Supporting Information

Efficient Radical C(sp^3)-H α-Oxyamination of Carbonyls Adjacent to Carbon Chalcogen Bond

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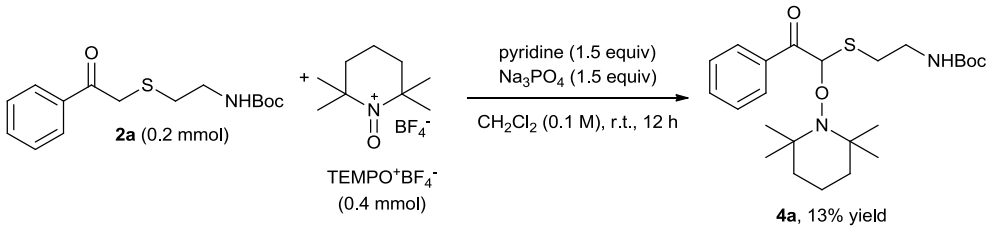
I. General Experiment Information and Materials

All commercial reagents were used without further purification unless otherwise noted. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker Avance 400 and 500MHz spectrometer. Tetramethylsilane (TMS) served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR. ^{1}H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet is10. The X-ray single-crystal diffraction was performed on Saturn 724+ instrument. High resolution mass spectra were obtained on an Ultima Global spectrometer with an ESI source.

II. Initial Exploration

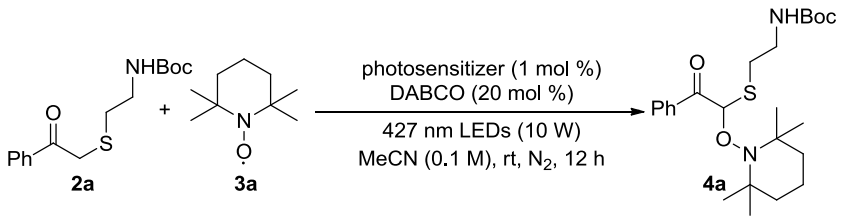


Scheme S1. Radical oxidative α-oxyamination of α-mercapoto carbonyl **2a** with $TEMPO^{+}BF_4^{-}$

To an oven-dried 10 mL tube equipped with a magnetic stir bar was added α-mercapoto ketone **2a** (0.2 mmol), $TEMPO^{+}BF_4^{-}$ (0.4 mmol), pyridine (0.3 mmol), Na_3PO_4 (0.4 mmol) in DCM (2 mL). The reaction mixture was then stirred at room temperature for 12 h. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired product **4a** (11.7 mg, 13% yield)**.**

III. Optimization

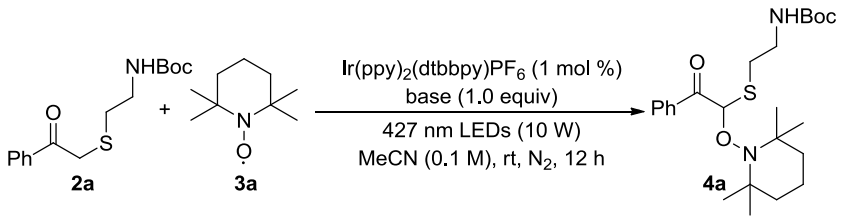
Table S1. Screening of different Photosensitizers.[a]



Entry	Photosensitizer	Yield (%)[b]
1	$Ir(ppy)_2(dtbbpy)PF_6$	75
2	$Ir(ppy)_3$	np
3	$Ru(bpy)_2Cl_2{\cdot}6H_2O$	27
4	Eosin Y	46
5	4CzIPN	56

[a] Reaction Conditions: **2a** (0.1 mmol), **3a** (0.2 mmol), photosensitizer (1 mol %) and DABCO (20 mol %) in CH_3CN (1.0 mL) at room temperature, 12 h. [b] Isolated product yield. np = no product.

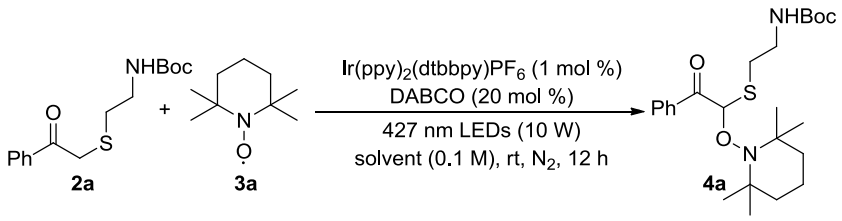
Table S2. Screening of different bases.[a]



Entry	Base	Yield (%)[b]
1[c]	DABCO	75
2	DABCO	73
3	quinuclidine	61
4	quinidine	59
5	pyridine	27
6	Na_3PO_4	16

[a] Reaction Conditions: **2a** (0.1 mmol), **3a** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol %) and base (0.1 mmol) in CH_3CN (1.0 mL) at room temperature, 12 h. [b] Isolated product yield. [c] DABCO (20 mol %).

Table S3. Screening of different solvents.[a]

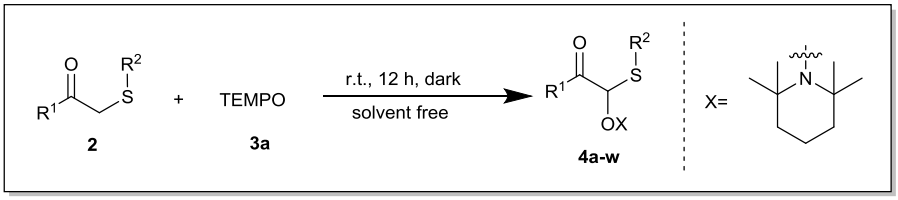


Entry	Solvent	Yield (%)[b]
1	CH_3CN	75
2	THF	59
3	DCM	27
4	DCE	30
5	DMF	59

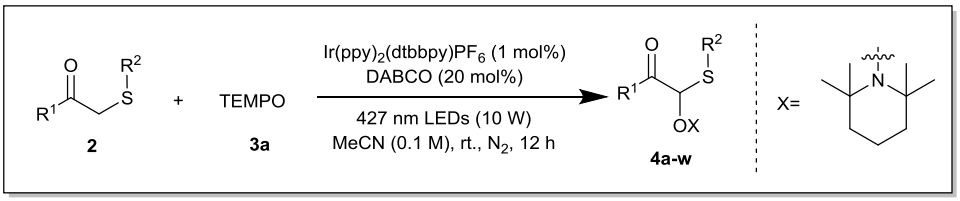
[a] Reaction Conditions: **2a** (0.1 mmol), **3a** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol %) and base (0.1 mmol) in CH_3CN (1.0 mL) at room temperature, 12 h. [b] Isolated product yield.

IV. Experimental Procedures and Characterization Data

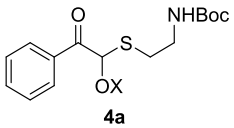
A) Radical C(sp^3)-H α-Oxyamination of α-Mercapoto Carbonyls 2 with 3a:



Reaction procedure I: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added α-mercapoto ketone **2** (0.2 mmol) and TEMPO (0.4 mmol). The reaction mixture was then stirred at room temperature for 12 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired product **4a-w.**



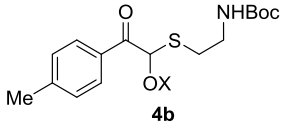
Reaction procedure II: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added α-mercapoto ketone **2** (0.2 mmol), TEMPO (0.4 mmol), DABCO (0.04 mmol) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous MeCN (2.0 mL) was added. The reaction mixture was irradiated by blue LEDs (427nm, 10W) at room temperature. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel gave the desired product.



4a

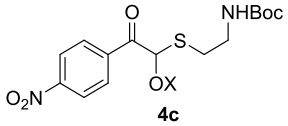
4a: Prepared according to the reaction procedure **I** above and obtained as light yellow oil (64.9 mg, 72%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 6.14 (s, 1H), 5.15 (br, 1H), 3.43 – 3.30 (m, 2H), 2.73 – 2.66 (m, 2H), 1.65 – 1.55 (m,

3H), 1.49 (s, 3H), 1.43 (s, 9H), 1.37 – 1.29 (m, 3H), 1.19 (s, 3H), 1.12 (s, 3H), 0.94 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 155.8, 134.7, 133.2, 128.6, 128.6, 89.4, 79.1, 60.6, 60.0, 41.1, 40.2, 34.9, 33.4, 30.6, 29.7, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3386, 2972, 2924, 1634, 1384, 1049, 404; HRMS (ESI) calcd for $C_{24}H_{38}N_2NaO_4S^+$ $(M+Na)^+$ 473.2450, found 473.2439.



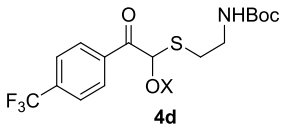
4b

4b: Prepared according to the procedure **I** above and obtained as light yellow oil (44.5 mg, 48%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.12 (s, 1H), 5.15 (br, 1H), 3.44 – 3.31 (m, 2H), 2.72 – 2.64 (m, 2H), 2.41 (s, 3H), 1.57 – 1.50 (m, 3H), 1.48 (s, 3H), 1.43 (s, 9H), 1.37 – 1.29 (m, 3H), 1.18 (s, 3H), 1.12 (s, 3H), 0.94 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 155.9, 144.1, 132.1, 129.4, 128.7, 89.4, 79.1, 60.6, 60.0, 41.1, 40.3, 34.9, 33.4, 30.7, 28.4, 21.7, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3385, 2972, 2852, 1681, 1607, 1507, 1191, 1056, 957, 785, 551, 529; HRMS (ESI) calcd for $C_{25}H_{40}N_2NaO_4S^+$ $(M+Na)^+$ 487.2606, found 487.2605.



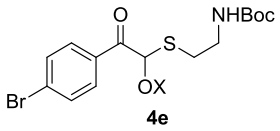
4c

4c: Prepared according to the procedure **I** above and obtained as yellow oil (18.3 mg, 37%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 2H), 6.06 (s, 1H), 5.02 (br, 1H), 3.40 – 3.35 (m, 2H), 2.72 – 2.64 (m, 2H), 1.58 – 1.54 (m, 3H), 1.49 (s, 3H), 1.44 (s, 9H), 1.34 – 1.29 (m, 3H), 1.19 (s, 3H), 1.09 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.5, 155.8, 150.3, 139.5, 129.9, 123.9, 90.3, 79.4, 60.8, 60.2, 40.8, 40.2, 34.8, 33.4, 31.1, 28.4, 20.6, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3671, 3389, 2986, 2901, 1406, 1251, 1055, 893; HRMS (ESI) calcd for $C_{24}H_{37}N_3NaO_6S^+$ $(M+Na)^+$ 518.2301, found 518.2299.



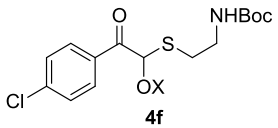
4d

4d: Prepared according to the procedure **I** above and obtained as light yellow oil (68.4 mg, 66%), eluent: petroleum ether/ethyl acetate (12:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 6.09 (s, 1H), 5.07 (br, 1H), 3.41 – 3.32 (m, 2H), 2.72 – 2.64 (m, 2H), 1.58 – 1.50 (m, 3H), 1.49 (s, 3H), 1.43 (s, 9H), 1.38 – 1.29 (m, 3H), 1.19 (s, 3H), 1.11 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 155.8, 137.6, 134.4 (q, *J* = 32.4 Hz), 129.0, 125.7 (q, *J* = 3.4 Hz), 123.5 (d, *J* = 270.8 Hz), 89.8, 79.3, 60.7, 60.1, 40.9, 40.2, 34.8, 33.4, 30.9, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3385, 2925, 1655, 1384, 1321, 1067; HRMS (ESI) calcd for $C_{25}H_{38}F_3N_2O_4S^+$ $(M+H)^+$ 519.2504, found 519.2499.



4e

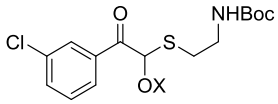
4e: Prepared according to the procedure **I** above and obtained as light yellow oil (63.4 mg, 60%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 6.04 (s, 1H), 5.09 (br, 1H), 3.41 – 3.26 (m, 2H), 2.72 – 2.62 (m, 2H), 1.58 – 1.50 (m, 3H), 1.47 (s, 3H), 1.43 (s, 9H), 1.33 – 1.31 (m, 3H), 1.18 (s, 3H), 1.10 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 155.8, 133.3, 132.0, 130.2, 128.4, 89.8, 79.2, 60.6, 60.05, 40.9, 40.2, 34.8, 33.4, 30.9, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3360, 2972, 2923, 1714, 1682, 1661, 1553, 1470, 1385, 1159, 1049, 519; HRMS (ESI) calcd for $C_{24}H_{37}BrN_2NaO_4S^+$ $(M+Na)^+$ 551.1555, found 551.1559.



4f

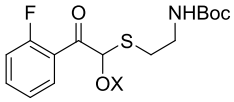
4f: Prepared according to the procedure **I** above and obtained as light yellow oil (71.6 mg, 74%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.05 (s, 1H), 5.09 (br, 1H), 3.40 – 3.31 (m, 2H), 2.71 – 2.63 (m, 2H), 1.58 – 1.50 (m, 3H), 1.48 (s, 3H), 1.43 (s, 9H),

1.36 – 1.26 (m, 3H), 1.18 (s, 3H), 1.10 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 155.8, 139.7, 132.9, 130.1, 129.0, 89.8, 79.2, 60.6, 60.1, 40.9, 40.2, 34.8, 33.4, 30.9, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3384, 2973, 2930, 1686, 1589, 1504, 1385, 1248, 1166, 1092, 1050, 909, 863, 778; HRMS (ESI) calcd for $C_{24}H_{38}ClN_2O_4S^+$ $(M+H)^+$ 485.2241, found 485.2237.



4g

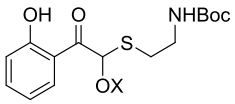
4g: Prepared according to the procedure **I** above and obtained as light yellow oil (66.8 mg, 69%), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 1H), 5.09 (br, 1H), 3.42 – 3.33 (m, 2H), 2.71 – 2.63 (m, 2H), 1.58 – 1.50 (m, 3H), 1.48 (s, 3H), 1.44 (s, 9H), 1.38 – 1.31 (m, 3H), 1.18 (s, 3H), 1.11 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 155.8, 136.3, 135.0, 133.1, 129.9, 128.7, 126.7, 89.5, 79.2, 60.7, 60.1, 40.9, 40.2, 34.8, 33.4, 30.8, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3662, 2973, 2901, 1406, 1251, 1054, 893; HRMS (ESI) calcd for $C_{24}H_{37}ClN_2NaO_4S^+$ $(M+Na)^+$ 507.2060, found 507.2061.



4h

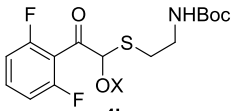
4h: Prepared according to the procedure **I** above and obtained as light yellow oil (60.9 mg, 65%), eluent: petroleum ether/ethyl acetate (12:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (t, *J* = 7.5 Hz, 1H), 7.52 (q, *J* = 7.0 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.11 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 6.25 (s, 1H), 5.12 (br, 1H), 3.43 – 3.30 (m, 2H), 2.66 – 2.58 (m, 2H), 1.56– 1.50 (m, 7H), 1.43 (s, 9H), 1.33 – 1.26 (m, 2H), 1.18 (d, *J* = 4.0 Hz, 6H), 1.01 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.3, 161.1 (d, *J* = 253.0 Hz), 155.8, 134.6 (d, *J* = 9.1 Hz), 131.2, 124.7, 123.7 (d, *J* = 12.5 Hz), 116.7 (d, *J* = 24.0 Hz), 91.5, 79.1, 60.6, 60.0, 41.0, 40.3, 34.8, 33.3, 29.3, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3385, 2973, 2928, 1713, 1696, 1481, 1453, 1365, 1271, 1209, 1169, 1067, 956, 878, 760; HRMS (ESI) calcd for $C_{24}H_{38}FN_2O_4S^+$ $(M+H)^+$ 469.2536, found

469.2529.



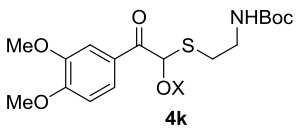
4i

4i: Prepared according to the procedure **I** or **II** above for 24 hand obtained as light yellow oil (37.3 mg, 40% for **I**, NP for **II**), eluent: petroleum ether/ethyl acetate (10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.00 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.10 (s, 1H), 5.09 (br, 1H), 3.45 – 3.30 (m, 2H), 2.78 – 2.74 (m, 2H), 1.71– 1.56 (m, 3H), 1.49 (s, 3H), 1.44 (s, 9H), 1.35 – 1.26 (m, 3H), 1.19 (s, 3H), 1.11 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 163.6, 155.8, 136.5, 129.7, 118.9, 118.8, 116.5, 89.2, 79.3, 60.7, 60.1, 41.0, 40.2, 34.8, 33.3, 31.2, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3670, 2972, 2902, 1713, 1664, 1453, 1393, 1250, 1159, 1066, 880, 756; HRMS (ESI) calcd for $C_{24}H_{38}N_2NaO_5S^+$ $(M+Na)^+$ 489.2399, found 489.2392.



4j

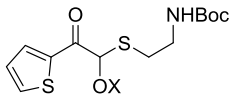
4j: Prepared according to the procedure **I** above and obtained as light yellow oil (68.1 mg, 70%), eluent: petroleum ether/ethyl acetate (12:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1H), 6.93 (t, *J* = 8.5 Hz, 2H), 5.98 (s, 1H), 5.08 (br, 1H), 3.46 – 3.33 (m, 2H), 2.79 – 2.69 (m, 2H), 1.58– 1.50 (m, 4H), 1.48 (s, 3H), 1.44 (s, 9H), 1.33 – 1.28 (m, 2H), 1.21 (s, 3H), 1.17 (s, 3H), 1.12 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2, 160.6 (dd, *J* = 6.8 Hz, *J* = 252.6 Hz) , 155.8, 132.6 (d, *J* = 20.9 Hz), 132.6, 116.0 (d, *J* = 35.9 Hz), 116.0, 112.1 (d, *J* = 25.0 Hz), 92.0, 79.1, 60.7, 60.3, 40.9, 40.3, 34.7, 33.5, 29.3, 28.4, 20.5, 17.0 ppm; IR(KBr, cm^{-1}): 3385, 2925, 1713, 1622, 1505, 1455, 1384, 1263, 1160, 1049, 788; HRMS (ESI) calcd for $C_{24}H_{37}F_2N_2O_4S^+$ $(M+H)^+$ 487.2442, found 487.2440.



4k

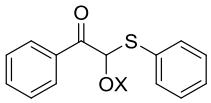
4k: Prepared according to the procedure **I** or **II** above for 24 h and obtained as light

yellow oil (70.4 mg, 69% for **I**, trace for **II**), eluent: petroleum ether/ethyl acetate (10:1 to 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 1H), 7.58 (s, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.08 (s, 1H), 5.20 (br, 1H), 3.95 (s, 6H), 3.43 – 3.32 (m, 2H), 2.71 (s, 2H), 1.70 – 1.54 (m, 3H), 1.49 (s, 3H), 1.43 (s, 9H), 1.38 – 1.26 (m, 3H), 1.19 (s, 3H), 1.12 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 155.9, 153.5, 149.1, 127.4, 123.2, 111.1, 110.1, 89.9, 79.1, 60.6, 60.0, 56.1, 56.0, 41.1, 40.2, 34.9, 33.4, 31.1, 28.4, 20.6, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3381, 2930, 1712, 1675, 1594, 1514, 1461, 1365, 1266, 1151, 1024, 955, 765, 637, 533; HRMS (ESI) calcd for $C_{26}H_{43}N_2O_6S^+$ $(M+H)^+$ 511.2842, found 511.2839.



4l

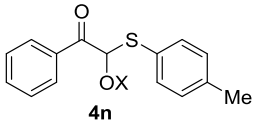
4l: Prepared according to the procedure **I** above for 24 h and obtained as yellow oil (59.3 mg, 65%), eluent: petroleum ether/ethyl acetate (8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 4.5 Hz, 1H), 7.65 (d, *J* = 4.5 Hz, 1H), 7.13 (t, *J* = 4.5 Hz, 1H), 5.92 (s, 1H), 5.13 (br, 1H), 3.45 – 3.31 (m, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 1.75– 1.55 (m, 3H), 1.47 (s, 3H), 1.43 (s, 9H), 1.37 – 1.26 (m, 3H), 1.18 (s, 3H), 1.12 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.4, 155.8, 141.0, 133.9, 132.6, 128.1, 90.5, 79.2, 60.6, 60.1, 41.0, 40.2, 34.8, 33.4, 31.0, 28.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3376, 2973, 2931, 1710, 1665, 1510, 1412, 1364, 1246, 1168, 1044, 909, 755, 721; HRMS (ESI) calcd for $C_{22}H_{37}N_2O_4S_2^+$ $(M+H)^+$ 457.2195, found 457.2191.



4m

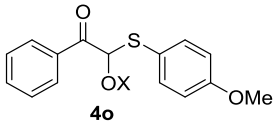
4m: Prepared according to the procedure **I** above and obtained as yellow oil (43.7 mg, 57%), eluent: petroleum ether/ethyl acetate (40:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.41 (m, 4H), 7.26 – 7.25 (m, 3H), 6.23 (s, 1H), 1.66 – 1.56 (m, 2H), 1.53 (s, 3H), 1.50 – 1.44 (m, 4H), 1.26 (s, 3H), 1.07 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 134.8, 133.4, 132.9,

132.5, 129.0, 128.8, 128.4, 128.1, 95.1, 60.8, 60.0, 40.2, 35.0, 33.4, 20.6, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3419, 2971, 2925, 1634, 1383, 1260, 1054, 1260, 1054, 689; HRMS (ESI) calcd for $C_{23}H_{30}NO_2S^+$ $(M+H)^+$ 384.1997, found 384.1994.



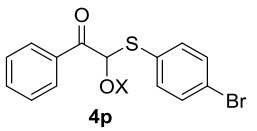
4n

4n: Prepared according to the procedure **I** above and obtained as yellow oil (61.2 mg, 77%), eluent: petroleum ether/ethyl acetate (40:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.19 (s, 1H), 2.31 (s, 3H), 1.66 – 1.62 (m, 1H), 1.56 (s, 3H), 1.51 – 1.43 (m, 4H), 1.33 – 1.28 (m, 1H), 1.26 (s, 3H), 1.06 (s, 3H), 0.94 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 138.3, 135.0, 133.8, 132.8, 129.6, 129.0, 128.6, 128.4, 95.1, 60.7, 60.0, 56.3, 40.2, 35.1, 33.4, 27.5, 21.2, 20.6, 17.0 ppm; IR(KBr, cm^{-1}): 2971, 2926, 1688, 1598, 1475, 1384, 1262, 1157, 1055, 905, 817, 704; HRMS (ESI) calcd for $C_{24}H_{32}NO_2S^+$ $(M+H)^+$ 398.2154, found 398.2154.



4o

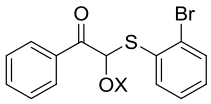
4o: Prepared according to the procedure **I** or **II** above and obtained as yellow oil (68.6 mg, 83% for **I**, trace for **II**), eluent: petroleum ether/ethyl acetate (40:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.15 (s, 1H), 3.78 (s, 3H), 1.58 (s, 3H), 1.52 – 1.31 (m, 6H), 1.27 (s, 3H), 1.06 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 160.1, 136.1, 135.1, 132.8, 128.9, 128.4, 122.2, 114.4, 95.0, 60.7, 60.0, 55.2, 40.3, 35.2, 33.4, 20.6, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3421, 2925, 1731, 1692, 1593, 1493, 1454, 1287, 1248, 1030, 827, 705; HRMS (ESI) calcd for $C_{24}H_{32}NO_3S^+$ $(M+H)^+$ 414.2103, found 414.2099.



4p

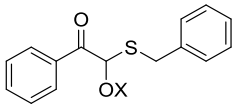
4p: Prepared according to the procedure **I** above and obtained as yellow oil (63.6 mg,

69%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.25 (s, 1H), 1.64 – 1.57 (m, 2H), 1.52 (s, 3H), 1.48 – 1.34 (m, 4H), 1.25 (s, 3H), 1.08 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 134.8, 134.7, 133.1, 131.9, 131.5, 128.9, 128.5, 122.6, 94.4, 60.9, 60.1, 40.2, 35.1, 33.4, 20.7, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 2927, 1688, 1471, 1384, 1263, 1056, 813, 704; HRMS (ESI) calcd for $C_{23}H_{29}BrNO_2S^+$ $(M+H)^+$ 462.1102, found 462.1097.



4q

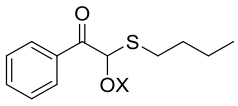
4q: Prepared according to the procedure **I** above and obtained as yellow oil (60.9 mg, 66%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.28 – 7.25 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 1.64 – 1.50 (m, 4H), 1.46 (s, 3H), 1.37 – 1.28 (m, 2H), 1.24 (s, 3H), 1.08 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9, 134.5, 134.4, 133.7, 133.1, 132.9, 129.2, 128.6, 128.4, 127.7, 126.1, 94.5, 60.9, 60.2, 40.2, 34.6, 33.4, 27.5, 20.6, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3387, 2928, 1685, 1449, 1382, 1264, 1057, 1021, 750, 705; HRMS (ESI) calcd for $C_{23}H_{29}BrNO_2S^+$ $(M+H)^+$ 462.1102, found 462.1095.



4r

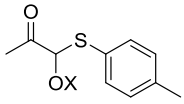
4r: Prepared according to the procedure **I** above for 24 hand obtained as colorless oil (46.1 mg), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.08 (s, 1H), 3.95 (d, *J* = 12.5 Hz, 1H), 3.81 – 3.72 (m, 1H), 1.60 – 1.52 (m, 4H), 1.48 (s, 3H), 1.39 – 1.31 (m, 2H), 1.17 (s, 3H), 1.15 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 137.2, 134.8, 133.0, 129.3, 128.8, 128.5, 128.4, 127.0, 89.8, 60.6, 59.9, 40.2, 34.8, 34.3, 33.4, 20.4,

20.2, 17.0 ppm; IR(KBr, cm^{-1}): 3418, 2962, 2930, 1676, 1597, 1494, 1377, 1230, 1168, 1067, 770, 739, 670, 639; HRMS (ESI) calcd for $C_{24}H_{31}NNaO_2S^+$ $(M+Na)^+$ 420.1973, found 420.1970.



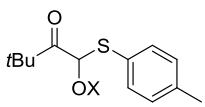
4s

4s: Prepared according to the procedure **I** above and obtained as yellow oil (42.1 mg, 58%), eluent: petroleum ether/ethyl acetate (40:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.01 (s, 1H), 2.68 – 2.47 (m, 2H), 1.61 – 1.51 (m, 4H), 1.49 (s, 3H), 1.42 – 1.29 (m, 6H), 1.19 (s, 3H), 1.10 (s, 3H), 0.94 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 134.9, 132.9, 128.7, 128.5, 90.1, 60.6, 59.8, 40.2, 34.8, 33.4, 31.6, 29.8, 27.4, 22.0, 20.4, 20.2, 17.1, 13.6 ppm; IR(KBr, cm^{-1}): 2971, 2926, 1680, 1453, 1384, 1260, 1051, 880; HRMS (ESI) calcd for $C_{21}H_{33}NNaO_2S^+$ $(M+Na)^+$ 386.2130, found 386.2126.



4t

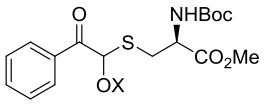
4t: Prepared according to the procedure **I** or **II** above at 45 °C for 72 h and obtained as yellow oil (37.5 mg, 56% for **I**, trace for **II**), eluent: petroleum ether/ethyl acetate (40:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.44 (s, 1H), 2.32 (s, 3H), 2.11 (s, 1H), 1.67 – 1.49 (m, 4H), 1.47 (s, 3H), 1.33 – 1.26 (m, 2H), 1.21 (s, 3H), 1.15 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 138.4, 133.7, 129.8, 128.2, 97.1, 60.7, 59.9, 56.2, 40.3, 35.3, 33.2, 27.5, 26.3, 21.2, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^-): 3241, 2927, 1714, 1633, 1431, 1110, 807, 617; HRMS (ESI) calcd for $C_{19}H_{30}NO_2S^+$ $(M+H)^+$ 336.1997, found 336.1997.



4u

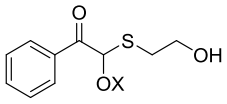
4u: Prepared according to the procedure **I** above at 45 °C for 72 h and obtained as

obtained as yellow oil (56.6 mg, 75%), eluent: petroleum ether/ethyl acetate (50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.84 (s, 1H), 2.34 (s, 3H), 1.66 – 1.53 (m, 3H), 1.50 (s, 3H), 1.45 – 1.33 (m, 3H), 1.25 (s, 3H), 1.24 (s, 9H), 1.12 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 137.7, 133.1, 129.3, 128.2, 90.8, 60.6, 60.0, 42.3, 40.3, 35.0, 33.6, 27.9, 21.2, 20.7, 20.3, 17.0 ppm; IR(KBr, cm$^-$): 2929, 1704, 1195, 1056, 784, 561, 536; HRMS (ESI) calcd for $C_{22}H_{35}NNaO_2S^+$ $(M+Na)^+$ 400.2286, found 400.2279.



4v

4v: Prepared according to the procedure **I** above and obtained as light yellow oil (69.1 mg, 68%, dr = 53:47), eluent: petroleum ether/ethyl acetate (8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 3H), 7.58 – 7.55 (m, 1.5H), 7.47 – 7.44 (m, 3H), 6.22 (s, 1H), 6.10 (s, 0.5H), 5.95 (d, *J* = 8.0 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 0.5H), 4.61 – 4.58 (m, 1H), 4.46 – 4.45 (m, 0.5H), 3.72 (s, 1.5H), 3.70 (s, 3H), 3.10 – 2.89 (m, 3H), 1.60 – 1.49 (m, 6H), 1.46 – 1.42 (m, 18H), 1.37 – 1.29 (m, 3H), 1.27 (s, 3H), 1.18 (s, 4.5H), 1.10 (s, 1.5H), 0.94 (s, 4.5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 189.9, 171.3, 171.2, 155,7, 134.7, 134.4, 133.3, 133.3, 128.8, 128.7, 128.6, 128.5, 89.7, 88.6, 79.9, 79.7, 60.7, 60.3, 60.0, 53.7, 52.5, 52.3, 40.4, 40.4, 40.2, 34.8, 34.5, 33.5, 32.3, 28.4, 28.3, 20.7, 20.6, 20.3, 17.0 ppm; IR(KBr, cm$^-$1): 3363, 2930, 1747, 1714, 1683, 1505, 1365, 1242, 1166, 1053, 912, 777, 705, 634, 582; HRMS (ESI) calcd for $C_{26}H_{41}N_2O_6S^+$ $(M+H)^+$ 509.2685, found 509.2685.

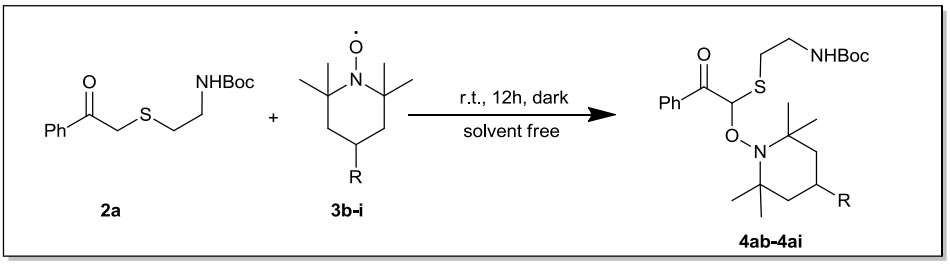


4w

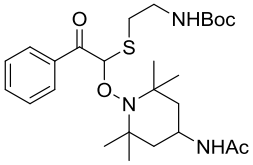
4w: Prepared according to the procedure **I** above and obtained as yellow oil (59.7 mg, 85%), eluent: petroleum ether/ethyl acetate (4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 12H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.17 (s, 1H), 3.88 – 3.81 (m, 2H), 2.84 – 2.73 (m, 3H), 1.60 – 1.56 (m, 2H), 1.51 (s, 3H), 1.44 – 1.32 (m, 4H), 1.19 (s, 3H), 1.11 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz,

$CDCl_3$) δ 190.6, 134.5, 133.3, 128.8, 128.7, 90.0, 62.6, 60.9, 60.1, 40.2, 35.0, 34.5, 33.4, 20.6, 20.3, 17.0 ppm; IR(KBr, cm^{-1}): 3418, 2931, 1682, 1597, 1448, 1379, 1262, 1237, 1179, 1132, 1045, 808, 704, 687; HRMS (ESI) calcd for $C_{19}H_{30}NO_3S^+$ $(M+H)^+$ 352.1946, found 352.1944.

B) Radical C(sp^3)-H α-Oxyamination of α-Mercapoto Carbonyls 2a with 3:

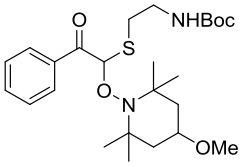


Reaction procedure III: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added α-mercapoto ketone **2a** (0.2 mmol) and various TEMPO radical **3** (0.4 mmol). The reaction mixture was then stirred at room temperature for 12 h in the dark. After reaction, purification of mixture by column chromatography on silica gel gave the desired product **4ab-4ai**.



4ab

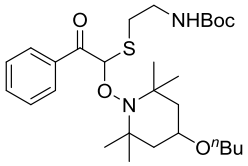
4ab: Prepared according to the procedure **III** above and obtained as light yellow oil (68.0 mg, 67% for **III**), eluent: petroleum ether/ethyl acetate (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.09 (s, 1H), 5.34 (d, *J* = 6.5 Hz, 1H), 5.12 (br, 1H), 4.14 – 4.12 (m, 1H), 3.42 – 3.30 (m, 2H), 2.72 – 2.64 (m, 2H), 1.94 (s, 3H), 1.89 (d, *J* = 13.0 Hz, 1H), 1.76 (d, *J* = 12.5 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 9H), 1.40 – 1.31 (m, 2H), 1.29 (s, 3H), 1.22 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 169.4, 155.8, 134.5, 133.3, 128.7, 128.6, 89.5, 79.2, 60.7, 60.3, 46.0, 46.0, 41.0, 40.9, 34.7, 33.3, 30.6, 28.4, 23.5, 21.1, 20.9 ppm; IR(KBr, cm^-): 3385, 2976, 2899, 1649, 1453, 1382, 1273, 1086, 1048, 880, 665, 434; HRMS (ESI) calcd for $C_{26}H_{41}N_3NaO_5S^+$ $(M+Na)^+$ 530.2665, found 530.2663.



4ac

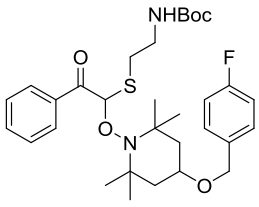
4ac: Prepared according to the procedure **III** above and obtained as light yellow oil

(72.0 mg, 75%), eluent: petroleum ether/ethyl acetate (10:1 to 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.15 (s, 1H), 5.11 (br, 1H), 3.47 – 3.40 (m, 2H), 3.00 (s, 3H), 2.72 – 2.64 (m, 2H), 1.97 – 1.95 (m, 1H), 1.84 – 1.82 (m, 1H), 1.53 (s, 3H), 1.43 (s, 9H), 1.40 – 1.31 (m, 3H), 1.24 (s, 3H), 1.18 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 155.8, 134.6, 133.3, 128.7, 128.5, 89.3, 79.2, 71.5, 60.8, 60.3, 55.8, 45.0, 41.1, 34.9, 33.5, 30.5, 28.4, 21.5, 21.3 ppm; IR(KBr, cm^{-1}): 3362, 2968, 2923, 1633, 1384, 1194, 1057, 870, 787, 561, 538; HRMS (ESI) calcd for $C_{25}H_{40}N_2NaO_5S^+$ $(M+Na)^+$ 503.2556, found 503.2556.



4ad

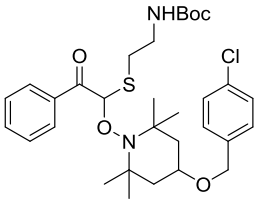
4ad: Prepared according to the procedure **III** above and obtained as light yellow oil (81.5 mg, 78% for **III**), eluent: petroleum ether/ethyl acetate (10:1 to 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.15 (s, 1H), 5.13 (br, 1H), 3.55 – 3.50 (m, 1H), 3.43 – 3.32 (m, 4H), 2.71 – 2.65 (m, 2H), 1.94 (d, *J* = 12.5 Hz, 1H), 1.81 (d, *J* = 12.5 Hz, 1H), 1.55 – 1.50 (m, 5H), 1.43 (s, 9H), 1.40 – 1.32 (m, 4H), 1.24 (s, 3H), 1.18 (s, 3H), 0.97 (s, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 155.8, 134.6, 133.3, 128.7, 128.5, 89.2, 79.2, 69.9, 68.1, 60.8, 60.3, 45.4, 41.1, 34.9, 33.5, 32.2, 30.5, 28.4, 21.5, 21.3, 19.4, 13.9 ppm; IR(KBr, cm^{-1}): 3383, 2971, 2928, 1714, 1682, 1505, 1454, 1384, 1249, 1050, 711; HRMS (ESI) calcd for $C_{28}H_{47}BrN_2O_5S^+$ $(M+H)^+$ 523.3206, found 523.3204.



4ae

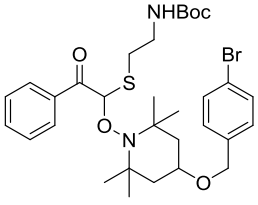
4ae: Prepared according to the procedure **III** above and obtained as light yellow oil (86.1 mg, 75% for **III**), eluent: petroleum ether/ethyl acetate (10:1 to 6:1); ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 6.5 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.15 (s, 1H), 5.09 (br, 1H), 4.47 (s, 2H), 3.69 – 3.64 (m, 1H), 3.40 – 3.32 (m, 2H), 2.68 – 2.67 (m, 2H), 1.99 (d, *J* = 12.5 Hz, 1H), 1.86 (d, *J* = 12.5 Hz, 1H), 1.53 (s, 3H), 1.51 – 1.47 (m, 3H), 1.43 (s, 9H), 1.22 (s, 3H), 1.17 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 162.3(d, *J* = 244.0 Hz), 155.8, 134.6, 134.4(d, *J* = 2.8 Hz), 133.4, 129.3 (d, *J* = 8.0 Hz), 128.7, 128.6, 115.3 (d, *J* = 21.3 Hz), 89.3, 79.2, 69.9, 69.6, 60.8, 60.4, 45.4, 41.1, 34.9, 33.5, 30.5, 28.4, 21.5, 21.3 ppm; IR(KBr, cm^{-1}): 3386, 2972, 2928, 1714, 1510, 1384, 1167, 1055, 823, 713; HRMS (ESI) calcd for $C_{31}H_{44}FN_2O_5S^+$ $(M+H)^+$ 575.2955, found 575.2956.



4af

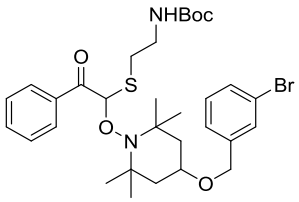
4af: Prepared according to the procedure **III** above and obtained as light yellow oil (59.0 mg, 50% for **III**), eluent: petroleum ether/ethyl acetate (10:1 to 6:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.15 (s, 1H), 5.09 (br, 1H), 4.47 (s, 2H), 3.69 – 3.64 (m, 1H), 3.43 – 3.30 (m, 2H), 2.71 – 2.64 (m, 2H), 2.00 – 1.97 (m, 1H), 1.87 – 1.84 (m, 1H), 1.54 (s, 3H), 1.51 – 1.47 (m, 2H), 1.43 (s, 9H), 1.22 (s, 3H), 1.17 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 155.8, 137.2, 134.6, 133.3, 133.3, 128.8, 128.7, 128.5, 89.3, 79.2, 70.0, 69.4, 60.8, 60.4, 45.3, 41.1, 34.9, 33.5, 30.5, 28.4, 21.5, 21.3 ppm; IR(KBr, cm^{-1}): 3384, 2973, 2929, 1712, 1684, 1493, 1364, 1247, 1168, 1086, 1016, 808, 711, 688; HRMS (ESI) calcd for $C_{31}H_{44}ClN_2O_5S^+$ $(M+H)^+$ 591.2659, found 591.2661.



4ag

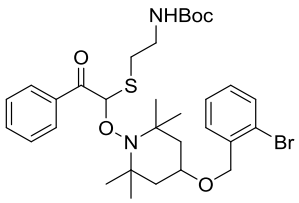
4ag: Prepared according to the procedure **III** above and obtained as light yellow oil

(83.7 mg, 66%), eluent: petroleum ether/ethyl acetate (10:1 to 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.15 (s, 1H), 5.07 (br, 1H), 4.45 (s, 2H), 3.66 (t, *J* = 10.5 Hz, 1H), 3.40 – 3.34 (m, 2H), 2.67 (s, 2H), 1.99 (d, *J* = 12.0 Hz, 1H), 1.86 (d, *J* = 12.0 Hz, 1H), 1.54 (s, 3H), 1.51 – 1.47 (m, 2H), 1.43 (s, 9H), 1.22 (s, 3H), 1.17 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 155.9, 137.8, 134.7, 133.4, 131.6, 129.2, 128.8, 128.6, 121.4, 89.3, 79.2, 70.1, 69.5, 60.8, 60.4, 45.4, 41.1, 35.0, 33.6, 30.6, 28.5, 21.6, 21.4 ppm; IR(KBr, cm^{-1}): 3386, 2972, 2922, 1633, 1384, 1251, 1050, 881; HRMS (ESI) calcd for $C_{31}H_{43}BrN_2NaO_5S^+$ $(M+Na)^+$ 657.1974, found 657.1975.



4ah

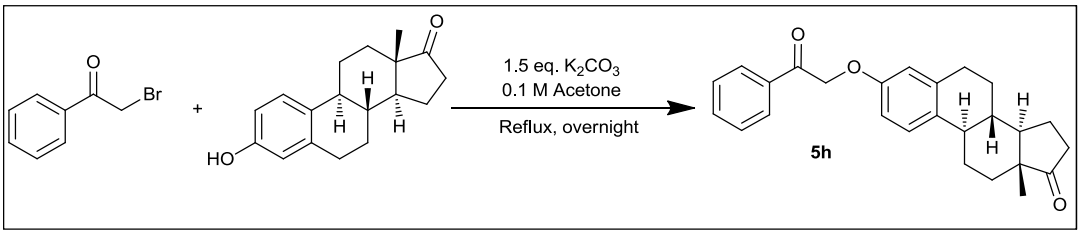
4ah: Prepared according to the procedure **III** above and obtained as light yellow oil (67.2 mg, 53%), eluent: petroleum ether/ethyl acetate (10:1 to 6:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.48 – 7.45 (m, 3H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.15 (s, 1H), 5.09 (br, 1H), 4.47 (s, 2H), 3.67 (t, *J* = 11.5 Hz, 1H), 3.41 – 3.34 (m, 2H), 2.68 – 2.67 (m, 2H), 2.00 (d, *J* = 12.5 Hz, 1H), 1.87 (d, *J* = 13.0 Hz, 1H), 1.54 (s, 3H), 1.52 – 1.48 (m, 2H), 1.43 (s, 9H), 1.23 (s, 3H), 1.17 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 155.8, 141.1, 134.7, 133.4, 130.6, 130.5, 130.0, 128.8, 128.6, 125.9, 122.6, 89.3, 79.2, 70.3, 69.5, 60.8, 60.4, 45.3, 41.1, 35.0, 33.5, 30.6, 28.5, 21.6, 21.3 ppm; IR(KBr, cm^{-}): 3386, 2972, 2923, 1686, 1383, 1250, 1160, 1054, 895; HRMS (ESI) calcd for $C_{31}H_{44}BrN_2O_5S^+$ $(M+H)^+$ 635.2154, found 635.2162.



4ai

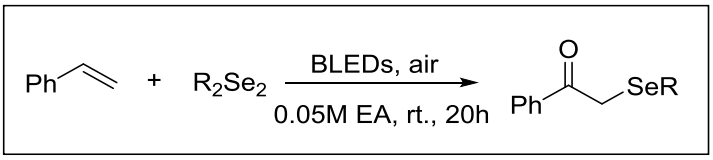
4ai: Prepared according to the procedure **III** above and obtained as light yellow oil (79.9 mg, 63%), eluent: petroleum ether/ethyl acetate (10:1 to 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 6.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.46 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.16 (s, 1H), 5.10 (br, 1H), 4.56 (s, 2H), 3.75 – 3.70 (m, 1H), 3.41 – 3.34 (m, 2H), 2.68 – 2.67 (m, 2H), 2.04 (d, *J* = 12.5 Hz, 1H), 1.91 (d, *J* = 12.5 Hz, 1H), 1.55 (s, 3H), 1.51 – 1.49 (m, 2H), 1.43 (s, 9H), 1.25 (s, 3H), 1.19 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 155.8, 138.0, 134.7, 133.4, 132.5, 130.9, 129.1, 128.9, 128.8, 128.6, 127.5, 122.7, 89.3, 79.2, 70.5, 69.7, 60.9, 60.4, 45.4, 41.1, 35.0, 33.6, 30.6, 28.5, 21.6, 21.3 ppm; IR(KBr, cm^{-1}): 3386, 2972, 2925, 1682, 1384, 1295, 1159, 1049, 752; HRMS (ESI) calcd for $C_{31}H_{43}BrN_2NaO_5S^+$ $(M+Na)^+$ 657.1974, found 657.1970.

C) Synthesis of α-Chalcogen Carbonyls 5h:

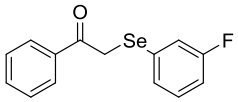


Reaction procedure IV: 2-Bromoacetophenone (0.5 mmol) and Estrone (0.5 mmol) were dissolved in 5mL Acetone, then K_2CO_3 (0.75mol) was added. The solution was stirred at reflux overnight. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1, v/v) gave the desired product **5h** (light yellow solid, 179 mg, 92% yield, dr = 1:0.23); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 0.23H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.70 (s, 1H), 6.64 (d, *J* = 9.0 Hz, 0.23H), 6.59 (s, 0.23H), 5.25 (s, 2H), 2.90 – 2.86 (m, 2.46H), 2.53 – 2.47 (m, 1.23H), 2.40 – 2.37 (m, 1H), 2.26 – 2.22 (m, 1.23H), 2.17 – 2.10 (m, 1.23H), 2.08 – 1.94 (m, 3.69H), 1.66 – 1.60 (m, 1.23H), 1.55 – 1.47 (m, 4.92H), 1.45 – 1.41 (m, 1.23H), 0.90 (s, 3.69H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.7, 156.1, 153.8, 138.0, 134.6, 133.8, 133.1, 128.8, 128.2, 126.5, 115.3, 114.9, 112.9, 112.2, 70.9, 50.4, 48.0, 44.0, 38.4, 38.3, 35.9, 31.6, 29.6, 29.5, 26.5, 25.9, 25.9, 21.6, 13.9 ppm.

D) Synthesis of α-Chalcogen Carbonyls 5k, 5n:

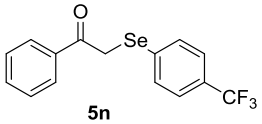


Reaction procedure V: Compound **5k**, **5n** were prepared according to a previous literature procedure with slight modifications.[1] More specifically, to a 50 mL round-bottomed flask with magnetic stir bar were added 2 mmol of styrene, 1 mmol diselenide and 20 mL of EA. The reaction mixture was stirred in air and irradiated with a 20W blue LEDs. After 20 hours, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel gave the desired product.



5k

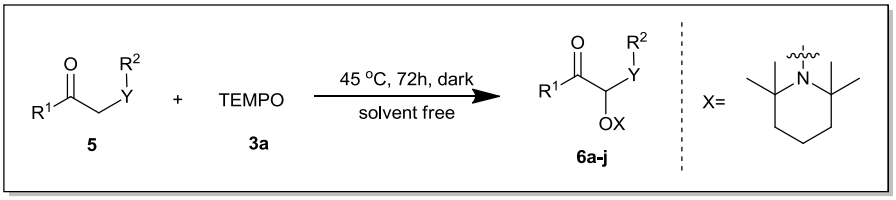
5k: Prepared according to the procedure **V** above and obtained as yellow oil (76.2 mg, 26%), eluent: petroleum ether/ethyl acetate (20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 70.60 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.03 – 7.00 (m, 1H), 4.25 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.7, 162.5 (d, *J* = 248.4 Hz), 135.3, 133.5, 130.7 (d, *J* = 7.0 Hz), 130.5 (d, *J* = 8.0 Hz), 129.1, 128.7, 120.4 (d, *J* = 19.6 Hz), 115.0 (d, *J* = 20.9 Hz), 32.7 ppm.



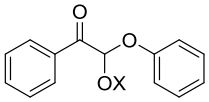
5n

5n: Prepared according to the general procedure **V** above and obtained as light yellow solid (78.9 mg, 23%), eluent: petroleum ether/ethyl acetate (20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 4.26 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ194.5, 135.2, 134.3, 133.6, 132.8, 129.9, 129.6, 128.8, 128.7, 125.9 (d, *J* = 3.4 Hz), 32.2 ppm.

E) Radical C(sp^3)-H α-Oxyamination of α-Chalcogen Carbonyls 5 with 3a:

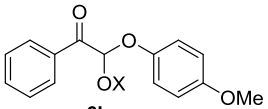


Reaction procedure VI: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added α-chalcogen carbonyls **5** (0.2 mmol) and TEMPO (0.4 mmol). The reaction mixture was then stirred at 45 °C for 72 h in the dark. After reaction, purification of mixture by column chromatography on silica gel gave the desired product **6a-t**. Compounds **6a**, **6b**, **6c** are known compounds.[2]



6a

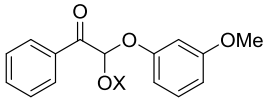
6a: Prepared according to the procedure **VI** above and obtained as white solid (58.8 mg, 80%), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.02 (s, 1H), 1.57 – 1.48 (m, 6H), 1.37 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 156.7, 133.5, 133.1, 130.5, 129.4, 128.3, 122.1, 116.8, 109.8, 61.2, 60.0, 40.2, 39.8, 33.8, 33.1, 20.9, 20.2, 17.1 ppm; IR(KBr, cm^{-1}): 3668, 3229, 2972, 1688, 1598, 1493, 1409, 1104, 893, 754, 690, 617; HRMS (ESI) calcd for $C_{23}H_{30}NO_3^+$ $(M+H)^+$ 368.2226, found 368.2226.



