Supporting Information

Catalyst-Controlled Cascade Synthesis of Bridged Bicyclic Tetrahydrobenz[*b*]azepin-4-ones

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Contents:

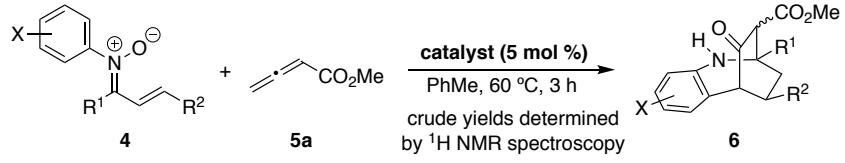
I. General Experimental Information.

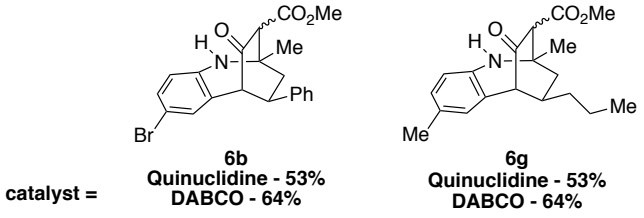
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 500 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. IR spectra were recorded at ambient temperature using ATR sampling. High resolution mass spectra were acquired on an LTQ FT spectrometer (ESI) or an VG 70-VSE spectrometer (EI), and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Medium pressure liquid chromatography was performed using force flow of the indicated solvent system down columns packed with 60 Å (40 – 60 μm) mesh silica gel (SiO_2). Samples purified by medium pressure liquid chromatography were dry-loaded onto celite. Flash chromatography was performed using glass columns packed with 60 Å (40 – 60 μm) mesh silica gel (SiO_2). Samples purified by flash chromatography were also dry-loaded onto celite. Unless otherwise noted, all reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. Unless otherwise noted, all reactions were performed under N_2 using standard Schlenk techniques. Toluene, THF, Et_2O, and MeCN were dried by filtration through alumina according to the procedure of Grubbs.[1] Nitrones **4a** and **4i** were prepared by known methods.[2,3] Allenes **5a**,[4] **5b**,[4b] **5c**,[5] and **5d**[6] were prepared by known methods.

II. Expanded Optimization Table for the Synthesis of 6a from 4a and 5a.

Entry[a]	Catalyst	Solvent	t (h)	T °C	% Yield **6a** (**8a**)[b]	dr[c]
1	**7**	C_6F_6	18	60	74	1:1[d]
2	quinine	C_6F_6	18	60	70	1:1[d]
3	quinine	toluene	18	60	73	2:1[d]
4	DABCO	toluene	18	60	57	1:1
5	DABCO	toluene	3	60	83	3:2
6	DABCO	DCE	3	60	80	3:2
7	DABCO	*i*-PrOAc	3	60	68	1:1
8	DABCO	MeOH	3	60	(68)	--
9	DABCO	THF	3	60	83	3:2
10	DABCO	MeCN	3	60	73	1:1
11	DABCO	toluene	3	80	66	1:1
12	DABCO	toluene	3	40	75	3:2
13	DABCO	toluene	3	25	50	3:2
14	DBU	toluene	3	60	56	1:1
15	quinuclidine	toluene	3	60	92	1:1
16	DMAP	toluene	3	60	68	1:1
17	morpholine	toluene	3	60	52	20:1[e]
18	imidazole	toluene	3	60	56	2:1

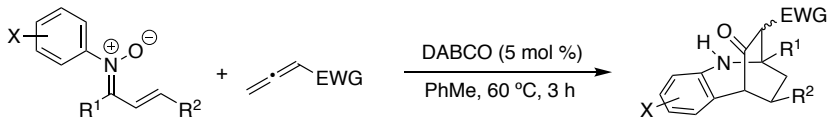
[a] Conditions: **4a** (1 equiv), **5a** (3 equiv), 0.12 M. [b] ^{1}H NMR spectral data for **8a** matched literature values.[2] [c] dr determined by ^{1}H NMR spectroscopy. [d] % ee = trace. [e] Purification of the crude **6a** on silica gel gave **6a** as a 3:2 mixture of diastereomers.





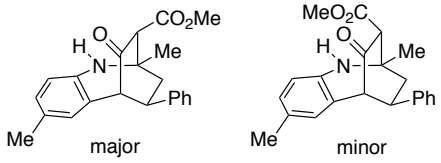
catalyst =

III. Synthesis of Bicyclic Benz[*b*]azepin-4-ones 6 (Scheme 2).



4 **5** **6**

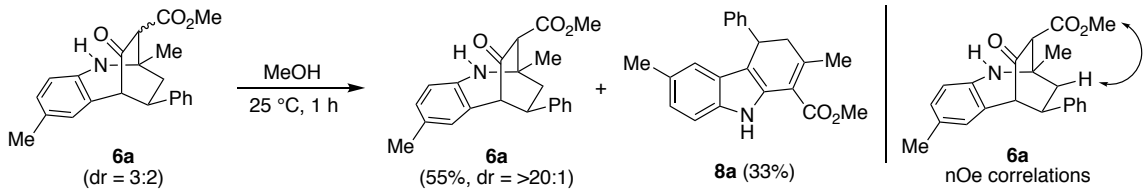
General Procedure A: A 5 mL conical vial was charged with nitrone **4** (1.0 equiv) and DABCO (5 mol %). A solution of allenoate **5** (3 equiv) in toluene (0.120 mM) was then added to these solids via syringe and the vial was capped with Teflon-lined screw cap. The reaction mixture in the closed vial was then stirred at 60 °C for 3 h. At this time, the reaction mixture was concentrated under vacuum, the residue was dry-loaded onto celite (~300 mg) using CH_2Cl_2 (~2 mL), and the crude material was purified by medium pressure chromatography (0 – 5% acetone, 2% NEt_3, 2% benzene, in petroleum ether) to give bicyclic benzazepinone **6**. The addition of 2% benzene to the column chromatography conditions for the purification of **6** resulted in complete separation of **6** from trace amounts of **8**. The removal of benzene from the purification conditions results in partial contamination of **6** by **8** and diminished yields. No solvents, such as CCl_4, were used that could affect the purity of compounds **6** without being noticeably present in the ^{1}H NMR spectra.



6a (dr = 3:2)

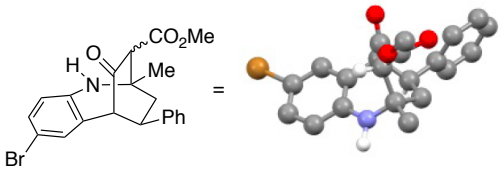
Bicyclic Benzazepinone 6a: Bicyclic benzazepinone **6a** was prepared by general procedure **A**. Nitrone **4a** (0.0300 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (5% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6a** as a light yellow amorphous solid (0.0314 g, 77%, d.r. = 3:2). ^{1}H NMR (500 MHz, $CDCl_3$) (*major diastereomer*): δ 7.34-7.31 (m, 2H), 7.25-7.23 (m, 2H), 7.18-7.17 (m, 1H), 6.89-6.87 (m, 1H), 6.69-6.67 (m, 1H), 6.50-6.49 (m, 1H), 4.11- 4.09 (m, 1H), 3.94-3.87 (m, 1H), 3.79 (s, 3H), 3.49 (s, 1H), 3.38 (s, 1H), 2.51-2.46 (m, 1H), 2.41-2.37 (m, 1H), 2.17 (s, 3H), 1.36 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (minor diastereomer, diagnostic peaks): δ 4.06 (s, 1H), 3.58 (s, 1H), 3.47 (s, 3H), 2.64-2.58 (m, 1H), 1.81-1.76 (m, 1H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*major diastereomer*): δ 205.1, 169.6, 145.5, 141.5, 130.5, 129.5, 129.0, 128.4, 127.0, 126.7, 121.2, 116.5, 64.8, 61.5, 55.7, 52.2, 47.4, 44.0, 26.9, 20.2; ^{13}C NMR (125 MHz, $CDCl_3$) (minor diastereomer, diagnostic peaks): δ 203.1, 167.9, 142.4, 116.7, 65.5, 61.0, 45.8, 28.6; IR (thin film) 3390, 3026, 2949, 2922, 2858, 1737, 1706, 1504, 1285, 1149; HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}NO_3$ $(M+H)^+$ 350.1756, found 350.1743. Major diastereomer assigned in analogy to **6i** and via ^{1}H-^{1}H nOe experiments using the diastereoenriched sample discussed below.

Solvent Effect on Diastereomeric Ratio of 6a



A diastereomeric mixture of bicyclic benazepinone **6a** was observed to favor a single diastereomer in protic solvents with concomitant formation of dihydrocarbazole **8a**.

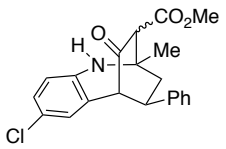
Bicyclic benzazepinone **6a** (0.0150 g, 0.0430 mmol) was dissolved in MeOH (0.50 mL, 0.86 M). The solution was allowed to stir at 25 °C for 1 h. After 1 h, MeOH was removed under vacuum to give the crude product as a yellow amorphous solid, which was identified by ^{1}H NMR spectroscopy as a mixture of **6a** (55%, dr = 20:1) and **8a** (33%). Yields were determined using CH_2Br_2 (7.0 µL, 0.1 mmol) as an ^{1}H NMR reference. ^{1}H NMR (500 MHz, $CDCl_3$) (diagnostic peaks for **6a**): δ 3.79 (s, 3H), 3.49-3.47 (m, 1H), 2.51-2.46 (m, 1H), 2.17 (s, 3H), 1.36 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (diagnostic peaks for **8a**): δ 9.31 (s, 1H), 4.33-4.30 (m, 1H), 3.94 (s, 3H), 3.03-3.01 (m, 1H), 2.80-2.75 (m, 1H), 2.28-2.27 (m, 6H).[2]



6b

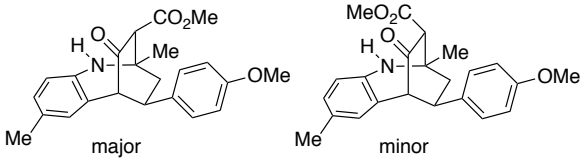
Bicyclic Benzazepinone 6b: Bicyclic benzazepinone **6b** was prepared by general procedure **A**. Nitrone **4b** (0.0327 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (5% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6b** as a light yellow amorphous solid (0.0295 g, 52%, d.r = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.23-7.22 (m, 2H), 7.16-7.12 (m, 2H), 7.00-6.97 (m, 1H), 6.46-6.44 (m, 1H), 4.24 (s, 1H), 4.03 (s, 1H), 3.91-3.84 (m, 1H), 3.79 (s, 3H), 3.44 (s, 1H), 2.53-2.48 (m, 1H), 2.44-2.39 (m, 1H), 1.37 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 4.18 (s, 1H), 3.55 (s, 1H), 3.52 (s, 3H), 3.39 (s, 1H), 2.65-2.61 (m, 1H), 1.83-1.78 (m, 1H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.3, 169.2, 144.9, 132.3, 131.5, 129.1, 127.0, 126.9, 126.5, 123.0, 117.9, 110.2, 65.0, 60.5, 55.8, 52.3, 47.2, 43.8, 28.5; ^{13}C NMR (125 MHz, $CDCl_3$): δ (*second diastereomer, diagnostic peaks*): 202.4, 167.7, 144.0, 65.7, 61.0, 55.5, 45.7, 26.9; IR (thin film) 3391, 3060, 3028, 2949, 2928, 2854, 1737, 1708, 1481, 1304; HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}NO_3Br$ $(M+H)^+$ 414.0705, found 414.0690.

Bicyclic benzazepinone **6b** was dissolved in CH_2Cl_2, layered with pentane, and placed in a -40 °C freezer. After 48 h, single crystals had formed. The supernatant was decanted and X-ray crystallography analysis confirmed the structure illustrated above.



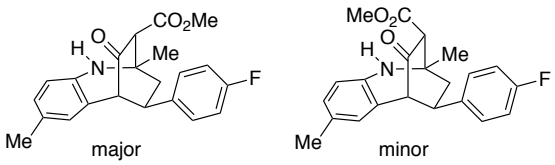
6c

Bicyclic Benzazepinone 6c: Bicyclic benzazepinone **6c** was prepared by general procedure **A**. Nitrone **4c** (0.0329 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (8% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6c** as a light yellow amorphous solid (0.0300 g, 69%, d.r = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 7.26-7.22 (m, 2H), 7.16-7.15 (m, 1H), 7.02-6.99 (m, 1H), 6.86-6.83 (m, 1H), 6.51-6.49 (m, 1H), 4.25 (s, 1H), 4.04 (s, 1H), 3.91-3.86 (m, 1H), 3.79 (s, 3H), 3.44 (s, 1H), 2.53-2.58 (m, 1H), 2.44-2.39 (m, 1H), 1.37 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 4.18 (s, 1H), 3.55 (s, 1H), 3.51 (s, 3H), 2.65-2.60 (m, 1H), 1.81-1.78 (m, 1H), 1.51 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4, 169.2, 144.9, 143.5, 129.5, 129.1, 128.7, 127.0, 126.9, 123.3, 122.5, 117.6, 65.0, 61.1, 55.8, 52.3, 47.2, 43.8, 26.9; ^{13}C NMR (125 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 202.4, 167.7, 145.0, 122.8, 117.5, 65.7, 60.6, 55.5, 26.9; IR (thin film) 3402, 3055, 3029, 2952, 1738, 1712, 1485, 1305, 1264, 1147; HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}NO_3Cl$ $(M+H)^+$ 370.1210, found 370.1209.



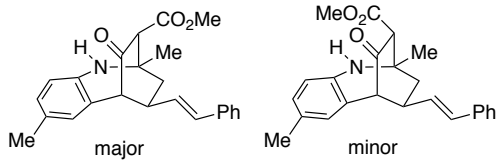
6d (dr = 3:2)

Bicyclic Benzazepinone 6d: Bicyclic benzazepinone **6d** was prepared by general procedure **A**. Nitrone **4d** (0.0328 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (8% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6d** as a light yellow amorphous solid (0.0309 g, 68%, d.r = 3:2). ^{1}H NMR (500 MHz, $CDCl_3$) (*major diastereomer*): δ 7.17-7.15 (m, 2H), 7.10-7.08 (m, 1H), 6.88-6.84 (m, 2H), 6.68-6.66 (m, 1H), 6.49 (m, 1H), 4.09-4.04 (m, 1H), 3.86-3.83 (m, 1H), 3.79 (s, 6H), 3.48 (s, 1H), 3.41 (s, 1H), 2.48-2.43 (m, 1H), 2.38-2.34 (m, 1H), 2.16 (s, 3H), 1.35 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*minor diastereomer*): δ 3.53 (s, 1H), 3.35 (s, 1H), 2.60-2.55 (m, 1H), 1.78-1.75 (m, 1H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.2, 169.7, 158.4, 141.4, 137.9, 130.5, 129.5, 128.1, 127.6, 121.4, 116.7, 114.2, 64.8, 62.0, 55.4, 55.0, 52.2, 46.6, 44.1, 26.9, 20.1; ^{13}C NMR (125 MHz, $CDCl_3$) (*minor diastereomer*): δ 203.3, 167.9, 142.4, 65.4, 61.4, 55.6, 47.5, 45.1, 28.6; IR (thin film) 3389, 2996, 2950, 2924, 2855, 2836, 1737, 1707 1512, 1305; HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}NO_4$ $(M+H)^+$ 380.1862, found 380.1847. Major diastereomer assigned in analogy to **6i** and **6a**.



6e (dr = 3:2)

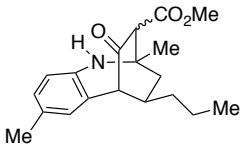
Bicyclic Benzazepinone 6e: Bicyclic benzazepinone **6e** was prepared by general procedure **A**. Nitrone **4e** (0.0322 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (8% acetone, 2% NEt_3 2% benzene, in petroleum ether) afforded **6e** as a light yellow amorphous solid (0.0298 g, 68%, d.r = 3:2). ^{1}H NMR (500 MHz, $CDCl_3$) (*major diastereomer*): δ 7.21-7.19 (m, 1H), 7.14-7.12 (m, 1H), 7.01-6.98 (m, 2H), 6.89-6.86 (m, 1H), 6.68-6.66 (m, 1H), 6.50-6.48 (m, 1H), 4.11-4.05 (m, 2H), 3.93-3.85 (m, 1H), 3.78 (s, 3H), 3.40 (s, 1H). 2.46-2.35 (m, 2H), 2.16 (s, 3H), 1.35 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*minor diastereomer*): δ 3.52 (s, 1H), 3.47 (s, 3H), 2.60-2.55 (m, 1H), 1.74-1.71 (m, 1H), 1.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*major diastereomer*): δ 205.0, 169.7, 161.6 (d, $J_{C\text{-}F}$ = 250.0 Hz), 141.4, 130.5, 129.6, 128.6, 128.5 (d, $J_{C\text{-}F}$ = 12.5 Hz), 128.2 (d, $J_{C\text{-}F}$ = 12.5 Hz), 120.9, 116.5, 115.7 (d, $J_{C\text{-}F}$ = 25.0 Hz), 64.8, 61.7, 55.5, 52.1, 46.5, 44.0, 26.9, 20.1; ^{13}C NMR (125 MHz, $CDCl_3$) (*minor diastereomer*): δ 203.2, 167.8, 167.8, 142.4, 121.2, 65.3, 61.1, 55.6, 52.1, 47.6, 45.2, 28.6, 20.2; IR (thin film) 3390, 2950, 2922, 2872, 1736, 1705, 1504, 1308, 1222, 1131; HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}NO_3F$ $(M+H)^+$ 368.1651, found 368.1662. Major diastereomer assigned in analogy to **6i** and **6a**.



6f (dr = 2:1)

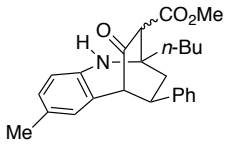
Bicyclic Benzazepinone 6f: Bicyclic benzazepinone **6f** was prepared by general procedure **A** with modified chromatography conditions. Nitrone **4f** (0.0410 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (5% EtOAc in hexanes, 2% TEA) afforded **6f** as a light yellow amorphous solid (0.0344 g, 65%, d.r = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.43-7.38 (m, 4H), 7.35-7.32 (m, 3H), 7.26-7.25 (m, 1H), 6.94-6.93 (m, 1H), 6.79 (s, 1H), 6.54-6.45 (m, 1H), 6.48-6.45 (m, 1H), 6.33-6.28 (m, 1H), 4.53 (s, 1H), 4.42 (s, 1H), 3.68-3.65 (m, 1H), 3.45 (s, 1H), 3.27 (s, 3H), 2.91-2.90 (m, 2H), 2.23 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 7.62-7.60 (m, 1H), 6.97-6.96 (m, 1H), 6.85 (s, 1H), 6.73-6.72 (m, 1H), 6.25-6.20 (m, 1H), 4.72 (s, 1H), 4.33 (s, 1H), 3.55 (s, 3H), 2.84-2.79 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 168.5, 145.4, 141.3, 136.9, 132.3, 130.6, 129.8, 129.7, 129.3, 128.6, 128.3, 127.5, 126.4, 126.2, 124.8, 119.4, 116.6, 66.2, 60.3, 60.2, 59.7, 51.8, 44.7, 39.1, 20.2; ^{13}C NMR (125 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 202.5, 168.4, 64.4, 61.5, 52.2, 44.8, 42.3, 20.3; IR (thin film) 3395, 3056, 3024, 2998, 2949, 2921, 1738, 1708,

1651, 1503; HRMS (ESI) *m/z* calcd. for $C_{29}H_{28}NO_3$ $(M+H)^+$ 438.2069, found 438.2065. Major diastereomer assigned in analogy to **6i** and **6a**.



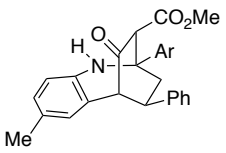
6g (dr = 1:1)

Bicyclic Benzazepinone 6g: Bicyclic benzazepinone **6g** was prepared by general procedure **A**. Nitrone **4g** (0.0263 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (8% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6g** as a light yellow amorphous solid (0.0190 g, 50%, d.r = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87-6.84 (m, 1H), 6.71-6.69 (m, 1H), 6.46-6.44 (m, 1H), 4.03 (s, 1H), 3.95 (s, 1H), 3.77 (s, 3H), 3.21-3.19 (m, 1H), 2.67-2.62 (m, 1H), 2.40-2.35 (m, 1H), 2.19 (s, 3H), 2.02-1.99 (m, 1H), 1.47(s, 3H), 1.41-1.33 (m, 4H), 0.93-0.90 (m, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 3.50 (s, 3H), 3.26 (s, 1H), 1.33 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.9, 169.5, 142.3, 130.4, 129.2, 128.0, 121.8, 116.6, 65.4, 60.8, 55.9, 52.1, 44.7, 41.9, 39.7, 29.0, 20.2, 19.9, 13.9; ^{13}C NMR (125 MHz, $CDCl_3$) (*second diastereomer*): δ 205.9, 168.1, 141.5, 121.5, 116.2, 55.5, 52.0, 40.7, 27.2; IR (thin film) 3395, 2954, 2929, 2871, 1738, 1711, 1505, 1310, 1259, 1139; HRMS (ESI) *m/z* calcd. for $C_{19}H_{26}NO_3$ $(M+H)^+$ 316.1913, found 316.1908.



6h (dr = 1:1)

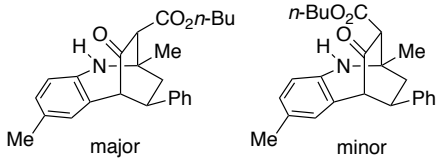
Bicyclic Benzazepinone 6h: Bicyclic benzazepinone **6h** was prepared by general procedure **A**. Nitrone **4h** (0.0352 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (8% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6h** as a light yellow amorphous solid (0.0305 g, 65%, d.r = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.25-7.23 (m, 2H), 7.19-7.18 (m, 1H), 6.90-6.87 (m, 1H), 6.70-6.67 (m, 1H), 6.53-6.50 (m, 1H), 4.13 (s, 1H), 3.98 (s, 1H), 3.93-3.86 (m, 1H), 3.79 (s, 3H), 2.45-2.43 (m, 2H), 2.18-2.17 (s, 3H), 1.78-1.70 (m, 3H), 1.46-1.27 (m, 3H), 0.97-0.90 (m, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 4.08 (m, 1H), 3.49 (s, 3H), 3.60 (s, 1H), 2.58-2.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.6, 169.7, 145.6, 141.6, 130.3, 129.4, 128.3, 128.2, 127.0, 126.6, 121.2, 116.4, 63.8, 61.5, 58.4, 52.2, 47.2, 44.1, 38.9, 25.0, 23.0, 20.2, 14.1; ^{13}C NMR (125 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 203.4, 168.0, 145.6, 142.5, 63.3, 60.9, 58.1, 52.1, 20.2, 13.9; IR (thin film) 3399, 3059, 3025, 2952, 2929, 2861, 1737, 1707, 1504, 1307; HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}NO_3$ $(M+H)^+$ 392.2226, found 392.2218.



6i (dr = >20:1)

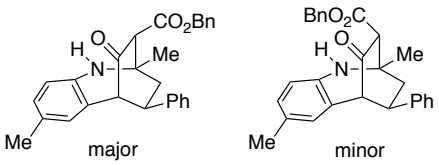
Ar = *p*-OMe(C_6H_4)

Bicyclic Benzazepinone 6i: Bicyclic benzazepinone **6i** was prepared by general procedure **A** with modified chromatography conditions. Nitrone **4i** (0.0473 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (0 – 5% EtOAc, 2% NEt_3 in hexane) afforded **6i** as a light yellow amorphous solid (0.0305 g, 58%, dr = 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.43 (m, 2H), 7.37-7.35 (m, 2H), 7.32-7.31 (m, 2H), 7.28-7.26 (m, 1H), 6.94-6.88 (m, 3H), 6.72 (s, 1H), 6.57-6.55 (m, 1H), 4.53 (s, 1H), 4.43 (s, 1H), 4.02-4.00 (t, *J*= 10.0 Hz, 1H), 3.81 (s, 3H), 3.55 (s, 1H), 3.31 (s, 3H), 3.11-3.06 (m, 1H), 2.97-2.95 (m, 1H), 2.20 (s, 3H). Spectral data for this compound were consistent with those previously reported in the literature.[3]



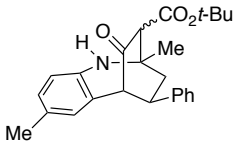
6j (dr = 3:2)

Bicyclic Benzazepinone 6j: Bicyclic benzazepinone **6j** was prepared by general procedure **A**. Nitrone **4a** (0.0309 g, 0.120 mmol) was treated with allenoate **5b** (0.0505 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (5% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6j** as a light yellow amorphous solid (0.0376 g, 80%, d.r = 3:2). ^{1}H NMR (500 MHz, $CDCl_3$) (*major diastereomer*): δ 7.33-7.30 (m, 2H), 7.26-7.22 (m, 2H), 7.19-7.17 (m, 1H), 6.89-6.85 (m, 1H), 6.68-6.67 (m, 1H), 6.50-6.47 (m, 1H), 4.22 (s, 1H), 4.04 (s, 1H), 3.90-3.88 (m, 1H), 3.46 (s, 1H), 2.51-2.47 (m, 1H), 2.41-2.37 (m, 1H), 2.17 (s, 3H), 1.67-1.64 (m, 2H), 1.41-1.37 (m, 2H), 1.30-1.22 (m, 2H), 0.93 (t, *J* = 5.0 Hz, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*minor diastereomer, diagnostic peaks*): δ 4.22-4.17 (m, 1H), 3.57 (s, 1H), 3.35 (s, 1H), 2.61-2.56 (m, 1H), 1.78-1.74 (m, 1H), 1.52 (s, 3H), 1.26-1.22 (m, 2H), 0.80 (t, *J* = 10.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*major diastereomer*): δ 205.1, 169.2, 145.5, 141.5, 130.5, 130.5, 129.4, 128.8, 127.0, 126.6, 121.3, 116.5, 65.2, 65.0, 61.6, 55.6, 47.3, 44.0, 30.5, 27.0, 20.2, 18.9, 13.7; ^{13}C NMR (125 MHz, $CDCl_3$) (*minor diastereomer, diagnostic peaks*): δ 203.4, 167.4, 145.6, 65.7, 65.1, 61.0, 55.6, 47.6, 46.1, 30.2, 20.2, 19.2, 14.1; IR (thin film) 3390, 3057, 3027, 2958, 2931, 2871, 1731, 1710, 1614, 1504; HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}NO_3$ $(M+H)^+$ 392.2226, found 392.2217. Major diastereomer assigned in analogy to **6i** and **6a**.



6k (dr = 3:2)

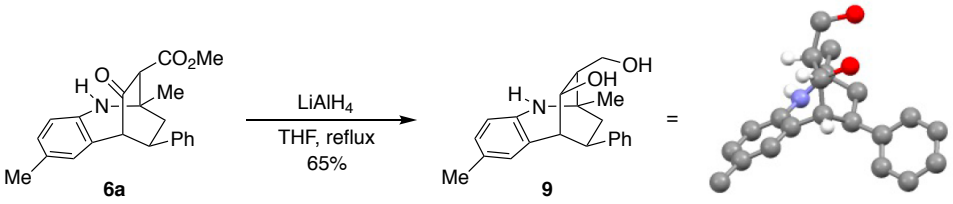
Bicyclic Benzazepinone 6k: Bicyclic benzazepinone **6k** was prepared by general procedure **A**. Nitrone **4a** (0.0300 g, 0.120 mmol) was treated with allenoate **5c** (0.0620 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (2% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6k** as a light yellow amorphous solid (0.0418 g, 82%, d.r = 3:2). ^{1}H NMR (500 MHz, $CDCl_3$) (*major diastereomer*): δ 7.37-7.32 (m, 3H), 7.30-7.26 (m, 2H), 7.22-7.20 (m, 3H), 7.18-7.16 (m, 1H), 7.10-7.05 (m, 1H), 6.88-6.87 (m, 1H), 6.67 (m, 1H), 6.48-6.47 (m, 1H), 5.24 (dd, *J* = 35.0 Hz, 10.0 Hz, 2H), 4.10-4.03 (m, 2H), 3.93-3.86 (m, 1H), 3.43 (s, 1H), 2.49- 2.45 (m, 1H), 2.39-2.34 (m, 1H), 2.16 (s, 3H), 1.31 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*minor diastereomer*): δ 6.82-6.81 (m, 1H), 6.41-6.39 (m, 1H), 4.95 (dd, *J* = 35.0 Hz, 10.0 Hz, 2H), 4.03 (s, 1H), 3.58 (s, 1H), 3.43 (s, 1H), 2.64-2.58 (m, 1H), 2.14 (s, 3H), 1.80-1.76 (m, 1H), 1.49 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) (*major diastereomer*): δ 205.0, 168.9, 145.5, 141.4, 135.2, 130.5, 129.7, 129.2, 128.8, 128.6, 128.2, 128.0, 127.0, 126.5, 121.4, 116.5, 67.2, 64.9, 61.6, 55.8, 47.3, 44.0, 26.9, 20.2; ^{13}C NMR (125 MHz, $CDCl_3$) (*minor diastereomer*): δ 202.8, 167.3, 142.3, 121.2, 116.7, 67.0, 65.8, 55.5, 28.6, 20.2; IR (thin film) 3389, 3061, 3029, 2922, 2858, 1732, 1708, 1503, 1302, 1258; HRMS (ESI) *m/z* calcd. for $C_{28}H_{28}NO_3$ $(M+H)^+$ 426.2069, found 426.2064. Major diastereomer assigned in analogy to **6i** and **6a**.



6l (dr = 1:1)

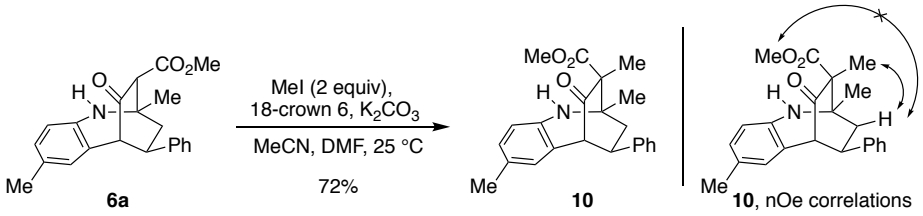
Bicyclic Benzazepinone 6l: Bicyclic benzazepinone **6l** was prepared by general procedure **A**. Nitrone **4a** (0.0300 g, 0.120 mmol) was treated with allenoate **5d** (0.0500 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. Chromatography (8% acetone, 2% NEt_3, 2% benzene, in petroleum ether) afforded **6l** as a light yellow amorphous solid (0.0295 g, 63%, d.r = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.26-7.17 (m, 3H), 6.87- 6.86 (m, 1H), 6.67-6.66 (m, 1H), 6.49-6.46 (m, 1H), 4.09 (br, 1H), 3.91-3.83 (m, 2H), 3.43 (s, 1H), 2.49-2.44 (m, 1H), 2.39-2.33 (m, 1H), 2.17-2.16 (m, 3H), 1.50 (s, 9H), 1.40 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 3.53 (s, 1H), 3.25 (s, 1H), 2.57-2.52 (m, 1H), 1.75-1.71 (m, 1H), 1.53 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.3, 168.1, 141.5, 130.5, 129.4, 128.9, 128.8, 128.2, 127.1, 126.6, 121.5, 116.4, 82.2, 65.9, 61.6, 55.5, 47.3, 44.2, 28.1, 26.8, 20.2; ^{13}C NMR (125 MHz, $CDCl_3$) (*second diastereomer, diagnostic peaks*): δ 204.0, 166.3, 145.5, 122.1, 82.0, 66.9, 61.0, 55.6, 28.7, 27.5, 20.3; IR (thin film) 3391, 3025, 2976, 2929, 2872, 1707, 1614, 1504, 1309, 1156; HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}NO_3$ $(M+H)^+$ 392.2226, found 392.2213.

IV. Derivatization of Bicyclic Benz[*b*]azepin-4-ones 6 (Scheme 3).



Reduction of Bicyclic Benazepinone 9: $LiAlH_4$ (0.0260 g, 0.684 mmol) was added to a flame-dried round bottom flask under nitrogen and diluted with THF (0.97 mL, 0.70M). Bicyclic benzazepinone **6a** (0.0400 g, 0.114 mmol) was dissolved in THF (0.88 mL, 0.13 M) and slowly added to the $LiAlH_4$ slurry. The reaction mixture was refluxed for 4 h, cooled to 25 °C, and then quenched with 20.0 µL H_2O and 20.0 µL 15% NaOH in H_2O. The resulting heterogeneous solution was then separated. The organic layer was washed with 0.10 mL H_2O, filtered through cotton with EtOAc (10.0 mL), and concentrated under vacuum. Chromatography (25% EtOAc in hexanes) afforded **9** as a light-yellow solid (0.0239 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.44 (m, 2H), 7.33-7.30 (m, 2H), 7.21-7.18 (m, 1H), 6.83-6.82 (m, 1H), 6.77-6.73 (m, 1H), 6.42-6.41 (m, 1H), 4.56-4.52 (m, 1H), 3.97-3.94 (m, 2H), 3.75-3.73 (m 1H), 3.05-3.04 (m, 1H), 2.66-2.61 (m, 1H), 2.37-2.27 (m, 2H), 2.22 (s, 3H), 2.17-2.07 (m, 2H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 143.7, 129.8, 128.4, 128.2, 128.0, 127.2, 126.7, 125.9, 115.9, 75.5, 61.9, 54.4, 52.2, 46.5, 42.4, 41.0, 26.1, 20.3; IR (thin film) 3558, 3383, 3024, 2960, 2916, 1499,1 476, 1451, 1303, 1264 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{26}NO_2$ $(M+H)^+$ 324.1964, found 324.1951, mp: 169-174 ºC.

