SUPPLEMENTARY INFORMATION FOR

Dynamic Kinetic Resolution in the Asymmetric Synthesis of Atropisomeric Biaryl [4] and [5]Helicenequinones

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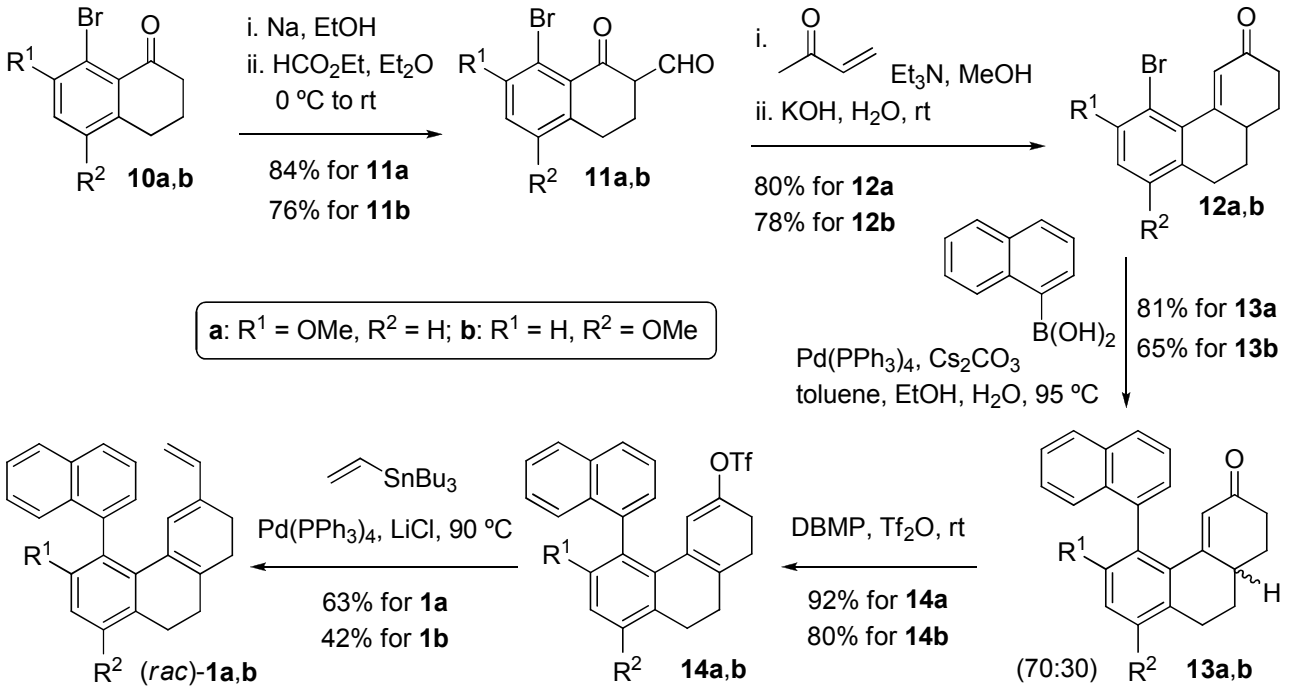
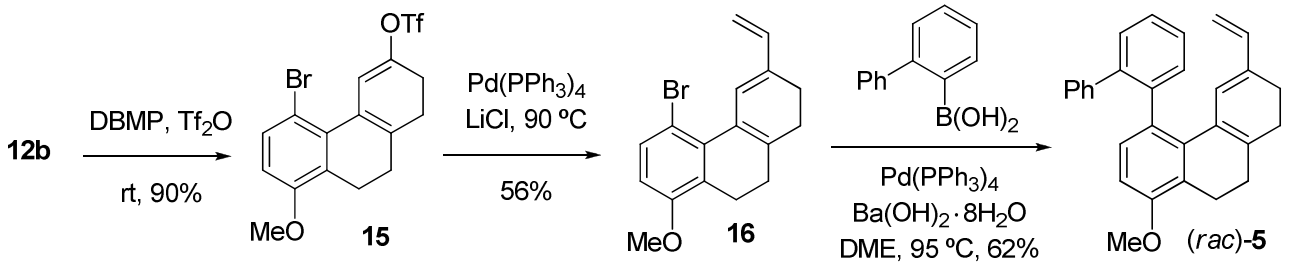
Synthesis of dienes (*rac*)-1a,b, (*rac*)-5 and (*rac*)-7

