Supporting Information For:

Reductive radical-initiated 1,2-C migration assisted by azidyl group

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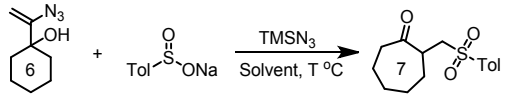
Contents

1. General Information

Reagents and Instruments: All reagents were purchased from commercial sources and used without purification unless otherwise mentioned. The products were purified by column chromatography over silica gel (300-400 size). ^{1}H, ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded at 25 °C on a Bruker 600 MHz, 150 MHz, and TMS was used as internal standard. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

2. Optimization of Reaction Conditions

Table S1. Optimization of the reaction conditions[a]



1ag **2a** **3ag**

entry	$TMSN_3$	**2a**	solvent	*T* (°C)	yield (%)[b]
1	4 eq.	4 eq.	DMSO:H_2O/2:1	50	58
2	4 eq.	4 eq.	DMSO:H_2O/3:1	50	55
3	4 eq.	4 eq.	DMSO:H_2O/1:1	50	49
4	4 eq.	4 eq.	DMF:H_2O/2:1	50	38
5	4 eq.	4 eq.	NMP:H_2O/2:1	50	41
6	4 eq.	4 eq.	DCM:H_2O/2:1	50	0[c]
7	4 eq.	4 eq.	CH_3CN:H_2O/2:1	50	43
8	4 eq.	4 eq.	CH_3CH_2OH:H_2O/2:1	50	52
9	4 eq.	4 eq.	DMSO:H_2O/2:1	70	44
10	4 eq.	4 eq.	DMSO:H_2O/2:1	30	54
11	3 eq.	4 eq.	DMSO:H_2O/2:1	50	56
12	4 eq.	3 eq.	DMSO:H_2O/2:1	50	39
13	**4 eq.**	**6 eq.**	**DMSO:H_2O/2:1**	**50**	**65**
14	4 eq.	7 eq.	DMSO:H_2O/2:1	50	64

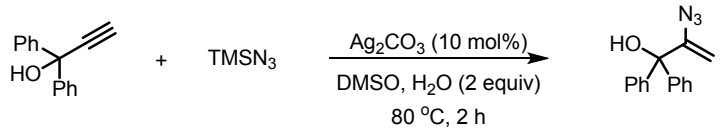
[a] Standard reaction conditions: **1ag** (0.5 mmol), $TMSN_3$ (2.0 mmol), **2a** (3.0 mmol), in H_2O (0.7 mL) and DMSO (1.4 mL) at 50 °C under air for 48 h. [b] Yield of isolated product. [c] No **3ag** was detected by ^{1}H NMR analysis of crude product. DCM = dichloromethane, DMSO = dimethyl sulfoxide, NMP = *N*-methyl pyrrolidone

To probe the feasibility of our proposed reaction, we investigated the reaction of 2-azidoallyl alcohols **1ag** with sodium *p*-toluenesulfinate **2a** in the presence of $TMSN_3$ in a DMSO/H_2O cosolvent system at 50 °C (Table S1, entry 1). Gratifyingly, after 48 h, the 1,2-migration product was isolated in 58% yield. We then optimized the other reaction parameters, including solvent, temperature and the amount of $TMSN_3$ and **2a**. Except for dichloromethane (DCM), the cosolvents of H_2O with dimethylsulfoxide (DMSO), dimethylformamide (DMF), *N*-methyl-2-

pyrrolidone (NMP), acetonitrile, or ethyl alcohol all afforded the desired product in moderate yields (entries 1-8). The yield decreased if the temperature was raised to 70 °C or reduced to 30 °C (entries 9 and 10). The reason might be that the quantity of byproducts was increased when the temperature was increased or lengthened the reaction timeextended (**1ag** was not observed after 72 h at 30 °C). The amounts of **2a** and $TMSN_3$ also were also important, and the results listed in entries 11-14 demonstrated that the yield of **3ag** was the highest (65%) when four equivalents of $TMSN_3$ and six equivalents of **2a** were used. After systematic screening of the reaction parameters, the conditions listed in entry 13 were found to be optimum for this reductive 1,2-carbon migration reaction.

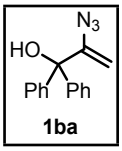
3. Typical Procedure for Synthesis of Substrates and Products

3.1 Typical procedure for the preparation of 2-azidoallyl alcohols



A-1 **1ba**, 83%

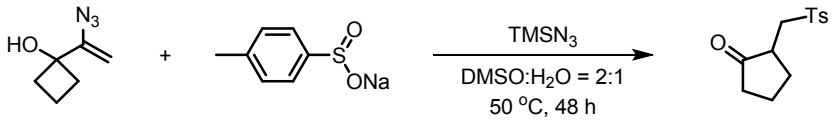
To a solution of ethynyl alcohol **A-1** (5.0 mmol, 1.041 g), $TMSN_3$ (7.5 mmol, 0.863 g), and H_2O (10.0 mmol, 0.180 g) in DMSO (10 mL), Ag_2CO_3 (0.5 mmol, 0.138 g) was added. The mixture was stirred at 80 °C for 2 h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 20:1) to afford 2-azidoallyl alcohol **1ba** (1.043 g, 83%).[1],[2]



1ba

2-Azido-1,1-diphenylprop-2-en-1-ol (1ba): Yellow solid; m.p. 26-28 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.37 (m, 4H), 7.34-7.28 (m, 6H), 5.01 (d, J = 2.4 Hz, 1H), 4.71 (d, J = 1.8 Hz, 1H), 3.05 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.96, 143.17, 128.09, 127.90, 127.60, 102.11, 80.67. **HRMS** (ESI) m/z calculated for $C_{15}H_{13}N_3NaO$ $[M+Na]^+$ 274.0960, found 274.0956.

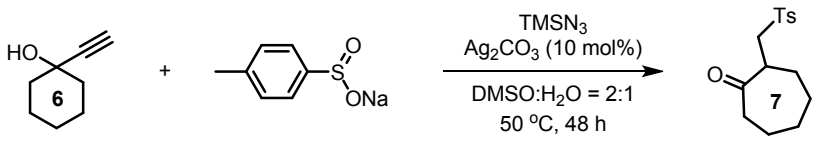
3.2 Typical procedure for the radical-initiated reductive 1,2-carbon migration



1aa **2a** **3aa**, 68%

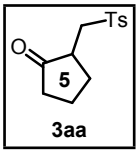
To a solution of 2-azidoallyl alcohol **1aa** (0.5 mmol, 0.070 g) and sodium *p*-tolylsulfinate (3.0 mmol, 0.534 g) in the co-solvent (DMSO 1.4 mL, H_2O 0.7 mL), $TMSN_3$ (2.0 mmol, 0.230 g) was added. The mixture was stirred at 50 °C for 48 h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 6:1) to afford product **3aa** (0.086 g, 68%).

3.3 Typical procedure for the 1,2-carbon migration from propargyl alcohols

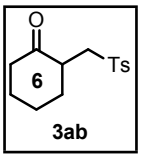


P-1 **2a** **3ag**, 54%

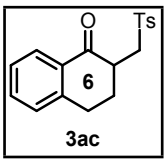
To a solution of propargyl alcohol **P-1** (0.5 mmol, 0.062 g), Ag_2CO_3 (0.05 mmol, 0.014 g) and sodium *p*-tolylsulfinate (3.0 mmol, 0.534 g) in the co-solvent (DMSO 1.4 mL, H_2O 0.7 mL), $TMSN_3$ (2.0 mmol, 0.230 g) was added. The mixture was stirred at 50 °C for 48 h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 6:1) to afford product **3ag** (0.076 g, 54%).



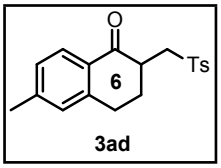
2-(Tosylmethyl)cyclopentanone (3aa): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 3.64 (dd, *J* = 14.2, 1.8 Hz, 1H), 2.91 (dd, *J* = 14.2, 10.2 Hz, 1H), 2.60-2.55 (m, 2H), 2.46 (s, 3H), 2.40-2.33 (m, 1H), 2.15-2.04 (m, 2H), 1.88-1.76 (m, 1H), 1.72-1.58 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 216.63, 144.94, 136.49, 130.03, 127.91, 56.68, 44.15, 36.72, 29.96, 21.66, 20.58. **HRMS** (ESI) m/z calculated for $C_{13}H_{16}NaO_3S$ $[M+Na]^+$ 275.0712, found 275.0708.



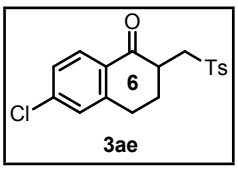
2-(Tosylmethyl)cyclohexanone (3ab): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.87 (dd, *J* = 14.4, 3.6 Hz, 1H), 3.07-3.02 (m, 1H), 2.82 (dd, *J* = 14.4, 7.7 Hz, 1H), 2.59-2.55 (m, 1H), 2.45 (s, 3H), 2.43-2.40 (m, 1H), 2.38-2.32 (m, 1H), 2.14-2.01 (m, 1H), 1.91-1.88 (m, 1H), 1.82-1.70 (m, 1H), 1.67-1.58 (m, 1H), 1.47 (qd, *J* = 12.9, 3.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.43, 144.74, 136.99, 129.93, 127.80, 55.42, 45.19, 41.85, 34.79, 27.73, 25.08, 21.65. **HRMS** (ESI) m/z calculated for $C_{14}H_{18}NaO_3S$ $[M+Na]^+$ 289.0869, found 289.0863.



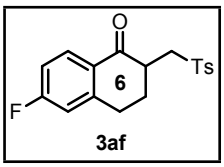
2-(Tosylmethyl)-3,4-dihydronaphthalen-1(2H)-one (3ac): Yellow solid; m.p: 97-98 °C;^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.44-7.38 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.20-7.16 (m, 1H), 4.08 (dd, *J* = 14.4, 2.2 Hz, 1H), 3.08-3.02 (m, 2H), 2.98-2.89 (m, 2H), 2.76-2.69 (m, 1H), 2.38 (s, 3H), 1.95 (qd, *J* = 13.2, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.79, 144.85, 143.91, 136.81, 133.90, 131.61, 130.03, 128.90, 127.91, 127.75, 126.80, 55.74, 43.11, 29.37, 28.98, 21.67. **HRMS** (ESI) m/z calculated for $C_{18}H_{18}NaO_3S$ $[M+Na]^+$ 337.0869, found 337.0873.



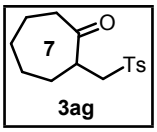
6-Methyl-2-(tosylmethyl)-3,4-dihydronaphthalen-1(2H)-one (3ad): Yellow solid; m.p: 49-50 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 4.15 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.12-3.04 (m, 2H), 3.02-2.98 (m, 1H), 2.94 (dt, *J* = 16.8, 3.6 Hz, 1H), 2.80-2.74 (m, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 2.04-1.95 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 195.44, 144.87, 144.80, 143.98, 136.84, 130.01, 129.30, 129.28, 127.90, 127.85, 127.82, 55.79, 43.03, 29.42, 28.94, 21.75, 21.66. **HRMS** (ESI) m/z calculated for $C_{19}H_{20}NaO_3S$ $[M+Na]^+$ 351.1034, found 351.1025.



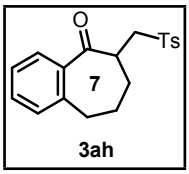
6-Chloro-2-(tosylmethyl)-3,4-dihydronaphthalen-1(2H)-one (3ae): Yellow solid; m.p: 71-72 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29-7.25 (m, 2H), 4.12 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.16-3.10 (m, 2H), 3.07-2.94 (m, 2H), 2.84-2.76 (m, 1H), 2.46 (s, 3H), 2.02 (qd, *J* = 13.0, 4.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.78, 145.44, 144.94, 140.30, 136.76, 130.06, 130.04, 129.44, 128.77, 127.90, 127.39, 55.61, 42.97, 29.10, 28.83, 21.68. **HRMS** (ESI) m/z calculated for $C_{18}H_{17}ClNaO_3S$ $[M+Na]^+$ 371.0479, found 371.0483.



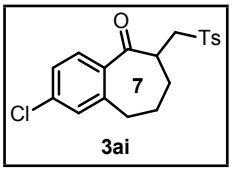
6-Fluoro-2-(tosylmethyl)-3,4-dihydronaphthalen-1(2H)-one (3af): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.98 (td, *J* = 8.6, 2.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 4.13 (dd, *J* = 14.4, 2.0 Hz, 1H), 3.16-3.10 (m, 2H), 3.04-2.97 (m, 2H), 2.82-2.78 (m, 1H), 2.46 (s, 3H), 2.02 (qd, *J* = 13.2, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.32, 165.96 (d, *J* = 253.5 Hz), 146.99 (d, *J* = 9.2 Hz), 144.89, 136.81, 130.95 (d, *J* = 9.9 Hz), 130.04, 128.27 (d, *J* = 2.6 Hz), 127.89, 115.20 (d, *J* = 21.5 Hz), 114.60 (d, *J* = 22.1 Hz), 55.64, 42.87, 29.16, 29.12, 21.66. **HRMS** (ESI) m/z calculated for $C_{18}H_{17}FNaO_3S$ $[M+Na]^+$ 355.0775, found 355.0778.



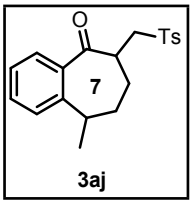
2-(Tosylmethyl)cycloheptanone (3ag): White solid; m.p: 58-59 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.83 (dd, *J* = 14.2, 6.0 Hz, 1H), 3.35-3.28 (m, 1H), 2.96 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.59 (dt, *J* = 16.0, 4.8 Hz, 1H), 2.45 (s, 3H), 2.43-2.38 (m, 1H), 2.05-1.98 (m, 1H), 1.91-1.87 (m, 1H), 1.85-1.69 (m, 3H), 1.65-1.56 (m, 1H), 1.50-1.44 (m, 1H), 1.32-1.23 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.43, 144.77, 136.93, 129.93, 127.90, 57.60, 45.38, 42.99, 31.69, 28.84, 28.43, 23.24, 21.65. **HRMS** (ESI) m/z calculated for $C_{15}H_{20}NaO_3S$ $[M+Na]^+$ 303.1025, found 303.1042.



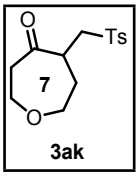
6-(Tosylmethyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (3ah): White solid; m.p: 84-85 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.44 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26-7.21 (m, 2H), 4.06 (dd, *J* = 14.4, 6.6 Hz, 1H), 3.59-3.54 (m, 1H), 3.13 (dd, *J* = 14.2, 5.0 Hz, 1H), 3.09-3.06 (m, 1H), 3.01-2.91 (m, 1H), 2.45 (s, 3H), 2.26-2.12 (m, 2H), 1.73-1.57 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 202.33, 144.73, 142.42, 138.43, 136.62, 131.86, 130.11, 129.95, 128.91, 128.09, 126.32, 57.00, 44.03, 33.32, 30.57, 25.35, 21.66. **HRMS** (ESI) m/z calculated for $C_{19}H_{20}NaO_3S$ $[M+Na]^+$ 351.1025, found 351.1033.



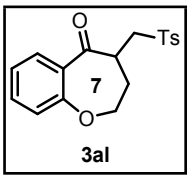
2-Chloro-6-(tosylmethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (3ai): White solid; m.p: 55-56 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.24-7.22 (m, 2H), 4.04 (dd, *J* = 14.2, 6.6 Hz, 1H), 3.56-3.51 (m, 1H), 3.12 (dd, *J* = 14.4, 5.0 Hz, 1H), 3.10-3.04 (m, 1H), 2.98-2.89 (m, 1H), 2.45 (s, 3H), 2.26-2.13 (m, 2H), 1.72-1.57 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.10, 144.81, 144.21, 137.99, 136.77, 136.60, 130.57, 130.04, 129.97, 128.06, 126.66, 56.90, 43.96, 33.08, 30.24, 25.12, 21.66. **HRMS** (ESI) m/z calculated for $C_{19}H_{19}ClNaO_3S$ $[M+Na]^+$ 385.0636, found 385.0645.



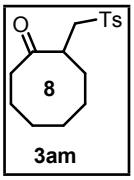
9-Methyl-6-(tosylmethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (3aj): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.44 (td, *J* = 7.8, 1.2 Hz, 1H), 7.38-7.33 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 4.02 (dd, *J* = 14.4, 4.8 Hz, 1H), 3.33-3.29 (m, 1H), 3.16-3.07 (m, 2H), 2.46 (s, 3H), 2.29-2.25 (m, 1H), 2.14-2.09 (m, 1H), 1.79-1.69 (m, 1H), 1.69-1.62 (m, 1H), 1.34 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.29, 144.75, 143.73, 139.11, 136.91, 131.98, 129.97, 128.67, 128.01, 126.51, 126.30, 57.51, 45.39, 35.69, 34.38, 27.77, 21.66, 20.32. **HRMS** (ESI) m/z calculated for $C_{20}H_{22}NaO_3S$ $[M+Na]^+$ 365.1182, found 365.1189.



5-(Tosylmethyl)oxepan-4-one (3ak): White solid; m.p: 84-85 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 4.11-4.02 (m, 2H), 3.86-3.75 (m, 2H), 3.75-3.67 (m, 1H), 3.56-3.48 (m, 1H), 2.99 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.87-2.76 (m, 1H), 2.64 (dt, *J* = 16.8, 3.6 Hz, 1H), 2.46 (s, 3H), 2.15-2.08 (m, 1H), 1.78-1.71 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.11, 145.01, 136.82, 130.03, 127.86, 65.92, 56.71, 45.20, 45.12, 39.80, 33.30, 21.67. **HRMS** (ESI) m/z calculated for $C_{14}H_{18}NaO_4S$ $[M+Na]^+$ 305.0818, found 305.0837.

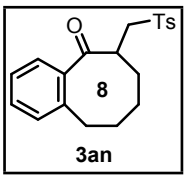


4-(Tosylmethyl)-3,4-dihydrobenzo[b]oxepin-5(2*H*)-one (3al): Yellow solid; m.p: 70-71 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.42 (td, *J* = 7.8, 1.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.07-7.03 (m, 2H), 4.57-4.53 (m, 1H), 3.98 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.83 (td, *J* = 12.6, 5.2 Hz, 1H), 3.76-3.71 (m, 1H), 3.18 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.85-2.77 (m, 1H), 2.44 (s, 3H), 1.89-1.77 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.29, 162.37, 144.84, 136.39, 133.93, 129.98, 129.61, 128.09, 127.72, 122.44, 120.30, 72.01, 56.07, 43.81, 34.56, 21.65. **HRMS** (ESI) m/z calculated for $C_{18}H_{18}NaO_4S$ $[M+Na]^+$ 353.0818, found 353.0833.



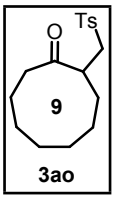
2-(Tosylmethyl)cyclooctanone (3am): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.82 (dd, *J* = 14.0, 8.4 Hz, 1H), 3.48-3.43 (m, 1H), 2.98 (dd, *J* = 14.0, 3.6 Hz, 1H), 2.69-2.66 (m, 1H), 2.45 (s, 3H), 2.34-2.26 (m, 1H), 2.16-2.07 (m, 1H), 1.95-1.90 (m, 1H), 1.84-1.75 (m, 1H), 1.70-

1.61 (m, 3H), 1.57-1.53 (m, 2H), 1.50-1.41 (m, 1H), 1.06-0.99 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.79, 144.82, 136.73, 129.94, 127.87, 58.29, 43.09, 42.53, 34.15, 28.18, 24.44, 24.42, 23.55, 21.66. **HRMS** (ESI) m/z calculated for $C_{16}H_{22}NaO_3S$ $[M+Na]^+$ 317.1182, found 317.1186.



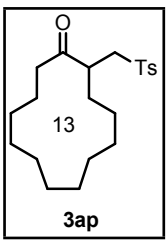
3an

6-(Tosylmethyl)-7,8,9,10-tetrahydrobenzo[8]annulen-5(6H)-one (3an): White solid; m.p: 82-83 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.41 (td, *J* = 7.8, 1.2 Hz, 1H), 7.28-7.23 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 3H), 4.07 (dd, *J* = 14.0, 7.4 Hz, 1H), 4.04-3.98 (m, 1H), 3.45-3.32 (m, 1H), 3.09 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.87 (dt, *J* = 15.0, 5.2 Hz, 1H), 2.41 (s, 3H), 2.05-1.98 (m, 1H), 1.87-1.79 (m, 2H), 1.74-1.65 (m, 2H), 1.56-1.48 (m, 1H), 1.41-1.31 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 204.08, 144.72, 139.40, 139.11, 136.44, 132.32, 131.62, 129.89, 128.21, 128.11, 126.41, 57.99, 44.87, 34.50, 32.24, 27.71, 22.34, 21.62. **HRMS** (ESI) m/z calculated for $C_{20}H_{22}NaO_3S$ $[M+Na]^+$ 365.1182, found 365.1188.



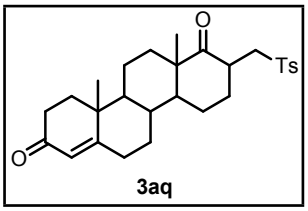
3ao

2-(Tosylmethyl)cyclononanone (3ao): Yellow solid; m.p: 61-64 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.76 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.54-3.32 (m, 1H), 3.00 (dd, *J* = 14.2, 4.4 Hz, 1H), 2.80-2.76 (m, 1H), 2.45 (s, 3H), 2.38-2.34 (m, 1H), 1.99-1.94 (m, 1H), 1.93-1.77 (m, 2H), 1.77-1.68 (m, 1H), 1.67-1.59 (m, 4H), 1.48-1.38 (m, 2H), 1.31-1.23 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.63, 144.81, 136.75, 129.94, 127.88, 58.26, 46.31, 43.12, 30.87, 26.68, 26.10, 24.26, 24.07, 23.57, 21.66. **HRMS** (ESI) m/z calculated for $C_{17}H_{24}NaO_3S$ $[M+Na]^+$ 331.1331, found 331.1344.



3ap

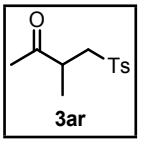
2-(Tosylmethyl)cyclotridecanone (3ap): Yellow solid; m.p: 67-68 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.73 (dd, *J* = 14.0, 9.2 Hz, 1H), 3.22-3.18 (m, 1H), 2.98 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.77-2.72 (m, 1H), 2.50-2.47 (m, 1H), 2.45 (s, 3H), 1.99-1.93 (m, 1H), 1.60-1.56 (m, 2H), 1.43-1.14 (m, 17H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.88, 144.81, 136.65, 129.93, 127.92, 57.59, 44.94, 41.72, 31.78, 26.68, 26.27, 25.97, 24.67, 24.55, 23.81, 23.75, 23.28, 21.70, 21.64. **HRMS** (ESI) m/z calculated for $C_{21}H_{32}NaO_3S$ $[M+Na]^+$ 387.1964, found 387.1971.



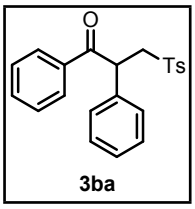
3aq

10a,12a-Dimethyl-2-(tosylmethyl)-2,3,4,4a,5,6,10,10a,10b,11,12,12a-dodecahydrochrysene-1,8(4b*H*,9*H*)-dione (3aq): White solid; m.p: 142-143 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 3.84 (dd, *J* = 14.4, 4.0 Hz, 1H), 3.52-3.38 (m, 1H), 2.78 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.65-2.54 (m, 1H), 2.45 (s, 3H), 2.41-2.23 (m, 4H), 2.12-1.99 (m, 2H), 1.96-1.82 (m, 1H), 1.73-1.63 (m, 4H), 1.61-1.47 (m, 2H), 1.41-1.32 (m, 2H), 1.18 (s, 3H), 1.15 (s, 3H), 1.01-0.92 (m, 2H), 0.89-0.84 (m, 1H). ^{13}C NMR (150

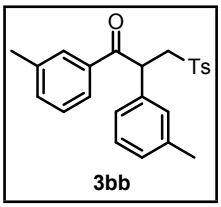
MHz, $CDCl_3$) δ 212.13, 199.27, 170.15, 144.74, 137.07, 129.90, 127.82, 123.71, 55.90, 52.77, 51.80, 48.33, 39.89, 38.61, 35.41, 35.23, 34.00, 33.88, 32.56, 32.34, 31.17, 23.31, 21.66, 19.75, 17.51, 16.56. **HRMS** (ESI) m/z calculated for $C_{28}H_{36}NaO_4S$ $[M+Na]^+$ 491.2227, found 491.2227.



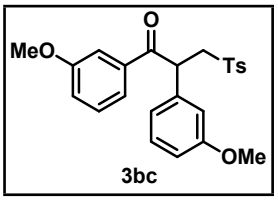
3-Methyl-4-tosylbutan-2-one (3ar): Yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.73 (dd, *J* = 14.2, 7.0 Hz, 1H), 3.24-3.20 (m, 1H), 2.96 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.45 (s, 3H), 2.21 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.20, 144.90, 136.68, 129.98, 127.92, 58.06, 40.97, 28.30, 21.65, 17.30. **HRMS** (ESI) m/z calculated for $C_{12}H_{16}NaO_3S$ $[M+Na]^+$ 263.0712, found 263.0719.



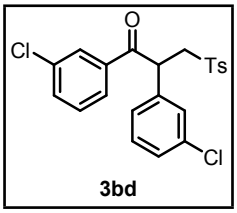
1,2-Diphenyl-3-tosylpropan-1-one (3ba): White solid; m.p: 90-91 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.25-7.21 (m, 6H), 7.20-7.18 (m, 1H), 5.28 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.42 (dd, *J* = 14.2, 8.8 Hz, 1H), 3.42 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.39 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 195.88, 144.70, 136.54, 136.44, 135.53, 133.41, 129.81, 129.38, 128.88, 128.58, 128.15, 128.11, 127.96, 59.34, 47.56, 21.61. **HRMS** (ESI) m/z calculated for $C_{22}H_{20}NaO_3S$ $[M+Na]^+$ 387.1025, found 387.1026.



1,2-Di-*m*-tolyl-3-tosylpropan-1-one (3bb): White solid; m.p: 99-100 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.66-7.57 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.21-7.18 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 11.2 Hz, 2H), 5.16 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.32 (dd, *J* = 14.2, 8.8 Hz, 1H), 3.33 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.12, 144.61, 139.11, 138.39, 136.48, 136.43, 135.58, 134.21, 129.75, 129.41, 129.21, 128.69, 128.63, 128.43, 128.10, 126.14, 125.30, 59.39, 47.46, 21.61, 21.37, 21.34. **HRMS** (ESI) m/z calculated for $C_{24}H_{24}NaO_3S$ $[M+Na]^+$ 415.1338, found 415.1337.

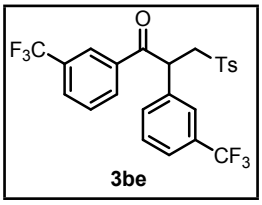


1,2-Bis(3-methoxyphenyl)-3-tosylpropan-1-one (3bc): Yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 1.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18-7.15 (m, 1H), 7.05 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.73-6.72 (m, 2H), 5.20 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.40 (dd, *J* = 14.2, 9.0 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.41 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.51, 160.17, 159.75, 144.70, 137.94, 136.84, 136.41, 130.41, 129.80, 129.56, 128.12, 121.49, 120.44, 120.02, 113.64, 113.37, 113.12, 59.24, 55.40, 55.24, 47.72, 21.61. **HRMS** (ESI) m/z calculated for $C_{24}H_{24}NaO_5S$ $[M+Na]^+$ 447.1237, found 447.1236.



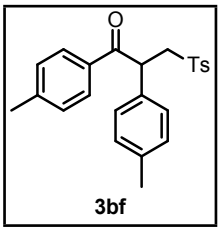
3bd

1,2-Bis(3-chlorophenyl)-3-tosylpropan-1-one (3bd): Yellow solid; m.p: 74-75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (t, *J* = 1.8 Hz, 1H), 7.80-7.75 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.51-7.49 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.28-7.23 (m, 2H), 7.21-7.16 (m, 3H), 7.14 (dt, *J* = 6.6, 1.8 Hz, 1H), 5.19 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.33 (dd, *J* = 14.2, 8.6 Hz, 1H), 3.43 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.41 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 194.43, 145.07, 137.70, 136.81, 136.11, 135.28, 135.17, 133.63, 130.73, 130.06, 129.92, 128.88, 128.49, 128.18, 128.06, 126.90, 126.44, 59.08, 47.22, 21.64. **HRMS** (ESI) m/z calculated for $C_{22}H_{18}Cl_2NaO_3S$ $[M+Na]^+$ 455.0246, found 455.0254.



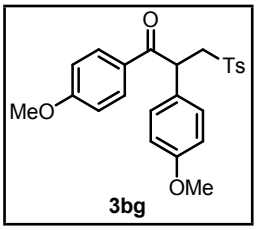
3be

3-Tosyl-1,2-bis(3-(trifluoromethyl)phenyl)propan-1-one (3be): Yellow solid; m.p: 76-77 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.51-7.45 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.36 (dd, *J* = 8.5, 4.2 Hz, 1H), 4.37 (dd, *J* = 14.2, 8.5 Hz, 1H), 3.49 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.40 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 194.41, 145.20, 136.63, 136.03, 135.65, 131.93 (q, *J* = 32.5 Hz), 131.87, 131.67, 130.17 (q, *J* = 3.0 Hz), 130.11, 129.96, 129.54, 128.02, 125.72 (q, *J* = 3.0 Hz), 125.27 (q, *J* = 3.0 Hz), 124.89 (q, *J* = 3.0 Hz), 123.51 (q, *J* = 273.0 Hz), 123.44 (q, *J* = 273.0 Hz), 59.08, 47.34, 21.56. **HRMS** (ESI) m/z calculated for $C_{24}H_{18}F_6NaO_3S$ $[M+Na]^+$ 523.0773, found 523.0776.



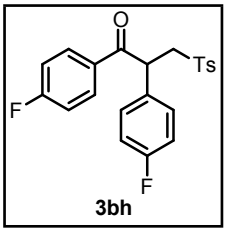
3bf

1,2-Di-*p*-tolyl-3-tosylpropan-1-one (3bf): Yllow solid; m.p: 85-86 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.21 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.37 (dd, *J* = 14.2, 8.6 Hz, 1H), 3.40 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.52, 144.57, 144.26, 137.68, 136.57, 133.74, 133.01, 129.99, 129.74, 129.26, 129.02, 128.09, 127.99, 59.32, 47.07, 21.64, 21.60, 21.00. **HRMS** (ESI) m/z calculated for $C_{24}H_{24}NaO_3S$ $[M+Na]^+$ 415.1338, found 415.1345.

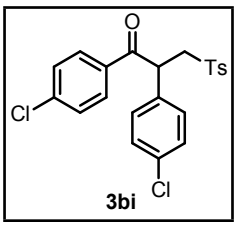


3bg

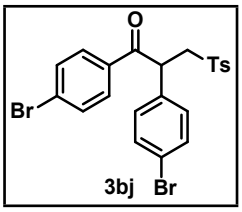
1,2-Bis(4-methoxyphenyl)-3-tosylpropan-1-one (3bg): Yellow solid; m.p: 88-89 °C;^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.18 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.34 (dd, *J* = 14.2, 8.8 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.40 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.45, 163.69, 159.16, 144.53, 136.60, 131.21, 129.71, 129.20, 128.87, 128.45, 128.08, 114.69, 113.78, 59.38, 55.48, 55.23, 46.39, 21.59. **HRMS** (ESI) m/z calculated for $C_{24}H_{24}NaO_5S$ $[M+Na]^+$ 447.1237, found 447.1250.



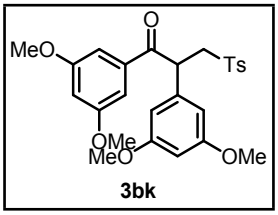
1,2-Bis(4-fluorophenyl)-3-tosylpropan-1-one (3bh): Yellow solid; m.p: 97-98 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 8.4 Hz, 2H), 5.25 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.34 (dd, *J* = 14.2, 8.5 Hz, 1H), 3.42 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.41, 165.92 (d, *J* = 254.6 Hz), 162.37 (d, *J* = 246.5 Hz), 144.90, 136.39, 132.05 (d, *J* = 3.3 Hz) , 131.72 (d, *J* = 2.8 Hz), 131.57 (d, *J* = 9.5 Hz), 129.87, 129.84 (d, *J* = 9.5 Hz), 128.03, 116.41 (d, *J* = 21.6 Hz), 115.89 (d, *J* = 21.8 Hz), 59.26, 46.60, 21.60. **HRMS** (ESI) m/z calculated for $C_{22}H_{18}F_2NaO_3S$ $[M+Na]^+$ 423.0837, found 423.0839.



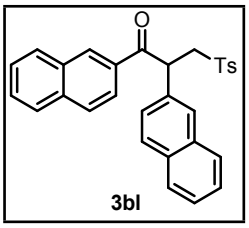
1,2-Bis(4-chlorophenyl)-3-tosylpropan-1-one (3bi): White solid; m.p: 89-90 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.21 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.30 (dd, *J* = 14.2, 8.4 Hz, 1H), 3.42 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.61, 144.96, 140.24, 136.33, 134.54, 134.30, 133.57, 130.23, 129.89, 129.64, 129.50, 129.08, 128.00, 59.04, 46.86, 21.63. **HRMS** (ESI) m/z calculated for $C_{22}H_{18}Cl_2NaO_3S$ $[M+Na]^+$ 455.0246, found 455.0243.



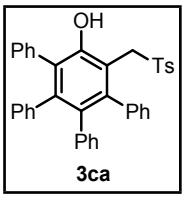
1,2-Bis(4-bromophenyl)-3-tosylpropan-1-one (3bj): White solid; m.p.: 101-103 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.12 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.21 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.35 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.75, 144.99, 136.28, 134.99, 133.93, 132.60, 132.10, 130.31, 129.90, 129.83, 129.05, 128.00, 122.43, 58.93, 46.92, 21.66. **HRMS** (ESI) m/z calculated for $C_{22}H_{18}Br_2NaO_3S$ $[M+Na]^+$ 544.9213, found 544.9221.



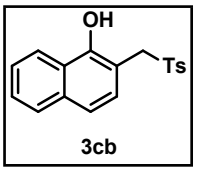
1,2-Bis(3,5-dimethoxyphenyl)-3-tosylpropan-1-one (3bk): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.34-7.14 (m, 2H), 7.03 (d, 2H), 6.59 (t, *J* = 1.8 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 2H), 6.27 (t, *J* = 1.8 Hz, 1H), 5.08 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.37 (dd, *J* = 14.2, 8.8 Hz, 1H), 3.78 (s, 6H), 3.70 (s, 6H), 3.39 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.21, 161.38, 160.76, 144.68, 138.62, 137.38, 136.43, 129.78, 128.12, 106.73, 106.08, 105.82, 99.79, 59.17, 55.55, 55.36, 48.00, 21.60. **HRMS** (ESI) m/z calculated for $C_{26}H_{28}NaO_7S$ $[M+Na]^+$ 507.1448, found 507.1449.



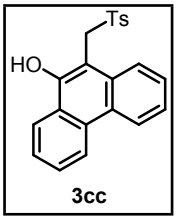
1,2-Di(naphthalen-2-yl)-3-tosylpropan-1-one (3bl): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.74-7.66 (m, 6H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.51-7.47 (m, 1H), 7.43-7.39 (m, 3H), 7.11 (d, *J* = 8.2 Hz, 2H), 5.61 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.51 (dd, *J* = 14.4, 8.2 Hz, 1H), 3.62 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.85, 144.68, 136.43, 135.66, 133.83, 133.49, 132.85, 132.71, 132.35, 130.89, 129.75, 129.72, 129.41, 128.80, 128.51, 128.06, 127.83, 127.70, 127.62, 127.56, 126.86, 126.55, 126.46, 125.57, 124.33, 59.33, 47.90, 21.51. **HRMS** (ESI) m/z calculated for $C_{30}H_{24}NaO_3S$ $[M+Na]^+$ 487.1338, found 487.1347.



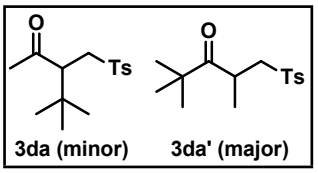
5',6'-Diphenyl-4'-(tosylmethyl)-[1,1':2',1''-terphenyl]-3'-ol (3ca): Yellow solid; m.p: 189-190 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.28-7.25 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.19-7.13 (m, 3H), 7.11-7.07 (m, 3H), 6.98-6.97 (m, 2H), 6.88-6.82 (m, 3H), 6.81-6.74 (m, 5H), 6.70 (d, *J* = 7.4 Hz, 2H), 4.49 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.94, 144.79, 143.99, 142.89, 139.96, 139.52, 138.77, 136.54, 136.14, 134.93, 131.46, 130.96, 130.94, 130.70, 129.72, 129.63, 128.31, 128.05, 127.35, 127.04, 126.72, 126.63, 126.56, 125.64, 125.24, 113.80, 57.06, 21.67. **HRMS** (ESI) m/z calculated for $C_{38}H_{30}NaO_3S$ $[M+Na]^+$ 589.1808, found 589.2803.



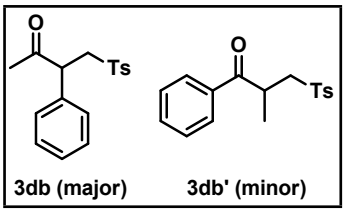
2-(Tosylmethyl)naphthalen-1-ol (3cb): Brown solid; m.p: 158-161 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.2 Hz, 1H), 7.92 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.54-7.51 (m, 2H), 7.26-7.24 (m, 3H), 6.68 (d, *J* = 8.4 Hz, 1H), 4.57 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ152.51, 145.43, 134.92, 133.95, 129.84, 128.57, 128.54, 127.37, 127.22, 126.47, 125.86, 122.87, 121.16, 109.51, 60.17, 21.70. **HRMS** (ESI) m/z calculated for $C_{18}H_{16}NaO_3S$ $[M+Na]^+$ 335.0711, found 335.0718.



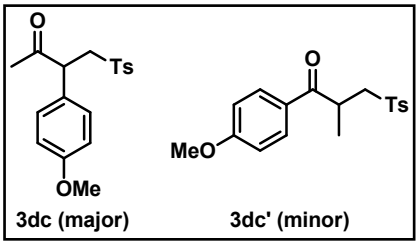
10-(Tosylmethyl)phenanthren-9-ol (3cc): White solid; m.p: 171-172 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.2 Hz, 1H), 8.58 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 1H), 7.76-7.66 (m, 4H), 7.44-7.41 (m, 1H), 7.34-7.30 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.94 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.87, 145.55, 134.44, 131.72, 131.09, 129.87, 128.60, 128.19, 127.02, 127.00, 126.88, 126.66, 124.36, 123.70, 122.98, 122.41, 122.17, 105.03, 55.16, 21.61. **HRMS** (ESI) m/z calculated for $C_{22}H_{18}NaO_3S$ $[M+Na]^+$ 385.0869, found 385.0870.



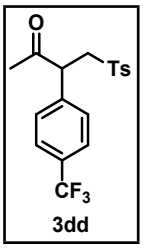
4,4-Dimethyl-3-(tosylmethyl)pentan-2-one (3da, minor): 2,4,4-trimethyl-1-tosylpentan-3-one (3da', major) = 1:3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2.67H, major (2H)+ minor (0.67H)), 7.37-7.34 (m, 2.67H, major (2H) + minor (0.67H)), 3.72 (dd, *J* = 12.4, 6.6 Hz, 1H, major), 3.69 (dd, *J* = 12.4, 6.6 Hz, 0.33H, minor), 3.51 (dd, *J* = 13.8, 6.6 Hz, 1H, major), 3.06 (dd, *J* = 13.8, 6.0 Hz, 0.67H, minor), 3.02 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.46 (s, 1H, minor), 2.45 (s, 3H, major), 2.30 (s, 1H, minor), 1.21 (d, *J* = 7.2 Hz, 3H, major), 1.19 (s, 9H, major), 0.92 (s, 3H, minor). ^{13}C NMR (150 MHz, $CDCl_3$) δ **3da**: 209.84, 144.93, 136.32, 129.98, 127.96, 56.31, 53.87, 33.97, 28.76, 27.53, 21.67; **3da'**: 216.14, 144.86, 136.89, 129.98, 127.82, 59.38, 44.91, 34.24, 26.63, 21.65, 19.05. **HRMS** (ESI) m/z calculated for $C_{15}H_{22}NaO_3S$ $[M+Na]^+$ 305.1192, found 305.1187.



3-Phenyl-4-tosylbutan-2-one (3db, major) : 2-methyl-1-phenyl -3-tosylpropan-1-one (3db', minor) = 2:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H, minor), 7.73 (d, *J* = 7.8 Hz, 1H, minor), 7.71 (d, *J* = 7.8 Hz, 2H, major), 7.58 (t, *J* = 7.2 Hz, 0.5H, minor), 7.46 (t, *J* = 7.2 Hz, 1H, major), 7.26-7.28 (m, 6H, major (4H)+minor (1H)), 7.12 (d, *J* = 7.2 Hz, 2H, major), 4.34-4.36 (m, 1H, major), 4.20 (dd, *J* = 13.8, 7.8 Hz, 1H, major), 4.18-4.12 (m, 0.5H, minor), 3.89 (dd, *J* = 14.0, 7.8 Hz, 0.5H, minor), 3.29 (dd, *J* = 13.8, 4.2 Hz, 1H, major), 3.16 (dd, *J* = 14.0, 5.0 Hz, 0.5H, minor), 2.42 (s, 3H, major), 2.40 (s, 1.5H, minor),2.10 (s, 3H, major), 1.34 (d, *J* = 7.2 Hz, 1.5H, minor). ^{13}C NMR (150 MHz, $CDCl_3$) δ **3db**: 204.09, 144.75, 136.59, 135.88, 133.56, 129.85, 129.34, 128.19, 127.92, 57.94, 52.76, 28.77, 21.61; **3db'**: 200.12, 144.84, 136.47, 134.96, 129.91, 128.77, 128.50, 128.16, 128.04, 58.73, 35.65, 21.60, 18.73. **HRMS** (ESI) m/z calculated for $C_{17}H_{18}NaO_3S$ $[M+Na]^+$ 325.0878, found 325.0874.

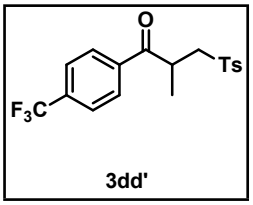


3-(4-Methoxyphenyl)-4-tosylbutan-2-one (3dc major): 1-(4-methoxyphenyl)-2-methyl-3-tosylpropan-1-one (3dc' minor) = 3:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 0.67H, minor), 7.65 (d, *J* = 7.8 Hz, 0.67H, minor), 7.61 (d, *J* = 7.8 Hz, 2H, major), 7.24-7.18 (m, 2.67H, major (2H)+minor (0.67H)), 6.96 (d, *J* = 8.4 Hz, 2H, major), 6.86 (d, *J* = 8.4 Hz, 0.67H, minor), 6.72 (d, *J* = 8.4 Hz, 2H, major), 4.22 (dd, *J* = 7.8, 4.8 Hz, 1H, major), 4.08 (dd, *J* = 14.4, 7.8 Hz, 1H, major), 4.06-4.00 (m, 0.33H, minor), 3.81 (s, 1H, minor), 3.79 (dd, *J* = 14.4, 7.2 Hz, 0.33H, minor), 3.69 (s, 3H, major), 3.20 (dd, *J* = 14.4, 4.8 Hz, 1H, major), 3.06 (dd, *J* = 14.4, 5.4 Hz, 0.33H, minor), 2.35 (s, 3H, major), 2.33 (s, 1H, minor), 2.02 (s, 3H, major), 1.25 (d, *J* = 7.2 Hz, 1H, minor). ^{13}C NMR (150 MHz, $CDCl_3$) δ **3dc**: 204.34, 159.47, 144.66, 136.70, 130.86, 129.82, 129.31, 127.92, 114.71, 58.02, 55.30, 51.93, 28.65, 21.64; **3dc'**: 198.56, 163.89, 144.76, 136.54, 129.86, 128.05, 127.87, 127.70, 113.94, 58.83, 55.56, 35.24, 21.64, 18.94. **HRMS** (ESI) m/z calculated for $C_{18}H_{20}NaO_4S$ $[M+Na]^+$ 355.0969, found 355.0980.



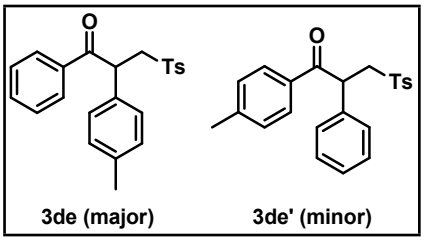
3dd

4-Tosyl-3-(4-(trifluoromethyl)phenyl)butan-2-one (3dd): Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.26-7.25 (m, 4H), 4.43 (t, *J* = 7.2 Hz, 1H), 4.12 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.35 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.33, 144.95, 139.60, 136.39, 130.54 (q, *J* = 32.4 Hz), 129.87, 128.73, 127.85, 126.23 (q, *J* = 3.8 Hz), 123.90 (q, *J* = 272.0 Hz), 57.77, 52.70, 28.92, 21.56. **HRMS** (ESI) m/z calculated for $C_{18}H_{17}F_3NaO_3S$ $[M+Na]^+$ 393.0742, found 393.0748.



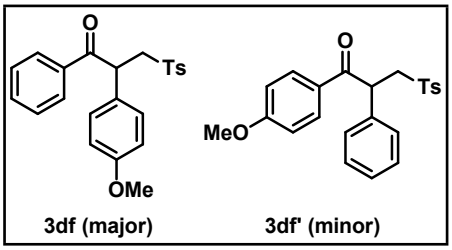
3dd'

2-Methyl-3-tosyl-1-(4-(trifluoromethyl)phenyl) propan-1-one (3dd'): Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.76-7.72 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.19-4.16 (m, 1H), 3.90 (dd, *J* = 14.4, 7.8 Hz, 1H), 3.17 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.42 (s, 3H), 1.35 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.43, 145.03, 137.81, 136.39, 134.81 (q, *J* = 32.6 Hz), 129.98, 128.88, 128.01, 125.86 (q, *J* = 3.8 Hz), 125.47 (q, *J* = 272.0 Hz), 58.71, 35.87, 21.63, 18.53. **HRMS** (ESI) m/z calculated for $C_{18}H_{17}F_3NaO_3S$ $[M+Na]^+$ 393.0742, found 393.0748.



3de (major) 3de' (minor)

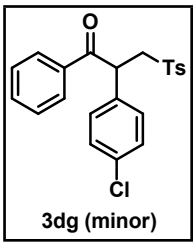
1-Phenyl-2-(p-tolyl)-3-tosylpropan-1-one (3de, major) : 2-phenyl-1-(p-tolyl)-3-tosylpropan-1-one (3de', minor) = 4:3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H, major), 7.80 (d, *J* = 7.8 Hz, 1.5H, minor), 7.68 (d, *J* = 7.8 Hz, 3.5H, major (2H)+minor (1.5H)), 7.48 (t, *J* = 7.8 Hz, 1.5H, minor), 7.37 (t, *J* = 7.8 Hz, 2H, major), 7.23-7.19 (m, 6H, major(2H)+minor(4H)), 7.18-7.16 (m, 1.75H, major(1H)+minor(0.75H)), 7.11 (d, *J* = 8.4 Hz, 2H, major), 7.03 (d, *J* = 7.8 Hz, 2H, major), 5.27-5.23 (m, 1.75H, major(1H)+minor(0.75H)), 4.42-4.37 (m, 1.75H, major(1H)+minor(0.75H)), 3.43-3.39 (m, 1.75H, major(1H)+minor(0.75H)), 2.38 (s, 5.25H, major(3H)+minor(2.25)), 2.34 (s, 2.25H, minor), 2.23 (s, 3H, major). ^{13}C NMR (150 MHz, $CDCl_3$) δ **3de**: 195.98, 144.65, 137.80, 136.48, 133.35, 130.06, 129.78, 129.33, 129.30, 128.88, 128.56, 128.11, 128.02, 59.35, 47.21, 21.61, 21.02; **3de'**: 195.43, 144.38, 136.80, 135.54, 133.47, 132.98, 129.79, 129.04, 128.88, 128.14, 128.02, 127.87, 125.98, 59.30, 47.42, 21.66, 21.02. **HRMS** (ESI) m/z calculated for $C_{23}H_{22}NaO_3S$ $[M+Na]^+$ 401.1180, found 401.1187.



