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Microwave-Assisted Intramolecular Aminopalladation-Triggered Domino Sequence: Atom Economical Route to 5,10-Dihydroindeno[1,2-*b*]indoles

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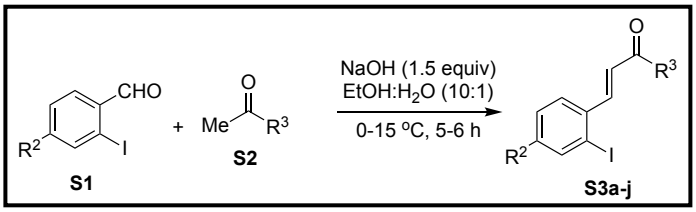
1. General Information

All reagents and solvents were purchased from commercial suppliers (Alfa Aesar, Sigma-Aldrich, Merck, SDFine, SRL, CDH) and used without further purification. All reactions were carried out in oven-dried glassware. The reactions were monitored by thin layer chromatography using Merck silica gel 60 F254 and visualized by UV detection or using molecular iodine or *p*-anisaldehyde stain. Silica gel (230-400 mesh) was used for flash column chromatography. Melting points were recorded on a melting point apparatus in capillaries and are uncorrected. 1H and 13C{1H} -NMR spectra were recorded in $CDCl_3$ at room temperature on a Brucker AC-400 spectrometer operating at 400 MHz for ^1H and 101 MHz for 13C{1H}. Chemical shifts (δ) are expressed in ppm using TMS as an internal standard and coupling constants (*J*) are given in Hz. Infrared (IR) spectra was recorded on Perkin-Elmer FTIR spectrophotometer using KBr. Elemental analyses were determined at the CAI de Microanalisis Elemental, Universidad Complutense, by using a Leco 932 CHNS combustion microanalyzer. Microwave-assisted synthesis was carried out in a CEM focused microwave synthesis system (Discover SP synthesizer) containing single-mode microwave cavity producing controlled irradiation at 2455 MHz. Reaction times refer to hold times at the temperatures indicated and not to total irradiation times. The temperature on the bottom of the reaction vessel was measured with an IR sensor located below the microwave cavity floor. The reactions were carried out under a pressure of 200 Pa and a power of 150 W in sealed reaction vessels.

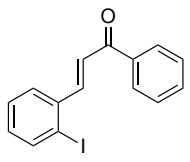
2. General Procedure for the Synthesis of Enones S3a-j



Compounds **S3** were prepared using the literature procedure.[1]

(*E*)-3-(2-Iodophenyl)-1-phenylprop-2-en-1-one (S3a)[1]

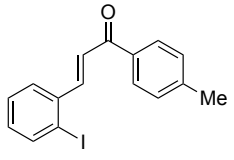
Pale yellow viscous liquid (91%, 3.03 g).



S3a

(*E*)-3-(2-Iodophenyl)-1-(*p*-tolyl)prop-2-en-1-one (S3b)[1]

Yellow viscous liquid (89%, 3.09 g).

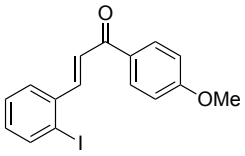


S3b

[1]M. Karuppasamy, B. S. Vachan, T. Jandial, S. B. Annes, N. Bhuvanesh, C. U. Maheswari, V. Sridharan, *Adv. Synth. Catal*., 2020, **362**, 2716– 2724.

(*E*)-3-(2-Iodophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (S3c)[1]

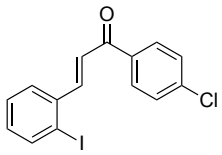
Colourless solid (93%, 3.38 g); mp: 95-97 °C.



S3c

(*E*)-1-(4-Chlorophenyl)-3-(2-iodophenyl)prop-2-en-1-one (S3d)[1]

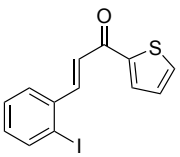
Off-white solid (65%, 2.39 g); mp: 71-73 °C.



S3d

(*E*)-3-(2-Iodophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (S3e)[1]

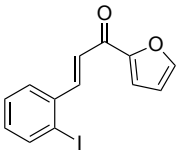
Pale brown viscous liquid (81%, 2.75 g).



S3e

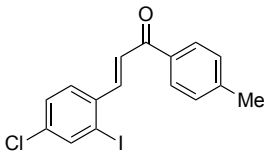
(*E*)-1-(Furan-2-yl)-3-(2-iodophenyl)prop-2-en-1-one (S3f)[1]

Pale brown viscous liquid (73%, 2.36 g).



S3f

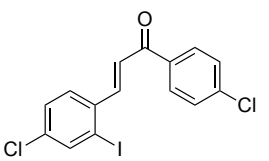
(*E*)-3-(4-Chloro-2-iodophenyl)-1-(*p*-tolyl)prop-2-en-1-one (S3g)



S3g

Colourless solid (3.41 g, 86%); mp: 114-116 °C; IR (KBr): 3052, 3002, 1860, 1682, 1611, 1442, 1326, 1281, 1169, 1052 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 15.5 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 15.5 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.08 (dd, *J* = 8.4, 1.9 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 146.0, 144.2, 141.0, 140.2, 135.0, 134.9, 131.1, 129.5, 128.9, 127.3, 126.1, 98.5, 21.8. Anal Calcd for $C_{16}H_{12}ClIO$: C, 50.23; H, 3.16. Found: C, 50.03; H, 3.08.

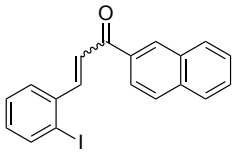
(*E*)-3-(4-Chloro-2-iodophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (S3h)



S3h

Off-white solid (3.62 g, 82%); mp: 145-147 °C; IR (KBr): 3062, 1900, 1692, 1611, 1442, 1299, 1252, 1189, 1065 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 15.5 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 15.5 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 146.9, 141.1, 139.8, 139.7, 135.9, 135.1, 131.4, 130.1, 129.1, 127.4, 125.5, 98.6. Anal Calcd for $C_{15}H_9Cl_2IO$: C, 44.70; H, 2.25. Found: C, 44.33; H, 2.22.

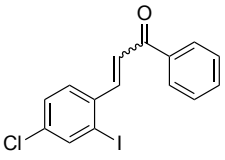
(*E/Z*)-3-(2-Iodophenyl)-1-(naphthalen-2-yl)prop-2-en-1-one (S3i)



S3i

Trans:*cis* = 1:0.62; Viscous liquid (2.70 g, 73%); IR (KBr): 3853, 2827, 1610, 1457, 1293, 1225, 1188, 1127, 1042 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.57 (s, *trans*, 1H), 8.42 (s, *cis*, 1H), 8.13 (dd, *J* = 8.6, 1.6 Hz, *trans*, 1H), 8.06 (d, *J* = 15.7 Hz, *trans*, 1H), 8.02 (d, *J* = 8.0 Hz, *trans*, 1H), 7.98-7.92 (m, *trans* & *cis*, 5H), 7.83-7.74 (m, *trans* & *cis*, 4H), 7.66-7.54 (m, *trans* & *cis*, 4H), 7.50 (d, *J* = 15.6 Hz, *trans*, 1H), 7.45 (t, *J* = 7.6 Hz, *trans*, 1H), 7.26 (d, *J* = 8.0 Hz, *cis*, 1H), 7.18 (d, *J* = 12.3 Hz, *cis*, 1H), 7.14-7.05 (m, *trans* & *cis*, 2H), 6.81-6.76 (m, *cis*, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ* 194.2, 190.3, 147.9, 142.8, 140.2, 139.7, 138.7, 138.5, 135.6, 135.2, 134.3, 132.6, 132.4, 131.5, 131.4, 130.4, 129.7, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.7, 127.6, 126.9, 126.7, 125.5, 124.6, 124.1, 101.8, 98.6. Anal Calcd for $C_{19}H_{13}IO$: C, 59.40; H, 3.41. Found: C, 59.12; H, 3.32. * Four aromatic carbons have merged with others.

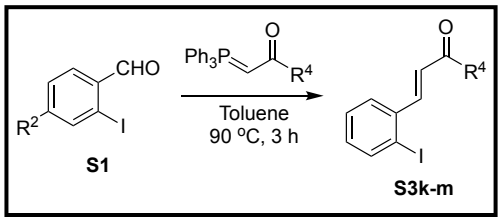
(*E/Z*)-3-(4-Chloro-2-iodophenyl)-1-phenylprop-2-en-1-one (S3j)



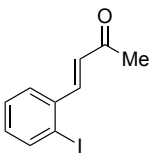
S3j

Trans:cis = 1:0.28; Viscous liquid (3.24 g, 81%); IR (KBr): 3051, 1896, 1670, 1603, 1446, 1307, 1262, 1186, 1091 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, *J* = 7.7 Hz, *trans*, 2H), 7.99 (t, *J* = 7.7 Hz, *cis*, 1H), 7.91 (d, *J* = 15.5 Hz, *trans*, 1H), 7.86 (s, *cis*, 1H), 7.85 (d, *J* = 8.4 Hz, *trans* & *cis*, 2H), 7.70-7.62 (m, *trans* & *cis*, 3H), 7.56-7.52 (m, *trans*, 2H), 7.49 (d, *J* = 7.4 Hz, *cis*, 1H), 7.42-7.36 (m, *trans & cis*, 2H), 7.23 (d, *J* = 2.1 Hz, *cis*, 1H), 7.09 (dd, *J* = 8.4, 2.2 Hz, *trans* 1H), 7.01 (d, *J* = 12.2 Hz, *cis*, 1H), 6.88 (dd, *J* = 8.4, 2.1 Hz, *cis*, 1H), 6.77 (d, *J* = 12.3 Hz, *cis*, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 189.8, 146.5, 142.2, 141.0, 141.1, 140.0, 139.7, 137.6, 137.2, 135.0, 134.2, 133.3, 133.2, 131.3, 130.2, 129.8, 128.8, 128.7, 128.6, 128.4, 128.3, 127.4, 126.0, 98.6, 95.6. Anal Calcd for $C_{15}H_{10}ClIO$: C, 48.88; H, 2.73. Found: C, 48.75; H, 2.69.

3. General Procedure for the Synthesis of Enones S3k-m



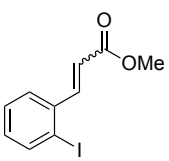
(*E*)-4-(2-Iodophenyl)but-3-en-2-one (S3k)[1]



S3k

Colourless solid (81%, 2.20 g), mp: 54-56 °C.

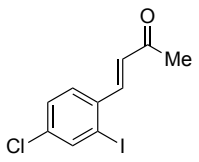
Methyl (*E*/*Z*)-3-(2-iodophenyl)acrylate (S3l)[1]



S3l

Trans:*cis* = 1:0.31; Colourless liquid (65%, 1.87 g).

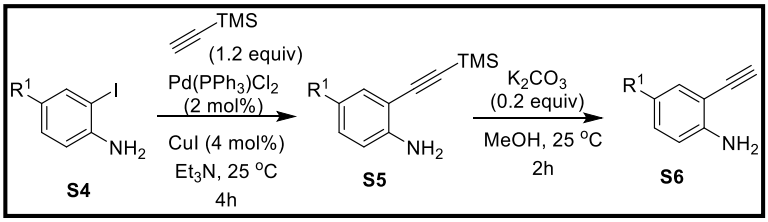
(*E*)-4-(4-Chloro-2-iodophenyl)but-3-en-2-one (S3m)



S3m

Off-white solid (2.81 g, 84%); mp: 121-123 °C; IR (KBr): 3049, 3005, 1889, 1685, 1604, 1446, 1307, 1266, 1178, 1085 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 16.1 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 2.4 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.2, 140.9, 139.4, 135.2, 131.4, 130.69, 127.3, 98.4, 27.6.Anal Calcd for $C_{10}H_8ClIO$: C, 39.18; H, 2.63. Found: C, 39.04; H, 2.61.

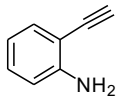
4. General Procedure for the Synthesis of 2-Alkynylanilines S6



Compounds **S6** were prepared using the literature procedure.[2]

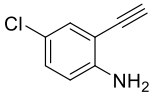
2-Ethynylaniline (S6a)[2]

Yellow oil (0.947 g, 81%)



S6a

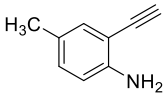
4-Chloro-2-ethynylaniline (S6b)[3]



S6b

Brown solid (1.19 g, 79%), mp: 56-58 °C.

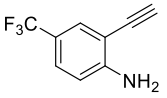
2-Ethynyl-4-methylaniline (S6c)[2]



S6c

Orange oil (0.95 g, 73%).

2-Ethynyl-4-(trifluoromethyl)aniline (S6d)[4]



S6d

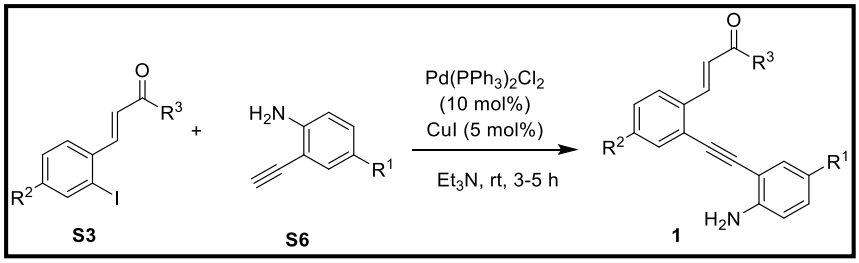
Brown oil (1.31 g, 71%).

[2]A. Isobe, J. Takagi, T. Katagiri, K. Uneyama, *Org. Lett*., 2008, **10**, 2657–2659.

[3]B. M. Trost, A. Mc Clory, *Angew. Chem. Int. Ed*., 2007, **46**, 2074–2077.

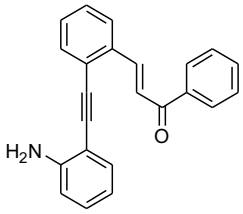
[4]X. Zhao, X. Song, H. Jin, Z. Zeng, Q. Wang, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal*., 2018, **360**, 2720–2726.

5. General Procedure for the Synthesis of Compounds 1



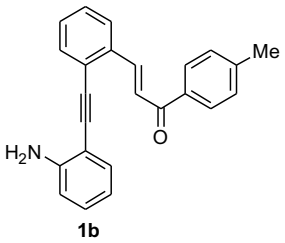
To a stirred solution of compound **S3** (1 mmol, 1.0 equiv) in Et_3N (15 mL) were added *2*-ethynylaniline **S6** (6 mmol, 1.2 equiv), $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 10 mol%) and CuI (0.05 mmol, 5 mol %) successively. The resulting mixture was stirred at room temperature for 3-5 h. After the completion of the reaction, as indicated by TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (2 × 20 mL). The organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to dryness under reduced pressure and the crude mixture was chromatographed over silica using petroleum ether and ethyl acetate mixture (85:15 to 80:20, v/ v) as the eluent to access the desired compounds **1a-t.**

(*E*)-3-(2-((2-Aminophenyl)ethynyl)phenyl)-1-phenylprop-2-en-1-one (1a)


1a

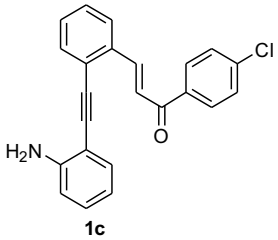
Pale brown solid (0.271 g, 84%); mp: 136-138°C; IR (KBr): 3452, 3369, 2191, 1642, 1510, 1317, 1088 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, *J* = 15.8 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.80-7.78 (m, 1H), 7.66 (d, *J* = 15.8 Hz, 1H), 7.63-7.58 (m, 2H), 7.51-7.48 (m, 2H), 7.42-7.37 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.76-6.72 (m, 2H), 4.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 190.8, 148.2, 142.9, 138.1, 135.8, 132.7, 132.8, 132.4, 130.2, 130.0, 128.7, 128.6, 128.4, 126.7, 124.7, 123.9, 117.9, 114.6, 107.40, 92.9, 92.43. Anal Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.25; H, 5.23; N, 4.29.

(*E*)-3-(2-((2-Aminophenyl)ethynyl)phenyl)-1-(*p*-tolyl)prop-2-en-1-one (1b)


1b

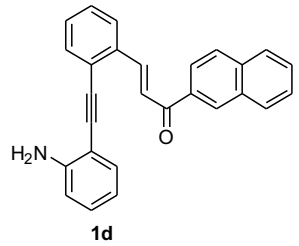
Pale yellow solid (0.302 g, 87%); mp: 96-98 °C; IR (KBr): 3431, 3342, 3045, 2216, 1681, 1470, 1301, 1193, 1052 cm^{-1}.^1H NMR ($CDCl_3$, 400 MHz) δ 8.40 (d, *J* = 15.6 Hz, 1H), 7.96-7.61 (m, 5H), 7.40-7.18 (m, 6H), 6.75 (d, *J* = 7.7 Hz, 2H), 4.42 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 148.2, 143.7, 142.5, 135.9, 135.5, 132.7, 132.4, 130.2, 129.9, 129.4, 128.8, 128.4, 126.6, 124.7, 123.9, 117.9, 114.6, 107.4, 92.8, 92.5, 21.7. Anal Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.29; H, 5.57; N, 4.06.

(*E*)-3-(2-((2-Aminophenyl)ethynyl)phenyl)-1-(4-chlorophenyl)prop-2-en-1-one (1c)


1c

Pale yellow solid (0.289 g, 81%); mp: 112-114 °C; IR (KBr): 3469, 3370, 2198, 1639, 1505, 1312, 1097 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, *J* = 15.8 Hz, 1H), 7.98-7.95 (m, 2H), 7.78-7.75 (m, 1H), 7.64-7.60 (m, 2H), 7.45 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.42-7.39 (m, 2H), 7.37 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.19 (td, *J* = 7.8, 1.5 Hz, 1H), 6.77-6.73 (m, 2H), 4.38 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 148.1, 143.5, 139.2, 136.4, 135.5, 132.8, 132.4, 130.3, 130.2, 130.0, 128.9, 128.5, 126.8, 124.7, 123.4, 118.0, 114.6, 107.3, 92.9, 92.4. Anal Calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91. Found: C, 76.89, H; 4.54, N, 3.97.

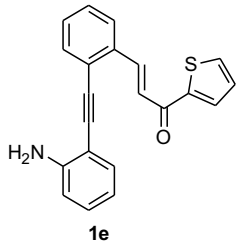
(*E*)-3-(2-((2-Aminophenyl)ethynyl)phenyl)-1-(naphthalen-2-yl)prop-2-en-1-one (1d)



1d

Yellow viscous liquid (0.314 g, 82%); IR (KBr): 3420, 3325, 3065, 2105, 1656, 1476, 1315, 1178, 1005 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.55 (s, 1H), 8.45 (d, *J* = 15.8 Hz, 1H), 8.12 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.95-7.83 (m, 5H), 7.64-7.61 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43-7.41 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 4.38 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 148.2, 142.9, 135.7, 135.6, 135.4, 132.9, 132.6, 132.4, 130.2, 130.7, 130.3, 129.2, 128.4, 128.5, 127.8, 126.9, 126.8, 126.4, 124.6, 124.5, 123.8, 117.9, 114.6, 107.4, 92.9, 92.5. Anal Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.66; H, 5.07; N, 3.69.

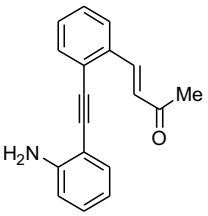
(*E*)-3-(2-((2-Aminophenyl)ethynyl)phenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1e)



1e

Pale yellow solid (0.240 g, 73%); mp: 128-130 °C; IR (KBr): 3371, 2911, 1665, 1564, 1477, 1413, 1304, 1221, 1072 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.47 (d, *J* = 15.7 Hz, 1H), 7.89 (d, *J* = 2.5 Hz, 1H), 7.80-7.78 (m, 1H), 7.71-7.70 (m, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 15.7 Hz, 1H), 7.44-7.40 (m, 3H), 7.20-7.16 (m, 2H), 6.76-6.71 (m, 2H), 4.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.2, 148.2, 145.4, 142.1, 135.6, 134.0, 132.7, 132.4, 132.1, 130.2, 130.1, 128.4, 128.3, 126.6, 124.8, 123.3, 117.9, 114.6, 107.4, 93.0, 92.4. Anal Calcd for $C_{21}H_{15}NOS$: C, 76.57; H, 4.59; N, 4.25. Found: C, 76.41; H, 4.48; N, 4.17.

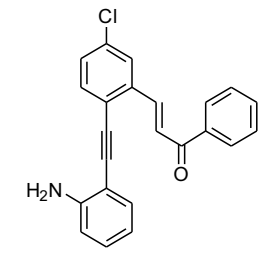
(*E*)-4-(2-((2-Aminophenyl)ethynyl)phenyl)but-3-en-2-one (1f)



1f

Pale yellow solid (0.211 g, 81%); mp: 94-96 °C; IR (KBr): 3450, 2188, 1656, 1487, 1369, 1331, 1223, 1174, 1102 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, *J* = 16.4 Hz, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.42-7.38 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.81-6.75 (m, 3H), 4.35 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 148.1, 141.5, 135.4, 132.7, 132.2, 130.3, 130.1, 128.6, 128.6, 126.1, 124.5, 118.1, 114.6, 107.4, 92.6, 92.2, 27.4. Anal Calcd for $C_{18}H_{15}NO$ C, 82.73; H, 5.79; N, 5.36. Found: C, 82.02, H; 5.65; N, 5.41.

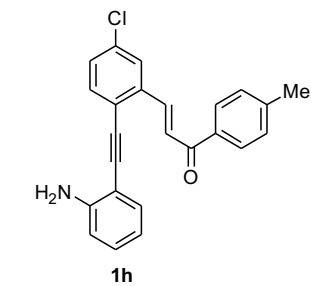
(*E*)-3-(2-((2-Aminophenyl)ethynyl)-5-chlorophenyl)-1-phenylprop-2-en-1-one (1g)



1g

Pale yellow solid (0.275 g, 77%); mp: 129-131 °C; IR (KBr): 3452, 3351, 2169, 1642, 1571, 1305, 1087 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, *J* = 15.8 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.54-7.49 (m, 3H), 7.38-7.35 (m, 2H), 7.18 (td, *J* = 8.2, 1.1 Hz, 1H), 6.73 (t, *J* = 8.0 Hz, 2H), 4.38 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 148.3, 141.4, 137.8, 137.3, 134.3, 133.7, 133.1, 132.4, 130.4, 130.0, 128.7, 128.6, 126.4, 124.6, 123.2, 117.9, 114.6, 107.1, 93.8, 91.4. Anal Calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91. Found: C, 76.92; H, 4.42; N, 3.85.

(*E*)-3-(2-((2-Aminophenyl)ethynyl)-5-chlorophenyl)-1-(*p*-tolyl)prop-2-en-1-one (1h)

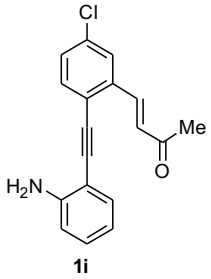


1h

Pale yellow solid (0.308 g, 83%); mp: 121-123 °C; IR (KBr): 3439, 3346, 3055, 2204, 1656, 1499, 1318, 1173, 1027 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, *J* = 1.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.63 (d, *J* = 15.8 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.37 (td, *J* = 8.3 , 1.8 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 8.1 Hz, 1H), 6.76-6.71 (m, 2H), 4.40 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 148.3, 144.0, 140.9,

137.4, 135.3, 134.3, 133.7, 132.4, 130.4, 129.9, 129.4, 128.8, 126.4, 124.7, 123.1, 117.9, 114.6, 107.1, 93.8, 91.5, 21.7. Anal Calcd for $C_{24}H_{18}ClNO$: C, 77.52; H, 4.88; N, 3.77. Found: C, 77.33; H, 4.81; N, 3.83.

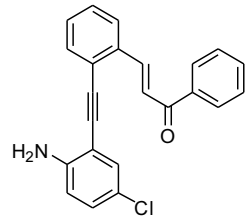
(*E*)-4-(2-((2-Aminophenyl)ethynyl)-5-chlorophenyl)but-3-en-2-one (1i)



1i

Pale brown solid (0.256 g, 87%); mp: 82-84 °C; IR (KBr): 3451, 2198, 1662, 1493, 1359, 1301, 1254, 1184, 1103 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 16.3 Hz, 1H), 7.65 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.41-7.35 (m, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.79-6.75 (m, 3H), 4.34 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 148.1, 139.9, 136.9, 134.5, 133.7, 132.2, 130.5, 130.1, 129.3, 126.1, 122.1, 118.2, 114.7, 107.1, 93.5, 91.3, 27.8. Anal Calcd for $C_{18}H_{14}ClNO$: C, 73.10; H, 4.77; N, 4.74. Found: C, 72.89; H, 4.72; N, 4.83.

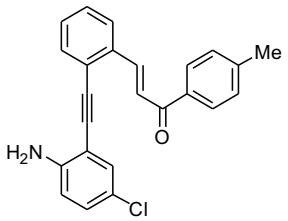
(*E*)-3-(2-((2-Amino-5-chlorophenyl)ethynyl)phenyl)-1-phenylprop-2-en-1-one (1j)



1j

Pale yellow solid (0.279 g, 78%); mp: 146-148 °C; IR (KBr): 3462, 3372, 2167, 1672, 1536, 1319, 1068 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J* = 15.8 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.81-7.78 (m, 1H), 7.65-7.60 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.43-7.40 (m, 2H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.12 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 4.29 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 190.9, 146.8, 142.7, 138.0, 135.9, 132.9, 132.8, 131.4, 130.1, 130.0, 128.8, 128.7, 128.6, 126.6, 124.2, 124.1, 122.2, 115.7, 108.7, 93.3, 91.4. Anal Calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91. Found: C, 77.02; H, 4.56; N, 3.85.

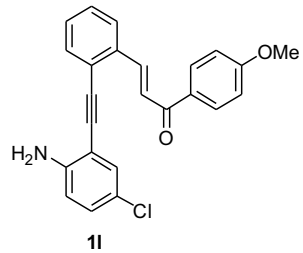
(*E*)-3-(2-((2-Amino-5-chlorophenyl)ethynyl)phenyl)-1-(*p*-tolyl)prop-2-en-1-one (1k)



1k

Pale yellow solid (0.372 g, 76%); mp: 130-131 °C; IR (KBr): 3352, 2967, 1681, 1611, 1451, 1322, 1251, 1163, 1042 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.34 (d, *J* = 15.8 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.80-7.77 (m, 1H), 7.65-7.59 (m, 2H), 7.42-7.38 (m, 2H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.30 (d,*J* = 8.0 Hz,2H), 7.11 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 4.38 (brs, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ* 190.3, 146.9, 143.9, 142.2, 136.0, 135.4, 132.8, 131.4, 130.1, 129.9, 129.4, 128.8, 126.6, 124.1, 124.0, 122.1, 115.7, 108.7, 93.3, 91.4, 21.7.Anal Calcd for $C_{24}H_{18}ClNO$: C, 77.52; H, 4.88; N, 3.77. Found: C, 77.32; H, 4.81; N, 3.78.*One aromatic carbon merged with others.

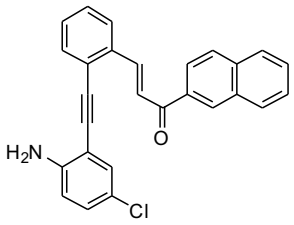
(*E*)-3-(2-((2-Amino-5-chlorophenyl)ethynyl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (1l)



1l

Pale brown solid (0.313 g, 81%); mp: 110-112 °C; IR (KBr): 3370, 3055, 1656, 1604, 1487, 1307, 1260, 1173, 1035 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, *J* = 15.8 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.78-7.76 (m, 1H), 7.67 (d, *J* = 15.8 Hz, 1H), 7.61-7.60 (m, 1H), 7.42-7.39 (m, 2H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.13-7.09 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 1H), 4.42 (brs, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 163.6, 146.9, 141.8, 136.1, 132.8, 132.0, 131.4, 130.9, 130.1, 129.8, 128.8, 126.7, 123.9, 122.1, 115.7, 115.6, 113.9, 108.7, 93.4, 91.3, 55.5. Anal Calcd for $C_{24}H_{18}ClNO_2$: C, 74.32; H, 4.68; N, 3.61. Found: C, 74.11; H, 4.57; N, 3.54.

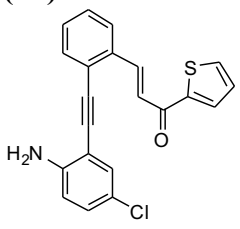
(*E*)-3-(2-((3-Aminonaphthalen-2-yl)ethynyl)phenyl)-1-(4-chlorophenyl)prop-2-en-1-one (1m)



1m

Pale yellow solid (0.318 g, 78%); mp: 127-129 °C; IR (KBr): 3428, 3340, 3055, 2192, 1668, 1476, 1324, 1178, 1021 cm^{-1}.^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (s, 1H), 8.44 (d, *J* = 15.8 Hz, 1H), 8.11 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.96-7.90 (m, 3H), 7.86-7.82 (m, 2H), 7.64-7.61 (m, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.44-7.43 (m, 2H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 4.32 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ* 190.4, 146.9, 142.6, 135.9, 135.5, 135.3, 132.9, 132.6, 131.4, 130.2, 130.1, 130.0, 129.6, 128.8, 128.7, 128.5, 127.8, 126.9, 124.5, 124.2, 123.9, 122.2, 115.8, 108.7, 93.3, 91.5. Anal Calcd for $C_{27}H_{18}ClNO$: C, 79.50; H, 4.45; N, 3.43. Found: C, 79.41; H, 4.32; N, 3.48. * One aromatic carbon merged with others.

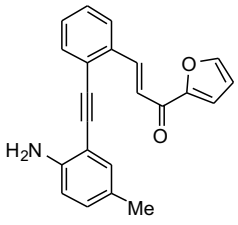
(*E*)-3-(2-((2-Amino-5-chlorophenyl)ethynyl)phenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1n)



1n

Pale brown solid (0.232 g, 64%); mp: 149-151 °C; IR (KBr): 3381, 2921, 1650, 1575, 1487, 1423, 1324, 1231, 1062 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, *J* = 15.7 Hz, 1H), 7.89-7.88 (m, 1H), 7.80-7.78 (m, 1H), 7.72-7.71 (m, 1H), 7.62-7.60 (m, 1H), 7.53 (d, *J* = 15.6 Hz, 1H), 7.43-7.41 (m, 2H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.20 (t, *J* = 2.1 Hz, 1H), 7.12 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 1H), 4.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.2, 146.9, 145.3, 141.9, 135.7, 134.2, 132.8, 132.1, 131.4, 130.2, 130.1, 128.7, 128.4, 126.6, 124.3, 123.3, 122.1, 115.7, 108.7, 93.2, 91.6. Anal Calcd for $C_{21}H_{14}ClNOS$: C, 69.32; H, 3.88; N, 3.85. Found: C, 69.08; H, 3.80; N, 3.77.

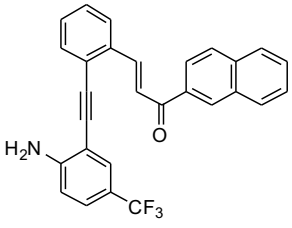
(*E*)-3-(2-((2-Amino-5-methylphenyl)ethynyl)phenyl)-1-(furan-2-yl)prop-2-en-1-one (1o)



1o

Pale brown solid (0.288 g, 88%); mp: 166-168 °C; IR (KBr): 3371, 3065, 2903, 1642, 1561, 1479, 1402, 1314, 1222, 1058 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, *J* = 15.8 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.66 (s, 1H), 7.61-7.56 (m, 2H), 7.40-7.38 (m, 2H), 7.35 (d, *J* = 3.1 Hz, 1H), 7.25 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.60-6.59 (m, 1H), 4.31 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 153.6, 146.7, 146.0, 142.1, 135.5, 132.7, 132.4, 131.1, 130.1, 128.3, 127.1, 126.7, 124.9, 122.83 117.8, 114.8, 112.6, 107.5, 93.3, 92.2, 20.3. Anal Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.42; H, 5.12; N, 4.27.

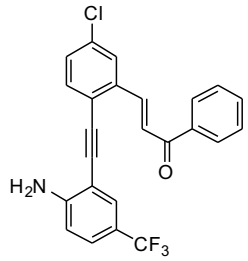
(*E*)-3-(2-((2-Amino-5-(trifluoromethyl)phenyl)ethynyl)phenyl)-1-(naphthalen-2-yl)prop-2-en-1-one (1p)



1p

Pale brown solid (0.313 g, 71%); mp: 153-155 °C; IR (KBr): 3480, 3364, 1656, 1615, 1586, 1342, 1173, 1143, 1085 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (s, 1H), 8.44 (d, *J* = 15.7 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.95-7.89 (m, 3H), 7.86-7.81 (m, 2H), 7.65-7.61 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.45-7.43 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 8.5 Hz 1H), 4.74 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ* 190.2, 150.7, 142.5, 135.9, 135.6, 135.3, 132.9, 132.5, 130.2, 130.1, 129.6 (q, *J* = 3.0 Hz), 129.5, 128.9, 128.7, 128.6, 127.8, 126.9 (q, *J* = 4.0 Hz), 126.9, 126.7, 124.4, 124.1, 123.9, 119.7 (q, *J* = 33.3 Hz), 113.9, 106.9, 93.3, 91.2. Anal Calcd for $C_{28}H_{18}F_3NO$: C, 76.18; H, 4.11; N, 3.17. Found: C, 75.96, H, 4.16, N, 3.21. *One aromatic carbon merged with others.

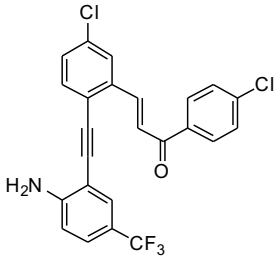
(*E*)-3-(2-((2-Amino-5-(trifluoromethyl)phenyl)ethynyl)-5-chlorophenyl)-1-phenylprop-2-en-1-one (1q)



1q

Pale yellow solid (0.293 g, 69%); mp: 131-133 °C; IR (KBr): 3055, 2373, 2315, 1843, 1720, 1493, 1423, 1377, 1190 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.29 (d, *J* = 15.8 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 1.0 Hz, 1H), 7.63-7.59 (m, 3H), 7.55-7.50 (m, 3H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.75 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ* 190.1, 150.7, 141.0, 137.7, 137.4, 134.9, 133.8, 133.2, 130.1, 129.7 (q, *J* = 4.0 Hz), 128.8, 128.6, 127.1 (q, *J* = 3.0 Hz), 126.4, 124.8, 122.5, 119.7 (q, *J* = 33.3 Hz), 114.1, 106.5, 92.2, 92.1. Anal Calcd for $C_{24}H_{15}ClF_3NO$: C, 67.69; H, 3.55; N, 3.29. Found: C, 67.61; H, 3.48; N, 3.29. *One aromatic carbon merged with others.

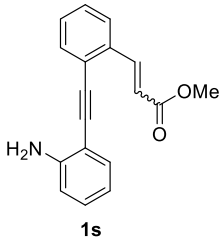
(*E*)-3-(2-((2-Amino-5-(trifluoromethyl)phenyl)ethynyl)-5-chlorophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (1r)



1r

Pale yellow solid (0.193 g, 70%); mp: 175-177 °C; IR (KBr): 3358, 2204, 1750, 1598, 1476, 1318, 1155, 1091, 1009 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, *J* = 15.7 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.64-7.54 (m, 3H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.40 (dd, *J* = 8.4, 1.8 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 4.74 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ* 188.6, 150.6, 141.5, 139.8, 137.2, 135.9, 134.9, 133.9, 130.3, 129.9, 129.7 (q, *J* = 4.0 Hz), 129.1, 127.2 (q, *J* = 4.0 Hz), 126.4, 124.0, 122.6, 119.8 (q, *J* = 33.3 Hz), 114.1, 106.5, 92.2, 92.1. Anal Calcd for $C_{24}H_{14}Cl_2F_3NO$: C, 62.63; H, 3.07; N, 3.04. Found: C, 62.44; H, 3.01; N, 2.98. *One aromatic carbon merged with others.

Methyl (*E/Z*)-3-(2-((2-aminophenyl)ethynyl)phenyl)acrylate (1s)

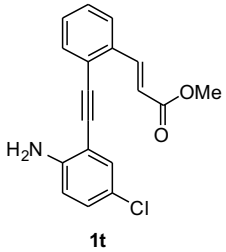


1s

Trans:*cis* = 1:0.31; Yellow oil (0.199 g, 64%); IR (KBr): 3362, 3079, 1681, 1662, 1479, 1322, 1239, 1181, 1049 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, *J* = 16.0 Hz, *trans*, 1H); 7.67-7.56 (m, *trans* & *cis*, 5H), 7.45-7.33 (m, *trans* & *cis*, 6H), 7.20-7.15 (m, *trans* & *cis*, 2H); 6.77-6.74 (m, *trans* & *cis*, 4H), 6,56 (d, *J* = 16.1 Hz, *trans*, 1H), 6.11 (d, *J* = 12.4 Hz, *cis*, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ* 167.4, 166.4, 148.1, 147.9, 142.8, 142.4, 136.8, 135.2, 132.6, 132.4, 132.2, 131.8, 130.2, 130.0, 129.9, 129.3, 128.6, 128.4, 127.7, 126.2, 124.3, 122.9, 114.6, 114.4, 107.7, 107.5, 92.9, 92.6, 92.2, 91.4, 51.8, 51.5.Anal Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.61; H, 5.34; N, 4.98. *Four aromatic carbons merged with others.

Methyl (*E*)-3-(2-((2-amino-5-chlorophenyl)ethynyl)phenyl)acrylate (1t)

Pale yellow solid (0.237 g, 76%); mp: 124-126 °C; IR (KBr): 3352, 3061, 1671, 1642, 1467, 1310, 1228, 1161, 1029 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.28 (d, *J* = 16.0 Hz, 1H), 7.67-7.65 (m, 1H), 7.59-7.56 (m, 1H), 7.40-7.37 (m, 3H), 7.12 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 1H), 6.54 (d, *J* = 16.1 Hz, 1H), 4.25 (brs, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 146.7, 142.6, 135.4, 132.6, 131.5, 130.1, 129.9, 128.8, 126.2, 123.8, 122.2, 119.6, 115.7, 108.8, 93.1, 91.2, 51.9. Anal Calcd for $C_{18}H_{14}ClNO_2$: C, 69.35; H, 4.53; N, 4.49. Found: C, 69.03; H, 4.43; N, 4.52.



