Electronic Supplementary Information

Addition of halide to π-bond directly from aqueous NaX solution: A general strategy for installation of two different functional groups

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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), bs (broad 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) as KBr pellets (solid sample) and in thin film on NaCl window (liquid sample). Optical rotation of the chiral compounds was measured in a polarimeter (Perkin Elmer 343) using standard 10 cm quartz cell in sodium-D lamp at ambient temperature. 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 μm) with maximum temperature 300° C. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Bruker). Single crystal X-ray diffraction studies of the crystalline heterocyclic compound were done in X-ray diffractometer (Bruker Smart Apex-II).

2. Generation of nanoreactor by self-assembled surfactant

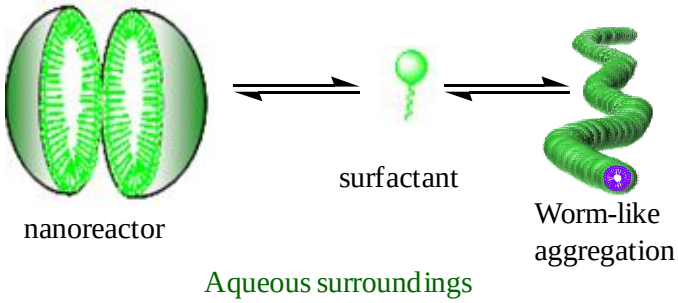


***Figure 1*:** Formation of nanoreactor by self-assembled aggregation

Nature uses well-defined reaction environment for the entire essential chemical reactions through construction of extremely complex assemblies in cell.[1] It provokes synthetic chemists how to use this idea to enhance the synthetic efficiency of chemical conversions in a designed self-assembled reactor of nanometer size. Above the CMC suitable surfactants can generate an organized media (AOM)[2] in water or organic solvents consisting of nanoreactor.[3] It is an unique example of such confined environment. Inside of the aqueous micelle (Figure 1) is sufficiently lipophilic in nature and makes both organic substrates and reagents soluble. Moreover, it not only brings them in close proximity toward enhancing the feasibility of chemical transformations but also protects water-labile reagents, reaction intermediates etc. from hydrolytic decomposition.[4] It simultaneously can exchange ionic, polar, non-polar organic and inorganic components through the interface thereby shifting the equilibrium in forward direction and making even the inaccessible chemical transformation feasible with much faster reaction rate and desired selectivities. Sphere-like assembly of amphiphilic surfactants formed on dissolving surfactants in water was confirmed by the inverted polarizing optical microscope image of its thin film (Figure 2).

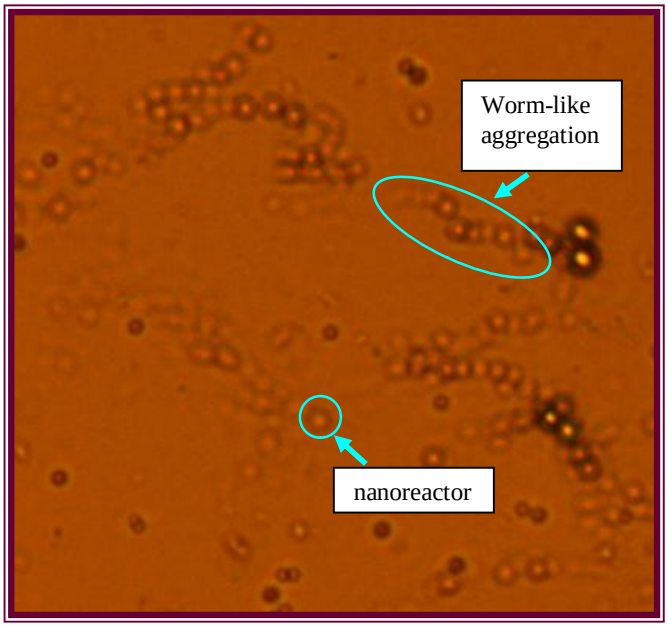
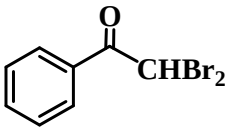


Figure 2: Polarizing optical microscope image of the nanoreactor formed in aqueous CTAB (10%)

3. **General procedure and characterization data of α,α-dihaloketones (3a-g)**

A solution of iodosobenzenediacetate (2.0 mmol) in water (10 mL) was taken in a round-bottom flask (25 mL) and stirred for 30 min. Alkyne **1** (1 mmol) was added under vigorous stirring followed by the addition of surfactant (CTAB/aliquat - 10 mol %). Progress of the reaction was monitored by TLC and the reaction was complete after 2.5-4.5 h depending on the substrates used. The post-reaction mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic portion was washed with brine solution (2 × 10 mL), dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with phenyl acetylene (**1a**, 102 mg, 1.0 mmol) afforded **3a** 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 83% (228 mg, 0.83 mmol). The α,α-dihaloketones (**3a-g**) were characterized by NMR, FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

3.1. **Compound 3a**[5]

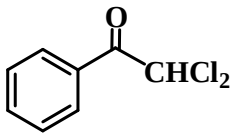


3a

Yield: 83 % (228 mg, 0.83 mmol).
Characteristic: viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.72 (1H, s), 7.48-7.54 (2H, m), 7.61-7.67 (1H, m), 8.07-8.10 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 39.6, 128.9, 129.7, 130.8, 134.4, 185.9.
EI-MS (m/z): 278 (M+2), 276 (M^+), 235, 171, 169, 145, 143, 120, 105, 90, 77.
IR (neat, cm^{-1}): 1091, 1475, 1601, 2926, 3446.

HR-MS (*m*/*z*) for $C_8H_6Br_2O$ (M^+): Calculated 275.8785, found 275.8772 (one of the peaks).

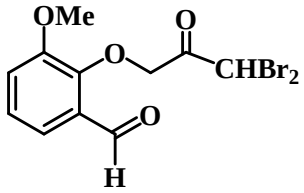
3.2. **Compound 3b**



3b

Yield: 65 % (122 mg, 0.65 mmol).
Characteristic: brown Oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.51 (1H, s), 7.36 (2H, m), 7.54 (1H, q, *J* = 8.1 Hz), 8.23 (1H, d, *J* = 7.8 Hz), 8.09 (1H, d, *J* = 7.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 66.4, 127.8, 128.9, 129.9, 133.3, 162.3.
EI-MS (m/z): 190 (M+2), 188 (M^+), 126, 107, 105, 96, 82, 58.
IR (neat, cm^{-1}): 1091, 1475, 1601, 2926, 3446.
HR-MS (*m*/*z*) for $C_8H_6Cl_2O$ (M^+): Calculated 187.9796, found 187.9725 (one of the peaks).

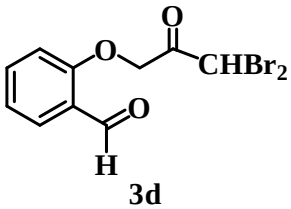
3.3. **Compound 3c**



3c

Yield: 80 % (291 mg, 0.80 mmol).
Characteristic: solid.
Melting Point: 83 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (3H, s), 5.05 (2H, s), 6.62 (1H, s), 7.08 (2H, d, *J* = 4.5 Hz), 7.35 (1H, m), 10.50 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1, 73.3, 108.8, 117.9, 119.0, 120.5, 124.6, 130.1, 152.5, 162.3, 190.4.
EI-MS (m/z): 365 (M+2), 363 (M^+), 303, 137, 120, 82, 51.
IR (KBr, cm^{-1}): 1041, 1169, 1454, 1661, 1690, 2902, 3431.
HR-MS (*m*/*z*) for $C_{11}H_{10}Br_2O_4$ (M+): Calculated 363.8946, found 363.8920 (one of the peaks).

3.4. **Compound 3d**

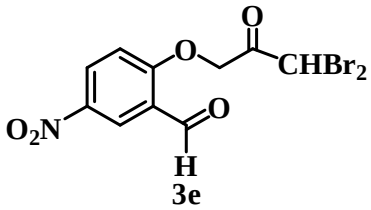


3d

Yield: 82 % (273 mg, 0.82 mmol).
Characteristic: yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.03 (2H, s), 6.77 (1H, s), 7.02 (1H, d, *J* = 8.4 Hz), 7.11 (1H, t, *J* = 7.2 Hz), 7.54-7.59 (1H, m), 7.89 (1H, dd, *J* = 1.8, 7.8 Hz), 10.58 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ 68.5, 107.2, 113.2, 120.4, 121.9, 125.6, 128.5, 135.7, 159.7, 189.6.
EI-MS (m/z): 336 (M+2), 334 (M^+), 332, 278, 276, 274, 253, 225, 211, 198, 185, 170, 118, 63.
IR (neat, cm^{-1}): 1036, 1103, 1161, 1283, 1456, 1479, 1595, 1697, 2863.
HR-MS (*m*/*z*) for $C_{10}H_8Br_2O_3$ (M^+): Calculated 333.8840, found 333.8820 (one of the peaks).

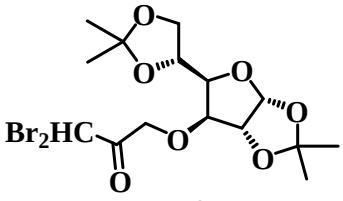
3.5. **Compound 3e**



3e

Yield: 78 % (295 mg, 0.78 mmol).
Characteristic: brown solid.
Melting Point: 78 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.08 (2H, s), 6.78 (1H, s), 7.07 (1H, d, *J* = 9.0 Hz), 8.37 (1H, dd, *J* = 2.7, 9.0 Hz), 8.67 (1H, d, *J* = 2.7 Hz), 10.46 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 69.2, 108.5, 113.5, 118.7, 124.6, 124.7, 125.4, 130.4, 163.2, 187.2.
EI-MS (m/z): 379 (M^+), 341, 281, 207, 186, 171, 152, 137, 82, 80, 53.
IR (KBr, cm^{-1}): 1011, 1070, 1277, 1343, 1593, 1690, 2927, 3465.
HR-MS (*m*/*z*) for $C_{10}H_7Br_2NO_5$ (M^+): Calculated 378.8691, found 378.8696 (one of the peaks).

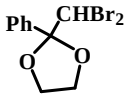
3.6. **Compound 3f**



(-) **3f**

Yield: 75 % (353 mg, 0.75 mmol).
Characteristic: brown oil.
$[\alpha]_D^{20}$ -13.90° (*c* 0.90, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (3H, s), 1.28 (3H, s), 1.35 (3H, s), 1.42 (3H, s), 3.88-3.93 (2H, m), 4.03-4.08 (2H, m), 4.27 (1H, dd, *J* = 6.0, 13.5 Hz), 4.35 (1H, s), 4.46 (1H, s), 4.55 (1H, d, *J* = 3.6 Hz), 5.83 (1H, d, *J* = 3.6 Hz), 6.60 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.4, 26.2, 26.7, 26.8, 67.3, 70.8, 72.5, 81.2, 81.9, 83.0, 105.2, 106.6, 109.0, 111.9, 122.2.
EI-MS (m/z): 472 (M^+), 281, 207, 96, 82, 58.
IR (neat, cm^{-1}): 1085, 1254, 1372, 1381, 1455, 1611, 1664, 2935, 2987.
HR-MS (*m*/*z*) for $C_{15}H_{22}Br_2O_7$ (M^+): Calculated 471.9732, found 471.9722 (one of the peaks).

3.7. **Compound 3g**



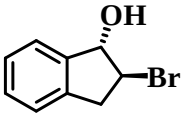
3g

Yield: 85 % (272 mg, 0.85 mmol).
Characteristic: viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (2H, t, *J* = 6.9 Hz), 4.24 (2H, t, *J* = 6.6 Hz), 5.73 (1H, s), 7.29 (3H, t, *J* = 3.0 Hz), 7.48-7.51 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 49.9, 66.7, 108.4, 126.9, 127.9, 129.0, 137.2.
EI-MS (m/z): 321 (M+2), 319 (M^+), 264, 262, 260, 184, 183, 181, 103, 76, 74.
IR (neat, cm^{-1}): 1029, 1043, 1162, 1443, 1471, 2869, 2924.
HR-MS (*m*/*z*) for $C_{10}H_{10}Br_2O_2$ (M^+): Calculated 319.9048, found 319.9120 (one of the peaks).

4. **General procedure and characterization data of 1,2-halohydrins (5a-i)**

A solution of iodosobenzenediacetate (2.0 mmol) in water (10 mL) was taken in a round-bottom flask (25 mL) and stirred for 30 min. Olefin **2** (1 mmol) was added under vigorous stirring followed by the addition of surfactant (CTAB/aliquat 10 mol %). Progress of the reaction was monitored by TLC and the reaction was complete after 1-2 h depending on the used substrate. The post-reaction mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic portion was washed with brine solution (2 × 10 mL), dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with indene (**2a**, 116 mg, 1.0 mmol) afforded **5a** after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:7, v/v) as an eluent in an isolated yield of 87% (184 mg, 0.87 mmol). The 1,2-bromohydrin (**5a-i**) were characterized by NMR, FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

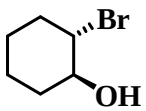
4.1. **Compound 5a**[6]



(±) **5a**

Yield: 87 % (184 mg, 0.87 mmol).
Characteristic: pale yellow solid.
Melting point: 119 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (1H, bs), 3.09-3.18 (1H, dd, *J* = 11.0, 16.0 Hz), 3.45-3.54 (1H, dd, *J* = 11.0, 23.0 Hz), 4.04-4.23 (1H, m), 5.23 (1H, d, *J* = 5.4 Hz), 7.12-7.22 (3H, m), 7.31-7.33 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 40.4, 54.5, 83.4, 124.0, 124.5, 127.6, 129.0, 139.7, 141.6.
EI-MS (m/z): 214 (M+2), 212 (M^+), 196, 194, 133, 115.
IR (KBr, cm^{-1}): 1064, 1166, 1344, 1465, 2924, 3234.
HR-MS (*m*/*z*) for C_9H_9BrO (M^+): calculated 211.9837, found 211.9830 (one of the peaks).

4.2. **Compound 5b**[7]

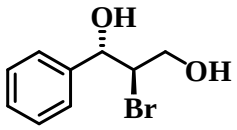


(±) **5b**

Yield: 72 % (128 mg, 0.72 mmol).

Characteristic: colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, m), 1.60-1.84 (3H, m), 2.04-2.08 (1H, m), 2.24-2.30 (1H, m), 2.50 (1H, bs), 3.49-3.57 (1H, m), 3.77-3.87 (1H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 24.1, 26.6, 33.5, 36.2, 61.8, 75.3.
EI-MS (m/z): 180 (M+2), 178 (M^+), 137, 134, 132, 100, 99, 83, 82, 81, 57.
IR (neat, cm^{-1}): 1075, 1120, 1450, 1494, 1606, 2860, 2937, 3433.
HR-MS (*m*/*z*) for $C_6H_{11}BrO$ (M^+): Calculated 177.9993, found 177.9990 (one of the peaks).

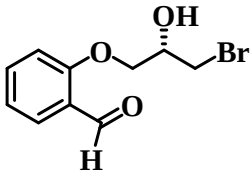
4.3. **Compound 5c**[8]



(±) **5c**

Yield: 82 % (188 mg, 0.82 mmol).
Characteristic: yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (1H, dd, *J* = 4.5, 7.8 Hz), 3.94 (1H, dd, *J* = 4.8, 12.3 Hz), 4.23 (1H, d, *J* = 6.3 Hz), 4.94 (1H, d, *J* = 5.7 Hz), 7.26-7.31 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 59.5, 64.2, 76.8, 126.5, 128.4, 128.6, 140.3.
EI-MS (m/z): 232 (M+2), 230 (M^+), 182, 184, 133, 107, 105, 79, 77.
IR (neat, cm^{-1}): 1077, 1453, 1494, 2925, 3399.
HR-MS (*m*/*z*) for $C_9H_{11}BrO_2$ (M^+): Calculated 229.9942, found 229.9918 (one of the peaks).

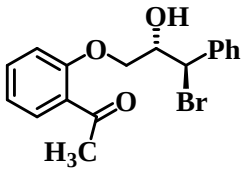
4.4. **Compound 5d**



(±) **5d**

Yield: 70 % (180 mg, 0.70 mmol).
Characteristic: viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.11 (1H, bs), 3.52-3.62 (1H, m), 3.98 (1H, d, *J* = 3.3 Hz), 4.11-4.24 (1H, m), 4.34 (2H, d, *J* = 3.6 Hz), 6.80-7.03 (2H, m), 7.45-7.56 (1H, m), 7.80-7.82 (1H, m), 10.29 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 50.6, 64.1, 69.3, 112.7, 121.6, 125.0, 129.9, 136.1, 159.9, 186.9.
EI-MS (m/z): 260 (M+2), 258 (M^+), 179, 165, 161, 136, 135, 121, 107, 105, 77.
IR (neat, cm^{-1}): 1242, 1455, 1484, 1599, 1686, 2927, 3433.
HR-MS (*m*/*z*) for $C_{10}H_{11}BrO_3$ (M^+): Calculated 257.9892, found 257.9881 (one of the peaks).

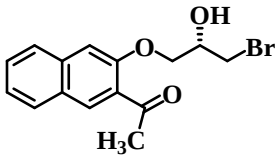
4.5. **Compound 5e**



(±) **5e**

Yield: 85 % (295 mg, 0.85 mmol).
Characteristic: yellow viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.68 (3H, s), 4.58-4.68 (1H, m), 4.72-4.81 (2H, m), 5.28 (1H, d, *J* = 10.2 Hz), 6.83 (1H, d, *J* = 8.7 Hz), 7.28-7.35 (6H, m), 7.38-7.52 (1H, m), 7.76-7.81 (1H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 32.2, 52.3, 52.5, 71.9, 114.6, 118.1, 127.8, 128.8, 129.2, 130.2, 133.3, 136.1, 139.1, 156.1, 197.8.
EI-MS (m/z): 348 (M^+), 252, 250, 203, 120, 105, 91, 79, 77.
IR (neat, cm^{-1}): 1066, 1149, 1225, 1395, 1454, 1481, 1588, 1678, 2924, 3032, 3065, 3338.
HR-MS (*m*/*z*) for $C_{17}H_{17}BrO_3$ (M^+): Calculated 348.0361, found 348.0345 (one of the peaks).

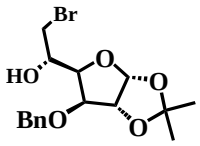
4.6. **Compound 5f**



(±) **5f**

Yield: 83 % (267 mg, 0.83 mmol).
Characteristic: yellowish oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.68 (3H, m), 3.87-3.97 (2H, m), 4.29-4.41 (2H, m), 4.48-4.56 (1H, m), 7.49-7.55 (2H, m), 7.58-7.63 (2H, m), 7.76-7.82 (1H, m), 8.29-8.33 (1H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 31.0, 32.7, 48.4, 123.3, 124.7, 125.1, 127.0, 127.9, 128.0, 128.3, 128.6, 136.5, 153.9, 200.5.
EI-MS (m/z): 322 (M^+), 282, 281, 207, 133, 115, 105, 82, 57.
IR (neat, cm^{-1}): 1074, 1244, 1272, 1337, 1360, 1681, 3058, 3436.
HR-MS (*m*/*z*) for $C_{15}H_{15}BrO_3$ (M^+): Calculated 322.0205, found 322.0299 (one of the peaks).