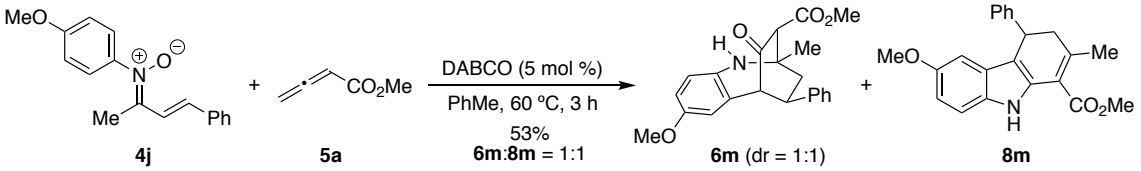
Reduced bicyclic benzazepinone **9** was dissolved in CH_2Cl_2, layered with pentane, and placed in a -40 °C freezer. After 24 h, single crystals had formed. The supernatant was decanted and X-ray crystallography analysis confirmed the structure illustrated above.



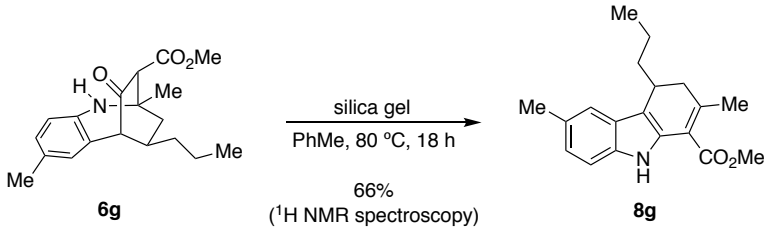
Methylated Bicyclic Benzazepinone 10: A scintillation vial was charged with **6a** (0.0306 g, 0.0860 mmol), 18-crown-6 (0.0680 g, 0.258 mmol, 3.0 equiv), and K_2CO_3 (0.0360 g, 0.258 mmol, 3.0 equiv). These reagents were diluted with MeCN (0.860 mL, 0.1 M) and DMF (0.009 mL). Methyl iodide (0.011 mL, 0.172 mmol, 2.0 equiv) was then added to the flask and the reaction mixture was stirred at 25 °C for 18 h. At this time reaction mixture was filtered through celite with EtOAc (15 mL) and the filtrate was concentrated under vacuum. The crude compound was purified by flash chromatography (10% EtOAc in hexanes) to afford **10** (0.0222 g, 72%)**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.24-7.21 (m, 1H), 7.18-7.16 (m, 2H), 6.83-6.81 (m, 1H) 6.67 (br, 1H), 6.45-6.43 (m, 1H), 4.10 (br, 1H), 3.91-3.87 (m, 1H), 3.57 (s, 1H), 3.19 (s, 3H), 2.37-2.32 (m, 1H), 2.16 (s, 3H), 1.88-1.83 (m, 1H), 1.53-1.50 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ

208.6, 172.2, 145.5, 142.2, 130.1, 128.9, 128.9, 128.0, 126.7, 126.6, 123.3, 116.2, 63.2, 61.0, 59.2, 51.9, 46.5, 44.6, 25.7, 20.2, 19.1; IR (thin film) 3390, 3025, 2992, 2946, 2855, 1727, 1711, 1503, 1452, 1379; HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}NO_3$ $(M+H)^+$, 364.1913 found 364.1912.

V. Mechanistic Experiments (Scheme 4).

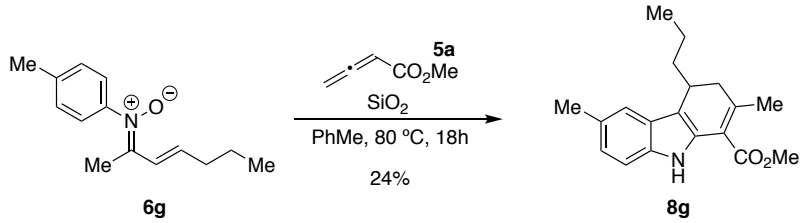


Synthesis of Bicyclic Benz[*b*]azepin-4-one 6m and Dihydrocarbazole 8m: A mixture of bicyclic benazepinone **6m** and dihydrocarbazole **8m** was prepared by general procedure A with alternative chromatography conditions. Nitrone **4j** (0.0321 g, 0.120 mmol) was treated with allenoate **5a** (0.0440 g, 0.360 mmol) in the presence of DABCO (0.0007 g, 0.006 mmol) in toluene (1.00 mL, 0.120 M) for 3 h at 60 °C. The crude material was purified by medium pressure chromatography (8% acetone, 2% NEt_3, 2% benzene, in petroleum ether) to afford a 1:1 of mixture **6m** and **8m** (0.0231 g, 53%, **6m**:**8m** = 1:1, dr for **6m** = 1:1) as a light yellow amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) (**6m**, *first diastereomer*): 7.34-7.18 (m, 5H), 6.70-6.67 (m, 1H), 6.55-6.52 (m, 1H), 6.45-6.43 (m, 1H), 4.06 (s, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 3.46 (s, 1H), 3.37 (s, 1H), 2.52-2.45 (m, 1H), 2.40-2.36 (m, 1H), 1.36 (s, 3H), N–*H* was too broad to be observed; ^{1}H NMR (500 MHz, $CDCl_3$) (**6m**, *second diastereomer, diagnostic peaks*): δ 3.70 (s, 3H), 3.49 (s, 3H), 2.63-2.56 (m, 1H), 1.79-1.75 (m, 1H), 1.51 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (**8m**): δ 9.30 (br, 1H), 7.34-7.18 (m, 6H), 6.75-6.74 (m, 1H), 6.28-6.26 (m, 1H), 4.32-4.29 (m, 1H), 3.68 (s, 3H), 3.60 (s, 1H), 3.58 (s, 3H), 2.99-2.94 (m, 1H), 2.84-2.78 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (**6m**, *first diastereomer*): δ 205.0, 167.9, 145.4, 138.7, 128.9, 128.5, 127.9, 127.0, 126.8, 122.4, 118.1, 114.6, 64.7, 61.6, 55.7, 52.2, 47.3, 45.8, 44.3, 28.6; ^{13}C NMR (125 MHz, $CDCl_3$) (**6m**, *second diastereomer, diagnostic peaks*): δ 203.0, 166.9, 152.9, 145.3, 117.7, 114.4, 65.2, 61.0; ^{13}C NMR (125 MHz, $CDCl_3$) (**8m**): δ 169.7, 153.8, 149.2, 144.5, 132.3, 131.1, 128.8, 128.5, 127.9, 126.8, 126.7,115.5, 111.8, 111.6, 100.5 55.6, 51.8, 45.8, 38.0, 23.0; IR (thin film) 3437, 3390, 3058, 3027, 2950, 2832, 1736, 1705, 1495, 1452; HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}NO_3$ $(M+H)^+$ 348.1600, found 348.1593; HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}NO_4$ $(M+H)^+$ 366.1705, found 366.1696.

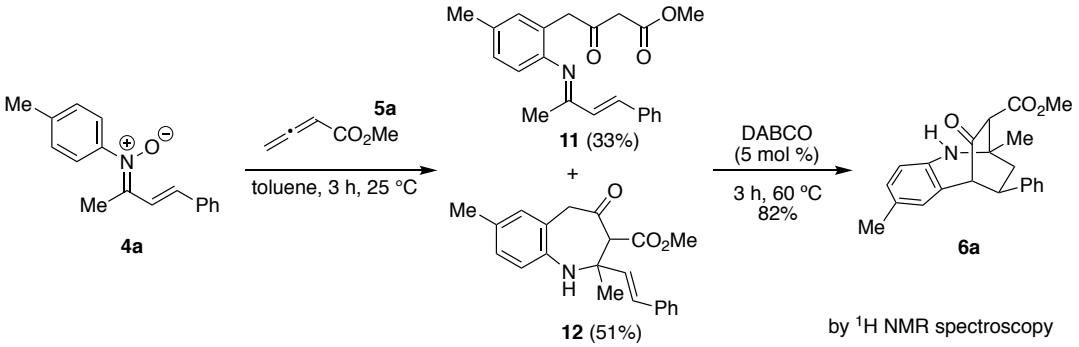


Conversion of Bicyclic Benz[*b*]azepin-4-one 6g to Dihydrocarbazole 8g: A Teflon-sealed reaction flask was charged with silica gel (0.136 g), flushed onto a Schlenk line, and placed under N_2 with a needle and a septum. A scintillation vial was charged with bicyclic benzazepinone **6g** (0.0429 g, 0.136 mmol, 1.0 equiv) and placed under N_2 with a needle and a septum. The bicyclic benzazepinone mixture was then diluted with toluene to form a 0.1 M solution. This solution was transferred to the reaction flask via syringe, the reaction vessel was sealed with a Teflon cap, and stirred at 25 ºC for 5 min. The reaction mixture was then heated to 80 ºC for 18 h. At this time, the reaction mixture was concentrated under vacuum and the crude

product mixture was identified as **8g** and quantified by ^{1}H NMR spectroscopy using CH_2Br_2 as a reference (66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (s, 1H), 7.28-7.22 (m, 2H), 6.95-6.94 (m, 1H), 3.92 (s, 3H), 3.06-3.05 (m, 1H), 2.88-2.83 (m, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 1.59-1.56 (m, 1H), 1.47- 1.44 (m, 2H), 1.32-1.27 (m, 2H), 0.91-0.88 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 149.5, 134.0, 130.5, 128.6, 126.6, 122.9, 118.1, 118.0, 112.4, 110.8, 51.6, 40.8, 37.2, 30.3, 23.4, 21.6, 20.5, 14.4. Spectral data match the product of the independent synthesis of **6g** from **4g** described below.



Independent Synthesis of Dihydrocarbazole 8g from 4g:[2] A Teflon-sealed reaction flask was charged with silica gel (0.200 g), flushed onto a Schlenk line, and placed under N_2 with a needle and a septum. A scintillation vial was charged with nitrone **4g** (0.0435 g, 0.200 mmol, 1.0 equiv) and allene **5a** (0.100 g, 0.600 mmol, 3.0 equiv) and placed under N_2 with a needle and a septum. The mixture was then diluted with toluene to form a 0.1 M solution. This solution was transferred to the reaction flask via syringe, the reaction vessel was sealed with a Teflon cap, and the reaction mixture was stirred at 25 ºC for 5 min. The reaction mixture was then heated to 80 ºC for 18 h. At this time, the solvent was removed from the reaction mixture under vacuum and the crude reaction mixture was purified by medium pressure chromatography (10% EtOAc in hexanes) to give **8g** as a yellow oil (0.0139 g, 24%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (s, 1H), 7.31-7.28 (m, 1H), 7.24-7.22 (m, 1H), 6.95-6.94 (m, 1H), 3.92 (s, 3H), 3.06-3.05 (m, 1H), 2.88-2.82 (m, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 1.59-1.54 (m, 1H), 1.48-1.39 (m, 2H), 1.31-1.29 (m, 2H), 0.91-0.88 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 149.5, 134.0, 130.5, 128.6, 126.6, 122.9, 118.1, 118.0, 112.4, 110.8, 51.6, 40.8, 37.2, 30.3, 23.4, 21.6, 20.5, 14.4; IR (thin film) 3449, 2954, 2924, 2869, 1745, 1720, 1694, 1595, 1574, 1434; HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}NO_2$ $(M+H)^+$ 298.1807, found 298.1805.



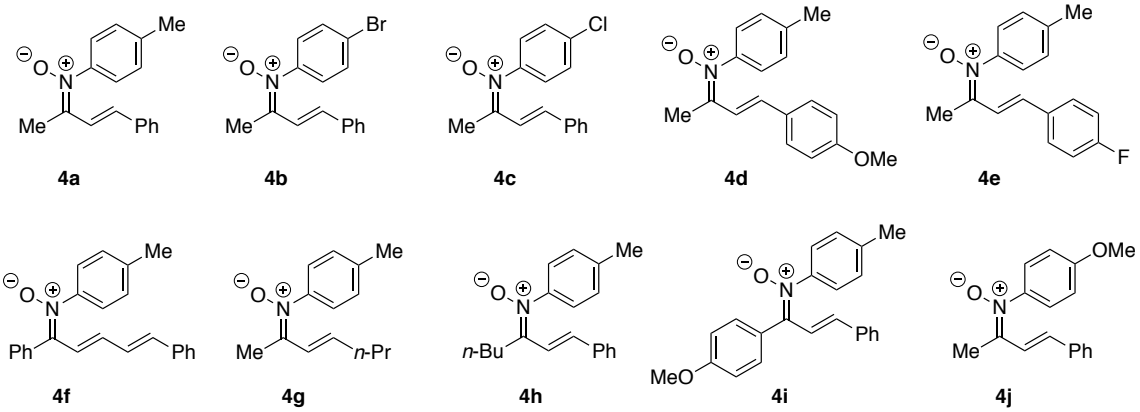
Effect of Catalyst on Cascade Intermediates.

Formation of Intermediates 11 and 12:[2,3] A Teflon-sealed reaction flask was charged with nitrone **4a** (0.0300 g, 0.120 mmol), allenoate **5a** (0.0440 g, 0.360 mmol), and toluene (1.0 mL). The mixture was stirred at 25 ºC for 3 h. After 3 h, the reaction mixture was concentrated under vacuum to give a crude product

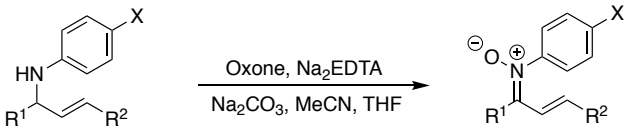
mixture, which was identified by ^{1}H NMR spectroscopy as a mixture of **11** (33%) and **12** (51%). Yields were determined by comparison to CH_2Br_2 (7.0 µL, 0.1 mmol), which was added as a reference. ^{1}H NMR (500 MHz, *diagnostic peaks* for **11***)* δ 7.59-7.57 (m, 2H), 3.69 (s, 3H), 3.51-3.50 (m, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 2.09 (s, 3H); ^{1}H NMR (500 MHz, *diagnostic peaks* for **12***)* δ 6.73-6.63 (m, 1H), 3.75 (s, 3H), 3.48 (s, 2H), 2.43 (s, 3H), 2.06 (s, 3H). This spectral data matched analogous spectra analyzed for different branches of the cascade reaction.[2,3]

Conversion of Intermediates 11 and 12 to Bicyclic Benzazepinone 6a: A Teflon-sealed reaction flask was charged with crude product mixture described above (0.0768 mmol) and treated with DABCO (0.0004 g, 0.004 mmol) and toluene (0.76 mL). The reaction mixture was heated at 60 ºC for 3 h. After 3 h, the reaction mixture was concentrated under vacuum to give a crude product, which was identified by ^{1}H NMR spectroscopy as **6a** (82%, dr = 1:1). Yields were determined by comparison to CH_2Br_2 (7.0 µL, 0.1 mmol), which was added as a reference. ^{1}H NMR (500 MHz, *major diastereomer, diagnostic peaks*): δ 7.34-7.31 (m, 2H), 7.25-7.23 (m, 2H), 7.18-7.17 (m, 1H), 6.89-6.87 (m, 1H), 6.69-6.67 (m, 1H), 6.50-6.49 (m, 1H), 4.11- 4.09 (m, 1H), 3.94-3.87 (m, 1H), 3.79 (s, 3H), 3.49 (s, 1H), 3.38 (s, 1H), 2.51-2.46 (m, 1H), 2.41-2.37 (m, 1H), 2.17 (s, 3H), 1.36 (s, 3H); ^{1}H NMR (500 MHz, $CDCl_3$) (minor diastereomer, diagnostic peaks): δ 4.06 (s, 1H), 3.58 (s, 1H), 3.47 (s, 1H), 2.64-2.58 (m, 1H), 1.81-1.76 (m, 1H), 1.50 (s, 3H). This spectral data matched the data described for **6a** above.

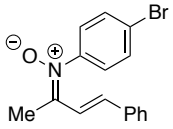
VI. Synthesis of Nitrones 4



Nitrones **4a**, **4c**, **4f**, and **4i** were prepared according to previously published procedures.[2,3,7]



General Procedure B: This procedure was adapted from the literature.[7] *N*-Allyl aniline **S-1** (1 equiv) was dissolved in a 1:4 mixture of THF:MeCN (0.54 M) and mixed with aqueous Na_2EDTA (0.14 equiv, 0.01 M). This mixture was then cooled to 0 ºC and mixed with $NaHCO_3$ (5 equiv). Oxone® (2.70 equiv) was added to the aniline and EDTA mixture in 12 portions over 2 h. The reaction mixture was then stirred at 25 °C for an additional 20 min before CH_2Cl_2 (20.0 mL) was added. The organic layer was separated from the rest of the reaction mixture and the aqueous layer was extracted with CH_2Cl_2 (3 x 15.0 mL). The combined organic layers were washed with brine (10.0 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The crude product was wet loaded on to celite with CH_2Cl_2 and purified by medium pressure chromatography (5% MeOH in CH_2Cl_2).

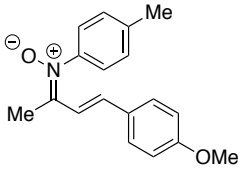


E:Z = 3:1

4b

Nitrone 4b: Nitrone **4b** was prepared by general procedure B using *N*-allyl aniline **S-1b** (1.725 g, 8.480 mmol), a 1:4 mixture of THF:MeCN (10.2 mL, 0.54 M), 0.01 M aq. Na_2EDTA (7.60 mL, 0.72 M), $NaHCO_3$ (2.290 g, 27.35 mmol), and oxone (4.540 g, 14.77 mmol). Chromatography (5% MeOH in CH_2Cl_2) afforded **XXb** as a yellow solid (0.398 g, 23%). ^{1}H NMR (500 MHz, $CDCl_3$) (*E*-isomer): δ 7.64-7.60 (m, 3H), 7.34-7.29 (m, 6H), 6.85-6.82 (m, 1H), 6.71-6.68 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E*-isomer): δ 144.4, 135.8, 133.4, 132.7, 129.1, 128.9, 127.7, 127.0, 126.2, 125.4, 120.6, 13.5; ^{1}H NMR (500 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 8.02-7.99 (m, 1H), 7.42-7.31 (m, 7H), 7.16-7.12 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 148.2, 138.3, 129.1, 125.4, 123.4, 120.2,

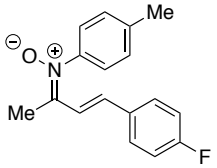
16.4; IR (thin film) 3170, 3080, 3055, 3023, 2974, 2922, 2852, 1488, 1474, 1304 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}NOBr$ $(M+H)^+$ 316.0337, found 316.0338; m.p: 98-102 °C.



E:Z = 3:1

4d

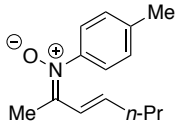
Nitrone 4d: Nitrone **4d** was prepared by general procedure B using *N*-allyl aniline **S-1d** (2.47, 9.24 mmol), a 1:4 mixture of THF:MeCN (17.0 mL, 0.54 M), 0.01 M aq. Na_2EDTA (12.8 mL, 0.72 M), $NaHCO_3$ (3.88 g, 46.2 mmol), and oxone (7.67 g, 24.9 mmol). Chromatography (5% MeOH in CH_2Cl_2) afforded **4d** as a solid (0.7466 g, 29%). ^1H NMR (500 MHz, $CDCl_3$) (*E*-isomer): δ 7.28-7.24 (m, 4H), 7.18-7.17 (m 2H), 6.81-6.79 (m, 2H), 6.75-6.72 (m, 1H), 6.62-6.59 (m, 1H), 3.77 (s, 3H), 2.49 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E*-isomer): δ 160.2, 147.7, 143.2, 139.4, 137.3, 132.1, 129.9, 128.3, 124.3, 119.2, 114.3, 55.3, 21.3, 13.4; ^1H NMR (500 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 7.93-7.90 (m, 1H), 7.55-7.54 (m, 1H), 7.07-7.03 (m,1H), 6.90, 6.88 (m, 1H), 3.82 (s, 3H), 2.38 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 160.6, 144.7, 144.0, 139.2,129.1, 128.9, 123.5, 118.5, 55.0, 21.2, 16.3; IR (thin film) 3035, 2953, 2836, 1597, 1507, 1493, 1462, 1441, 1319, 1208 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}NO_2$ $(M+H)^+$ 282.1494, found 282.1488; m.p: 120-122 °C.



E:Z = 3:1

4e

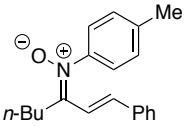
Nitrone 4e: Nitrone **4e** was prepared by general procedure B using *N*-allyl aniline **S-1e** (2.00 g, 7.43 mmol), a 1:4 mixture of THF:MeCN (13.8 mL, 0.54 M), 0.01 M aq. Na_2EDTA (10.3 mL, 0.72 M), $NaHCO_3$ (3.120 g, 37.15 mmol), and oxone (6.160 g, 20.05 mmol). Chromatography (5% MeOH in CH_2Cl_2) afforded **4e** as a yellow solid (1.550 g, 77%). ^1H NMR (500 MHz, $CDCl_3$) (*E*-isomer): δ 7.27-7.25 (m, 4H), 7.20-7.16 (m, 2H), 6.98-6.95 (m, 2H), 6.75-6.64 (m, 2H), 2.50 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E*-isomer): δ 162.8 (d, $J_{C\text{-}F}$ = 250.0 Hz) 147.3, 143.1, 139.6, 136.1, 129.9, 128.6 (d, $J_{C\text{-}F}$ = 12.5 Hz), 124.3, 123.4, 121.1, 115.9 (d, $J_{C\text{-}F}$ = 25.0 Hz) 21.2, 13.4; ^1H NMR (500 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 7.96-7.93 (m, 1H), 7.57-7.56 (m, 1H), 7.07-7.04 m, 2H), 2.39 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 163.2 (d, $J_{C\text{-}F}$ = 250.0 Hz), 139.4, 132.4, 129.3 (d, $J_{C\text{-}F}$ = 12.5 Hz), 120.5, 21.3, 16.3; IR (thin film) 3041, 2974, 2923, 1597, 1505, 1493, 1415, 1311, 1271, 1156 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}NO_F$ $(M+H)^+$ 270.1294, found 270.1284; m.p: 99-103 °C.



E:Z = 3:1

4g

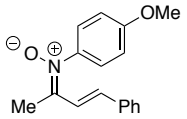
Nitrone 4g: Nitrone **4g** was prepared by general procedure B using *N*-allyl aniline **S-1g** (1.725 g, 8.480 mmol), a 1:4 mixture of THF:MeCN (15.7 mL, 0.54 M), 0.01 M aq. Na_2EDTA (11.8 mL, 0.72 M), $NaHCO_3$ (3.56 g, 42.4 mmol), and oxone (7.00 g, 22.9 mmol). Chromatography (5% MeOH in CH_2Cl_2) afforded **4g** as an oil (0.4189 g, 23%). ^{1}H NMR (500 MHz, $CDCl_3$) (*E*-isomer): δ 7.23-7.19 (m, 4H), 6.07-6.00 (m, 2H), 2.38-2.37 (m, 6H), 2.02-1.97 (m, 2H), 1.34-1.32 (m, 2H), 0.86-0.85 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E*-isomer): δ 143.1, 142.1, 139.2, 136.8, 129.8, 124.1, 123.4, 35.3, 22.1, 21.2, 13.6, 13.4; ^{1}H NMR (500 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 7.34-7.31 (m, 1H), 7.07-6.93 (m, 3H), 6.39-6.32(m, 1H), 2.29-2.26 (2H), 1.54-1.48 (m, 2H), 0.96-0.93 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 147.4, 143.1, 129.9, 123.9, 123.3, 35.6, 16.4, 13.8; IR (thin film) 3030, 2958, 2928, 2870, 1687, 1505, 1441, 1379, 1226, 1174 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{20}NO$ $(M+H)^+$ 218.1545, found 218.1539.



E:Z = 3:1

4h

Nitrone 4h: Nitrone **4h** was prepared by general procedure B using *N*-allyl aniline **S-1g** (1.60 g, 5.75 mmol), a 1:4 mixture of THF:MeCN (10.6 mL, 0.54 M), 0.01 M aq. Na_2EDTA (8.0 mL, 0.72 M), $NaHCO_3$ (2.40 g, 28.8 mmol), and oxone (4.75 g, 15.5 mmol). Chromatography (5% MeOH in CH_2Cl_2) afforded **4h** as an oil (0.4872 g, 29%). ^{1}H NMR (500 MHz, $CDCl_3$) (*E*-isomer): δ 7.26-7.23 (m, 9H), 6.78-6.68 (m 2H), 2.99-2.96 (m, 1H), 2.48 (s, 3H), 1.74-1.71 (m, 1H), 1.57-1.52 (m, 2H), 1.30-1.23 (m 2H), 1.03-1.00 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E*-isomer): δ 151.1, 143.4, 139.4, 137.3, 131.7, 129.8, 128.8, 127.6, 126.9, 124.3, 120.9, 27.8, 26.6, 23.1, 21.3, 14.0; ^{1}H NMR (500 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 7.93-7.90 (m, 1H), 7.62-7.60 (m, 2H), 7.39-7.36 (m, 3H), 7.19-7.16 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*Z*-isomer, diagnostic peaks): δ 149.1, 143.8, 139.1, 136.3, 130.0, 129.2, 128.6, 123.3, 119.5, 30.6, 29.3, 22.6, 21.2, 13.5; IR (thin film) 3056, 3025, 2955, 2927, 2869, 1509, 1483, 1447, 1298, 1225 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NO$ $(M+H)^+$ 294.1858, found 294.1854.

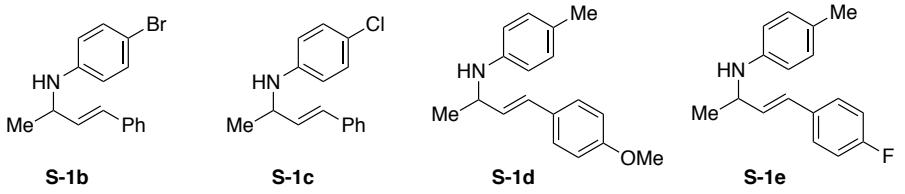


E:*Z* = 10:1

4j

Nitrone 4j: Nitrone **4j** was prepared by general procedure B with *N*-allyl aniline **S-1j** (3.73 g, 14.7 mmol), a 1:4 mixture of THF:MeCN (27.3 mL, 0.54 M), 0.01 M aq. Na_2EDTA (20.0 mL, 0.72 M), $NaHCO_3$ (6.78 g, 73.5 mmol), and oxone (12.2 g, 39.7 mmol). Chromatography (5% MeOH in CH_2Cl_2) afforded **4j** as an oil (1.19 g, 30%). ^1H NMR (500 MHz, $CDCl_3$) (*E*-isomer): δ 7.35-7.33 (m, 2H), 7.27-7.24 (m, 5H), 6.97-6.96 (m, 2H), 6.78-6.74 (m, 2H), 3.86 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E*-isomer): δ 160.1, 147.6, 138.8, 136.1, 132.4, 128.8, 128.8, 126.9, 125.8, 121.4, 114.4, 55.6, 13.6; IR (thin film) 3040, 3024, 2961, 2910, 2836, 1603, 1589, 1498,1384, 1298 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}NO_2$ $(M+H)^+$ 268.1338, found 268.1331.

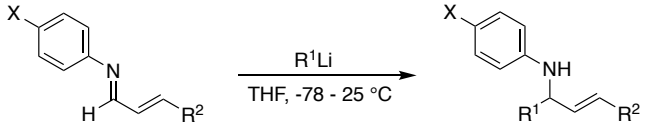
Synthesis of *N*-Allylanilines S-1



S-1b **S-1c** **S-1d** **S-1e**

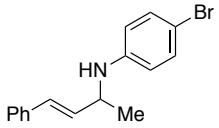
S-1g **S-1h** **S-1j**

N-Allylanilines **S-1c**[7] and **S-1j**[8] were prepared according to previously published procedures.



S-2 **S-1**

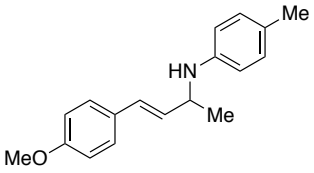
General Procedure C: This procedure was adapted from the literature.[2,7] An 250.0 mL round bottom flask was charged with *N*-aryl imine **S-2** (1.0 equiv), flushed onto a Schlenk line, dissolved in THF to form an 0.1 M solution, and cooled to -78 ºC with a dry ice/*i*-PrOH bath. An alkyl lithium reagent (1.5 equiv) was added dropwise to the imine solution and the mixture was stirred at -78 ºC for 30 min. The reaction quenched by the addition of aq. NH_4Cl (20.0 mL). The aqueous phase was extracted with Et_2O (2 x 20.0 mL). The combined organic fractions were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. Crude **S-1** was used for the synthesis of nitrone **4** without further purification.



S-1b

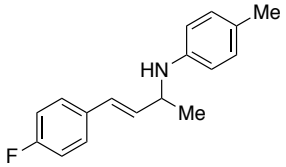
***N*-Allylaniline S-1b:** *N*-Allylaniline **S-1b** was prepared by general procedure C using *N*-aryl imine **S-2b** (2.00 g, 6.98 mmol), THF (70.0 mL), and MeLi (6.56 mL of a 1.60 M solution in Et_2O, 10.48 mmol). *N*-Allylaniline **S-1b** was isolated as an oil (1.730 g, 78%) and used without purification for the synthesis of

nitrone **4b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.35 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.23 (m, 3H), 6.57-6.52 (m, 3H), 6.20-6.15 (m, 1H), 4.12-4.07 (m, 1H), 3.67 (br, 1H), 1.40 (d, J = 5.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 136.8, 132.5, 131.9, 129.6, 128.6, 127.5, 126.3, 115.0, 108.9, 50.9, 22.0; IR (thin film) 3410, 3058, 3024, 2964, 2923, 2866, 1591, 1489, 1314, 1177 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{67}H_{17}NBr$ $(M+H)^+$, found 286.0232.



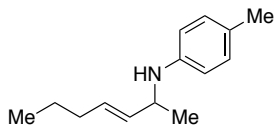
S-1d

***N*-Allylaniline S-1d:** *N*-allyl aniline **S-1d** was prepared by general procedure C using *N*-aryl imine **S-2d** (2.570 g, 10.22 mmol), THF (102.0 mL), MeLi (9.60 mL of a 1.60 M solution in Et_2O, 15.33 mmol). *N*-Allylaniline **S-1d** was isolated as an oil (2.4728 g, 90%) and used without purification for the synthesis of nitrone **4d**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 7.01-7.00 (m, 2H), 6.88-6.86 (m, 2H), 6.62-6.61 (m, 2H), 6.56-6.53 (m, 1H), 6.13-6.09 (m, 1H), 4.15-4.10 (m, 1H), 3.83 (s, 3H), 2.26 (s, 3H), 1.42 (d, J = 5.0 Hz, 3H), N–*H* was too broad to be observed; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 145.2, 131.3, 129.9, 129.7, 128.6, 127.5, 126.5, 113.9, 113.7, 55.3, 51.2, 22.2, 20.4; IR (thin film) 3399, 2966, 2916, 2865, 2834, 1606, 1577, 1508, 1462, 1315 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NO$ $(M+H)^+$ 268.1701, found 268.1701.



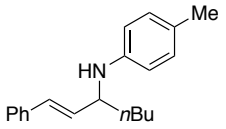
S-1e

***N*-Allylaniline S-1e:** N-Allylaniline **S-1e** was prepared by general procedure C using *N*-aryl imine **S-2e** (2.629 g, 10.98 mmol), THF (110.0 mL), and MeLi (10.30 mL of a 1.60 M solution in Et_2O, 15.33 mmol). *N*-Allylaniline **S-1e** was isolated as an oil (2.00 g, 68%) and used without purification for the synthesis of nitrone **4e**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.00-6.97 (m, 4H), 6.59-6.63 (m, 3H), 6.16-6.12 (m, 1H), 4.13-4.09 (m, 1H), 3.53 (br, 1H), 2.24 (s, 3H), 1.41 (m, 3H), N–*H* was too broad to be observed; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.2 (d, $J_{C\text{-}F}$ = 237.5 Hz), 145.1, 133.2, 129.7, 128.0, 127.7 (d, $J_{C\text{-}F}$ = 25.0 Hz), 126.6, 115.7, 115.4 (d, $J_{C\text{-}F}$ = 25.0 Hz), 113.6, 51.1, 22.1, 20.4; IR (thin film) 3398, 2981, 2938, 2871, 1736, 1616, 1518, 1507, 1372, 1044 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}NF$ $(M+H)^+$ 256.1502, found 256.1508.



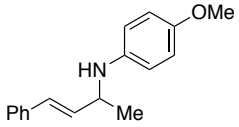
S-1g

***N*-Allylaniline S-1g:** *N*-Allylaniline **S-1g** was prepared by general procedure C using *N*-aryl imine **S-2g** (2.363, 12.60 mmol), THF (126.0 mL), and MeLi (11.80 mL of a 1.60 M solution in Et_2O, 18.90 mmol). *N*-Allylaniline **S-1g** was isolated as an oil (1.7250 g, 67%) and used without purification for the synthesis of nitrone **4g**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00-6.98 (m, 2H), 6.57-6.56 (m, 2H), 5.67-5.63 (m, 1H), 5.46-5.42 (m, 1H), 3.94-3.92 (m, 1H), 3.47 (br, 1H), 2.30 (s, 3H), 2.03-1.99 (m, 2H), 1.42-1.40 (m, 2H), 1.31-1.29 (m, 3H), 0.92-0.89 (m, 3H), N–*H* was too broad to be observed; ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4, 133.5, 130.3, 129.9, 129.6, 113.7, 50.9, 34.4, 22.5, 22.2, 20.4, 13.7; IR (thin film) 3400, 2957, 2924, 2869, 1641, 1614, 1514, 1371, 1299, 1253 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}N$ $(M+H)^+$ 204.1752, found 204.1749.



