Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of enaminones and their difluoroboron complexes through domino aryl migration

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Experimental

General information

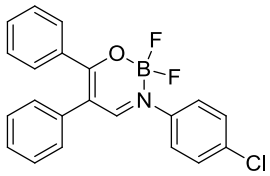
Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 (or $CDCl_3$) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-Q Ⅱ HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General procedure for the synthesis of 3

Example for the synthesis of **3a**: **3-(4-Chlorophenyl)-2,2-difluoro-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide**

Phenyl(3-phenyloxiran-2-yl)methanone (**1a**, 1 mmol) was introduced in a 25-mL reaction flask, 4-chloroaniline (**2a** 1.0 mmol), BF_3·Et_2O (1.2 mmol), and 1,4-dioxane (4.0 mL) were then successively added and stirred at 80 ^{o}C for 6 hours. After the completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was separated by column chromatography on silica gel (eluent, petroleum ether (b.p. 60-90 ^{o}C) /ethyl acetate 5:1 v/v) to afford the pure product **3a**.

3-(4-Chlorophenyl)-2,2-difluoro-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3a)



A yellow solid: 0.297 g, yield 78 %; Mp: 201-202 ^{o}C;

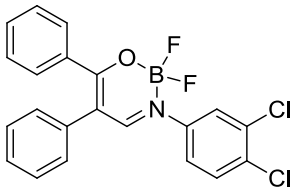
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.52 (s, 1H, CH), 7.72 (d, J = 8.8 Hz, 2H, Ar-H), 7.62-7.59 (m, 2H, Ar-H), 7.49-7.45 (m, 1H, Ar-H), 7.40-7.31 (m, 9H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.2, 164.9, 141.1, 135.4, 134.0, 133.1, 132.2, 130.5, 130.1, 129.8, 129.2, 128.7, 128.0, 125.8, 112.1;

IR (KBr, v, cm^{-1}): 1756, 1639, 1490, 1461, 1102, 843, 736, 569;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{15}BClFNO$, 364.0890 $[M-F]^{+}$; found: 364.0888.

3-(3,4-Dichlorophenyl)-2,2-difluoro-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3b)



A yellow solid: 0.299 g, yield 72 %; Mp: 182-183 ^{o}C;

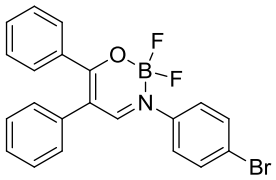
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.58 (s, 1H, CH), 8.03 (d, J = 2.4 Hz, 1H, Ar-H), 7.81 (d, J = 8.8 Hz, 1H, Ar-H), 7.70-7.68 (m, 1H, Ar-H), 7.50-7.46 (m, 1H, Ar-H), 7.40-7.32 (m, 9H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.9, 165.4, 142.0, 135.3, 133.9, 132.4, 132.2, 131.6, 131.1, 130.6, 130.2, 129.2, 128.8, 128.0, 126.0, 124.4, 112.2;

IR (KBr, v, cm^{-1}): 1614, 1575, 1418, 1273, 1018, 823, 701, 563;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{14}BCl_2FNO$, 398.0500 $[M-F]^+$; found: 398.0503.

3-(4-Bromophenyl)-2,2-difluoro-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3c)



A yellow solid: 0.369 g, yield 87 %; Mp: 196-198 ^{o}C;

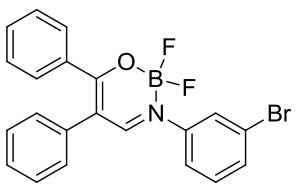
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.52 (s, 1H, CH), 7.75-7.72 (m, 2H, Ar-H), 7.65 (d, J = 8.8 Hz, 2H, Ar-H), 7.49-7.45 (m, 1H, Ar-H), 7.40-7.31 (m, 9H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.2, 164.8, 141.6, 135.4, 134.0, 132.7, 132.2, 130.5, 130.1, 129.2, 128.7, 128.0, 126.1, 121.6, 112.1;

IR (KBr, v, cm^{-1}): 1730, 1614, 1477, 1415, 1031, 832;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{15}BBrFNO$, 475.9614 $[M-F]^+$; found: 475.9611.

3-(3-Bromophenyl)-2,2-difluoro-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3d)



A yellow solid: 0.322 g, yield 76 %; Mp: 137-139 ^{o}C;

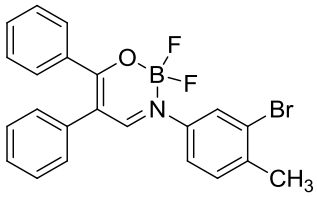
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.54 (s, 1H, CH), 7.93 (t, J = 1.6 Hz, 1H, Ar-H), 7.71-7.64 (m, 2H, Ar-H), 7.51-7.45 (m, 2H, Ar-H), 7.39-7.32 (m, 9H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.5, 165.3, 143.7, 135.4, 134.0, 132.2, 131.7, 131.4, 130.6, 130.1, 129.2, 128.8, 128.0, 126.8, 123.2, 122.4, 112.1;

IR (KBr, v, cm^{-1}): 1752, 1608, 1503, 1476, 1036, 819, 708, 552;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{15}BBrFNO$, 408.0394 $[M-F]^+$; found: 408.0397.

3-(3-Bromo-4-methylphenyl)-2,2-difluoro-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3e)



A yellow solid: 0.373 g, yield 85 %; Mp: 132-134 ^{o}C;

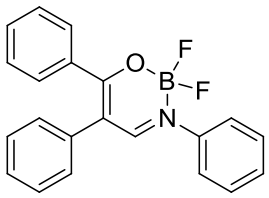
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.51 (s, 1H, CH), 7.95 (d, J = 2.0 Hz, 1H, Ar-H), 7.61 (d, J = 10.0 Hz, 1H, Ar-H), 7.51-7.45 (m, 2H, Ar-H), 7.39-7.31(m, 9H, Ar-H),2.40(s, 3H, CH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.1, 164.9, 141.3, 137.8, 135.4, 134.0, 132.1, 131.9, 130.6, 130.1, 129.2, 128.7, 127.9, 127.2, 124.7, 123.2, 97.2, 54.9;

IR (KBr, v, cm^{-1}): 1613, 1575, 1475, 1438, 1044, 833;

HRMS (APCI-TOF): m/z calcd for: $C_{22}H_{17}BBrFNO$, 422.0550 $[M-F]^+$; found : 422.0561.

2,2-Difluoro-3,5,6-triphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3f)



A yellow solid: 0.281 g, yield 81 %; Mp: 175-177 ^{o}C;

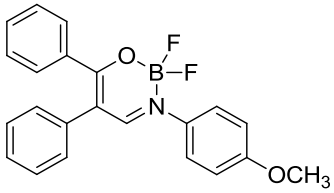
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.48 (s, 1H, CH), 7.67 (d, J = 8.0 Hz, 2H, Ar-H), 7.52 (t, J = 7.2 Hz, 2H, Ar-H), 7.46 (s, 2H, Ar-H), 7.39-7.30 (m, 9H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.7, 164.7, 142.4, 135.5, 134.1, 132.1, 130.5, 130.1, 129.8, 129.2, 128.7, 128.6, 127.9, 124.0, 111.9;

IR (KBr,v, cm^{-1}): 1611, 1574, 1476, 1438, 1038, 834, 695, 553;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{16}BFNO$, 328.1309 $[M-F]^+$; found: 328.1311.

2,2-Difluoro-3-(4-methoxyphenyl)-5,6-diphenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3g)



A yellow solid: 0.328 g, yield 87 %; Mp: 162-164 ^oC;

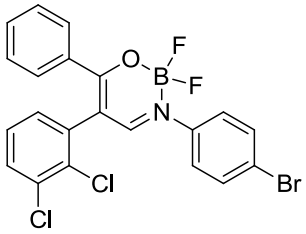
^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.41 (s, 1H, CH), 7.61(d, J = 9.2 Hz, 2H, Ar-H), 7.45–7.43 (m, 1H, Ar-H), 7.38-7.30 (m, 9H, Ar-H), 7.06 (d, J = 8.8 Hz, 2H, Ar-H), 3.81 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.8, 163.7, 159.5, 135.6, 135.4, 134.2, 131.9, 130.5, 130.0, 129.2, 128.7, 127.9, 125.1, 114.9, 97.2, 56.0;

IR (KBr,v, cm^{-1}): 1616, 1501, 1436, 1373, 1039, 822;

HRMS (APCI-TOF): m/z calcd for: $C_{22}H_{18}BFNO_2$, 358.1415 $[M-F]^+$; found: 358.1415.

3-(4-Bromophenyl)-5-(2,3-dichlorophenyl)-2,2-difluoro-6-phenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3h)



A yellow solid: 0.289 g, yield 74 %; Mp: 187-189 ^oC;

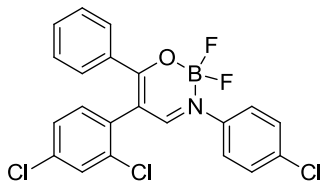
^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.58 (s, 1H, CH), 7.74 (d, J = 8.4 Hz, 2H, Ar-H), 7.67 (d, J = 8.0 Hz, 1H ,Ar-H), 7.60 (t, J = 8.4 Hz, 3H, Ar-H), 7.50-7.37 (m, 6H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 172.1, 164.6, 141.3, 136.4, 133.8, 132.8, 132.7, 132.7, 132.6, 132.4, 131.1, 129.2, 129.1, 129.0, 126.0, 121.7, 109.2;

IR (KBr, v, cm^{-1}): 1648, 1569, 1504, 1026, 1042, 827, 670, 528;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{13}BBrCl_2FNO$, 475.9614 $[M-F]^+$; found: 475.9611.

3-(4-Chlorophenyl)-5-(2,4-dichlorophenyl)-2,2-difluoro-6-phenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3i)



A yellow solid: 0.287 g, yield 64 %; Mp: 205-207 ^{o}C;

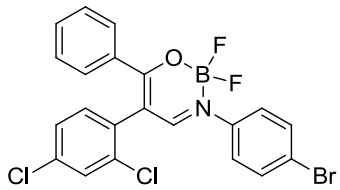
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.54 (s, 1H, CH), 7.70-7.60 (m, 6H, Ar-H), 7.53-7.49 (m, 2H, Ar-H), 7.42-7.37 (m, 4H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 172.2, 164.7, 140.9, 135.4, 134.9, 134.3, 133.9, 133.3, 133.1, 132.7, 129.9, 129.6, 129.3, 129.0, 128.5, 125.6, 108.1;

IR (KBr, v, cm^{-1}): 1675, 1593, 1507, 1469, 1134, 867;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{13}BCl_3FNO$, 432.0110 $[M-F]^+$; found: 432.0113.

3-(4-Bromophenyl)-5-(2,4-dichlorophenyl)-2,2-difluoro-6-phenyl-2*H*-1,3,2-oxazaborinin-3-ium -2-uide (3j)



A yellow solid: 0.330 g, yield 67 %; Mp: 186-188 ^{o}C;

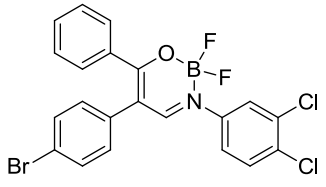
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.53 (s, 1H, CH), 7.74 (d, J = 8.8 Hz, 2H, Ar-H), 7.69-7.67 (m, 2H, Ar-H), 7.58 (d, J = 8.8 Hz, 2H, Ar-H), 7.53-7.48 (m, 4H, Ar-H), 7.41-7.36 (m, 6H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 172.3, 164.6, 141.3, 135.4, 134.9, 134.3, 133.9, 133.1, 132.8, 132.7, 129.6, 129.3, 129.0, 128.5, 125.9, 121.7, 108.1;

IR (KBr, v, cm^{-1}): 1684, 1601, 1542, 1501, 1146, 889;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{13}BBrCl_2FNO$, 475.9614 $[M-F]^+$; found: 475.9614.

5-(4-Bromophenyl)-3-(3,4-dichlorophenyl)-2,2-difluoro-6-phenyl-2*H*-1,3,2-oxazaborinin-3-ium -2-uide (3k)



A yellow solid: 0.384 g, yield 78 %; Mp: 184-186 ^{o}C;

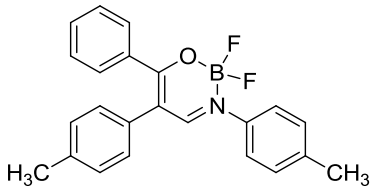
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.59 (s, 1H, CH), 8.03 (d, J = 2.4 Hz, 1H, Ar-H), 7.82 (d, J = 8.8 Hz, 1H, Ar-H), 7.70-7.67 (m, 1H, Ar-H), 7.56-7.49 (m, 3H, Ar-H), 7.41-7.30 (m, 6H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 172.2, 165.3, 142.0, 134.7, 133.7, 132.7, 132.5, 132.3, 132.1, 131.6, 131.2, 130.2, 128.9, 126.0, 124.4, 121.4, 111.1;

IR (KBr, v, cm^{-1}): 1612, 1575, 1469, 1370, 1009, 823;

HRMS (APCI-TOF): m/z calcd for: $C_{23}H_{20}BFNO$, 475.9614 $[M-F]^{+}$; found: 475.9615.

2,2-Difluoro-6-phenyl-3,5-di-p-tolyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3l)



A yellow solid: 0.288 g, yield 77 %; Mp: 154-156 ^{o}C;

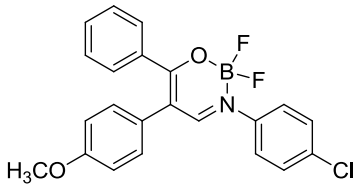
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.40 (s, 1H, CH), 7.55 (d, J = 8.0 Hz, 2H, Ar-H), 7.48-7.44 (m, 1H, Ar-H), 7.40-7.31 (m, 6H, Ar-H), 7.20 (d, J = 8.0 Hz, 2H, Ar-H), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 2.36 (s, 3H, CH_3), 2.30 (s, 3H, CH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.2, 164.1, 140.0, 138.2, 137.1, 134.2, 132.6, 131.9, 130.3, 130.3, 130.0, 129.8, 128.7, 123.7, 111.7, 21.2, 21.0;

IR (KBr,v, cm^{-1}): 1608, 1598, 1511, 1402, 1003, 846, 682, 531;

HRMS (APCI-TOF): m/z calcd for: $C_{23}H_{20}BFNO$, 357.1656 $[M-F]^{+}$; found: 357.1655.

3-(4-Chlorophenyl)-2,2-difluoro-5-(4-methoxyphenyl)-6-phenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3m)



A yellow solid: 0.329 g, yield 80 %; Mp: 179-181^{o}C;

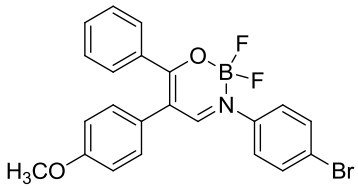
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.46 (s, 1H, CH), 7.71 (s, 2H, Ar-H), 7.61-7.59 (m, 2H, Ar-H), 7.47 (s, 1H, Ar-H), 7.42-7.34 (m, 4H, Ar-H), 7.25 (d, J = 8.8 Hz, 2H, Ar-H), 6.91 (d, J = 8.4 Hz, 2H, Ar-H), 3.75 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.7, 164.9, 159.1, 141.2, 134.2, 133.1, 132.1, 131.7, 130.0, 129.8, 128.7, 127.5, 125.8, 114.7, 111.7, 55.6;

IR (KBr, v, cm^{-1}): 1637, 1586, 1475, 1426, 1025, 851, 679, 540;

HRMS (APCI-TOF): m/z calcd for: $C_{22}H_{17}BClFNO_2$, 394.0995 $[M-F]^+$; found: 394.0997.

3-(4-Bromophenyl)-2,2-difluoro-5-(4-methoxyphenyl)-6-phenyl-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3n)



A yellow solid: 0.279 g, yield 68 %; Mp: 194-196 ^{o}C;

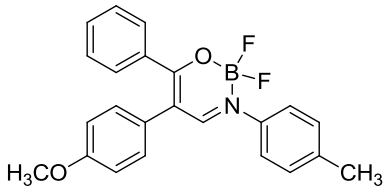
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.46 (s, 1H, CH), 7.73 (d, J = 8.8 Hz, 2H, Ar-H), 7.63 (d, J = 8.8 Hz, 2H, Ar-H), 7.47 (s, 1H, Ar-H), 7.42-7.34 (m, 4H, Ar-H), 7.25 (d, J = 8.8Hz, 2H, Ar-H), 6.91 (d, J = 8.8 Hz, 2H, Ar-H), 3.75 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.8, 164.9, 159.1, 141.6, 134.2, 132.7, 132.1, 131.7, 130.0, 128.7, 127.4, 126.1, 121.5, 114.7, 111.7, 55.6;

IR (KBr, v, cm^{-1}):1669, 1572, 1474, 1421, 1036, 834, 692, 551;

HRMS (APCI-TOF): m/z calcd for: $C_{22}H_{17}BBrFNO_2$, 438.0499 $[M-F]^+$; found: 438.0499.

2,2-Difluoro-5-(4-methoxyphenyl)-6-phenyl-3-(p-tolyl)-2*H*-1,3,2-oxazaborinin-3-ium-2-uide (3o)



A yellow solid: 0.274 g, yield 87 %; Mp: 154-156 ^{o}C;

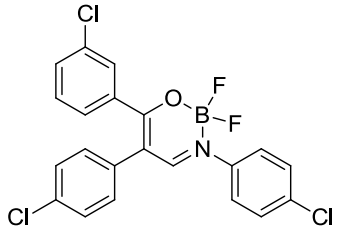
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.39 (s, 1H, CH), 7.55 (d, J = 8.0 Hz, 2H, Ar-H), 7.45 (s, 1H, Ar-H), 7.41-7.31 (m, 6H, Ar-H), 7.24 (d, J = 8.4 Hz, 2H, Ar-H), 6.90 (d, J = 8.4 Hz, 2H, Ar-H), 3.75 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.8, 169.9, 164.2, 159.1, 140.0, 138.2, 134.3, 131.8, 131.7, 130.3, 130.0, 128.7, 127.6, 123.7, 114.7, 55.6, 21.0;

IR (KBr, *v*, cm^{-1}): 1599, 1573, 1499, 1411, 1084, 826, 705, 538;

HRMS (APCI-TOF): m/z calcd for: $C_{23}H_{20}BFNO_2$, 372.1605 $[M-F]^+$; found: 372.1607.

6-(3-Chlorophenyl)-3,5-bis(4-chlorophenyl)-2,2-difluoro-2*H*-1,3,2-oxazaborinin-3-ium-2-uid (3p)



A yellow solid: 0.355 g, yield 79 %; Mp: 178-180 ^oC;

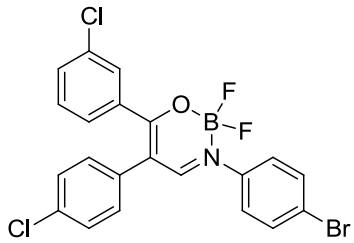
^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.57 (s, 1H, CH), 7.72 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.63-7.56 (m, 3H, Ar-H), 7.45-7.38 (m, 6H, Ar-H), 7.28 (d, *J* = 8.0Hz, 1H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.2, 165.2 141.0, 135.9, 133.9, 133.5, 133.4, 133.0, 132.4, 131.9, 130.8, 129.8, 129.6, 129.2, 128.8, 125.9, 111.3;

IR (KBr,*v*, cm^{-1}): 1613, 1564, 1500, 1380, 1033, 827;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{13}BCl_3FNO$, 432.0110 $[M-F]^+$; found: 432.0114.

3-(4-Bromophenyl)-6-(3-chlorophenyl)-5-(4-chlorophenyl)-2,2-difluoro-2*H*-1,3,2-oxazaborinin -3-ium-2-uide (3q)



A yellow solid: 0.409 g, yield 83 %; Mp: 183-185 ^oC;

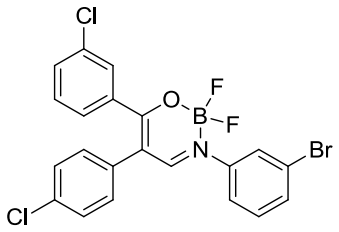
^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.57 (s, 1H, CH), 7.74 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.64 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.58-7.55 (m, 1H, Ar-H), 7.44-7.37 (m, 6H, Ar-H), 7.27 (d, *J* = 8.0 Hz, 1H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.2, 165.1, 141.4, 135.9, 133.9, 133.5, 133.0, 132.8, 132.4, 131.9, 130.8, 129.6, 129.2, 128.8, 126.1, 121.9,111.3;

IR (KBr, *v*, cm^{-1}): 1617, 1567, 1509, 1375, 1039, 826;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{13}BBrCl_2FNO$, 475.9614 $[M-F]^+$; found: 475.9610.

3-(3-Bromophenyl)-6-(3-chlorophenyl)-5-(4-chlorophenyl)-2,2-difluoro-2*H*-1,3,2-oxazaborinin -3-ium-2-uide (3r)



A yellow solid: 0.394 g, yield 80 %; Mp: 163-165 ^{o}C;

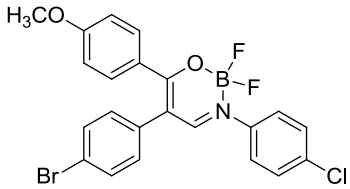
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.60 (s, 1H, CH), 7.94 (s, 1H, Ar-H), 7.69 (t, J = 8.0 Hz, 2H, Ar-H), 7.57 (d, J = 8.0 Hz, 1H, Ar-H), 7.52-7.38 (m, 7H, Ar-H), 7.28 (d, J = 8.0 Hz, 1H, Ar-H);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.5, 165.6, 143.5, 135.8, 133.9, 133.5, 133.0, 132.5, 132.0, 131.7, 131.6, 130.8, 129.6, 129.2, 128.8, 126.8, 123.3, 122.4, 111.3;

IR (KBr, v, cm^{-1}): 1614, 1568, 1506, 1379, 1030, 835, 692, 528;

HRMS (APCI-TOF): m/z calcd for: $C_{21}H_{13}BBrCl_2FNO$, 475.9614 $[M-F]^+$; found: 475.9618.

5-(4-Bromophenyl)-3-(4-chlorophenyl)-2,2-difluoro-6-(4-methoxyphenyl)-2*H*-1,3,2-oxazaborin in-3-ium-2-uide (3s)



A yellow solid: 0.372 g, yield 76 %; Mp: 164-166 ^{o}C;

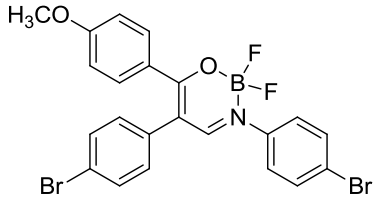
^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.42 (s, 1H, CH), 7.69 (d, J = 8.8 Hz, 2H, Ar-H), 7.61–7.55 (m, 4H, Ar-H), 7.41-7.37 (m, 2H, Ar-H), 7.35-7.32 (m, 2H, Ar-H),6.96-6.92 (m, 2H, Ar-H), 3.80 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.2, 164.0, 162.7, 141.2, 135.3, 132.9, 132.6, 132.5, 132.2, 129.8, 125.6, 121.3, 114.4, 110.2, 56.0;

IR (KBr,v, cm^{-1}): 1682, 1578, 1481, 1432, 1059, 846, 715, 570;

HRMS (APCI-TOF): m/z calcd for: $C_{22}H_{16}BBrClFNO_2$, 472.0110 $[M-F]^+$; found: 472.0109.

3-(3-Bromophenyl)-5-(4-bromophenyl)-2,2-difluoro-6-(4-methoxyphenyl)-2*H*-1,3,2-oxazaborin in-3-ium-2-uide (3t)



A yellow solid: 0.442 g, yield 83 %; Mp: 178-179 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.45 (s, 1H, CH), 7.91 (s, 1H, Ar-H), 7.68-7.63 (m, 2H, Ar-H), 7.57 (d, J = 8.4 Hz, 2H, Ar-H), 7.48 (t, J = 8.0 Hz, 1H, Ar-H), 7.40-7.33 (m, 4H, Ar-H), 6.95 (d, J = 8.8 Hz, 2H, Ar-H), 3.80 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 171.5, 164.4, 162.8, 143.8, 135.3, 132.7, 132.5, 132.2, 131.6, 131.1, 126.6, 125.5, 123.1, 122.4, 121.3, 114.4, 110.2, 56.0;

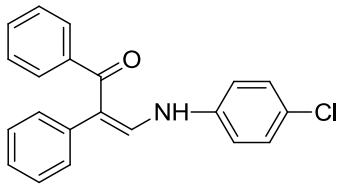
IR (KBr, v, cm^{-1}): 2981, 1589, 1473, 1372, 1133, 827, 703, 554;

HRMS (APCI-TOF): m/z calcd for: $C_{22}H_{16}BBr_2FNO_2$, 513.9625 $[M-F]^+$; found: 513.9618.

General procedure for the synthesis of compound 4a

Phenyl(3-phenyloxiran-2-yl)methanone (**1a**, 1 mmol) was introduced in a 25-mL reaction flask, 4-chloroaniline (**2a** 1.0 mmol), BF_3•Et_2O (1.2 mmol), and acetylacetone (1.2 mmol) as well as 1,4-dioxane (4.0 mL) were then successively added and stirred at 80 ^{o}C for 30 min After the completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was separated by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate 10:1 v/v) to afford the pure yellow solid **4a**.

(*Z*)-3-((4-Chlorophenyl)amino)-1,2-diphenylprop-2-en-1-one (4a) (major**)**



A yellow solid: 0.233 g, total yield 70 %; Mp: 158-159 ^{o}C;

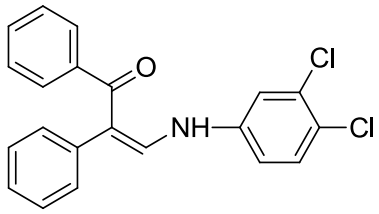
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.27 (d, J = 12.0 Hz, 1H, NH), 7.54 (d, J = 12.0 Hz, 1H, CH), 7.34-7.30 (m, 5H, Ar-H), 7.23-7.17 (m, 5H, Ar-H), 7.10-7.06 (m, 4H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.1, 141.1, 135.7, 135.2, 134.2, 125.7, 125.5, 125.1, 125.1, 124.0, 123.6, 123.3, 122.9, 121.4, 112.9, 108.1;

IR (KBr, v, cm^{-1}): 3454, 1661, 1371, 1232, 803, 646；

HRMS (EI-TOF): m/z calcd for: $C_{21}H_{15}ClNO$, 332.0842 $[M-H]^-$; found: 332.0841.

(*Z*)-3-((3,4-Dichlorophenyl)amino)-1,2-diphenylprop-2-en-1-one (4b) (major**)**



Yellow solid, Mp: 162-164 ^{o}C;

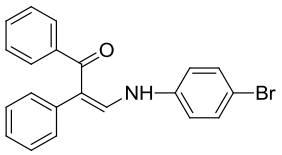
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.17 (d, J = 12.0 Hz, 1H, NH), 7.39 (d, J = 8.8 Hz, 2H, CH and Ar-H), 7.33-7.29 (m, 5H, Ar-H), 7.24-7.22 (m, 3H, Ar-H), 7.21 (s, 2H, Ar-H), 7.10 (d, J = 2.0 Hz, 1H, Ar-H), 6.98-6.95 (m, 1H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 195.2, 144.9, 140.2, 139.9, 139.6, 133.7, 131.3, 130.5, 129.8, 128.8, 128.4, 127.6, 126.7, 126.3, 117.8, 116.0, 113.7;

IR (KBr, v, cm^{-1}): 3428, 1653, 1475, 1225, 1015, 740;

HRMS (EI-TOF): m/z calcd for: $C_{21}H_{14}Cl_2NO$, 366.0453 $[M-H]^-$; found: 366.0455.

(*Z*)-3-((4-Bromophenyl)amino)-1,2-diphenylprop-2-en-1-one (4c) (major**)**



A yellow solid: 0.256 g, total yield 68 %; Mp: 185-186 ^{o}C;

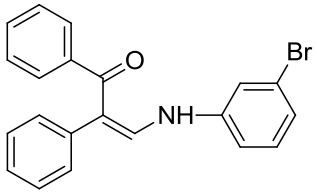
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.25 (d, J = 12.0 Hz, 1H, NH), 7.54 (d, J = 12.4 Hz, 1H, CH), 7.48-7.44 (m, 2H, Ar-H), 7.35-7.28 (m,4H, Ar-H), 7.22-7.19 (m, 4H, Ar-H), 7.11-7.08 (m, 2H, Ar-H), 7.04-7.00 (m, 2H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.2, 140.9, 135.7, 135.1, 134.7, 128.0, 125.5, 125.1, 124.0, 123.6, 122.9, 121.4, 113.3, 111.5, 108.2;

IR (KBr, v, cm^{-1}) : 3433, 1660, 1384, 1231, 802, 636；

HRMS (EI-TOF): m/z calcd for: $C_{21}H_{15}BrNO$, 376.0337 $[M-H]^-$; found: 376.0338.

(*Z*)-3-((3-Bromophenyl)amino)-1,2-diphenylprop-2-en-1-one (4d) (major**)**



Yellow solid, Mp: 103-105 ^{o}C;

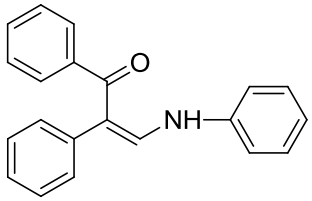
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.18 (d, J = 12.0 Hz, 1H, NH), 7.53 (d, J = 12.4 Hz, 1H, CH), 7.34-7.28 (m, 4H, Ar-H), 7.26-7.17 (m, 7H, Ar-H), 7.11-7.03 (m, 3H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 195.0, 145.3, 141.7, 140.4, 139.8, 131.1, 130.3, 129.9, 128.8, 128.4, 127.6, 126.5, 126.2, 123.6, 119.2, 115.4, 113.3;

IR (KBr, v, cm^{-1}): 3041, 1630, 1363, 1223, 1016, 765;

HRMS (EI-TOF): m/z calcd for: $C_{21}H_{15}BrNO$, 376.0337 $[M-H]^-$; found: 376.0338.

(*Z*)-1,2-Diphenyl-3-(phenylamino)prop-2-en-1-one (4e) (major**)**



Yellow solid, Mp: 90-92 ^{o}C;

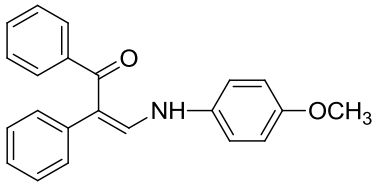
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.29 (d, J = 12.4 Hz, 1H, NH), 7.63 (d, J = 12.4 Hz, 1H, CH), 7.56-7.43 (m, 1H, Ar-H), 7.39-7.31 (m, 4H, Ar-H), 7.31-7.24 (m, 3H, Ar-H), 7.23-7.19 (m, 3H, Ar-H), 7.18-7.14 (m, 2H, Ar-H), 7.12-7.08 (m, 2H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 194.5, 146.4, 140.7, 140.2(3), 140.1(6), 129.9, 129.8, 128.8, 128.2, 127.6, 125.9, 123.8, 116.6, 112.4, 100.0;

IR (KBr, v, cm^{-1}): 3290, 1631, 1499, 1228, 1017, 747;

HRMS (EI-TOF): m/z calcd for: $C_{21}H_{16}NO$, 298.1232 $[M-H]^-$; found: 298.1233.

(*Z*)-3-((4-Methoxyphenyl)amino)-1,2-diphenylprop-2-en-1-one (4f) (major**)**



Yellow solid, Mp: 131-133 ^{o}C;

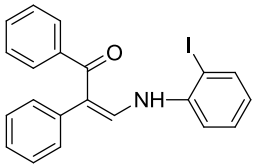
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.40 (d, J = 12.0 Hz, 1H, NH), 7.55 (d, J = 12.4 Hz, 1H, CH), 7.32 (d, J = 7.2 Hz, 2H, Ar-H), 7.30-7.25 (m, 1H, Ar-H), 7.20-7.16 (m, 5H, Ar-H), 7.10-7.08 (m, 4H, Ar-H), 6.91-6.89 (m, 2H, Ar-H), 3.80 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 193.9, 156.5, 147.6, 140.9, 140.3, 133.7, 129.9, 129.9, 128.8, 128.2, 127.5, 125.8, 118.2, 115.1, 111.6, 55.6;

IR (KBr, v, cm^{-1}): 3407, 1625, 1443, 1228, 1032, 748;

HRMS (EI-TOF): m/z calcd for: $C_{22}H_{18}NO_2$, 328.1338 $[M-H]^-$; found: 328.1336.