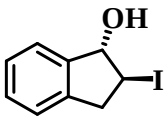
4.7. **Compound 5g**



(-) **5g**

Yield: 86 % (319 mg, 0.86 mmol).
Characteristic: viscous liquid.
$[\alpha]_D^{20}$ -40.23° (*c* 0.85, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (3H, s), 1.51 (3H, s), 3.62-3.70 (2H, m), 4.10 (1H, d, *J* = 2.7 Hz), 4.38-4.46 (3H, m), 4.69-4.73 (2H, m), 5.98 (1H, d, *J* = 3.9 Hz), 7.33-7.38 (5H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 26.4, 26.8, 34.7, 49.5, 71.8, 81.4, 82.1, 82.2, 104.7, 112.2, 128.0, 128.3, 128.7, 136.5.
EI-MS (m/z): 374 (M+2), 372 (M^+), 251, 249, 209, 207, 127, 91, 71, 69.
IR (neat, cm^{-1}): 1075, 1106, 1163, 1215, 1374, 1388, 1455, 2931, 2988.
HR-MS (*m*/*z*) for $C_{16}H_{21}BrO_5$ (M^+): Calculated 372.0572, found 372.0555 (one of the peaks).

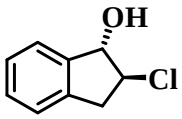
4.8. **Compound 5h**[8]



(±) **5h**

Yield: 80 % (208 mg, 0.80 mmol).
Characteristic: violet solid.
Melting point: 95 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.93 (1H, bs), 3.10-3.27 (1H, m), 3.46-3.55 (1H, m) 4.09-4.23 (1H, m), 5.32 (1H, d, *J* = 6.3 Hz), 7.11-7.41 (4H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 30.1, 42.3, 85.0, 123.8, 124.3, 127.5, 128.8, 140.9, 142.0.
EI-MS (m/z): 261 (M+1), 260 (M^+), 243, 242, 133, 116, 115, 105, 79.
IR (KBr, cm^{-1}): 1065, 1113, 1342, 1460, 2925, 3324.
HR-MS (*m*/*z*) for C_9H_9IO (M^+): Calculated 259.9698, found 259.9690 (one of the peaks).

4.9. **Compound 5i**



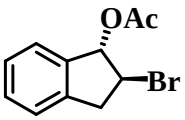
(±) **5i**

Yield: 71 % (119 mg, 0.71 mmol).
Characteristic: solid.
Melting point: 101 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (1H, dd, *J* = 7.2, 15.9 Hz), 3.44 (1H, dd, *J* = 7.2, 15.9 Hz), 4.18-4.25 (1H, m), 5.22 (1H, s), 7.13-7.40 (5H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 39.8, 64.6, 83.0, 124.1, 124.6, 127.6, 129.0, 139.0, 141.4.
EI-MS (m/z): 170 (M+2), 168 (M^+), 150, 133, 132, 131, 115, 105, 103, 77, 57.
IR (KBr, cm^{-1}): 1066, 1348, 1461, 2369, 3215, 3749.
HR-MS (*m*/*z*) for C_9H_9ClO (M^+): Calculated 168.0342, found 168.0340 (one of the peaks).

5. **General procedure and characterization data of 1,2-haloacetates (7a-f)**

A mixture of alkene **2** (1.0 mmol), anhydrous $MgSO_4$ (0.5 g) and dry dichloromethane (15 mL) were taken together in a round-bottom flask (25 mL) and content was cooled to 0^o C. $PhI(OAc)_2$ (644 mg, 2.0 mmol) and surfactant (CTAB/aliquat 10 mole%), NaBr (1.0 mm) were added successively. Then the content was allowed to attain room temperature. The reaction was complete after 1.5-2.5 h. The post-reaction mixture was extracted with dichloromethane (3 × 10 mL) and the combined organic portion was washed with brine solution (2 × 10 mL), dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with indene (**2a**, 116 mg, 1.0 mmol) afforded **7a** after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:8, v/v) as an eluent in an isolated yield of 75% (190 mg, 0.75 mmol). The 1,2-haloacetate (**7a**-**f**) were characterized by NMR, FT-IR and Mass (EI-MS and HR-MS) spectral analysis.

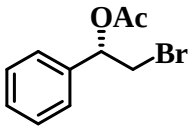
5.1. **Compound 7a**



(±) **7a**

Yield: 75 % (190 mg, 0.75 mmol).
Characteristic: colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (3H, s), 3.20 (1H, dd, *J* = 4.2, 17.1 Hz), 3.65 (1H, dd, *J* = 6.6, 17.1 Hz), 4.41-4.46 (1H, m), 6.27 (1H, d, *J* = 3.6 Hz), 7.19-7.42 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0, 41.4, 49.9, 83.9, 124.8, 125.8, 127.6, 129.7, 138.4, 141.2, 170.3.
EI-MS (m/z): 256 (M+2), 254 (M^+), 211, 195, 193, 173, 132, 131, 115, 103, 77.
IR (neat, cm^{-1}): 1018, 1048, 1227, 1371, 1740, 2926.
HR-MS (*m*/*z*) for $C_{11}H_{11}BrO_2$ (M^+): Calculated 253.9942, found 253.9930 (one of the peaks).

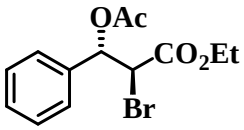
5.2. **Compound 7b**[8]



(±) **7b**

Yield: 71 % (171 mg, 0.71 mmol).
Characteristic: yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (3H, s), 3.56-3.76 (2H, m), 5.98 (1H, dd, *J* = 4.8, 7.8 Hz), 7.31-7.36 (5H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 20.9, 34.2, 74.8, 126.5, 128.7, 128.8, 137.7, 169.8.
EI-MS (m/z): 242 (M^+), 184, 182, 164, 162, 120, 107, 103, 79, 77.
IR (neat, cm^{-1}): 1074, 1237, 1494, 1747, 2926.
HR-MS (*m*/*z*) for $C_{10}H_{11}BrO_2$ (M^+): Calculated 241.9942, found 241.9935 (one of the peaks).

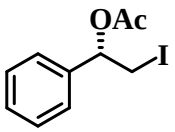
5.3. **Compound 7c**



(±) **7c**

Yield: 79 % (248 mg, 0.79 mmol).
Characteristic: yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (3H, t, *J* = 6.9 Hz), 2.04 (3H, s), 4.24-4.37 (2H, m), 4.51 (1H, d, *J* = 9.3 Hz), 6.15 (1H, d, *J* = 10.2 Hz), 7.32-7.42 (5H, m).
^{13}C NMR (75 MHz,$CDCl_3$): δ 13.9, 20.7, 46.4, 62.3, 75.5, 127.9, 128.5, 129.1, 136.0, 167.6, 168.6.
EI-MS (m/z): 314 (M^+), 254, 252, 193, 149, 147, 131, 120, 107, 103, 91, 77.
IR (neat, cm^{-1}): 1020, 1145, 1454, 1737, 2853, 2925.
HR-MS (*m*/*z*) for $C_{13}H_{15}BrO_4$ (M^+): Calculated 314.0154, found 314.0151 (one of the peaks).

5.4. **Compound 7d**

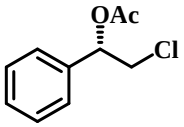


(±) **7d**

Yield: 84 % (243 mg, 0.84 mmol).
Characteristic: viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (3H, s), 3.42-3.48 (2H, m), 5.88 (1H, dd, *J* = 6.0, 7.5 Hz), 7.36 (5H, s).
^{13}C NMR (75 MHz,$CDCl_3$): δ 7.6, 20.9, 75.1, 126.3, 128.6, 128.7, 138.4, 169.6.
EI-MS (m/z): 289 (M^+), 184, 169, 162, 142, 120, 104, 91, 77.
IR (neat, cm^{-1}): 1049, 1240, 1453, 1494, 1722, 2926.
HR-MS (*m*/*z*) for $C_{10}H_{11}IO_2$ (M^+): Calculated 289.9804, found 289.9810 (one of the peaks).

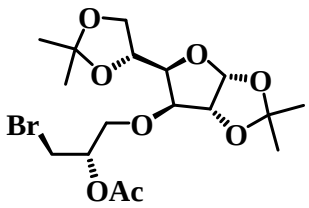
5.5. **Compound 7e**[9]



(±) **7e**

Yield: 71 % (140 mg, 0.71 mmol).
Characteristic: viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (3H, s), 3.62-3.69 (2H, m), 5.89 (1H, dd, *J* = 4.8, 7.8 Hz), 7.26 (5H, s).
^{13}C NMR (75 MHz,$CDCl_3$): δ 20.9, 46.4, 75.0, 126.6, 128.6, 128.8, 137.2, 170.0.
EI-MS (m/z): 200 (M+2), 198 (M^+), 163, 162, 140, 139, 138, 122, 120, 121, 107, 103, 79, 77.
IR (neat, cm^{-1}): 1024, 1229, 1373, 1403, 1455, 1746, 2855, 2928.
HR-MS (*m*/*z*) for $C_{10}H_{11}ClO_2$ (M^+): Calculated 198.0448, found 198.0344 (one of the peaks).

5.6. **Compound 7f**



(±) **7f** dr: 60: 40

Yield: 76 % (332 mg, 0.76 mmol).
Characteristic: viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (3H, s), 1.33 (3H, s), 1.41 (3H, s), 1.48 (3H, s), 2.10 (3H, s), 3.50-3.60 (1H, m), 3.71-3.79 (1H, m), 3.93-4.41 (7H, m), 5.43 (1H, t, *J* = 3.6 Hz), 5.06-5.10 (1H, m), 5.86 (1H, d, *J* = 3.6 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 20.8, 26.7, 26.8, 29.8, 30.2, 30.7, 30.8, 46.9, 53.3, 64.4, 67.4, 67.5, 69.0, 69.1, 69.2, 69.4, 70.8, 71.1, 71.3, 71.5, 72.2, 72.3, 81.2, 82.4, 82.5, 82.9, 83.0, 83.7, 105.2, 109.0, 11.95, 169.9, 170.1.
EI-MS (m/z): 440 (M+2), 438 (M^+), 385, 357, 199, 201, 127, 101, 72, 51.
IR (neat, cm^{-1}): 1078, 1216, 1256, 1373, 1456, 1618, 1720, 2935, 2981, 3450.
HR-MS (*m*/*z*) for $C_{17}H_{27}BrO_8$ (M^+): Calculated 438.0889, found 438.0852 (one of the peaks).

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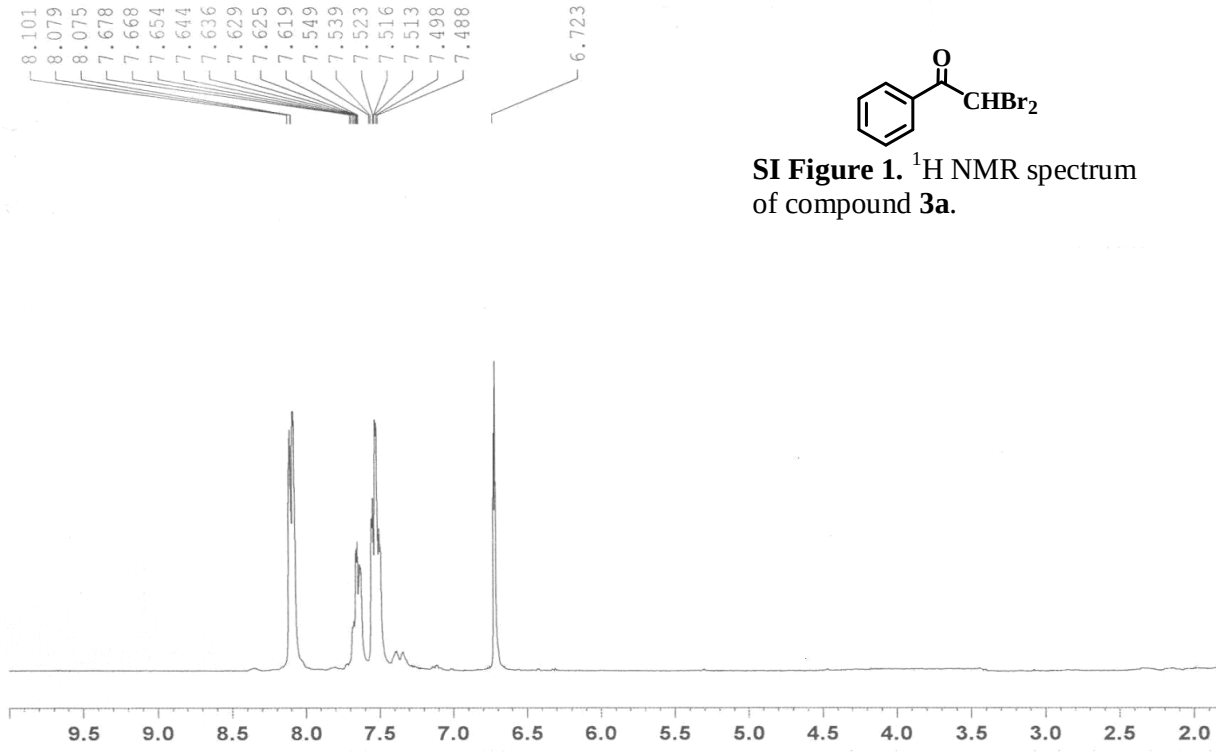
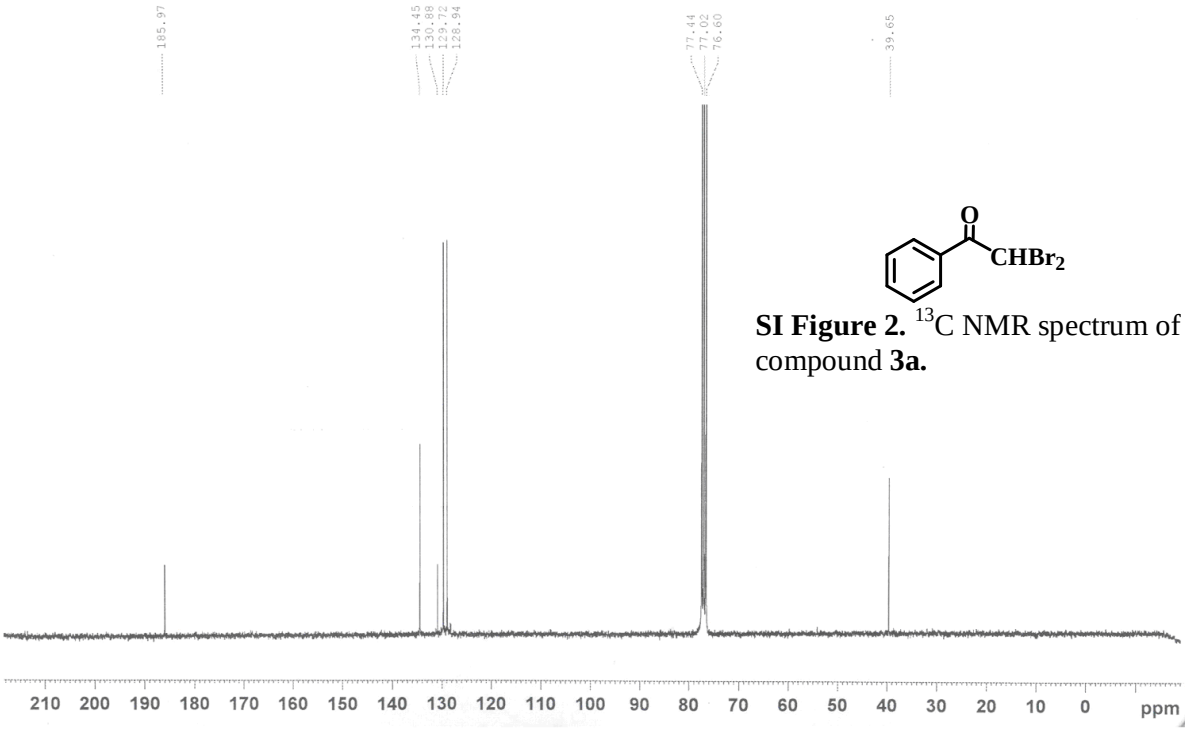
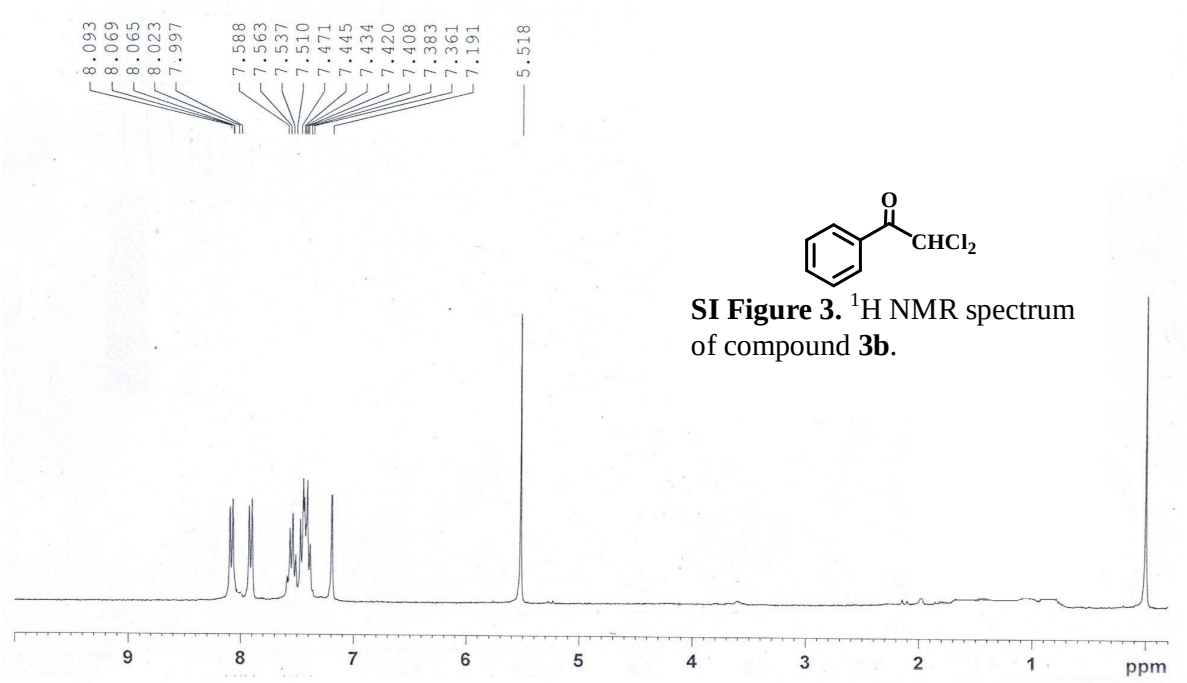
6. ^{1}H and ^{13}C spectra of the compounds (3a-g, 5a-i and 7a-f)



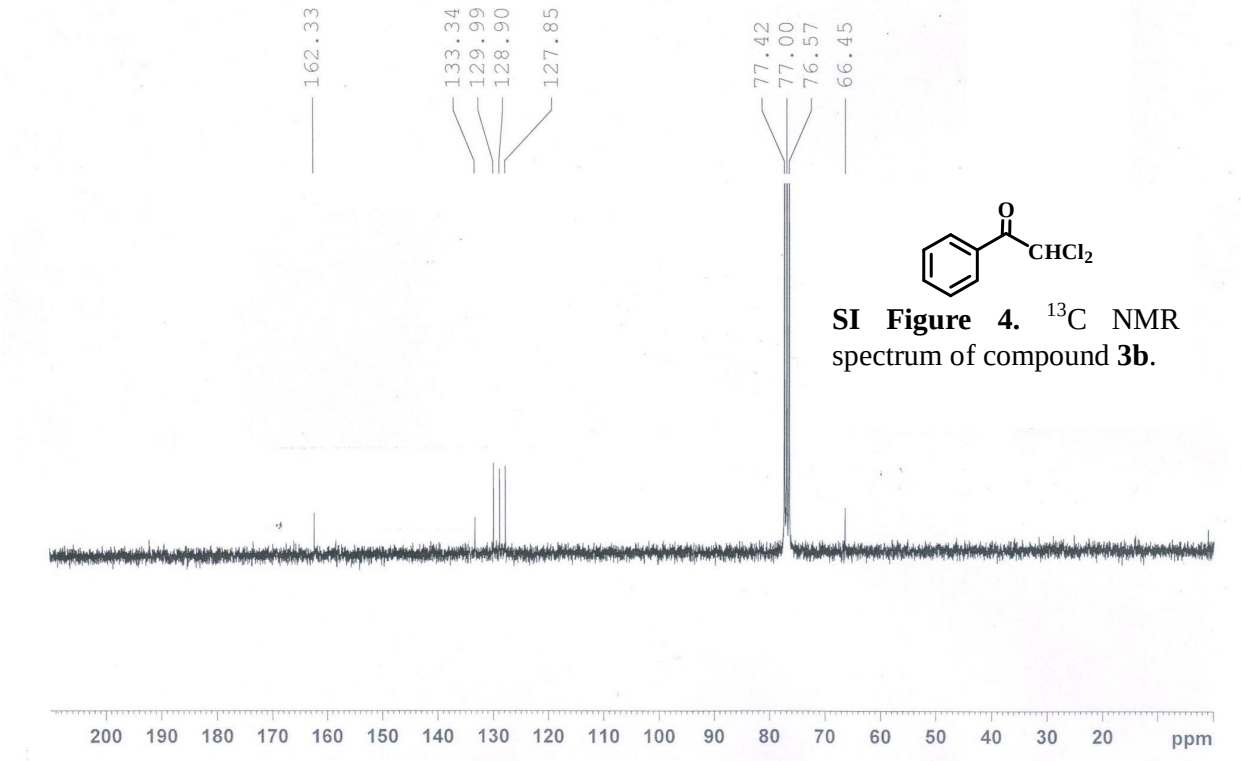
SI Figure 1. ^{1}H NMR spectrum of compound **3a**.