S-1h

***N*-Allylaniline S-1h:** *N*-Allylaniline **S-1h** was prepared by general procedure C using *N*-aryl imine **S-2a** (1.50, 6.77 mmol), THF (67.0 mL), and *n*-BuLi (6.35 mL of a 2.50 M solution in hexanes, 10.17 mmol). *N*-Allylaniline **S-1h** was isolated as an oil (1.69 g, 89%) and using without purification for the synthesis of nitrone **4h**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.22-7.20 (m, 1H), 6.98-6.96 (m, 2H), 6.59-6.55 (m, 3H), 6.16-6.12 (m, 1H), 3.93-3.91 (m, 1H), 2.23 (s, 3H), 1.70-1.67 (m, 2H), 1.45-1.37 (m, 4H), 0.94-0.91 (m, 3H), N–*H* was too broad to be observed; ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4, 137.2, 132.6, 130.0, 129.7, 128.6, 128.5, 127.3, 126.3, 113.5, 56.0, 36.1, 28.2, 22.7, 20.4, 14.1; IR (thin film) 3406, 3023, 2954, 2927, 2858, 1615, 1516, 1494, 1315, 1256 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}N$ $(M+H)^+$ 280.2065, found 280.2663.



S-1j

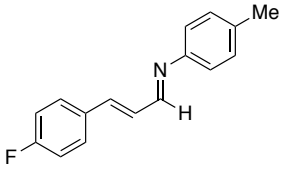
***N*-Allylaniline S-1j:** *N*-Allylaniline **S-1j** was prepared by general procedure C using *N*-aryl imine **S-2j** (3.77, 15.89 mmol), THF (160.0 mL), and MeLi (14.80 mL of a 1.60 M solution in Et_2O, 23.8 mmol). *N*-Allylaniline **S-1j** was isolated as an oil (3.73 g, 93%) and used without purification for the synthesis of nitrone **4j**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.38 (m, 2H), 7.33-7.30 (m, 2H), 7.26-7.22 (m, 1H), 6.81-6.79 (m, 2H), 6.67-6.65 (m, 2H), 6.61-6.58 (m, 1H), 6.26-2.22 (m, 1H). Spectral data for this compound were consistent with those found in the literature.[9]

Synthesis of *N*-Aryl Imines S-2

N-Aryl Imines **S-2b**,[10] **S-2c**,[7] **S-2d**,[7] and **S-2j**[10] were prepared according to previously published procedures.

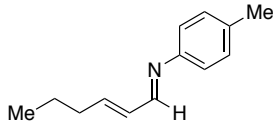
S-3 **S-2**

General Procedure D: A 0.4 M solution of aniline (1.05 equiv, 12.5 mmol) in Et_2O (30 mL) was mixed with anhydrous $MgSO_4$ (5.0 g). α,β-Unsaturated aldehyde **S-3** (1.0 equiv, 12.0 mmol) was added dropwise to the resulting slurry and the reaction mixture was stirred at 25 °C for 18 h under N_2. The reaction mixture was then filtered over cotton with Et_2O (20.0 mL) and concentrated under vacuum to give crude *N*-aryl imine **S-2**. *N*-Aryl imine **S-2** was used for the preparation of *N*-allylanilines **S-1** without purification.



S-2e

***N*-Aryl Imine S-2e:** *N*-Aryl imine **S-2e** was prepared by general procedure D using 4-toluidine (1.34g, 12.5 mmol), Et_2O (30.0 mL), $MgSO_4$ (5.00 g), and 4-fluorocinnamaldehyde (**S-3e**) (1.80 g, 12.0 mmol). *N*-Aryl imine **S-2e** was isolated as a yellow solid (2.629 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27-8.26 (m, 1H), 7.52-7.50 (m, 2H), 7.20-7.18 (m, 2H), 7.12-7.04 (m, 6H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4 (d, $J_{C\text{-}F}$ = 250.0 Hz), 160.5, 149.0, 142.1, 136.1, 132.1($J_{C\text{-}F}$ = 12.5 Hz), 129.8, 129.2 (d, $J_{C\text{-}F}$ = 12.5 Hz), 128.5, 120.8, 116.0 (d, $J_{C\text{-}F}$ = 25.0 Hz), 21.3; IR (thin film) 3024, 2980, 2922, 2869, 1703, 1696, 1627, 1598, 1538, 1501 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}NF$ $(M+H)^+$ 240.1189, found 240.1180; m.p: 111-115 °C.



S-2g

***N*-Aryl Imine S-2g:** *N*-Aryl imine **S-2g** was prepared by general procedure D using 4-toluidine (1.340 g, 15.50 mmol), Et_2O (30.0 mL), $MgSO_4$ (5.00 g), and 2-hexenal (**S-3g**) (1.40 mL, 12.0 mmol). *N*-Aryl imine **S-2g** was isolated as an oil (1.8847 g, 84%) and used without further purification for the synthesis of **S-1g**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08-8.06 (m, 1H), 7.16-7.15 (m, 2H), 7.06-7.01 (m, 2H), 6.47-6.36 (m, 2H), 2.35 (s, 3H), 2.29-2.24 (m, 2H), 1.56-1.51 (m, 2H), 0.99-0.96 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 149.3, 148.1, 135.5, 131.4, 129.7, 120.7, 34.9, 21.7, 21.0, 13.7; IR (thin film) 3022, 2958, 2927, 2869, 1644, 1612, 1504, 1455, 1396, 1298 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}N$ $(M+H)^+$, 268.2058.

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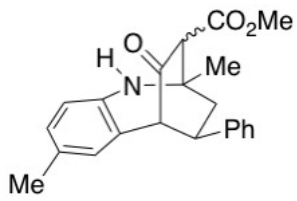

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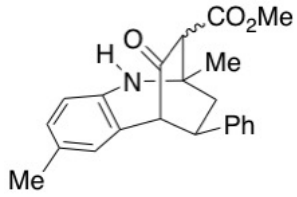
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H
N
Me
Ph
Me

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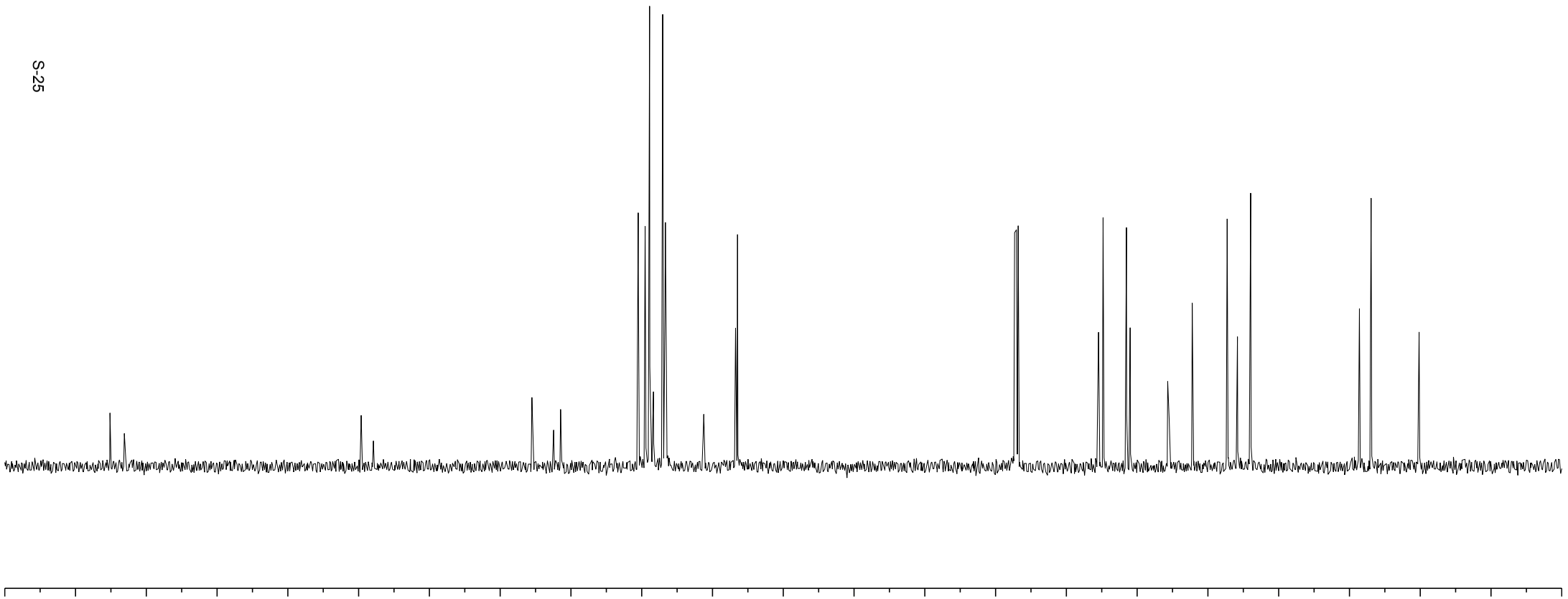
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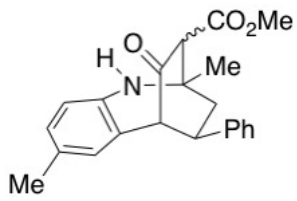
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H
N
Me
Ph
Me

6a (dr = 3:2)

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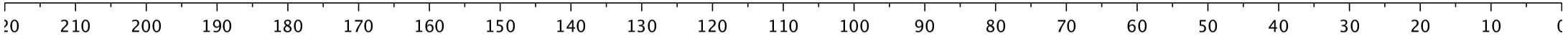
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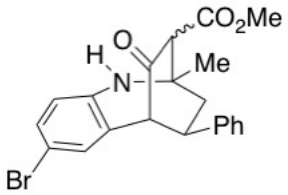

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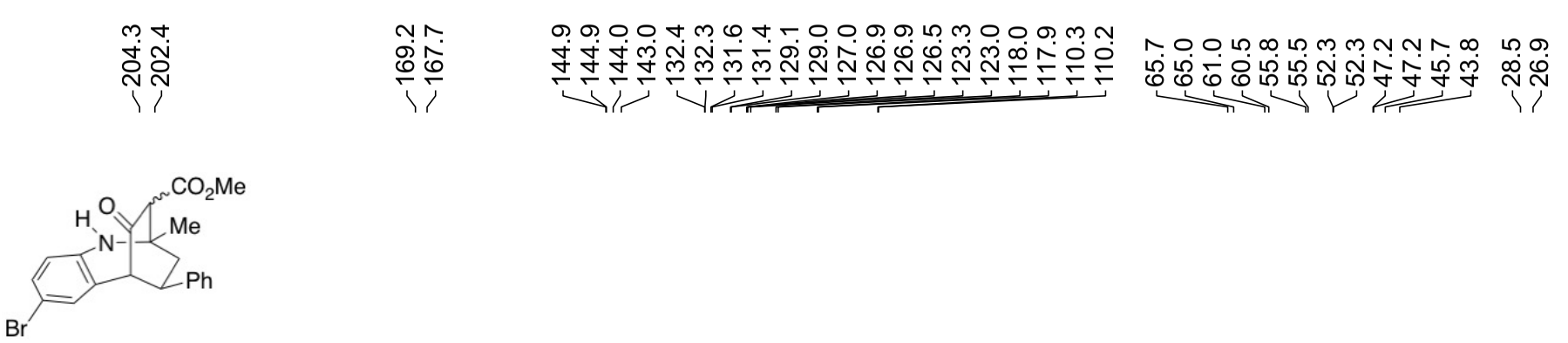
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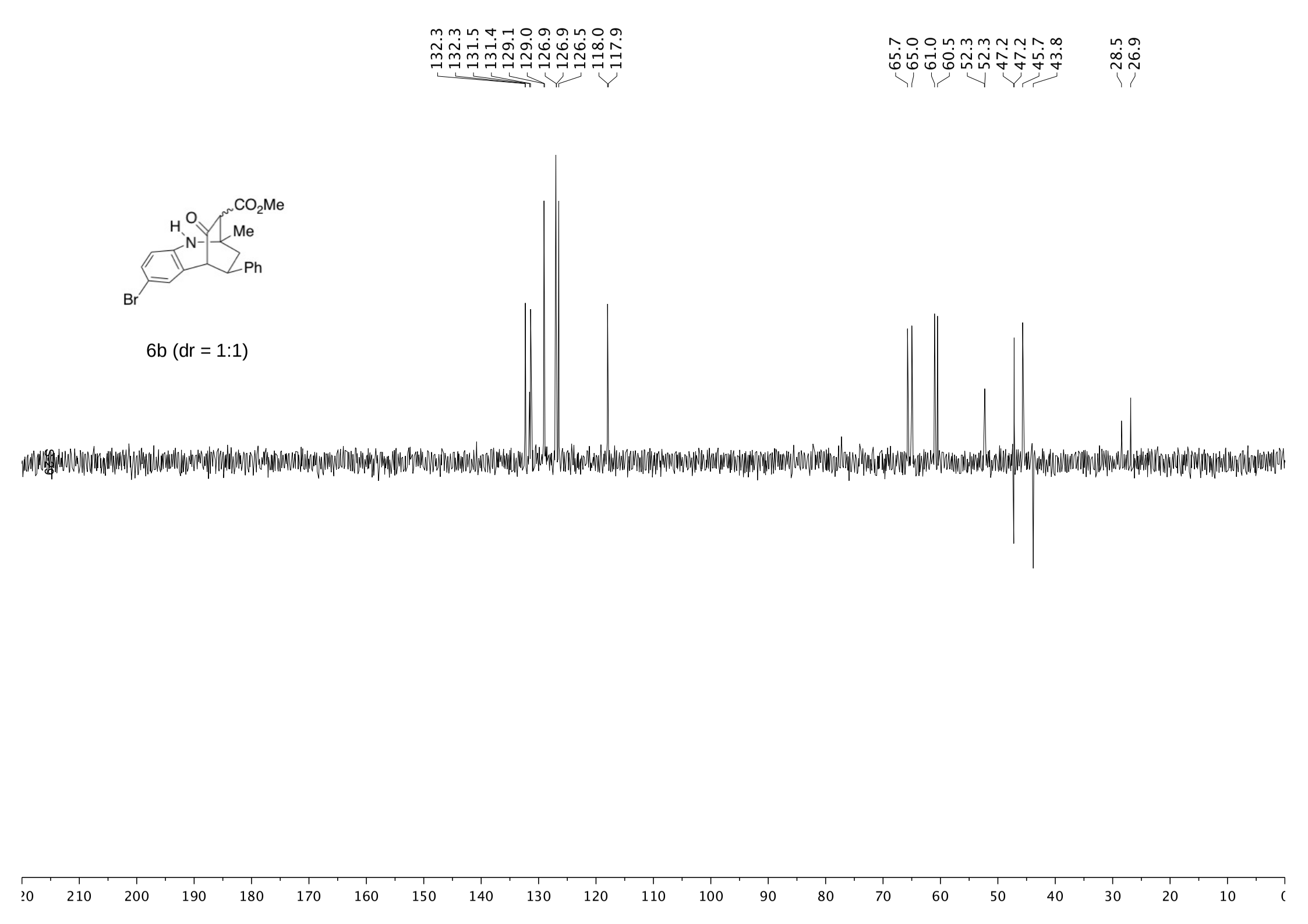
Br

6b (dr = 1:1)

f1 (ppm)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O
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Me
Ph
Br
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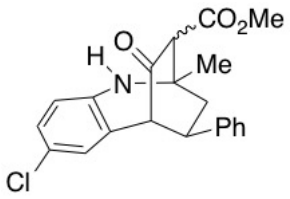

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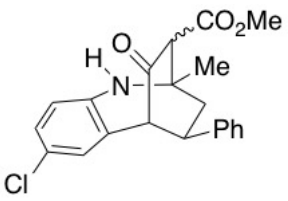
CO2Me
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N
Me
Ph
Cl

6c (dr = 1:1)

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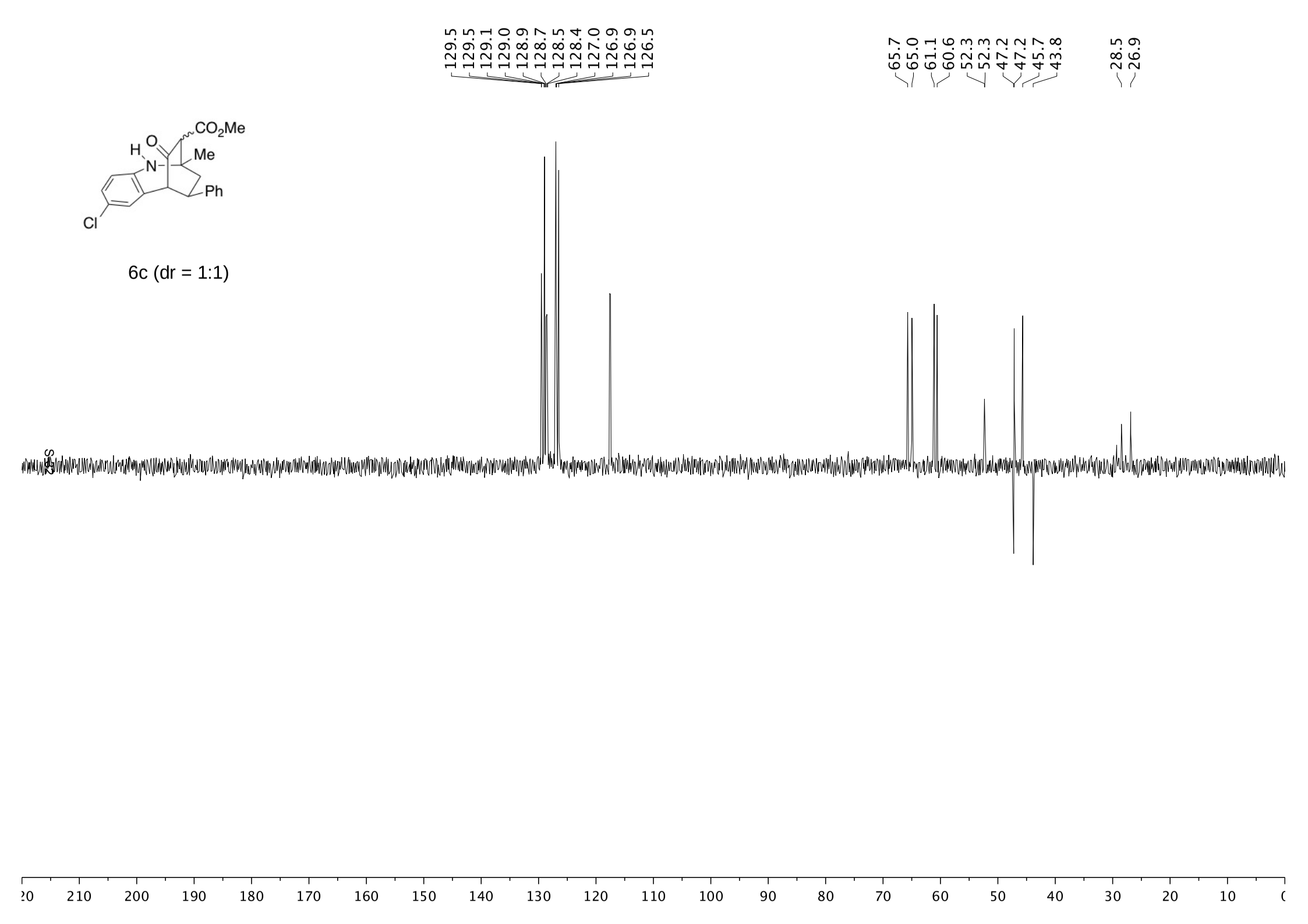
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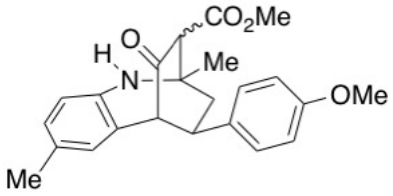

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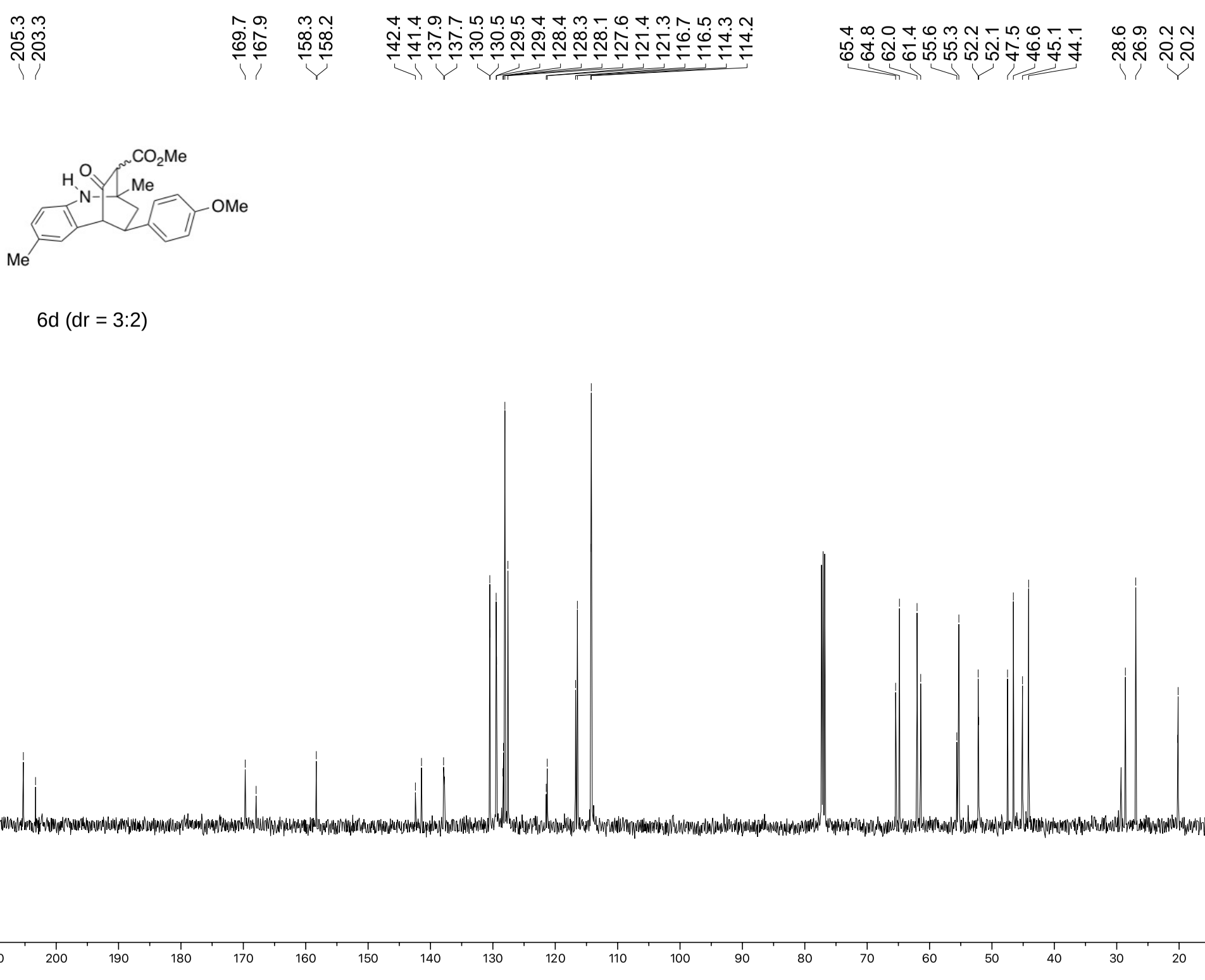
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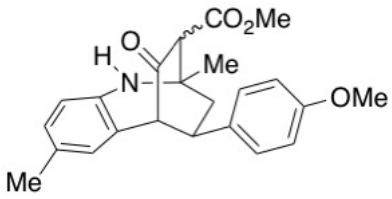
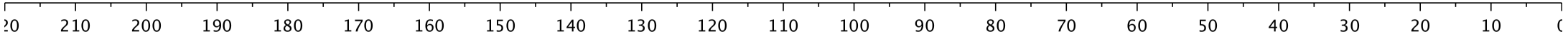
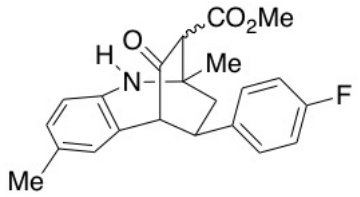
167.9
158.3
158.2
142.4
141.4
137.9
137.7
130.5
130.5
129.5
129.4
128.4
128.3
128.1
127.6
121.4
121.3
116.7
116.5
114.3
114.2
65.4
64.8
62.0
61.4
55.6
55.3
52.2
52.1
47.5
46.6
45.1
44.1
28.6
26.9
20.2
20.2
CO2Me
O
H
N
Me
OMe
Me
6d (dr = 3:2)
S-34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


CO2Me
O
H
N
Me
OMe
Me

6d (dr = 3:2)

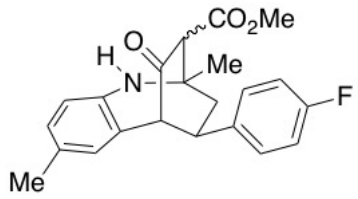
130.5
130.5
129.5
129.4
128.1
127.6
116.7
116.4
114.3
114.2
65.4
64.8
62.0
61.4
55.3
52.2
52.1
47.5
46.6
45.1
44.1
28.6
27.0
20.2
20.2


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

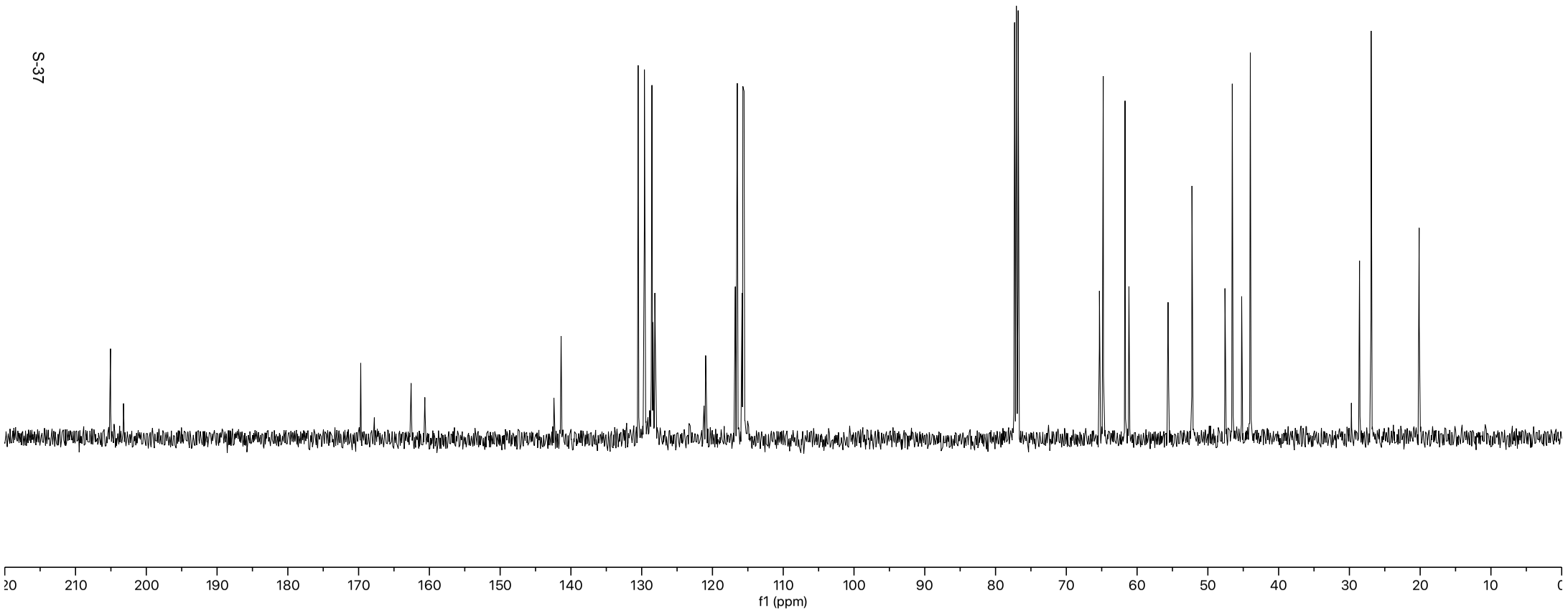


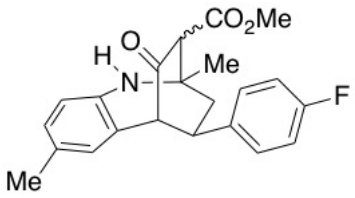
6e (dr = 3:2)

205.1
203.2
169.7
167.8
162.6
160.6
142.4
141.4
130.5
130.5
129.6
129.5
128.6
128.6
128.5
128.4
128.1
128.1
121.2
121.0
116.8
116.5
115.8
115.7
115.6
115.5
65.3
64.8
61.7
61.2
55.6
55.5
52.2
52.2
47.6
46.6
45.2
44.0
28.6
26.9
20.2
20.1

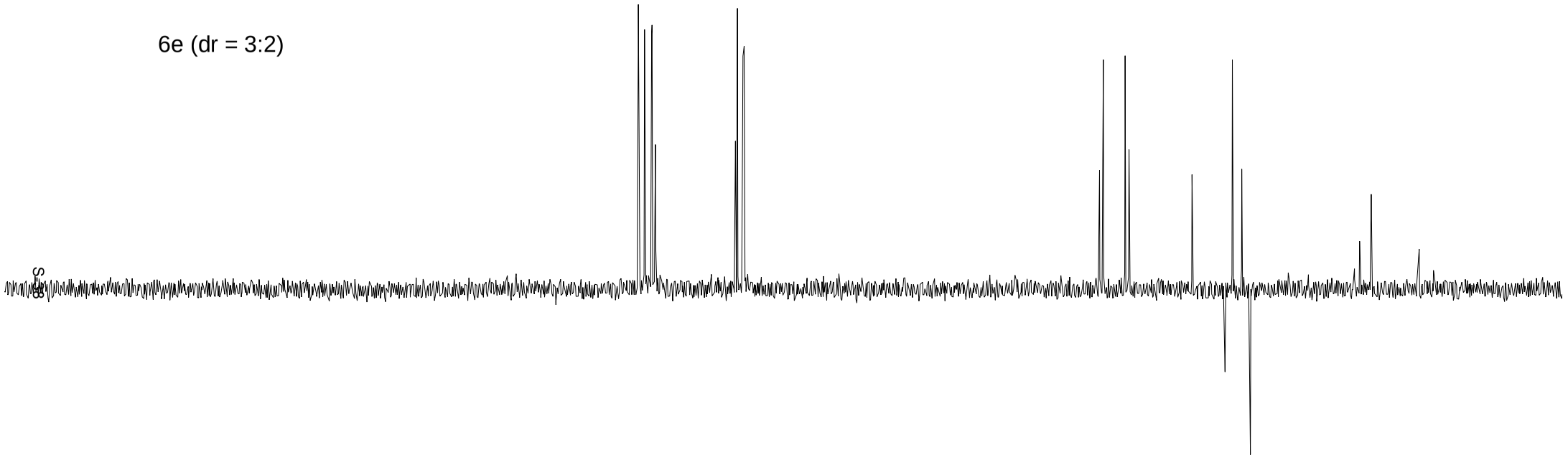


6e (dr = 3:2)





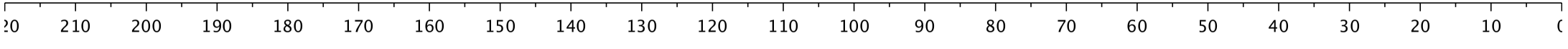
6e (dr = 3:2)

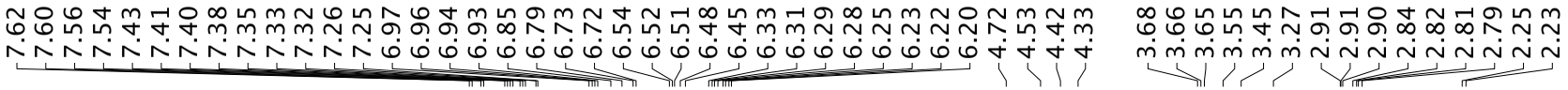


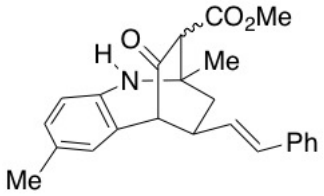
130.5 130.4 129.6 129.5 128.6 128.5 128.1 128.1 116.8 116.5 115.8 115.7 115.6 115.5