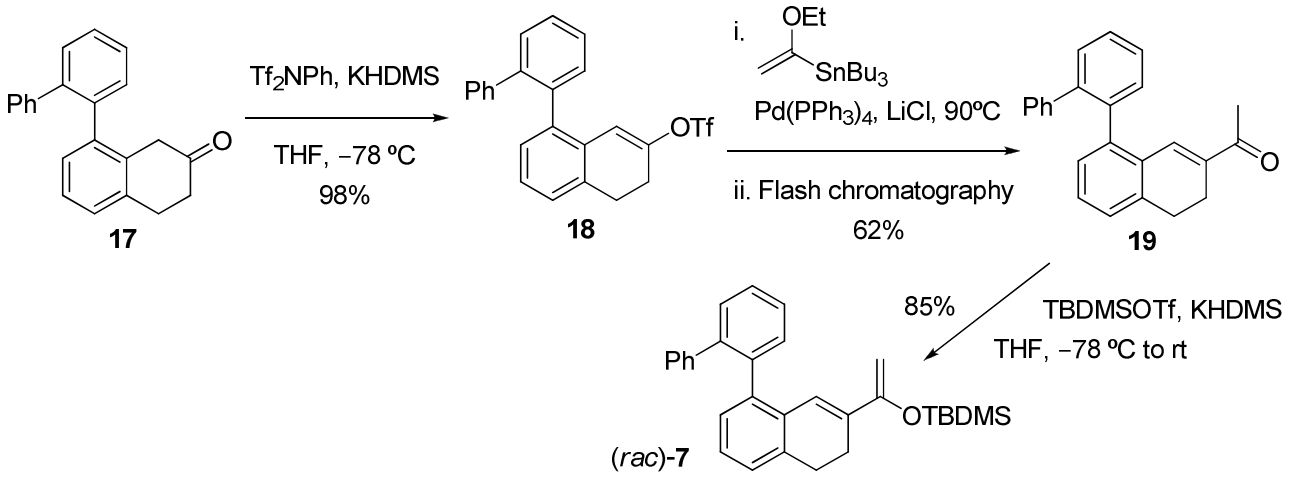
Synthesis of dienes (*rac*)-1a,b



Synthesis of diene (*rac*)-5



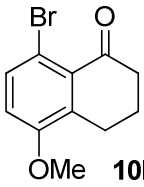
Synthesis of diene (*rac*)-7



Experimental Procedures

Melting points were obtained in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. All reactions were monitored by thin layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. Ethyl ether, CH_2Cl_2, THF and CH_3CN were dried over 4Å molecular sieves. All other reagent quality solvents were used without purification. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2, and solvent drying with $MgSO_4$.

8-Bromo-5-methoxy-3,4-dihydronaphthalen-1(*2H*)-one (10b)



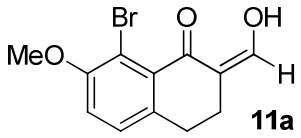
10b

To a vigorously stirred solution of commercially available 5-methoxy-1-tetralone (3.4 g, 18.9 mmol) in CH_3CN (105 mL), NBS (4.1 g, 22.6 mmol) was added. After 48 h, the solvent was evaporated and the residue purified by flash chromatography (eluent CH_2Cl_2) to give **10b** as a yellow solid, in 96% yield: m.p. 52-53 ºC; ^{1}H NMR δ 2.07-2.16 (m, 2H), 2.70 (dd, J = 6.7 and 6.8 Hz, 1H), 2.93 (dd, J = 6.2 and 6.3 Hz, 1H), 3.88 (s, 3H), 6.85 (d, J = 8.7 Hz, 1H), 7.53 (d, J = 8.7 Hz, 1H); ^{13}C NMR δ 22.0, 23.6, 39.9, 55.9, 111.3, 114.5, 131.4, 133.4, 136.0, 156.0, 197.2; MS (EI): *m/z* (%) 76 (37), 198 (48), 226 (51), 254 (M^+, 100), 256 (M^+ + 2, 96); HRMS (EI) calcd for $C_{11}H_{11}O_2Br$ (M^+) 253.9942 found 253.9932.