1t

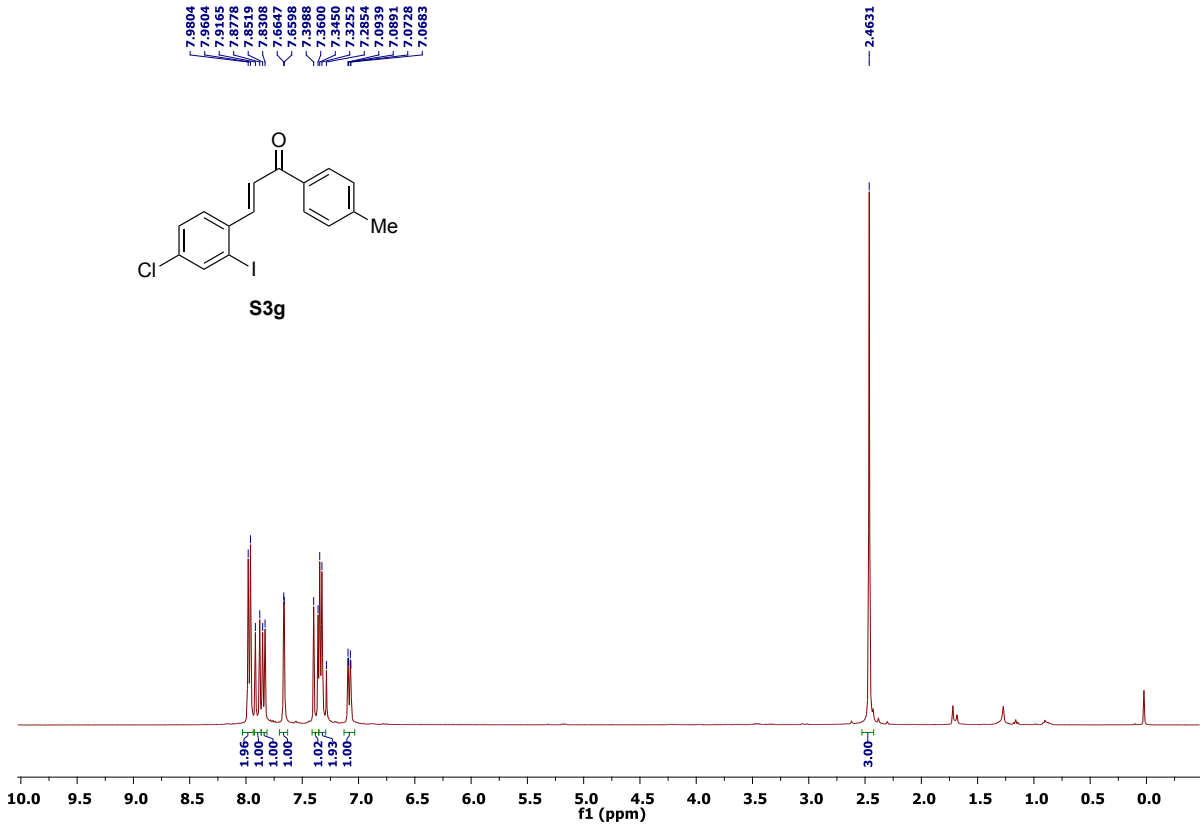
6. Optimization Table (Additional Entries)

Table S1. Optimization of the reaction conditions to access indene-fused indole **2a**

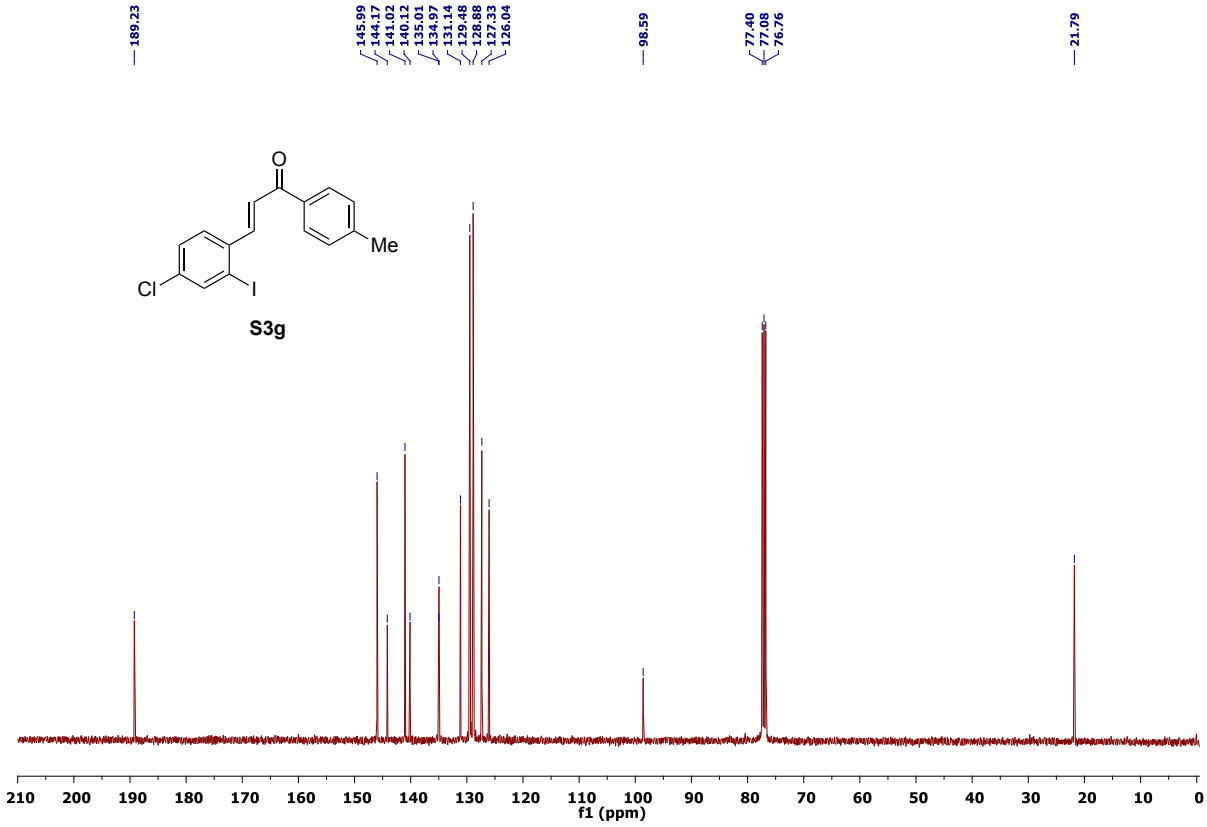
Entry	**Catalyst (10 mol%)**	**Solvent**	**Temp. (˚C)**	**Time (min)**	**Yield of 2a (%)[b]**	**Yield of 3a (%)[c]**
1	$PdCl_2$	THF	25	24 h	27	33
2	$PdCl_2$	Dioxane	25	36 h	39	32
3	$PdCl_2$	DCM	25	48 h	trace	41
4	$PdCl_2$	DCE	25	24 h	29	21
5	$PdCl_2$	Toluene	25	48 h	-	-
6	$PdCl_2$	DMSO	25	24 h	49	22
7	$PdCl_2$	MeCN	25	36 h	51	25

7. Copies of ^{1}H and ^{13}C NMR Spectra

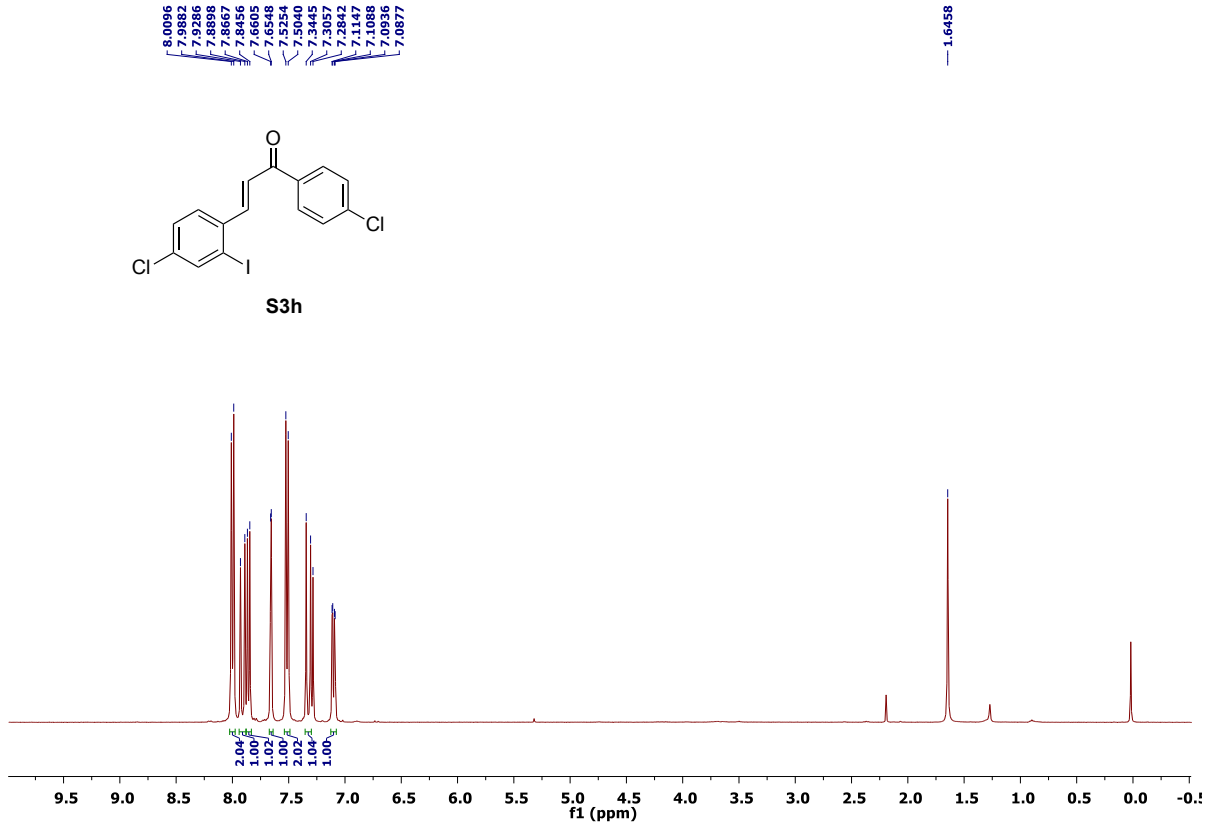
^{1}H NMR spectrum of compound **S3g** ($CDCl_3$, 400 MHz)



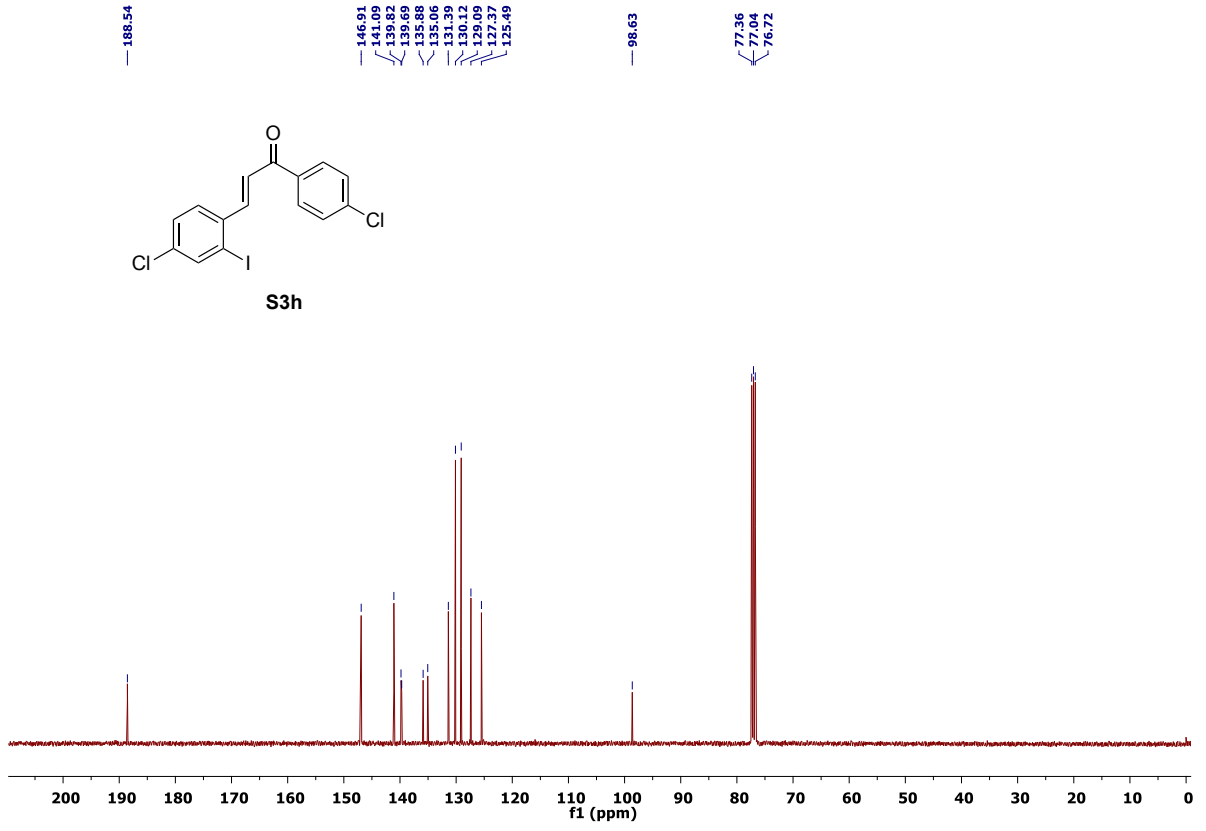
$^{13}C\{^{1}H\}$ NMR spectrum of compound **S3g** ($CDCl_3$, 101 MHz)



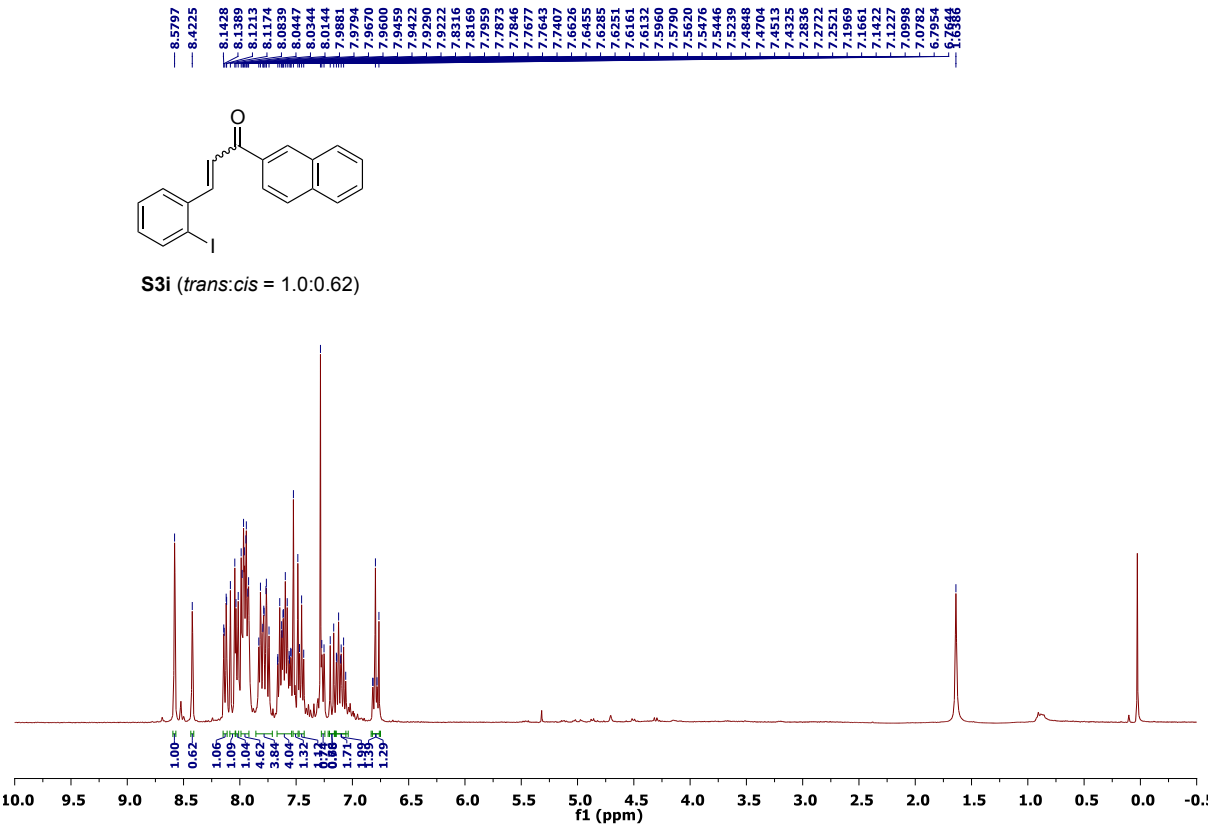
^{1}H NMR spectrum of compound **S3h** ($CDCl_3$, 400 MHz)



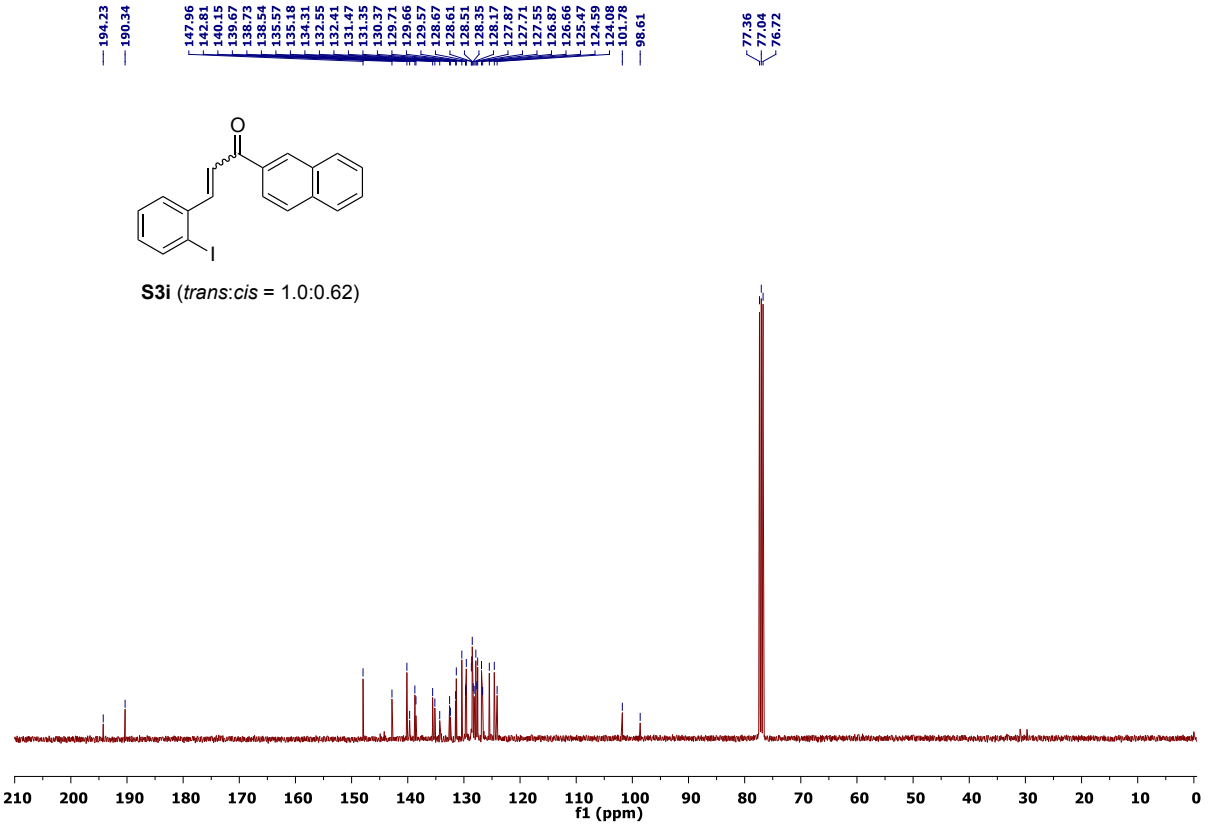
^{13}C{^{1}H} NMR spectrum of compound **S3h** ($CDCl_3$, 101 MHz)



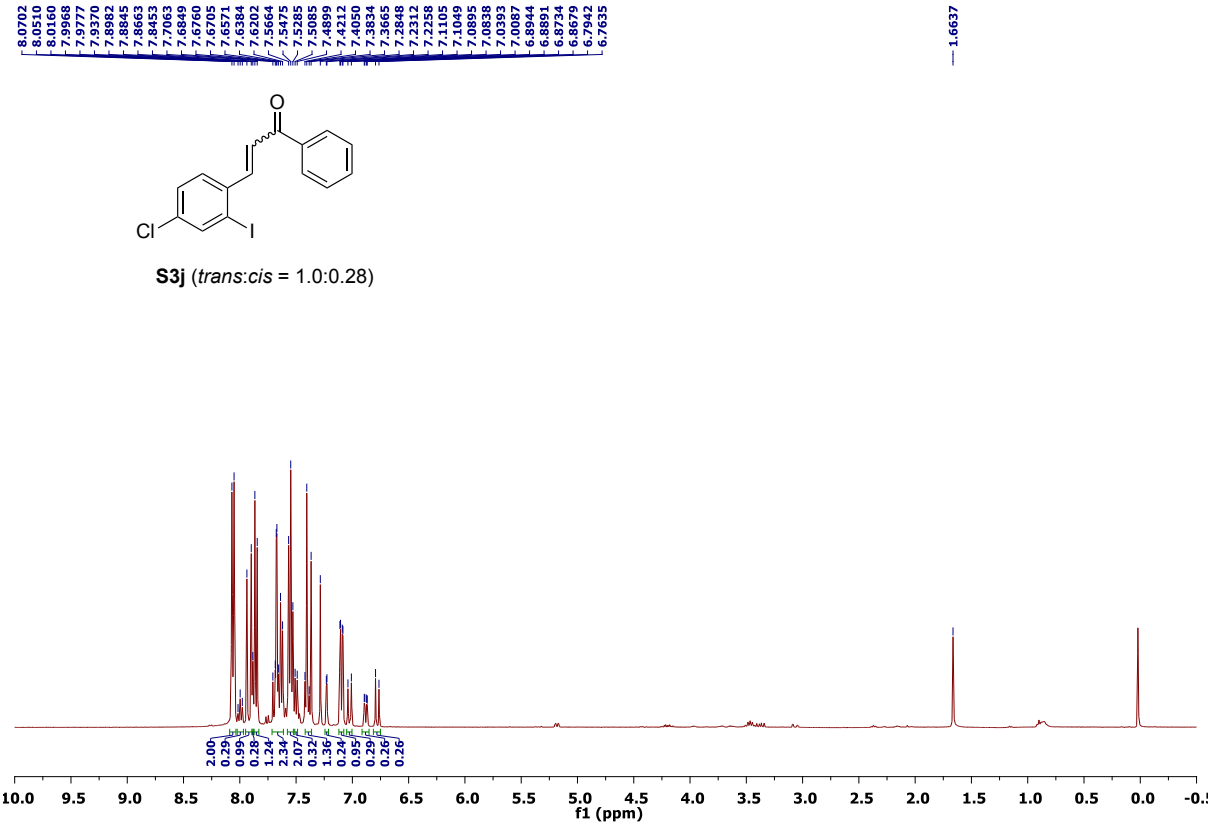
^{1}H NMR spectrum of compound **S3i** ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR spectrum of compound **S3i** ($CDCl_3$, 101 MHz)

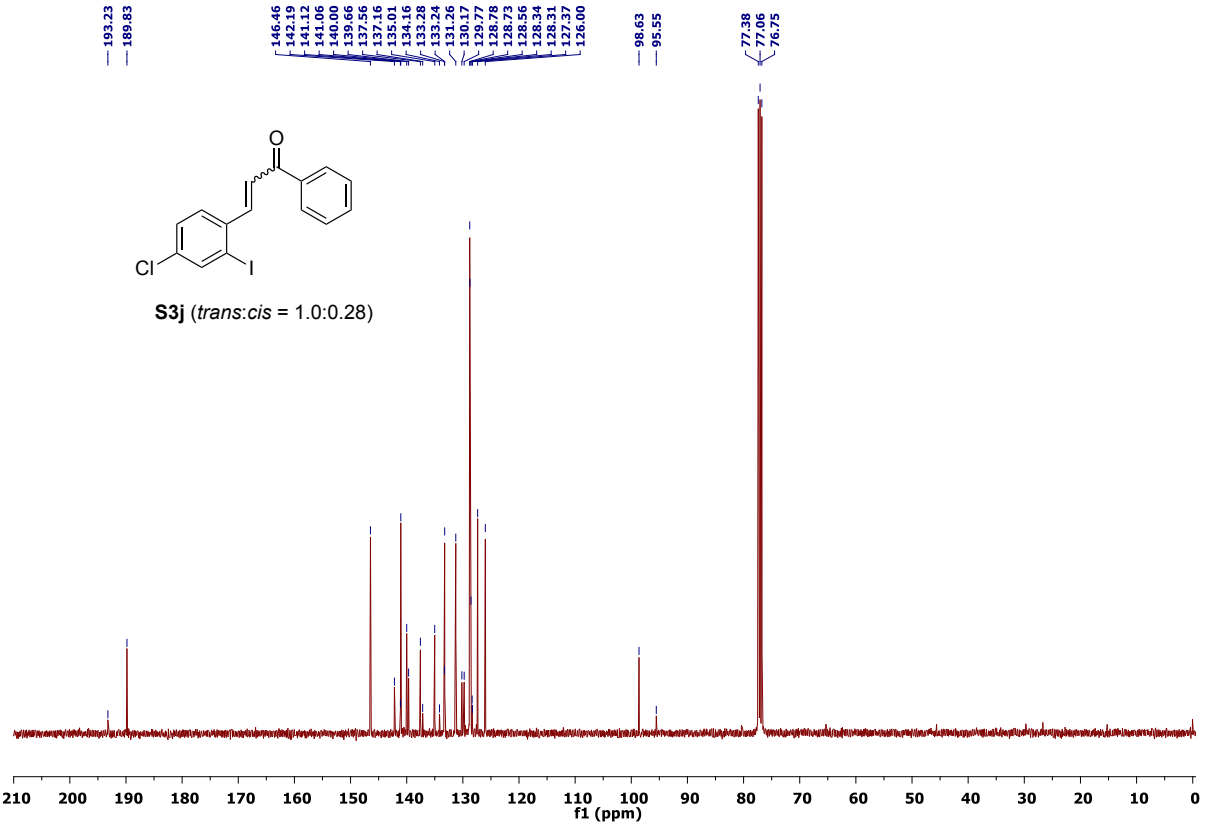


^{1}H NMR spectrum of compound **S3j** ($CDCl_3$, 400 MHz)



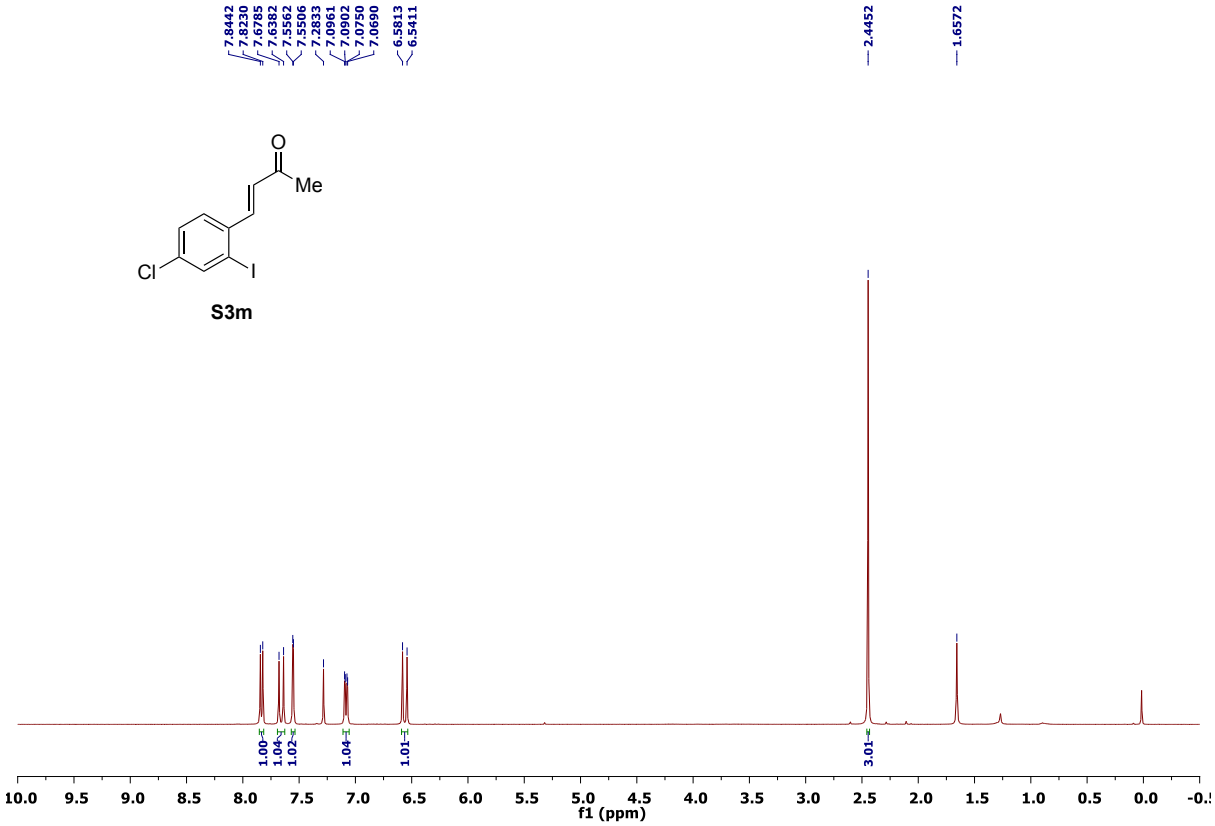
S3j (*trans*:*cis* = 1.0:0.28)

^{13}C{^{1}H} NMR spectrum of compound **S3j** ($CDCl_3$, 101 MHz)

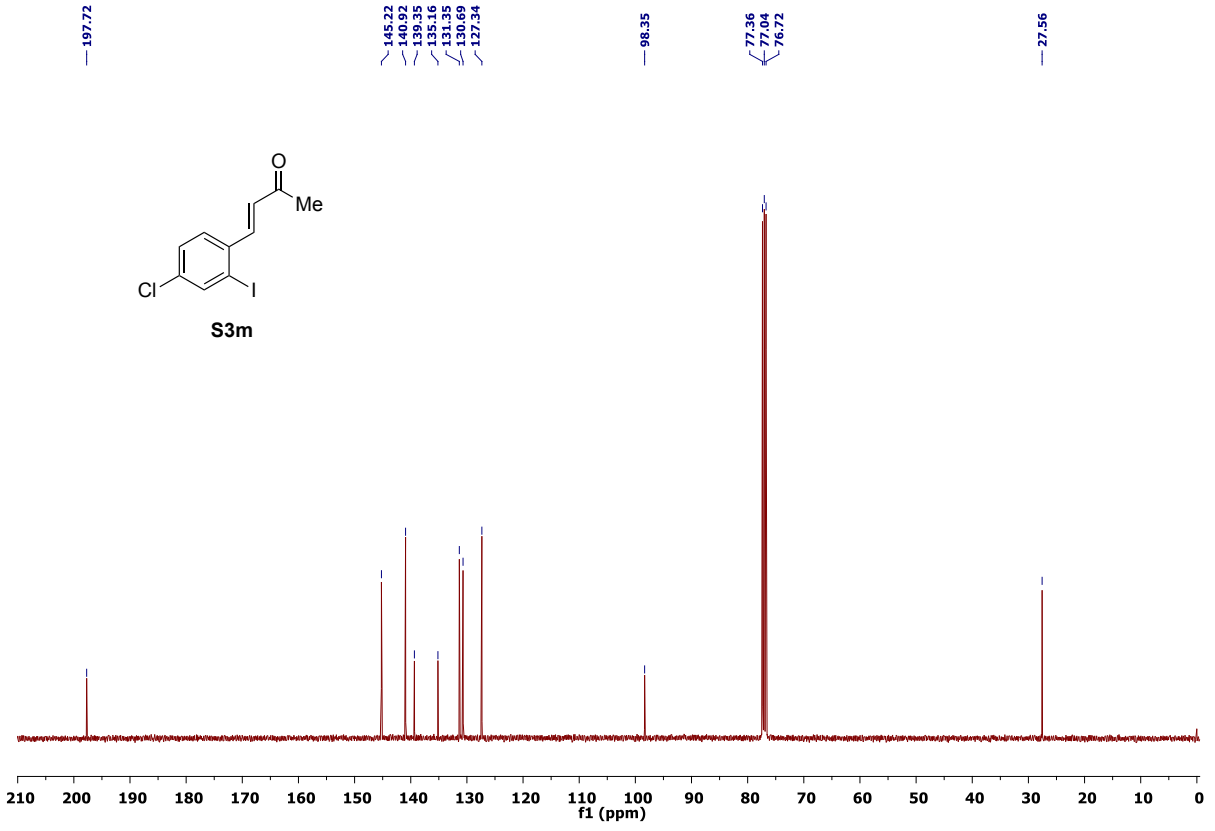


S3j (*trans*:*cis* = 1.0:0.28)

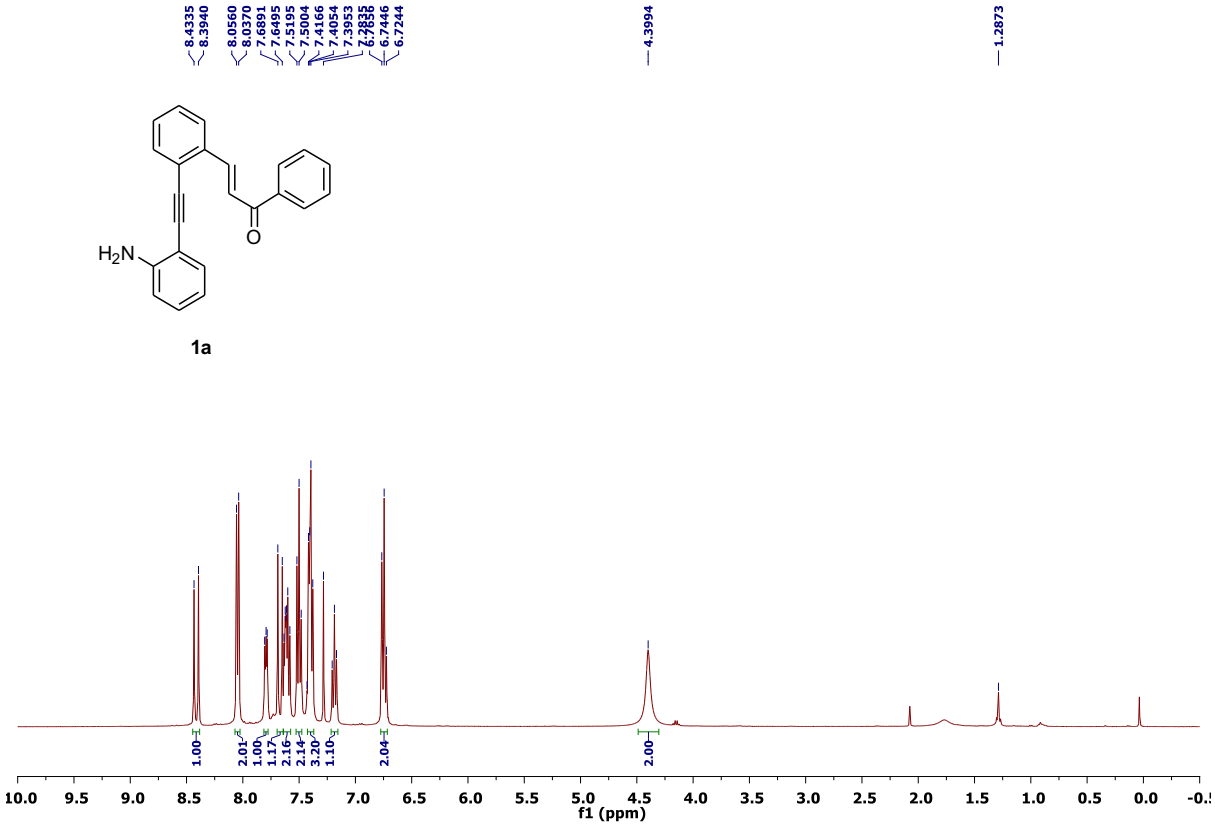
^{1}H NMR spectrum of compound **S3m** ($CDCl_3$, 400 MHz)



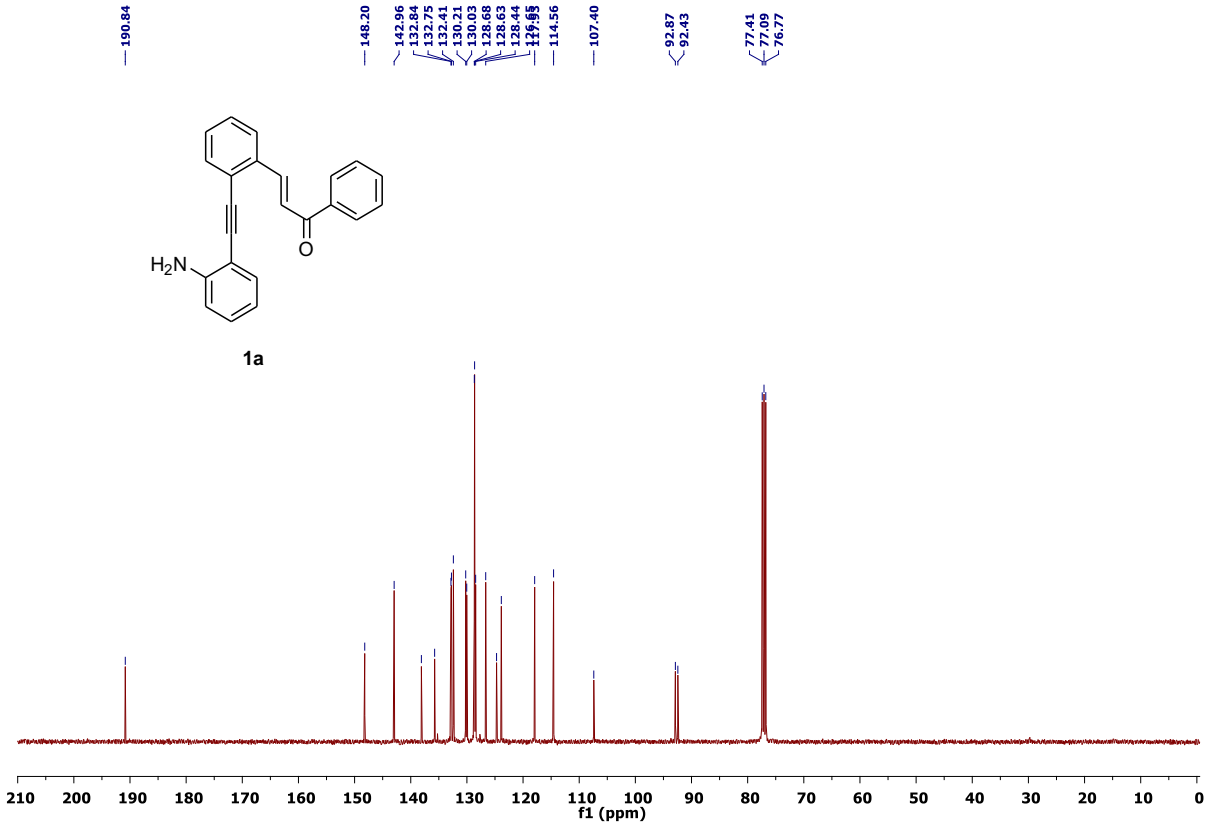
^{13}C{^{1}H} NMR spectrum of compound **S3m** ($CDCl_3$, 101 MHz)



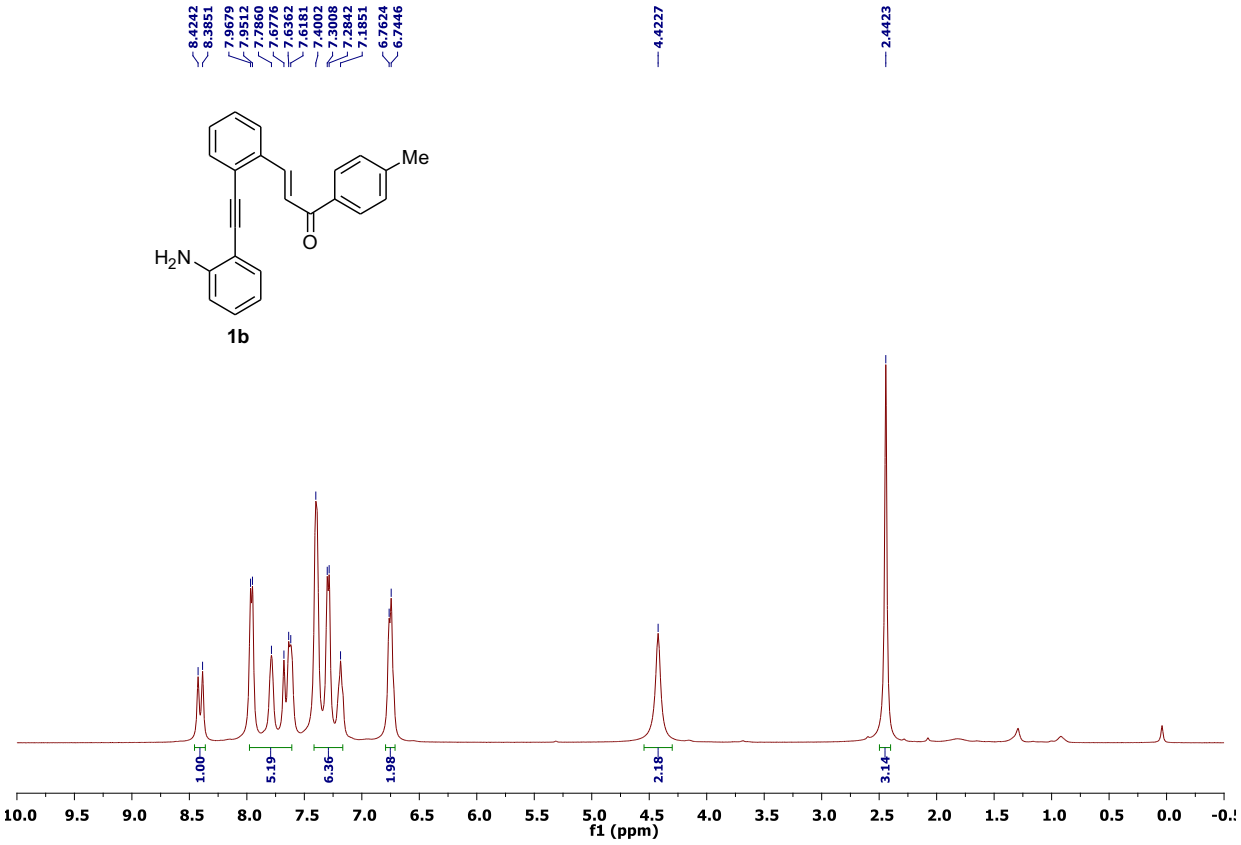
^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400 MHz)



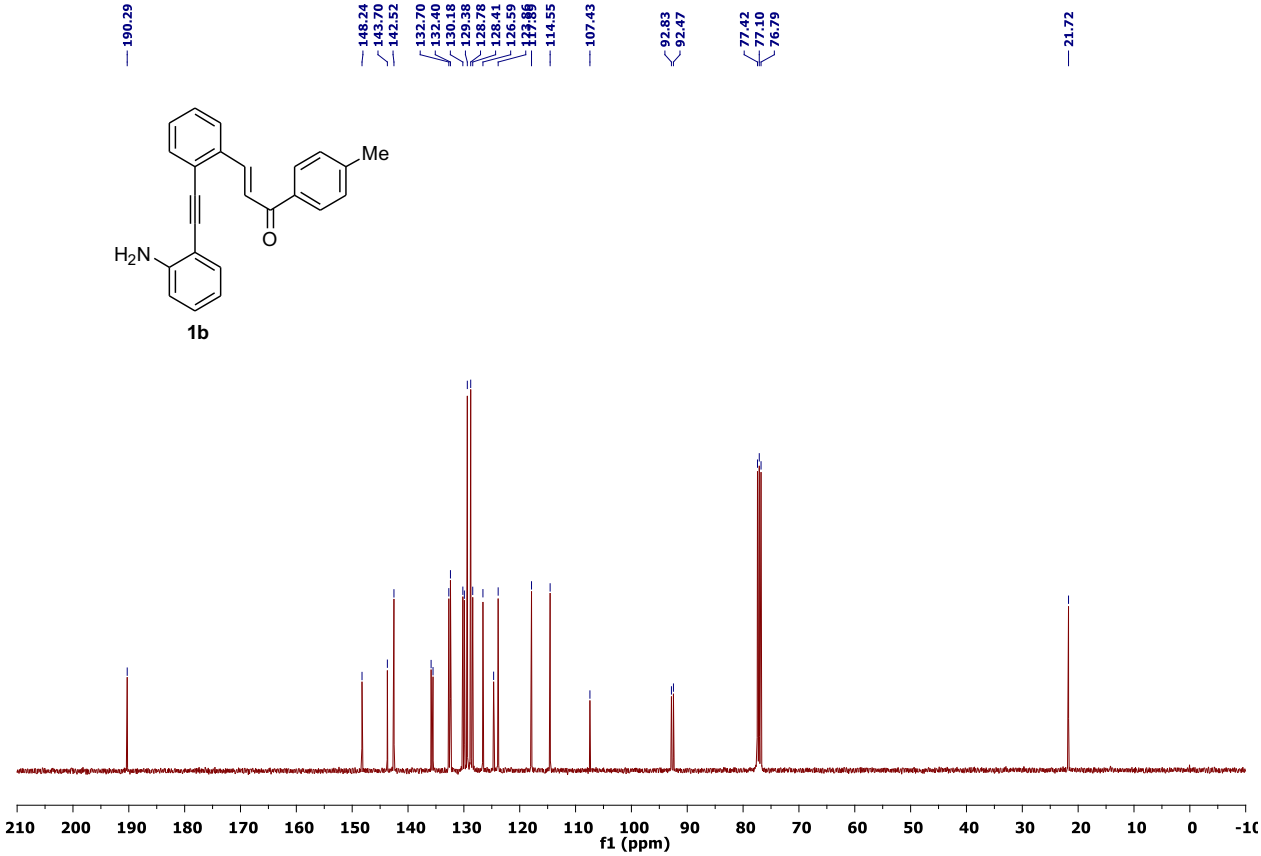
^{13}C{^{1}H} NMR spectrum of compound **1a** ($CDCl_3$, 101 MHz)



