Supporting Information

Phosphine-Controlled Divergent Reactions of MBH-Carbonates with Azaheptafulvenes: Access to o-Anilinyl diene and Benzazepine Derivatives

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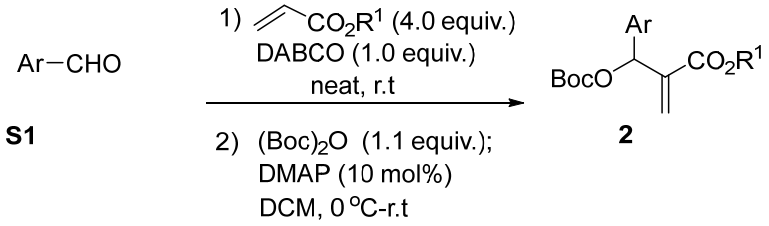
A. General information

Unless otherwise specified, all reactions were carried out with dry solvents in anhydrous conditions. All solvents were dried by activated molecular sieve (3 Å). All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm). High resolution mass spectra (HRMS) were recorded on a Waters TOF MS GCT Premier using ESI ionization. Petroleum ether (PE) refers to the fraction with boiling point in the range 60 – 90 °C. Troponimines **1** were prepared according to the literature procedure [1].

B. Synthesis of Morita-Baylis-Hillman carbonates

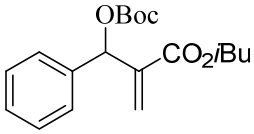
Morita-Baylis-Hillman carbonates **2a**, **2b**, **2d**–**2p**, **2r**–**2u**, **2w** and **2y** are known compounds and the characterization data are in agreement with those reported in the literature. The new compounds **2c**, **2q**, **2v** and **2x** were prepared by following the reported literature procedure.



Step1: To the neat mixture of aldehyde **S1** (1.0 equiv.) and acrylate (4.0 equiv.) was added DABCO (1.0 equiv.), then the resulting slurry was stirred vigorously at room temperature. After specified time, the reaction mixture was diluted with DCM. Then the solution was washed with 4 N aqueous HCl, followed by saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum to get the crude product that was purified by flash column chromatography to give Morita-Baylis-Hillman alcohols.

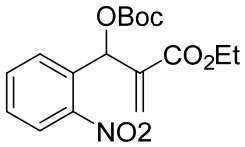
Step2: The solution of Morita-Baylis-Hillman alcohols (1.0 equiv.) and DMAP (10 mol%) in DCM (0.6 M) was stirred at 0 °C for 10 minutes. To the cooled solution, a DCM solution of $(Boc)_2O$ was then added dropwise (1.1 equiv.) at 0 °C. The resulting solution was stirred at room temperature for 2 h and then stirred at room temperature overnight. Subsequently, the solvent was removed in vacuo and the crude mixture was purified by column chromatography to afford pure Morita-Baylis-Hillman carbonates **2**.

Isobutyl 2-(((tert-butoxycarbonyl)oxy)(phenyl)methyl)acrylate (2c)



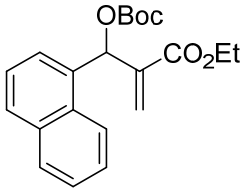
The title compound was prepared according to the general procedure to afford **2c** (72% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.37 – 7.28 (m, 4H), 6.48 (d, *J* = 3.7 Hz, 1H), 6.44 (d, *J* = 3.2 Hz, 1H), 5.90 (d, *J* = 3.3 Hz, 1H), 3.95 – 3.82 (m, 2H), 1.94 – 1.84 (m, 1H), 1.46 (d, *J* = 2.7 Hz, 9H), 0.86 (dd, *J* = 6.6, 3.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 152.3, 139.7, 137.5, 128.4, 127.9, 127.7, 125.8, 82.5, 75.8, 71.0, 27.7, 27.6, 19.0. **IR** (KBr): ν 2969, 2875, 1747, 1725, 1631, 1277, 1254, 1159, 1086, 882, 701 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{20}H_{24}NO_5$ $[M+H]^+$ = 335.1853, found = 335.1856.

Ethyl 2-(((tert-butoxycarbonyl)oxy)(2-nitrophenyl)methyl)acrylate (2q)



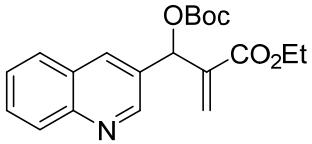
The title compound was prepared according to the general procedure to afford **2q** (68% yield) as a white solid. M.p. 90.6 – 93.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.50 (ddd, *J* = 8.5, 5.9, 2.8 Hz, 1H), 7.16 (s, 1H), 6.43 (s, 1H), 5.53 (s, 1H), 4.20 (qd, *J* = 7.2, 2.3 Hz, 2H), 1.46 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 152.0, 147.9, 138.7, 133.5, 133.3, 129.2, 128.6, 127.9, 125.1, 83.2, 71.1, 61.3, 27.7, 14.0. **IR** (KBr): ν 2927, 2856, 1741, 1713, 1586, 1465, 1383, 1353, 1304, 1152, 1102, 954, 736 cm^{-1}. **HRMS** (ESI): m/z calcd for $C_{20}H_{24}NO_5$ $[M+H]^+$ = 352.1391, found = 352.1401.

Ethyl 2-(((tert-butoxycarbonyl)oxy)(naphthalen-1-yl)methyl)acrylate (2v)



The title compound was prepared according to the general procedure to afford **2v** (57% yield) as a pale green solid. M.p. 43.6 – 55.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$ δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.34 (s, 1H), 6.47 (s, 1H), 5.72 (s, 1H), 4.18 (q, *J* = 7.4, 2H), 1.47 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.6, 139.4, 133.8, 133.3, 130.9, 129.2, 128.7, 127.6, 126.5, 125.8, 125.2, 123.5, 82.7, 72.4, 61.0, 27.7, 14.0. **IR** (KBr): ν 2815, 1740, 1719, 1597, 1352, 1277, 1253, 1157, 1088, 884, 777 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{20}H_{24}NO_5$ $[M+H]^+$ = 357.1697, found = 357.1692.

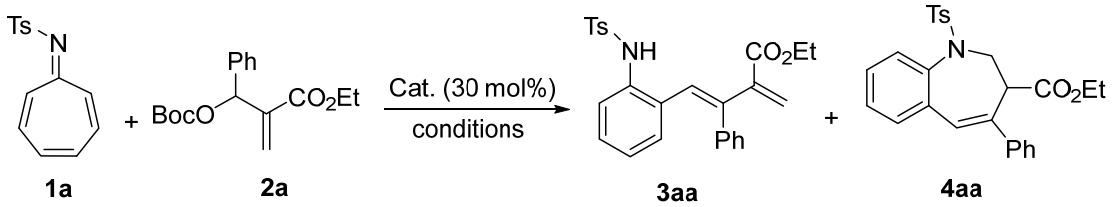
Ethyl 2-(((tert-butoxycarbonyl)oxy)(quinolin-3-yl)methyl)acrylate (2x)



The title compound was prepared according to the general procedure to afford **2x** (56% yield) as green viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 2.2 Hz, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.58 – 7.50 (m, 1H), 6.67 (s, 1H), 6.50 (s, 1H), 6.08 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 1.45 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 152.2, 150.2, 147.9, 139.0, 135.0, 130.6, 129.9, 129.2, 128.0, 127.5, 126.9, 125.9, 83.1, 73.9, 61.1, 27.7, 14.0. **IR** (KBr): ν 2832, 1747, 1716, 1631, 1364, 1276, 1254, 1157, 1088, 777 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{20}H_{24}NO_5$ $[M+H]^+$ = 358.1649, found = 358.1662.

C. Optimization of the cascade reaction for 3aa

Table 1. Optimization of the cascade reaction for **3aa** [a]

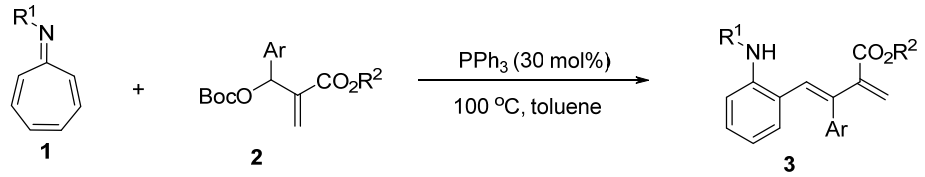


1a **2a** **3aa** **4aa**

Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Proportion[b] (**3aa**/**4aa**)	**3aa** Yield (%) [c]
1	PPh_3	toluene	a.t.	24	-	-
2	PPh_3	Toluene	40	24	> 19/1	27
3	PPh_3	Toluene	60	24	7.3/1	51
4	PPh_3	Toluene	80	12	7.3/1	58
5	PPh_3	Toluene	100	12	5/1	70
6	PPh_3	Toluene	120	12	2.4/1	38
7	$P(4\text{-}MeOC_6H_4)_3$	Toluene	a.t.	8	6.5/1	54
8	$P(4\text{-}MeOC_6H_4)_3$	Toluene	60	6	3.3/1	75
9	$P(4\text{-}MeOC_6H_4)_3$	Toluene	80	6	3.2/1	75
10	$P(4\text{-}MeOC_6H_4)_3$	Toluene	100	6	2.9/1	66
11	DPPE	Toluene	a.t.	72	2.1/1	47[e]
12	DPPE	Toluene	60	12	3.2/1	74[e]
13	DPPE	Toluene	80	12	3.2/1	67
14	DPPE	Toluene	100	12	1.6/1	59
15	DPPP	Toluene	a.t.	48	1.9/1	65[e]
16	DPPP	Toluene	60	12	3.1/1	75[e]
17	DPPP	Toluene	80	12	3.5/1	69
18	DPPP	Toluene	100	12	1.9/1	60
19	PPh_3	Mesitylene	100	12	2.5/1	52
20	PPh_3	*o*-dichlorobenzene	100	12	4.6/1	65
21	PPh_3	MeCN	100	12	4.6/1	70
22	PPh_3	1, 4-Dioxane	100	12	6.8/1	41
23	PPh_3	1, 2-DCE	100	12	2.5/1	42
24	PPh_3	DMF	100	12	5.1/1	51
25[d]	PPh_3	Toluene	100	12	4/1	44
26[e]	PPh_3	Toluene	100	12	3.3/1	56

[a] Unless otherwise stated, reactions were carried out with **1a** (0.1 mmol), **2a** (0.15 mmol) and 30 mol% of catalyst in 1.0 mL of solvent.[b] Determined by ^1H NMR analysis of crude product. [c] Isolated yield.[d] 20 mol% of catalyst was used. [e] 40 mol% of catalyst was used.

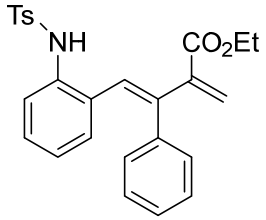
D. General procedure for synthesis of *o*-aminophenyl diene 3



To a dry sealed tube with a magnetic stirring bar was added the corresponding troponimine **1** (0.10 mmol, 1.0 equiv.), MBH-carbonate **2** (0.15 mmol, 1.5 equiv.) and toluene (1.0 mL). Once the solid dissolve completely, PPh_3 (8.0 mg, 30 mol%) was added at room temperature. Then the reaction mixture was stirred at 100 °C for 12 – 16 h. When the starting material was consumed monitored by TLC, the reaction solution was purified by column chromatography directly on silica gel with PE/EA as eluent to afford **3**.

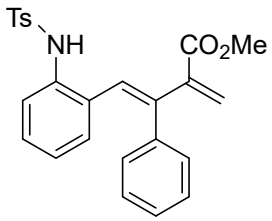
E. Analytic data for the products 3

Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-phenylbut-3-enoate (3aa)



The title compound was prepared according to the general procedure to afford **3aa** (31.4 mg, 70% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.08 (m, 4H), 6.95 – 6.86 (m, 2H), 6.86 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.80 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.66 (br, 1H), 6.35 (s, 1H), 6.23 (d, *J* = 1.5 Hz, 1H), 5.58 (d, *J* = 1.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 143.7, 143.4, 142.6, 137.3, 136.8, 134.2, 130.6, 129.8, 129.6, 129.0, 128.3, 127.9, 127.2, 127.1, 125.0, 124.9, 122.8, 61.0, 21.5, 13.9. **IR** (KBr): ν 3266, 3058, 3027, 2981, 2928, 1718, 1598, 1486, 1402, 1335, 1305, 1164, 1092, 920, 846, 814, 778, 703, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{25}NO_4S$ $[M+H]^+$ = 448.1577, found = 448.1579.

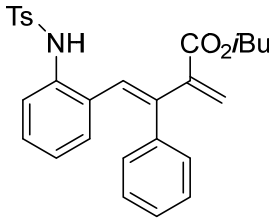
Methyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-phenylbut-3-enoate (3ab)



The title compound was prepared according to the general procedure to afford **3ab** (29.5 mg, 68% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.39 (dd, *J*

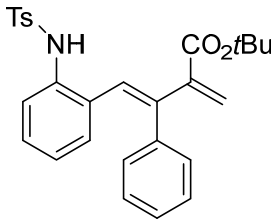
= 8.2, 1.2 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.08 (m, 4H), 6.93 – 6.88 (m, 2H), 6.86 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.66 (br, 1H), 6.37 (s, 1H), 6.24 (d, *J* = 1.3 Hz, 1H), 5.60 (d, *J* = 1.4 Hz, 1H), 3.70 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 143.7, 143.0, 142.4, 137.2, 136.8, 134.2, 130.5, 129.7, 129.6, 129.0, 128.4, 128.3, 127.9, 127.5, 127.2, 125.3, 125.0, 122.7, 52.2, 21.5. **IR** (KBr): ν 3295, 2920, 2851, 1723, 1597, 1484, 1332, 1305, 1162, 1091, 917, 813, 779, 703, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{23}NO_4S$ $[M+H]^+$ = 434.1421, found = 434.1422.

Isobutyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-phenylbut-3-enoate(3ac)



The title compound was prepared according to the general procedure to afford **3ac** (31.2 mg, 66% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.09 (m, 4H), 6.94 – 6.90 (m, 2H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.81 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.60 (s, 1H), 6.34 (s, 1H), 6.27 (d, *J* = 1.5 Hz, 1H), 5.60 (d, *J* = 1.5 Hz, 1H), 3.85 (d, *J* = 6.5 Hz, 2H), 2.39 (s, 3H), 1.85 – 1.72 (m, 1H), 0.80 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 143.7, 143.3, 142.7, 137.2, 136.8, 134.2, 130.6, 129.8, 129.6, 129.0, 128.4, 128.3, 128.0, 127.5, 127.2, 125.01, 124.98, 122.7, 71.2, 27.6, 21.5, 19.0. **IR** (KBr): ν 3260, 3057, 3026, 2961, 2874, 2832, 1719, 1598, 1487, 1364, 1336, 1164, 1092, 919, 813, 777, 752, 702, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{28}H_{29}NO_4S$ $[M+H]^+$ = 476.1890, found = 476.1895.

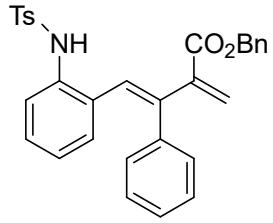
Tert-butyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-phenylbut-3-enoate(3ad)



The title compound was prepared according to the general procedure to afford **3ad** (37.1 mg, 78% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.42 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.09 (m, 4H), 6.95 – 6.90 (m, 2H), 6.87 (td, *J* = 7.5, 1.2 Hz, 1H), 6.81 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.63 (br, 1H), 6.27 (s, 1H), 6.14 (d, *J* = 1.6 Hz, 1H), 5.51 (d, *J* = 1.6 Hz, 1H), 2.39 (s, 3H), 1.23 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6,

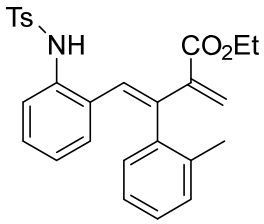
145.0, 143.7, 143.2, 137.6, 136.7, 134.2, 130.7, 129.8, 129.6, 129.0, 128.29, 128.26, 127.8, 127.1, 126.3, 125.0, 124.0, 122.8, 81.3, 27.6, 21.5. **IR** (KBr): ν 3249, 3061, 3027, 2979, 2931, 1714, 1599, 1485, 1368, 1335, 1306, 1164, 1092, 920, 850, 812, 753, 701, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{28}H_{29}NO_4S$ $[M+H]^+$ = 476.1890, found = 476.1895.

Benzyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-phenylbut-3-enoate (3ae)



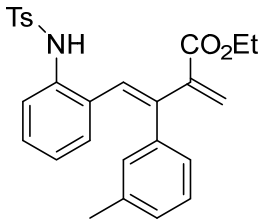
The title compound was prepared according to the general procedure to afford **3ae** (27.1 mg, 54% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.23 – 7.06 (m, 8H), 6.91 – 6.83 (m, 3H), 6.78 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.64 (s, 1H), 6.34 (s, 1H), 6.30 (d, *J* = 1.4 Hz, 1H), 5.63 (d, *J* = 1.4 Hz, 1H), 5.10 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 143.7, 143.0, 142.4, 137.1, 136.7, 135.5, 134.2, 130.6, 129.7, 129.6, 129.0, 128.44, 128.41, 128.38, 128.1, 128.0, 127.9, 127.2, 125.1, 125.0, 122.9, 66.8, 21.5. **IR** (KBr): ν 3294, 3028, 2920, 2851, 1721, 1581, 1493, 1333, 1194, 1163, 1091, 915, 813, 751, 699, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{28}H_{29}NO_4S$ $[M+H]^+$ = 510.1734, found = 510.1732.

Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(o-tolyl)but-3-enoate (3af)



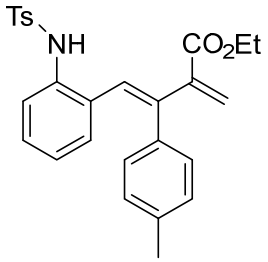
The title compound was prepared according to the general procedure to afford **3af** (35.1 mg, 76% yield) as a white solid. M.p. 108.2 – 110.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.17 – 6.98 (m, 4H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.64 (br, 1H), 6.59 – 6.56 (m, 2H), 6.07 (s, 1H), 5.32 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.97 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 143.8, 142.8, 141.1, 136.7, 136.7, 136.1, 134.1, 130.4, 129.8, 129.7, 129.6, 129.5, 128.2, 127.8, 127.2, 125.88, 125.86, 125.8, 125.0, 122.9, 61.1, 21.6, 19.5, 14.0. **IR** (KBr): ν 3280, 2924, 2854, 1721, 1598, 1484, 1334, 1305, 1191, 1163, 1092, 924, 813, 756, 733, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_4S$ $[M+H]^+$ = 462.1734, found = 462.1742.

Ethyl(E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(m-tolyl)but-3-enoate (3ag)



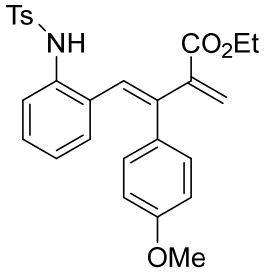
The title compound was prepared according to the general procedure to afford **3ag** (31.8 g, 69% yield) as a pale yellow solid. M.p. 73.8 – 76.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.92 – 6.79 (m, 2H), 6.76 (s, 1H), 6.72 – 6.64 (m, 2H), 6.33 (s, 1H), 6.21 (d, *J* = 1.5 Hz, 1H), 5.57 (d, *J* = 1.5 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 143.7, 143.5, 142.6, 137.9, 137.2, 136.8, 134.0, 130.5, 129.8, 129.6, 129.4, 128.7, 128.24, 128.17, 127.1, 127.0, 126.2, 125.0, 124.8, 122.8, 61.0, 21.5, 21.2, 13.9. **IR** (KBr): ν 3280, 2923, 2855, 1721, 1599, 1493, 1484, 1334, 1305, 1163, 1092, 922, 813, 756, 709, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_4S$ $[M+H]^+$ = 462.1734, found = 462.1733.

Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(p-tolyl)but-3-enoate (3ah)



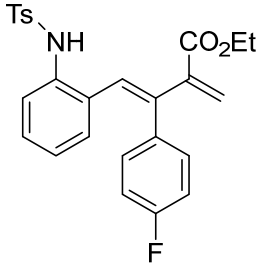
The title compound was prepared according to the general procedure to afford **3ah** (28.6 g, 62% yield) as a pale yellow solid. M.p. 74.8 – 79.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 (td, *J* = 7.8, 1.8 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 3.2 Hz, 1H), 6.29 (s, 1H), 6.21 (d, *J* = 1.5 Hz, 1H), 5.57 (d, *J* = 1.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.27 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 143.7, 143.5, 142.5, 137.8, 136.7, 134.2, 134.0, 130.5, 129.9, 129.6, 129.1, 128.8, 128.2, 127.1, 127.0, 125.0, 124.4, 122.8, 61.0, 21.5, 21.2, 13.9. **IR** (KBr): ν 3268, 2923, 2853, 1721, 1572, 1485, 1334, 1161, 1092, 916, 847, 814, 757, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_4S$ $[M+H]^+$ = 462.1734, found = 462.1732.

Ethyl (E)-3-(4-methoxyphenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3ai)



The title compound was prepared according to the general procedure to afford **3ai** (35.6 g, 74% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 (td, *J* = 8.1, 7.6, 1.9 Hz, 1H), 6.92 (td, *J* = 7.4, 1.2 Hz, 1H), 6.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.85 – 6.81 (m, 2H), 6.71 – 6.63 (m, 3H), 6.26 (s, 1H), 6.21 (d, *J* = 1.5 Hz, 1H), 5.58 (d, *J* = 1.6 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 2.38 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 159.2, 143.7, 143.6, 142.1, 136.7, 134.0, 130.5, 130.2, 129.9, 129.6, 129.5, 128.2, 127.1, 126.9, 125.0, 124.0, 122.6, 113.8, 61.0, 55.1, 21.5, 13.9. **IR** (KBr): ν 3285, 2929, 2837, 1720, 1605, 1511, 1485, 1334, 1163, 1092, 922, 837, 814, 757, 705, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_5S$ $[M+H]^+$ = 478.1683, found = 478.1680.

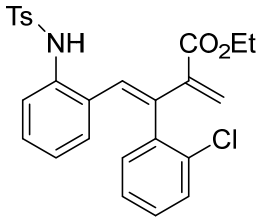
Ethyl (E)-3-(4-fluorophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)pheny-l)but-3-enoate (3aj)



The title compound was prepared according to the general procedure to afford **3aj** (22.1 mg, 47% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.63 – 7.57 (m, 2H), 7.41 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (td, *J* = 7.7, 1.6 Hz, 1H), 6.92 – 6.73 (m, 5H), 6.77 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.68 (s, 1H), 6.37 (s, 1H), 6.25 (d, *J* = 1.4 Hz, 1H), 5.61 (d, *J* = 1.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 162.2 (d, $^1J_{C\text{-}F}$ = 248.0 Hz), 143.8, 143.3, 141.6, 136.7, 134.3, 133.3 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 130.8 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 130.5, 129.6, 129.5, 128.5, 127.3, 127.2, 125.1, 125.0, 122.6, 115.3 (d, $^2J_{C\text{-}F}$= 21.6 Hz), 61.1, 21.5, 13.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.30. **IR** (KBr): ν 3268, 3068, 2982, 2927, 2855, 1720, 1600, 1508, 1486, 1335, 1164, 1092, 918, 842, 815, 758, 706, 662 cm^{-1}; **HRMS**

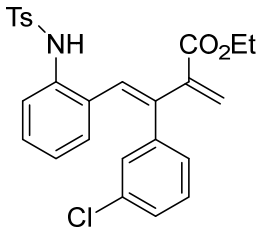
(ESI): m/z calcd for $C_{26}H_{24}FNO_4S$ $[M+H]^+$ = 466.1483, found = 466.1485.

Ethyl (Z)-3-(2-chlorophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3ak)



The title compound was prepared according to the general procedure to afford **3ak** (22.1 mg, 46% yield) as a pale yellow solid. M.p. 96.2 – 99.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.42 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.14 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.92 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.78 (td, *J* = 7.7, 1.3 Hz, 1H), 6.75 (s, 1H), 6.66 – 6.60 (m, 2H), 6.17 (d, *J* = 1.1 Hz, 1H), 5.40 (d, *J* = 1.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 143.8, 141.3, 139.4, 136.8, 136.4, 134.4, 133.5, 131.5, 129.7, 129.6, 129.6, 129.5, 129.0, 128.4, 127.8, 127.2, 126.9, 126.6, 124.8, 122.5, 61.1, 21.6, 14.0. **IR** (KBr): ν 3287, 2925, 2853, 1721, 1598, 1493, 1334, 1306, 1163, 1092, 923, 814, 754, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}ClNO_4S$ $[M+H]^+$ = 482.1188, 484.1158, found = 482.1193, 484.1172.

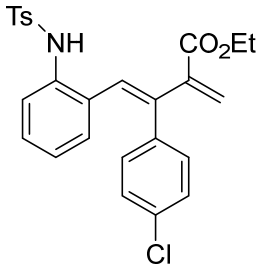
Ethyl (E)-3-(3-chlorophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3al)



The title compound was prepared according to the general procedure to afford **3al** (22.4 mg, 46% yield) as a pale yellow solid. M.p. 96.2 – 99.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.40 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.09 (m, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.91 (t, *J* = 1.9 Hz, 1H), 6.87 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 – 6.70 (m, 3H), 6.42 (s, 1H), 6.27 (d, *J* = 1.4 Hz, 1H), 5.62 (d, *J* = 1.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 143.9, 142.9, 141.2, 139.3, 136.6, 134.4, 134.1, 130.5, 129.7, 129.5, 129.3, 129.0, 128.6, 127.9, 127.7, 127.4, 127.2, 125.9, 125.1, 122.9, 61.1, 21.5, 13.9. **IR** (KBr): ν 3301, 2923, 2852, 1721, 1598, 1483, 1333, 1162, 1092, 916, 812,

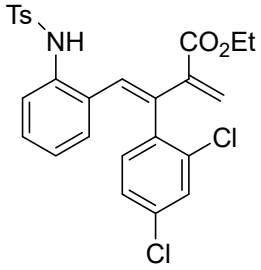
755, 708, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}ClNO_4S$ $[M+H]^+$ = 482.1188, 484.1188, found = 482.1195, 484.1167.

Ethyl (E)-3-(4-chlorophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3am)



The title compound was prepared according to the general procedure to afford **3am** (25.6 mg, 53% yield) as a white solid. M.p. 69.1 – 70.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.77 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.68 (s, 1H), 6.39 (s, 1H), 6.26 (d, *J* = 1.4 Hz, 1H), 5.63 (d, *J* = 1.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 143.9, 143.1, 141.5, 136.7, 135.9, 134.4, 133.7, 130.5, 130.4, 129.7, 129.3, 128.6, 128.5, 127.6, 127.2, 125.6, 125.1, 122.5, 61.1, 21.5, 13.9. **IR** (KBr): ν 3268, 2980, 2925, 1720, 1485, 1334, 1305, 1162, 1091, 916, 836, 813, 754, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}ClNO_4S$ $[M+H]^+$ = 482.1188, 484.1158, found = 482.1195, 484.1167.

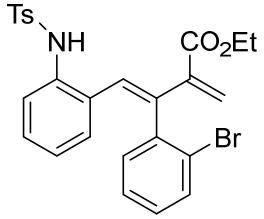
Ethyl (Z)-3-(2,4-dichlorophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3an)



The title compound was prepared according to the general procedure to afford **3an** (29.4 mg, 57% yield) as a pale yellow solid. M.p. 87.6 – 91.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.77 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.68 (br, 1H), 6.39 (s, 1H), 6.26 (d, *J* = 1.4 Hz, 1H), 5.63 (d, *J* = 1.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 143.9, 143.1, 141.5, 136.7, 135.9, 134.4, 133.7, 130.5, 130.4, 129.7, 129.3, 128.6, 128.5, 127.6, 127.2, 125.6,

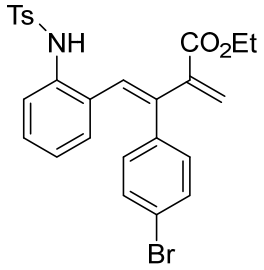
125.1, 122.5, 61.1, 21.5, 13.9. **IR** (KBr): ν 3280, 2925, 2853, 1721, 1584, 1334, 1163, 1092, 923, 814, 757, 705, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{23}Cl_2NO_4S$ $[M+H]^+$ = 516.0798, 518.0796, found = 516.0801, 518.0782.

Ethyl (Z)-3-(2-bromophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3ao)



The title compound was prepared according to the general procedure to afford **3ao** (25.5 mg, 48% yield) as a pale yellow solid. M.p. 107.3 – 111.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.48 – 7.40 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.93 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.74 (s, 1H), 6.66 (s, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.17 (s, 1H), 5.38 (s, 1H), 4.25 (q, *J* = 7.1, Hz, 2H), 2.40 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 143.8, 141.1, 140.7, 138.4, 136.8, 134.5, 133.0, 131.8, 129.6, 129.5, 129.1, 128.4, 127.6, 127.23, 127.17, 127.0, 124.8, 123.8, 122.5, 61.1, 21.6, 14.1. **IR** (KBr): ν 3270, 2956, 2924, 2853, 1721, 1598, 1486, 1334, 1162, 1092, 921, 813, 751, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}BrNO_4S$ $[M+H]^+$ = 526.0683, 528.0662, found = 526.0700, 528.0672.

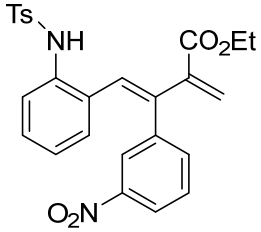
Ethyl (E)-3-(4-bromophenyl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3ap)



The title compound was prepared according to the general procedure to afford **3ap** (24.8 mg, 47% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.39 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.21 (s, 1H), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 – 6.73 (m, 4H), 6.41 (s, 1H), 6.26 (d, *J* = 1.4 Hz, 1H), 5.63 (d, *J* = 1.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 143.9, 143.0, 141.6, 136.7, 136.3, 134.4, 131.5, 130.7, 130.5, 129.7, 129.2, 128.6, 127.7,

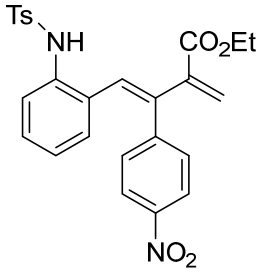
127.2, 125.5, 125.1, 122.5, 61.2, 21.6, 13.9. **IR** (KBr): ν 3270, 2922, 2852, 1721, 1585, 1483, 1332, 1158, 1090, 915, 832, 812, 751, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}BrNO_4S$ $[M+H]^+$ = 526.0683, 528.0662, found = 526.0689, 528.0679.

Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(3-nitrophe-nyl)but-3-enoate (3ar)



The title compound was prepared according to the general procedure to afford **3ar** (22.0 mg, 44% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.86 (t, *J* = 2.0 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.32 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.21 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H), 6.84 (td, *J* = 7.6, 1.2 Hz, 1H), 6.69 (s, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 6.36 (d, *J* = 1.3 Hz, 1H), 5.74 (d, *J* = 1.3 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 148.1, 144.0, 142.4, 140.3, 139.6, 136.6, 135.4, 134.7, 130.5, 129.8, 129.3, 129.1, 128.9, 128.6, 127.4, 127.2, 125.4, 123.9, 123.3, 122.5, 61.2, 21.5, 13.9. **IR** (KBr): ν 3250, 3113, 2982, 2925, 2853, 1720, 1598, 1529, 1492, 1348, 1162, 1092, 907, 813, 757, 701, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}N_2O_6S$ $[M+H]^+$ = 493.1428, found = 493.1433.

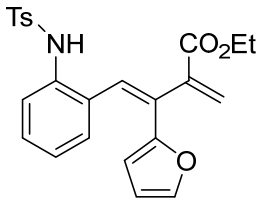
Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(4-nitrophe-nyl)but-3-enoate (3as)



The title compound was prepared according to the general procedure to afford **3as** (28.0 mg, 57% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.69 – 7.63 (m, 2H), 7.38 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.15 (td, *J* = 7.8, 1.6 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.85 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 (s, 1H), 6.66 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.59 (s, 1H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.74 (d, *J* = 1.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 147.0, 144.8, 144.2, 142.5, 140.7,

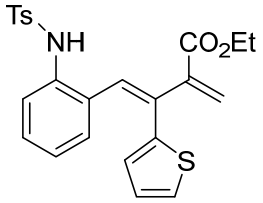
136.8, 134.8, 130.6, 130.1, 129.8, 129.3, 129.2, 128.6, 127.8, 127.3, 125.4, 123.5, 123.1, 61.4, 21.6, 14.0. **IR** (KBr): ν 3262, 3112, 2982, 2926, 1720, 1597, 1518, 1343, 1162, 1092, 914, 854, 814, 753, 706, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}N_2O_6S$ $[M+H]^+$ = 493.1428, found = 493.1428.

Ethyl (Z)-3-(furan-2-yl)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-3-enoate (3at)



The title compound was prepared according to the general procedure to afford **3at** (16.7 mg, 38% yield) as a colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 3H), 7.30 – 7.24 (m, 1H), 7.18 (d, *J* = 1.8 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.00 (m, 2H), 6.88 (s, 1H), 6.38 (d, *J* = 1.4 Hz, 1H), 6.18 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.91 (s, 1H), 5.77 (d, *J* = 1.4 Hz, 1H), 5.69 (d, *J* = 3.5 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 150.4, 143.6, 142.3, 140.8, 136.5, 134.3, 132.6, 129.5, 129.1, 128.7, 127.6, 127.2, 125.1, 123.4, 122.0, 111.3, 110.8, 61.4, 21.5, 14.1. **IR** (KBr): ν 3286, 2919, 2850, 1721, 1598, 1493, 1335, 1165, 1092, 916, 813, 741, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{24}H_{23}NO_5S$ $[M+H]^+$ = 438.1370 found = 438.1772.

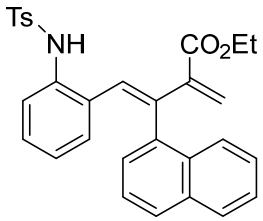
Ethyl (Z)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(thiophen-2-yl)but-3-enoate (3au)



The title compound was prepared according to the general procedure to afford **3au** (26.2 mg, 58% yield) as a pale yellow solid. M.p. 74.9 – 78.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.35 – 7.20 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.04 (m, 3H), 7.03 (s, 1H), 6.82 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.71 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.42 (d, *J* = 1.4 Hz, 1H), 6.06 (s, 1H), 5.79 (d, *J* = 1.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 143.6, 142.4, 139.2, 136.5, 136.3, 134.8, 129.8, 129.7,

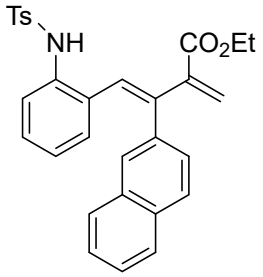
129.5, 129.1, 128.3, 128.2, 127.9, 127.5, 127.1, 126.4, 124.9, 124.1, 121.2, 61.6, 21.5, 14.1. **IR** (KBr): ν 3269, 3106, 3070, 2981, 2927, 1720, 1598, 1486, 1402, 1335, 1165, 1092, 920, 844, 813, 753, 706, 663 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{24}H_{23}NO_5S$ $[M+H]^+$ = 454.1141, found = 454.1147.

Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(naphthalen-1-yl)but-3-enoate (3av)



The title compound was prepared according to the general procedure to afford **3av** (23.0 mg, 46% yield) as a pale yellow solid. M.p. 113.2 – 117.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.72 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.44 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 (s, 1H), 7.23 (s, 1H), 7.00 – 6.95 (m, 1H), 6.94 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.88 (s, 1H), 6.78 (d, *J* = 3.1 Hz, 1H), 6.56 (td, *J* = 7.6, 1.2 Hz, 1H), 6.46 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.06 (d, *J* = 1.1 Hz, 1H), 5.27 (d, *J* = 1.1 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 143.8, 142.8, 140.1, 136.7, 135.2, 134.1, 133.5, 131.5, 129.9, 129.6, 129.2, 128.3, 128.2, 128.1, 127.74, 127.66, 127.2, 126.3, 125.8, 125.6, 125.3, 124.9, 122.8, 61.2, 21.6, 14.0. **IR** (KBr): ν 3301, 3040, 2923, 2852, 1720, 1598, 1492, 1333, 1162, 1092, 922, 805, 781, 756, 706, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{30}H_{27}NO_4S$ $[M+H]^+$ = 498.1734, found = 498.1736.

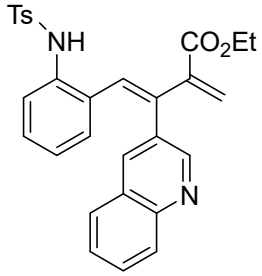
Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(naphthalen-1-yl)but-3-enoate (3aw)



The title compound was prepared according to the general procedure to afford **3aw** (33.5 mg, 67% yield) as a pale yellow solid. M.p. 112.9 – 116.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.44 – 7.35 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 (s, 1H), 7.23 (s, 1H), 6.98 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.94 (td, *J* = 7.7, 1.6 Hz, 1H), 6.90 (s, 1H), 6.87 (s, 1H), 6.55 (td, *J* = 7.6, 1.2 Hz, 1H), 6.46 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.06 (d, *J* = 1.0 Hz,

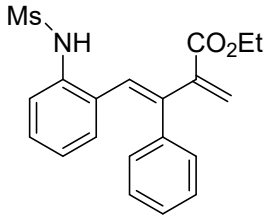
1H), 5.27 (d, *J* = 1.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 143.8, 142.8, 140.0, 136.7, 135.2, 134.1, 133.5, 131.5, 130.0, 129.6, 129.4, 129.2, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.2, 126.30, 126.26, 125.8, 125.6, 125.2, 124.9, 122.9, 61.1, 21.5, 14.0. **IR** (KBr): ν 3266, 3044, 2980, 2925, 1719, 1597, 1485, 1334, 1162, 1092, 918, 805, 780, 756, 706, 664 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{30}H_{27}NO_4S$ $[M+H]^+$ = 498.1734, found = 498.1737.

Ethyl (E)-2-methylene-4-(2-((4-methylphenyl)sulfonamido)phenyl)-3-(quinolin-3-yl)but-3-enoate (3ax)



The title compound was prepared according to the general procedure to afford **3ax** (26.2 mg, 53% yield) as a green viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.2 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 2.2 Hz, 1H), 7.71 – 7.60 (m, 4H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.73 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.61 (s, 1H), 6.38 (d, *J* = 1.3 Hz, 1H), 5.77 (d, *J* = 1.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 151.2, 146.9, 144.0, 142.9, 139.2, 136.6, 135.4, 134.7, 131.0, 130.5, 129.7, 129.7, 129.4, 129.2, 129.0, 128.3, 127.9, 127.4, 127.2, 127.0, 126.9, 125.5, 123.1, 61.2, 21.6, 13.9. **IR** (KBr): ν 3267, 3038, 2980, 2925, 2853, 1720, 1598, 1493, 1333, 1161, 1092, 917, 814, 788, 755, 662 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{29}H_{26}N_2O_4S$ $[M+H]^+$ = 499.1686, found = 499.1689.

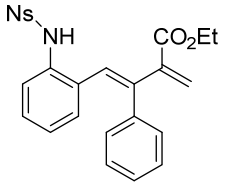
Ethyl (E)-2-methylene-4-(2-(methylsulfonamido)phenyl)-3-phenylbut-3-enoate (3ba)



The title compound was prepared according to the general procedure to afford **3ba** (23.6 mg, 64% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.13 – 7.06 (m, 2H), 7.06 (d, *J* = 1.7 Hz, 1H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80

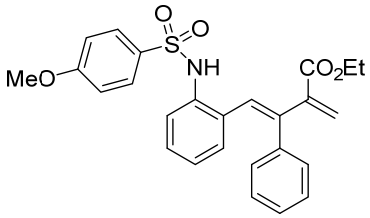
(s, 1H), 6.54 (s, 1H), 6.34 (d, *J* = 1.3 Hz, 1H), 5.80 (d, *J* = 1.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 143.1, 142.6, 137.5, 134.0, 130.8, 129.1, 128.7, 128.6, 128.5, 128.1, 127.9, 125.4, 124.8, 120.7, 61.2, 39.2, 13.9. **IR** (KBr): ν 3278, 3024, 2979, 2929, 2852, 1720, 1599, 1485, 1326, 1154, 1097, 970, 918, 761, 702 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{20}H_{21}NO_4S$ $[M+H]^+$ = 372.1264, found = 372.1271.

Ethyl (E)-2-methylene-4-(2-((4-nitrophenyl)sulfonamido)phenyl)-3-phenylbut-3-eno-ate (3ca)



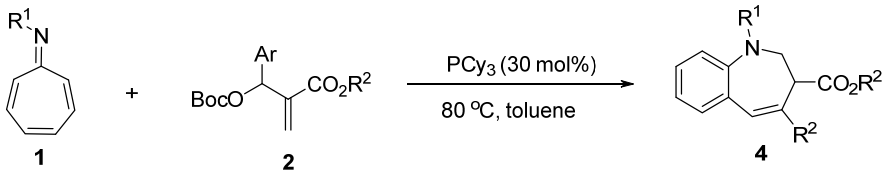
The title compound was prepared according to the general procedure to afford **3ca** (28.8 mg, 60% yield) as a yellow solid. M.p. 125.5 – 129.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 – 8.21 (m, 2H), 7.91 – 7.84 (m, 2H), 7.36 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.25 – 7.04 (m, 4H), 6.97 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.95 – 6.89 (m, 3H), 6.87 (dt, *J* = 7.8, 1.1 Hz, 1H), 6.41 (s, 1H), 6.24 (d, *J* = 1.2 Hz, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 150.1, 145.3, 142.9, 142.4, 137.1, 132.9, 130.8, 130.4, 129.0, 128.5, 128.4, 128.2, 127.5, 125.9, 125.0, 124.2, 123.4, 61.2, 13.9. **IR** (KBr): ν 3286, 3027, 2980, 2926, 2853, 1720, 1605, 1530, 1484, 1349, 1310, 1168, 1091, 925, 855, 778, 736, 702, 684 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{20}H_{21}NO_4S$ $[M+H]^+$ = 479.1271, found = 479.1272.

Ethyl (E)-4-(2-((4-methoxyphenyl)sulfonamido)phenyl)-2-methylene-3-phenylbut-3-enoate (3da)



The title compound was prepared according to the general procedure to afford **3da** (32.0 mg, 71% yield) as a pale yellow solid. M.p. 96.6 – 101.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.08 (m, 4H), 6.94 – 6.82 (m, 5H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.67 – 6.60 (m, 1H), 6.38 (d, *J* = 1.9 Hz, 1H), 6.24 (d, *J* = 1.7 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 4.11 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.82 (d, *J* = 1.7 Hz, 3H), 1.10 (td, *J* = 7.2, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 163.0, 143.4, 142.6, 137.3, 134.2, 131.2, 130.6, 129.7, 129.3, 129.0, 128.3, 127.8, 127.2, 124.95, 124.88, 122.7, 114.1, 61.0, 55.5, 13.9. **IR** (KBr): ν 3280, 2927, 2851, 1721, 1596, 1494, 1333, 1302, 1156, 1093, 916, 833, 752, 701 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{22}NO_4S$ $[M+H]^+$ = 464.1526, found = 464.1534.

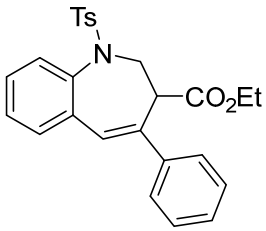
F. General procedure for synthesis of 4



To a dry sealed tube with a magnetic stirring bar was added the corresponding troponimines **1** (0.1 mmol, 1.0 equiv.), MBH-carbonates **2** (0.1 mmol, 1.0 equiv.) and toluene (1.0 mL). Once the solid dissolve completely, the catalyst PCy_3 (8.4 mg, 30 mol%) was added at room temperature. Then the reaction mixture was stirred at 80 °C for 3 – 6 h and monitored by TLC. The reaction solution was purified by column chromatography directly on silica gel with PE/EA as eluent to afford **4**.

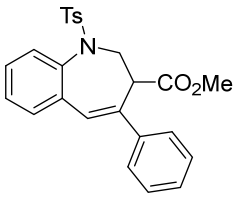
G. Analytic data for 4

Ethyl 4-phenyl-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4aa)



The title compound was prepared according to the general procedure to afford **4aa** (41.6 mg, 93% yield) as a white solid. M.p. 110.2 – 112.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 1H), 7.56 – 7.50 (m, 2H), 7.31 – 7.18 (m, 6H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.05 (m, 2H), 6.33 (d, *J* = 1.4 Hz, 1H), 4.60 (dd, *J* = 14.4, 5.6 Hz, 1H), 4.16 (ddd, *J* = 9.7, 5.6, 1.5 Hz, 1H), 3.94 (dd, *J* = 14.4, 9.7 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 143.4, 142.1, 139.8, 138.6, 137.9, 133.3, 132.2, 129.8, 129.4, 128.9, 128.1, 127.9, 127.6, 127.5, 127.1, 126.5, 61.0, 52.1, 49.6, 21.4, 13.7. **IR** (KBr): ν 3027, 2925, 1728, 1630, 1597, 1349, 1304, 1162, 1093, 1030, 813, 767, 696 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{25}NO_4S$ $[M+H]^+$ = 448.1577, found = 448.1582.

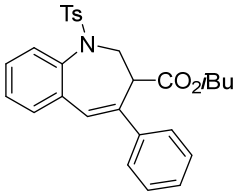
Methyl 4-phenyl-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ab)



The title compound was prepared according to the general procedure to afford **4ab** (36.7 mg, 85% yield) as a white solid. M.p. 110.1 – 112.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 1H), 7.57 – 7.50 (m, 2H), 7.31 – 7.24 (m, 5H), 7.23 – 7.18 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.04 (m, 2H), 6.35 (d, *J* = 1.3 Hz, 1H), 4.58 (dd, *J* = 14.4, 5.5 Hz, 1H), 4.17 (ddd, *J* = 9.4, 5.5, 1.4

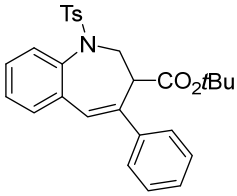
Hz, 1H), 3.97 (dd, *J* = 14.4, 9.4 Hz, 1H), 3.39 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 143.5, 142.1, 139.6, 138.6, 137.9, 133.2, 132.2, 130.0, 129.5, 128.8, 128.2, 128.0, 127.6, 127.5, 127.1, 126.4, 52.2, 52.1, 49.6, 21.4. **IR** (KBr): ν 3027, 2953, 2926, 1737, 1630, 1597, 1401, 1349, 1161, 1093, 814, 765, 696, 662 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{23}NO_4S$ $[M+H]^+$ = 434.1421, found = 434.1421.

Isobutyl 4-phenyl-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ac)



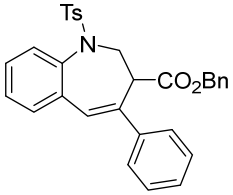
The title compound was prepared according to the general procedure to afford **4ac** (35.3 mg, 74% yield) as a white solid. M.p. 83.8 – 87.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 1H), 7.56 – 7.50 (m, 2H), 7.31 – 7.18 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.09 (dt, *J* = 7.7, 1.4 Hz, 2H), 6.34 (d, *J* = 1.4 Hz, 1H), 4.61 (dd, *J* = 14.4, 5.6 Hz, 1H), 4.17 (ddd, *J* = 9.7, 5.6, 1.4 Hz, 1H), 3.96 (dd, *J* = 14.4, 9.7 Hz, 1H), 3.56 (d, *J* = 6.6 Hz, 2H), 2.31 (s, 3H), 1.67 – 1.57 (m, 1H), 0.72 (d, *J* = 2.1 Hz, 3H), 0.70 (d, *J* = 2.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 143.4, 142.1, 139.7, 138.5, 137.8, 133.3, 132.1, 129.8, 129.4, 128.9, 128.2, 127.9, 127.5, 127.1, 126.4, 71.2, 52.3, 49.6, 27.4, 21.4, 18.9, 18.8. **IR** (KBr): ν 3028, 2958, 2873, 1728, 1630, 1351, 1291, 1217, 1162, 1093, 813, 766, 696 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{28}H_{29}NO_4S$ $[M+H]^+$ = 476.1890, found = 476.1894.

Tert-butyl 4-phenyl-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ad)



The title compound was prepared according to the general procedure to afford **4ad** (34.6 mg, 73% yield) as a white solid. M.p. 99.6 – 105.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 1H), 7.56 – 7.48 (m, 2H), 7.36 – 7.17 (m, 6H), 7.15 – 7.05 (m, 4H), 6.29 (d, *J* = 1.4 Hz, 1H), 4.62 (dd, *J* = 14.4, 5.6 Hz, 1H), 4.05 (ddd, *J* = 9.9, 5.6, 1.5 Hz, 1H), 3.87 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.29 (s, 3H), 1.06 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 143.3, 142.3, 140.4, 138.5, 137.9, 133.5, 132.1, 129.41, 129.38, 129.2, 128.0, 127.8, 127.5, 127.4, 127.0, 126.7, 81.4, 52.2, 50.4, 27.3, 21.4. **IR** (KBr): ν 3027, 2977, 2929, 1726, 1351, 1304, 1162, 1094, 809, 764, 697 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{28}H_{29}NO_4S$ $[M+H]^+$ = 476.1890, found = 476.1896.

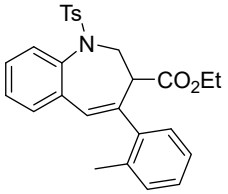
Benzyl 4-phenyl-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ae)



The title compound was prepared according to the general procedure to afford **4ae** (35.6 mg, 70%

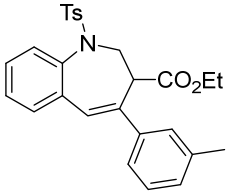
yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 1H), 7.55 – 7.49 (m, 2H), 7.31 – 7.18 (m, 8H), 7.21 – 7.13 (m, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.08 – 7.02 (m, 2H), 7.01 – 6.96 (m, 2H), 6.34 (d, *J* = 1.4 Hz, 1H), 4.81 (s, 2H), 4.59 (dd, *J* = 14.5, 5.6 Hz, 1H), 4.23 (ddd, *J* = 9.5, 5.6, 1.5 Hz, 1H), 3.98 (dd, *J* = 14.5, 9.5 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 143.4, 142.0, 139.5, 138.6, 137.8, 135.1, 133.1, 132.2, 130.0, 129.4, 128.7, 128.4, 128.21, 128.18, 128.1, 127.9, 127.6, 127.5, 127.1, 126.5, 66.9, 52.1, 49.7, 21.4. **IR** (KBr): ν 2923, 1727, 1630, 1586, 1349, 1162, 1093, 813, 766, 696 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{31}H_{27}NO_4S$ $[M+H]^+$ = 510.1734, found = 510.1731.

Ethyl 4-(o-tolyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4af)



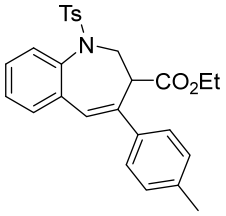
The title compound was prepared according to the general procedure to afford **4af** (37.64 mg, 81% yield) as a white solid. M.p. 104.5 – 103.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 3H), 7.28 – 7.16 (m, 5H), 7.15 – 7.11 (m, 2H), 7.07 (dp, *J* = 8.6, 4.0 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 2.2 Hz, 1H), 4.56 (dd, *J* = 14.7, 5.1 Hz, 1H), 4.11 (ddd, *J* = 11.0, 5.1, 2.2 Hz, 1H), 3.85 – 3.70 (m, 3H), 2.38 (s, 3H), 2.21 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 143.6, 141.7, 139.0, 138.3, 135.2, 132.6, 132.2, 131.1, 130.3, 129.7, 128.5, 127.84, 127.77, 127.3, 127.2, 127.1, 125.2, 60.8, 51.3, 50.5, 21.5, 19.7, 13.5. **IR** (KBr): ν 2925, 2854, 1731, 1630, 1492, 1351, 1304, 1162, 1093, 763 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_4S$ $[M+H]^+$ = 462.1734, found = 462.1737.

