

Supporting Information

Intramolecular through-space charge transfer between benzofuran and ynone groups on a naphthalene spacer

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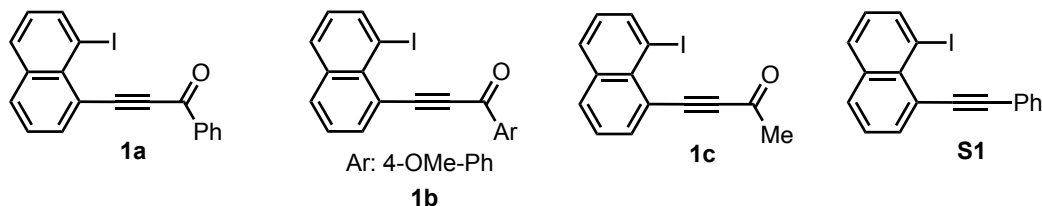
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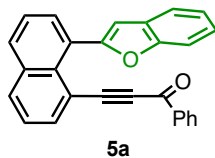
General Information: All reactions were performed using oven-dried glassware under an inert atmosphere of nitrogen. Reactions were monitored by thin-layer chromatography (TLC) using aluminum-backed plates pre-coated with silica gel (Silicycle, Silica Gel 60 F₂₅₄). UV light and KMnO₄ staining solutions were used for TLC visualization. Flash column chromatography was performed on Silicycle 40-63 µm (230-400 mesh) flash silica gel. NMR spectra were measured using a Bruker spectrometer at 400 MHz for ¹H NMR spectra and 100 MHz for ¹³C NMR spectra and calibrated from internal standard (TMS, 0 ppm) or residual solvent signals (chloroform at 7.26 ppm for ¹H spectra, and at 77.16 ppm and for ¹³C spectra). ¹H NMR data are reported as follows: chemical shift (parts per million, ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, app = apparent), coupling constant (Hz). Infrared (FTIR) spectra were recorded on a Bruker Alpha-Platinum-ATR spectrometer with only selected peaks reported. Mass spectral analyses were performed at UNAM-National Nanotechnology Research Center and Institute of Materials Science and Nanotechnology, Bilkent University. XRD analysis was performed at the Scientific and Technological Research Application and Research Center, Sinop University, Türkiye. UV-vis absorption spectra were recorded using a Varian Cary 5000 spectrophotometer, and emission spectra were recorded using a Varian Cary Eclipse fluorescence spectrometer. Cyclic voltammograms of **5a**, **5b** and **6** (ca. 1 mM concentration) were taken by using Gamry Reference 3000 potentiostat. Three-electrode system was utilized for cyclic voltammetry experiment; glassy carbon (GC) as working electrode for the experiments where DCM was used as solvent and platinum (Pt) coil electrode for the experiments where THF was used as solvent, graphite rod as counter electrode and Ag wire as reference electrode. As supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) was used in DCM solution, and 0.1 M tetrabutylammonium perchlorate (NBu₄ClO₄) was used in THF solution. Scan rate of voltammograms was 50 mV/s, and potential window for the scans were 0 V to 1.5 V for DCM solutions and -2.0 V to 0 V for THF solutions.

Materials: Anhydrous CH₂Cl₂, THF and 1,4-dioxane were purchased from Acros Organics (AcroSeal®) and used as received. Anhydrous THF, which was used for the cyclic voltammetry (CV) measurements, was obtained by refluxing over Na and benzophenone followed by distillation under nitrogen. In addition, prior to each CV measurement, anhydrous THF was deoxygenated by the application of freeze-pump-thaw technique for three cycles. All other commercially available reagents were used as received unless stated otherwise.

Iodonaphthalene derivatives **1a**, **1b**, **1c** and **S1** were prepared following our previously reported procedures.¹



Synthesis of Compounds 5-10:



An oven-dried, round bottom flask was evacuated with vacuum and refilled with nitrogen three times. Iodonaphthalene **1a** (133 mg, 0.348 mmol) was dissolved in 1.0 mL of anhydrous 1,4-dioxane. Then, benzofuran-2-boronic acid (134 mg, 0.83 mmol) and Pd(PPh₃)₄ (20 mg, 0.017 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (1.0 mL). Finally, K₃PO₄ (222 mg, 1.05 mmol) and 1.0 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C with a condenser for 6.5 h. After full consumption of iodonaphthalene **1a** was observed by TLC, the reaction mixture was cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (only hexanes) gave product **5a** as orange oil (91 mg, 70% yield).

$R_f = 0.48$ (EtOAc:hexanes = 1:4)

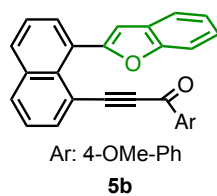
TLC Visualization: UV active; stains with KMnO₄ solution.

¹H NMR (400 MHz; CDCl₃) δ : 8.03 (2H, d, $J = 8.2$ Hz), 7.94 (1H, d, $J = 7.0$ Hz), 7.75 (1H, d, $J = 6.7$ Hz), 7.70 (2H, d, $J = 7.3$ Hz), 7.63 – 7.49 (3H, m), 7.33 (2H, t, $J = 7.7$ Hz), 7.21 (1H, d, $J = 8.1$ Hz), 7.16 (1H, d, $J = 7.3$ Hz), 6.99 (1H, td, $J = 8.0, 1.2$ Hz), 6.93 (1H, t, $J = 7.4$ Hz), 6.87 (1H, s).

¹³C NMR (100 MHz; CDCl₃) δ : 176.8, 155.8, 154.2, 136.3, 135.6, 134.3, 133.6, 132.5, 131.7, 131.3, 131.1, 129.4, 129.3, 128.7, 128.0, 126.0, 125.7, 124.4, 122.9, 121.0, 117.7, 111.9, 107.0, 91.9.

FTIR ν_{max} (ATR, film)/cm⁻¹ 3060, 2956, 2921, 2851, 2188, 1733, 1635, 1616, 1598, 1450, 1372, 1354, 1258, 1228, 1175, 1097, 1019, 952, 907.

HRMS (+ESI) Calcd for C₂₇H₁₇O₂ [M+H]⁺ 373.1223, found: 373.1216.



An oven-dried, round bottom flask was evacuated with vacuum and refilled with nitrogen three times. Iodonaphthalene **1b** (140 mg, 0.34 mmol) was dissolved in 1.5 mL of anhydrous 1,4-dioxane. Then, benzofuran-2-boronic acid (110 mg, 0.68 mmol) and Pd(PPh₃)₄ (19.6 mg, 0.017 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (1.5 mL). Finally, K₃PO₄ (217 mg, 1.02 mmol) and 1.5 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C with a condenser for 4.5 h. After full consumption of iodonaphthalene **1b** was observed by TLC, the reaction mixture was cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (EtOAc:hexanes = 1:9) gave product **5b** as red oil (88 mg, 64% yield).

R_f = 0.25 (EtOAc:hexanes = 1:6)

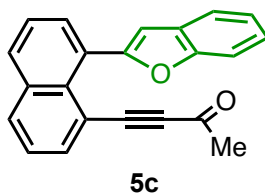
TLC Visualization: UV active; stains rapidly with KMnO₄ solution.

¹H NMR (400 MHz; CDCl₃) δ: 8.02 (2H, d, *J* = 8.2 Hz), 7.93 (1H, d, *J* = 7.2 Hz), 7.75 (1H, d, *J* = 6.9 Hz), 7.66 (2H, d, *J* = 8.5 Hz), 7.61 (1H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.8 Hz), 7.22 (2H, t, *J* = 7.9 Hz), 7.01 (1H, t, *J* = 7.4 Hz), 6.95 (1H, t, *J* = 7.5 Hz), 6.87 (1H, s), 6.80 (2H, d, *J* = 8.7 Hz), 3.88 (3H, s).

¹³C NMR (100 MHz; CDCl₃) δ: 175.5, 164.0, 155.8, 154.2, 135.5, 134.2, 132.4, 131.7, 131.6, 131.1, 131.0, 129.8, 129.3, 128.6, 125.9, 125.6, 124.3, 122.8, 121.0, 117.8, 113.2, 111.8, 106.9, 91.5, 91.1, 55.6.

FTIR ν_{max} (ATR, film)/cm⁻¹ 3054, 2921, 2851, 2188, 1738, 1664, 1598, 1573, 1508, 1457, 1421, 1371, 1256, 1236, 1162, 1108, 1028, 953, 882, 829, 750.

HRMS (+ESI) Calcd for C₂₈H₁₉O₂ [M+H]⁺ 403.1329, found: 403.1324.



An oven-dried, 25-mL Schlenk tube was evacuated with vacuum and refilled with nitrogen three times. Iodonaphthalene **1c** (30.0 mg, 0.094 mmol) was dissolved in 1.0 mL of anhydrous 1,4-dioxane. Then, benzofuran-2-boronic acid (30.4 mg, 0.187 mmol) and Pd(PPh₃)₄ (5.4 mg, 0.0047 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (0.5 mL). Finally, K₃PO₄ (59.9 mg, 0.282 mmol) and 0.75 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C for 2 h. After full consumption of iodonaphthalene **1c** was observed by TLC, the reaction mixture was cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (EtOAc:hexanes = 1:19→1:9) gave product **5c** as yellow oil (19.3 mg, 66% yield).

R_f = 0.18 (EtOAc:hexanes = 1:19)

TLC Visualization: UV active; stains with KMnO₄ solution.

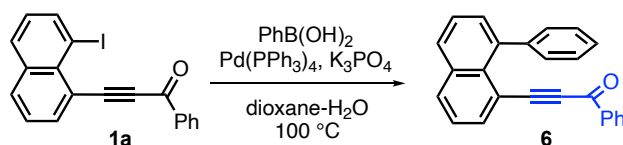
¹H NMR (400 MHz; CDCl₃) δ : 8.01 (2H, ddd, J = 8.2, 2.3, 1.3 Hz), 7.89 (1H, dd, J = 7.2, 1.2 Hz), 7.74 (1H, dd, J = 7.0, 1.2 Hz), 7.65 (1H, dd, J = 6.8, 1.8 Hz), 7.59 (1H, dd, J = 8.1, 7.2 Hz), 7.54-7.50 (2H, m), 7.35-7.27 (2H, m), 6.95 (1H, s), 1.40 (3H, s).

¹³C NMR (100 MHz; CDCl₃) δ : 184.3, 156.5, 154.8, 136.9, 134.3, 132.1, 132.0, 131.7, 131.2, 129.8, 128.5, 126.0, 125.7, 124.7, 123.3, 121.4, 117.5, 112.2, 106.3, 93.2, 89.0, 31.1.

FTIR ν_{\max} (ATR, film)/cm⁻¹ 3057, 2923, 2852, 2182, 1663, 1450, 1371, 1269, 1256.

HRMS (+APCI) Calcd for C₂₂H₁₅O₂ [M+H]⁺ 311.1067, found: 311.1069.

Note: Due to the shielding ring current effect of the benzofuran group, the -CH₃ singlet signal is observed at 1.40 ppm in the ¹H-NMR spectrum of **5c**.



An oven-dried, round bottom flask was evacuated with vacuum and refilled with nitrogen three times. Iodonaphthalene **1a** (35 mg, 0.092 mmol) was dissolved in 1.0 mL of anhydrous 1,4-dioxane. Then, phenylboronic acid (22.9 mg, 0.188 mmol) and Pd(PPh₃)₄ (5.4 mg, 0.005 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (1.0 mL). Finally, K₃PO₄ (60 mg, 0.28 mmol) and 1.0 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C with a condenser for 3.5 h. After full

consumption of iodonaphthalene **1a** was observed by TLC, the reaction mixture was cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (EtOAc:hexanes = 1:7) gave product **6** as yellow-orange solid (31 mg, 100% yield).

R_f = 0.47 (only hexanes)

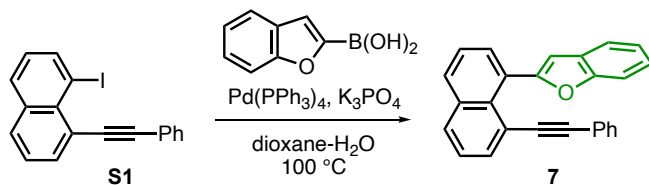
TLC Visualization: UV active; stains slowly with KMnO₄ solution.

¹H NMR (400 MHz; CDCl₃) δ : 8.02 (1H, dd, J = 8.2, 1.1 Hz), 7.92 (1H, dd, J = 8.2, 1.2 Hz), 7.88 – 7.85 (3H, m), 7.59 – 7.55 (2H, m), 7.51 (1H, dd, J = 8.1, 7.3 Hz), 7.46 (1H, dd, J = 7.1, 1.3 Hz), 7.44 – 7.40 (4H, m), 7.17 (2H, app t, J = 7.6 Hz), 7.05 (1H, tt, J = 7.5, 1.2 Hz).

¹³C NMR (100 MHz; CDCl₃) δ : 177.8, 141.9, 140.5, 136.9, 135.6, 134.4, 133.8, 131.6, 131.2, 130.4, 130.3, 129.8, 128.7, 128.3, 128.1, 128.0, 126.1, 125.2, 117.8, 94.6, 93.3.

FTIR ν_{\max} (ATR, film)/cm⁻¹ 3056, 2957, 2925, 2853, 2182, 1730, 1635, 1597, 1579, 1503, 1490, 1448, 1426, 1371, 1353, 1313, 1277.

HRMS (+ESI) Calcd for C₂₅H₁₇O [M+H]⁺ 333.1274, found: 333.1267.



An oven-dried, round bottom flask was evacuated with vacuum and refilled with nitrogen three times. Iodonaphthalene **S1** (35 mg, 0.099 mmol) was dissolved in 0.5 mL of anhydrous 1,4-dioxane. Then, benzofuran-2-boronic acid (32.1 mg, 0.198 mmol) and Pd(PPh₃)₄ (5.7 mg, 0.005 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (1.5 mL). Finally, K₃PO₄ (63 mg, 0.30 mmol) and 1.0 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C with a condenser for 5 h. After full consumption of iodonaphthalene **S1** was observed by TLC, the reaction mixture was cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (only hexanes) gave **7** as a slightly impure solid. Further recrystallization from heptane gave pure product **7** as yellow solid (25 mg, 74% yield).

R_f = 0.25 (only hexanes)

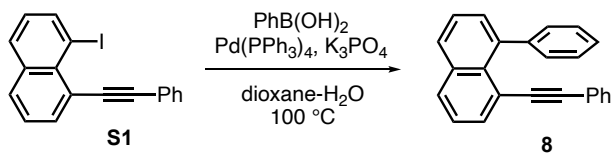
TLC Visualization: UV active; stains with KMnO₄ solution.