6b

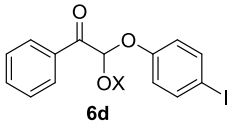
6b: Prepared according to the procedure **VI** above and obtained as colorless oil (59.6 mg, 75%), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.91 (s, 1H), 3.73 (s, 3H), 1.51 – 1.49 (m, 5H), 1.39 (s, 3H), 1.35 – 1.28 (m, 1H), 1.21 (s, 3H), 1.14 (s, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 154.8, 150.7, 133.4, 133.2, 130.4, 128.3, 118.2,

114.5, 110.6, 61.2, 60.0, 55.6, 40.2, 39.8, 33.8, 33.1, 20.9, 20.2, 17.1 ppm; IR(KBr, cm^{-1}): 2962, 2933, 1680, 1508, 1450, 1379, 1284, 1215, 1116, 1004, 832, 758, 718, 688; HRMS (ESI) calcd for $C_{24}H_{32}NO_4^+$ $(M+H)^+$ 398.2331, found 398.2325.



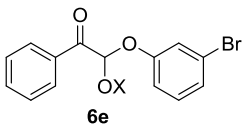
6c

6c: Prepared according to the procedure **VI** above and obtained as white solid (62.0 mg, 78%), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.62 (s, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 3.75 (s, 3H), 1.61 – 1.48 (m, 5H), 1.37 (s, 3H), 1.34 – 1.28 (m, 1H), 1.21 (s, 3H), 1.17 (s, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 160.7, 157.9, 133.5, 133.1, 130.5, 129.9, 128.3, 109.7, 109.0, 108.0, 103.1, 61.2, 60.0, 55.3, 40.2, 39.9, 33.7, 33.1, 20.9, 20.2, 17.1 ppm; IR(KBr, cm^-): 2924, 1649, 1452, 1097, 956, 603, 502; HRMS (ESI) calcd for $C_{24}H_{32}NO_4^+$ $(M+H)^+$ 398.2331, found 398.2328.



6d

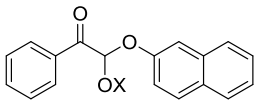
6d: Prepared according to the procedure **VI** above and obtained as white solid (64.1 mg, 65%, M.P. = 140-142 ^{o}C), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.98 (s, 1H), 1.59 – 1.43 (m, 6H), 1.32 (s, 3H), 1.20 (s, 3H), 1.14 (s, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 156.6, 138.3, 133.6, 133.0, 130.4, 128.3, 119.2, 109.7, 84.7, 61.3, 60.1, 40.2, 39.8, 33.7, 33.1, 20.9, 20.2, 17.1 ppm; IR(KBr, cm^{-1}): 2964, 1677, 1585, 1484, 1228, 1123, 982, 826, 757, 716, 684; HRMS (ESI) calcd for $C_2H_{29}NO_3^+$ $(M+H)^+$ 494.1192, found 494.1186.



6e

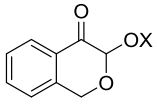
6e: Prepared according to the procedure **VI** above and obtained as white solid (43.6

mg, 49%, M.P. = 135-137 °C), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.23 (s, 1H), 7.10 (d, *J* = 4.5 Hz, 2H), 6.98 – 6.96 (m, 1H), 5.99 (s, 1H), 1.59 – 1.46 (m, 6H), 1.34 (s, 3H), 1.21 (s, 3H), 1.17 (s, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 157.4, 133.7, 132.8, 130.6, 130.4, 128.4, 125.3, 122.7, 120.4, 115.3, 109.7, 61.3, 60.1, 40.2, 39.8, 33.7, 33.1, 20.9, 20.2, 17.0 ppm; IR (KBr, cm^{-1}): 2924, 2388, 1650, 1449, 1094, 965, 603, 502; HRMS (ESI) calcd for $C_{23}H_{29}BrNO_3^+$ $(M+H)^+$ 446.1331, found 446.1323.



6f

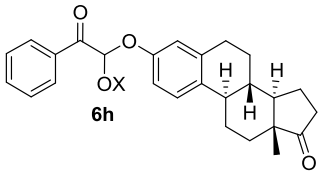
6f: Prepared according to the procedure **VI** above and obtained as light yellow oil (66.8 mg, 80%), eluent: petroleum ether/ethyl acetate (30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.68 (m, 3H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.37 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.18 (s, 1H), 1.58 – 1.46 (m, 5H), 1.39 (s, 3H), 1.34 – 1.31 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H), 1.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 154.5, 134.3, 133.6, 133.1, 130.5, 129.5, 128.3, 127.6, 127.2, 126.4, 124.2, 119.2, 110.7, 109.8, 61.3, 60.1, 40.2, 39.9, 33.9, 33.2, 21.0, 20.3, 17.1 ppm; IR (KBr, cm^{-1}): 2970, 2389, 1649, 1407, 1078, 966, 603, 502; HRMS (ESI) calcd for $C_{27}H_{32}NO_3^+$ $(M+H)^+$ 418.2382, found 418.2376.



6g

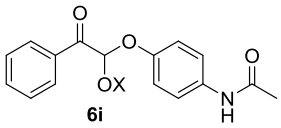
6g: Prepared according to the procedure **VI** above 60 °C and obtained as white solid (49.1 mg, 81%, M.P. = 141-144 °C), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.44 (s, 1H), 5.36 (d, *J* = 16.0 Hz, 1H), 4.76 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 5H), 1.35 – 1.26 (m, 7H), 1.13 (s, 3H), 1.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.8, 141.4, 133.8, 128.9, 127.6, 127.1, 123.9, 103.6,

61.6, 61.1, 59.8, 40.8, 40.4, 33.7, 33.0, 20.6, 20.1, 17.0 ppm; IR (KBr, cm^{-1}): 2926, 1699, 1605, 1459, 1282, 1101, 1063, 1024, 983, 761, 733, 691, 570; HRMS (ESI) calcd for $C_{18}H_{26}NO_3^+$ $(M+H)^+$ 304.1913, found 304.1914.



6h

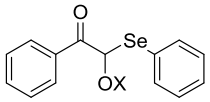
6h: Prepared according to the procedure **VI** above at 60 °C and obtained as light yellow solid (58.7 mg, 54%, M.P. = 90-92 °C), eluent: petroleum ether/ethyl acetate (6:1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 1H), 6.82 (t, J = 6.5 Hz, 1H), 6.73 (d, J = 4.5 Hz, 1H), 5.95 (s, 1H), 2.85 – 2.84 (m, 2H), 2.52 – 2.46 (m, 1H), 2.36 – 2.34 (m, 1H), 2.23 – 2.21 (m, 1H), 2.16 – 2.09 (m, 1H), 2.06 – 2.01 (m, 1H), 1.98 – 1.93 (m, 2H), 1.65 – 1.45 (m, 10H), 1.40 (s, 3H), 1.35 – 1.28 (m, 2H), 1.21 (s, 3H), 1.16 (s, 3H), 1.01 (s, 3H), 0.88 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 154.6, 137.8, 133.4, 133.1, 130.5, 128.2, 126.3, 116.7, 116.7, 114.3, 114.2, 109.9, 61.1, 60.0, 50.4, 48.0, 44.0, 40.2, 39.8, 38.3, 35.9, 33.9, 33.1, 31.6, 29.6, 26.5, 25.8, 21.6, 20.9, 20.2, 17.1, 13.8 ppm; IR (KBr, cm^{-1}): 2930, 2870, 1740, 1687, 1497, 1452, 1275, 1132, 1005, 987, 956, 818, 732, 711, 629, 579; HRMS (ESI) calcd for $C_{35}H_{45}NNaO_4^+$ $(M+Na)^+$ 566.3246, found 566.3247.



6i

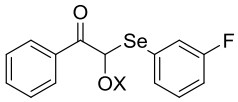
6i: Prepared according to the procedure **VI** above at 80 °C and obtained as white solid (61.1 mg, 72%, M.P. = 85-87 °C), eluent: petroleum ether/ethyl acetate (1:1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 7.15 (br, 1H), 6.98 (d, J = 8.5 Hz, 2H), 5.97 (s, 1H), 2.13 (s, 3H), 1.61 – 1.46 (m, 6H), 1.35 (s, 3H), 1.20 (s, 3H), 1.15 (s, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 168.1, 153.5, 133.5, 133.0, 132.2, 130.4, 128.3, 121.6, 117.3, 110.0, 61.2, 60.0, 40.2, 39.8, 33.7, 33.1, 24.4, 20.9, 20.2, 17.1 ppm; IR (KBr, cm^{-1}): 3415, 2932, 1686, 1617, 1509, 1450, 1217, 1181, 1006,

985, 835, 782, 712, 686; HRMS (ESI) calcd for $C_{25}H_{33}N_2O_4^+$ $(M+H)^+$ 425.2440, found 425.2431.



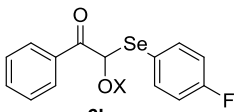
6j

6j: Prepared according to the procedure **VI** above and obtained as yellow oil (44.8 mg, 52%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 6.51 (s, 1H), 1.67 – 1.55 (m, 2H), 1.53 (s, 3H), 1.47 – 1.42 (m, 4H), 1.24 (s, 3H), 1.05 (s, 3H), 0.94 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 135.4, 134.8, 132.8, 128.9, 128.9, 128.4, 128.3, 92.8, 60.8, 60.2, 40.2, 35.4, 33.4, 20.5, 20.3, 17.0 ppm; IR (KBr, cm^{-1}): 3668, 3228, 2971, 1681, 1435, 1104, 875, 738, 617, 469; HRMS (ESI) calcd for $C_{23}H_{29}NNaO_2Se^+$ $(M+Na)^+$ 454.1261, found 454.1265.



6k

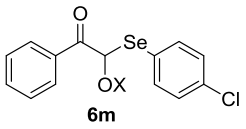
6k: Prepared according to the procedure **VI** above and obtained as yellow oil (47.5 mg, 53%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.21 (m, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 1.58 – 1.56 (m, 2H), 1.51 (s, 3H), 1.44 – 1.29 (m, 4H), 1.24 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 162.2 (d, *J* = 248.4 Hz), 134.6, 133.0, 130.7, 130.2 (d, *J* = 7.0 Hz), 130.1 (d, *J* = 7.8 Hz), 128.8, 128.5, 122.0 (d, *J* = 21.9 Hz), 115.3 (d, *J* = 21.0 Hz), 92.6, 60.9, 60.1, 40.2, 35.4, 33.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^-): 2932, 1682, 1588, 1470, 1261, 1121, 1055, 779, 702, 680; HRMS (ESI) calcd for $C_{23}H_{29}FNNaO_2Se^+$ $(M+Na)^+$ 472.1167, found 472.1165.



6l

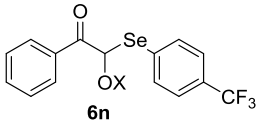
6l: Prepared according to the procedure **VI** above and obtained as yellow oil (48.4 mg,

54%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 4H), 6.93 (t, *J* = 8.5 Hz, 2H), 6.52 (s, 1H), 1.65 – 1.51 (m, 5H), 1.48 – 1.31 (m, 4H), 1.24 (s, 3H), 1.06 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 163.2 (d, *J* = 247.4 Hz), 137.8 (d, *J* = 8.1 Hz), 134.8, 132.9, 128.7, 128.5, 123.0, 116.2 (d, *J* = 21.5 Hz), 92.3, 60.8, 60.2, 40.2, 35.4, 33.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-}): 2931, 1682, 1583, 1486, 1196, 1055, 785, 703, 561; HRMS (ESI) calcd for $C_{23}H_{28}FNNaO_2Se^{+}$ $(M+Na)^{+}$ 472.1167, found 472.1158.



6m

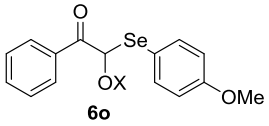
6m: Prepared according to the procedure **VI** above and obtained as yellow oil (45.5 mg, 50%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.44 – 7.39 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 1.64 – 1.56 (m, 2H), 1.52 (s, 3H), 1.48 – 1.31 (m, 4H), 1.23 (s, 3H), 1.06 (s, 3H), 0.94 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 136.7, 134.8, 134.7, 133.0, 129.1, 128.7, 128.5, 126.7, 92.4, 60.8, 60.2, 40.2, 35.4, 33.4, 20.5, 20.3, 17.0 ppm; IR(KBr, cm^{-}): 2931, 1682, 1472, 1381, 1195, 1055, 813, 785, 702; HRMS (ESI) calcd for $C_{23}H_{28}ClNNaO_2Se^{+}$ $(M+Na)^{+}$ 488.0871, found 488.0867.



6n

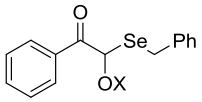
6n: Prepared according to the procedure **VI** above and obtained as yellow oil (40.9 mg, 41%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 6.60 (s, 1H), 1.57 – 1.54 (m, 2H), 1.50 (s, 3H), 1.45 – 1.32 (m, 4H), 1.23 (s, 3H), 1.08 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 134.7, 134.5, 133.8, 133.1, 130.2, 129.9, 128.7, 128.5, 125.6 (q, *J* = 3.5 Hz), 92.3, 60.9, 60.2, 40.2, 35.4, 33.4, 20.5, 20.3, 16.9 ppm; IR(KBr, cm^{-}): 2932, 1683, 1601, 1324, 1195, 1128, 1056, 829, 784, 703; HRMS (ESI) calcd for

$C_{24}H_{28}F_3NNaO_2Se^+$ $(M+Na)^+$ 522.1135, found 522.1135.



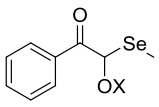
6o

6o: Prepared according to the procedure **VI** above and obtained as yellow oil (59.9 mg, 65%), eluent: petroleum ether/ethyl acetate (15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.46 (s, 1H), 3.79 (s, 3H), 1.56 (s, 3H), 1.51 – 1.30 (m, 6H), 1.24 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 160.1, 137.6, 135.0, 132.7, 128.8, 128.4, 118.6, 114.6, 92.5, 60.7, 60.1, 55.2, 40.2, 35.5, 33.3, 20.5, 20.4, 160.1, 137.6, 135.0, 132.7, 128.8, 128.4, 118.6, 114.6, 92.5, 60.7, 60.1, 55.2, 40.2, 35.5, 33.3, 20.5, 20.3, 17.0 ppm; IR(KBr, cm$^-$): 2931, 1681, 1589, 1489, 1247, 1174, 1029, 823, 796, 702; HRMS (ESI) calcd for $C_{24}H_{31}NNaO_3Se^+$ $(M+Na)^+$ 484.1367, found 484.1368.



6p

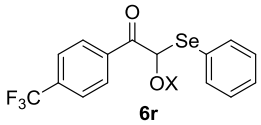
6p: Prepared according to the procedure **VI** above and obtained as light yellow solid (32.9 mg, 37%, M.P. = 78-81 °C), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 6.39 (s, 1H), 4.00 (t, *J* = 11.0 Hz, 1H), 3.85 (t, *J* = 11.5 Hz, 1H), 1.55 – 1.49 (m, 2H), 1.41 (s, 3H), 1.37 – 1.17 (m, 4H), 1.11 (d, *J* = 6.0 Hz, 6H), 0.96 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 137.3, 133.8, 132.0, 128.5, 127.7, 127.7, 127.6, 125.9, 86.1, 59.8, 59.1, 39.4, 34.3, 32.5, 27.7, 19.5, 19.4, 16.2 ppm; IR(KBr, cm$^-$): 2929, 1668, 1598, 1494, 1226, 1062, 794, 756, 696; HRMS (ESI) calcd for $C_{24}H_{31}NNaO_2Se^+$ $(M+Na)^+$ 468.1418, found 468.1419.



6q

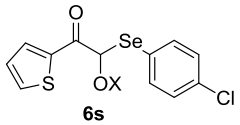
6q: Prepared according to the procedure **VI** above and obtained as light yellow solid

(39.8 mg, 54%, M.P. = 83-86 °C), eluent: petroleum ether/ethyl acetate (50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 6.41 (s, 1H), 2.04 (s, 3H), 1.58 – 1.55 (m, 2H),1.48 (s, 3H), 1.44 – 1.24 (m, 4H), 1.19 (s, 3H), 1.12 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 134.7, 132.8, 128.5, 128.4, 85.0, 60.7, 59.9, 40.2, 35.2, 33.3, 20.4, 20.2, 17.0 ppm; IR(KBr, cm$^-$): 2928, 1668, 1596, 1466, 1228, 1131, 1050, 732, 704; HRMS (ESI) calcd for $C_{18}H_{27}NNaO_2Se^+$ $(M+Na)^+$ 392.1105, found 392.1104.



6r

6r: Prepared according to the procedure **VI** above and obtained as light yellow solid (51.8 mg, 52%, M.P. = 84-85 °C), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.26 – 7.23 (m, 2H), 6.51 (s, 1H), 1.65 – 1.55 (m, 4H), 1.52 – 1.32 (m, 4H), 1.25 (s, 3H), 1.05 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 137.7, 135.5, 134.0 (q, *J* = 33.1 Hz), 129.2, 129.1, 128.6, 128.2, 125.4, 124.7, 92.7, 60.8, 60.2, 40.2, 35.4, 33.4, 20.5, 20.4, 17.0 ppm; IR(KBr, cm$^-$): 2933, 1678, 1579, 1410, 1320, 1128, 1066, 861, 769, 705, 691; HRMS (ESI) calcd for $C_{24}H_{28}F_3NNaO_2Se^+$ $(M+Na)^+$ 522.1135, found 522.1143.



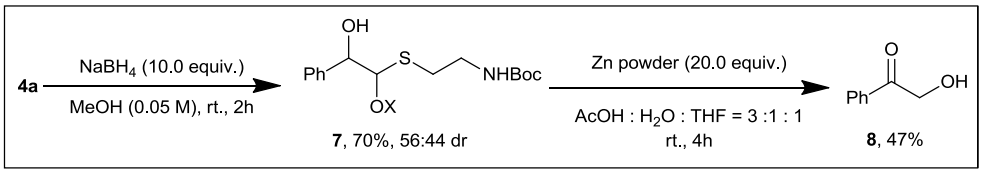
6s

6s: Prepared according to the procedure **VI** above and obtained as yellow oil (33.2 mg, 38%), eluent: petroleum ether/ethyl acetate (40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 3.5 Hz, 1H), 7.60 (d, *J* = 4.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.29 – 7325 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 4.0 Hz, 1H), 6.27 (s, 1H), 1.54 – 1.51 (m, 5H), 1.43 – 1.32 (m, 4H), 1.23 (s, 3H), 1.05 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.8, 138.8, 133.4, 131.4, 130.7, 126.7, 126.6, 126.1, 125.7, 91.5, 58.6, 58.1, 38.0, 33.2, 31.2, 18.4, 18.2, 14.8 ppm; IR(KBr, cm$^-$): 2931, 1661, 1577, 1438, 1259, 1059, 1038, 792, 736, 690; HRMS (ESI) calcd for

$C_{21}H_{27}NNaO_2SSe^+$ $(M+Na)^+$ 460.0825, found 460.0817.

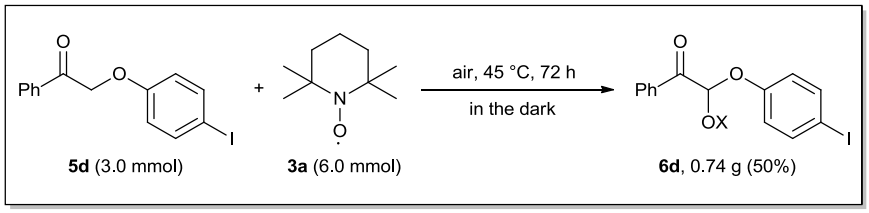
F) Gram-scale reaction and transformation of α-alkoxyamine carbonyls

Reaction procedure VII for gram-scale reaction of 4a: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added α-mercapoto ketone **2a** (3 mmol) and TEMPO (6 mmol). The reaction mixture was then stirred at room temperature for 24 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired product **4a** (1.15 g, 85% yield).

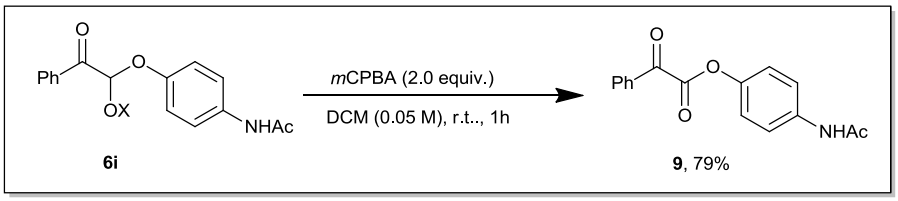


Reaction procedure VIII for transformation of 4a: Compound **4a** (1 mmol) was dissolved in 20 mL MeOH. Then, $NaBH_4$ (10 mmol) was added slowly. The reaction mixture was then stirred at room temperature for 2 h. After reaction, the mixture was quenched by H_2O slowly. The mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 6:1, v/v) gave the desired product **7** (colorless oil , 317mg, 70% yield, dr = 56 : 44); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 3.6H), 7.36 – 7.32 (m, 3.6H), 7.31 – 7.28 (m, 1.8H), 6.94 (br, 1H), 5.22 – 5.18 (m, 2.6H), 4.97 (d, *J* = 8.5 Hz, 1H), 4.85 (br, 0.8H), 4.85 (br, 1H), 3.29 (s, 0.8H), 3.21 (s, 1H), 3.00 – 2.91 (m, 1.6H), 2.78 – 2.76 (m, 1H), 2.70 – 2.65 (m, 0.8H), 2.56 – 2.51 (m, 1H), 1.64 – 1.60 (m, 1.6H), 1.58 (s, 2.4H), 1.55 – 1.52 (m, 3.6H), 1.46 (s, 3H), 1.44 (s, 7.2H), 1.43 (s, 9H), 1.32 – 1.26 (m, 5.4H), 1.21 (d, *J* = 6.0 Hz, 5.4H), 1.07 (s, 5.4H), 0.88 – 0.84 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 140.7, 140.4, 128.1, 128.1, 127.8, 127.6, 127.0, 96.6, 91.4, 79.3, 78.0, 75.2, 61.6, 61.0, 40.3, 40.0, 35.2, 34.6, 33.8, 32.5, 32.3, 28.4, 28.4, 20.9, 17.1 ppm; IR (KBr, cm^{-1}): 3252, 2927, 1714, 1505, 1453, 1109, 699, 617; HRMS (ESI) calcd for $C_{24}H_{41}N_2O_4S^+$ $(M+H)^+$ 453.2787, found 453.2787.

Compound **7** (0.6 mmol) was dissolved in a mixed solvent (AcOH : H_2O : THF = 3 : 1 : 1, 12 mL), then Zn powder (12 mmol) was added. After that, the mixture was stirred at room temperature for 4 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1, v/v) gave the desired product **8** (white solid, 38.4 mg, 47% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 4.89 (s, 2H), 3.55 (br, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 134.3, 133.4, 129.0, 127.7, 65.5 ppm.



Reaction procedure IX for gram-scale reaction of 5d: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added α-chalcogen carbonyls **5d** (3.0 mmol) and TEMPO (6.0 mmol). After that, the reaction mixture was then stirred at 45 ℃ for 72 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 30:1, v/v) gave the desired product **6d** (white solid, 0.74 g, 50%).



Reaction procedure X for transformation of 6i: Compound **6i** (0.1 mmol) was dissolved in DCM (2 ml), then *m*CPBA (0.2 mmol) was added. The mixture was stirred at room temperature for 1 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 1:1, v/v) gave the desired product **9** (white solid, 22.4 mg, 79% yield, M.P. = 160-164 ℃); ^{1}H NMR (500 MHz, DMSO) δ 10.11 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.70 – 7.65 (m, 4H), 7.32 (d, *J* = 8.5 Hz, 2H), 2.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 190.4, 173.6, 166.8, 149.8, 143.1, 140.8, 137.1,

135.3, 134.5, 126.9, 125.2, 29.2 ppm; IR (KBr, cm^{-1}): 3264, 2928, 1763, 1680, 1615, 1555, 1502, 1189, 1164, 813, 741, 714, 682; HRMS (ESI) calcd for $C_{16}H_{14}NO_4^+$ $(M+H)^+$ 284.0923, found 284.0927.

V. Cyclic Voltammetry (CV) Experiment

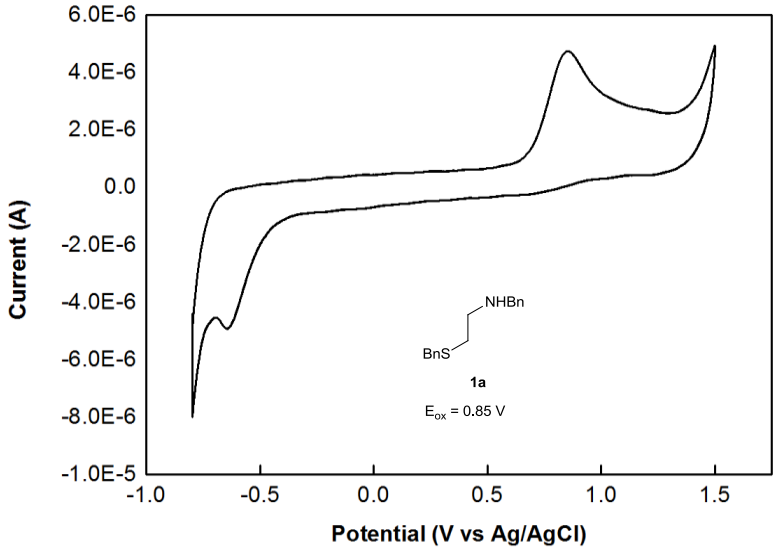


Fig. S1. Cyclic voltammograms of **1a** (2×10^{-2} M) in electrolyte solution (0.3 M nBu$_4$NPF$_6$ in CH$_3$CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

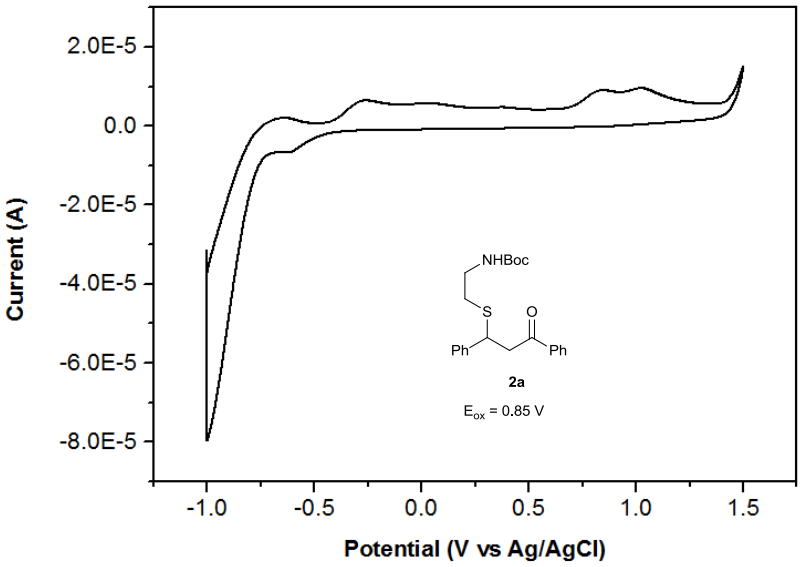
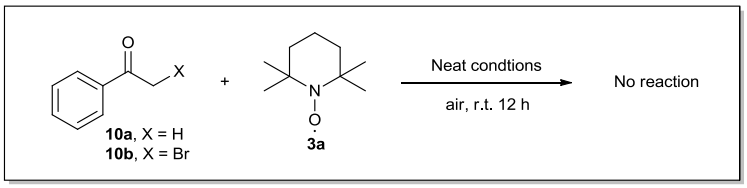
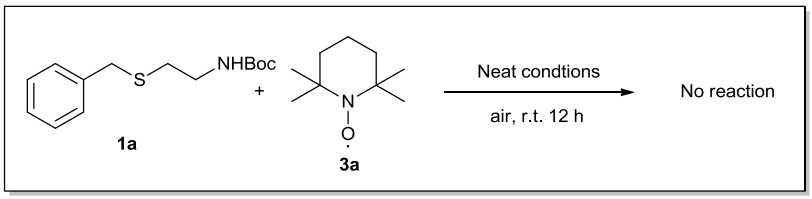


Fig. S1. Cyclic voltammograms of **2a** (2×10^{-2} M) in electrolyte solution (0.3 M nBu$_4$NPF$_6$ in CH$_3$CN) using a glassy carbon working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.

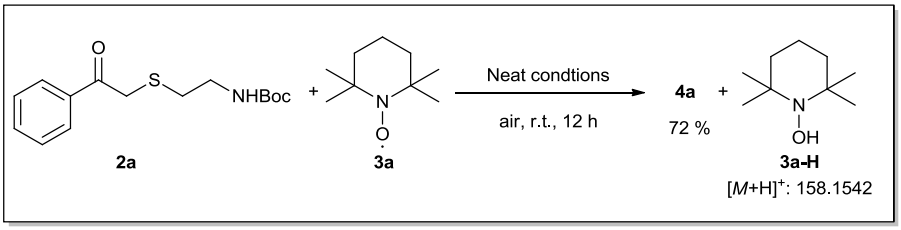
VI. Control Experiments



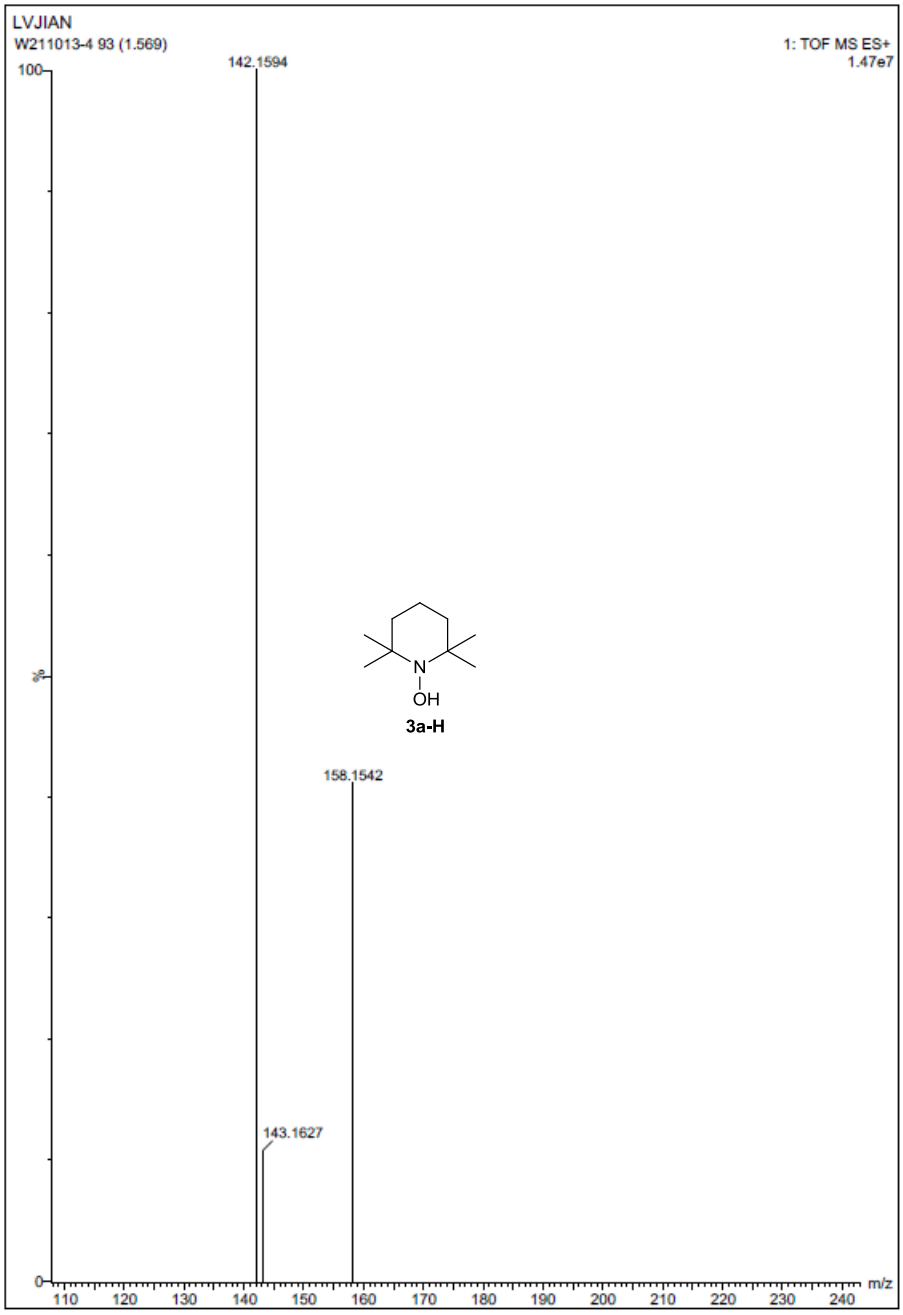
A) Radical C(sp^3)-H α-oxyamination of other carbonyls 10: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added ketone **10** (0.2 mmol) and TEMPO radical **3a** (0.4 mmol). No reaction was observed.



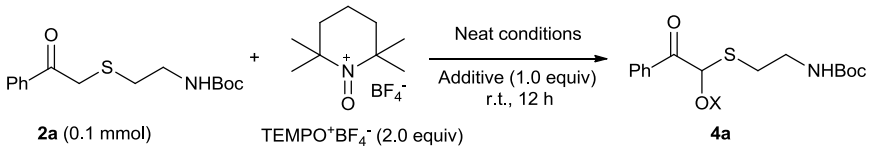
B) Radical C(sp^3)-H α-oxyamination of other thioether 1a: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added ketone **1a** (0.2 mmol) and TEMPO radical **3a** (0.4 mmol). No reaction was observed.



C) ESI experiment of radical C(sp^3)-H α-oxyamination of α-mercapto carbonyl 2a: To an oven-dried 10 mL tube equipped with a magnetic stir bar was added ketone **2a** (0.2 mmol) and TEMPO radical **3a** (0.4 mmol). The mixture was analyzed by LC-MS. The product **4a** was isolated in 72% yield.



D) Disproportionated effect in oxidative radical C(sp^3)-H α-oxyamination of 2 (see Scheme 3D) under the neat conditions: a) For entry 1: To an oven-dried 10 mL tube equipped with a magnetic stir bar was charged with α-mercapoto carbonyl **2a** (0.1 mmol), $TEMPO^+BF_4^-$ (0.20 mmol). The sample was then stirred at room temperature for 12 h. Trace product **4a** was observed. b) For entry 2: To an oven-dried 10 mL tube equipped with a magnetic stir bar was charged with α-mercapoto carbonyl **2a** (0.1 mmol), $TEMPO^+BF_4^-$ (0.10 mmol) and TEMPOH **3a-H** (0.1 mmol). The sample was then stirred at room temperature for 12 h. The mixture was directly loaded onto silica gel column and eluted with ethyl acetate/petroether to give the target product **4a**. Trace product **4a** was observed.



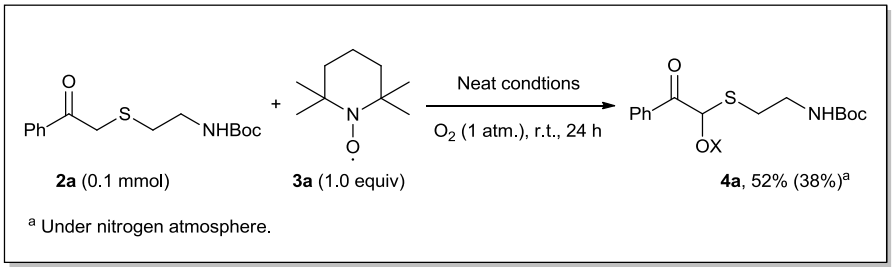
2a (0.1 mmol) $TEMPO^+BF_4^-$ (2.0 equiv) **4a**

Entry	Additive (**A**)	p*K*a of H**A**	Yield (%)
1	none	-	trace
2[a]	**3a-H**	14.9	trace

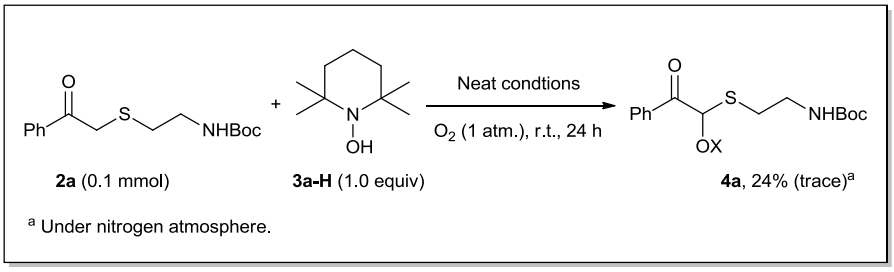
X =

[a] $TEMPO^+BF_4^-$ (1.0 equiv)

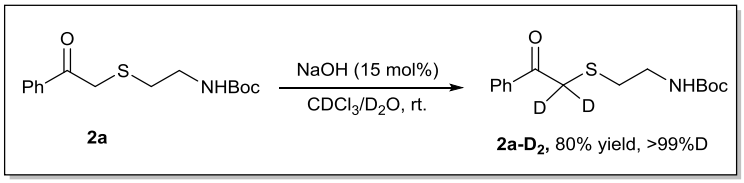
E) O_2 effect in radical C(sp^3)-H α-oxyamination of α-mercapoto carbonyl 2a: a) To an oven-dried 10 mL tube equipped with a magnetic stir bar was added **2a** (0.1 mmol) and TEMPO **3a** (0.1 mmol) under the oxygen or nitrogen atmosphere (1 atm.). The reaction mixture was then stirred room for 24 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 30:1, v/v) gave the desired product **4a** (52% for O_2, and 38% for N_2).



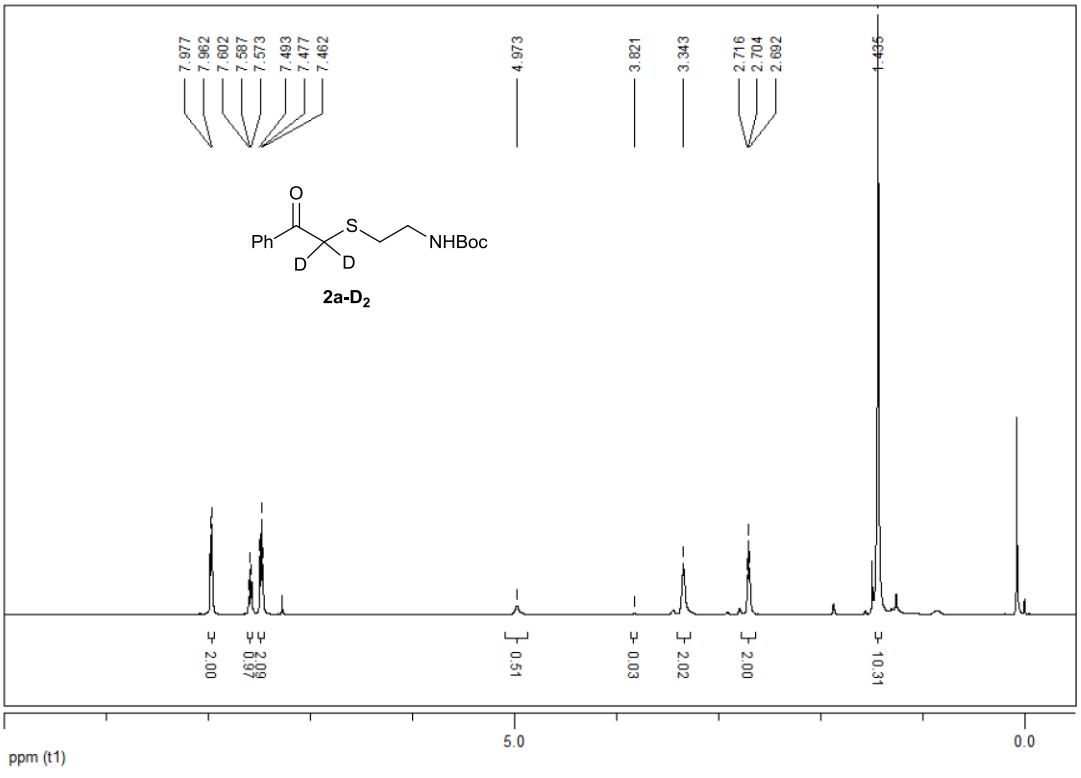
b) To an oven-dried 10 mL tube equipped with a magnetic stir bar was added **2a** (0.1 mmol) and TEMPOH **3a-H** (0.2 mmol) under the oxygen or nitrogen atmosphere (1 atm). The reaction mixture was then stirred room for 24 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 30:1, v/v) gave the desired product **4a** (24% for O_2, and trace for N_2).

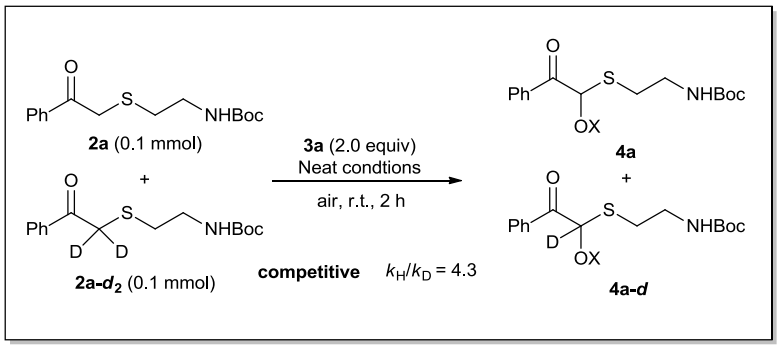


F) Deuterium-labeling experiment

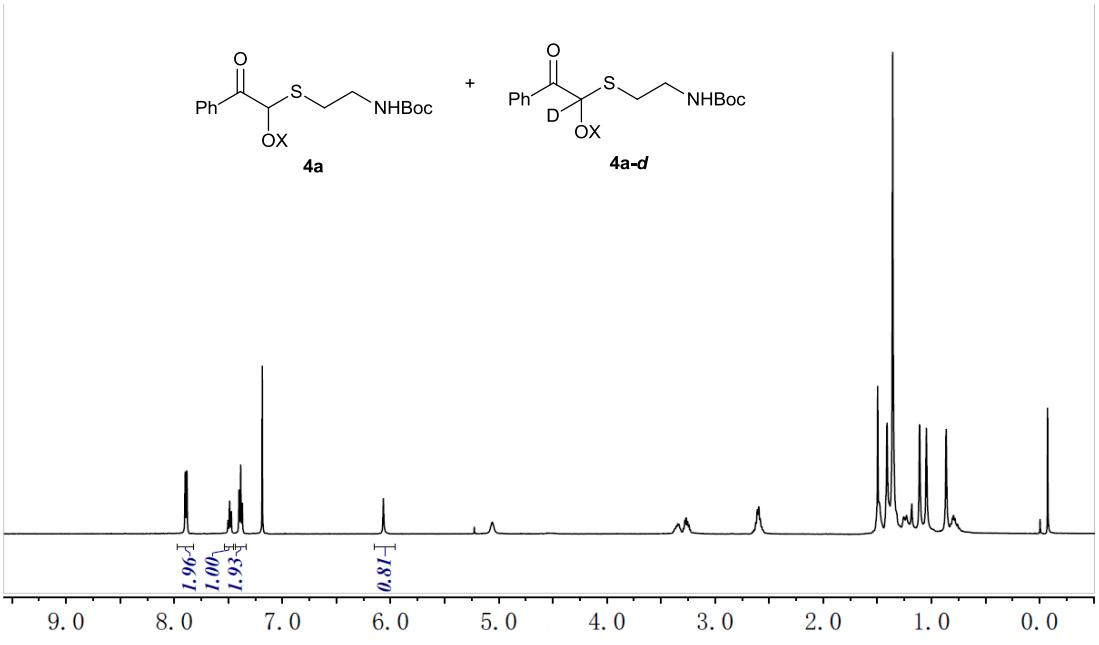


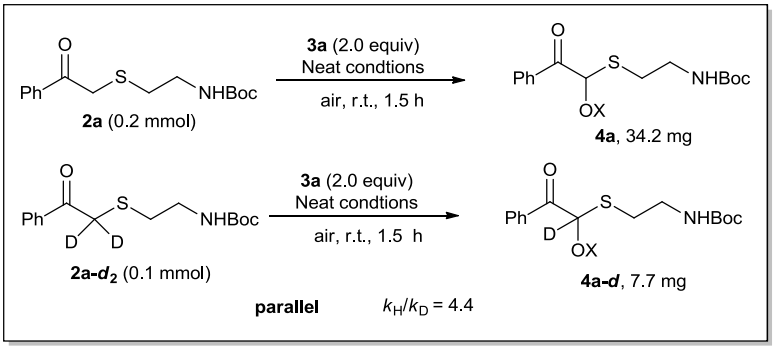
Synthesis for **2a-*d*$_2$**: To an oven-dried 20 mL Schlenk tube equipped with a magnetic stir bar was added α-mercapoto ketone **2a** (1.5 mmol) and NaOH (15 mo%). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then 6 mL mixed solution ($CDCl_3/D_2O$ = 1/3, v/v) was added. After that, the reaction mixture was stirred at room temperature for 24h. After reaction, the mixture was concentrated under vacuum. After that, 6 mL mixed solution ($CDCl_3/D_2O$ = 1/3, v) was added and stirred for another 24h. After reaction, the mixture was diluted with DCM. The aqueous layer was extracted with DCM. The combined organic layer was dried over anhydrous $NaSO_4$, filtered and concentrated *in vacuo* gave the desired product **2a-*d*$_2$** (yellow oil, 357 mg, >99% D). Compound **2a-*d*$_2$** was analyzed by ^{1}H-NMR.





Competition reaction: To an oven-dried 5 mL round flask was added compound **2a** (0.1 mmol), **2a-*d*$_2$** (0.1 mmol) and TEMPO (0.4 mmol), then dry DCM (2 mL) was added. After that, DCM was thoroughly removed *in vacuo*. The mixture was stirred at room temperature for 2 h. After reaction, the mixture was concentrated under vacuum. Purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired product **4a**/**4a-*d***, light yellow oil (9.0 mg, 10% yield), which was analyzed by ^{1}H NMR. A kinetic isotopic effect of this reaction was determined to be k_H/k_D = 4.3.

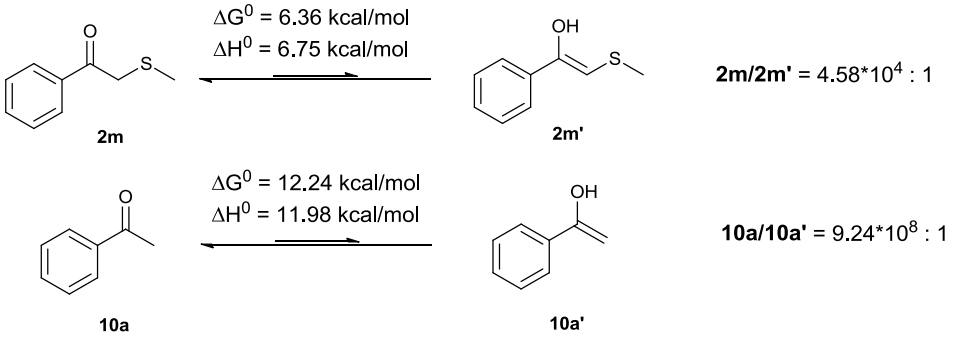




Parallel reaction: To an oven-dried 5 mL tube equipped with a magnetic stir bar was added α-mercapoto ketone **2a** (0.2 mmol) and TEMPO (0.4 mmol). The reaction mixture was then stirred at room temperature for 1.5 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired product **4a**, light yellow oil (34.2 mg, 38% yield).

To an oven-dried 5 mL tube equipped with a magnetic stir bar was added α-mercapoto ketone **2a-*d*$_2$** (0.2 mmol) and TEMPO (0.4 mmol). The reaction mixture was then stirred at room temperature for 1.5 h in the dark. After reaction, purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired product **4a-*d***, light yellow oil (7.7 mg, 9% yield). A kinetic isotopic effect of these two reactions was determined to be $k_H/k_D = 4.4$.

G) DFT for keto and enol tautomers



Scheme S2. keto and enol tautomers ratio

The geometry optimizations were conducted using the Gaussian 09 program[3] with M06-2X functional[4] and def2-SVP[5] basis set in SMD[6] solvation model of acetonitrile. Frequency calculations were performed on the resultant geometries to verify the nature of the optimized stationary points. The single point energy was calculated with def2-tzvpp basis set using M06-2X functional with the same SMD solvation model.