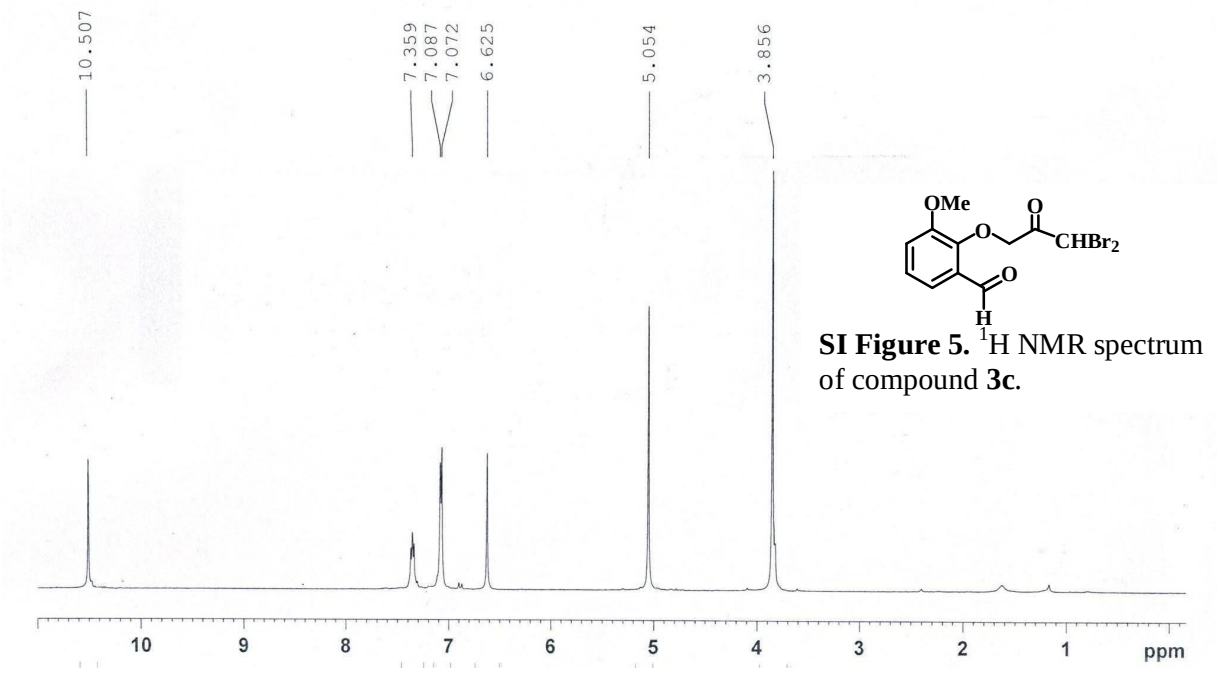
SI Figure 2. ^{13}C NMR spectrum of compound **3a.**



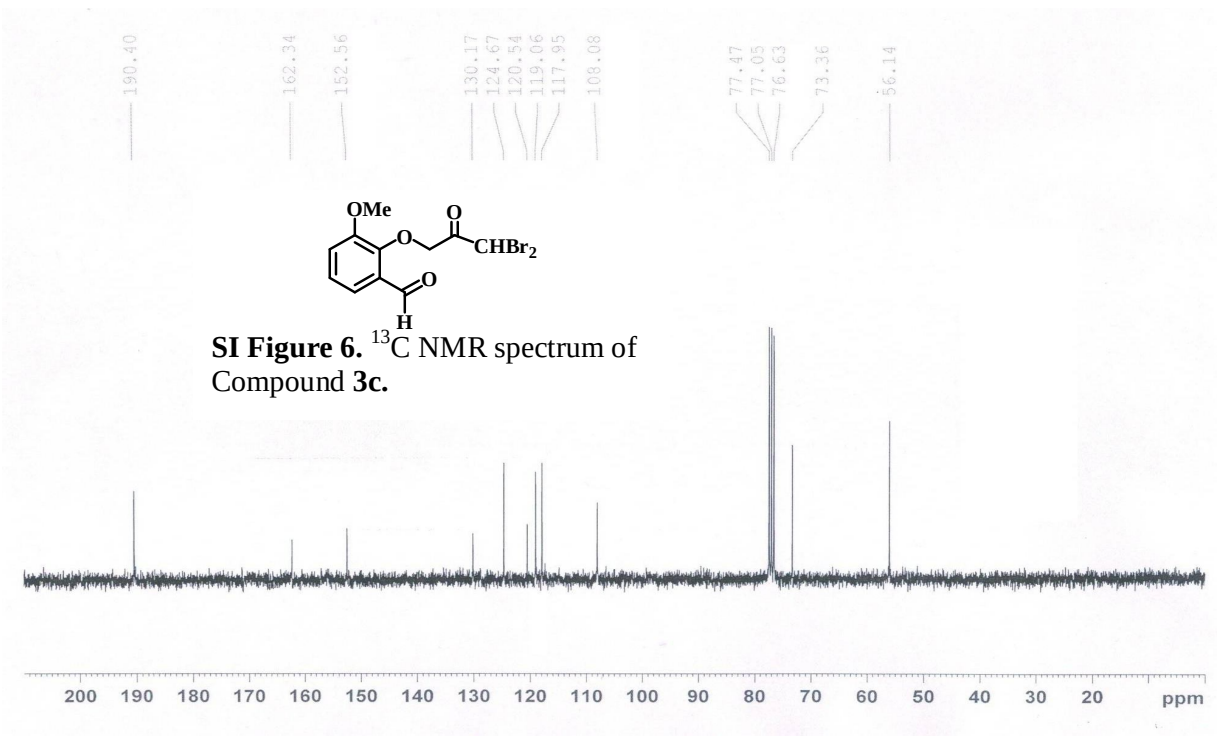
SI Figure 3. ^{1}H NMR spectrum of compound **3b**.



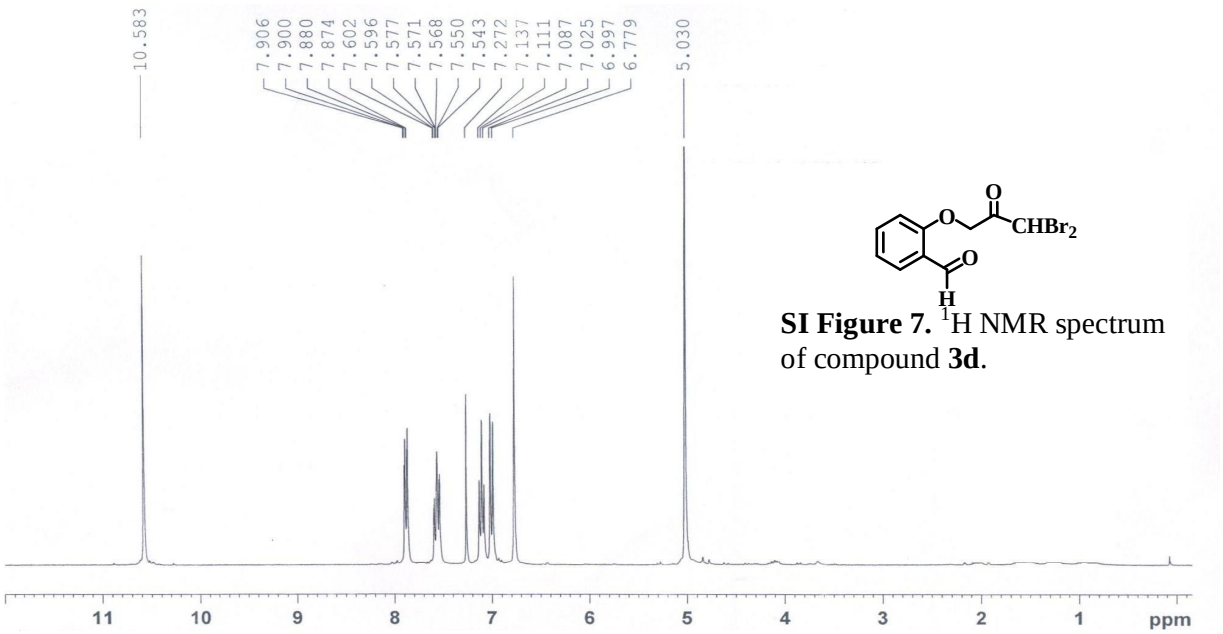
SI Figure 4. ^{13}C NMR spectrum of compound **3b**.



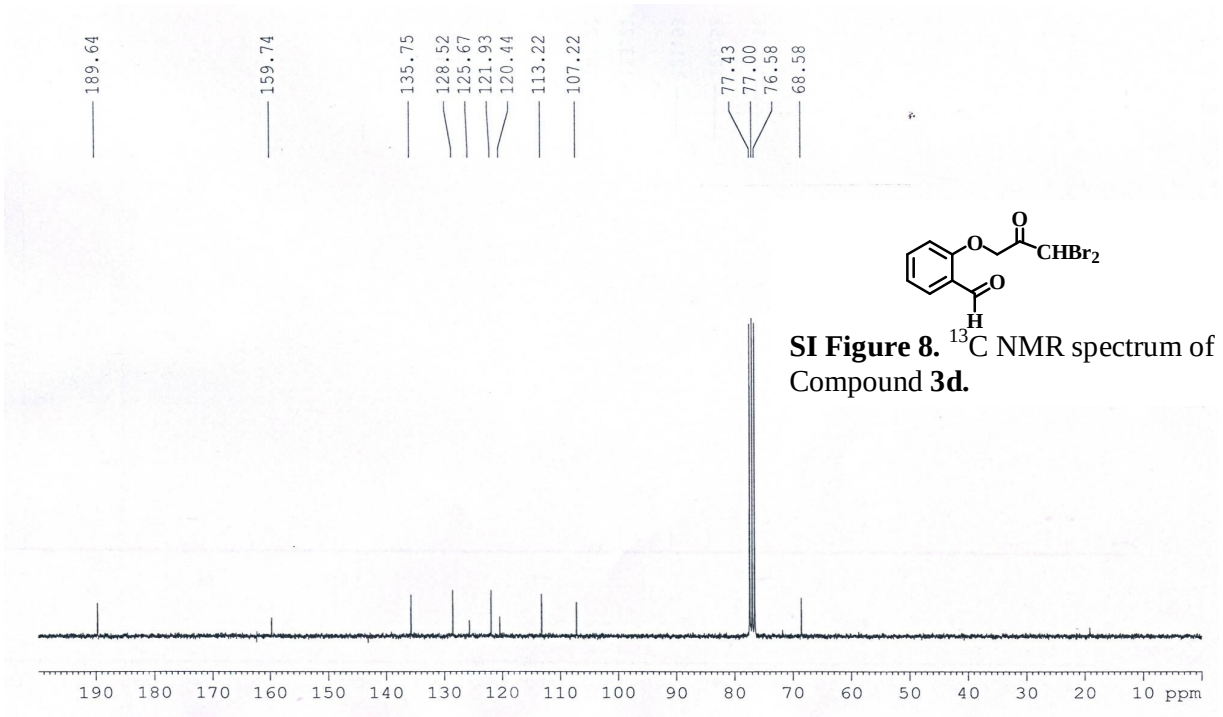
SI Figure 5. ^{1}H NMR spectrum of compound **3c**.



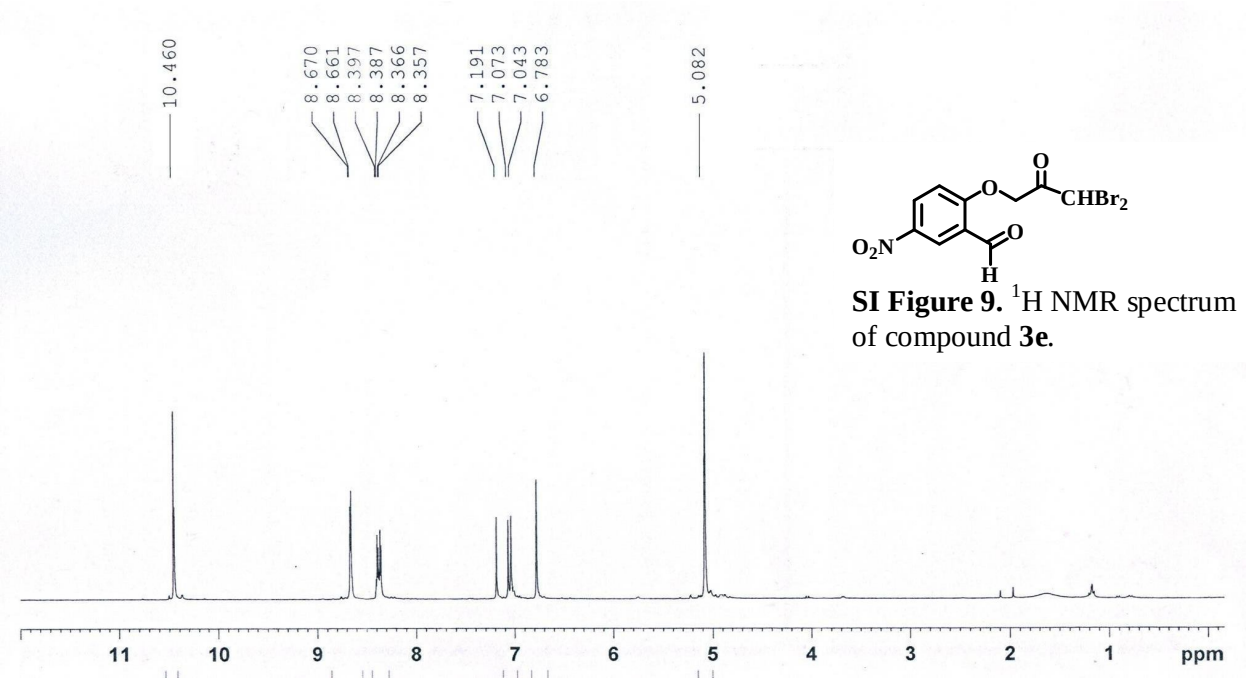
SI Figure 6. ^{13}C NMR spectrum of Compound **3c.**



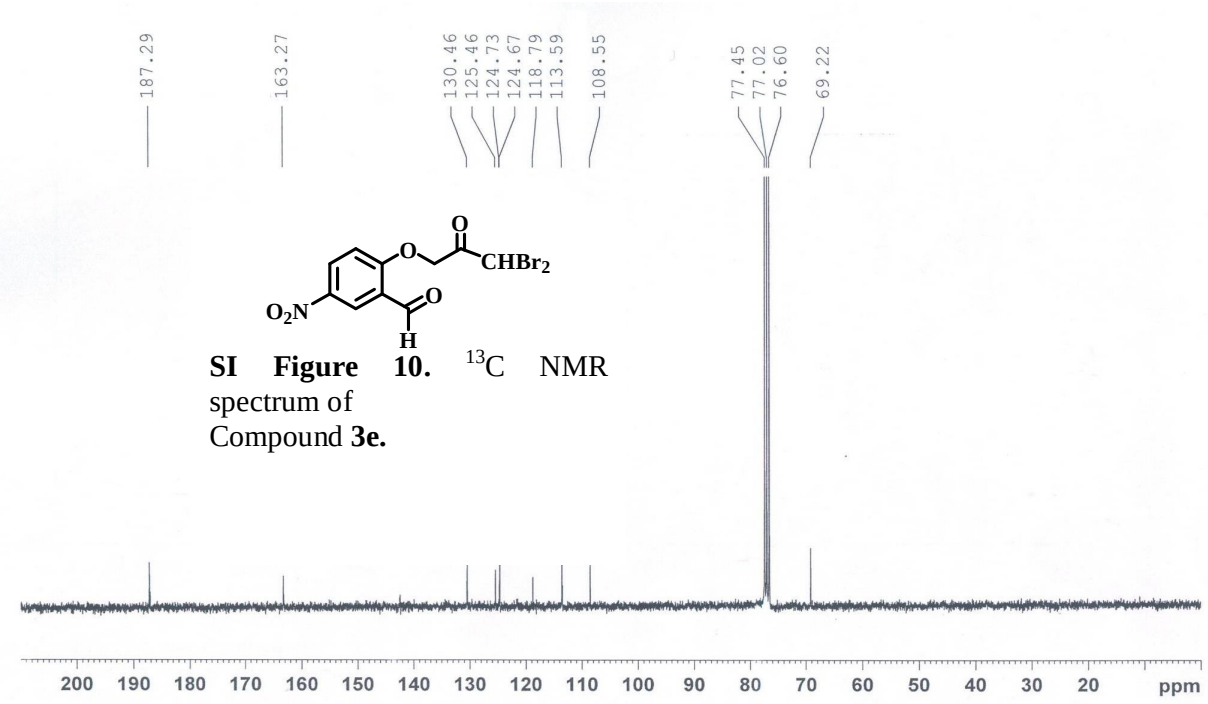
SI Figure 7. ^{1}H NMR spectrum of compound **3d**.



