Supporting Information

Indole-Catalyzed Bromolactonization in Lipophilic Solvent: a Solid-Liquid Phase Transfer Approach

*Tao Chen, Thomas Jian Yao Foo, Ying-Yeung Yeung **

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

E-mail: chmyyy@nus.edu.sg; Fax: +65-6779-1691; Tel: +65-6516-7760

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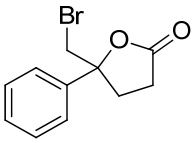
(A) General. All reactions were carried by standard procedures under atmosphere. Commercially available reagents from Alfa Aesar and Aldrich were used as received. Infrared spectra were recorded on a BIO-RAD FTS 165 FT-IR spectrophotometer and reported in wave numbers (cm-1). Melting points were determined on a BÜCHI B-540b melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz), Bruker DPX300 (300 MHz). Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements. High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merk 60 (0.040-0.063 mm) mesh silica gel. Indole catalyst **1** and substrate **5** were prepared according to the literature procedure.[1,2]

(B) General Procedure for the Indole-Catalyzed Bromolactonization. To a mixture of alkenoic acid **5** (0.5 mmol, 1.0 equiv) and indole catalyst **1a** (1 mg, 0.005 mmol, 0.01 equiv) in hexane (5 mL) at 25 ^{o}C was added *N*-bromosuccinimide (107 mg, 0.6 mmol, 1.2 equiv) in the absence of light. The resulting mixture was vigorously stirred at 25 ^{o}C and monitored by TLC. The reaction was quenched with saturated aqueous Na_2SO_3 (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to yield the corresponding lactone **6**.

Compound 6a (X = Br)



5-(Bromomethyl)-5-phenyldihydrofuran-2(3*H*)-one

Colorless oil.

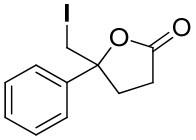
IR (KBr): 2961, 1783, 1448, 1162, 1034, 932 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.43-7.32 (m, 5H), 3.74 (d, *J* = 11.3 Hz, 1H), 3.69 (d, *J* = 11.3 Hz, 1H), 2.88-2.75 (m, 2H), 2.61-2.47 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.47, 140.67, 128.79, 128.61, 124.84, 86.37, 40.98, 32.32, 29.00;

HRMS (ESI) calcd for $C_{11}H_{12}BrO_2$ $[M + H]^+$: 255.0015; found: 255.0018.

Compound 6a (X = I)



5-(Iodomethyl)-5-phenyldihydrofuran-2(3*H*)-one

Yellow oil.

IR (KBr): 2956, 1788, 1448, 1153, 1026, 929 cm^{-1};

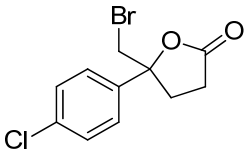
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.39-7.30 (m, 5H), 3.62 (s, 2H), 2.80-2.43 (m, 4H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.18, 140.48, 128.65, 128.40, 124.69, 85.86, 33.77, 29.06, 16.28;

HRMS (ESI) calcd for $C_{11}H_{12}IO_2$ $[M + H]^+$: 302.9876; found: 302.9879.

Compound 6b

5-(Bromomethyl)-5-(4-chlorophenyl)dihydrofuran-2(3*H*)-one



Colorless oil.

IR (KBr)): 2961, 1783, 1492, 1417, 1160, 1012 cm^{-1};

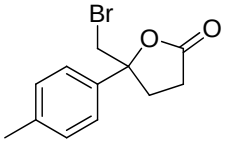
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.40-7.33 (m, 4H), 3.70 (d, *J* = 11.3 Hz, 1H), 3.65 (d, *J* = 11.3 Hz, 1H), 2.84-2.72 (m, 2H), 2.61-2.49 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.10, 139.20, 134.70, 129.00, 126.41, 85.93, 40.55, 32.34, 28.93;

HRMS (ESI) calcd for $C_{11}H_9BrClO_2$ $[M - H]^-$: 286.9480; found: 286.9489.

Compound 6c

5-(Bromomethyl)-5-(*p*-tolyl)dihydrofuran-2(3*H*)-one



Colorless oil.

IR (KBr)): 2959, 1779, 1514, 1161, 1040, 931 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.29 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.73 (d, *J* = 11.3 Hz, 1H), 3.67 (d, *J* = 11.3 Hz, 1H), 2.85-2.73 (m, 2H),

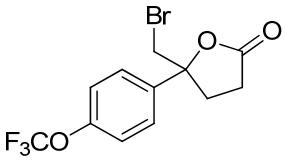
2.59-2.49 (m, 2H), 2.36 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) δ 175.58, 138.56, 137.65, 129.45, 124.80, 86.43, 41.03, 32.27, 29.05, 21.01;

HRMS (ESI) calcd for $C_{12}H_{12}BrO_2$ [M - H]$^-$: 267.0026; found: 267.0015.

Compound 6d

5-(Bromomethyl)-5-(4-trifluoromethoxyphenyl)dihydrofuran-2(3*H*)-one



Colorless oil.

IR (KBr)): 3033, 1770, 1509, 1256, 1164, 1012 cm^{-1};

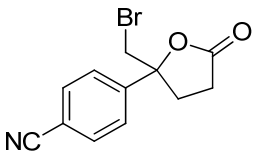
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.48-7.44 (m, 2H), 7.27-7.24 (m, 2H), 3.72 (d, *J* = 11.3 Hz, 1H), 3.66 (d, *J* = 11.3 Hz, 1H), 2.87-2.74 (m, 2H), 2.64-2.51 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.05, 149.30, 139.38, 126.66, 121.20, 118.64, 85.87, 40.58, 32.41, 28.96;

HRMS (ESI) calcd for $C_{12}H_9BrF_3O_3$ [M - H]$^-$: 336.9693; found: 336.9679.

Compound 6e

5-(Bromomethyl)-5-(4-cyanophenyl)dihydrofuran-2(3*H*)-one



White solid; mp 154–155 °C

IR (KBr)): 2960, 2233, 1789, 1175, 1050, 847 cm^{-1};

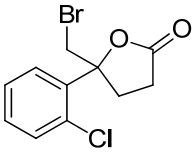
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.74-7.70 (m, 2H), 7.57-7.53(m, 2H), 3.71 (d, *J* = 11.3 Hz, 1H), 3.66 (d, *J* = 11.3 Hz, 1H), 2.88-2.75 (m, 2H), 2.63-2.51 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 174.59, 145.81, 132.64, 125.90, 118.01, 112.81, 85.69, 39.93, 32.44, 28.76;

HRMS (ESI) calcd for $C_{12}H_9BrNO_2$ $[M - H]^-$: 277.9822; found: 277.9814.

Compound 6f

5-(Bromomethyl)-5-(2-chlorophenyl)dihydrofuran-2(3*H*)-one



Yellow oil.

IR (KBr)): 2965, 1790, 1470, 1418, 1158, 1009 cm^{-1};

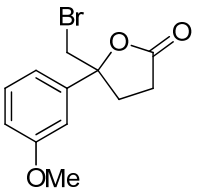
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.74-7.71 (m, 1H), 7.44-7.40 (m, 1H), 7.34-7.29 (m, 2H), 4.22 (d, *J* = 11.3 Hz, 1H), 3.81 (d, *J* = 11.3 Hz, 1H), 3.05-2.48 (m, 4H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.24, 138.21, 131.36, 130.07, 130.04, 127.51, 127.43, 86.44, 39.03, 31.72, 29.07;

HRMS (ESI) calcd for $C_{11}H_9BrClO_2$ $[M - H]^-$: 286.9480; found: 286.9471.

Compound 6g

5-(Bromomethyl)-5-(3-methoxyphenyl)dihydrofuran-2(3*H*)-one



Colorless oil.

IR (KBr)): 2961, 1790, 1602, 1458, 1245, 1160, 1038 cm^{-1};

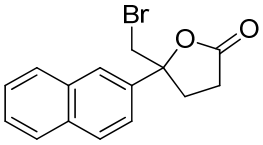
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.34-7.26 (m, 1H), 6.96-6.86 (m, 3H), 3.81 (s, 3H), 3.73 (d, *J* = 11.3 Hz, 1H), 3.68 (d, *J* = 11.3 Hz, 1H), 2.86-2.70 (m, 2H), 2.64-2.46 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.51, 159.81, 142.30, 129.91, 117.01, 113.83, 110.85, 86.30, 55.3, 40.93, 32.35, 29.02;

HRMS (ESI) calcd for $C_{12}H_{12}BrO_3$ $[M - H]^-$: 282.9974; found: 282.9975.

Compound 6h

5-(Bromomethyl)-5-(naphthalen-2-yl)dihydrofuran-2(3*H*)-one



Colorless oil.

IR (KBr)): 3058, 1771, 1600, 1157, 1035, 932 cm^{-1};

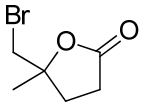
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.94 -7.82 (m, 4H), 7.56-7.50 (m, 2H), 7.43 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.80 (s, 2H), 2.94-2.47 (m, 4H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.53, 137.70, 132.89, 132.76, 128.84, 128.20, 127.54, 126.78, 124.14, 122.25, 86.50, 40.74, 32.29, 28.98;

HRMS (ESI) calcd for $C_{15}H_{12}BrO_2$ $[M - H]^-$: 303.0026; found: 303.0015.

Compound 6i

5-(Bromomethyl)-5-methyldihydrofuran-2(3*H*)-one



Colorless oil.

IR (KBr): 2979, 1771, 1455, 1382, 1168, 1075 cm^{-1};

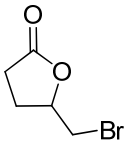
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 3.53 (d, *J* = 10.8 Hz, 1H), 3.46 (d, *J* = 10.9 Hz, 1H), 2.77-2.56 (m, 2H), 2.42-2.32 (m, 1H), 2.12-2.02 (m, 1H), 1.56 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 175.77, 84.01, 39.43, 31.49, 29.14, 25.35;

HRMS (ESI) calcd for $C_6H_{10}BrO_2$ $[M + H]^+$: 192.9859; found: 192.9861.

Compound 6j

5-(Bromomethyl)oxolan-2-one



Colorless oil.

IR (KBr): 2924, 2852, 1774, 1338, 1167, 1022 cm^{-1};

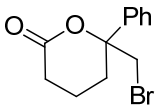
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 4.77-4.69 (m, 1H), 3.58-3.49 (m, 2H), 2.70-2.36 (m, 3H), 2.16-2.04 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 176.15, 77.78, 34.06, 28.28, 26.07;

HRMS (ESI) calcd for $C_5H_8BrO_2$ $[M + H]^+$: 178.9702; found: 178.9710.

Compound 6k

6-(bromomethyl)-6-phenyltetrahydro-2*H*-pyran-2-one



Colorless oil.

IR (KBr): 2951, 1731, 1494, 1358 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.44-7.31 (m, 5H), 3.68 (d, *J* = 11.2 Hz, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 2.56-2.31 (m, 4H), 1.89-1.78 (m, 1H), 1.68-1.50 (m, 1H);

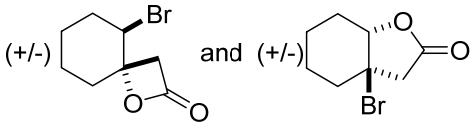
^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 170.41, 140.23, 128.95, 128.48, 125.33, 85.08, 41.48, 30.00, 29.03, 16.16;

MS (ESI) calcd for $C_{12}H_{12}BrO_2$ $[M-H]^-$: 267.0021; found : 267.1

Compound 6l+6l'

(+/-) 5-Bromo-1-oxaspiro[3.5]nonan-2-one

and (+/-) 3a-Bromohexahydrobenzofuran-2(3*H*)-one



Colorless oil.

IR (KBr): 2944, 2864, 1831, 1750, 1450, 1407 cm^{-1}

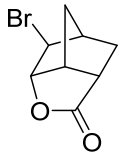
^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm): 4.67 (t, *J* = 4.6 Hz, 1H), 4.34 (dd, J_1 = 3.8 Hz, J_2 = 6.8 Hz, 4H), 3.43 (d, *J* = 16.4 Hz, 4H), 3.09 (d, *J* = 16.4 Hz, 4H), 3.03 (d, *J* = 17.1 Hz, 1H), 2.93 (d, *J* = 17.1 Hz, 1H), 2.34-2.17 (m, 10H), 2.06-1.84 (m, 12H), 1.78-1.68 (m. 9H), 1.65-1.48 (m. 14H);

^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm) 173.32, 166.90, 84.37, 78.15, 58.84, 54.56, 46.99, 46.75, 37.17, 32.76, 32.49, 25.59, 22.28, 21.96, 21.39, 19.58;

HRMS (EI) calcd for $C_8H_{11}{}^{79}BrO_2$ $[M]^+$: 217.9942; found: 217.9862.

Compound 6m

6-Bromohexahydro-2*H*-3,5-methanocyclopenta[*b*]furan-2-one



Colorless oil.

IR (KBr): 2986, 2889, 1768, 1452, 1344 cm^{-1}

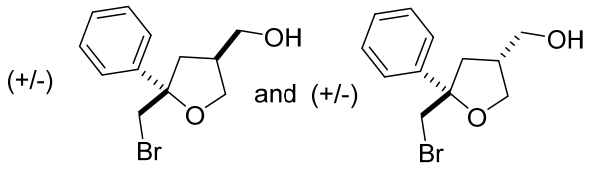
^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm) 4.92 (d, J = 5.0 Hz, 1H), 3.84 (d, J = 2.2 Hz, 1H), 3.23 (t, J = 4.4 Hz, 1H), 2.67 (d, J = 2.6 Hz, 1H), 2.56 (dd, J_1 = 4.4 Hz, J_2 =11.2 Hz, 1H), 2.33 (dd, J = 1.1, J_2 =11,5 Hz, 1H), 2.17-2.11(m, 1H), 1.81-1.73(m, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm) 179.17, 87.63, 53.43, 45.85, 45.49, 37.52, 35.72, 33.94;

HRMS (EI) calcd for $C_8H_9{}^{79}BrO_2[M]^+$: 215.9786, found: 215.9791;

Compound 6n and 6n'

(5-(Bromomethyl)-5-phenyltetrahydrofuran-3-yl)methanol



Colorless oil.

IR (KBr): 3408, 2872, 1601 1447 cm^{-1}

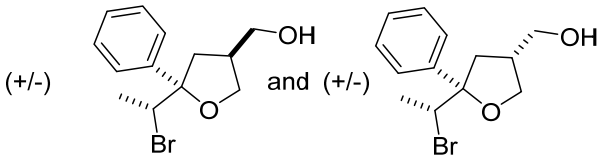
^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm): 7.42-7.26 (m, 25H), 4.25 (dd, J_1 = 7.3 Hz, J_2 = 8.6 Hz, 1H), 4.06-4.03 (t, 4H), 3.86 (dd, J_1 = 6.7 Hz, J_2 = 8.7 Hz, 4H), 3.69 (d, J = 6.3 Hz, 8H), 3.66 (s, 8H), 3.60 (s, 2H), 3.50-3.40 (m, 2H), 2.80-2.72 (m, 1H), 2.64 (dd, J_1 = 8.7 Hz, J_2 = 12.9 Hz, 1H), 2.47-2.40 (m. 8H), 2.21-2.08 (m. 6H);

^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm) 144.18, 143.06, 128.35, 128.32, 127.56, 127.45, 125.50, 125.42, 85.75, 85.45, 71.04, 70.55, 64.29, 64.10, 42.87, 42.48, 41.83, 41.55, 39.45, 39.06;

HRMS (ESI) calcd for $C_{12}H_{15}{}^{79}BrO_2\ Na^+$ $[M+Na]^+$: 293.0148, found: 293.0140;

Compound 6o and 6o'

(5-(1-Bromoethyl)-5-phenyltetrahydrofuran-3-yl)methanol



Colorless oil.

IR (KBr): 3415, 3024, 1677, 1376 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm): 7.54-7.52 (m, 2H), 7.37-7.34 (m, 2H), 7.32-7.28 (m, 1H), 4.35 (q, J = 6.9 Hz, 1H), 3.94-3.91 (m, 1H), 3.81 (dd, J_1 = 7.0 Hz, J_2 = 8.6 Hz, 1H), 3.70-3.64 (m, 2H), 2.65 (dd, J_1 = 7.6 Hz, J_2 = 12.6 Hz, 1H), 2.40-2.31 (m, 1H), 2.07 (dd, J_1 = 9.5 Hz, J_2 = 12.6 Hz, 1H), 1.50 (q, J = 6.8 Hz, 3H);

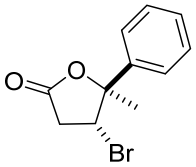
^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm) 140.69, 127.86, 127.56, 127.05, 88.88, 70.33,

64.53, 57.41, 41.24, 38.43, 21.75;

HRMS (ESI) calcd for $C_{13}H_{17}{}^{79}BrO_2\ Na^+$ $[M+Na]^+$: 307.0304, found: 307.0301;

Compound 6p

4-Bromo-5-methyl-5-phenyldihydrofuran-2(3*H*)-one



Yellow oil.

IR (KBr): 3000, 1788, 1496, 1379, 1197, 950 cm^{-1};

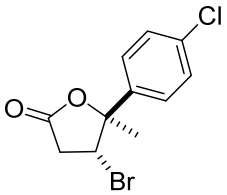
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.42-7.30 (m, 5H), 4.72 (dd, *J* = 6.7, 4 Hz, 1H), 3.13-2.86 (m, 2H), 1.86 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 172.28, 160.43, 139.17, 128.75, 128.25, 124.68, 119.18, 88.84, 26.23.

HRMS (EI) calcd for $C_{11}H_{11}BrO_2$ $[M]^+$: 253.9942; found:253.9939.

Compound 6q

4-Bromo-5-(4-chlorophenyl)-5-methyldihydrofuran-2(3*H*)-one



White solid; mp 101–103 °C

IR (KBr): 2921, 1780, 1489, 1375 cm^{-1};

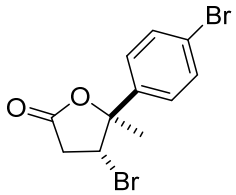
^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm) 7.37 (s, 4H), 4.63 (dd, J_1= 4.9 Hz, J_2= 7.0 Hz, 1H), 3.13-2.92 (m, 2H), 1.86 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm) 172.44, 140.10, 134.59, 129.17, 125.66, 87.89, 51.60, 39.96, 27.29;

HRMS (EI) calcd for $C_{11}H_{10}{}^{79}Br^{35}ClO_2[M]^+$: 287.9553, found: 287.9561.

Compound 6r

4-Bromo-5-(4-bromophenyl)-5-methyldihydrofuran-2(3*H*)-one



White solid; mp 114–116 °C

IR (KBr): 2981, 1777, 1490, 1374 cm^{-1};

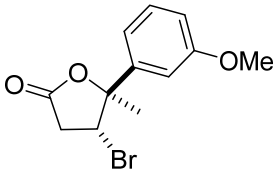
^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm): 7.53 (d, J = 8.5, 2H), 7.31 (d, J = 8.5, 2H), 4.62 (dd, J_1 = 4.9 Hz, J_2 = 6.9 Hz, 1H), 3.13-2.92 (m, 2H), 1.85 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm): 172.40, 140.65, 132.14, 125.96, 122.70, 87.90, 51.52, 39.96, 27.24;

HRMS (EI) calcd for $C_{11}H_{10}{}^{79}Br_2O_2[M]^+$: 331.9048, found: 331.9049.

Compound 6s

4-Bromo-5-(3-methoxyphenyl)-5-methyldihydrofuran-2(3*H*)-one



IR (KBr): 2976, 1699, 1376, 1331 cm^{-1};

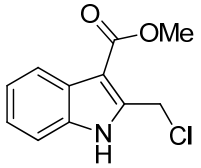
^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm): 7.31 (t, J = 8.0, 1H), 6.98-6.95 (m, 1H), 6.94-6.93 (m, 1H), 6.88-6.86 (m, 1H), 4.72 (dd, J_1 = 3.9 Hz, J_2 = 6.8 Hz, 1H), 3.81 (s, 3H); 3.13-2.89 (m, 2H), 1.86 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm): 172.92, 159.99, 143.15, 130.11, 116.35, 113.57, 110.25, 88.24, 55.34, 52.50, 40.27, 27.61;

HRMS (EI) calcd for $C_{12}H_{13}{}^{79}BrO_3[M]^+$：284.0048, found: 284.0048.

Compound 11

Methyl 2-(chloromethyl)-1H-indole-3-carboxylate



Violet solid; mp 87–89 °C

IR (KBr): 2919, 1675, 1460, 1355 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): (δ, ppm) 9.05 (s, 1H), 8.11-8.09 (m, 1H), 7.38-7.36 (m, 1H), 7.27-7.24 (m, 2H), 5.19 (s, 2H), 3.94 (s, 3H);

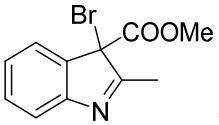
^{13}C NMR (125 MHz, $CDCl_3$): (δ, ppm) 165.73, 140.54, 134.81, 126.49, 123.60, 122.26, 121.85, 111.27, 105.18, 51.18, 37.96.

HRMS (EI) calcd for $C_{11}H_9ClNO_2$ $[M-H]^-$：222.0327, found: 222.0320.

(C) Procedure for the preparation compound 2. To a mixture of indole **1a** (5 mmol, 945 mg, 1.0 equiv) in dichloromethane or chloroform (10 mL) at 25 ^{o}C was added *N*-bromosuccinimide (1.070 g, 6 mmol, 1.2 equiv). After 5 minutes, the solution was concentrated *in vacuo* at 25 ^{o}C followed by the addition of hexane (10 mL). The clear yellow solution of hexane containing species **2** was separated by filtration. The solvent was removed under reduced pressure to yield compound **2** in 95% yield as orange oil.

Compound 2

Methyl 3-bromo-2-methyl-3*H*-indole-3-carboxylate



Orange oil.

IR (KBr): 2954, 1732, 1584, 1376, 965, 786 cm^{-1};

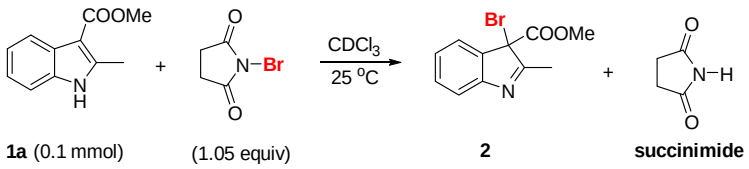
^{1}H NMR (300 MHz, $CDCl_3$): (δ, ppm) 7.60-7.57 (m, 1H), 7.48-7.46 (m, 1H), 7.39-7.33 (m, 1H), 7.24-7.18 (m, 1H), 3.74 (s, 3H), 2.54 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): (δ, ppm) 176.95, 166.25, 153.34, 136.24, 130.84, 126.71, 124.68, 120.86, 59.11, 54.01, 16.67;

DEPT-135 (75 MHz, $CDCl_3$): δ 130.84, 126.71, 124.68, 120.86, 54.00, 16.66.

HRMS (ESI) calcd for $C_{11}H_{10}BrNNaO_2$ $[M + Na]^+$: 289.9787; found: 289.9791, 291.9769.