General procedure for the α-formylation of 1-tetralones. Method A.

To a solution of the corresponding 1-tetralone **10a**,**b** (3.2 g, 12.6 mmol) in dry Et_2O (12.6 mL) under argon, an excess of sodium metal (6 or 7 pieces of ca. 0.5 cm), ethyl formate (1.46 mL, 18.9 mmol) and EtOH (0.15 mL) were added at 0 ºC. After stirring for 30 min at 0 ºC and overnight at rt, the mixture was treated with water at 0 ºC and stirred 30 min. The organic phase was washed with water, and the combined aqueous extracts treated with HCl until acidity. The solution was extracted with Et_2O and washed with sodium bicarbonate. After workup and flash chromatography, pure α-formyl derivatives **11a**,**b** were obtained.

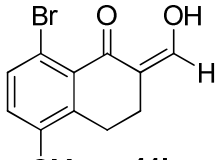
8-Bromo-2-(hydroxymethylene)-7-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (11a)



11a

Compound **11a** was obtained from 1-tetralone **10a**[1] following method A (eluent hexane/EtOAc 3:1) as a yellow solid, in 84% yield: m.p. 84-86 ºC; ^{1}H NMR δ 2.44 (dd, *J* = 6.9 and 5.6 Hz, 2H), 2.81 (dd, *J* = 6.9 and 8.6 Hz, 2H), 3.92 (s, 3H), 6.98 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.79 (d, 9.2 Hz, 1H); ^{13}C NMR δ 23.9, 30.0, 56.8, 110.6, 112.1, 115.5, 127.9, 132.0, 137.1, 155.8, 170.0, 187.1; MS (EI): *m/z* (%) 115 (85), 131 (85), 174 (95), 255 (47), 281 (M^+, 100), 283 (M^+ + 2, 88); HRMS (EI) calcd for $C_{12}H_{11}O_3Br$ (M^+) 281.9892, found 281.9897.

8-Bromo-2-(hydroxymethylene)-5-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (11b)



11b

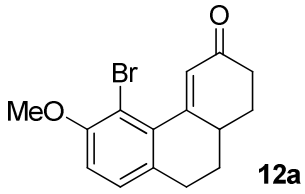
Compound **11b** was obtained from 1-tetralone **10b** following method A (eluent hexane/EtOAc 1:1) as a yellow solid, in 76% yield: m.p. 90-91 ºC; ^{1}H NMR δ 2.43 (dd, *J* = 6.5 and 7.1 Hz, 2H), 2.87 (dd, *J* = 6.5 and 7.1 Hz, 2H), 3.86 (s, 3H), 6.85 (d, *J* = 8.9 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR δ 22.5, 22.9, 55.9, 110.1, 111.7, 114.9, 131.2, 133.7, 134.5, 155.5, 169.8, 186.6; MS (EI): *m/z* (%) 115 (51), 139 (59), 174 (84), 253 (82), 282 (M^+, 100), 284 (M^+ + 2, 96); HRMS (EI) calcd for $C_{12}H_{11}O_3Br$ (M^+) 281.9891, found 281.9881.

(1) Bohlmann, F.; Fritz, G. *Chem. Ber.* **1976**, *109*, 3371-3374.

General procedure for the Robinson Annulation. Method B.

