Supporting Information

Multifunctional Catalysis: Stereoselective Construction of α-Methylidene-γ-Lactams *via* Amidation/Rauhut-Currier Sequence

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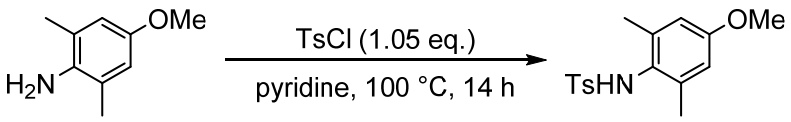
Contents

1. General information

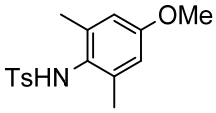
^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR or Bruker AVANCE II (^{1}H-NMR 400 or 600 MHz, ^{13}C-NMR 100 or 150 MHz. ^{1}H-NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of $CHCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C-NMR spectra reported in ppm relative to the central line of triplet for $CDCl_3$ at 77 ppm. ESI-MS spectra were obtained with JMS-T100LC (JEOL). Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector). FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). Column chromatography on SiO_2 was performed with Kanto Silica Gel 60 (40-100 μm). Commercially available organic and inorganic compounds were used without further purification.

2. Procedure for the preparation of 7l.



6l **7l** Quant.

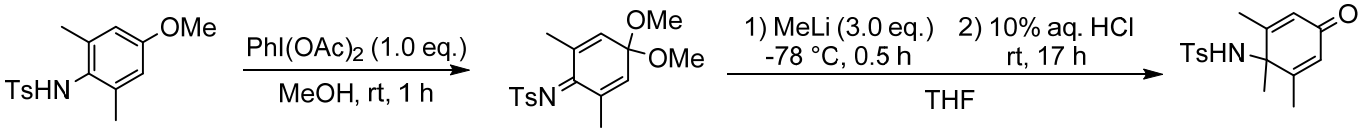
A solution of **6l** (8.67 mmol) and TsCl (9.10 mmol) in pyridine (29 mL) was heated to 100 °C. After 14 h, the solution was cooled to room temperature followed by evaporation in *vacuo*. The crude mixture was dissolved with EtOAc (40 mL) and washed with 10% aq. HCl (30 mL). The separated organic layer was dried over Na_2SO_4, evaporated in *vacuo,* giving pure product **7l** as white solid quantitatively.



7l

7l; Quant.; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.54 (s, 2H), 5.80 (s, 1H), 3.76 (s, 3H), 2.42 (s, 3H), 1.99 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.4, 143.5, 139.3, 137.7, 129.6, 127.2, 125.3, 113.7, 55.2, 21.6, 19.0; HRMS (ESI) calcd for $C_{16}H_{19}NO_3SNa$ m/z = 328.0978, found m/z = 328.0977 [$(M+Na)^+$]; IR (KBr): ν 3283, 2361, 1517, 1327, 543 cm^{-1}.

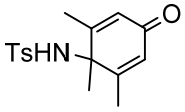
3. Procedure for the preparation of 2l.



7l **8l** Not isolated **2l** 17% from **7l**

To a solution of **7l** (3.08 mmol) in MeOH (15 mL) was added $PhI(OAc)_2$ (3.08 mmol) at 0 °C and stirred at room temperature. After 1 h, saturated $NaHCO_3$ aq. was added to the reaction solution to quench. EtOAc (50 mL) was added to the reaction mixture and washed with brine (30 mL). The organic layer was separated and dried over Na_2SO_4. Evaporation of solvent followed by dried in *vacuo* gave **8l** as crude product. This crude product was dissolved in THF (10 mL) and reacted with MeLi (1.13M ether solution, 8.2 mL) at -78 °C. After 0.5 h, 10% aq. HCl (10 mL) was added to reaction mixture, and then it

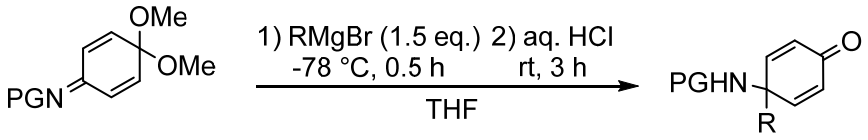
warmed to room temperature and stirred for 17 h. The reaction mixture was dissolved with EtOAc (30 mL) and the organic phase was washed with saturated $NaHCO_3$ aq. The separated organic layer was dried over Na_2SO_4, evaporated, dried in *vacuo* affording crude product which was purified by silica gel column chromatography. Pure **2l** was obtained as yellow solid in 17% overall yield from **7l**.



2l

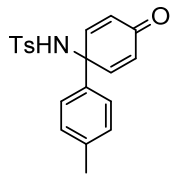
2l; 17% yield; Yellow solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.04 (s, 2H), 5.09 (s, 1H), 2.43 (s, 3H), 1.79 (s, 6H), 1.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.0, 159.3, 144.0, 137.0, 129.4, 128.3, 127.7, 59.2, 26.3, 21.6, 18.6; HRMS (ESI) calcd for $C_{16}H_{19}NO_3SNa$ m/z = 328.0978 , found m/z = 328.0980 [$(M+Na)^+$]; IR (KBr): ν 3087, 2867, 1670, 1607, 1455, 1330, 988, 633 cm^{-1}.

4. General procedure for the preparation of dienones 2.



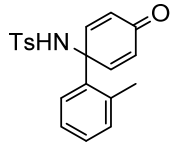
8 **2**

A solution of **8** (5.0 mmol) in THF (10 mL) was added to a solution of the corresponding Grignard reagents (7.5 mmol) in THF (7.5 mL) at -78 °C. After 0.5 h, the reaction mixture was acidified by aq. HCl, then, increased to room temperature. After 3 h, the organic layer was extracted with EtOAc and dried in *vacuo*. The resulting crude product was purified by silica gel column chromatography, followed by recrystallization to provide dienones **2** as a solid. Starting material **8a** (PG = Ts), **8b** (PG = Ms), known dienones **2a**, and **2g** were synthesized according to the following literatures.[1-4]



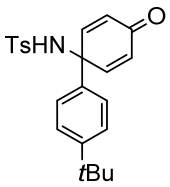
2b

2b; 63% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 10.1 Hz, 2H), 6.05 (d, *J* = 10.1 Hz, 2H), 5.27 (s, 1H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.0, 148.9, 144.2, 139.3, 137.4, 134.7, 130.1, 129.6, 127.8, 127.7, 125.6, 59.6, 21.6, 21.0; HRMS (ESI) calcd for $C_{20}H_{19}NO_3SNa$ m/z = 376.0978; found m/z = 376.0969 [$(M+Na)^+$]; IR (KBr): ν 3092, 2893, 1661, 1616, 1338, 1163, 962 cm^{-1}.



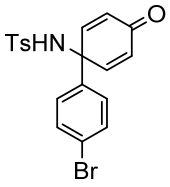
2c

2c; 73% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.31 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.19-7.27 (m, 4H), 7.11-7.15 (t, *J* = 8.0 Hz, 1H), 6.98 (dt, *J* = 11.0, 2.5 Hz, 2H), 6.07 (dt, *J* = 11.0, 2.5 Hz, 2H), 5.10 (s, 1H), 2.61 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.7, 147.2, 144.3, 137.5, 137.2, 135.7, 134.0, 129.7, 129.5, 128.3, 127.9, 126.9, 126.7, 60.4, 22.0, 21.7; HRMS (ESI) calcd for $C_{20}H_{19}NO_3SNa$ m/z = 376.0978; found m/z = 376.0980 [$(M+Na)^+$]; IR (KBr): ν 3115, 2875, 1662, 1616, 1334, 753 cm^{-1}.



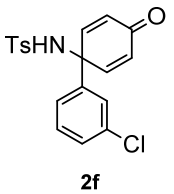
2d

2d; 51% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.34 (s, 4H), 7.25 (d, *J* = 8.2 Hz, 3H), 6.78 (d, *J* = 10.1 Hz, 2H), 6.05 (d, *J* = 10.1 Hz, 2H), 5.44 (s, 1H), 2.42 (s, 3H), 1.28 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.9, 152.5, 148.9, 144.2, 137.4, 134.5, 129.6, 127.8, 127.7, 126.4, 125.5, 59.5, 34.6, 31.1, 21.6 HRMS (ESI) calcd for $C_{23}H_{25}NO_3SNa$ m/z = 418.1447; found m/z = 418.1440 [$(M+Na)^+$]; IR (KBr): ν 3095, 2953, 1664, 1618, 1340, 722 cm^{-1}.



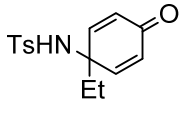
2e

2e; 45% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.24-7.30 (m, 4H), 6.76 (d, *J* = 10.5 Hz, 2H), 6.05 (d, *J* = 10.5 Hz, 2H), 5.82 (s, 1H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.6, 147.9, 144.4, 137.1, 136.8, 132.4, 129.7, 128.0, 127.8, 127.6, 123.3, 59.4, 21.6; HRMS (ESI) calcd for $C_{19}H_{16}BrNO_3SNa$ m/z = 439.9926; found m/z = 439.9921 [$(M+Na)^+$]; IR (KBr): ν 3107, 2899, 1662, 1617, 1335, 712 cm^{-1}.



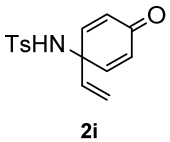
2f

2f; 40% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 1.8 Hz, 1H), 7.25-7.34 (m, 5H), 6.77 (d, *J* = 10.1 Hz, 2H), 6.09 (d, *J* = 10.1 Hz, 2H), 5.41 (s, 1H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.5, 147.7, 144.5, 139.7, 137.2, 135.4, 130.6, 129.7, 129.4, 128.3, 127.8, 126.2, 124.0, 59.4, 21.6; HRMS (ESI) calcd for $C_{19}H_{16}ClNO_3SNa$ m/z = 396.0432; found m/z = 396.0432 [$(M+Na)^+$]; IR (KBr): ν 3094, 2881, 1656, 1619, 1336, 1155, 857 cm^{-1}.



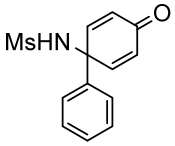
2h

2h; 43% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 10.1 Hz, 2H), 6.09 (d, *J* = 10.1 Hz, 1H), 5.25 (s, 1H) , 2.42 (s, 3H), 1.76 (q, *J* = 7.6 Hz, 2H), 0.79 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.0, 149.2, 144.2, 137.4, 129.6, 127.8, 58.1, 33.4, 21.6, 7.5; HRMS (ESI) calcd for $C_{15}H_{17}NO_3SNa$ m/z = 314.0821; found m/z = 314.0811 [$(M+Na)^+$]; IR (KBr): ν 3133, 2971, 2775, 1661, 1615, 1320, 1181, 869 cm^{-1}.



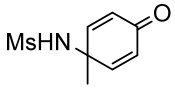
2i

2i; 13% yield; White solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 10.8 Hz, 2H), 6.06 (d, *J* = 10.8 Hz, 2H), 5.89 (s, 1H), 5.62 (dd, *J* = 17.2, 10.3 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.9, 147.8, 144.3, 137.2, 135.1, 129.6, 128.2, 127.7, 117.7, 58.4, 21.5 HRMS (ESI) calcd for $C_{15}H_{15}NO_3SNa$ m/z = 312.0665; found m/z = 312.0659 [$(M+Na)^+$]; IR (KBr): ν 3088, 2878, 1661, 1616, 1334, 1160, 998, 555 cm^{-1}.



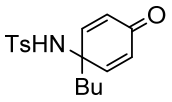
2j

2j; 31% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47-7.52 (m, 2H), 7.33-7.41 (m, 3H), 7.08-7.12 (m, 2H), 6.32-6.36 (m, 2H), 5.75 (s, 1H), 3.02 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.8, 148.9, 137.5, 129.4, 129.2, 128.2, 125.8, 59.8, 43.0; HRMS (ESI) calcd for $C_{13}H_{13}NO_3SNa$ m/z = 286.0508; found m/z = 286.0510 [$(M+Na)^+$]; IR (KBr): ν 3153, 2881, 1661, 1613, 1336, 1161, 980, 756 cm^{-1}.



2k

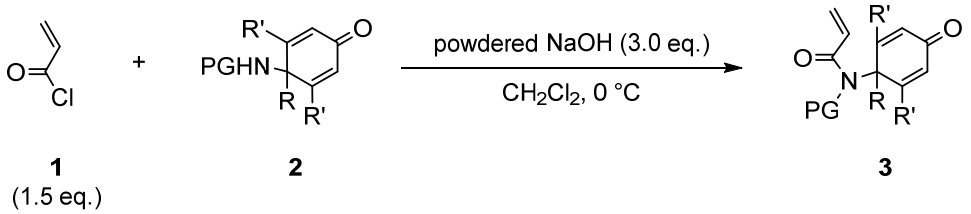
2k; 57% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 10.4 Hz, 2H), 6.29 (d, *J* = 10.4 Hz, 2H), 5.30 (s, 1H), 3.00 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.5, 150.5, 128.6, 54.6, 43.0, 27.4; HRMS (ESI) calcd for $C_8H_{11}NO_3SNa$ m/z = 224.0352; found m/z = 224.0348 [$(M+Na)^+$]; IR (KBr): ν 3293, 2986, 1712, 1671, 1631, 1139, 594 cm^{-1}.



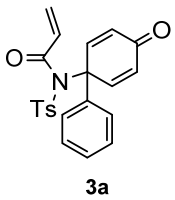
2m

2m; 12% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 10.1 Hz, 2H), 6.05 (d, *J* = 10.1 Hz, 2H), 5.68 (s, 1H), 2.41 (s, 3H), 1.70-1.66 (m, 2H), 1.24-1.10 (m, 4H), 0.80 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.2, 149.7, 144.1, 137.4, 129.6, 129.2, 127.7, 57.6, 40.1, 25.1, 22.4, 21.6, 13.7; HRMS (ESI) calcd for $C_{17}H_{21}NO_3SNa$ m/z = 342.1134; found m/z = 342.1128 [$(M+Na)^+$]; IR (KBr): ν 3117, 2934, 1659, 1614, 1343, 1161, 873 cm^{-1}.

5. General procedure for the preparation of acrylamide 3.

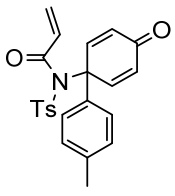


A round bottom flask was charged with a dichloromethane solution of dienone **2** (10 mL, 1.0 mmol) and powdered NaOH (3.0 mmol). Then, acrolylchloride (1.5 mmol) was added to the reaction vesicle at 0 °C. The reaction mixture was stirred vigorously 1 h at 0 °C. The reaction was then quenched with water, extracted with dichloromethane, and dried over Na_2SO_4. The combined solvent was removed in *vacuo* and the obtained crude product was quickly purified by silica gel column chromatography using hexane/ethyl acetate as an eluent to give the desired product **3** as a yellow oil or white solid. (**3** is not so stable in silica gel)



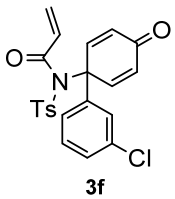
3a

3a; 63% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61-7.64 (m, 2H), 7.24-7.33 (m, 9H), 6.94 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.21 (dd, *J* = 16.9, 1.1 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 2H), 5.78 (dd, *J* = 10.1, 1.1 Hz, 1H), 2.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.7, 169.4, 147.9, 145.7, 138.9, 134.7, 133.2, 130.9, 129.8, 129.4, 128.6, 128.5, 127.6, 125.0, 65.6, 21.7; HRMS (ESI) calcd for $C_{22}H_{19}NO_4SNa$ m/z = 416.0927; found m/z = 416.0927 [$(M+Na)^+$]; IR (KBr): ν 3030, 2368, 1702, 1670, 1397, 1349, 1191, 1176, 989, 751, 661 cm^{-1}.



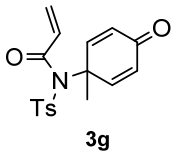
3b

3b; 12% yield; Pale yellow oil; ^{1}H-NMR (400 MHz $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.31-7.26 (m, 4H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.92 (dd, *J* = 17.4, 10.1 Hz, 1H), 6.23 (dd, *J* = 17.4, 0.9 Hz, 1H), 6.02 (d, *J* = 10.1 Hz, 2H), 5.78 (dd, *J* = 10.1, 0.9 Hz, 1H), 2.44 (s, 3H), 2.28 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.8, 169.5, 148.1, 145.6, 138.6, 136.4, 135.5, 133.3, 130.8, 130.1, 129.7, 128.5, 127.4, 124.9, 65.4, 21.7, 21.0; HRMS (ESI) calcd for $C_{23}H_{21}NO_4SNa$ m/z = 430.1083; found m/z = 430.1082 [$(M+Na)^+$]; IR (KBr): ν 3033, 2921, 1703, 1666, 1496, 1355, 1177, 984 cm^{-1}.

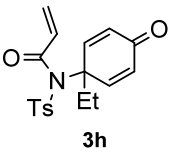


3f

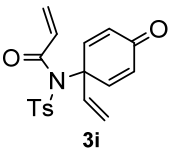
3f; 4% yield; Pale yellow oil; ^{1}H-NMR (400 MHz $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.18-7.31 (m, 8H), 6.96 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.24 (dd, *J* = 16.9, 1.1 Hz, 1H), 6.06 (d, *J* = 10.5 Hz, 2H), 5.83 (dd, *J* = 10.1, 1.1 Hz, 1H), 2.45 (s, 3H) ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.4, 169.3, 147.2, 145.9, 140.7, 136.2, 135.3, 133.0, 131.3, 130.5, 129.9, 128.8, 128.4, 128.1, 125.3, 123.1, 65.1, 21.7; HRMS (ESI) calcd for $C_{22}H_{18}ClNO_4SNa$ m/z = 450.0537; found m/z = 450.0536 [$(M+Na)^+$]; IR (KBr): ν 3035, 2925, 1705, 1660, 1354, 1179, 980 cm^{-1}.



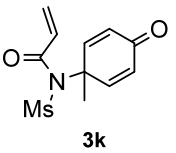
3g; 65% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.25-7.27 (m, 2H), 7.07-7.11 (m, 2H), 6.75 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.45 (dd, *J* = 16.9, 1.4 Hz, 1H), 5.92-6.00 (m, 3H), 2.41 (s, 3H), 1.54 (s, 3H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 184.2, 170.1, 150.2, 145.2, 136.4, 133.7, 131.5, 129.6, 128.1, 127.2, 60.1, 26.7, 21.5; HRMS (ESI) calcd for $C_{17}H_{17}NO_4SNa$, m/z = 354.0770; found m/z = 354.0774 [$(M+Na)^+$]; IR (KBr): ν 3044, 1672, 1345, 1182, 973, 866, 666, 592 cm^{-1}.



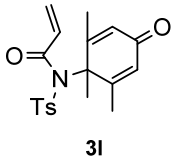
3h; 43% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 10.1 Hz, 2H), 6.81 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.49 (dd, *J* = 16.9, 0.9 Hz, 1H), 6.01 (d, *J* = 10.1 Hz, 2H), 5.96 (dd, *J* = 10.1, 0.9 Hz, 1H), 2.41 (s, 3H), 1.93 (q, *J* = 7.3 Hz, 2H), 0.74 (t, *J* = 7.3 Hz, 3H,); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.6, 170.8, 148.6, 145.4, 136.5, 134.5, 131.5, 129.6, 128.8, 128.5, 64.1, 31.0, 21.6, 8.2; HRMS (ESI) calcd for $C_{18}H_{19}NO_4SNa$ m/z = 368.0927; found m/z = 368.0912 [$(M+Na)^+$]; IR (KBr): ν 3042, 1677, 1340, 1180, 865, 656, 590 cm^{-1}.



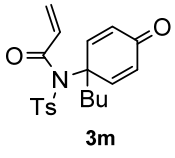
3i; 53% yield; White solid; ^{1}H-NMR (600 MHz $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 10.0 Hz, 2H), 6.84 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.42 (dd, *J* = 16.9, 1.4 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 2H), 5.89 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.69 (dd, *J* = 17.2, 10.3 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.7, 169.3, 147.0, 145.5, 136.5, 134.9, 133.3, 131.3, 129.8, 128.3, 128.0, 117.1, 64.2, 21.7; HRMS (ESI) calcd for $C_{18}H_{17}NO_4SNa$ m/z = 366.0770; found m/z = 366.0766 [$(M+Na)^+$]; IR (KBr): ν 3063, 2252, 1699, 1670, 1631, 1400, 1177, 663 cm^{-1}



3k; 12% yield; White solid; ^{1}H-NMR (400 MHz $CDCl_3$) δ 7.19 (d, *J* = 10.1 Hz, 2H), 6.44-6.46 (m, 2H), 6.26 (d, *J* = 10.1 Hz, 2H), 5.90 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.26 (s, 3H), 1.79 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.1, 169.3, 150.3, 132.5, 131.9, 128.1, 60.7, 44.5, 26.8; HRMS (ESI) calcd for $C_{11}H_{13}NO_4SNa$ m/z = 278.0457; found m/z = 278.0453 [$(M+Na)^+$]; IR (KBr): ν 3025, 2937, 1702, 1667, 1626, 1350, 1180, 862 cm^{-1}.



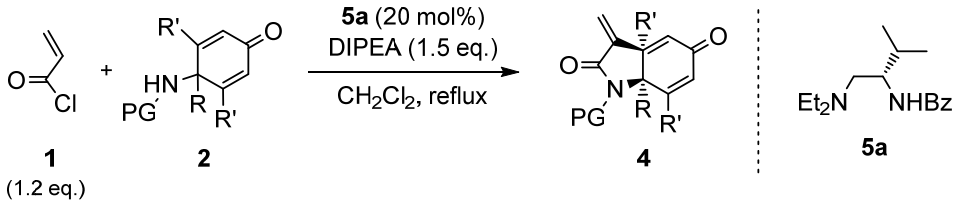
3l; 45% yield; White solid; ^{1}H-NMR (400 MHz $CDCl_3$ at 60 °C) δ 7.87 (br, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.79 (dd, *J* = 16.3, 10.3 Hz, 1H), 6.36 (d, *J* = 16.3 Hz, 1H), 6.04 (s, 2H), 5.76 (d, *J* = 10.3 Hz, 1H), 2.45 (s, 3H), 1.92 (s, 6H), 1.82 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.5, 162.1, 145.2, 137.4, 131.4, 129.8, 128.4, 126.9, 77.3, 77.0, 76.7, 27.5, 21.2, 19.7 (Some peaks are broad out or overlapped); HRMS (ESI) calcd for $C_{19}H_{21}NO_4SNa$ m/z = 382.1083; found m/z = 382.1086 [$(M+Na)^+$]; IR (KBr): ν 3092, 2991, 1666, 1623, 1353, 1190, 964, 819 cm^{-1}.



3m; 33% yield; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55-7.58 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.08 (dt, *J* = 11.0, 2.5 Hz, 2H), 6.81 (dd, *J* = 16.9, 11.0 Hz, 1H), 6.48 (dd, *J* = 16.9, 2.5 Hz, 1H), 5.94-6.01 (m, 3H), 2.41 (s, 3H), 1.83-1.87 (m, 2H), 1.06-1.20 (m, 4H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.7, 170.8, 149.0, 145.4, 136.5, 134.6, 131.4, 129.6, 128.6, 128.5, 63.6, 37.7, 25.7, 22.4, 21.6, 13.7; HRMS (ESI) calcd for $C_{20}H_{23}NO_4SNa$ m/z = 396.1240; found m/z = 396.1239 [$(M+Na)^+$]; IR (KBr): ν 3253, 3122, 2958, 1662, 1616, 1512, 1338, 1159, 814 cm^{-1}.

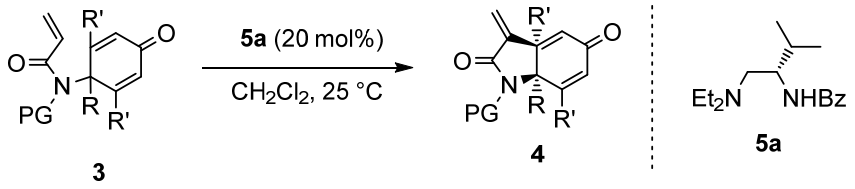
6. General procedure for the preparation of α-methylidene-γ-lactam 4.

One pot process (Method A)

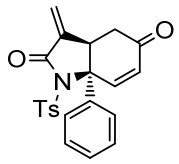


Acryloylchloride **1** (0.12 mmol) was added to a mixture of dienone **2** (0.10 mmol), DIPEA (0.15 mmol) and catalyst **5a** (0.02 mmol, 20 mol%) in dichloromethane (0.5 mL) under reflux conditions. After the full conversion of **2** as determined by TLC, crude reaction mixture was directly purified by silica gel column chromatography using hexane-ethyl acetate as an eluent to provide the corresponding product **4** as a white solid.

Stepwise process (Method B)

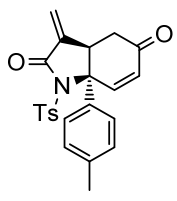


The chiral amine catalyst **5a** (0.02 mmol, 20 mol%) was added to a dichloromethane solution of acrylamide **3** (0.10 mmol, 0.5 mL) at 25 °C. After the full conversion of **3** on TLC, the reaction mixture was directly purified by silica-gel column chromatography using hexane-ethyl acetate as eluents to provide the corresponding product **4** as a white solid.



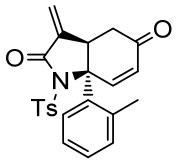
4a

4a; 92% yield for **Method A**, 95% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.51 (dd, *J* = 10.4, 1.6 Hz, 1H), 7.48-7.37 (m, 5H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.33 (d, *J* = 10.4 Hz, 1H), 6.24 (d, *J* = 3.7 Hz, 1H), 5.44 (d, *J* = 2.7 Hz, 1H), 3.45-3.37 (m, 1H), 2.74-2.54 (m, 2H), 2.45 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.6, 165.8, 145.7, 144.6, 139.4, 138.3, 135.4, 130.3, 129.3, 129.2, 128.9, 128.8, 125.8, 120.7, 69.9, 48.7, 35.0, 21.7; HRMS (ESI) calcd for $C_{22}H_{19}NO_4SNa$ m/z = 416.0927; found m/z = 416.0921 [$(M+Na)^+$]; IR (KBr): ν 3056, 2925, 2300, 1720, 1691, 1366, 1240, 1172, 1062, 909, 700 cm^{-1}; $[\alpha]_D^{24}$ = -39 (c 0.71, $CHCl_3$) for 96% ee; Enantiomeric excess: 80% for **Method A**, 96% for **Method B**, determined by HPLC (Daicel Chiralpak IC, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 225 nm) first peak (Minor): t_R = 9.5 min, second peak (Major): t_R = 14.1 min.



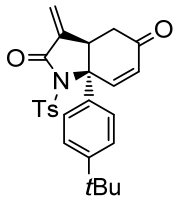
4b

4b; 50% yield for **Method A**, 85% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.50 (dd, *J* = 10.5, 1.8 Hz, 1H), 7.24-7.34 (m, 6H), 6.31 (d, *J* = 10.5 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 5.43 (d, *J* = 3.2 Hz, 1H), 3.38-3.40 (m, 1H), 2.56-2.70 (m, 2H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.6, 165.8, 145.6, 144.8, 138.8, 138.5, 136.5, 135.6, 130.1, 129.6, 129.3, 129.2, 125.7, 120.5, 77.3, 77.0, 76.7, 69.9, 48.8, 35.1, 21.7, 21.2; HRMS (ESI) calcd for $C_{23}H_{21}NO_4SNa$ m/z = 430.1083; found m/z = 430.1084 [$(M+Na)^+$]; IR (KBr): ν 2925, 2852, 1725, 1691, 1359, 660, 544 cm^{-1}; $[\alpha]_D^{24}$ = -42 (c 0.85, $CHCl_3$) for 92% ee; Enantiomeric excess: 78% for **Method A,** 92% for **Method B**, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 220 nm) first peak (Minor): t_R = 18.8 min, second peak (Major): t_R = 32.8 min.



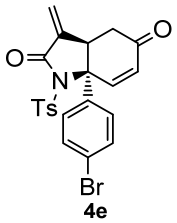
4c

4c; 81% yield for **Method A**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.61 (dd, *J* = 10.5, 1.8 Hz, 1H), 7.28-7.38 (m, 6H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.24 (d, *J* = 10.5 Hz, 1H), 5.49 (d, *J* = 3.2 Hz, 1H), 3.75 (m, 1H), 2.58-2.73 (m, 2H), 2.43 (s, 3H), 2.25 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.7, 165.4, 146.0, 145.7, 138.3, 136.2, 135.4, 135.2, 133.8, 129.4, 129.2, 129.1, 128.8, 128.0, 126.3, 121.5, 70.3, 44.2, 35.6, 21.7, 21.1; HRMS (ESI) calcd for $C_{23}H_{21}NO_4SNa$ m/z = 430.1083; found m/z = 430.1083 [$(M+Na)^+$]; IR (KBr): ν 1725, 1693, 1341, 1155, 575 cm^{-1}; $[\alpha]_D^{24}$ = -35 (c 1.0, $CHCl_3$) for 86% ee; Enantiomeric excess: 86%, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 221 nm) first peak (Minor): t_R = 12.6 min, second peak (Major): t_R = 22.3 min.



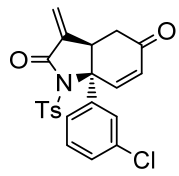
4d

4d; 61% yield for **Method A**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.52 (dd, *J* = 10.5, 1.8 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.29-7.32 (m, 4H), 6.31 (d, *J* = 10.5 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 5.42 (d, *J* = 3.2 Hz, 1H), 3.42 (t, *J* = 1.6 Hz, 1H), 2.56-2.70 (m, 2H), 2.45 (s, 3H), 1.36 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.7, 165.8, 151.8, 145.5, 144.9, 138.6, 136.3, 135.7, 130.1, 129.3, 129.1, 125.8, 125.5, 120.4, 69.8, 48.7, 35.2, 34.7, 31.3, 21.7; HRMS (ESI) calcd for $C_{26}H_{27}NO_4SNa$ m/z = 472.1553; found m/z = 472.1551 [$(M+Na)^+$]; IR (KBr): ν 1732, 1693, 1359, 1150, 580 cm^{-1}; $[\alpha]_D^{27}$ = -46 (c 4.1, $CHCl_3$) for 76% ee; Enantiomeric excess: 76%, determined by HPLC (Daicel Chiralpak IC, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 225 nm) first peak (Minor): t_R = 6.9 min, second peak (Major): t_R = 14.8 min.



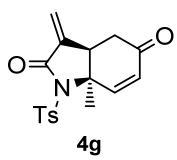
4e

4e; 87% yield for **Method A**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.32 (dd, *J* = 19.0, 8.2 Hz, 4H), 6.32-6.34 (m, 1H), 6.24 (d, J = 3.2 Hz, 1H), 5.45 (d, J = 3.2 Hz, 1H), 3.34-3.36 (m, 1H), 2.55-2.72 (m, 2H), 2.46 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.1, 165.6, 145.9, 143.8, 138.8, 138.0, 135.3, 132.2, 130.6, 129.5, 129.2, 127.5, 123.0, 121.0, 69.4, 48.6, 34.9, 21.8; HRMS (ESI) calcd for $C_{22}H_{18}BrNO_4SNa$ m/z = 494.0032; found m/z = 494.0021 [$(M+Na)^+$]; IR (KBr): ν 1732, 1693, 1359, 1150, 580 cm^{-1}; $[\alpha]_D^{27}$ = -70 (c 4.1, $CHCl_3$) for 74% ee; Enantiomeric excess: 74%, determined by HPLC (Daicel Chiralpak IC, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 225 nm) first peak (Minor): t_R = 6.9 min, second peak (Major): t_R = 12.2 min.



4f

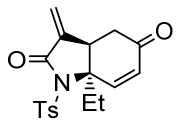
4f; 81% yield for **Method A**, 93% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.31-7.48 (m, 7H), 6.34 (dd, *J* = 10.5, 0.9 Hz, 1H), 6.26 (d, *J* = 3.0 Hz, 1H), 5.46 (d, *J* = 3.0 Hz, 1H), 3.36-3.38 (m, 1H), 2.57-2.74 (m, 2H), 2.46 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.0, 165.5, 145.9, 143.8, 141.6, 138.0, 135.3, 135.1, 130.6, 130.3, 129.5, 129.1, 126.1, 124.1, 120.9, 69.4, 48.6, 34.9, 21.7; HRMS (ESI) calcd for $C_{22}H_{18}ClNO_4SNa$ m/z = 450.0537; found m/z = 450.0537 [$(M+Na)^+$]; IR (KBr): ν 2364, 1725, 1699, 1358, 1150, 782 cm^{-1}; $[\alpha]_D^{24}$ = -33 (c 1.0, $CHCl_3$) for 94% ee; Enantiomeric excess: 79% for **Method A**, 94% for **Method B**, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 220 nm) first peak (Minor): t_R = 14.4 min, second peak (Major): t_R = 40.1 min.



4g

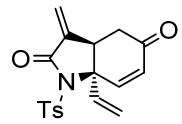
4g; 66% yield for **Method A**, 95% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J* = 8.4 Hz), 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 10.6, 1.4 Hz, 1H), 6.17 (d, *J* = 2.8 Hz, 1H), 6.02 (d, *J* = 10.6 Hz, 1H), 5.45 (d, *J* = 2.8 Hz, 1H), 3.14-3.21 (m, 1H), 2.70-2.81 (m, 2H), 2.44 (s, 3H), 1.98 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 165.3, 146.8, 145.5, 138.4, 135.9, 129.6, 128.6, 128.1, 120.8,

64.7, 45.2, 36.2, 25.1, 21.7; HRMS (ESI) calcd for $C_{17}H_{17}NO_4SNa$ m/z = 354.0770; found m/z = 354.0775 [(M+Na)$^+$]; IR (KBr): ν 2967, 1722, 1684, 1350, 1167, 805, 661, 583 cm^{-1}; $[\alpha]_D^{25}$ = -58 (c 1.1, $CHCl_3$) for 94% ee; Enantiomeric excess: 82% for **Method A**, 94% for **Method B**, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 215 nm) first peak (Major): t_R = 18.1 min, second peak (Minor): t_R = 28.1 min.



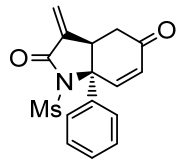
4h

4h; 71% yield for **Method A**, 90% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 10.5 Hz, 1H), 6.16 (d, *J* = 2.4 Hz, 1H), 6.12 (d, *J* = 10.5 Hz, 1H), 5.47 (d, *J* = 2.4 Hz, 1H), 3.30-3.39 (m, 1H), 2.55-2.70 (m, 2H), 2.37-2.48 (m, 4H), 2.11-2.22 (m, 1H), 1.09 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.9, 165.7, 146.5, 145.5, 139.0, 135.6, 129.5, 129.3, 128.9, 120.9, 68.2, 40.5, 37.9, 30.3, 21.7, 8.8; HRMS (ESI) calcd for $C_{18}H_{19}NO_4SNa$ m/z = 368.0927; found m/z = 368.0926 [(M+Na)$^+$]; IR (KBr): ν 2972, 2359, 1725, 1688, 1353, 1155, 665 cm^{-1}; $[\alpha]_D^{23}$ = -48 (c 2.5, $CHCl_3$) for 92% ee; Enantiomeric excess: 70% for **Method A**, 92% for **Method B**, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 221 nm) first peak (Major): t_R = 14.6 min, second peak (Minor): t_R = 18.4 min.



4i

4i; 51% yield for **Method A**, 95% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 10.7, 1.7 Hz, 1H), 6.17-6.24 (m, 3H), 5.50 (d, *J* = 10.7 Hz, 1H), 5.44 (d, *J* = 2.7 Hz, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 3.18 (m, 1H), 2.75 (m, 2H), 2.45 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.4, 165.1, 145.6, 143.6, 138.0, 136.8, 135.8, 130.4, 129.7, 128.8, 120.9, 117.3, 68.3, 44.1, 34.5, 21.7; HRMS (ESI) calcd for $C_{18}H_{17}NO_4SNa$ m/z = 366.0770; found m/z = 366.0760 [(M+Na)$^+$]; IR (KBr): ν 3003, 2357, 1735, 1690, 1515, 1362, 1173, 666 cm^{-1}; $[\alpha]_D^{22}$ = -71 (c 0.38, $CHCl_3$) for 96% ee; Enantiomeric excess: 80% for **Method A**, 96% for **Method B**, determined by HPLC (Daicel Chiralpak IA, hexane/2-propanol = 9/1; flow rate 1.0 ml/min; 25°C; 225 nm) first peak (Major): t_R = 29.4 min, second peak (Minor): t_R = 33.7 min.

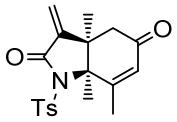


4j

4j; 93% yield for **Method A**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.47 (m, 5H), 7.26 (d, *J* = 10.4 Hz, 1H), 6.31-6.37 (m, 2H), 5.56 (d, *J* = 2.7 Hz, 1H), 3.47 (q, *J* = 2.7 Hz, 1H), 3.36 (s, 3H), 2.63-2.78 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 166.8, 143.5, 139.4, 138.1, 130.6, 129.2, 128.8, 125.1, 121.5, 69.7, 48.6, 43.1, 34.7; HRMS (ESI) calcd for $C_{16}H_{15}NO_4SNa$ m/z = 340.0614; found m/z = 340.0616 [(M+Na)$^+$]; IR (KBr): ν 2354, 1731, 1672, 1353, 1145, 750 cm^{-1}; $[\alpha]_D^{24}$ = -90 (c 1.1, $CHCl_3$) for 73% ee; Enantiomeric excess: 73%, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 216 nm) first peak (Minor): t_R = 13.6 min, second peak (Major): t_R = 20.8 min.