65.3 64.8 61.7 61.1 52.2 52.2 47.6 46.5 45.2 44.0

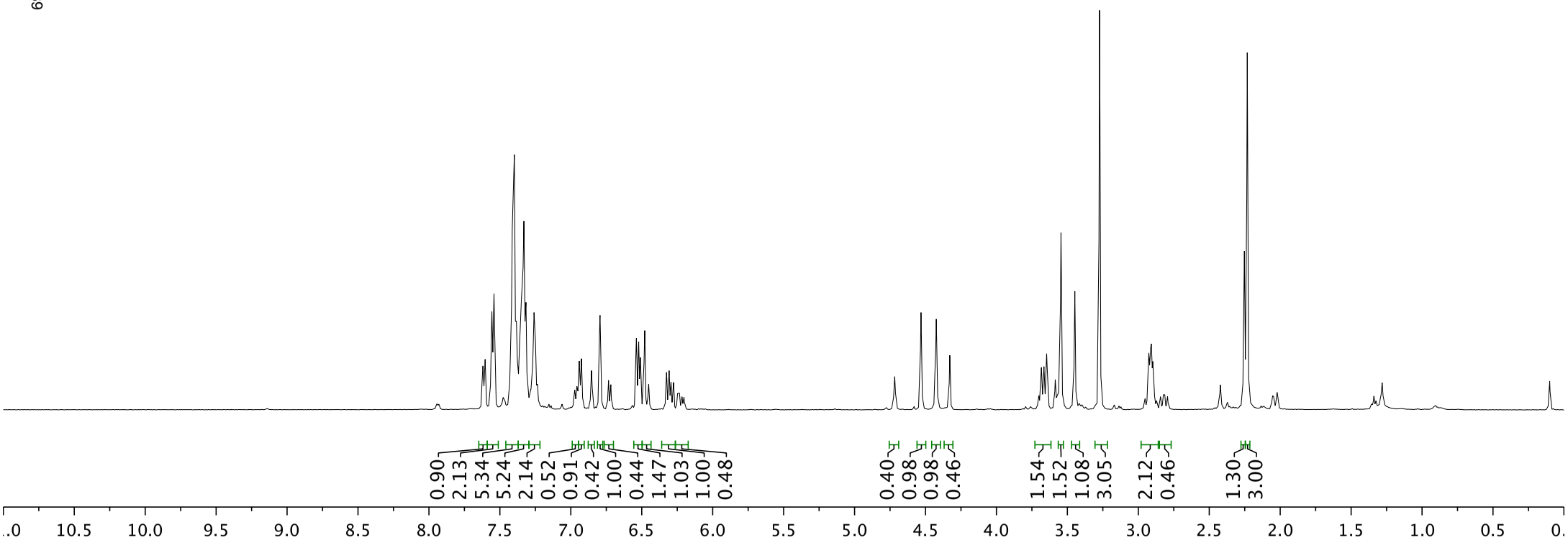
28.6 26.9 20.2 20.1

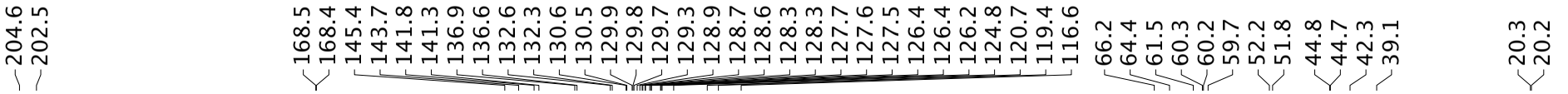


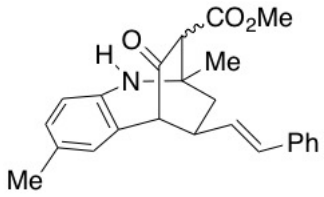

7.62
7.60
7.56
7.54
7.43
7.41
7.40
7.38
7.35
7.33
7.32
7.26
7.25
6.97
6.96
6.94
6.93
6.85
6.79
6.73
6.72
6.54
6.52
6.51
6.48
6.45
6.33
6.31
6.29
6.28
6.25
6.23
6.22
6.20
4.72
4.53
4.42
4.33
3.68
3.66
3.65
3.55
3.45
3.27
2.91
2.91
2.90
2.84
2.82
2.81
2.79
2.25
2.23


CO2Me
H
O
N
Me
Ph
Me

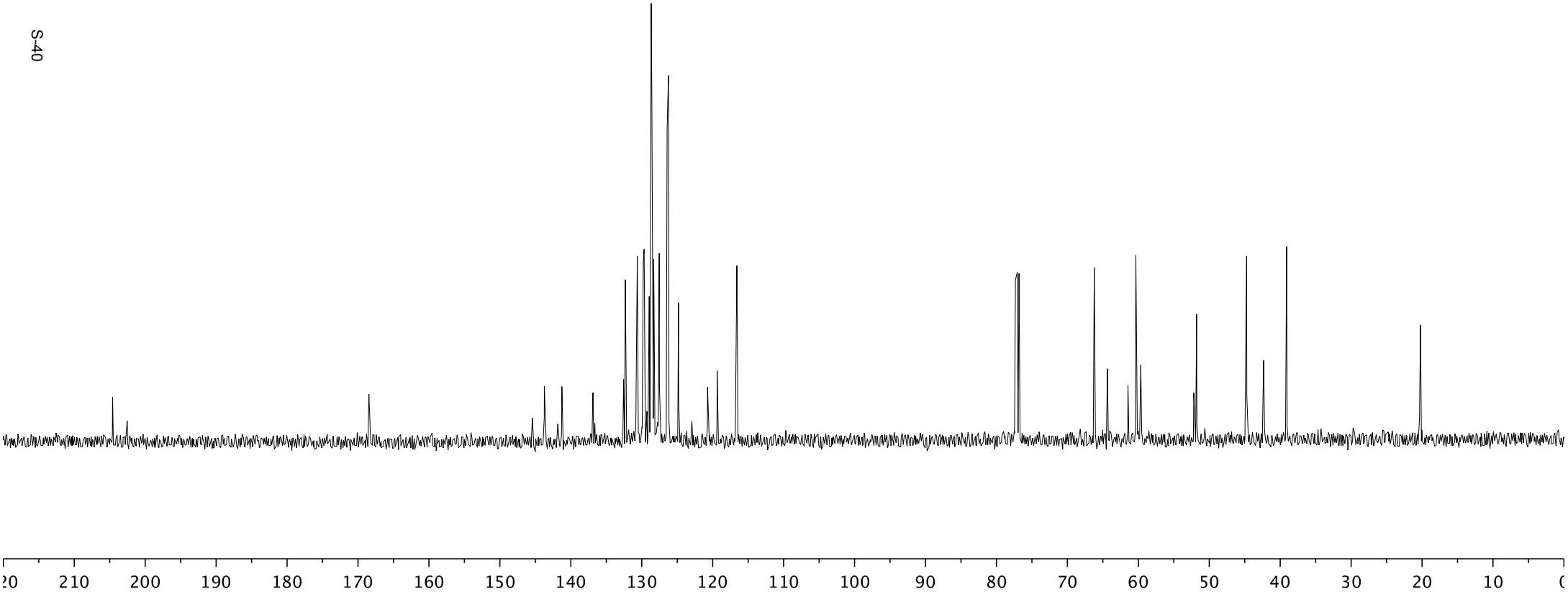
6f (dr = 2:1)

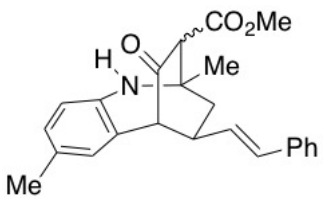

0.90
2.13
5.34
5.24
2.14
0.52
0.91
0.42
1.00
0.44
1.47
1.03
1.00
0.48
0.40
0.98
0.98
0.46
1.54
1.52
1.08
3.05
2.12
0.46
1.30
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


204.6
202.5
168.5
168.4
145.4
143.7
141.8
141.3
136.9
136.6
132.6
132.3
130.6
130.5
129.9
129.8
129.7
129.3
128.9
128.7
128.6
128.3
128.3
127.7
127.6
127.5
126.4
126.4
126.2
124.8
120.7
119.4
116.6
66.2
64.4
61.5
60.3
60.2
59.7
52.2
51.8
44.8
44.7
42.3
39.1
20.3
20.2


CO2Me
O
H
N
Me
Ph
Me

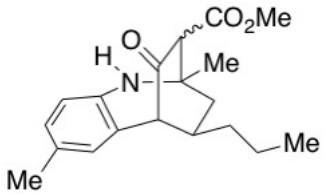
6f (dr = 2:1)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

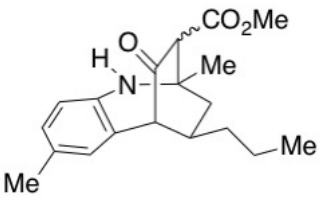

CO2Me
H
O
N
Me
Ph
Me

6f (dr = 2:1)

132.6
132.3
130.6
130.5
129.9
129.8
129.7
128.9
128.7
128.6
128.3
127.7
127.6
127.5
126.4
126.4
126.2
124.8
119.4
116.6
66.2
64.3
60.3
59.6
52.2
51.8
44.8
44.7
42.3
39.1
20.3
20.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

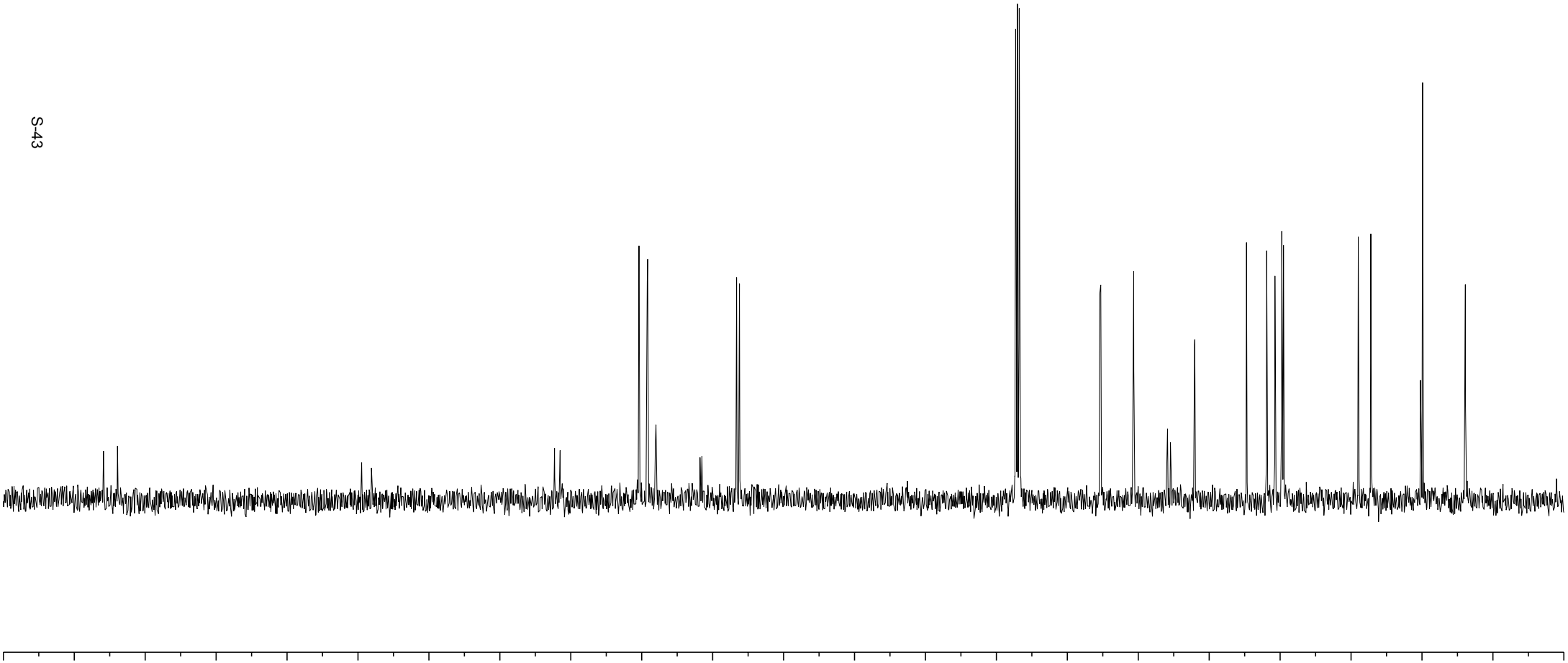


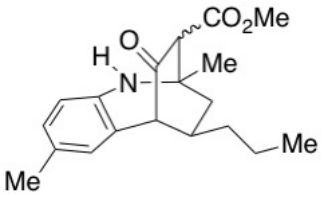
6g (dr = 1:1)



6g (dr = 1:1)

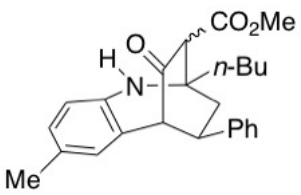
205.9
203.9
169.5
168.1
142.3
141.5
130.4
130.4
129.2
129.2
128.1
128.0
121.8
121.5
116.6
116.2
65.4
65.3
60.8
60.6
55.9
55.5
52.1
52.0
44.7
41.9
40.7
39.8
39.7
39.5
29.0
27.2
20.2
20.1
19.9
19.8
13.9
13.9



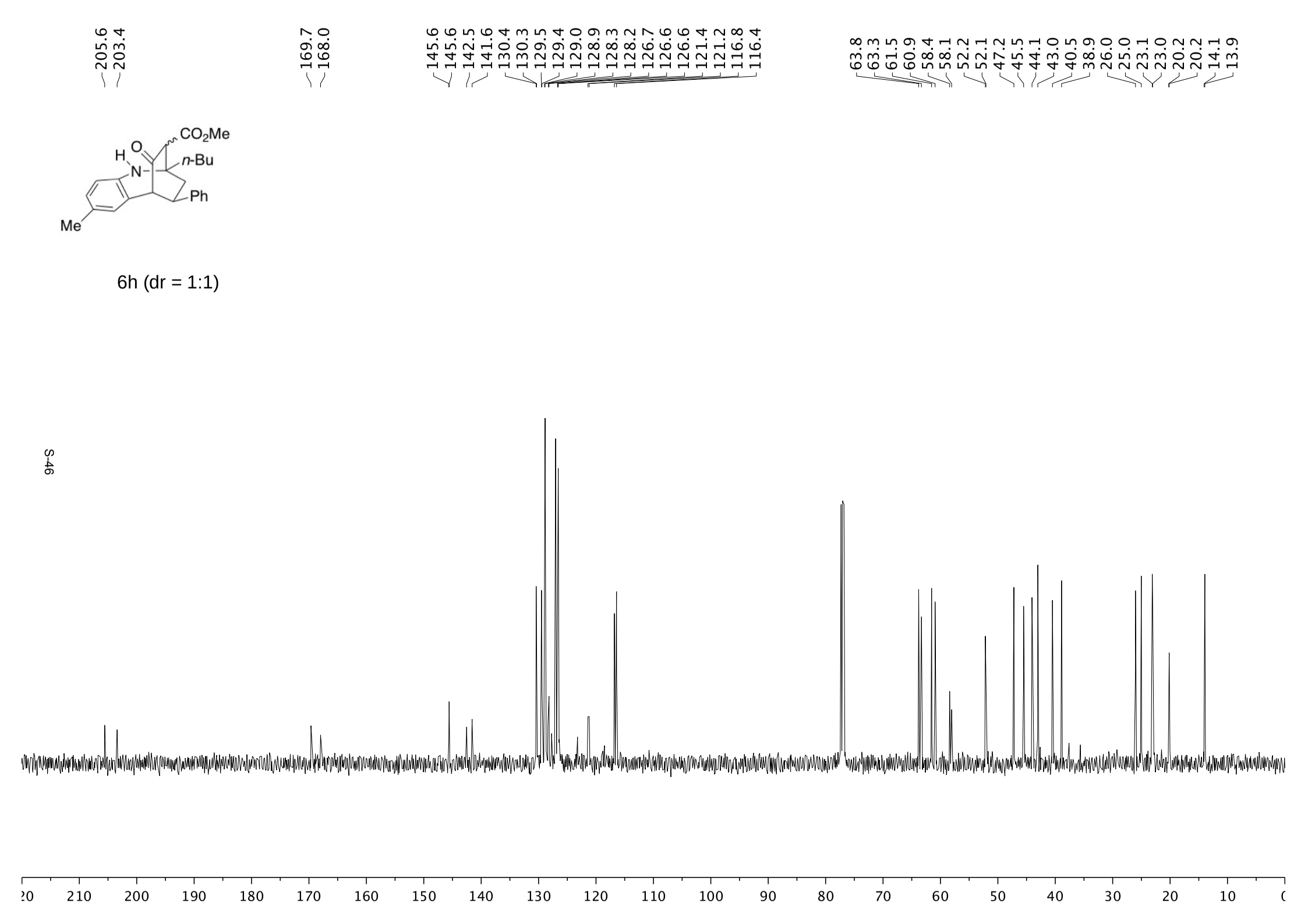

CO2Me
O
H
N
Me
Me
Me

6g (dr = 1:1)

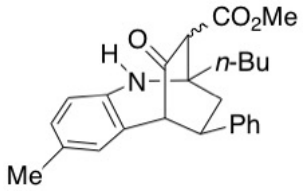
130.4
130.4
129.2
129.2
116.6
116.2
65.4
65.3
60.8
60.6
52.1
52.0
44.7
41.9
40.7
39.8
39.7
39.5
29.0
27.2
20.2
20.1
20.0
19.9
13.9
13.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



6h (dr = 1:1)

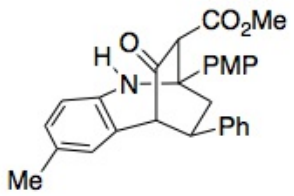

205.6
203.4
169.7
168.0
145.6
145.6
142.5
141.6
130.4
130.3
129.5
129.4
129.0
128.9
128.3
128.2
126.7
126.6
126.6
121.4
121.2
116.8
116.4
63.8
63.3
61.5
60.9
58.4
58.1
52.2
52.1
47.2
45.5
44.1
43.0
40.5
38.9
26.0
25.0
23.1
23.0
20.2
20.2
14.1
13.9
CO2Me
O
H
N
n-Bu
Ph
Me
S-46
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

6h (dr = 1:1)


CO2Me
O
H
N
n-Bu
Ph
Me

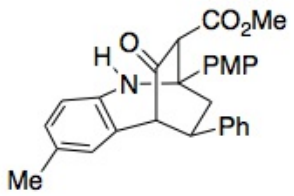
6h (dr = 1:1)

130.4
130.3
129.5
129.4
129.0
128.9
127.0
126.7
126.6
126.6
116.8
116.4
63.8
63.3
61.5
60.9
52.2
52.1
47.2
45.5
44.1
43.0
40.5
38.9
26.0
25.0
23.1
23.0
20.2
20.2
14.0
13.9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

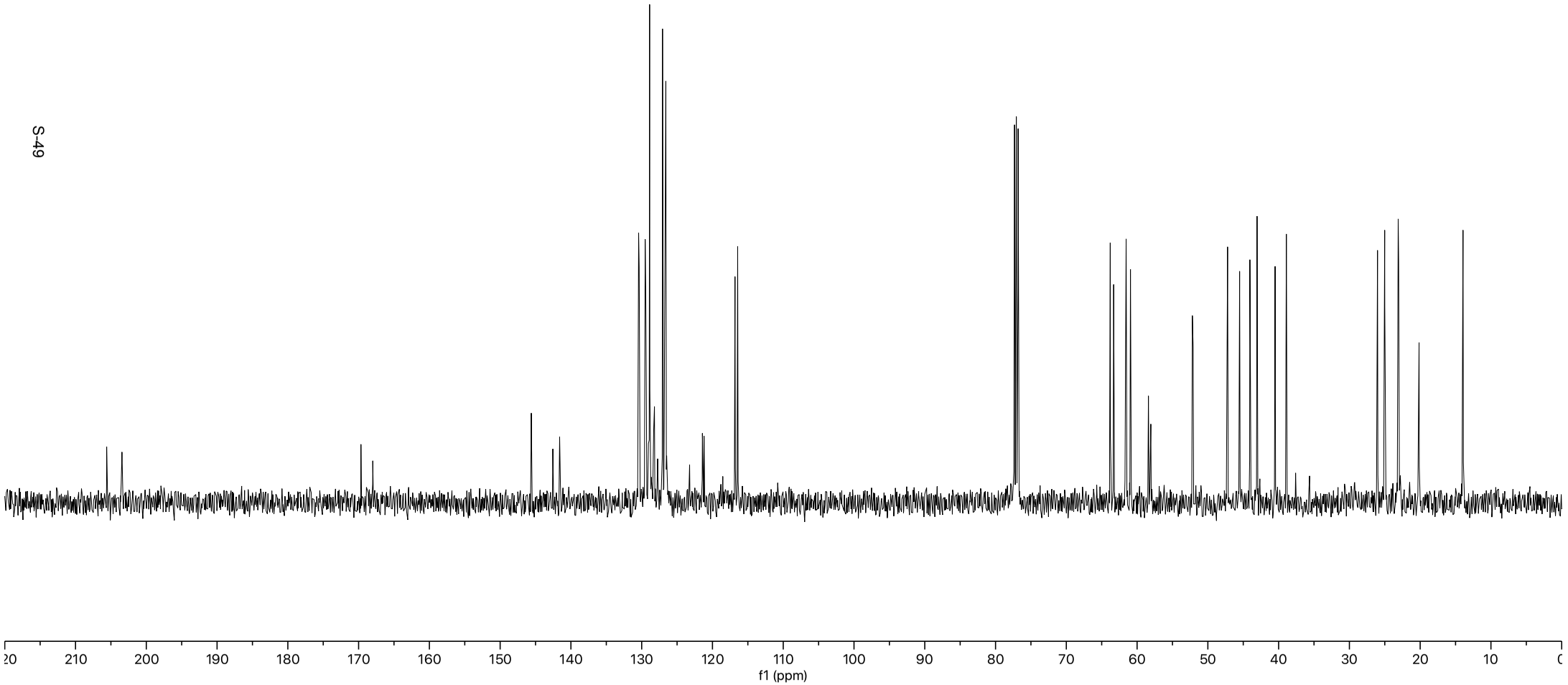


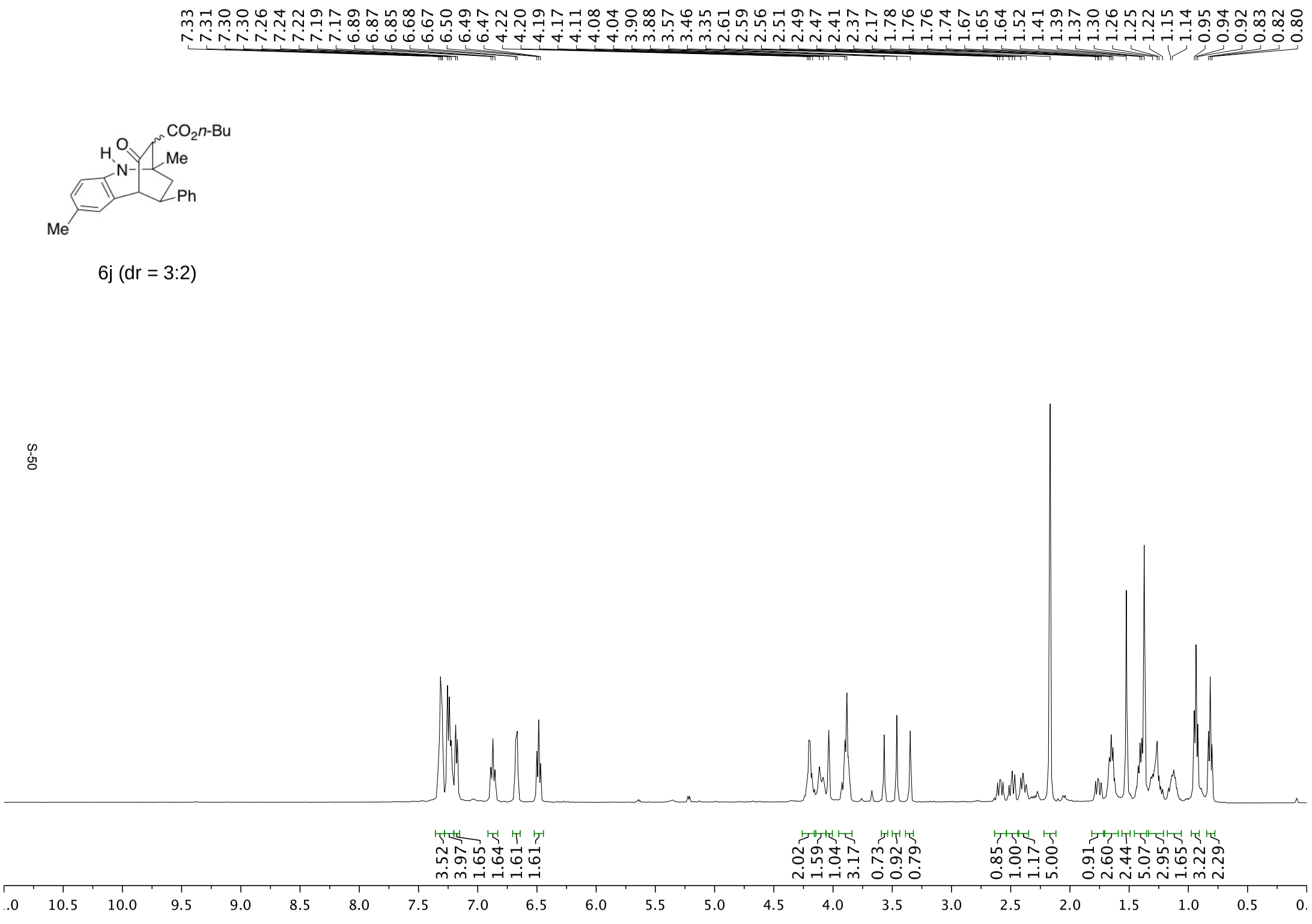
6i (dr = 20:1)

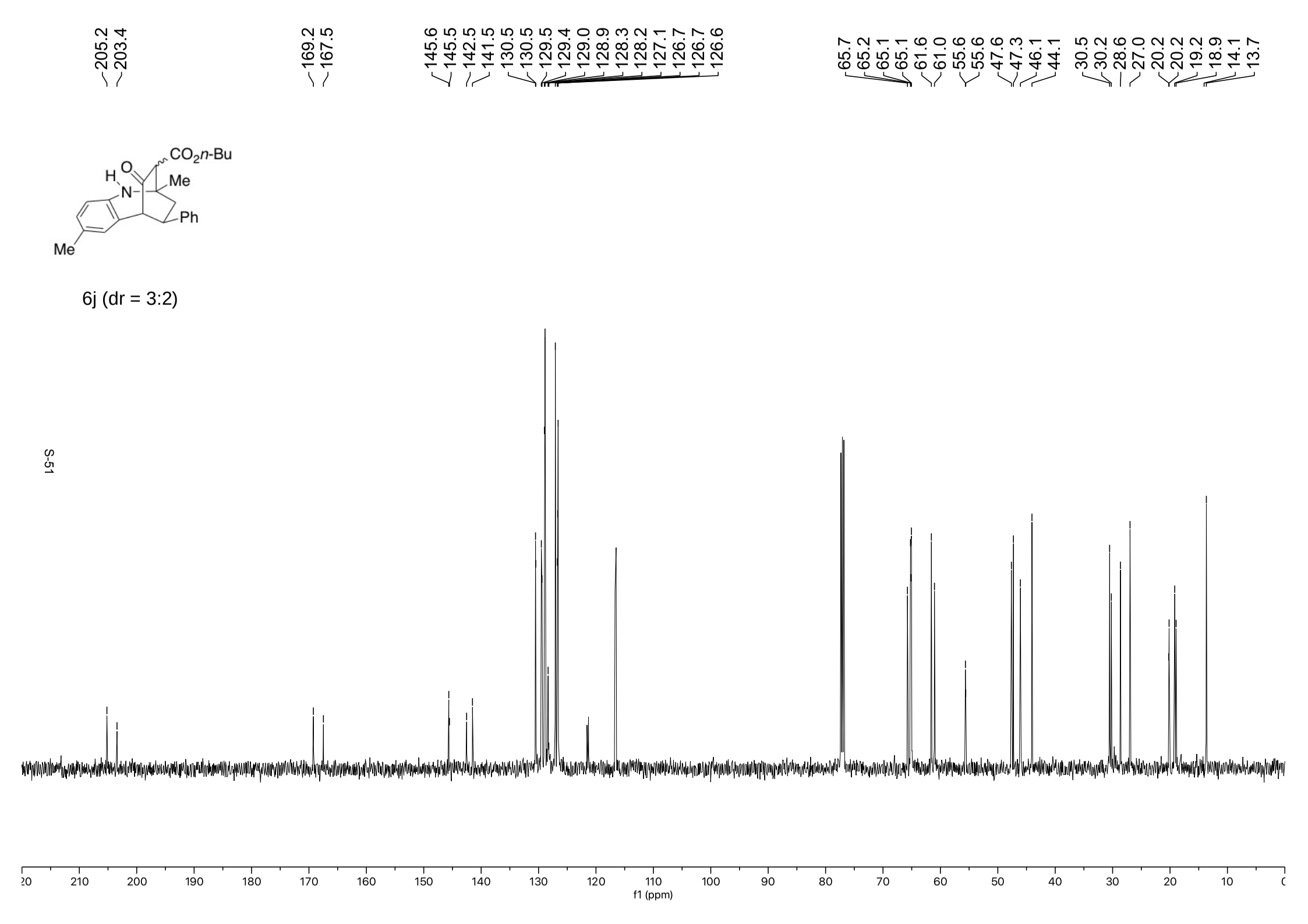
205.6
203.4
169.7
168.0
145.6
145.6
142.6
141.6
130.4
130.4
129.5
129.4
129.0
128.9
128.3
128.2
127.1
126.7
126.6
126.6
121.4
121.2
116.8
116.4
63.8
63.3
61.5
60.9
58.4
58.1
52.2
52.1
47.2
45.5
44.1
43.0
40.5
38.9
26.0
25.0
23.1
23.0
20.2
20.2
14.0
13.9

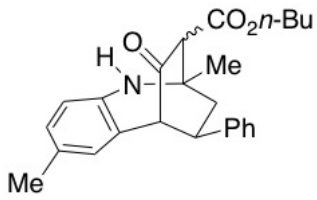


6i (dr = 20:1)



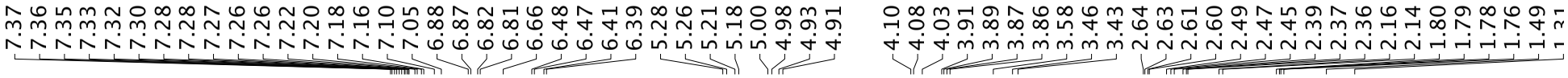

7.33 7.31 7.30 7.30 7.26 7.24 7.22 7.19 7.17 6.89 6.87 6.85 6.68 6.67 6.50 6.49 6.47 4.22 4.20 4.19 4.17 4.11 4.08 4.04 3.90 3.88 3.57 3.46 3.35 2.61 2.59 2.56 2.51 2.49 2.47 2.41 2.37 2.17 1.78 1.76 1.76 1.74 1.67 1.65 1.64 1.52 1.41 1.39 1.37 1.30 1.26 1.25 1.22 1.15 1.14 0.95 0.94 0.92 0.83 0.82 0.80
CO2n-Bu
O
H
N
Me
Ph
Me
6j (dr = 3:2)
S-50
3.52 3.97 1.65 1.64 1.61 1.61 2.02 1.59 1.04 3.17 0.73 0.92 0.79 0.85 1.00 1.17 5.00 0.91 2.60 2.44 5.07 2.95 1.65 3.22 2.29
10.5 10.0 9.5 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

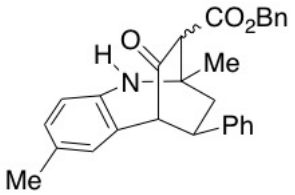

205.2
203.4
169.2
167.5
145.6
145.5
142.5
141.5
130.5
130.5
129.5
129.4
129.0
128.9
128.3
128.2
127.1
126.7
126.7
126.6
65.7
65.2
65.1
65.1
61.6
61.0
55.6
55.6
47.6
47.3
46.1
44.1
30.5
30.2
28.6
27.0
20.2
20.2
19.2
18.9
14.1
13.7
CO2n-Bu
O
H
N
Me
Ph
Me
6j (dr = 3:2)
S-51
f1 (ppm)


CO_2n-Bu
H
O
N
Me
Ph
Me

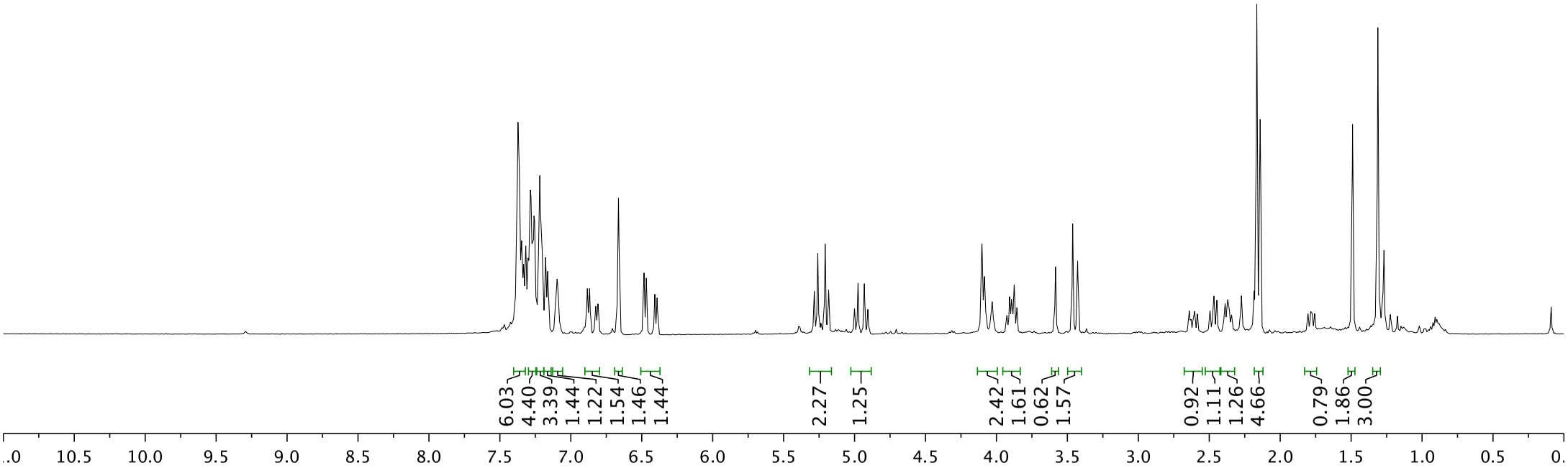
6j (dr = 3:2)

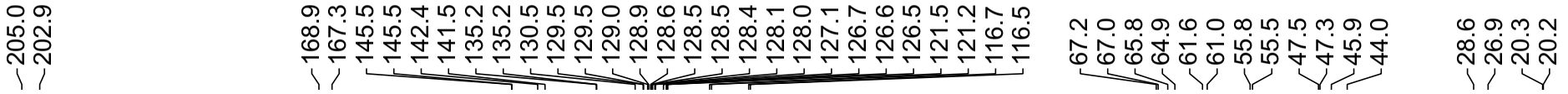
130.5
130.5
129.5
129.4
128.9
128.8
127.1
126.7
126.6
126.6
116.7
116.5
65.7
65.2
65.1
65.0
61.6
61.0
47.6
47.3
46.1
44.0
30.5
30.2
28.6
27.0
20.2
20.2
19.2
18.9
13.9
13.7
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