To a stirred mixture of the corresponding α-formyl 1-tetralone **11a**,**b** (2.18 g, 7.73 mmol) in anhydrous methanol (31 mL) at 0 ºC, Et_3N (2.1 mL) was added dropwise. After complete dissolution, methyl vinyl ketone (0.76 mL, 9.27 mmol) was added at 0 ºC and the reaction mixture stirred at room temperature for 20 h. After neutralization with acetic acid (0.92 mL), the solvents were evaporated and the residue redissolved in dioxane (17.5 mL). After addition of a solution of KOH (1.4 g) in water (16 mL), the mixture was vigorously stirred for 3.5 h at room temperature. Then, the solution was diluted with water, saturated with NaCl, and extracted with CH_2Cl_2. After workup and flash chromatography, pure tetrahydrophenanthrenones **12a**,**b** were obtained.

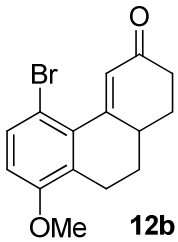
5-Bromo-6-methoxy-1,2,10,10a-tetrahydrophenanthren-3(9*H*)-one (12a)



12a

Compound **12a** was obtained from α-formyl-1-tetralone **11a** following method B (eluent hexane/EtOAc 3:1) as a white solid, in 80% yield: m.p. 89-90 ºC; ^{1}H NMR δ 1.69-2.03 (m, 3H), 2.14 (m, 1H), 2.39-2.70 (m, 3H), 2.80 (m, 1H), 3.88 (s, 3H), 6.51 (d, *J* = 2.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ 27.8, 28.8, 30.2, 34.8, 37.7, 56.6, 110.6, 112.3, 126.5, 129.1, 135.3, 137.1, 155.1, 157.7, 199.4; MS (EI): *m/z* (%) 128 (28), 171 (48), 199 (100), 306 (M^+, 46), 308 (M^+ + 2, 88); HRMS (EI) calcd for $C_{15}H_{15}O_2Br$ (M^+) 306.0255, found 306.0261.

5-Bromo-6-methoxy-1,2,10,10a-tetrahydrophenanthren-3(9*H*)-one (12b).



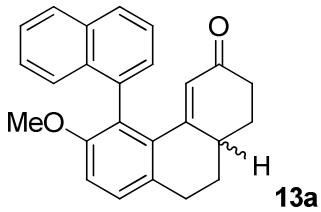
12b

Compound **12b** was obtained from α-formyl-1-tetralone **11b** following method B (eluent hexane/EtOAc 2:1) as a white solid, in 78% yield: m.p. 108-110 ºC; ^{1}H NMR δ 1.72-1.99 (m, 3H), 2.15-2.24 (m, 1H), 2.27-2.37 (m, 1H), 2.43-2.58 (m, 2H), 2.69-2.78 (m, 1H), 3.04 (dt, *J* = 5.5, 16.2 Hz, 1H), 3.8 (s, 3H), 6.57 (d, *J* = 2.1 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR δ 21.2, 28.5, 29.6, 34.8, 36.9, 55.8, 111.2, 111.8, 128.6, 131.6, 132.2, 136.1, 155.2, 158.0, 199.6; MS (EI): *m/z* (%) 115 (20), 128 (33), 171 (50), 199 (100), 306 (M^+, 40), 307 (M^+ + 2, 39); HRMS (EI) calcd for $C_{15}H_{15}O_2Br$ (M^+) 306.0255, found 306.0245.

General procedure for the Suzuki Coupling. Method C.

To a mixture of bromo derivatives **12a**,**b** (635 mg, 2.06 mmol), naphtyl boronic acid (1.23 g, 7.20 mmol), $CsCO_3$ (1.55 g, 4.73 mmol) and $Pd(PPh_3)_4$ (190 mg, 8% mol) under argon, toluene (10 mL), EtOH (10 mL) and H_2O (6 mL) were added. The reaction mixture was heated to 100 ºC for 12 h, filtered with celite and washed with water. After workup and flash chromatography, pure biaryls **13a**,**b** were obtained.