(*Z*)-3-((2-Iodophenyl)amino)-1,2-diphenylprop-2-en-1-one (4g) (major**)**



Yellow solid, Mp: 116-118 ^{o}C;

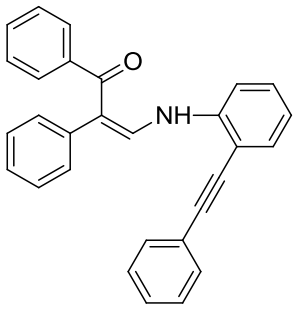
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.30 (d, J = 11.6 Hz, 1H, NH), 7.86-7.84 (m, 1H, CH), 7.57 (d, J = 12.0 Hz, 1H, Ar-H), 7.42-7.36 (m, 3H, Ar-H), 7.34-7.30 (s, 1H, Ar-H), 7.25-7.22 (m, 1H, Ar-H), 7.21-7.17 (m, 5H, Ar-H), 7.13-7.11 (m, 2H, Ar-H), 6.82-6.78 (m, 1H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 195.1, 144.8, 141.7, 140.5, 140.1, 140.0, 130.3, 129.8, 129.5, 128.9, 128.3, 127.6, 126.1, 124.8, 114.8, 113.8, 88.3;

IR (KBr, v, cm^{-1}): 3272, 1625, 1439, 1227, 1016, 751;

HRMS (EI-TOF): m/z calcd for: $C_{21}H_{15}INO$, 424.0199 $[M-H]^-$; found: 424.0200.

(*Z*)-1,2-Diphenyl-3-((2-(phenylethynyl)phenyl)amino)prop-2-en-1-one (4h) (major**)**



Yellow solid, Mp: 161-163 ^{o}C;

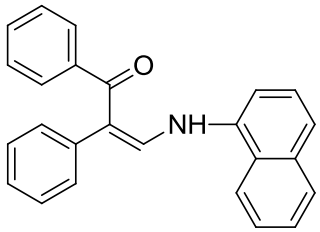
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.75 (d, J = 12.4 Hz, 1H, NH), 7.95-7.92 (m, 2H, CH and Ar-H), 7.73 (d, J = 12.0 Hz, 1H, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.40-7.36 (m, 5H, Ar-H), 7.32-7.28 (m, 2H, Ar-H), 7.26 (s, 1H, Ar-H), 7.23-7.13 (m, 7H, Ar-H), 7.05-7.01 (m, 1H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 194.4, 144.1, 141.7, 140.7, 140.3, 132.8, 132.2, 130.1, 129.9, 129.6, 129.0, 128.4, 128.3, 127.5, 126.0, 122.7, 113.5, 112.9, 112.7, 97.0, 84.6;

IR (KBr, v, cm^{-1}): 3415, 1668, 1484, 1242, 1046, 746;

HRMS (EI-TOF): m/z calcd for: $C_{29}H_{20}NO$, 398.1545 $[M-H]^-$; found: 398.1546.

(*Z*)-3-(Naphthalen-1-ylamino)-1,2-diphenylprop-2-en-1-one (4i)



Yellow solid, Mp: 147-149 ^{o}C;

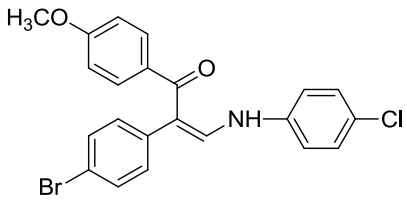
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 13.27 (d, J = 11.6 Hz, 1H, NH), 8.28 (d, J = 8.4 Hz, 1H ,CH), 7.89-7.83 (m, 2H, Ar-H), 7.64-7.54 (m, 3H, Ar-H), 7.47-7.44 (m, 1H, Ar-H), 7.41-7.39 (m, 2H, Ar-H), 7.35-7.29 (m, 2H, Ar-H), 7.25-7.22 (m, 4H, Ar-H), 7.20-7.19 (m, 1H,, Ar-H), 7.17-7.15 (m, 2H, Ar-H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 194.9, 147.6, 140.7, 140.1, 136.4, 134.4, 130.2, 129.9, 128.9, 128.5, 128.3, 127.6, 126.8, 126.7, 126.0, 125.8, 125.0, 124.3, 121.0, 113.3, 111.2；

IR (KBr, v, cm^{-1}): 3431, 1683, 1454, 1230, 1048, 771;

HRMS (EI-TOF): m/z calcd for: $C_{25}H_{18}NO$, 348.1389 $[M-H]^-$; found: 348.1411.

***(Z)*-2-(4-Bromophenyl)-3-((4-chlorophenyl)amino)-1-(4-methoxyphenyl)prop-2-en-1-one (4j) (**major**)**



Yellow solid, Mp: 173-174 ^{o}C;

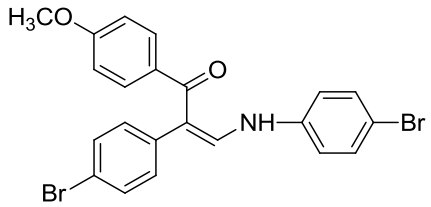
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.13 (d, J = 12.0 Hz, 1H, NH), 7.46 (d, J = 12.0 Hz, 1H, CH), 7.37-7.29 (m, 6H, Ar-H), 7.04 (d, J = 8.8 Hz, 2H, Ar-H), 6.99 (d, J = 8.8 Hz, 2H, Ar-H), 6.72 (d, J = 8.8 Hz, 2H, Ar-H), 3.79 (s, 3H, OCH_3);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 193.4, 161.5, 145.3, 139.4, 138.9, 132.5, 131.5, 131.2, 131.0, 129.8, 128.7, 120.0, 117.6, 113.0, 111.7, 55.3;

IR (KBr, v, cm^{-1}): 3442, 1661, 1454, 1234, 830, 596；

HRMS (EI-TOF): m/z calcd for: $C_{22}H_{16}BrClNO_2$, 440.0053 $[M-H]^-$; found: 440.0056.

(*Z*)-2-(4-Bromophenyl)-3-((4-bromophenyl)amino)-1-(4-methoxyphenyl)prop-2-en-1-one (4k) (major**)**



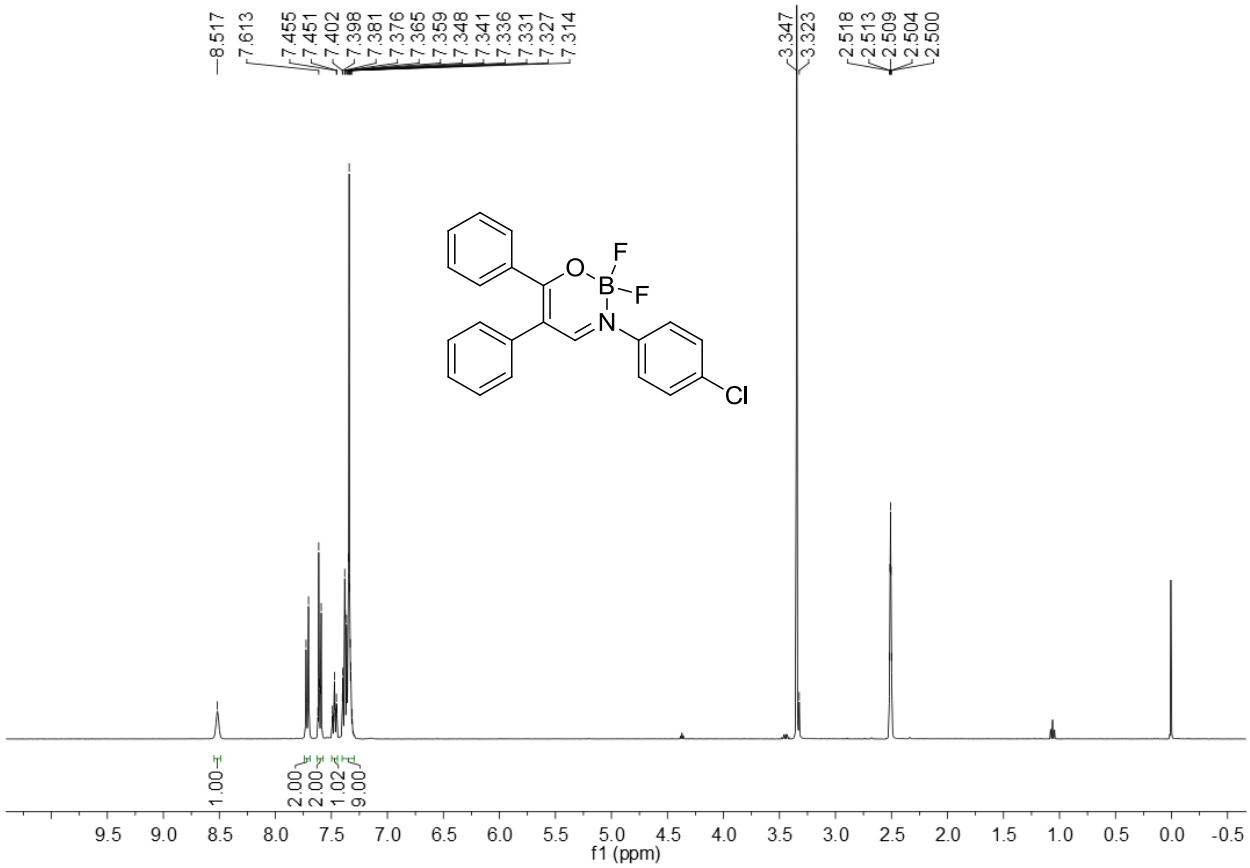
Yellow solid, Mp: 162-163 ^oC;

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 12.14 (d, J = 12.4 Hz, 1H, NH), 7.50-7.47(m, 3H, CH and Ar-H), 7.39 (d, J = 8.4 Hz, 2H, Ar-H), 7.34 (d, J = 8.8 Hz, 2H, Ar-H), 7.02 (d, J = 8.4 Hz, 4H, Ar-H), 6.75 (d, J = 8.8 Hz, 2H, Ar-H), 3.82 (s, 3H, OCH_3);

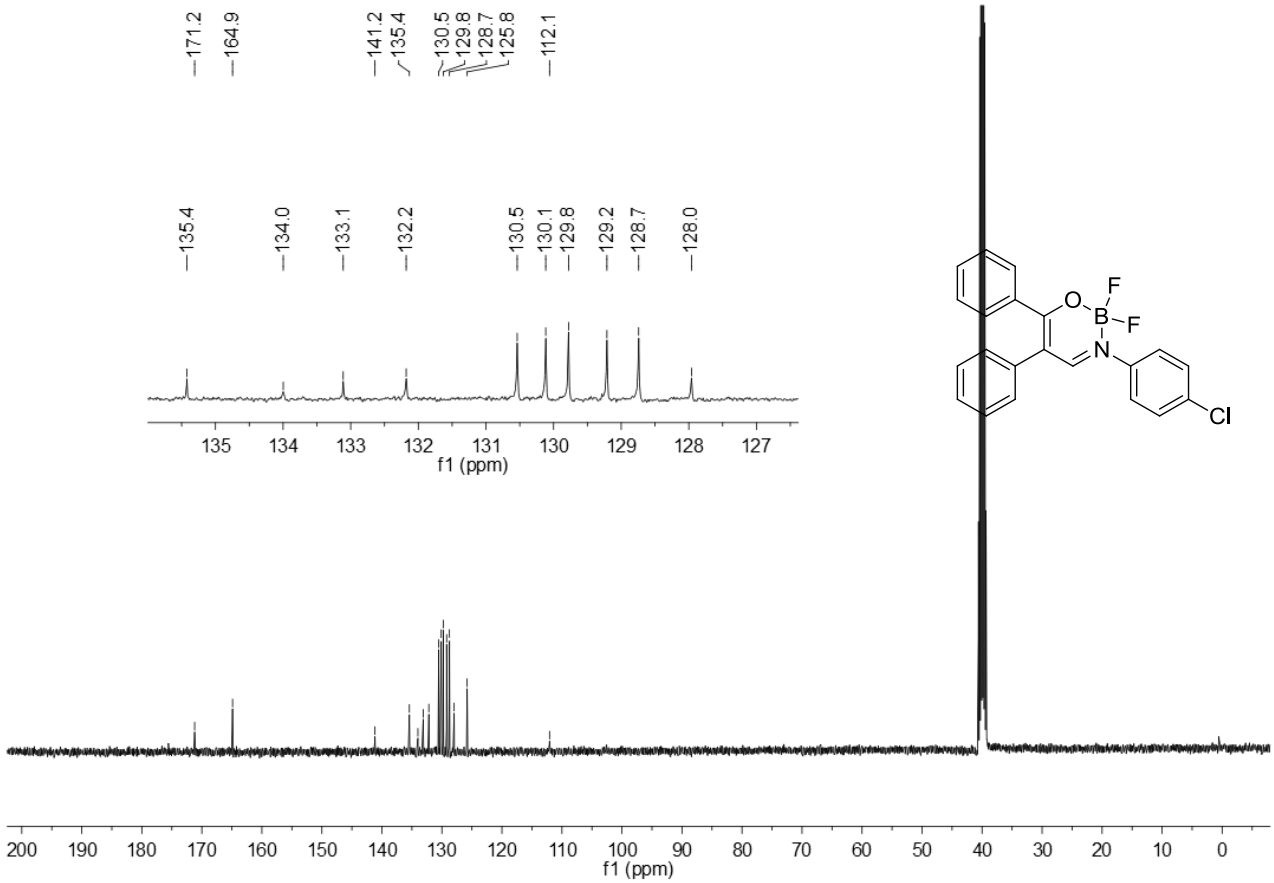
^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 193.4, 161.5, 145.1, 139.4, 139.34, 132.7, 132.5, 131.5, 131.2, 131.0, 120.1, 117.9, 116.2, 113.0, 111.8, 55.3;

IR (KBr, v, cm^{-1}): 3444, 1661, 1489, 1236, 829, 613；

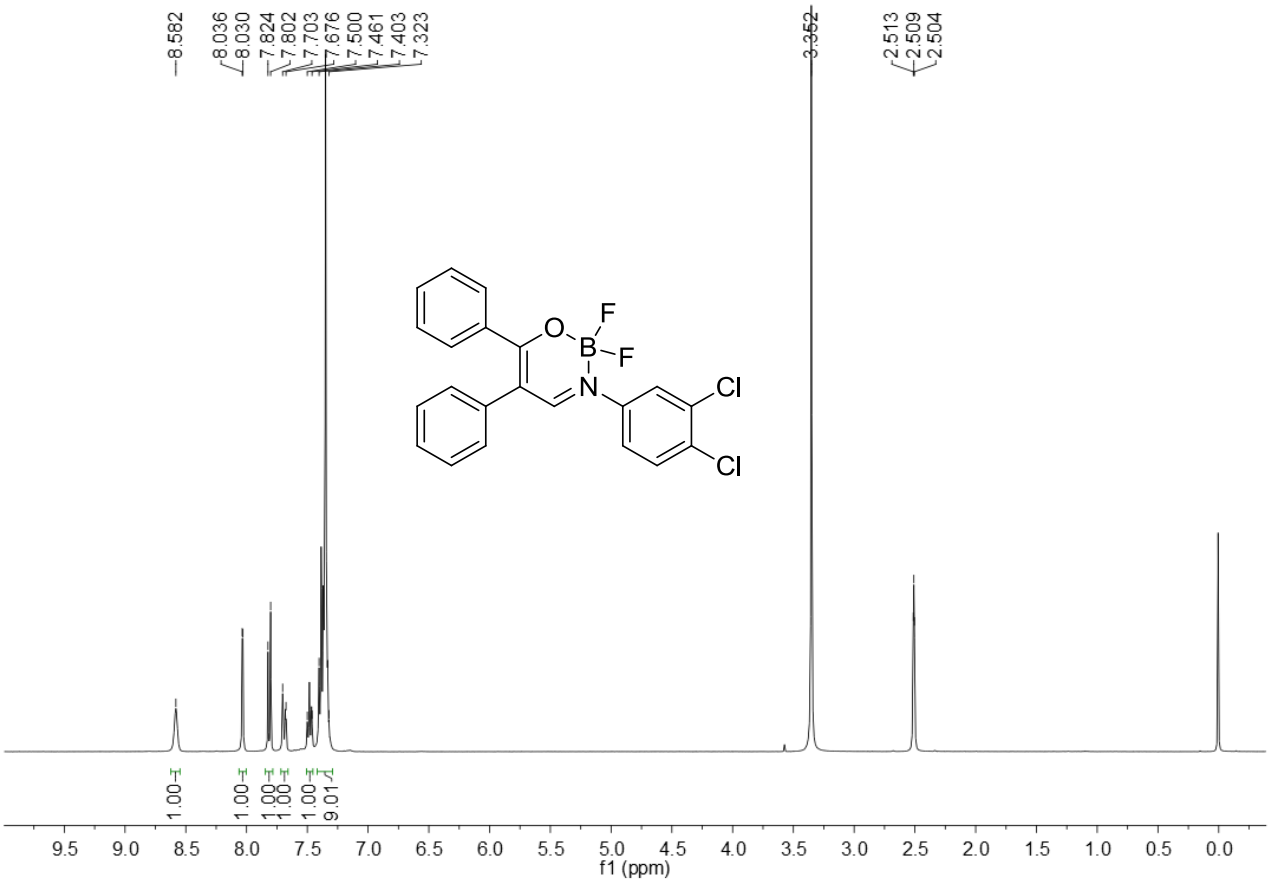
HRMS (EI-TOF): m/z calcd for: $C_{22}H_{16}Br_2NO_2$, 485.9528 $[M-H]^-$; found: 485.9527.



