Electronic Supplementary Information

A fast and selective decarboxylative difunctionalization and cyclization for easy access to *gem*-dihalo alcohol, ether, ester and bromo-1,4-dioxane

Saikat Khamarui, Deblina Sarkar, Palash Pandit and Dilip K. Maiti*

Department of Chemistry, University of Calcutta, University College of Science,
92, A. P. C. Road, Kolkata-700009, India

*Corresponding author. Fax: 91-33-2351 9755, Tel: 91-33-2350 1014
dkmchem@caluniv.ac.in

Serial No.	Content	Page Numbers
1.	Materials and methods	S-2
2.	General procedure for regioselective synthesis of α,α-dibromohydrin	S-2
3.	Characterization data of α,α-dibromohydrin (**2a-r**)	S-3
4.	General procedure for synthesis of α,α-(dibromomethyl)arylmethylbromide	S-9
5.	Characterization data of α,α-(dibromomethyl)arylmethylbromide (**5a**)	S-9
6.	General procedure for synthesis of α,α-(dibromomethyl)arylmethylmethylether	S-9
7.	Characterization data of α,α-(dibromomethyl)arylmethylmethylether (**6a-r**)	S-10
8.	Synthesis of α,α-(dichloromethyl)phenylmethylalcohol and methylether	S-16
9.	Characterization data of α,α-(dichloromethyl)phenylmethylalcohol and methylether **(8a-b)**	S-16
10.	Synthesis of α,α-(dibromomethyl)phenylmethylpropergylether	S-17
11.	Characterization data of α,α-(dibromomethyl)phenylmethylpropergylether	S-17
12.	General procedure for synthesis of α,α-(dibromomethyl)phenylmethylester	S-18
13.	Characterization data of α,α-(dibromomethyl)phenylmethylester **(10a-b)**	S-18
14.	General procedure for stereoselective synthesis of bromo-1,4-dioxane	S-19
15.	Characterization data of bromo-1,4-dioxane **(11a-f)**	S-20

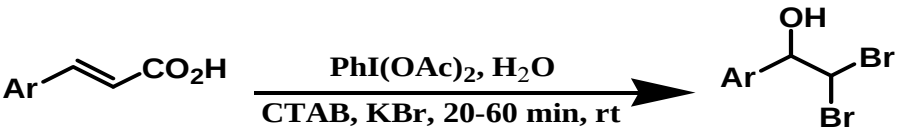
16. DLS study of the reaction mixture in protic solvents S-22

17. NMR spectra of the compounds **(2a-r, 5, 6a-r, 8a-b, 9, 10a-b, 11a-f)** S-23

1. Materials and Methods

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5. Petroleum ether used in our experiments was in the boiling range of 60°-80° C. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Melting points are reported uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) in thin film on NaCl window (liquid sample). EI-MS analysis was performed in GC-MS machine (Perkin Elmer Clarus 600) using column Elite 5 MS (30 m x 0.25 mm x 0.25 um) with maximum temperature 300 ºC. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Bruker).

2. General procedure for regioselective synthesis of α,α-dibromohydrin

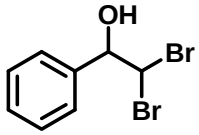


(**1**) (**2**)

To a stirred solution of α,β-unsaturated carboxylic acid (1 mmol) in water (5 ml) CTAB (36 mg, 10 mol%) and KBr (240 mg, 2 mmol) were added. The resultant mixture was stirred at room temperature (rt) for 5 min and iodosobenzene diacetate (2 mmol, 644 mg) was charged. The content of the reaction mixture was stirred at rt until the starting material was completely consumed. Progress of the reaction was monitored by thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2 x 15 mL) and the combined organic layer was washed successively with saturated sodium bicarbonate solution (1 x 10 mL) and brine (1 x 10 mL). It was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) afforded 2,2-dibromo-1-phenyl-ethanol (**2a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:19, v/v) as an eluent in an yield of 88% (246 mg, 0.88 mmol). The α,α-dibromohydrins (**2a-r**) were characterized by means of NMR (^{1}H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

3. Characterization data of α,α-dibromohydrin (2a-r)

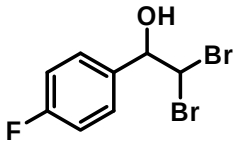
3.1. Compound 2a



2a

Yield: 88% (246 mg, 0.88 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.88 (1H, brs), 4.99 (1H, d, *J* = 5.1 Hz), 5.73 (1H, d, *J* = 5.1 Hz), 7.30-7.36 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.0, 78.9, 126.9, 128.4, 128.9, 137.9.
EI-MS (m/z): 281 (M+2), 279 (M^+), 119, 108, 107, 91, 79, 77, 51.
FT-IR (neat, cm^{-1}): 1066, 1452, 1611, 2855, 2923, 3433.
HR-MS (*m*/*z*) for $C_8H_8Br_2O$ (M^+): Calculated 277.8942, found 277.8939 (one of the peaks).

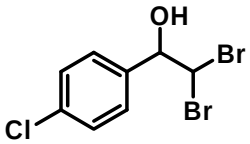
3.2. Compound 2b



2b

Yield: 83% (247 mg, 0.83 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63 (1H, brs), 5.03 (1H, d, *J* = 5.1 Hz), 5.74 (1H, d, *J* = 5.1 Hz), 7.07 (2H, t, *J* = 8.7 Hz), 7.41 (2H, dd, *J* = 8.7, 5.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 51.7, 79.2, 115.2, 115.5, 129.7, 129.8, 132.1, 161.4.
EI-MS (m/z): 298 (M+2), 296 (M^+), 203, 202, 201, 151, 149, 93, 76, 75, 74.
FT-IR (neat, cm^{-1}): 1096, 1536, 1608, 2993, 3223.
HR-MS (*m*/*z*) for $C_8H_7Br_2FO$ (M^+): Calculated 295.8848, found 295.8845 (one of the peaks).

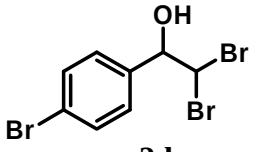
3.3. Compound 2c



2c

Yield: 80% (251 mg, 0.80 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (1H, s), 5.35 (1H, d, *J* = 6.9 Hz), 5.96 (1H, d, *J* = 6.9 Hz), 7.35 (2H, d, *J* = 8.4 Hz), 7.43 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.2, 78.5, 128.7, 130.0, 135.4, 135.7.
EI-MS (m/z): 314 (M+2), 312 (M^+), 218, 216, 139, 137, 102, 101, 75, 74.
FT-IR (neat, cm^{-1}): 1094, 1409, 1491, 1594, 2925.
HR-MS (*m*/*z*) for C_8H_7BrClO (M^+): Calculated 311.8552, found 311.8559 (one of the peaks).

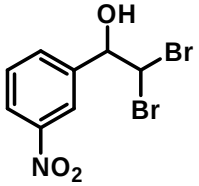
3.4. Compound 2d



2d

Yield: 82% (294 mg, 0.82 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.99 (1H, brs), 5.01 (1H, d, *J* = 5.1 Hz), 5.74 (1H, d, *J* = 5.1 Hz), 7.31 (2H, d, *J* = 8.4 Hz), 7.52 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 51.4, 78.3, 123.0, 128.6, 131.6, 136.8.
EI-MS (m/z): 358 (M+2), 356 (M^+), 281, 208, 207, 160, 133, 77, 73, 55.
FT-IR (neat, cm^{-1}): 1010, 1072, 1487, 2929, 3448.
HR-MS (*m*/*z*) for $C_8H_7Br_3O$ (M^+): Calculated 355.8047, found 355.8040 (one of the peaks).

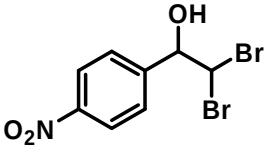
3.5. Compound 2e



2e

Yield: 72% (234 mg, 0.72 mmol).
Characteristic:Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (1H, brs), 5.39 (1H, d, *J* = 5.7 Hz), 5.78 (1H, d, *J* = 5.7 Hz), 7.51-7.62 (1H, m), 7.99 (1H, d, *J* = 7.8 Hz), 8.13 (1H, t, *J* = 6.9 Hz), 8.55 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 57.6, 79.3, 122.9, 123.7, 129.7, 134.6, 136.5, 137.5.
EI-MS (m/z): 325 (M+2), 323 (M^+), 229, 227, 183, 181, 102, 101, 77, 76, 75, 74, 63, 62, 51.
FT-IR (neat, cm^{-1}): 1098, 1348, 1598, 2929, 3398.
HR-MS (*m*/*z*) for $C_8H_7Br_2NO_3$ (M^+): Calculated 322.8793, found 322.8798 (one of the peaks).

3.6. Compound 2f

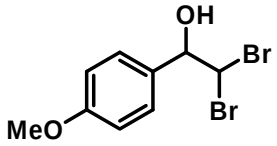


2f

Yield: 75% (243 mg, 0.75 mmol).
Characteristic**:** Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (1H, brs), 5.40 (1H, d, *J* = 5.4 Hz), 5.92 (1H, d, *J* = 5.4 Hz), 7.83 (2H, d, *J* = 8.7 Hz), 8.24 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 51.2, 82.7, 126.3, 126.5, 128.5, 133.3, 137.3.
EI-MS (m/z): 324 (M+2), 322 (M^+), 229, 181, 103, 102, 101, 90, 76, 75, 51.

FT-IR (neat, cm^{-1}): 1122, 1288, 1346, 1520, 1723, 2960.
HR-MS (*m*/*z*) for $C_8H_7Br_2NO_3$ (M^+): Calculated 322.8793, found 322.8787 (one of the peaks).

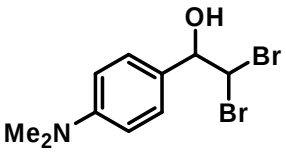
3.7. Compound 2g



2g

Yield: 92% (285 mg, 0.92 mmol).
Characteristic:Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.52 (1H, brs), 3.81 (3H, s), 4.99 (1H, d, *J* = 5.1 Hz), 5.75 (1H, d, *J* = 5.1 Hz), 6.90 (2H, d, *J* = 8.7 Hz), 7.34 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 55.3, 78.6, 113.8, 128.2, 130.0, 160.0.
EI-MS (m/z): 310 (M+2), 308 (M^+), 215, 214, 139, 137, 122, 121, 109, 94, 89, 77, 63.
FT-IR (neat, cm^{-1}): 1252, 1513, 1610, 3003, 3435.
HR-MS (*m*/*z*) for $C_9H_{10}Br_2O_2$ (M^+): Calculated 307.9048, found 307.9045 (one of the peaks).

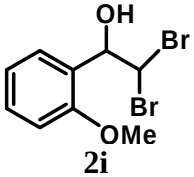
3.8. Compound 2h



2h

Yield: 85% (274 mg, 0.85 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73 (1H, brs), 2.82 (6H, s), 4.08 (1H, d, *J* = 6.6 Hz), 5.75 (1H, d, *J* = 6.6 Hz), 7.07 (1H, d, *J* = 8.4 Hz), 7.31 (1H, dd, *J* = 8.1, 2.1 Hz), 7.51-7.54 (1H, m), 7.69-7.75 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 44.0, 47.4, 48.2, 111.9, 120.0, 127.6, 129.0, 131.7, 133.4.
EI-MS (m/z): 323 (M+2), 321 (M^+), 281, 208, 207, 191, 160, 135, 133, 96, 73, 45, 44, 43.
FT-IR (neat, cm^{-1}): 1218, 1731, 2941, 3401.
HR-MS (*m*/*z*) for $C_{10}H_{13}Br_2NO$ (M^+): Calculated 320.9364, found 320.9369 (one of the peaks).

3.9. Compound 2i

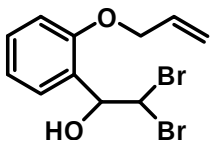


2i

Yield: 92% (285 mg, 0.92 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.2 (1H, brs), 3.87 (3H, s), 5.28 (1H, d, *J* = 6.3 Hz), 6.11 (1H, d, *J* = 6.3 Hz), 6.89 (1H, d, *J* = 8.1 Hz), 7.01(1H, t, *J* = 6.9 Hz), 7.33 (1H, t, *J* = 7.5 Hz), 7.48 (1H, d, *J* = 6.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 51.5, 55.4, 75.4, 110.4, 120.8, 126.4, 128.5, 129.7, 156.0.
EI-MS (m/z): 310 (M+2), 308 (M^+), 149, 138, 137, 121, 118, 107, 105, 91, 89, 79, 77, 63, 51.

FT-IR (neat, cm^{-1}): 746, 1052, 1232, 1471, 2931, 3433.
HR-MS (*m*/*z*) for $C_9H_{10}Br_2O_2$ (M^+): Calculated 307.9048, found 307.9042 (one of the peaks).

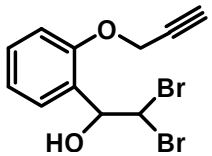
3.10. Compound 2j



2j

Yield: 91% (306 mg, 0.91 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (1H, s), 4.58 (2H, t, *J* = 4.2 Hz), 5.01 (1H, d, *J* = 2.7 Hz), 5.32 (1H, d, *J* = 10.5 Hz), 5.43 (1H, d, *J* = 17.5 Hz), 5.84 (1H, d, *J* = 2.7 Hz), 6.01-6.12 (1H, m), 6.87 (1H, d, *J* = 8.4 Hz), 7.02 (1H, t, *J* = 7.5 Hz), 7.32 (1H, t, *J* = 7.5 Hz), 7.46 (1H, d, *J* = 7.5 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 52.3, 69.2, 79.1, 111.5, 117.3, 120.8, 125.3, 128.1, 129.6, 132.7, 155.9.
EI-MS (m/z): 336 (M+2), 334 (M^+), 242, 240, 238, 205, 188, 160, 120, 105, 77, 58, 55.
FT-IR (neat, cm^{-1}): 651, 1090, 1413, 1767, 2929, 3432.
HR-MS (*m*/*z*) for $C_{11}H_{12}Br_2O_2$ (M^+): Calculated 333.9204, found 333.9215 (one of the peaks).

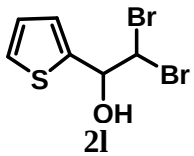
3.11. Compound 2k



2k

Yield: 91% (304 mg, 0.91 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67 (1H, brs), 2.54 (1H, t, *J* = 2.4 Hz), 4.76 (2H, d, *J* = 2.4 Hz), 5.31 (1H, d, *J* = 5.4 Hz), 6.12 (1H, d, *J* = 5.4 Hz), 7.04-7.10 (2H, m), 7.31-7.37 (1H, m), 7.55 (1H, dd, *J* = 12.3, 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.2, 58.5, 76.0, 79.2, 82.0, 111.9, 121.5, 125.8, 128.3, 129.5, 154.9.
EI-MS (m/z): 334 (M+2), 332 (M^+), 207, 162, 161, 121, 118, 105, 89, 79, 78, 63, 51, 44.
FT-IR (neat, cm^{-1}): 1057, 1216, 1727, 2912, 3298, 3412.
HR-MS (*m*/*z*) for $C_{11}H_{10}Br_2O_2$ (M^+): Calculated 331.9048, found 331.9041 (one of the peaks).

3.12. Compound 2l

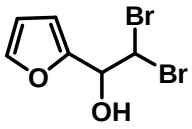


2l

Yield: 79% (226 mg, 0.79 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.00 (1H, brs), 5.22 (1H, d, *J* = 4.8 Hz), 5.75 (1H, d, *J* = 4.8 Hz), 6.96 (2H, dd, *J* = 4.8, 3.6 Hz), 7.08 (1H, d, *J* = 3.3 Hz), 7.27 (1H, d, *J* = 5.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 51.1, 75.5, 126.0, 126.5, 126.7, 126.9, 129.5, 140.8.
EI-MS (m/z): 285 (M+2), 283 (M^+), 190, 114, 113, 108, 107, 97, 85, 58, 45, 44.
FT-IR (neat, cm^{-1}): 1038, 1147, 1436, 2858, 2921, 3433.

HR-MS (*m*/*z*) for $C_6H_6Br_2OS$ (M^+): Calculated 283.8506, found 283.8516 (one of the peaks).

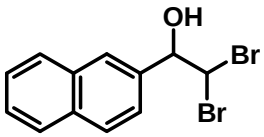
3.13. Compound 2m



2m

Yield: 73% (197 mg, 0.73 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): 2.11 (1H, brs), 5.38 (1H, d, *J* = 5.4 Hz), 5.97 (1H, d, *J* = 5.4 Hz), 6.63 (1H, dd, *J* = 3.6, 1.5 Hz), 7.29 (1H, d, *J* = 3.6 Hz), 7.72 (1H, d, *J* = 0.6 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.3, 76.0, 106.1, 112.0, 138.6, 154.3.
EI-MS (m/z): 280 (M+2), 278 (M^+), 174, 98, 97, 96, 88, 87, 74, 73, 51, 45.
FT-IR (neat, cm^{-1}): 1049, 1263, 1589, 2936, 3348.
HR-MS (*m*/*z*) for $C_6H_6Br_2O_2$ (M^+): Calculated 267.8735, found 267.8744 (one of the peaks).

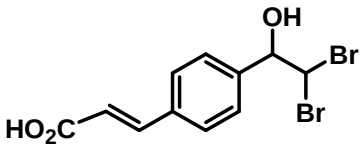
3.14. Compound 2n



2n

Yield: 80% (264 mg, 0.80 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (1H, s), 4.62 (1H, d, *J* = 5.4 Hz), 5.72 (1H, d, *J* = 5.4 Hz), 7.42-7.47 (3H, m), 7.79-7.82 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.6, 80.0, 124.8, 126.4, 126.5, 127.8, 127.9, 128.1, 128.3, 132.9, 133.6, 134.0.
EI-MS (m/z): 330 (M+2), 328 (M^+), 230, 229, 197, 169, 102, 101, 90, 89, 76, 75, 74, 63, 51.
FT-IR (neat, cm^{-1}): 1097, 1461, 1509, 2827, 2930, 3480.
HR-MS (*m*/*z*) for $C_{12}H_{10}Br_2O$ (M^+): Calculated 327.9098, found 327.9092 (one of the peaks)

3.15. Compound 2o

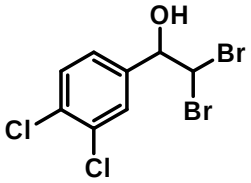


2o

Yield: 76% (266 mg, 0.76 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.68 (1H, d, *J* = 5.7 Hz), 5.99 (1H, d, *J* = 5.7 Hz), 6.99 (1H, t, *J* = 8.7 Hz), 7.24 (1H, dd, *J* = 8.4, 1.8 Hz), 7.46 (1H, d, *J* = 3.3 Hz), 7.54 (1H, d, *J* = 2.1Hz), 7.63-7.69 (1H, m), 7.97 (1H, d, *J* = 2.1), 10.95 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 45.3, 75.7, 119.9, 127.7, 128.8, 129.8, 130.5, 133.0, 136.0, 152.6, 169.1.

EI-MS (m/z): 350 (M+2), 348 (M^+), 267, 212, 210, 209, 135, 133, 96, 77, 74, 73, 53, 51.
FT-IR (neat, cm^{-1}): 746, 1078, 1484, 2958, 3362.
HR-MS (*m*/*z*) for $C_{11}H_{10}Br_2O_3$ (M^+): Calculated 347.8997, found 347.8991 (one of the peaks).

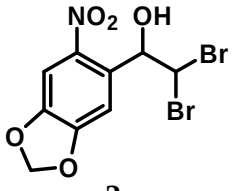
3.16. Compound 2p



2p

Yield: 69% (240 mg, 0.69 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.62 (1H, d, *J* = 2.4 Hz), 4.29 (1H, d, *J* = 2.4 Hz), 7.14 (1H, dd, *J* = 8.4, 2.1 Hz), 7.38 (1H, d, *J* = 2.1 Hz), 7.45 (1H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8, 61.0, 118.2, 125.0, 127.7, 130.7, 133.2, 135.3.
EI-MS (m/z): 347 (M+2), 345 (M^+), 232, 199, 189, 161, 147, 75, 74, 73, 44, 43.
FT-IR (neat, cm^{-1}): 1137, 1485, 1745, 2928, 3265.
HR-MS (*m*/*z*) for $C_8H_6Br_2Cl_2O$ (M^+): Calculated 345.8162, found 345.8156 (one of the peaks).

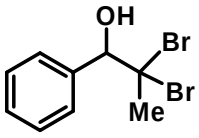
3.17. Compound 2q



2q

Yield: 62% (228 mg, 0.62 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65 (1H, brs), 4.60 (1H, d, *J* = 2.7 Hz), 4.89 (1H, d, *J* = 2.7 Hz), 6.16 (2H, s), 7.02 (1H, s), 7.68 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 74.4, 103.3, 105.5, 106.1, 129.4, 148.1, 153.0, 167.9.
EI-MS (m/z): 368 (M+2), 366 (M^+), 269, 154, 108, 102, 95, 94, 44.
FT-IR (neat, cm^{-1}): 1228, 1496, 1746, 3006, 3387.
HR-MS (*m*/*z*) for $C_9H_7Br_2NO_5$ (M^+): Calculated 366.8691, found 366.8688 (one of the peaks).

3.18. Compound 2r

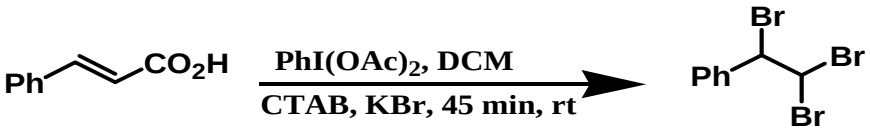


2r

Yield: 61% (179 mg, 0.61 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (3H, s), 4.56 (1H, s), 7.24-7.32 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 68.1, 91.3, 125.8, 128.3, 129.0, 130.9, 140.6.

EI-MS (m/z): 294 (M+2), 292 (M^+), 227, 203, 202, 184, 98, 97, 84, 83, 51, 44, 43.
FT-IR (neat, cm^{-1}): 1263, 1526, 1603, 2788, 2930, 3304.
HR-MS (*m*/*z*) for $C_9H_{10}Br_2O$ (M^+): Calculated 291.9098, found 291.9094 (one of the peaks).

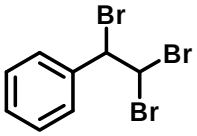
4. Synthesis of α,α-(dibromomethyl)phenylmethybromide



(1a) **(5a)**

To a stirred solution of *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) in water (5 mL) CTAB (10 mmol%, 36 mg) and KBr (240 mg, 2 mmol) were added.The resultant mixture was stirred at room temperature for 5 min and iodosobenzene diacetate (644 mg, 2 mmol) was added. The content of the reaction mixture was stirred at rt and the starting material was completely consumed after 45 min. The progress of the reaction was monitored by thin layer chromatography (TLC). The post reaction mixture was washed successively with saturated sodium bicarbonate solution (2 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, compound (1,2,2-tribromoethyl)-benzene (**5a**) was obtained after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:49, v/v) as an eluent in an yield of 76% (260 mg, 0.76 mmol). The α,α-(dibromomethyl)arylmethyl bromide was characterized by NMR (^1H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

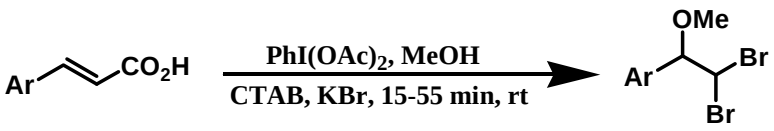
5. Characterization data of α,α-(dibromomethyl)phenylmethylbromide:
5.1. Compound 5a



5a

Yield: 76% (260 mg, 0.76 mmol).
Characteristic: Yellow oil.
^1H NMR (300 MHz, $CDCl_3$): δ 5.40 (1H, d, *J* = 7.2 Hz), 6.02 (1H, d, *J* = 7.2 Hz), 7.38-7.43 (3H, m), 7.47-7.50 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 46.6, 58.6, 118.1, 128.5, 128.6, 129.5, 137.4.
EI-MS (m/z): 342 (M+2), 340 (M^+), 265, 263, 261, 184, 182, 169, 103, 102, 77, 75, 63, 51, 50.
FT-IR (neat, cm^{-1}): 702, 1139, 1415, 3142, 3494.
HR-MS (*m*/*z*) for $C_8H_7Br_3$ (M^+): Calculated 339.8098, found 339.8094 (one of the peaks).

6. General procedure for synthesis of α,α-(dibromomethyl)arylmethylmethylether

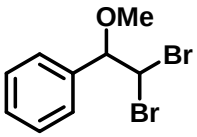


(1) **(6)**

To a stirred solution of α, β-unsaturated carboxylic acid (1 mmol) in methanol (5 mL) CTAB (36 mg , 10 mmol%) and KBr (240 mg, 2 mmol) were added. The content of the reaction mixture was stirred at room temperature for 5 min followed by addition of iodosobenzene diacetate (644 mg, 2 mmol). Stirring was continued until the starting material was completely consumed. The reaction was monitored by thin layer chromatography (TLC). Solvent was removed in a rotary evaporator under reduced pressure at room temperature. The post reaction mixture was extracted with EtOAc (2 x 15 mL). It was washed successively with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure. Thus, the reaction with p-methoxy *trans*-cinnamic acid (**1g**, 178 mg, 1.0 mmol) afforded 1-(2,2-dibromo-1-methoxy-ethyl)-4-methoxy-benzene (**6g**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:49, v/v) as an eluent in an yield of 92% (298 mg, 0.92 mmol). The α,α-(dibromomethyl)arylmethylmethylether (**6a-q**) and α,α-(dibromoethyl)arylmethylmethylether (**6r**) were characterized by means of NMR (^{1}H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

7. Characterization data of α,α-(dibromoalkyl)arylmethylmethylether (6a-r)

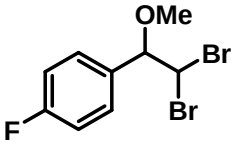
7.1. Compound 6a



6a

Yield: 90% (264 mg, 0.90 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (3H, s), 4.52 (1H, d, *J* = 5.1 Hz), 5.69 (1H, d, *J* = 5.1 Hz), 7.39 (5H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 58.0, 87.6, 127.9, 128.3, 129.0, 136.5.
EI-MS (m/z): 294 (M+2), 292(M^+), 293, 261, 220, 137, 119, 106, 105, 91, 79, 77, 65, 55.
FT-IR (neat, cm^{-1}): 709, 1099, 1643, 2916, 3416.
HR-MS (*m*/*z*) for $C_9H_{10}Br_2O$ (M^+): Calculated 291.9098, found 291.9096 (one of the peaks).

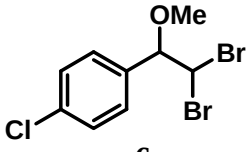
7.2. Compound 6b



6b

Yield: 89% (278 mg, 0.89 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (3H, s), 4.50 (1H, d, *J* = 5.1 Hz), 5.66 (1H, d, *J* = 5.1 Hz), 7.08 (2H, t, *J* = 8.7 Hz), 7.36-7.41 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.1, 58.0, 86.8, 115.2, 115.5, 129.7, 129.8, 132.1, 161.4.
EI-MS (m/z): 312 (M+2), 310 (M^+), 139, 123, 109, 101, 95, 82, 80, 79, 57.
FT-IR (neat, cm^{-1}):1095, 1223, 1509, 1605, 2930.
HR-MS (*m*/*z*) for $C_9H_9Br_2FO$ (M^+): Calculated 309.9004, found 309.9008 (one of the peaks).

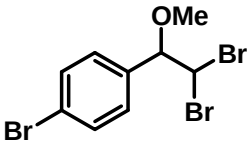
7.3. Compound 6c



6c

Yield: 83% (272 mg, 0.83 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (3H, s), 5.35 (1H, d, *J* = 6.9 Hz), 5.96 (1H, d, *J* = 6.9 Hz), 7.35 (2H, d, *J* = 8.4 Hz), 7.43 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 46.2, 57.2, 86.7, 128.7, 130.0, 135.4, 135.7.
EI-MS (m/z): 328 (M+2), 326 (M^+), 232, 230, 153, 149, 116, 115, 90, 89, 88.
FT-IR (neat, cm^{-1}): 1090, 1141, 1495, 1560, 3334.
HR-MS (*m*/*z*) for $C_9H_9Br_2ClO$ (M^+): Calculated 325.8709, found 325.8712 (one of the peaks).

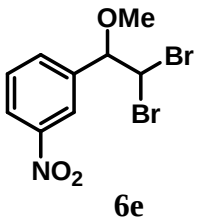
7.4. Compound 6d



6d

Yield: 84% (313 mg, 0.84 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.39 (3H, s), 4.48 (1H, d, *J*= 5.1 Hz), 5.65 (1H, d, *J*= 5.1 Hz), 7.28 (2H, d, *J*= 8.4 Hz), 7.52 (2H, d, *J*= 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 46.9, 58.1, 86.9, 123.1, 129.7, 131.5, 135.4.
EI-MS (m/z): 372 (M+2), 370 (M^+), 201, 199, 183, 118, 102, 93, 91,89,76,75,63,51.
FT-IR (neat, cm^{-1}): 1101, 1484,1590, 2927, 3443.
HR-MS (*m*/*z*) for $C_9H_9Br_3O$ (M^+): Calculated 369.8203, found 369.8209 (one of the peaks).

7.5. Compound 6e

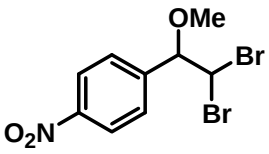


6e

Yield: 73% (247 mg, 0.73 mmol).
Characteristic:Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.99 (3H, s), 5.39 (1H, d, *J* = 6.3 Hz), 5.78 (1H, d, *J* = 6.3 Hz), 7.51-7.62 (1H, m), 7.99 (1H, d, *J* = 7.8 Hz), 8.13 (1H, t, *J* = 6.9 Hz), 8.55 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.2, 58.3, 87.1, 122.9, 123.7, 129.7, 134.6, 136.5, 137.5.
EI-MS (m/z): 339 (M+2), 337 (M^+), 237, 235, 169, 168, 116, 115, 76, 75, 74, 51.
FT-IR (neat, cm^{-1}): 1095, 1153, 1407, 1595, 3026.

HR-MS (*m*/*z*) for $C_9H_9Br_2NO_3$ (M^+): Calculated 336.8949, found 336.8945 (one of the peaks).

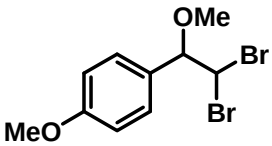
7.6. Compound 6f



6f

Yield: 72% (244 mg, 0.72 mmol).
Characteristic**:** Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41 (3H, s), 4.87 (1H, d, *J* = 5.7 Hz), 6.10 (1H, d, *J* = 5.7 Hz), 7.83 (2H, d, *J* = 8.7 Hz), 8.24 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.8, 58.3, 88.2, 126.3, 126.5, 128.0, 128.5, 133.3, 137.3.
EI-MS (m/z): 339 (M+2), 337 (M^+), 255, 253, 178, 177, 101, 99, 76, 75, 74, 53, 51.
FT-IR (neat, cm^{-1}): 1123, 1287, 1428, 1637, 3323.
HR-MS (*m*/*z*) for $C_9H_9Br_2NO_3$ (M^+): Calculated 336.8949, found 336.8952 (one of the peaks).

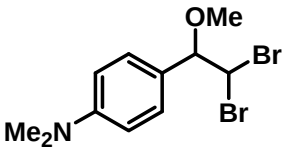
7.7. Compound 6g



6g

Yield: 92% (298 mg, 0.92 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.37 (3H, s), 3.82 (3H, s), 4.47 (1H, d, *J* = 5.1 Hz), 5.65 (1H, d, *J* = 5.1 Hz), 6.91 (2H, d, *J* = 8.1 Hz), 7.31 (2H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.1, 55.2, 57.8, 87.2, 113.7, 128.4, 129.2, 160.1.
EI-MS (m/z): 324 (M+2), 322 (M^+), 292, 152, 151, 136, 135, 90, 89,77, 63.
FT-IR (neat, cm^{-1}): 1093, 1247, 1510, 1608, 2831, 2931, 2997.
HR-MS (*m*/*z*) for $C_{10}H_{12}Br_2O_2$ (M^+): Calculated 321.9204, found 321.9208 (one of the peaks).

7.8. Compound 6h

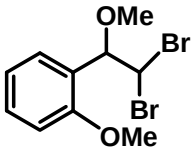


6h

Yield: 85% (286 mg, 0.85 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.82 (6H, s), 3.39 (3H, s), 4.43 (1H, d, *J* = 5.1 Hz), 5.63 (1H, d, *J* = 5.1 Hz), 6.60 (1H, d, *J* = 8.4 Hz), 7.07 (1H, d, *J* = 8.4 Hz), 7.19 (1H, d, *J* = 8.4 Hz), 7.59 (1H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 44.0, 47.4, 48.7, 58.1, 111.9, 120.0, 127.6, 129.0, 131.7, 133.4.
EI-MS (m/z): 337 (M+2), 335 (M^+), 208, 207, 133, 115, 77, 73, 72, 45, 44, 43.
FT-IR (neat, cm^{-1}): 695, 1094, 1423, 2947, 3429, 3820.

HR-MS (*m*/*z*) for $C_{11}H_{15}Br_2NO$ (M^+): Calculated 334.9520, found 334.9527 (one of the peaks).

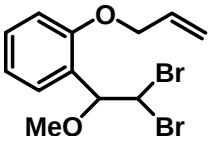
7.9. Compound 6i



6i

Yield: 90% (291 mg, 0.90 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.48 (3H, s), 3.85 (3H, s), 4.95 (1H, d, *J* = 3.0 Hz), 5.89 (1H, d, *J* = 3.0 Hz), 6.89 (1H, d, *J* = 8.1 Hz), 7.01(1H, t, *J* = 7.2 Hz), 7.34 (1H, t, *J* = 7.5 Hz), 7.45 (1H, d, *J* = 6.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.4, 55.4, 58.6, 82.3, 110.3, 120.6, 125.0, 128.1, 129.7, 156.9.
EI-MS (m/z): 324 (M+2), 322 (M^+), 152, 151, 133, 131, 121, 105, 91, 89, 77, 63, 51.
FT-IR (neat, cm^{-1}): 1122, 1251, 1466, 2938, 3414.
HR-MS (*m*/*z*) for $C_{10}H_{12}Br_2O_2$ (M^+): Calculated 321.9204, found 321.9201 (one of the peaks).

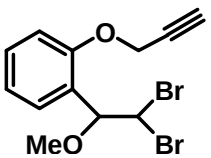
7.10. Compound 6j



6j

Yield: 92% (322 mg, 0.92 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.50 (3H, s), 4.58 (2H, t, *J* = 4.2 Hz), 5.01 (1H, d, *J* = 2.7 Hz), 5.32 (1H, d, *J* = 10.5 Hz), 5.43 (1H, d, *J* = 17.5 Hz), 5.93 (1H, d, *J* = 2.7 Hz), 5.99-6.12 (1H, m), 6.87 (1H, d, *J* = 8.4 Hz), 7.02 (1H, t, *J* = 7.5 Hz), 7.32 (1H, t, *J* = 7.5 Hz), 7.46 (1H, d, *J* = 7.5 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 47.3, 58.6, 68.6, 82.3, 111.5, 117.3, 120.8, 125.3, 128.1, 129.6, 132.7, 155.9.
EI-MS (m/z): 350 (M+2), 348 (M^+), 207, 177, 160, 115, 91, 82, 80, 77, 55, 51.
FT-IR (neat, cm^{-1}): 1454, 1487, 1600, 2829, 2930, 3078.
HR-MS (*m*/*z*) for $C_{12}H_{14}Br_2O_2$ (M^+): Calculated 347.9361, found 347.9369 (one of the peaks).

7.11. Compound 6k

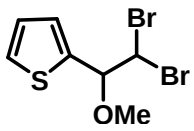


6k

Yield: 91% (317 mg, 0.91 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (1H, t, *J* = 2.4 Hz), 3.48 (3H, s), 4.75 (2H, d, *J* = 2.4 Hz), 4.97 (1H, d, *J* = 3.0 Hz), 5.89 (1H, d, *J* = 3.0 Hz), 7.00-7.09 (2H, m), 7.32-7.38 (1H, m), 7.48 (1H, dd, *J* = 7.8, 1.5 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 47.2, 56.0, 58.5, 76.0, 78.1, 82.0, 111.9, 121.5, 125.8, 128.3, 129.5, 154.9.
EI-MS (m/z): 348 (M+2), 346 (M^+), 176, 175, 145, 121, 91, 89, 77, 69, 63, 51,45.
FT-IR (neat, cm^{-1}): 1119, 1226, 1477, 2918, 3276.

HR-MS (*m*/*z*) for $C_{12}H_{12}Br_2O_2$ (M^+): Calculated 345.9204, found 345.9209 (one of the peaks).

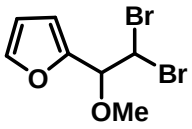
7.12. Compound 6l



6l

Yield: 79% (237 mg, 0.79 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (3H, s), 5.10 (1H, d, *J* = 5.4 Hz), 6.01 (1H, d, *J* = 5.4 Hz), 6.96 (1H, dd, *J* = 4.8, 3.6 Hz), 7.08 (1H, d, *J* = 3.3 Hz), 7.27 (1H, d, *J* = 5.1 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 48.2, 57.4, 86.9, 126.0, 126.5, 126.7, 126.9, 129.5, 140.8.
EI-MS (m/z): 300 (M+2), 298 (M^+), 204, 128, 127, 121, 120, 107, 106, 58, 51, 45.
FT-IR (neat, cm^{-1}): 1069, 1248, 1376, 2856, 2949, 3366.
HR-MS (*m*/*z*) for $C_7H_8Br_2OS$ (M^+): Calculated 297.8663, found 297.8668 (one of the peaks).

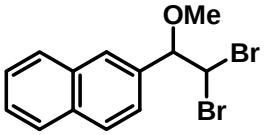
7.13. Compound 6m



6m

Yield: 76% (216 mg, 0.76 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.39 (3H, s), 5.43 (1H, d, *J* = 5.1 Hz), 5.97 (1H, d, *J* = 5.1 Hz), 6.63 (1H, dd, *J* = 3.6, 1.5 Hz), 7.31 (1H, d, *J* = 3.6 Hz), 7.75 (1H, d, *J* = 0.6 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 48.2, 56.9, 87.7, 106.1, 113.7, 139.6, 155.7.
EI-MS (m/z): 284 (M+2), 282 (M^+), 219, 218, 188, 187, 121, 97, 96, 84, 53.
FT-IR (neat, cm^{-1}): 1069, 1336, 1539, 2889, 3240.
HR-MS (*m*/*z*) for $C_7H_8Br_2O_2$ (M^+): Calculated 281.8891, found 281.8890 (one of the peaks).

7.14. Compound 6n

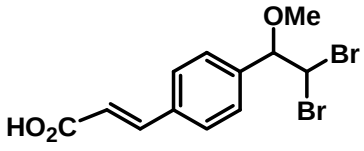


6n

Yield: 76% (261 mg, 0.76 mmol).
Characteristic: White semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.37 (3H, s), 4.62 (1H, d, *J* = 5.4 Hz), 5.72 (1H, d, *J* = 5.4 Hz), 7.42-7.47 (3H, m), 7.79-7.82 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.4, 58.1, 87.8, 124.8, 126.4, 126.5, 127.8, 127.9, 128.1, 128.3, 132.9, 133.6, 134.0.
EI-MS (m/z): 344 (M+2), 342 (M^+), 184, 172, 171, 152, 141, 128, 127, 77, 76.
FT-IR (neat, cm^{-1}): 1097, 1461, 1508, 2827, 2929, 3056.

HR-MS (*m*/*z*) for $C_{13}H_{12}Br_2O$ (M^+): Calculated 341.9255, found 341.9258 (one of the peaks).

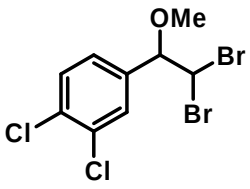
7.15. Compound 6o



6o

Yield: 75% (273 mg, 0.75 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (3H, s), 4.49 (1H, d, *J* = 5.1 Hz), 5.66 (1H, d, *J* = 5.1 Hz), 6.81 (1H, d, *J* = 14.1 Hz), 7.06 (1H, d, *J* = 8.1 Hz), 7.33 (4H, q, *J* = 8.4 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 47.1, 58.0, 87.2, 116.3, 126.0, 128.4, 136.5, 144.7, 170.5.
EI-MS (m/z): 364 (M+2), 362 (M^+), 281, 227, 225, 209, 207, 115, 102, 96, 77, 76, 73, 63, 51.
FT-IR (neat, cm^{-1}): 1069, 1594, 2927, 3420.
HR-MS (*m*/*z*) for $C_{12}H_{12}Br_2O_3$ (M^+): Calculated 361.9153, found 361.9154 (one of the peaks).

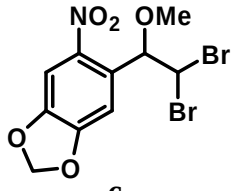
7.16. Compound 6p



6p

Yield: 70% (254 mg, 0.70 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.46 (1H, d, *J* = 1.8 Hz), 3.84 (3H, s), 4.07 (1H, d, *J* = 1.8 Hz), 7.14 (1H, dd, *J* = 8.4, 2.1 Hz), 7.38 (1H, d, *J* = 2.1 Hz), 7.45 (1H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.7, 56.5, 56.6, 118.1, 125.0, 127.7, 130.7, 133.2, 135.2.
EI-MS (m/z): 361 (M+2), 359 (M^+), 246, 201, 199, 191, 189, 161, 159, 125, 123, 75, 74, 73, 44, 32, 28.
FT-IR (neat, cm^{-1}): 1215, 1334, 1449, 1754, 2924, 3036, 3478.
HR-MS (*m*/*z*) for $C_9H_8Br_2Cl_2O$ (M^+): Calculated 359.8319, found 359.8311(one of the peaks).

7.17. Compound 6q

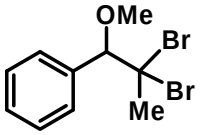


6q

Yield: 66% (253 mg, 0.66 mmol).
Characteristic: Brown oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (1H, d, *J* = 1.5 Hz), 3.87 (3H, s), 4.65 (1H, d, *J* = 1.5 Hz), 6.16 (2H, s), 7.00 (1H, s), 7.68 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8, 55.5, 56.6, 103.3, 105.5, 106.1, 129.4, 148.1, 153.0, 167.9.

EI-MS (m/z): 382 (M+2), 380 (M^+), 281, 207, 135, 119, 105, 96, 94, 79, 52, 44, 32, 28.
FT-IR (neat, cm^{-1}): 1330, 1524, 1614, 1749, 2918, 3122.
HR-MS (*m*/*z*) for $C_{10}H_9Br_2NO_5$ (M^+): Calculated 380.8852, found 380.8847 (one of the peaks).

