

Oxidative Fragmentations and Skeletal Rearrangements of Oxindole Derivatives

Hendrik F. T. Klare, Alexander F. G. Goldberg, Douglas C. Duquette,
and Brian M. Stoltz*

*The Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering,
Division of Chemistry and Chemical Engineering, California Institute of Technology,
1200 East California Boulevard, MC 101-20, Pasadena, CA 91125, USA
stoltz@caltech.edu*

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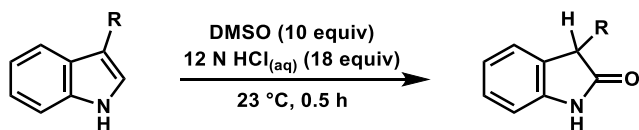
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Materials and Methods

Unless stated otherwise, reactions were performed in flame-dried or oven-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina).¹ Sodium carbonate and cesium carbonate were flame-dried in vacuo prior to use. Commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. SiliaFlash P60 Academic Silica gel (particle size 0.040–0.063 mm) was used for flash chromatography. ¹H and ¹³C NMR spectra were recorded on a Varian 400 (at 400 MHz and 100 MHz, respectively) or on a Varian Mercury 500 (at 500 MHz and 126 MHz, respectively) and are reported relative to CHCl₃ as the residual solvent resonance (δ 7.26 & 77.16 ppm, respectively) or tetramethylsilane (0.00 ppm). Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MM) ionization mode; HRMS were also acquired using a JEOL JMS-600H with fast atom bombardment (FAB). Optical rotations were recorded on a JASCO P-2000 Polarimeter. Analytical SFC was performed with a Mettler SFC supercritical CO₂ analytical chromatography system utilizing Chiralpak (AD-H) or Chiralcel (OD-H and OJ-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 254 nm. CCDC 1495039 contains the supplemental crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

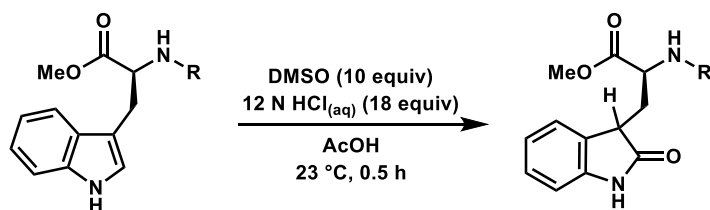
¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

General Experimental Procedures



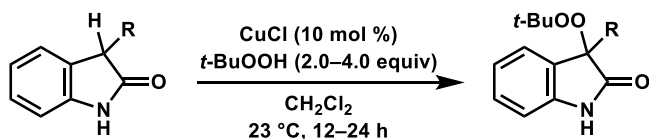
General Procedure A. Indole oxidation.

According to a procedure reported by Savige and Fontana,² the indole is dissolved in dimethyl sulfoxide (10 equiv) and concentrated hydrochloric acid (12 N, 18 equiv) is added dropwise at ambient temperature. Reaction progress is monitored by LCMS and is typically complete in less than 30 minutes. The reaction mixture is neutralized (pH > 6) with concentrated ammonium hydroxide and extracted with dichloromethane. The combined organic phases are dried over sodium sulfate, filtered, and concentrated. The residue is purified by column chromatography to afford the oxindole product.



General Procedure B. Tryptophan methyl ester oxidation.

In order to prevent methyl ester hydrolysis, a modified procedure is used for tryptophan methyl ester derivatives. The indole is dissolved in dimethyl sulfoxide (10 equiv) and glacial acetic acid (5 mL/mmol indole) is added, followed by dropwise addition of concentrated hydrochloric acid (12 N, 18 equiv) at ambient temperature. Reaction progress is monitored by LCMS and is typically complete in less than 30 minutes. The reaction mixture is neutralized (pH > 6) with concentrated ammonium hydroxide and extracted with dichloromethane. The combined organic phases are dried over sodium sulfate, filtered, and concentrated. The residue is purified by column chromatography to afford the oxindole product.

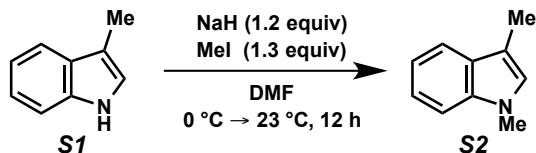


General Procedure C. Oxindole Peroxidation.

A schlenk tube is flame dried, cooled under a stream of argon gas, and charged with oxindole (1 equiv) and copper(I) chloride (0.1 equiv). The tube is sealed, then evacuated and backfilled with argon (three times). Dichloromethane (5 mL/mmol oxindole) is added, followed by dropwise addition of *tert*-butyl hydroperoxide (6 M in decane, 2 equiv). The reaction is stirred at ambient temperature, and monitored by LCMS. If the reaction is incomplete after 12 h, an additional portion of *tert*-butyl hydroperoxide (6 M in decane, 2 equiv) is added, and stirred for an additional 12 h. Upon completion, the reaction mixture is dry-loaded onto silica gel, and purified directly by column chromatography to afford the 3-(*tert*-butylperoxy)oxindole product.

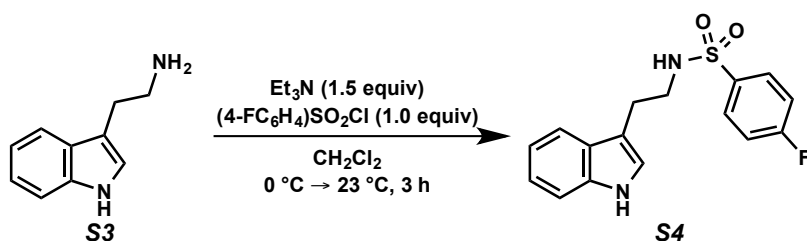
² Savige, W. E., Fontana, A. *Methods Enzymol.* **1977**, *47*, 442–453.

Indole Characterization Data



1,3-Dimethylindole (S2)

Sodium hydride (0.576 g, 24 mmol, 1.2 equiv) was suspended in DMF (20 mL) and cooled in an ice-water bath. To this suspension was added dropwise a solution of 3-methylindole (2.624 g, 20 mmol, 1.0 equiv) in DMF (30 mL). The reaction mixture was warmed to ambient temperature and stirred for an hour, affording an orange solution. The reaction mixture was then cooled again in an ice-bath and methyl iodide (1.62 mL, 26 mmol, 1.3 equiv) was added dropwise; a white precipitate was observed. The heterogeneous mixture was warmed slowly to ambient temperature and stirred for 12 hours, at which point, complete consumption of starting material was observed by TLC. The reaction was quenched by addition of saturated aqueous ammonium chloride (25 mL) and extracted with diethyl ether (4 x 25 mL). The combined organic extracts were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash chromatography on SiO₂ (5% Et₂O in hexanes) to afford 1,3-dimethylindole (2.85 g, 98% yield) as a colorless solid, with spectral data matching those reported in the literature.³

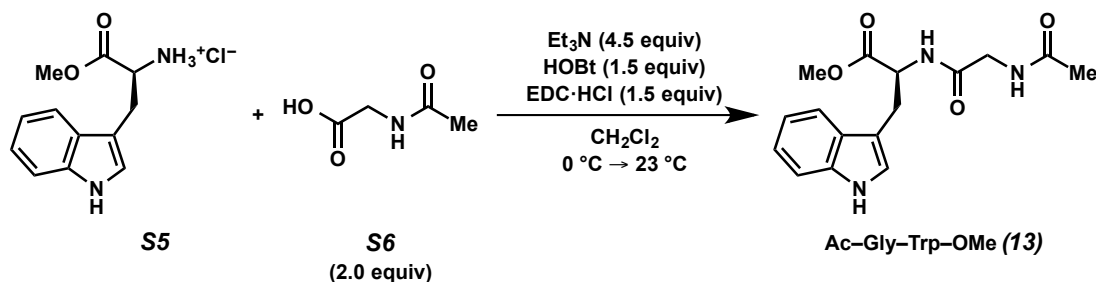


N-(4-Fluorobenzene)sulfonyl-3-(2-aminoethyl)indole (S4)

To a 200 mL round-bottomed flask was added tryptamine (1.6 g, 10 mmol, 1.0 equiv), CH₂Cl₂ (100 mL), and Et₃N (2.1 mL, 15 mmol, 1.5 equiv). The solution was cooled in an ice-bath and 4-fluorobenzenesulfonyl chloride (2.0 g, 10.3 mmol, 1.0 equiv) was added in a single portion. The ice-bath was then removed and the reaction allowed to warm to 23 °C. After stirring for additional 3 hours, the reaction was quenched with 1 N HCl (100 mL). The mixture was then washed with 1 N HCl (2 x 100 mL), the organic layer dried over anhydrous Na₂SO₄, filtered, and concentrated to afford a tan solid that was triturated from Et₂O/hexanes to afford **S4** as an off-white solid (2.26 g, 71% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.04 (s, 1H), 7.76–7.68 (m, 2H), 7.42–7.40 (m, 1H), 7.37 (ddd, *J* = 8.2, 8.2, 0.9 Hz, 1H), 7.20 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.11–7.01 (m, 3H), 6.99 (d, *J* = 2.3 Hz, 1H), 4.41 (t, *J* = 6.0 Hz, 1H), 3.30 (td, *J* = 6.4, 6.2 Hz, 2H), 2.96 (td, *J* = 6.6, 0.8 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 165.1 (d, *J* = 254.3 Hz), 136.6, 136.0, 135.9, 129.8 (d, *J* = 9.5 Hz), 126.9, 122.7, 122.6, 119.8, 118.6, 116.3 (d, *J* = 22.6 Hz), 111.6, 111.5, 77.4, 43.2, 25.6; ¹⁹F NMR (282 MHz, CDCl₃) δ –105.5; IR (Neat Film, NaCl) 3400,

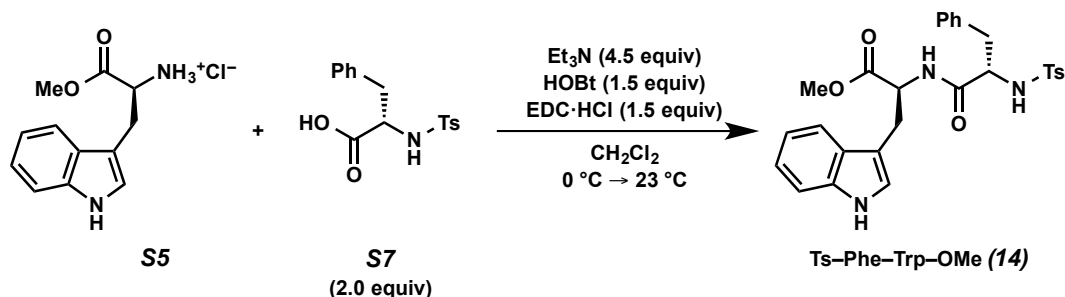
³ Barluenga, J.; Fañanás, F. J.; Sanz, R.; Fernández, Y. *Chem. Eur. J.* **2002**, *8*, 2034–2046.

3295, 3052, 1592, 1491, 1320, 1152, 1090, 836; HRMS (MM ESI-APCI) m/z calc'd for $C_{16}H_{15}FN_2O_2S$ $[M]^+$: 318.0838, found: 318.0845.



Ac-Gly-Trp-OMe (13)

To a 100 mL round-bottom flask is added tryptophan methyl ester hydrochloride (1.0 g, 3.96 mmol, 1.0 equiv) and dichloromethane (20 mL), and the mixture is cooled in an ice-bath. To the stirring mixture is added triethylamine (2.5 mL, 17.7 mmol, 4.5 equiv), HOBT (802 mg, 5.94 mmol, 1.5 equiv), *N*-acetylglycine (927 mg, 7.92 mmol, 2.0 equiv), then EDC·HCl (922 mg, 5.94 mmol, 1.5 equiv). The mixture was then warmed to ambient temperature and monitored by LCMS. Upon completion, the mixture was treated with 1 N HCl (25 mL) and a white precipitate was observed, which was filtered, washed with water, and dried to yield Ac-Gly-Trp-OMe as a white solid (286.7 mg, 0.903 mmol, 23% yield), with spectral data matching those reported in the literature.⁴

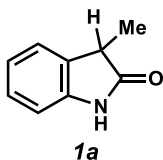


Ts-Phe-Trp-OMe (14)

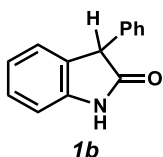
Prepared as in Ac-Gly-Trp-OMe, using tryptophan methyl ester hydrochloride (656 mg, 2.58 mmol, 1.0 equiv) and *N*-tosylphenylalanine⁵ (1.64 g, 5.13 mmol, 2.0 equiv), to obtain Ts-Phe-Trp-OMe as a white solid (387.4 mg, 27% yield). R_f = 0.20 (EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.26 (s, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.39–7.29 (m, 2H), 7.21–7.01 (m, 7H), 6.96–6.85 (m, 3H), 6.77 (d, J = 7.9 Hz, 1H), 4.87–4.74 (m, 1H), 3.97–3.86 (m, 1H), 3.62 (s, 3H), 3.29–3.10 (m, 2H), 2.92–2.70 (m, 2H), 2.35 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.6, 169.8, 143.7, 136.1, 136.0, 135.3, 129.7, 129.3, 128.7, 127.4, 127.1, 127.0, 123.2, 122.2, 119.6, 118.4, 111.4, 109.4, 57.6, 53.0, 52.4, 38.2, 27.5, 21.5; IR (Neat Film, NaCl) 3285, 3057, 2928, 1736, 1649, 1533, 1431, 1219, 1034, 742 cm⁻¹; HRMS (MM ESI-APCI) m/z calc'd for $C_{28}H_{30}N_3O_5S$ $[M+H]^+$: 520.1901; found: 520.1909. $[\alpha]_D^{25}$ -100.6 (0.88, CHCl₃).

⁴ Hashizume, K.; Shimonishi, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3806–3810.

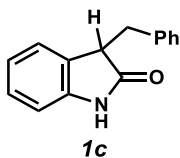
⁵ Han, Z.-J.; Wang, R.; Zhou, Y.-F.; Liu, L. *Eur. J. Org. Chem.* **2005**, 934–938.

Oxindole Characterization Data**3-Methyloxindole (1a)**

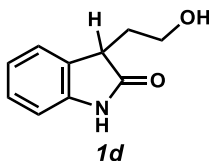
Prepared according to General Method A, using 3-methylindole (5.25 g, 40 mmol), to afford oxindole **1a** (4.18 g, 71% yield). $R_f = 0.44$ (1:1 EtOAc:hexanes). Characterization data matches those reported in the literature.⁶

**3-Phenyloxindole (1b)**

Prepared according to the method of Trost and coworkers. Characterization data matches those reported in the literature.⁷

**3-Benzyloxindole (1c)**

Prepared according to General Method A, using 3-benzylindole (207.3 mg, 1.0 mmol), to afford oxindole **1c** (189.8 mg, 85% yield). $R_f = 0.44$ (1:1 EtOAc:hexanes). Characterization data matches those reported in the literature.⁸

**3-(2-Hydroxyethyl)oxindole (1d)**

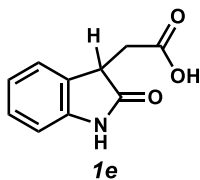
Prepared according to General Method A, using 3-(2-hydroxyethyl)indole (161.2 mg, 1.0 mmol), to afford oxindole **1d** (134.7 mg, 76% yield). $R_f = 0.21$ (3:1 EtOAc:hexanes). Characterization data matches those reported in the literature.⁹

⁶ Smith, III, A. B.; Liu, Z. *Org. Lett.* **2008**, *10*, 4363–4365.

⁷ Trost, B. M.; Xie, J.; Sieber, J. D. *J. Am. Chem. Soc.* **2011**, *133*, 20611–20622.

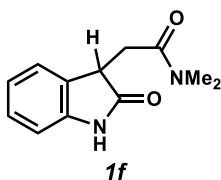
⁸ Grigg, R.; Whitney, S.; Sridharan, V.; Keep, A.; Derrick, A. *Tetrahedron* **2009**, *65*, 4375–4383.

⁹ RajanBabu, T. V.; Chenard, B. L.; Petti, M. A. *J. Org. Chem.* **1986**, *51*, 1704–1712.



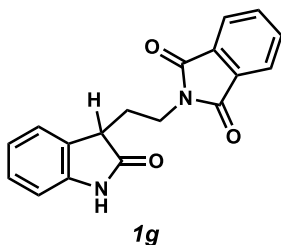
2-(Oxindol-3-yl)acetic acid (**1e**)

Prepared according to General Method A, using 3-indoleacetic acid (175.2 mg, 1.0 mmol), to afford oxindole **1e** (97.5 mg, 51% yield): $R_f = 0.5$ (1:3 MeOH:CH₂Cl₂); ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.32 (s, 1H), 10.36 (s, 1H), 7.20 (d, $J = 7.3$ Hz, 1H), 7.14 (m, 1H), 6.90 (ddd, $J = 7.7, 7.5, 1.0$ Hz, 1H), 6.79 (d, $J = 7.7$ Hz, 1H), 3.63–3.57 (m, 1H), 2.88 (dd, $J = 17.0, 4.7$ Hz, 1H), 2.68 (dd, $J = 17.0, 7.1$ Hz, 1H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 178.6, 172.6, 143.3, 129.8, 128.1, 124.0, 121.6, 109.6, 42.2, 34.4; IR (Neat Film, NaCl) 3231, 2918, 1708, 1622, 1469, 1402, 1338, 1224, 1167, 749 cm⁻¹; HRMS (MM ESI-APCI) m/z calc'd for C₁₀H₈NO₃ [M-H]⁻ 190.0510; found: 190.0503.



N,N-Dimethyl-2-(oxindol-3-yl)acetamide (**1f**)

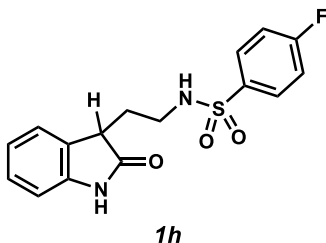
Prepared according to General Method A, using *N,N*-dimethyl-2-(indol-3-yl)acetamide (202.3 mg, 1.0 mmol), to afford oxindole **1f** (157.1 mg, 72% yield): $R_f = 0.20$ (EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.74 (br s, 1H), 7.31 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.23–7.14 (m, 1H), 7.02–6.94 (m, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.95 (dd, $J = 9.0, 3.3$ Hz, 1H), 3.12 (dd, $J = 16.6, 3.3$ Hz, 1H), 2.99 (d, $J = 8.5$ Hz, 6H), 2.76 (ddd, $J = 16.7, 9.0, 2.7$ Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 180.2, 170.0, 141.5, 130.0, 127.9, 124.7, 122.3, 109.6, 42.6, 37.1, 35.7, 34.5; IR (Neat Film, NaCl) 3221, 2923, 1711, 1622, 1469, 1404, 1335, 749 cm⁻¹; HRMS (MM ESI-APCI) m/z calc'd for C₁₂H₁₅N₂O₂ [M+H]⁺: 219.1128; found 219.1132.



2-(2-(2-Oxindol-3-yl)ethyl)isoindoline-1,3-dione (**1g**)

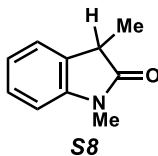
Prepared according to General Method A, using 2-(2-(2-indol-3-yl)ethyl)isoindoline-1,3-dione (290.4 mg, 1.0 mmol), to afford oxindole **1g** (199.1 mg, 65% yield): $R_f = 0.23$ (1:1 EtOAc:hexanes). Characterization data matches those reported in the literature.¹⁰

¹⁰ Ma, S.; Han, X.; Krishnan, S.; Virgil, S. C.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 8037–8041.



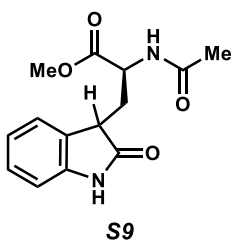
***N*-(4-Fluorobenzene)sulfonyl-3-(2-aminoethyl)oxindole (1h)**

Prepared according to General Method A, using *N*-(4-fluorobenzene)sulfonyl-3-(2-aminoethyl)indole (318.4 mg, 1.0 mmol), to afford oxindole **1h** (277.5 mg, 83% yield): $R_f = 0.19$ (1:1 EtOAc:hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.08 (s, 1H), 7.92–7.83 (m, 2H), 7.26–7.21 (m, 1H), 7.20–7.13 (m, 3H), 7.05 (dd, $J = 7.6, 7.6, 1.0$ Hz, 1H), 6.91–6.85 (d, $J = 7.6$ Hz, 1H), 5.86 (dd, $J = 7.1, 5.1$ Hz, 1H), 3.52 (dd, $J = 8.3, 4.9$ Hz, 1H), 3.26–3.18 (m, 1H), 3.18–3.10 (m, 1H), 2.30–2.22 (m, 1H), 2.07–1.96 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 179.9, 164.9 (d, $J = 254.4$ Hz), 141.0, 136.1, 129.7 (d, $J = 9.3$ Hz), 128.5, 128.3, 124.0, 122.8, 116.3 (d, $J = 22.5$), 110.0, 43.9, 40.7, 29.9; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -105.62; IR (Neat Film, NaCl) 3271, 2878, 1701, 1622, 1592, 1471, 1328, 1152, 1091, 838 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{SF}$ $[\text{M}+\text{H}]^+$: 335.0860; found: 335.0865.



1,3-Dimethyloxindole (S8)

Prepared according to General Method A, using 1,3-dimethylindole (**S2**, 1.45 g, 10 mmol, 1.0 equiv) to afford oxindole **S8** (1.32 g, 82% yield) as an off-white solid: $R_f = 0.28$ (3:1 hexanes:EtOAc). Characterization data matches those reported in the literature.¹¹

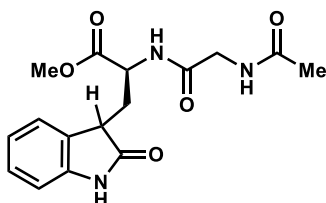


***N*-Acetyloxindolyalanine methyl ester (Ac-Oia-OMe) (S9)**

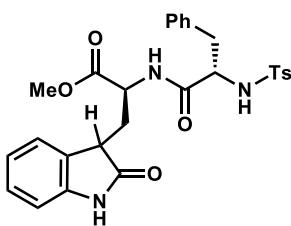
Prepared according to General Method B, using *N*-acetyltryptophan methyl ester (**12**, 1.042 g, 4.0 mmol), to afford the oxindole **S9** as a mixture of diastereomers, **S9a** and **S9b** (1.018 g, 92% yield, dr = 1.5:1.0 by $^1\text{H NMR}$ integration): $R_f = 0.36, 0.26$ (EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.07 (s, 1H), 7.42 (dd, $J = 13.5, 7.7$ Hz, 1H), 7.24–7.19 (m, 1H), 7.10–6.97 (m, 2H), 6.92–6.84 (m, 1H), 4.93 (ddd, $J = 10.0, 8.0, 4.6$ Hz, 0.7H, **S9a**), 4.75 (ddd, $J = 8.0, 7.1, 4.4$ Hz, 0.5H, **S9b**), 3.75 (s, 1H, **S9b**), 3.68 (s, 1.7H, **S9a**), 3.59–

¹¹ Szabó-Pusztay, K.; Szabó, L. *Synthesis* **1979**, 276–277.

3.50 (m, 1H), 2.53 (ddd, $J = 14.8, 7.1, 3.7$ Hz, 0.5H, **S9a**), 2.44–2.27 (m, 0.7H, **S9b**; 1H, **S9a/S9b**), 2.01 (s, 1.6H, **S9a**), 1.99 (s, 1H, **S9b**); ^{13}C NMR (126 MHz, CDCl_3 , **S9a**) δ 180.0, 172.3, 170.6, 141.3, 128.8, 128.3, 124.6, 122.8, 110.0, 52.5, 50.5, 43.1, 32.5, 23.0; ^{13}C NMR (126 MHz, CDCl_3 , **S9b**) δ 180.4, 172.3, 170.3, 141.3, 128.5, 128.3, 123.9, 122.9, 110.1, 52.6, 50.5, 43.5, 31.6, 22.9; IR (Neat Film, NaCl) 3275, 3077, 1706, 1661, 1540, 1471, 1219, 752, 732 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 277.1183; found: 277.1190; >99% ee (*vide infra*), $[\alpha]_{\text{D}}^{25} -29.2$ (c 2.41, CHCl_3).

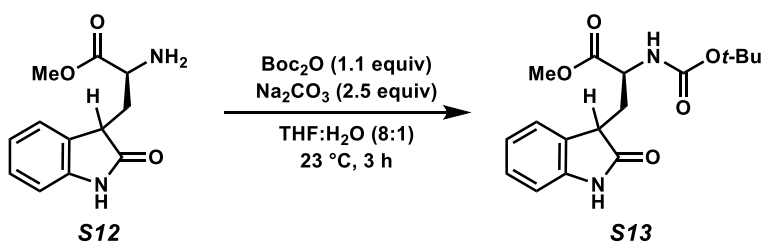
**S10****Ac-Gly-Oia-OMe (S10)**

Prepared according to General Method B, using Ac-Gly-Trp-OMe (**13**, 158.7 mg, 0.5 mmol), to afford the oxindole as a mixture of diastereomers, **S10a** and **S10b** (148 mg, 89% yield, dr not determined): $R_f = 0.31, 0.21$ (9:1 CH_2Cl_2 :MeOH); ^1H NMR (500 MHz, CDCl_3) δ 8.64 (s, 1H), 7.41 (ddd, $J = 7.9, 1.3, 0.7$ Hz, 1H), 7.28–7.23 (m, 1H), 7.17 (ddd, $J = 8.2, 7.1, 1.3$ Hz, 1H), 7.11 (ddd, $J = 8.1, 7.1, 1.1$ Hz, 1H), 6.54 (d, $J = 7.9$ Hz, 1H), 6.24 (dd, $J = 4.5, 4.5$ Hz, 1H), 4.90 (ddd, $J = 7.9, 5.6, 5.6$ Hz, 1H), 3.86 (d, $J = 5.1$ Hz, 2H), 3.75–3.66 (m, 1H), 3.70 (s, 3H), 3.36–3.21 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.8, 170.5, 168.5, 134.4, 127.5, 122.6, 122.3, 120.5, 117.9, 110.8, 106.1, 52.7, 52.4, 42.9, 26.4, 22.9; IR (Neat Film, NaCl) 3285, 3057, 2928, 1736, 1649, 1533, 1431, 1219, 1034, 742 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$: 334.1397; found: 334.1401; 99% ee (*vide infra*), $[\alpha]_{\text{D}}^{25} -80.6$ (c 0.79, MeOH).

**S11****Ts-Phe-Oia-OMe (S11)**

Prepared according to General Method B, using Ts-Phe-Trp-OMe (**14**, 519.6 mg, 1.0 mmol), to afford the oxindole as a mixture of diastereomers, **S11a** and **S11b** (454 mg, 85% yield, dr = 1.5:1.0 by ^1H NMR integration): $R_f = 0.12$ (1:1 hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 8.20 (s, 0.6H), 8.03 (s, 0.4H), 7.63–7.54 (m, 2H), 7.44 (d, $J = 7.9$ Hz, 0.6H), 7.34 (d, $J = 7.4$ Hz, 0.6H), 7.26–7.18 (m, 1H), 7.17–7.10 (m, 4H), 7.10–7.04 (m, 2.6H), 7.00 (ddd, $J = 7.7, 4.4, 1.9$ Hz, 2H), 6.90 (dd, $J = 7.7, 2.9$ Hz, 1H), 5.70 (d, $J = 8.7$ Hz, 0.6H), 5.46 (d, $J = 8.4$ Hz, 0.4H), 4.81 (ddd, $J = 9.3, 7.9, 4.8$ Hz, 0.7H), 4.54 (ddd, $J = 8.7, 8.7, 3.9$ Hz, 0.5H), 4.05 (dddd, $J = 23.3, 8.3, 6.3, 6.3$ Hz, 1H), 3.71 (s, 1.3H), 3.63 (s, 1.7H), 3.50 (dd, $J = 8.4, 3.8$ Hz, 0.5H), 3.13 (dd, $J = 6.6, 6.6$ Hz, 0.7H), 3.06–2.96 (m, 1.4H), 2.88 (dd, $J = 6.3, 2.6$ Hz, 0.8H), 2.51 (ddd, $J = 14.7, 9.0, 3.6$ Hz,

0.6H), 2.41–2.23 (m, 4.5H); ^{13}C NMR (126 MHz, CDCl_3) δ 180.2, 180.1, 171.4, 171.3, 170.7, 170.4, 143.5, 143.4, 141.4, 141.1, 136.6, 136.4, 135.6, 135.6, 129.6, 129.6, 129.6, 129.5, 128.7, 128.5, 128.4, 128.4, 128.4, 127.9, 127.1, 127.1, 126.8, 126.7, 124.9, 123.9, 122.9, 122.8, 110.3, 110.2, 60.4, 57.8, 57.7, 52.6, 52.6, 52.5, 50.4, 50.2, 43.1, 42.6, 38.8, 38.6, 32.4, 31.3, 21.4, 21.4, 21.1, 14.2; IR (Neat Film, NaCl) 3285, 1738, 1698, 1540, 1328, 1157, 1090 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_6\text{S}$ $[\text{M}+\text{H}]^+$: 536.1850; found: 536.1849; $[\alpha]_{\text{D}}^{25}$ -100.6 (c 0.88, CHCl_3).

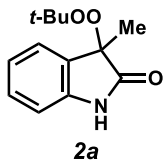


N-tert-Butylcarboxyoxindolylalanine methyl ester (Boc–Oia–OMe) (**S13**)

To a solution of oxindole **S12**¹² (3.89 g, 16.6 mmol, 1.00 equiv) in an 8:1 mixture of THF:H₂O (166 mL) were added Boc₂O (3.98 g, 18.3 mmol, 1.10 equiv) followed by Na₂CO₃ (4.40 g, 41.5 mmol, 2.50 equiv) in a single portion. The reaction mixture was stirred at ambient temperature (23 °C) until complete consumption of starting material was observed by TLC (3 h). The reaction was diluted with EtOAc (200 mL) and H₂O (100 mL), transferred to a separatory funnel and the phases were separated. The aqueous layer was extracted with EtOAc (3 x 75 mL). The combined organic fractions were washed with brine (100 mL), dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash chromatography on SiO₂ (1:4 EtOAc:hexanes → 2:3 EtOAc:hexanes) to afford the oxindole as a mixture of diastereomers **S13a** and **S13b** (4.53 g, 81% yield, 1.7:1.0 d.r. by ^1H NMR integration) as a colorless oil: R_f = 0.39 (1:1 EtOAc:hexanes); ^1H NMR (500 MHz, CDCl_3) δ 9.10 (s, 0.3H, **S13a**), 9.05 (s, 0.5H, **S13b**), 7.45 (d, J = 7.4 Hz, 0.5H), 7.26–7.17 (m, 1.4H), 7.05 (ddd, J = 7.3, 6.9, 4.5 Hz, 1H), 6.90 (dd, J = 10.9, 7.9 Hz, 1H), 5.84 (d, J = 8.7 Hz, 0.3H, **S13b**), 5.58 (d, J = 8.7 Hz, 0.64H, **S13a**), 4.69 (ddd, J = 8.9, 8.9, 5.6 Hz, 0.5H, **S13a**), 4.55 (ddd, J = 7.0, 7.0, 6.5 Hz, 0.3H, **S13b**), 3.73 (s, 1.1H, **S13b**), 3.69 (s, 1.8H, **S13a**), 3.59–3.52 (m, 1H), 2.45–2.39 (m, 1H), 2.38–2.23 (m, 1H), 1.44 (s, 5.4H, **S13a**), 1.40 (s, 3H, **S13b**); ^{13}C NMR (126 MHz, CDCl_3) δ 180.6, 180.3, 172.9, 172.7, 155.8, 155.4, 141.6, 141.5, 129.2, 128.5, 128.3, 124.9, 124.2, 122.9, 110.2, 110.1, 80.2, 79.9, 52.6, 51.8, 51.7, 43.3, 42.9, 33.6, 32.2, 28.4 (mixture of diastereomers); IR (Neat Film, NaCl) 3292, 2977, 2252, 1709, 1623, 1517, 1487, 1473, 1437, 1366, 1227, 1169, 1052, 1026, 912, 752, 733 cm^{-1} ; HRMS (EI+) m/z calc'd for $\text{C}_{17}\text{H}_{22}\text{O}_5\text{N}_2$ $[\text{M}]^+$: 334.1529; found: 334.1526; >99% ee (*vide infra*), $[\alpha]_{\text{D}}^{25}$ -182.4 (c 1.76, CHCl_3).

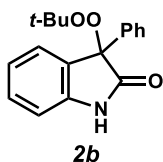
¹² von Nussbaum, F.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2175–2178.

Peroxyoxindole Characterization Data



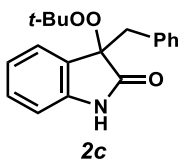
3-(*tert*-Butylperoxy)-3-methyloxindole (**2a**)

Prepared according to General Method C, using oxindole **1a** (294.4 mg, 2.0 mmol), to afford peroxyoxindole **2a** (432 mg, 92% yield): $R_f = 0.64$ (3:1 hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.95 (s, 1H), 7.31 (d, $J = 7.2$ Hz, 1H), 7.24 (ddd, $J = 7.7, 7.5, 1.3$ Hz, 1H), 7.04 (ddd, $J = 7.7, 7.5, 1.0$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 1.54 (s, 3H), 1.11 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 177.9, 140.8, 130.0, 129.4, 124.2, 122.4, 110.2, 82.3, 80.4, 26.4, 20.3; IR (Neat Film, NaCl) 3261, 2983, 2928, 1733, 1622, 1471, 1362, 1197, 1145, 752 cm^{-1} ; HRMS (FAB) m/z calc'd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$ $[\text{M}]^+$: 235.1208; found: 235.1203. The characterization data matches those reported in the literature.¹³ CCDC 1495039 contains the supplementary crystallographic data for this compound.



3-(*tert*-Butylperoxy)-3-phenyloxindole (**2b**)

Prepared according to General Method C, using oxindole **1b** (418.5 mg, 2.0 mmol), to afford peroxyoxindole **2b** (581 mg, 98% yield): $R_f = 0.68$ (4:1 hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.93 (s, 1H), 7.51–7.43 (m, 2H), 7.41–7.26 (m, 5H), 7.10 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 1H), 1.21 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 176.7, 141.9, 136.2, 129.9, 129.1, 129.0, 128.6, 127.1, 126.5, 122.6, 110.5, 86.7, 81.0, 26.7; IR (Neat Film, NaCl) 3251, 2978, 1731, 1622, 1474, 1362, 1194, 752 cm^{-1} ; HRMS (FAB) m/z calc'd for $\text{C}_{18}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 298.1443; found: 298.1451.

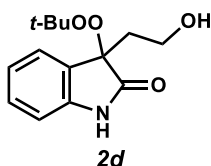


3-(*tert*-Butylperoxy)-3-benzyloxindole (**2c**)

Prepared according to General Method C, using oxindole **1c** (44.6 mg, 0.2 mmol), to afford peroxyoxindole **2c** (48.6 mg, 78% yield): $R_f = 0.31$ (4:1 hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.37 (s, 1H), 7.22–7.10 (m, 4H), 7.06–7.00 (m, 2H), 6.98–6.90 (m, 2H), 6.73 (d, $J = 8.0$ Hz, 1H), 3.35 (d, $J = 13.3$ Hz, 1H), 3.05 (d, $J = 13.2$ Hz, 1H), 1.13 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 177.0, 141.1, 133.6, 130.9, 129.5, 127.9, 127.7, 127.0, 125.8, 121.9, 110.0, 85.7, 80.7, 40.5, 26.6; IR (Neat Film, NaCl)

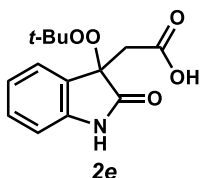
¹³ Kong, D.-L.; Cheng, L.; Yue, T.; Wu, H.-R.; Feng, W.-C.; Wang, D.; Liu, L. *J. Org. Chem.* **2016**, *81*, 5337–5344.

3260, 2978, 2928, 1738, 1634, 1474, 1402, 1192, 730 cm^{-1} ; HRMS (FAB) m/z calc'd for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ $[\text{M}]^+$: 311.1521; found: 311.1522. The characterization data matches those reported in the literature.¹³



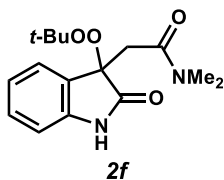
3-(*tert*-Butylperoxy)-3-(2-hydroxyethyl)oxindole (**2d**)

Prepared according to General Method C, using oxindole **1d** (35.4 mg, 0.2 mmol), to afford peroxyoxindole **2d** (45.2 mg, 85% yield): $R_f = 0.17$ (1:1 hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 9.01 (s, 1H), 7.27 (d, $J = 7.5$ Hz, 1H), 7.26–7.19 (m, 1H), 7.03 (ddd, $J = 7.5, 7.3, 1.0$ Hz, 1H), 6.86 (d, $J = 7.7$ Hz, 1H), 3.89 (m, 1H), 3.61 (m, 1H), 2.97 (s, 1H), 2.31 (ddd, $J = 14.6, 7.0, 4.5$ Hz, 1H), 2.07 (dddd, $J = 14.5, 7.0, 4.5, 1.0$ Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 178.0, 141.2, 129.8, 128.8, 124.6, 122.7, 110.5, 84.5, 80.8, 57.9, 37.3, 26.5; IR (Neat Film, NaCl) 3260, 2983, 2933, 1726, 1621, 1471, 1362, 1194, 1051, 749 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{14}\text{H}_{20}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 266.1387; found: 266.1385.



2-(3-(*tert*-Butylperoxy)oxindol-3-yl)acetic acid (**2e**)

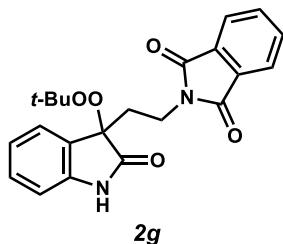
Prepared according to General Method C, using oxindole **1e** to afford peroxyoxindole **2e** (81% yield): $R_f = 0.68$ (4:1 hexanes:EtOAc); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 10.33 (s, 1H), 7.34–7.29 (m, 1H), 7.22–7.15 (m, 1H), 6.90 (dd, $J = 7.5, 7.5, 1.0$ Hz, 1H), 6.77–6.71 (m, 1H), 2.99 (d, $J = 15.6$ Hz, 1H), 2.90 (d, $J = 15.7$ Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 174.0, 169.3, 143.5, 129.8, 127.2, 125.0, 121.0, 109.4, 81.7, 79.9, 40.4, 26.1; IR (Neat Film, NaCl) 2924, 2853, 1728, 1621, 1471, 1191, 755 cm^{-1} ; HRMS (FAB) m/z calc'd for $\text{C}_{14}\text{H}_{18}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 280.1185; found: 280.1194.



N,N-Dimethyl-2-(3-(*tert*-butylperoxy)oxindol-3-yl)acetamide (**2f**)

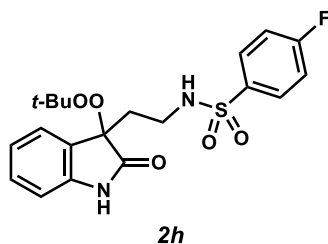
Prepared according to General Method C, using oxindole **1f** (43.6 mg, 0.2 mmol), to afford peroxyoxindole **2f** (52.2 mg, 85% yield): $R_f = 0.29$ (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 8.10 (s, 1H), 7.26 (d, $J = 7.3$ Hz, 1H), 7.20 (ddd, $J = 7.7, 7.5, 1.3$ Hz, 1H), 6.96 (ddd, $J = 7.8, 7.5, 1.0$ Hz, 1H), 6.80 (ddd, $J = 7.8, 7.7, 0.8$ Hz, 1H), 3.25 (s, 2H), 3.02 (s, 3H), 2.79 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 175.2, 167.6, 142.4, 129.7, 128.3, 124.4, 121.8, 109.8, 82.7, 80.6, 37.5, 37.4, 35.2, 26.3; IR (Neat Film, NaCl)

3260, 2978, 2928, 1738, 1634, 1474, 1402, 1192, 730 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 307.1652; found: 307.1653.



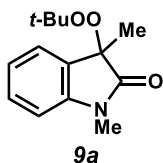
2-(2-(2-Oxindol-3-yl)ethyl)isoindoline-1,3-dione (**2g**)

Prepared according to General Method C, using oxindole **1g** (60.9 mg, 0.2 mmol), to afford peroxyoxindole **2g** (68.7 mg, 88% yield): R_f = 0.45 (1:1 hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 8.44 (s, 1H), 7.78–7.68 (m, 2H), 7.68–7.60 (m, 2H), 7.35 (d, J = 7.5 Hz, 1H), 7.10 (ddd, J = 7.7, 7.5, 1.2 Hz, 1H), 6.87 (ddd, J = 7.7, 7.5, 1.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 3.93 (ddd, J = 14.1, 7.7, 7.5 Hz, 1H), 3.76 (ddd, J = 14.1, 7.9, 5.3 Hz, 1H), 2.57–2.49 (ddd, J = 13.9, 7.8, 7.5 Hz, 1H), 2.34 (ddd, J = 13.9, 7.5, 5.3 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 175.9, 167.8, 141.3, 133.8, 131.9, 129.6, 127.8, 124.8, 123.0, 122.3, 110.3, 83.8, 80.6, 32.7, 31.9, 26.4; IR (Neat Film, NaCl) 3290, 2978, 2928, 1713, 1622, 1469, 1397, 1362, 1189 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 395.1601; found: 395.1619.



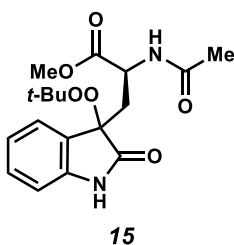
N-(4-Fluorobenzene)sulfonyl-3-(2-aminoethyl)-3-(*tert*-butylperoxy)oxindole (**2h**)

Prepared according to General Method C, using oxindole **1h** (33.4 mg, 0.1 mmol), to afford peroxyoxindole **2h** (36.2 mg, 86% yield): R_f = 0.44 (1:1 hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 8.63 (s, 1H), 7.89–7.81 (m, 2H), 7.30–7.25 (m, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.18–7.08 (m, 2H), 7.06 (ddd, J = 7.7, 7.5, 1.0 Hz, 1H), 6.88 (ddd, J = 7.8, 7.5, 0.8 Hz, 1H), 6.02 (ddd, J = 7.8, 7.7, 3.3 Hz, 1H), 3.14–3.02 (m, 2H), 2.30 (ddd, J = 14.7, 7.9, 5.5 Hz, 1H), 2.06–1.97 (m, 1H), 1.07 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 176.9, 164.9 (d, J = 255 Hz), 141.1, 135.8 (d, J = 3.2 Hz), 130.0, 129.8 (d, J = 9.2 Hz), 127.7, 124.6, 122.7, 116.2 (d, J = 22.5 Hz), 110.6, 84.0, 80.8, 38.3, 33.4, 26.4; ^{19}F NMR (282 MHz, CDCl_3) δ -105.79; IR (Neat Film, NaCl) 3275, 2983, 2933, 1726, 1622, 1592, 1491, 1471, 1330, 1165, 1152, 1090, 735; HRMS (FAB) m/z calc'd for $\text{C}_{20}\text{H}_{24}\text{FN}_2\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 423.1390; found, 423.1386.



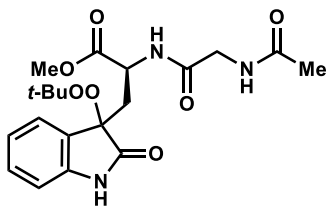
1,3-Dimethyl-3-(*tert*-butylperoxy)oxindole (**9a**)

Prepared according to General Method C, with minor modifications, using 1,3-dimethyl-oxindole (**S8**, 161.2 mg, 1.0 mmol, 1.0 equiv) and copper(I) bromide (28.7 mg, 0.2 mmol, 0.2 equiv), to afford oxindole **9a** (240 mg, 96% yield) as a yellow oil: $R_f = 0.72$ (1:1 hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.36–7.28 (m, 2H), 7.06 (ddd, $J = 7.8, 7.5, 1.0$ Hz, 1H), 6.80 (ddd, $J = 7.8, 7.5, 0.7$ Hz, 1H), 3.19 (s, 3H), 1.51 (s, 3H), 1.09 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 175.3, 143.7, 129.8, 129.5, 124.0, 122.5, 108.0, 81.9, 80.3, 26.5, 26.3, 20.4. IR (Neat Film, NaCl) 2980, 2931, 17535, 1616, 1495, 1472, 1364, 1244, 1196, 1122, 752 cm^{-1} ; HRMS (EI) m/z calc'd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$ [M^+]: 249.1365; found: 249.1358.