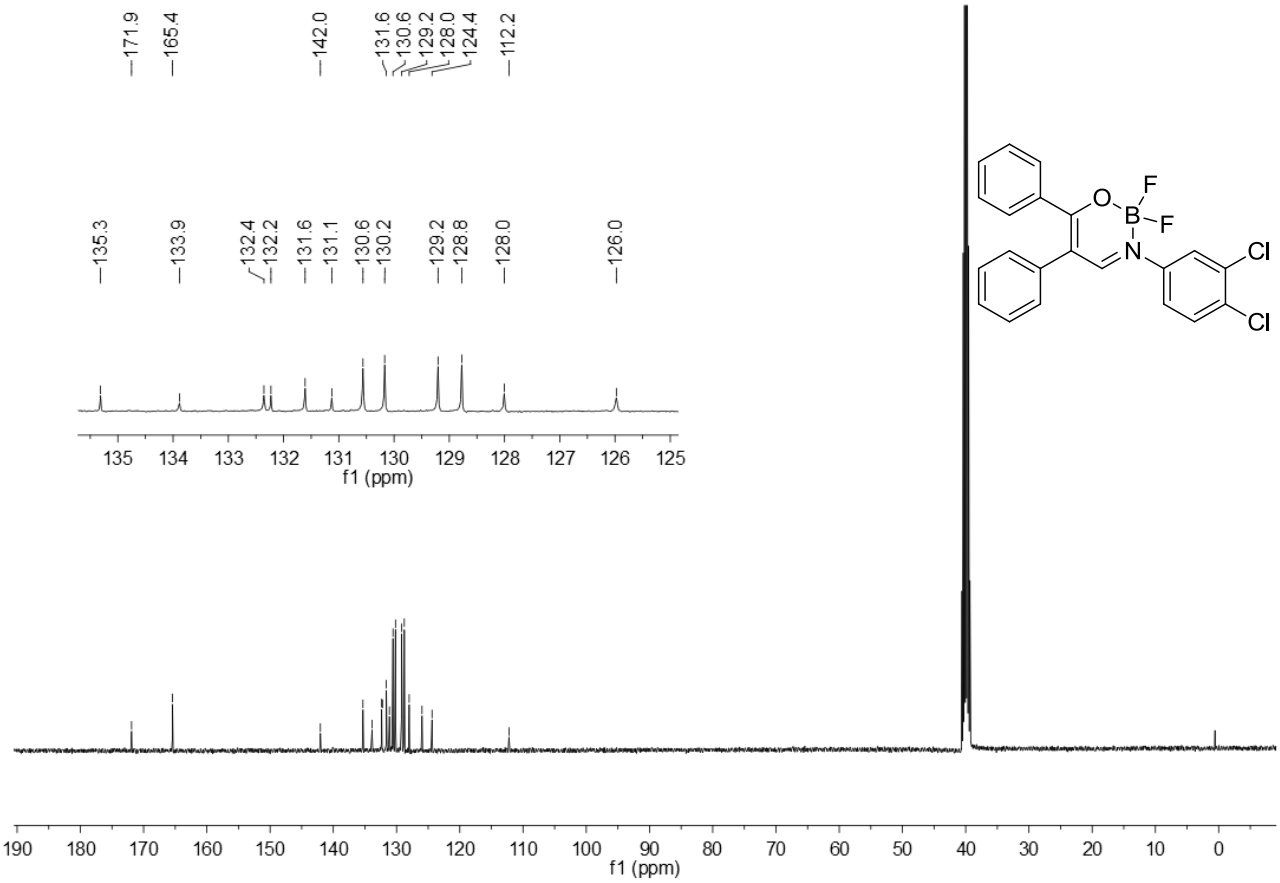
^{1}H NMR Spectrum of Compound 3a



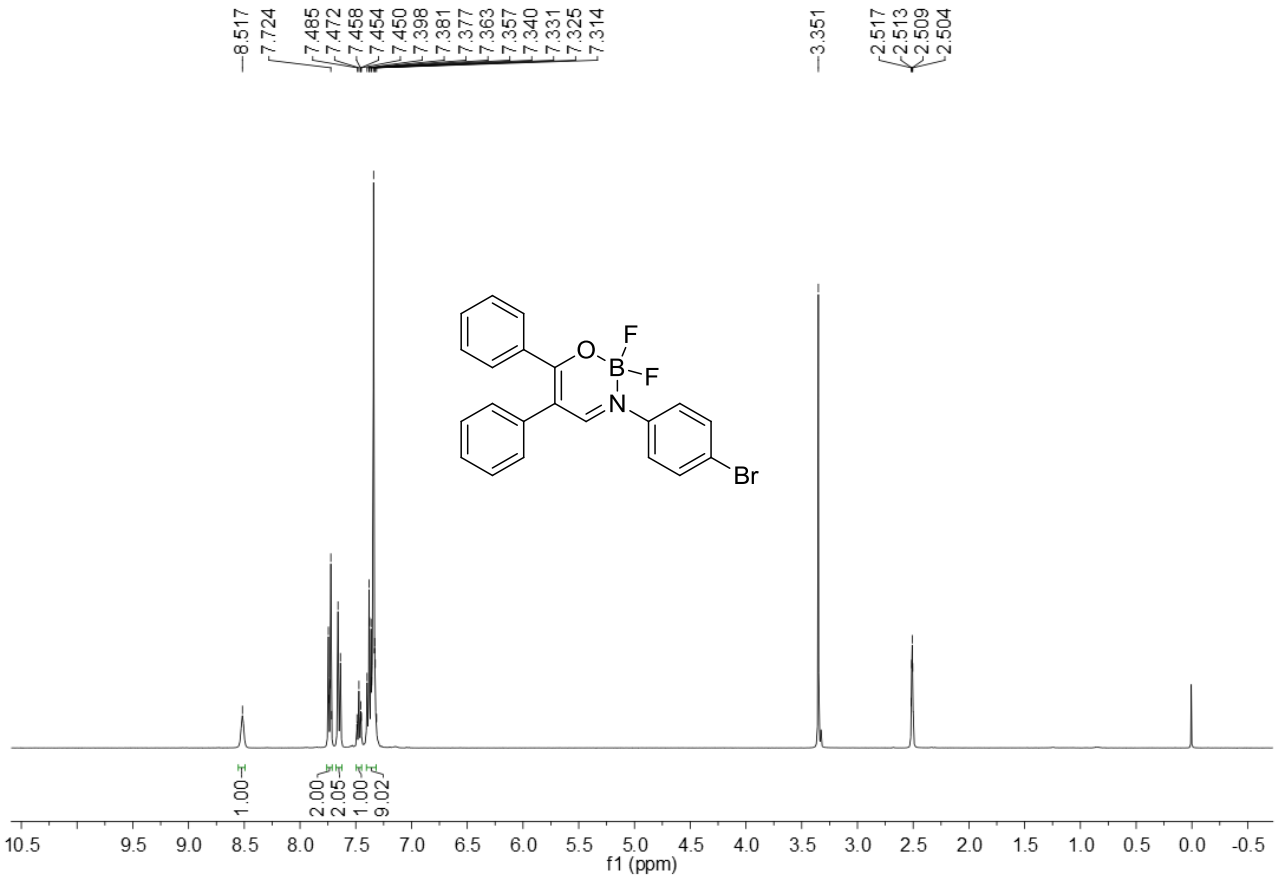
^{13}C NMR Spectrum of Compound 3a



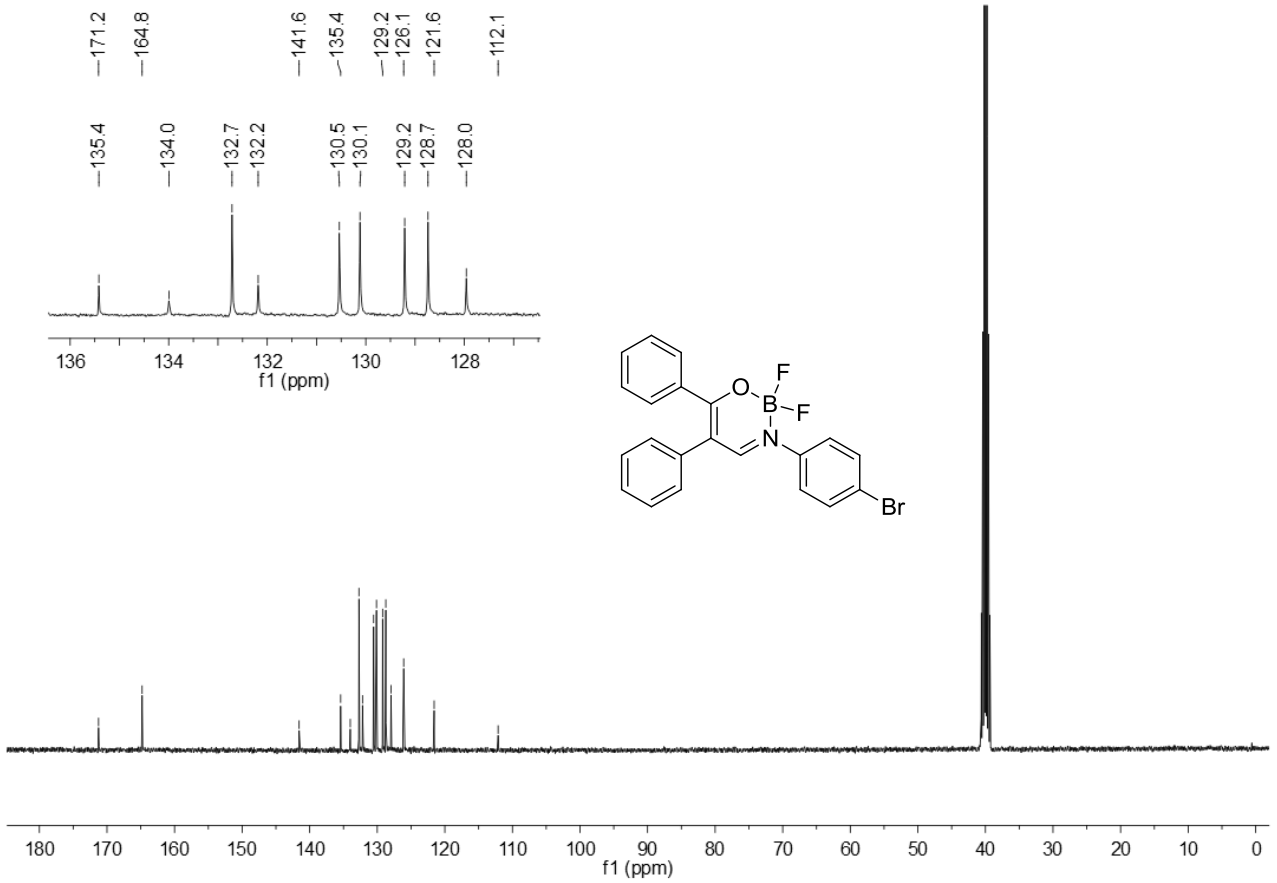
^{1}H NMR Spectrum of Compound 3b



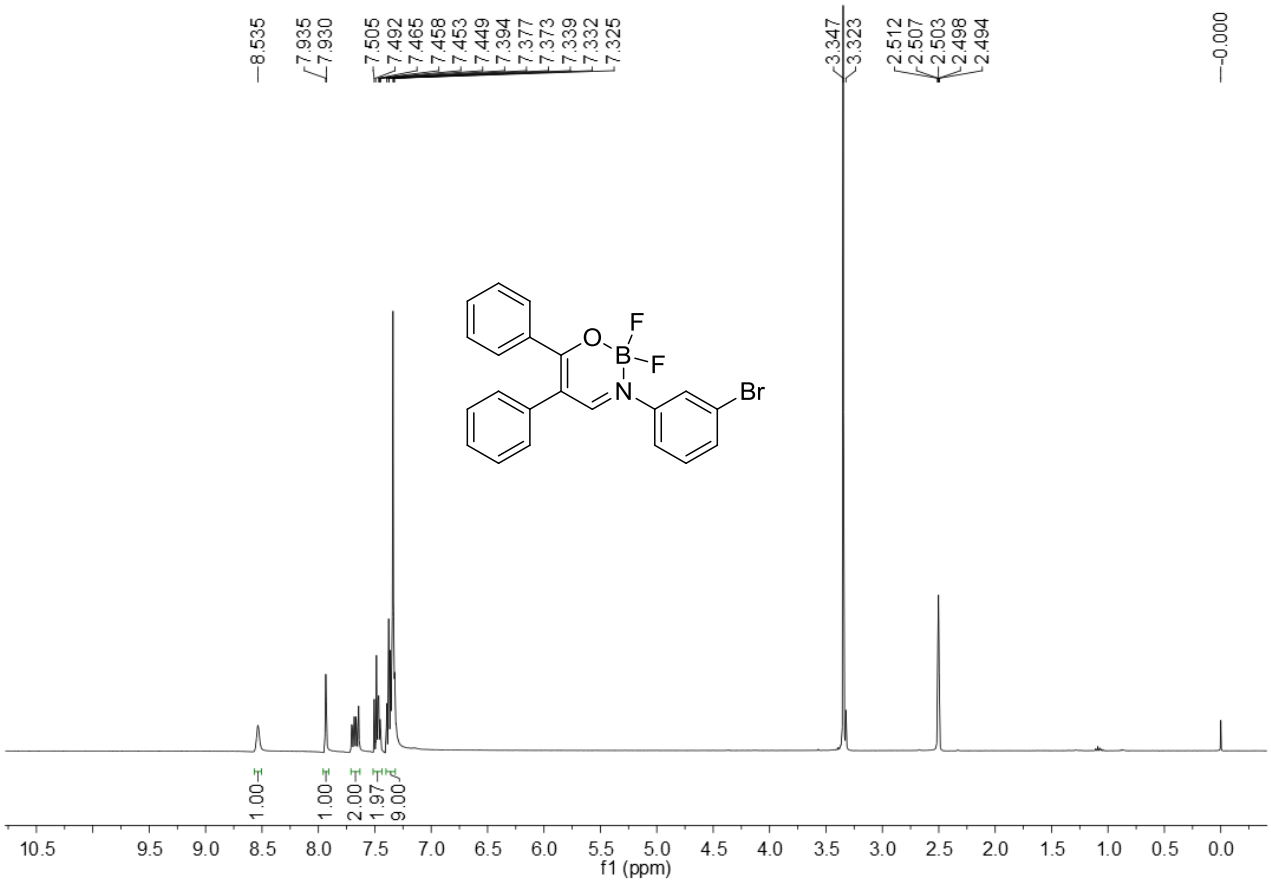
^{13}C NMR Spectrum of Compound 3b



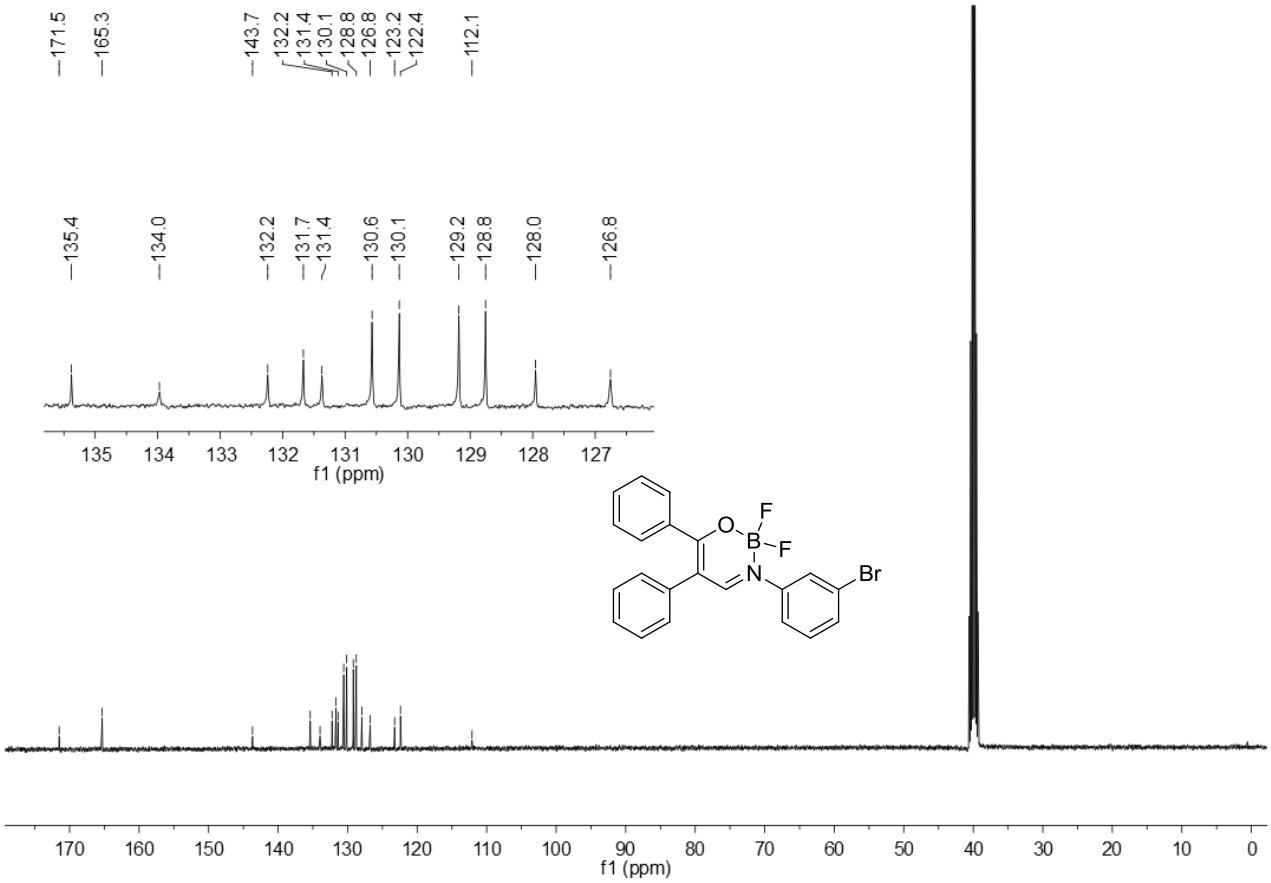
^{1}H NMR Spectrum of Compound 3c



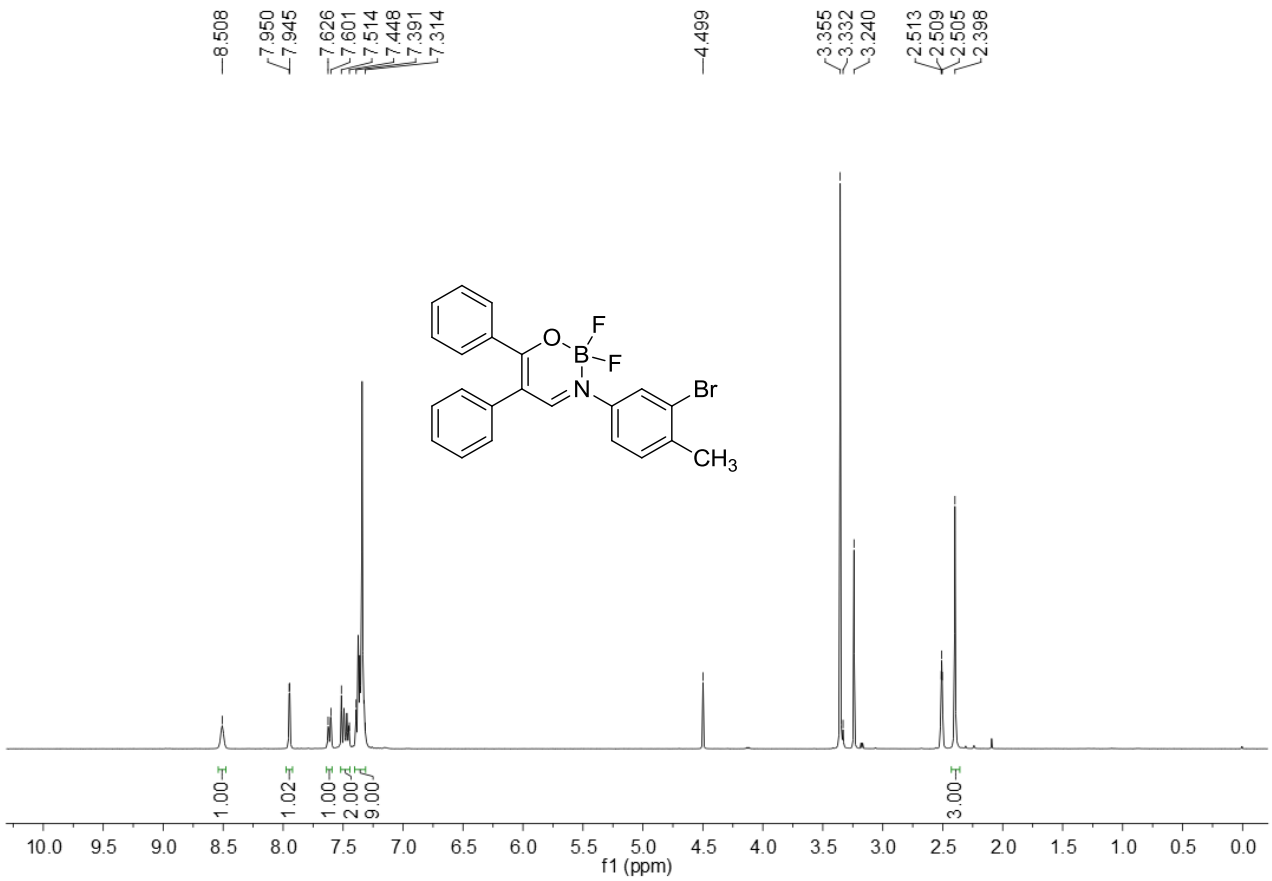
^{13}C NMR Spectrum of Compound 3c



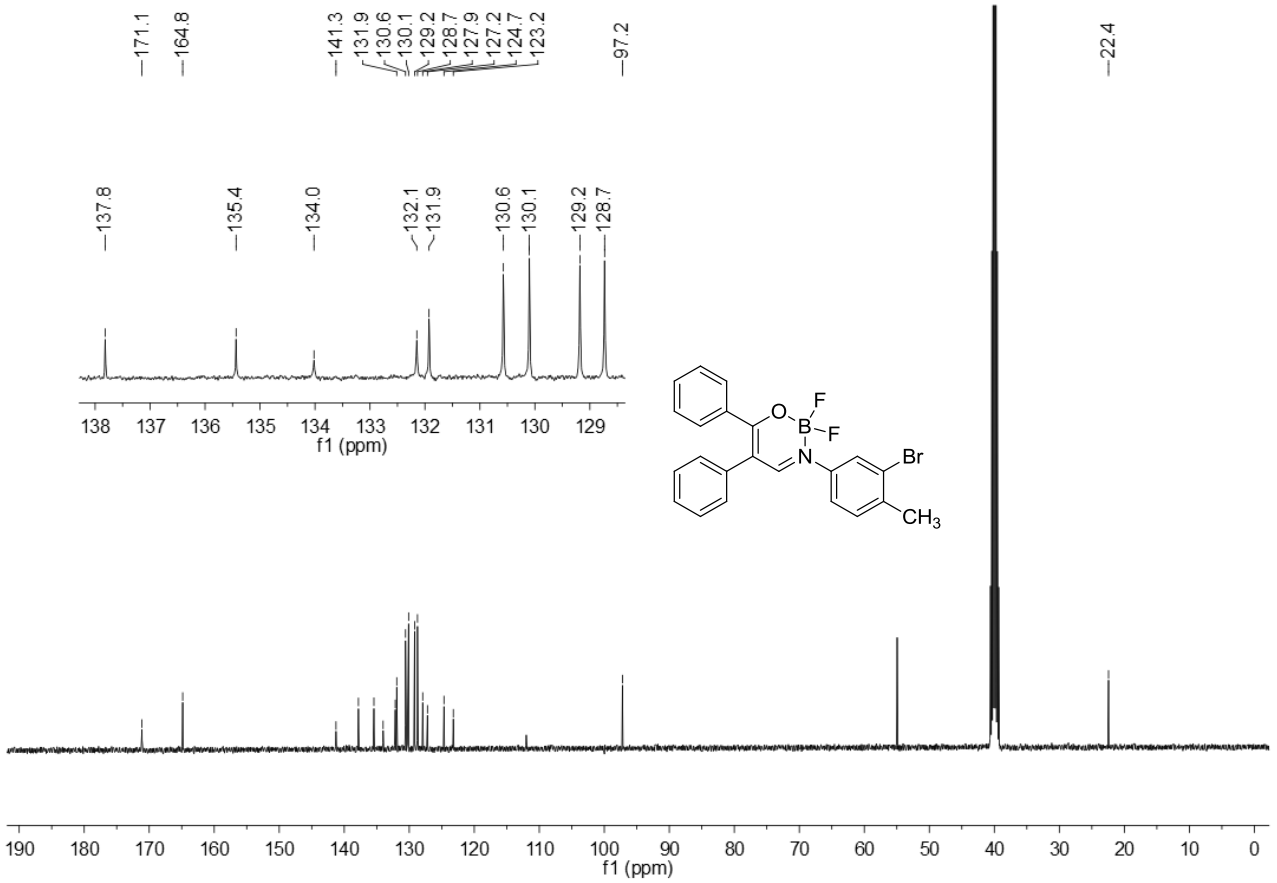
^{1}H NMR Spectrum of Compound 3d



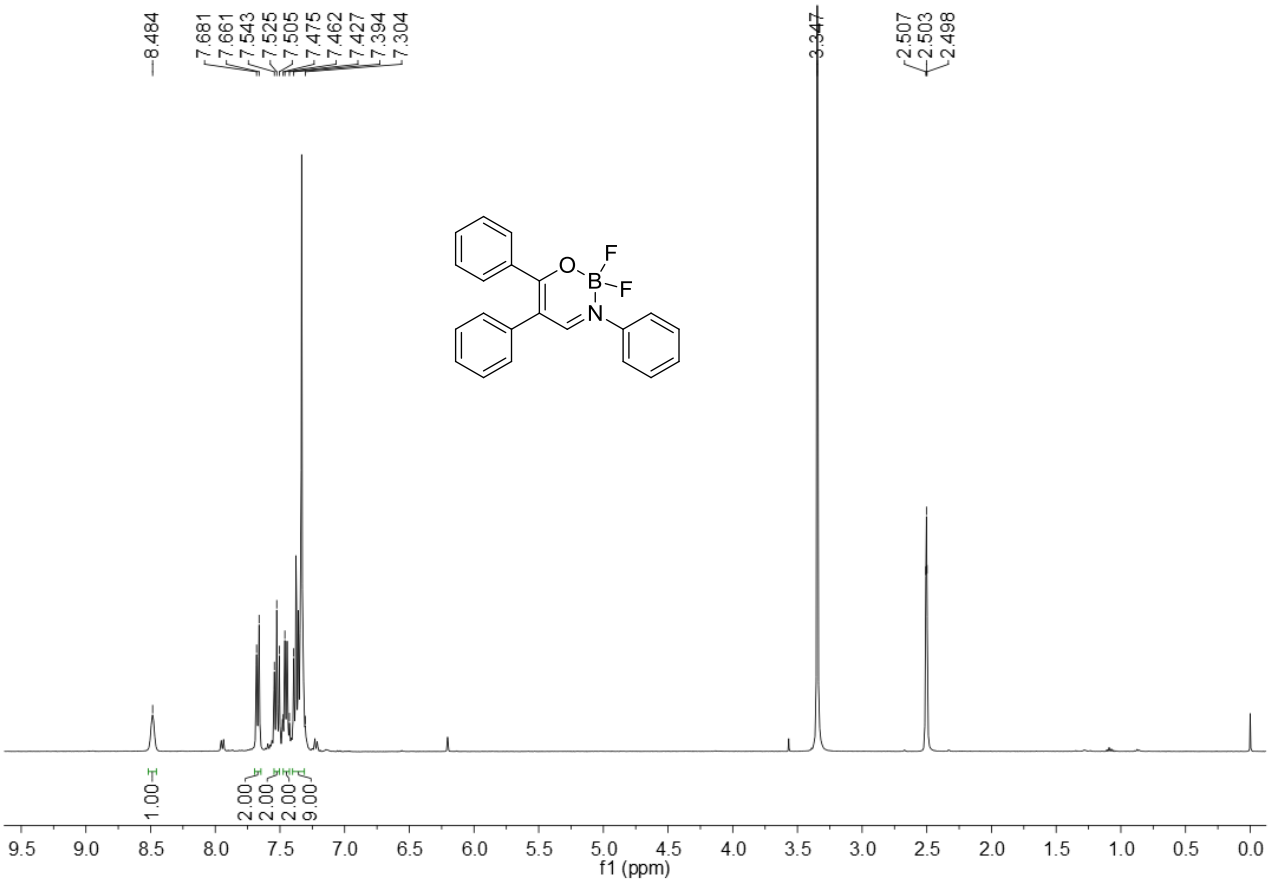
^{13}C NMR Spectrum of Compound 3d



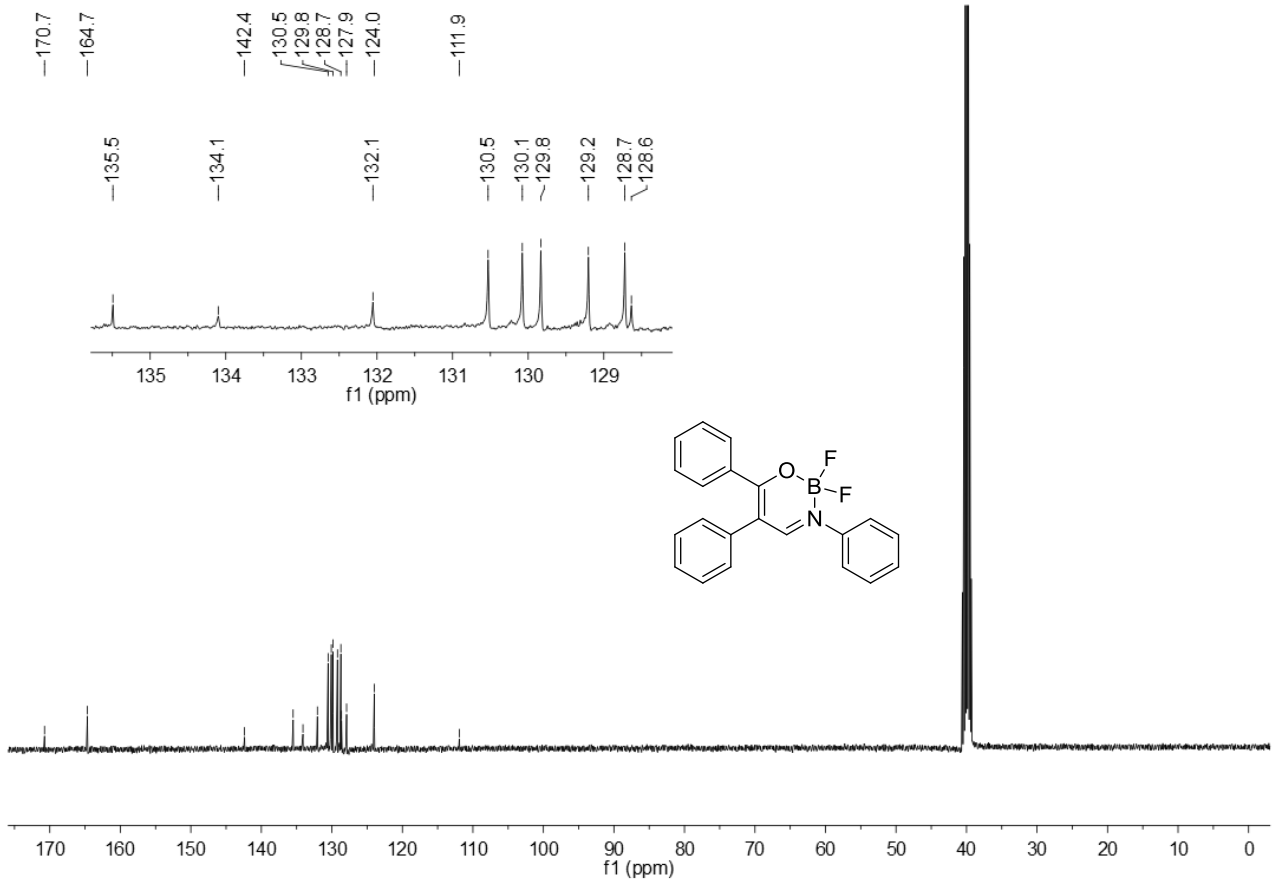
^{1}H NMR Spectrum of Compound 3e



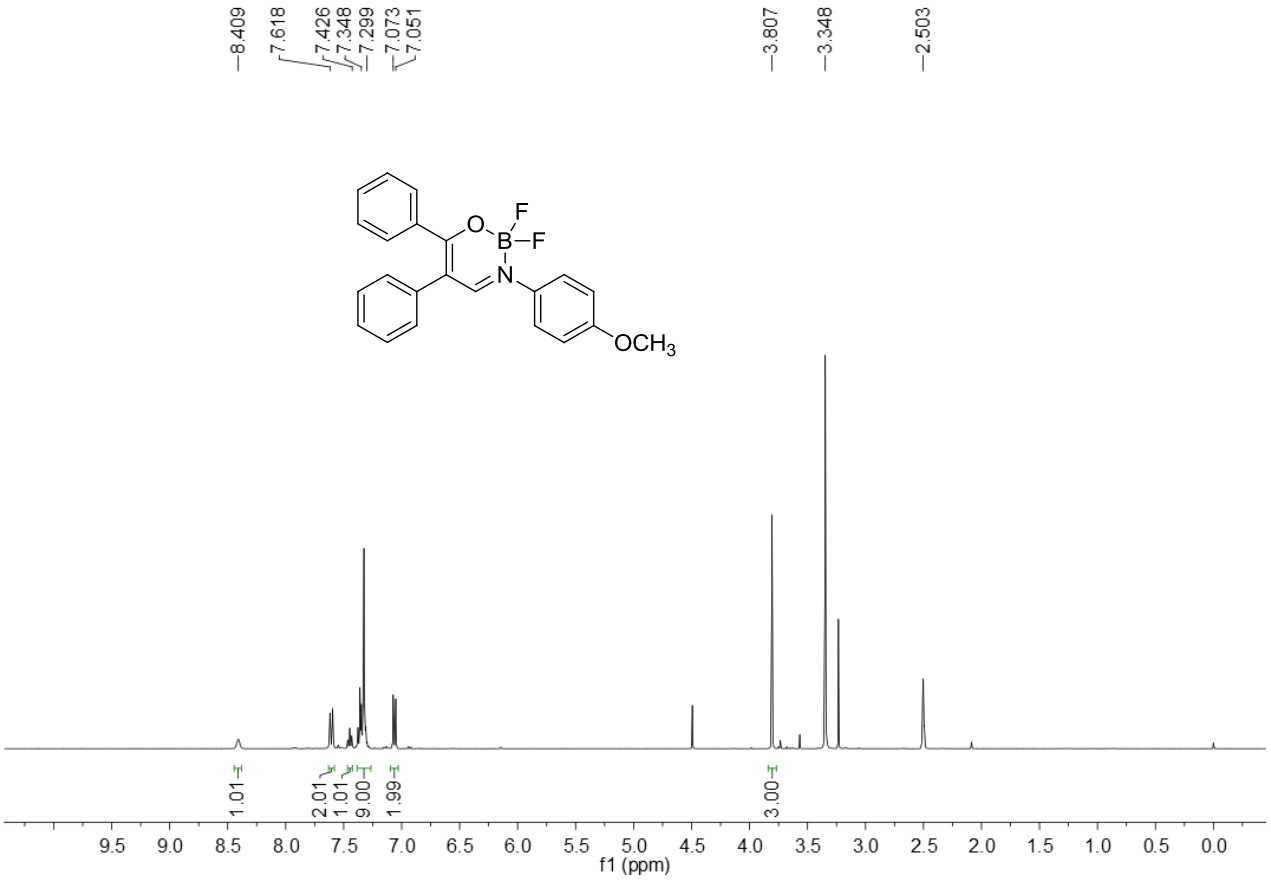
^{13}C NMR Spectrum of Compound 3e