¹H NMR (400 MHz; CDCl₃) δ: 7.99 (1H, d, *J* = 8.1 Hz), 7.92 (1H, d, *J* = 8.2 Hz), 7.88 (1H, d, *J* = 7.1 Hz), 7.69 (1H, d, *J* = 6.9 Hz), 7.60 – 7.46 (4H, m), 7.23 – 7.18 (2H, m), 7.07 (1H, t, *J* = 7.2 Hz), 6.99 – 6.94 (3H, m), 6.47 (2H, d, *J* = 7.2 Hz).

¹³C NMR (100 MHz; CDCl₃) δ: 157.3, 155.3, 135.3, 134.5, 131.7, 131.6, 131.2, 131.1, 129.9, 129.5, 128.9, 127.7, 127.5, 125.8, 125.4, 124.2, 123.1, 122.8, 121.0, 120.7, 111.9, 105.7, 95.2, 88.5.

FTIR ν_{\max} (ATR, film)/cm⁻¹ 3053, 2963, 2923, 2850, 1733, 1668, 1597, 1566, 1489, 1474, 1450, 1426, 1371, 1304, 1255, 1178, 1053, 962, 882.

HRMS (+ESI) Calcd for C₂₆H₁₇O [M+H]⁺ 345.1274, found: 345.1264



An oven-dried, round bottom flask was evacuated with vacuum and refilled with nitrogen three times. Iodonaphthalene **S1** (35 mg, 0.099 mmol) was dissolved in 1.0 mL of anhydrous 1,4-dioxane. Then, phenylboronic acid (24.1 mg, 0.198 mmol) and Pd(PPh₃)₄ (5.7 mg, 0.005 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (1.0 mL). Finally, K₃PO₄ (63 mg, 0.30 mmol) and 1.0 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C with a condenser for 4.5 h. After full consumption of iodonaphthalene **S1** was observed by TLC, the reaction mixture was cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (only hexanes) gave product **8** as white solid with a brown tinge (24 mg, 80% yield).

R_f = 0.42 (only hexanes)

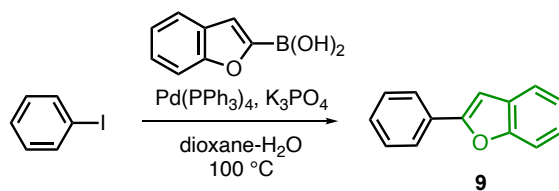
TLC Visualization: Weakly UV active; stains slowly with KMnO₄ solution.

¹H NMR (400 MHz; CDCl₃) δ: 7.92 (1H, d, *J* = 8.2 Hz), 7.89 (1H, d, *J* = 8.2 Hz), 7.81 (1H, d, *J* = 7.2 Hz), 7.55 – 7.47 (4H, m), 7.41 – 7.36 (3H, m), 7.28 (1H, app t, *J* = 8.0 Hz), 7.22 – 7.18 (3H, m), 7.03 – 7.01 (2H, m).

¹³C NMR (100 MHz; CDCl₃) δ: 143.0, 140.8, 135.0, 134.7, 131.8, 130.6, 130.5, 130.3, 129.7, 128.7, 127.8, 127.6, 127.4, 125.5, 125.3, 123.7, 120.8, 98.1, 90.3.

FTIR ν_{\max} (ATR, film)/cm⁻¹ 3079, 2249, 1570, 1373.

HRMS (+APCI) Calcd for C₂₄H₁₇ [M+H]⁺ 305.1325, found: 305.1326.



Anhydrous 1,4-dioxane was deoxygenated by purging nitrogen gas for 15 min. An oven-dried, round bottom flask was evacuated with vacuum and refilled with nitrogen three times. Iodobenzene (183 mg, 100 μ L, 0.90 mmol) was dissolved in 1.0 mL of anhydrous 1,4-dioxane. Then, benzofuran-2-boronic acid (159 mg, 0.98 mmol) and Pd(PPh₃)₄ (56.6 mg, 0.049 mmol) were added sequentially. The walls of the flask were washed with additional 1,4-dioxane (4.0 mL). Finally, K₃PO₄ (624 mg, 2.94 mmol) and 2.5 mL of distilled water were added. The resulting reaction mixture was stirred in an oil bath at 100 °C with a condenser for 4.5 h. The reaction mixture was then cooled down to ambient temperature and quenched with distilled water. Then, the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (only hexanes) gave product **9** as white solid (70 mg, 40% yield). The NMR spectroscopic data match those reported in the literature.²

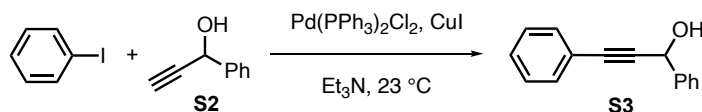
R_f = 0.69 (only hexanes)

TLC Visualization: UV active; stains slowly with KMnO₄ solution.

¹H NMR (400 MHz; CDCl₃) δ : 7.93 (2H, d, *J* = 7.4 Hz), 7.64 (1H, d, *J* = 7.4 Hz), 7.60 (1H, d, *J* = 7.9 Hz), 7.50 (2H, t, *J* = 7.5 Hz), 7.41 (1H, t, *J* = 7.3 Hz), 7.34 (1H, t, *J* = 7.5 Hz), 7.30 (1H, t, *J* = 7.3 Hz), 7.07 (1H, s).

¹³C NMR (100 MHz; CDCl₃) δ : 156.0, 155.0, 130.6, 129.4, 128.9, 128.7, 125.1, 124.4, 123.1, 121.0, 111.3, 101.4.

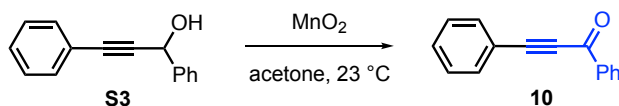
FTIR ν_{max} (ATR, film)/cm⁻¹ 3053, 2926, 2854, 2200, 1642, 1491, 1455, 1443, 1264.



An oven-dried 25-mL Schlenk tube was evacuated with vacuum and refilled with nitrogen three times. Iodobenzene (100 mg, 55 μ L, 0.49 mmol) and alkyne **S2** (65 mg, 0.50 mmol) were

dissolved in 1.5 mL of Et₃N. Then, Pd(PPh₃)₂Cl₂ (24.5 mg, 0.035 mmol) and CuI (13.3 mg, 0.070 mmol) were added sequentially. The walls of the flask were washed with additional Et₃N (2.5 mL). The reaction mixture was stirred at 23 °C for 4 h. After the completion of the reaction, Et₃N was removed under reduced pressure. Distilled water was added to the mixture, and the aqueous phase was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography (EtOAc:hexanes = 1:4) gave pure product **S3** (47 mg, 46% yield). The ¹H-NMR spectroscopic data match those reported in the literature.³

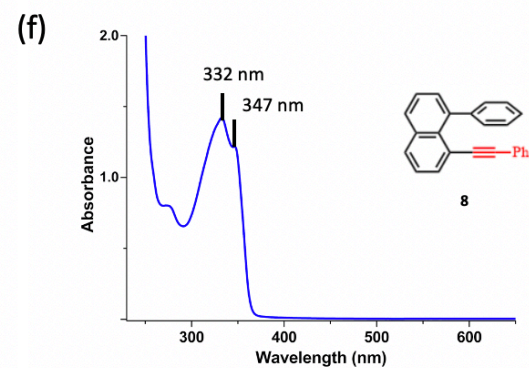
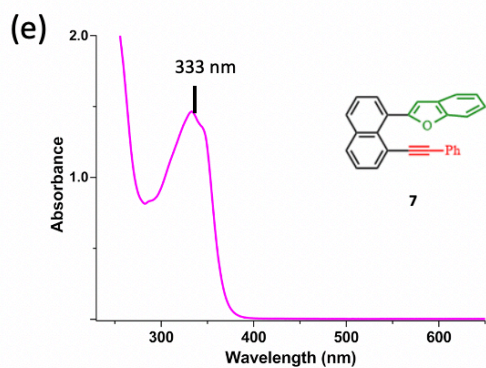
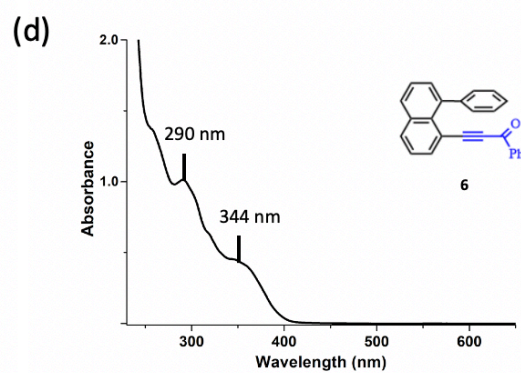
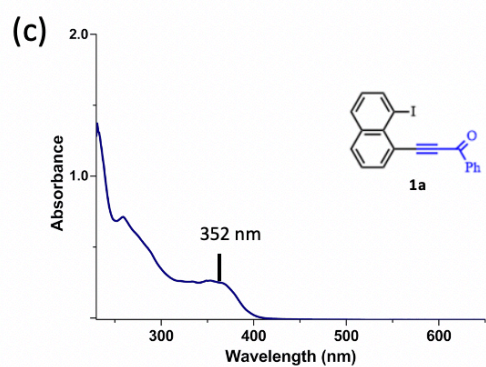
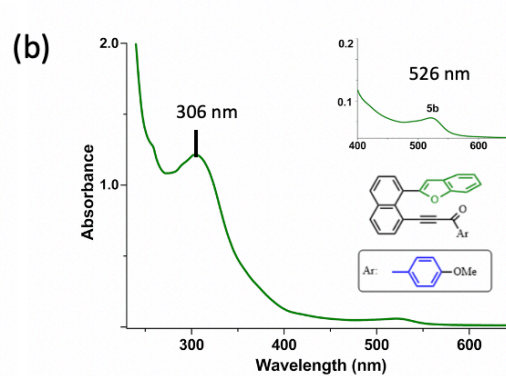
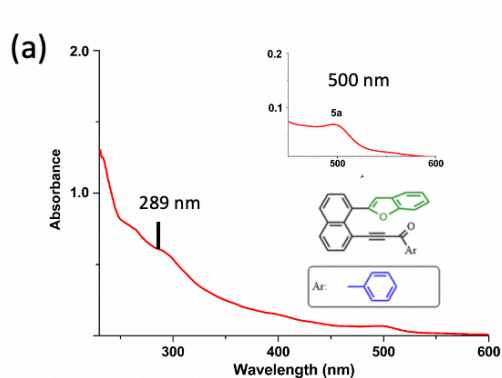
¹H NMR (400 MHz; CDCl₃) δ: 7.64 (2H, d, *J* = 7.2 Hz), 7.50 – 7.48 (2H, m), 7.42 (2H, t, *J* = 7.2 Hz), 7.38 – 7.31 (4H, m), 5.70 (1H, s), 2.48 (1H, s).



To a solution of the propargylic alcohol **S3** (47 mg, 0.23 mmol) in 10 mL of acetone in a 20-mL vial was added MnO₂ (393 mg, 4.52 mmol) at 23 °C. The reaction mixture was stirred for 3 h and then filtered to remove all solids. All volatiles were then removed under reduced pressure. Purification by flash column chromatography (EtOAc:hexanes = 1:7) gave pure ynone product **10** (17 mg, 36% yield). The ¹H-NMR spectroscopic data match those reported in the literature.⁴

¹H NMR (400 MHz; CDCl₃) δ: 8.23 (2H, d, *J* = 7.7 Hz), 7.69 (2H, d, *J* = 7.0 Hz), 7.64 (1H, t, *J* = 7.3 Hz), 7.54 – 7.47 (3H, m), 7.43 (2H, t, *J* = 7.6 Hz).

UV-VIS Absorption and Emission Spectra:



(h)

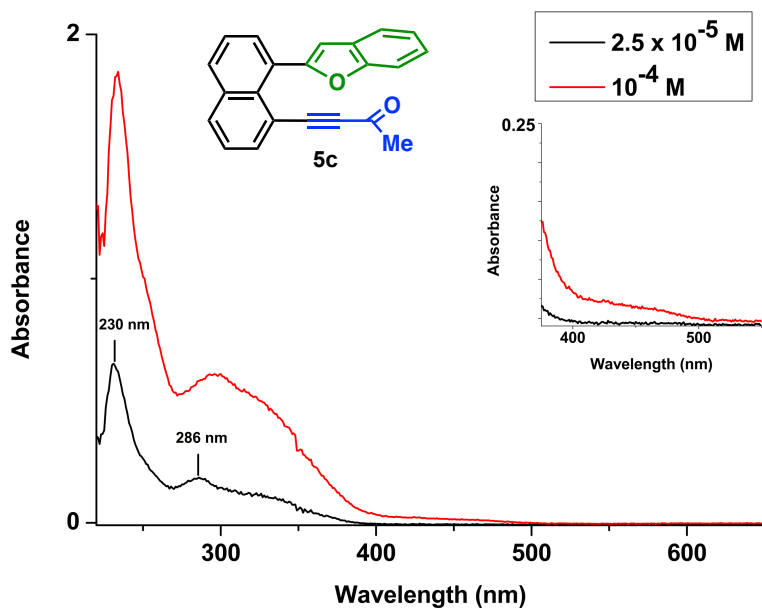


Figure S1. (a)-(g) UV-vis absorption spectra of **5-8** and **1a** in CH_2Cl_2 ($2.5 \times 10^{-5} \text{ M}$); (h) UV-vis absorption spectra of **5c** in CH_2Cl_2 ($2.5 \times 10^{-5} \text{ M}$ and $1.0 \times 10^{-4} \text{ M}$).

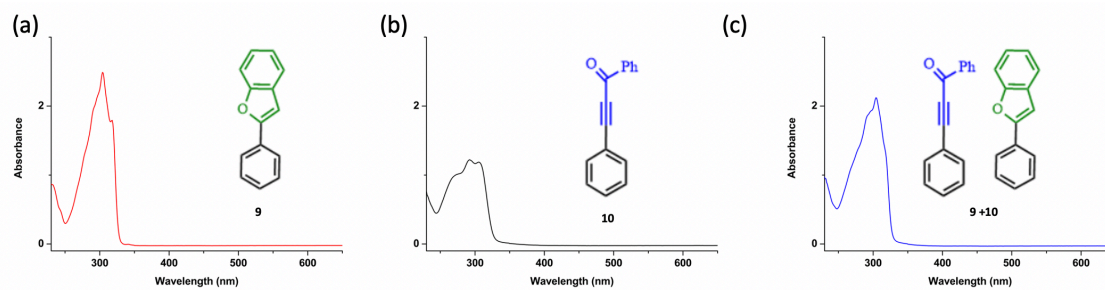


Figure S2. UV-vis absorption spectra of **9**, **10** and 1:1 mixture of **9** and **10** in CH_2Cl_2 ($1.0 \times 10^{-3} \text{ M}$).