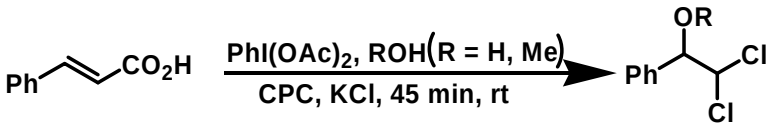
7.18. Compound 6r



6r

Yield: 60% (184 mg, 0.60 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (3H, s), 3.27 (3H, s), 5.10 (1H, s), 7.24-7.32 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 53.3, 67.5, 94.3, 125.8, 128.3, 129.0, 130.9, 140.6.
EI-MS (m/z): 308 (M+2), 306 (M^+), 207, 148, 105, 103, 90, 89, 77, 44, 43, 40, 32, 29, 28, 27.
FT-IR (neat, cm^{-1}): 1282, 1454, 1726, 2852, 2924, 3399.
HR-MS (*m*/*z*) for $C_{10}H_{12}Br_2O$ (M^+): Calculated 305.9255, found 305.9260 (one of the peaks).

8. Synthesis of α,α-(dichloromethyl)phenylmethylalcohol and methylether

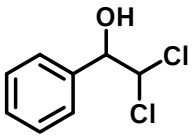


(1a) **(8)**

To a stirred solution of *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) in water or methanol (5 mL) cetyl pyridinium chloride (CPC) (10 mmol%, 26 mg) and KCl (150 mg, 2 mmol) were added.The resultant mixture was stirred at room temperature for 5 min and iodosobenzene diacetate (644 mg, 2 mmol) was added. The content of the reaction mixture was stirred at rt and the starting material was completely consumed after 45 min. The progress of the reaction was monitored by thin layer chromatography (TLC). Solvent was removed in a rotary evaporator under reduced pressure at room temperature in case of methanol. The post reaction mixture was extracted with EtOAc (2 x 15 mL). It was washed successively with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure. Thus, compound α,α-(dichloromethyl)phenylmethylmethylether (**8b**) was obtained after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:9, v/v) as an eluent in an yield of 74% (152 mg, 0.74 mmol). The α,α-(dichloromethyl)phenylmethylalcohol (**8a**) and methylether (**8b**) was characterized by NMR (^{1}H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

9. Characterization data of α,α-(dichloromethyl)phenylmethylalcohol and methylether (8a-b)

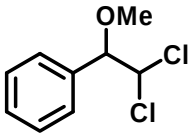
9.1. Compound 8a



8a

Yield: 60% (115 mg, 0.60 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.40 (1H, d, *J* = 7.8 Hz), 5.04 (1H, d, *J* = 7.8 Hz), 7.35-7.43 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 55.0, 73.3, 126.9, 128.5, 128.8, 138.7.
EI-MS (m/z): 190 (M^+), 185, 125, 92, 75, 51, 48, 32, 27.
FT-IR (neat, cm^{-1}): 1025,1500, 1728, 2928, 3500.
HR-MS (*m*/*z*) for $C_8H_8Cl_2O$ (M^+): Calculated 189.9952, found 189.9957 (one of the peaks).

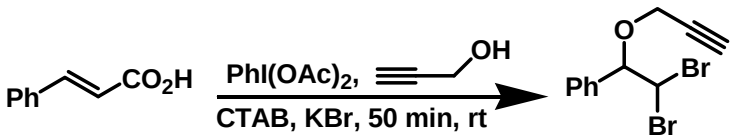
9.2. Compound 8b



8b

Yield: 74% (152 mg, 0.74 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.78 (3H, s), 4.40 (1H, d, *J* = 7.8 Hz), 5.04 (1H, d, *J* = 7.8 Hz), 7.37-7.41 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 53.1, 59.0, 75.3, 126.9, 128.5, 128.8, 138.7.
EI-MS (m/z): 206 (M+2), 204 (M^+), 196, 161, 108, 107, 105, 79, 77, 51, 32, 28.
FT-IR (neat, cm^{-1}): 1019, 1438, 1746, 2926, 3463.
HR-MS (*m*/*z*) for $C_9H_{10}Cl_2O$ (M^+): Calculated 204.0109, found 204.0112 (one of the peaks).

10. Synthesis of α,α-(dibromomethyl)phenylmethylpropergylether



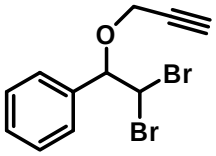
(1a) **(9)**

To a stirred solution of *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) in propergyl alcohol (5 mL) CTAB (36 mg , 10 mmol%) and KBr (240 mg, 2 mmol) were added. The content of the reaction mixture was stirred at room temperature for 5 min followed by addition of iodosobenzene diacetate (644 mg, 2 mmol). Stirring was continued until the starting material was completely consumed. The reaction was monitored by thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2

x15 mL) and washed successively with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and of brine (1 x 10 mL).The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure. Thus, compound α,α-(dibromomethyl)phenylmethylpropergylether (**9**) was obtained after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:13, v/v) as an eluent in an yield of 62% (197 mg, 0.62 mmol). The α,α-(dichloromethyl)phenylmethylether was characterized by NMR (^{1}H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

11. Characterization data of α,α-(dibromomethyl)phenylmethylpropergylether

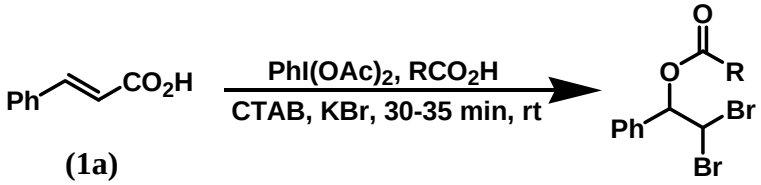
11.1. Compound 9



9

Yield: 62% (197 mg, 0.62 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (1H, t, *J* = 2.7 Hz), 3.72- 3.77 (2H, m), 4.36 (1H, d, *J* = 5.1 Hz), 4.82 (1H, d, *J* = 5.1 Hz), 7.30-7.43 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.6, 56.0, 76.3, 78.4, 82.0, 127.7, 128.6, 130.0, 136.3.
EI-MS (m/z): 318 (M+2), 316 (M^+), 310, 207, 195, 179, 178, 147, 103, 96, 59, 58, 45, 44, 32, 28.
FT-IR (neat, cm^{-1}): 1371, 1462, 1617, 1743, 2850, 2919, 3302.
HR-MS (*m*/*z*) for $C_{11}H_{10}Br_2O$ (M^+): Calculated 315.9104, found 315.9098 (one of the peaks).

12. General procedure for synthesis of α,α-(dibromomethyl)phenylmethylester

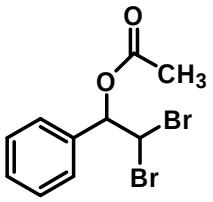


(1a) **(10)**

To a stirred solution of *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) in carboxylic acid (acetic acid and L-lactic acid) (5 mL) CTAB (36 mg , 10 mmol%) and KBr (240 mg, 2 mmol) were added. The content of the reaction mixture was stirred at room temperature for 5 min followed by addition of iodosobenzene diacetate (644 mg, 2 mmol). Stirring was continued until the starting material was completely consumed. The reaction was monitored by thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2 x 15 mL). It was washed successively with saturated aqueous sodium bicarbonate solution till effervescence ceased and brine (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure. Thus, the reaction with *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) in acetic acid afforded α,α-(dibromomethyl)phenylmethylacetate **(10a)**. After purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:9, v/v) as an eluent in an yield of 78% (251 mg, 0.78 mmol). The α,α-(dibromomethyl)phenylmethylacetate (**10a)** and α,α-(dibromomethyl)phenylmethyllactate (**10b)** were characterized by means of NMR (^{1}H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

13. Characterization data of α,α-(dibromomethyl)phenylmethylester (10a-b)

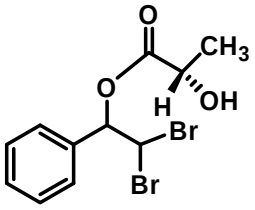
13.1. Compound 10a



10a

Yield: 78% (251 mg, 0.78 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (3H, s), 5.82 (1H, d, *J* = 5.7 Hz), 6.17 (1H, d, *J* = 5.7 Hz), 7.38-7.44 (5H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 45.5, 78.3, 127.7, 128.4, 129.3, 133.5, 169.2.
EI-MS (m/z): 321 (M+2), 319 (M^+), 198, 182, 161, 149, 107, 103, 79, 77, 51, 43.
FT-IR (neat, cm^{-1}): 1024, 1219,1372, 1748, 2928, 3034, 3482.
HR-MS (*m*/*z*) for $C_{10}H_{10}Br_2O_2$ (M^+): Calculated 319.9048, found 319.9045 (one of the peaks).

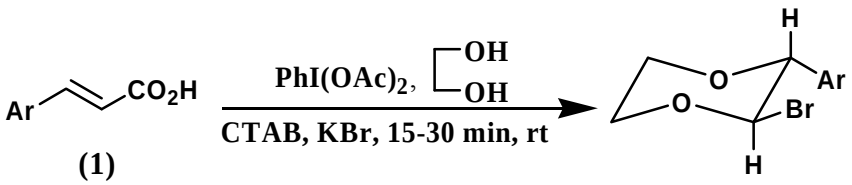
13.2. Compound 10b



10b (mixture of two diastereomers, dr= 1:1)

Yield: 81% (285 mg, 0.81 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (3H, d, *J* = 6.9 Hz), 1.59 (3H, d, *J* = 6.9 Hz), 4.40 (1H, q, *J* = 6.9 Hz), 4.49 (1H, q, *J* = 6.9 Hz), 5.80-5.84 (1H, m), 6.20-6.24 (1H, m), 7.41 (5H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.1, 20.5, 44.7, 44.8, 66.7, 66.9, 79.3, 79.4, 127.4, 127.5, 128.6, 129.6, 134.9, 173.8, 174.0.
EI-MS (m/z): 351 (M+2), 349 (M^+), 263, 184, 151, 107, 103, 102, 77, 76, 51, 45, 44, 32, 28.
FT-IR (neat, cm^{-1}): 1125, 1496, 1748, 2851, 2925, 3433.
HR-MS (*m*/*z*) for $C_{11}H_{12}Br_2O_3$ (M^+): Calculated 349.9153, found 349.9144 (one of the peaks).

14. General procedure for stereoselective synthesis of bromo-1,4-dioxane

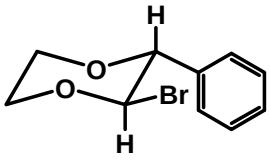


(1) **(±) 11**

To a stirred solution of α,β-unsaturated carboxylic acid (1 mmol) in ethylene glycol (5 mL) CTAB (36 mg, 10 mmol%) and KBr (240 mg, 2 mmol) were added.The resultant mixture was stirred at room temperature for 5 min and iodosobenzene diacetate (644 mg, 2 mmol) was added. The content of the reaction mixture was stirred until the starting material was completely consumed. The progress of the reaction was monitored by thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2 x15 mL) and washed successively with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and of brine (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with *trans*-cinnamic acid (**1a**, 148 mg, 1.0 mmol) afforded 2-bromo-3-phenyl-1,4-dioxane (**11a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1: 9, v/v) as an eluent in an isolated yield of 90% (218 mg, 0.90 mmol). The bromo-1,4-dioxane (**11a-f**) were characterized by means of NMR (^{1}H and ^{13}C), FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

15. Characterization data of bromo-1,4-dioxane (11a-f)

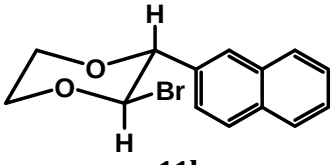
15.1. Compound 11a



11a

Yield: 90% (218 mg, 0.90 mmole).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.59-3.70 (2H, m), 3.81 (2H, t, *J* = 4.5 Hz), 4.72 (1H, d, *J* = 5.4 Hz), 5.74 (1H, d, *J* = 5.4 Hz), 7.42 (5H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.9, 61.7, 71.6, 86.3, 127.8, 128.5, 129.2, 136.6.
EI-MS (m/z): 244 (M+2), 242 (M^+), 184, 182, 152, 151, 107, 103, 102, 91, 79, 77, 73, 51.
FT-IR (neat, cm^{-1}): 583, 695, 1087, 2908, 3396.
HR-MS (*m*/*z*) for $C_{10}H_{11}BrO_2$ (M^+): Calculated 241.9942 , found 241.9939 (one of the peaks).

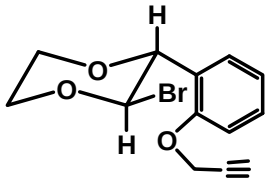
15.2. Compound 11b



11b

Yield: 88% (257 mg, 0.88 mmole).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.59-3.71 (2H, m), 3.81 (2H, t, *J* = 4.2 Hz), 4.85 (1H, d, *J* = 5.7 Hz), 5.81 (1H, d, *J* = 5.7 Hz), 7.48-7.55 (3H, m), 7.85-7.89 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.7, 61.7, 71.6, 86.5, 124.5, 126.5, 126.7, 127.8, 128.1, 128.5, 132.9, 133.6, 134.0.
EI-MS (m/z): 294 (M+2), 292 (M^+), 281, 207, 195, 160, 133, 96, 77, 73, 44, 43.
FT-IR (neat, cm^{-1}): 871, 1092, 1391, 2922, 3394, 3790.
HR-MS (*m*/*z*) for $C_{14}H_{13}BrO_2$ (M^+): Calculated 292.0099, found 292.0107 (one of the peaks).

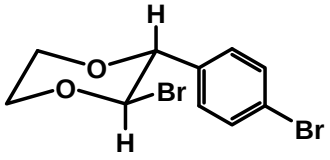
15.3. Compound 11c



11c

Yield: 90% (267 mg, 0.90 mmole).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54 (1H, t, *J* = 2.4 Hz), 3.59-3.65 (1H, m), 3.71-3.78 (1H, m), 3.80-3.84 (2H, m), 4.76 (1H, d, *J* = 2.4 Hz), 5.12 (1H, d, *J* = 3.3 Hz), 5.93 (1H, d, *J* = 3.3 Hz), 7.00-7.08 (2H, m), 7.32-7.37 (1H, m), 7.48 (1H, d, *J* = 6.3 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 56.0, 61.7, 71.8, 78.0, 80.6, 112.0, 121.7, 125.9, 128.4, 129.8, 154.7.
EI-MS (m/z): 298 (M +2), 296 (M^+), 207, 205, 161, 128, 121, 118, 105, 89, 77, 63, 51, 45, 44, 43.
FT-IR (neat, cm^{-1}): 656, 1072, 1234, 1466, 2916, 3293, 3694.
HR-MS (*m*/*z*) for $C_{13}H_{13}BrO_3$ (M^+): Calculated 296.0048, found 296.0049 (one of the peaks).

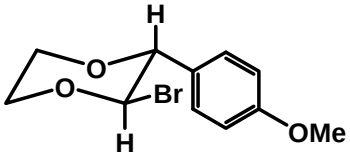
15.4. Compound 11d



11d

Yield: 85% (274 mg, 0.85 mmole).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.55-3.66 (2H, m), 3.78 (2H, t, *J* = 4.2 Hz), 4.65 (1H, d, *J* = 5.4 Hz), 5.67 (1H, d, *J* = 5.4 Hz), 7.29 (2H, d, *J* = 8.4 Hz), 7.53 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.0, 61.6, 71.6, 85.6, 129.5, 131.7, 135.6.
EI-MS (m/z): 322 (M+2), 320 (M^+), 281, 231, 207, 195, 185, 167, 160, 102, 77, 75, 51, 45, 44, 43.
FT-IR (neat, cm^{-1}): 727, 1079, 1412, 2926, 3429.
HR-MS (*m*/*z*) for $C_{10}H_{10}Br_2O_2$ (M^+): Calculated 319.9048, found 319.9043 (one of the peaks).

15.5. Compound 11e

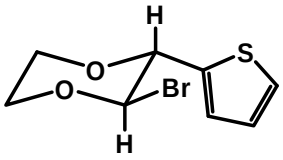


11e

Yield: 92% (251 mg, 0.92 mmole).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.55-3.61 (2H, m), 3.76 (2H, t, *J* = 4.5 Hz), 3.81 (3H, s), 4.63 (1H, d, *J* = 5.7 Hz), 5.67 (1H, d, *J* = 5.7 Hz), 6.91 (2H, d, *J* = 8.7 Hz), 7.31 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.4, 55.3, 61.6, 71.3, 85.8, 113.9, 128.5, 129.0, 160.1.
EI-MS (m/z): 274 (M+2), 272 (M^+), 212, 195, 182, 181, 137, 121, 90, 89, 77, 63, 45, 44.

FT-IR (neat, cm^{-1}): 1082, 1250, 2927, 3401, 3838.
HR-MS (*m*/*z*) for $C_{11}H_{13}BrO_3$ (M^+): Calculated 272.0048, found 272.0041 (one of the peaks).

15.6. Compound 11f



11f

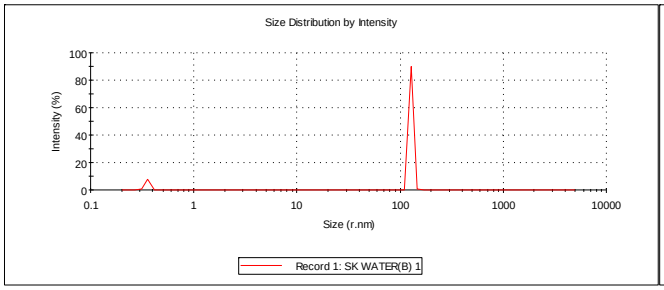
Yield: 88% (219 mg, 0.88 mmole).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63-3.69 (2H, m), 3.77 (2H, t, *J* = 4.2 Hz), 4.94 (1H, d, *J* = 5.4 Hz), 5.74 (1H, d, *J* = 5.4 Hz), 7.02 (1H, dd, *J* = 4.8, 3.6 Hz), 7.15 (1H, d, *J* = 3.6 Hz), 7.36 (1H, dd, *J* = 5.1, 0.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.4, 61.6, 71.7, 82.4, 126.7, 128.1, 129.4, 139.4.
EI-MS (m/z): 250 (M+2), 248 (M^+), 190, 188, 157, 113, 109, 108, 97, 85, 82, 69, 65, 63, 58, 51, 45.
FT-IR (neat, cm^{-1}): 701, 1083, 1581, 2920, 3382, 3845.
HR-MS (*m*/*z*) for $C_8H_9BrO_2S$ (M^+): Calculated 247.9507, found 247.9509 (one of the peaks).

16. DLS study of the reaction mixture in protic solvent

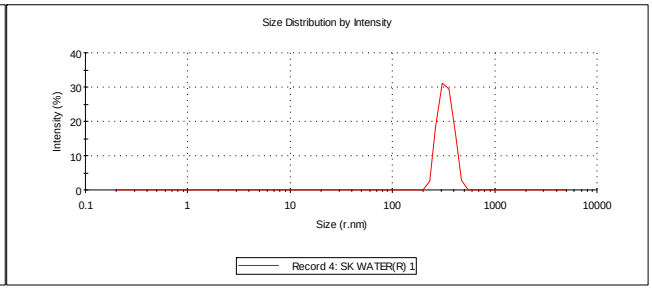
Above the CMC concencentration, suitable surfactants can generate an organized media in water or other protic organic solvents like methanol, ethanol etc. Inside of the surfactant-assembled spherical micelle is sufficiently lipophilic in nature and makes both organic substrates and reagents soluble. It was confirmed by DLS (Dynamic Light Scattering) experiment of the solutions containg surfactant and solvent as well as the reaction mixture. Large enhancement of the size of CTAB-assembled nanoreactor in water (127.7 nm), methanol 260.1) and ethylene glycol (106.7) were observed after the addition of organic Lewis acid-like oxidant $PhI(OAc)_2$, the precursor *trans*-cinnamic acid (**1a**) and KBr. The radii of the nanoreactors in the reaction mixtures became 333.5 nm (water), 383.5 nm (methanol) and 666.6 nm (ethylene glycol) (Figure 1). Interestingly, size of the nanoreactors were also increased from water to ethylene glycols.

Table 1: DLS data of the difunctionalization process

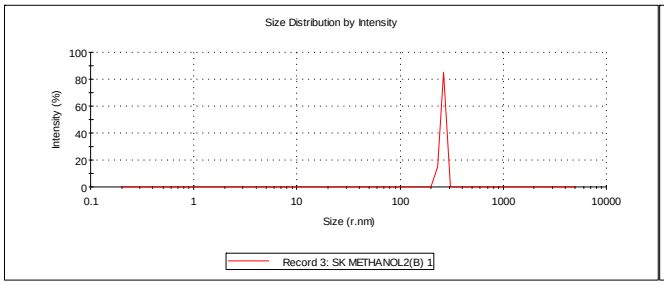
Composition	**Water medium R (width) nm**	**Methanol medium R (width) nm**	**Ethylene glycol medium R (width) nm**
Solvent + CTAB	**127.7 (9.43)**	**260.1 (13.01)**	**106.7 (13.63)**
Solvent + CTAB + *trans*-cinnamic acid + $PhI(OAc)_2$ + KBr	**333.5 (55.30)**	**383.5 (31.76)**	**666.6 (98.79)**



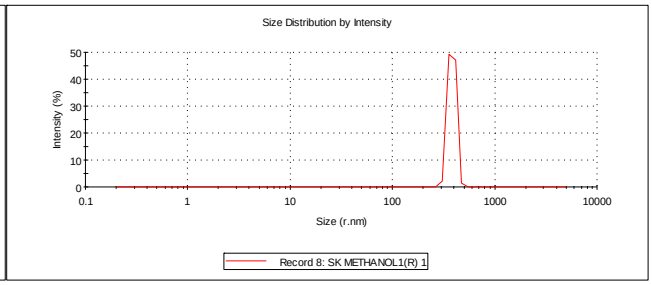
(a) DLS data (127.7 nm) of aqueous CTAB (10 mol%)



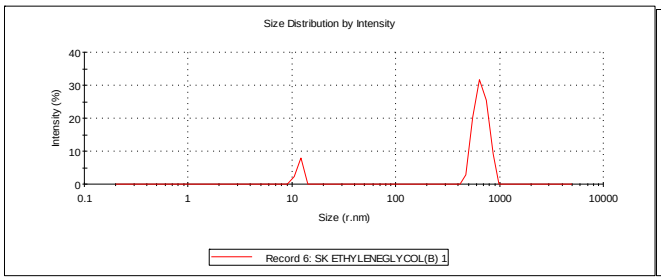
(b) DLS data (333.5 nm) of aqueous reaction mixture



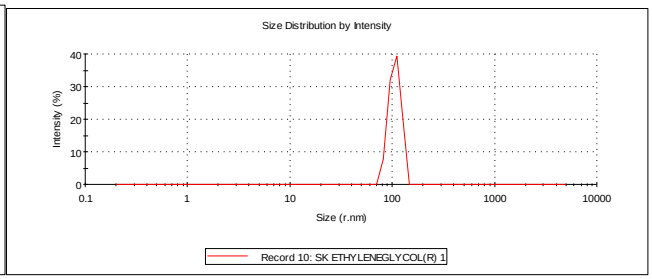
(c) DLS data (260.1 nm) of CTAB (10 mol%) in methanol



(d) DLS data (383.5 nm) of the reaction mixture in methanol



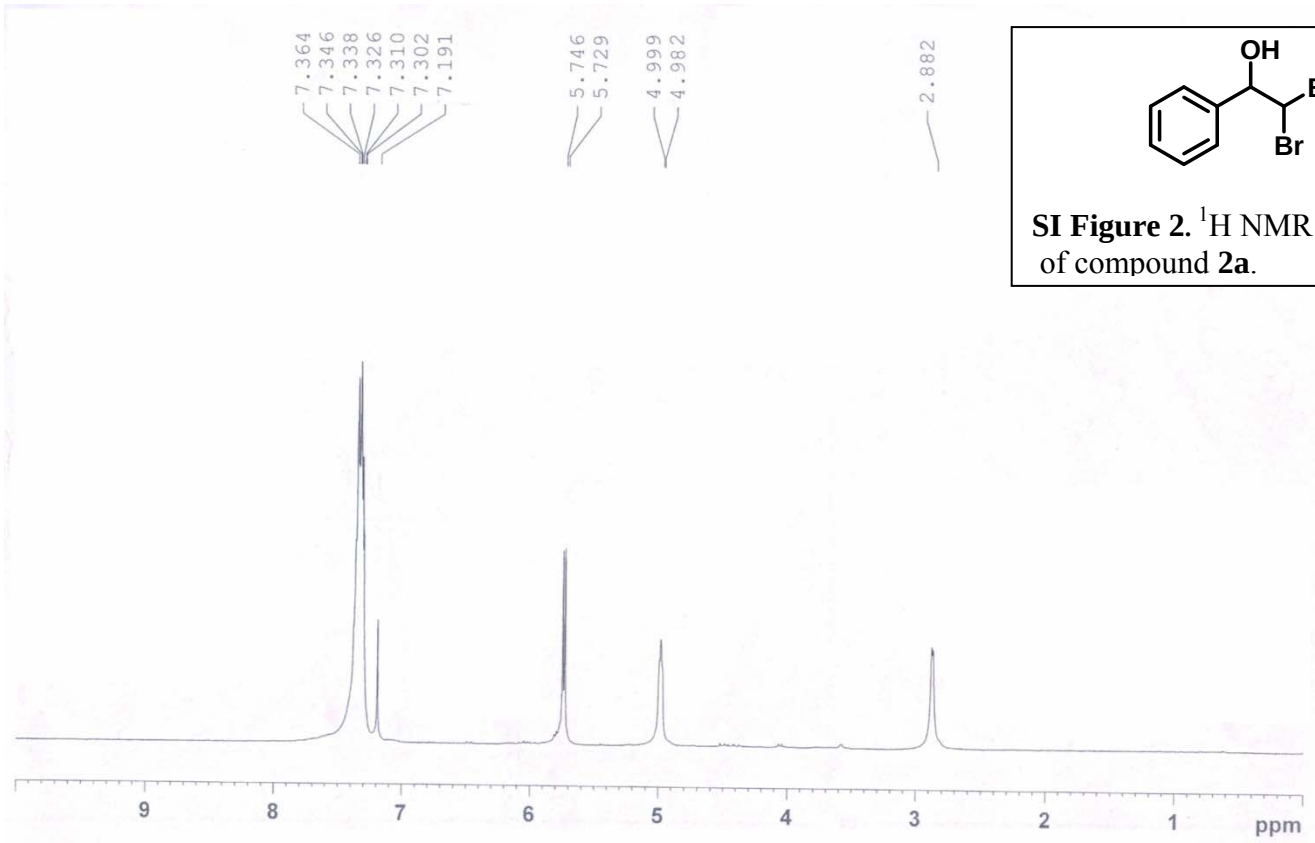
(e) DLS data (106.7 nm) of CTAB (10 mol%) in ethylene glycol



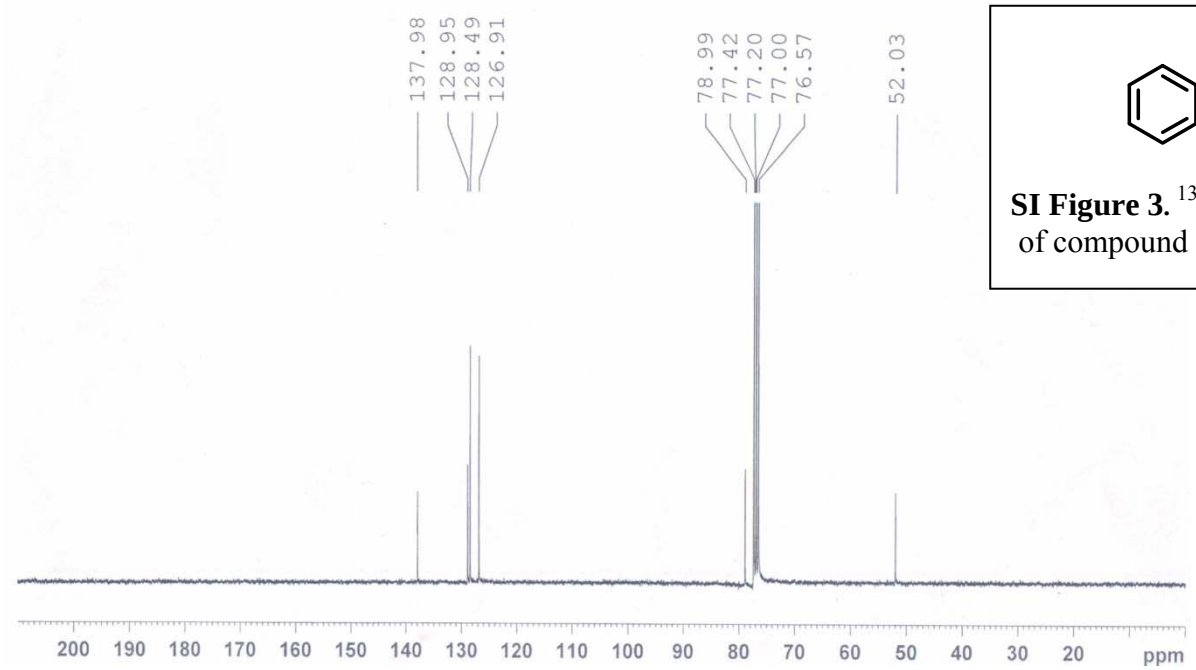
(f) DLS data (666.6 nm) of CTAB (10 mol%) in ethylene glycol

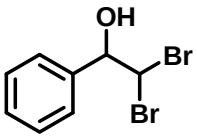
Figure 1: DLS data

17. ^{1}H and ^{13}C spectra of the compounds (2a-r, 5, 6a-r, 8a-b, 9, 10a-b, 11a-f)

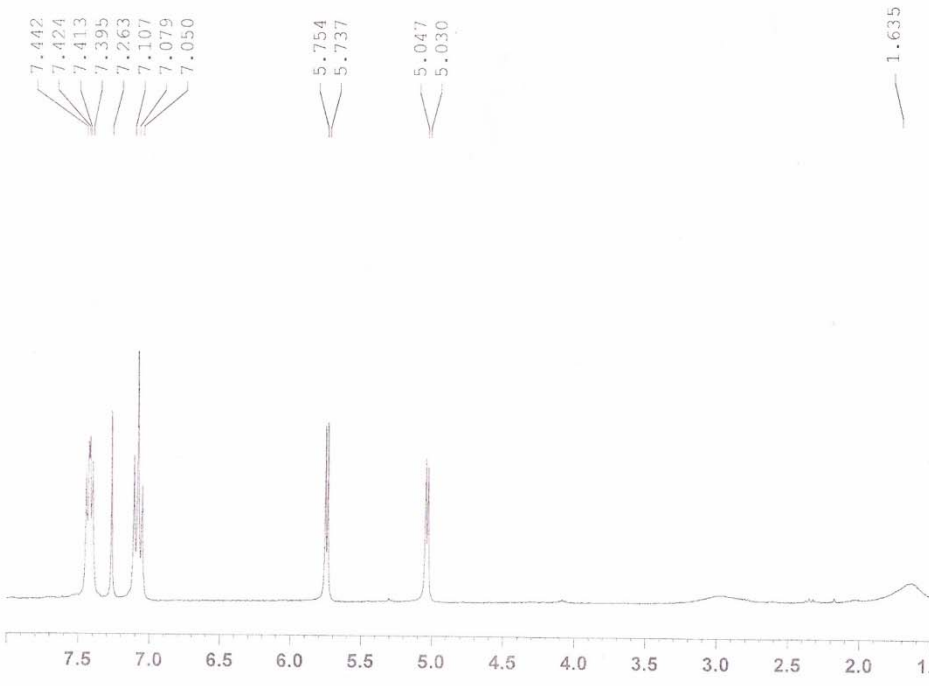


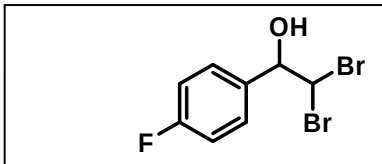
SI Figure 2. ^{1}H NMR spectrum of compound **2a**.



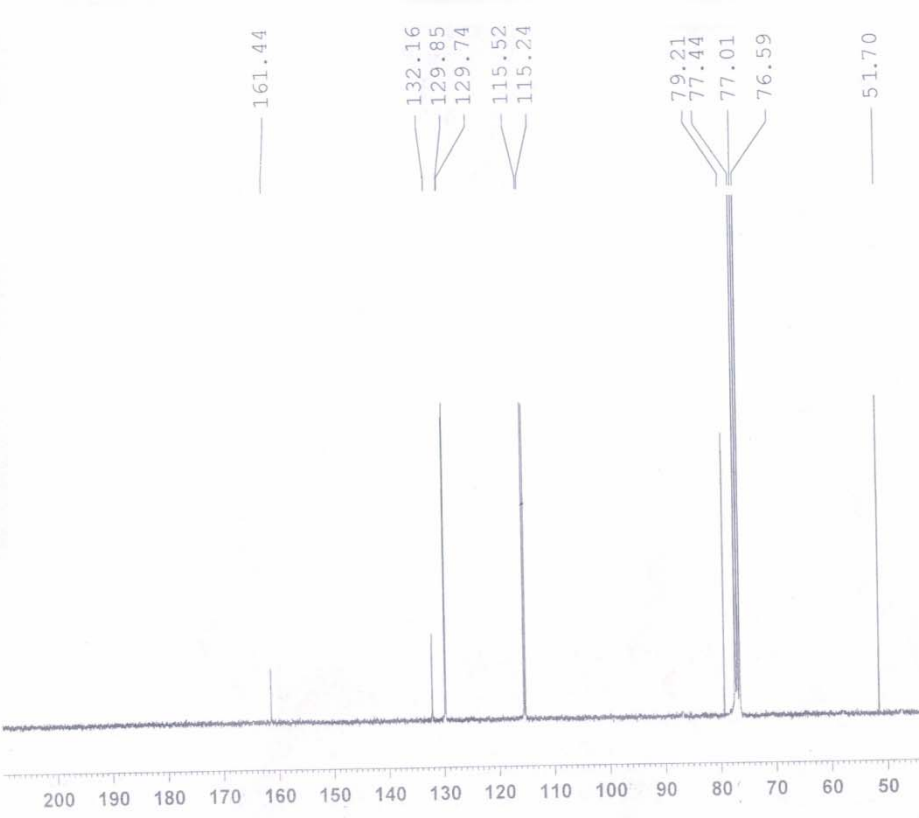


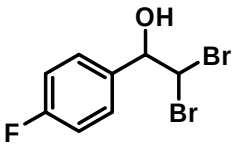
SI Figure 3. ^{13}C NMR spectrum of compound **2a**.



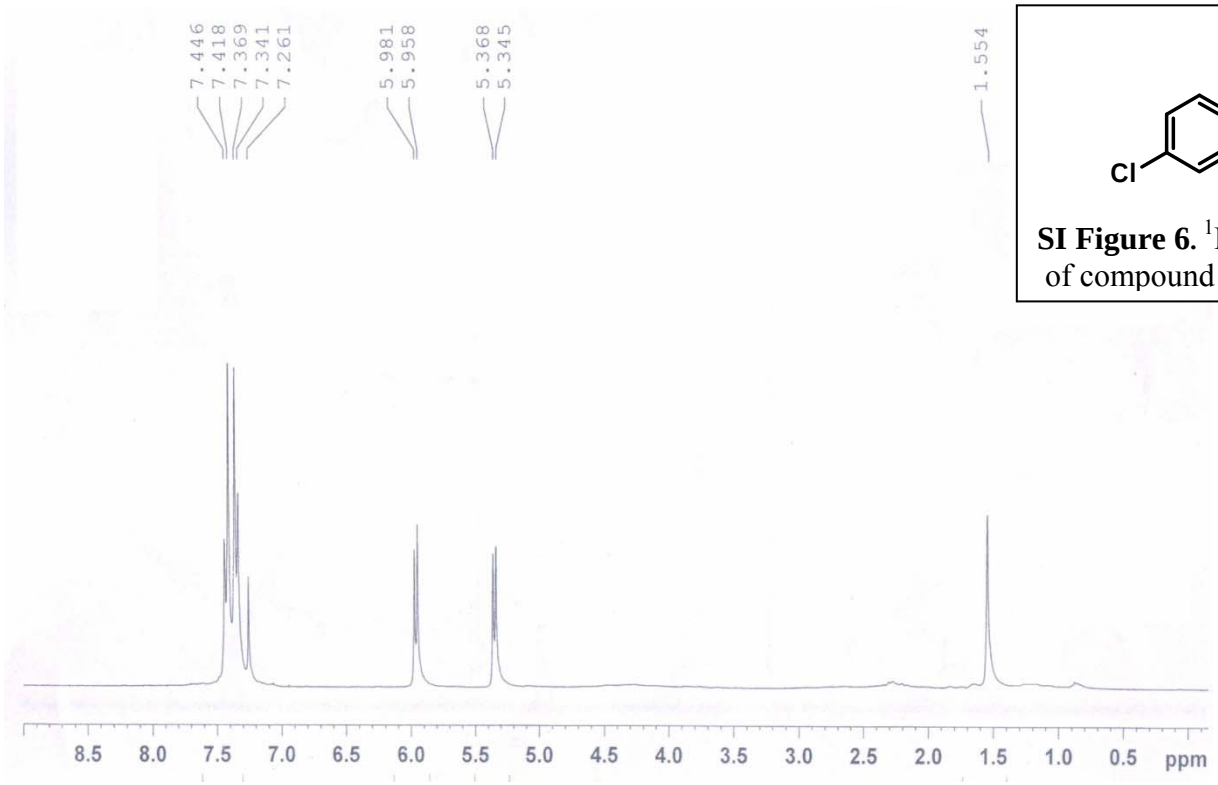


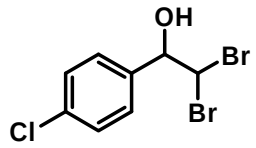
SI Figure 4. ^{1}H NMR spectrum of compound **2b**.



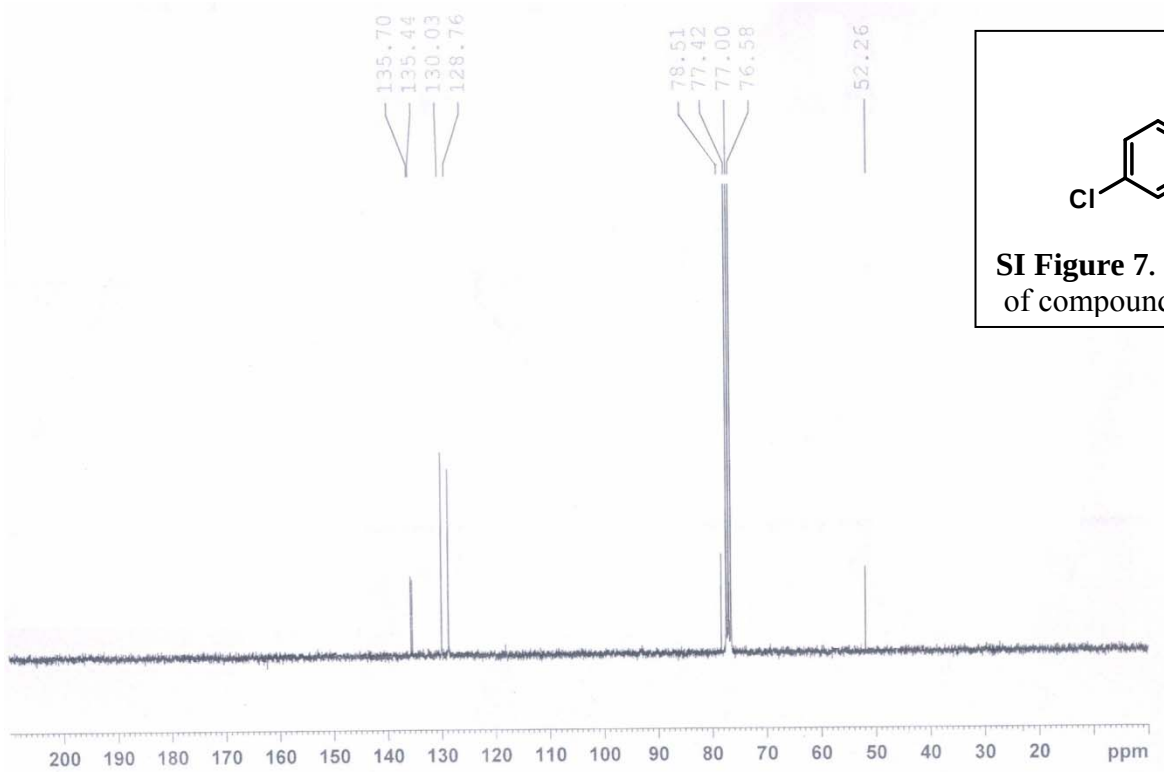


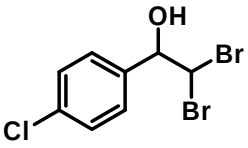
SI Figure 5. ^{13}C NMR spectrum of compound **2b**.



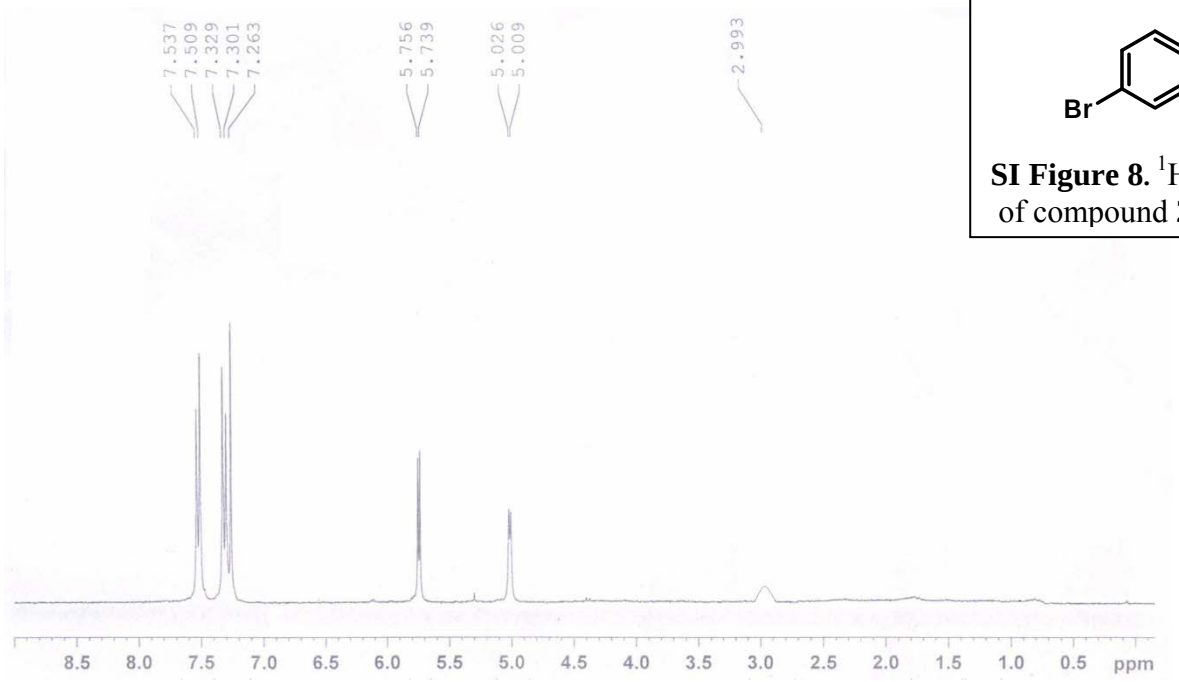


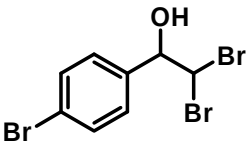
SI Figure 6. ^{1}H NMR spectrum of compound **2c**.