VII. X-ray Structure

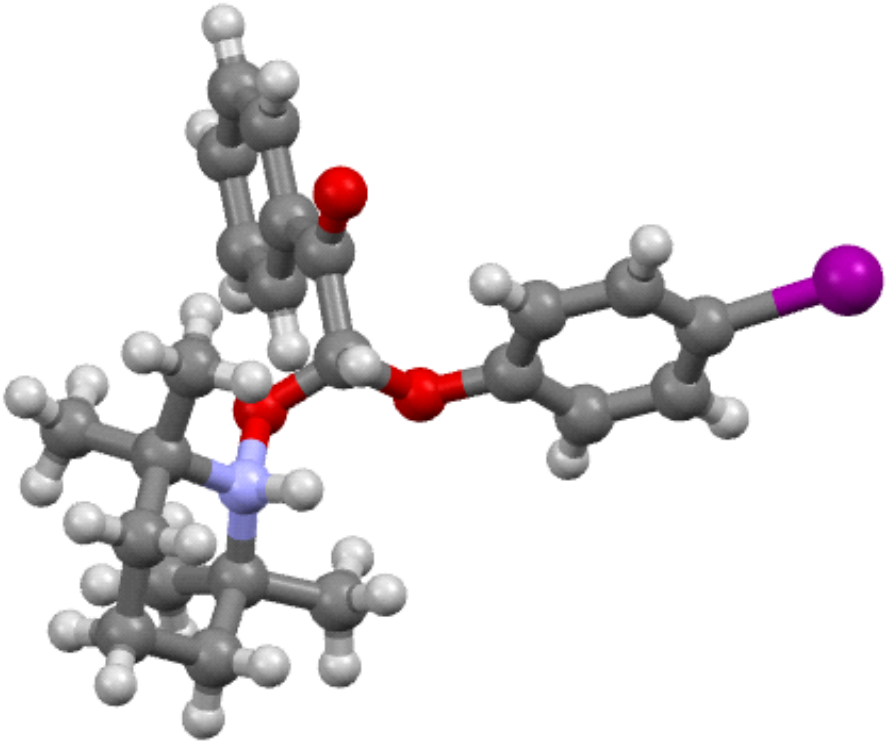
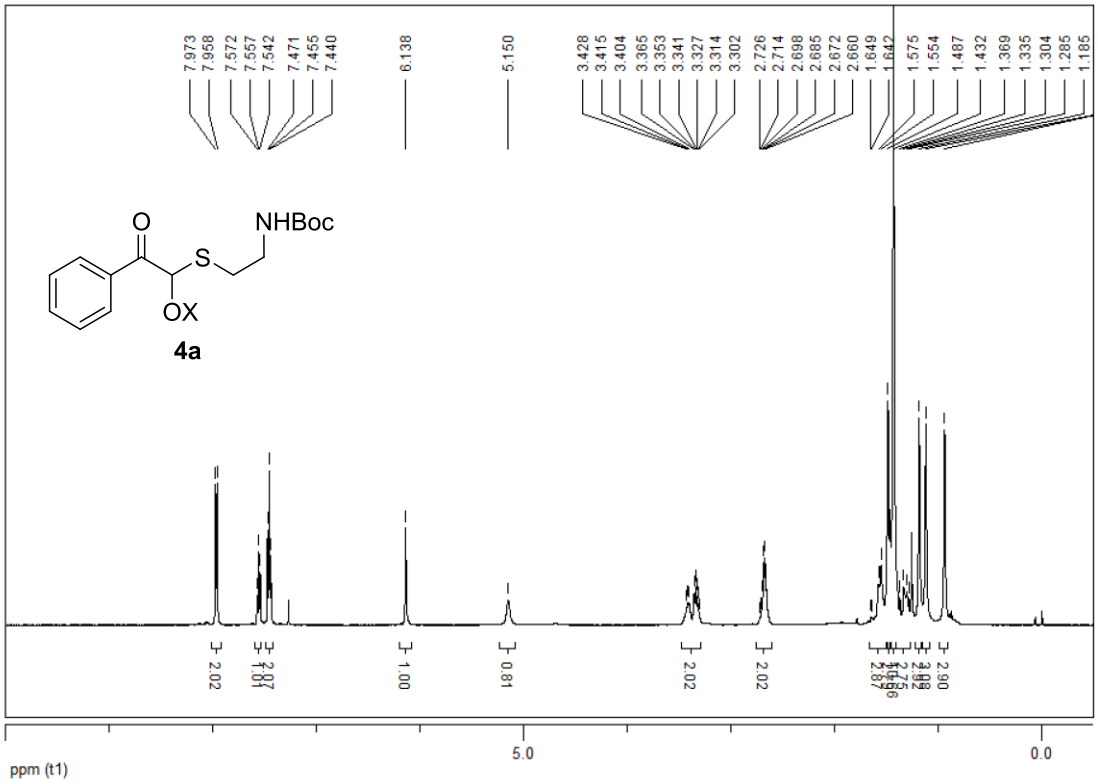


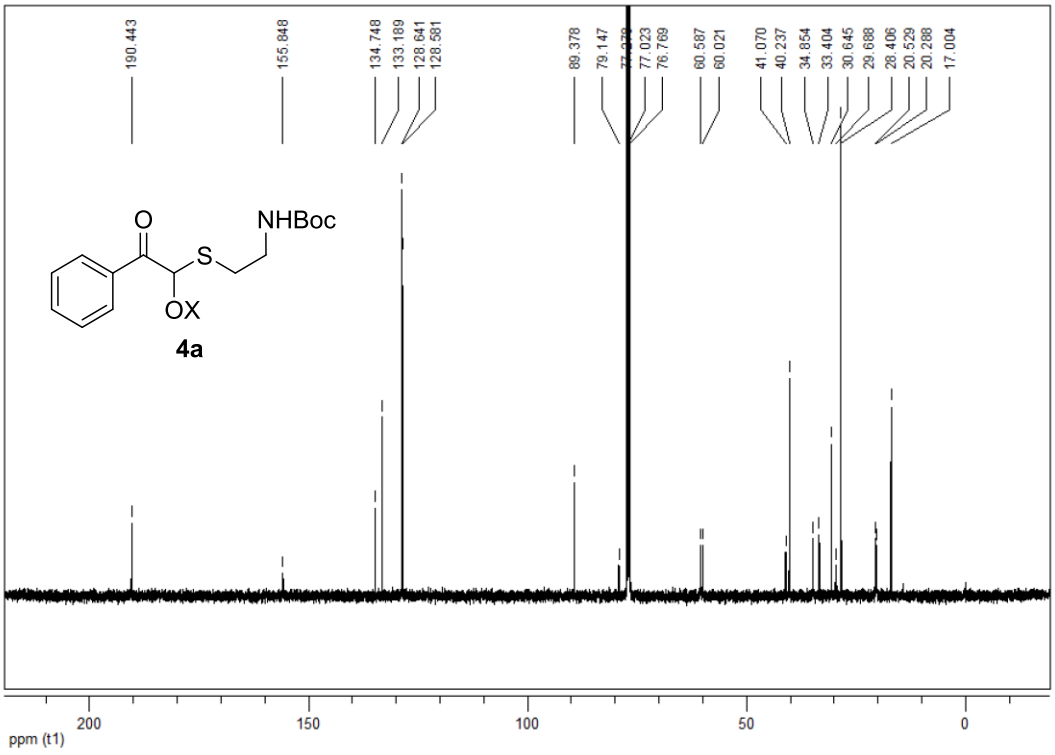
Fig. S3. X-ray structure of compound 6d (CCDC 218506)

VIII. NMR Spectrum

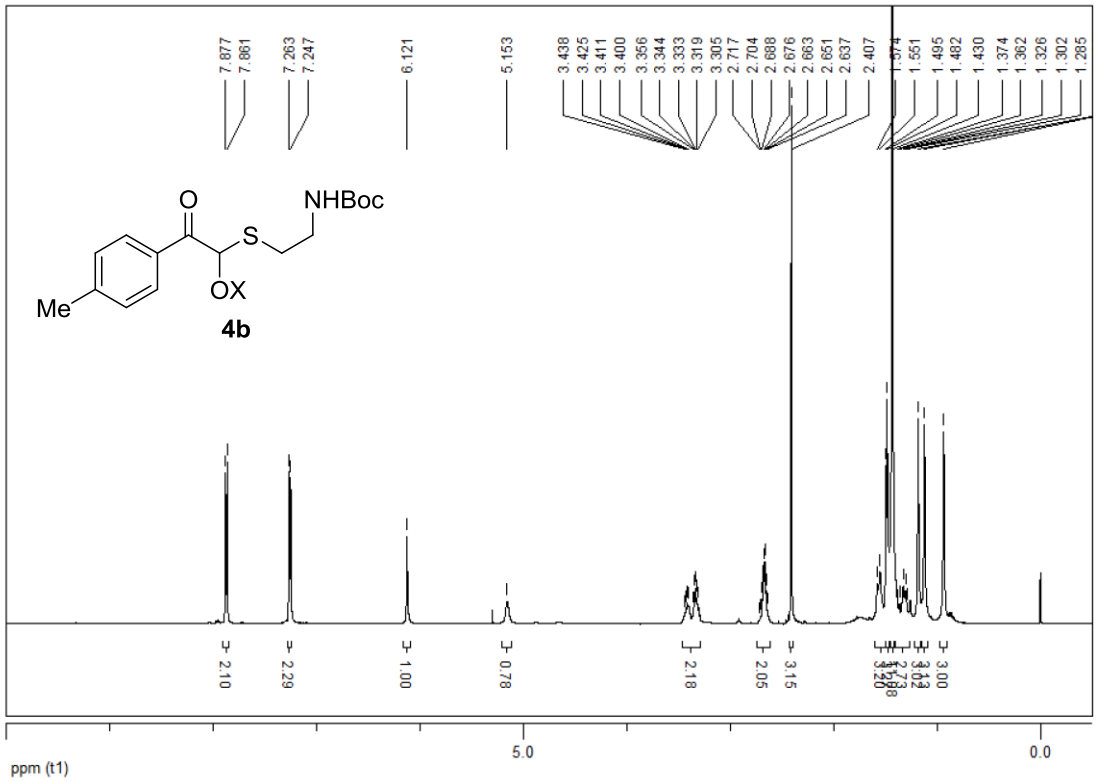
^{1}H NMR (500 MHz, $CDCl_3$)



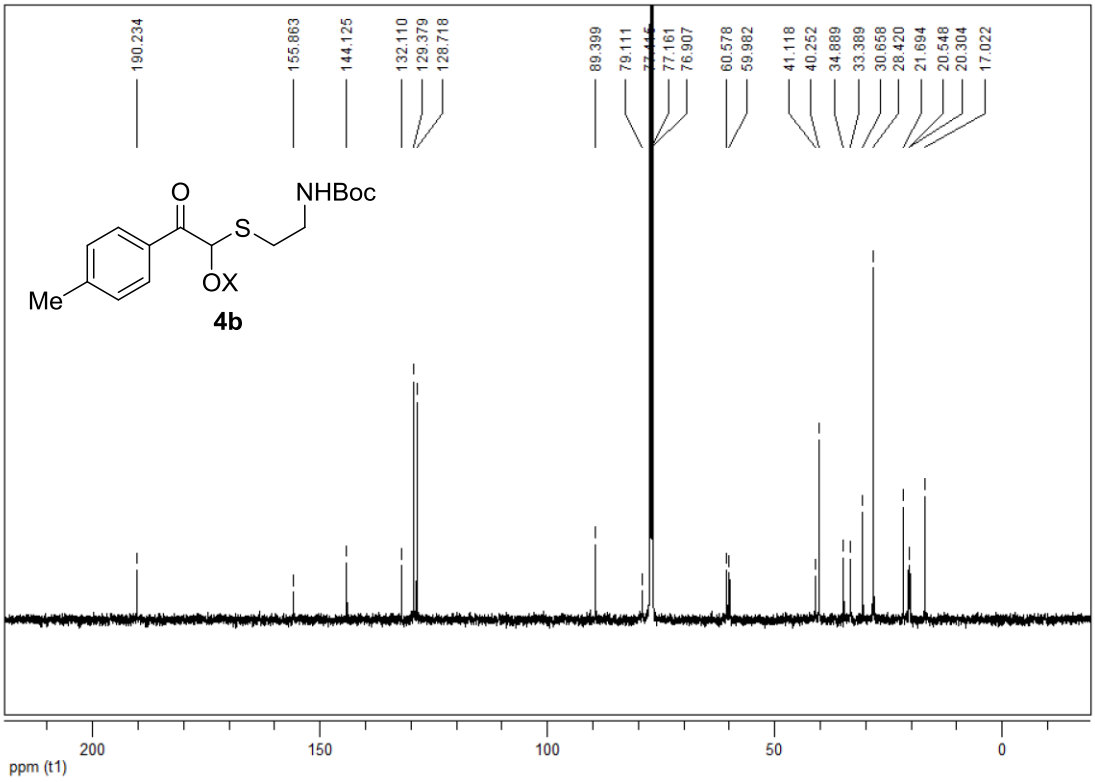
^{13}C NMR (125 MHz, $CDCl_3$)



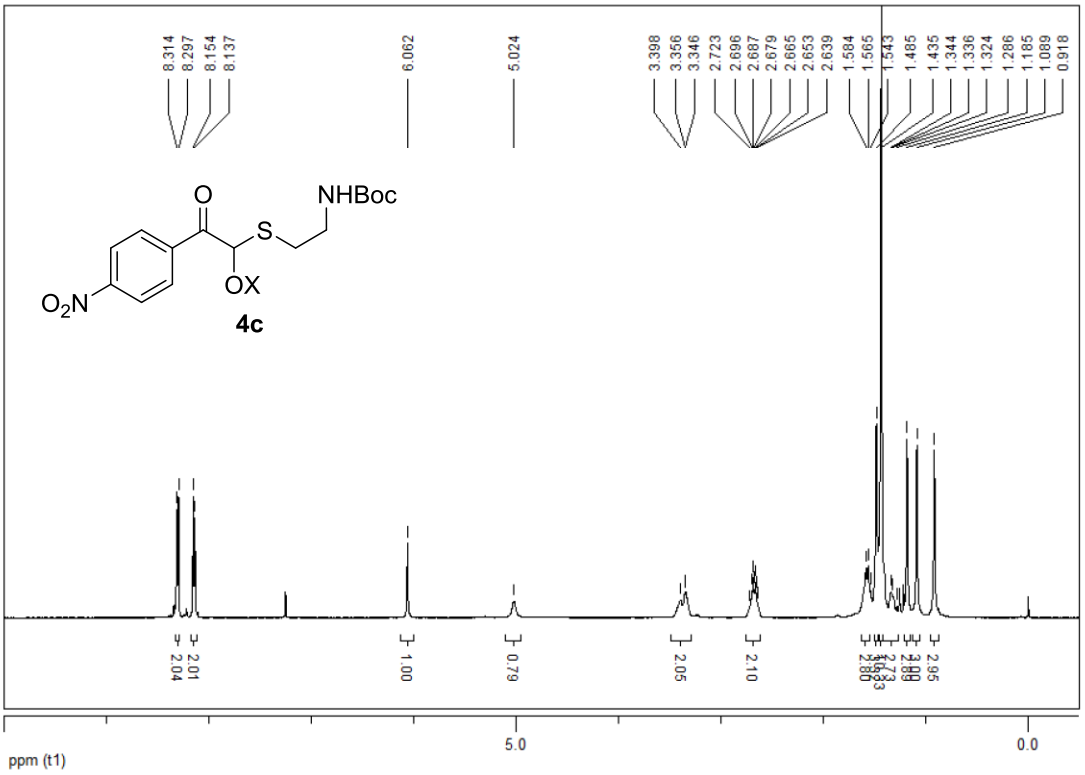
^{1}H NMR (500 MHz, $CDCl_3$)



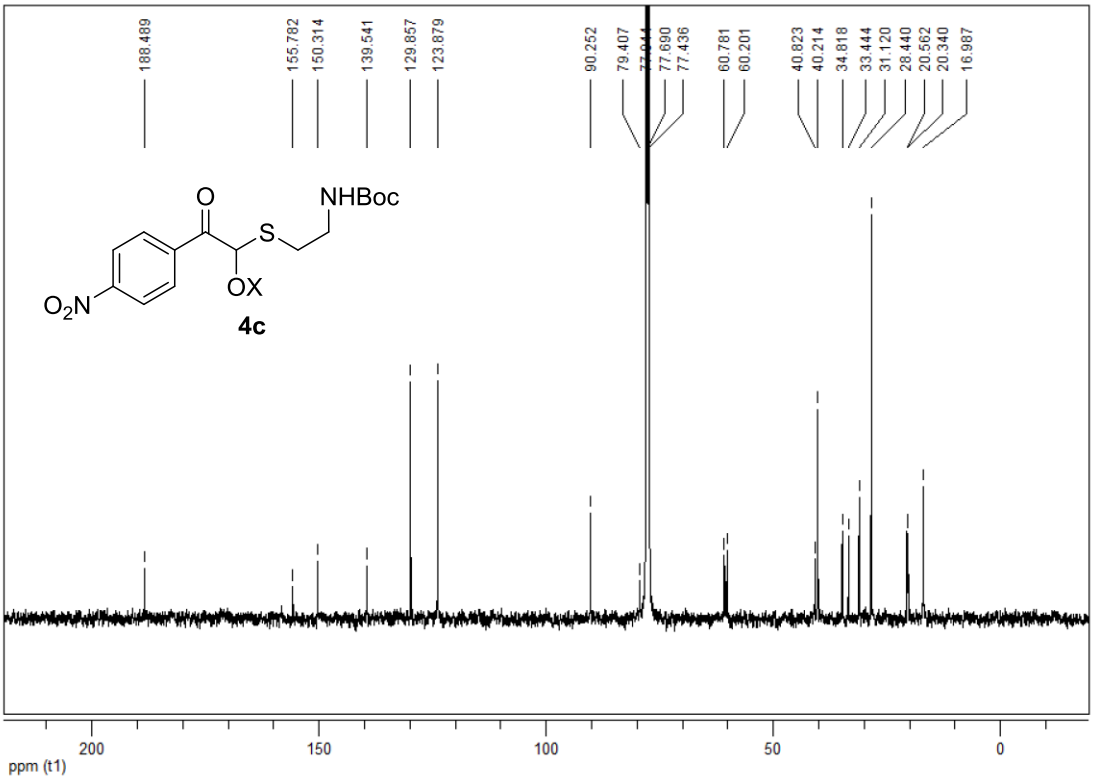
^{13}C NMR (125 MHz, $CDCl_3$)



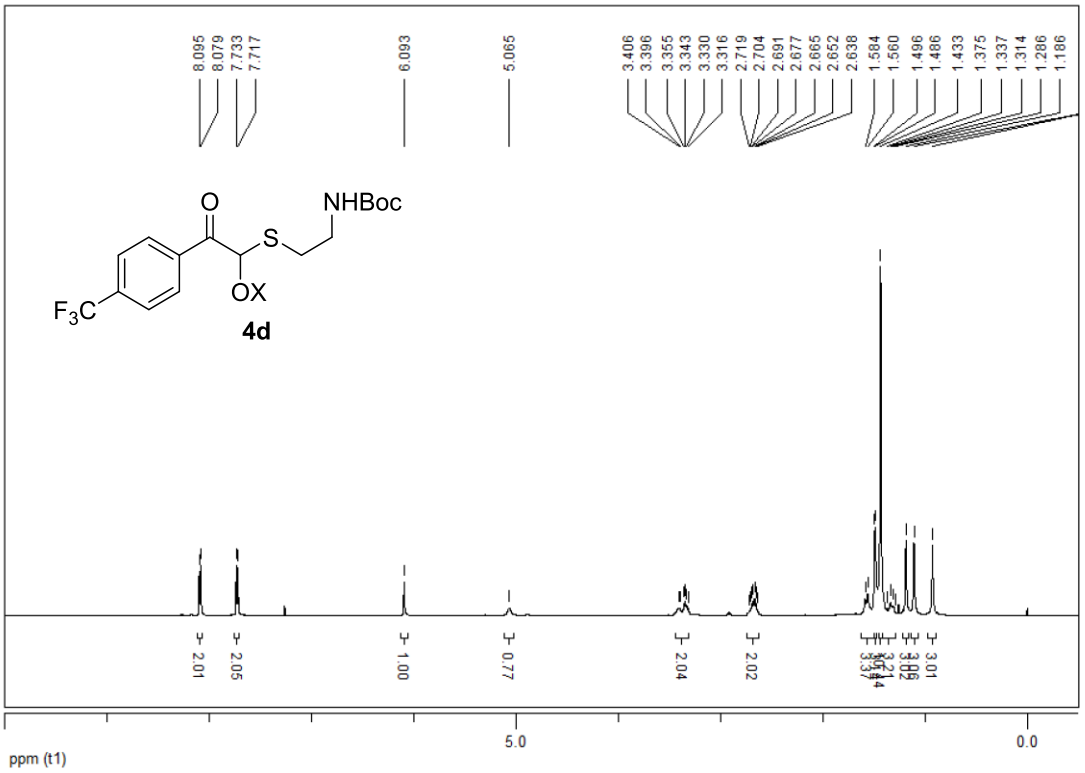
^{1}H NMR (500 MHz, $CDCl_3$)



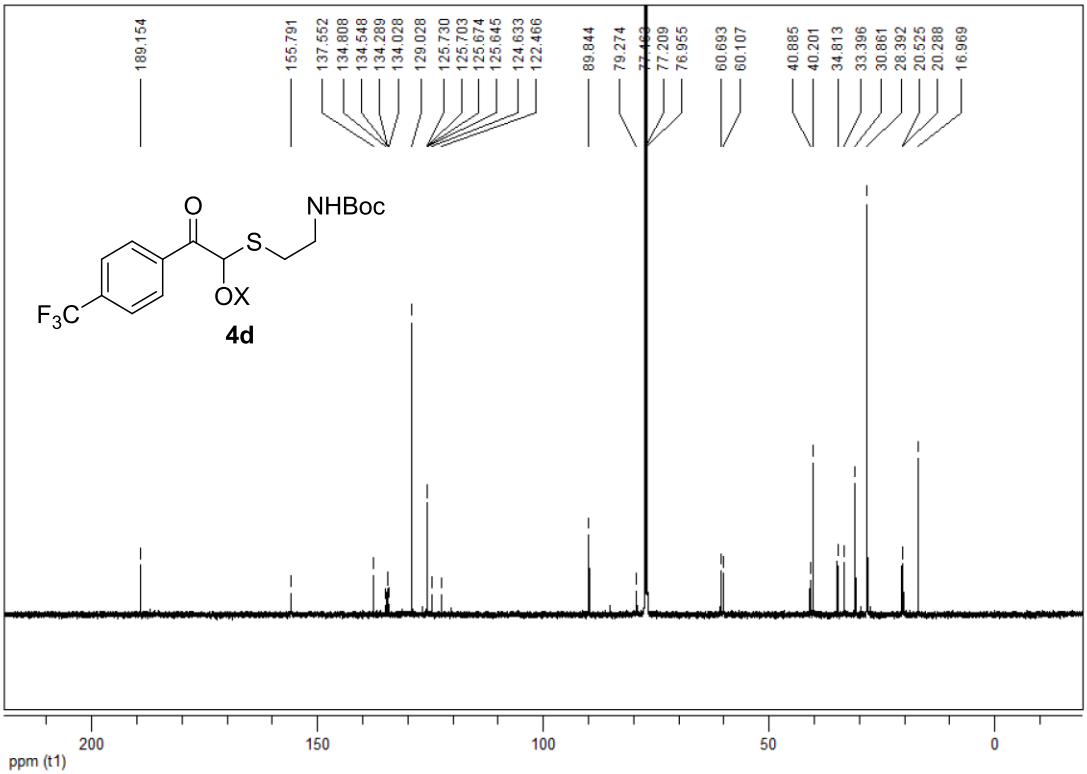
^{13}C NMR (125 MHz, $CDCl_3$)



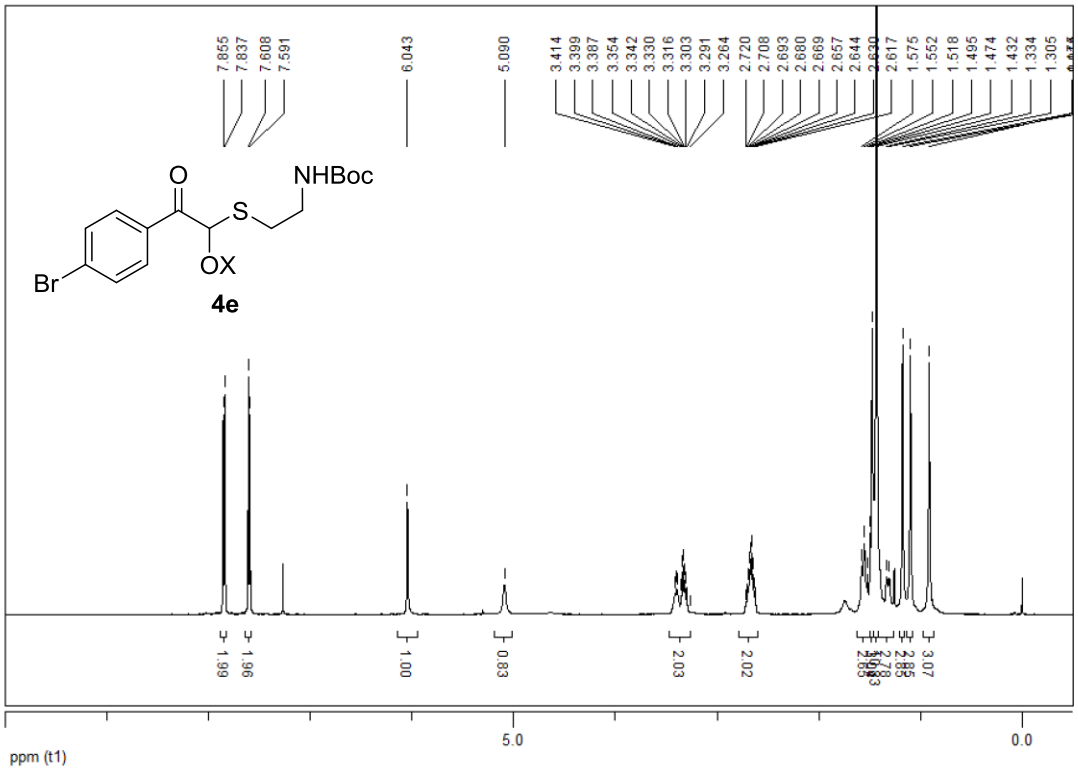
^{1}H NMR (500 MHz, $CDCl_3$)



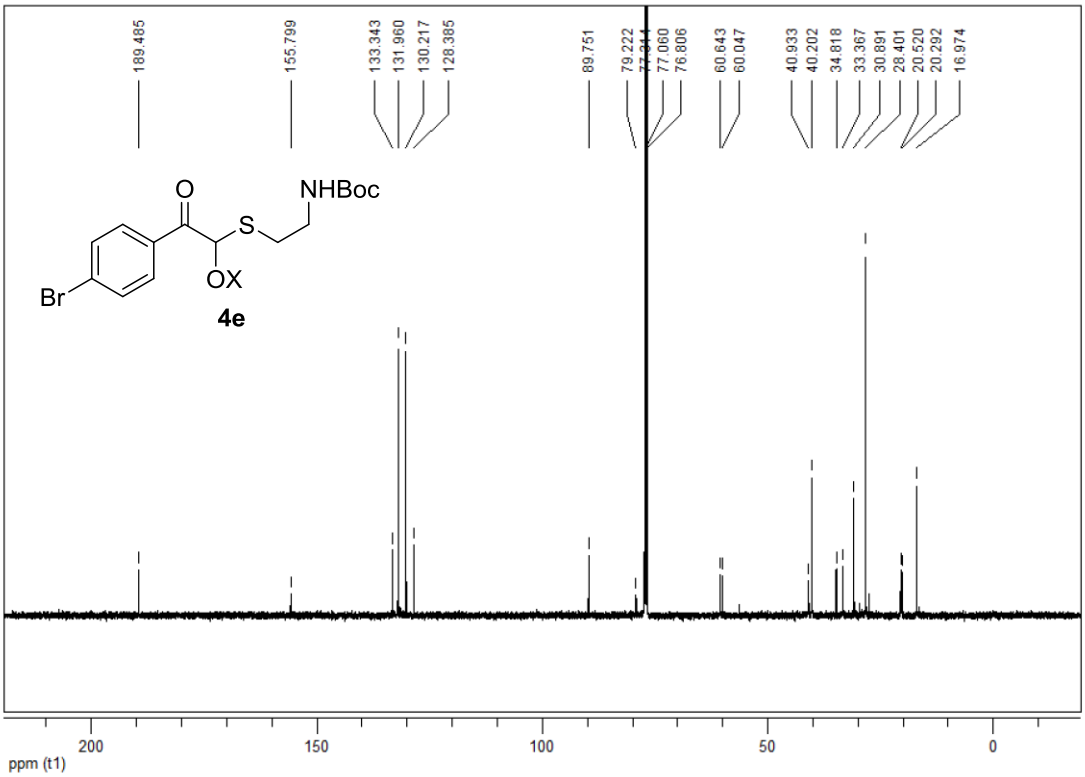
^{13}C NMR (125 MHz, $CDCl_3$)



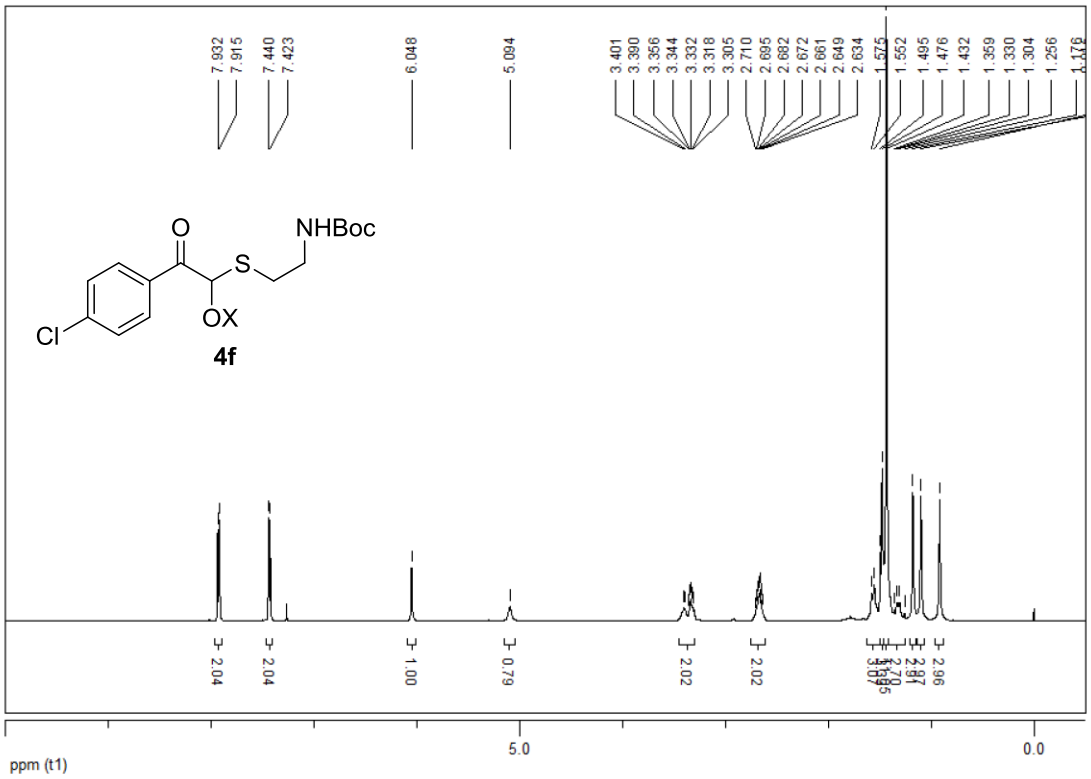
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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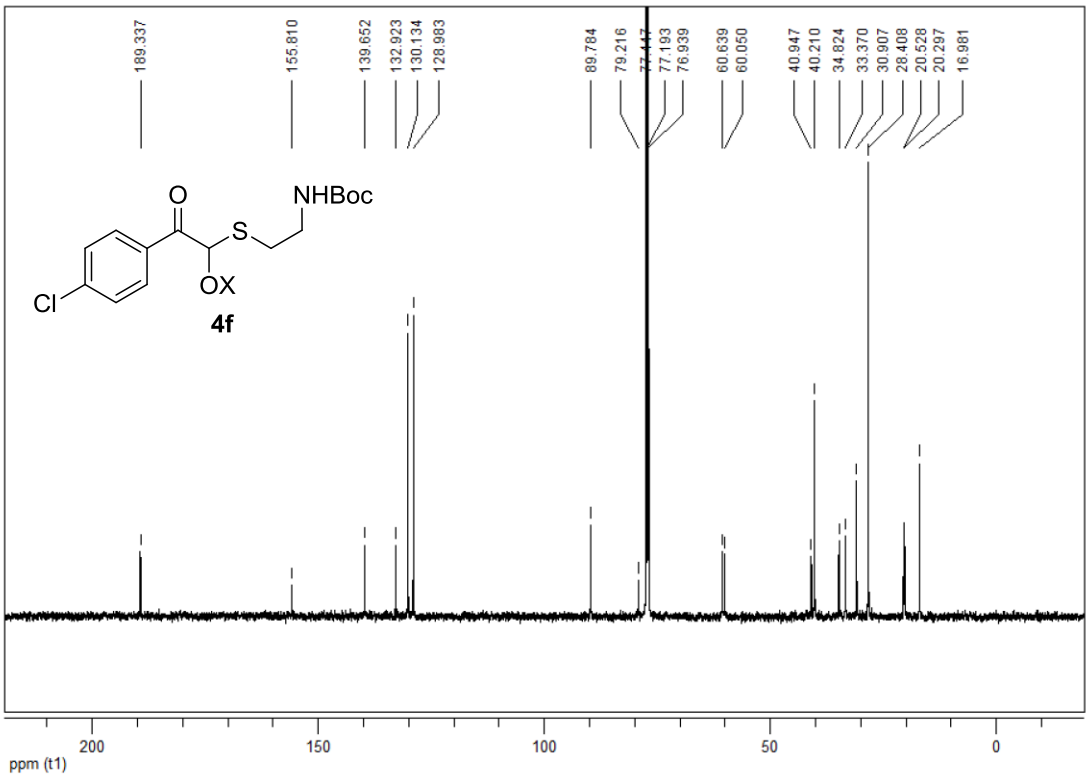

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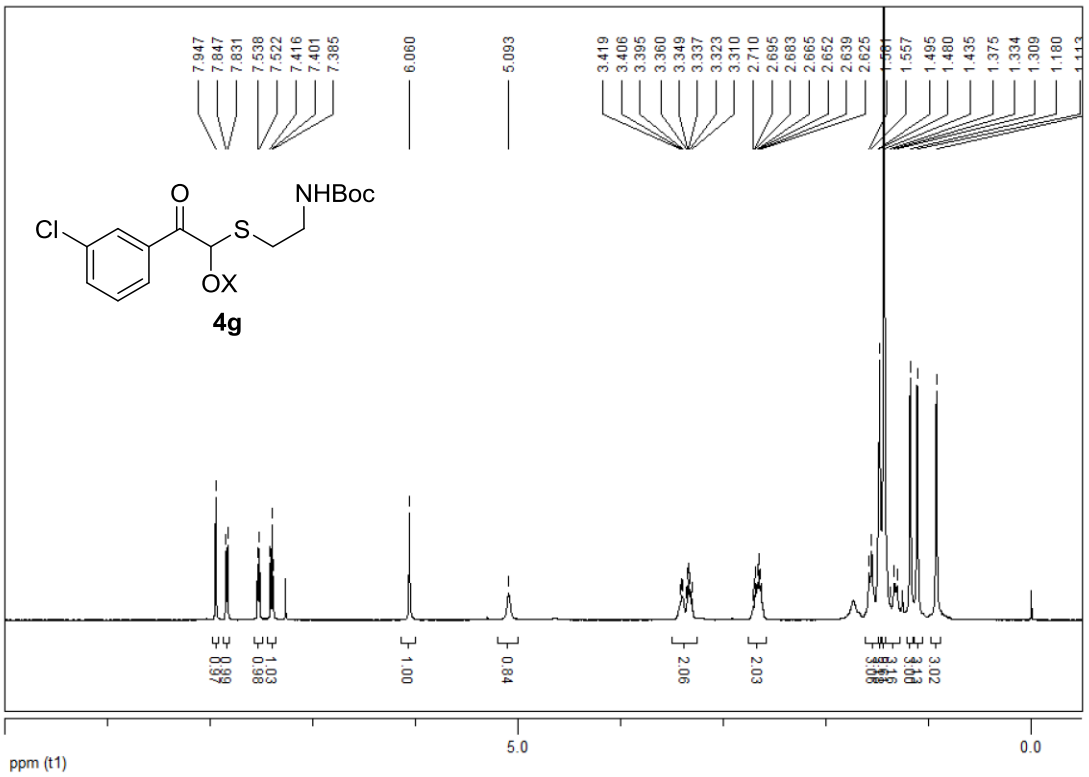
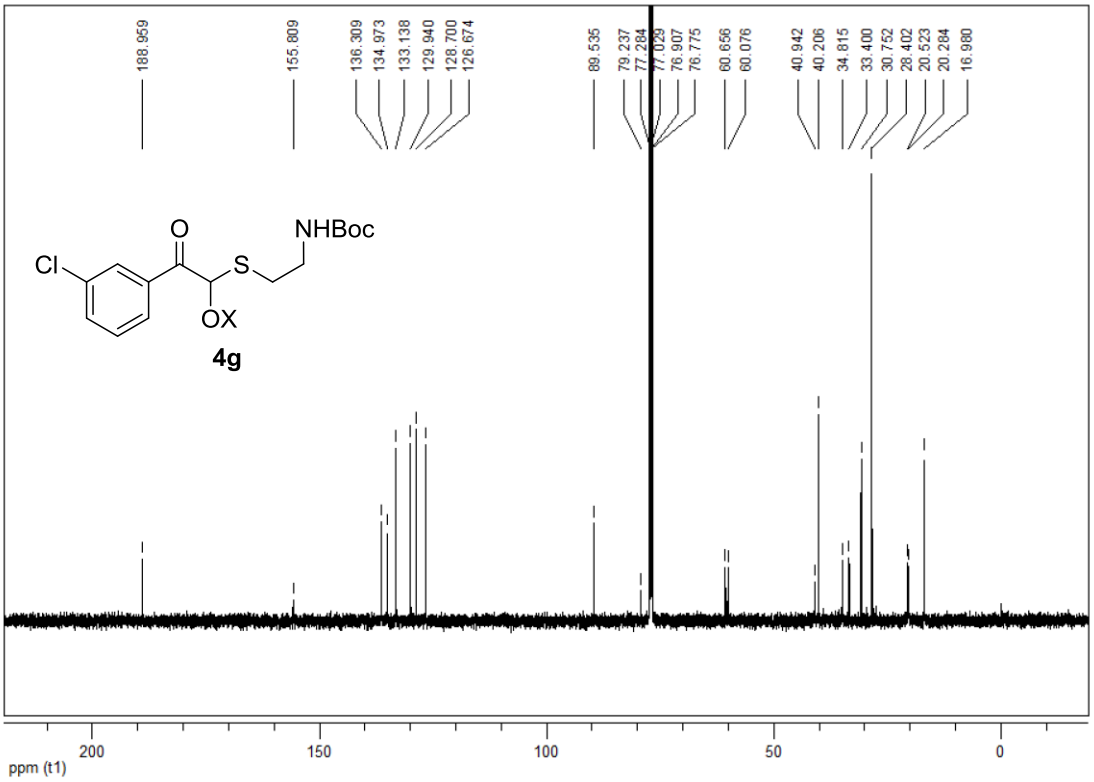


^{13}C NMR (125 MHz, $CDCl_3$)



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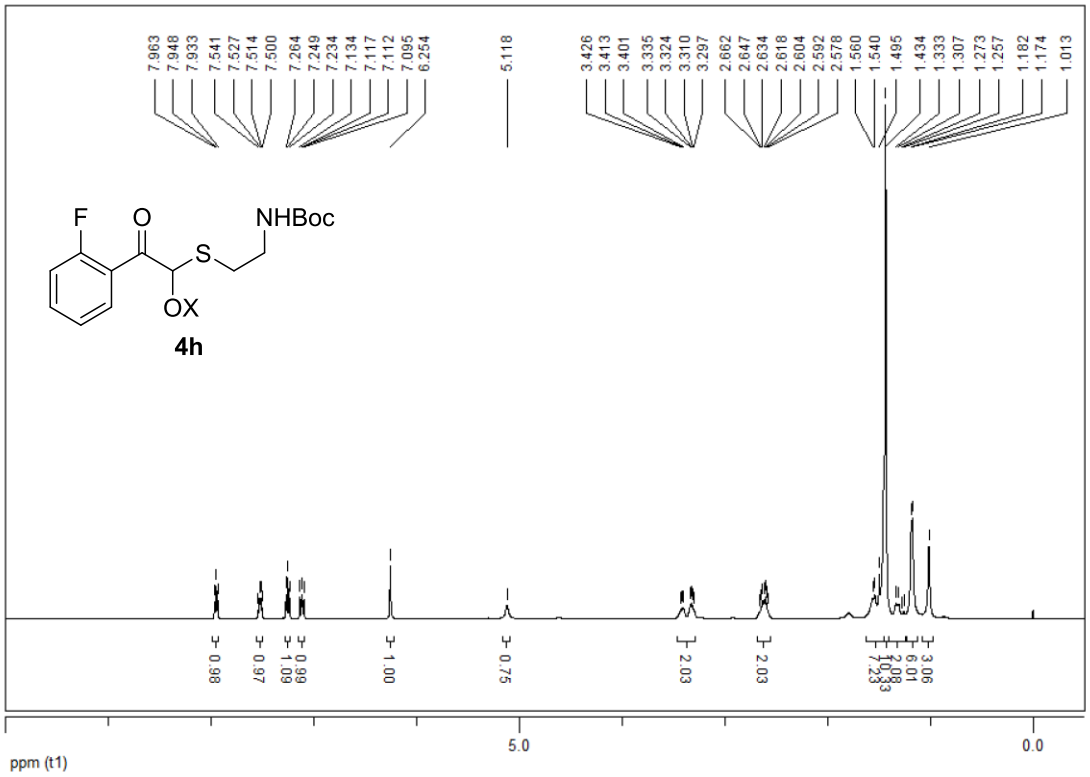

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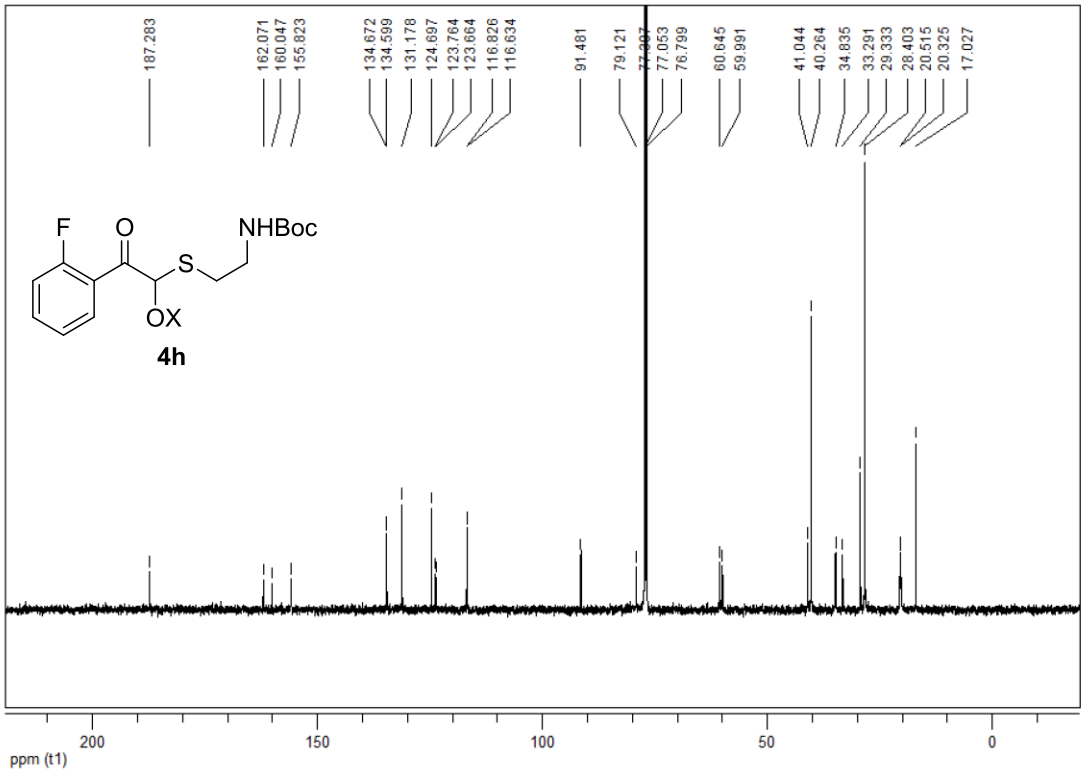

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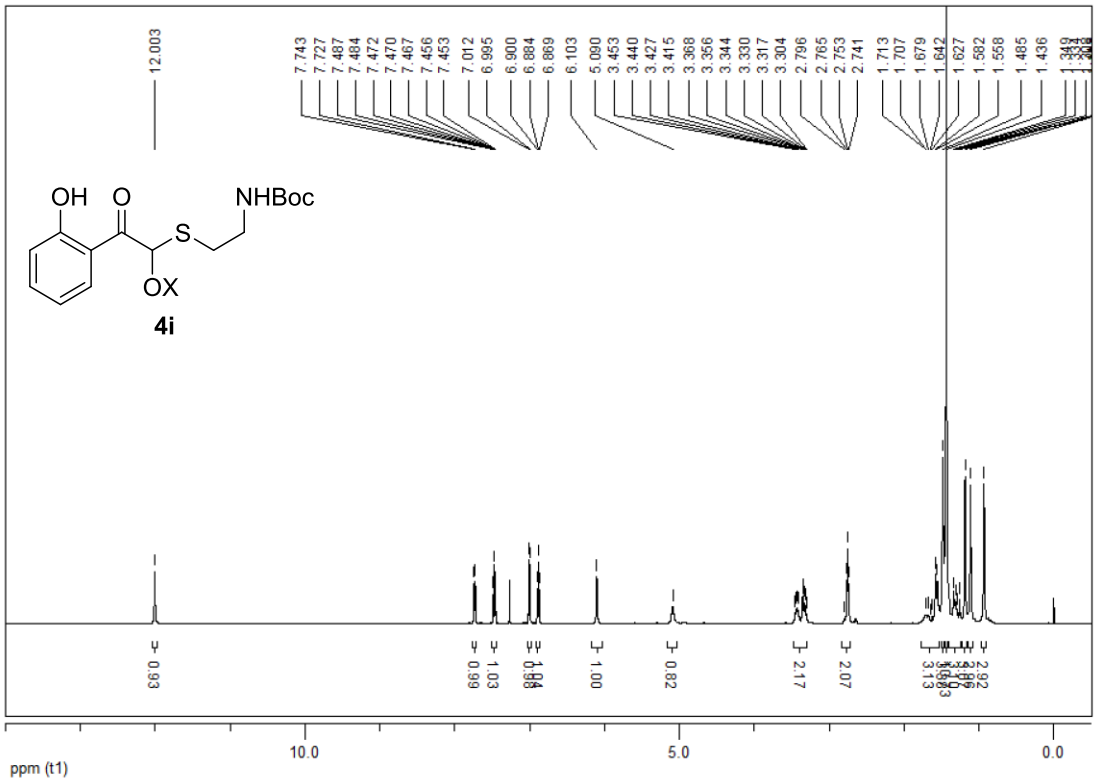

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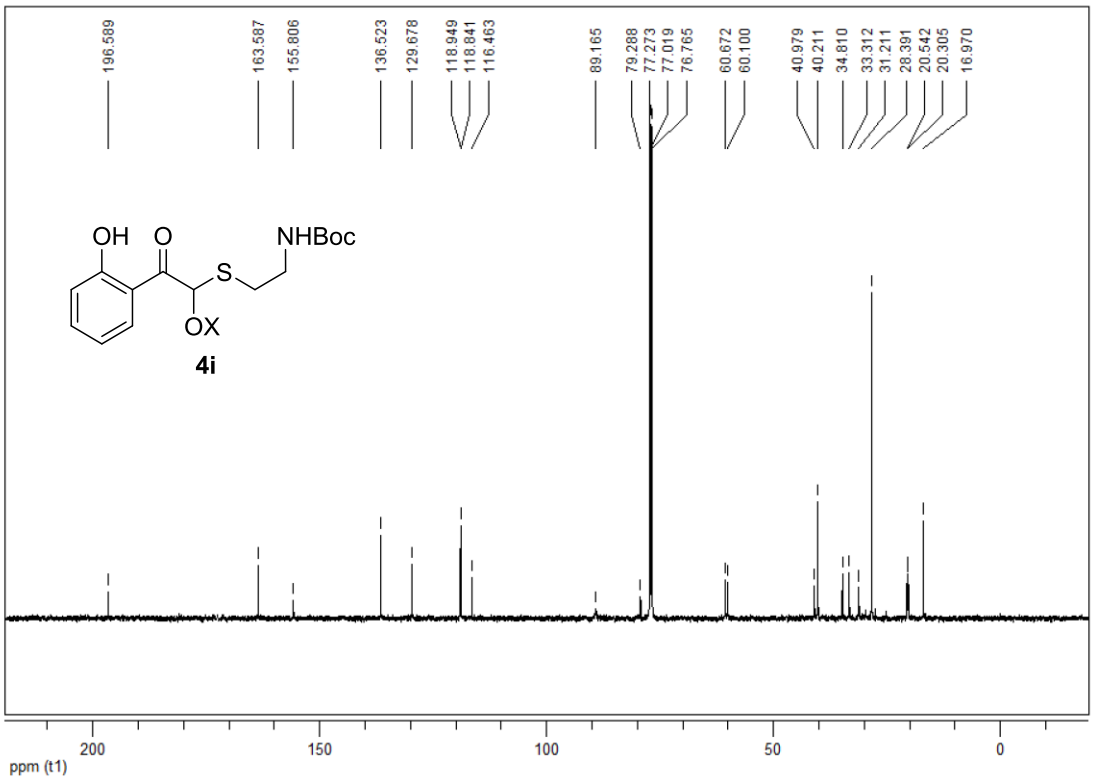

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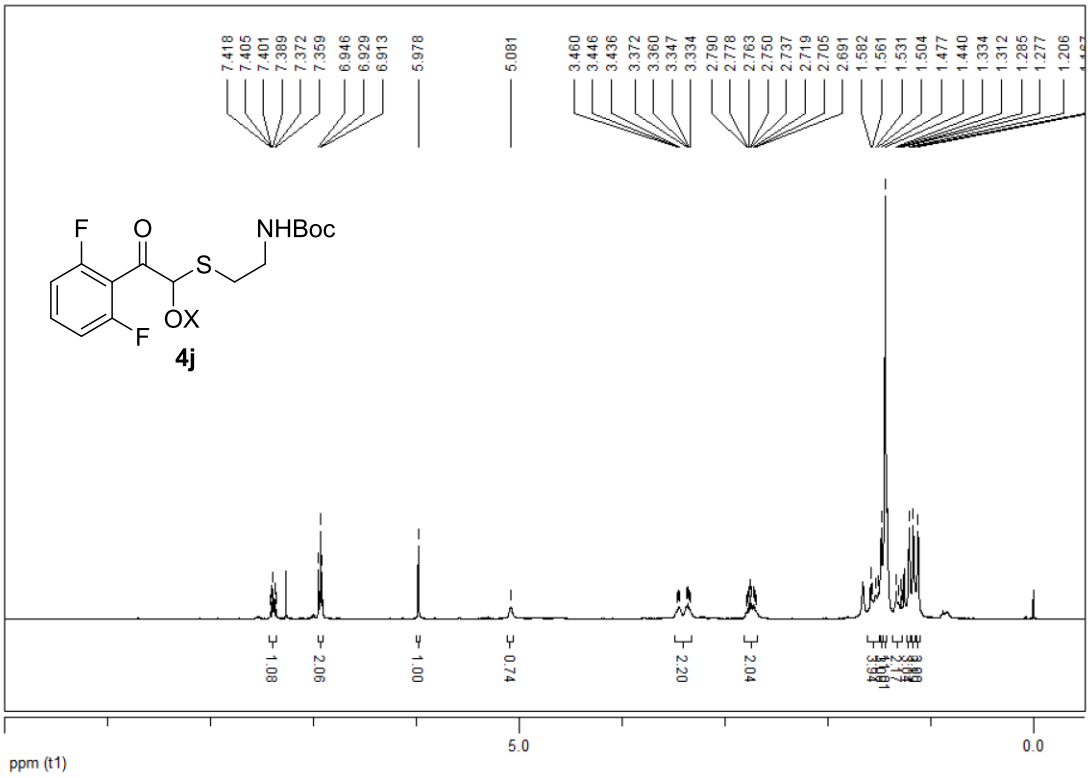