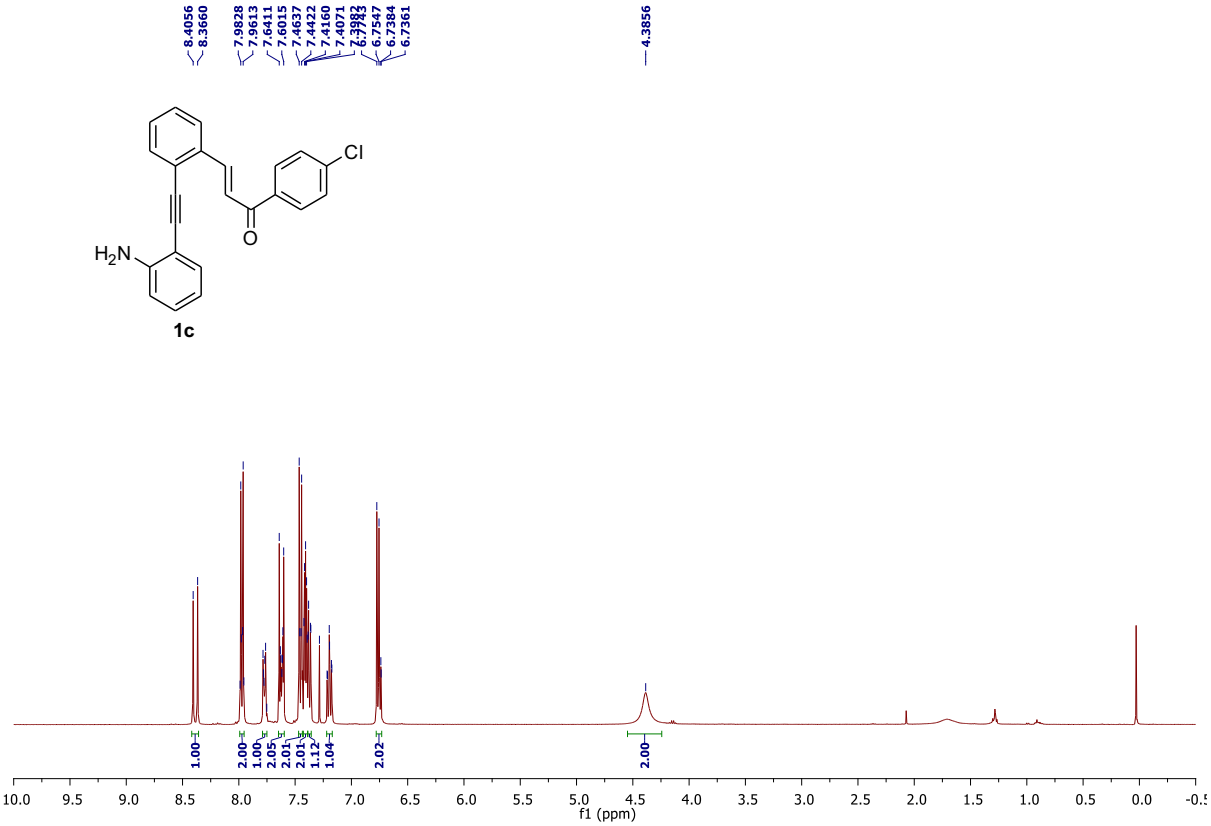
^{1}H NMR spectrum of compound **1b** ($CDCl_3$, 400 MHz)



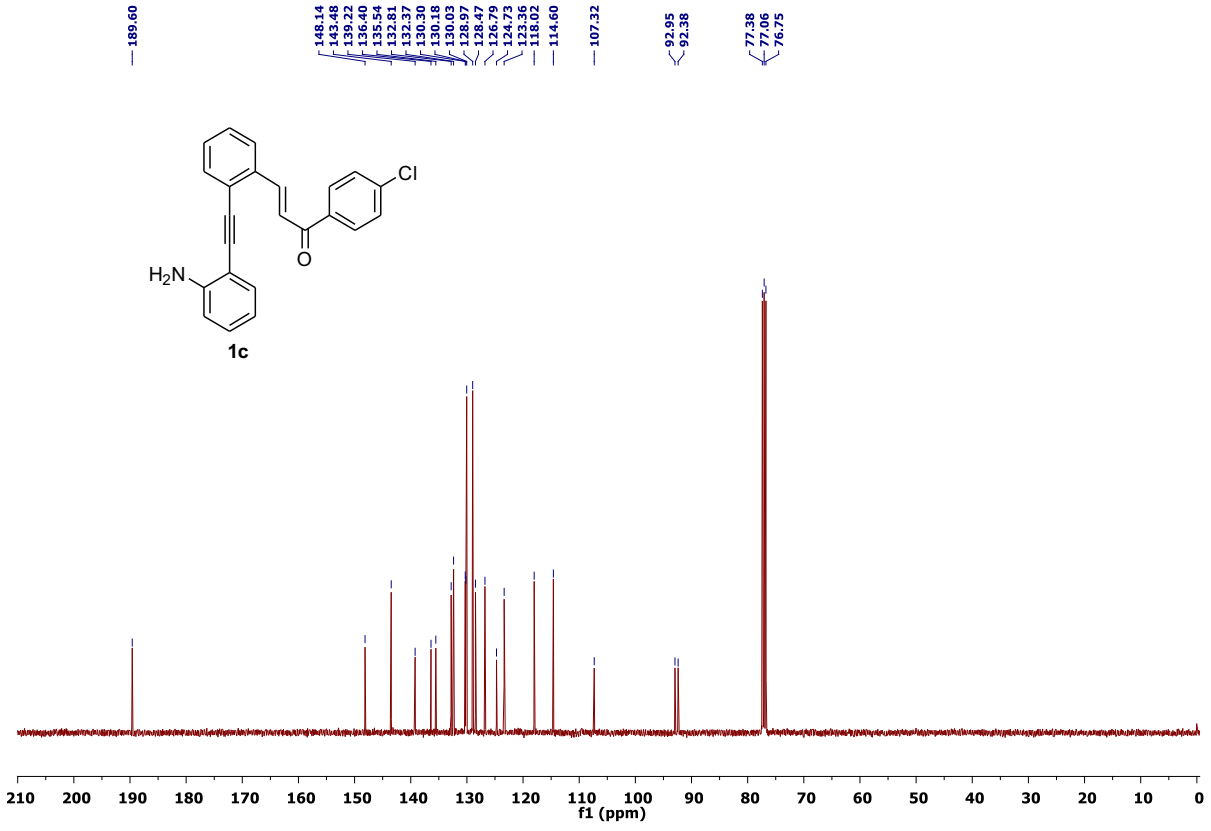
^{13}C{^{1}H} NMR spectrum of compound **1b** ($CDCl_3$, 101 MHz)



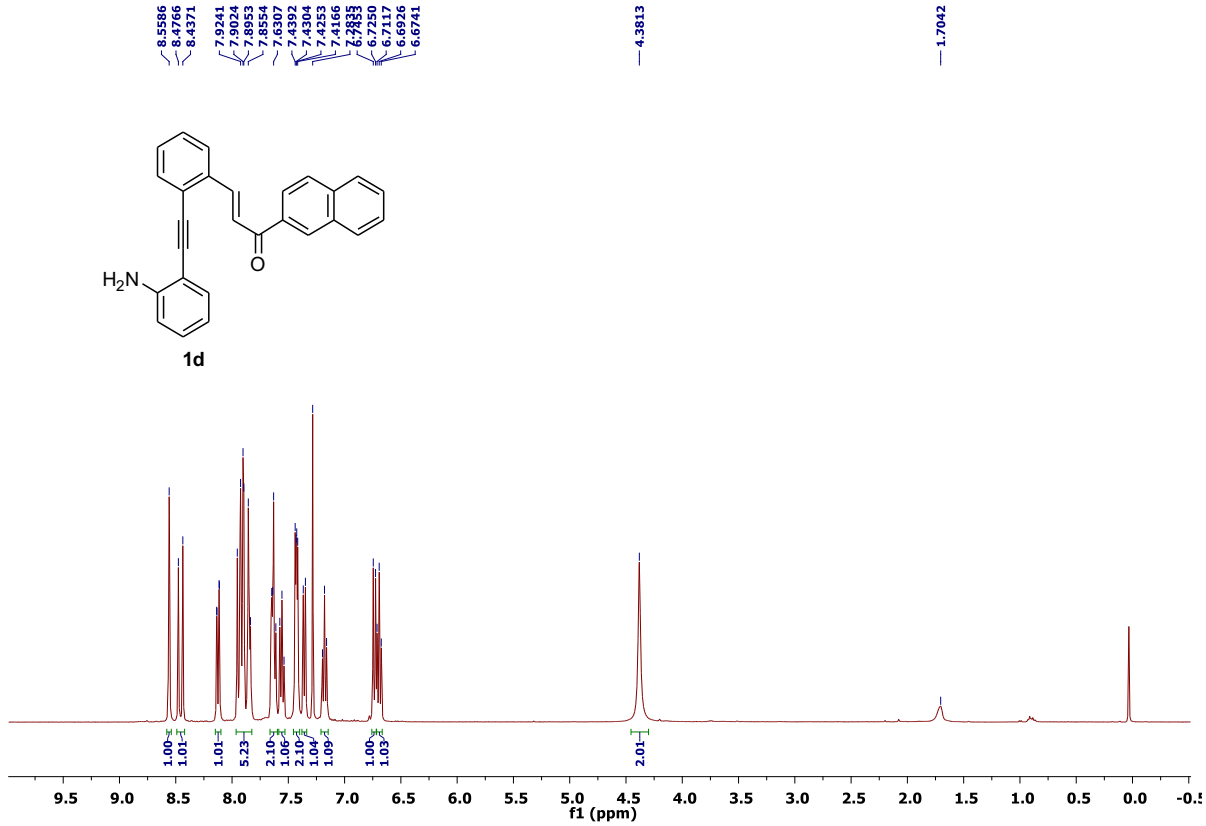
^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 400 MHz)



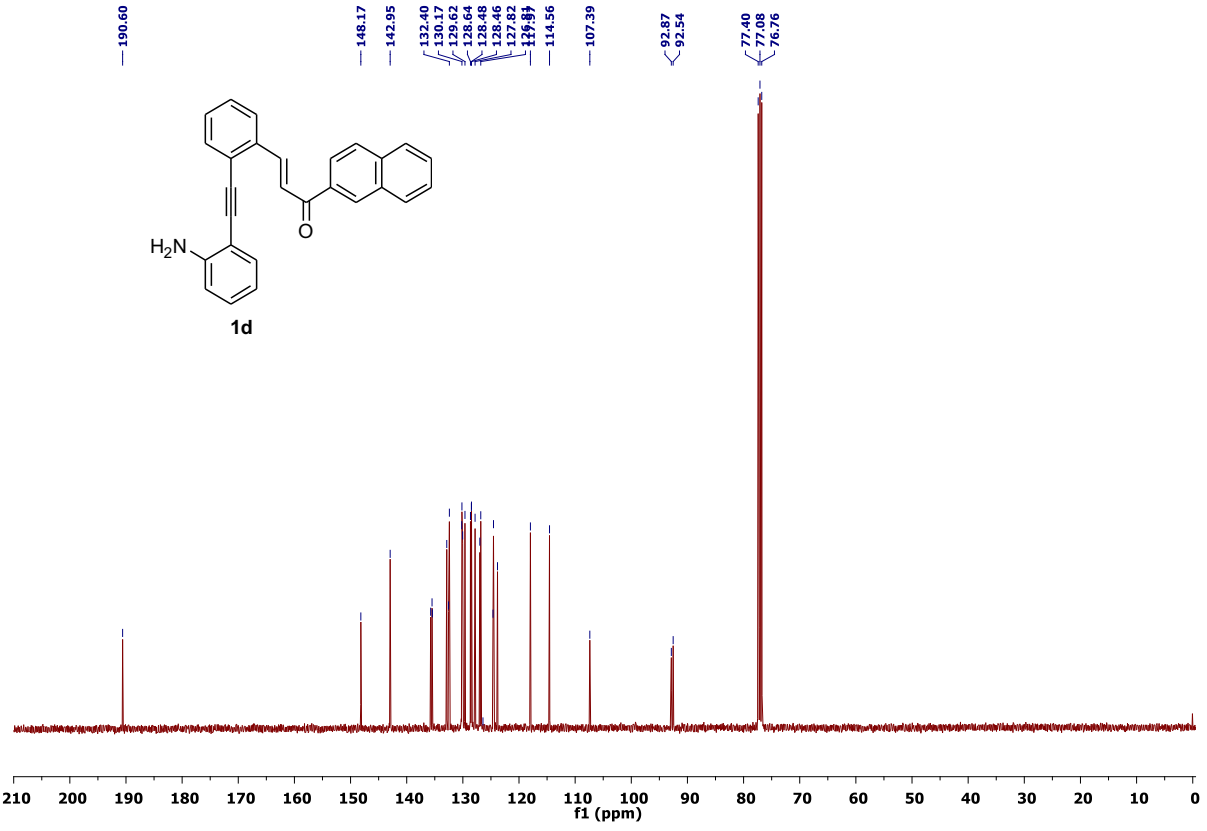
^{13}C{^{1}H} NMR spectrum of compound **1c** ($CDCl_3$, 101 MHz)



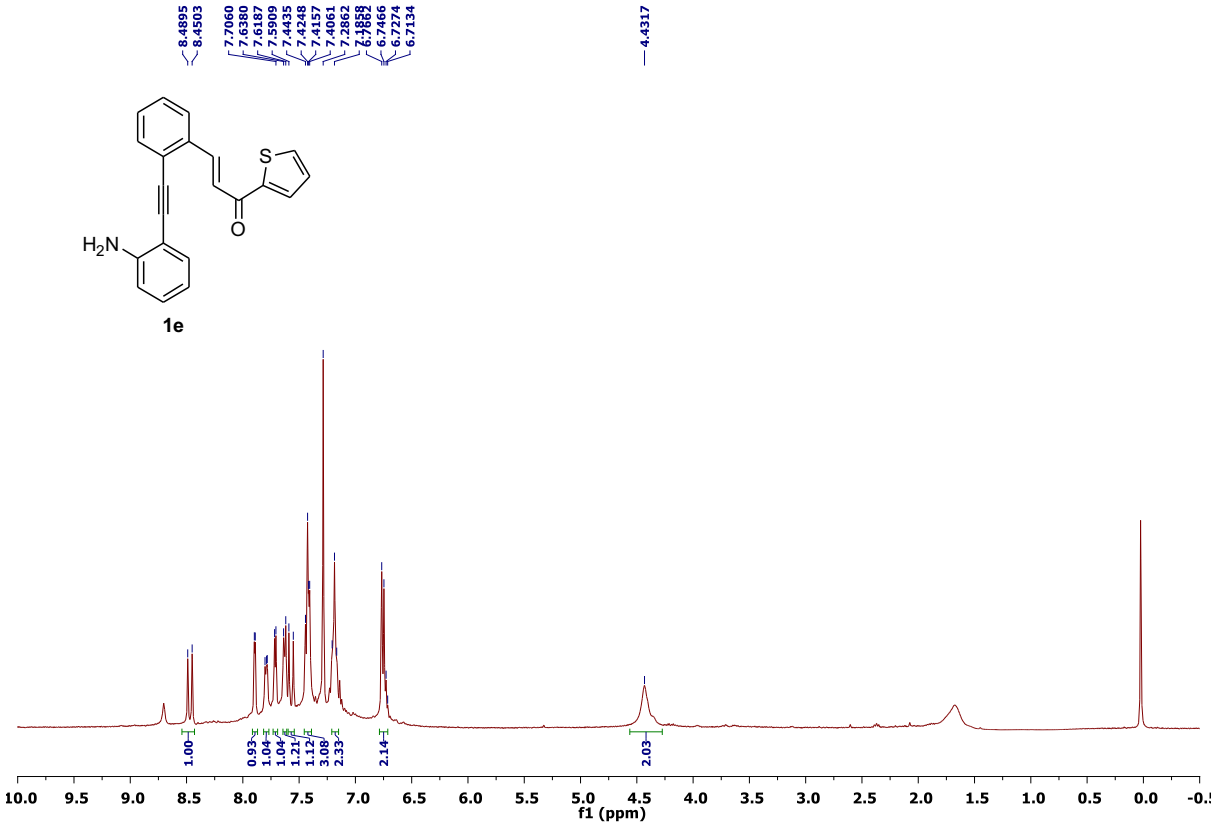
^{1}H NMR spectrum of compound **1d** ($CDCl_3$, 400 MHz)



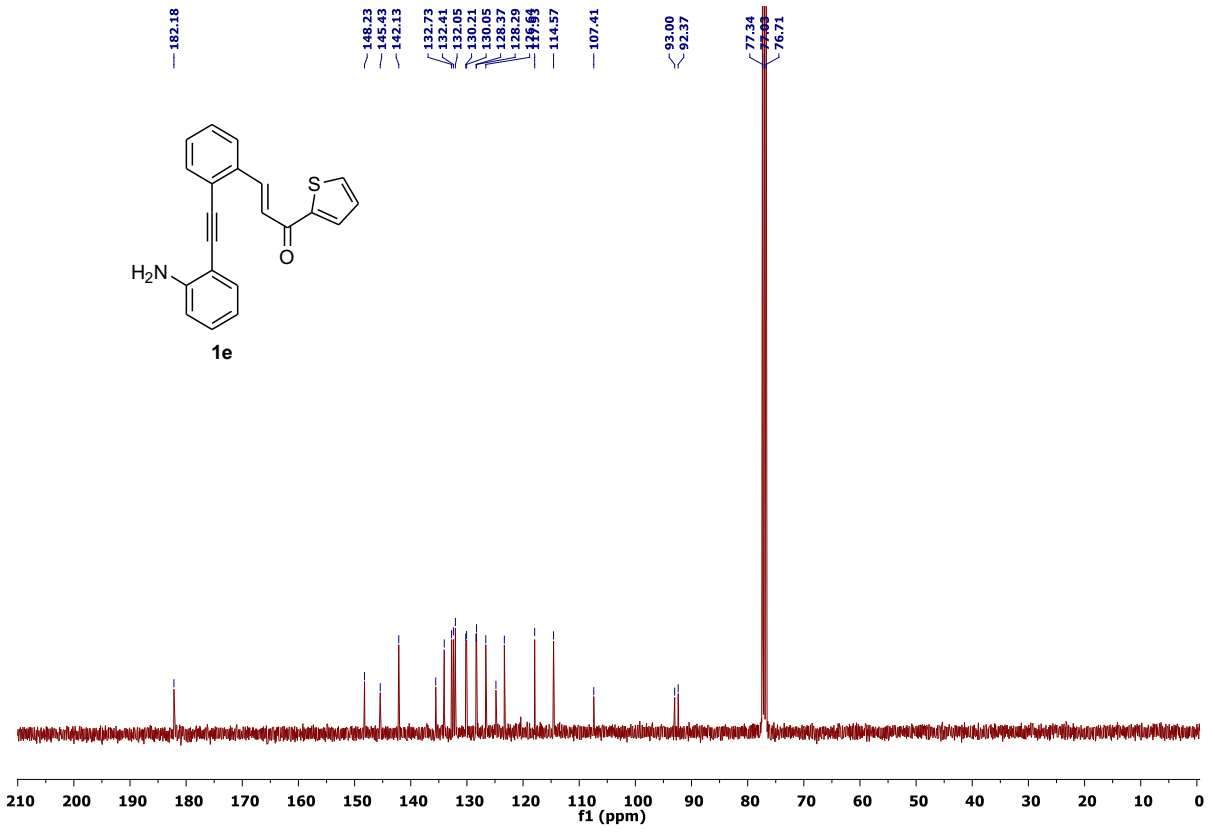
^{13}C{^{1}H} NMR spectrum of compound **1d** ($CDCl_3$, 101 MHz)



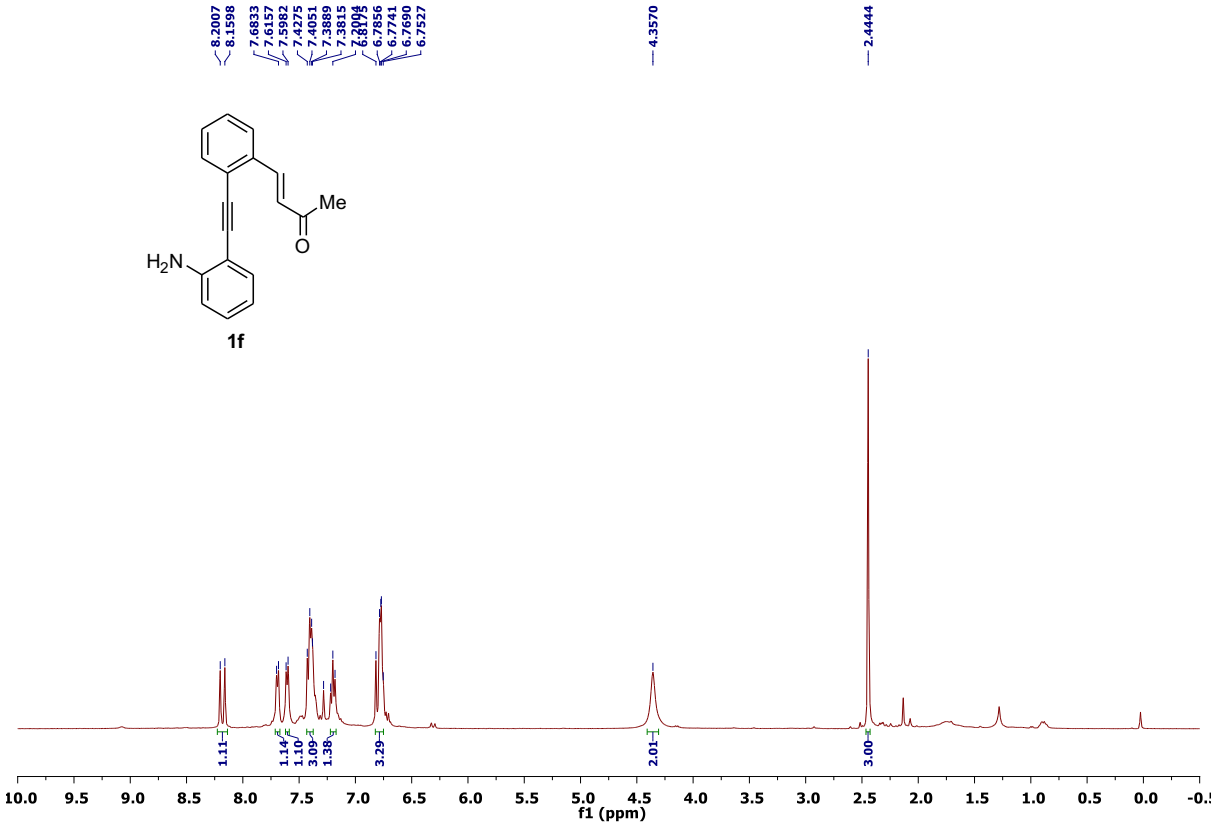
^{1}H NMR spectrum of compound **1e** ($CDCl_3$, 400 MHz)



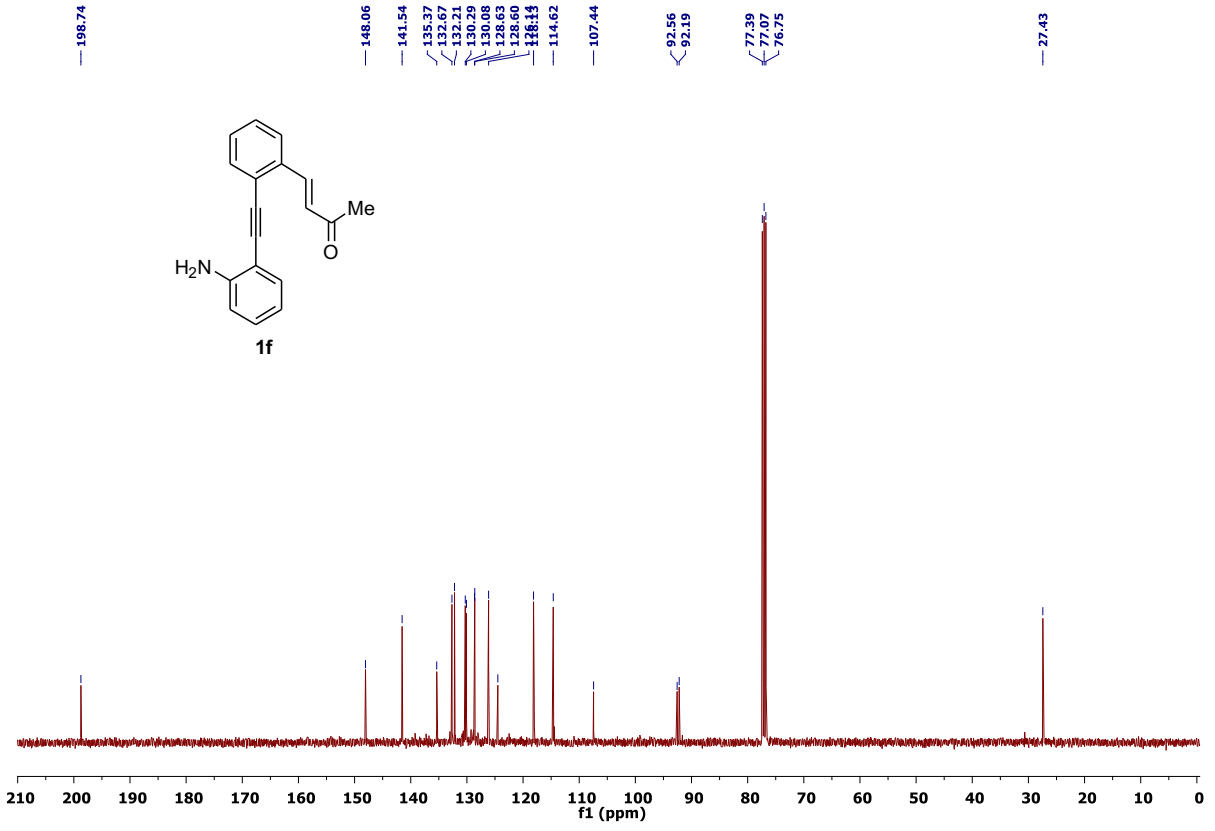
^{13}C{^{1}H} NMR spectrum of compound **1e** ($CDCl_3$, 101 MHz)



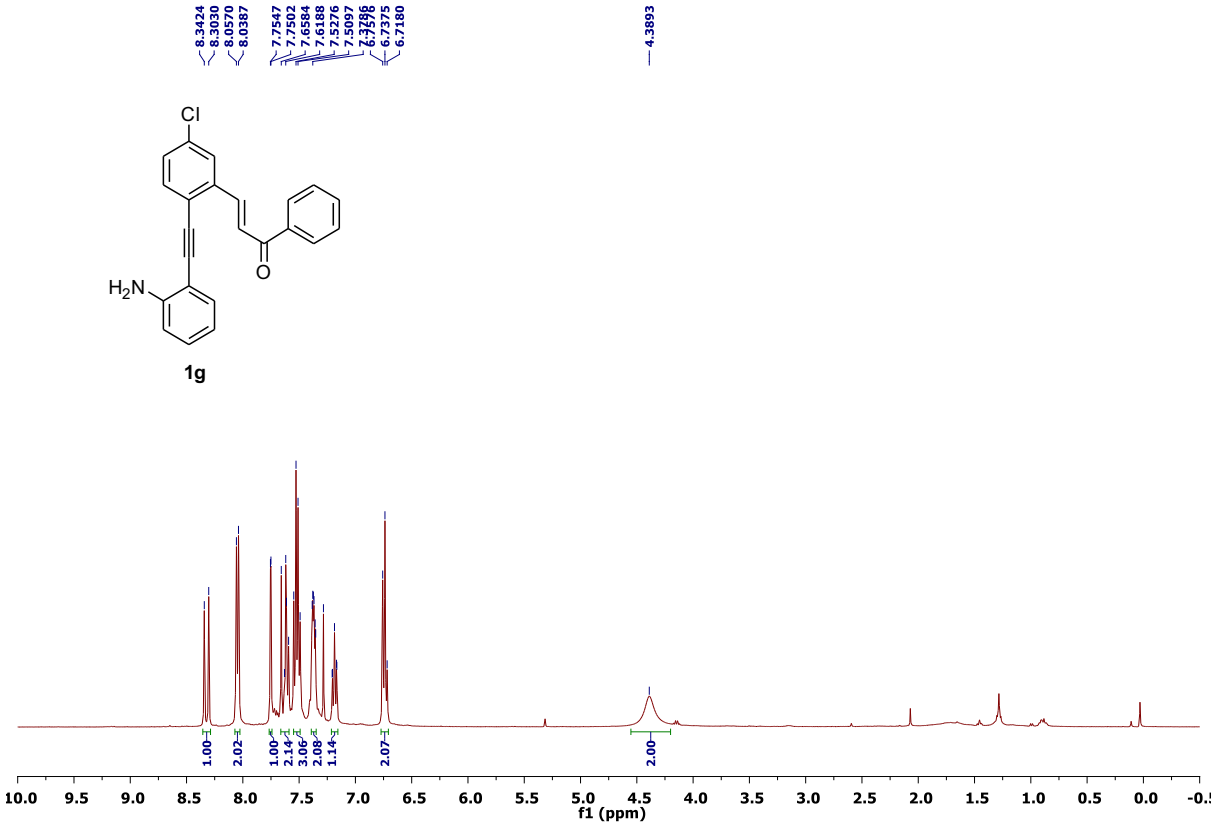
^{1}H NMR spectrum of compound **1f** ($CDCl_3$, 400 MHz)



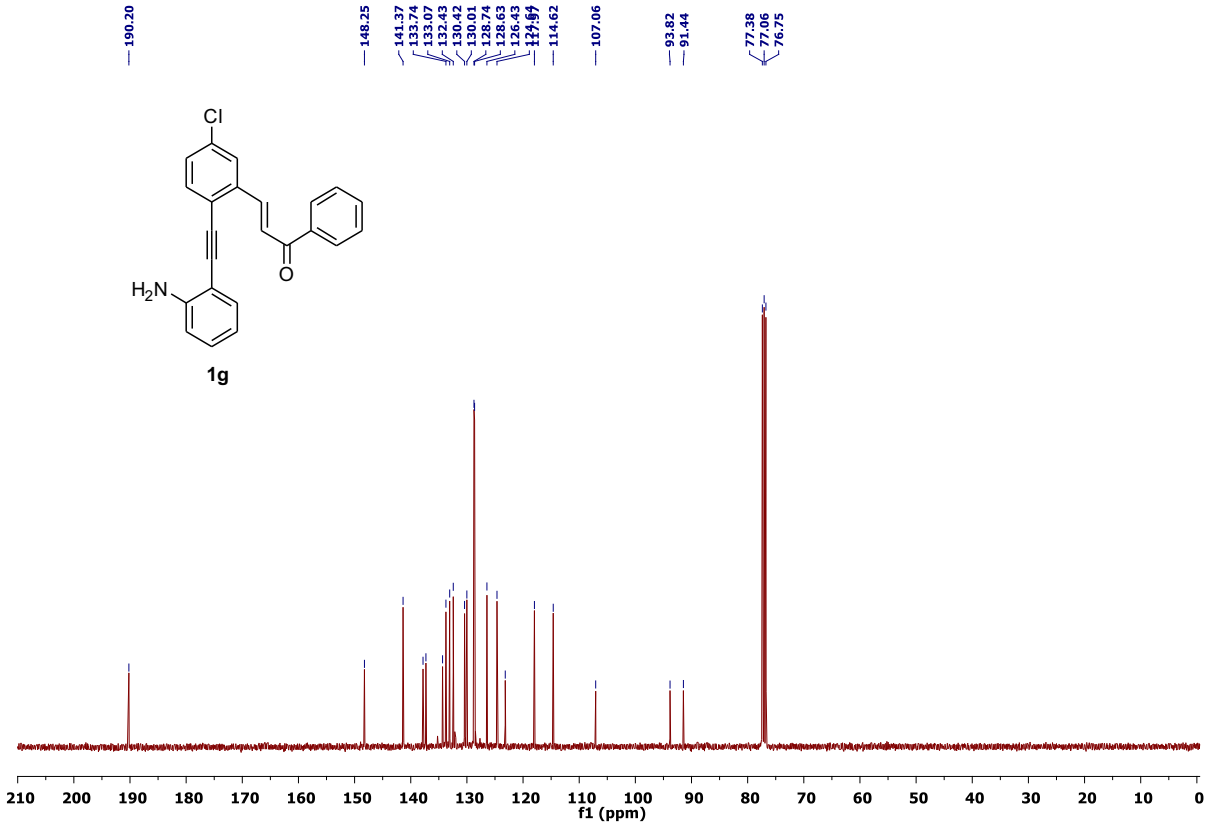
^{13}C{^{1}H} NMR spectrum of compound **1f** ($CDCl_3$, 101 MHz)



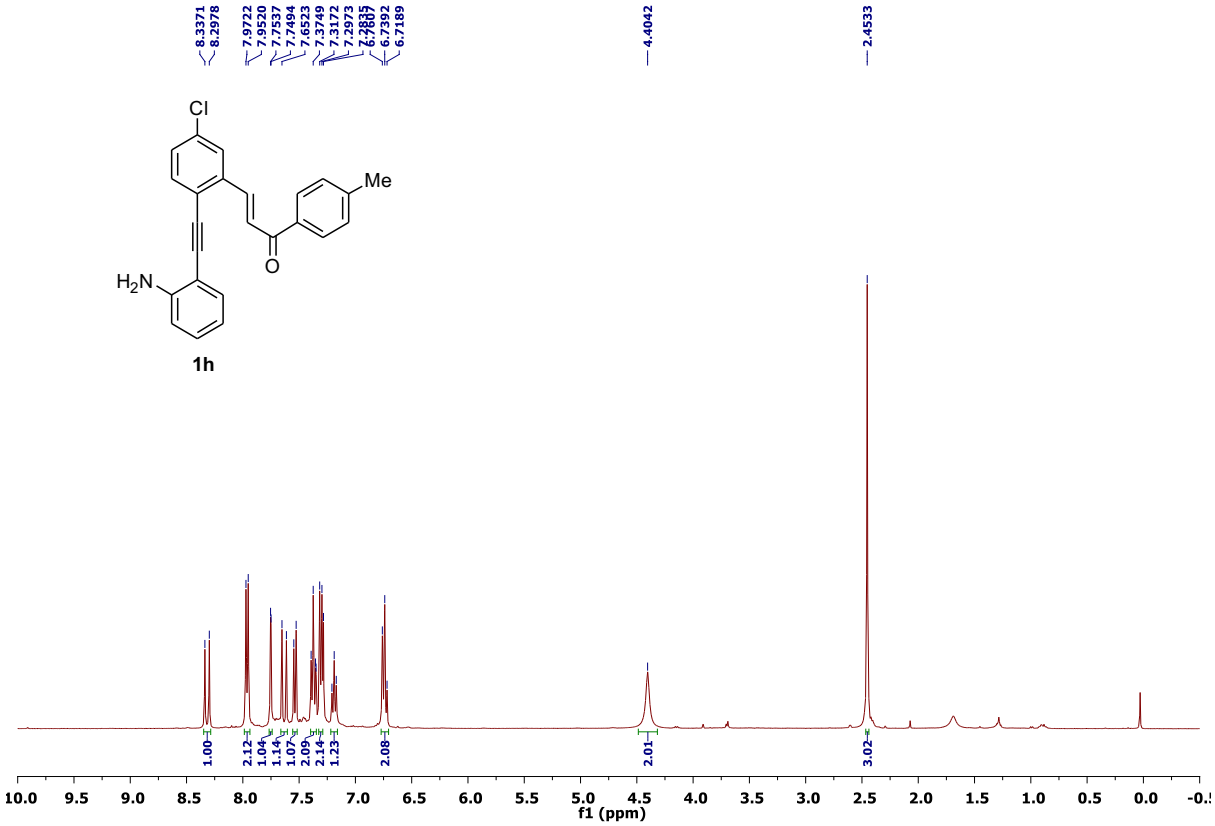
^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz)



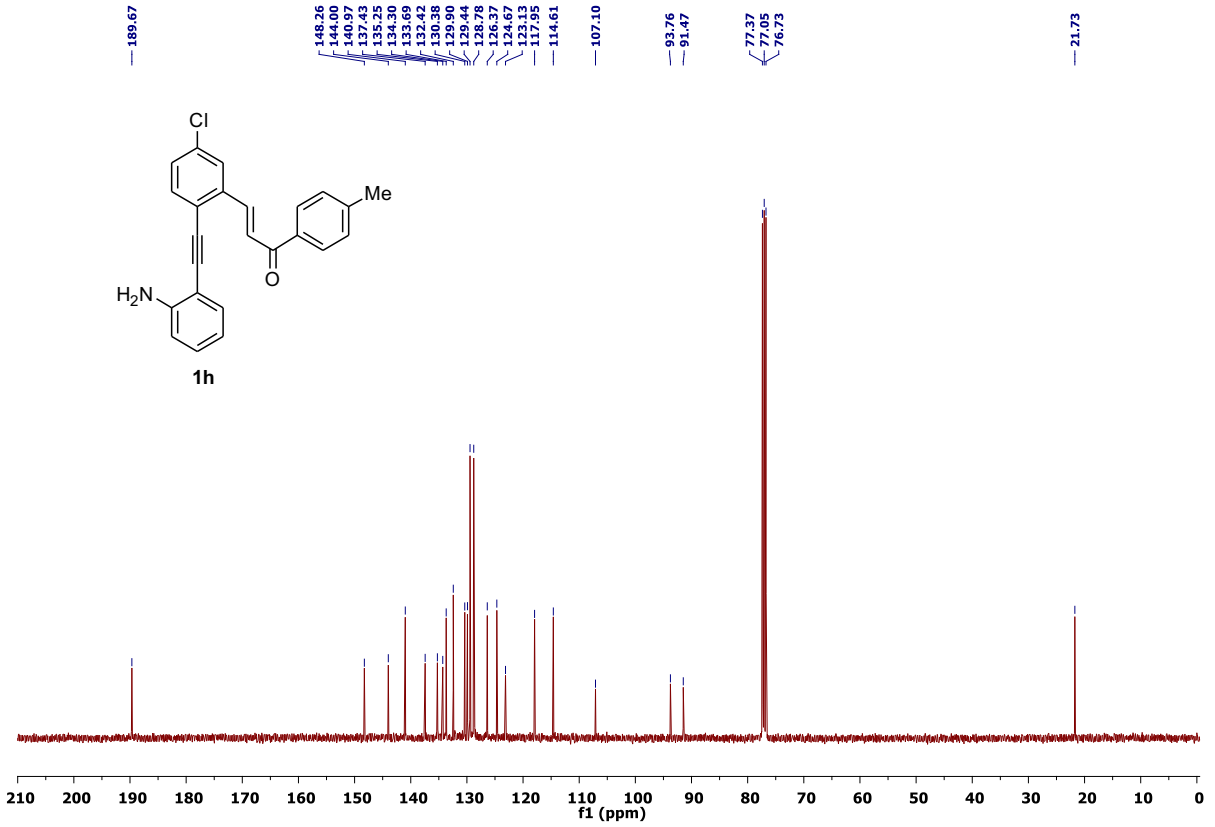
^{13}C{^{1}H} NMR spectrum of compound **1g** ($CDCl_3$, 101 MHz)



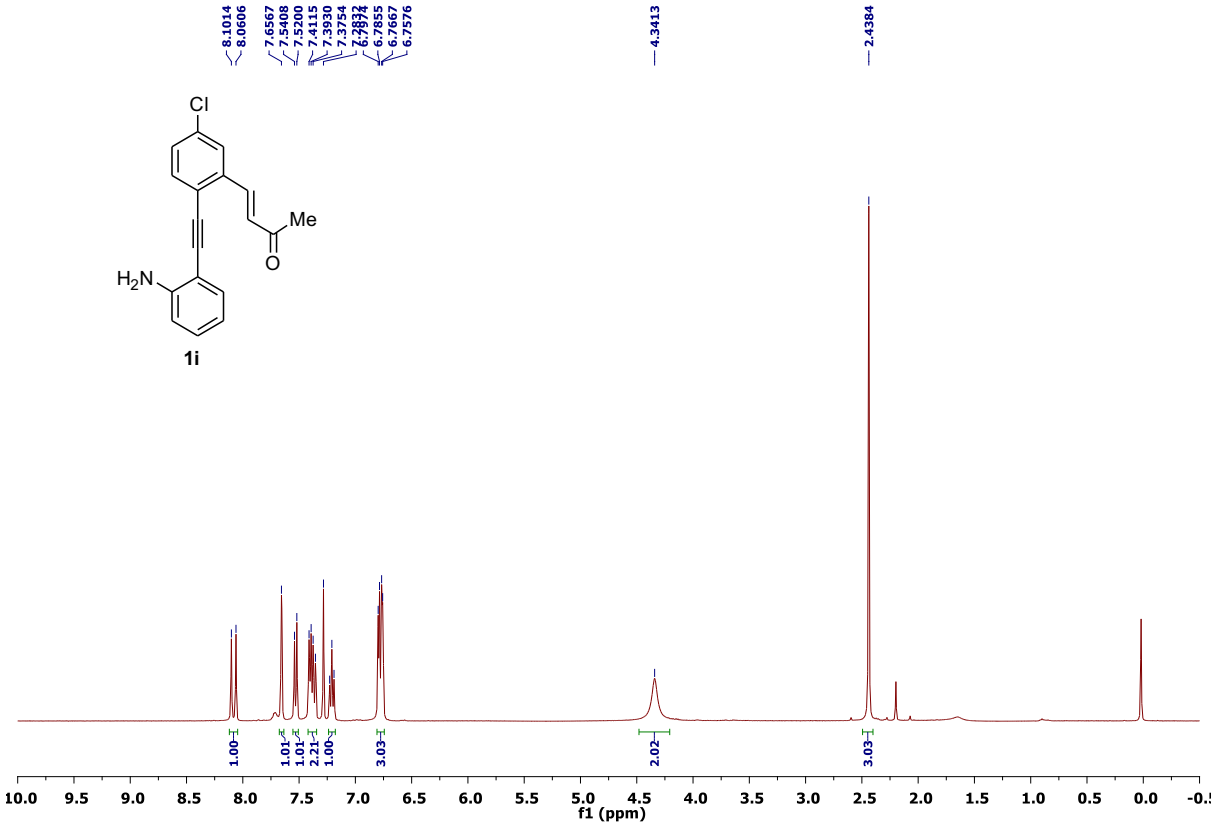
^{1}H NMR spectrum of compound **1h** ($CDCl_3$, 400 MHz)