Ethyl 4-(m-tolyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate（4ag）



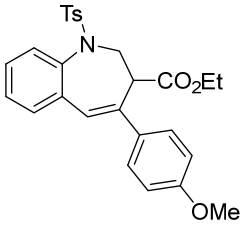
The title compound was prepared according to the general procedure to afford **4ag** (42.0 mg, 91% yield) as a white solid. M.p. 113.2 – 117.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.65 – 7.58 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.13 (m, 4H) 7.05 (d, *J* = 7.5 Hz, 1H), 6.87 – 6.86 (m, 2H), 4.59 (dd, *J* = 14.4, 5.5 Hz, 1H), 4.12 (ddd, *J* = 9.6, 5.5, 1.4 Hz, 1H), 3.94 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.85 (qd, *J* = 7.1, 2.8 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 143.3, 142.1, 139.9, 138.5, 137.9, 137.6, 133.4, 132.1, 129.5, 129.4, 129.0, 128.2, 127.9, 127.8, 127.5, 127.2, 127.1, 123.6, 60.9, 52.2, 49.6, 21.4, 21.4, 13.7. **IR** (KBr): ν 2850, 1726, 1630, 1586, 1346, 1302, 1162, 1093, 815, 710, 664 cm^{-1}; **HRMS**(ESI): m/z calcd for $C_{27}H_{27}NO_4S$ $[M+H]^+$ = 462.1734, found = 462.1737.

Ethyl 4-(p-tolyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ah)



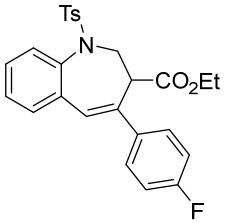
The title compound was prepared according to the general procedure to afford **4ah** (39.2 mg, 85% yield) as a pale yellow solid. M.p. 111.4 – 114.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.31 (s, 1H), 4.59 (dd, *J* = 14.4, 5.5 Hz, 1H), 4.17 – 4.09 (m, 2H), 3.93 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 143.4, 139.7, 139.3, 138.5, 137.9, 137.3, 133.4, 132.1, 129.4, 129.2, 128.9, 128.8, 127.8, 127.5, 127.1, 126.4, 61.0, 52.2, 49.6, 21.4, 21.0, 13.7. **IR** (KBr): ν 2980, 2924, 1728, 1630, 1597, 1401, 1350, 1304, 1161, 1093, 813, 708 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_4S$ $[M+H]^+$ = 462.1734, found = 462.1740.

Ethyl 4-(4-methoxyphenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ai)



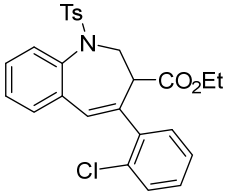
The title compound was prepared according to the general procedure to afford **4ai** (26.2 mg, 55% yield) as a white solid. M.p. 95.2 – 96.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.04 – 6.99 (m, 2H), 6.83 – 6.76 (m, 2H), 6.28 (s, 1H), 4.58 (dd, *J* = 14.4, 5.5 Hz, 1H), 4.12 (ddd, *J* = 9.8, 5.5, 1.3 Hz, 2H), 3.89 (dd, *J* =14.4, 5.5 Hz, 1H), 3.86 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.32 (s, 3H), 0.93 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 159.1, 143.4, 139.3, 138.4, 137.9, 134.6, 133.4, 132.1, 129.4, 128.9, 128.8, 127.7, 127.6, 127.5, 127.1, 113.4, 61.0, 55.3, 52.0, 49.7, 21.4, 13.8. **IR** (KBr): ν 2979, 2934, 2837, 1732, 1631, 1606, 1512, 1350, 1162, 1094, 1032, 910, 815, 709, 655 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{27}NO_5S$ $[M+H]^+$ = 478.1683, found = 468.1684.

Ethyl 4-(4-fluorophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4aj)



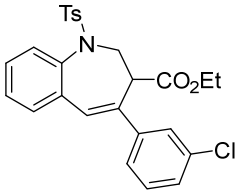
The title compound was prepared according to the general procedure to afford **4aj** (38.4 mg, 83 % yield) as a white solid. M.p.81.2 – 84.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.56 – 7.50 (m, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.03 (m, 2H), 7.02 – 6.90 (m, 2H), 6.30 (d, *J* = 1.5 Hz, 1H), 4.58 (dd, *J* = 14.5, 5.6 Hz, 1H), 4.13 (ddd, *J* = 9.9, 5.6, 1.5 Hz, 1H), 3.94 – 3.89 (m, 1H), 3.86 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 162.2 (d, $^1J_{C-F}$ = 247.1 Hz), 143.5, 138.7, 138.2 (d, $^4J_{C-F}$ = 3.3 Hz), 137.9, 133.0, 132.2, 130.0, 129.4, 128.8, 128.2 (d, $^3J_{C-F}$ = 8.0 Hz), 128.0, 127.6, 127.1, 114.9 (d, $^2J_{C-F}$ = 21.4 Hz), 61.1, 51.9, 49.9, 21.4, 13.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.44. **IR** (KBr): ν 2981, 2930, 1732, 1630, 1600, 1509, 1352, 1304, 1163, 1095, 835, 814, 758, 709, 655 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_4S$ $[M+H]^+$ = 466.1483, found = 466.1487.

Ethyl 4-(2-chlorophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ak)



The title compound was prepared according to the general procedure to afford **4ak** (42.0 mg, 87 % yield) as a pale yellow solid. M.p. 115.4 – 117.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 3H), 7.36 – 7.30 (m, 1H), 7.26 – 7.15 (m, 7H), 7.05 – 6.95 (m, 1H), 6.36 (d, *J* = 2.1 Hz, 1H), 4.59 (dd, *J* = 14.7, 5.1 Hz, 1H), 4.30 (ddd, *J* = 10.3, 5.1, 2.1 Hz, 1H), 3.89 (dd, *J* = 14.7, 10.3 Hz, 1H), 3.85 – 3.79 (m, 2H), 2.36 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 143.6, 141.0, 139.2, 137.7, 137.3, 132.9, 132.6, 132.5, 131.5, 130.8, 129.6, 129.5, 128.7, 128.2, 127.3, 127.2, 127.0, 126.4, 61.0, 50.5, 50.3, 21.5, 13.6. **IR** (KBr): ν 2980, 2926, 1729, 1630, 1597, 1350, 1305, 1161, 1093, 813, 758, 688, 655 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}ClNO_4S$ $[M+H]^+$ = 482.1188, 484.1158, found = 482.1193, 484.1172.

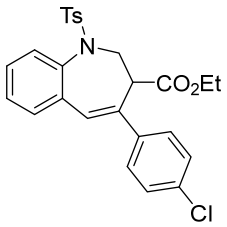
Ethyl 4-(3-chlorophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4al)



The title compound was prepared according to the general procedure to afford **4al** (45.2 mg, 94 % yield) as a white solid. M.p. 97.4 – 99.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 1H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.52 (d, J = 2.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.15 (m, 5H), 7.01

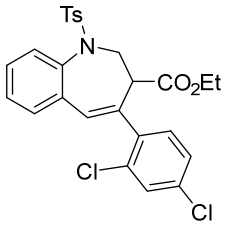
– 6.96 (m, 1H), 6.94 (d, J = 2.3 Hz, 1H), 6.31 (s, 1H), 4.60 (ddd, *J* = 14.4, 5.5, 2.4 Hz, 1H), 4.07 (dd, *J* = 9.4, 6.2 Hz, 1H), 3.95 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.91 – 3.82 (m, 2H), 2.35 (s, 3H), 0.94 (td, *J* = 7.1, 2.4 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 143.9, 143.6, 138.7, 138.4, 138.0, 133.9, 132.9, 132.3, 130.7, 129.5, 129.4, 129.2, 128.3, 127.7, 127.5, 127.1, 126.8, 124.7, 61.2, 52.1, 49.4, 21.5, 13.7. **IR** (KBr): ν 2925, 1730, 1630, 1592, 1351, 1305, 1162, 1094, 813, 785, 691, 657 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}ClNO_4S$ $[M+H]^+$ = 482.1188, 484.1158, found = 482.1195, 484.1167.

Ethyl 4-(4-chlorophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4am)



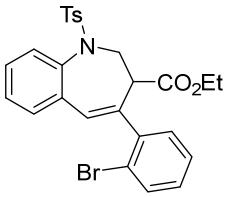
The title compound was prepared according to the general procedure to afford **4am** (43.4 mg, 90 % yield) as a white solid. M.p. 93.6 – 95.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.32 (d, *J* = 1.4 Hz, 1H), 4.58 (dd, *J* = 14.5, 5.6 Hz, 1H), 4.13 (ddd, *J* = 9.8, 5.7, 1.5 Hz, 1H), 3.94 – 3.81 (m, 3H), 2.32 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 143.5, 140.7, 138.7, 138.5, 137.9, 133.4, 132.9, 132.3, 130.3, 129.5, 128.8, 128.3, 128.2, 127.9, 127.6, 127.1, 61.2, 51.9, 49.7, 21.4, 13.8. **IR** (KBr): ν 2982, 2930, 1732, 1632, 1597, 1492, 1401, 1351, 1305, 1162, 1094, 815, 758, 689, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}ClNO_4S$ $[M+H]^+$ = 482.1188, 484.1158, found = 482.1194, 484.1175.

Ethyl 4-(2,4-dichlorophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4an)



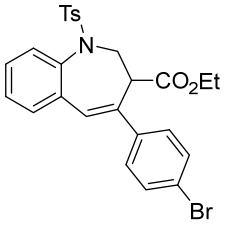
The title compound was prepared according to the general procedure to afford **4an** (41.3 mg, 80% yield) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 3H), 7.36 (t, *J* = 1.7 Hz, 1H), 7.26 – 7.14 (m, 6H), 6.94 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.34 (s, 1H), 4.56 (dd, *J* = 14.8, 5.1 Hz, 1H), 4.25 (ddd, *J* = 10.1, 5.0, 1.8 Hz, 1H), 3.93 – 3.82 (m, 3H), 2.37 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 143.6, 139.6, 139.3, 137.7, 136.2, 133.8, 133.4, 133.0, 131.6, 131.3, 129.6, 129.3, 128.4, 127.3, 127.2, 127.1, 126.7, 61.1, 50.5, 50.4, 21.5, 13.7. **IR** (KBr): ν 3063, 2980, 2958, 2926, 1732, 1597, 1493, 1351, 1306, 1162, 1099, 815, 764, 708, 691, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{23}Cl_2NO_4S$ $[M+H]^+$ = 516.0798, 518.0769, found = 516.0794, 518.0784.

Ethyl 4-(2-bromophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ao)



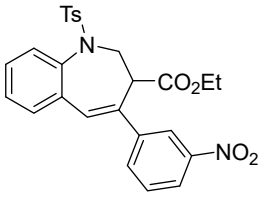
The title compound was prepared according to the general procedure to afford **4ao** (36.3 mg, 69% yield) as a white solid. M.p. 127.5 – 132.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.64 – 7.59 (m, 1H), 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28 – 7.19 (m, 6H), 7.11 (td, *J* = 7.7, 1.8 Hz, 1H), 6.97 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.36 (d, *J* = 2.1 Hz, 1H), 4.55 (dd, *J* = 14.7, 5.1 Hz, 1H), 4.31 (ddd, *J* = 10.3, 5.0, 2.1 Hz, 1H), 3.92 (dd, *J* = 15.4, 9.6 Hz, 1H), 3.84 (qd, *J* = 7.1, 2.3 Hz, 2H), 2.37 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 143.6, 142.8, 139.4, 138.5, 137.8, 133.0, 132.8, 132.7, 131.4, 130.7, 129.6, 128.8, 128.2, 127.4, 127.0, 126.9, 122.6, 61.0, 50.8, 50.3, 21.5, 13.6. **IR** (KBr): ν 2979, 2926, 2854, 1731, 1630, 1597, 1493, 1350, 1305, 1161, 1094, 814, 760, 709, 680, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}BrNO_4S$ $[M+H]^+$ = 526.0683, 528.0662, found = 526.0683, 528.0673.

Ethyl 4-(4-bromophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ap)



The title compound was prepared according to the general procedure to afford **4ap** (36.5 mg, 70% yield) as a white solid. M.p. 107.1 – 110.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 5.8, 3.5 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.47 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 (dd, *J* = 5.8, 3.5 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.03 – 6.96 (m, 2H), 6.36 (d, *J* = 1.4 Hz, 1H), 4.62 (dd, *J* = 14.5, 5.6 Hz, 1H), 4.17 (ddd, *J* = 9.9, 5.6, 1.5 Hz, 1H), 3.99 – 3.86 (m, 3H), 2.36 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 143.6, 142.8, 139.4, 138.5, 137.8, 133.0, 132.8, 132.7, 131.4, 130.7, 129.6, 128.8, 128.2, 127.4, 127.0, 126.9, 122.6, 61.0, 50.8, 50.3, 21.5, 13.6. **IR** (KBr): ν 2921, 2852, 1727, 1631, 1597, 1493, 1485, 1348, 1304, 1161, 1093, 814, 757, 709, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}BrNO_4S$ $[M+H]^+$ = 526.0683, 528.0662, found = 526.0699, 528.0670.

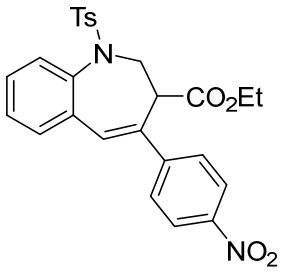
Ethyl 4-(3-nitrophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ar)



The title compound was prepared according to the general procedure to afford **4ar** (47.4 mg, 96% yield) as a pale yellow solid. M.p. 116.2 – 118.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.08

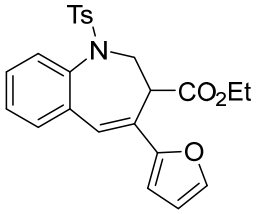
(m, 1H), 7.87 – 7.86 (m, 1H), 7.68 – 7.61 (m, 1H), 7.58 – 7.52 (m, 2H), 7.50 – 7.44 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 1.5 Hz, 1H), 4.64 (dd, *J* = 14.6, 5.6 Hz, 1H), 4.19 (ddd, *J* = 9.9, 5.7, 1.5 Hz, 1H), 3.98 – 3.83 (m, 3H), 2.31 (s, 3H), 0.93 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 148.0, 143.9, 143.9, 138.9, 137.9, 137.3, 132.6, 132.6, 132.3, 131.9, 129.6, 129.2, 129.0, 128.7, 127.7, 127.0, 122.3, 121.5, 61.3, 51.8, 49.5, 21.4, 13.8. **IR** (KBr): ν 2916, 2850, 1727, 1630, 1581, 1530, 1493, 1347, 1161, 1092, 812, 711, 656 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}N_2O_6S$ $[M+H]^+$ = 493.1428, found = 493.1425.

Ethyl 4-(4-nitrophenyl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4as)



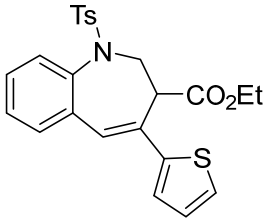
The title compound was prepared according to the general procedure to afford **4as** (47.6 mg, 97% yield) as a yellow solid. M.p. 148.2 – 149.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.25 – 7.24 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.46 (s, 1H), 4.60 (dd, *J* = 14.6, 5.6 Hz, 1H), 4.23 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.97 – 3.83 (m, 3H), 2.32 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 148.9, 146.9, 143.7, 139.0, 137.9, 137.6, 132.7, 132.4, 132.2, 129.5, 128.8, 128.6, 127.7, 127.3, 127.1, 123.5, 61.4, 51.9, 49.6, 21.4, 13.8. **IR** (KBr): ν 2925, 2853, 1728, 1630, 1593, 1514, 1345, 1162, 1094, 852, 814, 760, 710, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}N_2O_6S$ $[M+H]^+$ = 493.1428, found = 493.1430.

Ethyl 4-(furan-2-yl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4at)



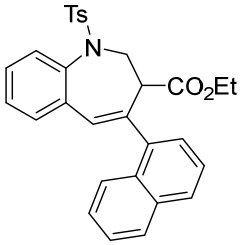
The title compound was prepared according to the general procedure to afford **4at** (43.3 mg, 98% yield) as a yellow solid. M.p. 73.4 – 76.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.45 – 7.38 (m, 2H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 6.36 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.24 (d, *J* = 3.4 Hz, 1H), 4.55 (dd, *J* = 14.6, 6.1 Hz, 1H), 4.15 – 3.99 (m, 3H), 3.93 (dd, *J* = 14.6, 9.8 Hz, 1H), 2.25 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 153.8, 143.4, 141.9, 139.0, 137.1, 132.9, 132.5, 129.1, 128.4, 128.0, 127.6, 126.9, 125.1, 111.5, 106.6, 61.5, 52.6, 47.8, 21.4, 14.0. **IR** (KBr): ν 2925, 2853, 1731, 1630, 1597, 1493, 1350, 1290, 1163, 1096, 912, 808, 739, 709, 691, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{23}NO_5S$ $[M+H]^+$ = 438.1370, found = 438.1374.

Ethyl 4-(thiophen-2-yl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4au)



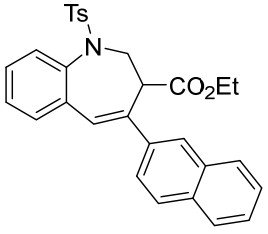
The title compound was prepared according to the general procedure to afford **4au** (40.9 mg, 90% yield) as a yellow solid. M.p. 99.8 – 102.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.28 – 7.17 (m, 3H), 7.15 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.93 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.86 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.55 (s, 1H), 4.58 (dd, *J* = 14.5, 5.9 Hz, 1H), 4.17 (ddd, *J* = 9.4, 5.9, 1.1 Hz, 1H), 4.05 – 3.91 (m, 3H), 2.25 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 145.5, 143.5, 138.8, 137.2, 132.9, 132.7, 132.3, 129.3, 128.6, 128.04, 127.96, 127.6, 127.3, 126.9, 124.4, 123.9, 61.4, 52.6, 49.9, 21.4, 13.9. **IR** (KBr): ν 2979, 2929, 1731, 1597, 1493, 1349, 1290, 1162, 1093, 911, 812, 757, 709, 692, 656 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{23}NO_4S_2$ $[M+H]^+$ = 454.1141, found = 454.1139.

Ethyl 4-(naphthalen-1-yl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4av)



The title compound was prepared according to the general procedure to afford **4av** (28.9 mg, 58% yield) as a white solid. M.p. 124.8 – 126.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.48 – 7.38 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.24 (m, 5H), 7.24 – 7.18 (m, 1H), 6.88 (br, 1H), 6.43 (s, 1H), 4.61 (dd, *J* = 14.7, 5.2 Hz, 1H), 4.25 (dd, *J* = 9.6, 4.6 Hz, 1H), 3.97 (dd, *J* = 14.6, 10.8 Hz, 1H), 3.57 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 0.56 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 143.6, 140.0, 139.2, 138.4, 133.7, 132.6, 132.4, 132.3, 129.7, 128.13, 128.06, 127.7, 127.4, 127.2, 126.0, 125.7, 125.6, 124.8, 60.8, 52.1, 51.1, 21.6, 13.3. **IR** (KBr): ν 2924, 1727, 1630, 1592, 1493, 1350, 1304, 1161, 1094, 802, 778, 709, 691 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{30}H_{27}NO_4S$ $[M+H]^+$ = 498.1734, found = 498.1735.

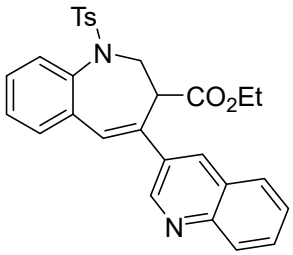
Ethyl 4-(naphthalen-2-yl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4aw)



The title compound was prepared according to the general procedure to afford **4aw** (36.8 mg, 74%

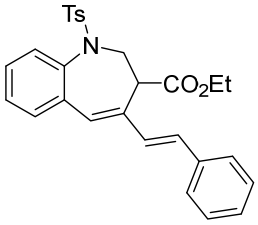
yield) as a white solid. M.p. 126.9 – 131.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.61 (m, 3H), 7.48 – 7.39 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.24 – 7.18 (m, 1H), 6.88 (br, 1H), 6.43 (s, 1H), 4.61 (dd, *J* = 14.7, 5.3 Hz, 1H), 4.26 (ddd, *J* = 10.9, 5.4, 2.0 Hz, 1H), 3.97 (dd, *J* = 14.6, 10.8 Hz, 1H), 3.57 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 0.56 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 143.6, 140.0, 139.2, 138.4, 133.7, 132.6, 132.4, 132.3, 131.2, 129.7, 128.12, 128.05, 127.7, 127.4, 127.2, 126.0, 125.7, 125.6, 124.7, 60.8, 52.1, 51.1, 21.6, 13.3. **IR** (KBr): ν 2978, 2926, 2854, 1730, 1630, 1493, 1350, 1304, 1162, 1095, 911, 803, 799, 709, 691, 659 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{30}H_{27}NO_4S$ $[M+H]^+$ = 498.1734, found = 498.1737.

Ethyl 4-(quinolin-3-yl)-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ax)



The title compound was prepared according to the general procedure to afford **4ax** (45.0 mg, 90% yield) as a yellow solid. M.p. 71.6 – 73.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.71 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.65 (dt, *J* = 7.1, 3.6 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.34 – 7.27 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 1.6 Hz, 1H), 4.67 (dd, *J* = 14.6, 5.7 Hz, 1H), 4.34 (ddd, *J* = 10.1, 5.8, 1.6 Hz, 1H), 3.96 (dd, *J* = 14.6, 10.0 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 149.1, 147.2, 143.7, 138.9, 138.0, 136.4, 134.9, 132.7, 132.6, 132.6, 131.9, 129.6, 129.5, 129.1, 128.9, 128.5, 127.8, 127.7, 127.2, 127.1, 61.3, 51.8, 49.7, 21.4, 13.7. **IR** (KBr): ν 3054, 2980, 2930, 1731, 1596, 1568, 1349, 1305, 1162, 1093, 910, 814, 753, 709, 692, 655 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{29}H_{26}N_2O_4S$ $[M+H]^+$ = 499.1686, found = 499.1685.

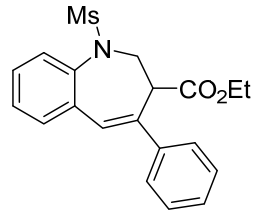
Ethyl (E)-4-styryl-1-tosyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ay)



The title compound was prepared according to the general procedure to afford **4ay** (24.8 mg, 52% yield) as a yellow solid. M.p. 89.3 – 93.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 7.39 – 7.30 (m, 4H), 7.26 – 7.16 (m, 4H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 16.4 Hz, 1H), 6.45 (d, *J* = 16.4 Hz, 1H), 6.36 (s, 1H), 4.55 (dd, *J* = 14.6, 6.0 Hz, 1H), 4.24 – 4.02 (m, 3H), 3.88 (dd, *J* = 14.6, 10.1 Hz, 1H), 2.24 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR**

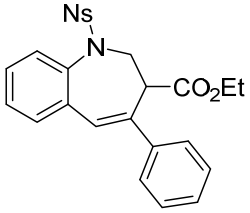
(101 MHz, $CDCl_3$) δ 171.1, 143.4, 139.4, 137.3, 137.0, 136.9, 132.8, 132.6, 132.2, 129.3, 128.7, 128.5, 128.1, 128.0, 127.7, 127.4, 127.1, 126.4, 61.5, 52.1, 47.6, 21.4, 14.1. **IR** (KBr): ν 2730, 1727, 1630, 1581, 1493, 1347, 1303, 1161, 1101, 963, 813, 749, 710, 654 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{28}H_{27}NO_4S$ $[M+H]^+$ = 474.1734, found = 474.1743.

Ethyl 1-(methylsulfonyl)-4-phenyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ba)



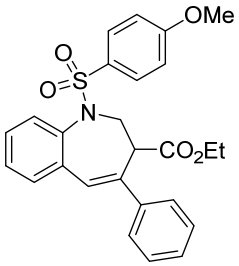
The title compound was prepared according to the general procedure to afford **4ba** (30.5 mg, 81% yield) as a white solid. M.p. 135.2 – 139.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.27 (m, 6H), 6.79 (s, 1H), 4.39 – 4.27 (m, 2H), 4.13 (td, *J* = 10.6, 4.4 Hz, 1H), 3.93 (q, *J* = 7.2 Hz, 2H), 2.89 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 142.4, 140.1, 138.4, 132.9, 132.5, 130.2, 128.5, 128.3, 127.93, 127.87, 127.7, 126.5, 61.2, 51.2, 50.5, 40.2, 13.7. **IR** (KBr): ν 3054, 3023, 2980, 2934, 1731, 1630, 1570, 1572, 1493, 1343, 1154, 962, 760, 699 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{20}H_{21}NO_4S$ $[M+H]^+$ = 372.1264, found = 372.1266.

Ethyl 1-((4-nitrophenyl)sulfonyl)-4-phenyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4ca)



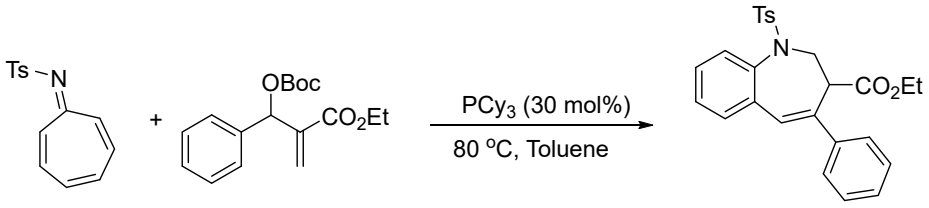
The title compound was prepared according to the general procedure to afford **4ca** (32.7 mg, 68% yield) as a yellow solid. M.p. 124.1 – 128.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 2H), 7.78 – 7.71 (m, 2H), 7.67 – 7.59 (m, 1H), 7.42 – 7.31 (m, 2H), 7.30 – 7.23 (m, 3H), 7.23 – 7.17 (m, 1H), 7.09 – 7.02 (m, 2H), 6.25 (s, 1H), 4.65 (dd, *J* = 14.2, 5.7 Hz, 1H), 4.20 (dd, *J* = 14.2, 8.8 Hz, 1H), 4.09 (ddd, *J* = 8.8, 5.7, 1.0 Hz, 1H), 3.84 (qd, *J* = 7.1, 1.9 Hz, 2H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 149.8, 145.8, 141.1, 140.0, 137.1, 134.1, 131.9, 129.7, 129.3, 128.6, 128.5, 128.4, 128.3, 128.1, 126.0, 123.9, 61.3, 53.8, 48.8, 13.7. **IR** (KBr): ν 2978, 2928, 2869, 1728, 1630, 1605, 1530, 1349, 1306, 1168, 1095, 855, 766, 738, 698, 610 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{22}N_2O_6S$ $[M+H]^+$ = 479.1271, found = 479.1276.

Ethyl 1-((4-methoxyphenyl)sulfonyl)-4-phenyl-2,3-dihydro-1H-benzo[b]azepine-3-carboxylate (4da)



The title compound was prepared according to the general procedure to afford **4da** (37.6 mg, 81% yield) as a white solid. M.p. 85.2 – 86.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.59 – 7.53 (m, 2H), 7.31 – 7.23 (m, 5H), 7.23 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 6.82 – 6.75 (m, 2H), 6.35 (d, *J* = 1.5 Hz, 1H), 4.59 (dd, *J* = 14.5, 5.5 Hz, 1H), 4.20 (ddd, *J* = 9.8, 5.6, 1.5 Hz, 1H), 3.94 (dd, *J* = 14.5, 9.7 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 162.8, 142.1, 139.7, 138.6, 133.2, 132.3, 132.2, 129.8, 129.2, 128.9, 128.1, 127.9, 127.6, 127.5, 126.5, 113.9, 61.0, 55.5, 52.0, 49.6, 13.7. **IR** (KBr): ν 2928, 2842, 1728, 1630, 1595, 1496, 1349, 1305, 1157, 1093, 908, 832, 805, 767, 697 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{25}NO_5S$ $[M+H]^+$ = 479.1271, found = 479.1276.

H. Gram scale synthesis of 4aa



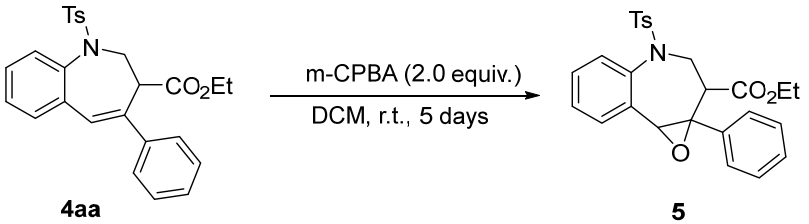
1a 4 mmol

2a 4 mmol

4aa 1.11 g, 62% yield

To a dried 100 mL round-bottomed flask with a magnetic stirring bar was added **1a** (1.2 g, 4.0 mmol, 1.0 equiv.), **2a** (1 g, 4.0 mmol, 1.0 equiv.), followed by the addition of toluene (40 mL). Allow the solid to dissolve completely, PCy_3 (336 mg, 30 mol%) was added at room temperature. Then the reaction mixture was stirred at 80 ºC for 3 h and monitored by TLC. The reaction solution was concentrated under reduced pressure and then purified directly by column chromatography directly on silica gel with PE/EA as eluent to afford **4aa** (1.11 g, 62% yield).

I. Transformation of the product 4aa



4aa
0.5 mmol

5
130.0 mg, 57% yield

m-Chloroperbenzoic acid (170 mg, 1.0 mmol, 2.0 equiv.) was added to a solution of **4aa** (220 mg, 0.5 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 5 days and monitored by TLC. CH_2Cl_2 was then added, and the solution was washed with NaOH (2 N), dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography directly on silica gel with PE/EA as eluent to give the targeted products **5** (130 mg, 57% yield) as a white solid. M.p.158.2 – 159.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.27 (m, 8H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.84 (t, *J* = 13.0 Hz, 1H), 4.03 – 3.87 (m, 2H), 3.74 (dd, *J* = 13.4, 6.5 Hz, 1H), 3.53 (s, 1H), 2.59 (dd, *J* = 12.7, 6.4 Hz, 1H), 2.33 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 143.6, 136.9, 136.7, 135.4, 134.4, 130.4, 129.8, 129.6, 129.5, 129.3, 128.3, 128.2, 127.4, 126.1, 61.2, 60.9, 60.4, 49.6, 47.4, 21.5, 13.8. **IR** (KBr): ν 3036, 2925, 1728, 1630, 1598, 1493, 1348, 1163, 1115, 1092, 1064, 938, 903, 815, 760, 710, 661 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{26}NO_5S$ $[M+H]^+$ = 464.1526, found = 464.1530.

J. X-Ray crystallographic analysis

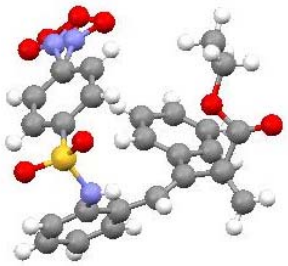


Figure 1. X-ray structure of **3ca**

The title compound was recrystallized from hexane/DCM, by slow evaporation of solvent.

Table 2. Crystal data and structure refinement for **3ca** (CCDC 2269752)

Empirical formula	C25 H22 N2 O6 S	
Formula weight	478.50	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.452(3) Å	α= 90.
	b = 17.525(4) Å	β= 108.347(3).
	c = 9.769(2) Å	γ = 90.
Volume	2348.4(9) $Å^3$	
Z	4	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	1000	
Crystal size	0.210 x 0.180 x 0.170 mm^3	
Theta range for data collection	1.485 to 27.530°.	
Index ranges	-18<=h<=18, -19<=k<=22, -12<=l<=11	
Reflections collected	14426	
Independent reflections	5381[R(int) = 0.0312]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5381/ 44 / 339	
Goodness-of-fit on F^2	1.133	
Final R indices [I>2sigma(I)]	R1 = 0.0527, wR2 = 0.1642	
R indices (all data)	R1 = 0.0660, wR2 = 0.1795	
Largest diff. peak and hole	0.470 and -0.467 e.$Å^{-3}$	

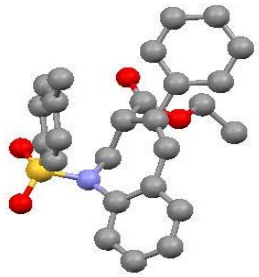


Figure 2. X-ray structure of **4aa**

The title compound was recrystallized from hexane/DCM, by slow evaporation of solvent.

Table 3. Crystal data and structure refinement for **4aa** (CCDC 2269753)

Empirical formula	C26 H25 N O4 S	
Formula weight	447.53	
Temperature	296K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.622(5)Å	α= 63.485(6).
	b = 11.052(6)Å	β=68.532(6).
	c = 12.153(6)Å	γ =70.726(6)
77.611(4).		
Volume	1164.0(10) $Å^3$	
Z	2	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.171 mm^{-1}	
F(000)	472	
Crystal size	0.22 x 0.20 x 0.19 mm^3	
Theta range for data collection	1.939 to 27.581°.	
Index ranges	-13<=h<=12, -14<=k<=13, -14<=l<=15	
Reflections collected	7258	
Independent reflections	5202 [R(int) = 0.0159]	
Completeness to theta = 25.242°	98.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5202/ 0 /291	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1446	
R indices (all data)	R1 = 0.0600, wR2 = 0.1581	
Largest diff. peak and hole	0.287 and -0.382 $e.Å^{-3}$	

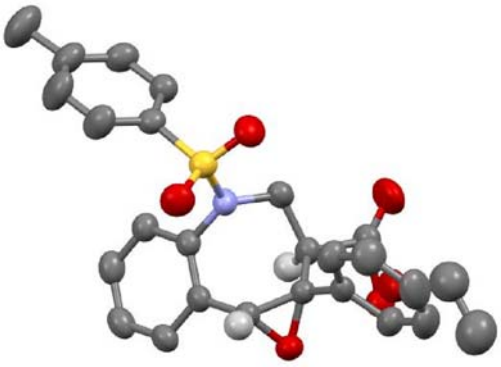


Figure 3. X-ray structure of **5**

The title compound was recrystallized from hexane/DCM, by slow evaporation of solvent.

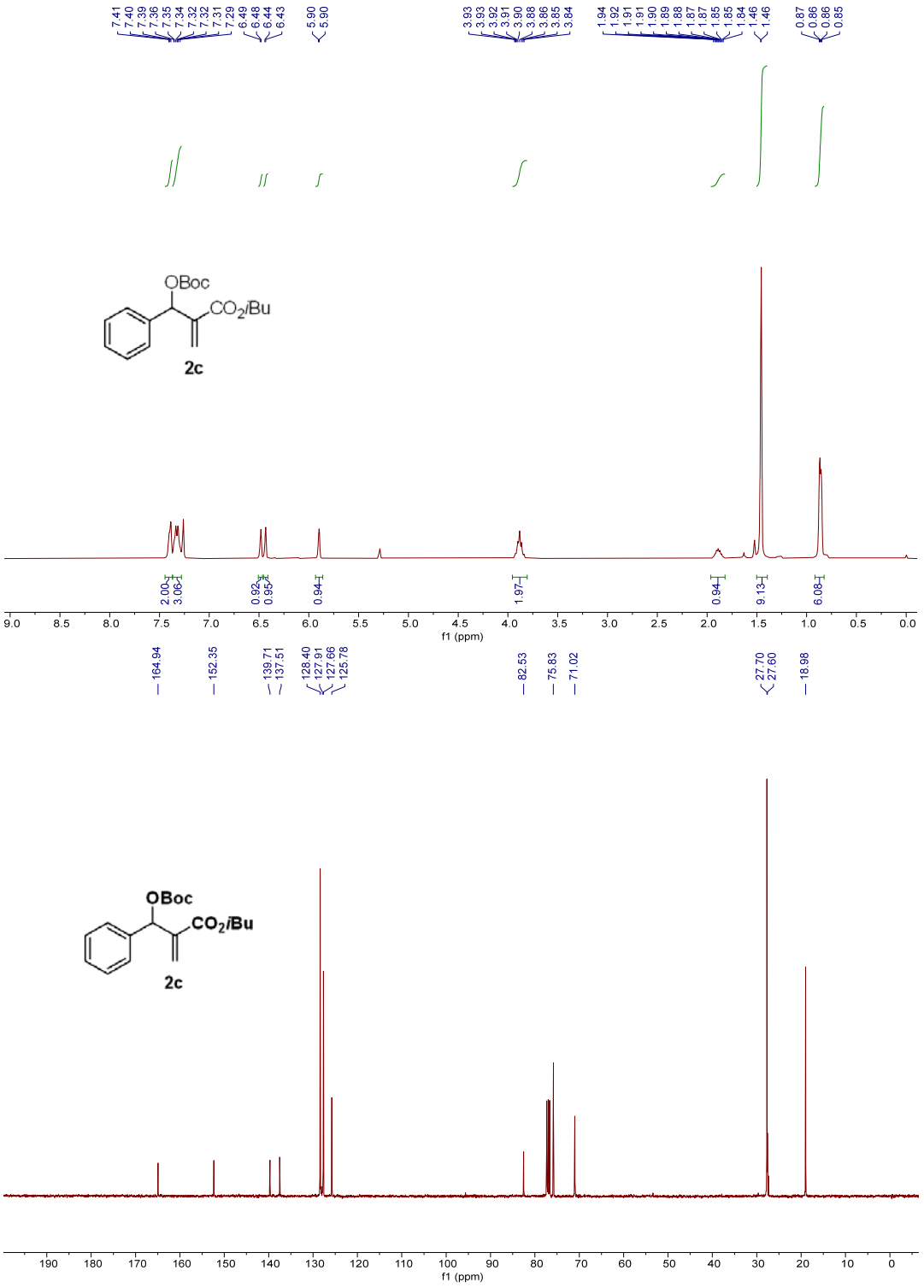
Table 3. Crystal data and structure refinement for **5** (CCDC 2377466)

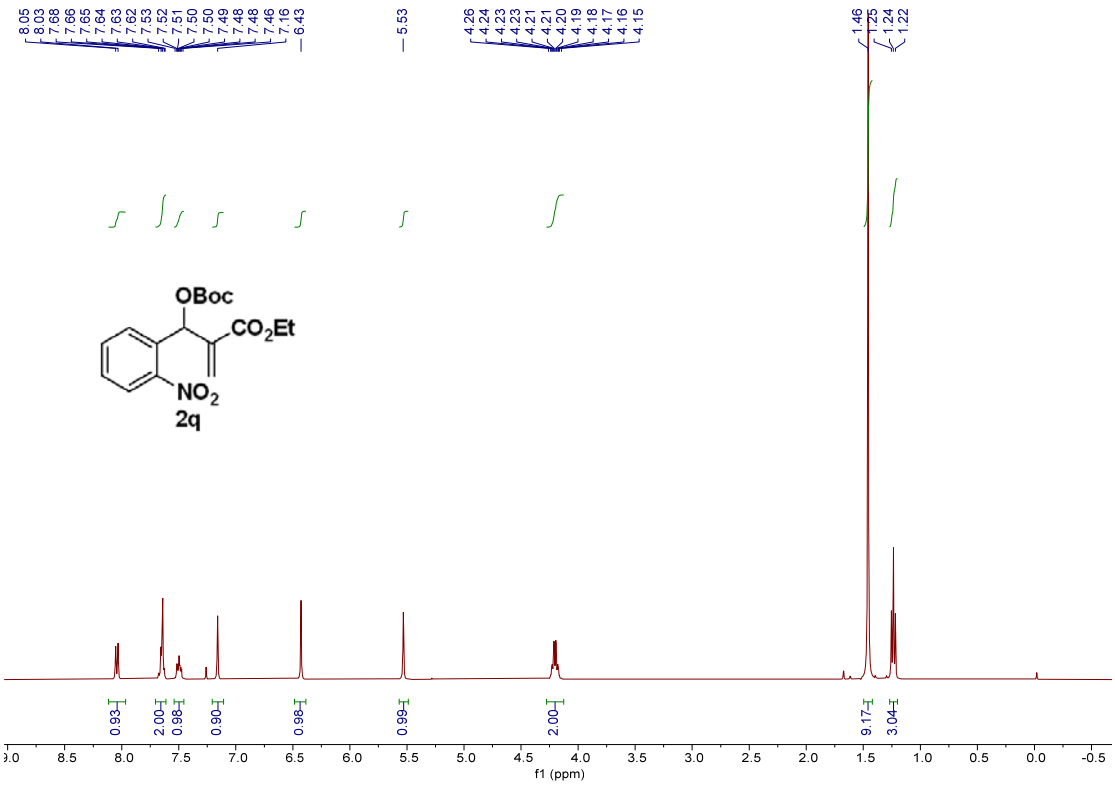
Empirical formula	C26 H25 N O5 S	
Formula weight	463.53	
Temperature	293K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.5226(3) Å	α = 90.
	b = 8.5185(3) Å	β = 91.414(3).
	c = 25.6829(6) Å	γ = 90.
Volume	2301.43(12) $Å^3$	
Z	4	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.171 mm^{-1}	
F(000)	976.0	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	3.443 to 74.620°.	
Index ranges	-13<=h<=12, -10<=k<=10, -31<=l<=28	
Reflections collected	21772	
Independent reflections	4571 [R(int) = 0.0439]	
Completeness to theta = 67.684°	97 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5202/ 24 /311	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1632	
R indices (all data)	R1 = 0.0639, wR2 = 0.1738	
Largest diff. peak and hole	0.816 and -0.573 $e.Å^{-3}$	

K. Reference

[1] R. Manzano, A. Romaniega, L. Prieto, E. Díaz, E. Reyes, U. Uria, L. Carrillo, and J. L. Vicario, *Org. Lett.,***2020**, *22*, 4721–4725.