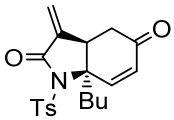
4k

4k 74% yield for **Method A**, 83% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 10.5, 1.6 Hz, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 6.01 (d, *J* = 10.5 Hz, 1H), 5.57 (d, J = 3.2 Hz, 1H), 3.39 (s, 3H), 3.26 (qd, J = 3.2, 1.6 Hz, 1H), 2.83 (d, J = 5.0 Hz, 2H), 1.93 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.1, 166.6, 145.9, 138.1, 128.4, 121.7, 64.9, 45.1, 43.1, 36.1, 25.2; HRMS (ESI) calcd for $C_{11}H_{13}NO_4SNa$ m/z = 278.0463; found m/z = 278.0449 [(M+Na)$^+$]; IR (KBr): ν 3013, 2926, 2357, 1722, 1684, 1357, 1231, 1164, 971 cm^{-1}; $[\alpha]_D^{22}$ = -130 (c 0.21, $CHCl_3$) for 90% ee; Enantiomeric excess: 63% for **Method A**, 90% for **Method B**, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 215 nm) first peak (Major): t_R = 17.9 min, second peak (Minor): t_R = 46.5 min.



4l

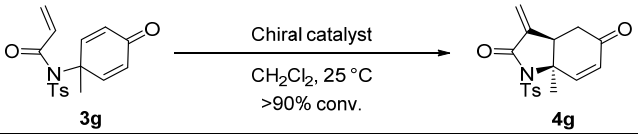
4l; 53% yield for **Method A**, 81% yield for **Method B**; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.01 (s, 1H), 5.84 (s, 1H), 5.29 (s, 1H), 2.62 (m, 2H), 2.44 (s, 3H), 2.31 (d, *J* = 1.4 Hz, 3H), 1.88 (s, 3H), 0.95 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.4, 160.1, 145.4, 144.0, 135.5, 129.5, 128.7, 127.3, 118.4, 73.2, 48.5, 41.7, 24.8, 21.7, 21.3, 17.6; HRMS (ESI) calcd for $C_{19}H_{21}NO_4SNa$ m/z = 382.1083; found m/z = 382.1080 [$(M+Na)^+$]; IR (KBr): ν 3743, 3650, 2971, 2366, 1741, 1677, 1356, 1173, 1089, 816, 663 cm^{-1}; $[\alpha]_D^{26}$ = -87 (c 0.31, $CHCl_3$) for 98% ee; Enantiomeric excess: 84% for **Method A**, 98% for **Method B**, determined by HPLC (Daicel Chiralpak AD-H, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 216 nm) first peak (Major): t_R = 10.1 min, second peak (Minor): t_R = 11.9 min.



4m

4m; 90% yield for **Method B**; Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, J = 0.9 Hz, 1H), 6.16 (d, *J* = 2.3 Hz, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 5.46 (d, *J* = 2.3 Hz, 1H), 3..40-3.33 (m, 1H), 2.72-2.55 (m, 2H), 2.44 (s, 3H), 2.41-2.29 (m, 1H), 2.21-2.02 (m, 1H), 1.49-1.22 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.9, 165.7, 146.7, 145.5, 139.1, 135.6, 129.5, 129.1, 128.9, 120.9, 67.8, 41.1, 38.0, 37.3, 26.4, 22.8, 21.7, 13.9; HRMS (ESI) calcd for $C_{20}H_{23}NO_4SNa$ m/z = 396.1240; found m/z = 396.1236 [$(M+Na)^+$]; IR (KBr): ν 2922, 2853, 2361, 1729, 1697, 1355, 1086, 802, 590 cm^{-1}; $[\alpha]_D^{25}$ = -39 (c 0.36, $CHCl_3$) for 89% ee; Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak ID, hexane/EtOH = 2/1; flow rate 1.0 ml/min; 25°C; 215 nm) first peak (Minor): t_R = 11.5 min, second peak (Major): t_R = 14.3 min.

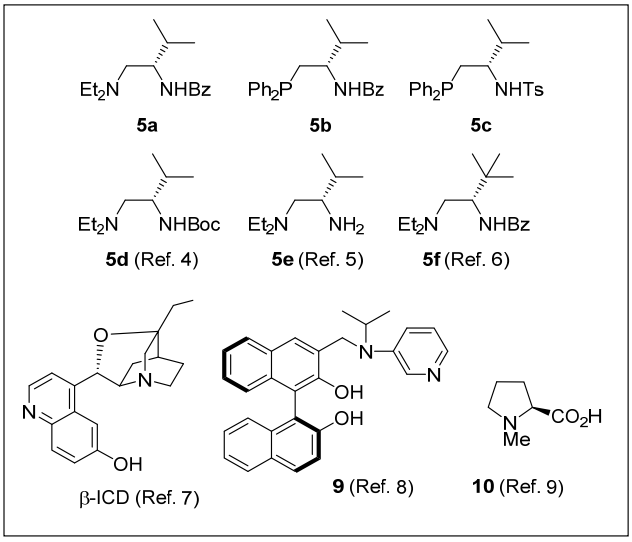
7. Screening of chiral catalysts.



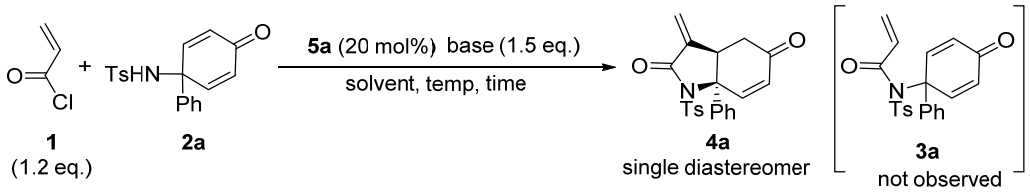
3g **4g**

entry	chiral amine	time (h)	NMR yield (%)[a]	ee (%)[b]
1	**5a**	48	97 (95)[c]	94
2	**5b**	0.1	18[d]	90
3	**5c**	0.1	12[d]	90
4	**5d**	48	87	67
5	**5e**	48	95	39
6	**5f**	48	93	90
7	β-ICD	96	87	70
8	**9**	1.5	97	7
9	**10**	96	40	15

[a] 1,3,5-Trimethoxybenzene was used as an internal standard.
[b] Determined by HPLC (Daicel Chiralpak AD-H)
[c] Isolated yield.
[d] Polymerization of **3g** mainly proceeded.



8. Further optimization of reaction conditions.

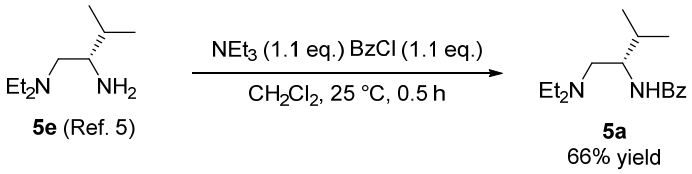


1 (1.2 eq.) **2a** **4a** single diastereomer **3a** not observed

entry	base	solvent	temp. (°C)	time (h)	NMR yield (%)[a]	ee (%)[b]
1[c]	-	CH_2Cl_2	25	17	84	85
2	proton sponge	CH_2Cl_2	25	72	51	64
3	proton sponge	$CHCl_3$	25	72	44	63
4	proton sponge	toluene	25	72	0	-
5	proton sponge	THF	25	72	0	-
6	tetramethylguanidine	CH_2Cl_2	25	48	5>	-
7	DBU	CH_2Cl_2	25	12	25	0
8	DIPEA	CH_2Cl_2	25	12	82	76
9	DIPEA	$CHCl_3$	25	12	24	83
10	DIPEA	PhCl	25	12	67	59
11	DIPEA	CH_2Cl_2	reflux	8	95 (92)[d]	80
12[e]	DIPEA	CH_2Cl_2	reflux	24	85	78
13	DIPEA	CH_2Cl_2	-20	60	72	81

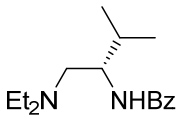
[a] 1,3,5-Trimethoxybenzene was used as an internal standard.
[b] Determined by HPLC (Daicel Chiralpak IC).
[c] 150 mol% of **5a** was used.
[d] Isolated yield.
[e] 10 mol% of **5a** was used.

9. Synthesis of amine catalyst 5a



5e (Ref. 5) **5a** 66% yield

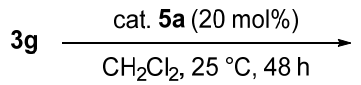
A solution of **5e** (0.32 mmol) and triethylamine (0.35 mmol) in dichloromethane (1.6 mL) was treated with benzoylchloride (0.35 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 0.5 h. The reaction was quenched with saturated $NaHCO_3$ aq. (3 mL) followed by extraction with EtOAc (3 mL). The separated organic layer was dried over Na_2SO_4 and reduced in *vacuo*. The obtained residue was purified by silica gel column chromatography using hexane, ethyl acetate, and triethylamine (10:10:1) mixed eluent, giving **5a** in 66% yield as a white solid.



5a

5a; White solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76-7.78 (m, 2H), 7.40-7.50 (m, 3H), 6.42 (d, J = 6.0 Hz, 1H), 4.03 (qd, J = 7.3, 5.0 Hz, 1H), 2.45-2.62 (m, 6H), 2.15-2.23 (m, 1H), 0.95-1.00 (m, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.6, 135.3, 131.1, 128.5, 126.8, 53.0, 52.3, 47.0, 29.8, 18.6, 17.9, 11.8; HRMS (ESI) calcd for $C_{16}H_{26}NO_4SNa$ m/z = 285.1937; found m/z = 285.1938 [$(M+Na)^+$]; IR (KBr): ν 3313, 2964, 1634, 1546, 1187, 696 cm^{-1}; $[\alpha]_D^{26}$ = +18 (c 1.0, $CHCl_3$) for >99% ee.

10. Procedure for reuse of catalyst 5a in the stereoselective RC reaction of 3g[a,b]



Cycle	1st	2nd	3rd	4th	5th
Results	95% 94% ee	95% 94% ee	95% 94% ee	95% 94% ee	95% 94% ee

[a] Reaction conditions: **3e** (0.10 mmol), cat. 5a (20 mol%) and CH_2Cl_2 (0.5 mL).

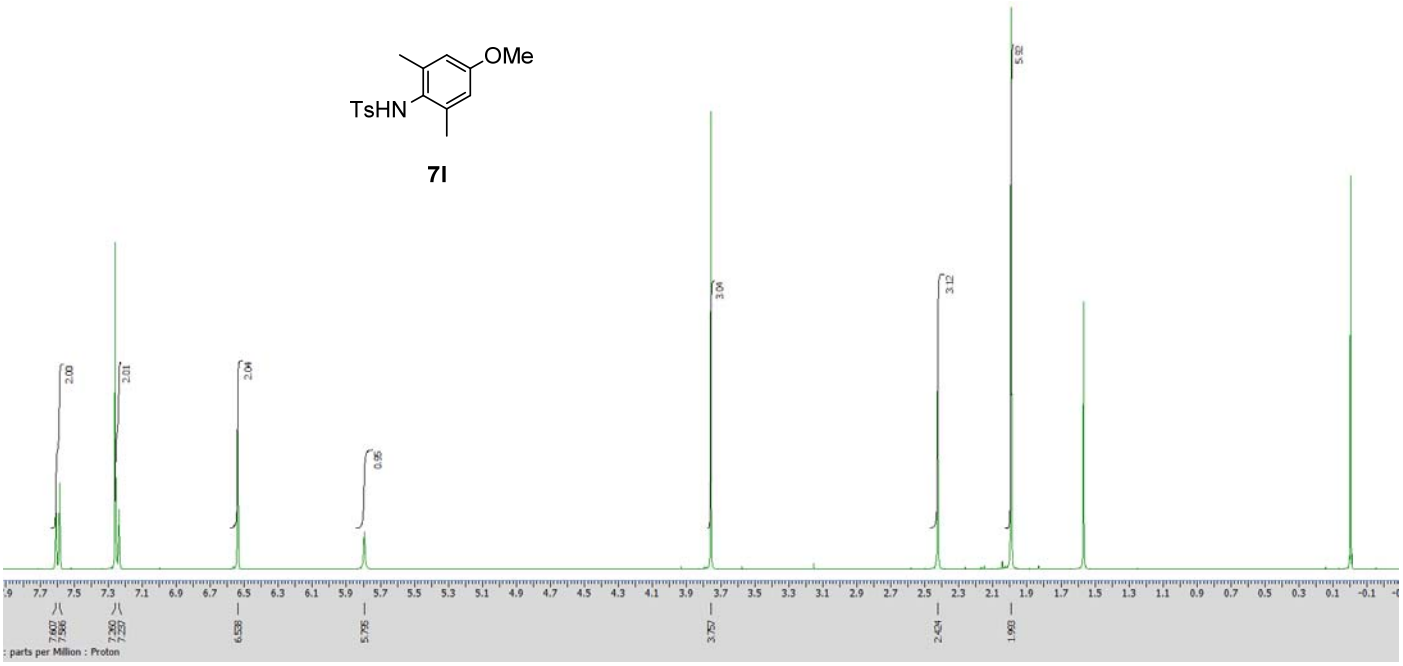
[b] Determined by HPLC (Daicel Chiralpak AD-H).

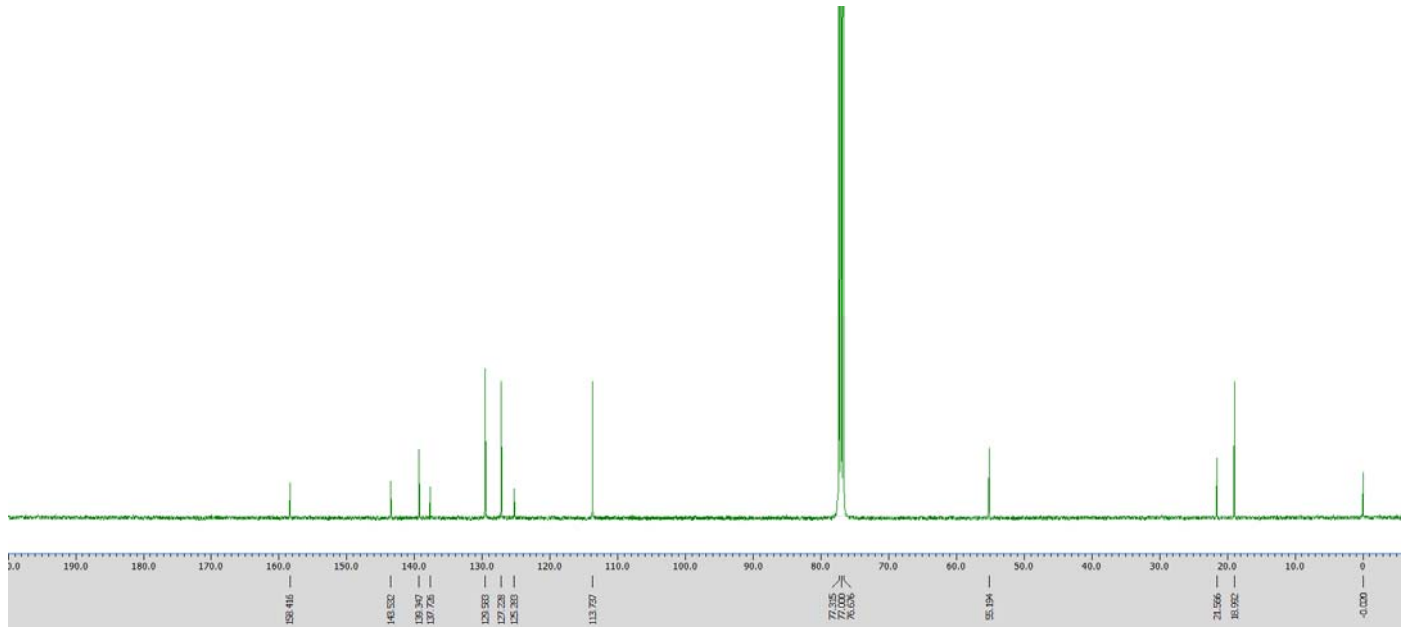
After the full conversion of **3g**, diethyl ether (1.5 mL) and saturated aq. NH_4Cl (2.0 mL) was added to the reaction mixture. Evaporation of the separated organic layer gave product **4g**. To the aqueous layer was basified with saturated aq. $NaHCO_3$ followed by extraction using $CHCl_3$-MeOH (4:1) mixed solvent (2 mL×2). Evaporation of the organic layer gave catalyst **5a**, which can be used for the next reaction without further purification.

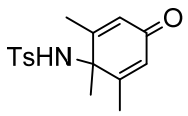
11. References

1. S. C. Banfield; M. A. Kerr, *Can. J. Chem.* **2004**, *82*, 131.
2. I. G. C. Coutts; N. J. Culbert; M. Edwards; J. A. Hadfield; D. R. Musto; V. H. Pavlidis; D. J. Richards, *J. Chem. Soc., Perkin Trans 1* **1985**, 1829.
3. R. Tello-Aburto; K. A. Kalstabakken; A. M. Harned, *Org. Biomol. Chem.* **2013**, *11*, 5596.
4. M. L. Richmond; C. T. Seto, *J. Org. Chem.* **2003**, *68*, 7505.
5. S. Hu; L. Zhang; J. Li; S. Luo; J.-P. Cheng, *Eur. J. Org. Chem.* **2011**, 3347.
6. D. Wang; C. Xu; L. Zhang; S. Luo, *Org. Lett.* **2015**, *17*, 576.
7. A. Nakano; S. Kawahara; S. Akamatsu; K. Morokuma; M. Nakatani; Y. Iwabuchi; K. Takahashi; J. Ishihara; S. Hatakeyama, *Tetrahedron*, **2006**, *62*, 381.
8. K. Matsui; S. Takizawa; H. Sasai, *J. Am. Chem. Soc*. **2005**, *127*, 3680.
9. L. Aurelio; J. S. Box; R. T. C. Brownlee; A. B. Hughes; M. M. Sleebs, *J. Org. Chem*. **2003**, *68*, 2652.

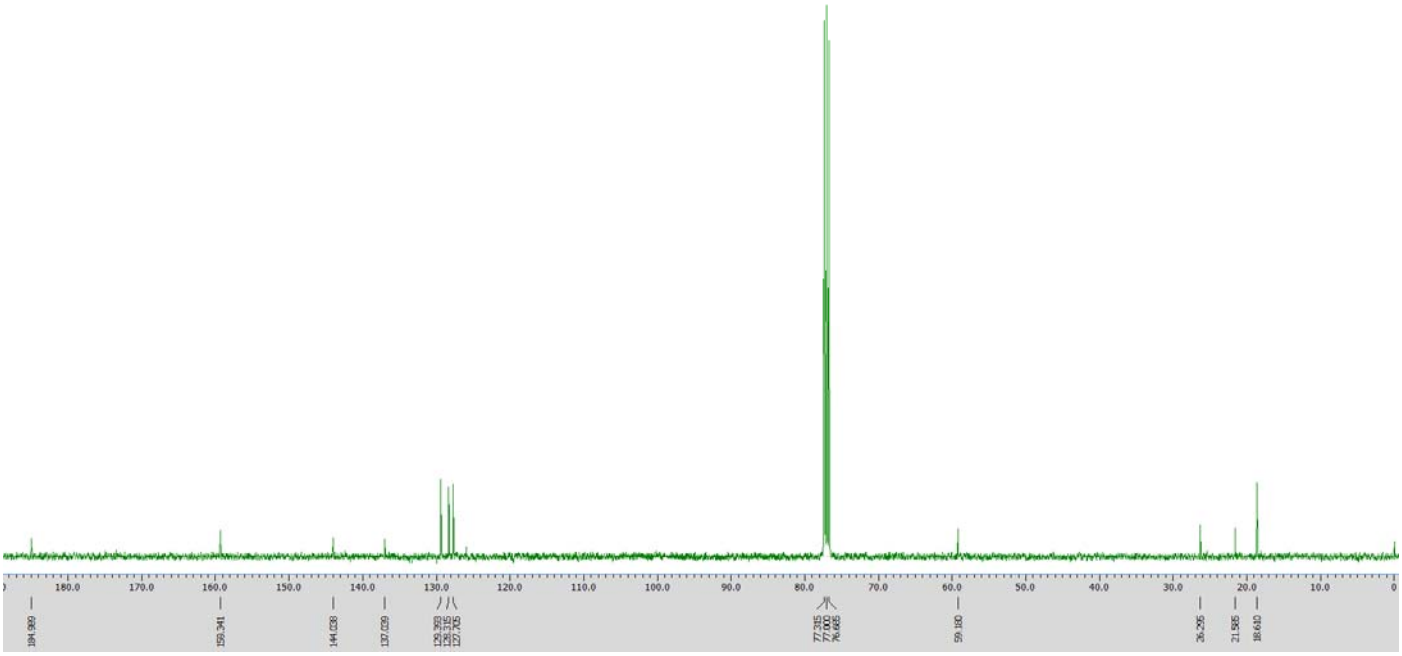
12. ^{1}H- and ^{13}C-NMR spectra

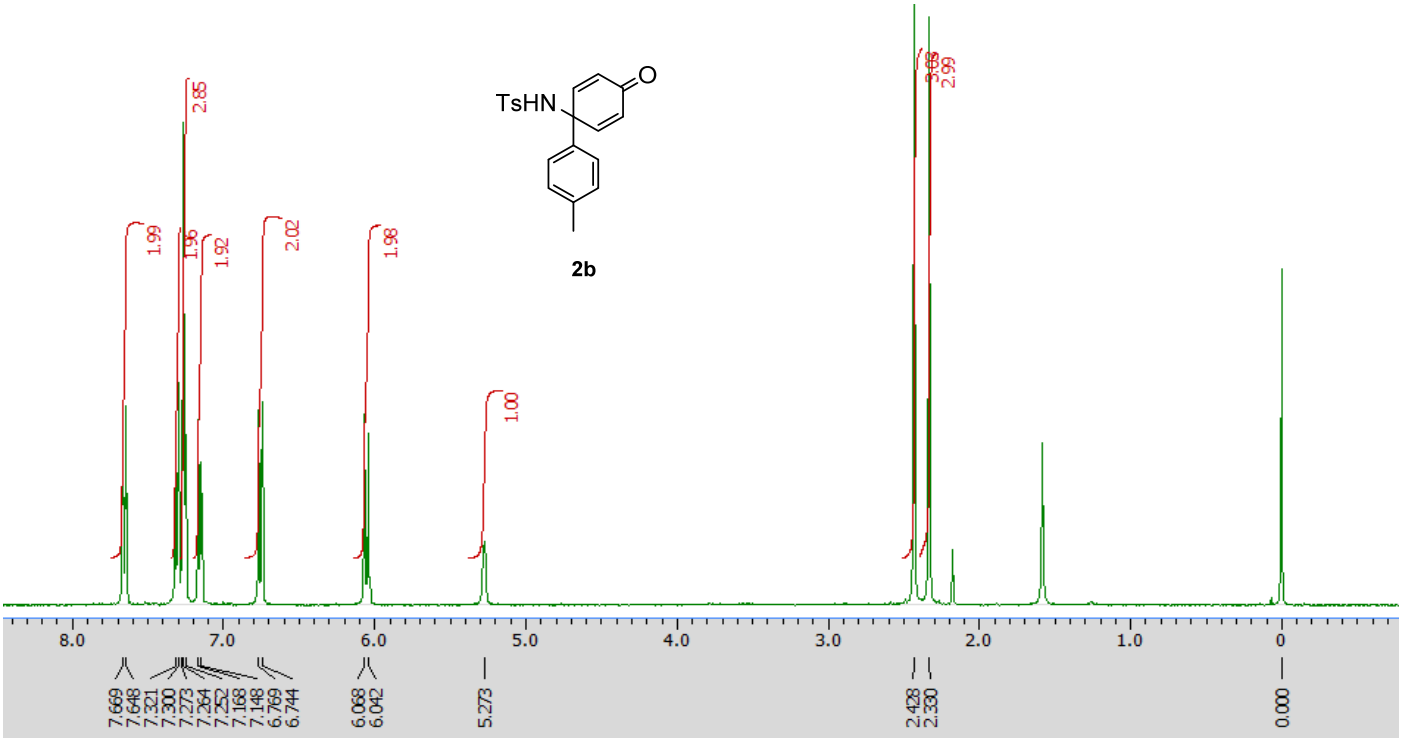






2l

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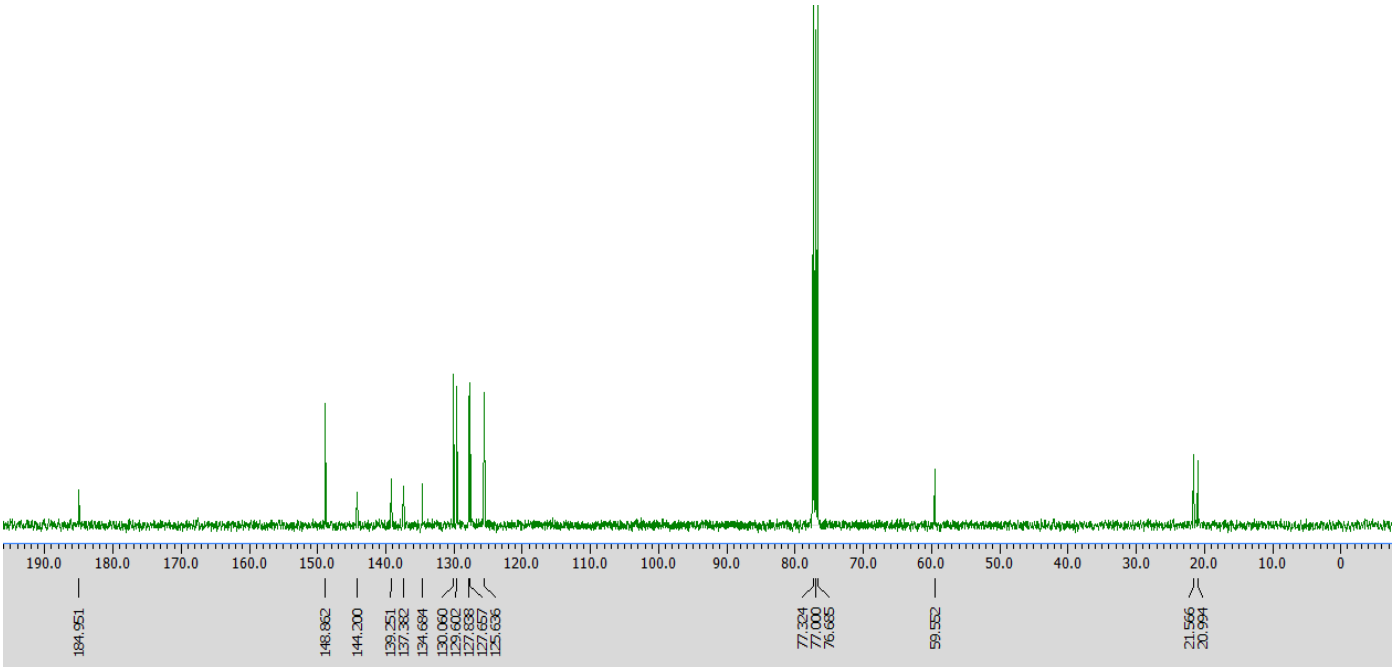
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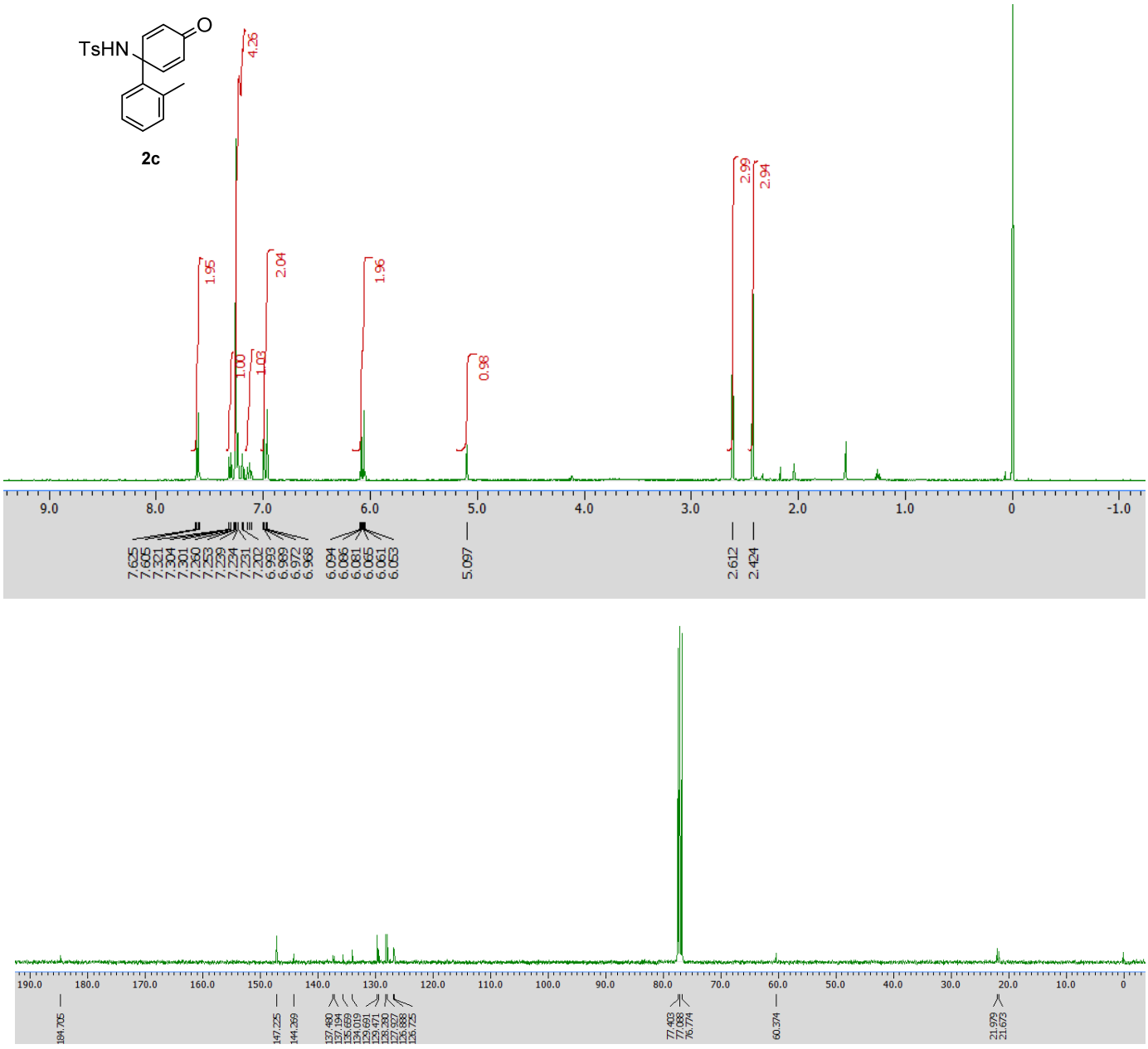
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2.424

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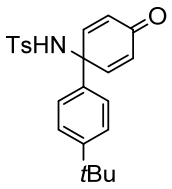
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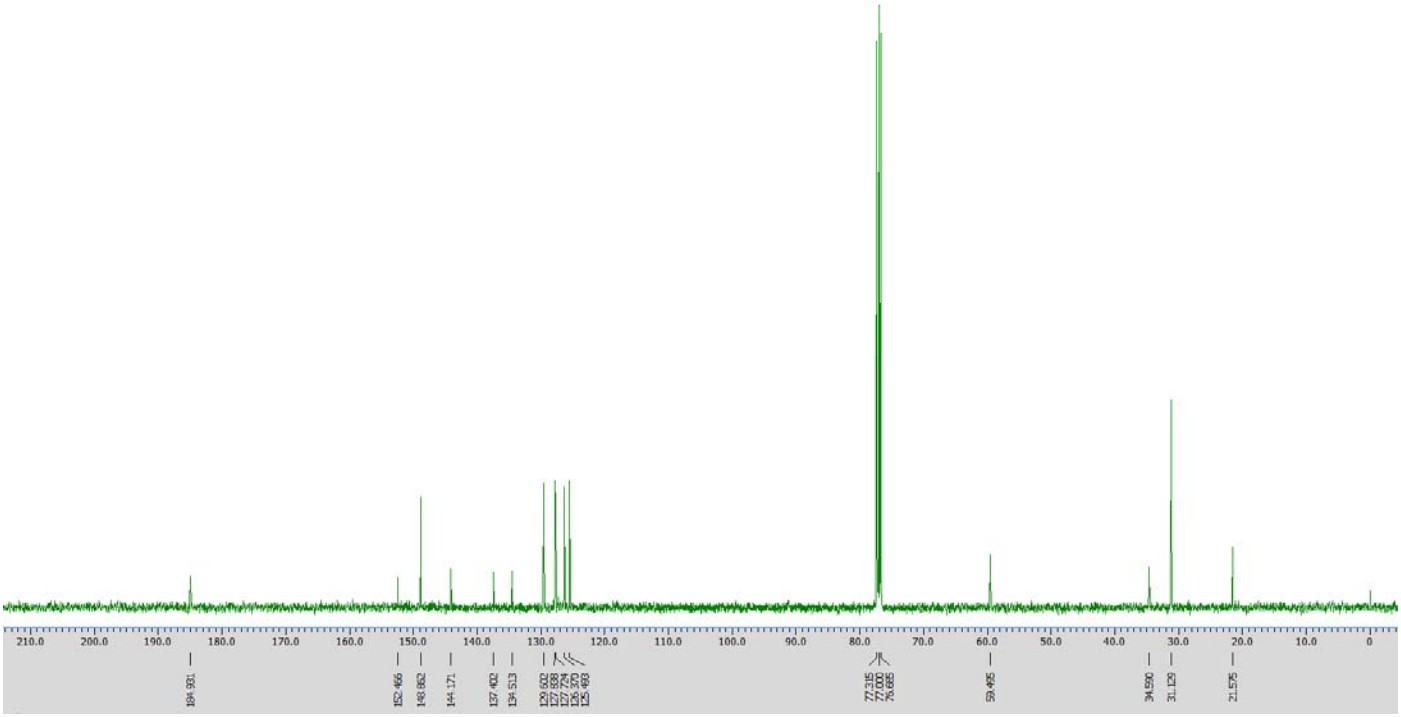
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140.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
196.981
152.466
148.862
144.171
137.402
134.513
129.602
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127.774
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125.469
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77.000
76.685
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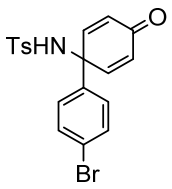
34.590
31.129
21.575