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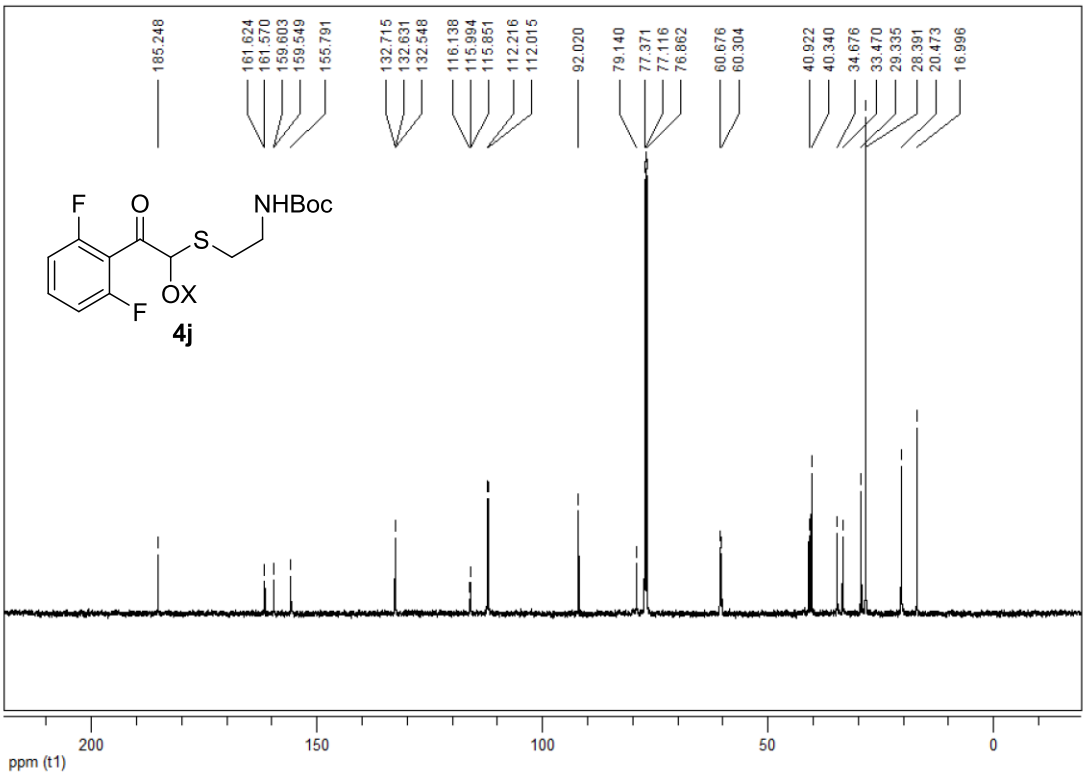

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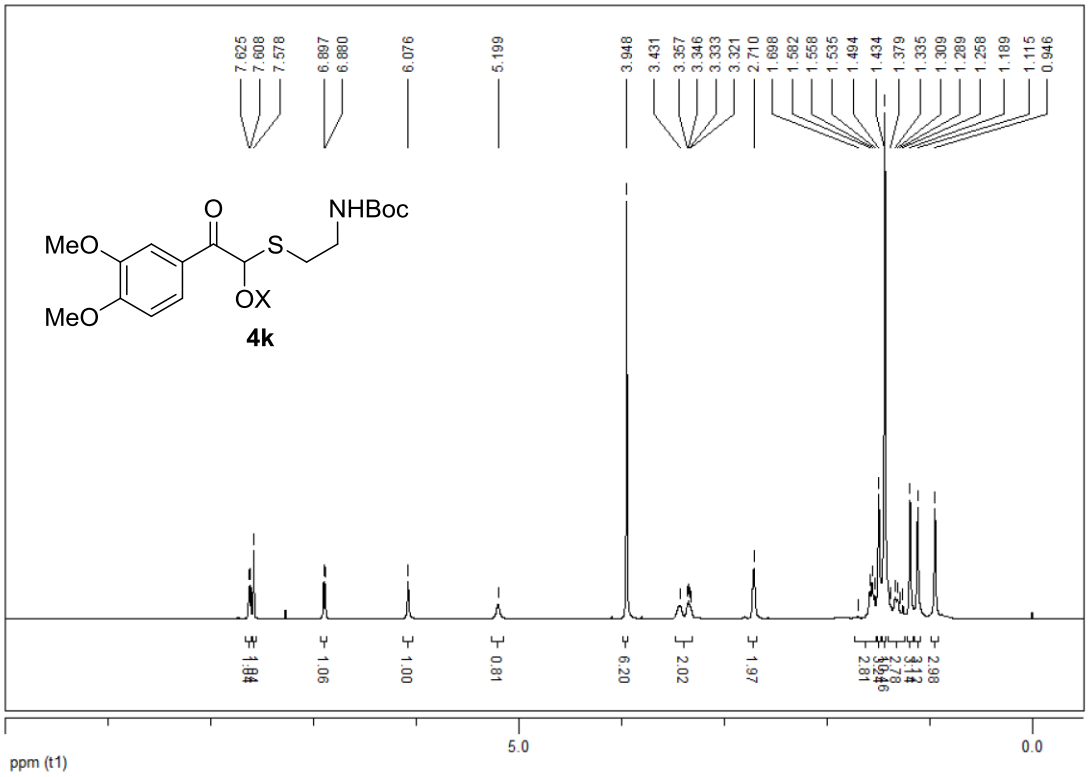

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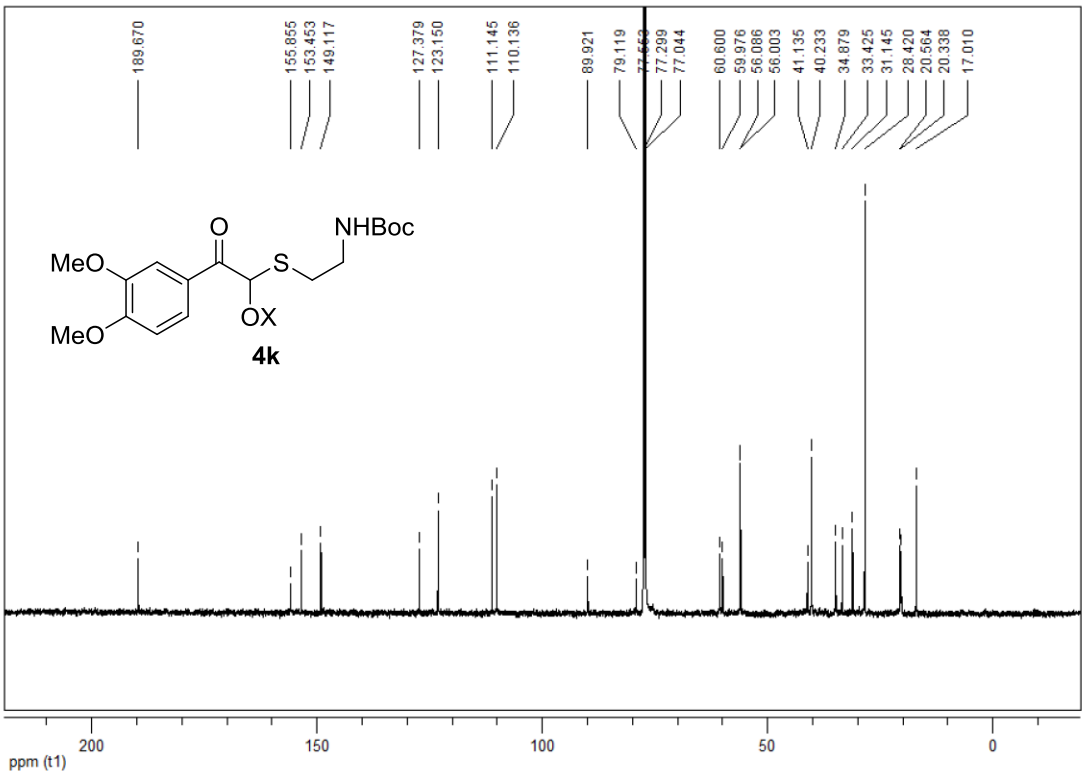
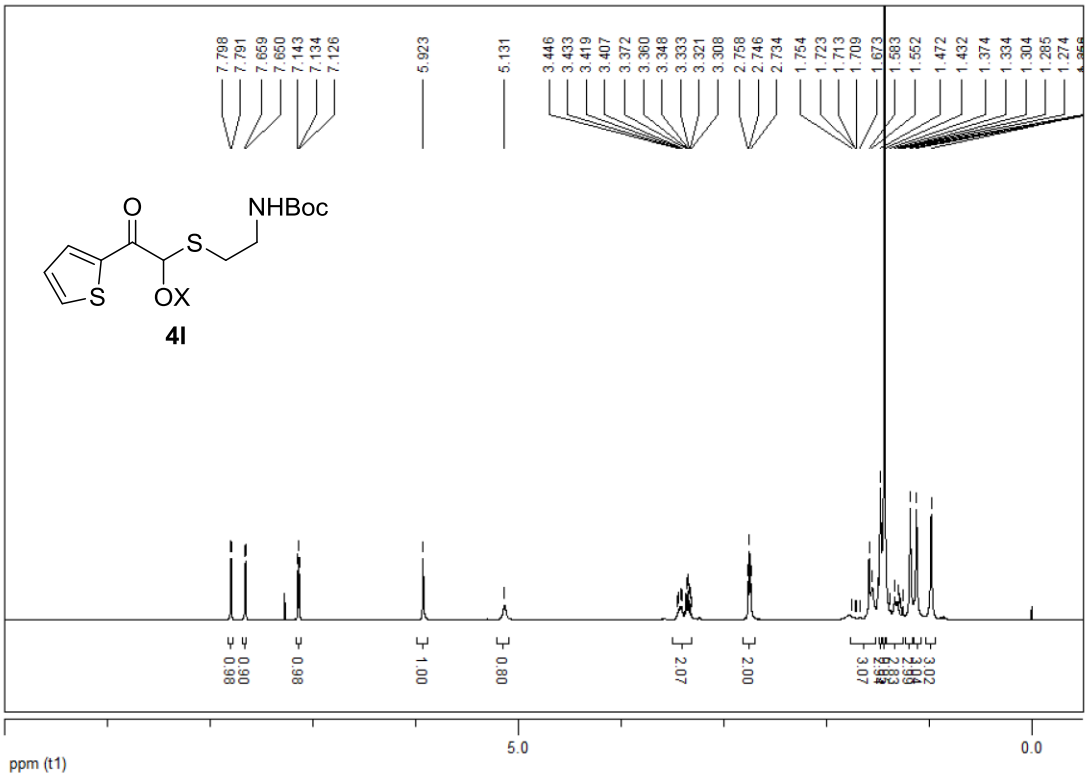
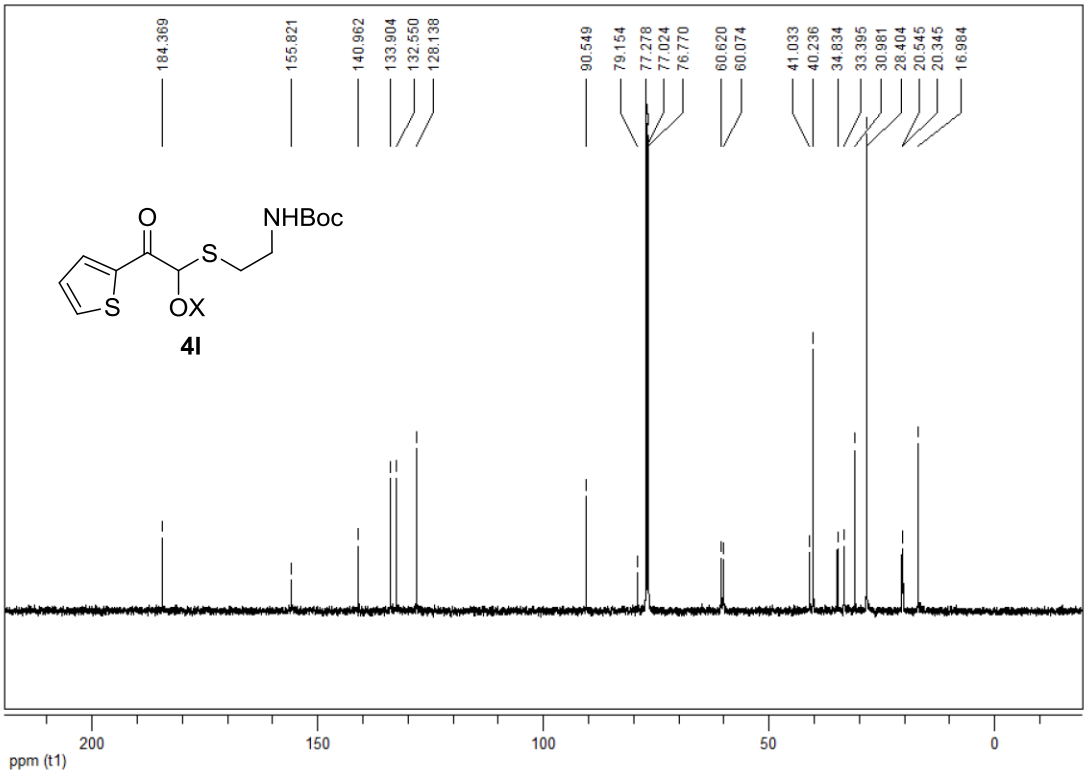


^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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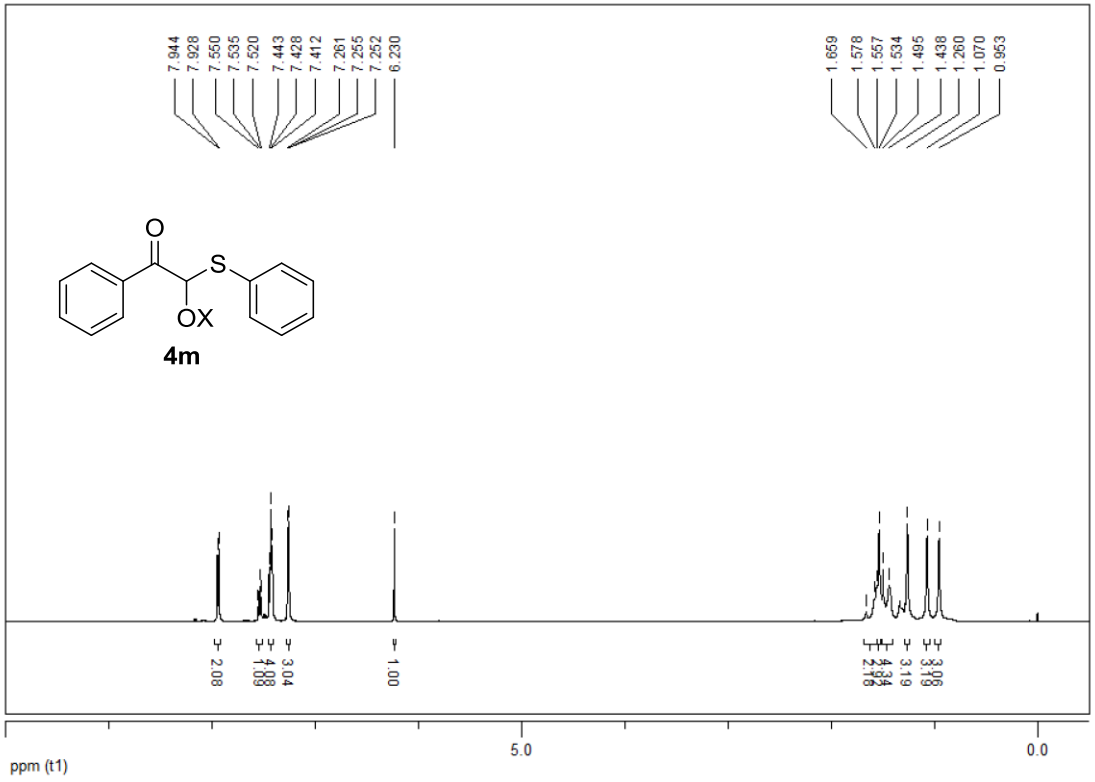

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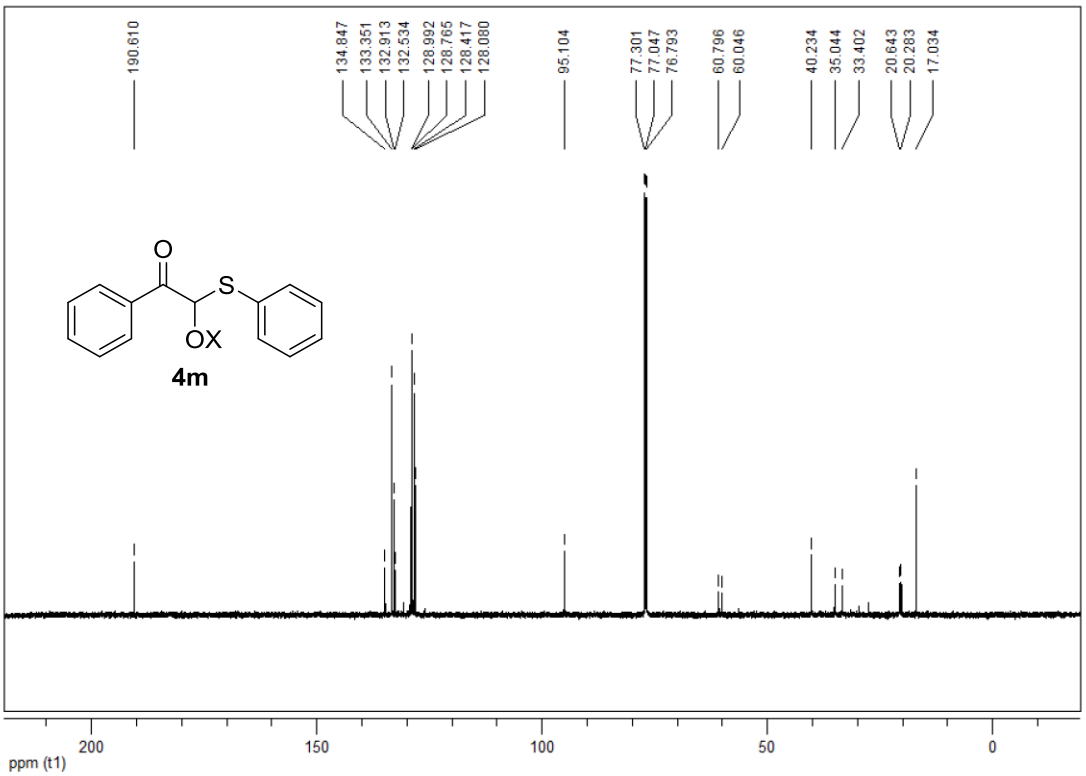

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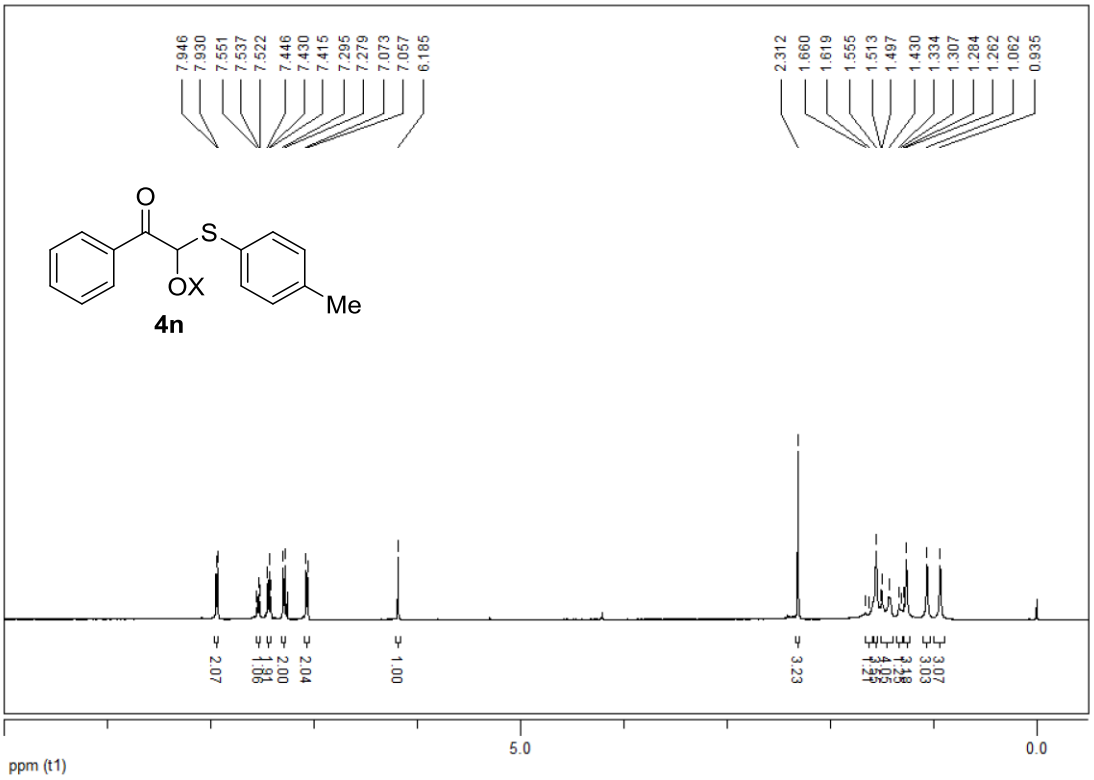

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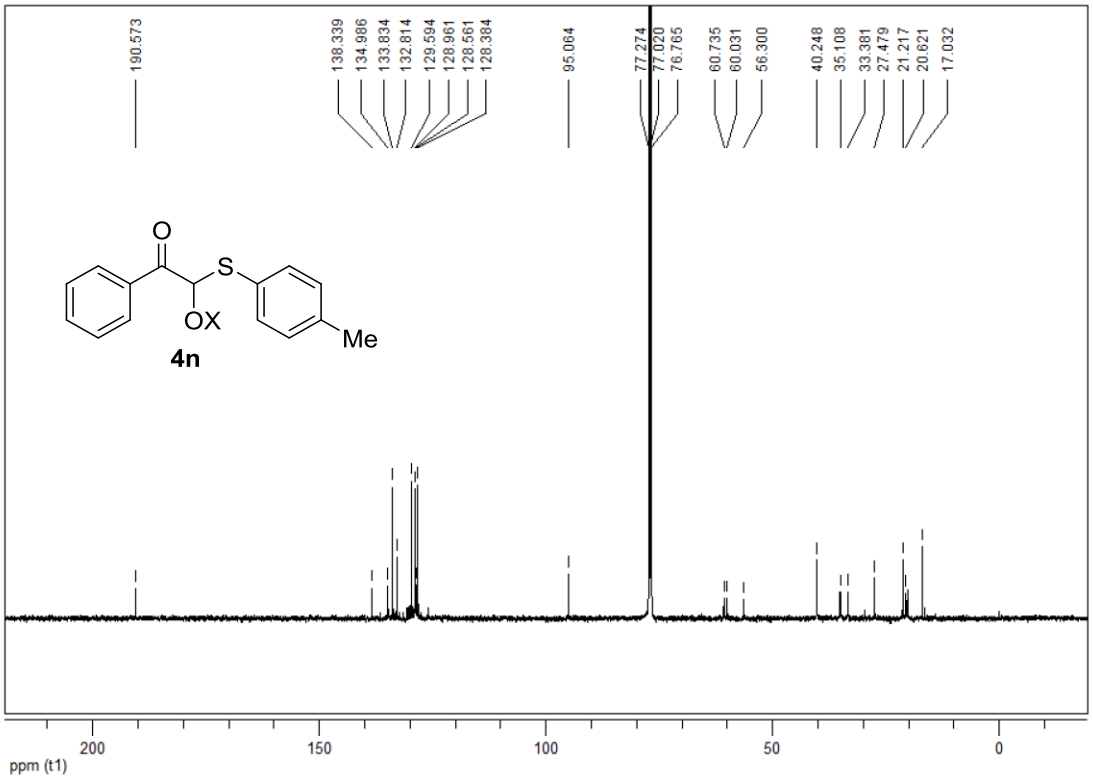

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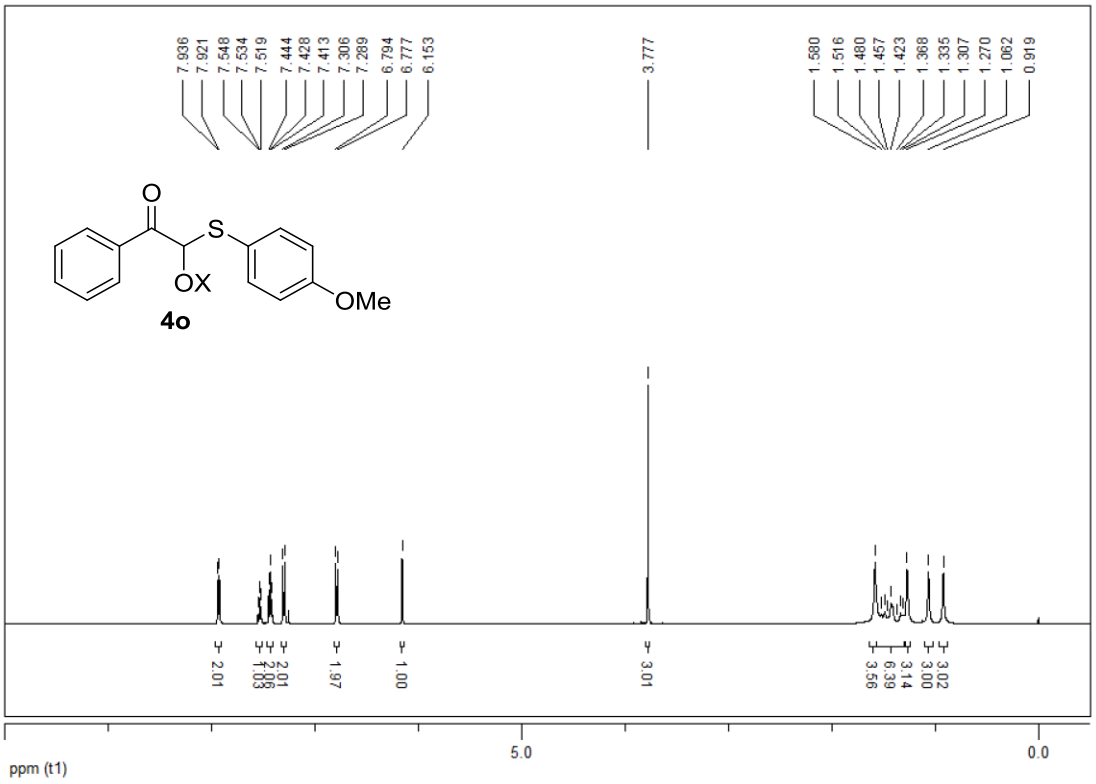

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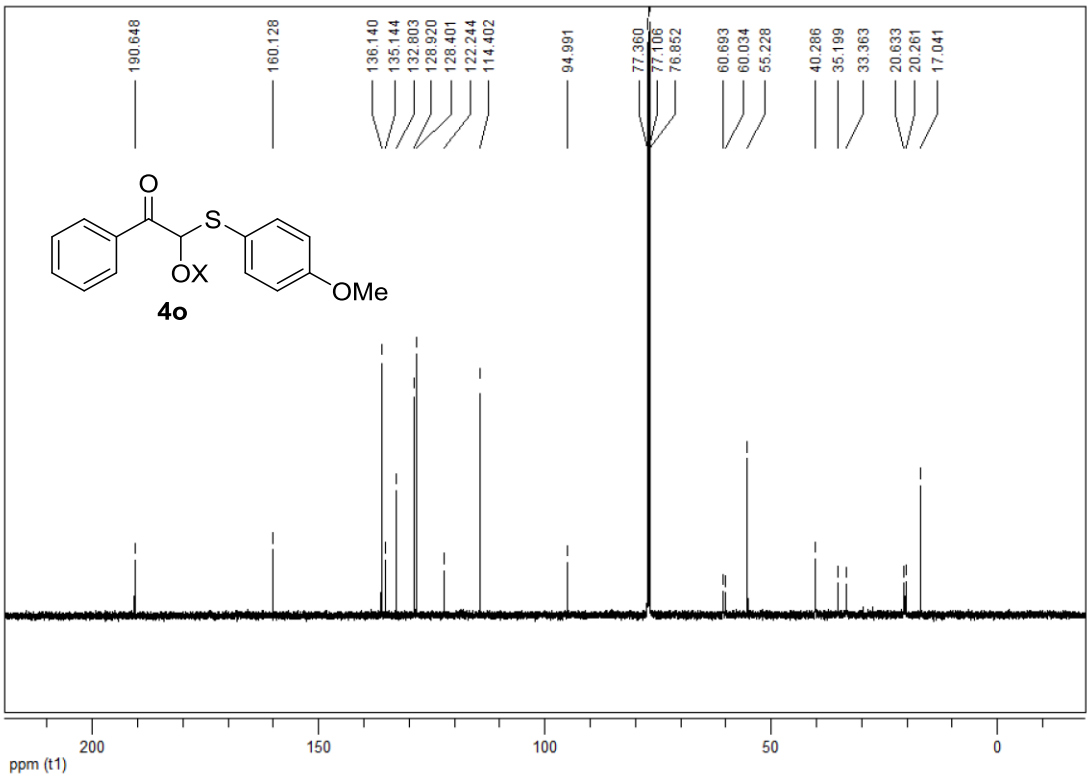

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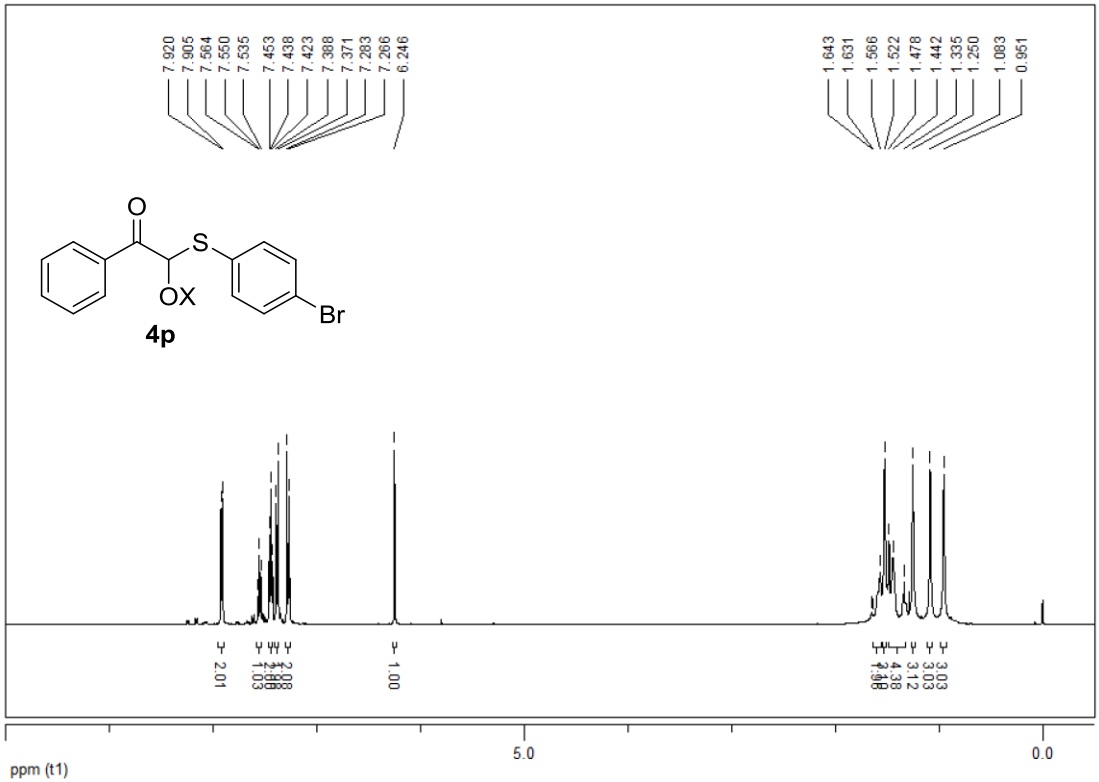

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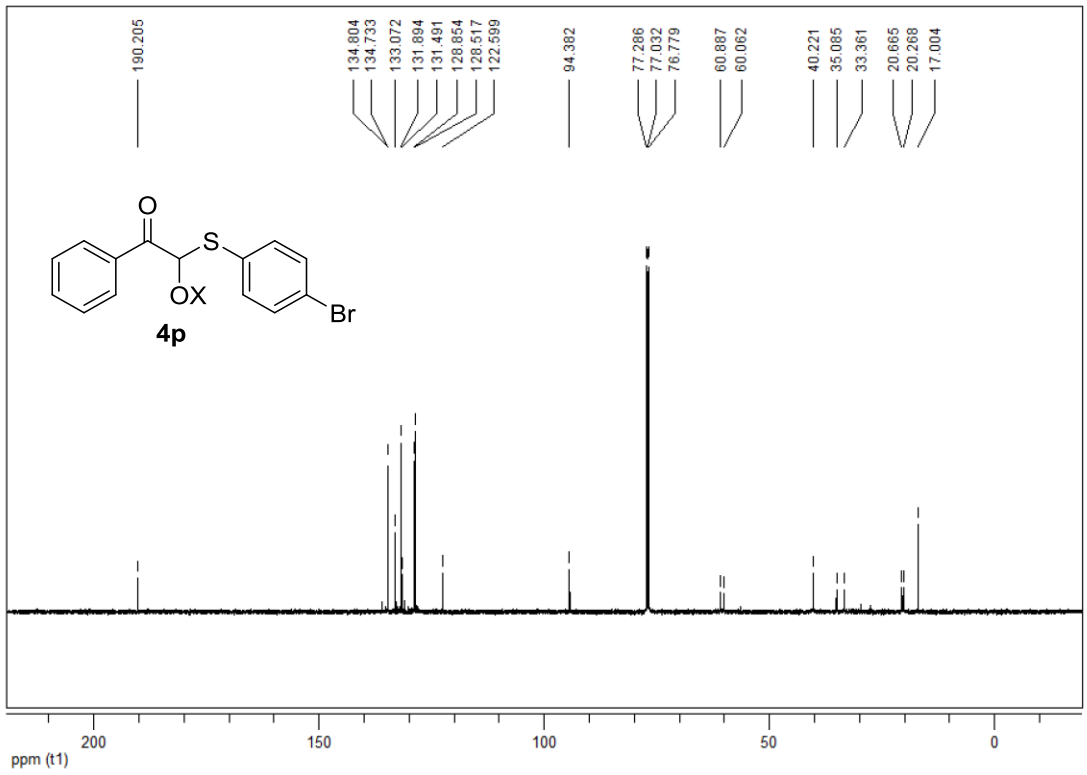

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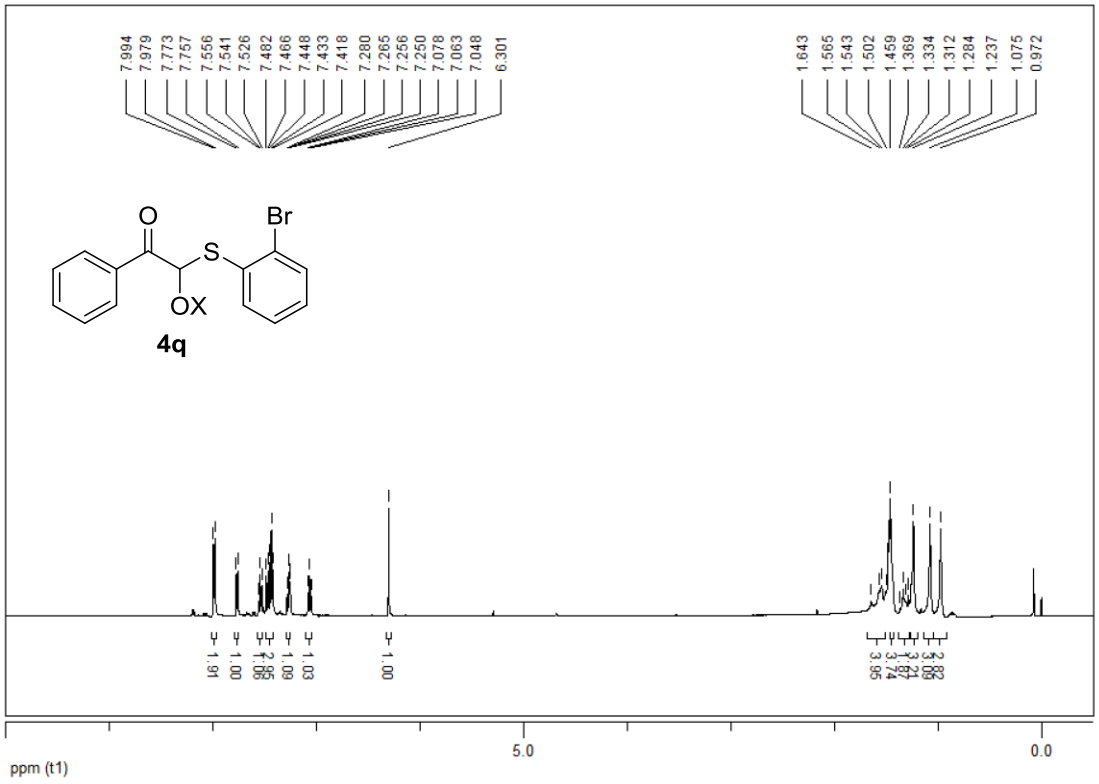

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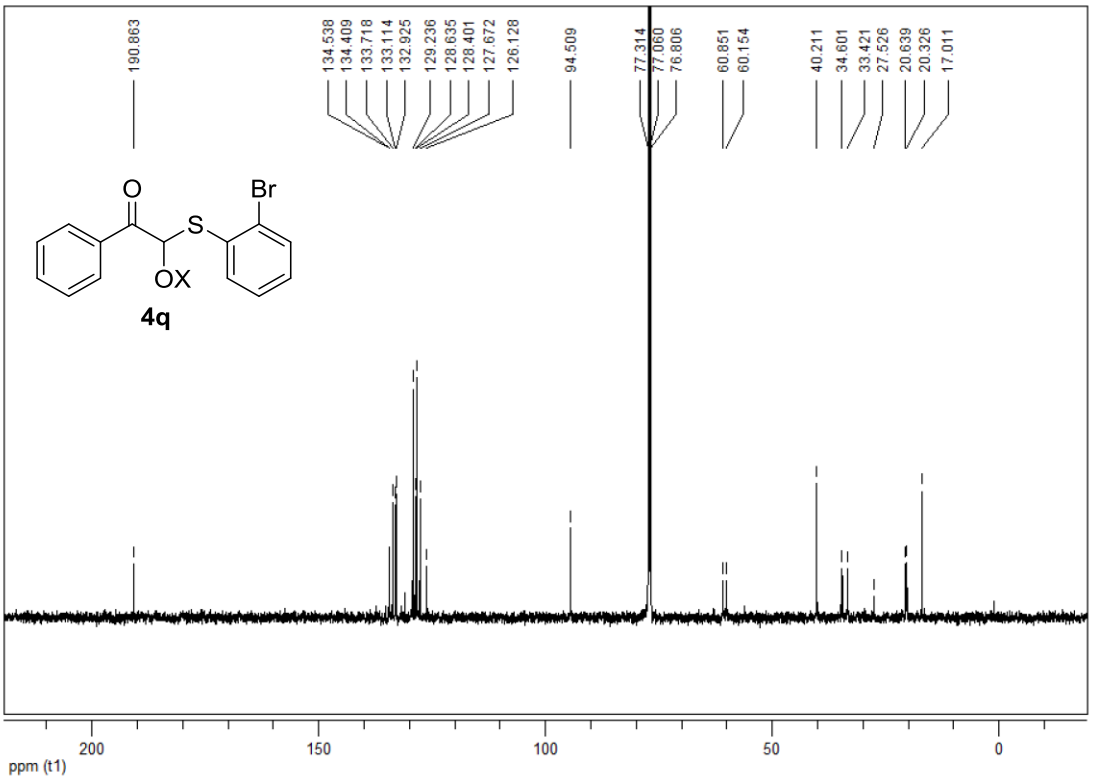

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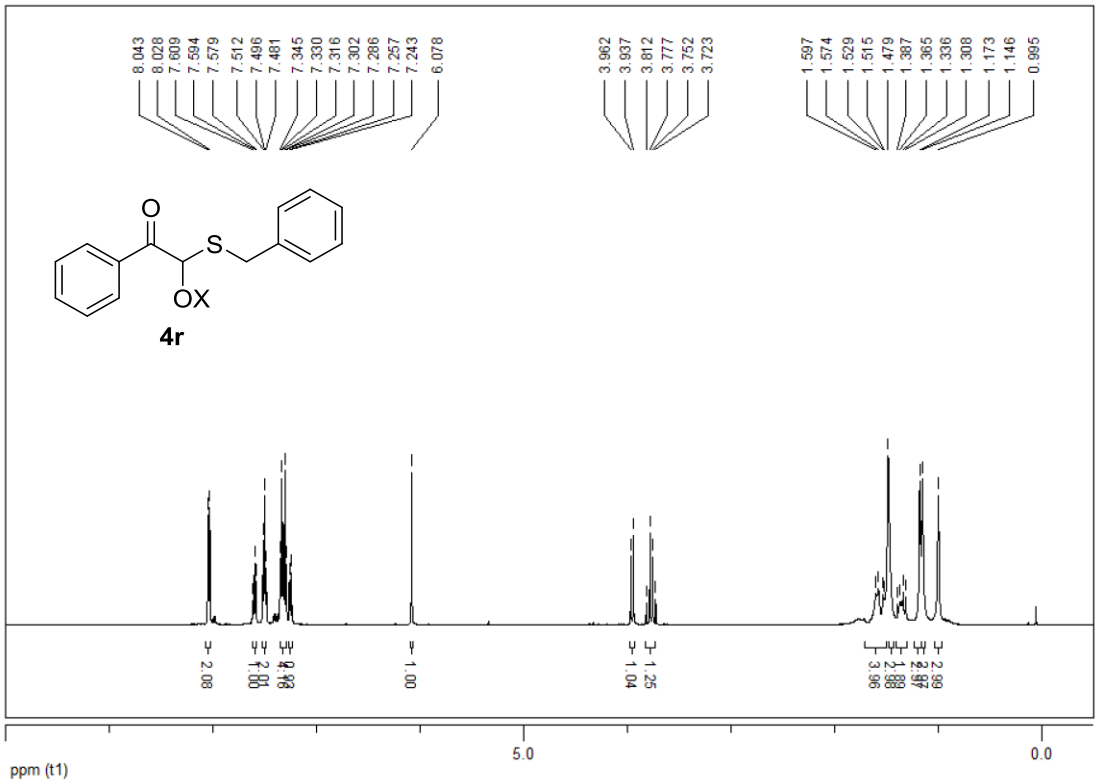

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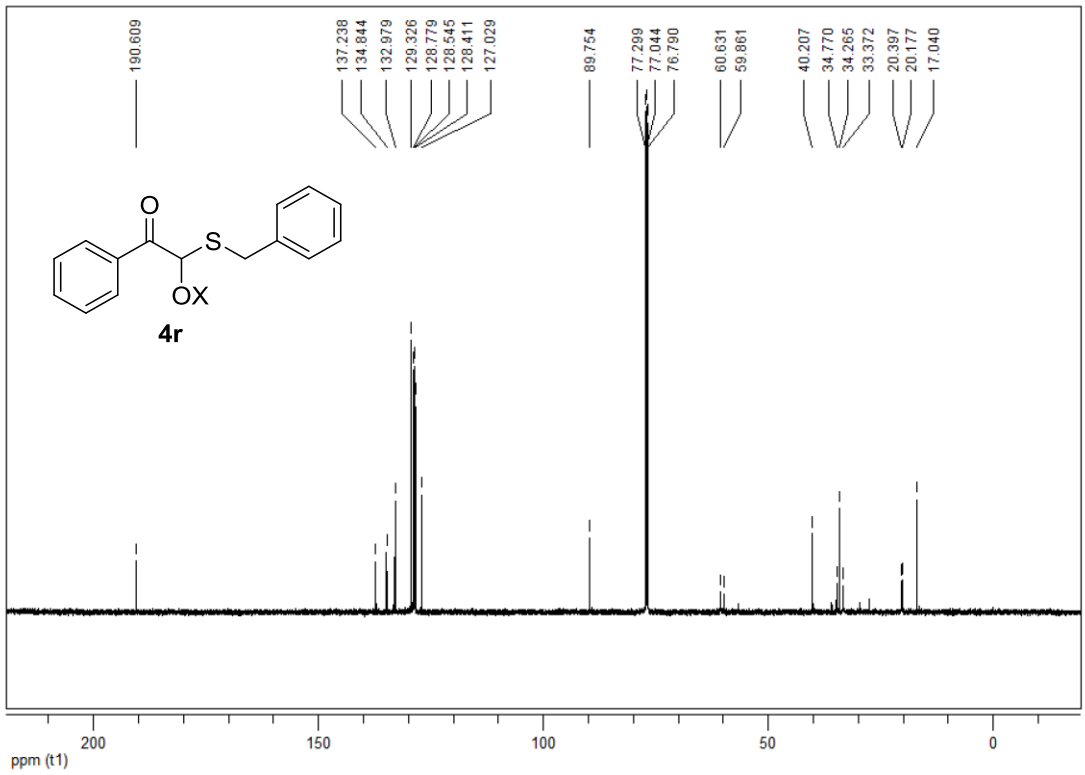

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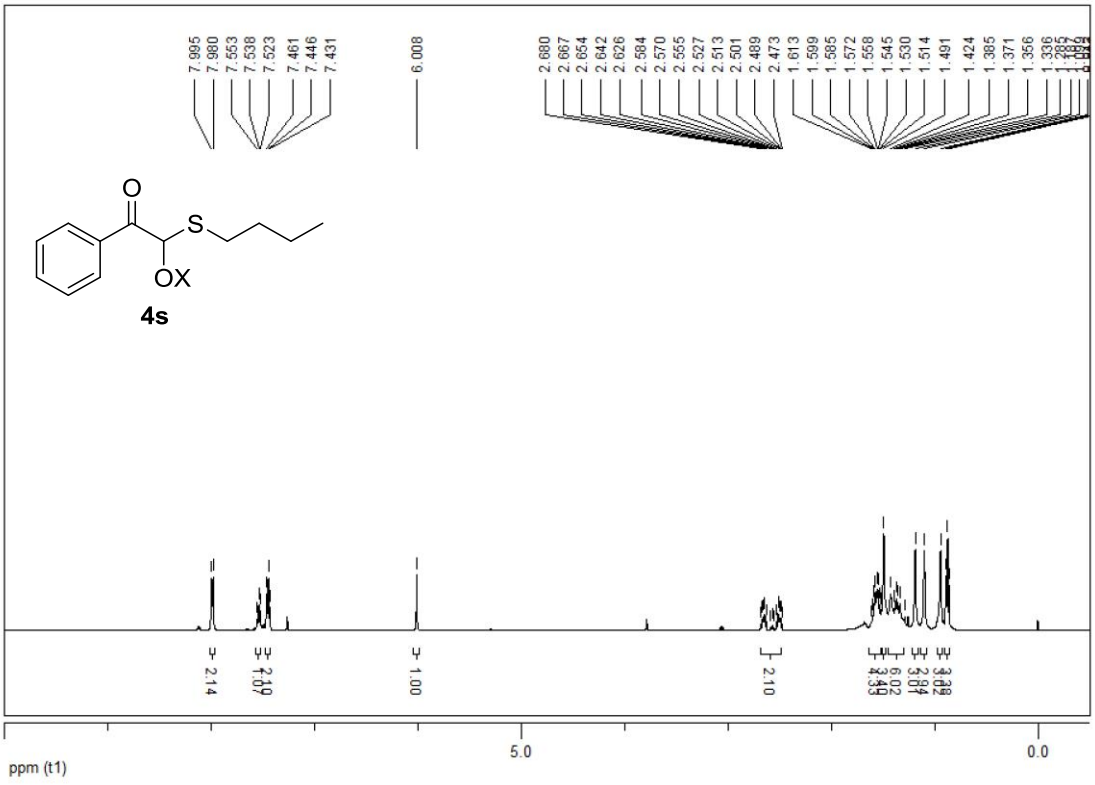