N-Acetylperoxyoxindolyalanine methyl ester (Ac-*t*Oia-OMe) (**15**)

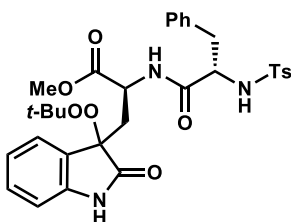
Prepared according to General Method C, using oxindole **S9** (2.763 g, 10.0 mmol), to afford the peroxyoxindole as a mixture of diastereomers, **15a** and **15b** (3.47 g, 95% yield, dr = 1.4:1.0 by $^1\text{H NMR}$ integration): $R_f = 0.49, 0.38$ (EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.85 (d, $J = 3.6$ Hz, 1H), 7.39–7.30 (m, 1H), 7.29–7.21 (m, 1H), 7.11–7.03 (m, 1H), 6.91–6.76 (m, 2H), 4.80 (ddd, $J = 8.3, 8.3, 4.5$ Hz, 0.6H), 4.55 (ddd, $J = 8.4, 8.3, 4.5$ Hz, 0.4H), 3.72 (s, 1.2H), 3.64 (s, 1.8H), 2.61 (dd, $J = 14.5, 8.4$ Hz, 0.4H), 2.54–2.40 (m, 1.6H), 1.98 (s, 1.2H), 1.94 (s, 1.8H), 1.09 (s, 5H), 1.08 (s, 4H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3 , **15a**) δ 176.8, 171.8, 170.4, 141.5, 130.4, 127.6, 125.0, 123.0, 110.5, 84.1, 81.1, 52.7, 48.5, 35.6, 26.5, 23.0; $^{13}\text{C NMR}$ (126 MHz, CDCl_3 , **15b**) δ 176.4, 172.0, 170.0, 141.3, 130.1, 128.0, 125.2, 122.8, 110.5, 83.9, 81.0, 52.6, 48.8, 35.3, 26.5, 23.1; IR (Neat Film, NaCl) 3290, 2978, 1733, 1659, 1619, 1545, 1471, 1360, 1192, 910, 752, 730 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_6$ [$\text{M}+\text{H}$] $^+$: 365.1707; found: 365.1714; >99% ee, $[\alpha]_{\text{D}}^{25} -37.3$ (c 1.89, CHCl_3); SFC conditions (**15a**): 10% IPA, 2.5 mL/min, OJ-H column, $\lambda = 254$ nm, t_{R} (min): major = 2.03, minor = 3.00; (**15b**): 10% IPA, 2.5 mL/min, OJ-H column, $\lambda = 254$ nm, t_{R} (min): major = 3.59, minor = 2.39.



16

Ac-Gly-tOia-OMe (16)

Prepared according to General Method C, using Ac-Gly-Oia-OMe (**S10**, 33.4 mg, 0.1 mmol), to afford the oxindole as a mixture of diastereomers, **16a** and **16b** (34 mg, 81% yield, dr = 1.4:1.0 by ^1H NMR integration): $R_f = 0.25$ (9:1 CH_2Cl_2 :MeOH); ^1H NMR (500 MHz, CDCl_3) δ 9.37 (s, 0.7H, **16a**), 9.15 (s, 0.5H, **16b**), 7.41–7.25 (m, 2H), 7.26–7.19 (m, 1H), 7.09–6.98 (m, 1.3H), 6.89–6.78 (m, 1.5H), 4.74 (ddd, $J = 7.6, 7.6, 4.5$ Hz, 0.6H, **16a**), 4.35 (ddd, $J = 9.2, 9.2, 4.5$ Hz, 0.5H, **16b**), 3.92 (m, 1H), 3.83 (dd, $J = 4.7, 4.7$ Hz, 1H), 3.69 (s, 1.2H, **16b**), 3.59 (s, 1.7H, **16a**), 2.70 (dd, $J = 14.6, 4.5$ Hz, 0.6H, **16a**), 2.59–2.50 (m, 0.9H, **16b**), 2.46 (dd, $J = 14.7, 7.9$ Hz, 0.6H, **16a**), 2.08 (s, 1.2H), 1.99 (s, 1.9H), 1.06 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 176.8, 176.4, 171.9, 171.5, 171.3, 171.0, 169.4, 169.1, 142.0, 141.8, 130.5, 130.2, 127.7, 126.8, 125.3, 124.9, 122.8, 122.5, 110.8, 110.7, 84.1, 83.6, 80.9, 52.8, 52.7, 49.0, 48.6, 42.9, 42.8, 35.1, 34.6, 26.5, 26.5, 23.2, 23.0; IR (Neat Film, NaCl) 3300, 2953, 1733, 1634, 1585, 1523, 1449, 1315, 1263, 1246, 1214, 1061, 922, 749 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{20}\text{H}_{28}\text{N}_3\text{O}_7$ $[\text{M}+\text{H}]^+$: 422.1922; found: 422.1925; 99% ee, $[\alpha]_{\text{D}}^{25} +57.8$ (c 4.05, CHCl_3); SFC conditions (**16a**): 20% IPA, 2.5 mL/min, OJ-H column, $\lambda = 254$ nm, t_{R} (min): major = 4.74, minor = 5.53; (**16b**): 20% IPA, 2.5 mL/min, OJ-H column, $\lambda = 254$ nm, t_{R} (min): major = 5.89, minor = 4.53.

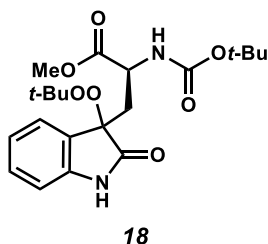


17

Ts-Phe-tOia-OMe (17)

Prepared according to General Method C, using Ts-Phe-Oia-OMe (**S11**, 267.8 mg, 0.5 mmol), to afford the oxindole as a mixture of diastereomers, **17a** and **17b** (264 mg, 85% yield, dr = 1.3:1.0 by ^1H NMR integration): $R_f = 0.33, 0.23$ (1:1 hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 8.31 (s, 0.5H, **17a**), 8.18 (s, 0.4H, **17b**), 7.61–7.56 (m, 1H), 7.48 (d, $J = 8.3$ Hz, 1H), 7.32–7.23 (m, 3H), 7.17–7.02 (m, 6H), 7.00–6.91 (m, 2H), 6.87 (d, $J = 7.8, 0.5$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 0.6H, **17a**), 5.66 (d, $J = 8.0$ Hz, 0.6H, **17a**), 5.58 (d, $J = 8.5$ Hz, 0.5H, **17b**), 4.69–4.64 (m, 0.6H, **17a**), 4.37–4.31 (m, 0.5H, **17b**), 4.03 (ddd, $J = 8.6, 7.4, 5.3$ Hz, 0.5H, **17b**), 3.91 (ddd, $J = 8.1, 7.9, 5.4$ Hz, 0.6H, **17a**), 3.68 (s, 1.4H, **17a**), 3.51 (s, 1.6H, **17b**), 3.09 (dd, $J = 14.2, 5.4$ Hz, 0.6H, **17a**), 2.88 (dd, $J = 14.1, 5.2$ Hz, 0.5H, **17b**), 2.84–2.74 (m, 1H), 2.71 (dd, $J = 14.5, 5.1$ Hz, 0.6H, **17a**), 2.53 (dd, $J = 14.3, 9.8$ Hz, 0.5H, **17b**), 2.43 (ddd, $J = 14.1, 10.2, 5.0$ Hz, 1H), 2.38 (s, 1.6H, **17a**), 2.36 (s, 1.2H, **17b**), 1.07 (d, $J = 2.1$ Hz, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 176.5,

176.1, 170.9, 170.6, 170.1, 170.0, 143.6, 143.5, 141.5, 141.5, 136.7, 136.2, 136.2, 135.7, 130.5, 130.3, 129.8, 129.7, 129.5, 128.6, 128.5, 127.3, 127.3, 127.1, 126.9, 126.8, 126.7, 125.5, 124.9, 123.0, 122.6, 83.9, 83.4, 81.0, 80.9, 58.0, 57.7, 52.7, 52.5, 49.5, 48.7, 38.7, 37.8, 35.2, 34.6, 26.5, 26.5, 21.7, 21.6 (mixture of diastereomers); IR (Neat Film, NaCl) 3270, 2988, 1738, 1619, 1333, 1189, 1157, 1090, 754 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{32}\text{H}_{38}\text{N}_3\text{O}_8\text{S}$ $[\text{M}+\text{H}]^+$: 624.2374; found: 624.2379; $[\alpha]_{\text{D}}^{25}$ -180.4 (c 2.23, CHCl_3).



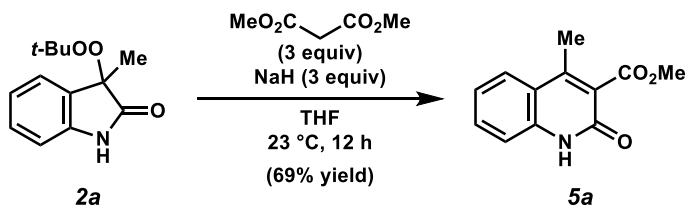
***N*-tert-Butylcarboxyperoxyoxindolylalanine methyl ester (Boc-*t*Oia-OMe) (18)**

Prepared according to General Method C, using oxindole **S13** (2.32 g, 6.94 mmol), to afford peroxyoxindole as a mixture of separable diastereomers, **18a** and **18b** (2.79 g, 95% yield, dr = 1.7:1).

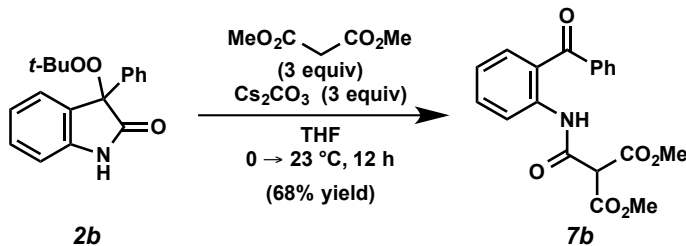
Major diastereomer (**18a**): R_f = 0.39 (1:1 EtOAc:hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.75 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.27 (ddd, J = 7.7, 7.5, 1.2 Hz, 1H), 7.07 (dd, J = 7.7, 7.6 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 5.32 (d, J = 8.8 Hz, 1H), 4.28 (d, J = 4.9 Hz, 1H), 3.69 (s, 3H), 2.47 (m, 2H), 1.38 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 175.9, 172.4, 155.1, 141.2, 130.3, 127.3, 125.3, 122.9, 110.1, 83.8, 81.0, 79.9, 52.6, 50.1, 35.5, 28.4, 26.5; IR (Neat Film, NaCl) 3279, 2979, 1733, 1622, 1472, 1366, 1165, 1058, 913, 870, 753, 734 cm^{-1} ; HRMS (FAB+) m/z calc'd for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_7$ $[\text{M}+\text{H}]^+$: 423.2131; found: 423.2152; >99% ee (*vide infra*), $[\alpha]_{\text{D}}^{25}$ -76.1 (c 0.51, CHCl_3).

Minor diastereomer (**18b**): R_f = 0.43 (1:1 EtOAc:hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.85 (s, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.27 (ddd, J = 7.7, 7.4, 1.2 Hz, 1H), 7.07 (dd, J = 7.7, 7.5 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 5.51 (d, J = 7.8 Hz, 1H), 4.52 (ddd, J = 7.2, 6.7, 6.7 Hz, 1H), 3.65 (s, 3H), 2.43 (d, J = 6.4 Hz, 2H), 1.43 (s, 9H), 1.11 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 175.8, 172.3, 155.2, 141.0, 130.0, 127.8, 125.5, 122.9, 110.2, 83.8, 81.0, 80.0, 52.6, 50.1, 35.8, 28.5, 26.5; IR (Neat Film, NaCl) 3325, 2979, 1739, 1623, 1472, 1366, 1167, 1058, 912, 863, 754, 734 cm^{-1} ; HRMS (FAB+) m/z calc'd for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_7$ $[\text{M}+\text{H}]^+$: 423.2131; found: 423.2148; >99% ee (*vide infra*), $[\alpha]_{\text{D}}^{25}$ $+48.9$ (c 0.58, CHCl_3).

Characterization Data of Peroxyoxindole Fragmentation Products

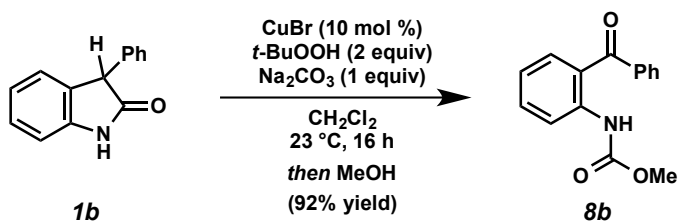
Methyl 4-methylquinolin-2(1*H*)-one-3-carboxylate (**5a**)

To a suspension of sodium hydride (7.2 mg, 0.3 mmol, 3.0 equiv) in THF (0.5 mL) was added dimethylmalonate (34 μ L, 0.3 mmol, 3.0 equiv) dropwise. The resulting solution was transferred, dropwise, to a second flask containing a solution of 3-*tert*-butylperoxy-3-methylindole (**2a**, 23.6 mg, 0.1 mmol, 1.0 equiv) in THF (1.5 mL). The resulting yellow suspension was stirred at ambient temperature for 12 h, and complete consumption of starting material was observed. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by column chromatography on SiO₂ (50% \rightarrow 75% EtOAc in hexanes) to afford quinolin-2(1*H*)-one **5a** (15 mg, 69% yield). The characterization data matches those reported in the literature.¹⁴ Oxindole **4a** was observed as a minor side-product.¹⁰

Dimethyl 2-((2-benzoylphenyl)carbamoyl)malonate (**7b**)

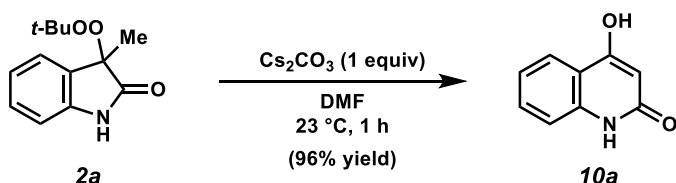
To an ice-cooled solution of 3-*tert*-butylperoxy-3-phenylindole (**2b**, 29.8 mg, 0.1 mmol, 1.0 equiv) in THF (1 mL) were added cesium carbonate (97.8 mg, 0.3 mmol, 3.0 equiv) and dimethylmalonate (34 μ L, 0.3 mmol, 3.0 equiv). The resulting yellow suspension was stirred at ambient temperature for 12 hour, and complete consumption of starting material was observed. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by column chromatography on SiO₂ (20% \rightarrow 25% EtOAc in hexanes) to afford malonate **7b** (24 mg, 68% yield) as a colorless oil: R_f = 0.45 (35% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 11.46 (s, 1H), 8.56 (d, J = 8.1 Hz, 1H), 7.79–7.71 (m, 2H), 7.66–7.53 (m, 3H), 7.48 (dd, J = 8.2, 6.9 Hz, 2H), 7.15 (ddd, J = 7.7, 7.7, 1.1 Hz, 1H), 4.54 (s, 1H), 3.85 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 198.8, 165.3, 161.2, 139.1, 138.4, 134.0, 133.3, 132.8, 130.3, 128.4, 125.1, 123.3, 122.4, 60.9, 53.7; IR (Neat Film, NaCl) 3292, 2954, 1742, 1695, 1645, 1598, 1582, 1521, 1447, 1265, 1157, 940, 925, 752 cm⁻¹; HRMS (MM ESI-APCI) m/z calc'd for C₁₉H₁₈NO₆ [M+H]⁺: 356.1129; found 356.1135.

¹⁴ Ritter, A.; Poschenrieder, H.; Bracher, F. *Z. Naturforsch.* **2009**, *64b*, 427–433.



Methyl (2-benzoylphenyl)carbamate (**8b**)

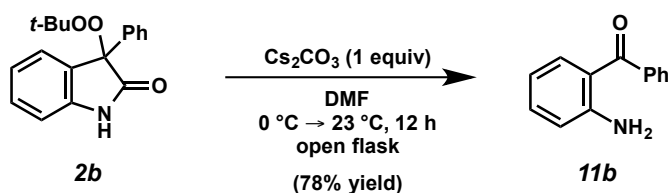
To a suspension of copper(I) bromide (2.9 mg, 0.02 mmol, 0.1 equiv), sodium carbonate (21.2 mg, 0.2 mmol, 1 equiv), and 3-phenyloxindole (**1b**, 41.9 mg, 0.2 mmol, 1.0 equiv) was added *tert*-butyl hydroperoxide (72.8 μL , 5.5 M in decane, 0.4 mmol, 2.0 equiv) dropwise at ambient temperature (23 $^\circ\text{C}$) with stirring. After 16 hours, complete conversion of starting material was observed, at which point methanol (2 mL) was added. After one hour, consumption of the intermediate peroxide was observed. The reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography on SiO_2 (7% EtOAc in hexanes) to afford carbamate **8b** (47.1 mg, 92% yield) as a colorless oil: $R_f = 0.65$ (35% EtOAc in hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 10.29 (s, 1H), 8.47–8.36 (m, 1H), 7.69 (dd, $J = 8.3, 1.4$ Hz, 2H), 7.62–7.42 (m, 5H), 7.08–6.97 (m, 1H), 3.78 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 199.4, 154.4, 141.0, 138.8, 134.3, 133.7, 132.4, 130.0, 128.4, 122.9, 121.3, 120.0, 52.5; IR (Neat Film, NaCl) 3300, 2953, 1733, 1634, 1585, 1523, 1449, 1315, 1263, 1246, 1214, 1061, 922, 749 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{15}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 256.0968; found: 256.0973.



4-Hydroxyquinolin-2(1H)-one (**10a**)

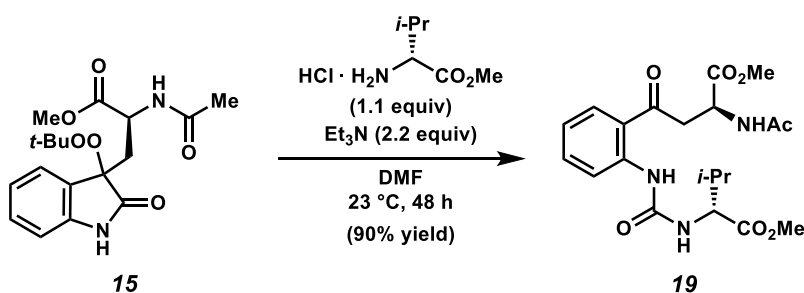
To a solution of 3-*tert*-butylperoxy-3-methyloxindole (**2a**, 47.1 mg, 0.2 mmol, 1.0 equiv) in DMF (2 mL) was added cesium carbonate (65.2 mg, 0.2 mmol, 1.0 equiv) in one portion. The suspension was stirred at ambient temperature for one hour, at which time complete consumption of starting material was observed. The reaction mixture was filtered through a plug of Celite and concentrated in vacuo. The residue was purified by flash chromatography on SiO_2 (9:1 CH_2Cl_2 :MeOH) to afford 4-hydroxyquinolin-2(1H)-one (**10a**, 31 mg, 96% yield) as a white solid; $R_f = 0.3$ (9:1 CH_2Cl_2 :MeOH). The characterization data matches those reported in the literature.¹⁵

¹⁵ Arya, K.; Agarwal, M. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 86–93.



2-Aminobenzophenone (**11b**)

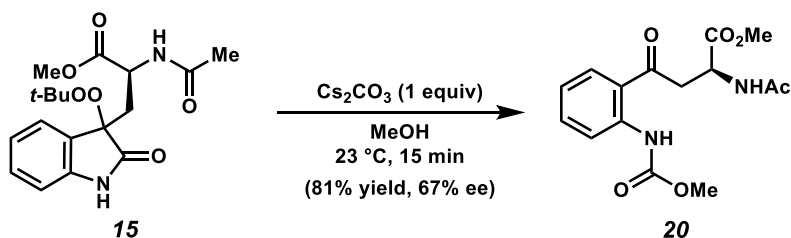
To an ice-cooled solution of 3-*tert*-butylperoxy-3-phenyloxindole (**2b**, 59.5 mg, 0.2 mmol, 1.0 equiv) in DMF (1 mL) was slowly added a suspension of cesium carbonate (65.2 mg, 0.2 mmol, 1.0 equiv) in DMF (1 mL) under an atmosphere of air. The reaction mixture was allowed to warm slowly to ambient temperature and stirred for 12 h, at which time consumption of starting material was observed by TLC and LCMS. The reaction mixture was filtered through Celite and the solvent was removed in vacuo. The residue was purified by flash chromatography on SiO_2 (9:1 hexanes:EtOAc) to afford 2-aminobenzophenone (31 mg, 78% yield) as a yellow solid. The characterization data matches those previously reported in the literature.¹⁶



Methyl (*S*)-2-acetamido-4-(2-(3-((*R*)-1-methoxy-3-methyl-1-oxobutan-2-yl)ureido)-phenyl)-4-oxobutanoate (**19**)

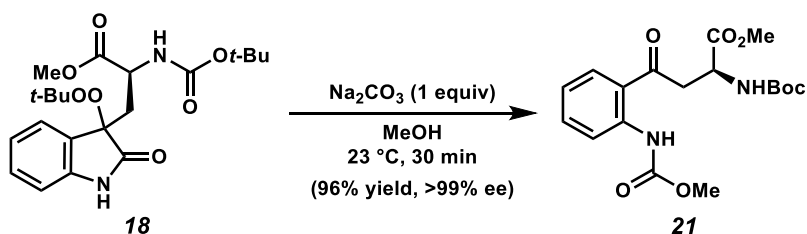
To a solution of peroxyoxindole **15** (54.7 mg, 0.15 mmol, 1.0 equiv) and D-valine methyl ester hydrochloride (27.7 mg, 0.165 mmol, 1.1 equiv) in DMF (1.5 mL) was added Et_3N (46 μL , 0.33 mmol, 2.2 equiv). The reaction mixture was stirred at ambient temperature ($23\text{ }^\circ\text{C}$) for 48 h, at which time complete consumption of starting material was observed. The crude reaction mixture was diluted with EtOAc (8 mL) and passed through a plug of SiO_2 using EtOAc as eluent. After removal of the solvents in vacuo, the residue was purified by flash chromatography on SiO_2 (9:1 EtOAc:hexanes \rightarrow 100% EtOAc) to afford valine-derived urea **19** (56.7 mg, 90% yield) as a colorless solid: $R_f = 0.48$ (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 10.65 (s, 1H), 8.38 (dd, $J = 8.7, 1.1$ Hz, 1H), 7.83 (d, $J = 8.9$ Hz, 1H), 7.60 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.41 (d, $J = 9.1$ Hz, 1H), 7.29 (ddd, $J = 8.6, 7.2, 1.5$ Hz, 1H), 6.80 (ddd, $J = 8.1, 7.2, 1.1$ Hz, 1H), 5.05 (ddd, $J = 9.0, 3.8, 3.8$ Hz, 1H), 4.91 (dd, $J = 9.6, 4.7$ Hz, 1H), 3.79 (s, 3H), 3.78 (dd, $J = 18.3, 4.1$ Hz, 1H), 3.72 (s, 3H), 3.32 (dd, $J = 18.3, 3.7$ Hz, 1H), 2.37–2.29 (m, 1H), 2.13 (s, 3H), 1.08 (d, $J = 6.9$ Hz, 3H), 0.97 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 200.5, 175.7, 171.9, 171.1, 155.2, 143.0, 134.8, 130.9, 120.4, 119.7, 119.6, 58.2, 52.7, 52.4, 47.1, 41.7, 31.7, 22.9, 19.4, 17.8; IR (Neat Film, NaCl) 3315, 2958, 1731, 1656, 1525, 1451, 1303, 1212 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{20}\text{H}_{28}\text{N}_3\text{O}_7$ [$\text{M}+\text{H}$] $^+$: 422.1922; found: 422.1929; $[\alpha]_D^{25} +270.8$ (c 0.93, CHCl_3).

¹⁶ Thakur, K. G.; Ganapathy, D.; Sekar, G. *Chem. Commun.* **2011**, 47, 5076–5078.



(S)-Methyl 2-acetamido-4-(2-((methoxycarbonyl)amino)phenyl)-4-oxobutanoate (20)

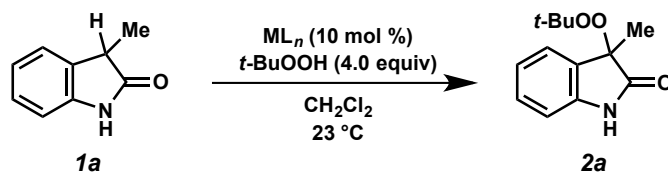
To a solution of peroxyoxindole **15** (36.5 mg, 0.1 mmol, 1.0 equiv) in methanol (1 mL) was added cesium carbonate (36.5 mg, 0.1 mmol, 1.0 equiv) in one portion. The reaction mixture was stirred at ambient temperature (23 °C) for 15 minutes, at which time complete consumption of starting material was observed. The reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography on SiO_2 (3:1 EtOAc:hexanes \rightarrow 100% EtOAc) to afford carbamate **20** (26 mg, 81% yield) as a colorless oil: R_f = 0.52 (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 11.01 (s, 1H), 8.51 (d, J = 8.6 Hz, 1H), 7.88 (dd, J = 8.2, 1.6 Hz, 1H), 7.59 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.09 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 6.63–6.57 (m, 1H), 4.98 (ddd, J = 7.9, 3.9, 3.9 Hz, 1H), 3.88–3.78 (m, 4H), 3.77 (s, 3H), 3.67 (dd, J = 18.2, 4.0 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 201.5, 171.6, 169.9, 154.1, 141.7, 135.8, 131.0, 121.6, 120.2, 119.2, 52.8, 52.4, 48.1, 41.7, 23.2; IR (Neat Film, NaCl) 3270, 2923, 1740, 1654, 1585, 1525, 1454, 1217 cm^{-1} ; HRMS (MM ESI-APCI) m/z calc'd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$: 323.1238; found: 323.1240; 67% ee, $[\alpha]_{\text{D}}^{25}$ +114.1 (c 0.25, CHCl_3); SFC conditions: 20% IPA, 2.5 mL/min, AD-H column, λ = 254 nm, t_{R} (min): major = 4.36, minor = 3.29.



Methyl (S)-2-((tert-butoxycarbonyl)amino)-4-(2-((methoxycarbonyl)amino)phenyl)-4-oxobutanoate (21)

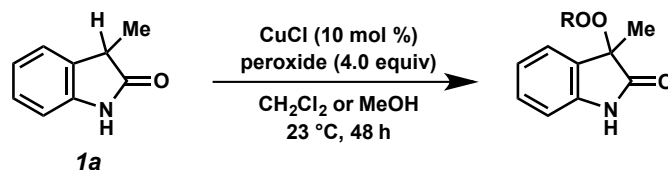
To a solution of peroxyoxindole **18** (211 mg, 0.5 mmol, 1.0 equiv) in MeOH (5.0 mL) was added Na_2CO_3 (53 mg, 0.5 mmol, 1.0 equiv). The mixture was stirred until complete consumption of starting material was observed by TLC (30 min). The crude reaction was passed through a plug of SiO_2 , flushed with EtOAc and purified by flash chromatography on SiO_2 (1:4 EtOAc:hexanes \rightarrow 3:7 EtOAc:hexanes) to afford carbamate **21** (183 mg, 96% yield) as a colorless oil: R_f = 0.15 (1:4 EtOAc:hexanes); ^1H NMR (500 MHz, CDCl_3) δ 11.01 (s, 1H), 8.48 (dd, J = 8.6, 1.1 Hz, 1H), 7.86 (dd, J = 8.2, 1.5 Hz, 1H), 7.56 (ddd, J = 8.7, 7.2, 1.6 Hz, 1H), 7.07 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 5.57 (d, J = 8.8 Hz, 1H), 4.68 (ddd, J = 8.5, 4.1, 4.1 Hz, 1H), 3.83–3.71 (m, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.58 (dd, J = 18.1, 4.1 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 201.6, 172.1, 155.7, 154.3, 141.8, 135.8, 131.1, 121.7, 120.5, 119.4, 80.3, 52.9, 52.5, 49.6, 42.3, 28.4; IR (Neat Film, NaCl) 3265, 2977, 2954, 1740, 1652, 1585, 1526, 1454, 1366, 1308, 1250, 1217, 1168, 1068, 756, 734 cm^{-1} ; HRMS (FAB+) m/z calc'd for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_7$ $[\text{M}+\text{H}]^+$: 381.1662; found: 381.1659; >99% ee, $[\alpha]_{\text{D}}^{25}$ -408.9 (c 0.25, CHCl_3); SFC cond.: 10% IPA, 2.5 mL/min, OD-H column, λ = 254 nm, t_{R} (min): major = 6.98, minor = 7.71.

Optimization of the Oxindole C–H Peroxidation

Table S1: Screening of Metal Salts^a

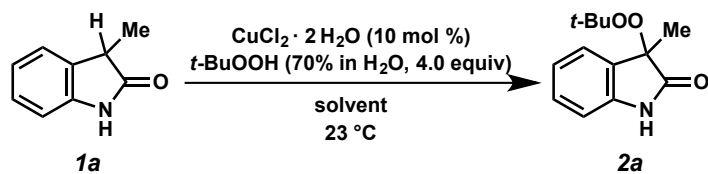
entry	metal catalyst	time [h]	conversion [%] ^b	yield [%] ^c
1	CuBr	48	>99	92
2	CuCl	48	>99	95
3	CuCl ₂	48	>99	87
4	CuCl ₂ · 2 H ₂ O	48	>99	91
5	FeCl ₃	12	>99	96
6	Rh ₂ (cap) ₄	48	>99	95
7	RuCl ₂ (PPh ₃) ₃	48	50	26
8	CoBr ₂	48	60	n.d.
9	NiCl ₂	48	10	n.d.
10	Pd(OAc) ₂	48	0	—
11	Pd(CO ₂ CF ₃) ₂	48	traces	n.d.
12	Pd(CO ₂ CF ₃) ₂ + ZnOTf ₂ (10 mol%)	48	traces	n.d.

^aAll reactions were conducted on a 0.1–0.2 mmol scale at a concentration of 0.1 M. ^bConversion was monitored by TLC and LC-MS analysis. ^cYields refers to isolated product after purification by flash chromatography on silica gel.

Table S2: Screening of Peroxides^a

entry	peroxide	conversion [%] ^b	yield [%] ^c
1	<i>t</i> -BuOOH	>99	92
2	AcOOH	0	—
3	H ₂ O ₂	0	—
4	O ₂ (1 atm)	0	—
5	<i>t</i> -BuOO <i>t</i> -Bu	0	—
6	<i>t</i> -BuOOBz	0	—
7	BzOOBz	0	—

^aAll reactions were conducted on a 0.1–0.2 mmol scale at a concentration of 0.1 M. ^bConversion was monitored by TLC and LC-MS analysis. ^cYield refers to isolated product after purification by flash chromatography on silica gel.

Table S3: Screening of Solvents^a

entry	solvent	time [h]	conversion [%] ^b	yield [%] ^c
1	CH_2Cl_2	48	>99	92
2	MeOH	48	>99	91
3	MeCN	24	>99	92
4	DMF	48	>99	80
5	DMSO	96	75	61
6	H_2O	96	traces	n.d.

^aAll reactions were conducted on a 0.1–0.2 mmol scale at a concentration of 0.1 M. ^bConversion was monitored by TLC and LC-MS analysis. ^cYield refers to isolated product after purification by flash chromatography on silica gel.

Figure S1: Direct Observation of the Isocyanate Intermediate by React IR Analysis. Baseline correction was not performed on the data, which shows rapid formation and consumption of the presumed 2-benzoylisocyanate intermediate, a known compound with a characteristic isocyanate IR band at $\nu = 2251 \text{ cm}^{-1}$ (▼: point of base addition).

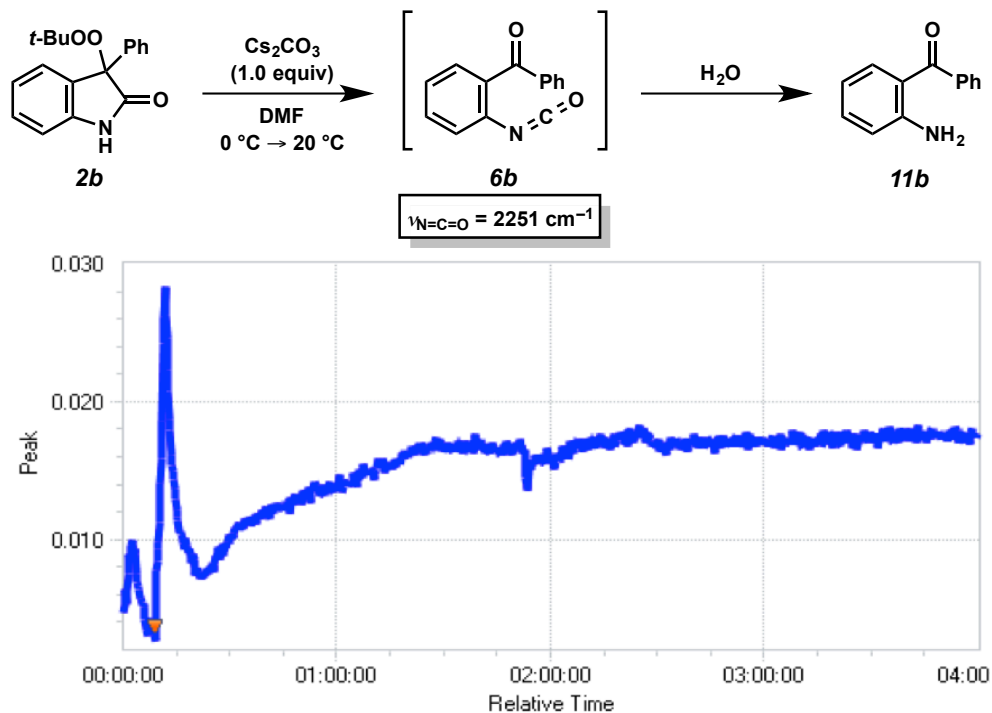


Table S4. Crystal Data and Structure Analysis Details for Peroxyoxindole 14a.

Empirical formula	C ₁₃ H ₁₇ N O ₃
Formula weight	235.27
Crystallization solvent	Et ₂ O / hexanes (2 drops of benzene)
Crystal shape	blade
Crystal color	colourless
Crystal size	0.10 x 0.16 x 0.41 mm

Data Collection

Preliminary photograph(s)	rotation
Type of diffractometer	Bruker APEX-II CCD
Wavelength	0.71073 Å MoK
Data collection temperature	100 K
Theta range for 9616 reflections used in lattice determination	2.20 to 27.49°
Unit cell dimensions	a = 16.7256(10) Å α = 90° b = 12.4161(7) Å β = 90° c = 25.1262(14) Å γ = 90°
Volume	5217.9(5) Å ³
Z	16
Crystal system	orthorhombic
Space group	P c a 21 (# 29)
Density (calculated)	1.198 g/cm ³
F(000)	2016
Theta range for data collection	2.0 to 29.5°
Completeness to theta = 25.000°	99.2%
Index ranges	-20 ≤ h ≤ 22, -16 ≤ k ≤ 15, -30 ≤ l ≤ 25
Data collection scan type	and scans
Reflections collected	41655
Independent reflections	10988 [R _{int} = 0.0560]
Reflections > 2 σ(I)	8290
Average σ(I)/(net I)	0.0680
Absorption coefficient	0.09 mm ⁻¹
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8792

Table S4 (cont.)**Structure Solution and Refinement**

Primary solution method	dual
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10988 / 1 / 629
Treatment of hydrogen atoms	mixed
Goodness-of-fit on F ²	1.01
Final R indices [I>2 (I), 8290 reflections]	R1 = 0.0452, wR2 = 0.0810
R indices (all data)	R1 = 0.0737, wR2 = 0.0890
Type of weighting scheme used	calc
Weighting scheme used	$w=1/[\sigma^2(F_o^2)+(0.0367P)^2+0.2379P]$ where $P=(F_o^2+2F_c^2)/3$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.6(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.21 and -0.23 e·Å ⁻³

Programs Used

Cell refinement	SAINT V8.34A (Bruker-AXS, 2007)
Data collection	APEX2 2011.2-3, APEX2 2013.2-0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.34A (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999), Olex2 (Dolomanov et al., 2009)

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for peroxyoxindole 14a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	-3313(1)	139(2)	-2141(1)	32(1)
O(2)	-2608(1)	-1216(1)	-2977(1)	21(1)
O(3)	-3108(1)	-2059(2)	-2724(1)	23(1)
N(1)	-4403(1)	-107(2)	-2686(1)	20(1)
C(1)	-3616(2)	-73(2)	-2572(1)	22(1)
C(2)	-3151(2)	-352(2)	-3085(1)	19(1)
C(3)	-3817(2)	-624(2)	-3469(1)	18(1)
C(4)	-3804(2)	-942(2)	-3993(1)	26(1)
C(5)	-4530(2)	-1147(3)	-4246(1)	32(1)
C(6)	-5244(2)	-1032(2)	-3971(1)	29(1)
C(7)	-5264(2)	-678(2)	-3450(1)	22(1)
C(8)	-4540(2)	-472(2)	-3208(1)	18(1)
C(9)	-2614(2)	571(2)	-3253(1)	31(1)
C(10)	-2796(2)	-3097(2)	-2896(1)	24(1)
C(11)	-2918(2)	-3256(3)	-3483(1)	34(1)
C(12)	-1930(2)	-3212(3)	-2732(1)	33(1)
C(13)	-3327(2)	-3857(3)	-2575(2)	43(1)
O(1B)	-4038(1)	-4583(2)	-288(1)	22(1)
O(2B)	-4737(1)	-4229(2)	794(1)	26(1)
O(3B)	-4110(1)	-3394(2)	840(1)	26(1)
N(1B)	-3045(1)	-5280(2)	242(1)	19(1)
C(1B)	-3801(2)	-4962(2)	132(1)	17(1)
C(2B)	-4319(2)	-5178(2)	634(1)	20(1)
C(3B)	-3701(2)	-5590(2)	1026(1)	21(1)
C(4B)	-3763(2)	-5924(2)	1546(1)	31(1)
C(5B)	-3079(2)	-6326(3)	1797(1)	37(1)
C(6B)	-2364(2)	-6404(2)	1529(1)	32(1)
C(7B)	-2290(2)	-6078(2)	1006(1)	26(1)
C(8B)	-2970(2)	-5665(2)	764(1)	18(1)
C(9B)	-4972(2)	-5998(2)	516(1)	25(1)
C(10B)	-4507(2)	-2359(2)	781(1)	26(1)
C(11B)	-5092(2)	-2197(3)	1242(1)	36(1)
C(12B)	-4920(2)	-2276(3)	249(1)	37(1)
C(13B)	-3801(2)	-1593(2)	816(1)	30(1)
O(1C)	-907(1)	-240(2)	-2271(1)	24(1)
O(2C)	38(1)	-1702(2)	-1588(1)	24(1)
O(3C)	-310(1)	-2599(2)	-1901(1)	24(1)
N(1C)	-1920(1)	-929(2)	-1754(1)	19(1)
C(1C)	-1152(2)	-705(2)	-1875(1)	17(1)
C(2C)	-628(2)	-1098(2)	-1405(1)	18(1)
C(3C)	-1229(2)	-1694(2)	-1066(1)	19(1)
C(4C)	-1144(2)	-2279(2)	-604(1)	26(1)
C(5C)	-1827(2)	-2690(3)	-358(1)	33(1)
C(6C)	-2571(2)	-2510(2)	-580(1)	33(1)
C(7C)	-2667(2)	-1928(2)	-1048(1)	25(1)
C(8C)	-1985(2)	-1528(2)	-1282(1)	18(1)
C(9C)	-250(2)	-139(2)	-1127(1)	25(1)

C(10C)	312(2)	-3413(2)	-1942(1)	21(1)
C(11C)	530(2)	-3828(3)	-1395(1)	30(1)
C(12C)	1030(2)	-2942(3)	-2231(1)	27(1)
C(13C)	-101(2)	-4275(2)	-2274(1)	30(1)
O(1D)	-6508(1)	-4768(2)	-179(1)	22(1)
O(2D)	-7479(1)	-3255(2)	-802(1)	20(1)
O(3D)	-7086(1)	-2418(2)	-469(1)	23(1)
N(1D)	-5521(1)	-4073(2)	-719(1)	19(1)
C(1D)	-6286(2)	-4295(2)	-579(1)	18(1)
C(2D)	-6838(2)	-3857(2)	-1023(1)	18(1)
C(3D)	-6258(2)	-3255(2)	-1373(1)	18(1)
C(4D)	-6367(2)	-2656(2)	-1827(1)	25(1)
C(5D)	-5699(2)	-2256(2)	-2094(1)	29(1)
C(6D)	-4937(2)	-2461(2)	-1901(1)	28(1)
C(7D)	-4819(2)	-3066(2)	-1444(1)	23(1)
C(8D)	-5488(2)	-3449(2)	-1186(1)	18(1)
C(9D)	-7246(2)	-4791(2)	-1307(1)	22(1)
C(10D)	-7648(2)	-1541(2)	-415(1)	21(1)
C(11D)	-7852(2)	-1069(3)	-952(1)	30(1)
C(12D)	-8394(2)	-1930(3)	-129(1)	28(1)
C(13D)	-7177(2)	-752(3)	-75(1)	36(1)

Table S6. Bond lengths [\AA] and angles [$^\circ$] for peroxyoxindole 14a.