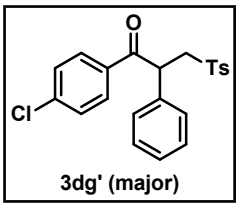
3df (major) 3df' (minor)

2-(4-Methoxyphenyl)-1-phenyl-3-tosylpropan-1-one (3df, major) : 1-(4-methoxyphenyl)-2-phenyl-3-tosylpropan-1-one (3df', minor) = 6:5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89-7.88 (m, 3.67H, major(2H)+minor(1.67H)), 7.69-7.68 (m, 3.67H, major(2H)+minor(1.67H)), 7.49 (t, *J* = 7.2 Hz, 1H, major), 7.37 (t, *J* = 7.8 Hz, 2H, major), 7.24-7.20 (m, 7H, major(2H)+minor(5H)), 7.19-7.17 (m, 0.83H, minor), 7.14 (d, *J* = 9.0 Hz, 2H, major), 6.85 (d, *J* =

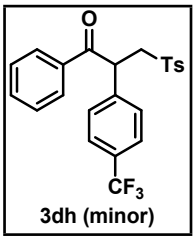
8.4 Hz, 1.67H, minor), 6.76 (d, *J* = 9.0 Hz, 2H, major), 5.23 (dd, *J* = 9.0, 4.2 Hz, 1.83H, major(1H)+minor(0.83H)), 4.42-4.35 (m, 1.83H, major(1H)+minor(0.83H)), 3.81 (s, 2.53H, minor), 3.71 (s, 3H, major), 3.43-3.40 (m, 1.83H, major(1H)+minor(0.83H)), 2.38 (s, 5.55H, major(3H)+minor(2.55H)). ^{13}C NMR (150 MHz, $CDCl_3$) δ **3df**: 196.05, 159.26, 144.63, 135.54, 133.33, 131.25, 129.78, 129.30, 128.86, 128.57, 128.11, 128.08, 114.77, 59.37, 55.23, 46.76, 21.60; **3df'**: 194.25, 163.76, 137.04, 136.52, 136.50, 129.76, 128.57, 128.45, 128.32, 128.11, 128.08, 127.83, 113.81, 59.33, 55.49, 47.19, 21.60. **HRMS** (ESI) m/z calculated for $C_{23}H_{22}NaO_4S$ $[M+Na]^+$ 417.1127, found 417.1136.



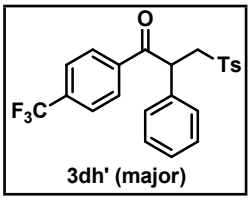
2-(4-Chlorophenyl)-1-phenyl-3-tosylpropan-1-one (3dg): White solid; m.p: 95-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.25-7.18 (m, 4H), 7.16 (d, J = 8.4 Hz, 2H), 5.27 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.31 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.44 (d, *J* = 14.4, 4.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.70, 144.86, 136.35, 135.22, 134.87, 134.09, 133.66, 129.84, 129.58, 129.52, 128.86, 128.71, 128.04, 59.12, 46.87, 21.61. **HRMS** (ESI) m/z calculated for $C_{22}H_{19}NaO_3S$ $[M+Na]^+$ 421.0638, found 421.0641.



1-(4-chlorophenyl)-2-phenyl-3-tosylpropan-1-one (3dg'): White solid; m.p: 94-95 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.26-7.24 (m, 4H), 7.22-7.20 (m, 3H), 5.22 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.40 (dd, *J* = 13.8, 8.4 Hz, 1H), 3.40 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.79, 144.81, 139.95, 136.43, 136.20, 133.87, 130.26, 129.86, 129.49, 128.96, 128.14, 128.09, 128.07, 59.23, 47.56, 21.62. **HRMS** (ESI) m/z calculated for $C_{22}H_{19}NaO_3S$ $[M+Na]^+$ 421.0636, found 421.0641.

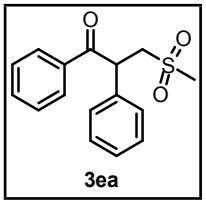


1-Phenyl-3-tosyl-2-(4-(trifluoromethyl)phenyl)propan-1-one (3dh): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.37 (dd, *J* = 7.8, 5.4 Hz, 1H), 4.31 (dd, *J* = 14.4, 7.8 Hz, 1H), 3.51 (dd, *J* = 14.4, 5.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.46, 144.91, 140.24, 136.26, 135.10 (q, *J* = 30.0 Hz), 133.84, 129.83, 128.88, 128.79, 128.72, 128.00, 126.22 (q, *J* = 3.0 Hz), 123.75 (q, *J* = 272.0 Hz), 59.01, 47.31, 21.55. **HRMS** (ESI) m/z calculated for $C_{23}H_{19}F_3NaO_3S$ $[M+Na]^+$ 455.0912, found 455.0905.

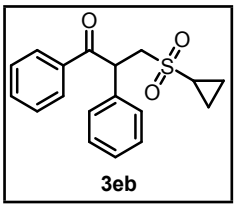


2-Phenyl-3-tosyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3dh'): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.28-7.26 (m, 4H), 7.24-7.21 (m, 3H), 5.27 (dd, *J* = 9.0, 3.6 Hz, 1H), 4.42 (dd, *J* = 13.8, 9.0 Hz, 1H),

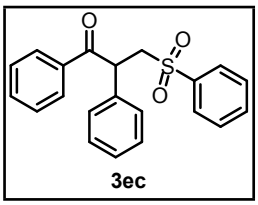
3.42 (dd, *J* = 13.8, 3.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.20, 144.90, 138.35, 136.41, 135.75, 134.60 (q, *J* = 30.0 Hz), 129.90, 129.60, 129.17, 128.30, 128.13, 128.05, 125.68 (q, *J* = 3.0 Hz), 123.45 (q, *J* = 273.0 Hz), 59.24, 47.87, 21.62. **HRMS** (ESI) m/z calculated for $C_{23}H_{19}F_3NaO_3S$ $[M+Na]^+$ 455.0910, found 455.0905.



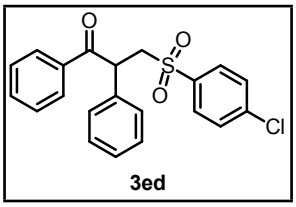
3-(methylsulfonyl)-1,2-diphenylpropan-1-one (3ea): White solid; m.p: 88-89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.32-7.35 (m, 4H), 7.25-7.28 (m, 1H), 5.29 (dd, *J* = 8.2, 5.0 Hz, 1H), 4.20 (dd, *J* = 14.4, 8.2 Hz, 1H), 3.41 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.57, 136.24, 135.26, 133.70, 129.69, 129.05, 128.77, 128.35, 128.31, 58.17, 48.48, 42.52. **HRMS** (ESI) m/z calculated for $C_{16}H_{16}NaO_3S$ $[M+Na]^+$ 311.0712, found 311.0720.



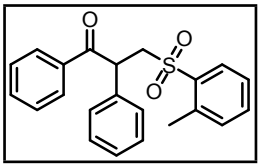
3-(cyclopropylsulfonyl)-1,2-diphenylpropan-1-one (3eb): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 5.31 (dd, *J* = 8.4, 4.5 Hz, 1H), 4.31 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.41 (dd, *J* = 14.4, 4.5 Hz, 1H), 2.19-2.11 (m, 1H), 1.24-1.17 (m, 1H), 1.14-1.08 (m, 1H), 0.98-0.92 (m, 1H), 0.86-0.79 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.50, 136.64, 135.42, 133.59, 129.53, 128.98, 128.76, 128.31, 128.18, 57.13, 47.95, 30.80, 5.51, 4.87. **HRMS** (ESI) m/z calculated for $C_{18}H_{18}NaO_3S$ $[M+Na]^+$ 337.0869, found 337.0873.



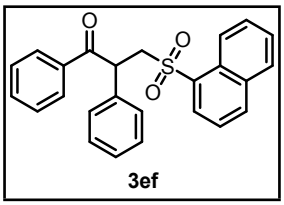
1,2-diphenyl-3-(phenylsulfonyl)propan-1-one (3ec): White solid; m.p: 100-101 °C; ^{1}H NMR (600MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.24-7.22 (m, 4H), 7.20-7.16 (m, 1H), 5.30 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.43 (dd, *J* = 14.2, 8.4 Hz, 1H), 3.46 (dd, *J* = 14.2, 3.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.83, 139.43, 136.42, 135.46, 133.74, 133.48, 129.42, 129.22, 128.91, 128.65, 128.17, 128.05, 128.04, 59.20, 47.54. **HRMS** (ESI) m/z calculated for $C_{21}H_{18}NaO_3S$ $[M+Na]^+$ 373.0869, found 373.0875.



3-((4-chlorophenyl)sulfonyl)-1,2-diphenylpropan-1-one (3ed): Yellow solid; m.p: 94-95 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44-7.35 (m, 4H), 7.29-7.13 (m, 5H), 5.28 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.40 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.48 (dd, *J* = 14.4, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.75, 140.47, 137.90, 136.15, 135.34, 133.60, 129.58, 129.48, 128.87, 128.69, 128.17, 128.12, 59.33, 47.67. **HRMS** (ESI) m/z calculated for $C_{21}H_{17}ClNaO_3S$ $[M+Na]^+$ 407.0479, found 407.0480.



1,2-Diphenyl-3-(o-tolylsulfonyl)propan-1-one (3ee): White solid; m.p.: 64-65 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86-7.85 (m, 3H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.26-7.23 (m, 4H), 7.20-7.15 (m, *2*H), 5.28 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.51 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.42 (dd, *J* = 14.4, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.86, 138.45, 137.17, 136.55, 135.47, 133.76, 133.41, 132.70, 130.09, 129.40, 128.85, 128.56, 128.09, 128.00, 126.37, 58.20, 47.39, 20.33. **HRMS** (ESI) m/z calculated for $C_{22}H_{20}NaO_3S$ $[M+Na]^+$ 387.1022, found 387.1031.



3-(naphthalen-1-ylsulfonyl)-1,2-diphenylpropan-1-one (3ef)： White solid; m.p: 106-107 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H) 7.11-7.00 (m, 5H), 5.28 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.54 (dd, *J* = 14.2, 8.6 Hz, 1H), 3.54 (dd, *J* = 14.2, 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.82, 136.27, 135.48, 135.32, 134.32, 134.13, 133.43, 130.55, 129.26, 129.21, 128.92, 128.88, 128.62, 128.13, 127.95, 127.10, 124.22, 124.16, 58.72, 47.48. **HRMS** (ESI) m/z calculated for $C_{25}H_{20}NaO_3S$ $[M+Na]^+$ 423.1025, found 423.1025.

4. Investigation of mechanism

4.1 Control experiments

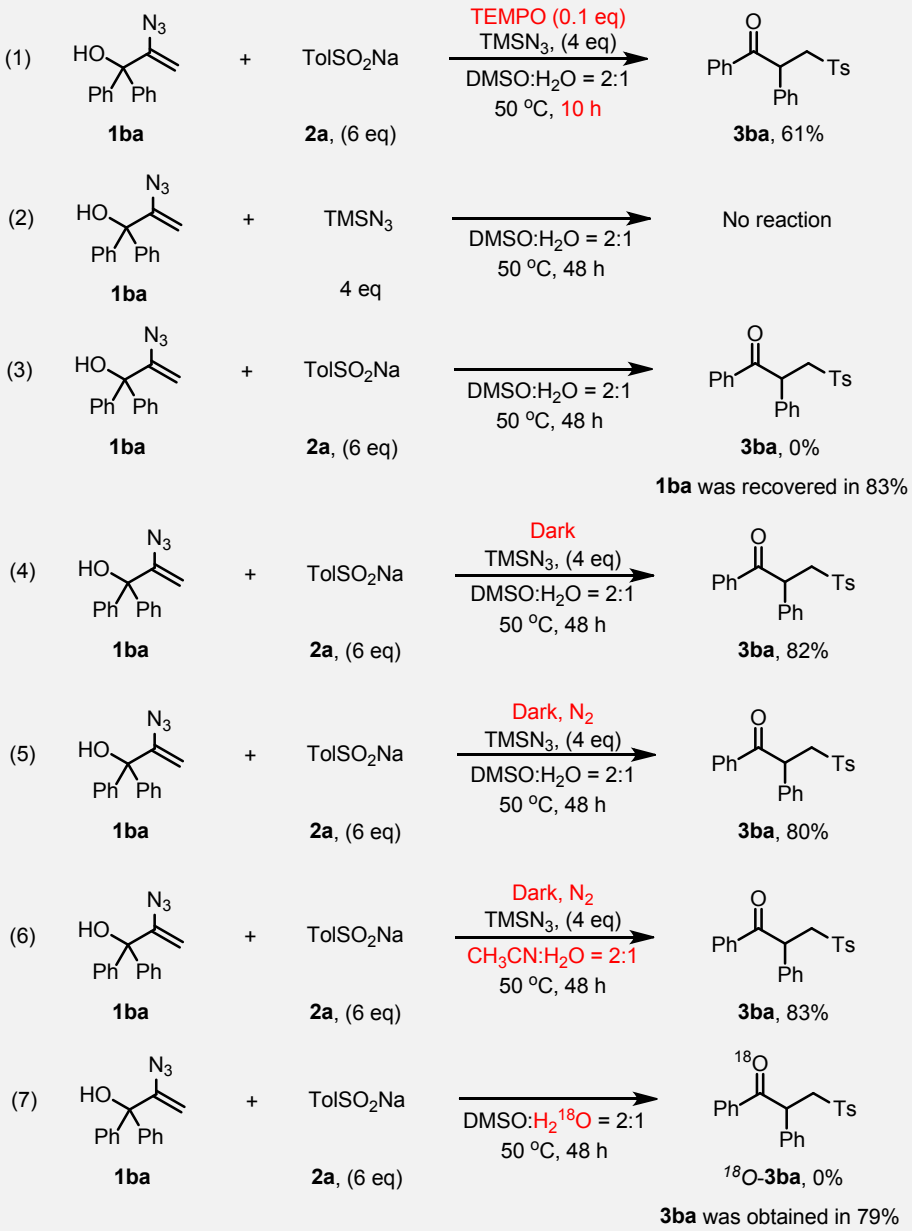
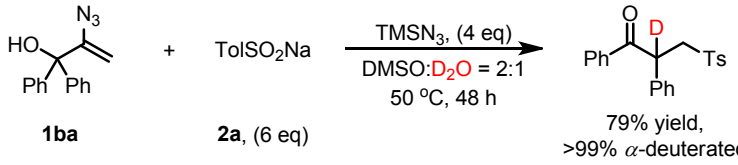


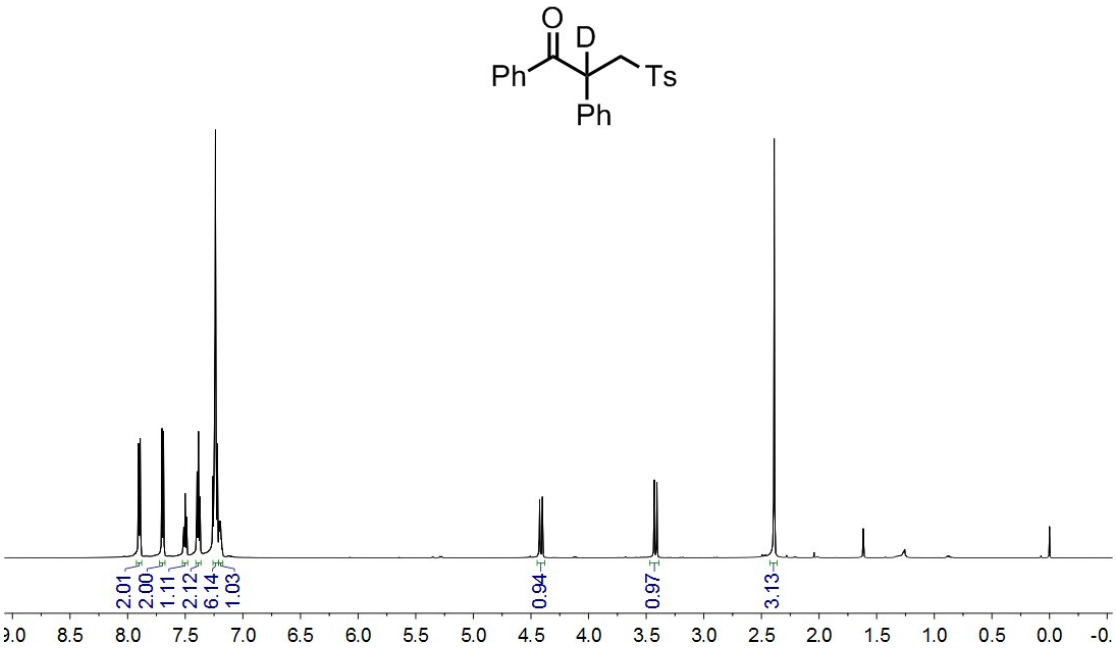
Figure S1. Control experiments

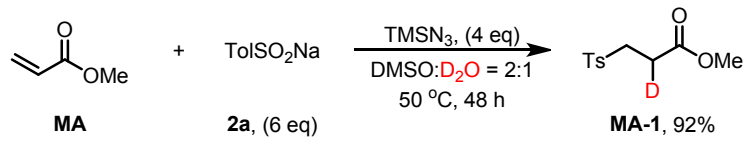
The catalytic amount of TEMPO were beneficial to accelerate the rate of the transformation,[3] despite the yield of desired product would be lowered (eq. 1). Further information on the generation of sulfonyl radical was obtained by submission of allylic alcohols (**1ba**) to various reaction conditions (eq. 2 and 3), which revealed a dual role of $TMSN_3$: in the absence of $TMSN_3$, no reaction took place, whereas in the presence of 4 equivalents, product **3ba** was afforded in high yield (84%). This implies that $TMSN_3$ plays a critical role in the generation of sulfonyl radical. Meanwhile, the results were listed in eq. 4-6 showed that solvent, oxygen, and light all did not affect the generation of sulfonyl radical. Therefore, the sulfonyl radical may be generated from the homolysis process under the action of $TMSN_3$. The experiment of eq. 7 demonstrated that the oxygen of carbonyl in the product was not from water.

4.2 Deuterium-labeling studies

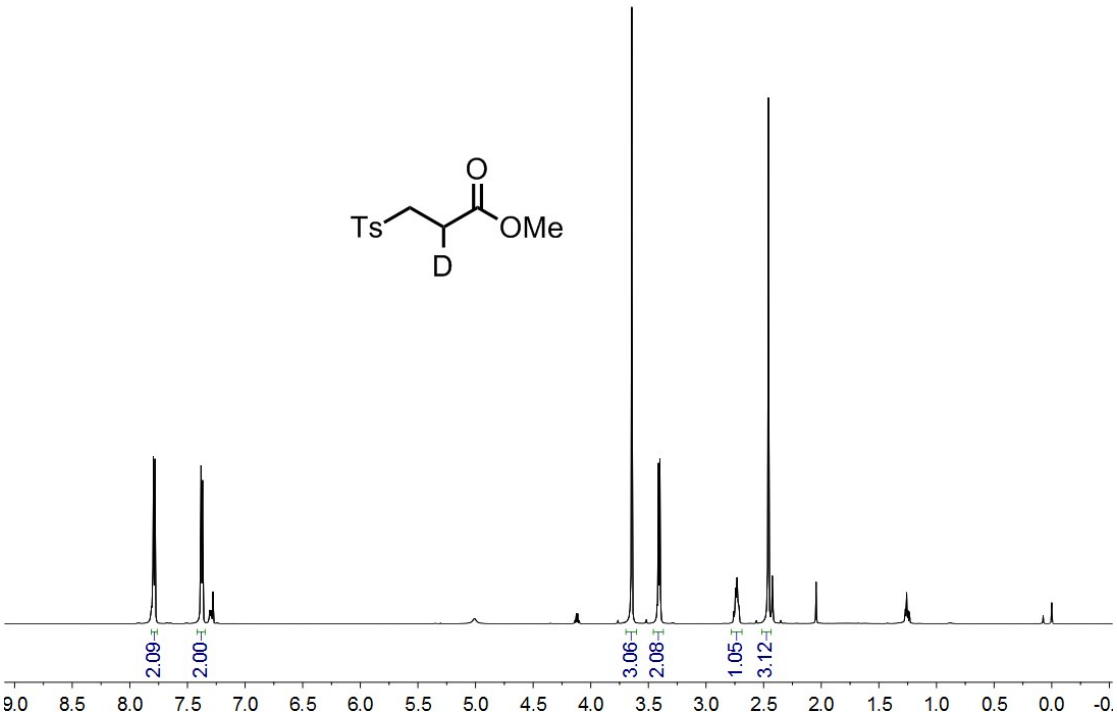


A Schlenk tube was placed compound **1ba** (0.5 mmol), $TolSO_2Na$ (3.0 mmol), $TMSN_3$ (2.0 mmol), D_2O (0.7 mL), and DMSO (1.4 mL). Then the mixture was stirred at 50 °C for 48h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 6:1) to afford deuterated product ***d*-3ba** in 79% yield.

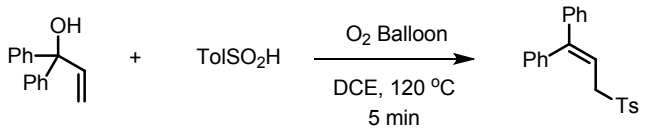




A Schlenk tube was placed compound **MA** (0.5 mmol), $TolSO_2Na$ (3.0 mmol), $TMSN_3$ (2.0 mmol), D_2O (0.7 mL), and DMSO (1.4 mL). Then the mixture was stirred at 50 °C for 48h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 10:1) to afford deuterated product **MA-1** in 92% yield.[4]

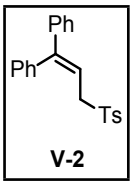


4.3 Research on the key intermediate



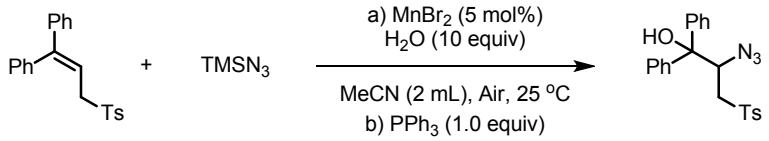
V-1 **V-2**

Allylic alcohol **V-1** (0.3 mmol) and *p*-toluene sulfonic acid (0.6 mmol) in dichloroethane (2 mL) were stirred at 120 °C with an O_2 balloon for 5 min. Upon completion of the reaction (as indicated by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum/ethyl acetate as the eluent to afford pure product **V-2** in 85% yield.[5]



V-2

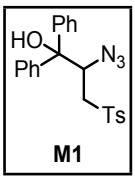
(3-Tosylprop-1-ene-1,1-diyl)dibenzene (V-2): Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.29-7.22 (m, 8H), 7.17-7.15 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.12 (t, *J* = 7.8 Hz, 1H), 3.90 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.60, 144.63, 140.59, 137.86, 135.81, 129.70, 129.27, 128.52, 128.33, 128.24, 127.77, 127.45, 114.28, 57.60, 21.66.



V-2 **M1**

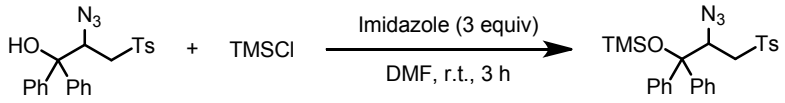
Compound **V-2** (0.3 mmol), $TMSN_3$ (0.6 mmol), $MnBr_2$ (0.015 mmol) and H_2O (3 mmol) in

MeCN (2 mL) at room temperature under ambient air. Monitoring the reaction by TLC to confirm whether the **V-2** disappeared or not. Then PPh_3 (0.3 mmol) was added and the mixture was stirred for 10 min. finally, the mixture was purified through column chromatography to afford the pure product **M1** in 82% yield.[6]



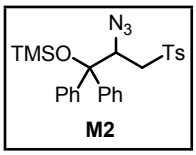
M1

2-Azido-1,1-diphenyl-3-tosylpropan-1-ol (M1): Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.38-7.34 (m, 6H), 7.29-7.26 (m, 3H), 7.23-7.22 (m, 1H), 4.97 (d, J = 9.0 Hz, 1H), 3.36-3.32 (m, 1H), 3.21 (d, J = 8.4 Hz, 1H), 2.77 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.97, 143.82, 136.69, 130.04, 128.87, 128.83, 127.85, 127.83, 127.78, 125.47, 125.25, 80.58, 64.04, 56.92, 21.69. **HRMS** (ESI) m/z calculated for $C_{22}H_{21}N_3NaO_3S$ $[M+Na]^+$ 430.1212, found 430.1201



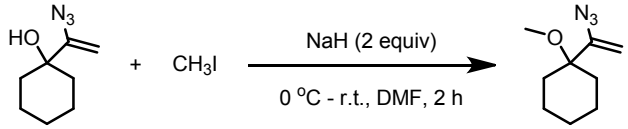
M1 (3 equiv) **M2**

Compound **M1** (0.3 mmol), TMSCl (0.9 mmol), and imidazole (0.9 mmol) in DMF (2 mL) was stirred at room temperature for 3 h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 10:1) to afford deuterated product **M2** in 94% yield.



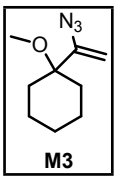
M2

(2-azido-1,1-diphenyl-3-tosylpropoxy)trimethylsilane (M2): White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 2H), 7.31-7.29 (m, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.26-7.23 (m, 6H), 7.19-7.16 (m, 2H), 4.75 (d, J = 9.6 Hz, 1H), 3.36 (d, J = 14.4 Hz, 1H), 2.65 (dd, J = 14.4, 9.6 Hz, 1H), 2.37 (s, 3H), -0.26 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.89, 140.60, 140.07, 135.54, 128.99, 127.36, 127.27, 127.20, 127.14, 127.04, 127.02, 127.00, 82.10, 62.26, 20.62, 0.59. **HRMS** (ESI) m/z calculated for $C_{25}H_{29}N_3NaO_3SSi$ $[M+Na]^+$ 502.1603, found 502.1597.



1ag 2 equiv **M3**

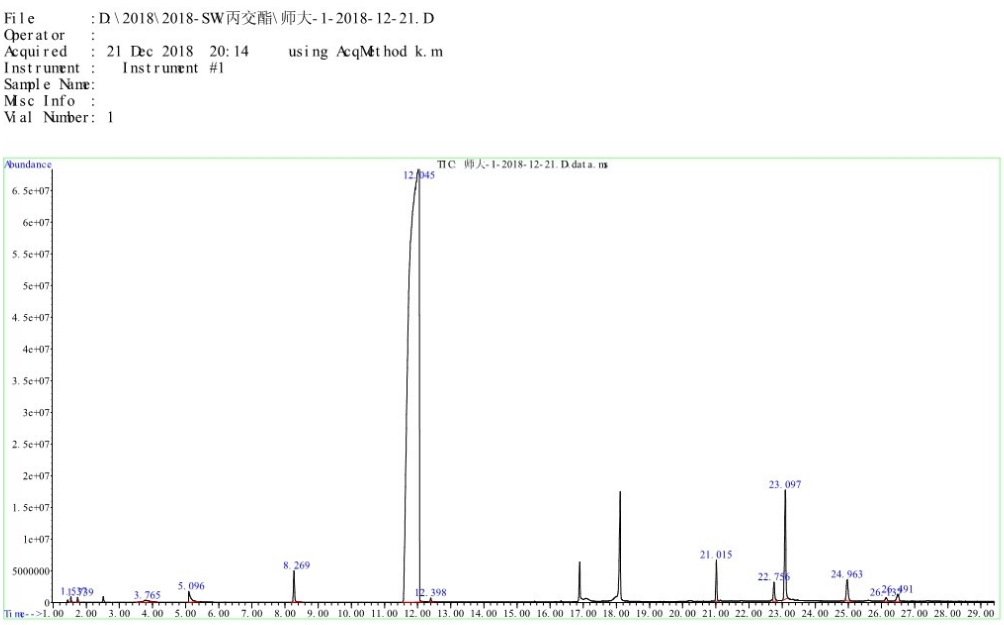
Compound **1ag** (0.3 mmol), and NaH (0.6 mmol) in DMF (2 mL) was stirred at 0 °C. After 0.5 h, CH_3I (0.6 mmol) was added to the reaction system. Then the reaction was stirred at room temperature for 2 h. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (petroleum ether:ethyl acetate = 15:1) to afford deuterated product **M3** in 96% yield.



1-(1-azidovinyl)-1-methoxycyclohexane (M3): Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.94 (d, *J* = 1.2 Hz, 1H), 4.87 (d, *J* = 1.2 Hz, 1H), 3.11 (s, 3H), 1.86-1.84 (m, 2H), 1.60-1.52 (m, 3H), 1.50-1.46 (m, 4H), 1.25-1.20 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.74, 99.42, 76.57, 49.55, 32.68, 25.57, 21.51. **HRMS** (ESI) m/z calculated for $C_9H_{15}N_3NaO$ $[M+Na]^+$ 204.1108, found 204.1113.

4.4 The detection of TMSOH and $(TMS)_2O$ by gas chromatography-mass spectrometer (GC-MS)

The Si-containing species in the reaction mixture were identified as TMSOH and $(TMS)_2O$ by GC-MS.



** Search Report Page 1 of 1 **

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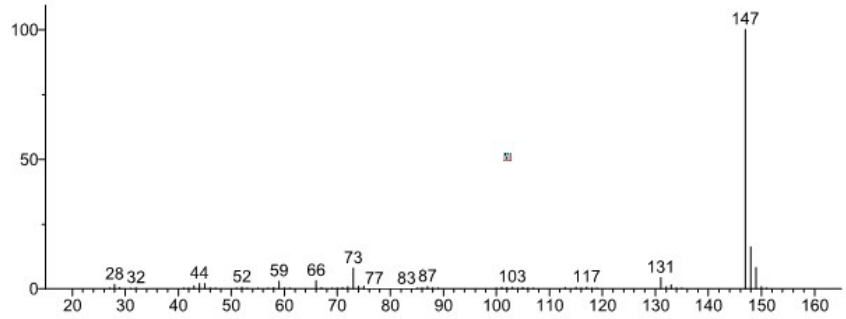
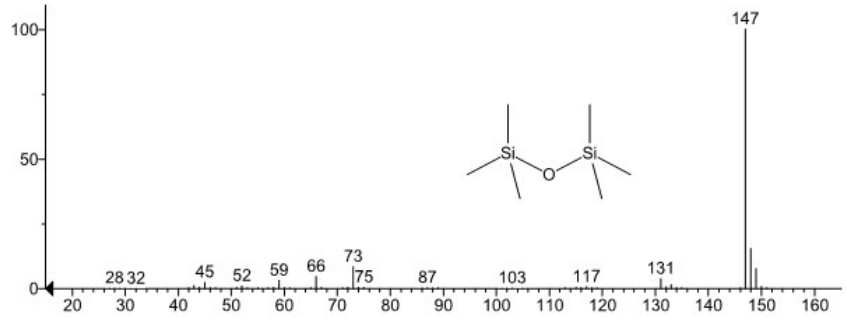
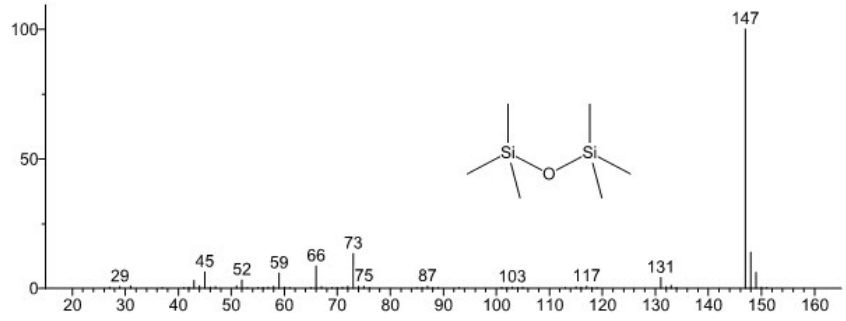
Compound in Library Factor = 256



Hit 1 : Disiloxane, hexamethyl-
C6H18OSi2; MF: 924; RMF: 925; Prob 84.1%; CAS: 107-46-0; Lib: replib; ID: 19826.

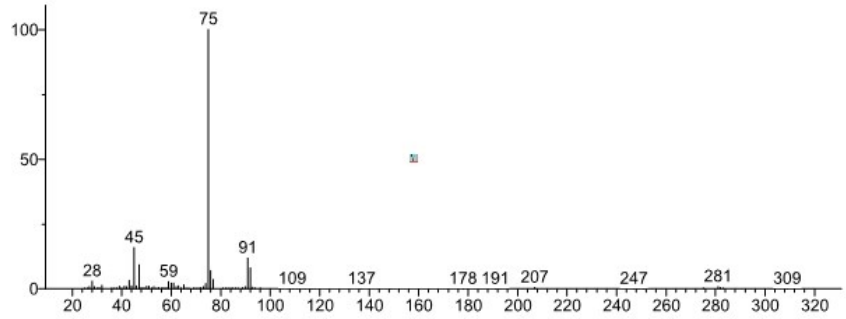


Hit 2 : Disiloxane, hexamethyl-
C6H18OSi2; MF: 913; RMF: 916; Prob 84.1%; CAS: 107-46-0; Lib: replib; ID: 19825.

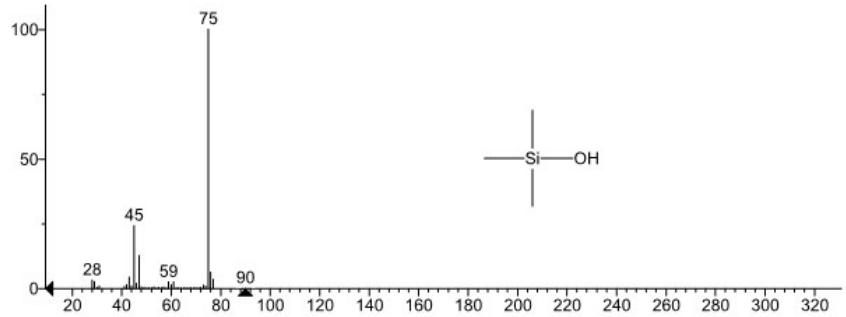


** Search Report Page 1 of 1 **

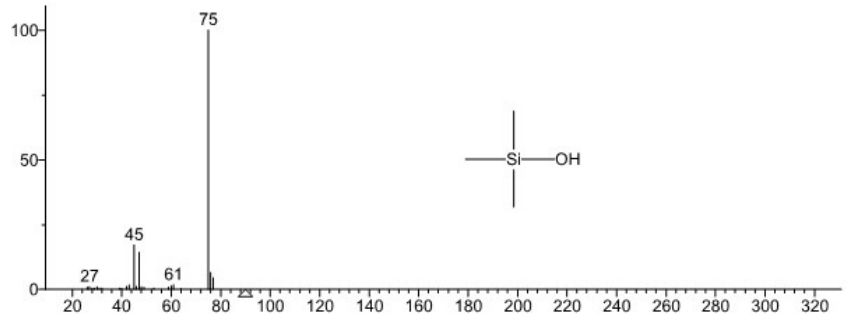
Unknown: Scan 670 (3.773 min): -1-2018-12-21.D\data.ms
Compound in Library Factor = -343



Hit 1 : Silanol, trimethyl-
C3H10OSi; MF: 761; RMF: 793; Prob 62.1%; CAS: 1066-40-6; Lib: mainlib; ID: 38640.

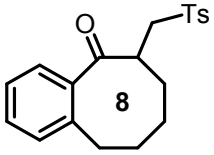


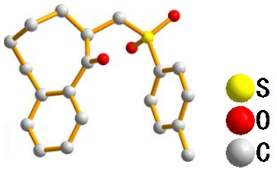
Hit 2 : Silanol, trimethyl-
C3H10OSi; MF: 737; RMF: 888; Prob 62.1%; CAS: 1066-40-6; Lib: replib; ID: 9172.



5. X-ray Structure of 3an and 3ba

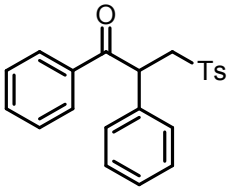
Table S2. Crystal Structure of 1,2-diphenyl-3-tosylpropan-1-one 3an (CCDC No. 1897875)

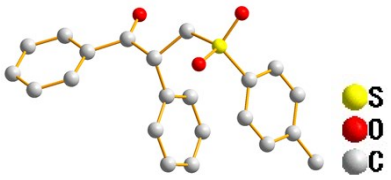




Empirical formula	C20 H22 O3 S
Temperature	293 K
Wavelength	0.71073 Å
Unit cell dimensions	a = 9.2575(7) Å b = 9.6845(7) Å c =10.1145(8)Å alpha = 79.903(6)deg. beta = 84.497(7) deg. gamma = 80.659(6) deg.
Volume	878.80(12)Å ^{3}
Z	2
Calculated density	1.294 g/m^3
Absorption coefficient	0.199 mm^{-1}
F(000)	364.0
Crystal size	0.15 × 0.12 × 0.1 mm^3
Theta range for data collection	7.622 to 58.388 deg.
Reflections collected / unique	6448 / 3958 [R(int) = 0.0181]
Data / restraints / parameters	3958 / 0 / 218
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R_1 = 0.0503, wR_2 = 0.1134
Rindices (all data)	R_1 = 0.0731, wR_2 = 0.1308

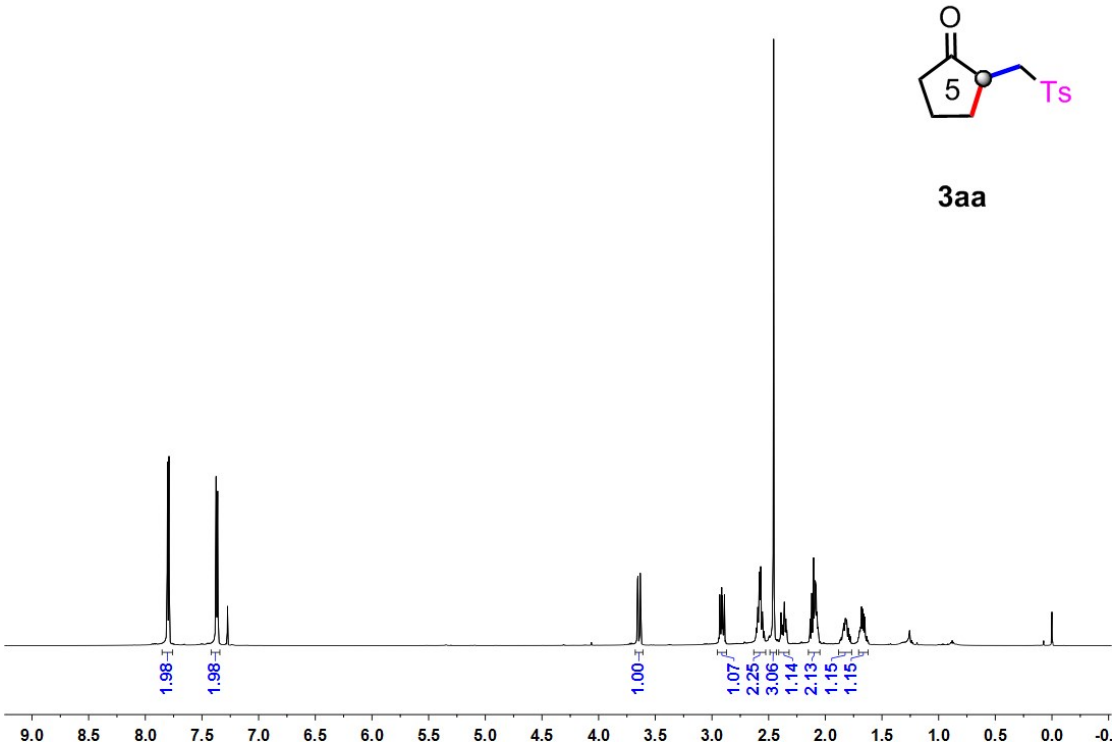
Table S3. Crystal Structure of 1,2-diphenyl-3-tosylpropan-1-one 3ba (CCDC No. 1897779)

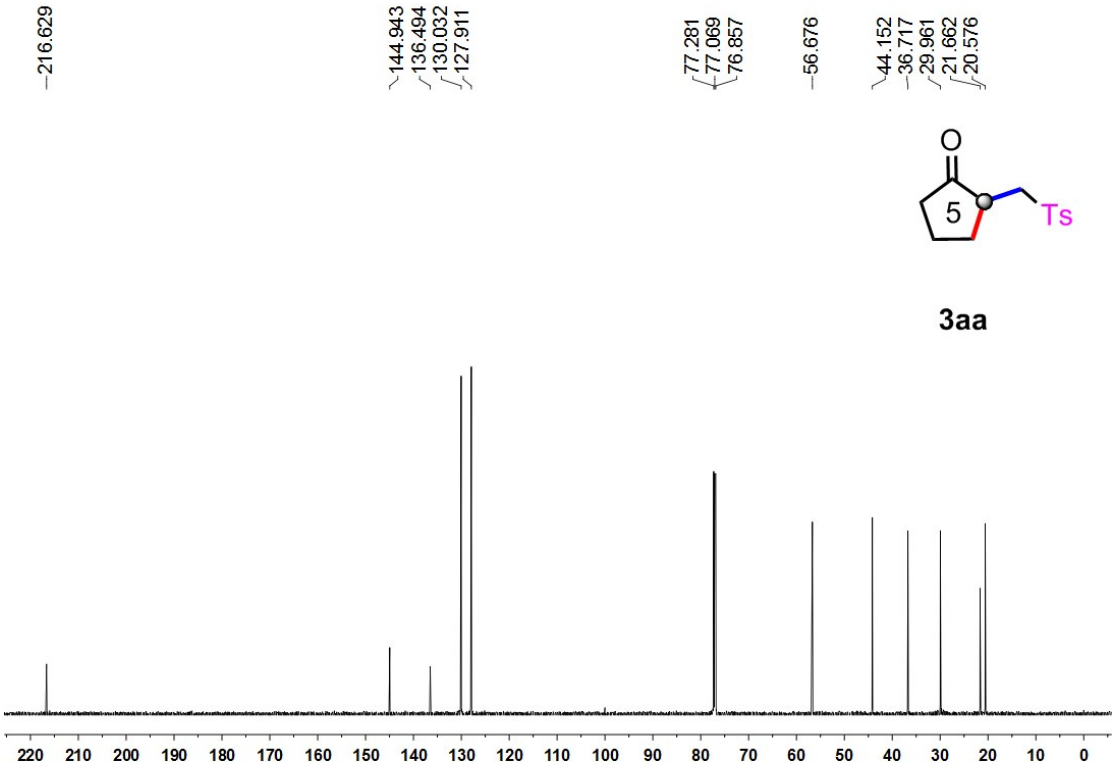


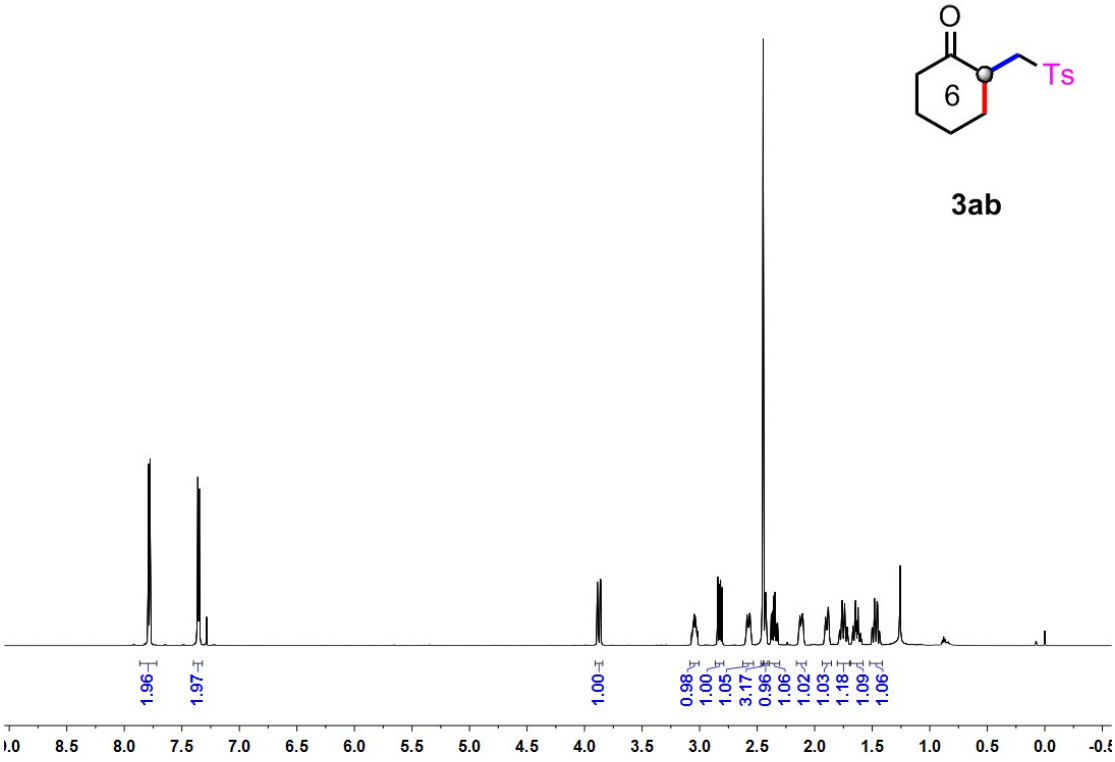


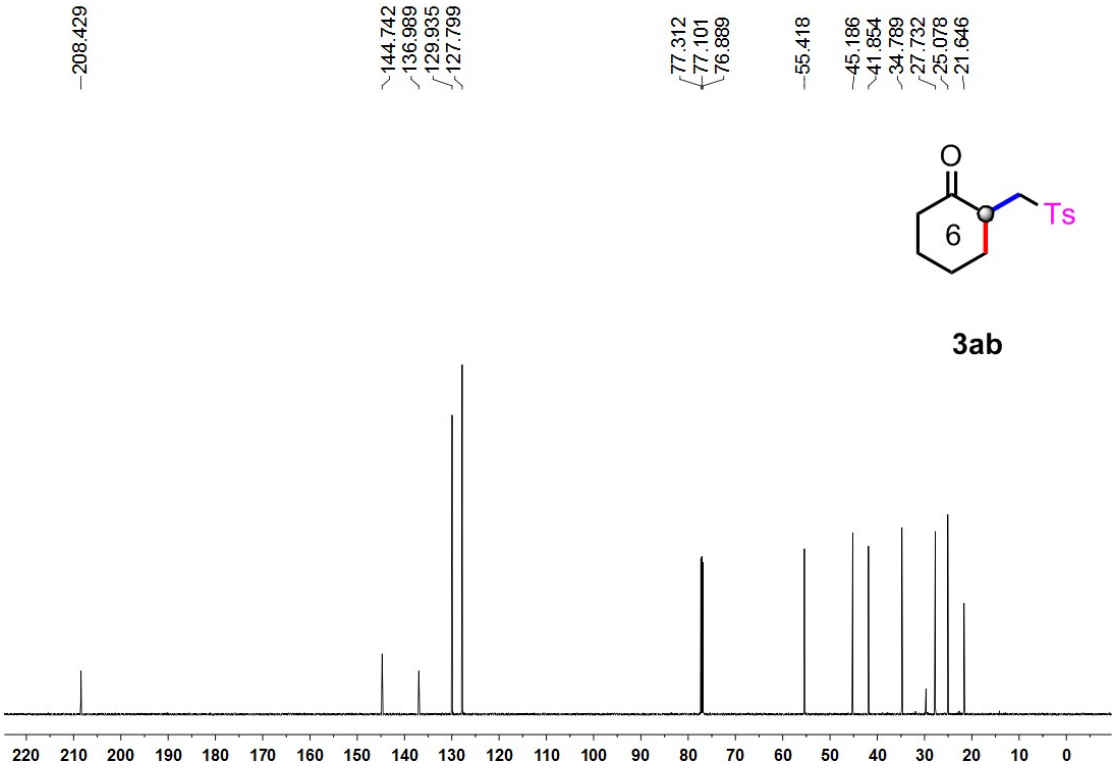
Empirical formula	C22H20O3S
Temperature	293 K
Wavelength	0.71073 Å
Unit cell dimensions	a = 19.855(3) Å b = 5.7928(7) Å c =16.427(2) Å alpha = 90.0 deg. beta = 105.359(13) deg. gamma = 90.0 deg.
Volume	1821.9(4) Å ^{3}
Z	4
Calculated density	1.329 g/m3
Absorption coefficient	0.196 mm-1
F(000)	768.0
Crystal size	0.15 × 0.12 × 0.1 mm^3
Theta range for data collection	7.06 to 58.402 deg.
Reflections collected / unique	7635 / 4207 [R(int) = 0.0293]
Data / restraints / parameters	4207 / 0 / 236
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R_1 = 0.0495, wR_2 = 0.0986
Rindices (all data)	R_1 = 0.0877, wR_2 = 0.1149