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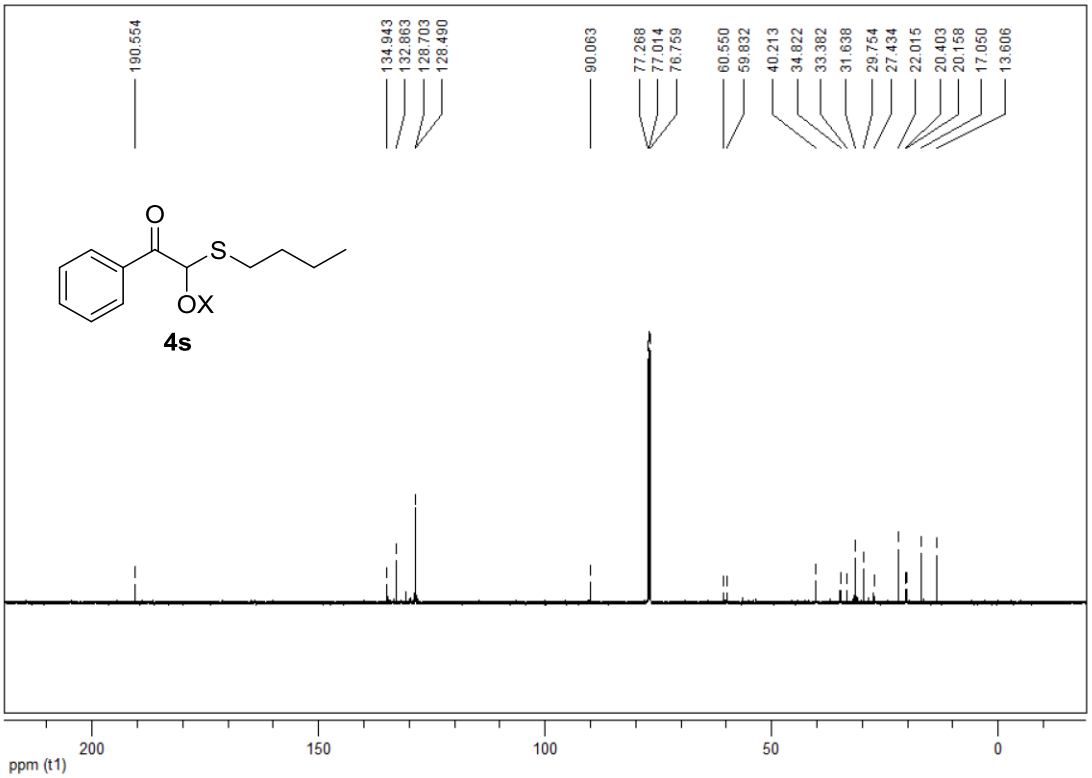
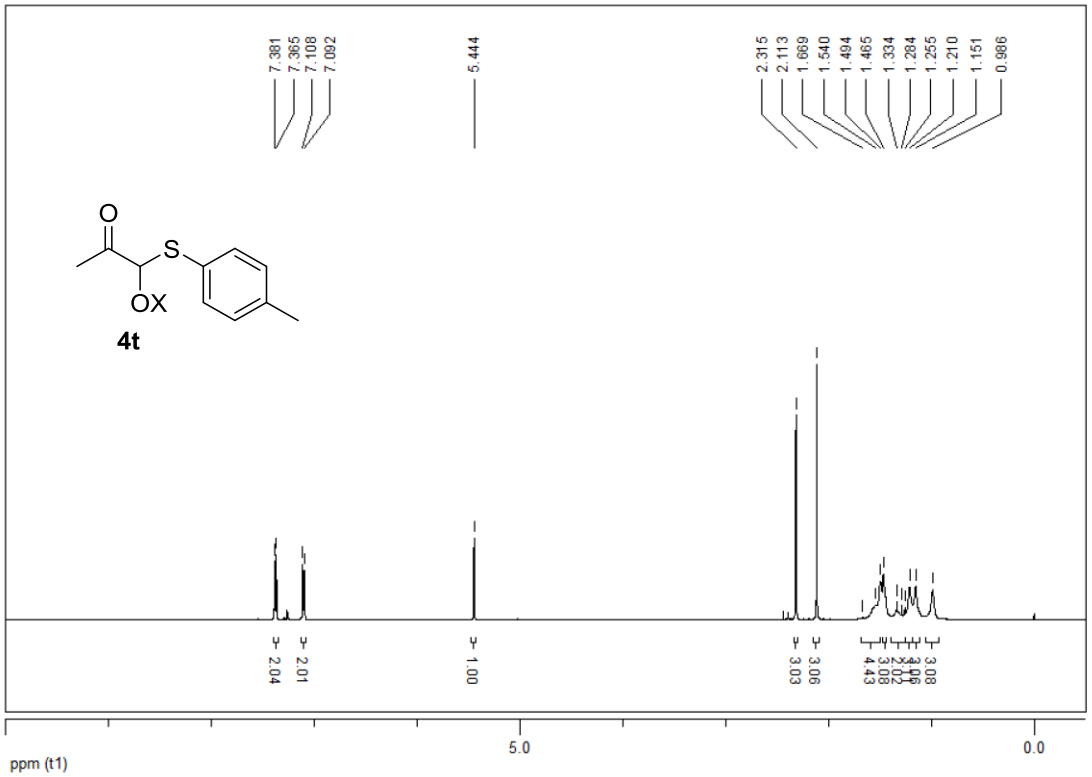


^{1}H NMR (500 MHz, $CDCl_3$)



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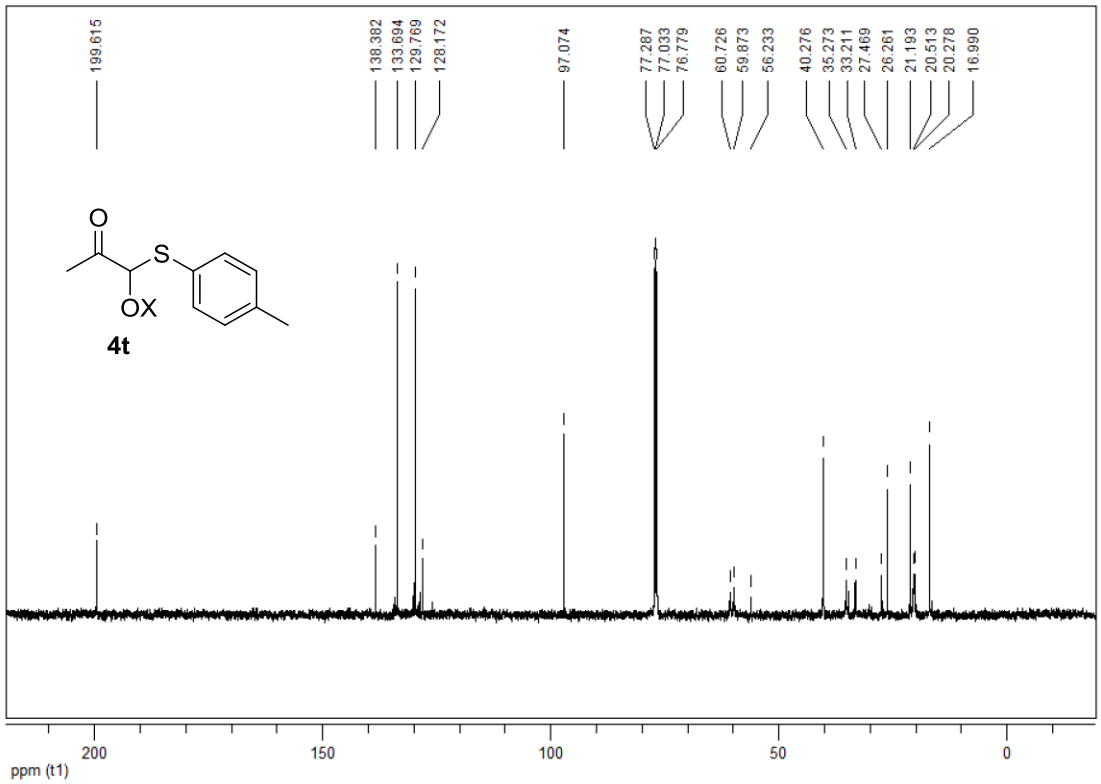

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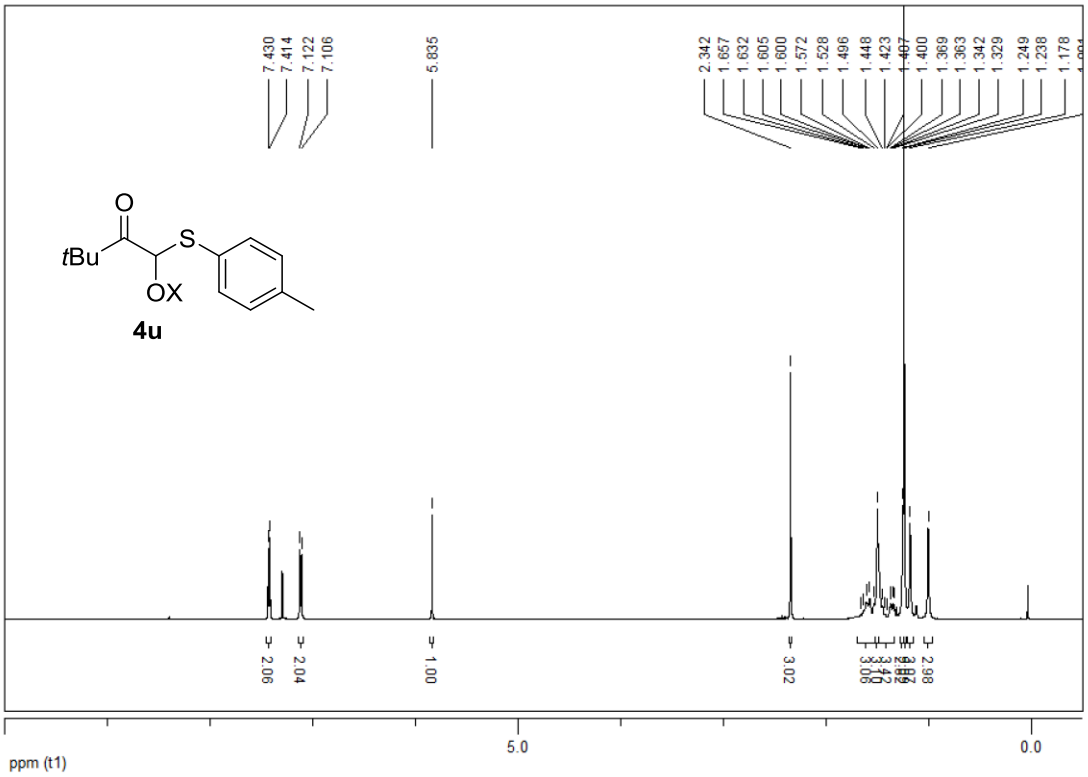

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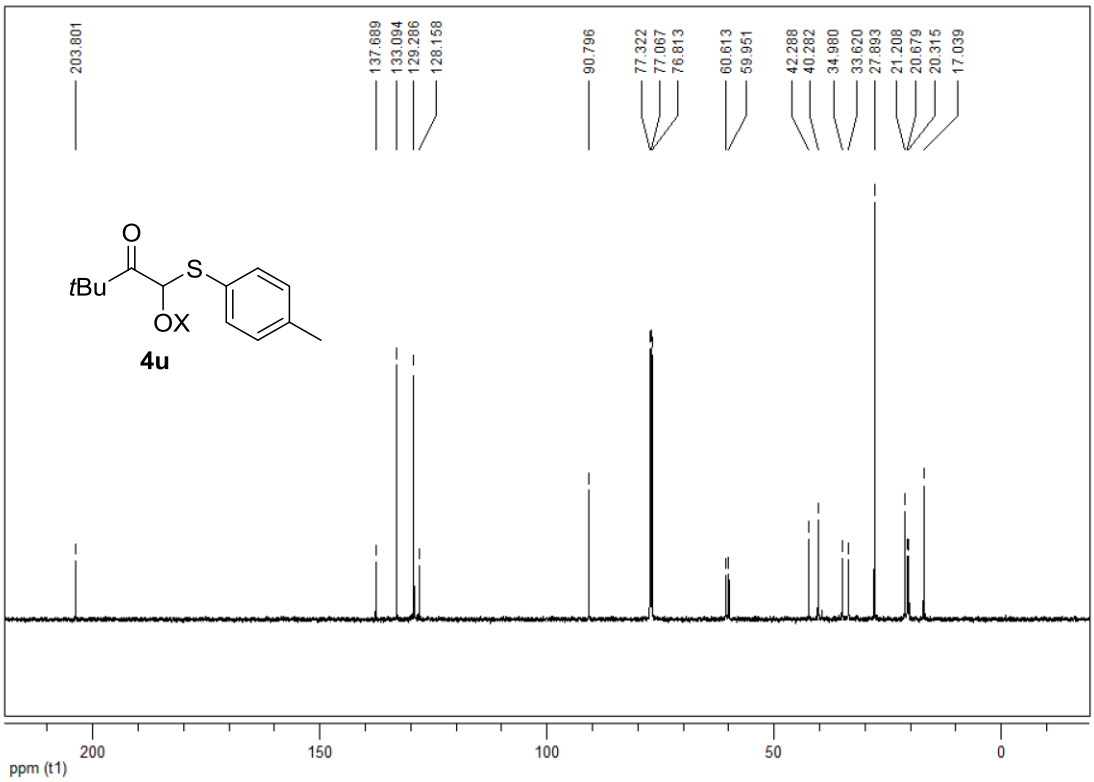

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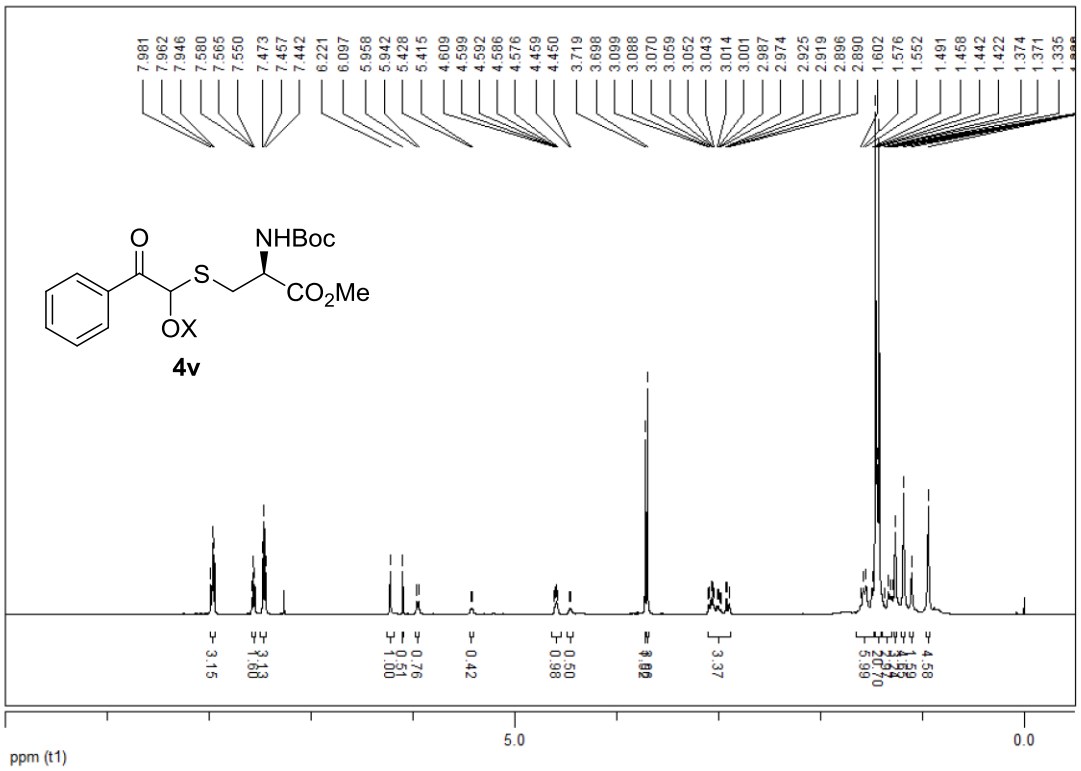

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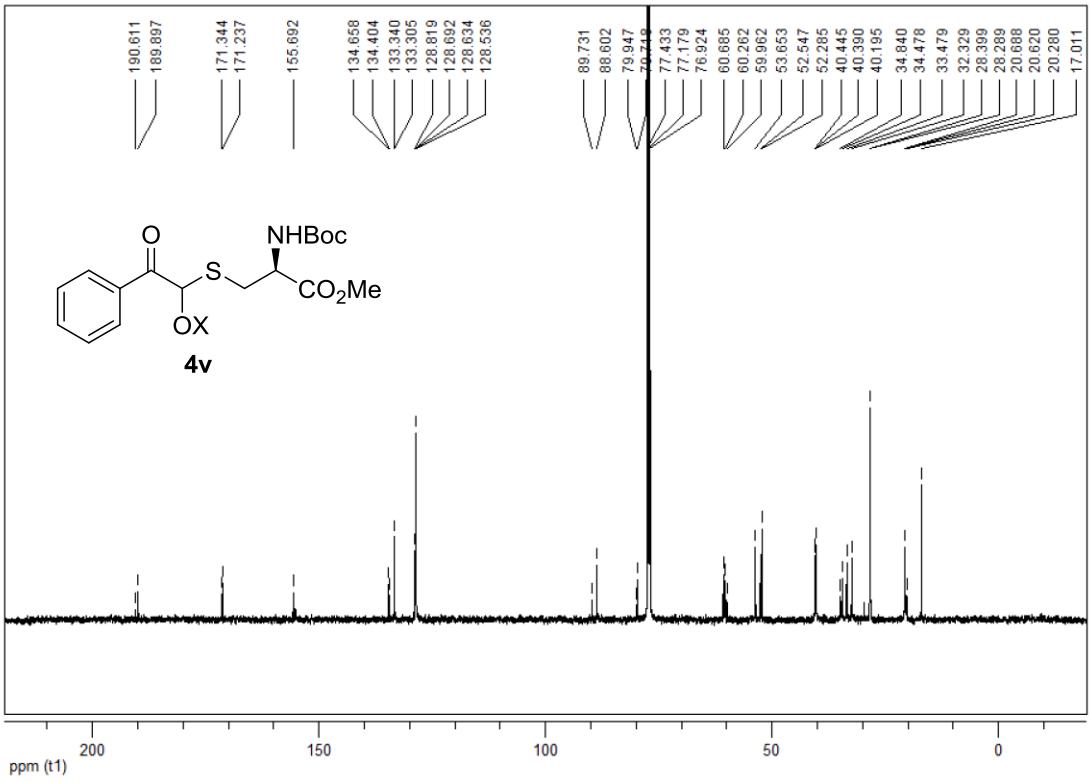

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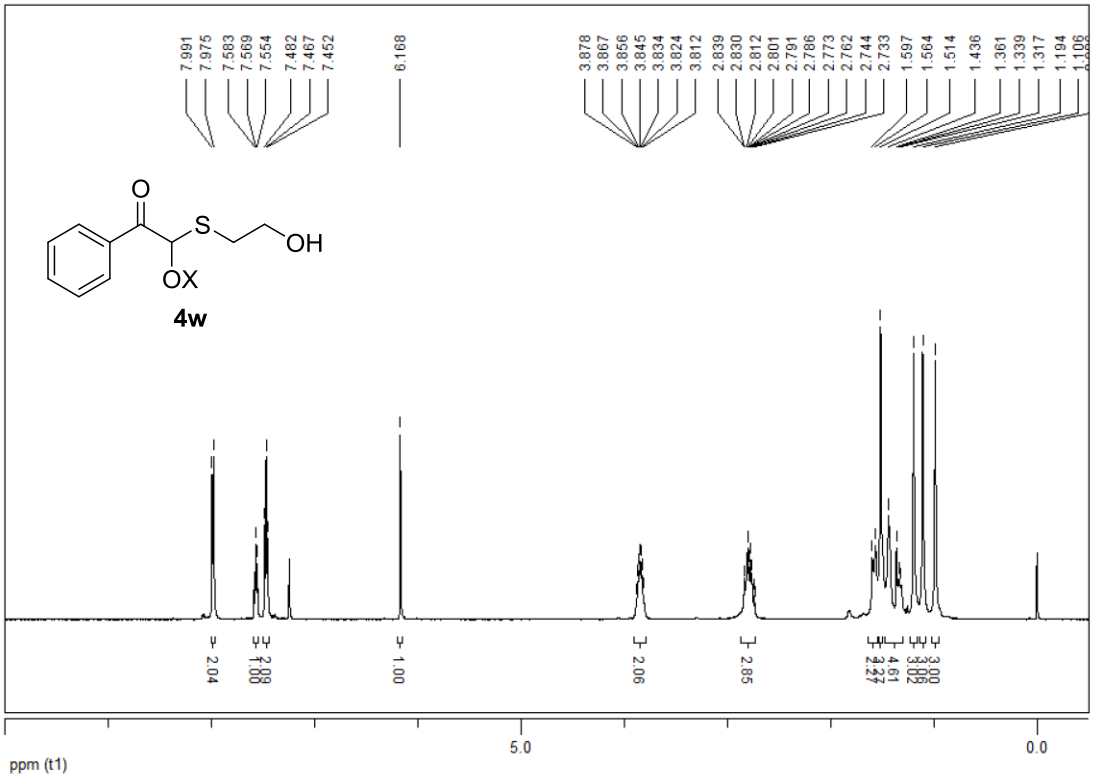

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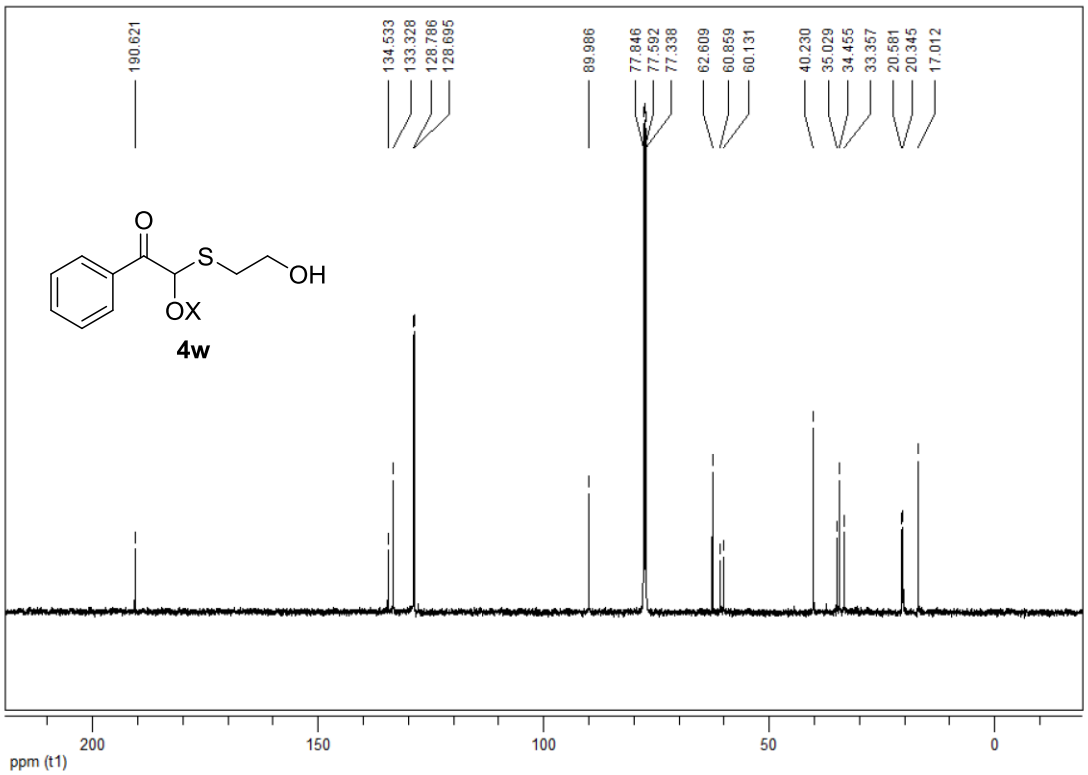

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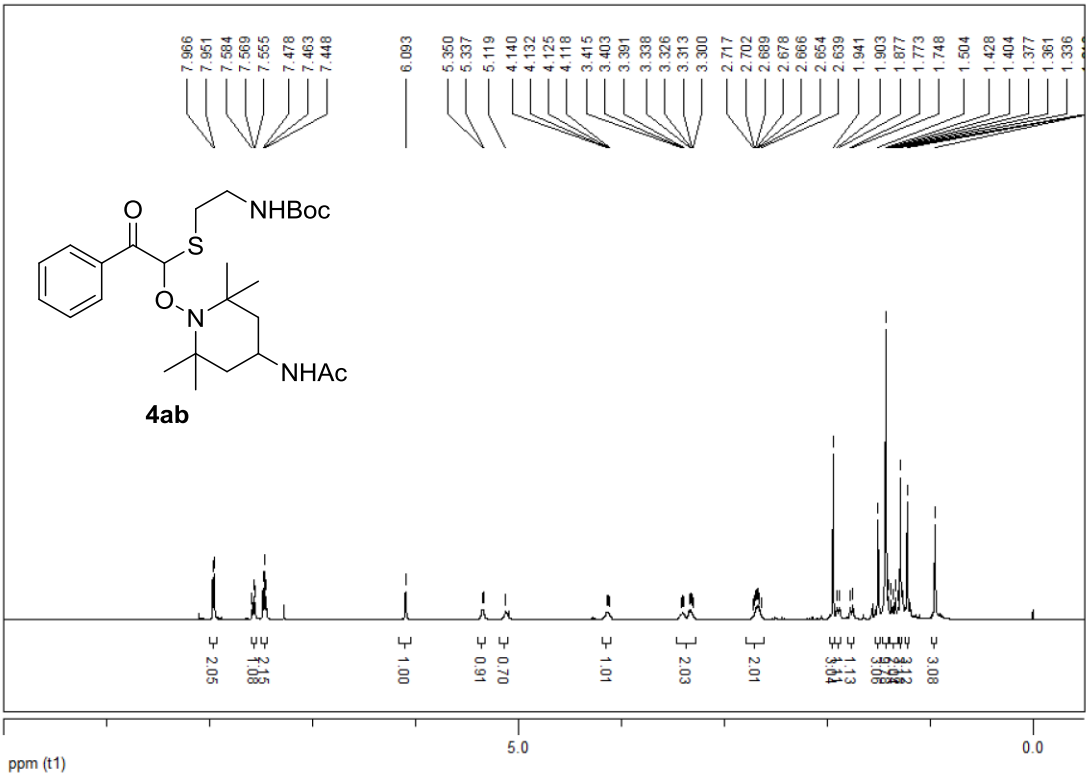

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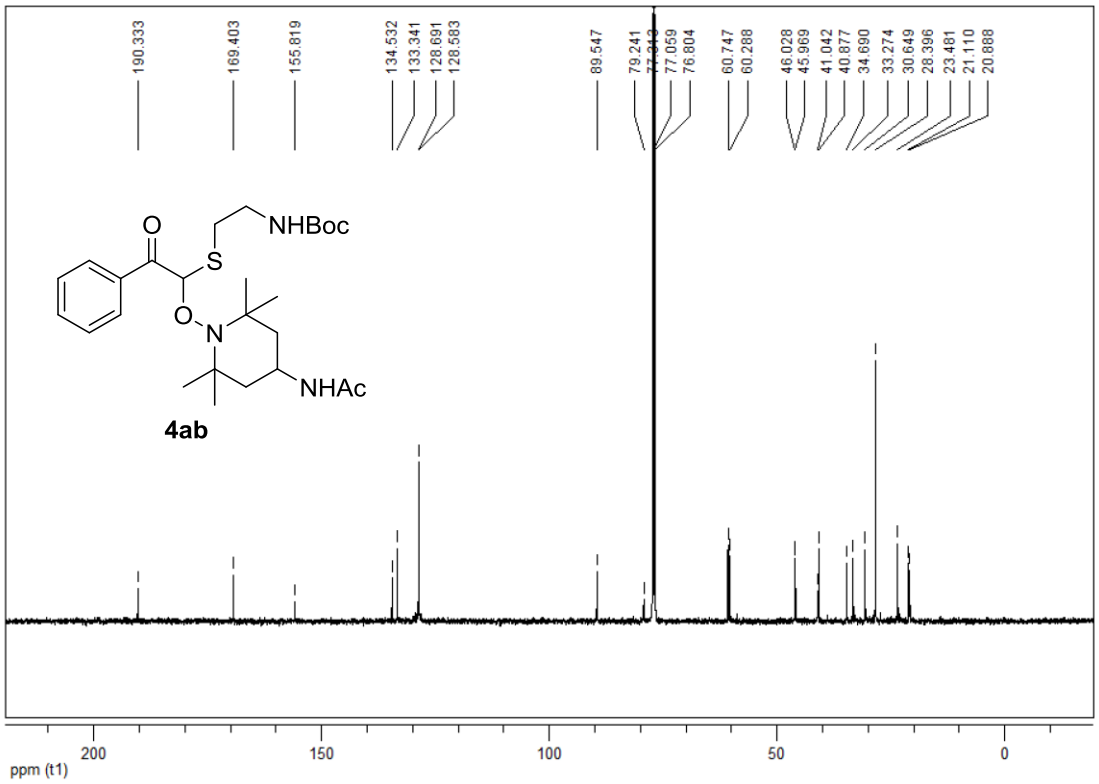

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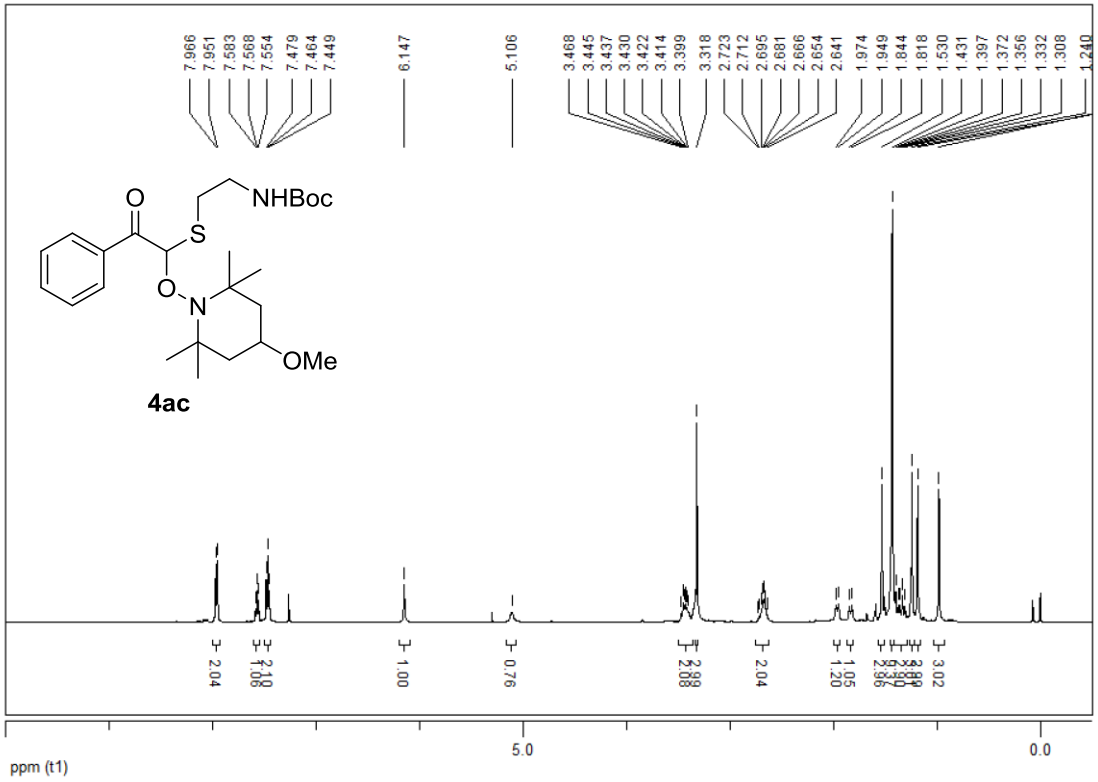

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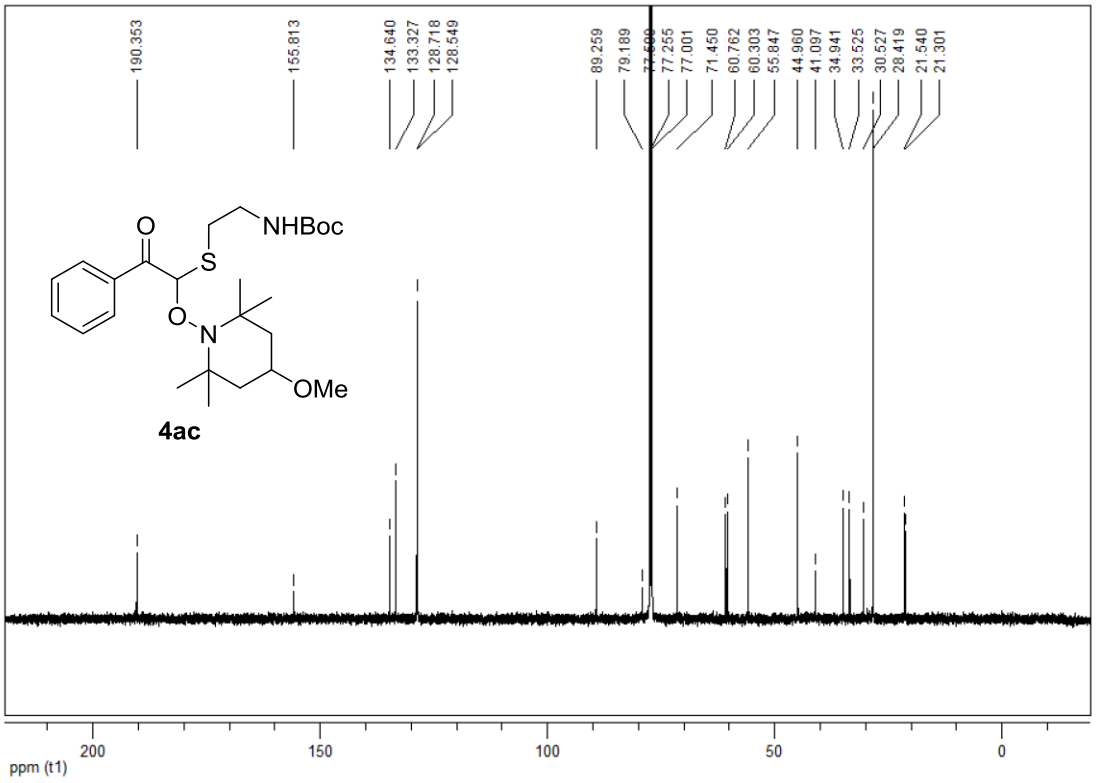

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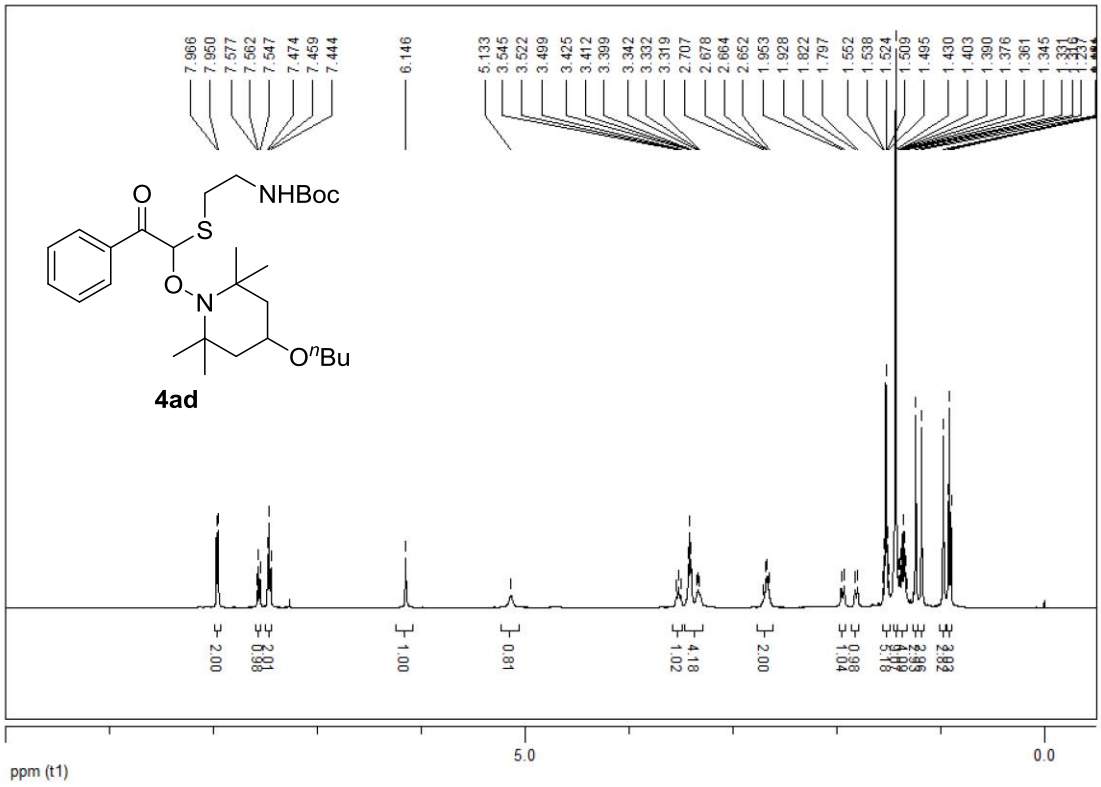

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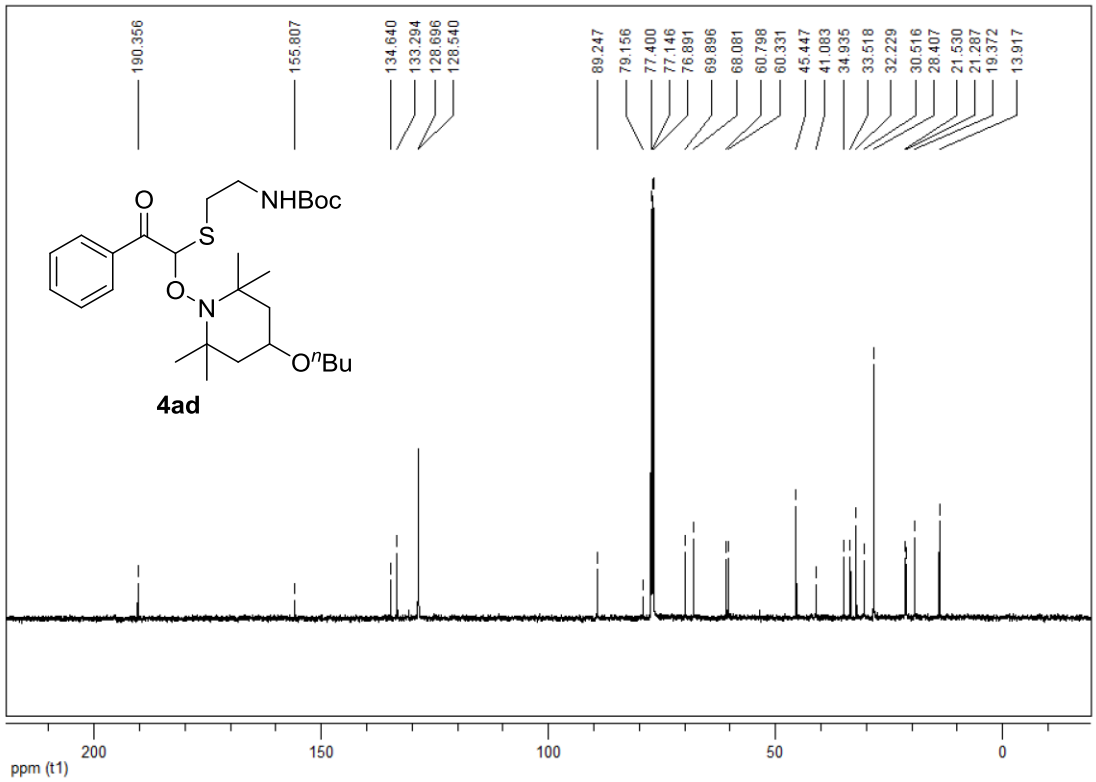

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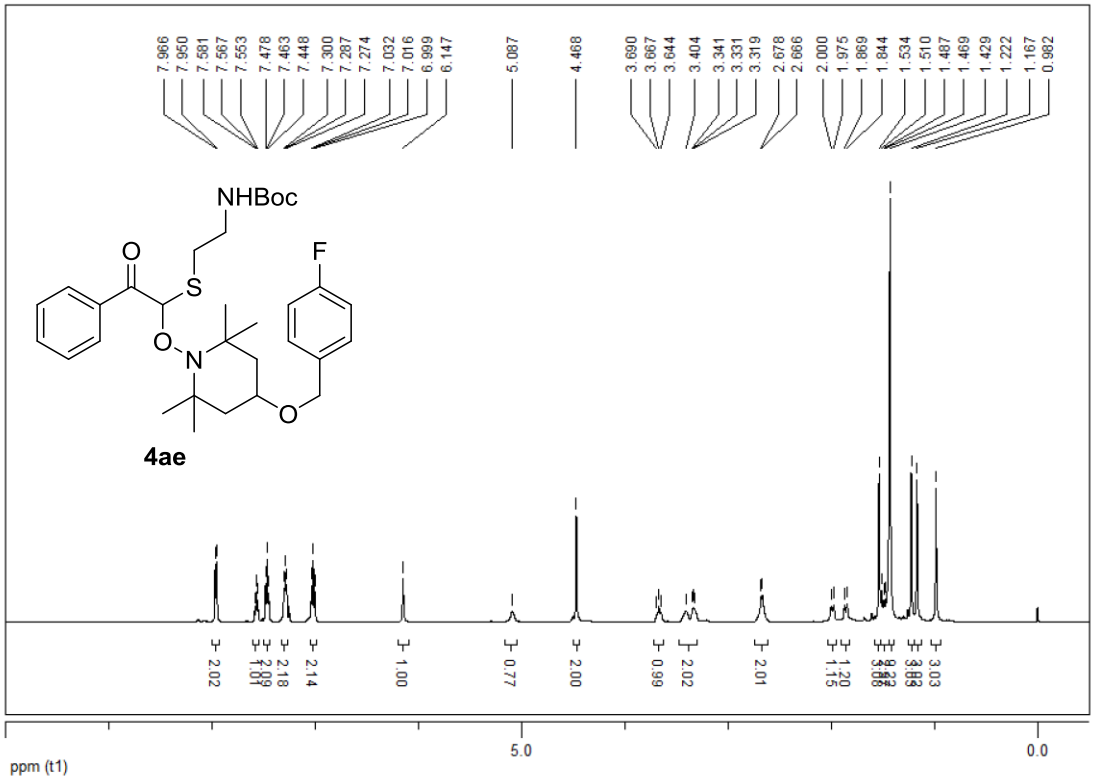
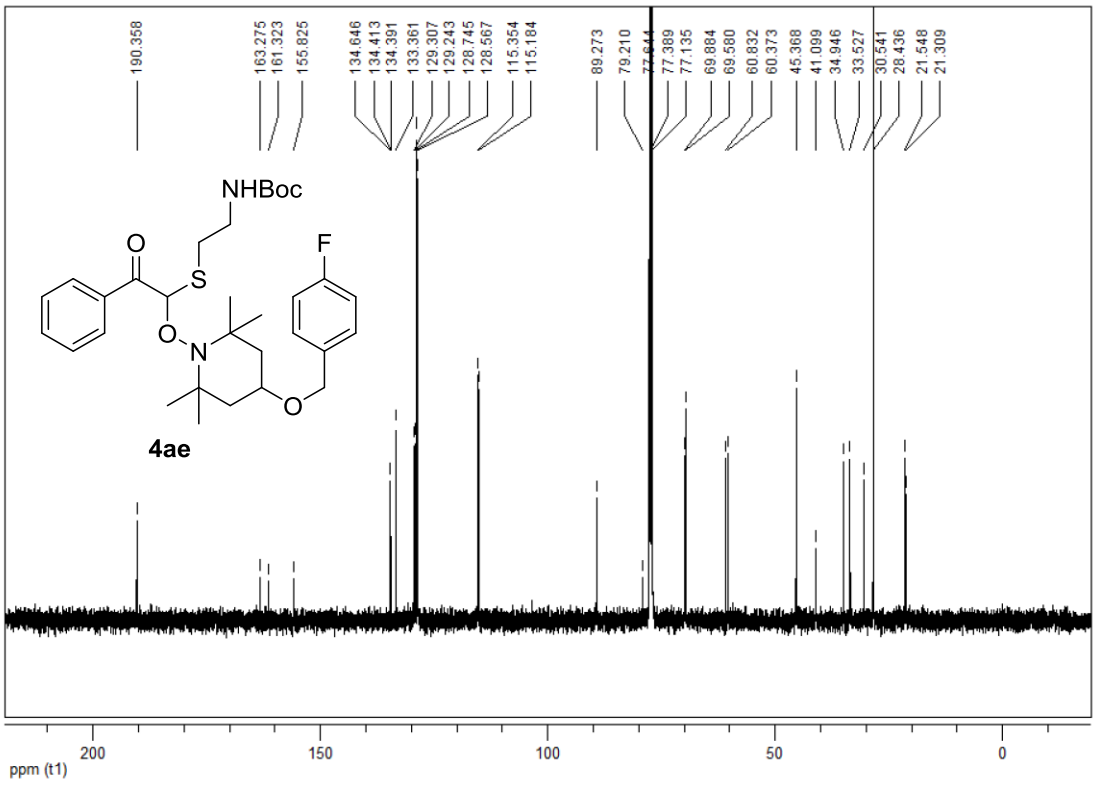


^{13}C NMR (125 MHz, $CDCl_3$)



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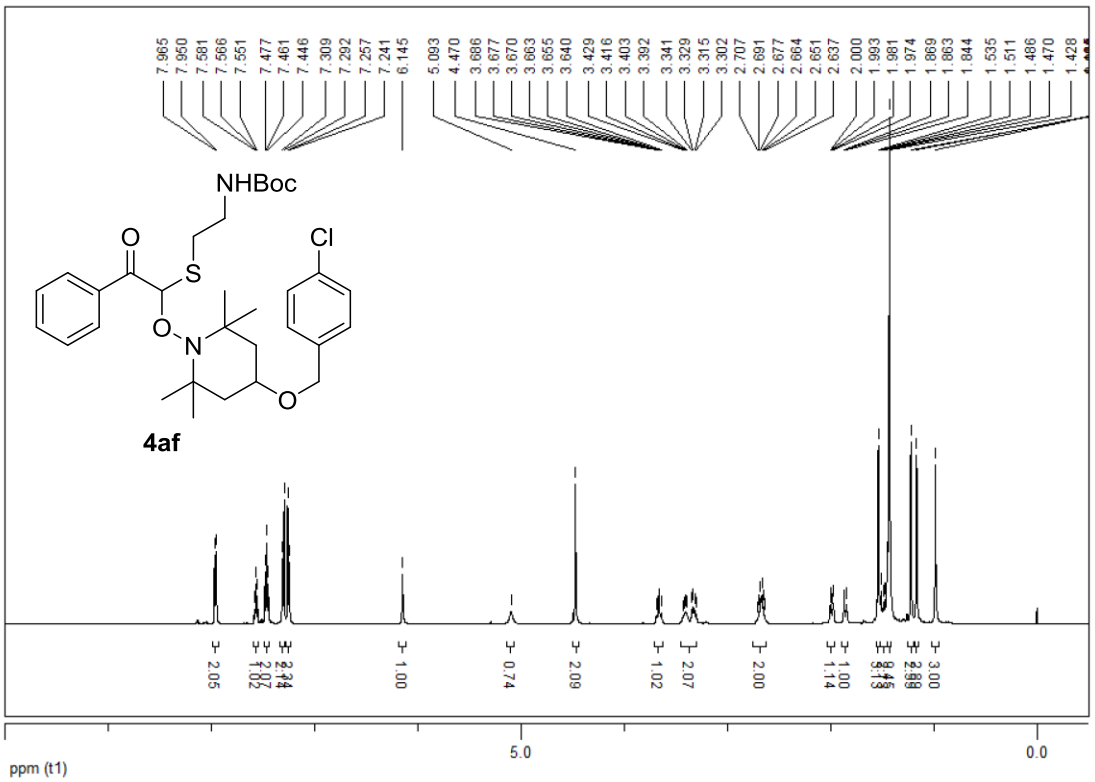

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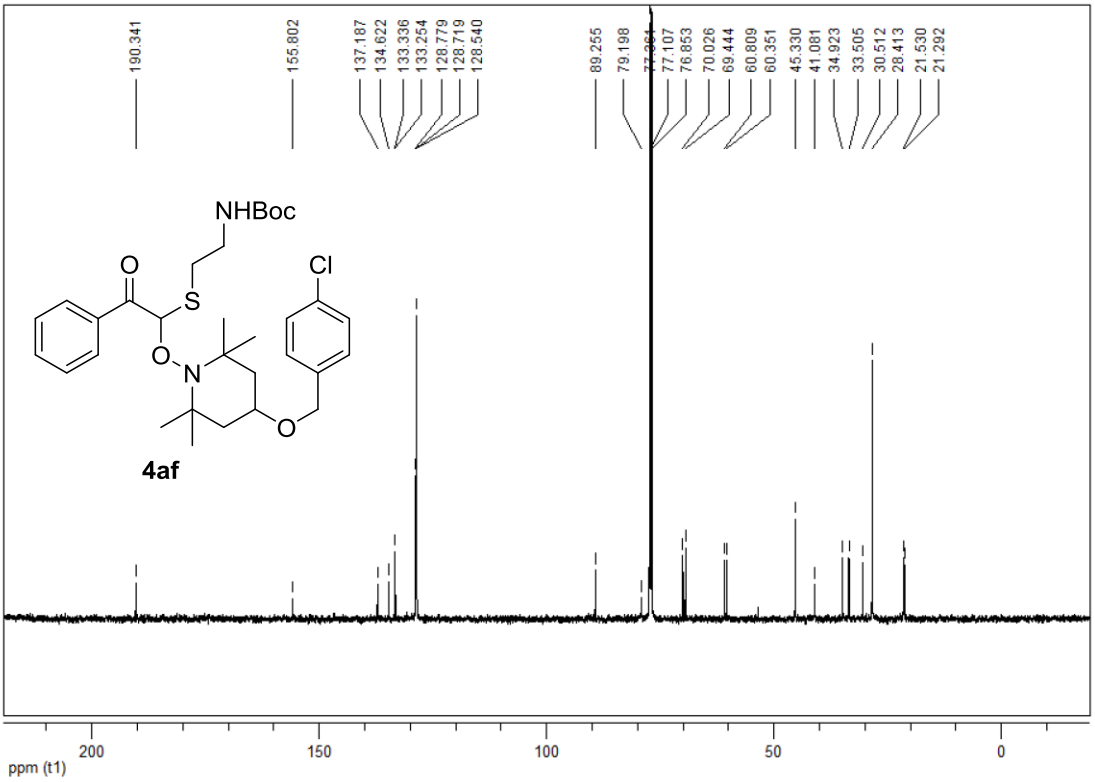