(D) Analysis of The Reactive Species 2



1a (0.1 mmol) (1.05 equiv) **2** **succinimide**

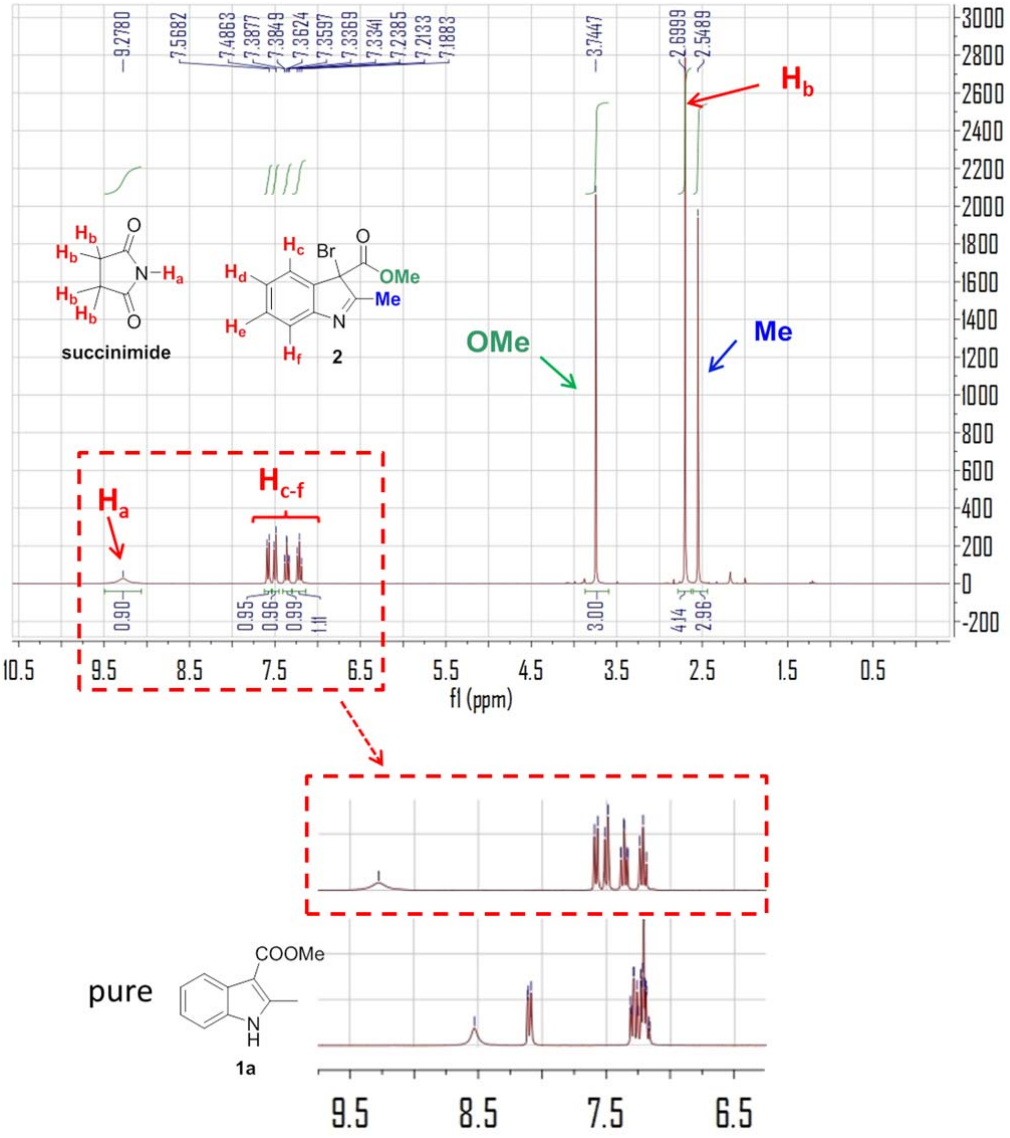


Figure S1. In situ Generation of Reactive Species **2** by Mixing **1a** and NBS in $CDCl_3$

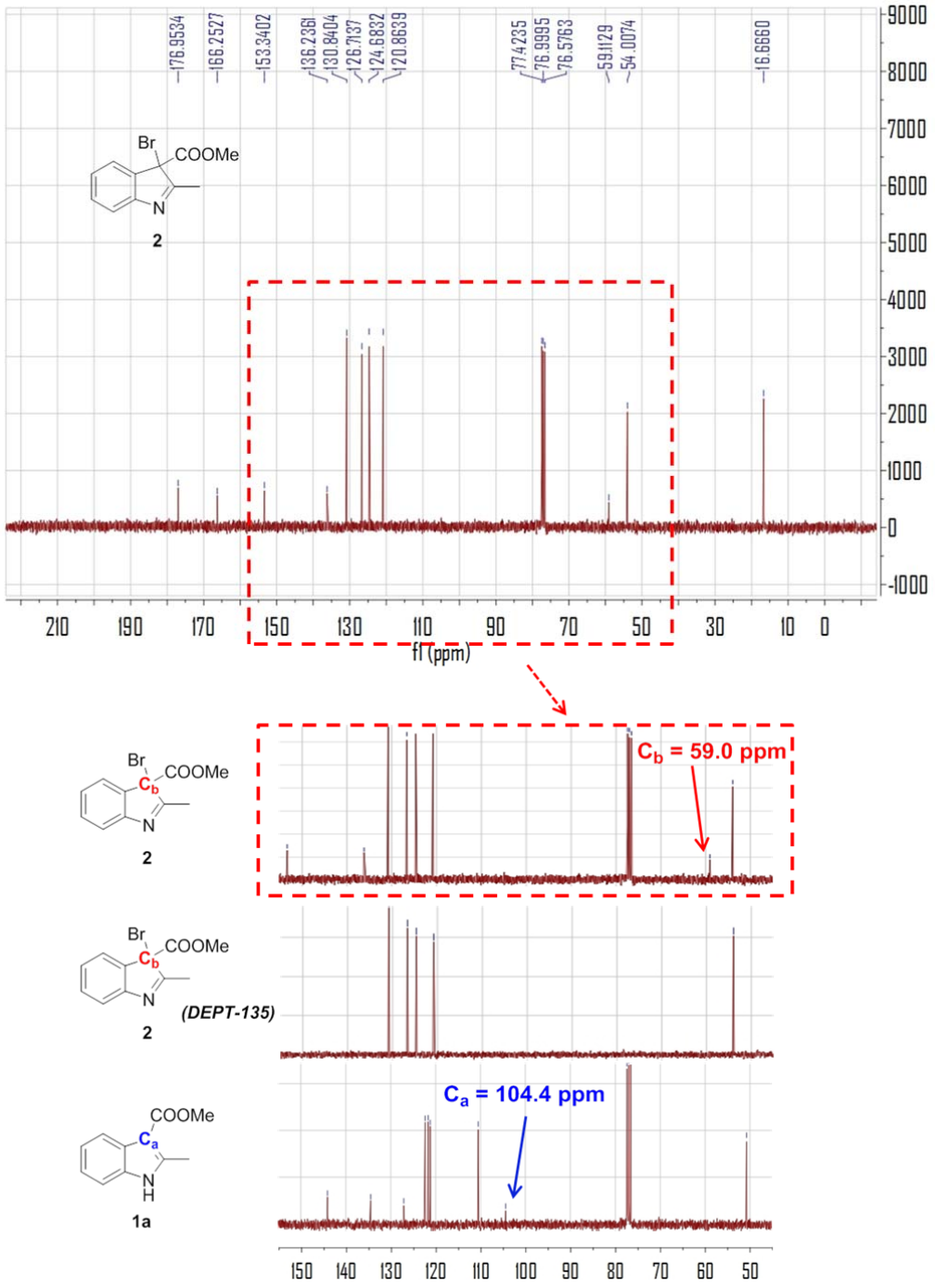
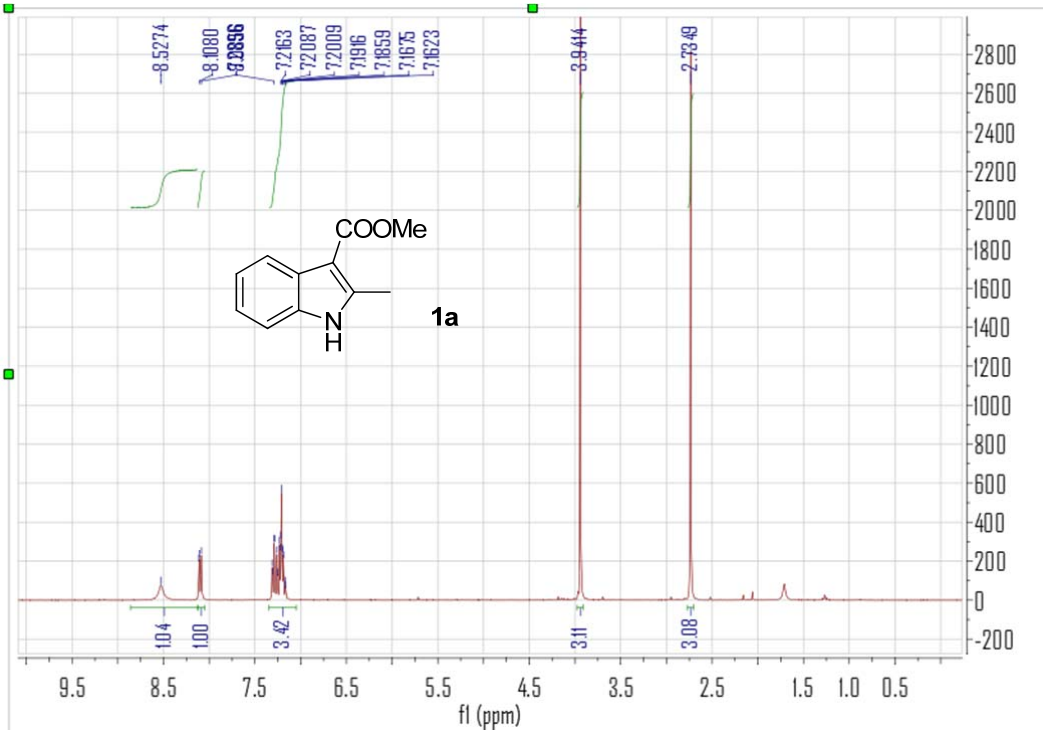
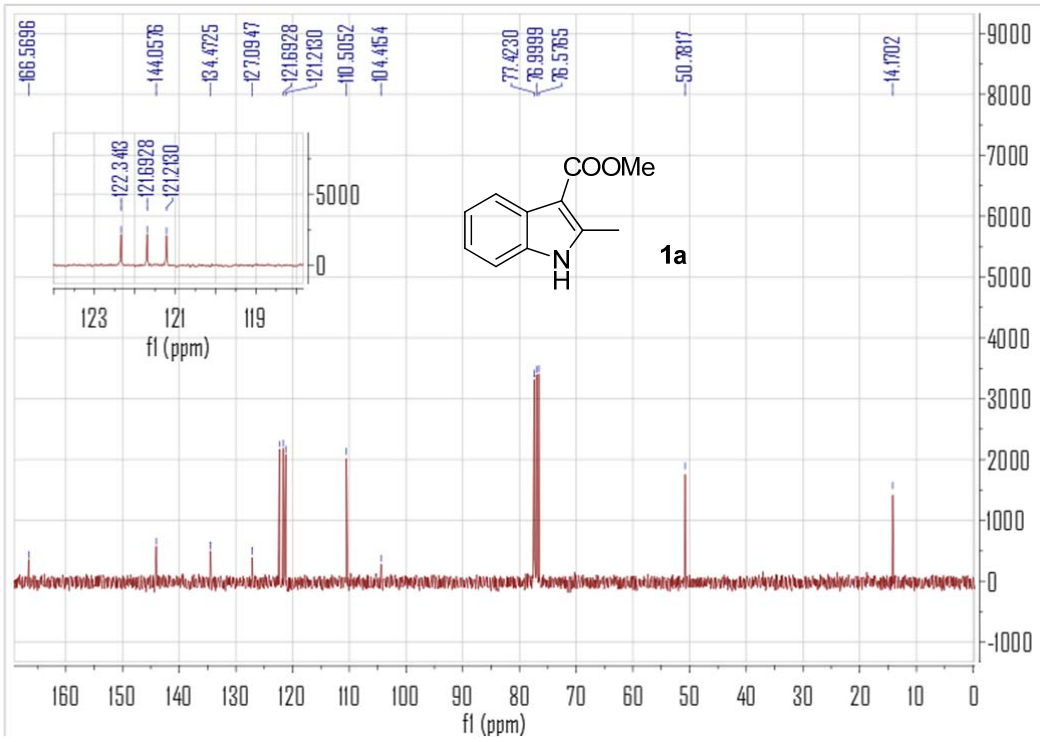
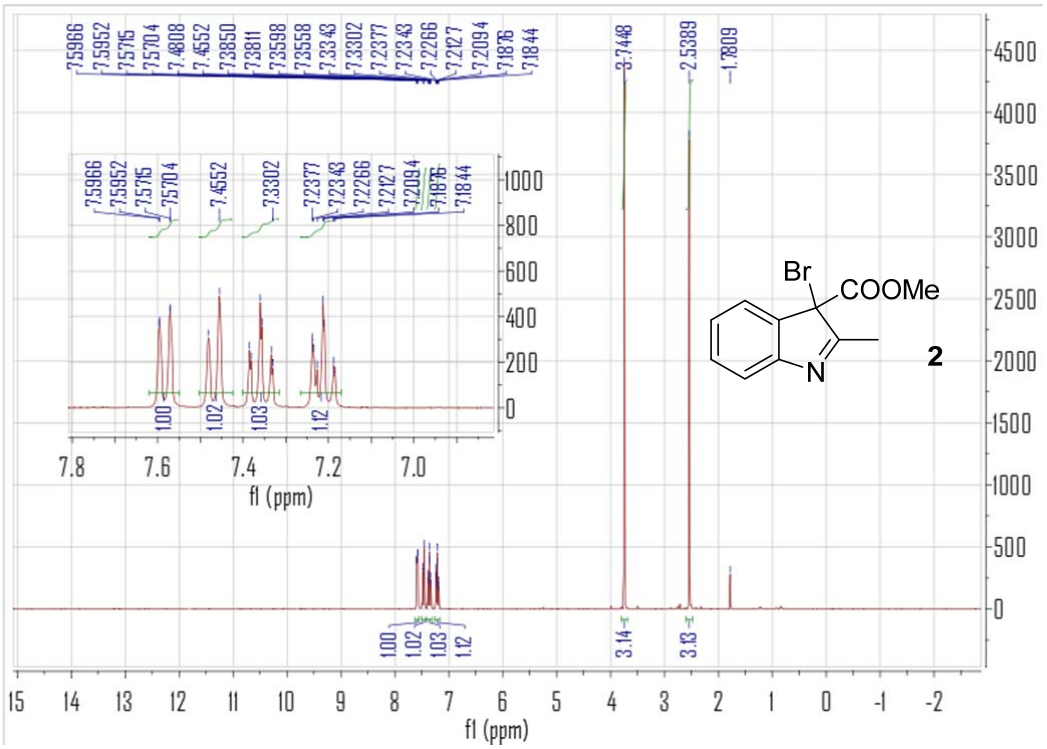
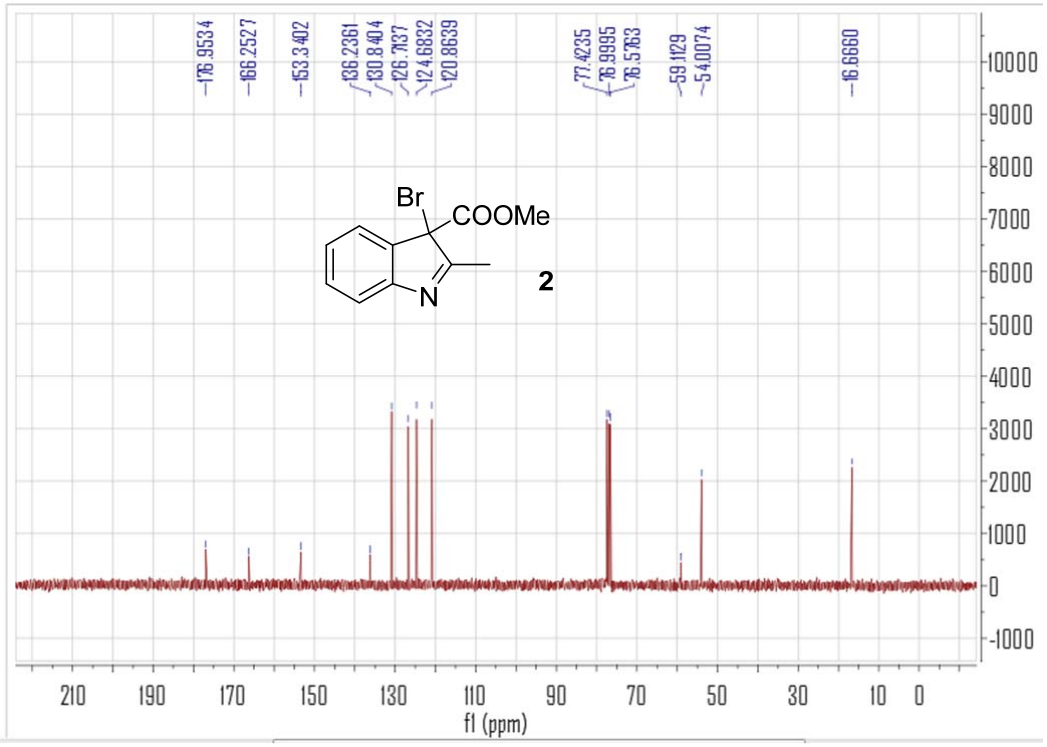


Figure S2. Comparison of ^{13}C NMR Spectra of **1a** and **2**

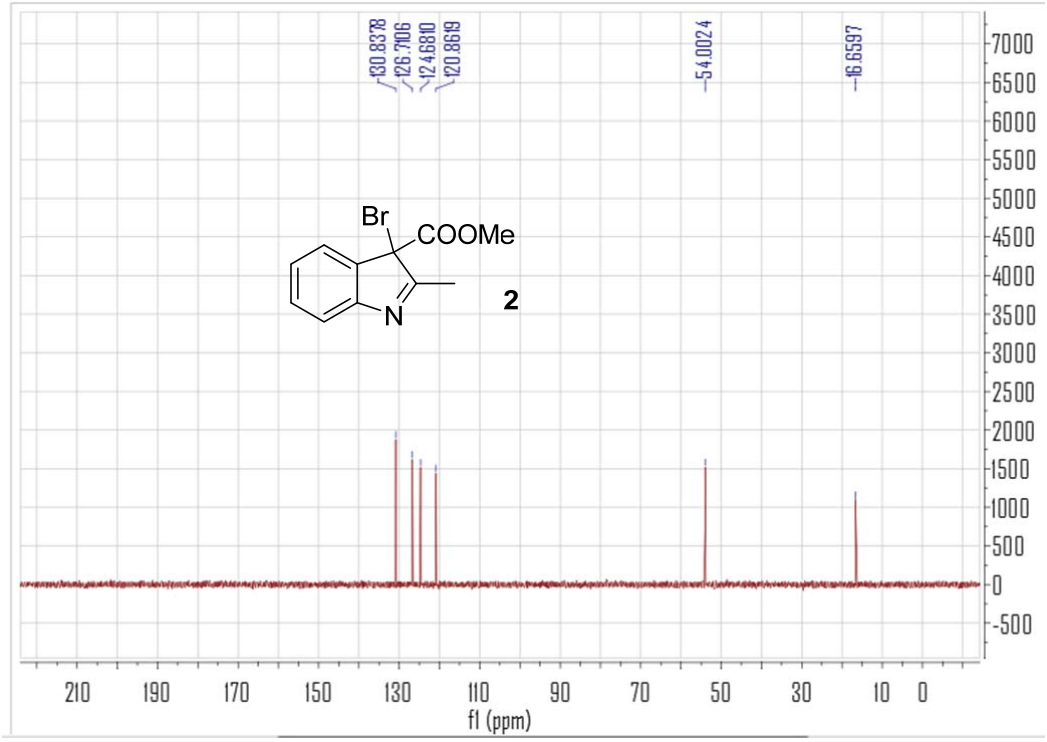

8.5274
8.1080
7.2163
7.2087
7.2009
7.1959
7.1859
7.1675
7.1623
3.9444
2.7349
COOMe
N
H
1a
10.4
1.00
3.42
3.11
3.08
f1 (ppm)


166.5696
144.0576
134.4725
127.0947
121.6928
121.2130
110.5052
104.4654
77.4230
76.9999
76.5765
50.7817
14.1702
122.3443
121.6928
121.2130
5000
0
123
121
119
f1 (ppm)
COOMe
N
H
1a
f1 (ppm)

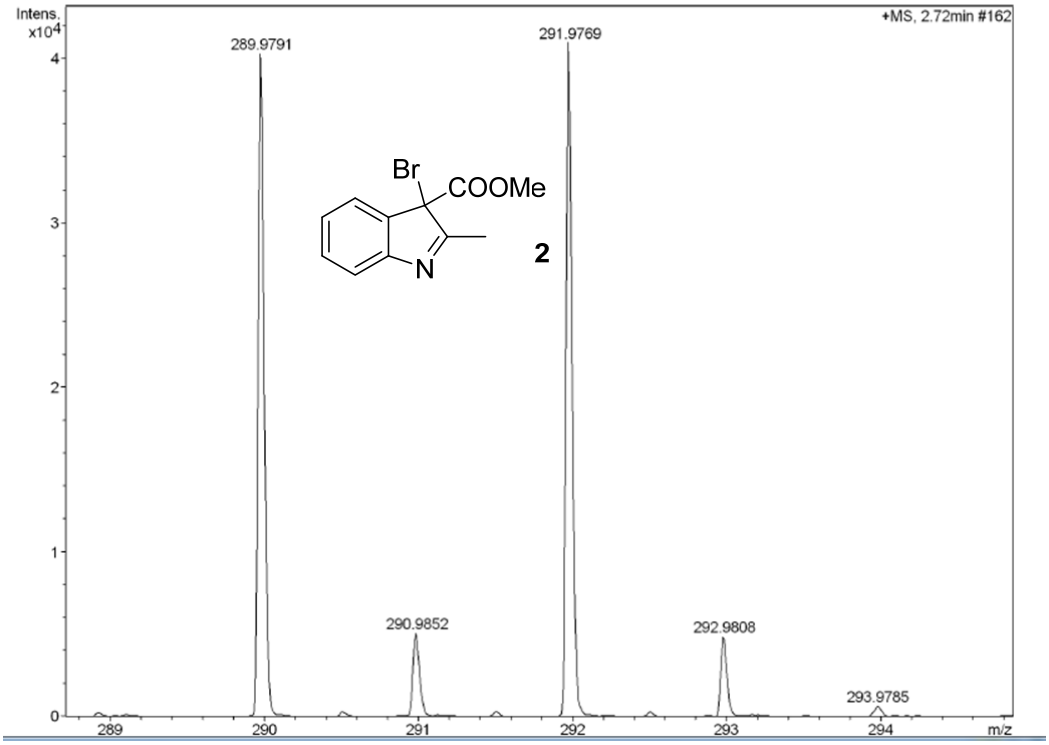

7.5966
7.5952
7.5715
7.5704
7.4808
7.4552
7.3850
7.3811
7.3598
7.3558
7.3343
7.3302
7.2377
7.2343
7.2266
7.2127
7.2094
7.1876
7.1844
3.7448
2.5389
1.7809
Br
COOMe
N
2
1.00
1.02
1.03
1.12
3.14
3.13
fl (ppm)


176.9534
166.2527
153.3402
136.2361
130.8404
126.7637
124.6832
120.8639
77.4235
76.9995
76.5763
59.1129
54.0074
16.6660
Br
COOMe
N
2
fl (ppm)

DEPT-135



HRMS



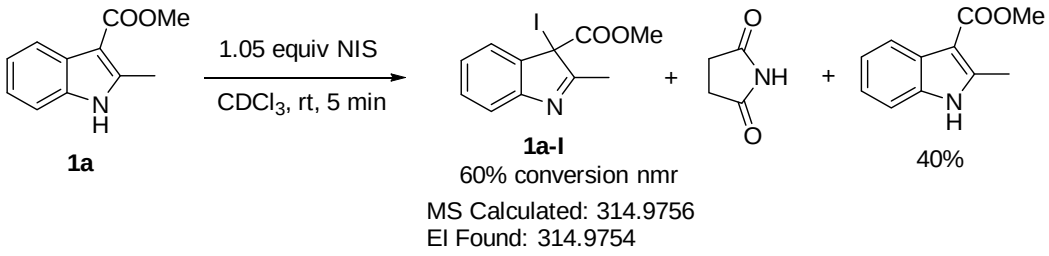
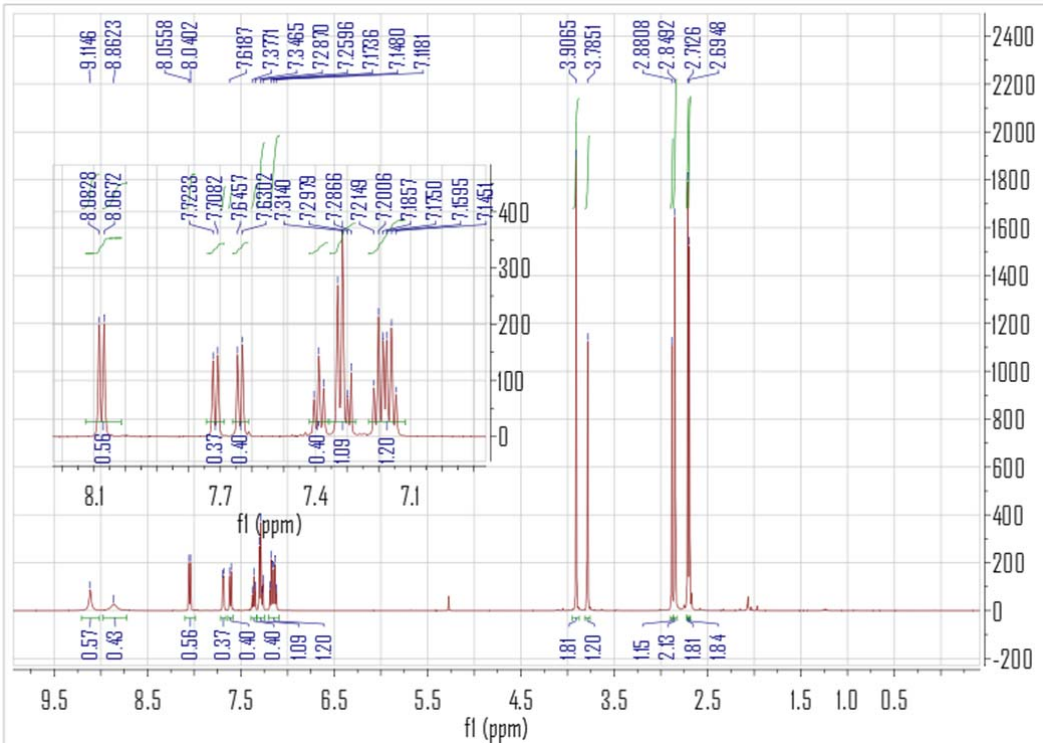
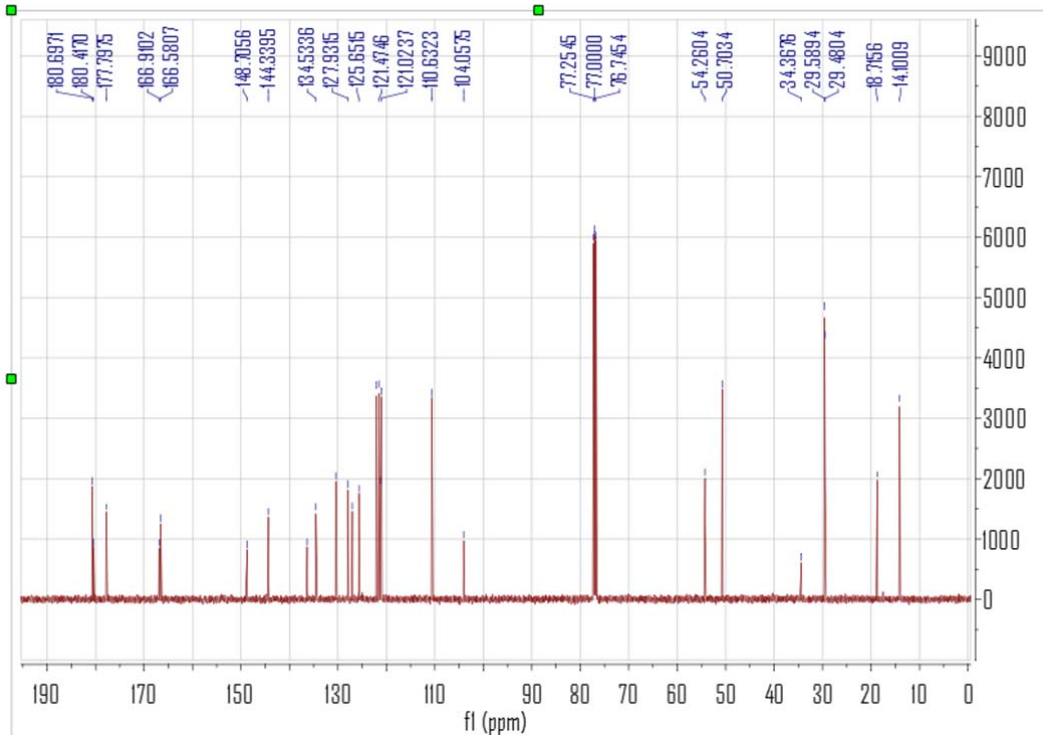