TsHN
O
Br

2e

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2.05
2.03
2.06
2.02
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.619
7.446
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6.064
6.038
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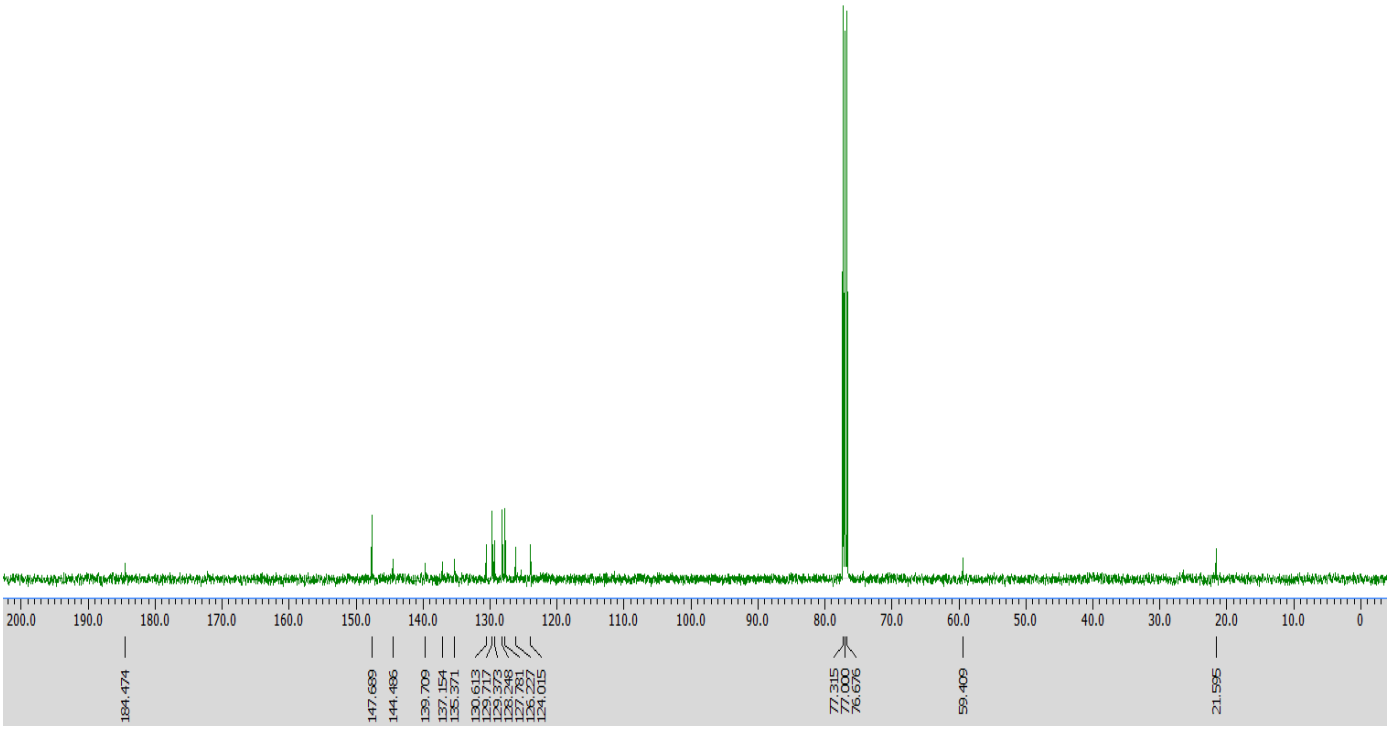
2.431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30.0
20.0
10.0
0
184.474
147.689
144.486
139.709
137.154
135.371
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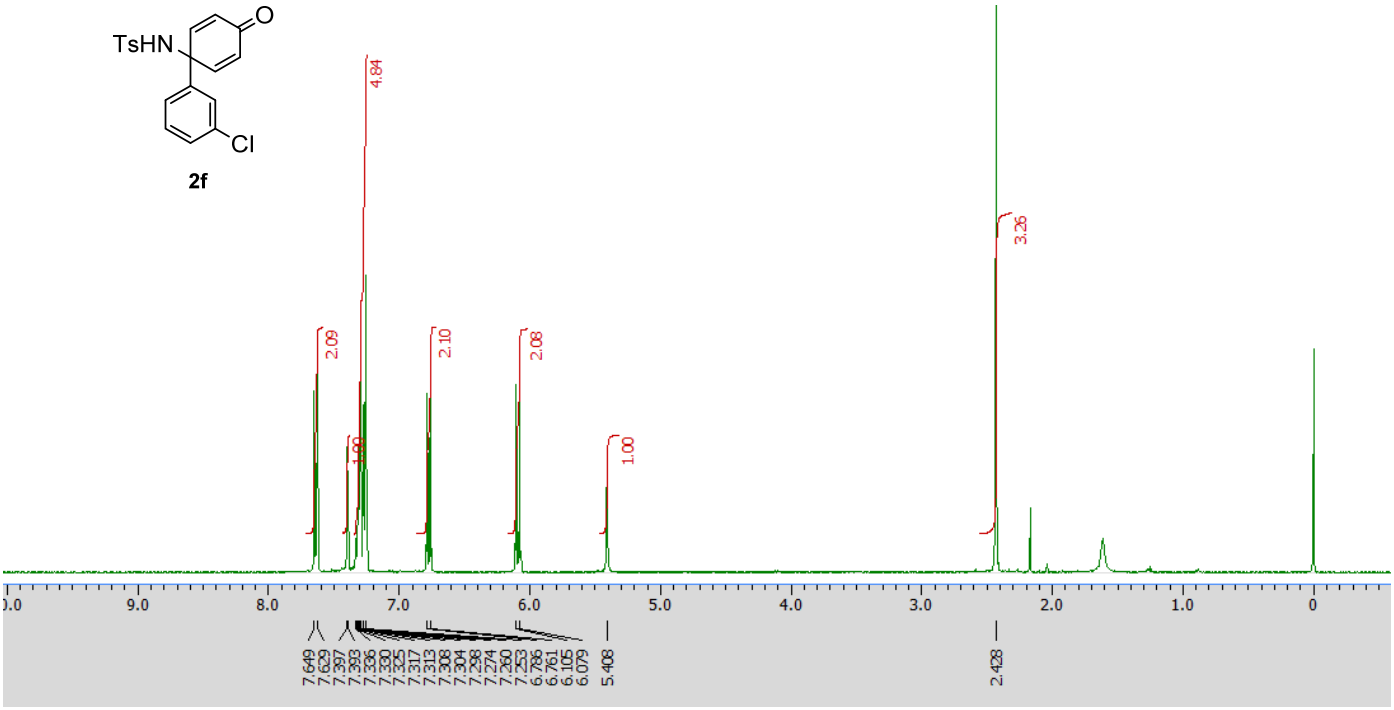
21.595


TsHN
O
Cl
2f
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2.08
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7.649
7.629
7.397
7.393
7.336
7.330
7.325
7.317
7.313
7.308
7.304
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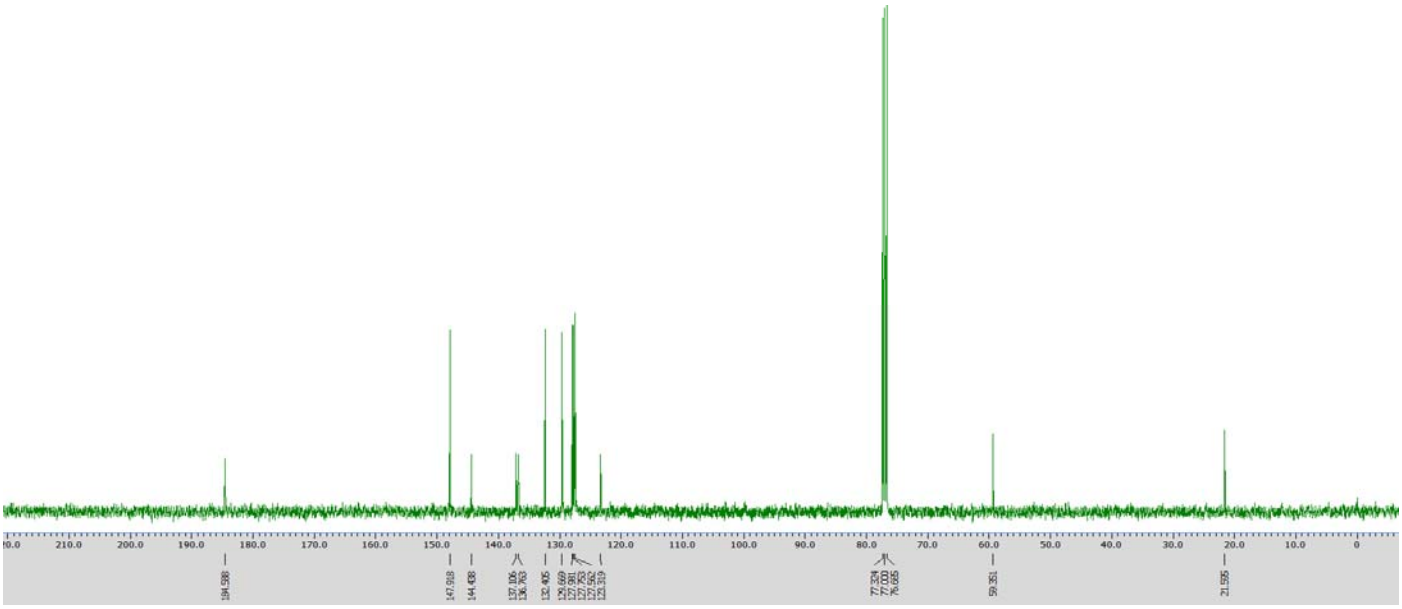
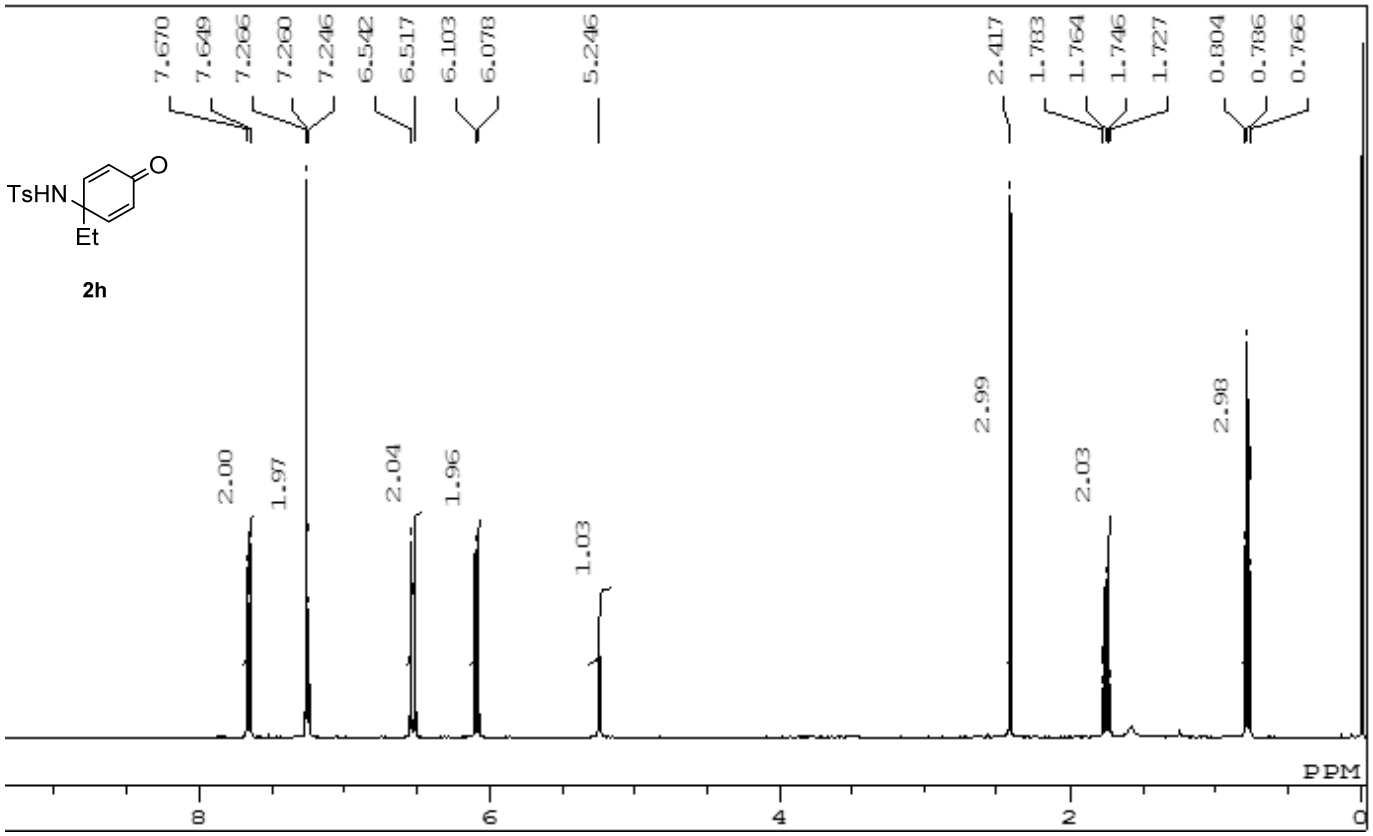
7.274
7.260
7.253
6.766
6.761
6.105
6.079
5.408
2.428

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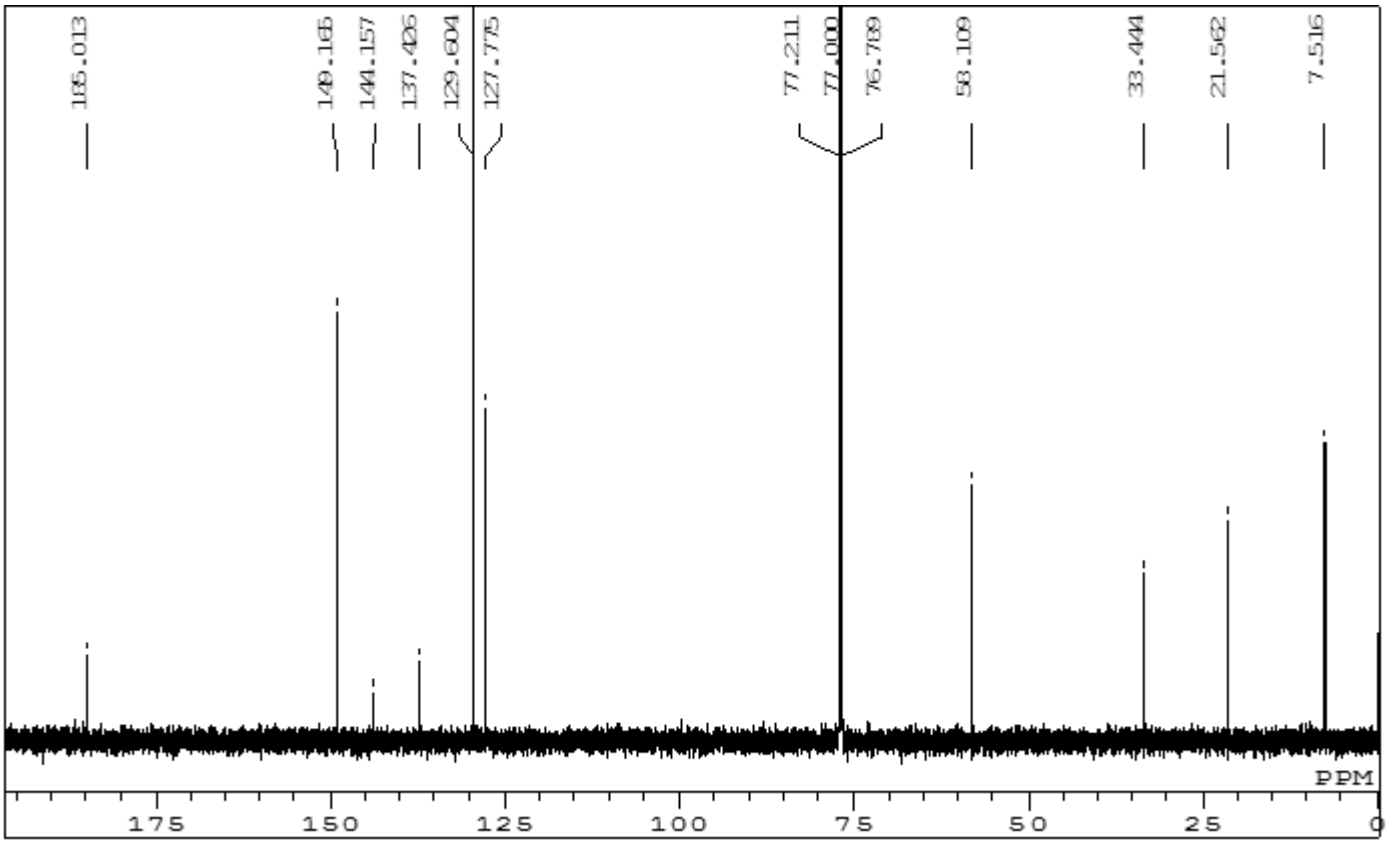
7.649
7.266
7.260
7.246
6.542
6.517
6.103
6.078
5.246
2.417
1.783
1.764
1.746
1.727
0.804
0.786
0.766
TsHN
Et
O
2h
2.00
1.97
2.04
1.96
1.03
2.99
2.03
2.98
PPM
8
6
4
2
0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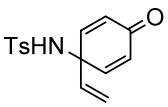
149.165
144.157
137.426
129.604
127.775
77.211
77.000
76.789
58.109
33.444
21.562
7.516
PPM
175
150
125
100
75
50
25
0


TsHN
O

2i

2.02
2.10
2.00
2.00
1.05
1.00
1.02
1.03
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.701
7.697
7.273
7.260
6.658
6.642
6.067
6.049
5.888
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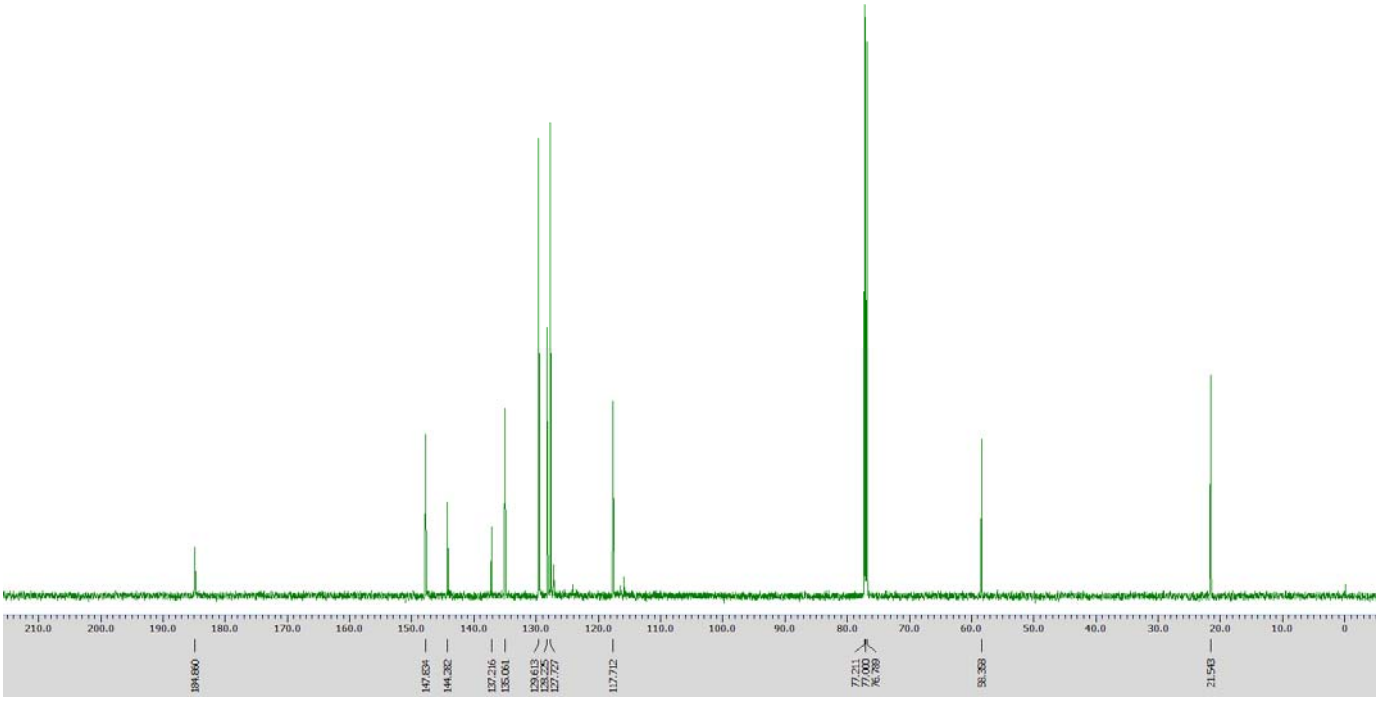
5.618
5.601
5.396
5.367
5.254
5.249
5.236
5.222
2.420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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
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20.0
10.0
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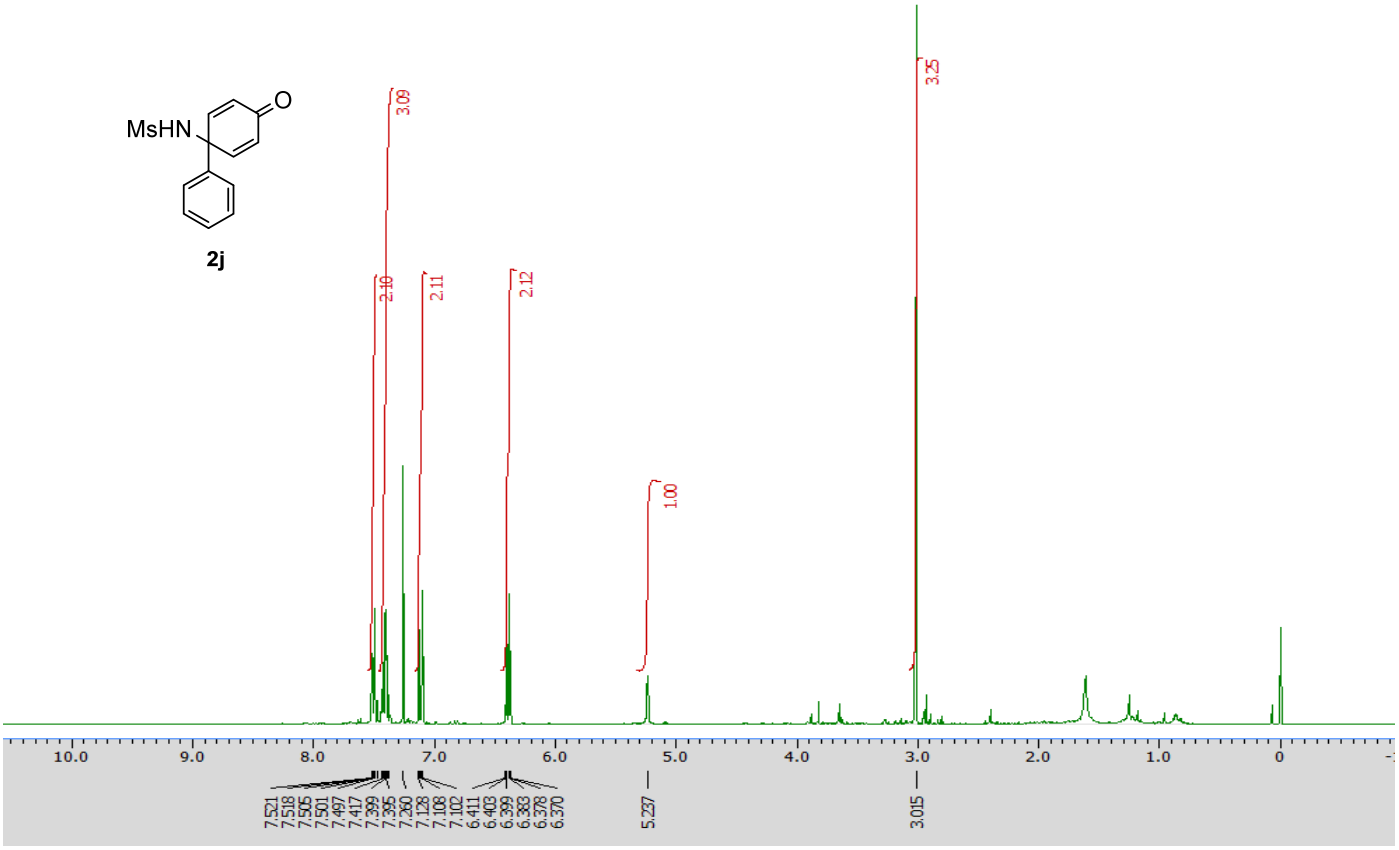
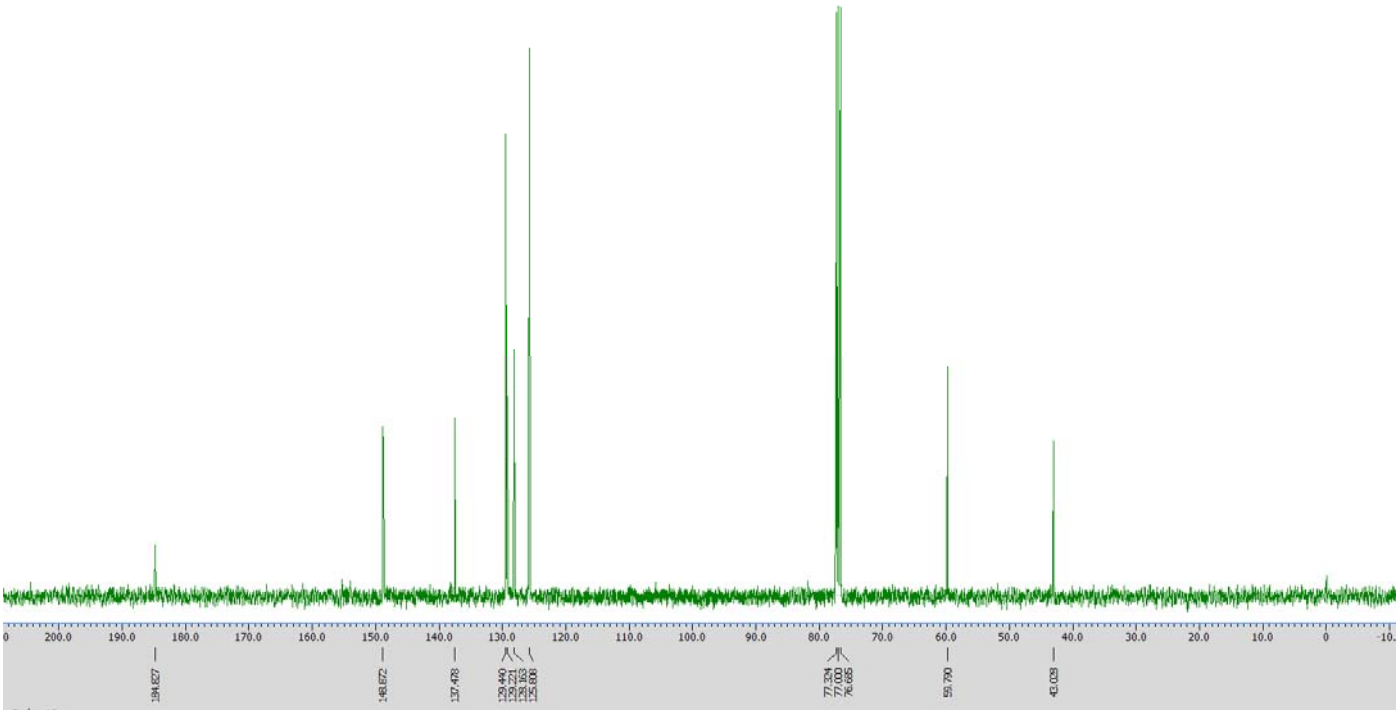
77.211
77.000
76.789
58.368
21.543


MsHN
O
2j
3.09
2.10
2.11
2.12
1.00
3.25
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.521
7.518
7.505
7.501
7.497
7.417
7.399
7.395
7.260
7.128
7.108
7.102
6.411
6.403
6.399
6.383
6.378
6.370
5.237
3.015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129.440
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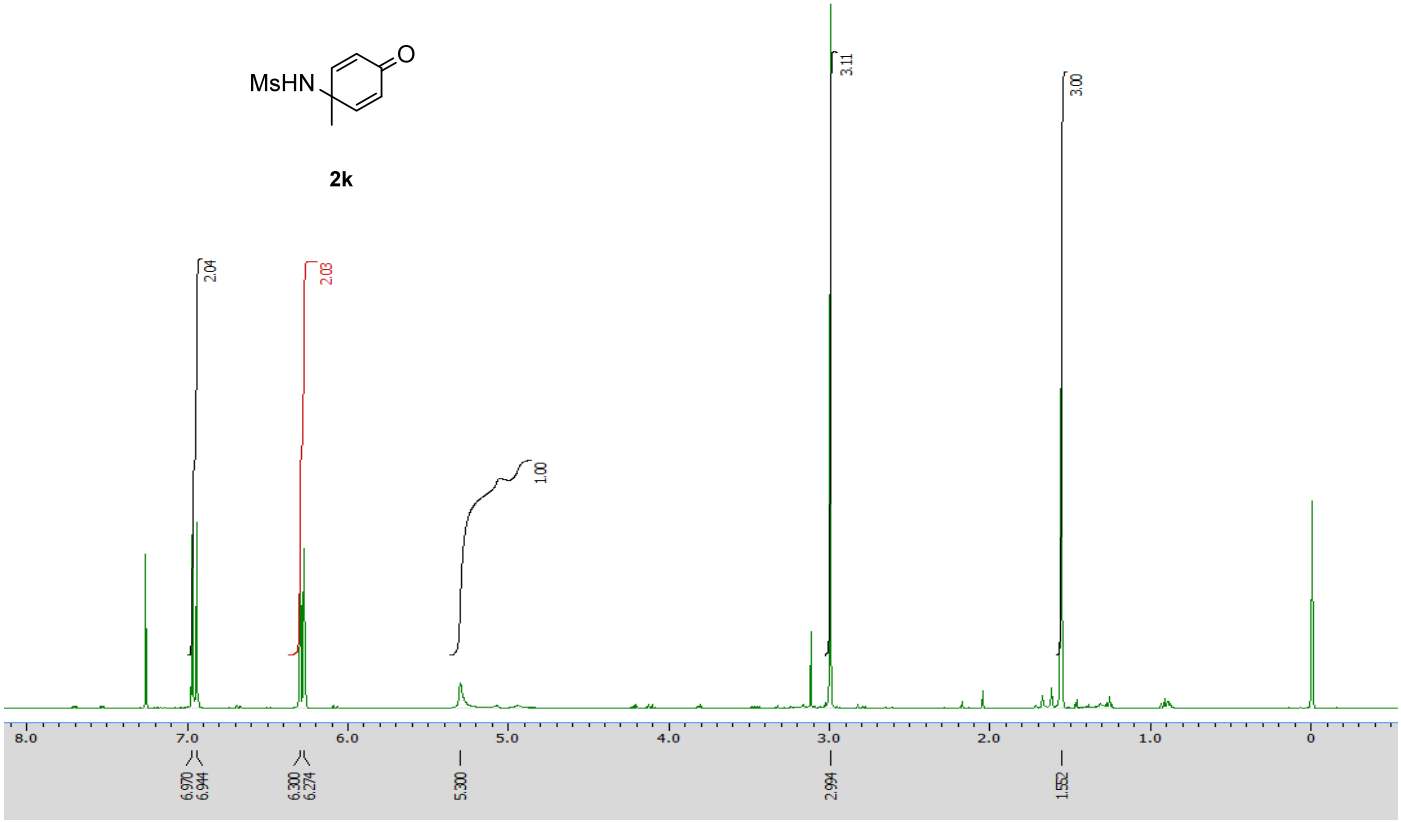
128.163
125.800
77.374
77.000
76.685
55.709
43.029


MsHN
O
2k
2.04
2.03
1.00
3.11
3.00
8.0
7.0
6.0
5.0
4.0
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2.0
1.0
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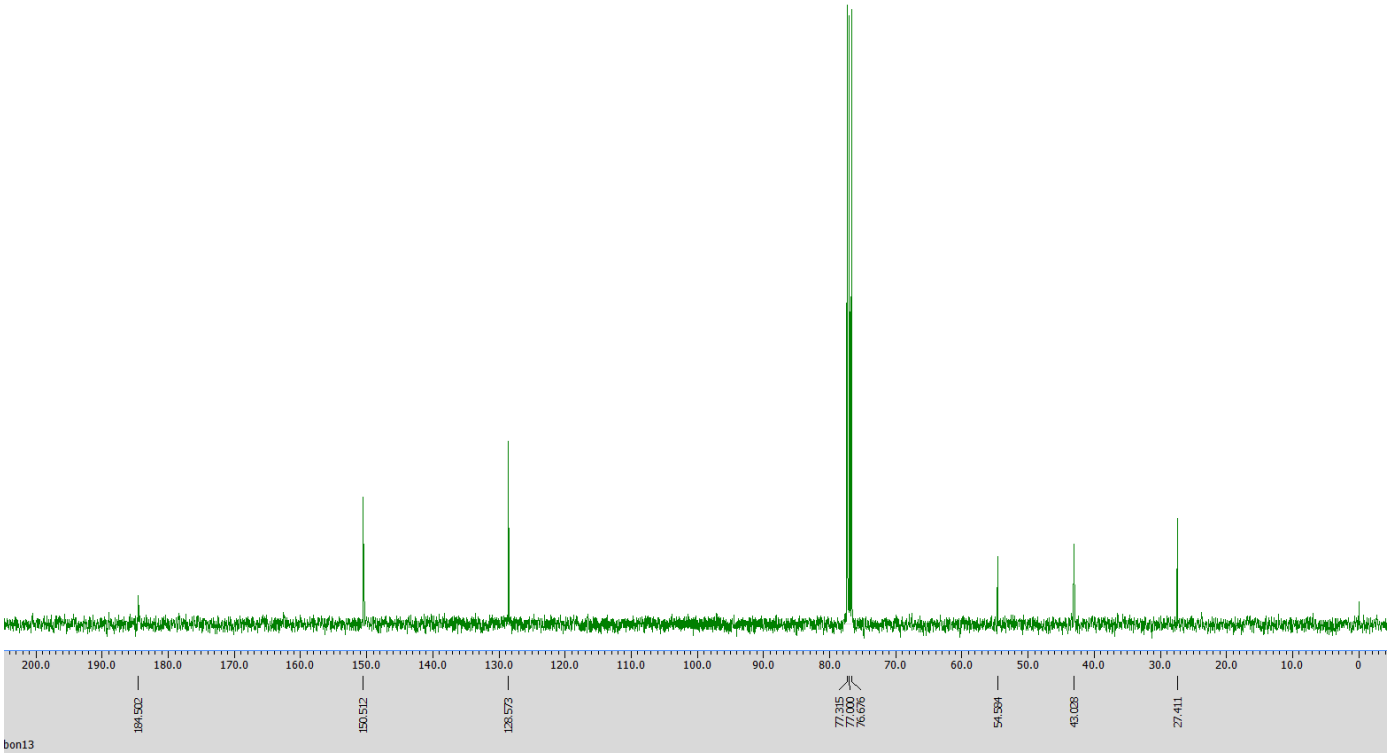
6.944
6.300
6.274
5.300
2.994
1.552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170.0
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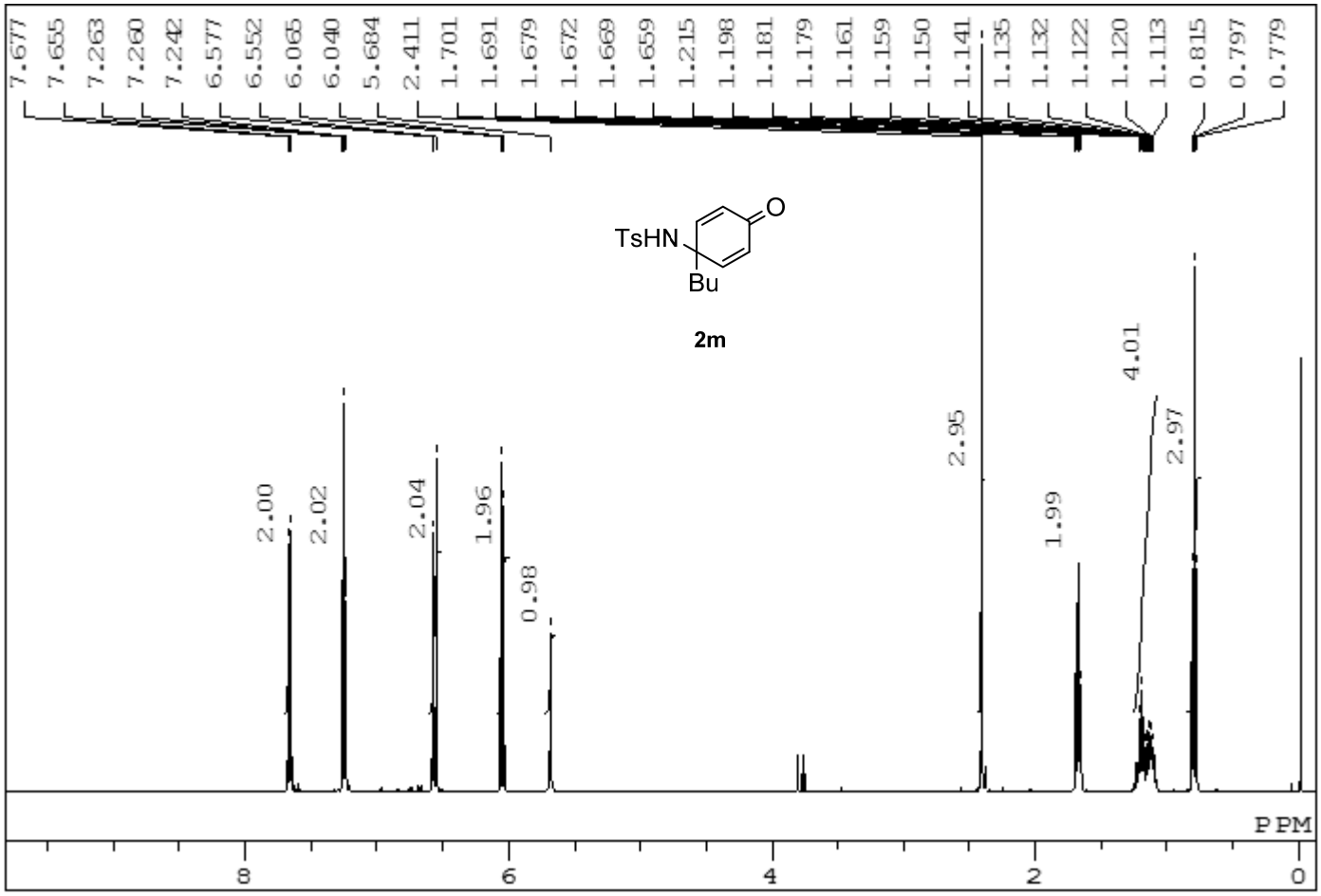
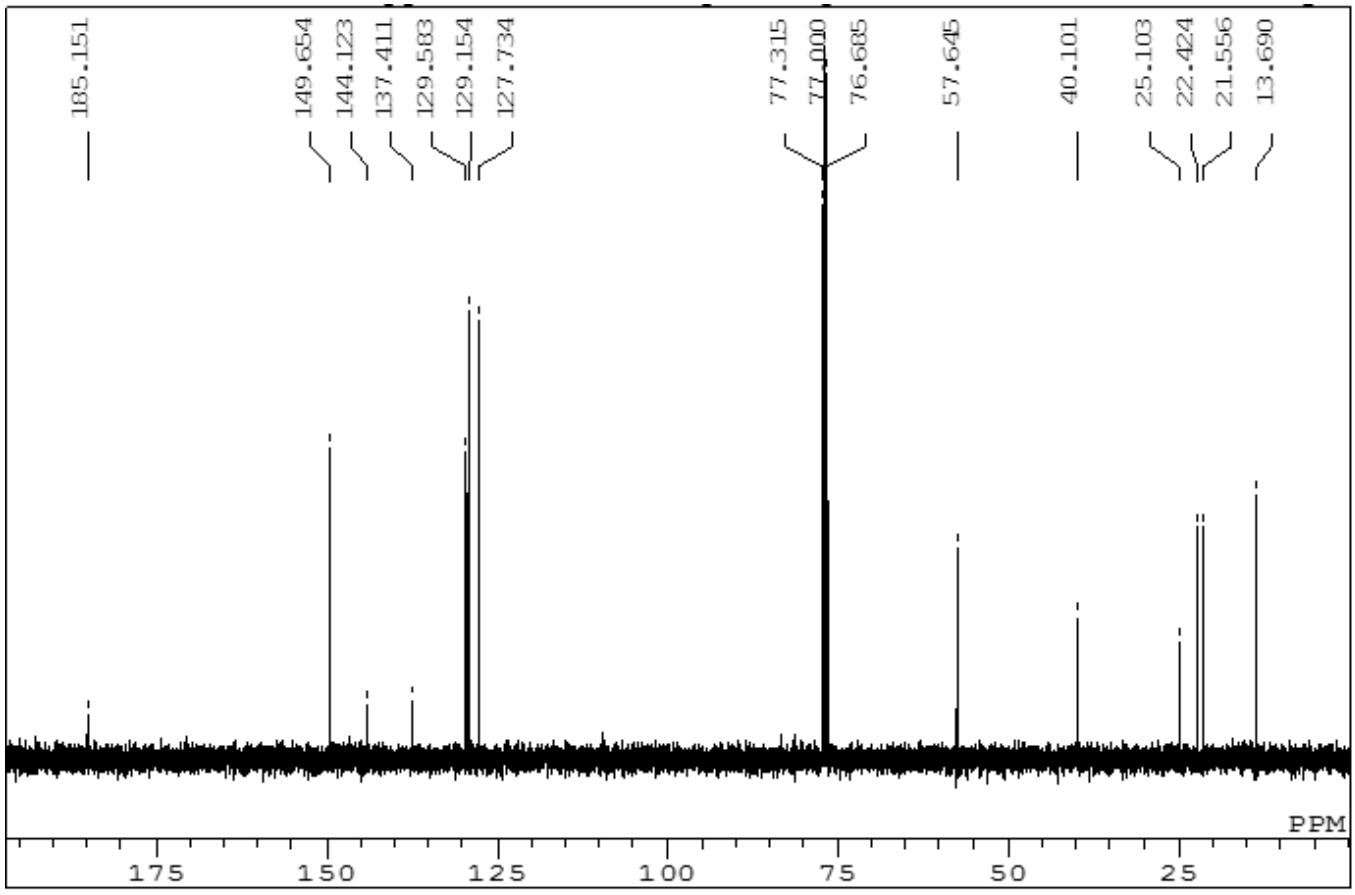
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.502
150.512
128.573
77.315
77.000
76.676
54.594
43.039
27.411
bon13