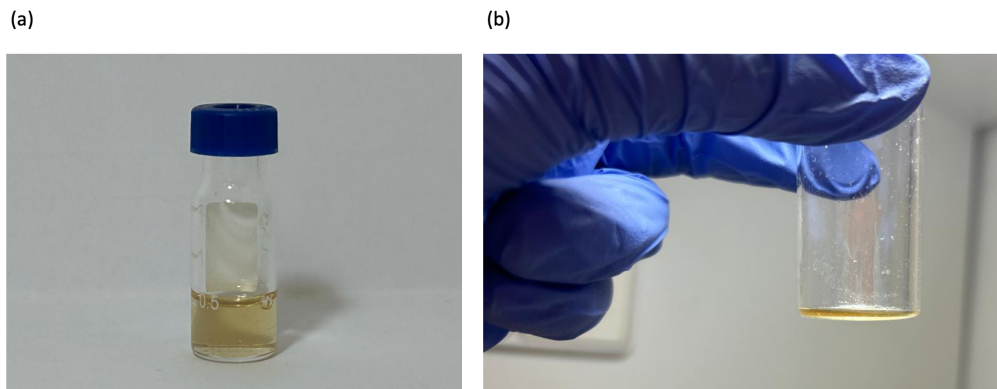


Figure S3. (a) Appearance of 1.0 M solution of 1:1 mixture of **9** and **10** in CH_2Cl_2 ; (b) Appearance of condensed 1:1 mixture of **9** and **10** obtained via the evaporation of solvent from a 1.0 M solution.

Table S1. Molar absorption coefficients of compounds **5-8** and **1a**.

compound	λ_{max} (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	compound	λ_{max} (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)
5a	289	2.39×10^4	1a	352	9.86×10^3
5a	500	2.69×10^3	6	290	4.05×10^4
5b	306	4.84×10^4	6	344	1.82×10^4
5b	526	2.40×10^3	7	333	5.86×10^4
5c	230	2.60×10^4	8	332	5.68×10^4
5c	286	7.34×10^3	8	347	4.87×10^4

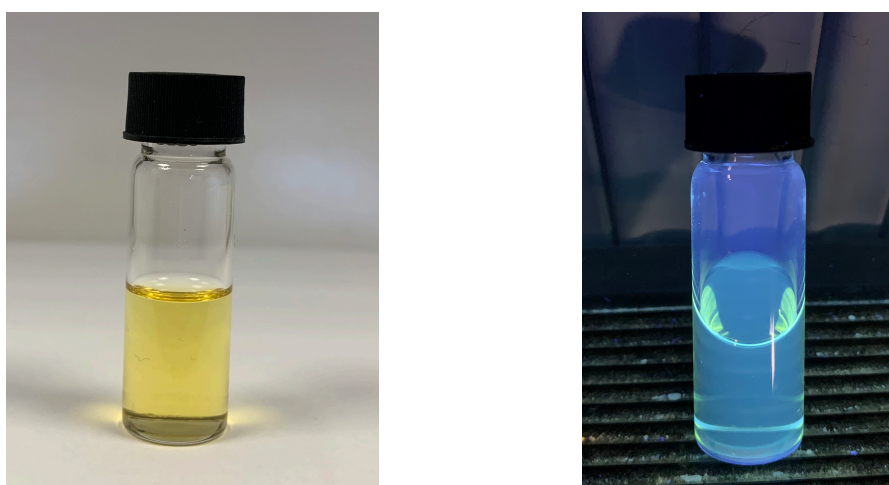


Figure S4. Appearance of compound **5c** in CH_2Cl_2 (1.0×10^{-2} M) (a) under daylight; (b) under UV light (366 nm).

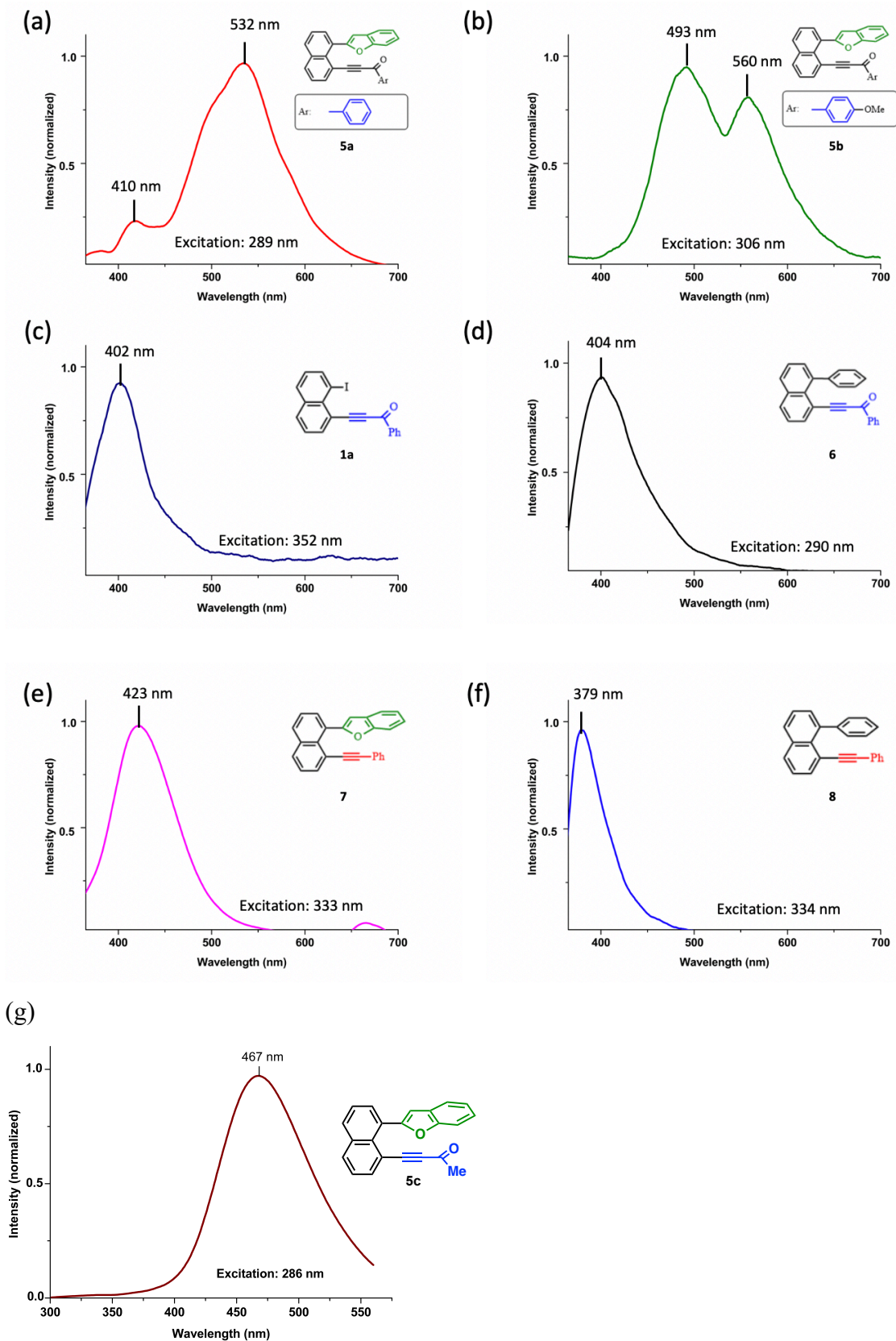


Figure S5. Photoluminescence (PL) spectra of **5-8** and **1a** in CH_2Cl_2 (2.5×10^{-5} M).

Determination of the Photoluminescence Quantum Yields of **5a** and **5b**:

The photoluminescence (PL) quantum yields of compounds **5a** and **5b** were measured based on published literature.⁵ The reference material used for quantum yield measurements was quinine sulfate in 0.5 M aqueous H₂SO₄ solution ($\Phi_{\text{PL}} = 0.546$).⁶ The absorbance of the reference material was measured for five concentrations provided that the absorbance value is not higher than 0.1 (Shimadzu UV-2550 spectrophotometer). The PL spectra of the compounds were recorded with excitation wavelength of 310 nm, excitation slitwidth of 10 nm, and emission slitwidth of 5 nm (measurements were done on Perkin Elmer LS 55). With these in hand, absorption vs PL emission peak areas were drawn. The same procedure was repeated for compounds **5a** and **5b**. Using the following equation, the PL quantum yields for **5a** and **5b** were calculated.

$$\Phi_S = \Phi_R \frac{\text{Slope}_S \eta_S^2}{\text{Slope}_R \eta_R^2}$$

In this equation, Φ_R is the PL quantum yield of reference compound, and Φ_S is PL quantum yield of compound of interest. Slope_S and Slope_R are the slopes obtained from the absorption versus PL emission peak areas of the sample and reference compound, respectively. Lastly, η_S and η_R are refractive indexes of the medium used for sample preparation.

The quantum yield measurements for **5a** and **5b** were performed and repeated multiple times. They were found to be 4.1% and 2.0%, respectively.

Cyclic Voltammetry Studies:

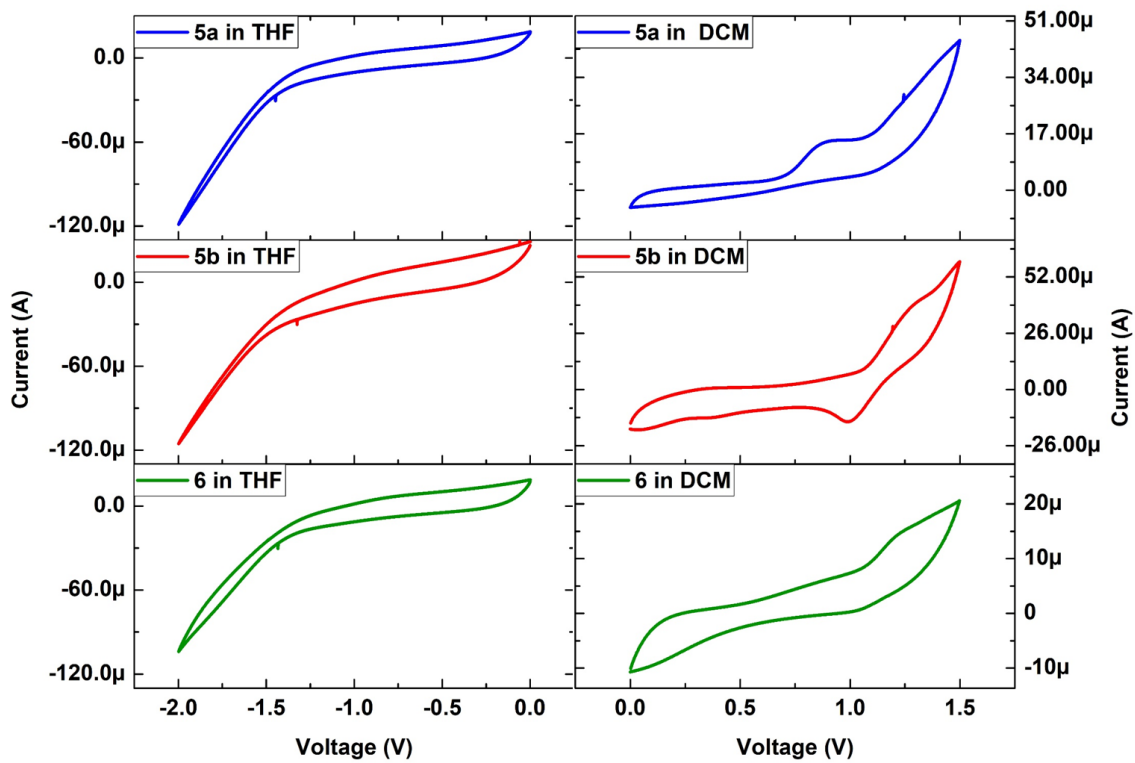


Figure S6. Cyclic voltammograms of **5a**, **5b** and **6** in THF and DCM.