Figure S3. In situ Generation of Reactive Species **1a-I** by Mixing **1a** and NIS in $CDCl_3$

^{1}H NMR

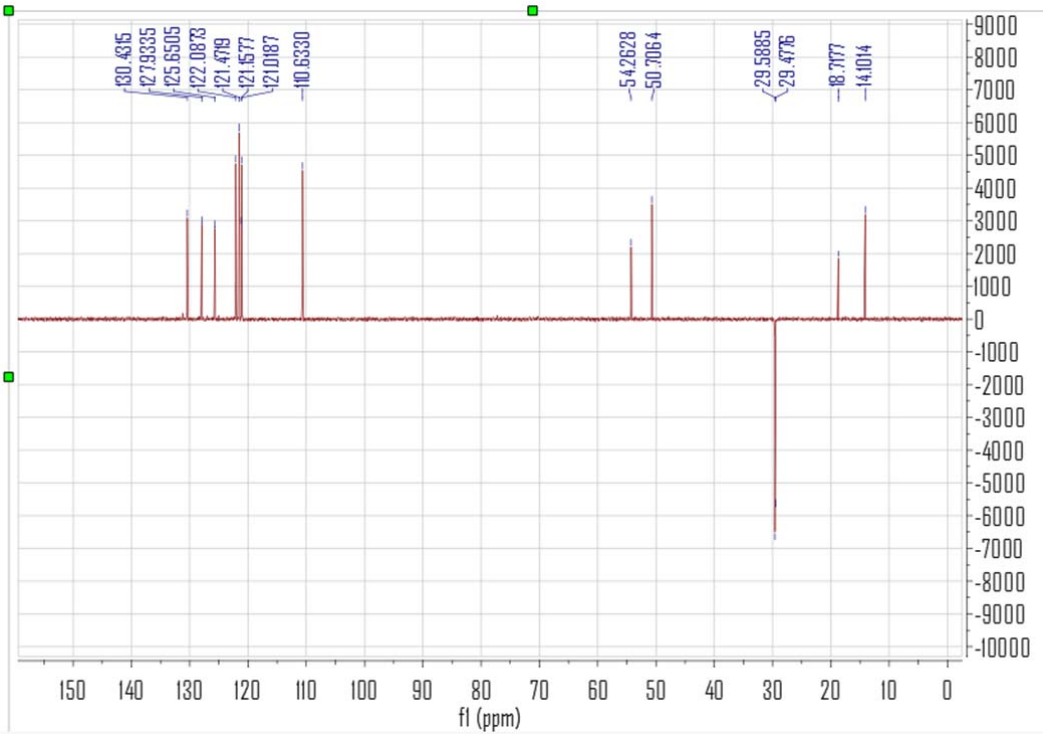


^{13}C NMR



δ =34.37ppm Carbon is quaternary carbon at 3-position.

DEPT135



(E) Studies of Indole Catalyst Analogues

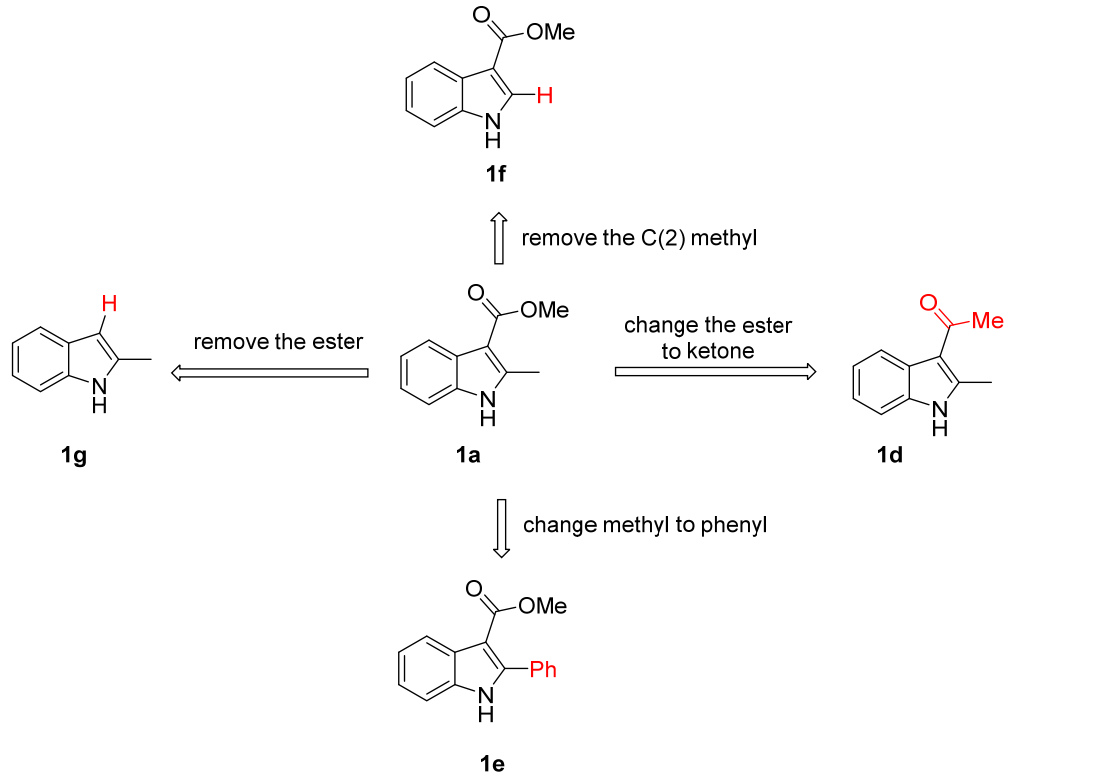
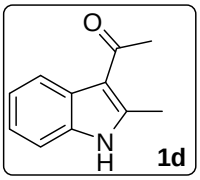


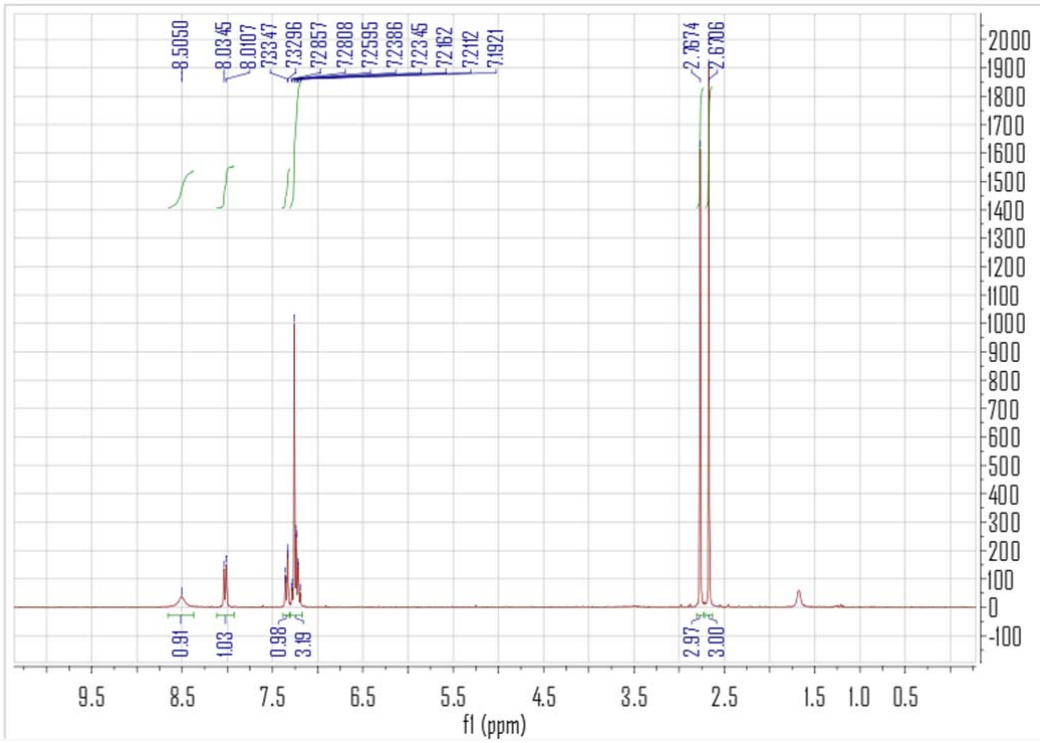
Figure S4. Generation of Reactive Species from Analogues of **1a**

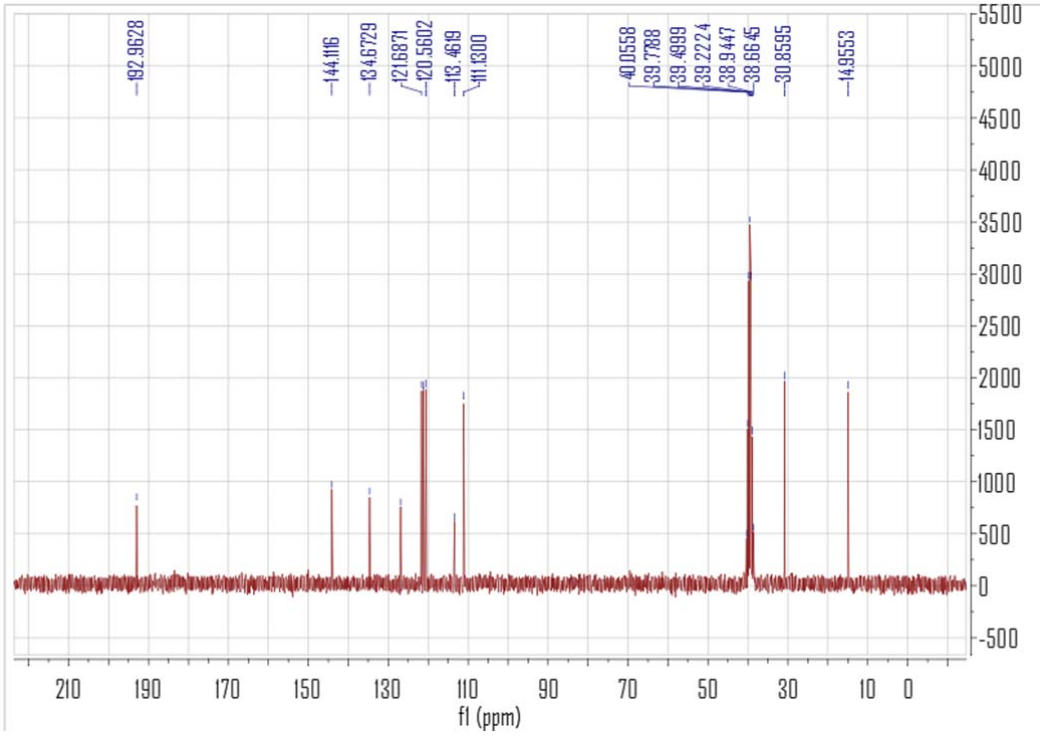
Note: We attempted to prepare the **1-Br** species from catalyst analogues **1d-1g** using the procedure in Section (C). Both **1d** and **1e** could give the corresponding **1d-Br** and **1e-Br** species smoothly. 1f and its brominated species showed very low solubility in lipophilic solvent. For **1g**, it reacted with NBS to give the 3-bromoindole **1g-Br**. The Br in **1g-Br** was found to be inactive towards electrophilic bromination reaction.