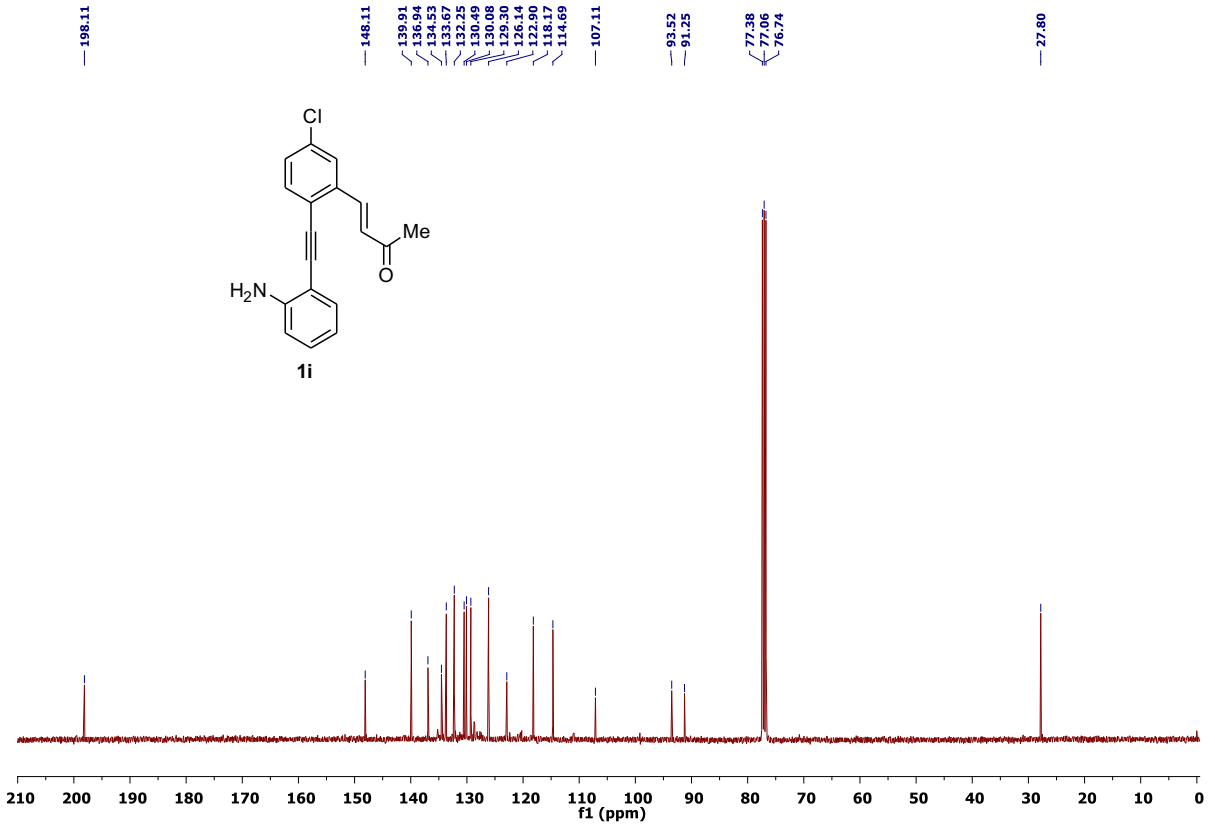
^{13}C{^{1}H} NMR spectrum of compound **1h** ($CDCl_3$, 101 MHz)



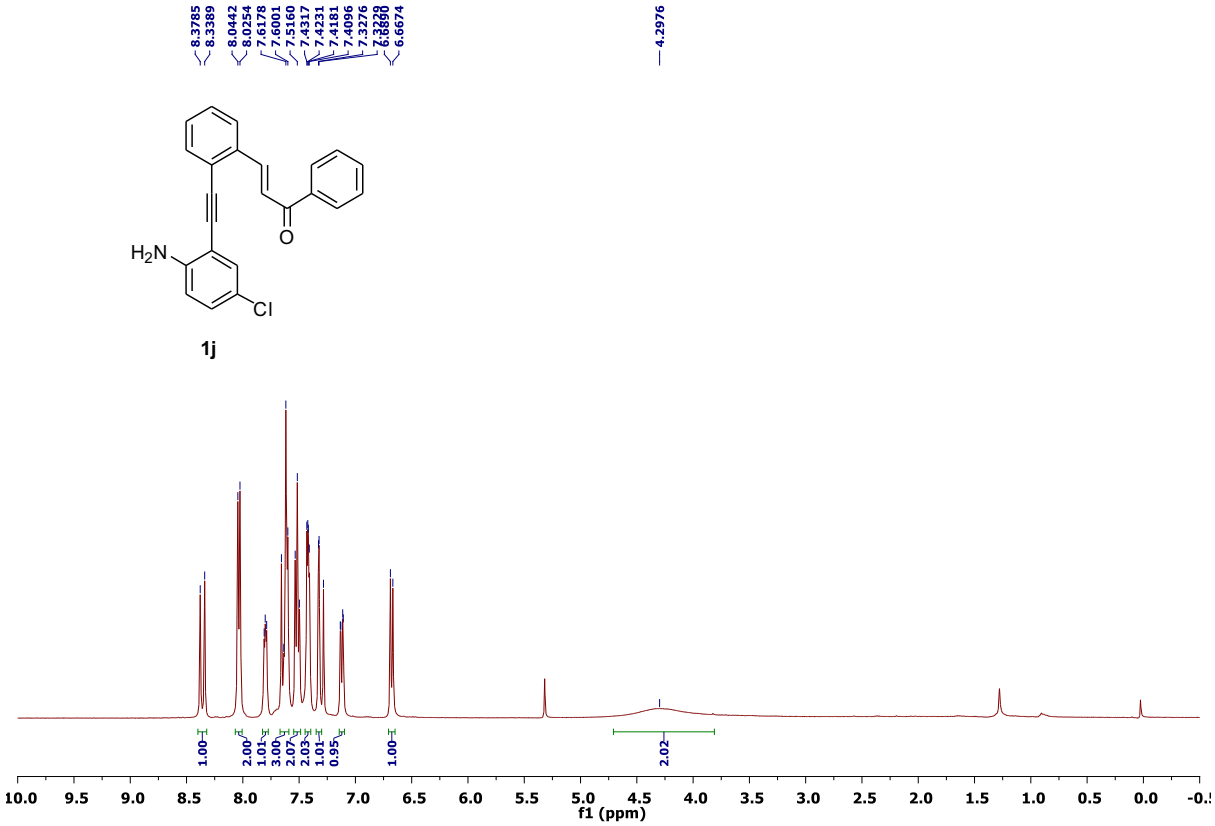
^{1}H NMR spectrum of compound **1i** ($CDCl_3$, 400 MHz)



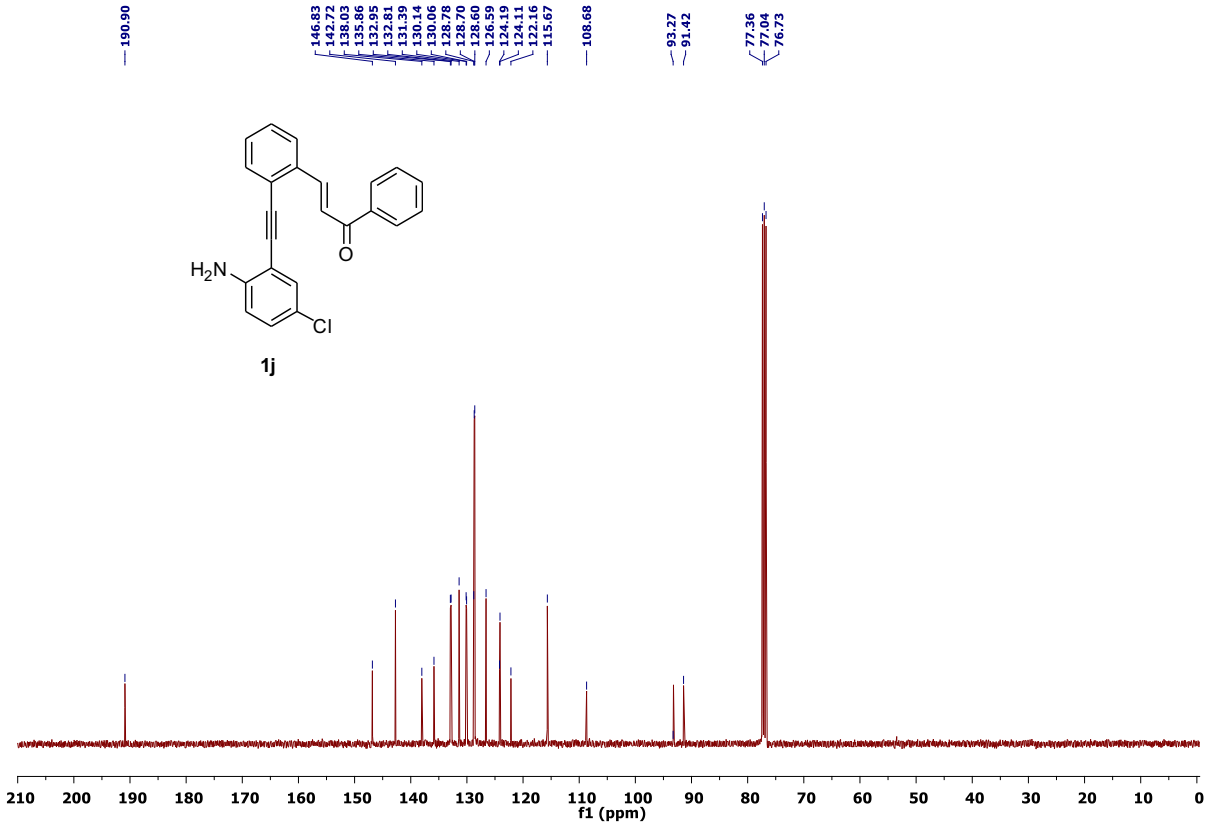
^{13}C{^{1}H} NMR spectrum of compound **1i** ($CDCl_3$, 101 MHz)



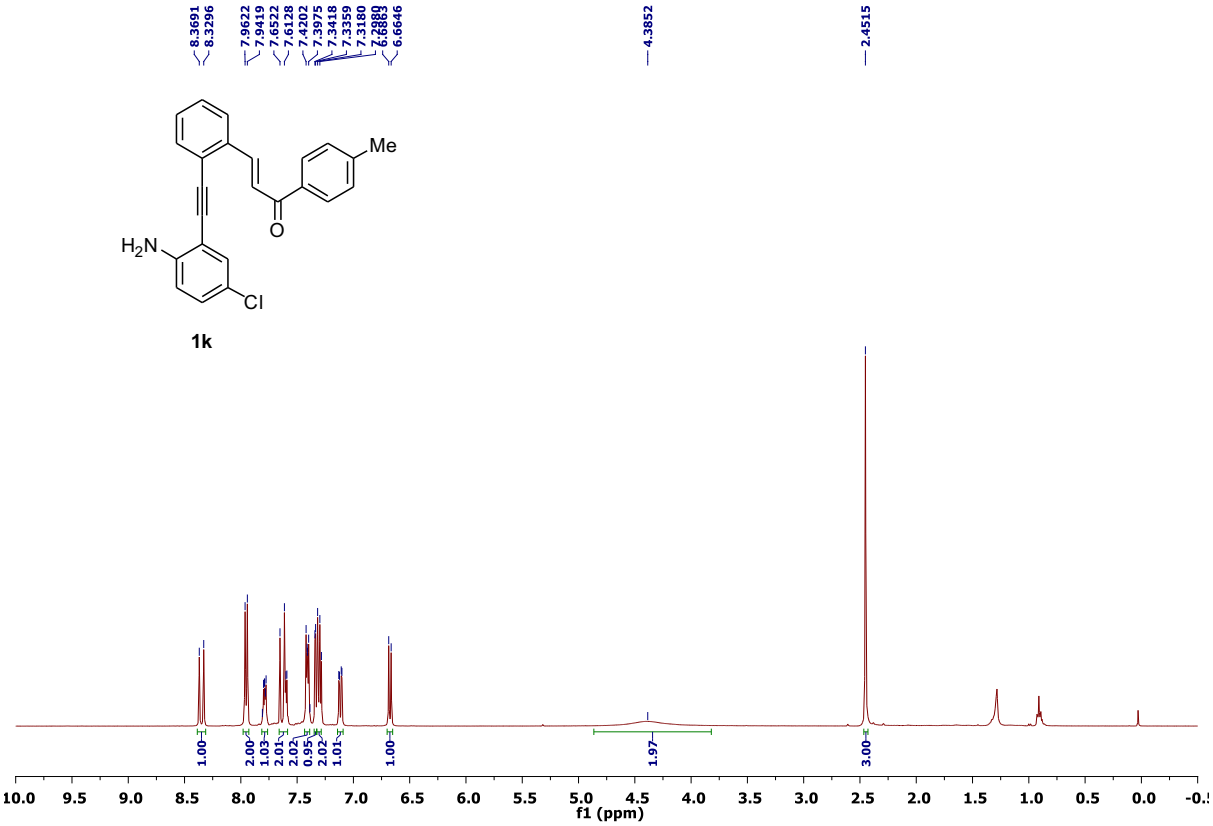
^{1}H NMR spectrum of compound **1j** ($CDCl_3$, 400 MHz)



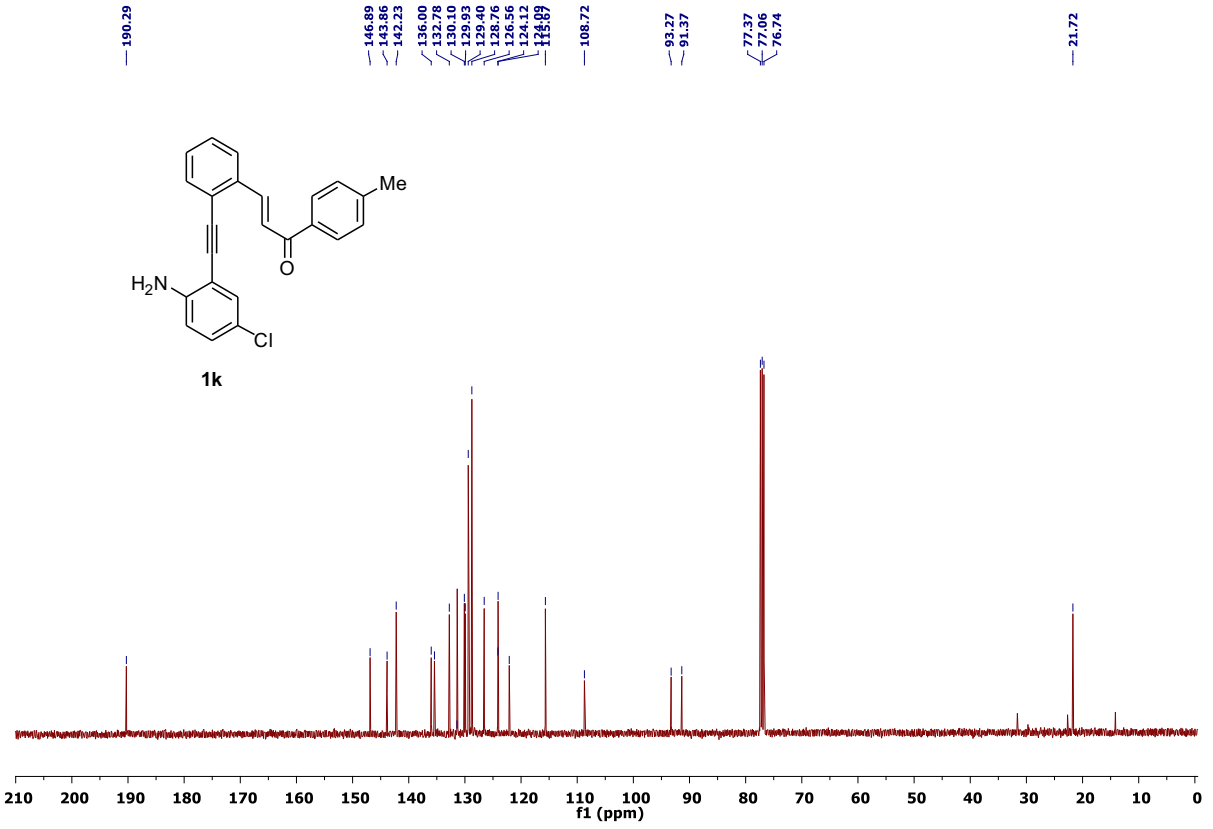
^{13}C{^{1}H} NMR spectrum of compound **1j** ($CDCl_3$, 101 MHz)



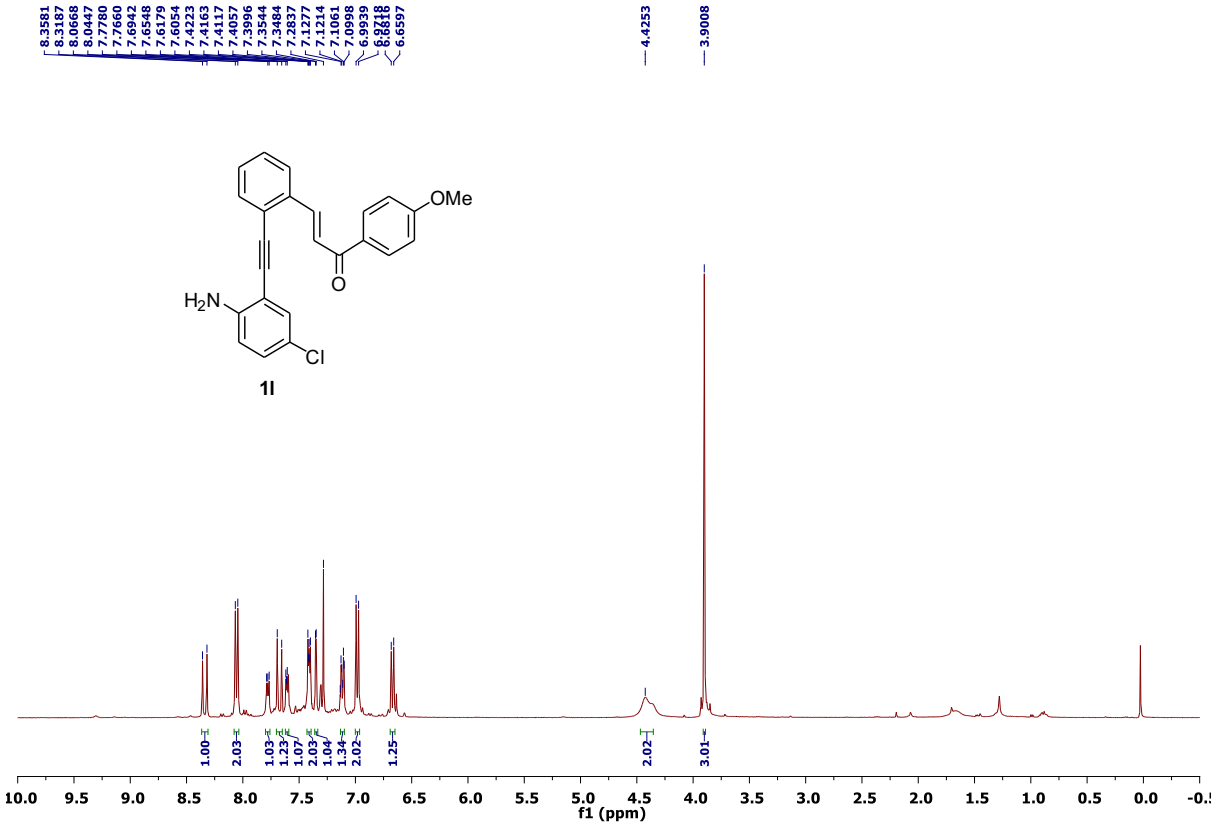
^{1}H NMR spectrum of compound **1k** ($CDCl_3$, 400 MHz)



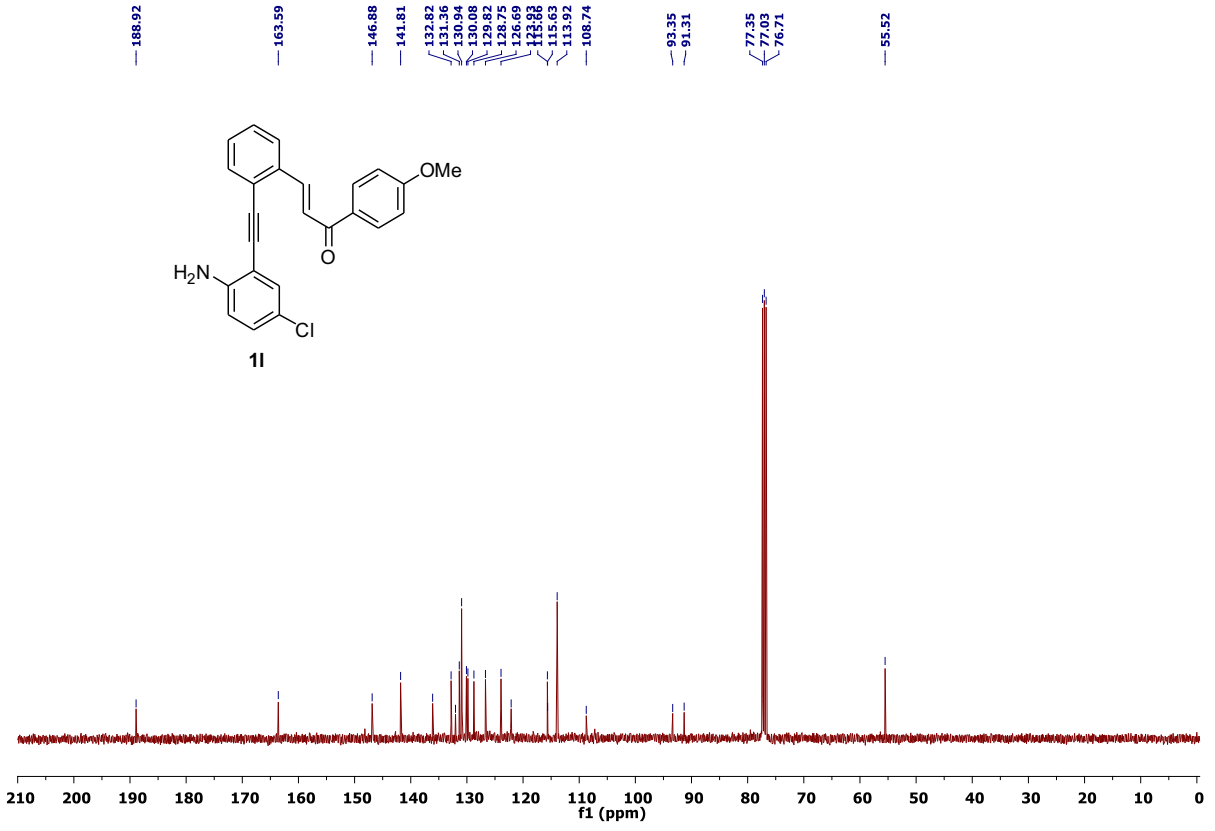
^{13}C{^{1}H} NMR spectrum of compound **1k** ($CDCl_3$, 101 MHz)



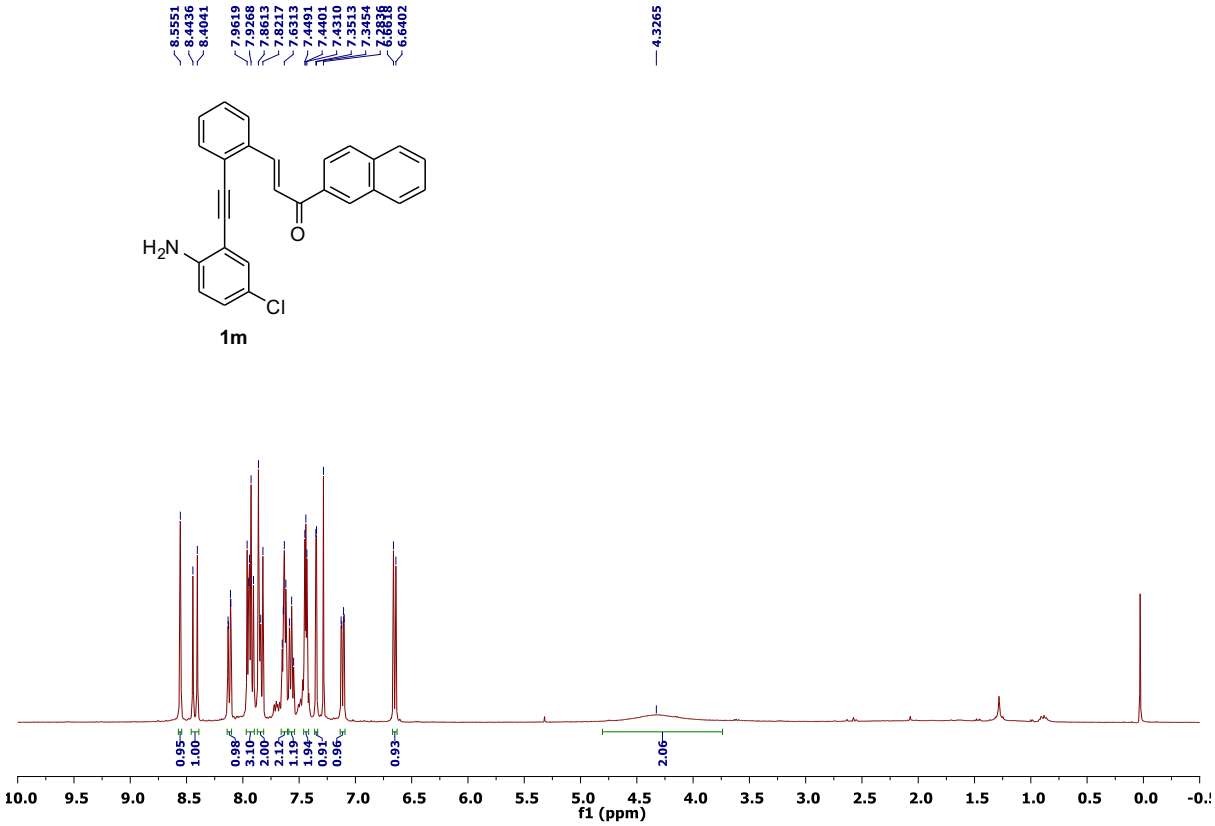
^{1}H NMR spectrum of compound **1l** ($CDCl_3$, 400 MHz)



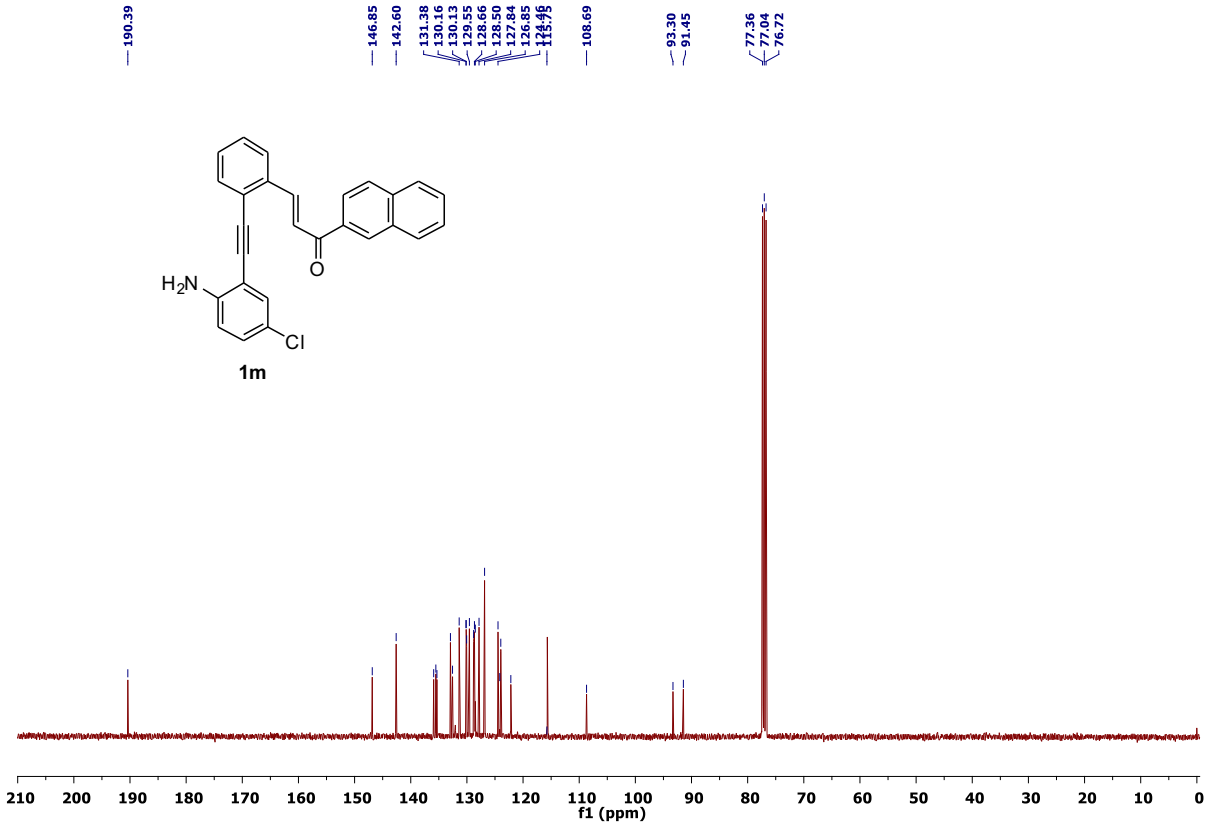
^{13}C{^{1}H} NMR spectrum of compound **1l** ($CDCl_3$, 101 MHz)



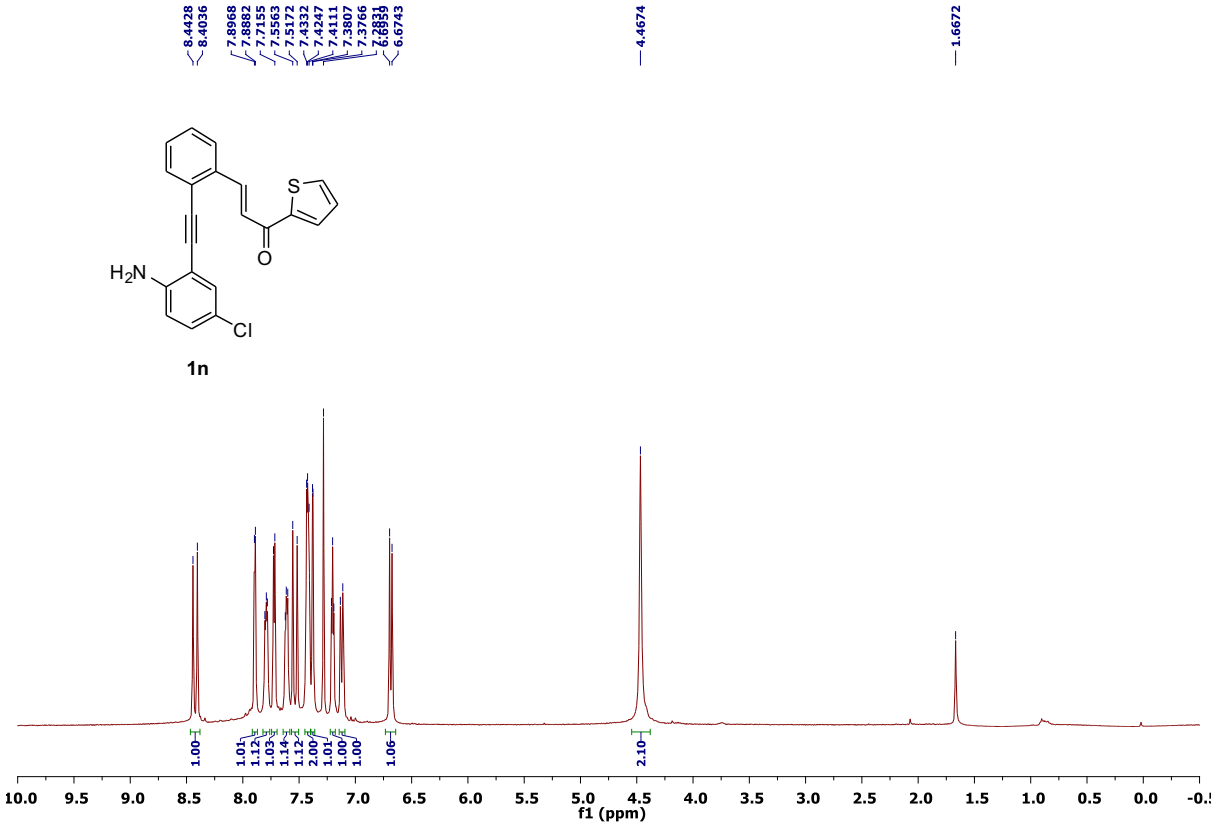
^{1}H NMR spectrum of compound **1m** ($CDCl_3$, 400 MHz)



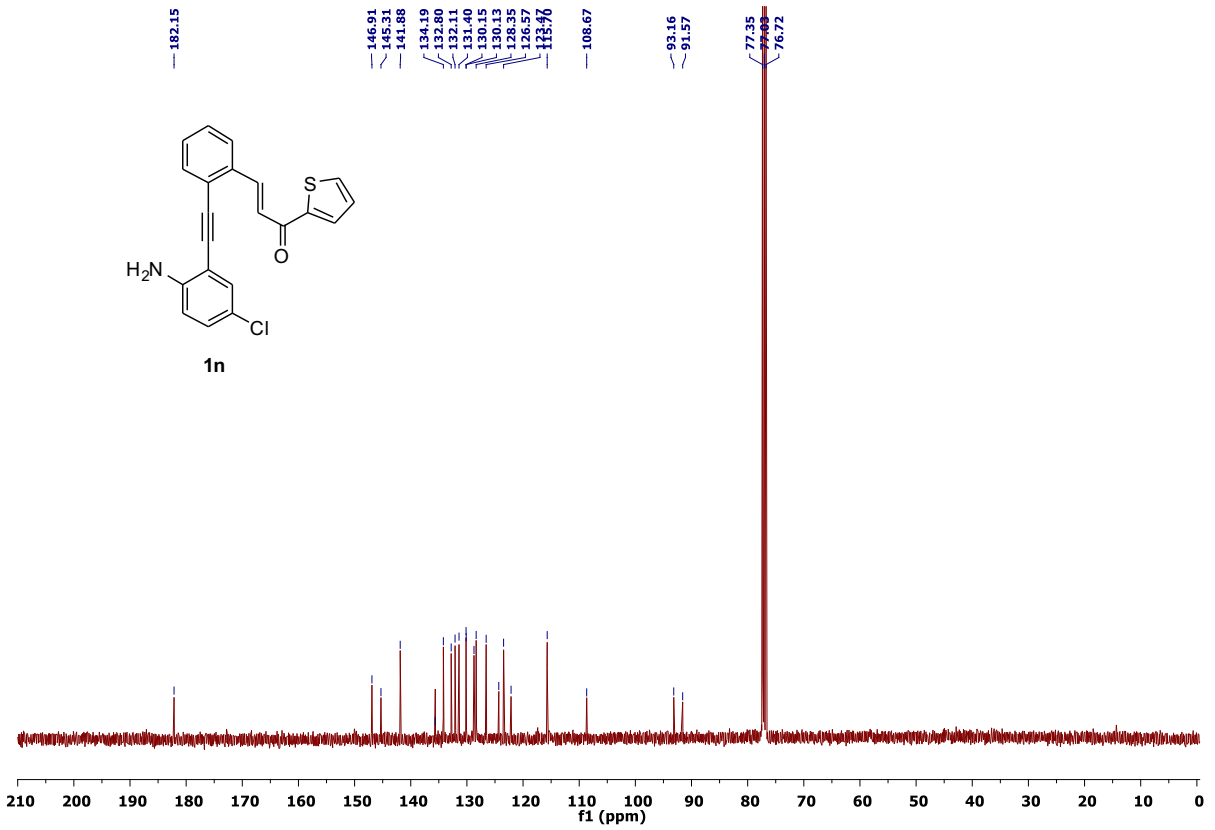
^{13}C{^{1}H} NMR spectrum of compound **1m** ($CDCl_3$, 101 MHz)



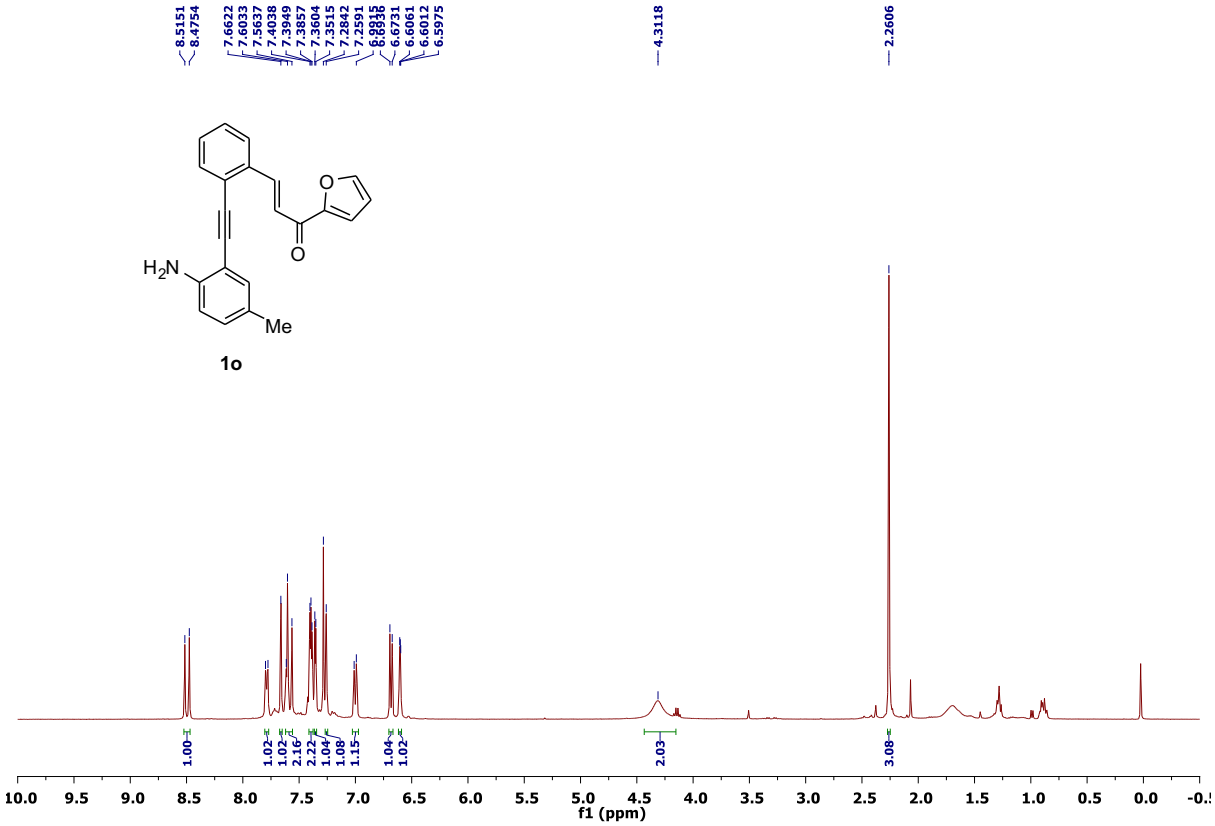
^{1}H NMR spectrum of compound **1n** ($CDCl_3$, 400 MHz)



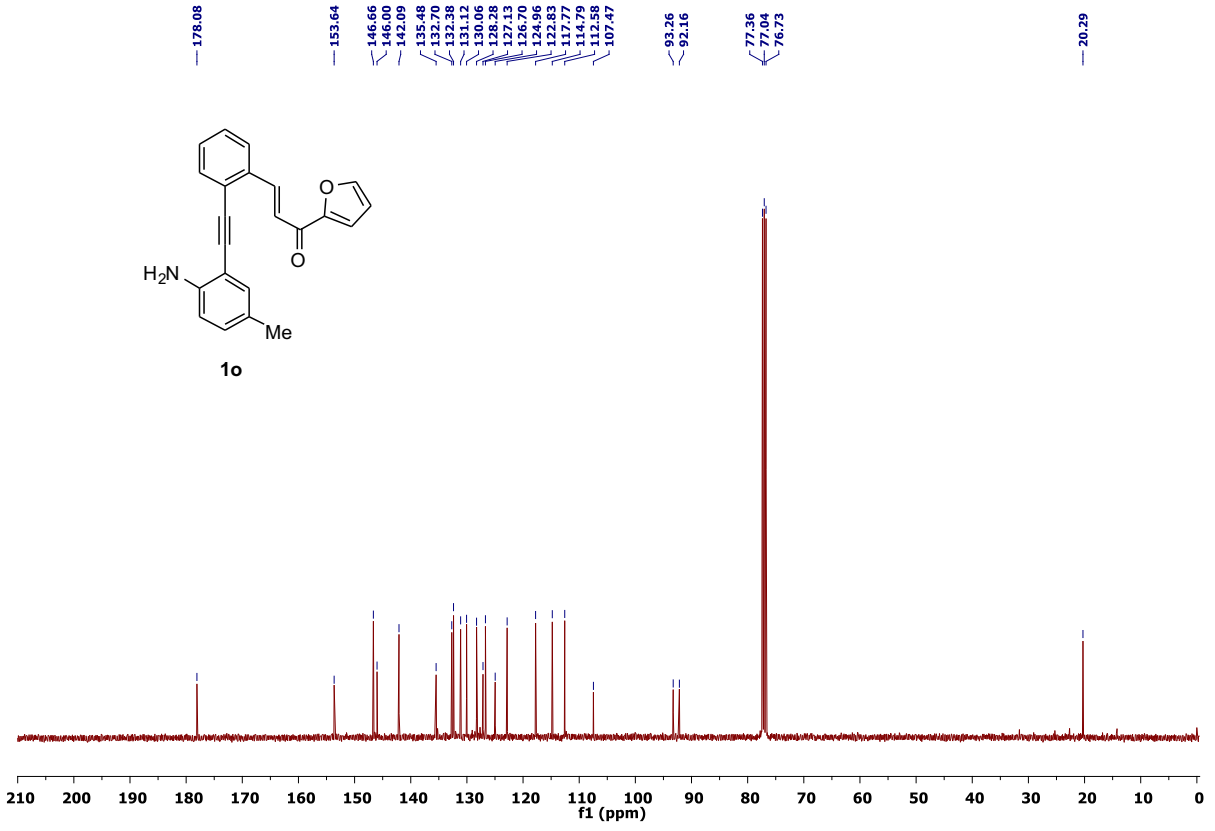
^{13}C{^{1}H} NMR spectrum of compound **1n** ($CDCl_3$, 101 MHz)