6. NMR Spectra of the Products






O
6
Ts
3ab
1.96
1.97
1.00
0.98
1.00
1.05
3.17
0.96
1.06
1.02
1.03
1.18
1.09
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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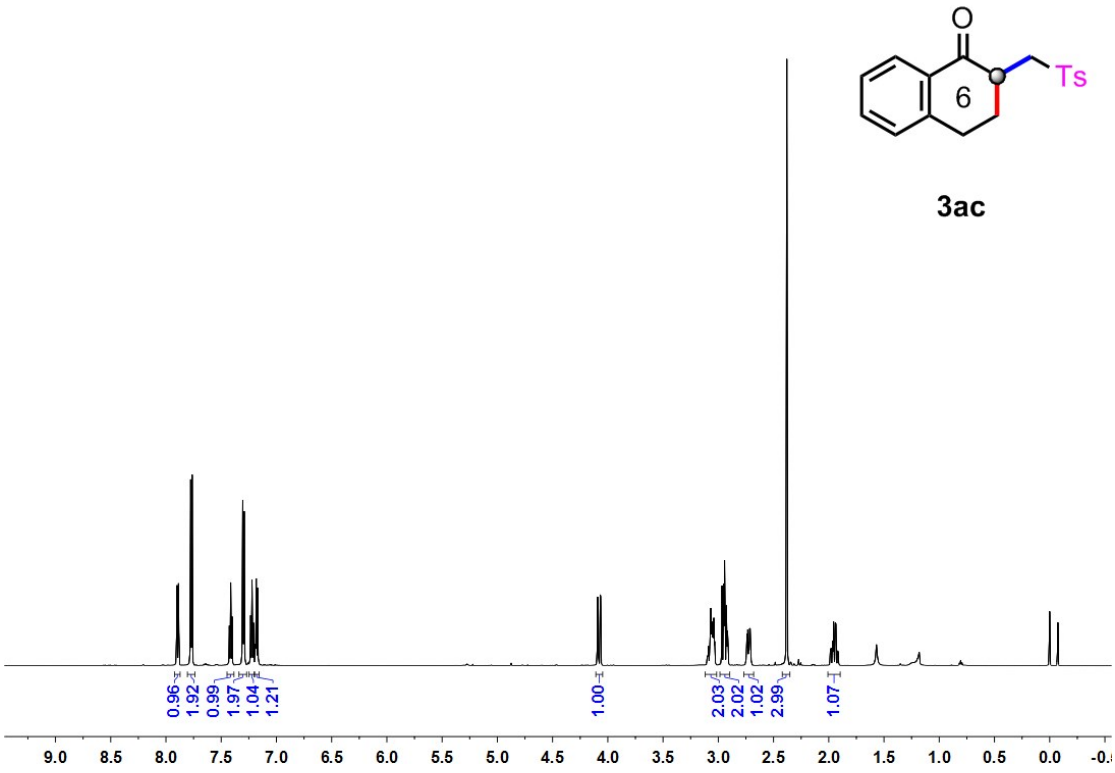
144.742
136.989
129.935
127.799
77.312
77.101
76.889
55.418
45.186
41.854
34.789
27.732
25.078
21.646
O
6
Ts
3ab
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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6
Ts
3ac
0.96
1.92
0.99
1.97
1.04
1.21
1.00
2.03
2.02
1.02
2.99
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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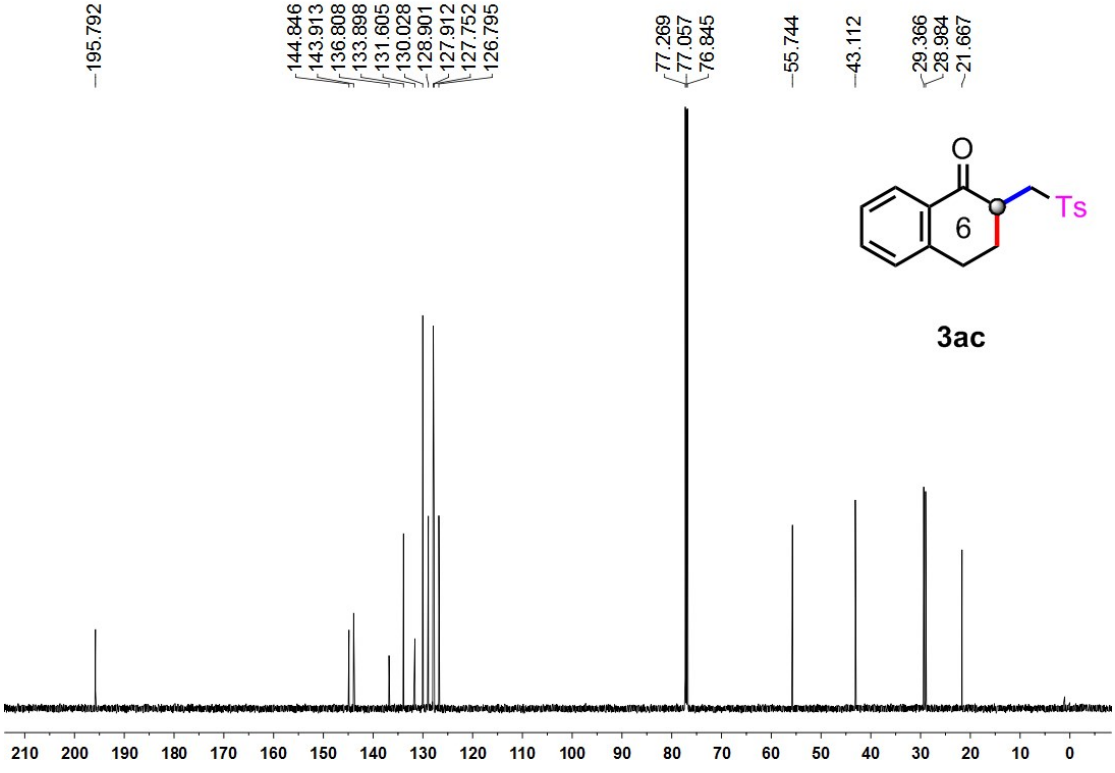
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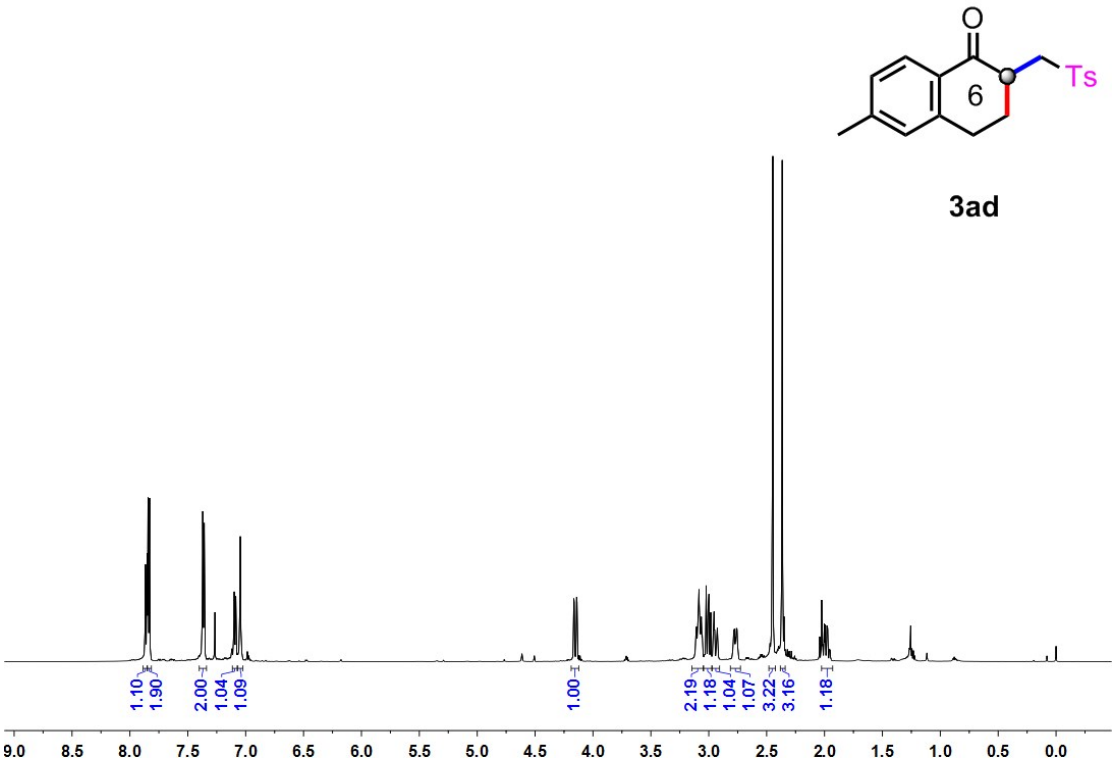
143.913
136.808
133.898
131.605
130.028
128.901
127.912
127.752
126.795
77.269
77.057
76.845
55.744
43.112
29.366
28.984
21.667
O
6
Ts
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
6
Ts
3ad
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1.90
2.00
1.04
1.09
1.00
2.19
1.18
1.04
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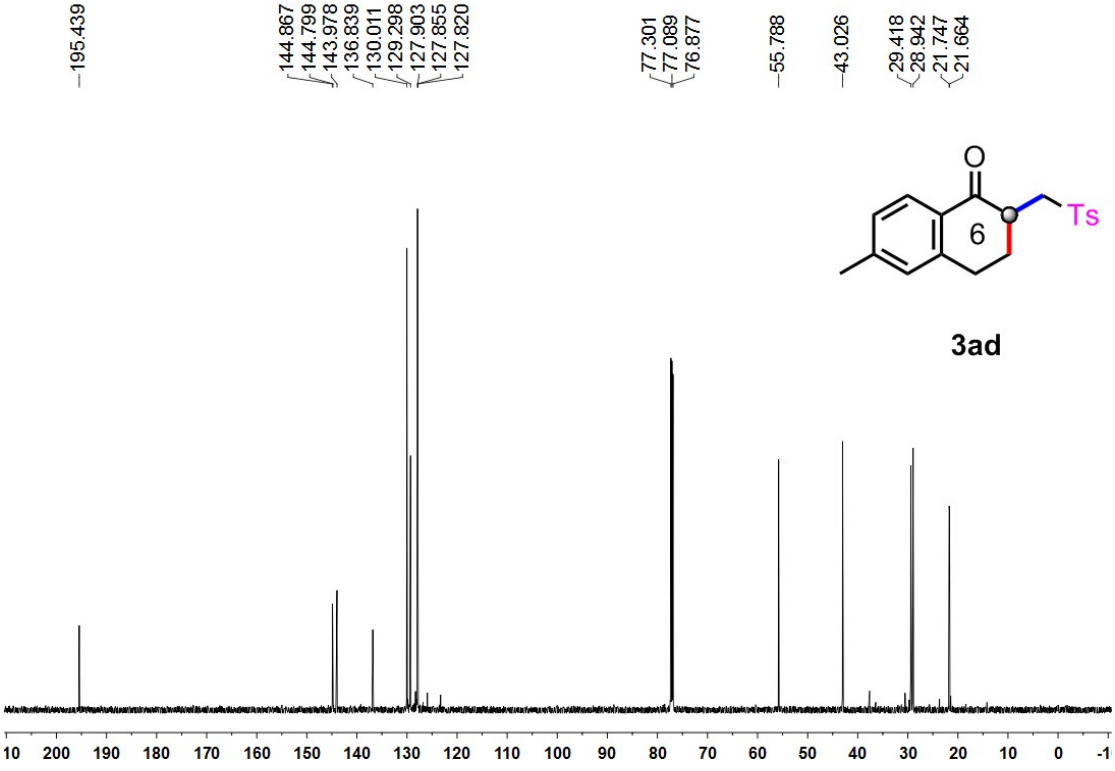
3.22
3.16
1.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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144.799
143.978
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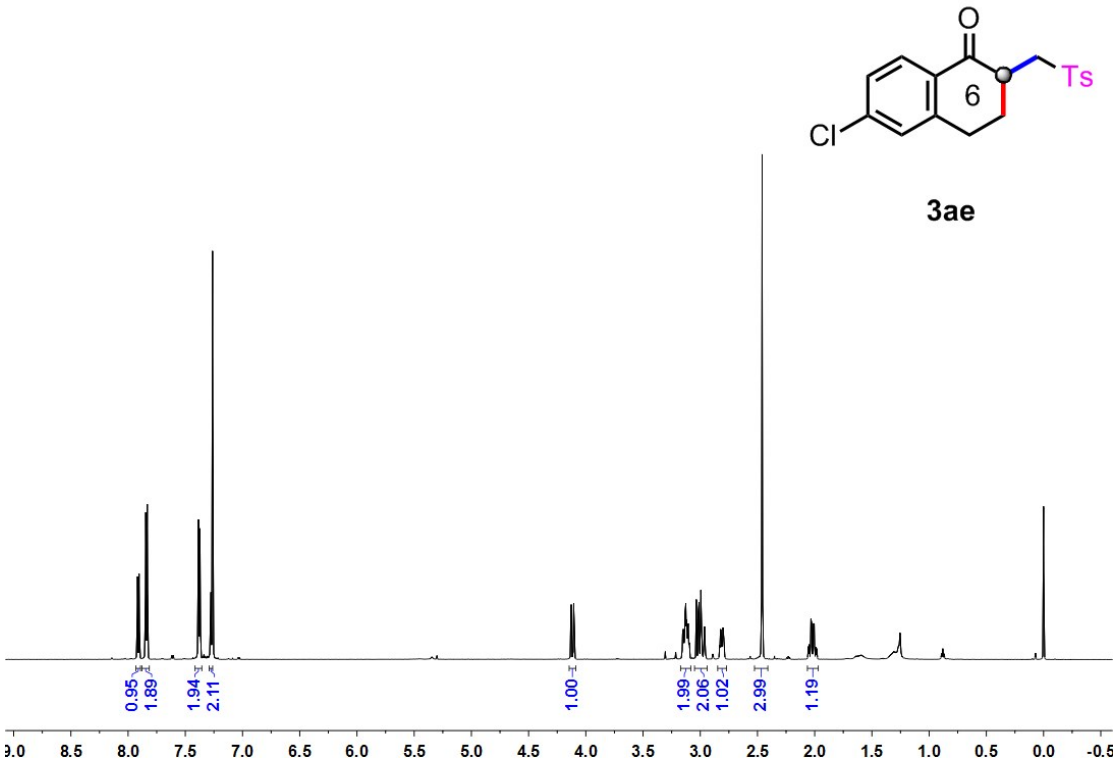
127.903
127.855
127.820
77.301
77.089
76.877
55.788
43.026
29.418
28.942
21.747
21.664
O
6
Ts
3ad
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


O
Ts
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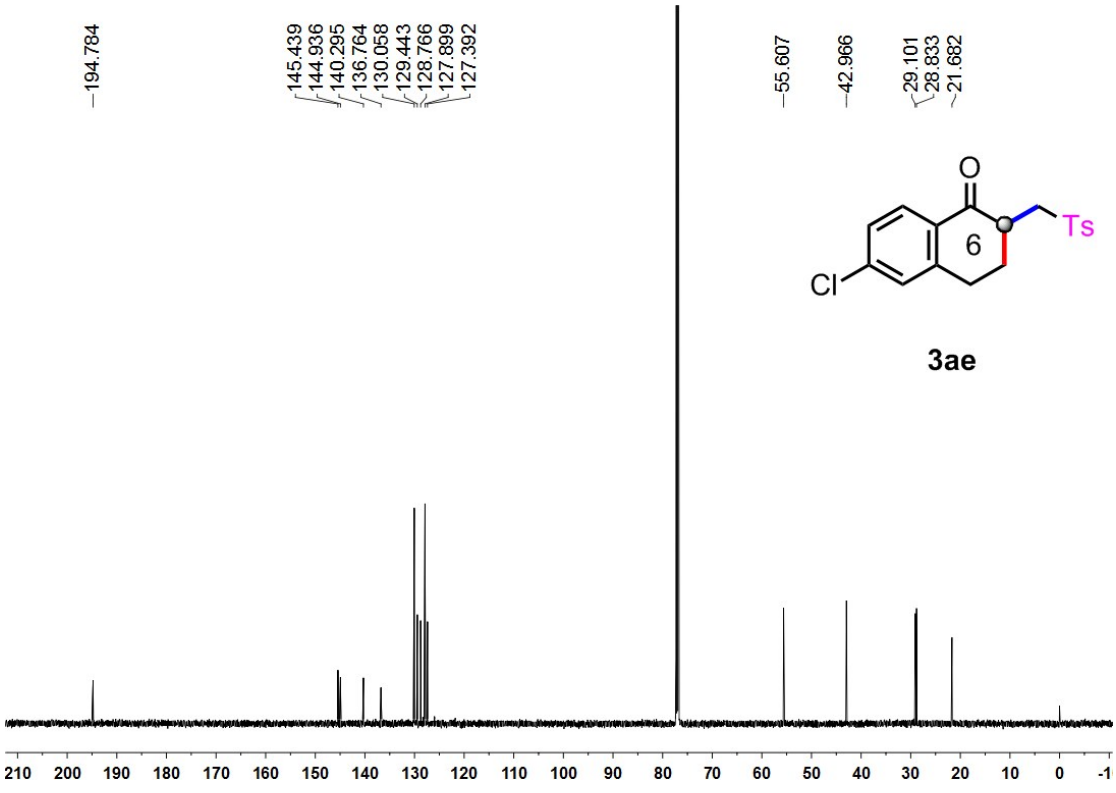
Cl
3ae
0.95
1.89
1.94
2.11
1.00
1.99
2.06
1.02
2.99
1.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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136.764
130.058
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127.899
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29.101
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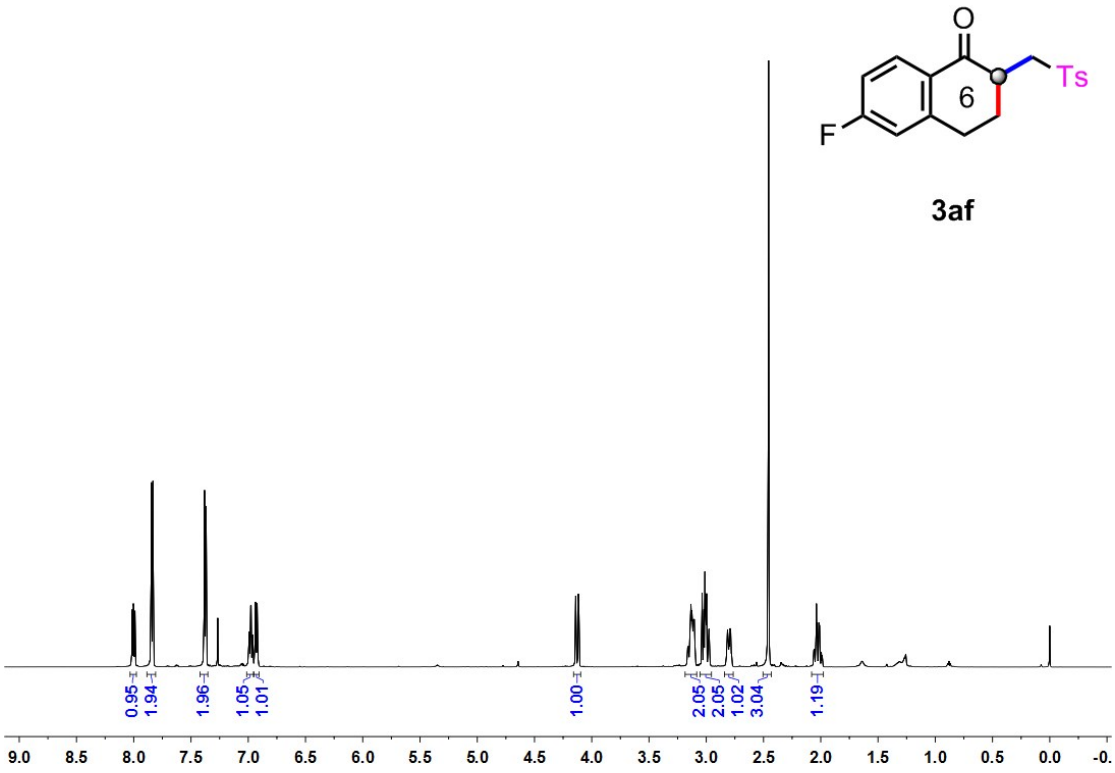
21.682
O
Ts
6
Cl
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