O(1)-C(1)	1.225(4)	C(6B)-H(6B)	0.9500
O(2)-O(3)	1.484(3)	C(6B)-C(7B)	1.381(4)
O(2)-C(2)	1.431(3)	C(7B)-H(7B)	0.9500
O(3)-C(10)	1.456(3)	C(7B)-C(8B)	1.387(4)
N(1)-H(1)	0.8800	C(9B)-H(9D)	0.9800
N(1)-C(1)	1.348(4)	C(9B)-H(9E)	0.9800
N(1)-C(8)	1.406(4)	C(9B)-H(9F)	0.9800
C(1)-C(2)	1.544(4)	C(10B)-C(11B)	1.529(4)
C(2)-C(3)	1.513(4)	C(10B)-C(12B)	1.507(4)
C(2)-C(9)	1.515(4)	C(10B)-C(13B)	1.520(4)
C(3)-C(4)	1.373(4)	C(11B)-H(11D)	0.9800
C(3)-C(8)	1.390(4)	C(11B)-H(11E)	0.9800
C(4)-H(4)	0.9500	C(11B)-H(11F)	0.9800
C(4)-C(5)	1.394(4)	C(12B)-H(12D)	0.9800
C(5)-H(5)	0.9500	C(12B)-H(12E)	0.9800
C(5)-C(6)	1.386(4)	C(12B)-H(12F)	0.9800
C(6)-H(6)	0.9500	C(13B)-H(13D)	0.9800
C(6)-C(7)	1.382(4)	C(13B)-H(13E)	0.9800
C(7)-H(7)	0.9500	C(13B)-H(13F)	0.9800
C(7)-C(8)	1.380(4)	O(1C)-C(1C)	1.222(3)
C(9)-H(9A)	0.9800	O(2C)-O(3C)	1.482(3)
C(9)-H(9B)	0.9800	O(2C)-C(2C)	1.419(3)
C(9)-H(9C)	0.9800	O(3C)-C(10C)	1.454(3)
C(10)-C(11)	1.501(4)	N(1C)-H(1C)	0.8800
C(10)-C(12)	1.513(4)	N(1C)-C(1C)	1.348(3)
C(10)-C(13)	1.527(4)	N(1C)-C(8C)	1.404(4)
C(11)-H(11A)	0.9800	C(1C)-C(2C)	1.549(4)
C(11)-H(11B)	0.9800	C(2C)-C(3C)	1.511(4)
C(11)-H(11C)	0.9800	C(2C)-C(9C)	1.519(4)
C(12)-H(12A)	0.9800	C(3C)-C(4C)	1.375(4)
C(12)-H(12B)	0.9800	C(3C)-C(8C)	1.393(4)
C(12)-H(12C)	0.9800	C(4C)-H(4C)	0.9500
C(13)-H(13A)	0.9800	C(4C)-C(5C)	1.395(4)
C(13)-H(13B)	0.9800	C(5C)-H(5C)	0.9500
C(13)-H(13C)	0.9800	C(5C)-C(6C)	1.381(5)
O(1B)-C(1B)	1.222(3)	C(6C)-H(6C)	0.9500
O(2B)-O(3B)	1.479(3)	C(6C)-C(7C)	1.388(5)
O(2B)-C(2B)	1.429(3)	C(7C)-H(7C)	0.9500
O(3B)-C(10B)	1.455(3)	C(7C)-C(8C)	1.376(4)
N(1B)-H(1B)	0.8800	C(9C)-H(9G)	0.9800
N(1B)-C(1B)	1.353(3)	C(9C)-H(9H)	0.9800
N(1B)-C(8B)	1.402(4)	C(9C)-H(9I)	0.9800
C(1B)-C(2B)	1.551(4)	C(10C)-C(11C)	1.513(4)
C(2B)-C(3B)	1.518(4)	C(10C)-C(12C)	1.520(4)
C(2B)-C(9B)	1.522(4)	C(10C)-C(13C)	1.522(4)
C(3B)-C(4B)	1.374(4)	C(11C)-H(11G)	0.9800
C(3B)-C(8B)	1.392(4)	C(11C)-H(11H)	0.9800
C(4B)-H(4B)	0.9500	C(11C)-H(11I)	0.9800
C(4B)-C(5B)	1.398(5)	C(12C)-H(12G)	0.9800
C(5B)-H(5B)	0.9500	C(12C)-H(12H)	0.9800
C(5B)-C(6B)	1.375(5)	C(12C)-H(12I)	0.9800

C(13C)-H(13G)	0.9800	C(4)-C(3)-C(8)	120.4(3)
C(13C)-H(13H)	0.9800	C(8)-C(3)-C(2)	108.0(2)
C(13C)-H(13I)	0.9800	C(3)-C(4)-H(4)	120.8
O(1D)-C(1D)	1.221(3)	C(3)-C(4)-C(5)	118.4(3)
O(2D)-O(3D)	1.488(3)	C(5)-C(4)-H(4)	120.8
O(2D)-C(2D)	1.420(3)	C(4)-C(5)-H(5)	119.8
O(3D)-C(10D)	1.445(3)	C(6)-C(5)-C(4)	120.4(3)
N(1D)-H(1D)	0.8800	C(6)-C(5)-H(5)	119.8
N(1D)-C(1D)	1.356(3)	C(5)-C(6)-H(6)	119.2
N(1D)-C(8D)	1.406(4)	C(7)-C(6)-C(5)	121.6(3)
C(1D)-C(2D)	1.546(4)	C(7)-C(6)-H(6)	119.2
C(2D)-C(3D)	1.509(4)	C(6)-C(7)-H(7)	121.4
C(2D)-C(9D)	1.523(4)	C(8)-C(7)-C(6)	117.1(3)
C(3D)-C(4D)	1.374(4)	C(8)-C(7)-H(7)	121.4
C(3D)-C(8D)	1.392(4)	C(3)-C(8)-N(1)	110.1(2)
C(4D)-H(4D)	0.9500	C(7)-C(8)-N(1)	127.9(3)
C(4D)-C(5D)	1.395(4)	C(7)-C(8)-C(3)	122.0(3)
C(5D)-H(5D)	0.9500	C(2)-C(9)-H(9A)	109.5
C(5D)-C(6D)	1.387(4)	C(2)-C(9)-H(9B)	109.5
C(6D)-H(6D)	0.9500	C(2)-C(9)-H(9C)	109.5
C(6D)-C(7D)	1.385(4)	H(9A)-C(9)-H(9B)	109.5
C(7D)-H(7D)	0.9500	H(9A)-C(9)-H(9C)	109.5
C(7D)-C(8D)	1.379(4)	H(9B)-C(9)-H(9C)	109.5
C(9D)-H(9J)	0.9800	O(3)-C(10)-C(11)	111.1(2)
C(9D)-H(9K)	0.9800	O(3)-C(10)-C(12)	110.2(2)
C(9D)-H(9L)	0.9800	O(3)-C(10)-C(13)	100.5(2)
C(10D)-C(11D)	1.512(4)	C(11)-C(10)-C(12)	112.7(3)
C(10D)-C(12D)	1.520(4)	C(11)-C(10)-C(13)	111.1(3)
C(10D)-C(13D)	1.519(4)	C(12)-C(10)-C(13)	110.7(3)
C(11D)-H(11J)	0.9800	C(10)-C(11)-H(11A)	109.5
C(11D)-H(11K)	0.9800	C(10)-C(11)-H(11B)	109.5
C(11D)-H(11L)	0.9800	C(10)-C(11)-H(11C)	109.5
C(12D)-H(12J)	0.9800	H(11A)-C(11)-H(11B)	109.5
C(12D)-H(12K)	0.9800	H(11A)-C(11)-H(11C)	109.5
C(12D)-H(12L)	0.9800	H(11B)-C(11)-H(11C)	109.5
C(13D)-H(13J)	0.9800	C(10)-C(12)-H(12A)	109.5
C(13D)-H(13K)	0.9800	C(10)-C(12)-H(12B)	109.5
C(13D)-H(13L)	0.9800	C(10)-C(12)-H(12C)	109.5
		H(12A)-C(12)-H(12B)	109.5
C(2)-O(2)-O(3)	104.58(17)	H(12A)-C(12)-H(12C)	109.5
C(10)-O(3)-O(2)	107.20(17)	H(12B)-C(12)-H(12C)	109.5
C(1)-N(1)-H(1)	124.2	C(10)-C(13)-H(13A)	109.5
C(1)-N(1)-C(8)	111.5(2)	C(10)-C(13)-H(13B)	109.5
C(8)-N(1)-H(1)	124.2	C(10)-C(13)-H(13C)	109.5
O(1)-C(1)-N(1)	126.7(3)	H(13A)-C(13)-H(13B)	109.5
O(1)-C(1)-C(2)	125.3(3)	H(13A)-C(13)-H(13C)	109.5
N(1)-C(1)-C(2)	107.9(3)	H(13B)-C(13)-H(13C)	109.5
O(2)-C(2)-C(1)	109.3(2)	C(2B)-O(2B)-O(3B)	104.56(17)
O(2)-C(2)-C(3)	114.9(2)	C(10B)-O(3B)-O(2B)	106.68(18)
O(2)-C(2)-C(9)	104.1(2)	C(1B)-N(1B)-H(1B)	124.0
C(3)-C(2)-C(1)	102.2(2)	C(1B)-N(1B)-C(8B)	111.9(2)
C(3)-C(2)-C(9)	115.2(3)	C(8B)-N(1B)-H(1B)	124.0
C(9)-C(2)-C(1)	111.2(2)	O(1B)-C(1B)-N(1B)	126.2(3)
C(4)-C(3)-C(2)	131.7(3)	O(1B)-C(1B)-C(2B)	126.0(3)

N(1B)-C(1B)-C(2B)	107.8(3)	H(13E)-C(13B)-H(13F)	109.5
O(2B)-C(2B)-C(1B)	111.2(2)	C(2C)-O(2C)-O(3C)	105.07(17)
O(2B)-C(2B)-C(3B)	115.3(2)	C(10C)-O(3C)-O(2C)	106.16(17)
O(2B)-C(2B)-C(9B)	104.7(2)	C(1C)-N(1C)-H(1C)	124.0
C(3B)-C(2B)-C(1B)	101.9(2)	C(1C)-N(1C)-C(8C)	111.9(2)
C(3B)-C(2B)-C(9B)	112.9(2)	C(8C)-N(1C)-H(1C)	124.0
C(9B)-C(2B)-C(1B)	111.0(2)	O(1C)-C(1C)-N(1C)	126.9(3)
C(4B)-C(3B)-C(2B)	132.0(3)	O(1C)-C(1C)-C(2C)	125.4(2)
C(4B)-C(3B)-C(8B)	119.7(3)	N(1C)-C(1C)-C(2C)	107.7(2)
C(8B)-C(3B)-C(2B)	108.2(2)	O(2C)-C(2C)-C(1C)	111.4(2)
C(3B)-C(4B)-H(4B)	120.8	O(2C)-C(2C)-C(3C)	116.5(2)
C(3B)-C(4B)-C(5B)	118.3(3)	O(2C)-C(2C)-C(9C)	103.7(2)
C(5B)-C(4B)-H(4B)	120.8	C(3C)-C(2C)-C(1C)	102.0(2)
C(4B)-C(5B)-H(5B)	119.5	C(3C)-C(2C)-C(9C)	113.6(2)
C(6B)-C(5B)-C(4B)	121.1(3)	C(9C)-C(2C)-C(1C)	109.9(2)
C(6B)-C(5B)-H(5B)	119.5	C(4C)-C(3C)-C(2C)	131.8(3)
C(5B)-C(6B)-H(6B)	119.2	C(4C)-C(3C)-C(8C)	120.0(3)
C(5B)-C(6B)-C(7B)	121.5(3)	C(8C)-C(3C)-C(2C)	108.2(2)
C(7B)-C(6B)-H(6B)	119.2	C(3C)-C(4C)-H(4C)	120.6
C(6B)-C(7B)-H(7B)	121.6	C(3C)-C(4C)-C(5C)	118.9(3)
C(6B)-C(7B)-C(8B)	116.8(3)	C(5C)-C(4C)-H(4C)	120.6
C(8B)-C(7B)-H(7B)	121.6	C(4C)-C(5C)-H(5C)	120.0
C(3B)-C(8B)-N(1B)	109.9(2)	C(6C)-C(5C)-C(4C)	120.0(3)
C(7B)-C(8B)-N(1B)	127.5(3)	C(6C)-C(5C)-H(5C)	120.0
C(7B)-C(8B)-C(3B)	122.5(3)	C(5C)-C(6C)-H(6C)	119.0
C(2B)-C(9B)-H(9D)	109.5	C(5C)-C(6C)-C(7C)	122.0(3)
C(2B)-C(9B)-H(9E)	109.5	C(7C)-C(6C)-H(6C)	119.0
C(2B)-C(9B)-H(9F)	109.5	C(6C)-C(7C)-H(7C)	121.5
H(9D)-C(9B)-H(9E)	109.5	C(8C)-C(7C)-C(6C)	117.0(3)
H(9D)-C(9B)-H(9F)	109.5	C(8C)-C(7C)-H(7C)	121.5
H(9E)-C(9B)-H(9F)	109.5	C(3C)-C(8C)-N(1C)	109.7(2)
O(3B)-C(10B)-C(11B)	109.4(2)	C(7C)-C(8C)-N(1C)	128.1(3)
O(3B)-C(10B)-C(12B)	111.0(2)	C(7C)-C(8C)-C(3C)	122.1(3)
O(3B)-C(10B)-C(13B)	101.0(2)	C(2C)-C(9C)-H(9G)	109.5
C(12B)-C(10B)-C(11B)	111.7(3)	C(2C)-C(9C)-H(9H)	109.5
C(12B)-C(10B)-C(13B)	111.4(3)	C(2C)-C(9C)-H(9I)	109.5
C(13B)-C(10B)-C(11B)	111.8(3)	H(9G)-C(9C)-H(9H)	109.5
C(10B)-C(11B)-H(11D)	109.5	H(9G)-C(9C)-H(9I)	109.5
C(10B)-C(11B)-H(11E)	109.5	H(9H)-C(9C)-H(9I)	109.5
C(10B)-C(11B)-H(11F)	109.5	O(3C)-C(10C)-C(11C)	110.1(2)
H(11D)-C(11B)-H(11E)	109.5	O(3C)-C(10C)-C(12C)	109.4(2)
H(11D)-C(11B)-H(11F)	109.5	O(3C)-C(10C)-C(13C)	101.7(2)
H(11E)-C(11B)-H(11F)	109.5	C(11C)-C(10C)-C(12C)	112.0(2)
C(10B)-C(12B)-H(12D)	109.5	C(11C)-C(10C)-C(13C)	111.5(2)
C(10B)-C(12B)-H(12E)	109.5	C(12C)-C(10C)-C(13C)	111.6(3)
C(10B)-C(12B)-H(12F)	109.5	C(10C)-C(11C)-H(11G)	109.5
H(12D)-C(12B)-H(12E)	109.5	C(10C)-C(11C)-H(11H)	109.5
H(12D)-C(12B)-H(12F)	109.5	C(10C)-C(11C)-H(11I)	109.5
H(12E)-C(12B)-H(12F)	109.5	H(11G)-C(11C)-H(11H)	109.5
C(10B)-C(13B)-H(13D)	109.5	H(11G)-C(11C)-H(11I)	109.5
C(10B)-C(13B)-H(13E)	109.5	H(11H)-C(11C)-H(11I)	109.5
C(10B)-C(13B)-H(13F)	109.5	C(10C)-C(12C)-H(12G)	109.5
H(13D)-C(13B)-H(13E)	109.5	C(10C)-C(12C)-H(12H)	109.5
H(13D)-C(13B)-H(13F)	109.5	C(10C)-C(12C)-H(12I)	109.5

H(12G)-C(12C)-H(12H)	109.5	C(8D)-C(7D)-C(6D)	117.5(3)
H(12G)-C(12C)-H(12I)	109.5	C(8D)-C(7D)-H(7D)	121.3
H(12H)-C(12C)-H(12I)	109.5	C(3D)-C(8D)-N(1D)	110.0(2)
C(10C)-C(13C)-H(13G)	109.5	C(7D)-C(8D)-N(1D)	127.9(3)
C(10C)-C(13C)-H(13H)	109.5	C(7D)-C(8D)-C(3D)	122.1(3)
C(10C)-C(13C)-H(13I)	109.5	C(2D)-C(9D)-H(9J)	109.5
H(13G)-C(13C)-H(13H)	109.5	C(2D)-C(9D)-H(9K)	109.5
H(13G)-C(13C)-H(13I)	109.5	C(2D)-C(9D)-H(9L)	109.5
H(13H)-C(13C)-H(13I)	109.5	H(9J)-C(9D)-H(9K)	109.5
C(2D)-O(2D)-O(3D)	104.68(18)	H(9J)-C(9D)-H(9L)	109.5
C(10D)-O(3D)-O(2D)	106.97(18)	H(9K)-C(9D)-H(9L)	109.5
C(1D)-N(1D)-H(1D)	124.3	O(3D)-C(10D)-C(11D)	110.8(2)
C(1D)-N(1D)-C(8D)	111.4(2)	O(3D)-C(10D)-C(12D)	109.9(2)
C(8D)-N(1D)-H(1D)	124.3	O(3D)-C(10D)-C(13D)	101.7(2)
O(1D)-C(1D)-N(1D)	126.7(3)	C(11D)-C(10D)-C(12D)	111.0(2)
O(1D)-C(1D)-C(2D)	125.5(2)	C(11D)-C(10D)-C(13D)	111.7(2)
N(1D)-C(1D)-C(2D)	107.8(2)	C(13D)-C(10D)-C(12D)	111.4(2)
O(2D)-C(2D)-C(1D)	110.8(2)	C(10D)-C(11D)-H(11J)	109.5
O(2D)-C(2D)-C(3D)	116.9(2)	C(10D)-C(11D)-H(11K)	109.5
O(2D)-C(2D)-C(9D)	104.2(2)	C(10D)-C(11D)-H(11L)	109.5
C(3D)-C(2D)-C(1D)	102.2(2)	H(11J)-C(11D)-H(11K)	109.5
C(3D)-C(2D)-C(9D)	113.1(2)	H(11J)-C(11D)-H(11L)	109.5
C(9D)-C(2D)-C(1D)	109.7(2)	H(11K)-C(11D)-H(11L)	109.5
C(4D)-C(3D)-C(2D)	131.9(3)	C(10D)-C(12D)-H(12J)	109.5
C(4D)-C(3D)-C(8D)	119.8(3)	C(10D)-C(12D)-H(12K)	109.5
C(8D)-C(3D)-C(2D)	108.1(2)	C(10D)-C(12D)-H(12L)	109.5
C(3D)-C(4D)-H(4D)	120.5	H(12J)-C(12D)-H(12K)	109.5
C(3D)-C(4D)-C(5D)	119.1(3)	H(12J)-C(12D)-H(12L)	109.5
C(5D)-C(4D)-H(4D)	120.5	H(12K)-C(12D)-H(12L)	109.5
C(4D)-C(5D)-H(5D)	119.9	C(10D)-C(13D)-H(13J)	109.5
C(6D)-C(5D)-C(4D)	120.2(3)	C(10D)-C(13D)-H(13K)	109.5
C(6D)-C(5D)-H(5D)	119.9	C(10D)-C(13D)-H(13L)	109.5
C(5D)-C(6D)-H(6D)	119.3	H(13J)-C(13D)-H(13K)	109.5
C(7D)-C(6D)-C(5D)	121.4(3)	H(13J)-C(13D)-H(13L)	109.5
C(7D)-C(6D)-H(6D)	119.3	H(13K)-C(13D)-H(13L)	109.5
C(6D)-C(7D)-H(7D)	121.3		

Table S7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for peroxyoxindole 14a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	291(11)	387(14)	271(14)	-139(11)	-130(10)	138(10)
O(2)	160(9)	152(10)	321(12)	29(9)	36(9)	10(8)
O(3)	217(10)	177(11)	304(12)	40(9)	86(9)	28(8)
N(1)	175(12)	248(14)	163(15)	-39(11)	-1(11)	53(10)
C(1)	238(15)	159(16)	260(20)	-9(14)	-59(15)	51(12)
C(2)	185(14)	135(15)	246(19)	-17(14)	5(13)	7(11)
C(3)	239(15)	133(14)	172(18)	8(13)	1(13)	16(11)
C(4)	326(17)	213(17)	230(20)	38(15)	31(14)	27(13)
C(5)	520(20)	270(18)	158(18)	-74(15)	-83(16)	37(15)
C(6)	340(18)	231(18)	310(20)	-10(15)	-138(15)	9(14)
C(7)	200(14)	195(16)	262(19)	29(14)	-40(13)	-7(12)
C(8)	234(14)	137(15)	166(17)	18(13)	-31(13)	10(11)
C(9)	260(16)	223(17)	440(20)	54(16)	33(15)	-15(13)
C(10)	224(15)	144(16)	350(20)	-14(14)	31(13)	37(12)
C(11)	367(18)	211(17)	430(20)	-61(16)	-28(16)	-29(14)
C(12)	276(16)	253(19)	460(20)	-18(16)	-29(16)	107(13)
C(13)	430(20)	211(19)	660(30)	104(18)	168(18)	51(15)
O(1B)	179(10)	275(12)	220(13)	34(10)	-25(9)	14(8)
O(2B)	161(10)	162(11)	449(14)	-13(10)	75(10)	2(8)
O(3B)	203(10)	162(11)	420(13)	-41(10)	0(10)	-4(8)
N(1B)	160(12)	232(13)	170(15)	-7(12)	19(10)	48(10)
C(1B)	176(14)	124(15)	210(20)	-33(13)	10(13)	-7(11)
C(2B)	194(14)	131(15)	270(20)	-35(13)	23(13)	0(11)
C(3B)	273(16)	150(15)	201(19)	-43(14)	14(13)	-4(12)
C(4B)	430(20)	254(18)	260(20)	13(16)	62(16)	-33(14)
C(5B)	600(20)	296(19)	210(20)	35(16)	-37(18)	-32(17)
C(6B)	470(20)	219(18)	280(20)	33(15)	-134(17)	40(15)
C(7B)	318(17)	170(16)	280(20)	-60(14)	-58(14)	40(13)
C(8B)	266(15)	102(14)	175(18)	-39(13)	0(13)	-3(11)
C(9B)	210(15)	206(16)	336(19)	-9(15)	40(14)	-23(12)
C(10B)	255(15)	151(16)	370(20)	-71(15)	-17(15)	42(12)
C(11B)	283(17)	275(19)	510(20)	-116(17)	56(16)	28(14)
C(12B)	378(19)	265(19)	470(20)	-64(16)	-136(17)	57(14)
C(13B)	279(16)	193(17)	440(20)	-41(15)	-1(15)	4(13)
O(1C)	250(11)	274(12)	207(13)	31(10)	21(10)	-43(9)
O(2C)	160(10)	228(12)	343(13)	-118(10)	-34(9)	12(8)
O(3C)	164(10)	224(11)	323(13)	-120(10)	-66(9)	34(8)
N(1C)	144(11)	205(13)	220(15)	35(12)	1(10)	12(10)
C(1C)	181(14)	143(15)	198(18)	-38(13)	14(13)	5(11)
C(2C)	150(13)	184(15)	201(17)	-45(13)	2(12)	21(11)
C(3C)	213(15)	171(15)	179(18)	-54(13)	13(13)	12(11)
C(4C)	376(18)	202(16)	202(19)	-18(14)	-37(15)	67(13)
C(5C)	540(20)	213(18)	220(20)	10(15)	51(16)	18(15)
C(6C)	406(19)	187(17)	390(20)	-38(16)	182(17)	-70(14)
C(7C)	232(15)	217(17)	310(20)	-28(15)	54(14)	-22(12)
C(8C)	227(14)	127(15)	180(17)	-40(13)	21(12)	1(11)
C(9C)	227(16)	245(17)	280(20)	-64(15)	-28(14)	-3(13)

C(10C)	156(13)	193(16)	267(19)	-26(14)	-1(13)	46(11)
C(11C)	283(16)	297(18)	317(19)	61(16)	-23(15)	0(14)
C(12C)	253(15)	274(17)	290(20)	-23(15)	79(14)	42(13)
C(13C)	236(15)	263(18)	390(20)	-76(16)	-9(15)	70(13)
O(1D)	180(10)	275(11)	216(13)	43(10)	8(9)	9(8)
O(2D)	156(9)	204(11)	234(12)	-88(9)	-35(8)	30(8)
O(3D)	187(10)	244(11)	262(12)	-127(10)	-60(9)	26(8)
N(1D)	136(11)	207(14)	219(15)	21(12)	-14(10)	3(10)
C(1D)	185(14)	158(15)	189(18)	-56(14)	10(12)	4(11)
C(2D)	174(14)	189(15)	179(17)	-15(13)	9(12)	23(12)
C(3D)	210(14)	181(15)	165(17)	-52(13)	1(13)	1(11)
C(4D)	287(16)	255(18)	195(18)	-37(15)	8(14)	12(13)
C(5D)	415(19)	215(17)	232(19)	31(14)	63(16)	-8(14)
C(6D)	354(18)	192(17)	300(20)	-2(15)	95(16)	-56(14)
C(7D)	188(14)	220(17)	290(20)	-37(15)	46(13)	-36(12)
C(8D)	219(14)	131(15)	193(18)	-47(13)	6(12)	7(11)
C(9D)	193(15)	243(17)	230(20)	-38(14)	-34(14)	-18(12)
C(10D)	245(15)	182(15)	203(18)	-16(14)	48(13)	29(12)
C(11D)	407(19)	208(17)	290(19)	10(15)	31(15)	-15(14)
C(12D)	303(16)	267(17)	255(19)	1(15)	78(14)	57(13)
C(13D)	400(19)	300(19)	380(20)	-128(16)	7(16)	-5(15)

Table S8. Hydrogen coordinates ($\times 10^3$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for peroxyindole 14a.

	x	y	z	U_{iso}
H(1)	-478	8	-246	23
H(4)	-331	-102	-418	31
H(5)	-454	-137	-461	38
H(6)	-573	-120	-415	35
H(7)	-576	-58	-327	26
H(9A)	-231	36	-357	46
H(9B)	-224	74	-296	46
H(9C)	-294	120	-334	46
H(11A)	-274	-398	-358	50
H(11B)	-261	-272	-368	50
H(11C)	-349	-318	-357	50
H(12A)	-188	-311	-235	50
H(12B)	-161	-267	-292	50
H(12C)	-174	-393	-283	50
H(13A)	-325	-372	-219	65
H(13B)	-319	-460	-266	65
H(13C)	-389	-373	-267	65
H(1B)	-265	-525	1	22
H(4B)	-426	-588	173	37
H(5B)	-311	-655	216	44
H(6B)	-191	-669	171	38
H(7B)	-180	-613	82	31
H(9D)	-527	-615	84	38
H(9E)	-473	-667	39	38
H(9F)	-533	-571	24	38
H(11D)	-550	-276	123	53
H(11E)	-534	-149	121	53
H(11F)	-480	-225	158	53
H(12D)	-454	-243	-4	56
H(12E)	-513	-155	20	56
H(12F)	-536	-280	24	56
H(13D)	-355	-165	117	46
H(13E)	-398	-85	76	46
H(13F)	-341	-178	54	46
H(1C)	-233	-72	-195	23
H(4C)	-63	-240	-46	31
H(5C)	-178	-309	-4	39
H(6C)	-303	-279	-41	39
H(7C)	-318	-181	-120	30
H(9G)	13	21	-137	38
H(9H)	3	-38	-81	38
H(9I)	-67	38	-103	38
H(11G)	4	-402	-120	45
H(11H)	82	-327	-120	45
H(11I)	87	-447	-143	45
H(12G)	126	-236	-202	41
H(12H)	86	-265	-257	41

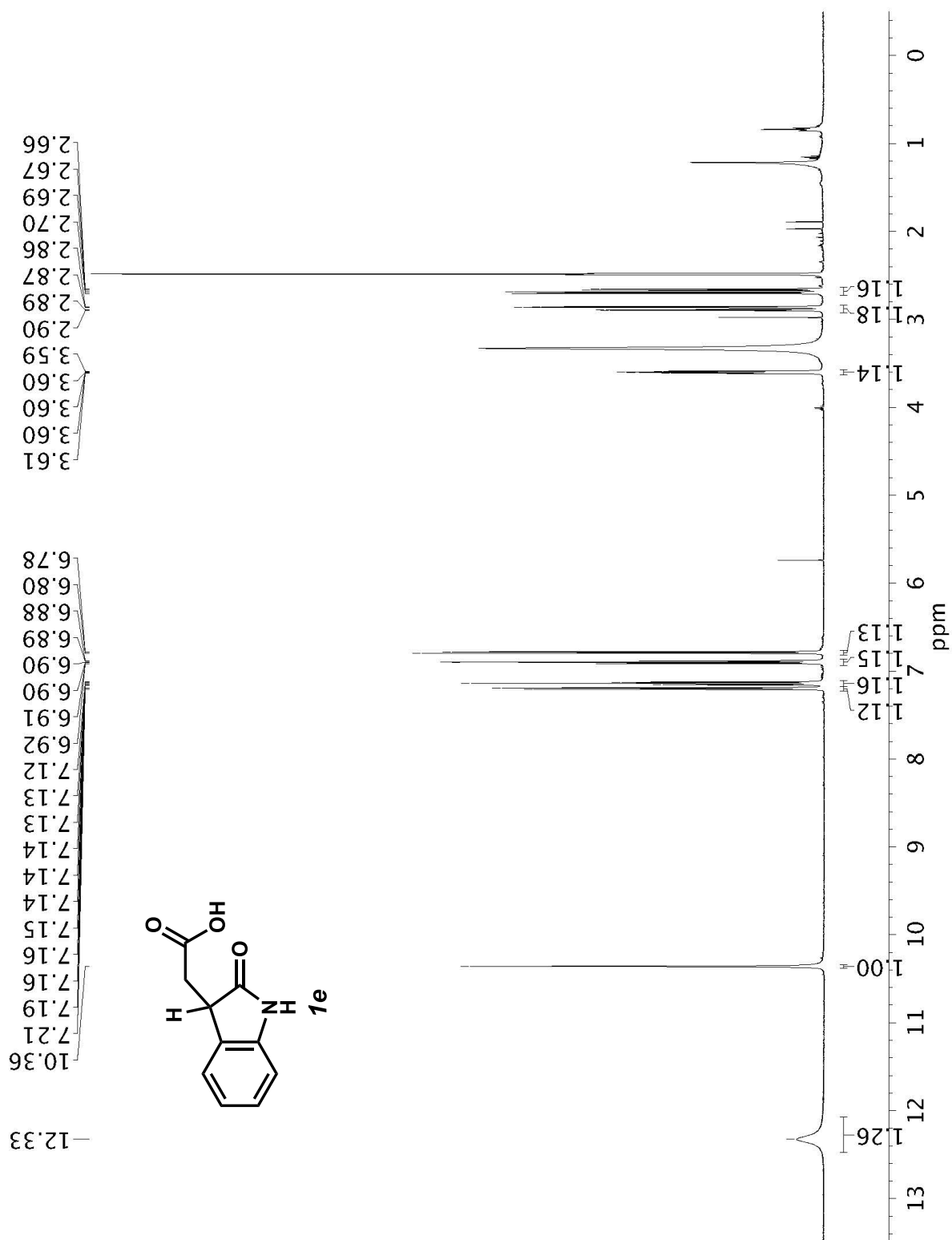
H(12I)	143	-351	-229	41
H(13G)	-25	-397	-262	44
H(13H)	-58	-452	-209	44
H(13I)	26	-488	-233	44
H(1D)	-510	-429	-54	22
H(4D)	-689	-252	-196	29
H(5D)	-576	-184	-241	34
H(6D)	-449	-218	-208	34
H(7D)	-430	-321	-132	28
H(9J)	-759	-518	-106	33
H(9K)	-684	-528	-145	33
H(9L)	-757	-451	-160	33
H(11J)	-815	-40	-90	45
H(11K)	-818	-158	-115	45
H(11L)	-736	-92	-115	45
H(12J)	-825	-222	22	41
H(12K)	-865	-249	-34	41
H(12L)	-876	-133	-8	41
H(13J)	-702	-110	26	54
H(13K)	-751	-12	1	54
H(13L)	-670	-52	-27	54

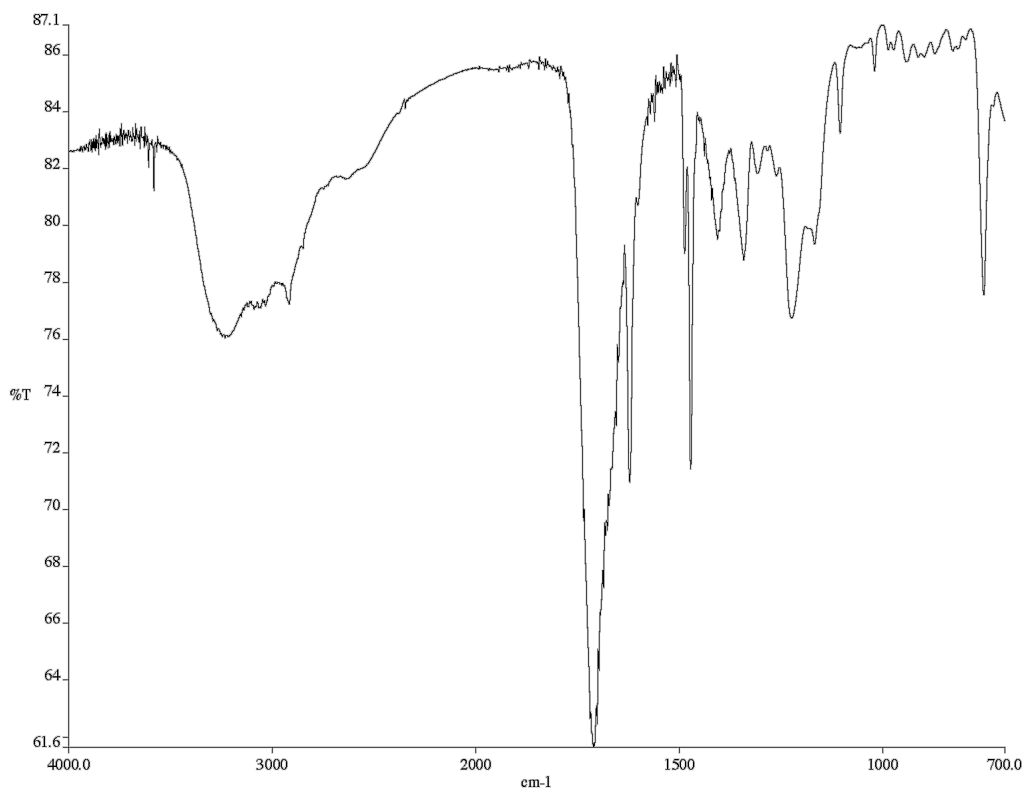
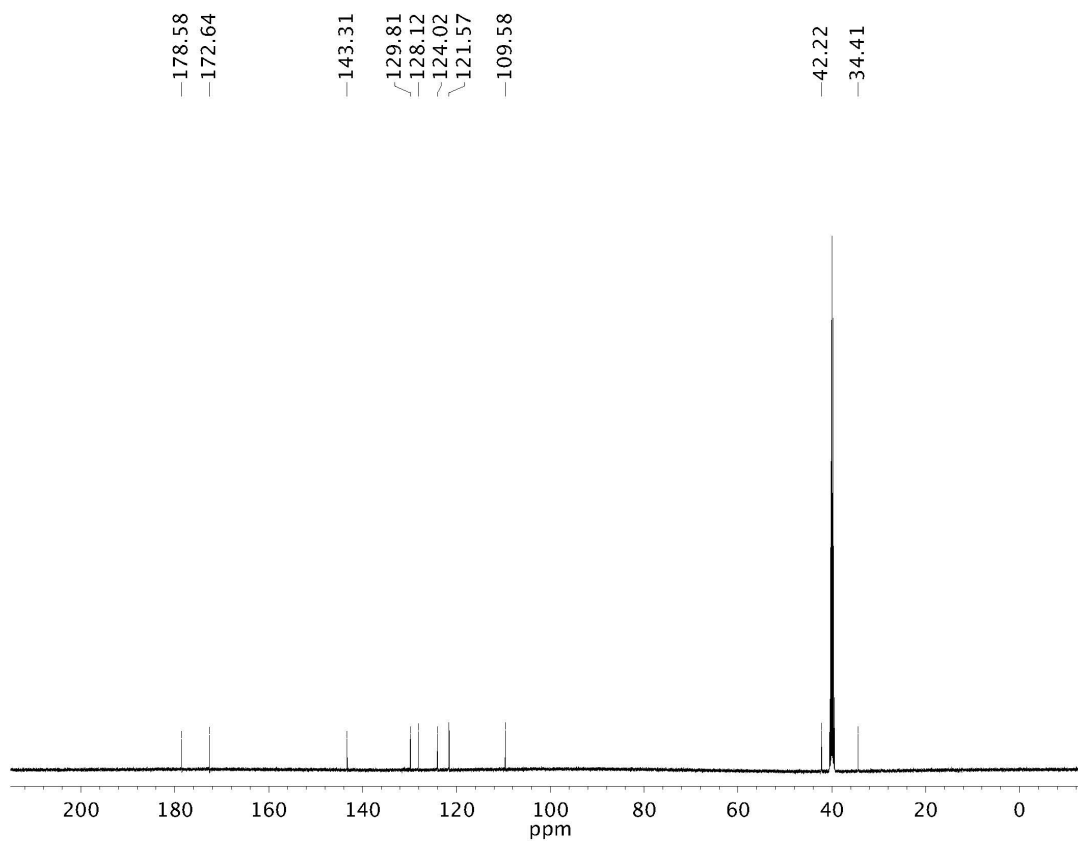
Table S9. Hydrogen bonds for peroxyoxindole 14a [\AA and $^\circ$].

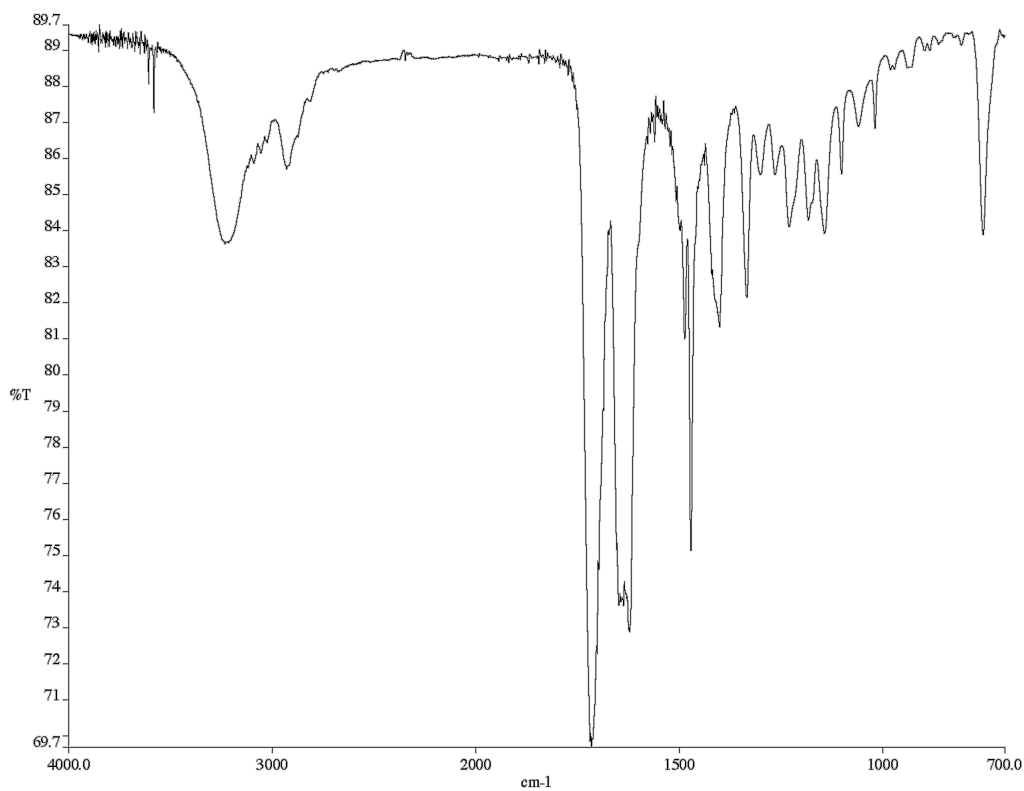
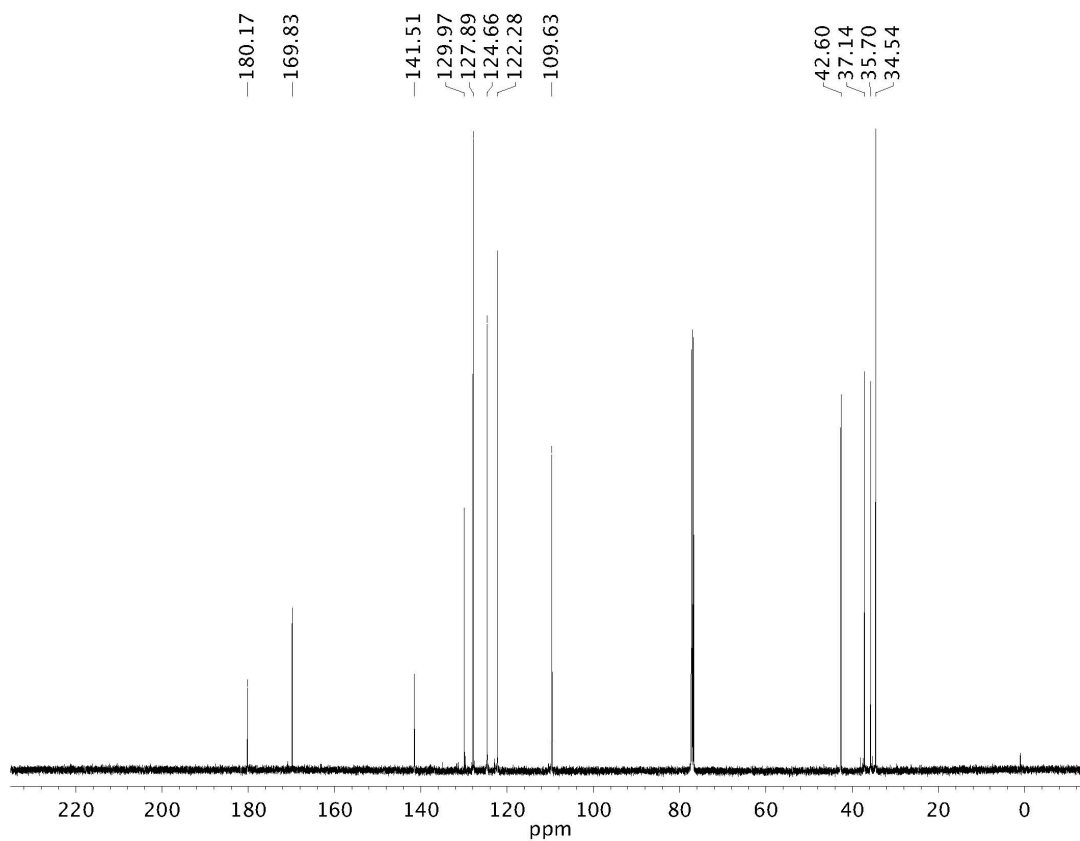
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1C)#1	0.88	1.95	2.758(3)	151.8
N(1B)-H(1B)...O(1D)#2	0.88	1.97	2.781(3)	153.2
N(1C)-H(1C)...O(1)	0.88	2.02	2.851(3)	157.2
N(1D)-H(1D)...O(1B)	0.88	1.92	2.779(3)	165.8

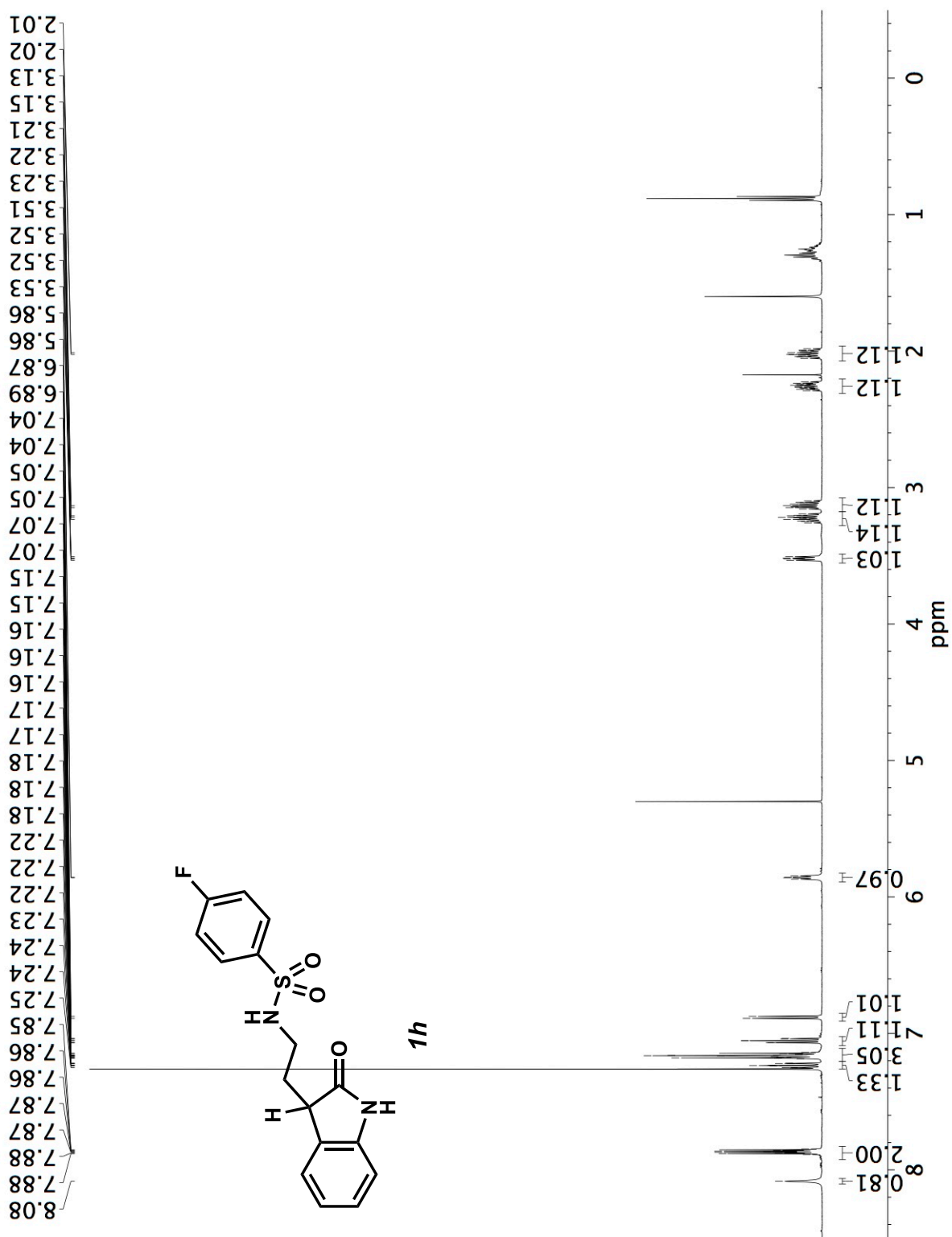
— Symmetry transformations used to generate equivalent atoms:

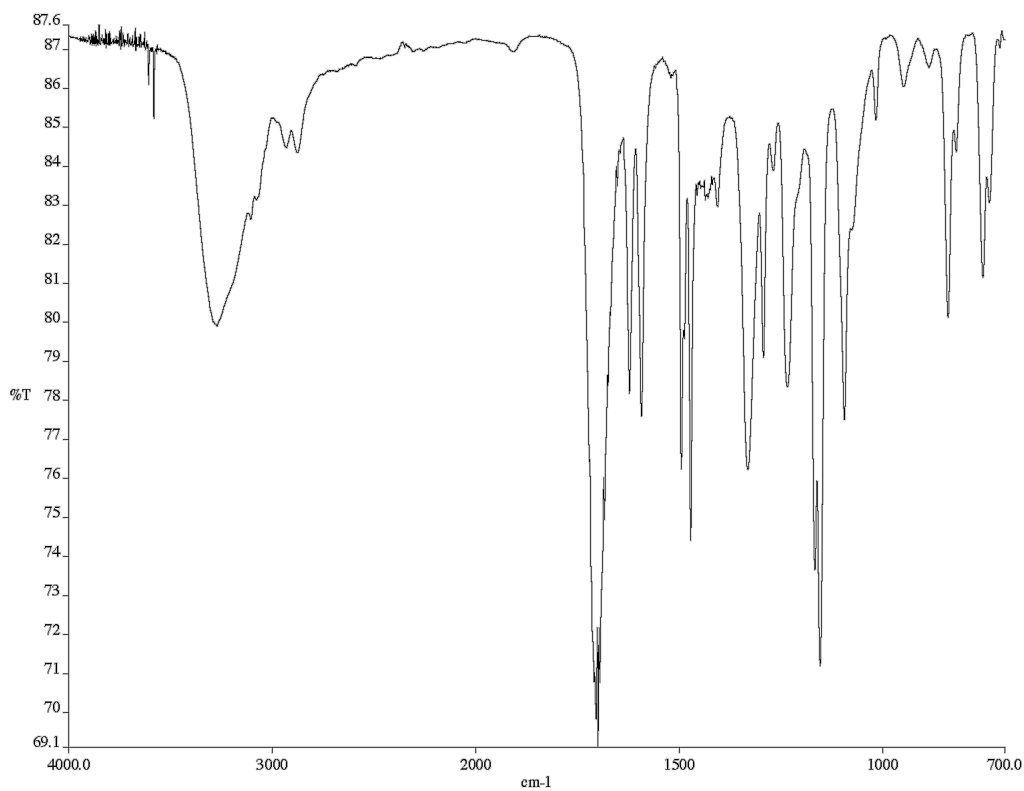
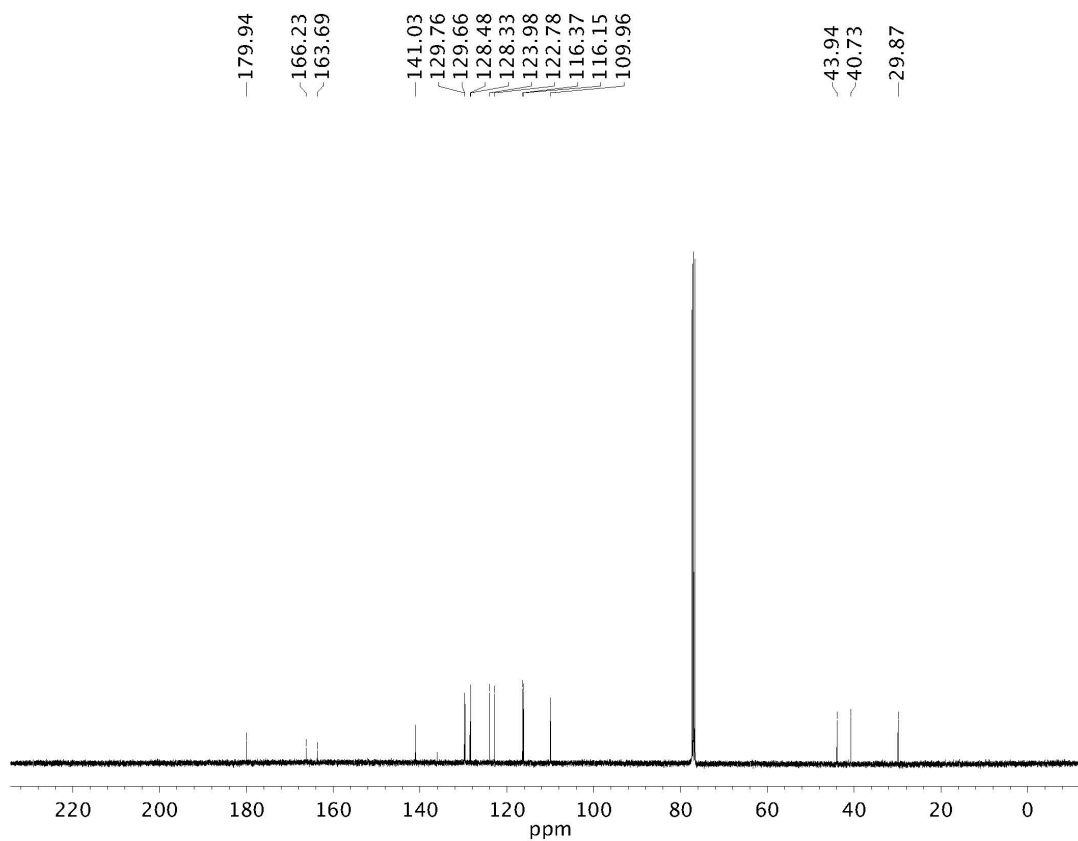
#1 $x-1/2, -y, z$ #2 $x+1/2, -y-1, z$

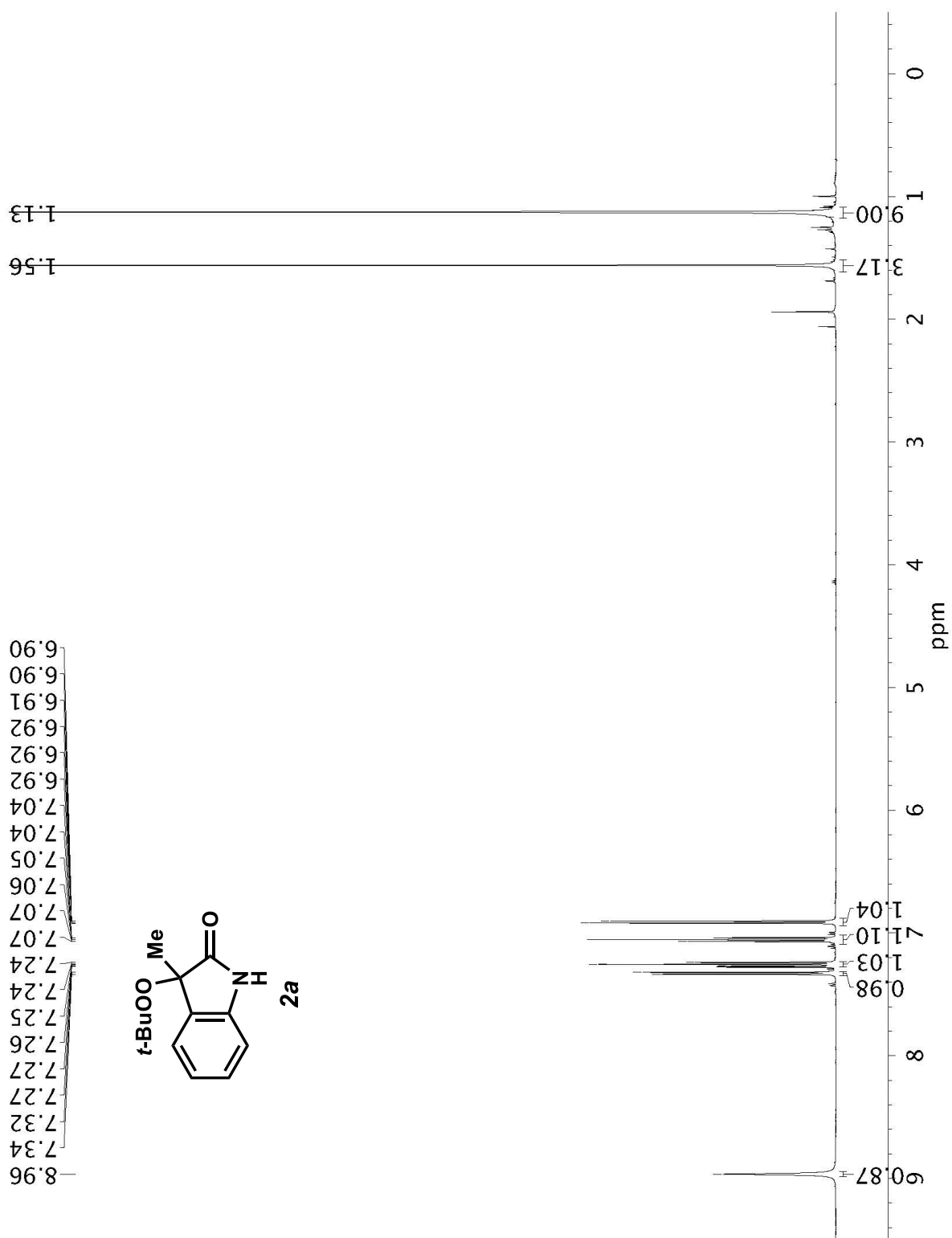
¹H NMR (500 MHz, DMSO) of compound 1e.