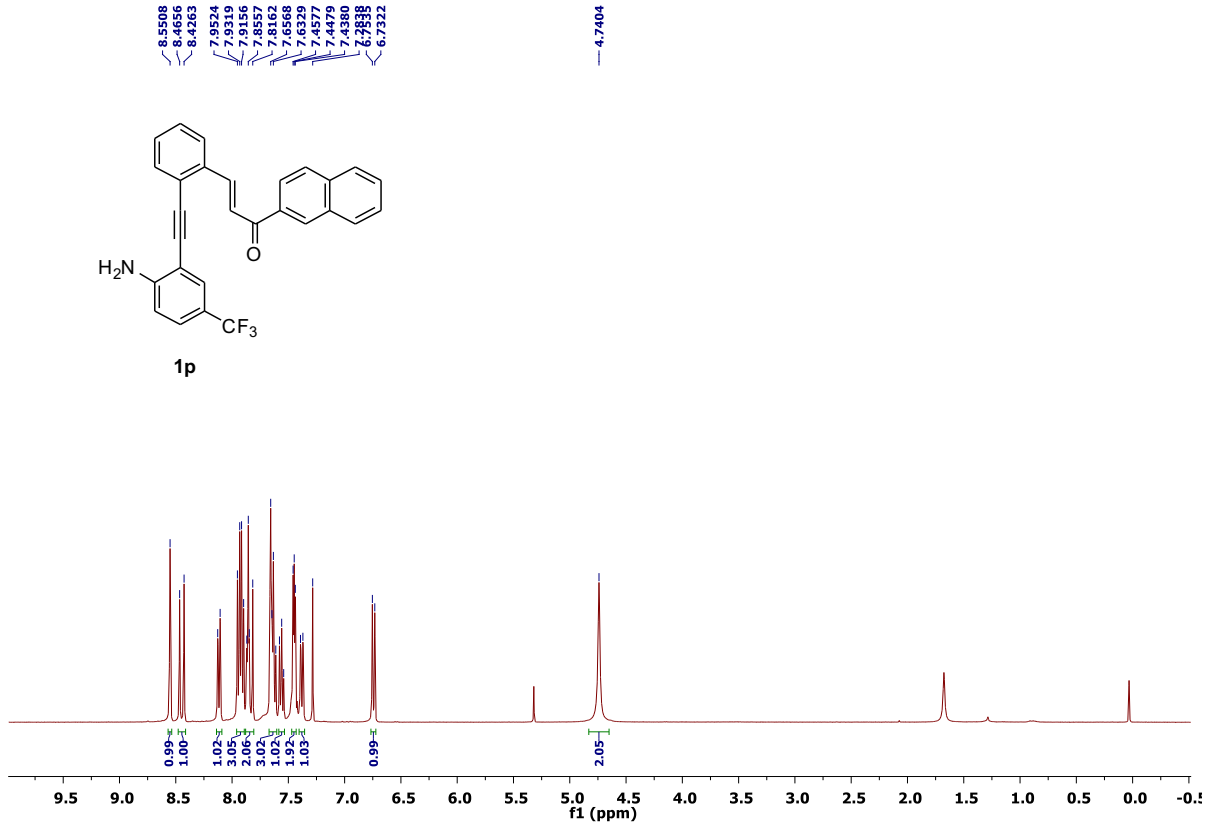
^{1}H NMR spectrum of compound **1o** ($CDCl_3$, 400 MHz)



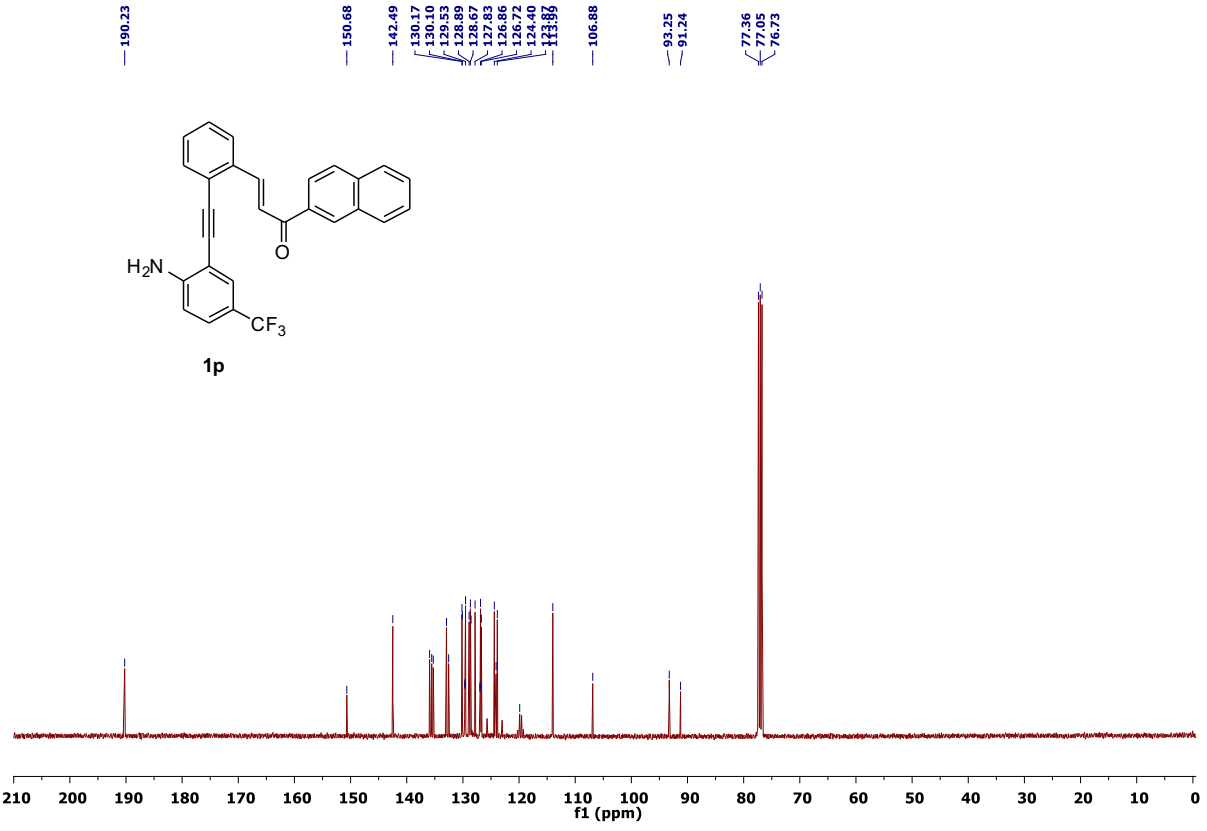
^{13}C{^{1}H} NMR spectrum of compound **1o** ($CDCl_3$, 101 MHz)



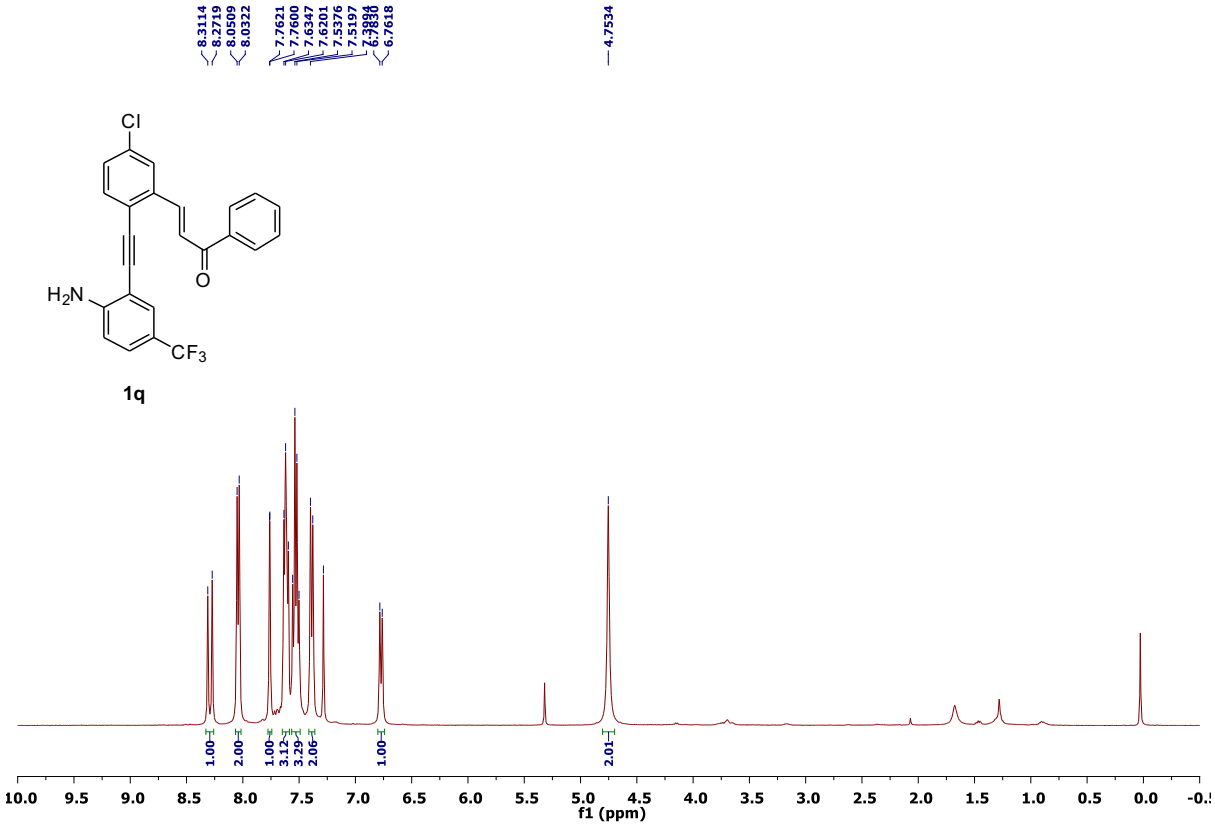
^{1}H NMR spectrum of compound **1p** ($CDCl_3$, 400 MHz)



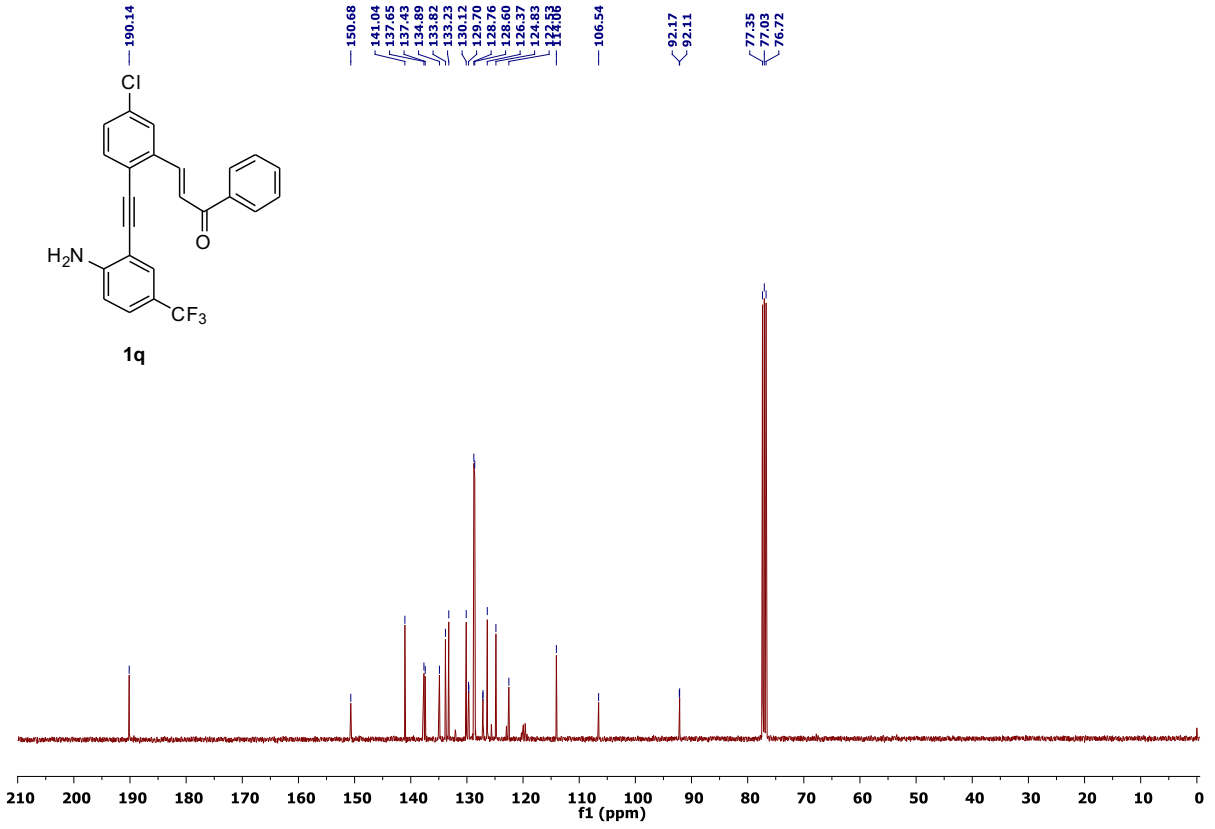
^{13}C{^{1}H} NMR spectrum of compound **1p** ($CDCl_3$, 101 MHz)



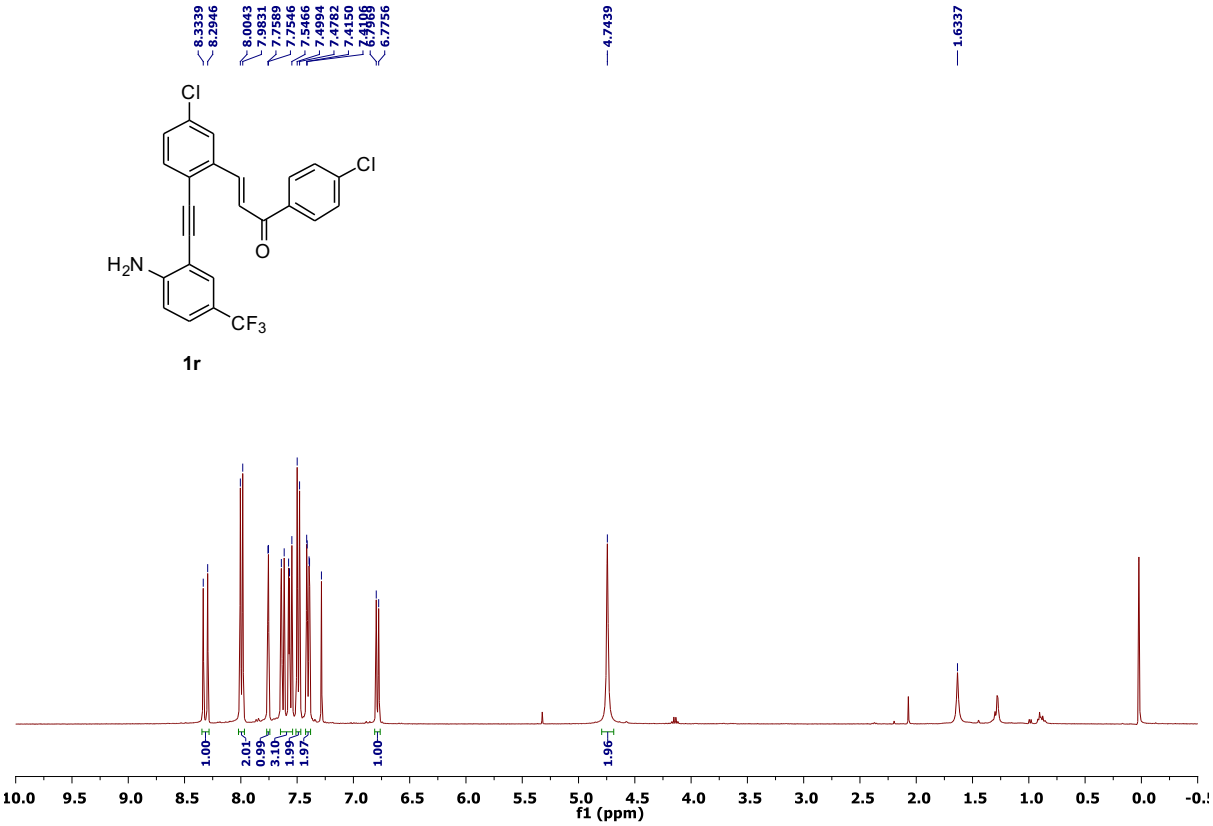
^{1}H NMR spectrum of compound **1q** ($CDCl_3$, 400 MHz)



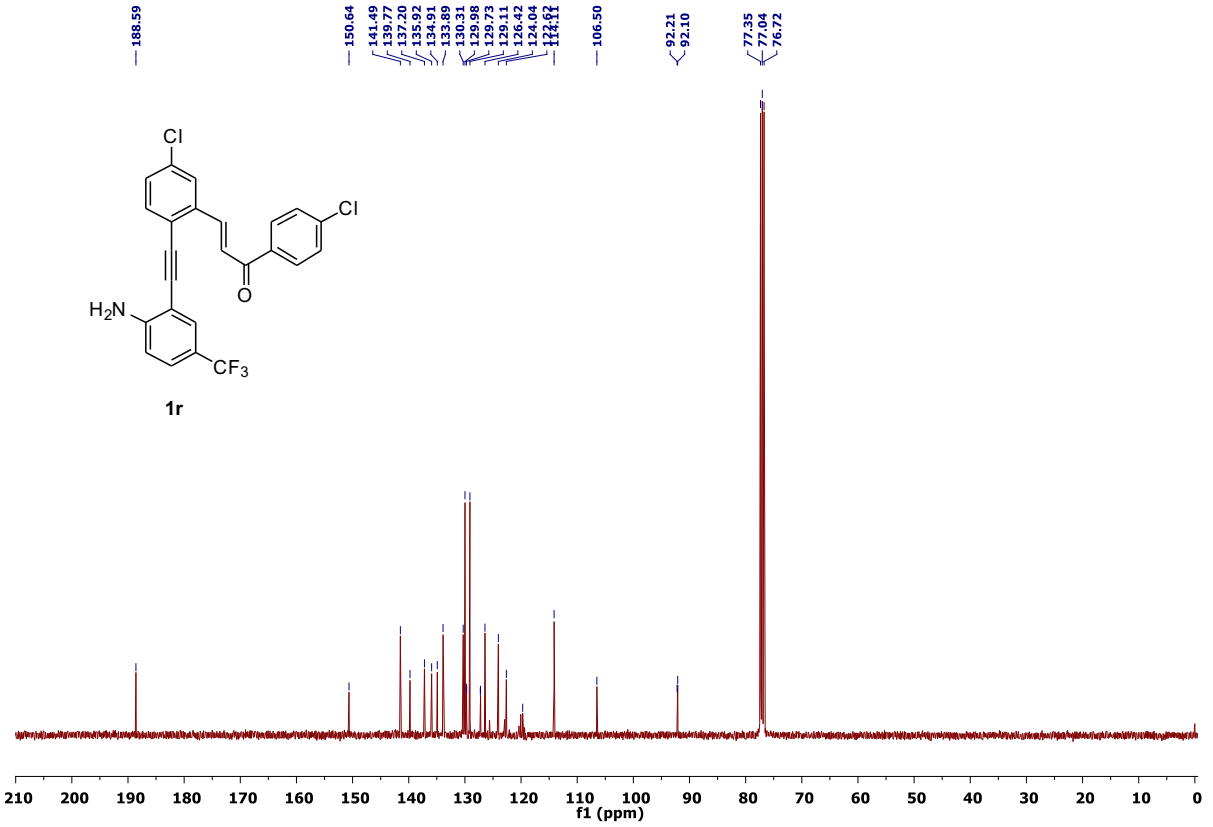
^{13}C{^{1}H} NMR spectrum of compound **1q** ($CDCl_3$, 101 MHz)



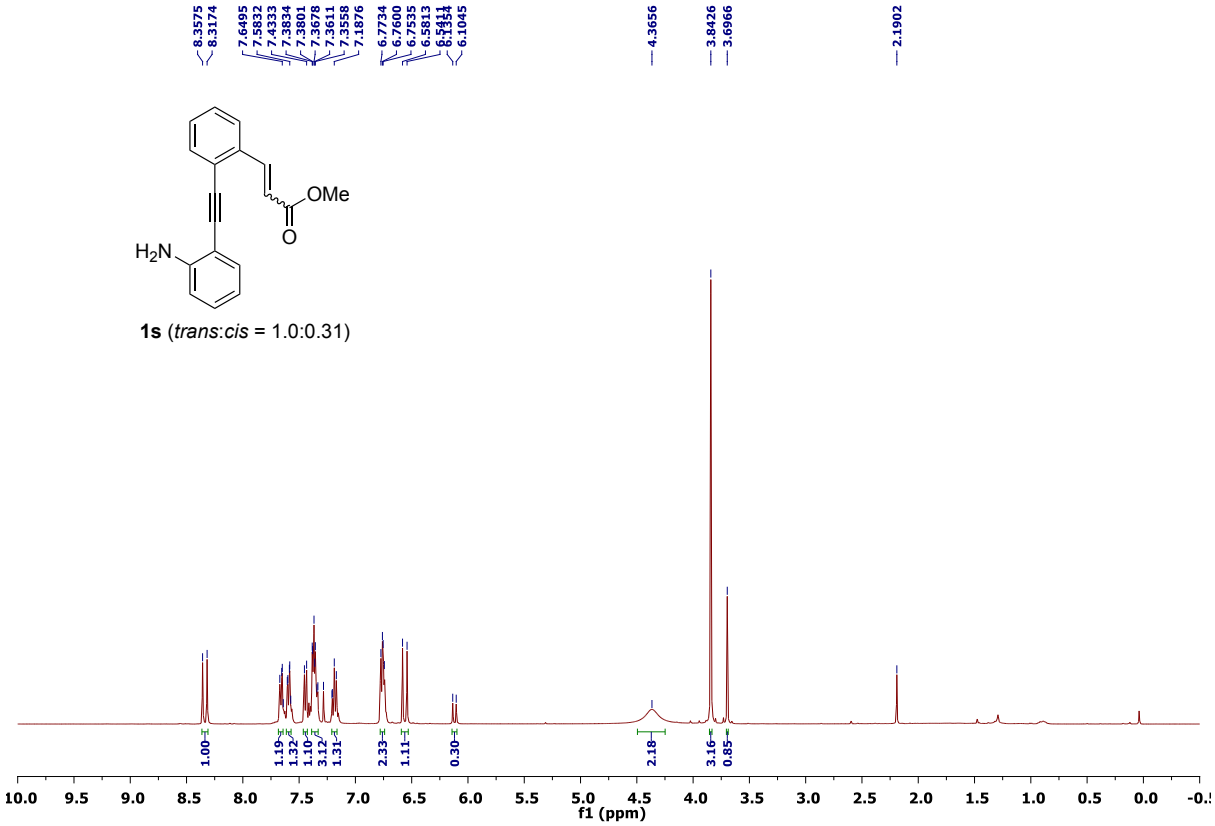
^{1}H NMR spectrum of compound **1r** ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR spectrum of compound **1r** ($CDCl_3$, 101 MHz)

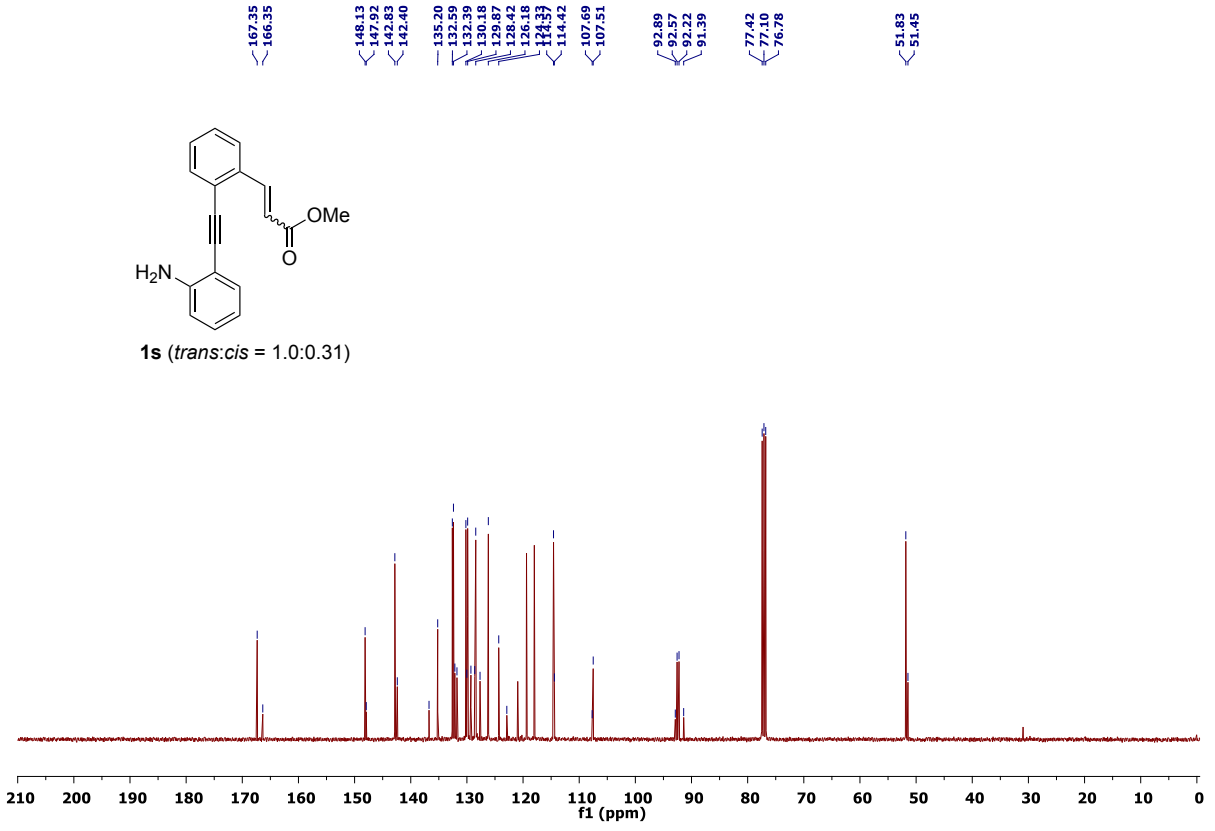


^{1}H NMR spectrum of compound **1s** ($CDCl_3$, 400 MHz)



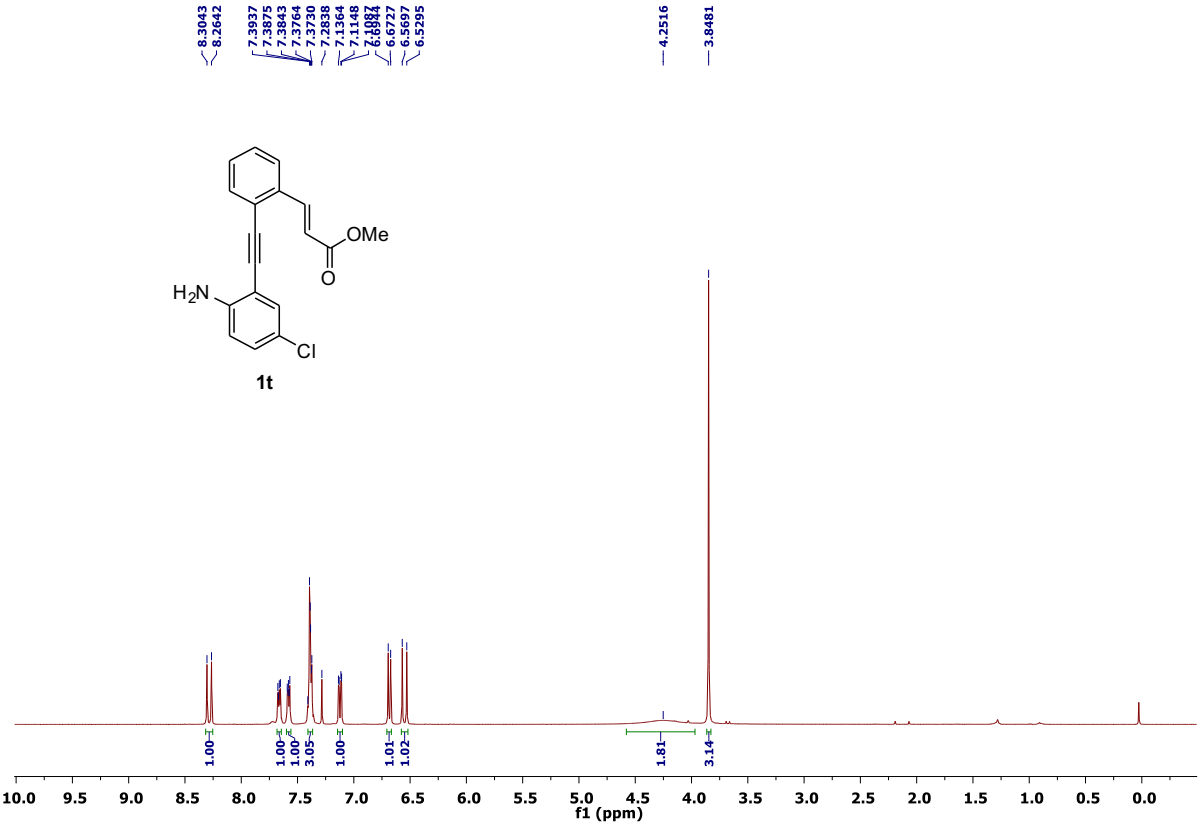
1s (*trans*:*cis* = 1.0:0.31)

^{13}C{^{1}H} NMR spectrum of compound **1s** ($CDCl_3$, 101 MHz)

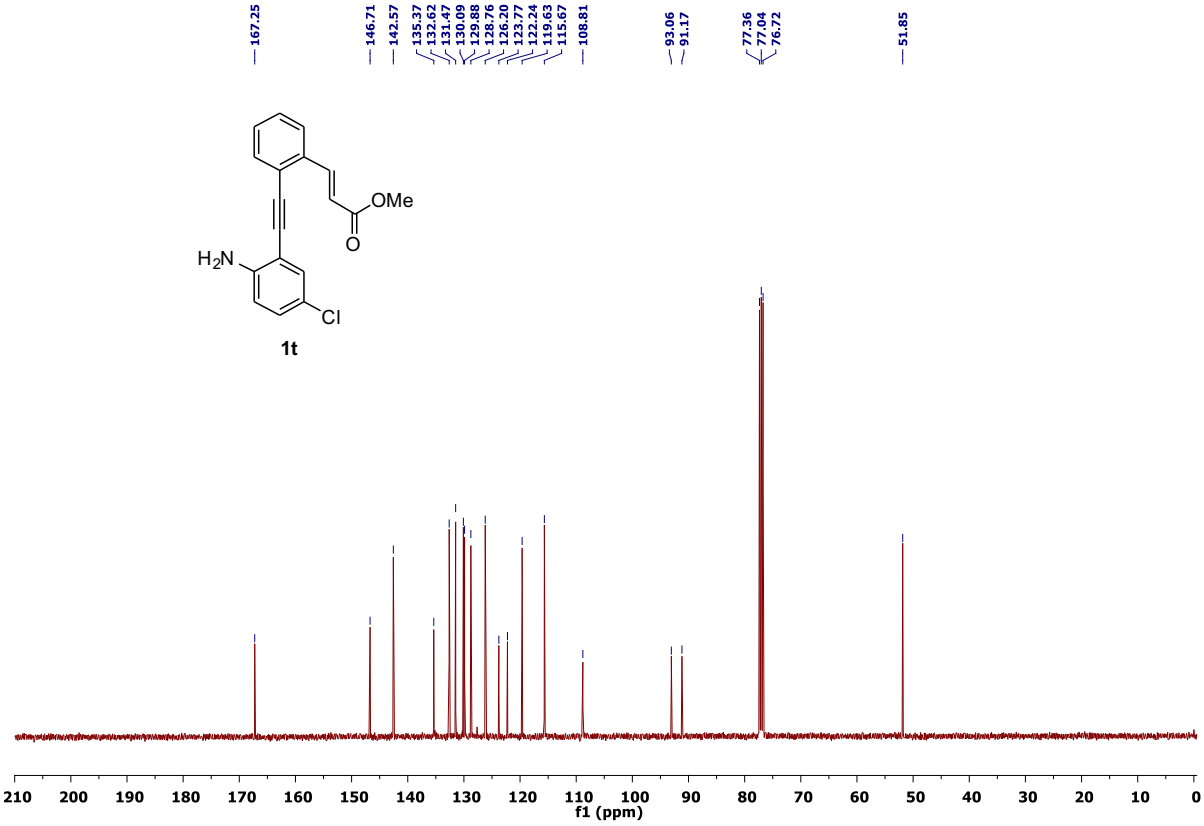


1s (*trans*:*cis* = 1.0:0.31)

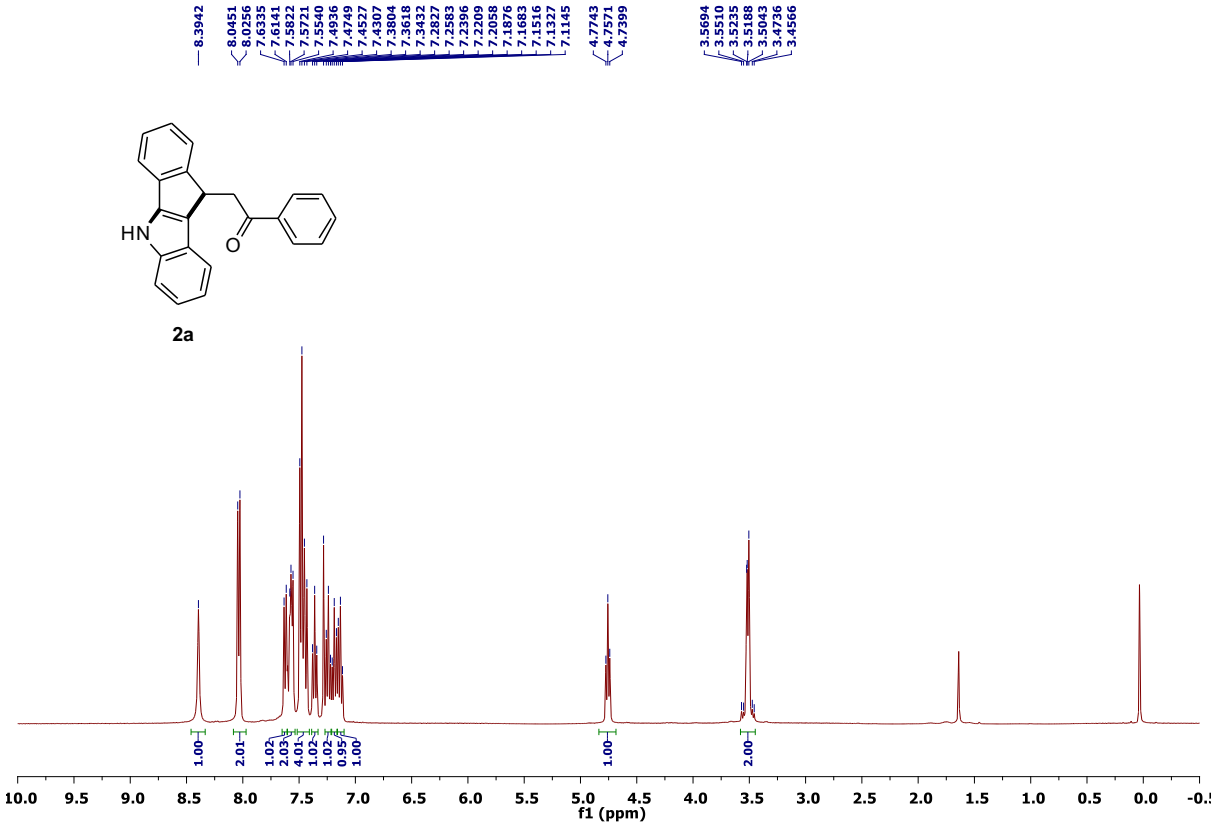
^{1}H NMR spectrum of compound **1t** ($CDCl_3$, 400 MHz)



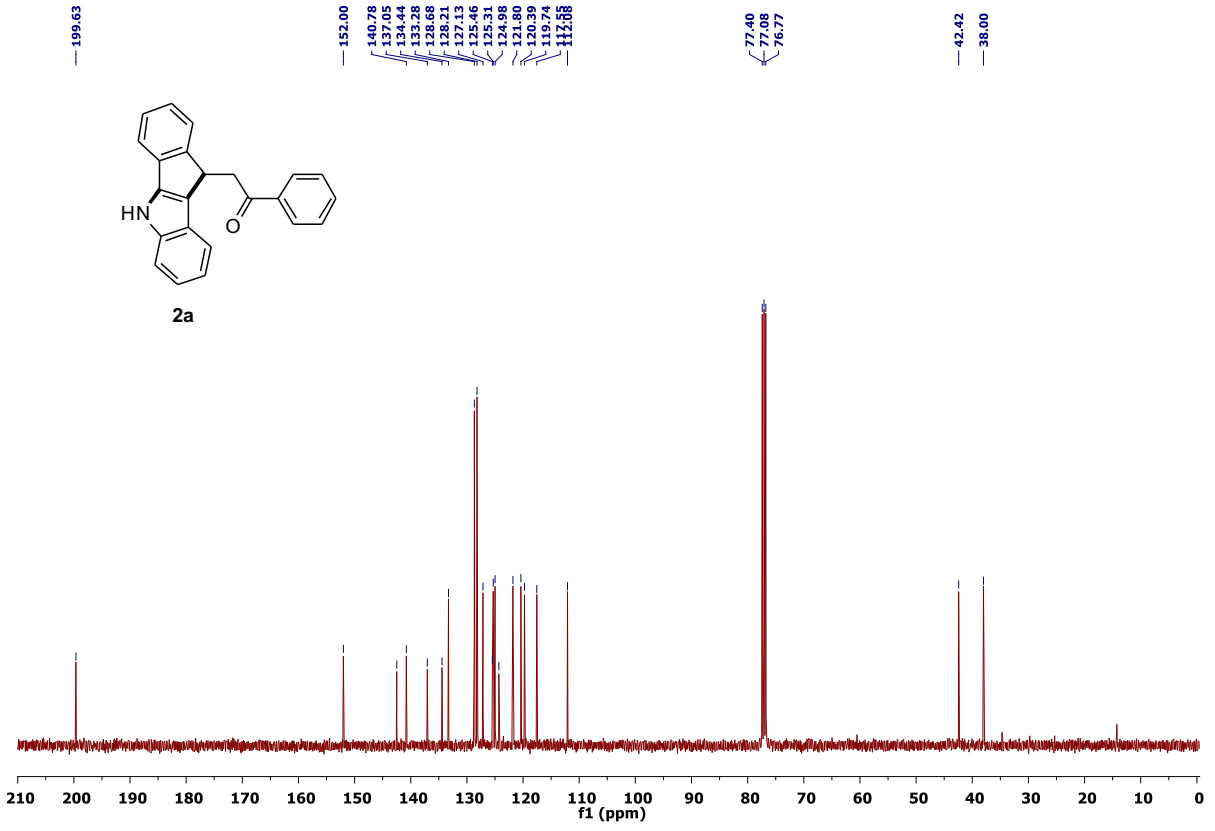
^{13}C{^{1}H} NMR spectrum of compound **1t** ($CDCl_3$, 101 MHz)



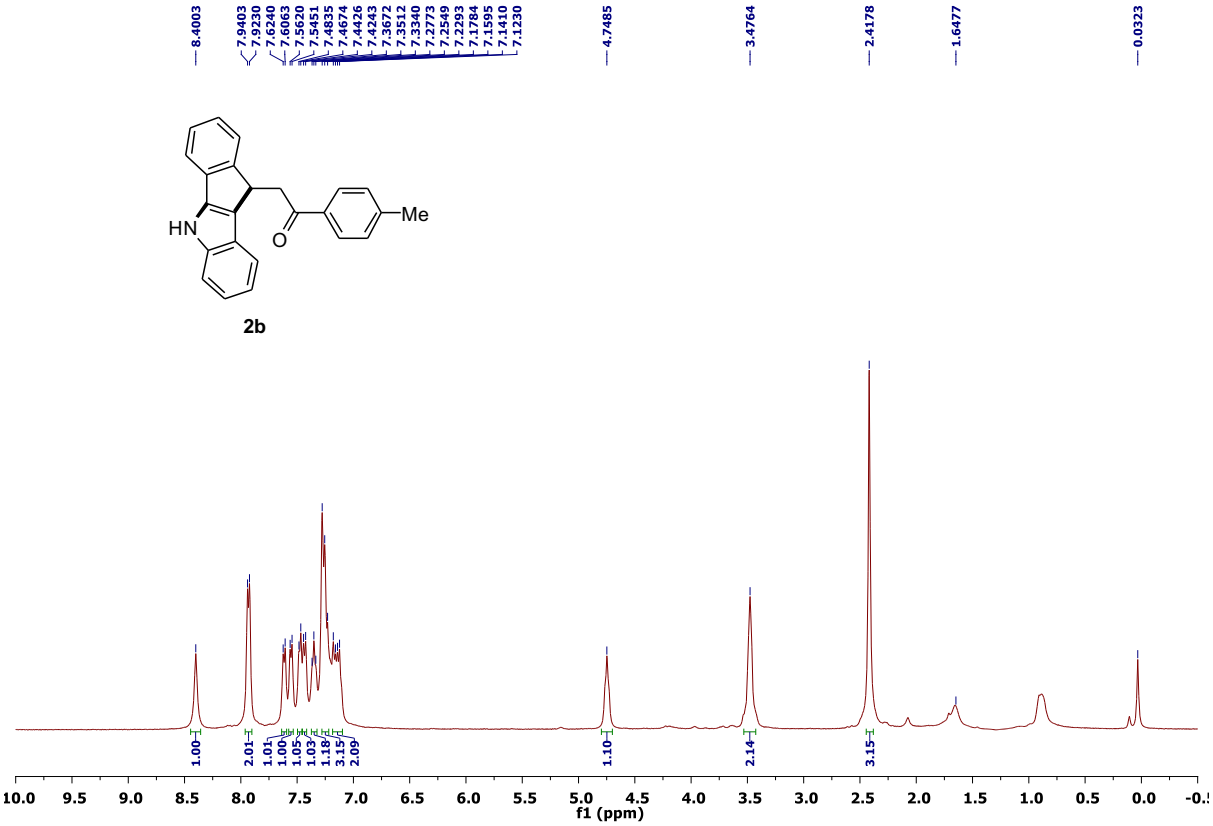
^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz)