7.677
7.655
7.263
7.260
7.242
6.577
6.552
6.065
6.040
5.684
2.411
1.701
1.691
1.679
1.672
1.669
1.659
1.215
1.198
1.181
1.179
1.161
1.159
1.150
1.141
1.135
1.132
1.122
1.120
1.113
0.815
0.797
0.779
TsHN
O
Bu
2m
2.00
2.02
2.04
1.96
0.98
2.95
1.99
4.01
2.97
PPM
8
6
4
2
0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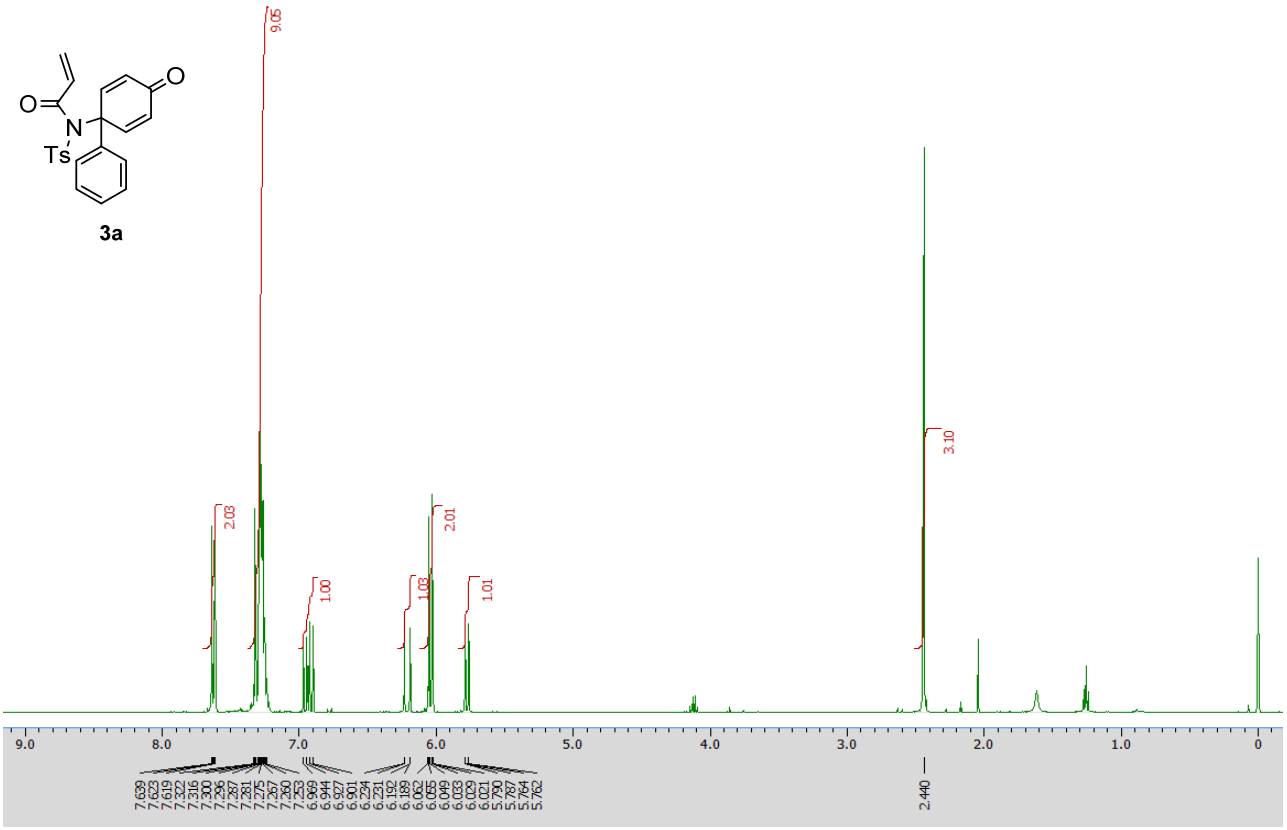
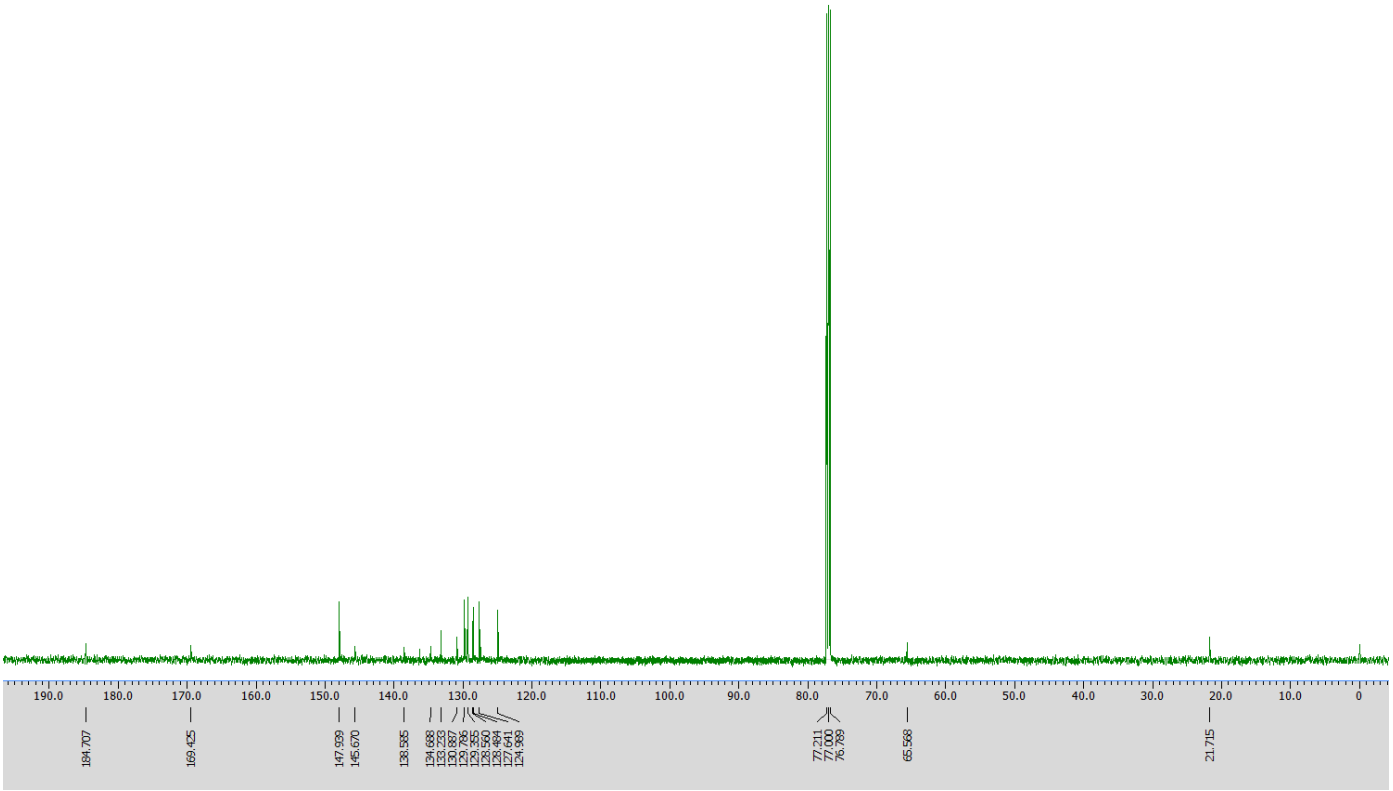
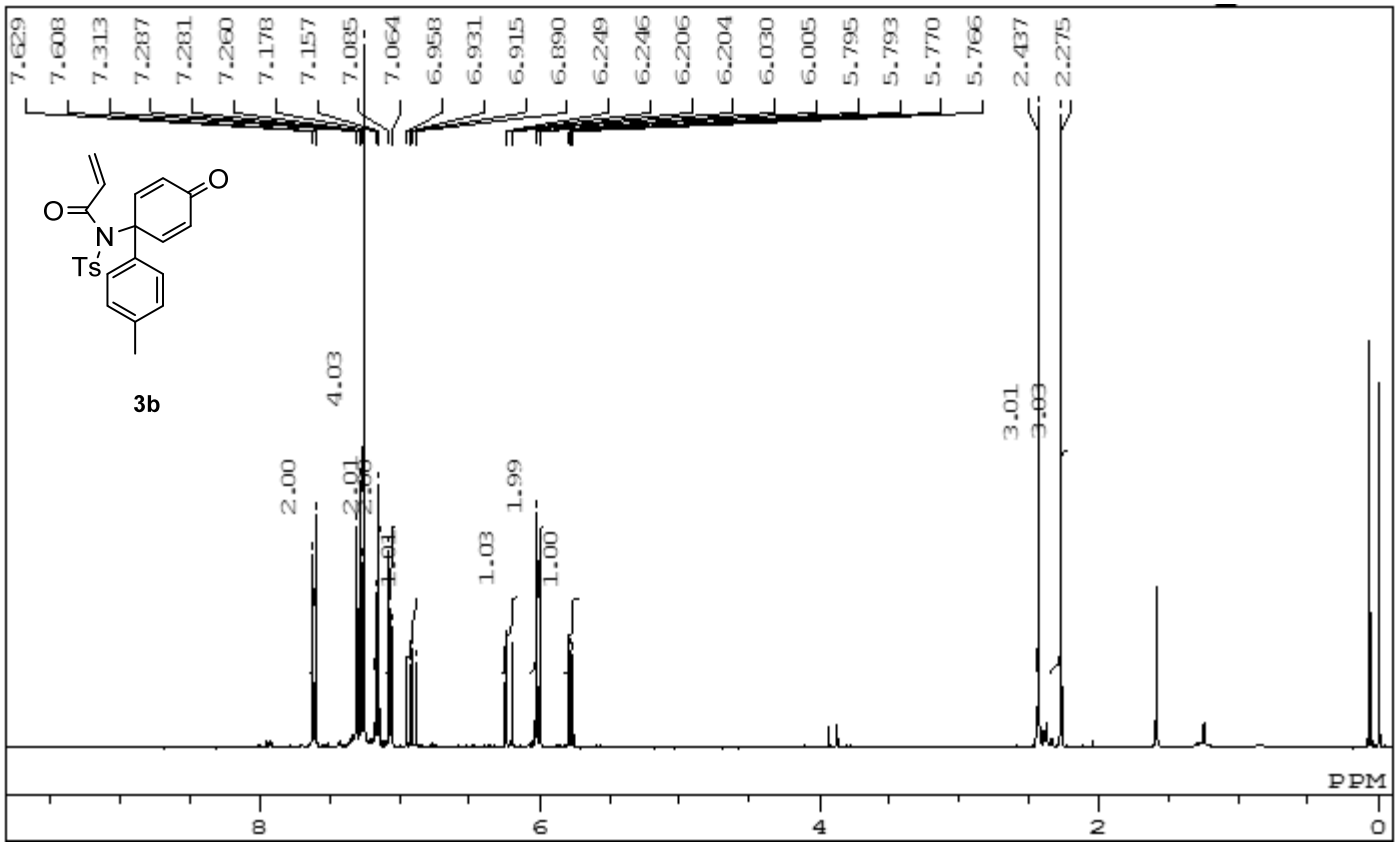
149.654
144.123
137.411
129.583
129.154
127.734
77.315
77.000
76.685
57.645
40.101
25.103
22.424
21.556
13.690
PPM
175
150
125
100
75
50
25


O
O
N
Ts
3a
9.05
2.03
1.00
1.03
2.01
1.01
3.10
2.440

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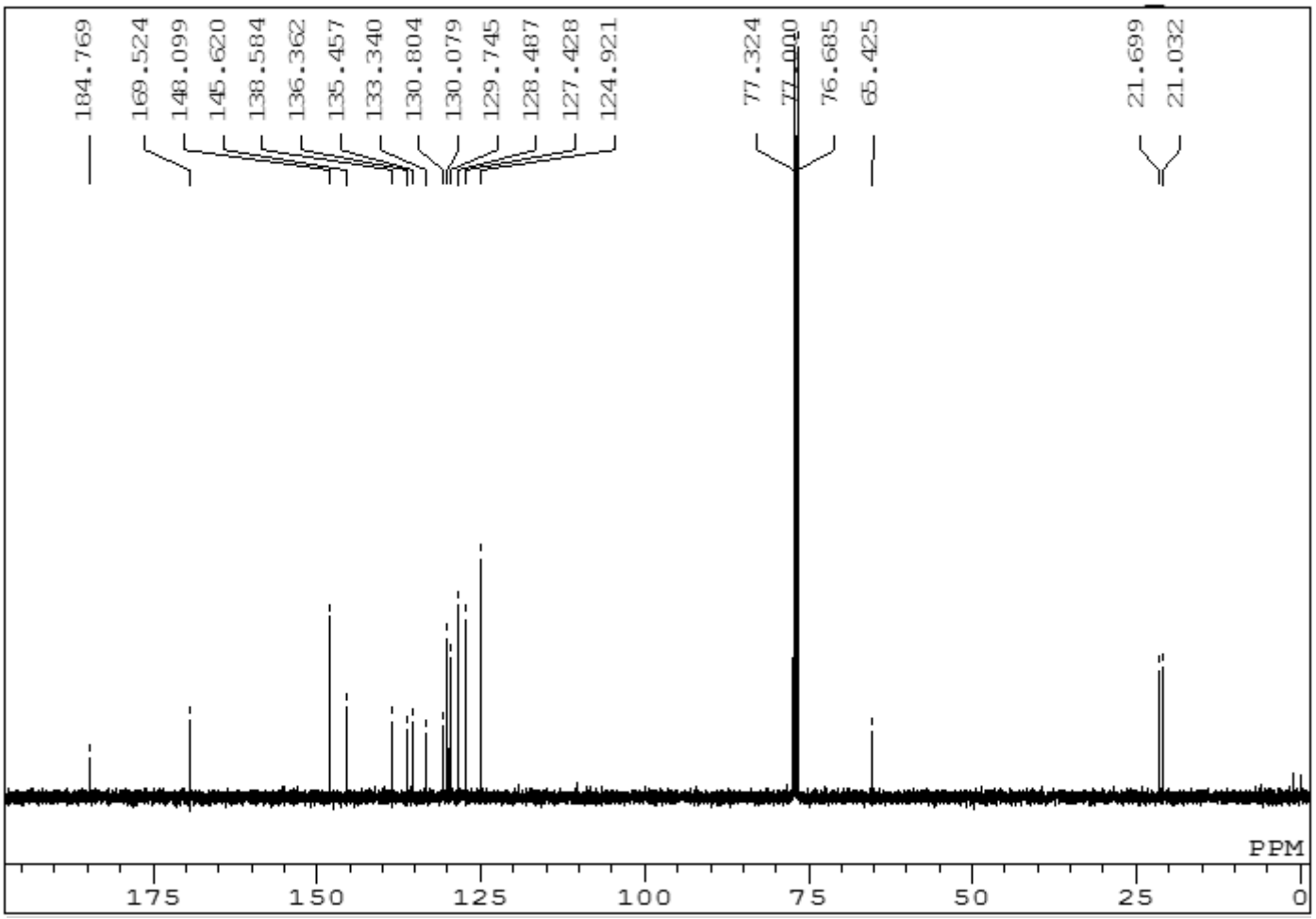
7.313
7.287
7.281
7.260
7.178
7.157
7.085
7.064
6.958
6.931
6.915
6.890
6.249
6.246
6.206
6.204
6.030
6.005
5.795
5.793
5.770
5.766
2.437
2.275
O
O
N
Ts
3b
4.03
2.00
2.01
2.06
1.04
1.03
1.99
1.00
3.01
3.03
PPM
8
6
4
2
0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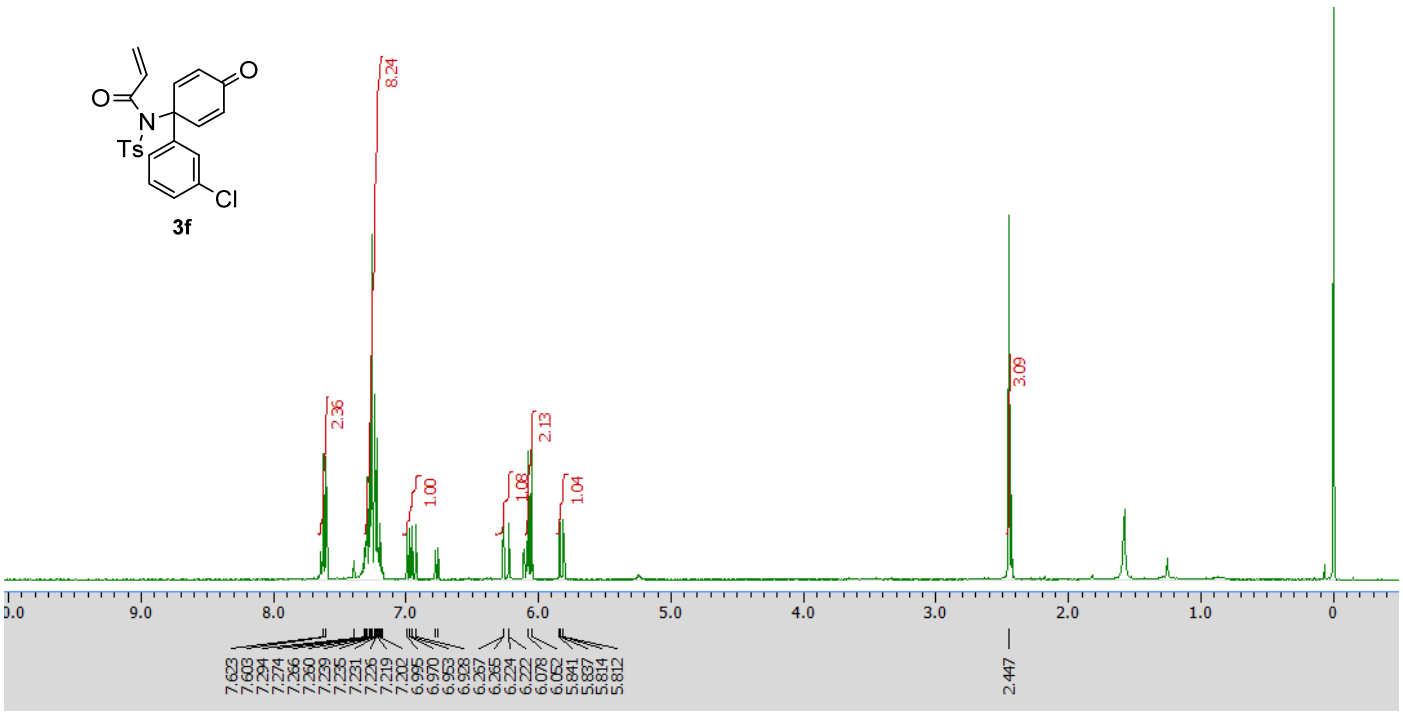
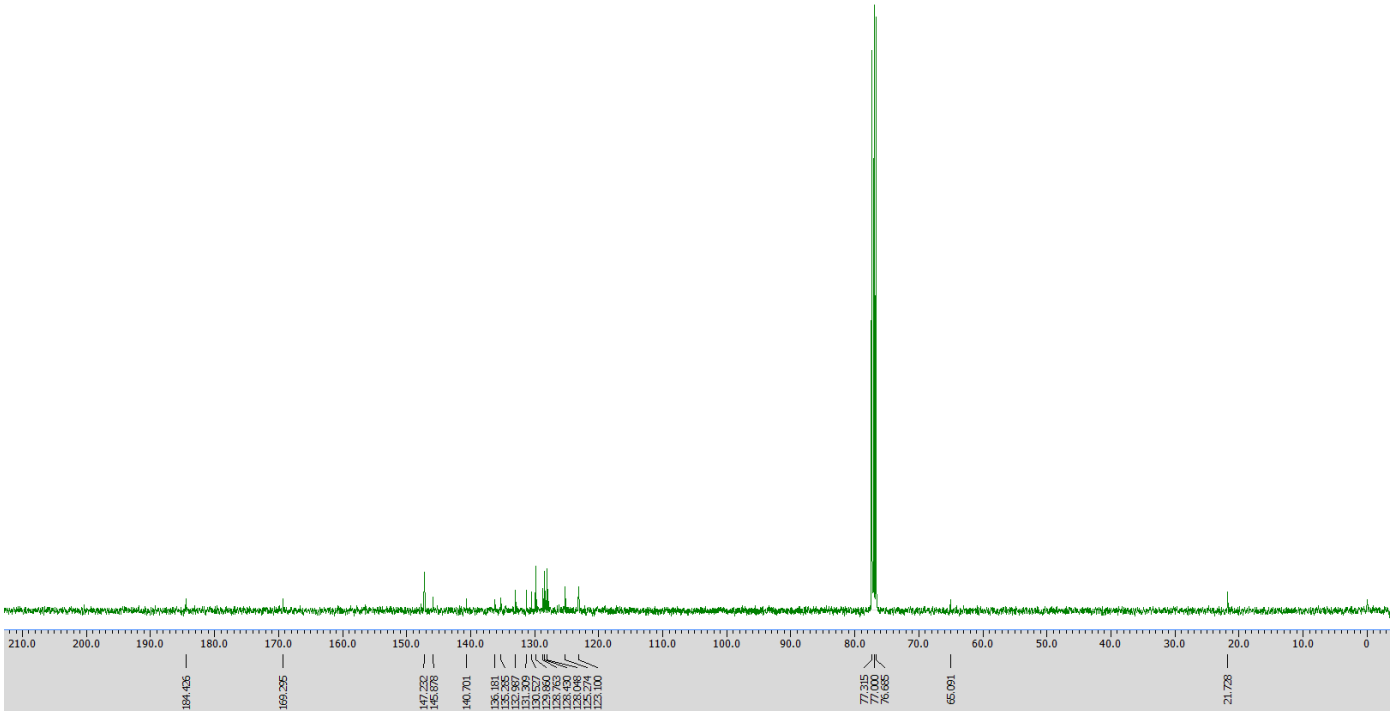
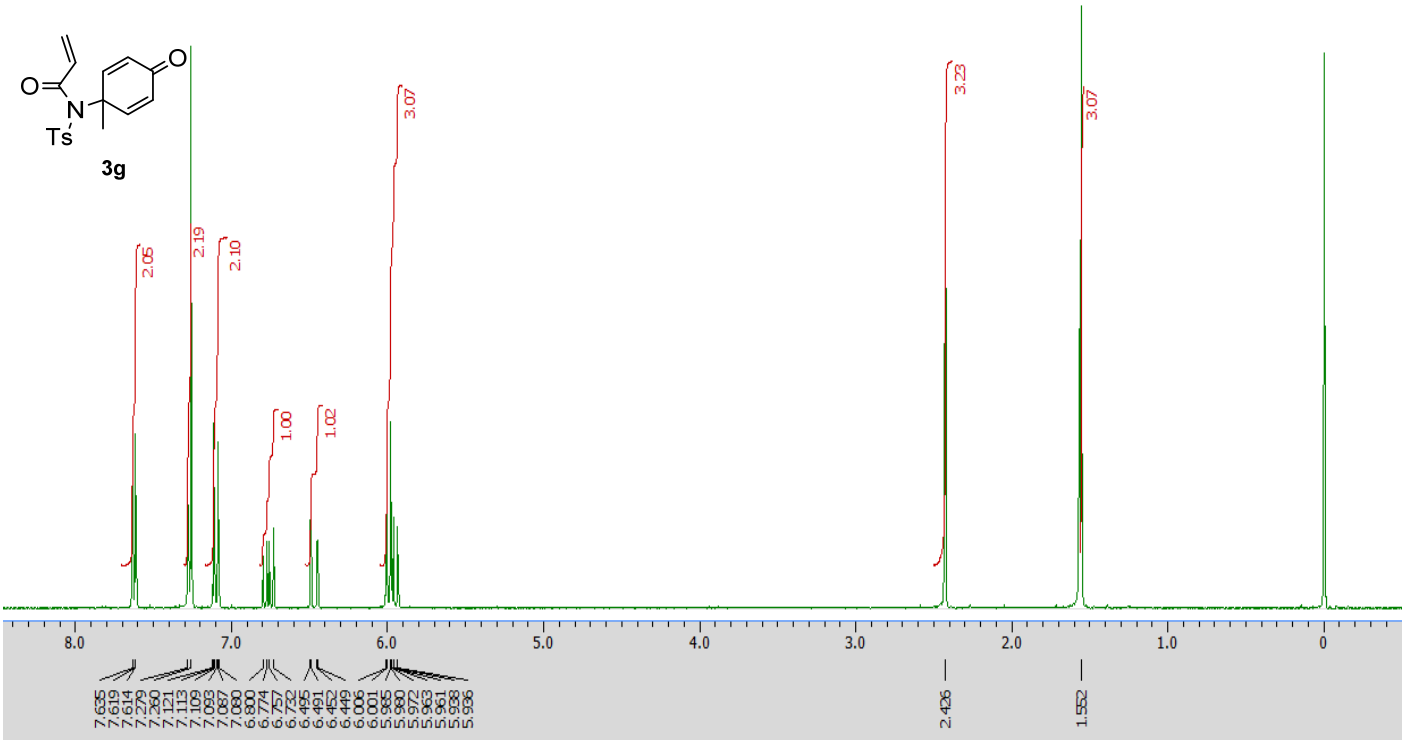
169.524
148.099
145.620
138.584
136.362
135.457
133.340
130.804
130.079
129.745
128.487
127.428
124.921
77.324
77.010
76.685
65.425
21.699
21.032
PPM
175
150
125
100
75
50
25
0


O
O
N
Ts
Cl
3f
8.24
2.36
1.00
1.08
2.13
1.04
3.09
2.447




3g
2.05
2.19
2.10
1.00
1.02
3.07
3.23
3.07
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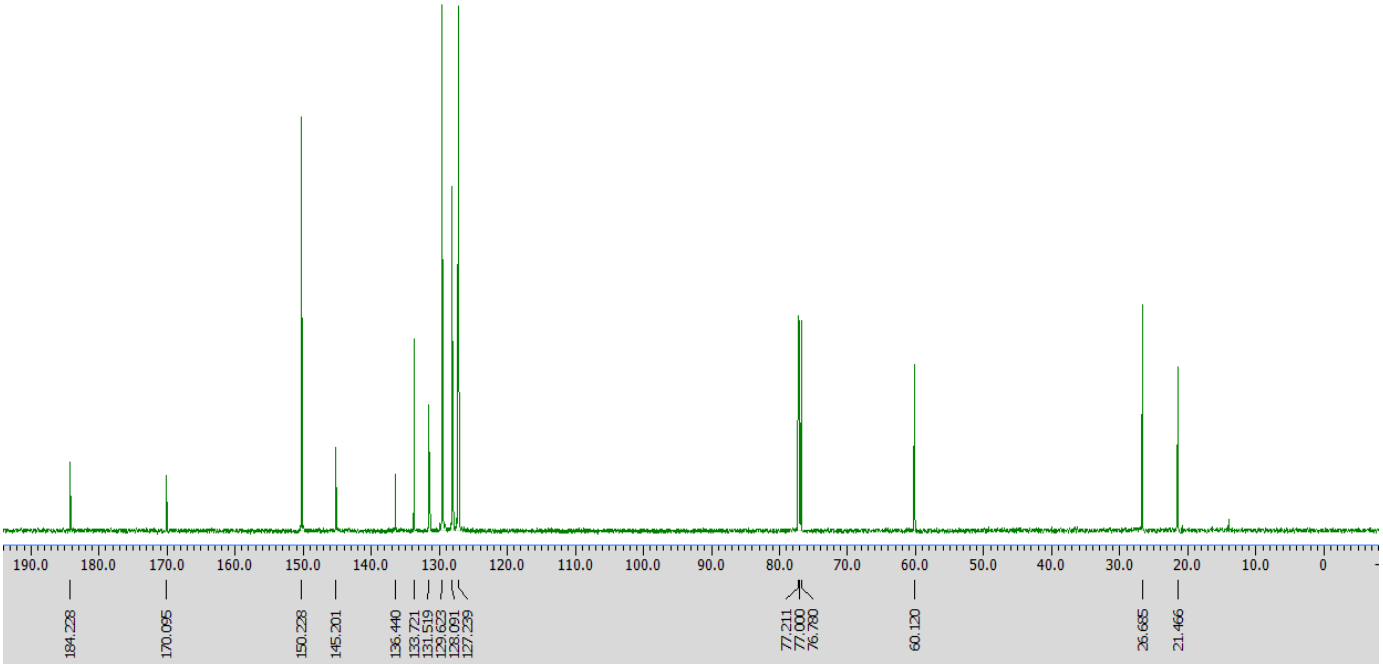
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.426
1.552


190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.228
170.095
150.228
145.201
136.440
133.721
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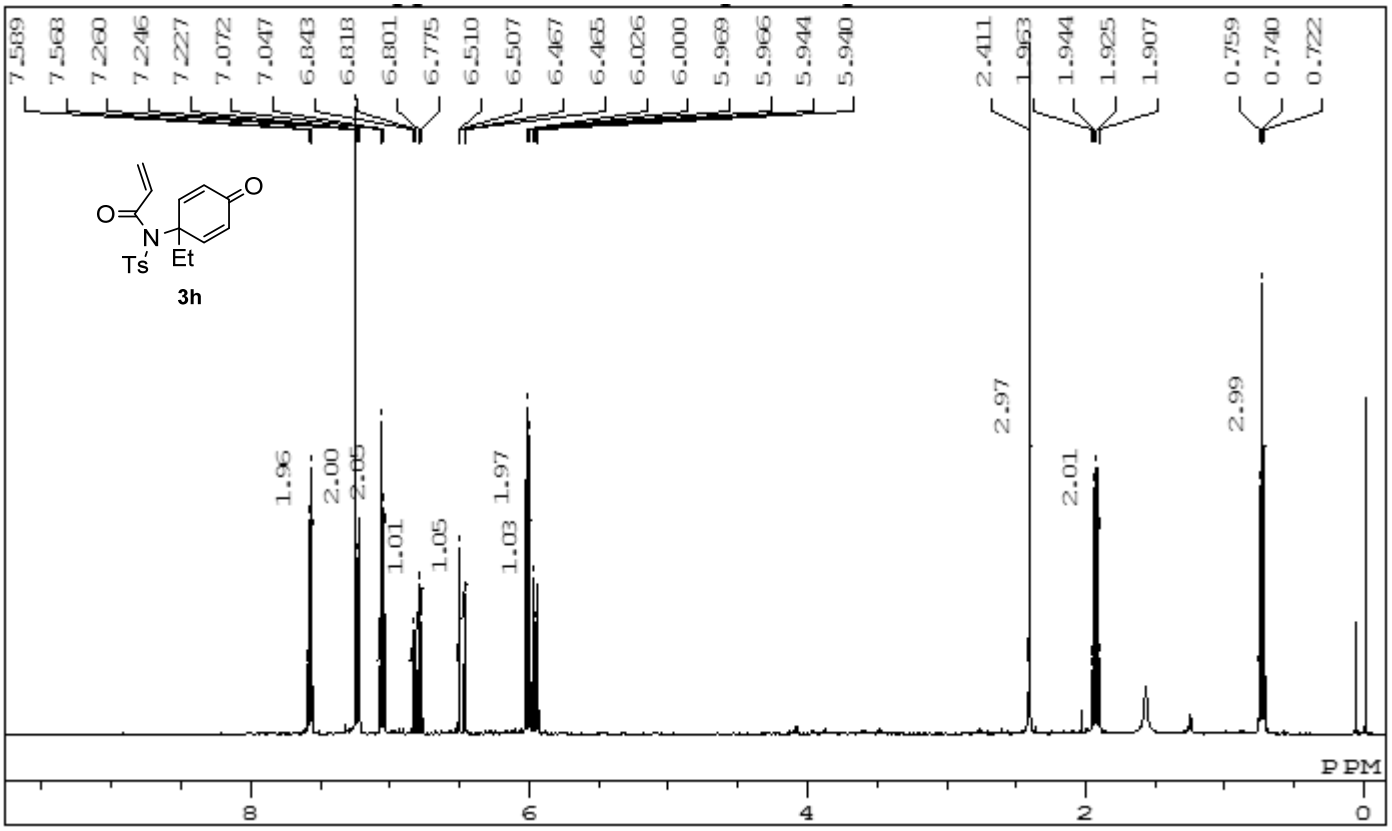
129.623
128.091
127.259
77.211
77.000
76.780
60.120
26.685
21.466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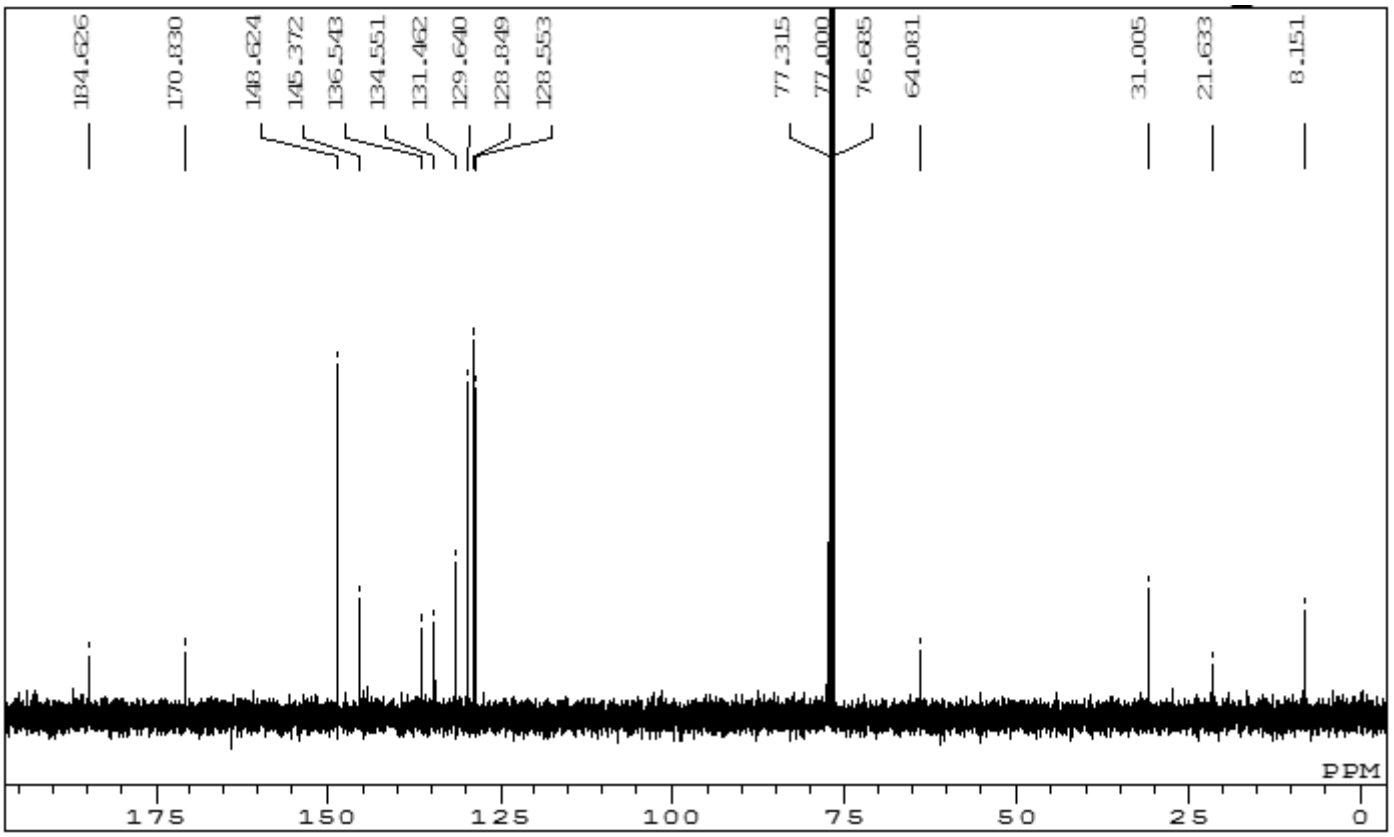
7.563
7.260
7.246
7.227
7.072
7.047
6.843
6.818
6.801
6.775
6.510
6.507
6.467
6.465
6.026
6.000
5.969
5.966
5.944
5.940
2.411
1.963
1.944
1.925
1.907
0.759
0.740
0.722
1.96
2.00
2.05
1.01
1.05
1.03
1.97
2.97
2.01
2.99
O
O
N
Ts
Et
3h
PPM
8
6
4
2
0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170.830
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145.372
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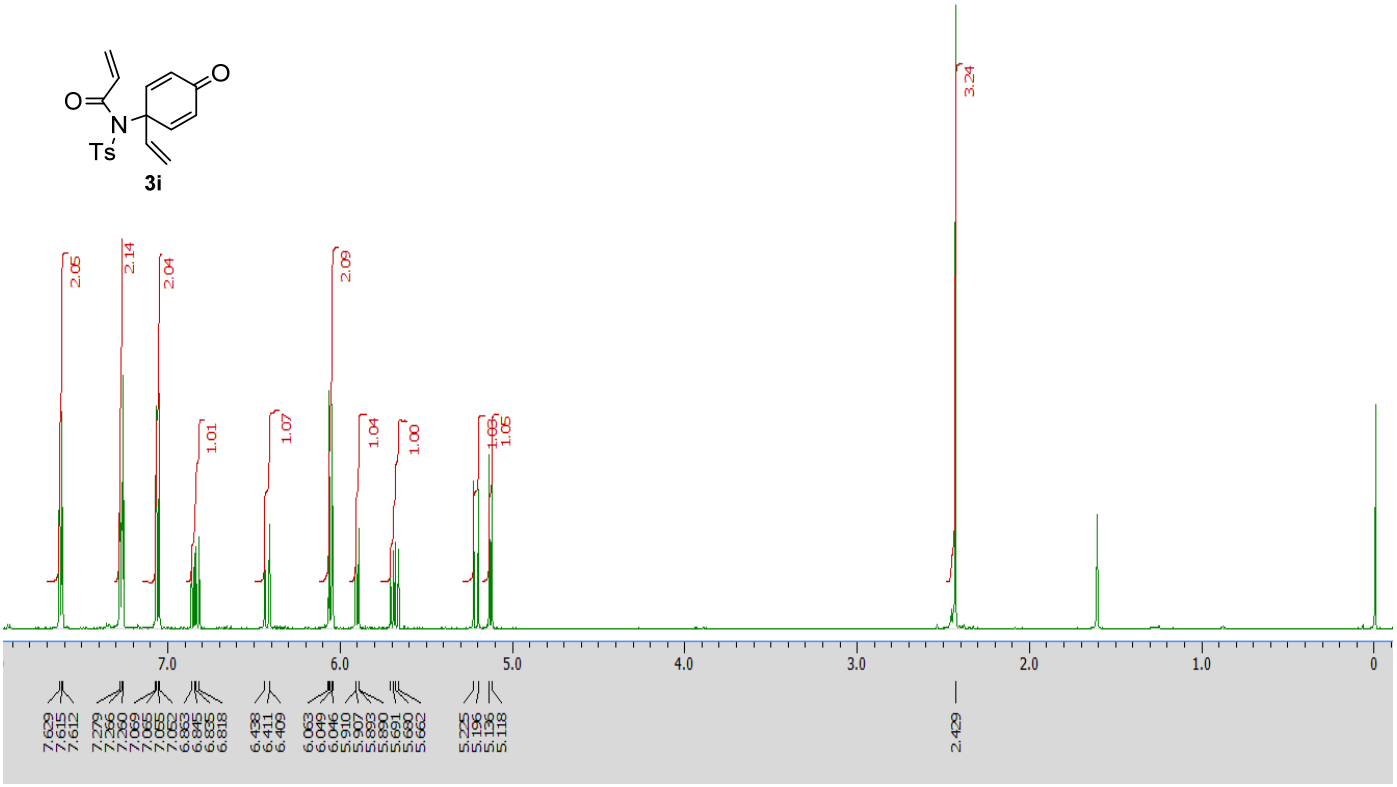
134.551
131.462
129.640
128.849
128.553
77.315
77.000
76.685
64.081
31.005
21.633
8.151
PPM
175
150
125
100
75
50
25
0