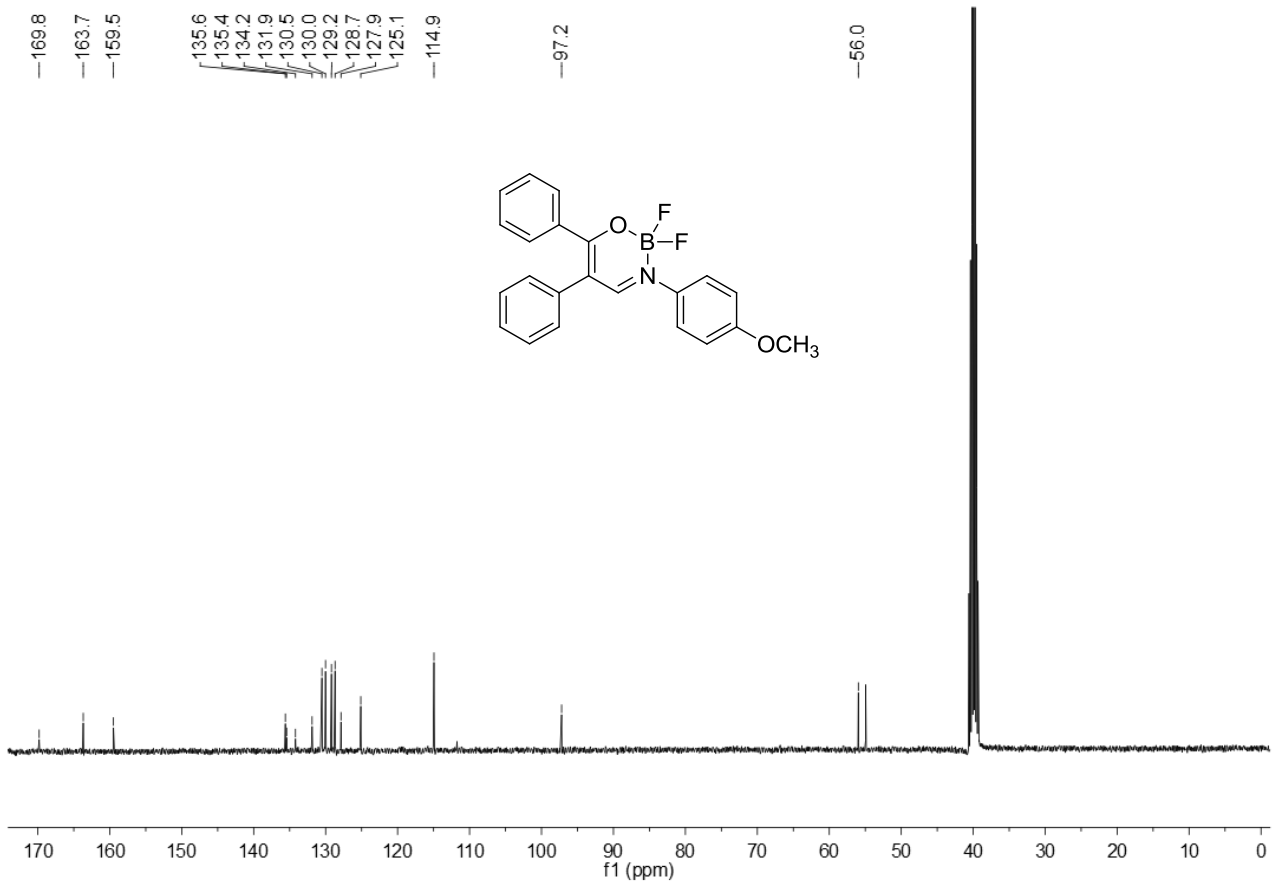
[1]H NMR Spectrum of Compound 3f



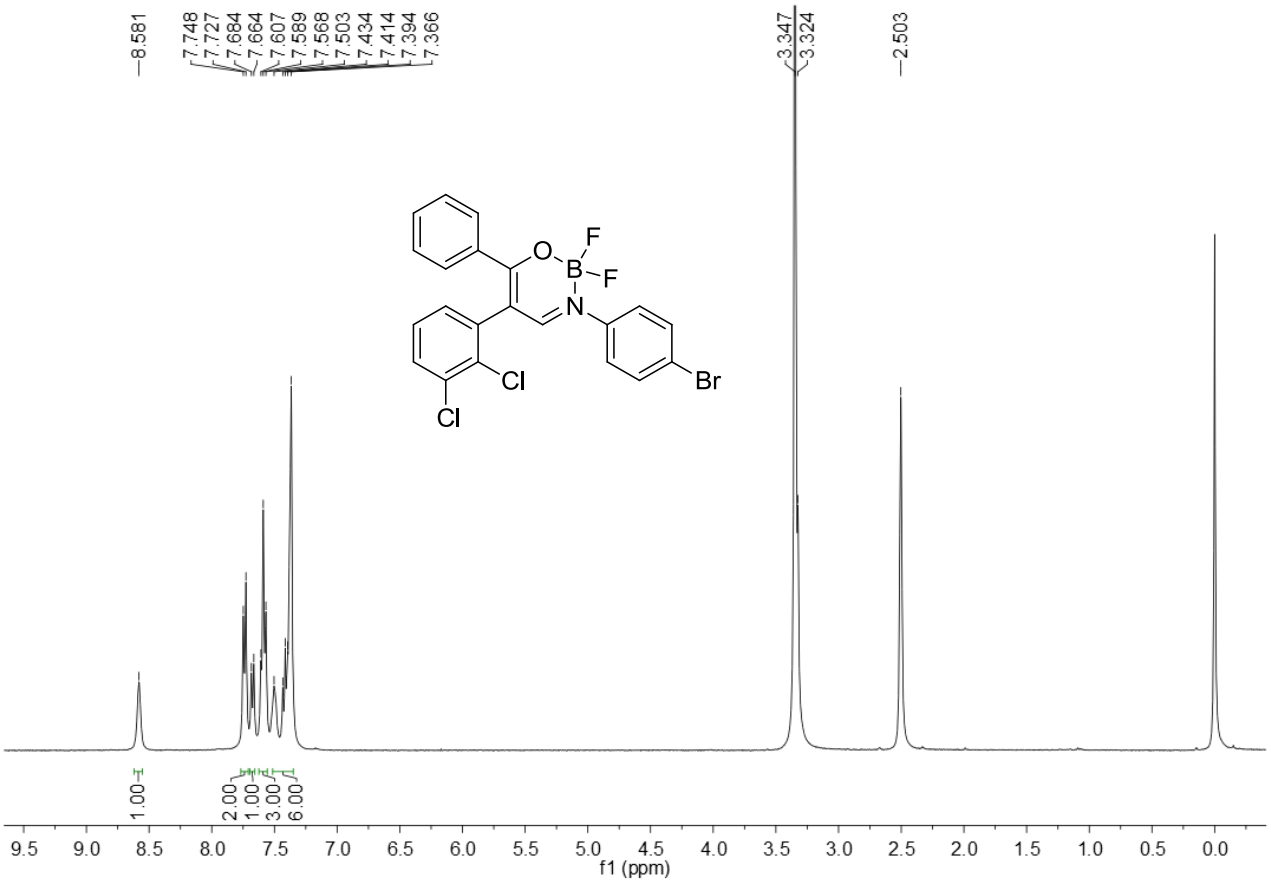
[13]C NMR Spectrum of Compound 3f



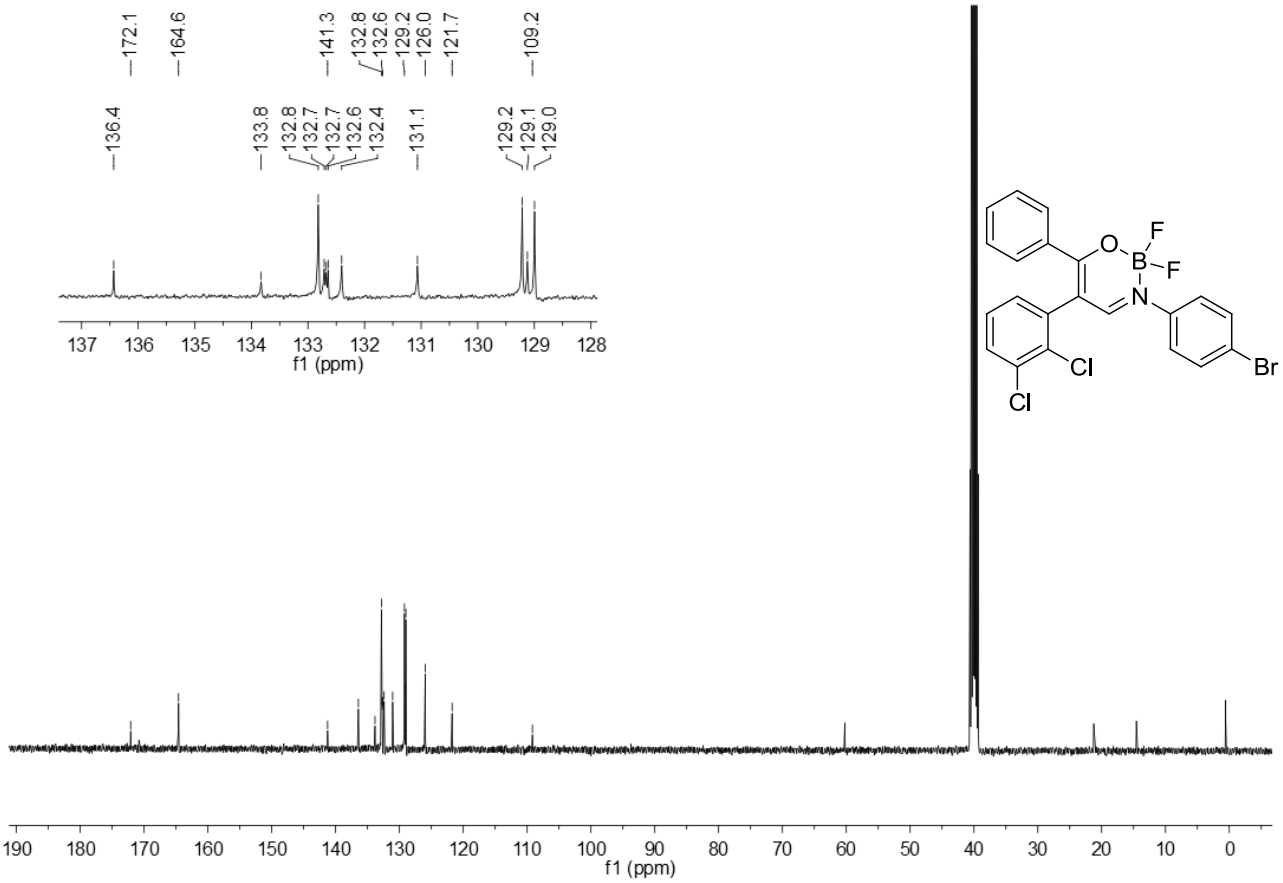
^{1}H NMR Spectrum of Compound 3g



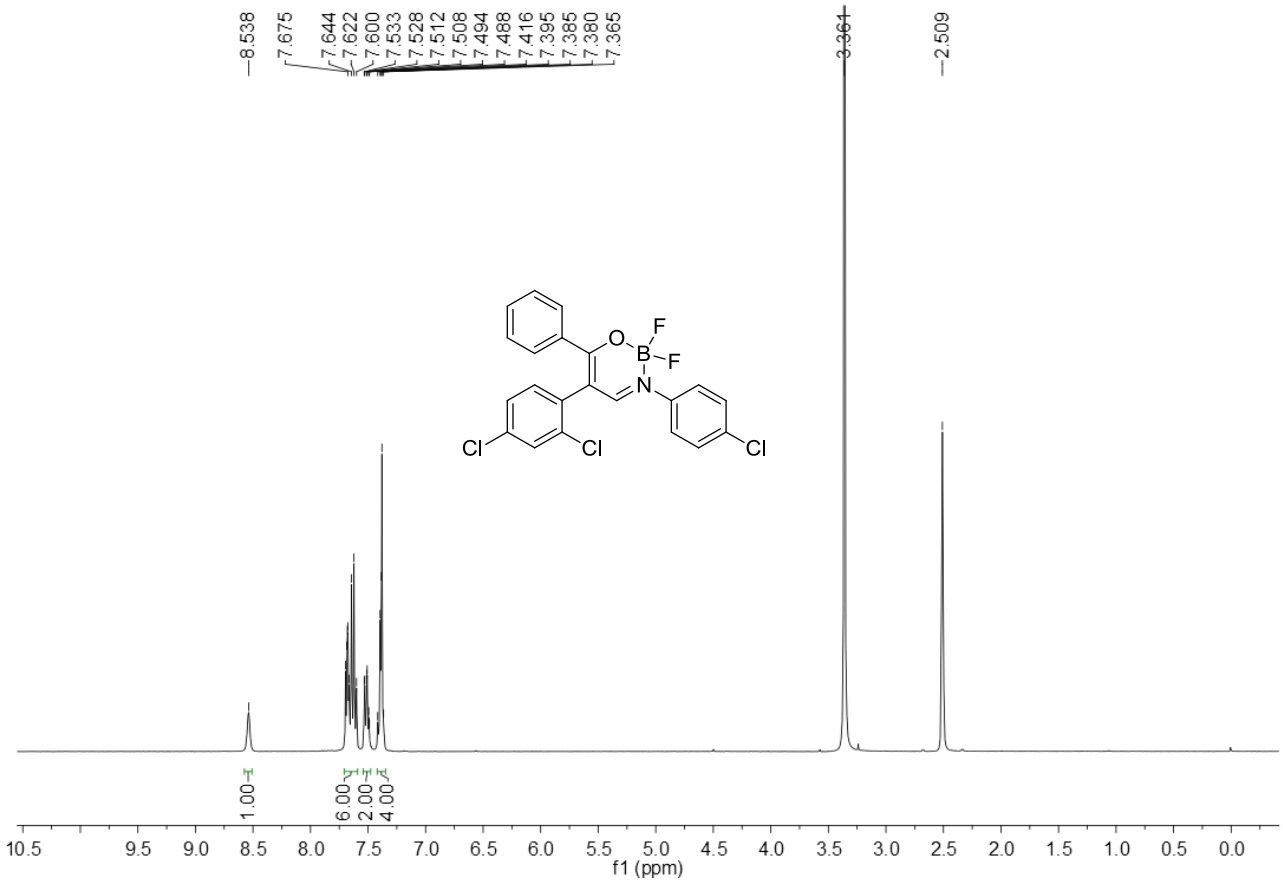
^{13}C NMR Spectrum of Compound 3g



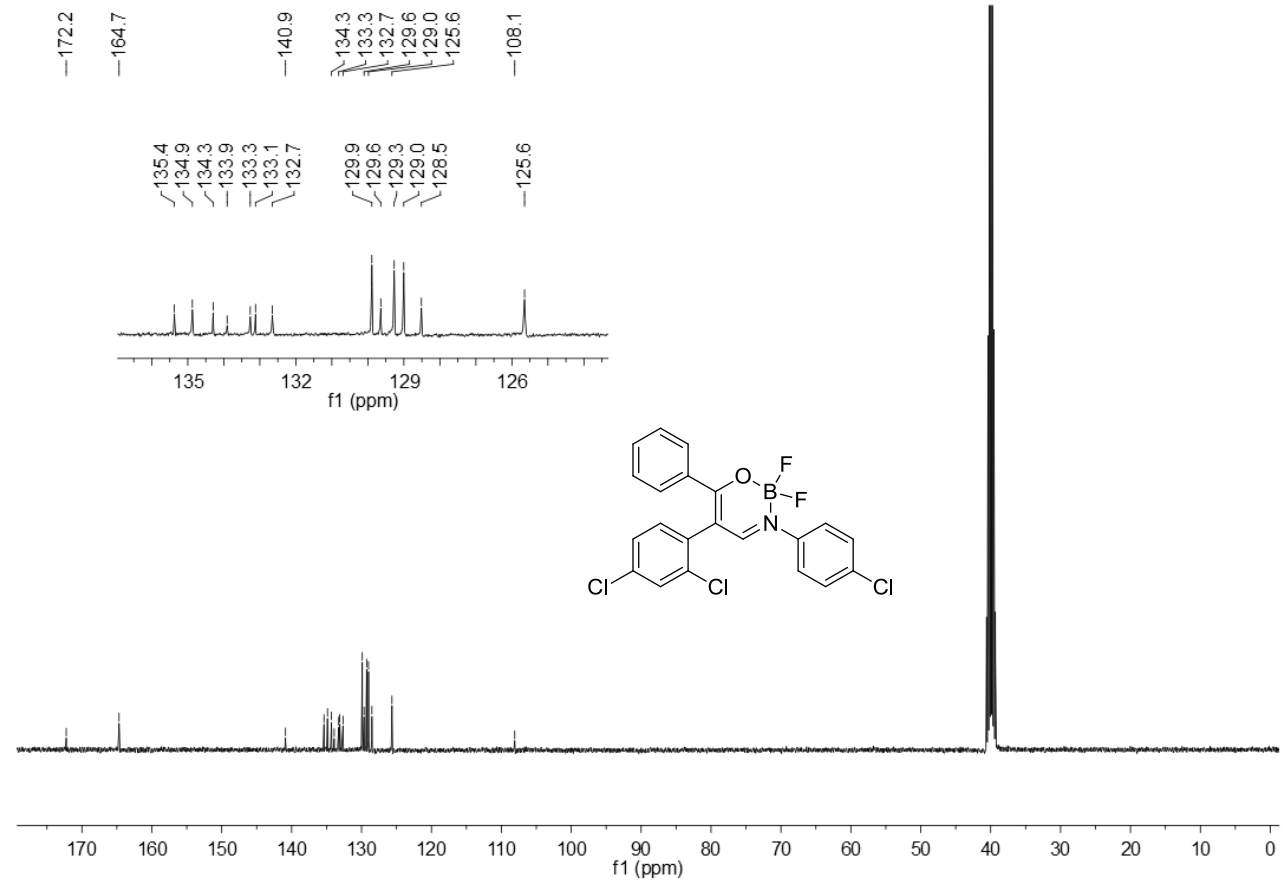
^{1}H NMR Spectrum of Compound 3h



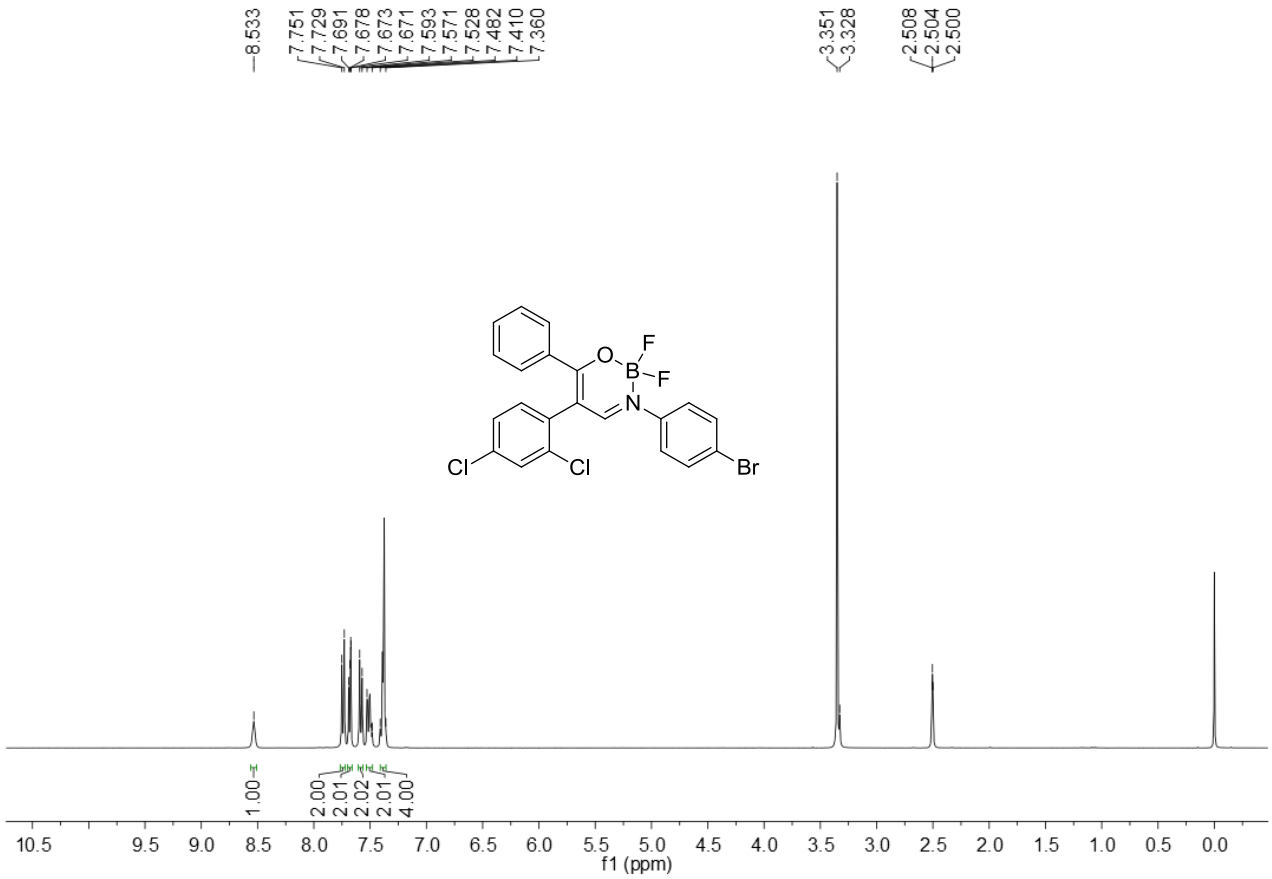
^{13}C NMR Spectrum of Compound 3h



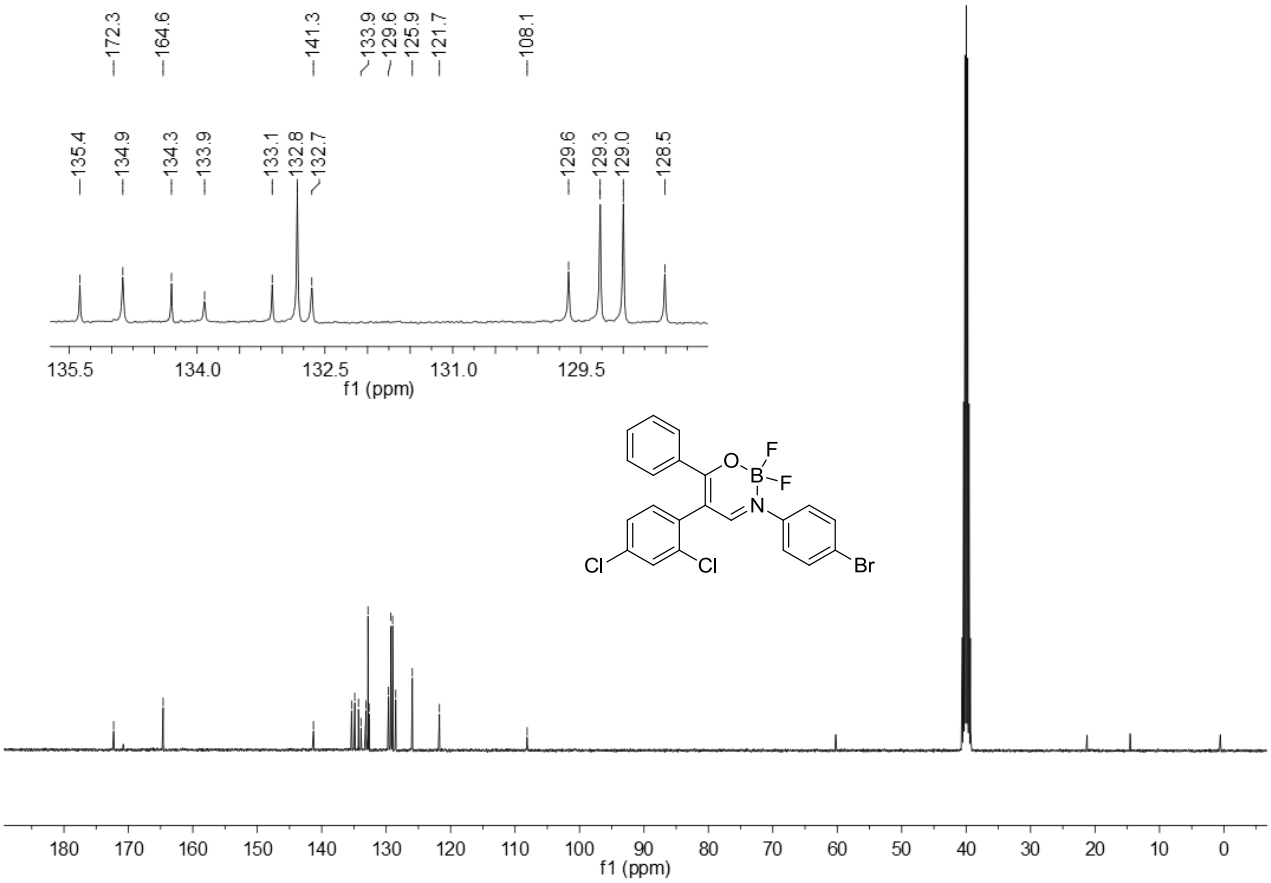
^{1}H NMR Spectrum of Compound 3i



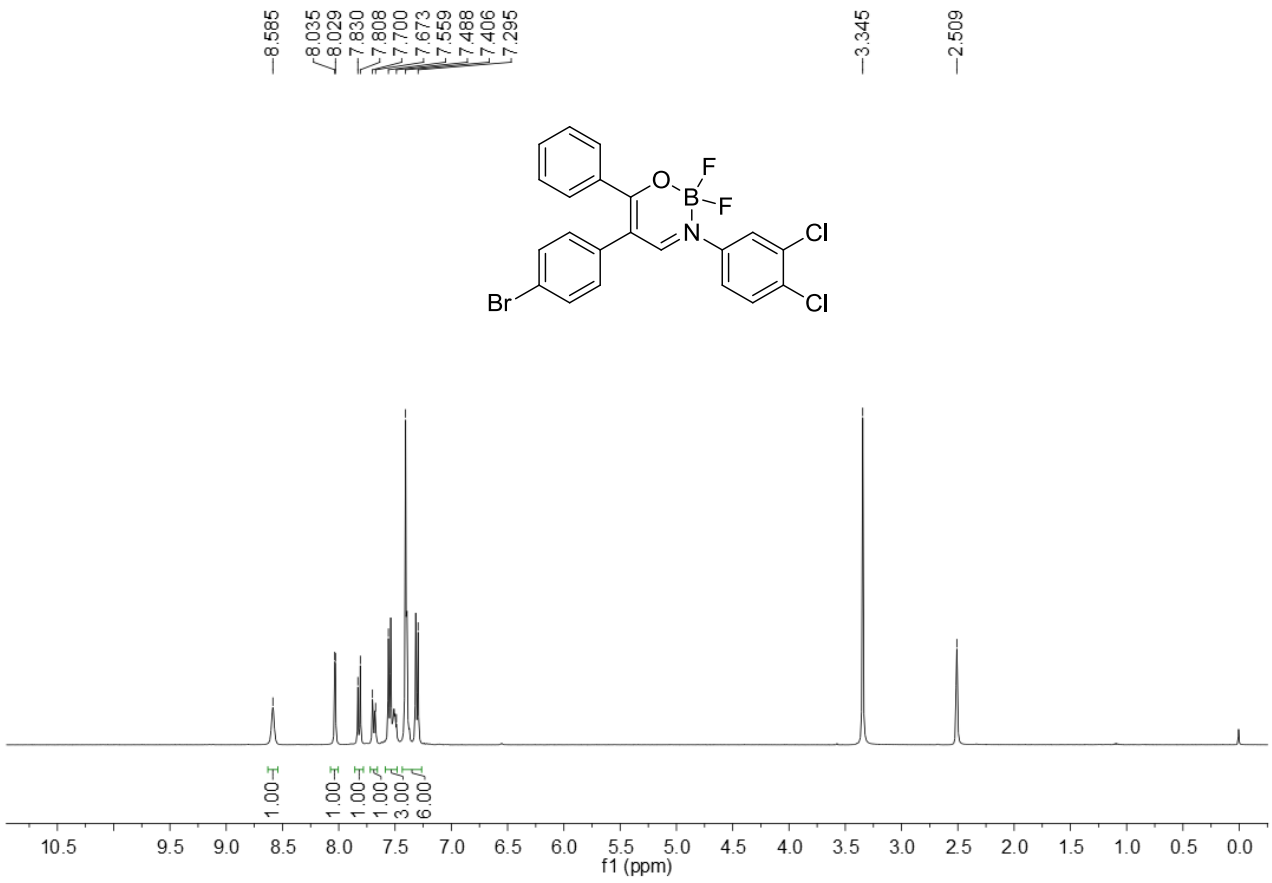
^{13}C NMR Spectrum of Compound 3i



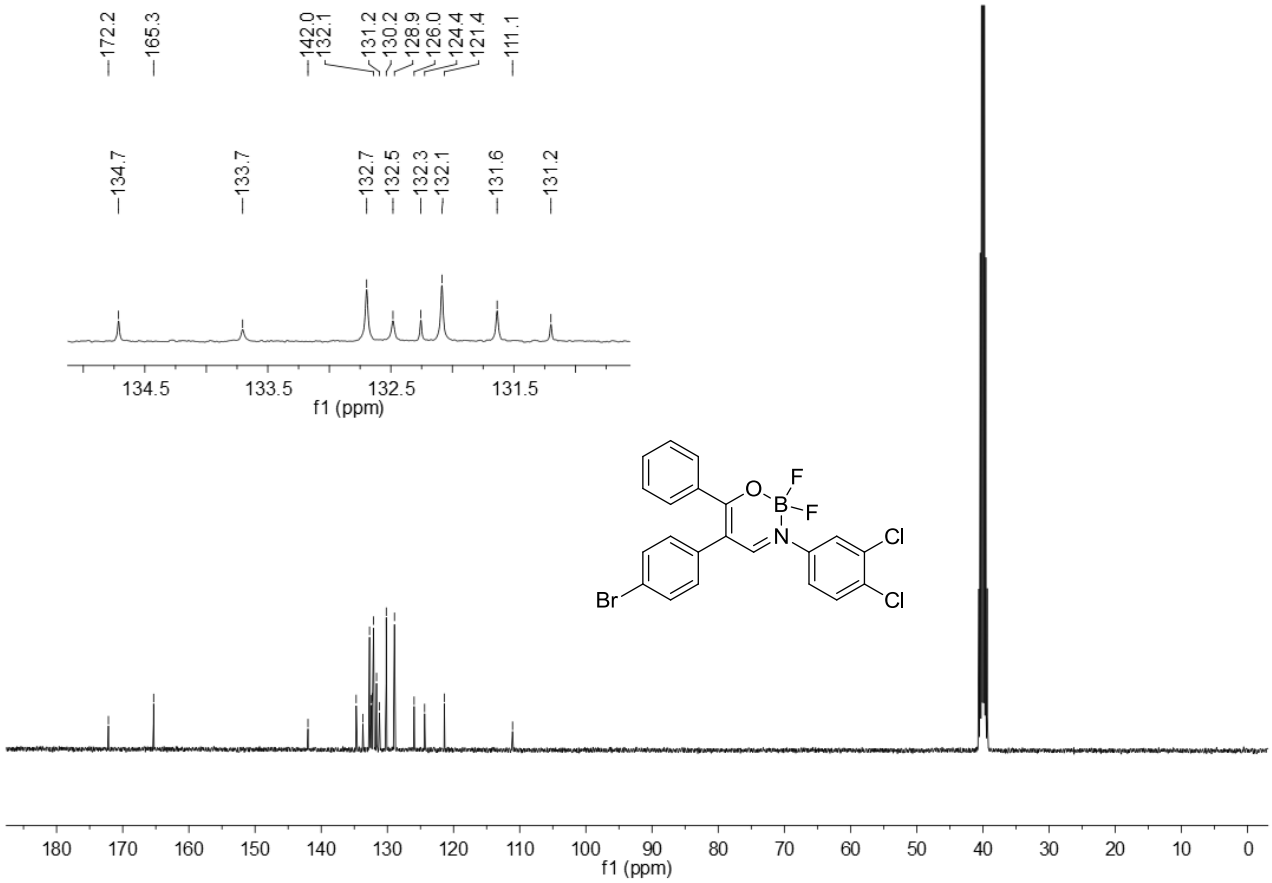
^{1}H NMR Spectrum of Compound 3j



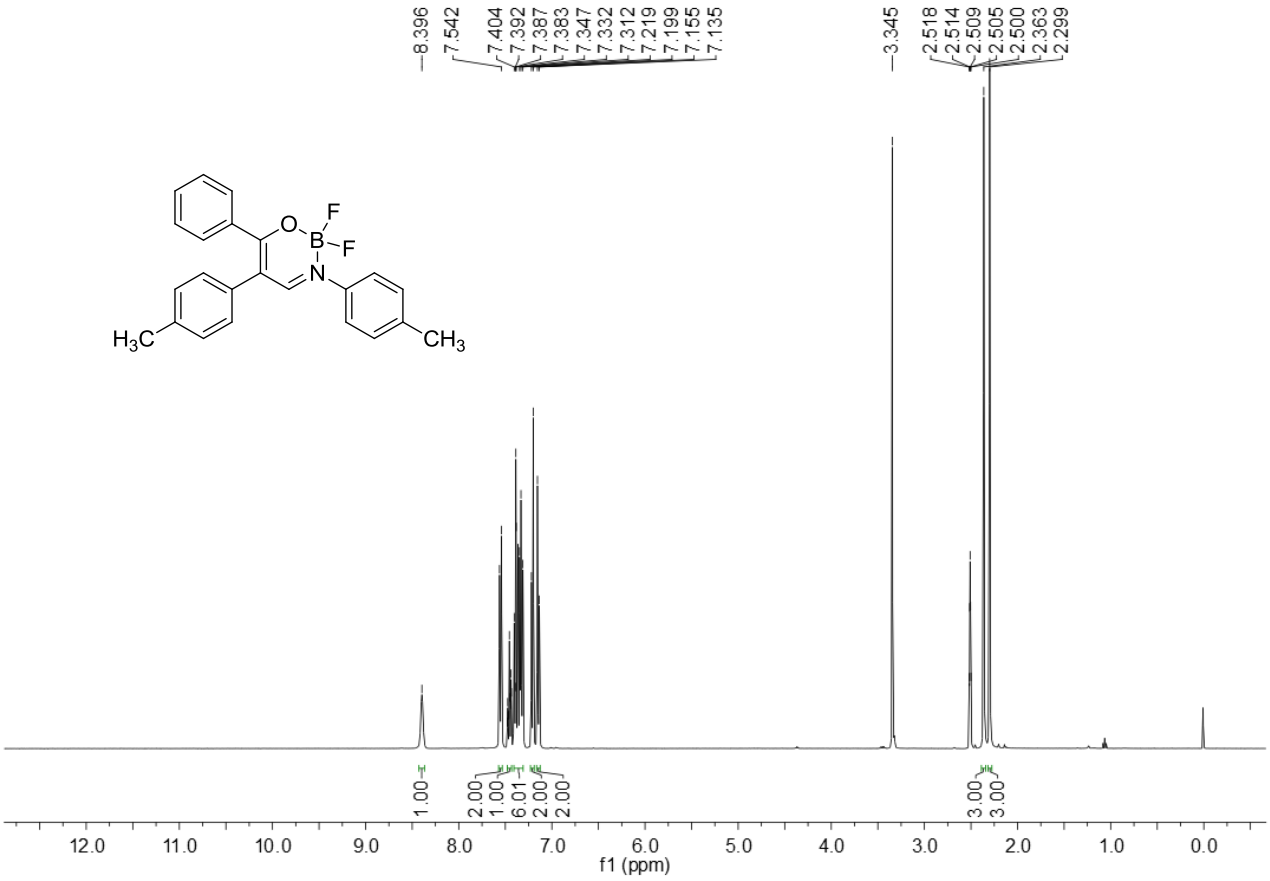
^{13}C NMR Spectrum of Compound 3j