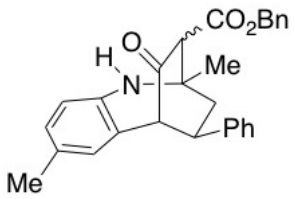

7.37
7.36
7.35
7.33
7.32
7.30
7.28
7.28
7.27
7.26
7.26
7.22
7.20
7.18
7.16
7.10
7.05
6.88
6.87
6.82
6.81
6.66
6.48
6.47
6.41
6.39
5.28
5.26
5.21
5.18
5.00
4.98
4.93
4.91
4.10
4.08
4.03
3.91
3.89
3.87
3.86
3.58
3.46
3.43
2.64
2.63
2.61
2.60
2.49
2.47
2.45
2.39
2.37
2.36
2.16
2.14
1.80
1.79
1.78
1.76
1.49


CO2Bn
H
O
N
Me
Ph
Me

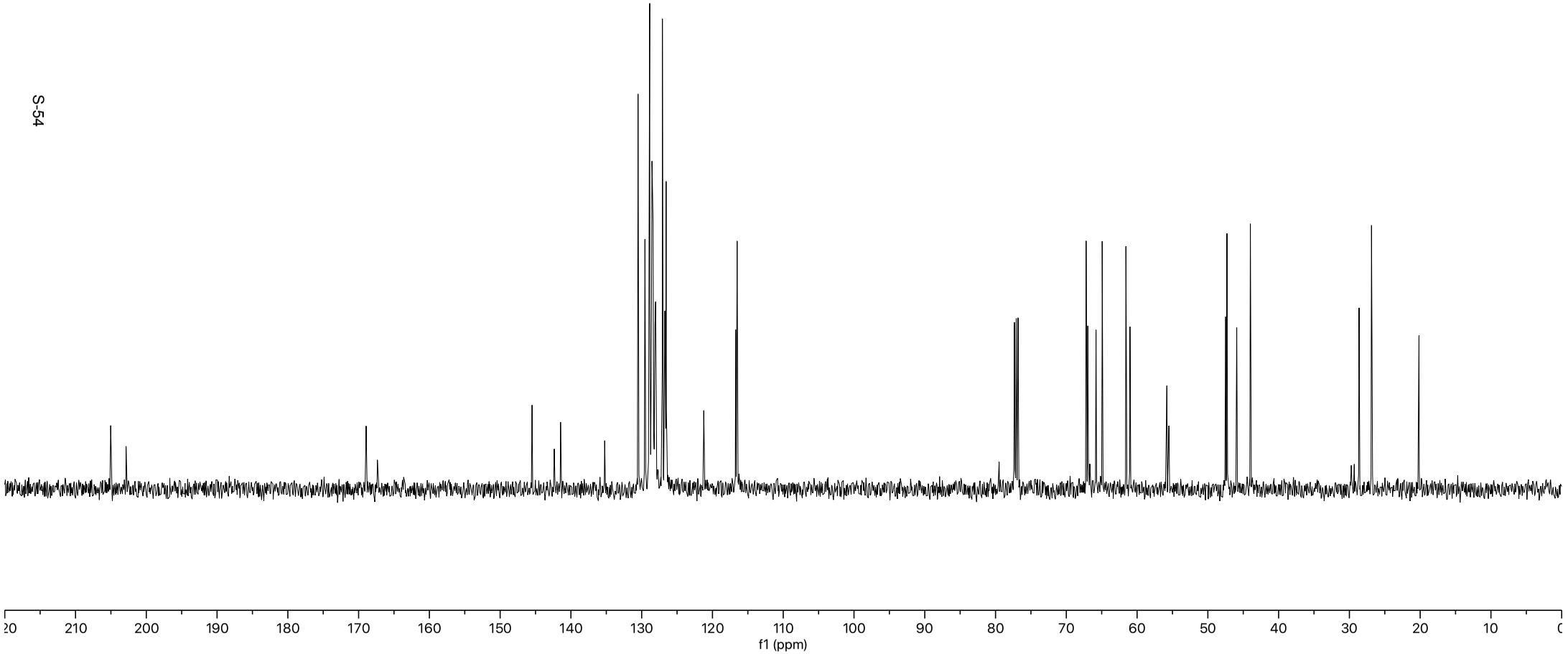
6k (dr = 3:2)

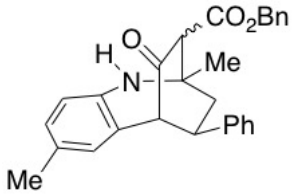

6.03
4.40
3.39
1.44
1.22
1.54
1.46
1.44
2.27
1.25
2.42
1.61
0.62
1.57
0.92
1.11
1.26
4.66
0.79
1.86
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


205.0
202.9
168.9
167.3
145.5
145.5
142.4
141.5
135.2
135.2
130.5
129.5
129.5
129.0
128.9
128.6
128.5
128.5
128.4
128.1
128.0
127.1
126.7
126.6
126.5
121.5
121.2
116.7
116.5
67.2
67.0
65.8
64.9
61.6
61.0
55.8
55.5
47.5
47.3
45.9
44.0
28.6
26.9
20.3
20.2


CO2Bn
O
H
N
Me
Ph
Me

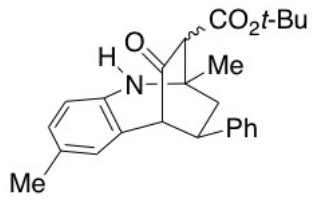
6k (dr = 3:2)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

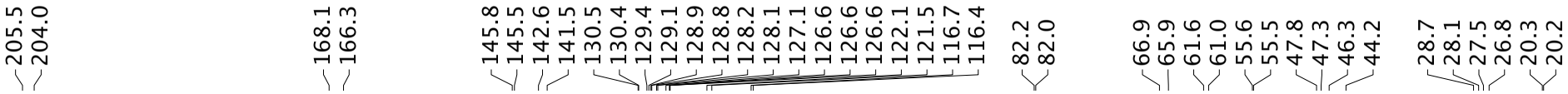

CO_2Bn
O
H
N
Me
Ph
Me

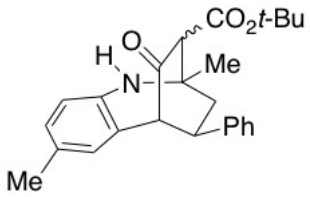
6k (dr = 3:2)

130.5
129.5
129.5
129.0
128.9
128.6
128.5
128.5
128.4
128.1
128.0
127.7
127.1
126.7
126.6
126.5
116.7
116.5
67.2
67.0
65.8
64.9
61.6
61.0
47.5
47.3
45.9
44.0
28.6
26.9
20.2
20.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

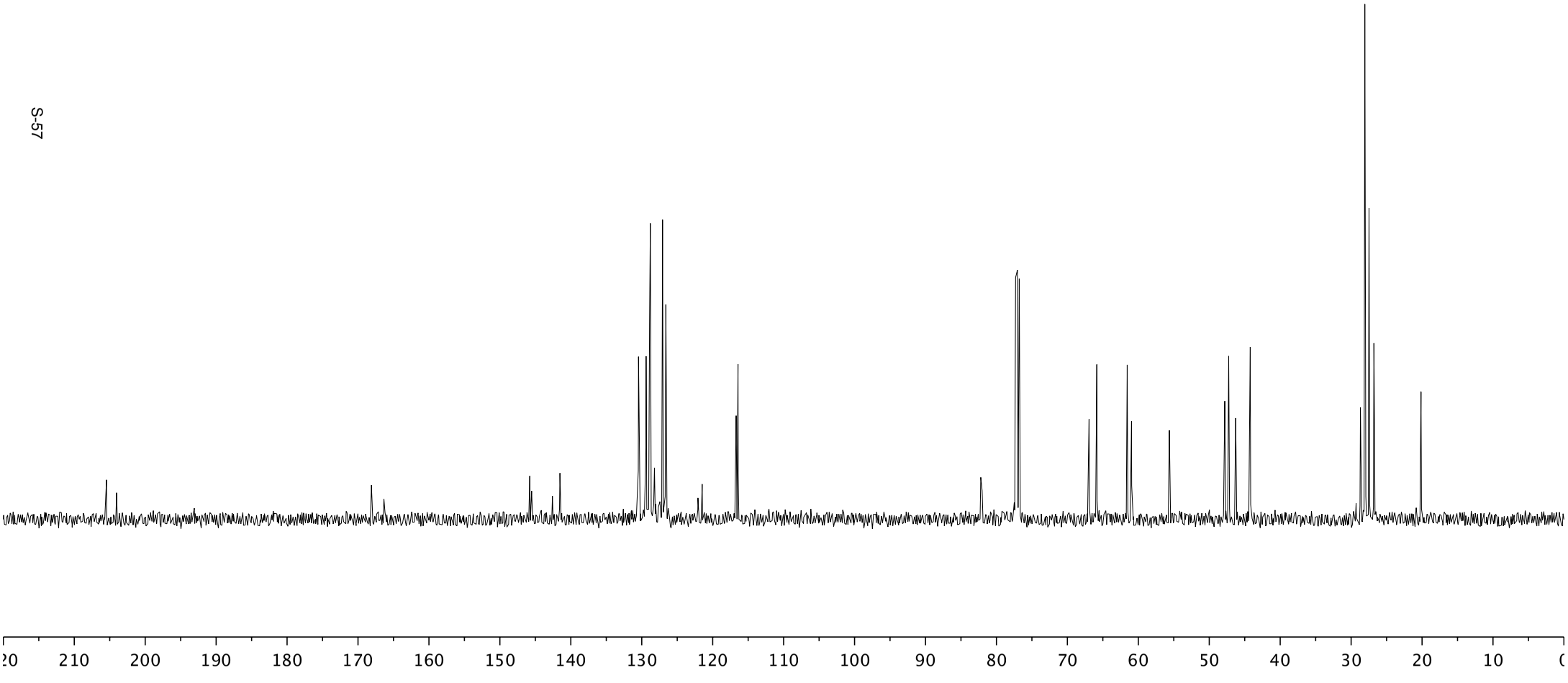


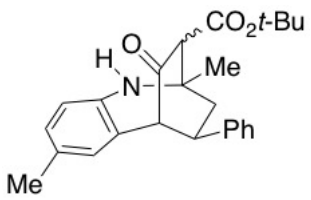
6l (dr = 1:1)


205.5
204.0
168.1
166.3
145.8
145.5
142.6
141.5
130.5
130.4
129.4
129.1
128.9
128.8
128.2
128.1
127.1
126.6
126.6
126.6
122.1
121.5
116.7
116.4
82.2
82.0
66.9
65.9
61.6
61.0
55.6
55.5
47.8
47.3
46.3
44.2
28.7
28.1
27.5
26.8
20.3
20.2


CO2t-Bu
O
H
N
Me
Ph
Me

6l (dr = 1:1)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



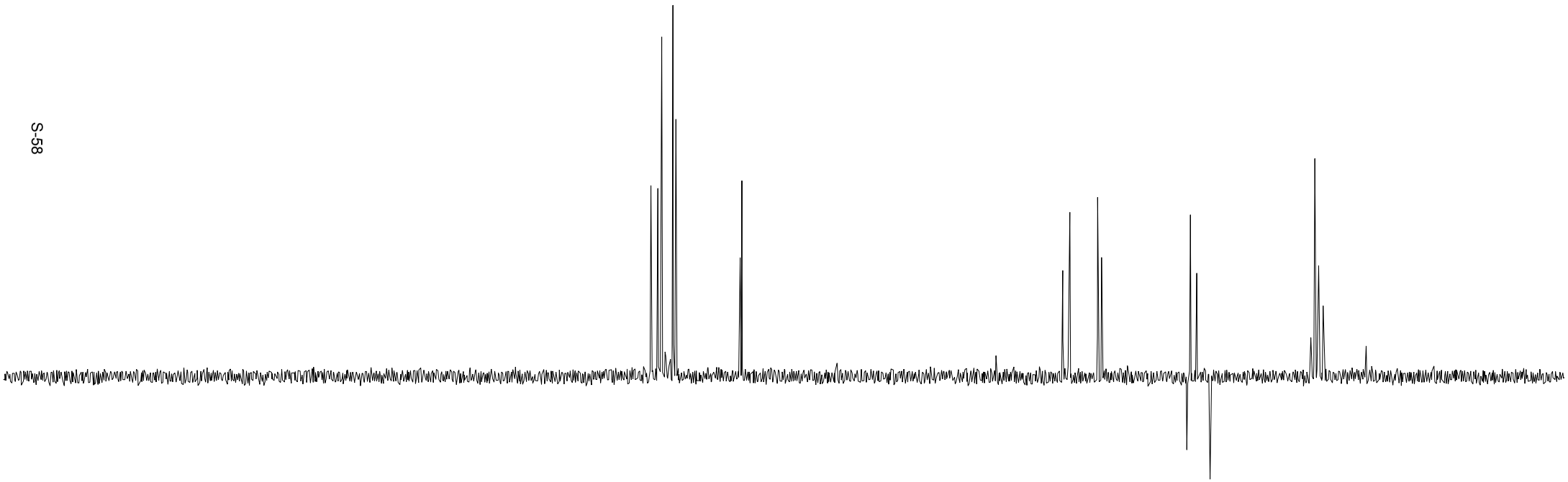
6l (dr = 1:1)

130.5
130.4
129.4
129.1
128.9
128.8
127.1
126.6
126.6
126.6
116.7
116.4

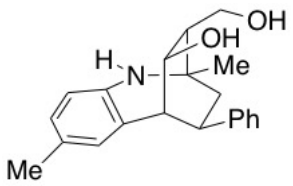
66.9
65.9
61.6
61.0

47.8
47.3
46.3
44.2

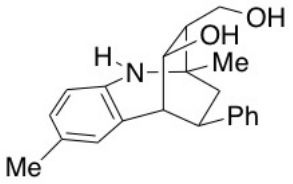
28.7
28.1
27.5
26.8
20.3
20.2



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

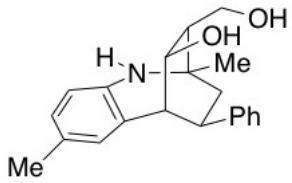


9 (dr = >20:1)


OH
OH
H
N
Me
Ph
Me

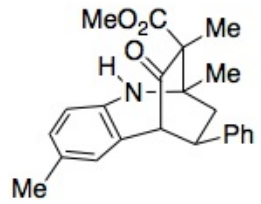
9 (dr = >20:1)

146.62
143.67
129.84
128.40
128.20
127.97
127.24
126.71
125.93
115.87
75.55
61.87
54.43
52.21
46.49
42.42
40.96
26.09
20.29
S-60
f1 (ppm)



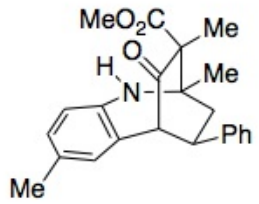
9 (dr = >20:1)

129.8
128.4
128.2
128.0
125.9
115.9
75.5
52.2
46.5
42.4
40.9
26.1
20.3

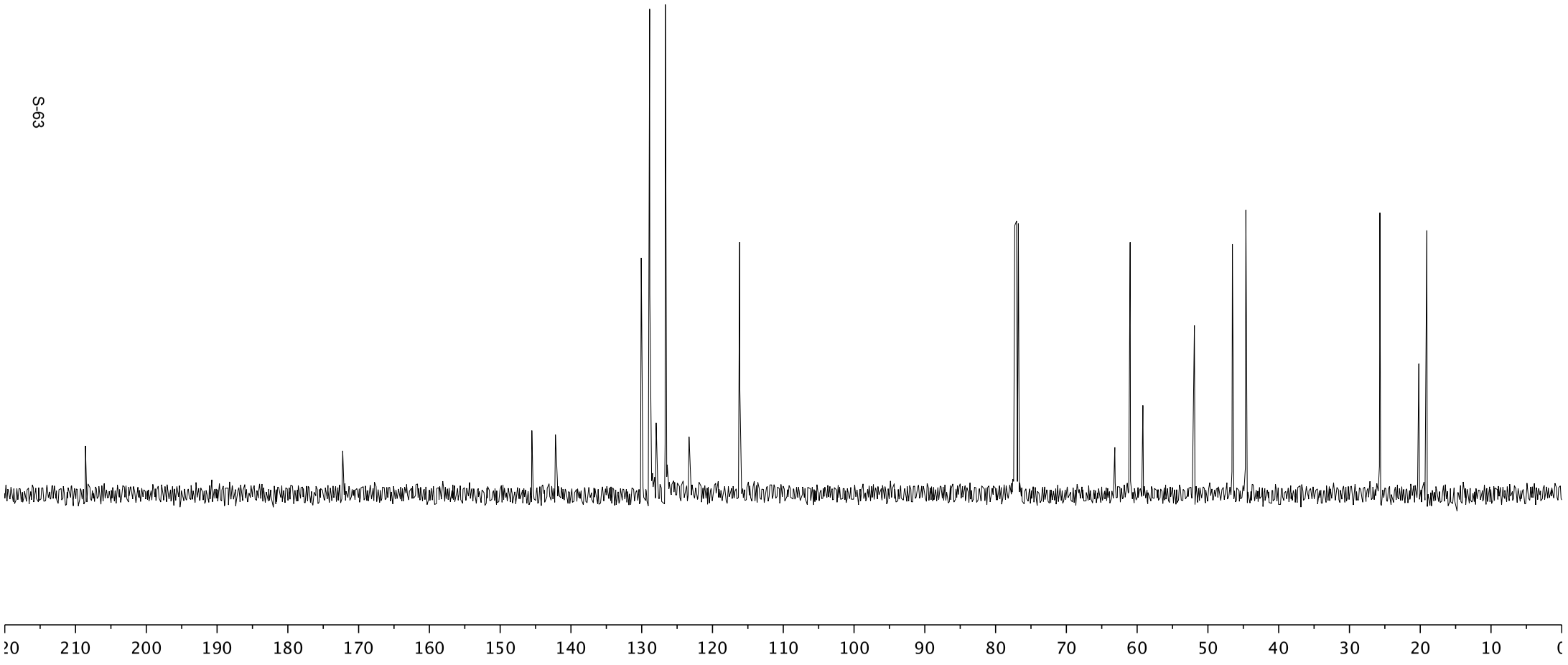


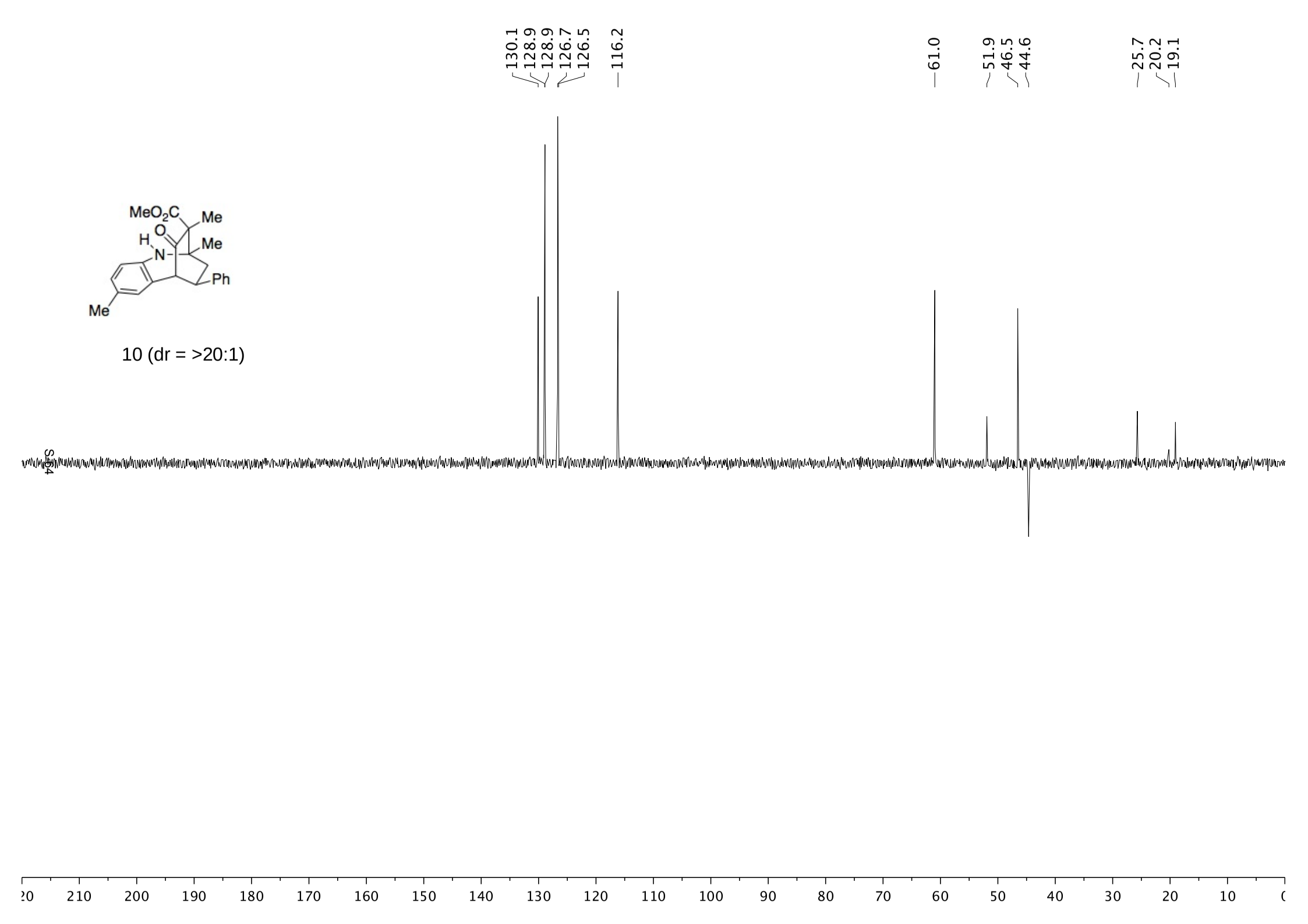
10 (dr = >20:1)

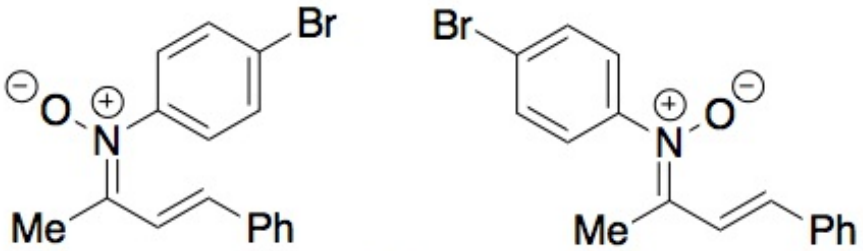
208.6
172.2
145.5
142.2
130.1
128.9
128.9
128.0
126.7
126.6
123.3
116.2
63.2
61.0
59.2
51.9
46.5
44.6
25.7
20.2
19.1



10 (dr = >20:1)



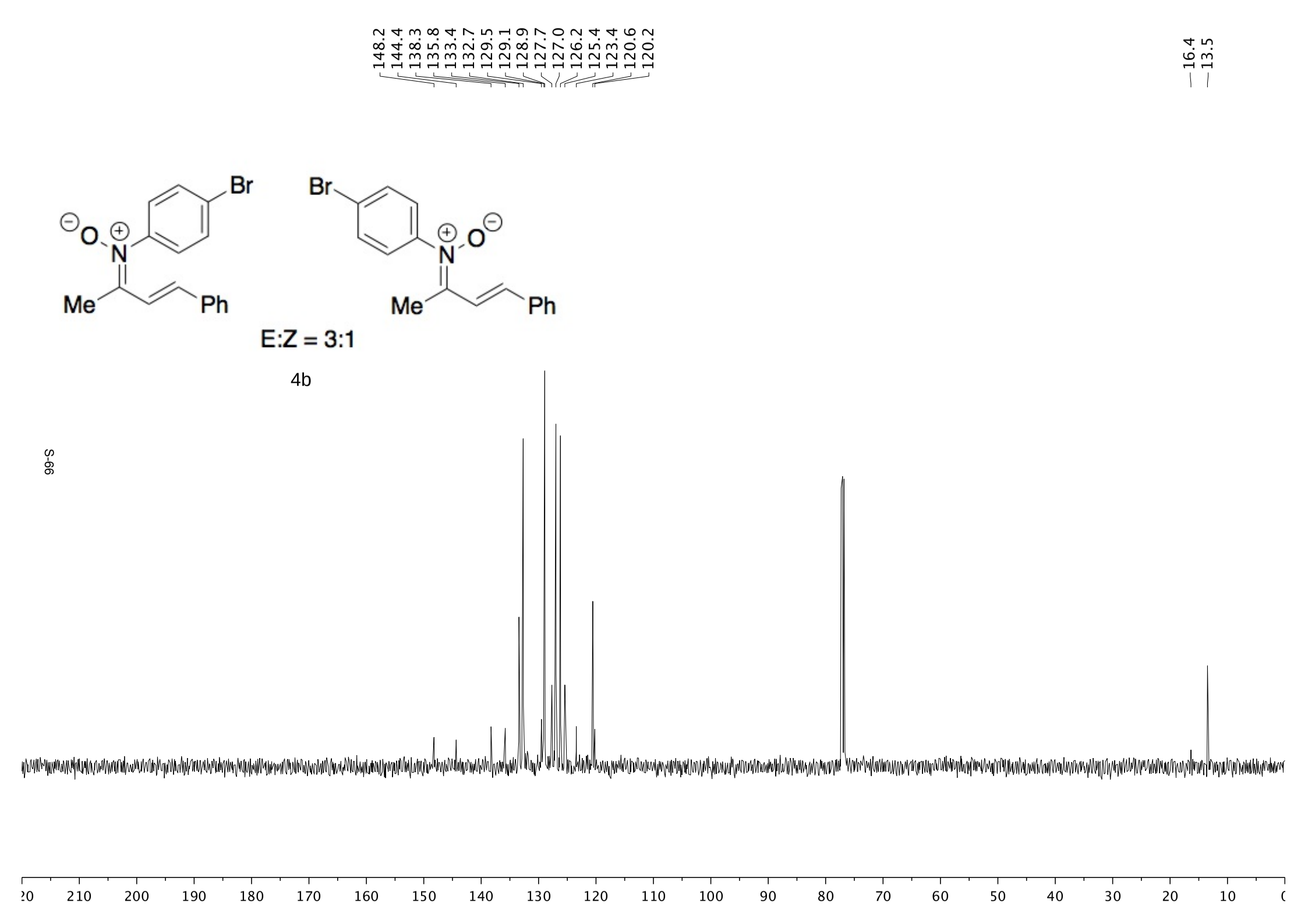

130.1
128.9
128.9
126.7
126.5
116.2
61.0
51.9
46.5
44.6
25.7
20.2
19.1
MeO2C
Me
O
H
N
Me
Me
Ph
10 (dr = >20:1)
S4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

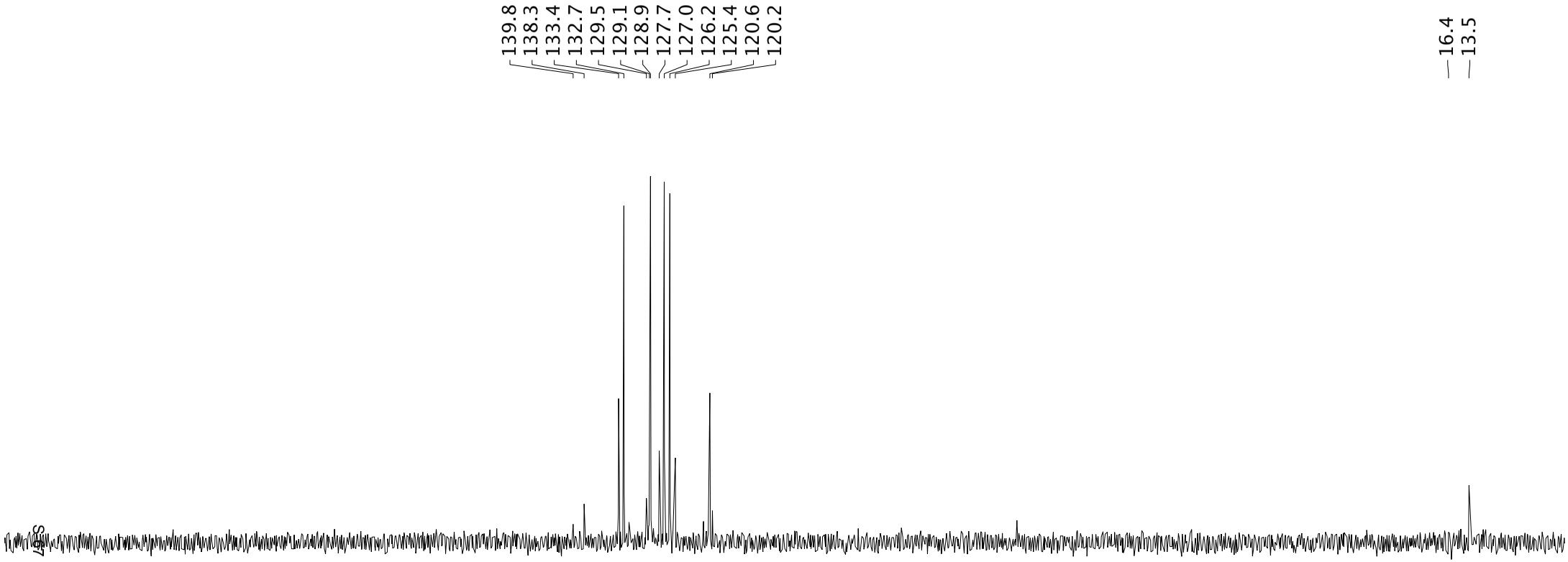

Br
O
N
Me
Ph
Br
N
O
Me
Ph

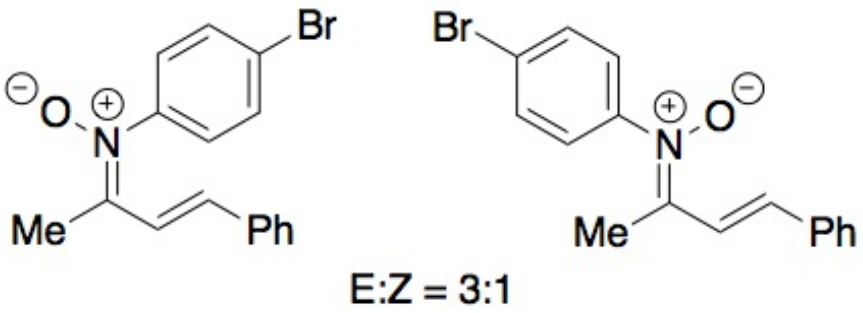
E:Z = 3:1

4b

8.02
7.99
7.64
7.62
7.60
7.42
7.37
7.34
7.31
7.29
7.26
7.16
7.12
6.85
6.82
6.71
6.68
2.52
2.08
S-65
0.25
2.95
7.13
0.52
1.05
1.08
3.00
0.71
10.5
10.0
9.5
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

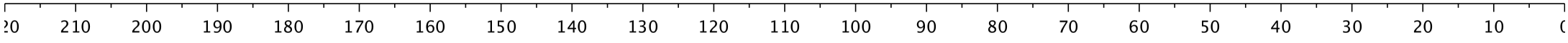

148.2
144.4
138.3
135.8
133.4
132.7
129.5
129.1
128.9
127.7
127.0
126.2
125.4
123.4
120.6
120.2
16.4
13.5
Br
O
N
Me
Ph
Br
O
N
Me
Ph
E:Z = 3:1
4b
S-66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

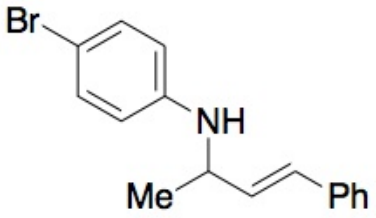

139.8
138.3
133.4
132.7
129.5
129.1
128.9
127.7
127.0
126.2
125.4
120.6
120.2
16.4
13.5