O
Ts
6
F
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1.94
1.96
1.05
1.01
1.00
2.05
2.05
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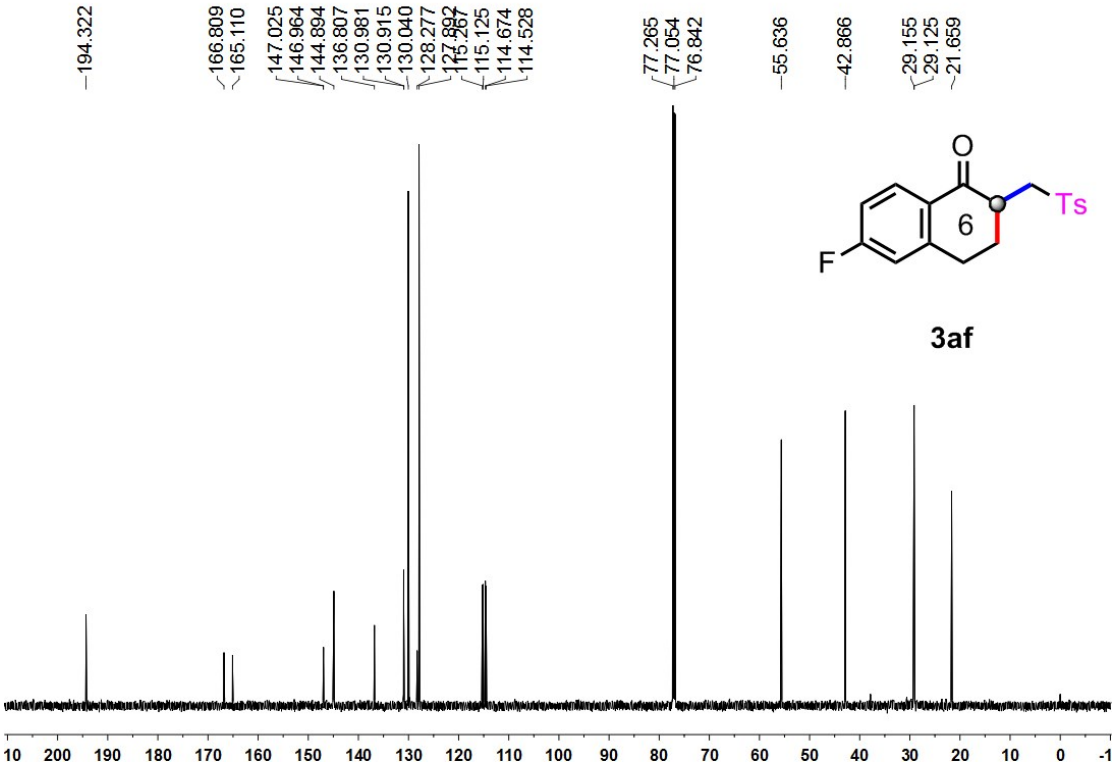
3.04
1.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.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128.277
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114.528
77.265
77.054
76.842
55.636
42.866
29.155
29.125
21.659
O
Ts
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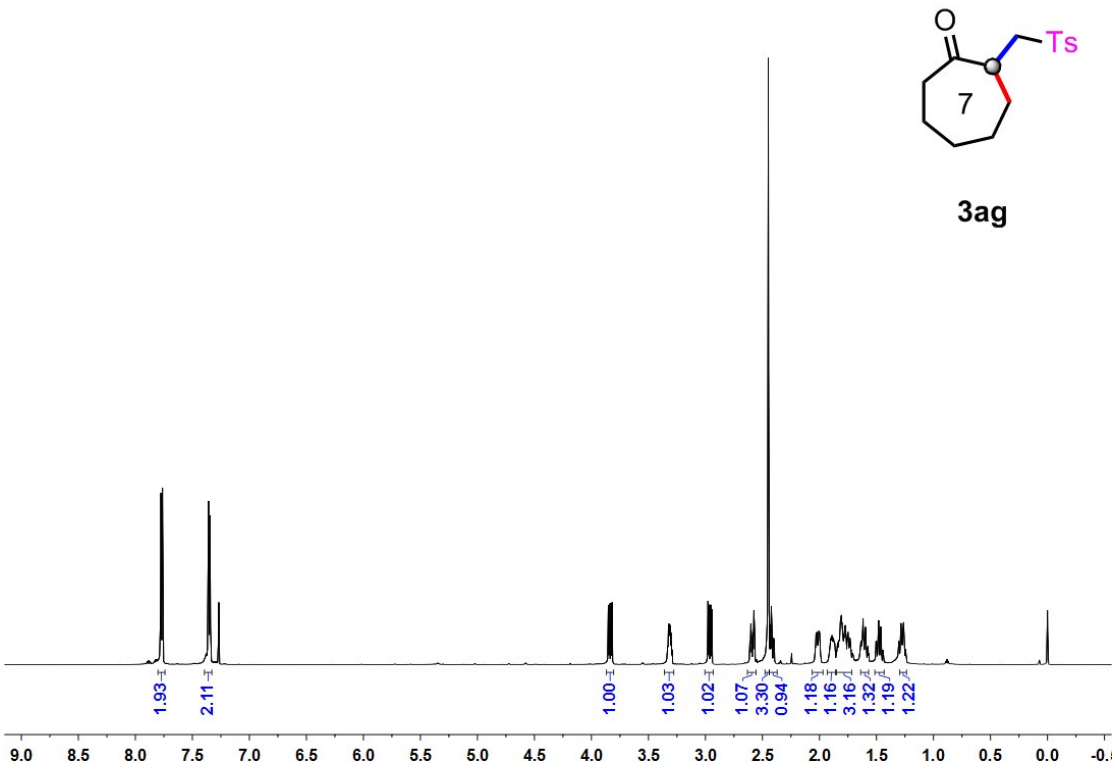
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1.32
1.19
1.22
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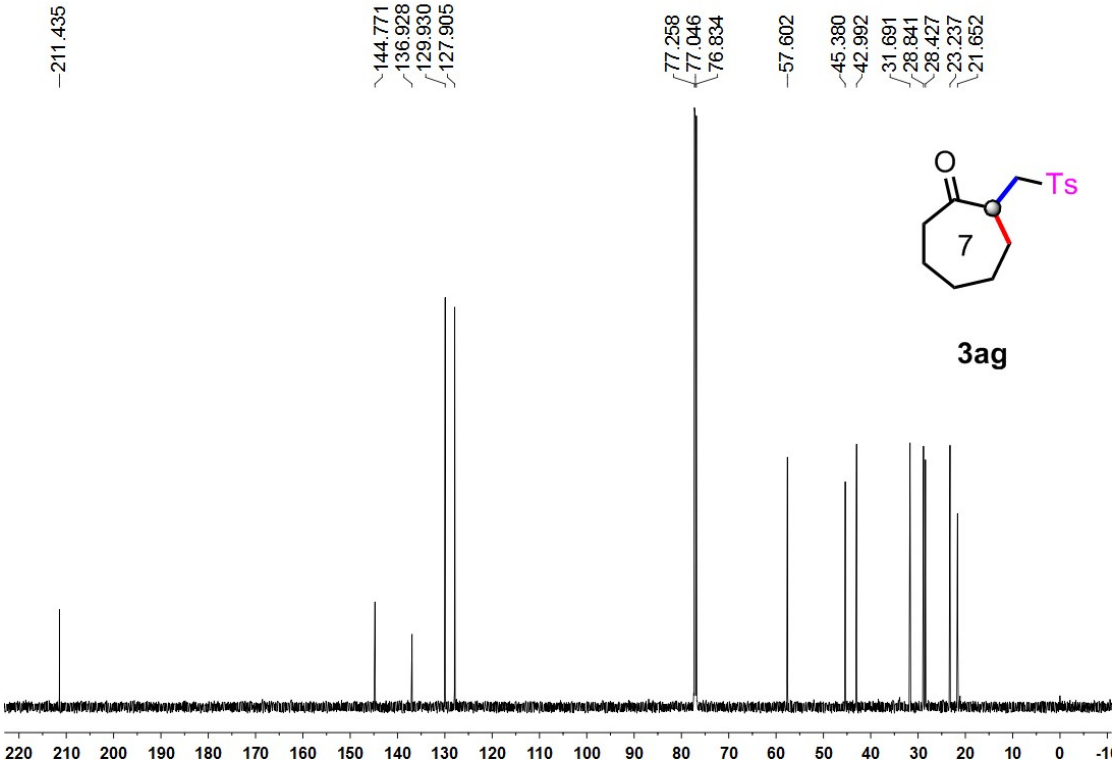
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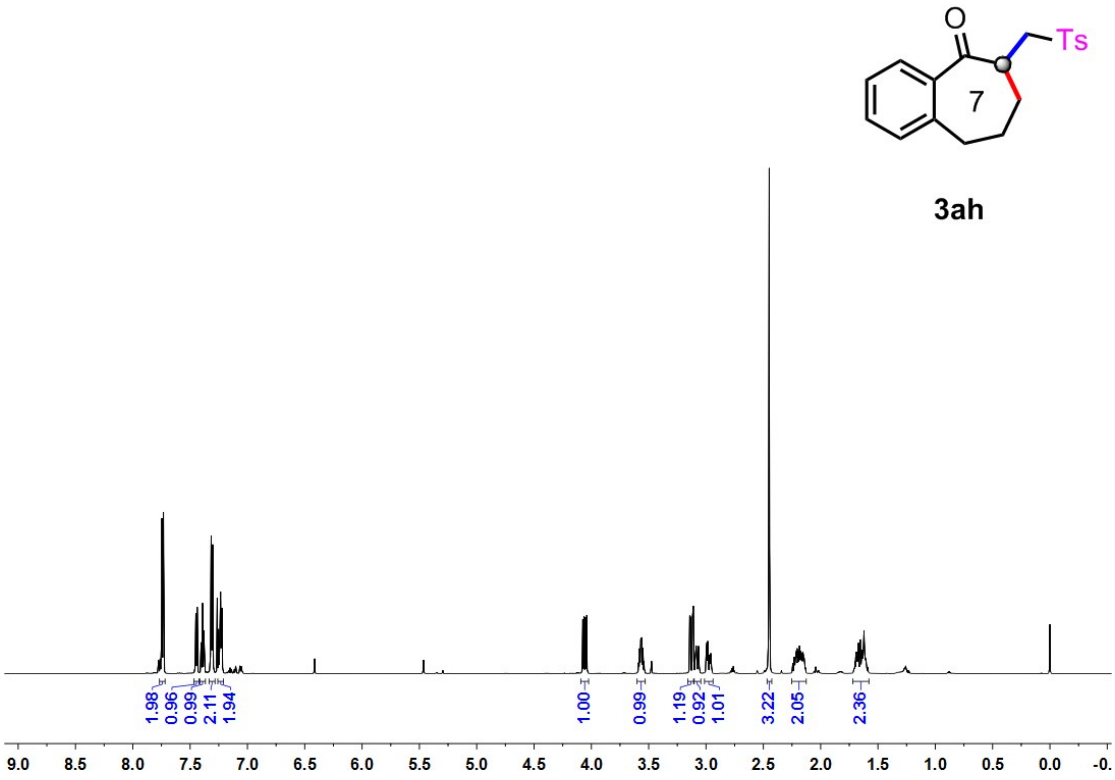
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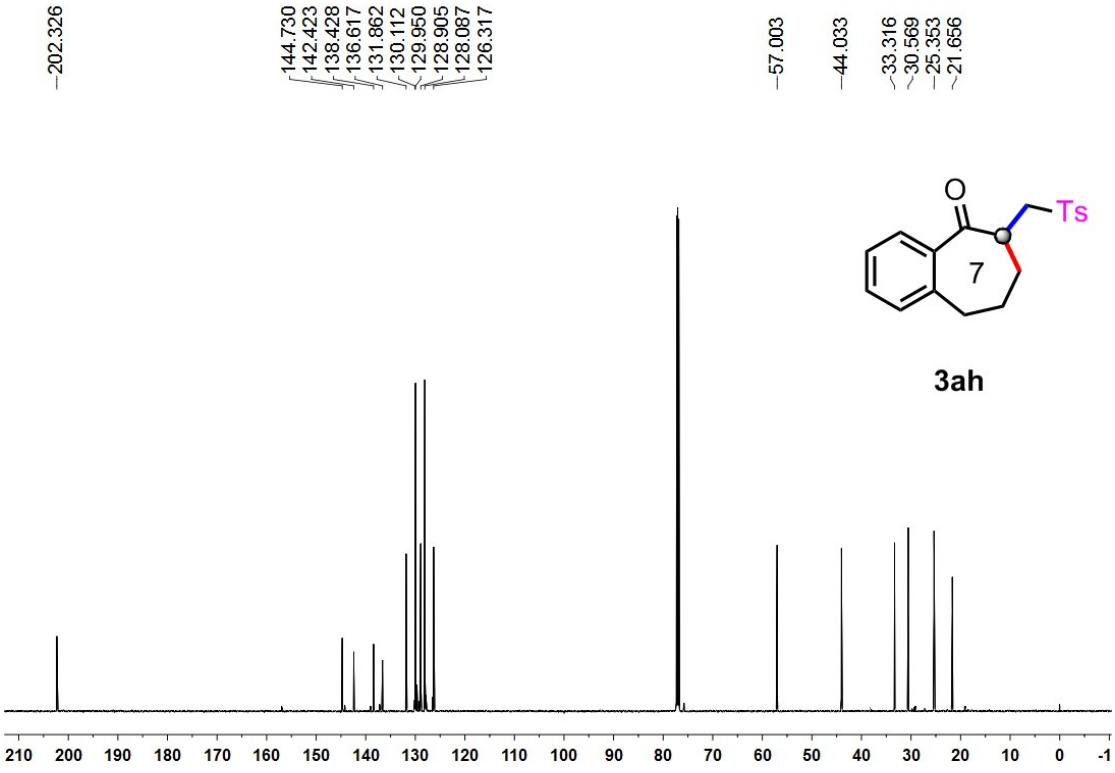
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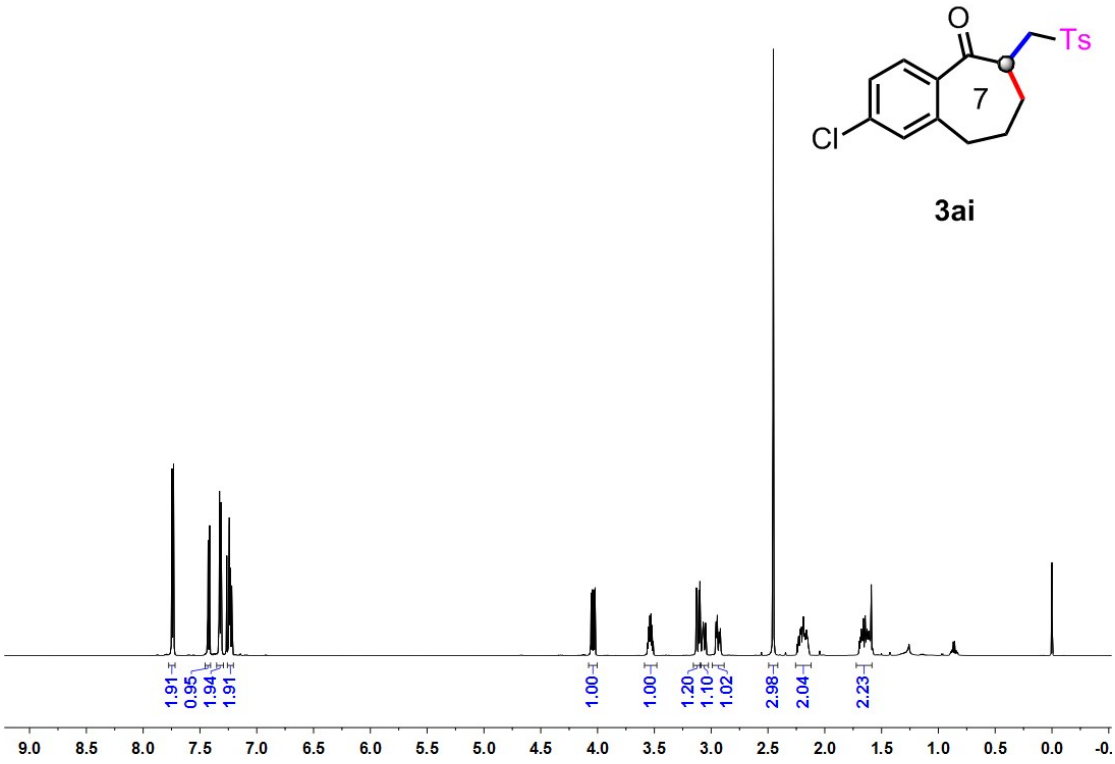
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2.23
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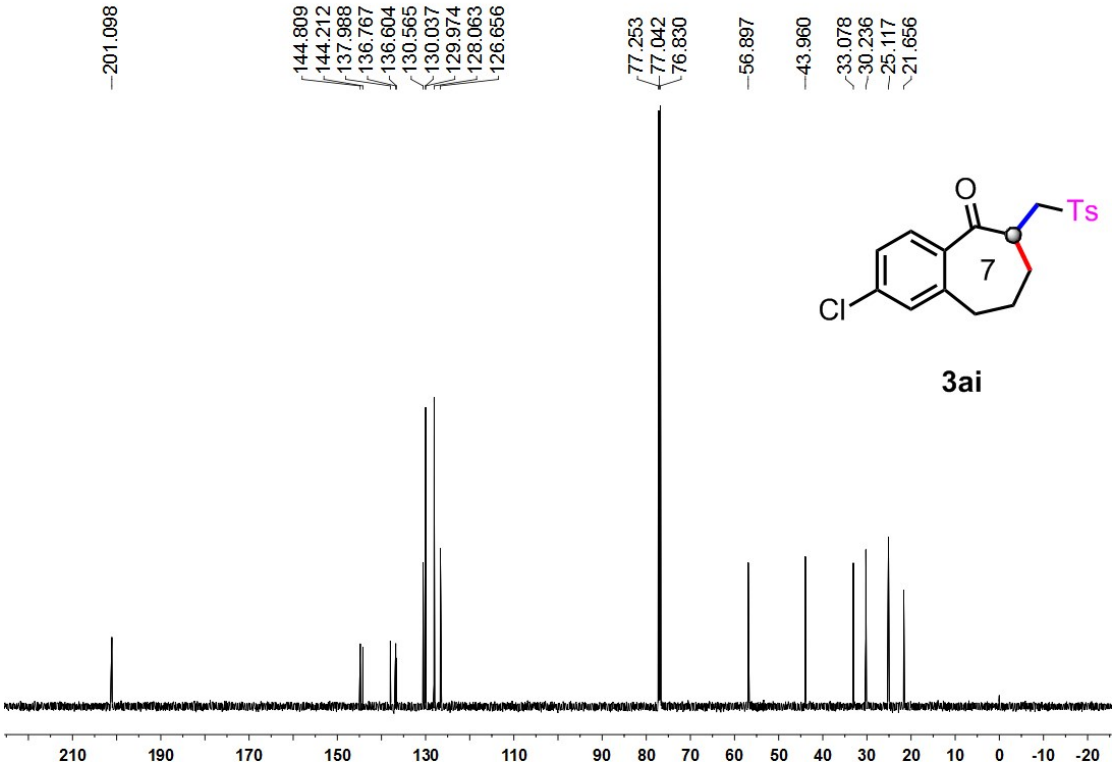
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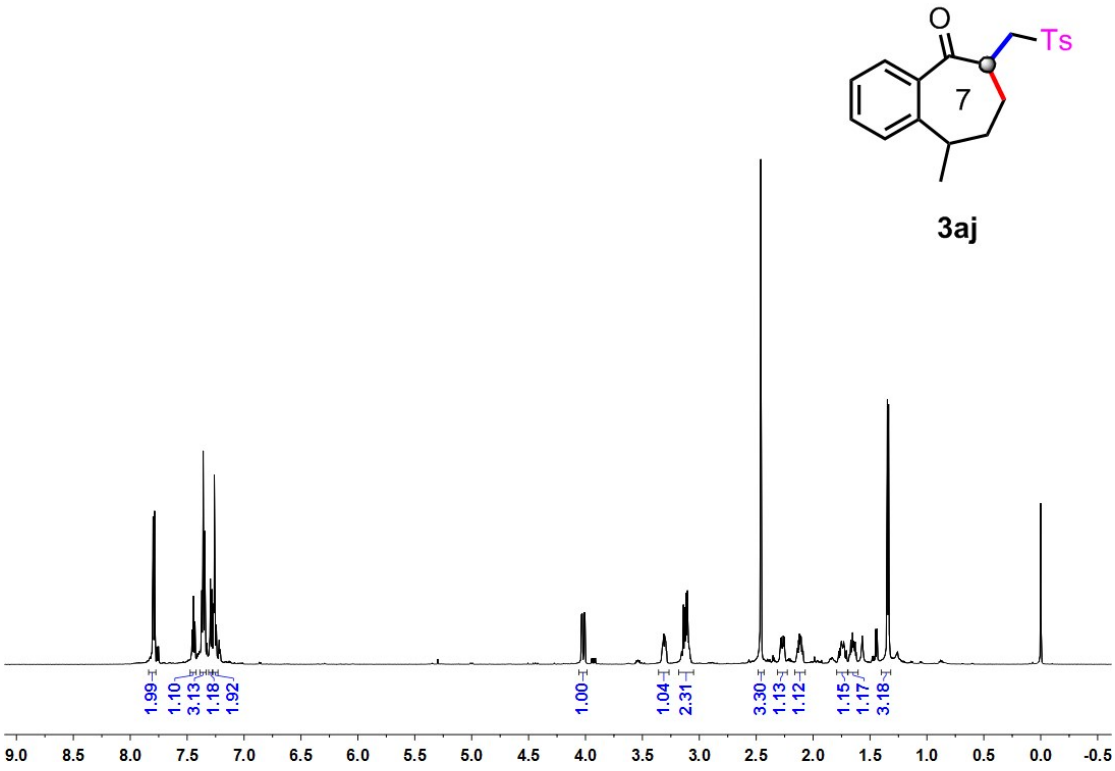
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1.12
1.15
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3.18
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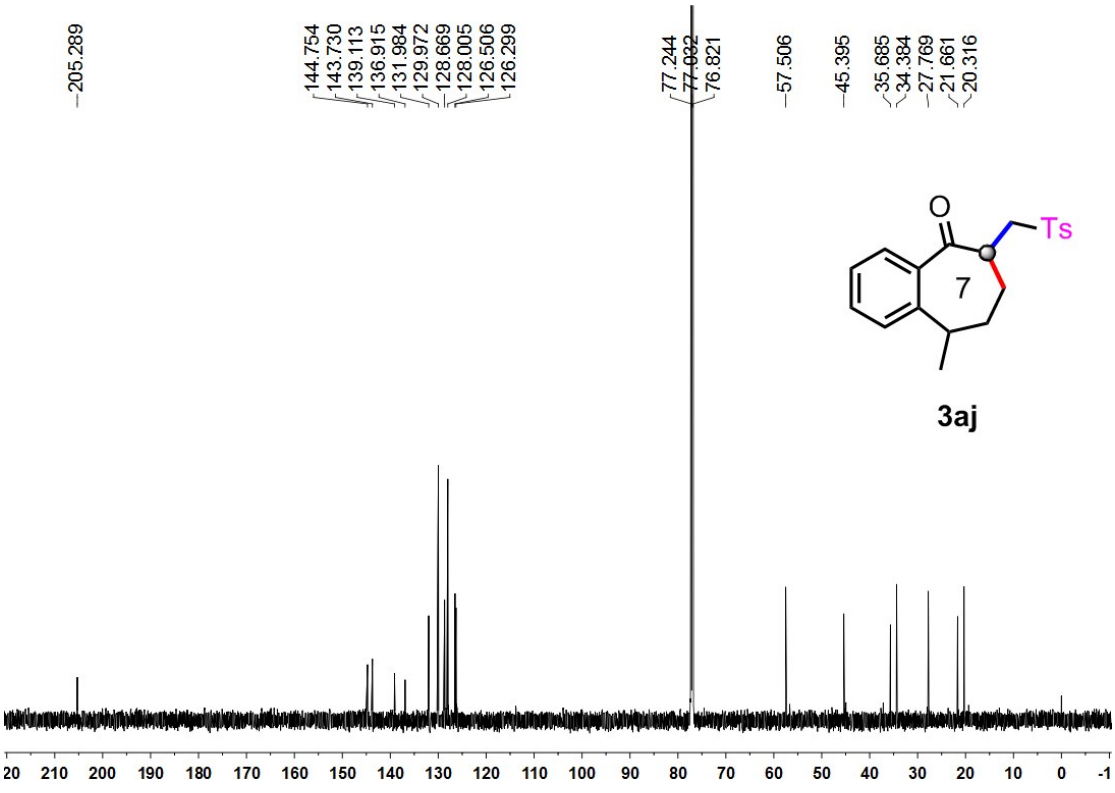
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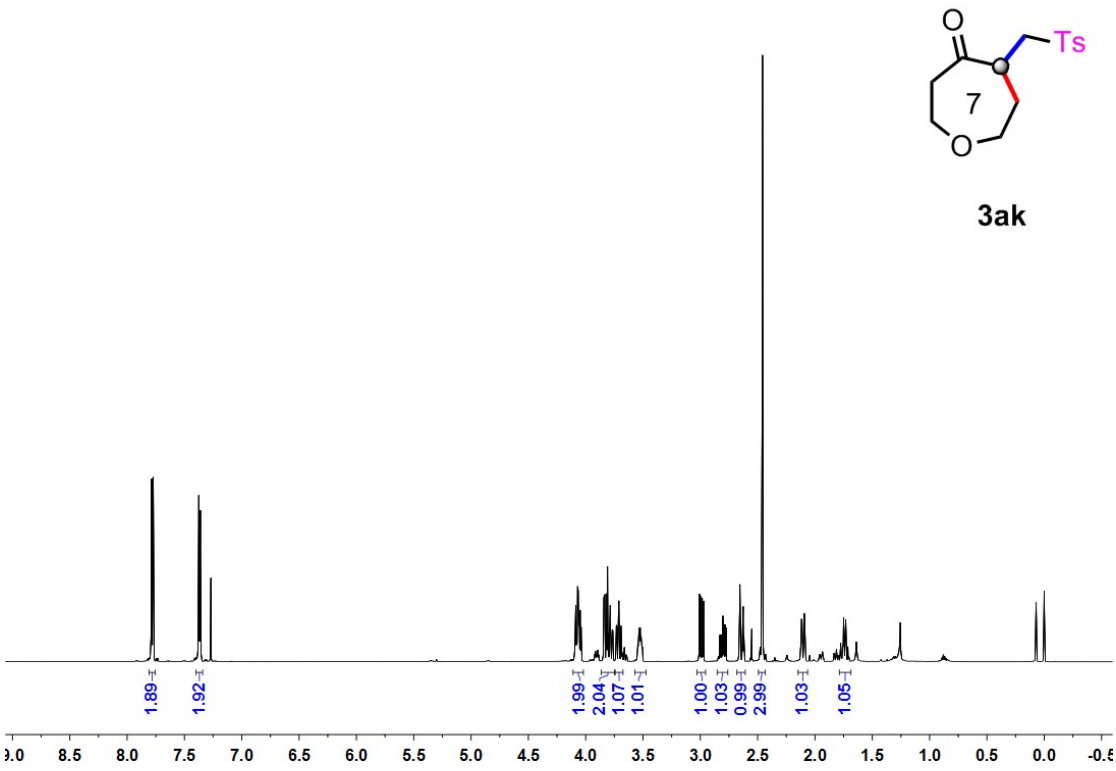
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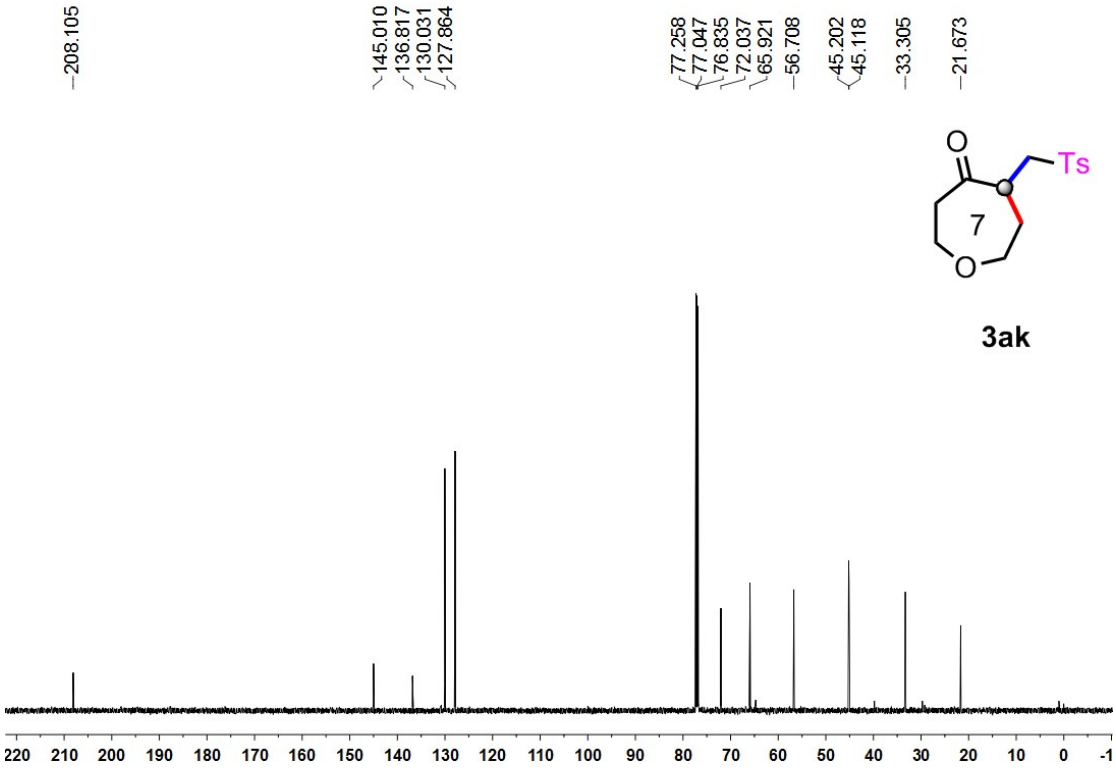
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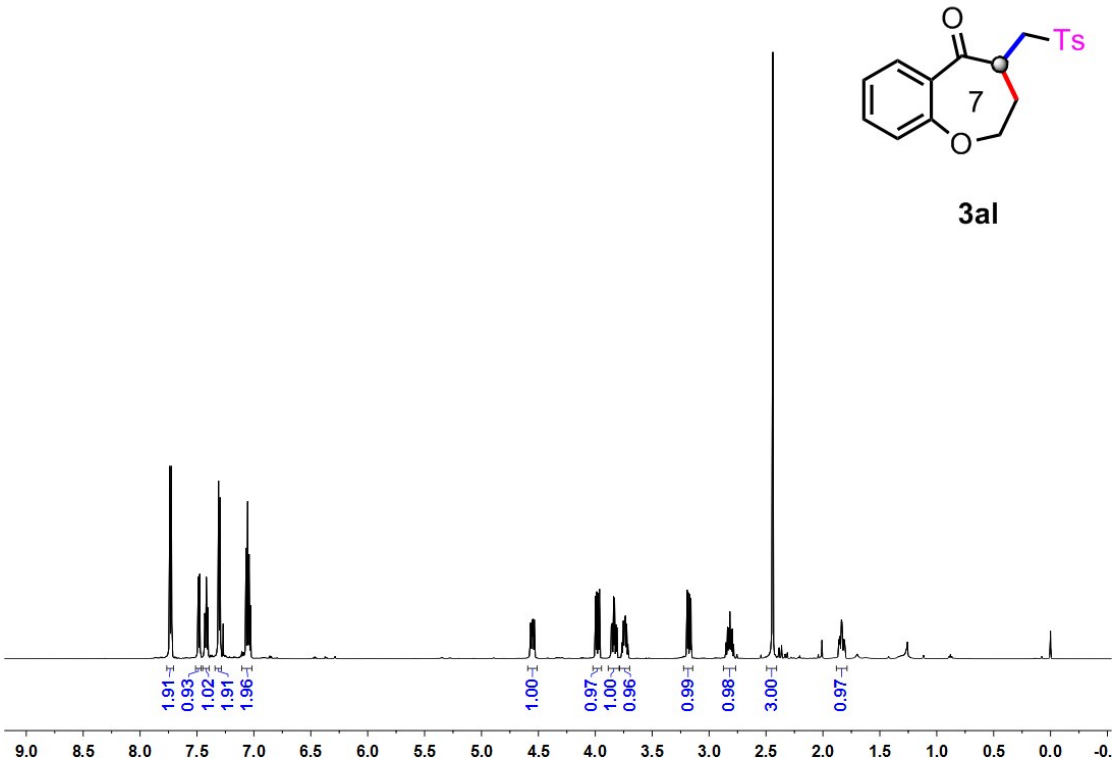
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3.00
0.97
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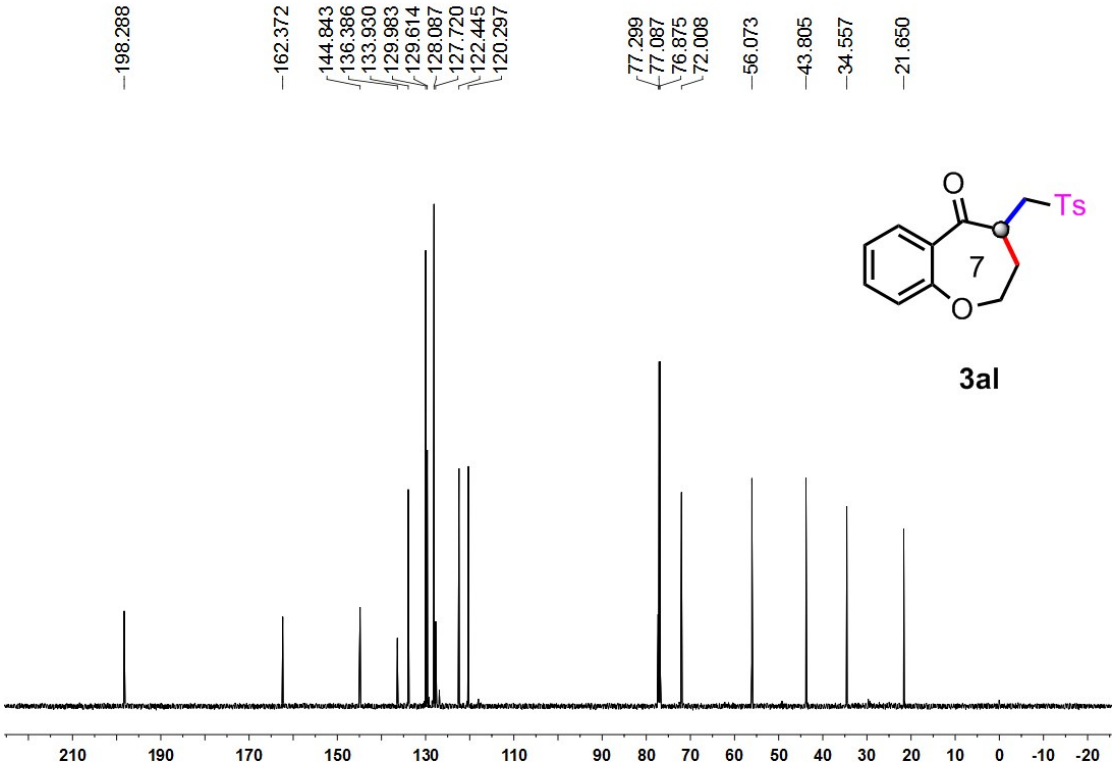
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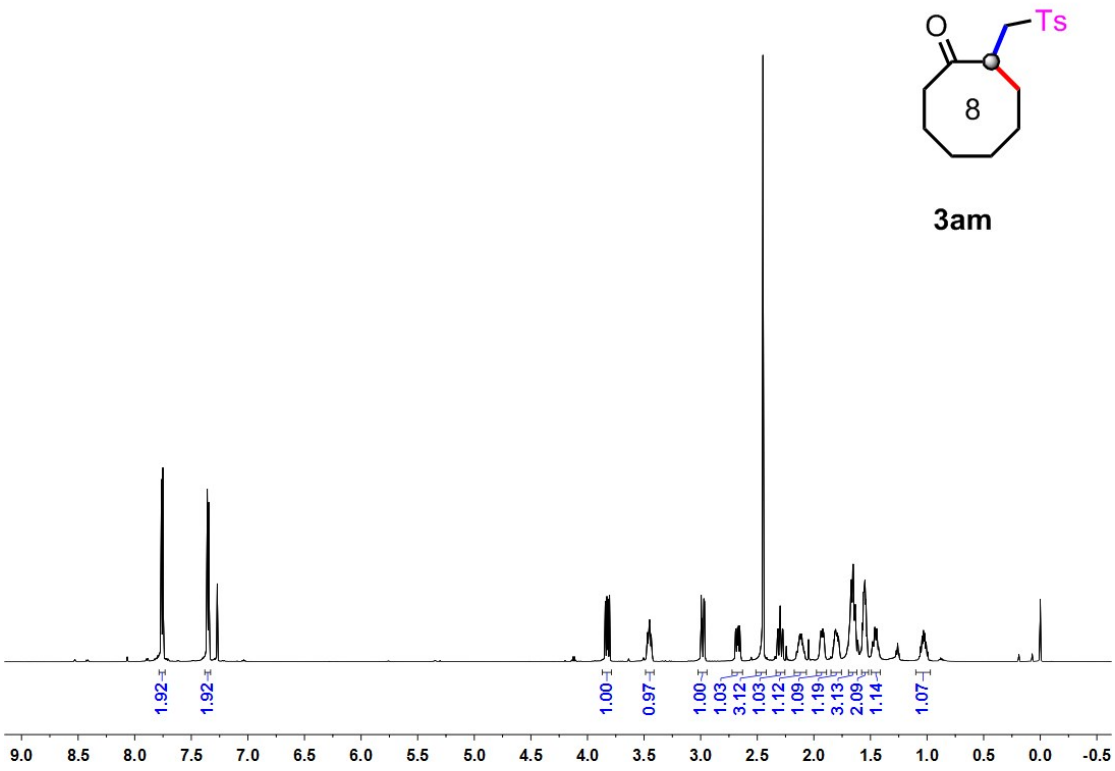
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1.03
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1.19
3.13
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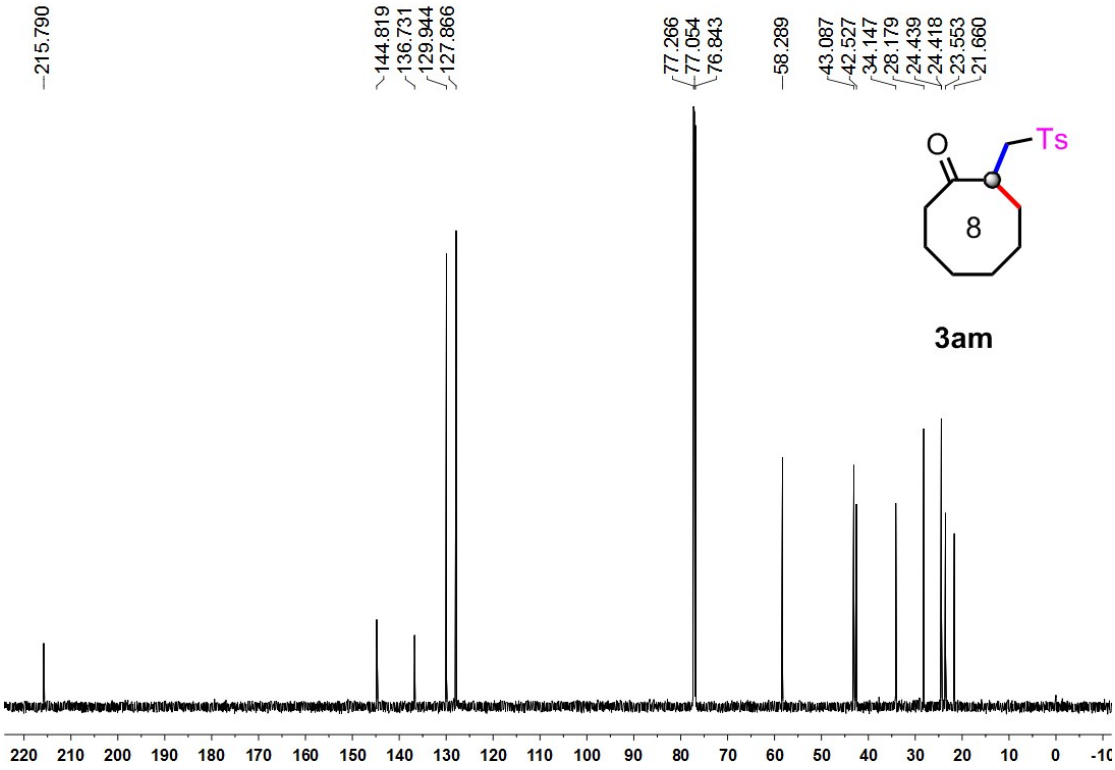
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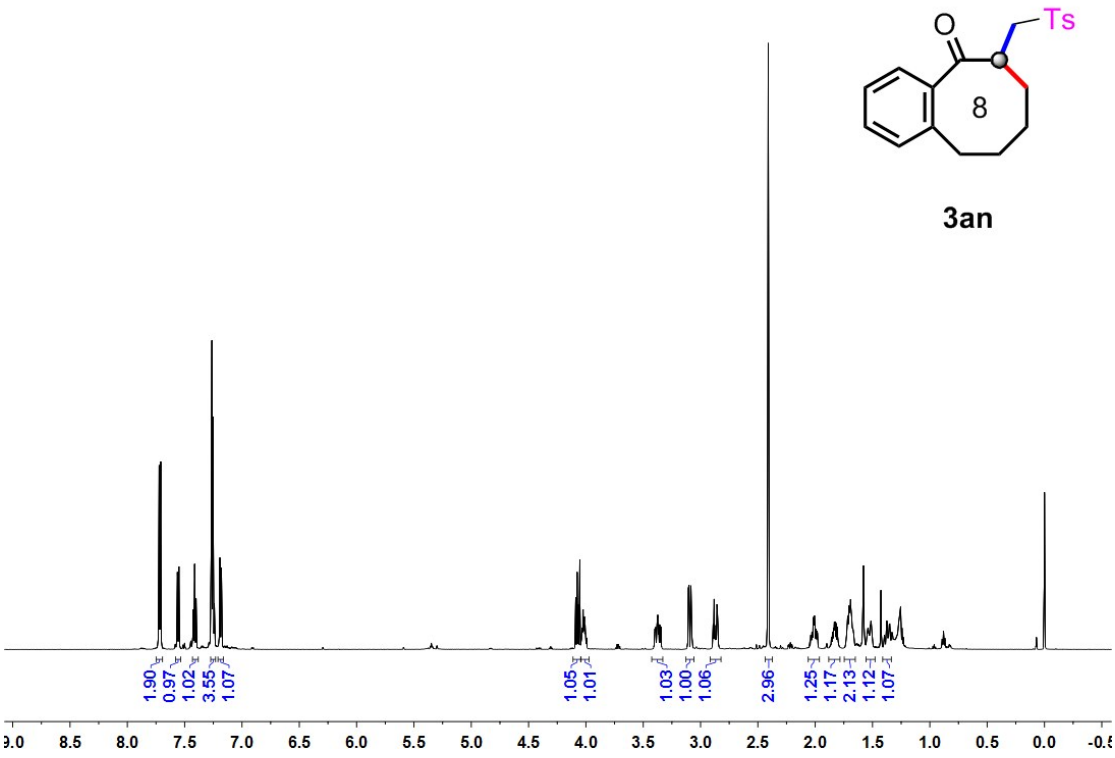
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1.03
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1.25
1.17
2.13
1.12
1.07
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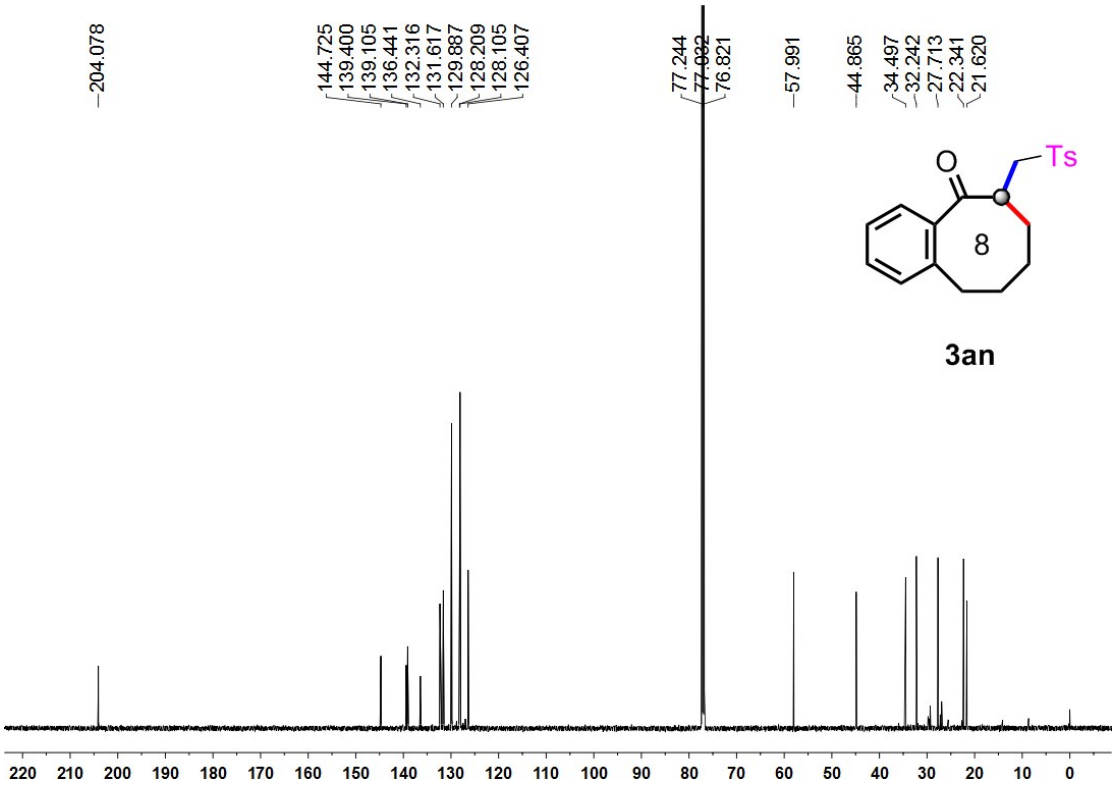
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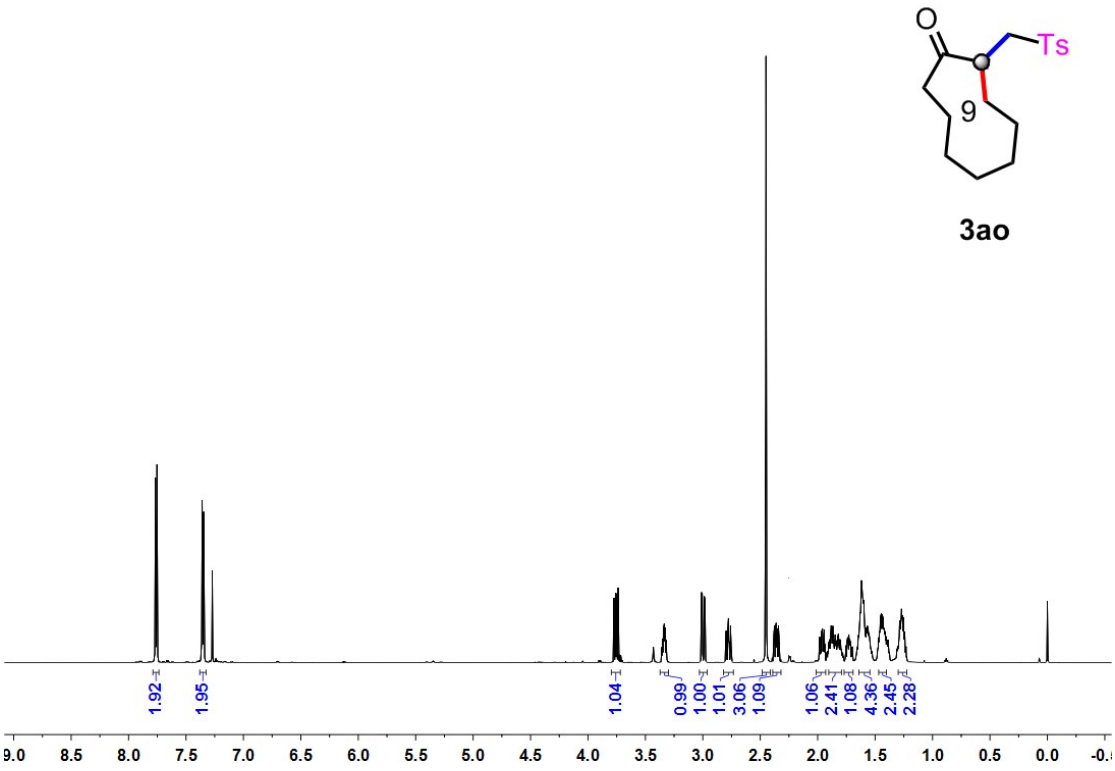
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1.09
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1.08
4.36
2.45
2.28
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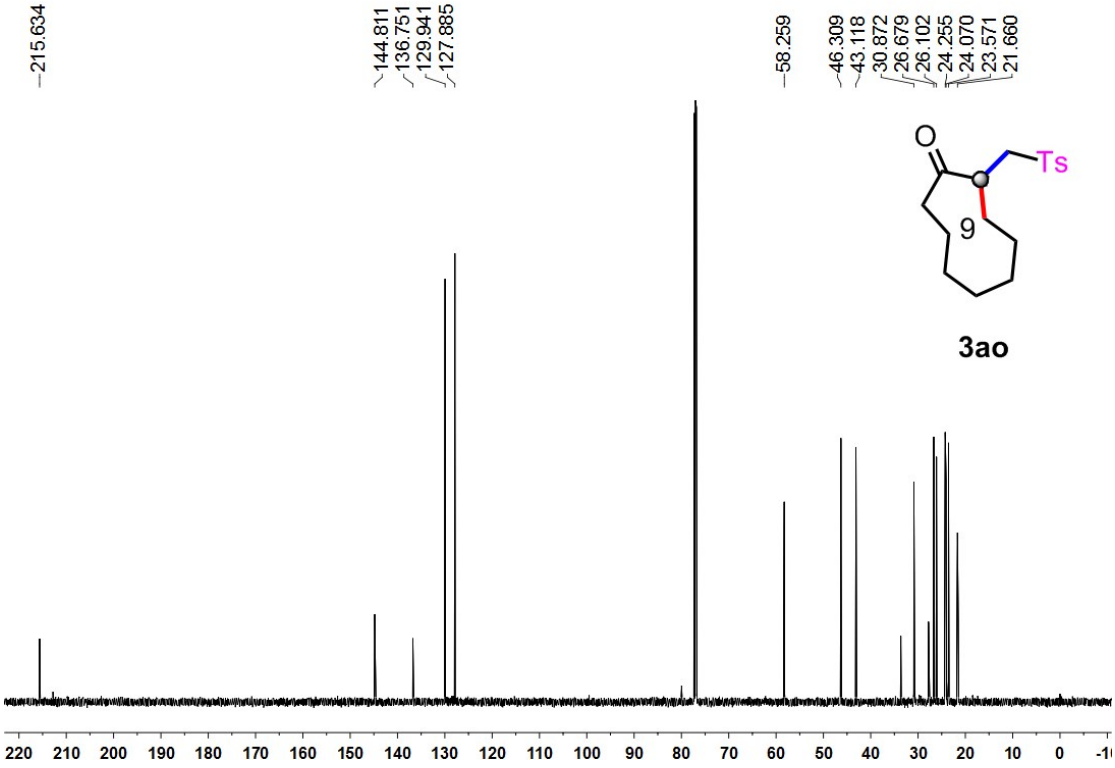
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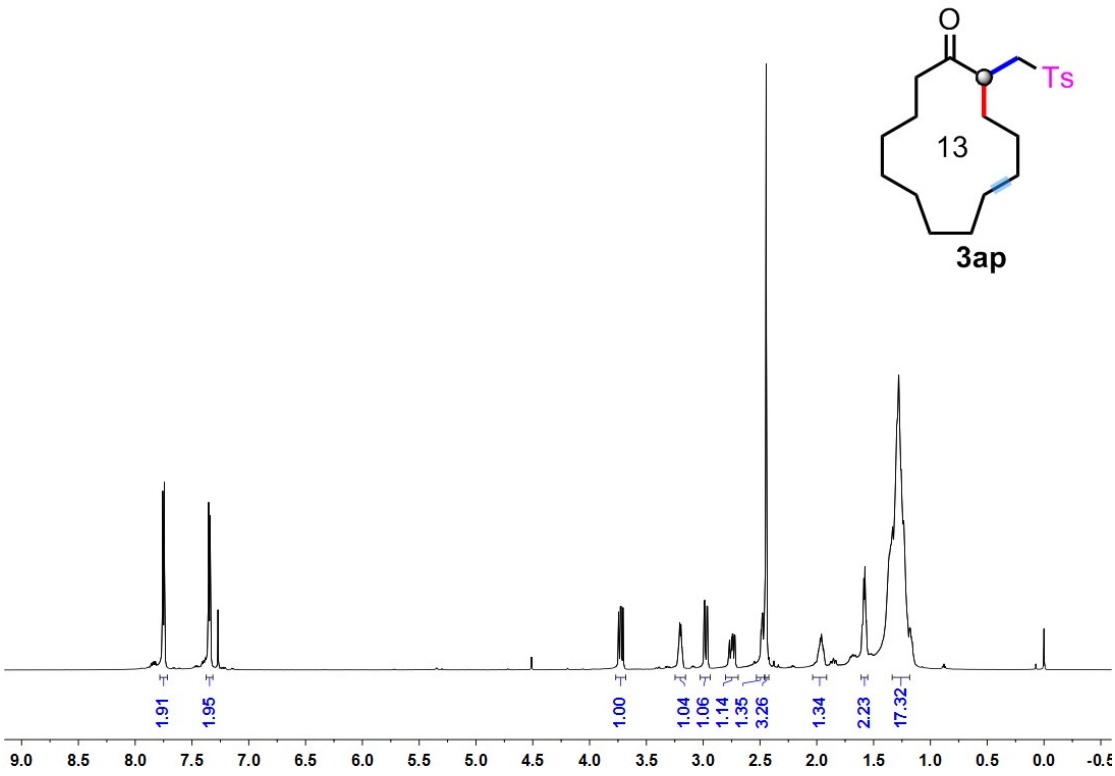
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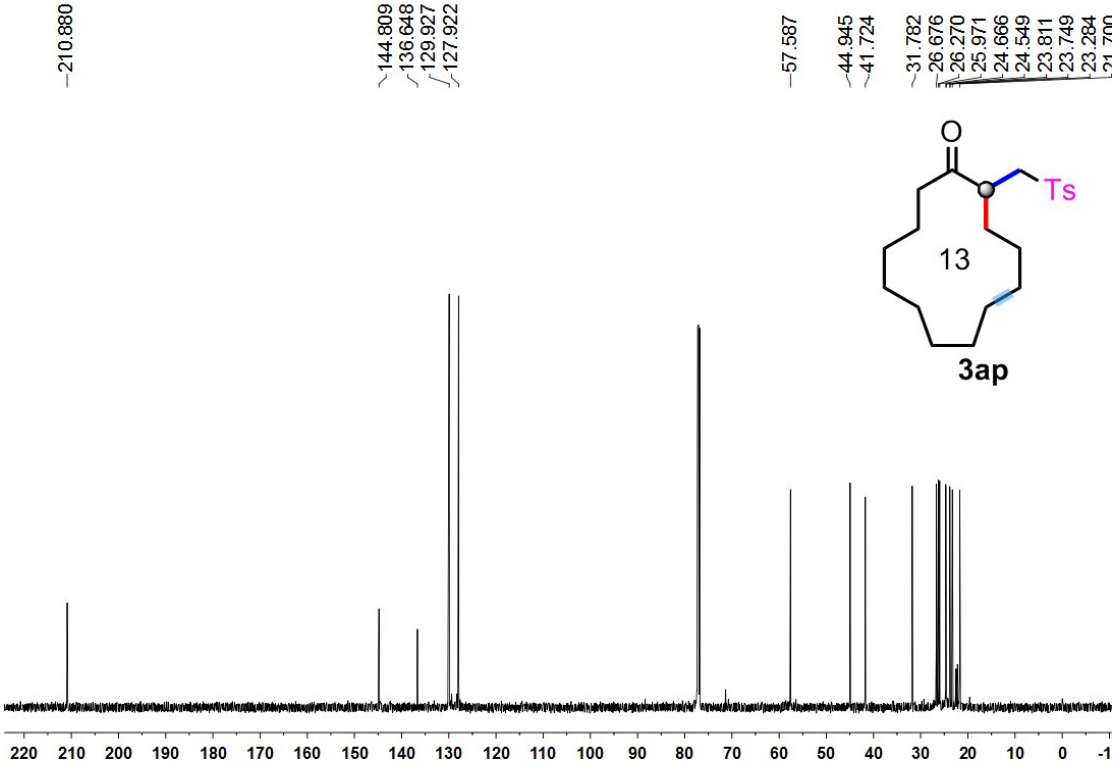
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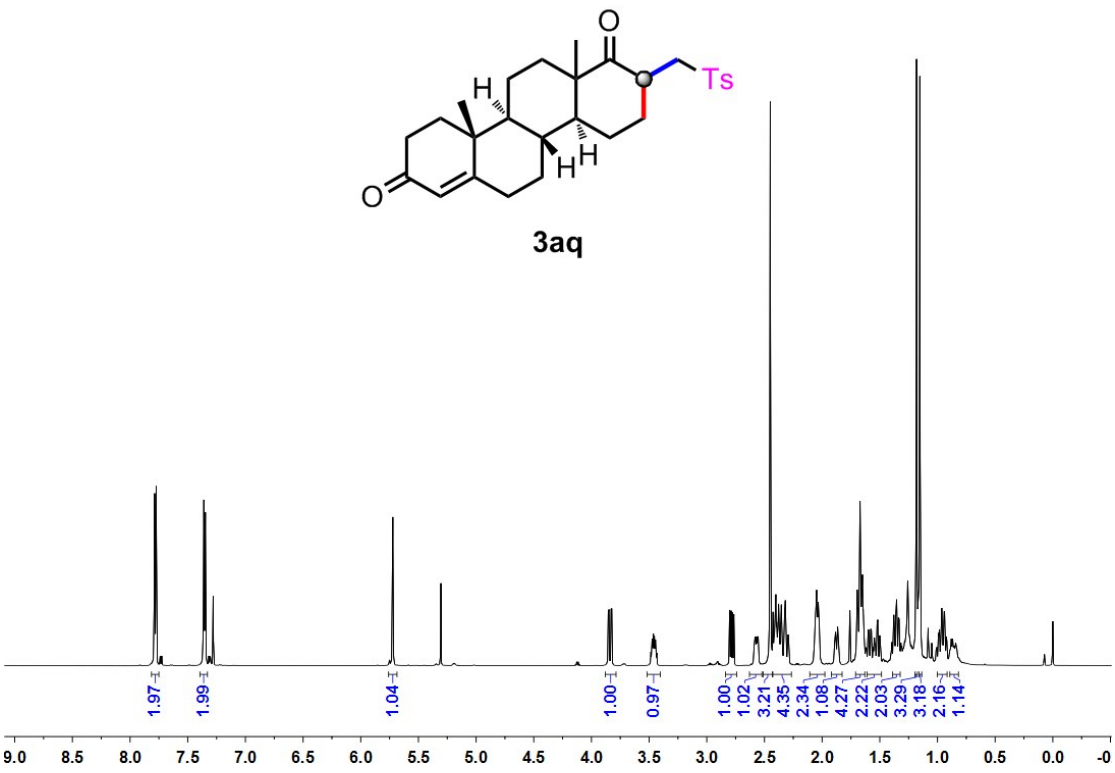
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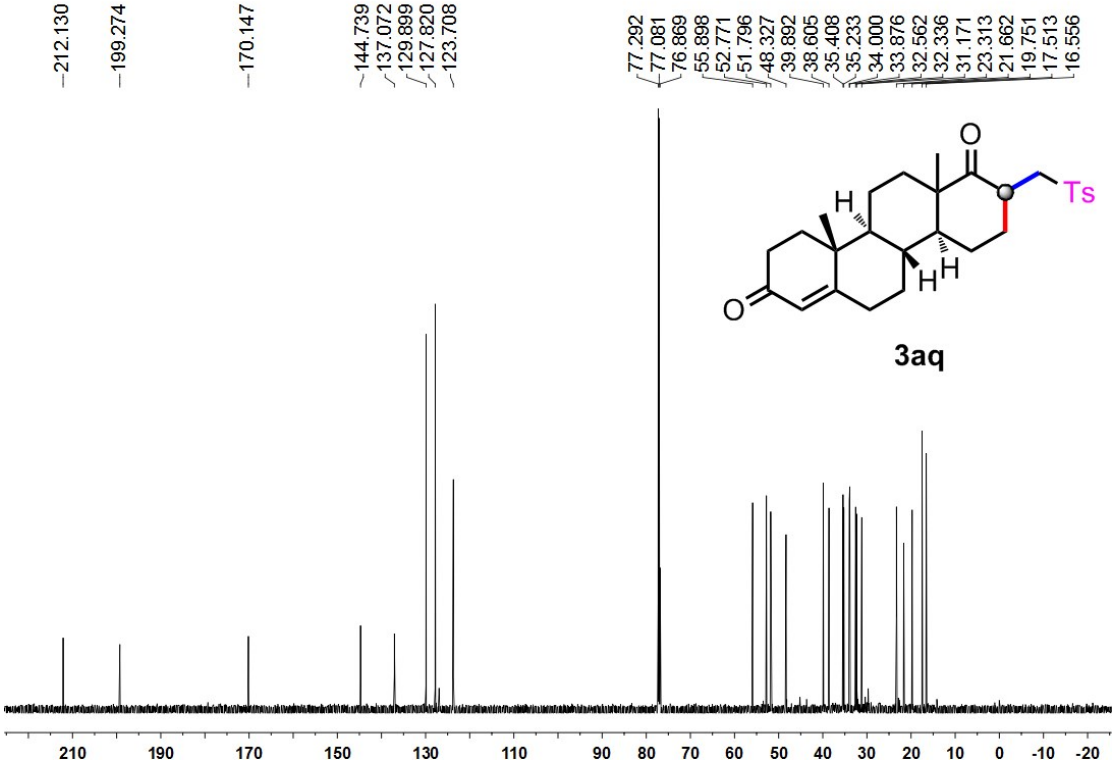
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17.513
16.556
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H
H
O
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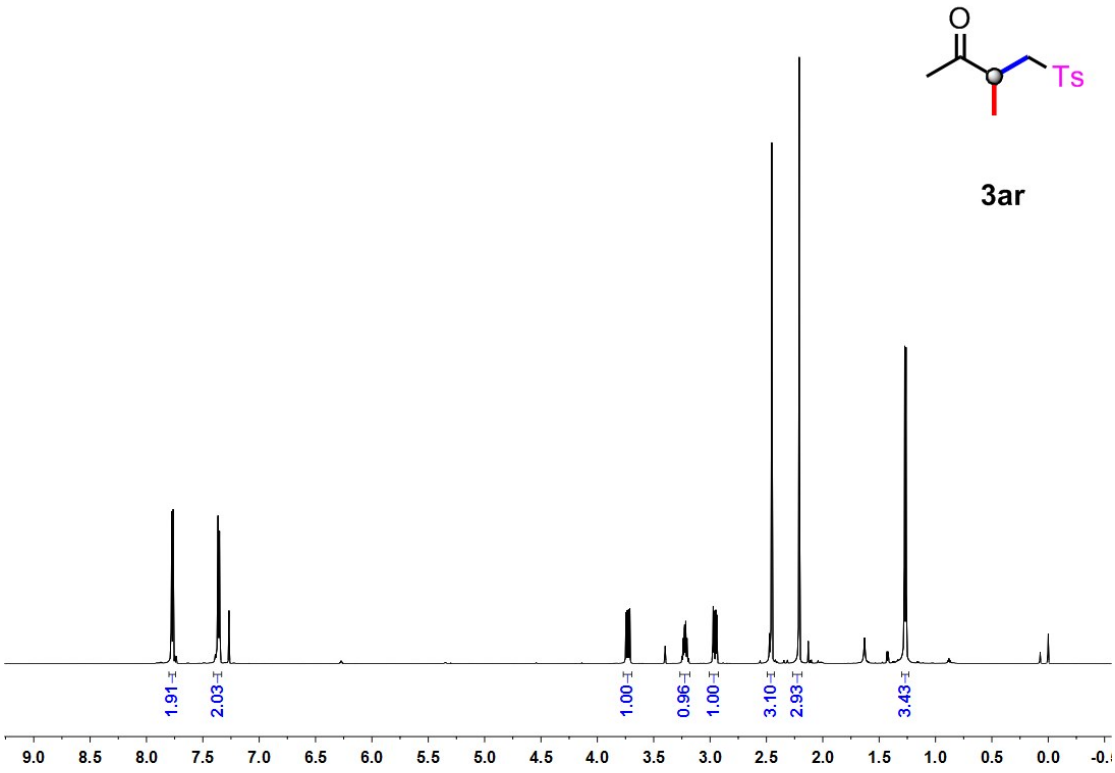
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3.43
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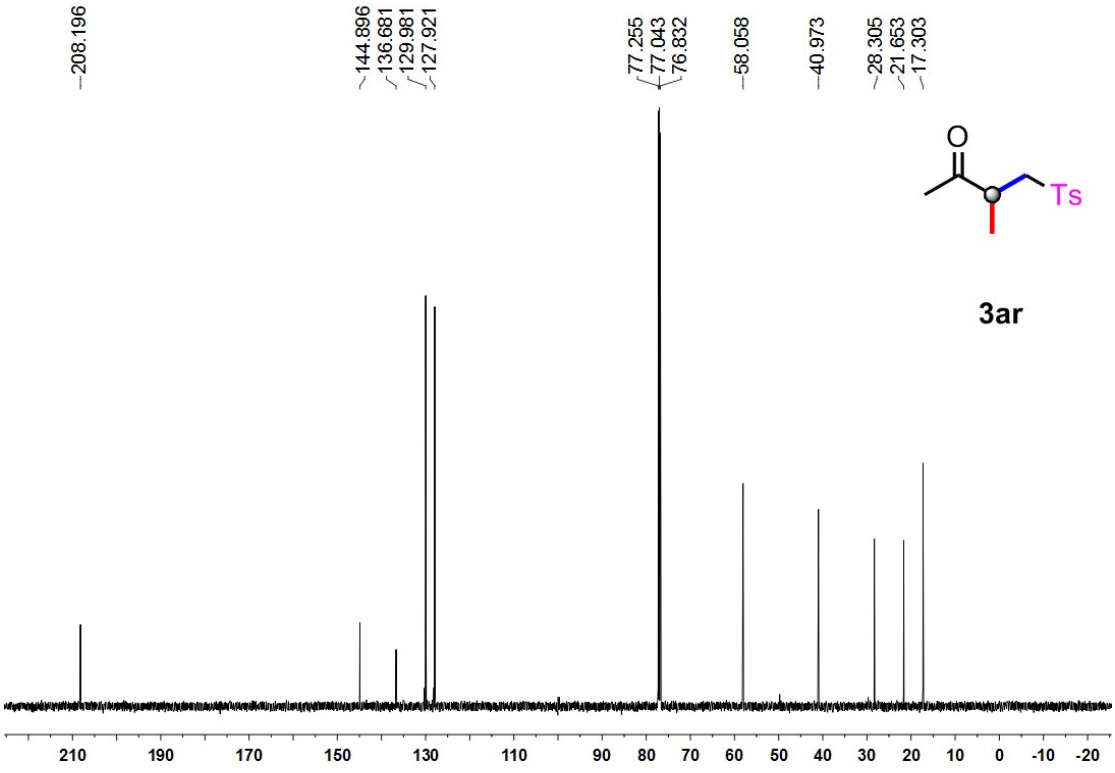
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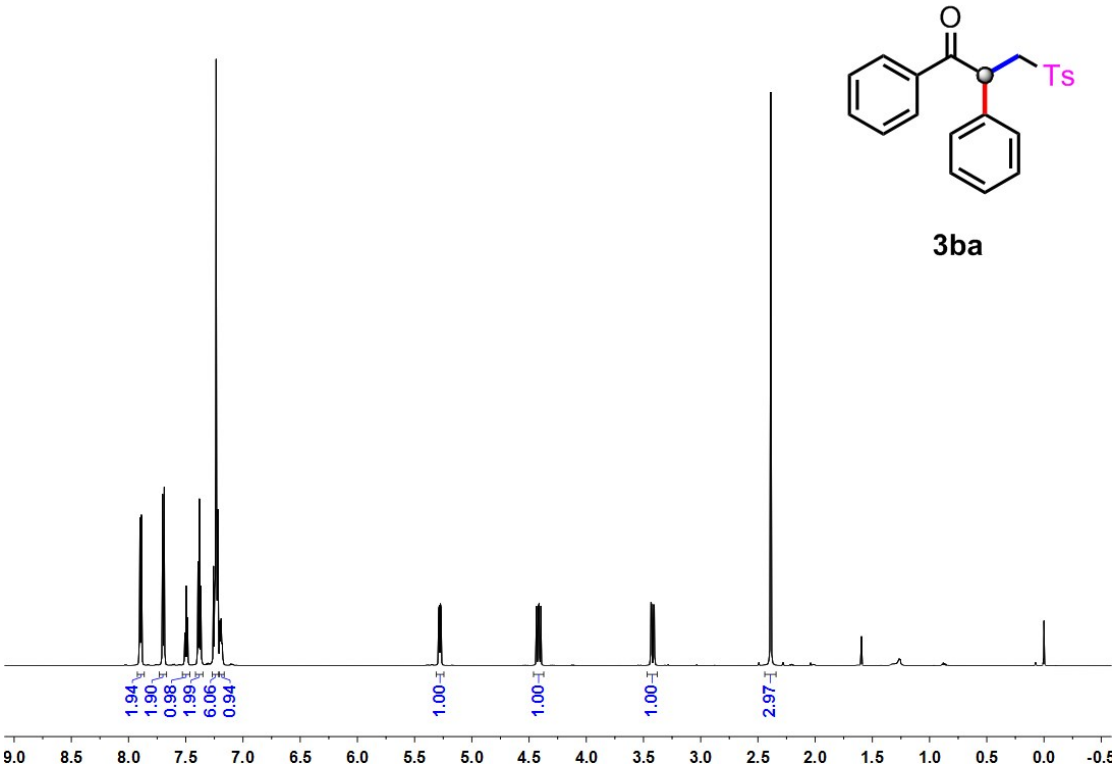
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6.5
6.0
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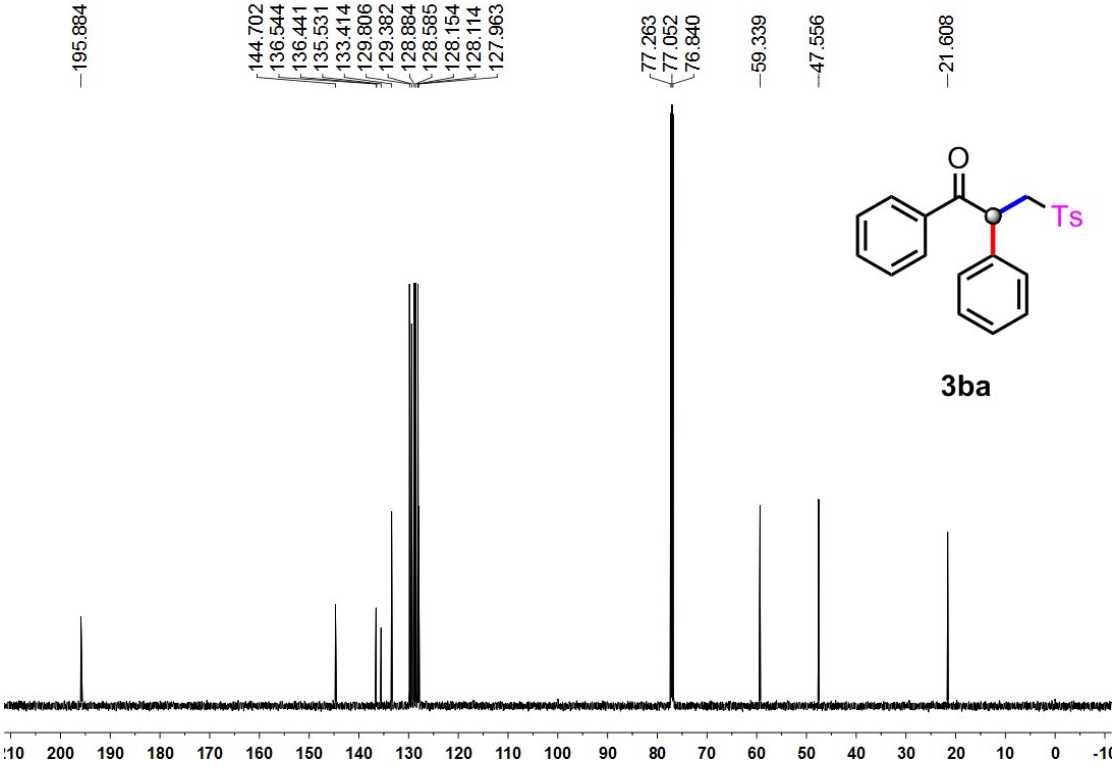
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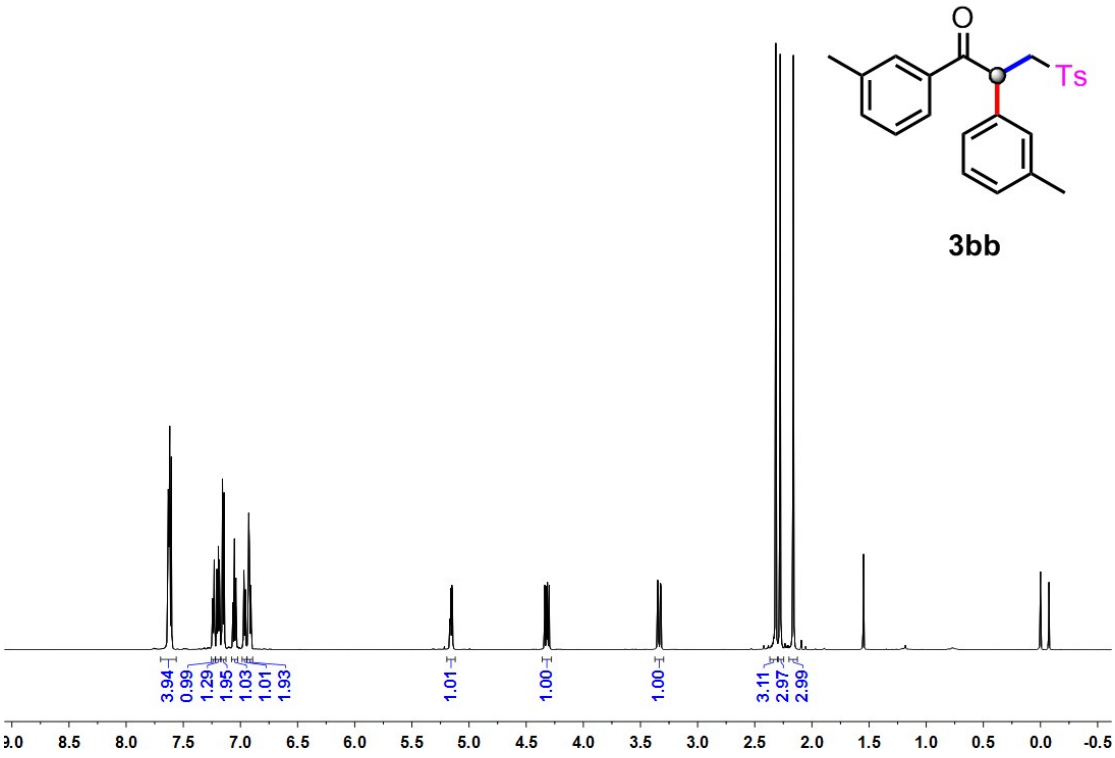
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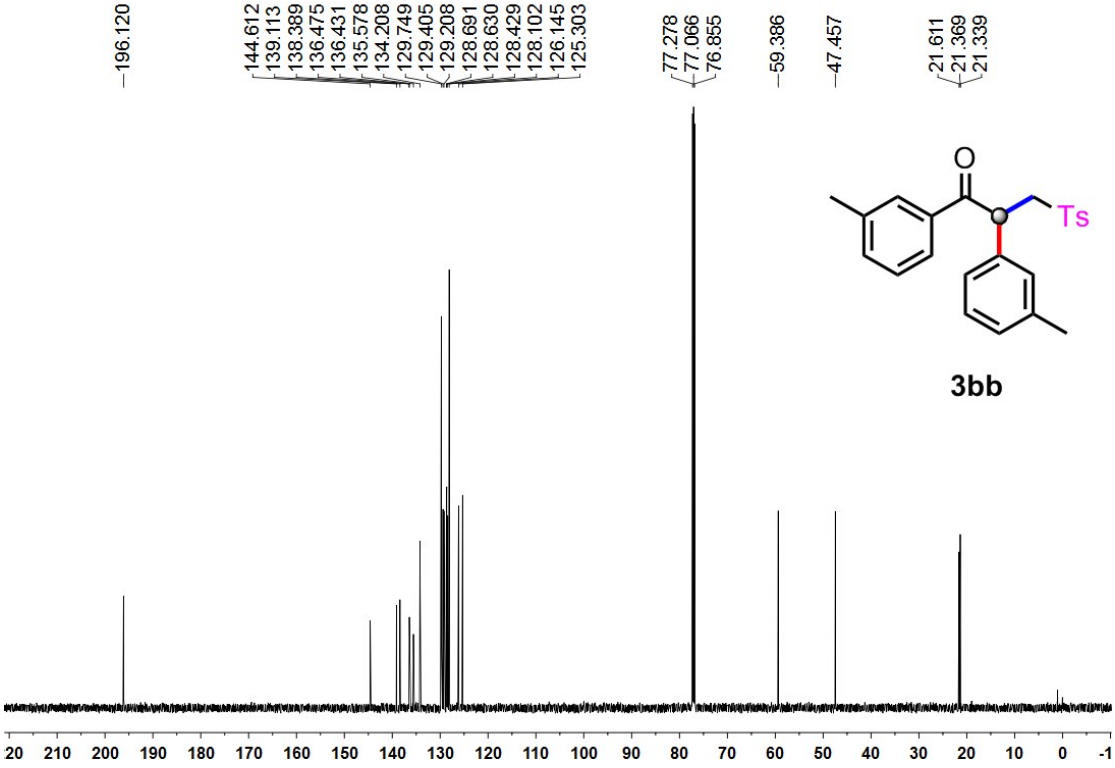
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21.339
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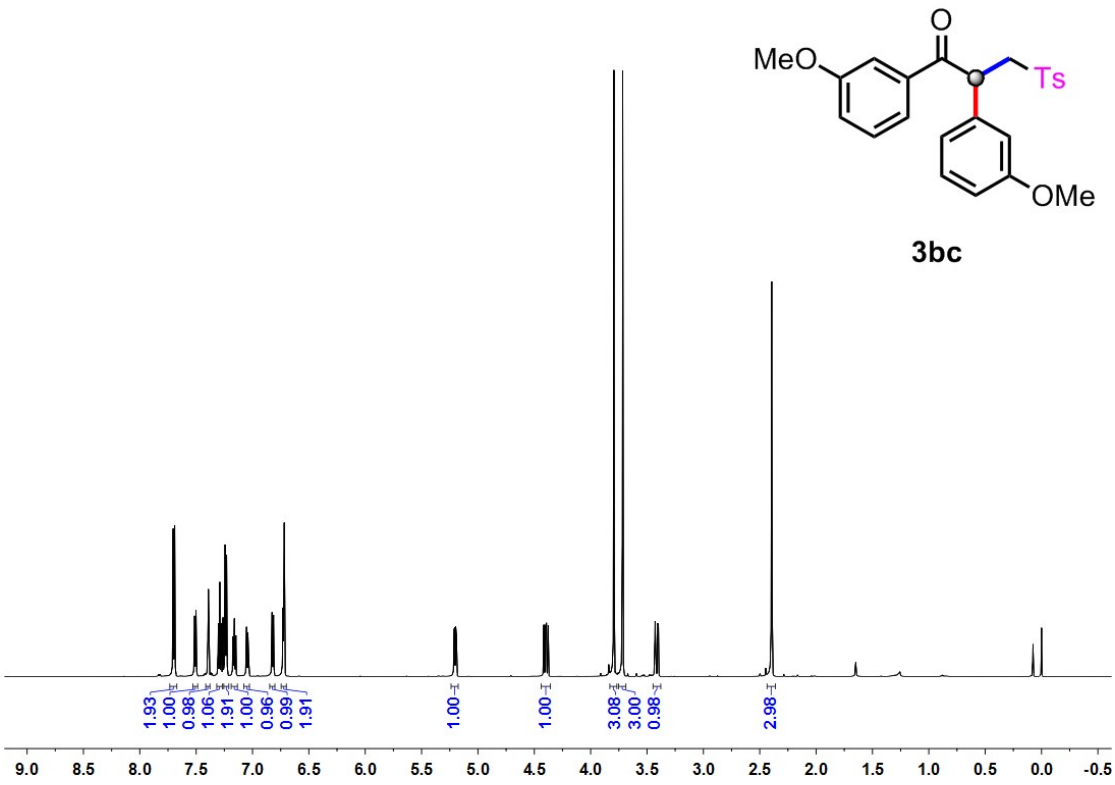
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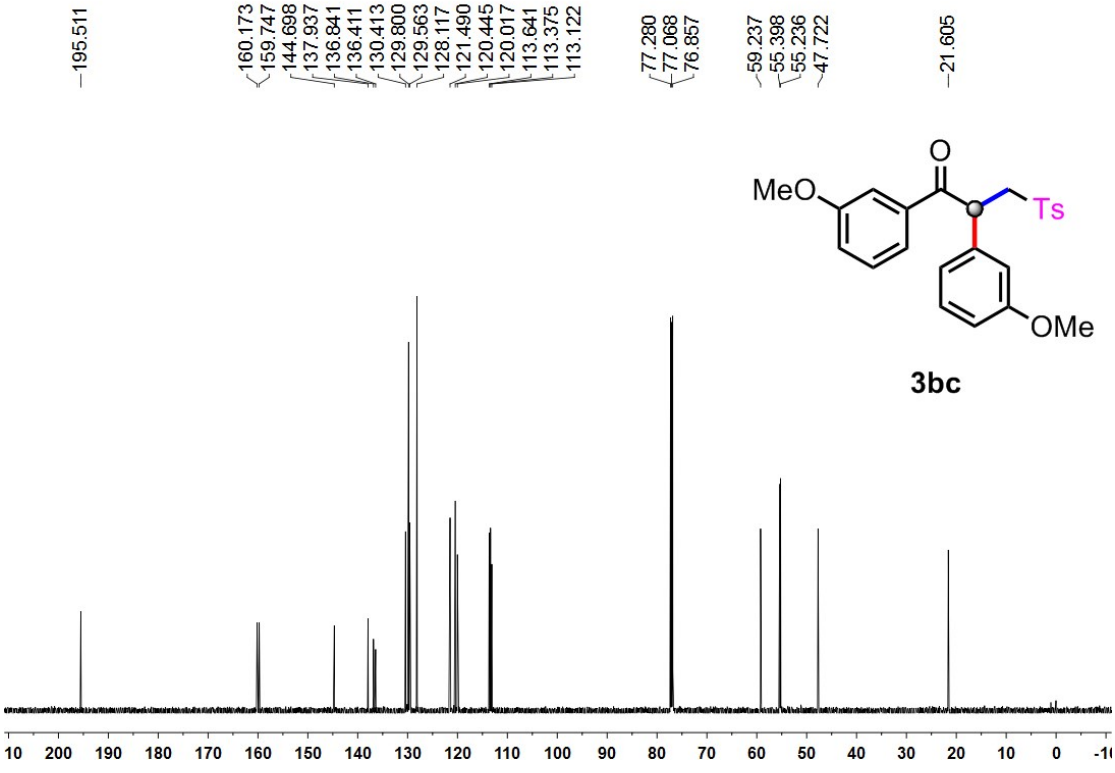
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55.236
47.722
21.605
MeO
O
Ts
OMe
3bc
10
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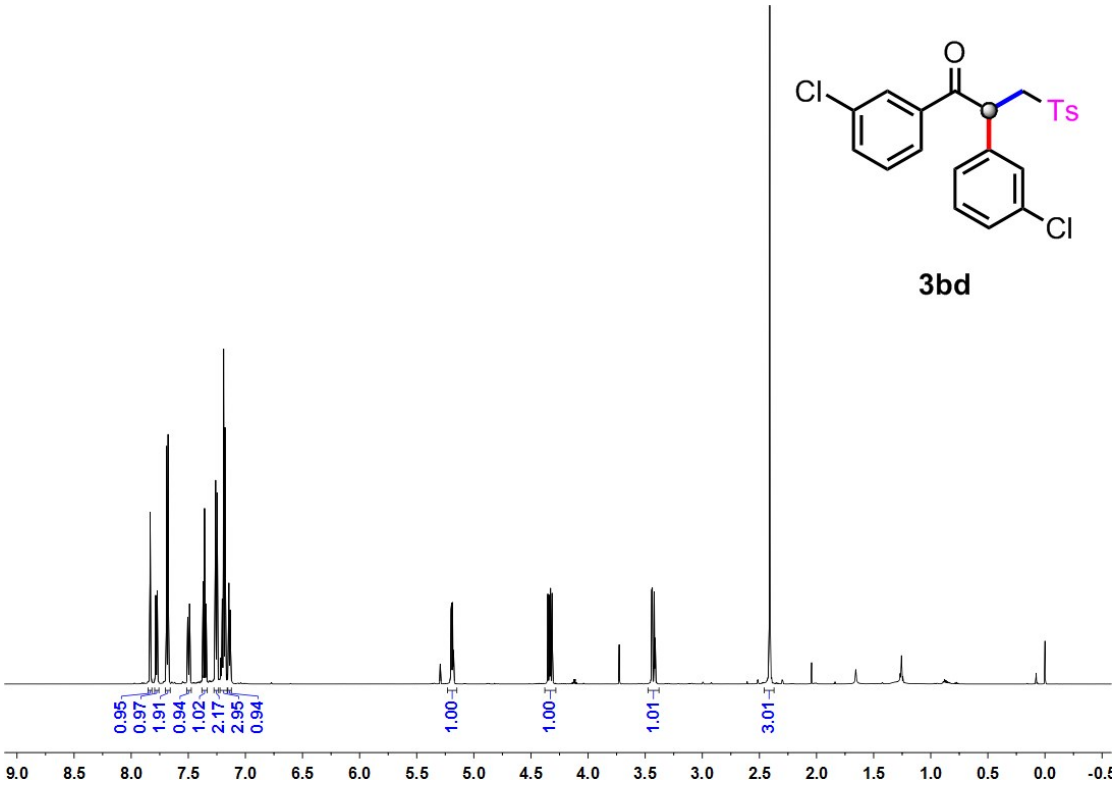
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1.00
1.01
3.01
9.0
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8.0
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7.0
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6.0
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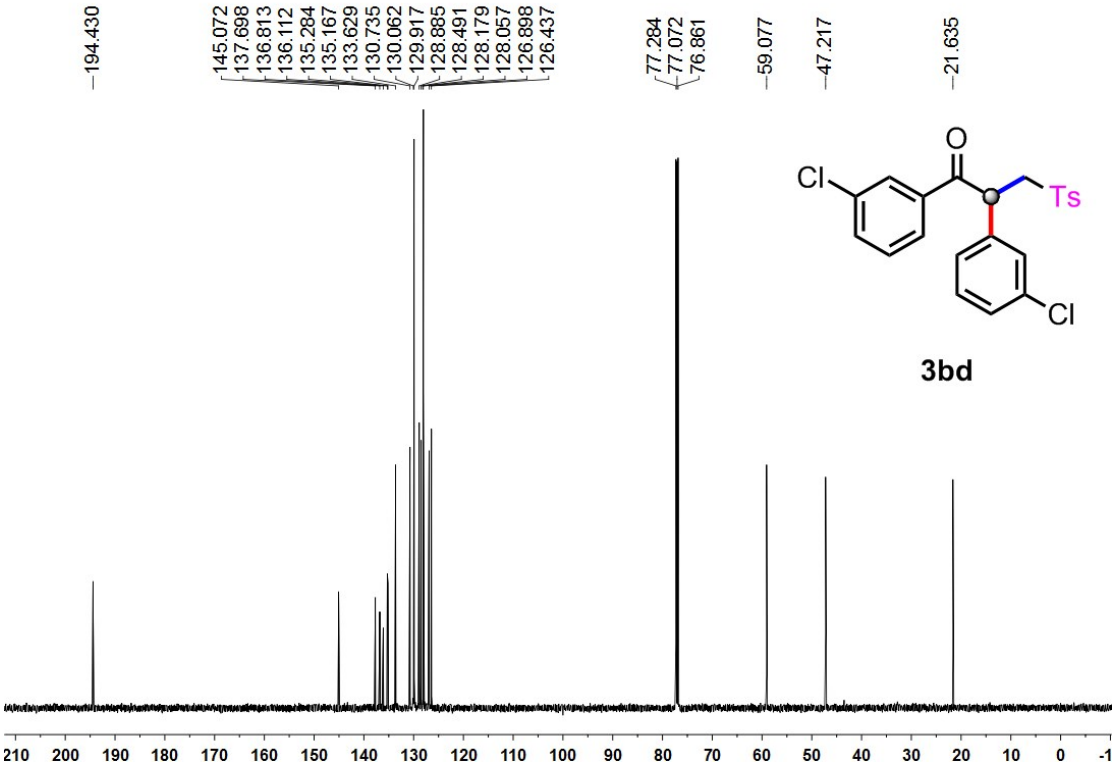
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21.635
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Ts
Cl
3bd
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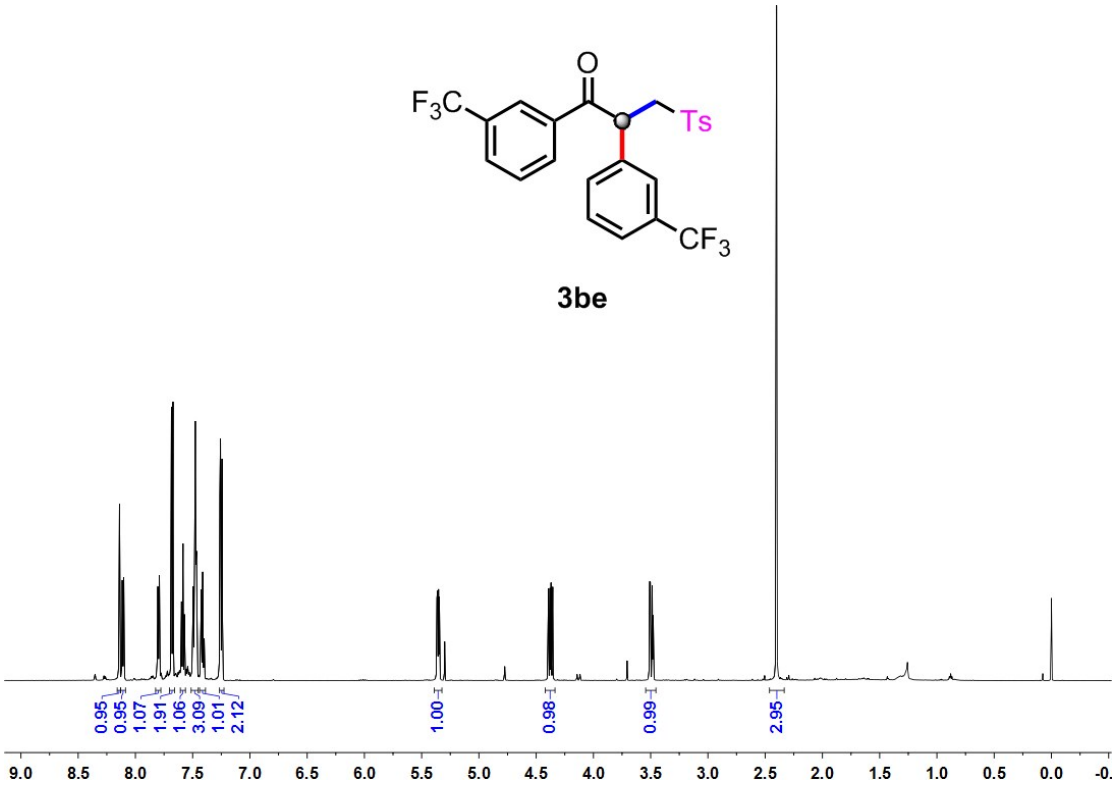
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1.00
0.98
0.99
2.95
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8.0
7.5
7.0
6.5
6.0
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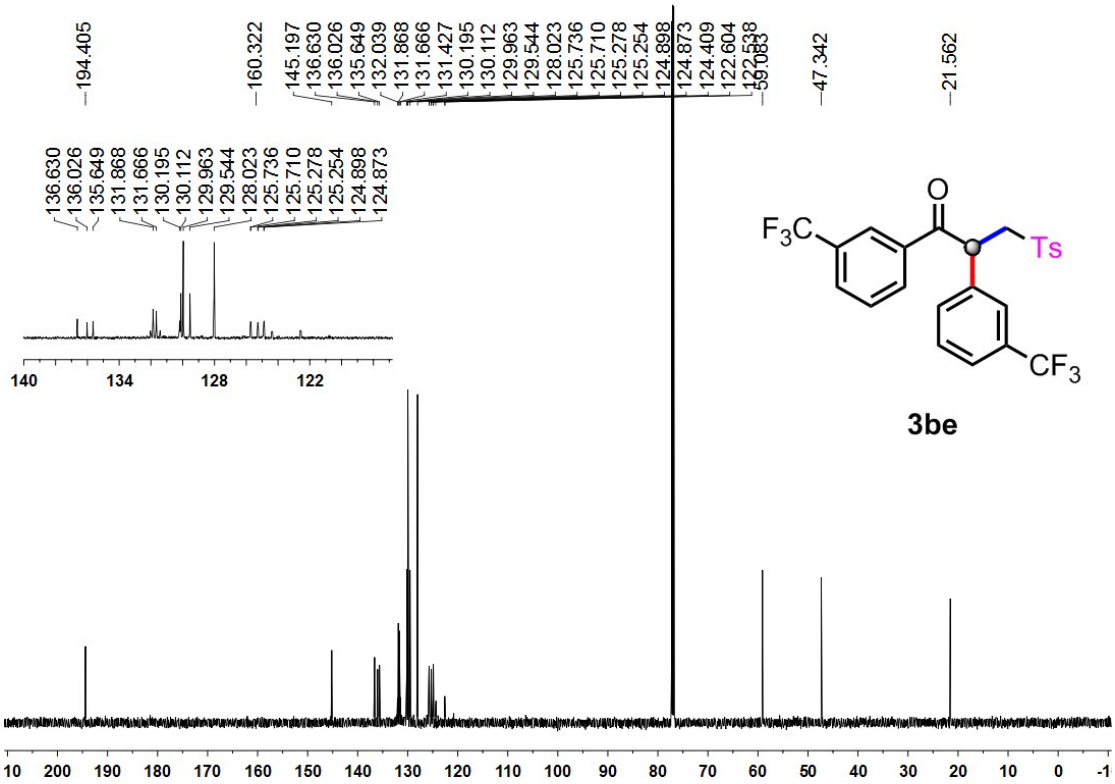
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125.254
124.898
124.873
124.409
122.604
122.538
59.083
47.342
21.562
140
134
128
122
O
F3C
Ts
CF3
3be
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200
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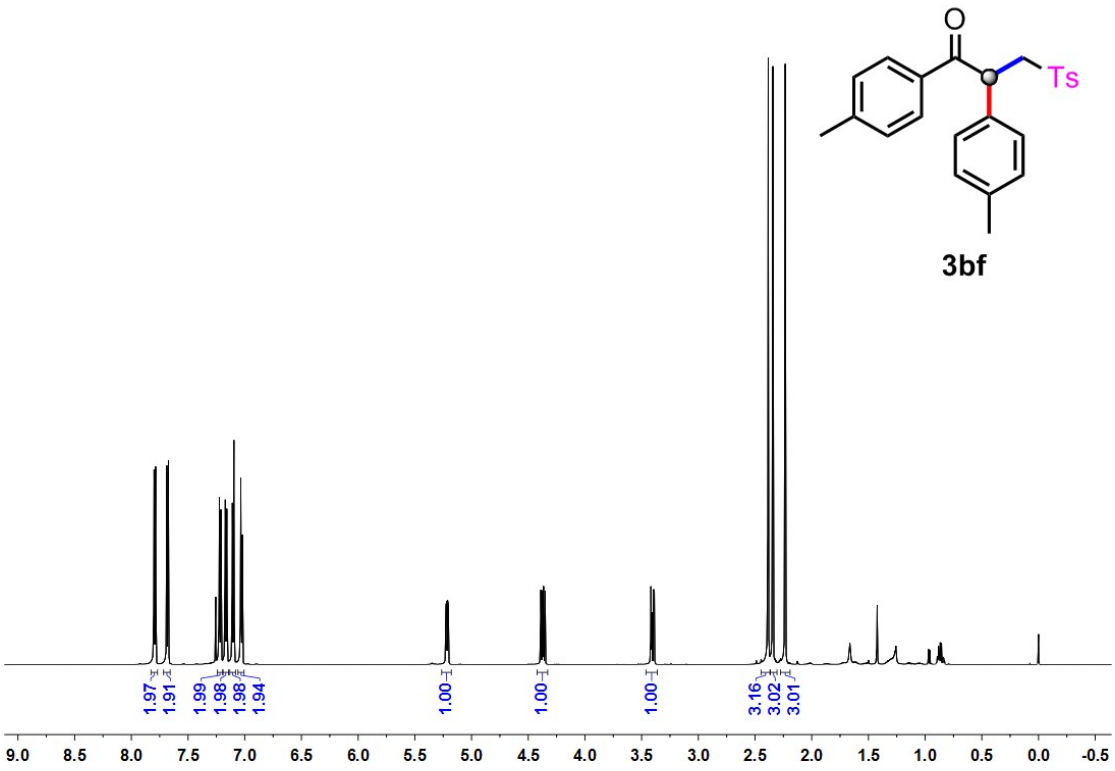
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1.99
1.98
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1.94
1.00
1.00
1.00
3.16
3.02
3.01
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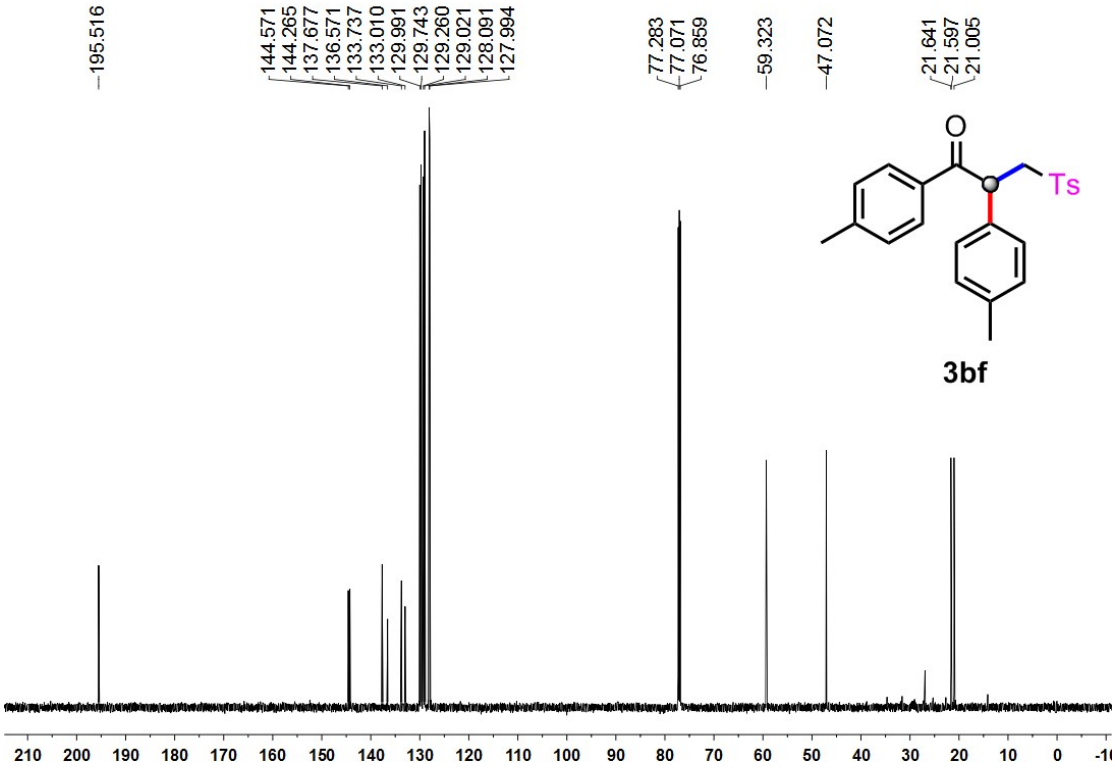
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129.260
129.021
128.091
127.994
77.283
77.071
76.859
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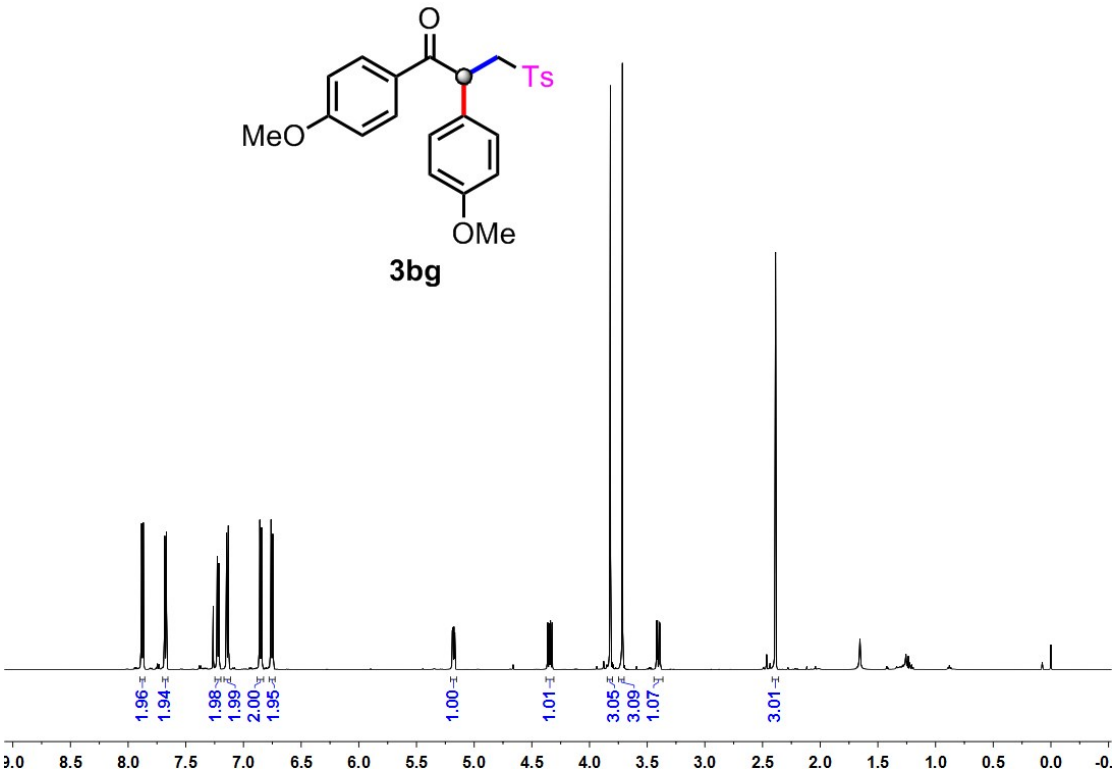
47.072
21.641
21.597
21.005
O
Ts
3bf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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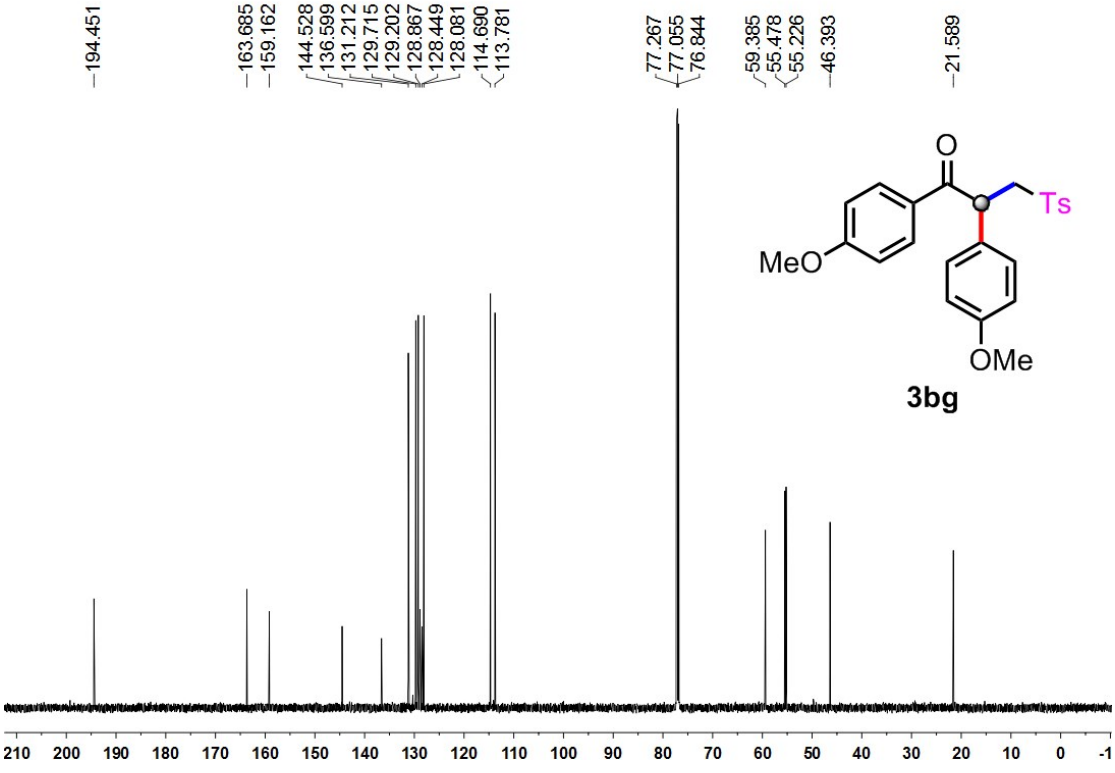
Ts
MeO
OMe
3bg
1.96
1.94
1.98
1.99
2.00
1.95
1.00
1.01
3.05
3.09
1.07
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.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129.202
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128.081
114.690
113.781
77.267
77.055
76.844
59.385
55.478
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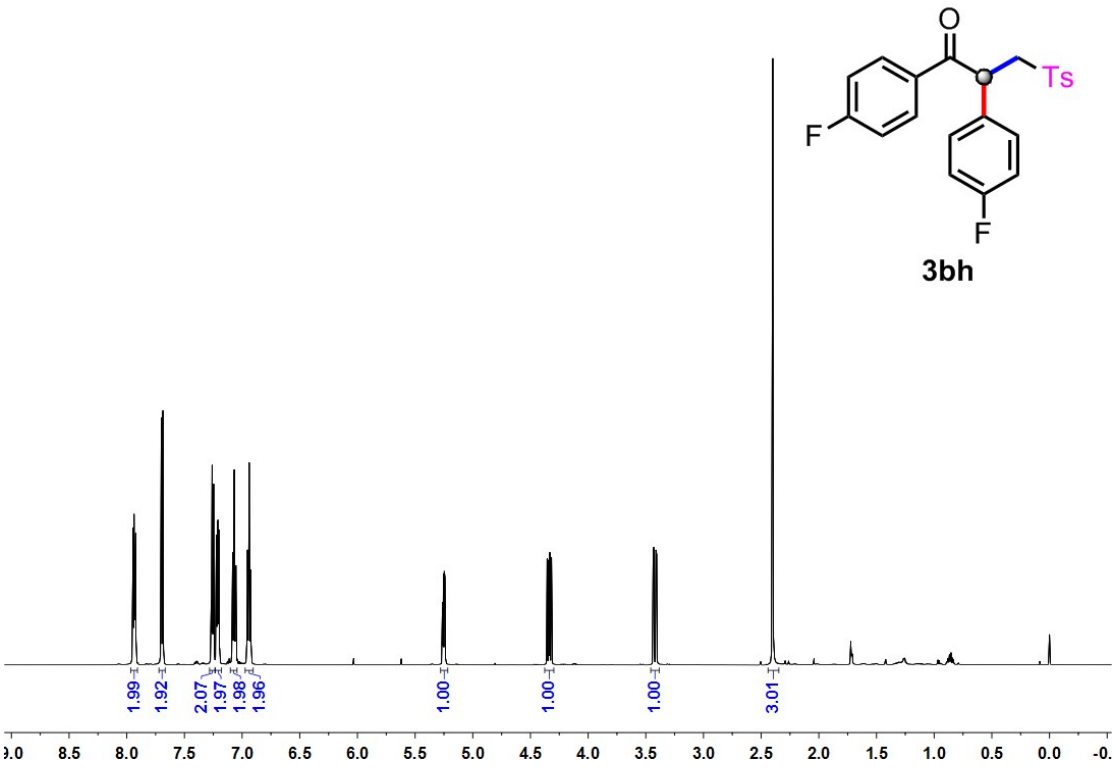
21.589
O
Ts
MeO
OMe
3bg
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1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Ts
F
F
3bh
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2.07
1.97
1.98
1.96
1.00
1.00
1.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
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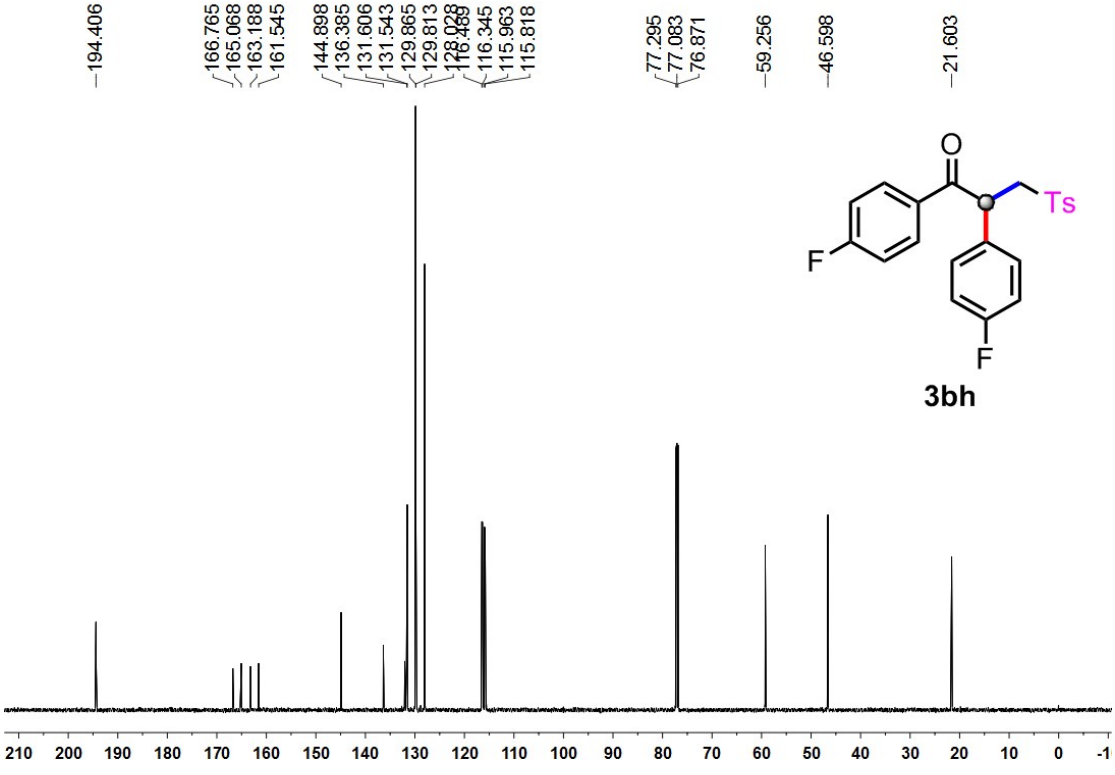
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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129.813
128.028
116.345
115.963
115.818
77.295
77.083
76.871
59.256
46.598
21.603
O
Ts
F
F
3bh
210
200
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180
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150
140
130
120
110
100
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80
70
60
50
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30
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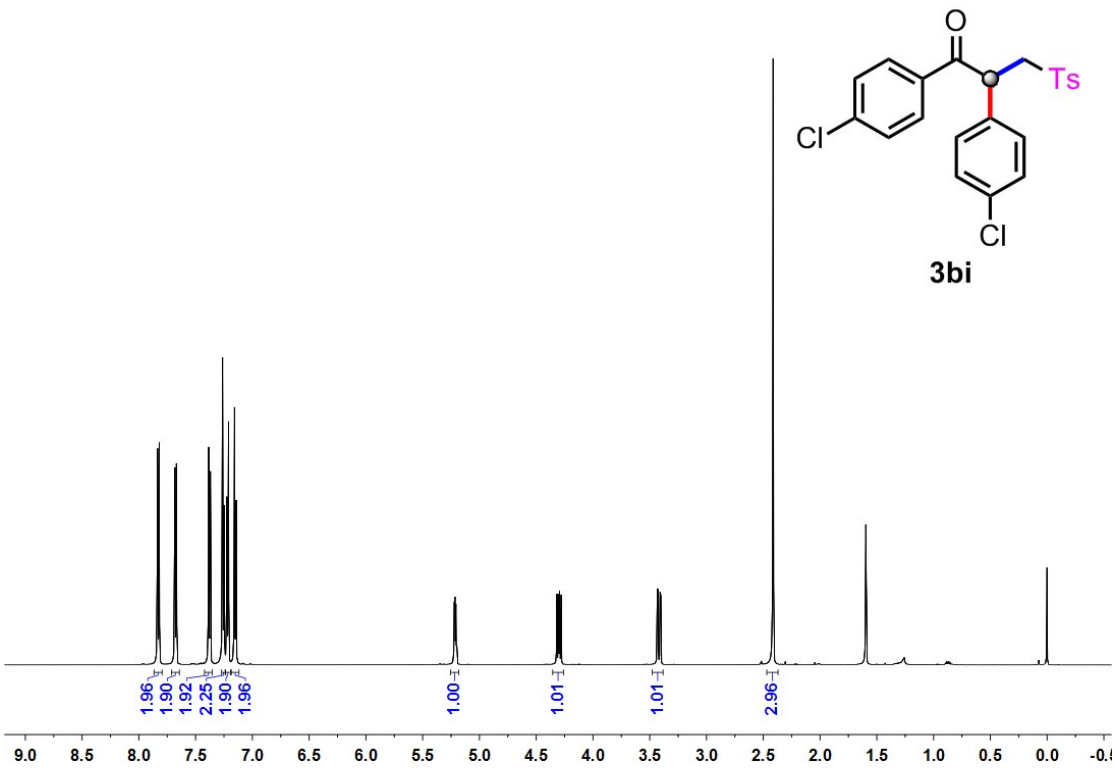
10
0