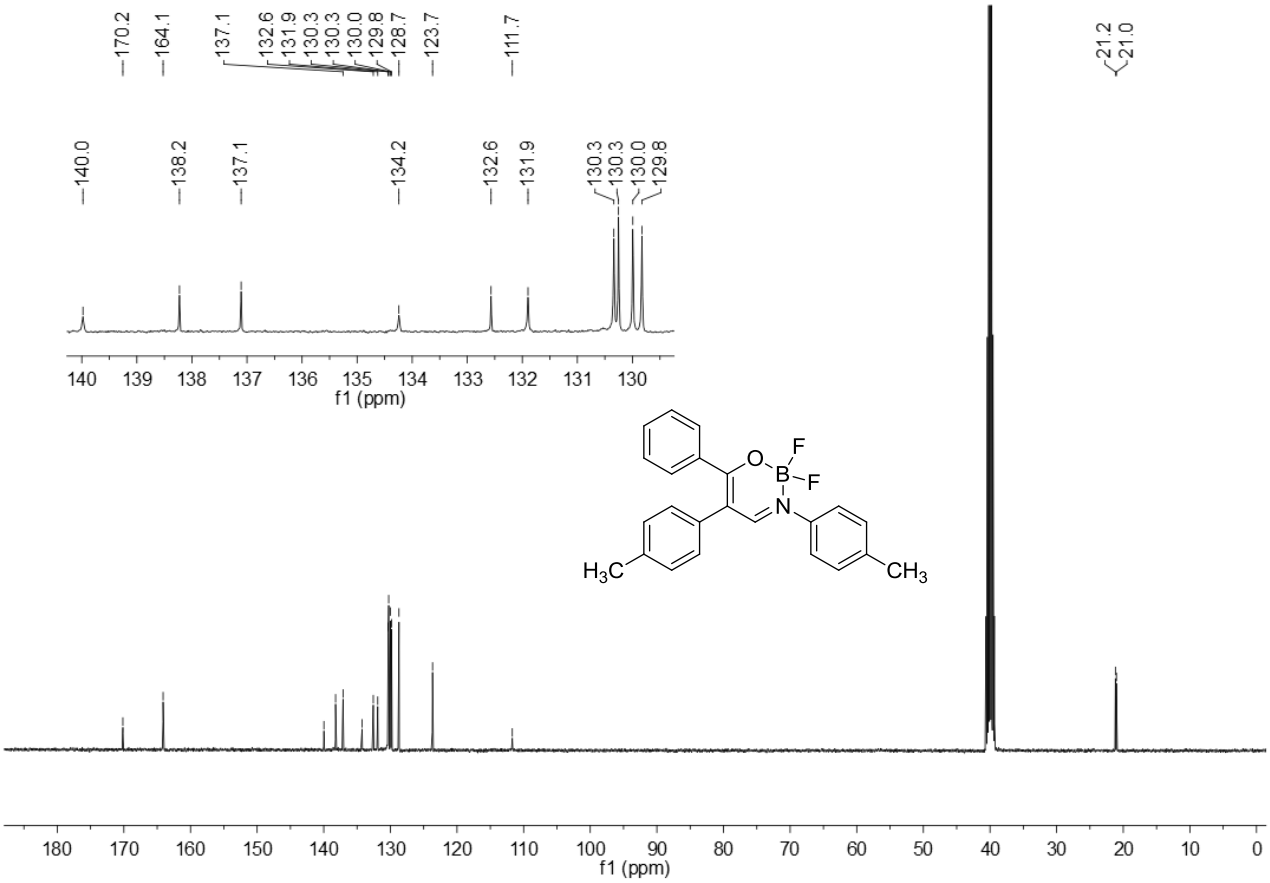
^{1}H NMR Spectrum of Compound 3k



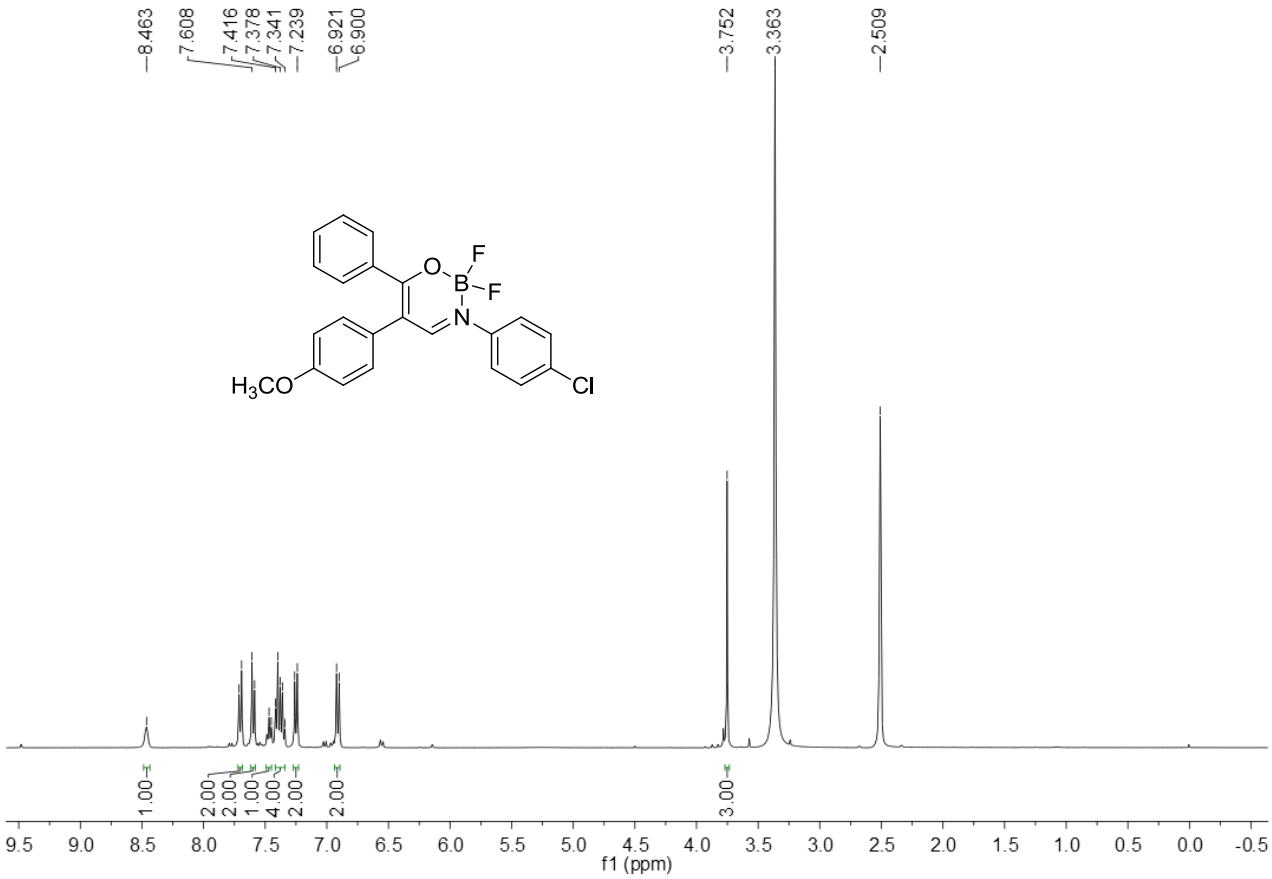
^{13}C NMR Spectrum of Compound 3k



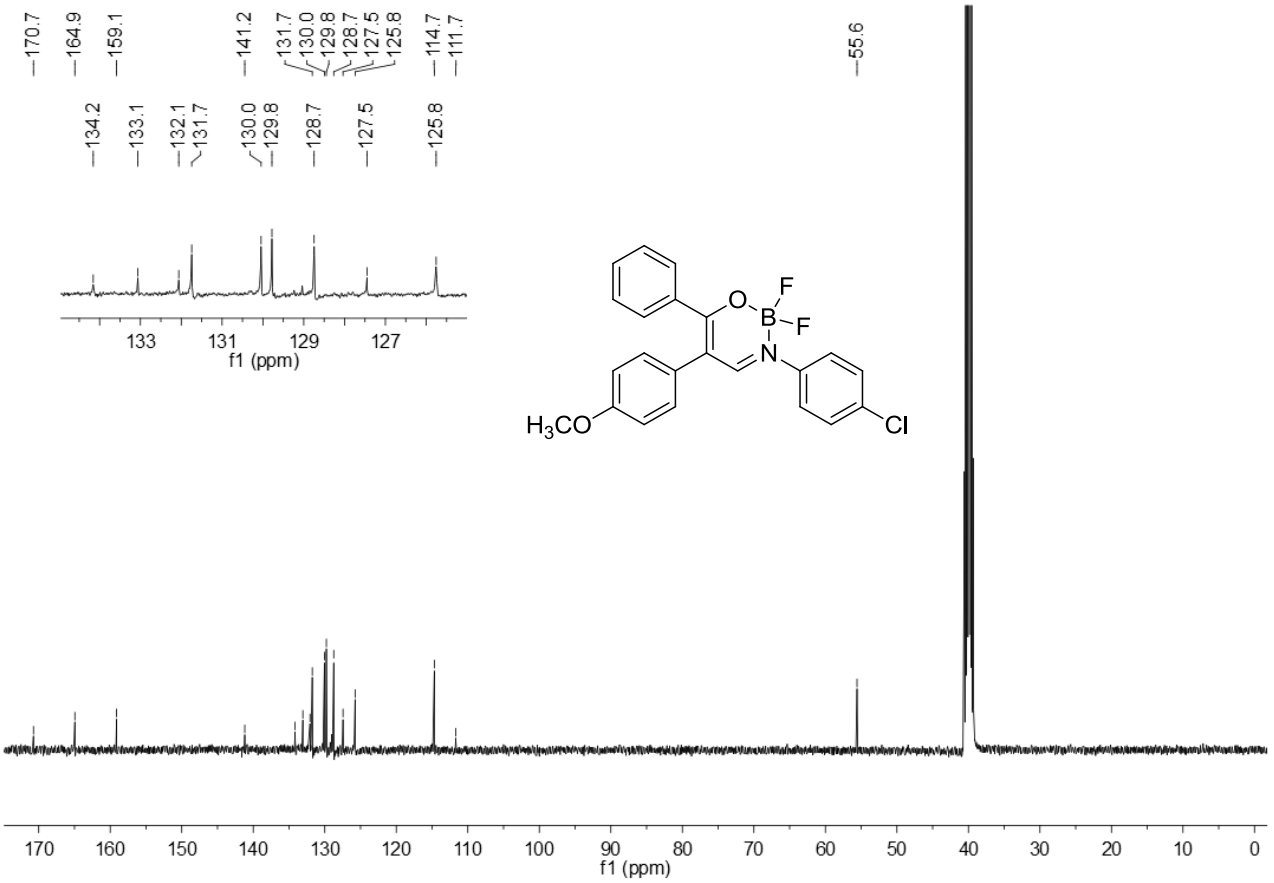
^{1}H NMR Spectrum of Compound3l



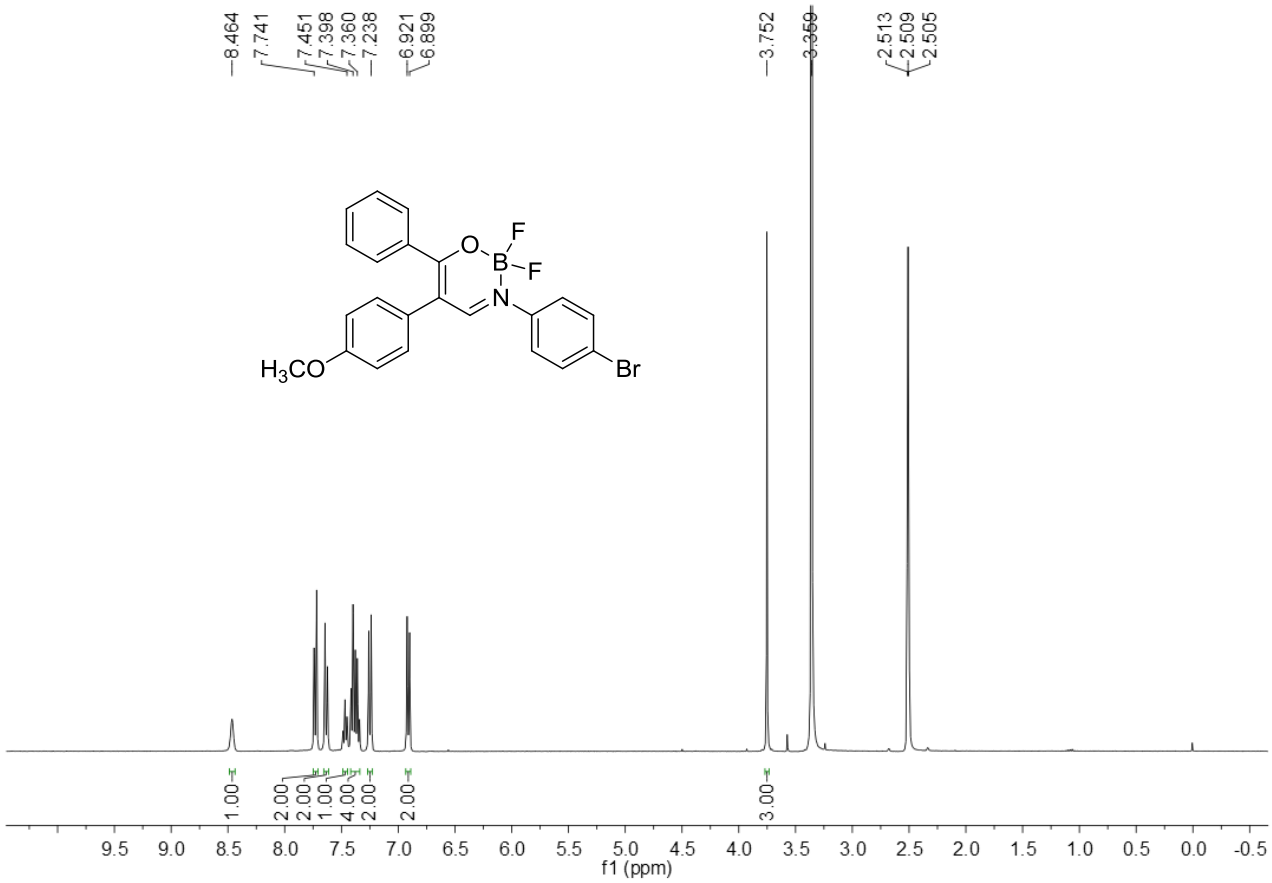
^{13}C NMR Spectrum of Compound 3l



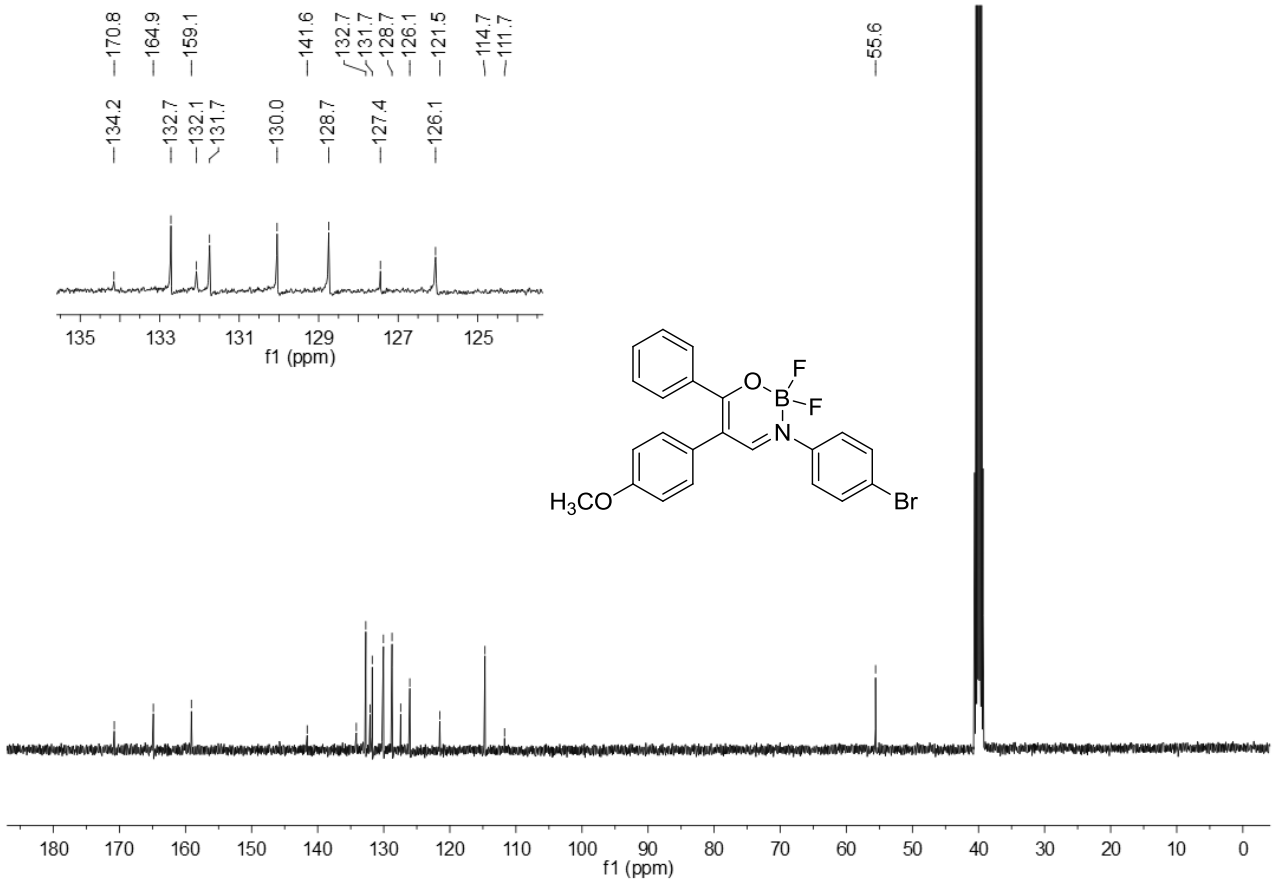
[1]H NMR Spectrum of Compound 3m



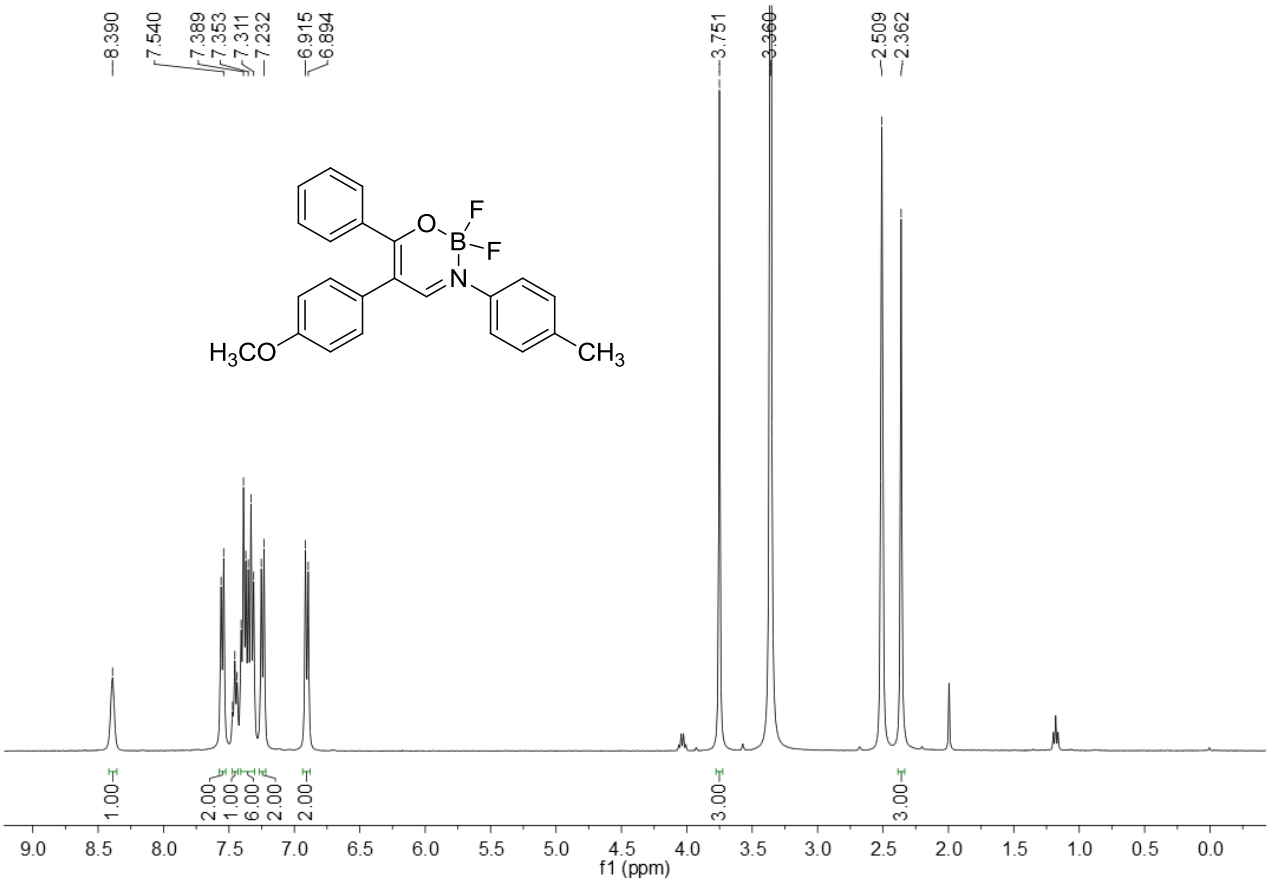
[13]C NMR Spectrum of Compound 3m



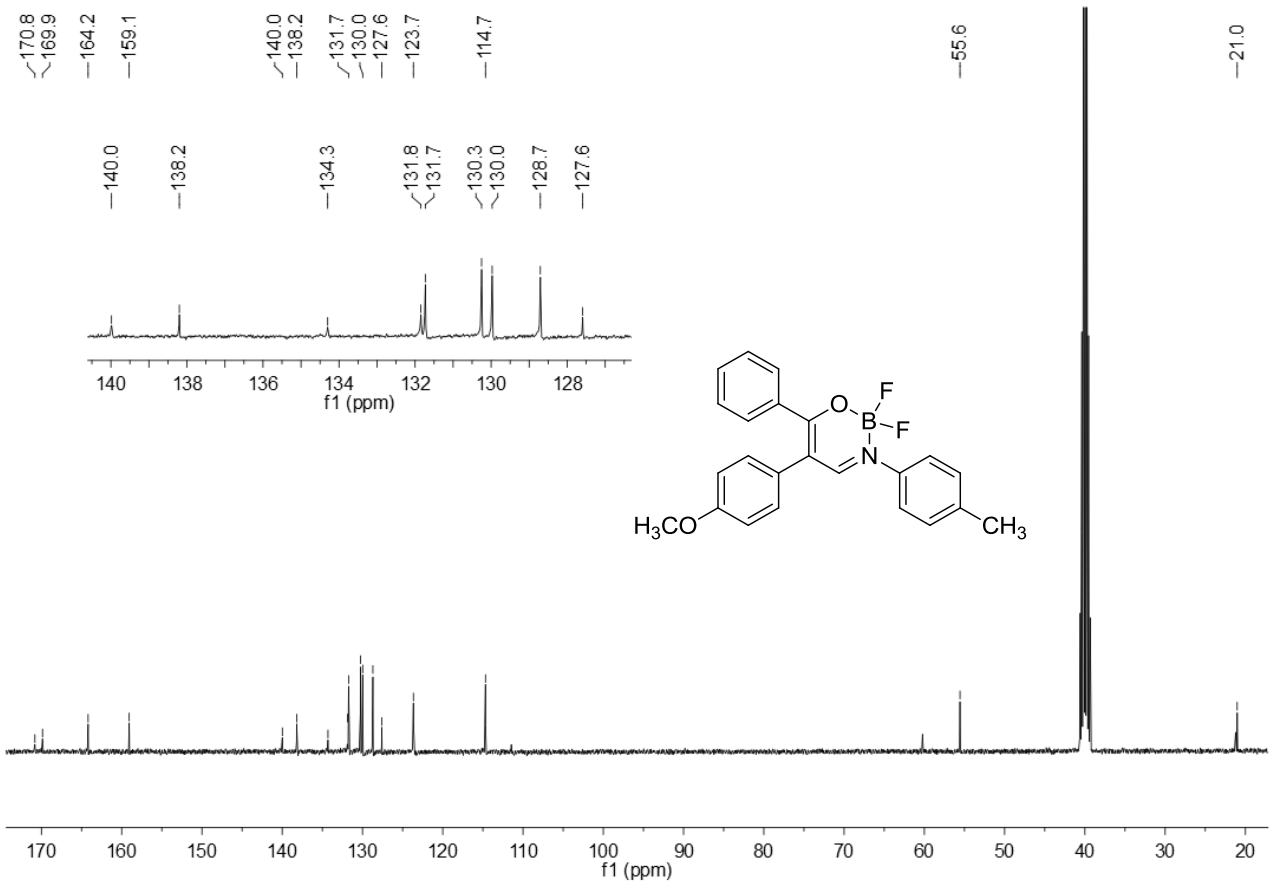
^{1}H NMR Spectrum of Compound 3n



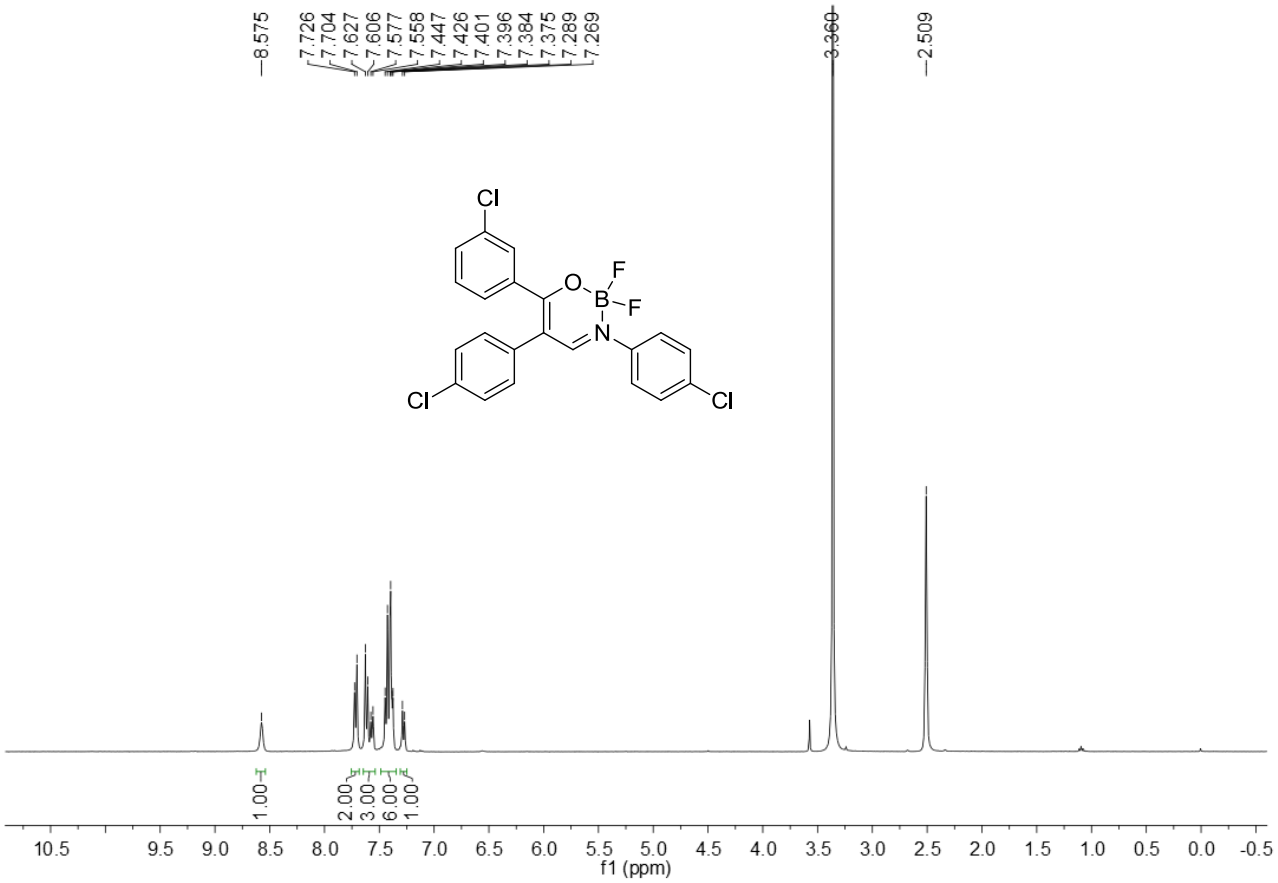
^{13}C NMR Spectrum of Compound 3n



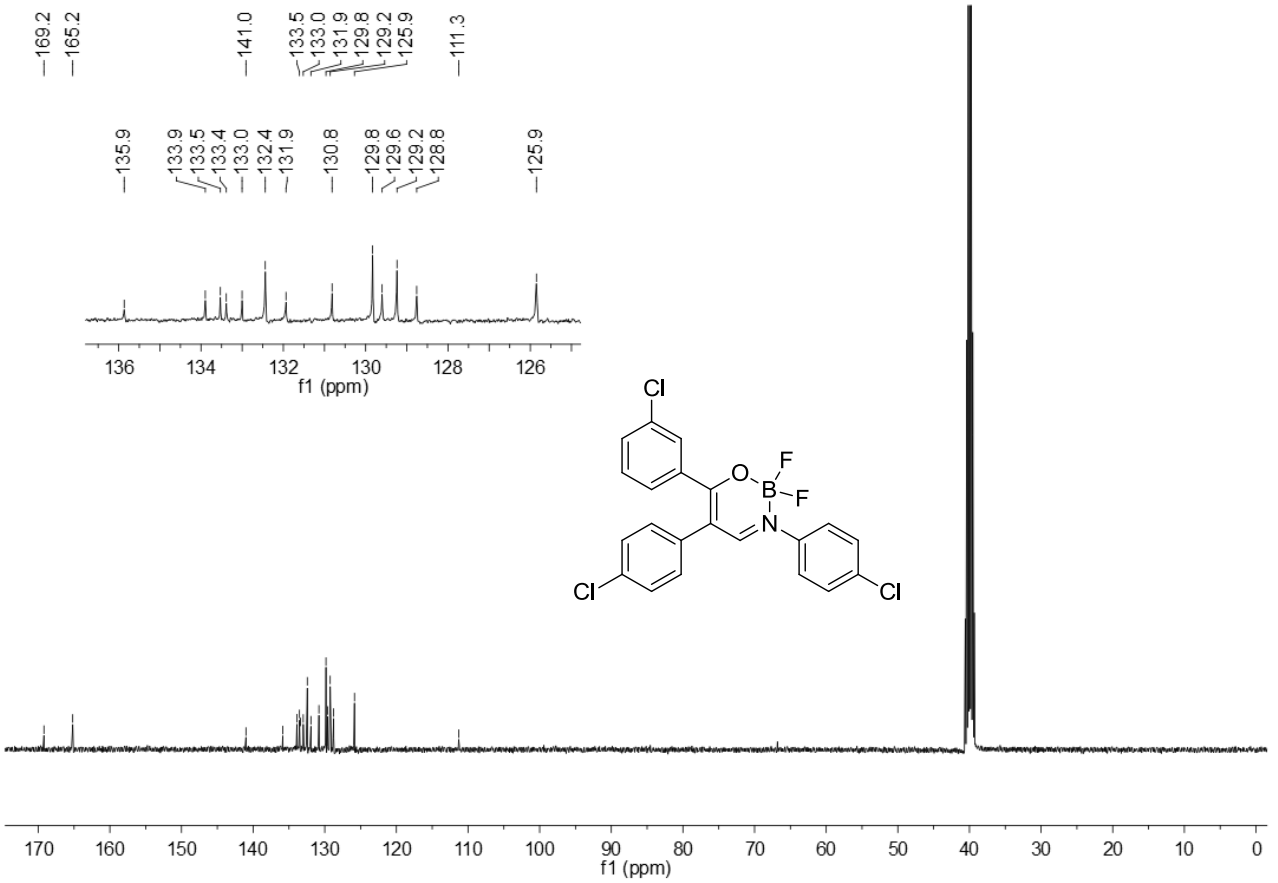
^{1}H NMR Spectrum of Compound 3o



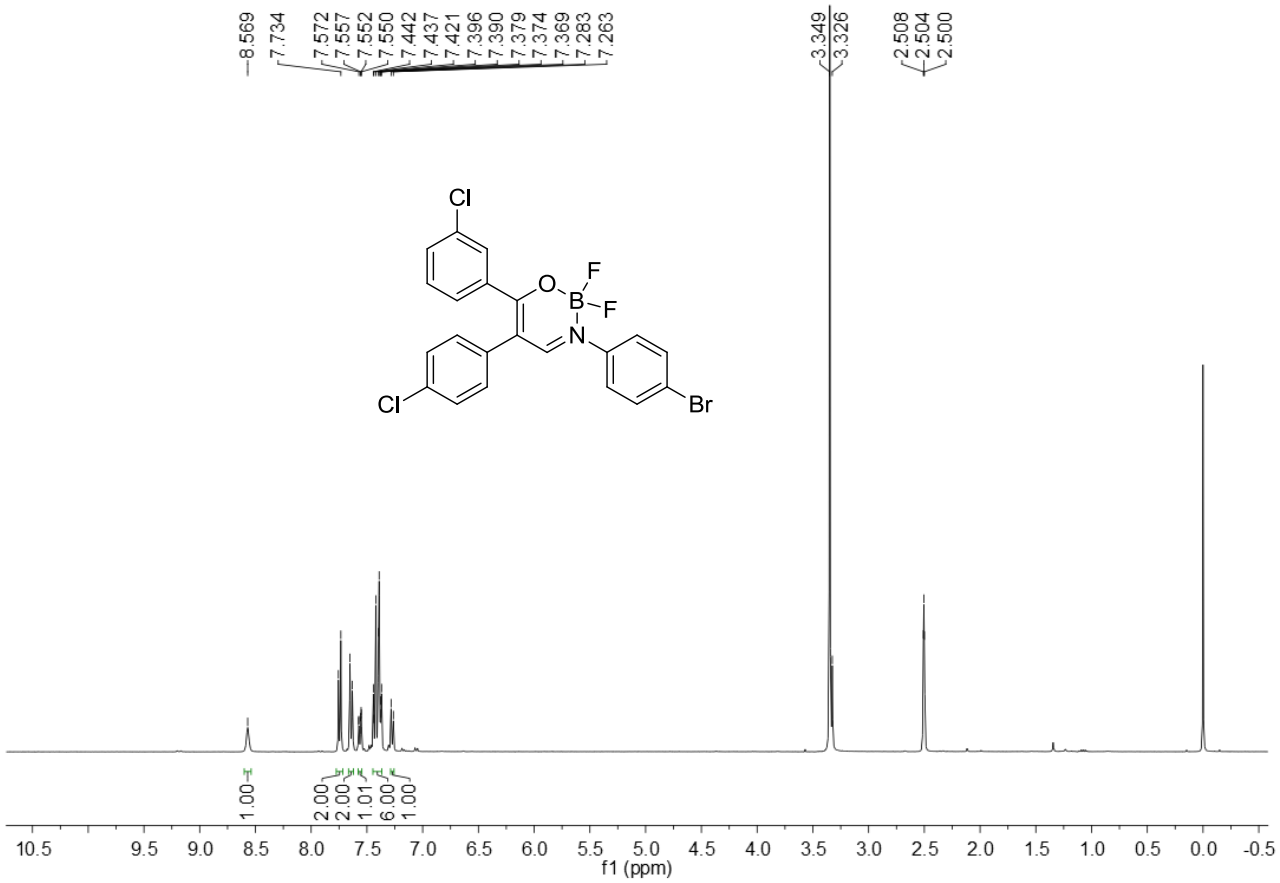
^{13}C NMR Spectrum of Compound 3o