Br
O
N
Me
Ph
Br
O
N
Me
Ph

E:Z = 3:1

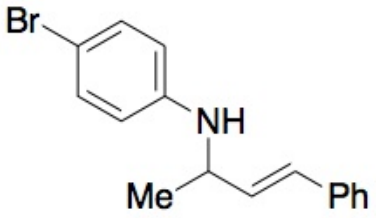
4b


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Br
NH
Me
Ph

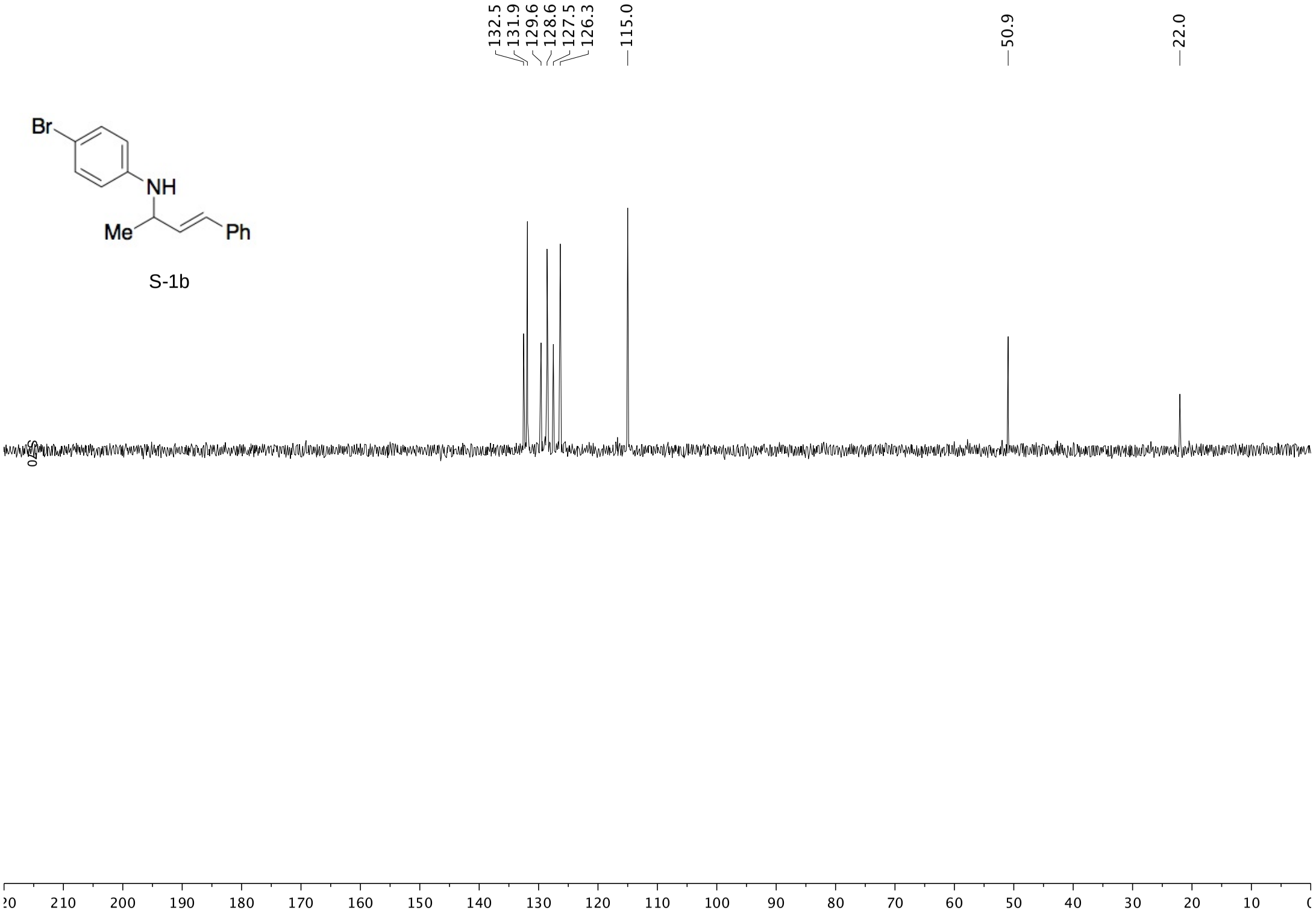
S-1b

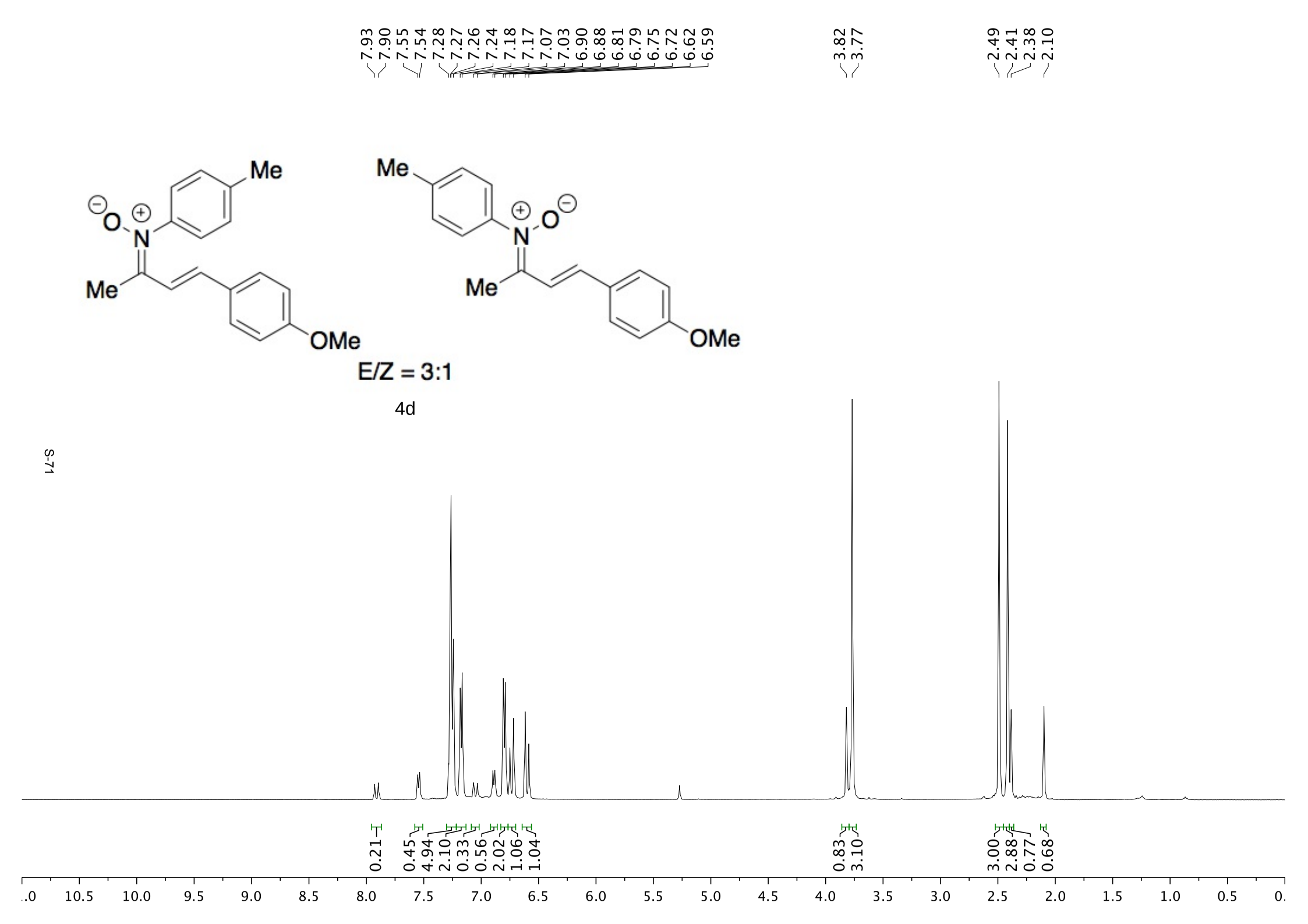
7.36
7.35
7.32
7.31
7.29
7.24
7.23
6.57
6.53
6.52
6.20
6.19
6.17
6.15
4.11
4.10
4.08
3.67
1.41
1.40
S-68
2.17
2.43
3.05
3.16
0.96
1.00
1.33
2.92
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

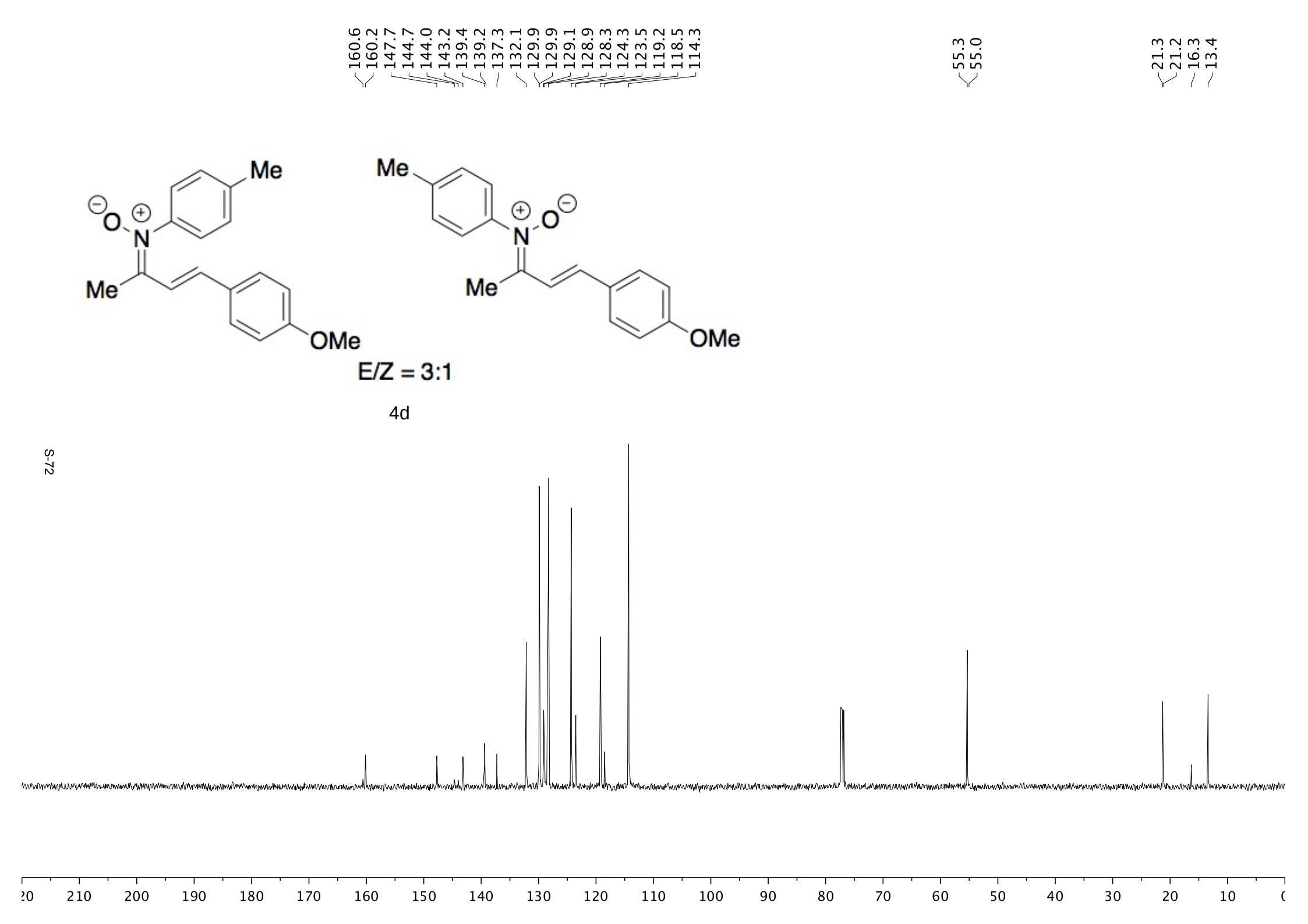

Br
NH
Me
Ph

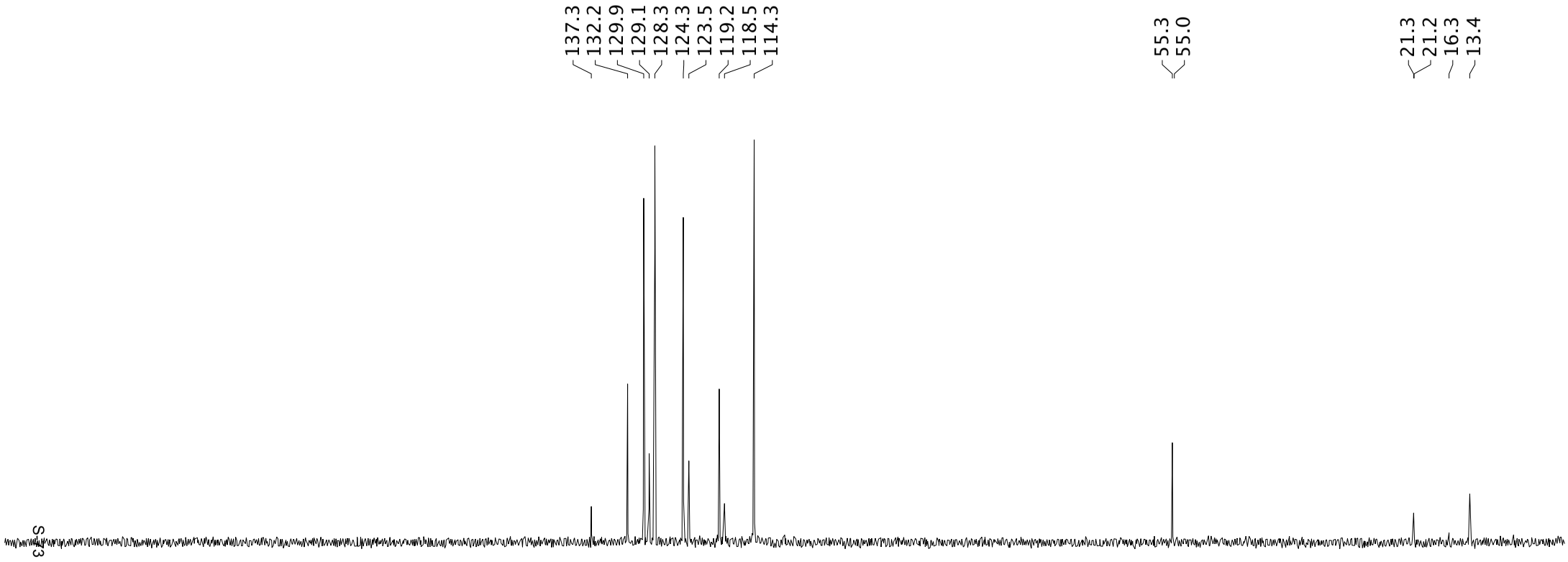
S-1b

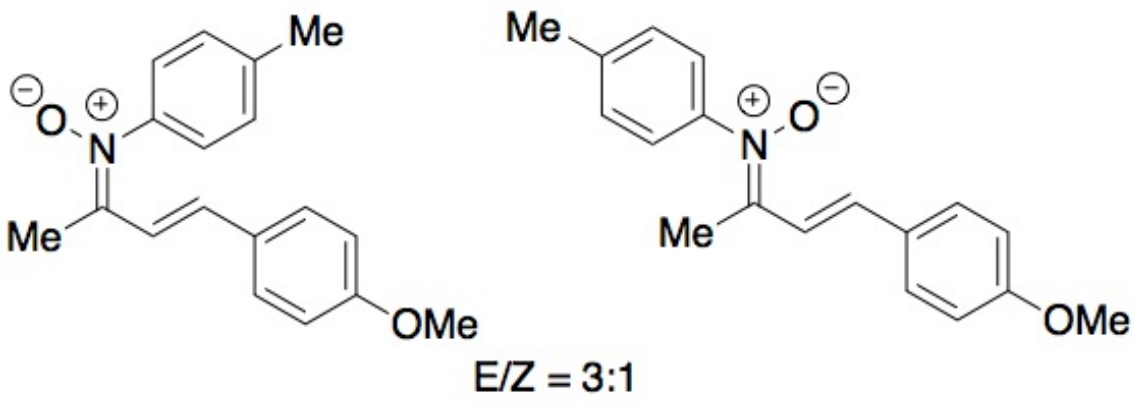
146.4
136.8
132.5
131.9
129.6
128.6
127.5
126.3
115.0
108.9
50.9
22.0
S-69
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


132.5
131.9
129.6
128.6
127.5
126.3
115.0
50.9
22.0
Br
NH
Me
Ph
S-1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.93
7.90
7.55
7.54
7.28
7.27
7.26
7.24
7.18
7.17
7.07
7.03
6.90
6.88
6.81
6.79
6.75
6.72
6.62
6.59
3.82
3.77
2.49
2.41
2.38
2.10
Me
O
N
Me
OMe
Me
O
N
Me
OMe
E/Z = 3:1
4d
S-71
0.21
0.45
4.94
2.10
0.33
0.56
2.02
1.06
1.04
0.83
3.10
3.00
2.88
0.77
0.68
10.5
10.0
9.5
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

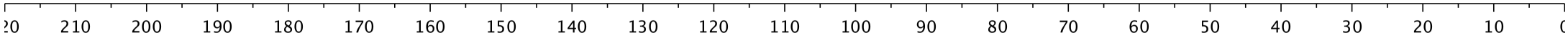

160.6
160.2
147.7
144.7
144.0
143.2
139.4
139.2
137.3
132.1
129.9
129.9
129.1
128.9
128.3
124.3
123.5
119.2
118.5
114.3
55.3
55.0
21.3
21.2
16.3
13.4
Me
O
N
Me
OMe
Me
O
N
Me
OMe
E/Z = 3:1
4d
S-72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

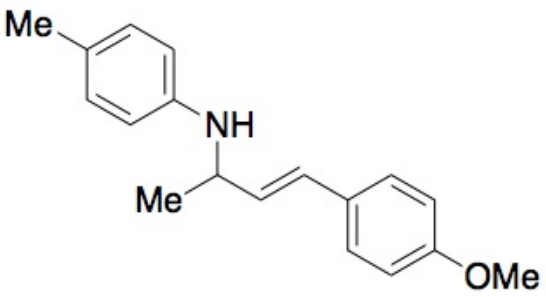

137.3
132.2
129.9
129.1
128.3
124.3
123.5
119.2
118.5
114.3
55.3
55.0
21.3
21.2
16.3
13.4
S3


Me
O
N
Me
OMe
Me
O
N
Me
OMe

E/Z = 3:1

4d


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Me
NH
Me
OMe

S-1d

7.30
7.29
7.26
6.99
6.97
6.85
6.83
6.60
6.58
6.54
6.51
6.11
6.10
6.07
6.06
4.15
4.11
4.10
4.09
3.80
2.24
1.40
1.38
2.25
2.20
2.07
1.99
0.96
0.96
1.00
3.24
3.35
2.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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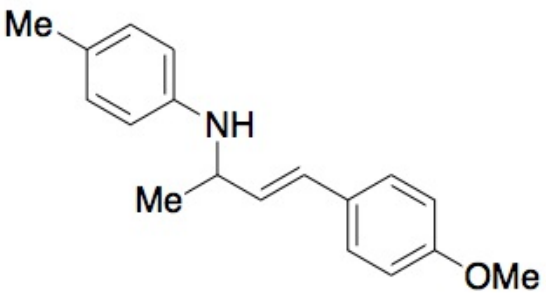
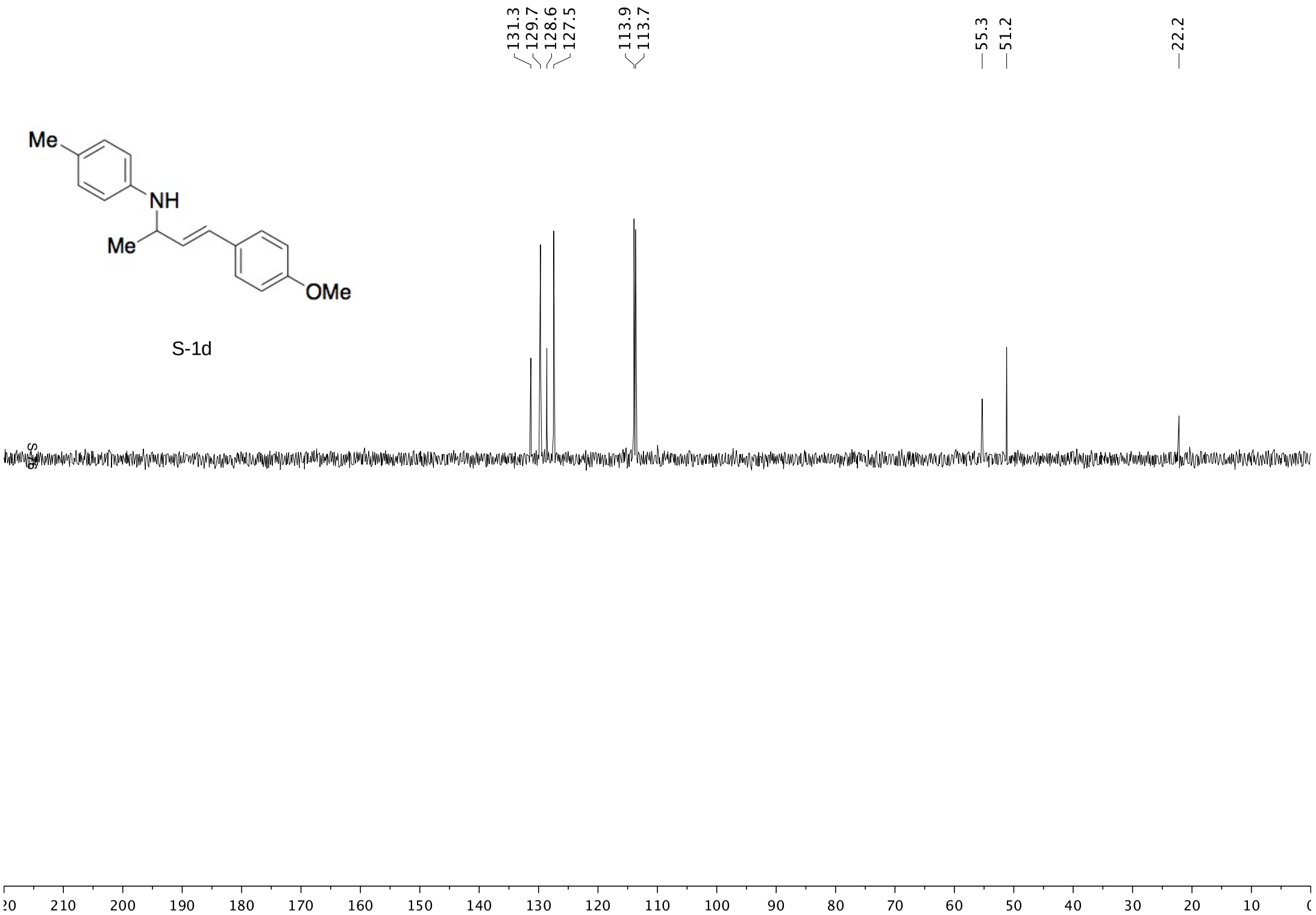
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


Me
NH
Me
OMe

S-1d

159.0
145.2
131.3
129.9
129.7
128.6
127.5
126.5
113.9
113.7
55.3
51.2
22.2
20.4
S-75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


131.3
129.7
128.6
127.5
113.9
113.7
55.3
51.2
22.2
Me
NH
Me
OMe
S-1d
210
200
190
180
170
160
150
140
130
120
110
100
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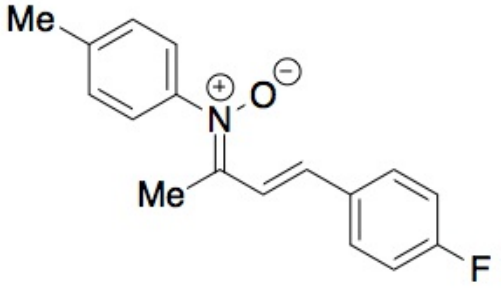
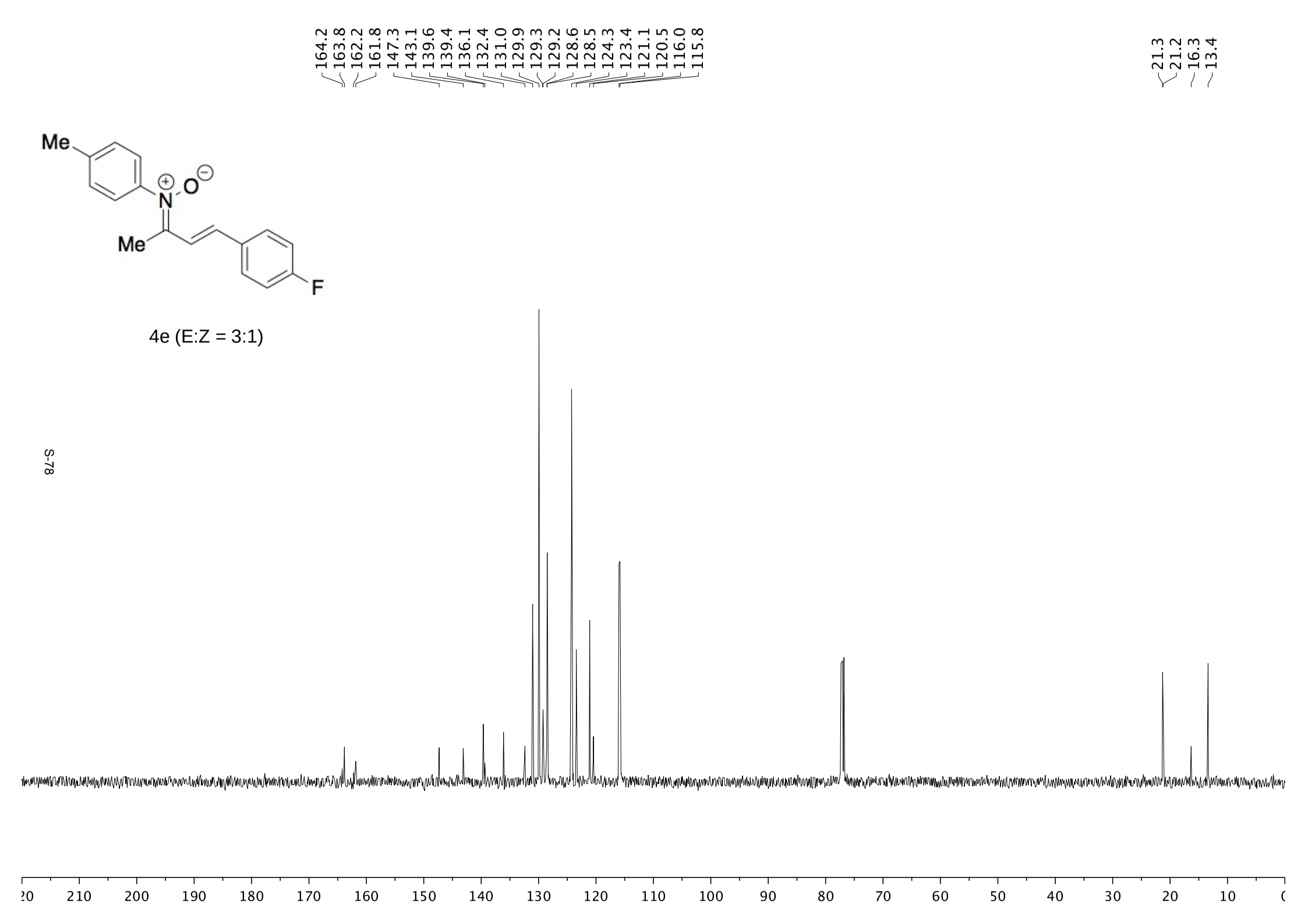
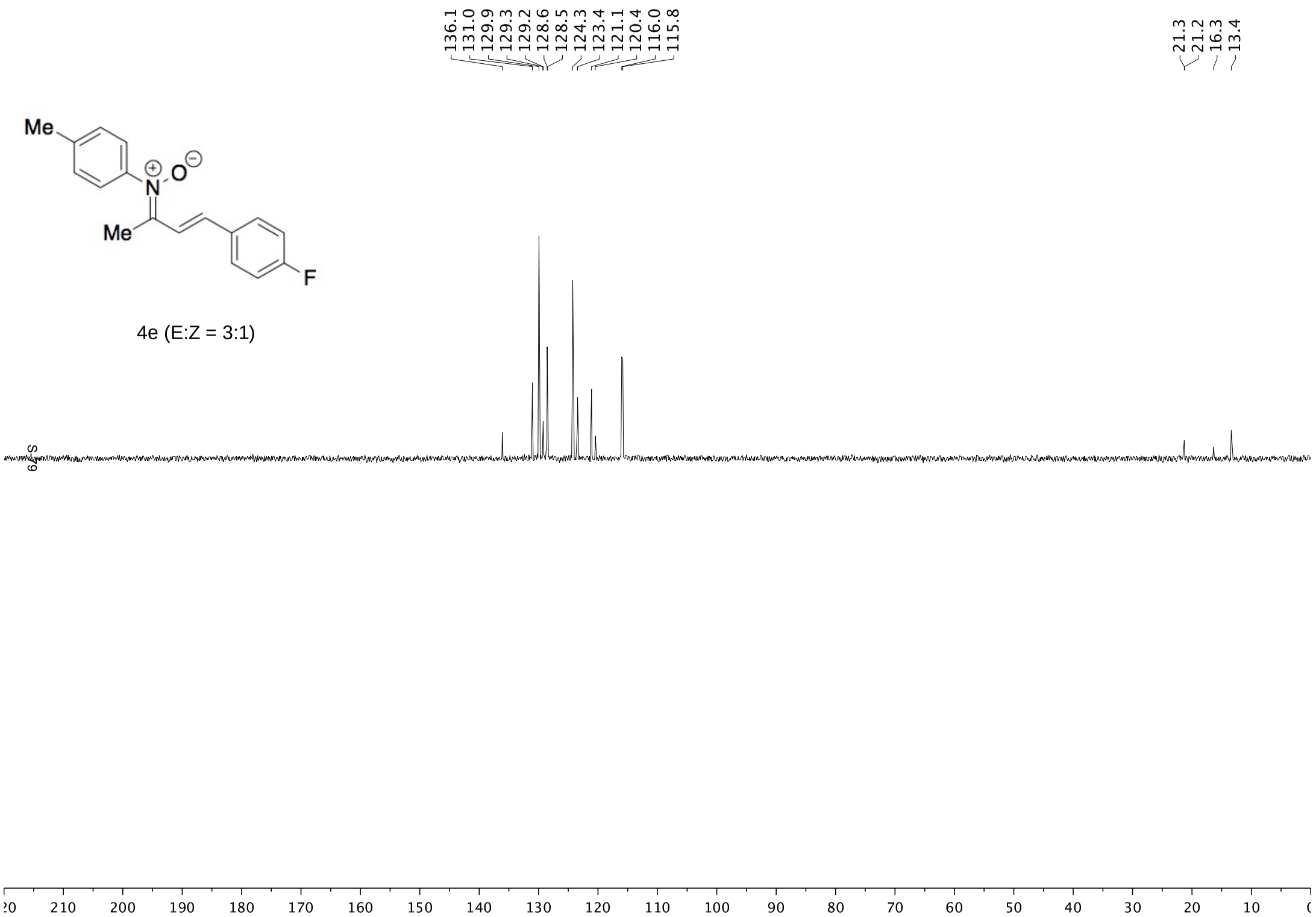
80
70
60
50
40
30
20
10

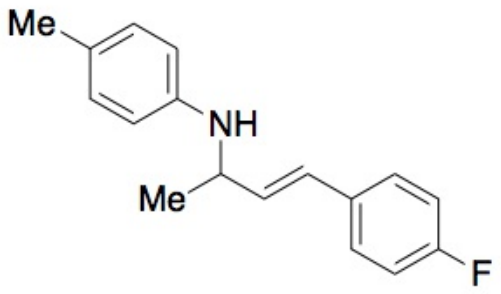

Me
O
N
Me
F

4e (E:Z = 3:1)

7.96
7.93
7.57
7.56
7.29
7.27
7.25
7.20
7.20
7.16
7.07
7.06
7.04
6.98
6.96
6.95
6.75
6.72
6.67
6.64
2.50
2.43
2.39
2.12
0.30
0.63
3.99
2.14
1.09
2.11
2.08
3.00
2.94
0.95
0.89
10.5
10.0
9.5
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

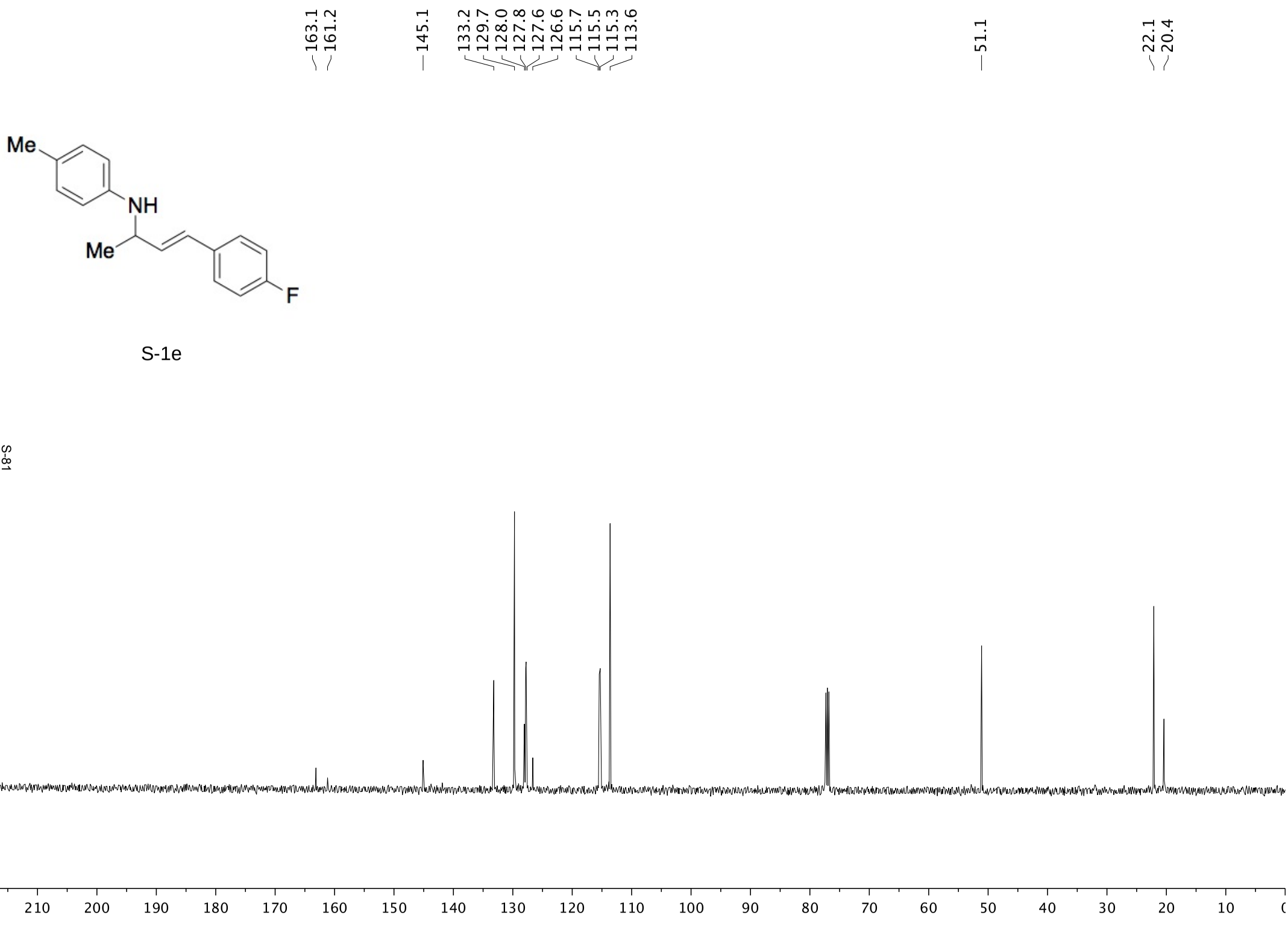

164.2
163.8
162.2
161.8
147.3
143.1
139.6
139.4
136.1
132.4
131.0
129.9
129.3
129.2
128.6
128.5
124.3
123.4
121.1
120.5
116.0
115.8
21.3
21.2
16.3
13.4
Me
O
N
Me
F
4e (E:Z = 3:1)
S-78
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