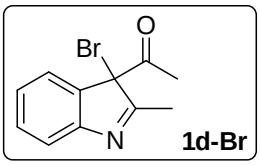


1d

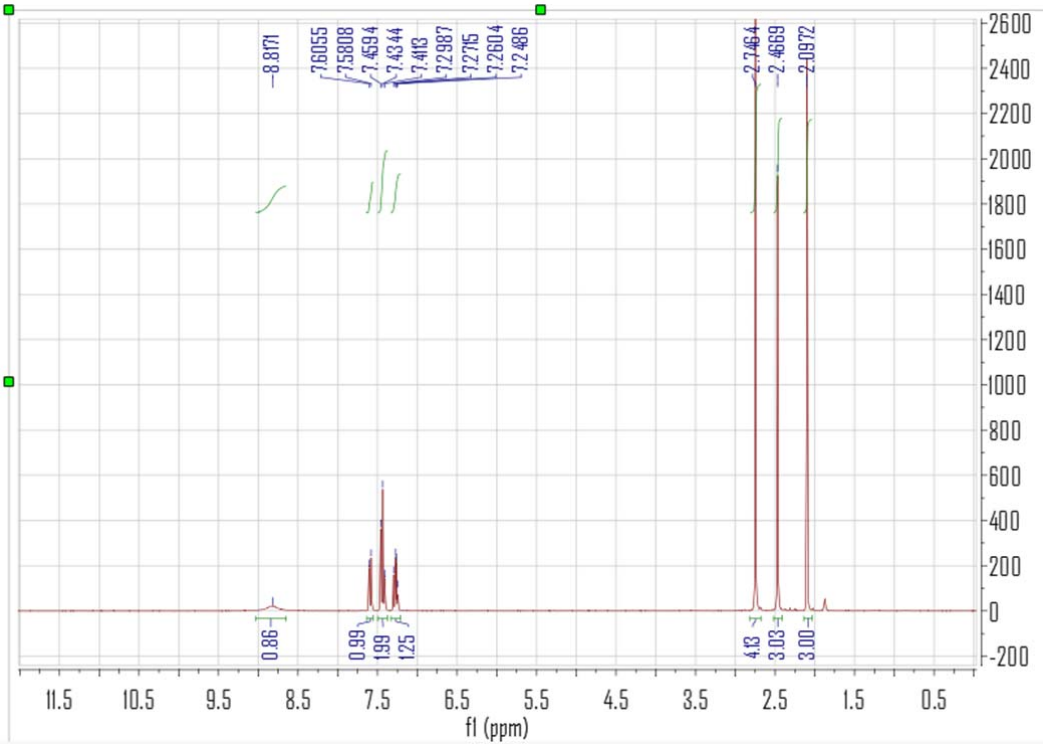
^{1}H NMR and ^{13}C NMR

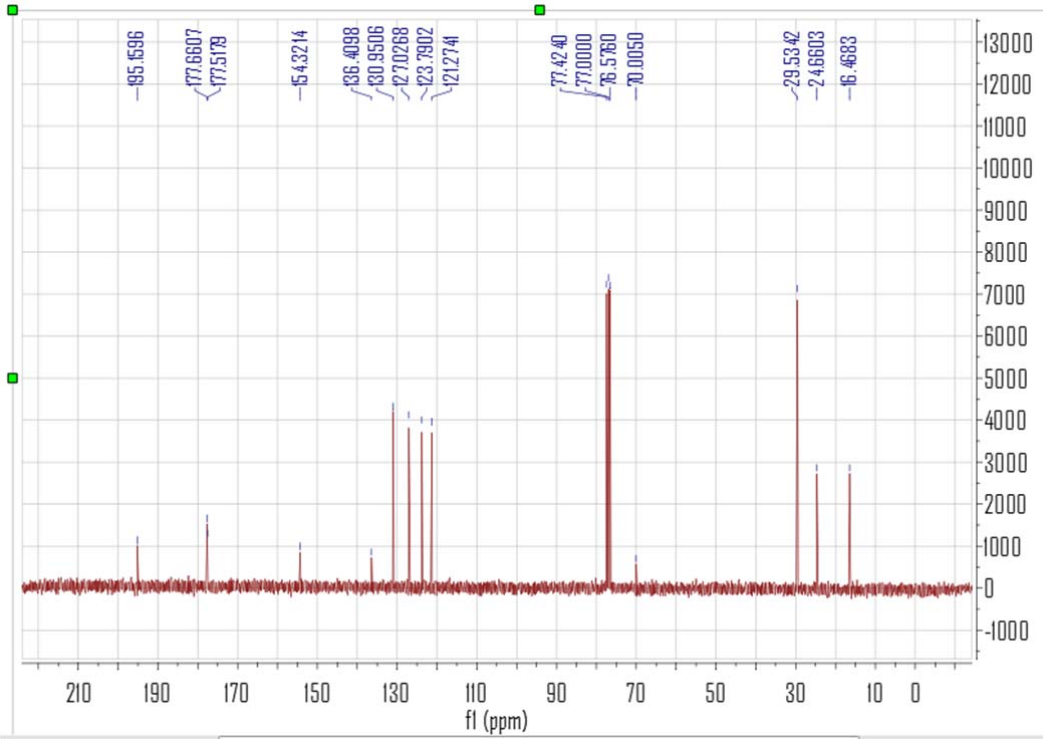




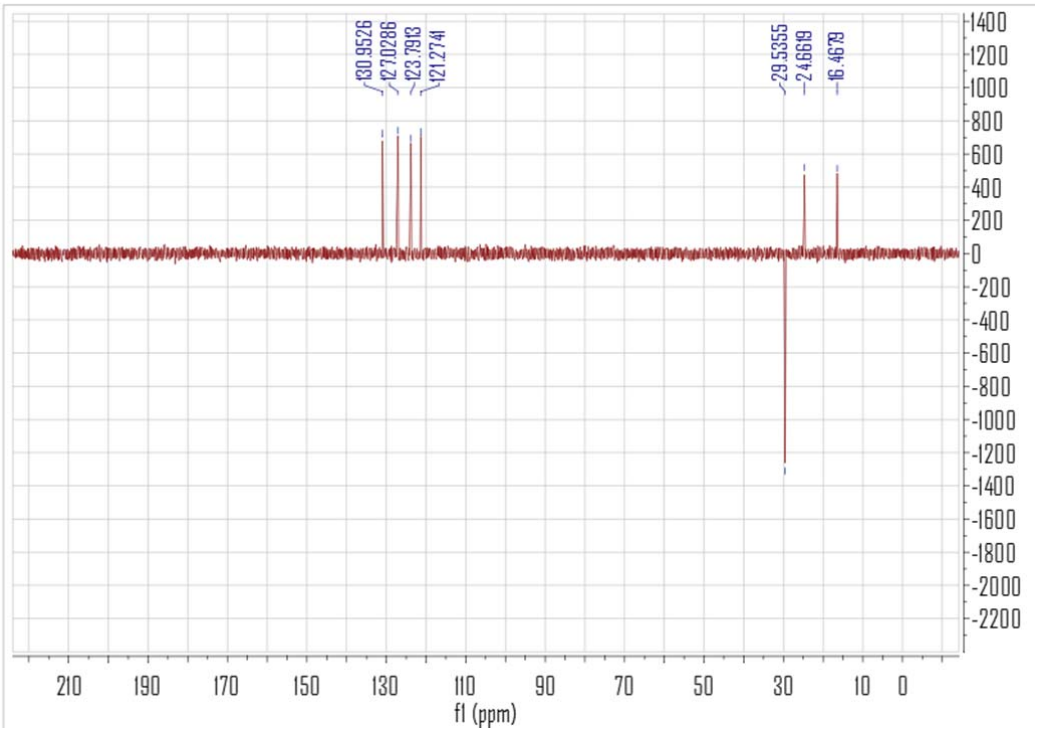


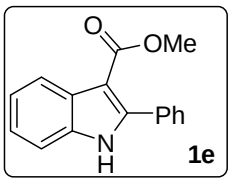
1d-Br ^{1}H NMR, ^{13}C NMR and DEPT135



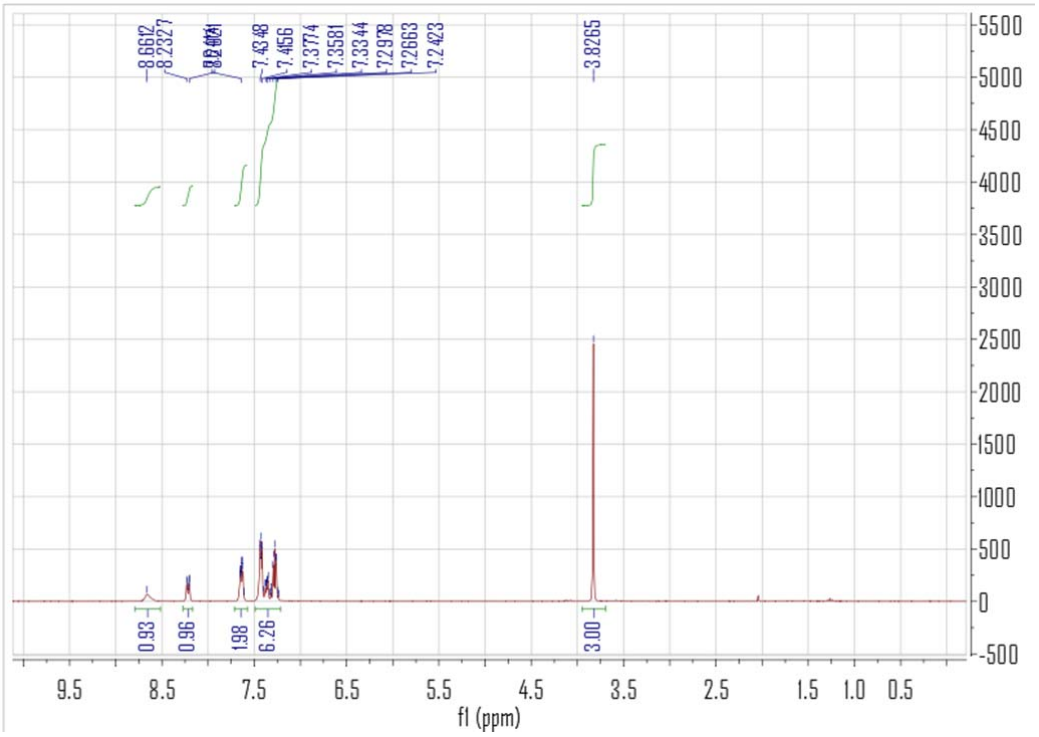


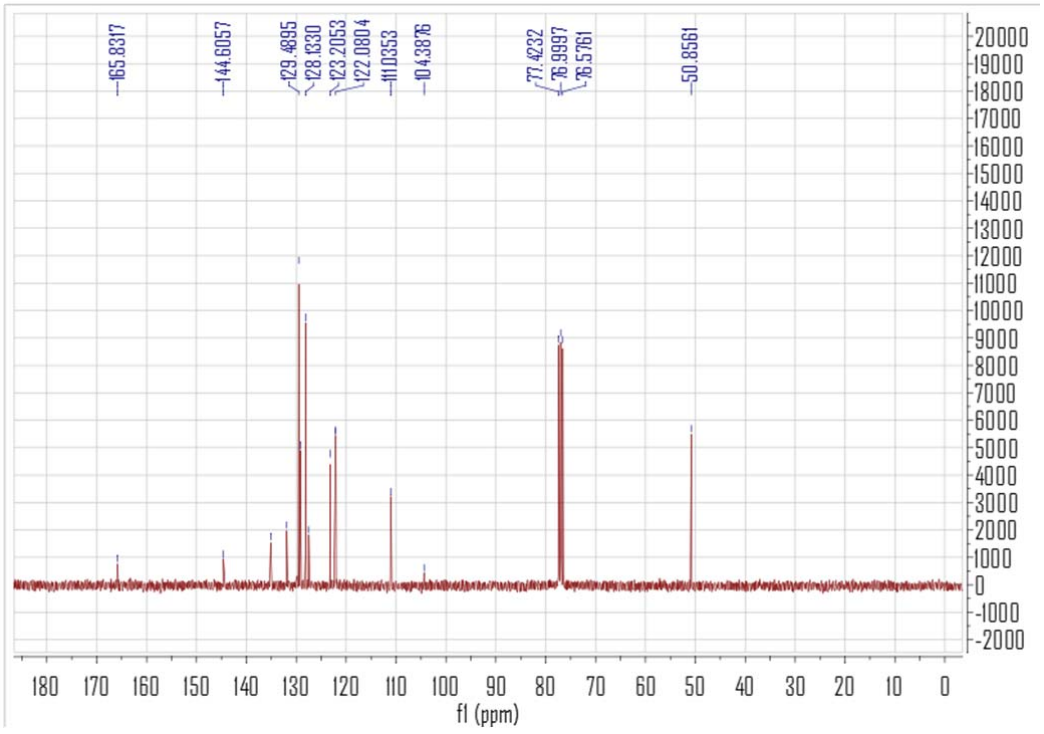
δ =70.00 ppm is quaternary carbon

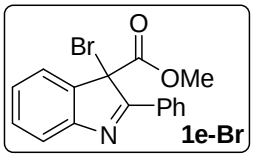




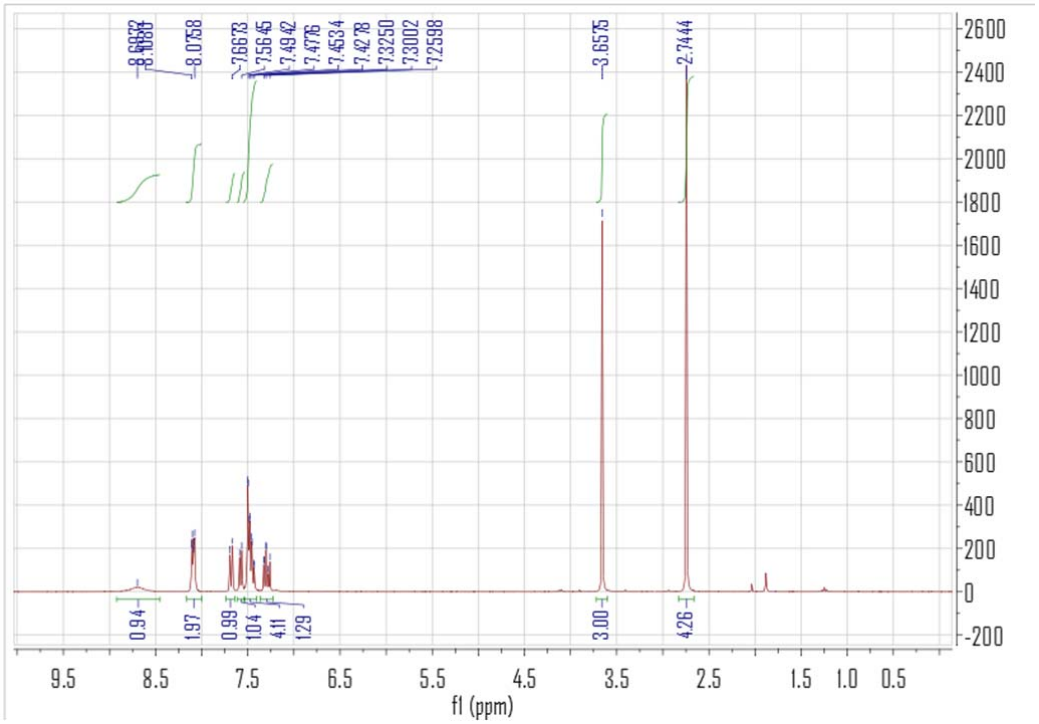
^{1}H NMR and ^{13}C NMR

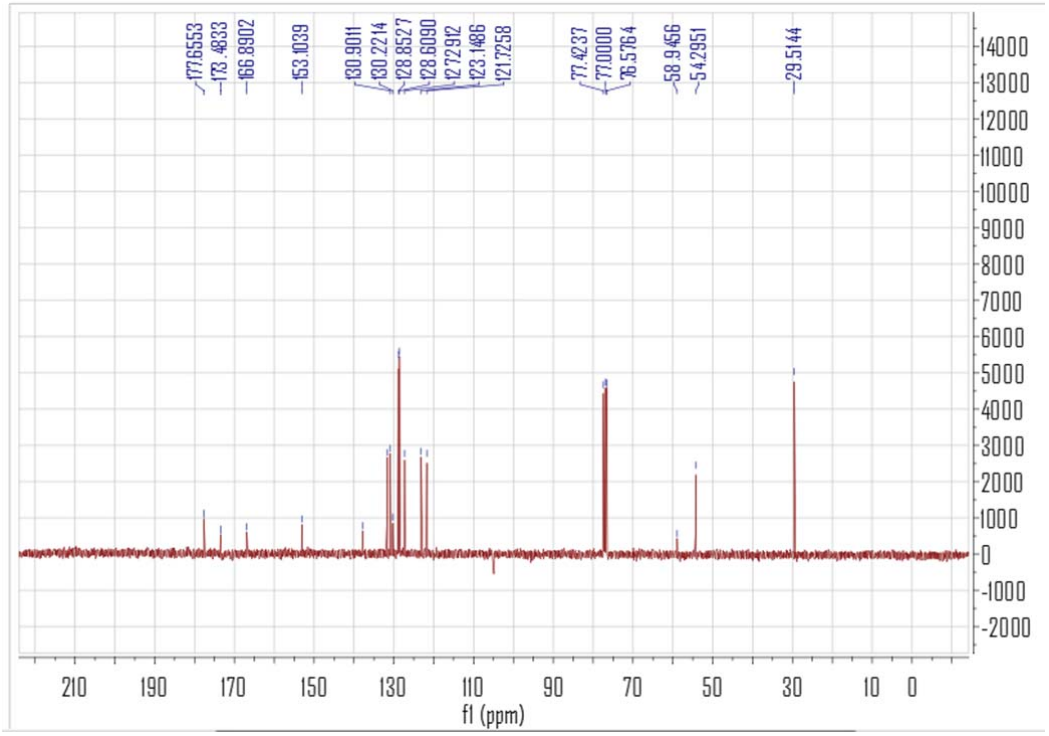




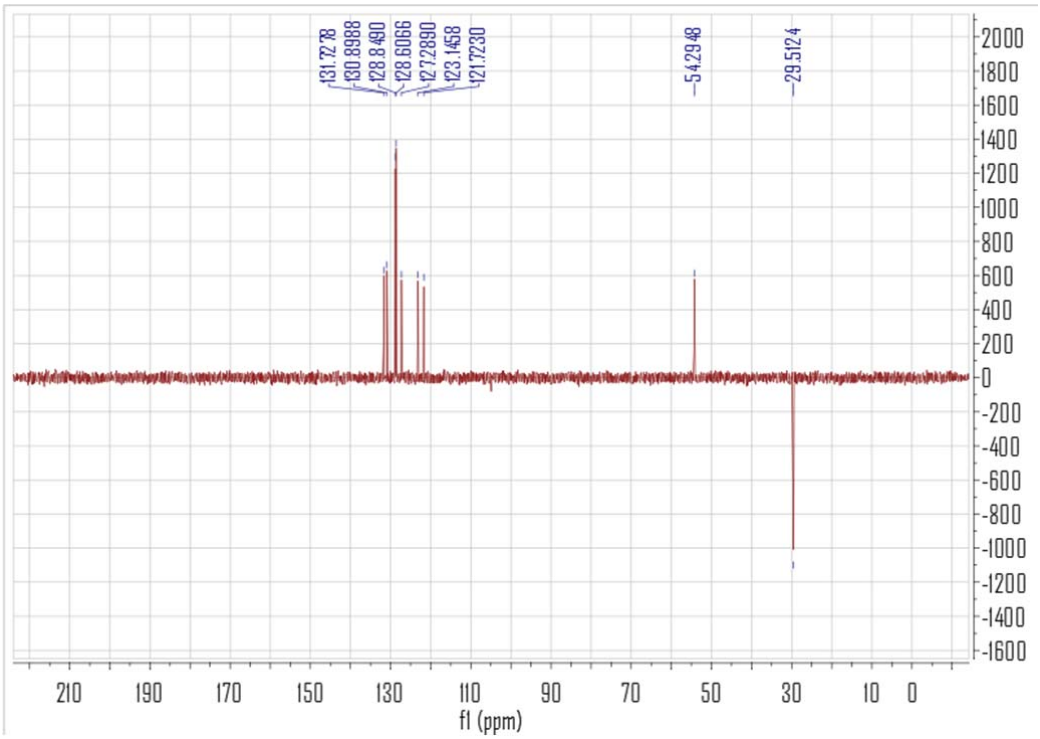


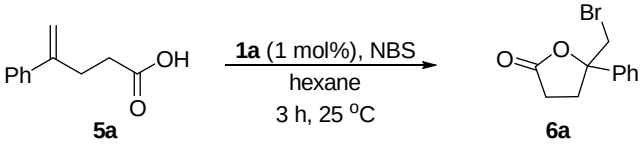
^{1}H NMR, ^{13}C NMR and DEPT135





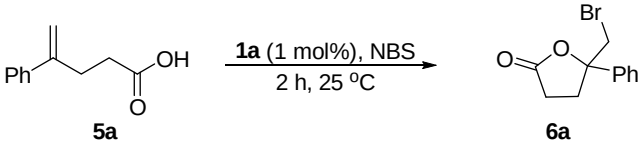
δ =58.95 ppm is quaternary carbon





entry	catalyst	yield (%)
1	**1a**	54
2	**1d**	30
3	**1e**	20
4	**1f**	34
5	**1g**	18

Figure S5. Comparison of the catalytic ability of different catalysts



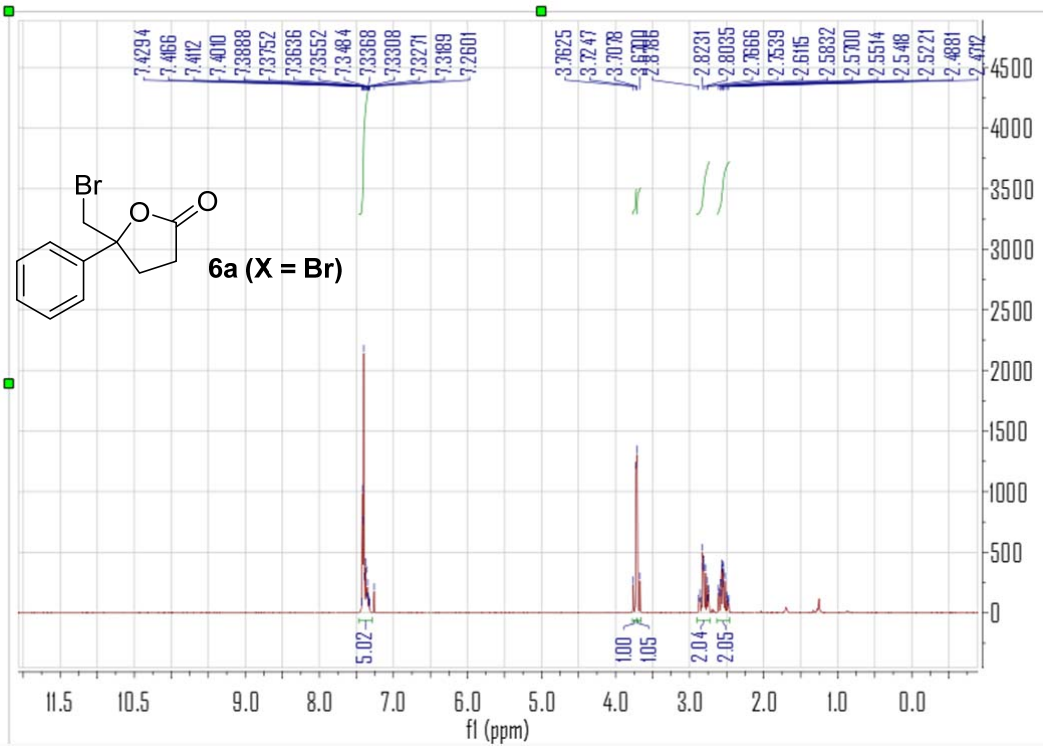
entry	solvent	yield (%)
1	CH_2Cl_2	92
2	THF	95
3	MeCN	96

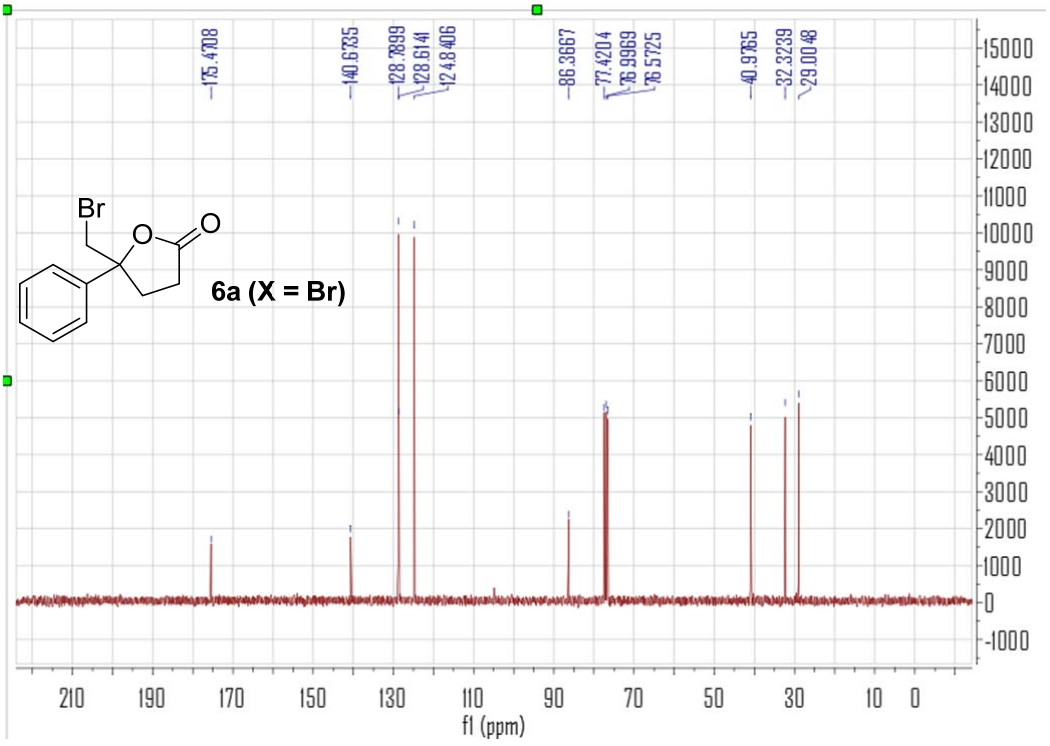
Figure S6. Generation of Reactive Species from Analogues of **1a**

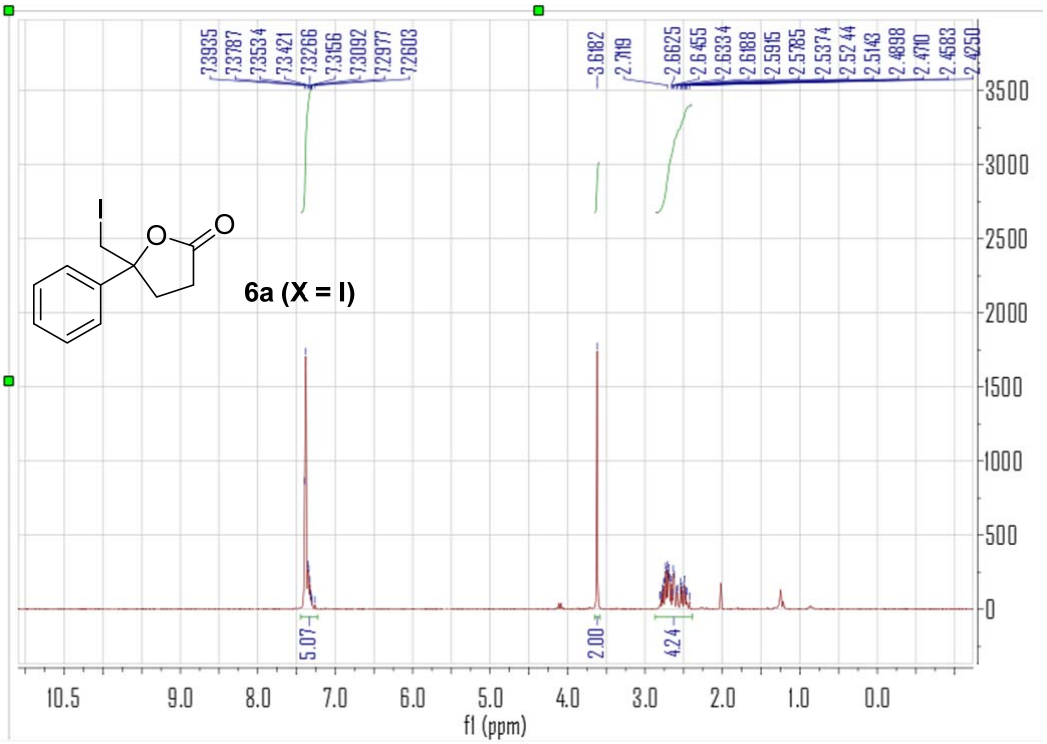
(F) References

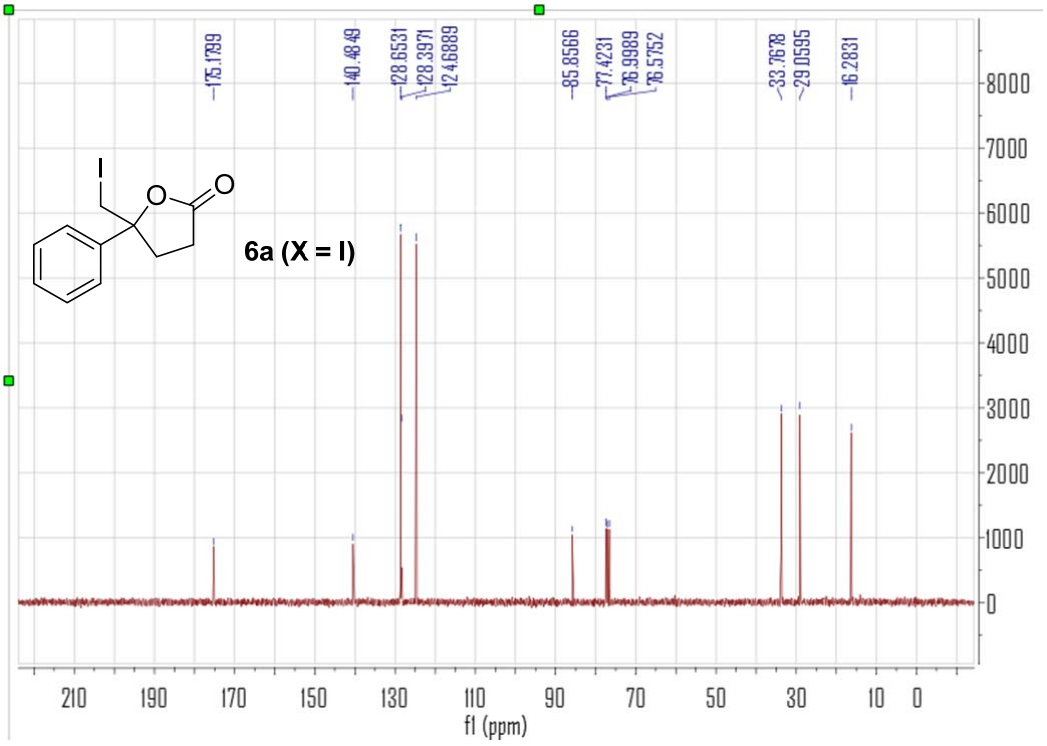
(1) Zhou, L.; Tan, C. K.; Jiang, X.; Chen, F.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 15474–15476.

(2) Wuertz, S.; Rakshit, S.; Neumann, J. J.; Dröege, T.; Glorius, F. *Angew. Chem. Int. Ed.* **2008**, *47*, 7230–7233.


7.4294
7.4166
7.4112
7.4010
7.3888
7.3752
7.3636
7.3552
7.3484
7.3368
7.3308
7.3271
7.3189
7.2601
3.7625
3.7247
3.7078
2.8231
2.8035
2.7666
2.7539
2.6115
2.5832
2.5700
2.5514
2.5418
2.5221
2.4881
Br
O
O
6a (X = Br)
5.02
1.00
1.05
2.04
2.05
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


175.4708
140.6735
128.7899
128.6141
124.8406
86.3667
77.4204
76.9969
76.5725
40.9765
32.3239
29.0048
Br
O
O
6a (X = Br)
210
190
170
150
130
110
90
70
50
30
10
0
f1 (ppm)