3i
2.05
2.14
2.04
1.01
1.07
2.09
1.04
1.00
1.03
1.05
3.24
7.629
7.615
7.612
7.279
7.266
7.260
7.069
7.065
7.055
7.052
6.863
6.845
6.835
6.818
6.438
6.411
6.409
6.063
6.049
6.046
5.910
5.907
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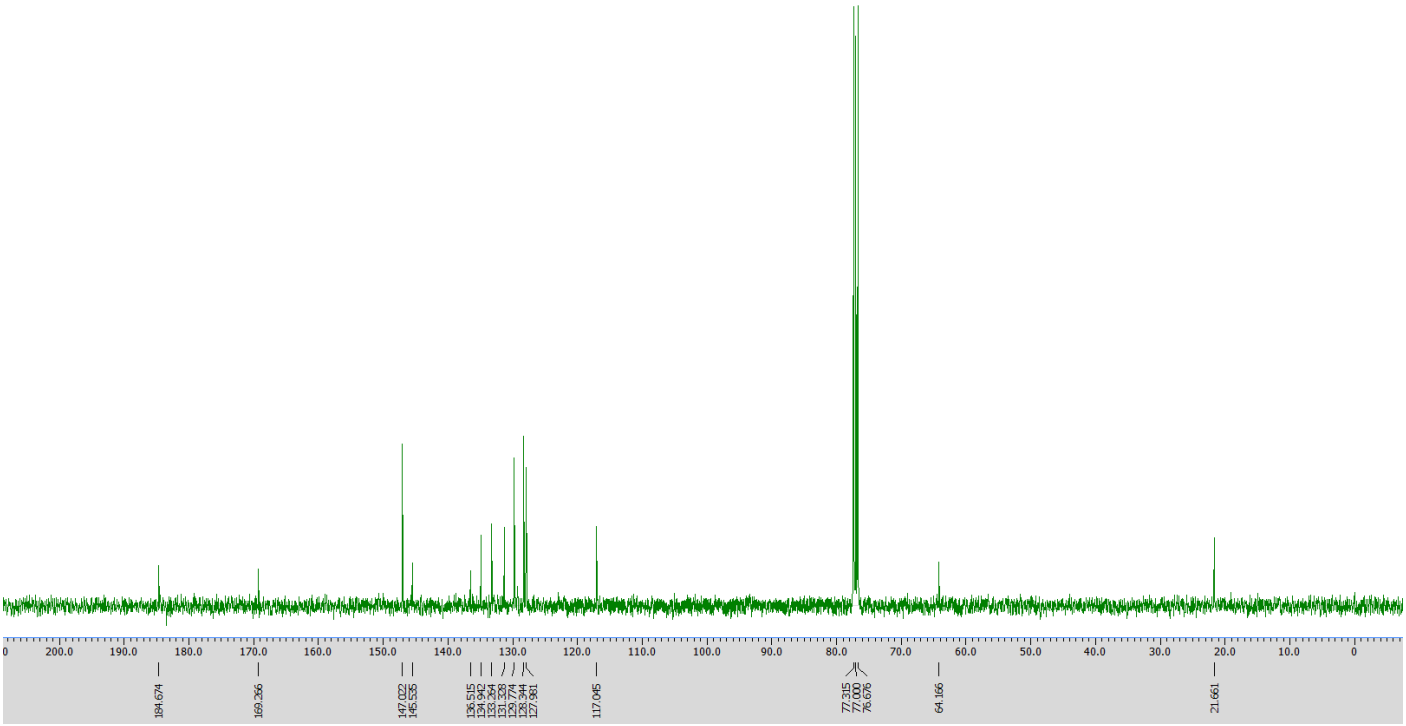
5.890
5.691
5.680
5.662
5.225
5.196
5.136
5.118
2.429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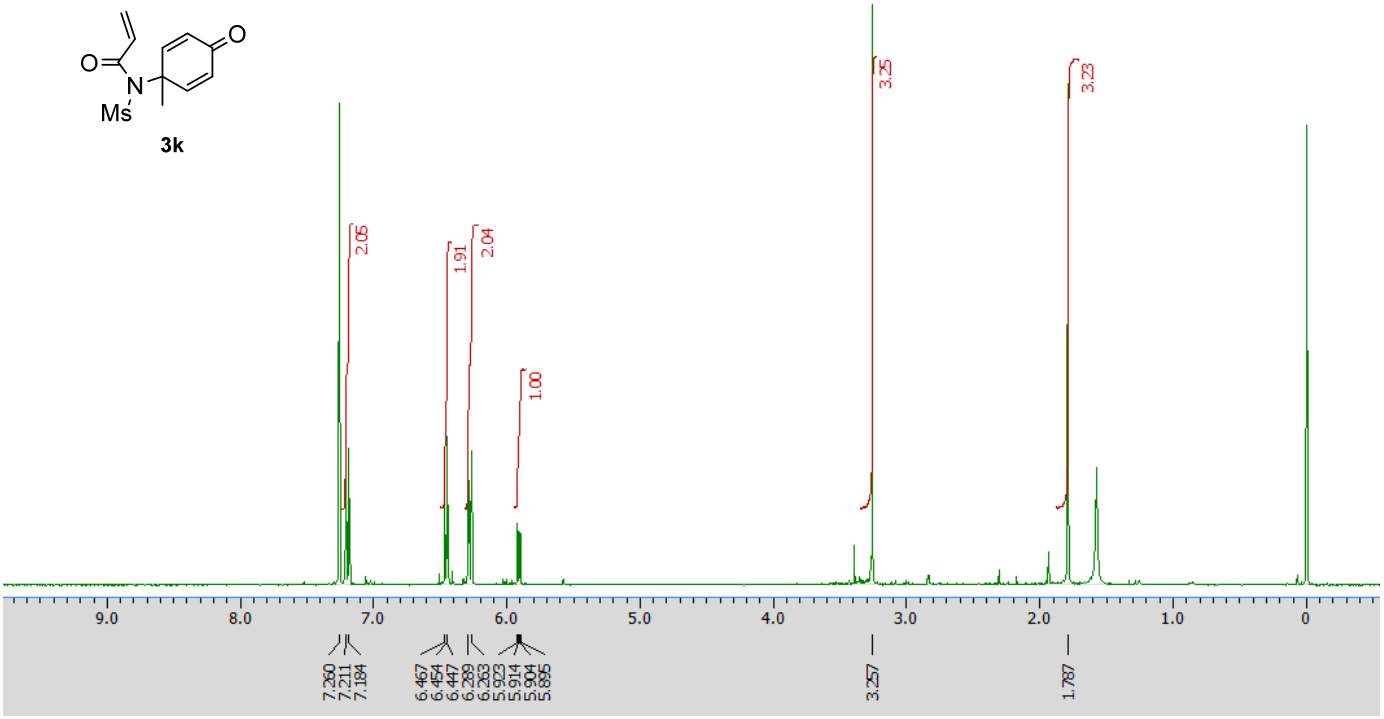
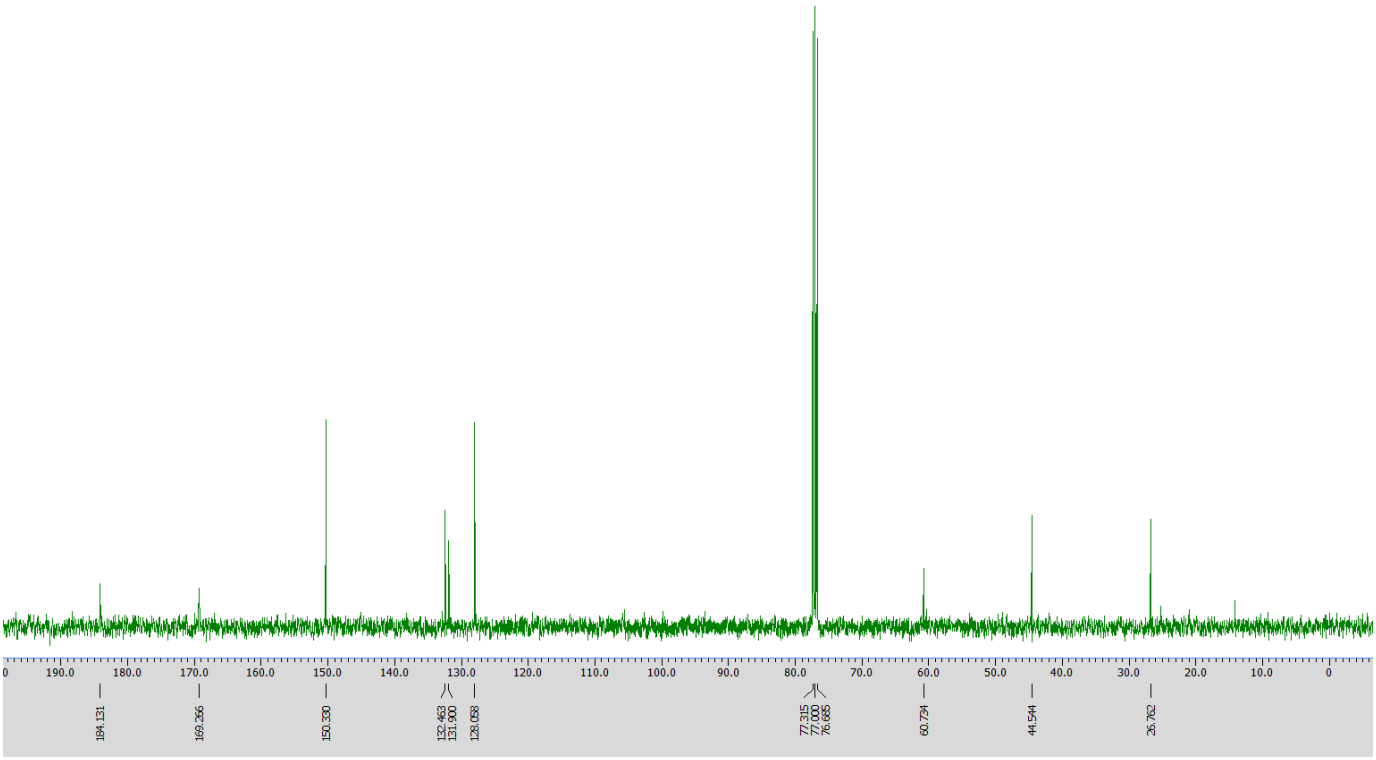
129.774
129.284
127.981
117.045
77.215
77.000
76.676
64.166
21.661


3k
2.05
1.91
2.04
1.00
3.25
3.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
7.211
7.184
6.467
6.454
6.447
6.289
6.263
5.923
5.914
5.904
5.895
3.257
1.787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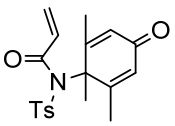
132.463
131.900
128.058
77.315
77.000
76.685
60.724
44.544
26.762


O
O
N
Ts

3l
(at 60 °C)

2.14
2.12
1.00
1.14
2.14
1.03
3.67
6.02
2.84
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.872
7.365
7.345
7.260
6.819
6.793
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6.379
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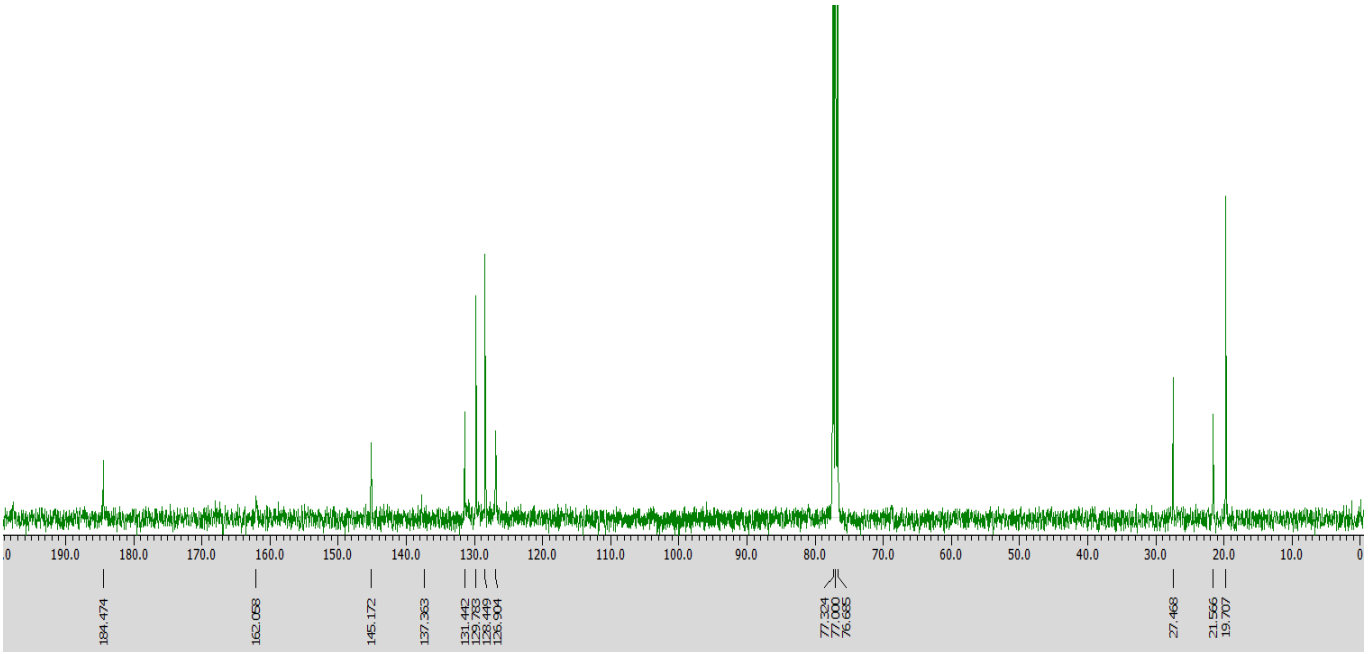
6.037
5.777
5.751
2.464
2.432
1.924
1.817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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.474
162.058
145.172
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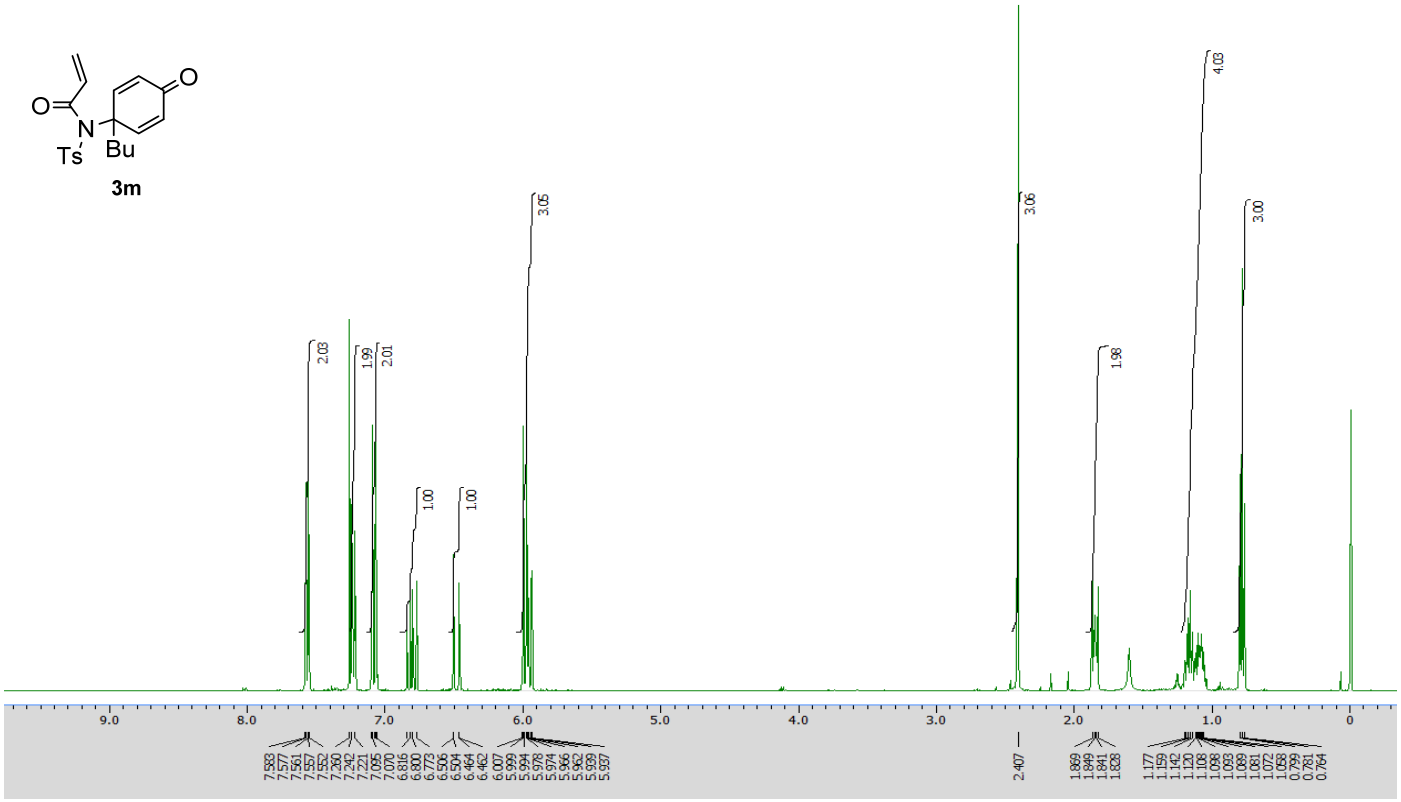
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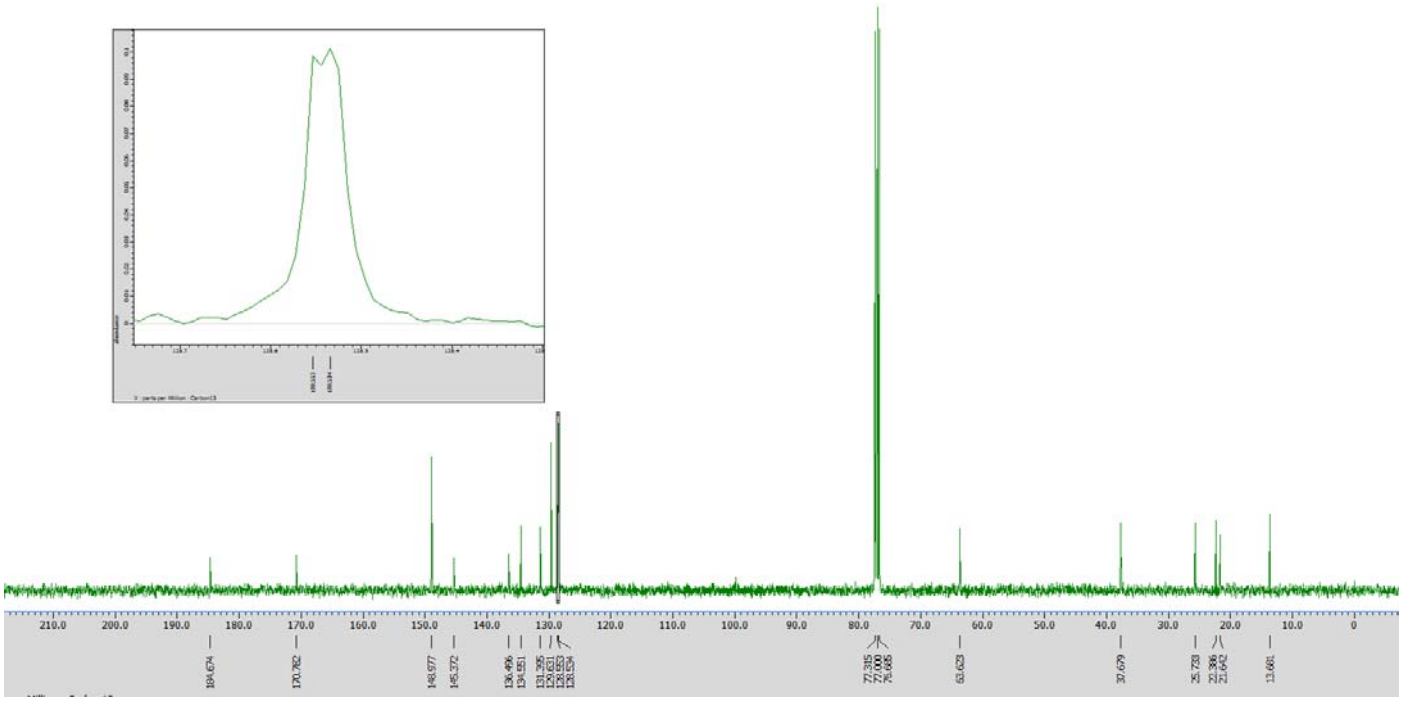

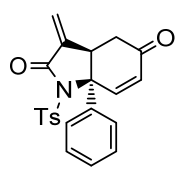
O
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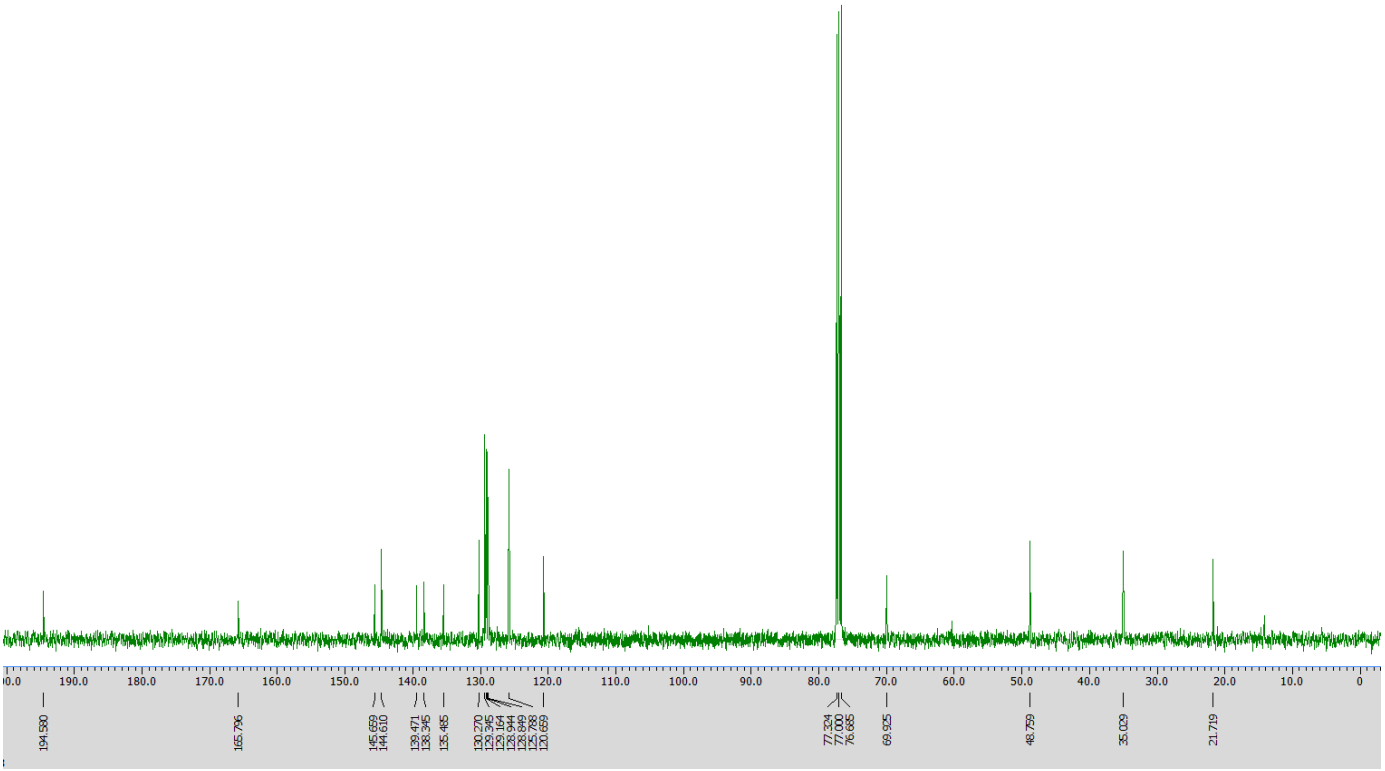
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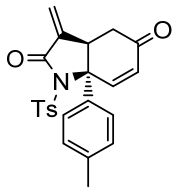

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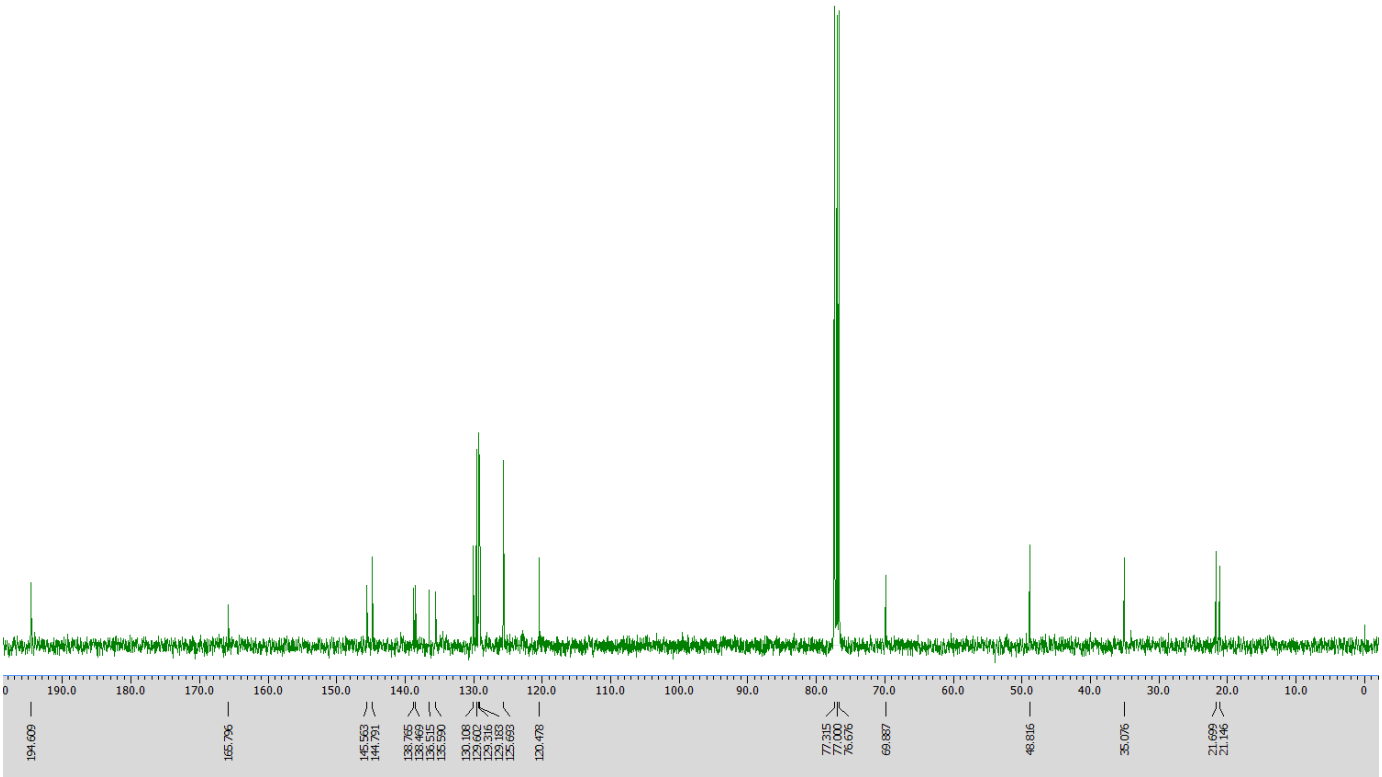

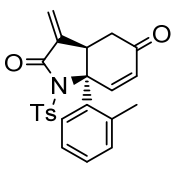

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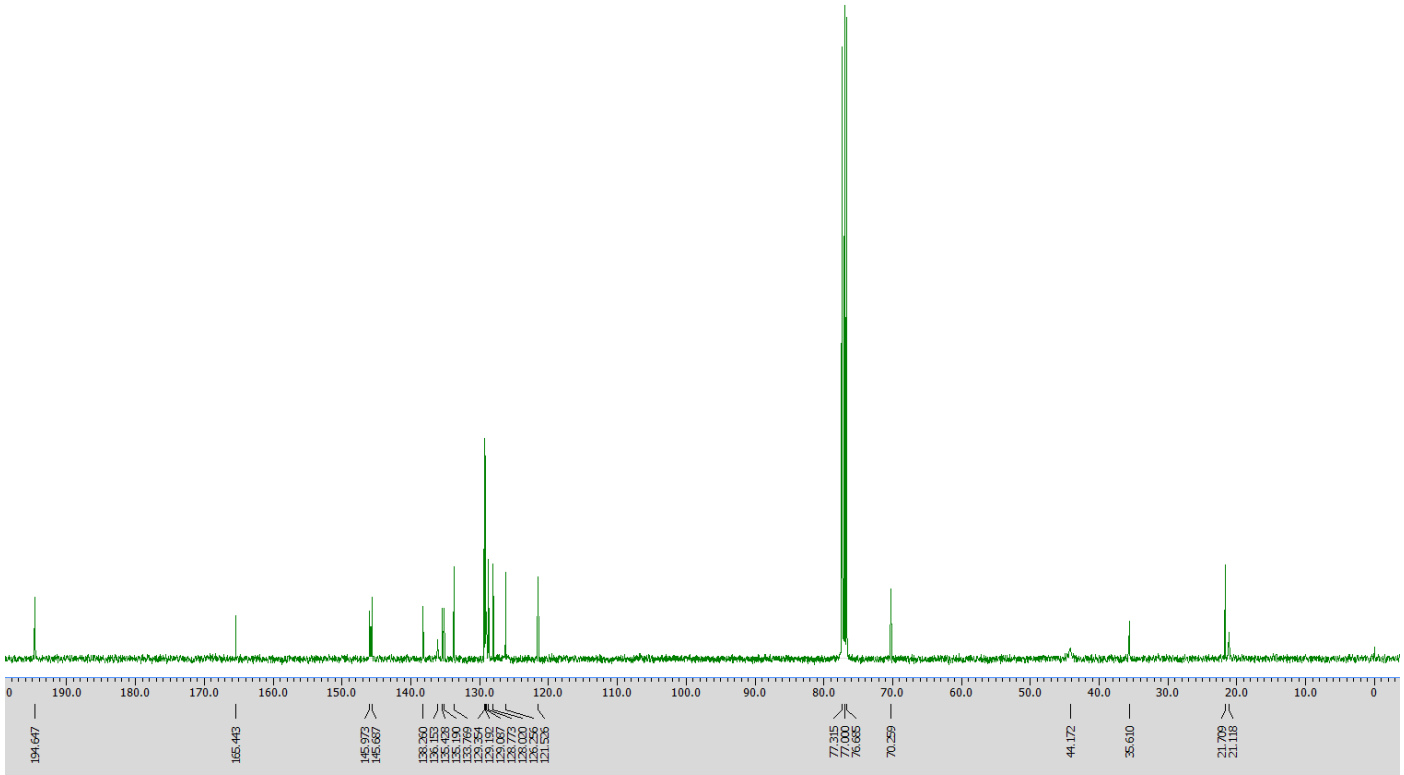