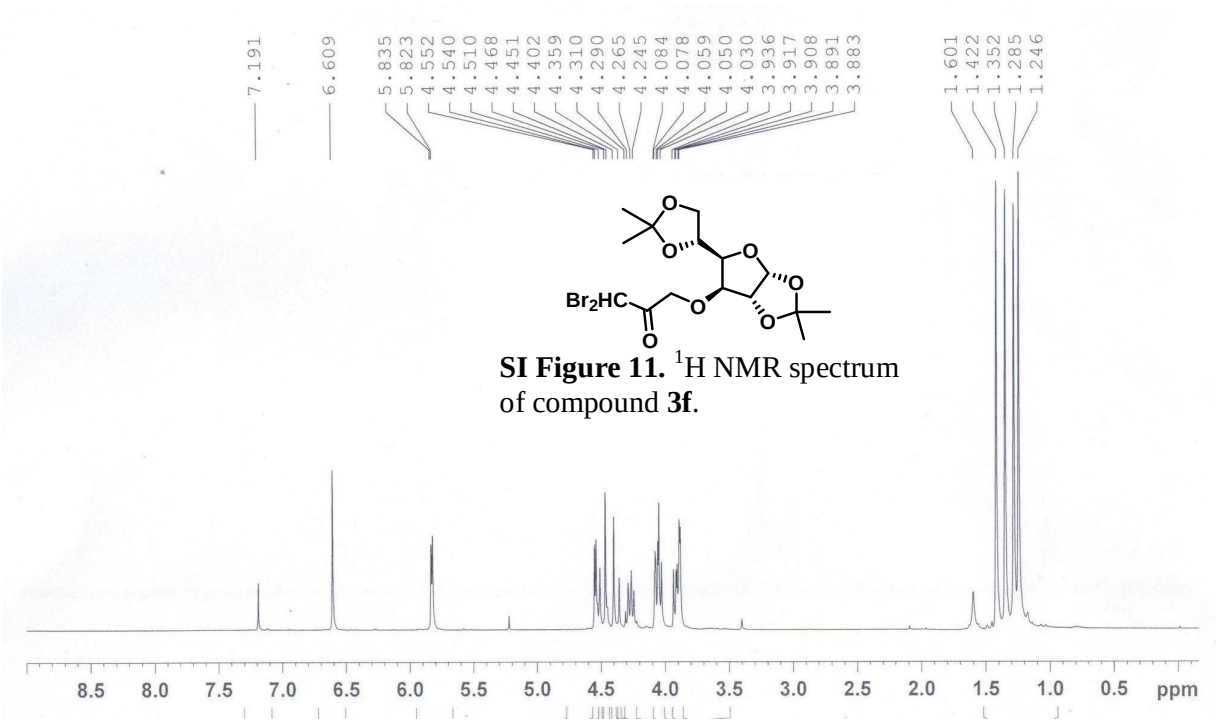
SI Figure 8. ^{13}C NMR spectrum of Compound **3d.**



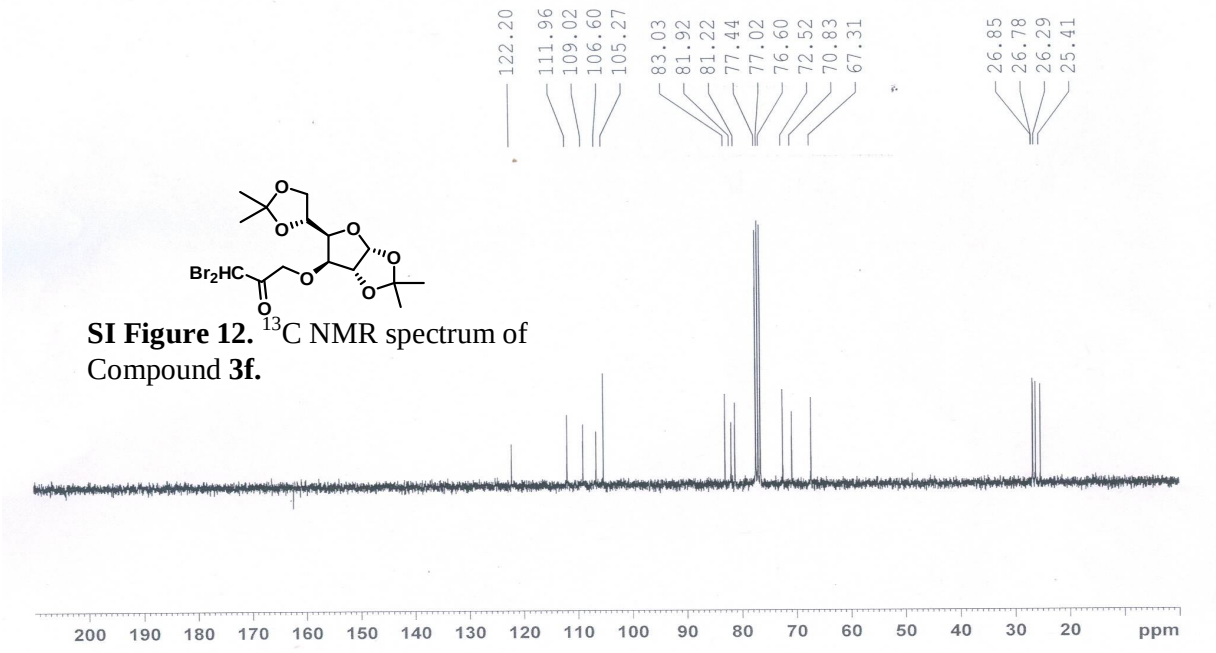
SI Figure 9. ^{1}H NMR spectrum of compound **3e**.



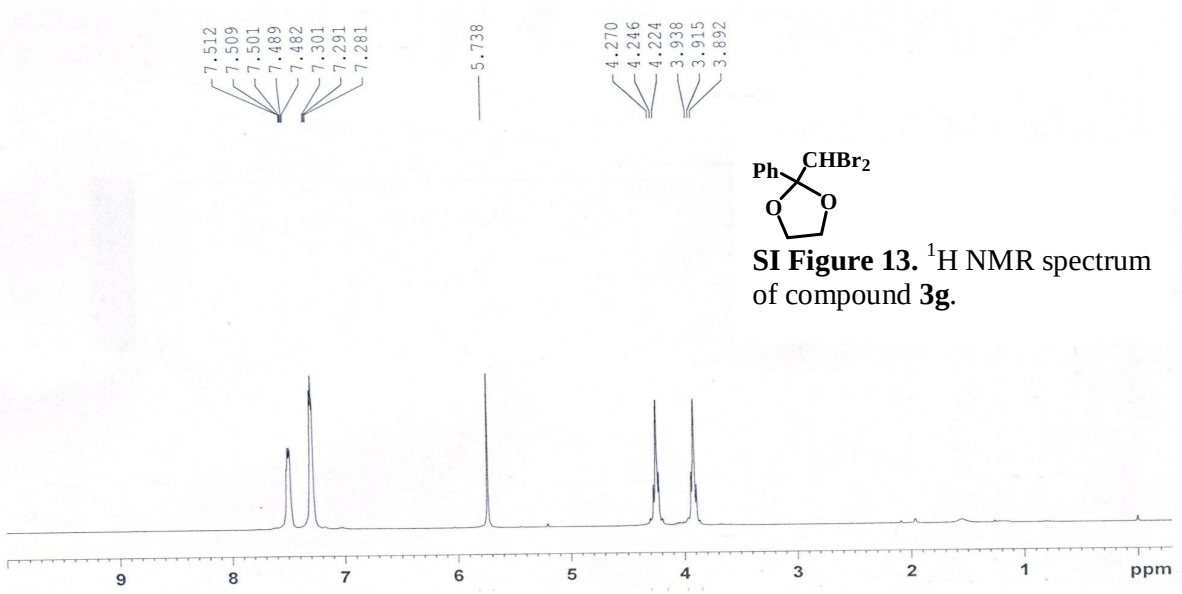
SI Figure 10. ^{13}C NMR spectrum of Compound **3e.**



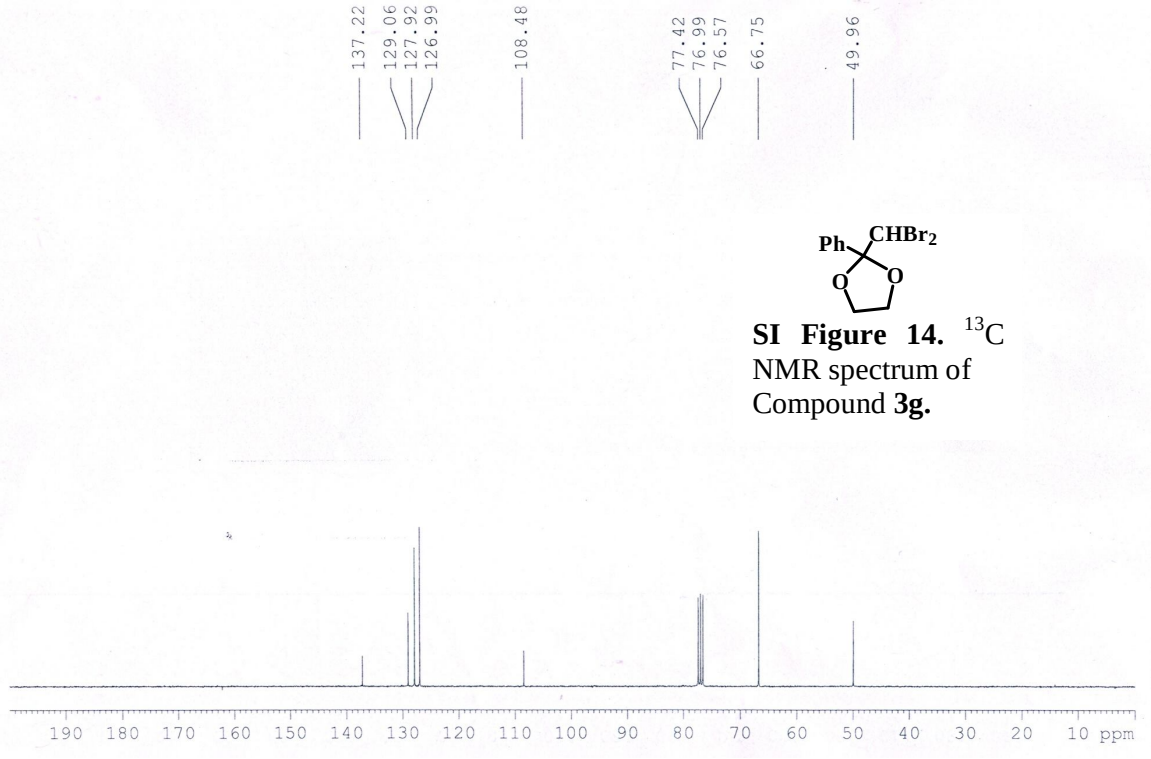
SI Figure 11. ^{1}H NMR spectrum of compound **3f**.



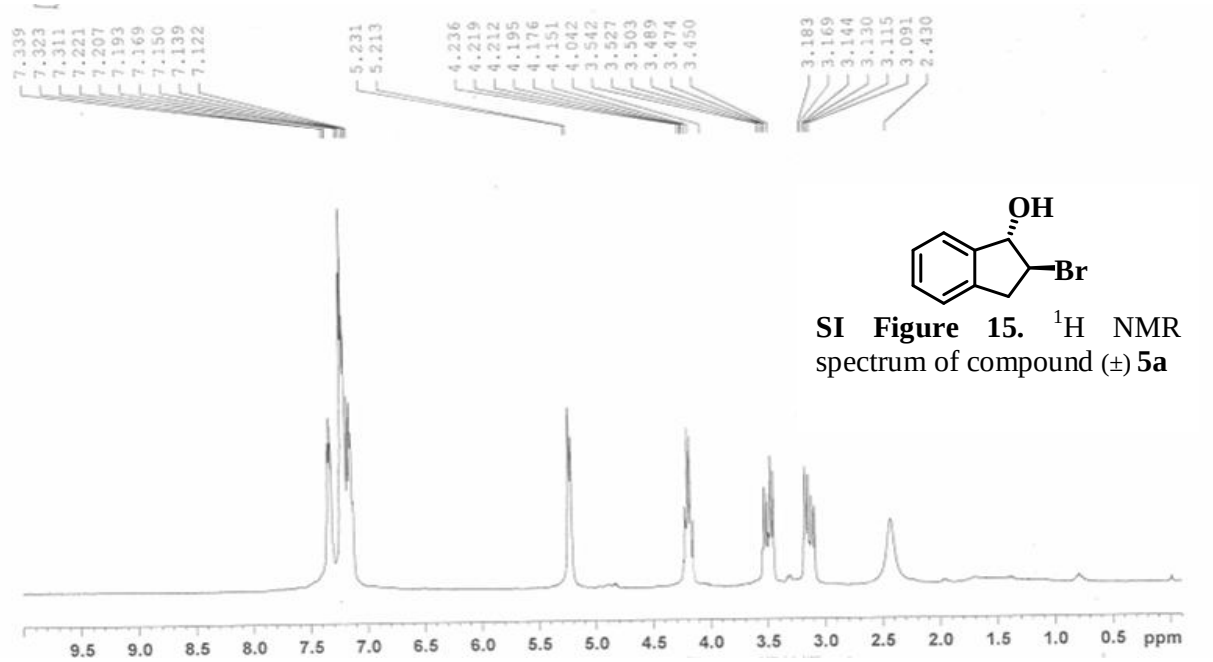
SI Figure 12. ^{13}C NMR spectrum of Compound **3f.**



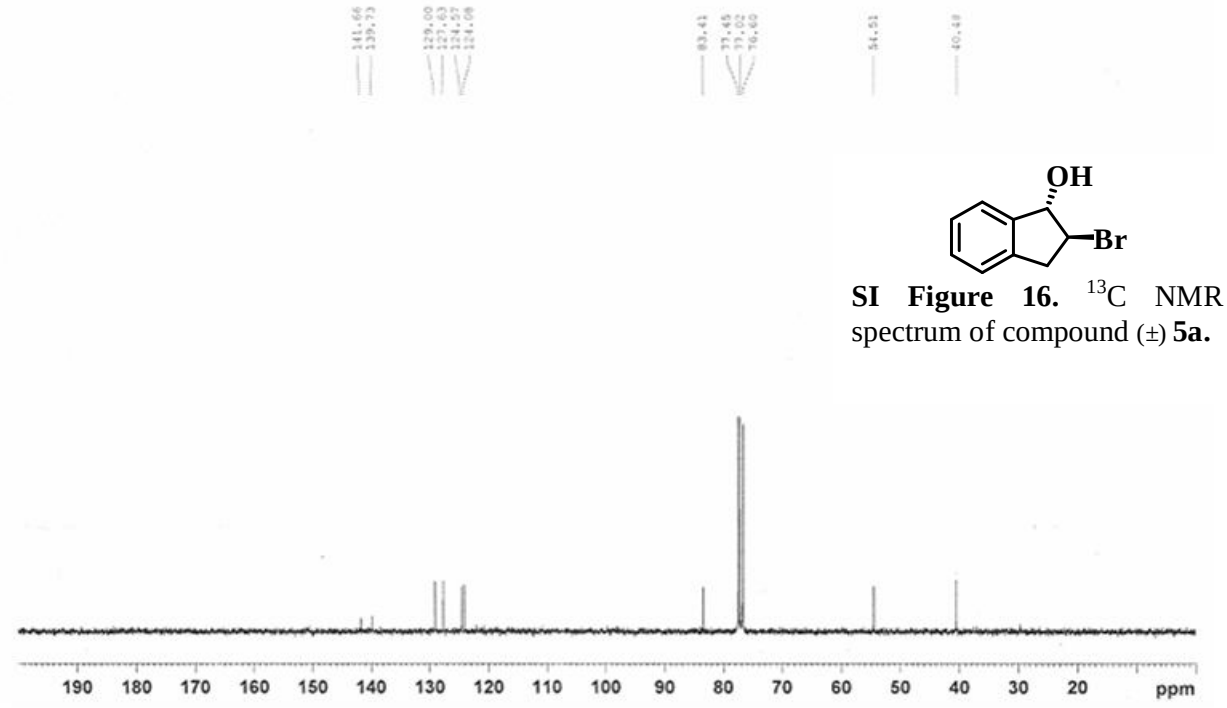
SI Figure 13. ^{1}H NMR spectrum of compound **3g**.



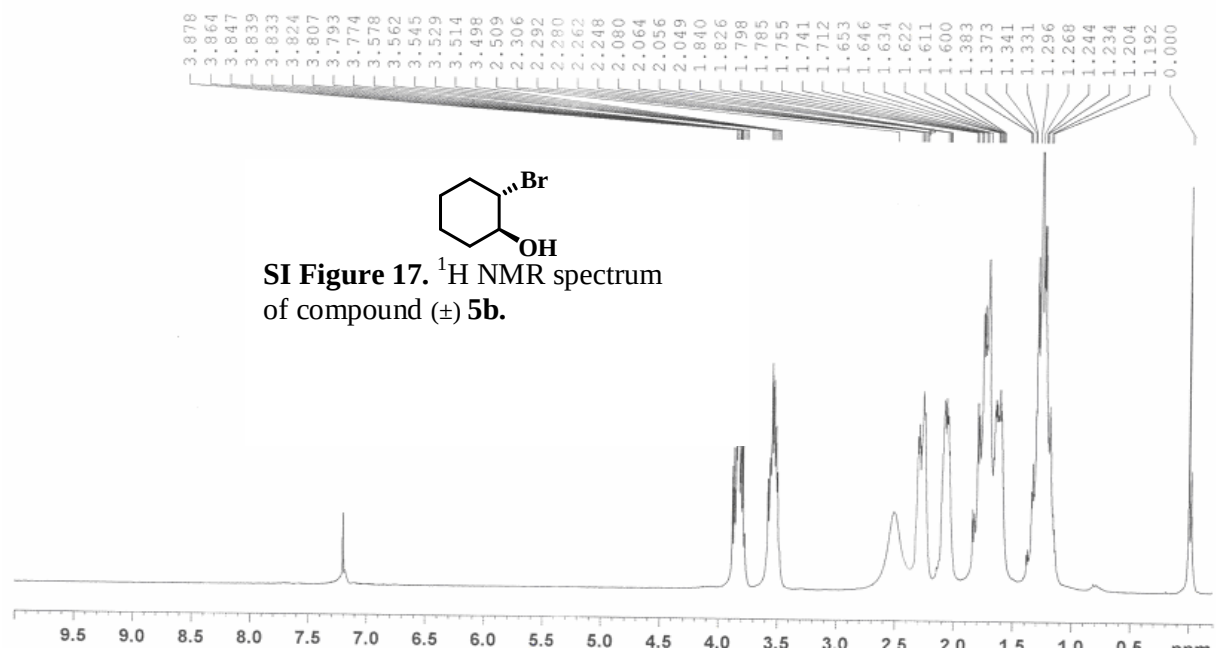
SI Figure 14. ^{13}C NMR spectrum of Compound **3g.**