L. NMR Spectra

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7.62
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7.52
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7.50
7.49
7.48
7.48
7.46
7.16
6.43
5.53
4.26
4.24
4.23
4.23
4.21
4.21
4.20
4.19
4.18
4.17
4.16
4.15
1.46
1.25
1.24
1.22
OBoc
CO2Et
NO2
2q
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0.90
0.98
0.99
2.00
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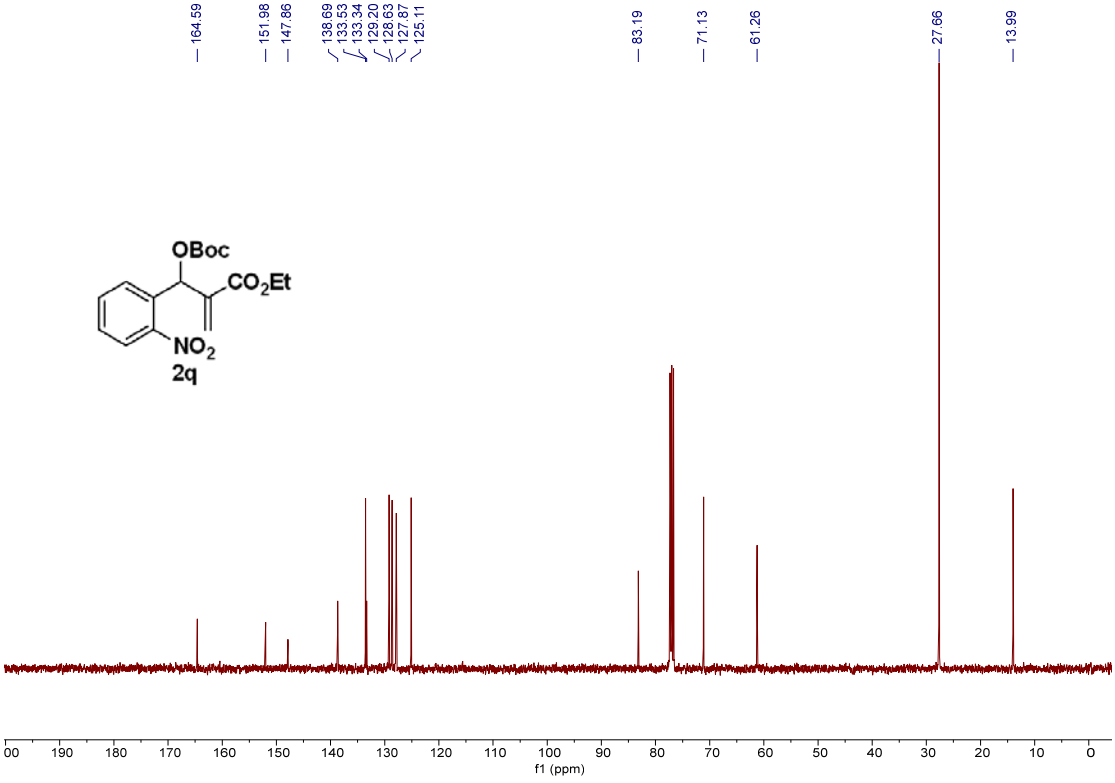
3.04
f1 (ppm)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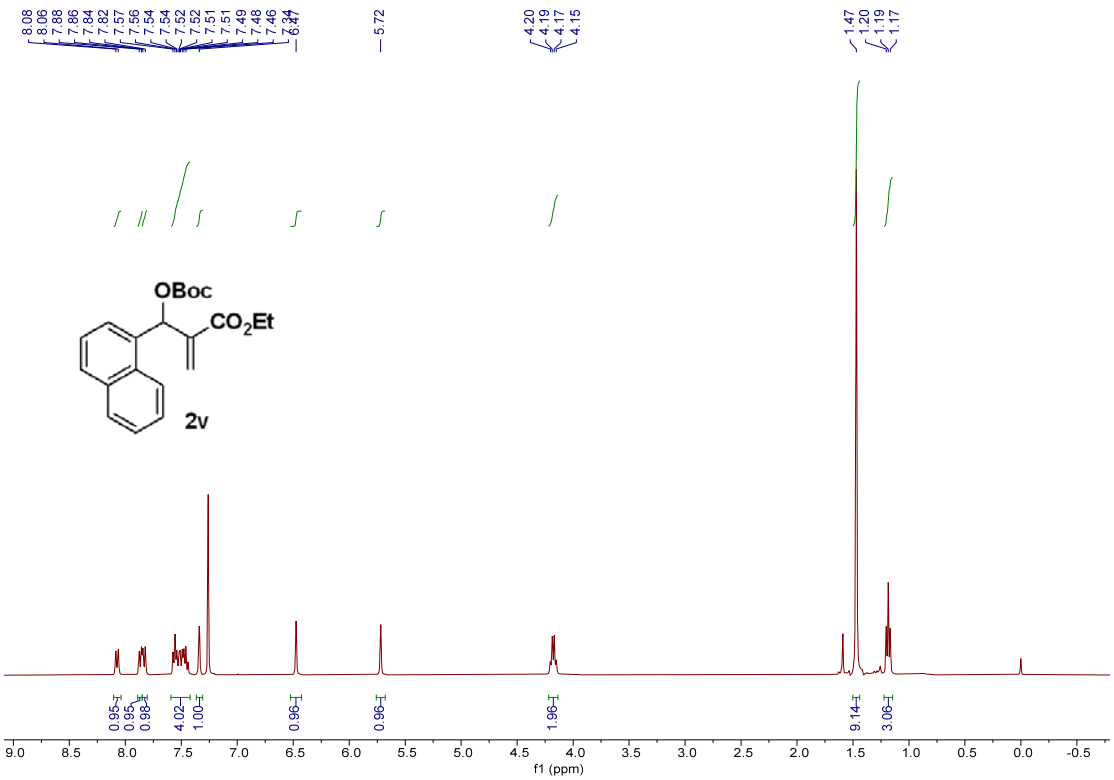
OBoc
CO2Et
NO2
2q
f1 (ppm)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4.15
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1.20
1.19
1.17
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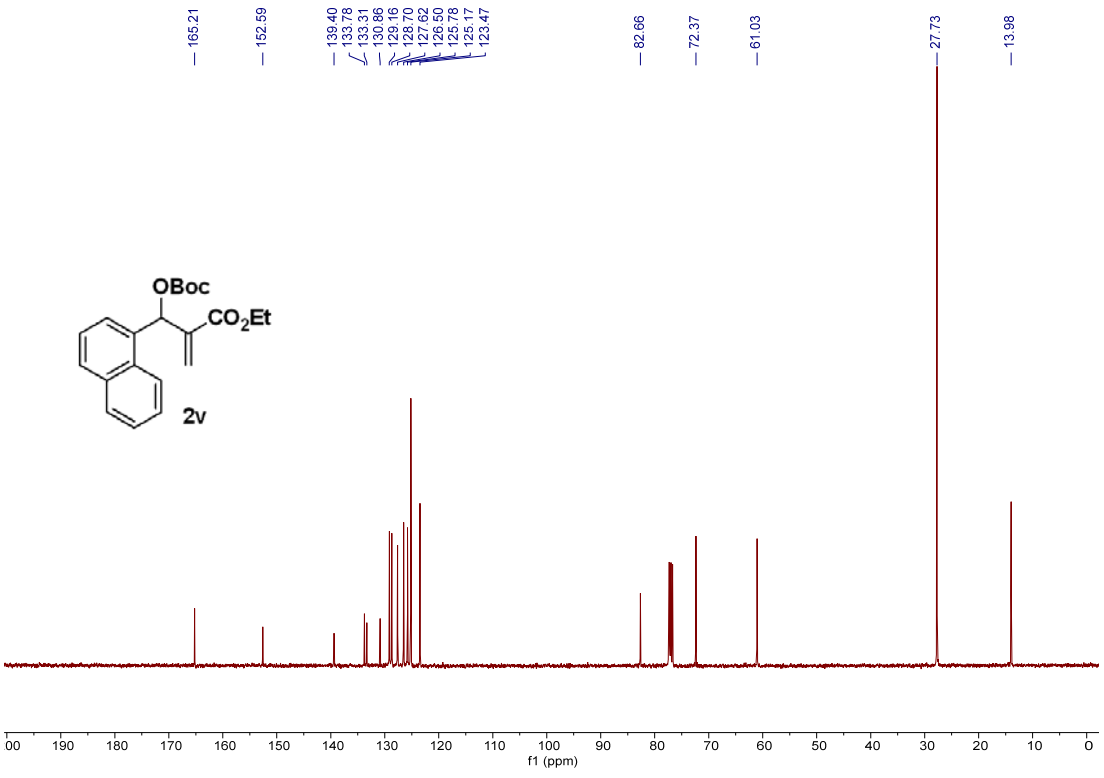
f1 (ppm)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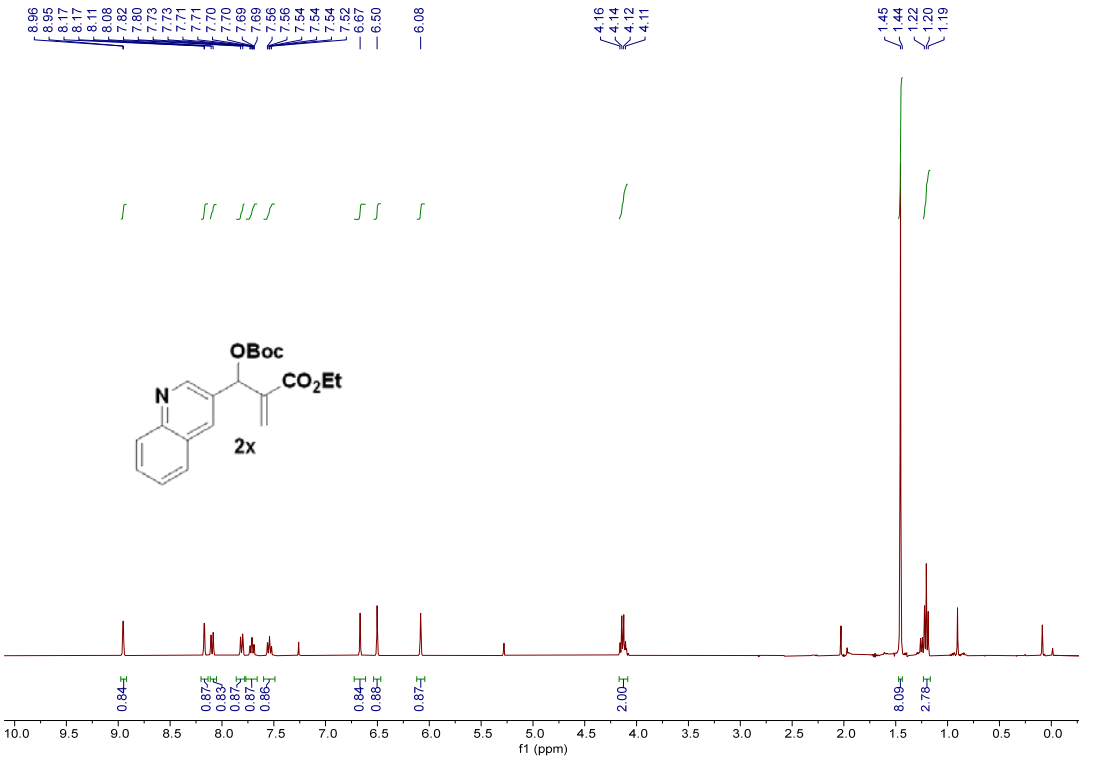
13.98
OBoc
CO2Et
2v
f1 (ppm)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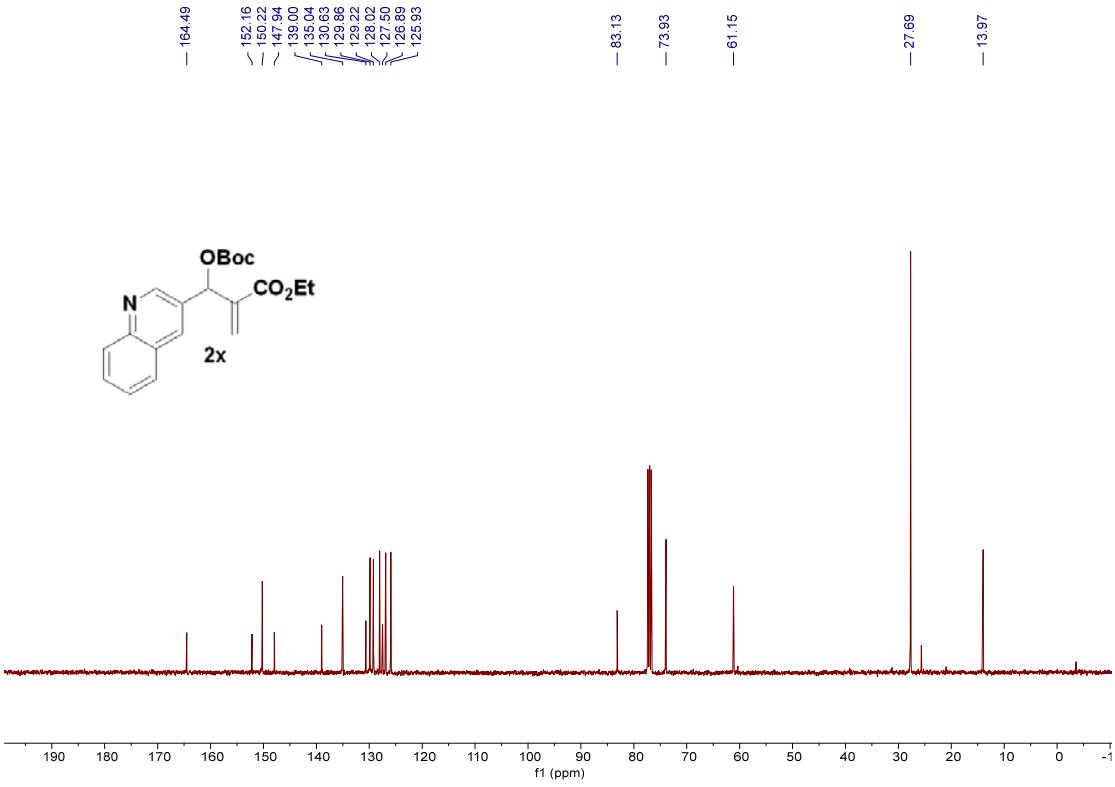
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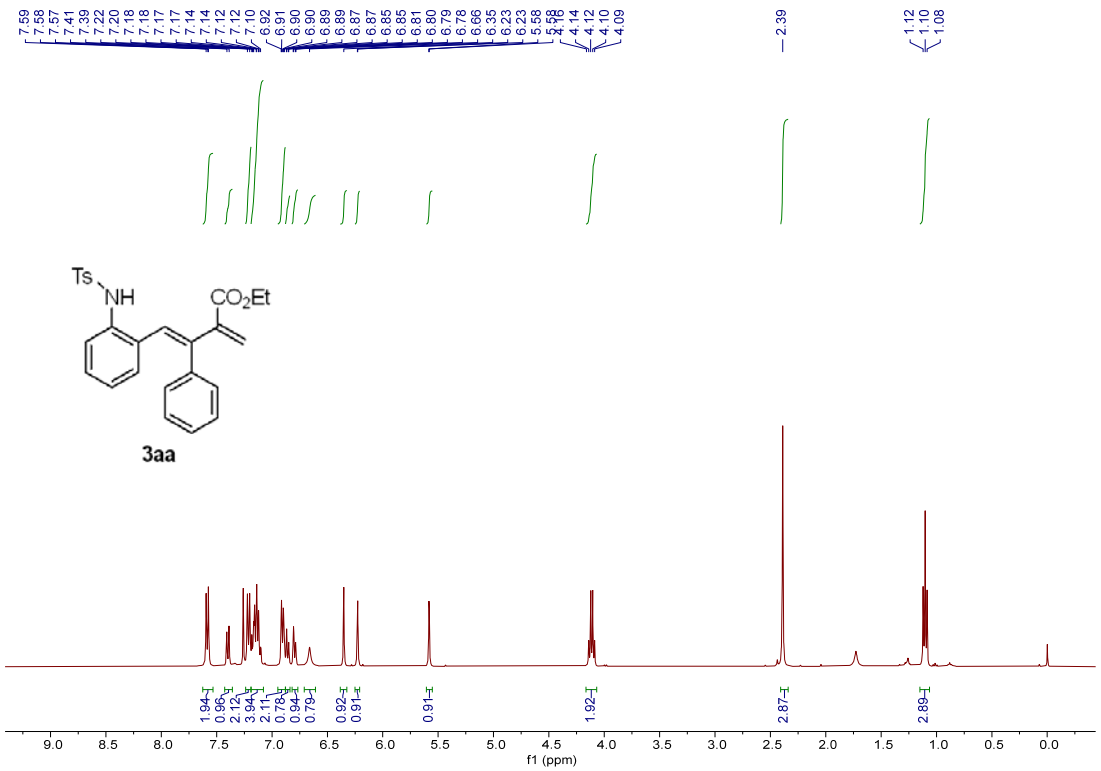
N
2x
f1 (ppm)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NH
CO2Et
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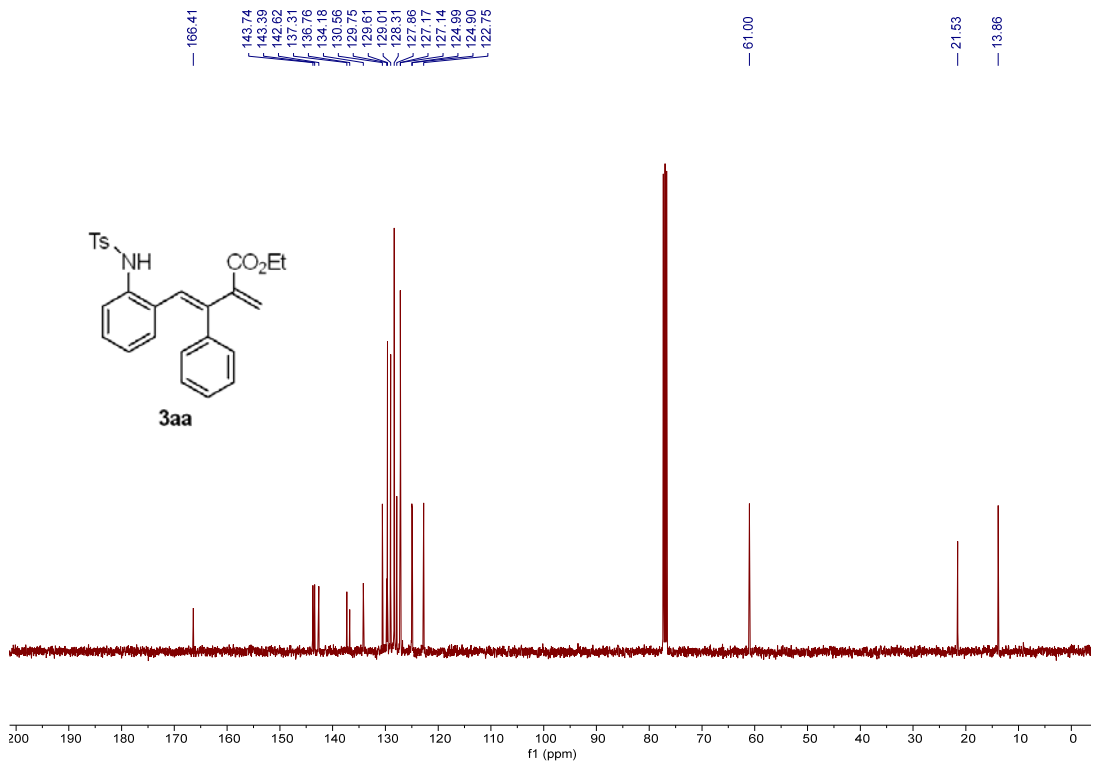
2.89
f1 (ppm)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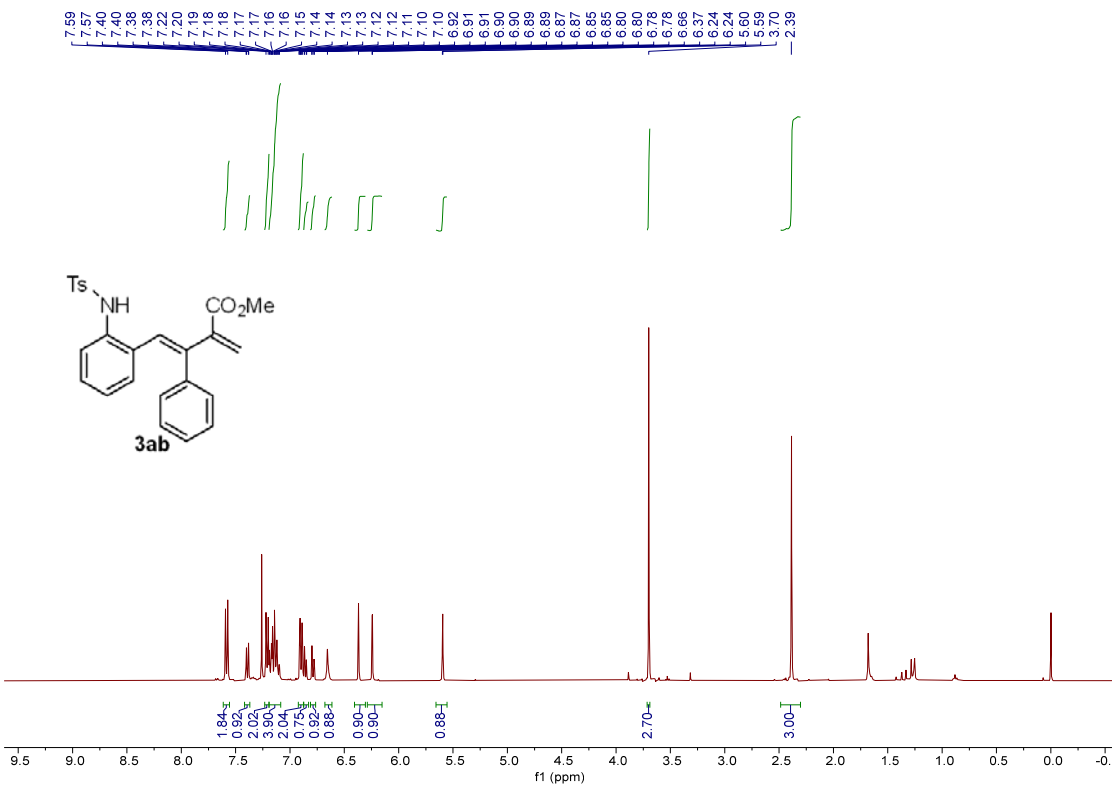
21.53
13.86
Ts
NH
CO2Et
3aa
f1 (ppm)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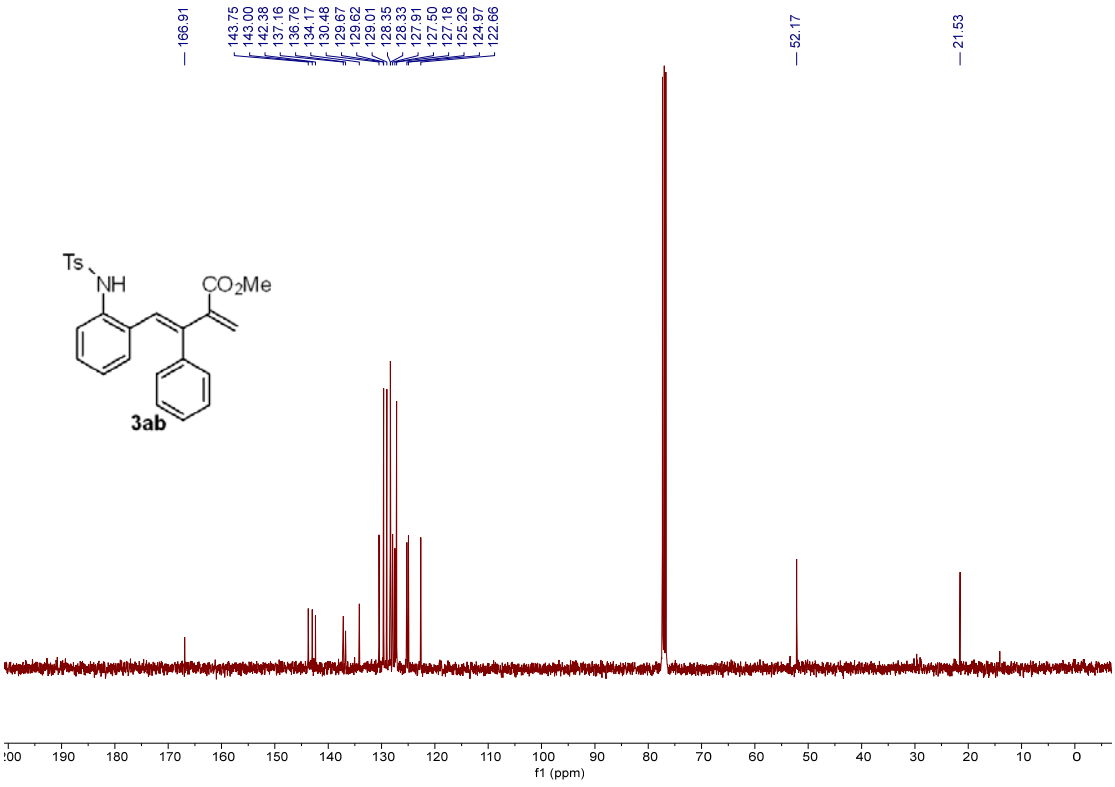
Ts
NH
CO2Me
3ab
1.84 0.92 2.02 3.90 2.04 0.75 0.92 0.88 0.90 0.90 0.88 2.70 3.00
f1 (ppm)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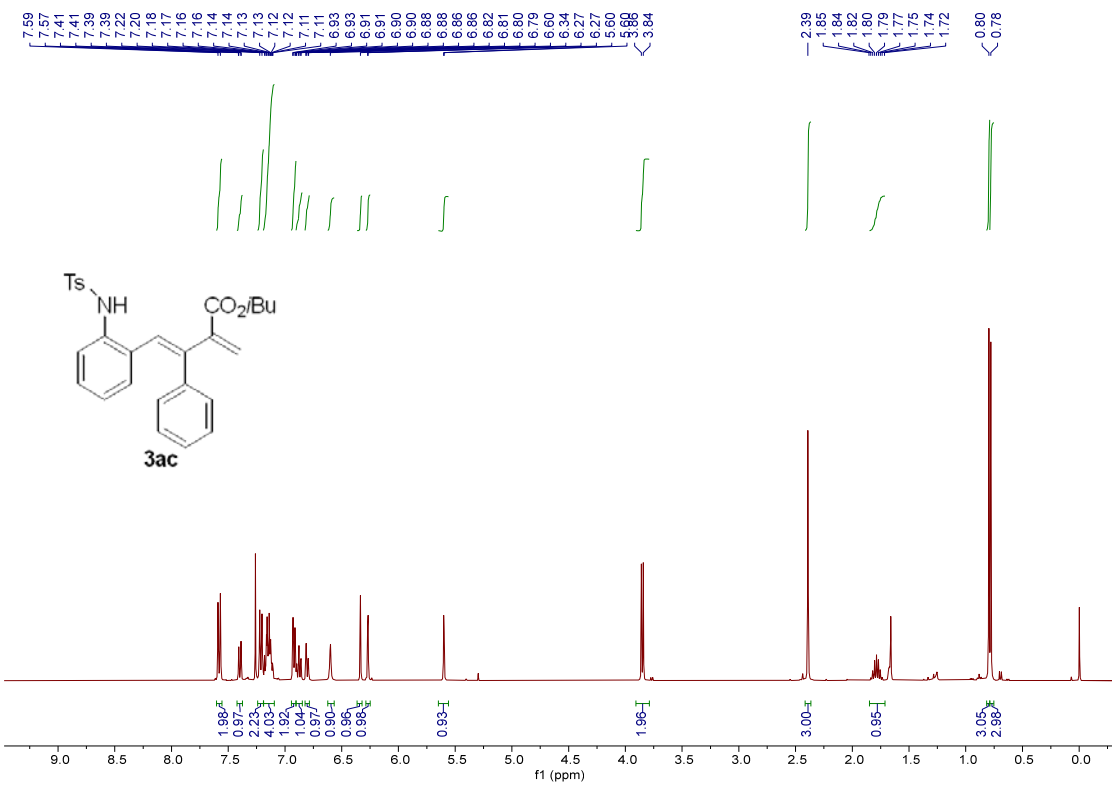
Ts
NH
CO2Me
3ab
f1 (ppm)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7.14
7.13
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7.12
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6.93
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6.91
6.91
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6.90
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6.88
6.86
6.86
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6.81
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3.84
2.39
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1.84
1.82
1.80
1.79
1.77
1.75
1.74
1.72
0.80
0.78
Ts
NH
CO2tBu
3ac
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0.97
2.23
4.03
1.92
1.04
0.97
0.90
0.96
0.98
0.93
1.96
3.00
0.95
3.05
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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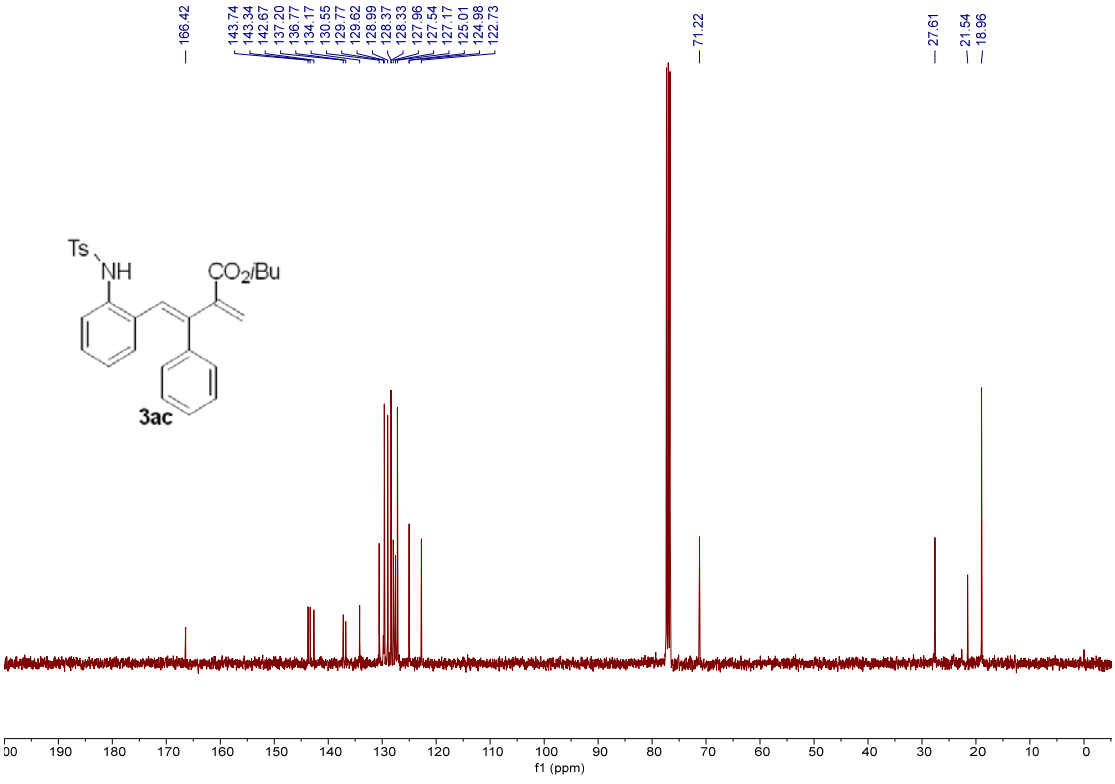
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127.54
127.17
125.01
124.98
122.73
71.22
27.61
21.54
18.96
Ts
NH
CO2tBu
3ac
190
180
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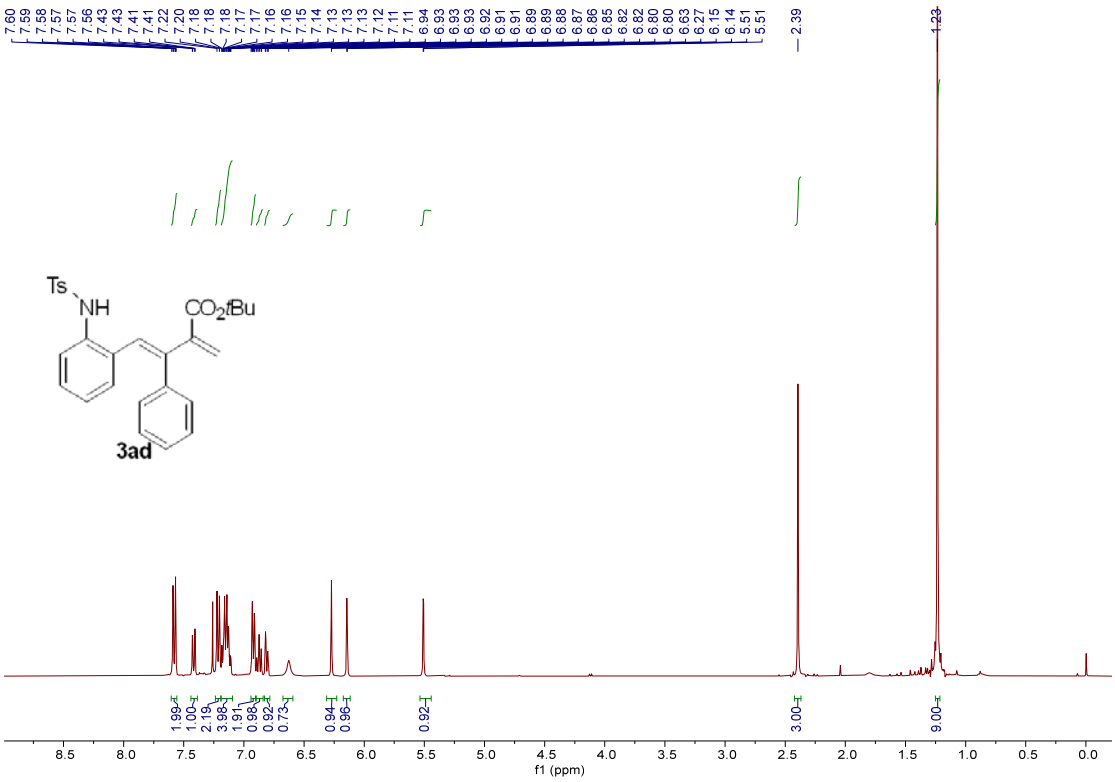
f1 (ppm)