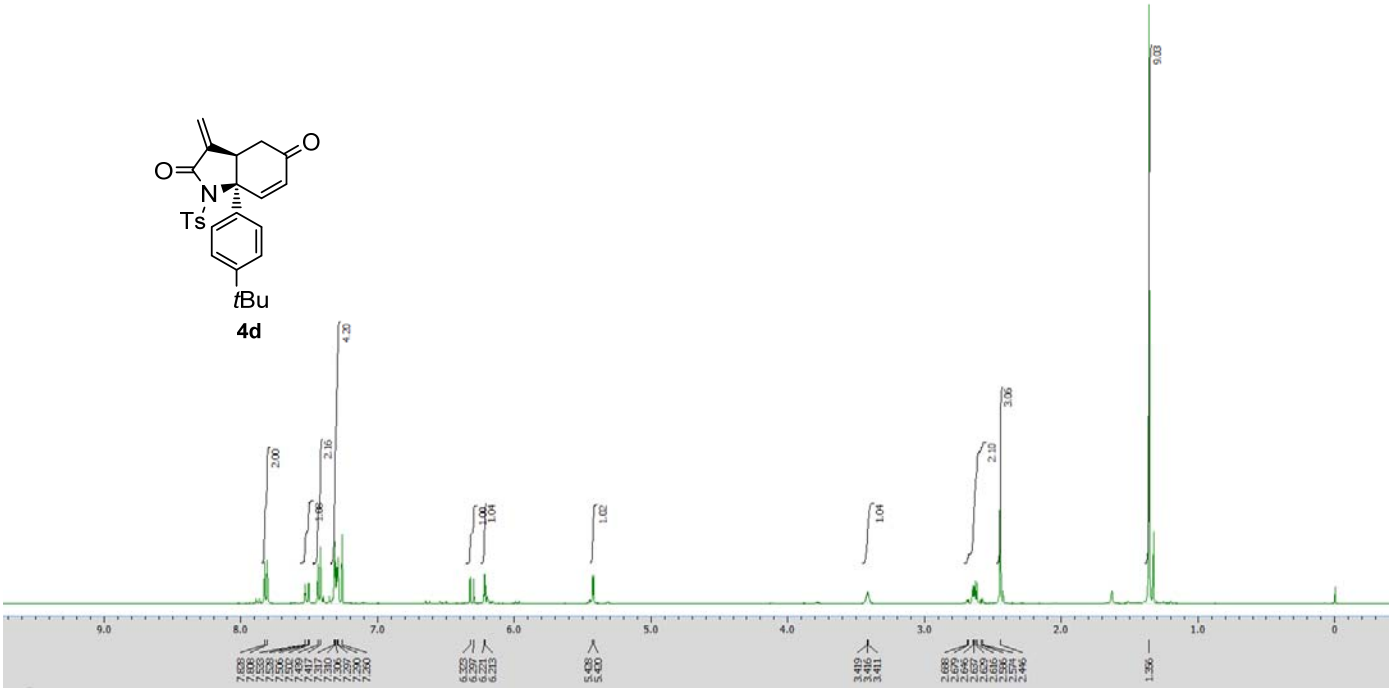

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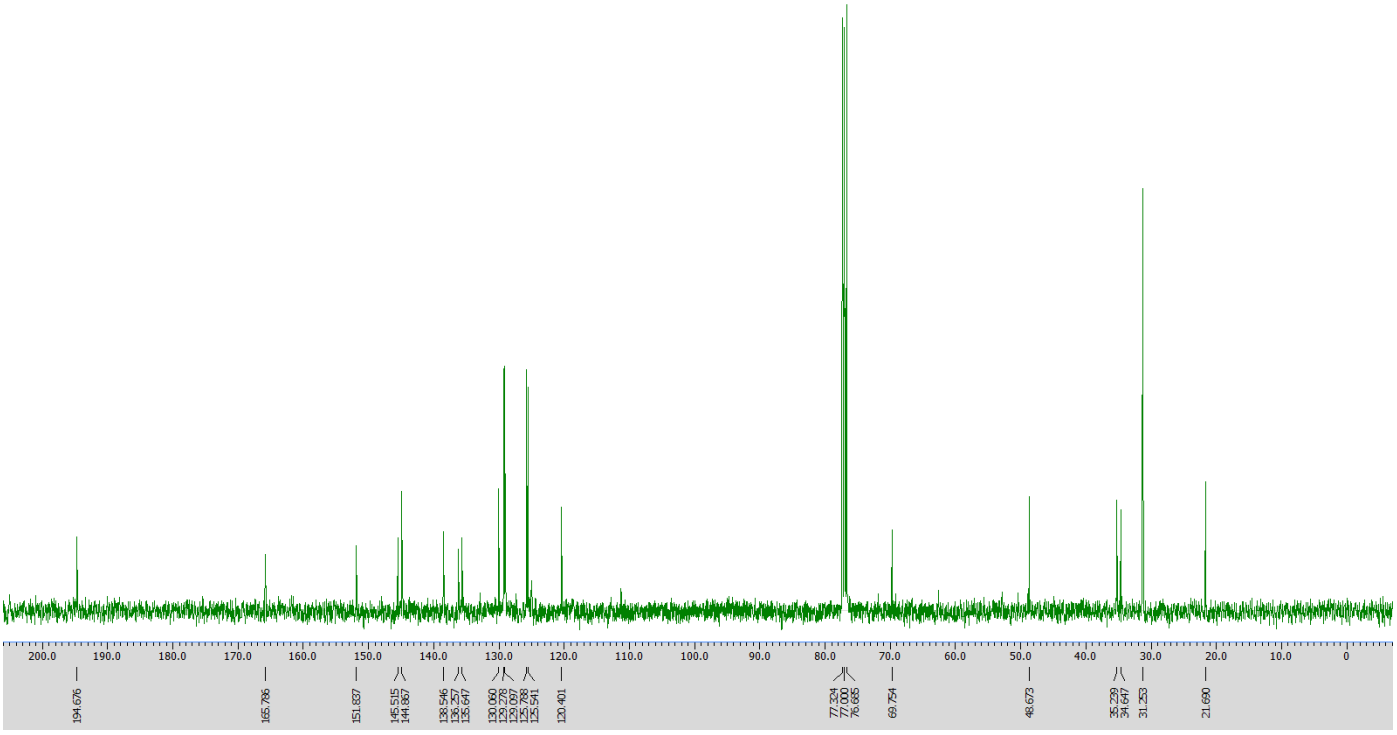

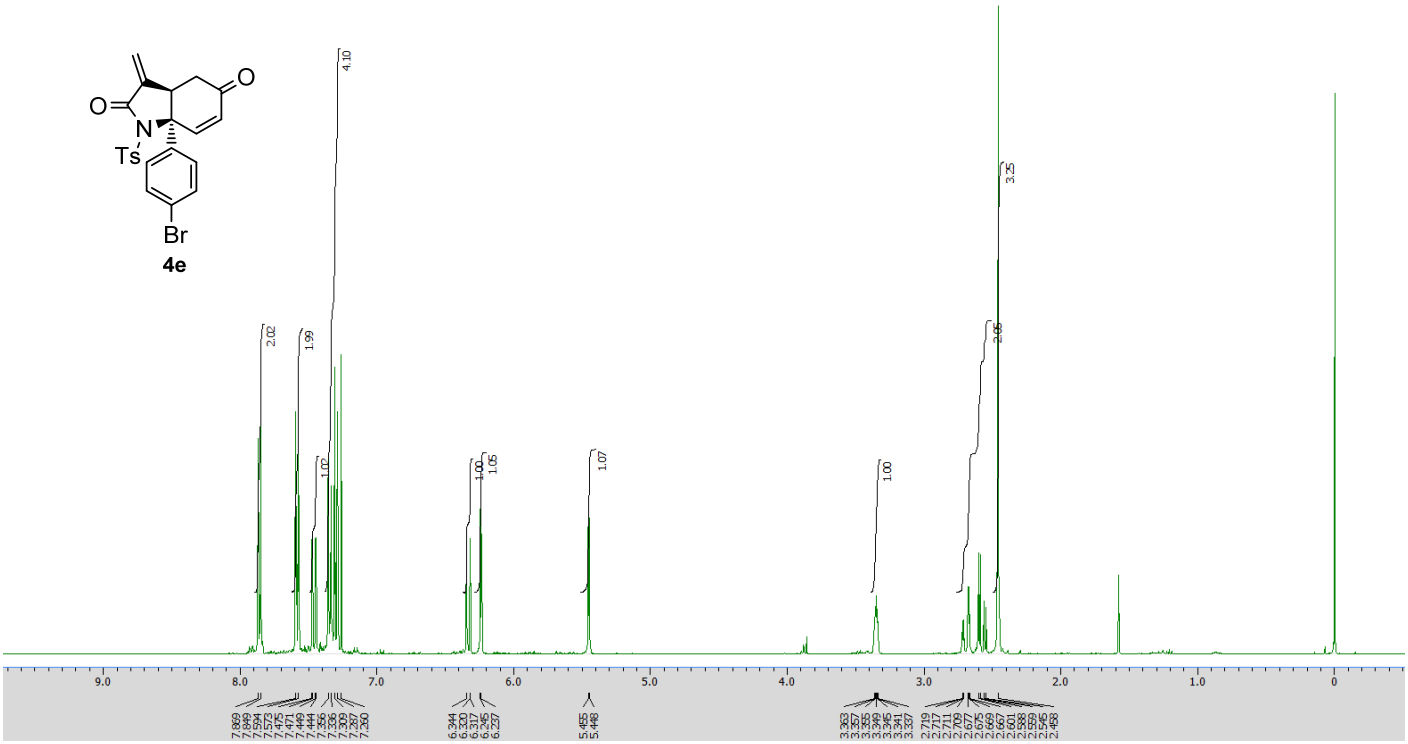
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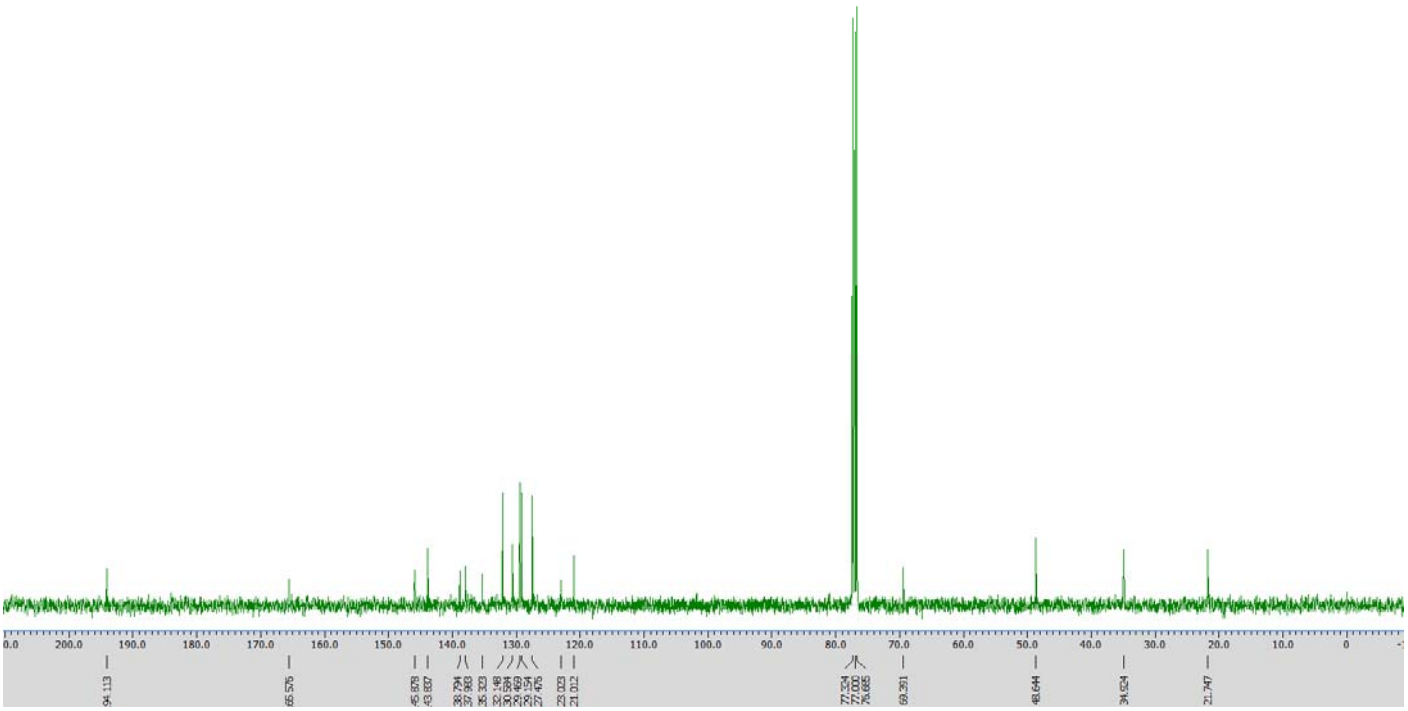

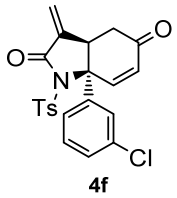

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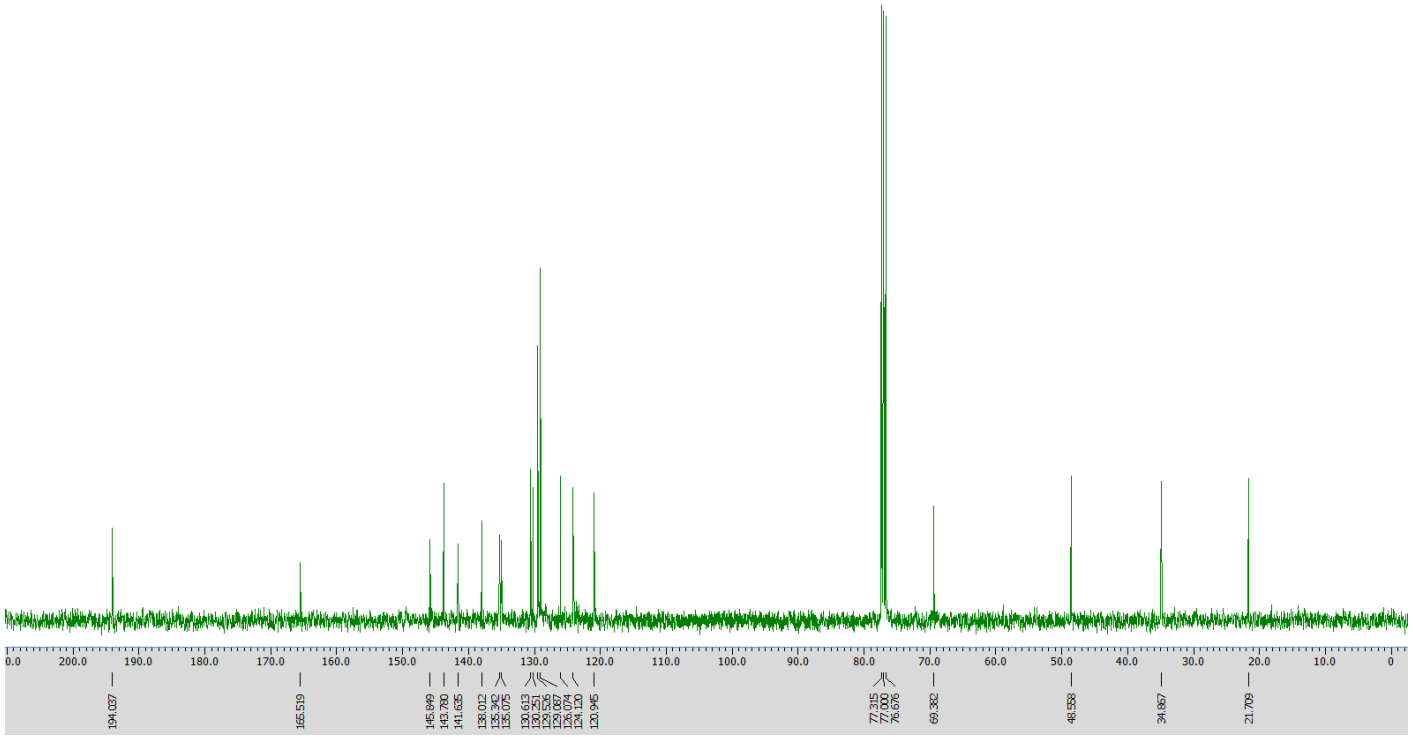

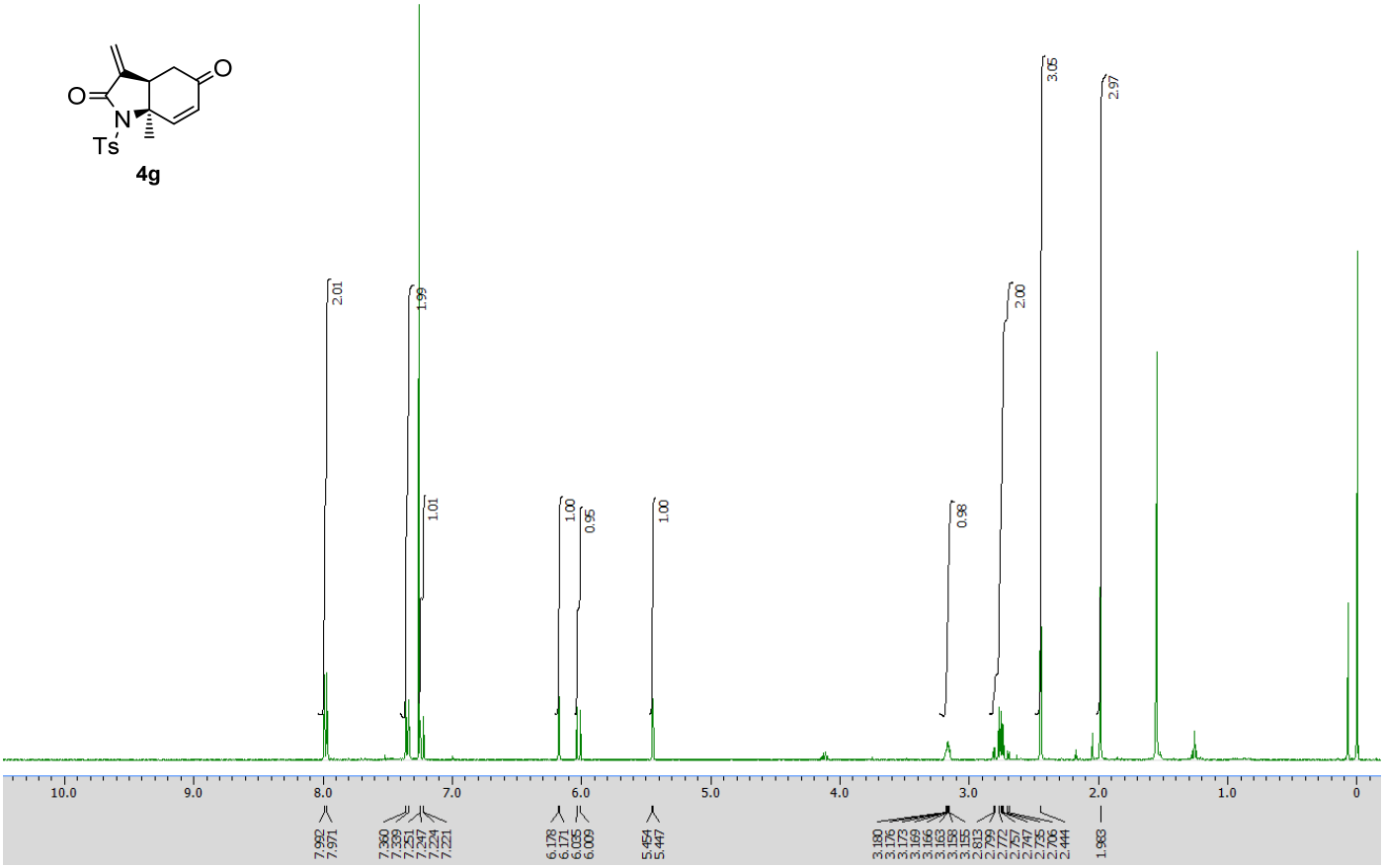
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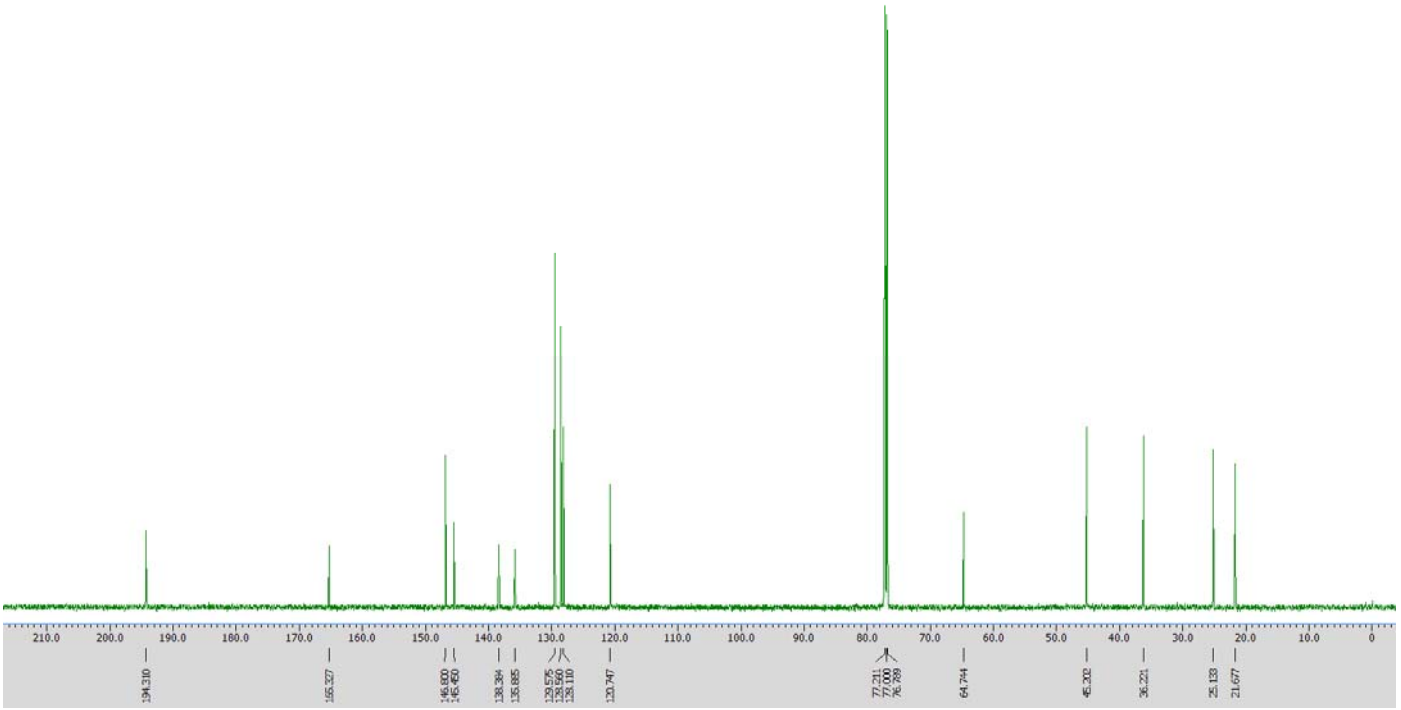

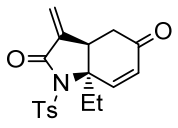
O
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4h

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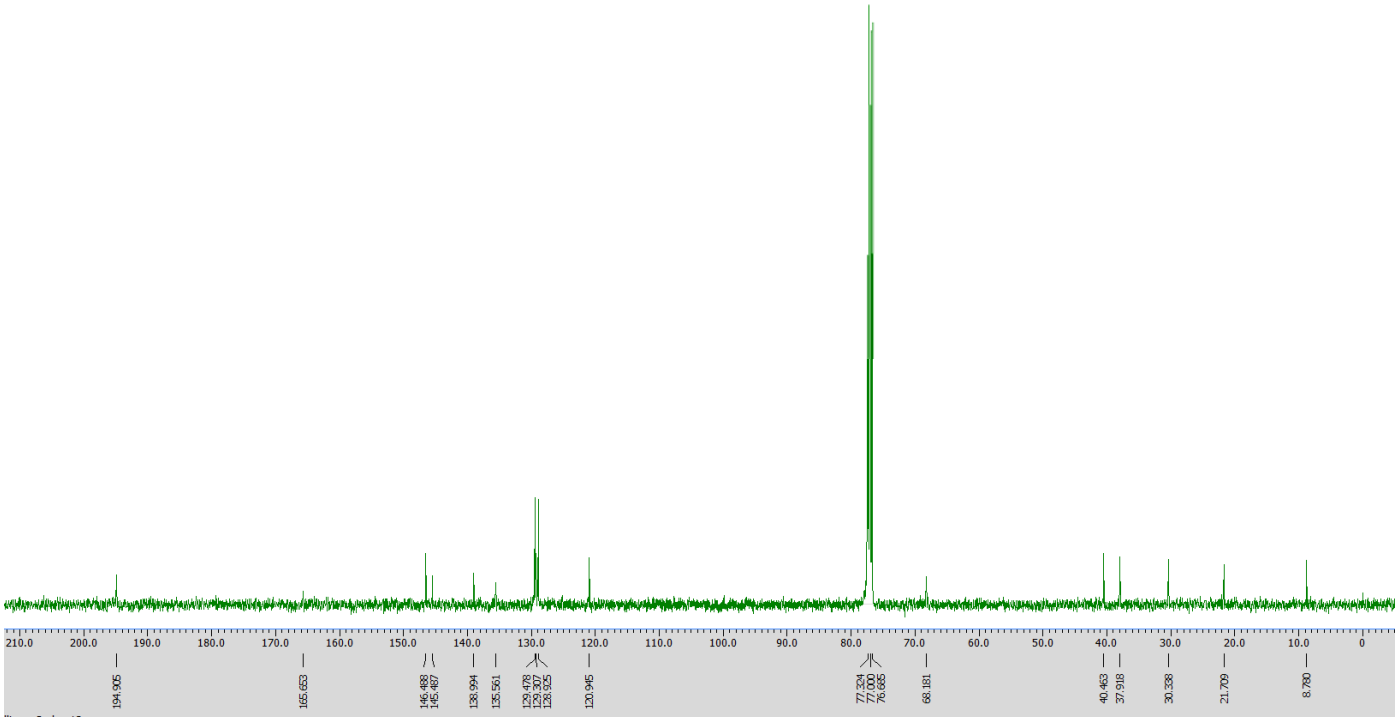
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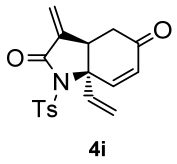
O
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4i

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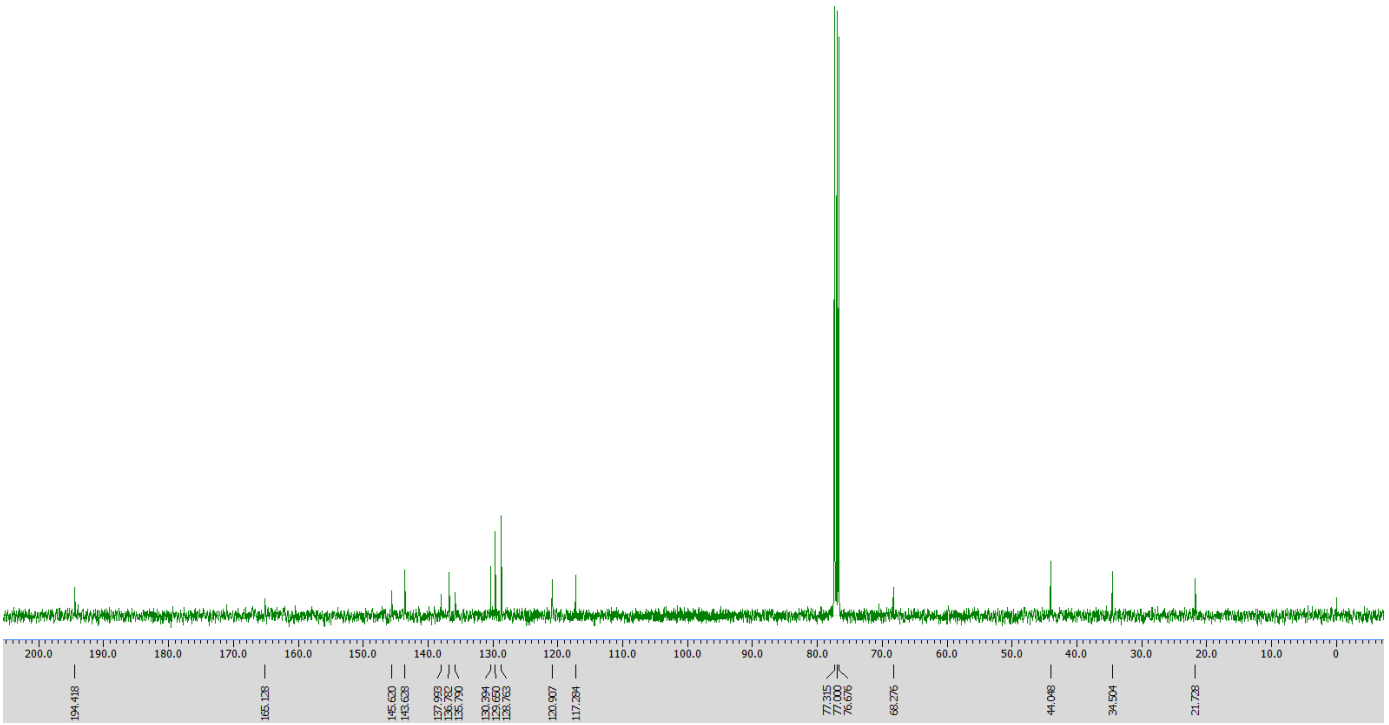
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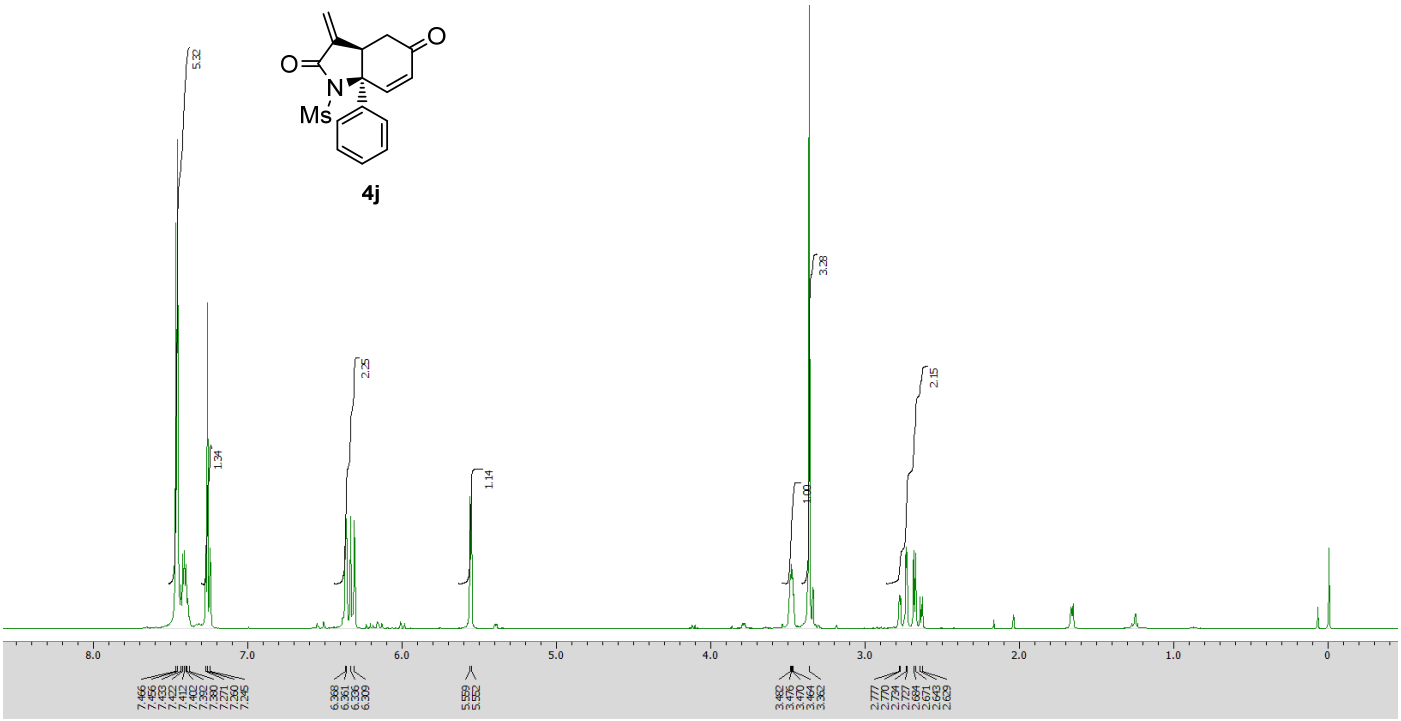
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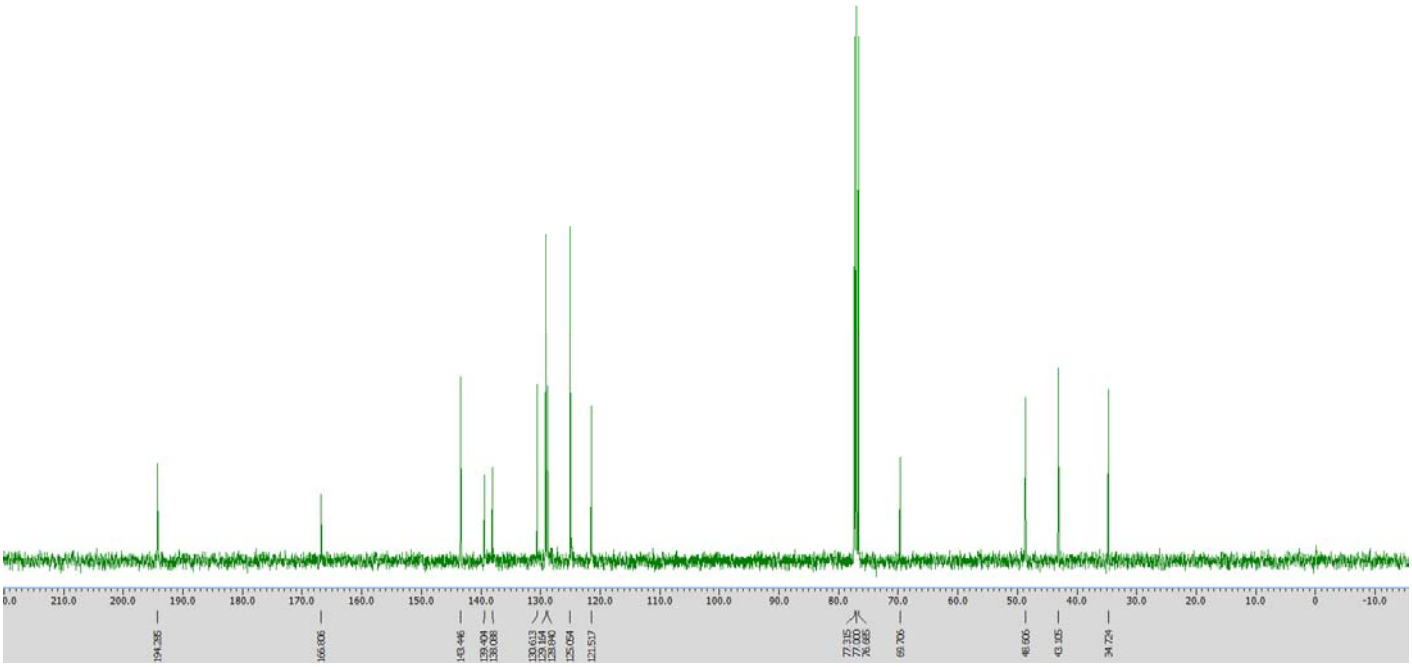
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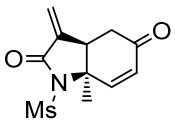
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Ms