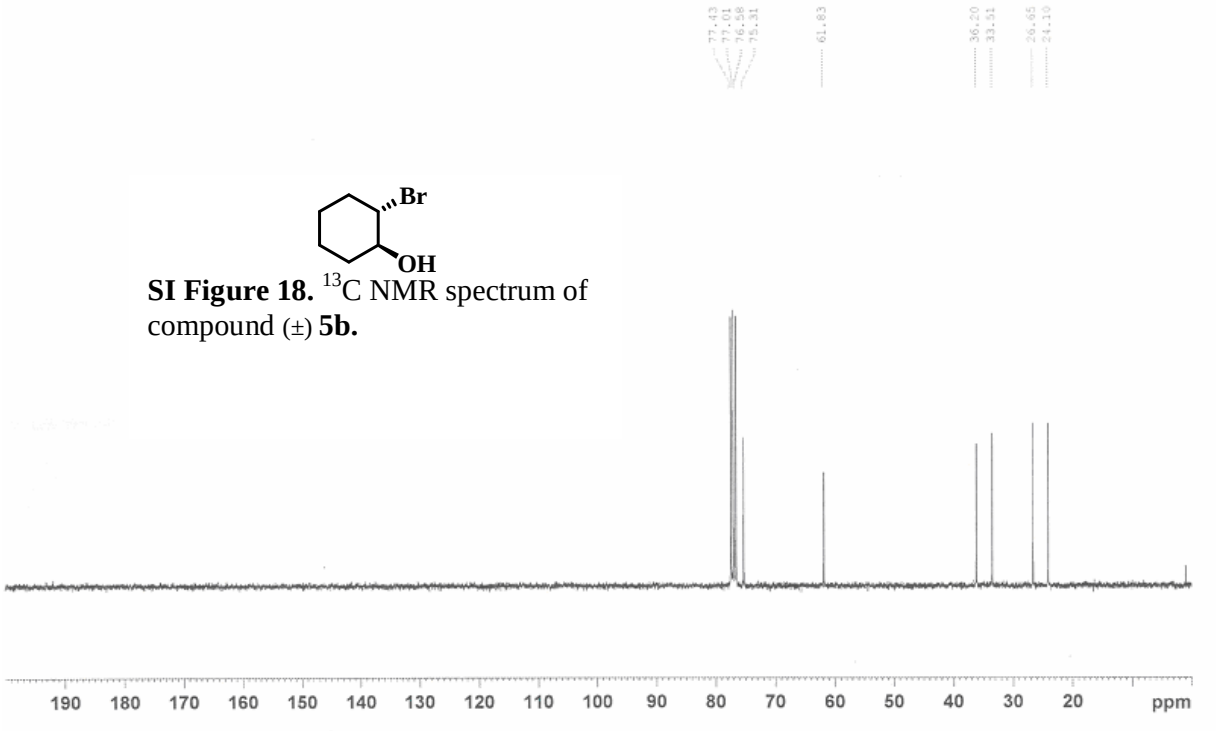
SI Figure 15. ^{1}H NMR spectrum of compound (±) **5a**



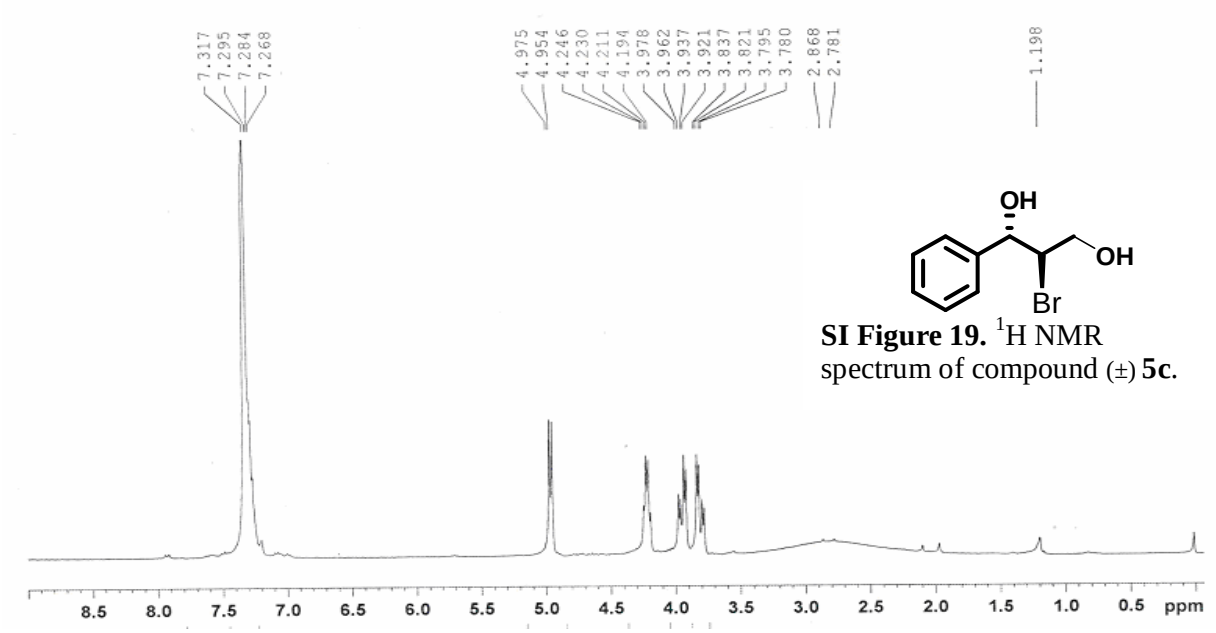
SI Figure 16. ^{13}C NMR spectrum of compound (±) **5a.**



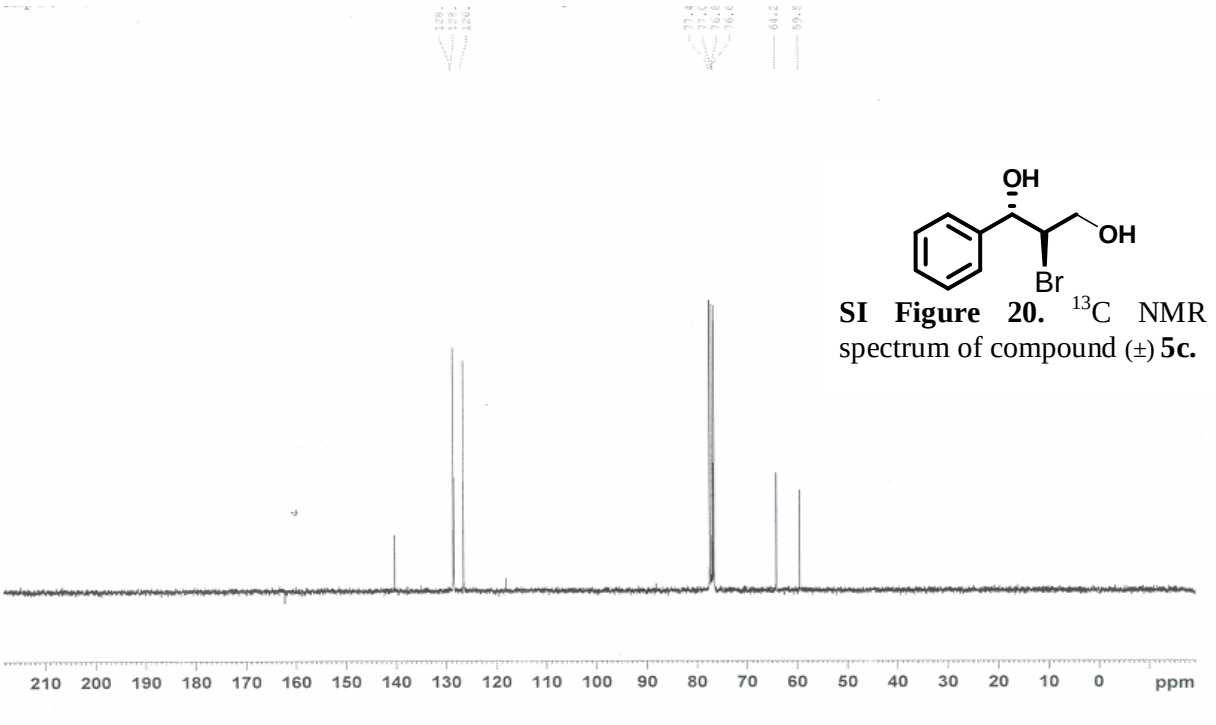
SI Figure 17. ^{1}H NMR spectrum of compound (±) **5b.**



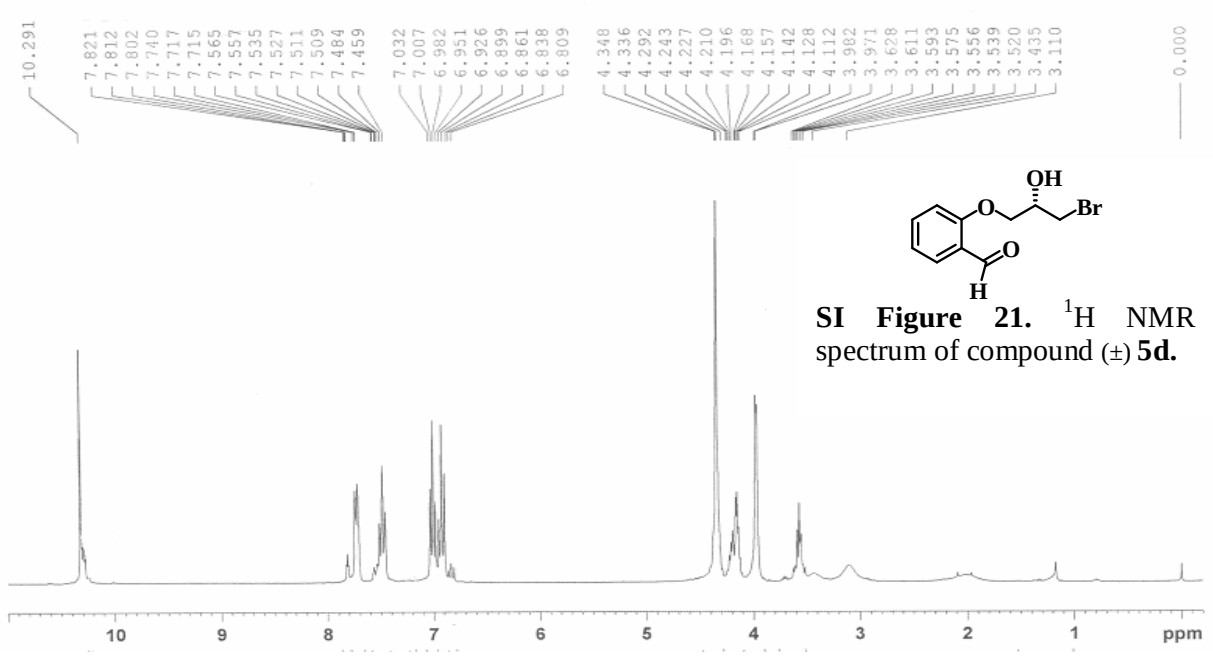
SI Figure 18. ^{13}C NMR spectrum of compound (±) **5b.**



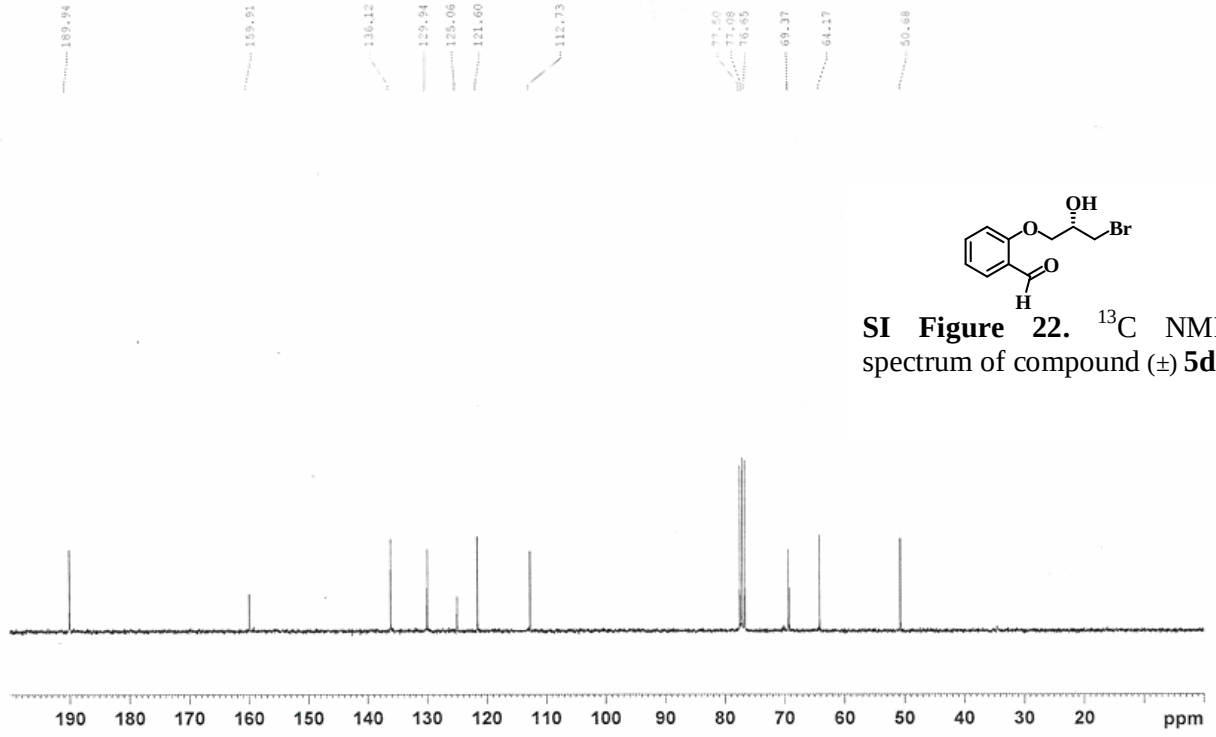
SI Figure 19. ^{1}H NMR spectrum of compound (±) **5c**.



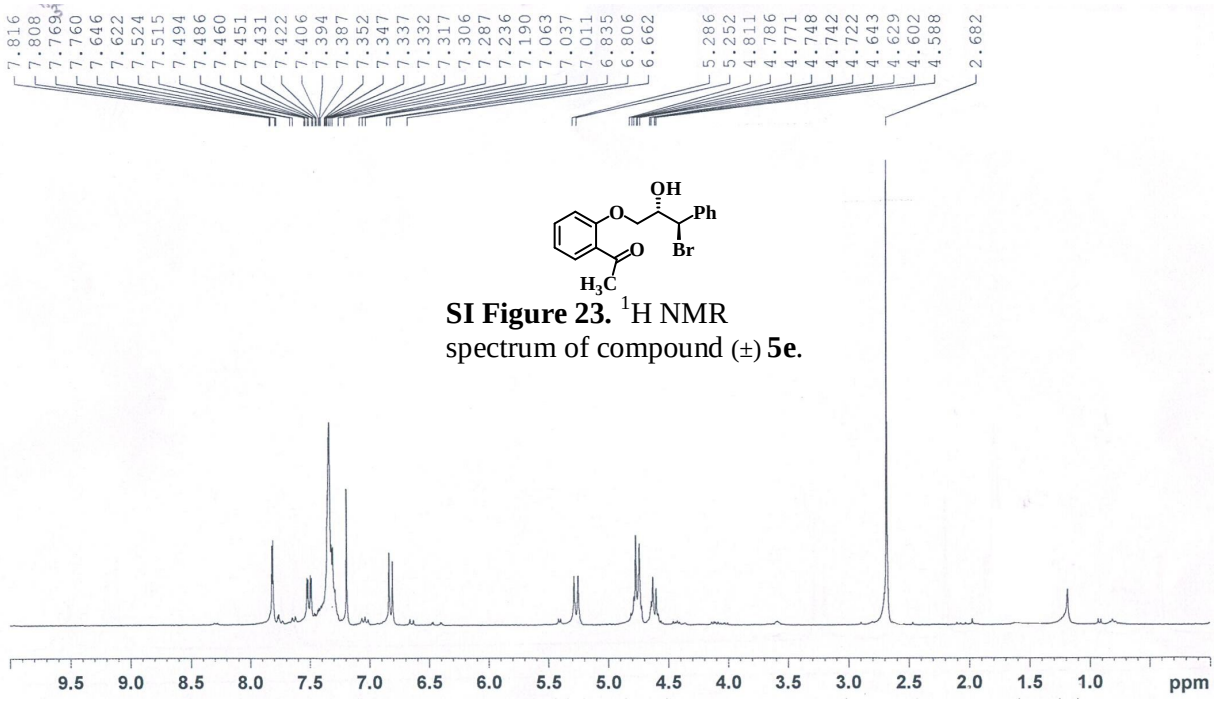
SI Figure 20. ^{13}C NMR spectrum of compound (±) **5c.**



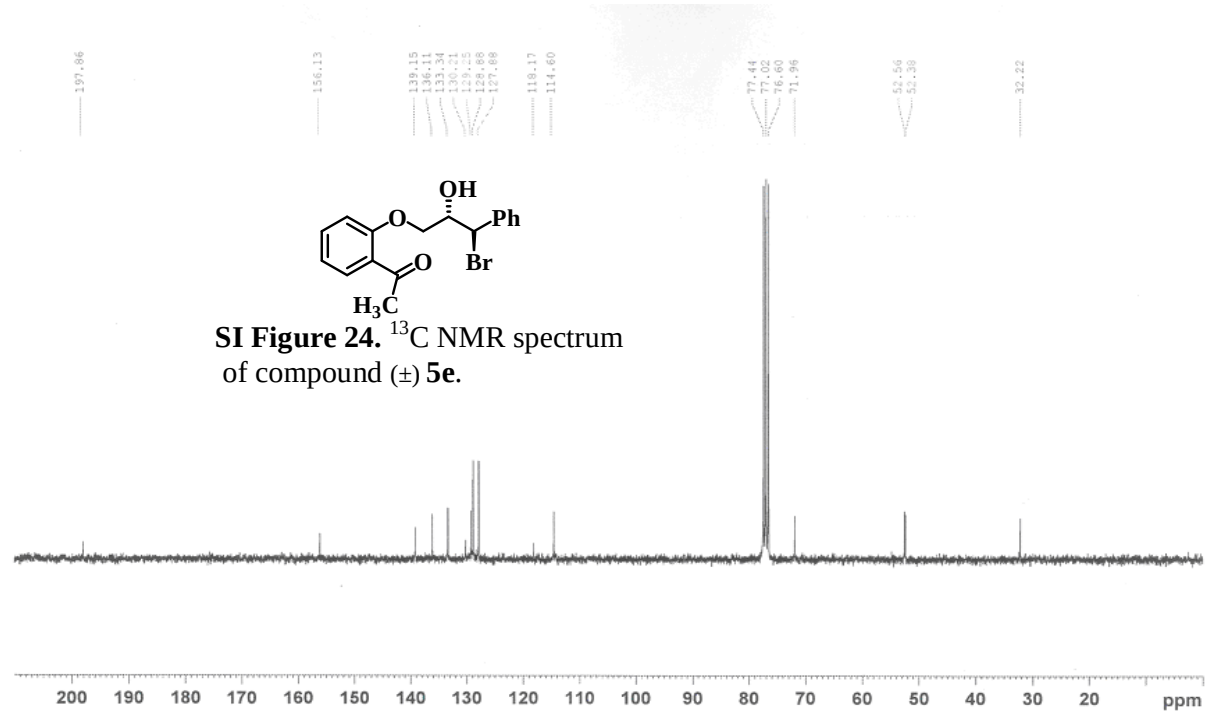
SI Figure 21. ^{1}H NMR spectrum of compound (±) **5d.**