Ts
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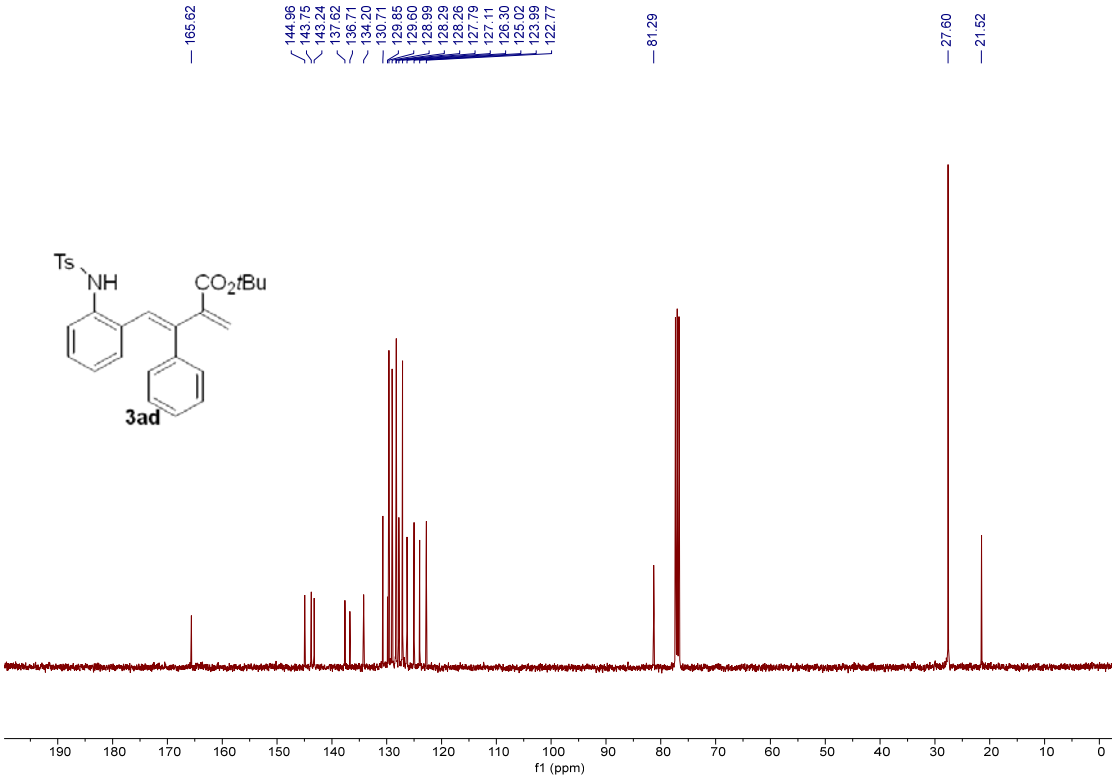
f1 (ppm)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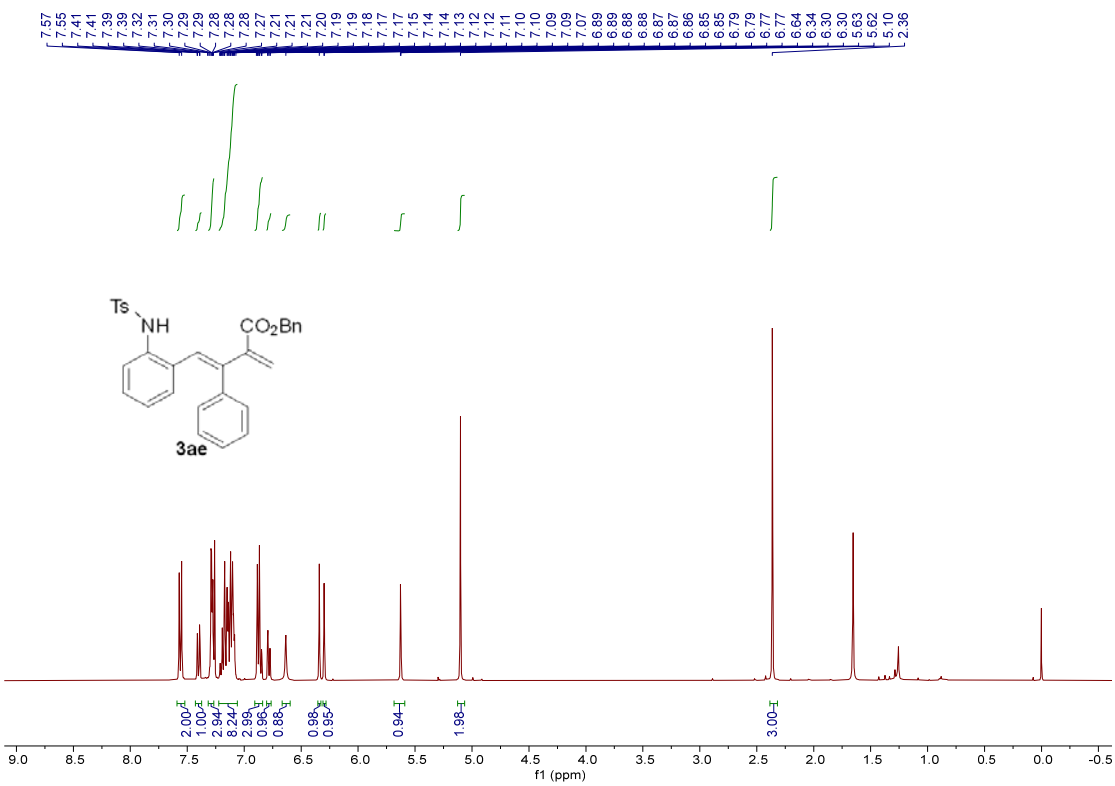
3ad
f1 (ppm)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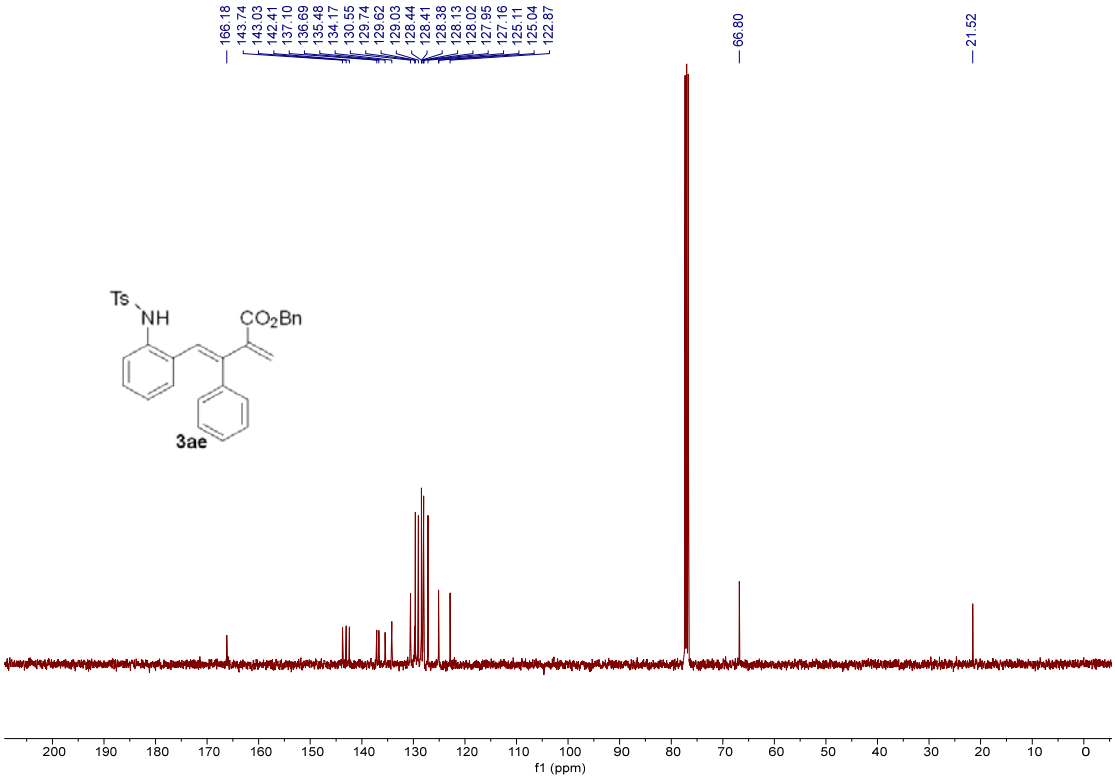
Ts
NH
CO2Bn
3ae
2.00 1.00 2.94 8.24 2.99 0.96 0.88 0.98 0.95 0.94 1.98 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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66.80
21.52
Ts
NH
CO2Bn
3ae
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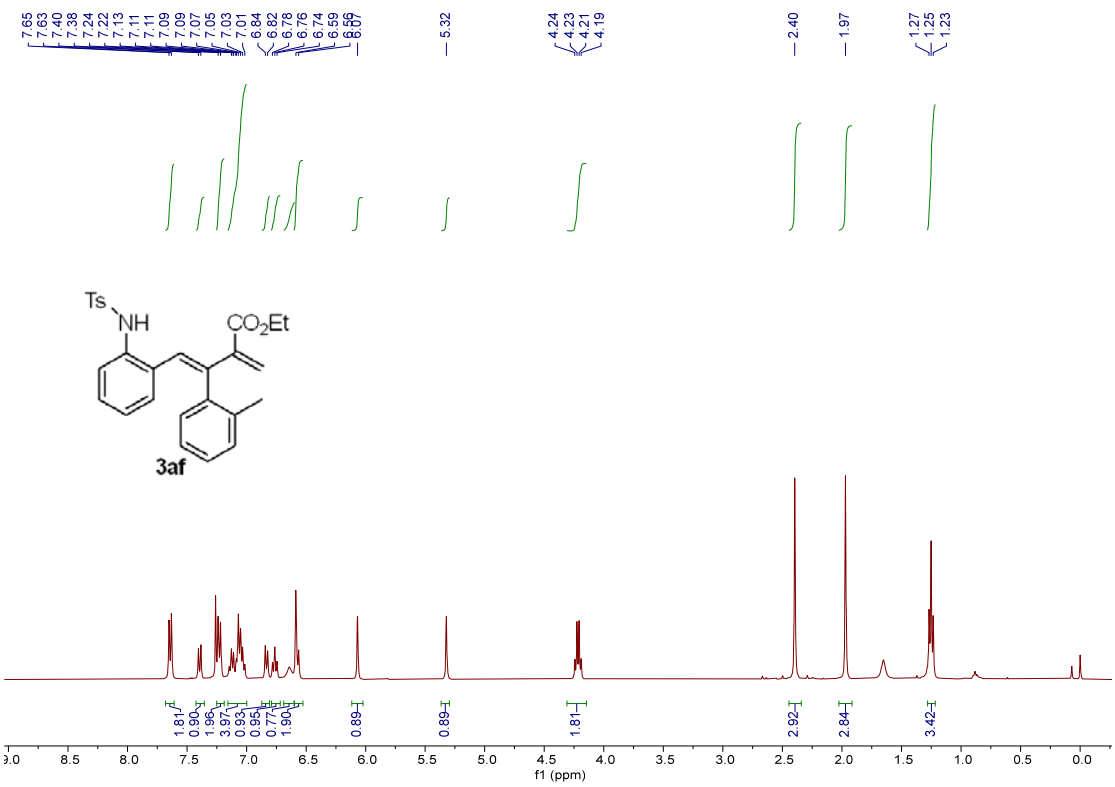
f1 (ppm)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7.07
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7.03
7.01
6.84
6.82
6.78
6.76
6.74
6.59
6.56
6.07
5.32
4.24
4.23
4.21
4.19
2.40
1.97
1.27
1.25
1.23
Ts
NH
CO2Et
3af
1.81
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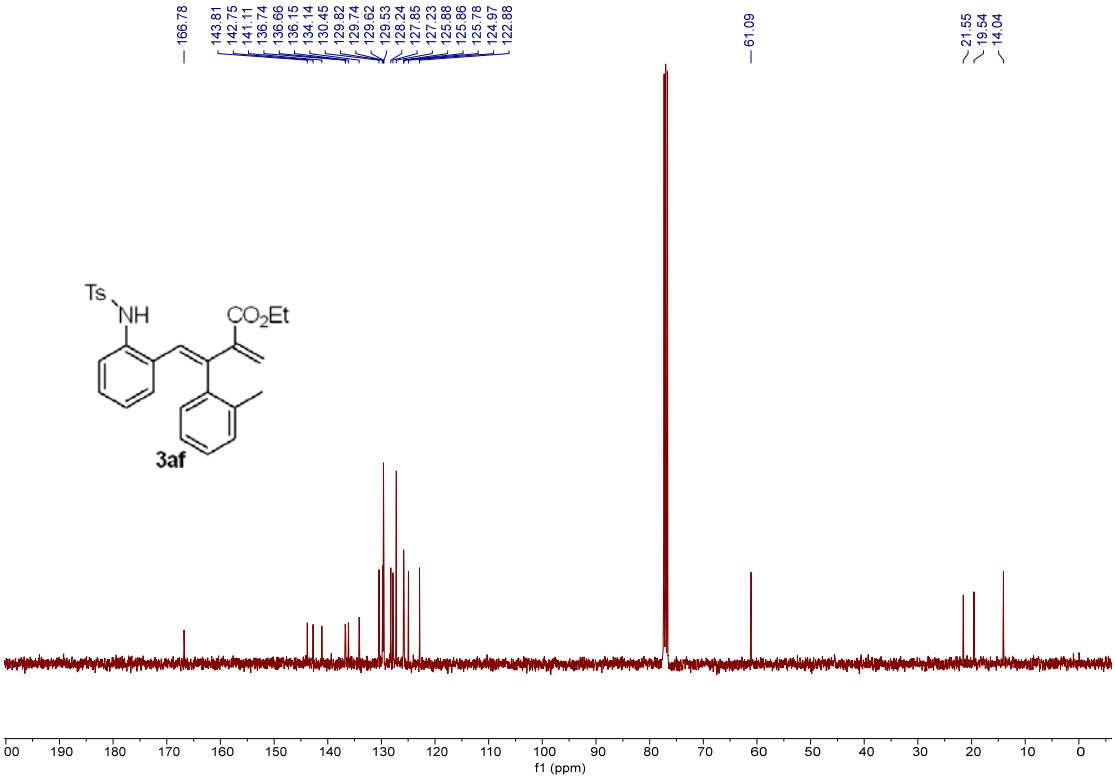
f1 (ppm)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127.23
125.88
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Ts
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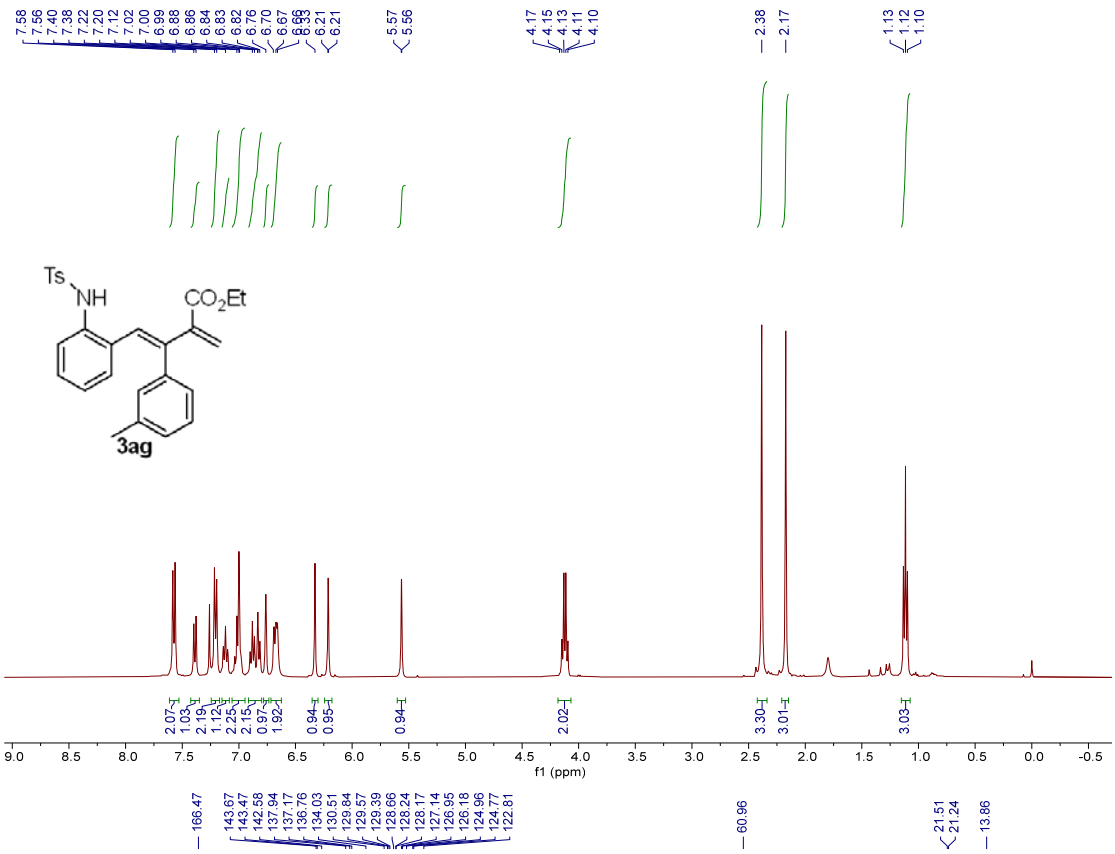
CO2Et
3af
f1 (ppm)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6.83
6.82
6.76
6.70
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6.21
6.21
5.57
5.56
4.17
4.15
4.13
4.11
4.10
2.38
2.17
1.13
1.12
1.10
Ts
NH
CO2Et
3ag
2.07
1.03
2.19
1.12
2.25
2.15
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1.92
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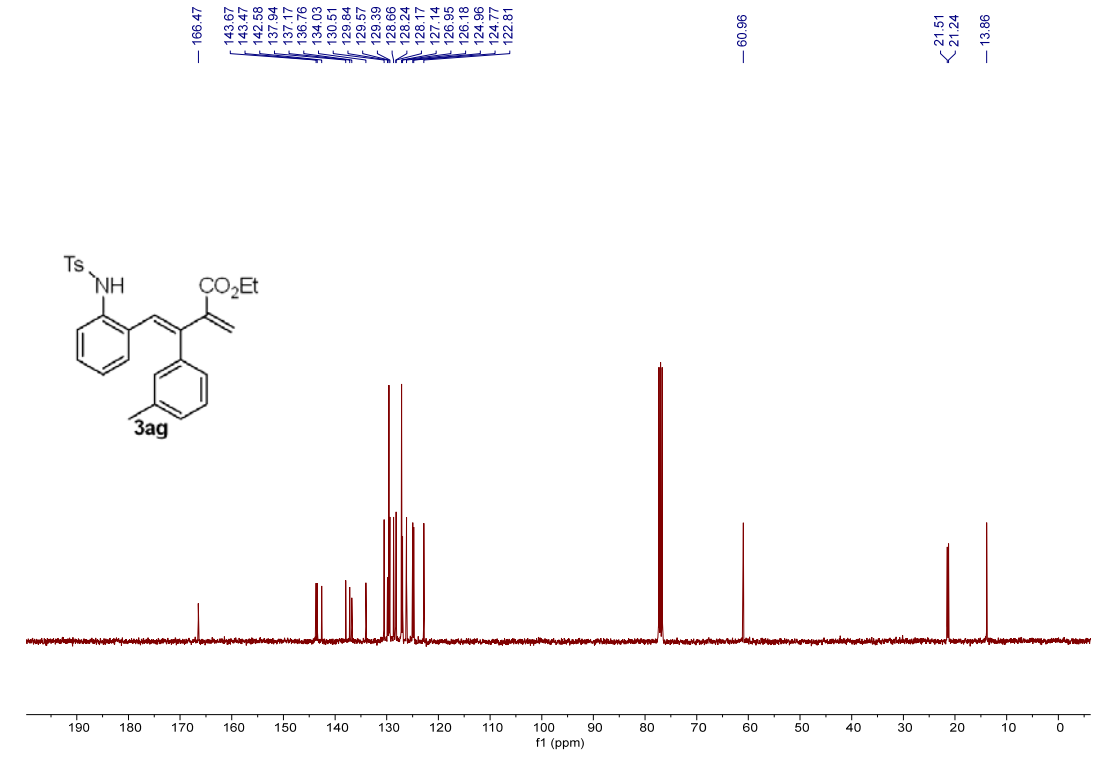
0.95
0.94
2.02
3.30
3.01
3.03
f1 (ppm)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129.57
129.39
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128.17
127.14
126.95
126.18
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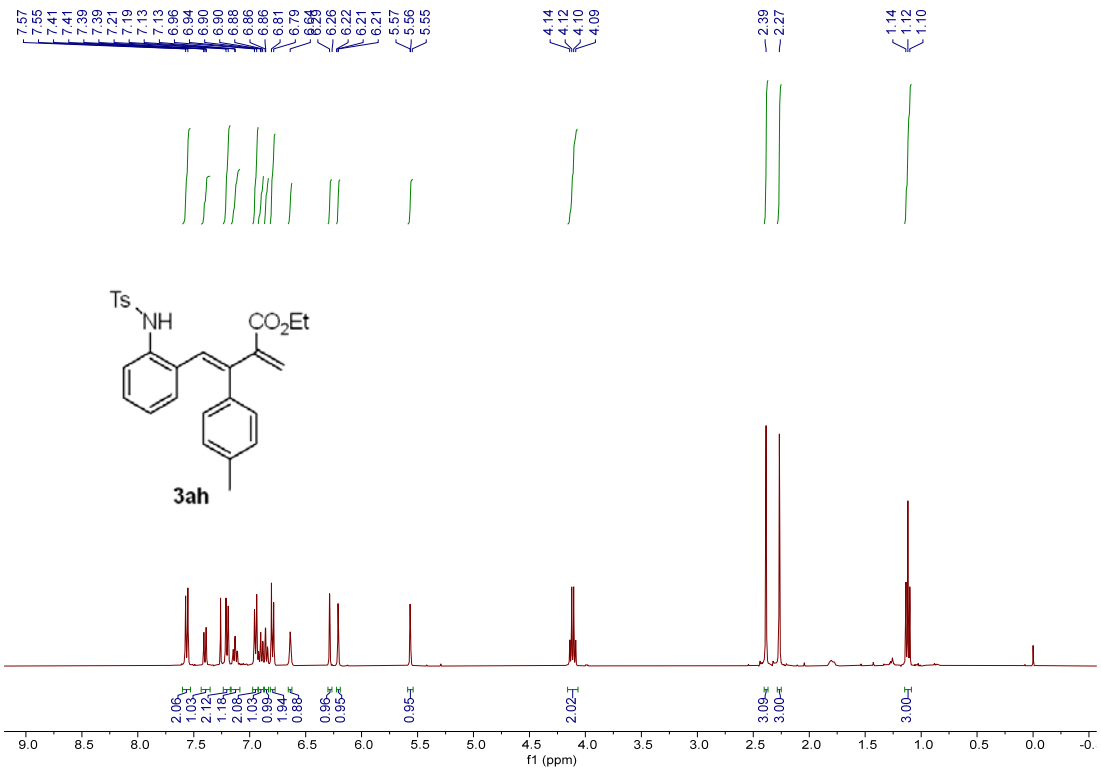
122.81
60.96
21.51
21.24
13.86
Ts
NH
CO2Et
3ag
f1 (ppm)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6.90
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6.86
6.81
6.79
6.26
6.22
6.21
5.57
5.56
5.55
4.14
4.12
4.10
4.09
2.39
2.27
1.14
1.12
1.10
Ts
NH
CO2Et
3ah
2.06
1.03
2.12
1.18
2.08
1.03
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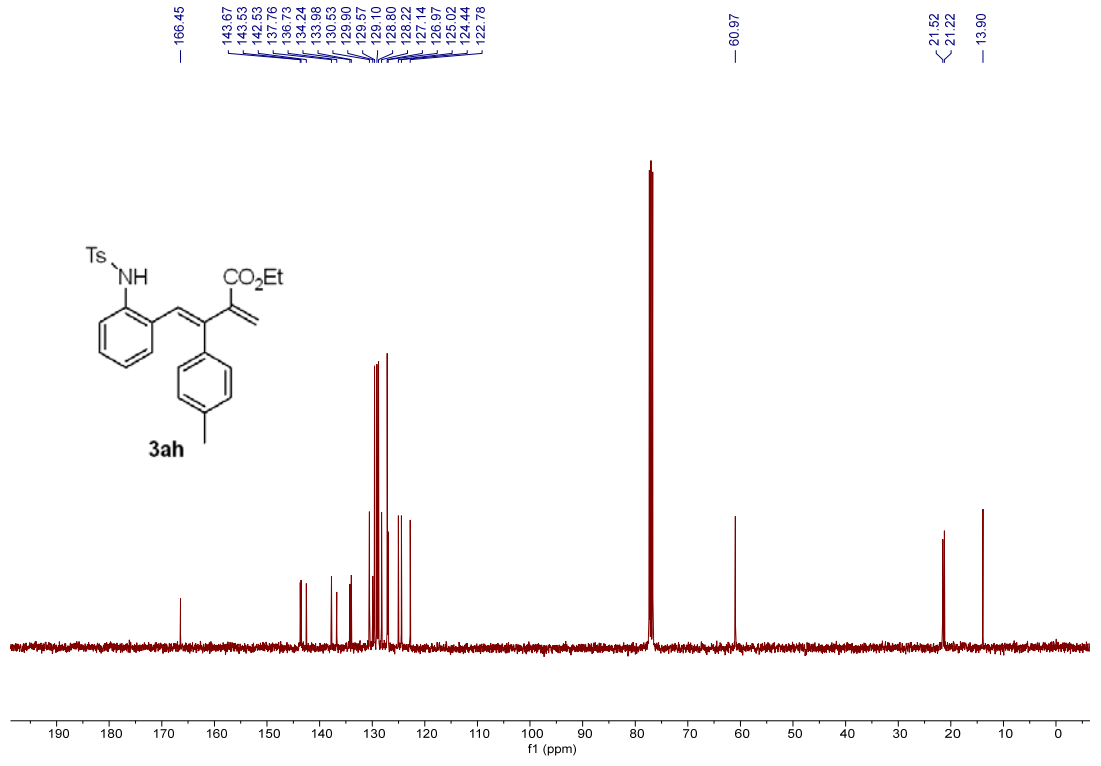
0.88
0.96
0.95
0.95
2.02
3.09
3.00
3.00
f1 (ppm)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127.14
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21.52
21.22
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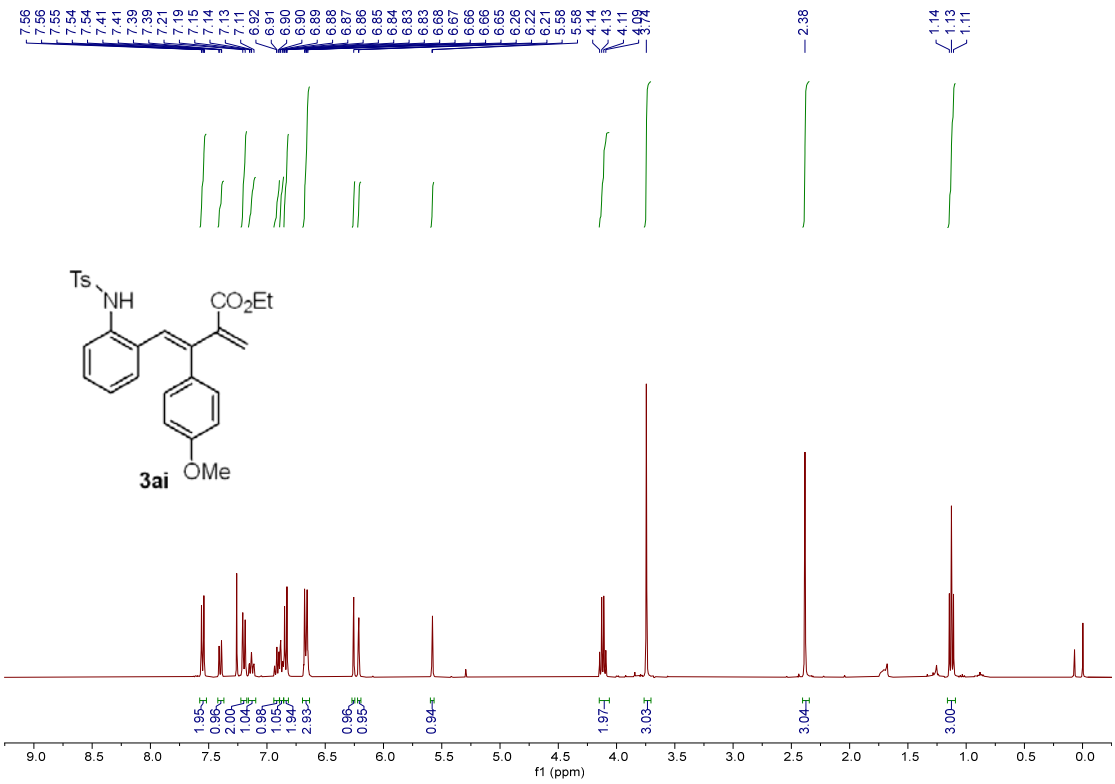
Ts
NH
CO2Et
3ah
f1 (ppm)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4.11
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1.13
1.11
Ts
NH
CO2Et
OMe
3ai
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2.00
1.04
0.98
1.05
1.94
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0.95
0.94
1.97
3.03
3.04
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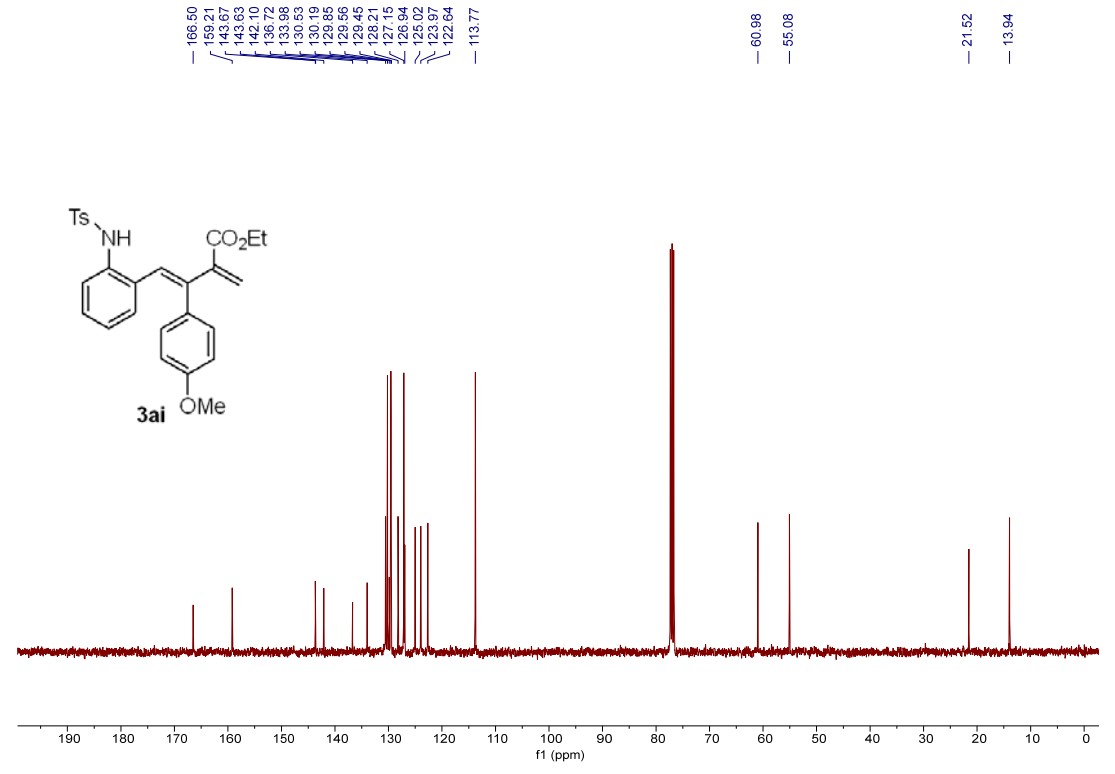
0.0
f1 (ppm)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127.15
126.94
125.02
123.97
122.64
113.77
60.98
55.08
21.52
13.94
Ts
NH
CO2Et
OMe
3ai
190
180
170
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150
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130
120
110
100
90
80
70
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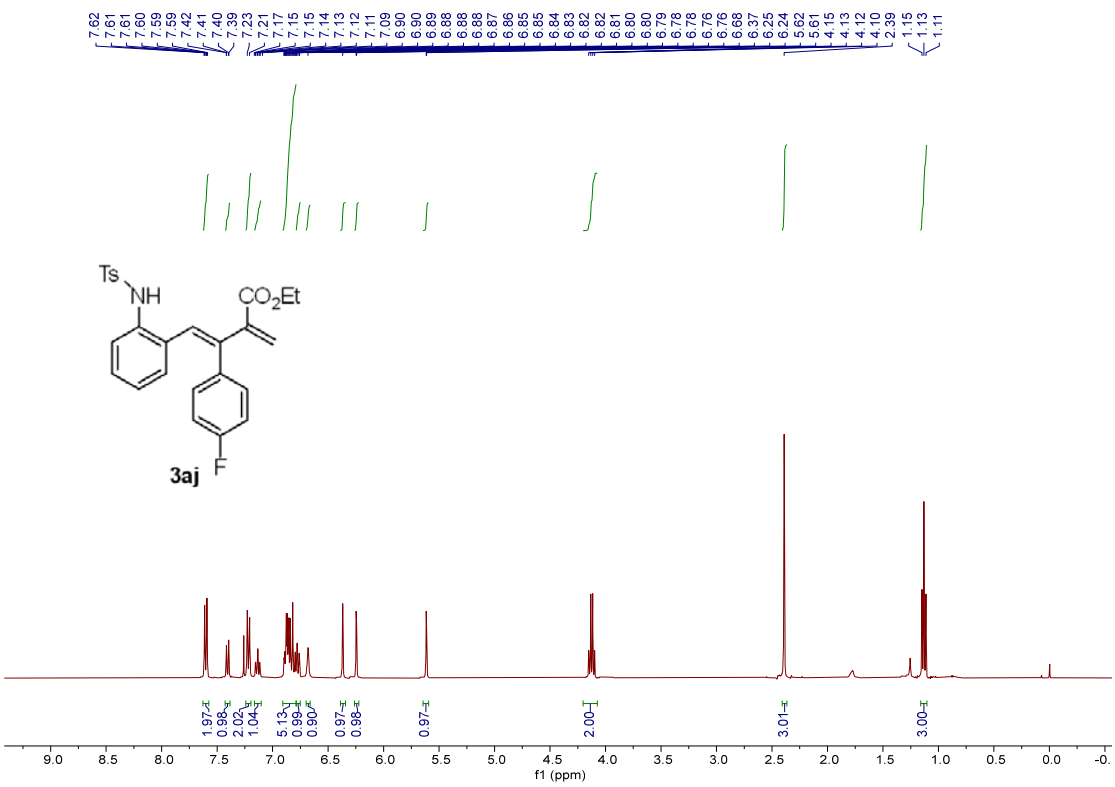
50
40
30
20
10
0
f1 (ppm)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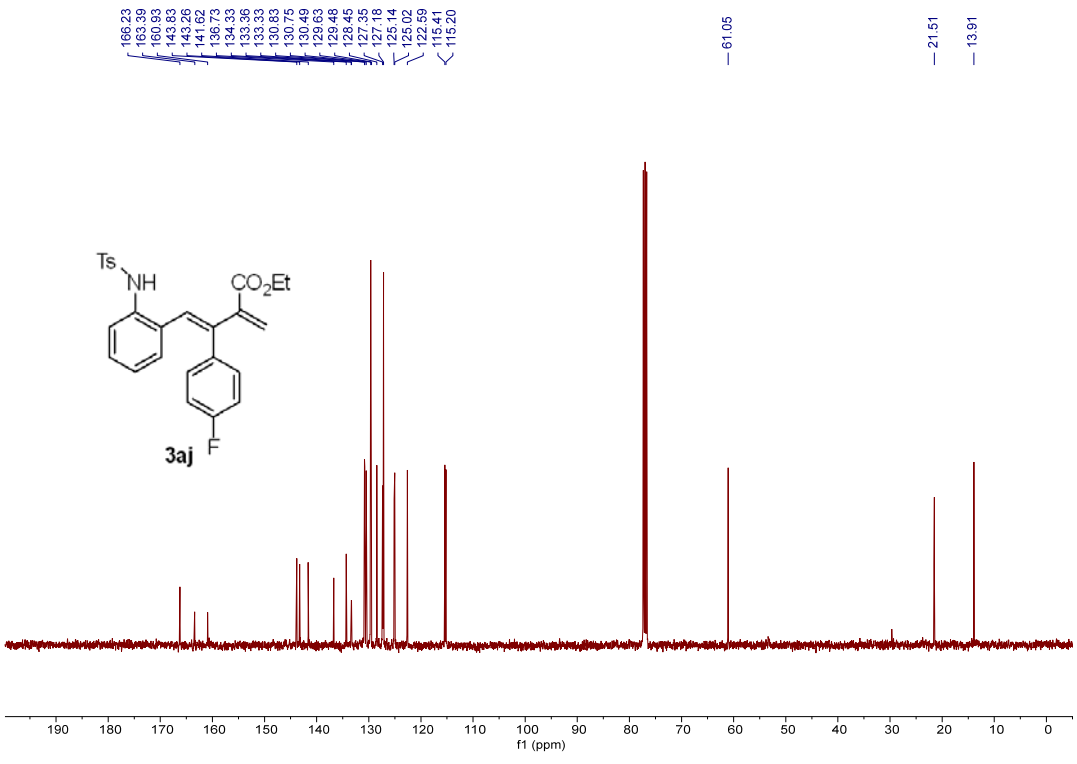
Ts
NH
CO2Et
F
3aj
1.97 0.98 2.02 1.04 5.13 0.99 0.90 0.97 0.98 0.97 2.00 3.01 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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61.05
21.51
13.91
Ts
NH
CO2Et
F
3aj
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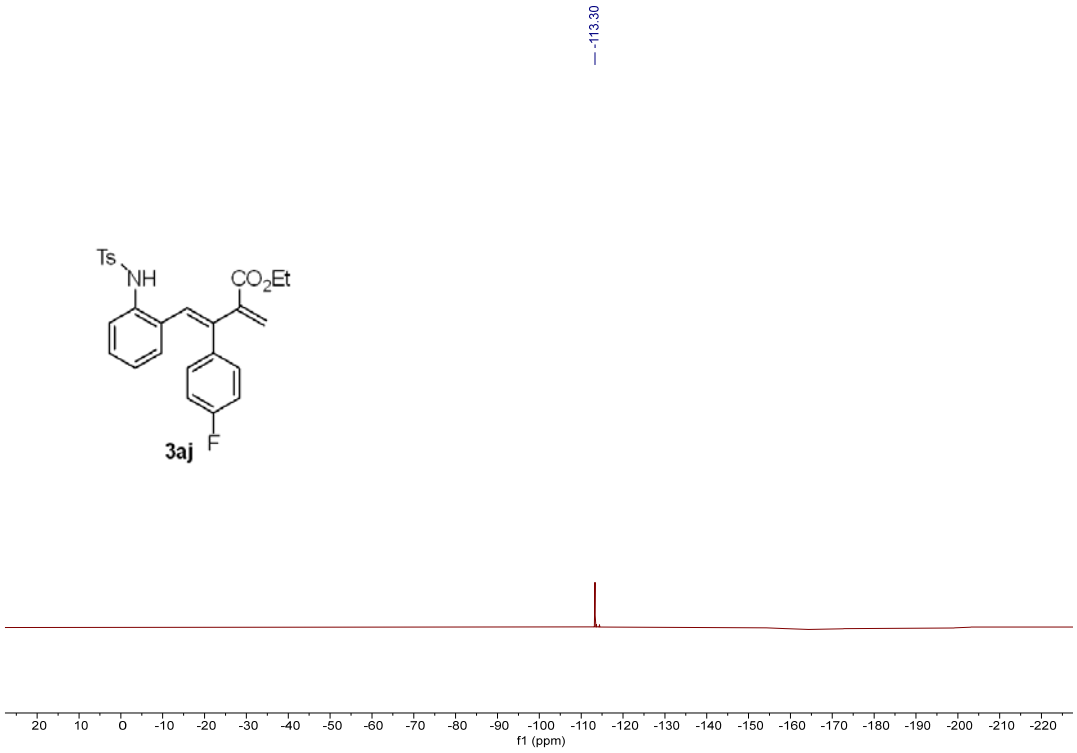
f1 (ppm)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F
3aj
20
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-20
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-80
-90
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-150
-160
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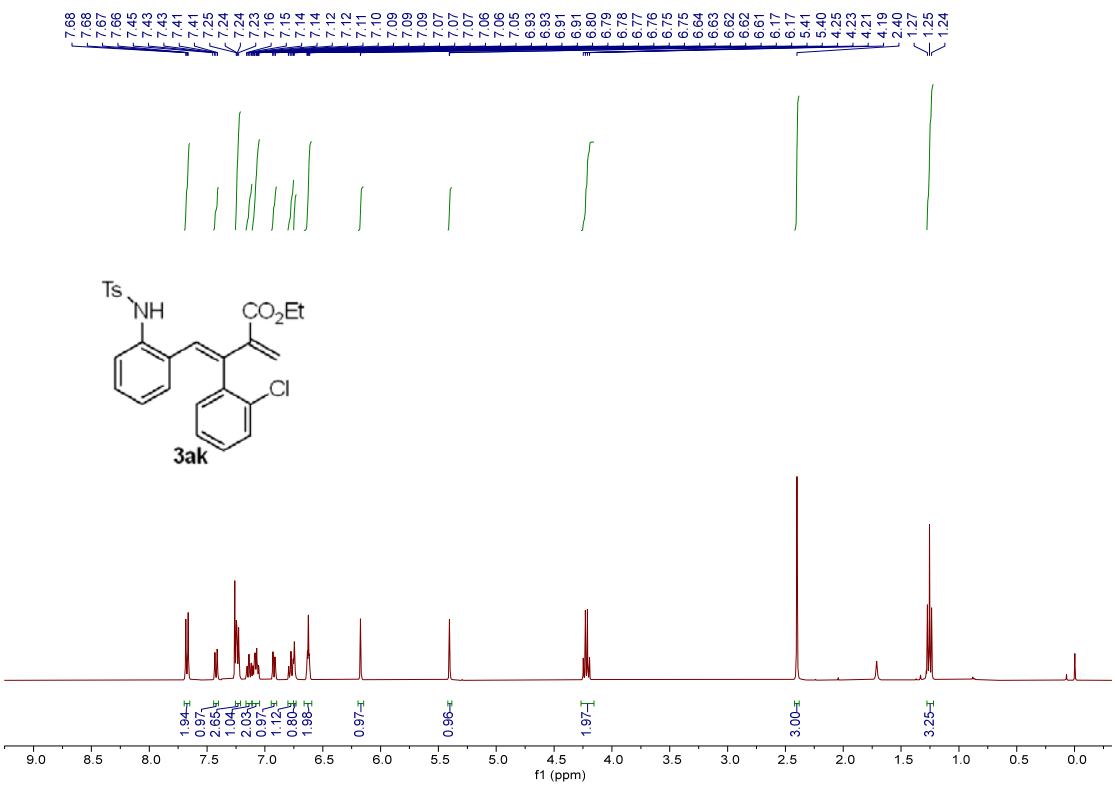
-180
-190
-200
-210
-220
f1 (ppm)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Ts
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CO2Et
Cl
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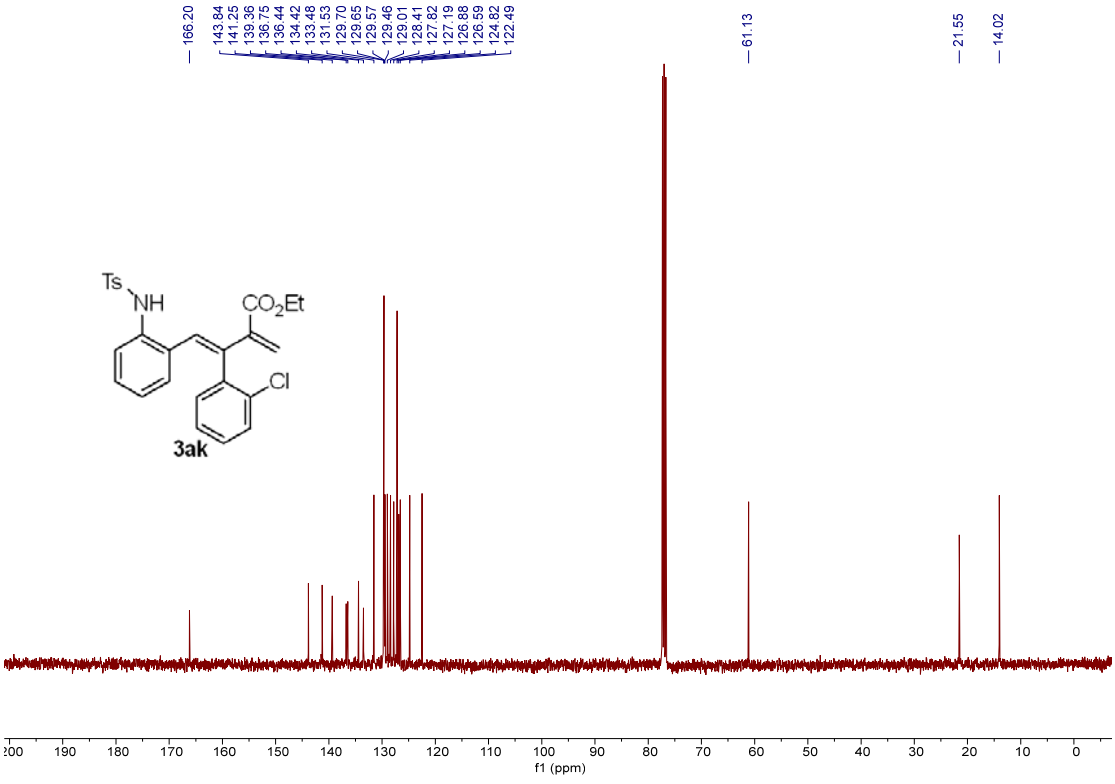
f1 (ppm)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127.19
126.88
126.59
124.82
122.49
61.13
21.55
14.02
Ts
NH
CO2Et
Cl
3ak
200
190
180
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110
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50
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10
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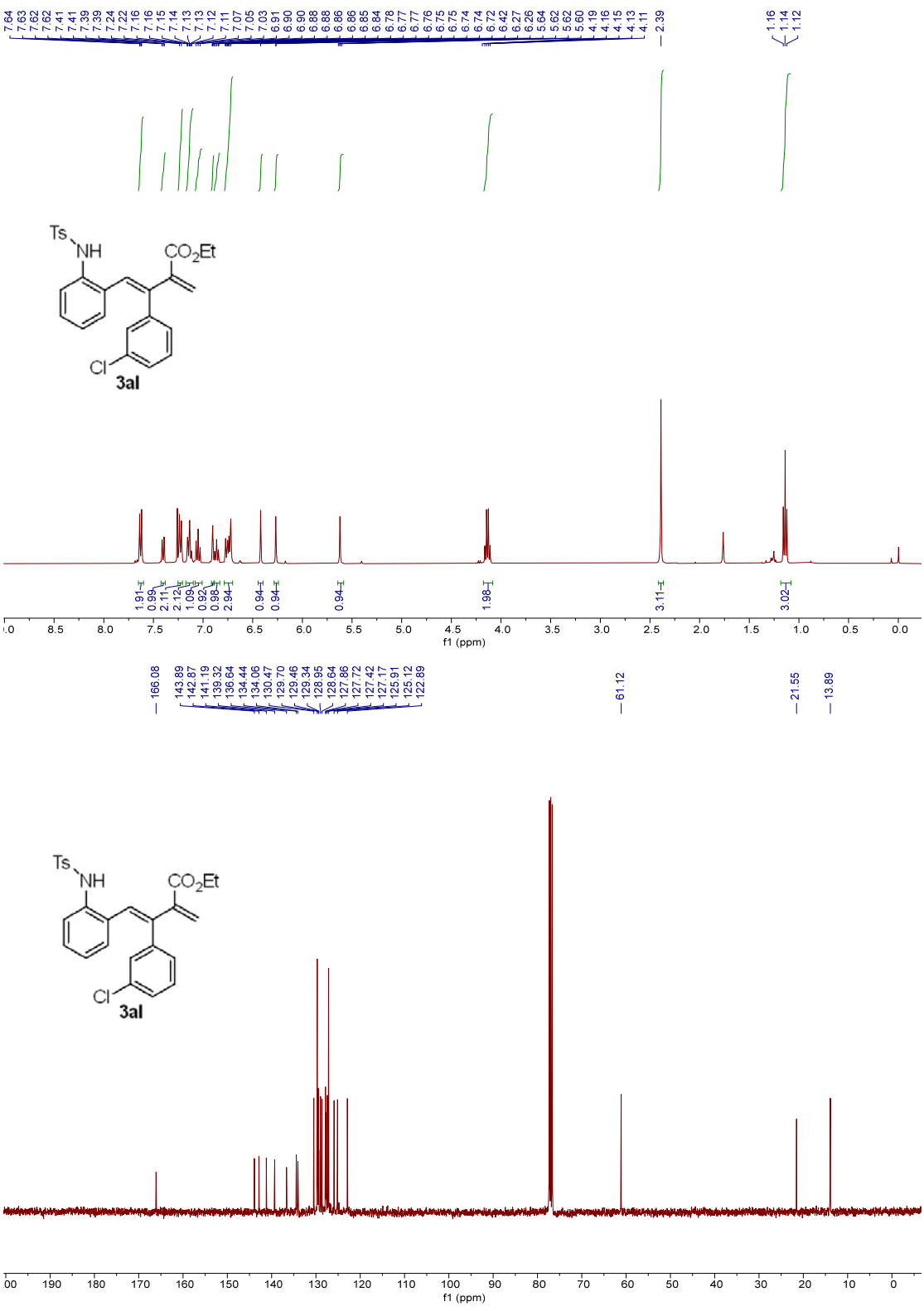
f1 (ppm)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f1 (ppm)
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Ts
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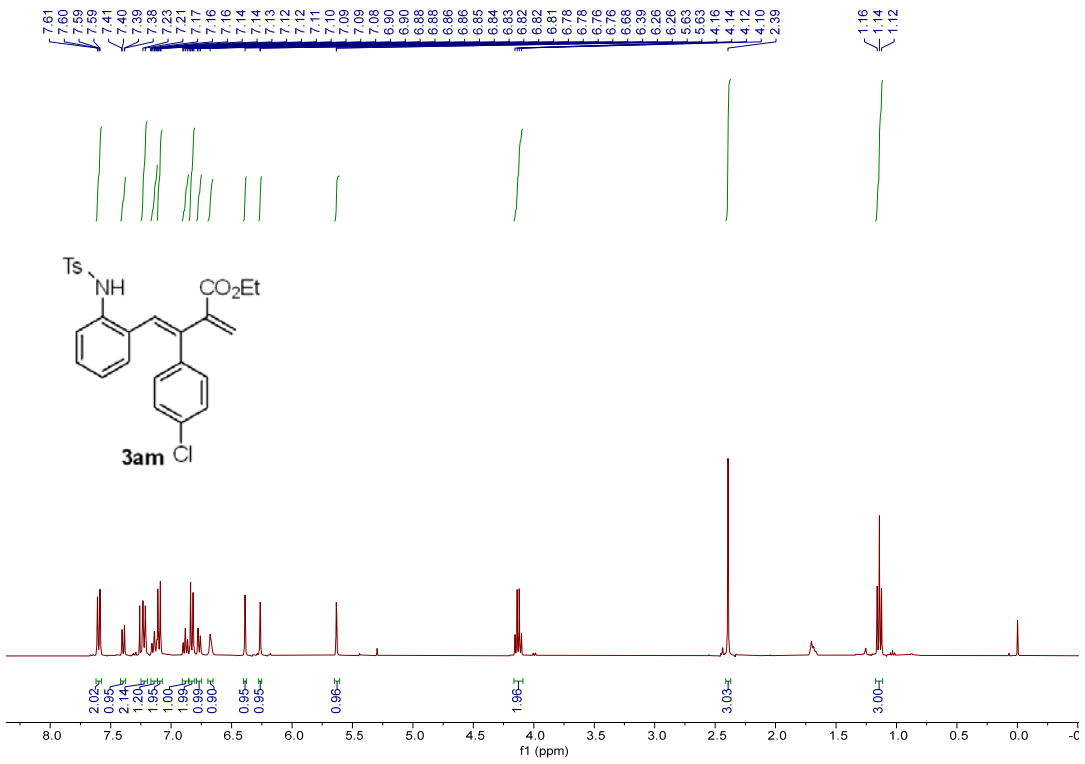
Cl
3al
f1 (ppm)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Ts
NH
CO2Et
Cl
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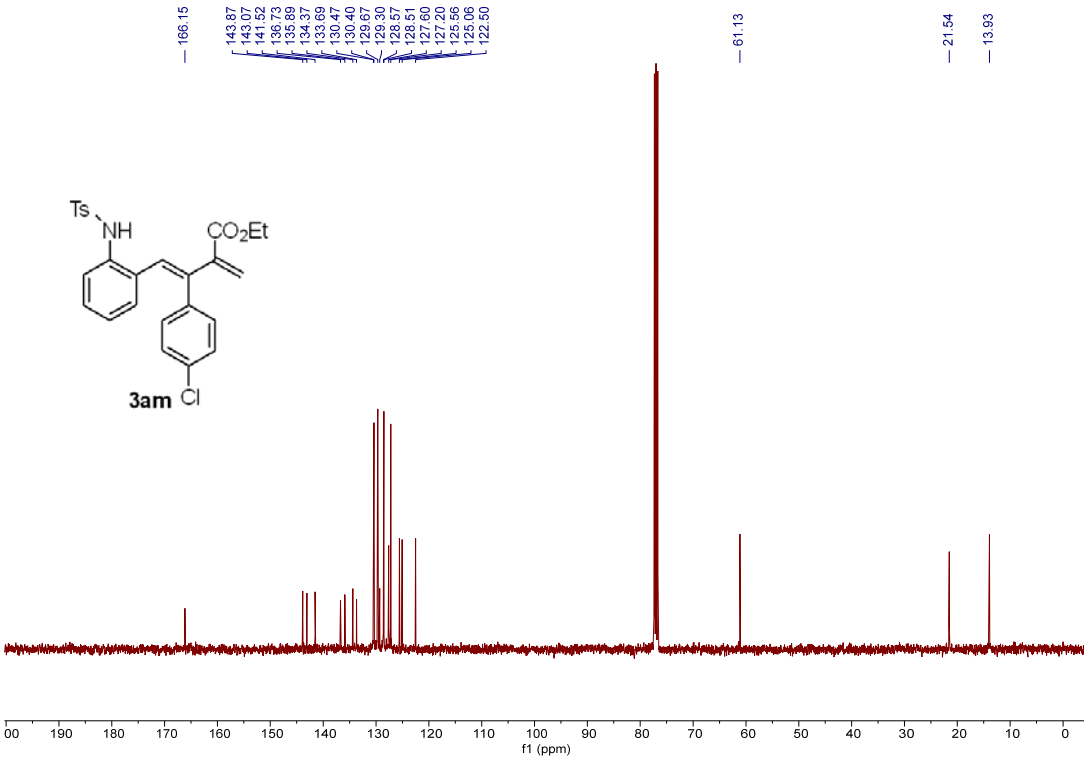
3.00
f1 (ppm)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Ts
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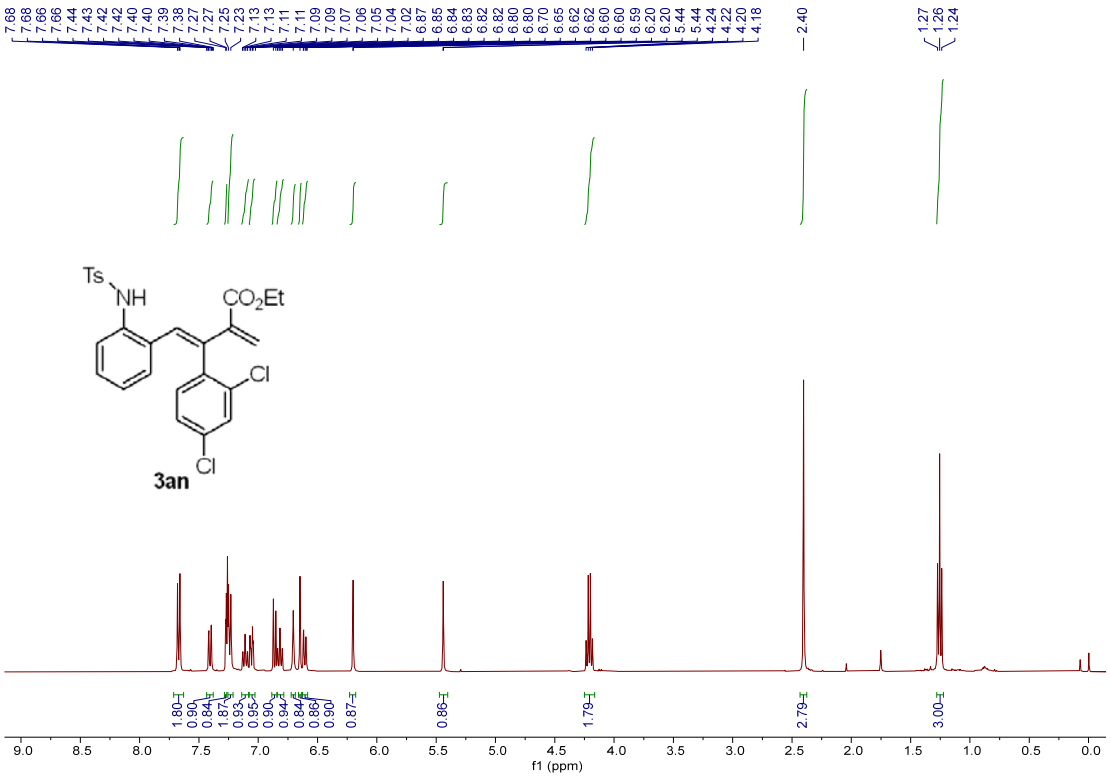
Cl
3am
f1 (ppm)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7.05
7.04
7.02
6.87
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6.84
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6.62
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6.60
6.59
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6.20
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4.22
4.20
4.18
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1.27
1.26
1.24
Ts
NH
CO2Et
Cl
Cl
3an
1.80
0.90
0.84
1.87
0.93
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0.90
0.87
0.86
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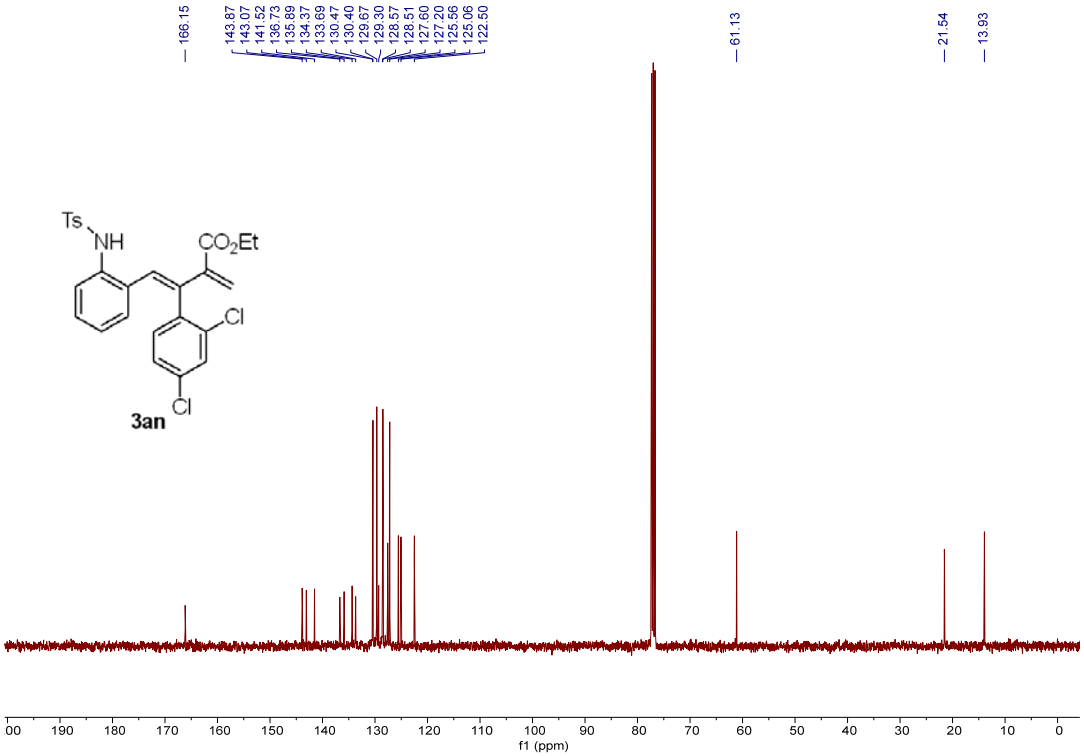
2.79
3.00
f1 (ppm)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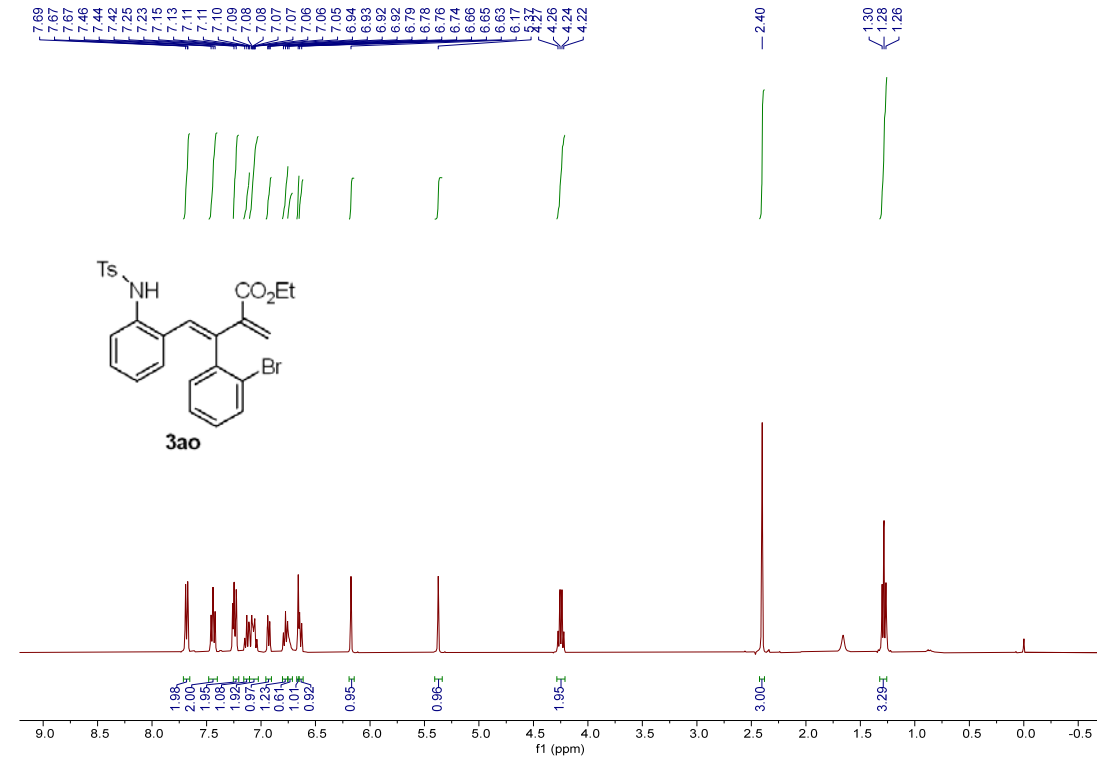
Ts
NH
CO2Et
Cl
Cl
3an
f1 (ppm)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Br
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0.61
1.01
0.92
0.95
0.96
1.95
3.00
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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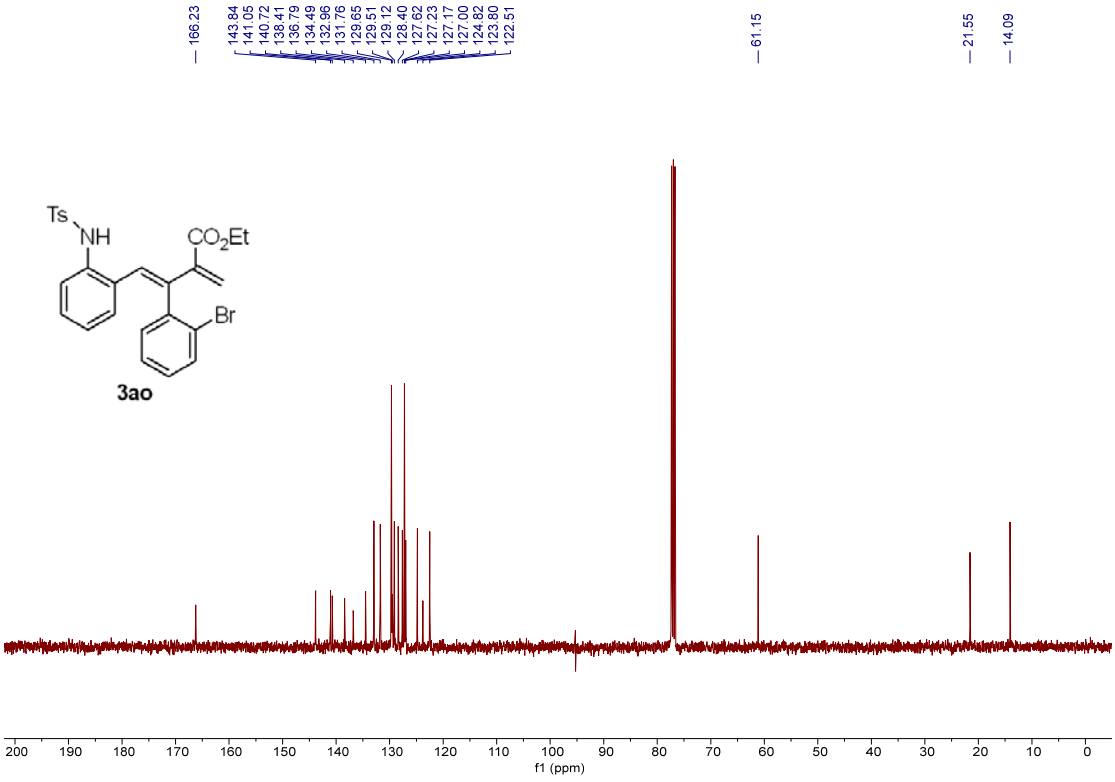
f1 (ppm)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127.23
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127.00
124.82
123.80
122.51
61.15
21.55
14.09
Ts
NH
CO2Et
Br
3ao
200
190
180
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90
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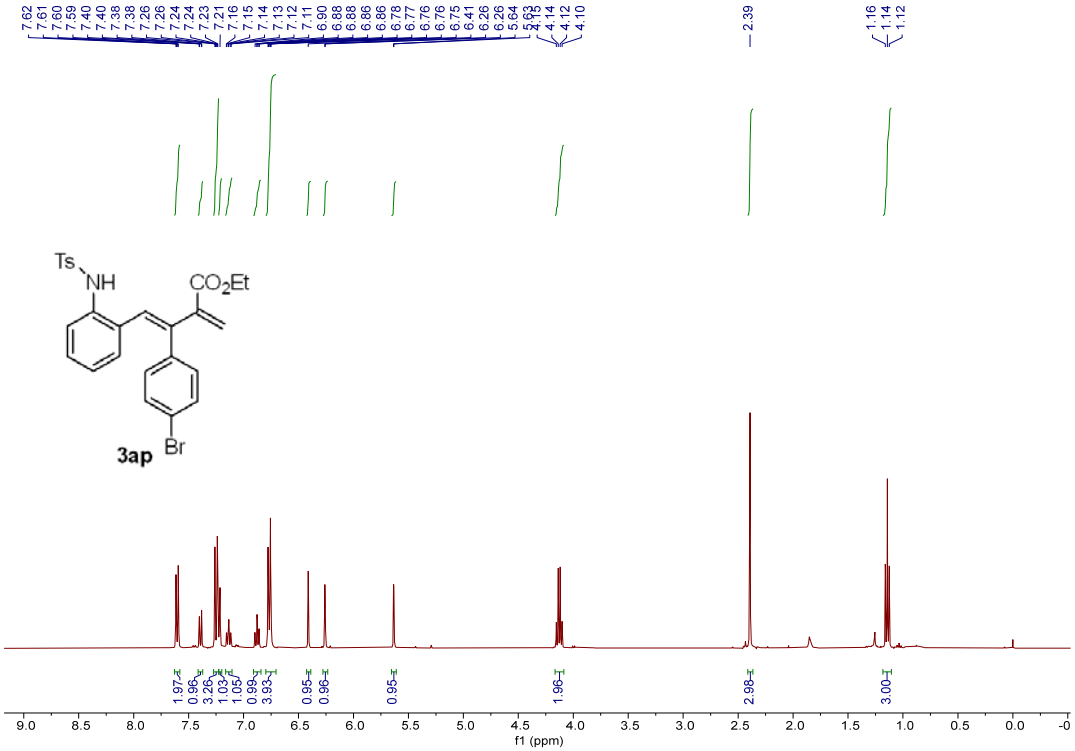
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6.88
6.86
6.86
6.78
6.77
6.76
6.76
6.75
6.41
6.26
6.26
5.64
5.63
4.15
4.14
4.12
4.10
2.39
1.16
1.14
1.12
Ts
NH
CO2Et
Br
3ap
1.97
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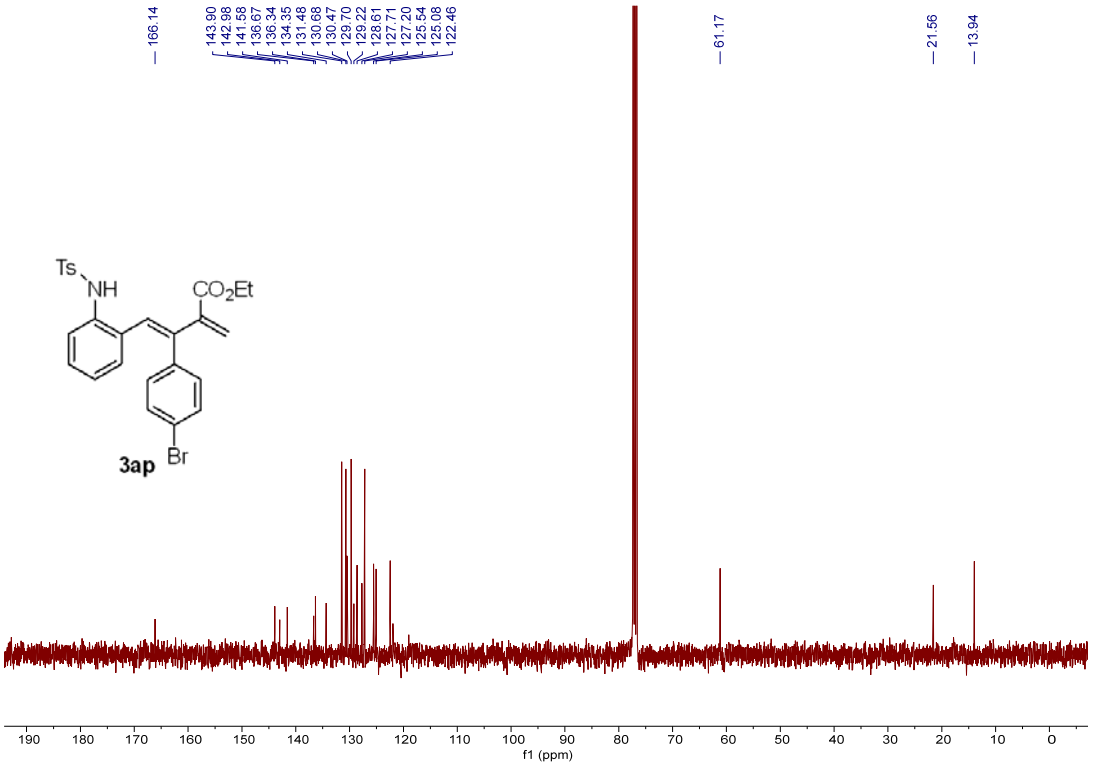
3.00
f1 (ppm)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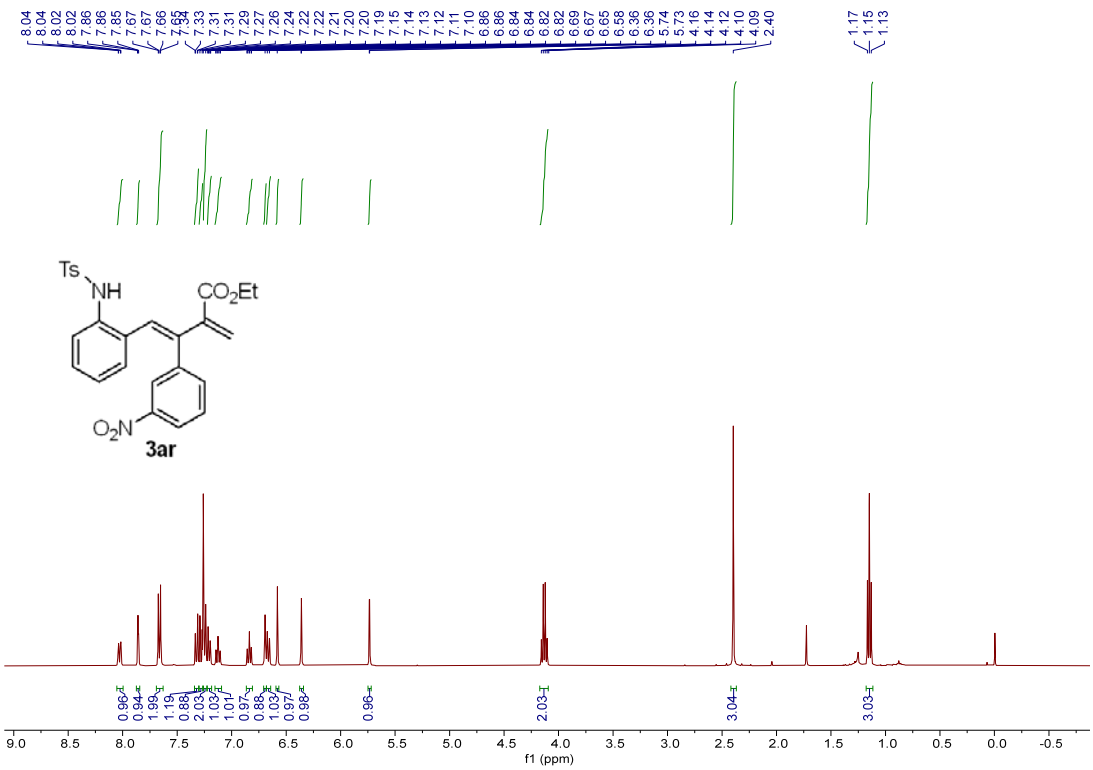
Ts
NH
CO2Et
Br
3ap
f1 (ppm)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7.26
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7.22
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7.13
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7.10
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6.86
6.84
6.84
6.82
6.82
6.69
6.67
6.65
6.58
6.36
6.36
5.74
5.73
4.16
4.14
4.12
4.10
4.09
2.40
1.17
1.15
1.13
Ts
NH
CO2Et
O2N
3ar
0.96
0.94
1.99
1.19
0.88
2.03
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1.01
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0.88
1.03
0.97
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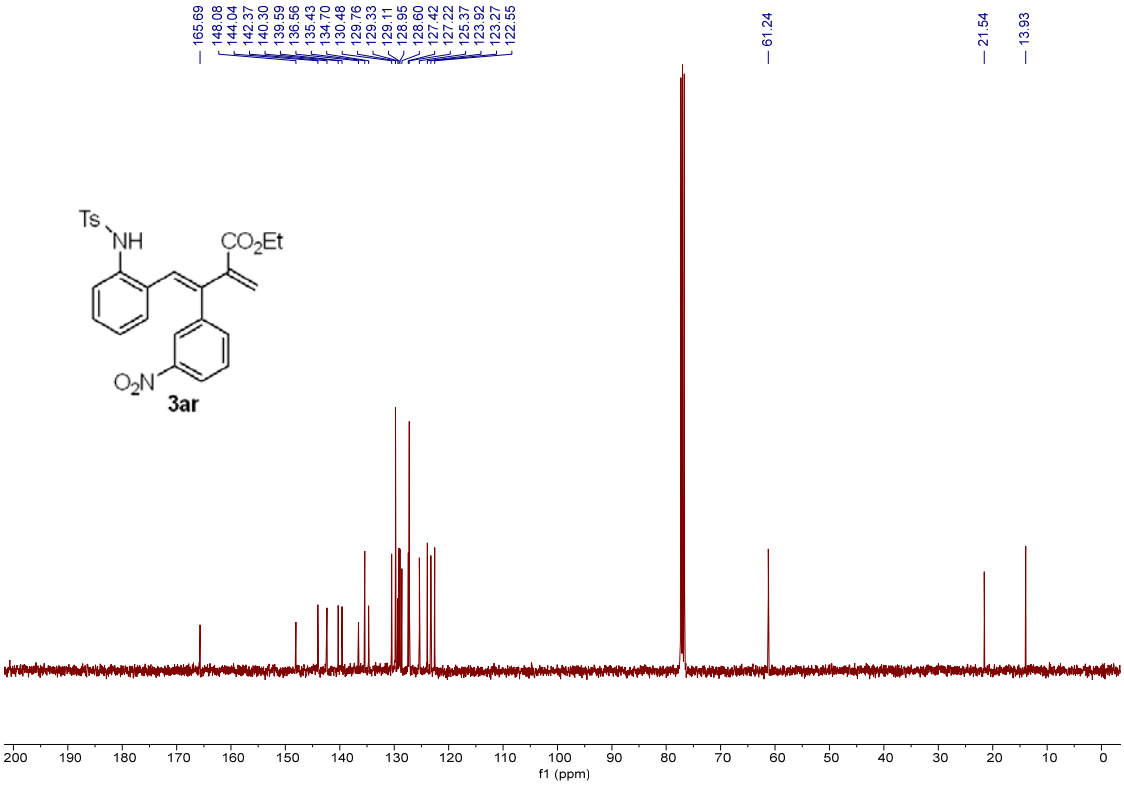
0.96
2.03
3.04
3.03
f1 (ppm)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128.95
128.60
127.42
127.22
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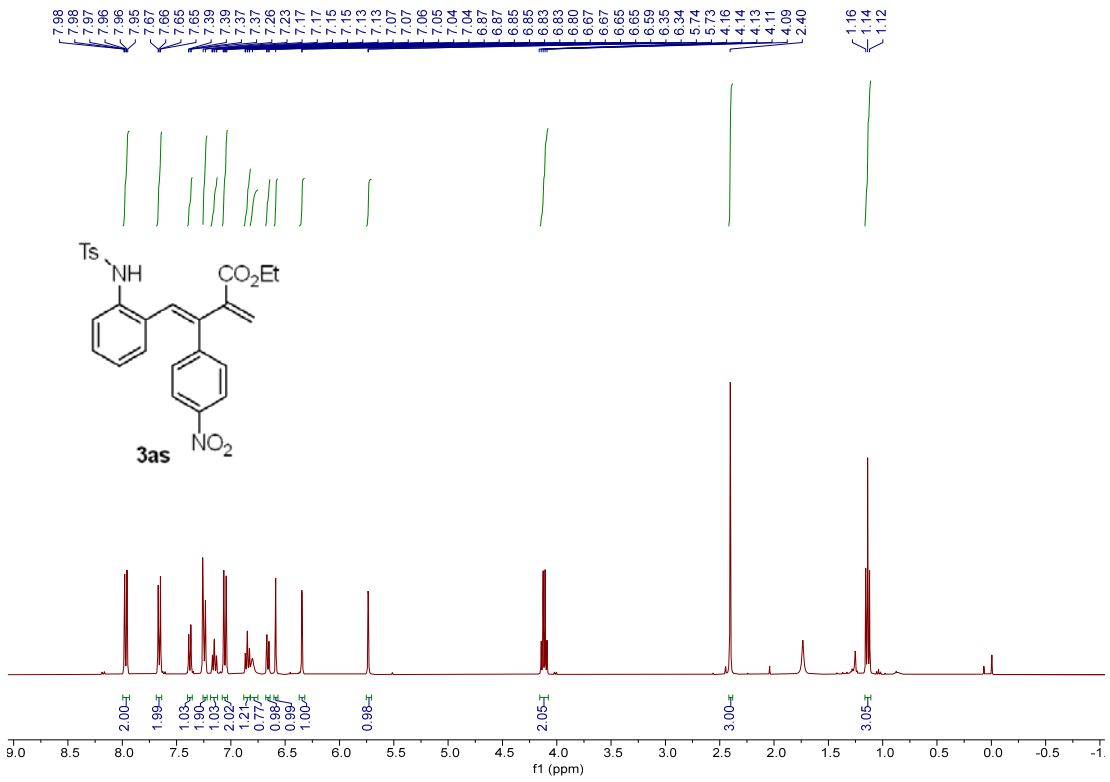
21.54
13.93
Ts
NH
CO2Et
O2N
3ar
f1 (ppm)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7.07
7.06
7.05
7.04
7.04
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6.65
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6.35
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4.13
4.11
4.09
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1.12
Ts
NH
CO2Et
NO2
3as
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1.03
1.90
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0.99
1.00
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2.05
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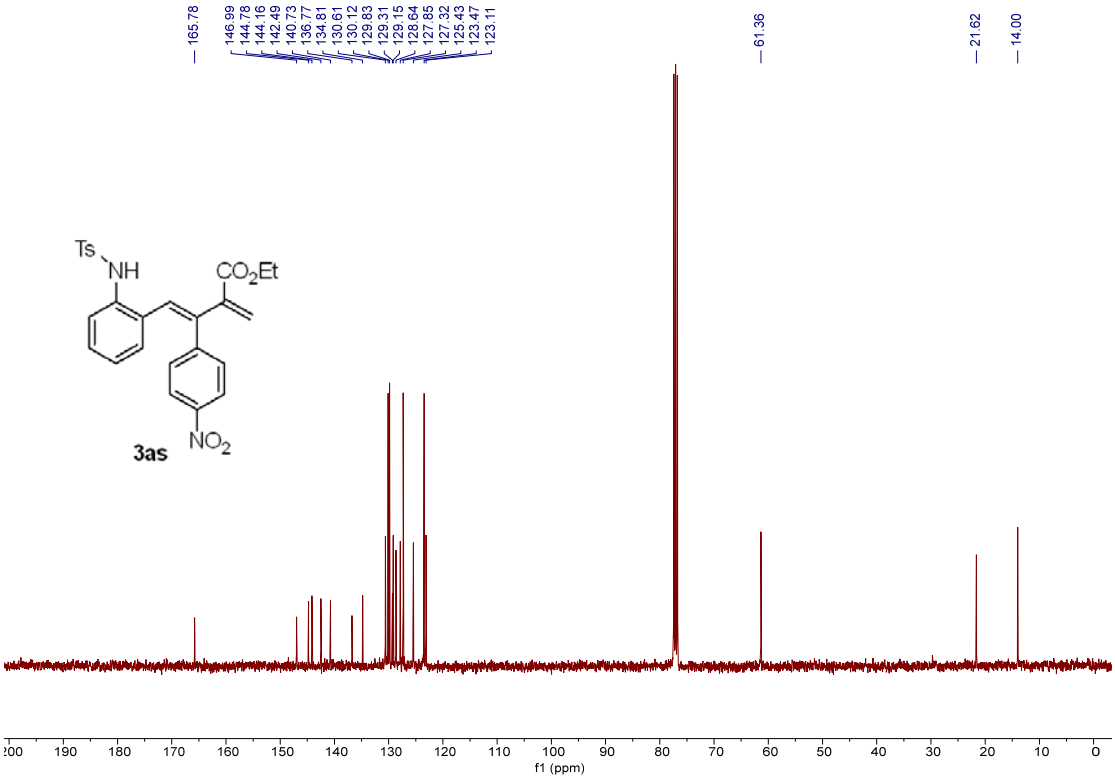
3.05
f1 (ppm)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128.64
127.85
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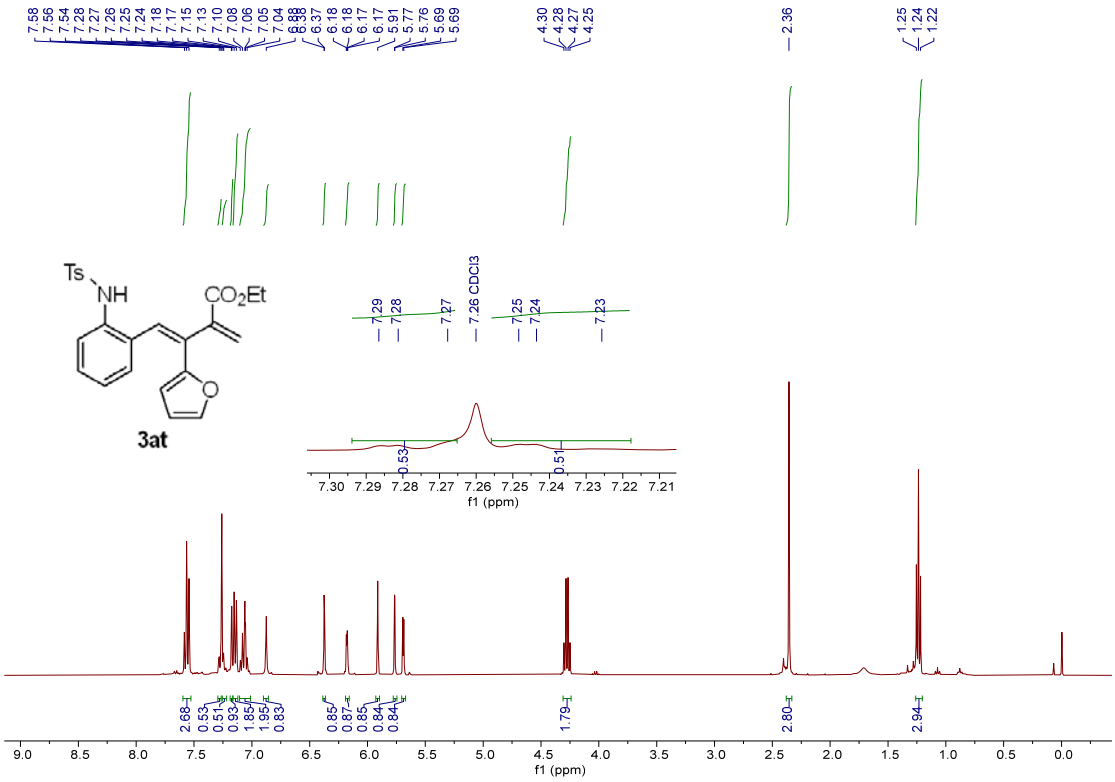
14.00
Ts
NH
CO2Et
NO2
3as
f1 (ppm)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7.04
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6.37
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6.18
6.17
6.17
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5.76
5.69
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4.28
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1.22
Ts
NH
CO2Et
O
3at
7.29
7.28
7.27
7.26 CDCl3
7.25
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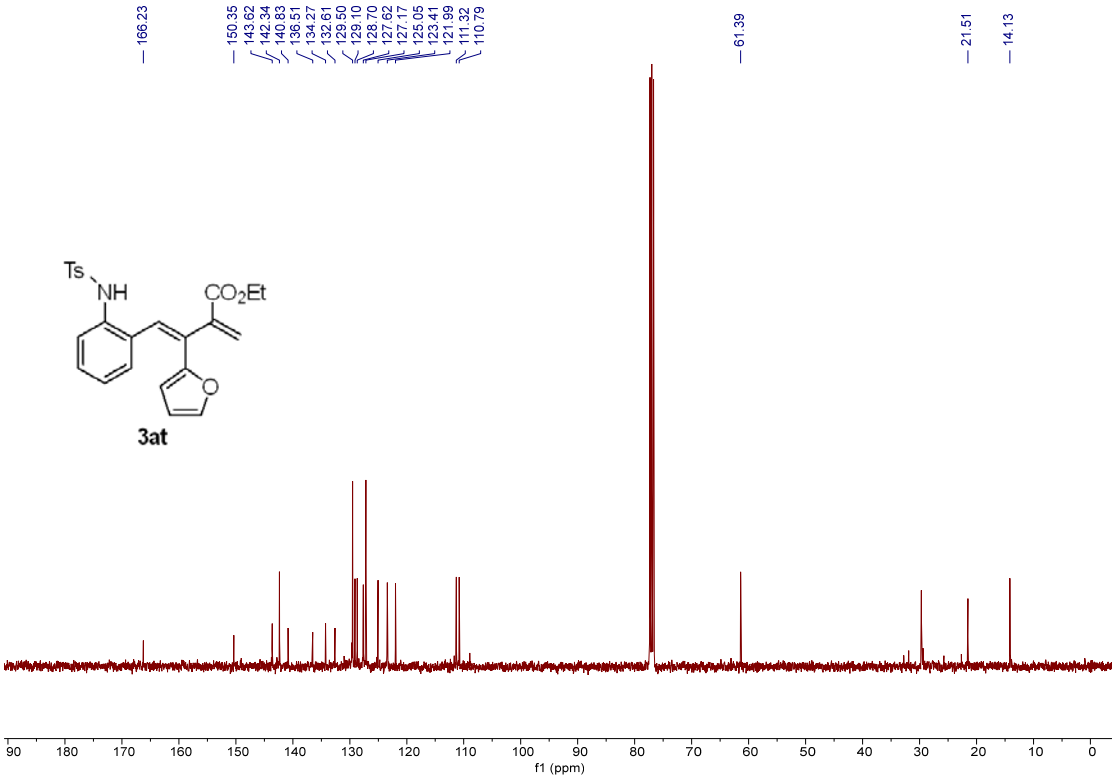
0.51
7.30 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.22 7.21
f1 (ppm)
2.68
0.53
0.51
0.93
1.85
1.95
0.83
0.85
0.87
0.85
0.84
0.84
1.79
2.80
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.05
123.41
121.99
111.32
110.79
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Ts
NH
CO2Et
O
3at
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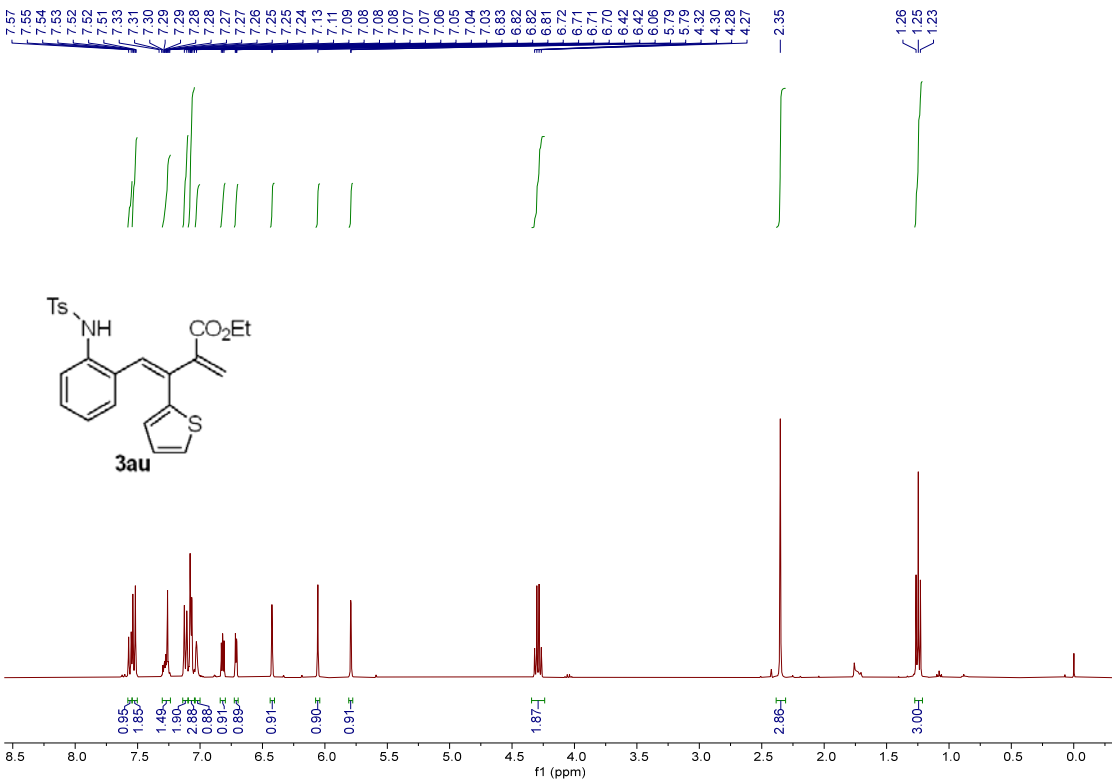
f1 (ppm)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7.05
7.04
7.03
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6.82
6.81
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6.71
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6.42
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4.28
4.27
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1.25
1.23
Ts
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CO2Et
S
3au
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0.91
0.90
0.91
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6.0
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3.0
2.5
2.0
1.5
1.0
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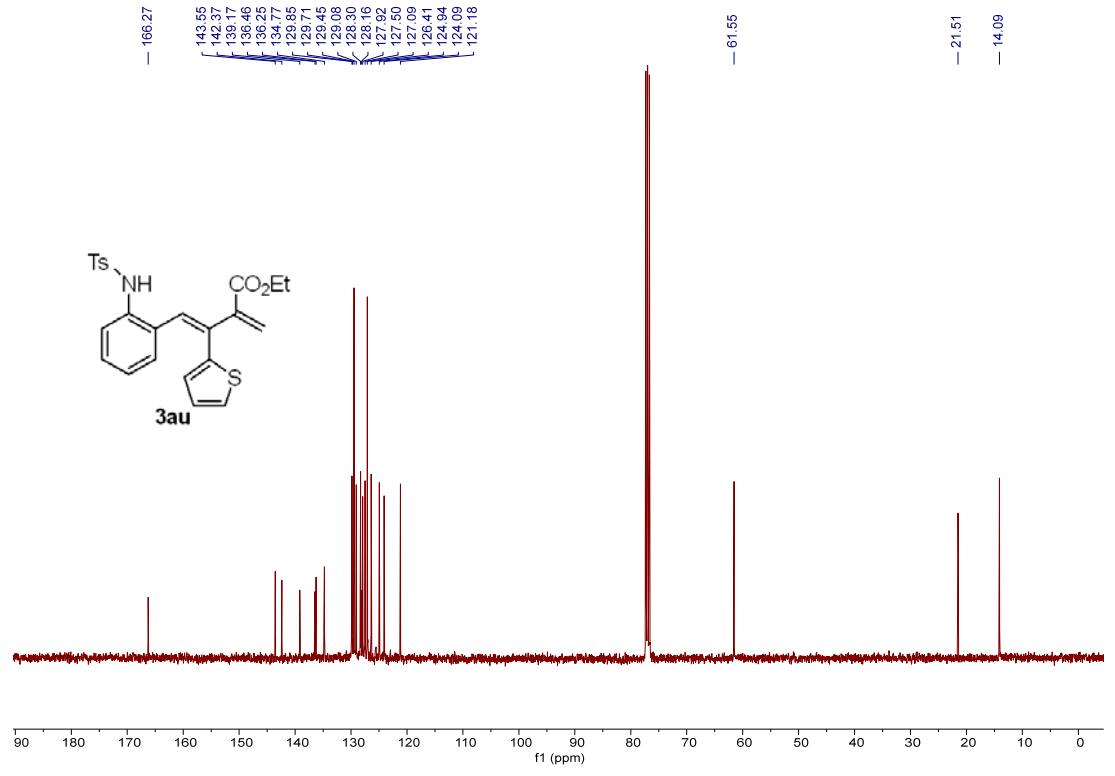
0.0
f1 (ppm)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127.50
127.09
126.41
124.94
124.09
121.18
61.55
21.51
14.09
Ts
NH
CO2Et
S
3au
90
180
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110
100
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50
40
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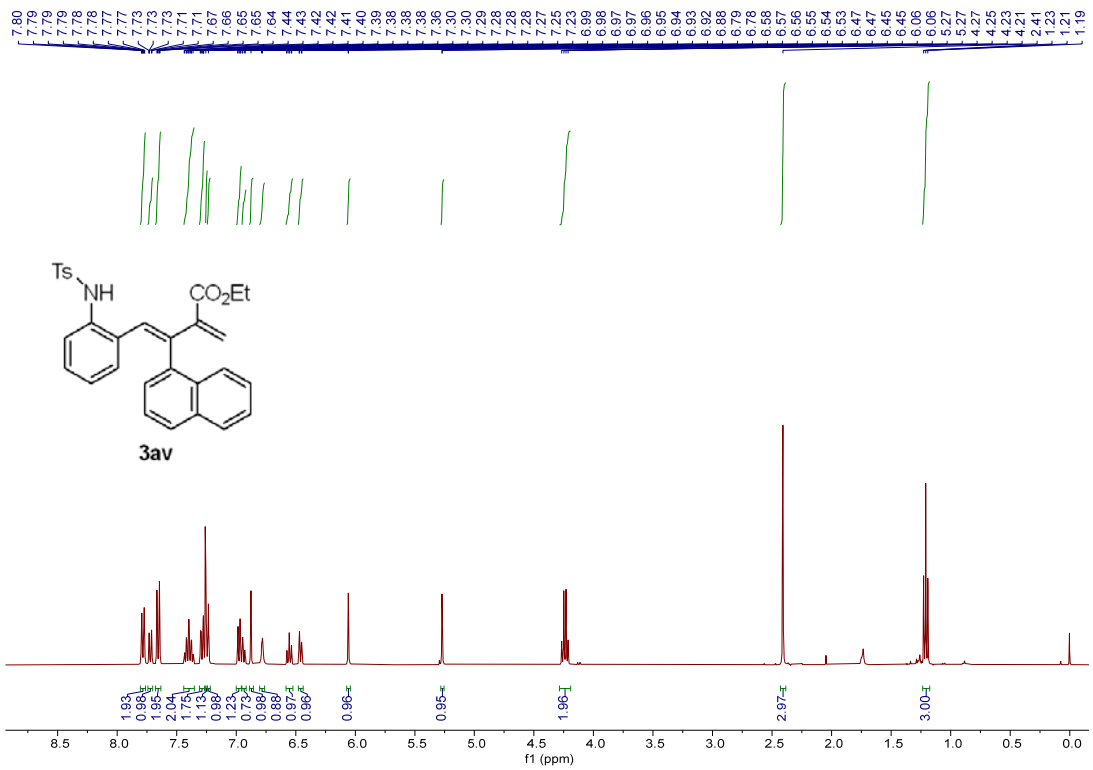
f1 (ppm)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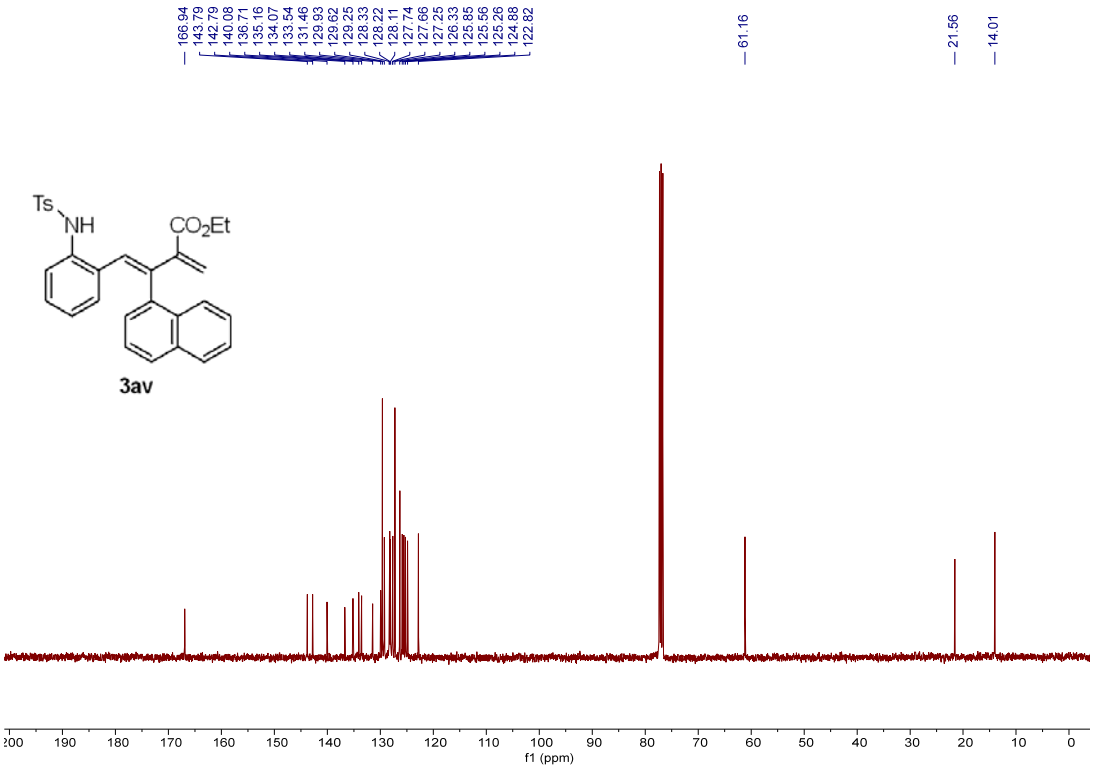
Ts NH CO2Et
3av
1.93 0.98 1.95 2.04 1.75 1.13 0.98 1.23 0.73 0.98 0.88 0.97 0.96 0.96 0.95 1.96 2.97 3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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61.16
21.56
14.01
Ts NH CO2Et
3av
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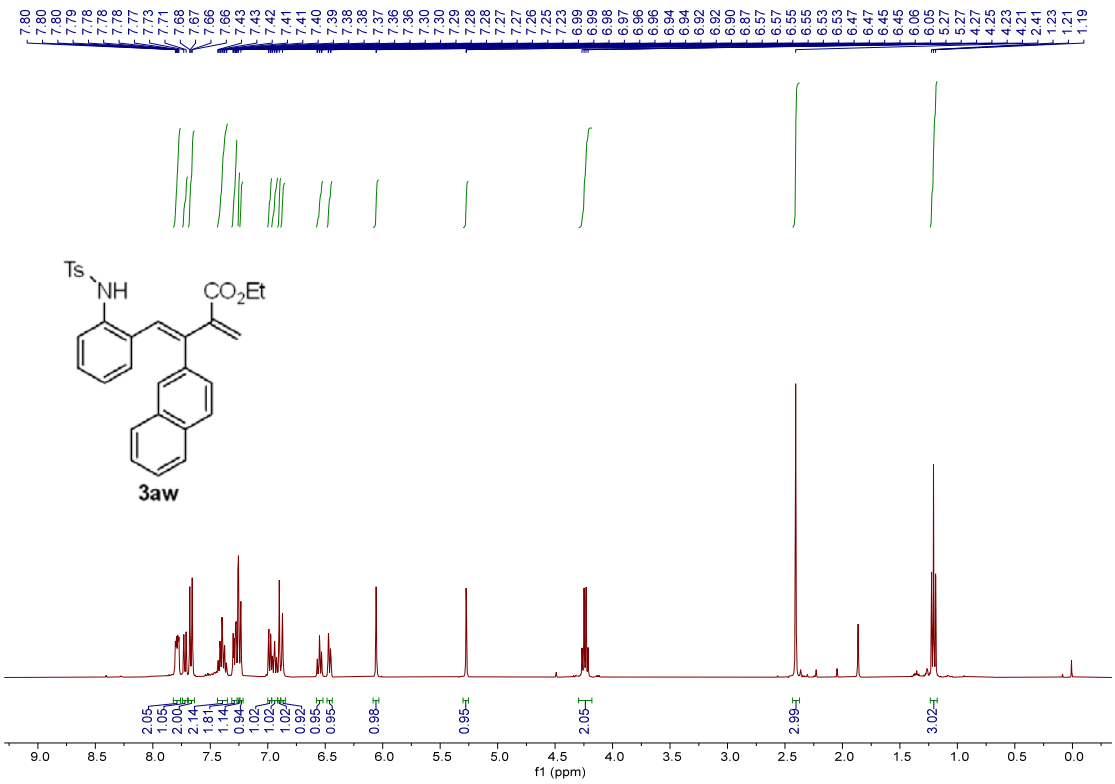
f1 (ppm)