4k

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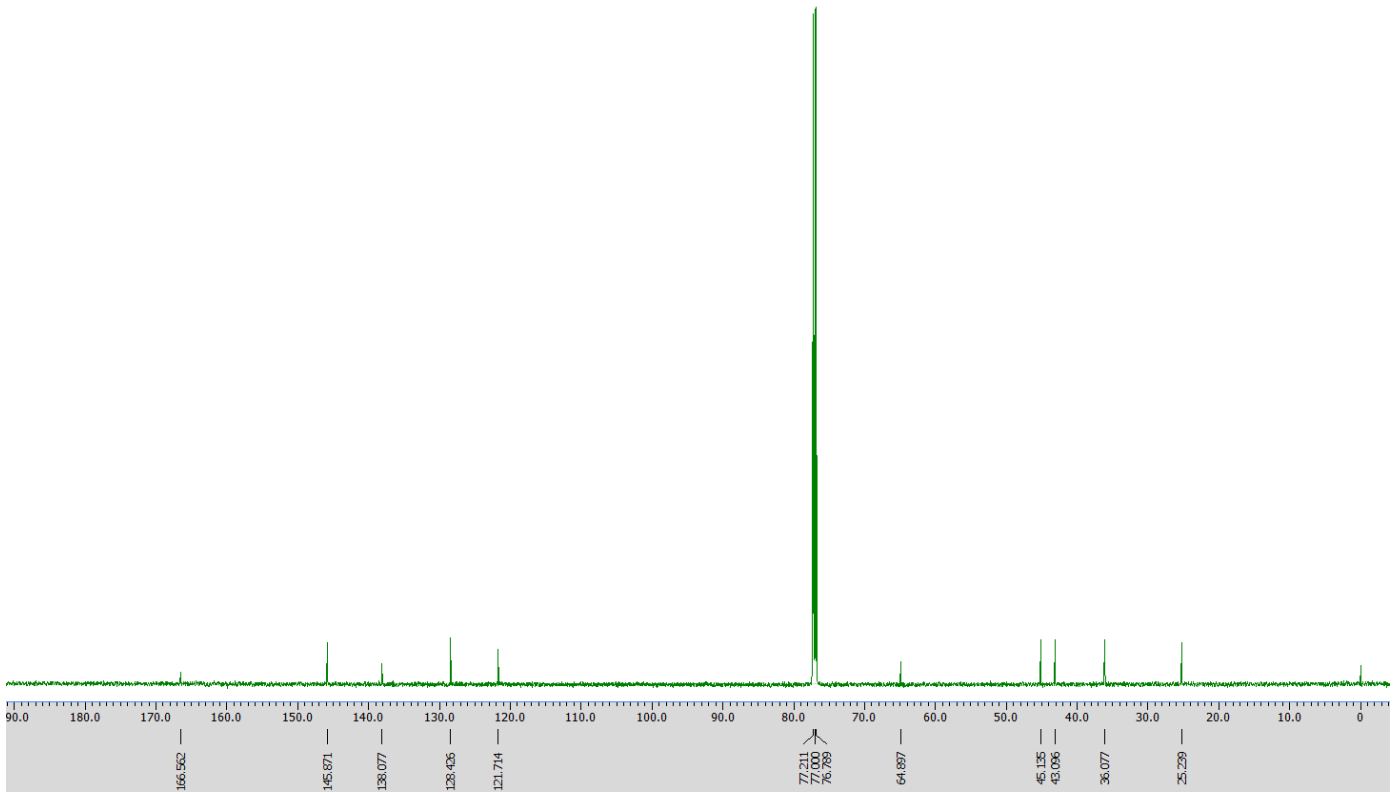
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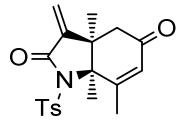
O
O
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Ts

4l

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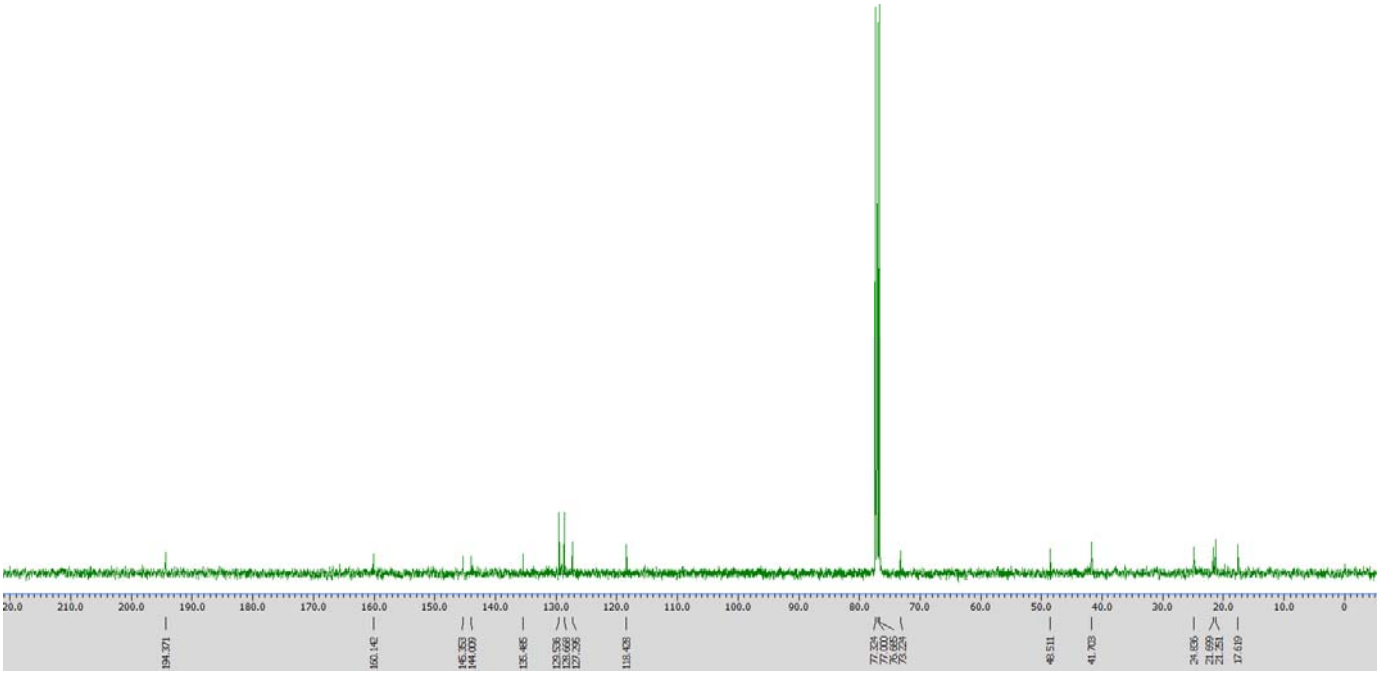
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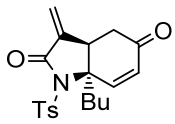

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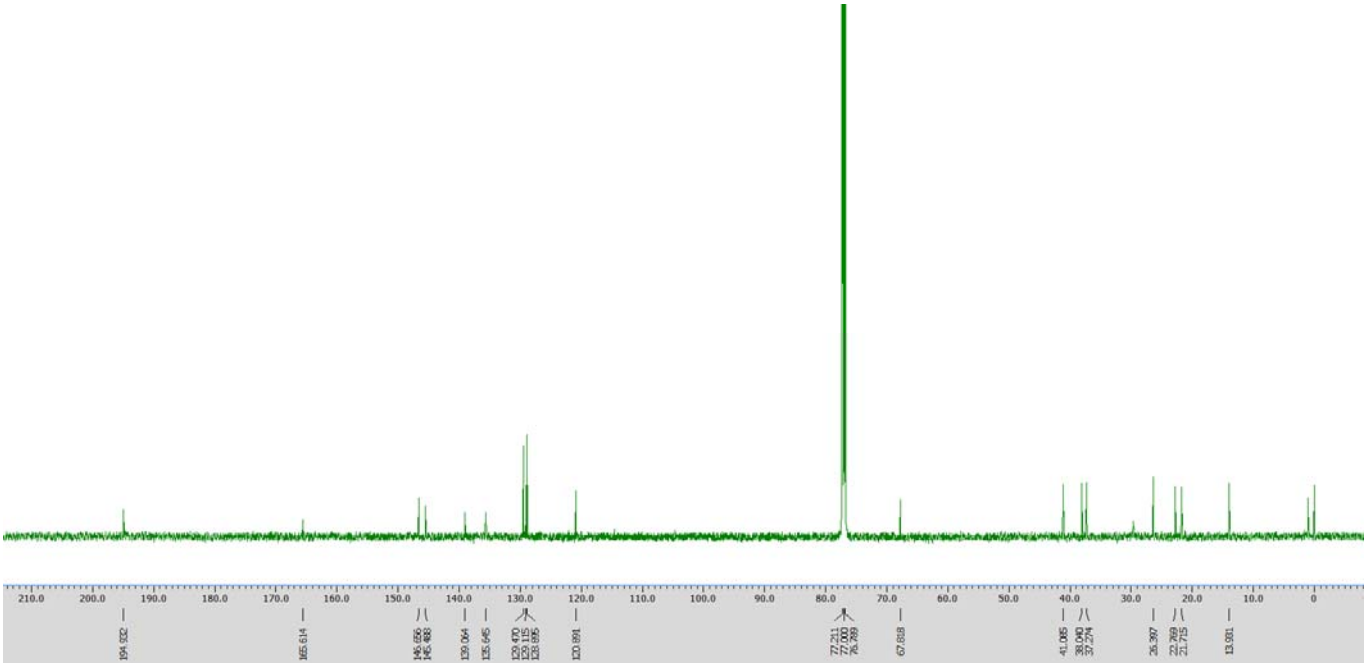

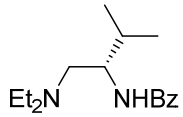

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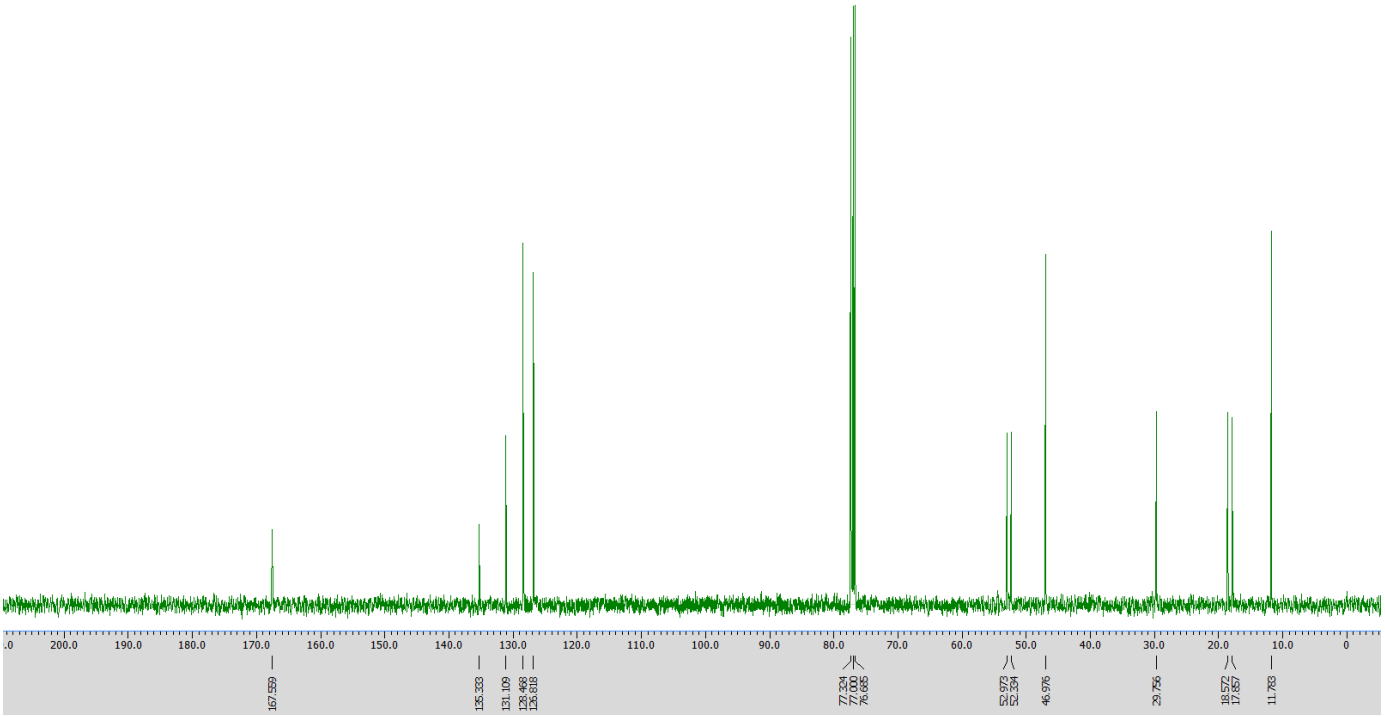
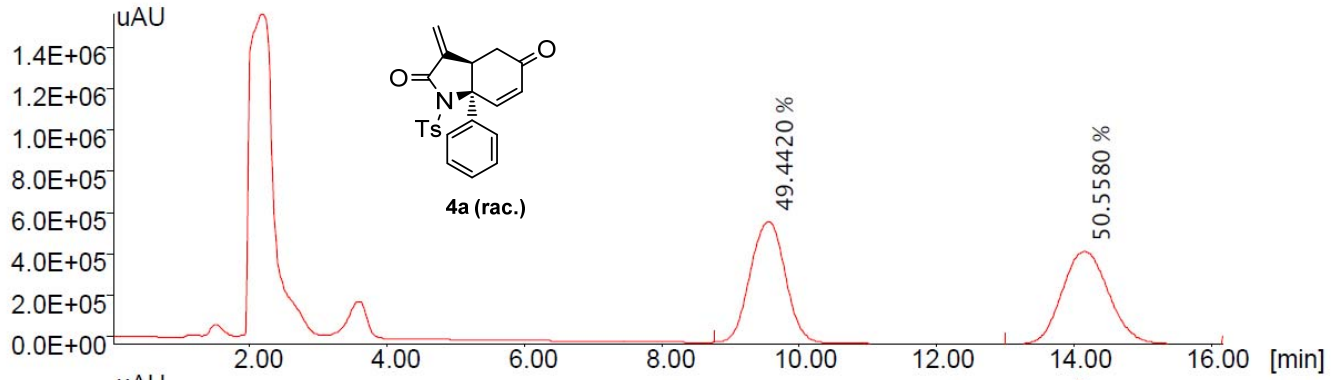
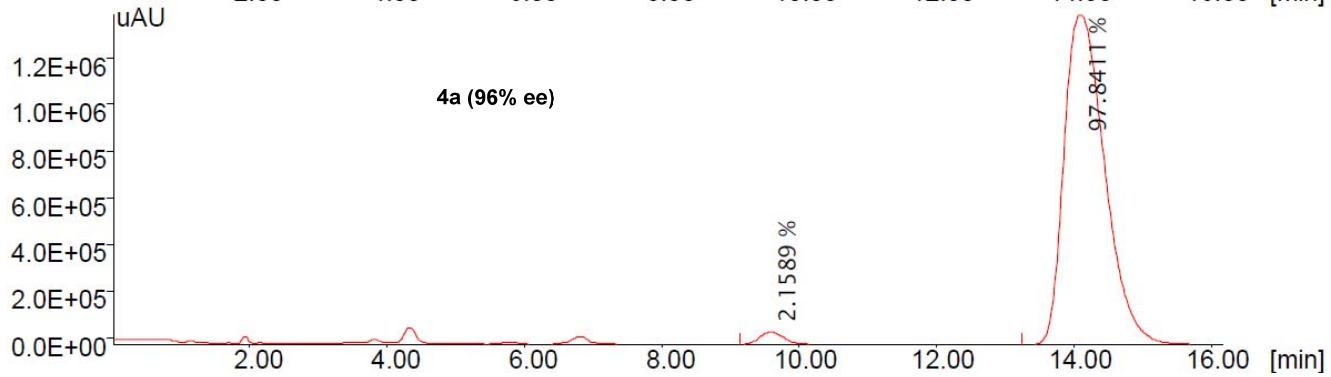
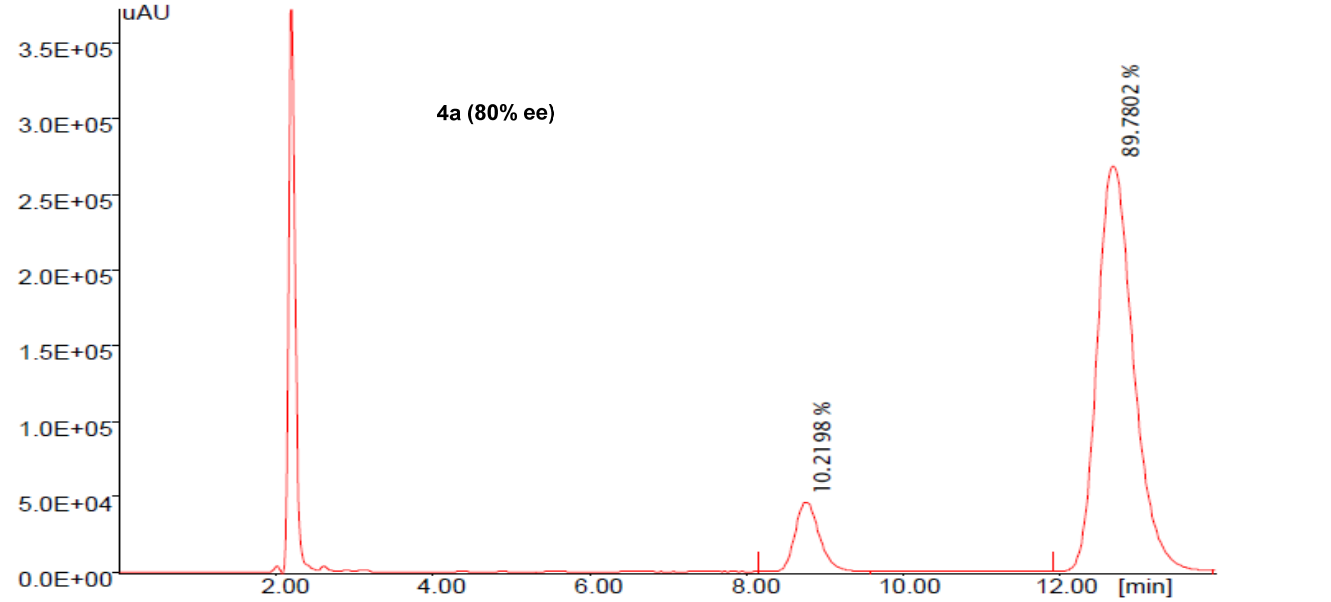


13. HPLC chart







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2		14.133	446529	20550545.906	50.56

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
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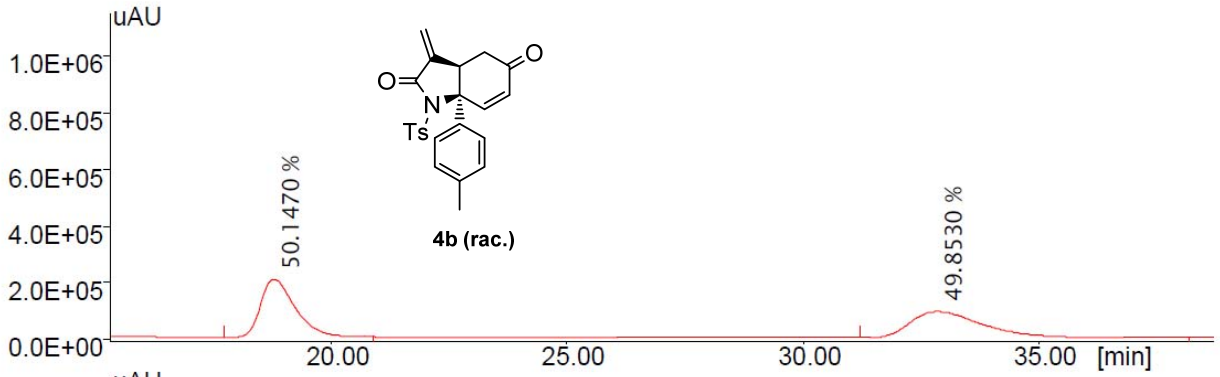
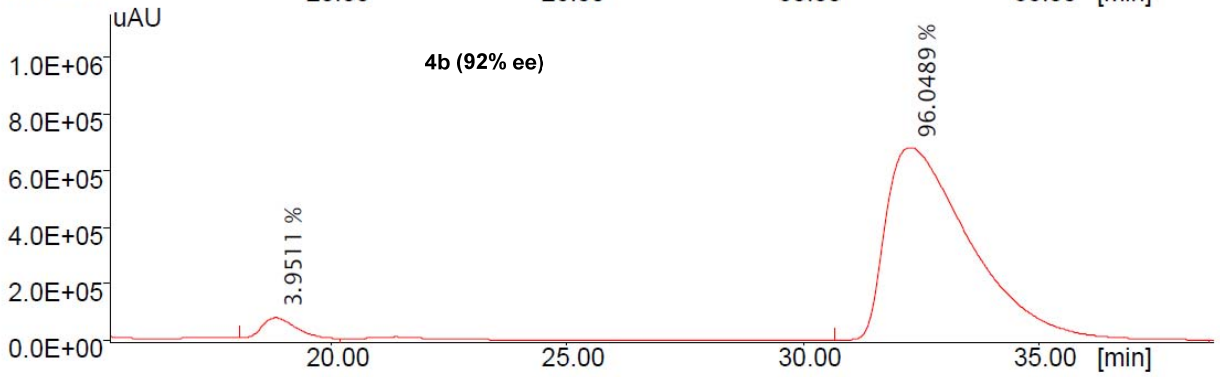
2		14.093	1410261	56568043.515	97.84

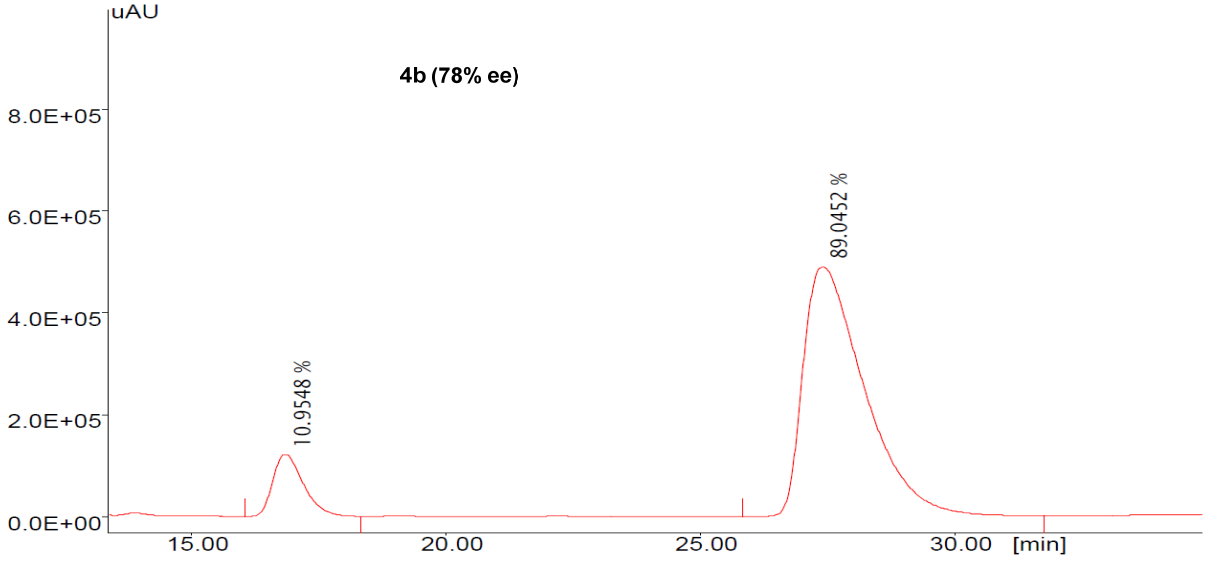
#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		8.760	45952	950077.764	10.22
2		12.680	268360	8346334.924	89.78



4b (rac.)



4b (92% ee)



4b (78% ee)

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2		32.827	93880	10076496.150	49.85

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
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#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
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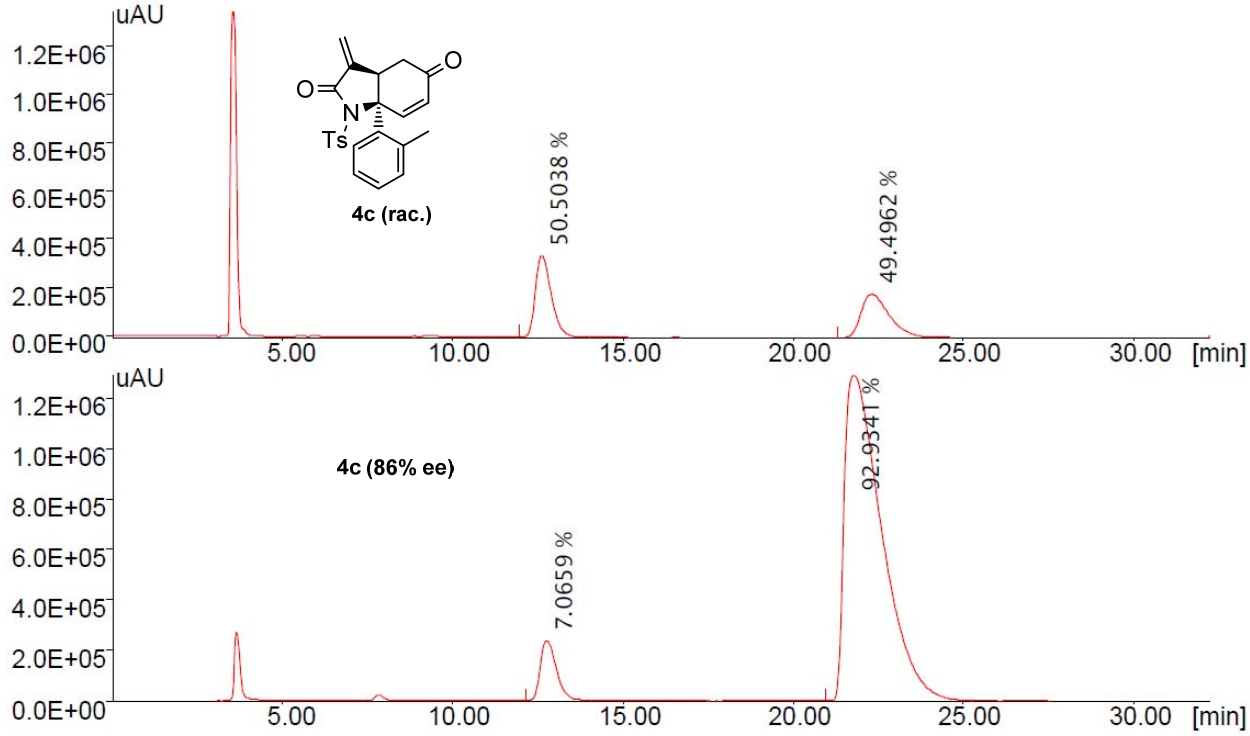

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2		22.280	178493	9955284.519	49.50

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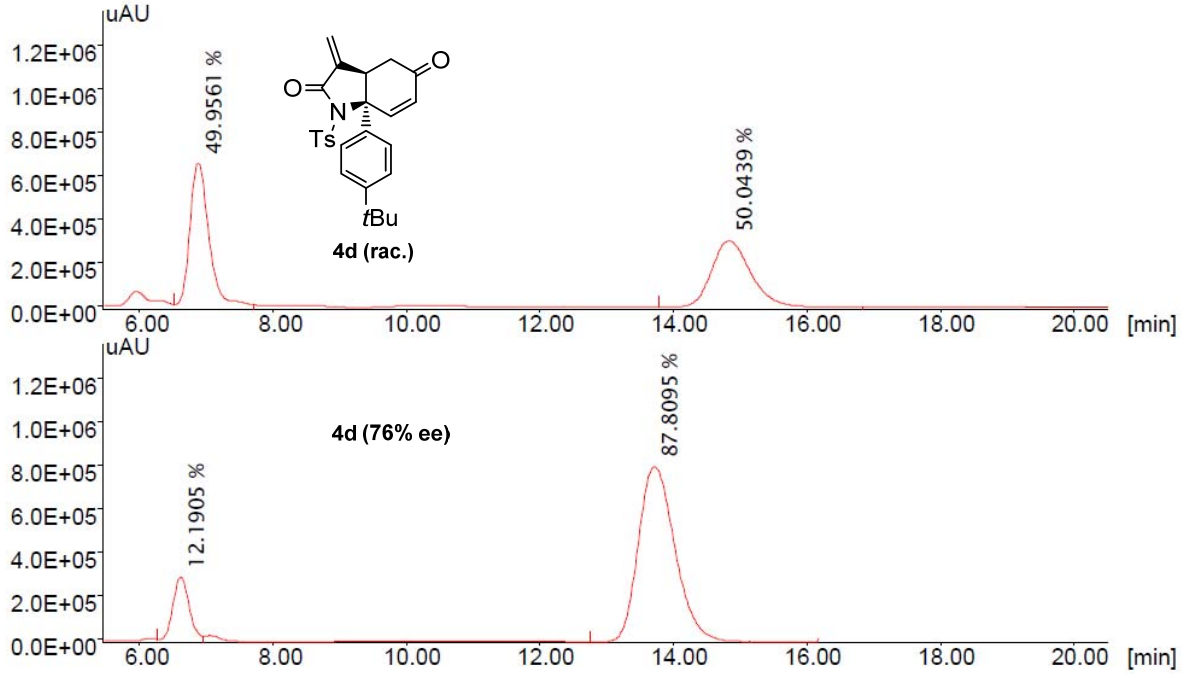
2		21.773	1287561	95190047.418	92.93



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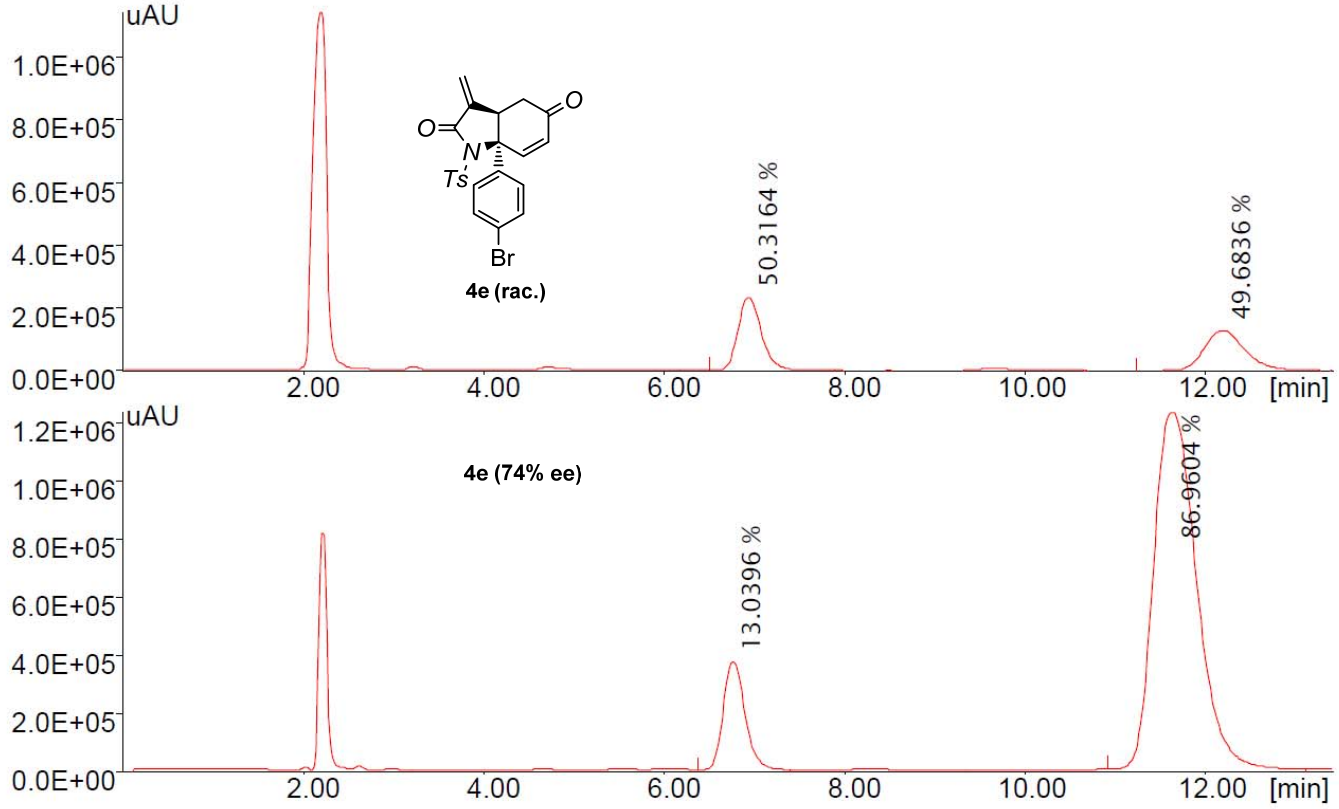
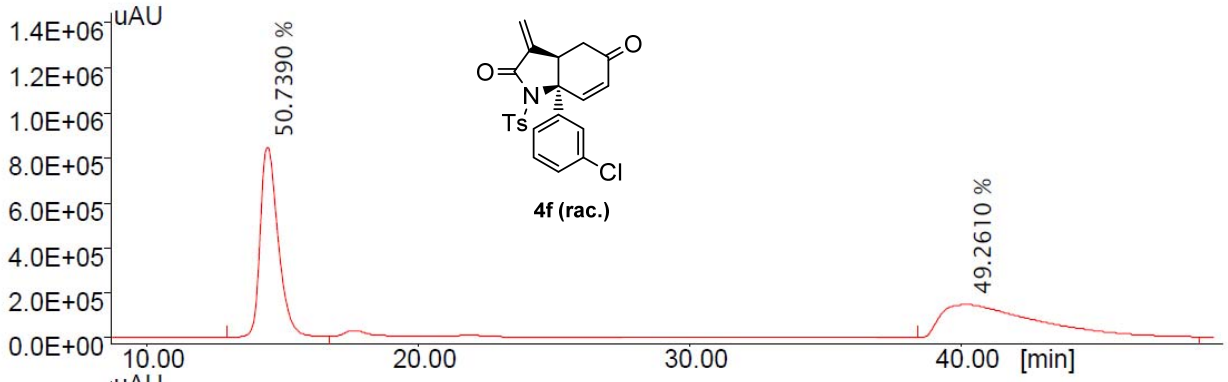
2		13.707	804244	29861253.839	87.81

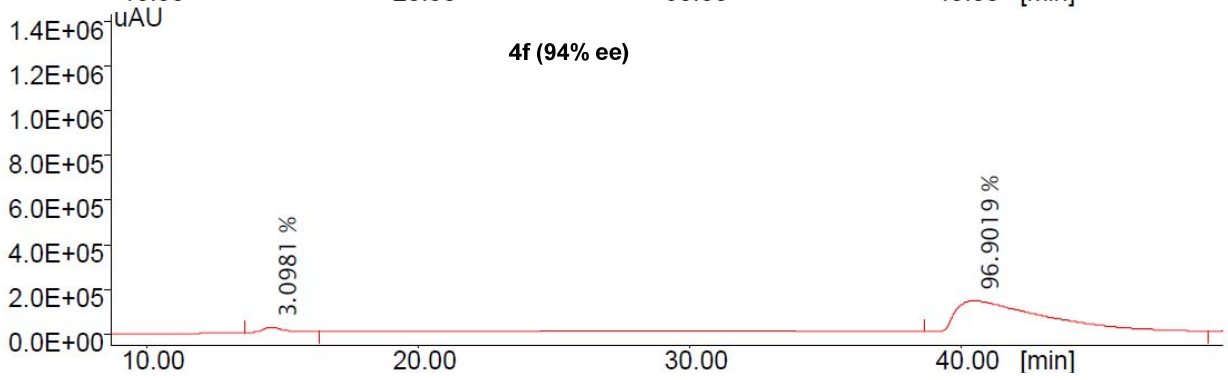


#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		6.947	233527	3970979.936	50.32
2		12.200	128469	3921046.458	49.68

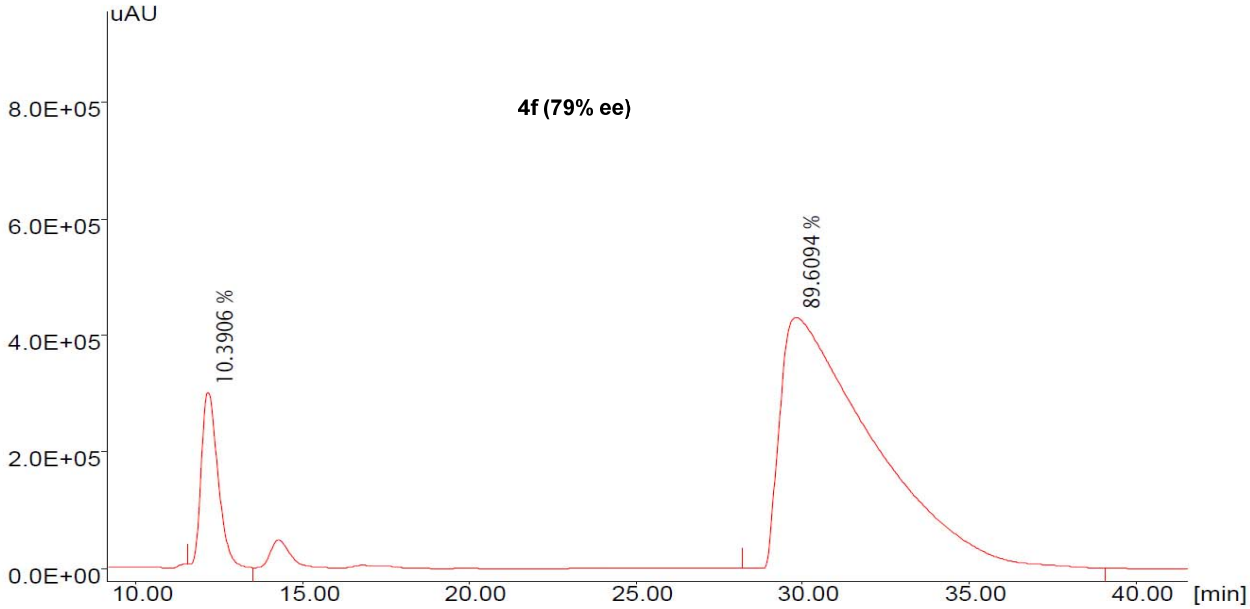
#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		6.773	371257	5871029.687	13.04
2		11.640	1223367	39153540.983	86.96



4f (rac.)