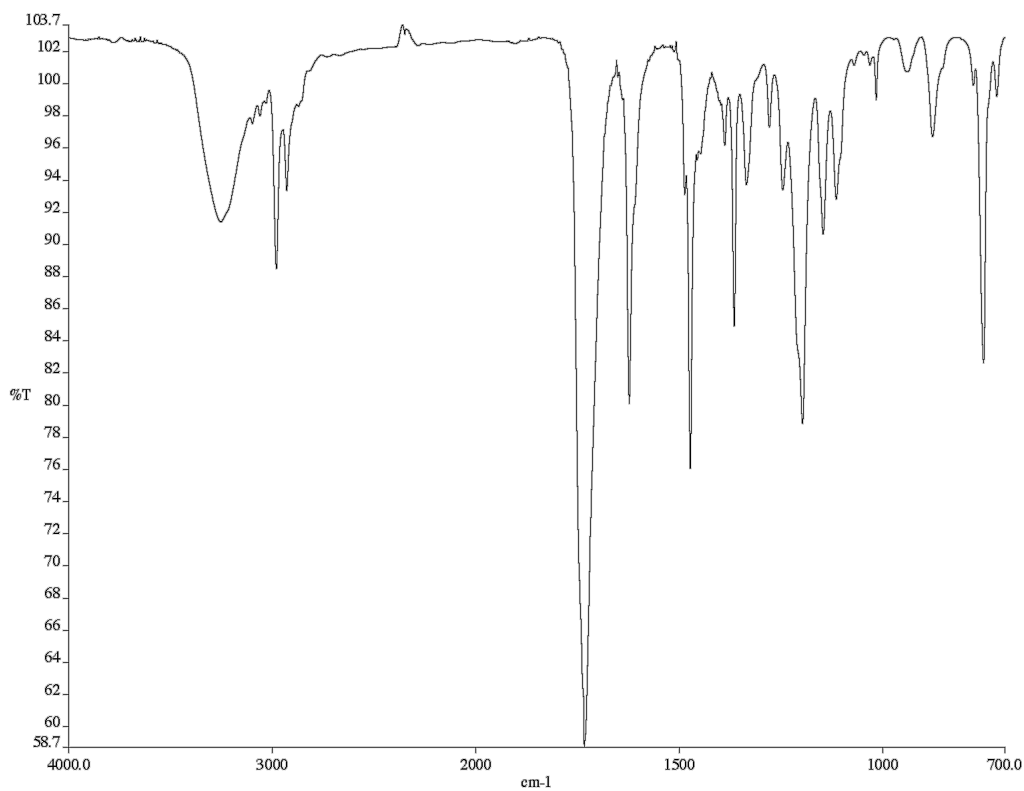
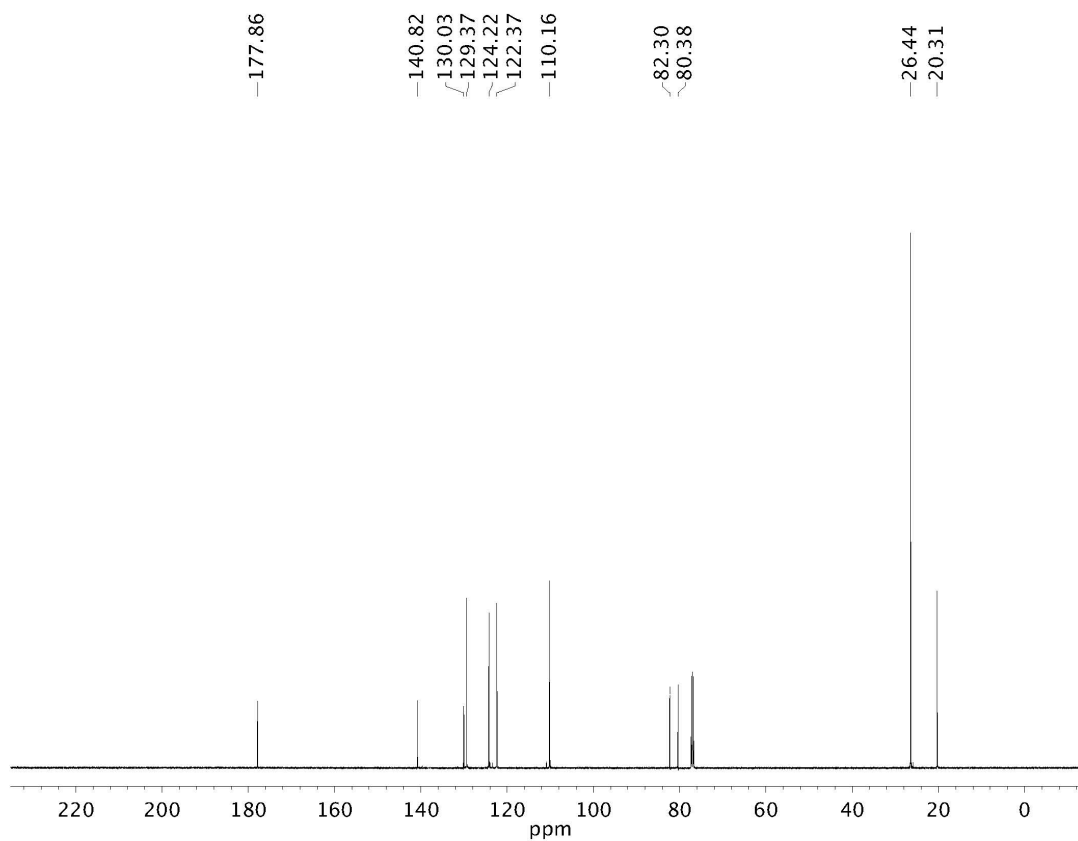
Infrared spectrum (Thin Film, NaCl) of compound **1e**.¹³C NMR (126 MHz, DMSO) of compound **1e**.

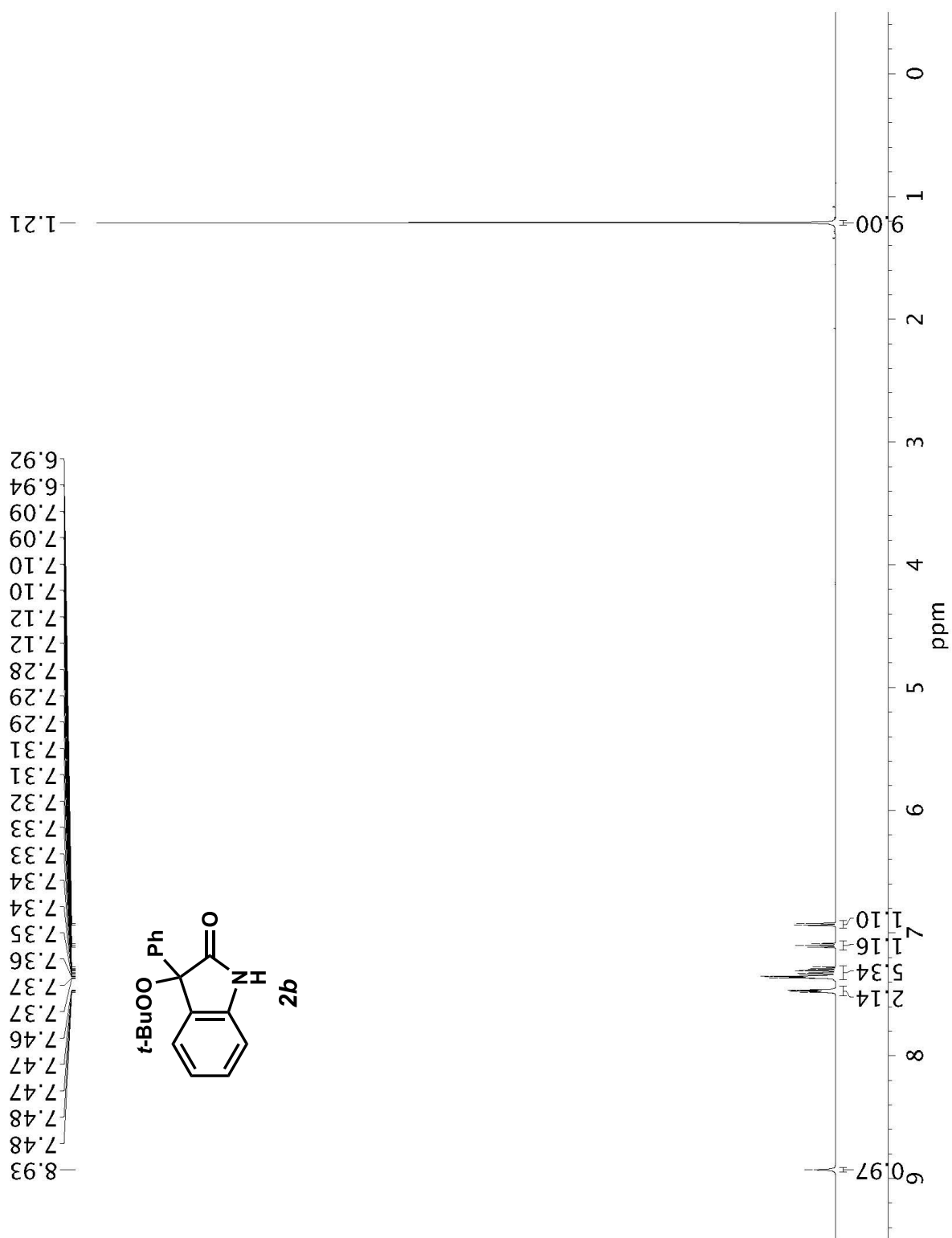
Infrared spectrum (Thin Film, NaCl) of compound **1f**.¹³C NMR (126 MHz, CDCl₃) of compound **1f**.

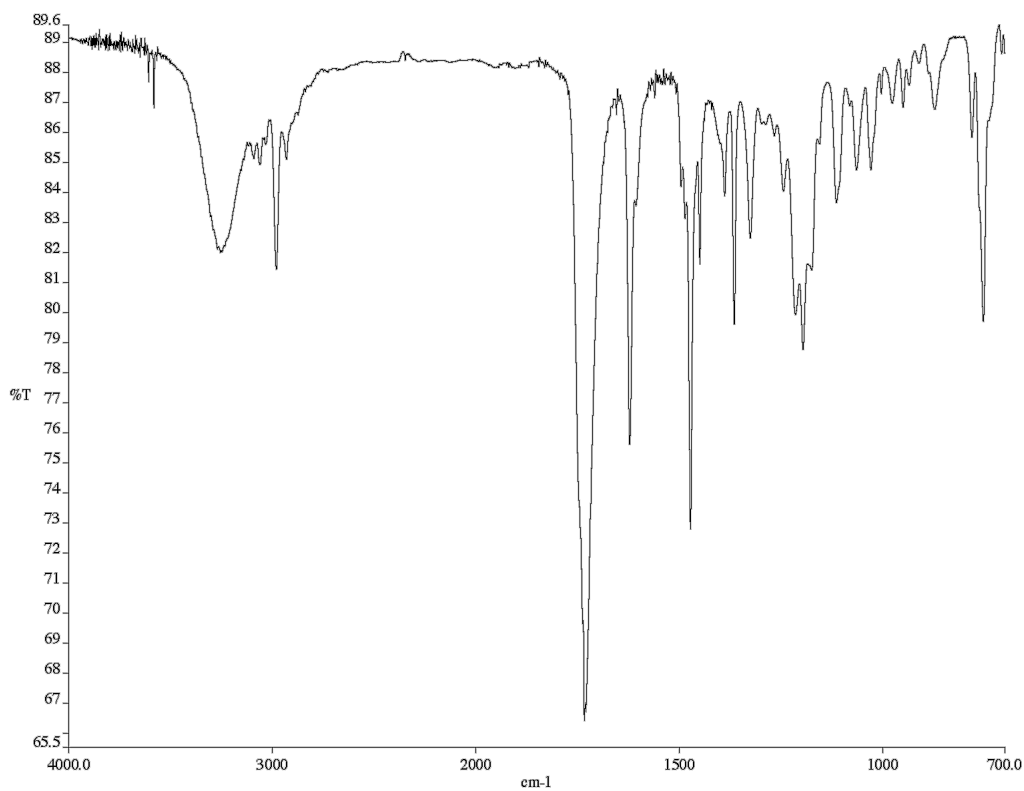
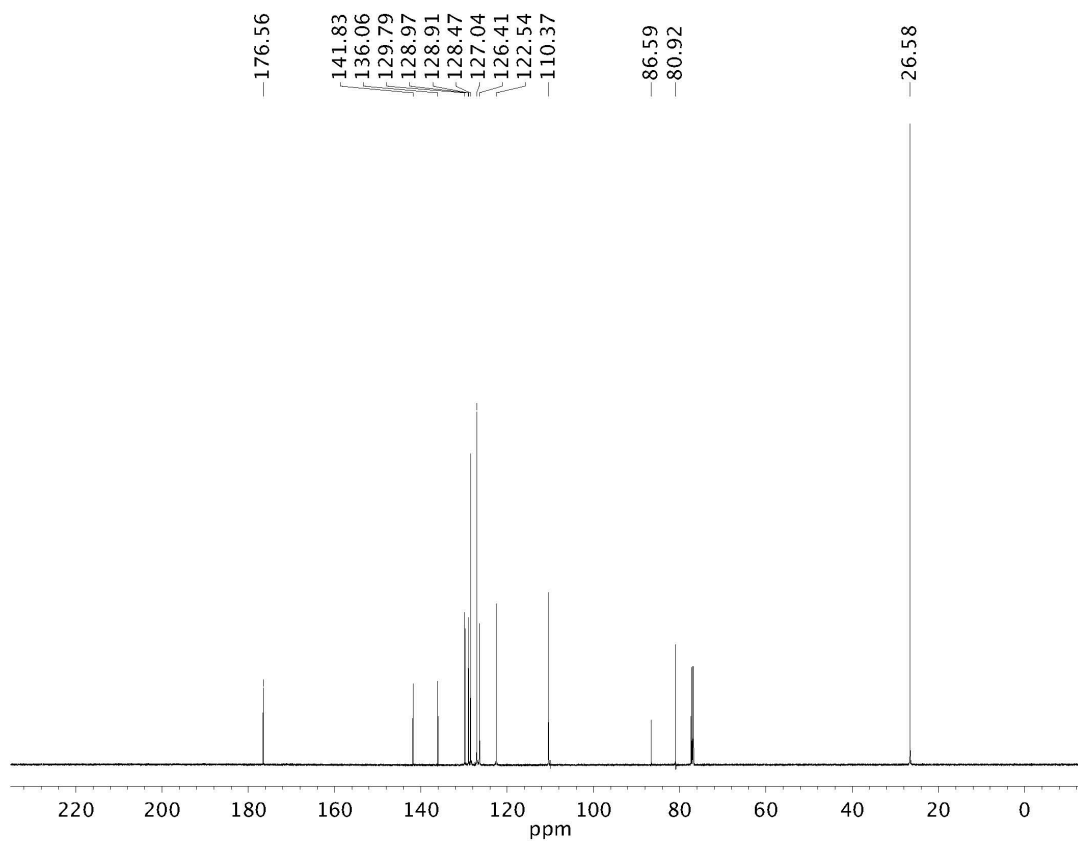


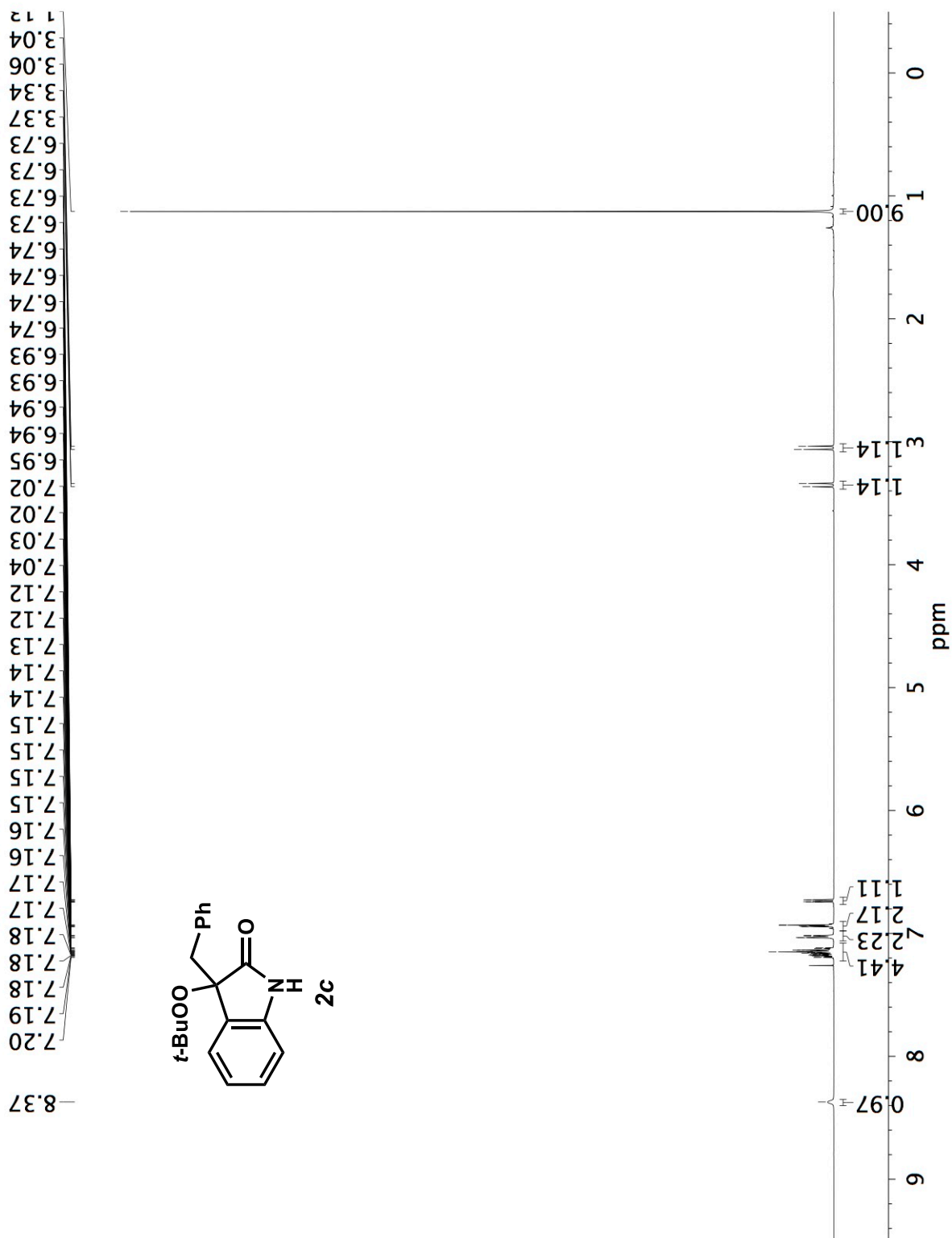
Infrared spectrum (Thin Film, NaCl) of compound **1h**.¹³C NMR (126 MHz, CDCl₃) of compound **1h**.

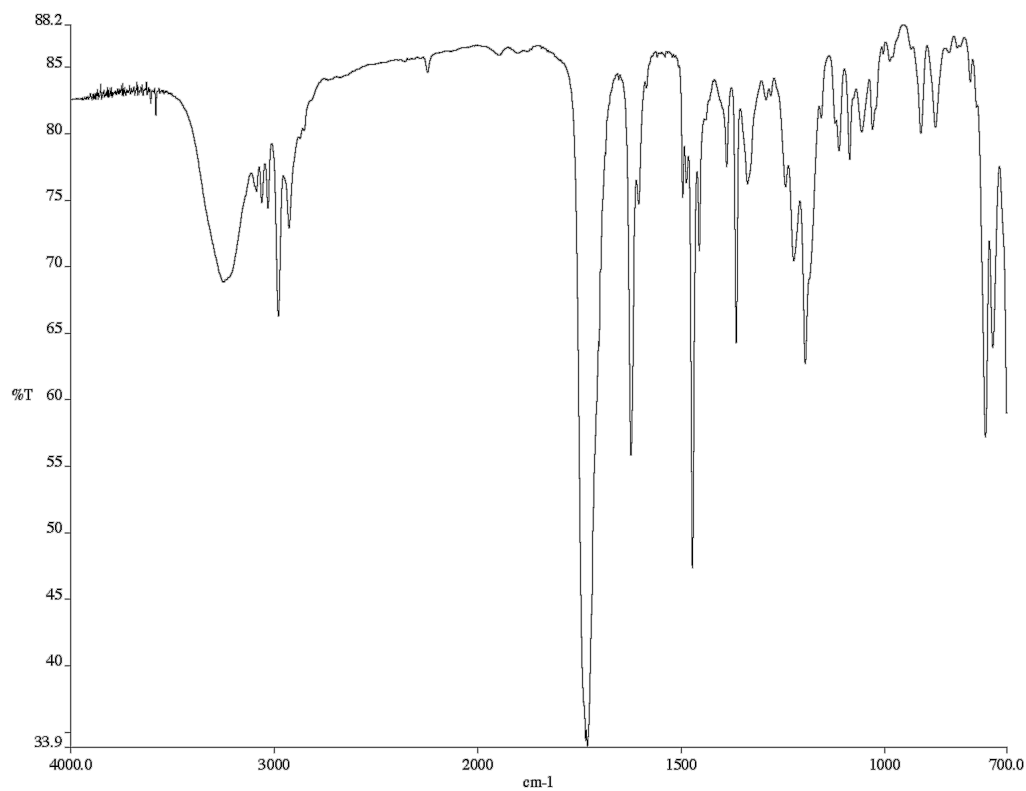
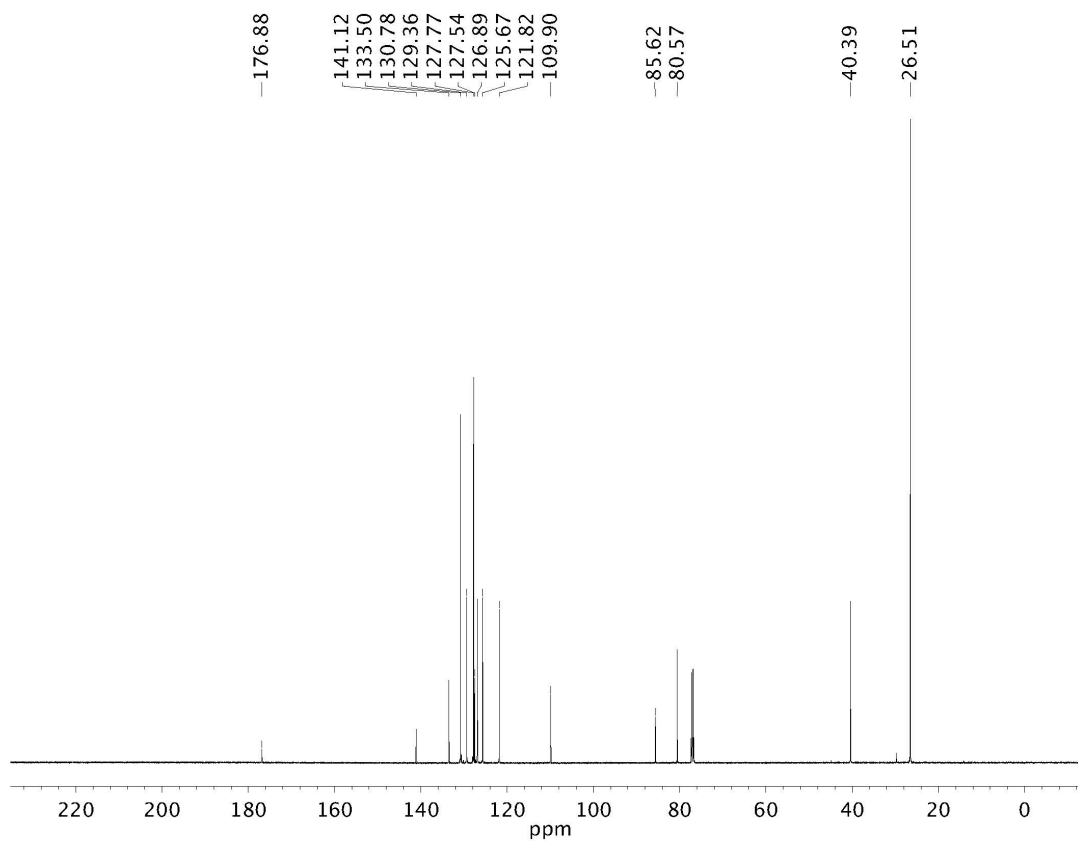


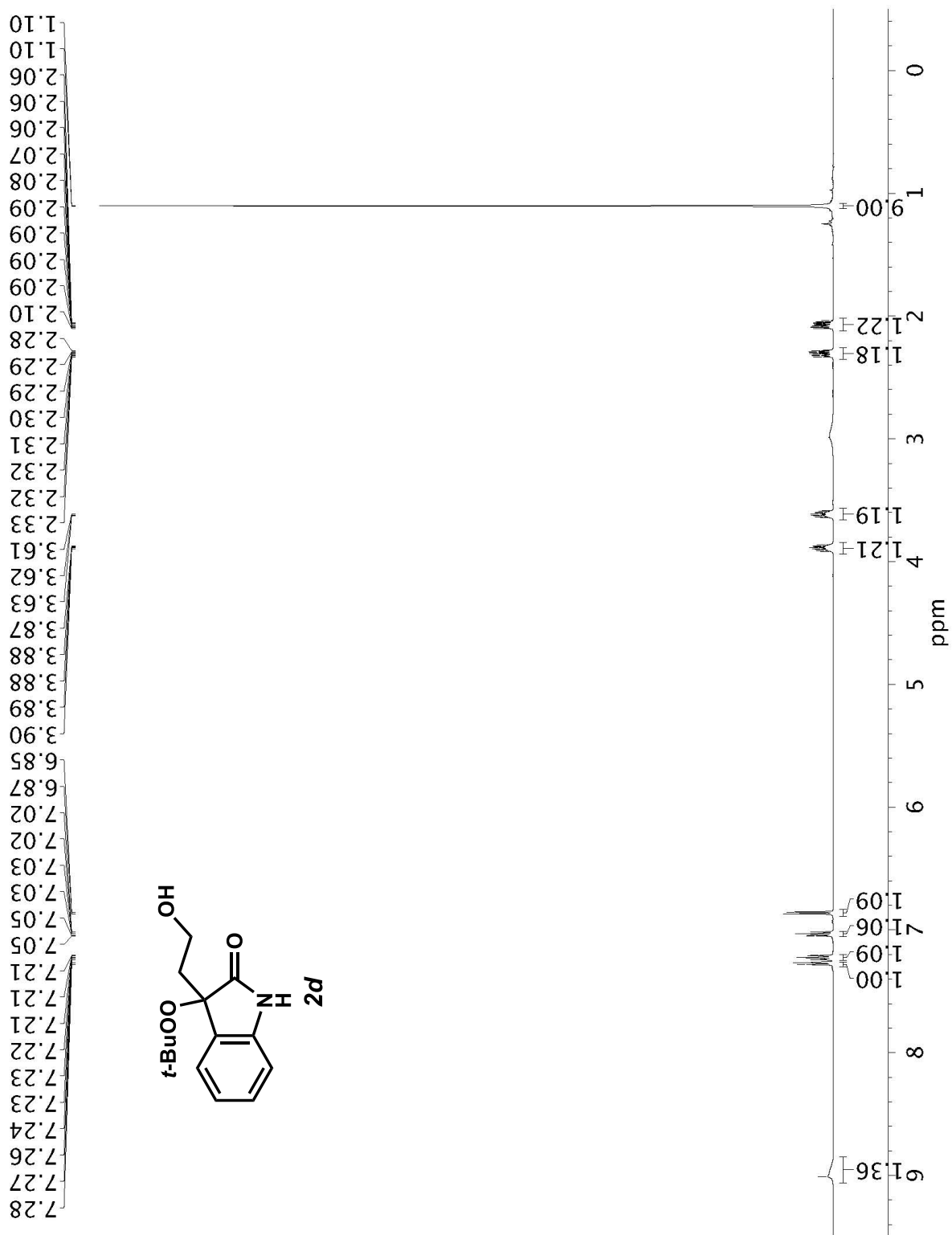
Infrared spectrum (Thin Film, NaCl) of compound **2a**.¹³C NMR (126 MHz, CDCl₃) of compound **2a**.

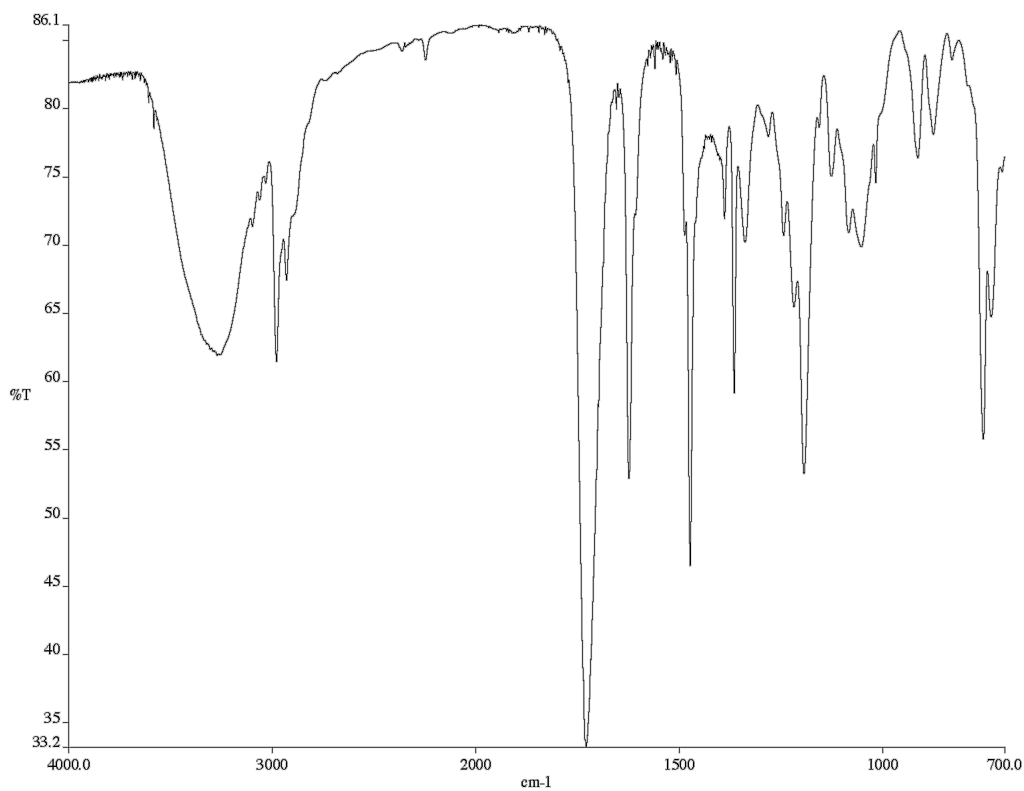
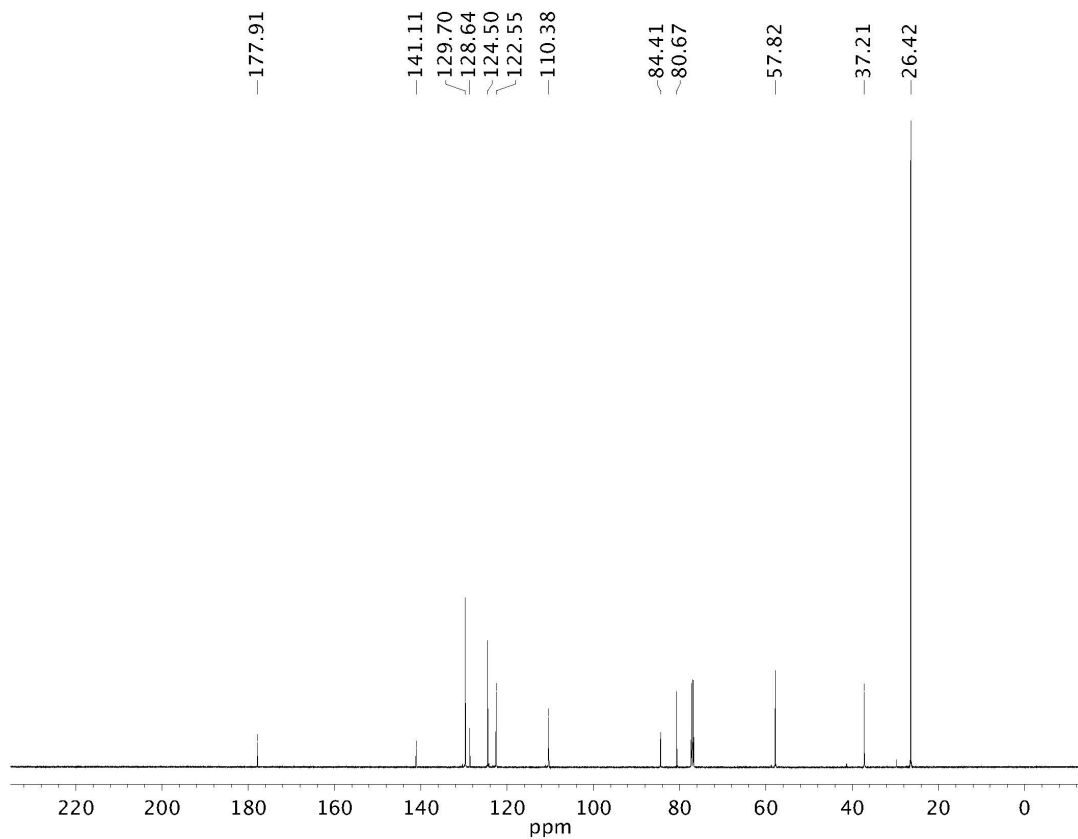


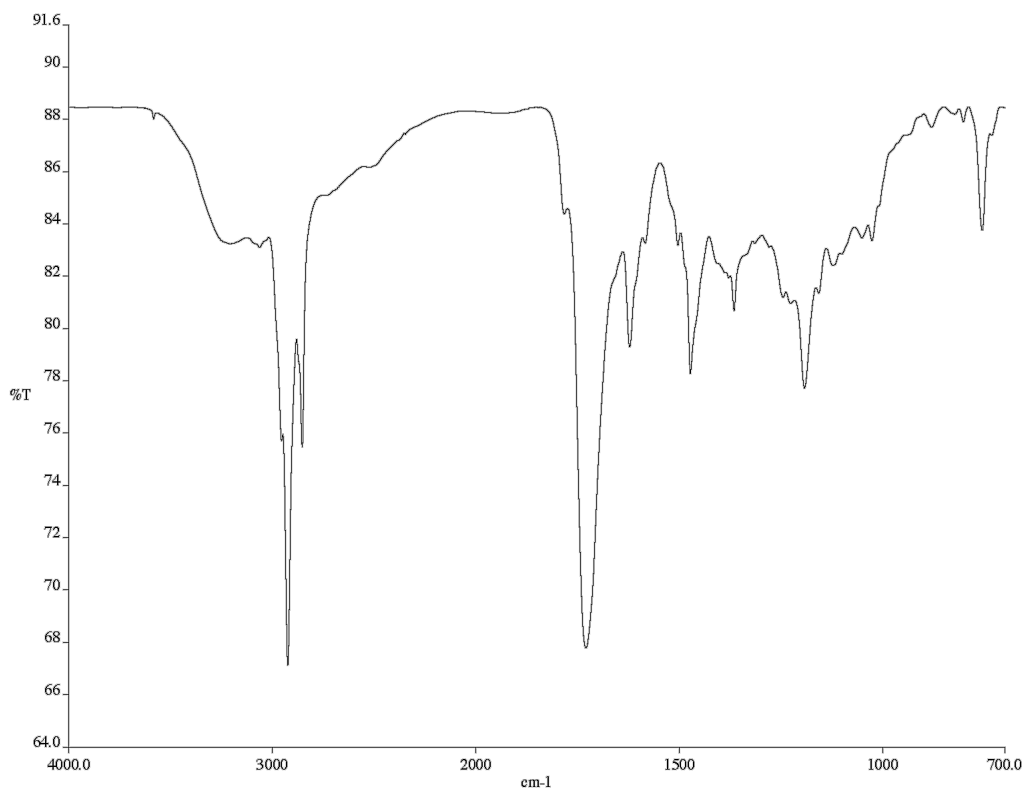
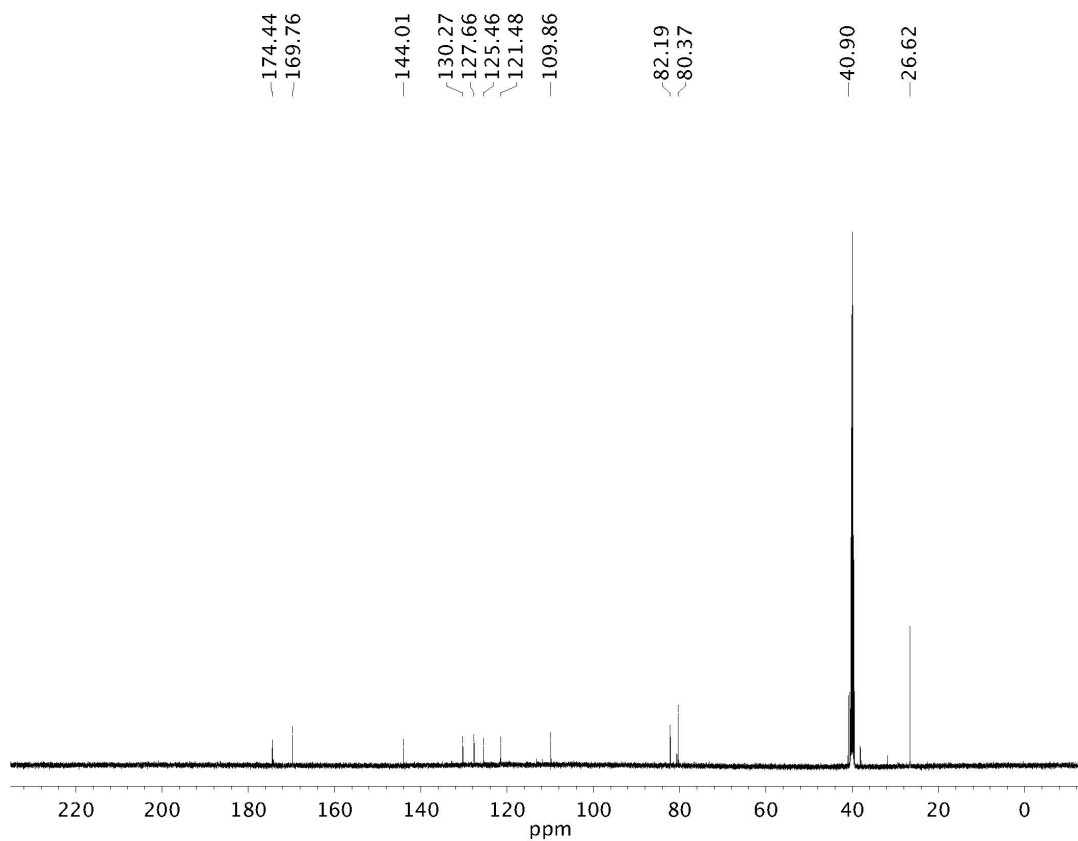
Infrared spectrum (Thin Film, NaCl) of compound **2b**.¹³C NMR (126 MHz, CDCl₃) of compound **2b**.