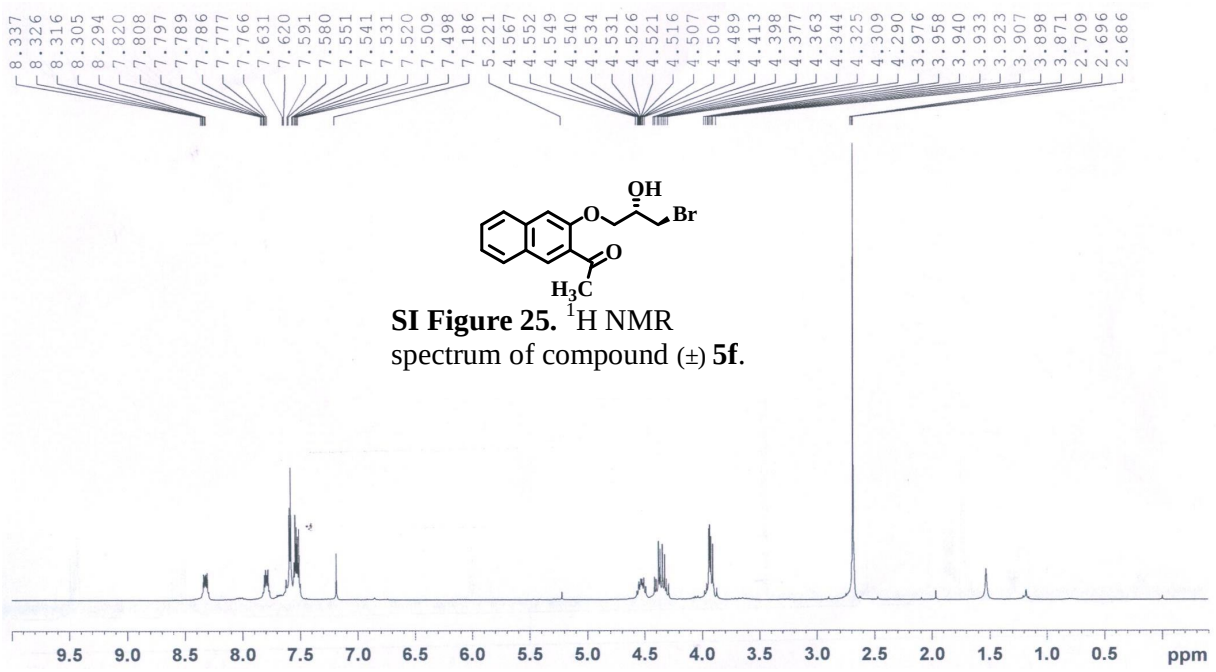
SI Figure 22. ^{13}C NMR spectrum of compound (±) **5d.**



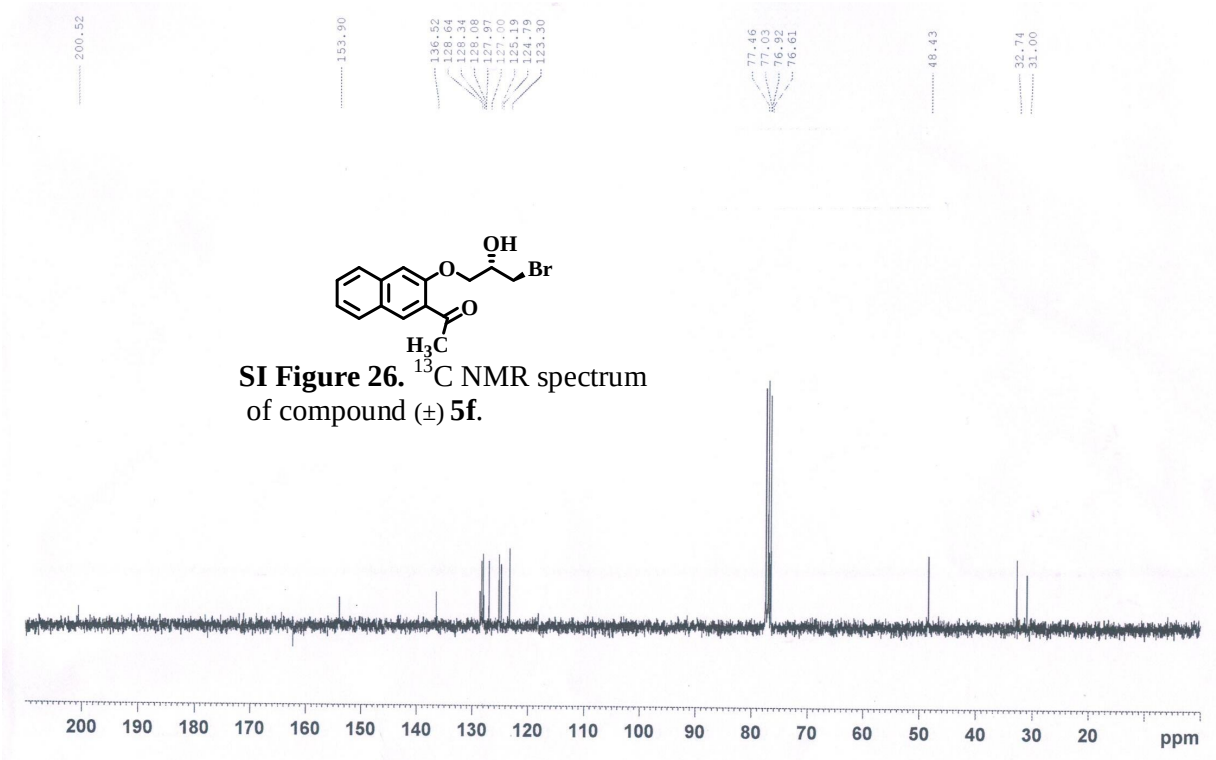
SI Figure 23. ^{1}H NMR spectrum of compound (±) **5e**.



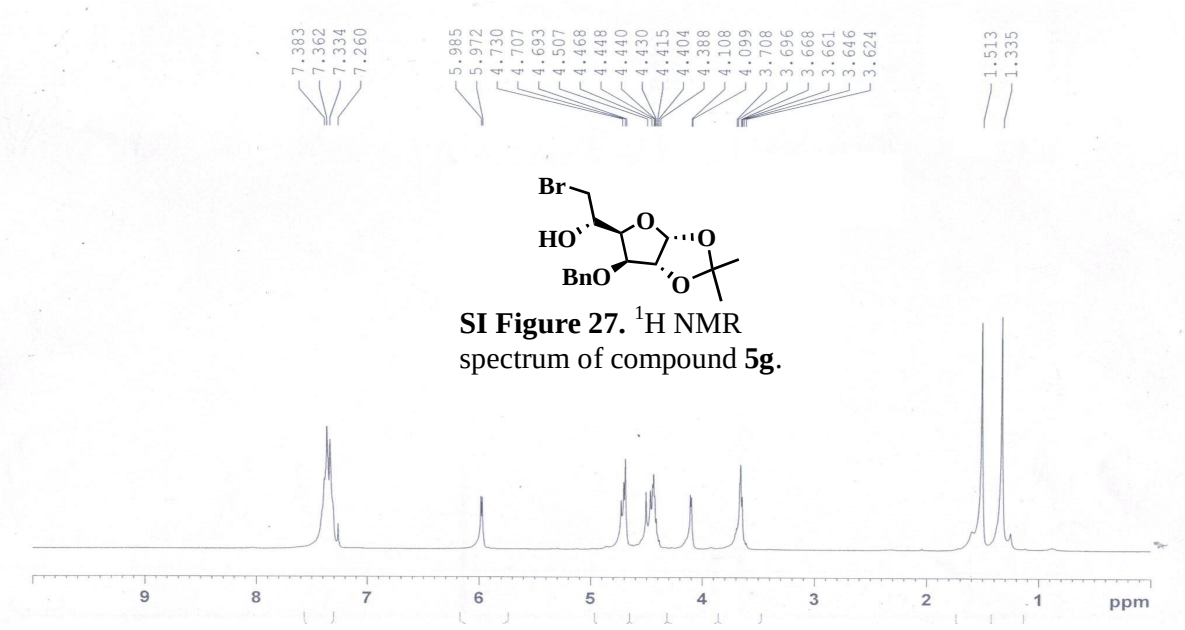
SI Figure 24. ^{13}C NMR spectrum of compound (±) **5e**.



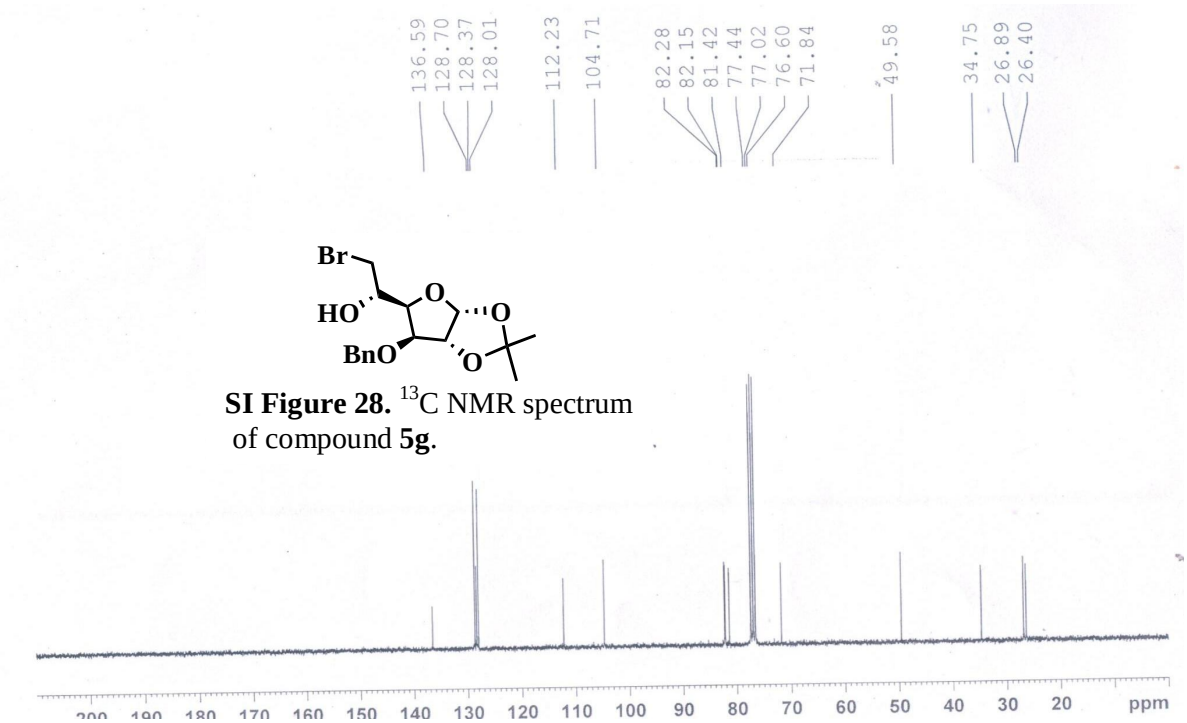
SI Figure 25. ^{1}H NMR spectrum of compound (±) **5f**.



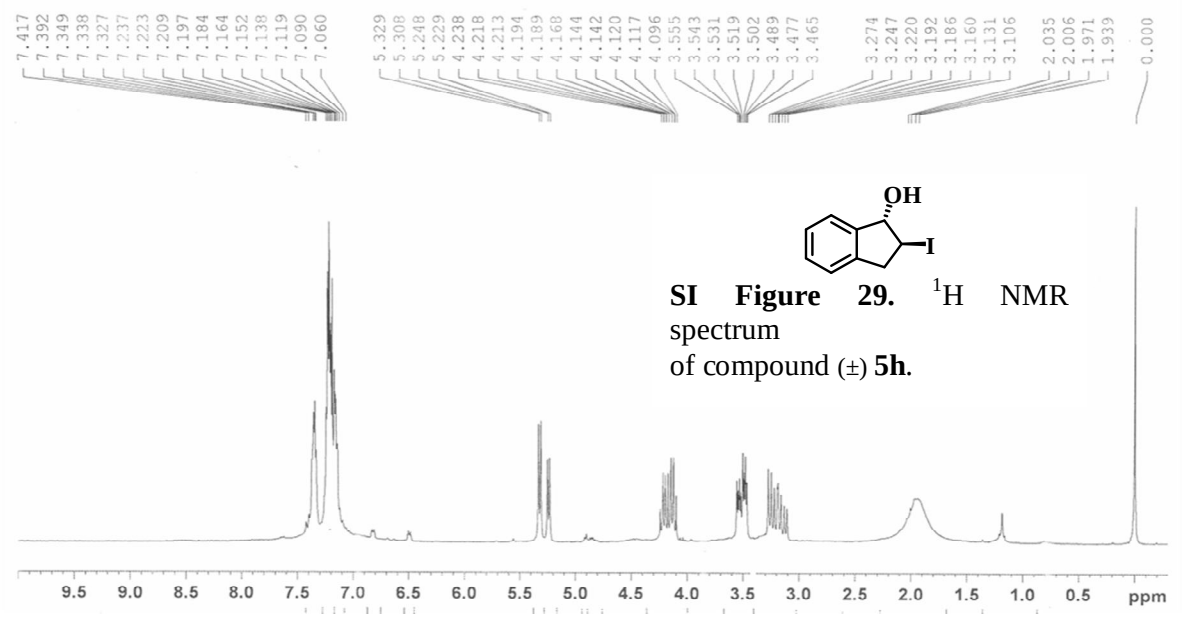
SI Figure 26. ^{13}C NMR spectrum of compound (±) **5f**.



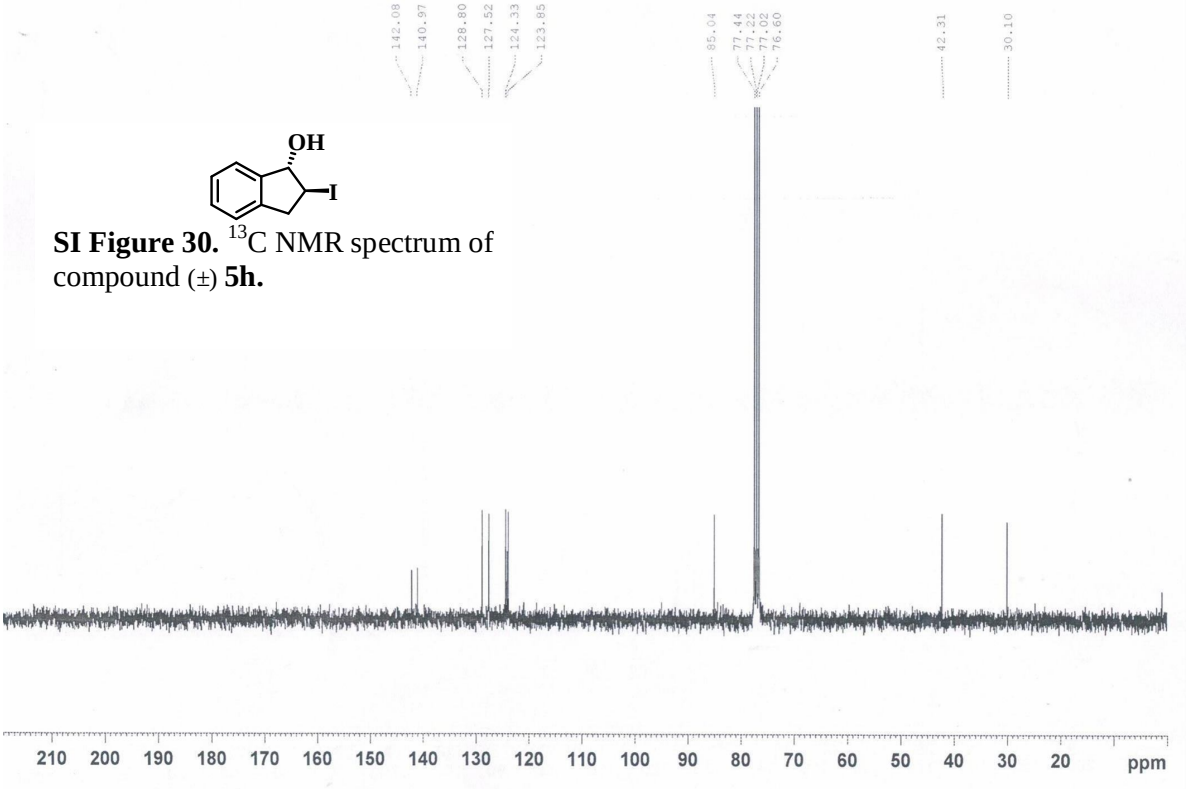
SI Figure 27. ^{1}H NMR spectrum of compound **5g**.



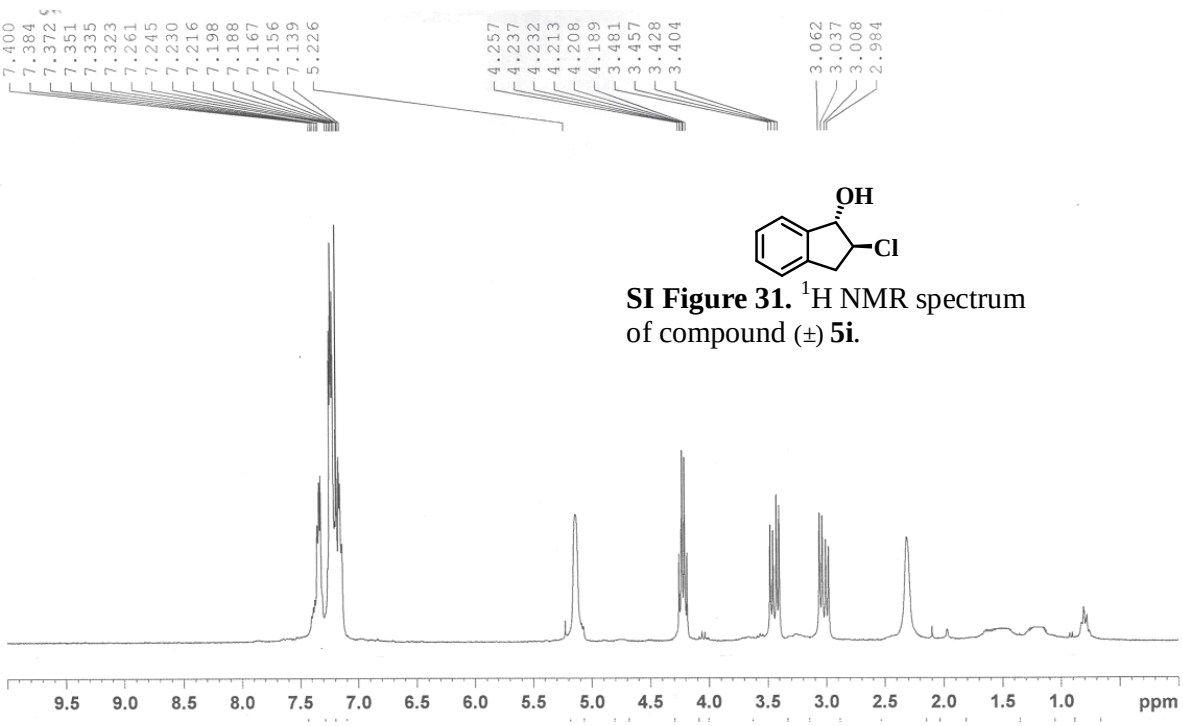
SI Figure 28. ^{13}C NMR spectrum of compound **5g**.