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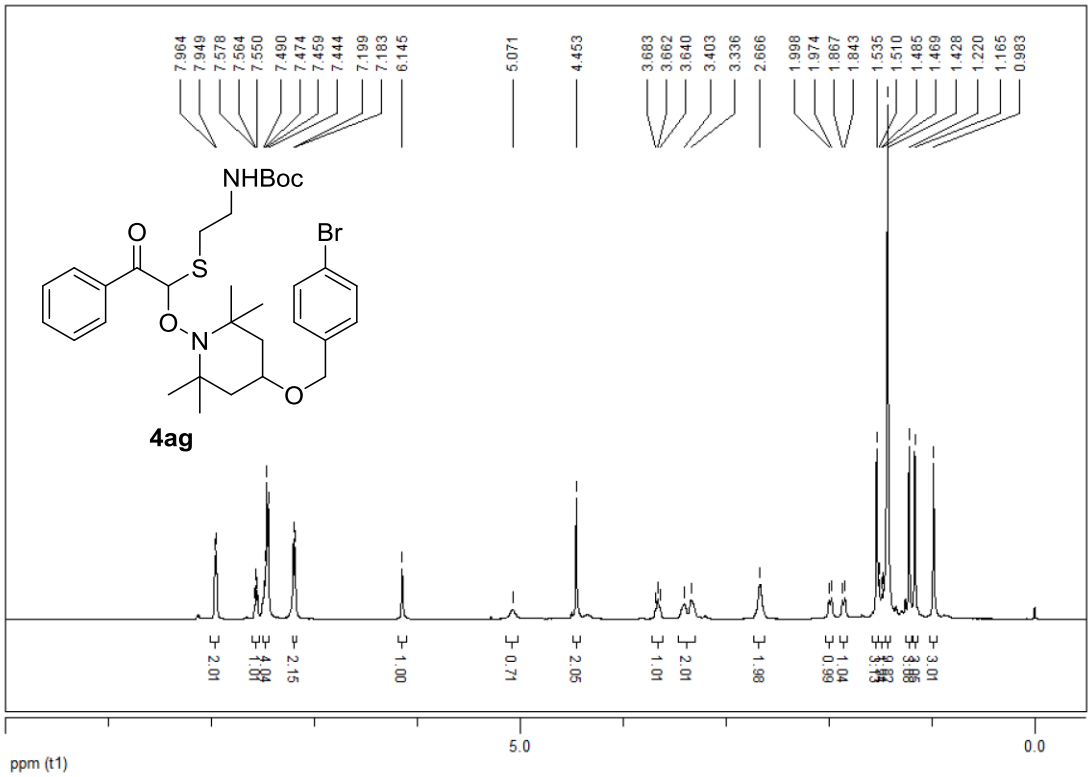

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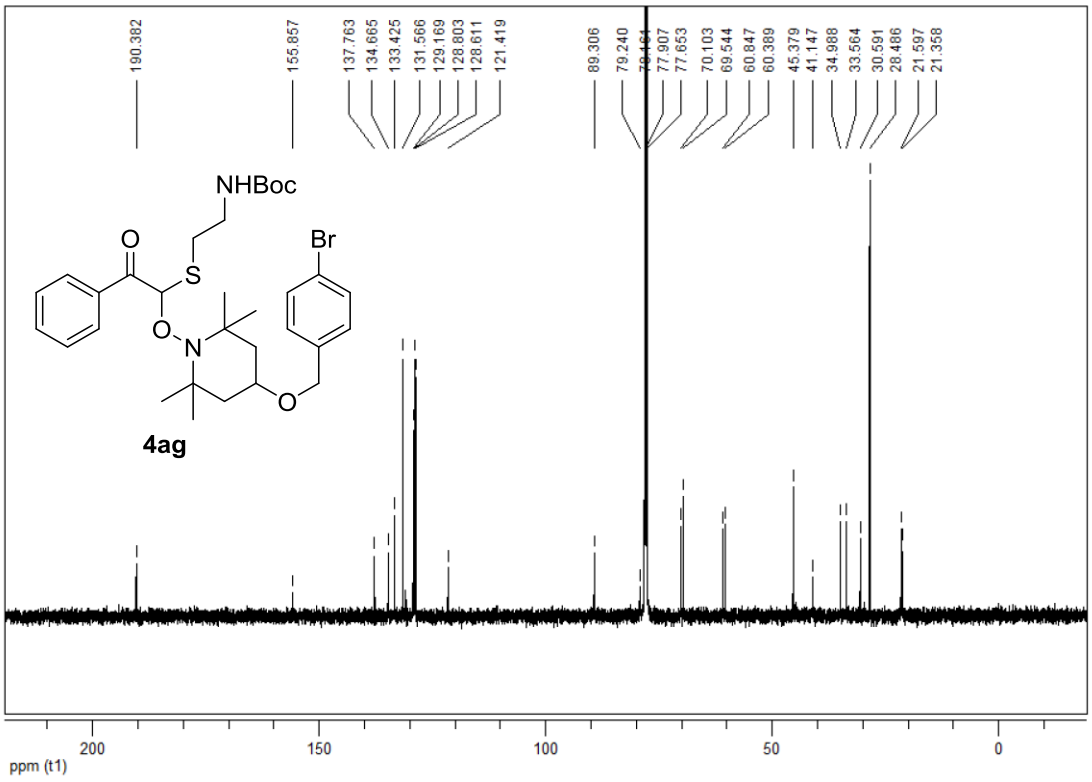

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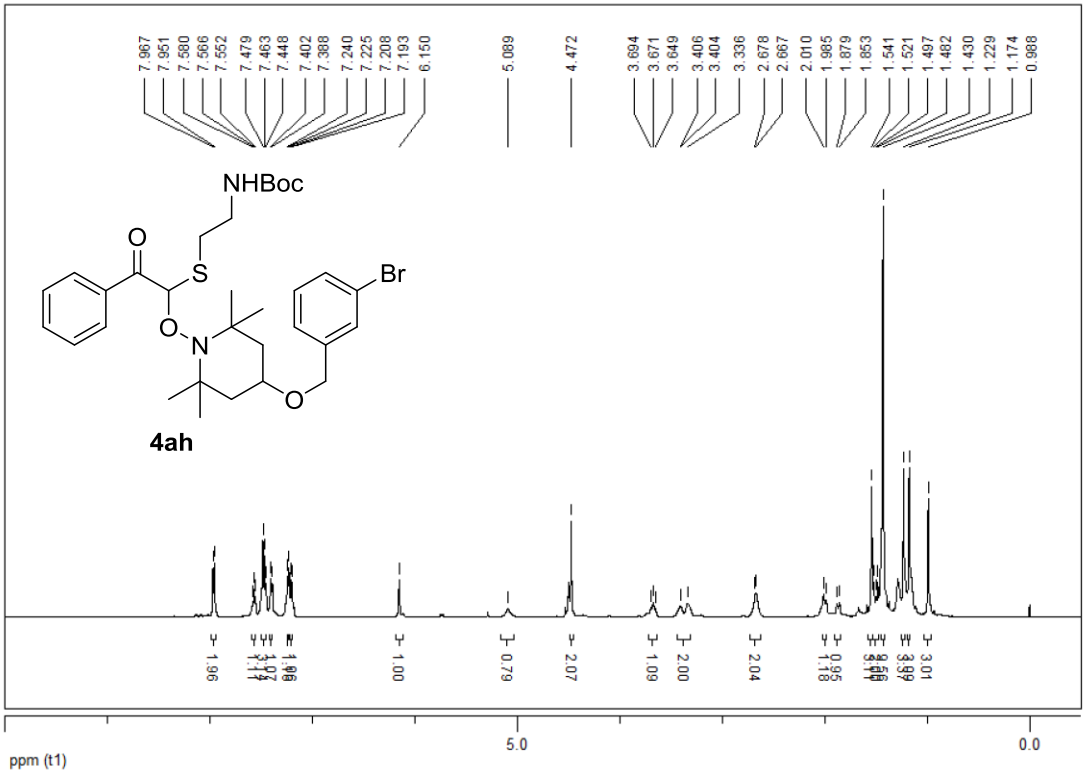

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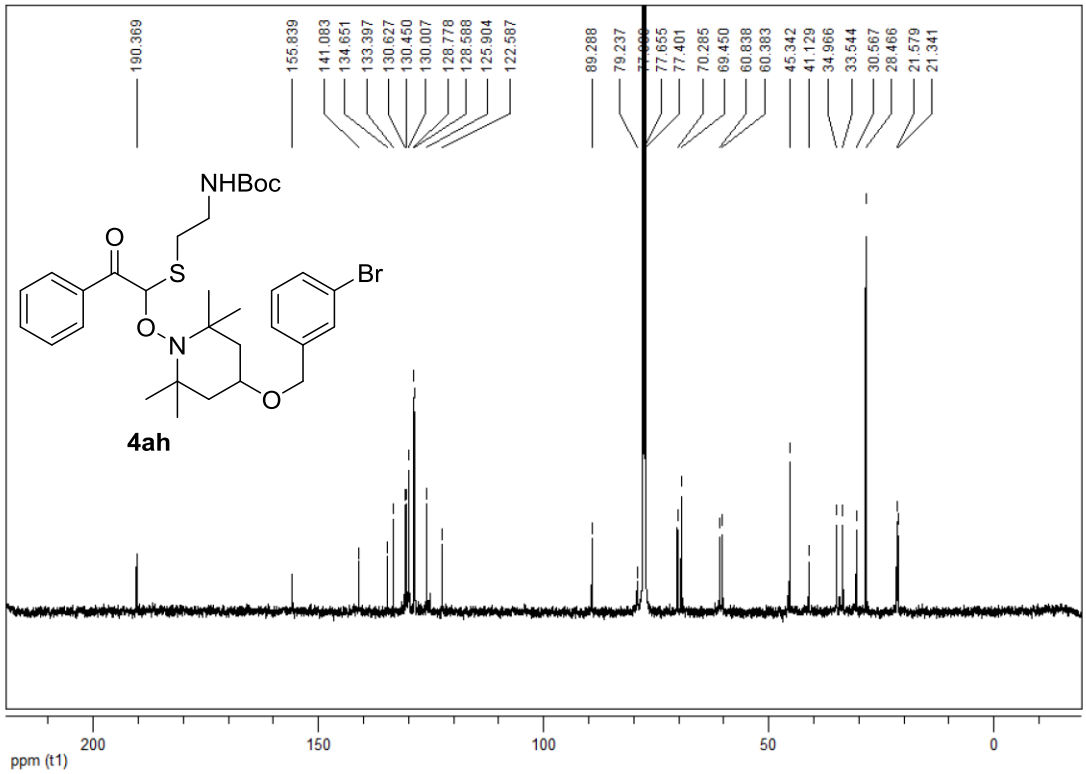

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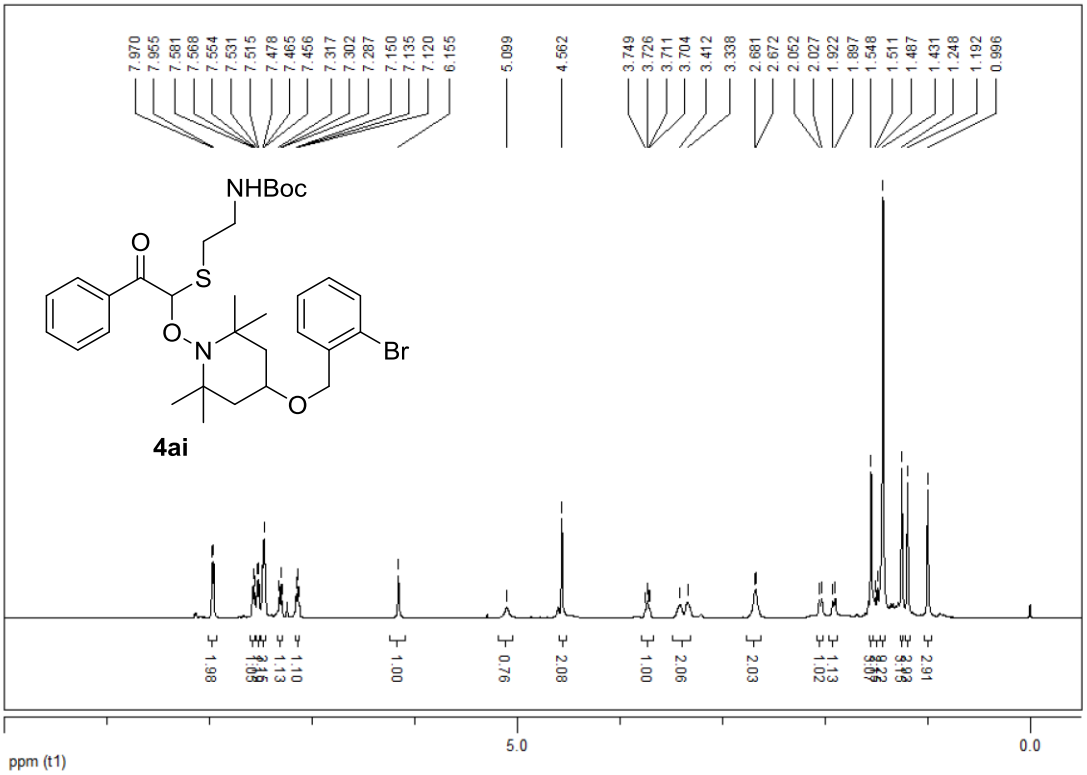

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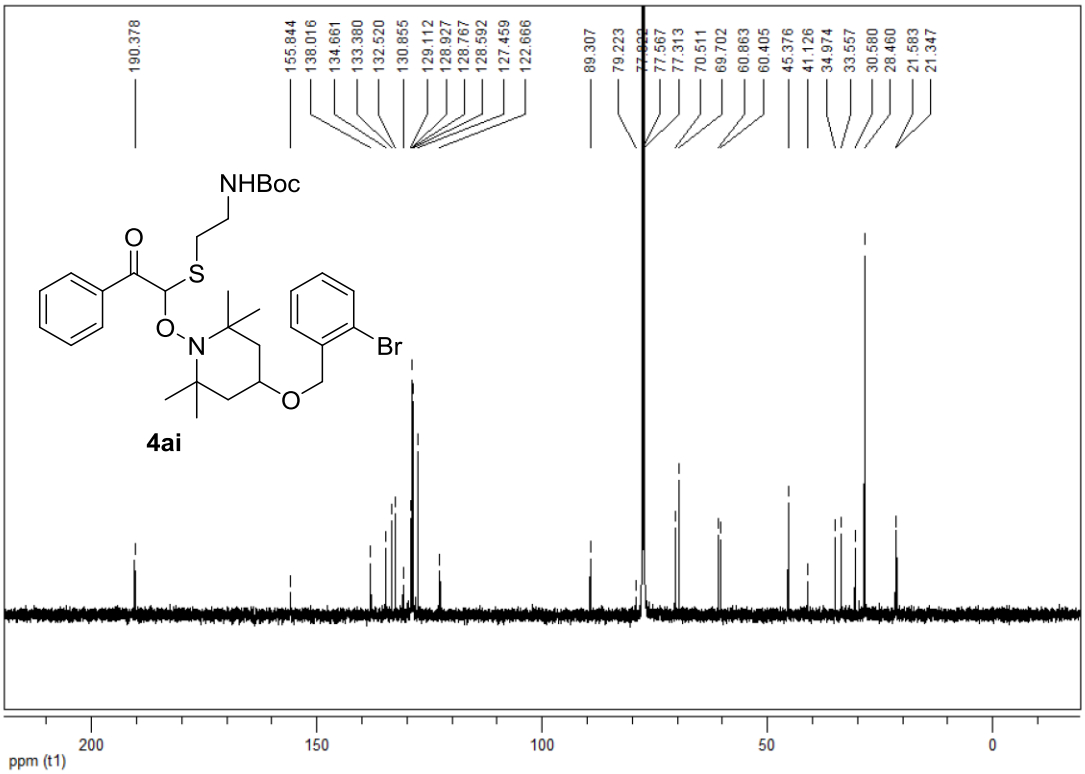

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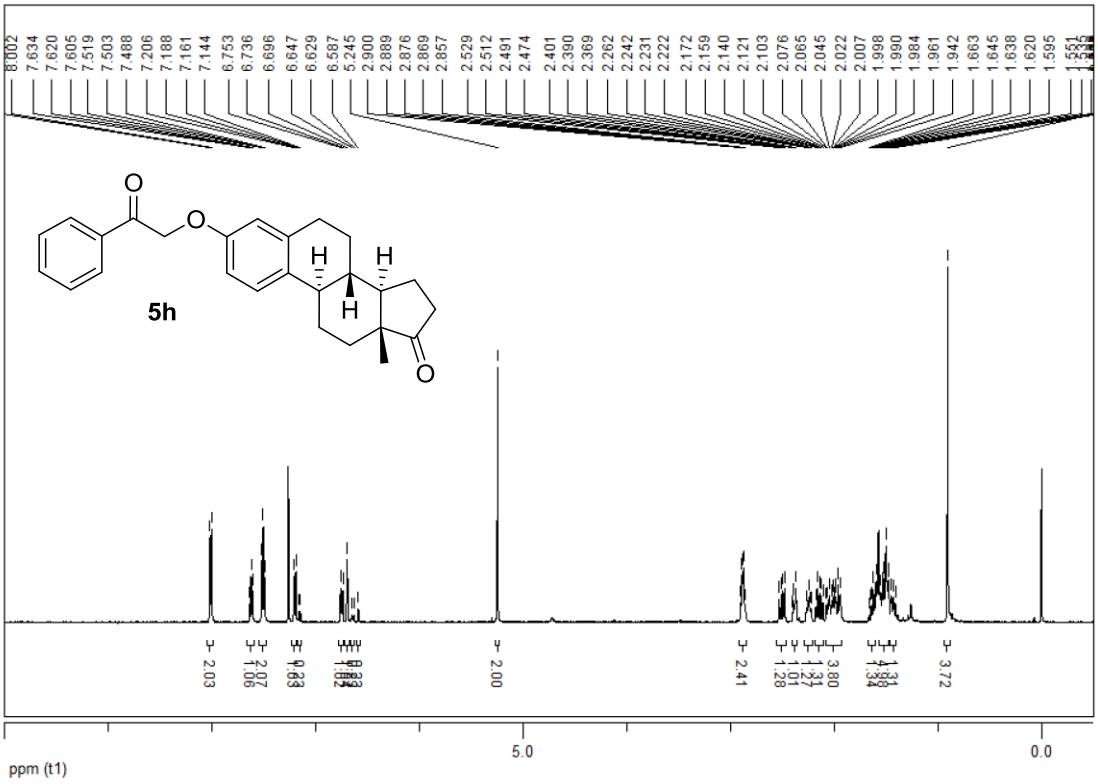

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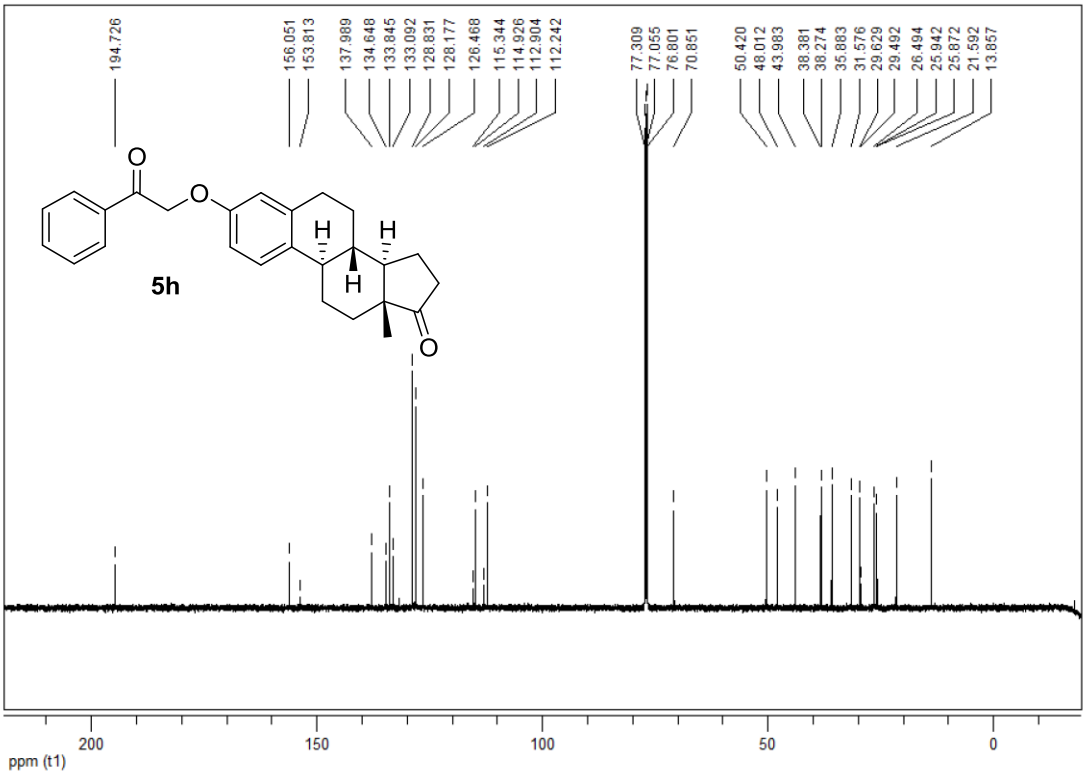

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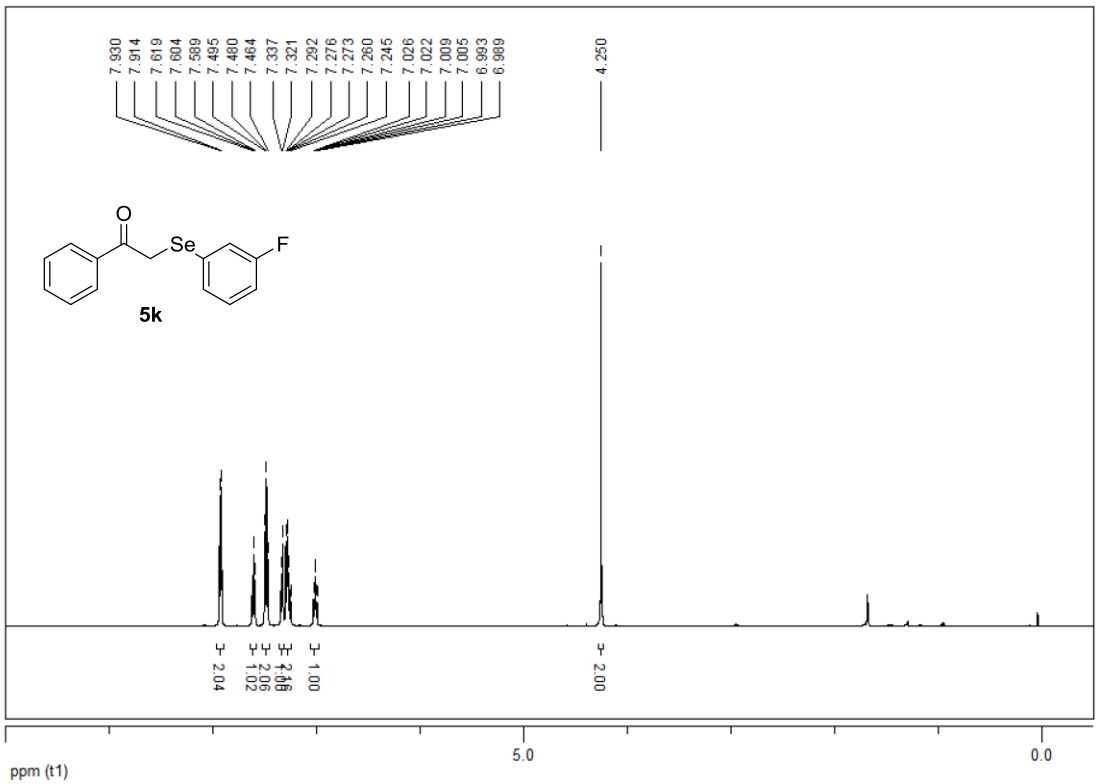

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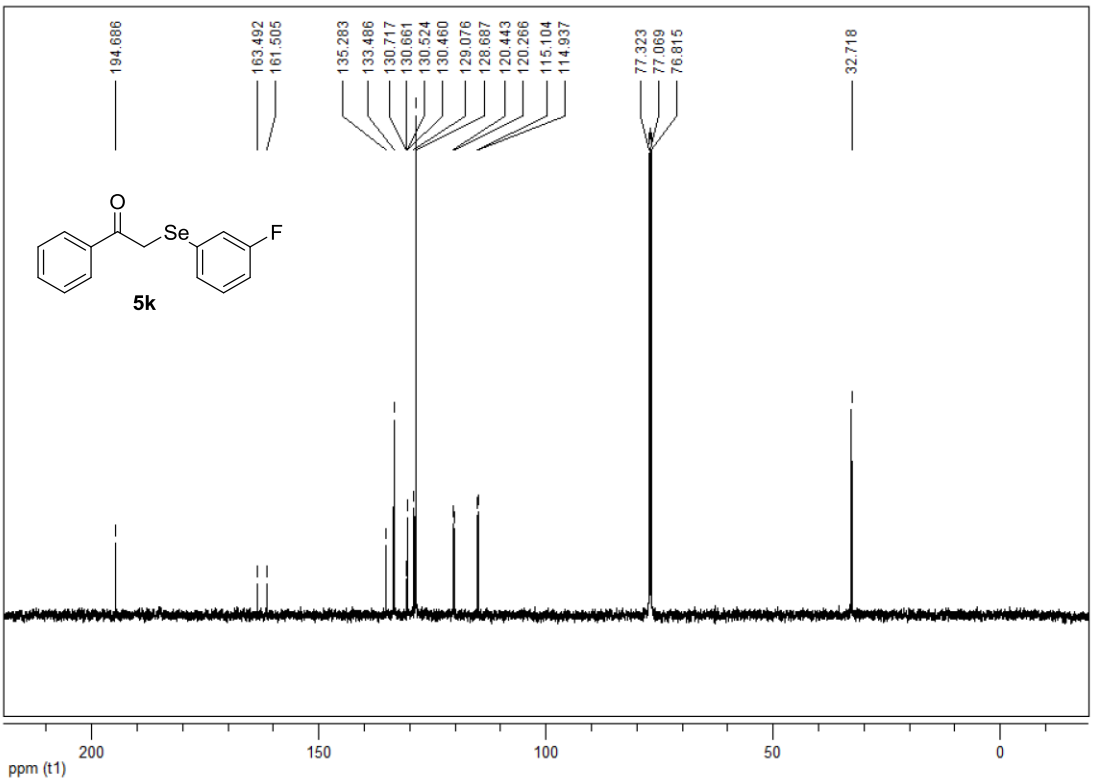

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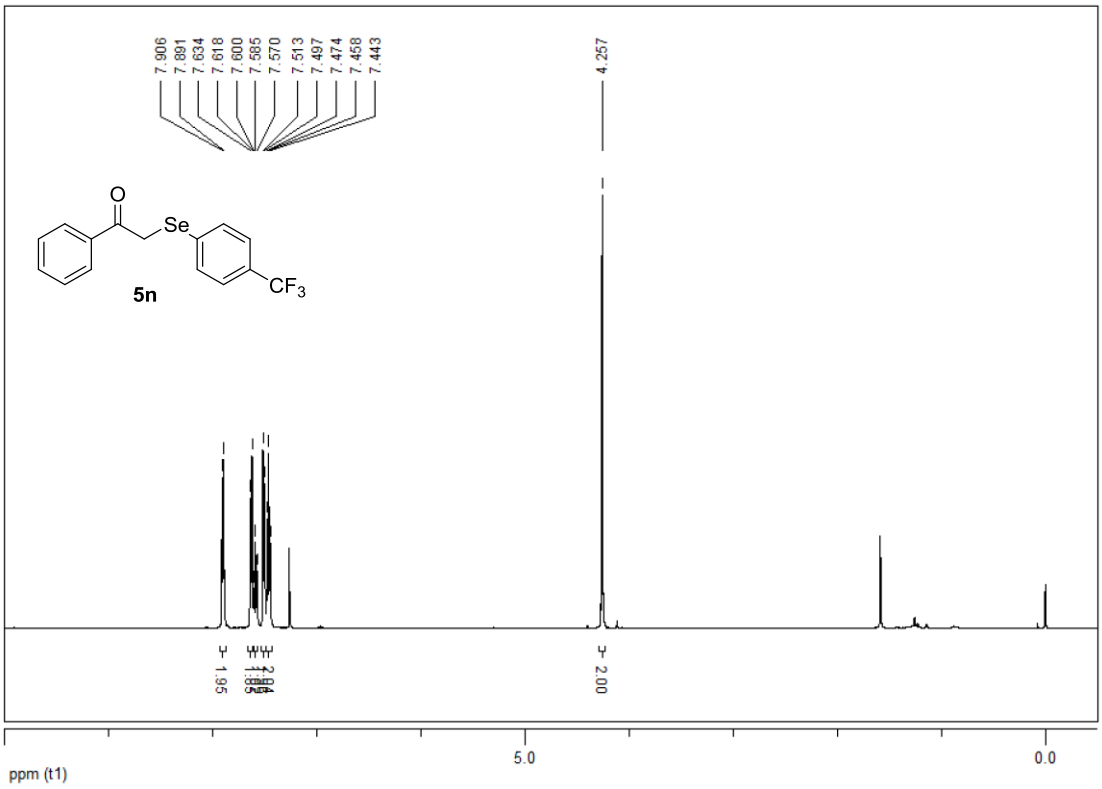

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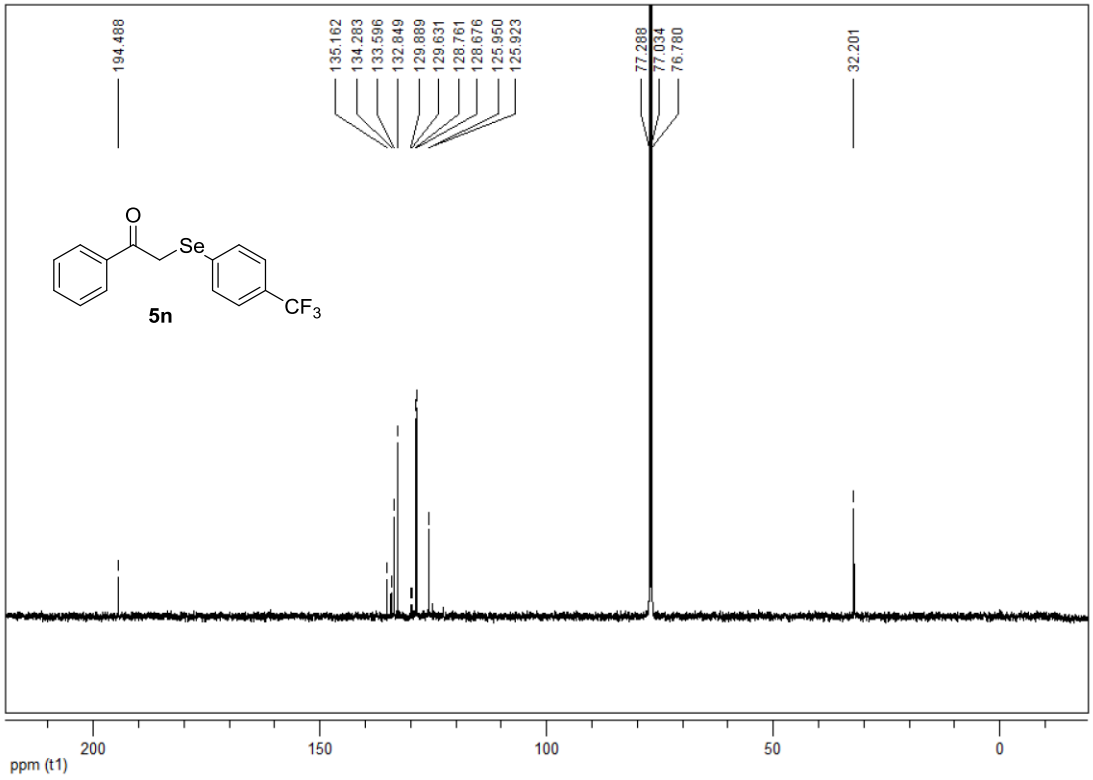

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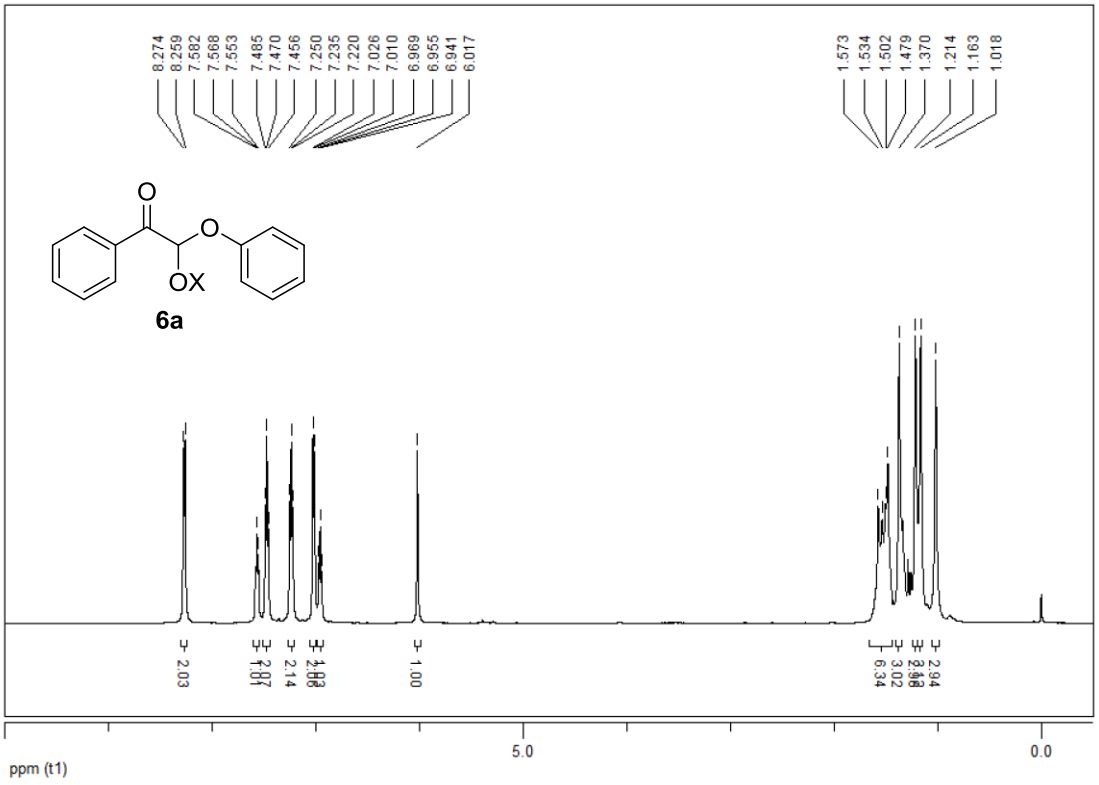

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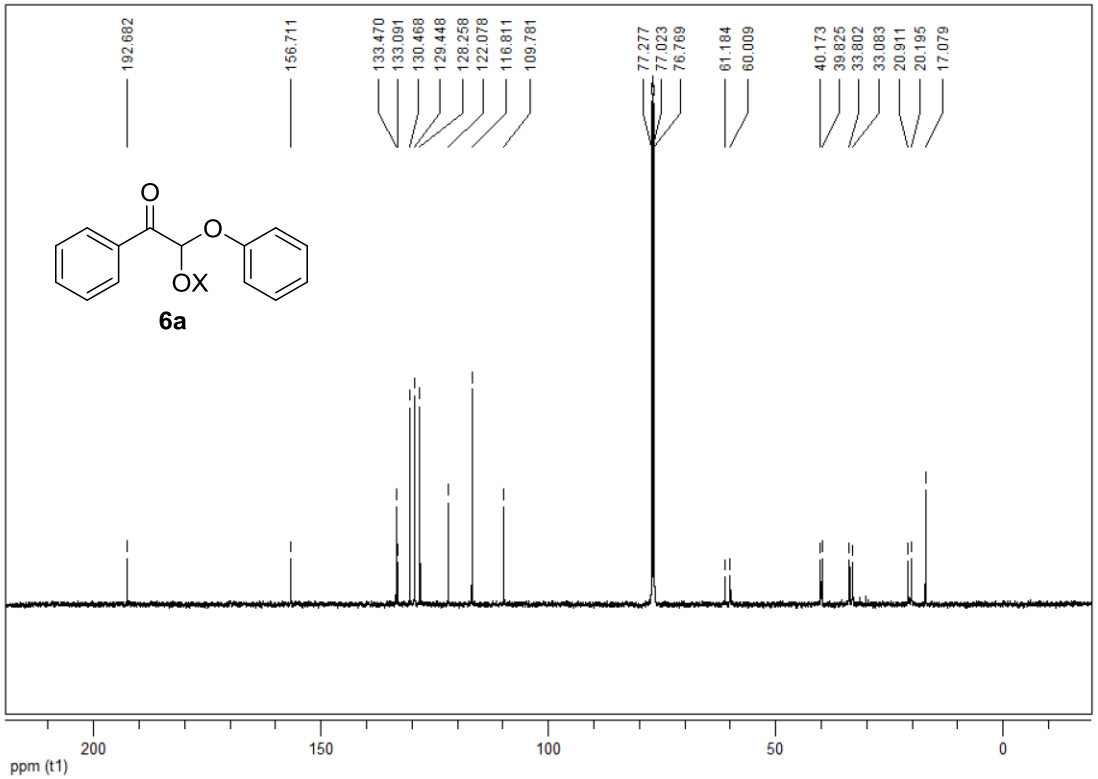

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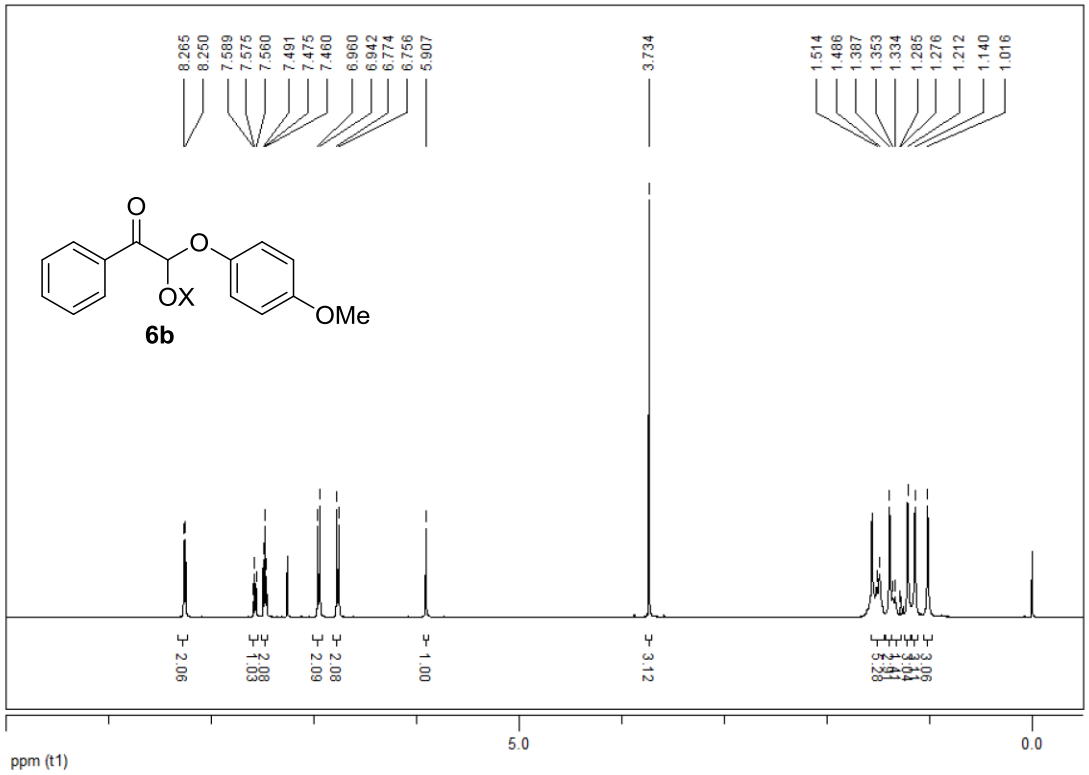

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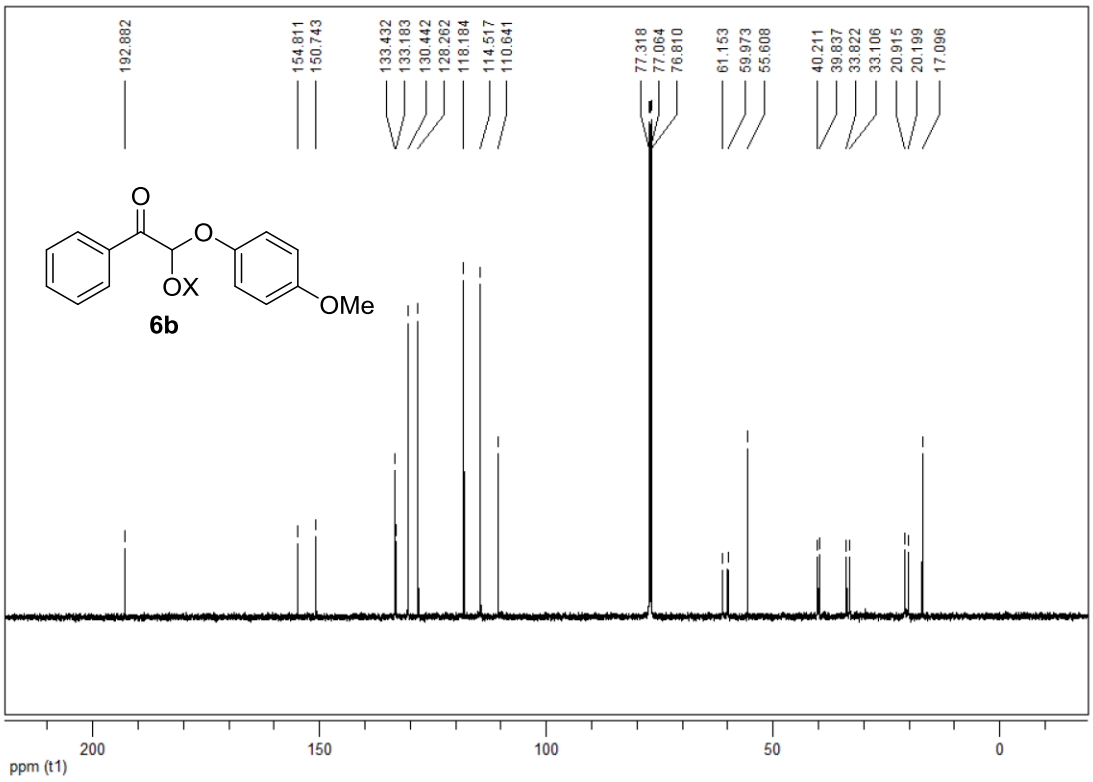

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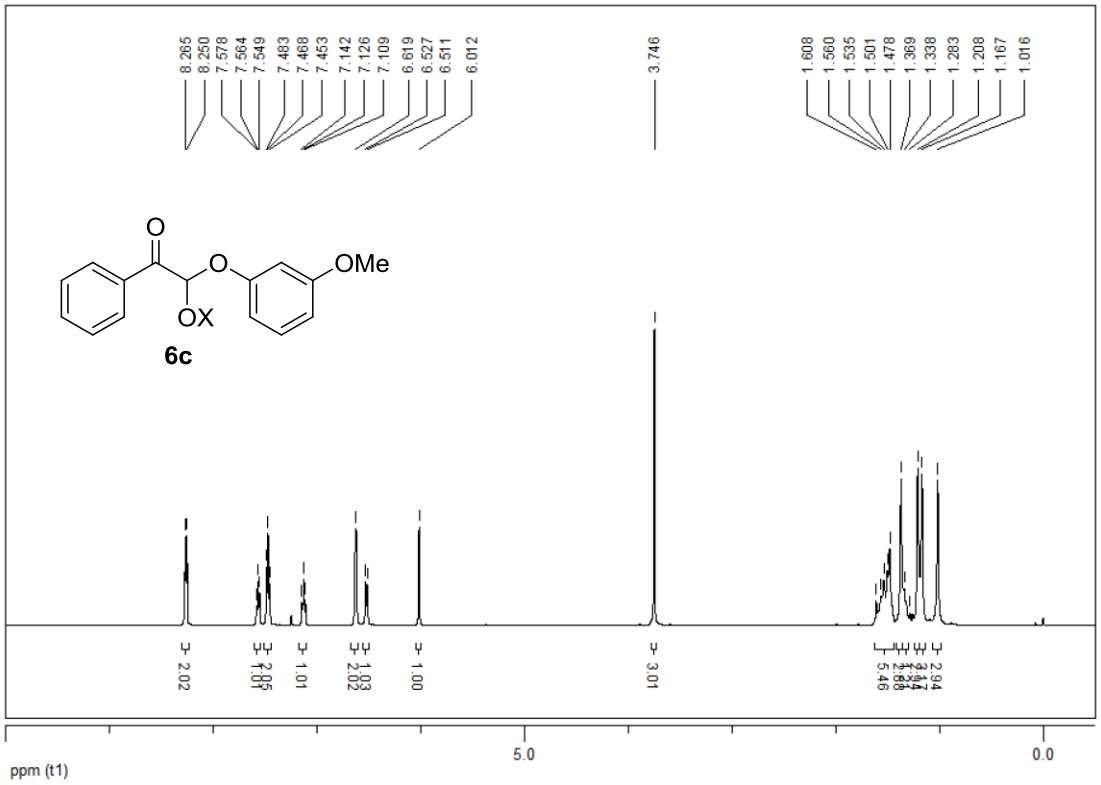

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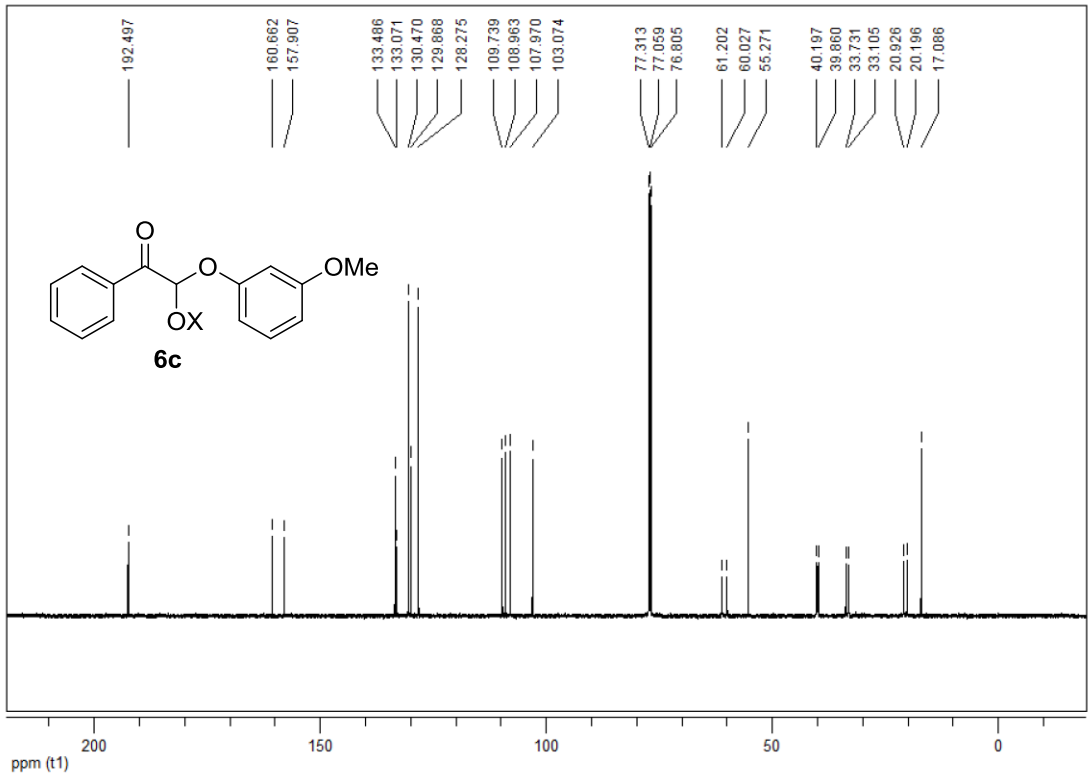

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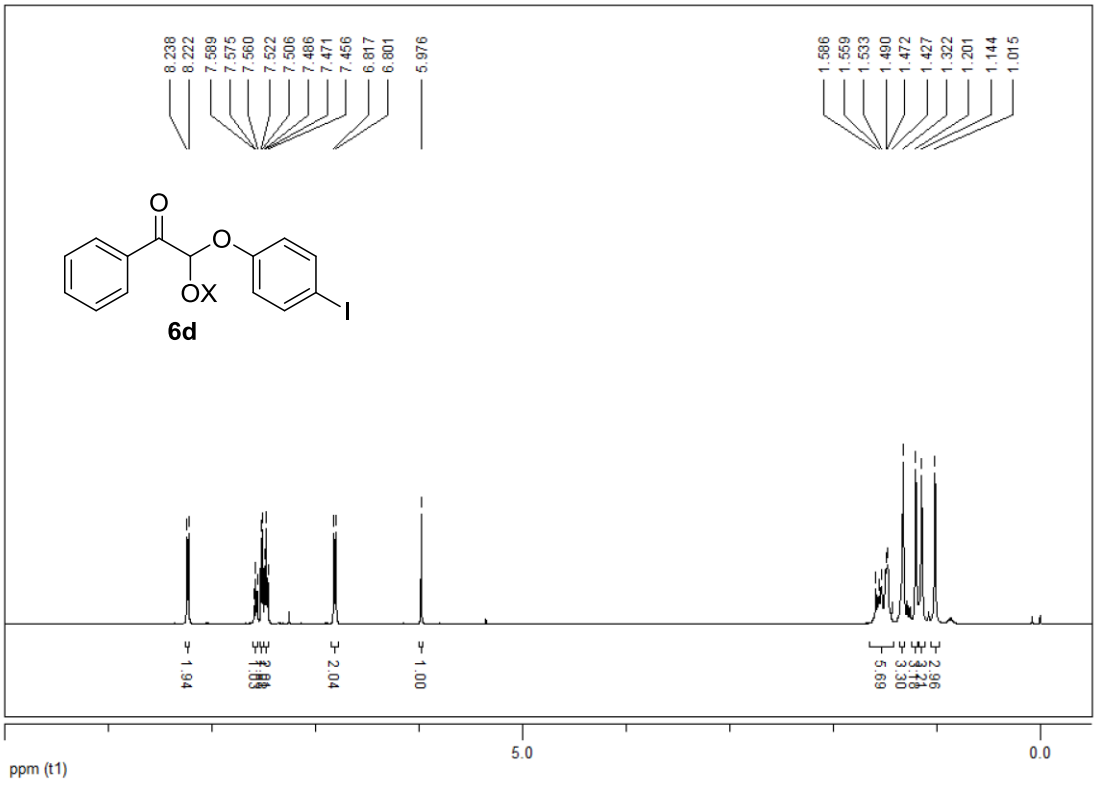