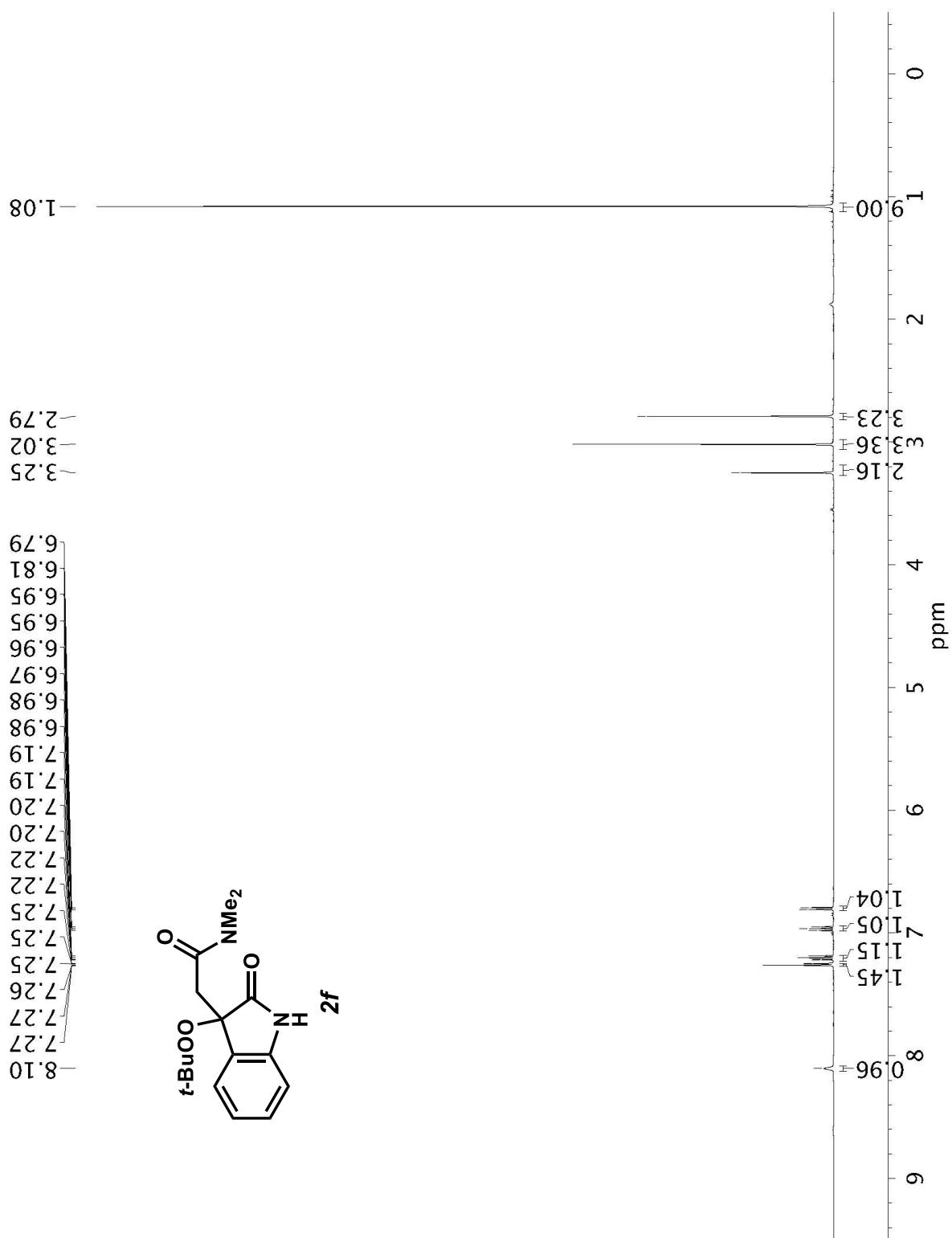


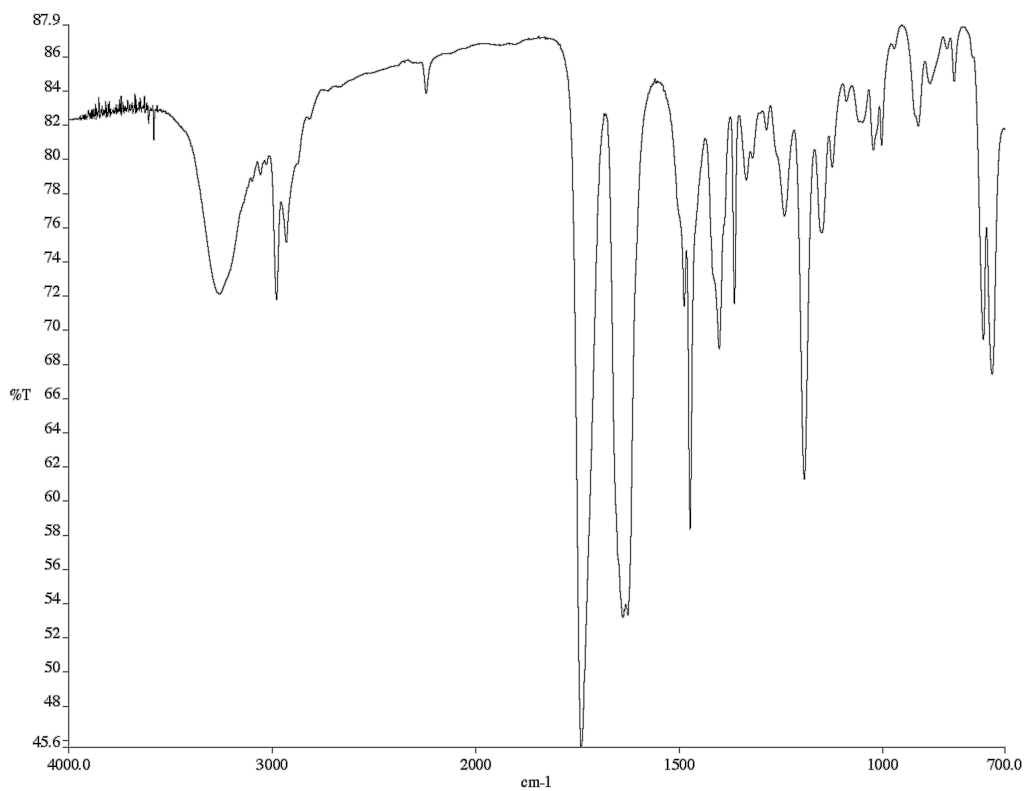
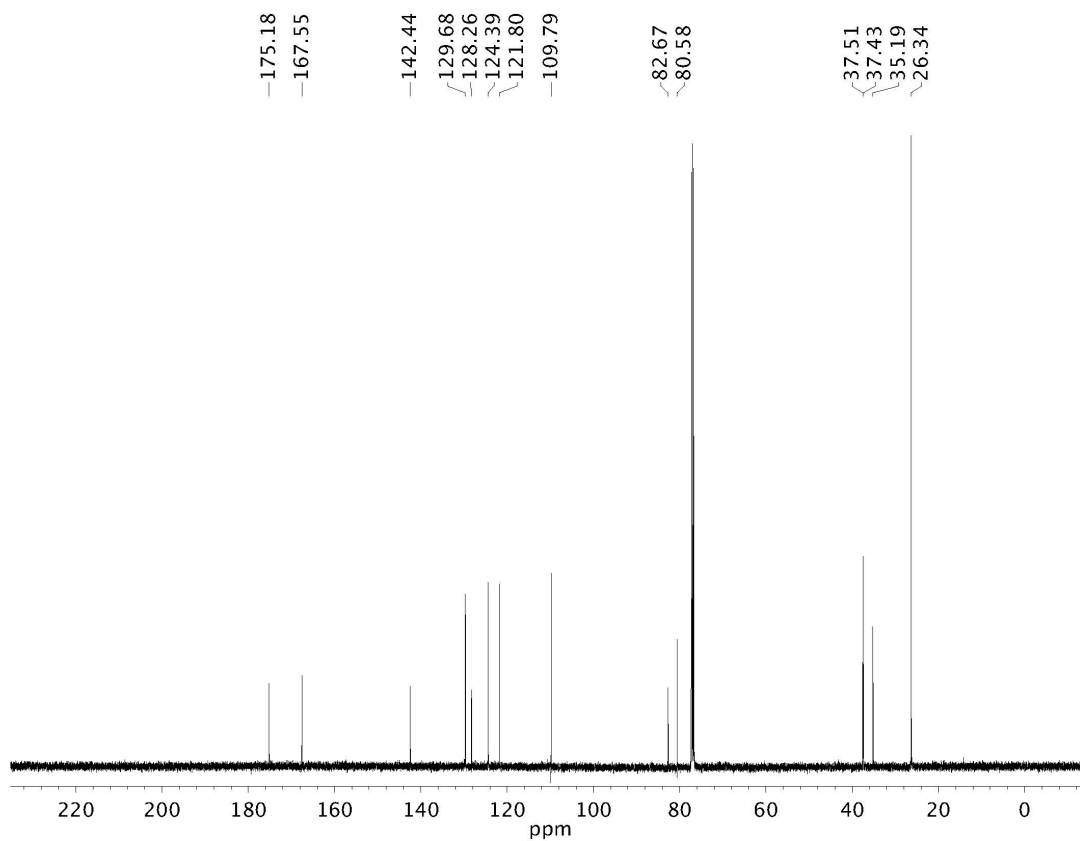
Infrared spectrum (Thin Film, NaCl) of compound **2c**.¹³C NMR (126 MHz, CDCl₃) of compound **2c**.

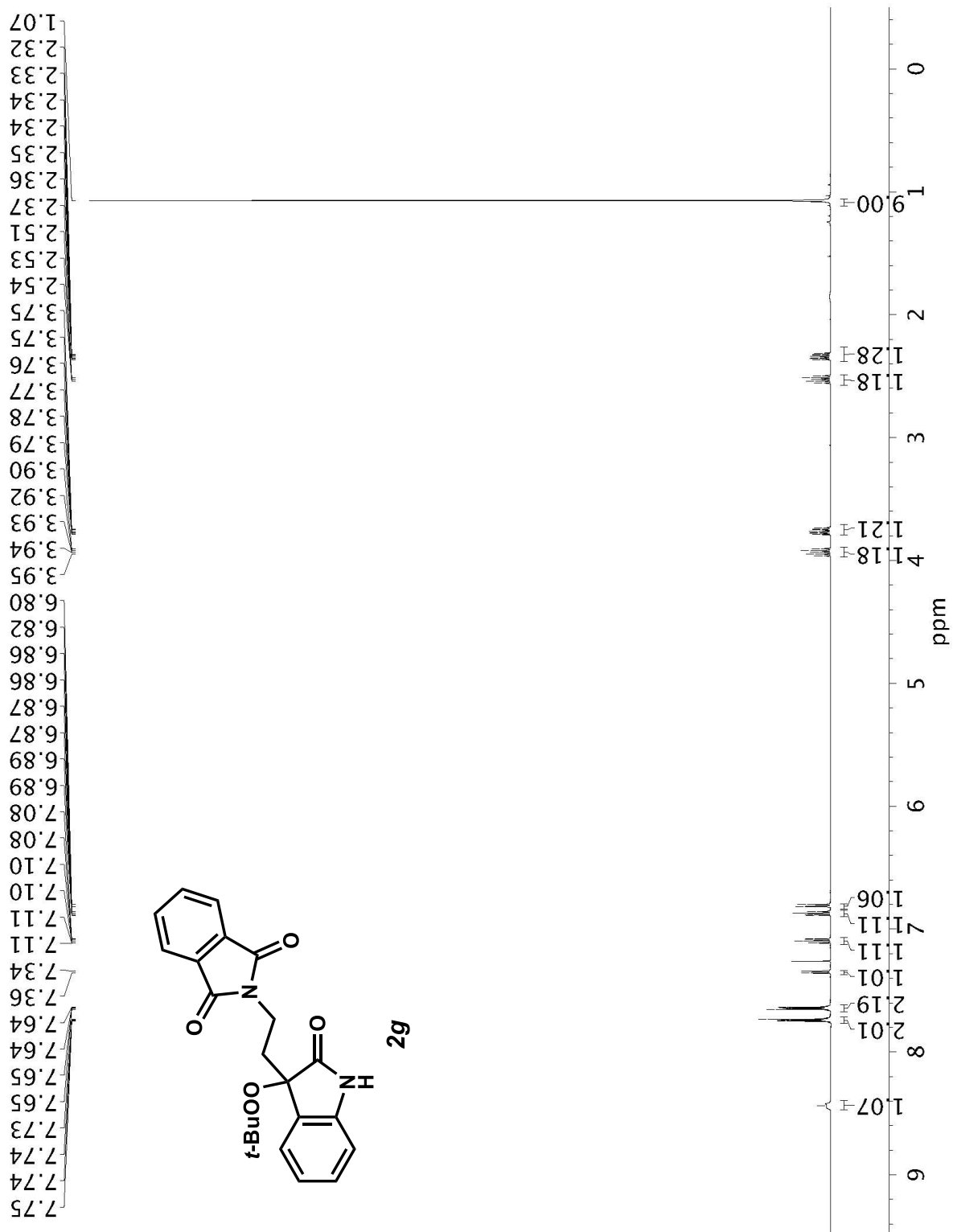
¹H NMR (500 MHz, CDCl₃) of compound **2d**.

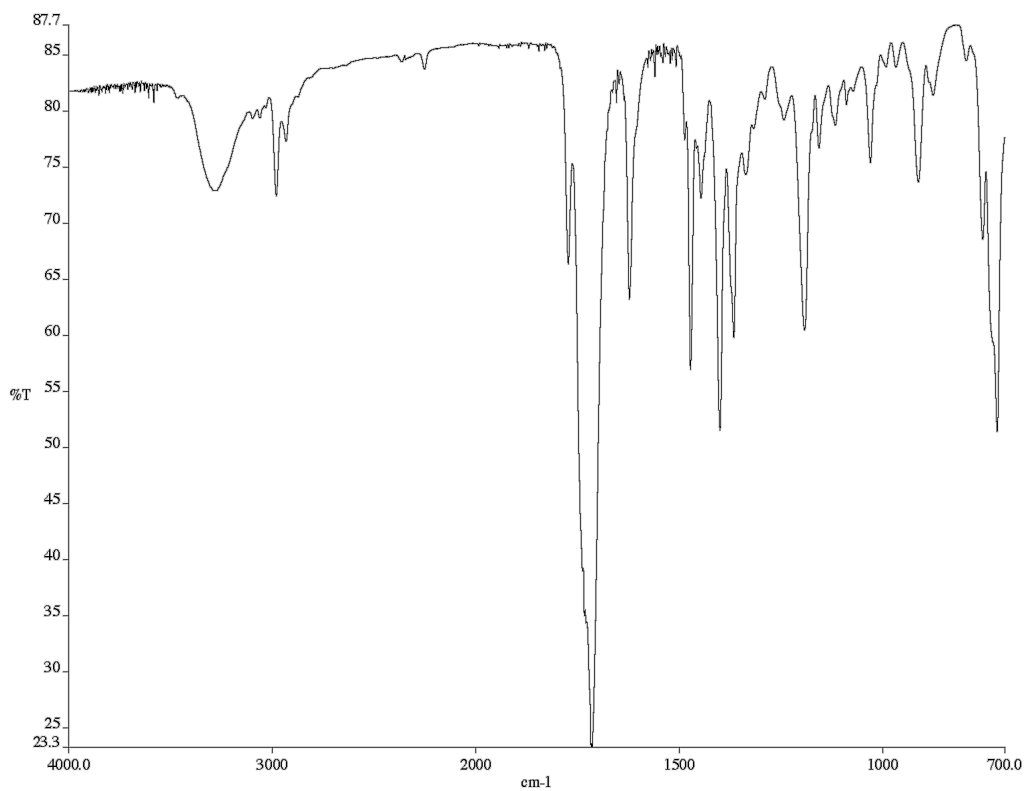
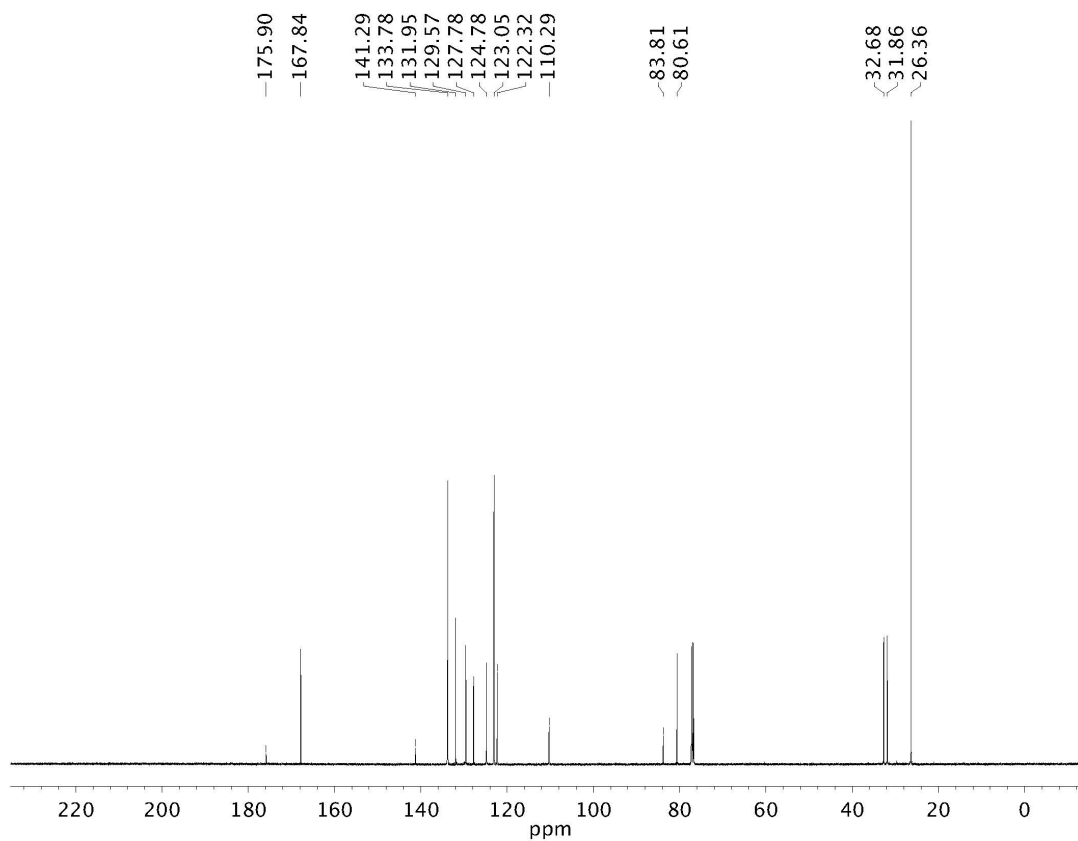
Infrared spectrum (Thin Film, NaCl) of compound **2d**.¹³C NMR (126 MHz, CDCl₃) of compound **2d**.

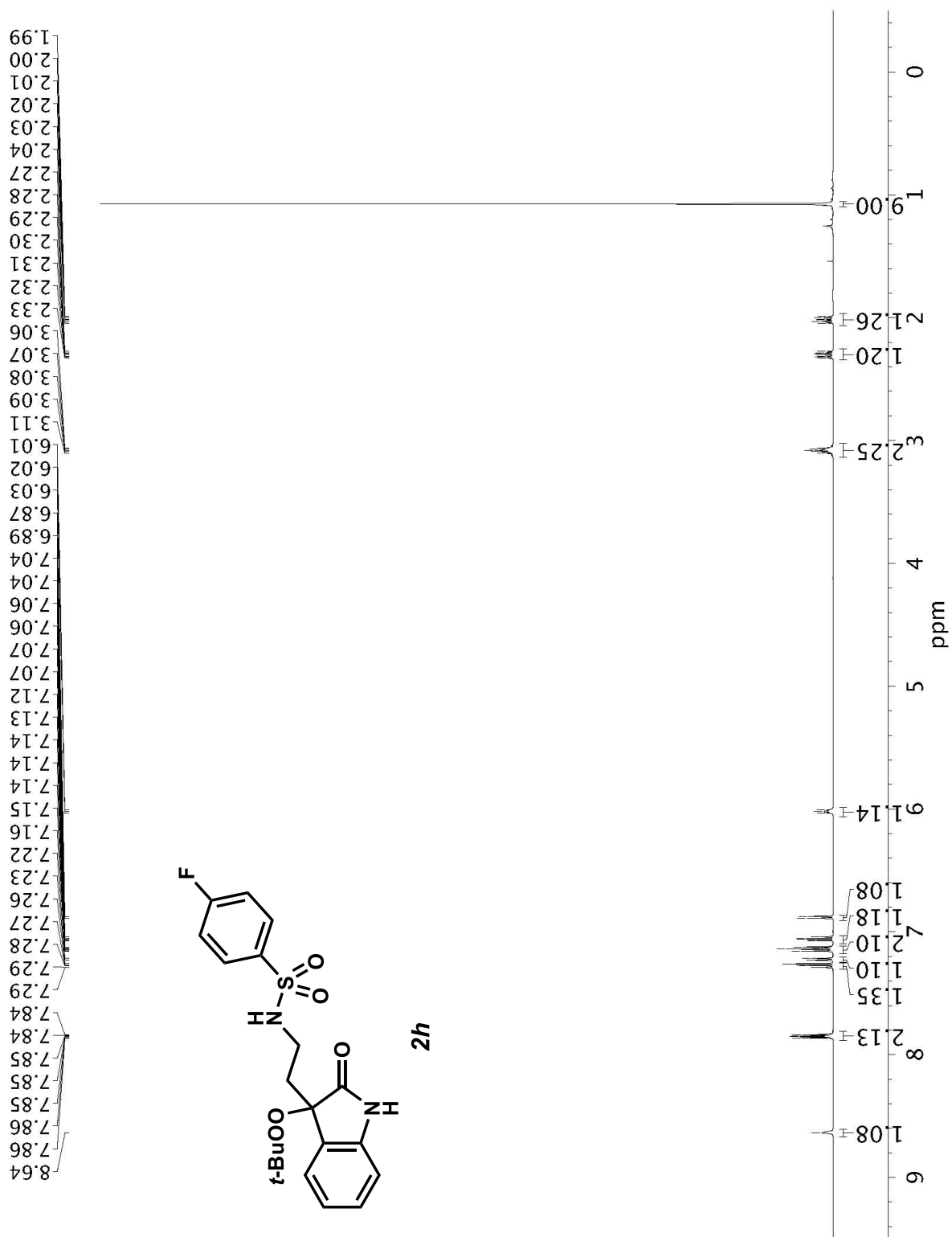
Infrared spectrum (Thin Film, NaCl) of compound **2e**.¹³C NMR (126 MHz, DMSO) of compound **2e**.

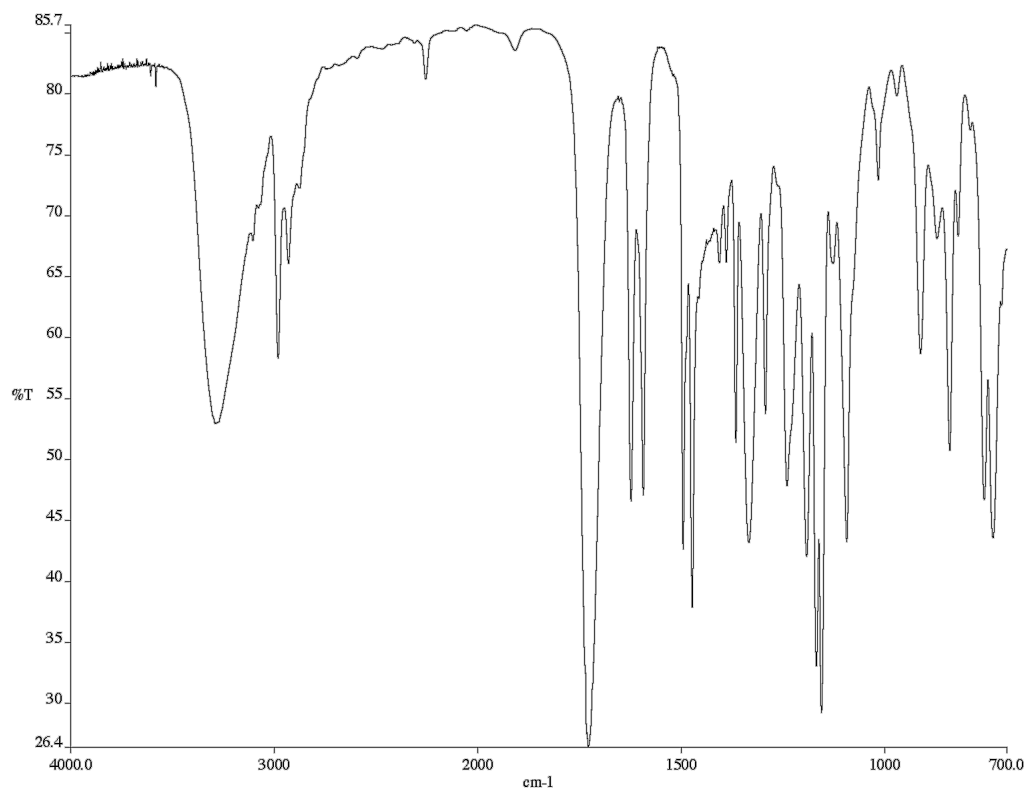
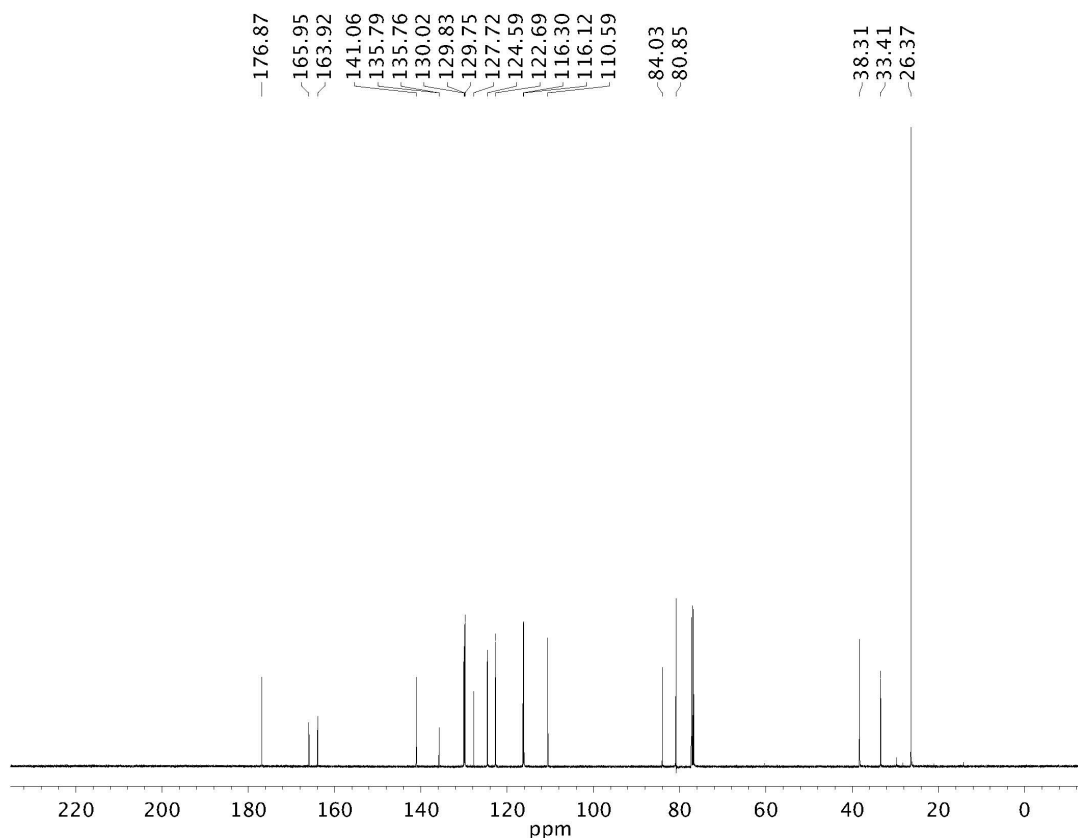


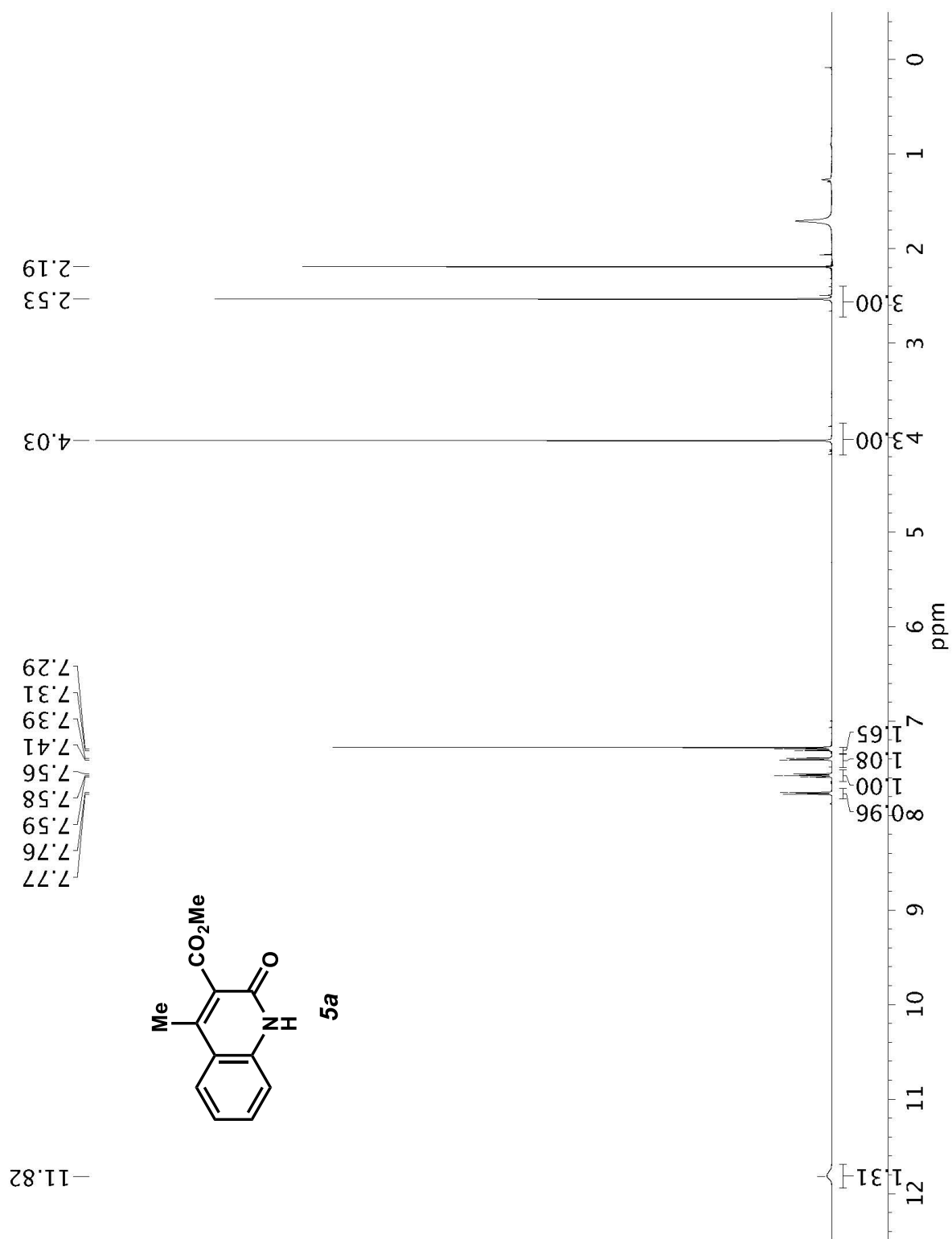
Infrared spectrum (Thin Film, NaCl) of compound **2f**.¹³C NMR (126 MHz, CDCl₃) of compound **2f**.

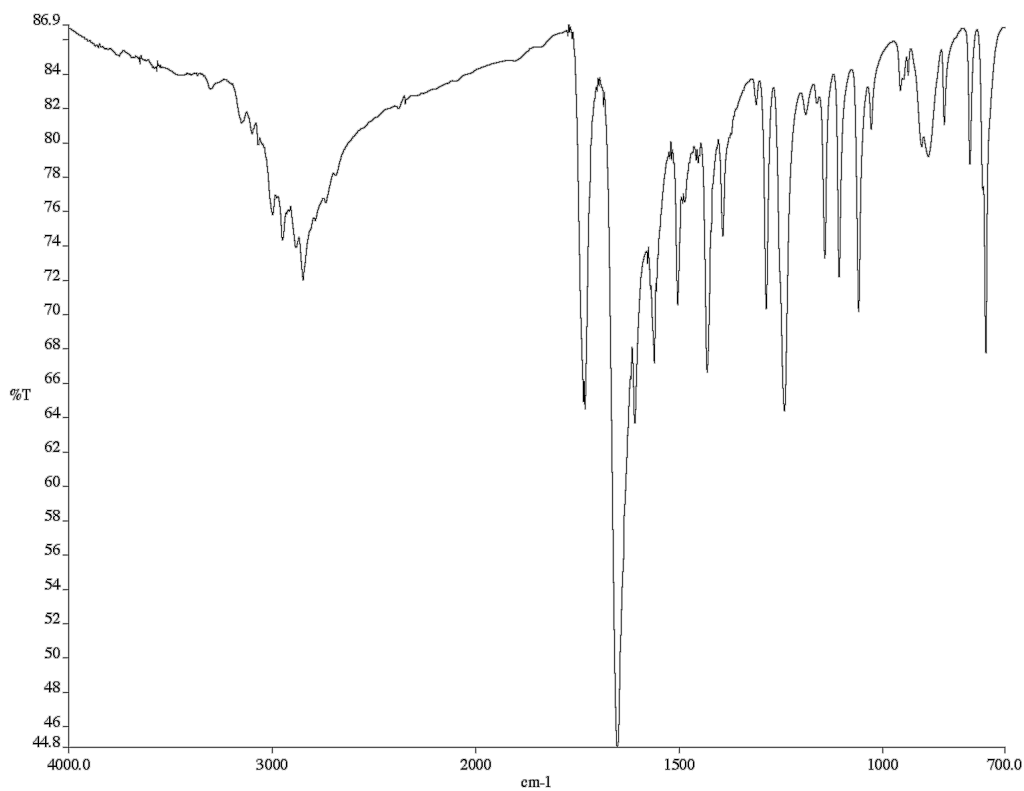
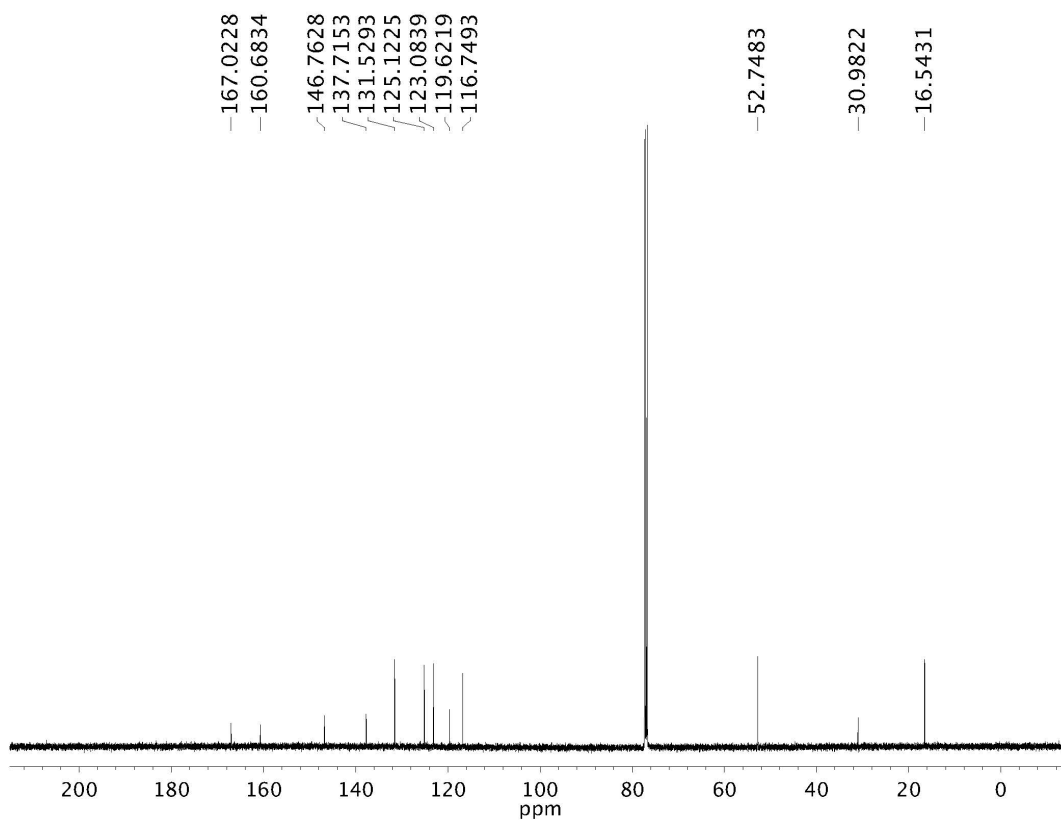


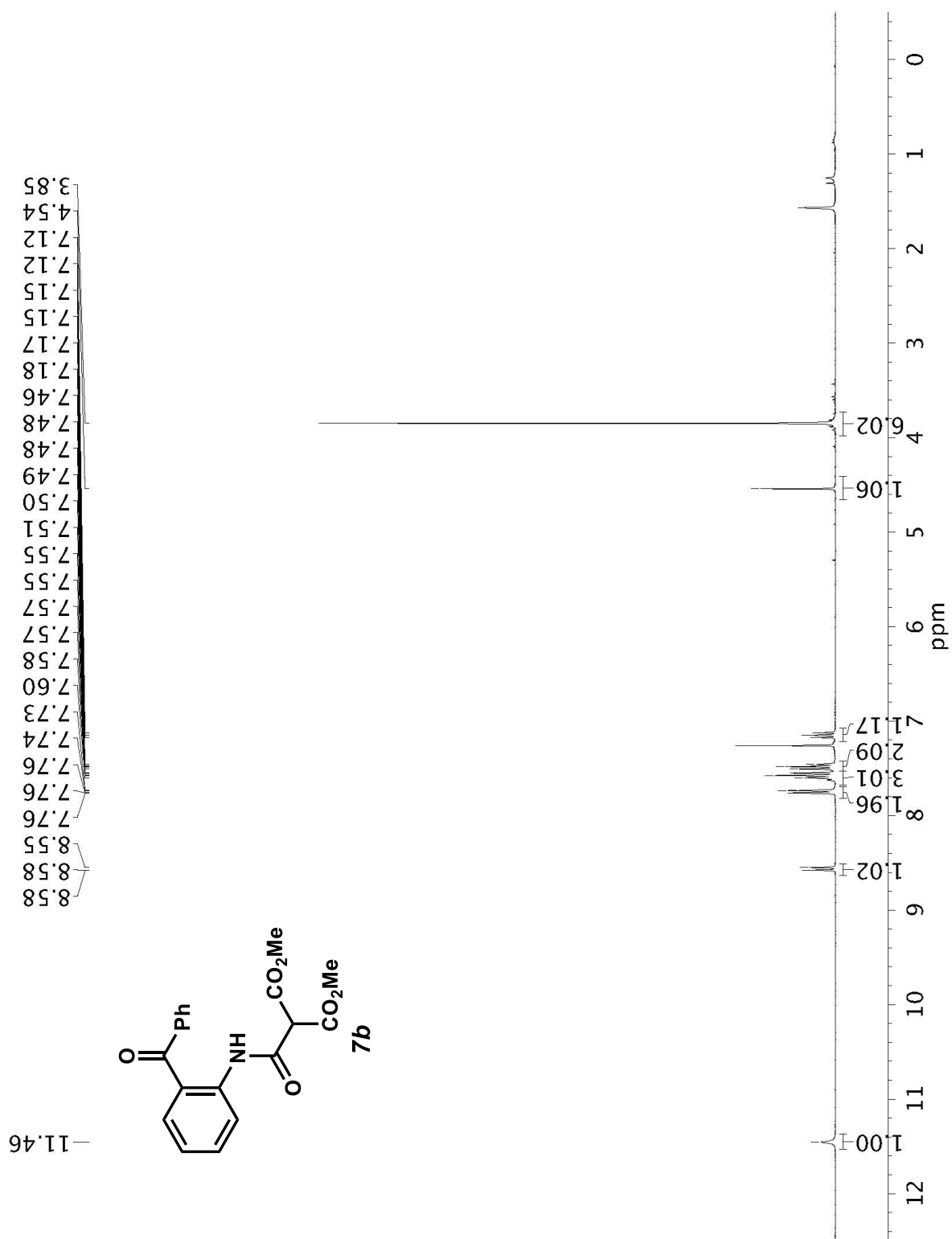
Infrared spectrum (Thin Film, NaCl) of compound **2g**.¹³C NMR (126 MHz, CDCl₃) of compound **2g**.

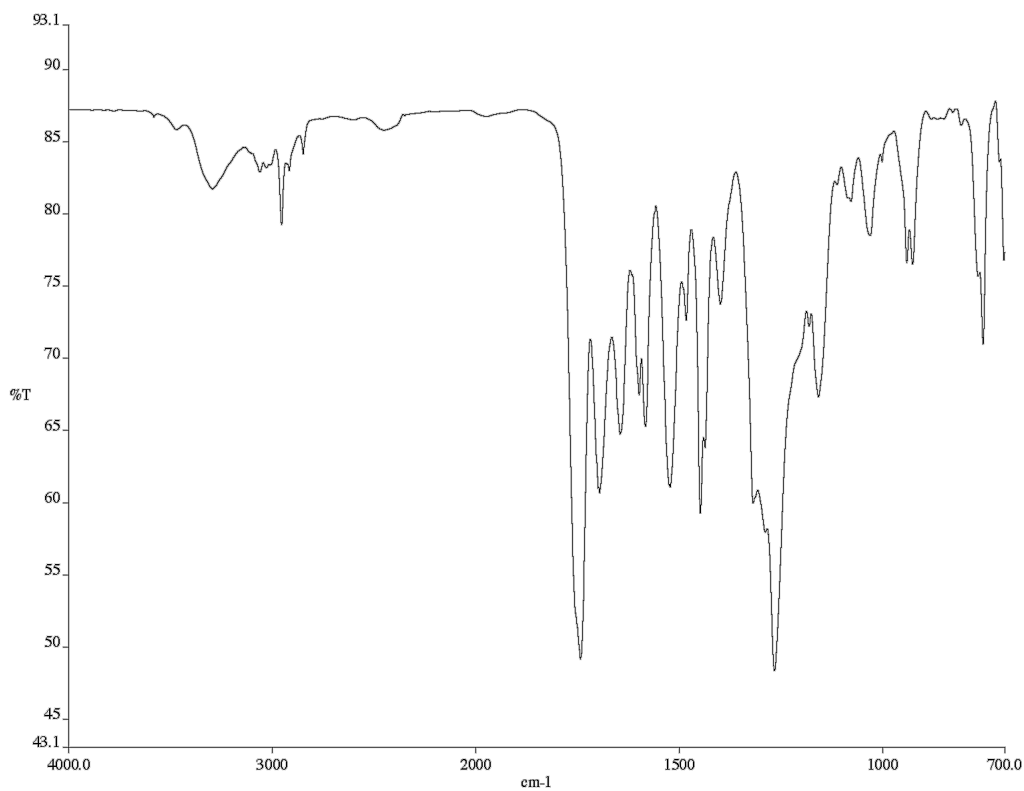
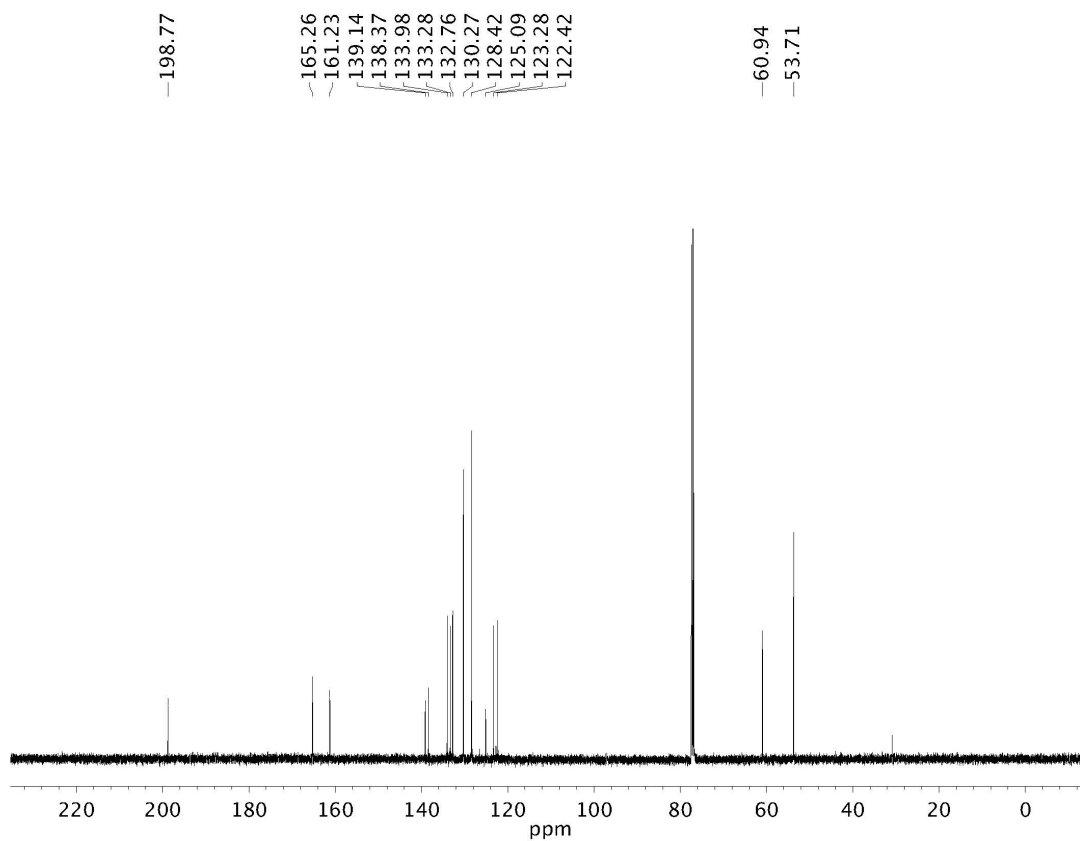


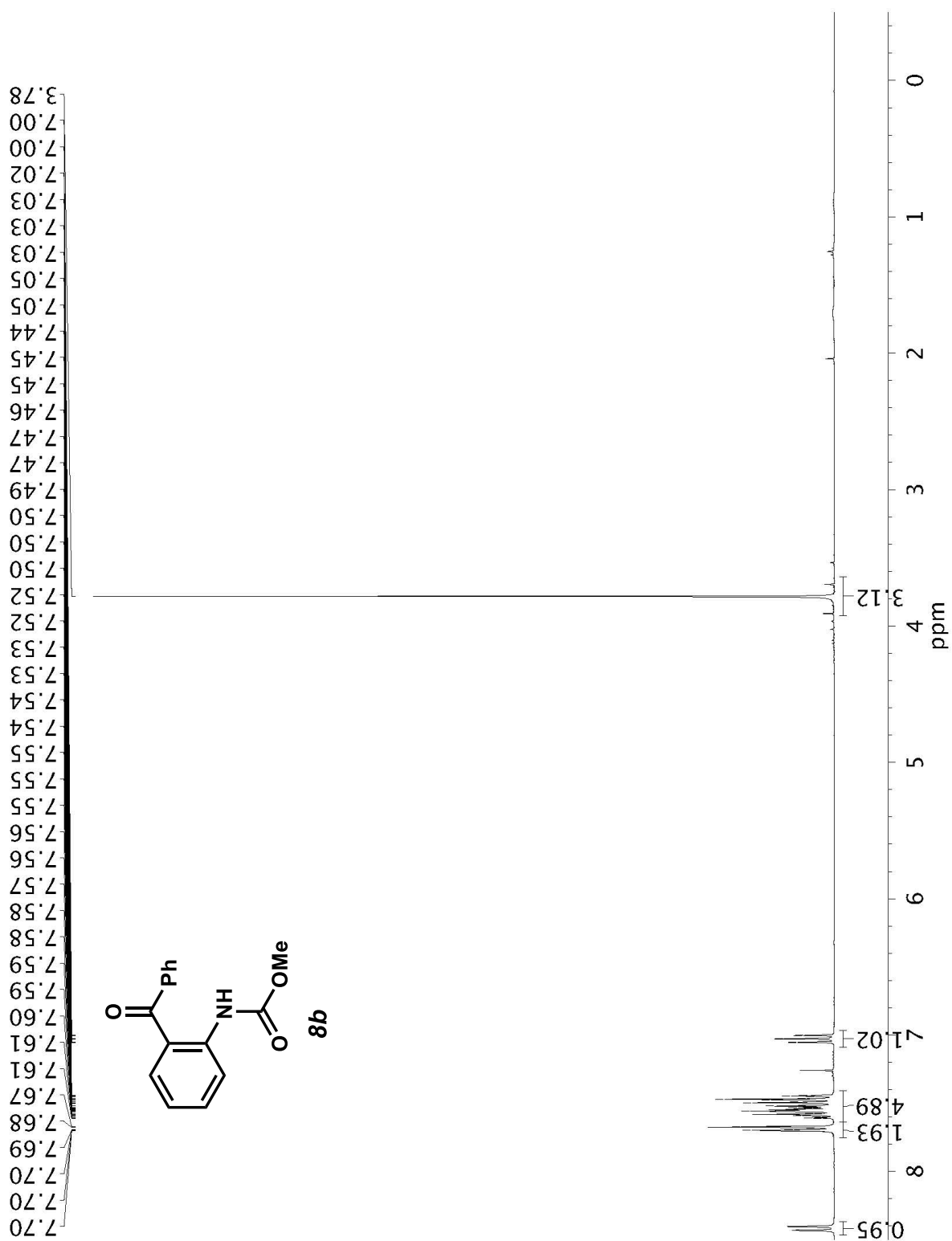
Infrared spectrum (Thin Film, NaCl) of compound **2h**.¹³C NMR (126 MHz, CDCl₃) of compound **2h**.