O
Ts
Cl
Cl
3bi
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1.90
1.92
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1.90
1.96
1.00
1.01
1.01
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
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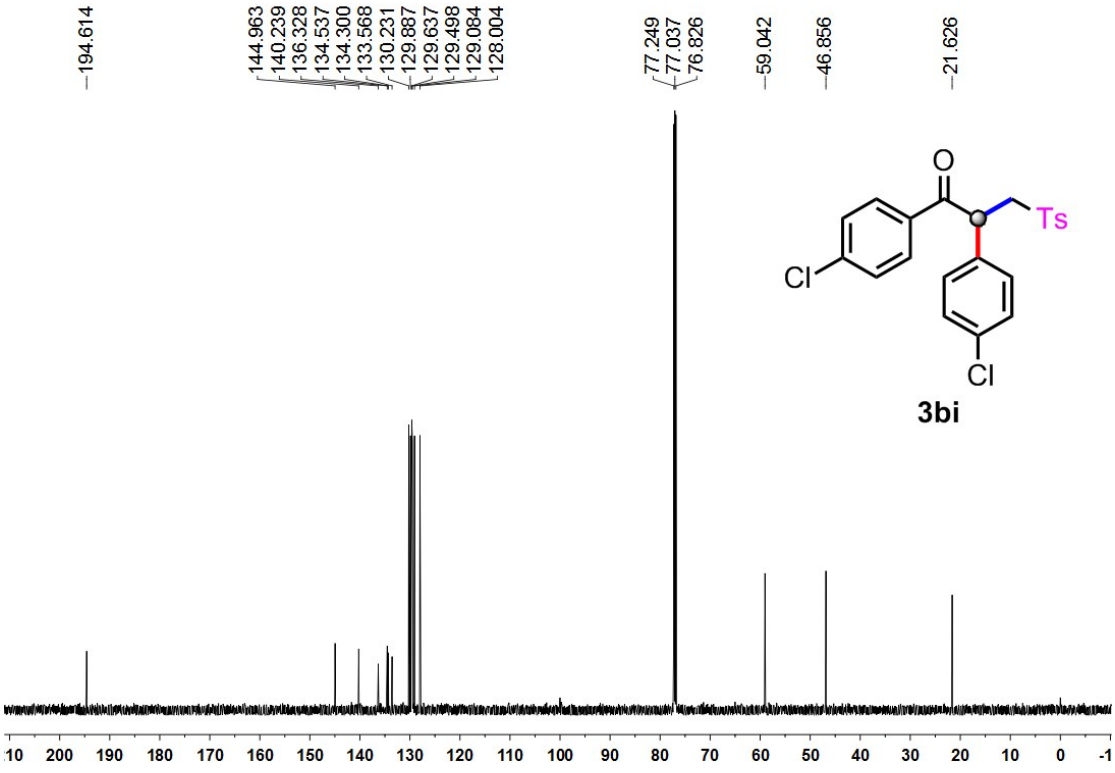
3.0
2.5
2.0
1.5
1.0
0.5
0.0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128.004
77.249
77.037
76.826
59.042
46.856
21.626
O
Ts
Cl
Cl
3bi
210
200
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150
140
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120
110
100
90
80
70
60
50
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30
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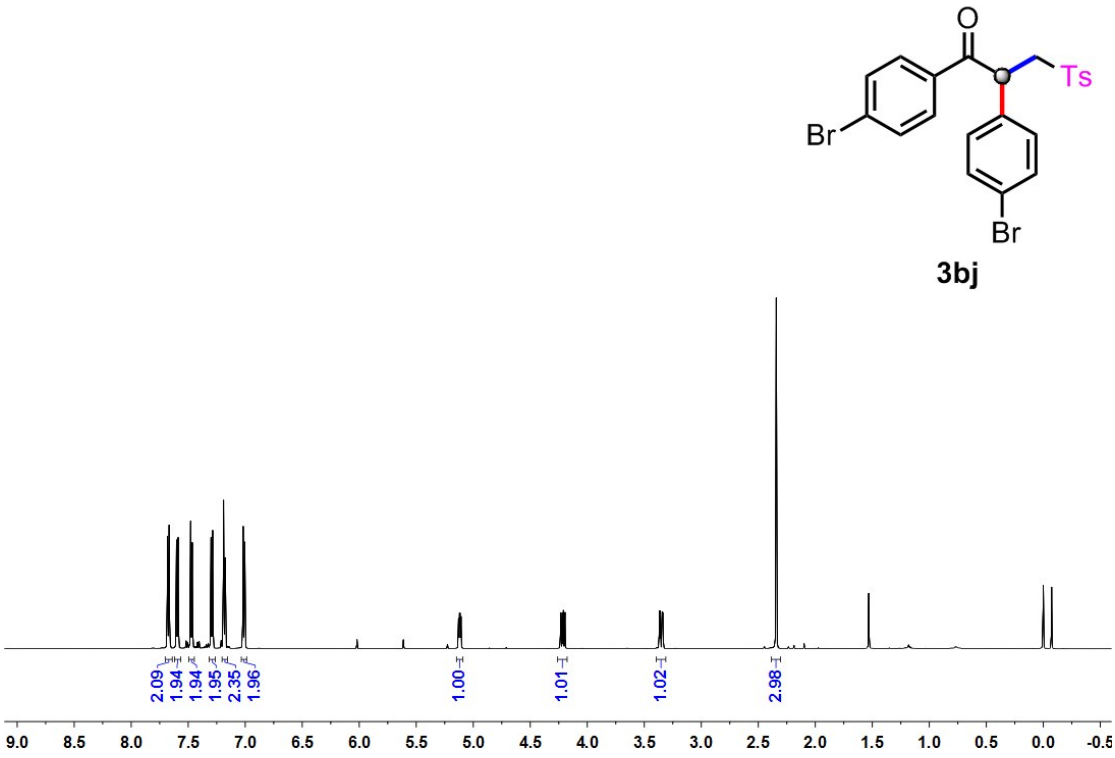
10
0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Ts
Br
Br
3bj
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1.94
1.95
2.35
1.96
1.00
1.01
1.02
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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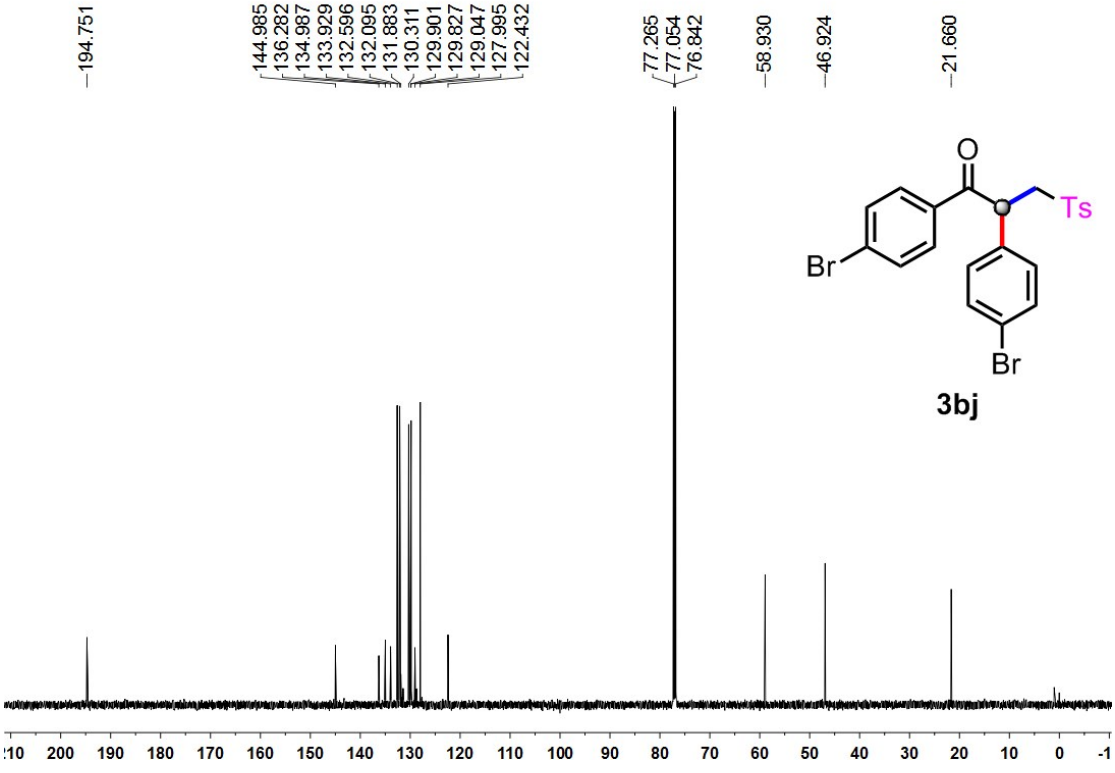
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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129.901
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129.047
127.995
122.432
77.265
77.054
76.842
58.930
46.924
21.660
O
Ts
Br
Br
3bj
210
200
190
180
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140
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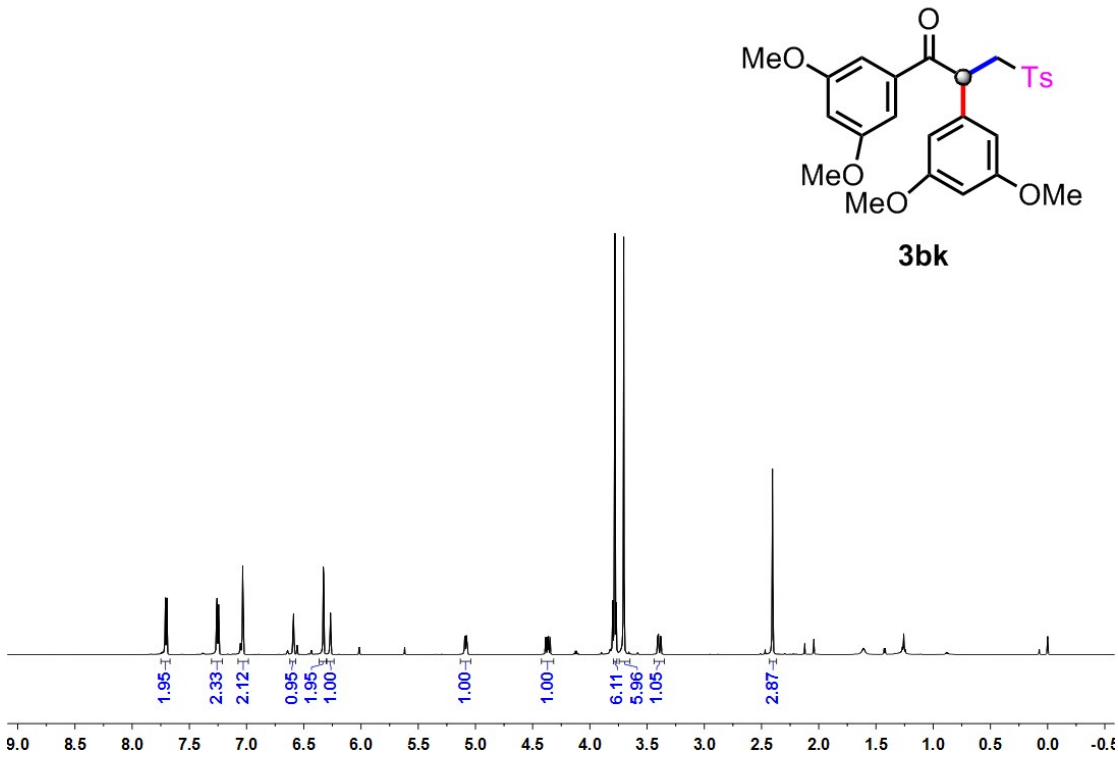
-1