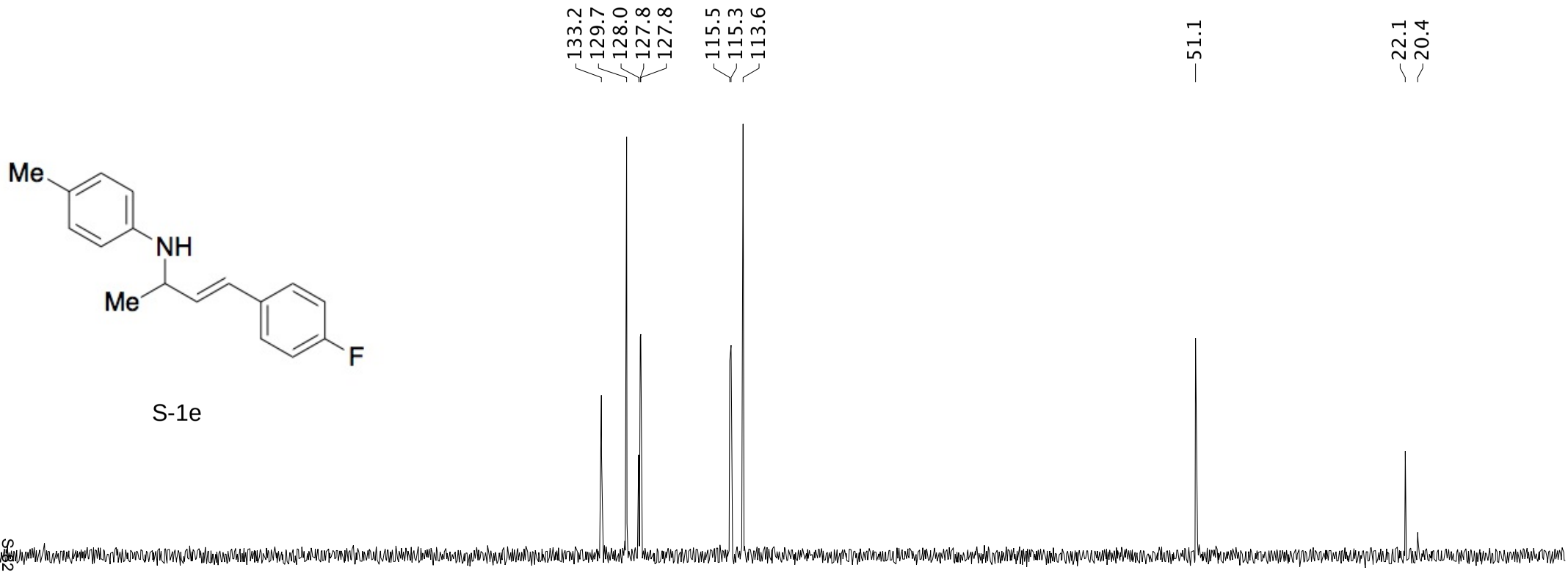

136.1
131.0
129.9
129.3
129.2
128.6
128.5
124.3
123.4
121.1
120.4
116.0
115.8
21.3
21.2
16.3
13.4
Me
N
O
Me
F
4e (E:Z = 3:1)
S29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

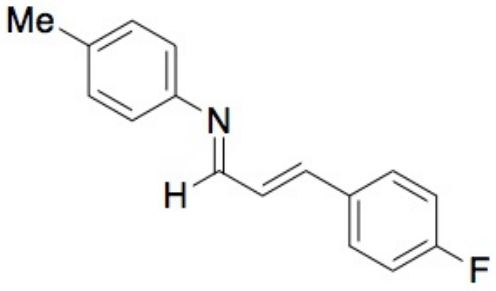

Me
NH
Me
F

S-1e

7.33
7.32
7.30
7.00
7.00
6.98
6.97
6.59
6.58
6.56
6.53
6.16
6.15
6.13
6.12
4.12
4.11
4.10
4.09
3.53
2.24
1.39
S-80
2.03
4.18
3.02
0.98
1.00
3.24
3.08
10.5
10.0
9.5
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

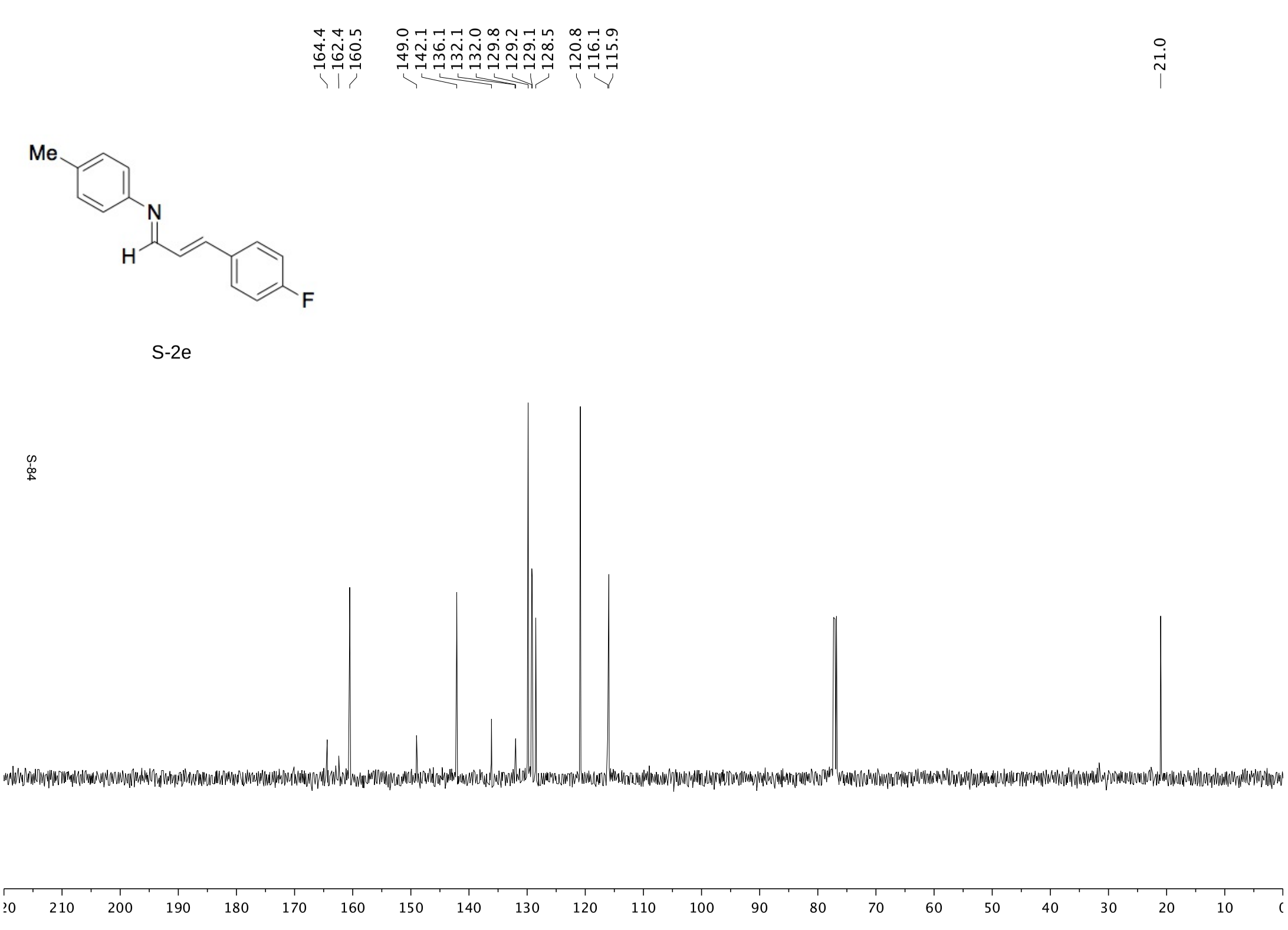

163.1
161.2
145.1
133.2
129.7
128.0
127.8
127.6
126.6
115.7
115.5
115.3
113.6
51.1
22.1
20.4
Me
NH
Me
F
S-1e
S-81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

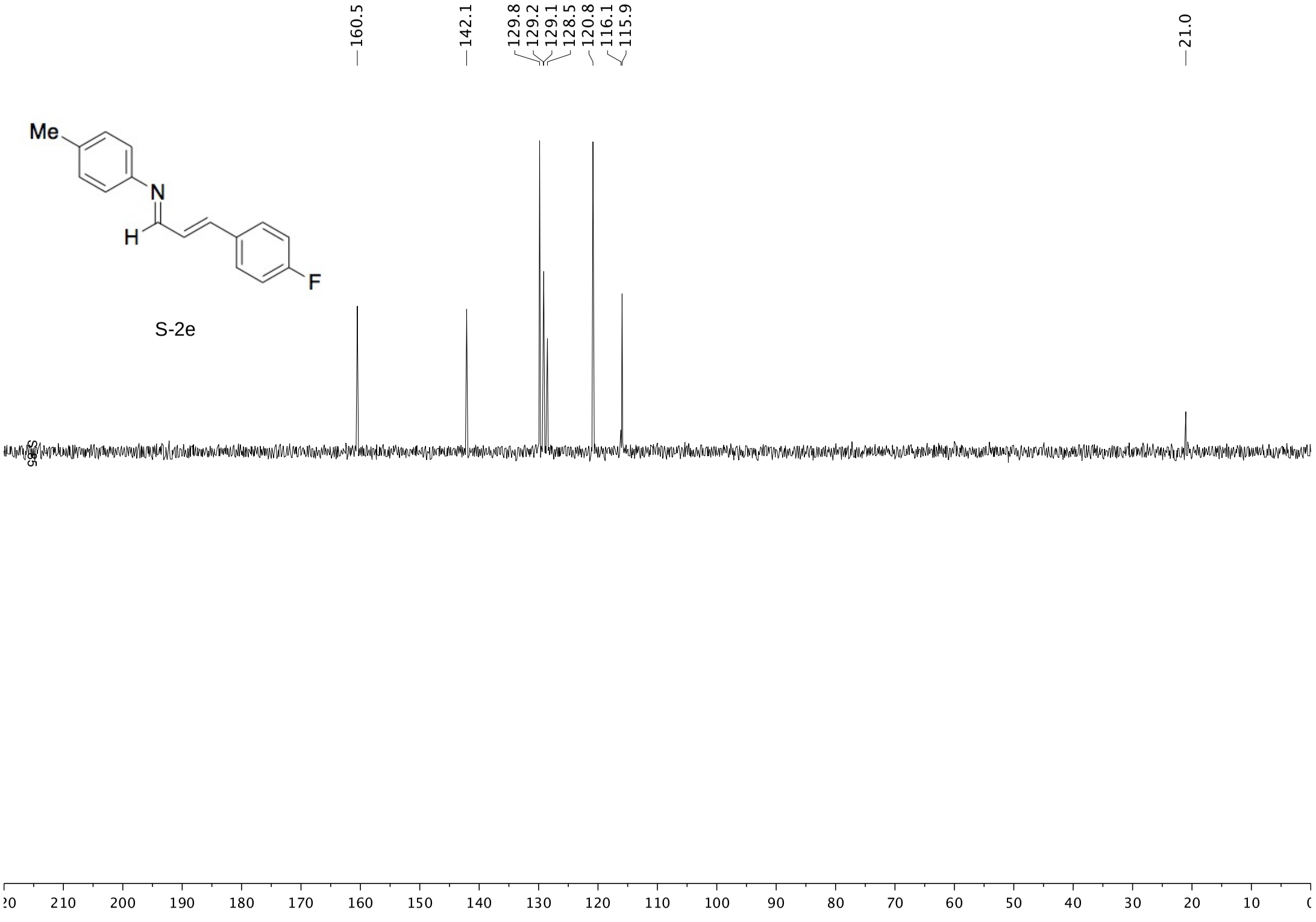

133.2
129.7
128.0
127.8
127.8
115.5
115.3
113.6
51.1
22.1
20.4
Me
NH
Me
F
S-1e

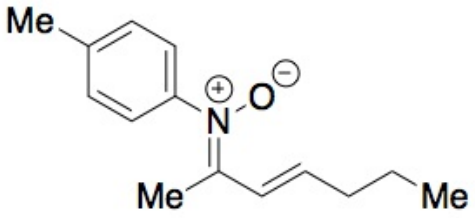

Me
N
H
F

S-2e

8.27
8.26
7.52
7.51
7.51
7.50
7.20
7.18
7.12
7.10
7.08
7.07
7.04
2.37
S-83
1.00
2.05
2.01
6.05
3.05
10.5
10.0
9.5
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

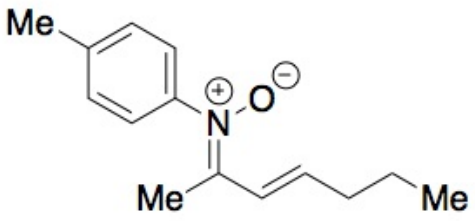

164.4
162.4
160.5
149.0
142.1
136.1
132.1
132.0
129.8
129.2
129.1
128.5
120.8
116.1
115.9
21.0
Me
N
H
F
S-2e
S-84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


160.5
142.1
129.8
129.2
129.1
128.5
120.8
116.1
115.9
21.0
Me
N
H
F
S-2e


Me
N
O
Me
Me

4g (E:Z = 3:1)

7.34
7.31
7.23
7.22
7.20
7.19
7.07
7.07
7.05
6.96
6.93
6.39
6.37
6.34
6.32
6.07
6.04
6.00
2.38
2.37
2.29
2.28
2.26
2.02
1.99
1.97
1.54
1.52
1.51
1.49
1.48
1.34
1.32
0.96
0.95
0.93
0.86
0.85
S-86
0.30
4.41
1.22
0.24
1.77
6.04
1.73
2.65
0.70
2.17
1.24
3.00
10.5
10.0
9.5
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

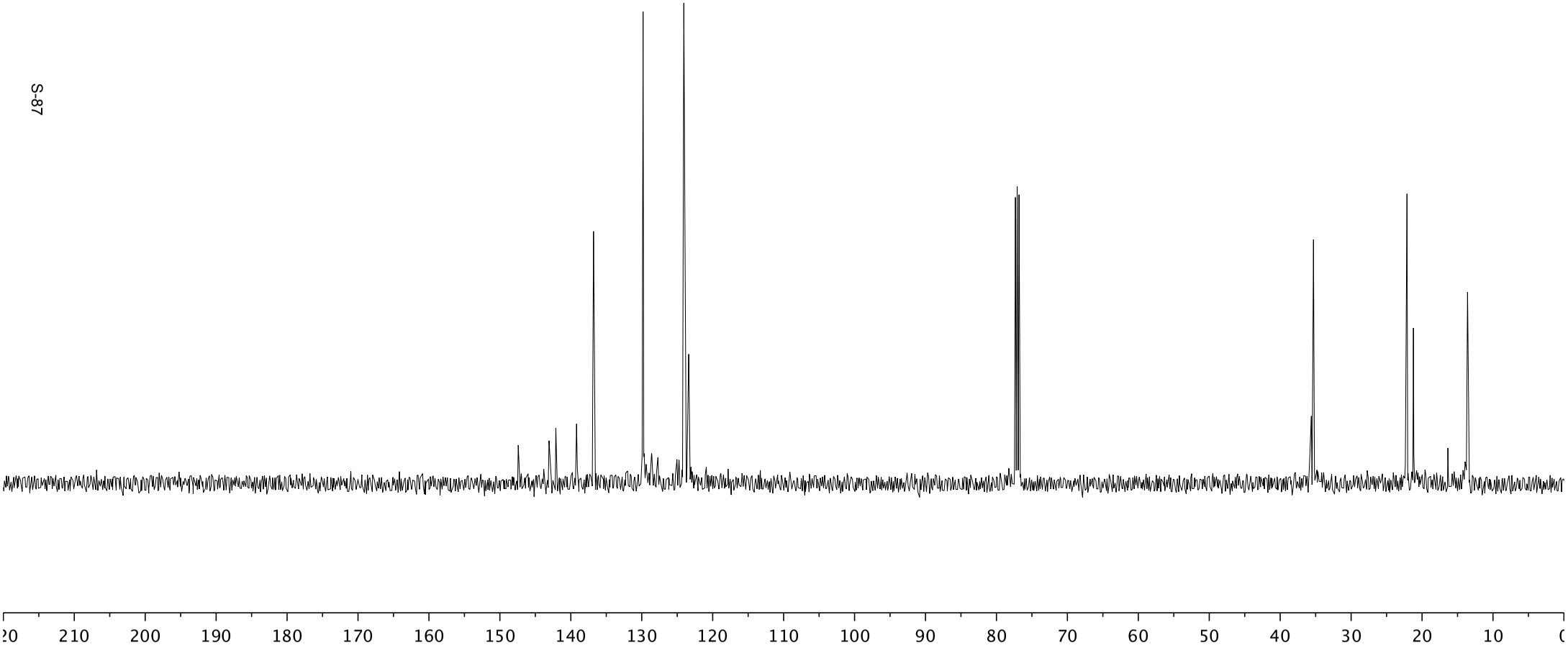


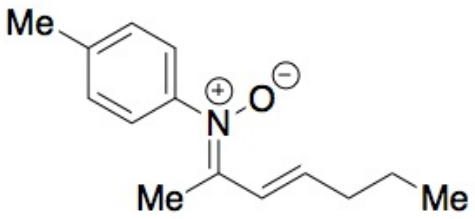
147.4
143.1
143.1
142.1
139.2
136.8
129.9
129.8
124.1
123.9
123.4
123.3

35.6
35.3

22.1
21.2
16.4
13.8
13.6
13.4

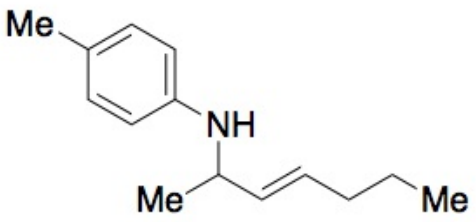
4g (E:Z = 3:1)




Me
N
O
Me
Me

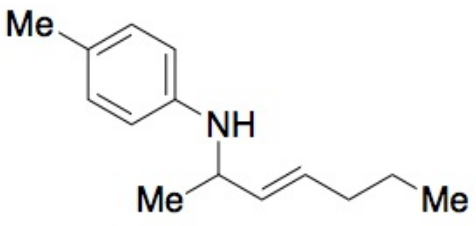
4g (E:Z = 3:1)

142.1
142.0
136.8
129.9
129.8
124.1
123.4
123.3
35.6
35.3
22.1
21.2
13.6
13.4
S-88
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
NH
Me
Me

S-1g

7.00
6.98
6.57
6.56
5.67
5.66
5.63
5.46
5.42
3.94
3.92
3.47
2.30
2.26
2.03
2.01
1.99
1.42
1.41
1.40
1.31
1.29
0.92
0.90
0.89
S-89
2.06
1.89
1.00
0.98
1.00
0.92
3.41
2.02
2.24
3.11
3.16
10.5
10.0
9.5
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

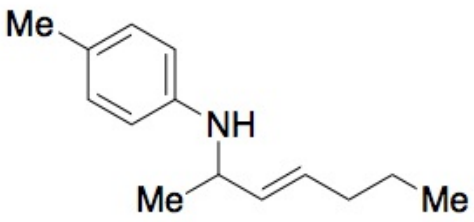


S-1g

145.3
133.5
130.3
129.9
129.6
113.7
50.9
34.4
22.5
22.2
20.4
13.6

S-90

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

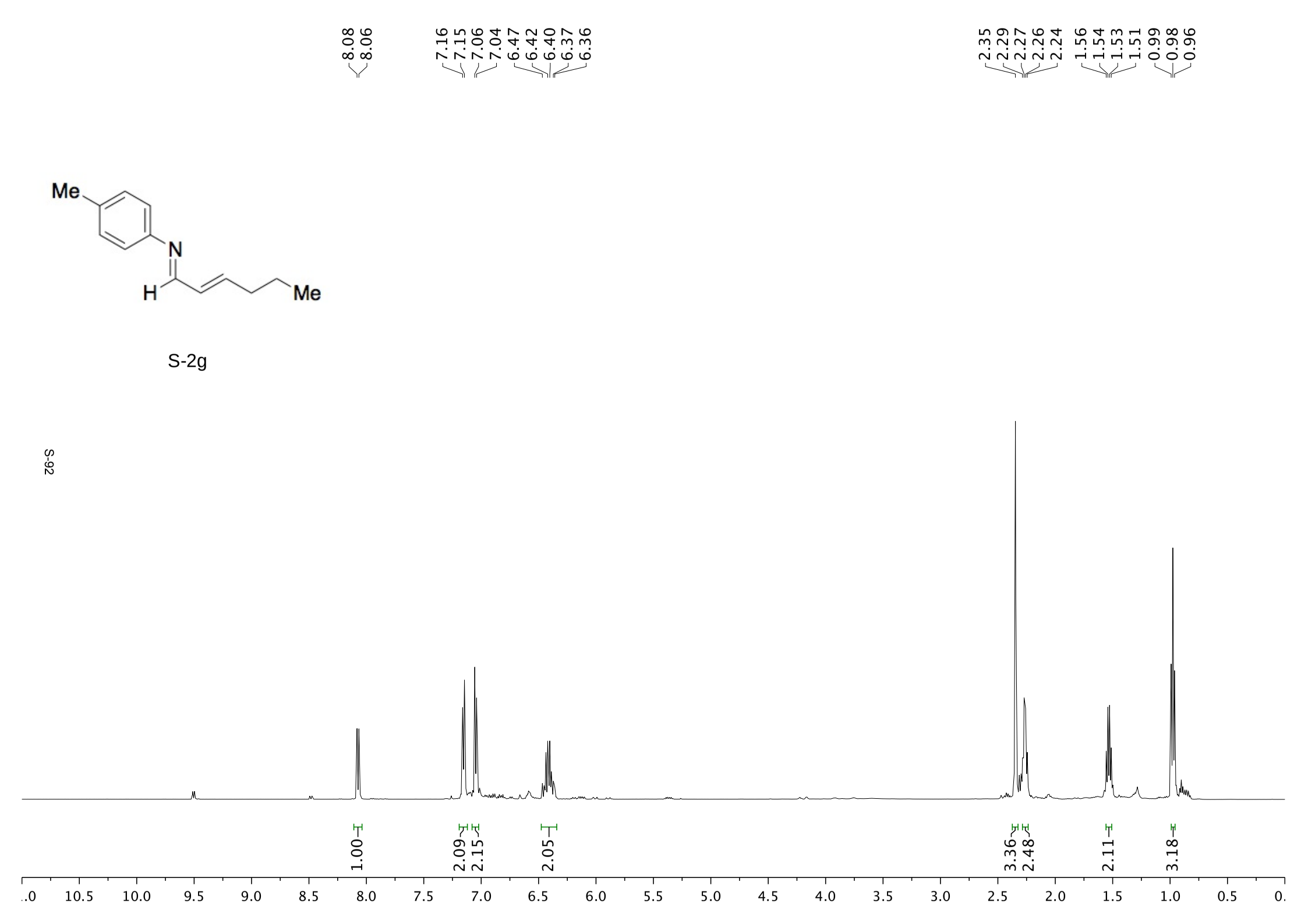


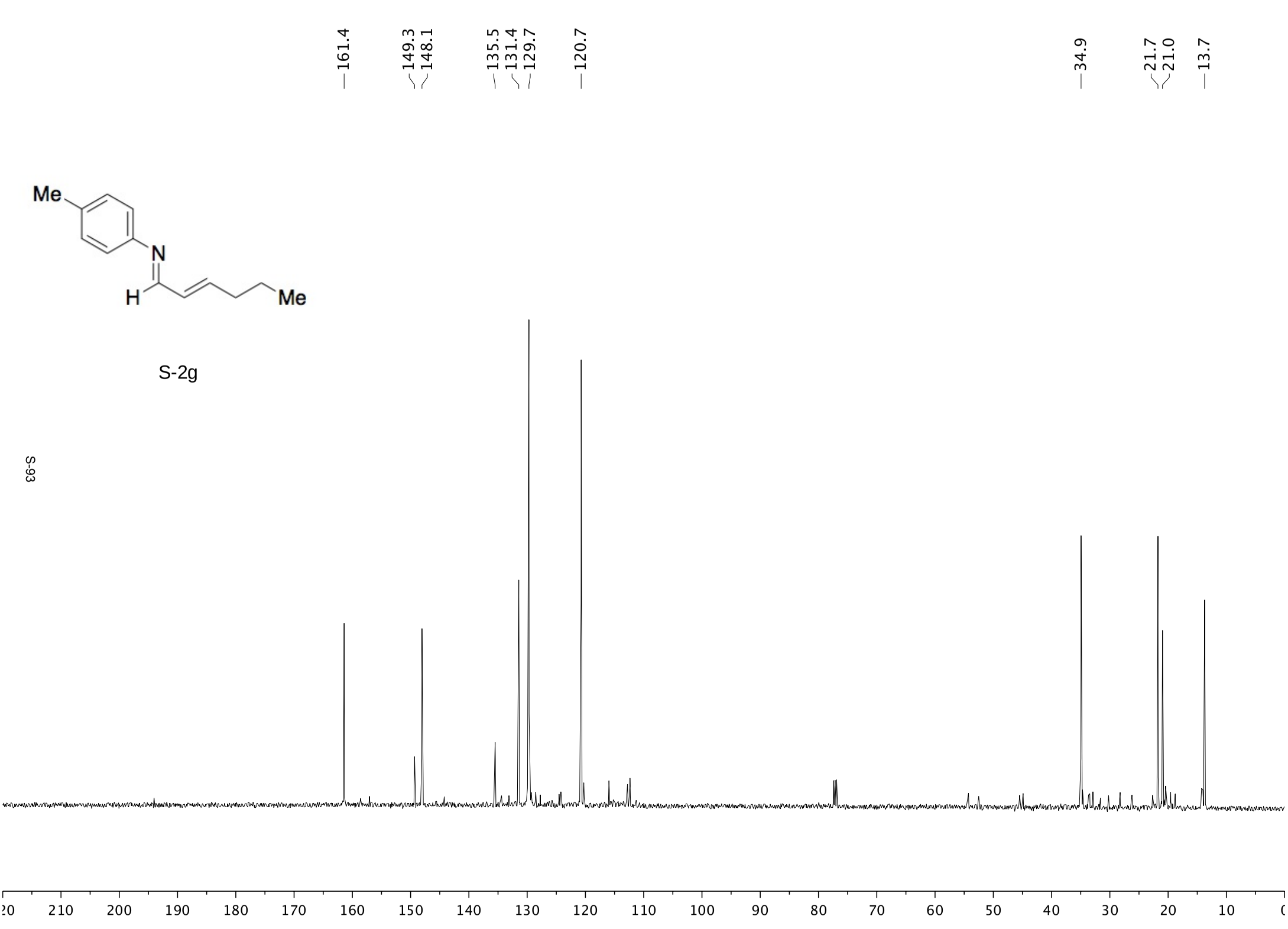
S-1g

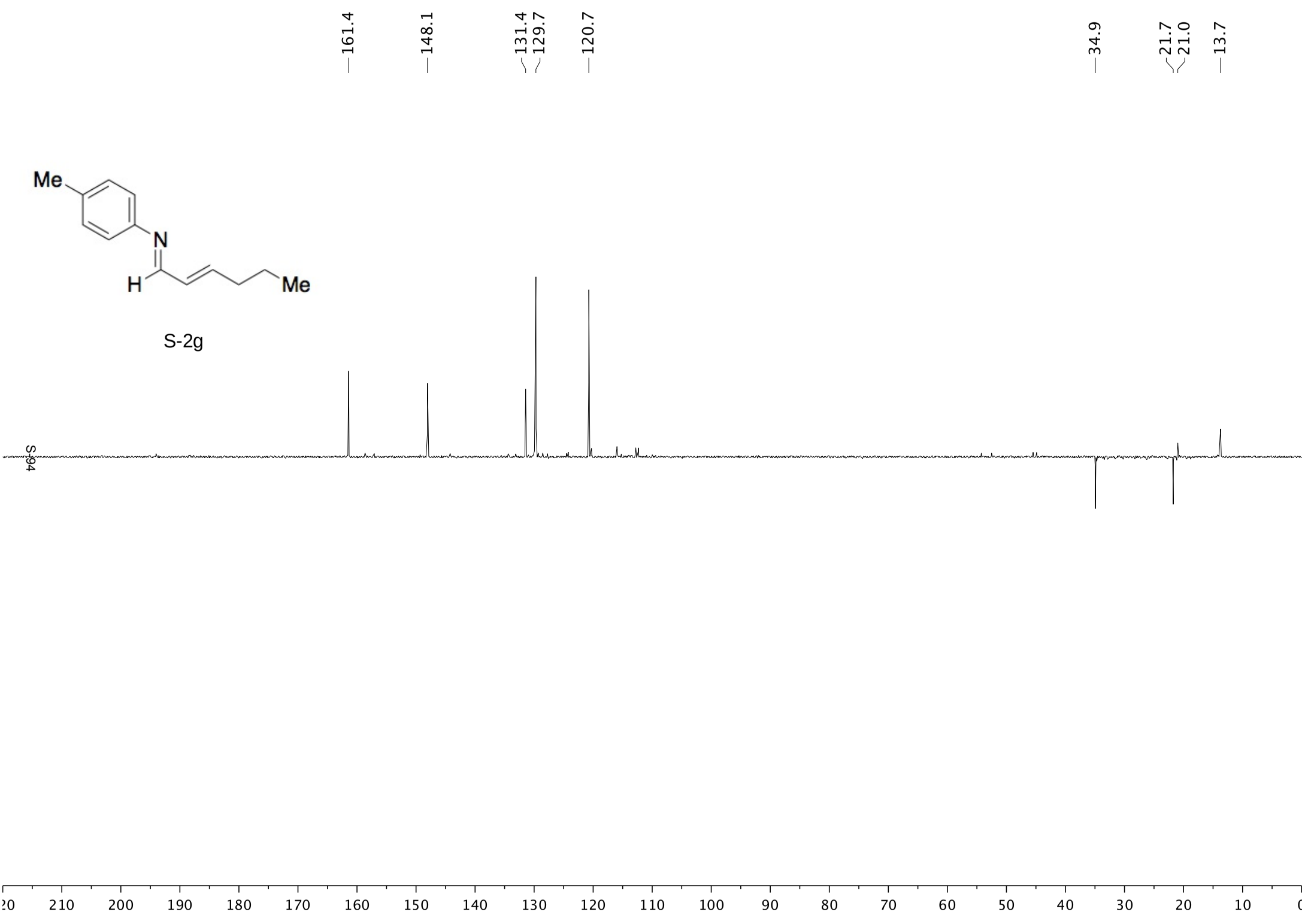
133.5
130.3
129.6
113.7
50.9
34.4
22.5
22.2
20.4
13.7

S1

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.08
8.06
7.16
7.15
7.06
7.04
6.47
6.42
6.40
6.37
6.36
2.35
2.29
2.27
2.26
2.24
1.56
1.54
1.53
1.51
0.99
0.98
0.96
Me
N
H
Me
S-2g
S-92
1.00
2.09
2.15
2.05
3.36
2.48
2.11
3.18
10.5
10.0
9.5
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


161.4
149.3
148.1
135.5
131.4
129.7
120.7
34.9
21.7
21.0
13.7
Me
N
H
Me
S-2g
S-93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