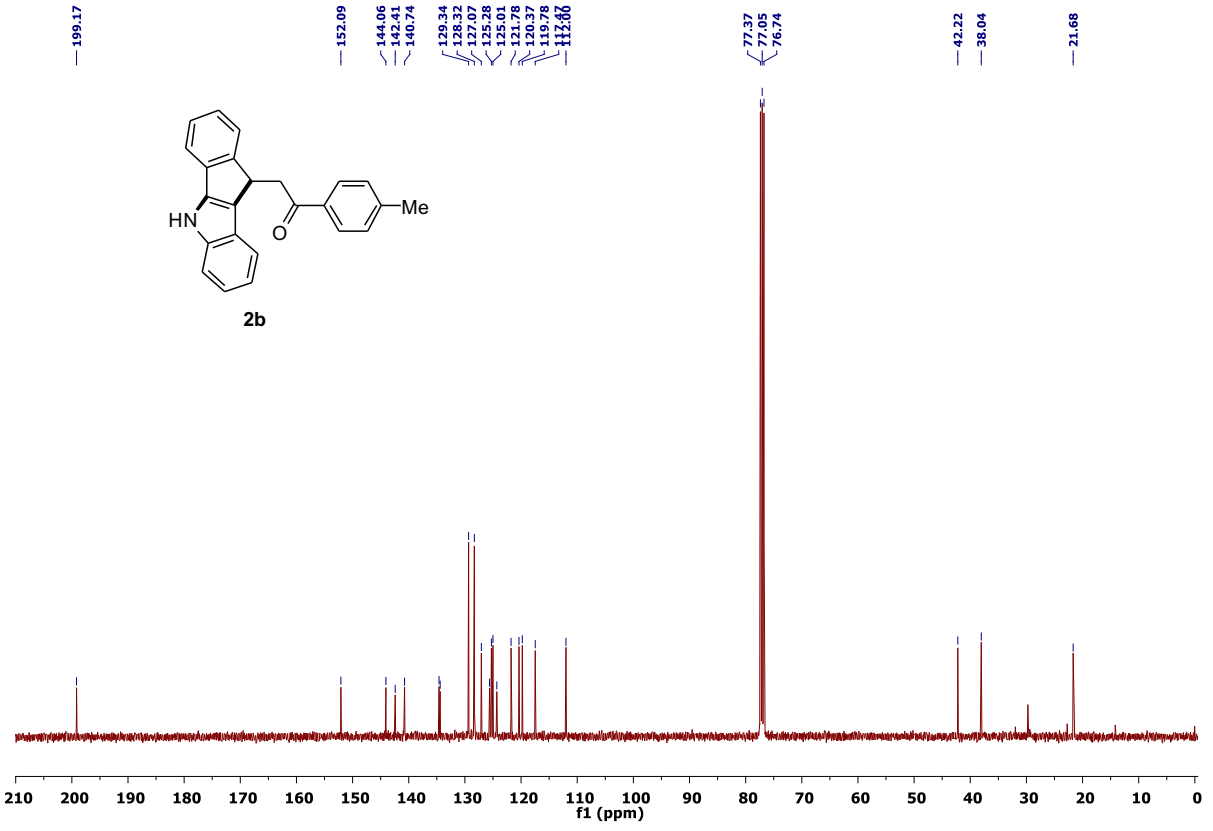
^{13}C{^{1}H} NMR spectrum of compound **2a** ($CDCl_3$, 101 MHz)



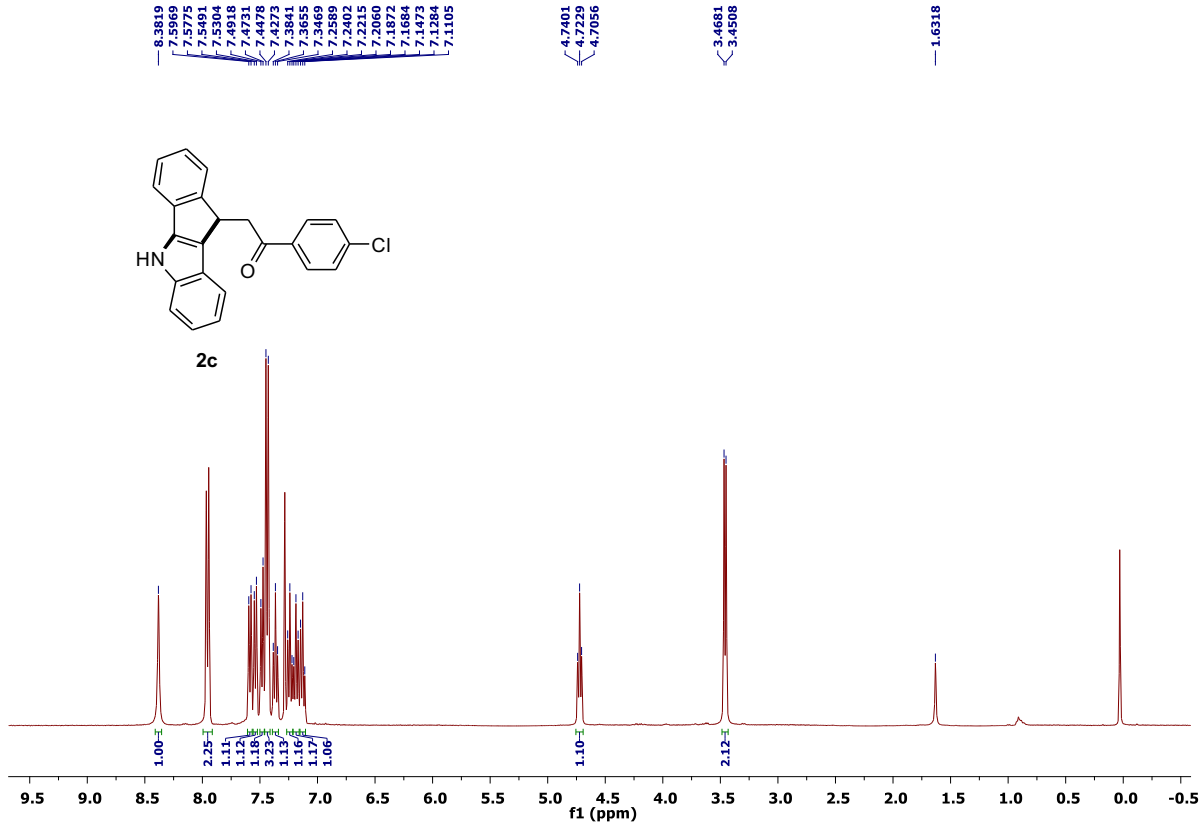
^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz)



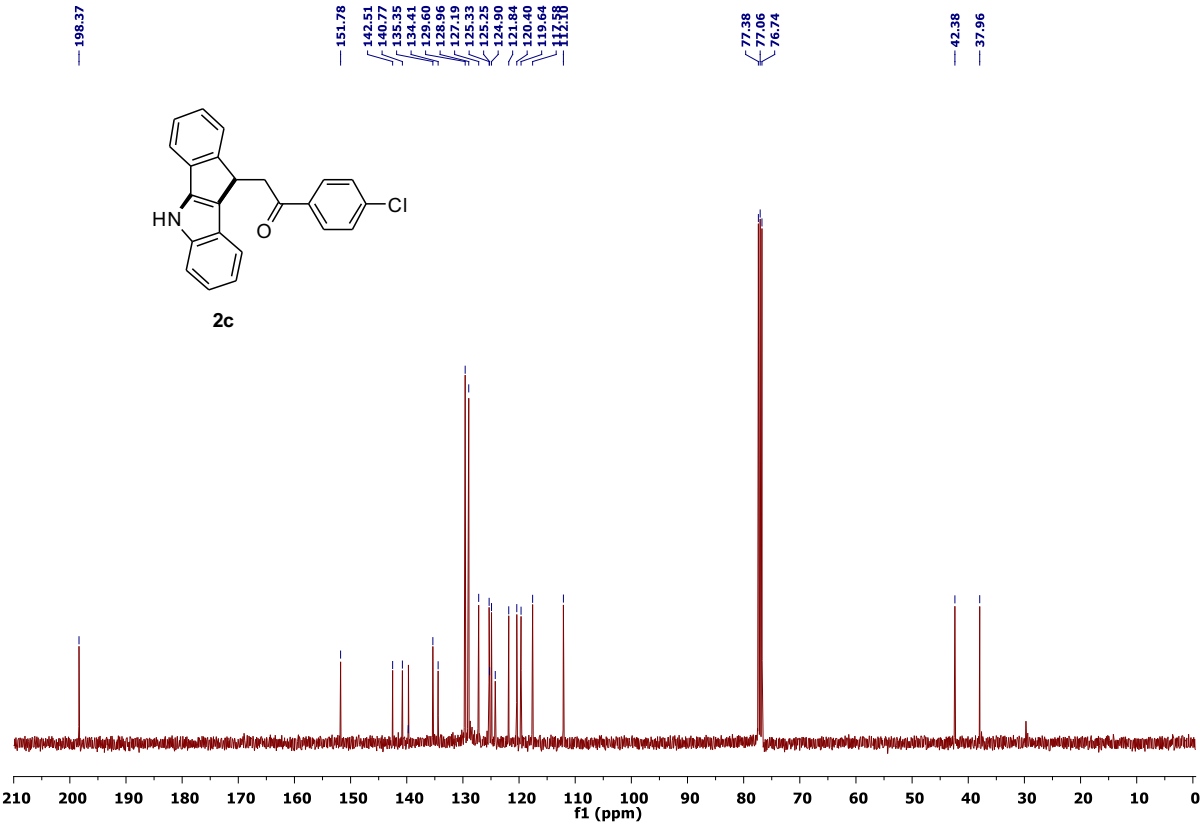
^{13}C{^{1}H} NMR spectrum of compound **2b** ($CDCl_3$, 101 MHz)



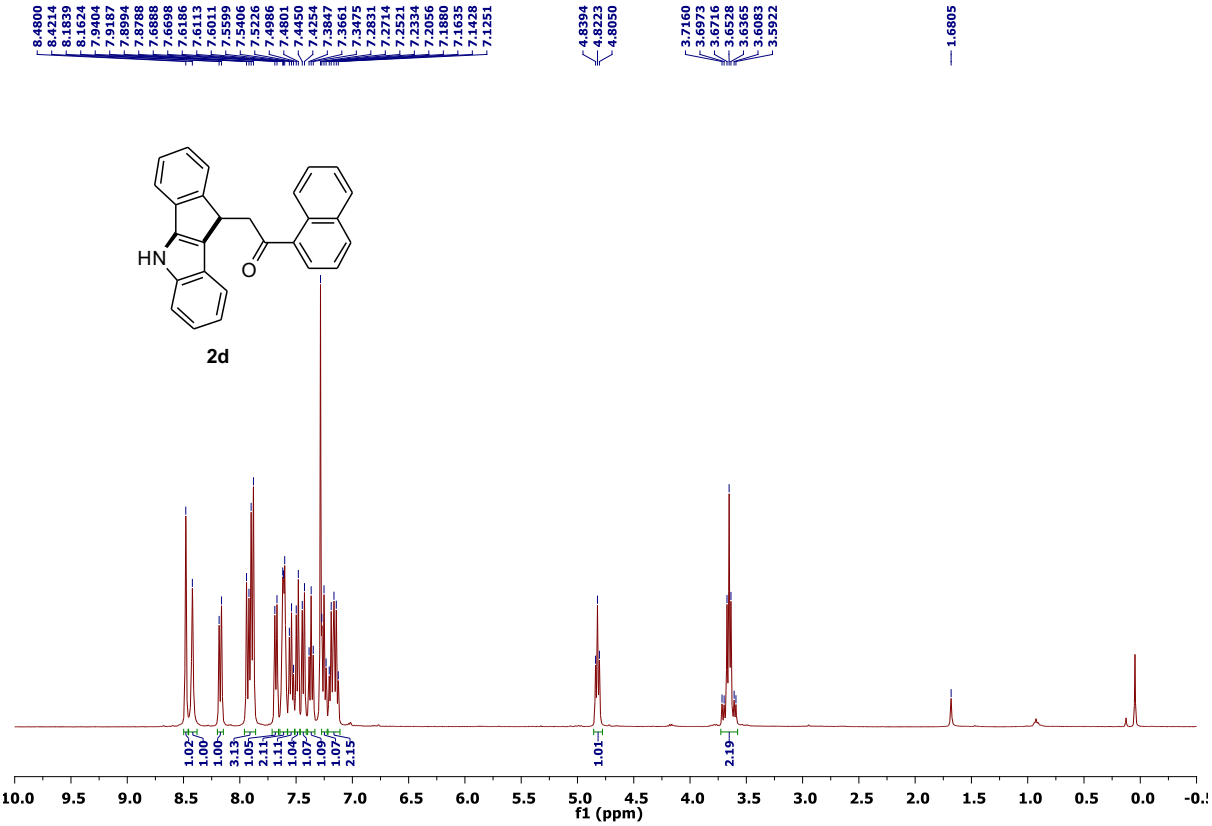
^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz)



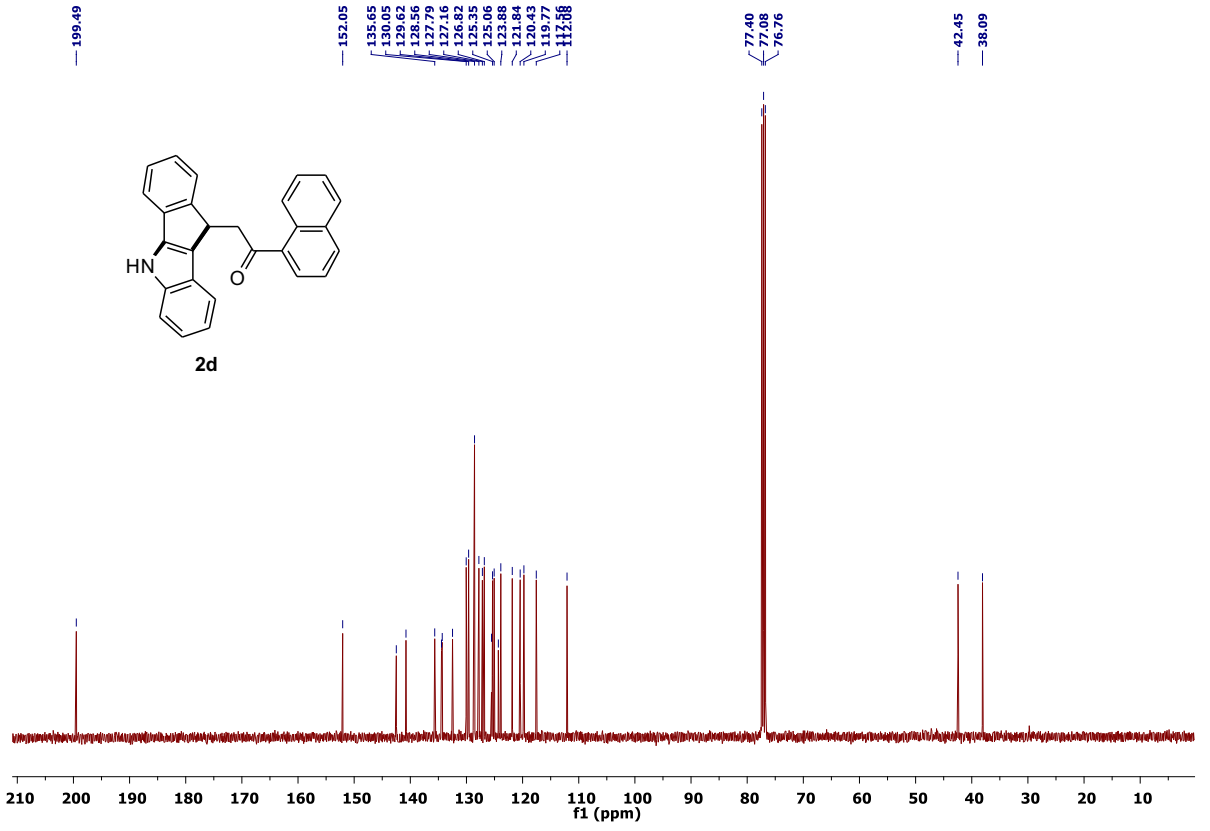
^{13}C{^{1}H} NMR spectrum of compound **2c** ($CDCl_3$, 101 MHz)



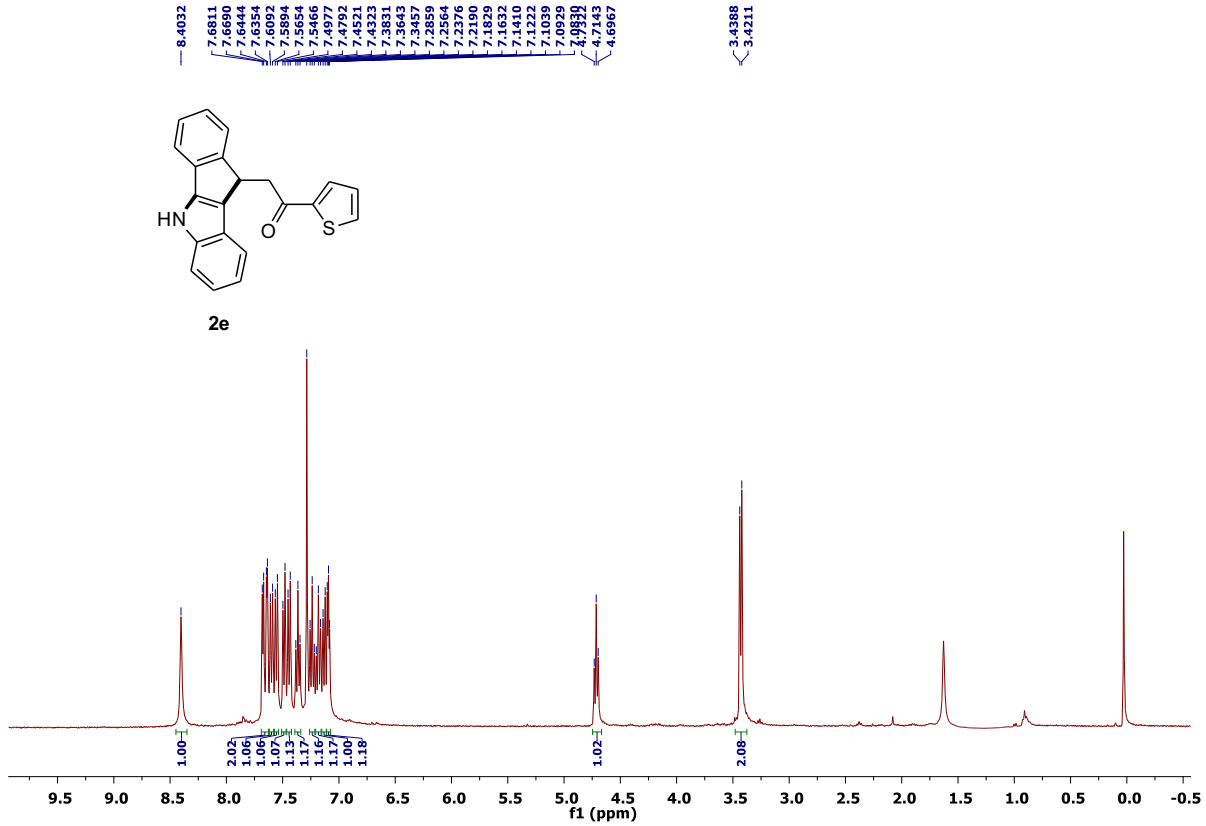
^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz)



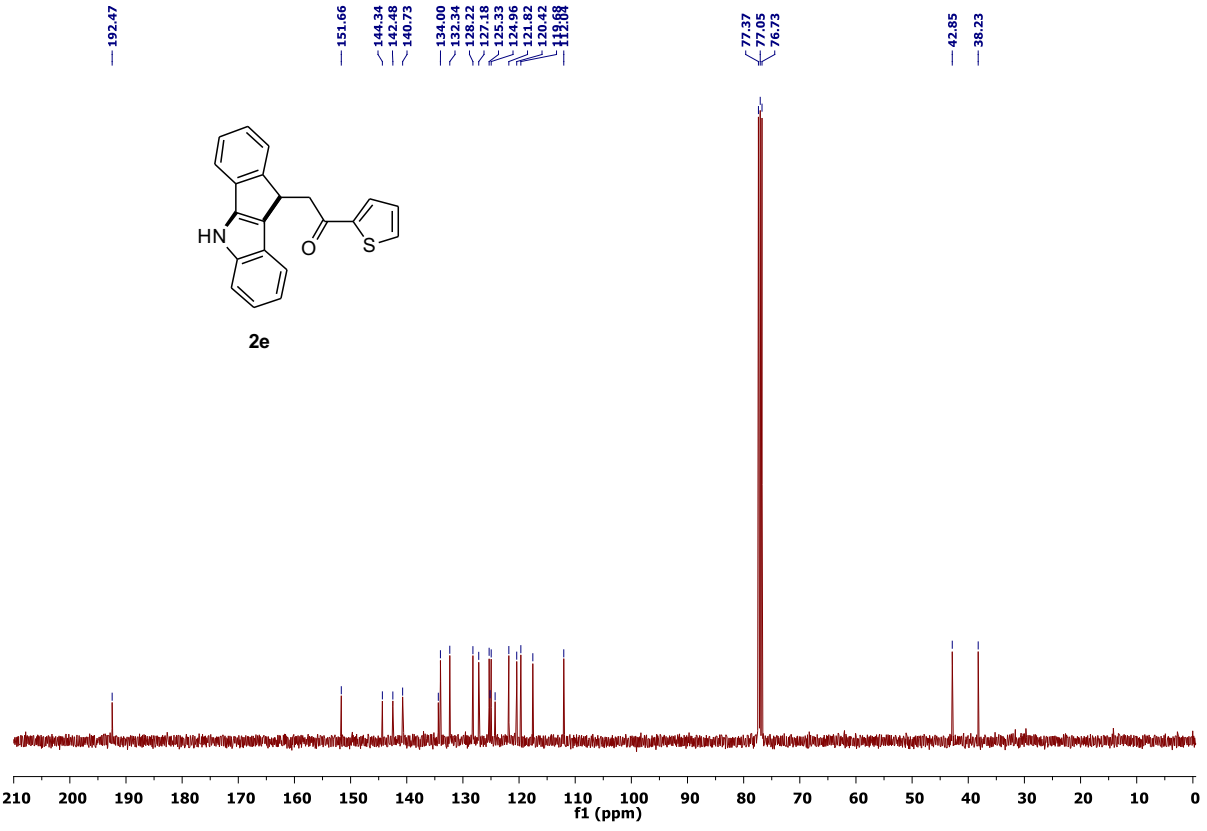
^{13}C{^{1}H} NMR spectrum of compound **2d** ($CDCl_3$, 101 MHz)



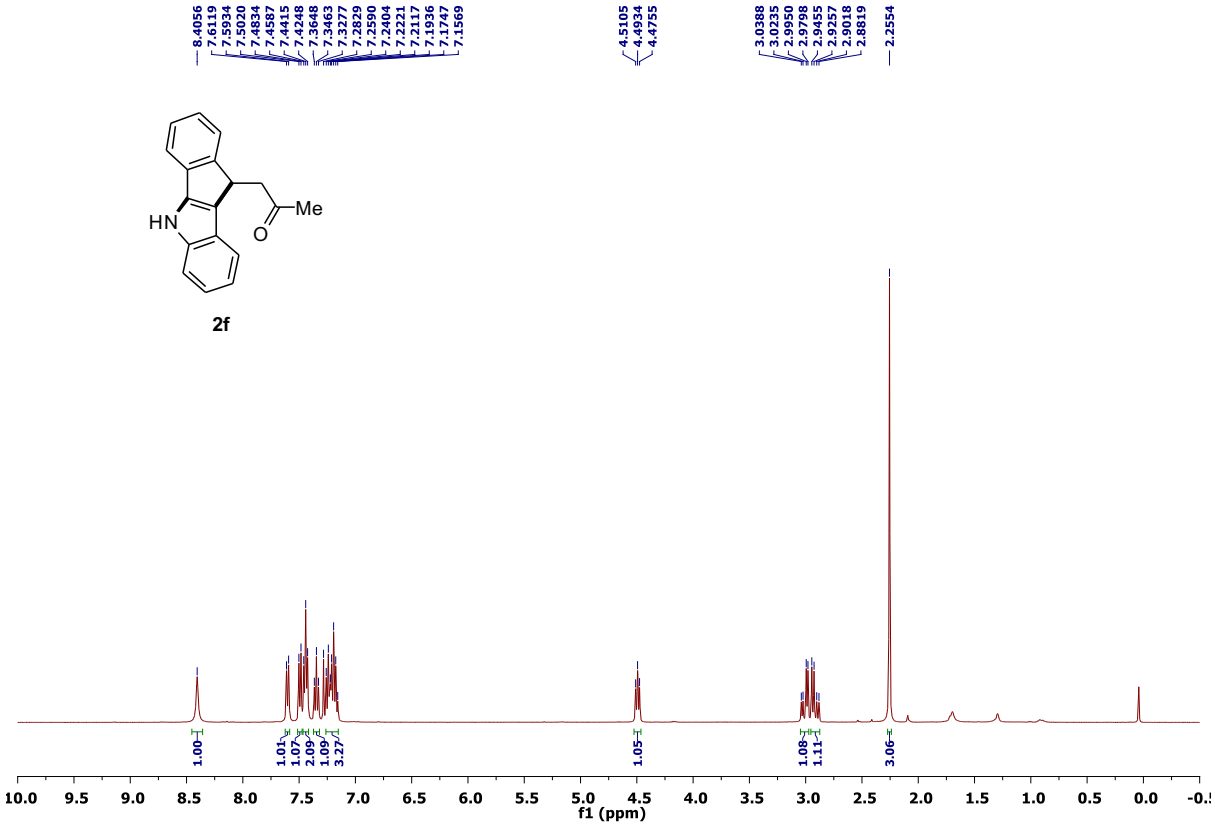
^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz)



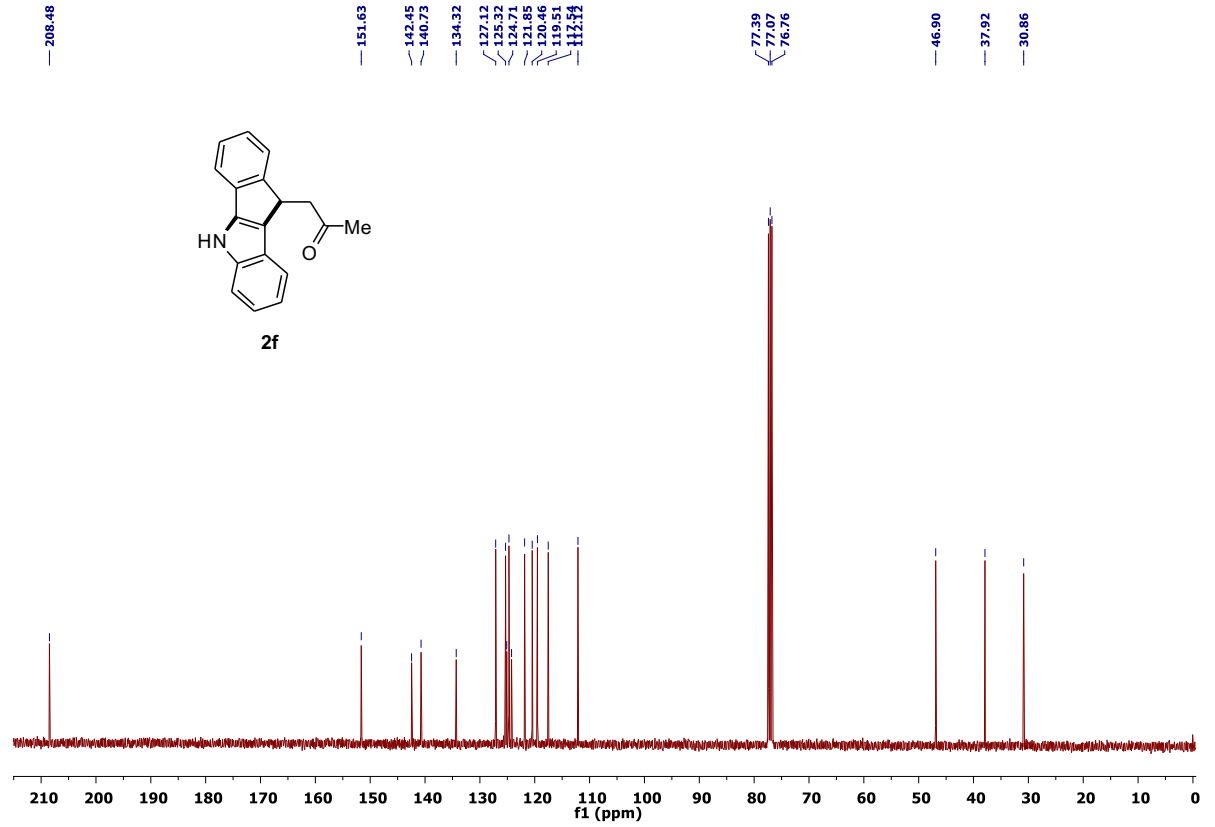
^{13}C{^{1}H} NMR spectrum of compound **2e** ($CDCl_3$, 101 MHz)



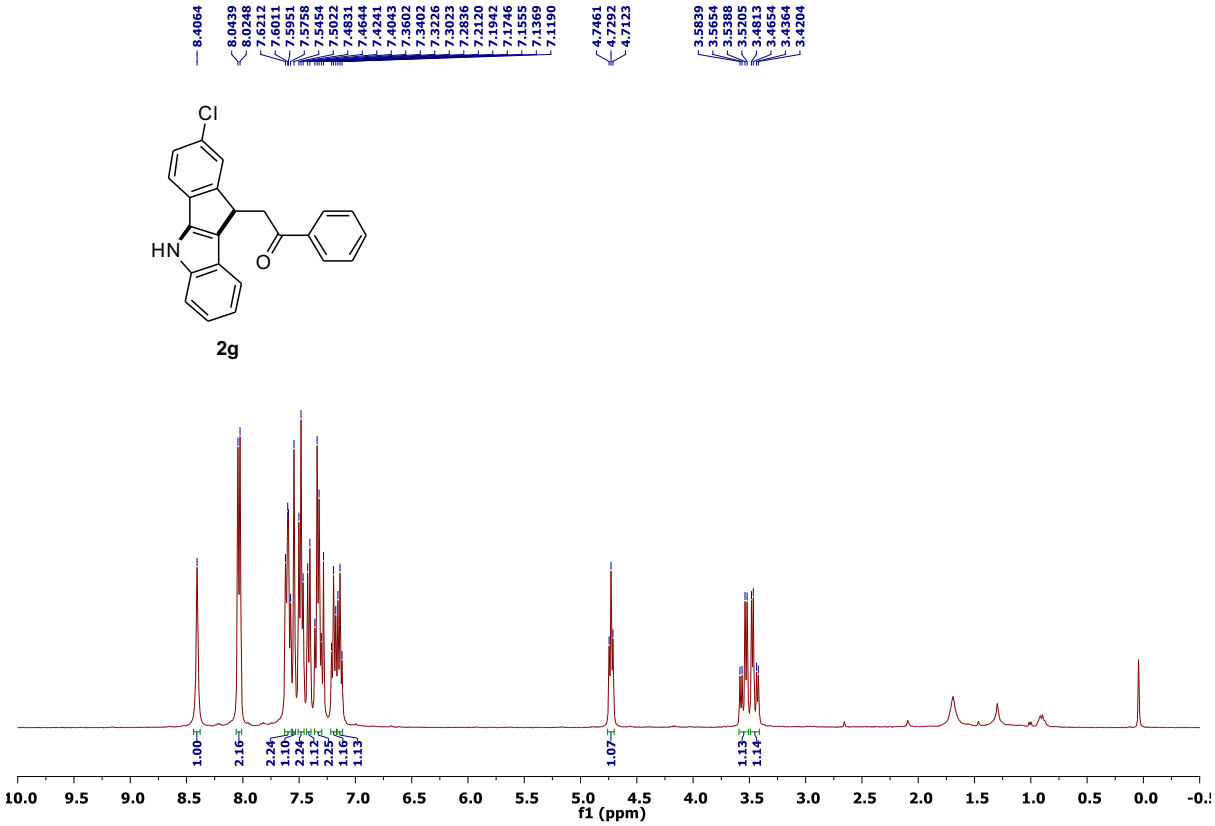
^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz)



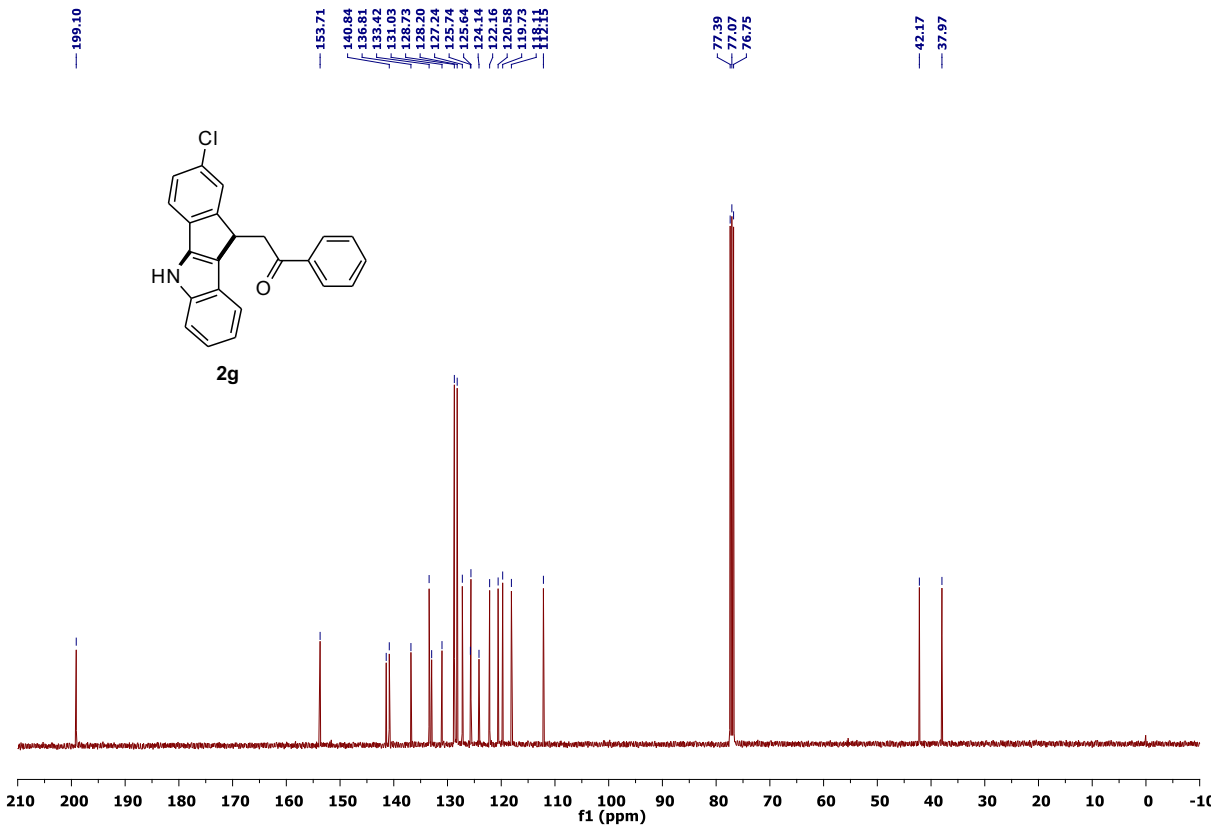
^{13}C{^{1}H} NMR spectrum of compound **2f** ($CDCl_3$, 101 MHz)



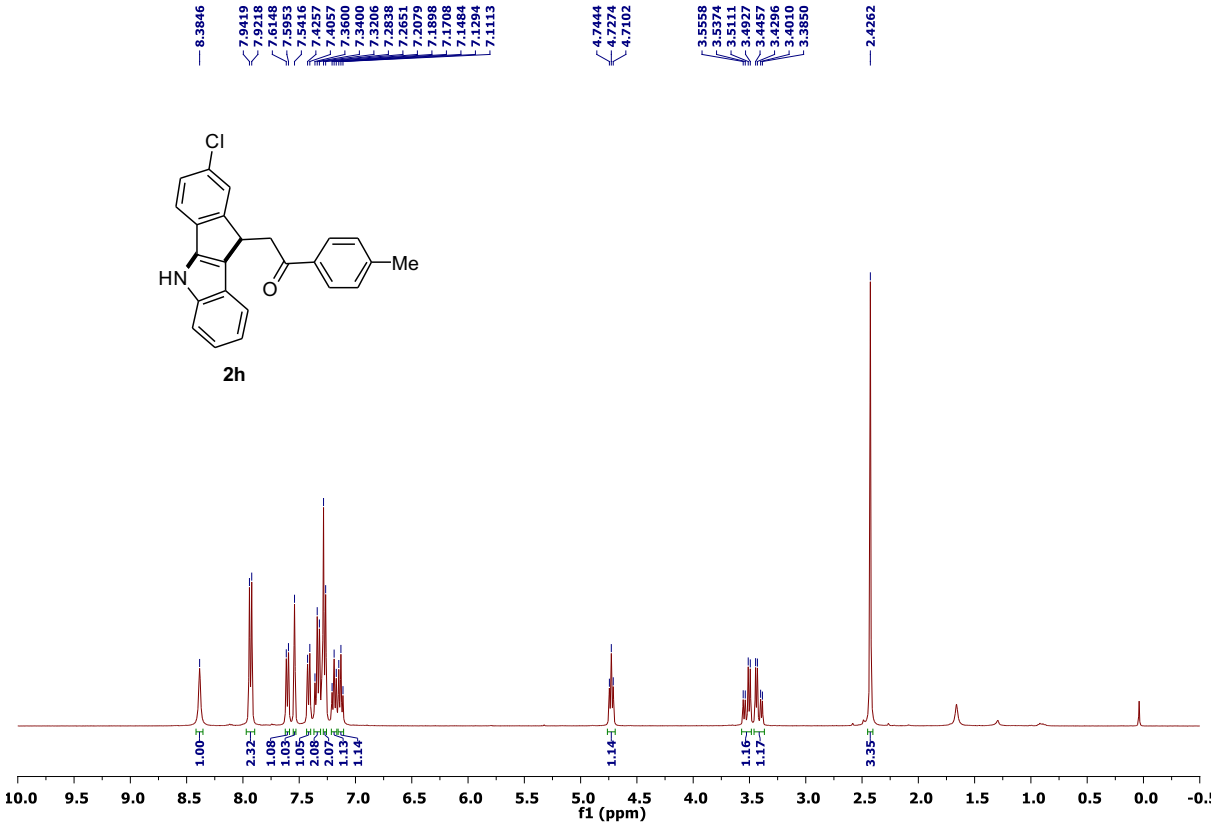
^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz)



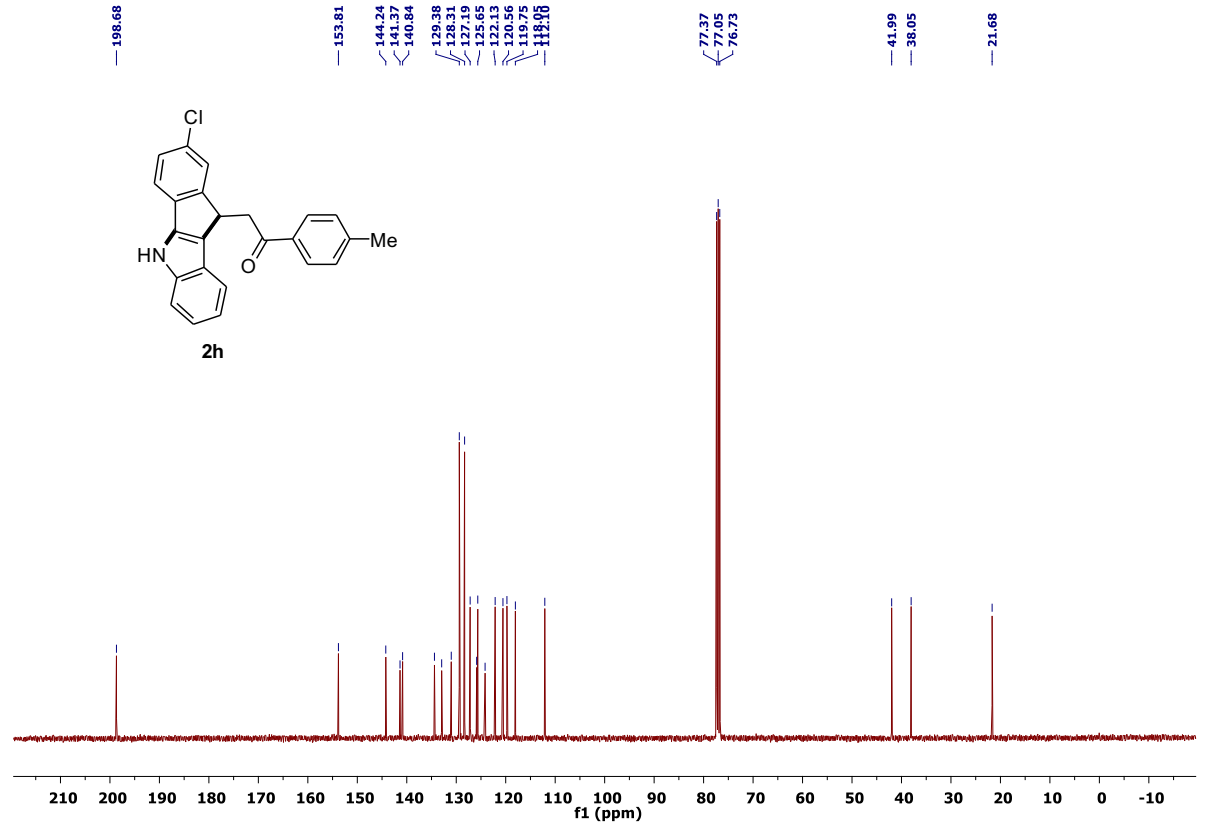
^{13}C{^{1}H} NMR spectrum of compound **2g** ($CDCl_3$, 101 MHz)



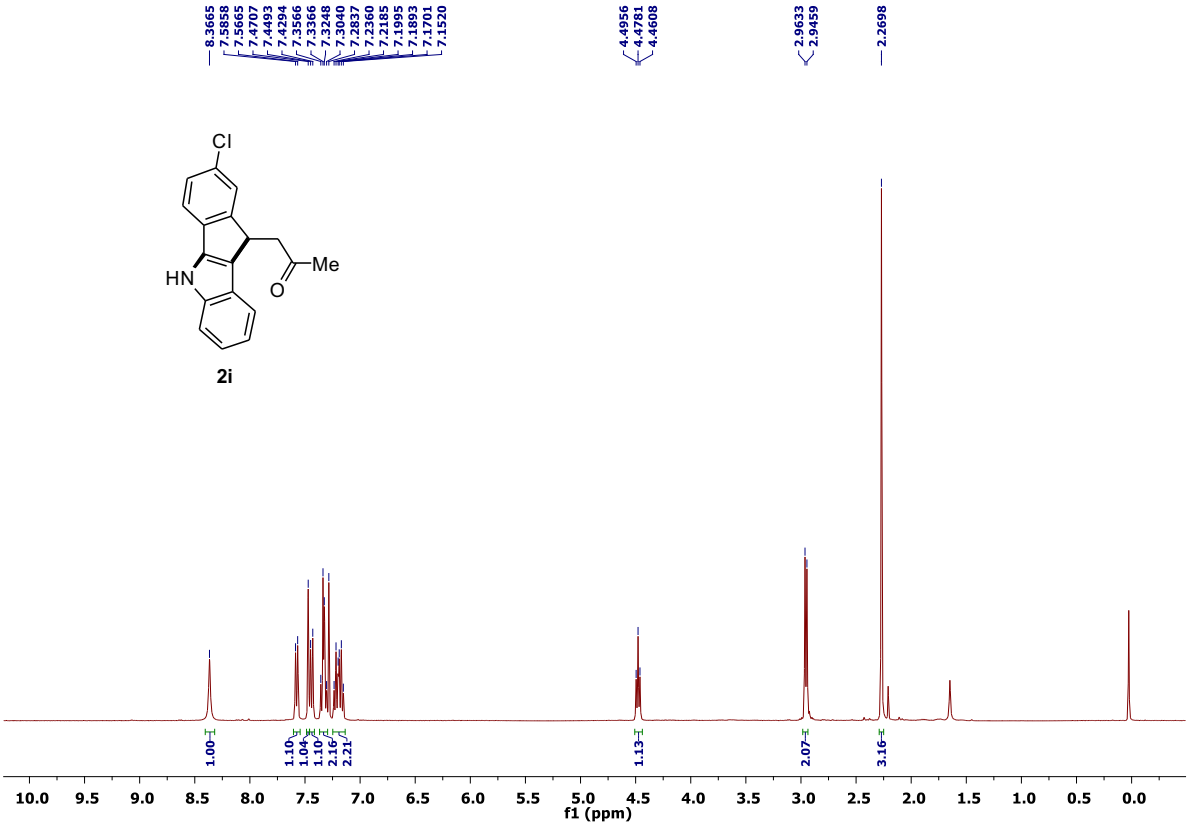
^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz)