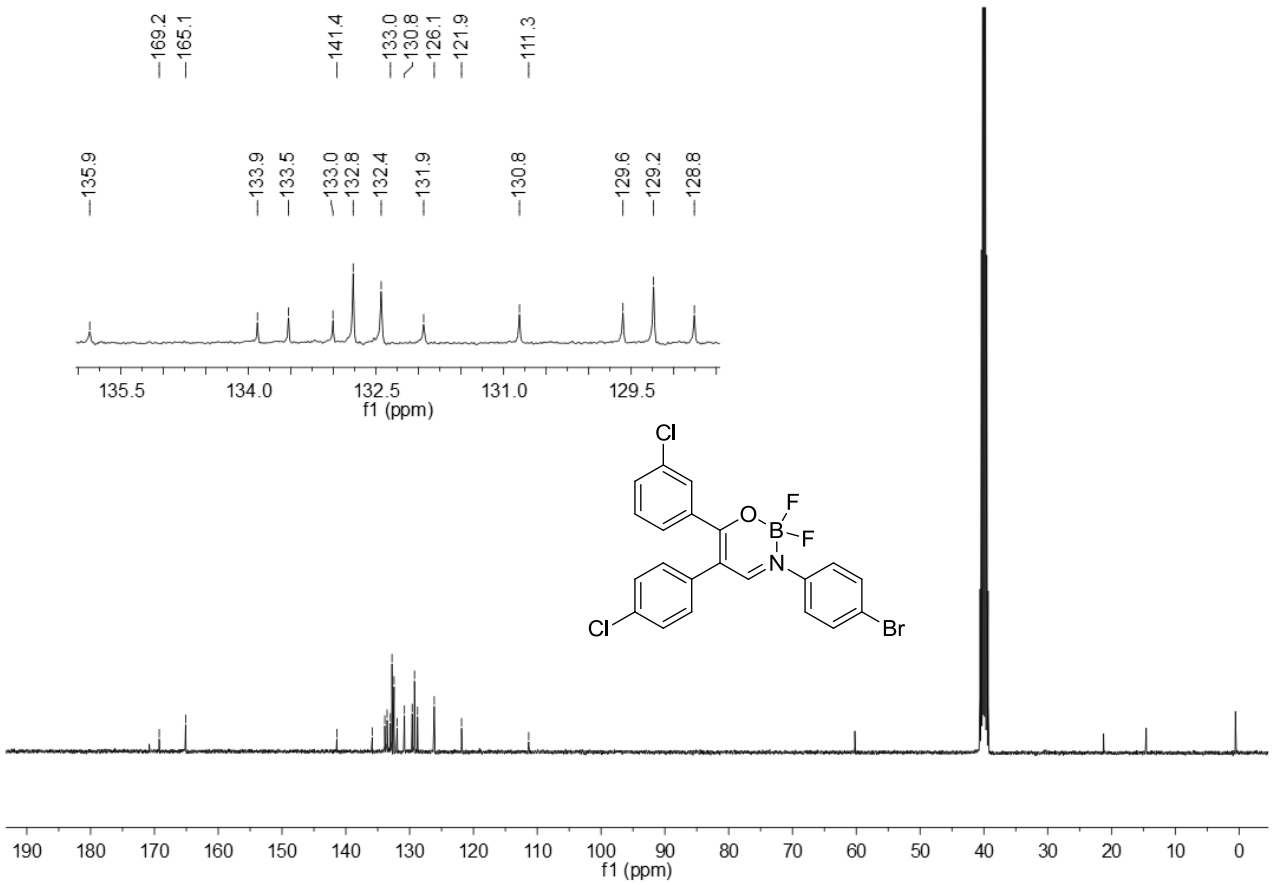
^{1}H NMR Spectrum of Compound 3p



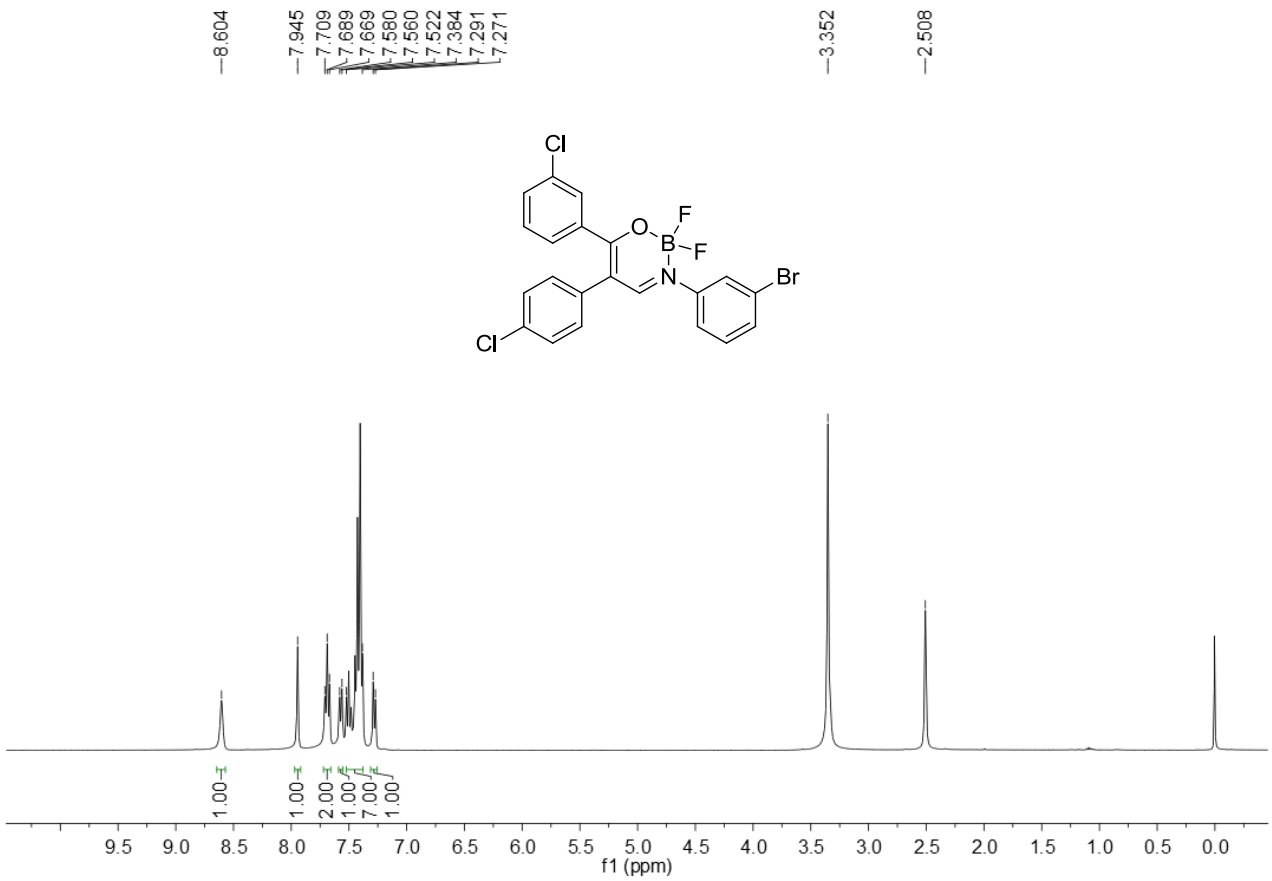
^{13}C NMR Spectrum of Compound 3p



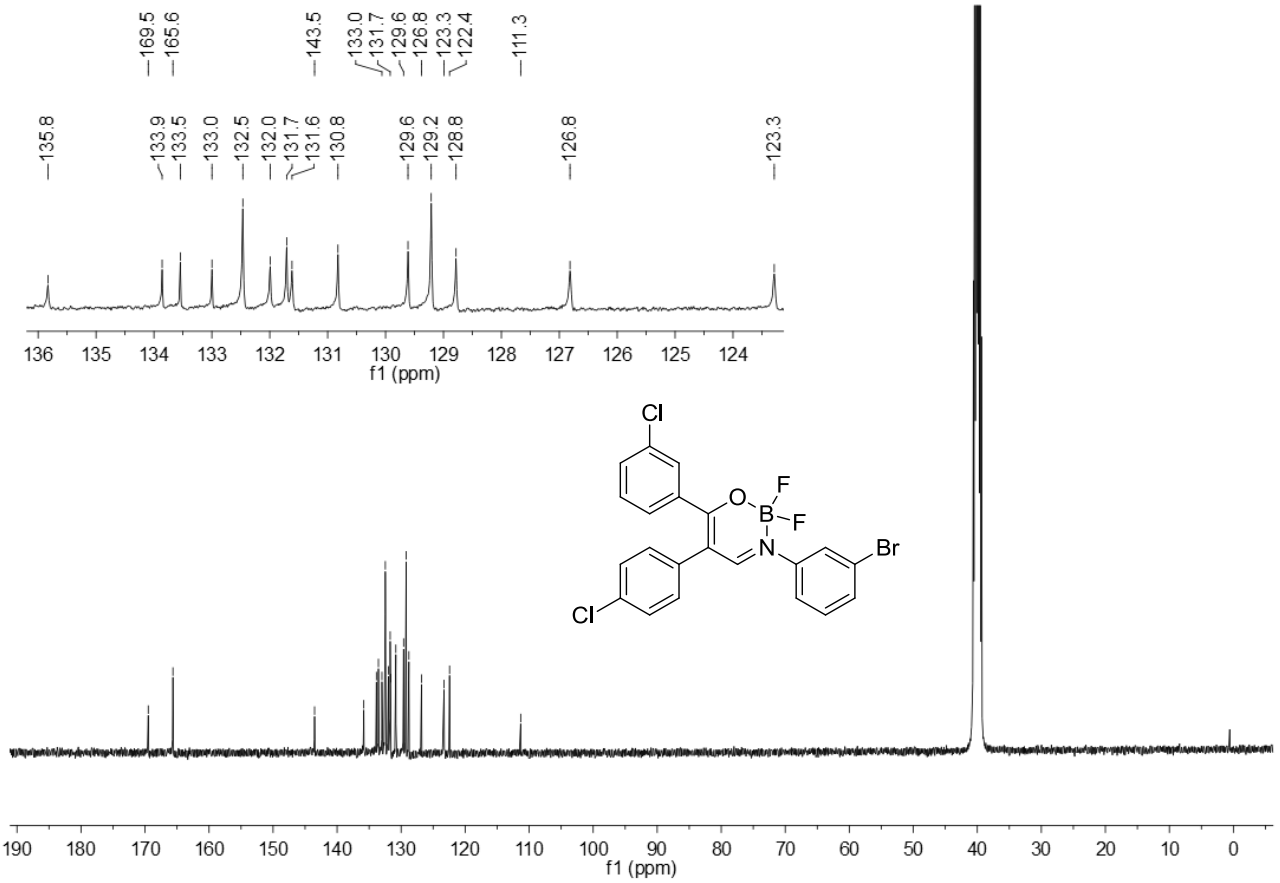
^{1}H NMR Spectrum of Compound 3q



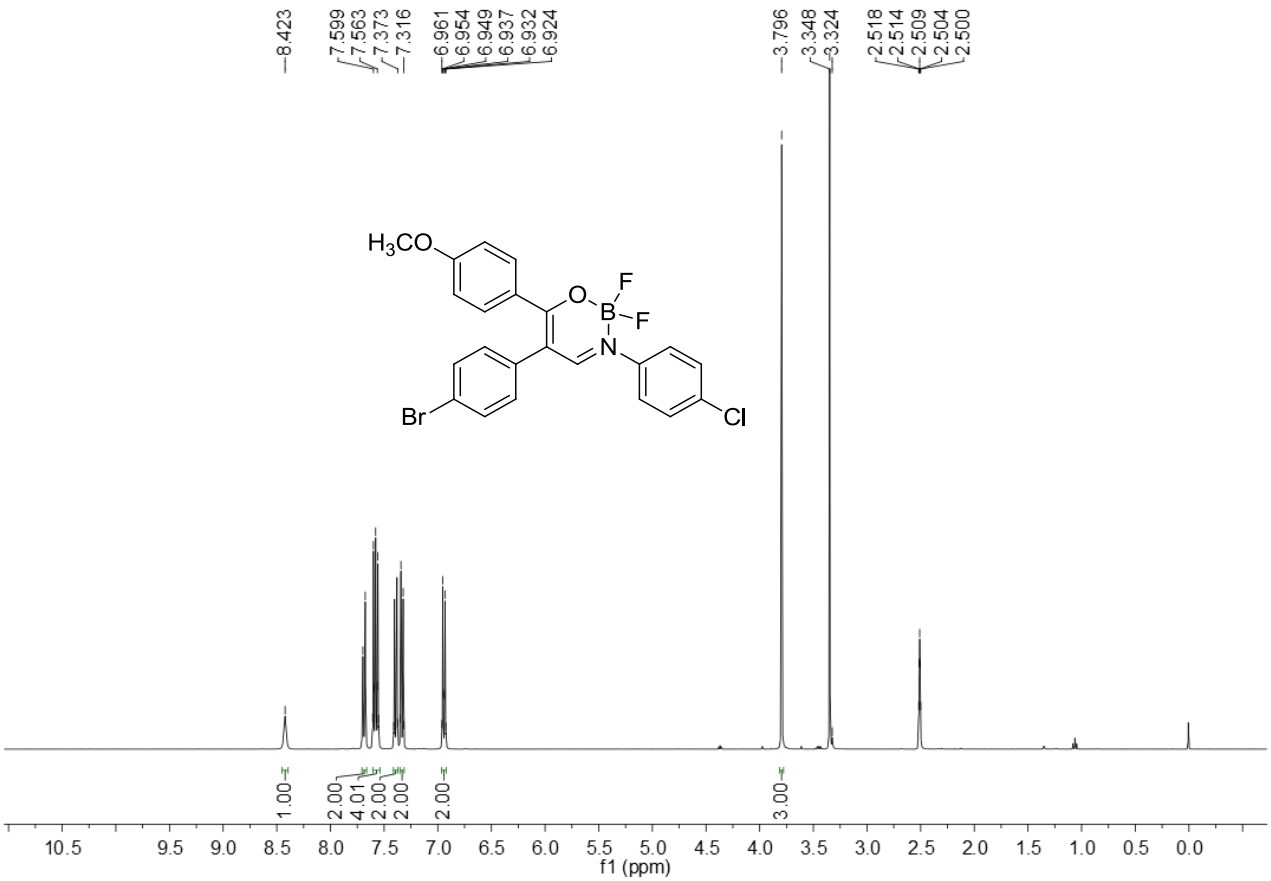
^{13}C NMR Spectrum of Compound 3q



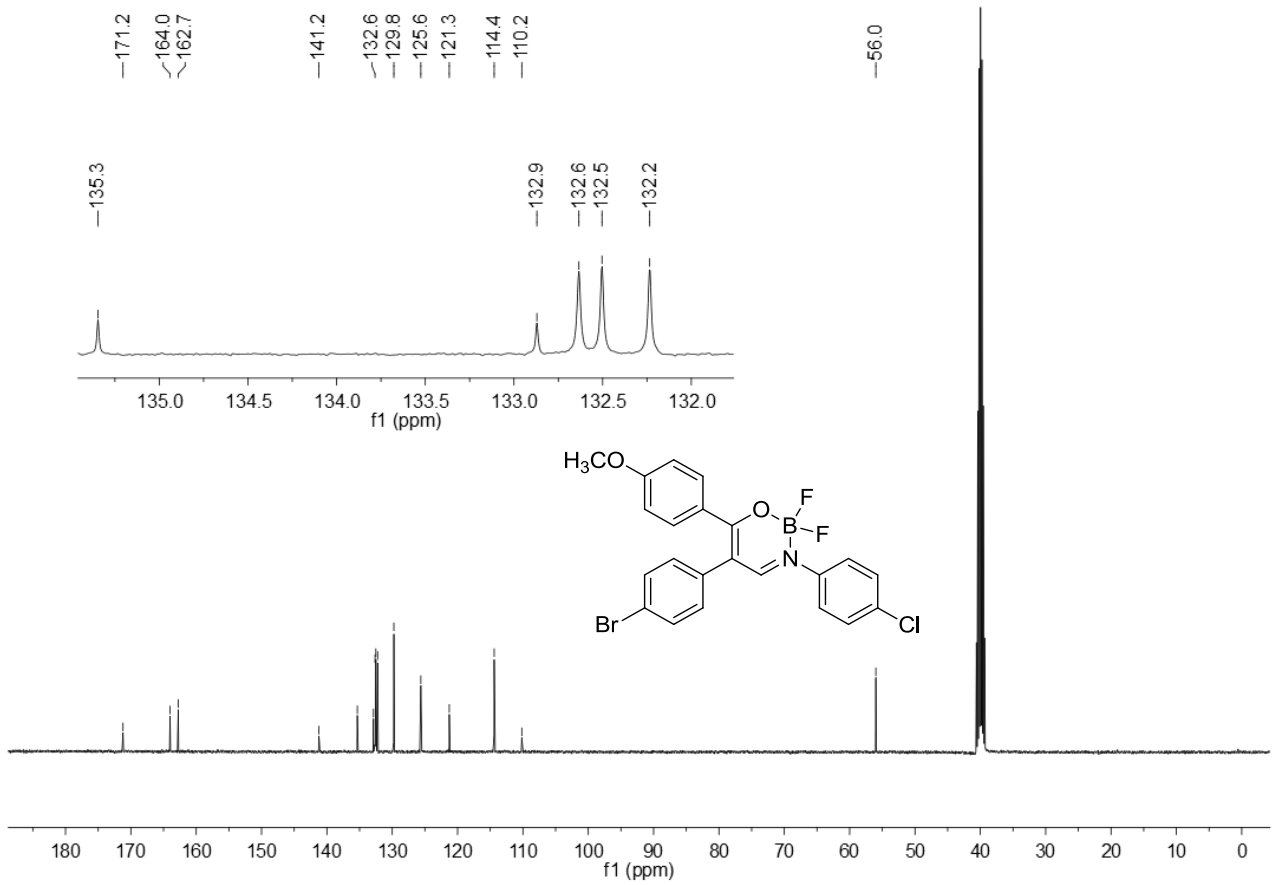
^{1}H NMR Spectrum of Compound 3r



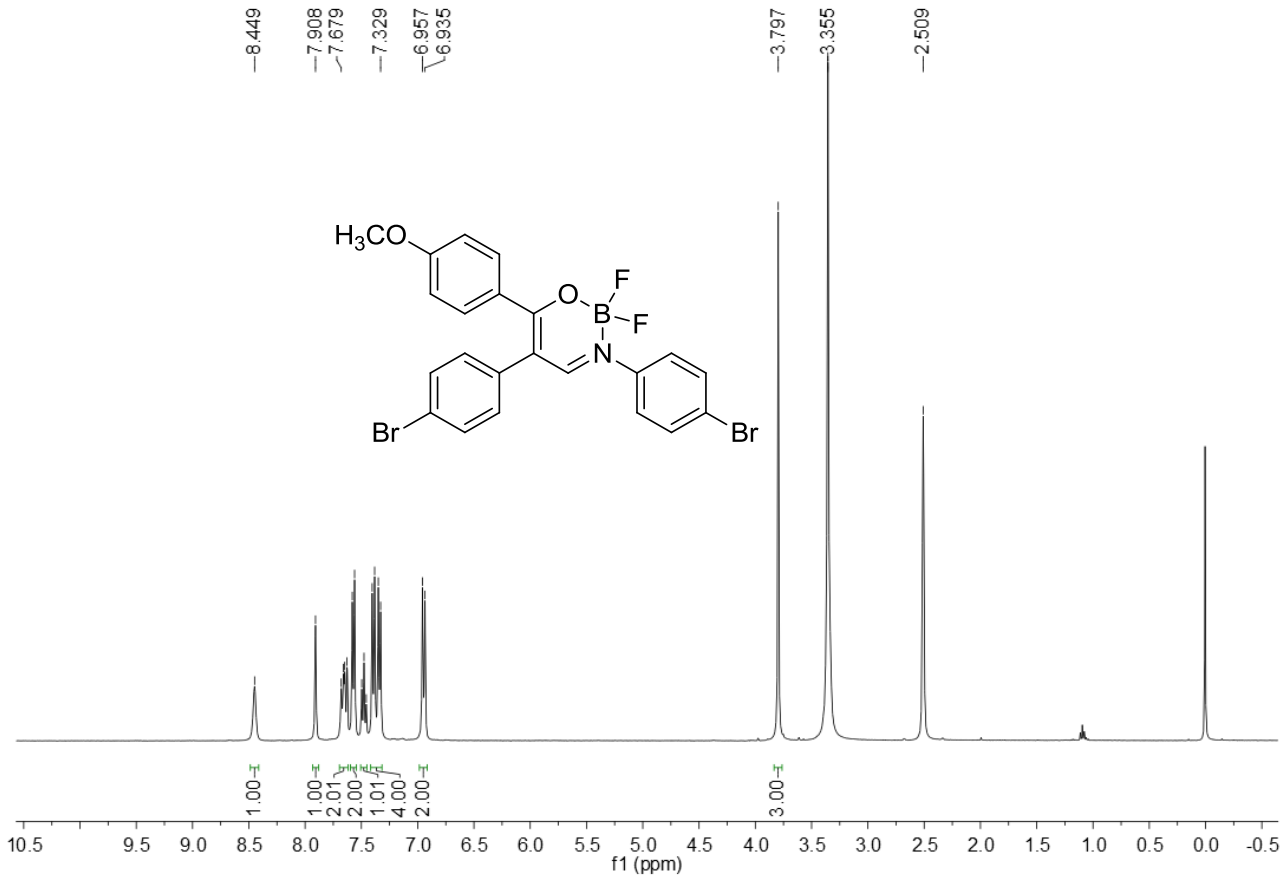
^{13}C NMR Spectrum of Compound 3r



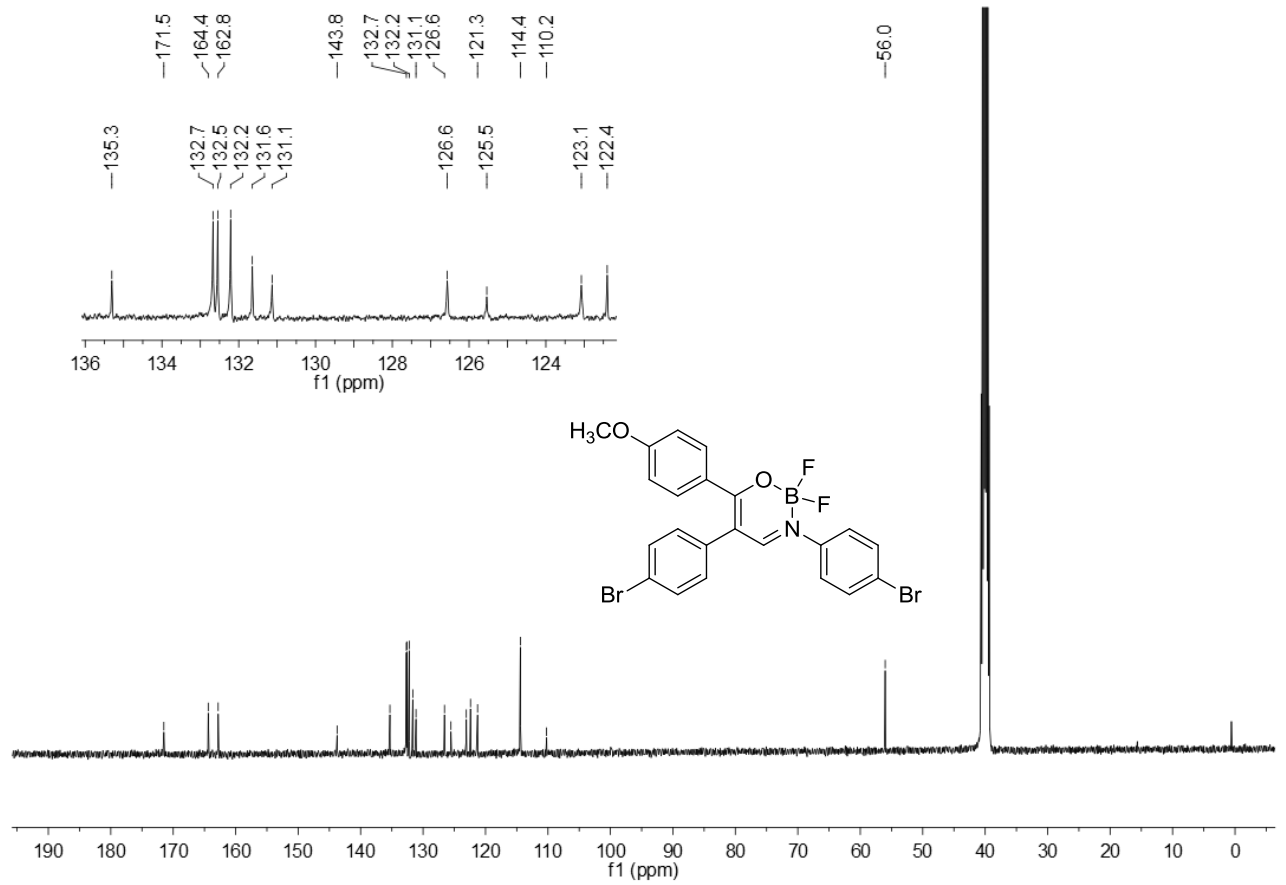
^{1}H NMR Spectrum of Compound 3s



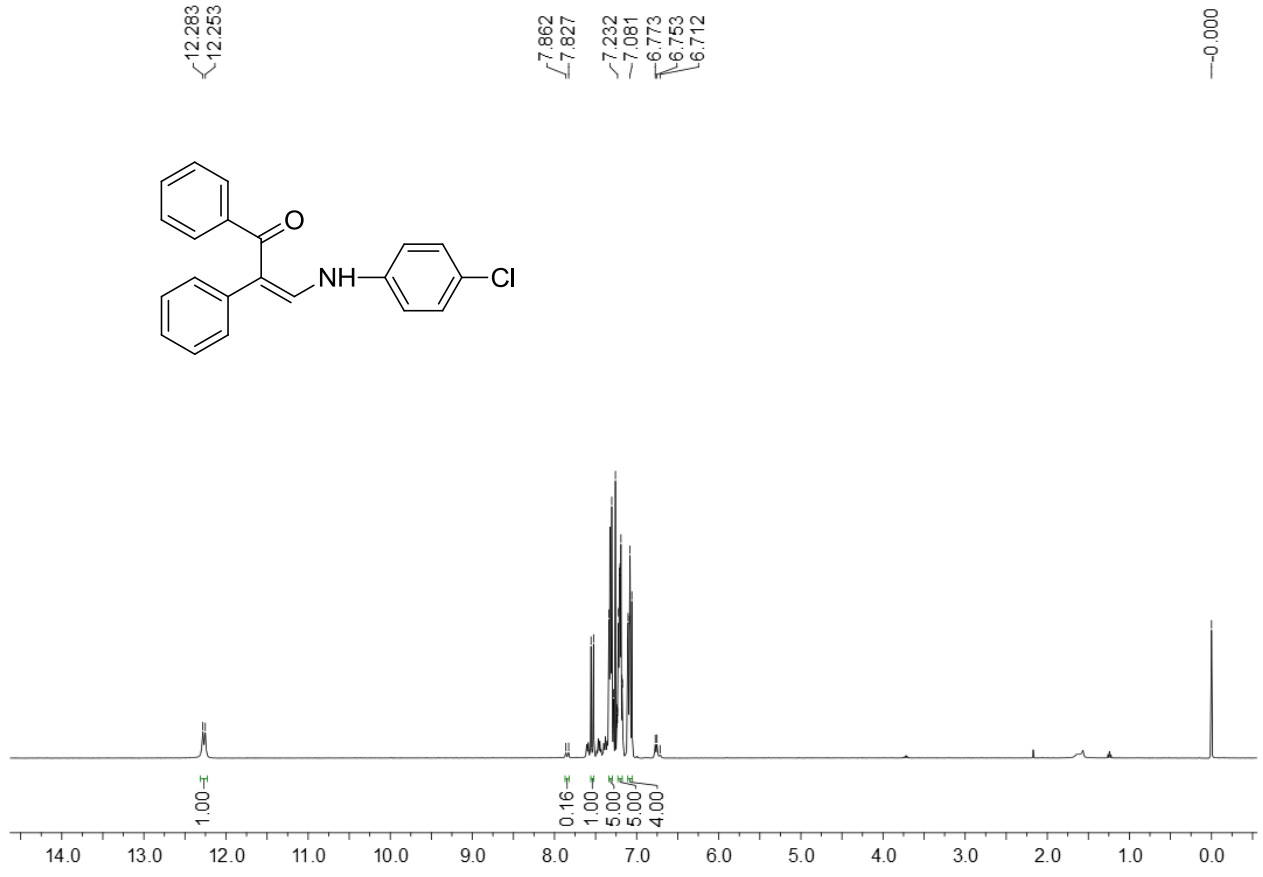
^{13}C NMR Spectrum of Compound 3s



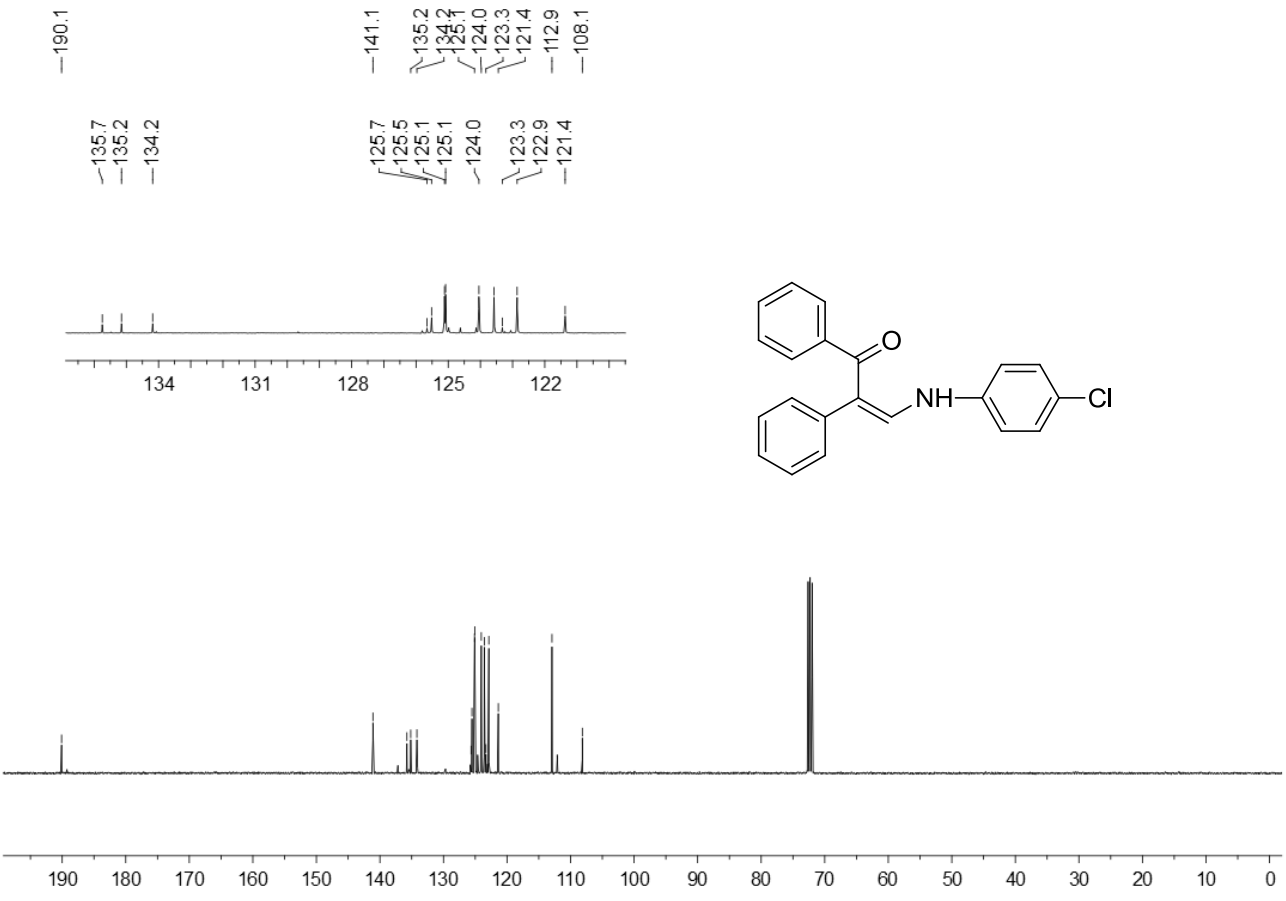
^{1}H NMR Spectrum of Compound 3t



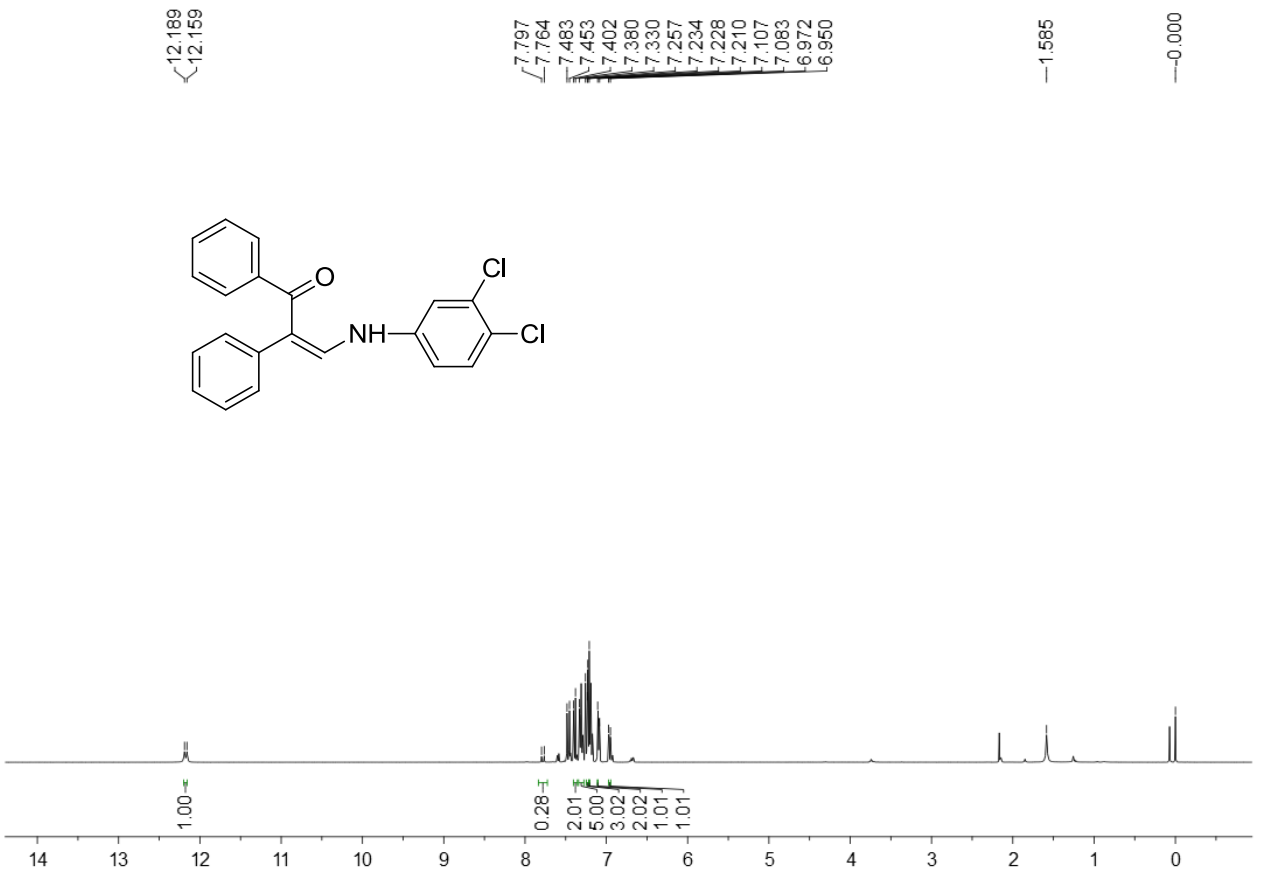
^{13}C NMR Spectrum of Compound 3t



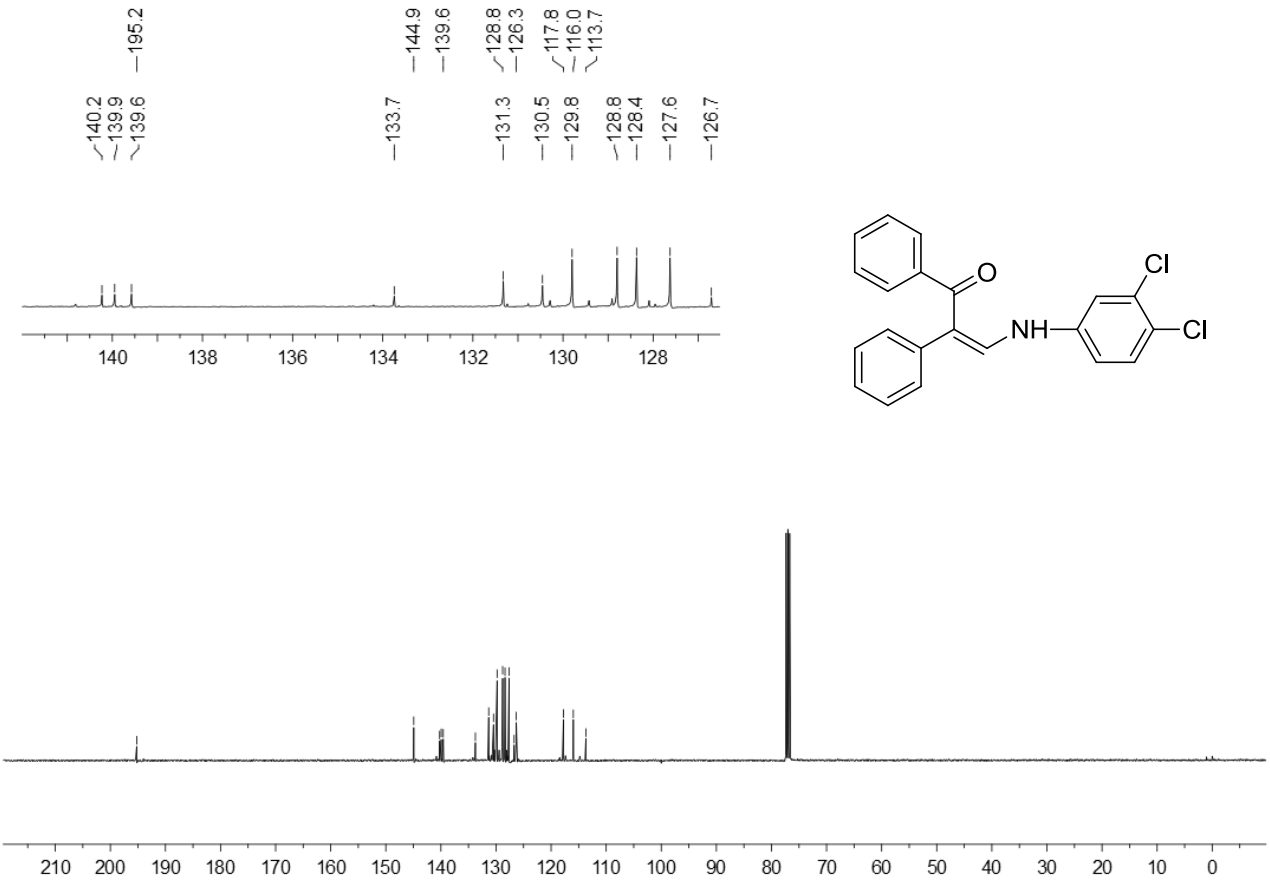