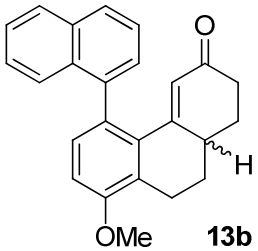
6-Methoxy-5-(1-naphthyl)-1,2,10,10a-tetrahydrophenanthren-3(9*H*)-one (13a)



13a

Compound **13a** was obtained, as a 70:30 mixture of diastereomers, from bromo derivative **12a** following method C (eluent hexane/EtOAc/CH_2Cl_2 6:1:2), as a yellow solid, in 81% yield: ^{1}H NMR δ 1.72-2.09 (m, 8H), 2.14-2.35 (m, 4H), 2.56-2.85 (m, 6H), 3.58 (s, 3H), 3.65 (s, 3H), 5.08 (d, *J* = 2.0 Hz, 1H), 5.42 (d, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 1.1 and 7.0 Hz, 1H), 7.22-7.27 (m, 4H), 7.34-7.47 (m, 5H), 7.51-7.58 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.78-7.81 (m, 1H), 7.85 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR δ 28.0, 29.5, 29.6, 29.9, 30.1, 34.9, 36.1, 37.0, 37.0, 37.4, 56.0, 56.2, 111.7, 112.7, 124.6, 125.2, 125.3, 125.5, 125.6, 125.7, 126.1, 126.4, 126.7, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.5, 128.6, 129.9, 131.8, 133.3, 133.4, 133.7, 133.9, 134.0, 135.6, 136.8, 136.9, 156.4, 156.5, 158.7, 158.8, 199.1, 199.2; MS (EI): *m/z* (%) 239 (34), 265 (46), 298 (34), 336 (44), 354 (M^+, 100); HRMS (EI) calcd for $C_{25}H_{22}O_2$ (M^+) 354.1620, found 354.1614.

8-Methoxy-5-(1-naphthyl)-1,2,10,10a-tetrahydrophenanthren-3(9*H*)-one (13b).



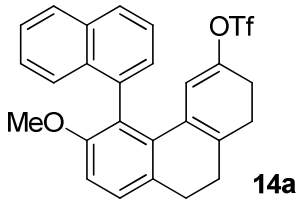
13b

Compound **13b** was obtained, as a 70:30 mixture of diastereomers, from bromo derivative **12b** following method C (eluent hexane/EtOAc/CH_2Cl_2 6:1:2), as a yellow solid, in 65% yield: ^{1}H NMR δ 1.70-1.86 (m, 3H), 1.90-1.97 (m, 1H), 2.01-2.23 (m, 6H), 2.28-2.39 (m, 1H), 2.65-2.83 (m, 5H), 3.03-3.18 (m, 2H), 3.96 (s, 6H), 5.31 (d, *J* = 2.0 Hz, 1H), 5.48 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 1.1 and 7.0 Hz, 1H), 7.17-7.19 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.26-7.29 (m, 2H), 7.31-7.35 (m, 1H), 7.39-7.45 (m, 3H), 7.47-7-53 (m, 1H), 7.55-7.59 (m, 2H), 7.82-7.85 (m, 3H), 7.93 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR δ 20.5, 20.8, 27.6, 28.0 (2C), 28.1, 33.6, 34.5, 34.8, 35.2, 54.2, (2C), 108.6, 109.4, 123.7, 123.9, 124.1, 124.2, 124.4 (2C), 124.5, 124.8, 125.6, 125.8, 126.1, 126.3, 126.4, 127.1, 127.2, 127.3, 128.4, 129.0, 129.6, 129.7, 129.9, 130.0, 130.6, 132.1, 132.6, 134.5, 138.1, 138.3, 154.2, 154.5, 157.4, 197.6 (2C); MS (EI): *m/z* (%) 239 (28), 252 (31), 298 (26), 336(30), 354 (M^+, 100); HRMS (EI) calcd for $C_{25}H_{22}O_2$ (M^+) 354.1620, found 354.1615.

General procedure for the enol triflate formation. Method D.

To a solution of the corresponding tetrahydrophenanthrenone (0.42 mmol) and di-*tert*-butylmethylpyridine (75 mg, 0.42 mmol) in CH_2Cl_2 (5.3 mL) at 0 ºC, triflic anhydride (74 μL, 0.42 mmol) was slowly added, under argon. After stirring for 30 minutes at rt, the solution was cooled to 0 ºC and hexane was added. After 10 minutes, the solution was filtered with celite, the solvent evaporated, and the resulting enol triflates were used in the next step without further purification.