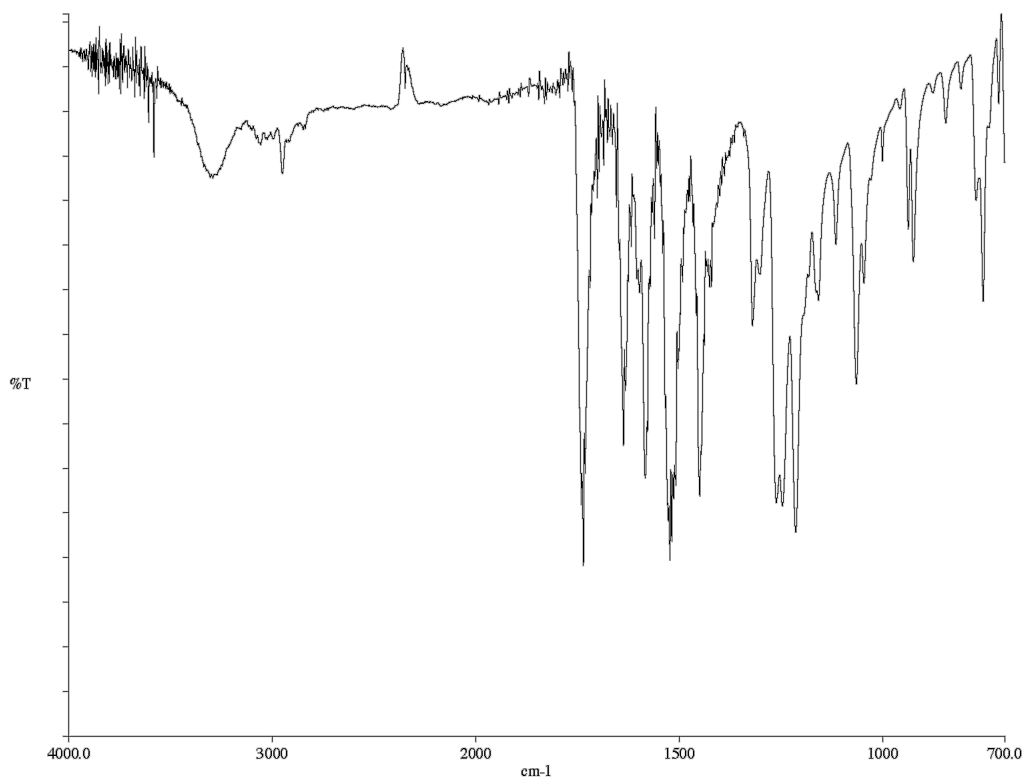
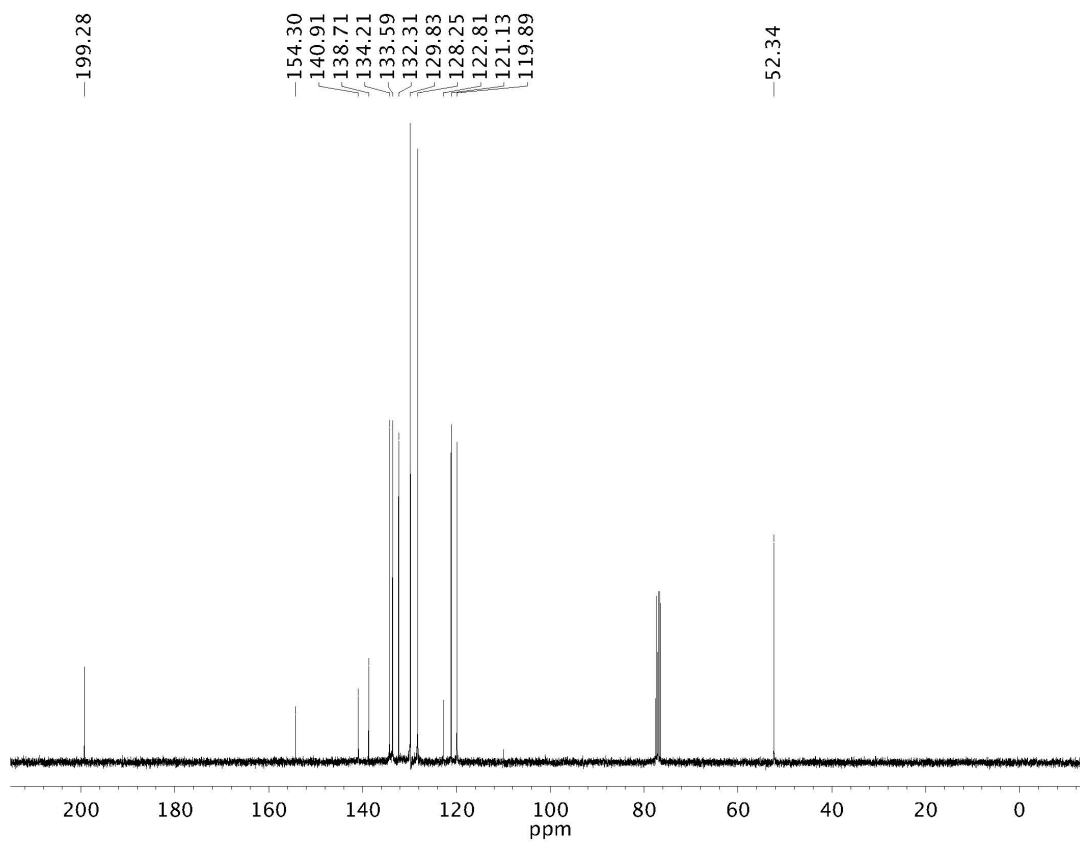


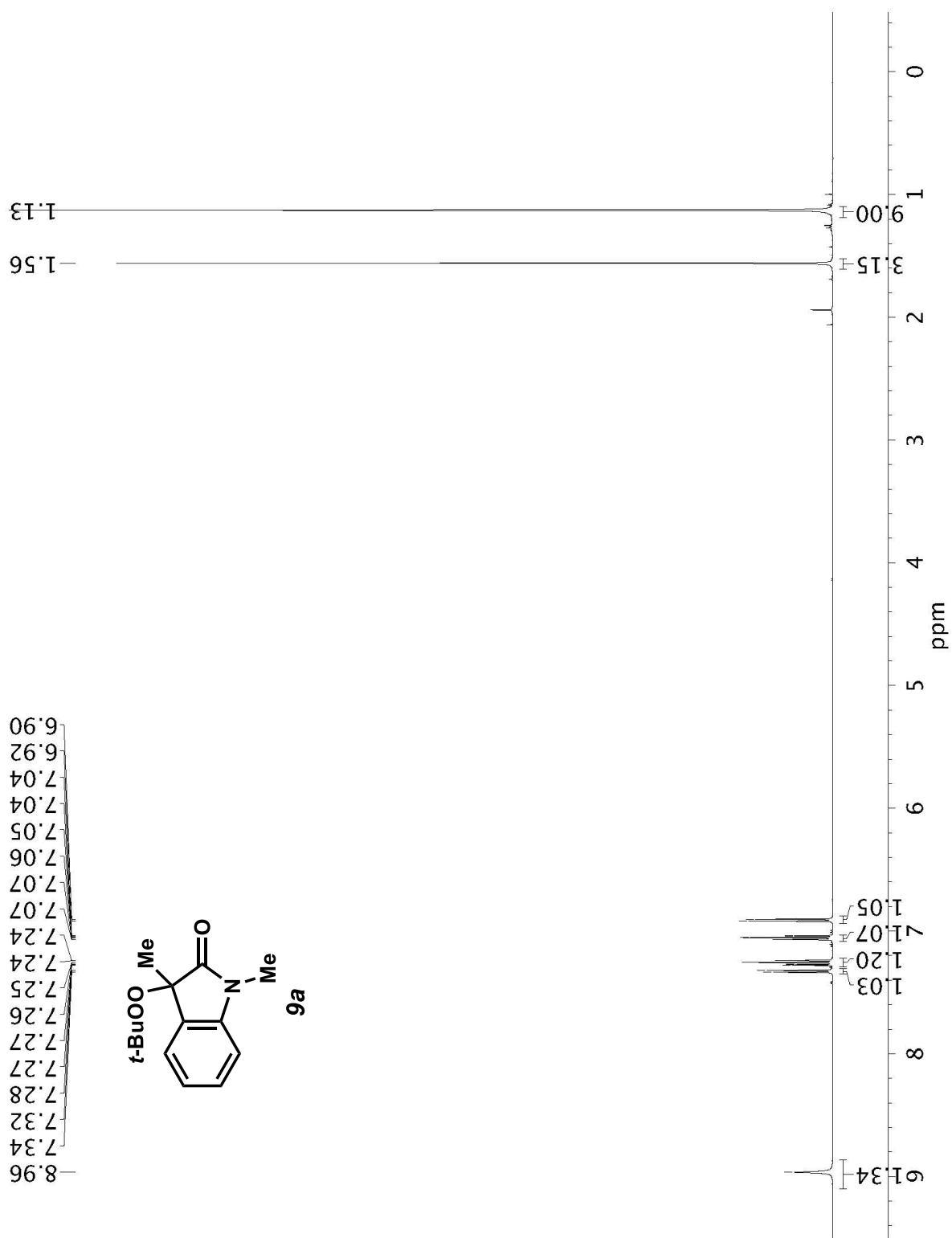
Infrared spectrum (Thin Film, NaCl) of compound **5a**.¹³C NMR (126 MHz, CDCl₃) of compound **5a**.

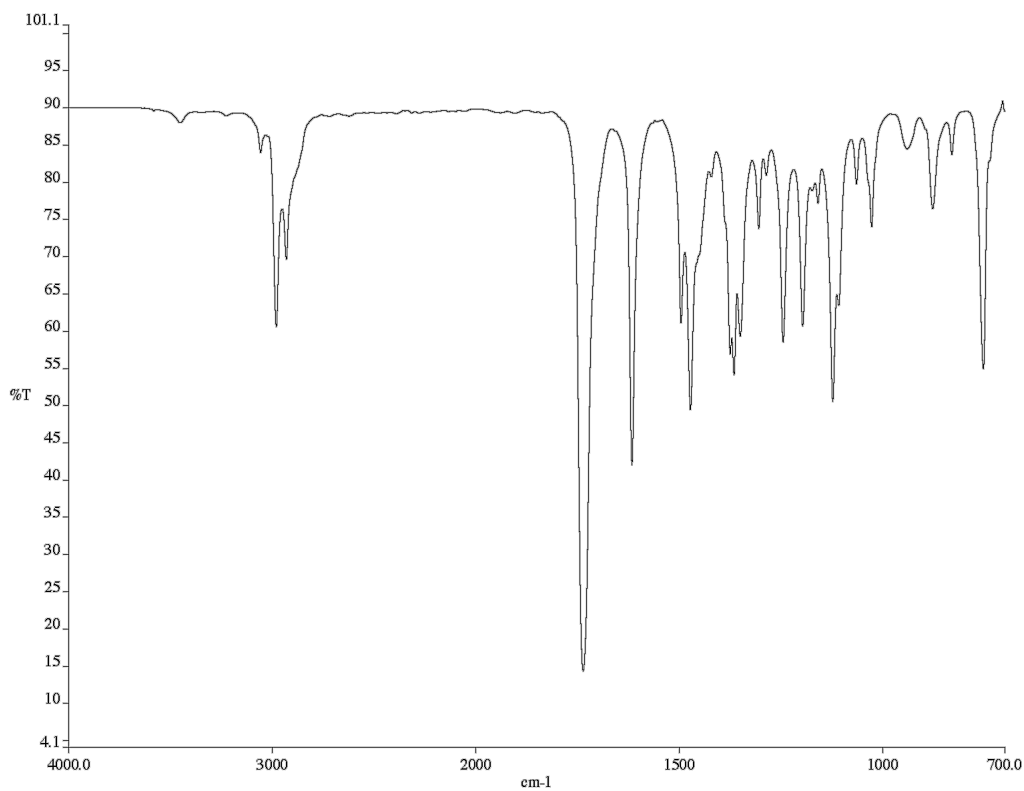
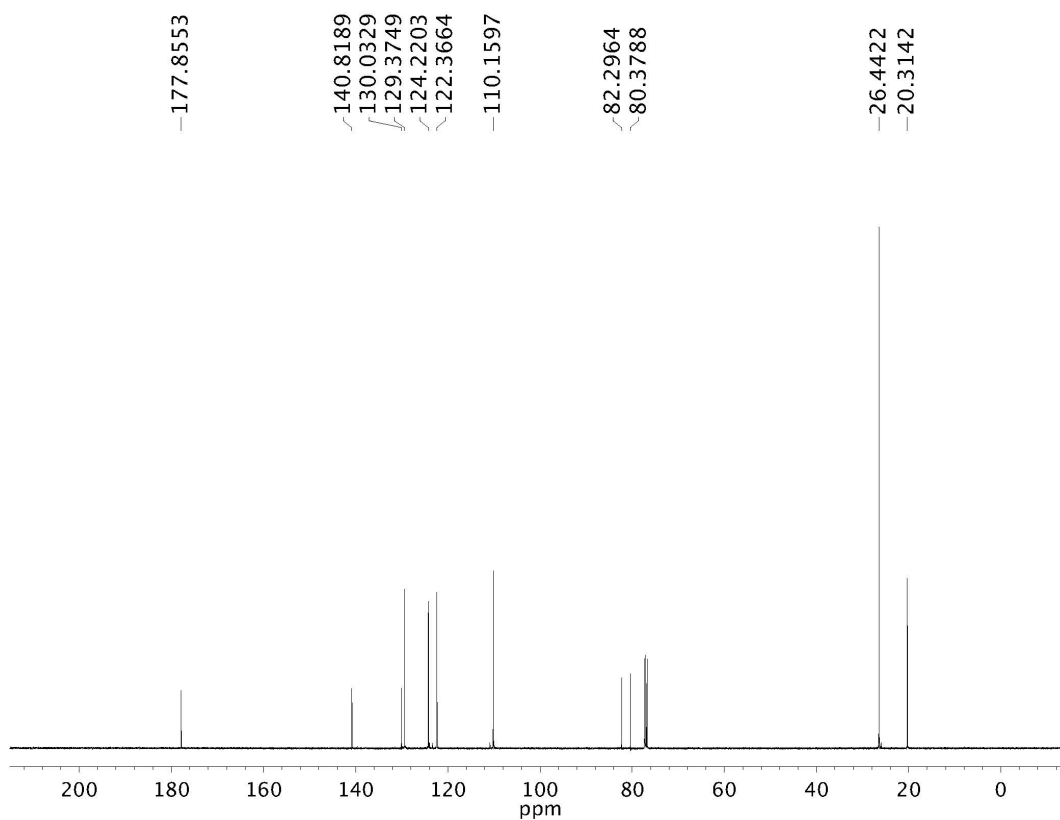


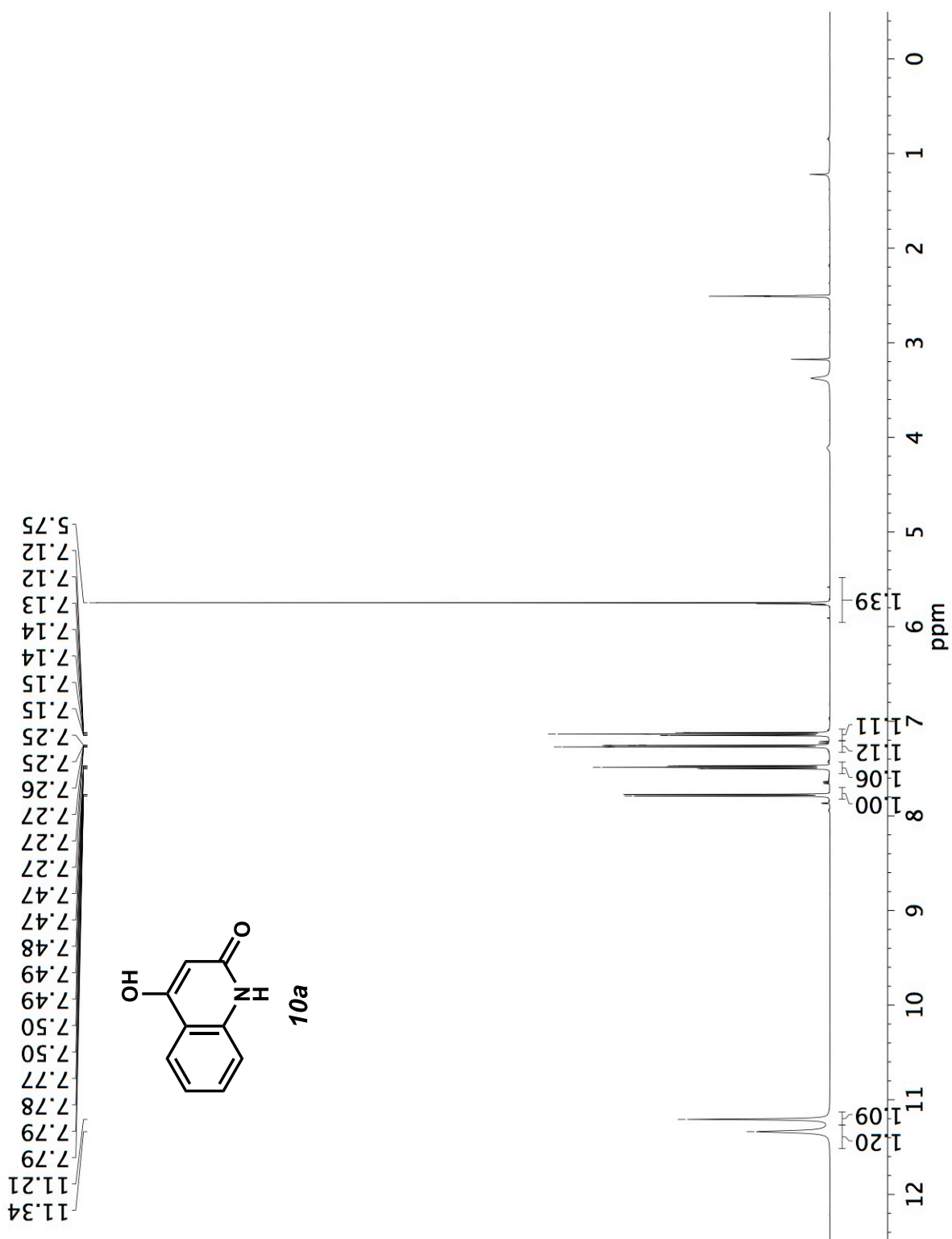
Infrared spectrum (Thin Film, NaCl) of compound **7b**.¹³C NMR (126 MHz, CDCl₃) of compound **7b**.

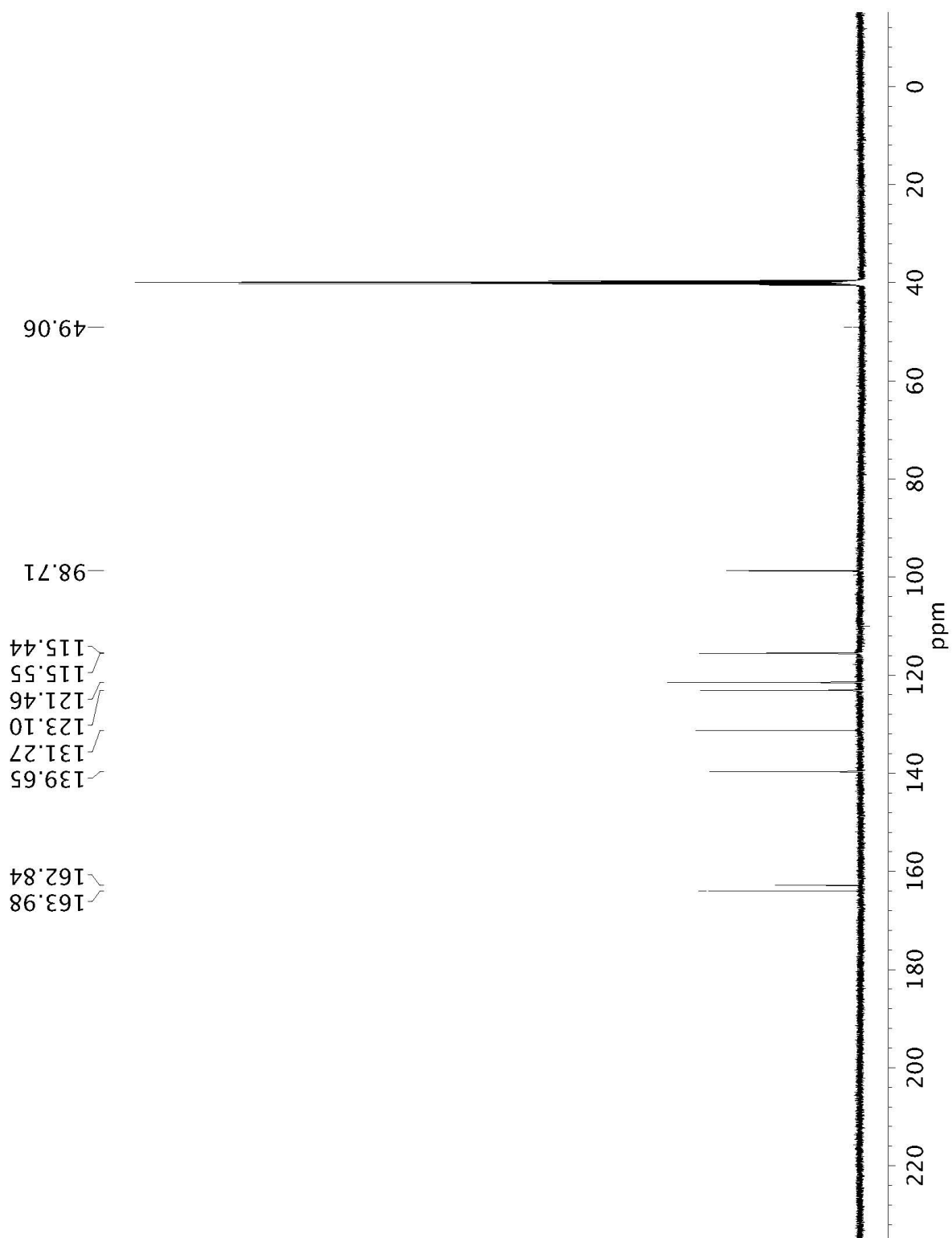


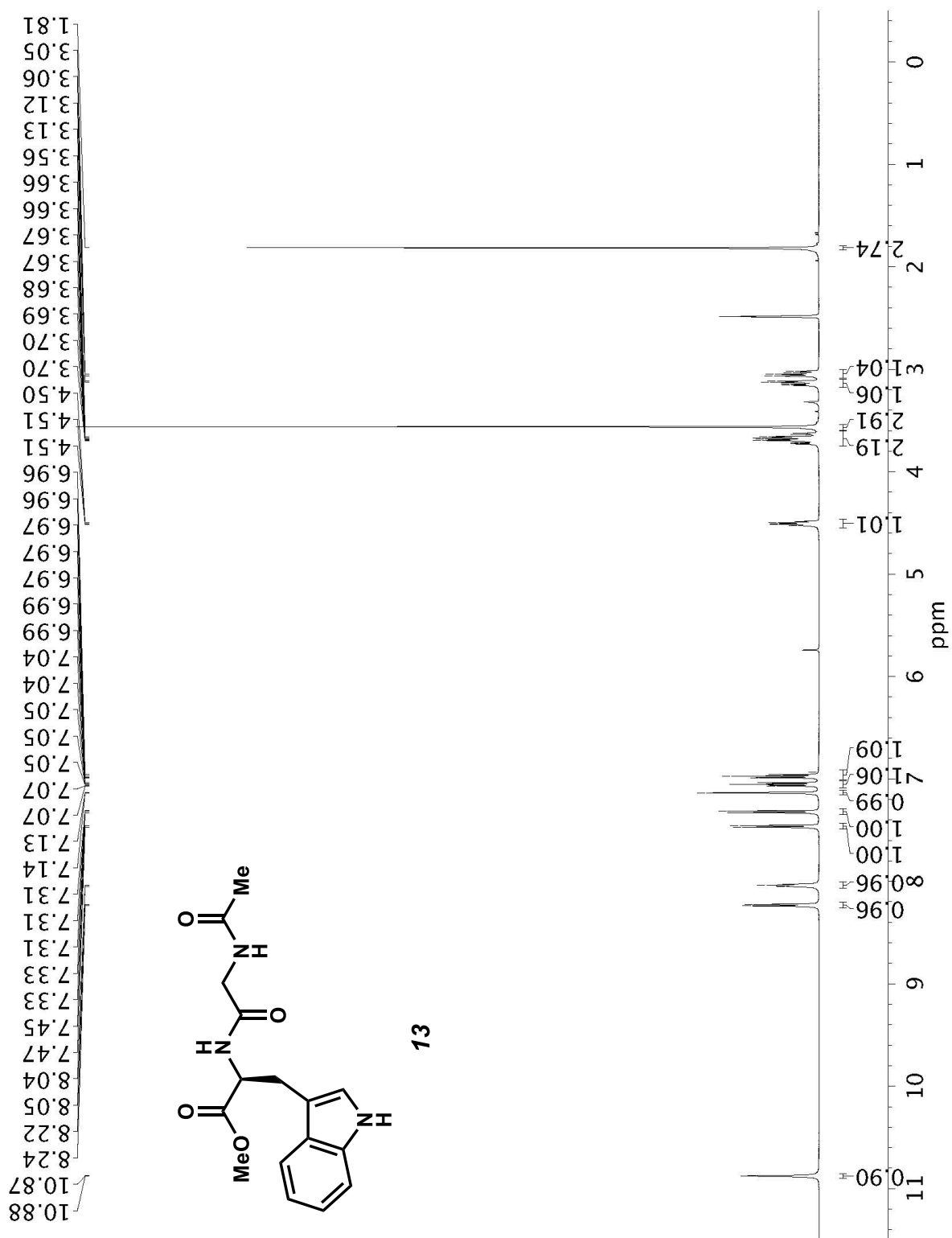
Infrared spectrum (Thin Film, NaCl) of compound **8b**.¹³C NMR (75 MHz, CDCl₃) of compound **8b**.

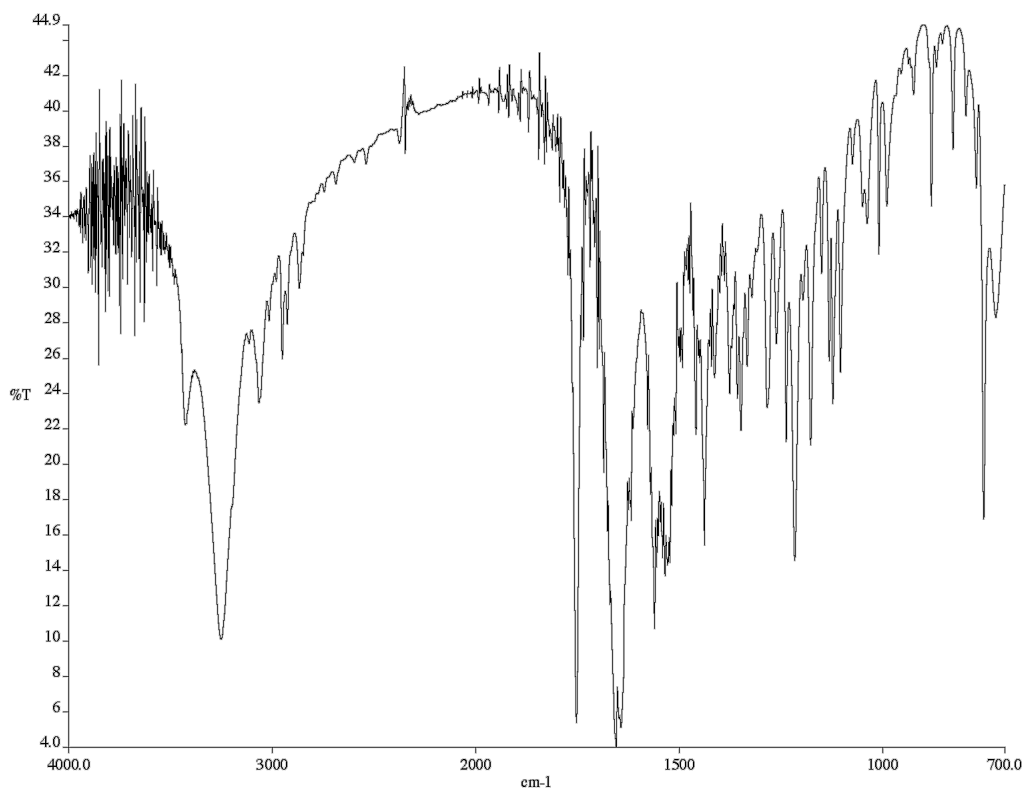
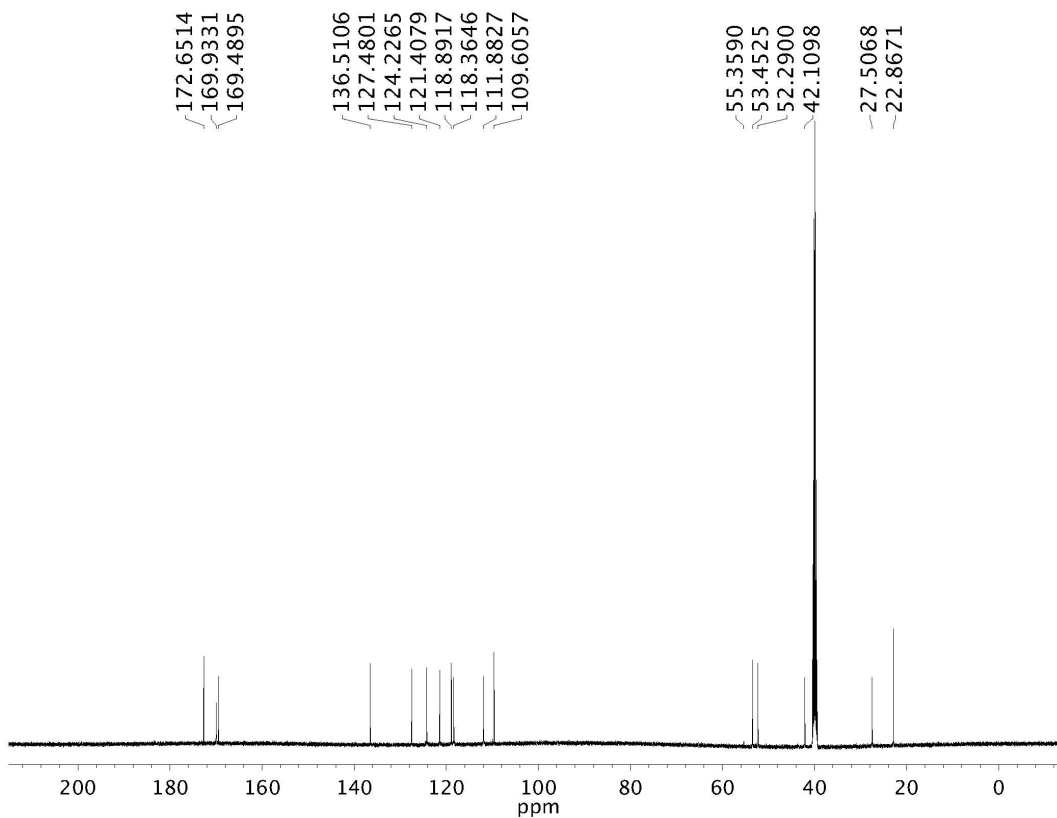


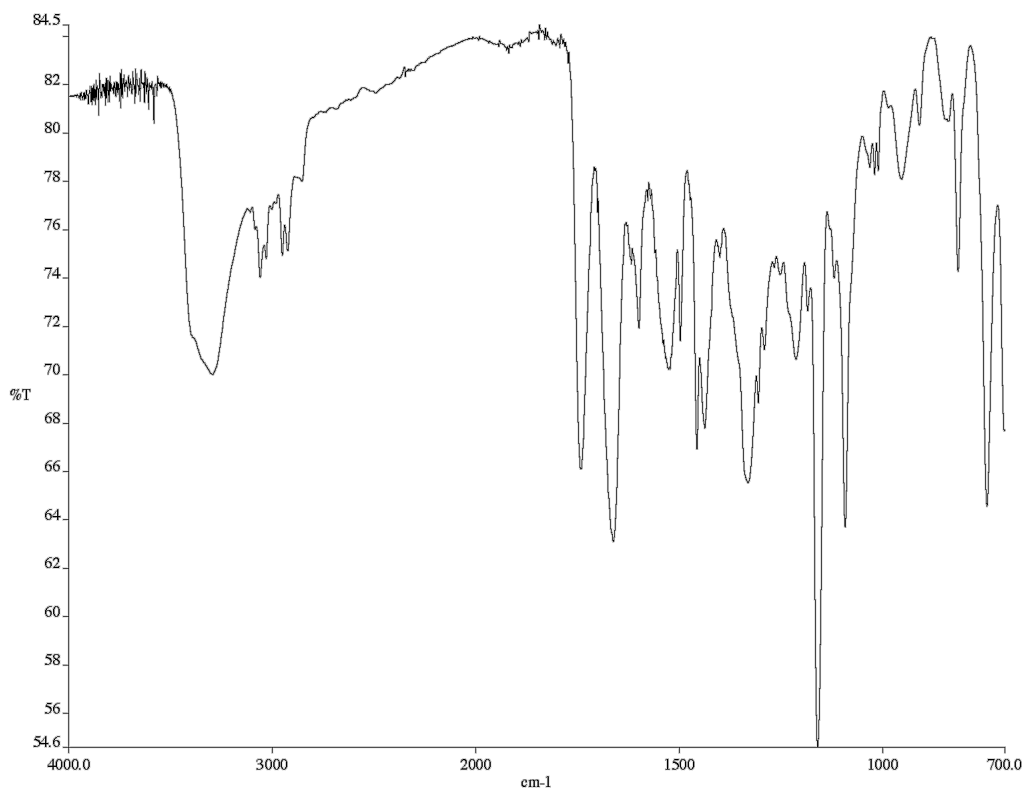
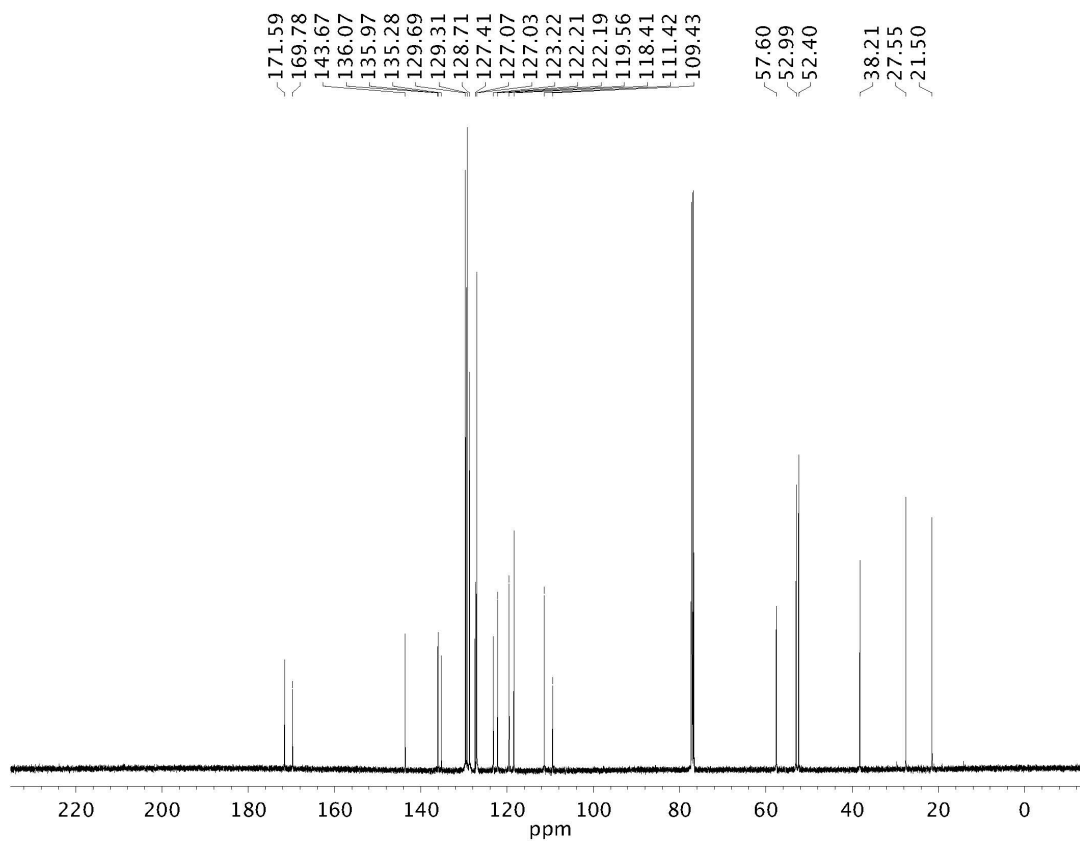
Infrared spectrum (Thin Film, NaCl) of compound **9a**.¹³C NMR (126 MHz, CDCl₃) of compound **9a**.