4f (94% ee)

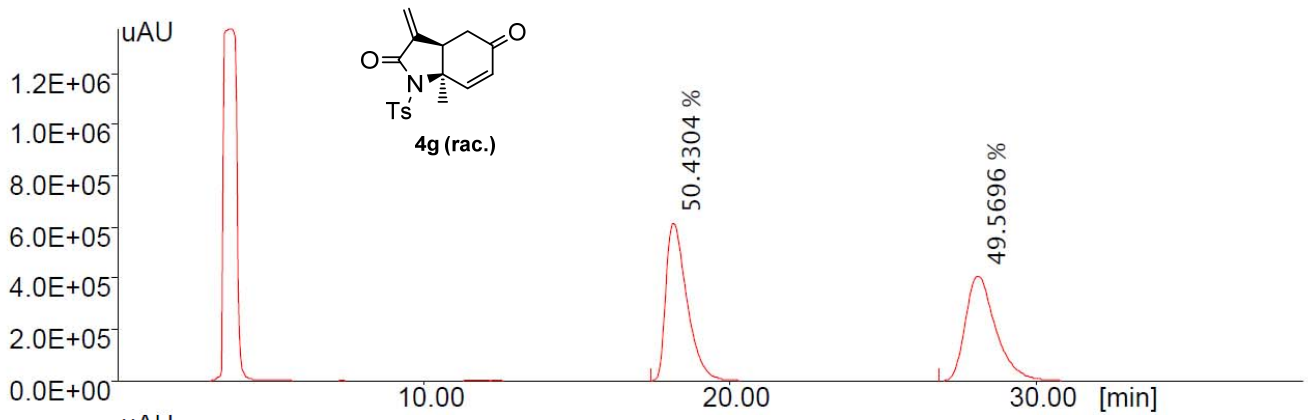


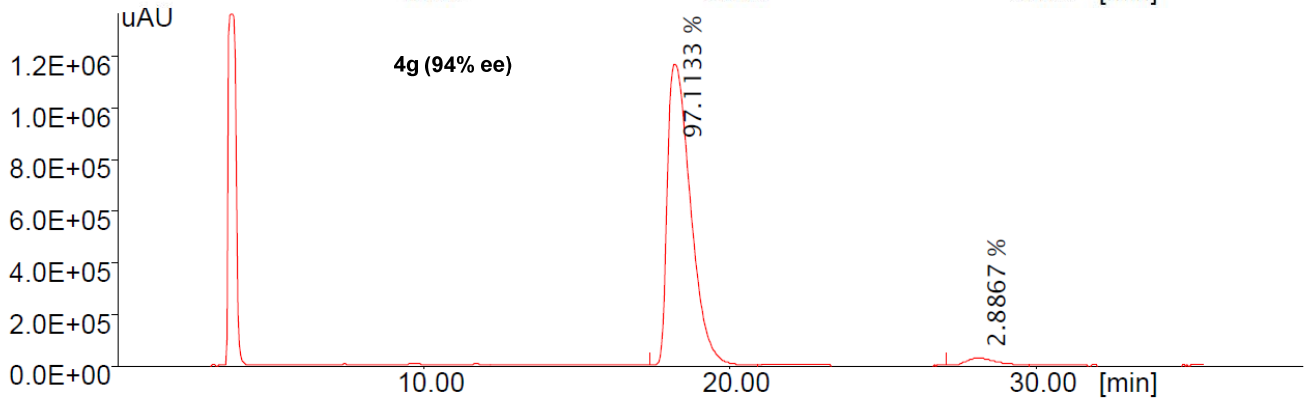
4f (79% ee)

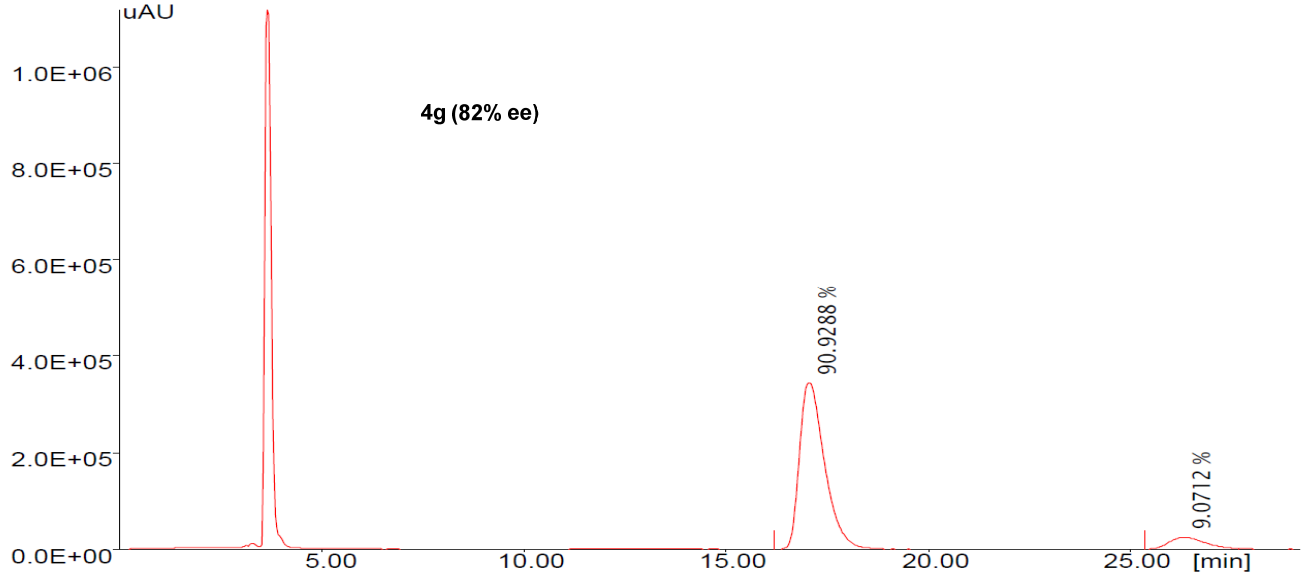
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		14. 427	840613	36228824. 497	50. 74
2		40. 147	145343	35173457. 324	49. 26

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		14. 573	21695	971896. 014	3. 10
2		40. 453	138148	30399156. 432	96. 90

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		12. 147	295724	9530832. 732	10. 39
2		29. 773	430333	82194808. 419	89. 61



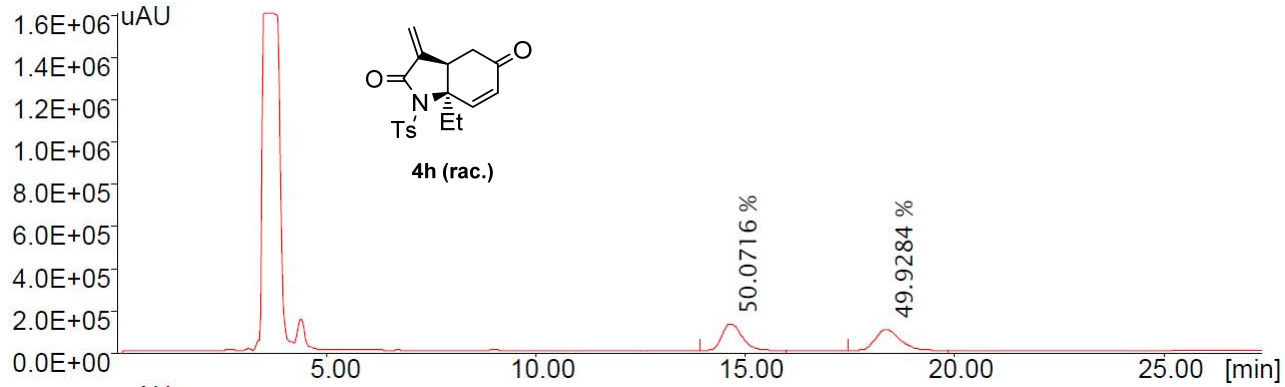


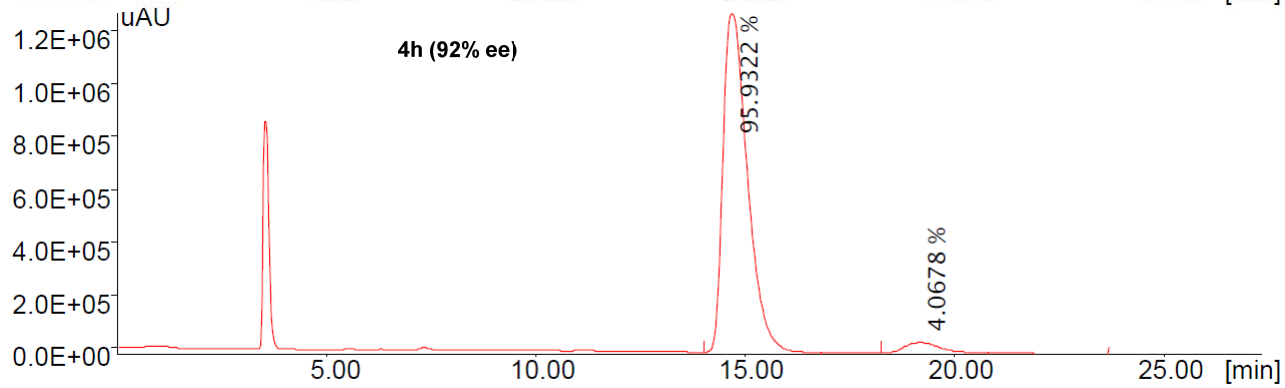


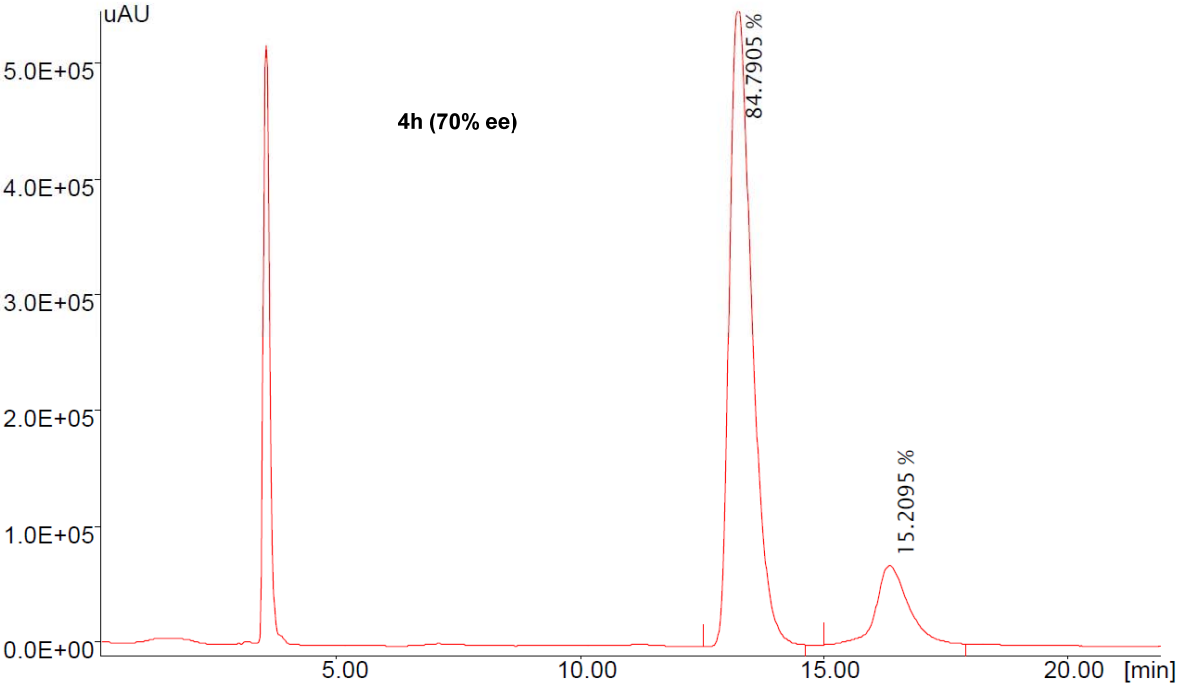
#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		18.133	613150	27859098.015	50.43
2		28.080	410582	27383544.809	49.57

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		18.187	1162312	58283592.868	97.11
2		28.093	27395	1732492.826	2.89

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		17.040	344297	14146381.811	90.93
2		26.293	24152	1411271.221	9.07



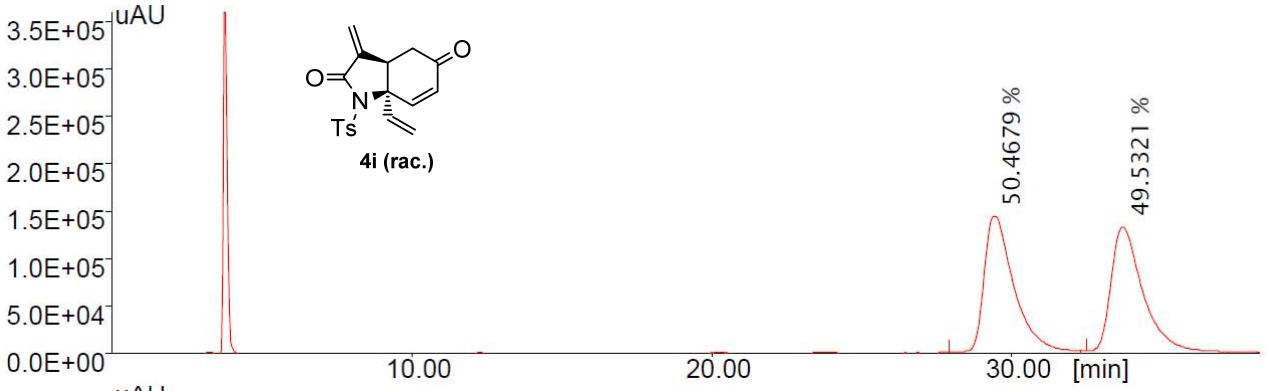


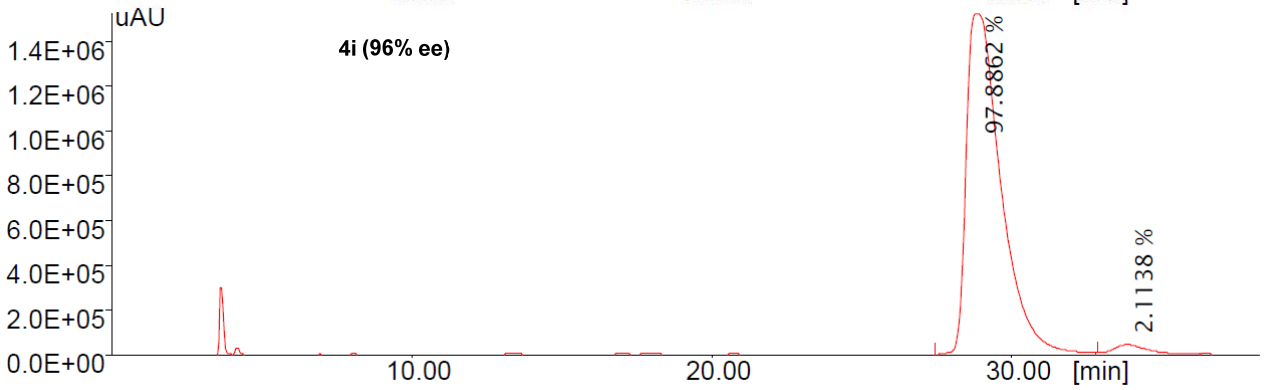


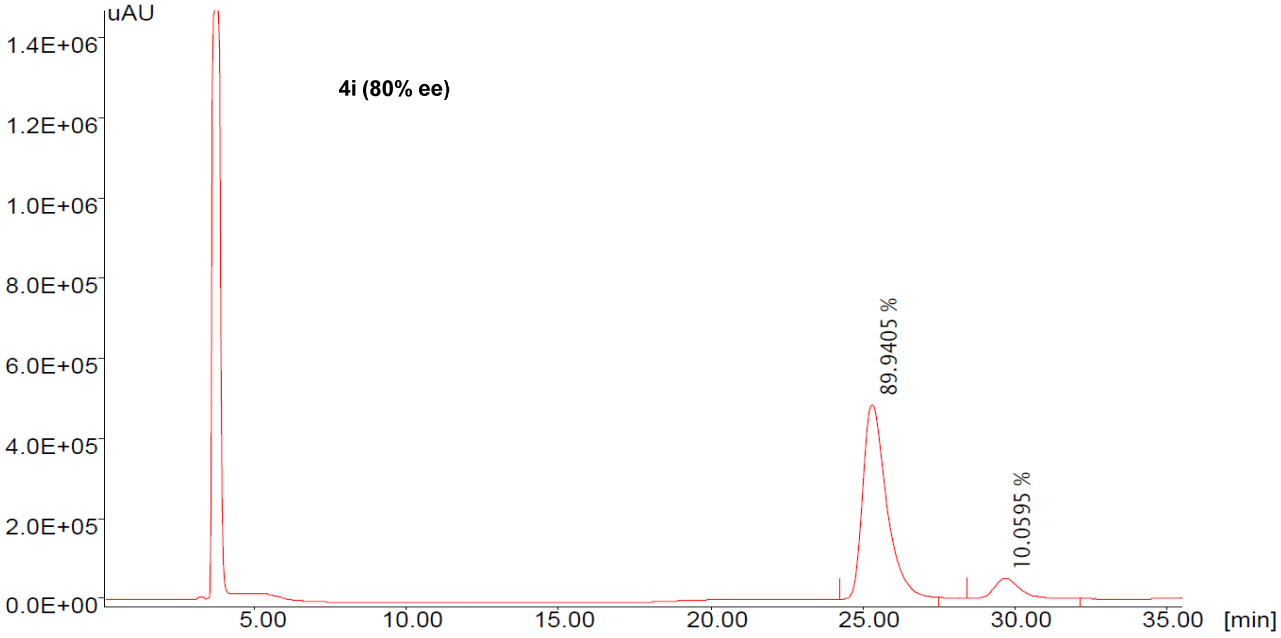
#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		14.640	125089	3898111.258	50.07
2		18.360	98438	3886970.458	49.93

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		14.667	1283043	49730612.341	95.93
2		19.147	37429	2108695.382	4.07

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		13.227	549000	16844465.728	84.79
2		16.333	67747	3021516.845	15.21



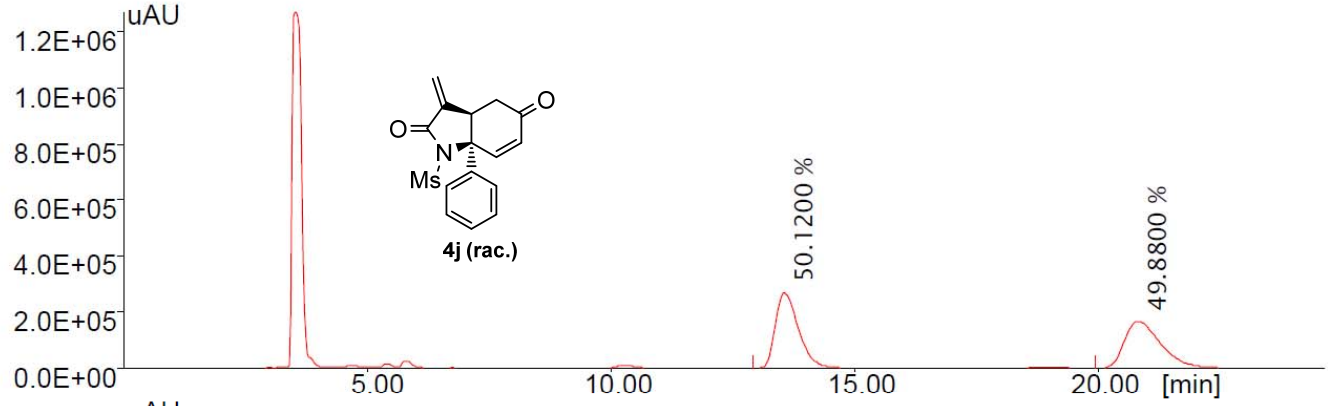


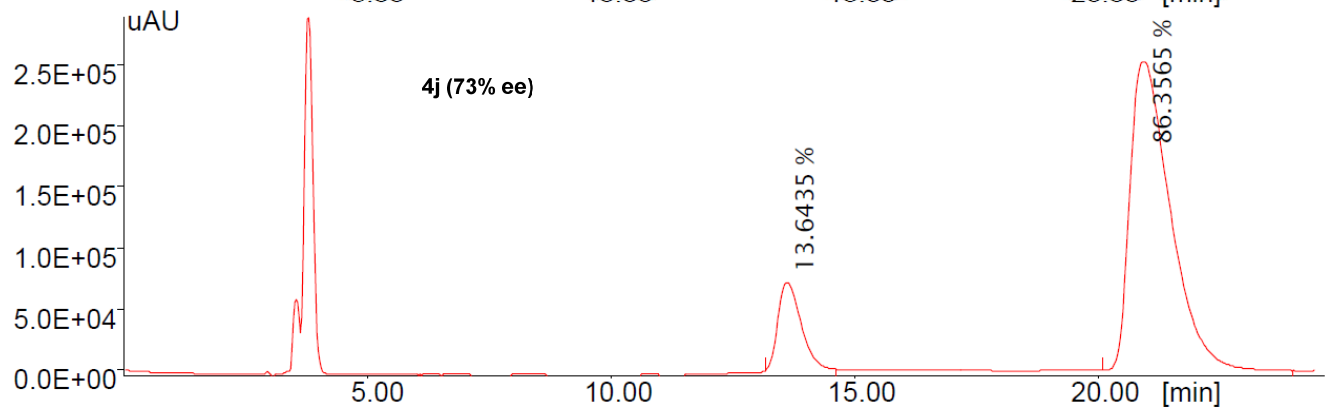


#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		29. 413	143779	9407331. 340	50. 47
2		33. 693	130658	9232909. 738	49. 53

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		28. 840	1521625	117079798. 940	97. 89
2		33. 827	37857	2528297. 438	2. 11

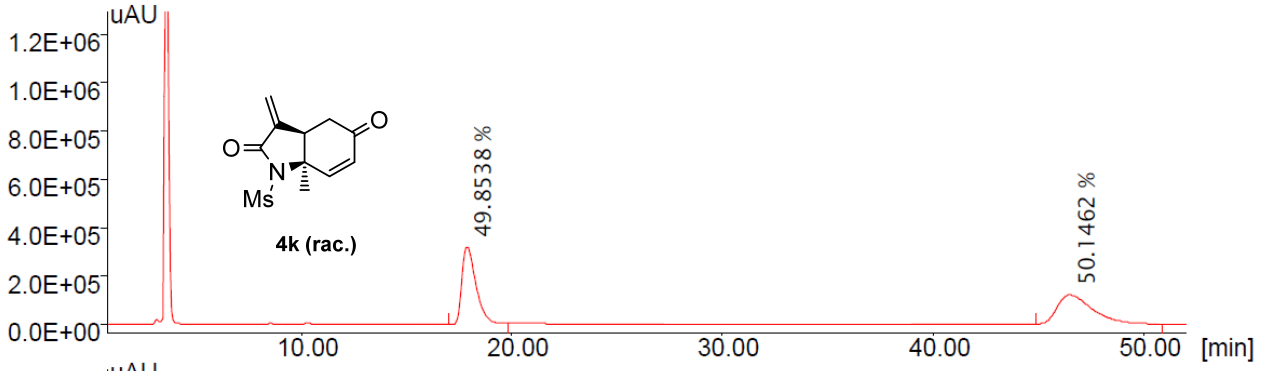
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		25. 293	482673	24870798. 069	89. 94
2		29. 667	50344	2781695. 869	10. 06

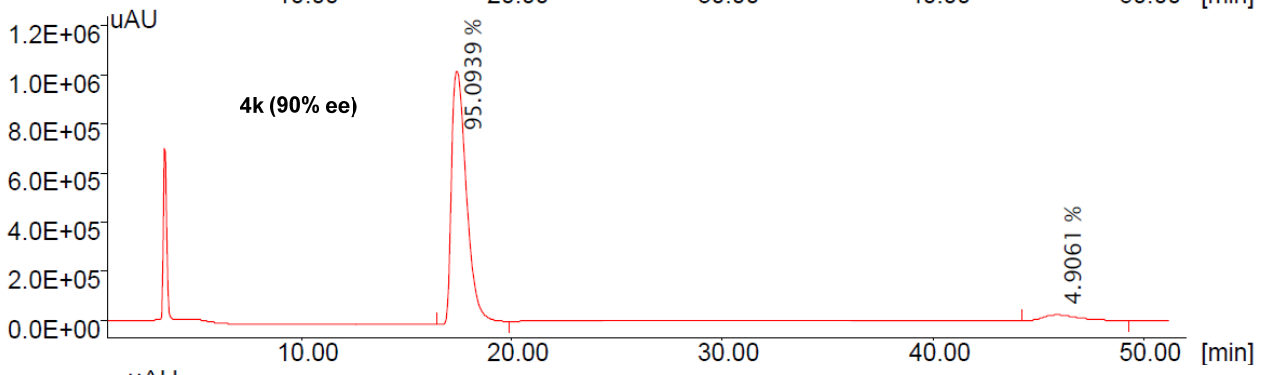


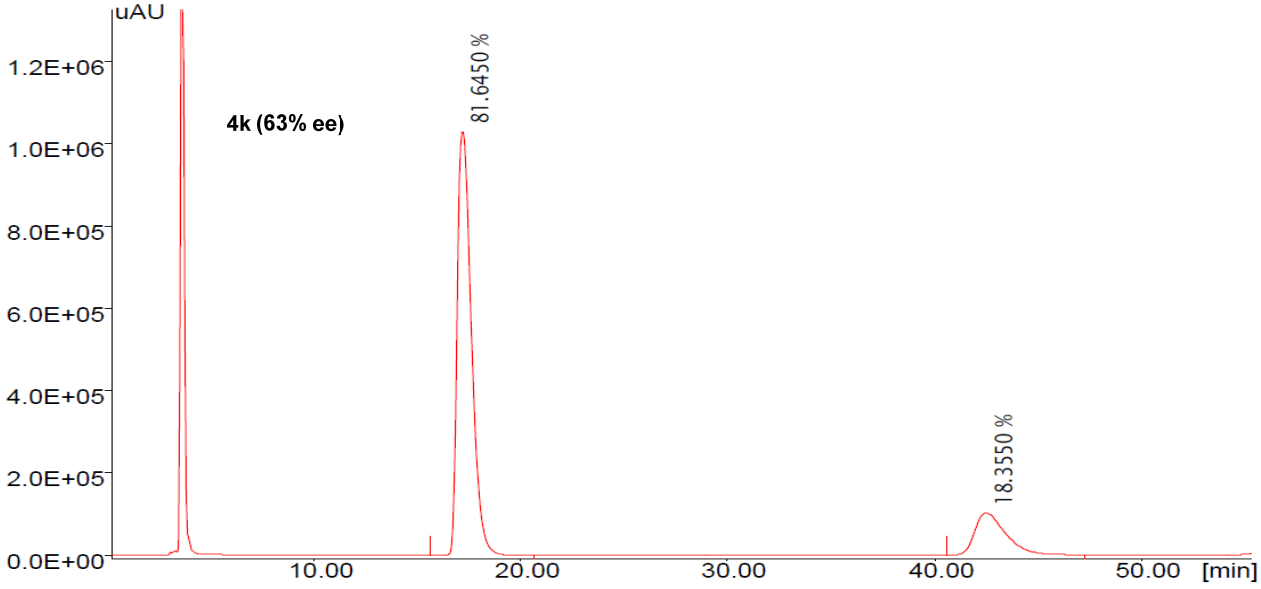


#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		13.560	267630	8452742.926	50.12
2		20.827	166091	8412256.925	49.88

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		13.627	71818	2230404.033	13.64
2		20.960	252684	14117326.610	86.36



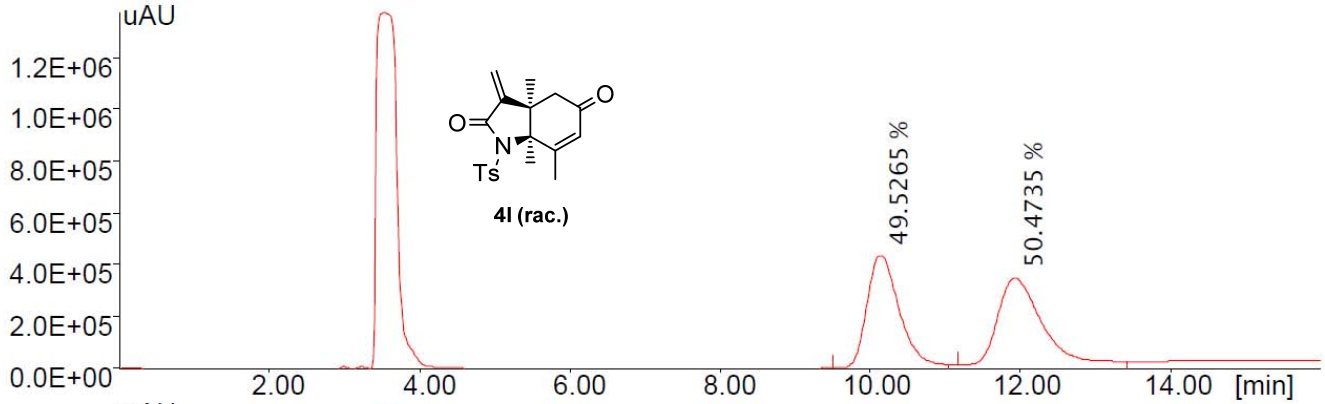


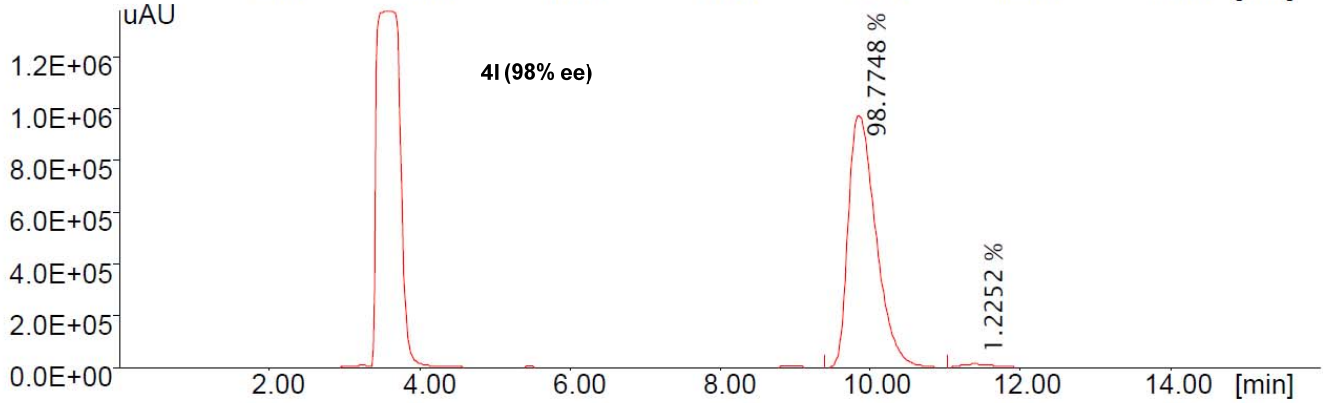


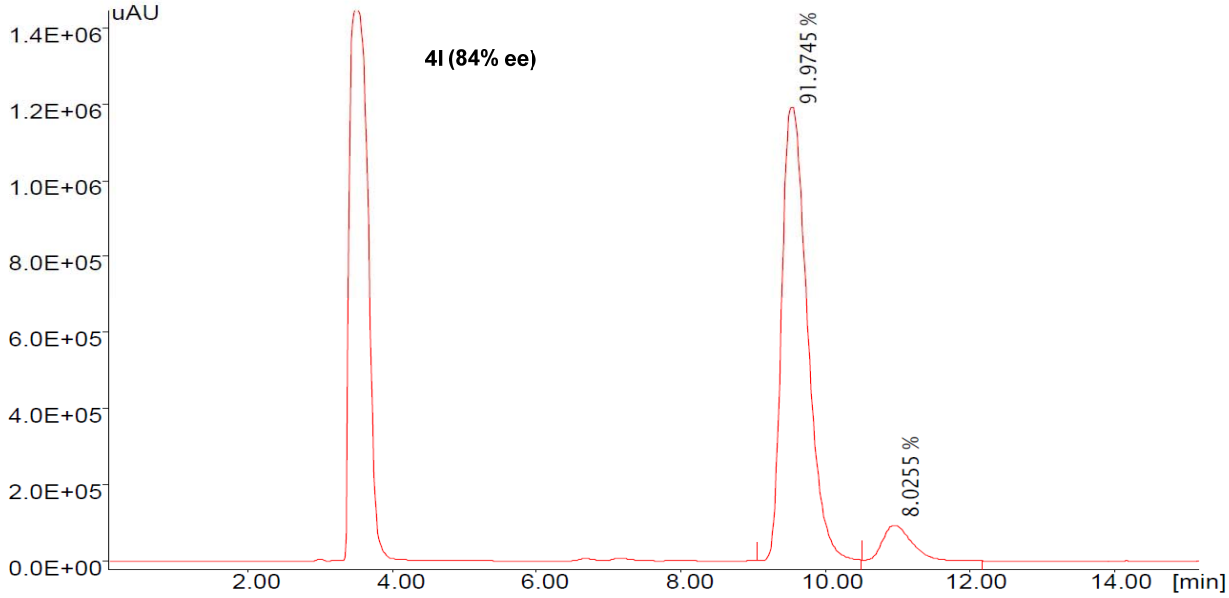
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		17. 853	318551	13562364. 078	49. 85
2		46. 467	120436	13641919. 003	50. 15

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		17. 387	1024454	46720348. 425	95. 09
2		45. 840	22720	2410388. 436	4. 91

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		17. 120	1028733	45109239. 379	81. 65
2		42. 480	101109	10141208. 151	18. 35



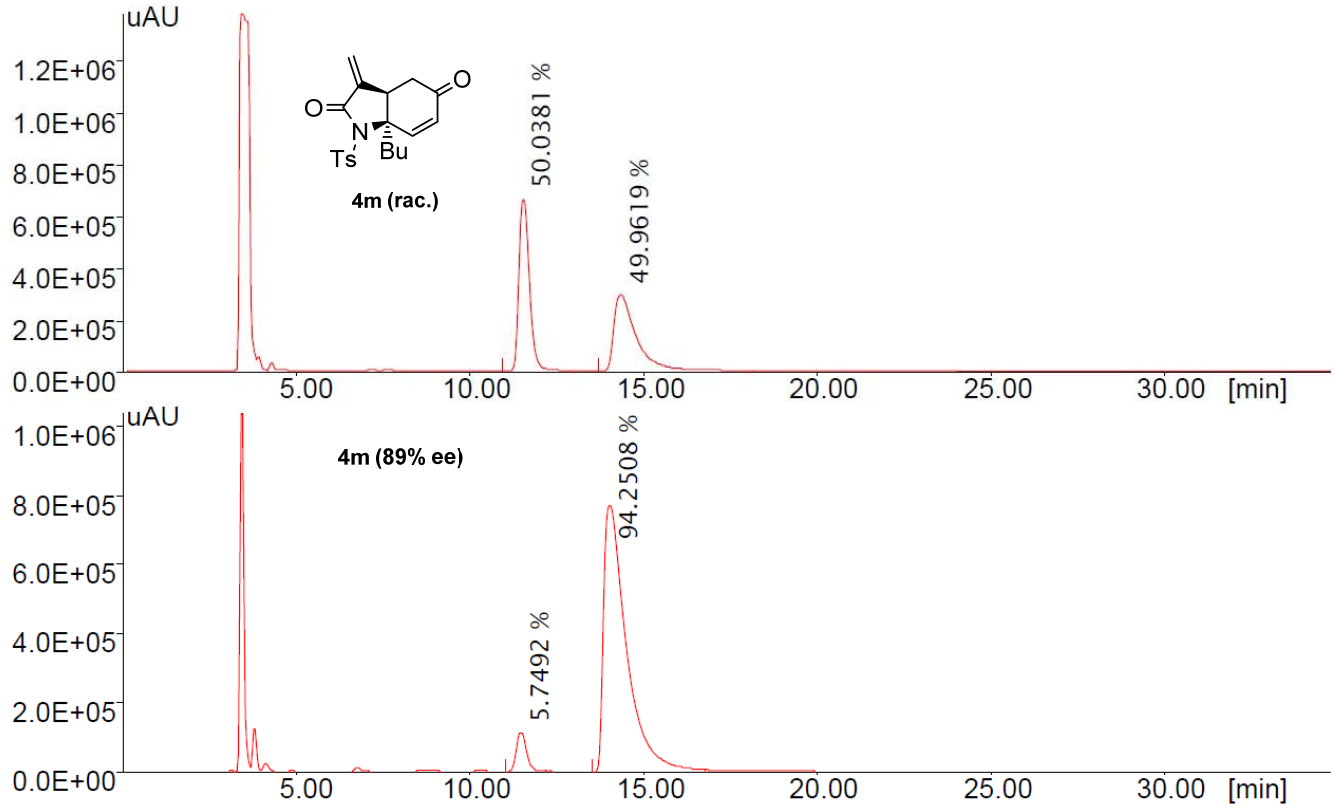




#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		10. 133	429406	12043453. 459	49. 53
2		11. 920	328455	12273732. 259	50. 47

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		9. 840	969215	23815322. 355	98. 77
2		11. 387	11531	295415. 604	1. 23

#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		9. 520	1190449	27885966. 816	91. 97
2		10. 947	90884	2433282. 686	8. 03



#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		11.507	660526	12350960.902	50.04
2		14.320	292508	12332138.517	49.96

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		11.440	112181	2021240.711	5.75
2		14.000	768822	33135606.494	94.25