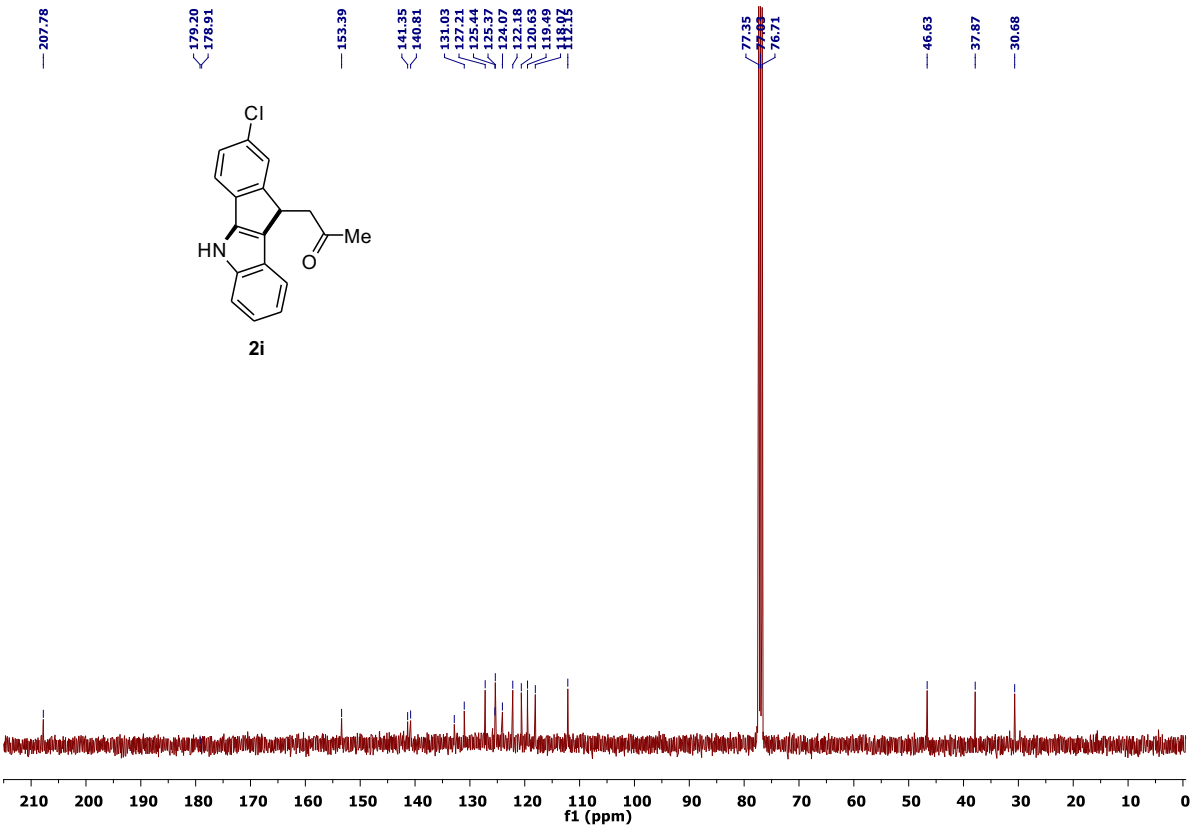
^{13}C{^{1}H} NMR spectrum of compound **2h** ($CDCl_3$, 101 MHz)



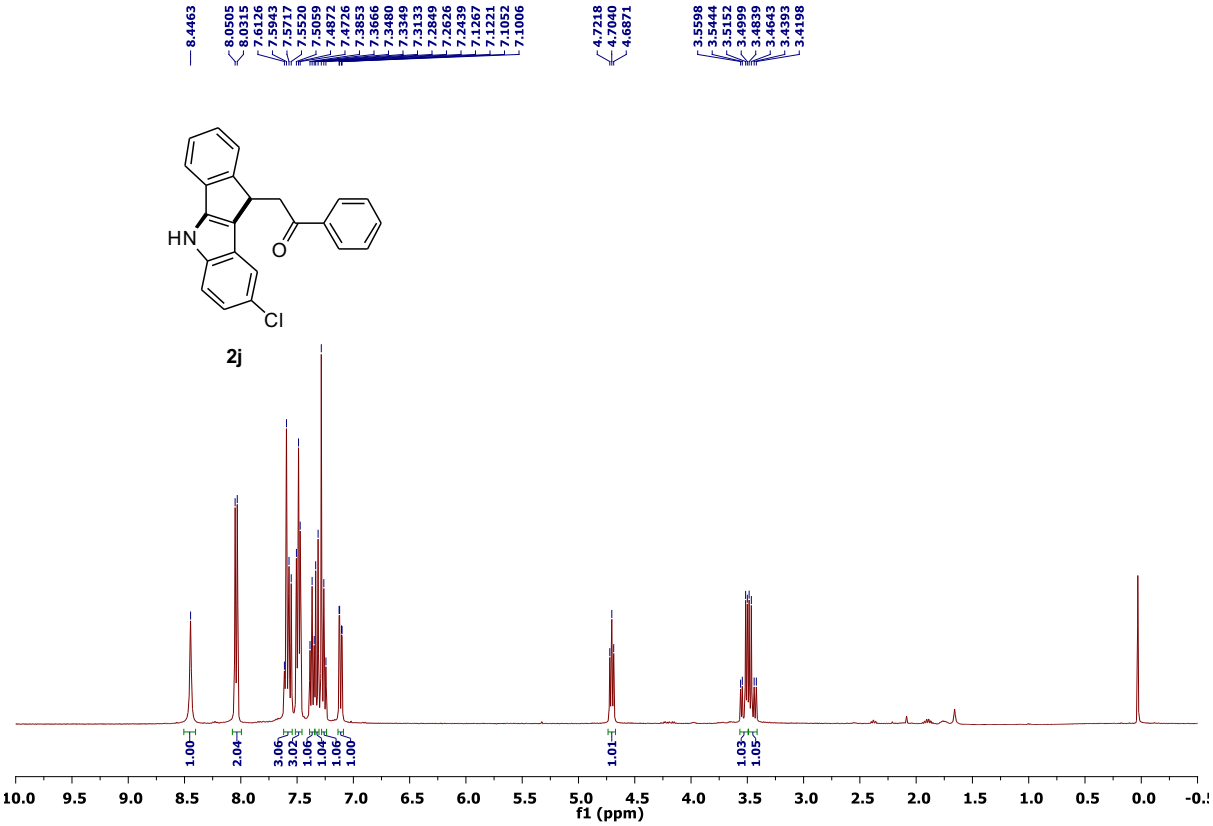
^{1}H NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz)



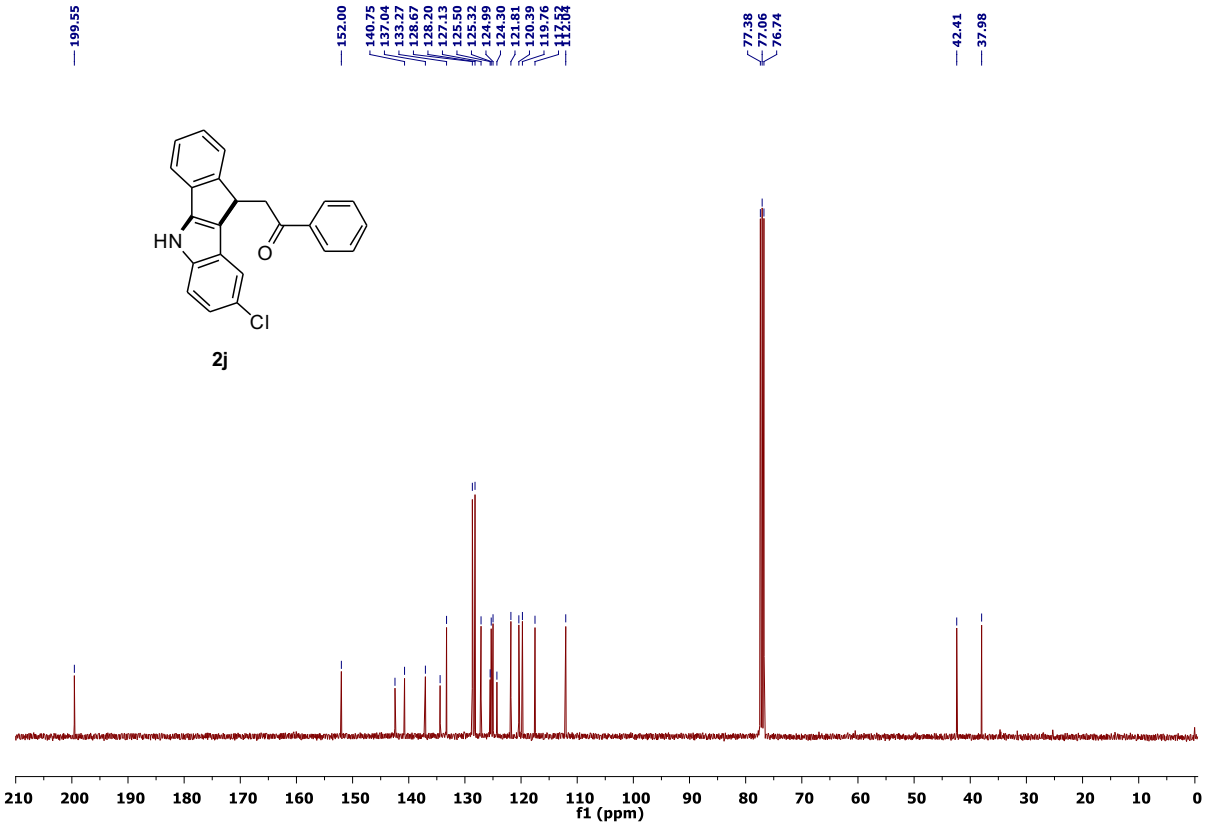
^{13}C{^{1}H} NMR spectrum of compound **2i** ($CDCl_3$, 101 MHz)



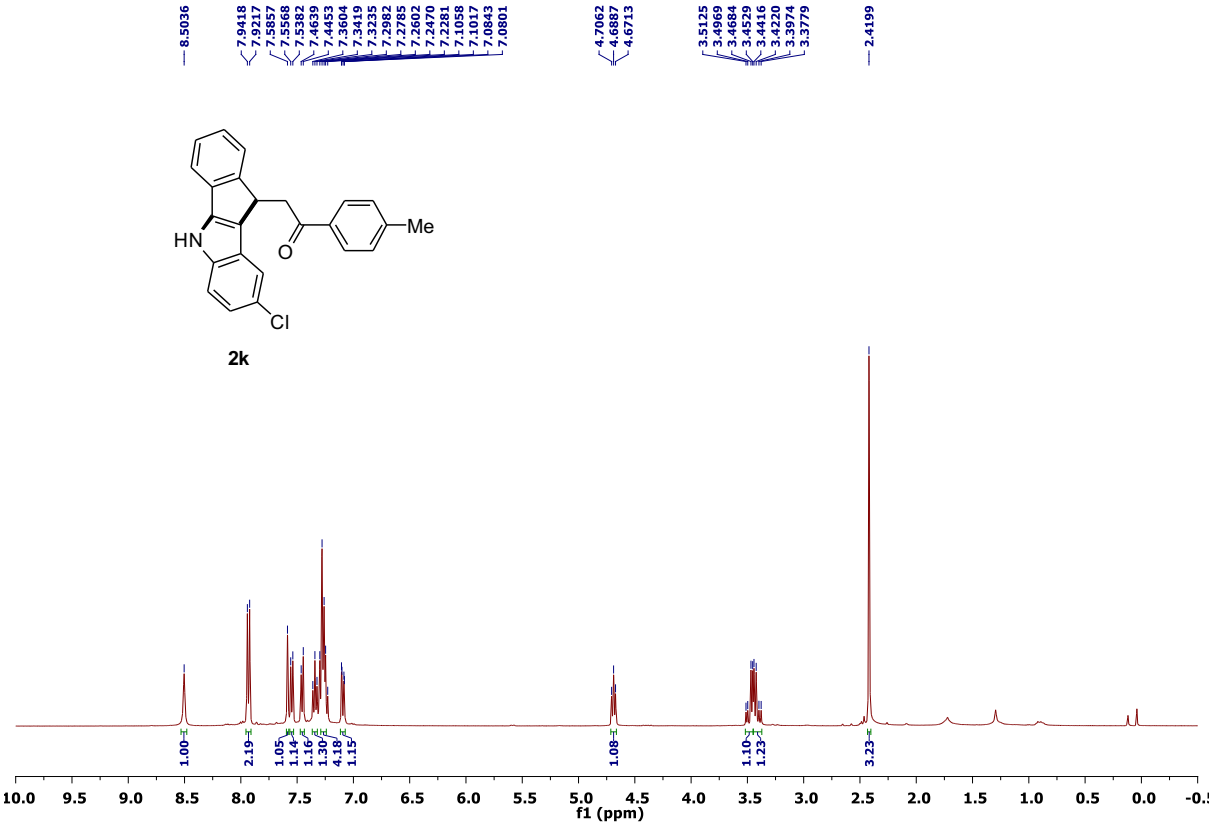
^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz)



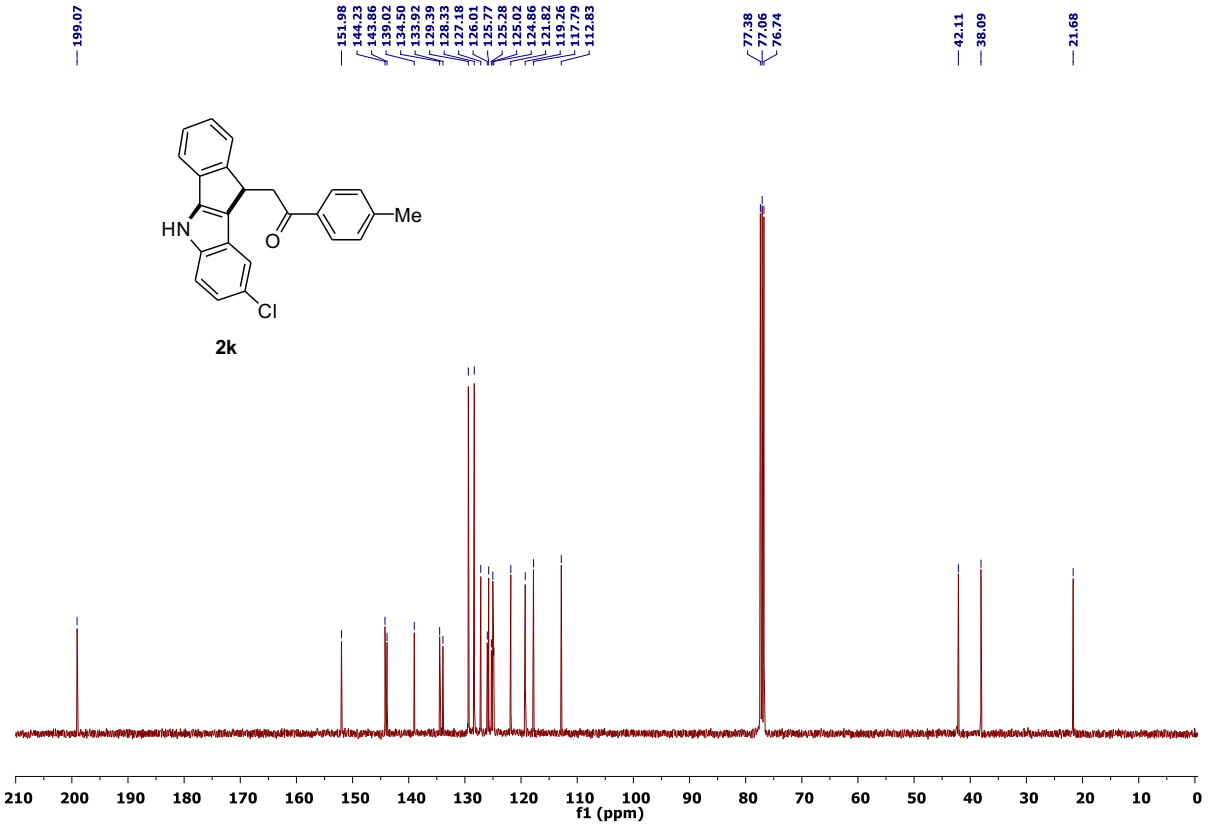
^{13}C{^{1}H} NMR spectrum of compound **2j** ($CDCl_3$, 101 MHz)



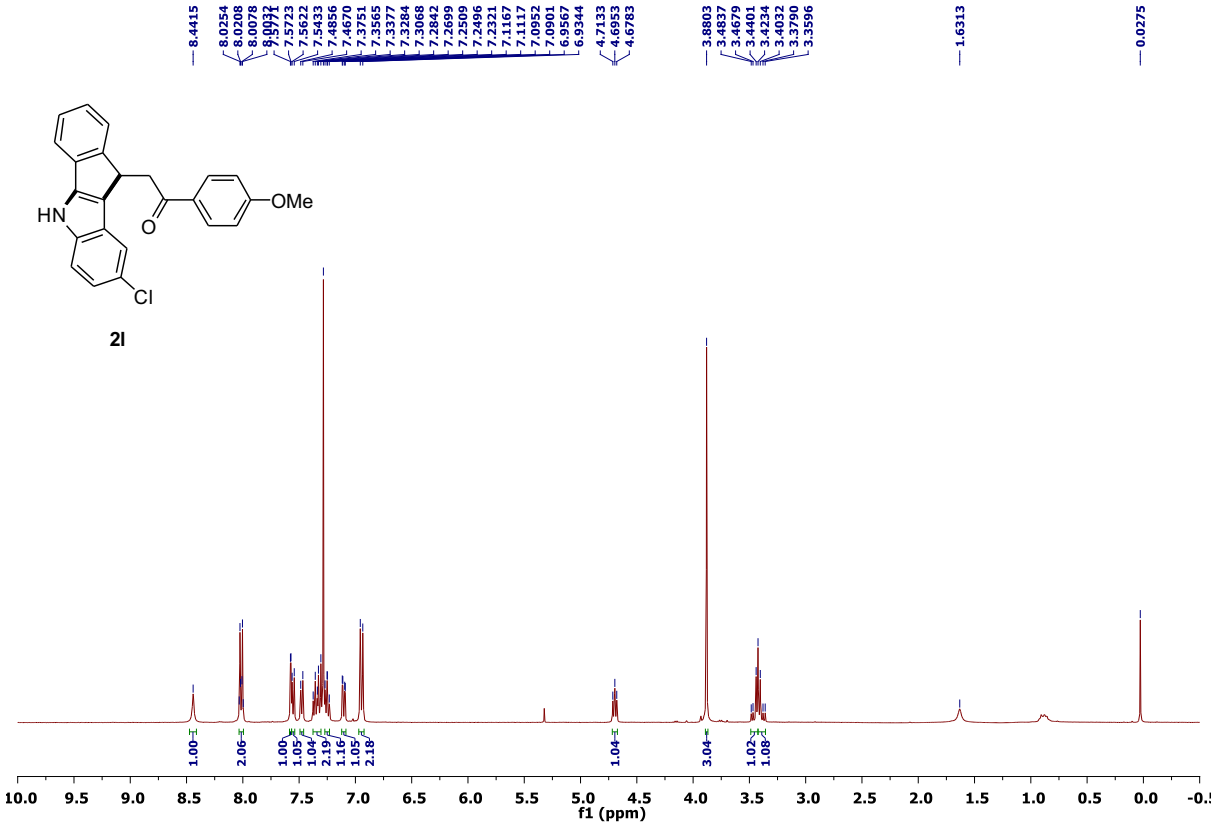
^{1}H NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz)



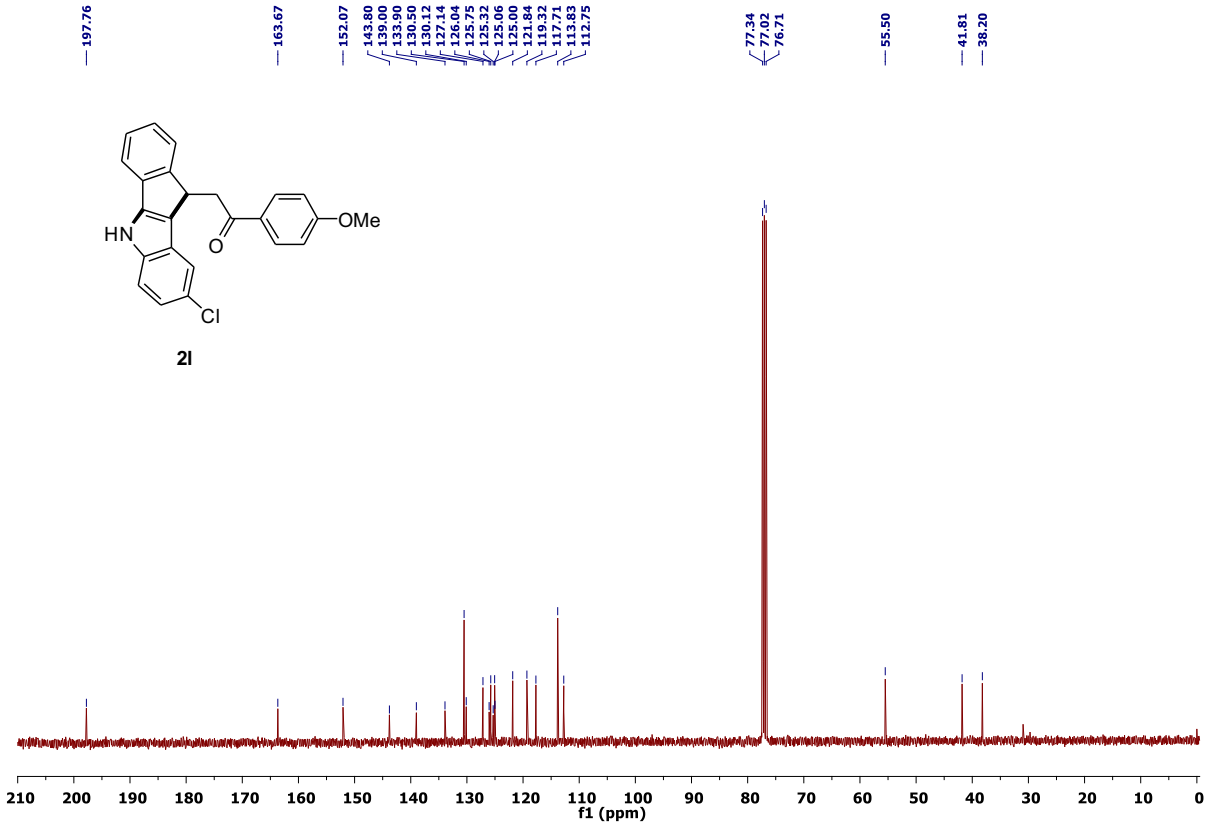
^{13}C{^{1}H} NMR spectrum of compound **2k** ($CDCl_3$, 101 MHz)



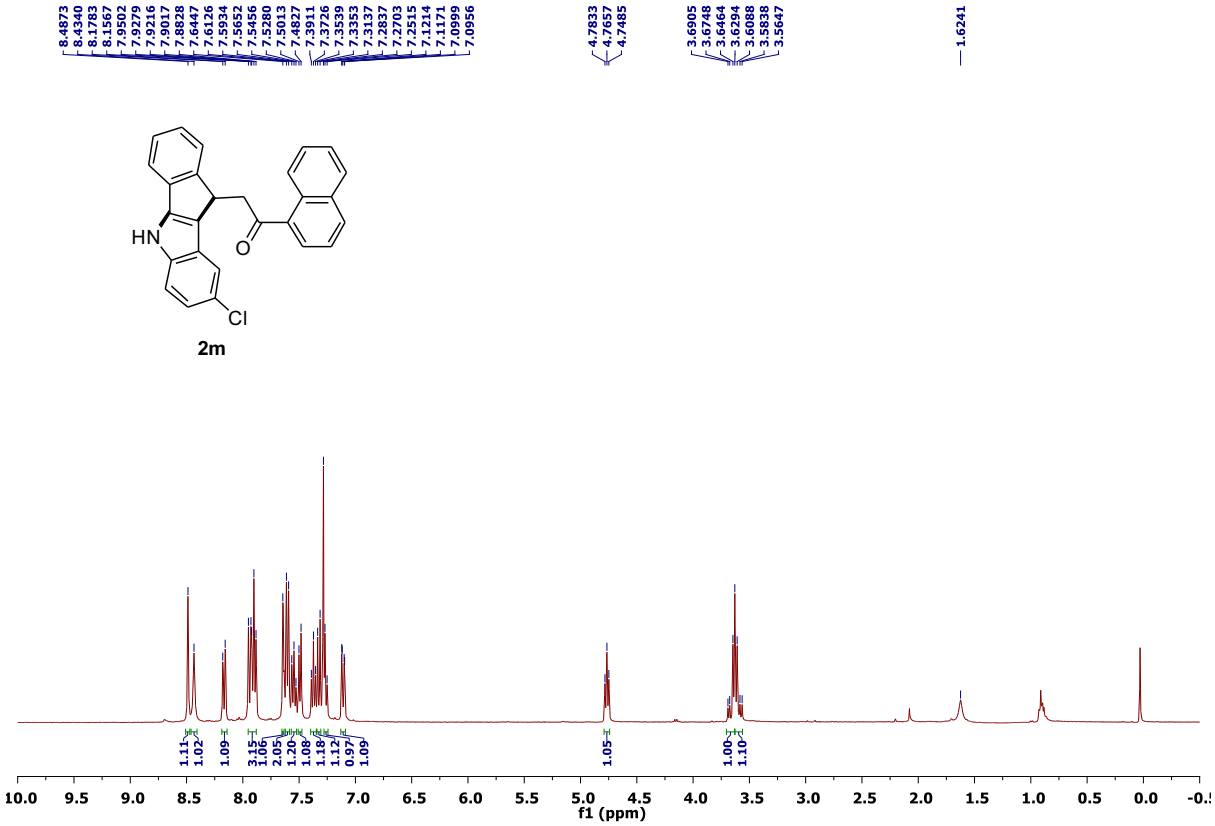
^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 400 MHz)



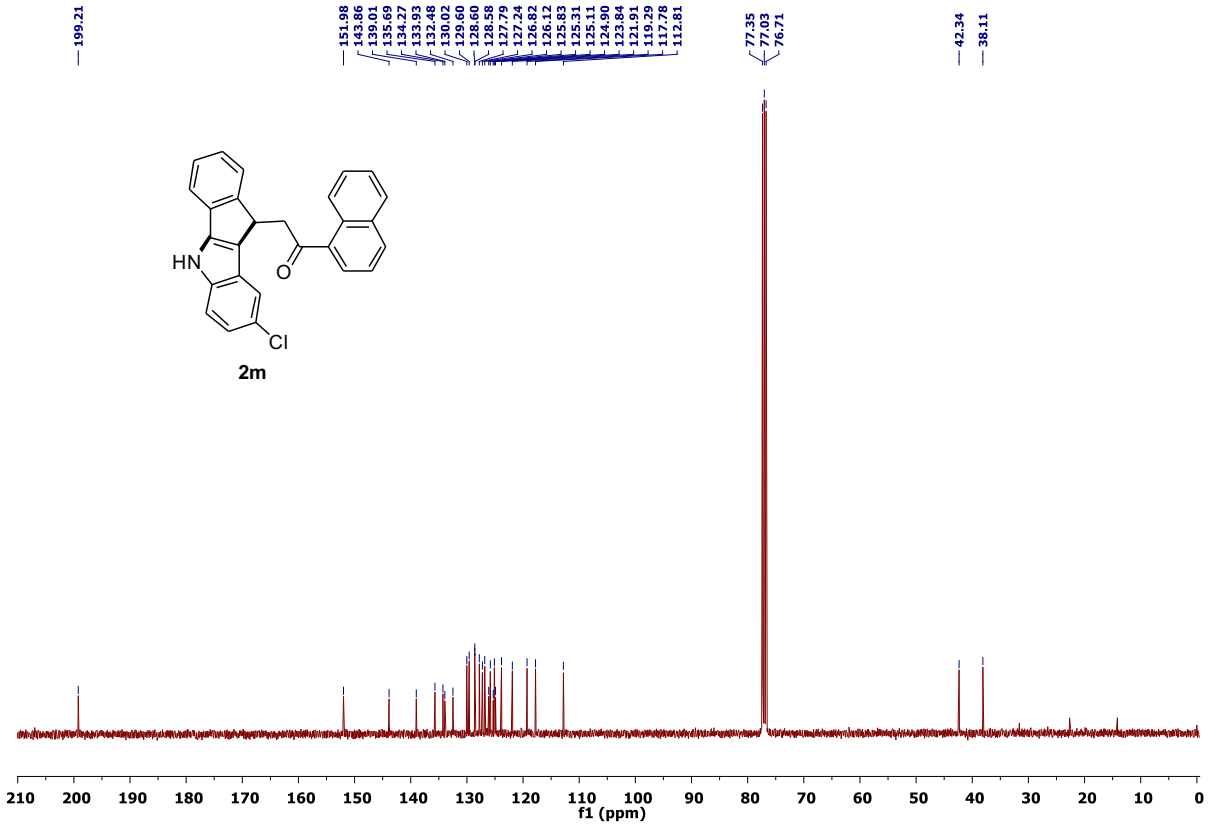
^{13}C{^{1}H} NMR spectrum of compound **2l** ($CDCl_3$, 101 MHz)



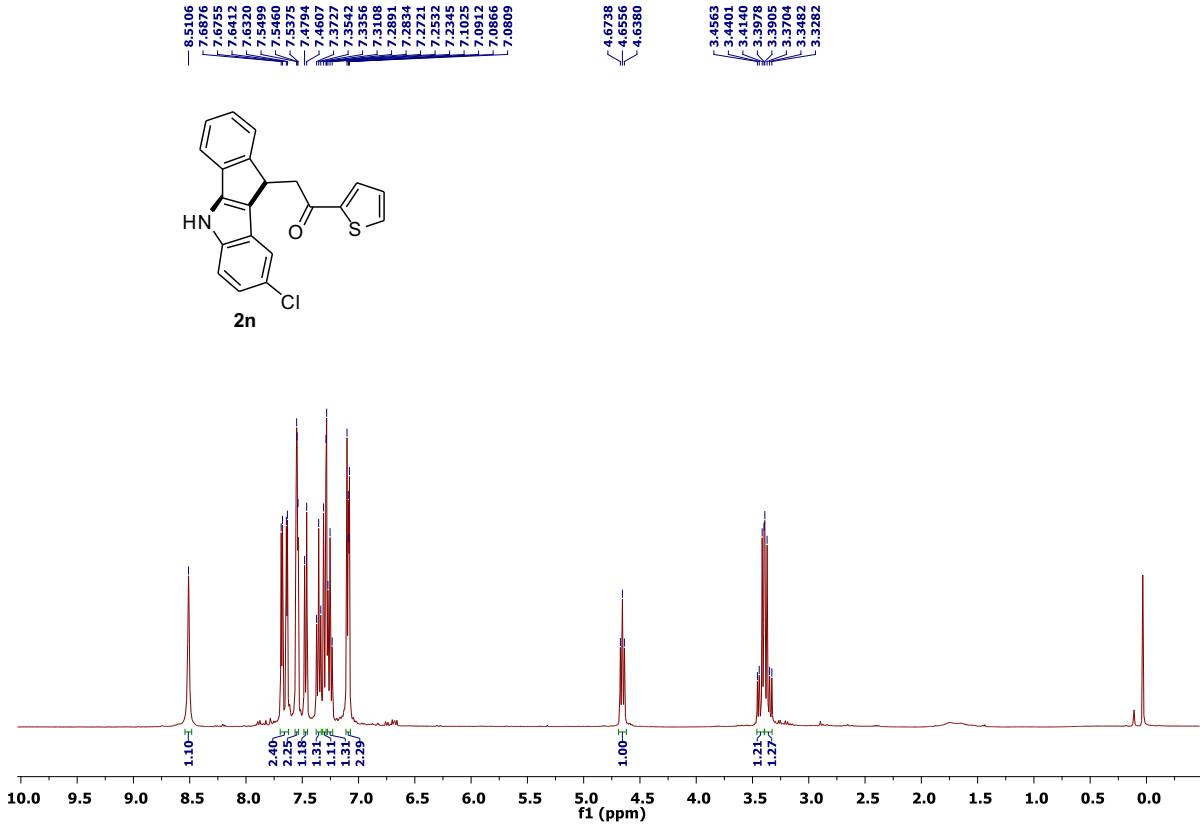
^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz)



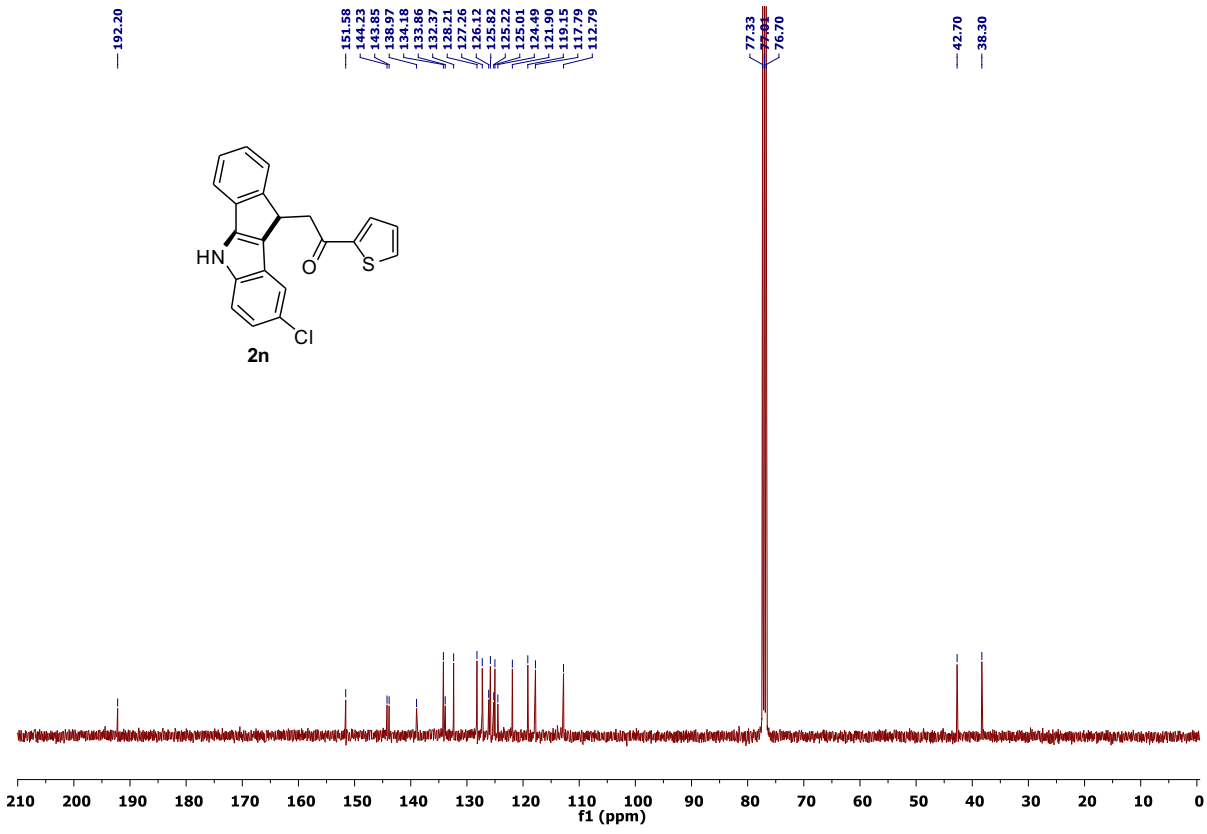
^{13}C{^{1}H} NMR spectrum of compound **2m** ($CDCl_3$, 101 MHz)



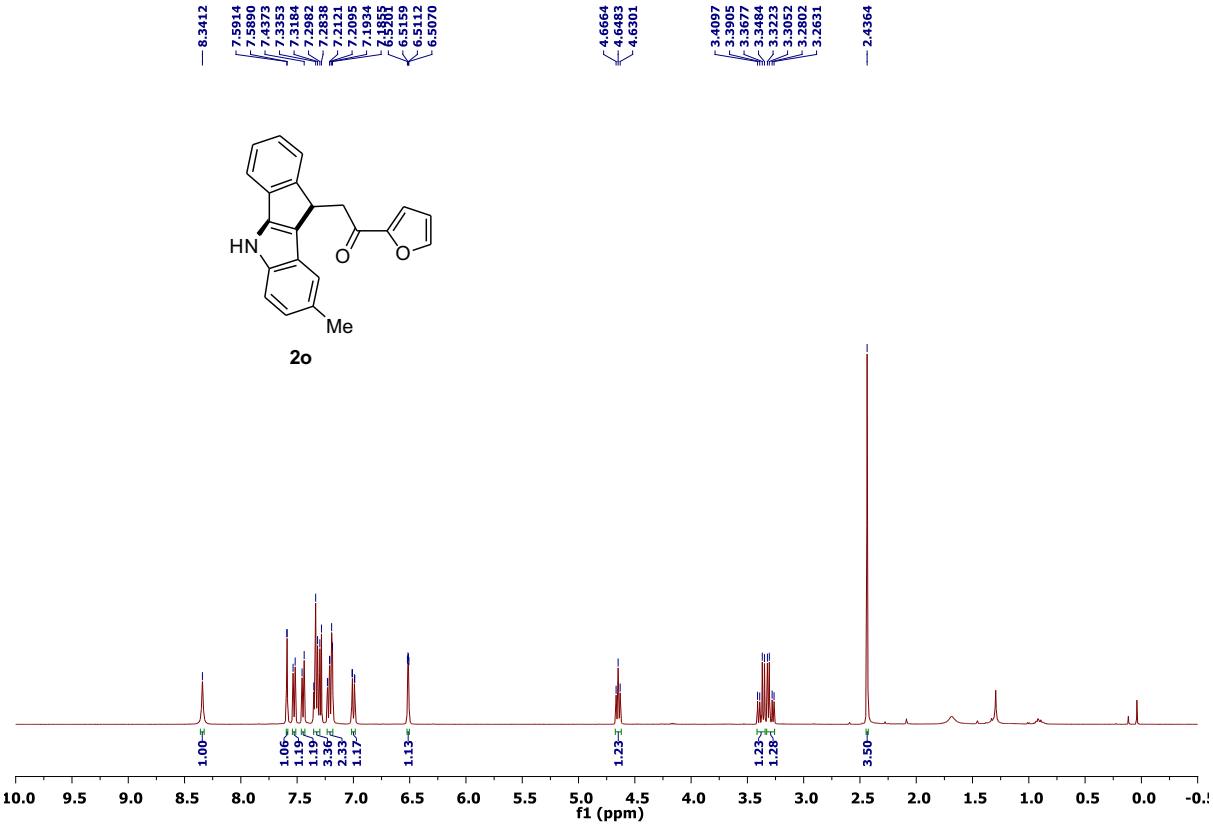
^{1}H NMR spectrum of compound **2n** ($CDCl_3$, 400 MHz)



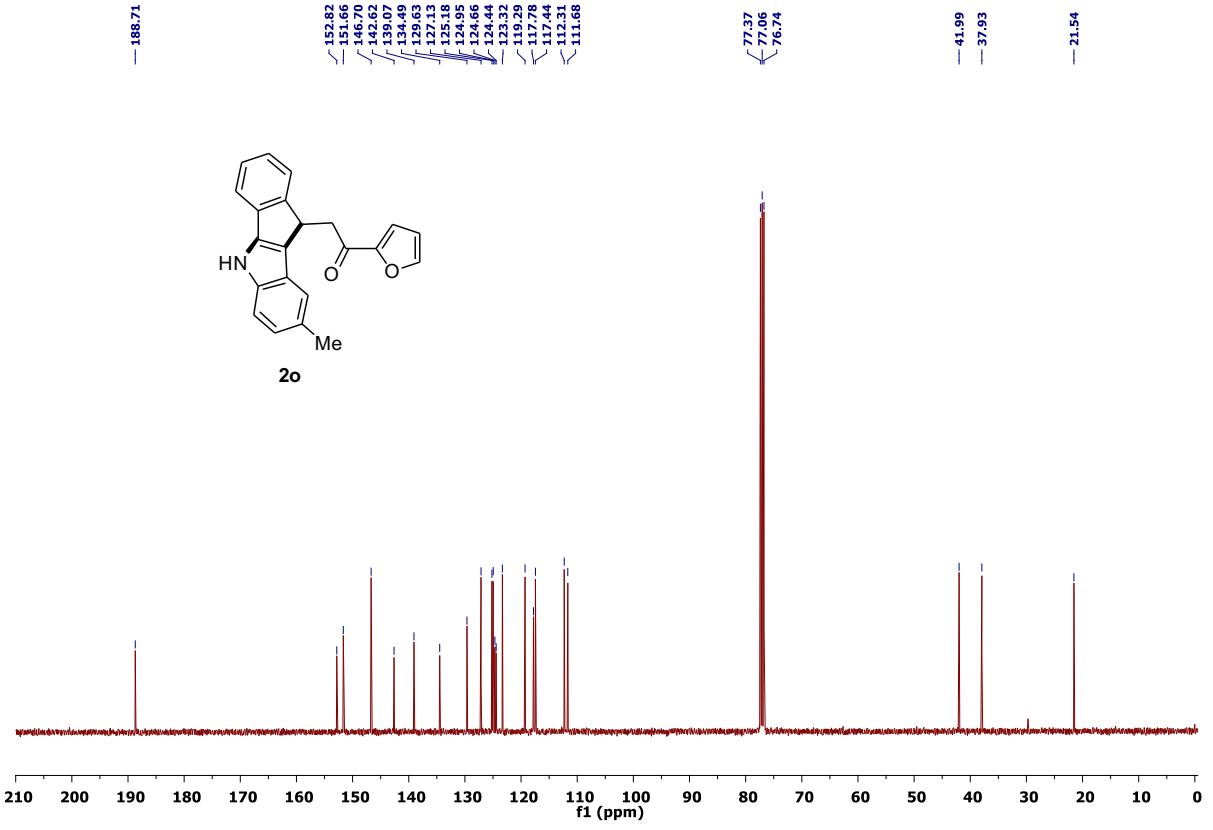
^{13}C{^{1}H} NMR spectrum of compound **2n** ($CDCl_3$, 101 MHz)