Ts
NH
CO2Et
3aw
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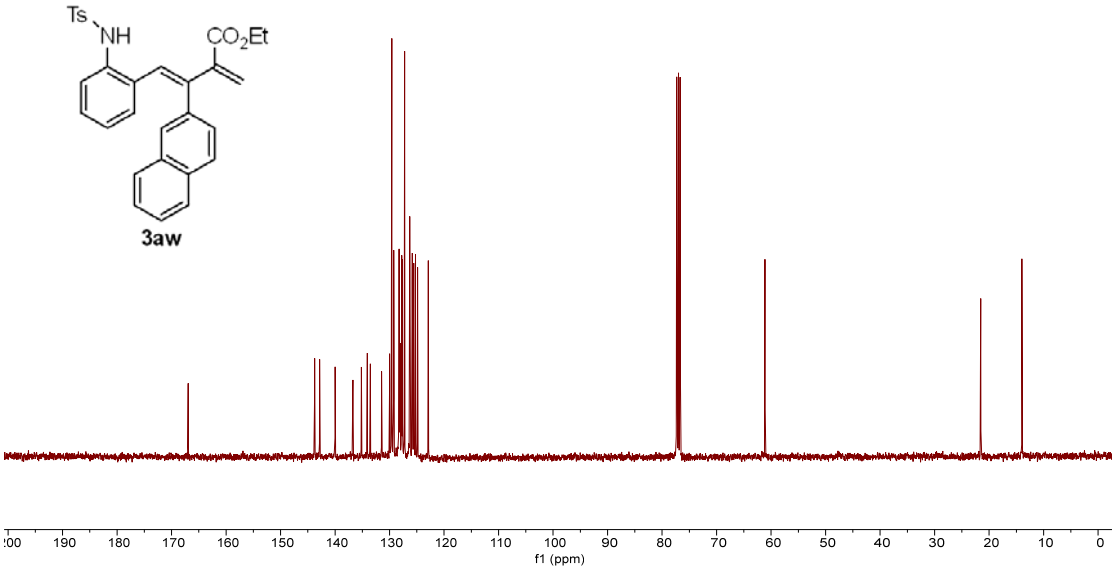
Ts
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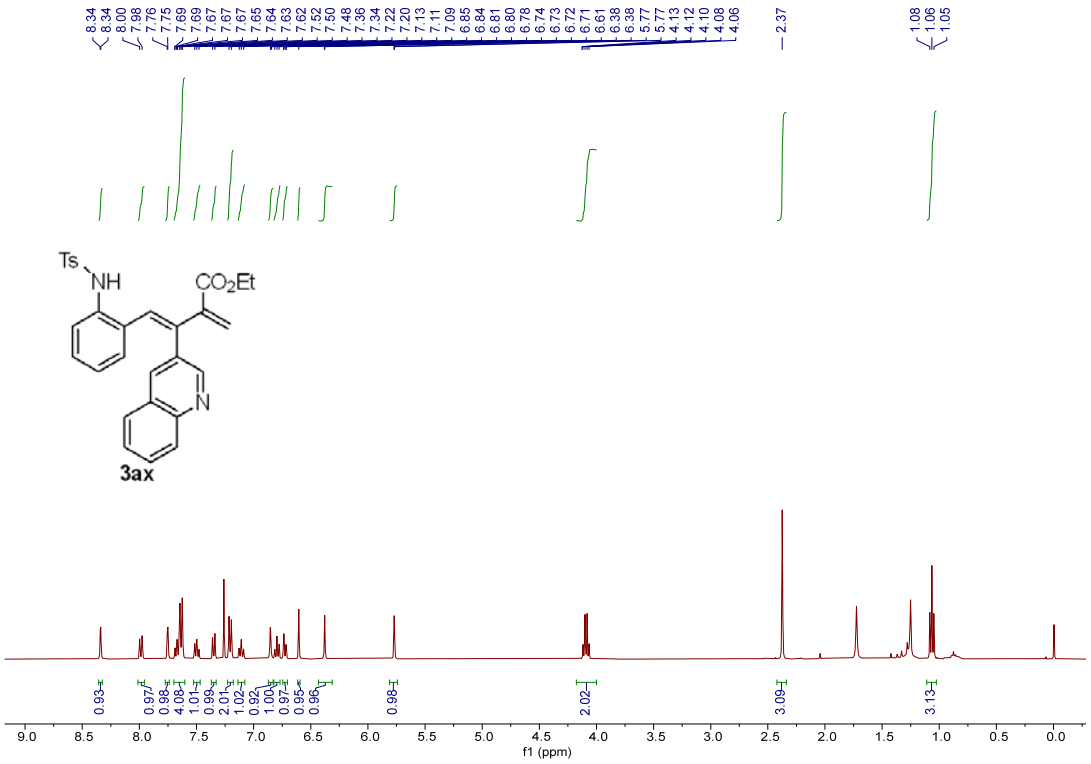
CO2Et
3aw
f1 (ppm)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7.11
7.09
6.85
6.84
6.81
6.80
6.78
6.74
6.73
6.72
6.71
6.61
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1.08
1.06
1.05
Ts
NH
CO2Et
N
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1.02
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1.00
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0.98
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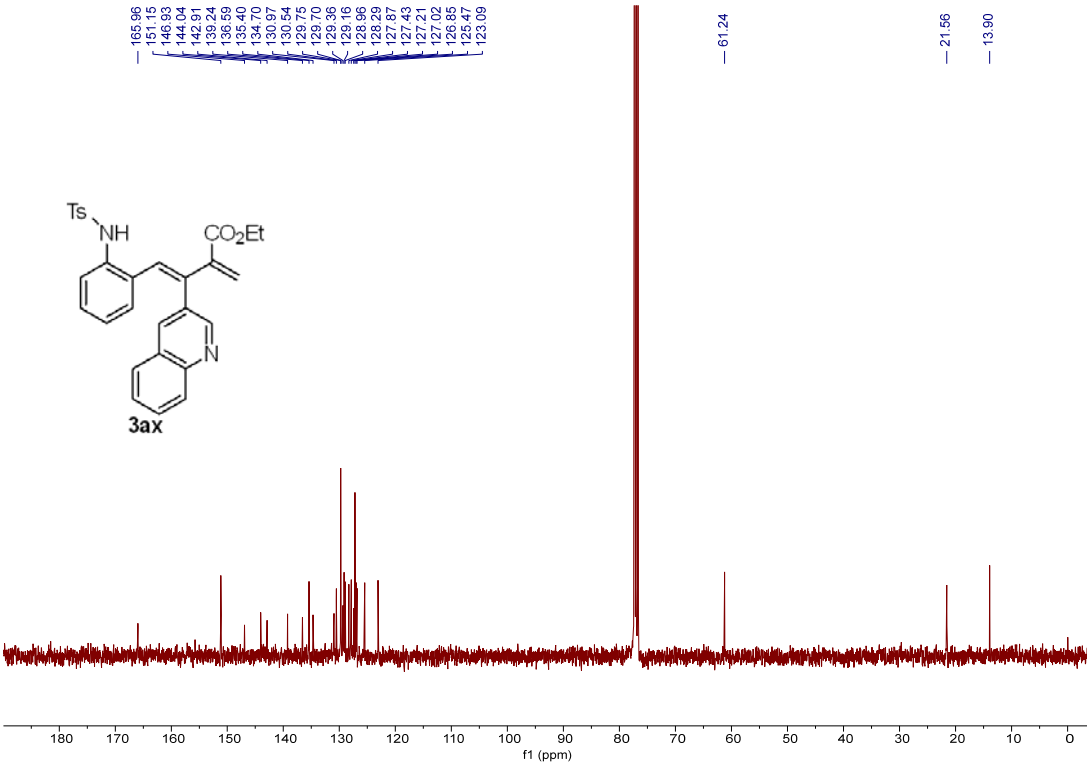
f1 (ppm)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129.36
129.16
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128.29
127.87
127.43
127.21
127.02
126.85
125.47
123.09
61.24
21.56
13.90
Ts
NH
CO2Et
N
3ax
180
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110
100
90
80
70
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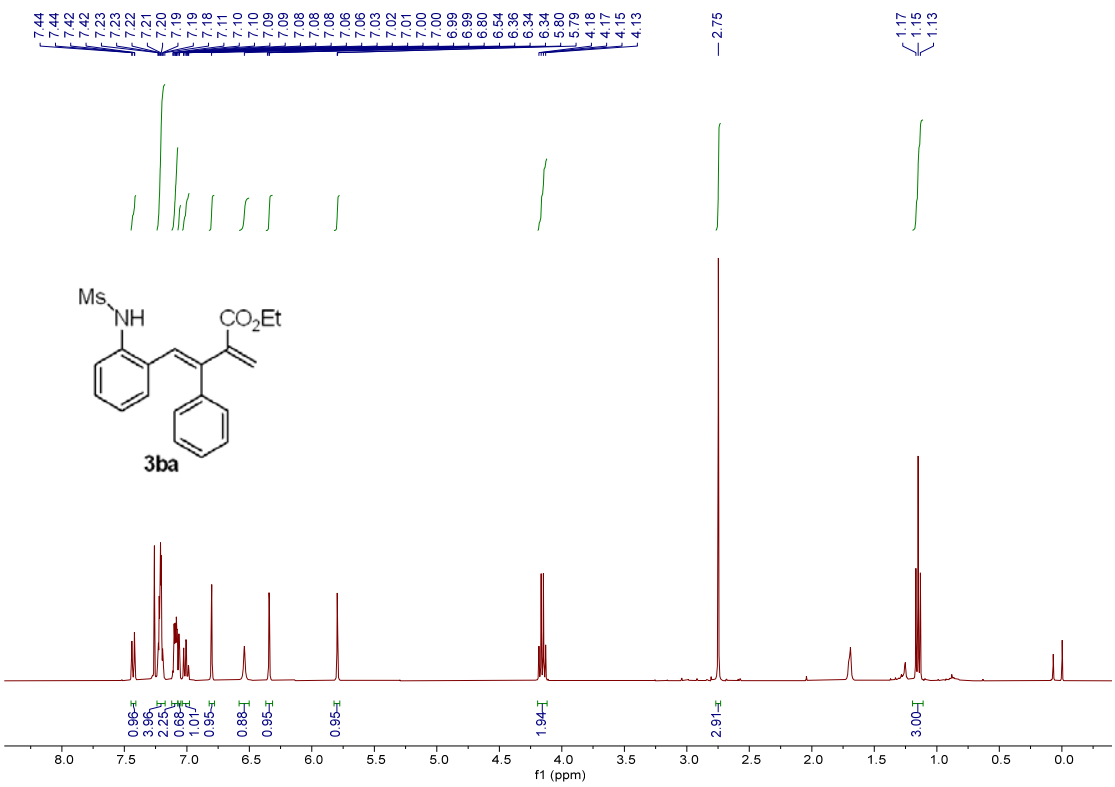
50
40
30
20
10
0
f1 (ppm)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7.00
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1.15
1.13
Ms
NH
CO2Et
3ba
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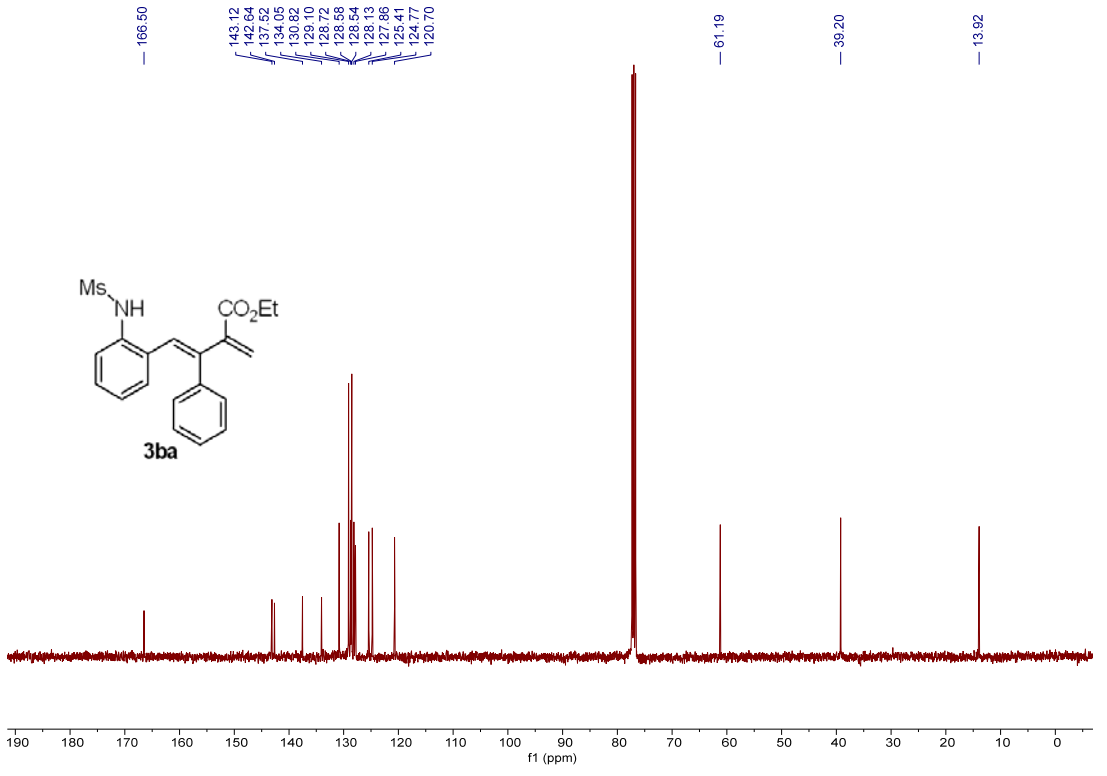
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Ms
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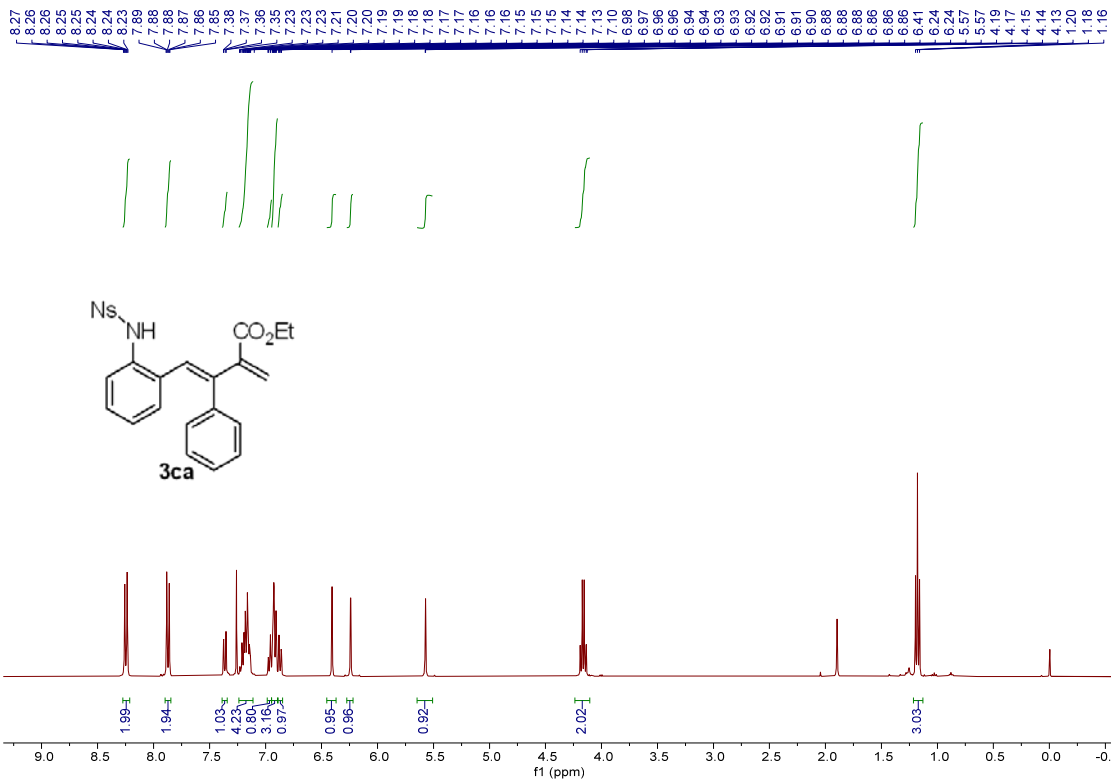
3ba
f1 (ppm)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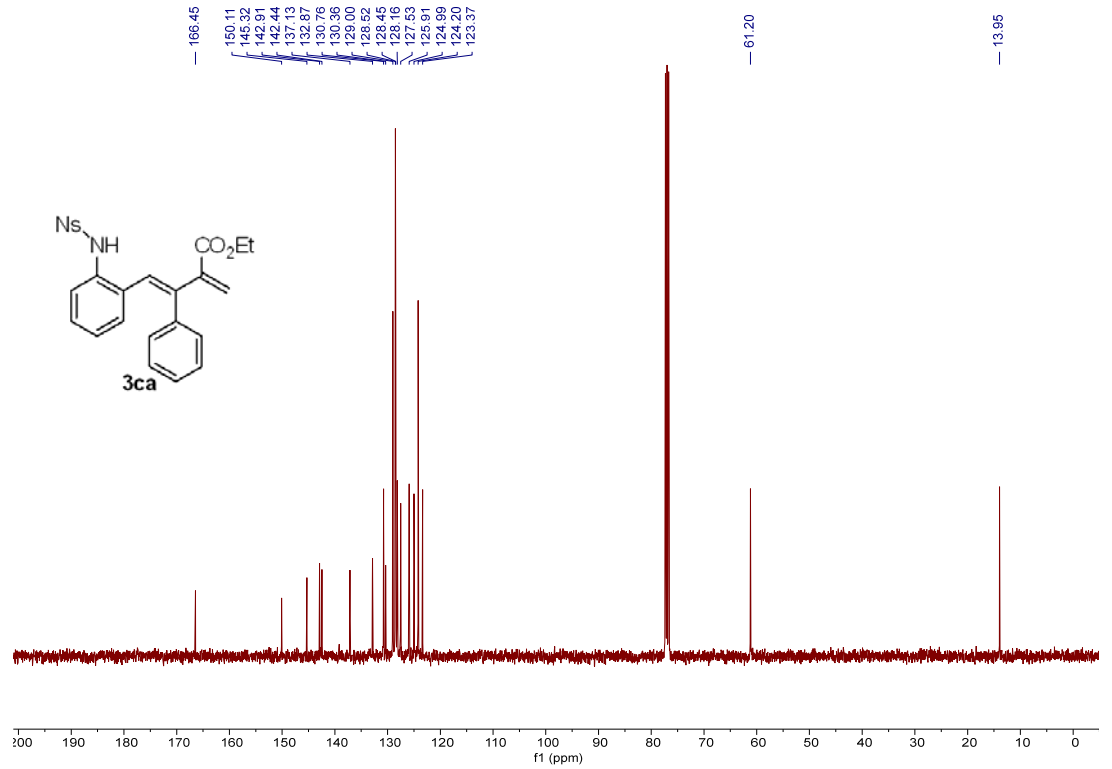
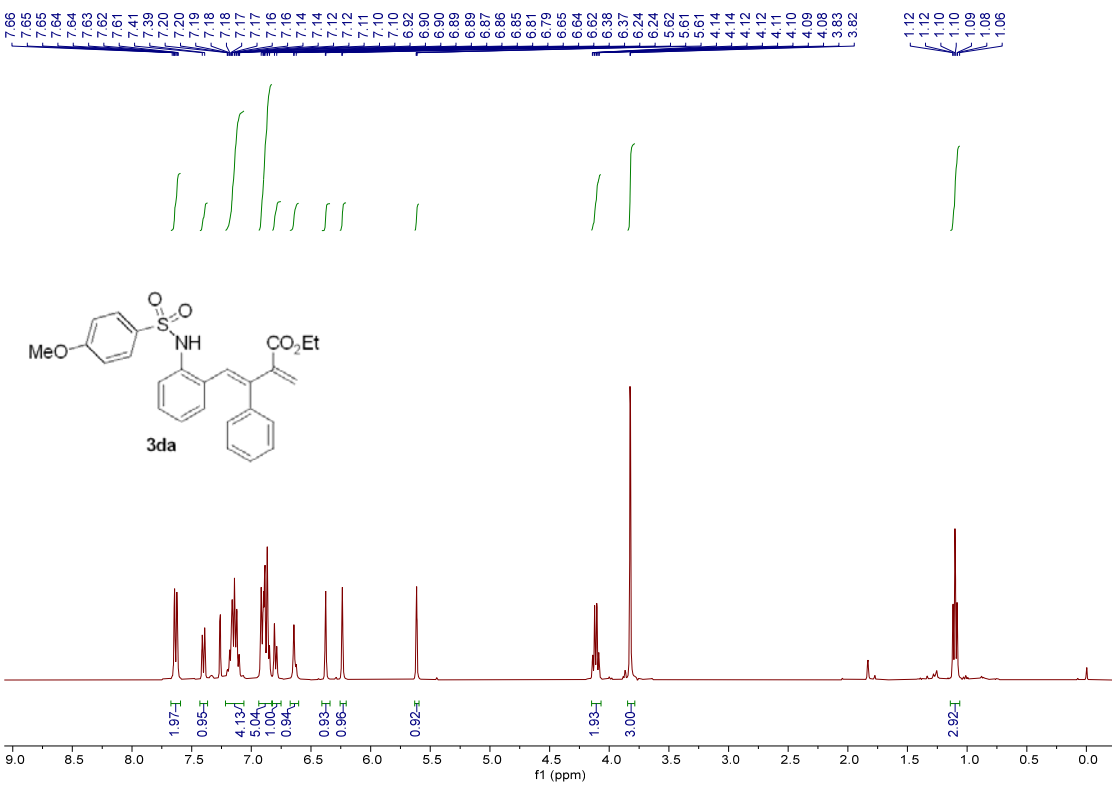
Ns
NH
CO2Et
3ca
1.99 1.94 1.03 4.23 0.80 3.16 0.97 0.95 0.96 0.92 2.02 3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.45 150.11 145.32 142.91 142.44 137.13 132.87 130.76 130.36 129.00 128.52 128.45 128.16 127.53 125.91 124.99 124.20 123.37 61.20 13.95
Ns
NH
CO2Et
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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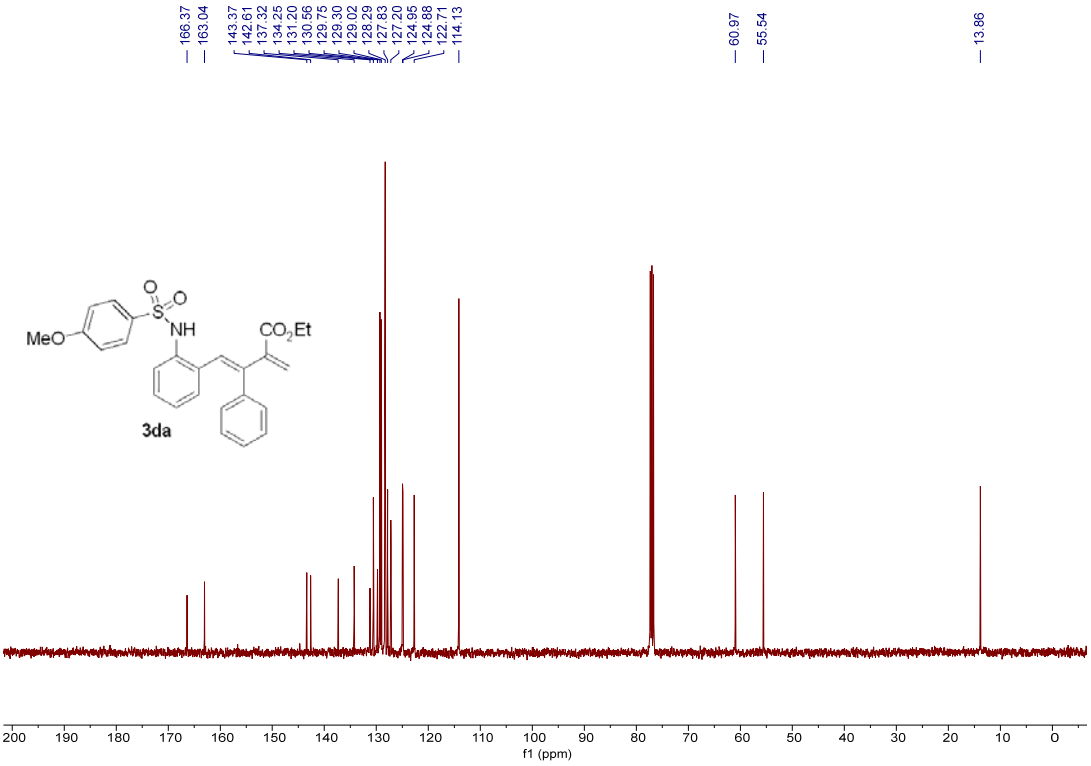
1.12 1.12 1.10 1.10 1.09 1.08 1.06
MeO
NH
CO2Et
3da
1.97 0.95 4.13 5.04 1.00 0.94 0.93 0.96 0.92 1.93 3.00 2.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.37 163.04 143.37 142.61 137.32 134.25 131.20 130.56 129.75 129.30 128.02 128.29 127.83 127.20 124.95 124.88 122.71 114.13
60.97 55.54
13.86
MeO
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CO2Et
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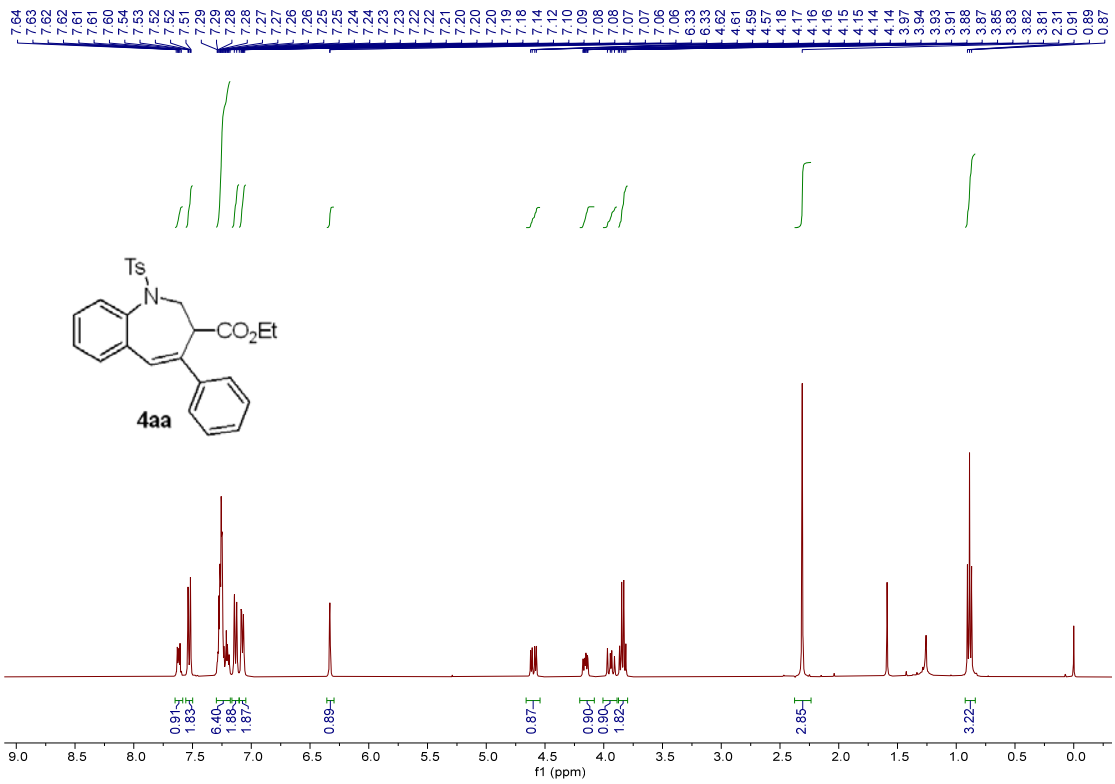
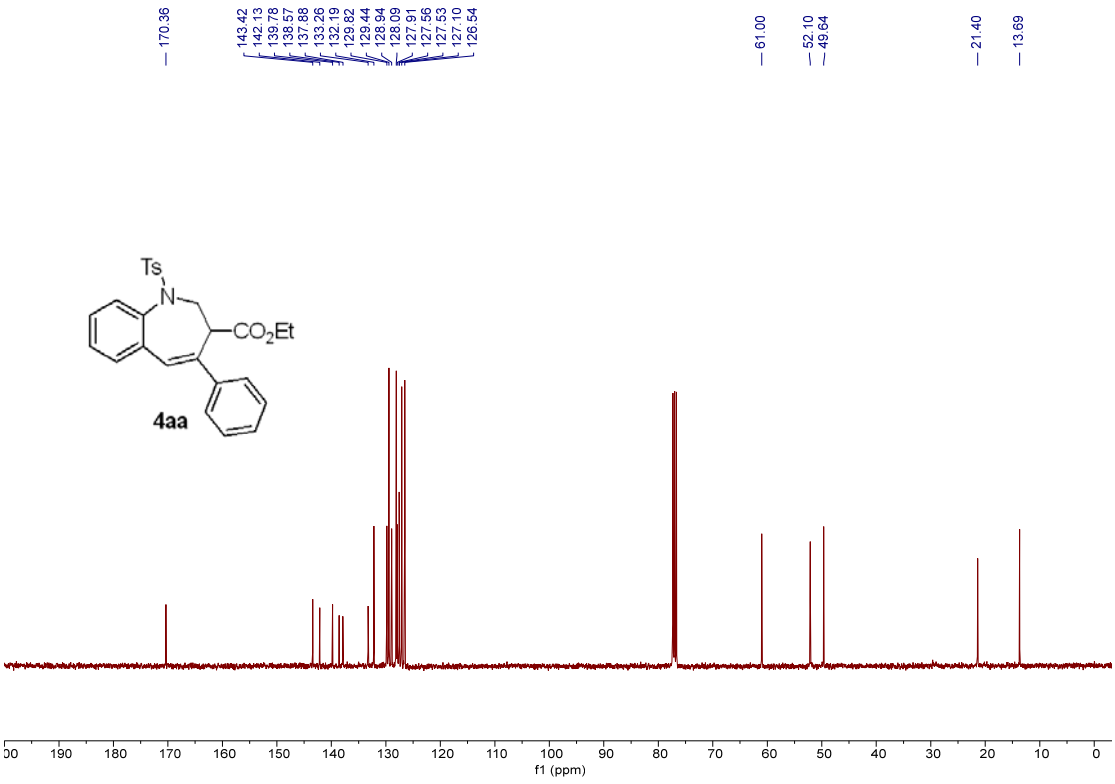
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ts
N
CO2Et
4aa
f1 (ppm)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N
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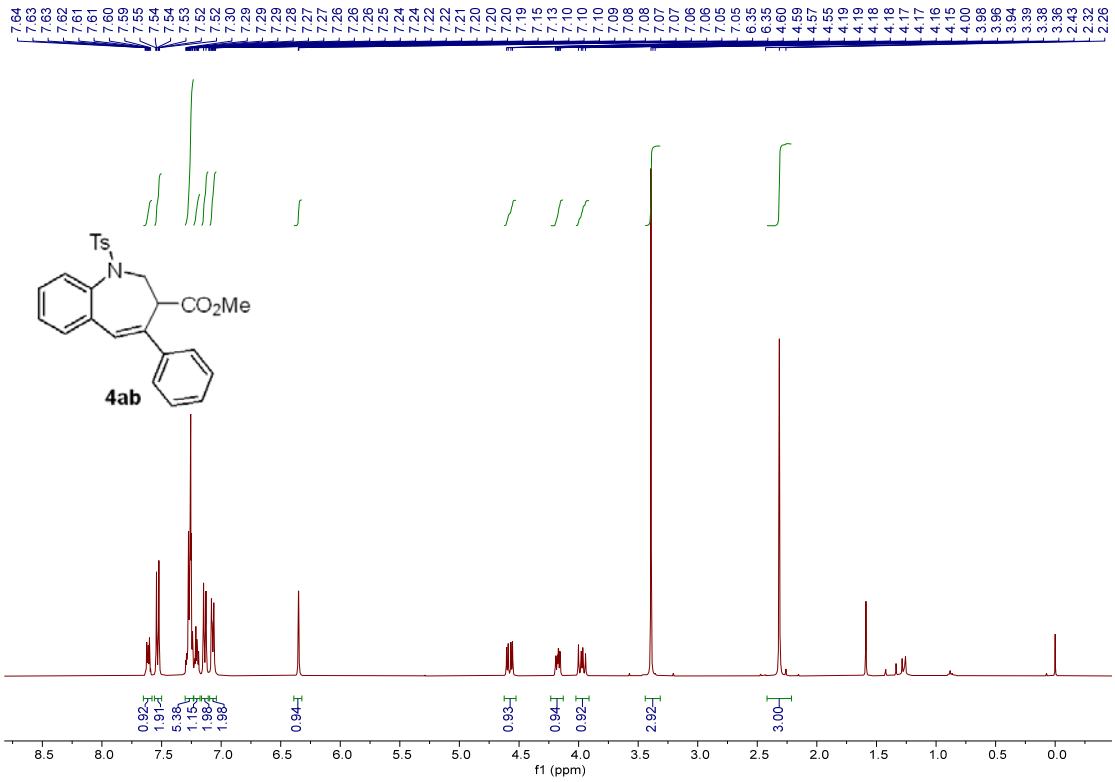
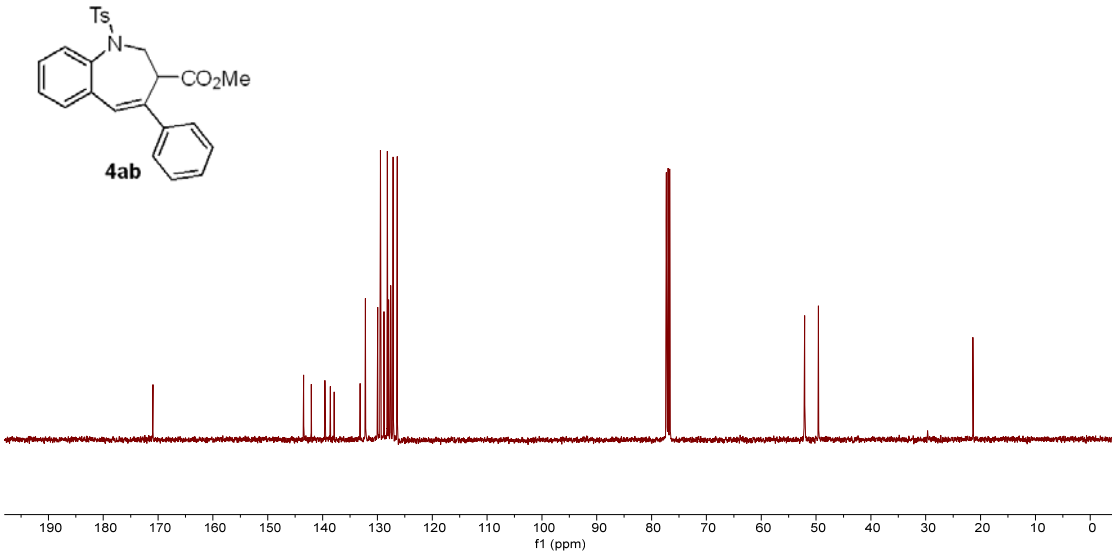
f1 (ppm)