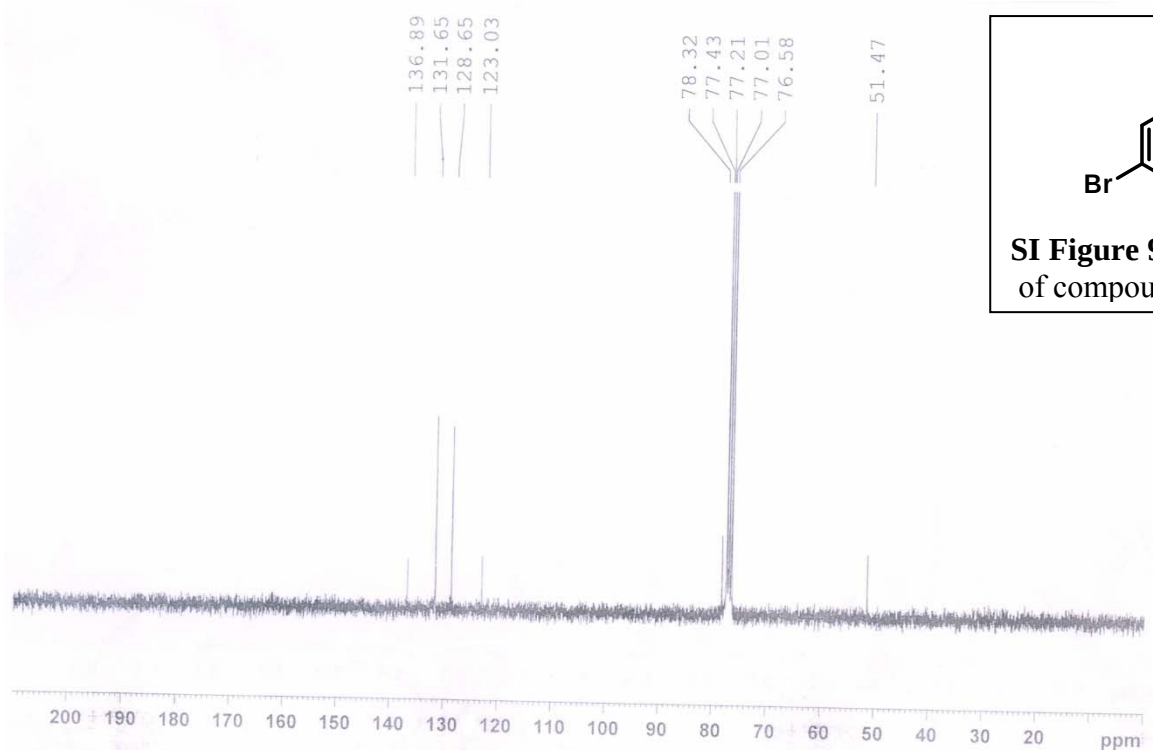


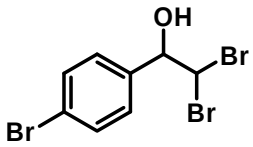
SI Figure 7. ^{13}C NMR spectrum of compound **2c**.



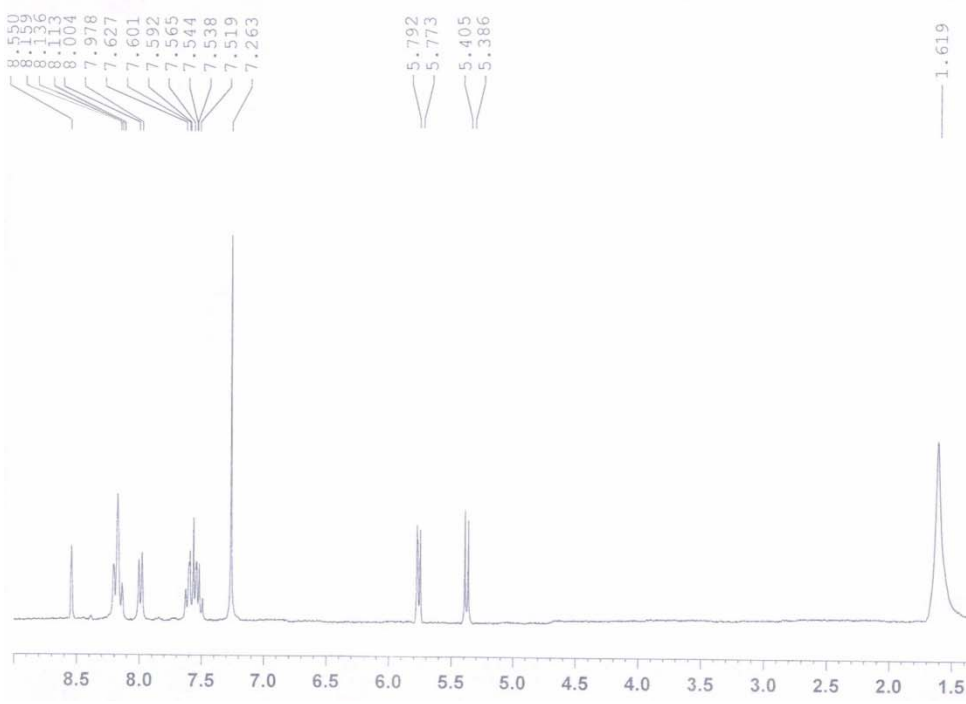


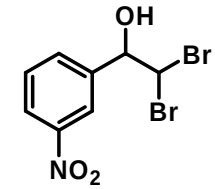
SI Figure 8. ^{1}H NMR spectrum of compound **2d**.



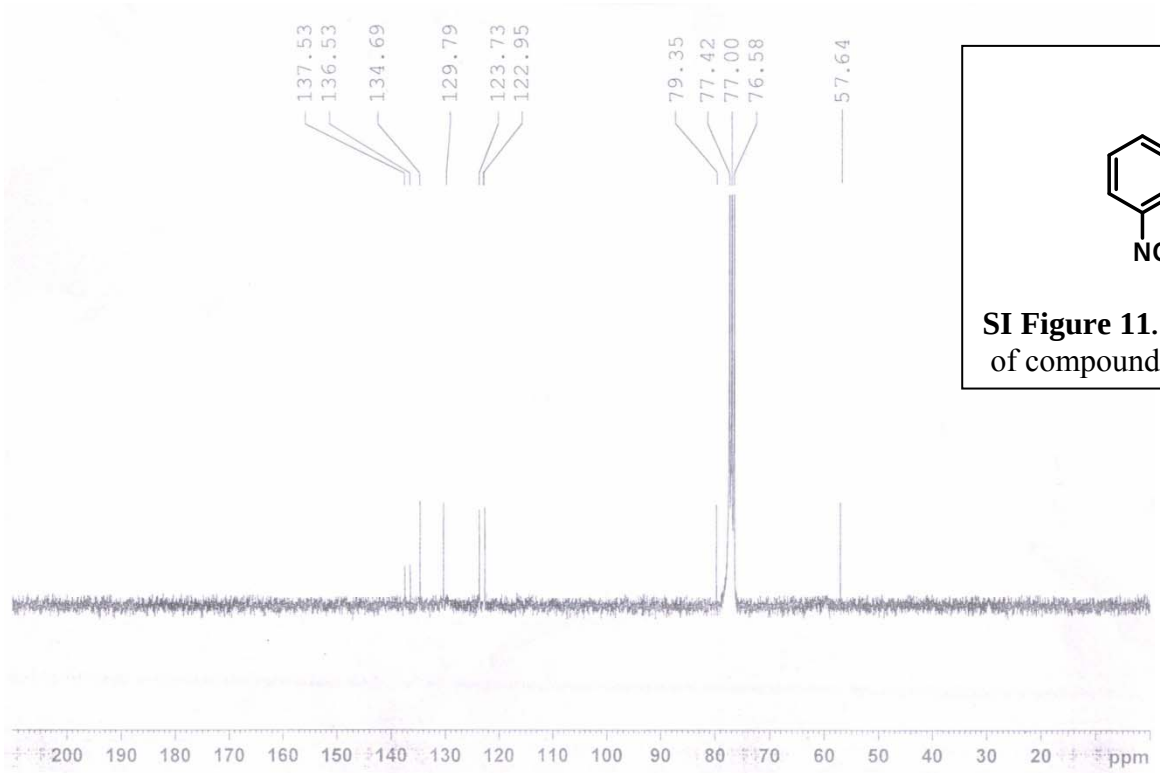


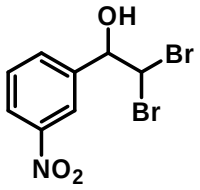
SI Figure 9. ^{13}C NMR spectrum of compound **2d**.



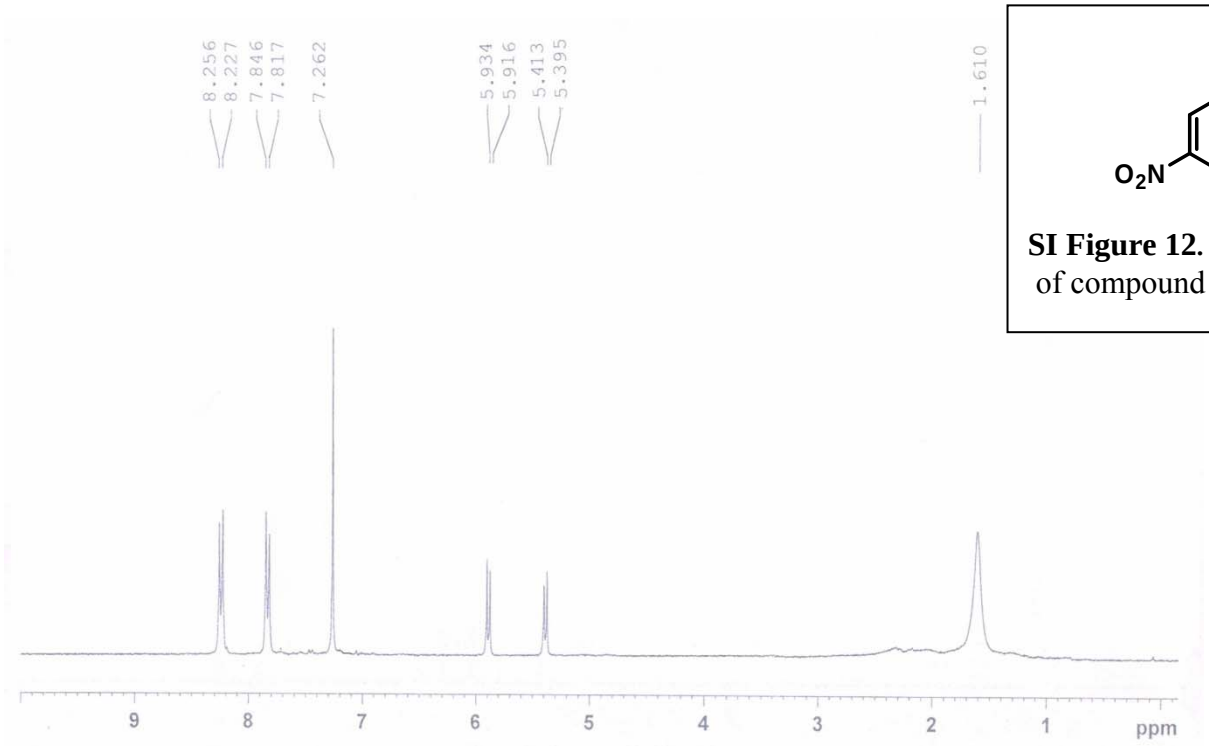


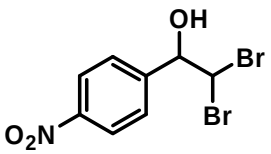
SI Figure 10. ^{1}H NMR spectrum of compound **2e**.



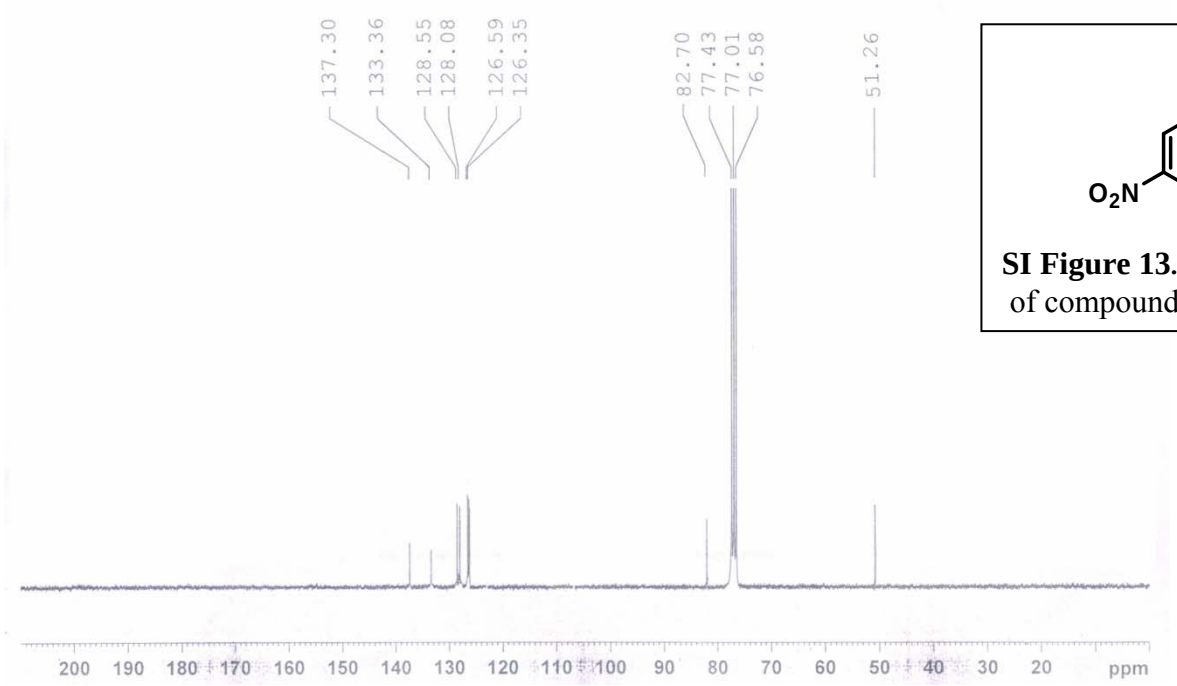


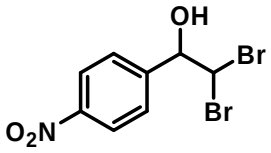
SI Figure 11. ^{13}C NMR spectrum of compound **2e**.



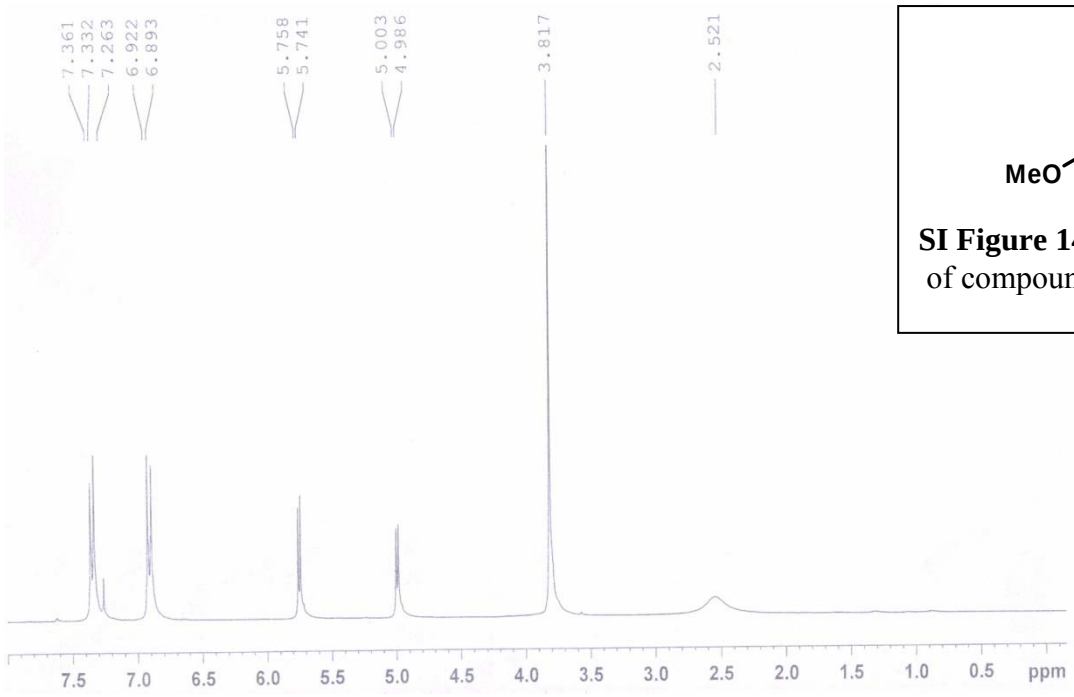


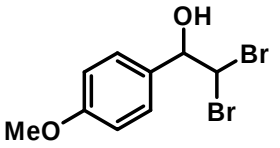
SI Figure 12. ^{1}H NMR spectrum of compound **2f**.



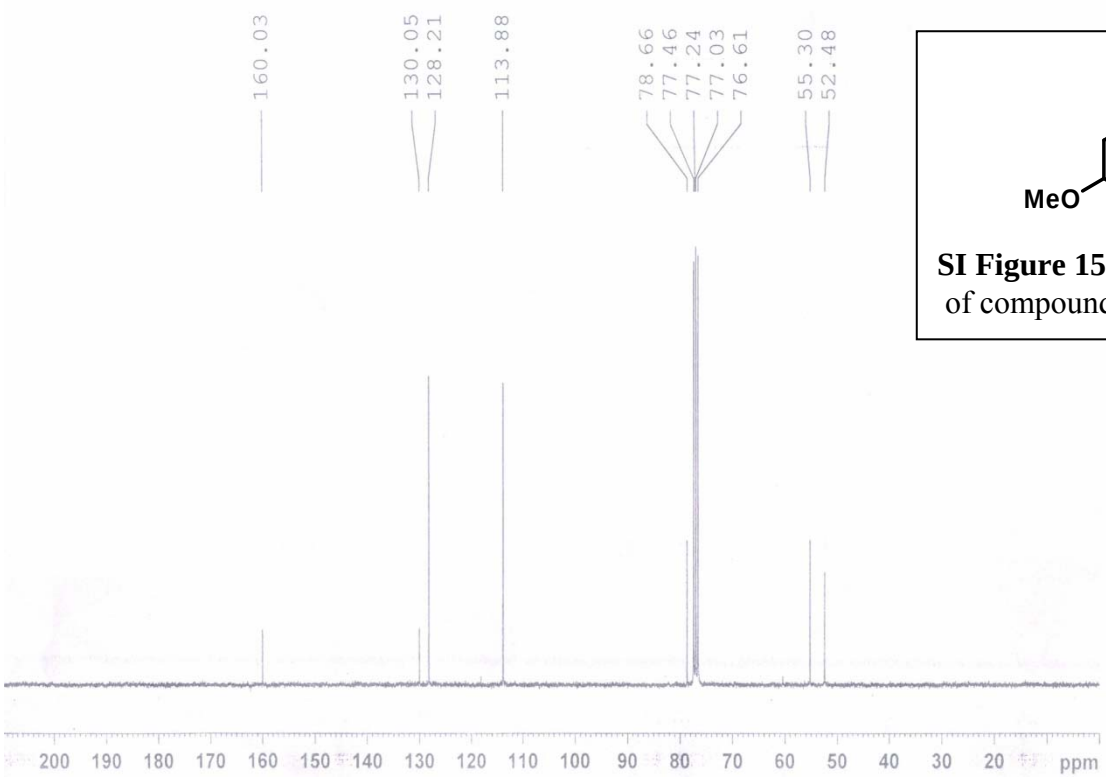


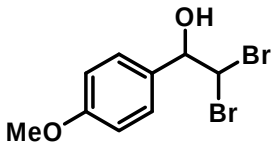
SI Figure 13. ^{13}C NMR spectrum of compound **2f**.



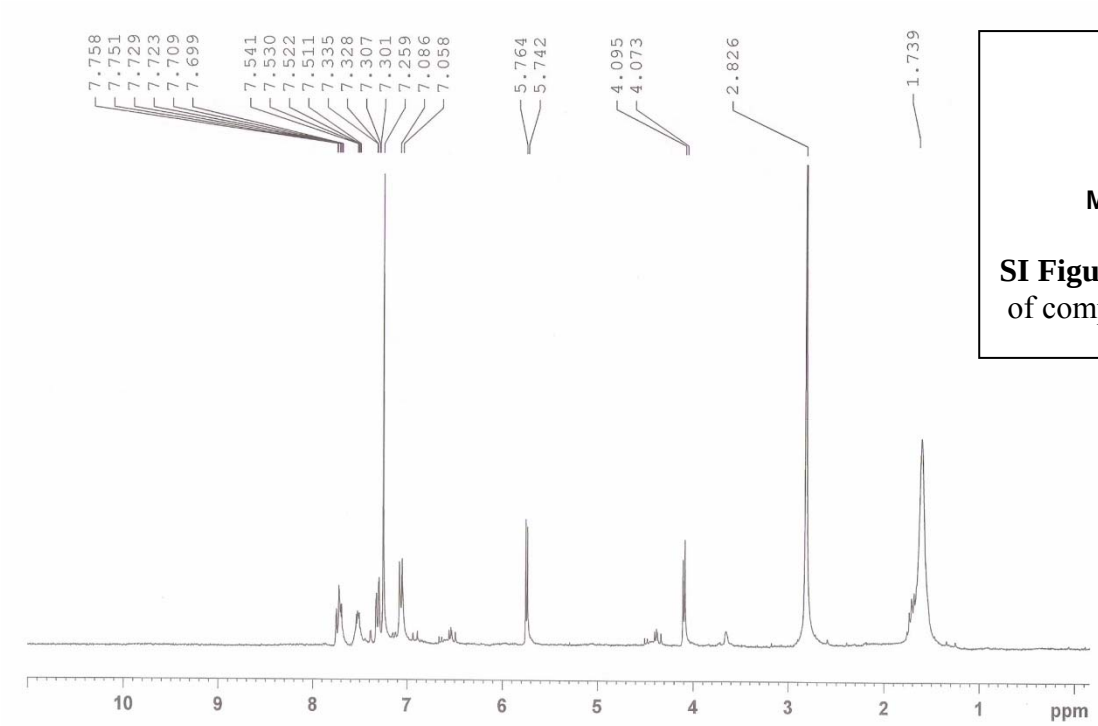


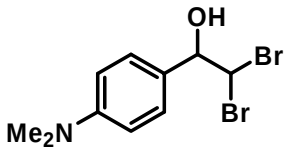
SI Figure 14. ^{1}H NMR spectrum of compound **2g**.



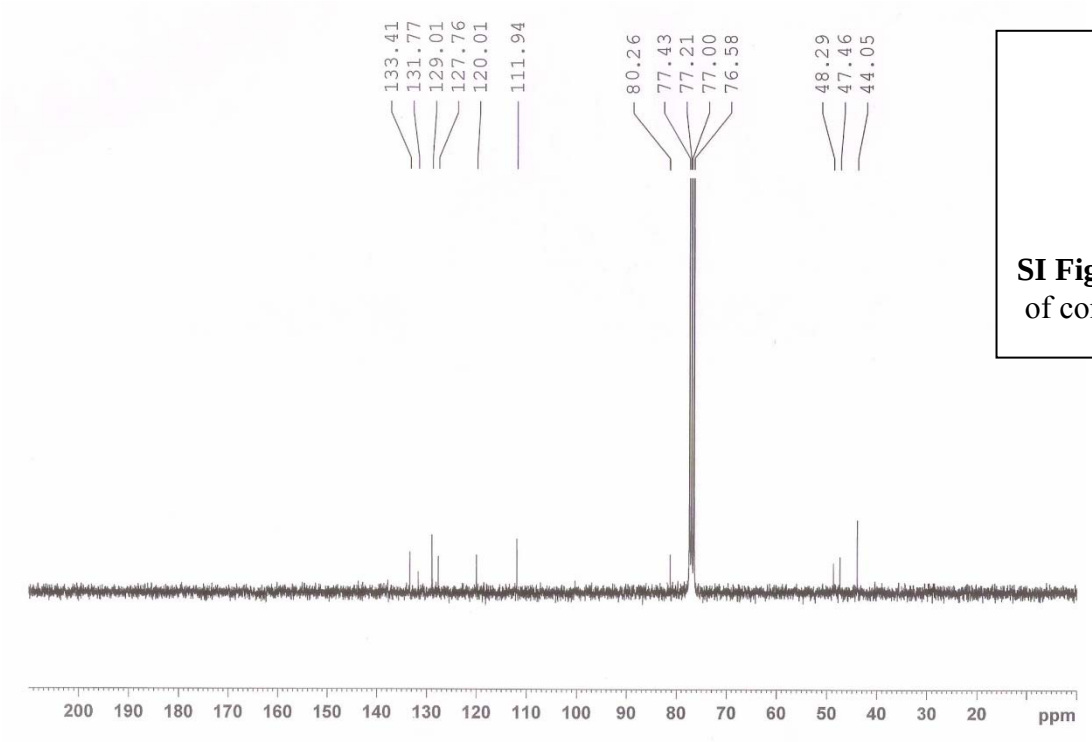


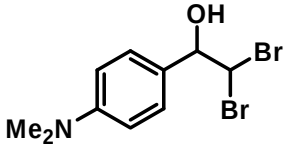
SI Figure 15. ^{13}C NMR spectrum of compound **2g**.



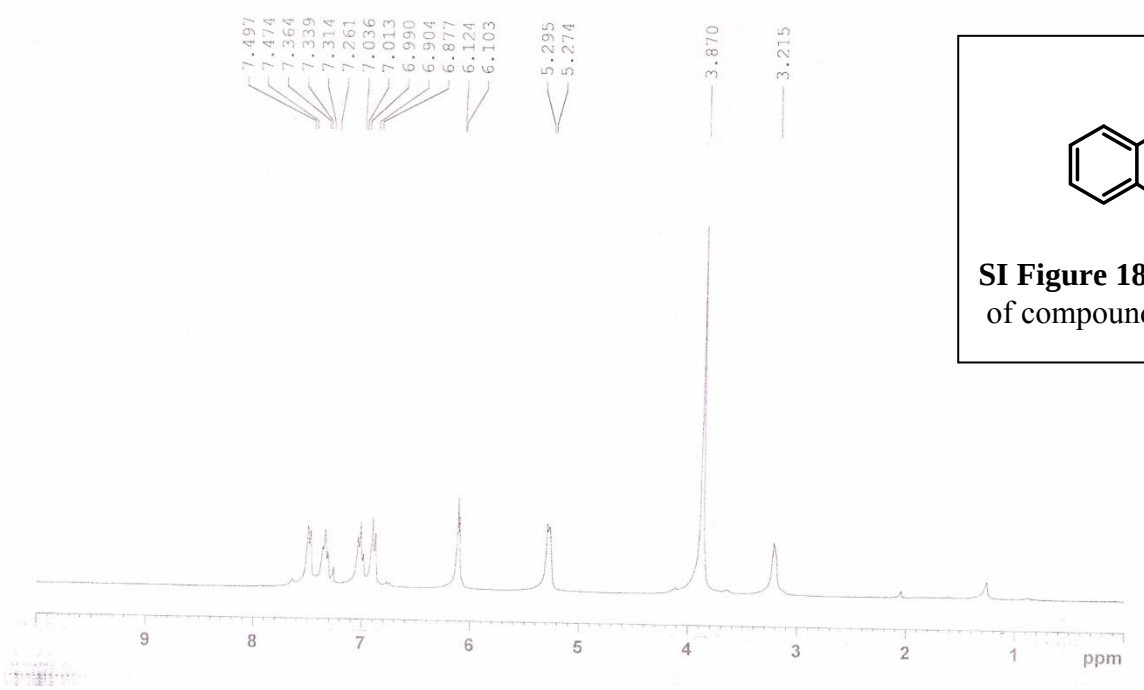


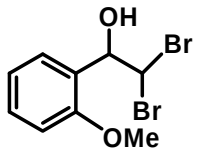
SI Figure 16. ^{1}H NMR spectrum of compound **2h**.



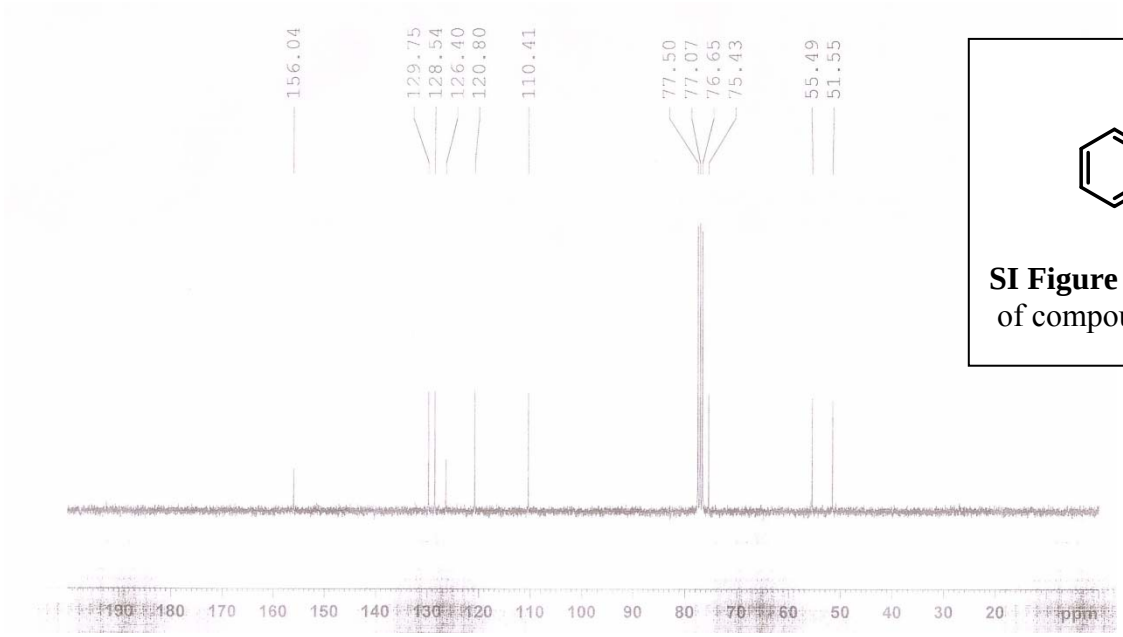


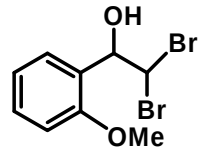
SI Figure 17. ^{13}C NMR spectrum of compound **2h**.



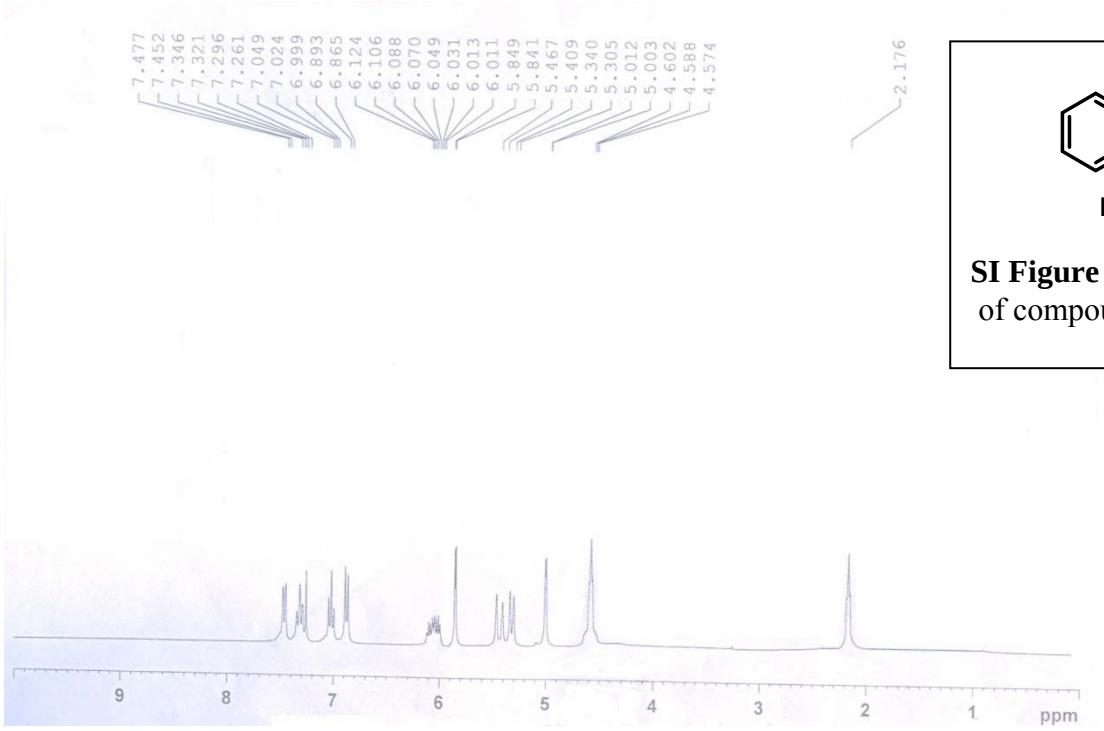


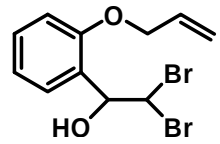
SI Figure 18. ^{1}H NMR spectrum of compound **2i**.



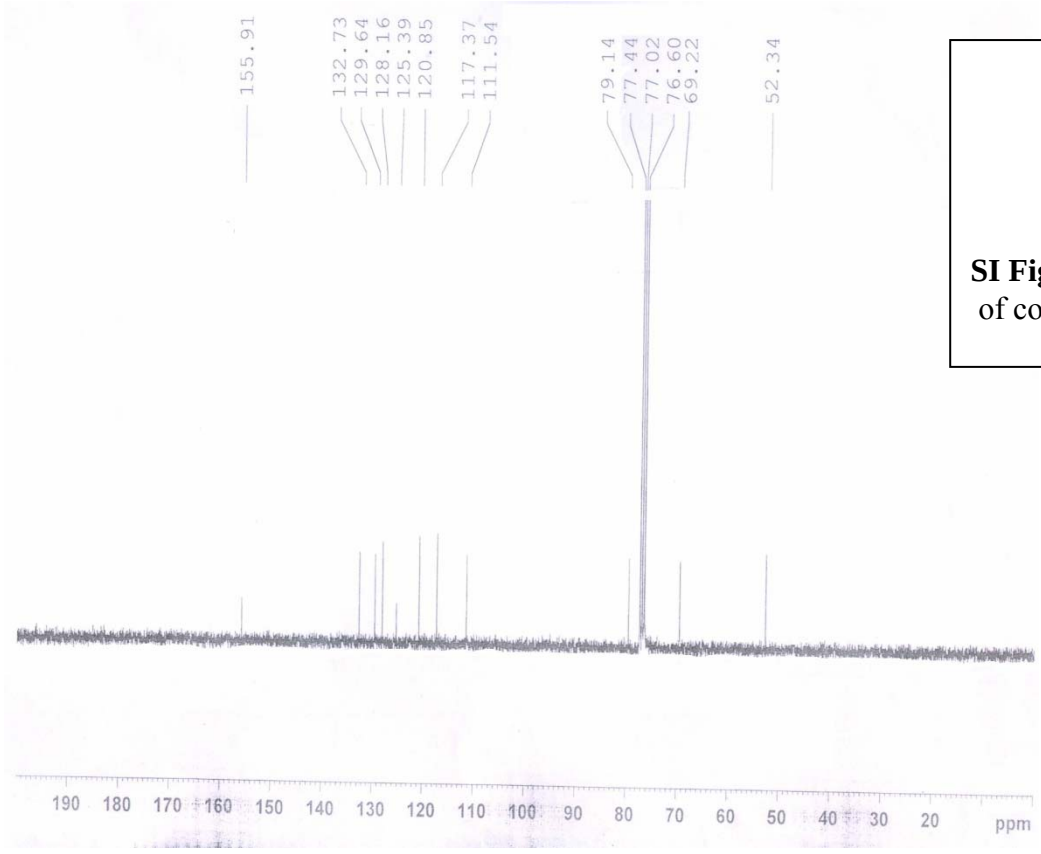


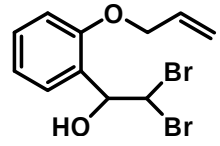
SI Figure 19. ^{13}C NMR spectrum of compound **2i**.



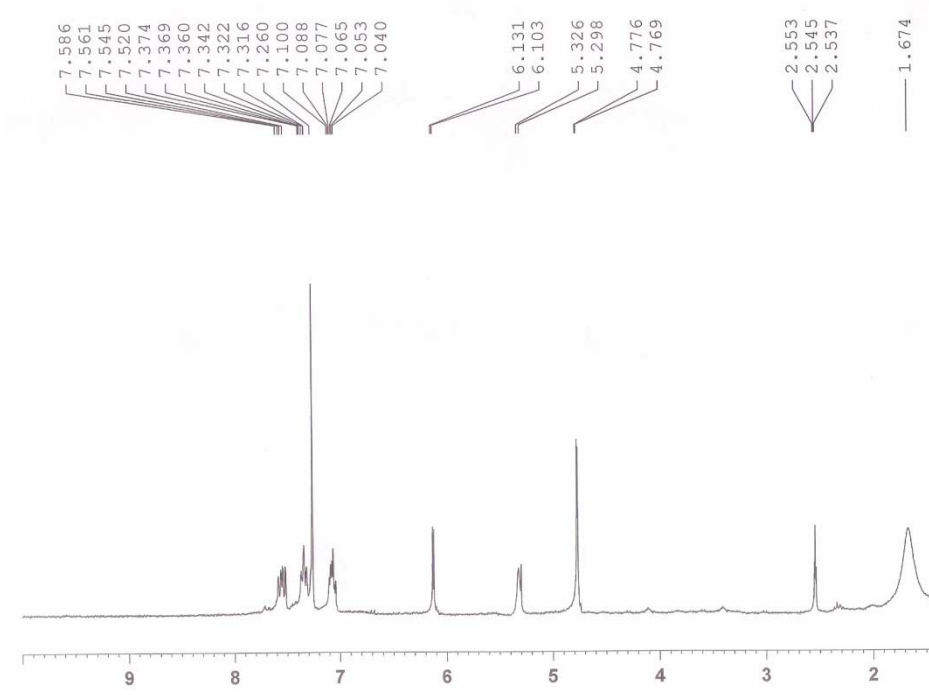


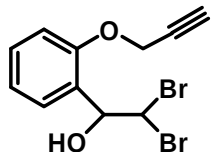
SI Figure 20. ^{1}H NMR spectrum of compound **2j**.



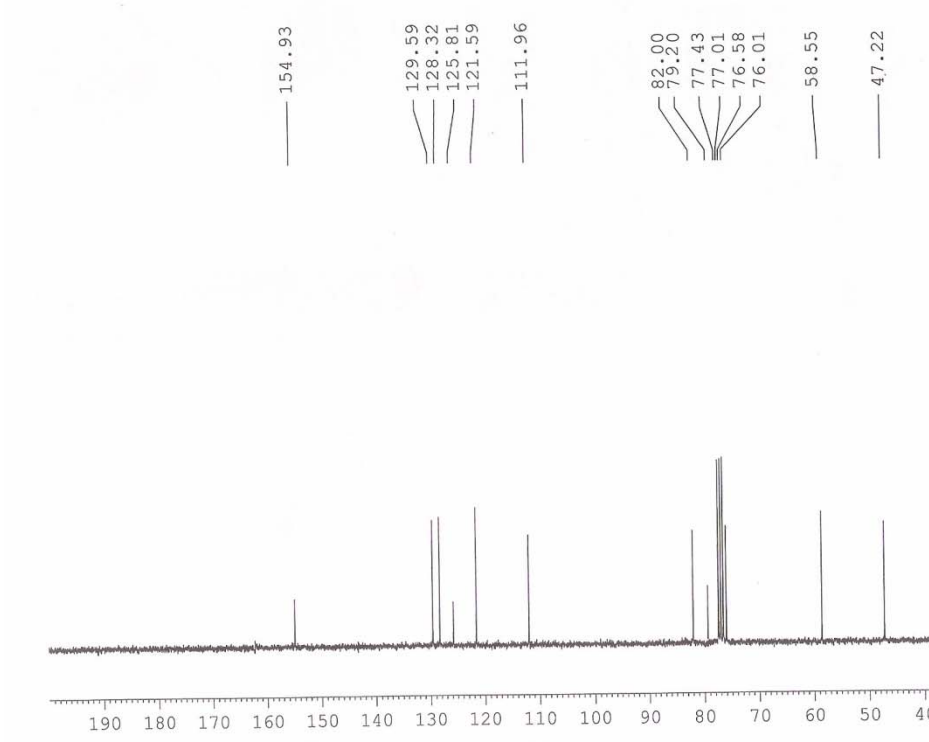


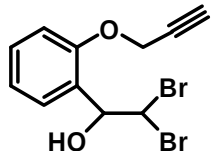
SI Figure 21. ^{13}C NMR spectrum of compound **2j**.