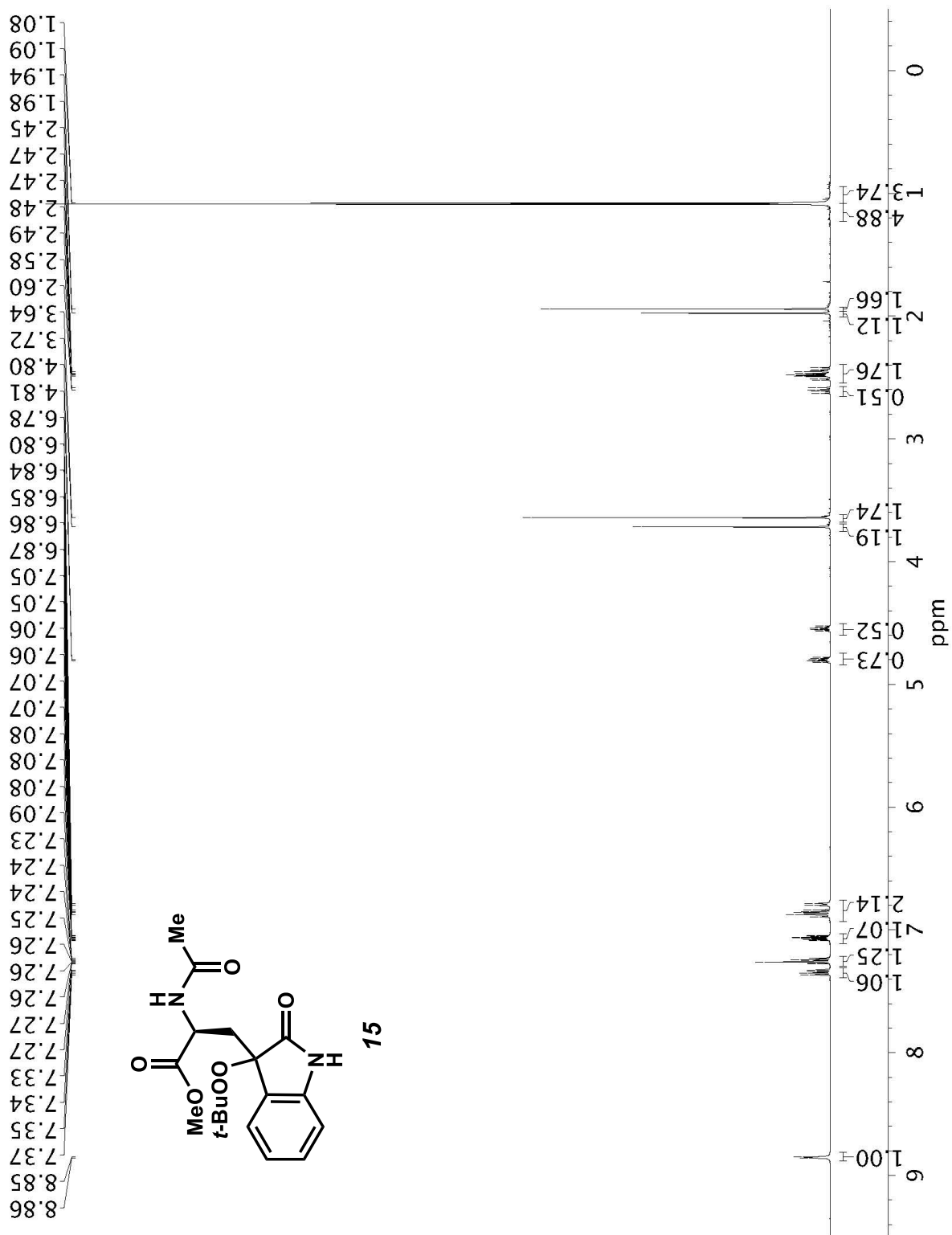


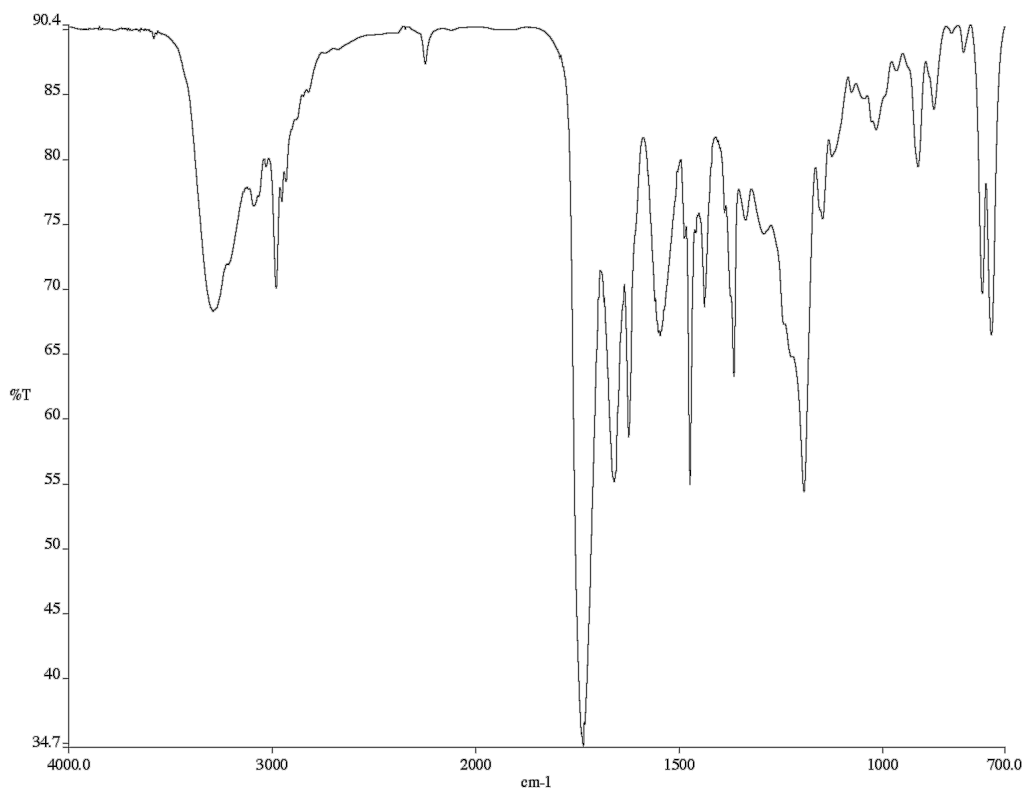
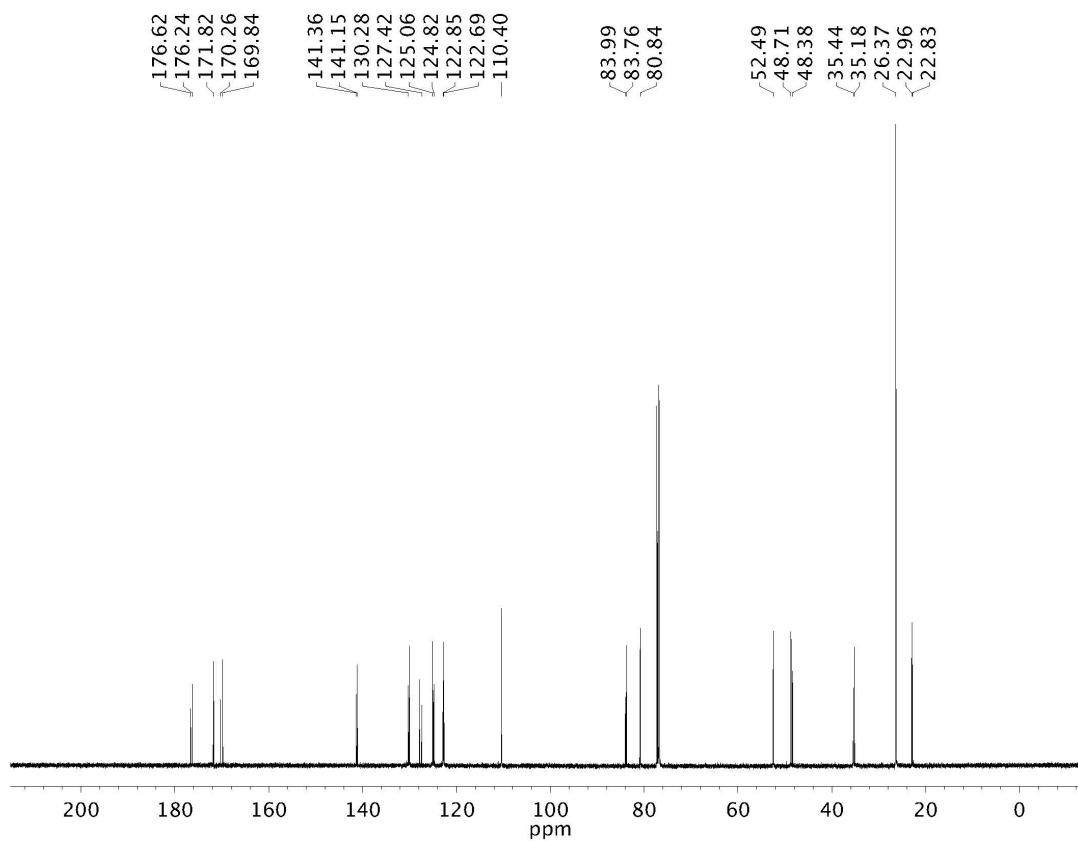


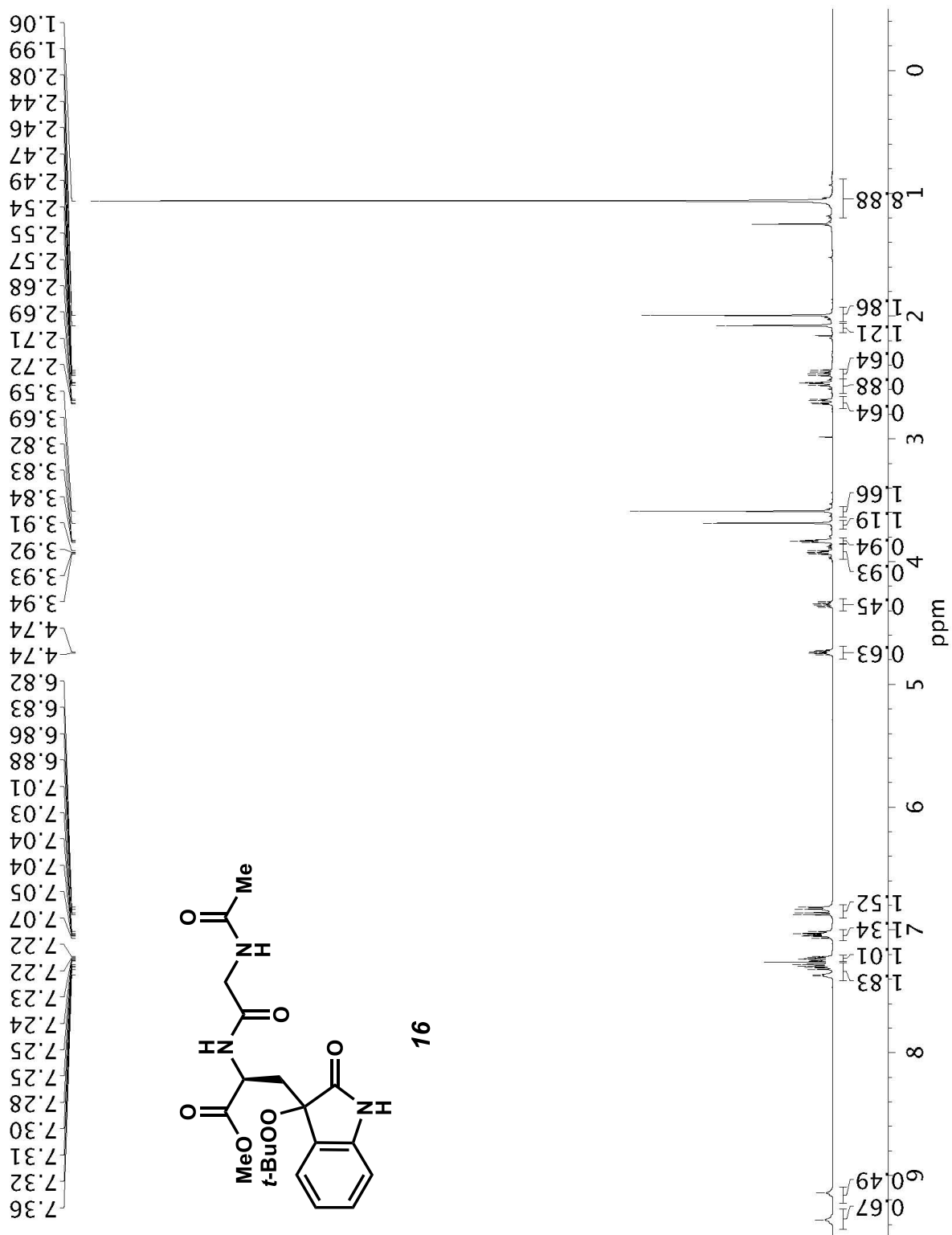


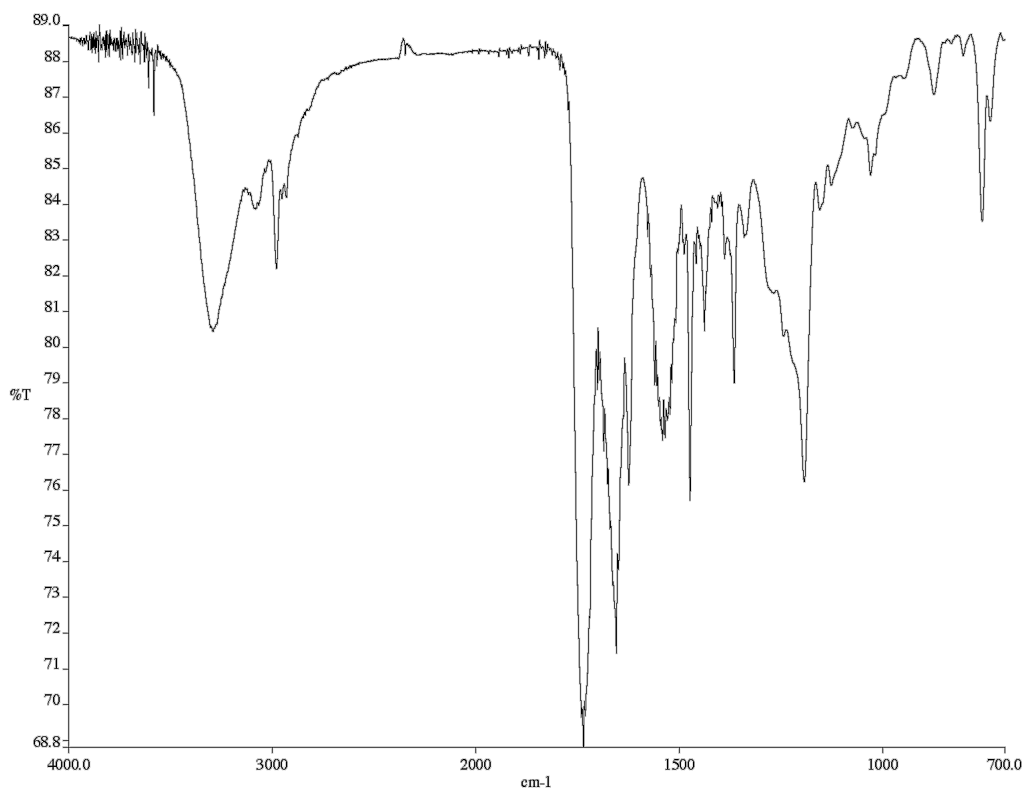
Infrared spectrum (Thin Film, NaCl) of compound **13**.¹³C NMR (126 MHz, DMSO) of compound **13**.

Infrared spectrum (Thin Film, NaCl) of compound **14**. ^{13}C NMR (126 MHz, CDCl_3) of compound **14**.

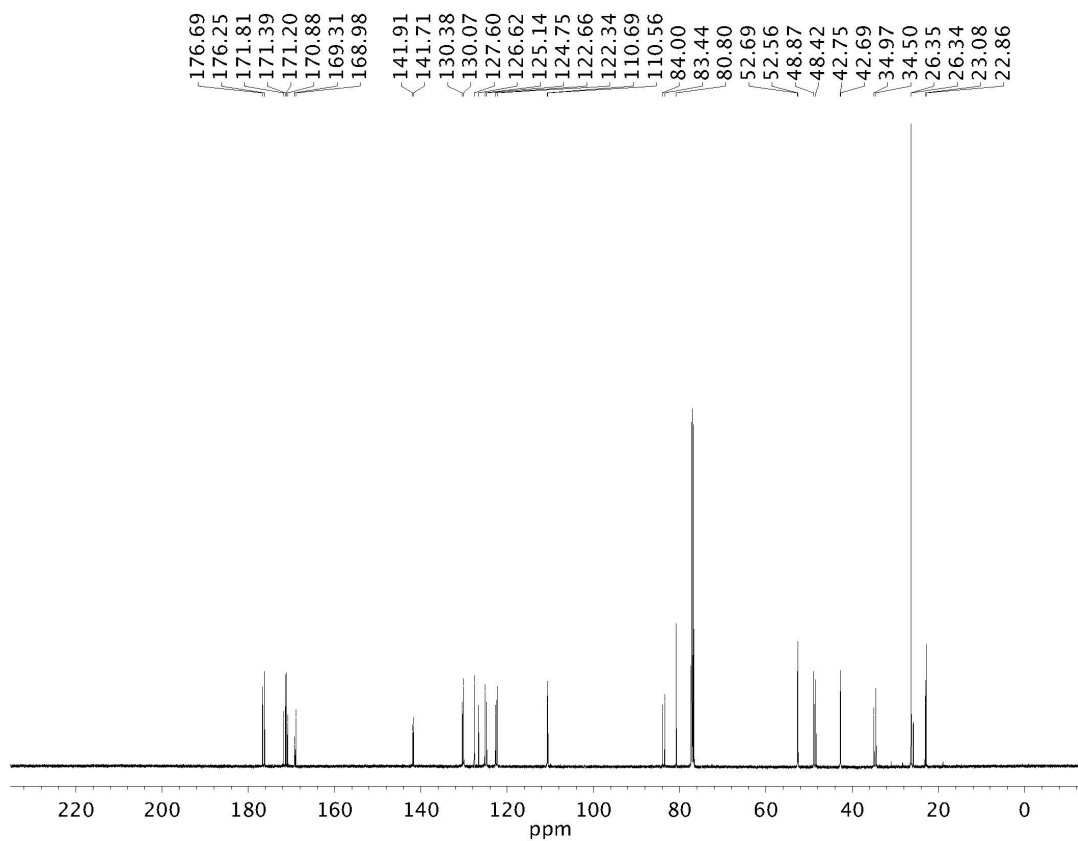


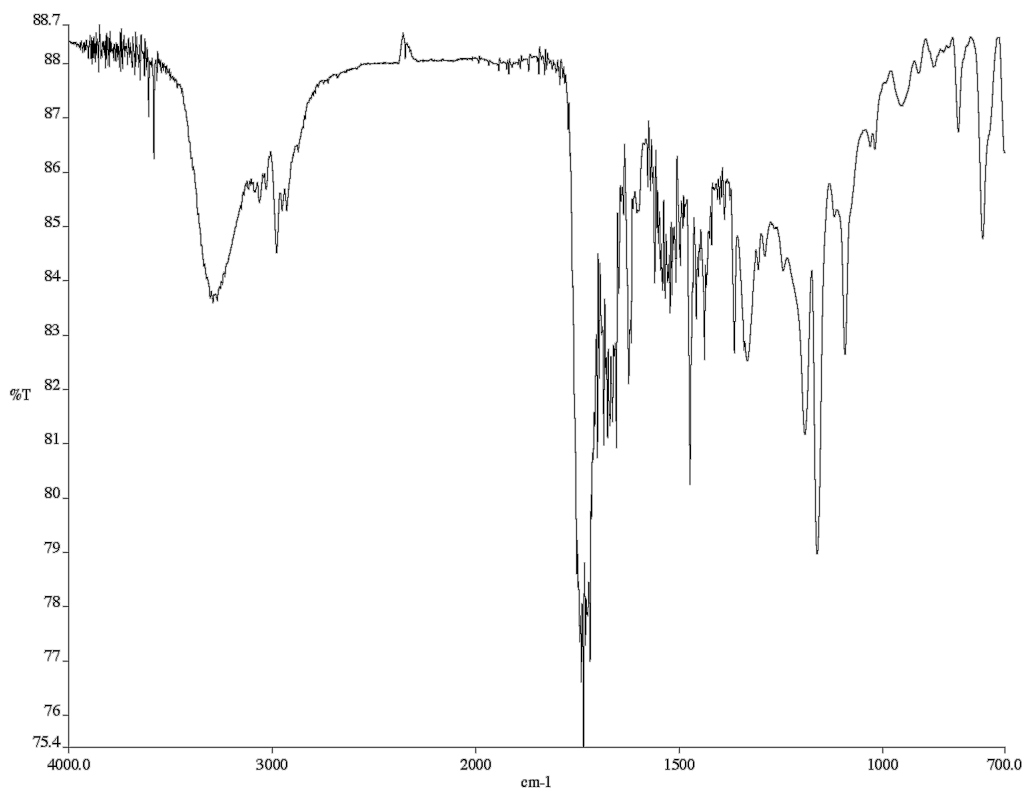
Infrared spectrum (Thin Film, NaCl) of compound **15**. ^{13}C NMR (126 MHz, CDCl_3) of compound **15**.



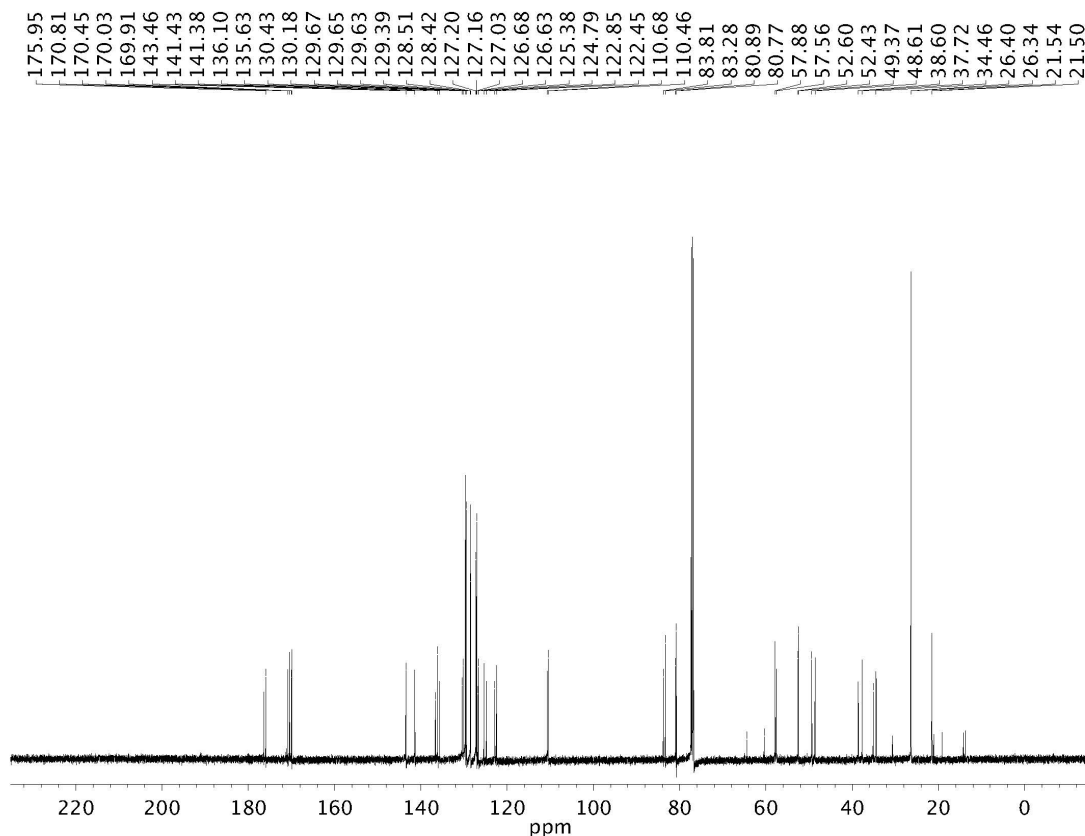


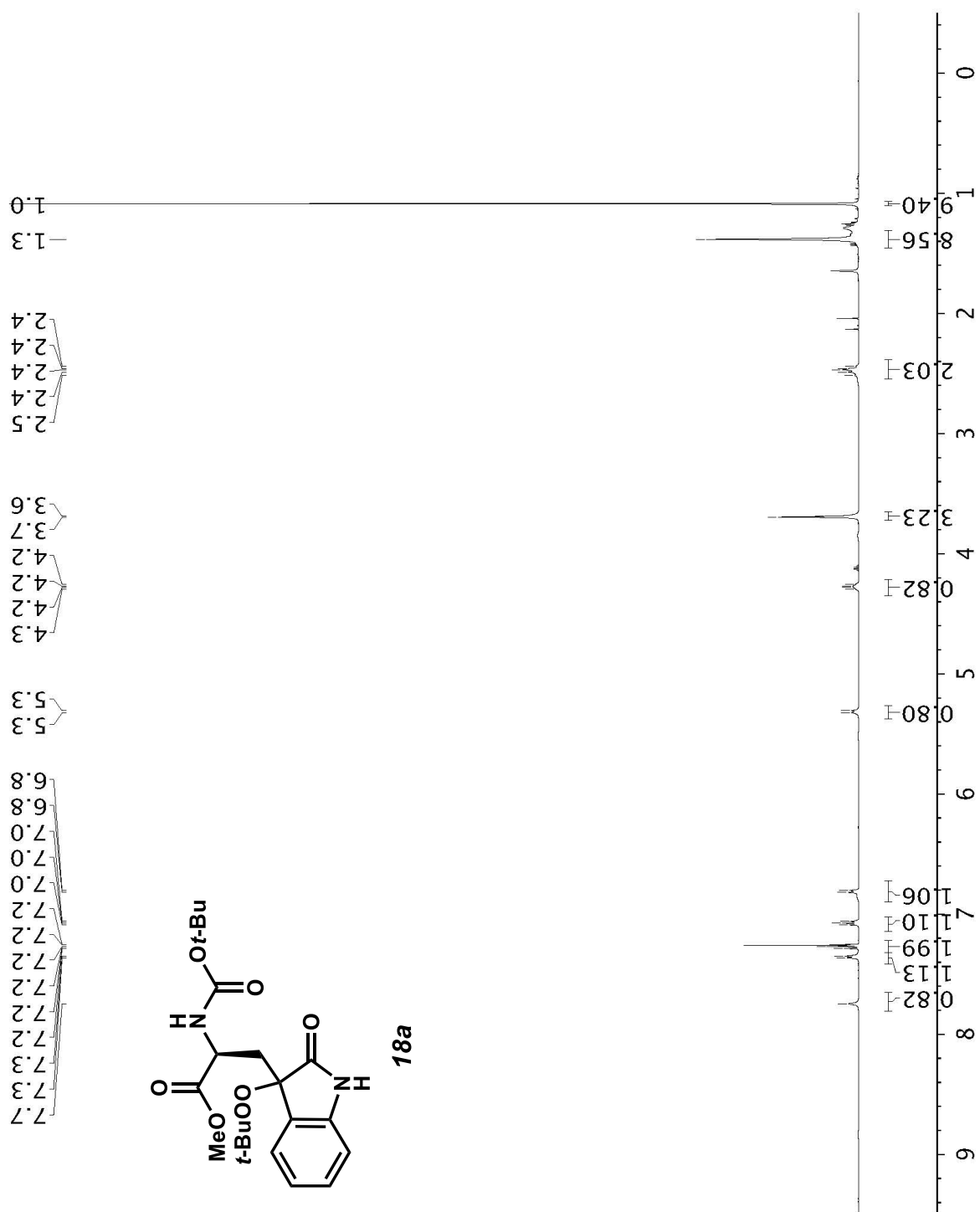
Infrared spectrum (Thin Film, NaCl) of compound 16.

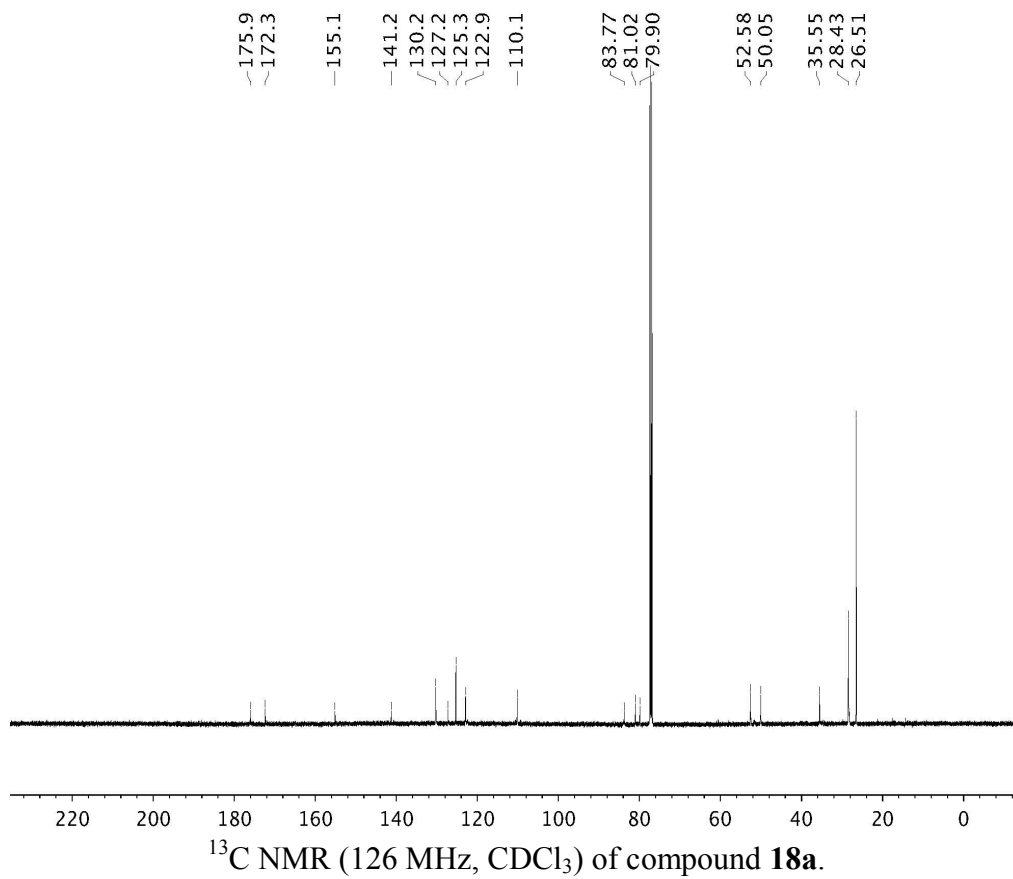
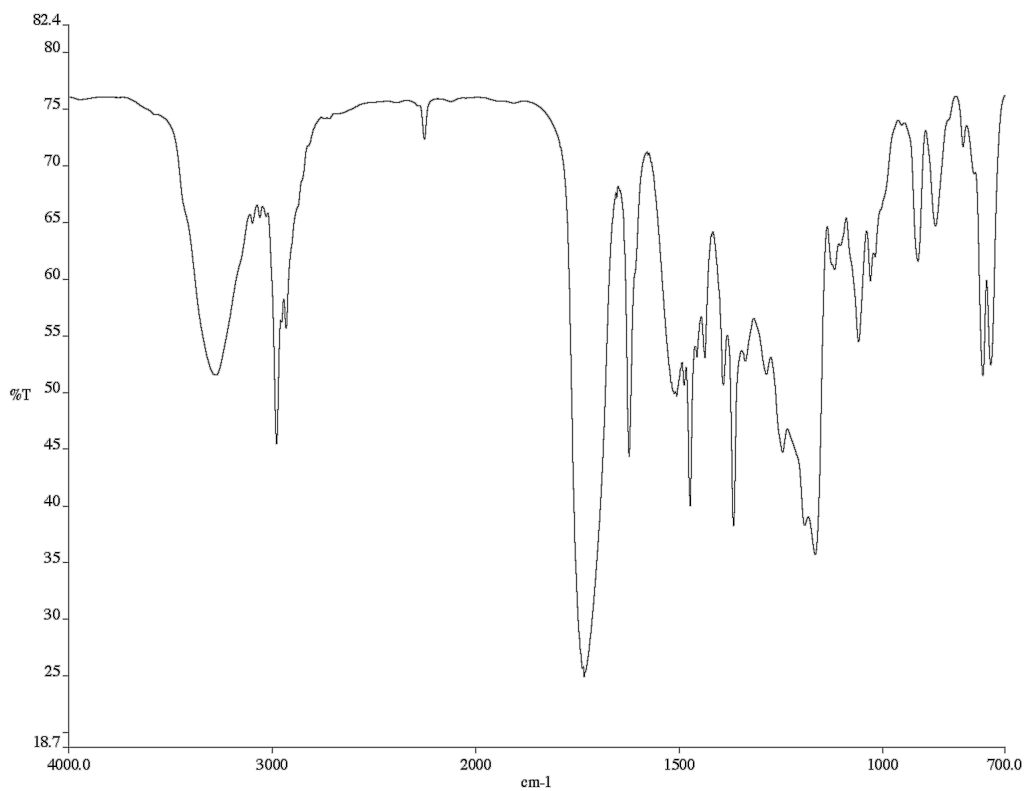
 ^{13}C NMR (126 MHz, CDCl_3) of compound 16.

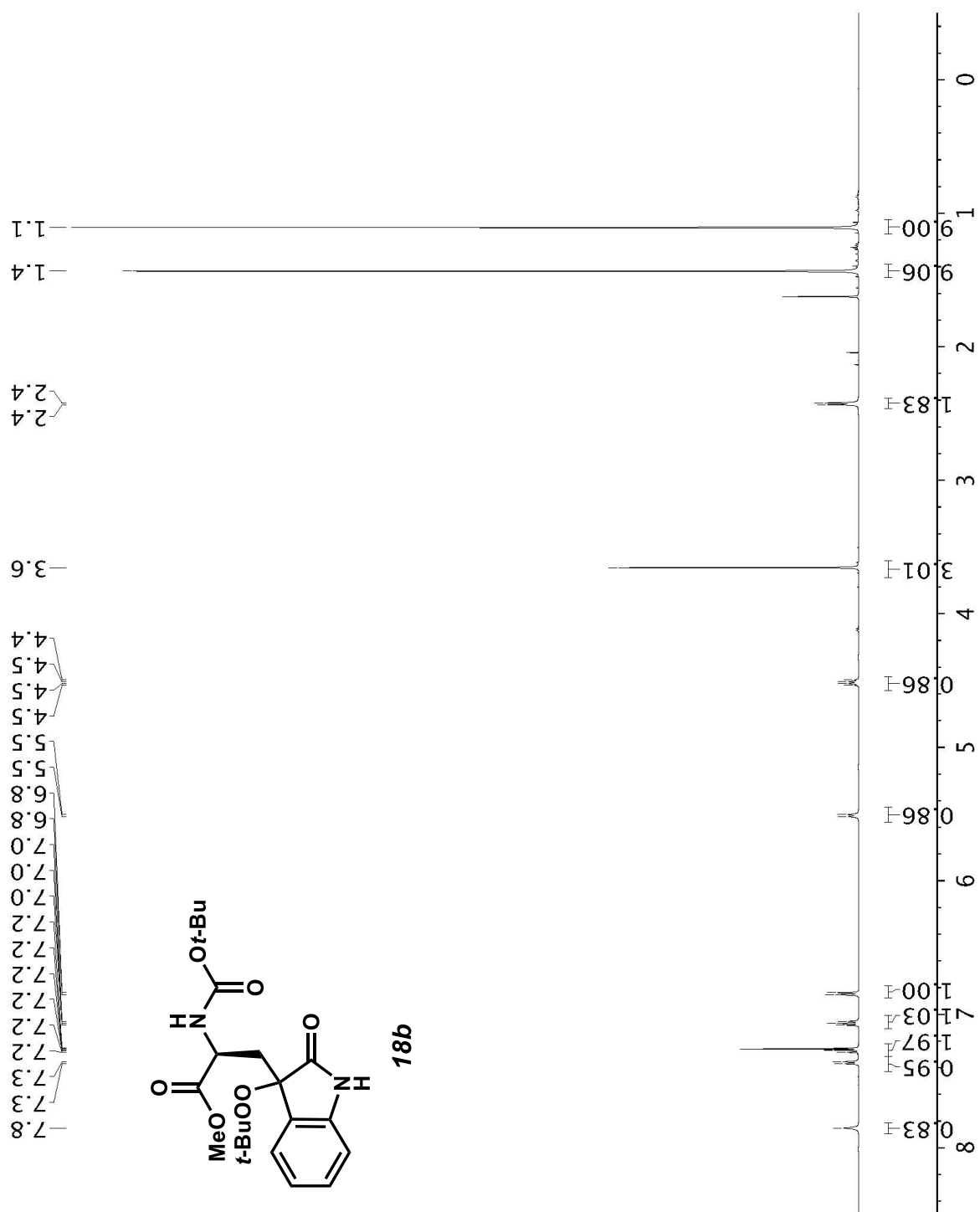


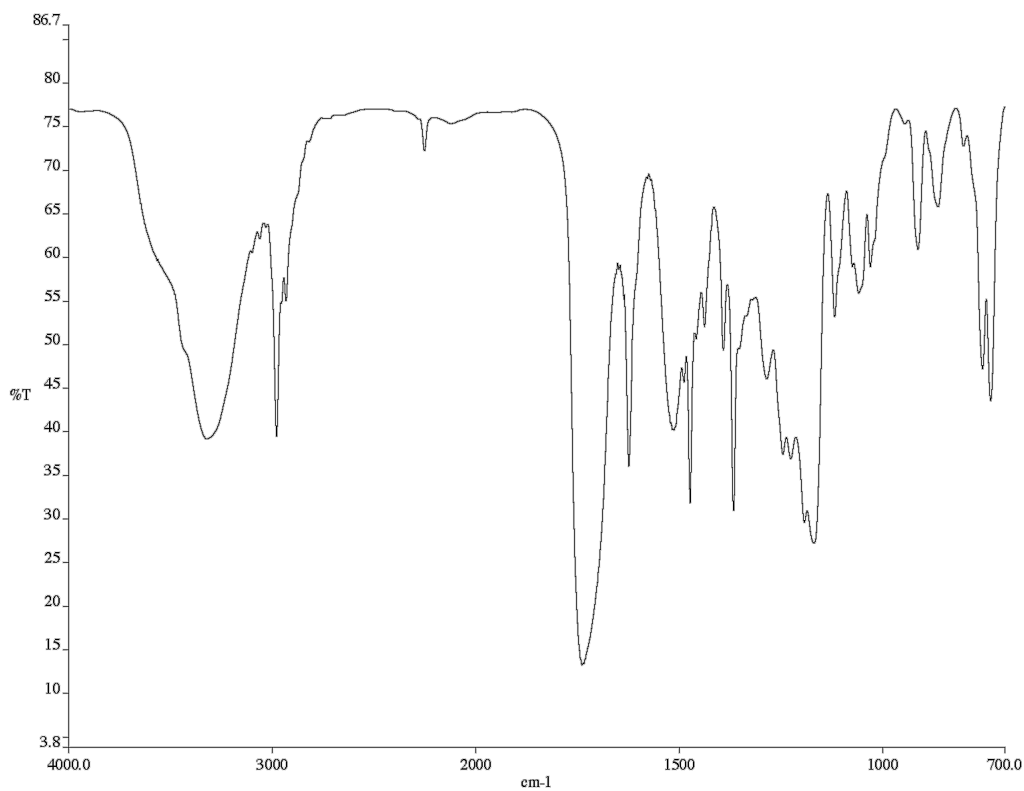
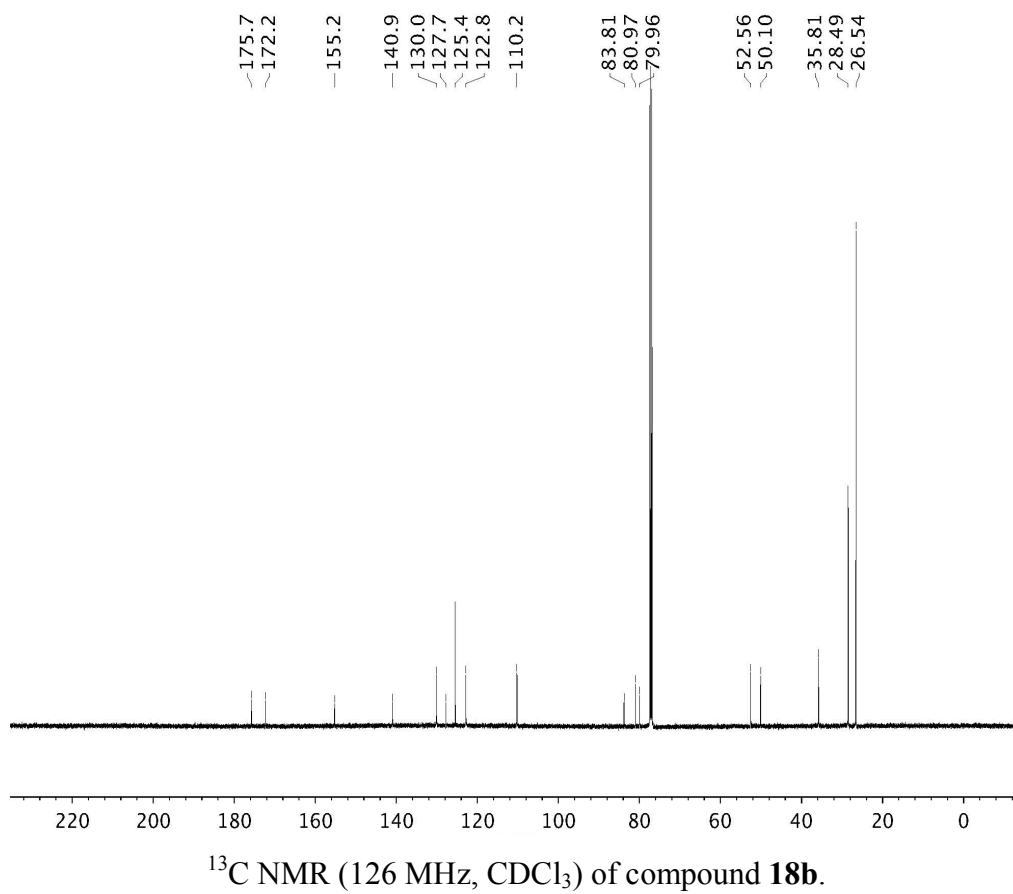
Infrared spectrum (Thin Film, NaCl) of compound 17.

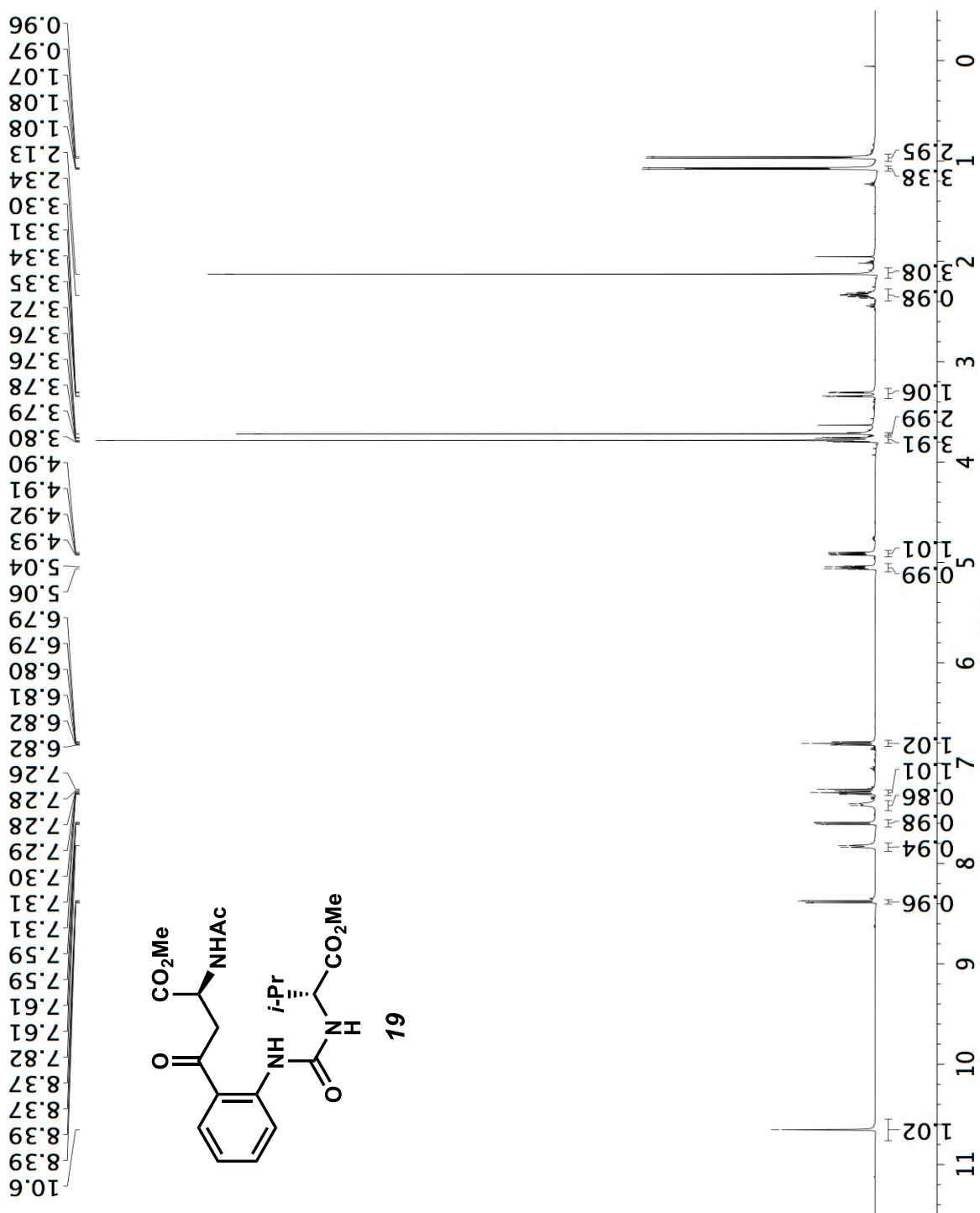
¹³C NMR (126 MHz, CDCl₃) of compound 17.

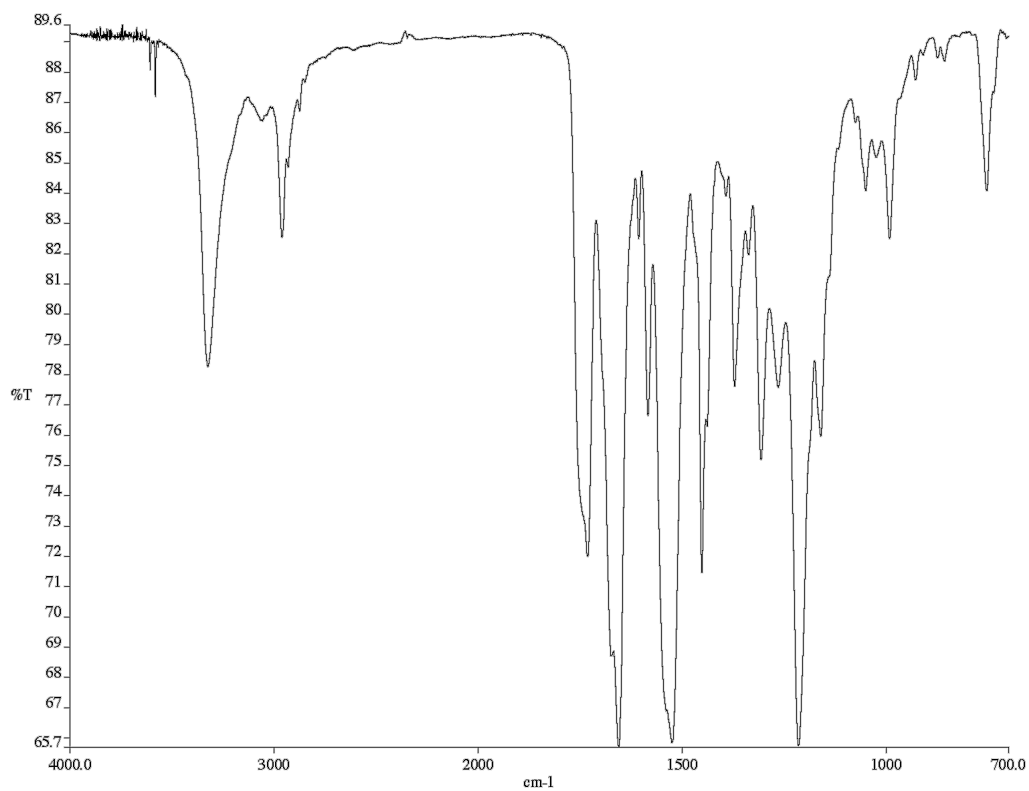




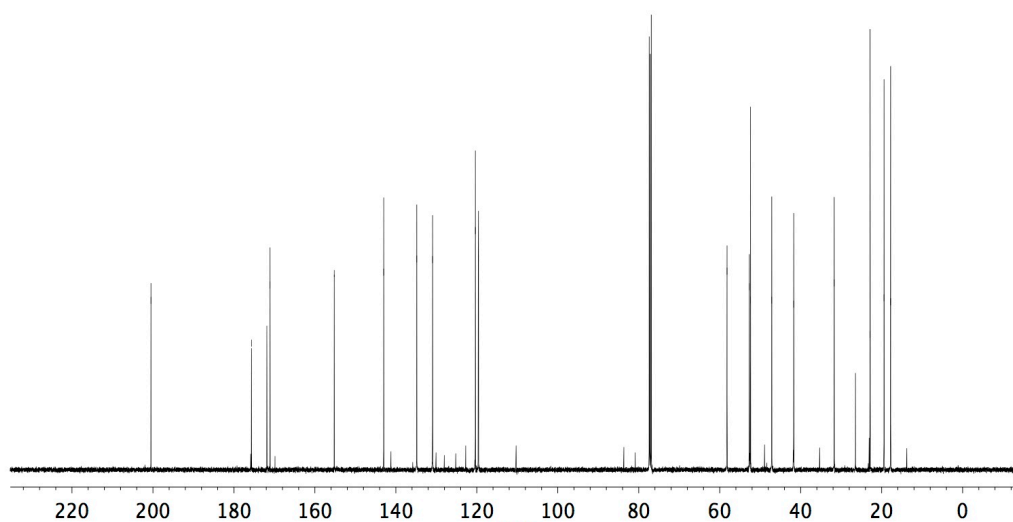


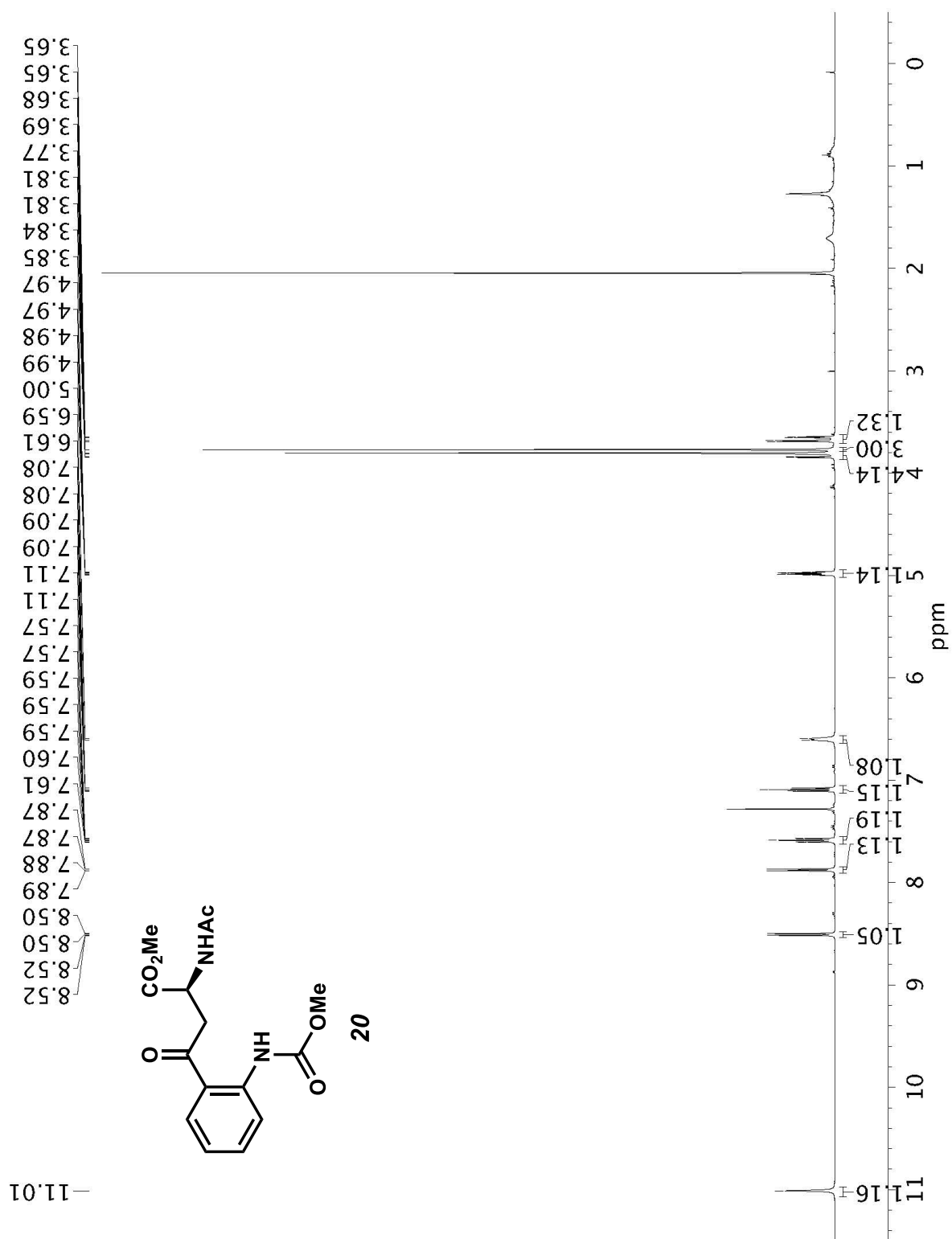
Infrared spectrum (Thin Film, NaCl) of compound **18b**.¹³C NMR (126 MHz, CDCl₃) of compound **18b**.