MeO
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Ts
MeO
MeO
OMe
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2.12
0.95
1.95
1.00
1.00
1.00
6.11
5.96
1.05
2.87
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8.5
8.0
7.5
7.0
6.5
6.0
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3.0
2.5
2.0
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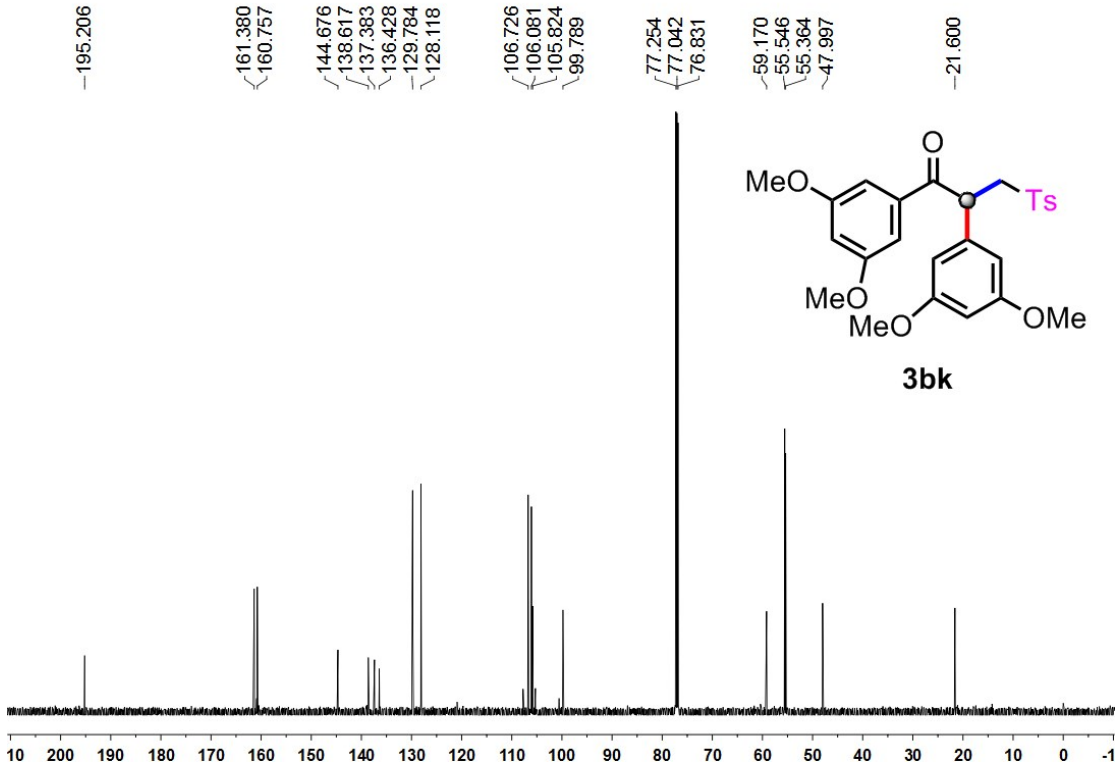
0.0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99.789
77.254
77.042
76.831
59.170
55.546
55.364
47.997
21.600
MeO
O
Ts
MeO
MeO
OMe
3bk
10
200
190
180
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150
140
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120
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100
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80
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60
50
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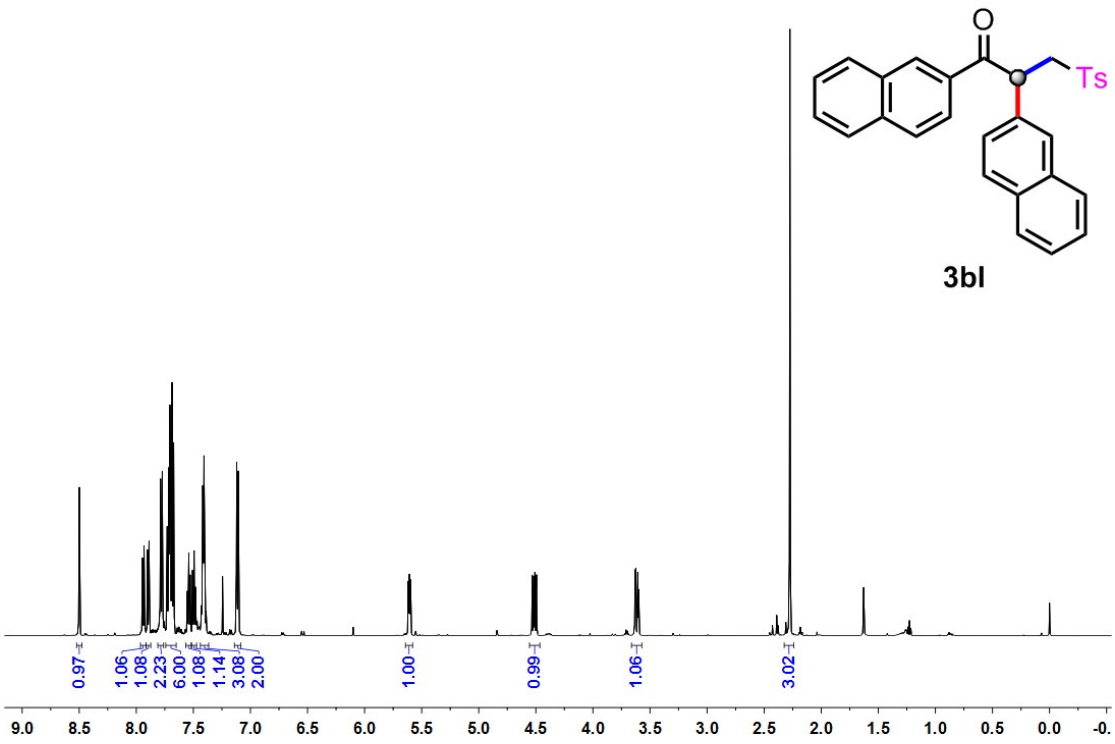
20
10
0
-1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Ts
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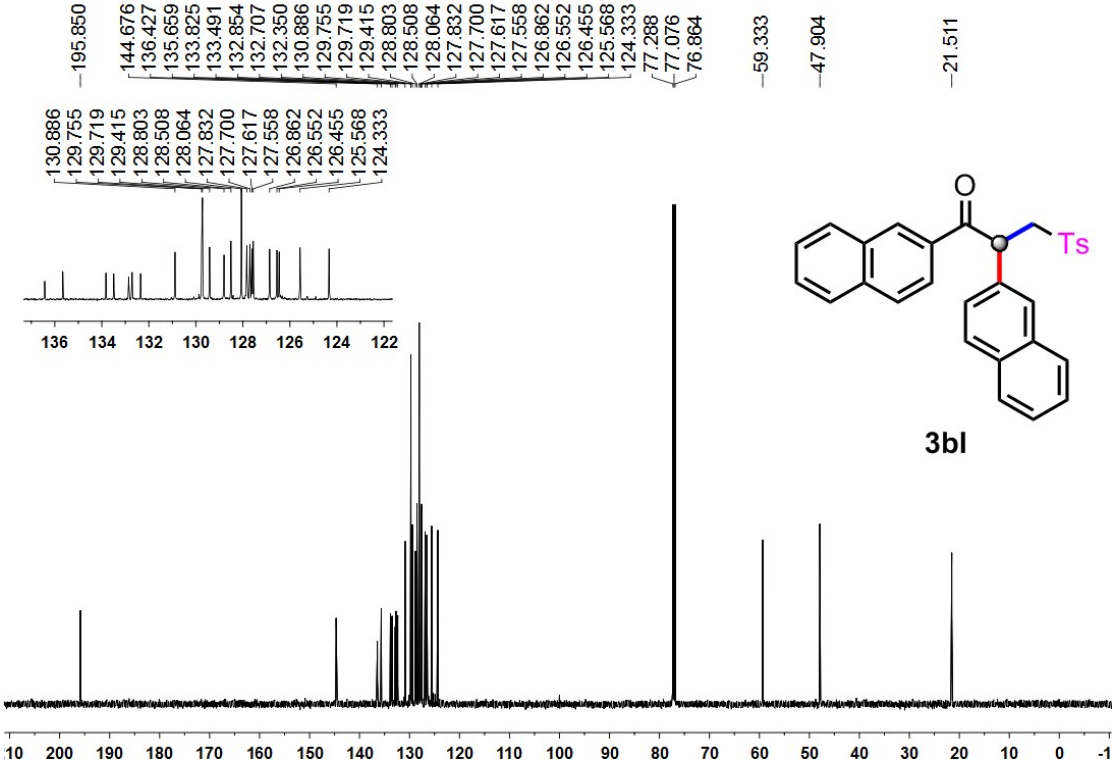
1.08
2.23
6.00
1.08
1.14
3.08
2.00
1.00
0.99
1.06
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.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129.719
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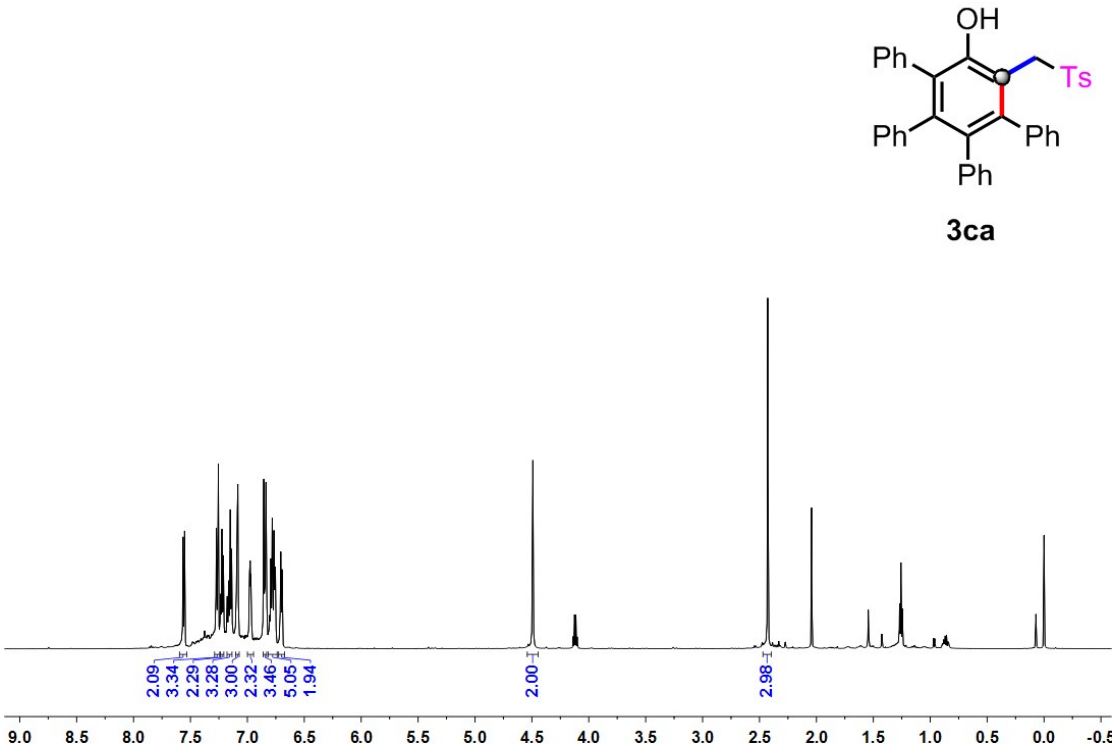
126.862
126.552
126.455
125.568
124.333
77.288
77.076
76.864
59.333
47.904
21.511
136 134 132 130 128 126 124 122
O
Ts
3bl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1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Ph
Ts
Ph
Ph
Ph
3ca
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3.28
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2.32
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5.05
1.94
2.00
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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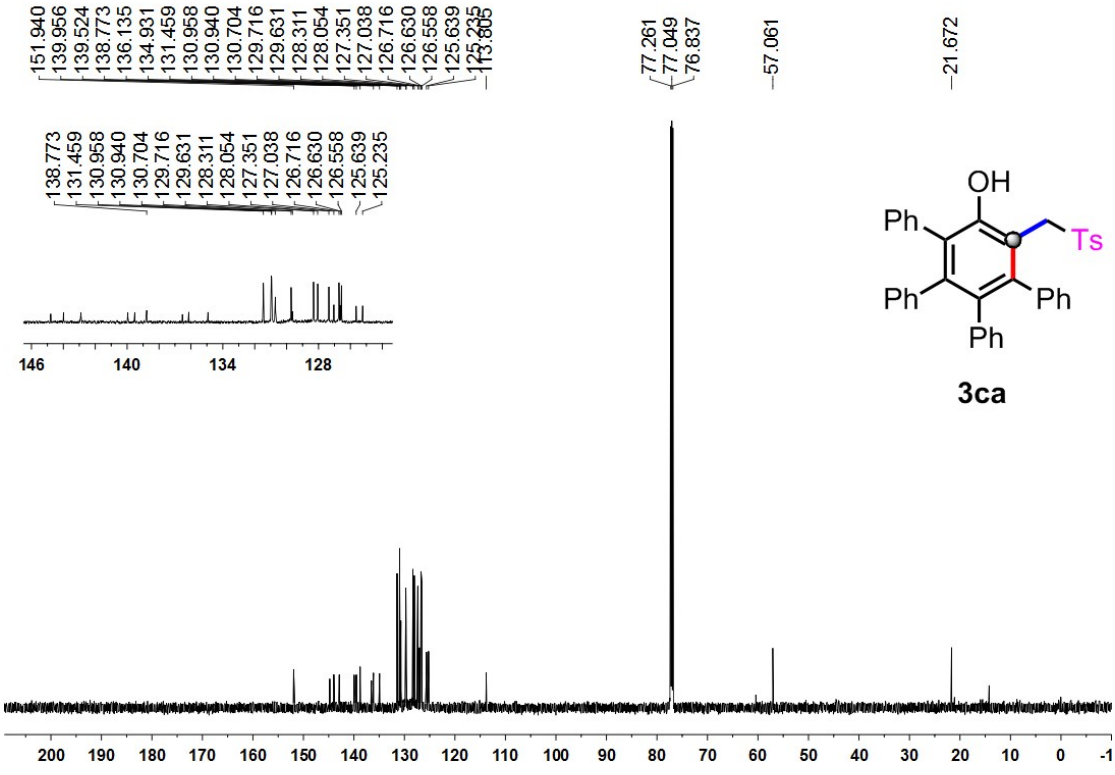
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126.558
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77.049
76.837
57.061
21.672
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140
134
128
OH
Ph
Ts
Ph
Ph
Ph
3ca
200
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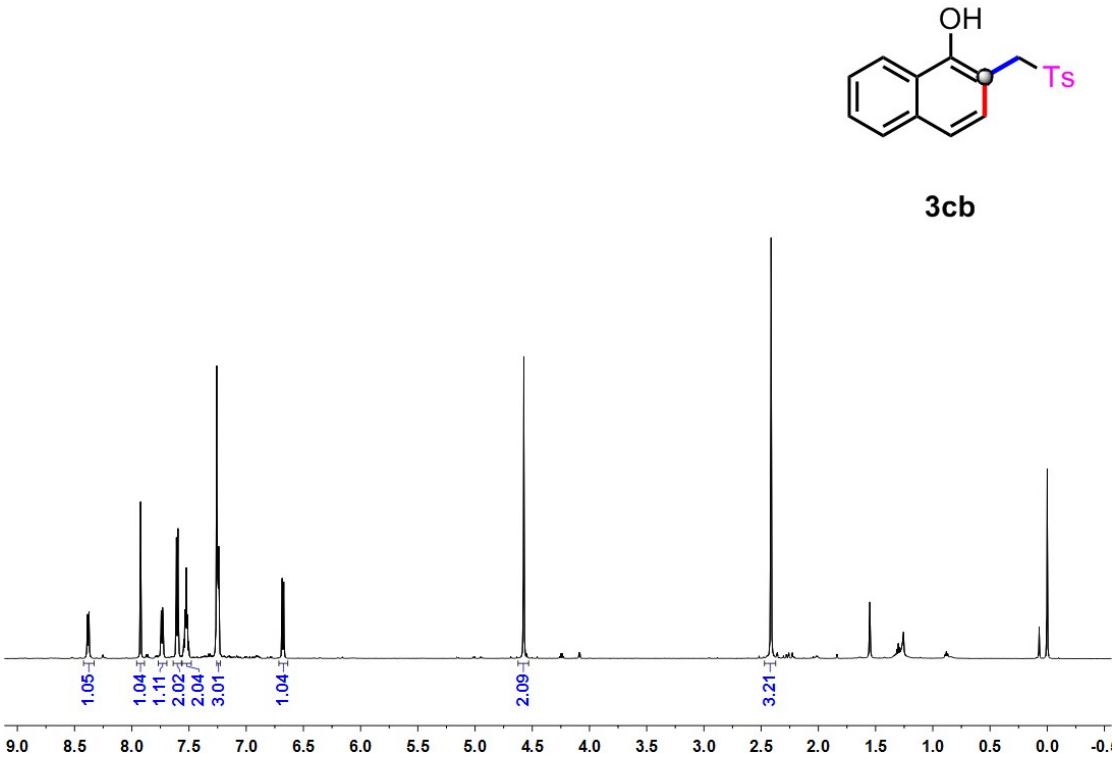
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3.01
1.04
2.09
3.21
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8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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1.0
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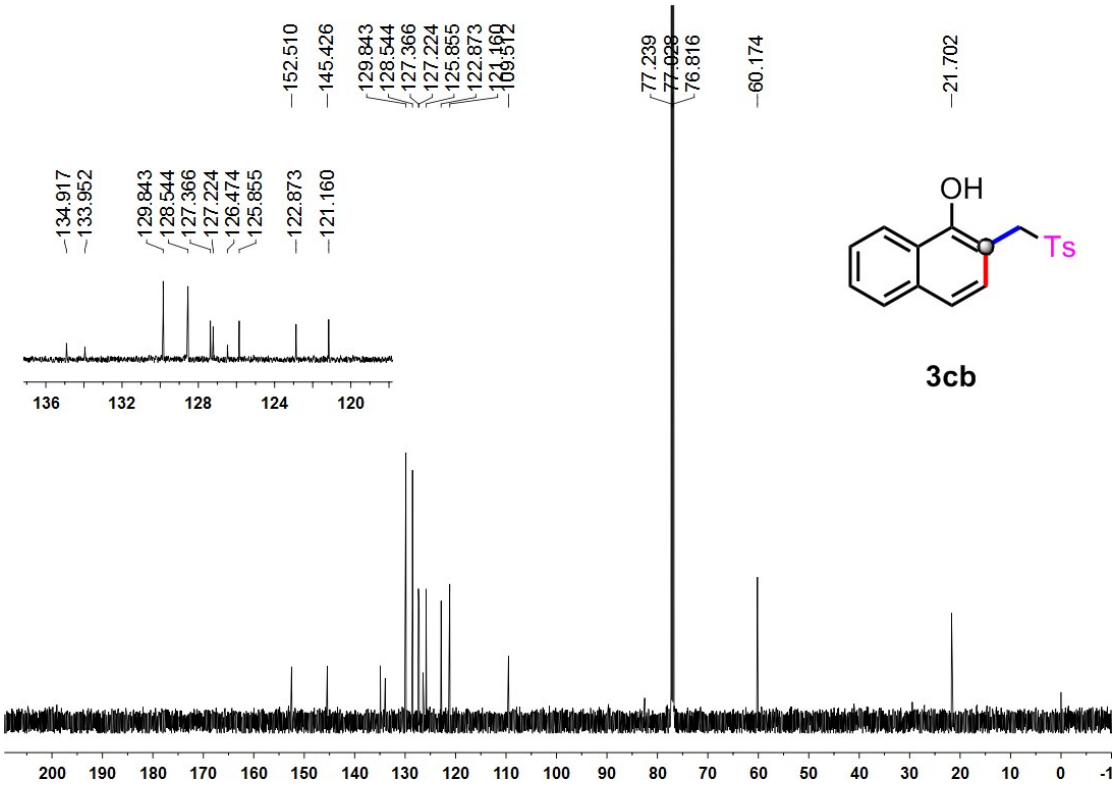
0.0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127.366
127.224
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121.160
77.239
76.816
60.174
21.702
134.917
133.952
129.843
128.544
127.366
127.224
126.474
125.855
122.873
121.160
136
132
128
124
120
OH
Ts
3cb
200
190
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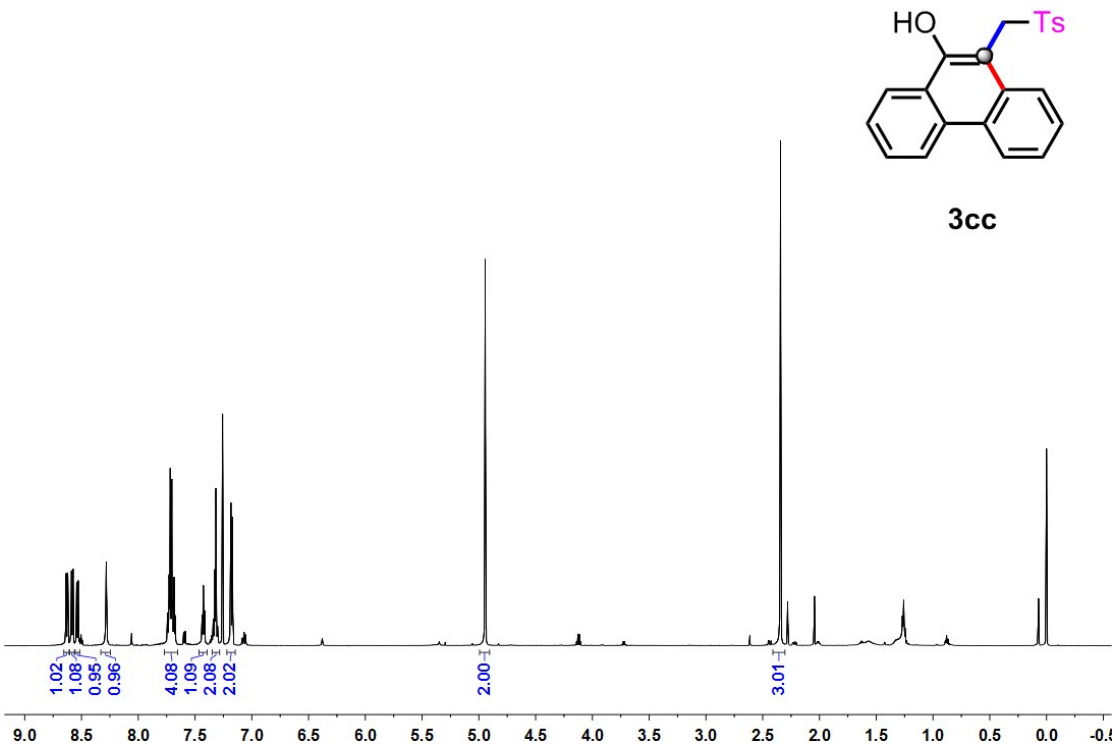
-1


HO
Ts
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0.96
4.08
1.09
2.08
2.02
2.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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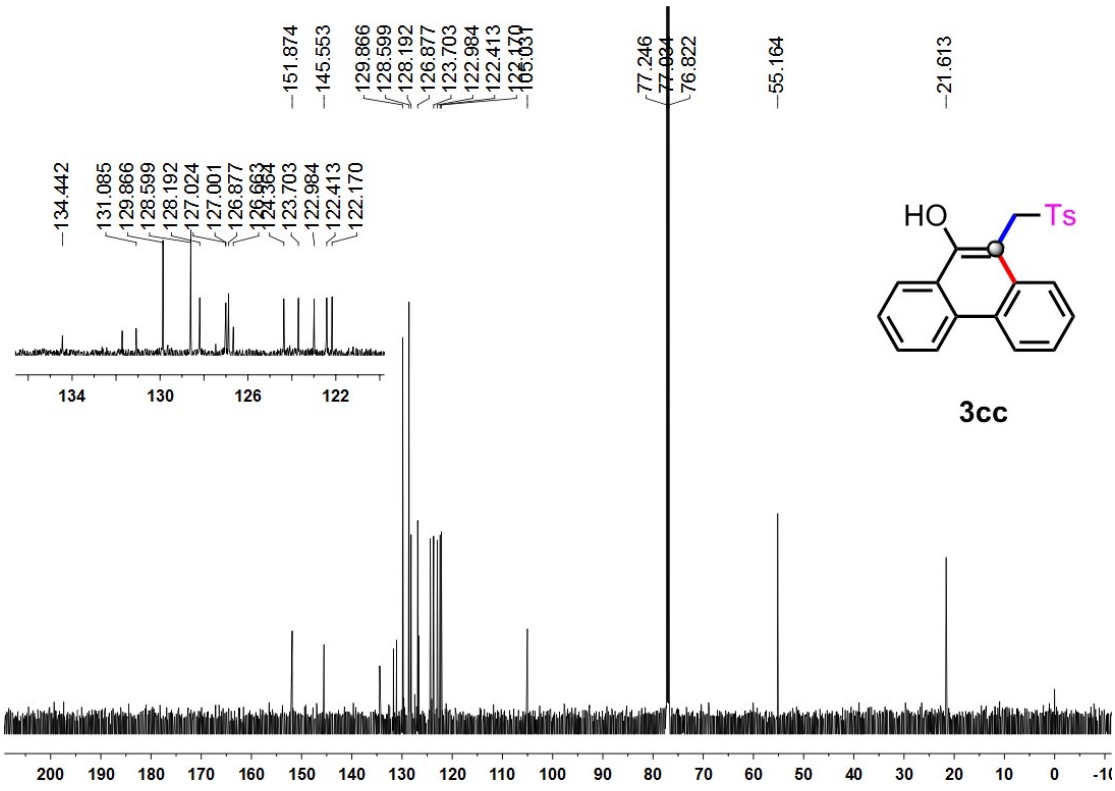
0.0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134.442
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129.866
128.599
128.192
127.024
127.001
126.877
123.703
122.984
122.413
122.170
134
130
126
122
HO
Ts
3cc
200
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150
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110
100
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70
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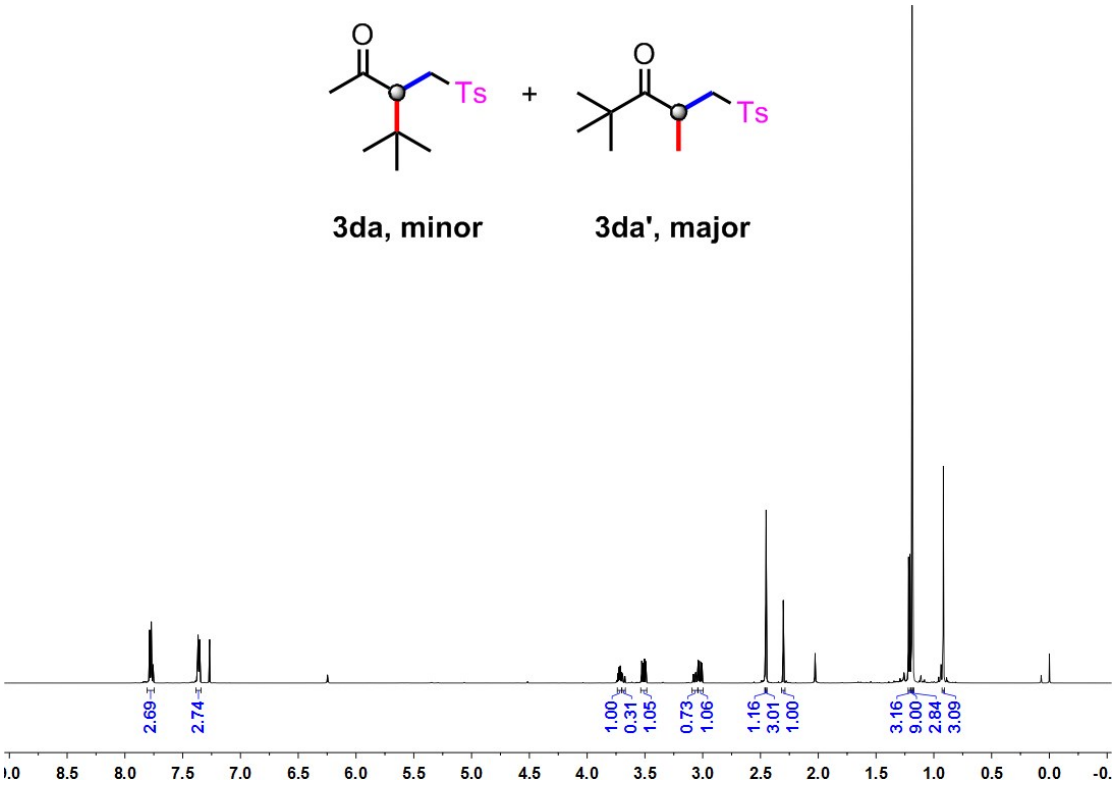
10
0