XYZ Coordinates of Optimized Structures with no Imaginary Frequencies:

5a

H	-0.782042	4.767282	-1.573416
C	-0.304821	4.357392	-0.689113
C	0.716043	5.027982	-0.016076
H	1.046987	5.995792	-0.382758
C	-0.682398	3.126264	-0.168911
O	-1.660469	2.309255	-0.666239
C	-1.688985	1.187845	0.145164
C	-0.772173	1.290882	1.150875
C	-0.090831	2.542831	0.968053
C	-2.773812	0.235623	-0.111602
C	-4.026745	0.774401	-0.383910
C	-5.183563	-0.024283	-0.440551
C	-5.092716	-1.371475	-0.183693
C	-3.832625	-1.980839	0.047567
C	-2.631620	-1.189171	0.016768
C	-1.373443	-1.898716	0.072837
C	-1.363106	-3.272835	0.315373
C	-2.552431	-4.011802	0.449053
C	-3.761602	-3.379242	0.285566
C	-0.128194	-1.324502	-0.250103
C	1.020490	-0.969220	-0.591842
C	2.281263	-0.452001	-1.037209
C	3.522680	-1.067965	-0.473023
C	3.479790	-2.093252	0.481599
C	4.663107	-2.636463	0.979686
C	5.894450	-2.157903	0.527557
C	5.943222	-1.133637	-0.423675
C	4.763416	-0.590546	-0.921797
O	2.324614	0.458479	-1.857336
H	-5.981825	-1.996313	-0.166536
H	-6.146559	0.436262	-0.640788
H	-4.110324	1.849446	-0.505509
H	2.518190	-2.457626	0.830158
H	4.626972	-3.431316	1.719383
H	6.816086	-2.581682	0.916955
H	6.902459	-0.762481	-0.774135
H	4.772493	0.205818	-1.658819
H	-0.608707	0.564750	1.934290
C	0.934341	3.238319	1.629200
C	1.323864	4.476402	1.128441
H	-0.404709	-3.781842	0.353059
H	-2.503596	-5.080196	0.637649
H	-4.689941	-3.943391	0.327389
H	2.117132	5.029240	1.624110
H	1.412623	2.819865	2.510163

5b

C	-2.272715	3.440273	0.984783
C	-1.615563	3.243278	2.214740
C	-0.371342	2.618231	2.278667
C	0.176428	2.207240	1.069542
C	-0.453910	2.388031	-0.177080
C	-1.708038	3.018069	-0.214636
C	0.448749	1.818806	-1.143352
C	1.520710	1.342515	-0.446609
O	1.382895	1.585734	0.906776
C	2.794620	0.758508	-0.886903
C	3.491868	1.452071	-1.866892
C	4.778067	1.058070	-2.286087
C	5.389831	-0.010648	-1.677761
C	4.714795	-0.767351	-0.683233
C	3.369641	-0.425559	-0.309624
C	2.687514	-1.314631	0.598459
C	3.379169	-2.377267	1.178475
C	4.721925	-2.646978	0.859939
C	5.367425	-1.871460	-0.073752
C	1.289037	-1.262626	0.879370
C	0.113417	-1.394517	1.166939
C	-1.264309	-1.561122	1.601774
O	-1.500430	-1.866135	2.768772
C	-2.339636	-1.376368	0.594128
C	-2.071933	-1.059932	-0.748968
C	-3.106418	-0.911437	-1.659013
C	-4.438291	-1.076012	-1.243565
C	-4.719721	-1.391491	0.095365
C	-3.671530	-1.538774	0.997541
H	0.146212	2.451982	3.217424
H	-2.088599	3.580458	3.132559
H	6.401872	-0.299726	-1.949698
H	5.293244	1.629011	-3.053116
H	3.045776	2.351156	-2.280689
H	-1.044248	-0.925734	-1.071986
H	-2.915831	-0.668933	-2.699694
O	-5.380057	-0.909346	-2.210390
H	-5.740796	-1.522098	0.434757
H	-3.868037	-1.784245	2.036274
H	0.311636	1.750032	-2.213801
H	2.845284	-3.024311	1.866766
H	5.228119	-3.484516	1.330875
H	6.391272	-2.092231	-0.364856
H	-3.242874	3.929420	0.975825
H	-2.226453	3.170565	-1.157093
C	-6.748474	-1.065388	-1.860703
H	-7.311839	-0.889390	-2.778614
H	-6.956866	-2.078936	-1.495052
H	-7.055022	-0.335718	-1.100402

5c

C	-0.015709	0.091647	-0.004993
C	0.008261	0.026652	1.413225
C	1.261968	-0.023098	2.114877
C	2.462343	-0.122576	1.320513
C	2.381627	-0.045585	-0.070060
C	1.149495	0.080846	-0.734672
C	1.224661	-0.002018	3.550971
C	0.002467	-0.053656	4.207561
C	-1.219765	-0.080619	3.507216
C	-1.213956	-0.007661	2.135888
C	2.417097	0.142103	4.397365
C	2.836454	-0.543839	5.498501
C	4.014320	0.128278	5.980601
C	4.210235	1.210605	5.099435
O	3.232250	1.230027	4.146015
C	4.923734	-0.057644	7.034458
C	5.982735	0.837135	7.162156
C	6.150328	1.908101	6.262649
C	5.260435	2.114276	5.209051
C	3.757769	-0.408980	1.844042
C	4.909785	-0.702717	2.108126
C	6.287189	-1.071598	2.378669
C	6.575174	-1.682483	3.734504
O	7.156185	-0.892566	1.537358
H	5.376455	2.931407	4.504909
H	6.989636	2.585621	6.390067
H	-2.146179	0.020240	1.577444
H	-2.155666	-0.116292	4.057091
H	-0.002754	-0.025343	5.292748
H	2.375883	-1.436667	5.898221
H	3.301067	-0.116776	-0.641851
H	1.125997	0.137938	-1.818864
H	-0.980298	0.145887	-0.503369
H	6.696415	0.708991	7.971257
H	4.804780	-0.880662	7.733751
H	7.609480	-2.033288	3.757572
H	6.421395	-0.936632	4.523011
H	5.889351	-2.512659	3.939011

6

C	-1.741425	2.674489	-1.337726
C	-3.020791	2.506301	-1.889098
C	-3.621289	3.568928	-2.578056
C	-2.952501	4.784710	-2.712894
C	-1.680077	4.945850	-2.160573
C	-1.075269	3.888314	-1.472966
C	-3.696501	1.183437	-1.717796
O	-3.155064	0.251146	-1.131094
C	-5.031601	1.034586	-2.264236
C	-6.148548	0.811008	-2.695685
C	-7.502027	0.736422	-3.135268
C	-8.202715	-0.523543	-3.377656
C	-9.650460	-0.514199	-3.590003
C	-10.134762	0.800862	-3.634932
C	-9.515452	1.862547	-3.470172
C	-8.155689	1.986667	-3.196601
C	-7.564287	-1.808290	-3.402611
C	-8.343288	-2.955891	-3.499714
C	-9.743313	-2.918823	-3.637135
C	-10.391331	-1.707013	-3.713217
C	-6.083056	-2.005680	-3.415219
H	-11.464278	-1.643544	-3.862738
H	-10.300728	-3.847674	-3.717825
H	-7.835661	-3.915911	-3.510805
H	-4.609549	3.436825	-3.008399
H	-3.422255	5.605120	-3.248505
H	-1.159012	5.893877	-2.265504
H	-0.085103	4.014715	-1.043608
H	-1.294553	1.839047	-0.808821
H	-7.616865	2.904440	-2.991068
C	-5.437492	-2.660717	-2.357787
C	-4.066618	-2.909530	-2.410553
C	-3.327349	-2.527243	-3.530520
C	-3.965463	-1.893089	-4.598197
C	-5.333483	-1.632239	-4.540951
H	-6.010564	-2.952576	-1.481892
H	-3.574347	-3.394174	-1.572292
H	-2.258751	-2.719662	-3.569504
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H	-5.829136	-1.140630	-5.373991

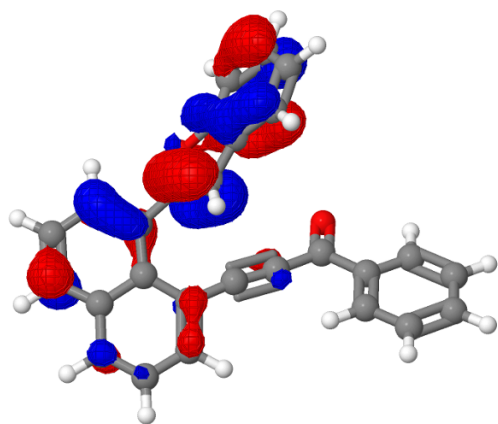
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C	0.533660	0.371801	4.914461
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C	-0.875880	-0.124325	6.827479
C	0.225937	-0.001552	7.668665
C	1.482560	0.307922	7.141722
C	1.629386	0.493238	5.764954
C	-1.878897	-0.065969	4.590205
C	-2.868466	-0.171850	3.888381
C	-4.150385	-0.280854	3.273515
C	-4.416665	-0.037674	1.875588
C	-5.793291	0.018331	1.461099
C	-6.833066	-0.271507	2.382564
C	-6.546729	-0.578613	3.691776
C	-5.213411	-0.561583	4.133915
C	-6.121729	0.385162	0.128524
C	-5.140751	0.686102	-0.783475
C	-3.787876	0.565832	-0.408688
C	-3.411296	0.192296	0.874324
C	-1.970605	-0.006234	1.090259
O	-1.566311	-1.257696	1.516553
C	-0.201074	-1.239569	1.534303
C	0.278434	0.012958	1.100063
C	-0.898722	0.789905	0.814408
C	1.666258	0.223275	1.046160
C	2.510105	-0.817934	1.423594
C	1.997805	-2.057671	1.852213
C	0.624587	-2.290504	1.915030
H	2.072244	1.175288	0.715059
H	3.586527	-0.674226	1.386058
H	2.684845	-2.847593	2.141880
H	0.212805	-3.237721	2.247001
H	-7.171537	0.429053	-0.150736
H	-5.395925	0.976572	-1.798532
H	-3.010757	0.724258	-1.149914
H	-7.861327	-0.237715	2.031630
H	-7.343181	-0.804677	4.395065
H	-4.989839	-0.745602	5.179728
H	-1.853815	-0.364144	7.233866
H	0.104152	-0.147246	8.738758
H	2.341726	0.402942	7.800294
H	2.604378	0.730623	5.347903
H	0.650976	0.510943	3.845451
H	-0.946815	1.815138	0.474609

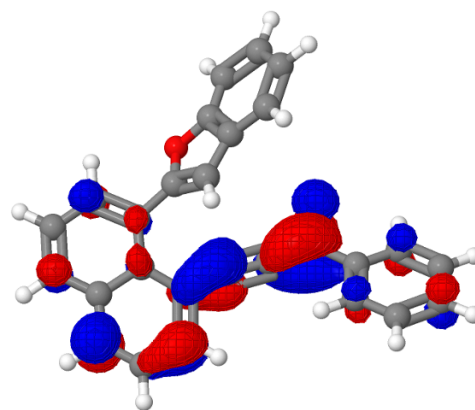
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C	-4.110104	2.068180	0.696191
C	-4.216765	1.473634	-0.578320
C	-3.080437	1.446703	-1.412650
C	-1.878432	1.999499	-0.978991
C	-1.783160	2.585022	0.286051
C	-2.903225	2.616363	1.120770
C	-5.455982	0.918935	-1.008414
C	-6.506335	0.438364	-1.393437
C	-7.838371	0.015882	-1.677733
C	-8.253444	-0.648566	-2.893216
C	-9.669989	-0.817042	-3.098428
C	-10.594675	-0.438793	-2.090089
C	-10.163507	0.120299	-0.910723
C	-8.792984	0.361003	-0.719252
C	-7.365677	-1.120055	-3.921404
C	-7.900579	-1.611457	-5.104488
C	-9.289356	-1.717184	-5.319780
C	-10.156022	-1.352162	-4.320456
C	-5.880781	-1.215449	-3.789534
H	-11.230415	-1.459529	-4.447559
H	-9.661133	-2.116658	-6.259272
H	-7.217182	-1.968304	-5.869630
H	-8.453166	0.854951	0.185325
H	-10.873043	0.404461	-0.138756
H	-11.654349	-0.596167	-2.275098
H	-3.156761	0.987381	-2.392310
H	-1.009922	1.972544	-1.631934
H	-0.842280	3.014378	0.619607
H	-2.836173	3.070510	2.105862
H	-4.982584	2.092466	1.342117
C	-5.299014	-2.048828	-2.820890
C	-3.920871	-2.251610	-2.790351
C	-3.096408	-1.626159	-3.729130
C	-3.662107	-0.793394	-4.696537
C	-5.043336	-0.593212	-4.727170
H	-5.936173	-2.549321	-2.097355
H	-3.489617	-2.904863	-2.036452
H	-2.022119	-1.789652	-3.707794
H	-3.030134	-0.302566	-5.432466
H	-5.481645	0.054147	-5.482026

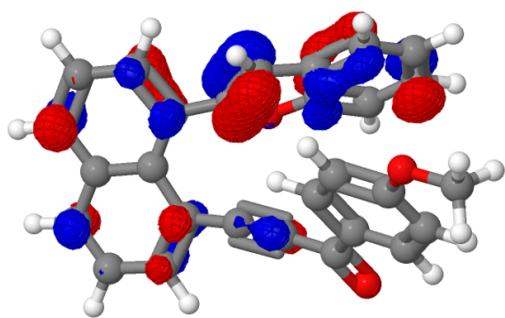
HOMOs and LUMOs of Compounds 5-8:



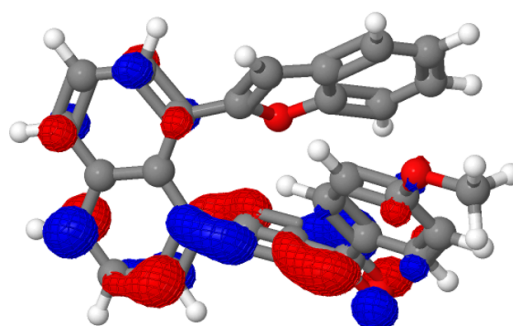
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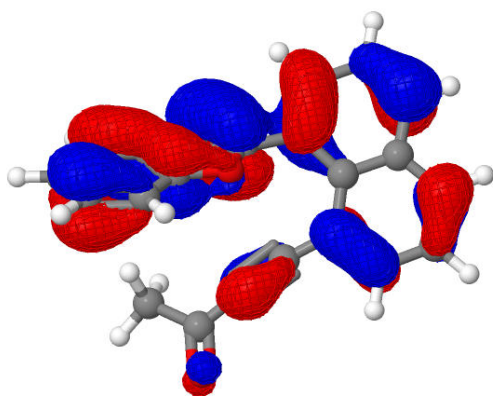
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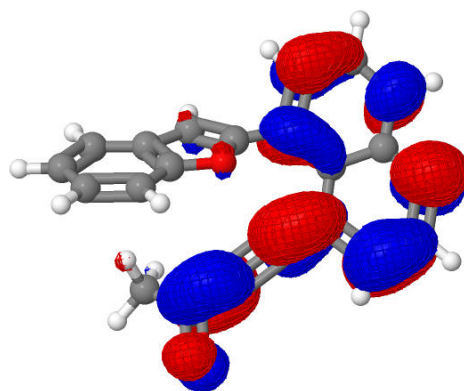
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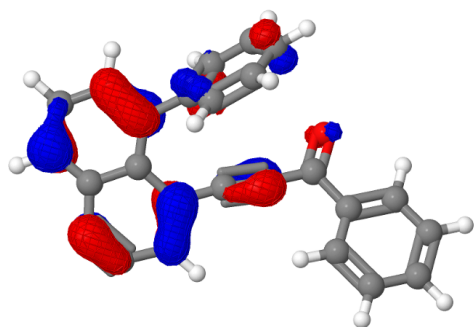
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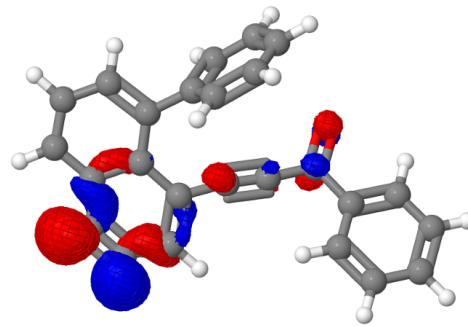
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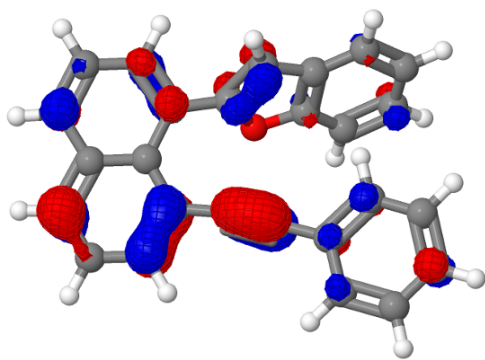
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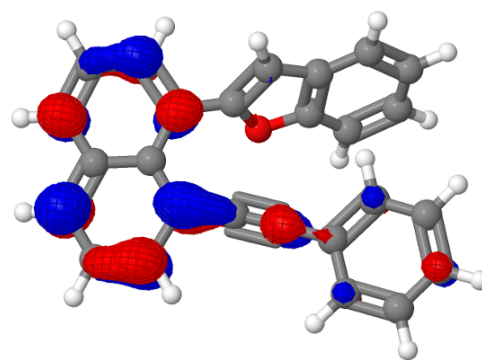
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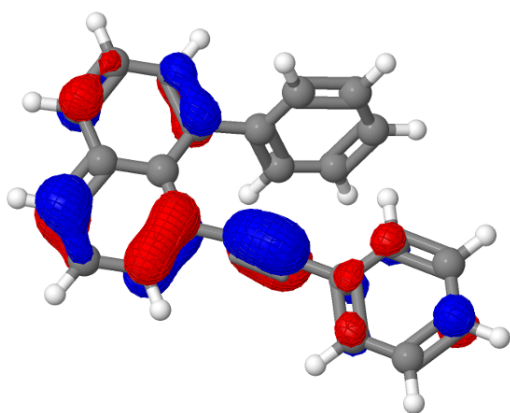
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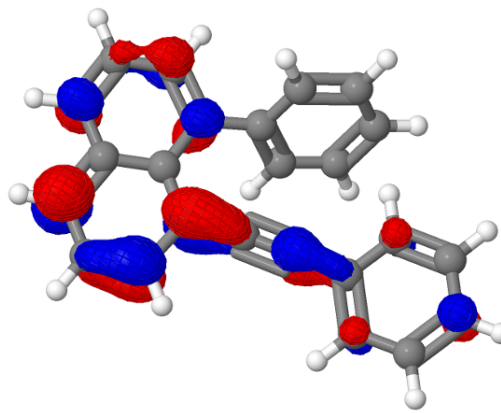
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LUMO of 7