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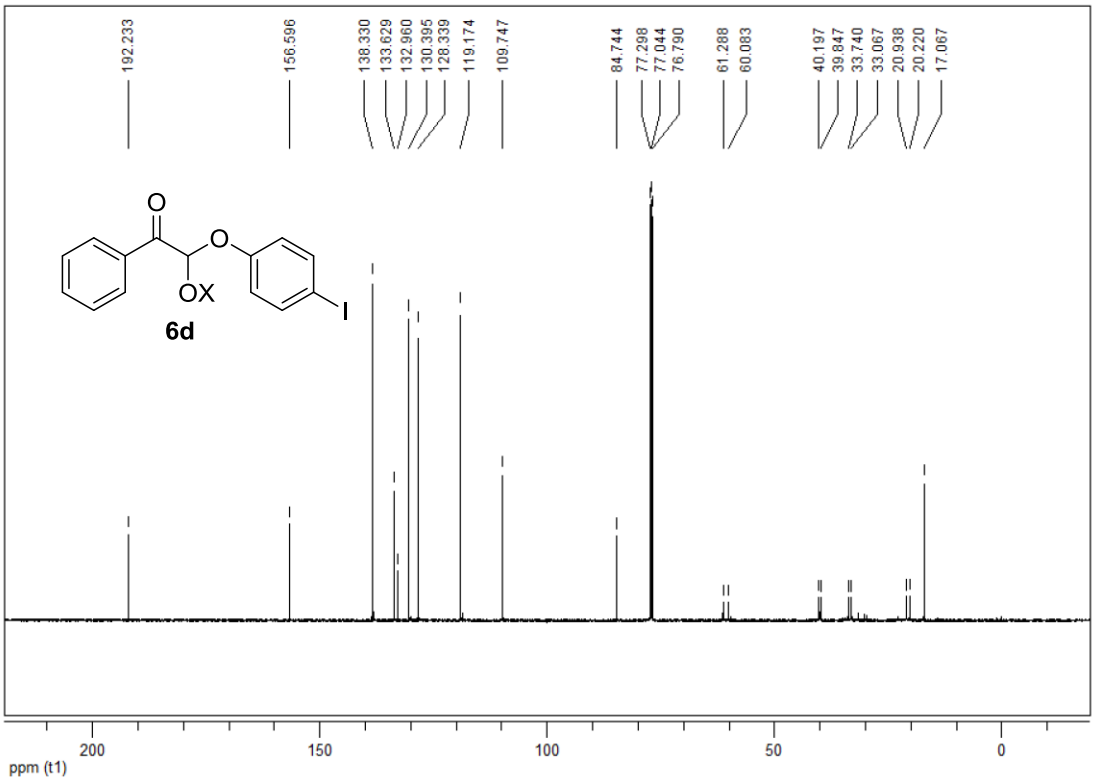

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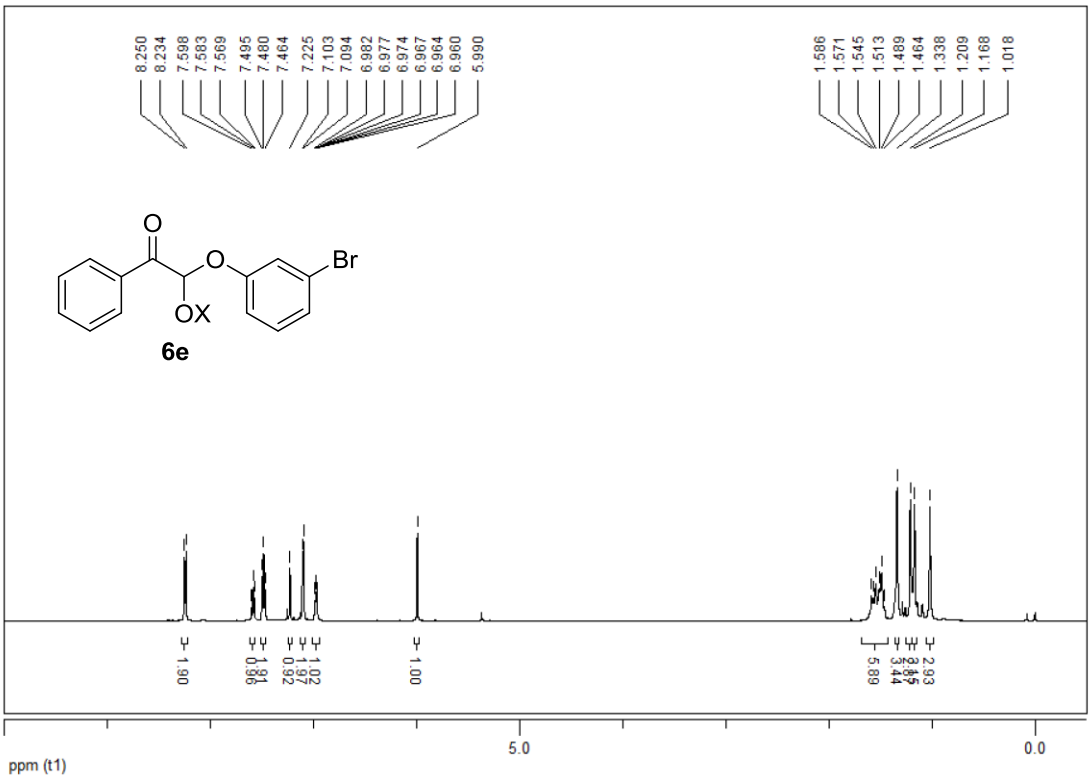

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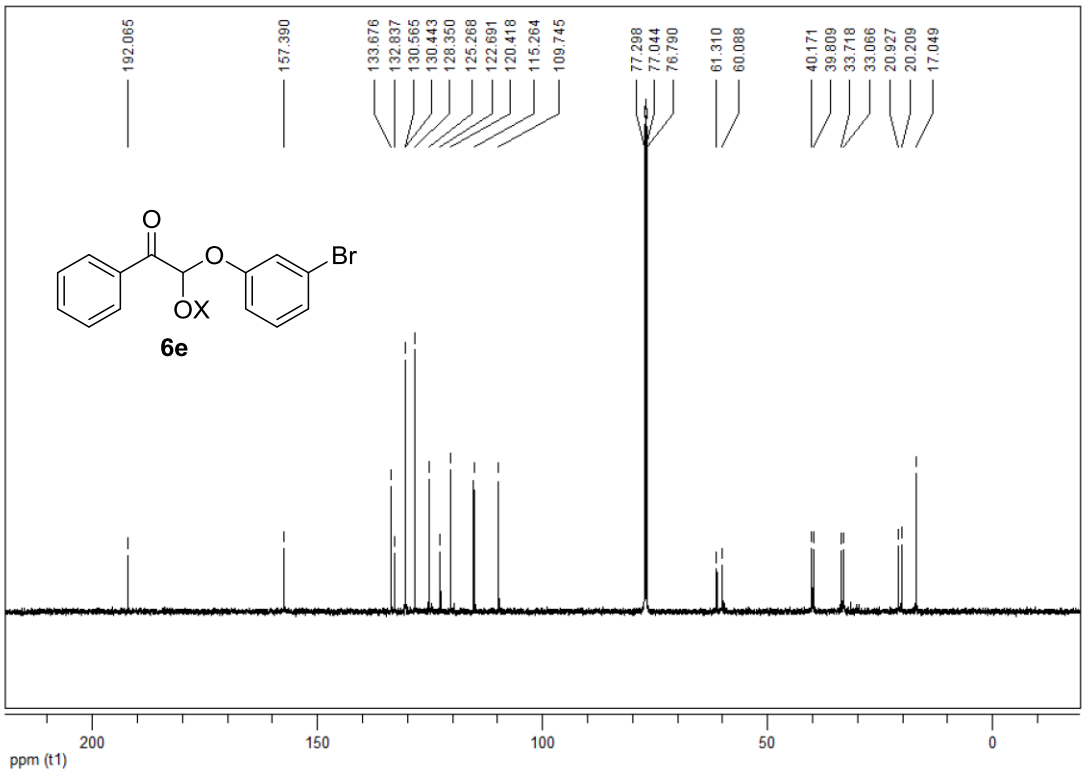

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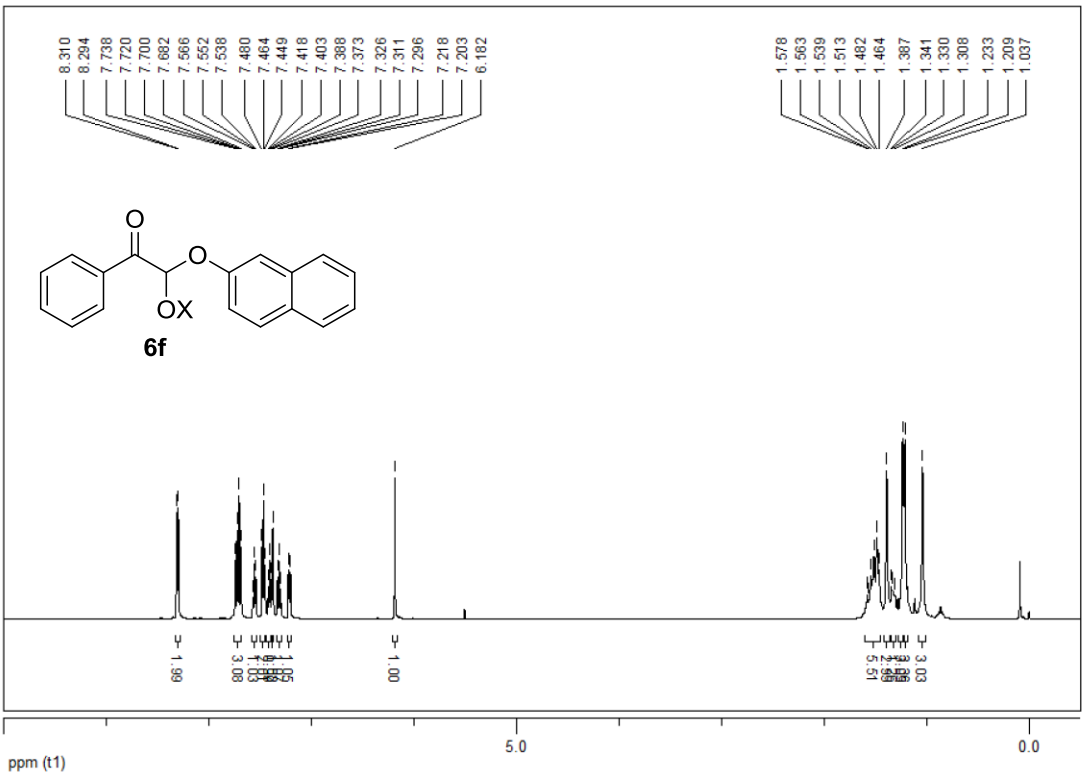

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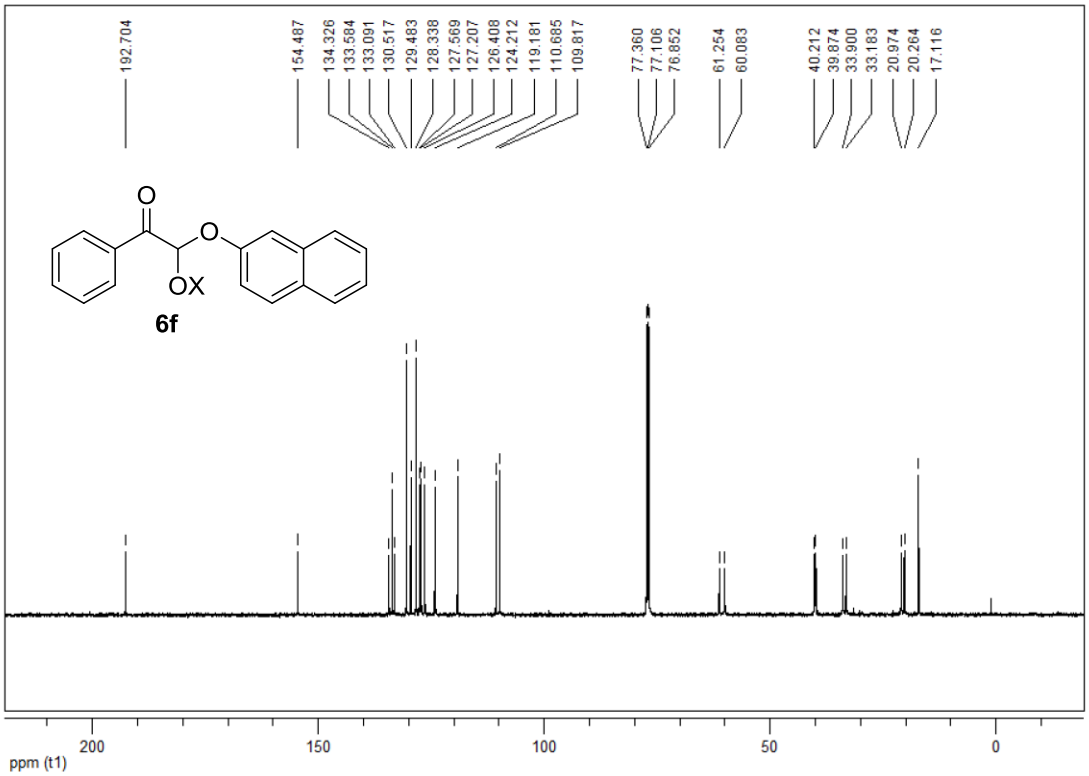

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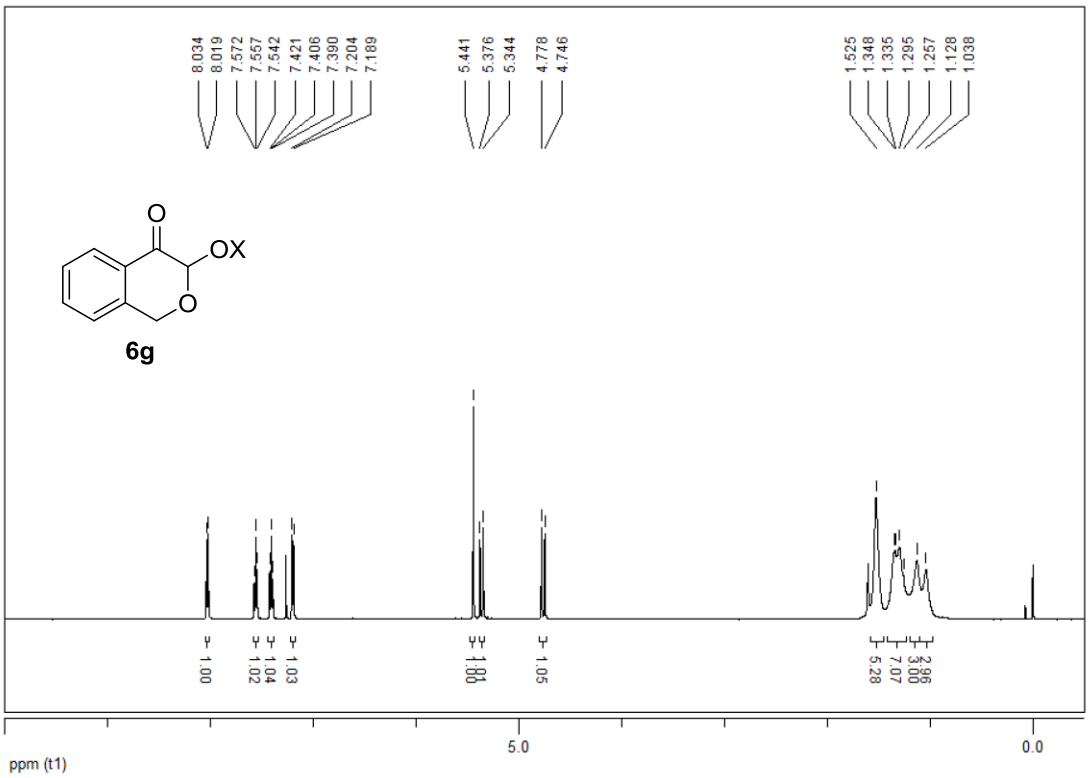

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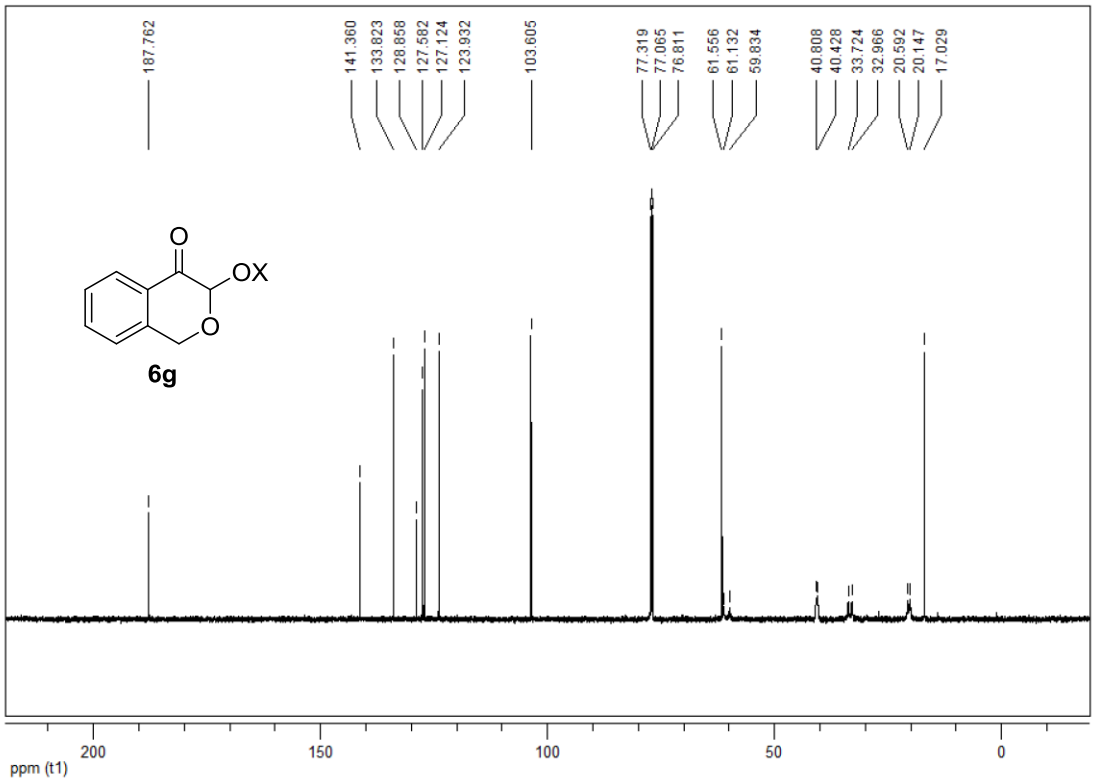

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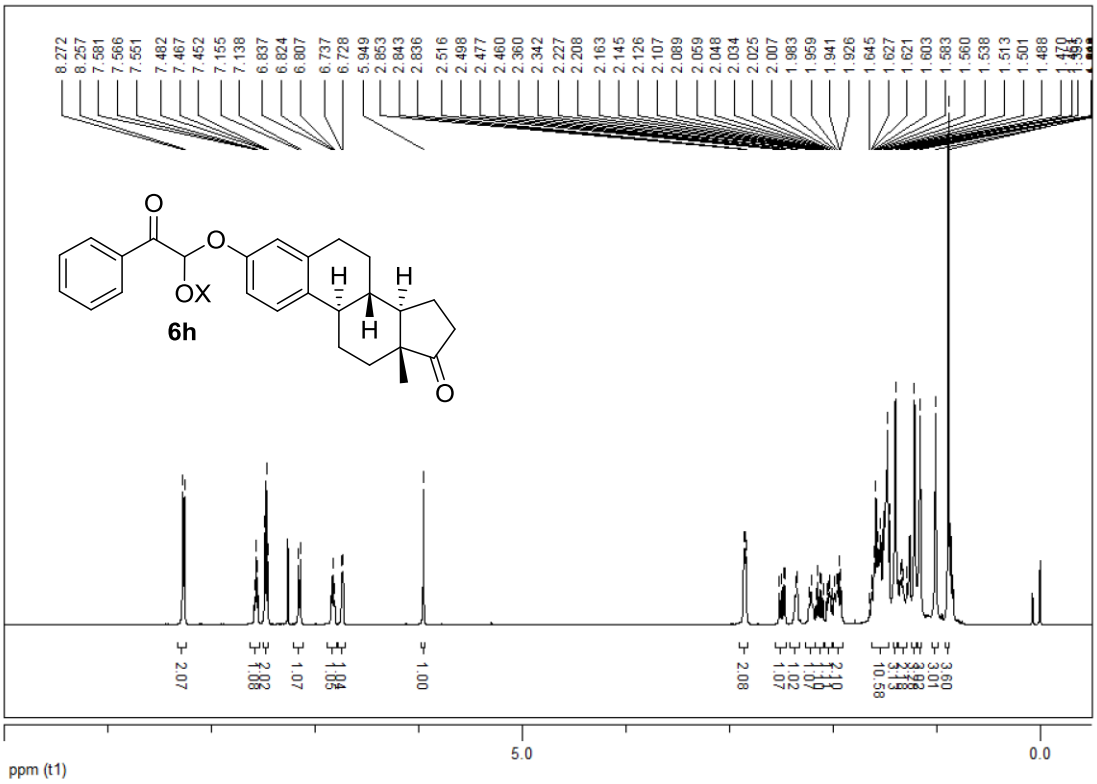

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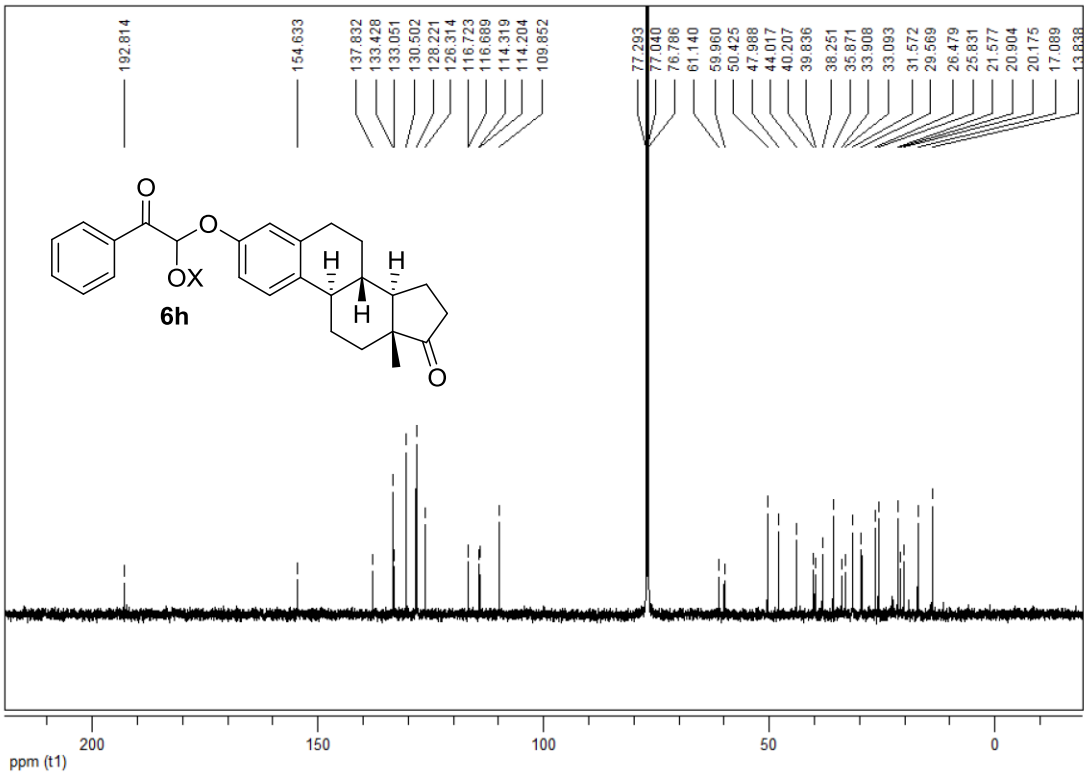

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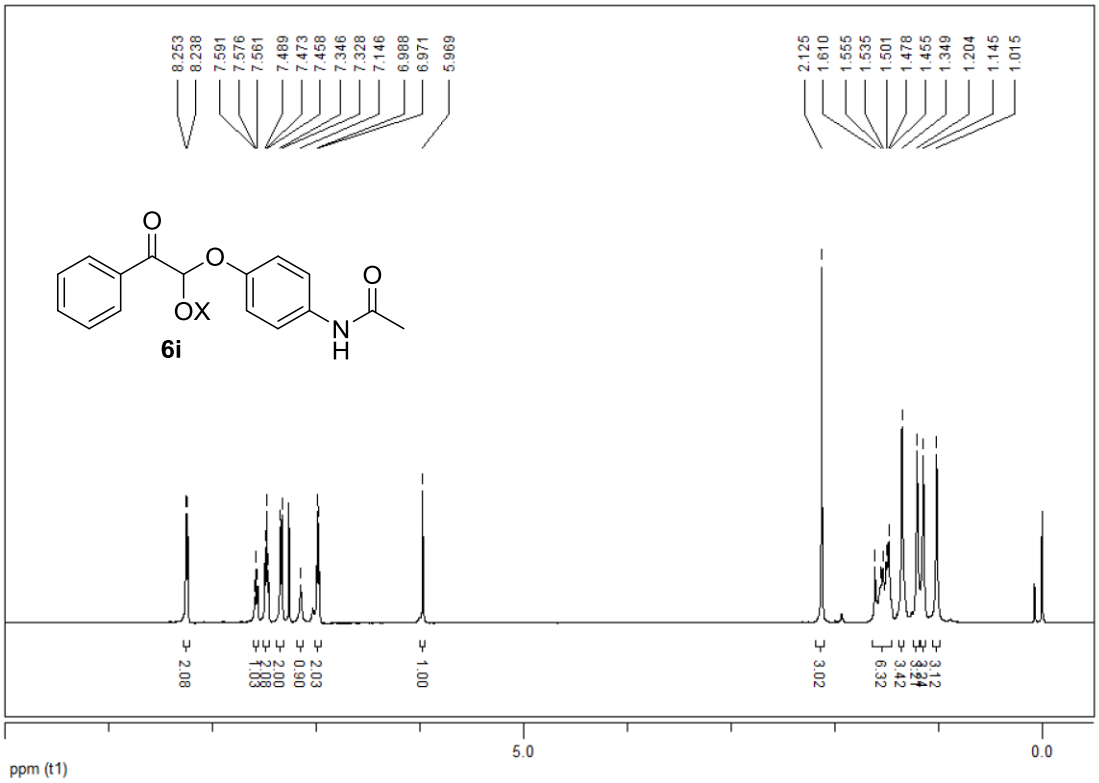

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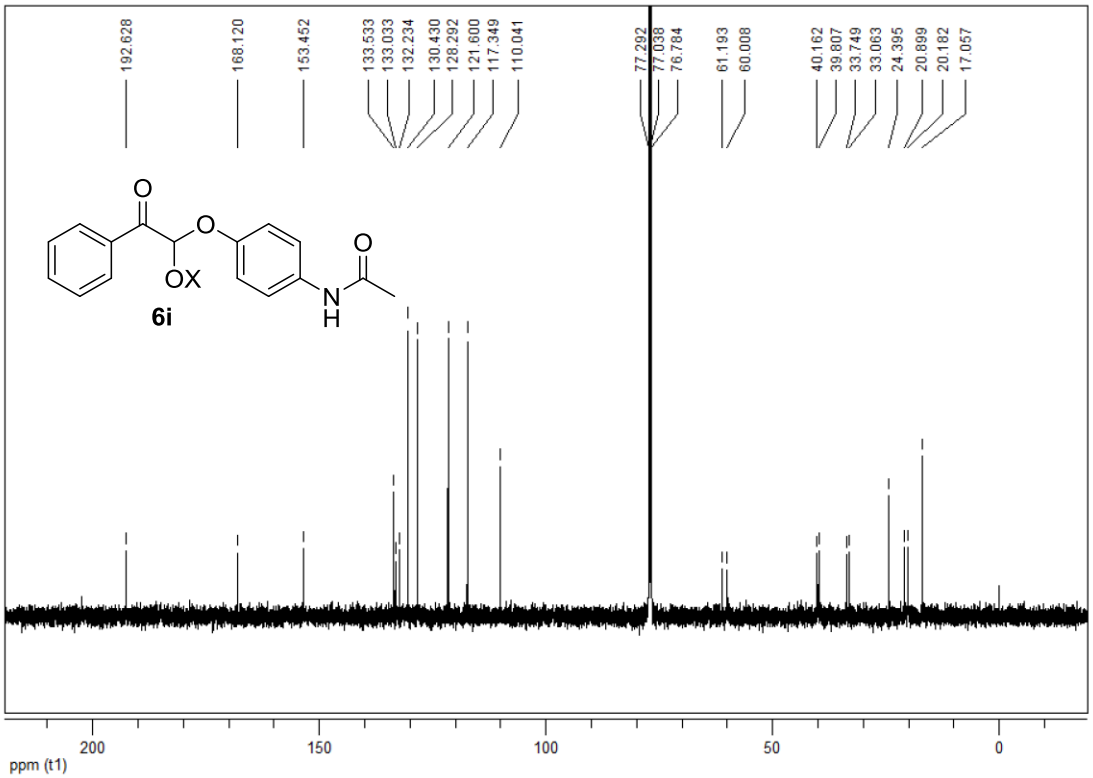

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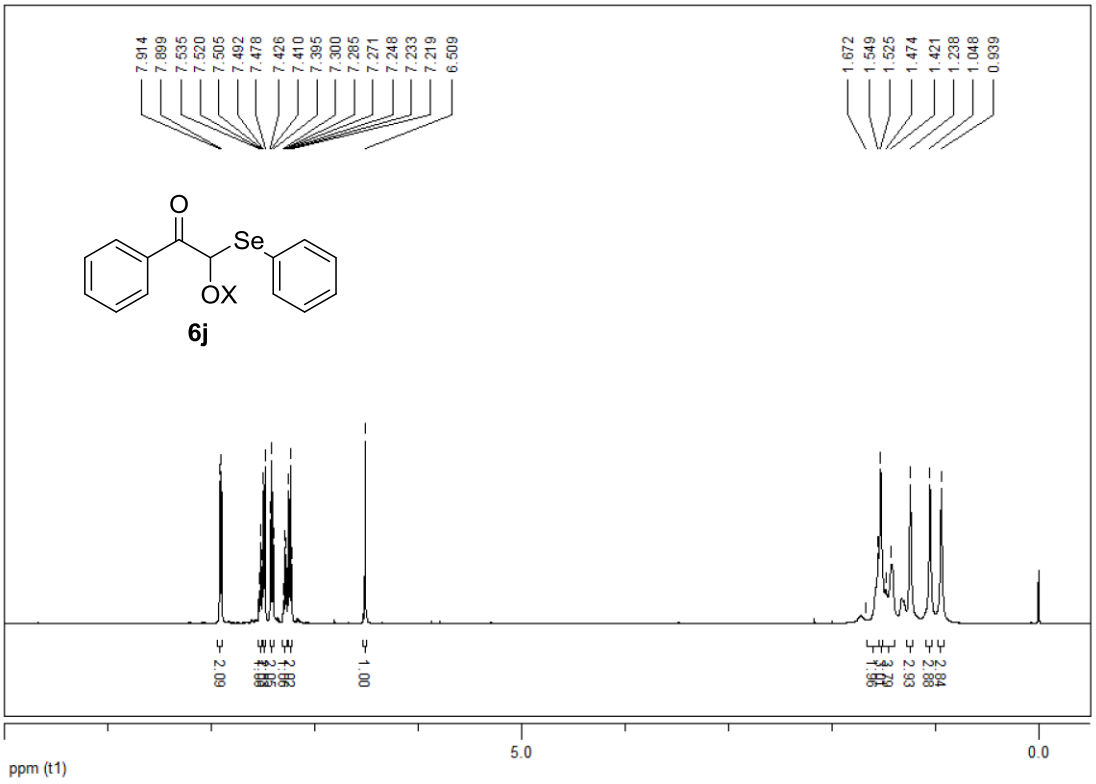

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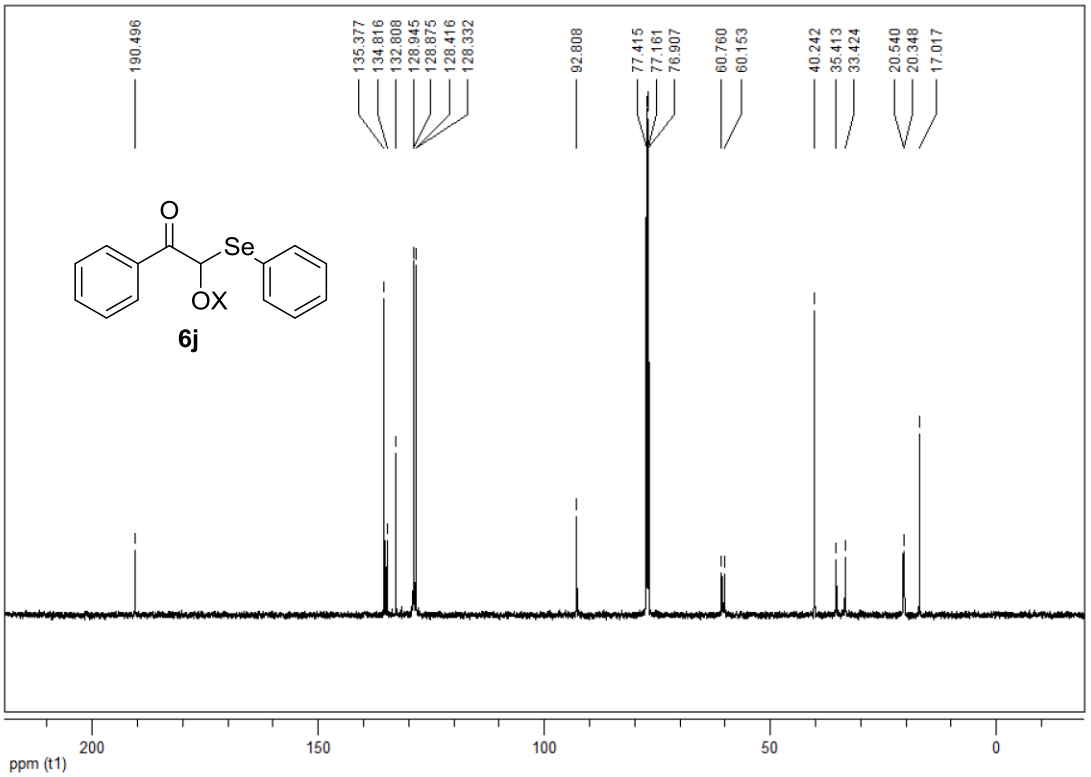

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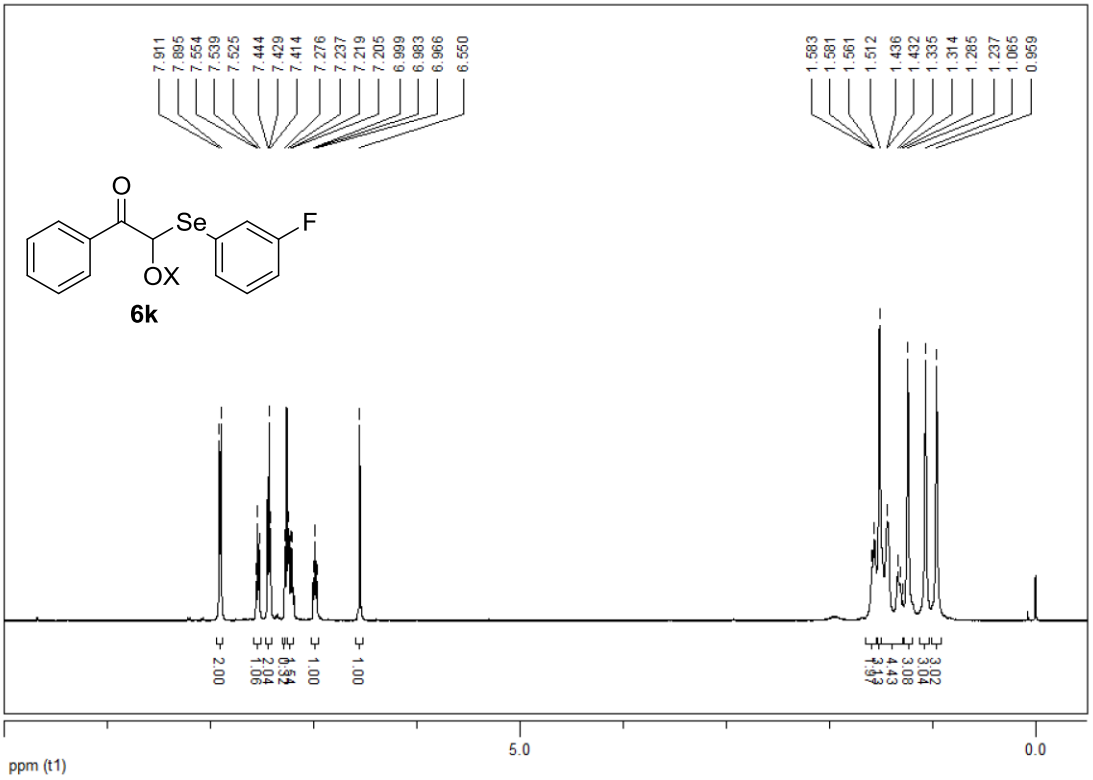

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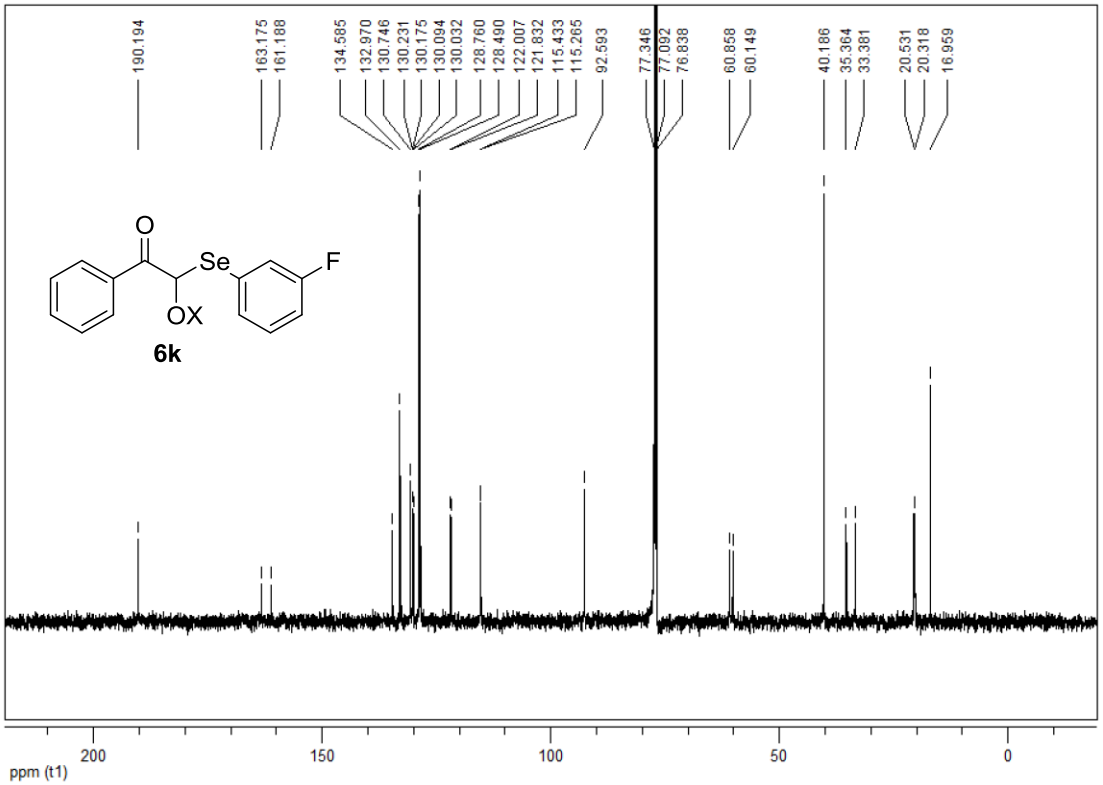

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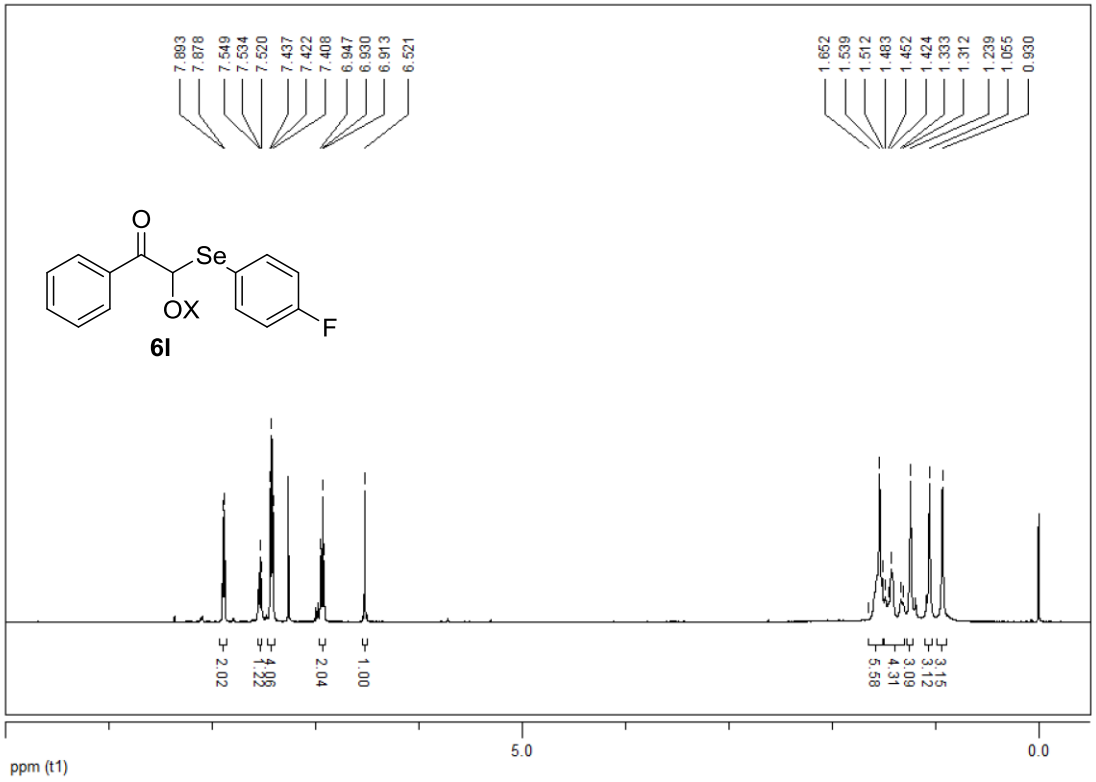

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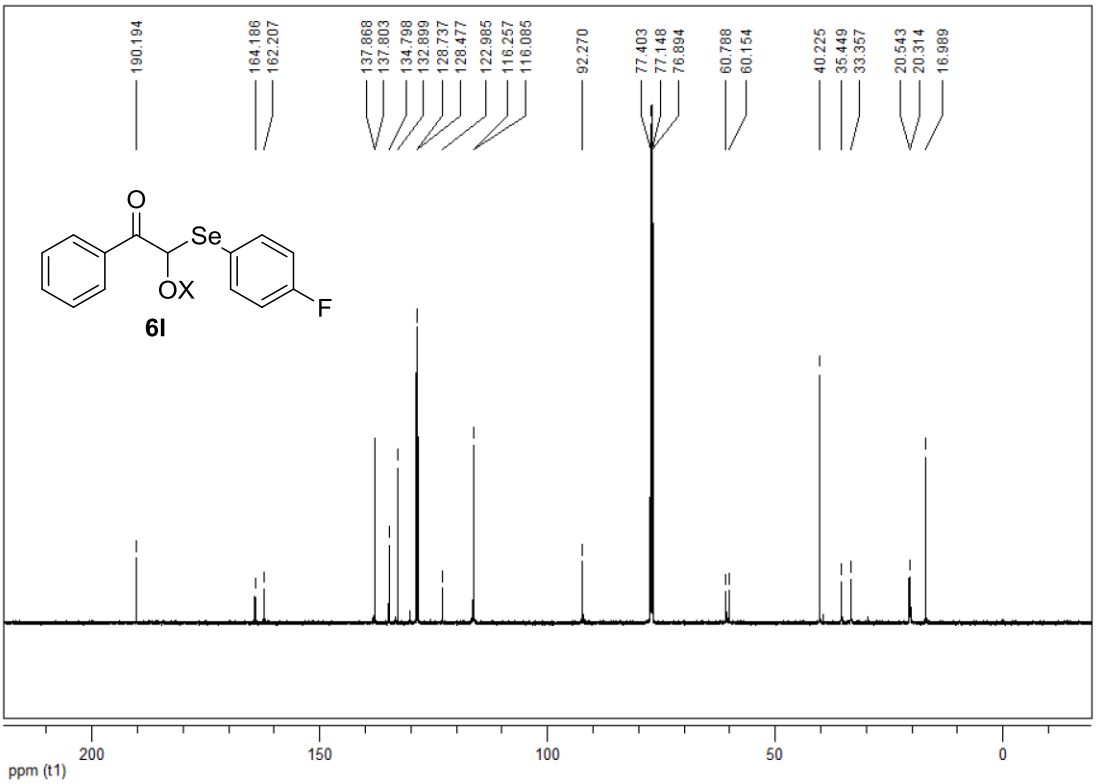

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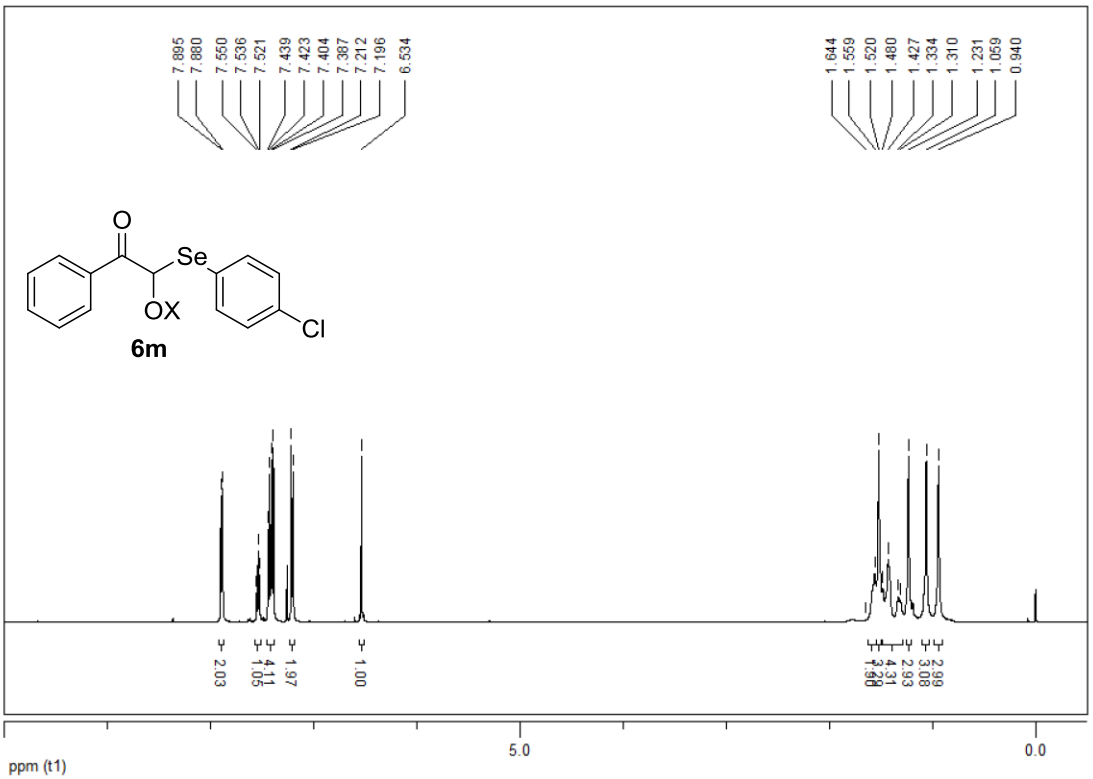

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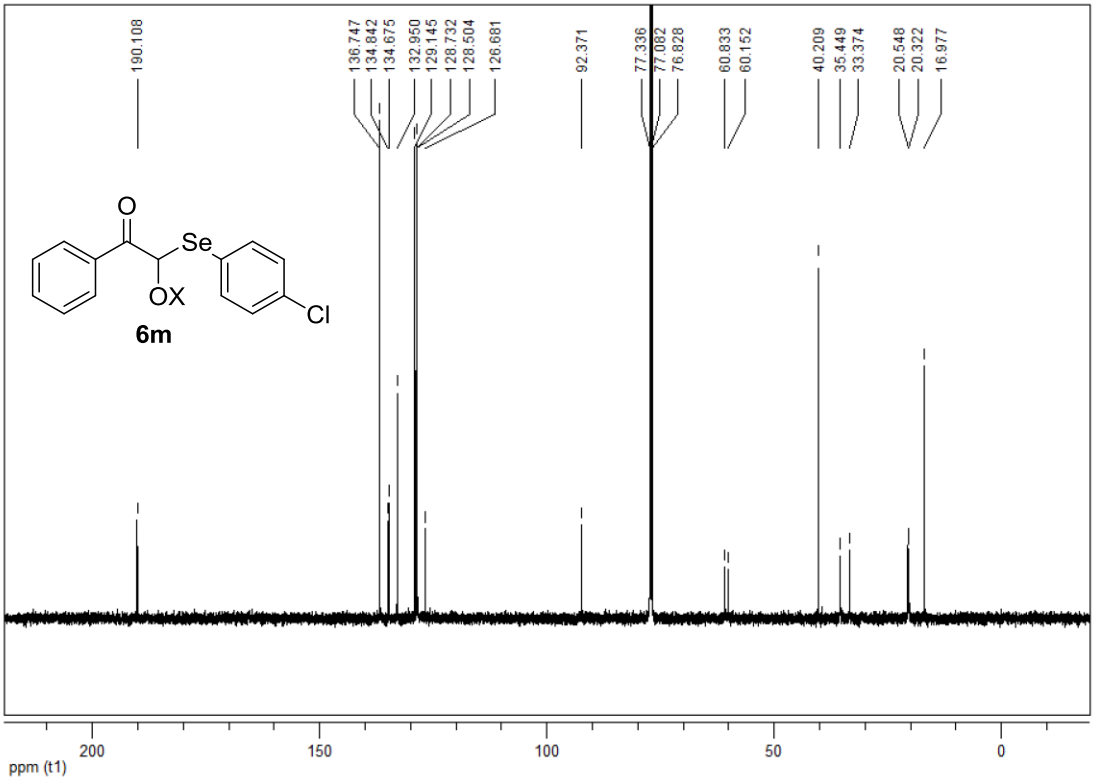