161.4
148.1
131.4
129.7
120.7
34.9
21.7
21.0
13.7
Me
N
H
Me
S-2g
S94
210
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150
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130
120
110
100
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80
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50
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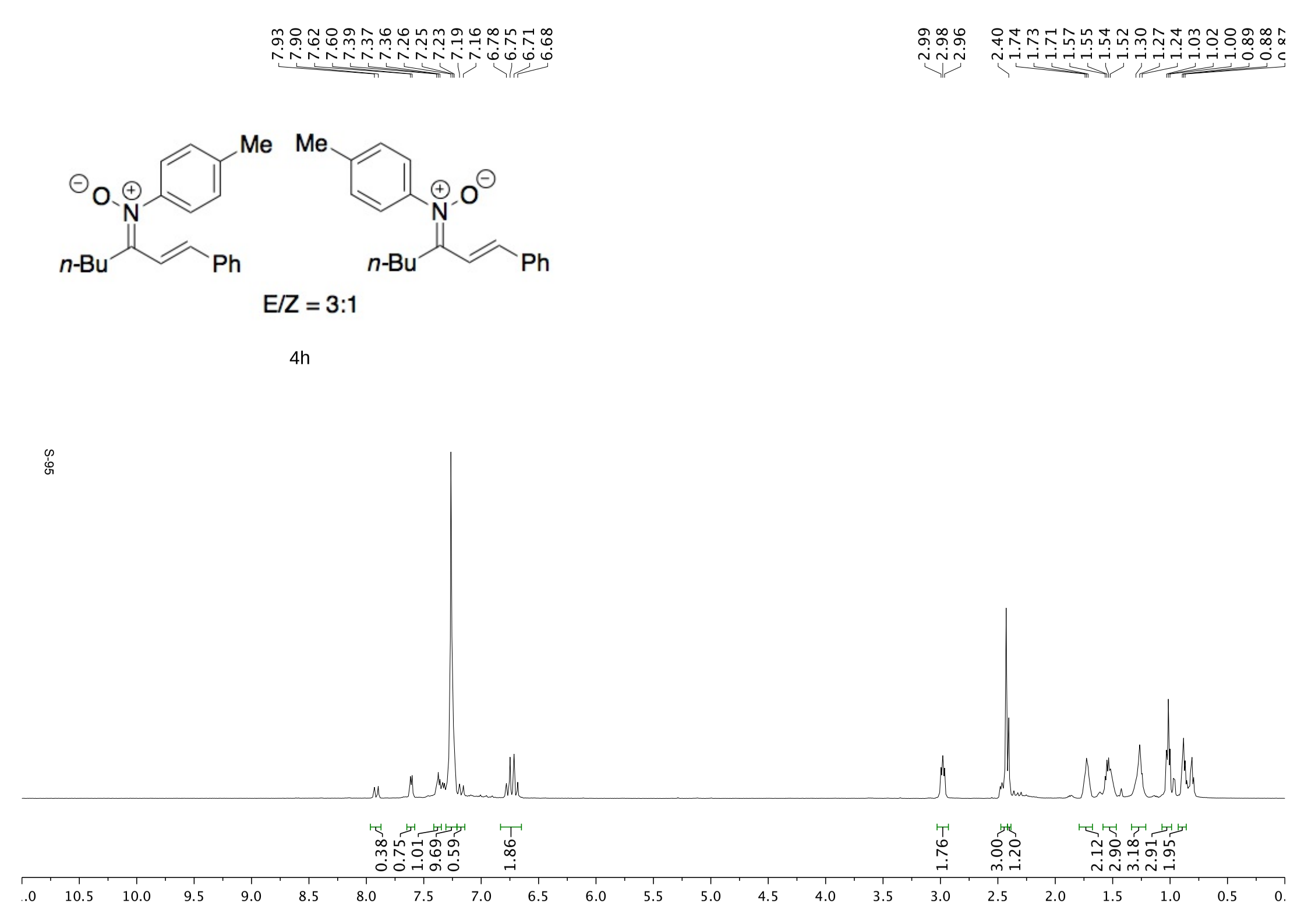
30
20
10


7.93
7.90
7.62
7.60
7.39
7.37
7.36
7.26
7.25
7.23
7.19
7.16
6.78
6.75
6.71
6.68
2.99
2.98
2.96
2.40
1.74
1.73
1.71
1.57
1.55
1.54
1.52
1.30
1.27
1.24
1.03
1.02
1.00
0.89
0.88
Me
Me
O
N
n-Bu
Ph
O
N
n-Bu
Ph
E/Z = 3:1
4h
S-95
0.38
0.75
1.01
9.69
0.59
1.86
1.76
3.00
1.20
2.12
2.90
3.18
2.91
1.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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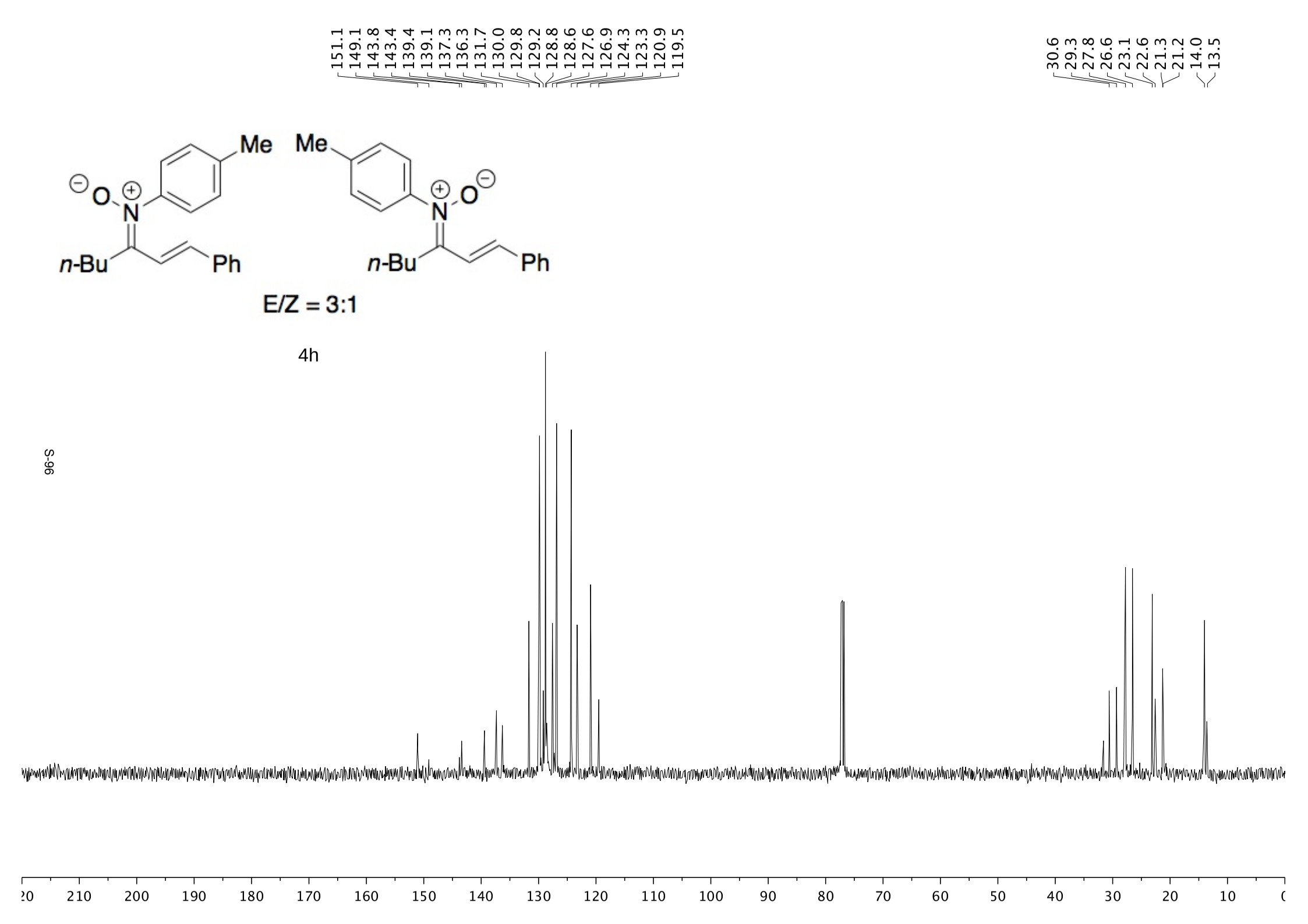
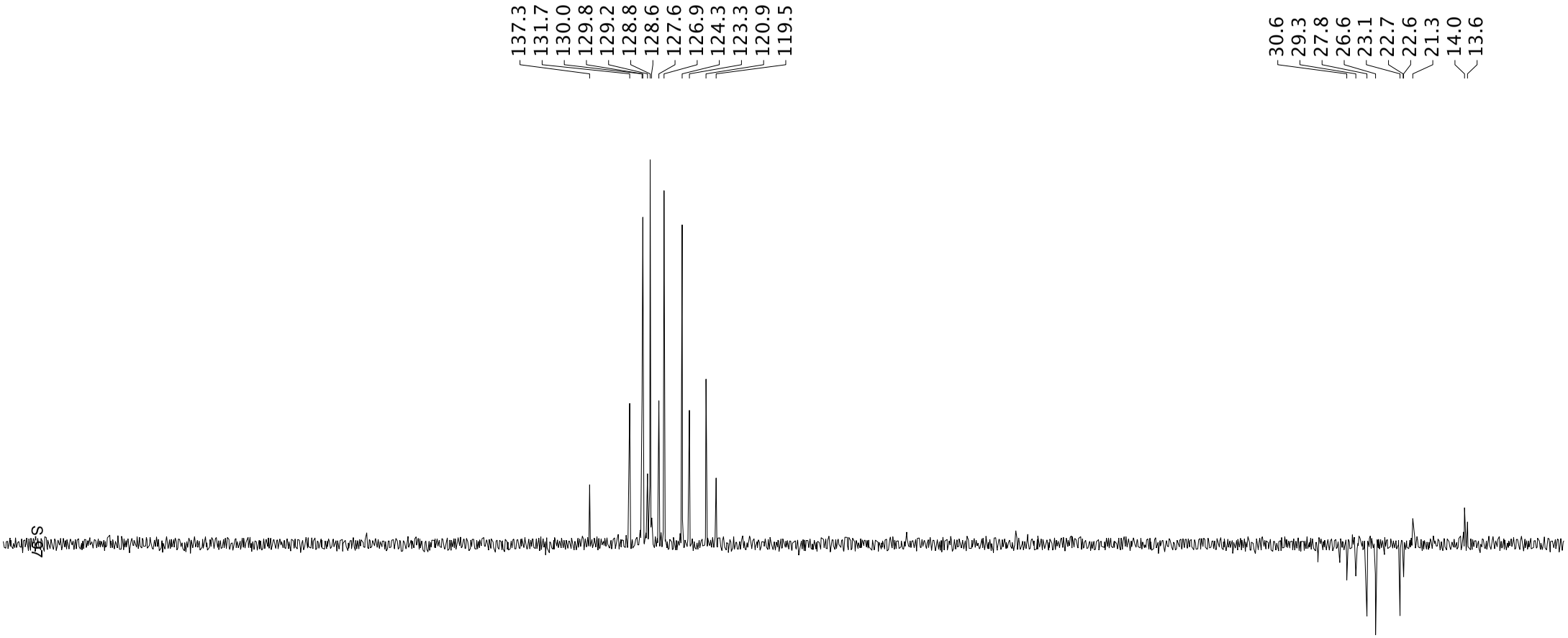
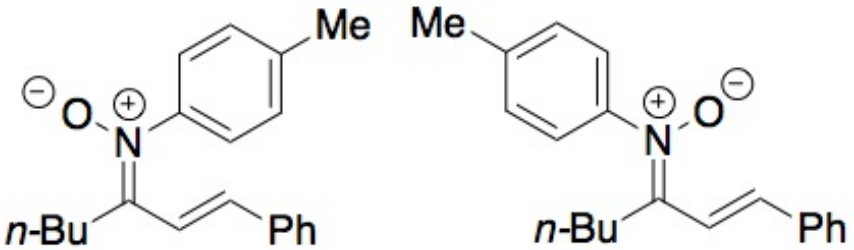
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

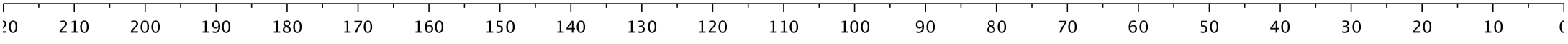

151.1
149.1
143.8
143.4
139.4
139.1
137.3
136.3
131.7
130.0
129.8
129.2
128.8
128.6
127.6
126.9
124.3
123.3
120.9
119.5
30.6
29.3
27.8
26.6
23.1
22.6
21.3
21.2
14.0
13.5
Me
O
N
n-Bu
Ph
Me
O
N
n-Bu
Ph
E/Z = 3:1
4h
S-96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

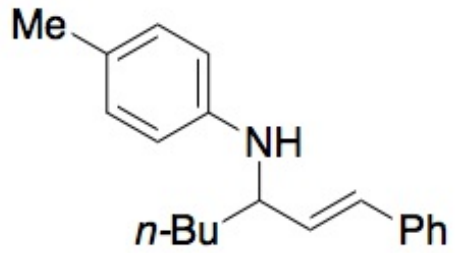

137.3
131.7
130.0
129.8
129.2
128.8
128.6
127.6
126.9
124.3
123.3
120.9
119.5
30.6
29.3
27.8
26.6
23.1
22.7
22.6
21.3
14.0
13.6
DMSO


Me
O
N
n-Bu
Ph
Me
O
N
n-Bu
Ph

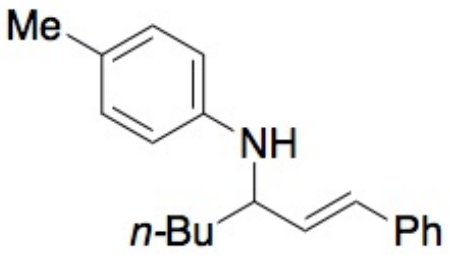
E/Z = 3:1

4h


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



S-1h

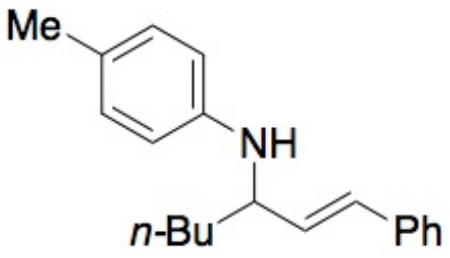


S-1h

145.4
137.2
132.6
130.0
129.7
128.6
128.5
127.3
126.3
113.5
56.0
36.1
28.2
22.7
20.4
14.1

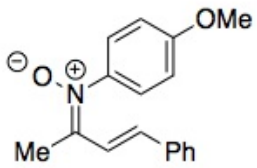
S-99

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


Me
NH
n-Bu
Ph

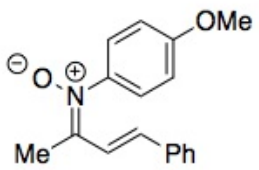
S-1h

132.6
130.0
129.7
128.5
127.3
126.3
113.5
56.0
36.1
28.2
22.7
14.1
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OMe
O
N
Me
Ph

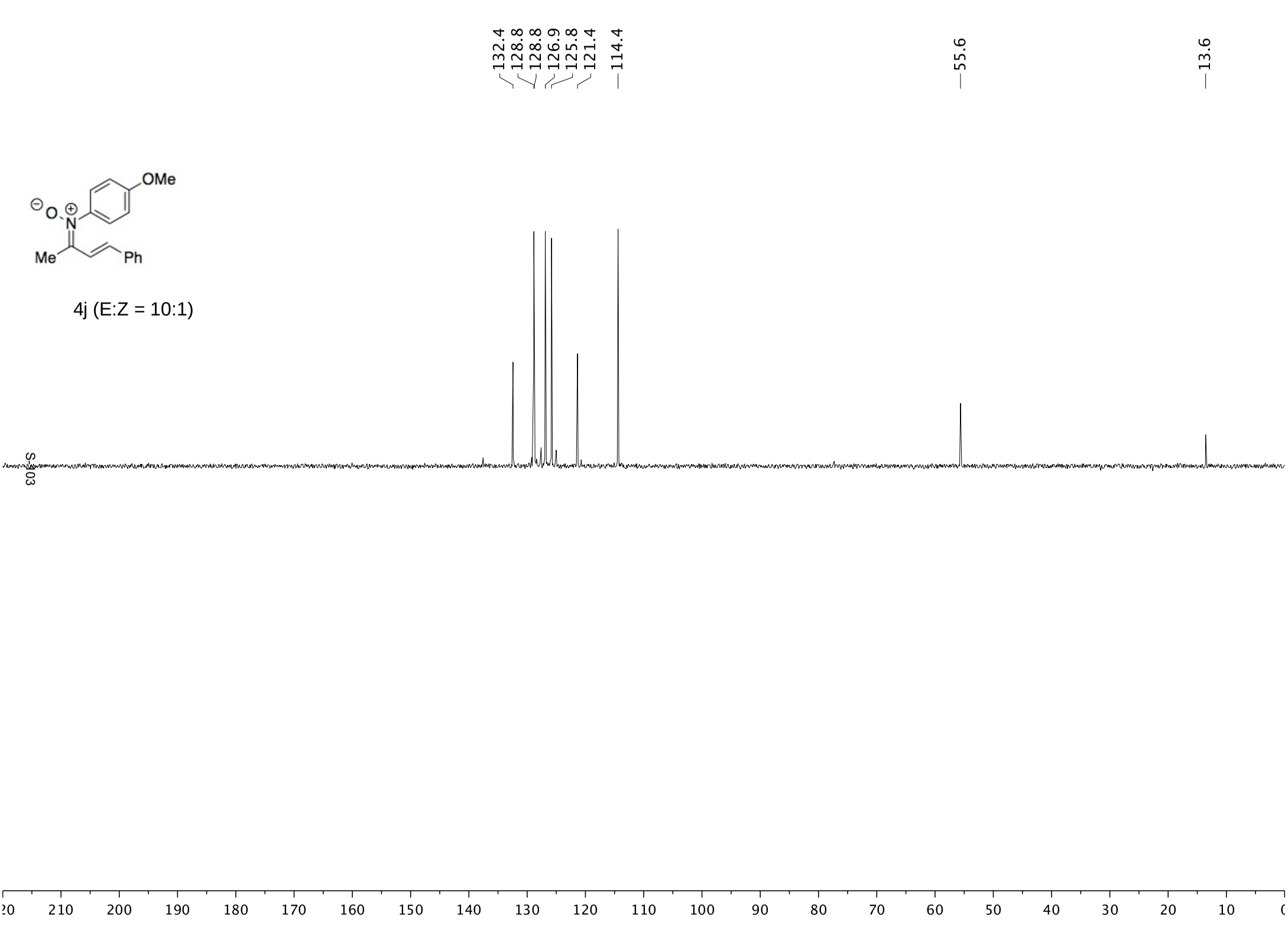
4j (E:Z = 10:1)

7.35
7.33
7.27
7.26
7.25
7.24
6.97
6.96
6.78
6.74
3.86
2.50
S-101
2.30
5.13
2.11
1.96
2.99
3.00
10.5
10.0
9.5
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


OMe
O
N
Me
Ph

4j (E:Z = 10:1)

160.1
147.6
138.8
136.1
132.4
128.8
128.8
126.9
125.8
121.4
114.4
55.6
13.6
S-102
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


132.4
128.8
128.8
126.9
125.8
121.4
114.4
55.6
13.6
OMe
Me
Ph
4j (E:Z = 10:1)
S-03
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


CO2Me
H
O
N
Me
Ph
Me
dr = 60:40
MeOH
1 h
CO2Me
H
O
N
Me
Ph
Me
55%
dr = >20:1
+
Ph
Me
Me
N
H
CO2Me
33%

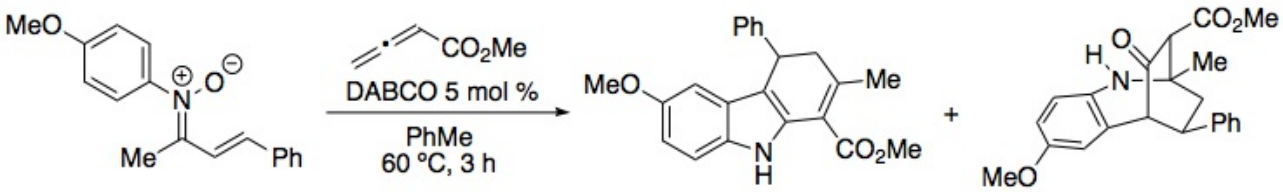
6a

6a

8a

S-104

9.31
7.34
7.32
7.31
7.26
7.23
7.17
6.92
6.89
6.88
6.73
6.67
6.50
6.49
4.93
4.33
4.31
4.30
4.09
4.06
3.94
3.79
3.49
3.47
3.03
3.01
2.99
2.80
2.78
2.75
2.51
2.48
2.46
2.28
2.27
2.17
1.36
CH2Br2
0.13
2.00
0.14
0.40
0.75
0.38
0.14
0.14
0.28
0.86
0.86
0.71
10.5
10.0
9.5
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



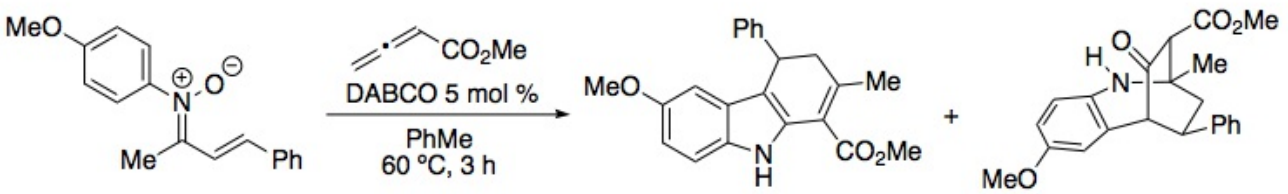
4m

8m

6m (dr = 1:1)

S-109

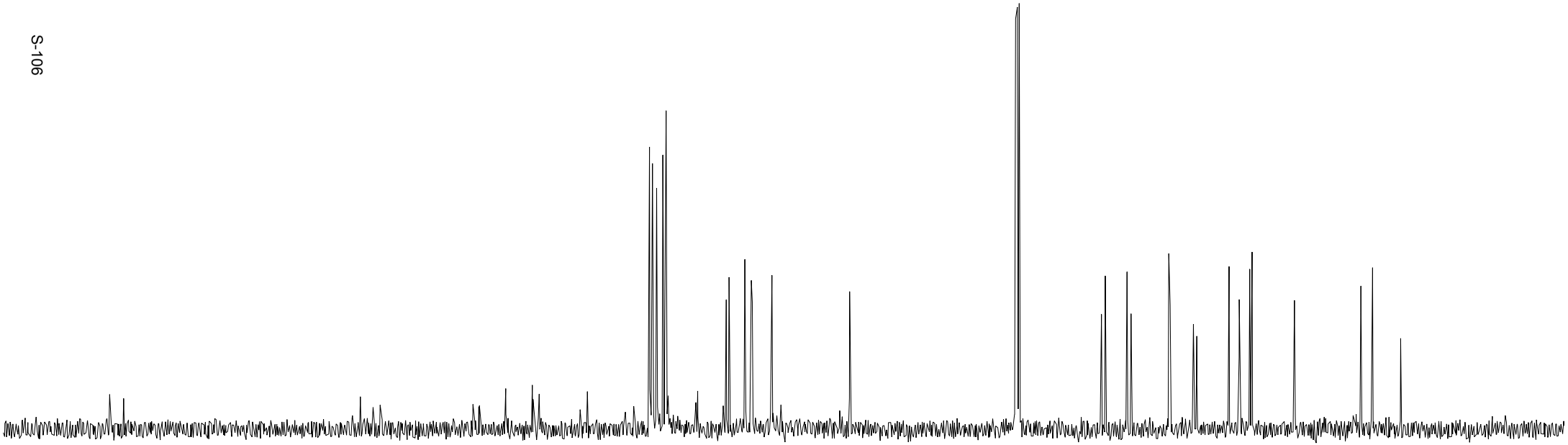

205.0
203.0
169.7
167.9
166.9
153.8
153.0
152.9
149.2
145.4
145.3
144.5
138.7
137.7
132.3
131.1
129.0
128.9
128.8
128.5
127.9
127.0
126.8
126.7
126.6
122.4
122.1
118.1
117.7
115.5
114.6
114.4
111.8
111.6
100.7
65.2
64.7
61.6
61.0
55.7
55.6
55.5
52.2
52.2
51.8
47.3
47.2
45.8
44.3
44.0
38.0
28.6
27.0
23.0

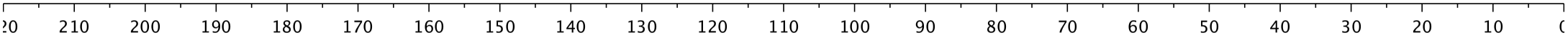

MeO
N
O
Me
Ph
CO2Me
DABCO 5 mol %
PhMe
60 °C, 3 h
Ph
MeO
Me
N
H
CO2Me
+
CO2Me
O
H
N
Me
Ph
MeO

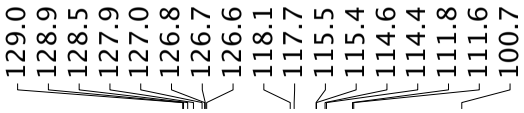
4m

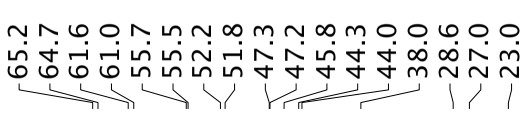
8m

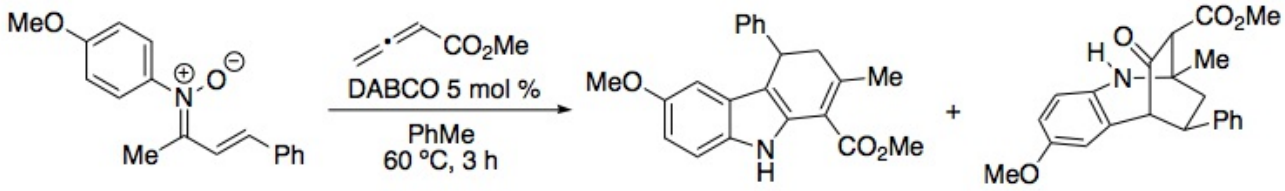
6m (dr = 1:1)




220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


129.0
128.9
128.5
127.9
127.0
126.8
126.7
126.6
118.1
117.7
115.5
115.4
114.6
114.4
111.8
111.6
100.7

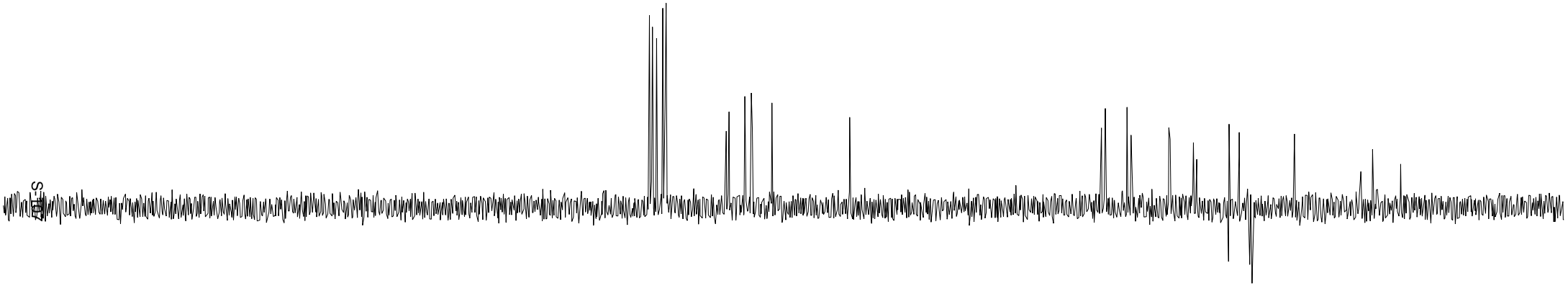

65.2
64.7
61.6
61.0
55.7
55.5
52.2
51.8
47.3
47.2
45.8
44.3
44.0
38.0
28.6
27.0
23.0

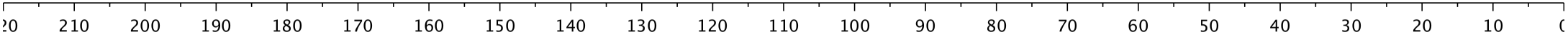

MeO
Me
Ph
CO2Me
DABCO 5 mol %
PhMe
60 °C, 3 h
Ph
MeO
Me
CO2Me
N
H
+
CO2Me
O
H
N
Me
Ph
MeO

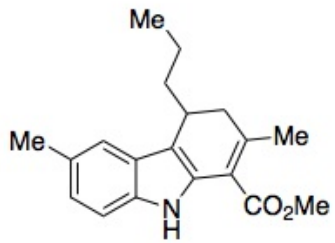
4m

8m

6m (dr = 1:1)

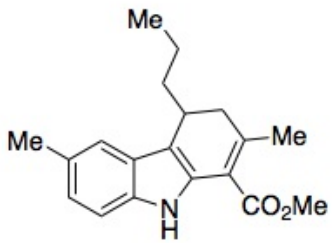



220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

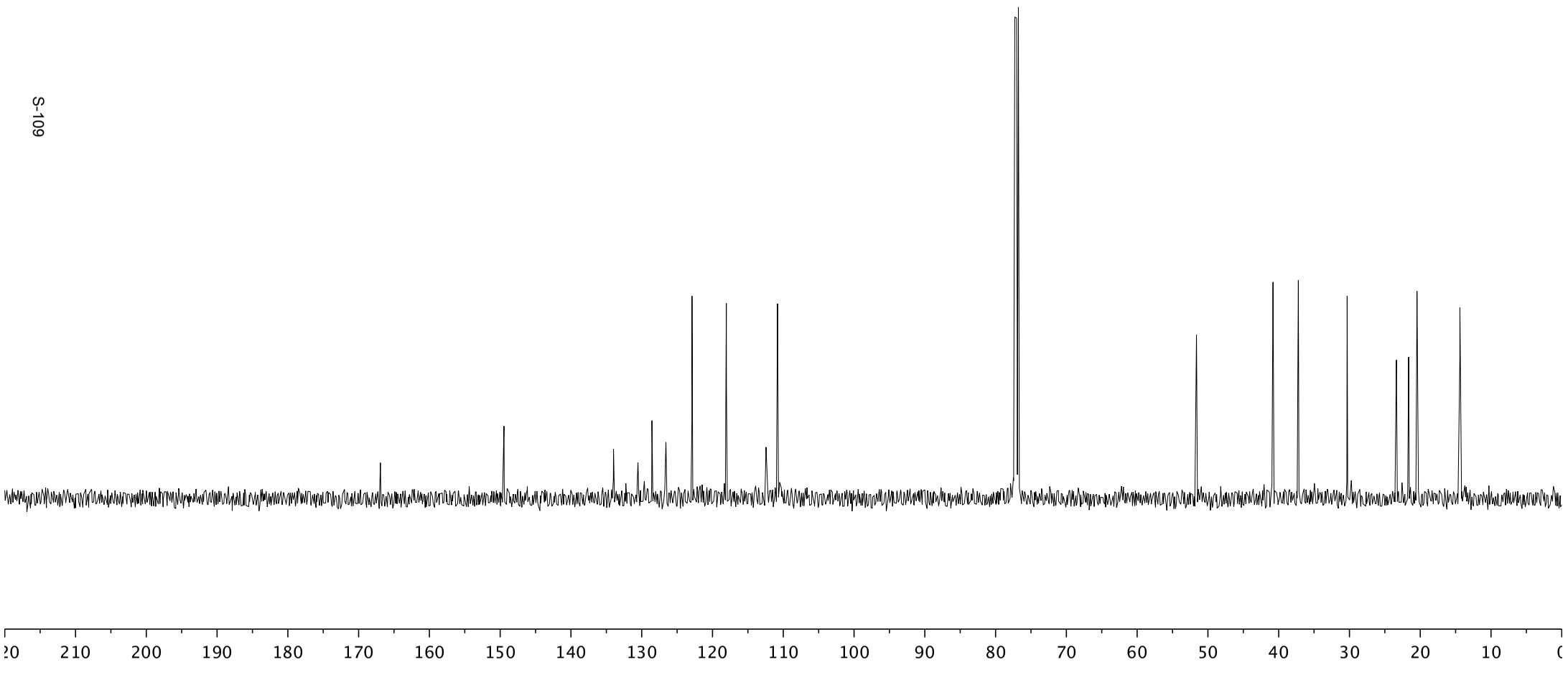

Me
Me
Me
N
H
CO2Me

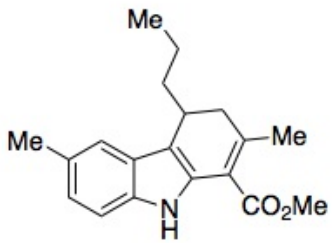
8g

9.16
7.28
7.24
7.22
6.95
6.94
3.92
3.06
3.05
2.88
2.84
2.82
2.45
2.31
1.59
1.57
1.54
1.48
1.44
1.39
1.31
1.29
0.91
0.89
0.88
S-108
0.99
1.41
1.27
1.35
3.32
1.19
1.24
3.30
3.04
1.51
2.35
2.20
3.03
10.5
10.0
9.5
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


Me
Me
Me
N
H
CO2Me

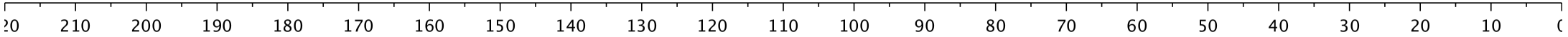
8g

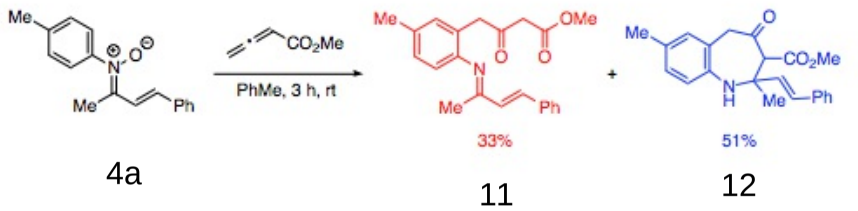

166.9
149.5
134.0
130.5
128.6
126.6
122.9
118.1
118.0
112.4
110.8
51.6
40.8
37.2
30.3
23.4
21.6
20.5
14.4
S-109
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Me
Me
Me
N
H
CO2Me

8g

122.9
118.0
110.8
51.6
40.8
37.2
30.3
23.4
21.6
20.5
14.4
S10


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



4a 11 12

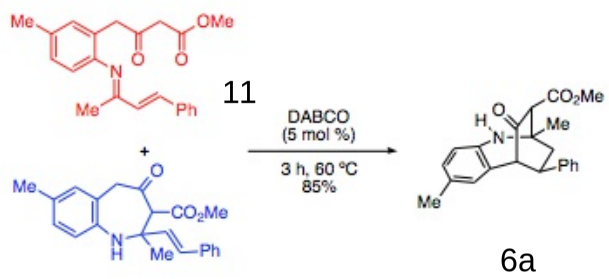
S-111

7.56 7.54 6.70 6.67 3.75 3.70 3.66 3.66 3.48 3.47 2.43 2.36 2.35 2.33 2.06

CH_2Cl

1.57 0.45 2.00 1.60 2.14 3.13 2.11 1.04 1.84 1.20 1.98

11.0 10.5 10.0 9.5 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.



11

12

DABCO
(5 mol %)

3 h, 60 °C
85%

6a