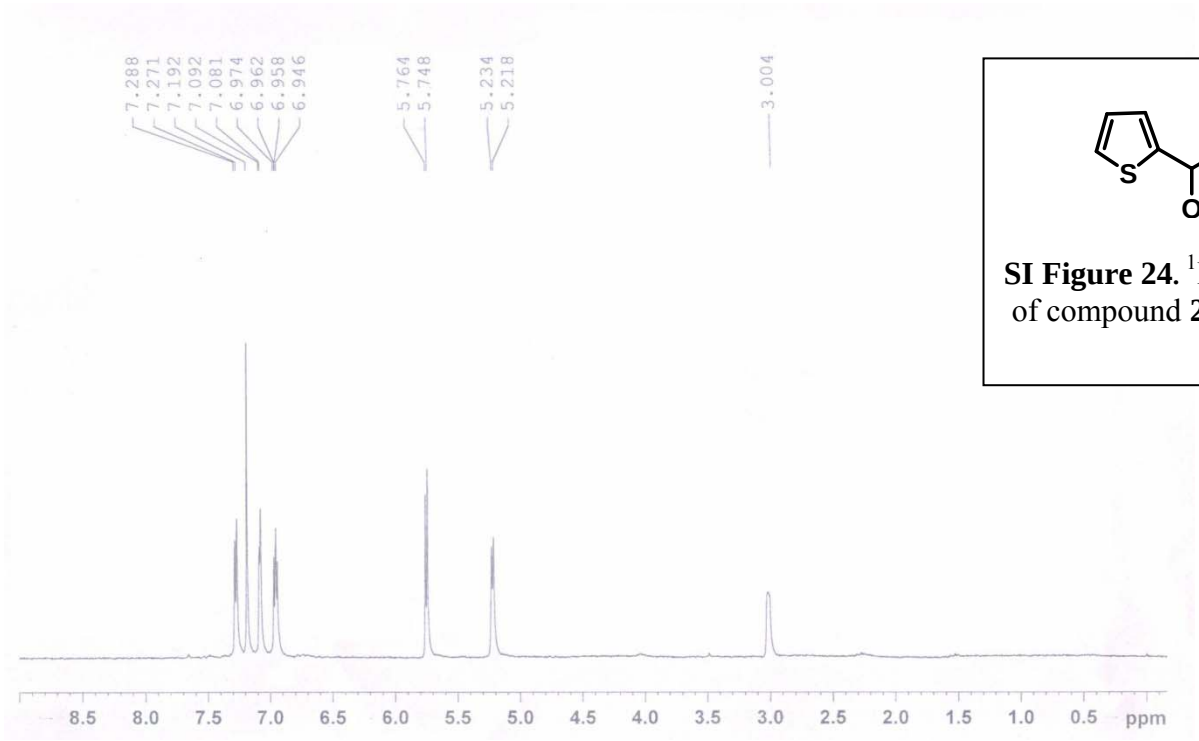


SI Figure 22. ^{1}H NMR spectrum of compound **2k**.

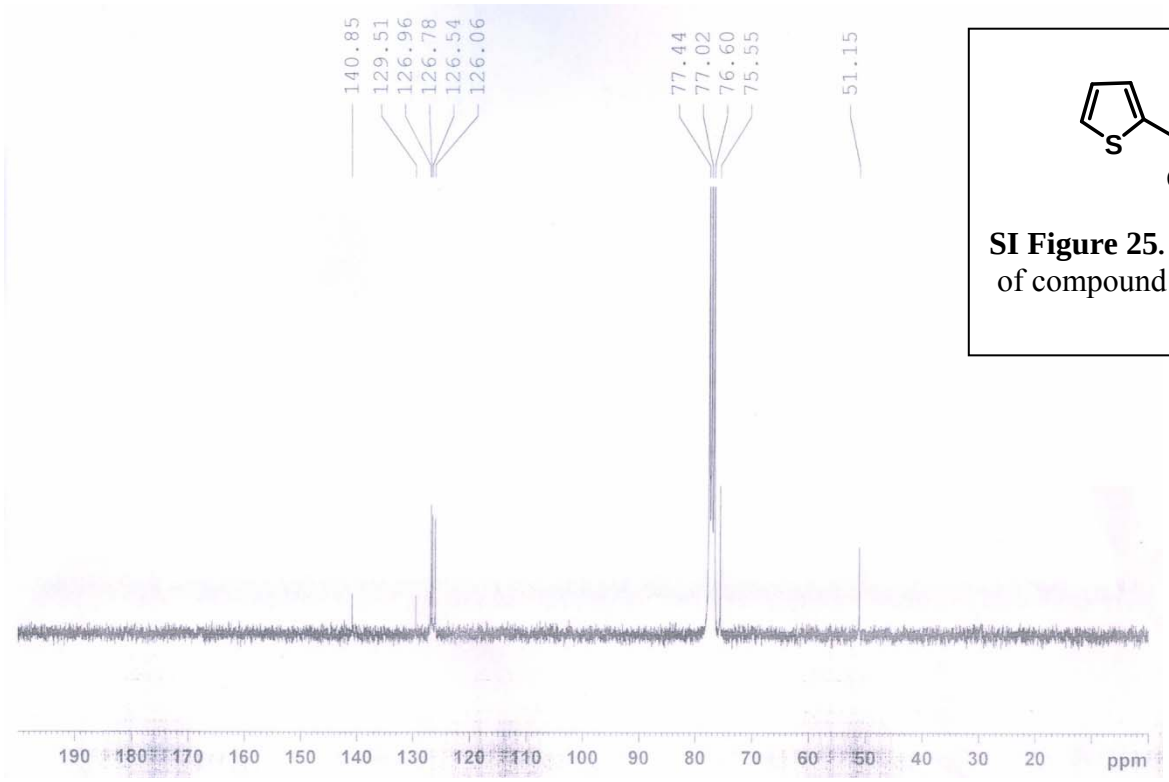


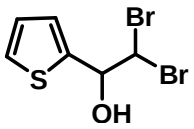


SI Figure 23. ^{13}C NMR spectrum of compound **2k**.

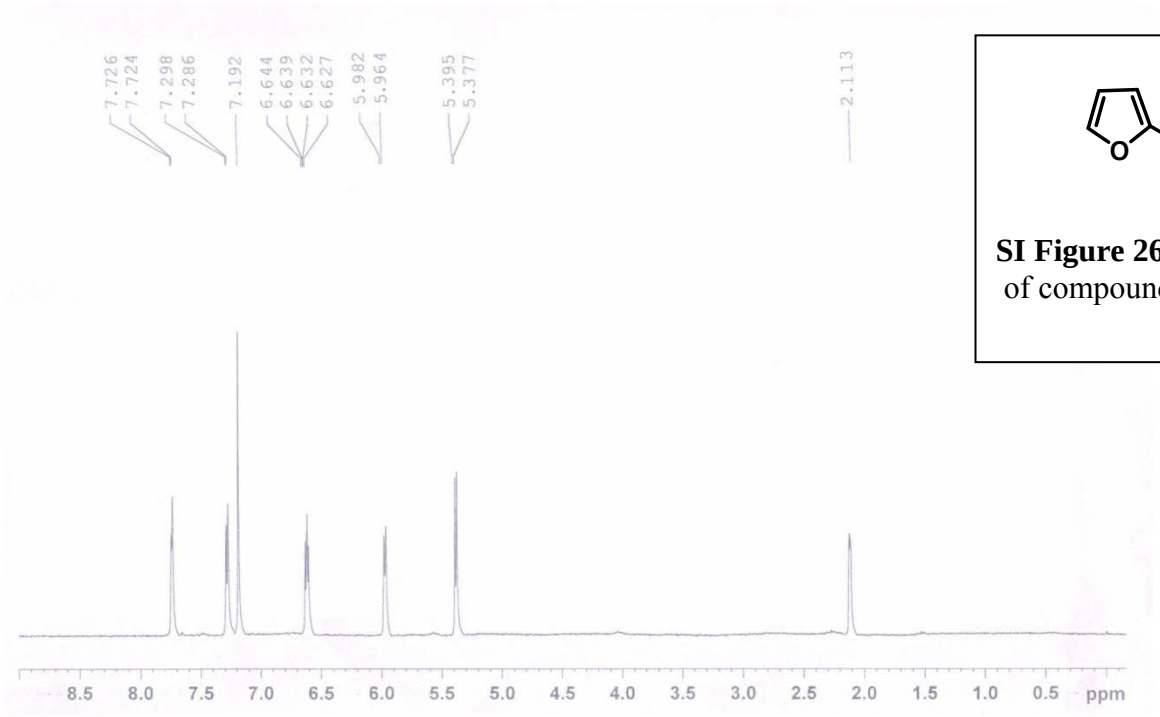


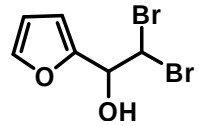
SI Figure 24. ^{1}H NMR spectrum of compound **2l**.



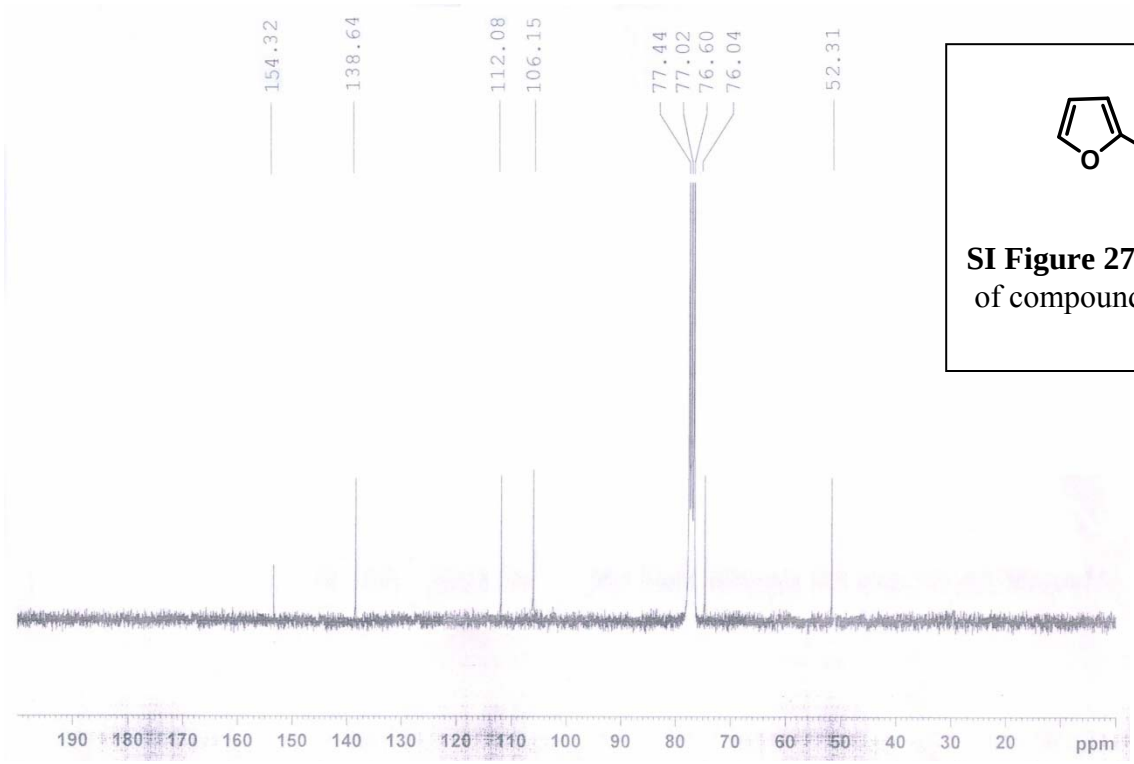


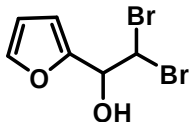
SI Figure 25. ^{13}C NMR spectrum of compound **2l**.



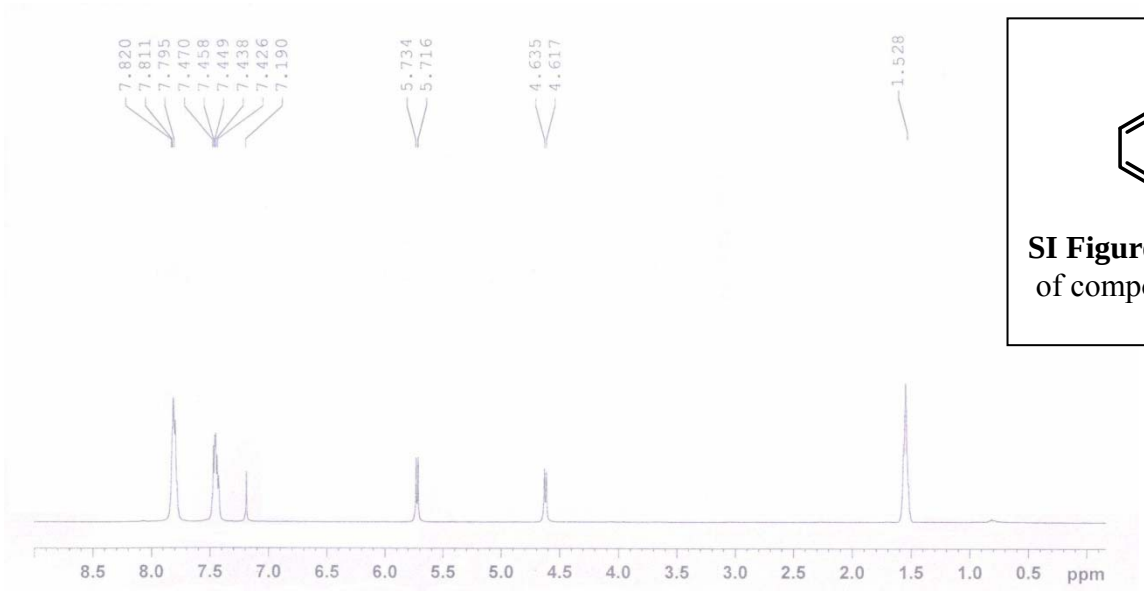


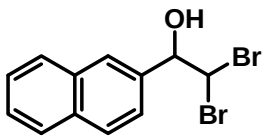
SI Figure 26. ^{1}H NMR spectrum of compound **2m**.



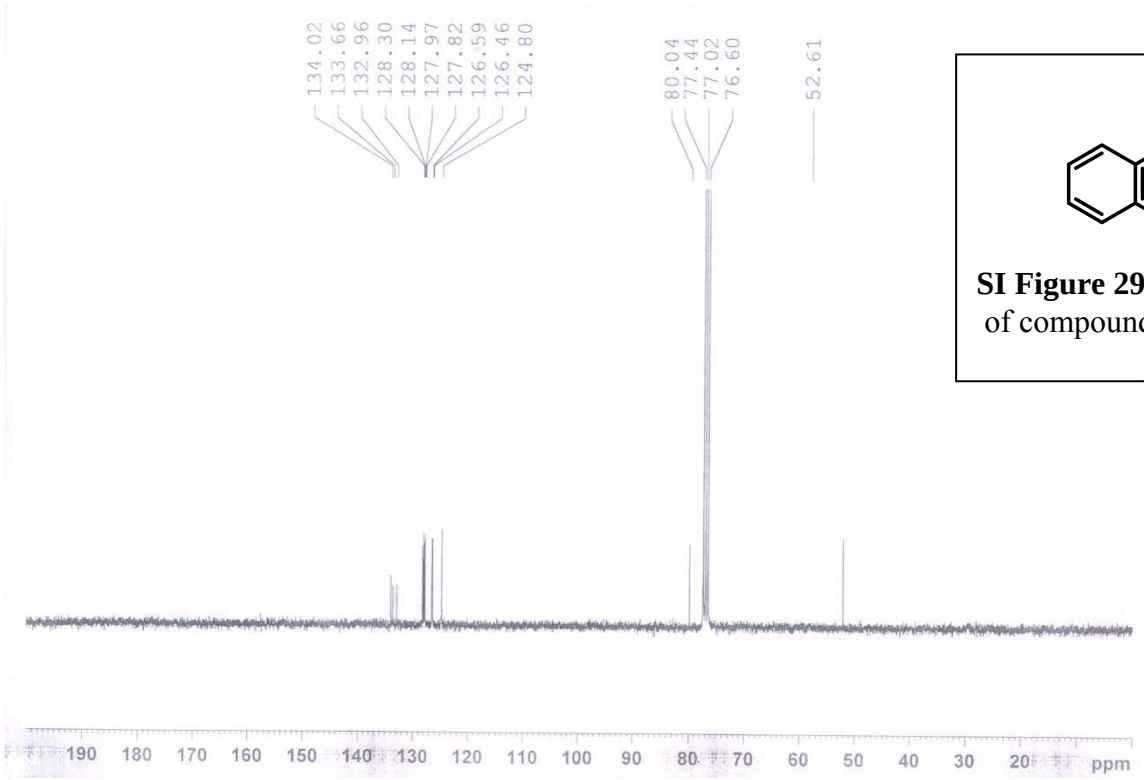


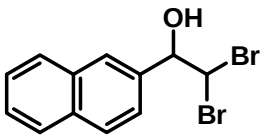
SI Figure 27. ^{13}C NMR spectrum of compound **2m**.



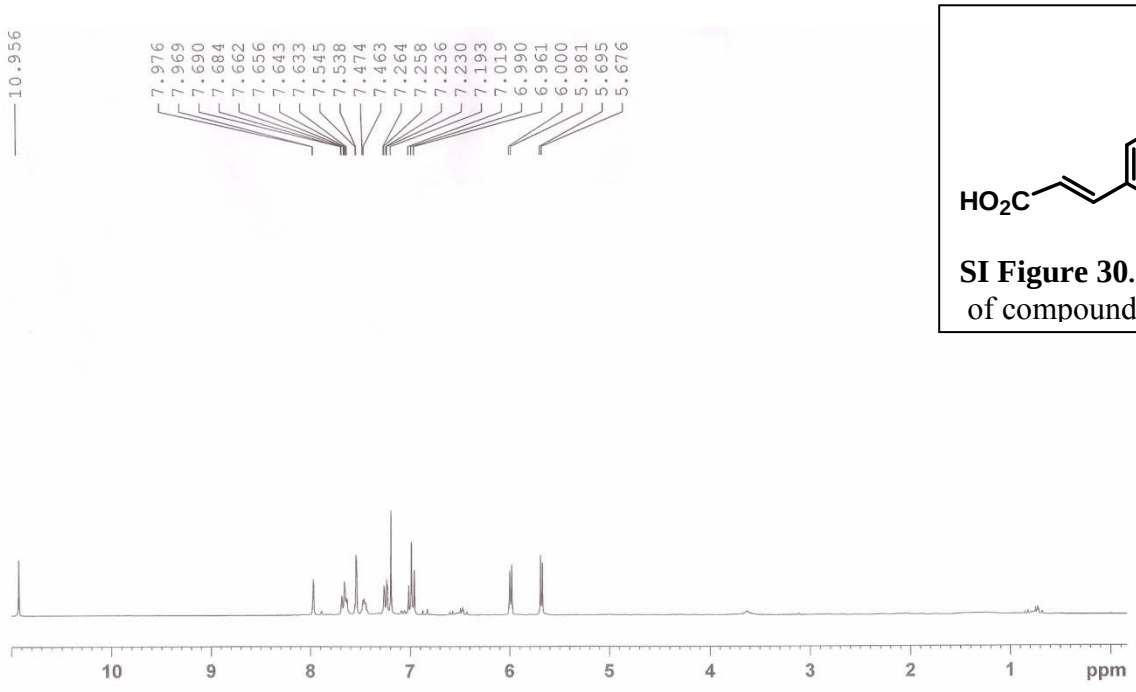


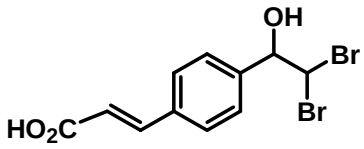
SI Figure 28. ^{1}H NMR spectrum of compound **2n**.



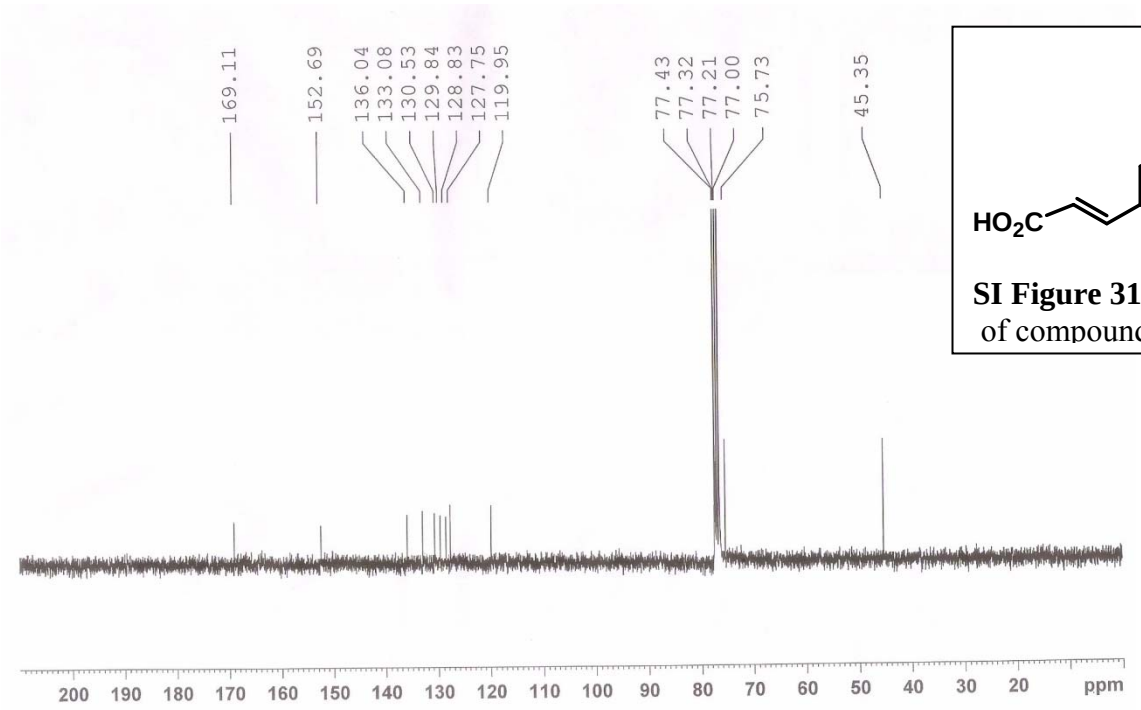


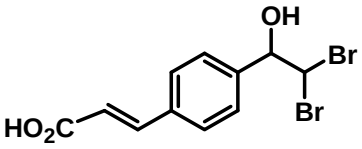
SI Figure 29. ^{13}C NMR spectrum of compound **2n**.



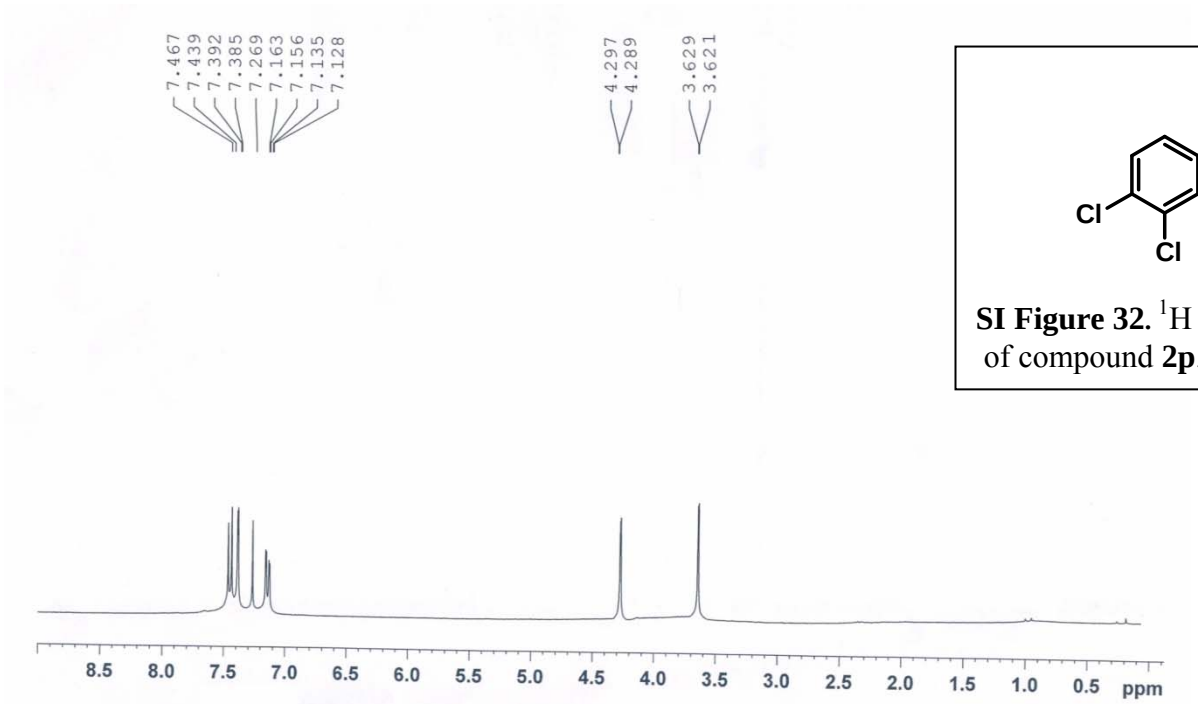


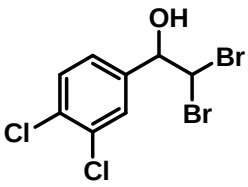
SI Figure 30. ^{1}H NMR spectrum of compound **2o**.



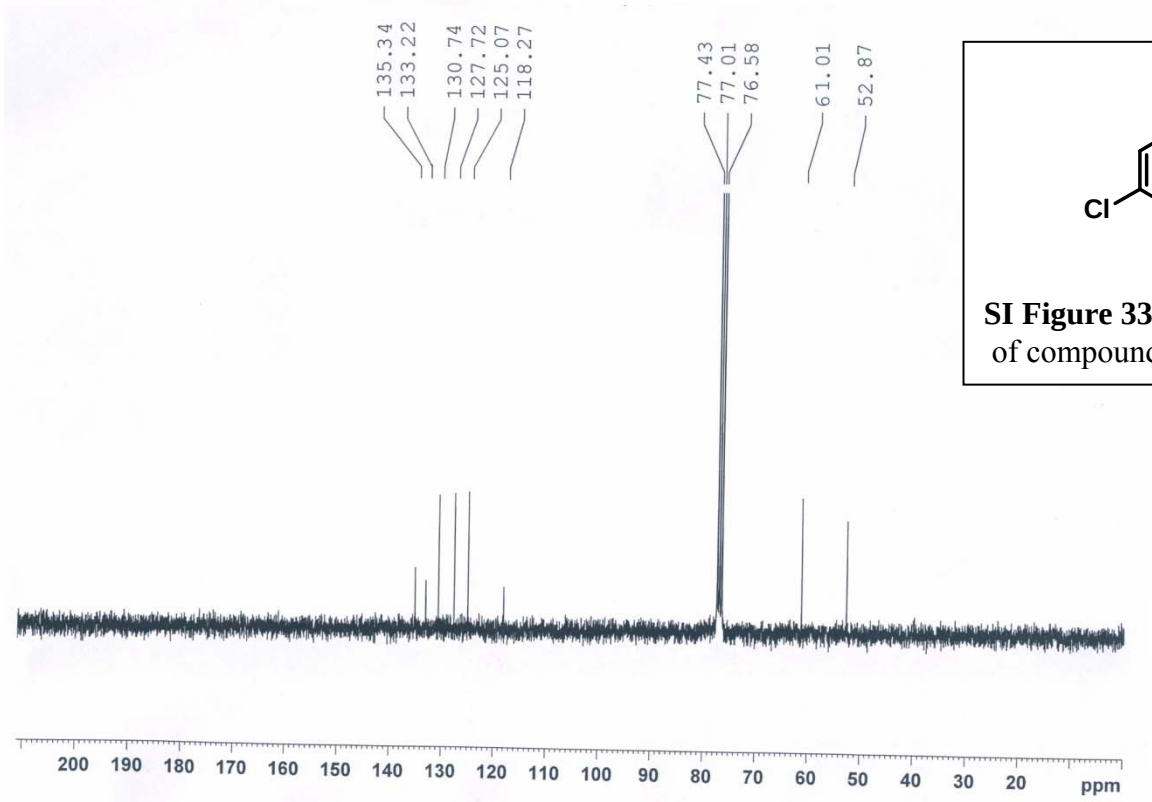


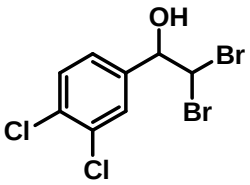
SI Figure 31. ^{13}C NMR spectrum of compound **2o**.



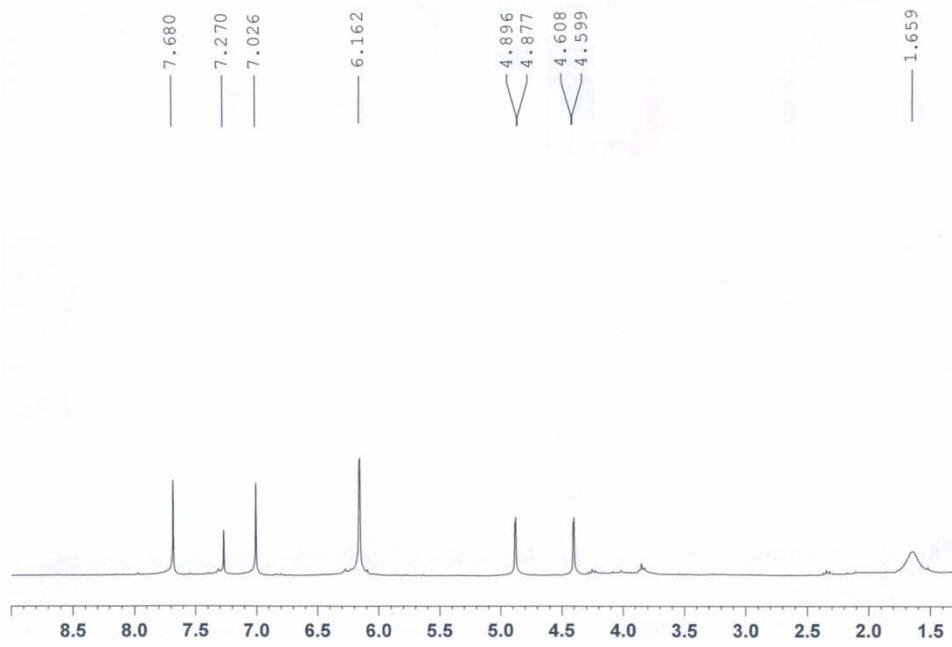


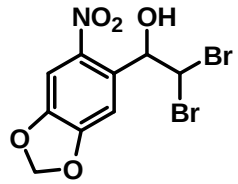
SI Figure 32. ^{1}H NMR spectrum of compound **2p**.



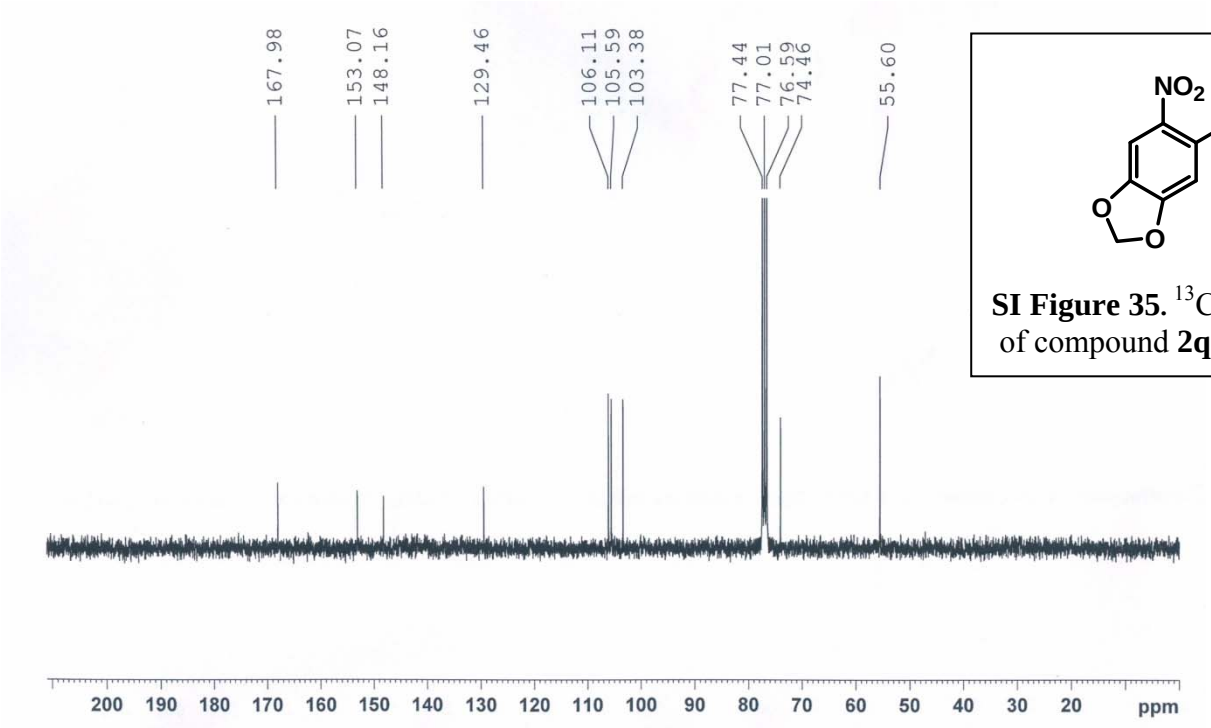


SI Figure 33. ^{13}C NMR spectrum of compound **2p**.

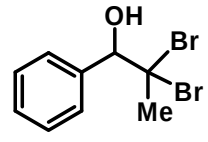




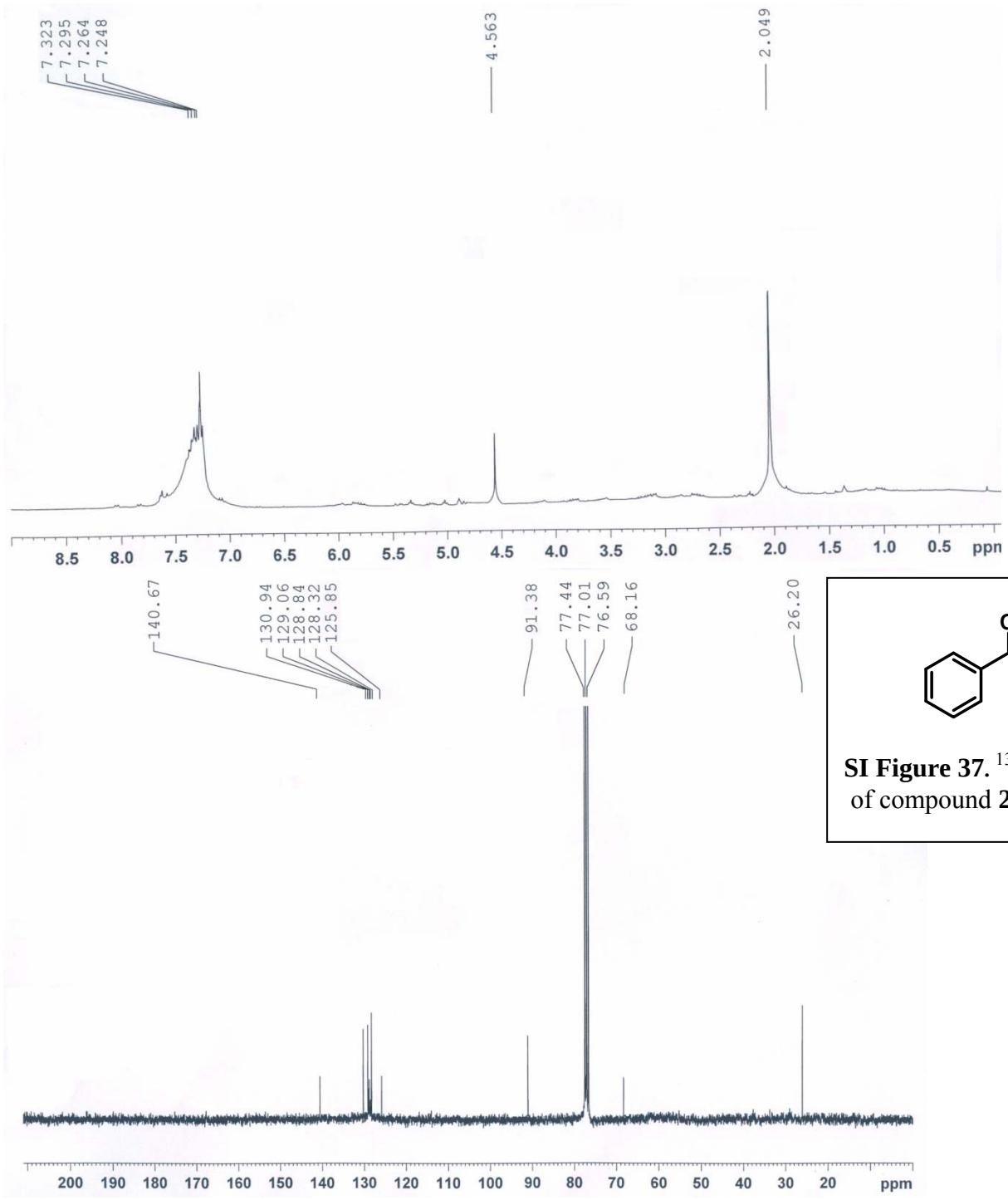
SI Figure 34. ^{1}H NMR spectrum of compound **2q**.



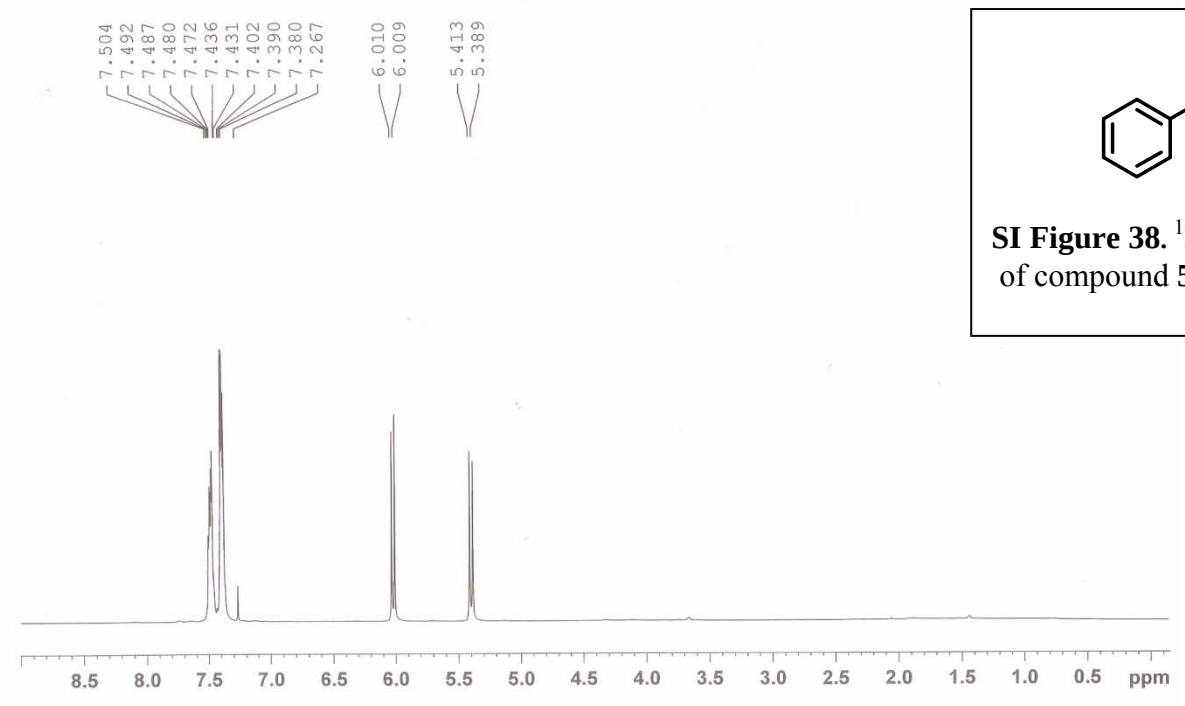
SI Figure 35. ^{13}C NMR spectrum of compound **2q**.

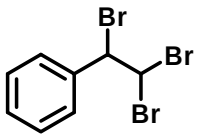


SI Figure 36. ^{1}H NMR spectrum of compound **2r**.

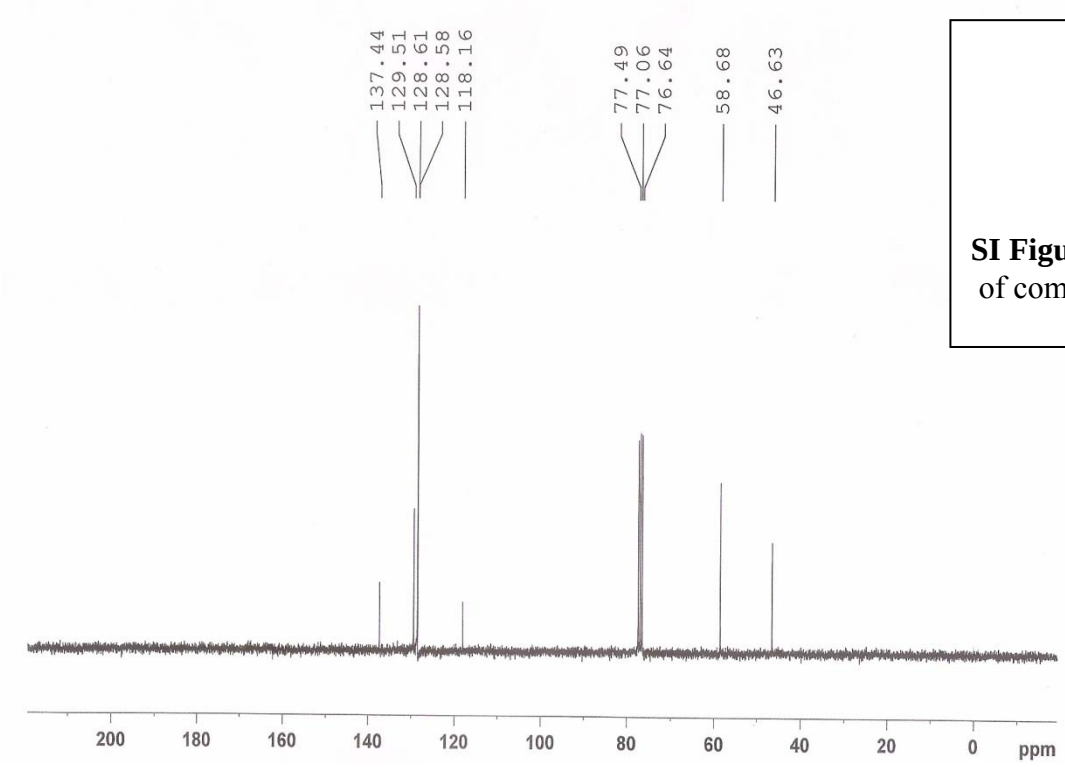


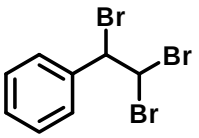
SI Figure 37. ^{13}C NMR spectrum of compound **2r**.