HOMO of 8



LUMO of 8

Figure S7. HOMO and LUMO images of compounds 5-8.

X-Ray Diffraction Analysis of Compound 7:

Suitable crystal of **7** was selected for data collection which was performed on a Bruker diffractometer equipped with a graphite-monochromatic Mo-K α radiation at 296 K. We used the following procedures for our analysis: solved by direct methods; SHELXS-2013;⁷ refined by full-matrix least-squares methods; SHELXL-2013;⁸ data collection: Bruker APEX2;⁹ molecular graphics: MERCURY;¹⁰ solution: WinGX.¹¹ Details of data collection and crystal structure determinations are given in Table S1.

Table S2. Crystal data and structure refinement parameters for **7**.

Empirical formula	C ₂₆ H ₁₆ O
Formula weight	344.39
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	5.8787 (3)
<i>b</i> (Å)	25.8705 (14)
<i>c</i> (Å)	12.0671 (6)
β (°)	101.194 (2)
<i>V</i> (Å ³)	1800.31 (16)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.271
μ (mm ⁻¹)	0.08
θ range (°)	2.3-27.5
Measured refls.	41927
Independent refls.	4132
<i>R</i> _{int}	0.062
<i>S</i>	1.08
R1/wR2	0.053/0.129
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ ⁻³)	0.25/-0.17
CCDC	2287262

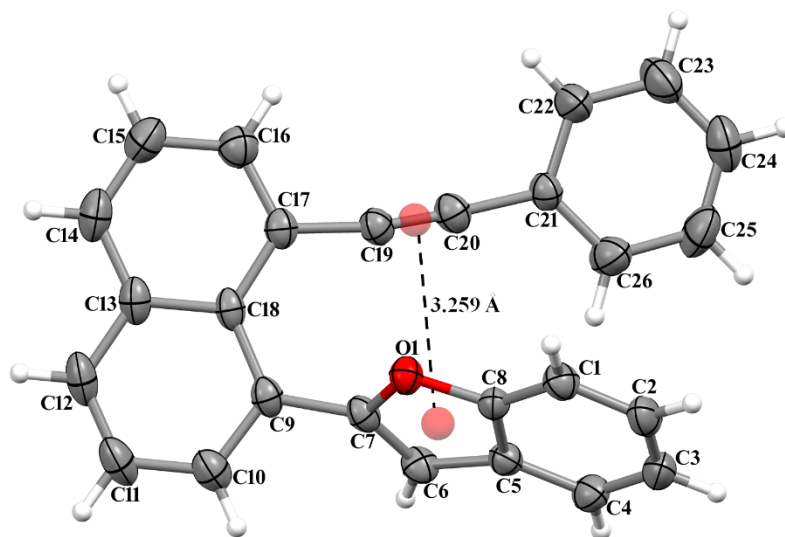


Figure S8. The molecular structure of 7, showing 40% probability displacement ellipsoids and the atomic numbering.

Solvatochromism Studies:

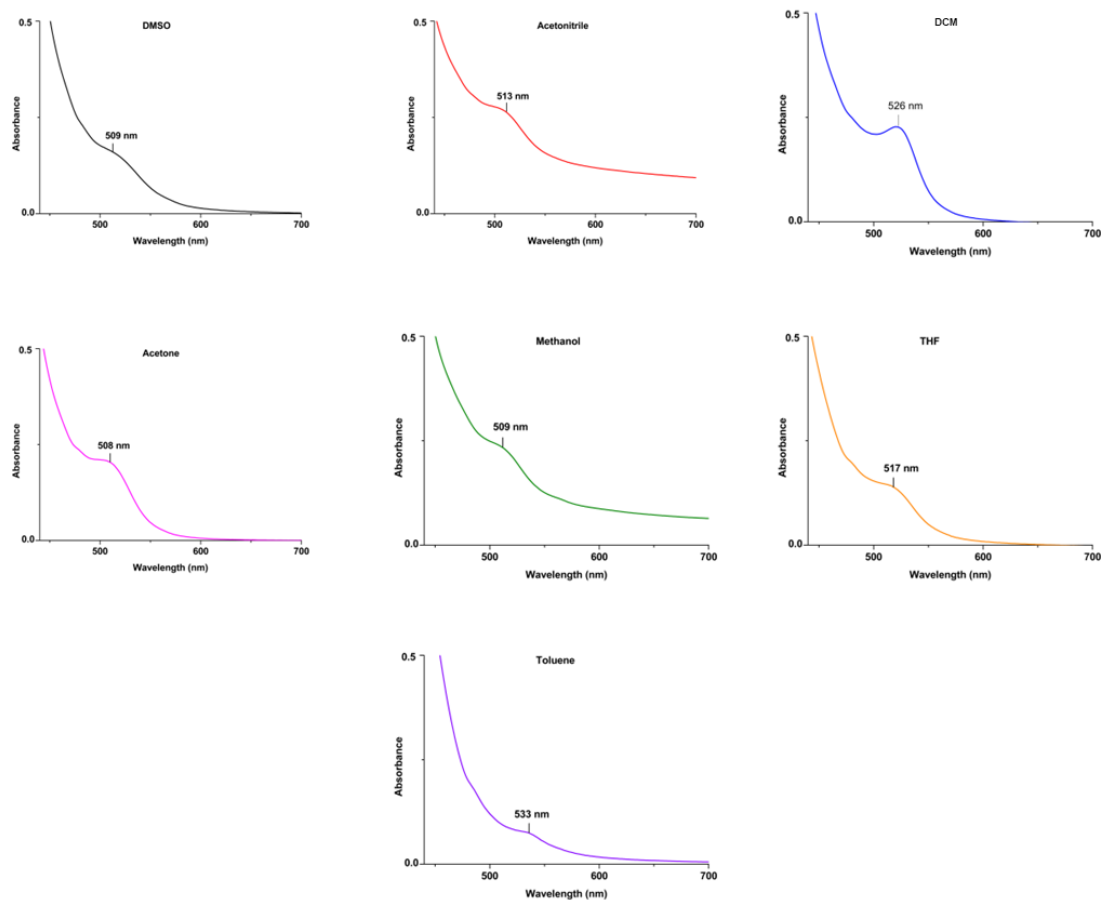


Figure S9. UV-vis absorption spectra of **5b** in different solvents.

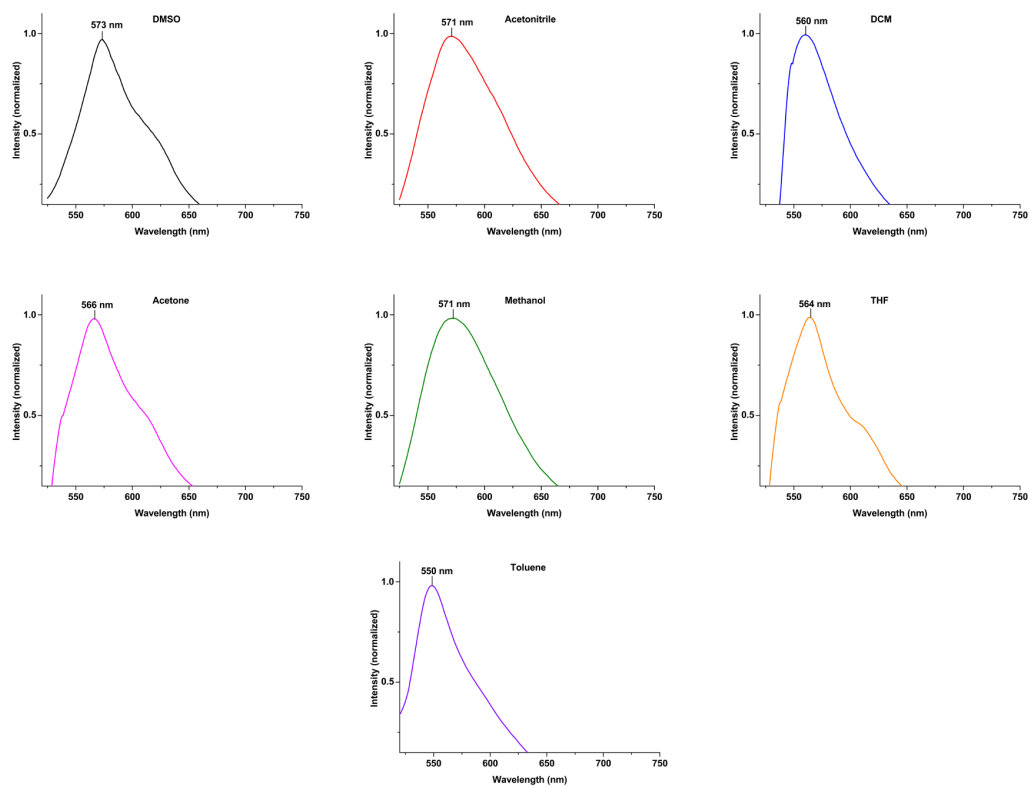


Figure S10. Photoluminescence (PL) spectra of **5b** in different solvents.

Table S3. Solvatochromism measurements for **5b** in different solvents.

Solvent	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	$\Delta\lambda$ (nm)	Absorption Energy (eV)	Emission Energy (eV)	Average Energy (eV)
DMSO	509	573	64	2.44	2.16	2.30
Methanol	509	571	62	2.44	2.17	2.31
Acetonitrile	513	571	58	2.42	2.17	2.30
Acetone	508	566	58	2.44	2.19	2.32
THF	517	564	47	2.40	2.20	2.30
DCM	526	560	34	2.36	2.21	2.29
Toluene	533	550	17	2.33	2.25	2.29

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra:

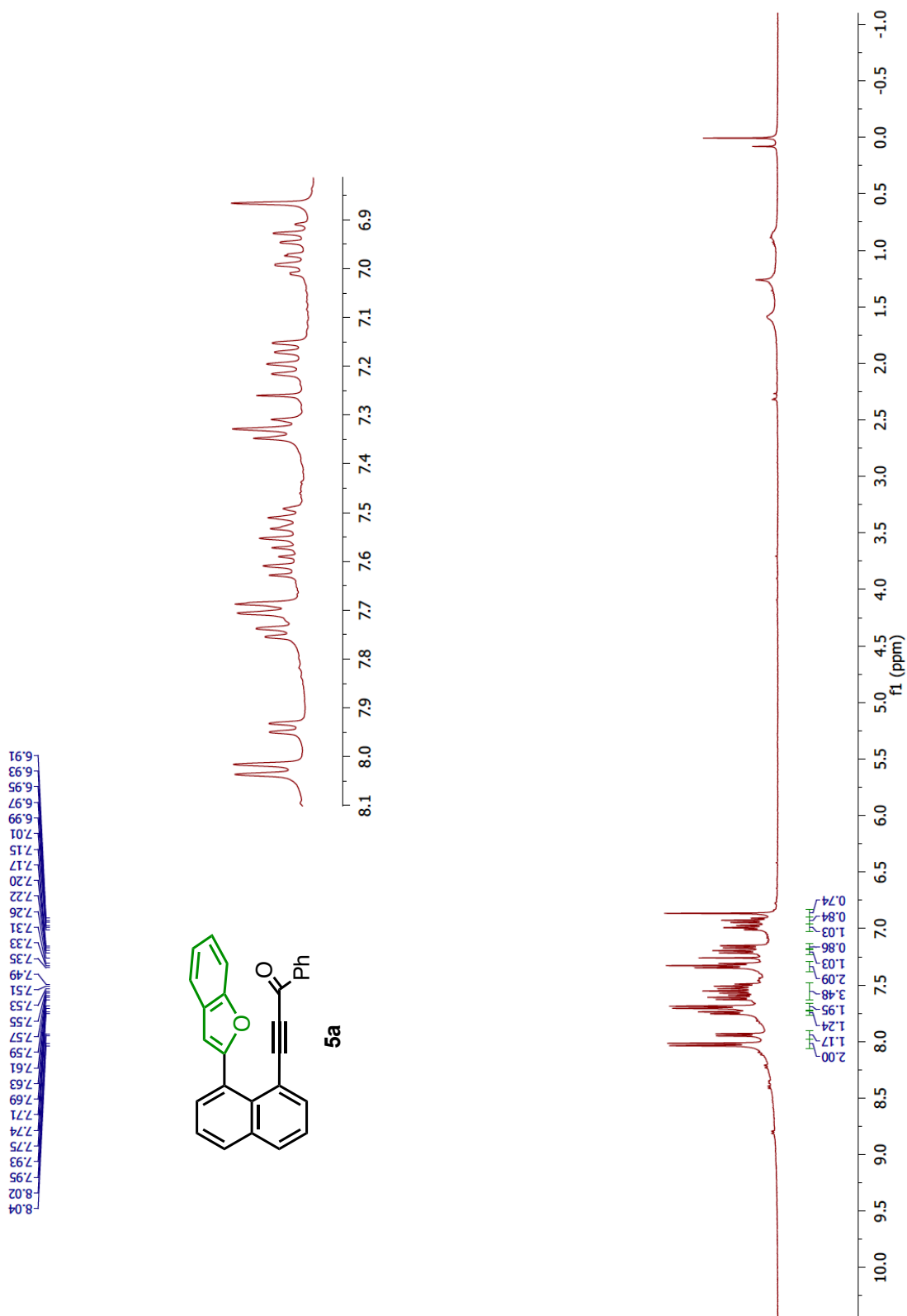


Figure S11. ^1H NMR spectrum of **5a** in CDCl₃.