7.3935
7.3787
7.3534
7.3421
7.3266
7.3156
7.3092
7.2977
7.2603
3.6182
2.719
2.6625
2.6455
2.6334
2.6188
2.5915
2.5785
2.5374
2.5244
2.5143
2.4898
2.4710
2.4583
2.4250
I
O
O
6a (X = I)
5.07
2.00
4.24
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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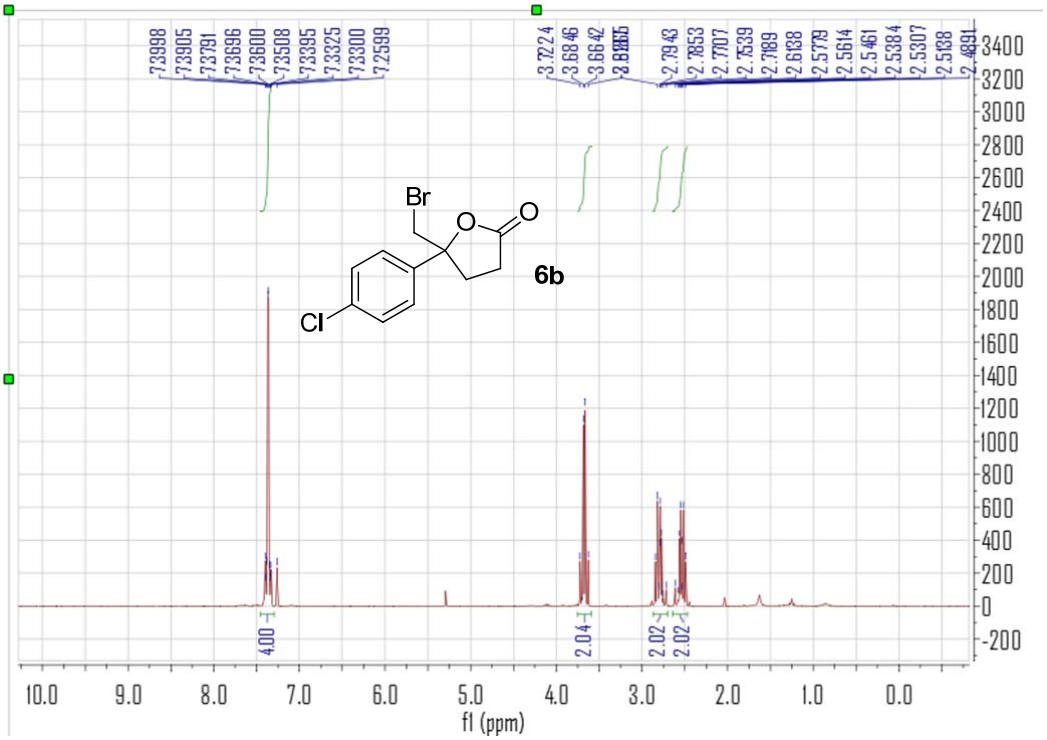
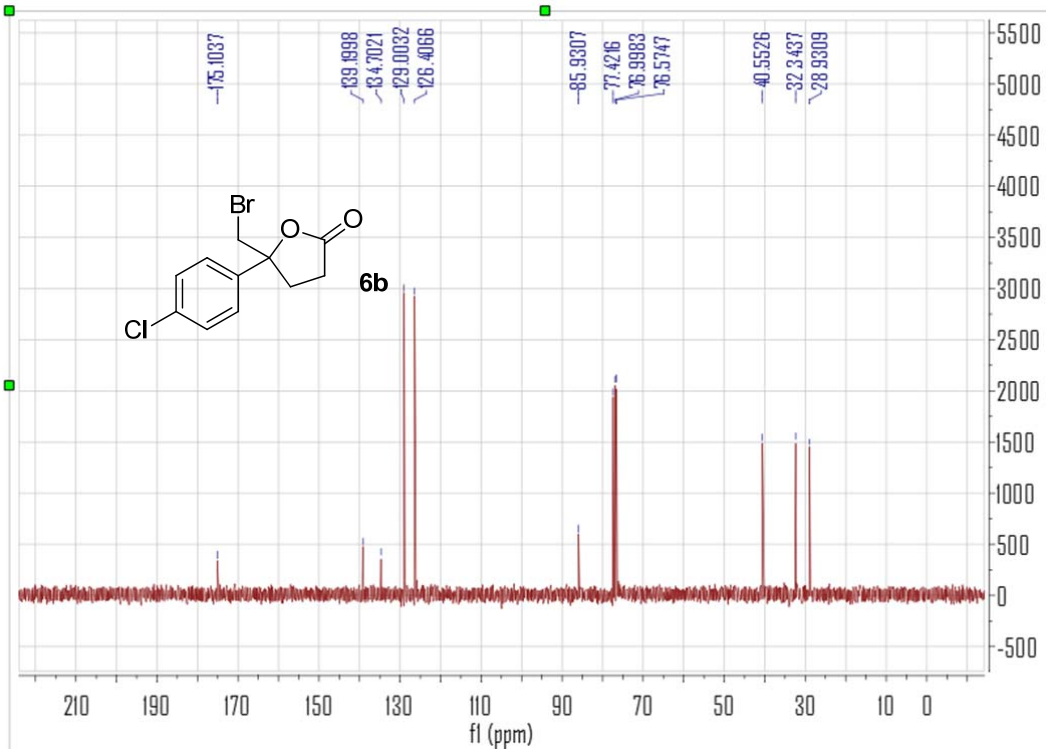
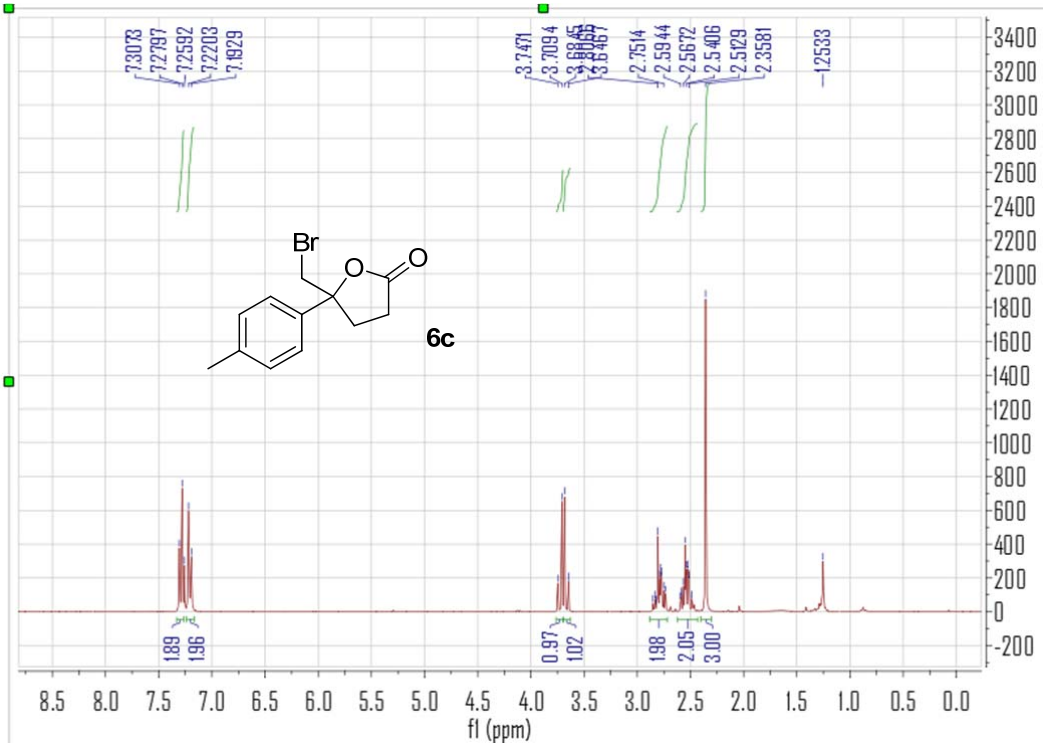
140.4849
128.6531
128.3971
124.6889
85.8566
77.4231
76.9989
76.5752
33.7678
29.0595
16.2831
I
O
O
6a (X = I)
210
190
170
150
130
110
90
70
50
30
10
0
f1 (ppm)


Br
O
O
Cl
6b
f1 (ppm)


Br
O
O
Cl
6b
f1 (ppm)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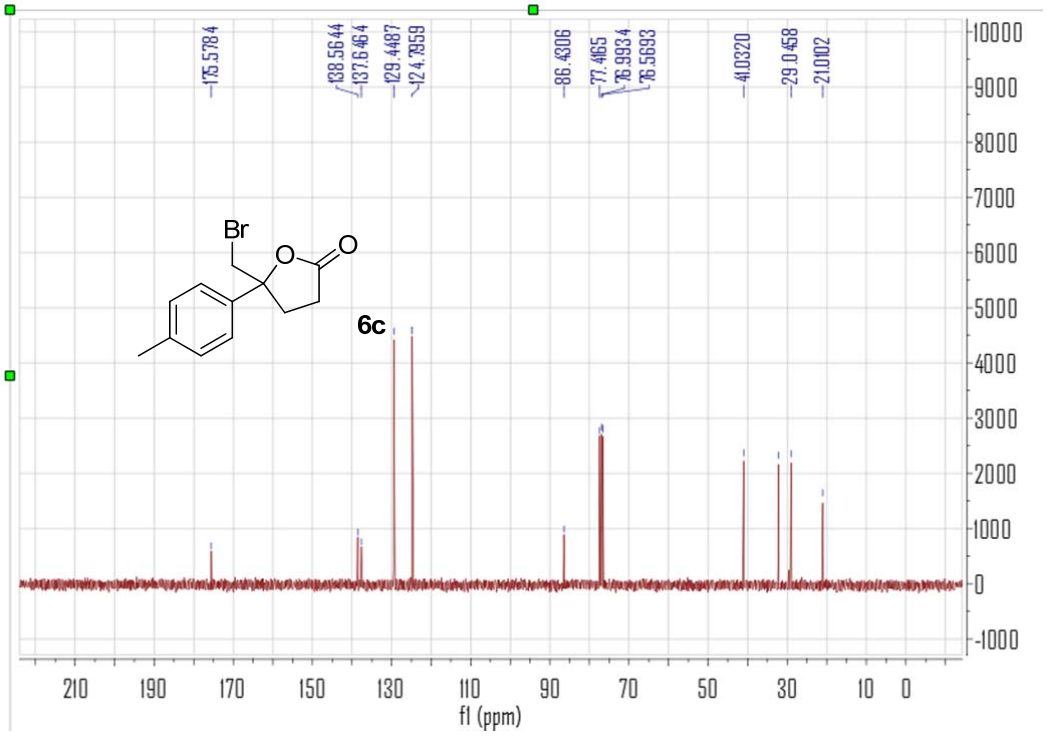
7.2797
7.2592
7.2203
7.1929
3.7471
3.7094
2.7514
2.5944
2.5672
2.5406
2.5129
2.3581
1.2533
Br
O
O
6c
1.89
1.96
0.97
1.02
1.98
2.05
3.00
f1 (ppm)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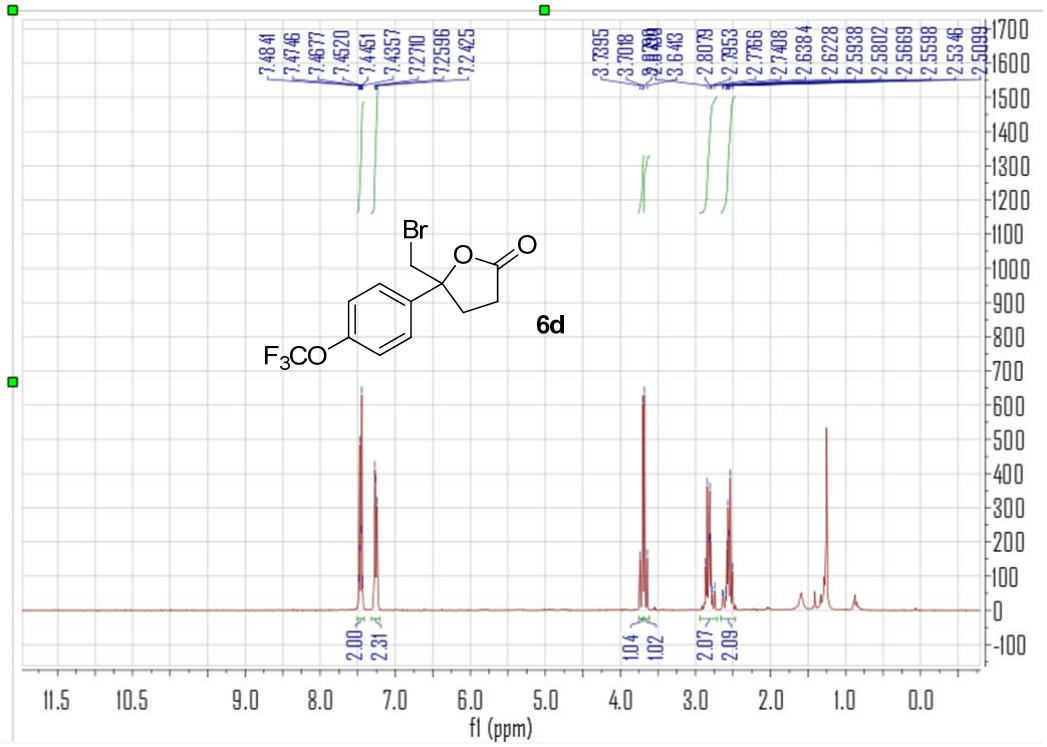
138.5644
137.6464
129.4487
124.7959
86.4306
77.4665
76.9934
76.5693
41.0320
29.0458
21.0002
Br
O
O
6c
f1 (ppm)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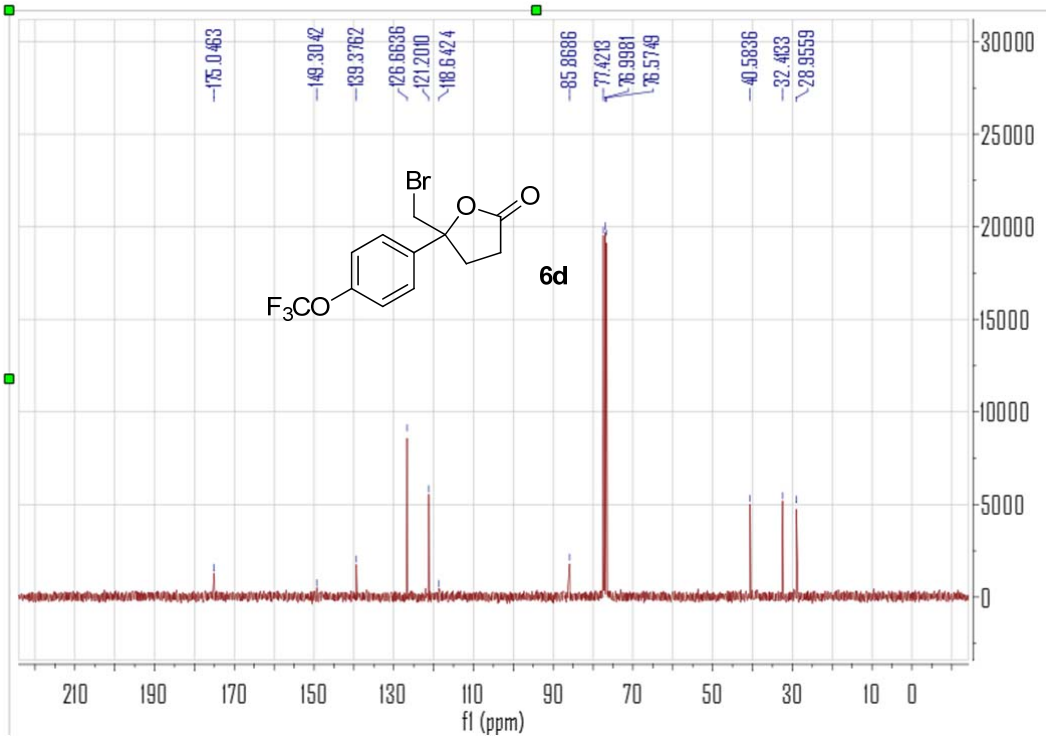
7.4677
7.4520
7.4451
7.4357
7.2710
7.2596
7.2425
3.7395
3.7018
3.6443
2.8079
2.7953
2.7766
2.7408
2.6384
2.6228
2.5938
2.5802
2.5669
2.5598
2.5346
2.5099
Br
O
O
F3CO
6d
2.00
2.31
10.4
1.02
2.07
2.09
f1 (ppm)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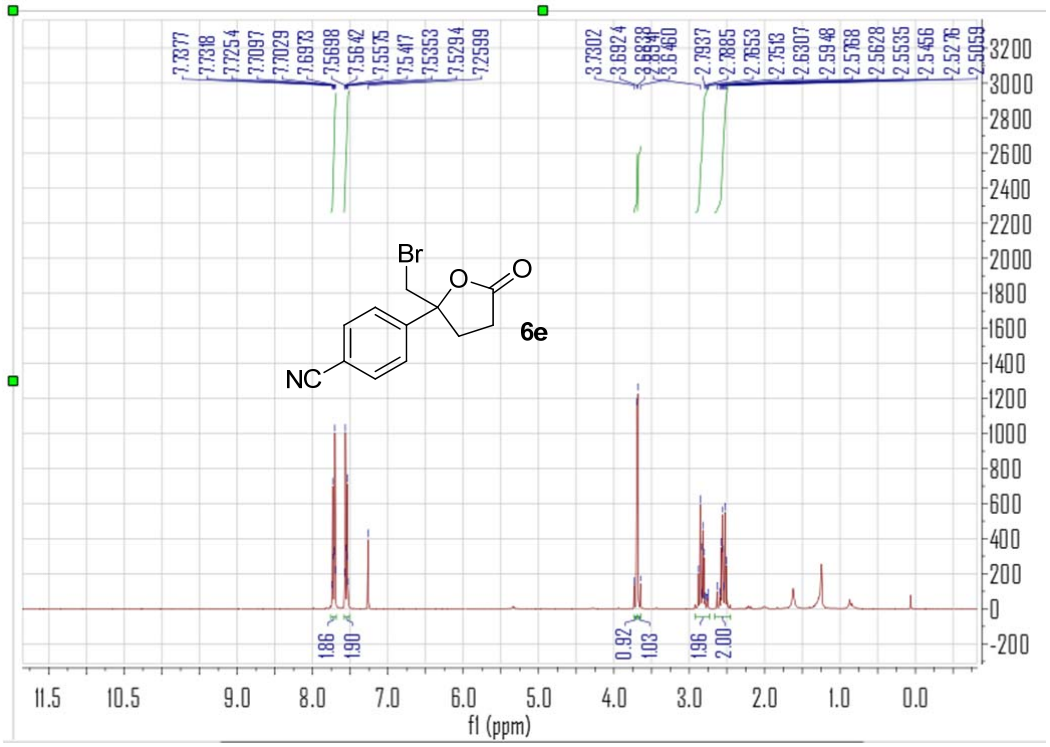
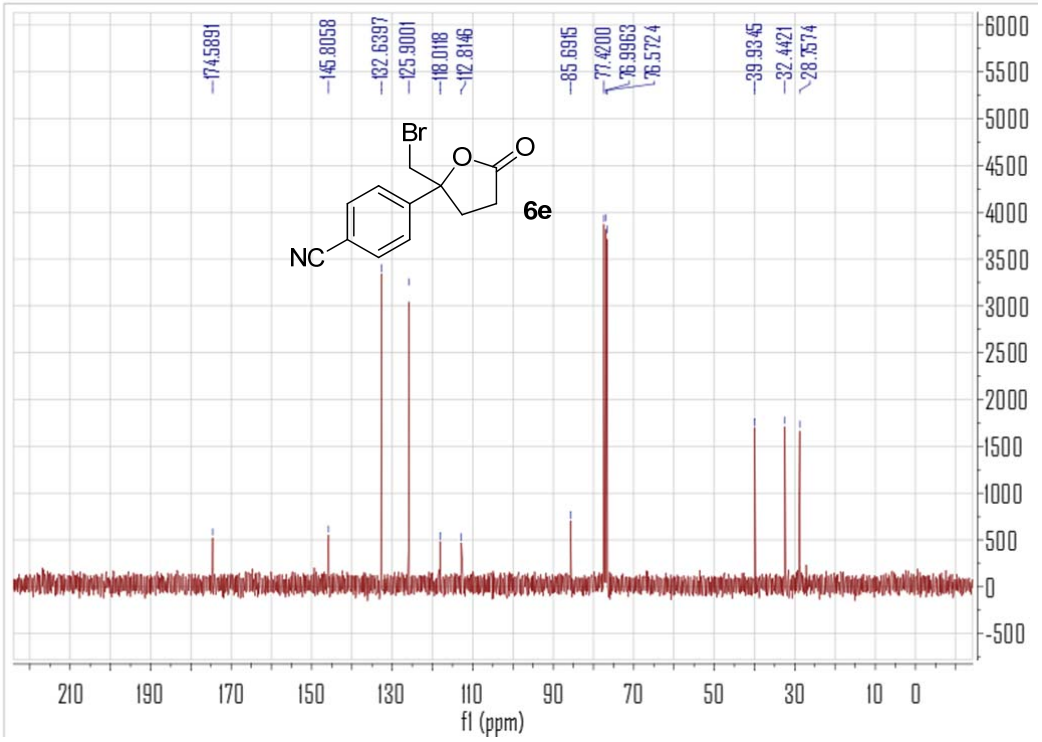
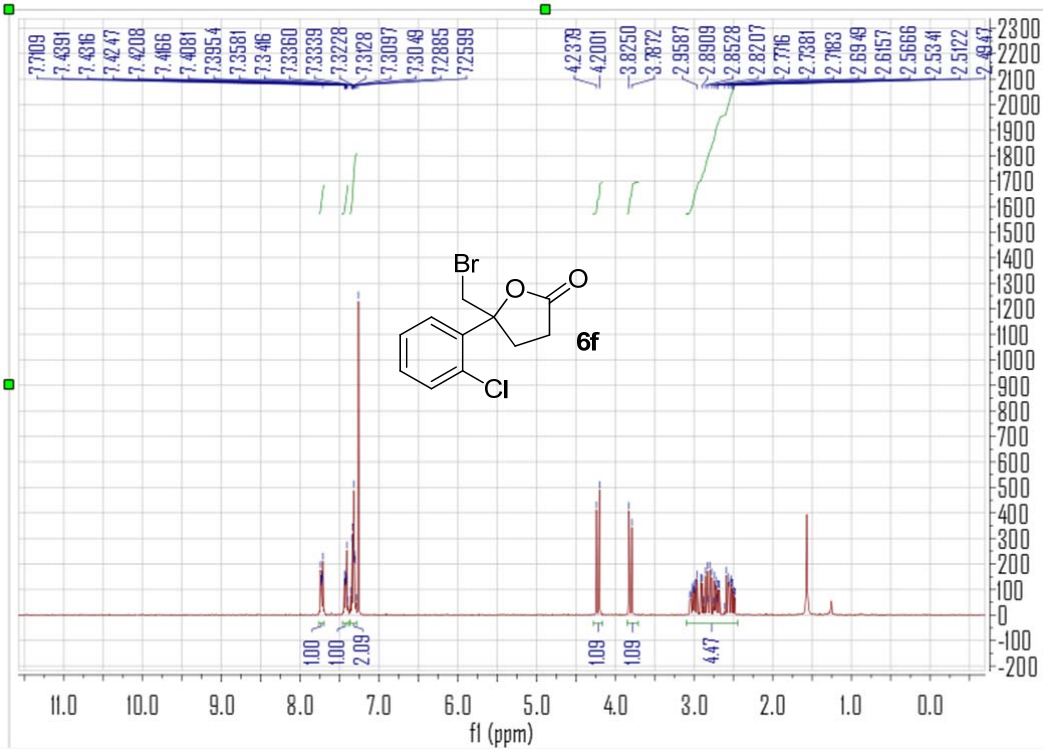
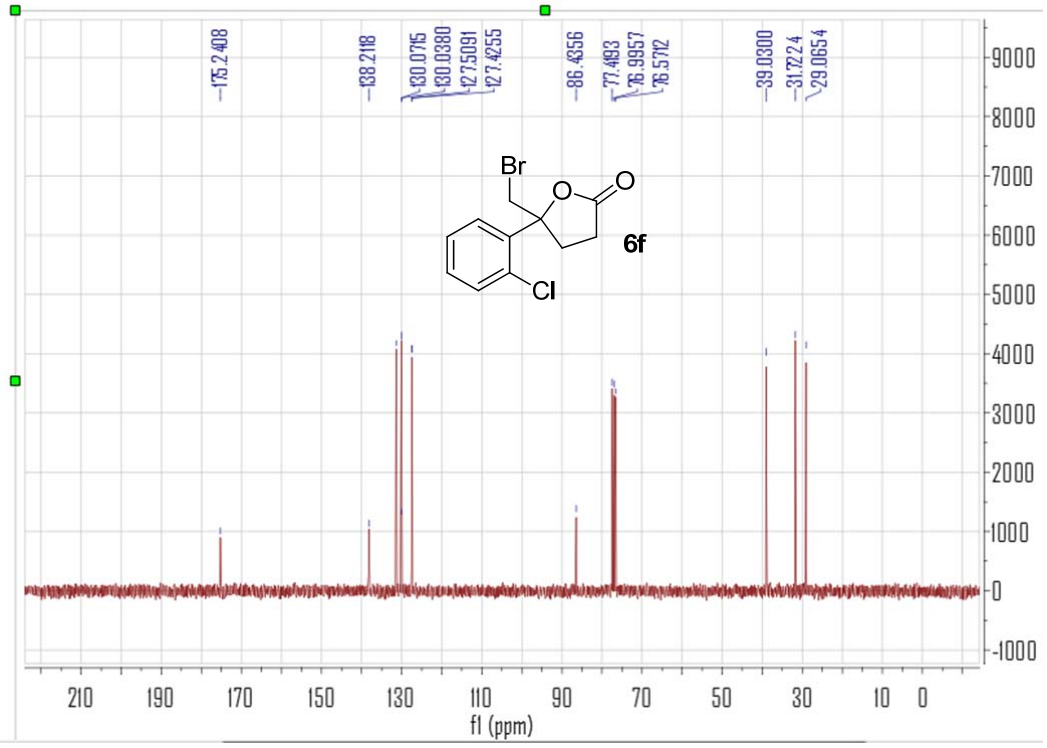
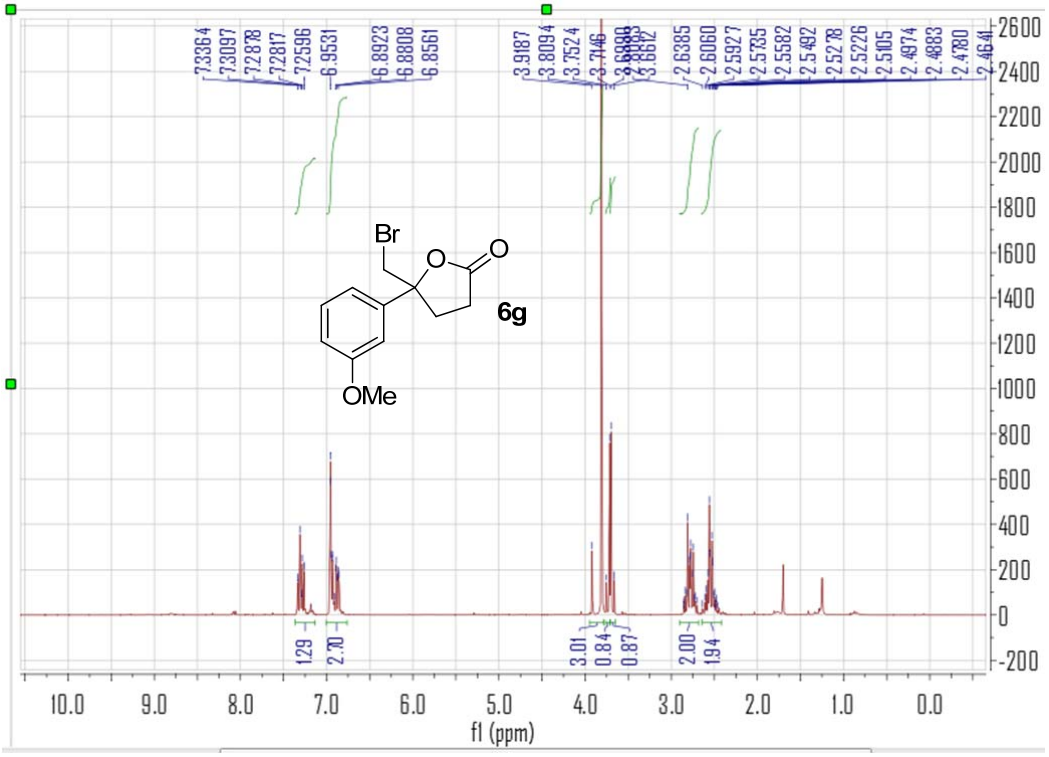
149.3042
139.3762
126.6636
121.2010
118.6424
85.8686
77.4213
76.9981
76.5749
40.5836
32.4633
28.9559
Br
O
O
F3CO
6d
f1 (ppm)