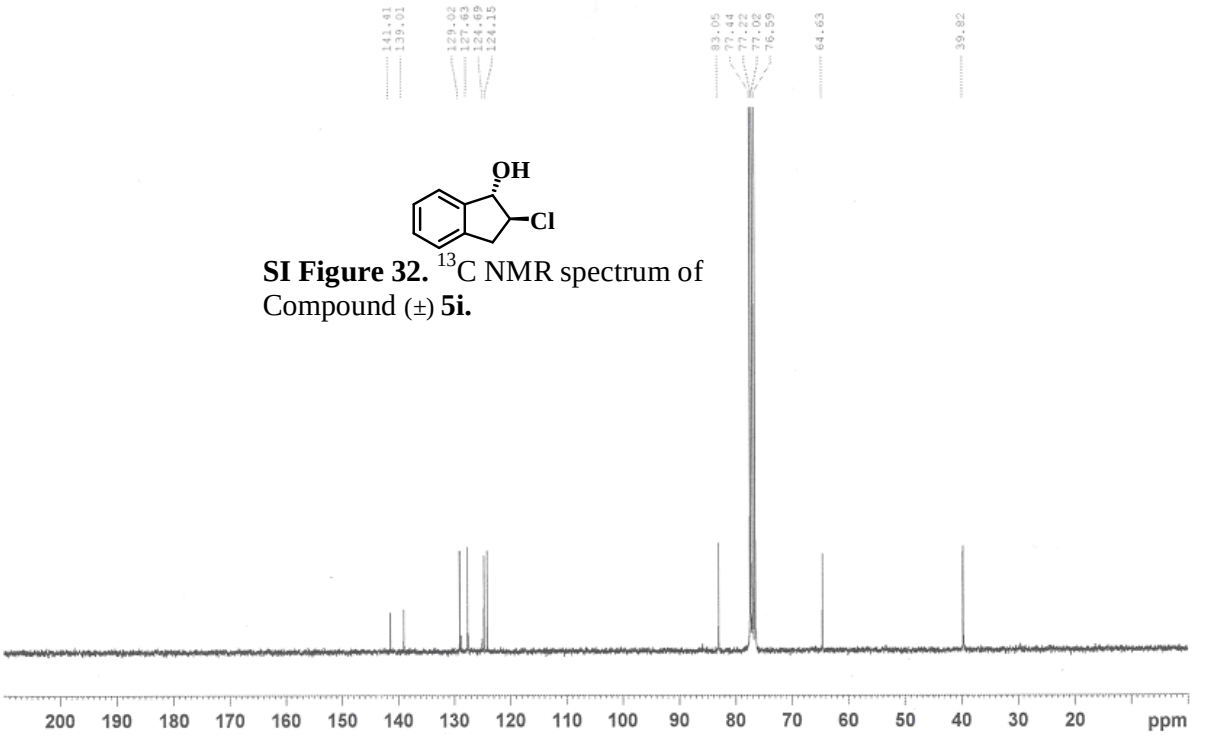
SI Figure 29. ^{1}H NMR spectrum of compound (±) **5h**.



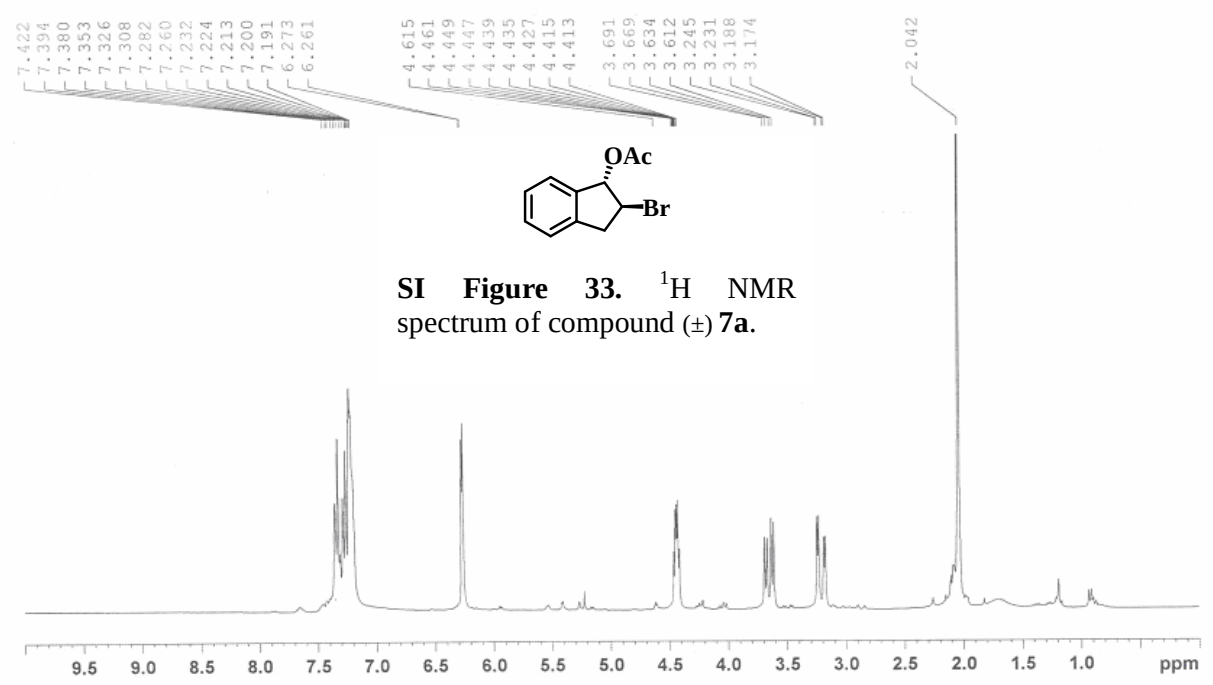
SI Figure 30. ^{13}C NMR spectrum of compound (±) **5h.**



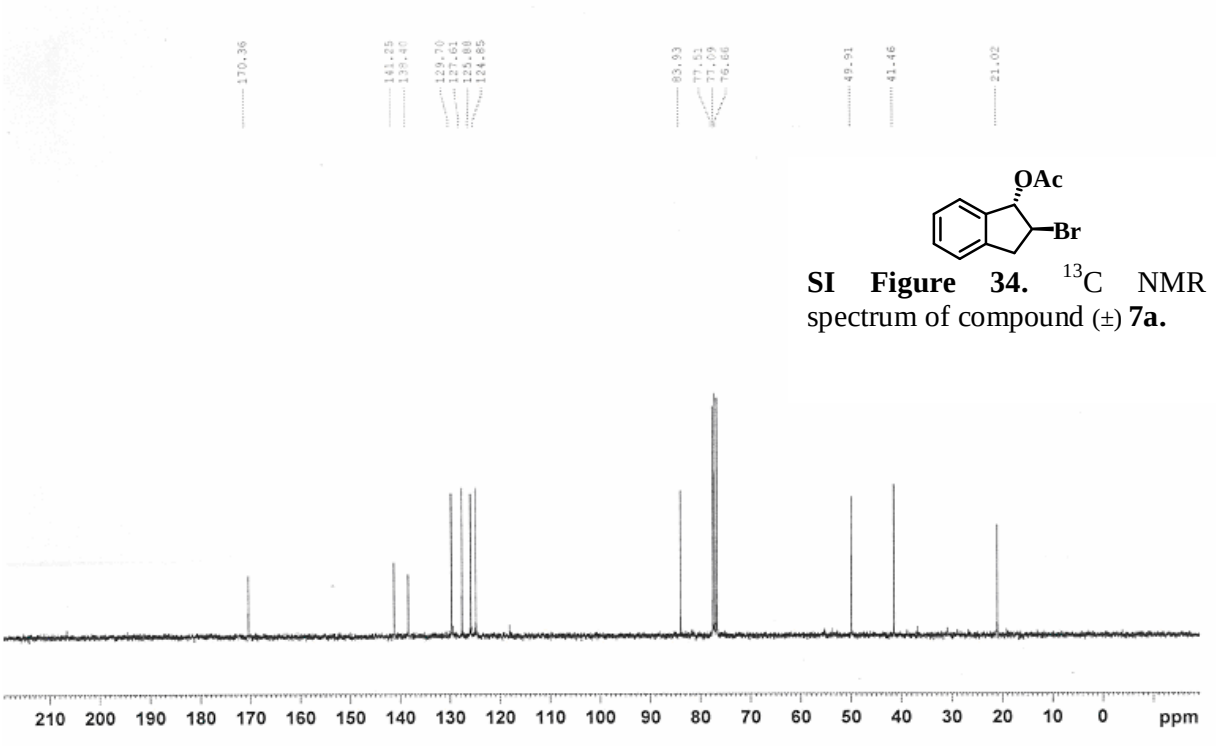
SI Figure 31. ^{1}H NMR spectrum of compound (±) **5i**.



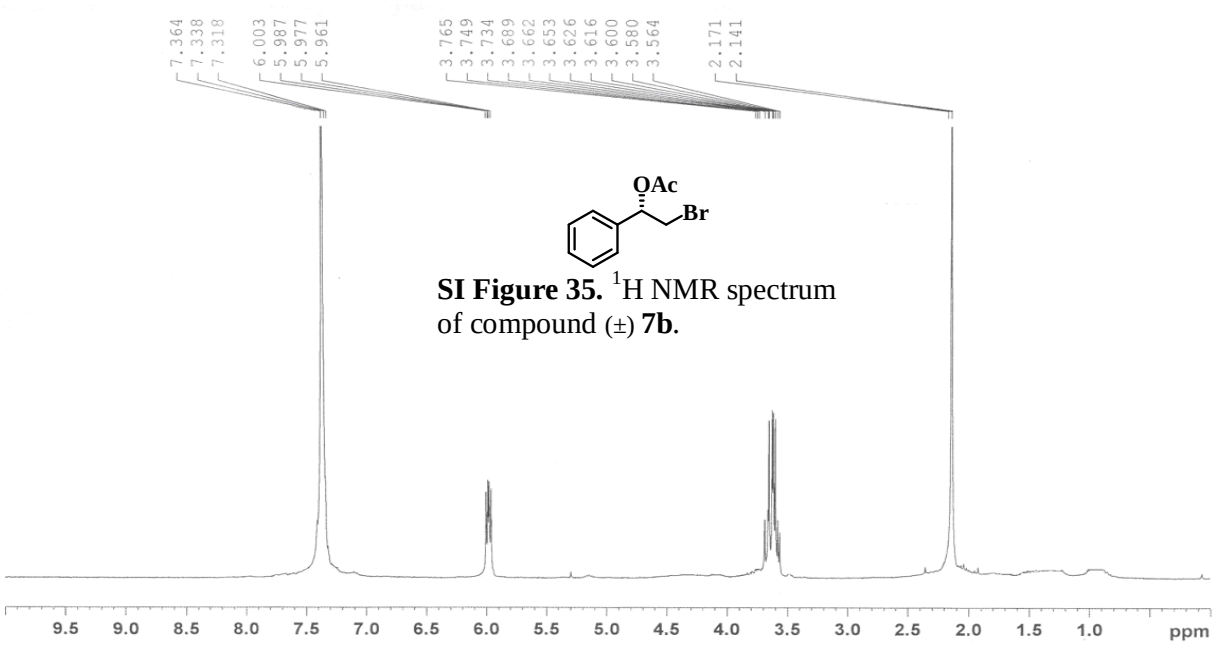
SI Figure 32. ^{13}C NMR spectrum of Compound (±) **5i.**



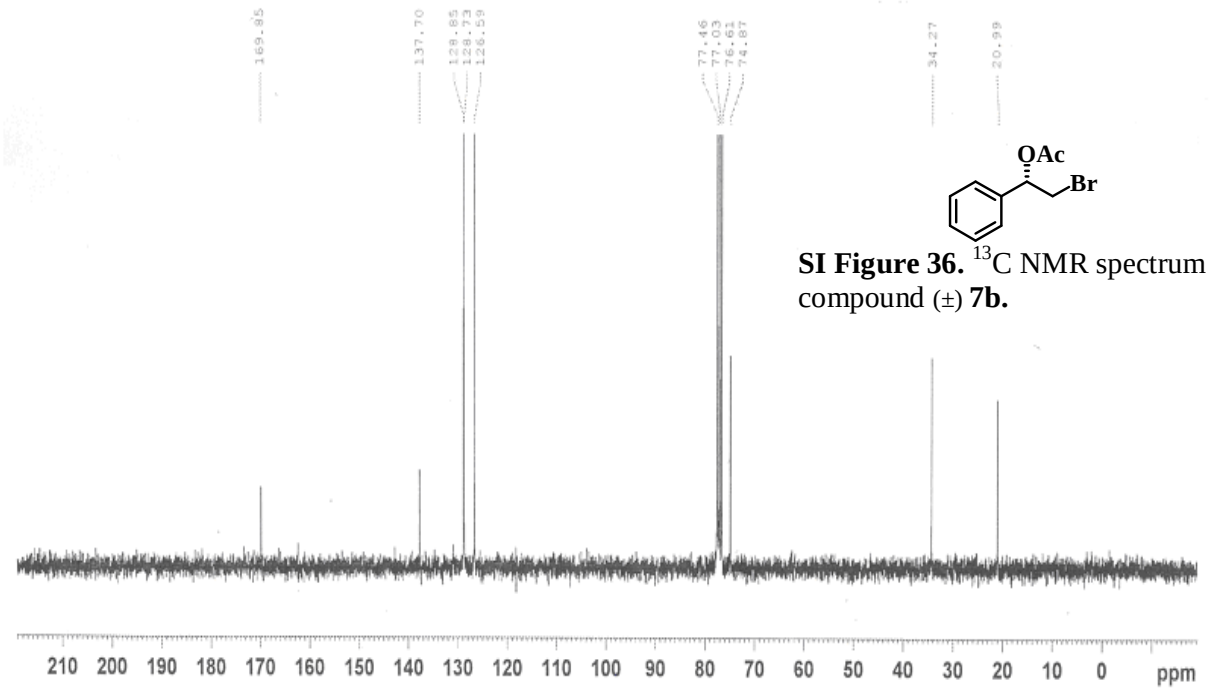
SI Figure 33. ^{1}H NMR spectrum of compound (±) **7a**.



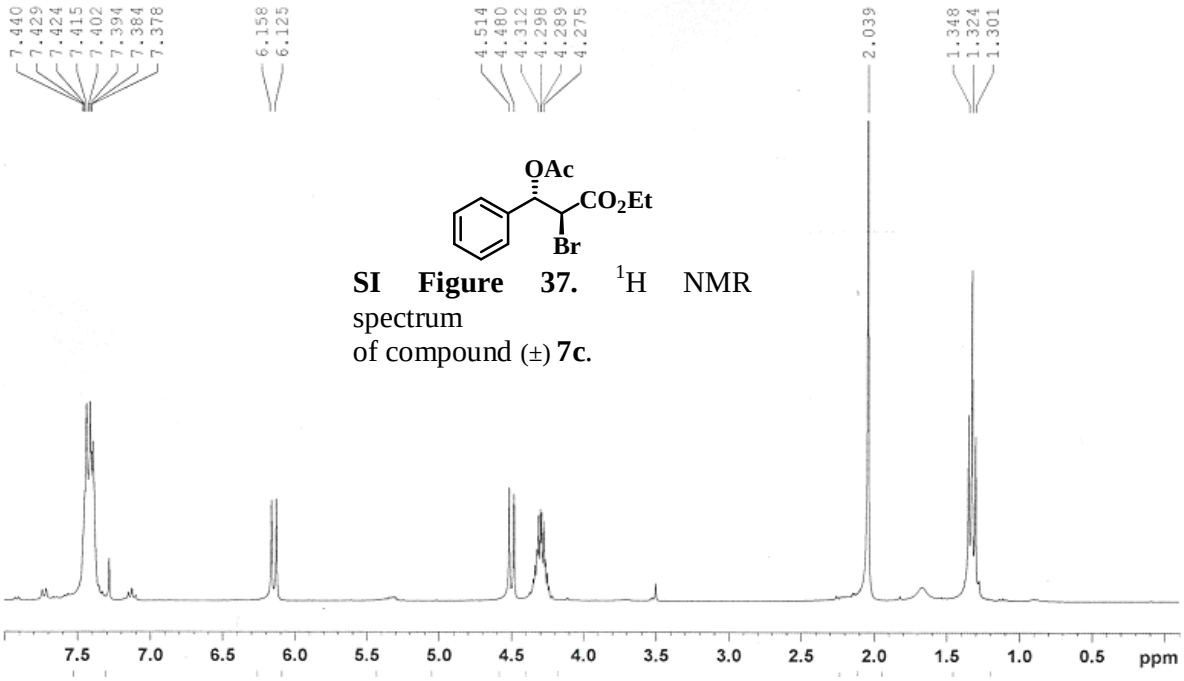
SI Figure 34. ^{13}C NMR spectrum of compound (±) **7a.**



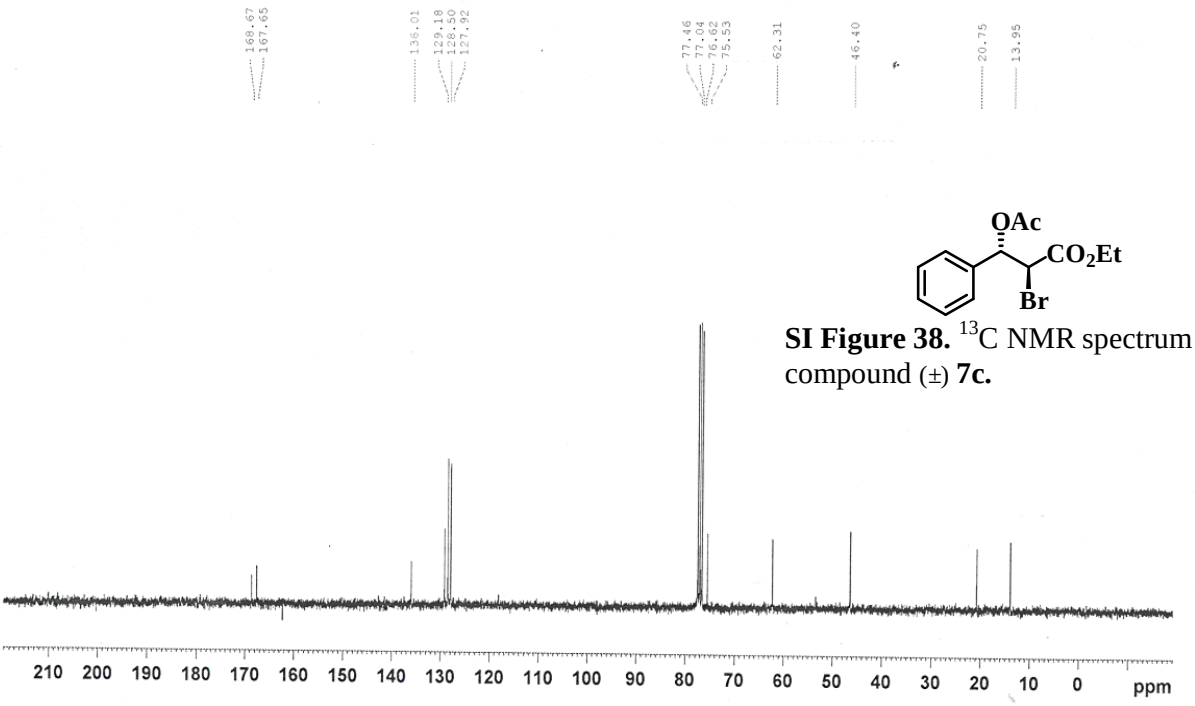
SI Figure 35. ^{1}H NMR spectrum of compound (±) **7b**.