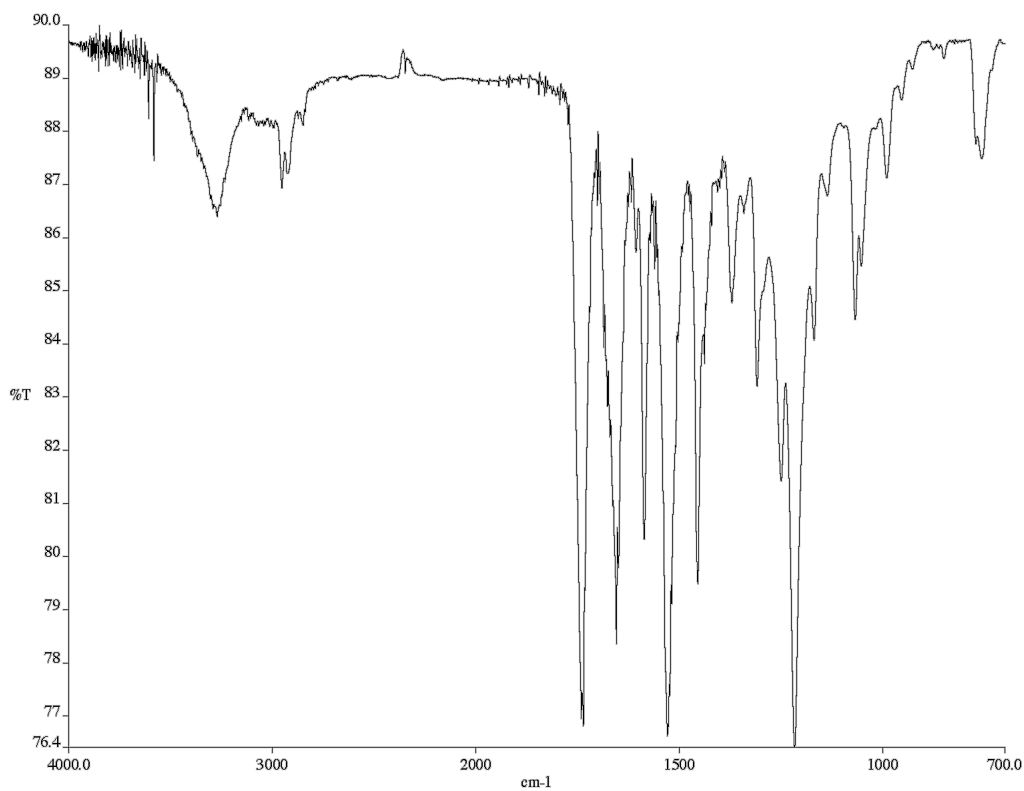
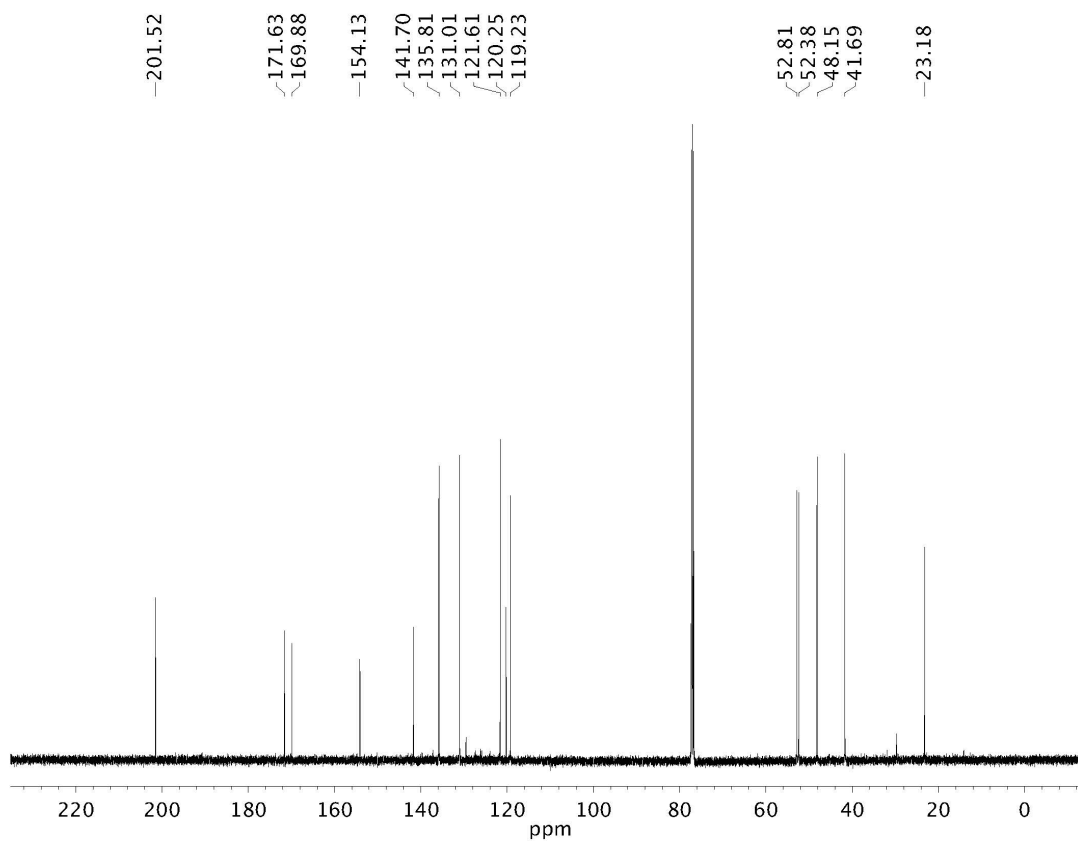


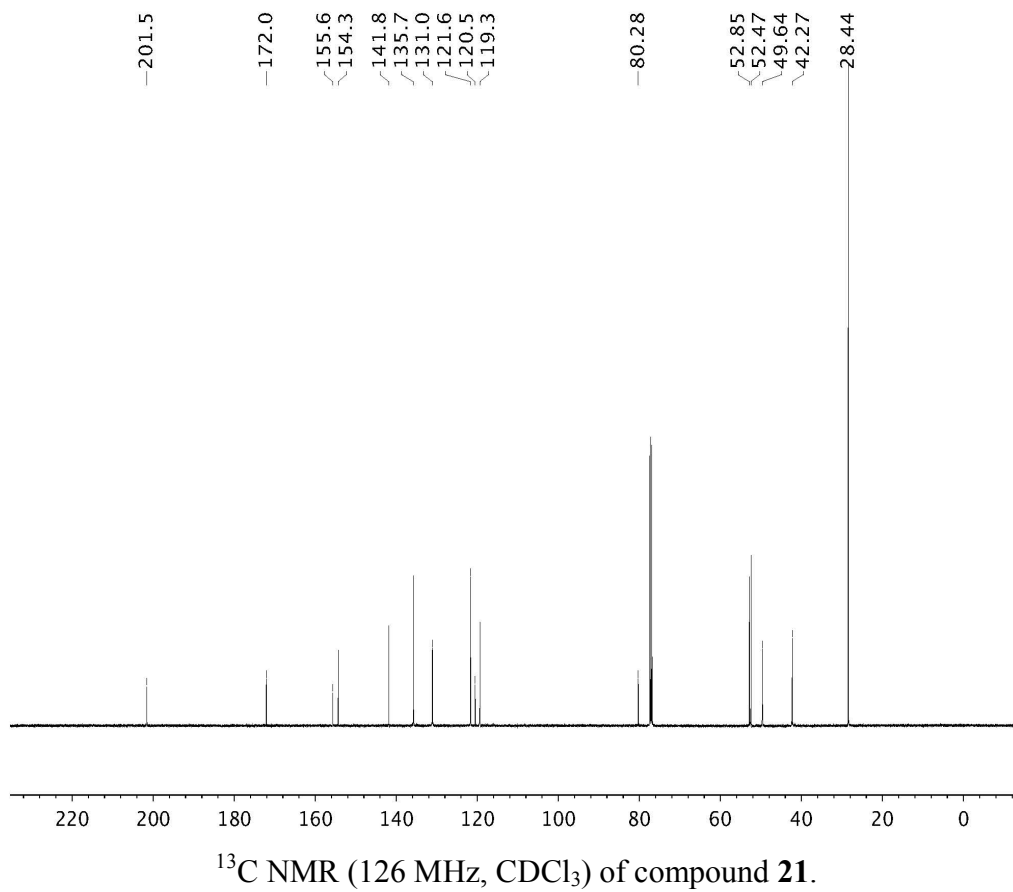
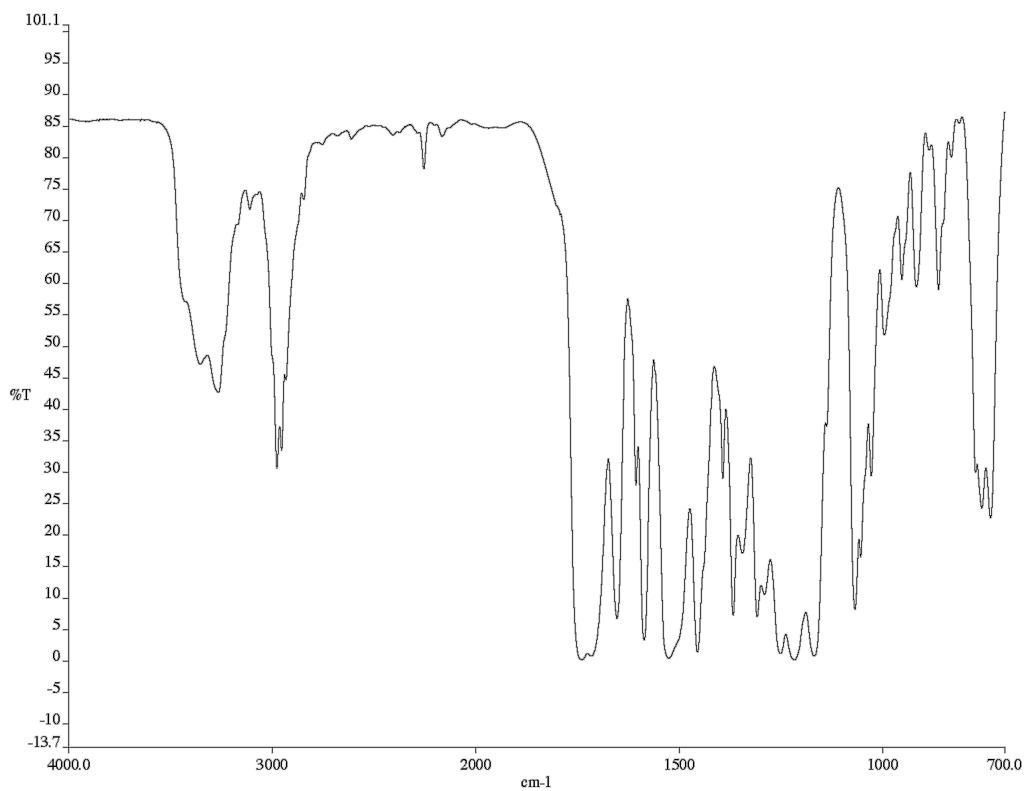
Infrared spectrum (Thin Film, NaCl) of compound **19**.

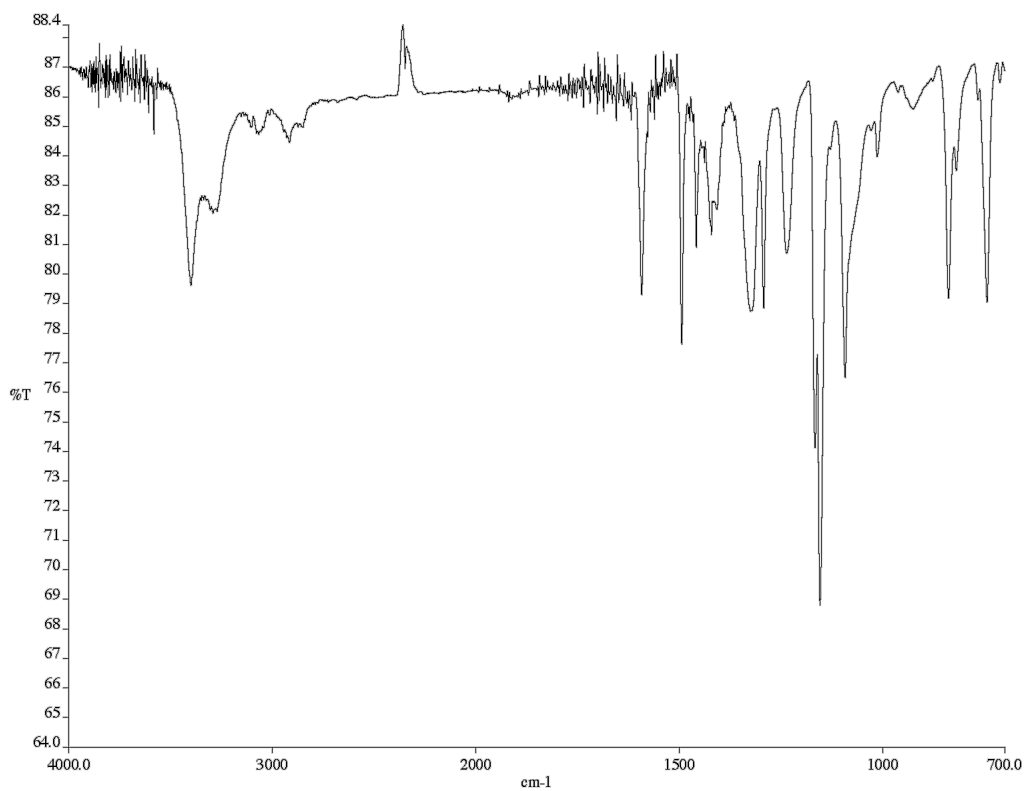
—200.4
—175.6
—171.8
—171.0
—155.2
—143.0
—134.8
—130.9
—120.3
—119.6
—119.5
—58.18
—52.69
—52.39
—47.14
—41.72
—31.72
—22.87
—19.42
—17.78

 ^{13}C NMR (126 MHz, CDCl_3) of compound **19**.

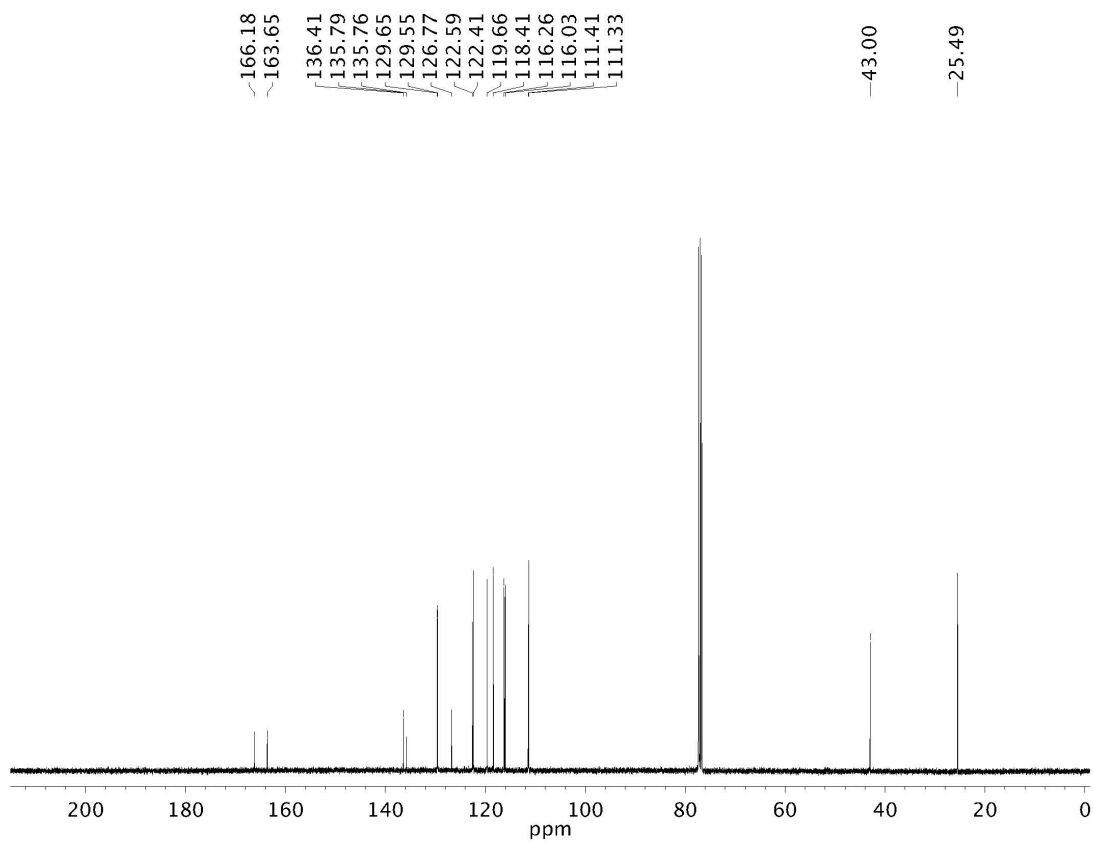


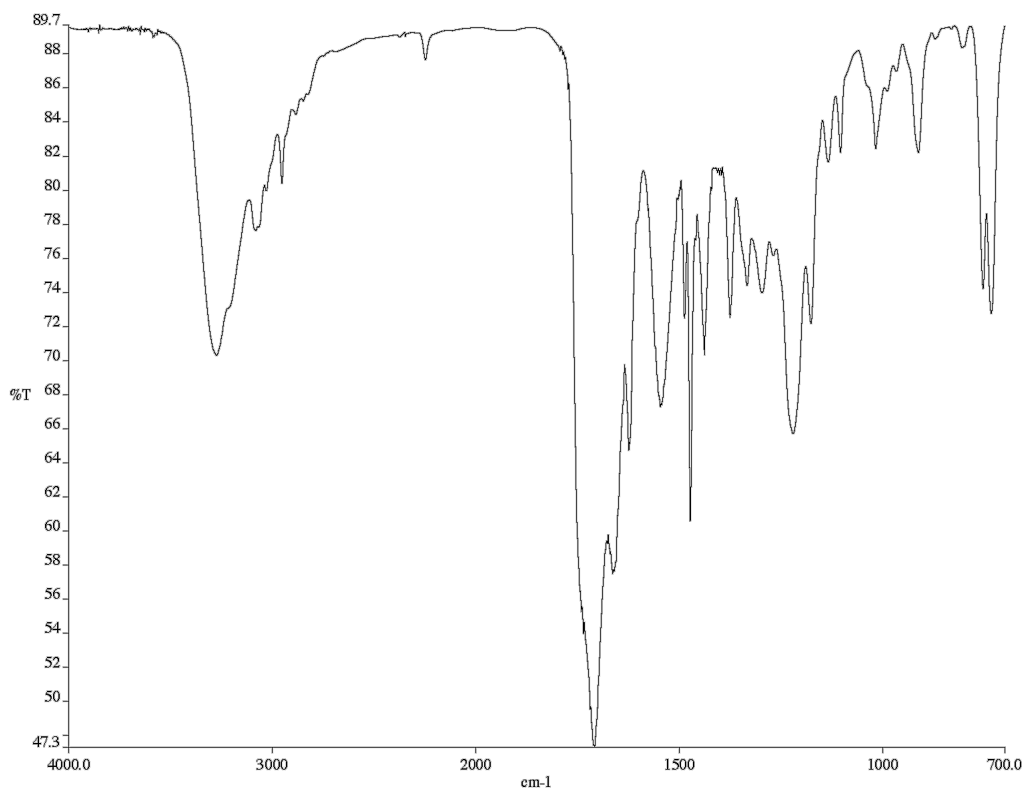
Infrared spectrum (Thin Film, NaCl) of compound **20**.¹³C NMR (126 MHz, CDCl₃) of compound **20**.



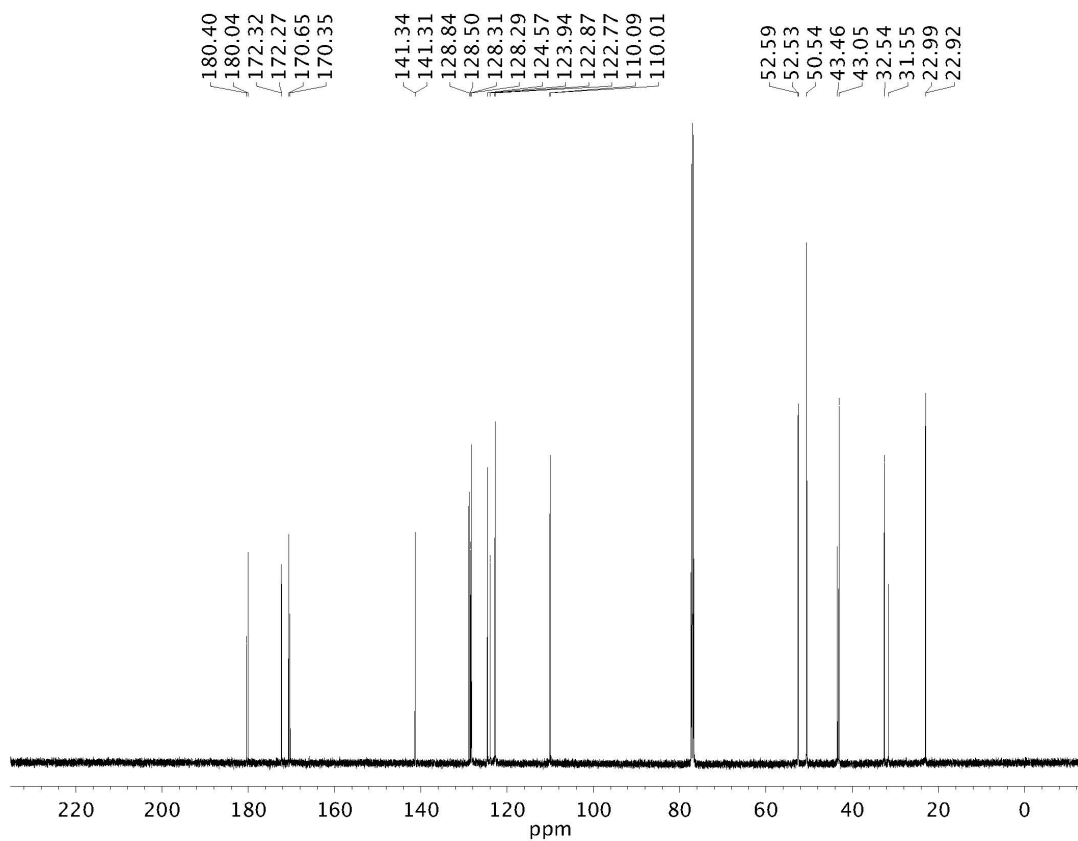


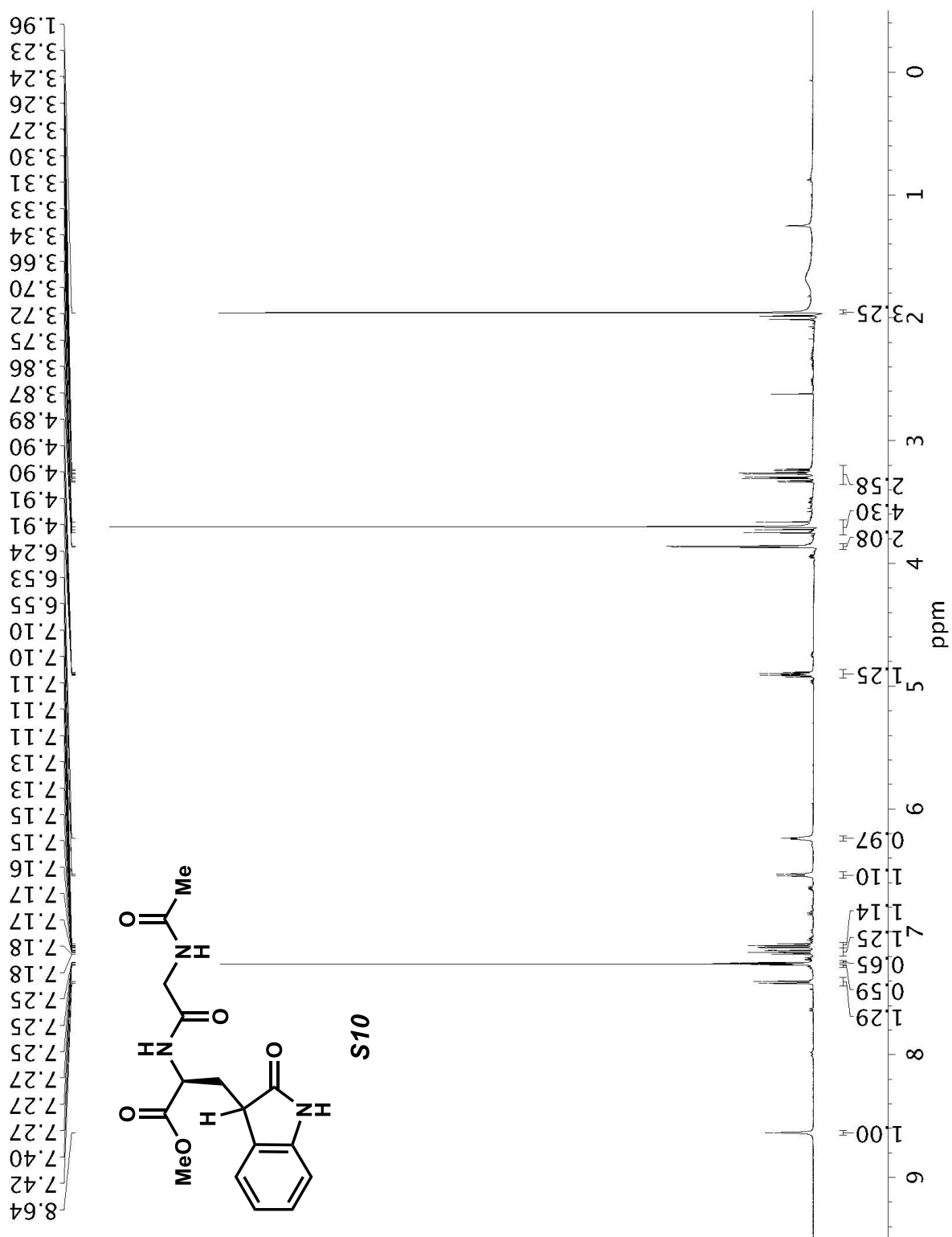
Infrared spectrum (Thin Film, NaCl) of compound S4.

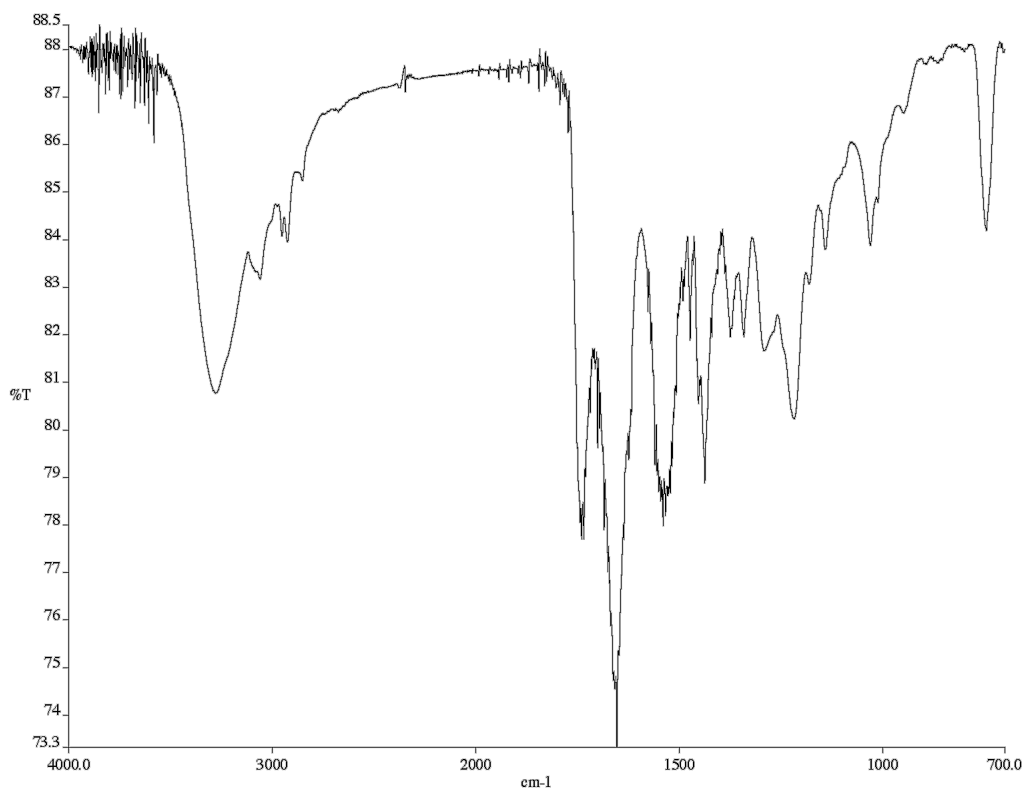
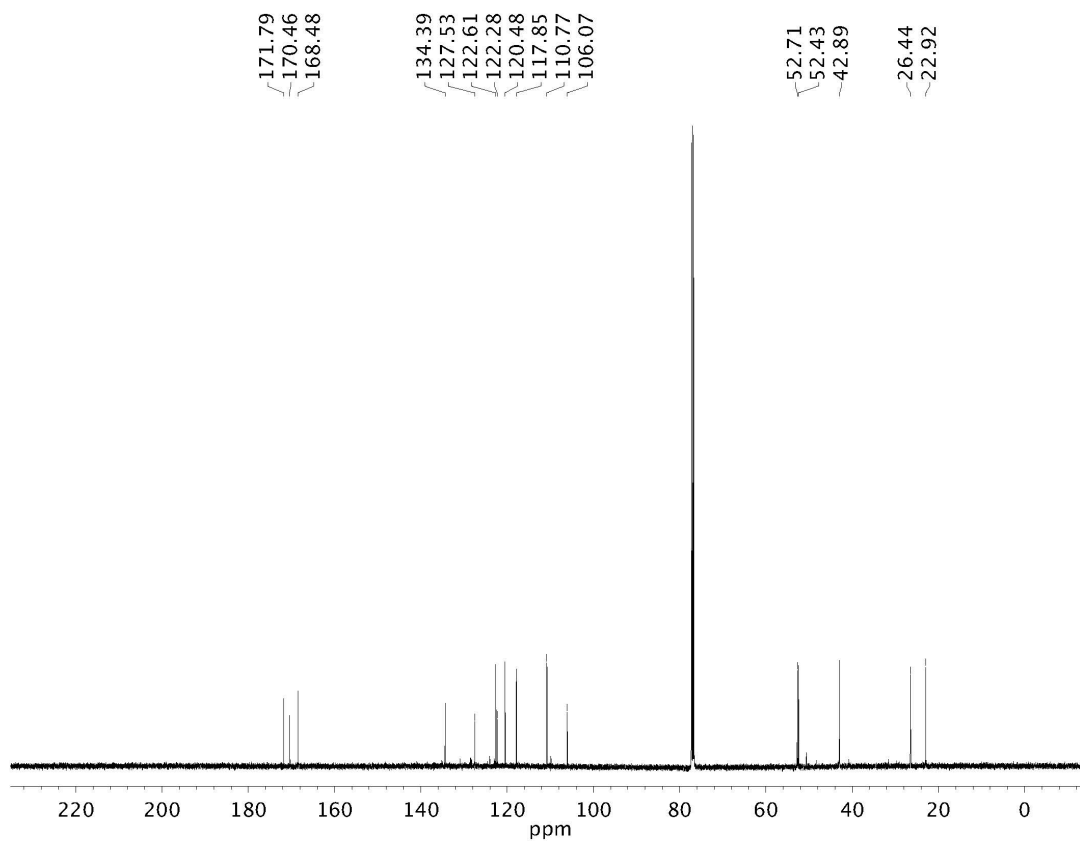
 ^{13}C NMR (100 MHz, CDCl_3) of compound S4.

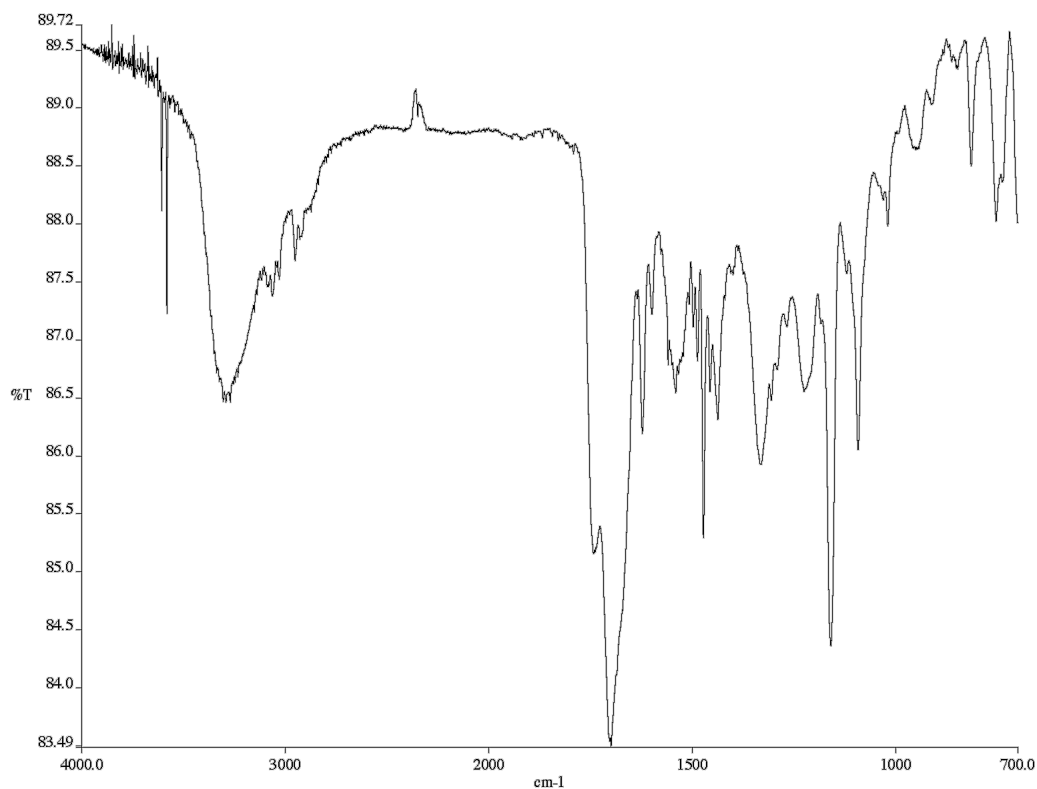


Infrared spectrum (Thin Film, NaCl) of compound S9.

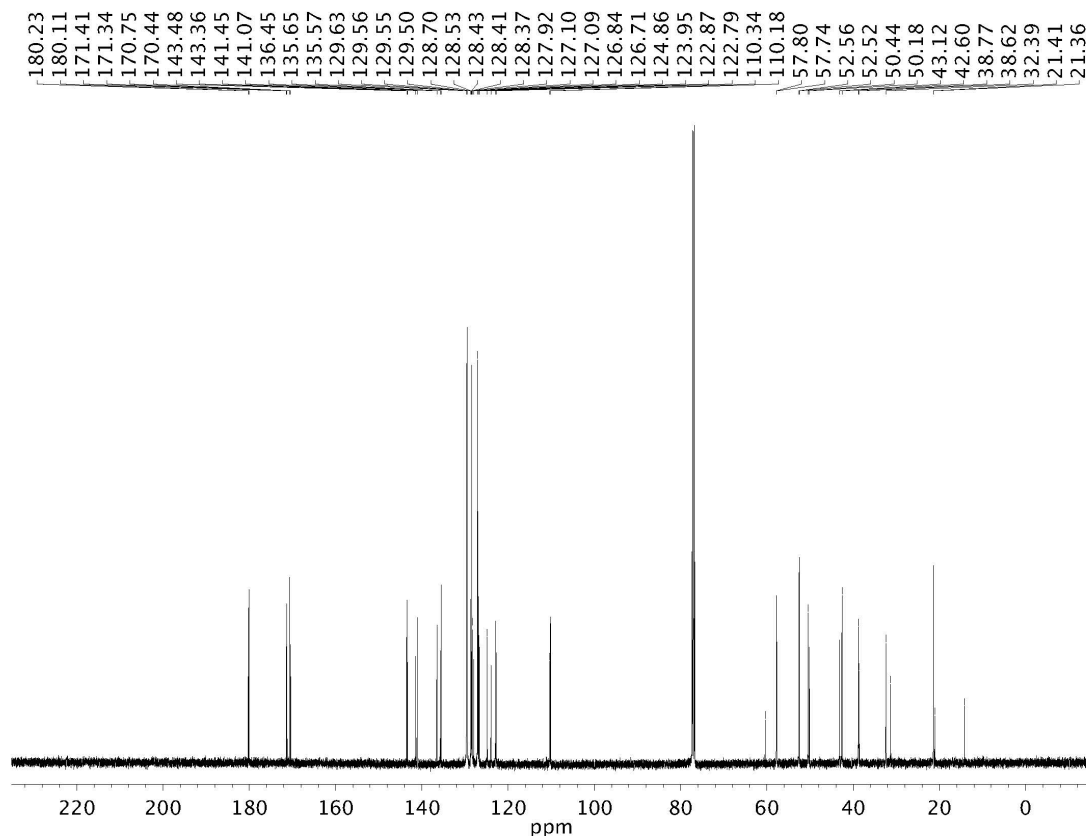
¹³C NMR (126 MHz, CDCl₃) of compound S9.

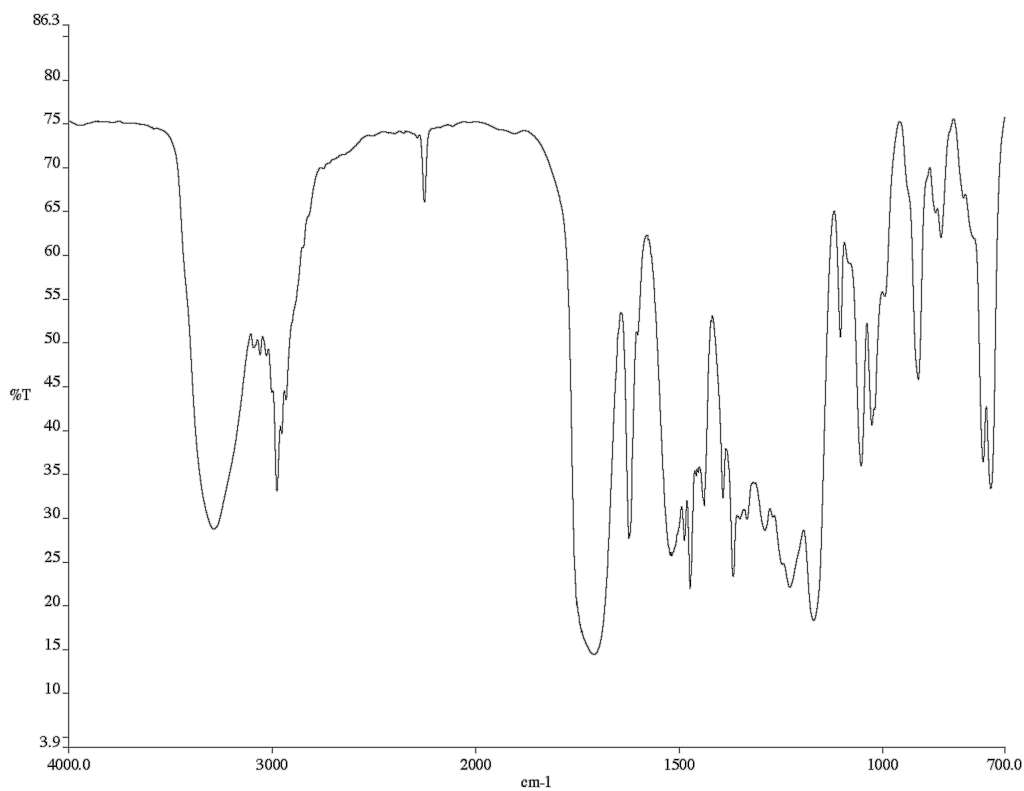
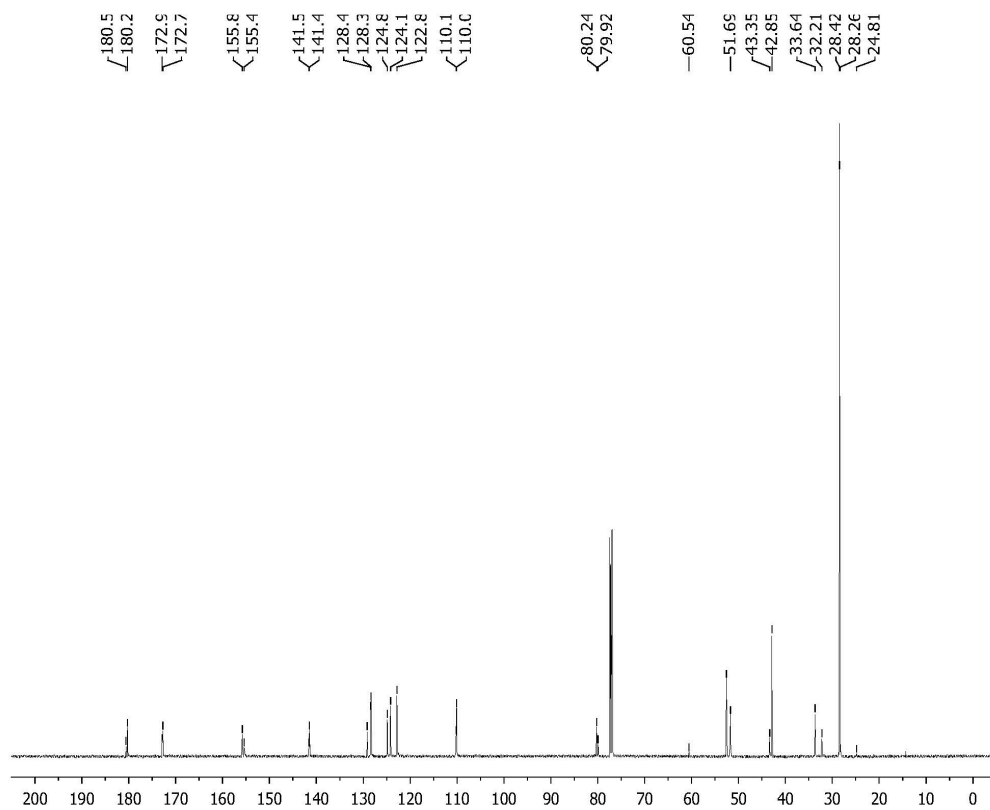


Infrared spectrum (Thin Film, NaCl) of compound **S10**.¹³C NMR (126 MHz, CDCl₃) of compound **S10**.



Infrared spectrum (Thin Film, NaCl) of compound S11.

¹³C NMR (126 MHz, CDCl₃) of compound S11.

Infrared spectrum (Thin Film, NaCl) of compound **S13**. ^{13}C NMR (126 MHz, CDCl_3) of compound **S13**.