Ts
+
Ts
3da, minor
3da', major
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2.74
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0.73
1.06
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1.00
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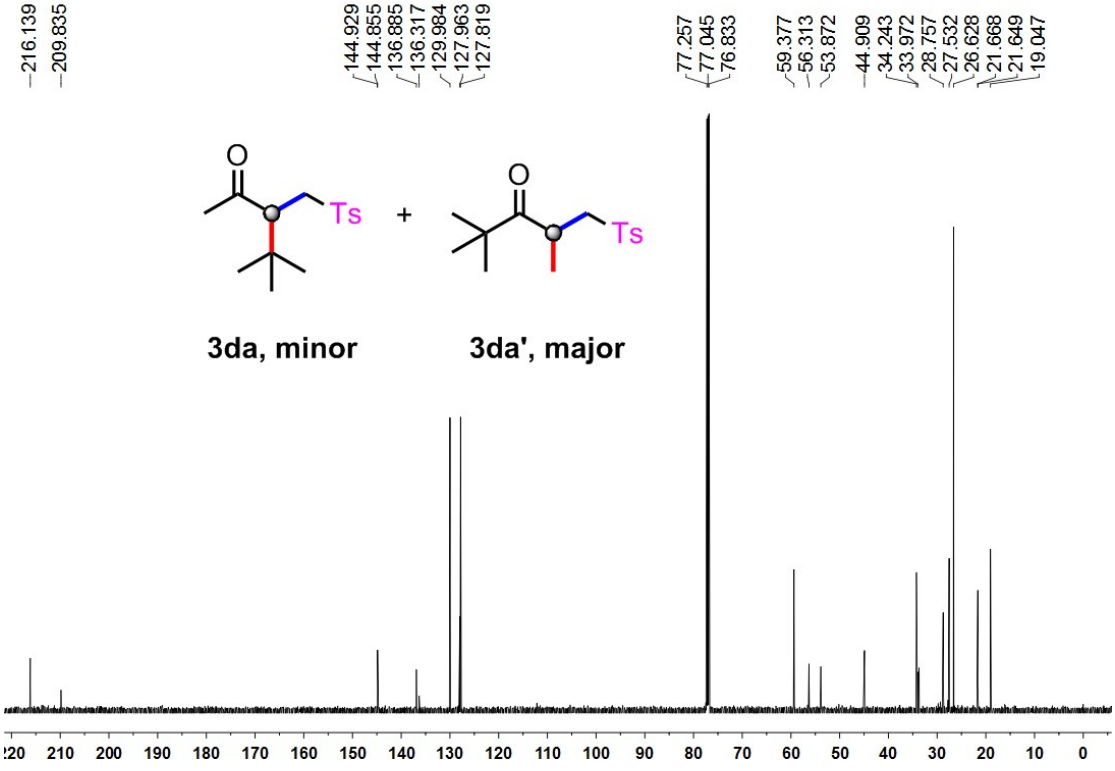
3.09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144.855
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136.317
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127.963
127.819
77.257
77.045
76.833
59.377
56.313
53.872
44.909
34.243
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19.047
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Ts
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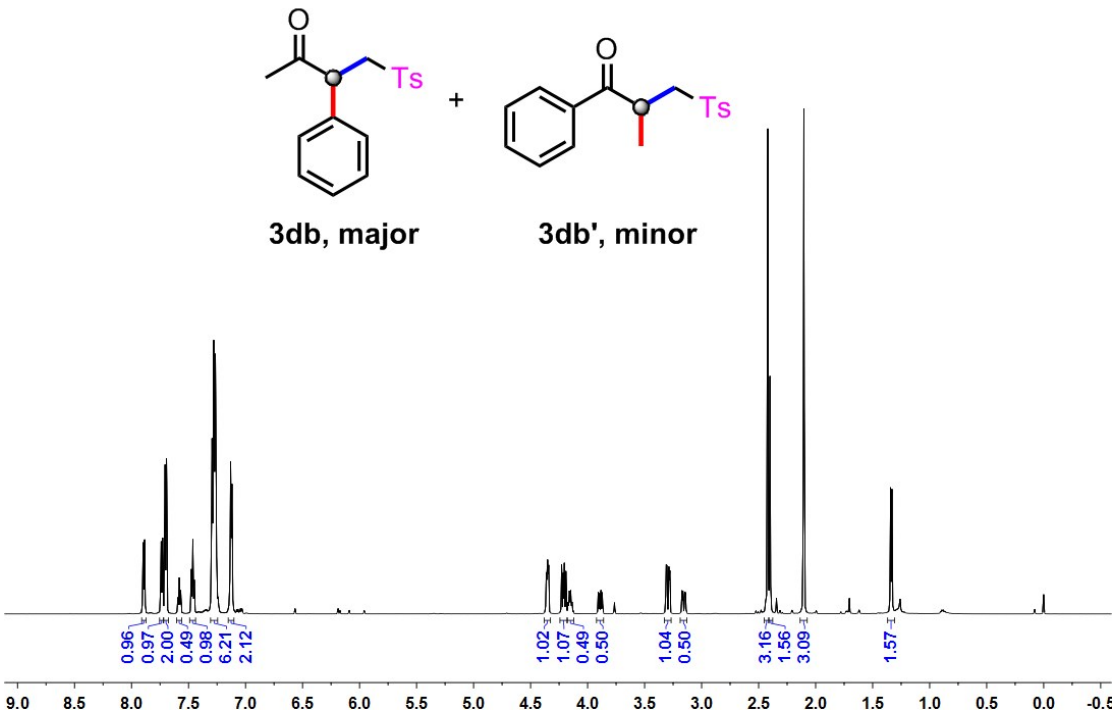
3da', major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Ts
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3db', minor
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0.49
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2.12
1.02
1.07
0.49
0.50
1.04
0.50
3.16
1.56
3.09
1.57
9.0
8.5
8.0
7.5
7.0
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6.0
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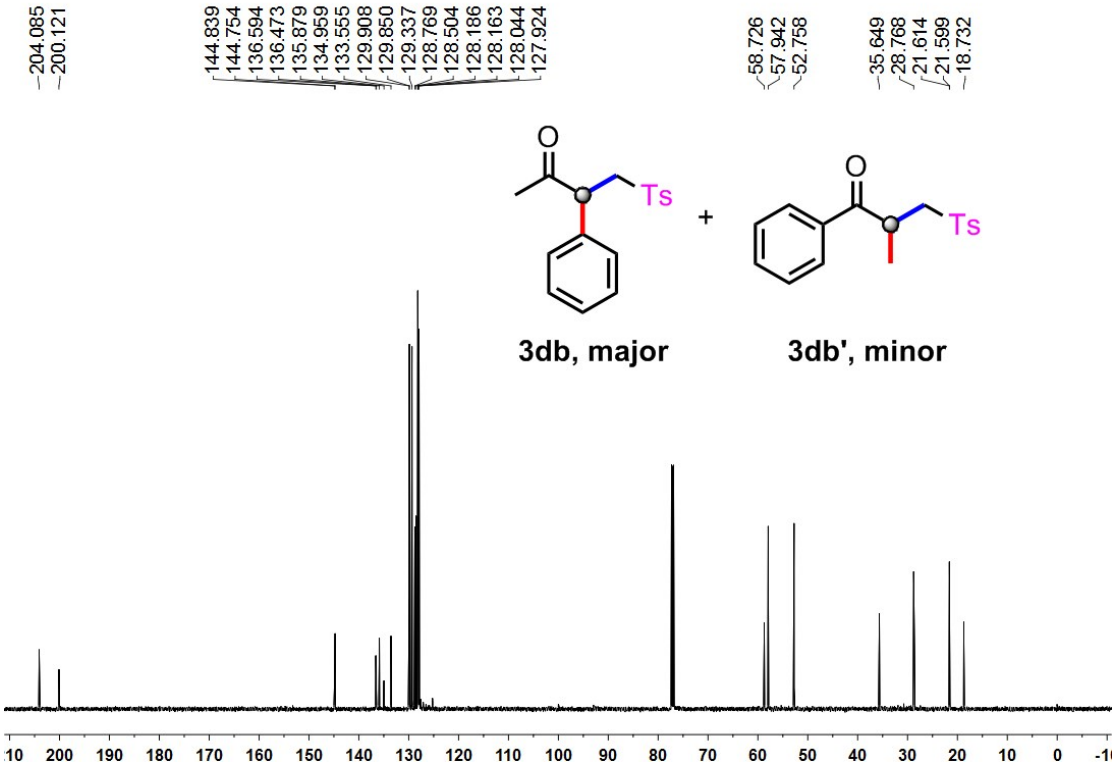
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128.769
128.504
128.186
128.163
128.044
127.924
58.726
57.942
52.758
35.649
28.768
21.614
21.599
18.732
Ts
+
Ts
3db, major
3db', minor
210
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70
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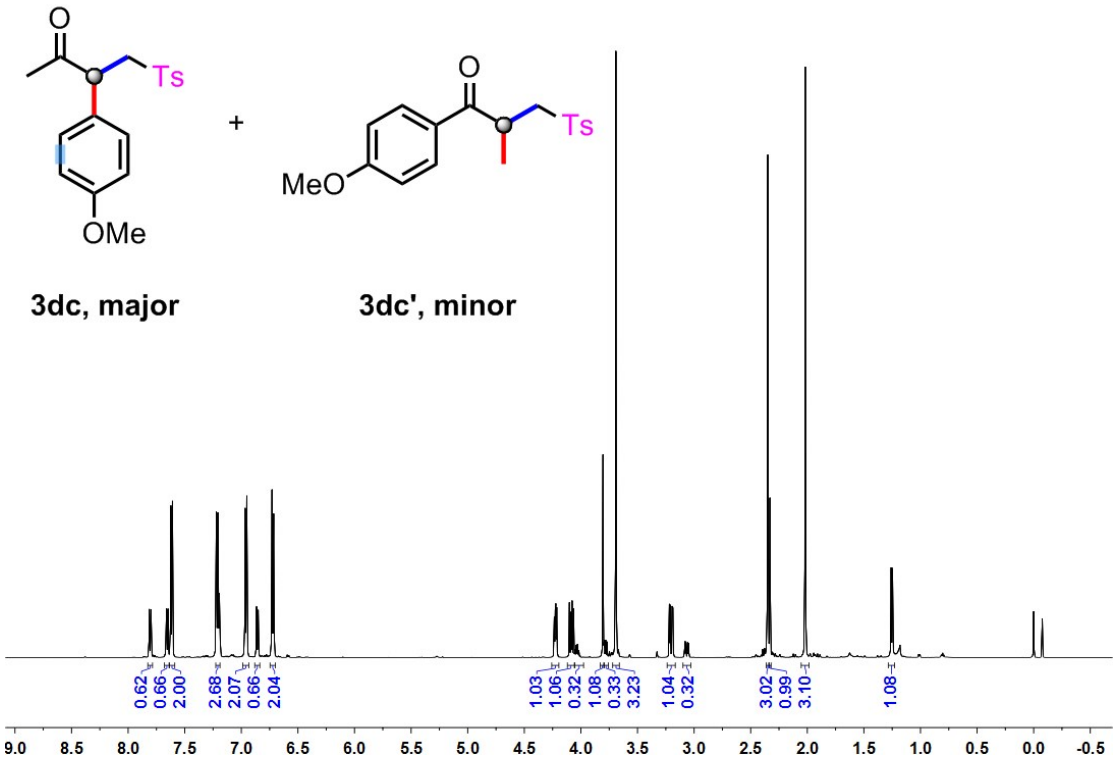
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MeO
Ts
3dc', minor
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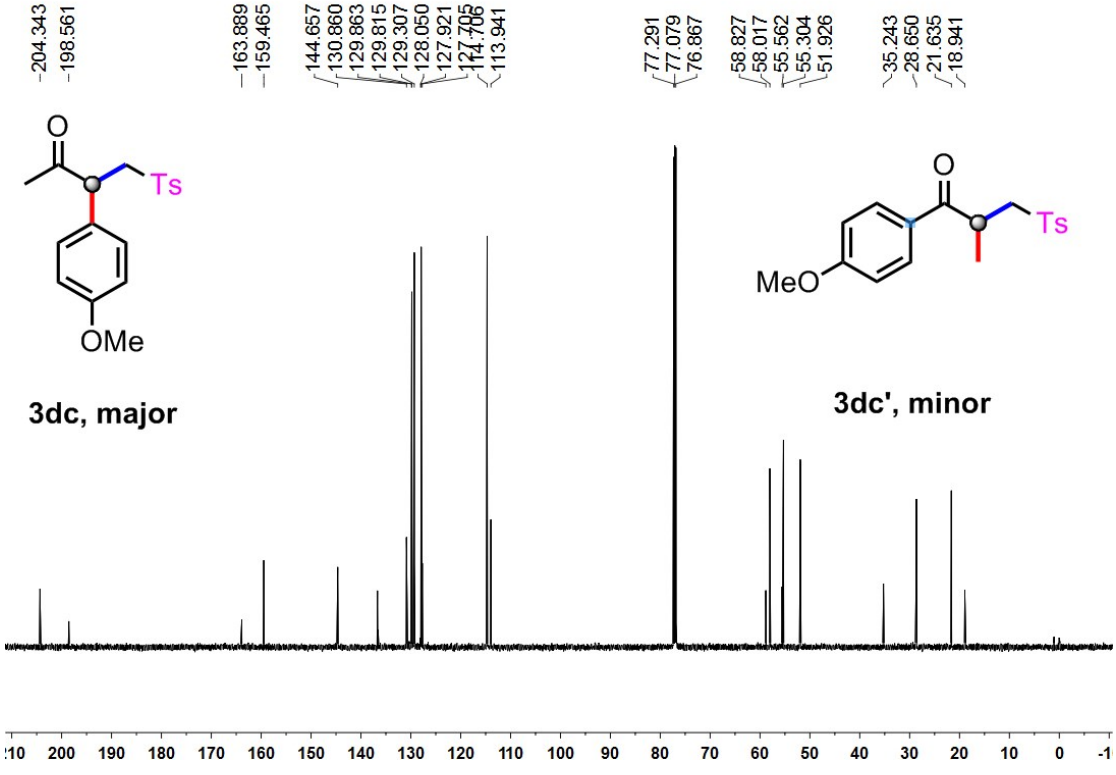
2.07
0.66
2.04
1.03
1.06
0.32
1.08
0.33
3.23
1.04
0.32
3.02
0.99
3.10
1.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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127.921
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114.706
113.941
77.291
77.079
76.867
58.827
58.017
55.562
55.304
51.926
35.243
28.650
21.635
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OMe
3dc, major
MeO
Ts
3dc', minor
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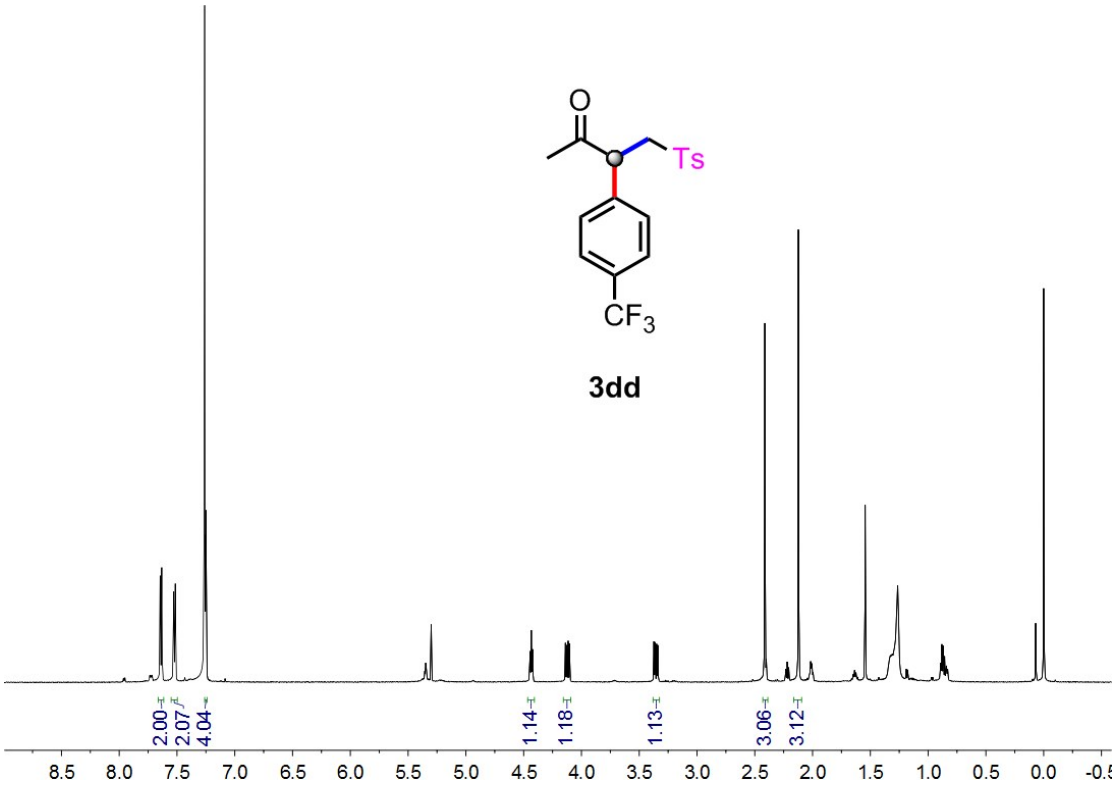
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Ts
CF3
3dd
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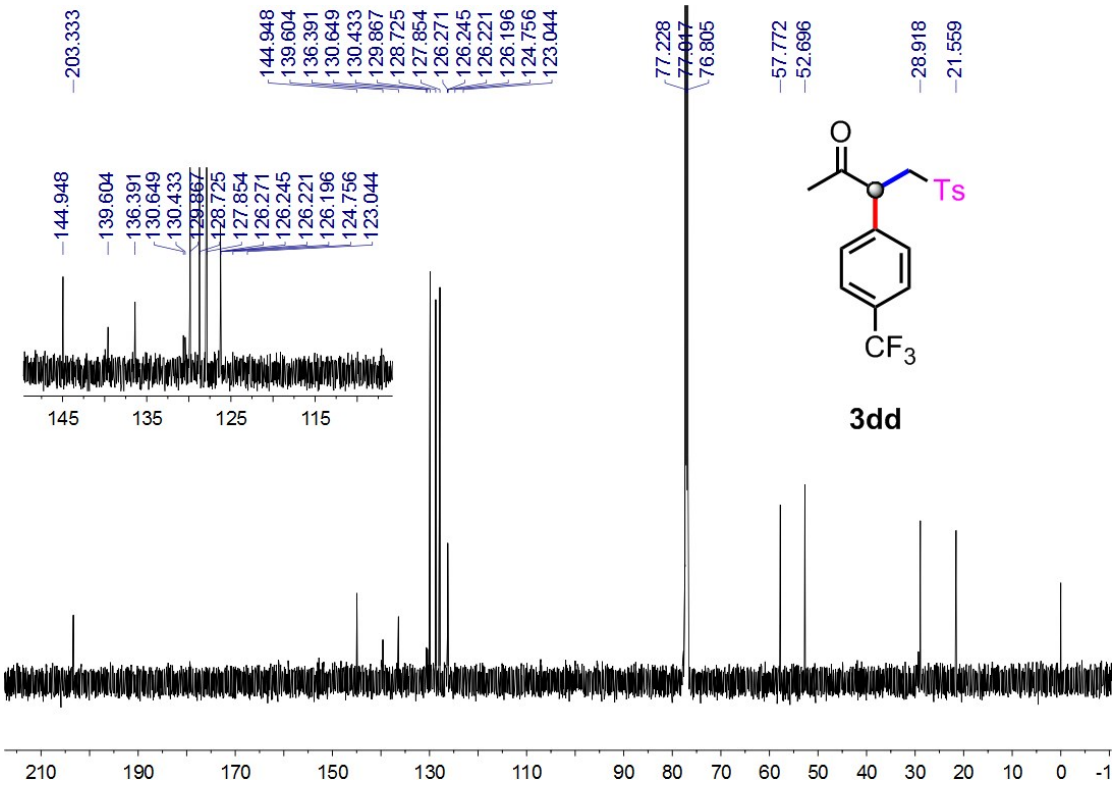
2.07
4.04
1.14
1.18
1.13
3.06
3.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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126.271
126.245
126.221
126.196
124.756
123.044
77.228
77.017
76.805
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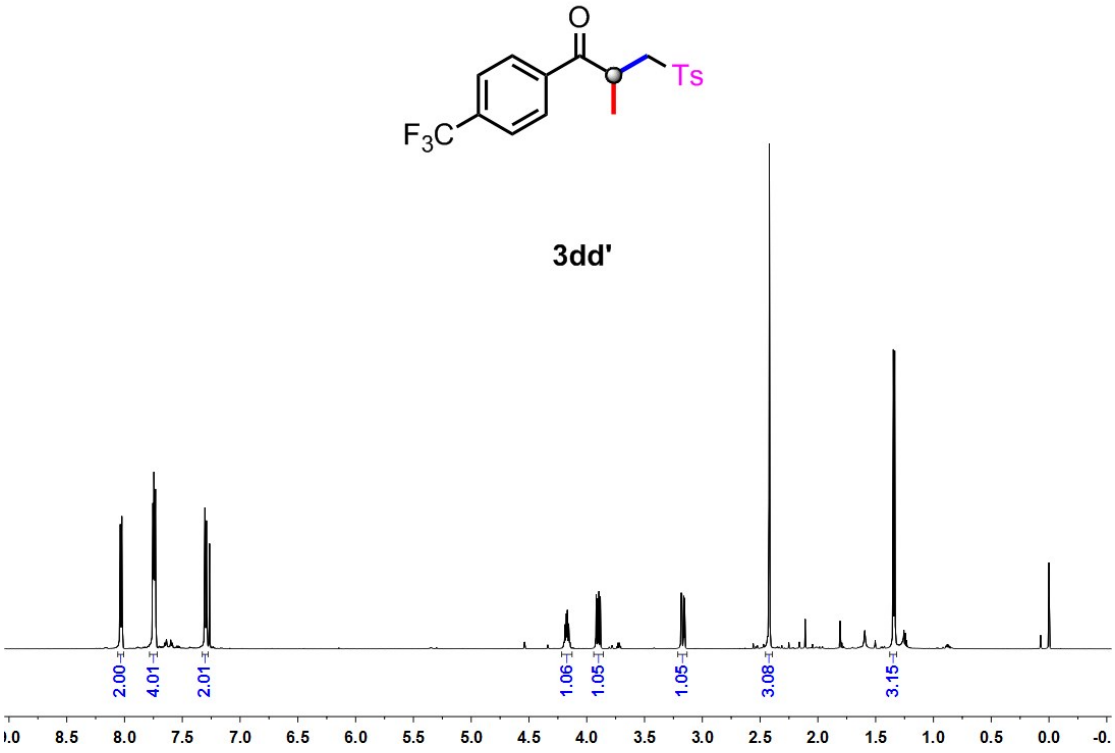
28.918
21.559
O
Ts
CF3
3dd
145 135 125 115
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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Ts
F3C
3dd'
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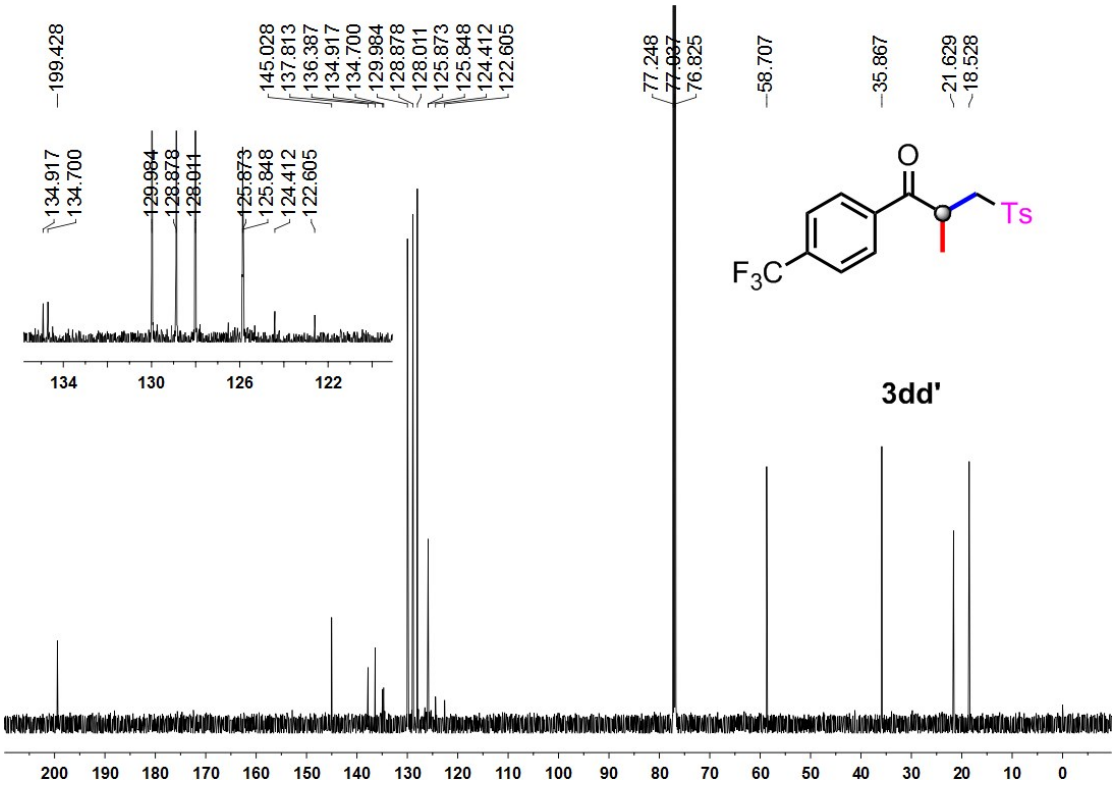
4.01
2.01
1.06
1.05
1.05
3.08
3.15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129.984
128.878
128.011
125.873
125.848
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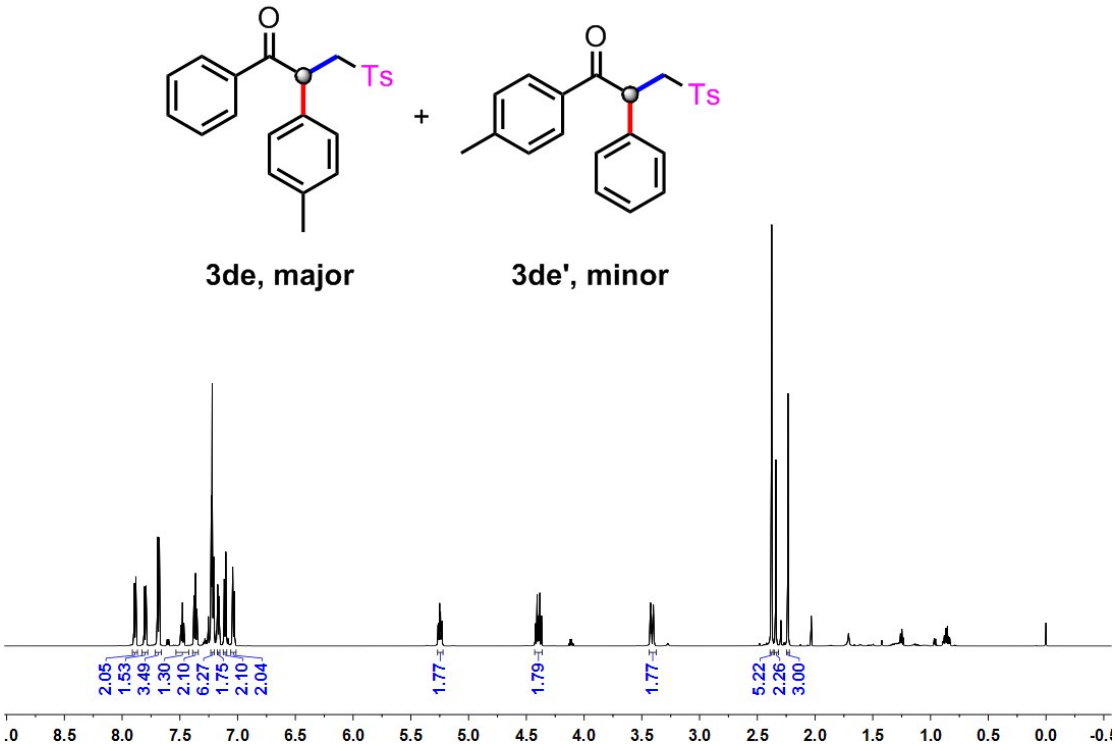
77.037
76.825
58.707
35.867
21.629
18.528
O
Ts
F3C
3dd'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+
Ts
3de, major
3de', minor
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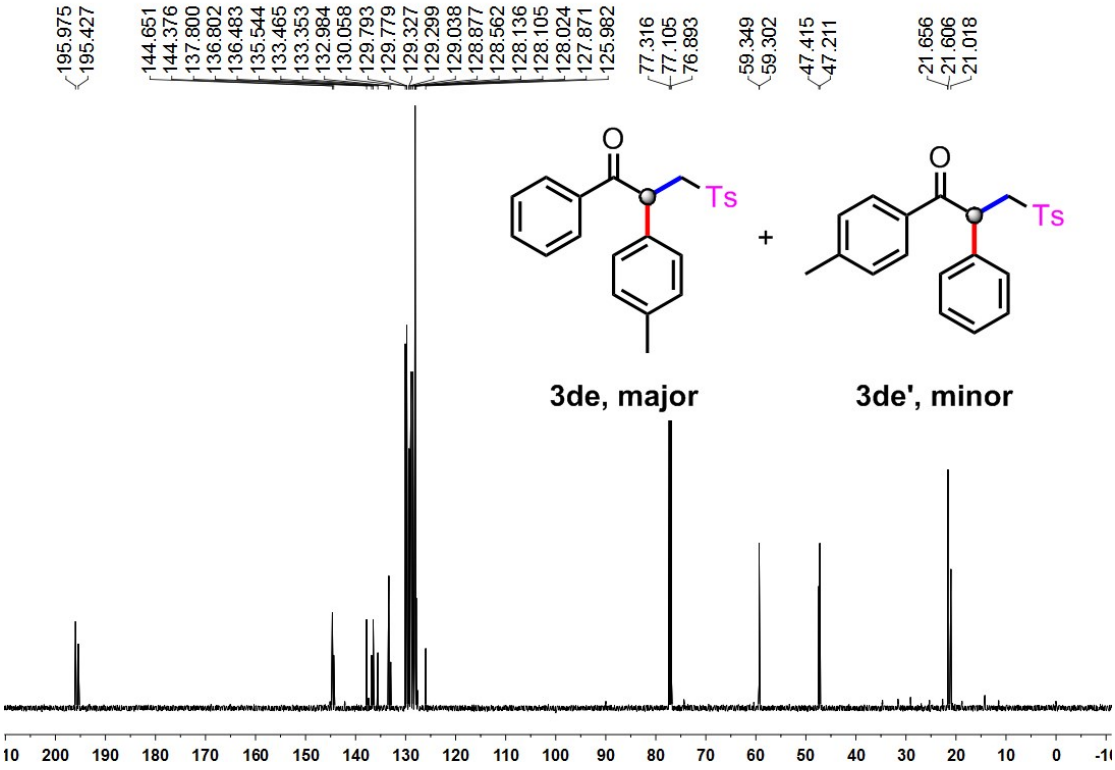
1.53
3.49
1.30
2.10
6.27
1.75
2.10
2.04
1.77
1.79
1.77
5.22
2.26
3.00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135.544
133.465
133.353
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129.793
129.779
129.327
129.299
129.038
128.877
128.562
128.136
128.105
128.024
127.871
125.982
77.316
77.105
76.893
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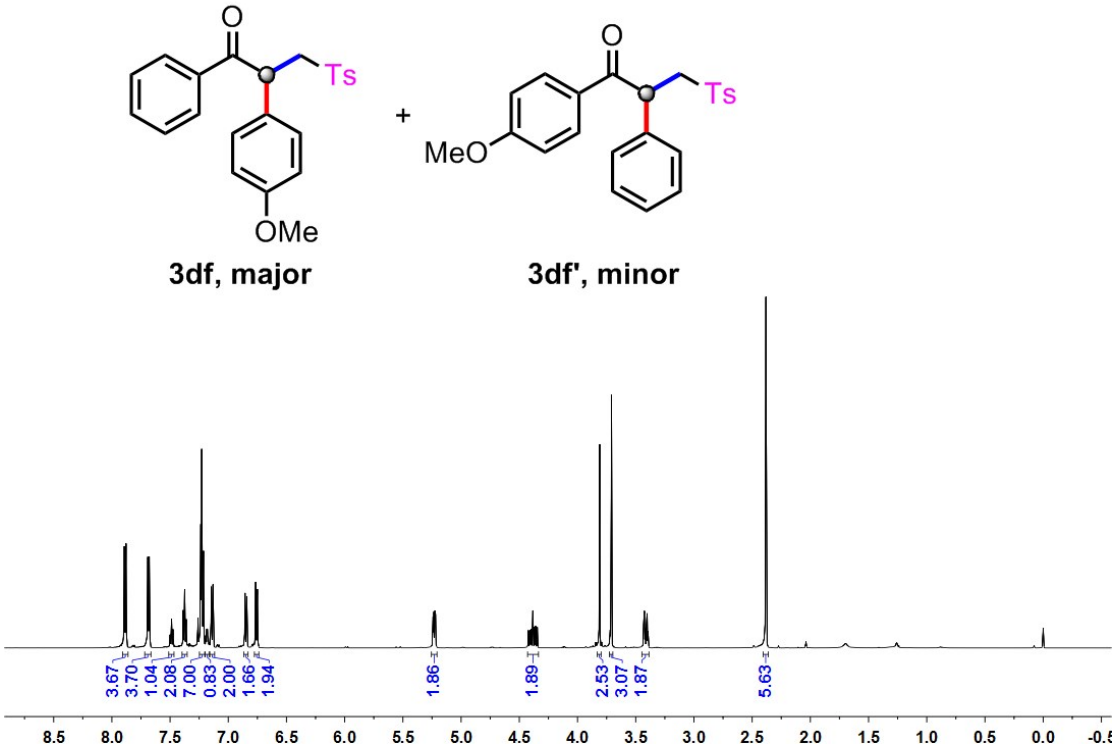
47.211
21.656
21.606
21.018
Ts
+
Ts
3de, major
3de', minor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Ts
OMe
+
MeO
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3df', minor
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3.70
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2.08
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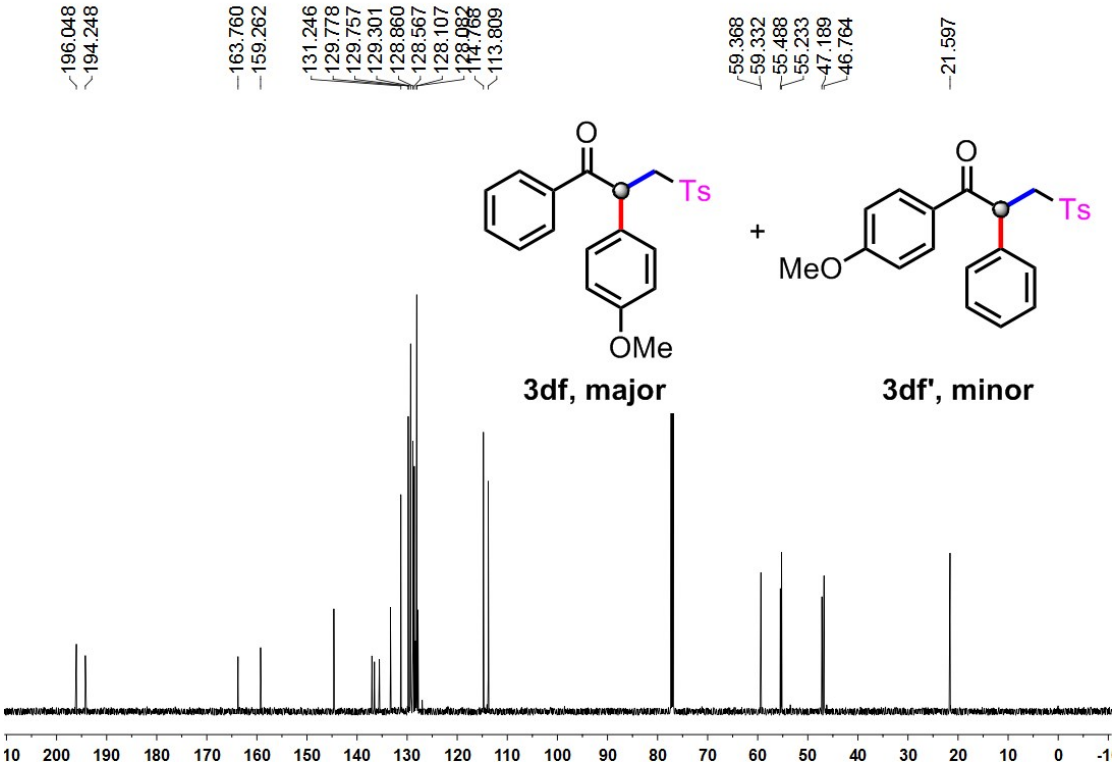
2.00
1.66
1.94
1.86
1.89
2.53
3.07
1.87
5.63
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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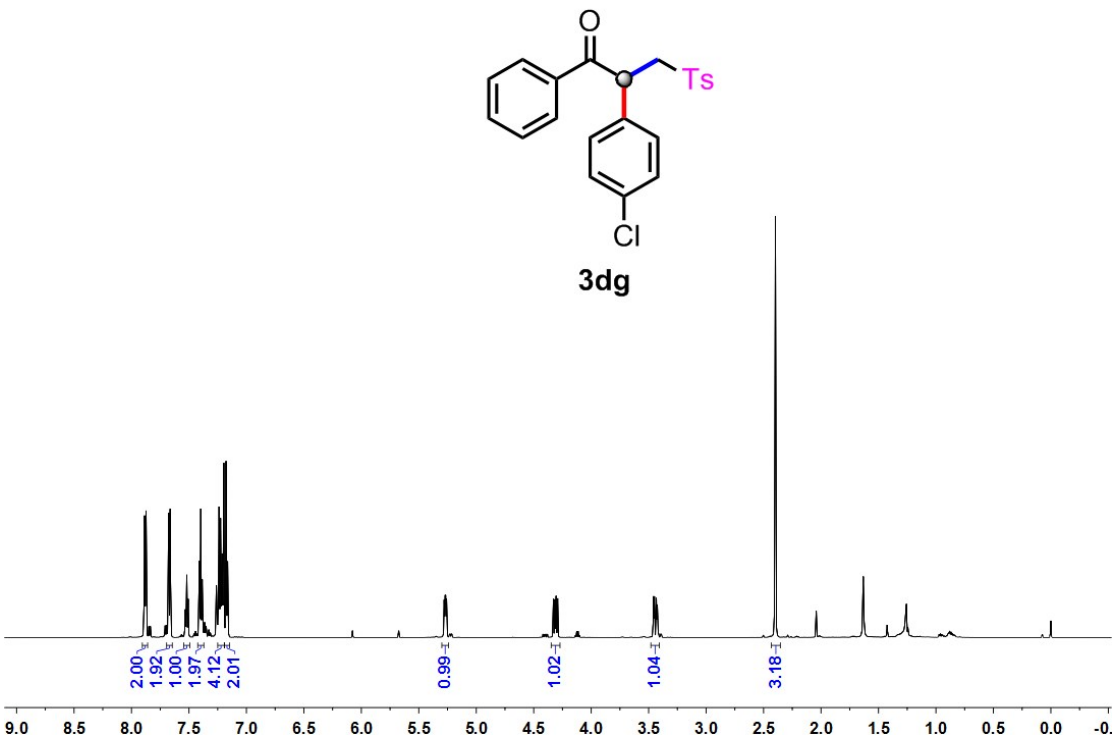
159.262
131.246
129.778
129.757
129.301
128.860
128.567
128.107
113.809
59.368
59.332
55.488
55.233
47.189
46.764
21.597
O
Ts
OMe
+
MeO
3df, major
3df', minor
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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Ts
Cl
3dg
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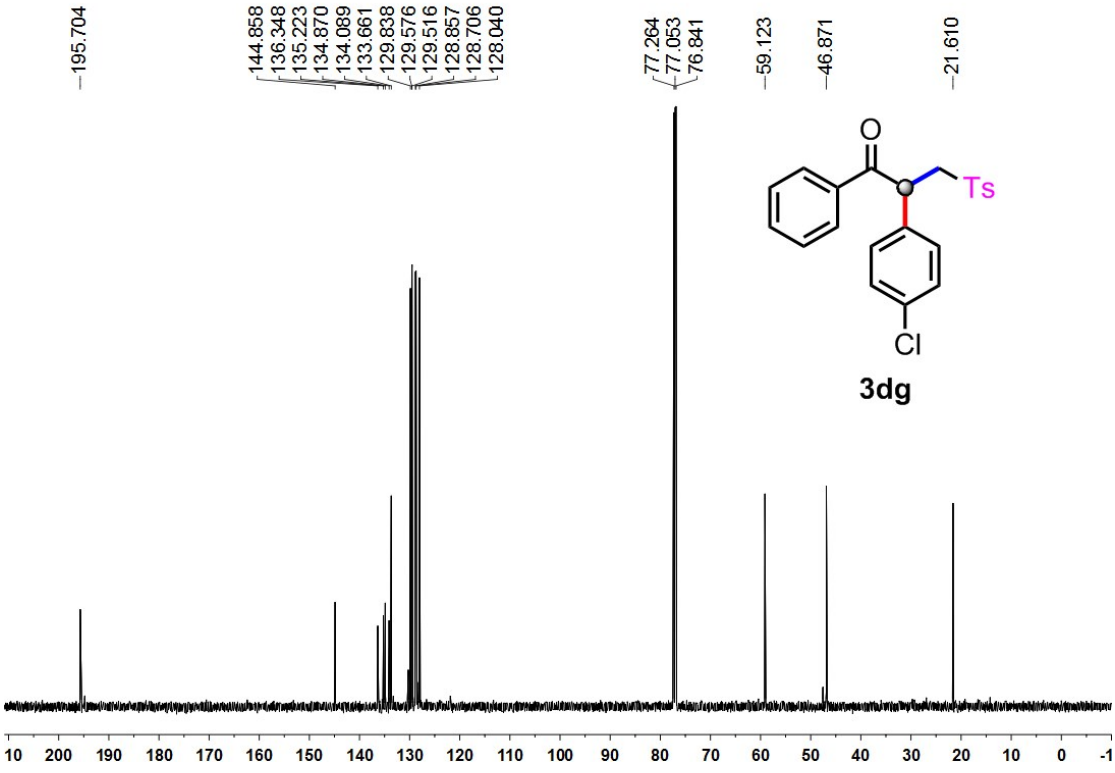
1.92
1.00
1.97
4.12
2.01
0.99
1.02
1.04
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.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129.838
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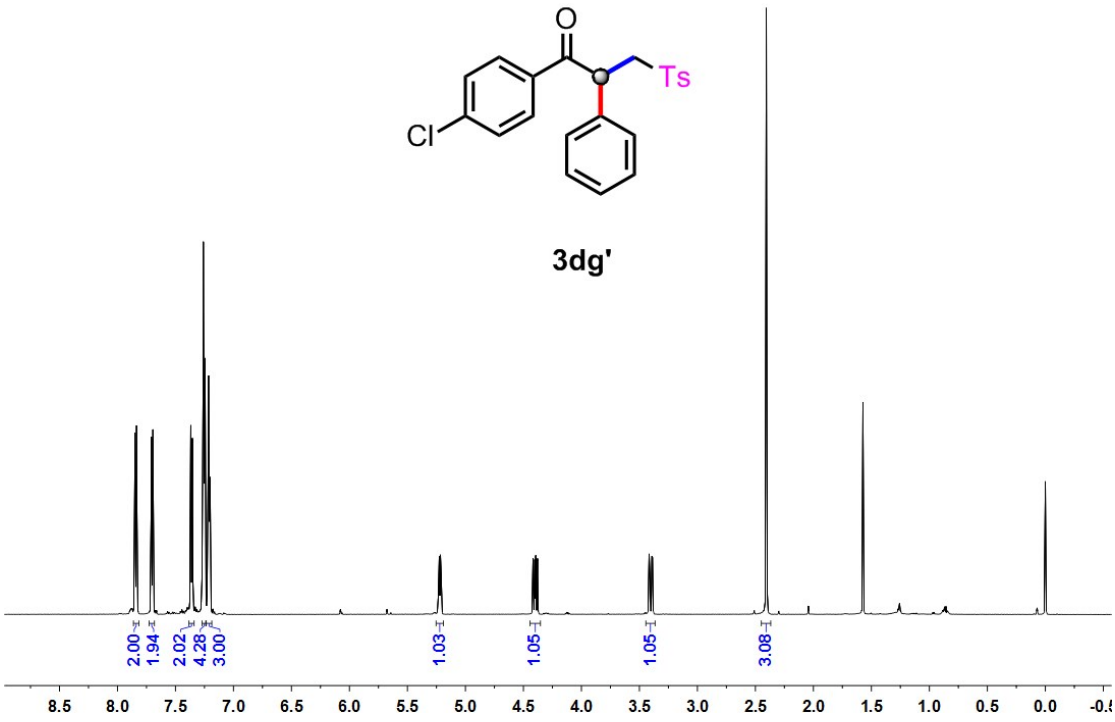
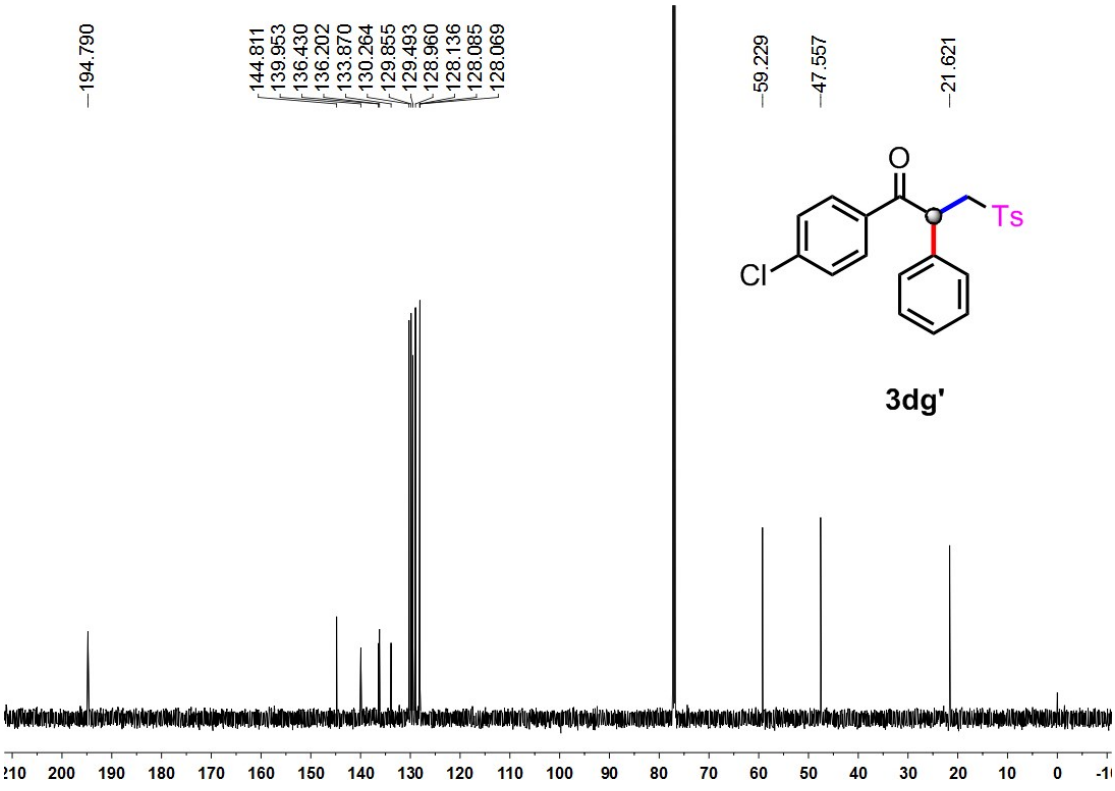
129.516
128.857
128.706
128.040
77.264
77.053
76.841
59.123
46.871
21.610
O
Ts
Cl
3dg
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


O
Ts
Cl
3dg'
2.00
1.94
2.02
4.28
3.00
1.03
1.05
1.05
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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128.960
128.136
128.085
128.069
59.229
47.557
21.621
O
Ts
Cl
3dg'
210
200
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150
140
130
120
110
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70
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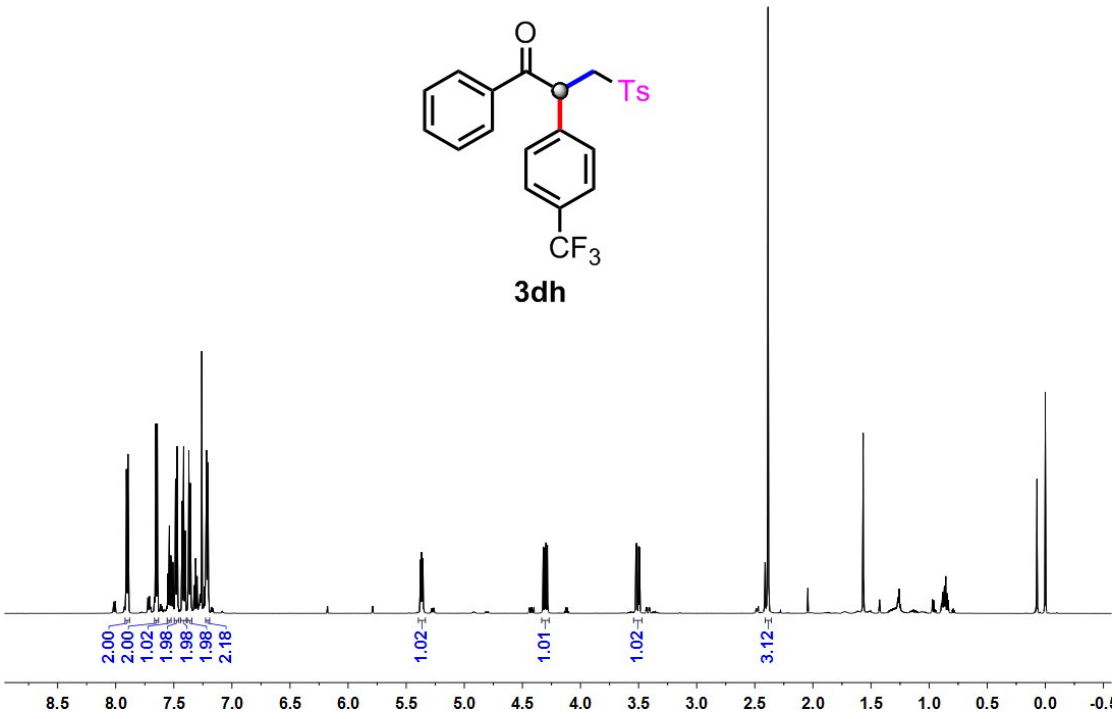
30
20
10
0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Ts
CF3
3dh
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2.00
1.02
1.98
1.98
1.98
2.18
1.02
1.01
1.02
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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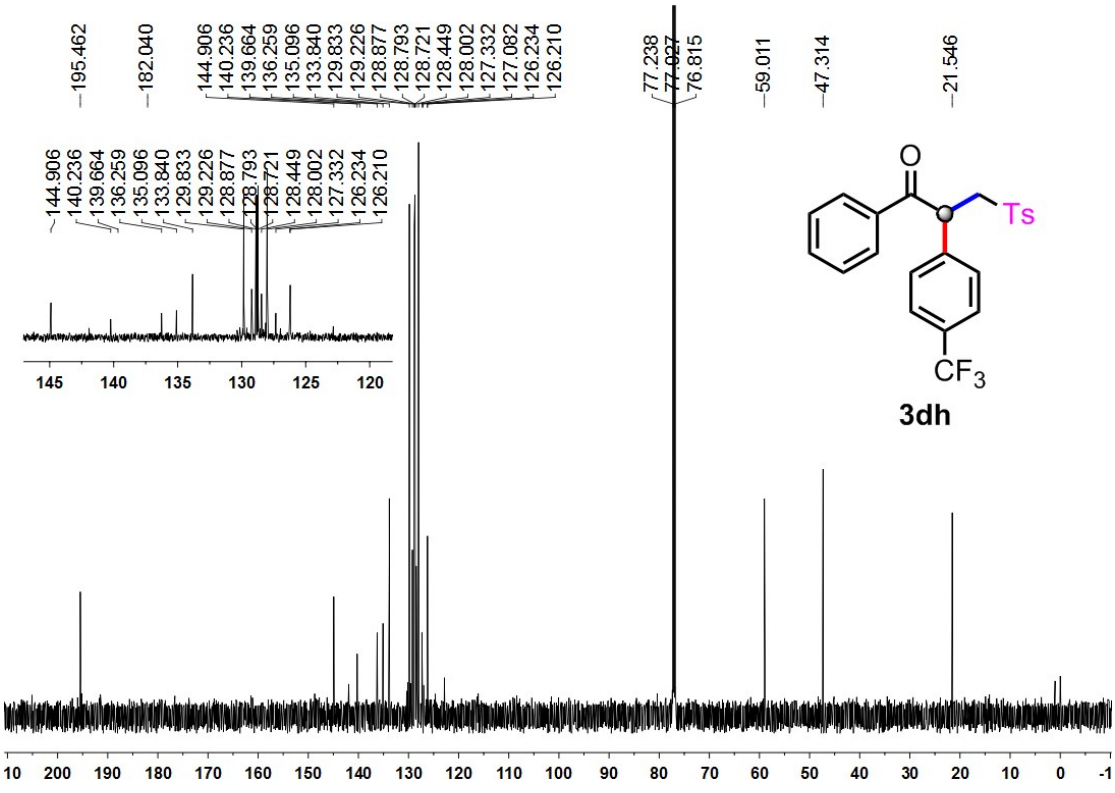
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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128.721
128.449
128.002
127.332
127.082
126.234
126.210
77.238
77.027
76.815
59.011
47.314
21.546
145
140
135
130
125
120
O
Ts
CF3
3dh
10
200
190
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140
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120
110
100
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60
50
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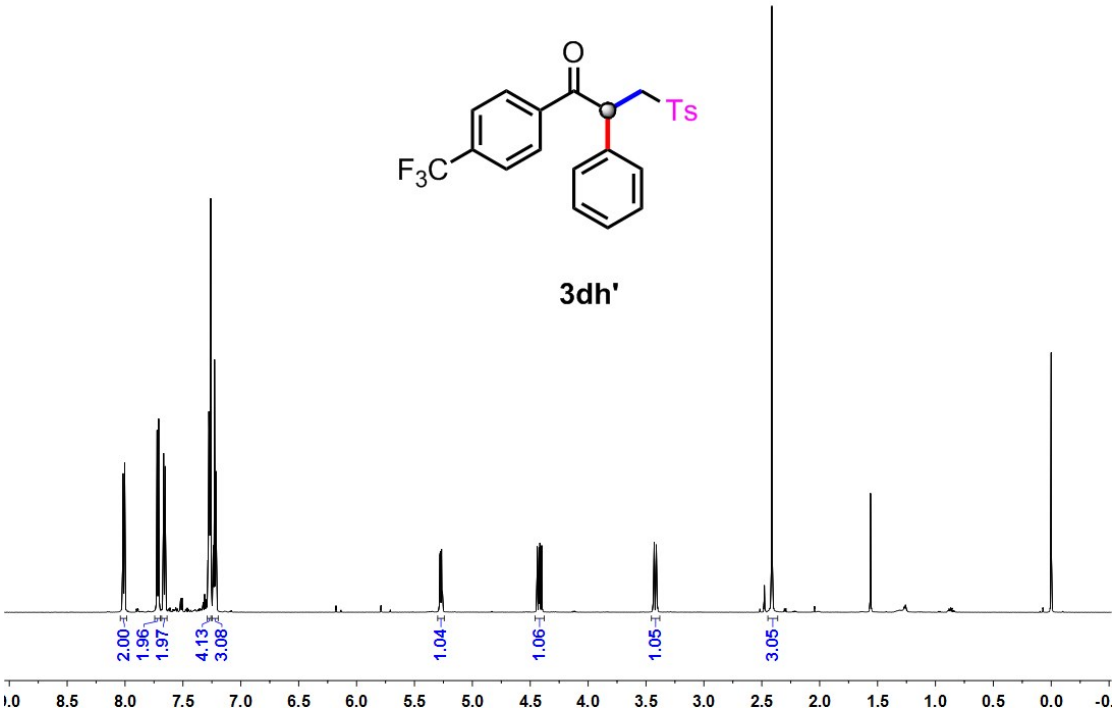
-1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Ts
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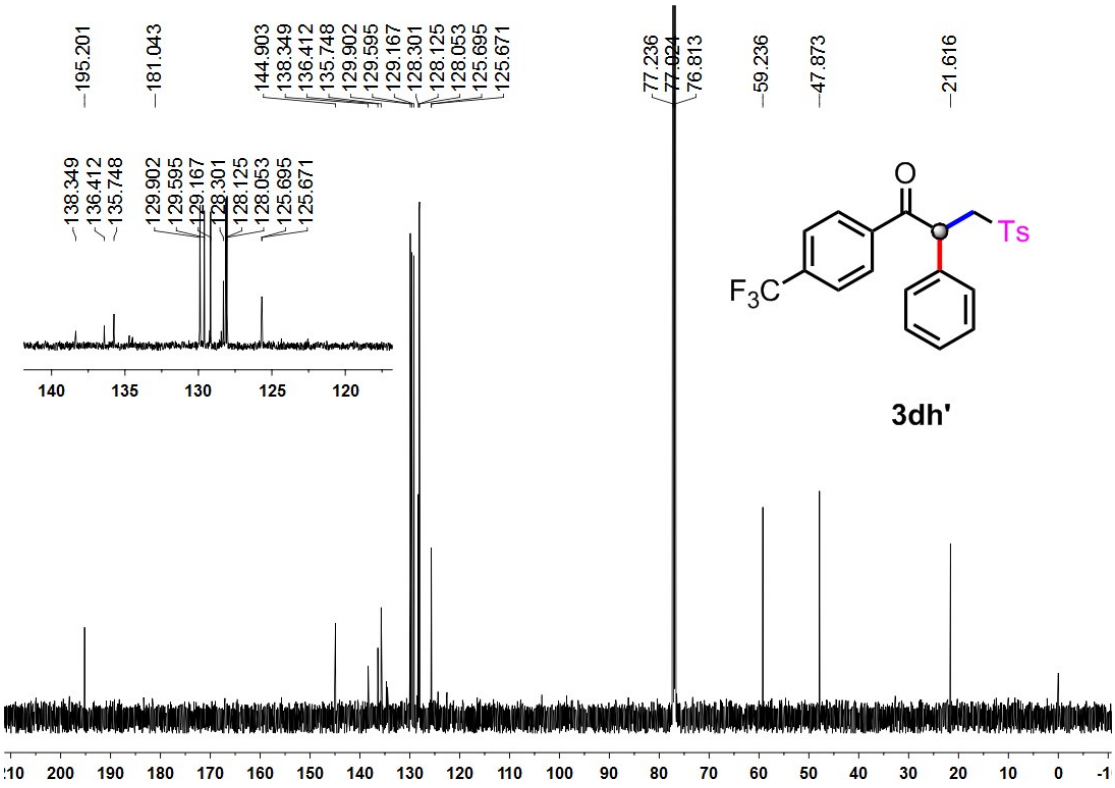
3.08
1.04
1.06
1.05
3.05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128.301
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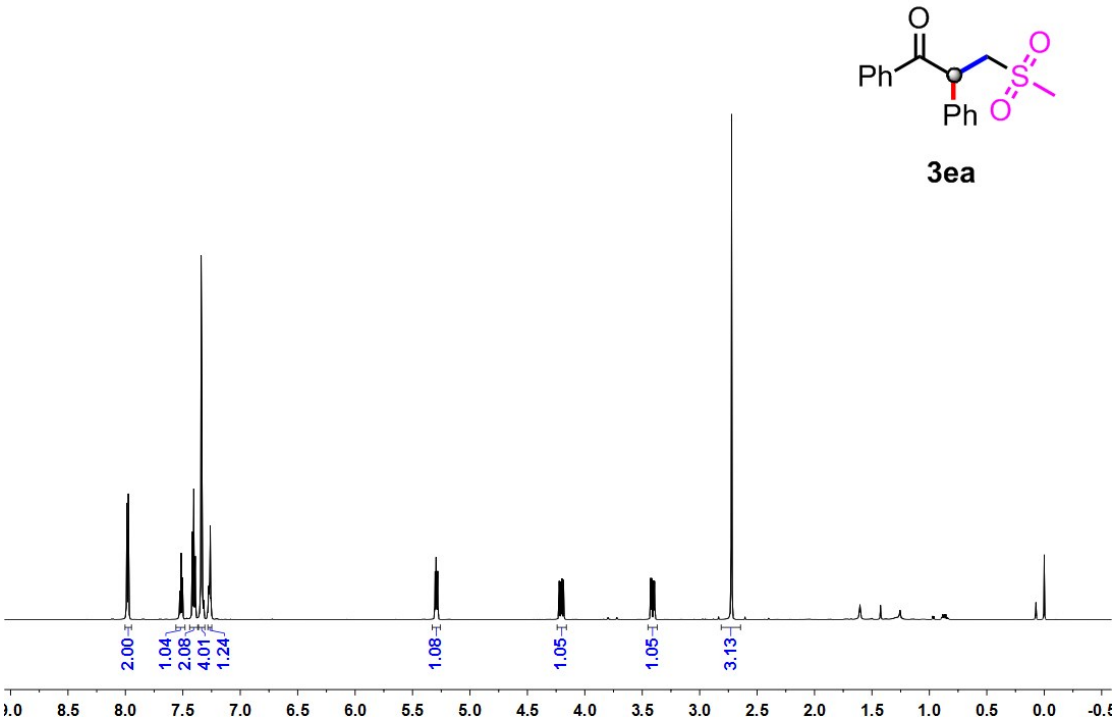
77.024
76.813
59.236
47.873
21.616
O
Ts
F3C
3dh'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1.04
2.08
4.01
1.24
1.08
1.05
1.05
3.13
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
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2.0
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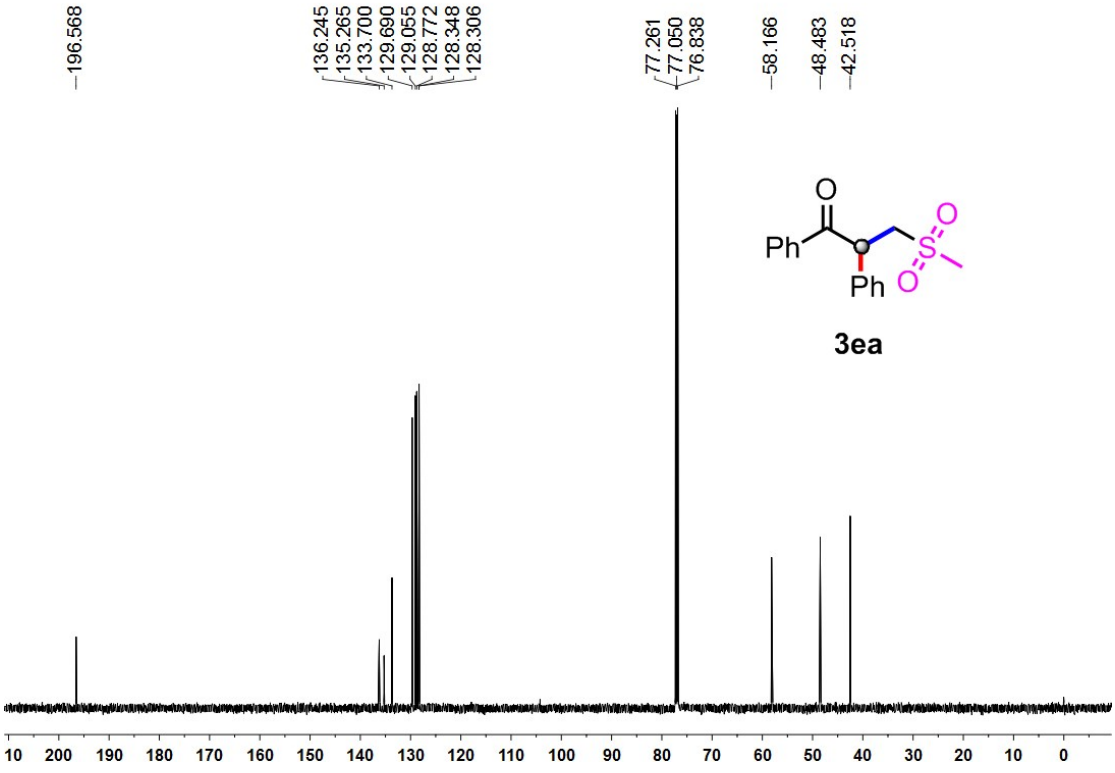
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77.261
77.050
76.838
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42.518
3ea
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50
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30
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10
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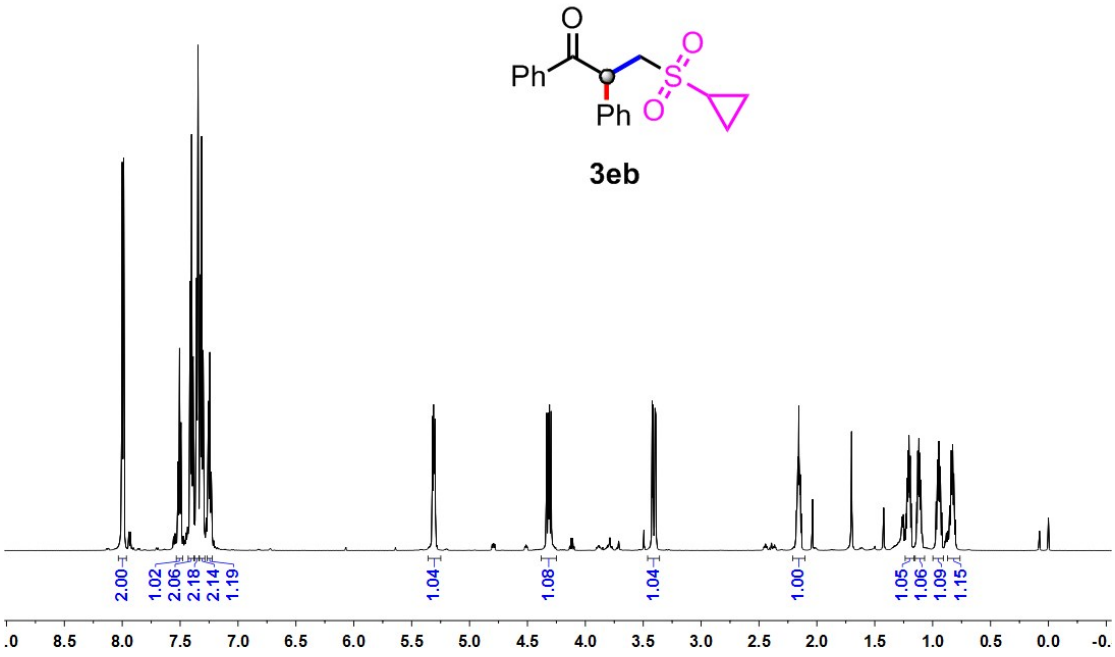
O
Ph
Ph
O=S=O
3eb
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1.02
2.06
2.18
2.14
1.19
1.04
1.08
1.04
1.00
1.05
1.06
1.09
1.15
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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1.0
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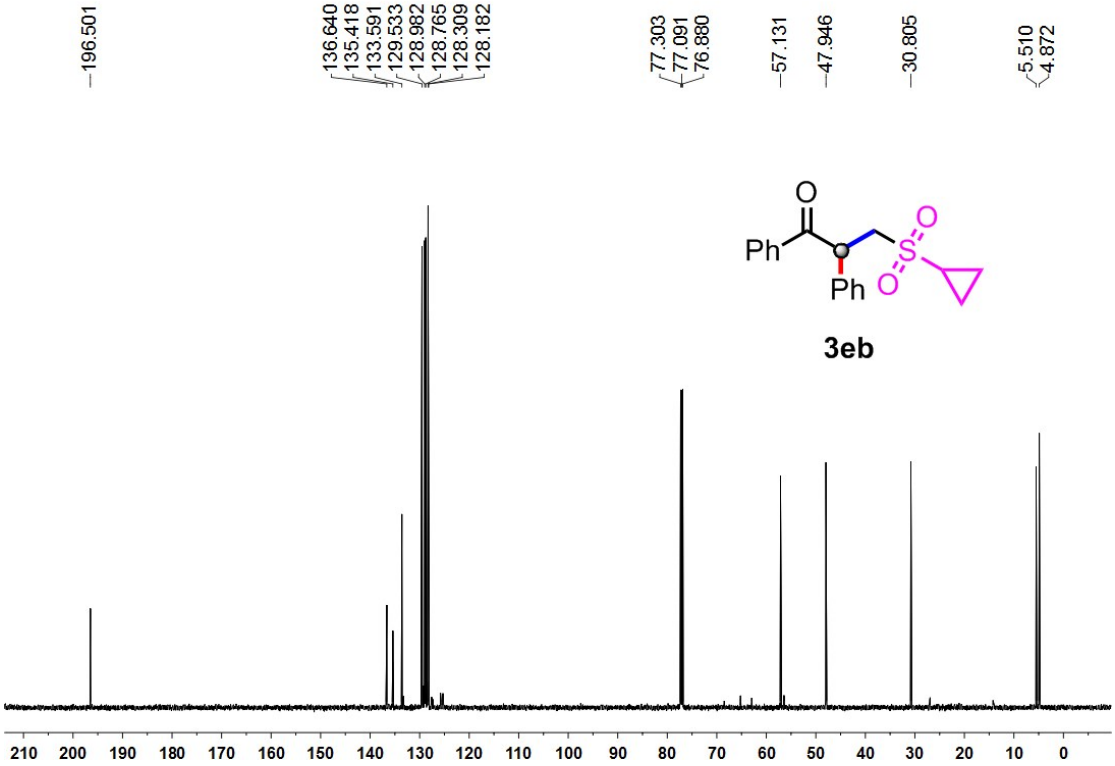
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128.309
128.182
77.303
77.091
76.880
57.131
47.946
30.805
5.510
4.872
O
Ph
Ph
O=S=O
3eb
210
200
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180
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150
140
130
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110
100
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70
60
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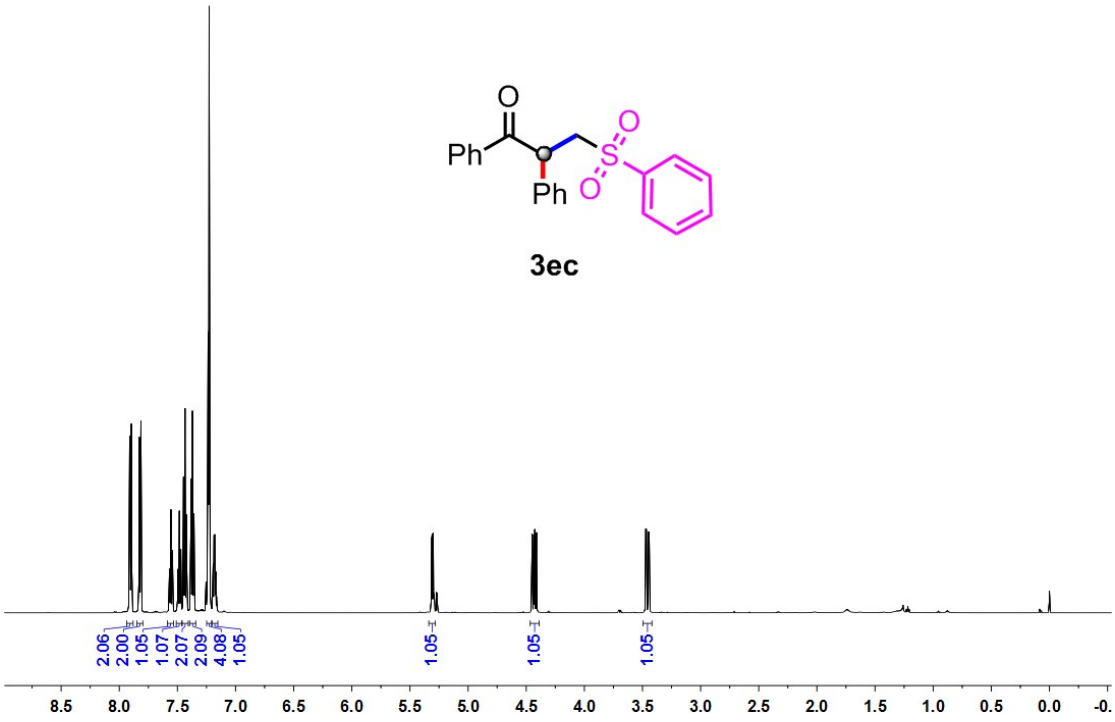
30
20
10
0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Ph
Ph
O
S
O
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2.00
1.05
1.07
2.07
2.09
4.08
1.05
1.05
1.05
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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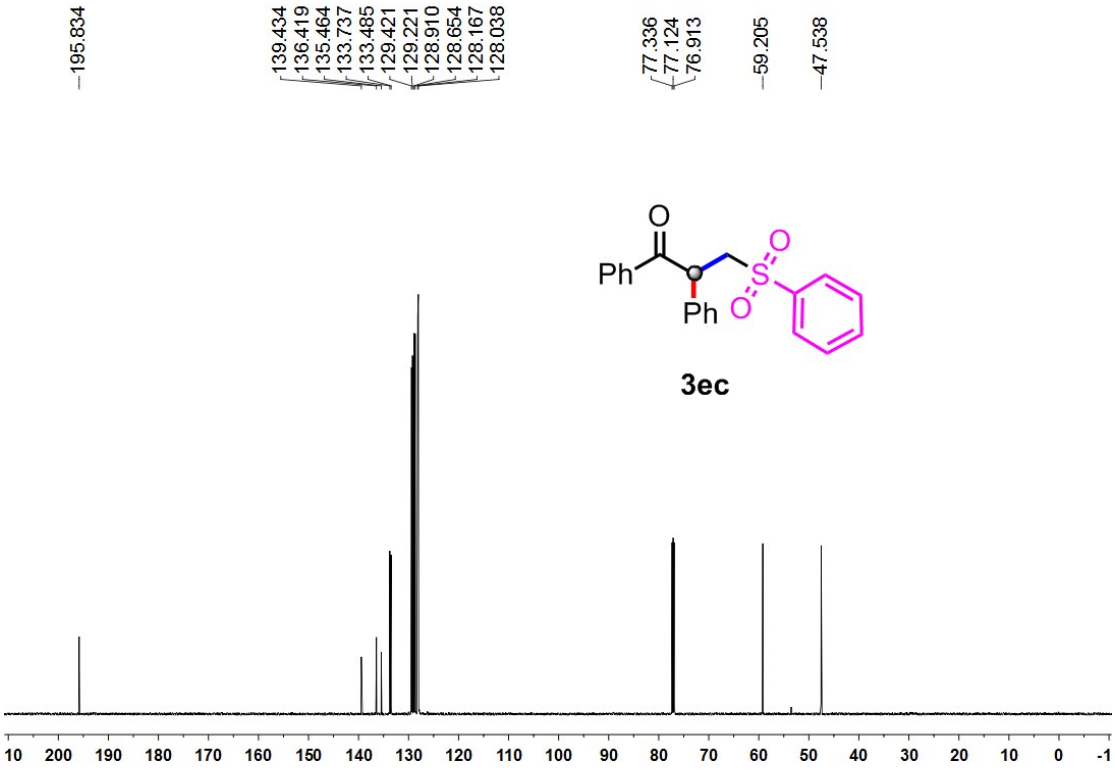
0.0
-0.