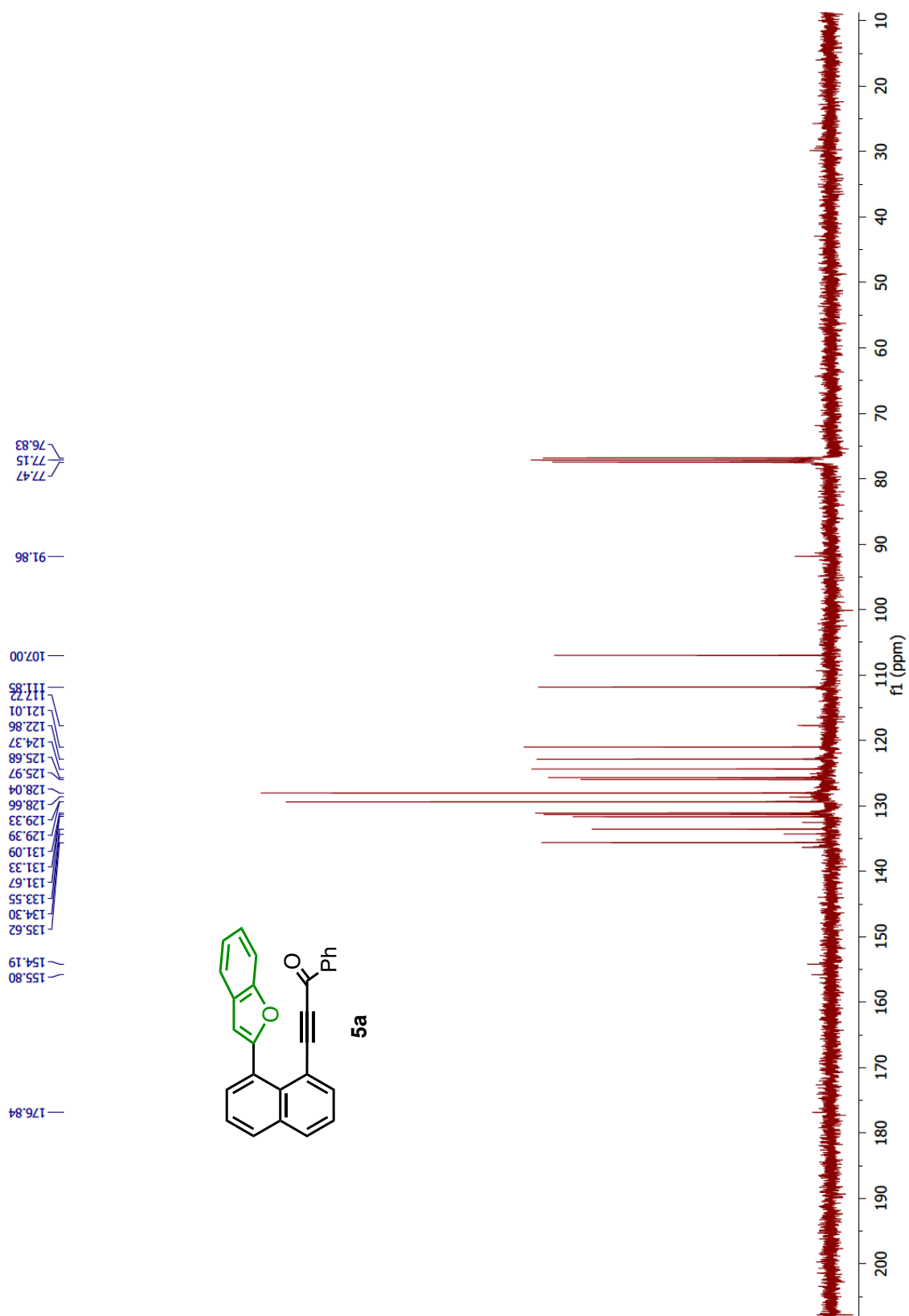


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5a** in CDCl_3 .

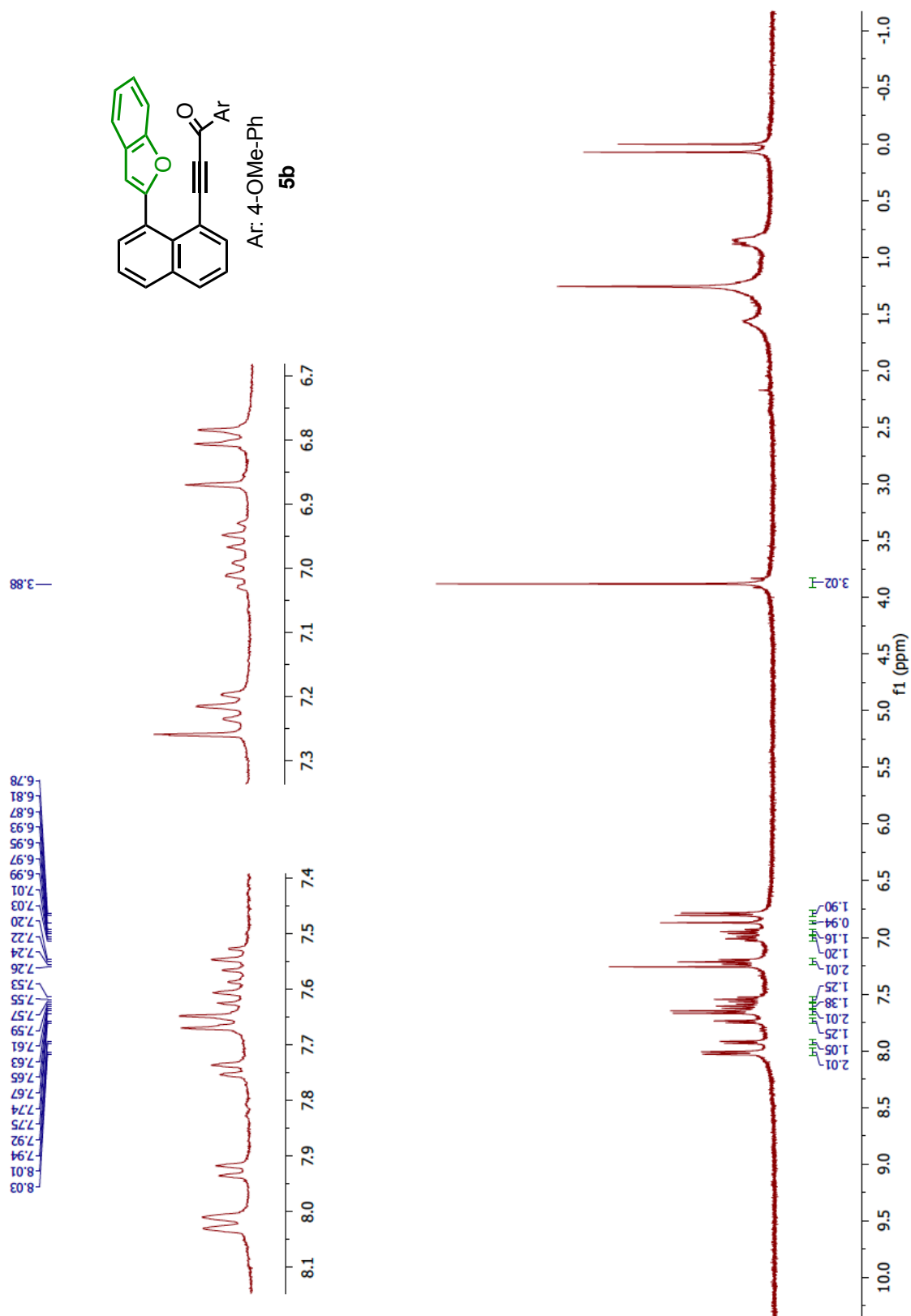


Figure S13. ^1H NMR spectrum of **5b** in CDCl_3 .

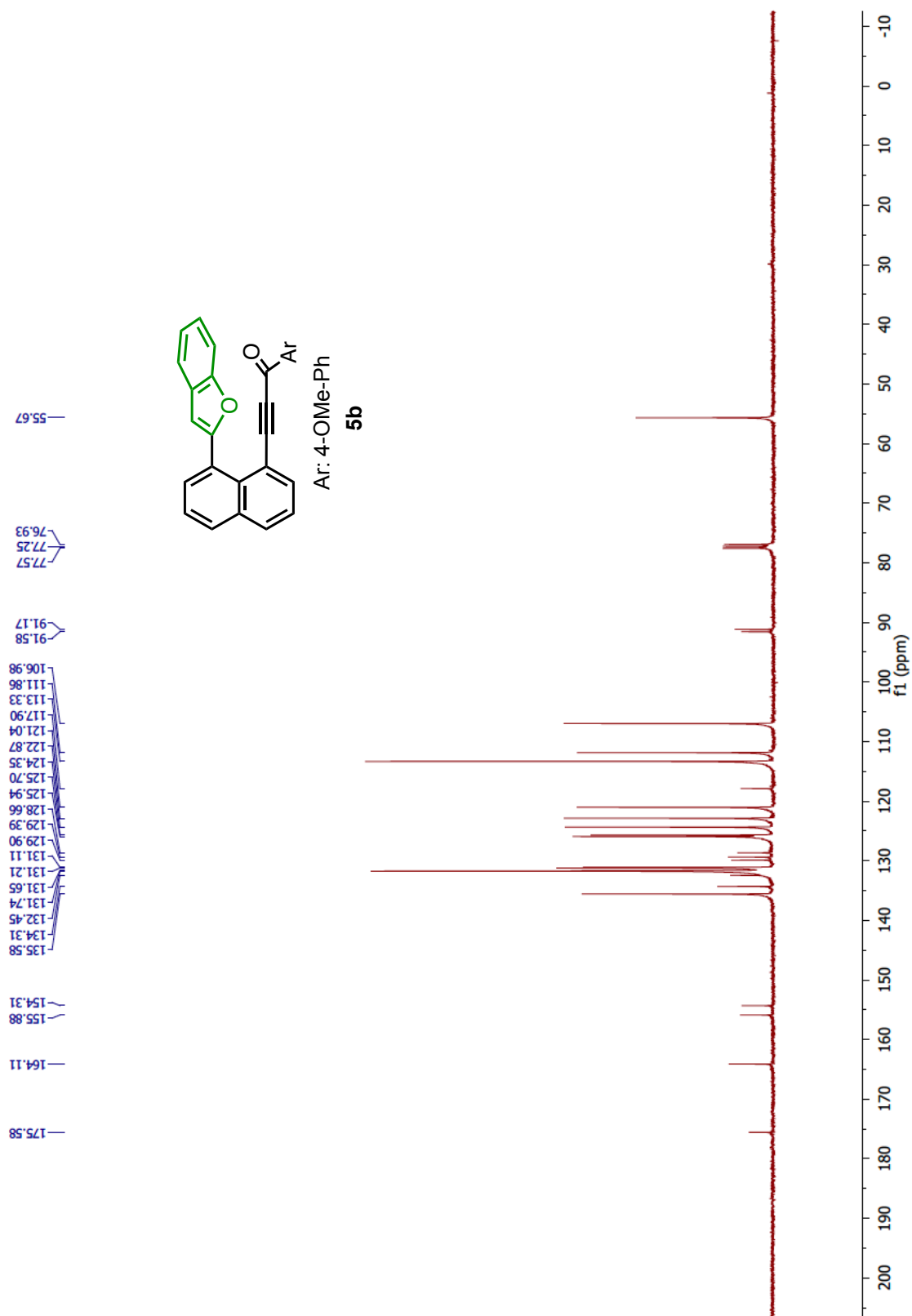


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5b** in CDCl_3 .