^{1}H NMR Spectrum of Compound 4a



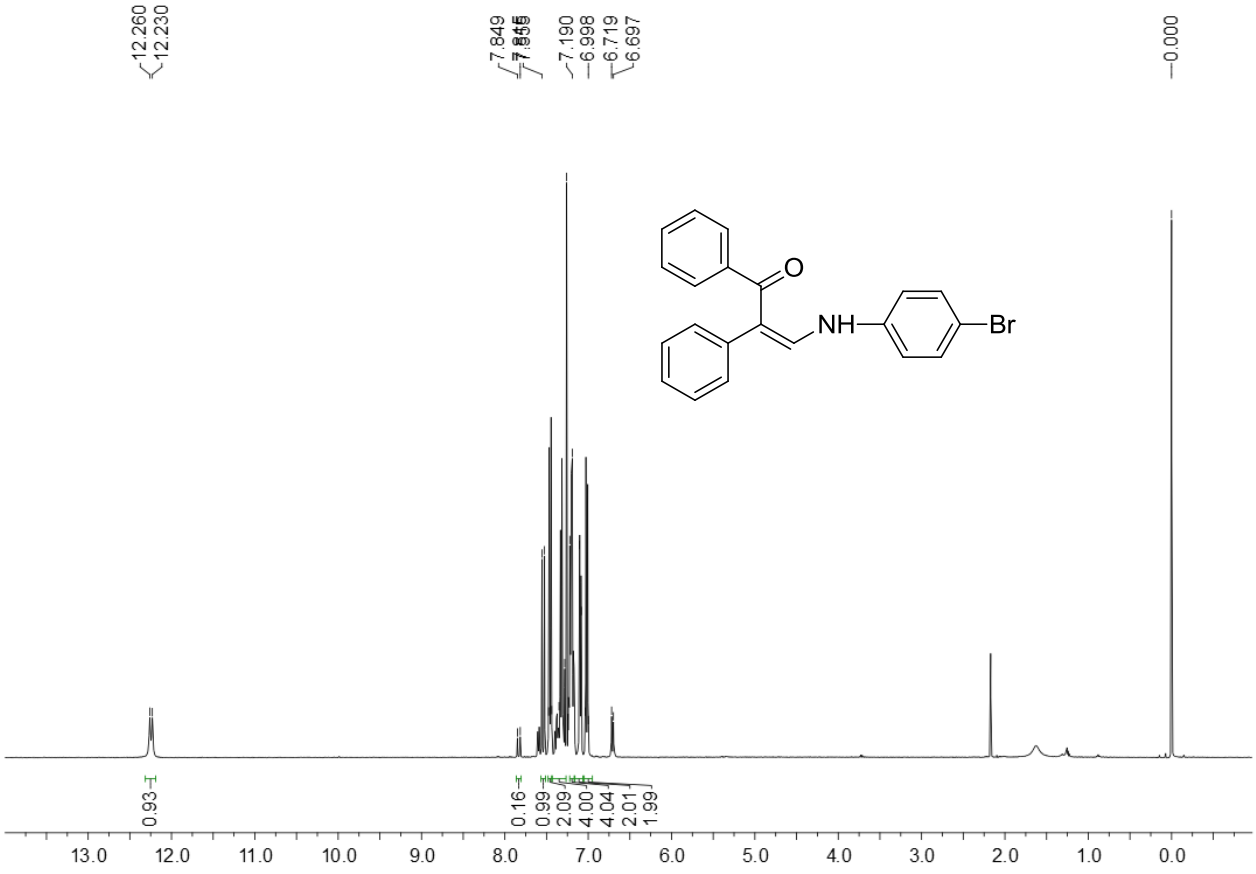
^{13}C NMR Spectrum of Compound 4a



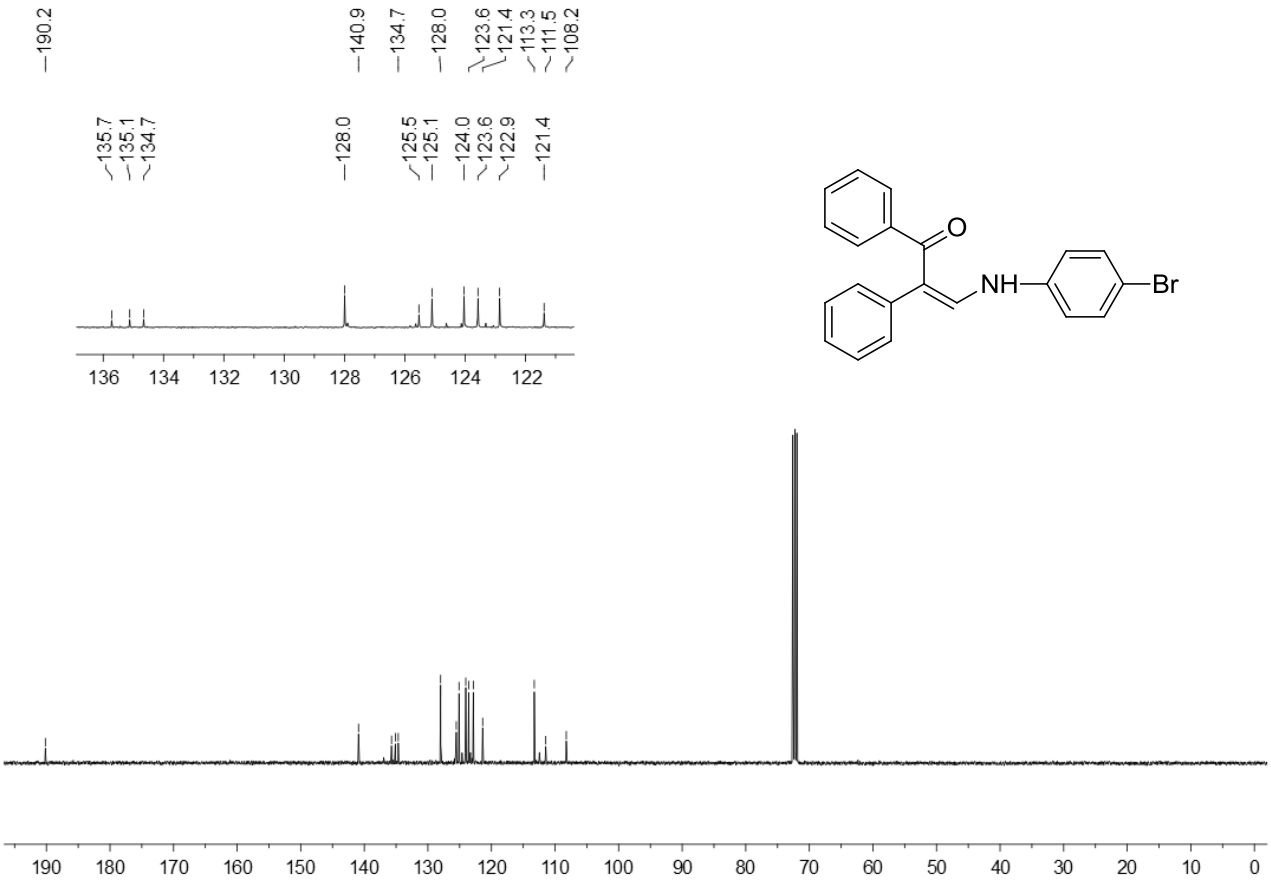
^{1}H NMR Spectrum of Compound 4b



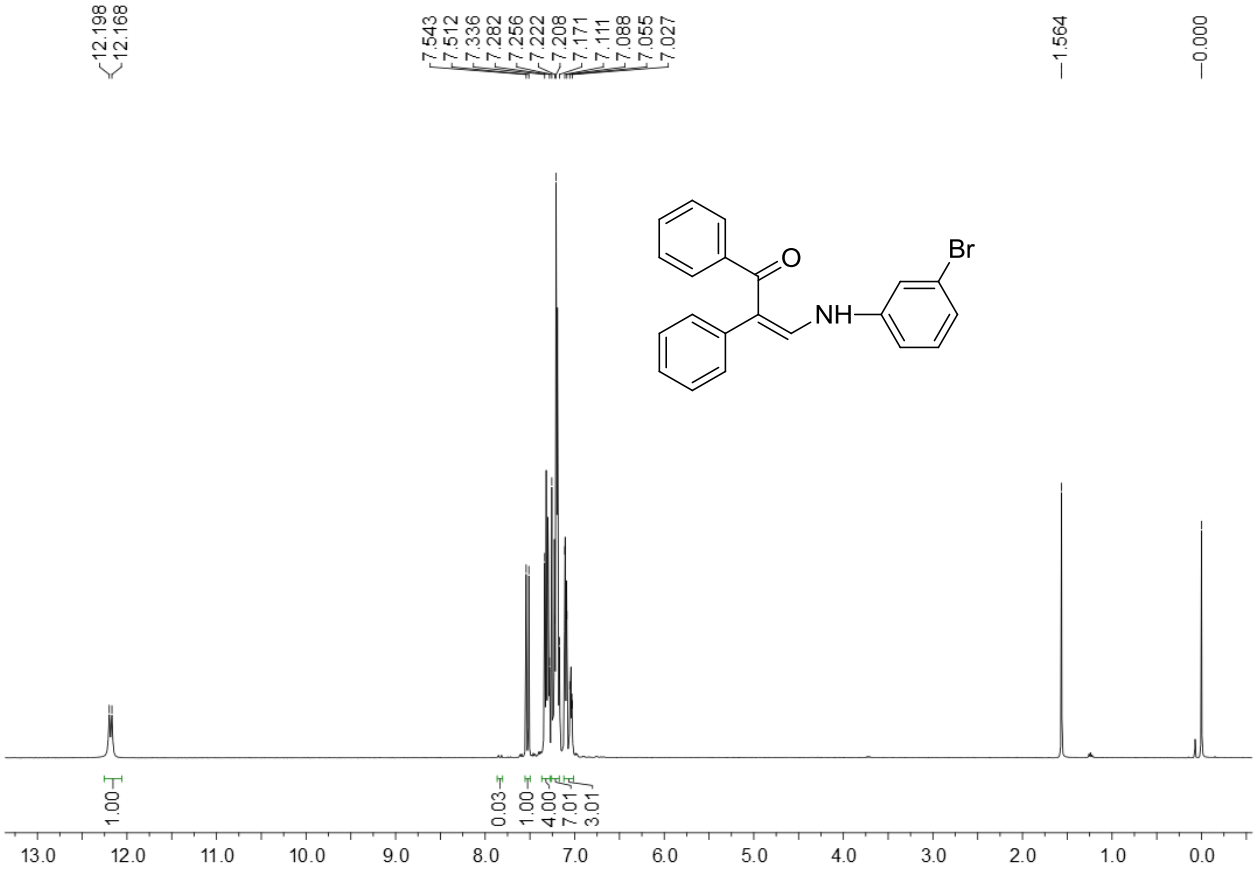
^{13}C NMR Spectrum of Compound 4b



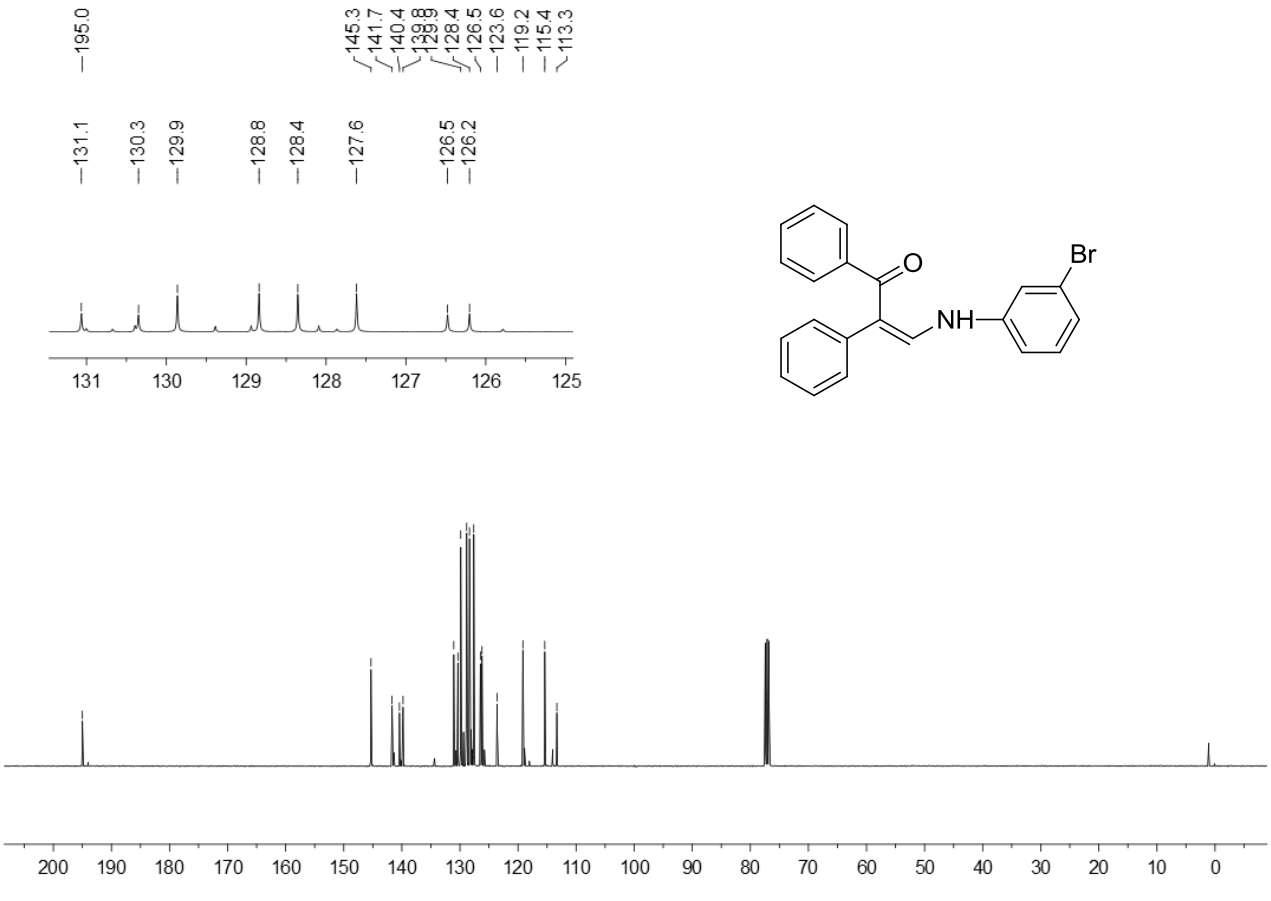
^{1}H NMR Spectrum of Compound 4c



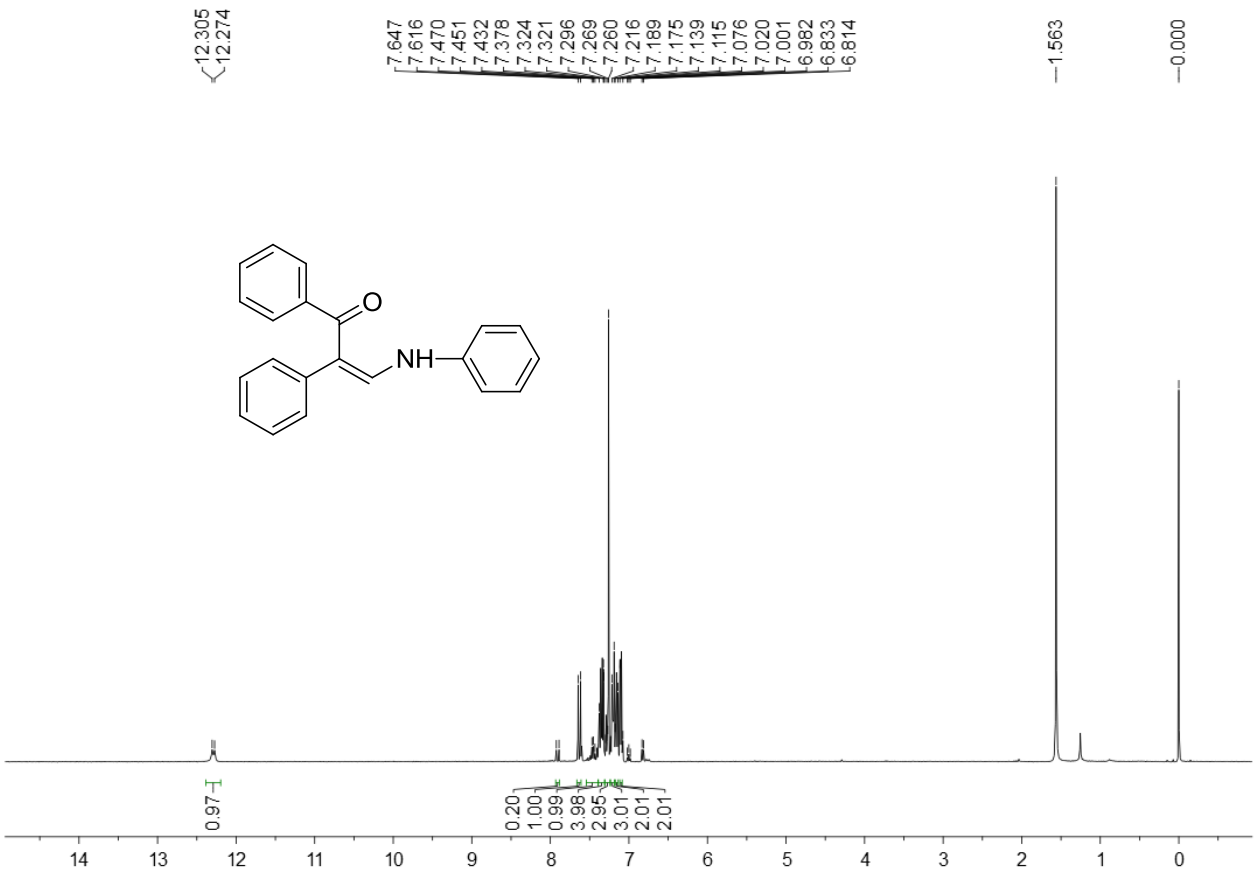
^{13}C NMR Spectrum of Compound 4c



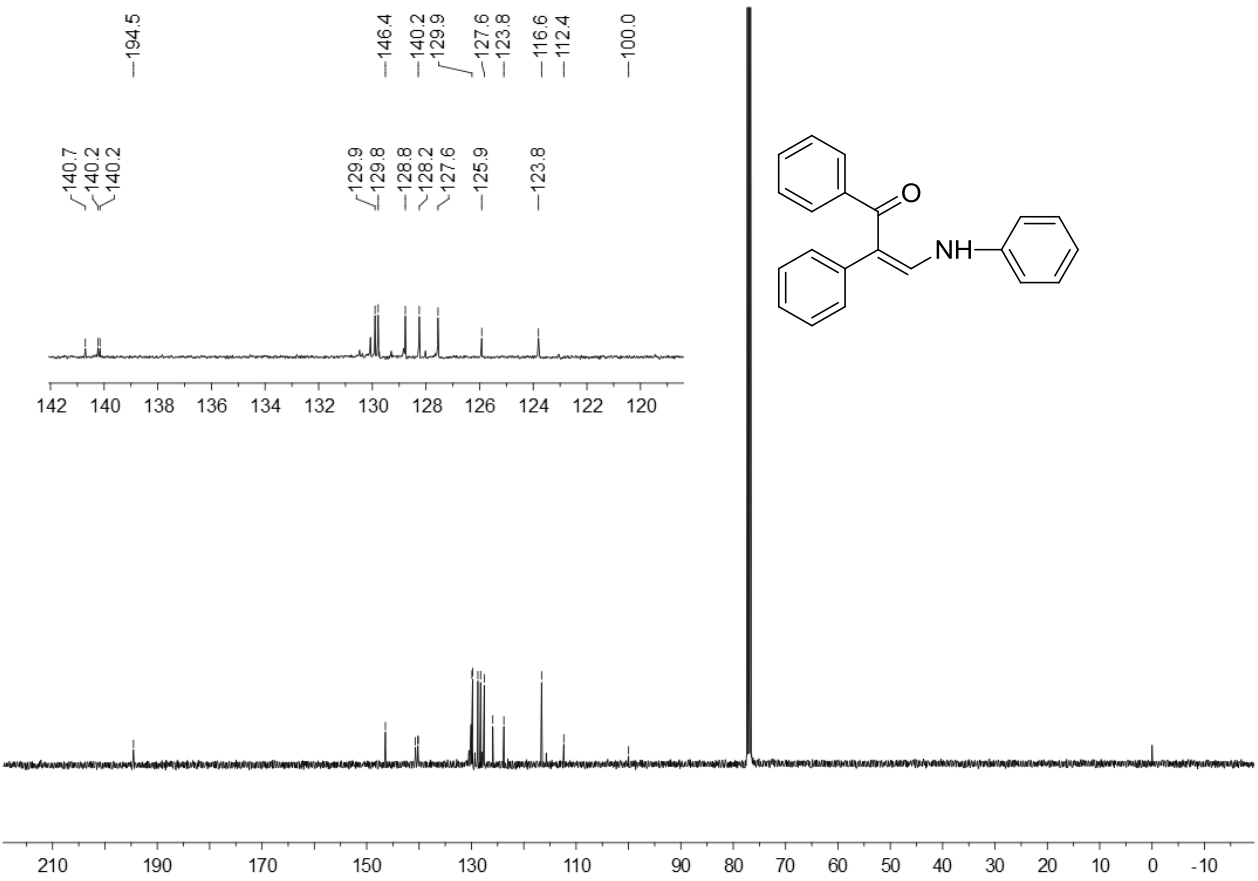
^{1}H NMR Spectrum of Compound 4d



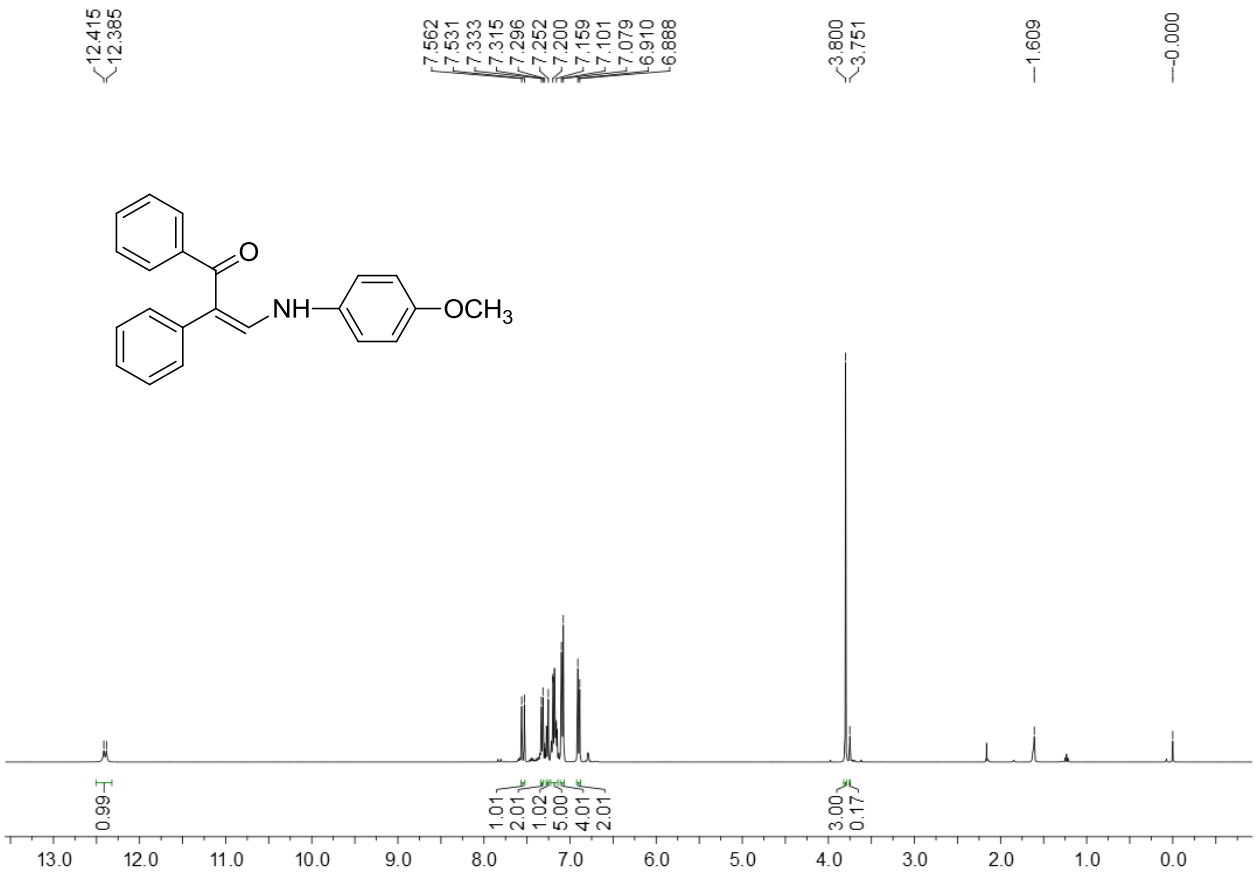
^{13}C NMR Spectrum of Compound 4d



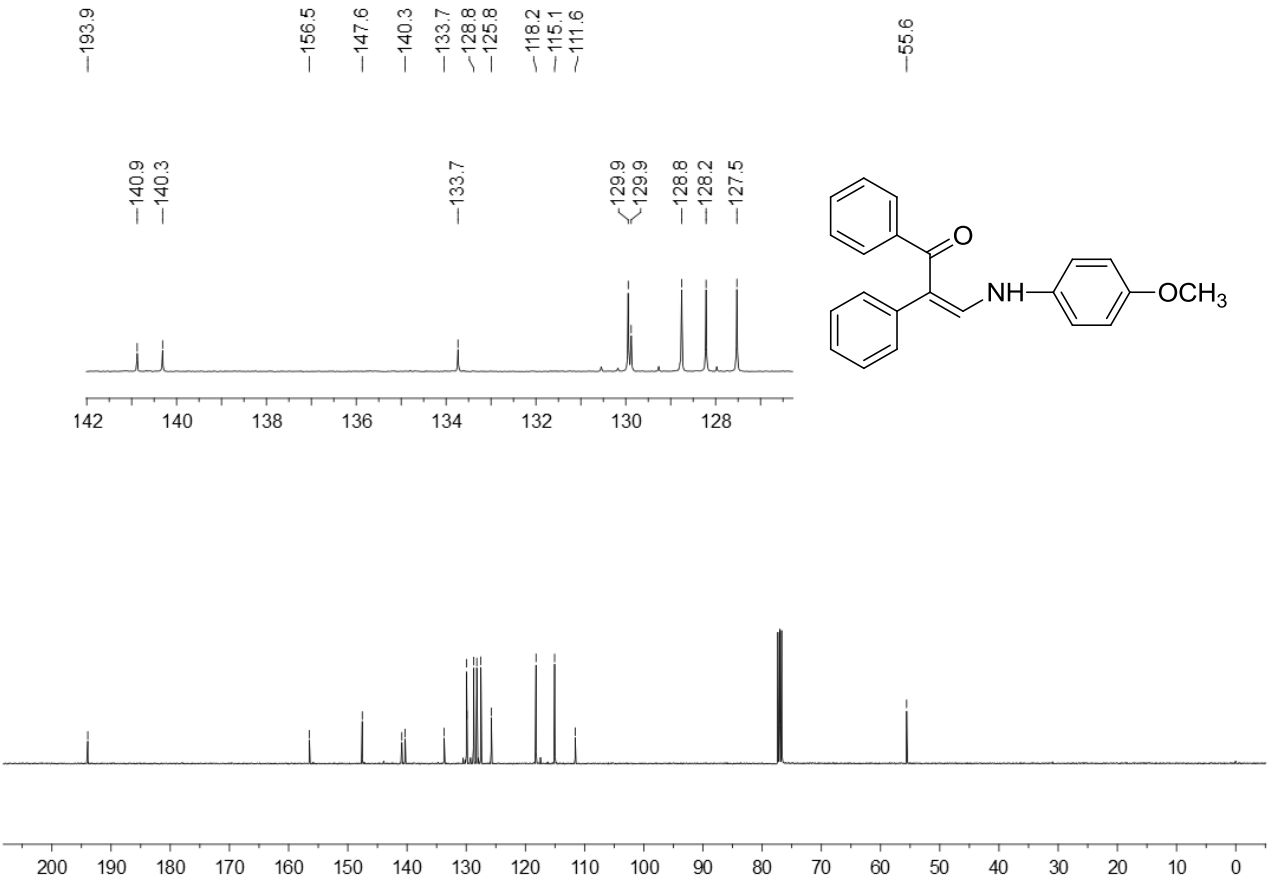
^{1}H NMR Spectrum of Compound 4e



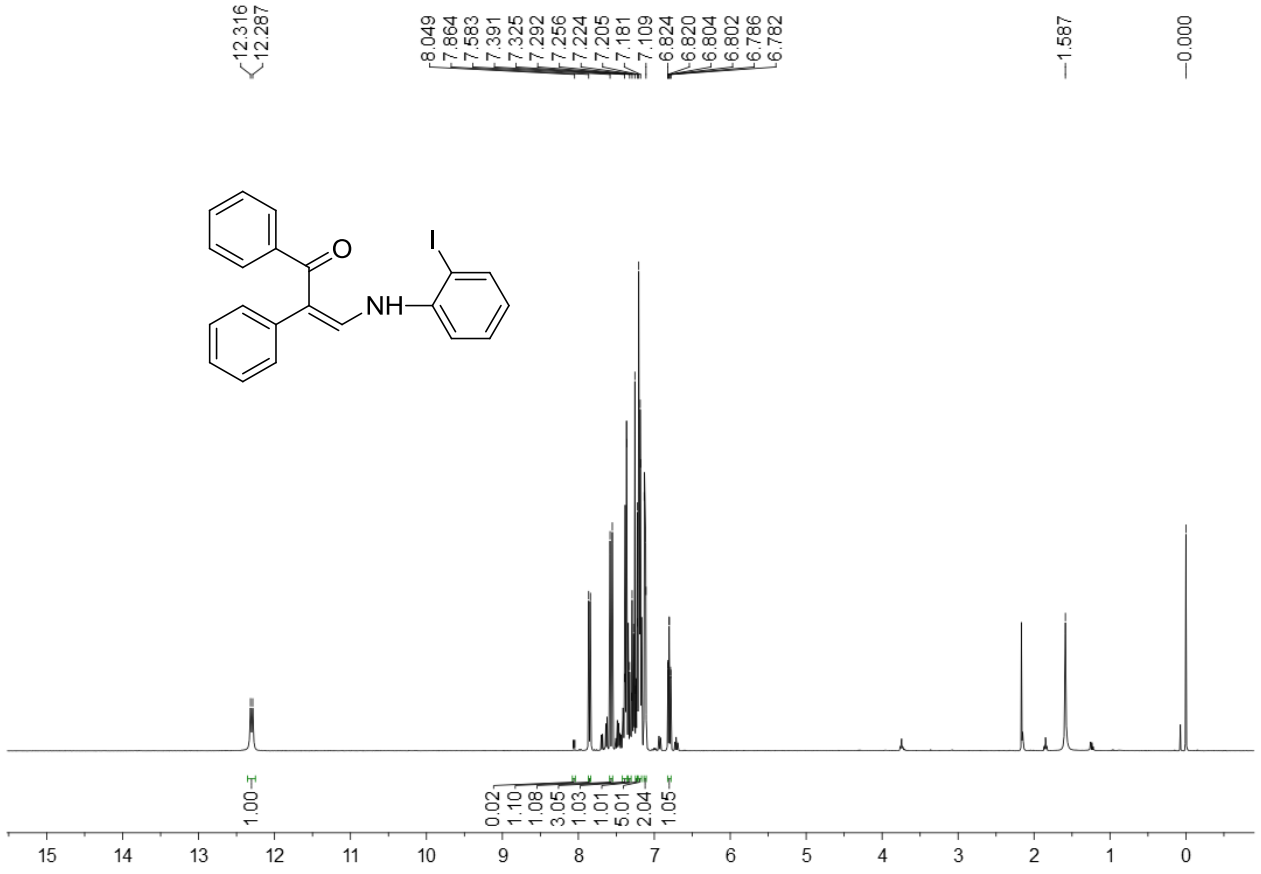
^{13}C NMR Spectrum of Compound 4e



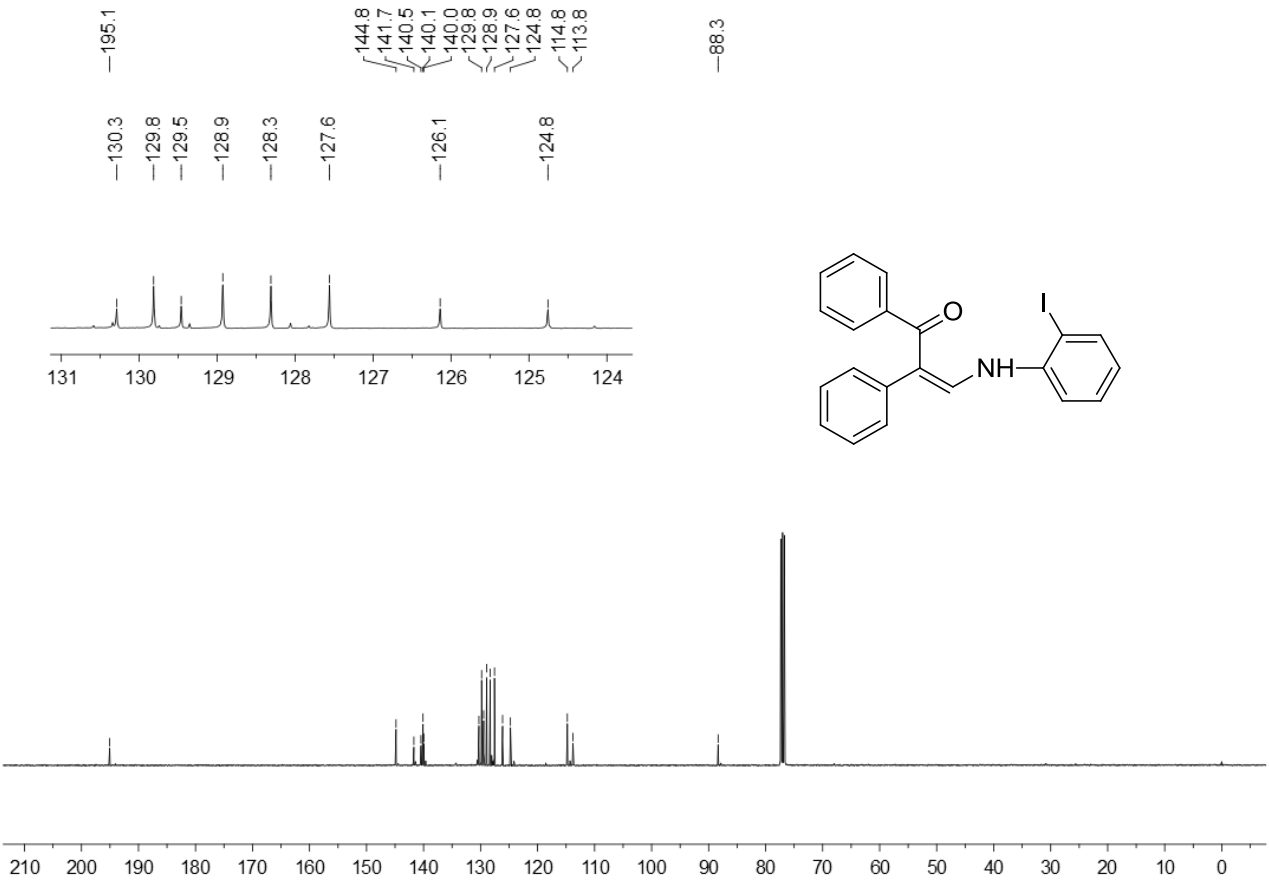