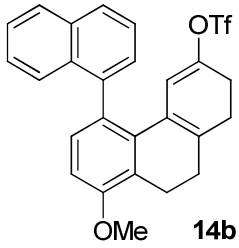
6-Methoxy-5-(1-naphthyl)-1,2,9,10-tetrahydrophenanthren-3-yl trifluoromethanesulfonate (14a).



14a

Compound **14a** was obtained from tetrahydrophenanthrenone **13a** (148 mg) following method D as a yellow oil, in 92% yield: ^{1}H NMR δ 2.04-2.13 (m, 1H), 2.20-2.52 (m, 5H), 2.72 (t, *J* = 6.7 Hz, 2H), 3.63 (s, 3H), 4.92 (s, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 7.24-7.28 (m, 2H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.43-7.51 (m, 3H), 7.85-7.90 (m, 2H); ^{13}C NMR δ 25.2, 28.6, 29.1, 29.9, 55.9, 108.9, 117.0, 118 (q, *J* = 322 Hz, 1C), 124.9, 125.0, 125.2, 125.5, 125.7, 125.8, 125.9, 127.2, 128.1, 128.3, 129.6, 132.6, 133.5, 134.6, 135.4, 137.5, 144.4, 156.6; MS (EI): *m/z* (%) 303 (26), 320 (17), 335 (100), 352 (19), 486 (M^+, 48); HRMS (EI) calcd for $C_{26}H_{21}O_4F_3S$ (M^+) 486.1112, found 486.1103.

8-Methoxy-5-(1-naphthyl)-1,2,9,10-tetrahydrophenanthren-3-yl trifluoromethanesulfonate (14b)



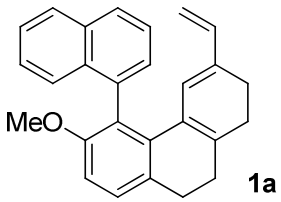
14b

Compound **14b** was obtained from tetrahydrophenanthrenone **13b** (148 mg) following method D as a yellow oil, in 80% yield: ^{1}H NMR δ 2.03-2.07 (m, 4H), 2.45-2.59 (m, 2H), 2.71-2.93 (m, 2H), 3.92 (s, 3H), 5.10 (s, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.32-7.38 (m, 2H), 7.41-7.49 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.81-7.89 (m, 2H); ^{13}C NMR δ 21.2, 25.2, 27.7, 28.9, 55.7, 109.2, 117.0, 125.3, 125.4, 125.7, 125.8, 125.9, 126.0, 127.5, 127.9, 128.4, 128.8, 130.7, 132.2, 133.8, 134.4, 136.9, 139.8, 144.8, 155.5; MS (FAB): *m/z* (%) 335 (100), 486 (M^+, 60); HRMS (EI) calcd for $C_{26}H_{21}O_4F_3S$ (M^+) 486.1113, found 486.1104.

General procedure for the Stille coupling: synthesis of dienes. *Method E*.

To a mixture of the corresponding enol triflate (0.267 mmol), LiCl (56 mg, 1.3 mmol) and $Pd(PPh_3)_4$ (15 mg, 5% mol) in dry THF (2.6 mL), under argon, vinyltributylstannane (84 mg, 0.267 mmol) was added dropwise. The reaction mixture was refluxed for the time indicated in each case, filtered with celite and washed with water. After workup and flash chromatography, pure 3-vinyl tetrahydrophenanthrenes were obtained.

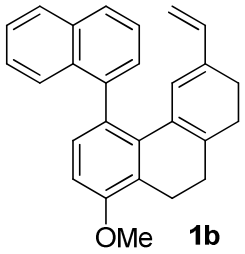
6-Methoxy-5-(1-naphthyl)-3-vinyl-1,2,9,10-tetrahydrophenanthrene (1a).