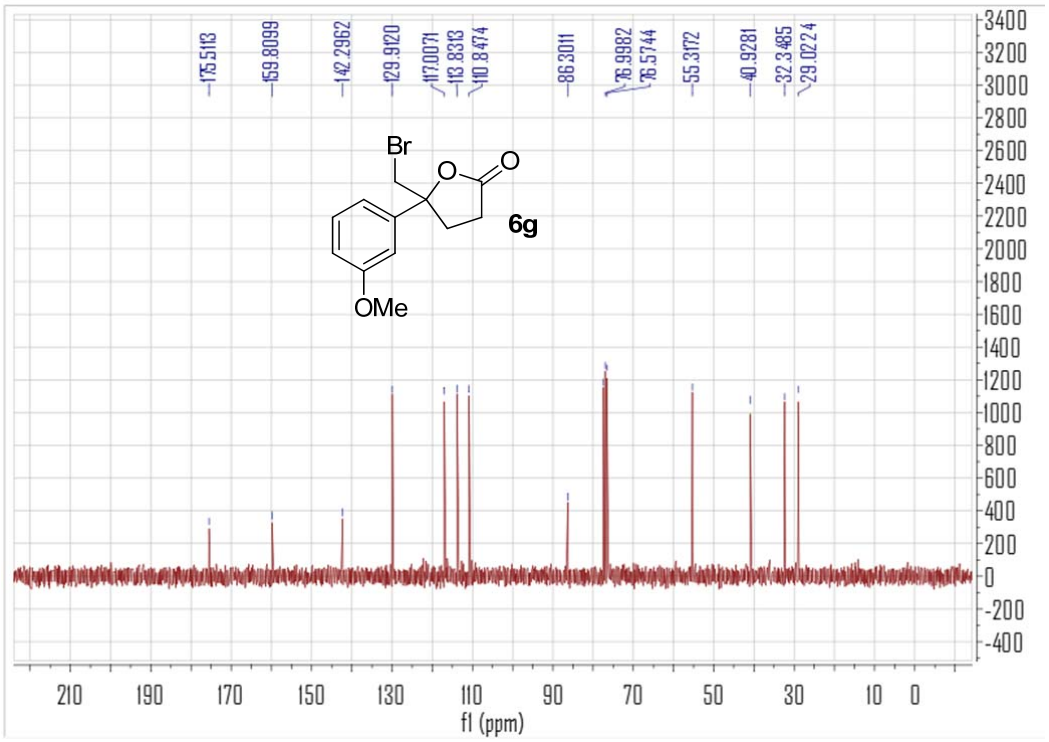

Br
O
O
6e
NC
f1 (ppm)

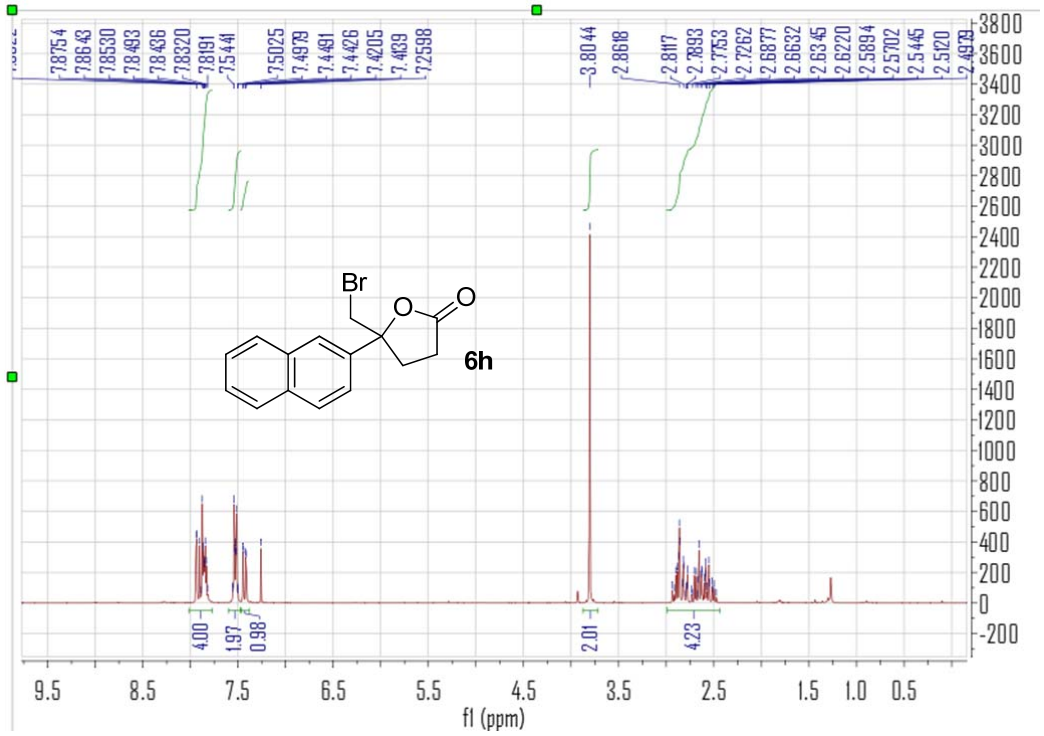

Br
O
O
6e
NC
f1 (ppm)


Br
O
O
6f
Cl
f1 (ppm)


Br
O
O
6f
Cl
f1 (ppm)


Br
O
O
6g
OMe
7.3364
7.3097
7.2878
7.2817
7.2596
6.9531
6.8923
6.8808
6.8561
3.9187
3.8094
3.7524
3.7146
3.6612
2.6385
2.6060
2.5927
2.5735
2.5582
2.5492
2.5278
2.5226
2.5105
2.4974
2.4883
2.4780
2.4641
1.29
2.70
3.01
0.84
0.87
2.00
1.94
f1 (ppm)


Br
O
O
6g
OMe
175.5113
159.8099
142.2962
129.9120
117.0071
113.8313
110.8474
86.3011
76.9982
76.5744
55.3172
40.9281
32.3485
29.0224
f1 (ppm)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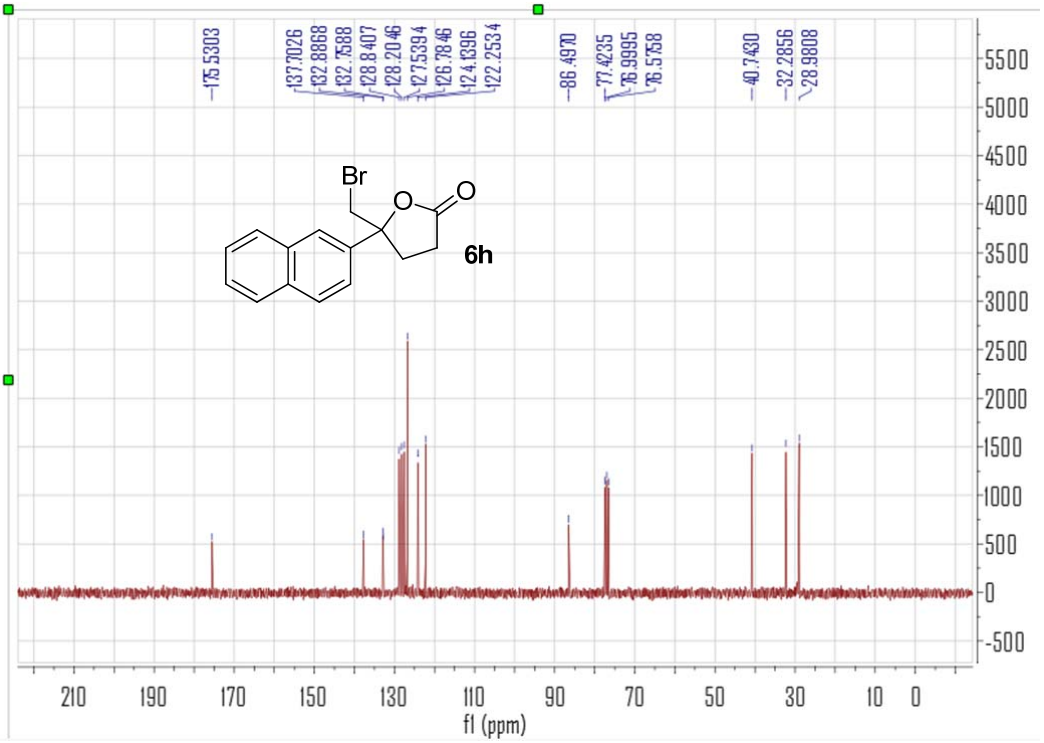
7.8643
7.8530
7.8493
7.8436
7.8320
7.8191
7.5441
7.5025
7.4979
7.4491
7.4426
7.4205
7.4139
7.2598
3.8044
2.8618
2.8117
2.7893
2.7753
2.7262
2.6877
2.6632
2.6345
2.6220
2.5894
2.5702
2.5445
2.5120
2.4979
Br
O
O
6h
4.00
1.97
0.98
2.01
4.23
f1 (ppm)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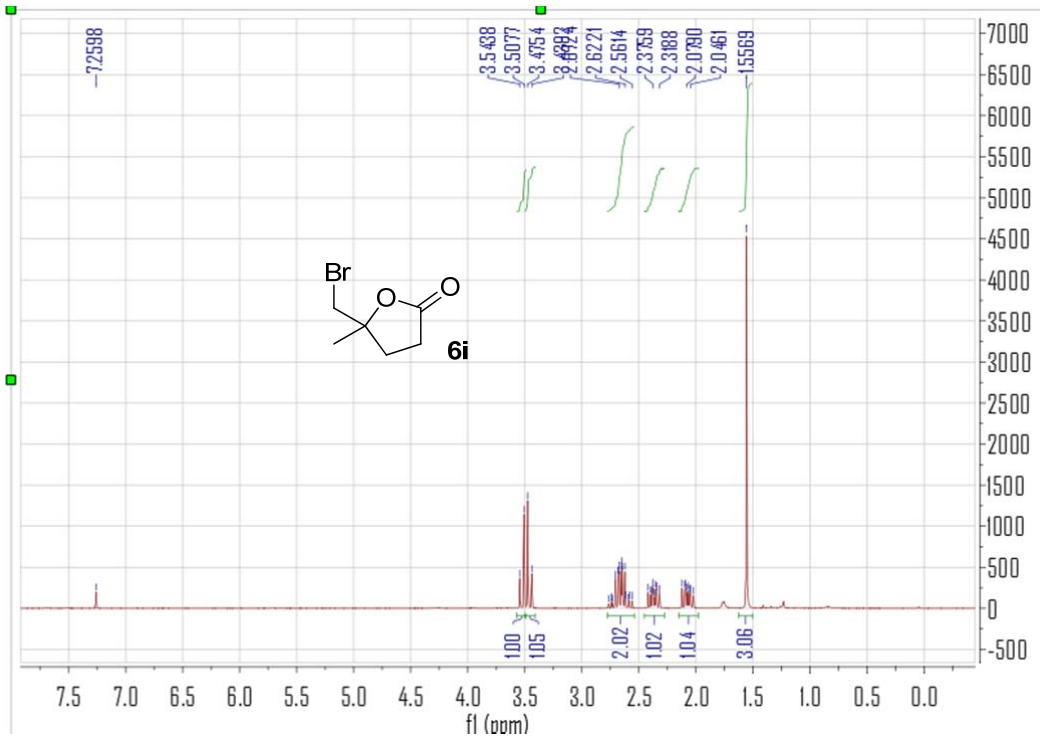
137.7026
132.8868
132.7588
128.8407
128.2046
127.5394
126.7846
124.1396
122.2534
86.4970
77.4235
76.9995
76.5758
40.7480
32.2856
28.9808
Br
O
O
6h
f1 (ppm)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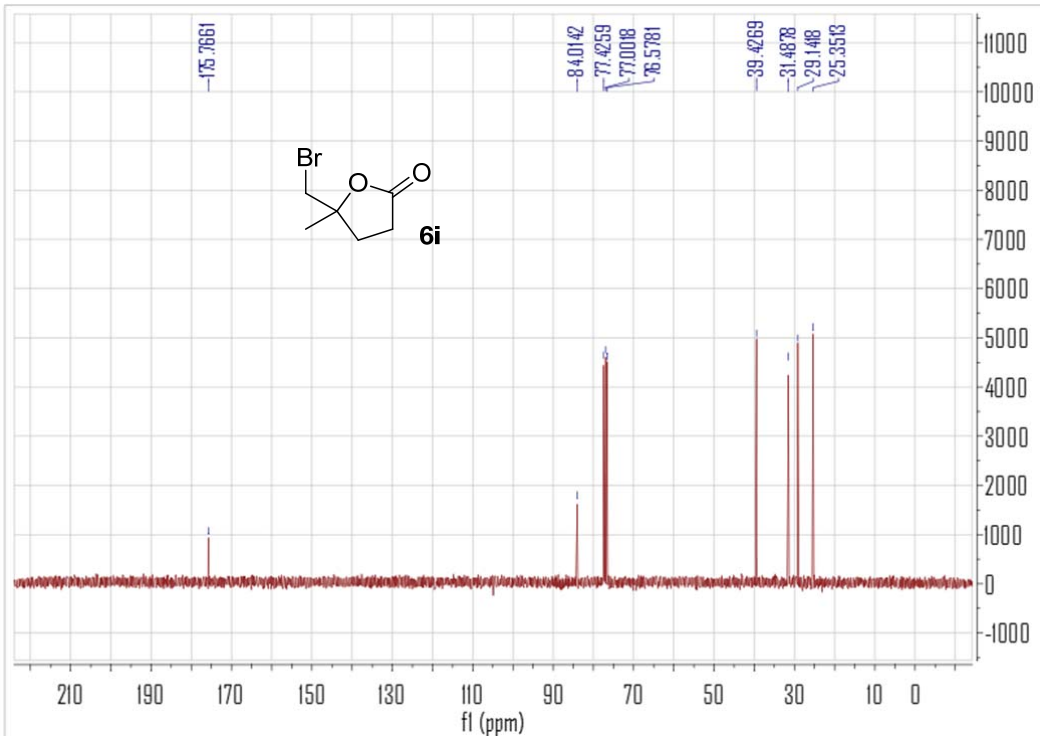
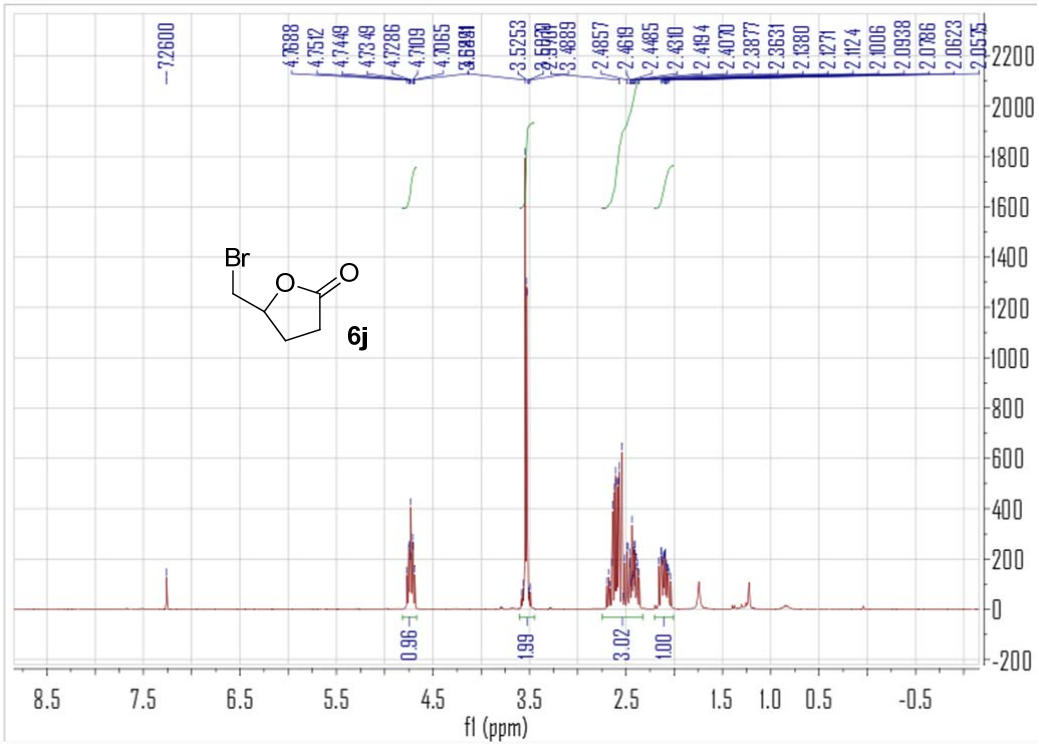
3.5438
3.5077
3.4754
2.6221
2.5614
2.3759
2.3188
2.0780
2.0461
1.5569
Br
O
O
6i
1.00
1.05
2.02
1.02
1.04
3.06
f1 (ppm)


175.7661
84.0142
77.4259
77.0018
76.5781
39.4269
31.4878
29.1498
25.3513
Br
O
O
6i
f1 (ppm)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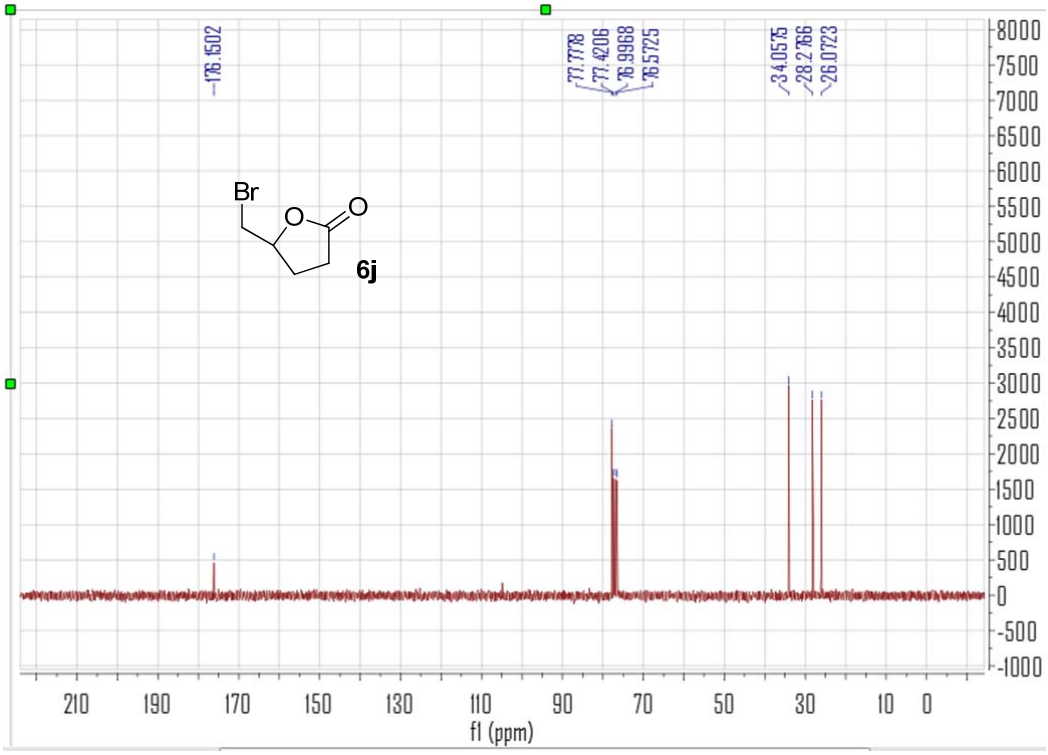
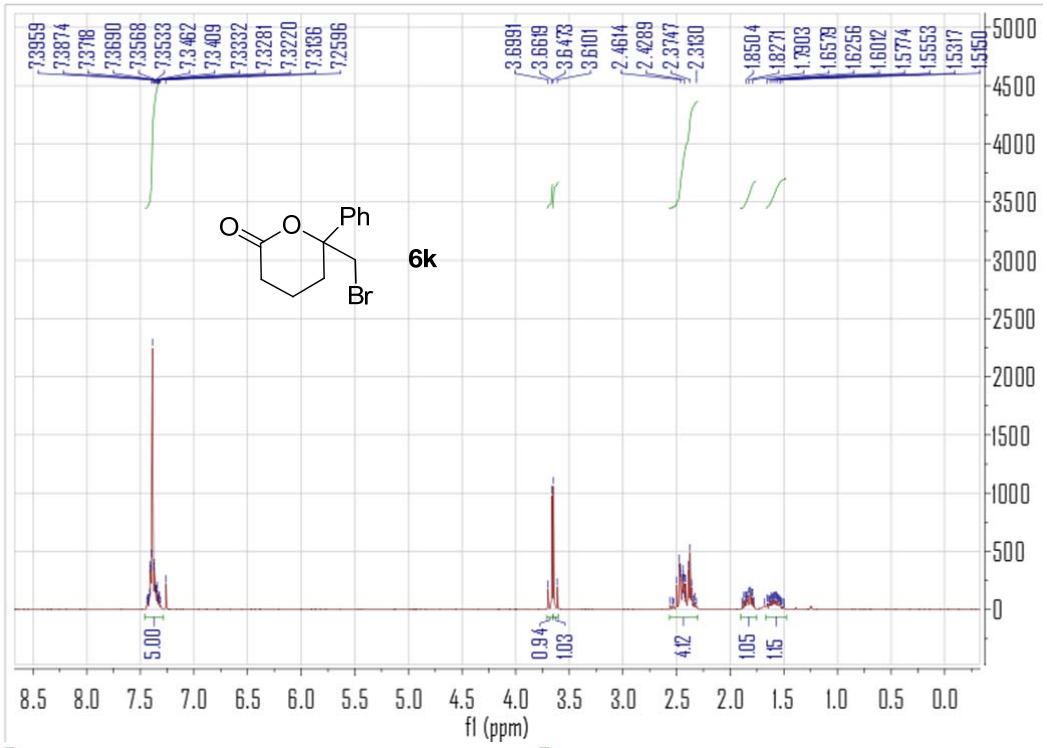
4.7688
4.7512
4.7449
4.7349
4.7286
4.7109
4.7065
3.5253
3.4889
2.4857
2.4619
2.4485
2.4310
2.4194
2.4070
2.3877
2.3631
2.1380
2.1271
2.1124
2.1006
2.0938
2.0786
2.0623
2.0575
Br
O
O
6j
0.96
1.99
3.02
1.00
f1 (ppm)