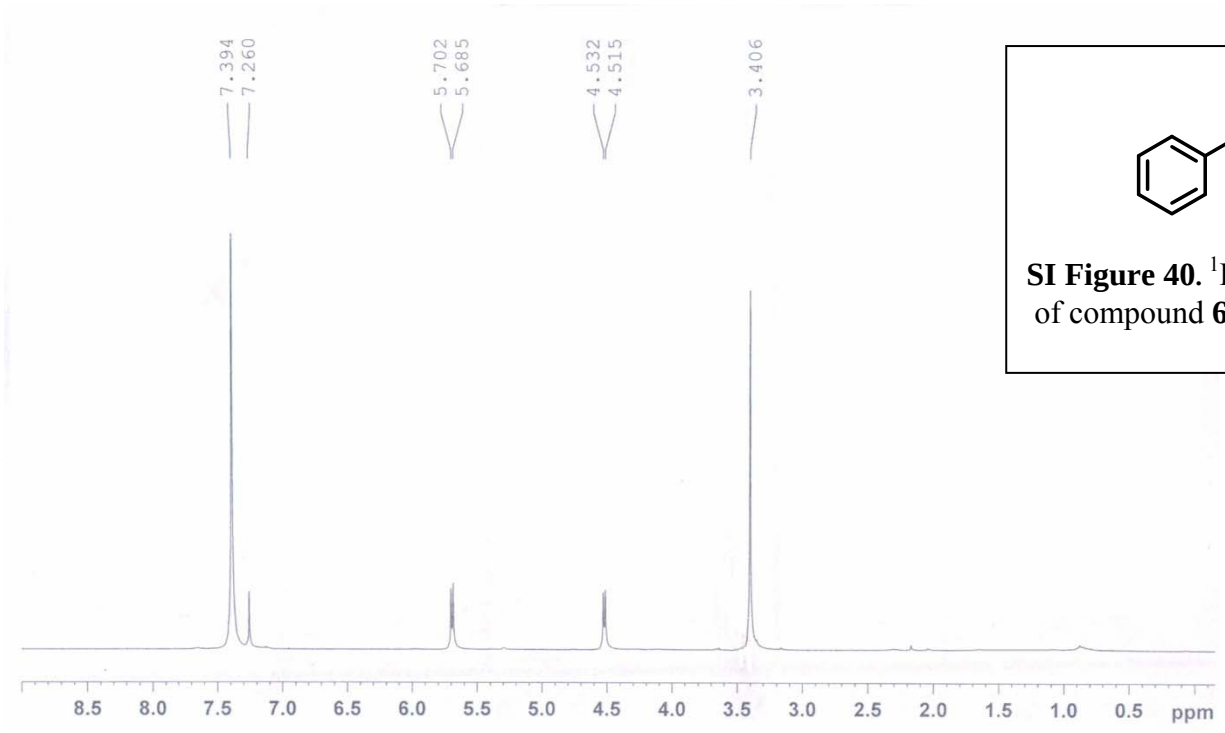


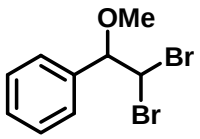
SI Figure 38. ^{1}H NMR spectrum of compound **5a**.



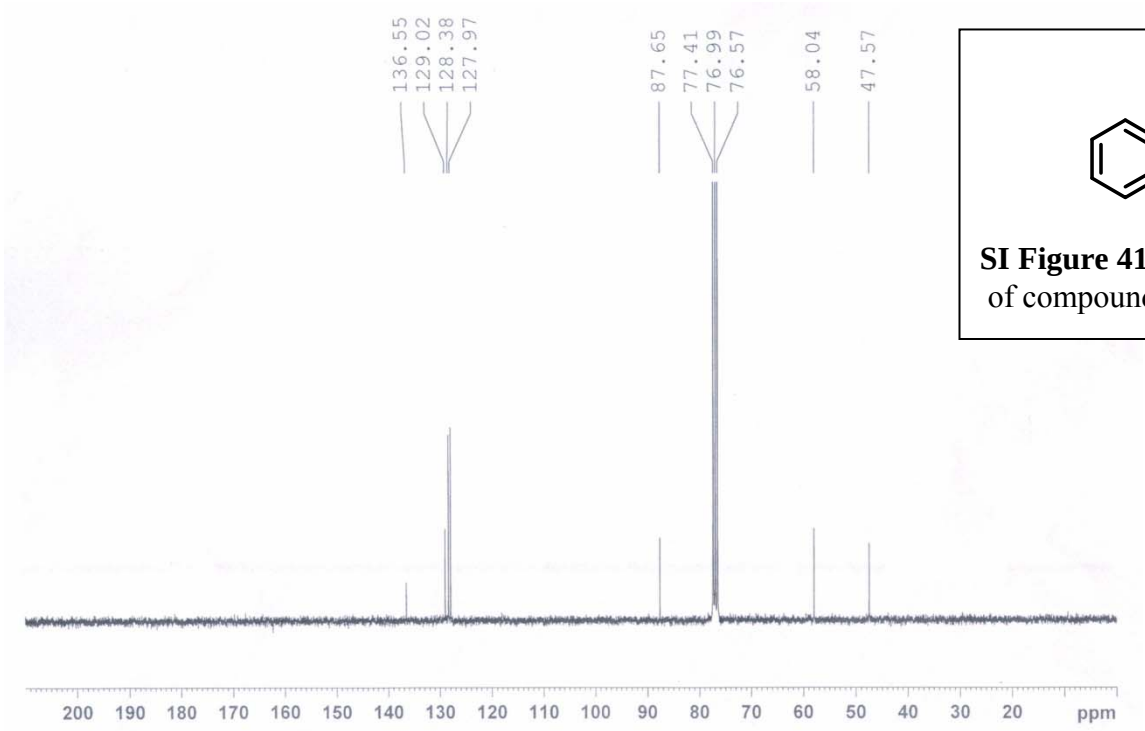


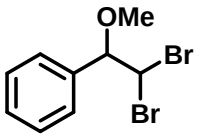
SI Figure 39. ^{13}C NMR spectrum of compound **5a**.



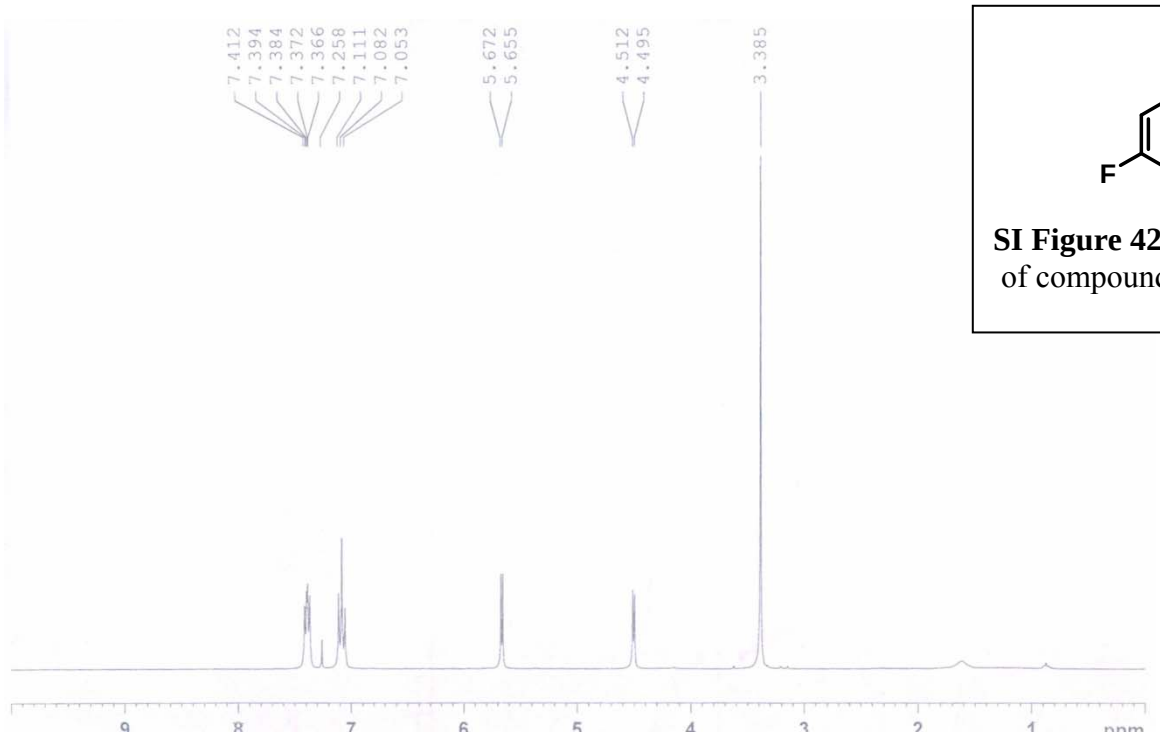


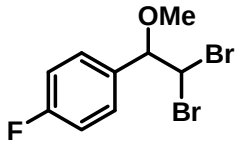
SI Figure 40. ^{1}H NMR spectrum of compound **6a**.



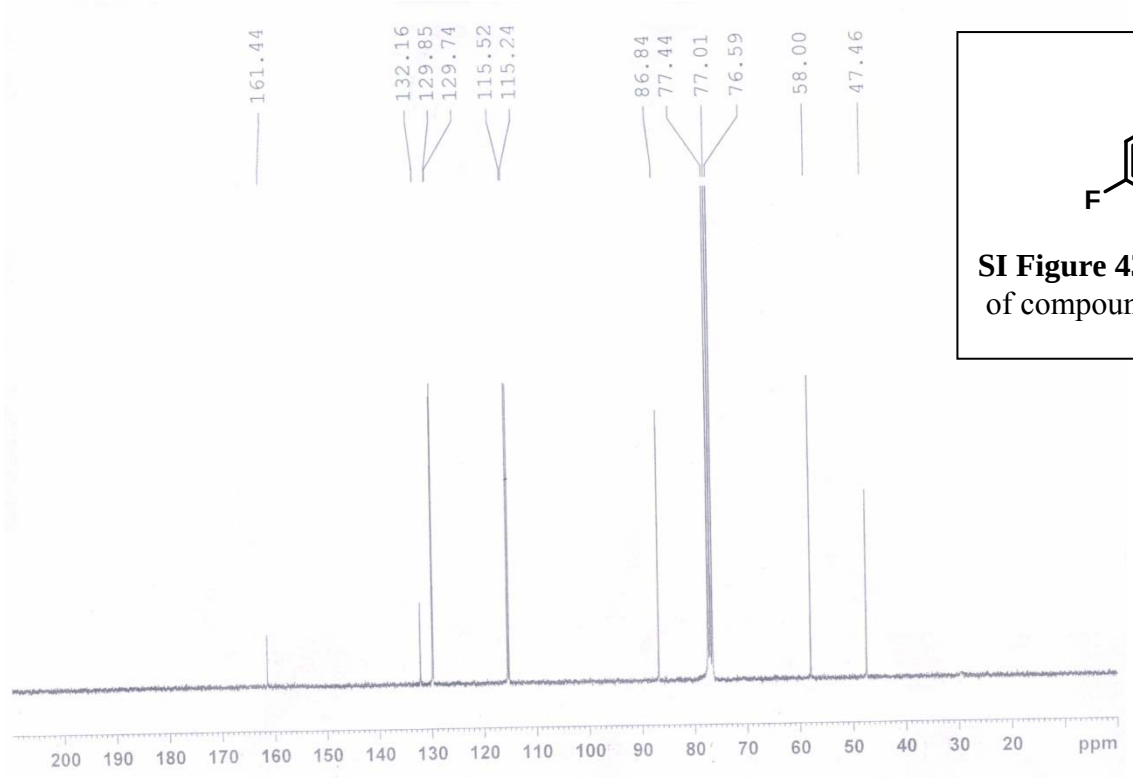


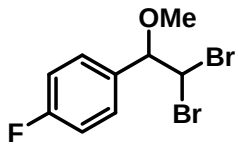
SI Figure 41. ^{13}C NMR spectrum of compound **6a**.



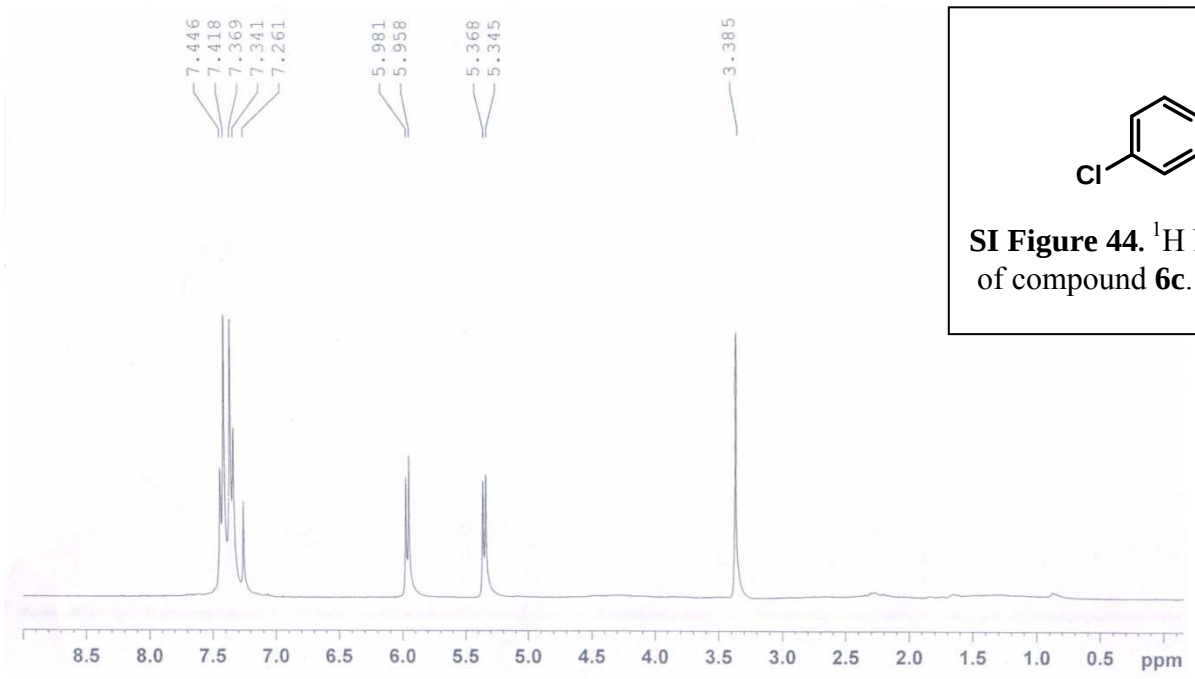


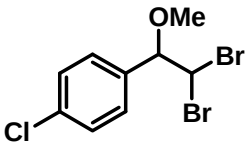
SI Figure 42. ^{1}H NMR spectrum of compound **6b**.



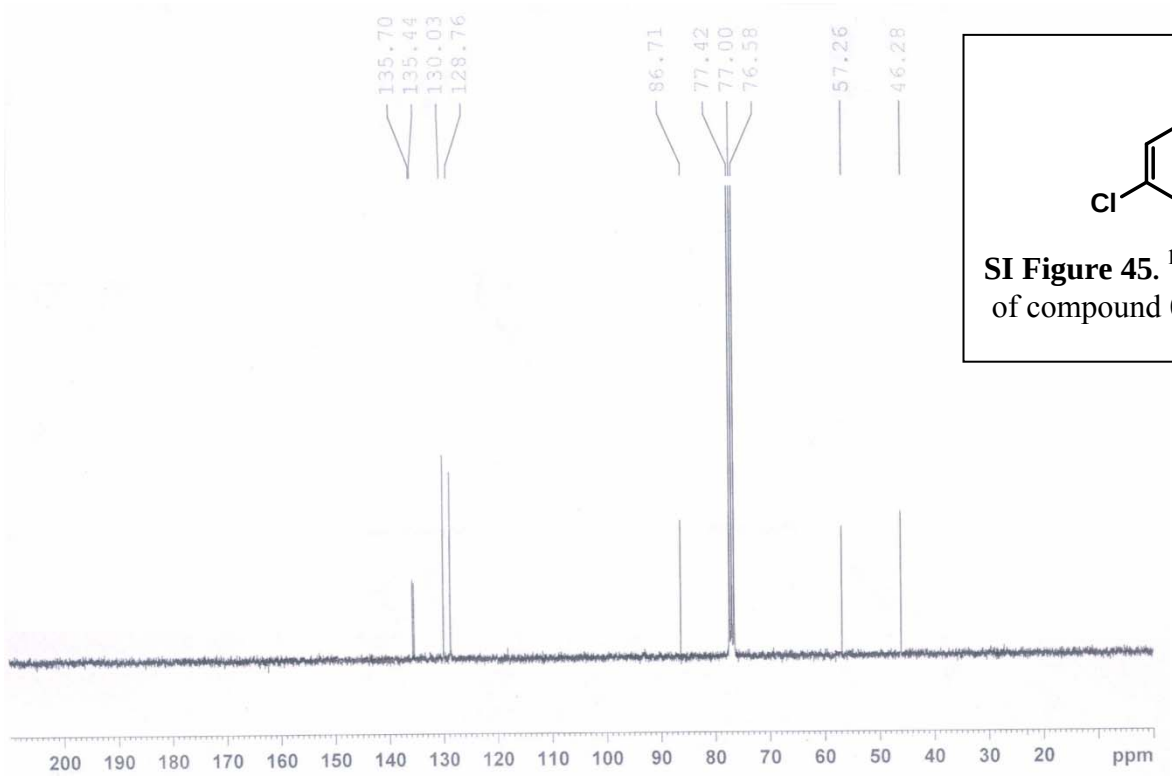


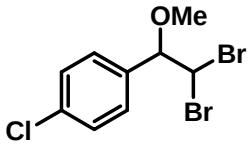
SI Figure 43. ^{13}C NMR spectrum of compound **6b**.



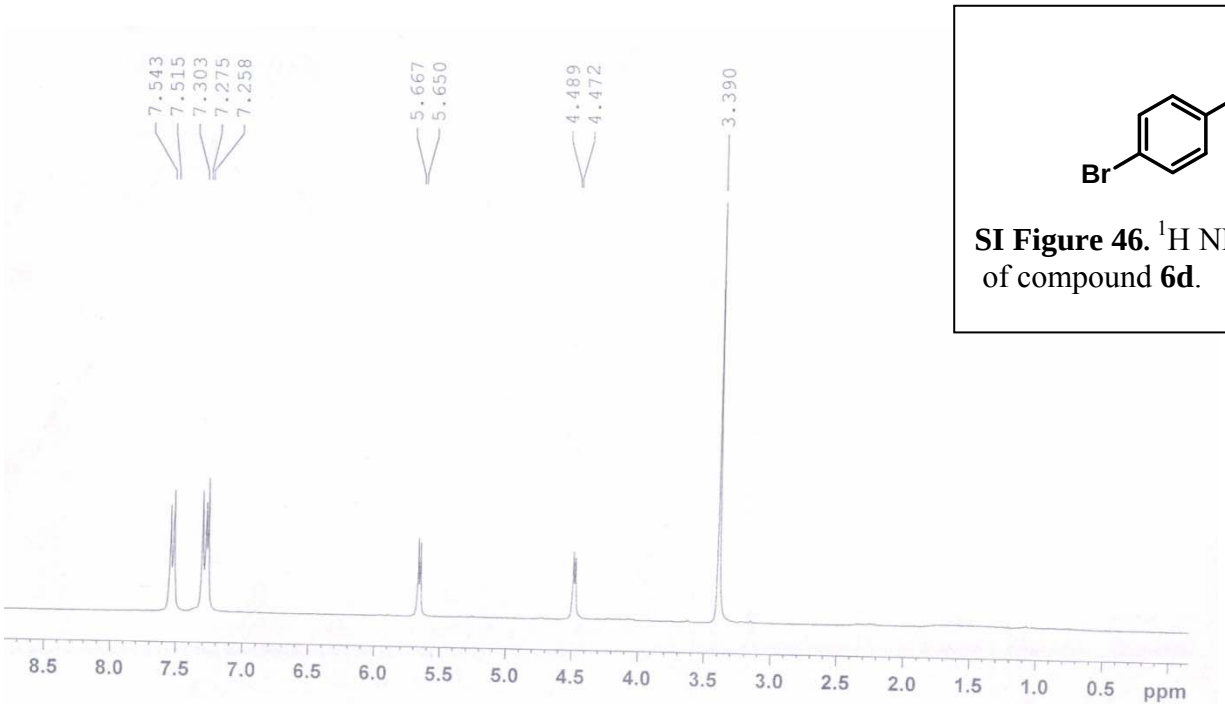


SI Figure 44. ^{1}H NMR spectrum of compound **6c**.

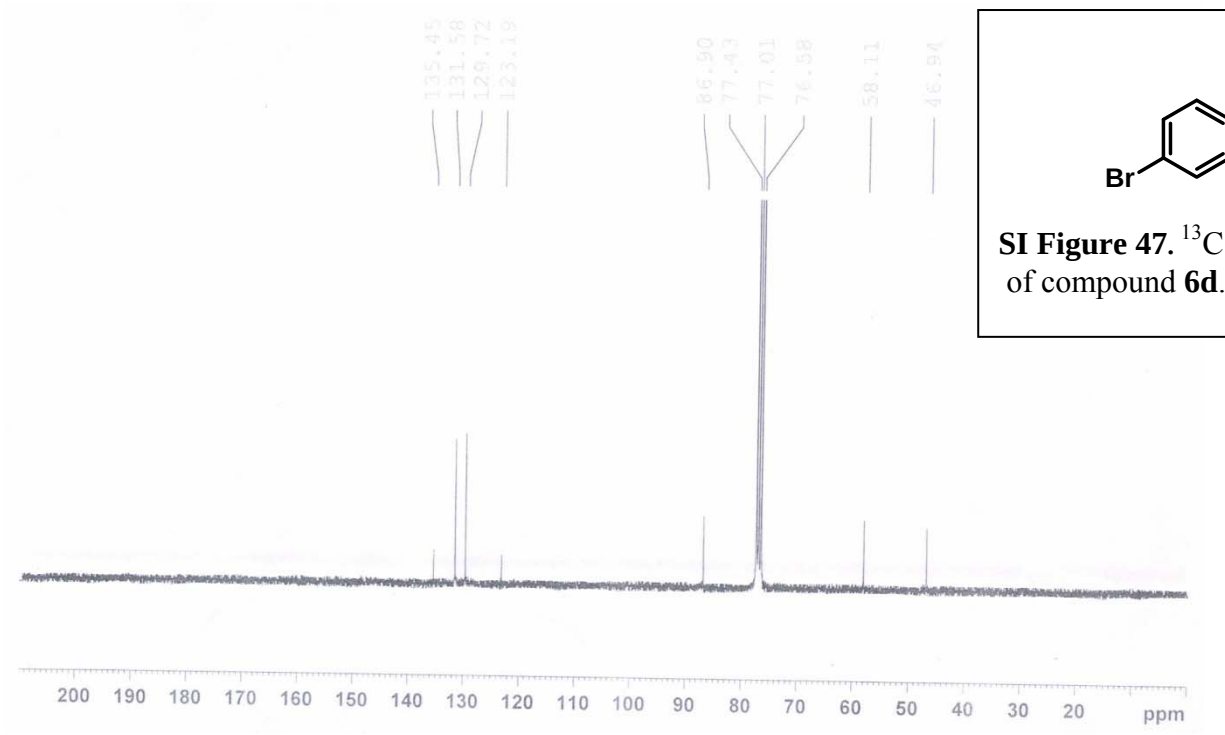


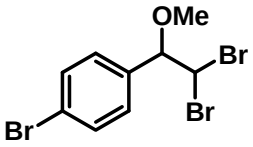


SI Figure 45. ^{13}C NMR spectrum of compound **6c**.

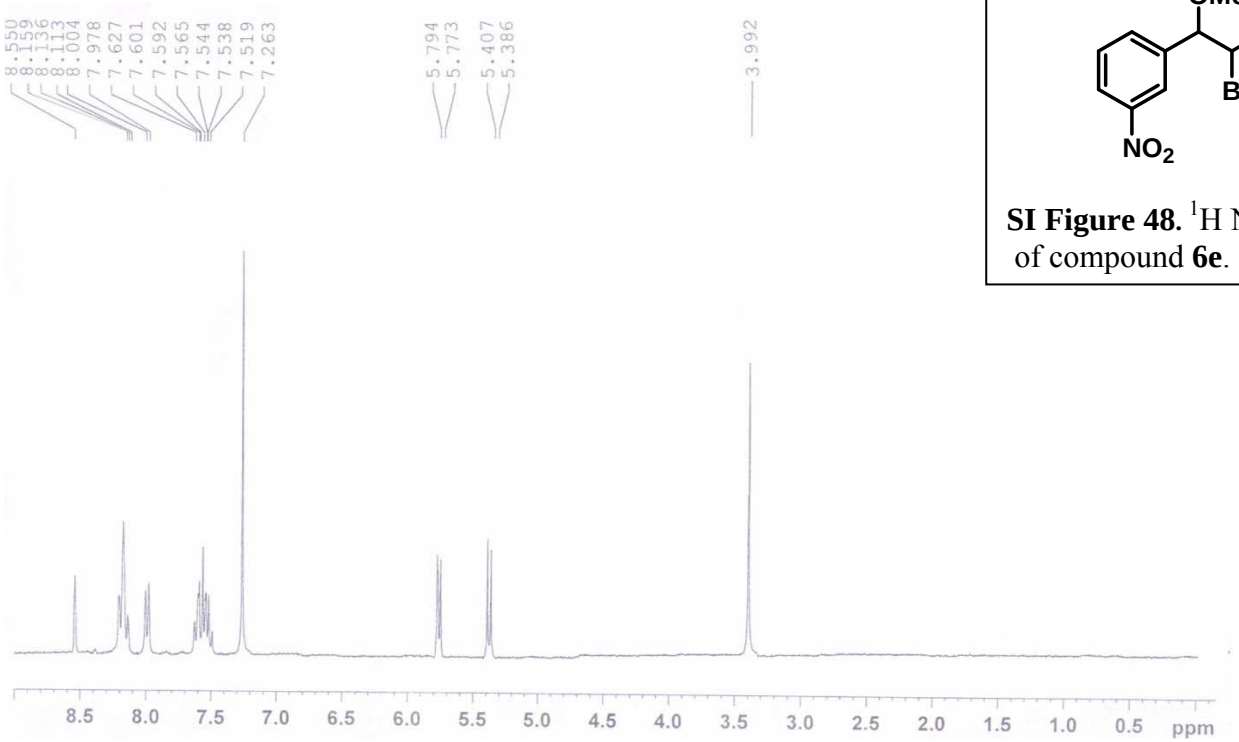


SI Figure 46. ^{1}H NMR spectrum of compound **6d**.

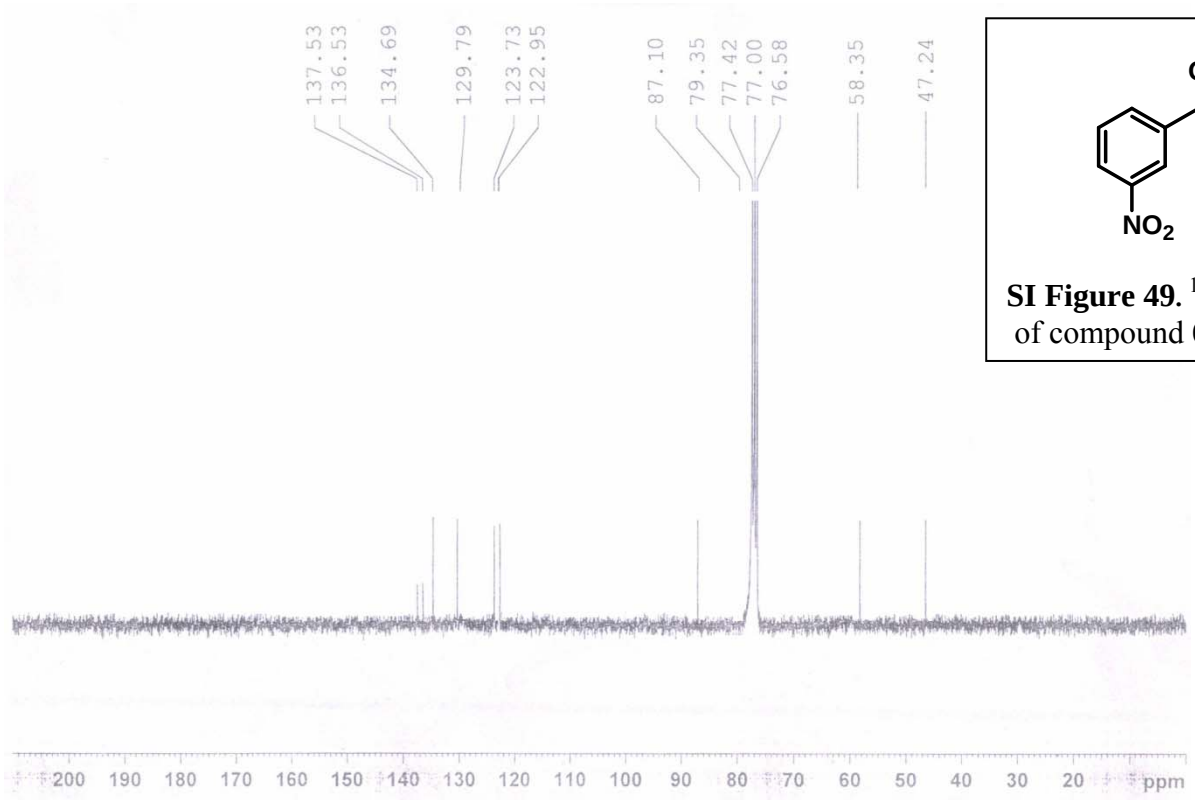




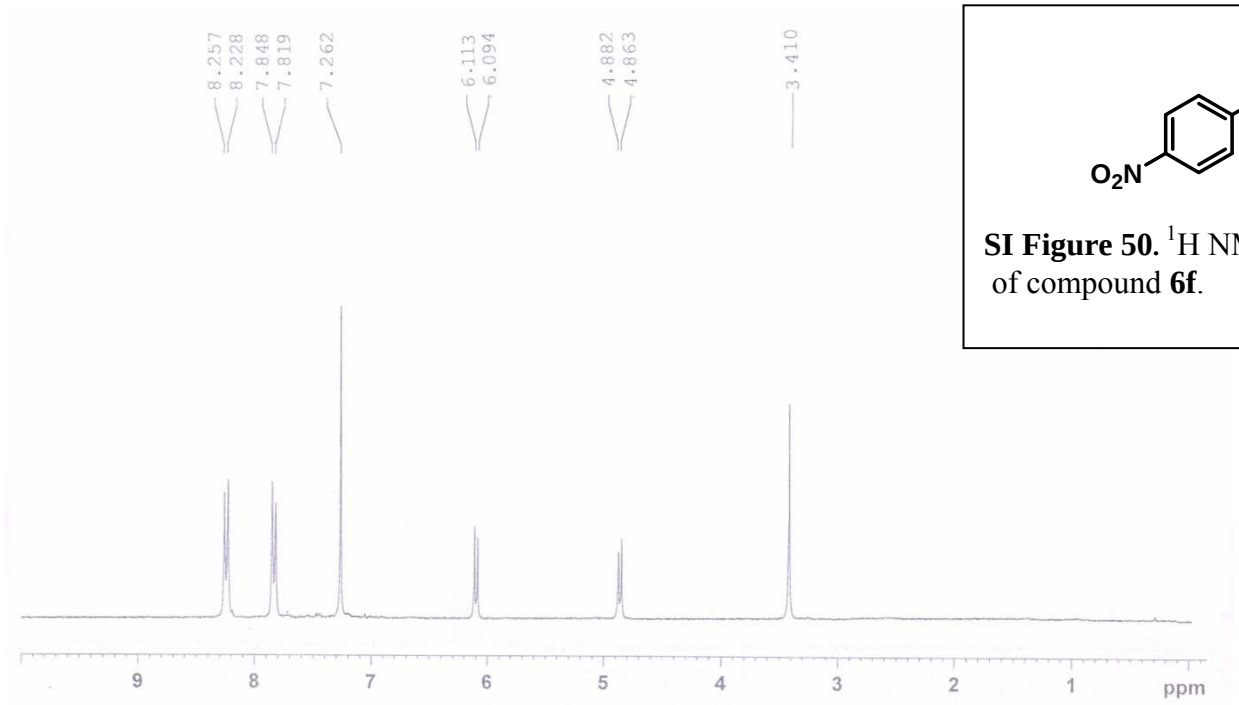
SI Figure 47. ^{13}C NMR spectrum of compound **6d**.



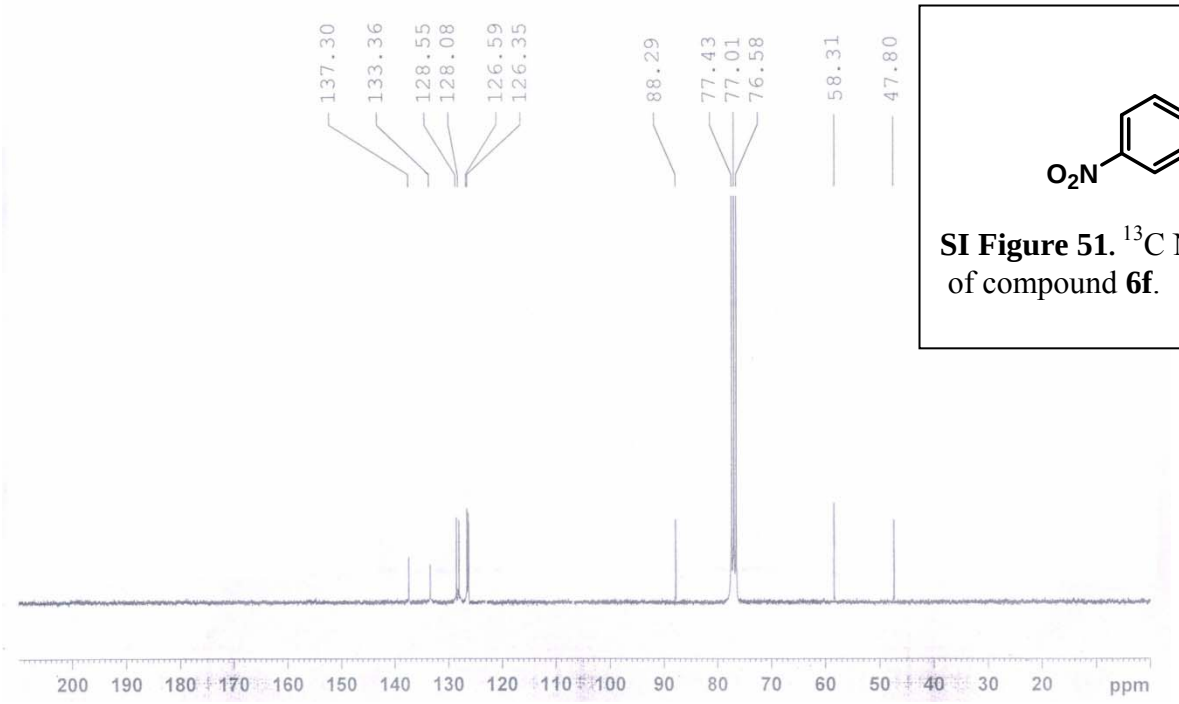
SI Figure 48. ^{1}H NMR spectrum of compound **6e**.



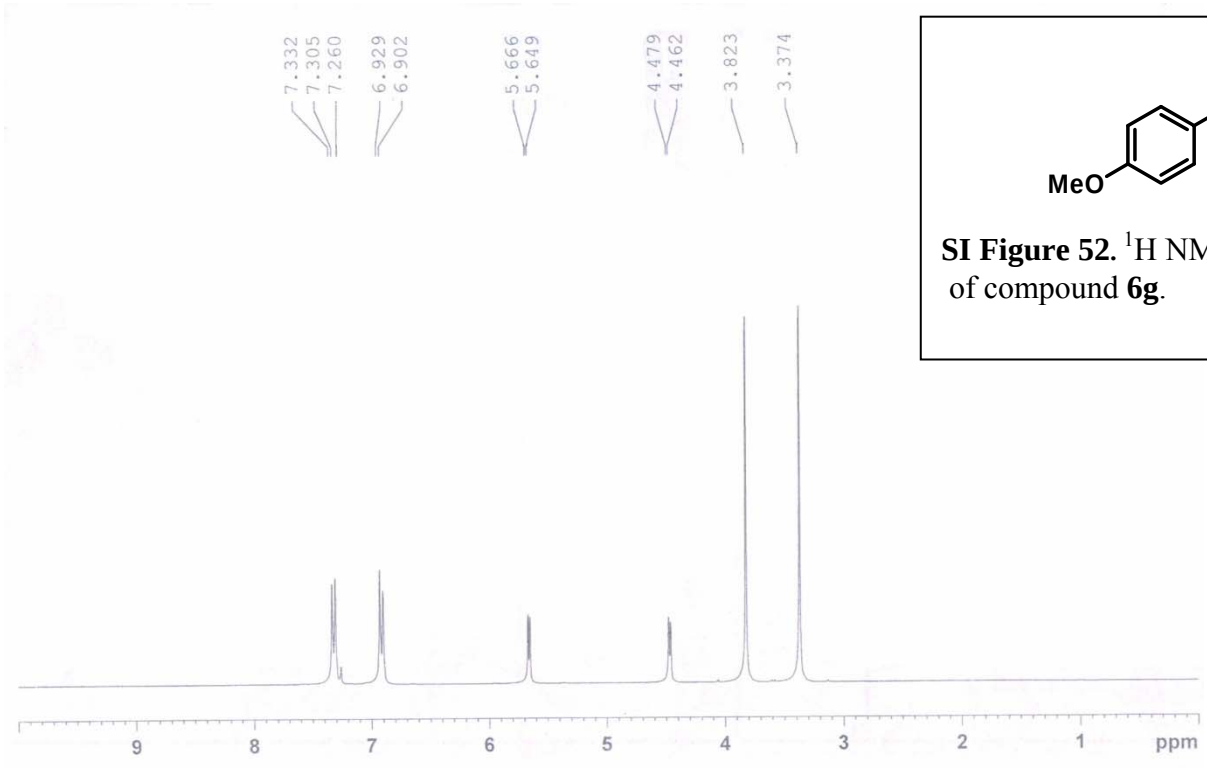
SI Figure 49. ^{13}C NMR spectrum of compound **6e**.



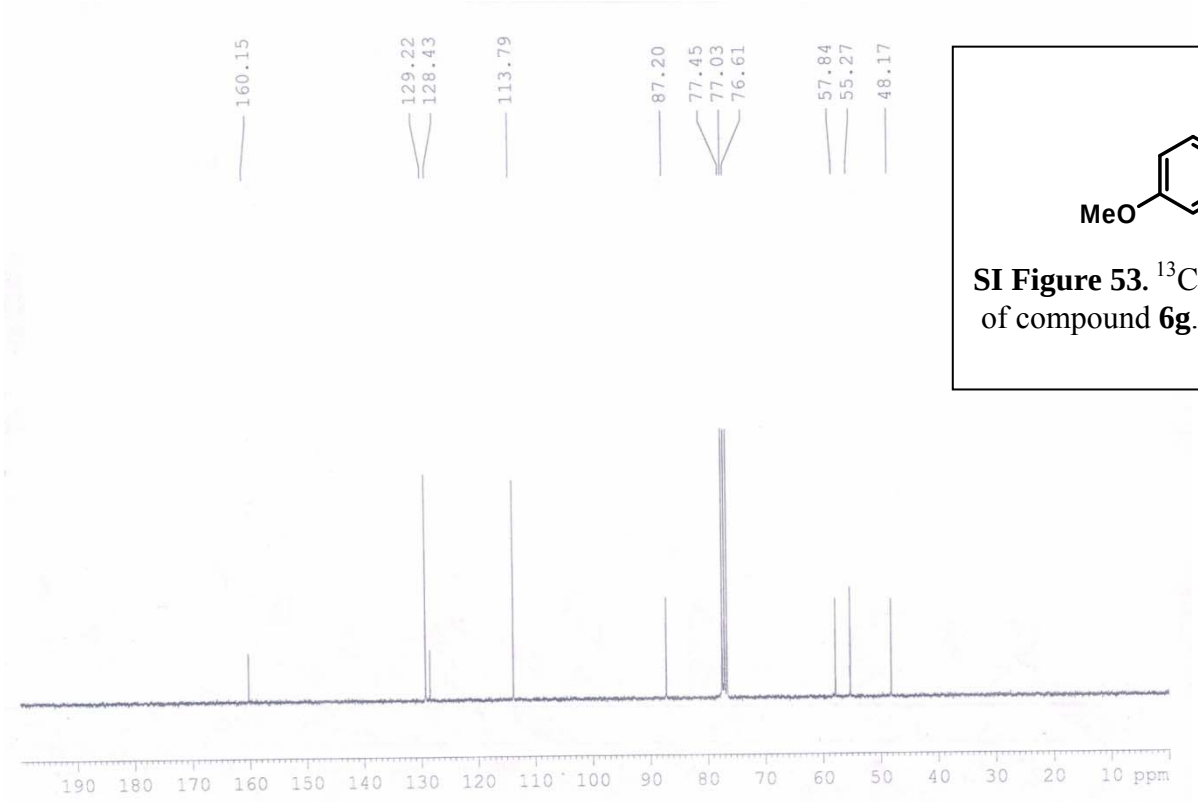
SI Figure 50. ^{1}H NMR spectrum of compound **6f**.

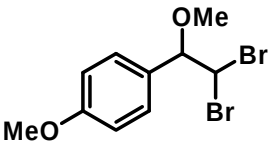


SI Figure 51. ^{13}C NMR spectrum of compound **6f**.