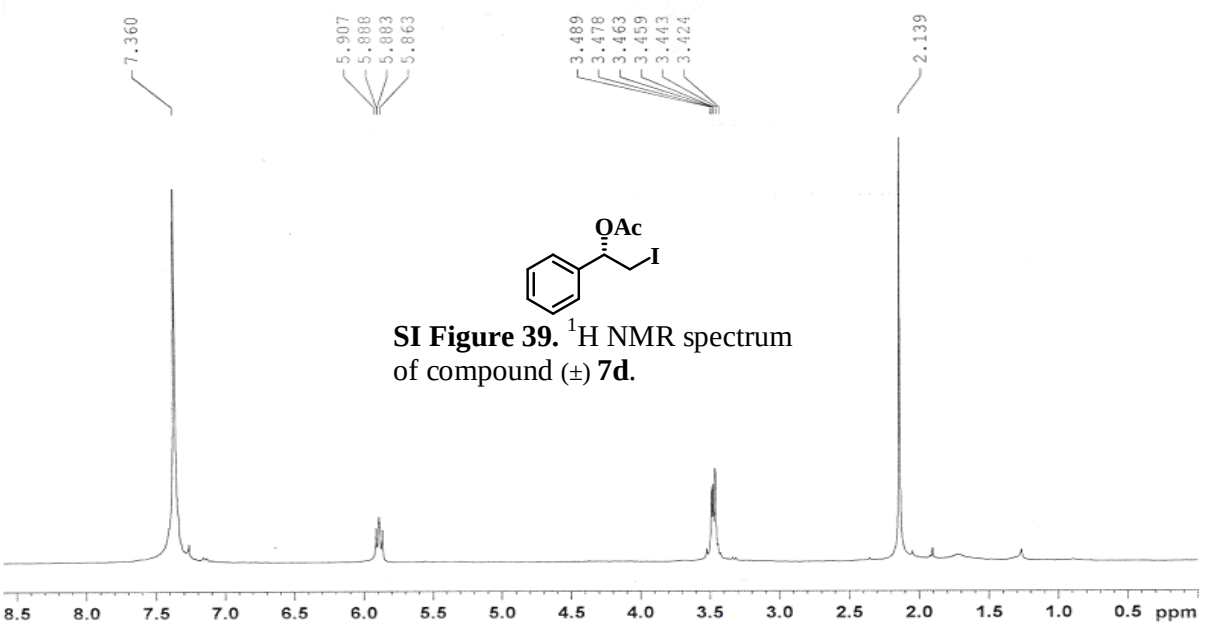
SI Figure 36. ^{13}C NMR spectrum of compound (±) **7b.**



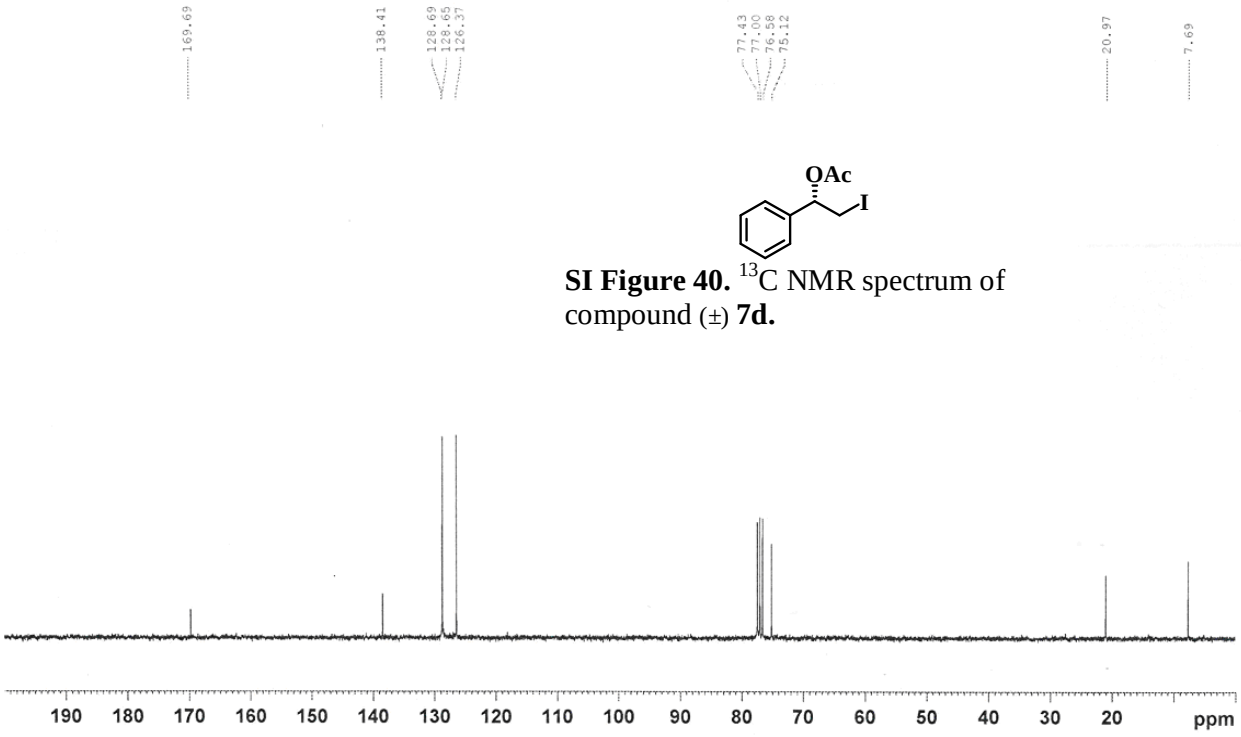
SI Figure 37. ^{1}H NMR spectrum of compound (±) **7c**.



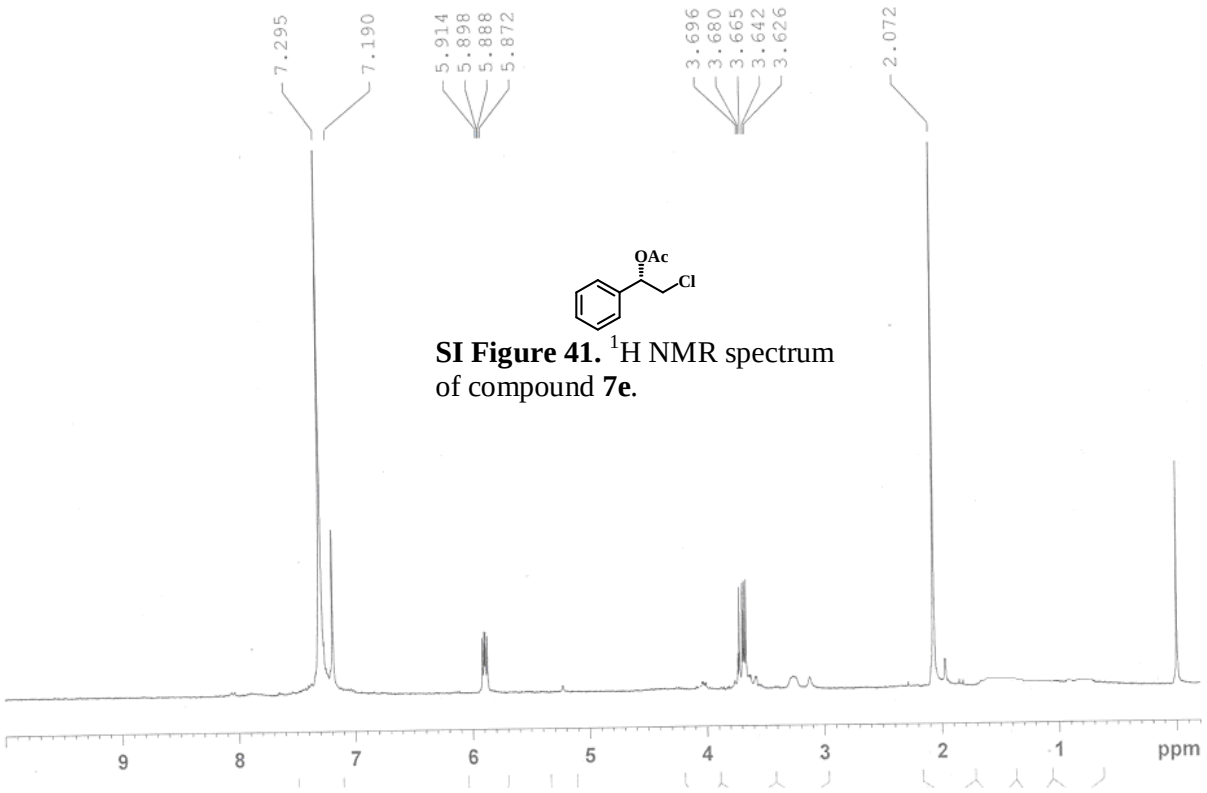
SI Figure 38. ^{13}C NMR spectrum of compound (±) **7c.**



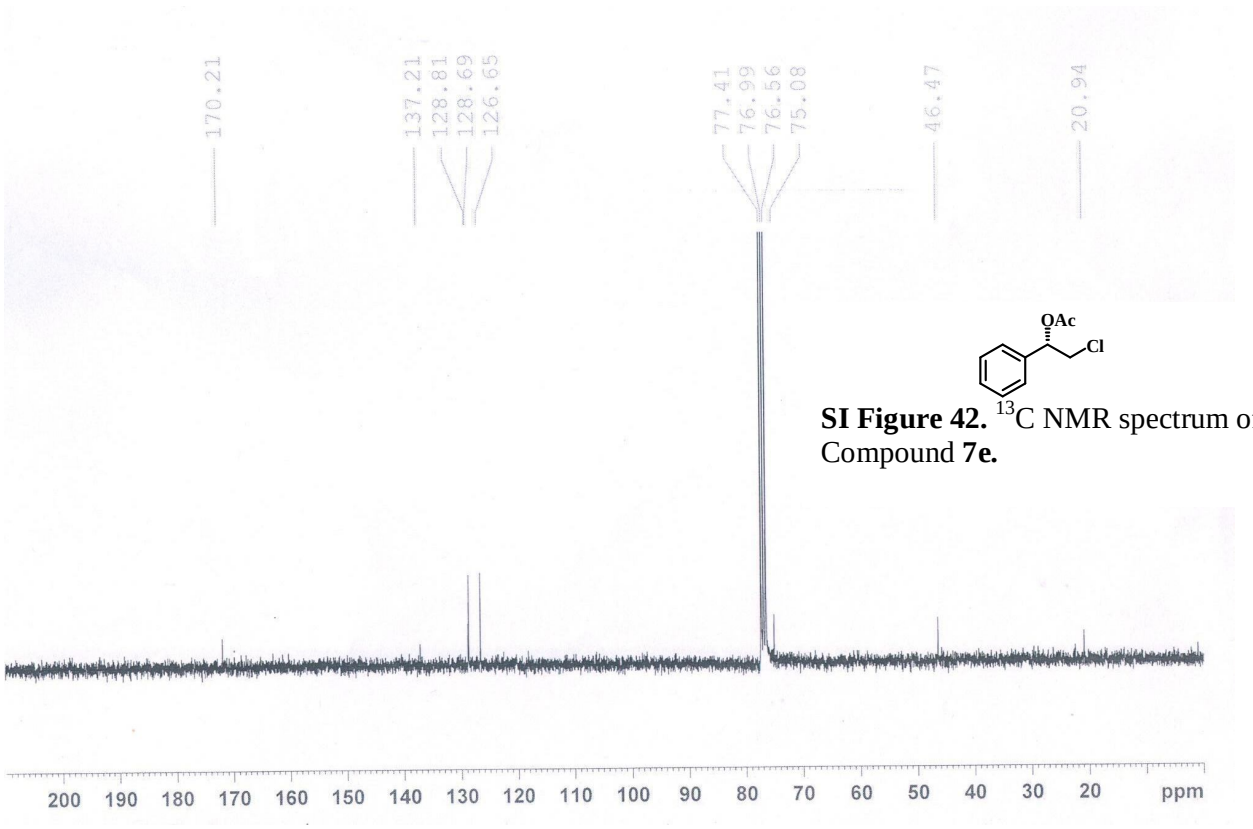
SI Figure 39. ^{1}H NMR spectrum of compound (±) **7d**.



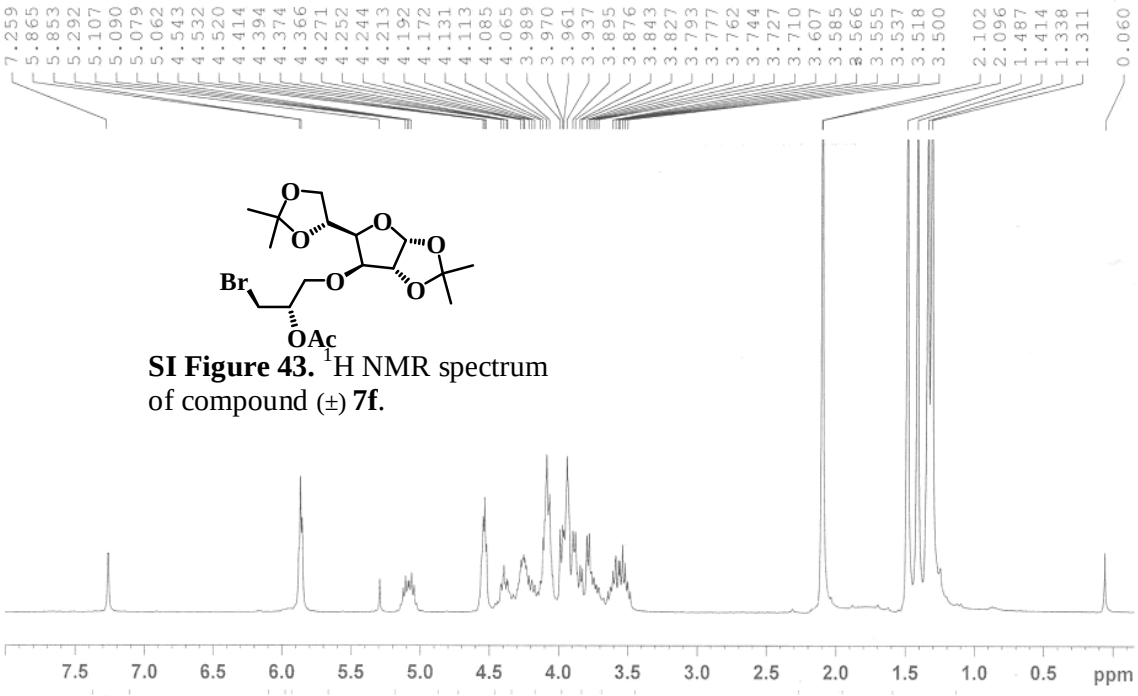
SI Figure 40. ^{13}C NMR spectrum of compound (±) **7d.**



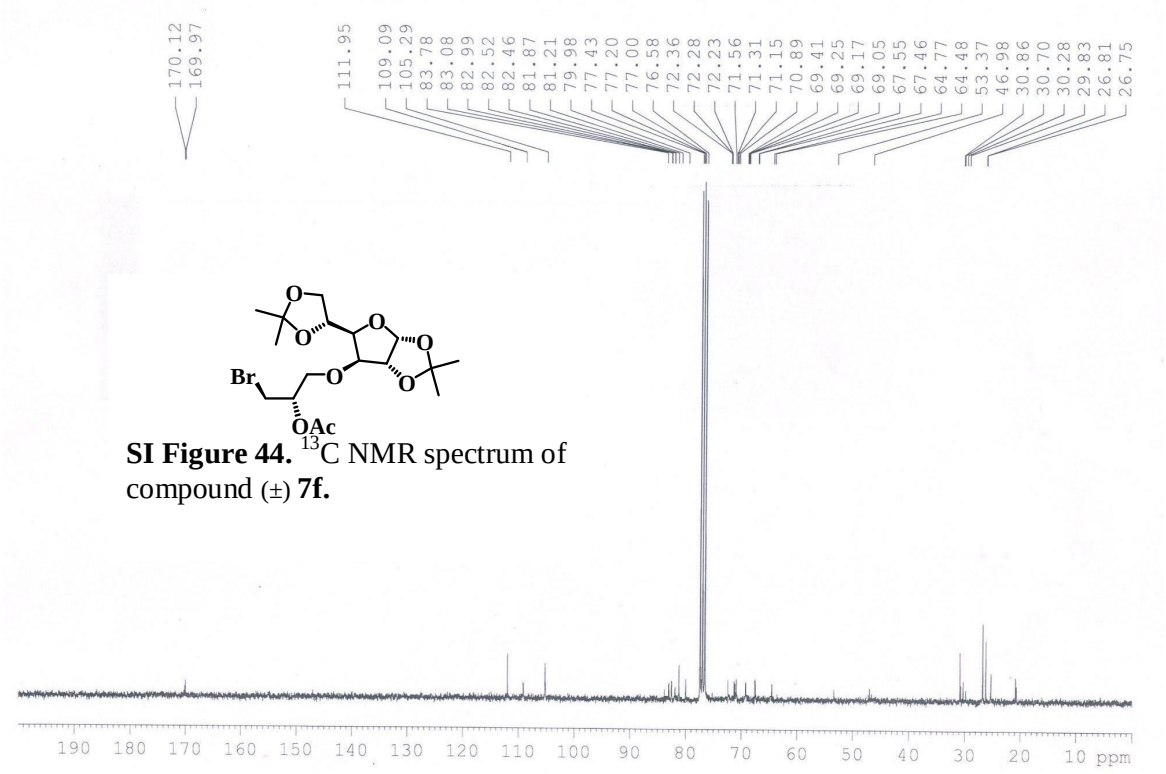
SI Figure 41. ^{1}H NMR spectrum of compound **7e**.



SI Figure 42. ^{13}C NMR spectrum of Compound **7e.**

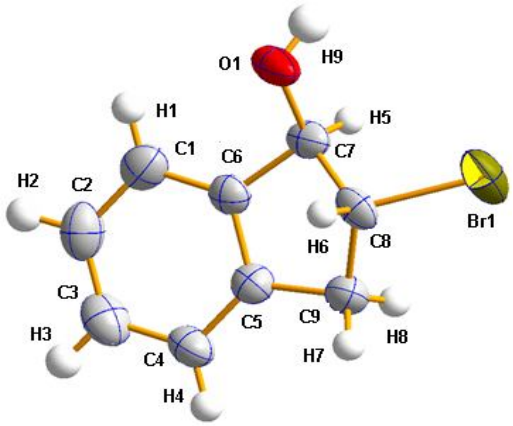


SI Figure 43. ^{1}H NMR spectrum of compound (±) **7f**.



SI Figure 44. ^{13}C NMR spectrum of compound (±) **7f.**

7. **Summary of data CCDC 799249 (compound 5a)**



. Chemical formula and formula weight (M):	C_9H_9BrO and 213.07
. Crystal system:	Monoclinic
. Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds:	a 12.286(8), b 4.978(3), c 14.499(9), 90.00, 106.853(8), 90.00, 848.7(9)
. Temperature:	296 (2)
. Space group symbol:	P21/n
. No. of formula units in unit cell (Z):	4
. Number of reflections measured and/or number of independent reflections, Rint:	1420
. Final R values (and whether quoted for all or observed data):	0.0528