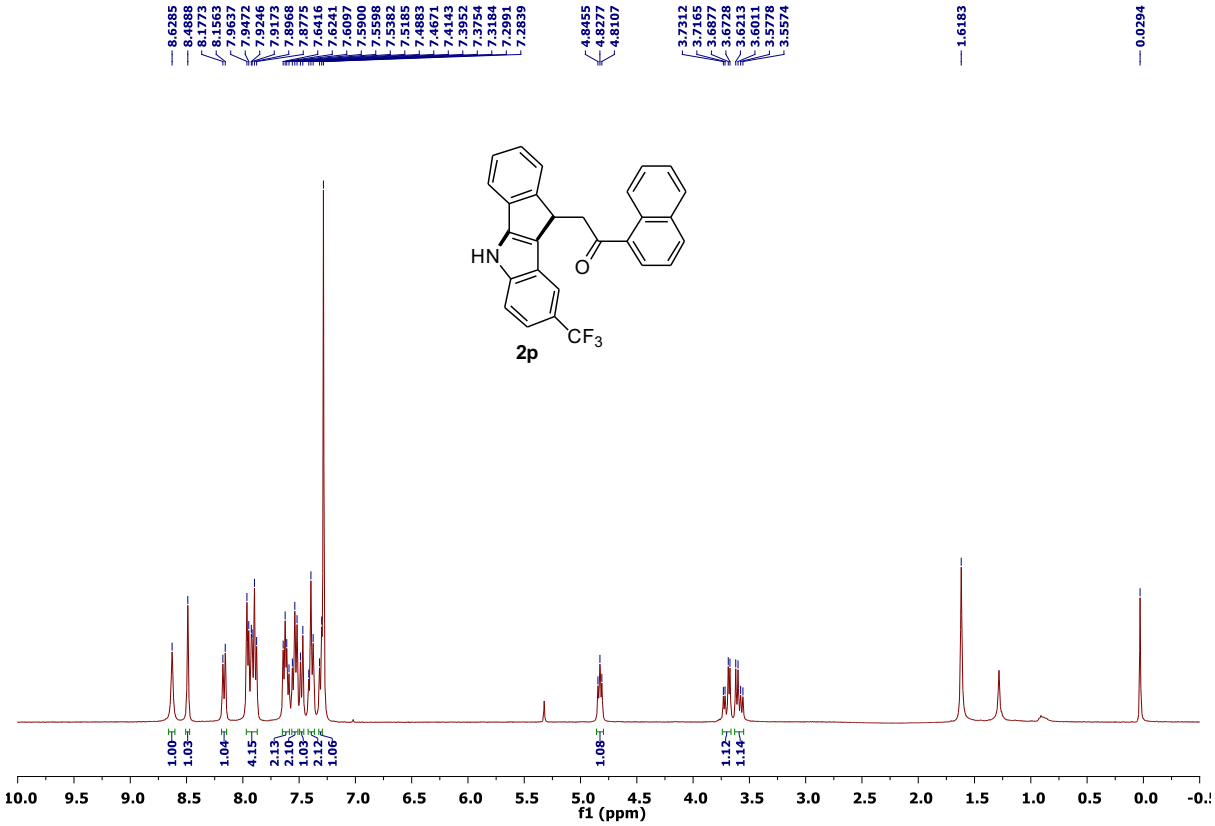
^{1}H NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz)



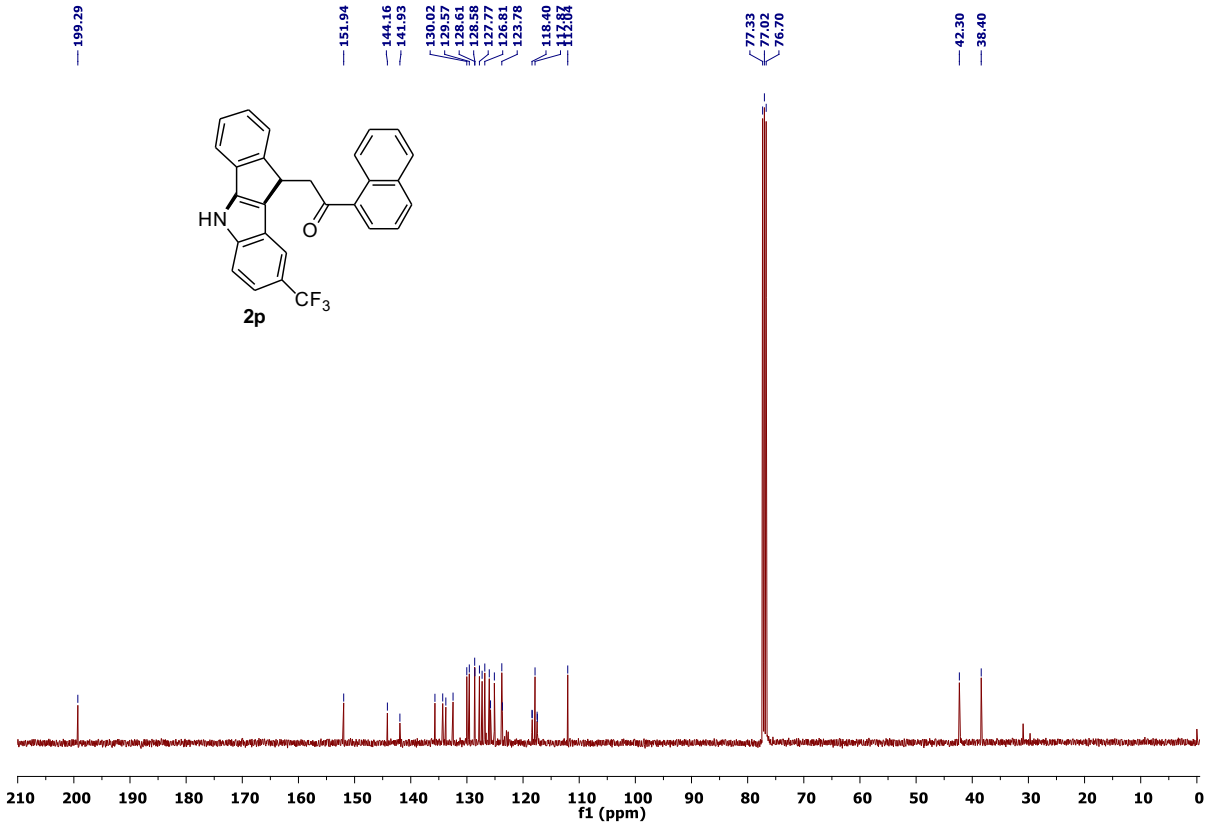
^{13}C{^{1}H} NMR spectrum of compound **2o** ($CDCl_3$, 101 MHz)



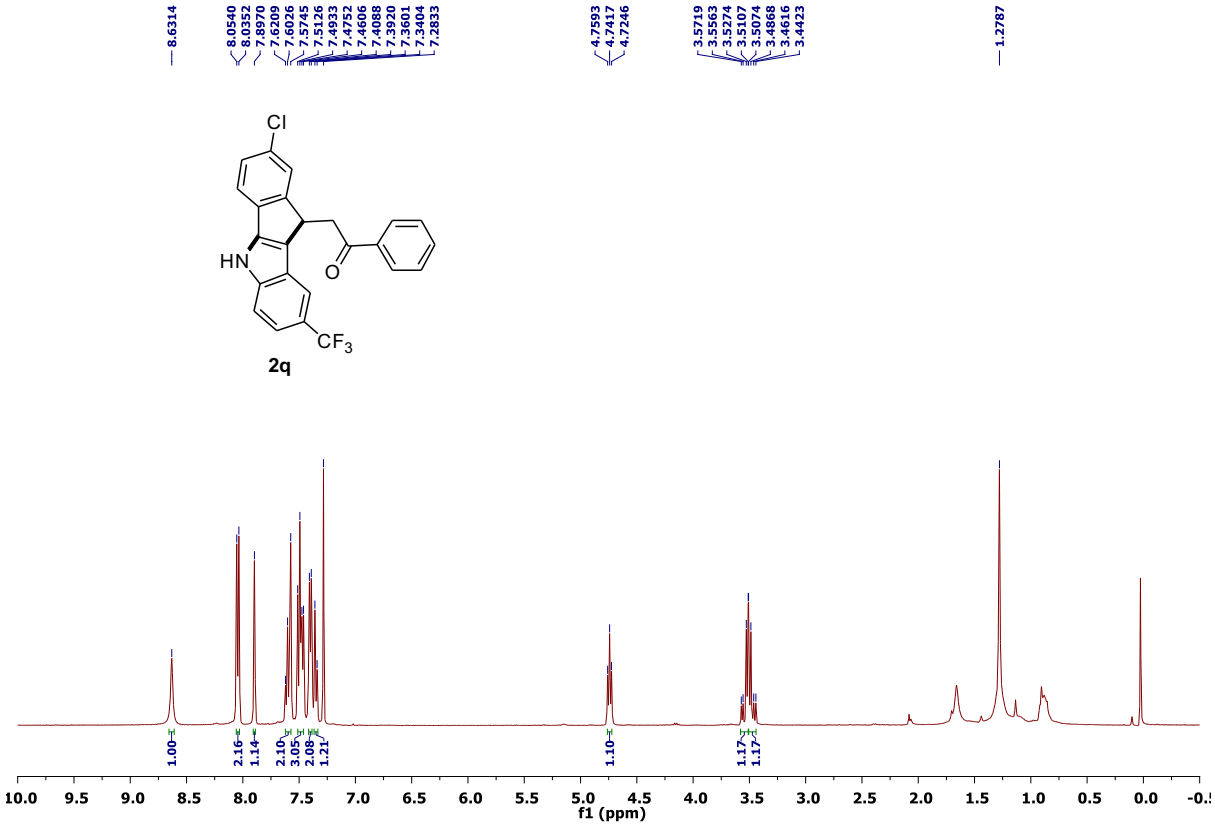
^{1}H NMR spectrum of compound **2p** ($CDCl_3$, 400 MHz)



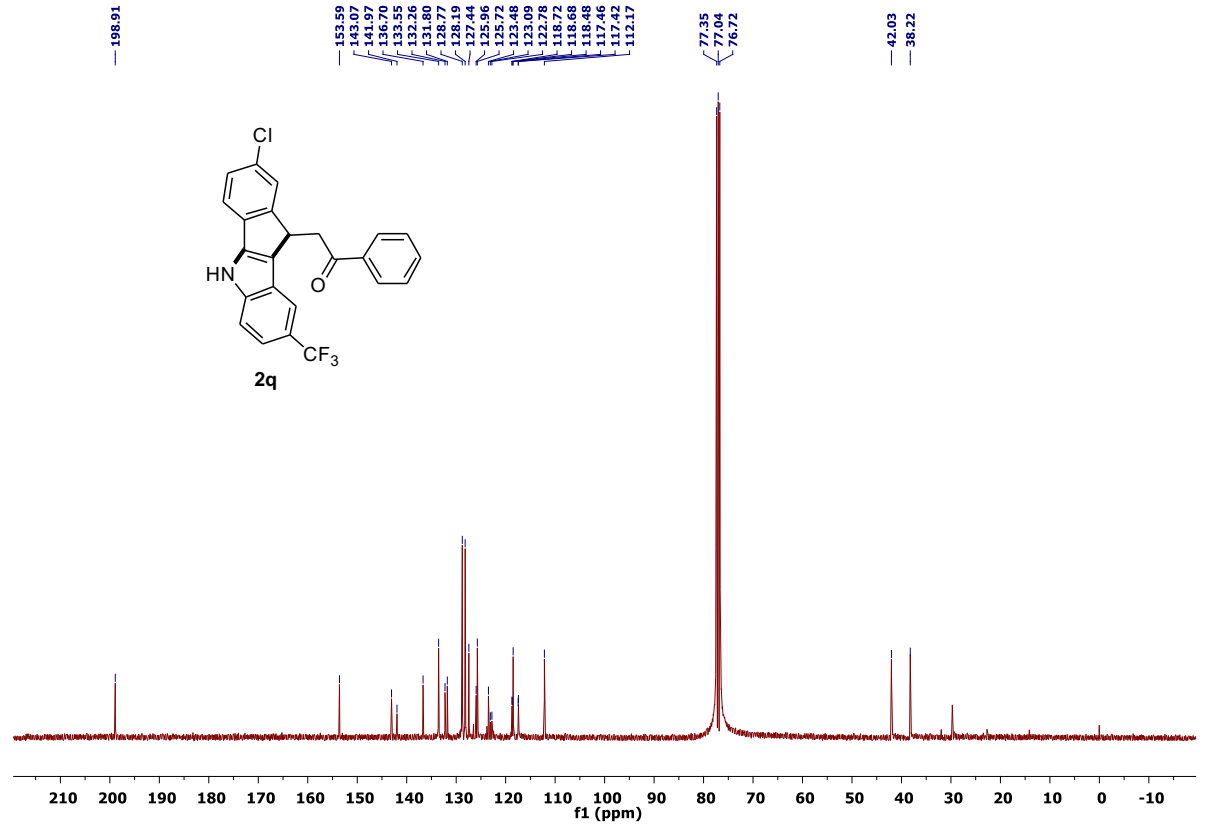
^{13}C{^{1}H} NMR spectrum of compound **2p** ($CDCl_3$, 101 MHz)



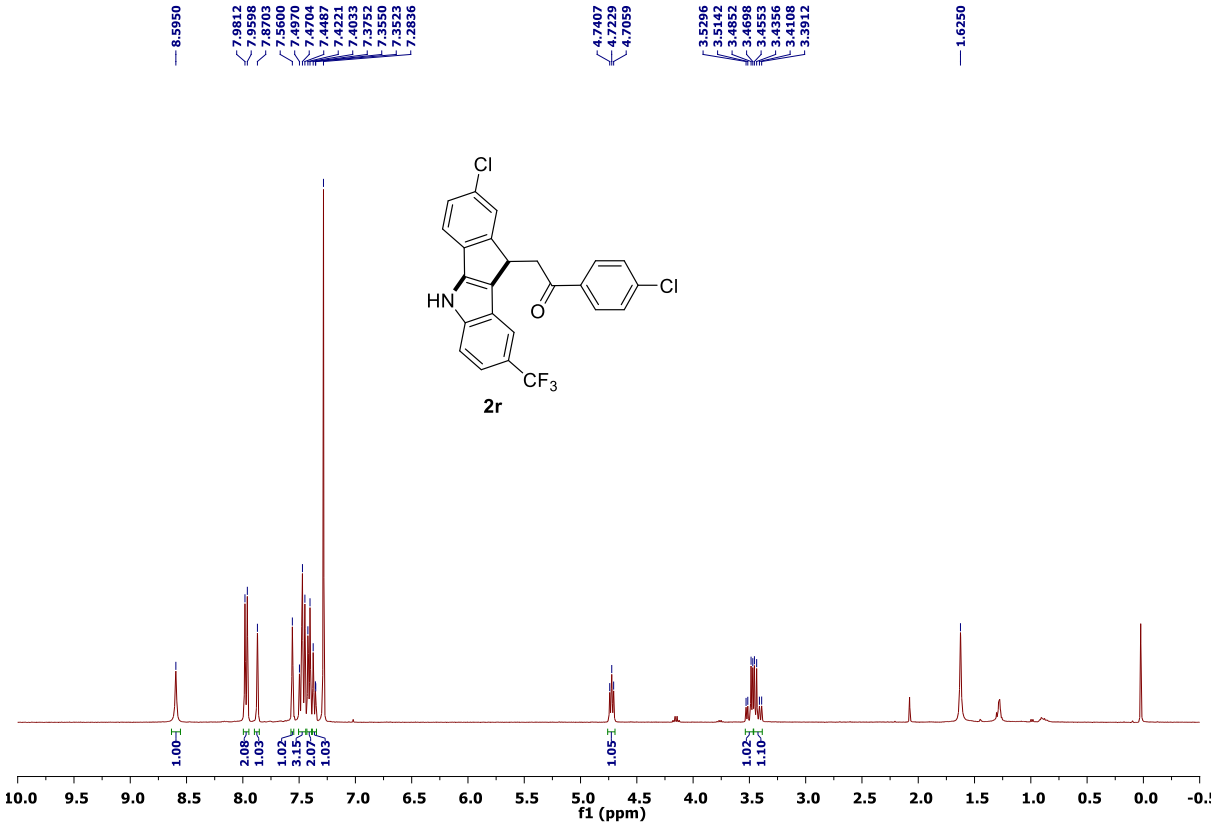
^{1}H NMR spectrum of compound **2q** ($CDCl_3$, 400 MHz)



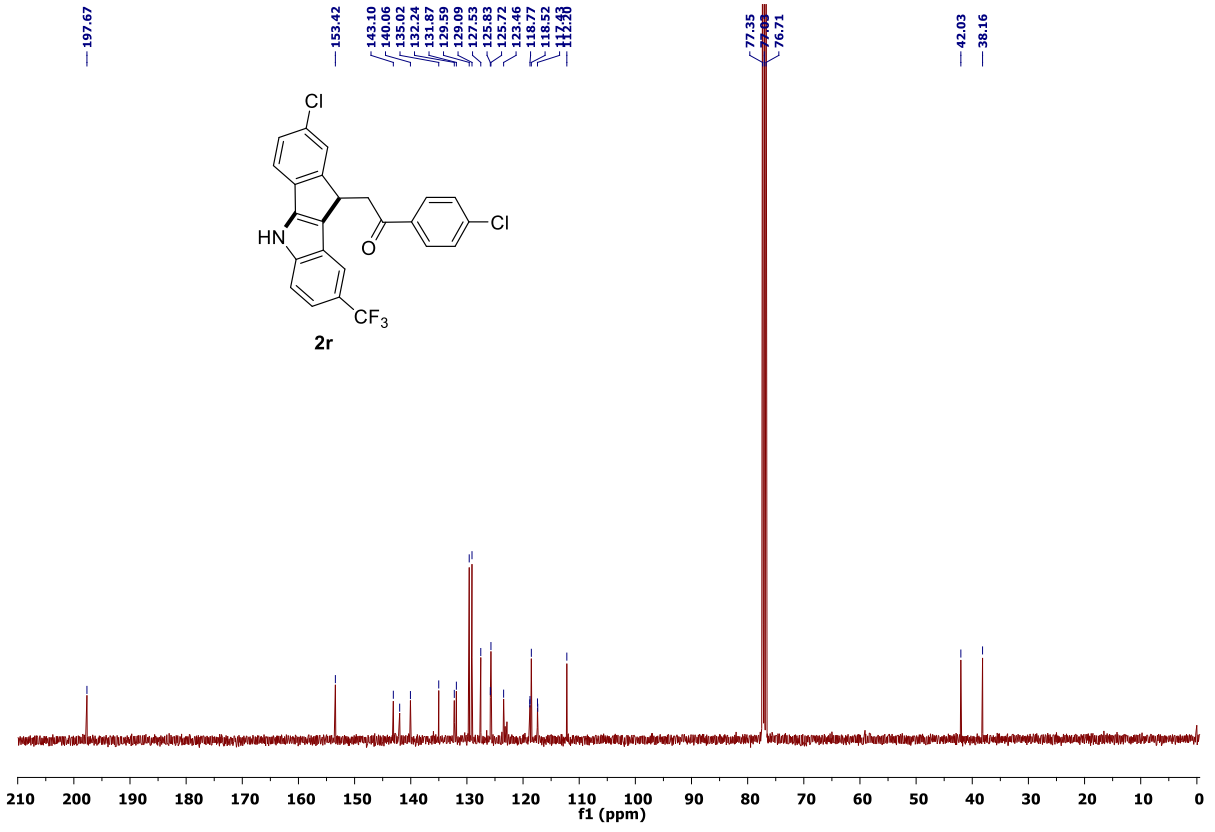
^{13}C{^{1}H} NMR spectrum of compound **2q** ($CDCl_3$, 101 MHz)



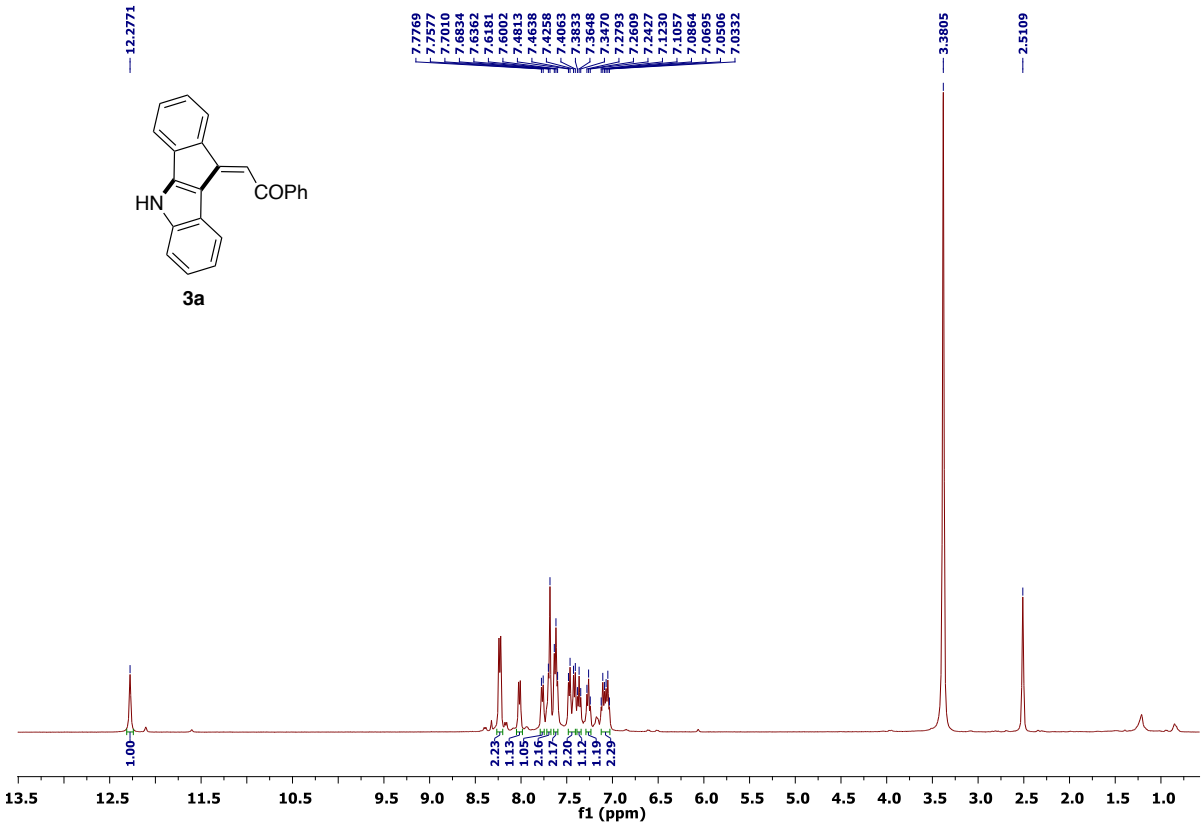
^{1}H NMR spectrum of compound **2r** ($CDCl_3$, 400 MHz)



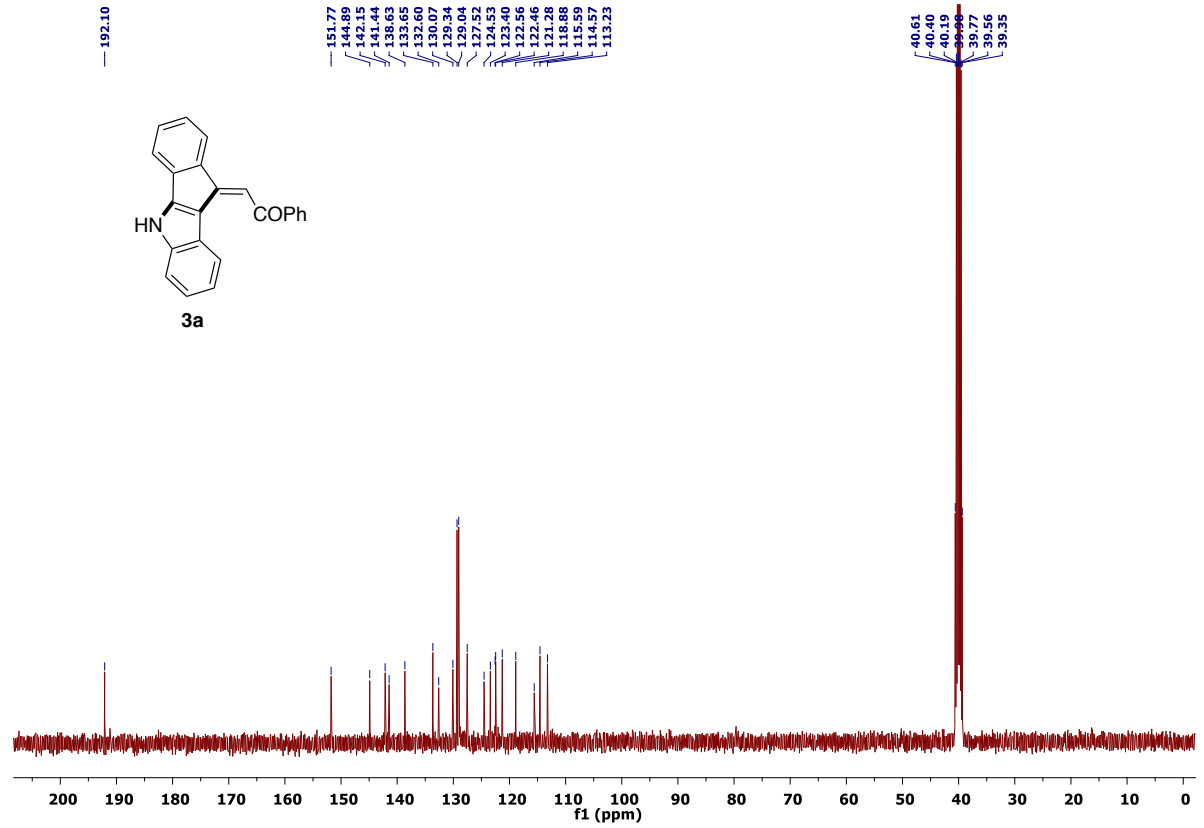
^{13}C{^{1}H} NMR spectrum of compound **2r** ($CDCl_3$, 101 MHz)



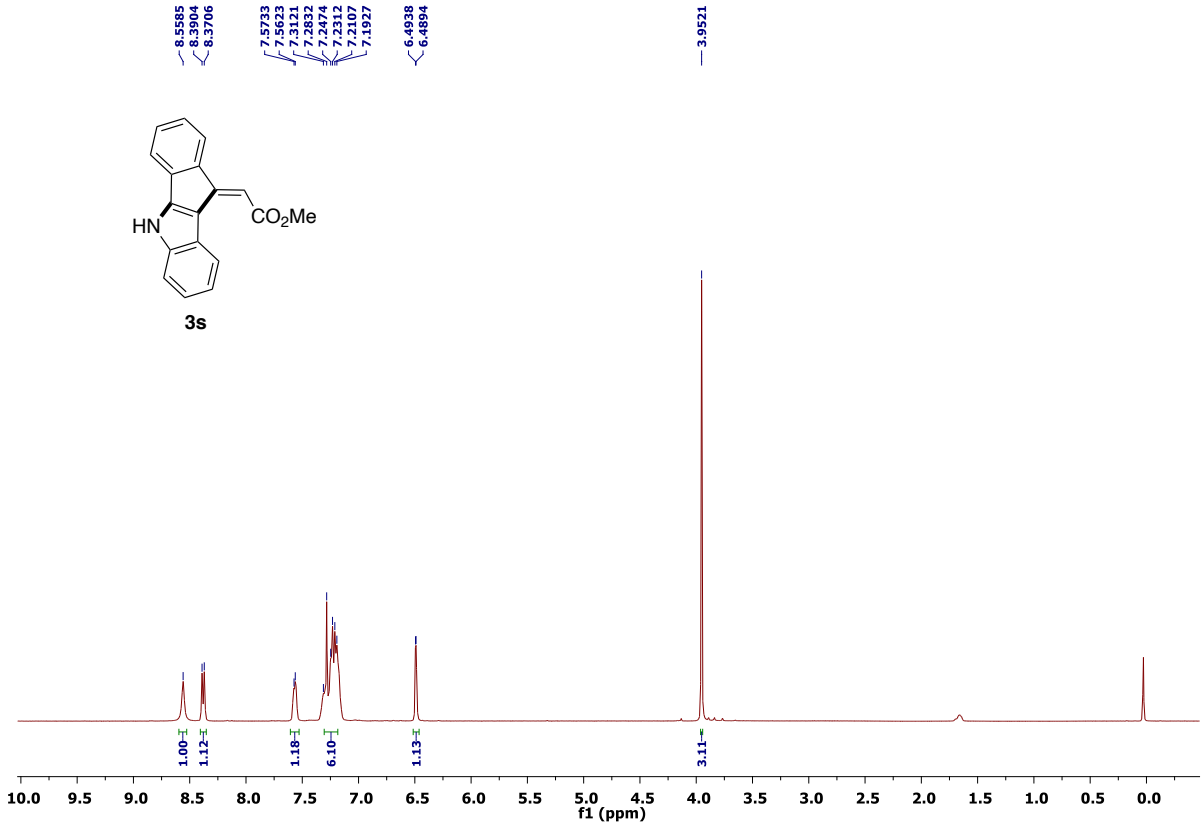
^{1}H NMR spectrum of compound **3a** (DMSO-d_6, 400 MHz)



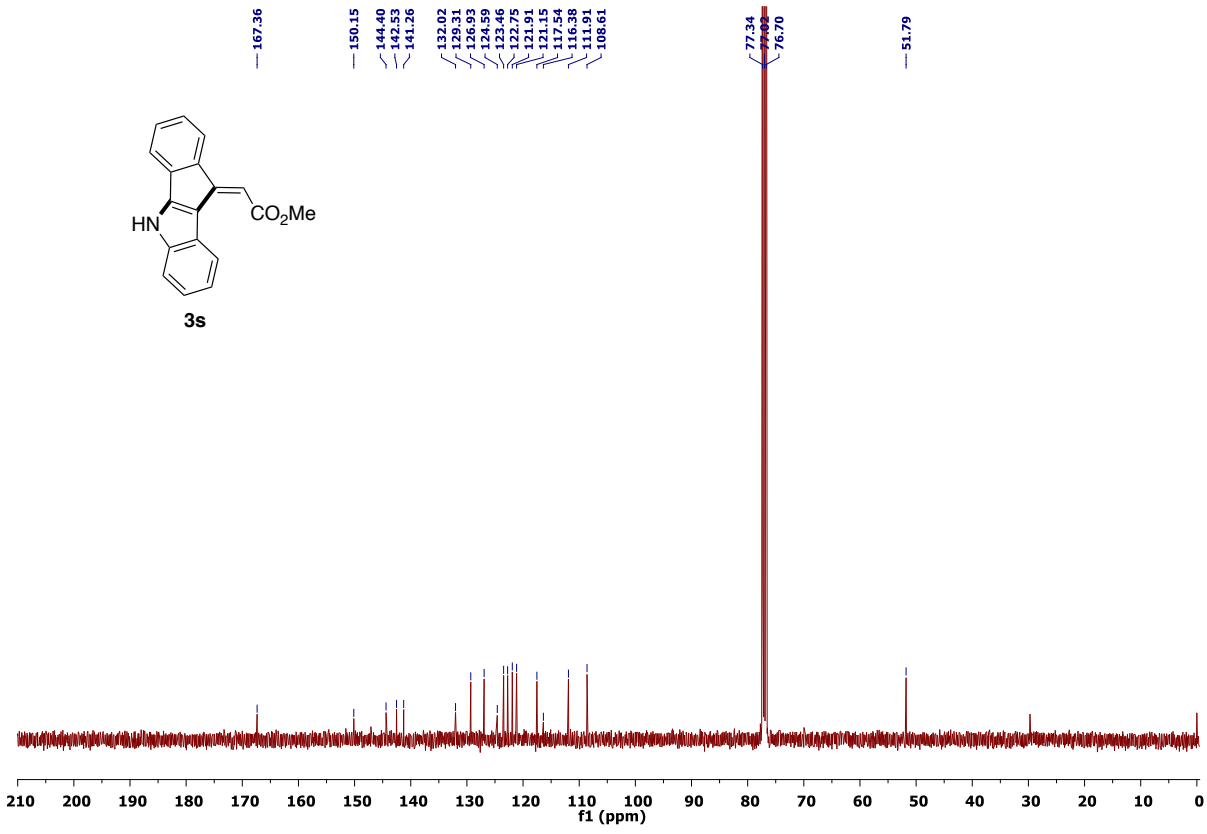
^{13}C{^{1}H} NMR spectrum of compound **3a** (DMSO-d_6, 101 MHz)



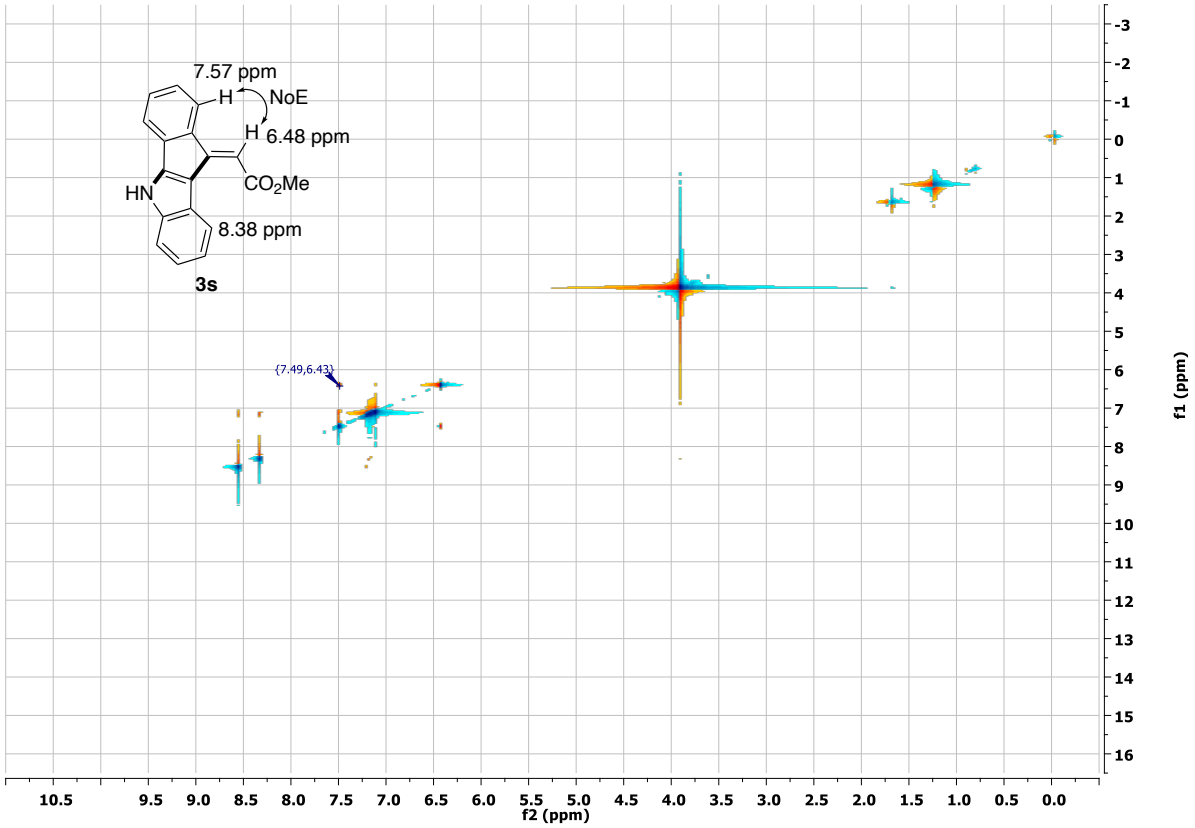
^{1}H NMR spectrum of compound **3s** ($CDCl_3$, 400 MHz)

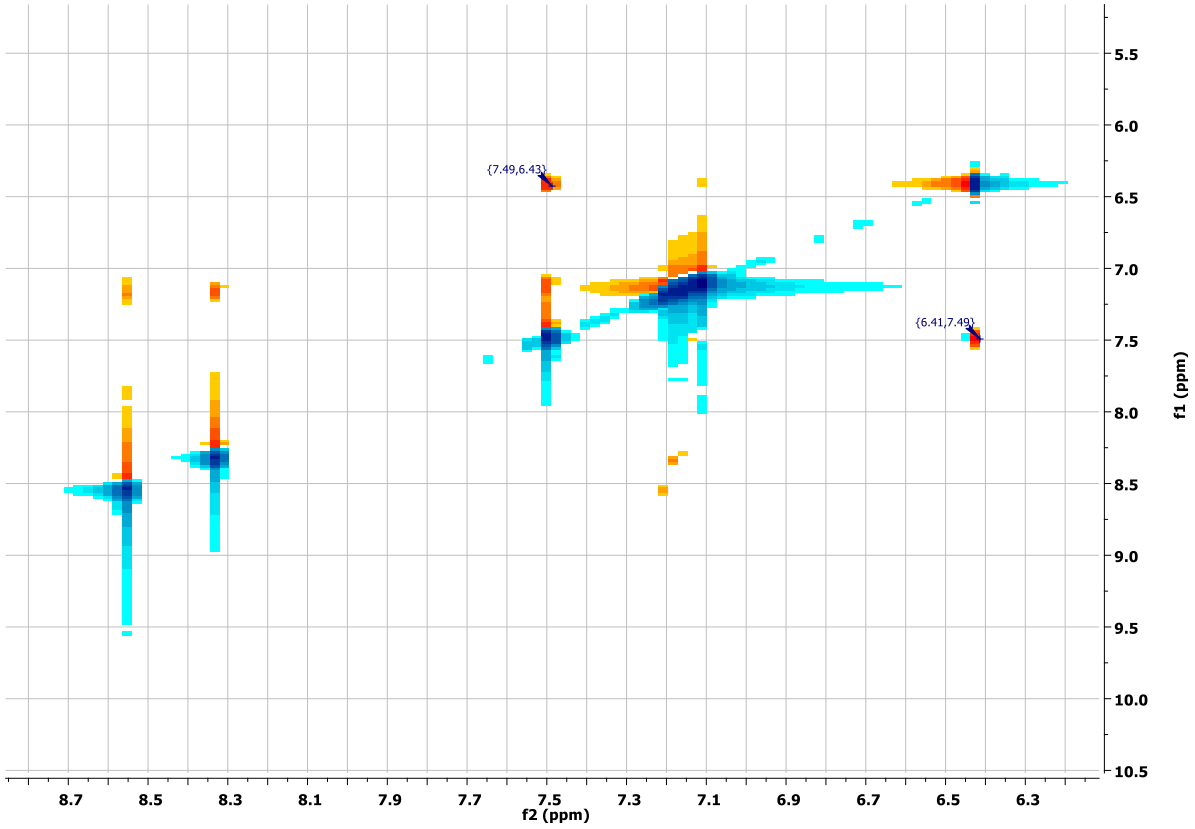


^{13}C{^{1}H} NMR spectrum of compound **3s** ($CDCl_3$, 101 MHz)

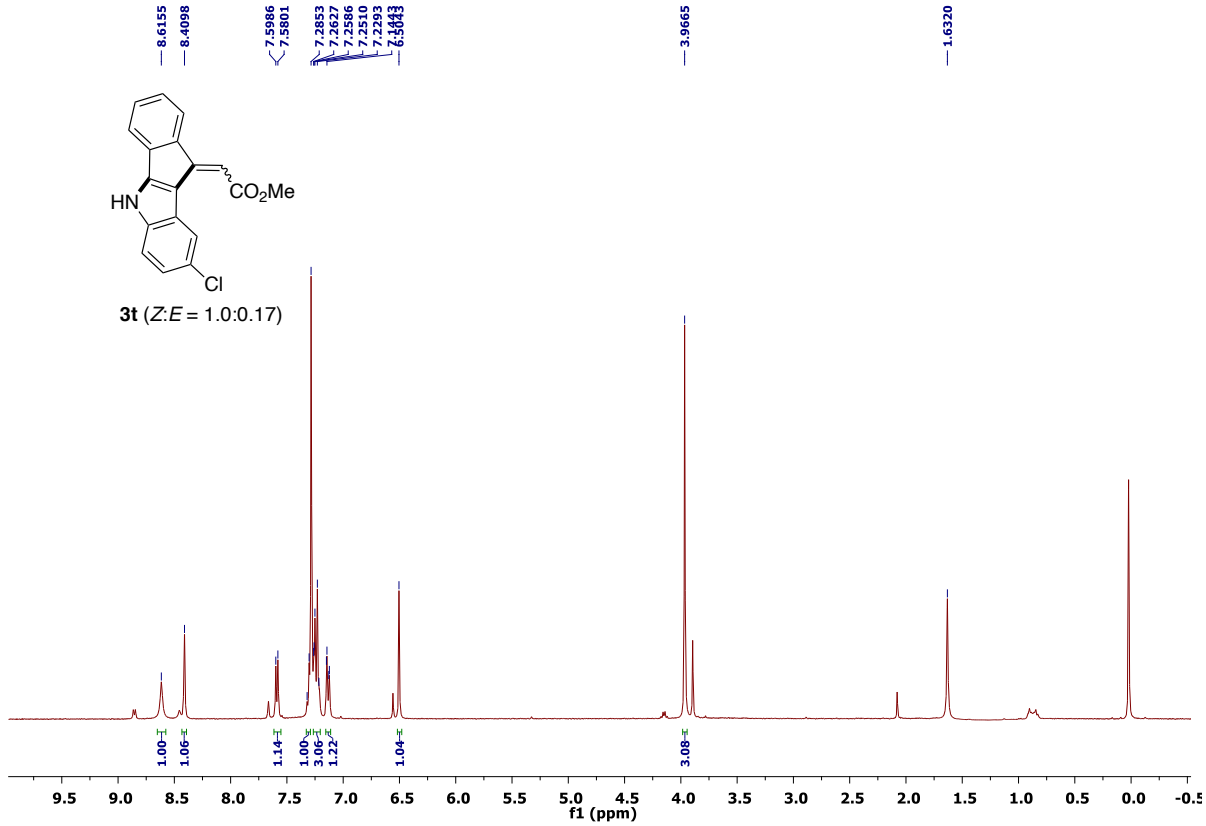


NOESY spectrum of compound **3s** ($CDCl_3$, 400 MHz)





^{1}H NMR spectrum of compound **3t** ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR spectrum of compound **3t** ($CDCl_3$, 101 MHz)