Ts
N
CO2Me
4ab
f1 (ppm)


Ts
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CO2Me
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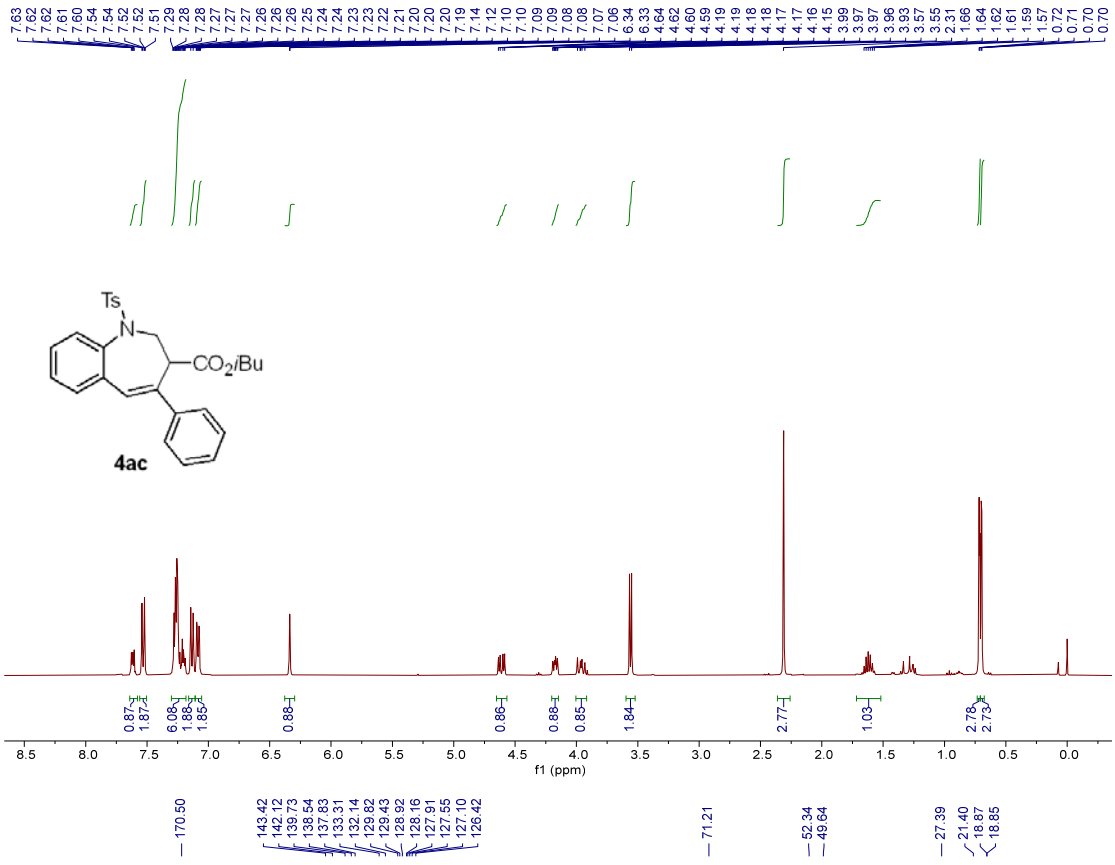
f1 (ppm)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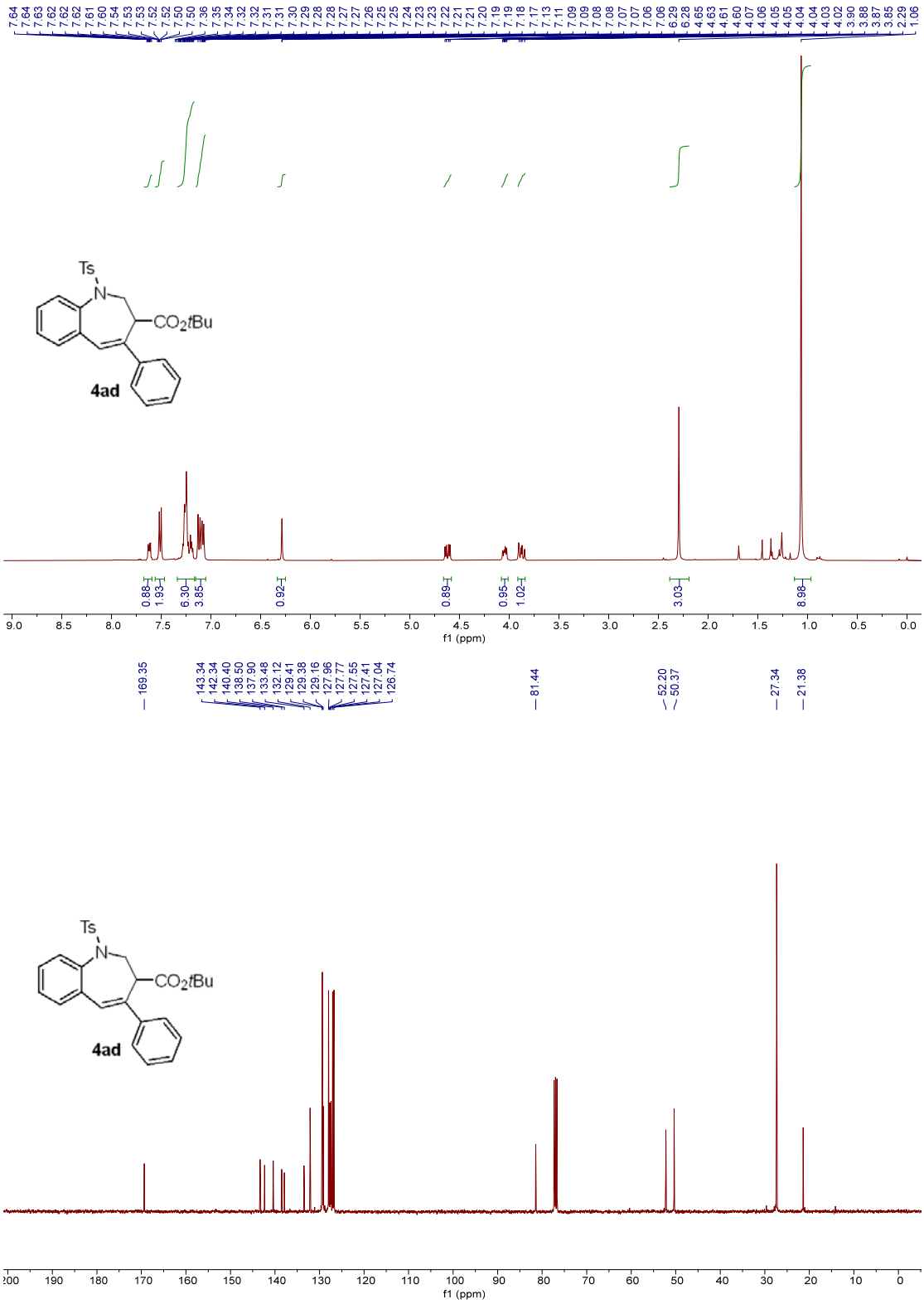
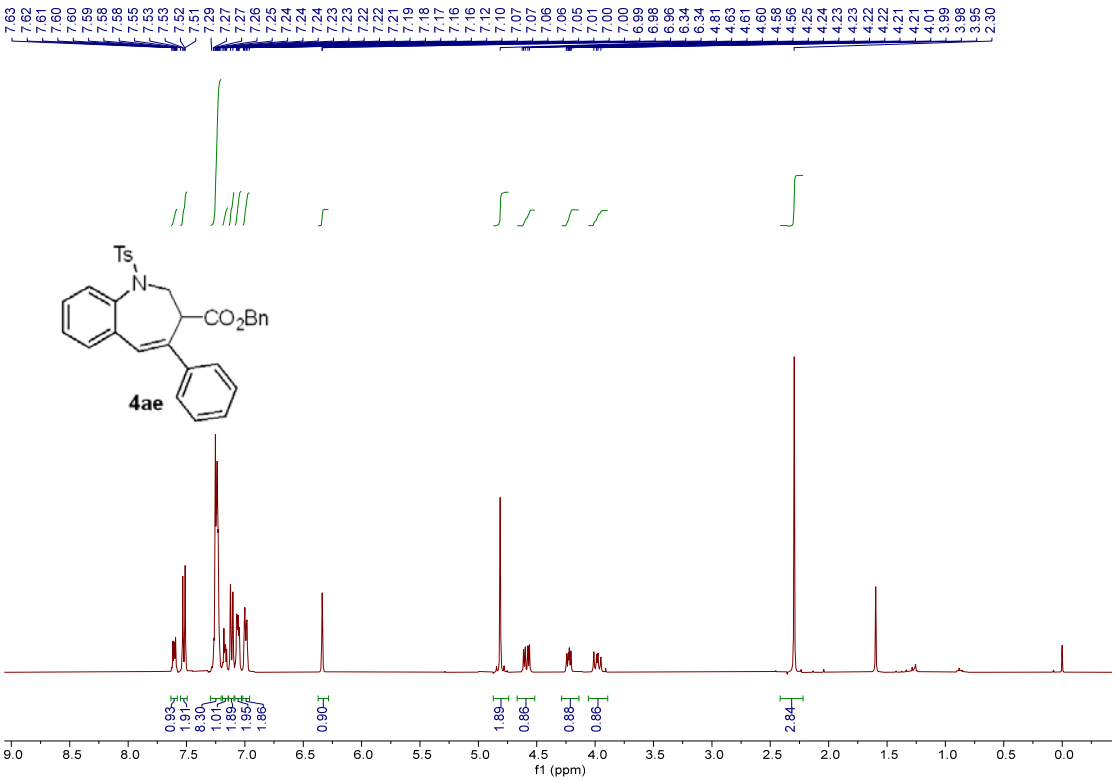
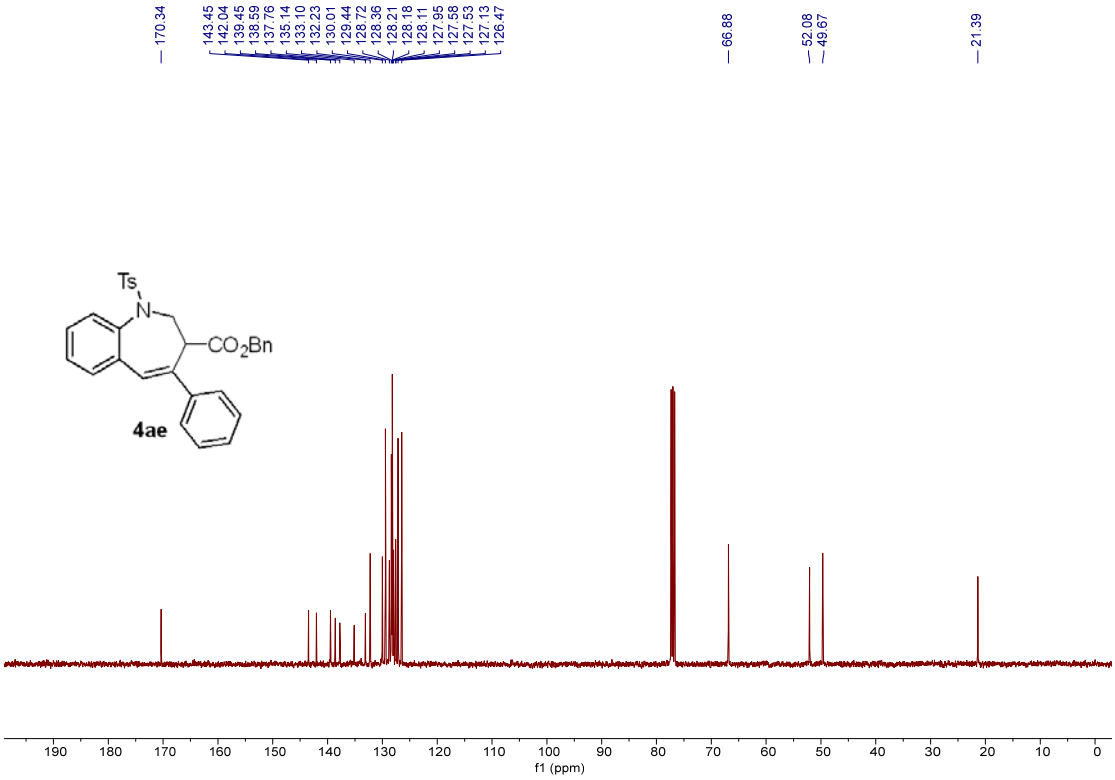
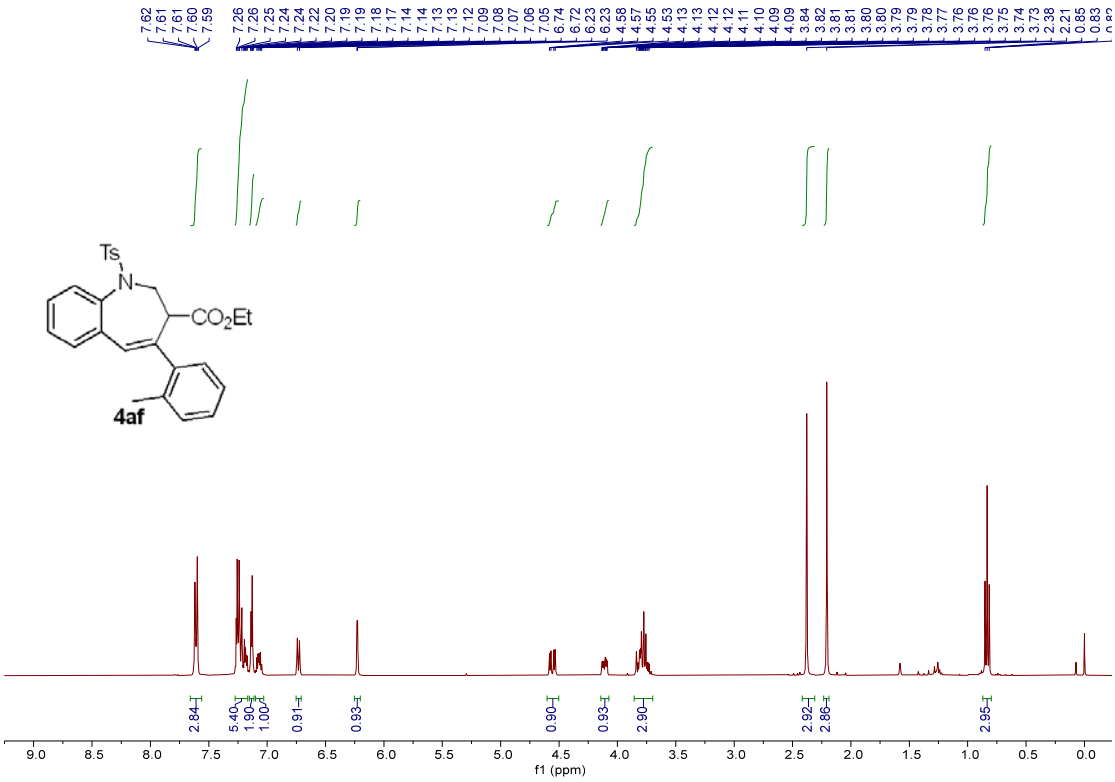
Ts
N
CO2iBu
4ac
0.87 1.87 6.08 1.88 1.85 0.88 0.86 0.88 0.85 1.84 2.77 1.03 2.78 2.73
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
170.50 143.42 142.12 139.73 138.54 137.83 133.31 132.14 129.82 129.43 128.92 128.16 127.91 127.55 127.10 126.42 71.21 52.34 49.64 27.39 21.40 18.87 18.85
Ts
N
CO2iBu
4ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ts
N
CO2tBu
4ad
f1 (ppm)


Ts
N
CO2Bn
4ae
f1 (ppm)


Ts
N
CO2Bn
4ae
f1 (ppm)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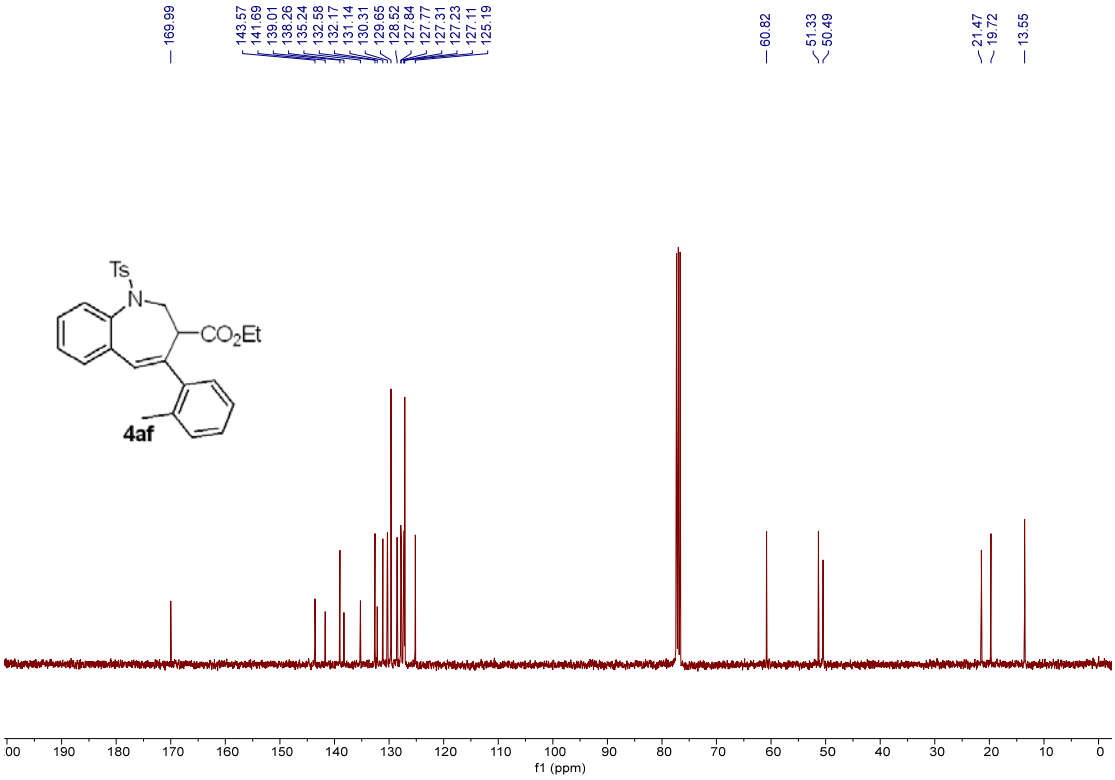
Ts
N
CO2Et
4af
2.84 5.40 1.90 1.00 0.91 0.93 0.90 0.93 2.90 2.92 2.86 2.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.99
143.57 141.69 139.01 138.26 135.24 132.58 132.17 131.14 130.31 129.65 128.52 127.84 127.77 127.31 127.23 127.11 125.19
60.82
51.33 50.49
21.47 19.72
13.55
Ts
N
CO2Et
4af
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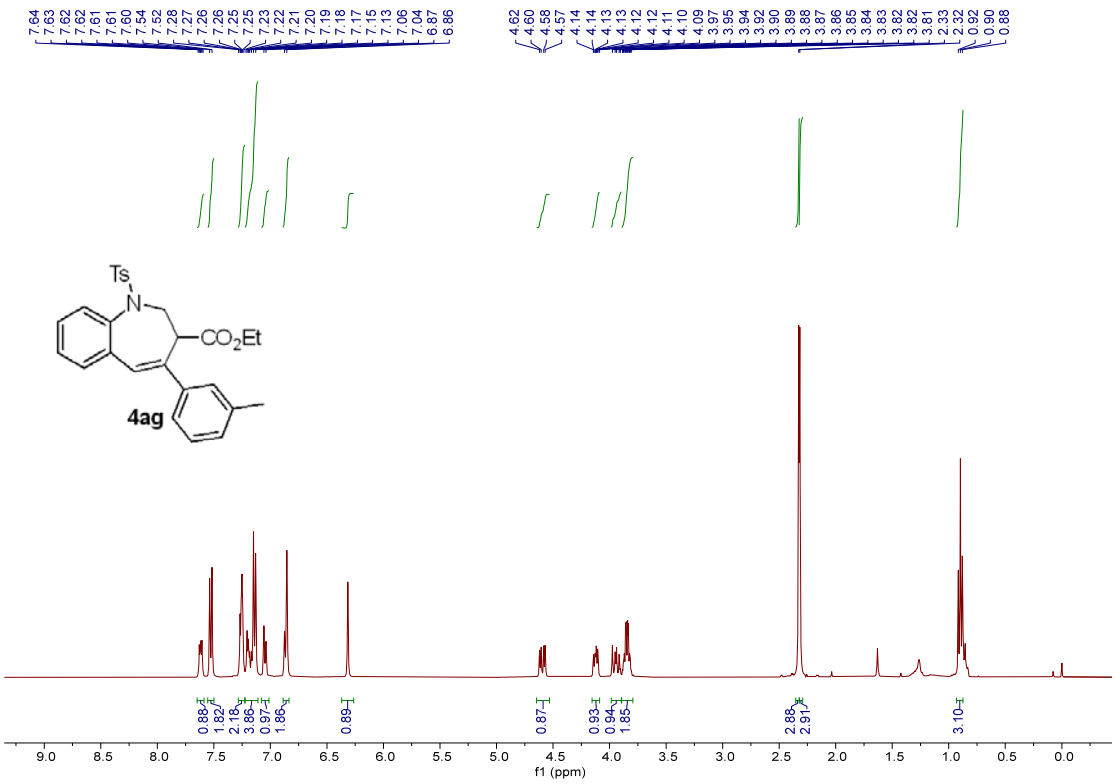
f1 (ppm)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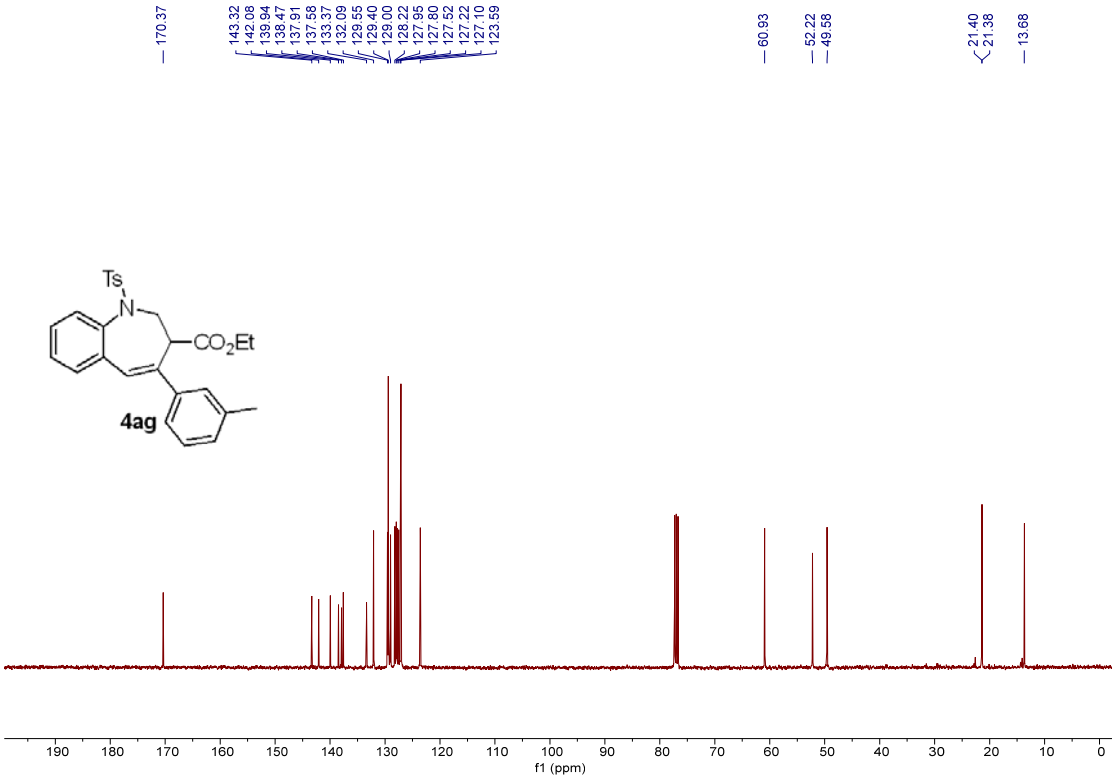
4.62 4.60 4.58 4.57 4.14 4.14 4.13 4.13 4.12 4.12 4.11 4.10 4.09 3.97 3.95 3.94 3.92 3.90 3.89 3.88 3.87 3.86 3.85 3.84 3.83 3.82 3.82 3.81 2.33 2.32 0.92 0.90 0.88
Ts
N
CO2Et
4ag
0.88 1.82 2.18 3.86 0.97 1.86 0.89 0.87 0.93 0.94 1.85 2.88 2.91 3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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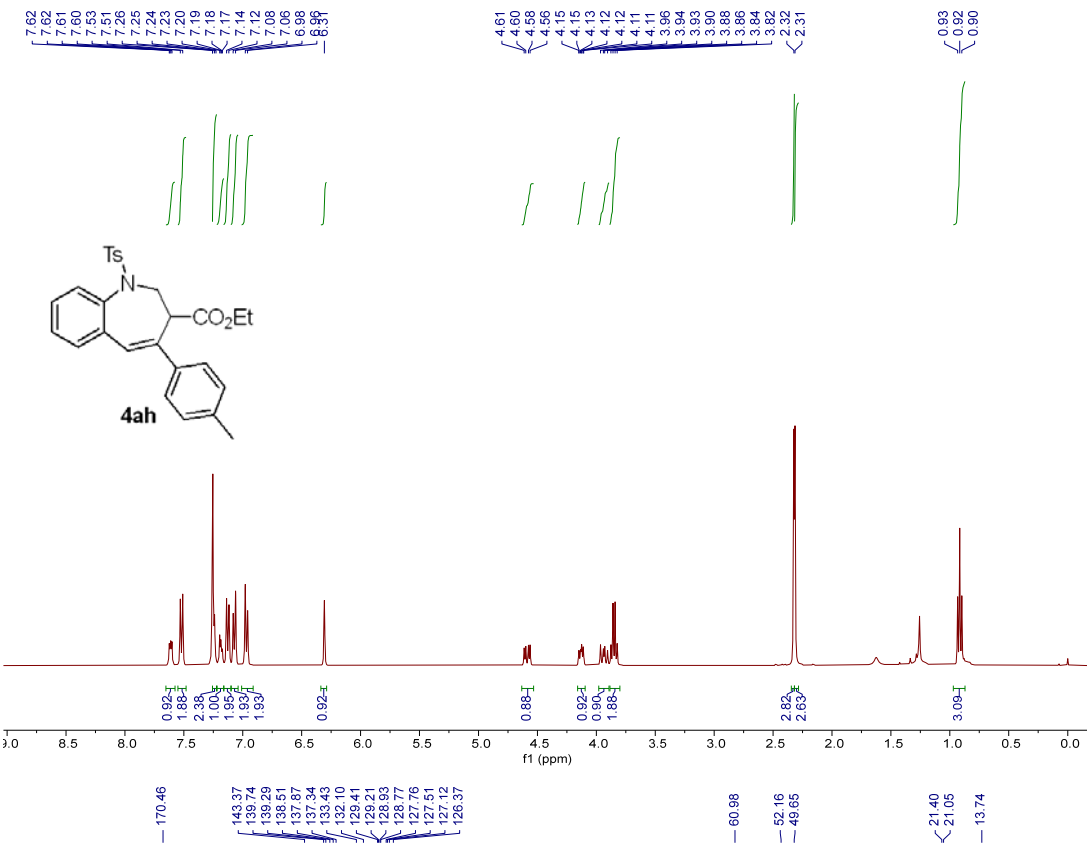
143.32 142.08 139.94 138.47 137.91 137.58 133.37 132.09 129.55 129.40 129.00 128.22 127.95 127.80 127.52 127.22 127.10 123.59
60.93
52.22 49.58
21.40 21.38
13.68
Ts
N
CO2Et
4ag
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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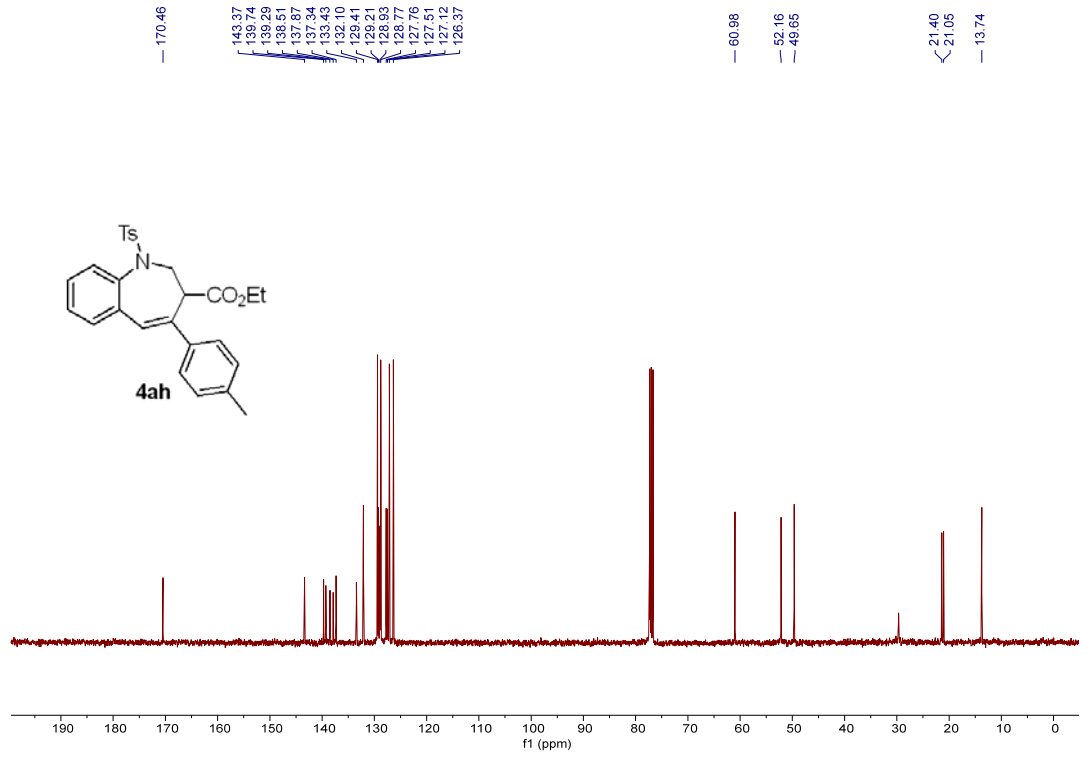
7.23
7.20
7.19
7.18
7.17
7.14
7.12
7.08
7.06
6.98
6.96
6.91
4.61
4.60
4.58
4.56
4.15
4.13
4.12
4.12
4.11
4.11
3.96
3.94
3.93
3.90
3.88
3.86
3.84
3.82
2.32
2.31
0.93
0.92
0.90
Ts
N
CO2Et
4ah
0.92
1.88
2.38
1.00
1.95
1.93
1.93
0.92
0.88
0.92
0.90
1.88
2.83
2.63
3.09
f1 (ppm)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128.77
127.76
127.51
127.12
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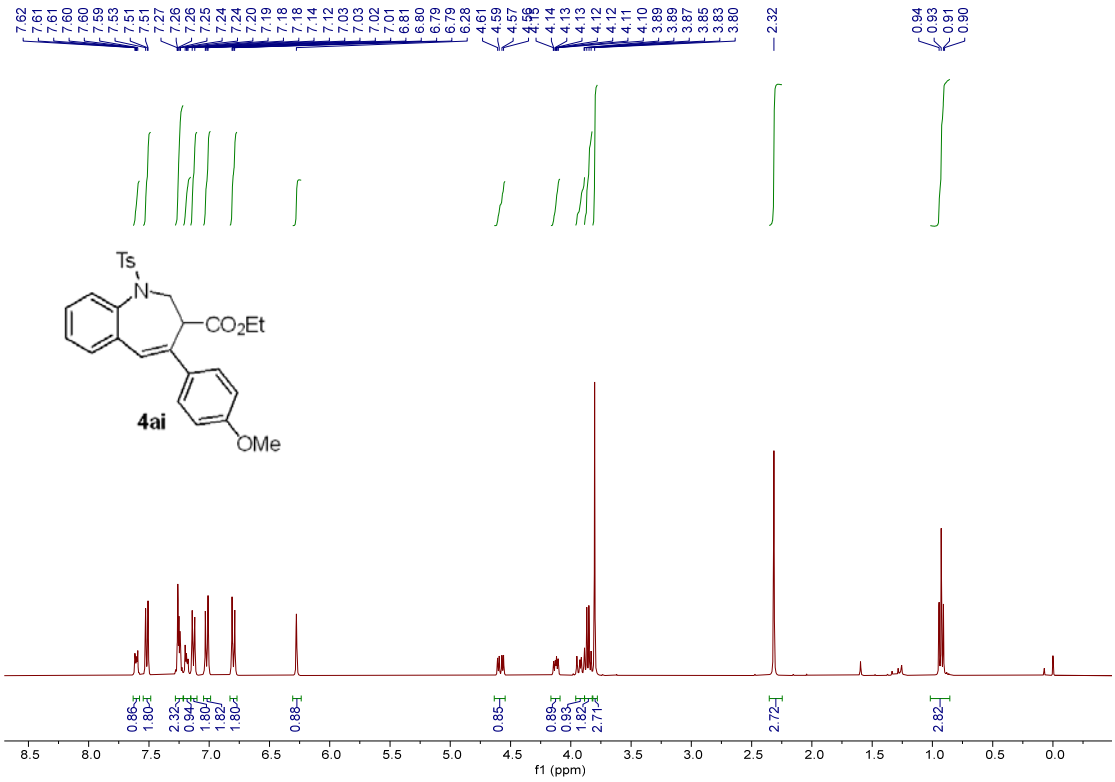
52.16
49.65
21.40
21.05
13.74
Ts
N
CO2Et
4ah
f1 (ppm)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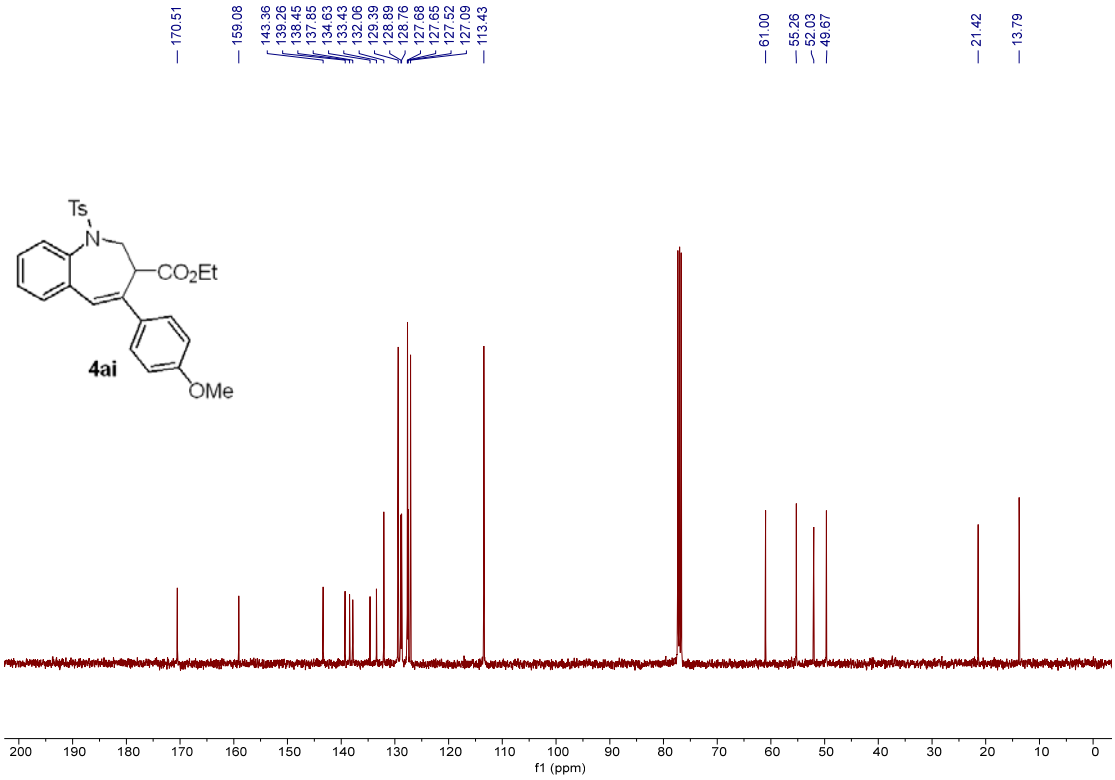
7.26
7.26
7.25
7.24
7.24
7.20
7.19
7.18
7.18
7.14
7.12
7.03
7.03
7.02
7.01
6.81
6.80
6.79
6.79
6.28
4.61
4.59
4.57
4.56
4.55
4.14
4.13
4.13
4.12
4.12
4.11
4.10
3.89
3.89
3.87
3.85
3.83
3.80
2.32
0.94
0.93
0.91
0.90
Ts
N
CO2Et
4ai
OMe
0.86
1.80
2.32
0.94
1.80
1.82
1.80
0.88
0.85
0.89
0.93
1.82
2.71
2.72
2.82
f1 (ppm)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134.63
133.43
132.06
129.39
128.89
128.76
127.68
127.65
127.52
127.09
113.43
61.00
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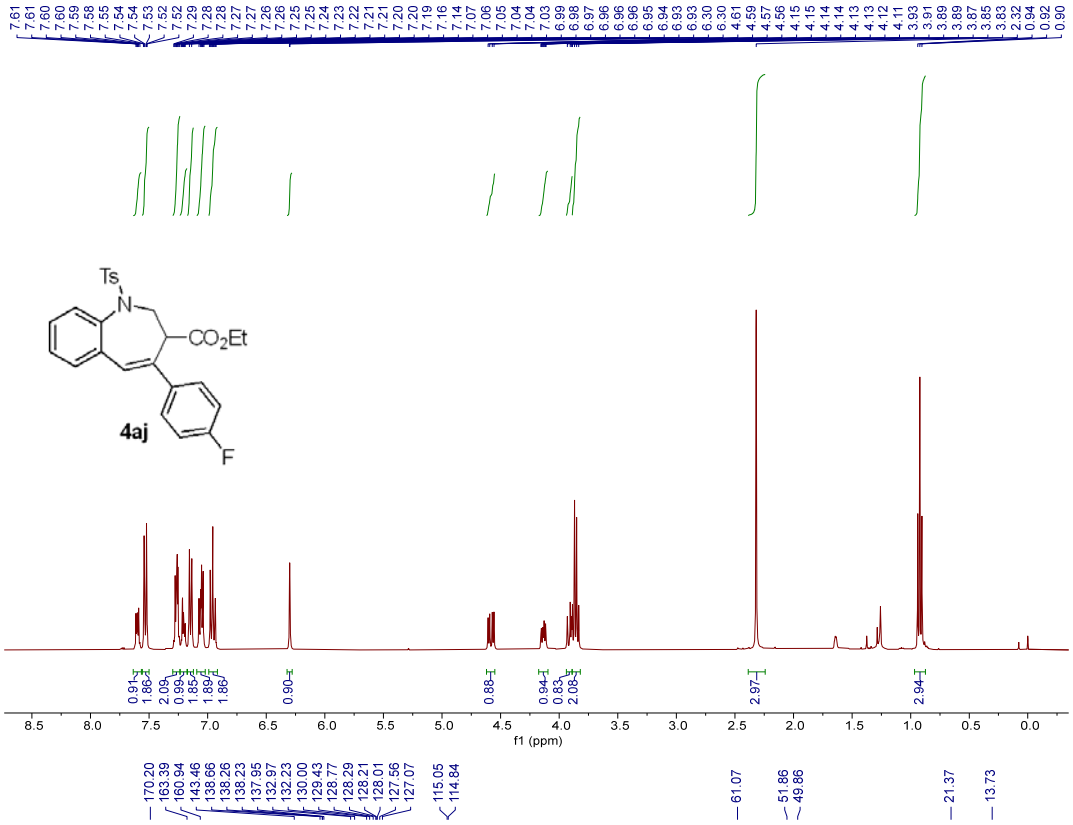
52.03
49.67
21.42
13.79
Ts
N
CO2Et
4ai
OMe
f1 (ppm)


Ts
N
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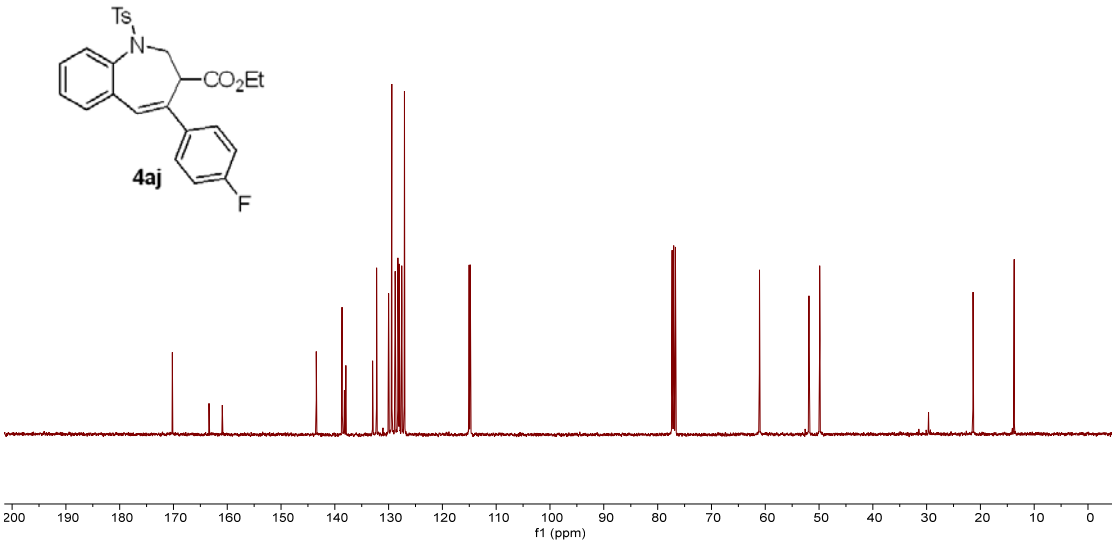
4aj
F
f1 (ppm)