3ec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47.538
10
200
190
180
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80
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50
40
30
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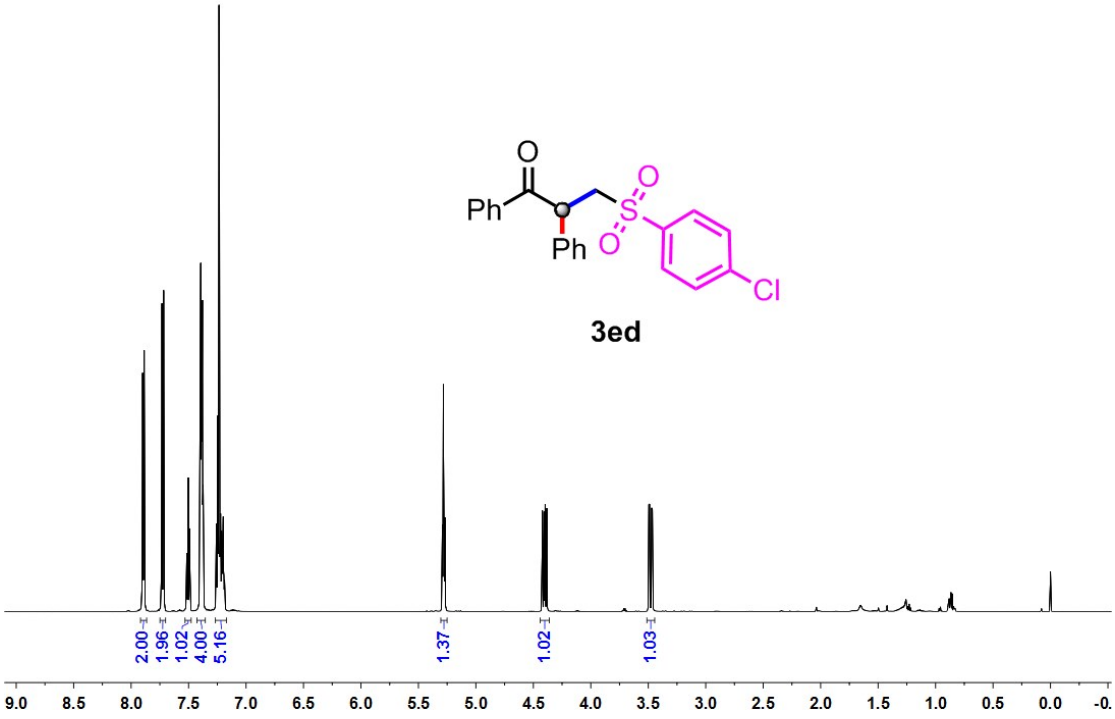
0
-1

3ec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Ph
Ph
O
O
S
Cl
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1.96
1.02
4.00
5.16
1.37
1.02
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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1.5
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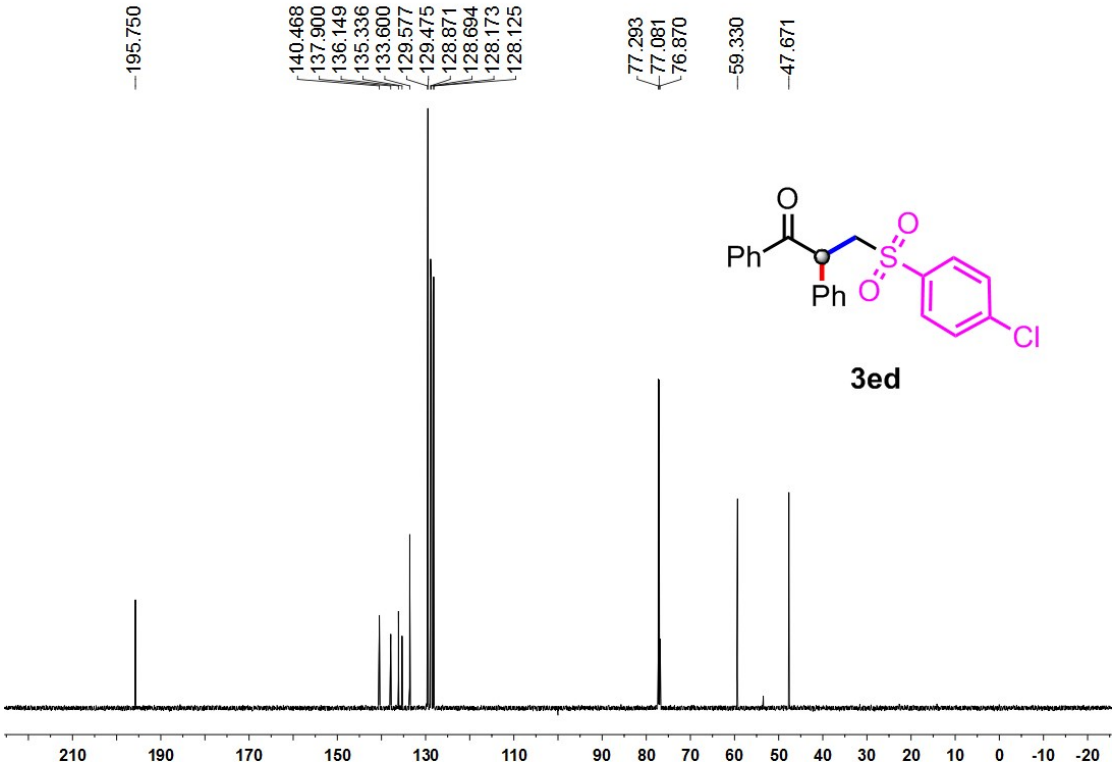
0.0

3ed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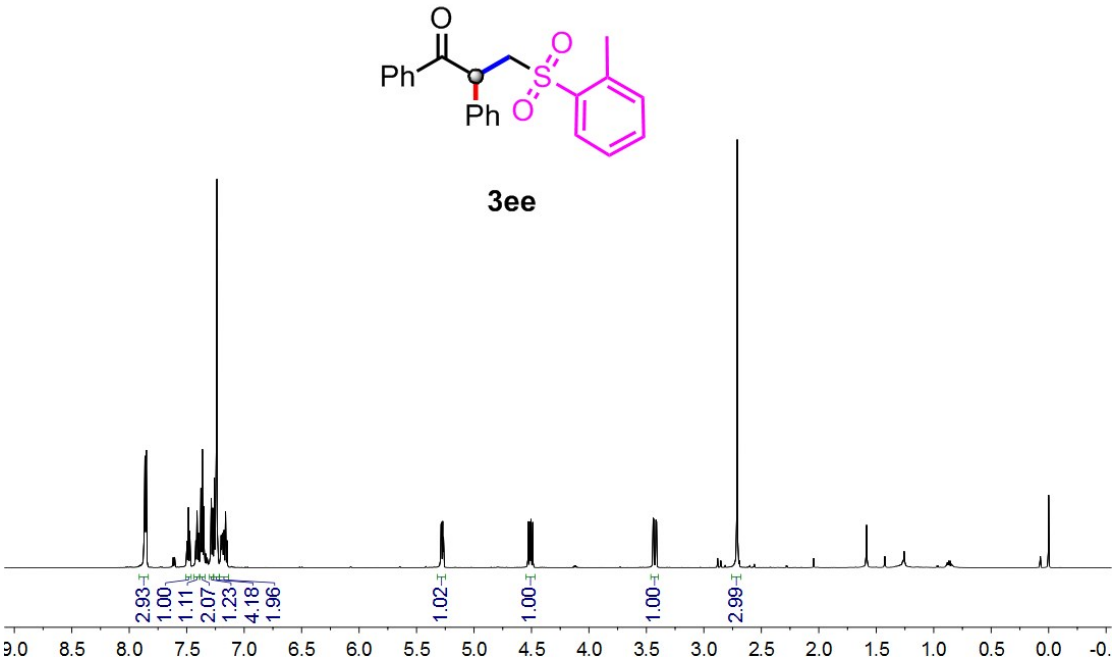
128.173
128.125
77.293
77.081
76.870
59.330
47.671
O
Ph
Ph
O
O
S
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20

3ed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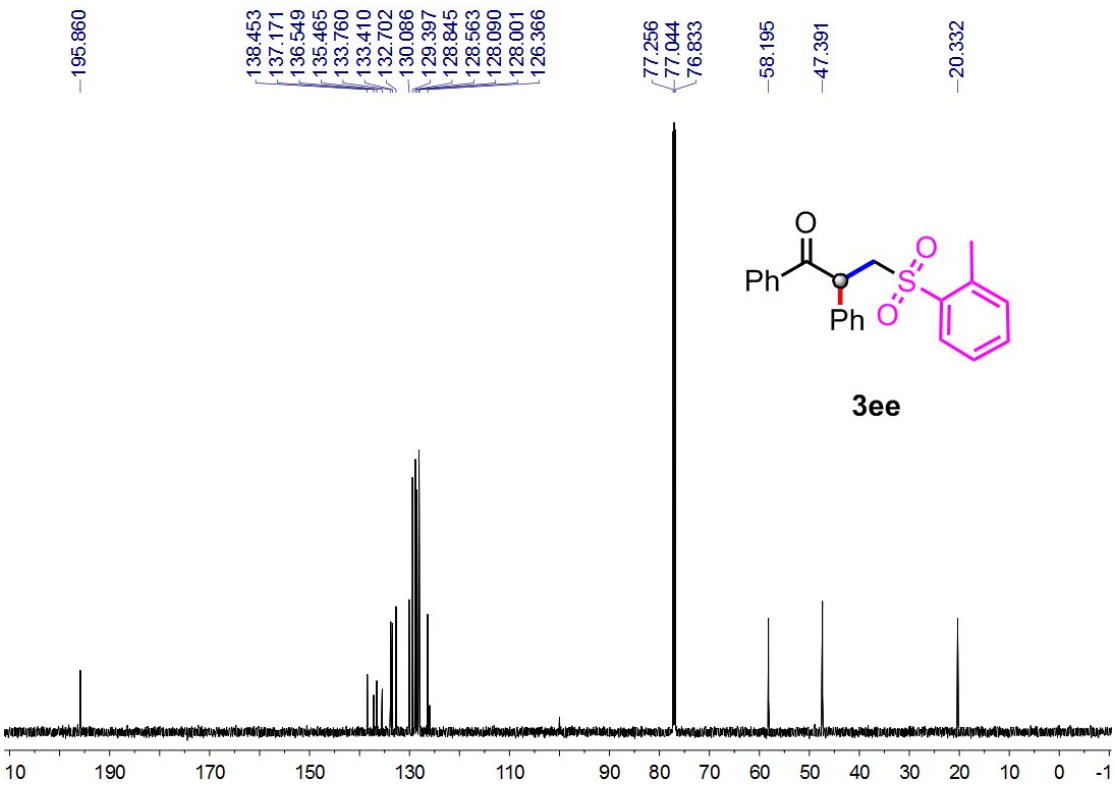
1.11
2.07
1.23
4.18
1.96
1.02
1.00
1.00
2.99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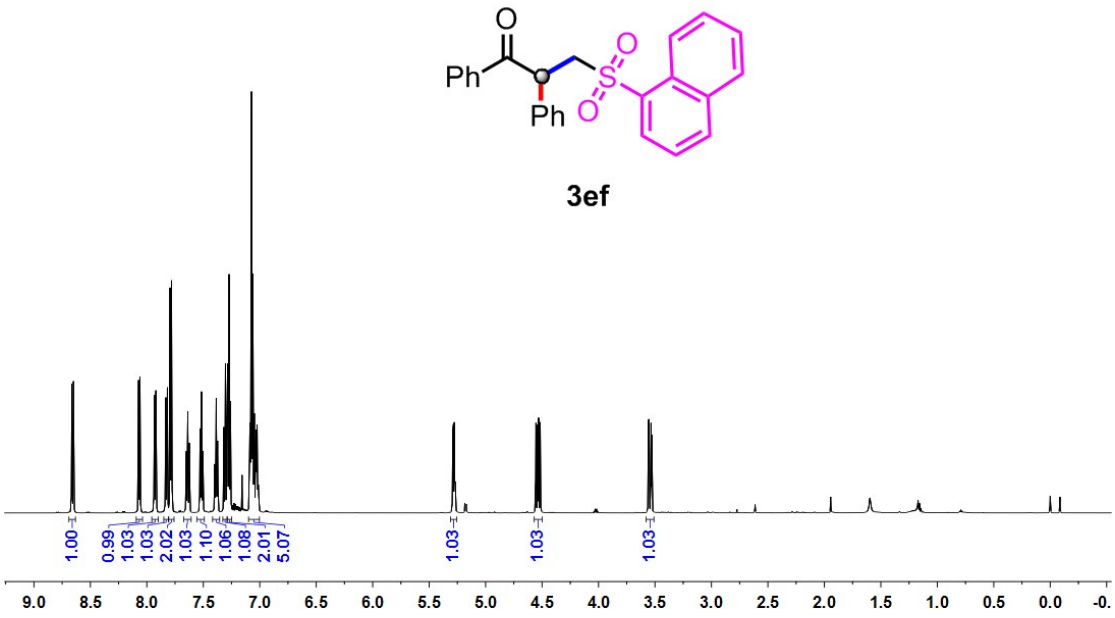
138.453
137.171
136.549
135.465
133.760
133.410
132.702
130.086
129.397
128.845
128.563
128.090
128.001
126.366
77.256
77.044
76.833
58.195
47.391
20.332
3ee


Ph
O
Ph
O
S
O
1.00
0.99
1.03
1.03
2.02
1.03
1.10
1.06
1.08
2.01
5.07
1.03
1.03
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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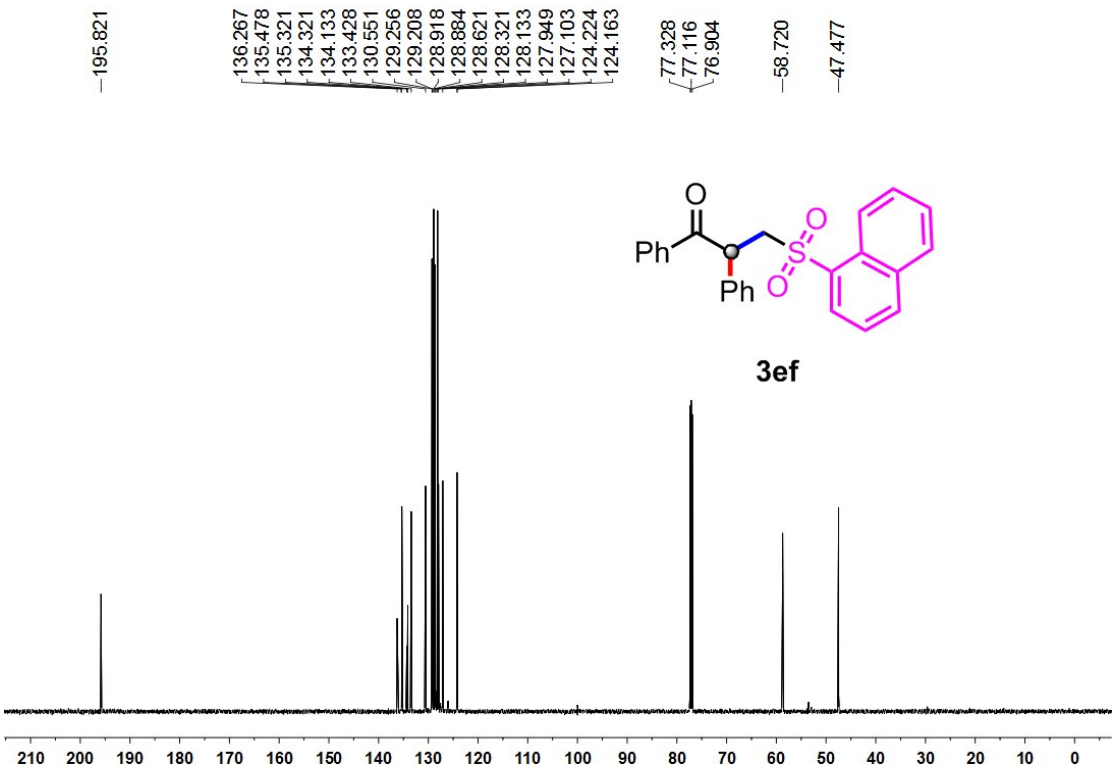
0.0
-0.

3ef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135.478
135.321
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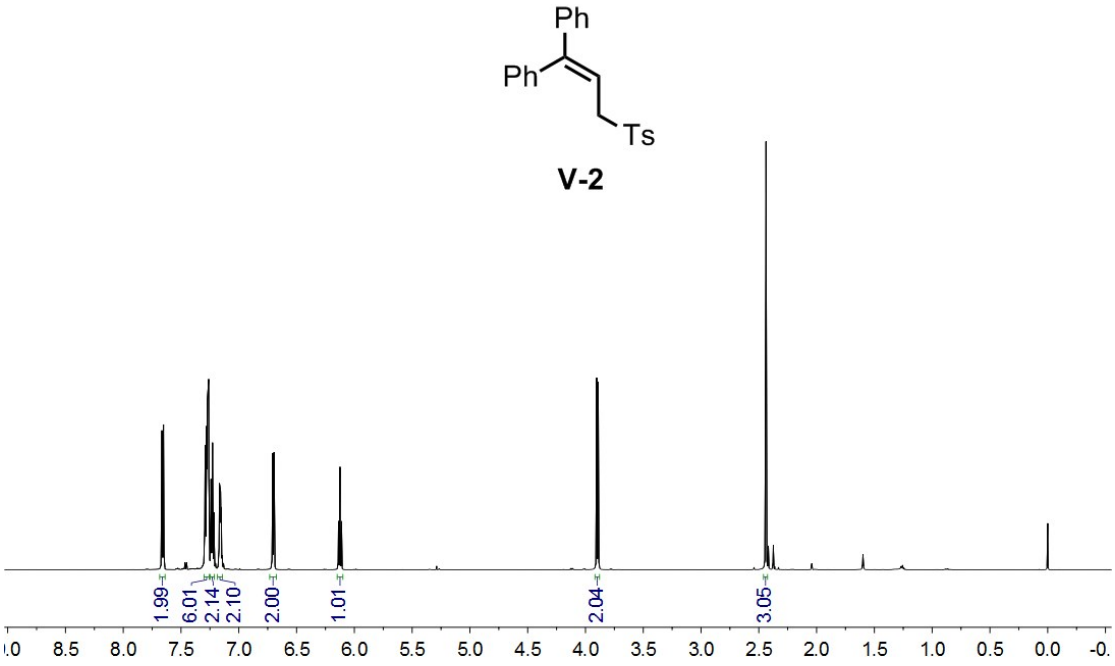
128.918
128.884
128.621
128.321
128.133
127.949
127.103
124.224
124.163
77.328
77.116
76.904
58.720
47.477
Ph
O
Ph
O
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3ef


Ph
Ph
Ts
V-2
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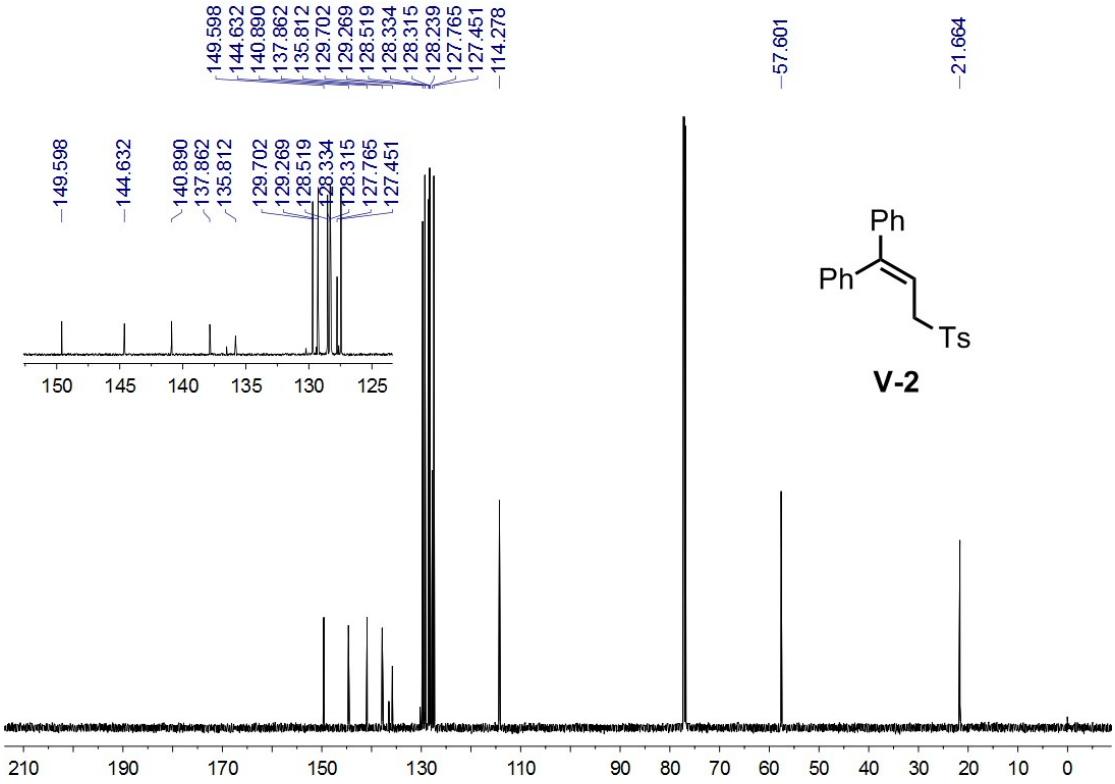
6.01
2.14
2.10
2.00
1.01
2.04
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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144.632
140.890
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135.812
129.702
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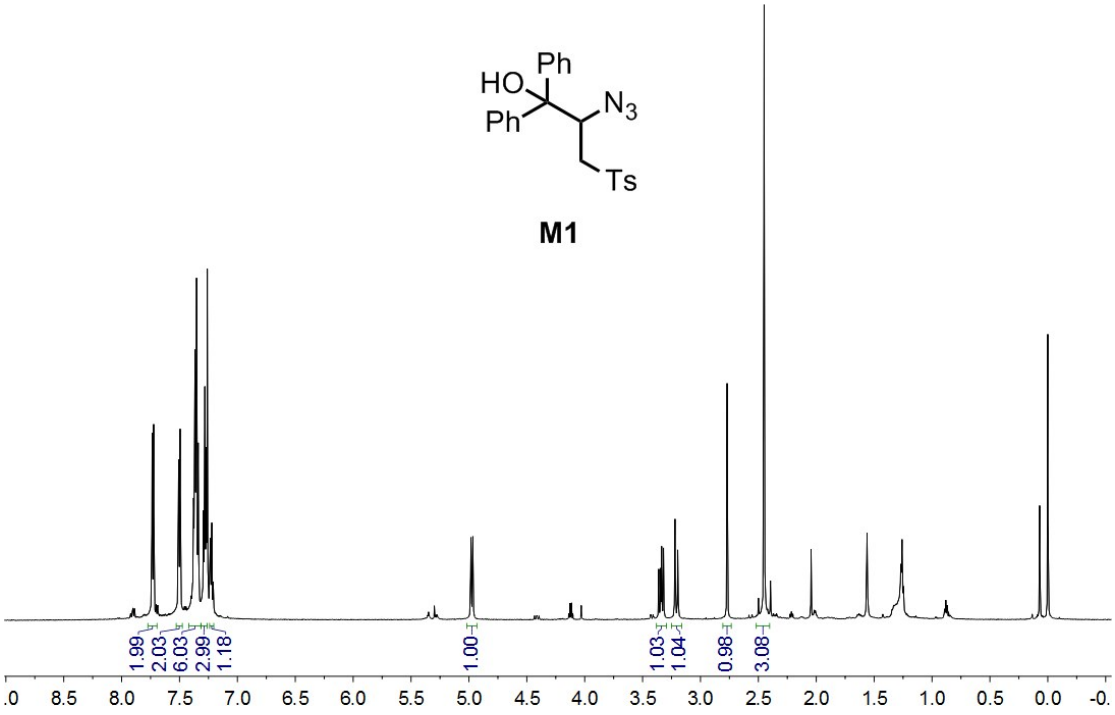
128.519
128.334
128.315
128.239
127.765
127.451
114.278
57.601
21.664
Ph
Ph
Ts
V-2
150 145 140 135 130 125
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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HO
N3
Ph
Ts
M1
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2.03
6.03
2.99
1.18
1.00
1.03
1.04
0.98
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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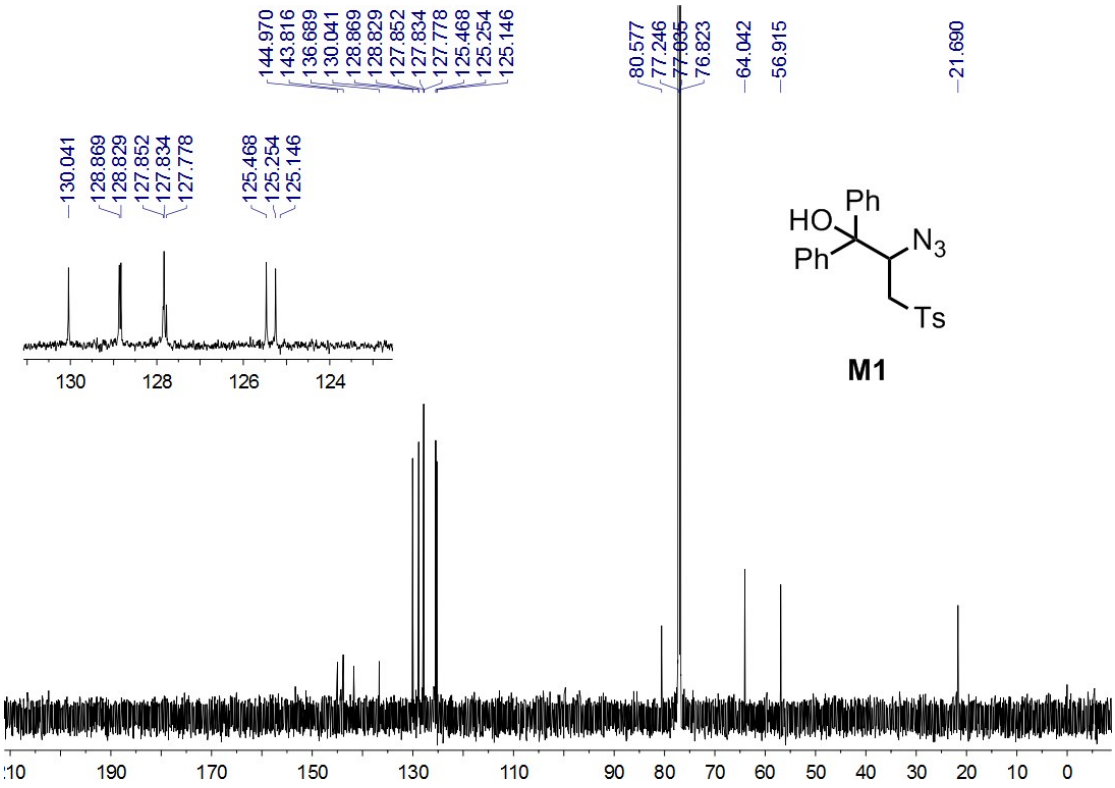
0.0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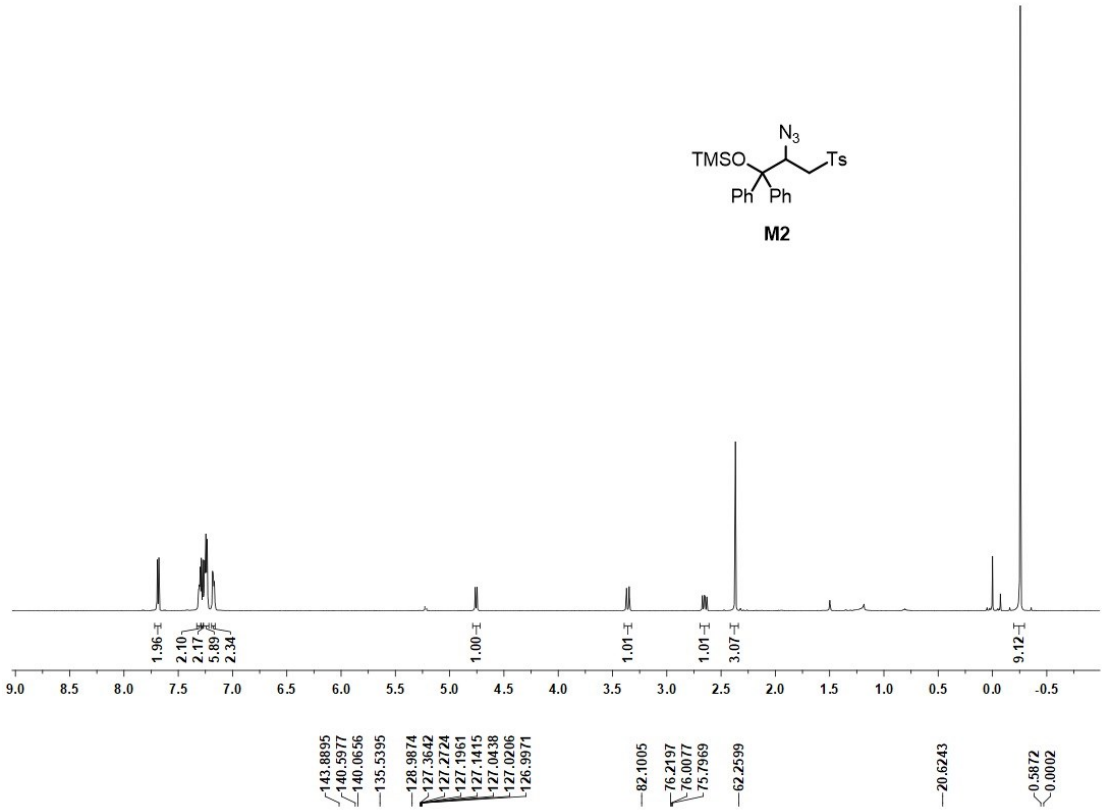
143.816
136.689
130.041
128.869
128.829
127.852
127.834
127.778
125.468
125.254
125.146
80.577
77.246
77.035
76.823
64.042
56.915
21.690
130.041
128.869
128.829
127.852
127.834
127.778
125.468
125.254
125.146
130
128
126
124
Ph
HO
N3
Ph
Ts
M1
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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TMSO
Ts
Ph
Ph
M2
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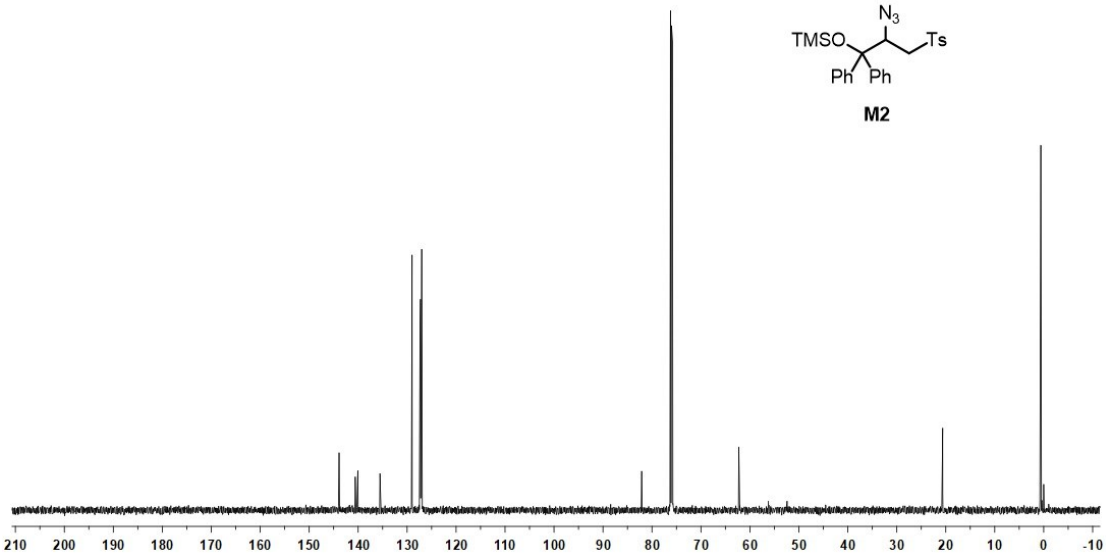
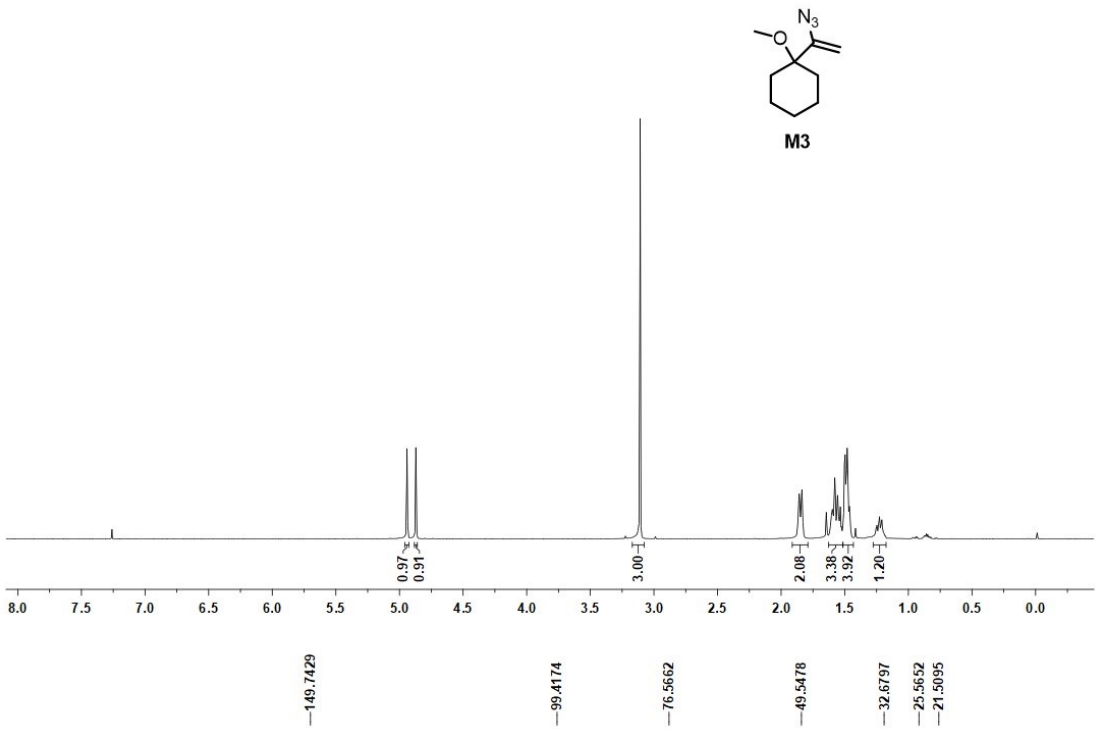
2.10
2.17
5.89
2.34
1.00
1.01
1.01
3.07
9.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
143.8895
140.5977
140.0656
135.5395
128.9874
127.3642
127.2724
127.1961
127.1415
127.0438
127.0206
126.9971
82.1005
76.2197
76.0077
75.7969
62.2599
20.6243
0.5872
0.0002


N3
TMSO
Ts
Ph
Ph
M2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


N3
O
M3
0.97
0.91
3.00
2.08
3.38
3.92
1.20
8.0
7.5
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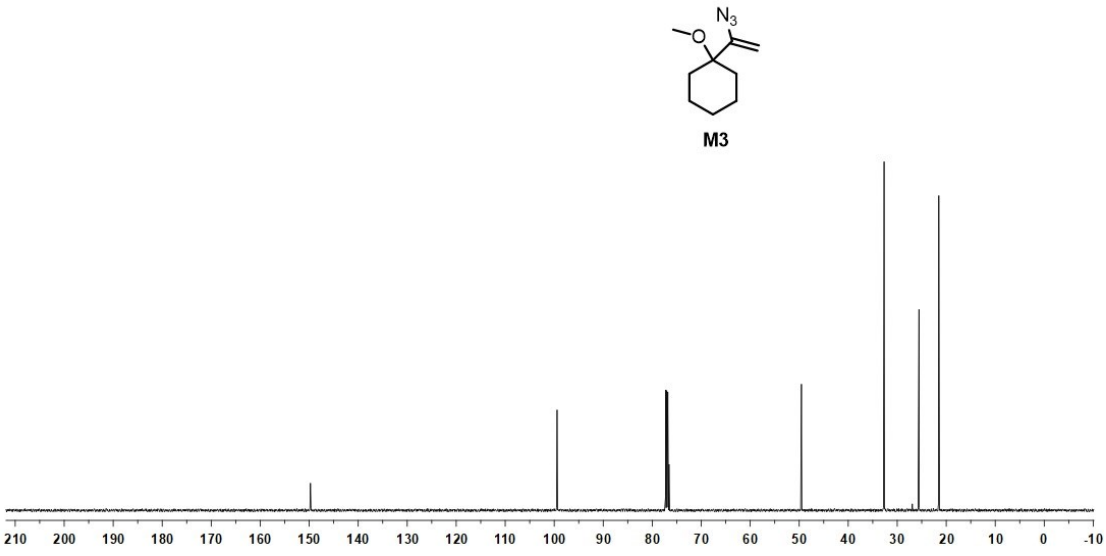
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


149.7429
99.4174
76.5662
49.5478
32.6797
25.5652
21.5095
N3
O
M3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

7. References

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