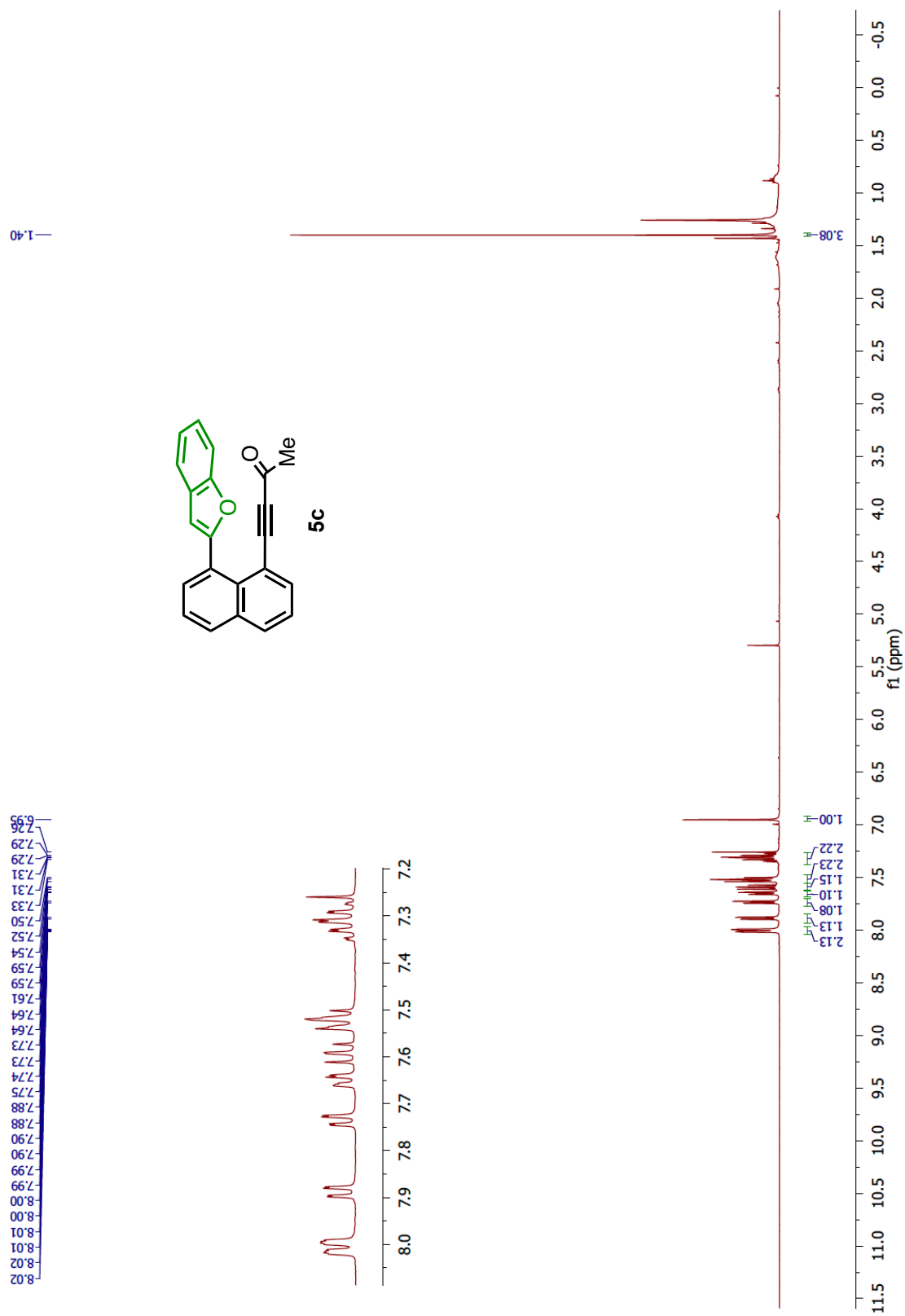


Figure S15. ^1H NMR spectrum of **5c** in CDCl_3 .

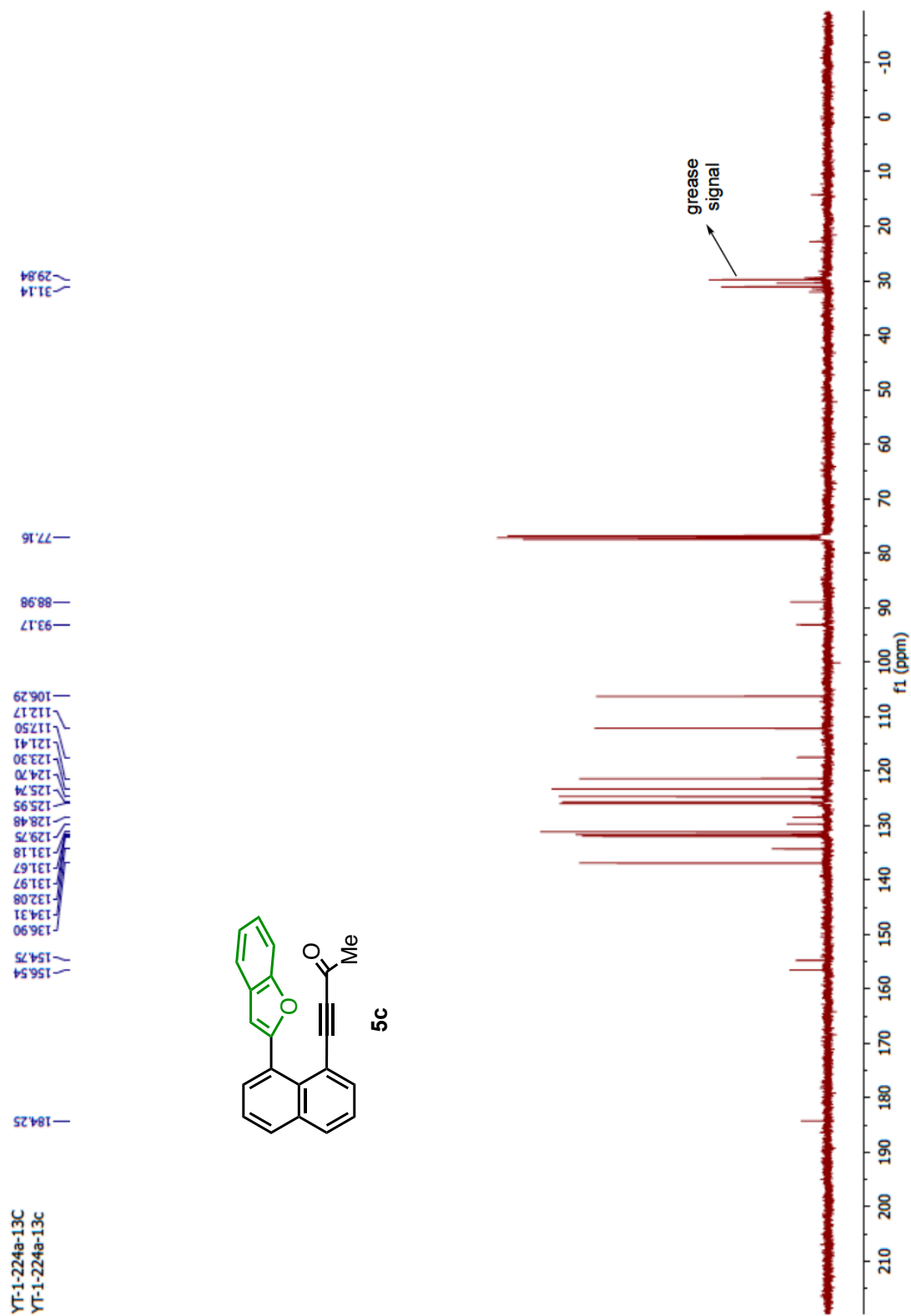


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5c** in CDCl_3 .

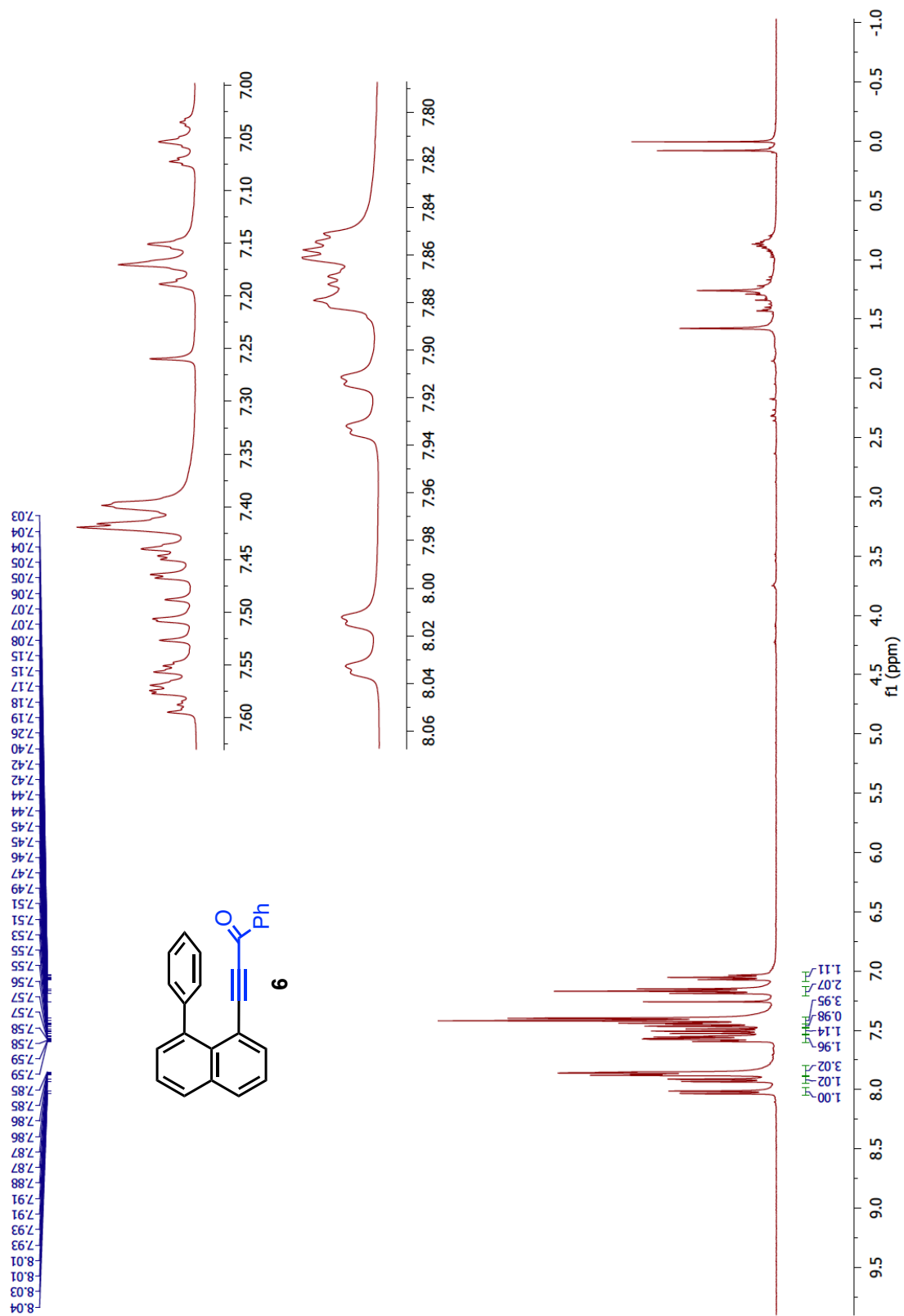


Figure S17. ^1H NMR spectrum of **6** in CDCl_3 .

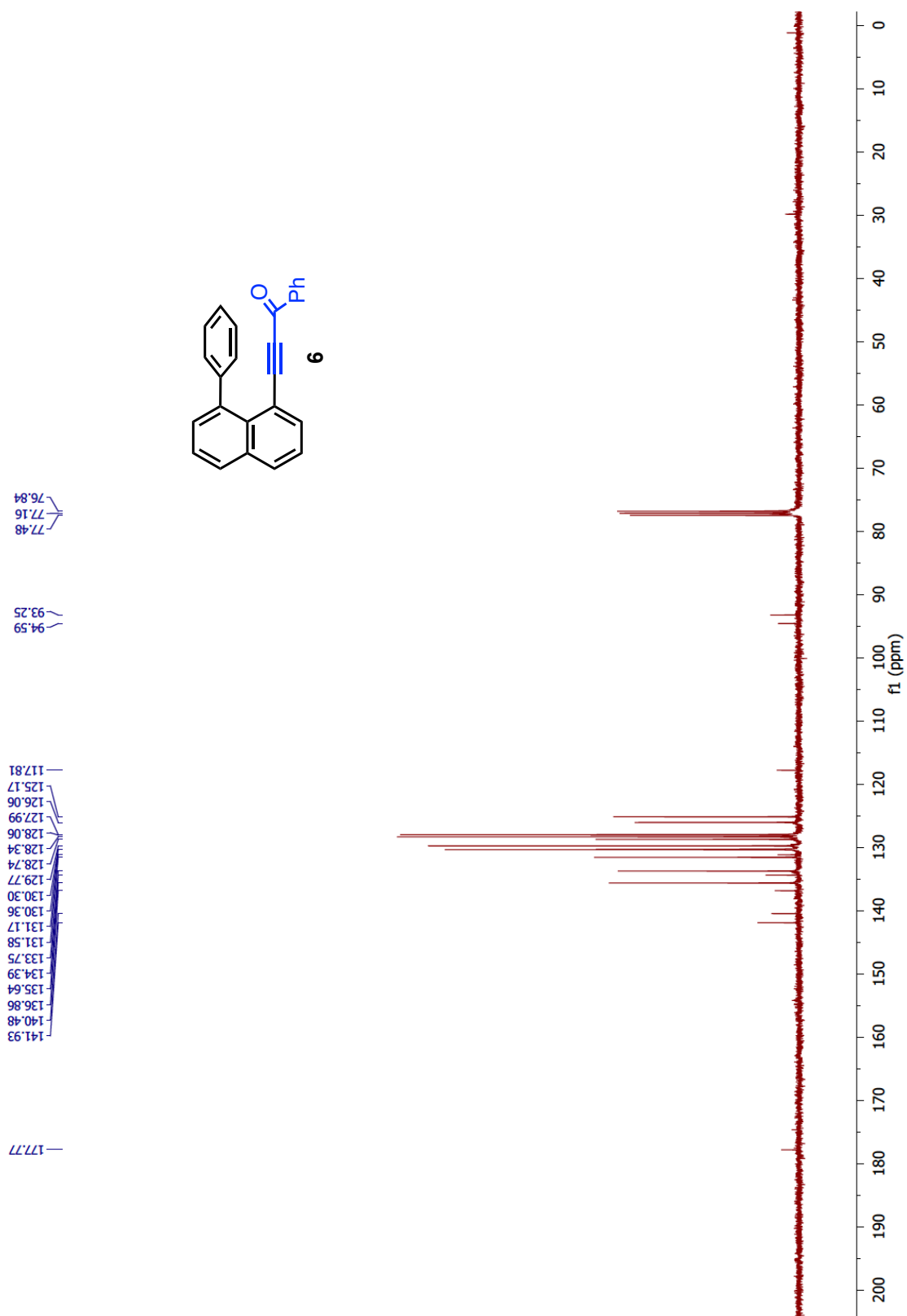


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in CDCl_3 .