176.1502
77.7778
77.4206
76.9968
76.5725
34.0575
28.2766
26.0723
Br
O
O
6j
f1 (ppm)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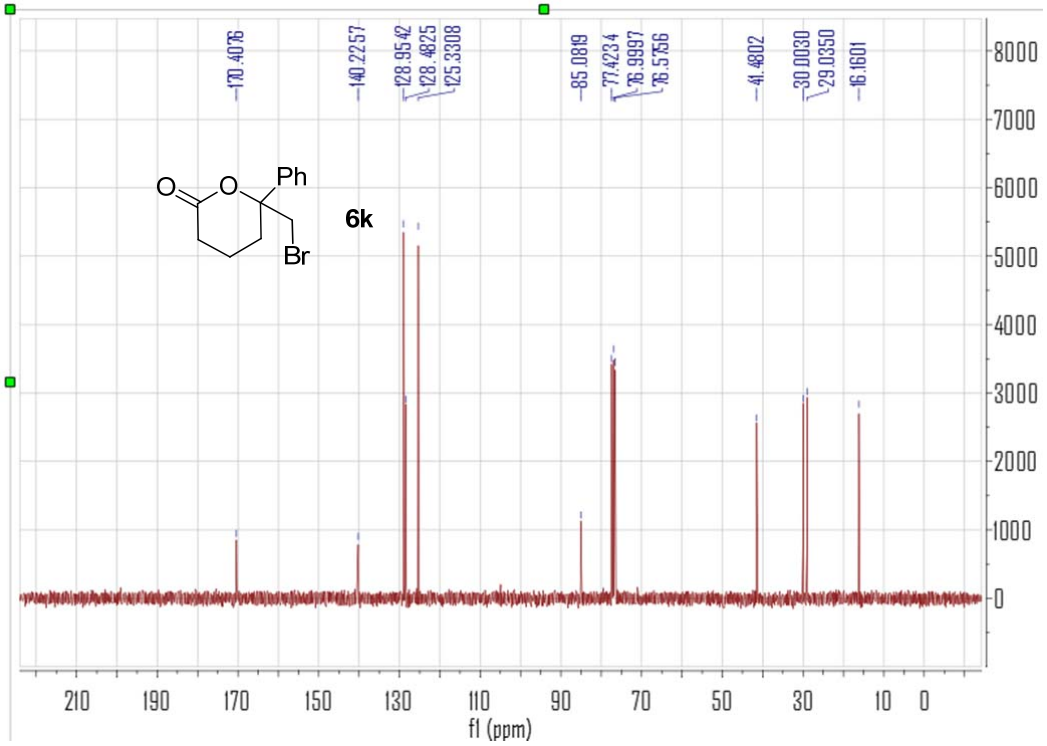
7.3874
7.3718
7.3690
7.3568
7.3533
7.3462
7.3409
7.3332
7.3281
7.3220
7.3166
7.2596
3.6991
3.6619
3.6473
3.6101
2.4614
2.4289
2.3747
2.3380
1.8504
1.8271
1.7803
1.6579
1.6256
1.6012
1.5774
1.5553
1.5317
1.5150
O
O
Ph
Br
6k
5.00
0.94
1.03
4.12
1.05
1.15
f1 (ppm)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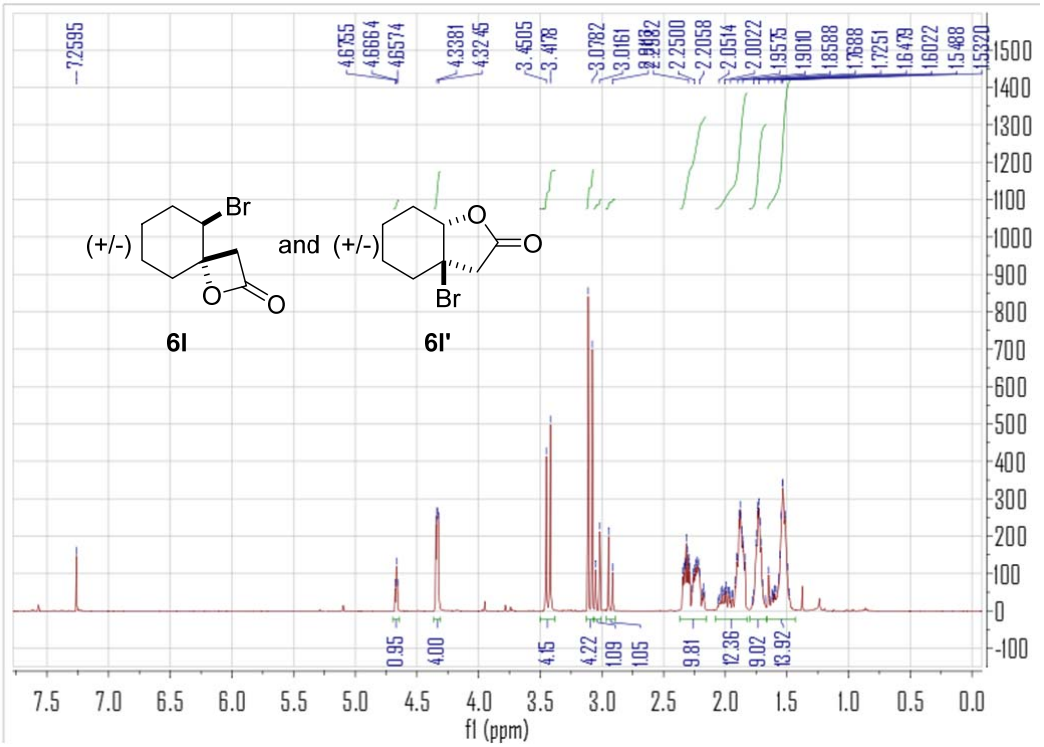
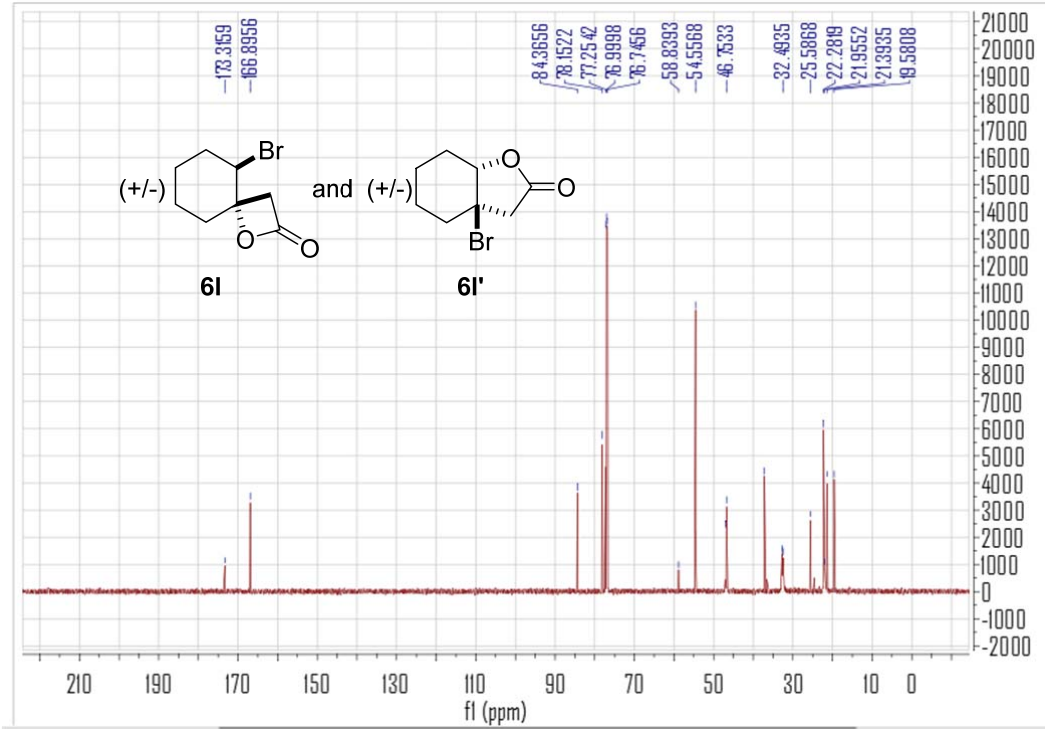
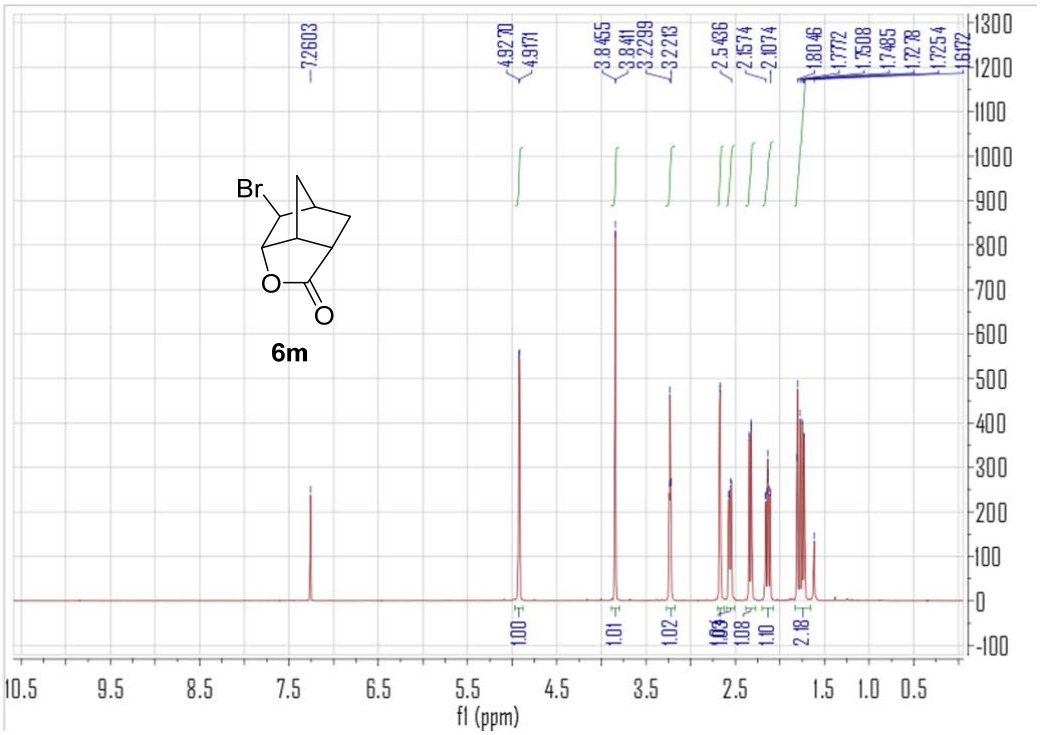
128.9542
128.4825
125.3308
85.0819
77.4234
76.9997
76.5756
41.4802
30.0030
29.0350
16.1601
O
O
Ph
Br
6k
f1 (ppm)


(+/-)
Br
O
O
and (+/-)
O
O
Br
6l
6l'
fl (ppm)


(+/-)
Br
O
O
and (+/-)
O
O
Br
6l
6l'
fl (ppm)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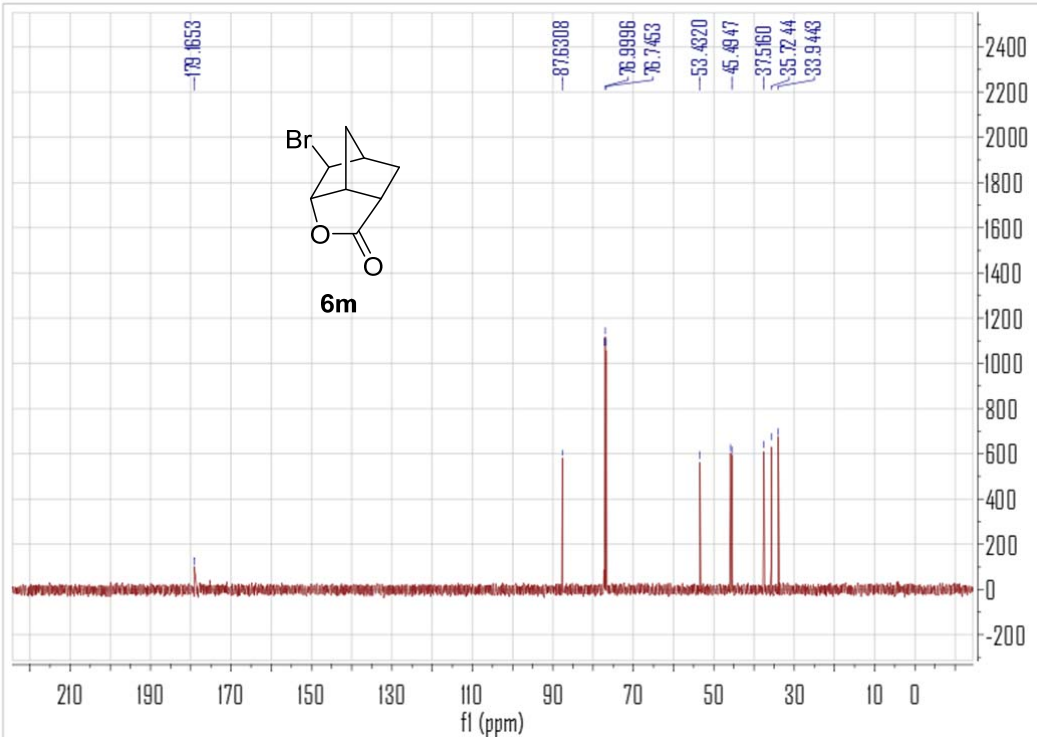
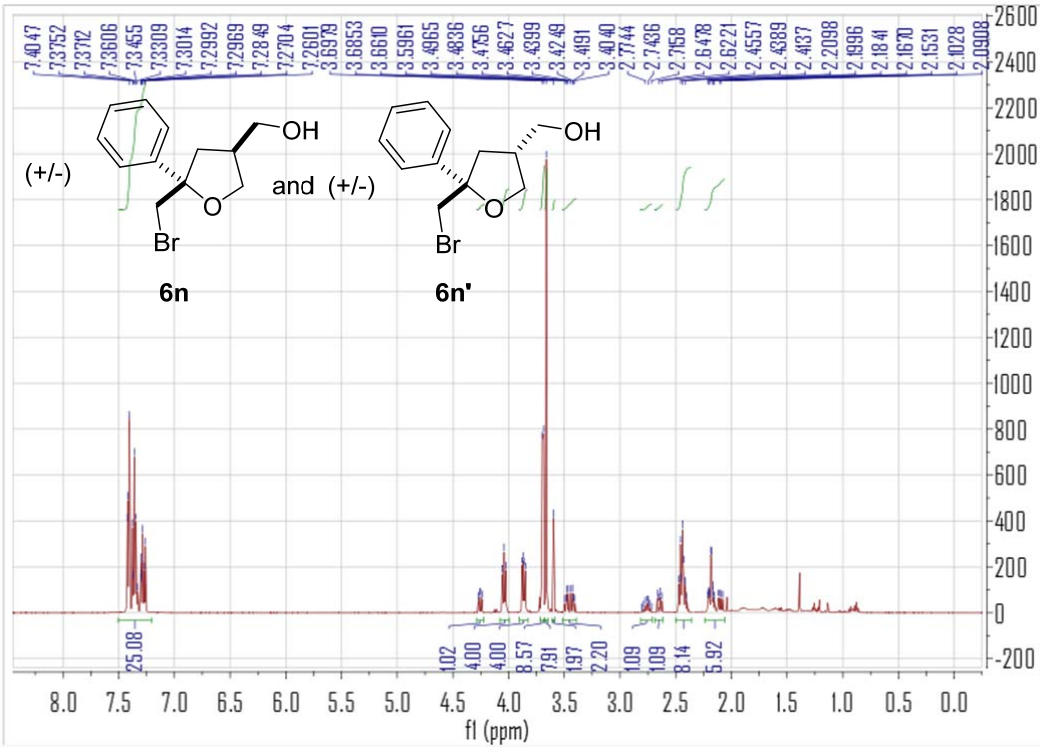
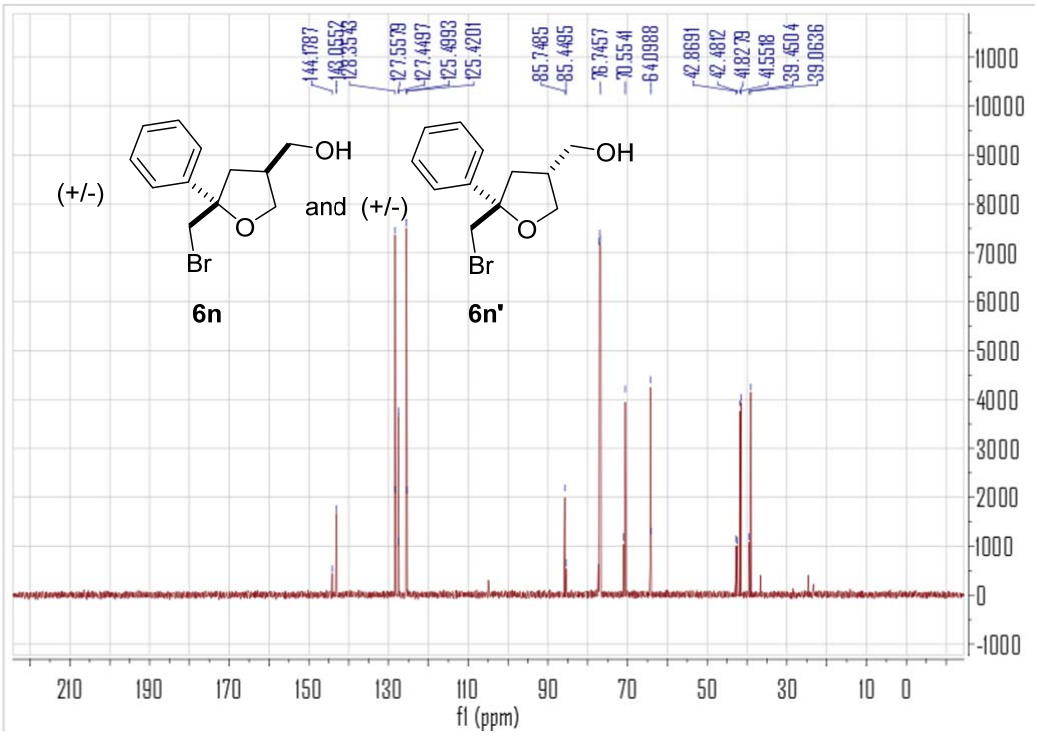
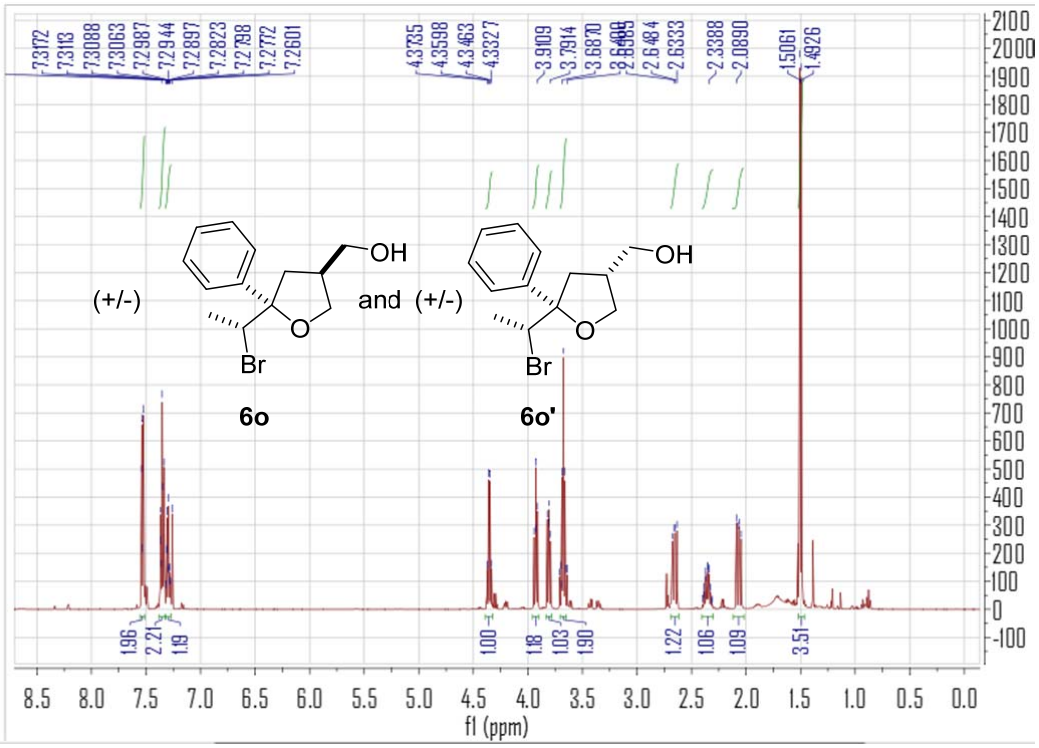
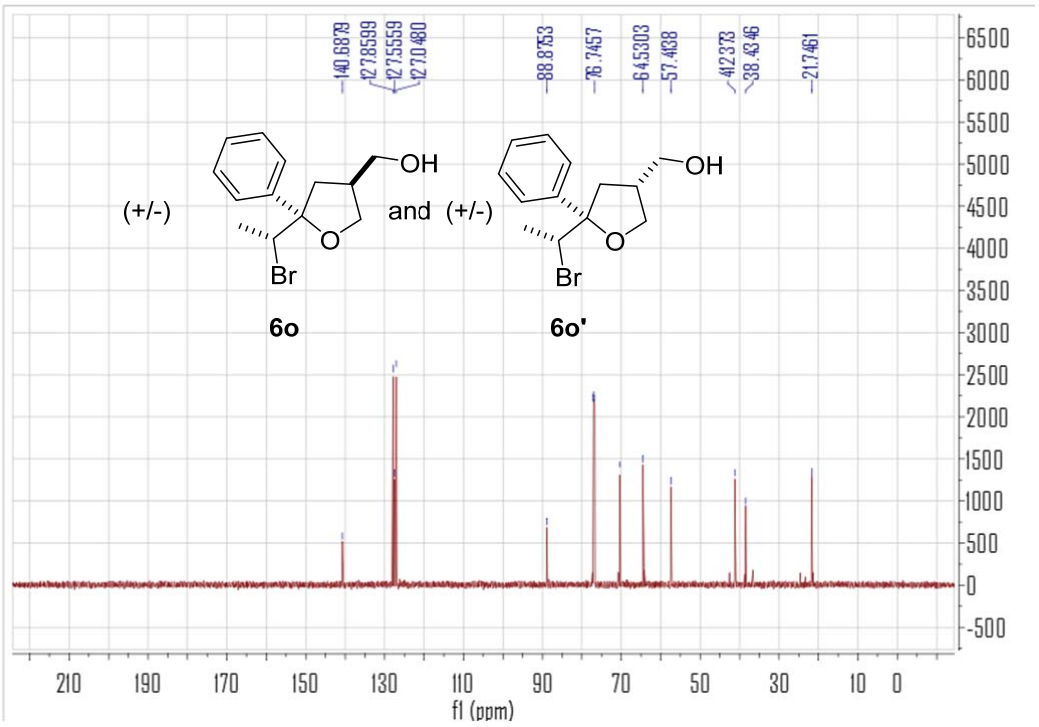
3.8455
3.8411
3.2299
3.2213
2.5436
2.1574
2.1074
1.8046
1.7772
1.7508
1.7485
1.7278
1.7254
1.6172
Br
O
O
6m
1.00
1.01
1.02
2.18
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
1.0
0.5
f1 (ppm)

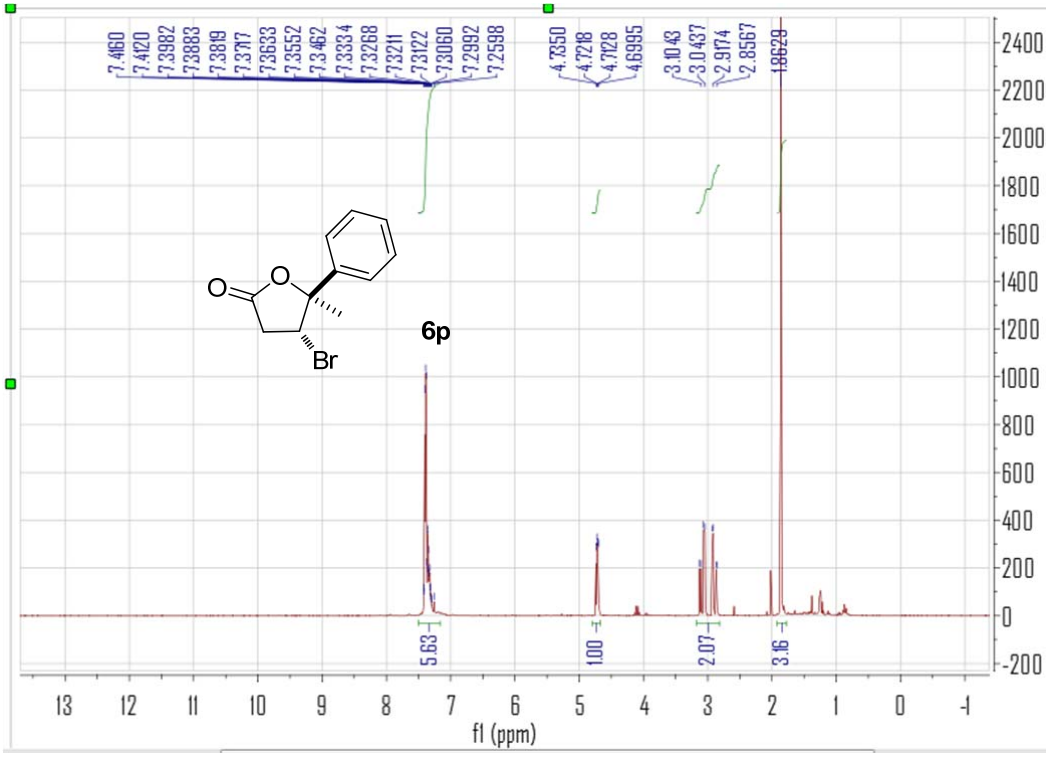

179.1653
87.6308
76.9996
76.7453
53.4320
45.4947
37.5160
35.7244
33.9443
Br
O
O
6m
210
190
170
150
130
110
90
70
50
30
10
0
f1 (ppm)


(+/-)
OH
Br
O
6n
and (+/-)
OH
Br
O
6n'
f1 (ppm)


(+/-)
OH
Br
O
6n
and (+/-)
OH
Br
O
6n'
f1 (ppm)


(+/-)
OH
Br
6o
and (+/-)
OH
Br
6o'
f1 (ppm)