^{1}H NMR Spectrum of Compound 4f



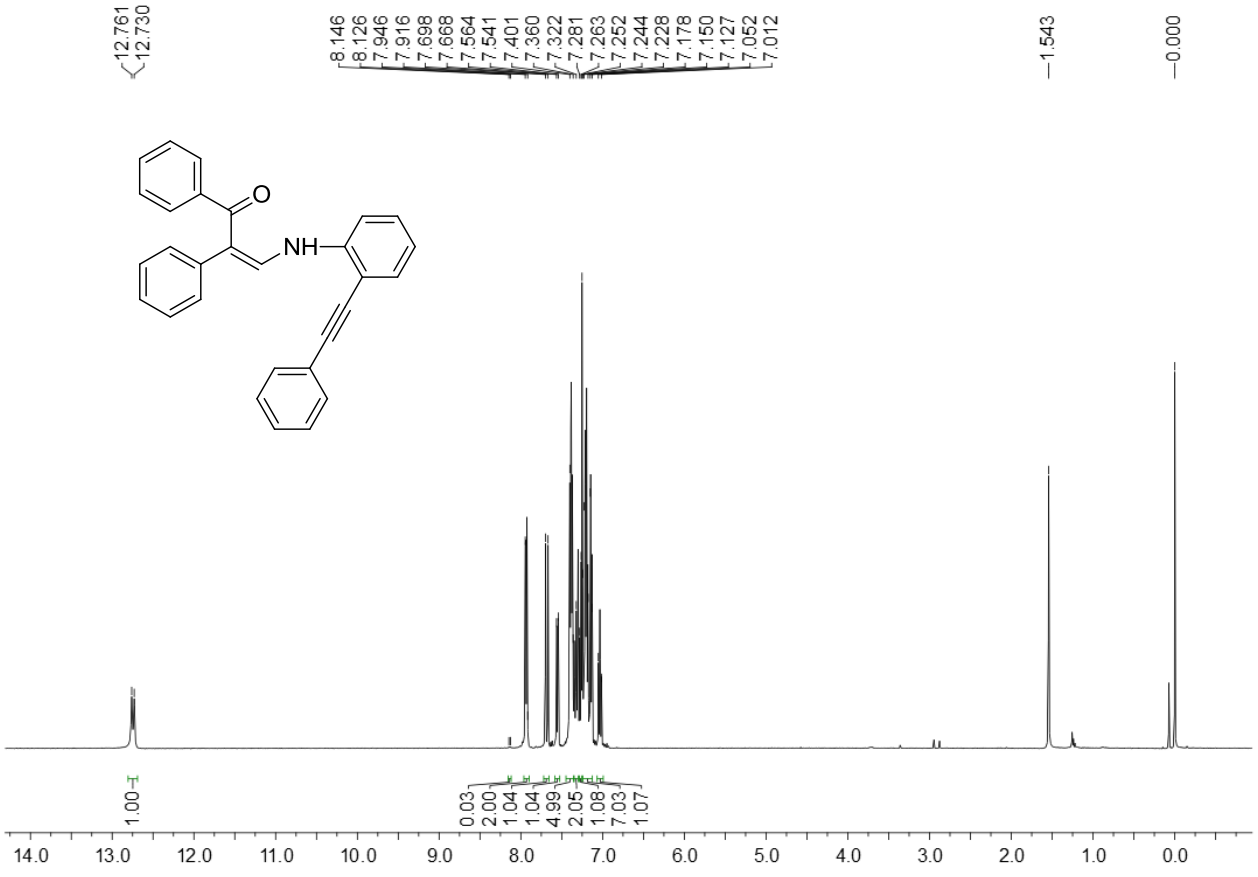
^{13}C NMR Spectrum of Compound 4f



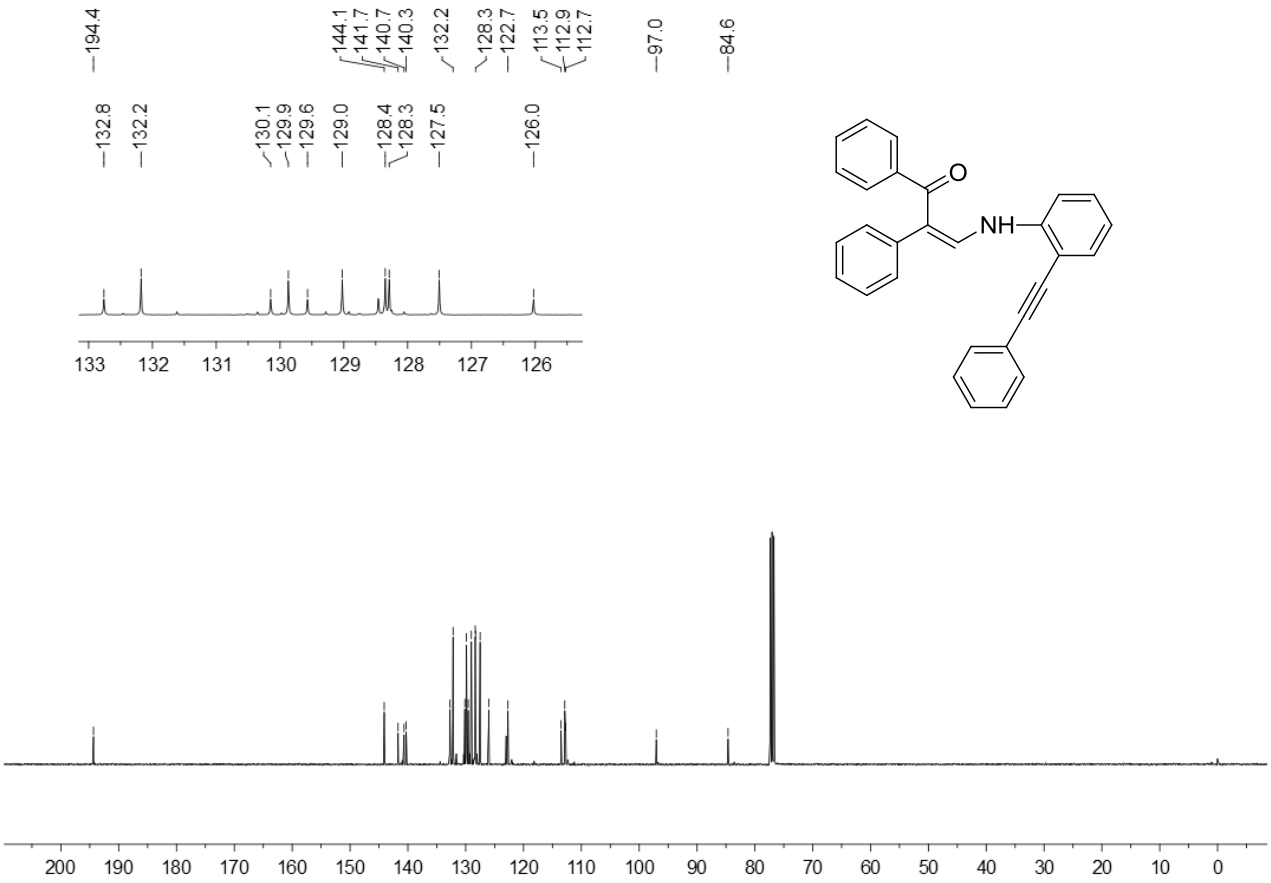
^{1}H NMR Spectrum of Compound 4g



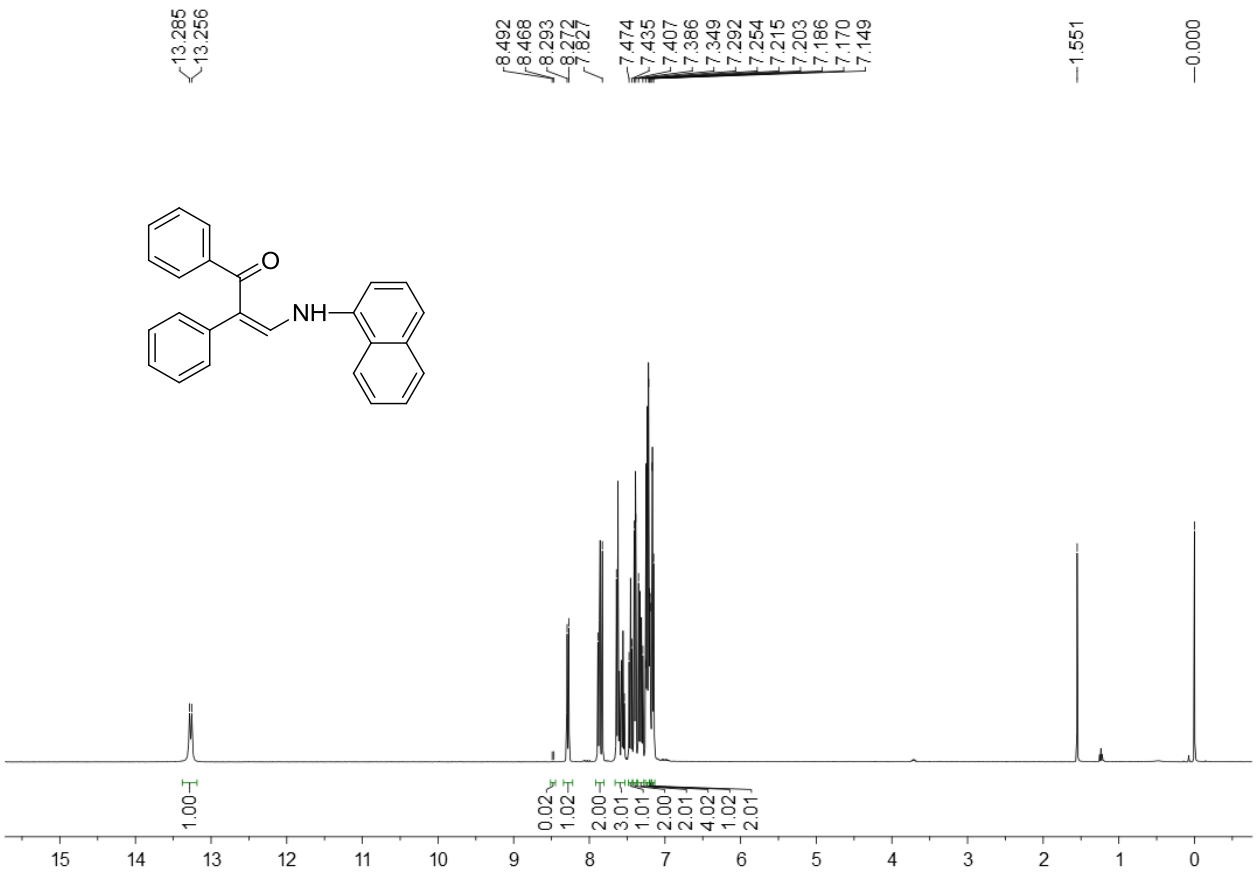
^{13}C NMR Spectrum of Compound 4g



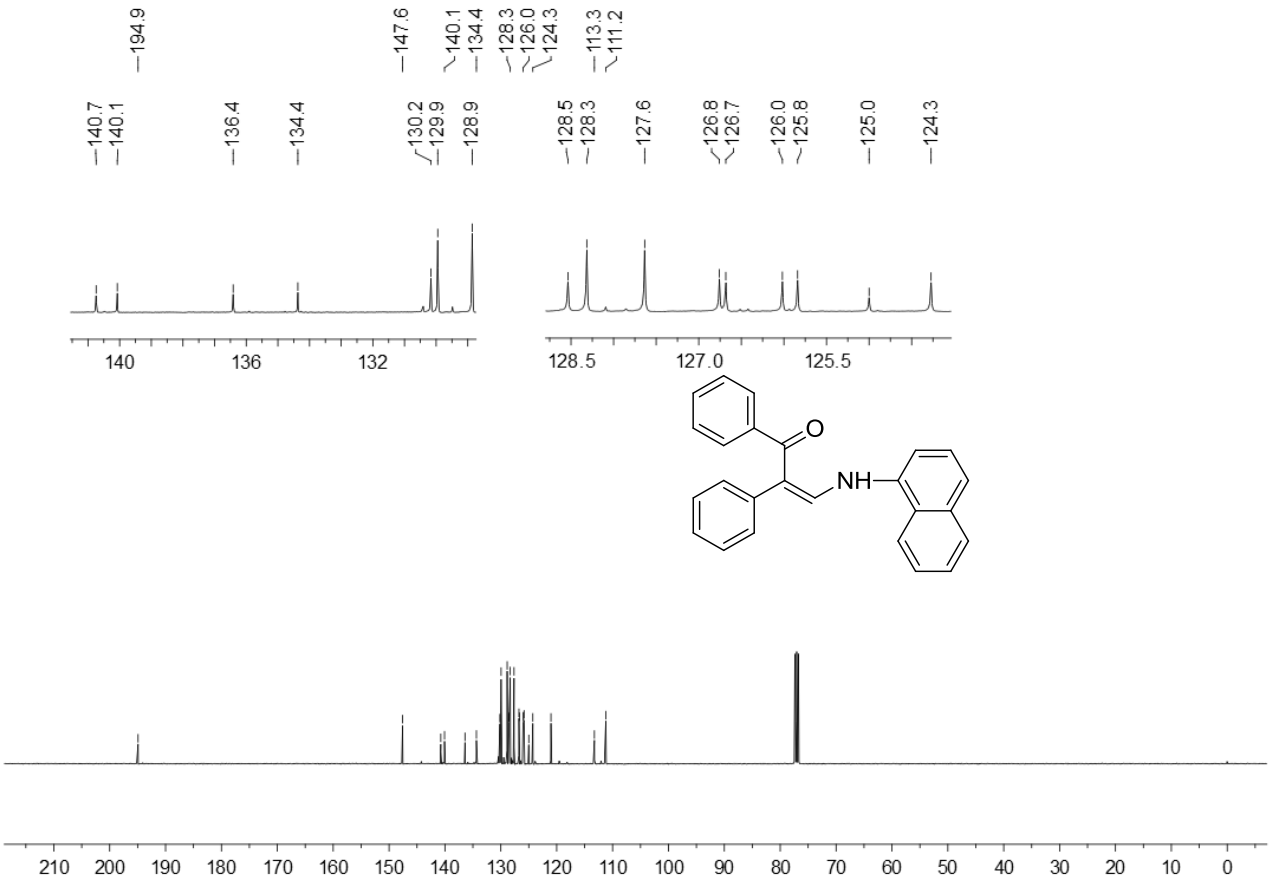
^{1}H NMR Spectrum of Compound 4h



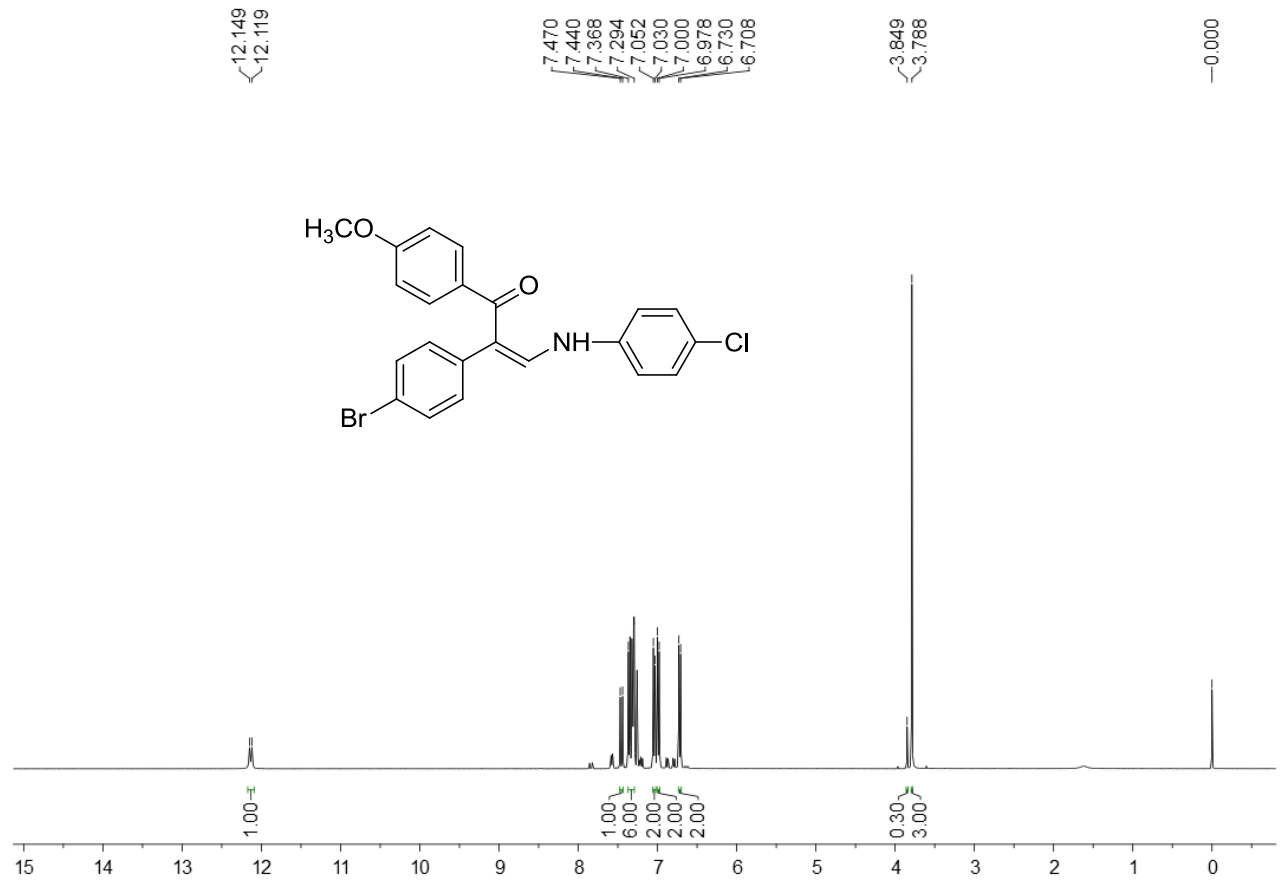
^{13}C NMR Spectrum of Compound 4h



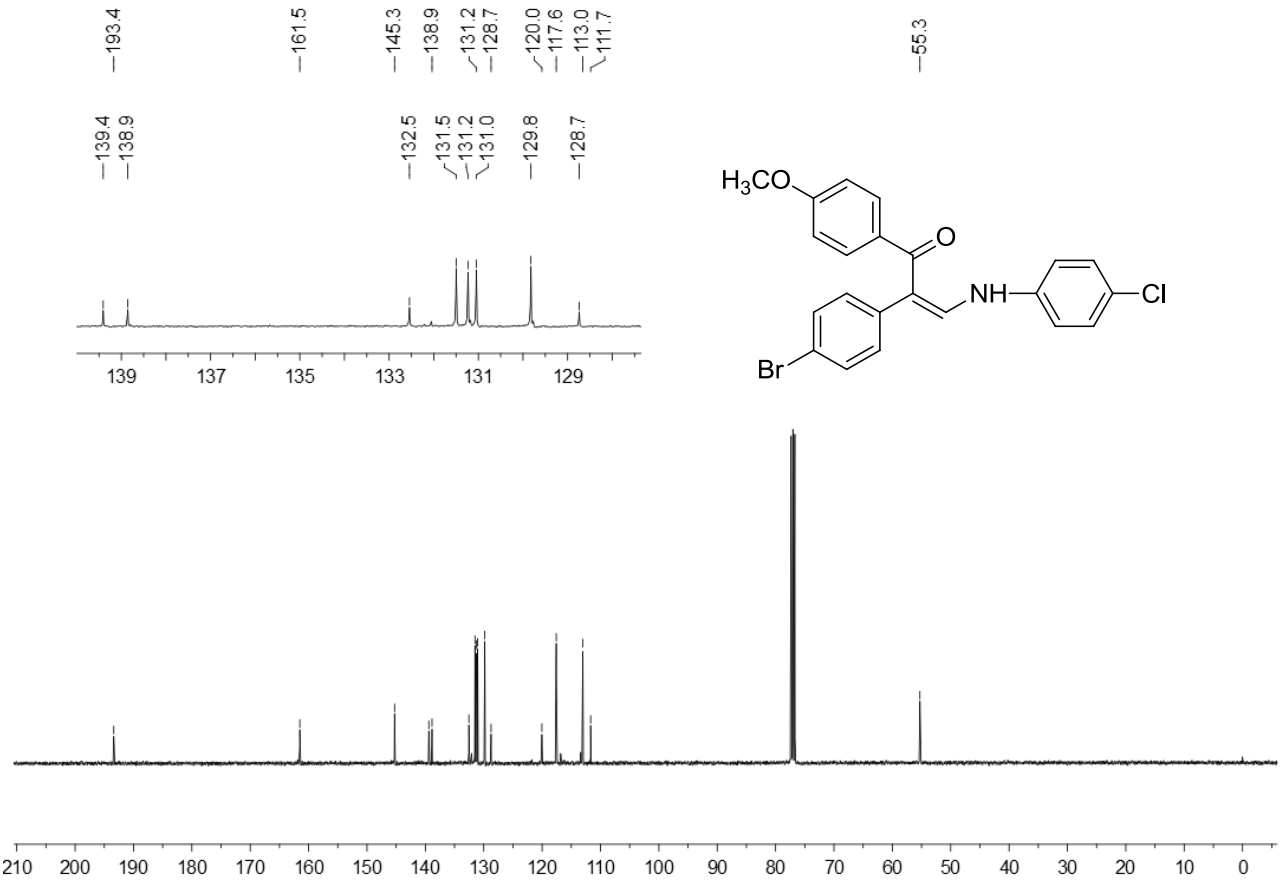
^{1}H NMR Spectrum of Compound 4i



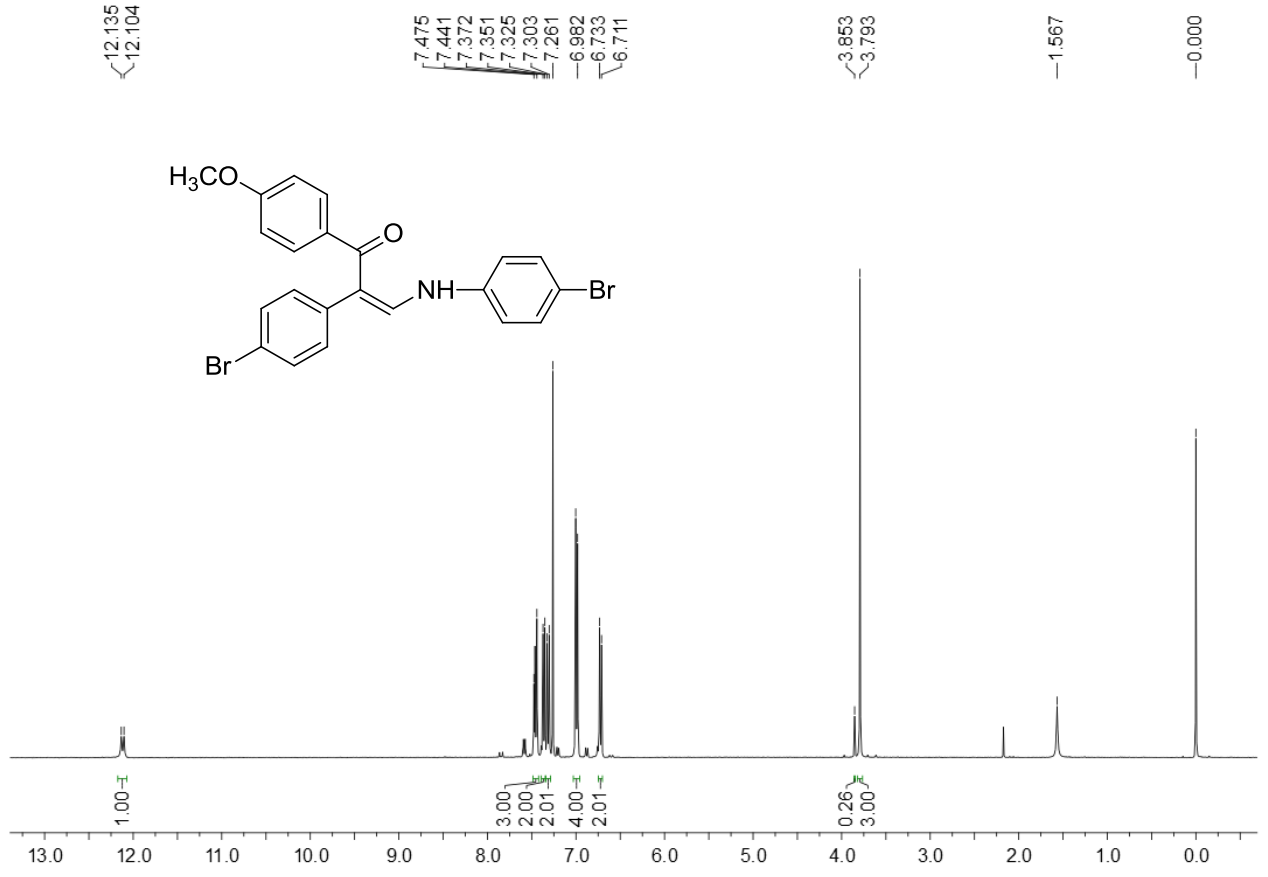
^{13}C NMR Spectrum of Compound 4i



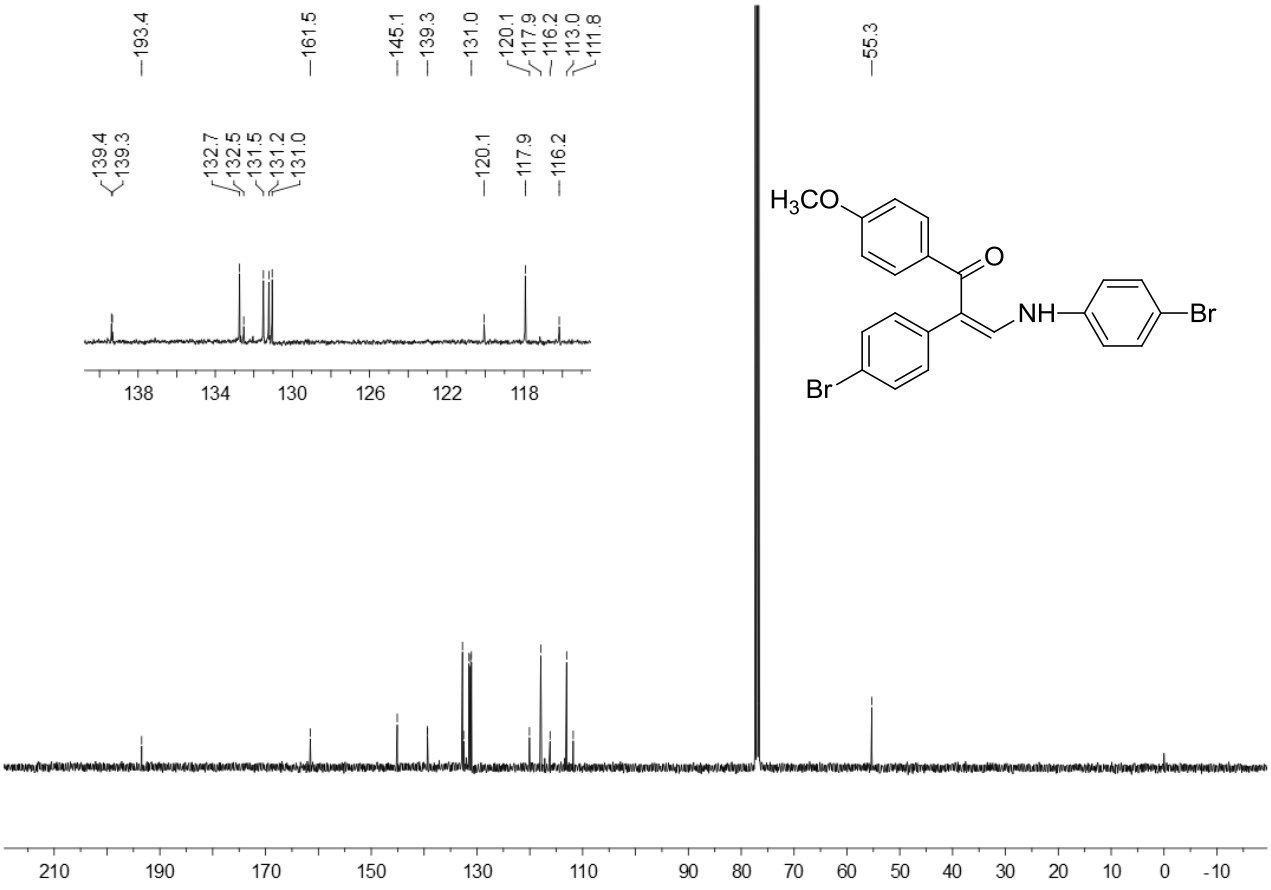
^{1}H NMR Spectrum of Compound 4j



^{13}C NMR Spectrum of Compound 4j



^{1}H NMR Spectrum of Compound 4k



^{13}C NMR Spectrum of Compound 4k