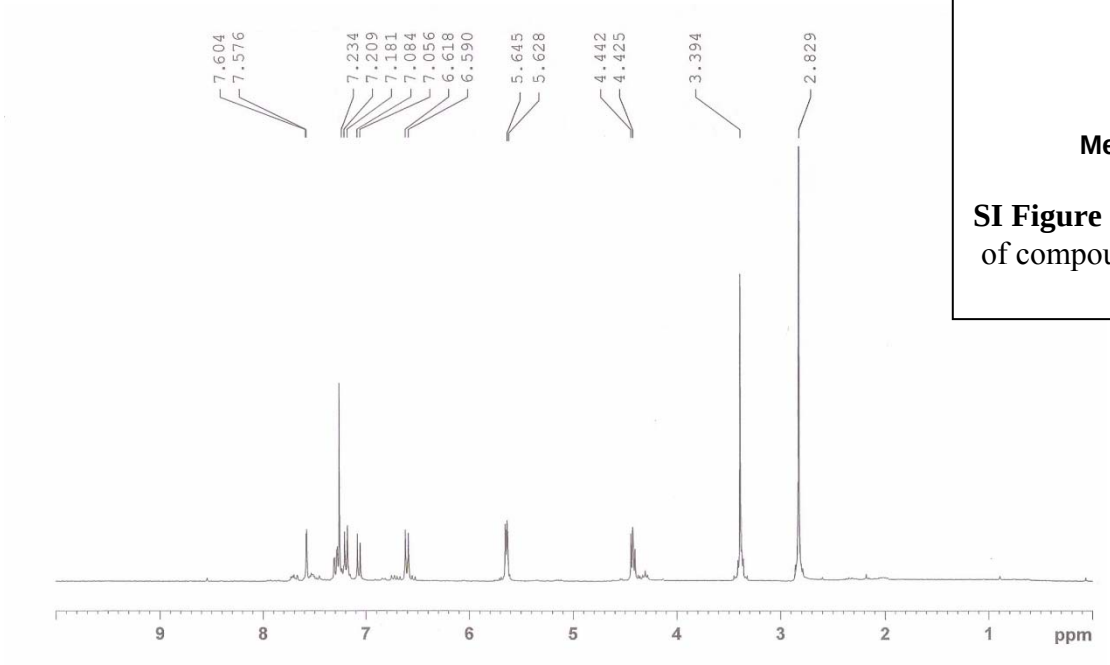


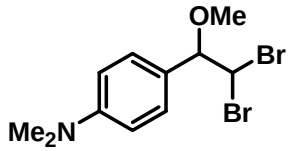
SI Figure 52. ^{1}H NMR spectrum of compound **6g**.



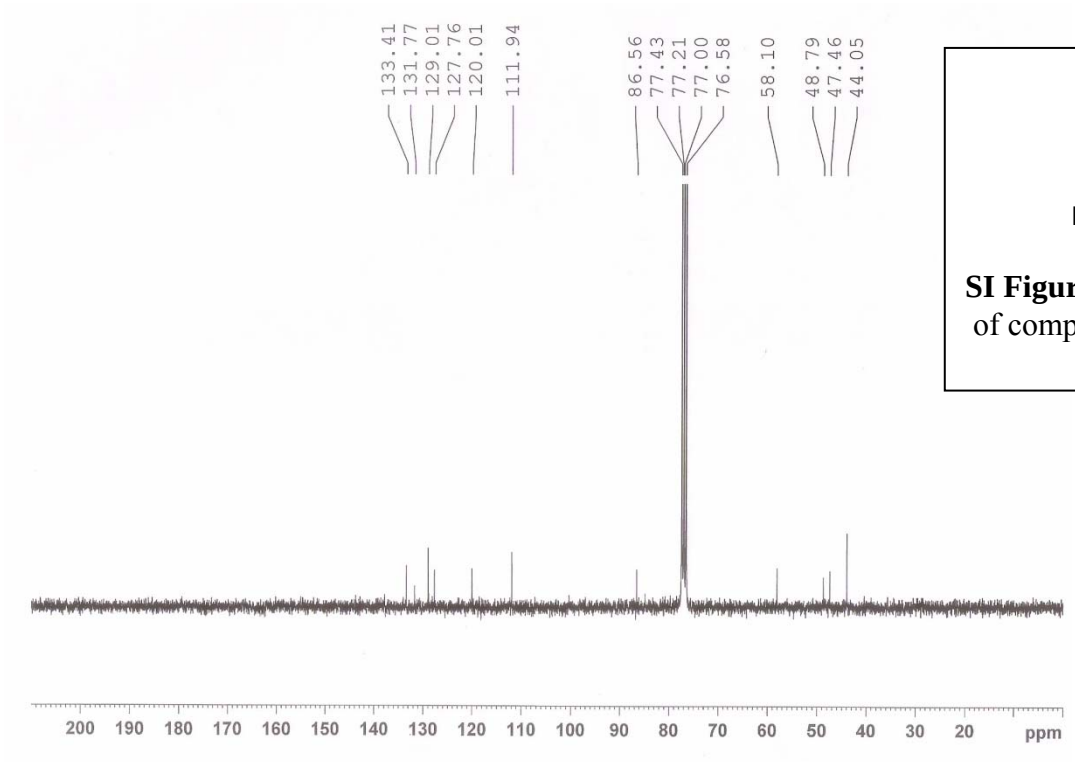


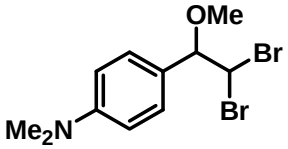
SI Figure 53. ^{13}C NMR spectrum of compound **6g**.



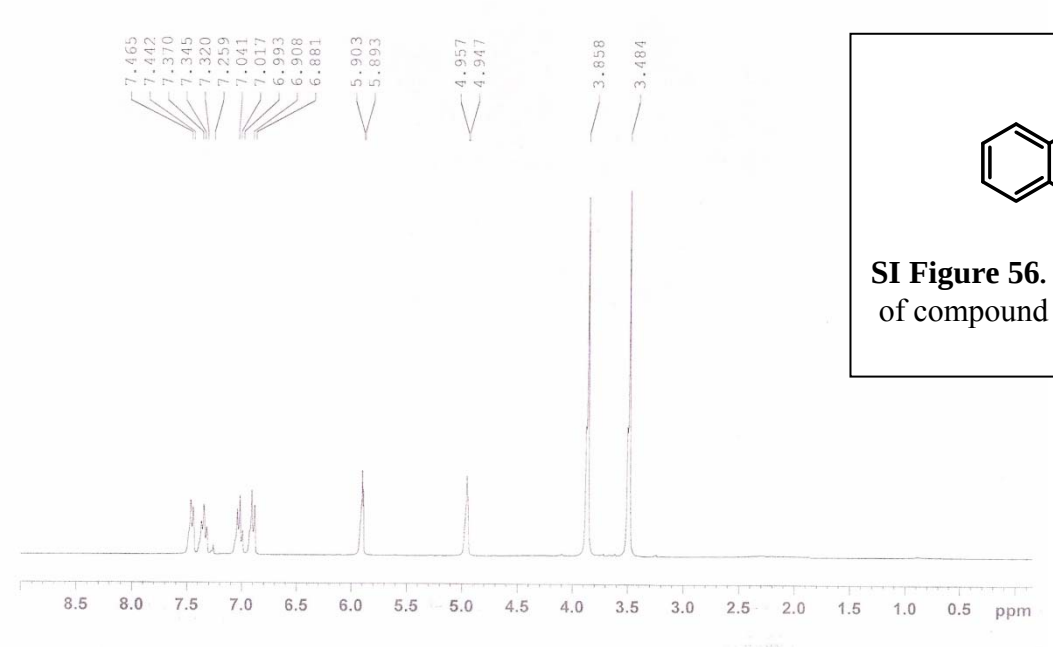


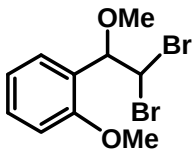
SI Figure 54. ^{1}H NMR spectrum of compound **6h**.



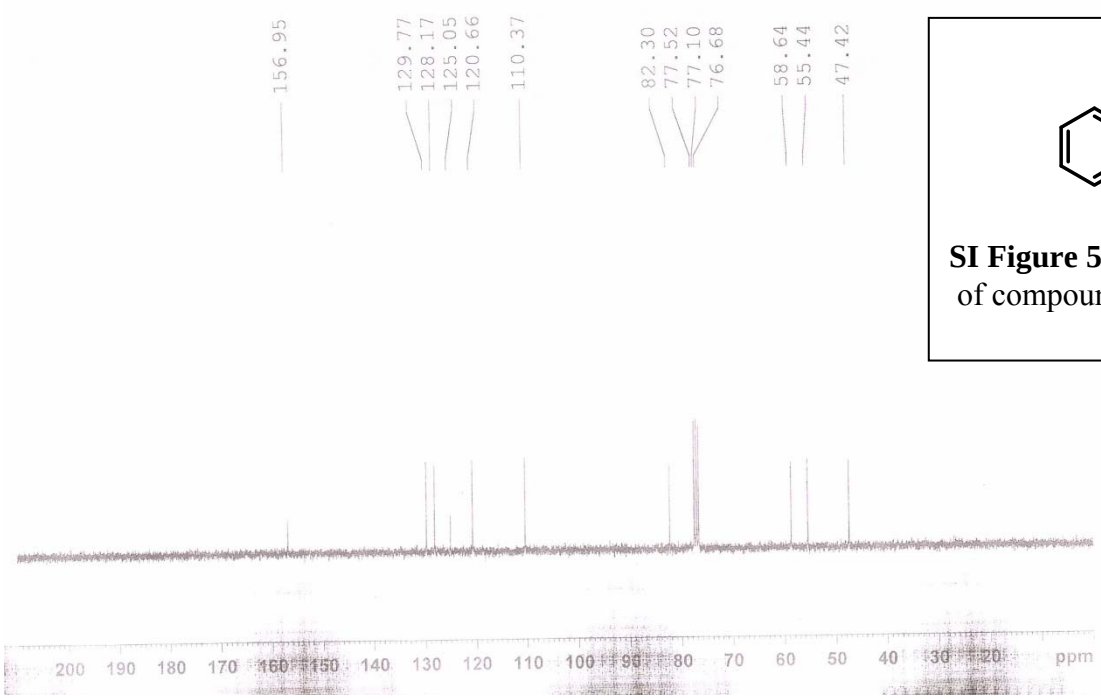


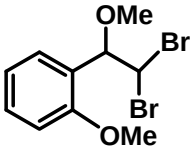
SI Figure 55. ^{13}C NMR spectrum of compound **6h**.



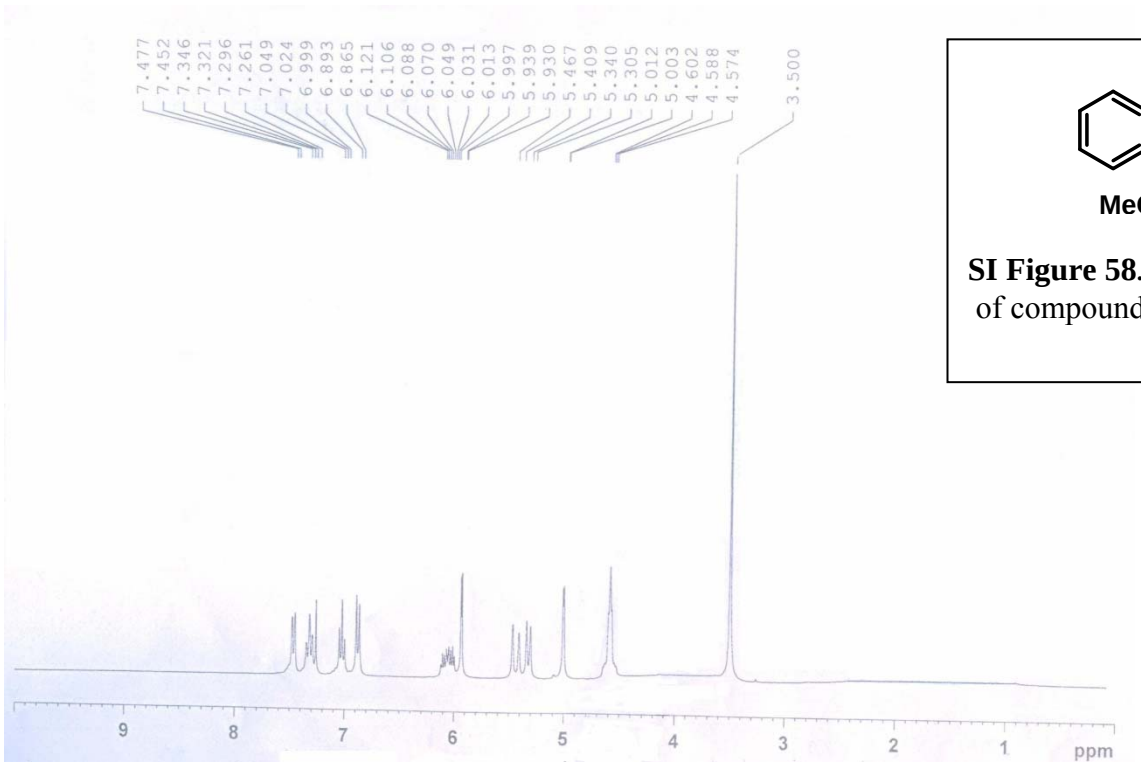


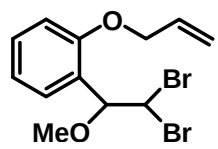
SI Figure 56. ^{1}H NMR spectrum of compound **6i**.



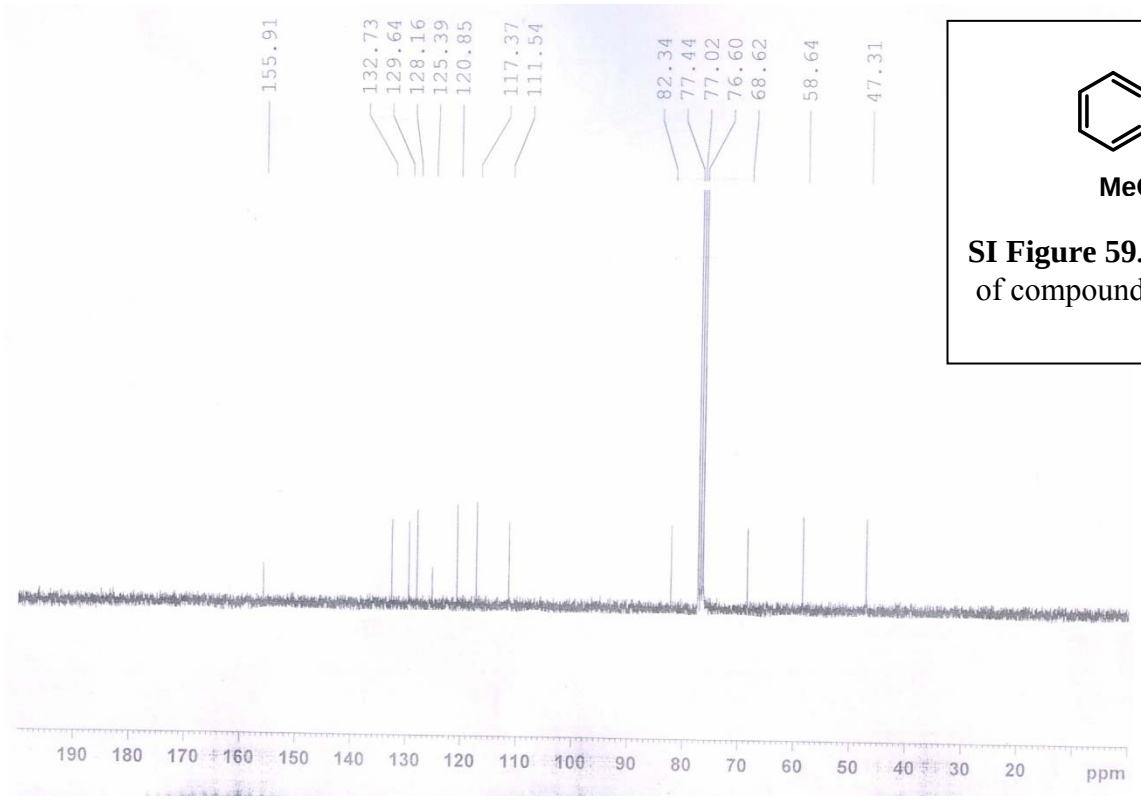


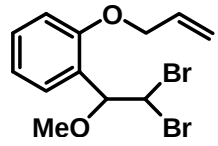
SI Figure 57. ^{13}C NMR spectrum of compound **6i**.



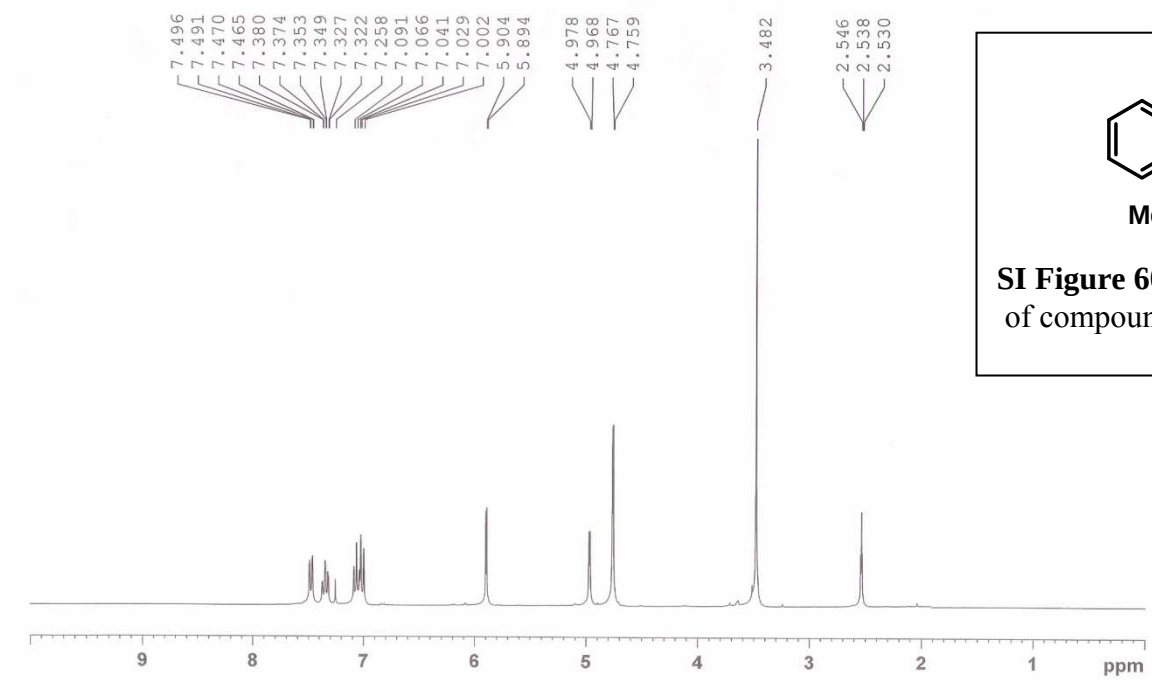


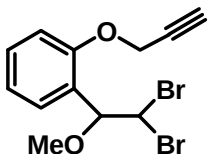
SI Figure 58. ^{1}H NMR spectrum of compound **6j**.



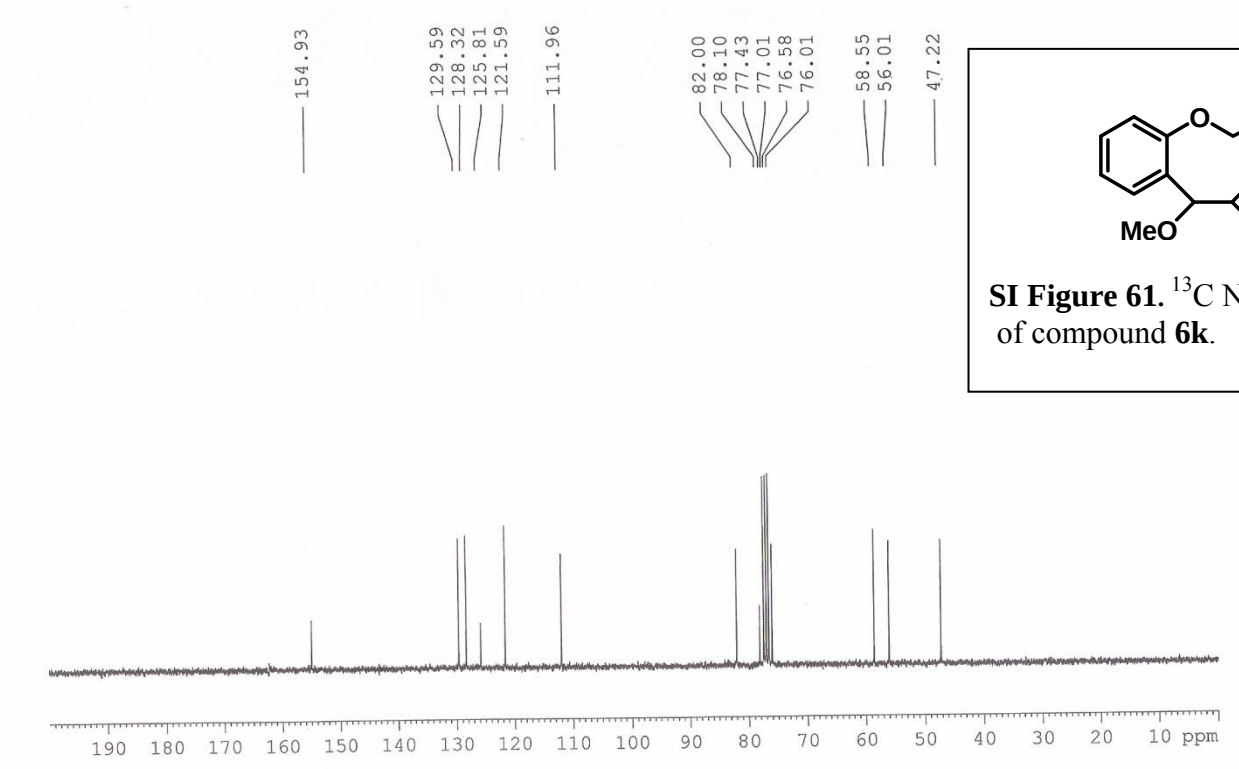


SI Figure 59. ^{13}C NMR spectrum of compound **6j**.

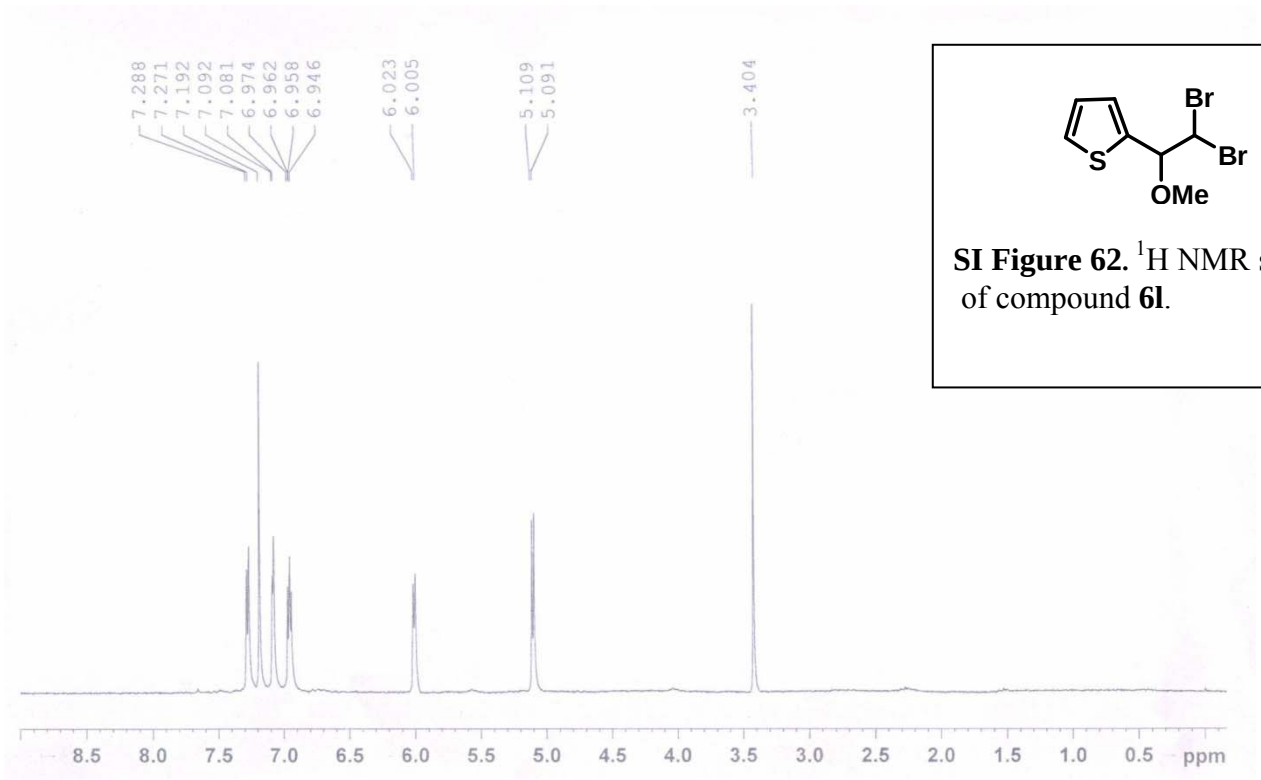




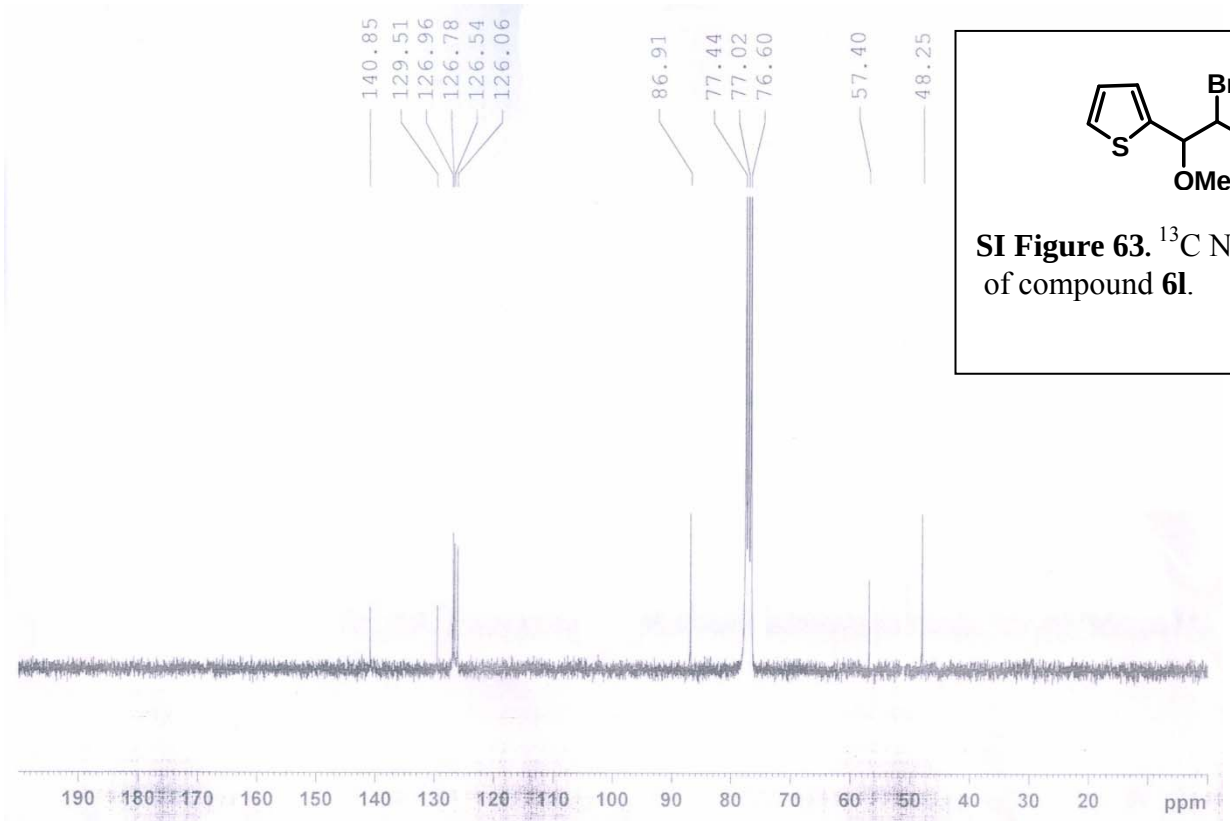
SI Figure 60. ^{1}H NMR spectrum of compound **6k**.



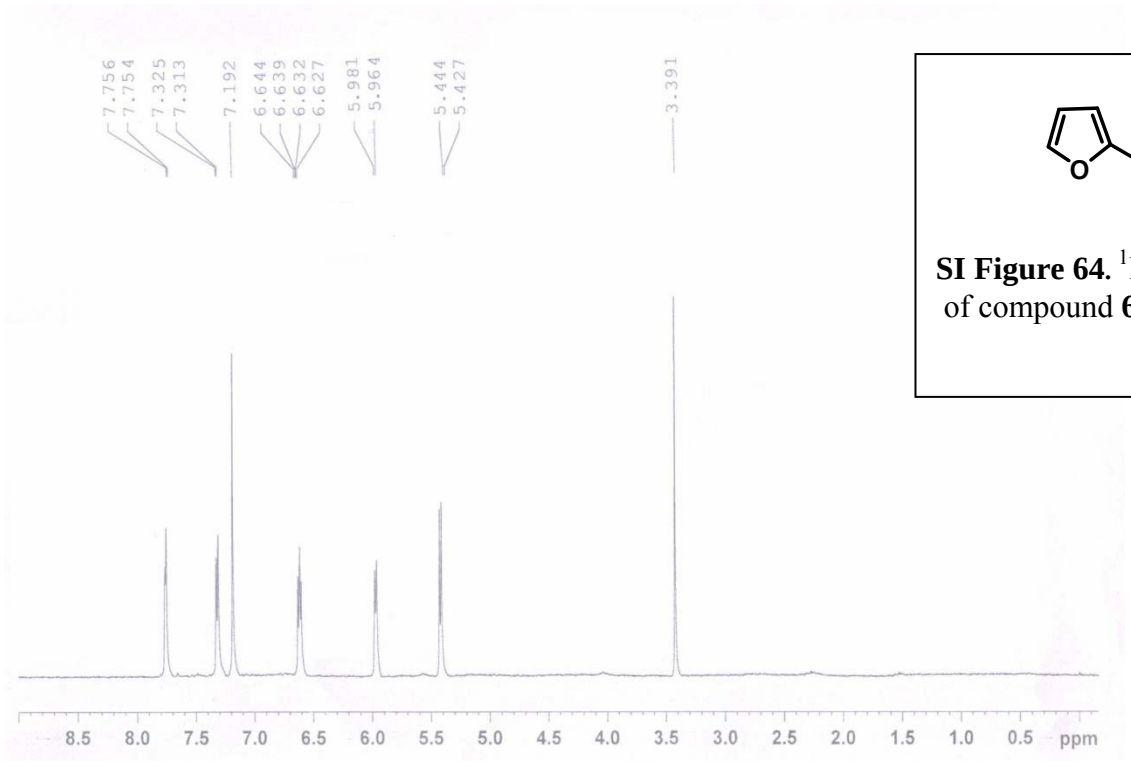
SI Figure 61. ^{13}C NMR spectrum of compound **6k**.

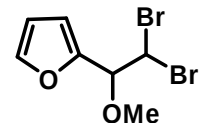


SI Figure 62. ^{1}H NMR spectrum of compound **6l**.

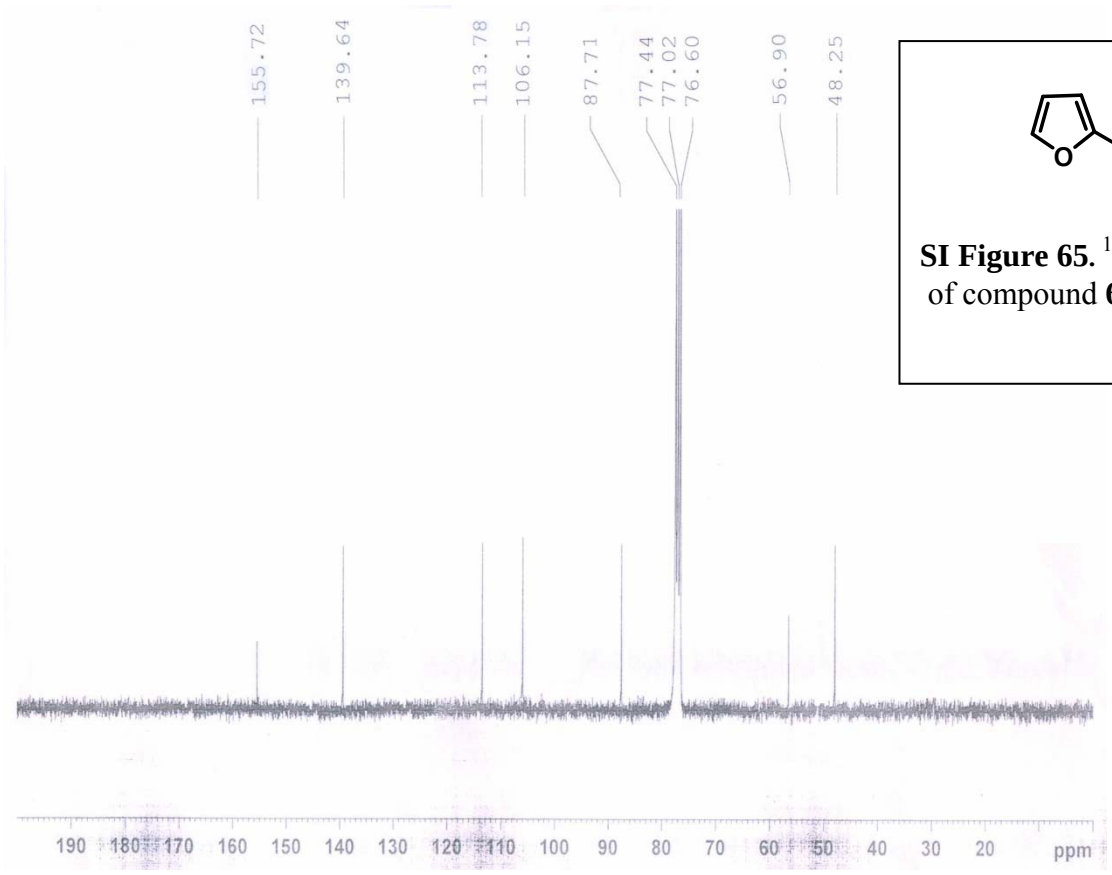


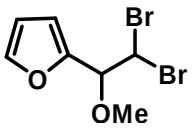
SI Figure 63. ^{13}C NMR spectrum of compound **6l**.



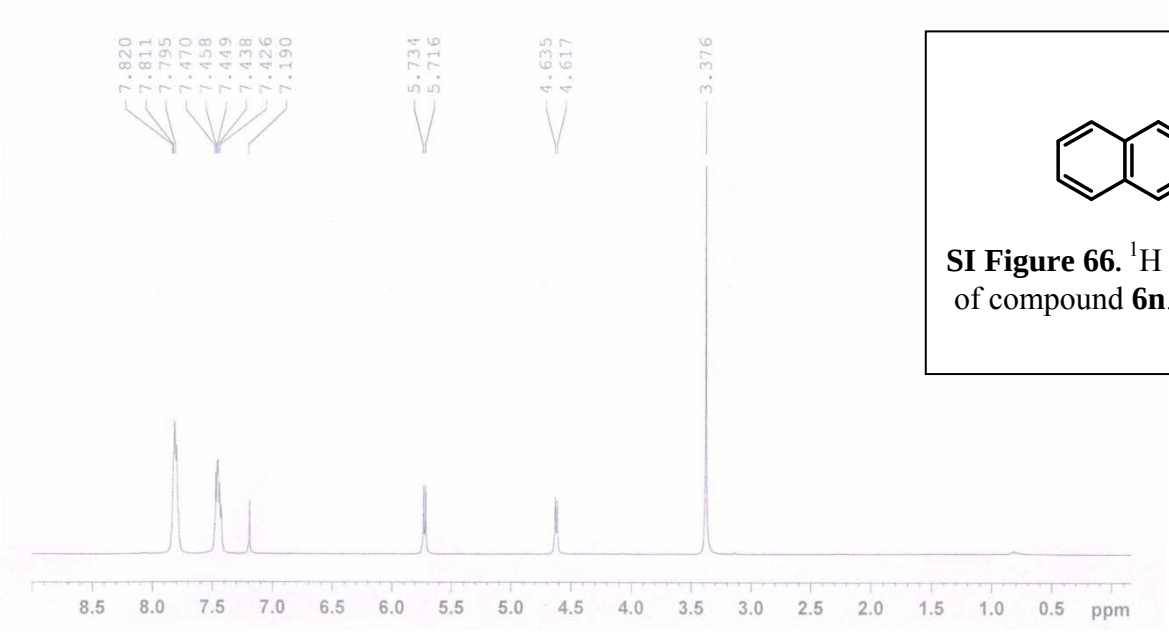


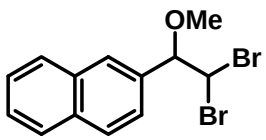
SI Figure 64. ^{1}H NMR spectrum of compound **6m**.



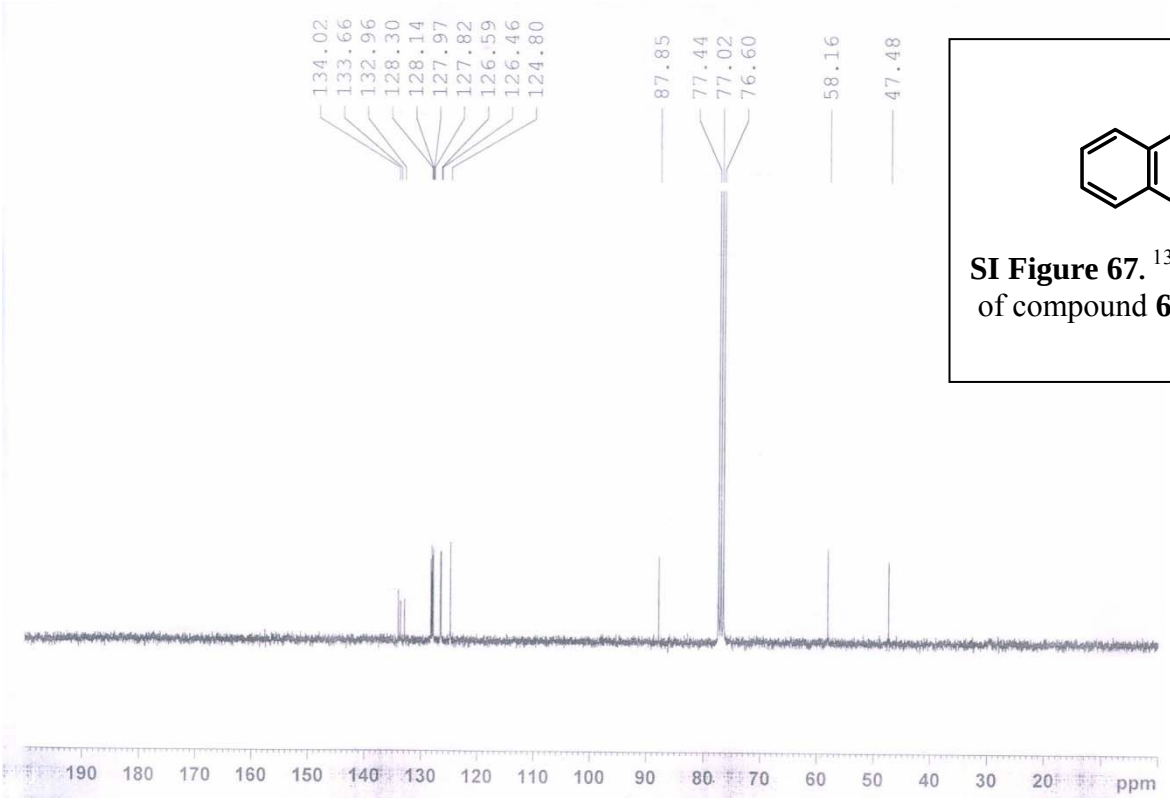


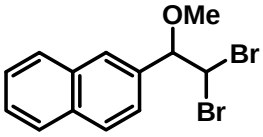
SI Figure 65. ^{13}C NMR spectrum of compound **6m**.



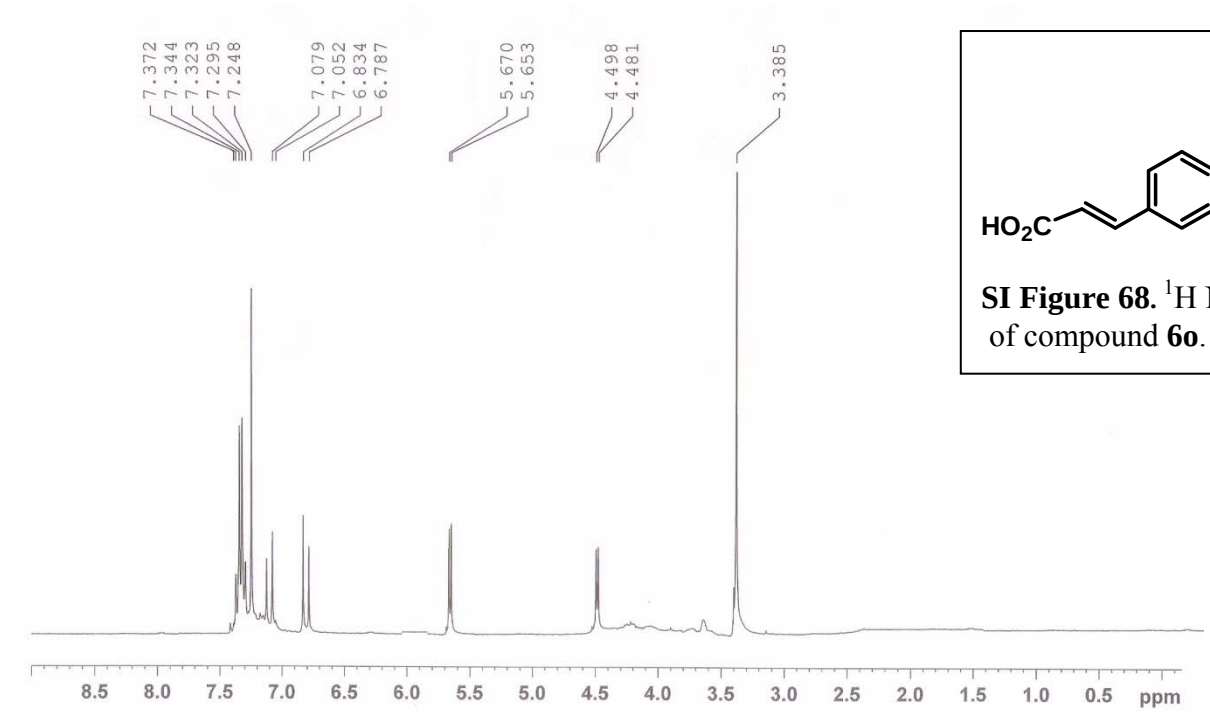


SI Figure 66. ^{1}H NMR spectrum of compound **6n**.