(+/-)
OH
Br
6o
and (+/-)
OH
Br
6o'
f1 (ppm)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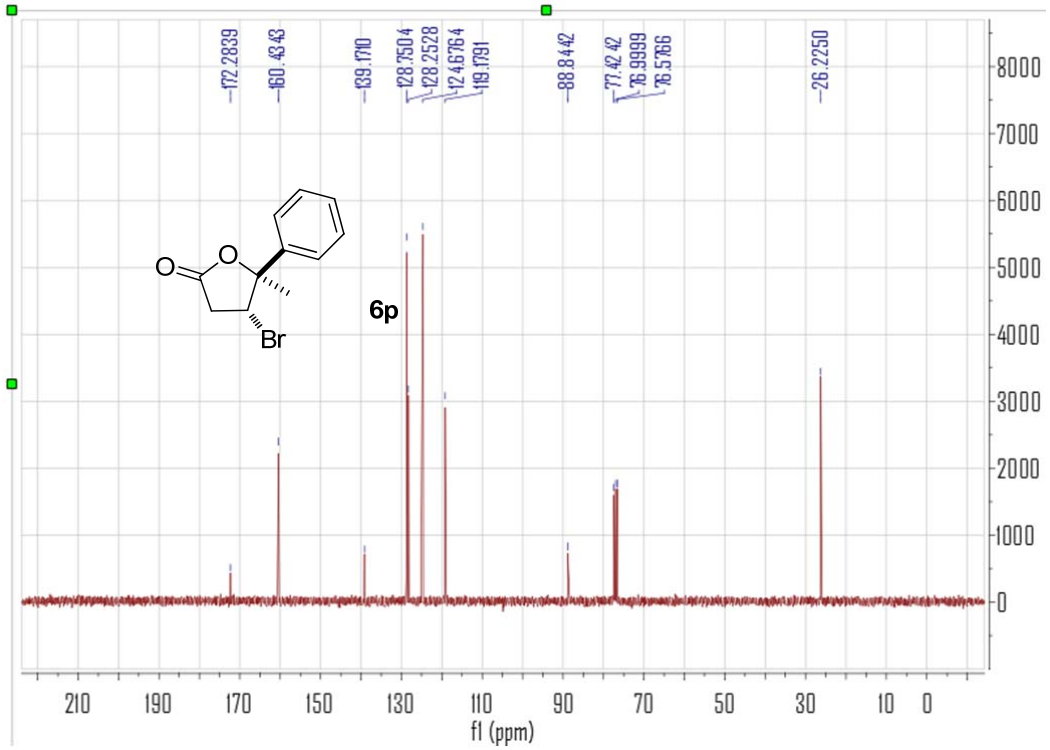
7.3982
7.3883
7.3819
7.3717
7.3633
7.3552
7.3462
7.3334
7.3268
7.3211
7.3122
7.3060
7.2992
7.2598
4.7350
4.7218
4.7128
4.6995
3.1043
3.0437
2.9774
2.8567
1.8629
O
O
Br
6p
5.63
1.00
2.07
3.16
f1 (ppm)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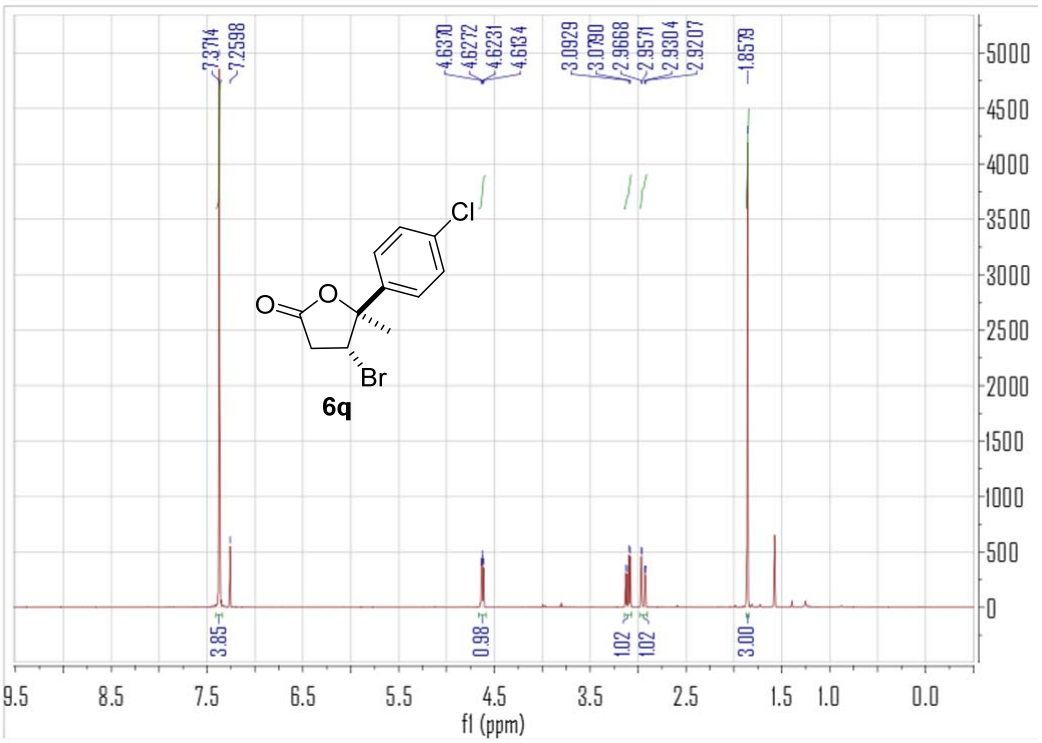
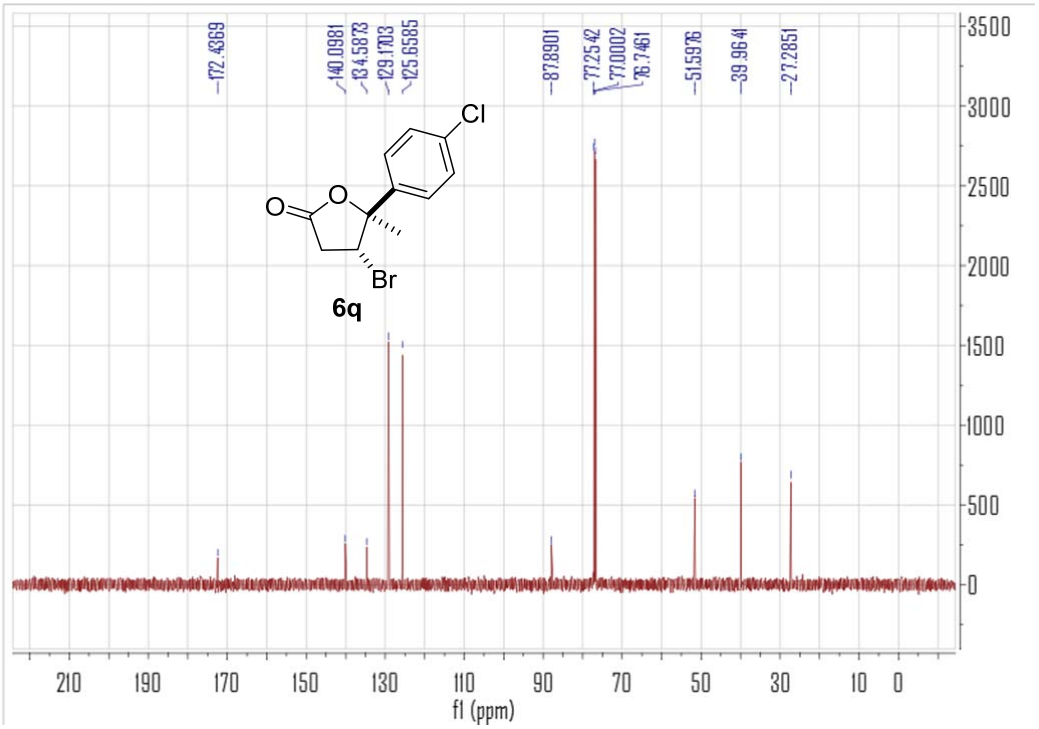
139.1710
128.7504
128.2528
124.6764
119.1791
88.8442
77.4242
76.9999
76.5766
26.2250
O
O
Br
6p
f1 (ppm)


7.3714
7.2598
4.6370
4.6272
4.6231
4.6134
3.0929
3.0790
2.9668
2.9571
2.9304
2.9207
1.8578
Cl
O
O
Br
6q
3.85
0.98
1.02
1.02
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
1.0
0.0
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0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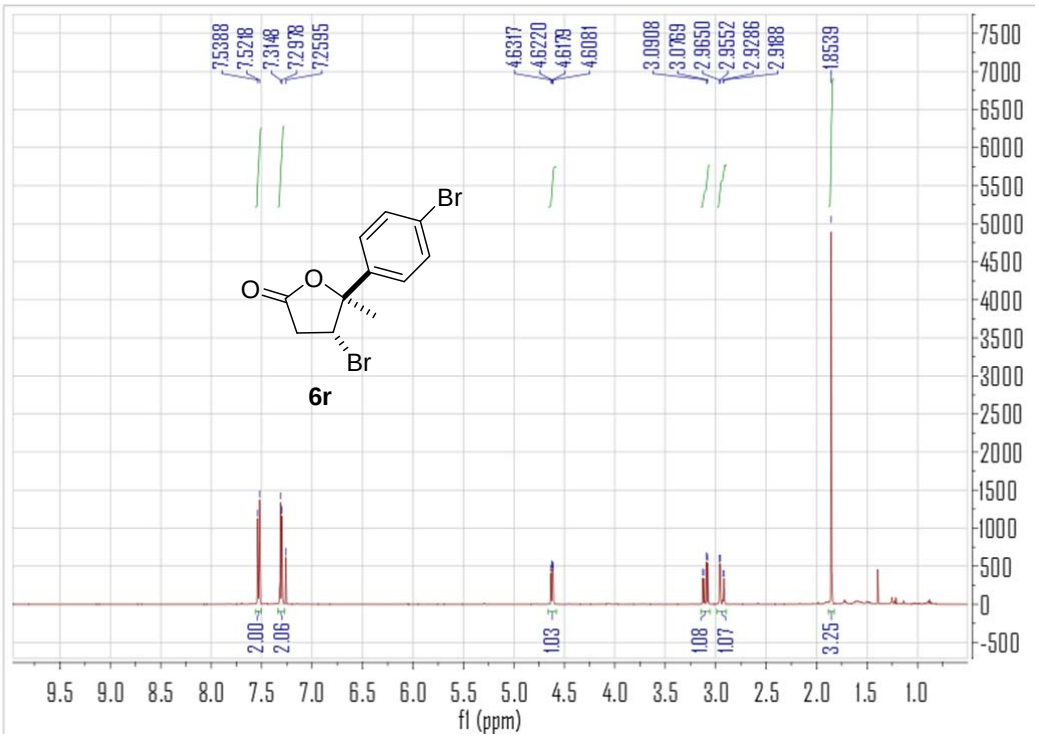
134.5873
129.1703
125.6585
87.8901
77.2542
77.0002
76.7461
51.5976
39.9641
27.2851
Cl
O
O
Br
6q
210
190
170
150
130
110
90
70
50
30
10
0
f1 (ppm)
3500
3000
2500
2000
1500
1000
500
0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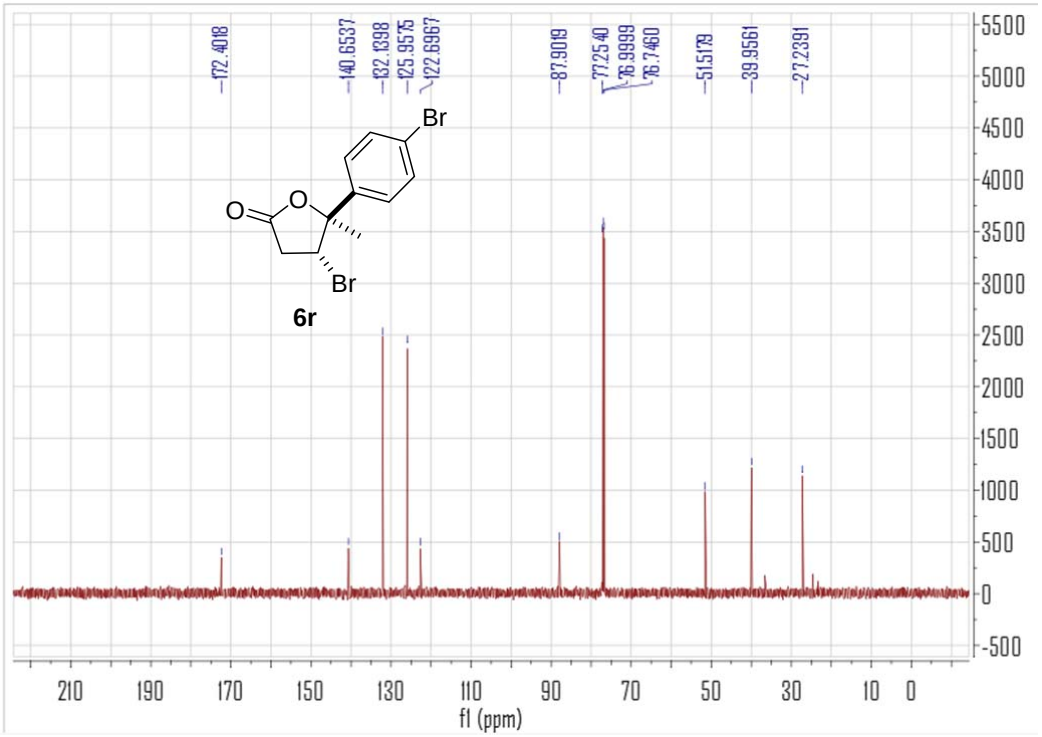
7.3148
7.2978
7.2595
4.6317
4.6220
4.6179
4.6081
3.0908
3.0769
2.9650
2.9552
2.9286
2.9168
1.8539
Br
O
O
Br
6r
2.00
2.06
1.03
1.08
1.07
3.25
fl (ppm)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132.1398
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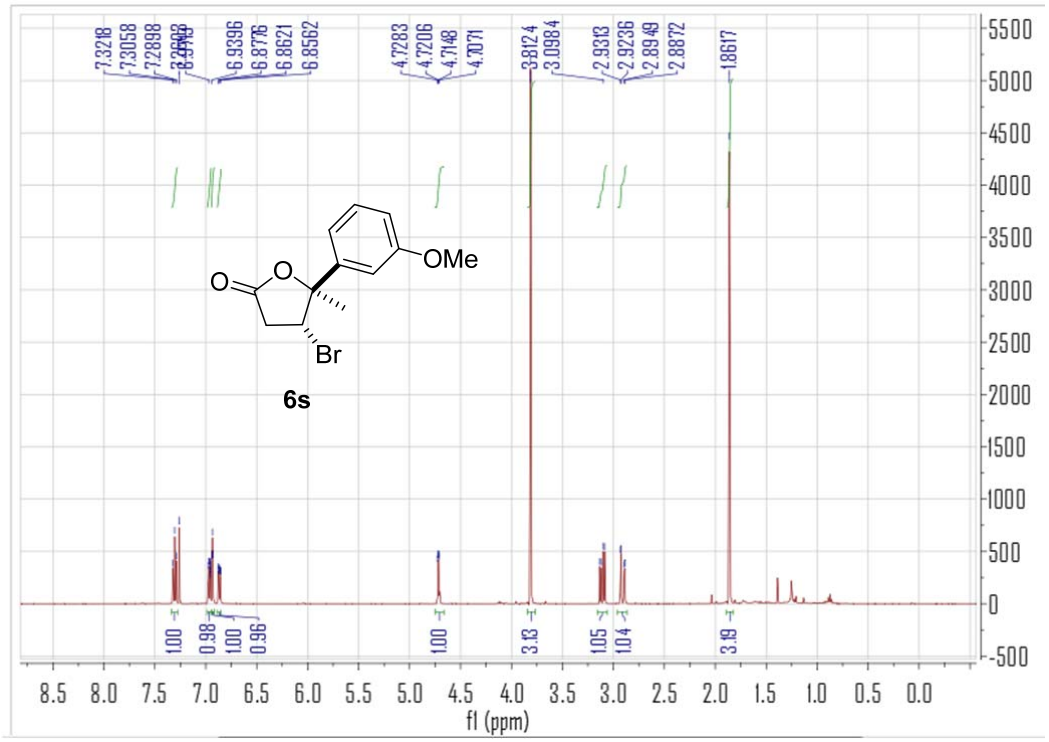
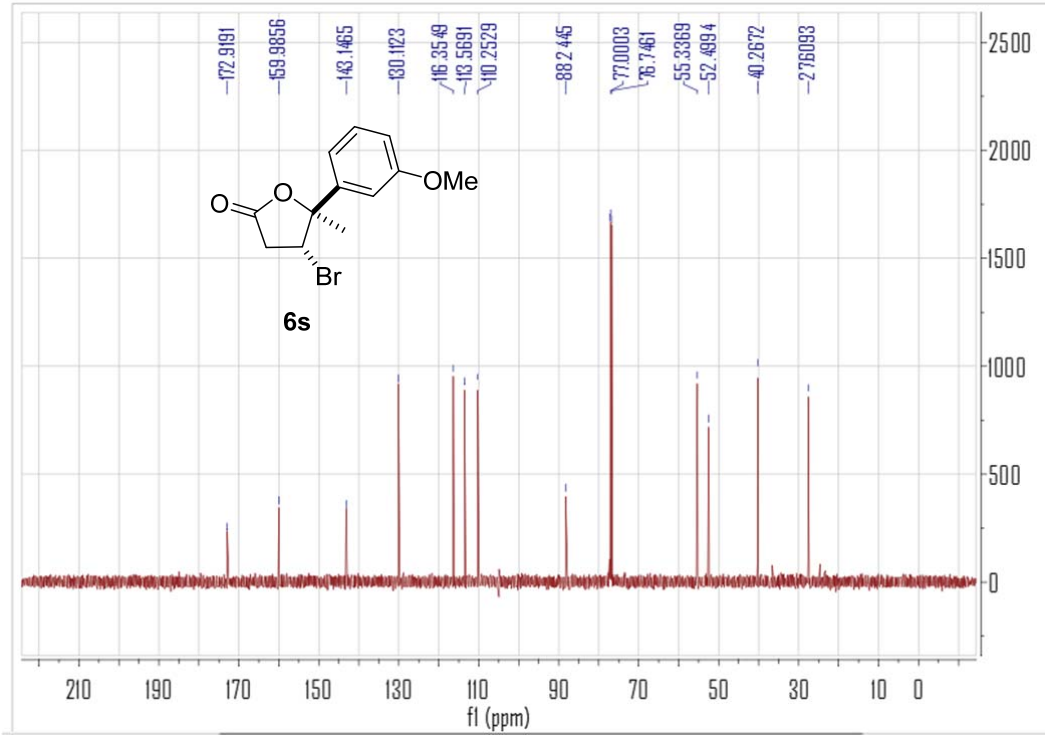
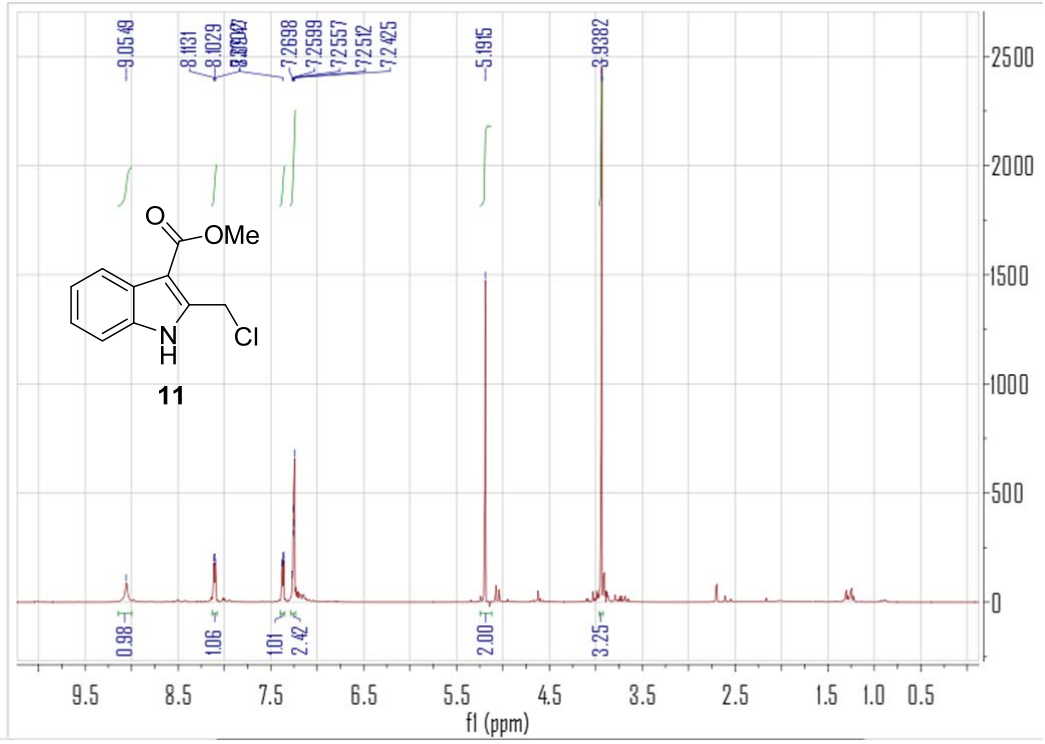
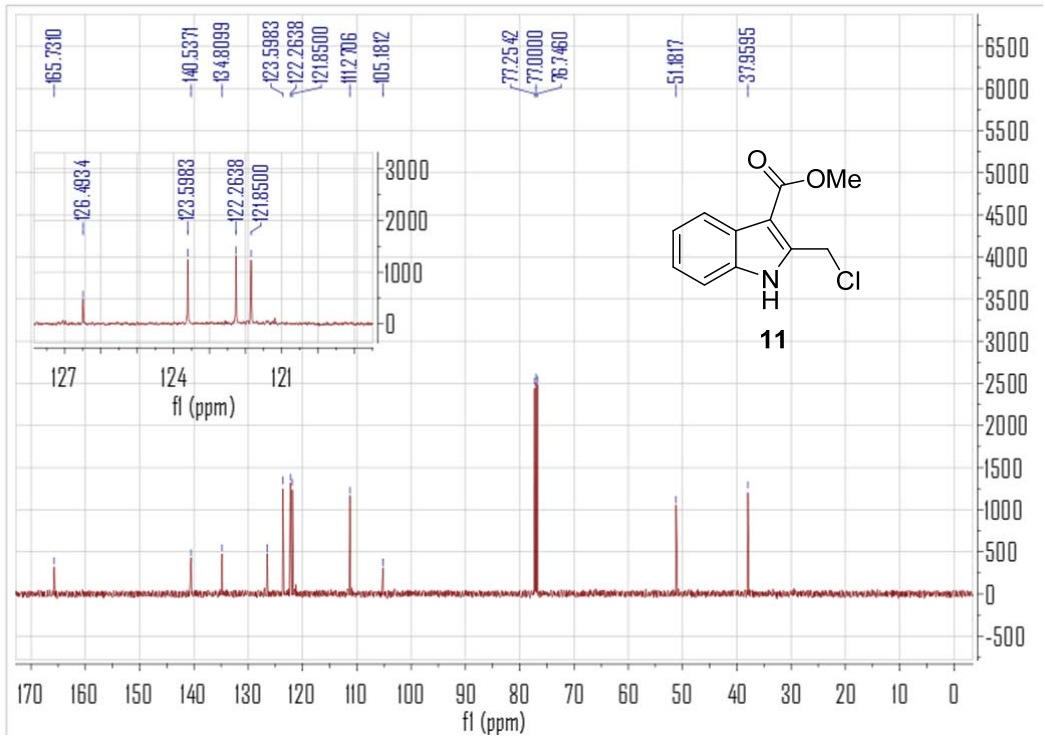
122.6967
87.9019
77.2540
76.9999
76.7460
51.5179
39.9561
27.2391
Br
O
O
Br
6r
fl (ppm)


7.3218
7.3058
7.2898
6.9396
6.8778
6.8621
6.8562
4.7283
4.7206
4.7148
4.7071
3.8124
3.0984
2.9313
2.9236
2.8949
2.8872
1.8617
OMe
O
O
Br
6s
1.00
0.98
1.00
0.96
1.00
3.13
1.05
1.04
3.19
fl (ppm)


172.9191
159.9856
143.1465
130.1123
116.3549
113.5691
110.2529
88.2445
77.0003
76.7461
55.3369
52.4994
40.2672
27.6093
OMe
O
O
Br
6s
fl (ppm)


9.05 49
8.1131
8.1029
7.2698
7.2599
7.2557
7.2512
7.2425
5.1915
3.9382
O
OMe
N
H
Cl
11
0.98
1.06
1.01
2.42
2.00
3.25
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
1.0
0.5
f1 (ppm)
2500
2000
1500
1000
500
0


165.7310
140.5371
134.8099
123.5983
122.2638
121.8500
111.2706
105.1812
77.2542
77.0000
76.7460
51.1817
37.9595
126.493 4
123.5983
122.2638
121.8500
3000
2000
1000
0
127
124
121
f1 (ppm)
O
OMe
N
H
Cl
11
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)