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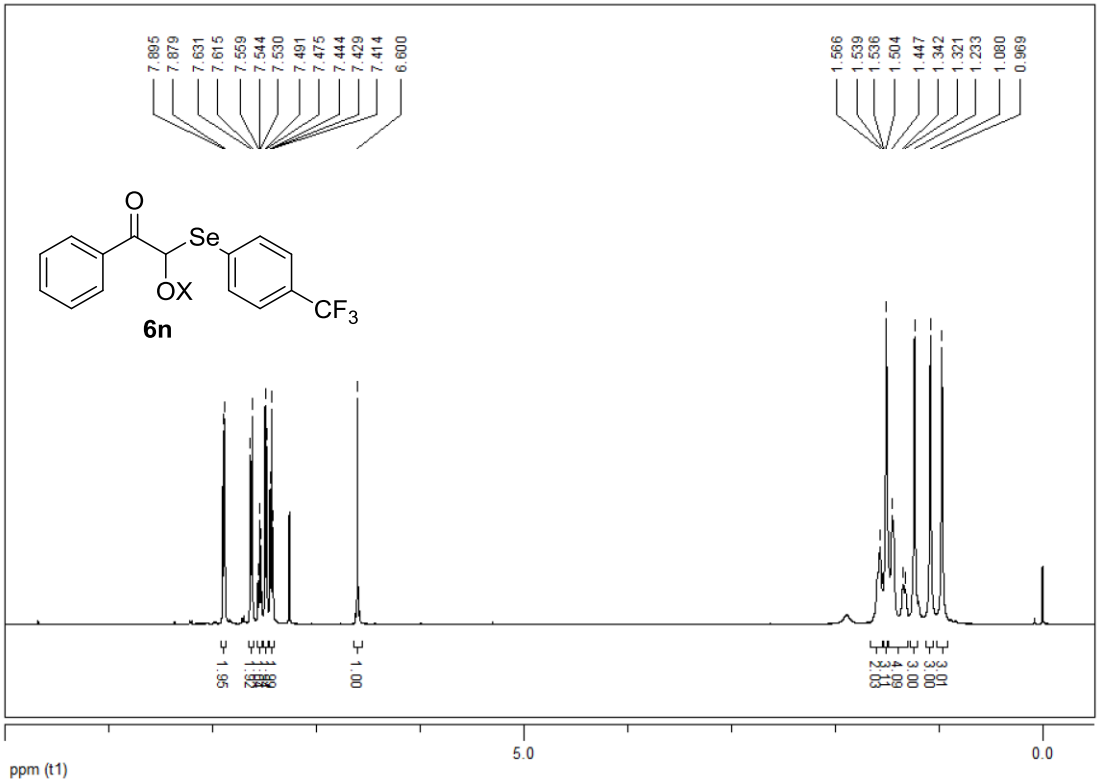

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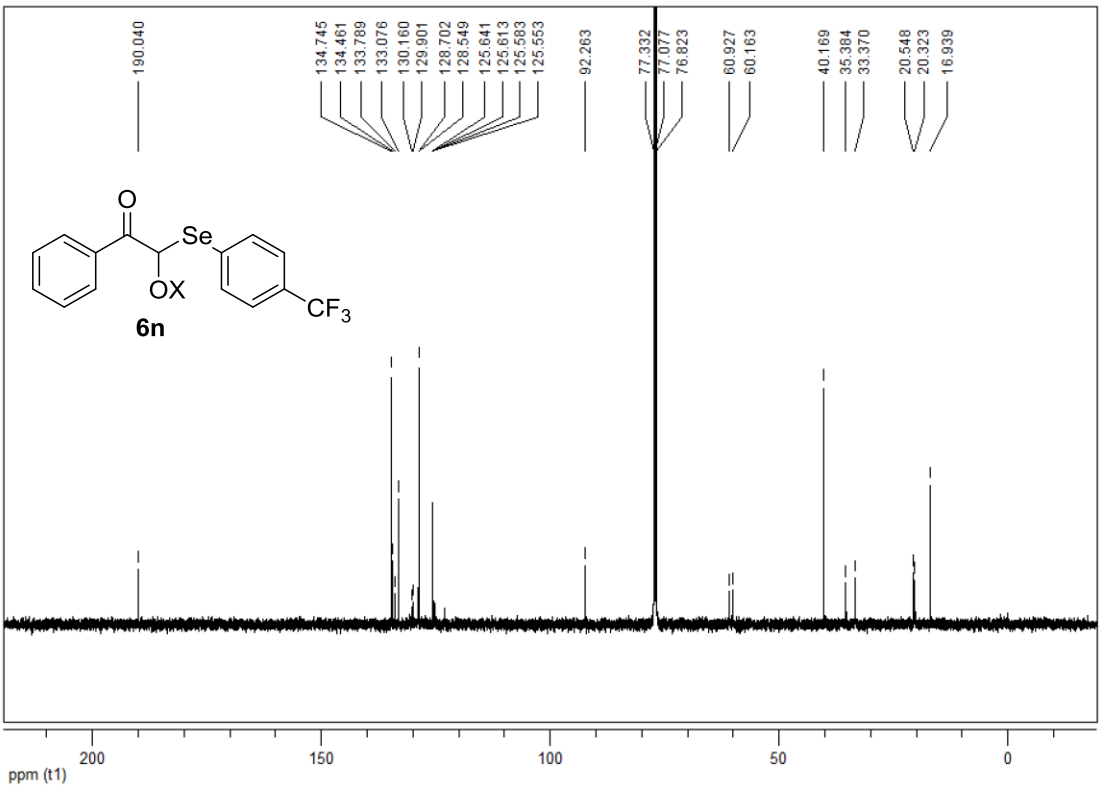

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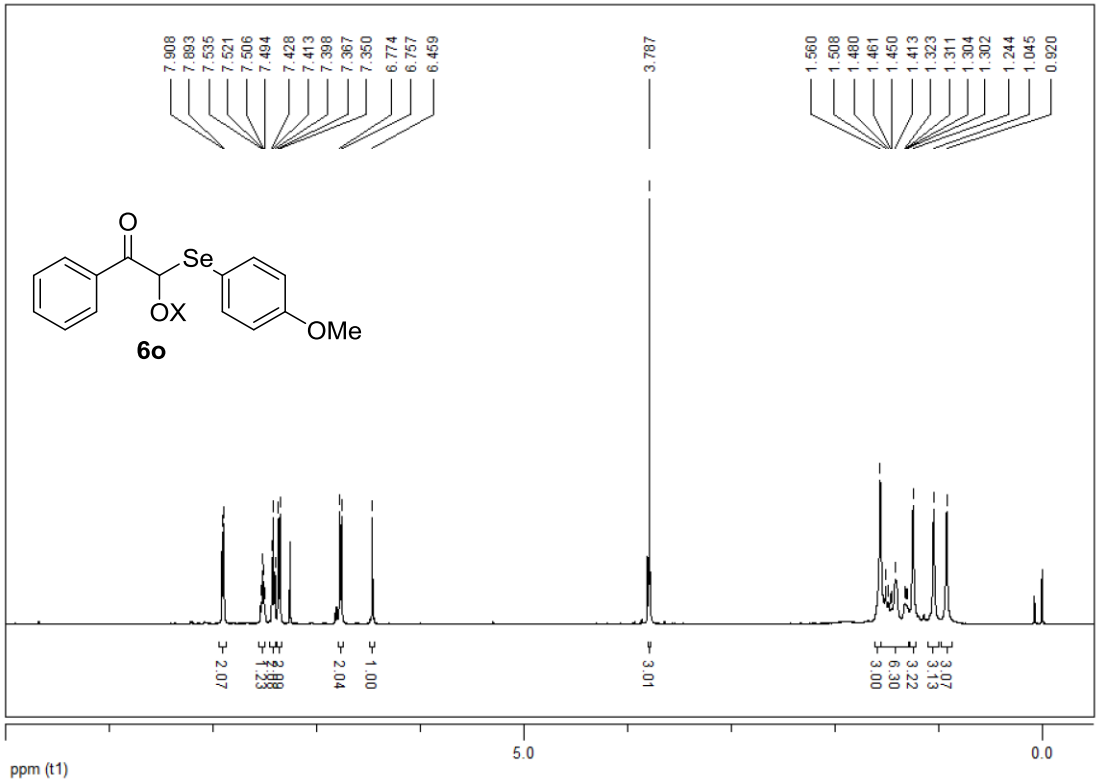

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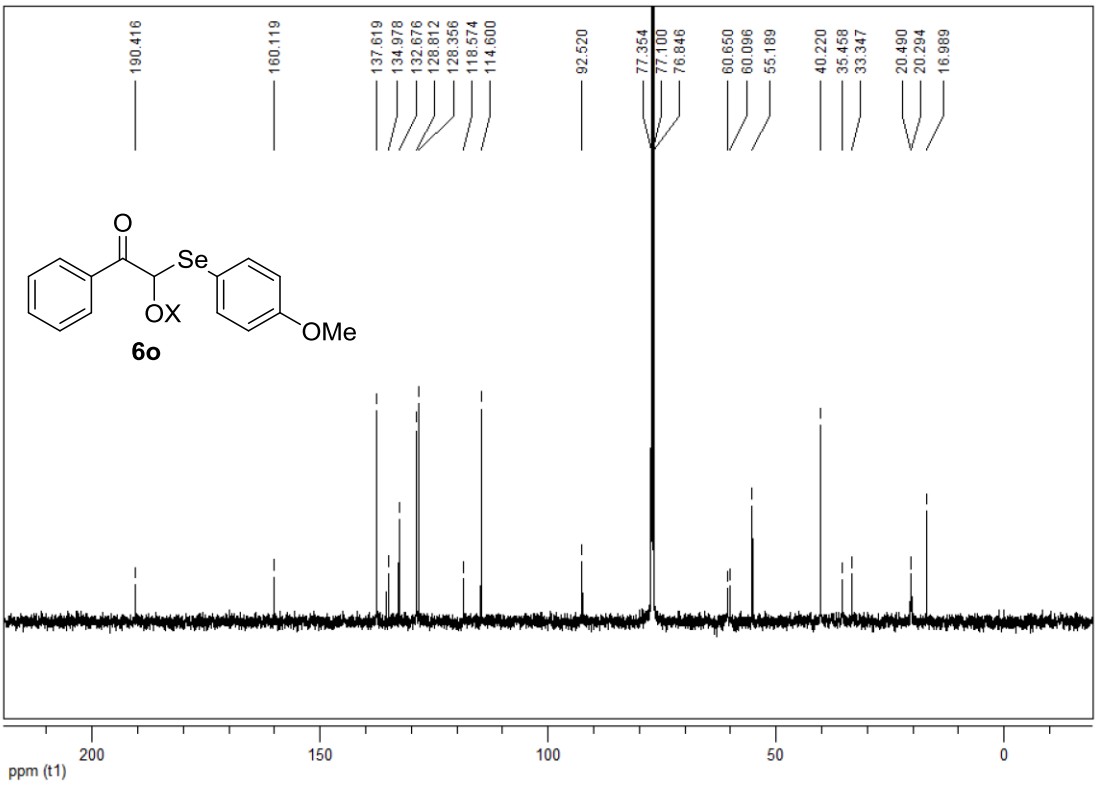

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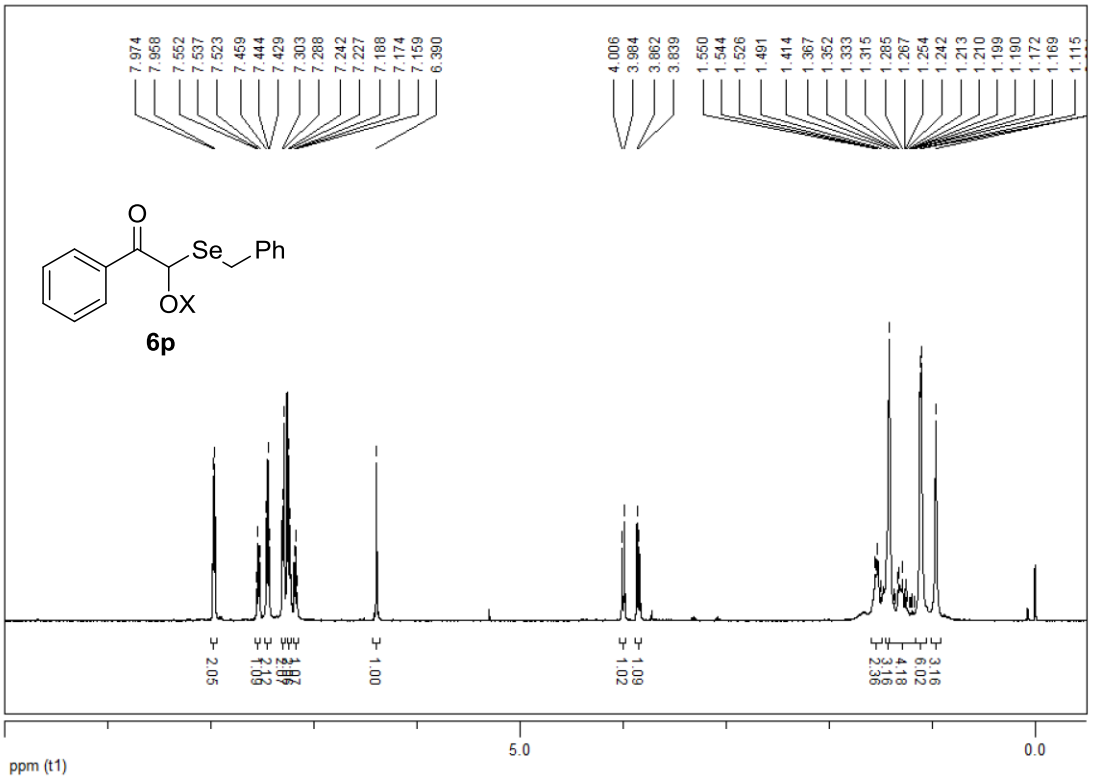

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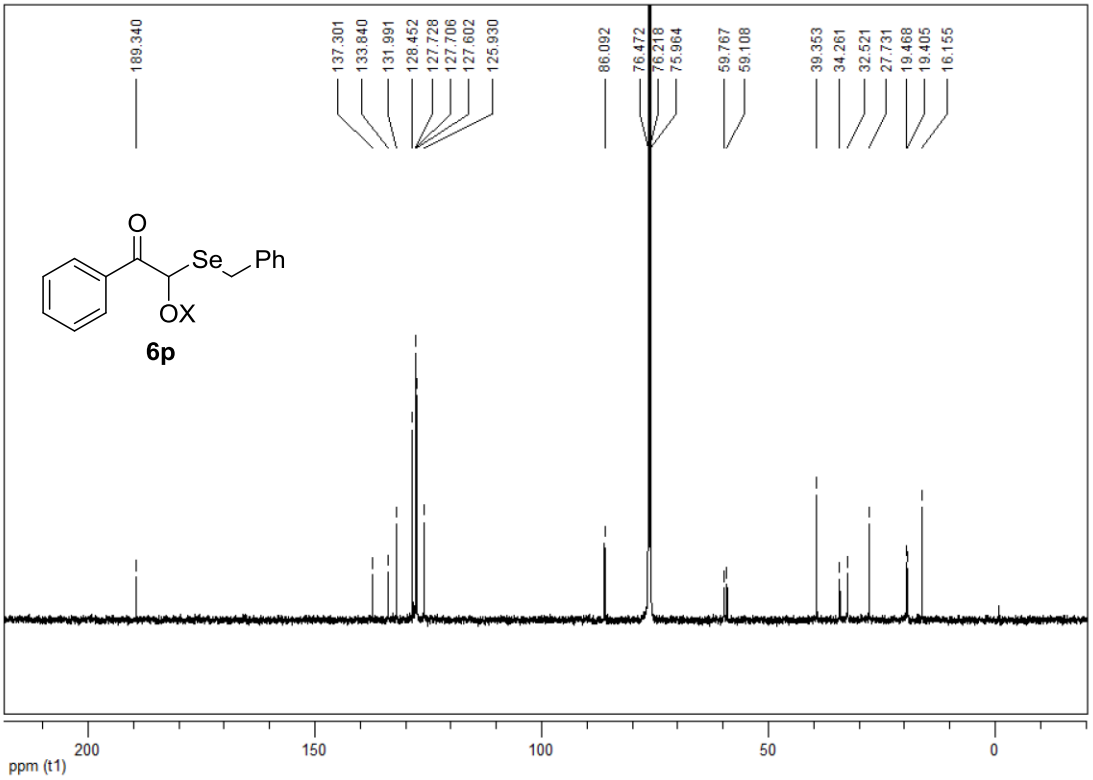

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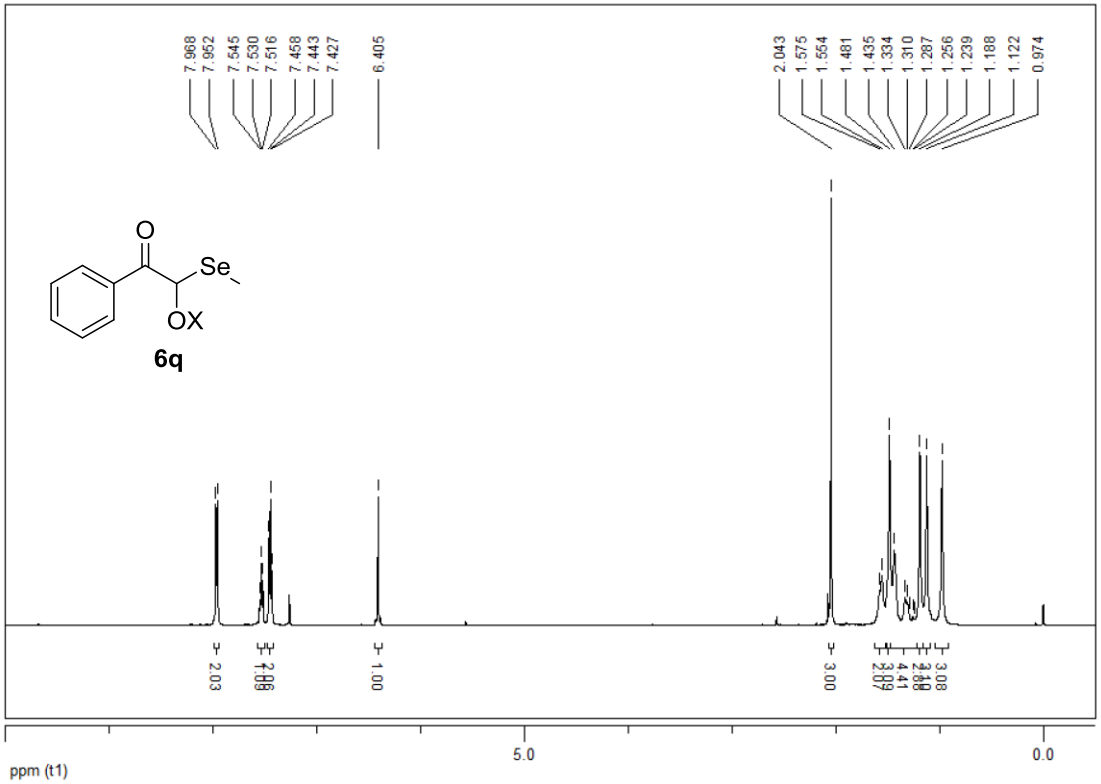

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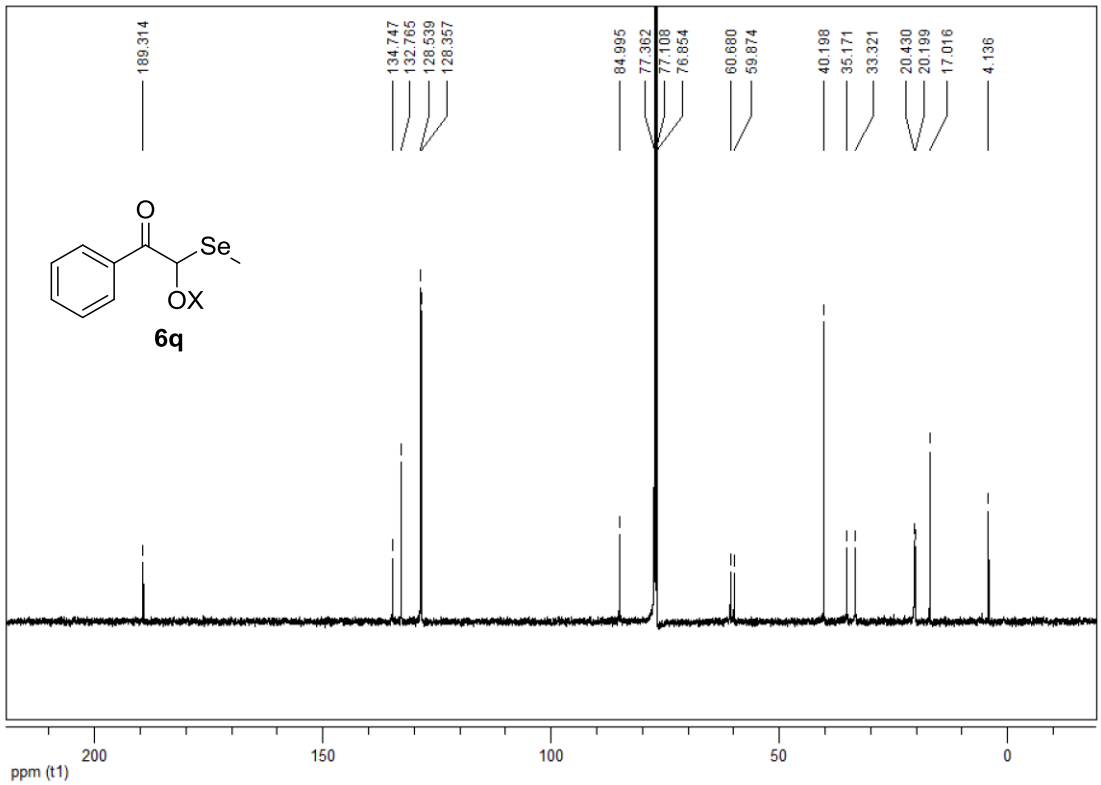

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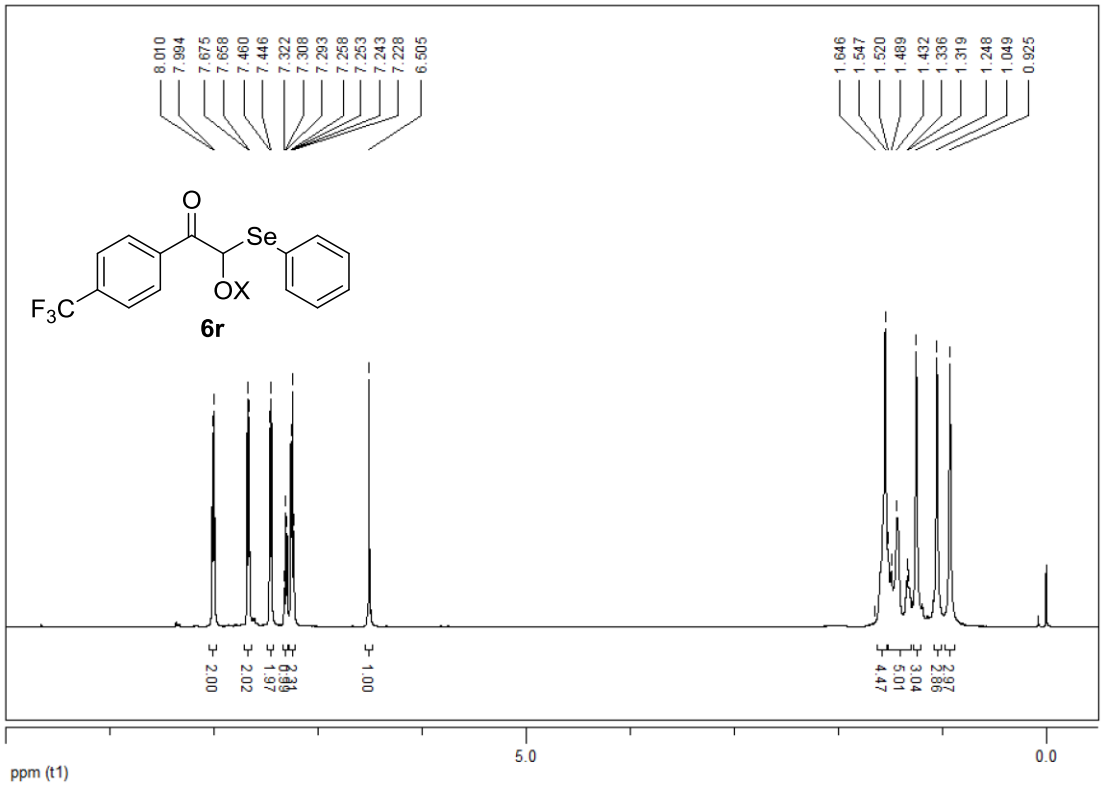

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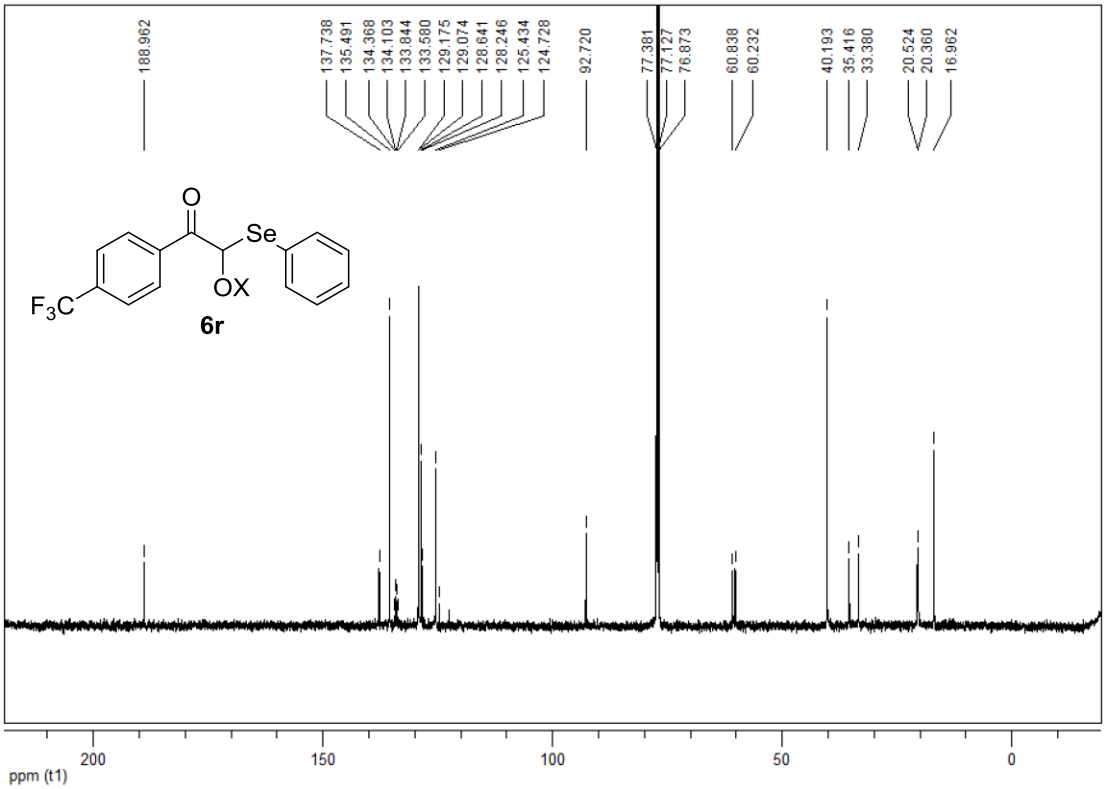

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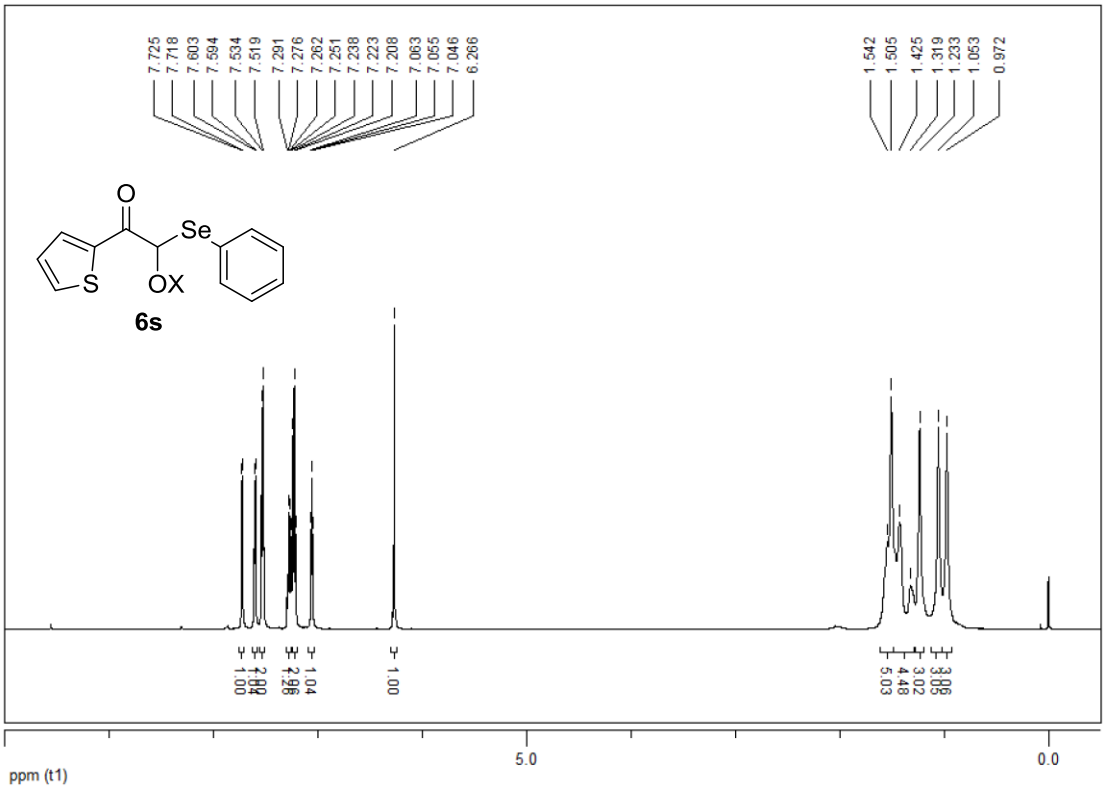

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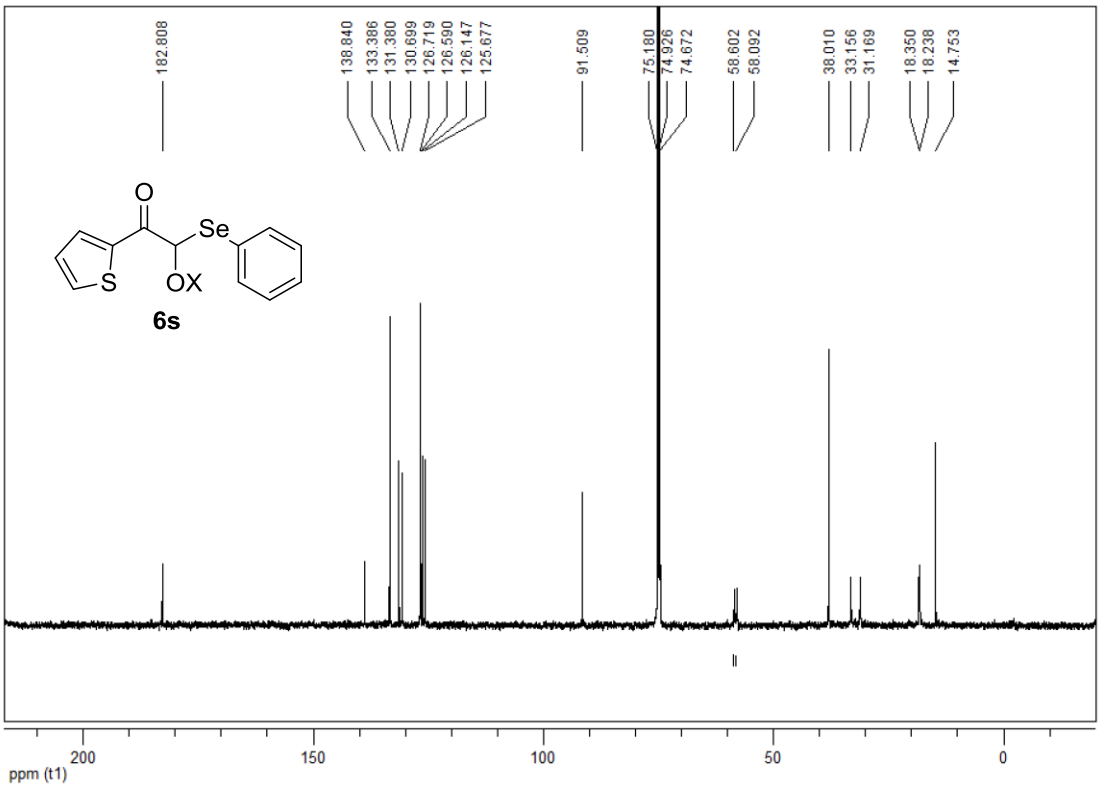

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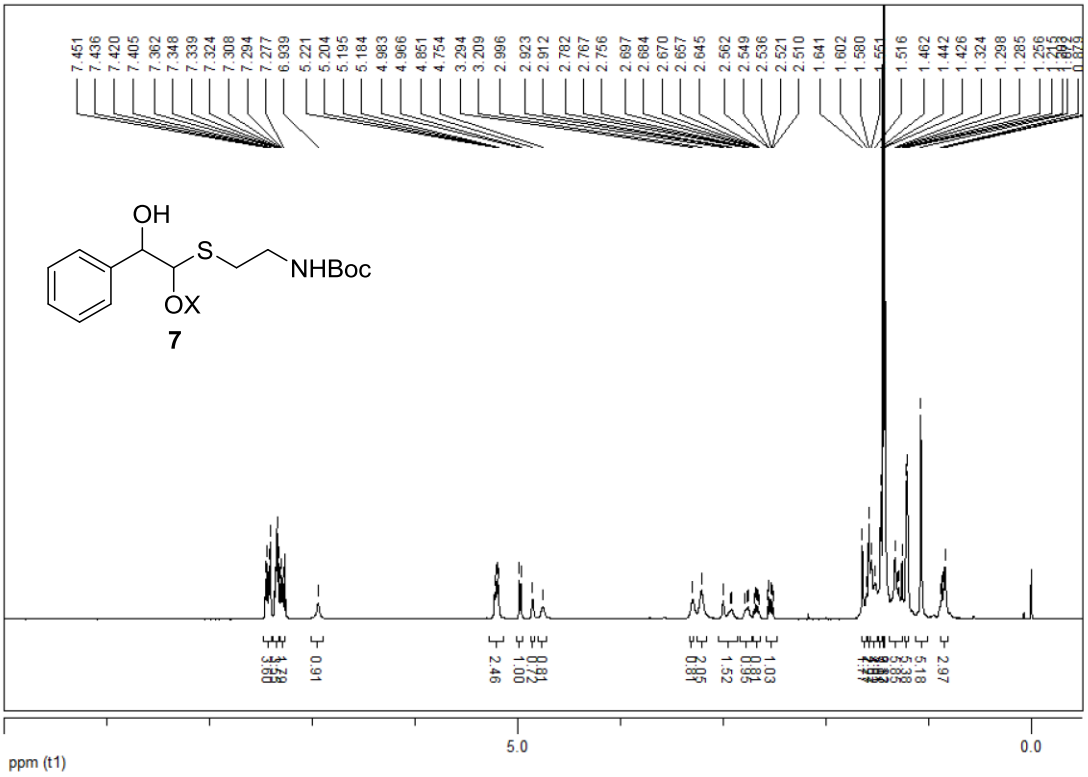

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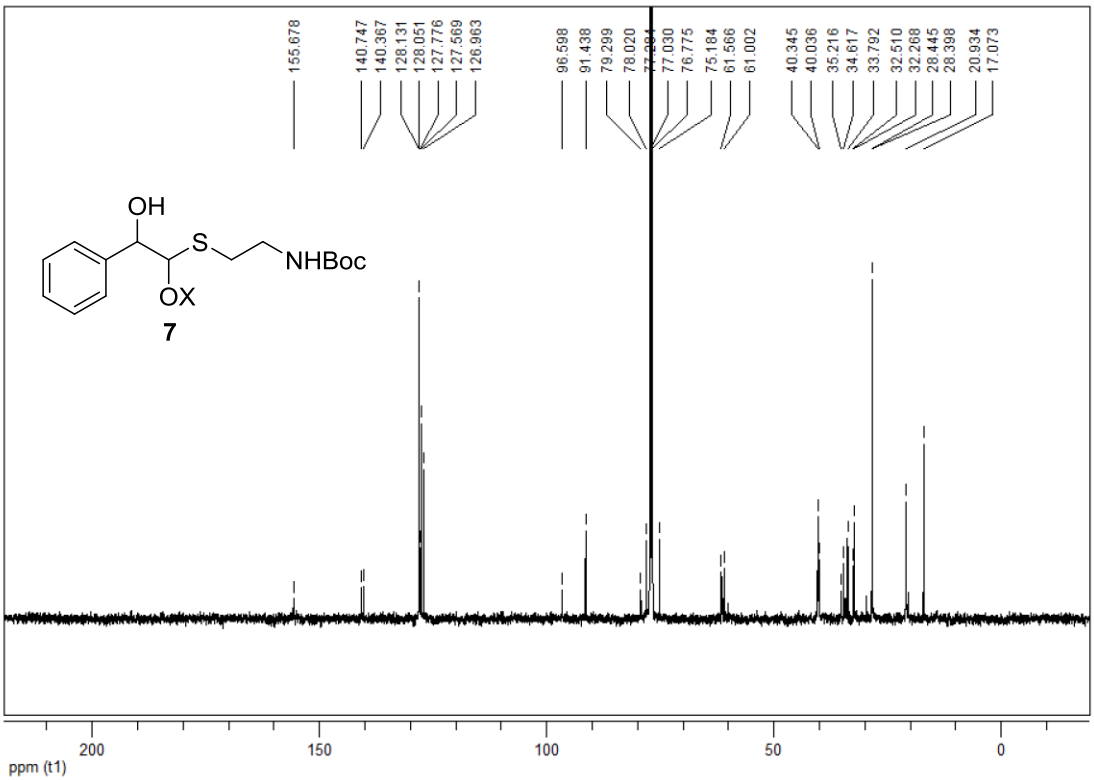

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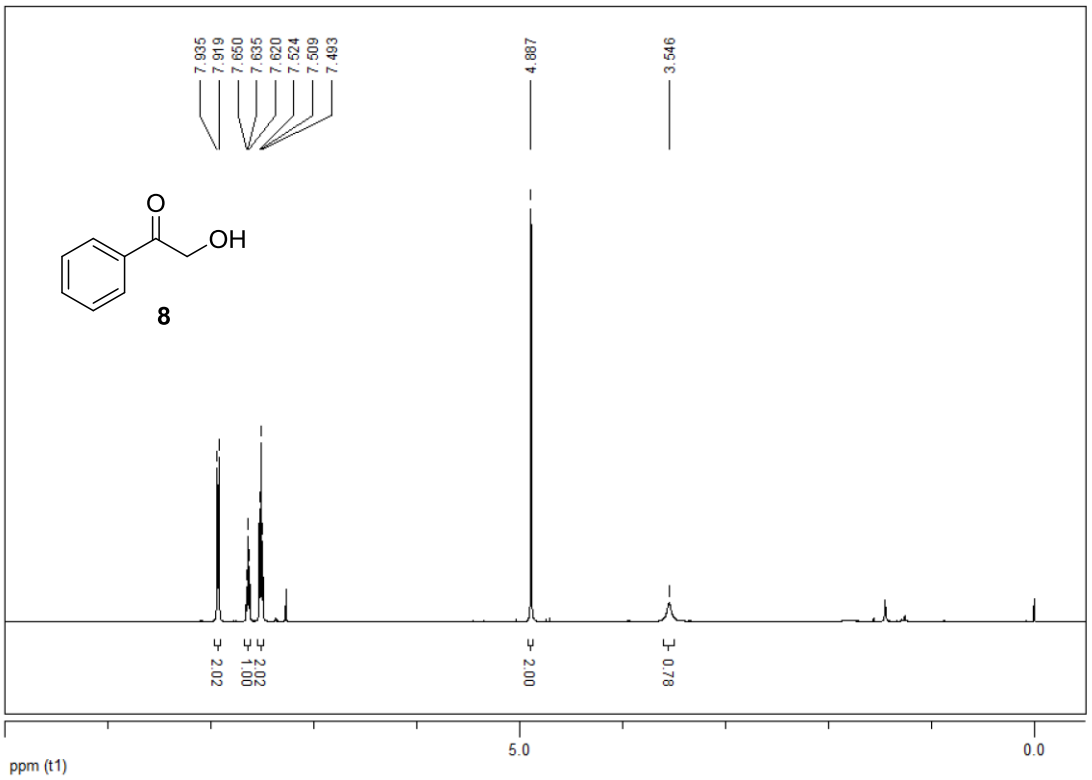

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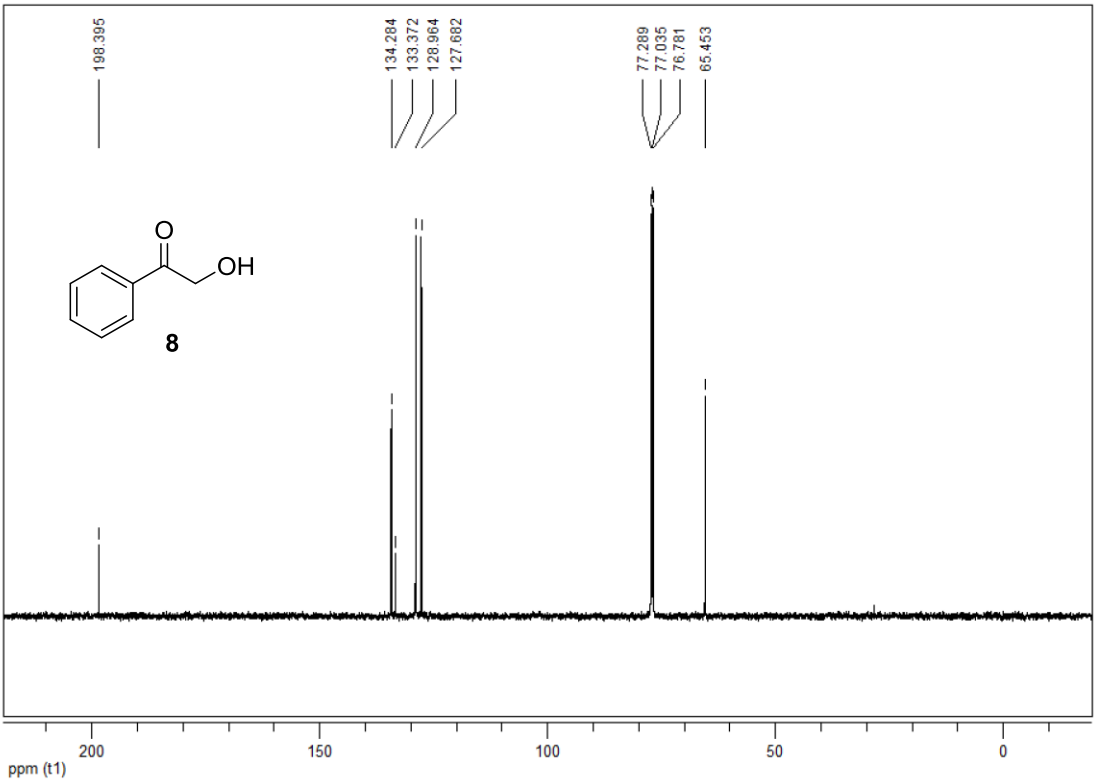

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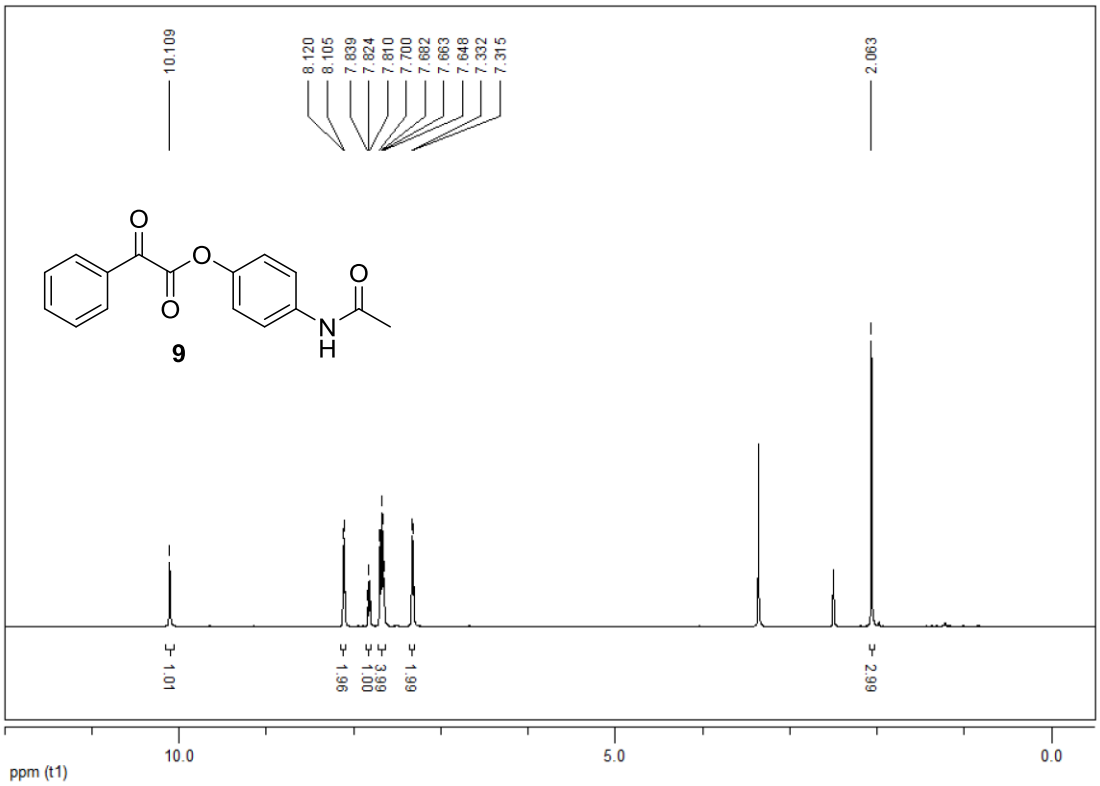

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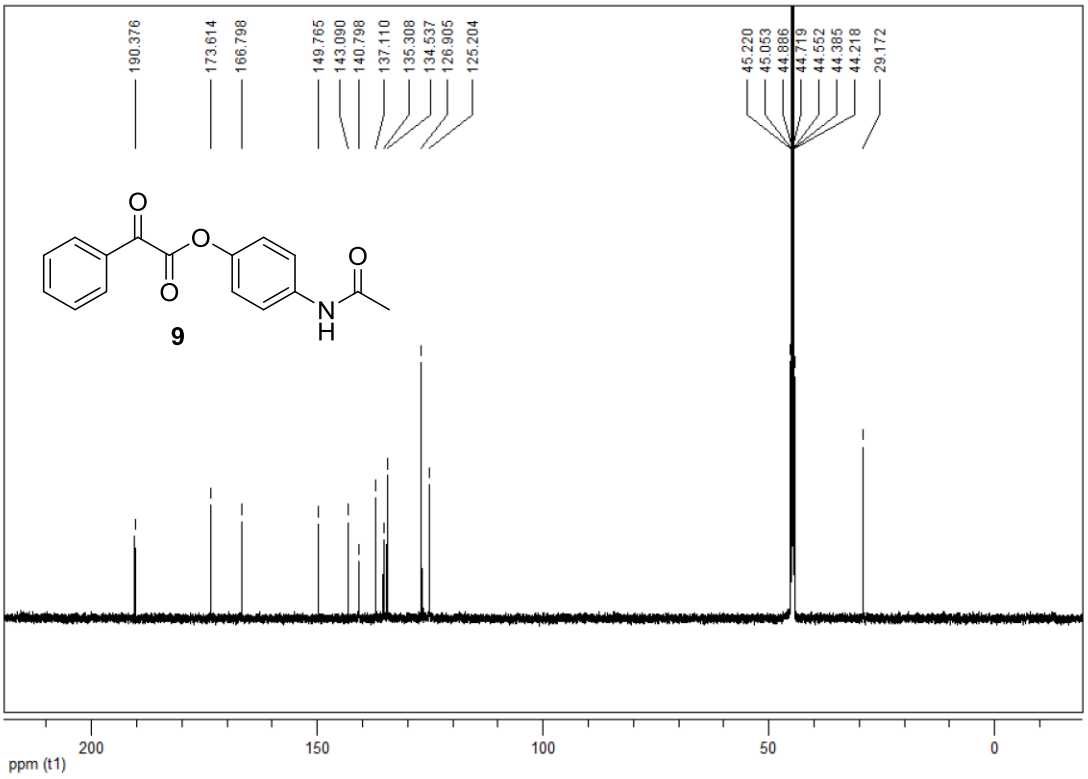

IX. Reference

1. G. -Q. Liu, W. Yi, P. -F. Wang, J. Liu, M. Ma, D. -Y. Hao, L. Ming, Y. Ling, *Green Chem.* 2021, **23**, 1840–1846.

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