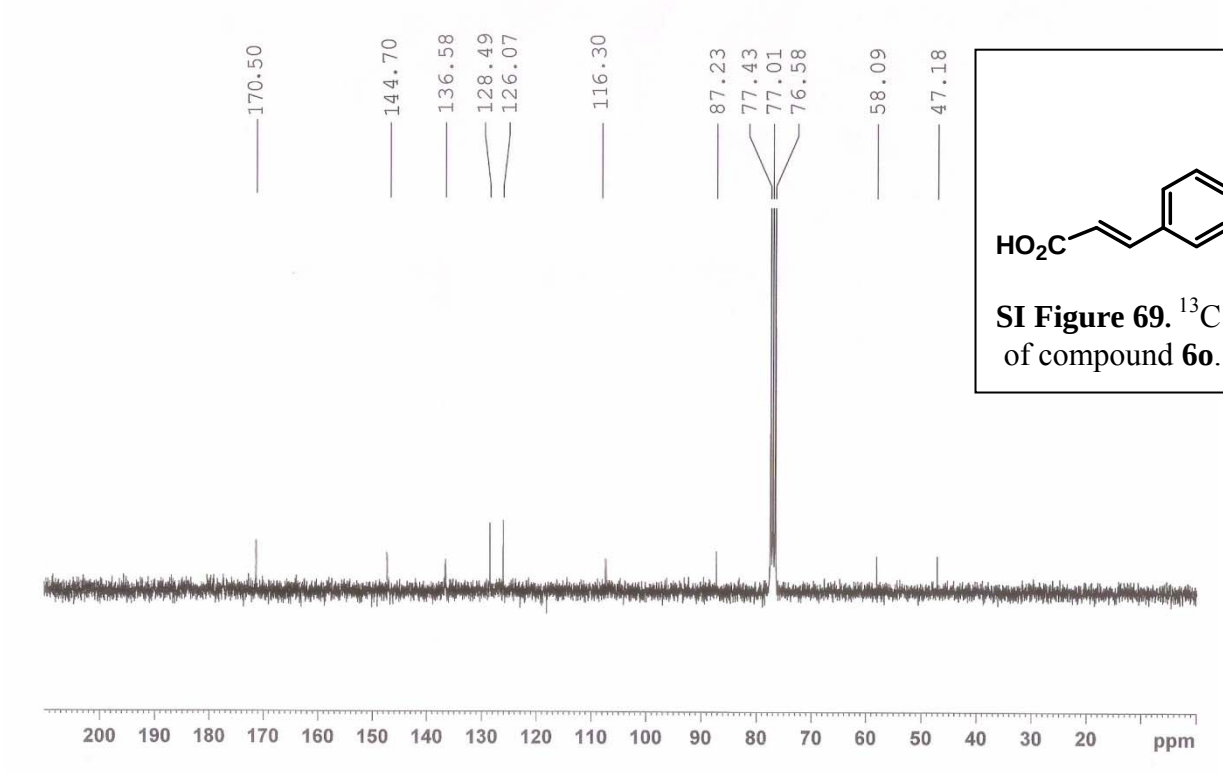




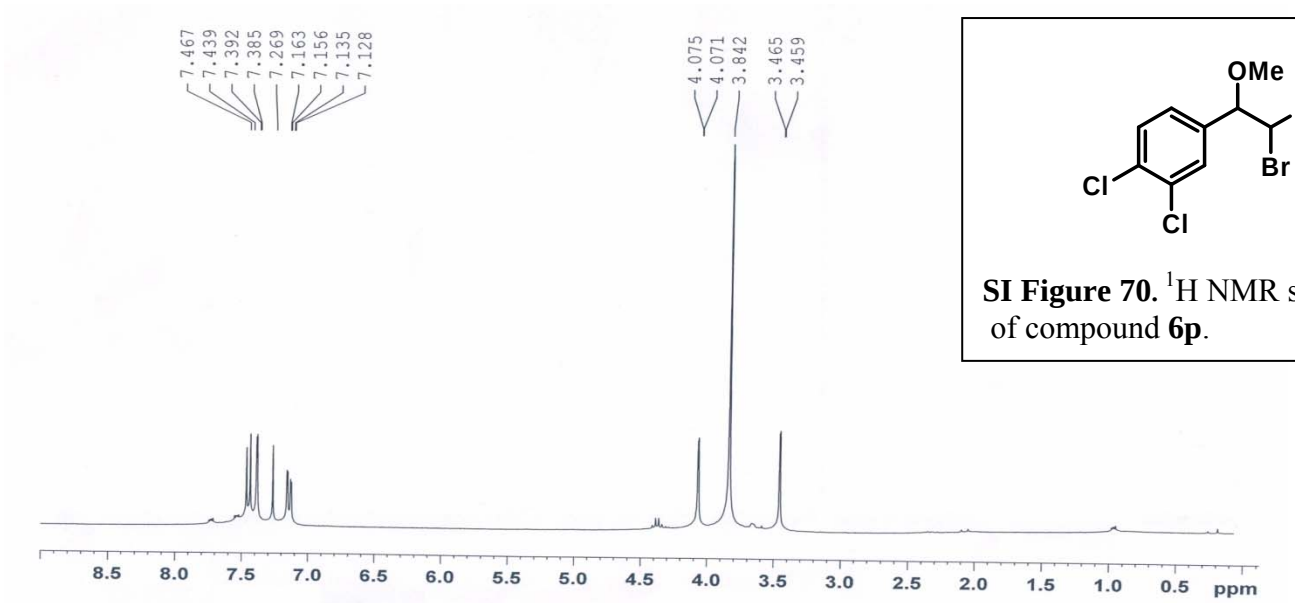
SI Figure 67. ^{13}C NMR spectrum of compound **6n**.



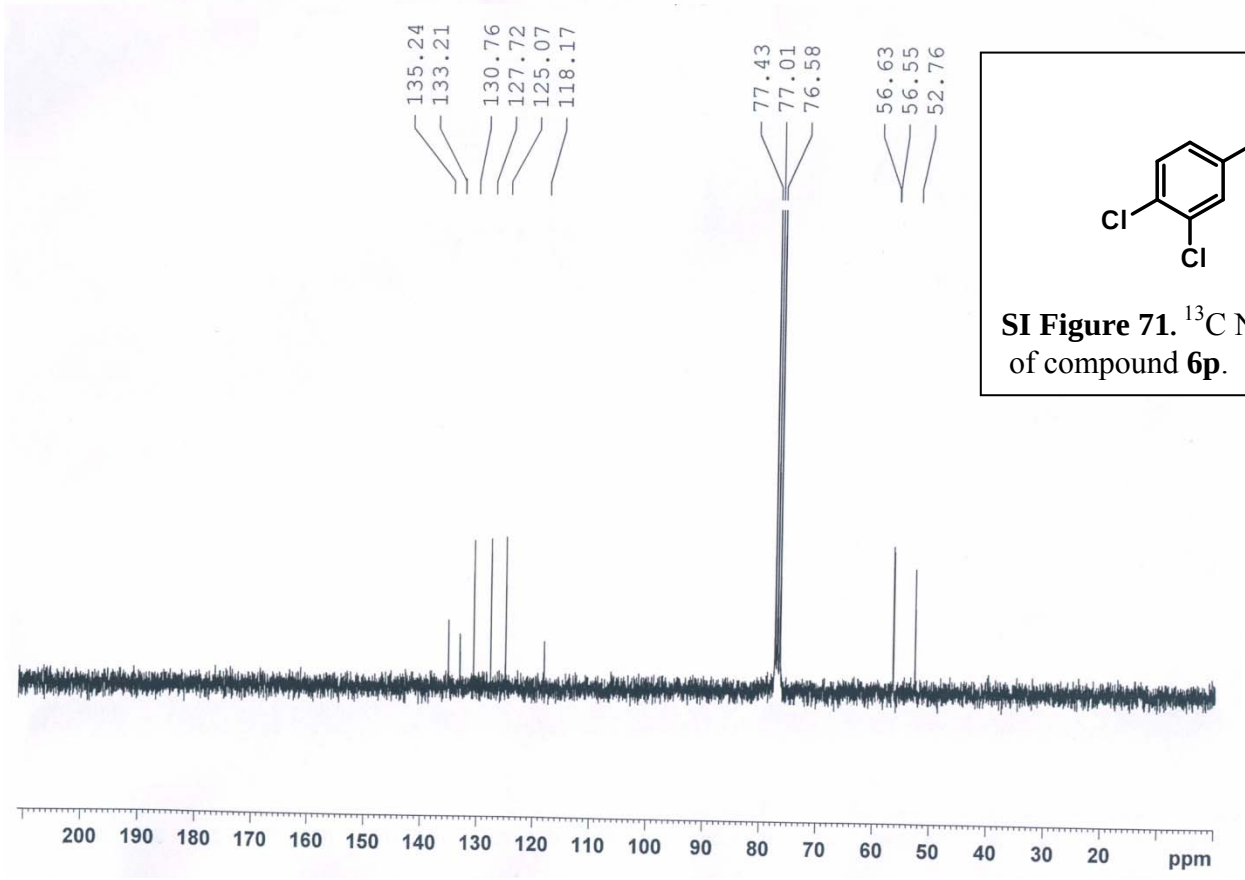
SI Figure 68. ^{1}H NMR spectrum of compound **6o**.



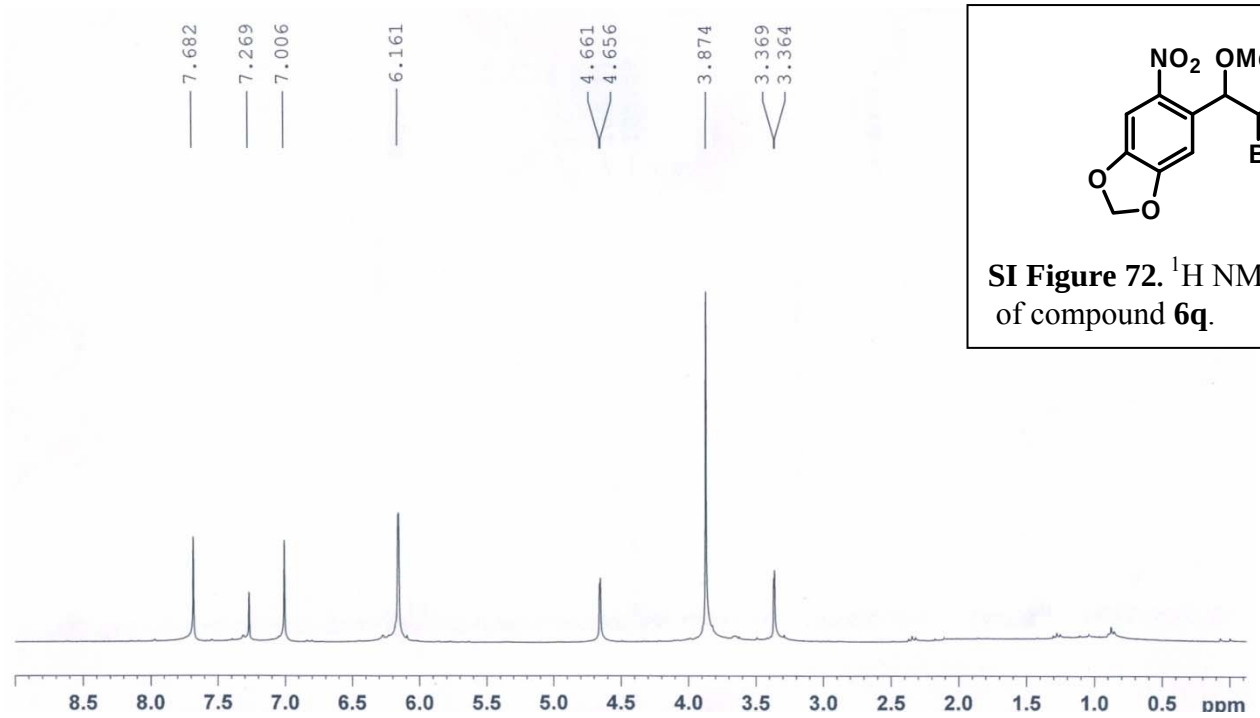
SI Figure 69. ^{13}C NMR spectrum of compound **6o**.



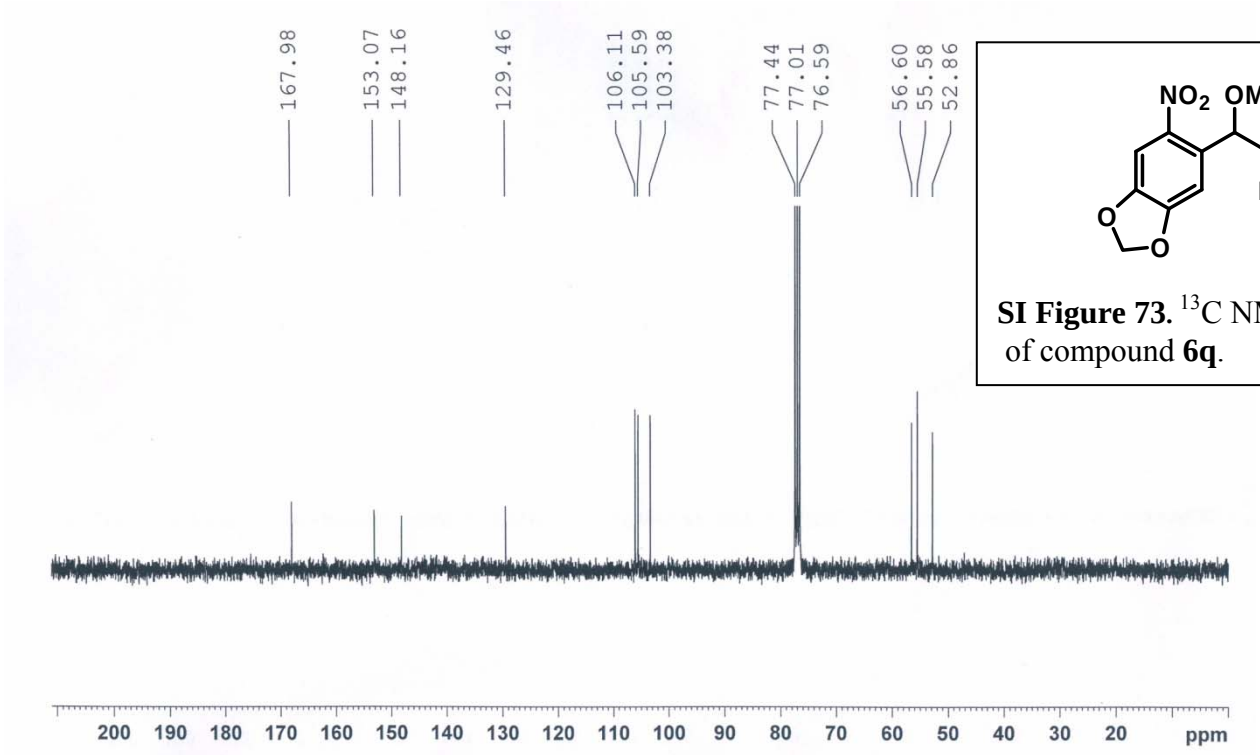
SI Figure 70. ^{1}H NMR spectrum of compound **6p**.



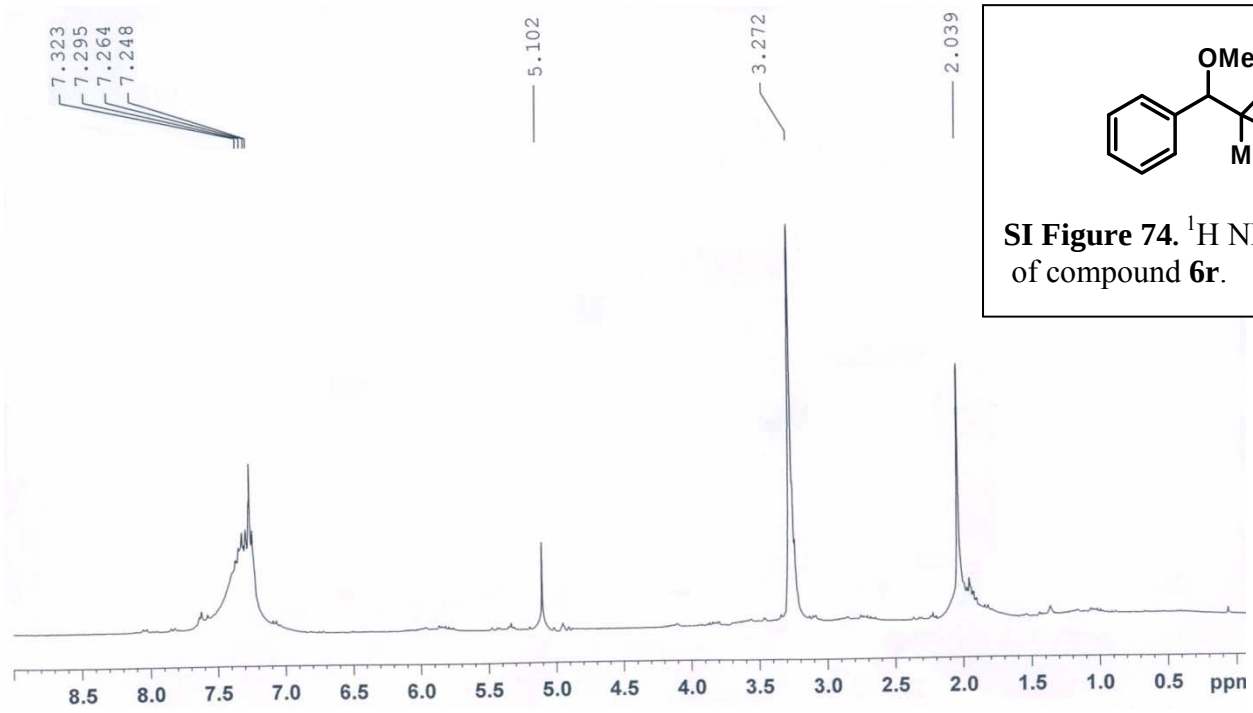
SI Figure 71. ^{13}C NMR spectrum of compound **6p**.



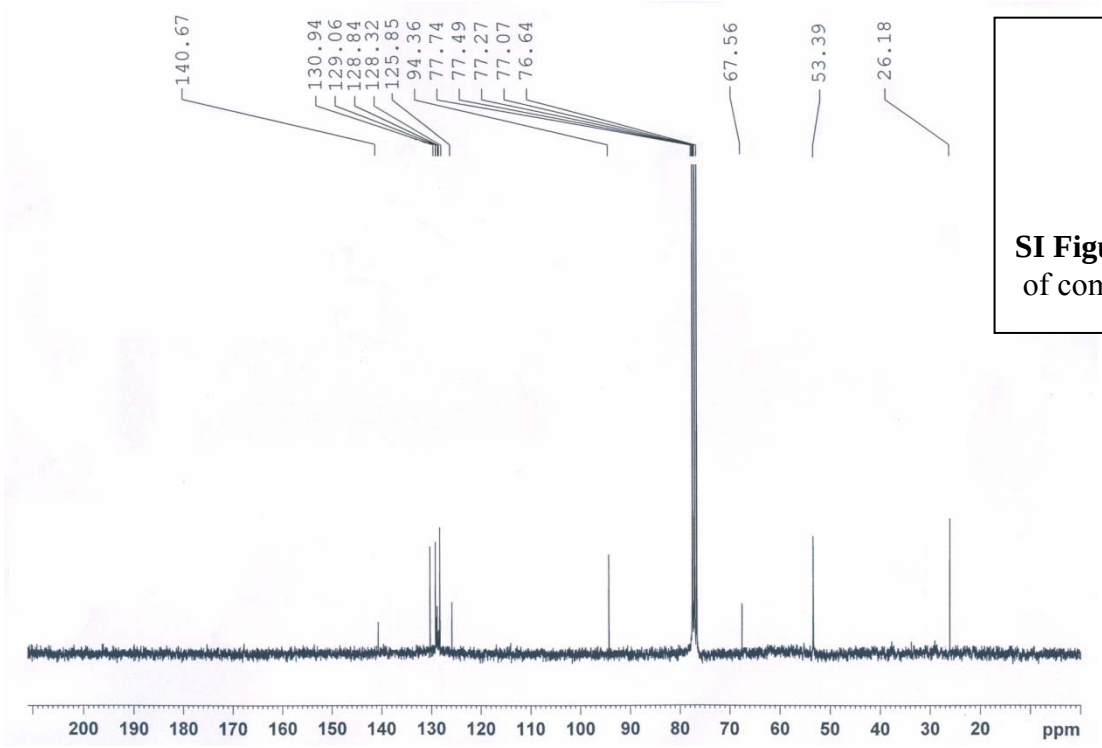
SI Figure 72. ^{1}H NMR spectrum of compound **6q**.

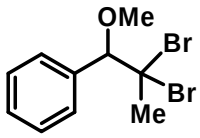


SI Figure 73. ^{13}C NMR spectrum of compound **6q**.

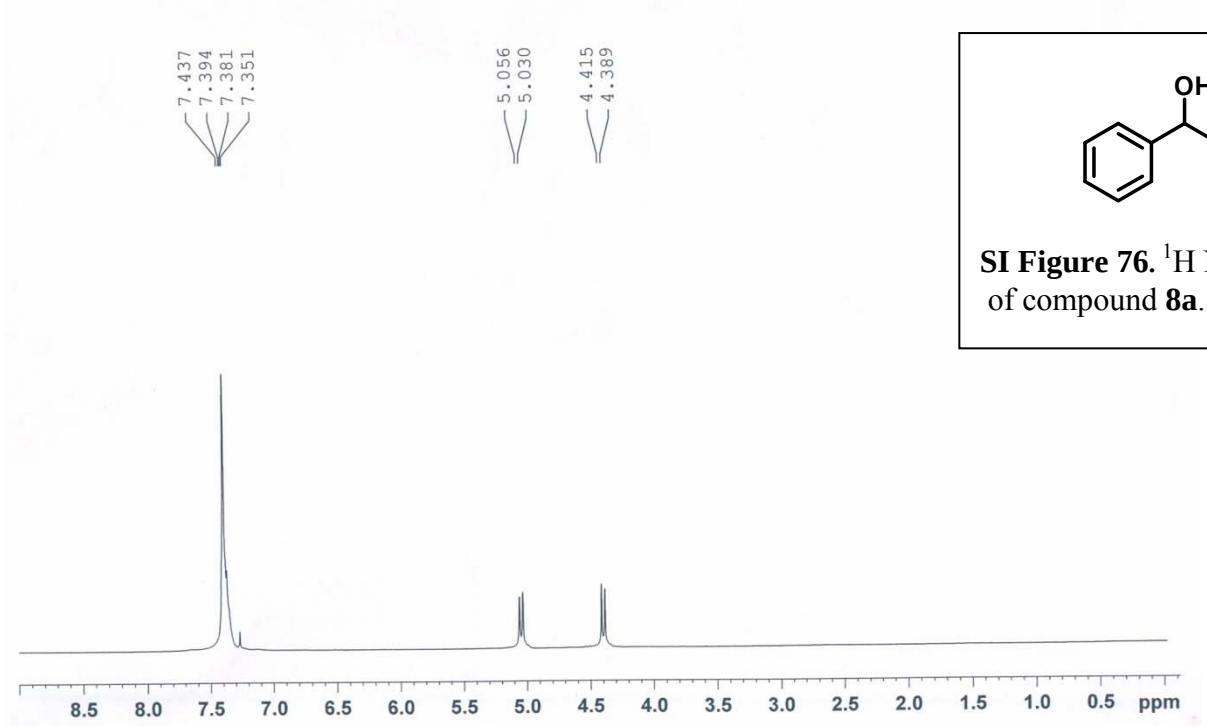


SI Figure 74. ^{1}H NMR spectrum of compound **6r**.

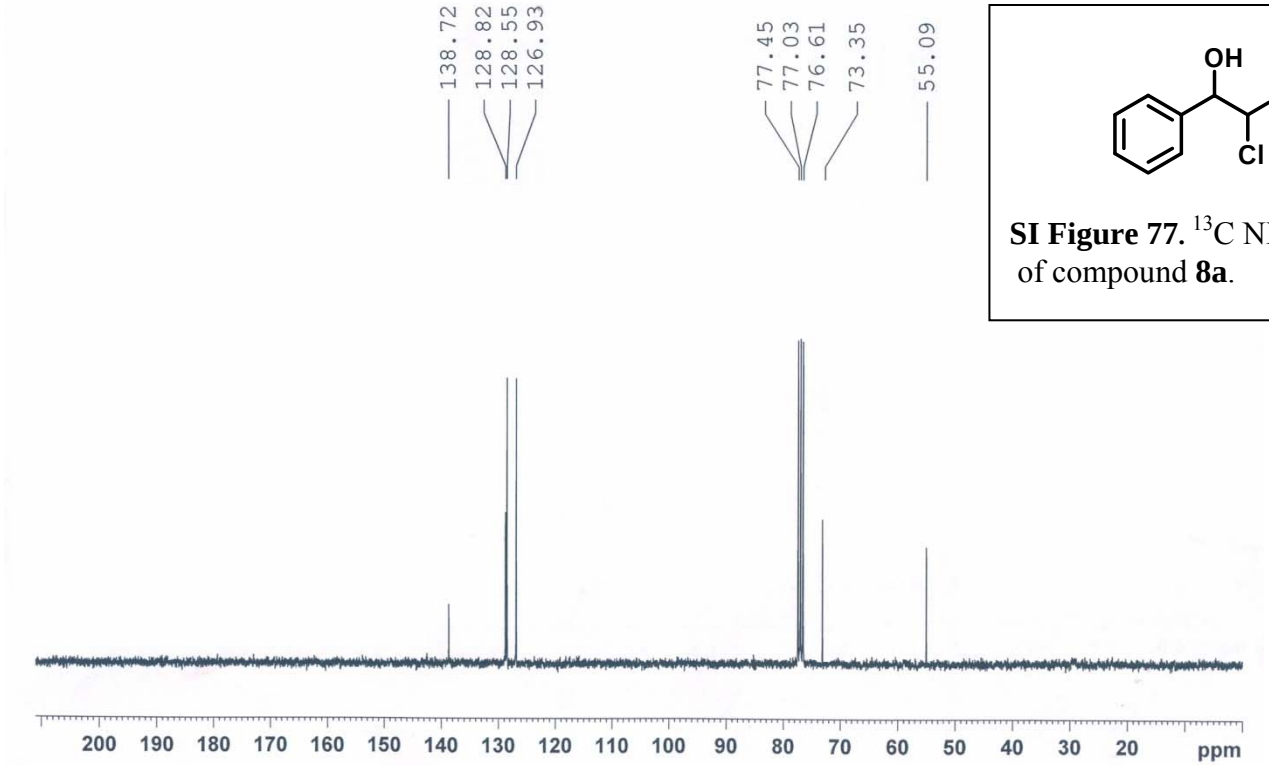




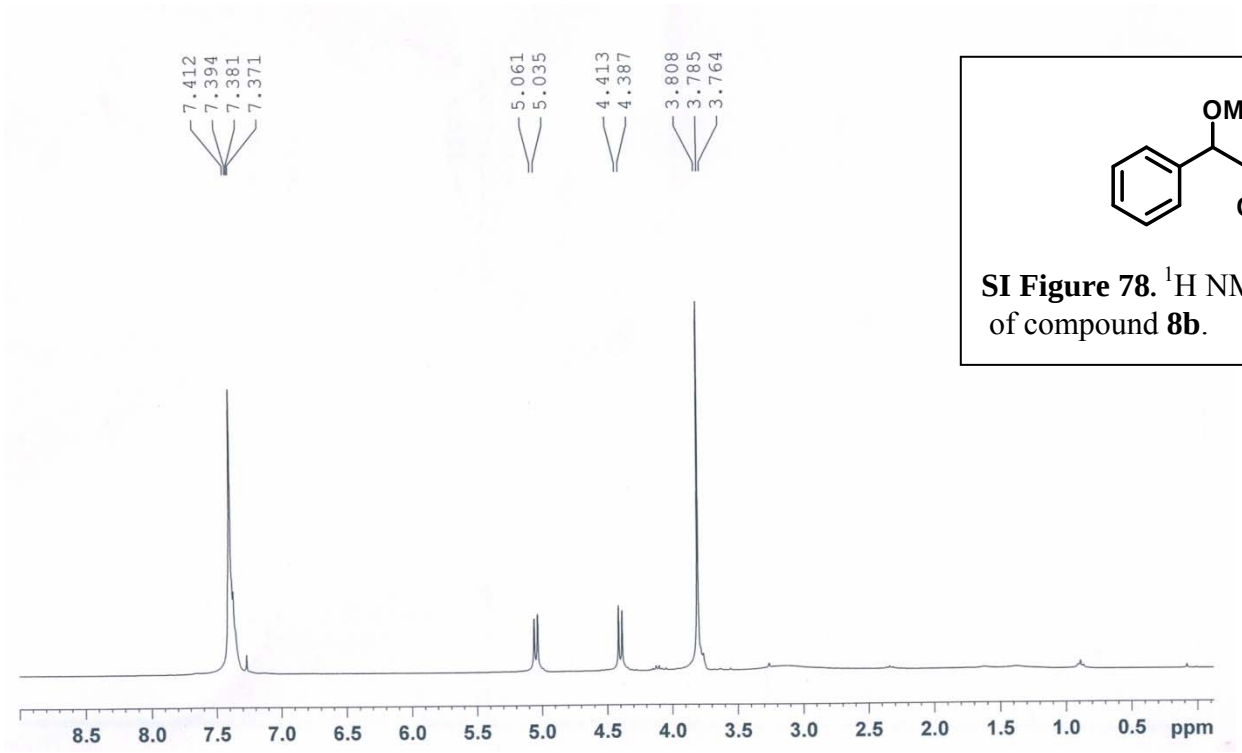
SI Figure 75. ^{13}C NMR spectrum of compound **6r**.



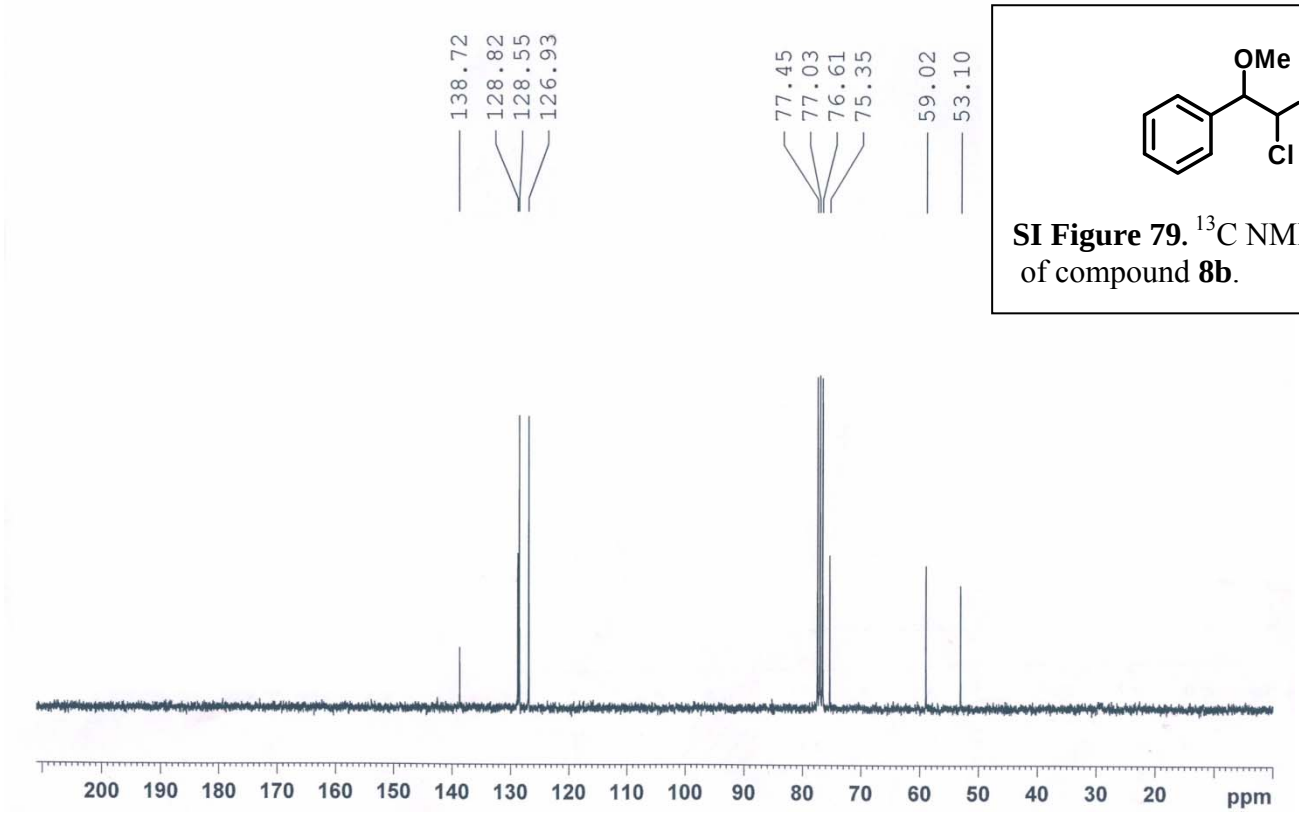
SI Figure 76. ^{1}H NMR spectrum of compound **8a**.



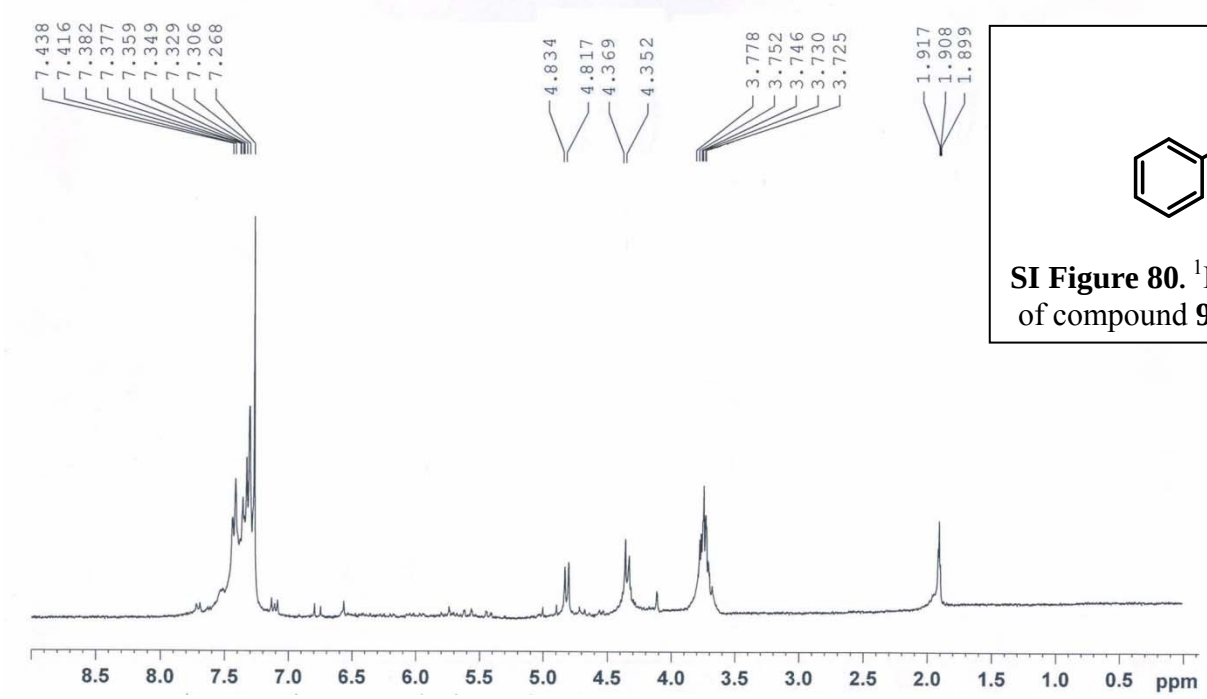
SI Figure 77. ^{13}C NMR spectrum of compound **8a**.

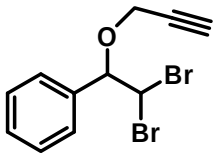


SI Figure 78. ^{1}H NMR spectrum of compound **8b**.

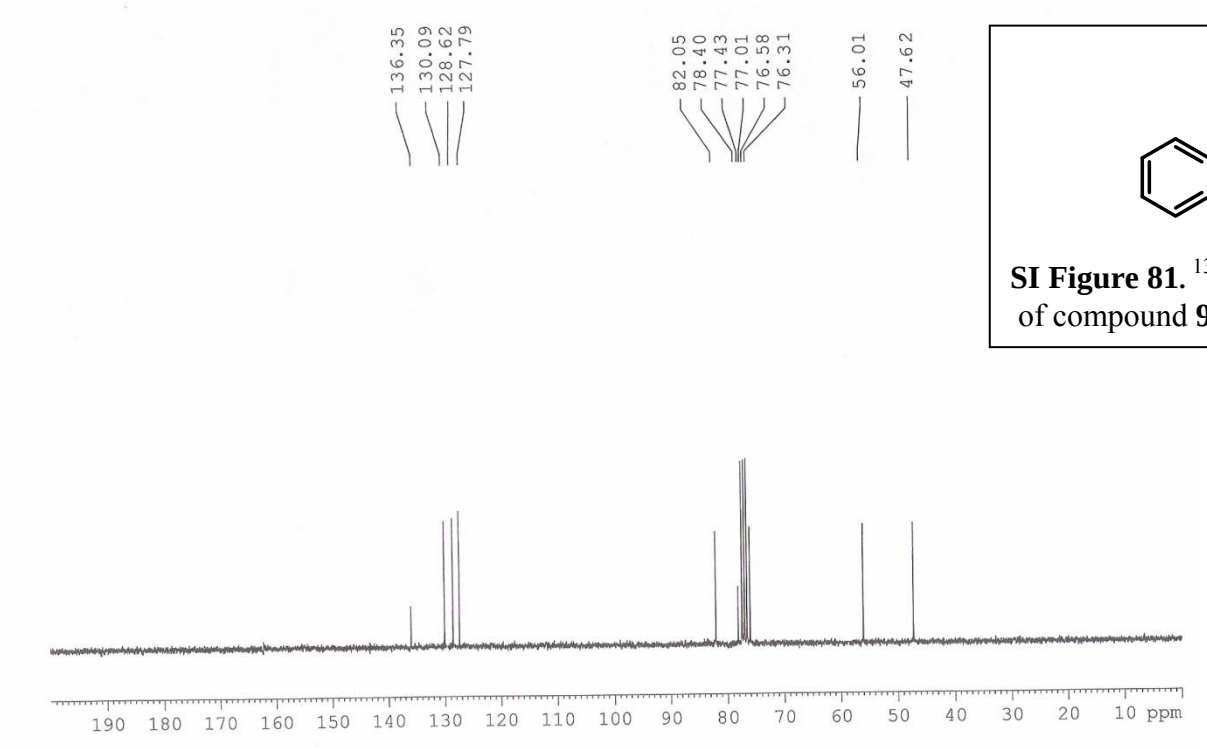


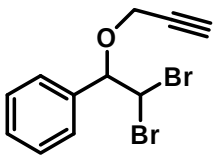
SI Figure 79. ^{13}C NMR spectrum of compound **8b**.



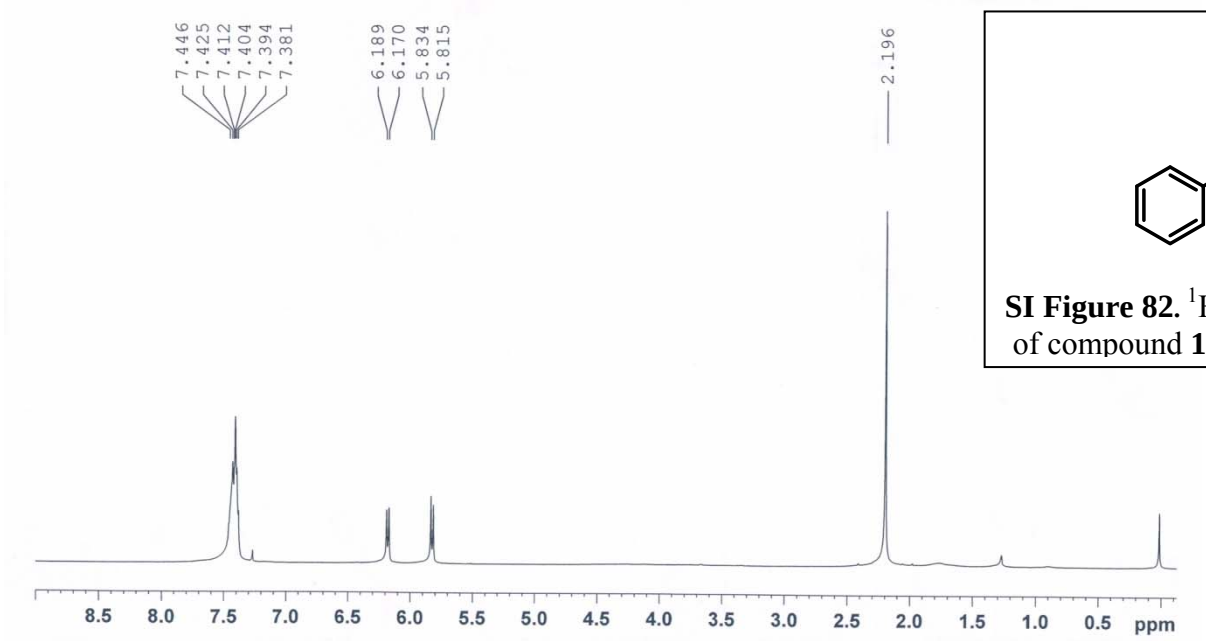


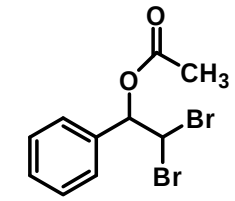
SI Figure 80. ^{1}H NMR spectrum of compound **9**.