Ts
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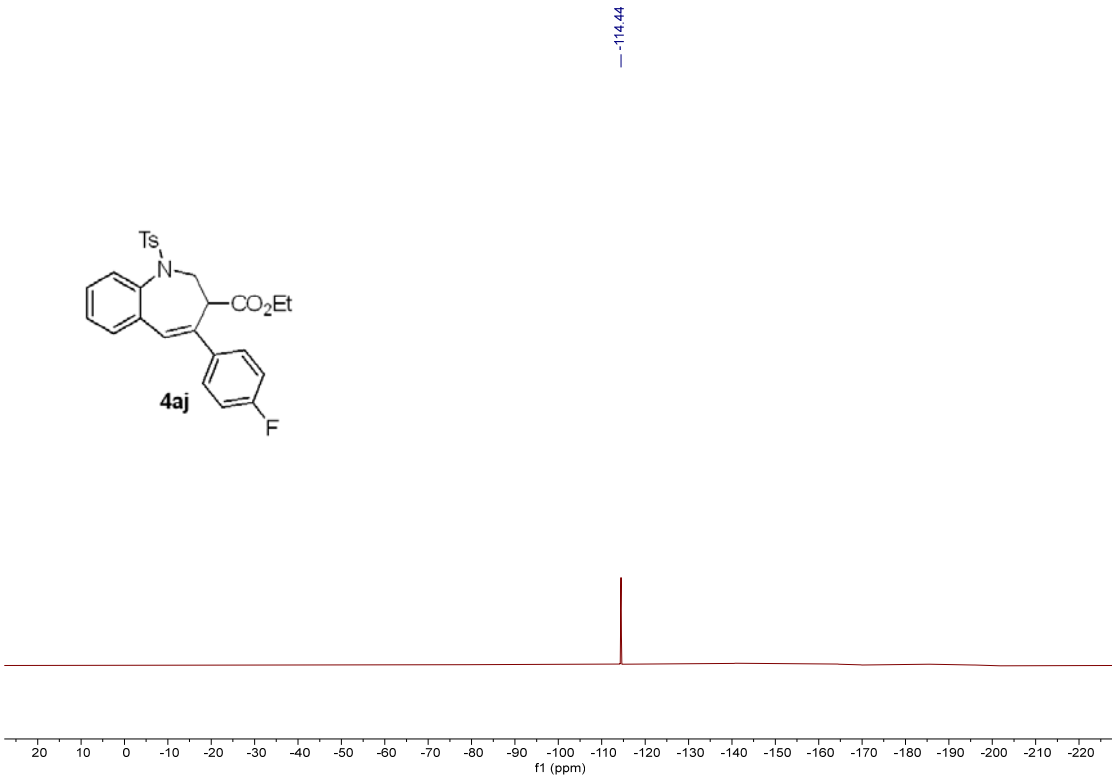
f1 (ppm)


-114.44
Ts
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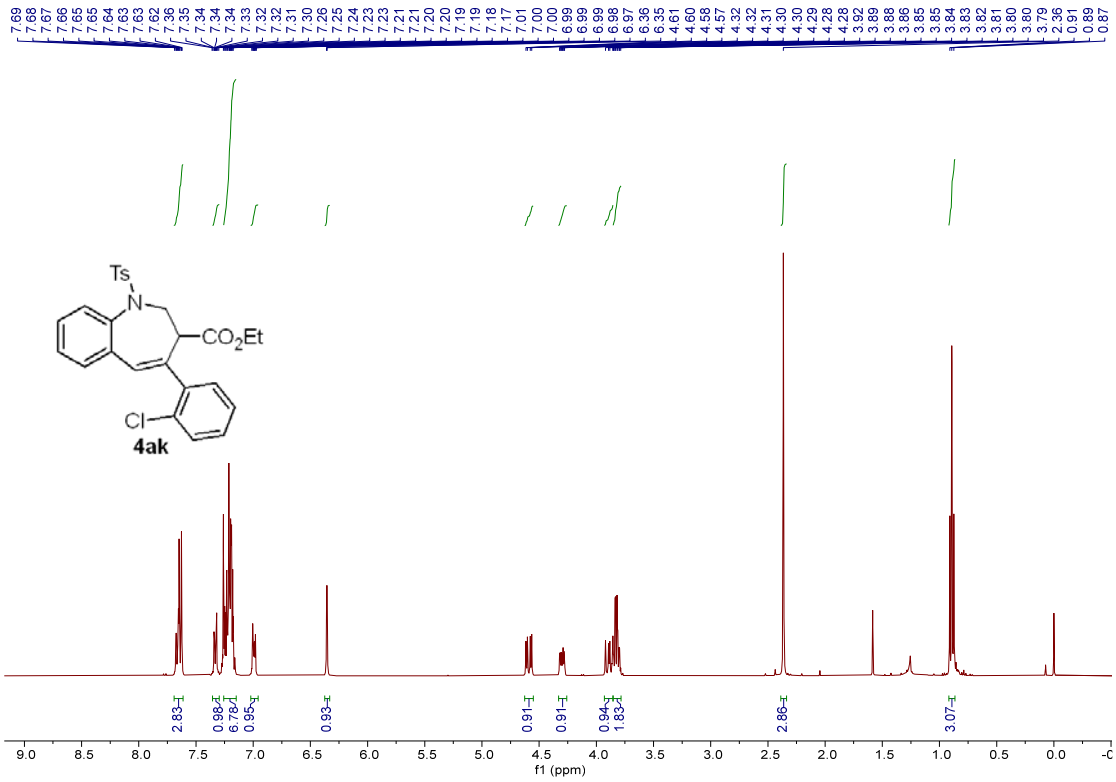
CO2Et
F
4aj
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)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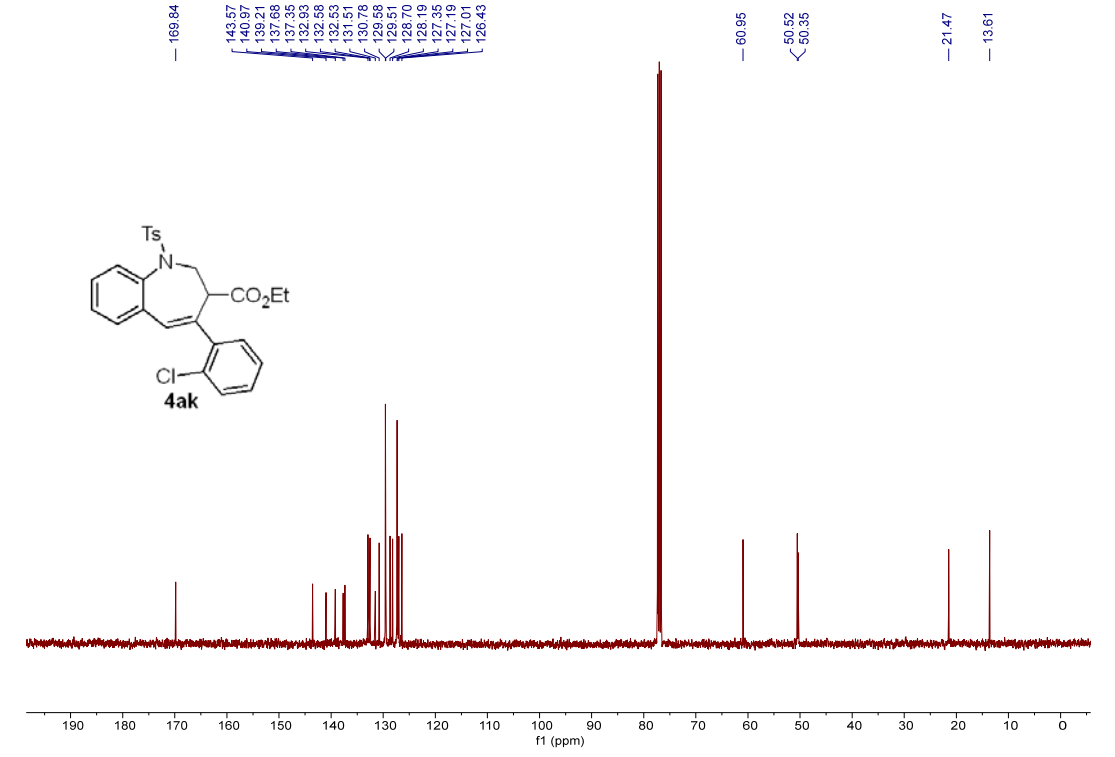
Cl
4ak
f1 (ppm)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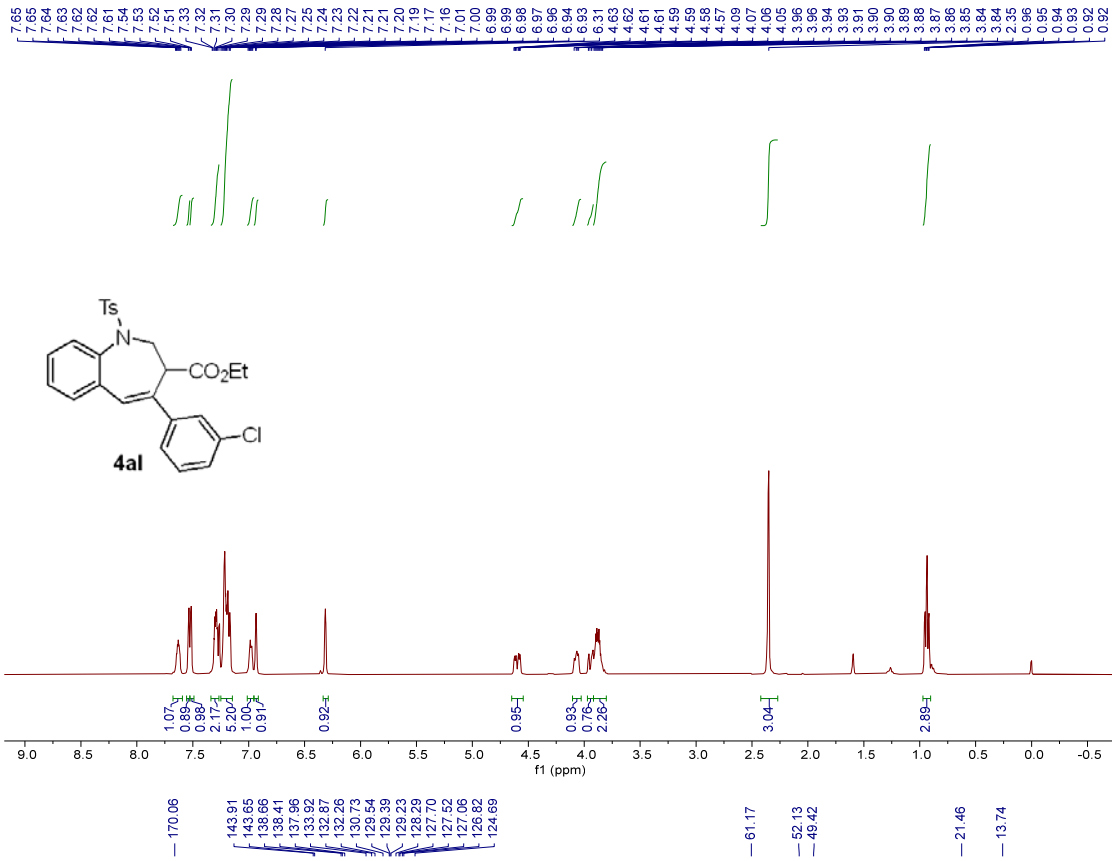
Cl
4ak
f1 (ppm)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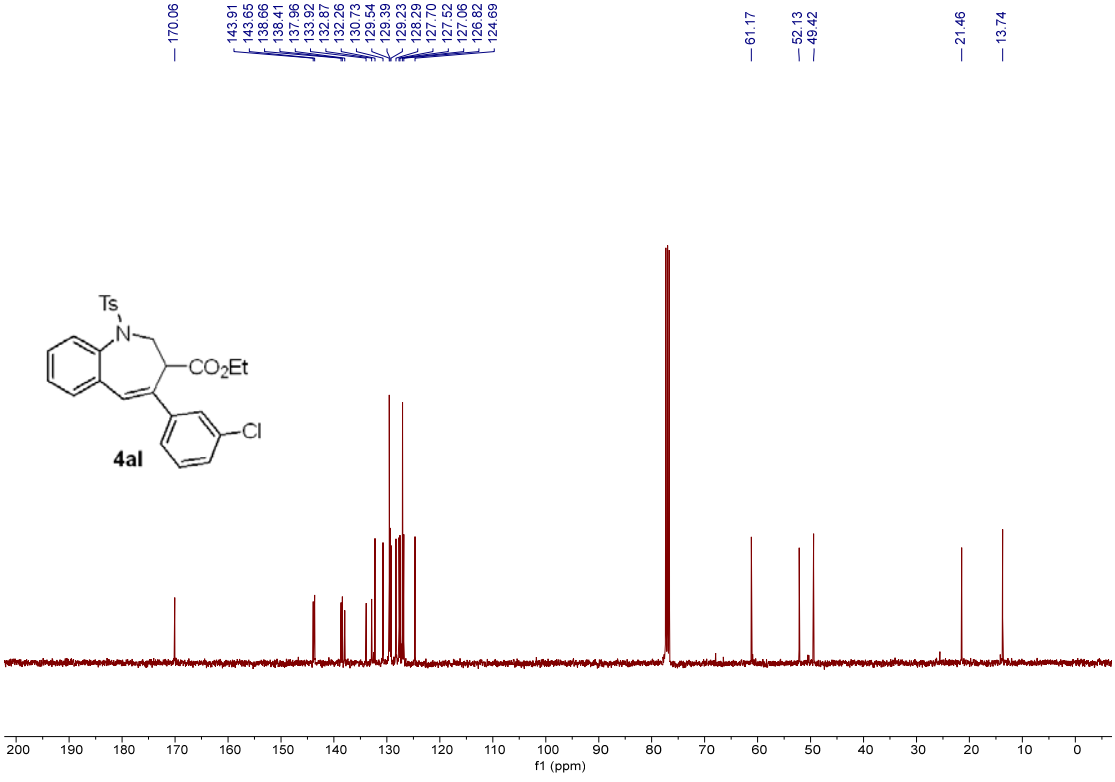
Ts
N
CO2Et
Cl
4al
1.07 0.89 0.98 2.17 5.20 1.00 0.91 0.92 0.95 0.93 0.76 2.26 3.04 2.89
f1 (ppm)


170.06
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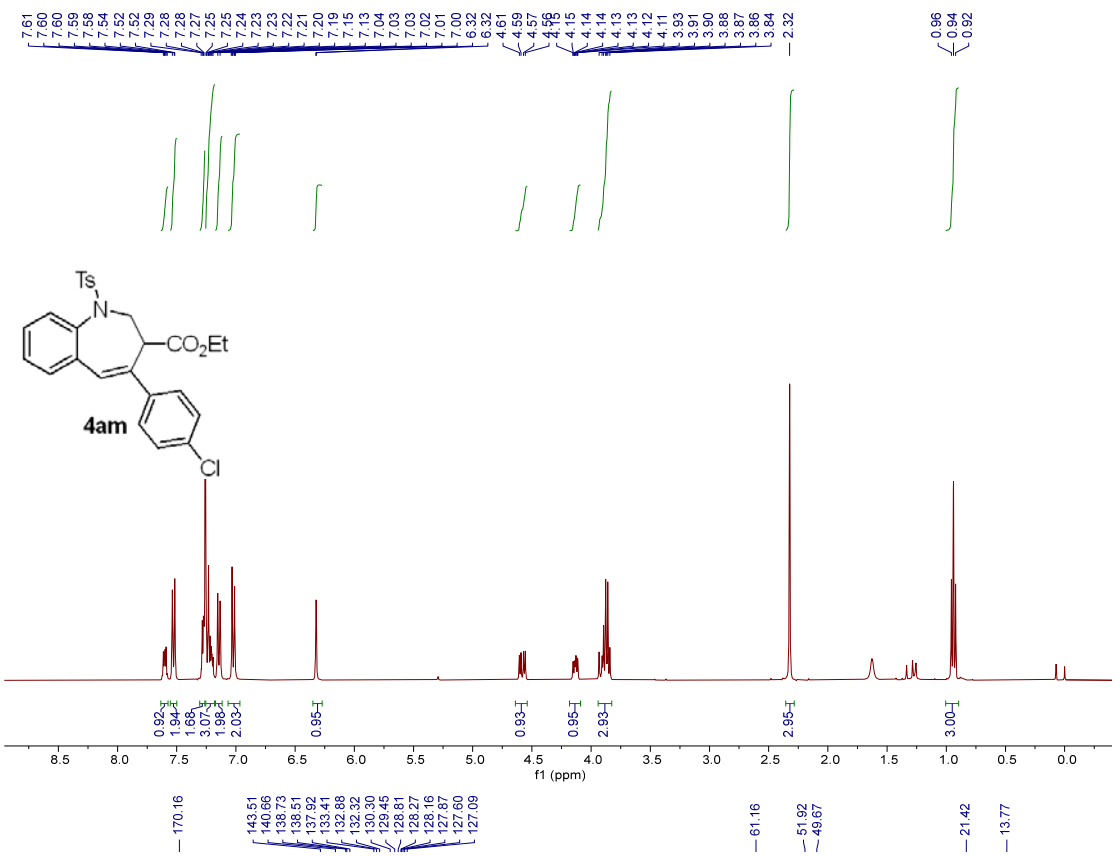
61.17
52.13 49.42
21.46
13.74
Ts
N
CO2Et
Cl
4al
f1 (ppm)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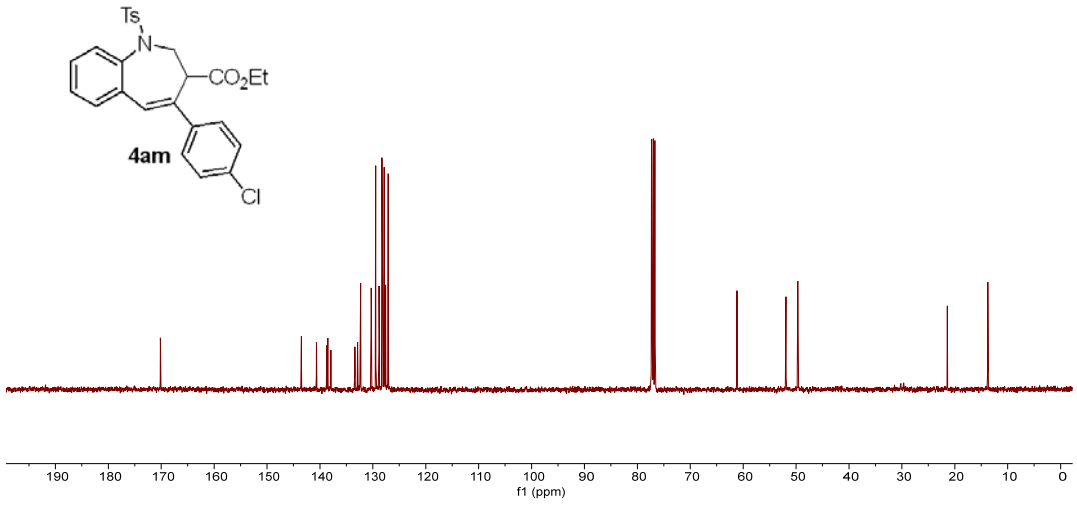
CO2Et
4am
Cl
f1 (ppm)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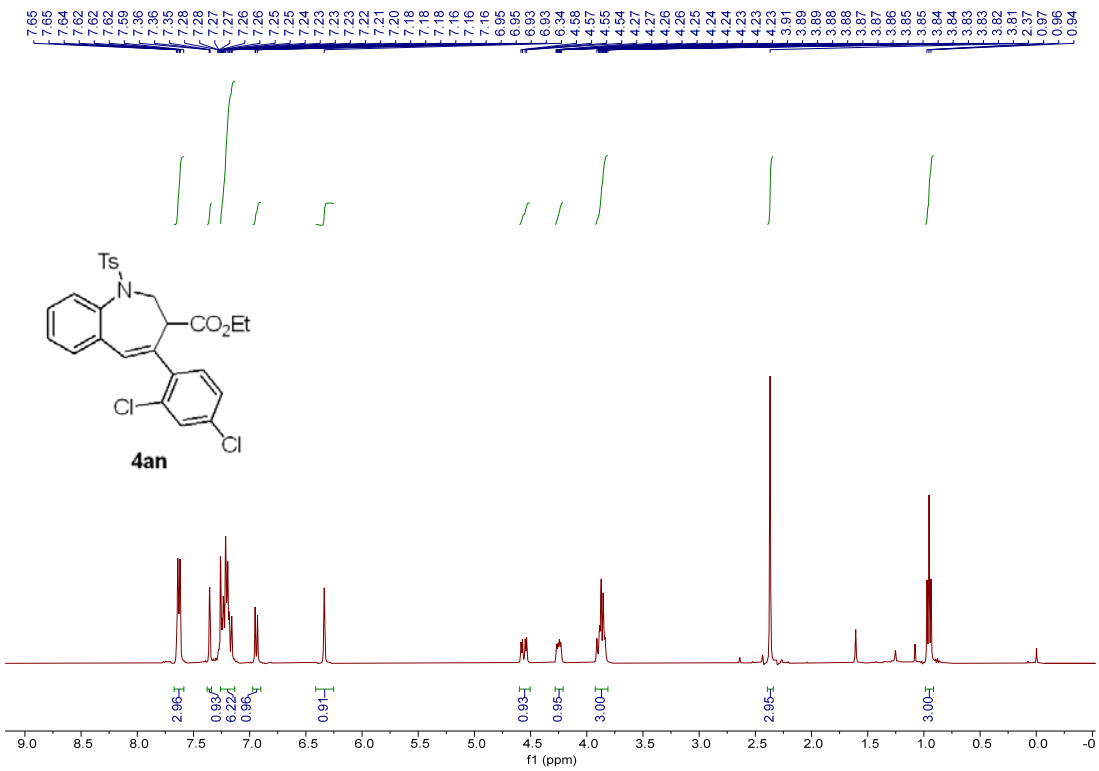
Cl
f1 (ppm)


Ts
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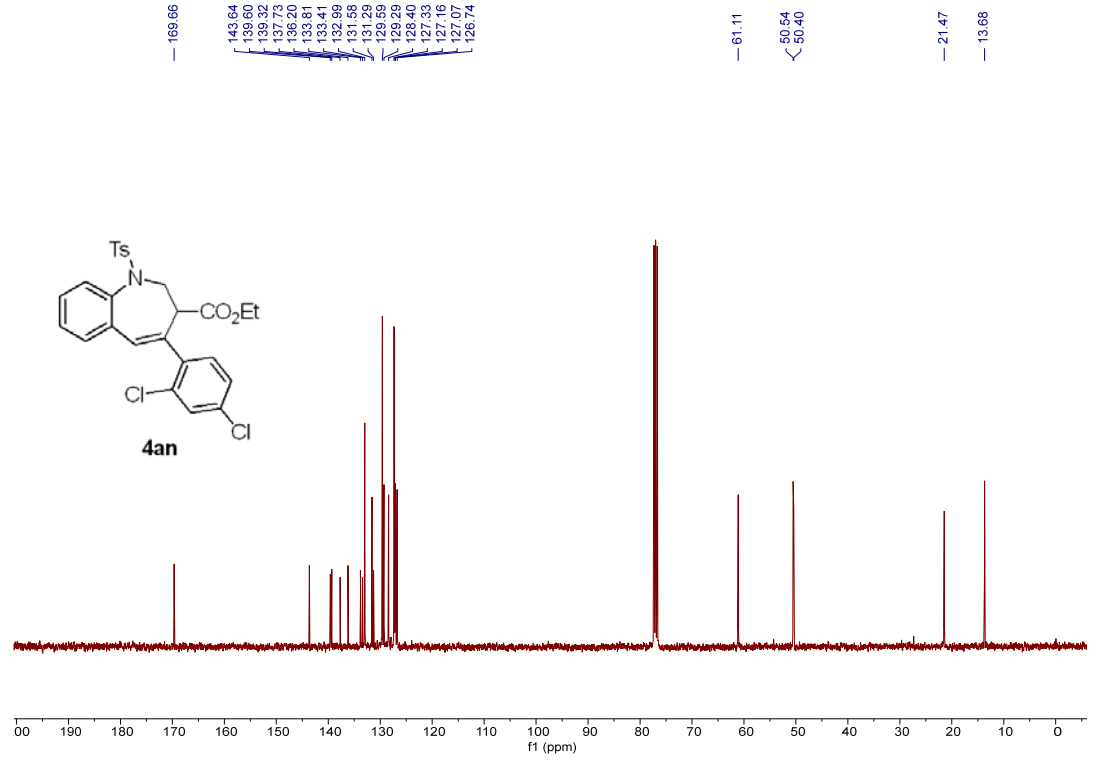
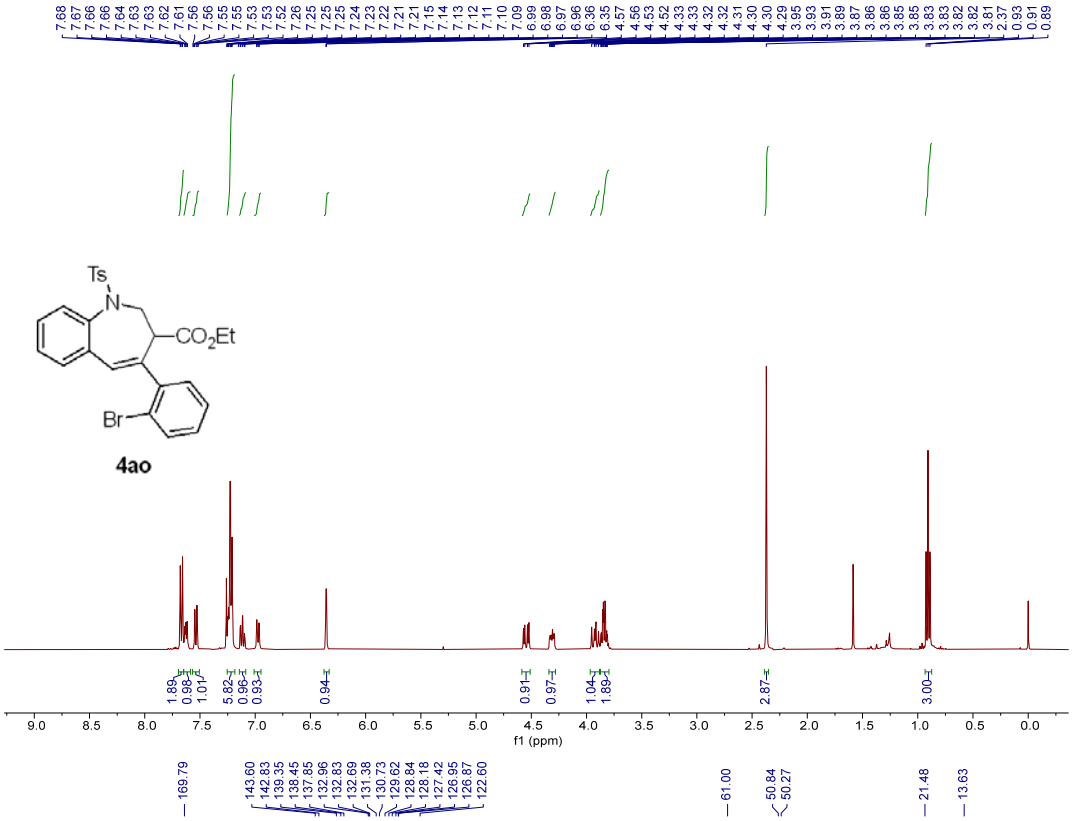
Cl
Cl
4an
f1 (ppm)


Ts
N
CO2Et
Cl
Cl
4an
f1 (ppm)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Br
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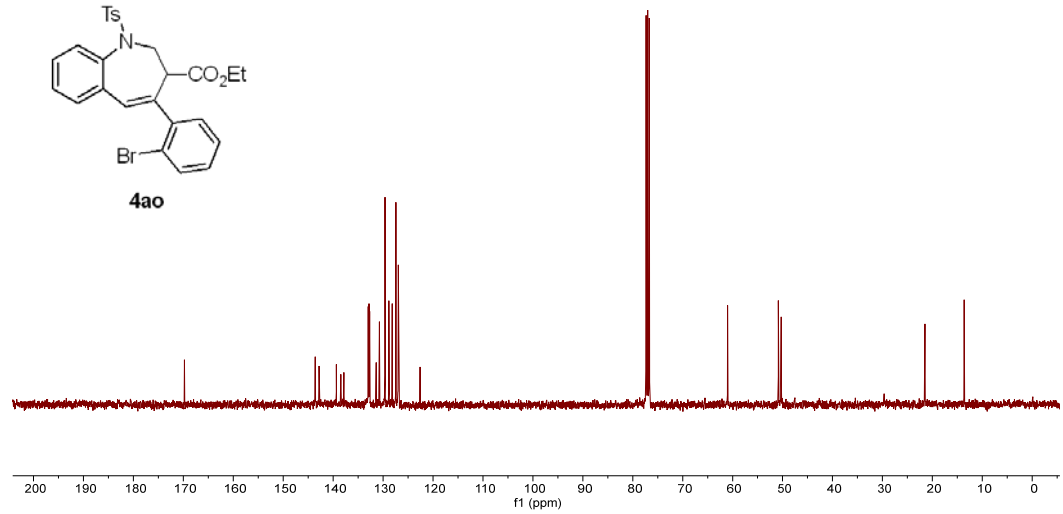
f1 (ppm)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Br
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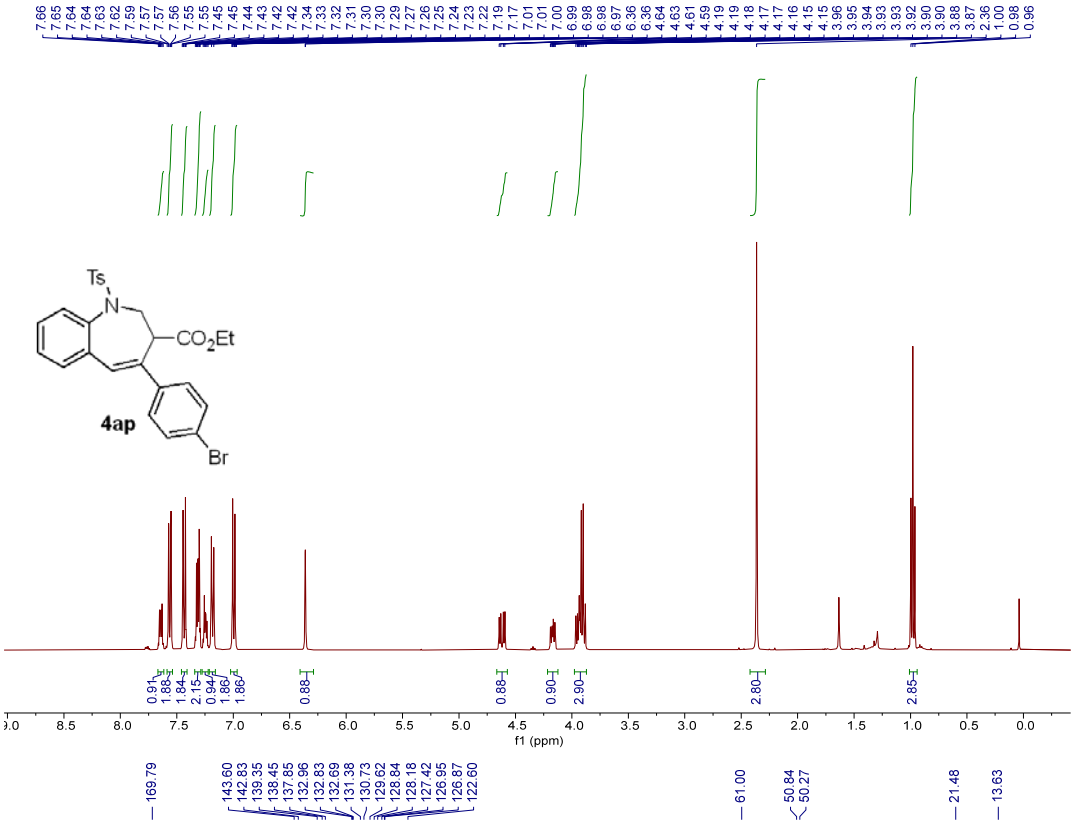
f1 (ppm)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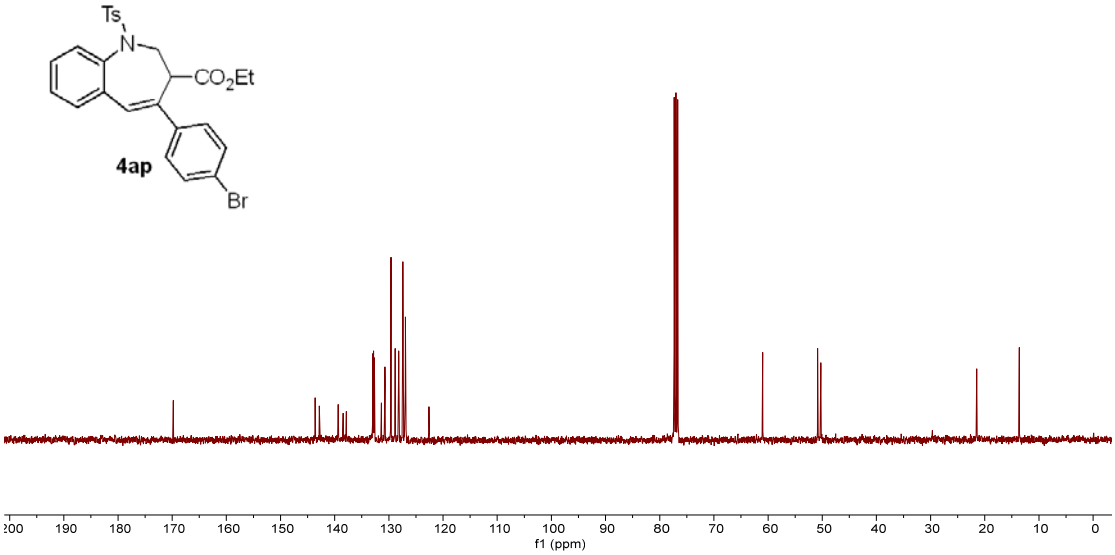
4ap
Br
f1 (ppm)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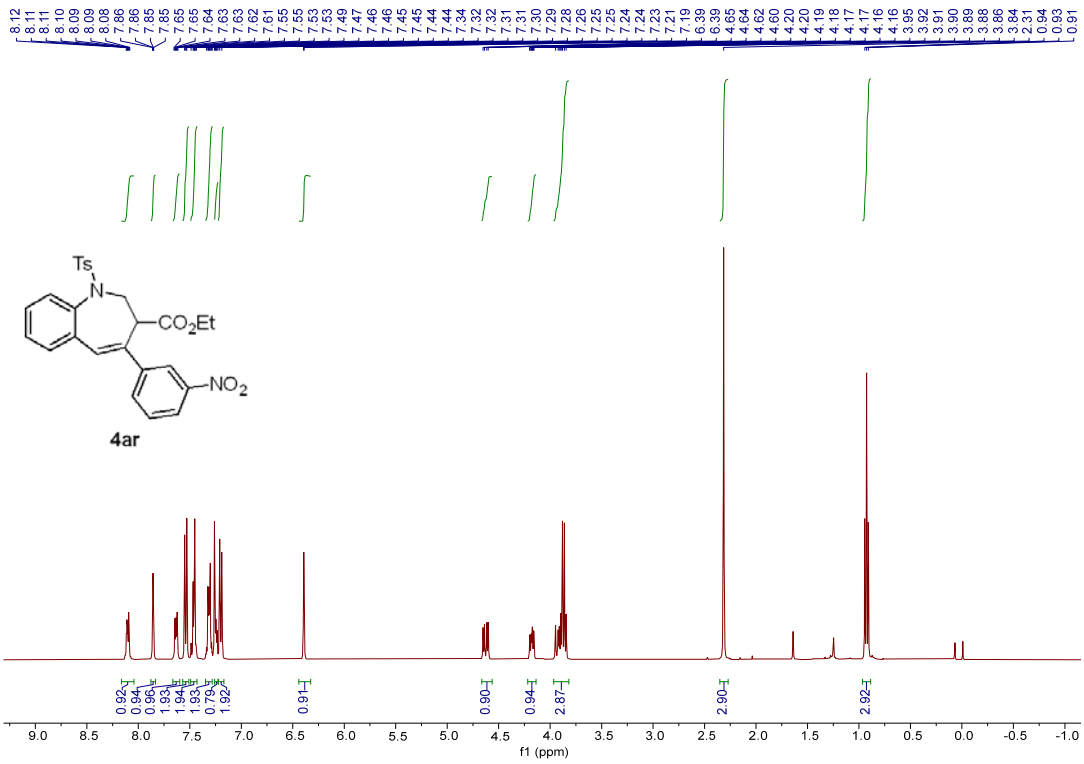
CO2Et
4ap
Br
f1 (ppm)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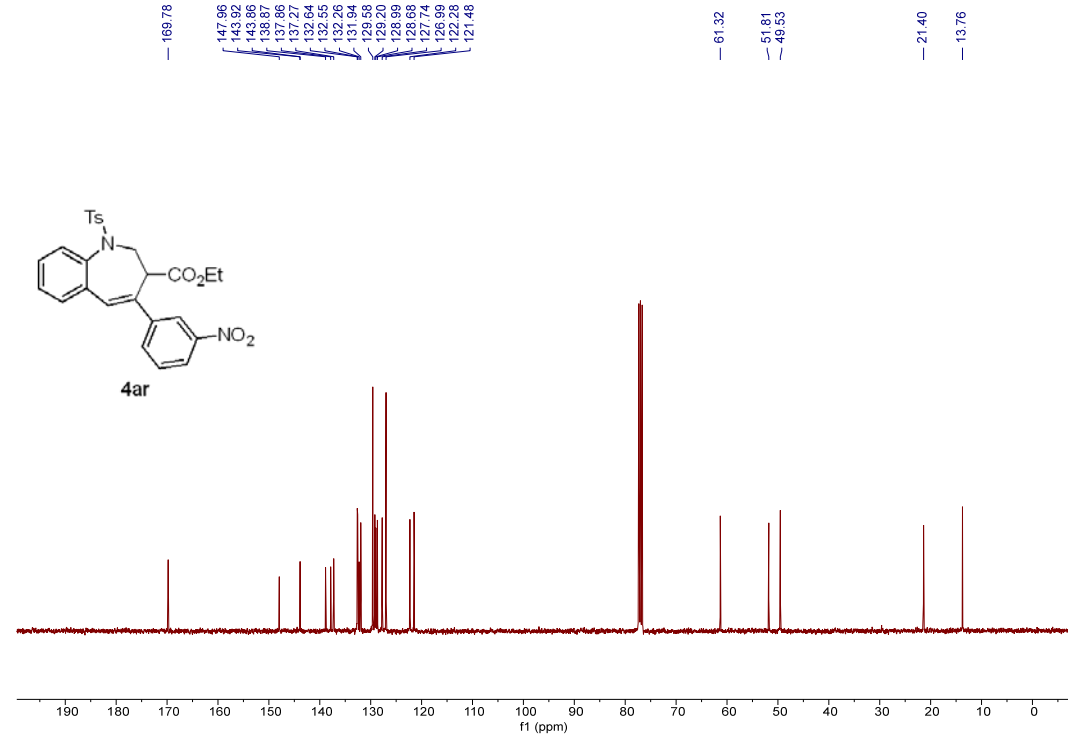
CO2Et
NO2
4ar
f1 (ppm)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NO2
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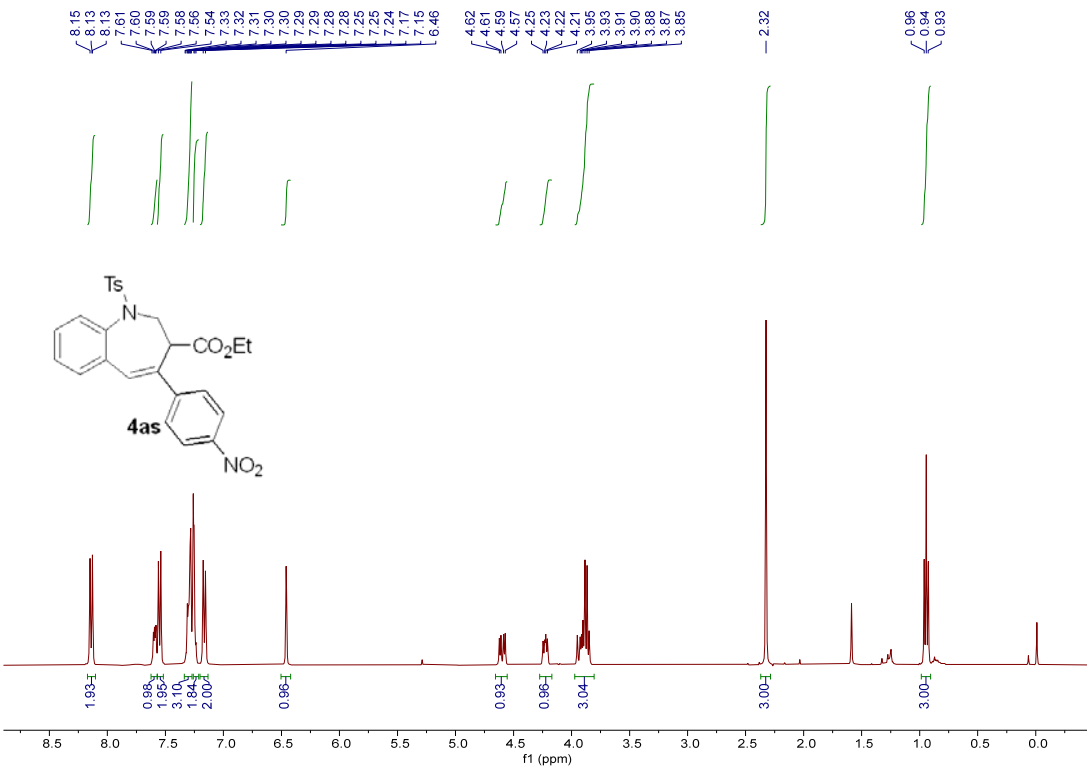
f1 (ppm)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7.30
7.29
7.29
7.28
7.28
7.25
7.25
7.24
7.17
7.15
6.46
4.62
4.61
4.59
4.57
4.25
4.23
4.22
4.21
3.95
3.93
3.91
3.90
3.88
3.87
3.85
2.32
0.96
0.94
0.93
Ts
N
CO2Et
4as
NO2
1.93
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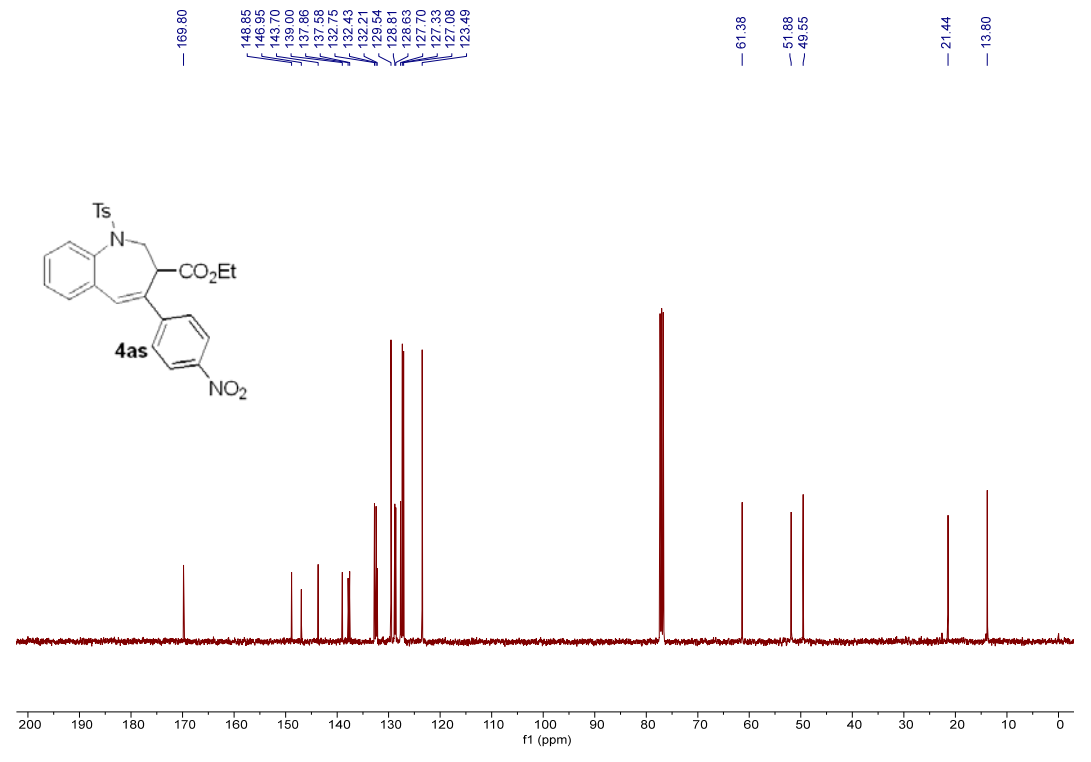
2.00
0.96
0.93
0.96
3.04
3.00
3.00
f1 (ppm)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146.95
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139.00
137.86
137.58
132.75
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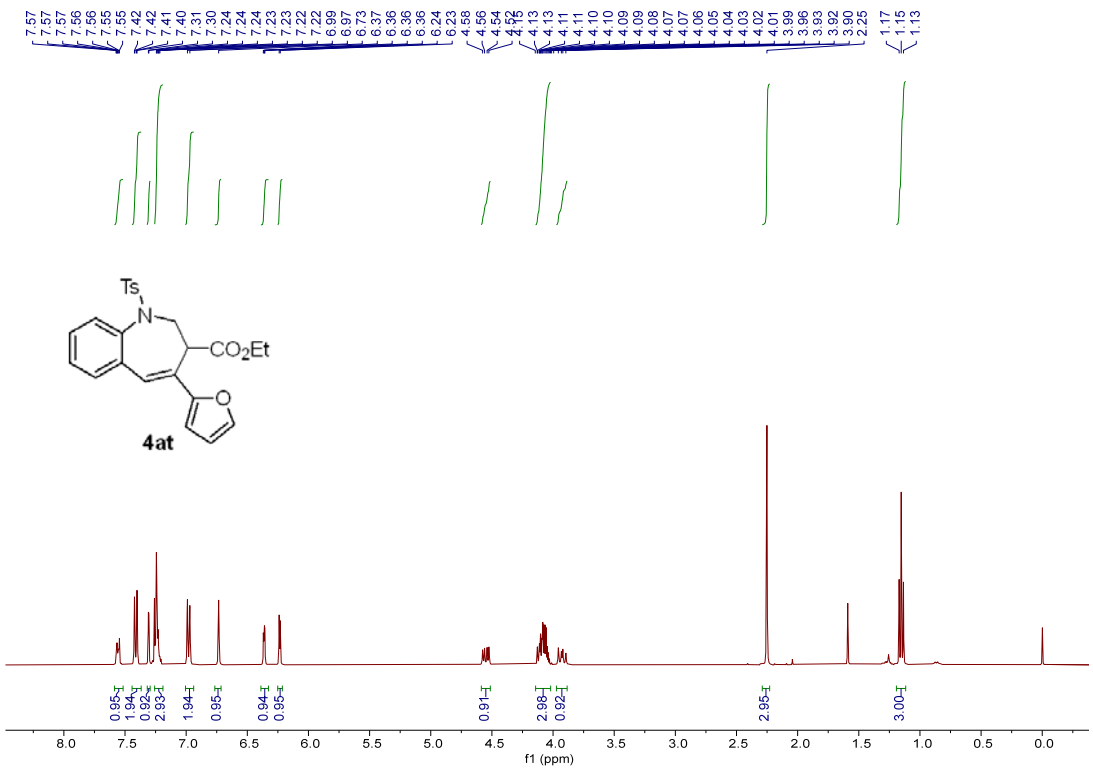
132.21
129.54
128.81
128.63
127.70
127.33
127.08
123.49
61.38
51.88
49.55
21.44
13.80
Ts
N
CO2Et
4as
NO2
f1 (ppm)