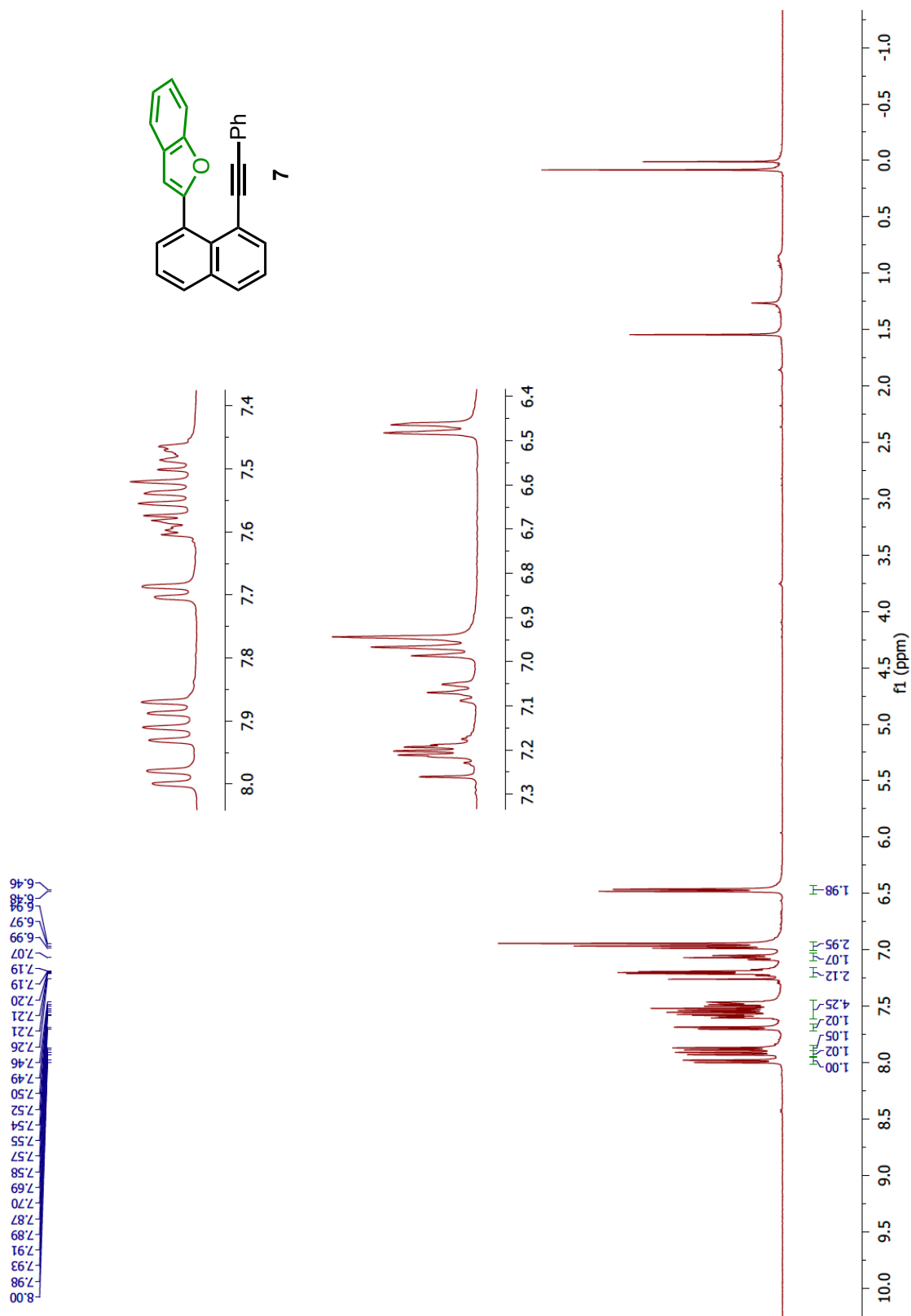


Figure S19. ¹H NMR spectrum of **7** in CDCl₃.

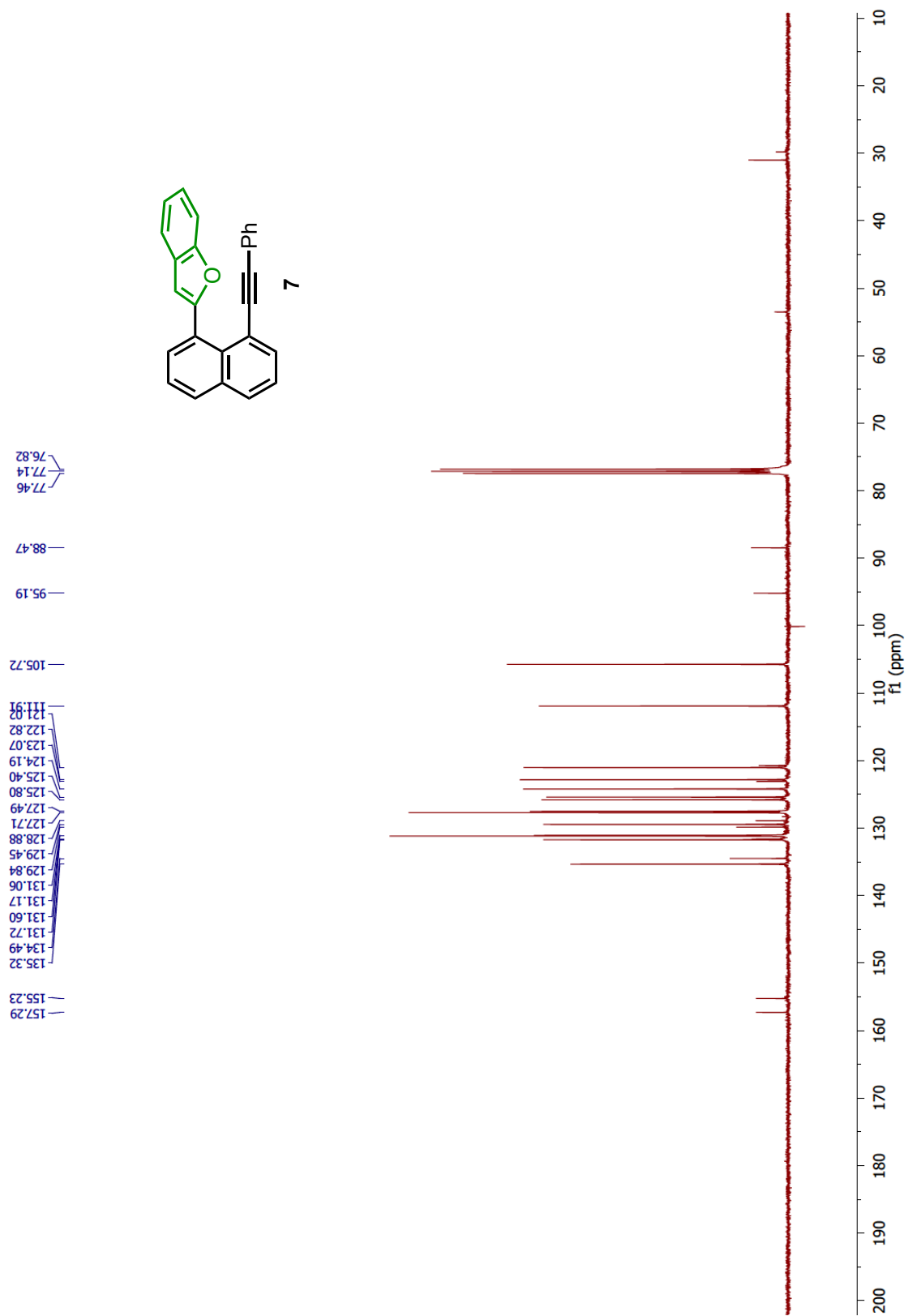


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 .

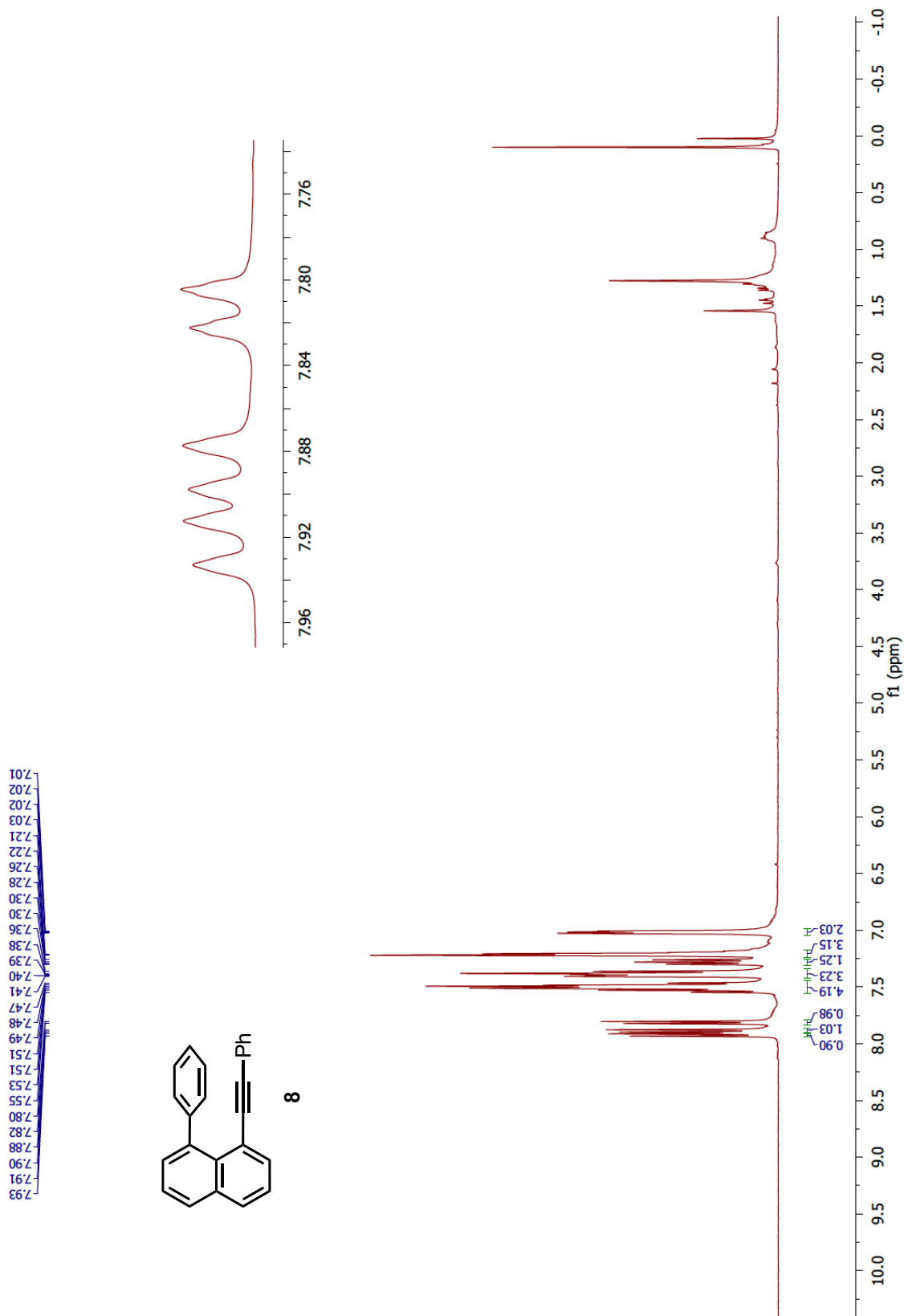


Figure S21. ¹H NMR spectrum of **8** in CDCl₃.

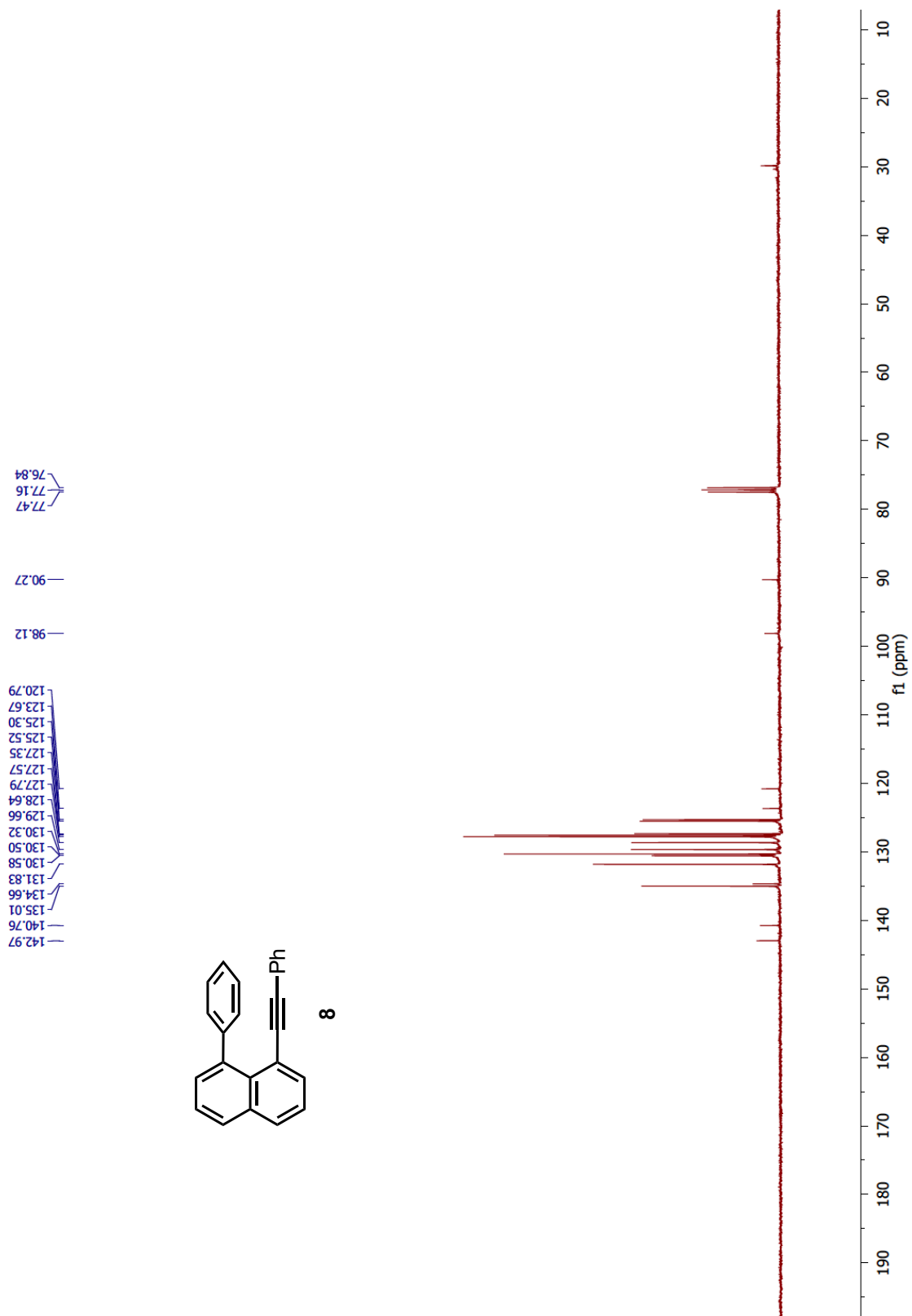


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 .

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