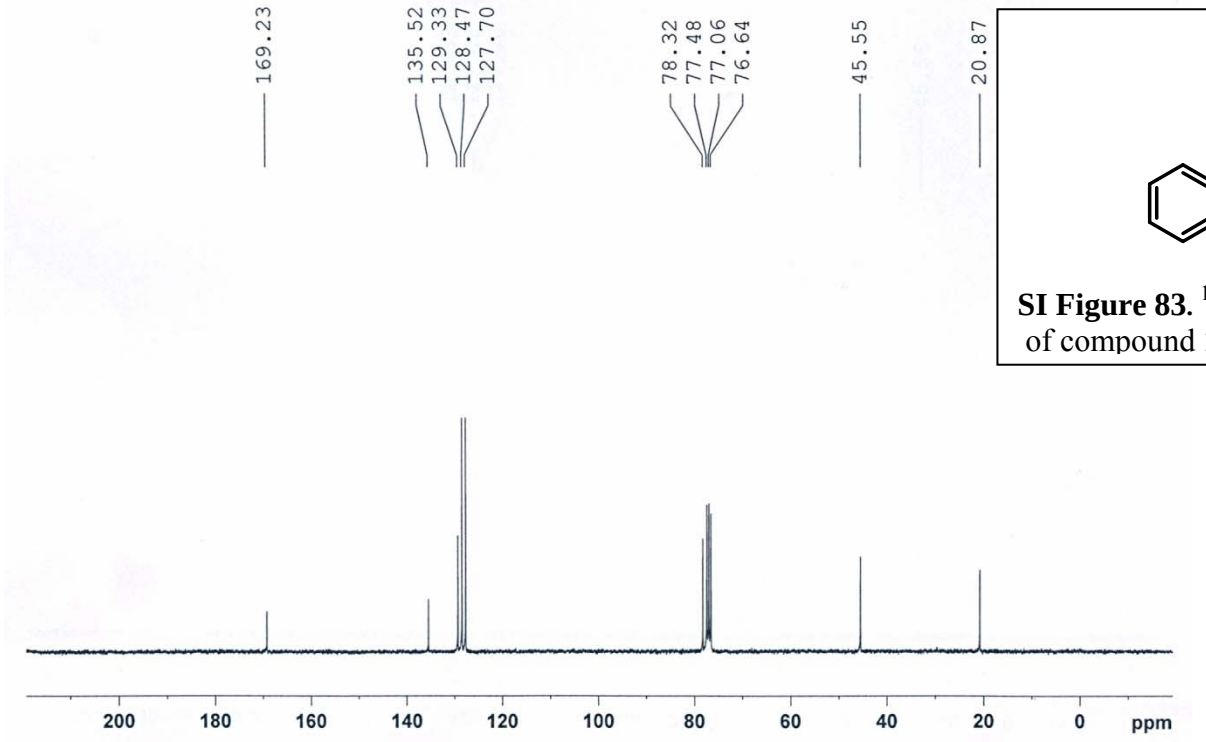


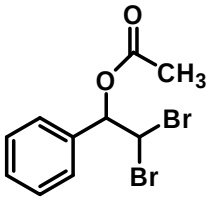
SI Figure 81. ^{13}C NMR spectrum of compound **9**.



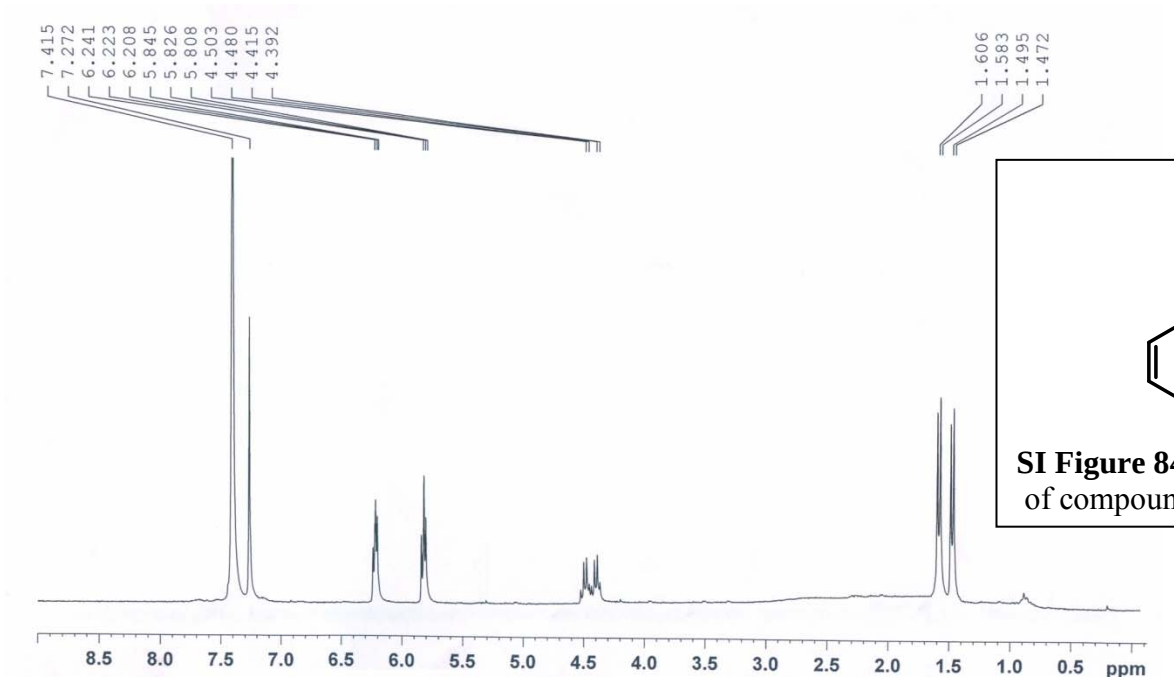


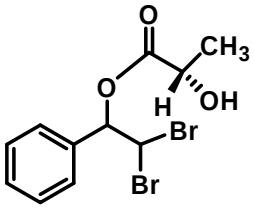
SI Figure 82. ^{1}H NMR spectrum of compound **10a**.



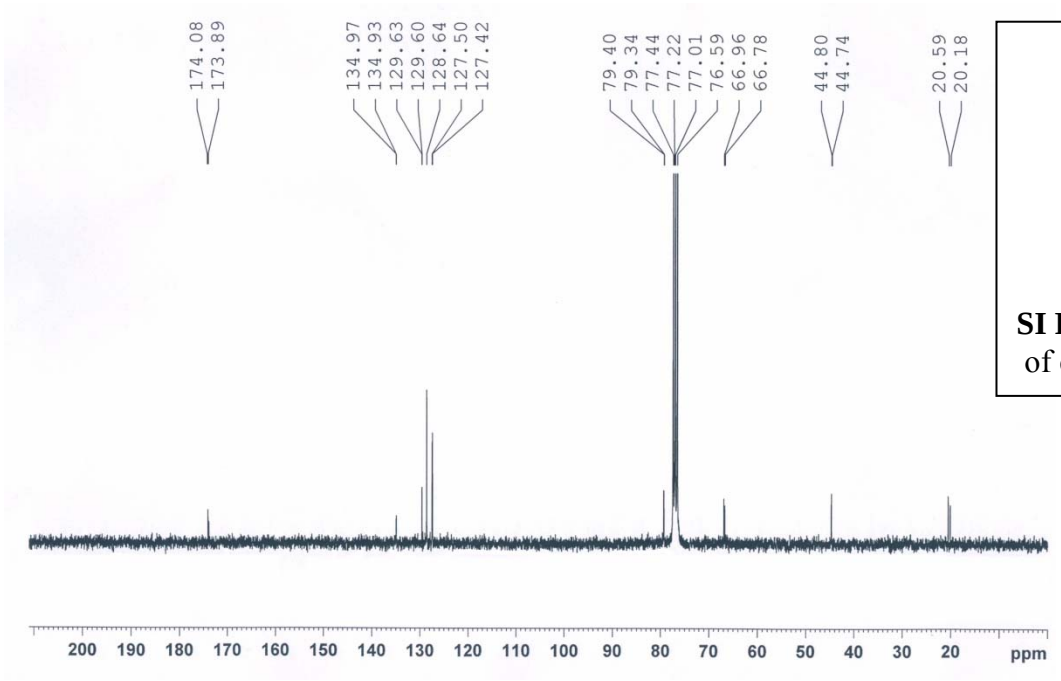


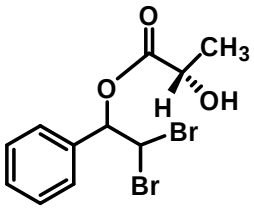
SI Figure 83. ^{13}C NMR spectrum of compound **10a**.



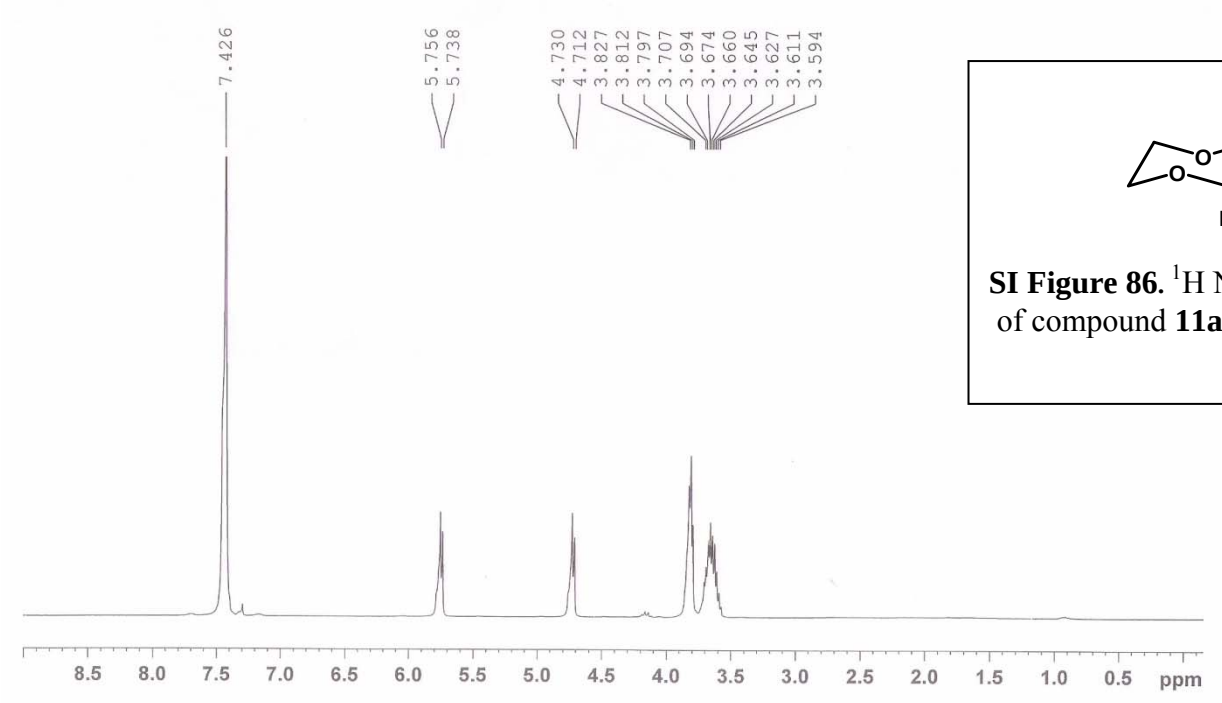


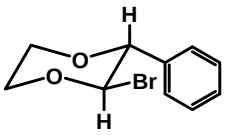
SI Figure 84. ^{1}H NMR spectrum of compound **10b**.



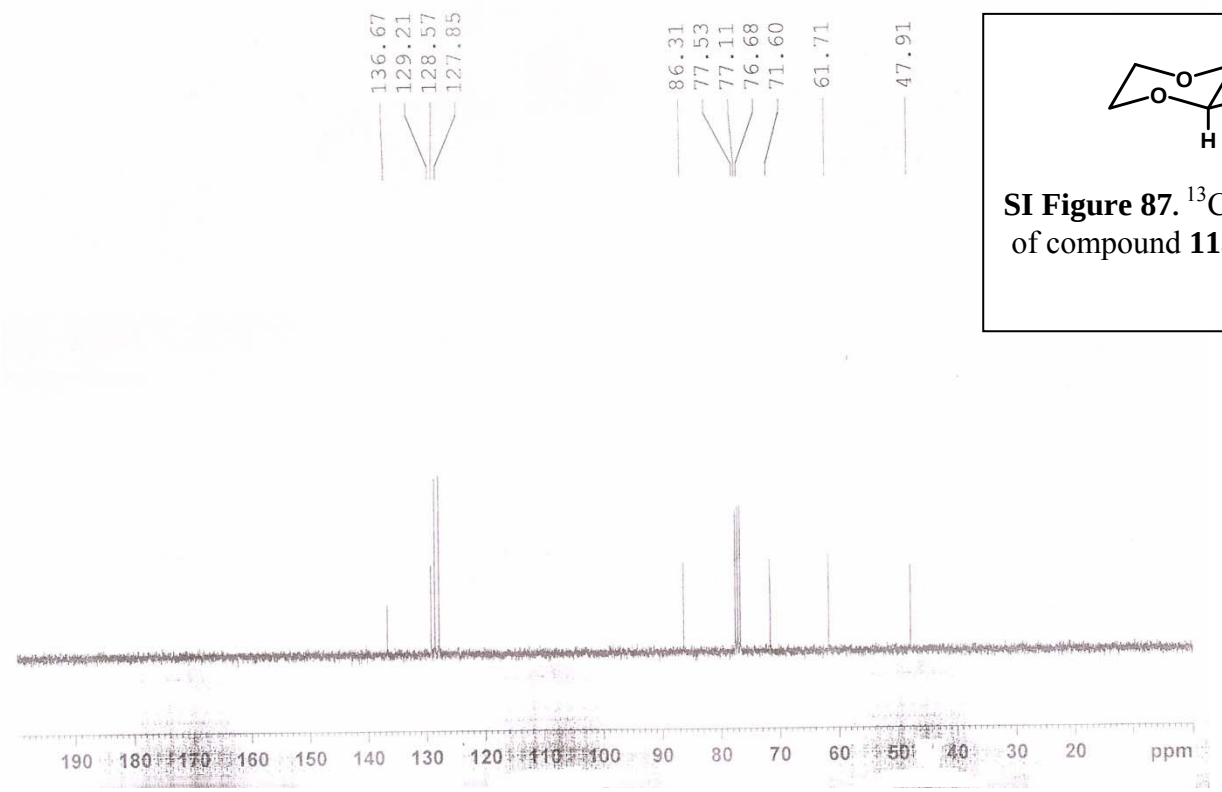


SI Figure 85. ^{13}C NMR spectrum of compound **10b**.

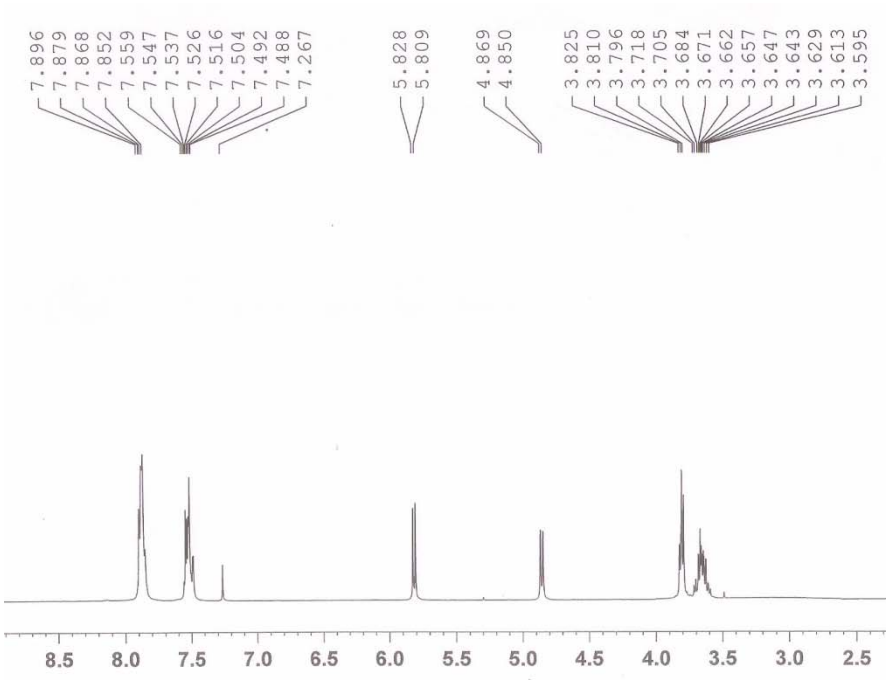


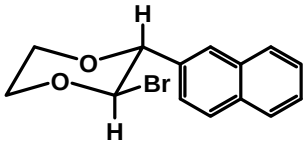


SI Figure 86. ^{1}H NMR spectrum of compound **11a**.

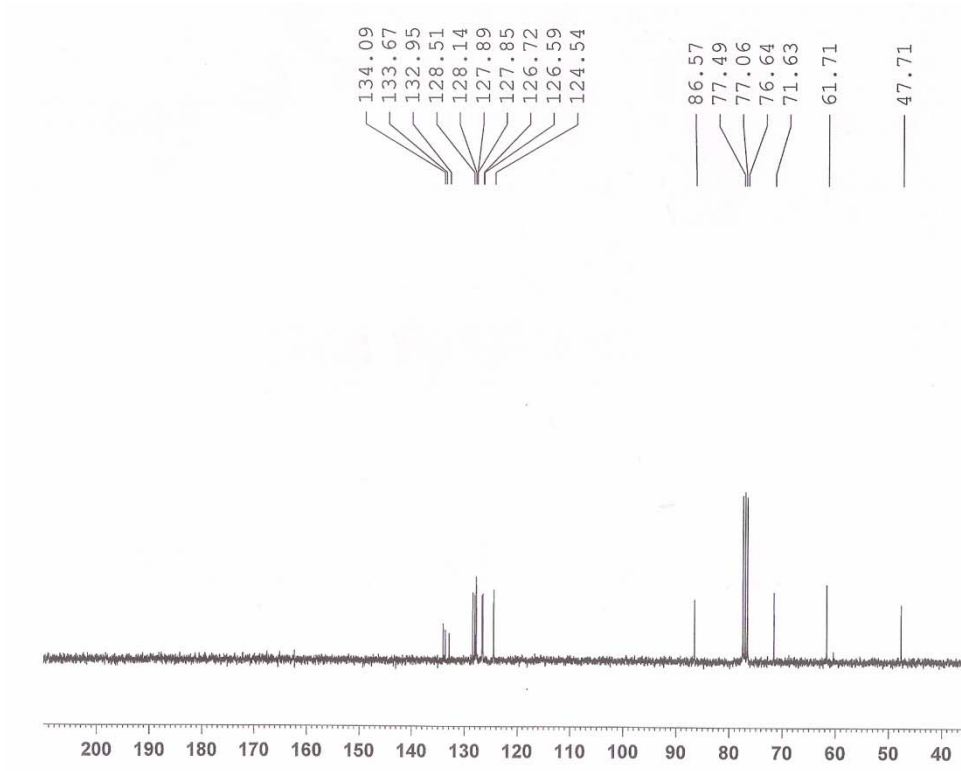


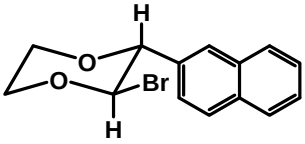
SI Figure 87. ^{13}C NMR spectrum of compound **11a**.



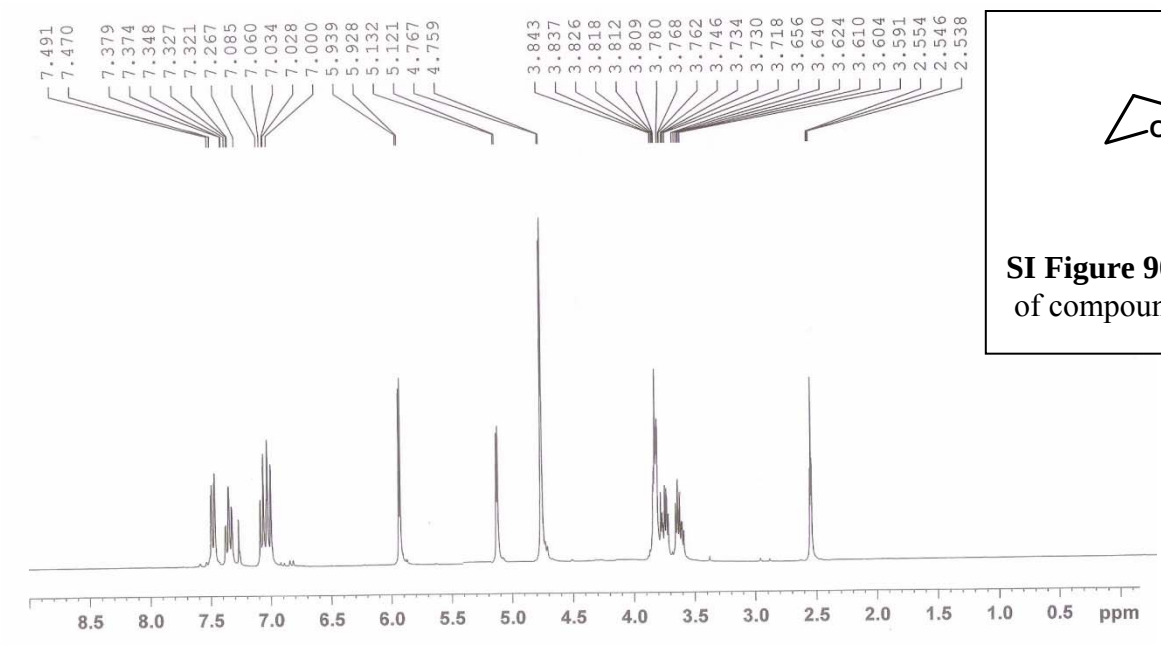


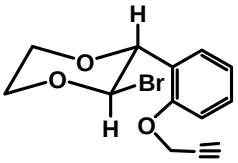
SI Figure 88. ^{1}H NMR spectrum of compound **11b**.



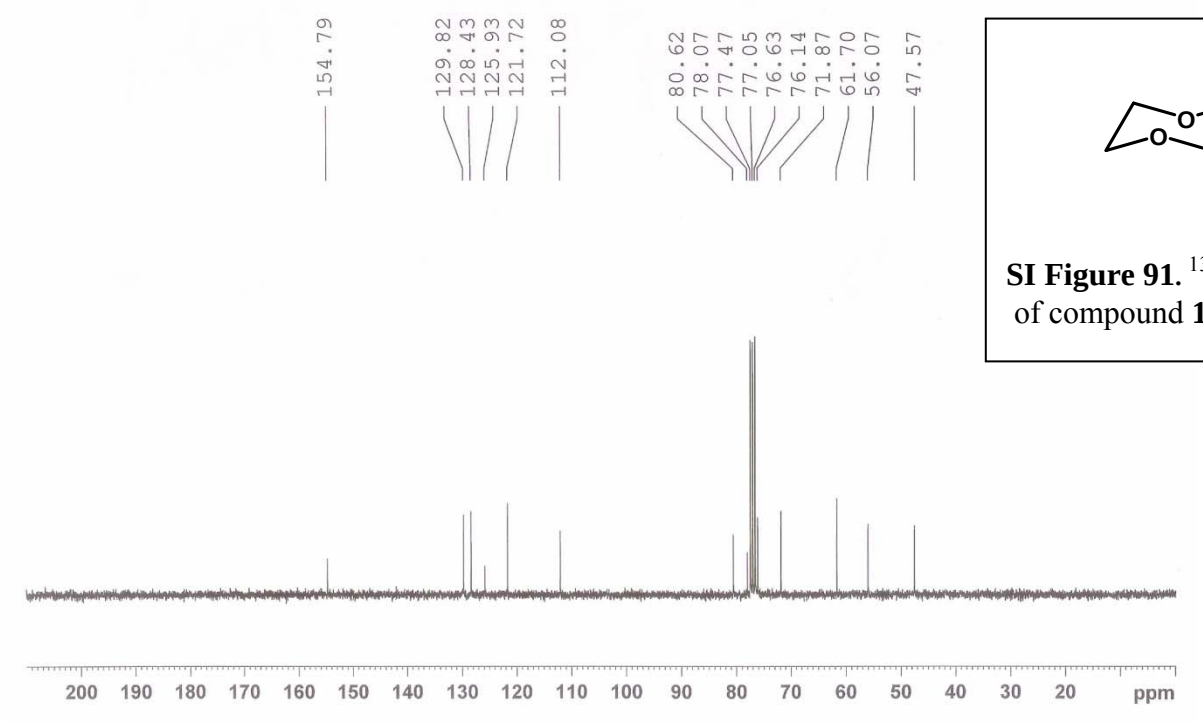


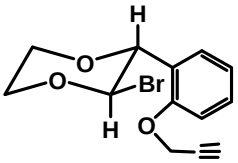
SI Figure 89. ^{13}C NMR spectrum of compound **11b**.



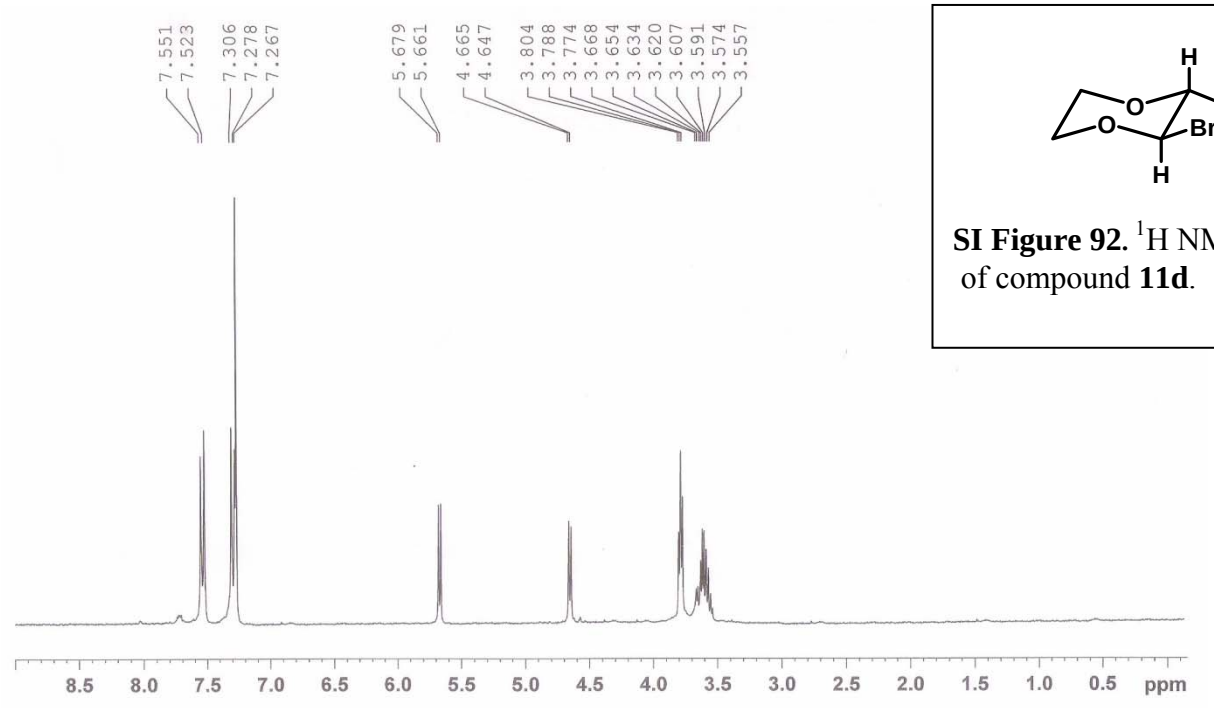


SI Figure 90. ^{1}H NMR spectrum of compound **11c**.

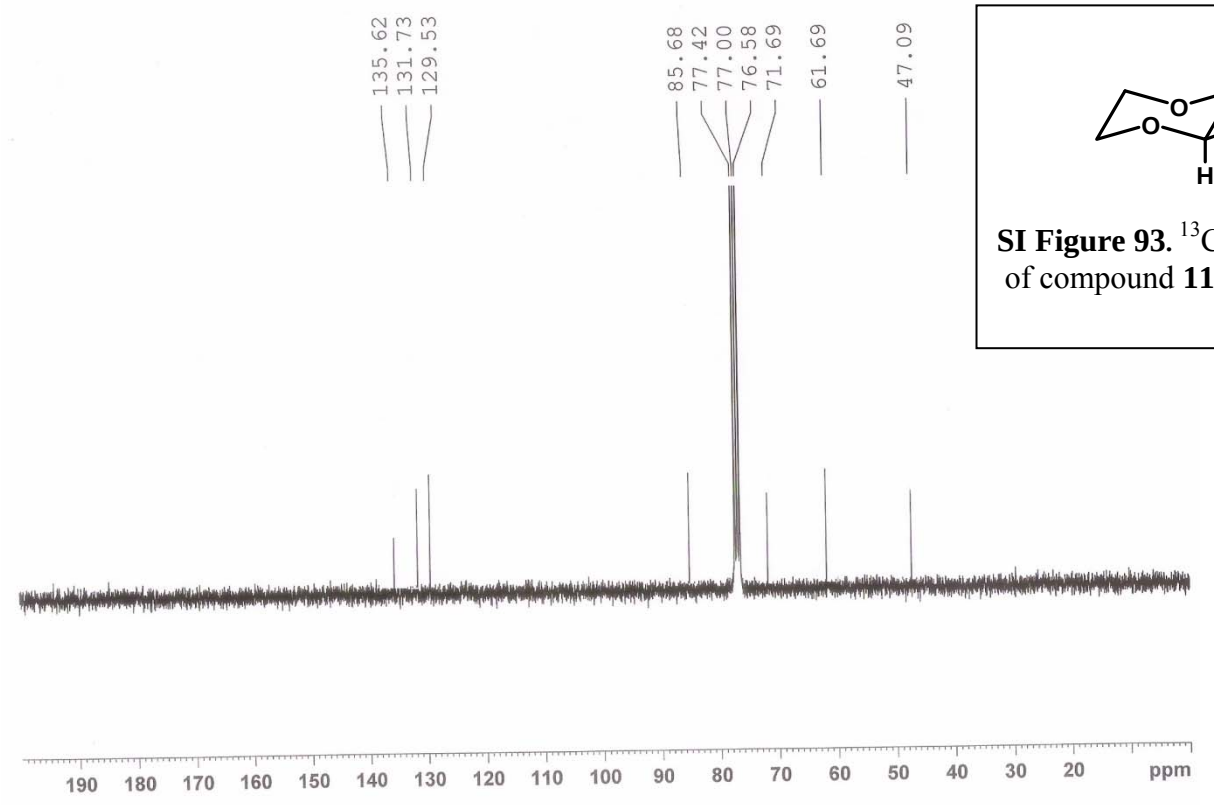


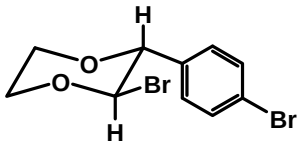


SI Figure 91. ^{13}C NMR spectrum of compound **11c**.

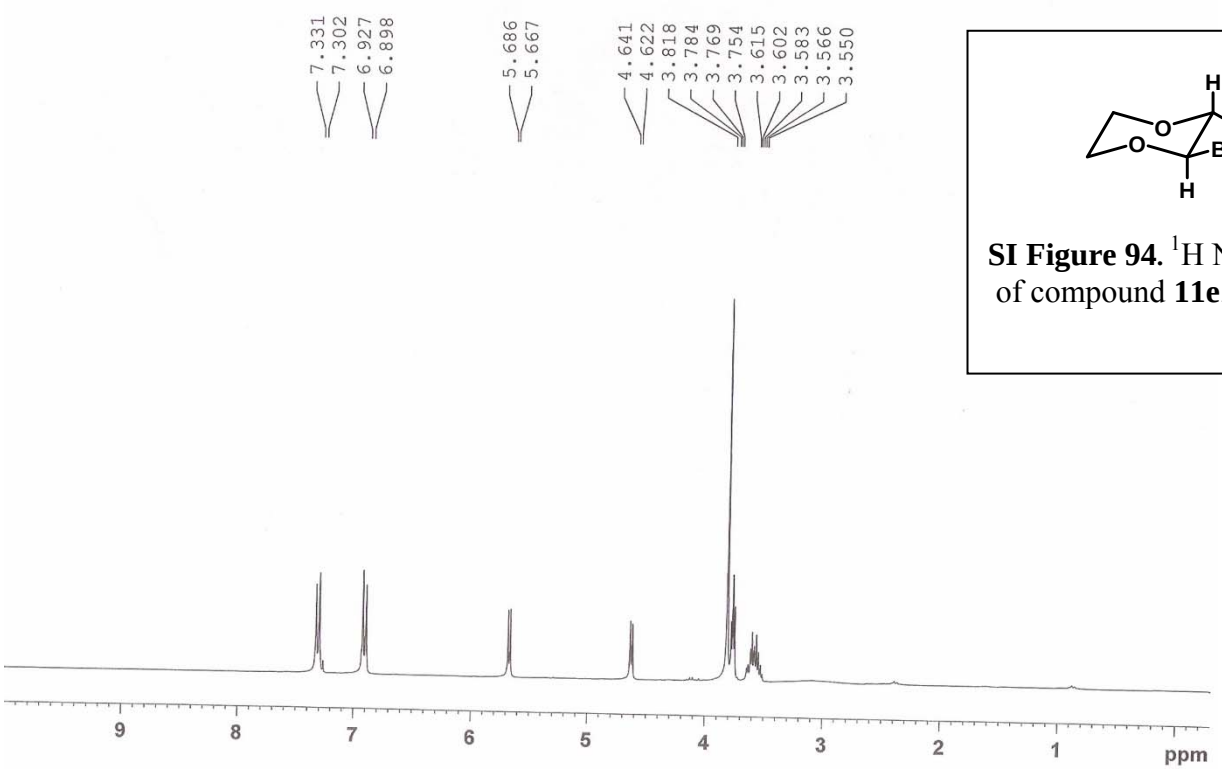


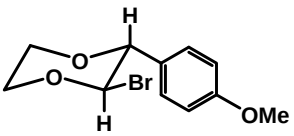
SI Figure 92. ^{1}H NMR spectrum of compound **11d**.



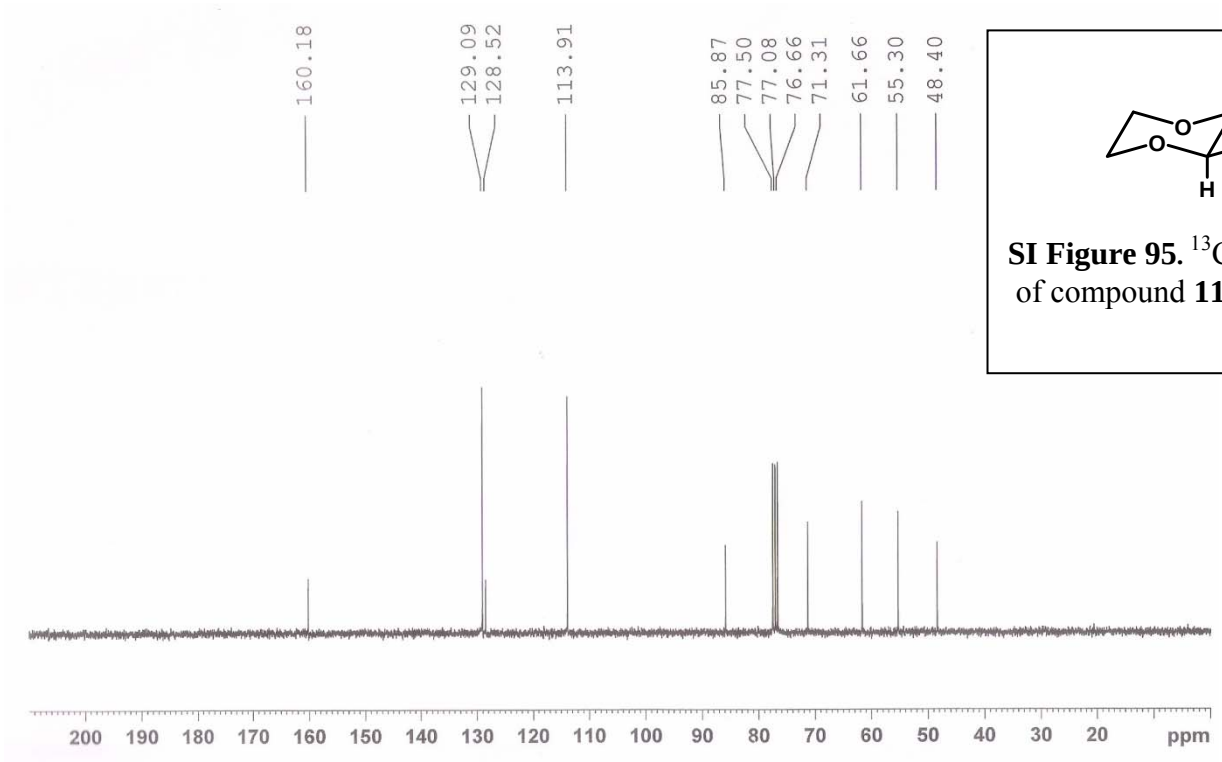


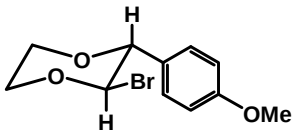
SI Figure 93. ^{13}C NMR spectrum of compound **11d**.



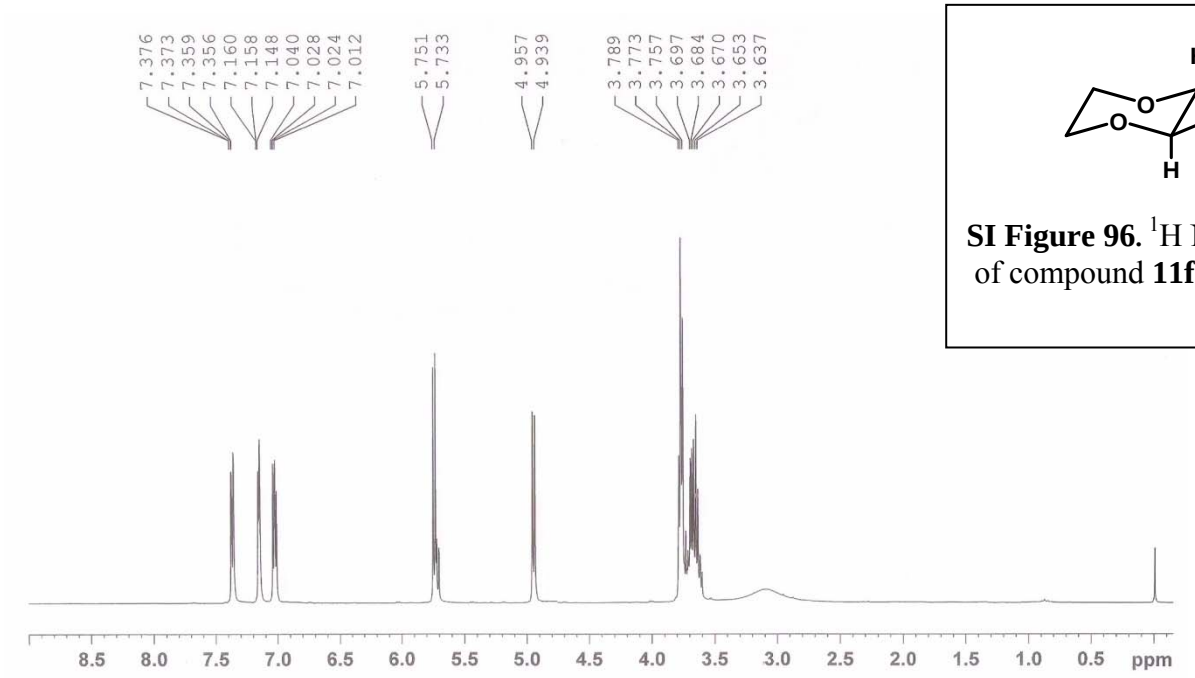


SI Figure 94. ^{1}H NMR spectrum of compound **11e**.

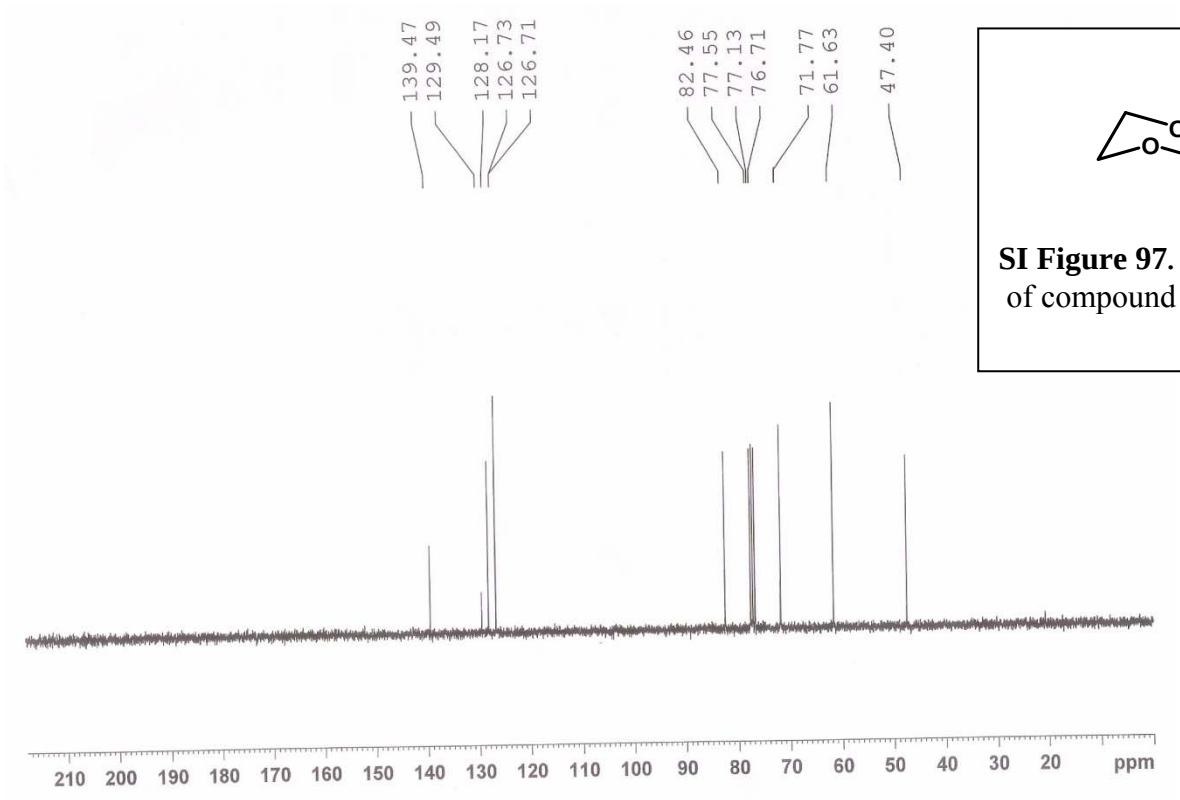


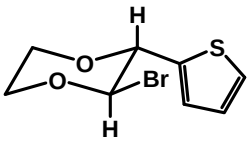


SI Figure 95. ^{13}C NMR spectrum of compound **11e**.



SI Figure 96. ^{1}H NMR spectrum of compound **11f**.





SI Figure 97. ^{13}C NMR spectrum of compound **11f**.