Ts
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CO2Et
O
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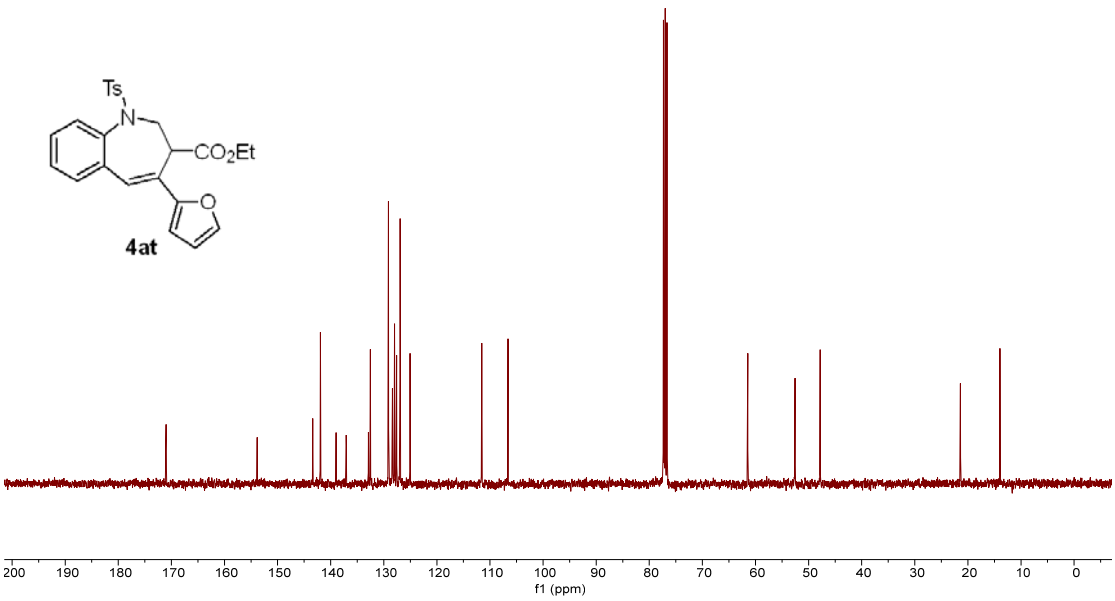
f1 (ppm)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O
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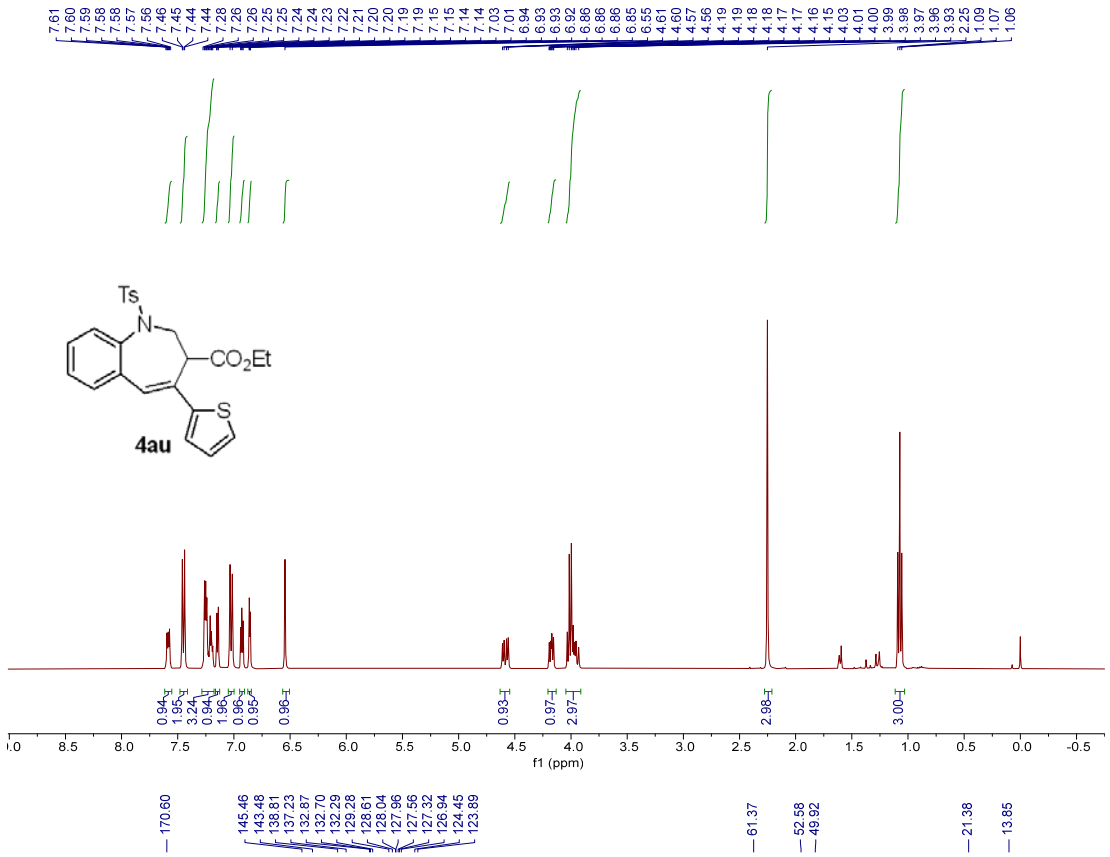
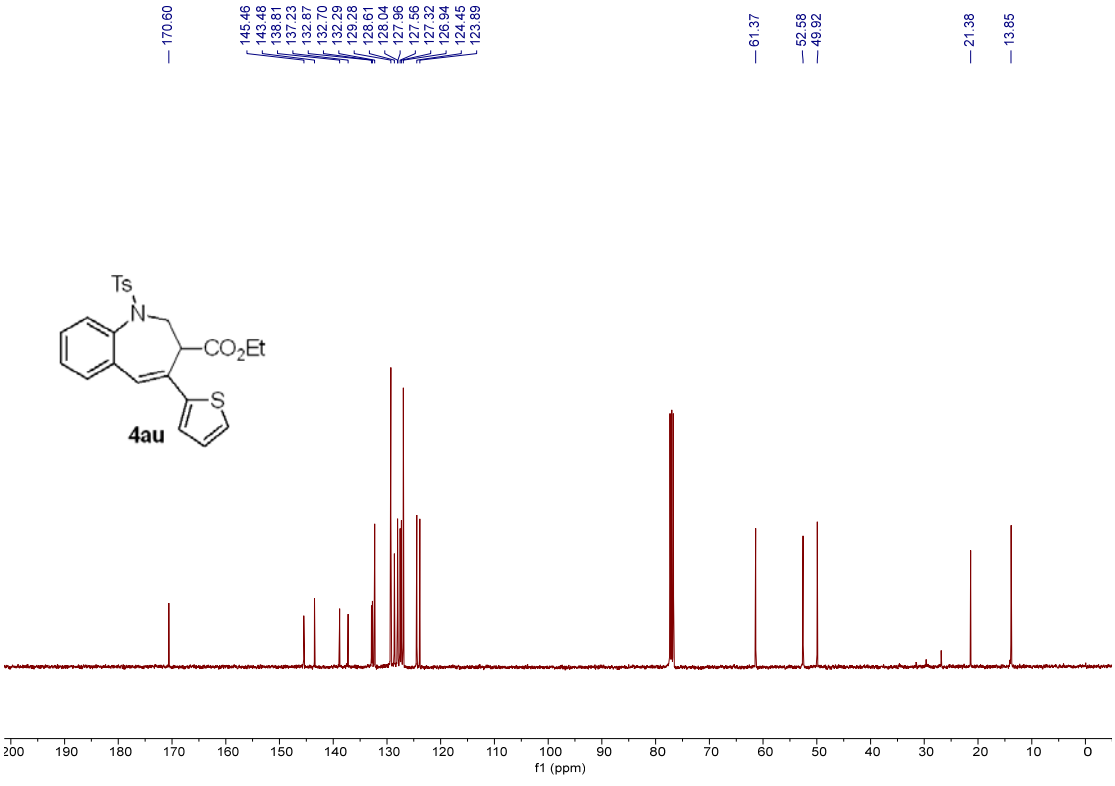
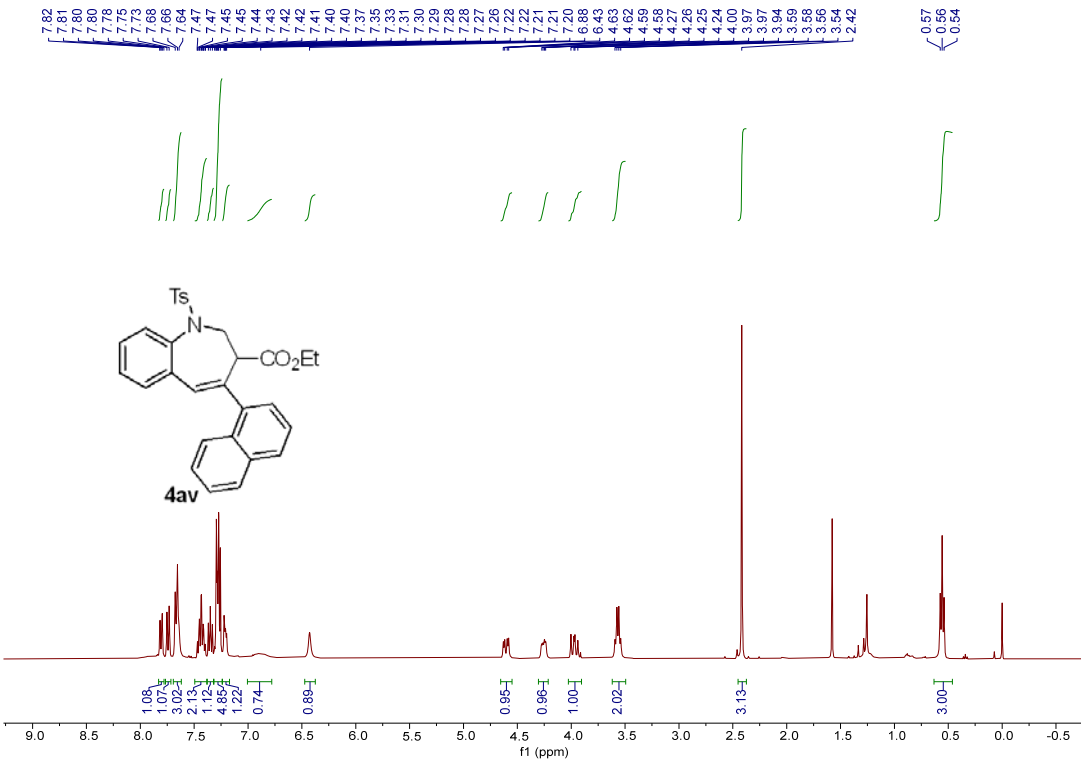
f1 (ppm)


7.61 7.60 7.59 7.58 7.58 7.57 7.56 7.46 7.45 7.44 7.44 7.28 7.26 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.21 7.20 7.20 7.19 7.19 7.15 7.15 7.14 7.14 7.03 7.01 6.94 6.93 6.93 6.92 6.86 6.86 6.86 6.85 6.55 4.61 4.60 4.57 4.56 4.19 4.19 4.18 4.18 4.17 4.17 4.16 4.15 4.03 4.01 4.00 3.99 3.98 3.97 3.96 3.93 2.25 1.09 1.07 1.06
Ts
N
CO2Et
S
4au
0.94 1.95 3.24 0.94 1.96 0.96 0.95 0.96 0.93 0.97 2.97 2.98 3.00
f1 (ppm)


170.60
145.46 143.48 138.81 137.23 132.87 132.70 132.29 129.28 128.61 128.04 127.96 127.56 127.32 126.94 124.45 123.89
61.37
52.58 49.92
21.38
13.85
Ts
N
CO2Et
S
4au
f1 (ppm)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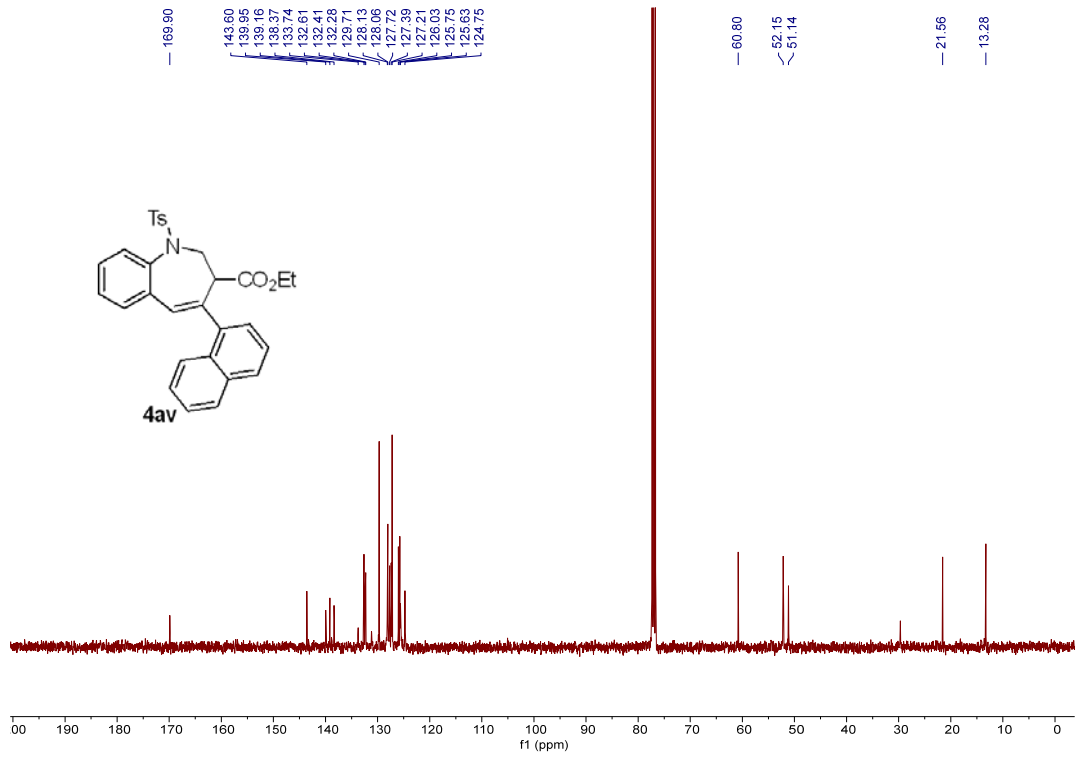
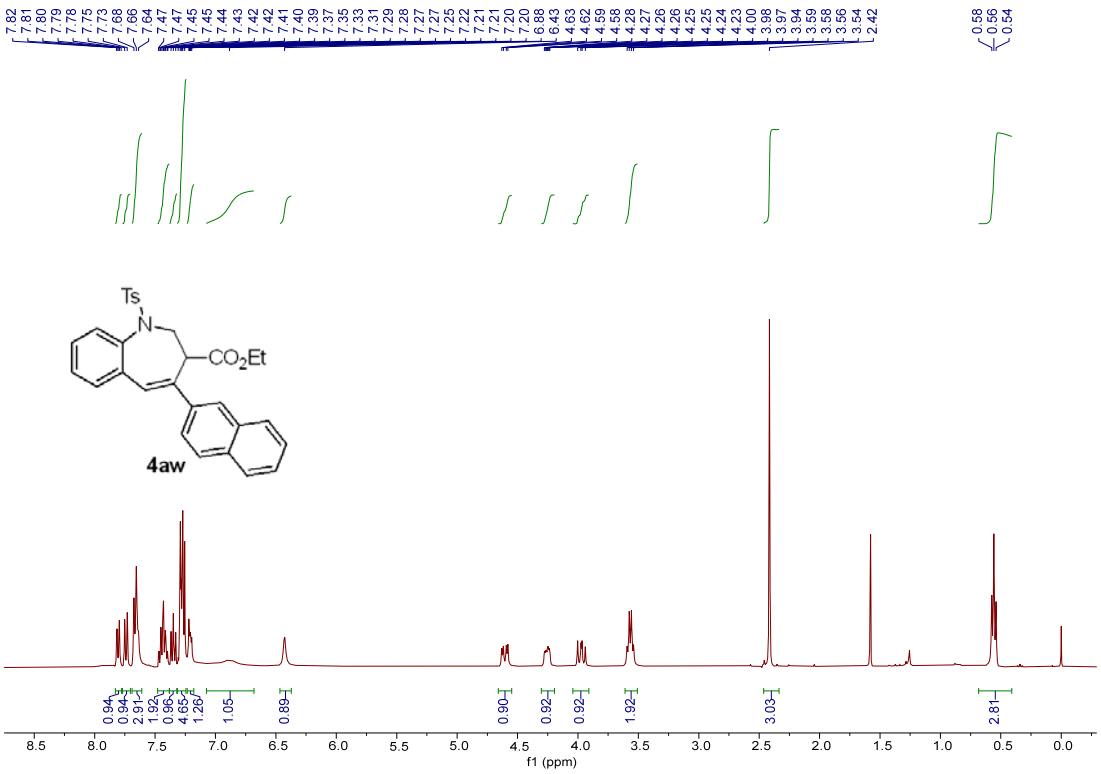
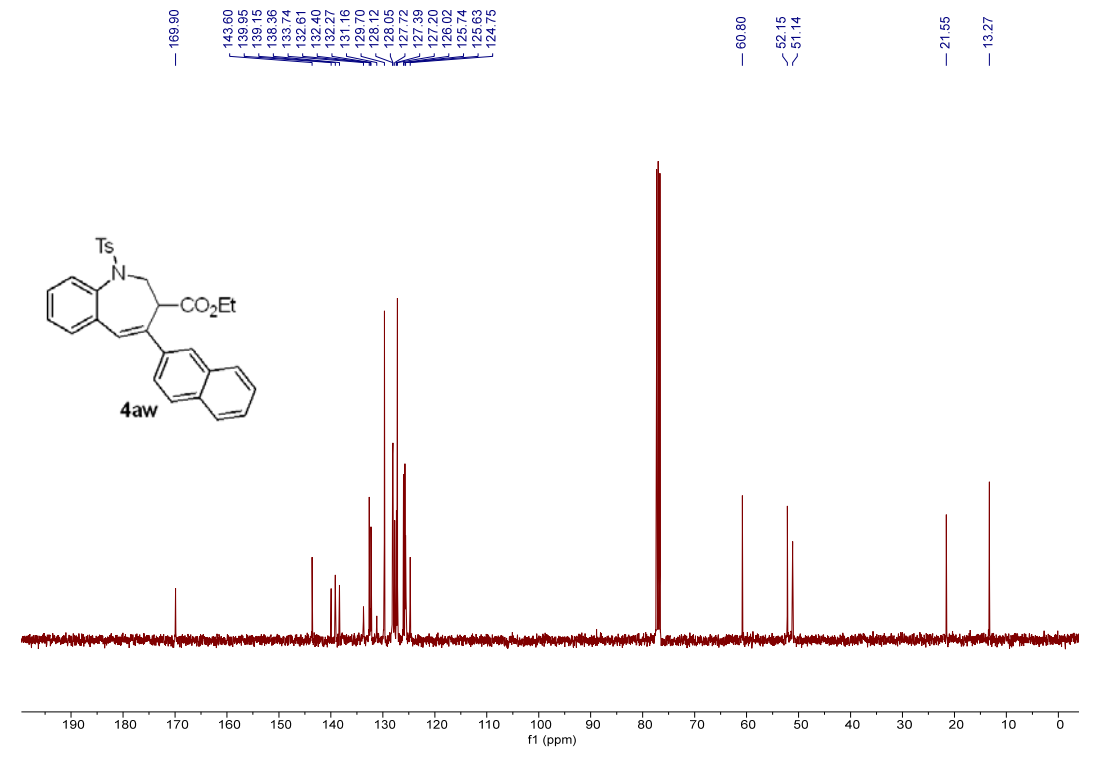
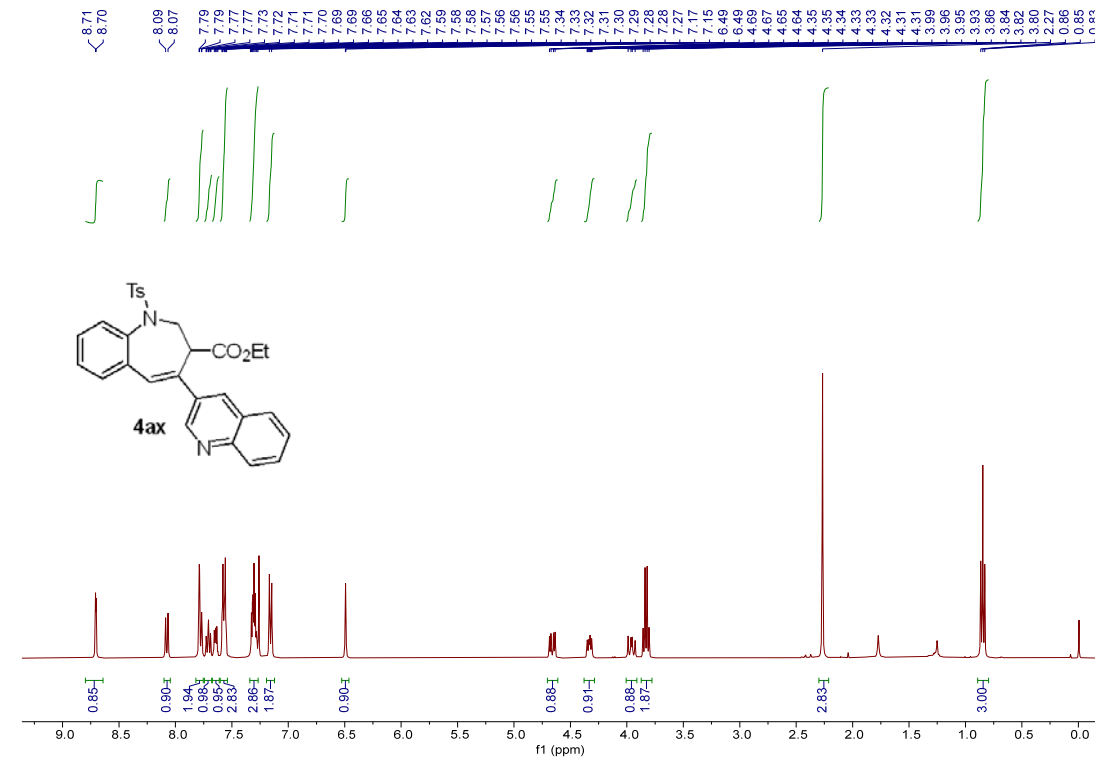
Ts
N
CO2Et
4av
1.08 1.07 3.02 2.13 1.12 4.85 1.22 0.74 0.89 0.95 0.96 1.00 2.02 3.13 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.90 143.60 139.95 139.16 138.37 133.74 132.61 132.41 132.28 129.71 128.13 128.06 127.72 127.39 127.21 126.03 125.75 125.63 124.75 60.80 52.15 51.14 21.56 13.28
Ts
N
CO2Et
4av
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.82 7.81 7.80 7.79 7.78 7.75 7.73 7.68 7.66 7.64 7.47 7.47 7.45 7.45 7.44 7.43 7.42 7.42 7.41 7.40 7.39 7.37 7.35 7.33 7.31 7.29 7.28 7.27 7.27 7.25 7.22 7.21 7.21 7.20 7.20 6.88 6.43 4.63 4.62 4.59 4.58 4.28 4.27 4.26 4.26 4.25 4.25 4.24 4.23 4.00 3.98 3.97 3.94 3.59 3.58 3.56 3.54 2.42
0.58 0.56 0.54
Ts
N
CO2Et
4aw
0.94 0.94 2.91 1.92 0.96 4.65 1.26 1.05 0.89 0.90 0.92 0.92 1.92 3.03 2.81
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
f1 (ppm)


169.90
143.60 139.95 139.15 138.36 133.74 132.61 132.40 132.27 131.16 129.70 128.12 128.05 127.72 127.39 127.20 126.02 125.74 125.63 124.75
60.80
52.15 51.14
21.55
13.27
Ts
N
CO2Et
4aw
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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4.31
4.31
3.99
3.96
3.95
3.93
3.86
3.84
3.82
3.80
2.27
0.86
0.85
Ts
N
CO2Et
4ax
N
0.85
0.90
1.94
0.98
0.95
2.83
2.86
1.87
0.90
0.88
0.91
0.88
1.87
2.83
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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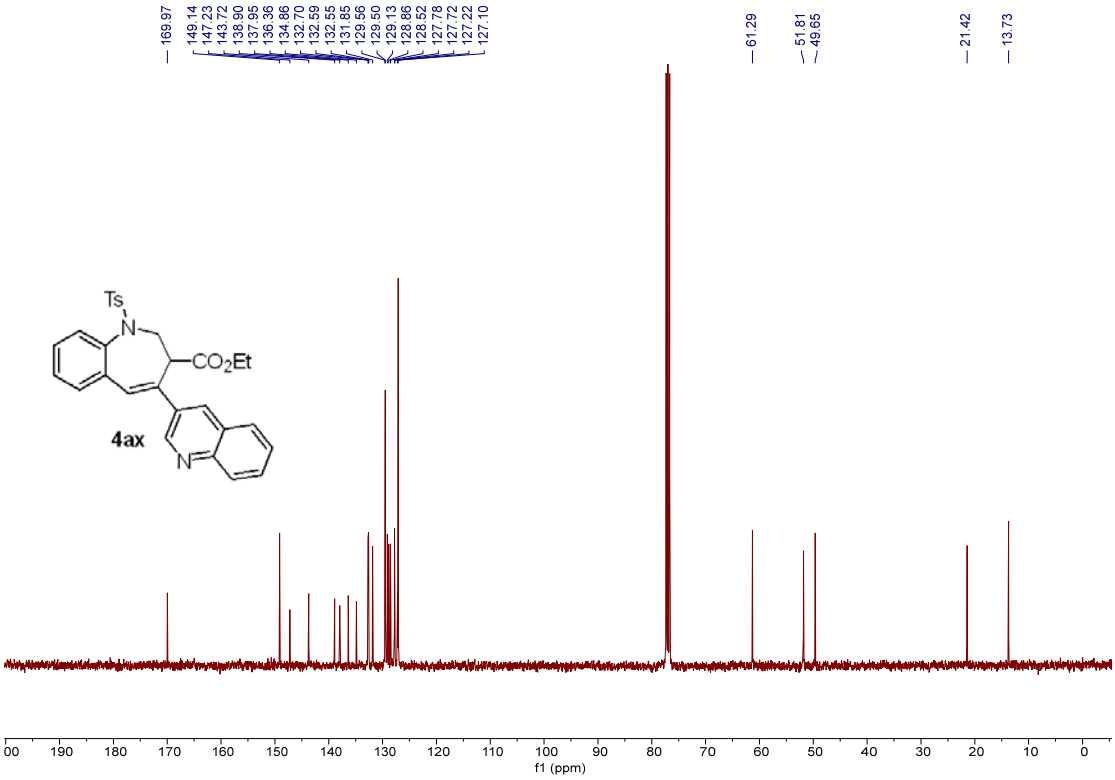
0.0
f1 (ppm)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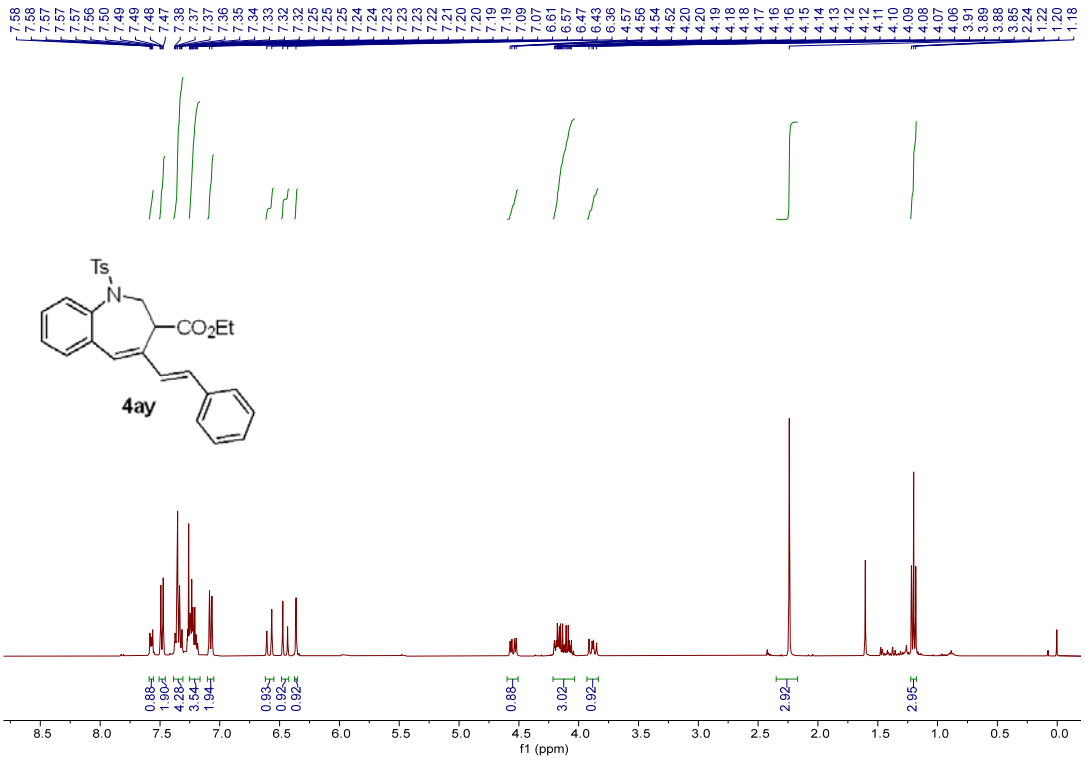
131.85
129.56
129.50
129.13
128.86
128.52
127.78
127.72
127.22
127.10
61.29
51.81
49.65
21.42
13.73
Ts
N
CO2Et
4ax
N
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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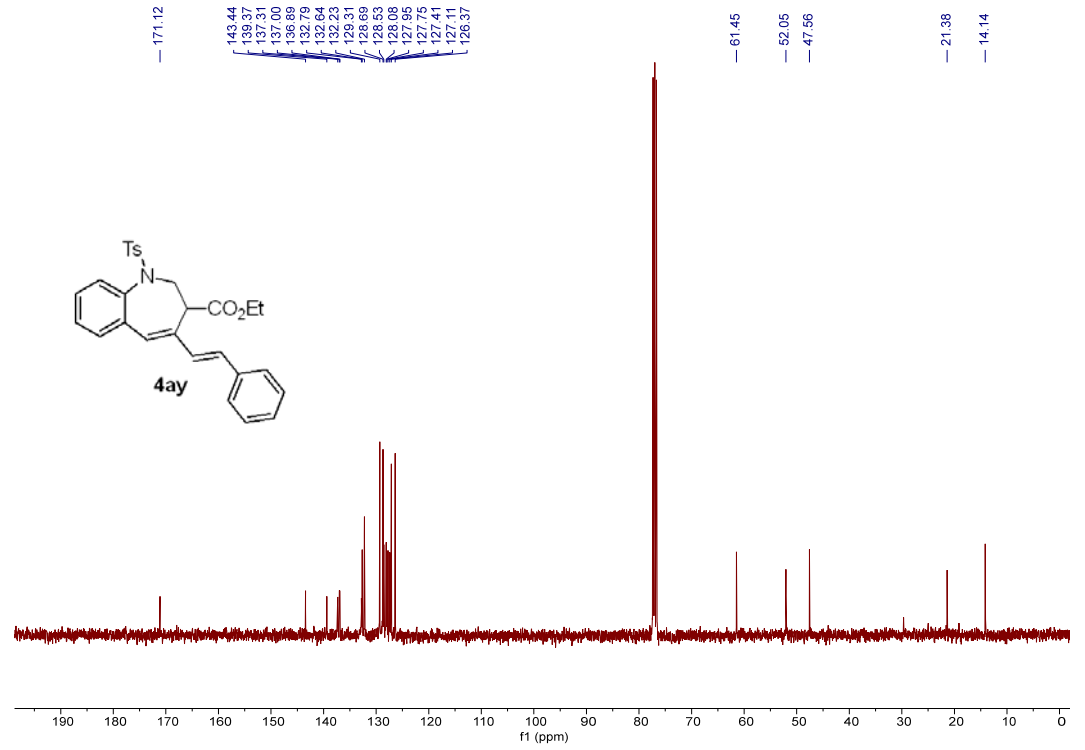
4ay
f1 (ppm)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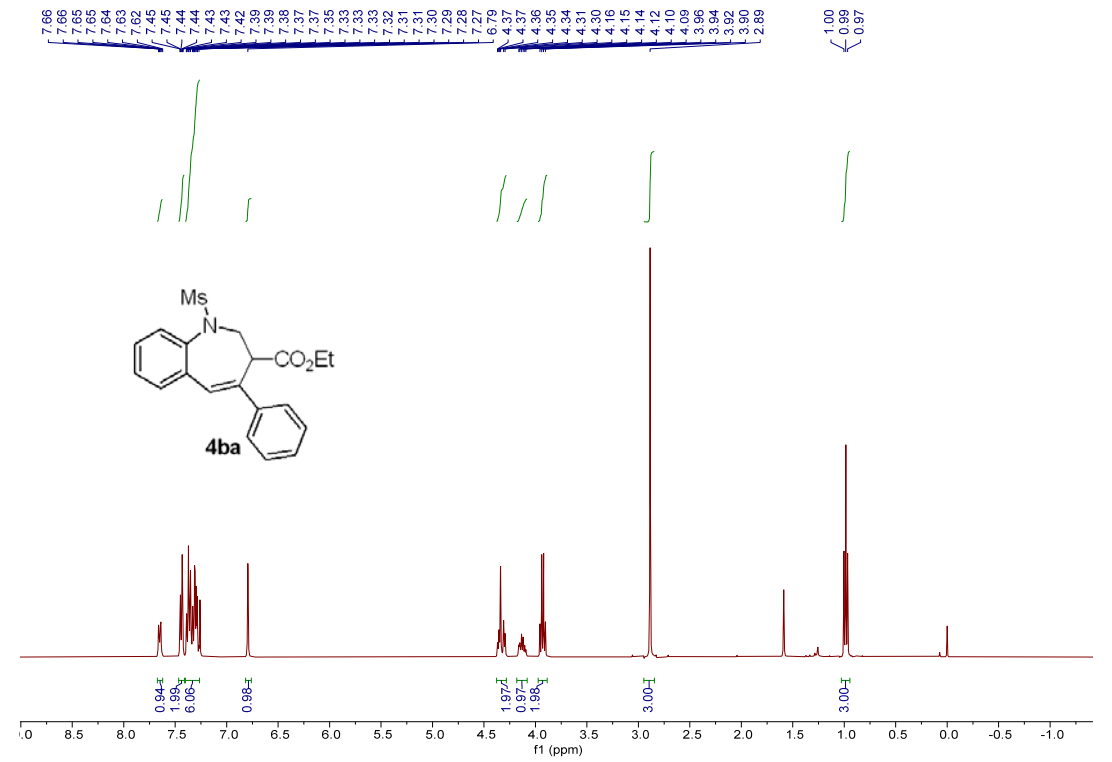
CO2Et
4ay
f1 (ppm)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7.39
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6.79
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4.16
4.15
4.14
4.12
4.10
4.09
3.96
3.94
3.92
3.90
2.89
1.00
0.99
0.97
Ms
N
CO2Et
4ba
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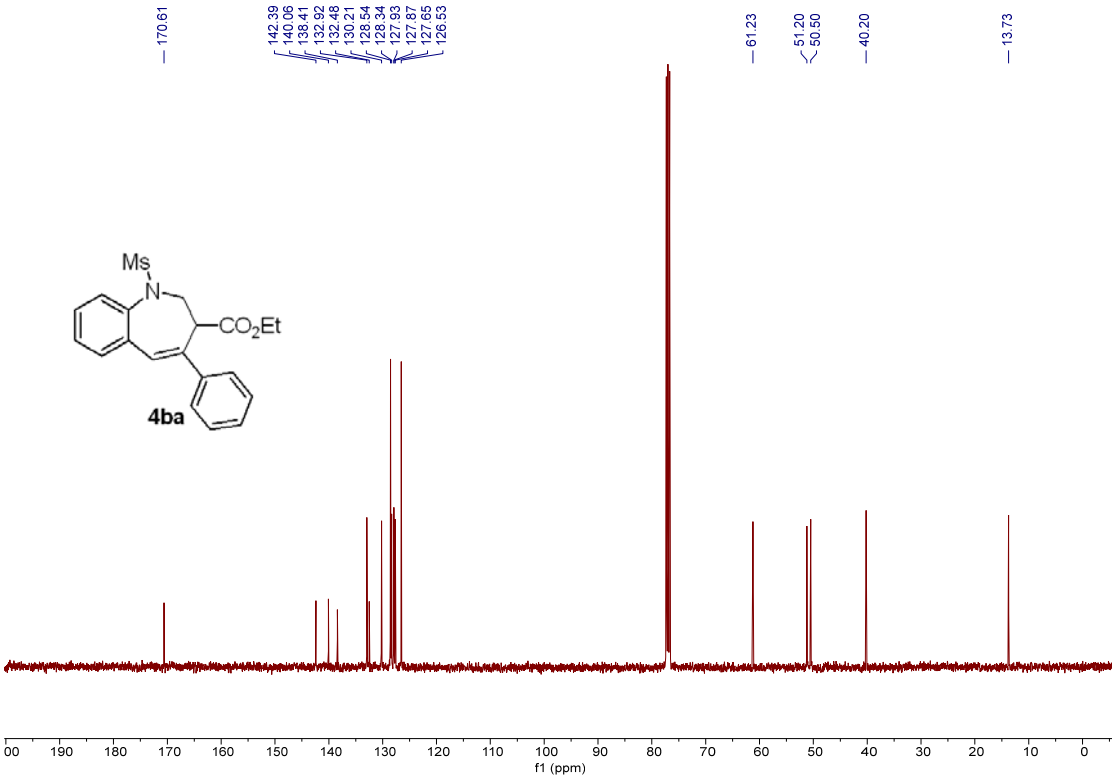
1.99
6.06
0.98
1.97
0.97
1.98
3.00
3.00
f1 (ppm)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138.41
132.92
132.48
130.21
128.54
128.34
127.93
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61.23
51.20
50.50
40.20
13.73
Ms
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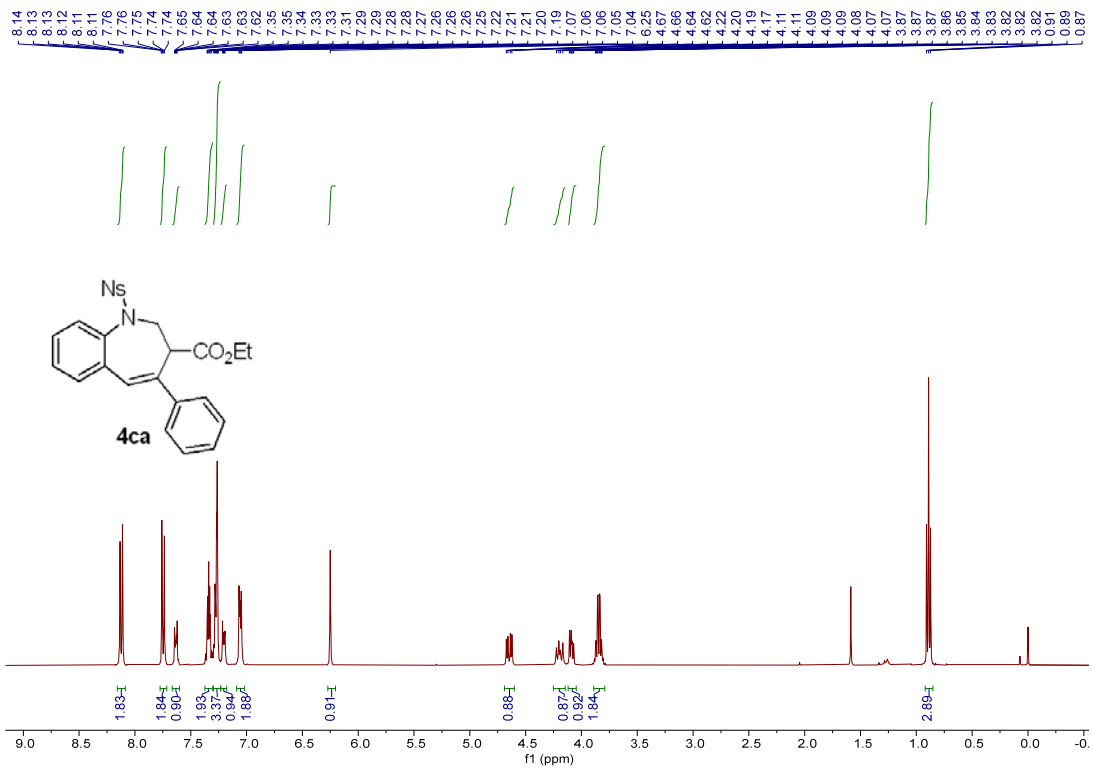
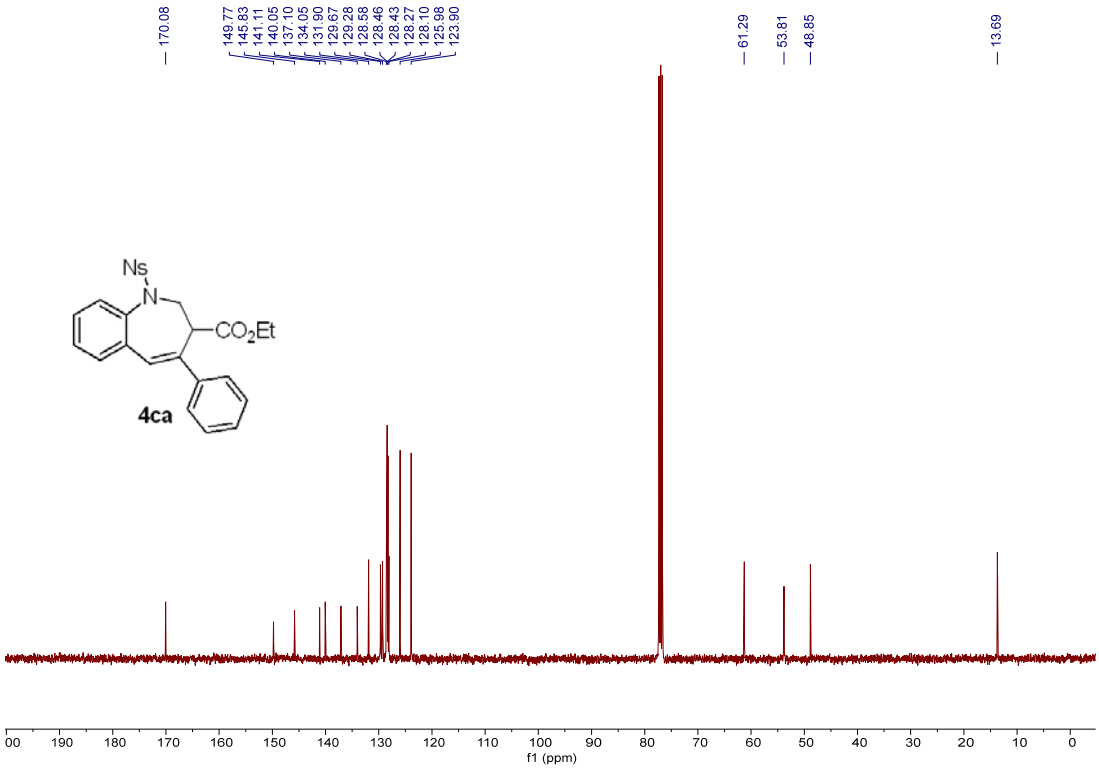
CO2Et
4ba
f1 (ppm)


Ns
N
CO2Et
4ca
f1 (ppm)


Ns
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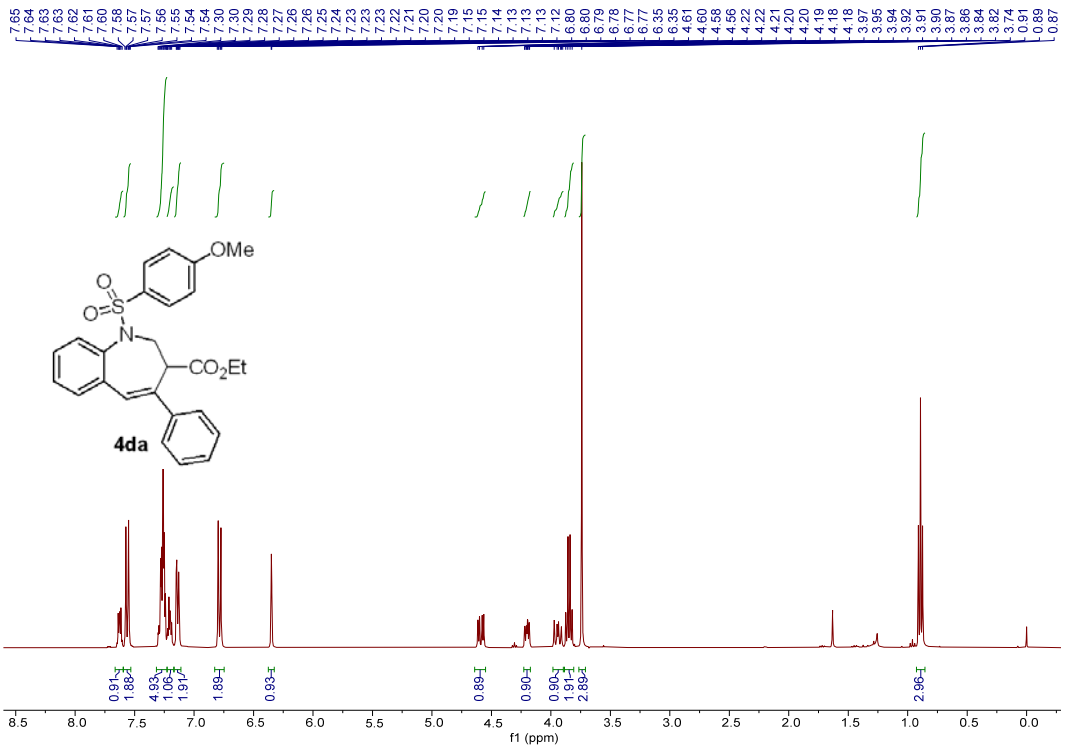
CO2Et
4ca
f1 (ppm)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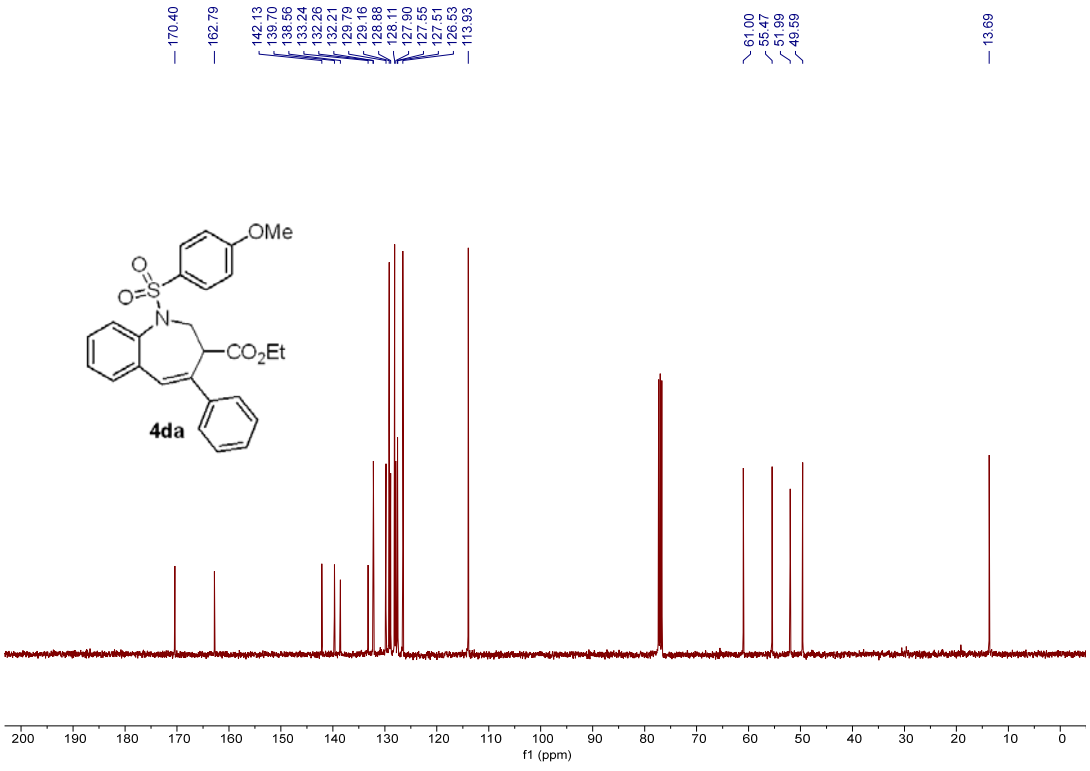
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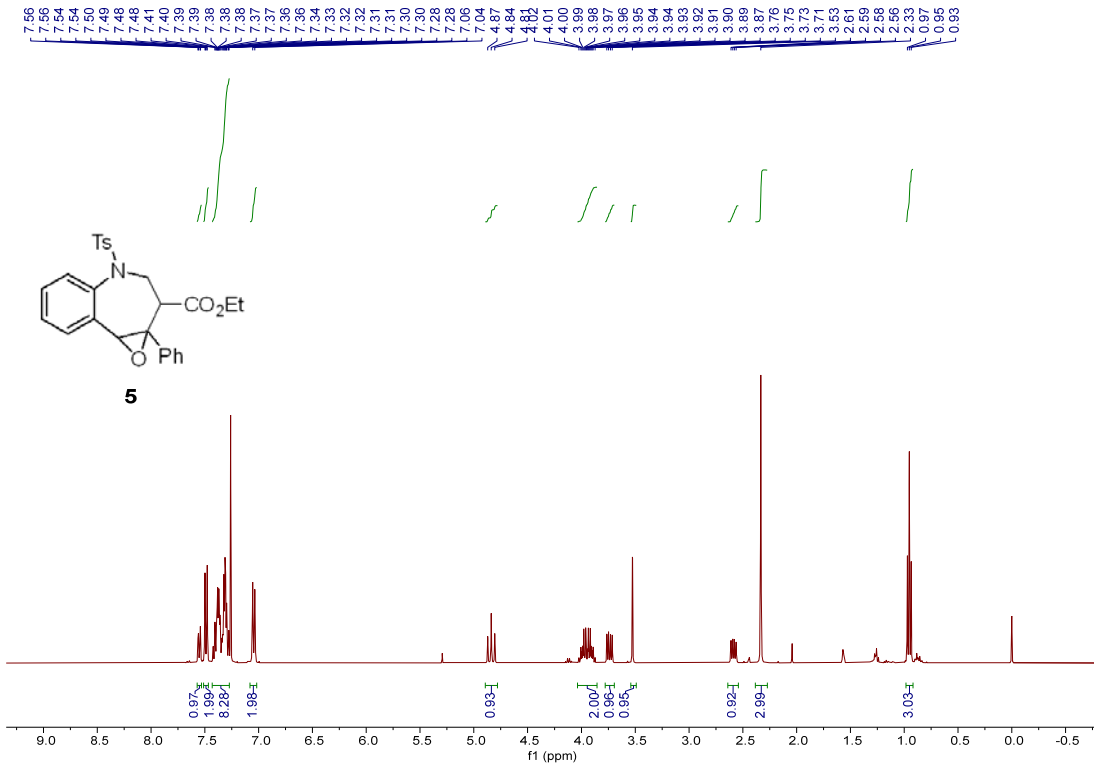
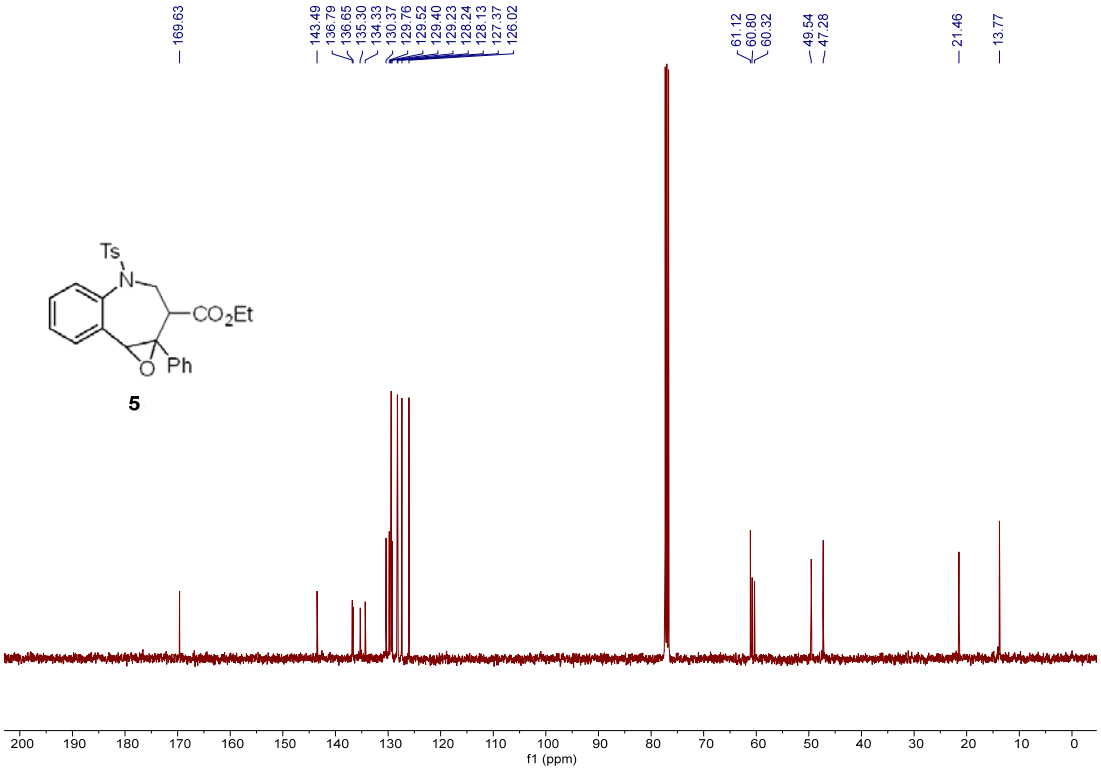
4da
f1 (ppm)


Ts
N
CO2Et
O
Ph
5
f1 (ppm)


Ts
N
CO2Et
O
Ph
5
f1 (ppm)