1a

Compound **1a** was obtained from enol triflate **14a** (129 mg) following method E (90 min, eluent hexane/ CH_2Cl_2 1:3) as a colourless oil, in 63% yield ^{1}H NMR δ 1.87-1.93 (m, 2H), 2.19-2.25 (m, 3H), 2.32-2.43 (m, 1H), 2.68-2.73 (m, 2H), 3.61 (s, 3H), 4.58 (d, *J* = 10.6 Hz, 1H), 4.76 (d, *J* = 17.3 Hz, 1H), 4.84 (s, 1H), 5.28 (dd, *J* = 10.6 and 17.3 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 7.21 (m, 1H), 7.23 (m, 1H), 7.31-7.44 (m, 3H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 20.6, 29.1, 29.2, 29.3, 55.9, 108.3, 109.3, 125.0, 125.1, 125.2, 125.5, 126.4, 127.0, 127.5, 128.0, 128.4, 128.8, 130.2, 131.1, 133.0, 133.3, 135.9, 136.3, 138.2, 139.3, 156.5; MS (EI): *m/z* (%) 165 (6), 239 (6), 289 (12), 364 (M^+, 100); HRMS (EI) calcd for $C_{27}H_{24}O_1$ (M^+) 364.1827, found 364.1815.

8-Methoxy-5-(1-naphthyl)-3-vinyl-1,2,9,10-tetrahydrophenanthrene (1b).



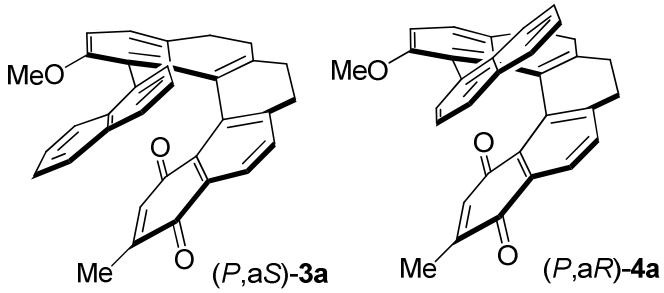
1b

Compound **1b** was obtained from enol triflate **14b** (129 mg) following method E (90 min, eluent hexane/ CH_2Cl_2 15:1 in Al_2O_3) as a colourless oil, in 42% yield: ^{1}H NMR δ 1.83 (ddd, *J* = 6.3, 9.7 and 16.2 Hz, 1H), 1.99 (ddd, *J* = 7.5, 8.4 and 16.2 Hz, 1H), 2.23-2.36 (m, 4H), 2.76 (ddd, *J* = 7.7, 8.0 and 15.5 Hz, 1H), 2.86 (ddd, *J* = 7.6, 7.9 and 7.5 Hz, 1H), 3.92 (s, 3H), 4.59 (d, *J* = 10.7 Hz, 1H), 4.75 (d, *J* = 17.3 Hz, 1H), 5.02 (s, 1H), 5.39 (dd, *J* = 10.7 and 17.3 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.31-7.45 (m, 4H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ 20.7, 21.3, 28.2, 29.1, 55.7, 108.6, 109.5, 125.1, 125.4, 125.5, 125.6, 126.3, 127.2, 127.5, 127.6, 128.0, 127.7, 128.9, 130.4, 131.4, 132.4, 133.5, 135.6, 138.2, 138.6, 140.7, 155.3; MS (EI): *m/z* (%) 144 (11), 165 (11), 289 (22), 335 (22), 364 (M^+, 100); HRMS (EI) calcd for $C_{27}H_{24}O_1$ (M^+) 364.1827, found 364.1840.

General procedure for the synthesis of 14-aryl-[5]helicenequinones. Method F.

To a mixture of the corresponding 3-vinyltetrahydrophenanthrene (0.11 mmol) and (S*S*)-5-methyl-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**2**)[2] (54 mg, 0.22 mmol) at –27 ºC, CH_2Cl_2 (5.5 mL) was rapidly added, under argon. The reaction mixture was stirred at the temperature and for the time indicated in each case. After elimination of the solvent and flash chromatography, the corresponding pure 14-aryl-[5]helicenequinones were obtained.

(*P*,a*S*)-13-Methoxy-3-methyl-14-(1-naphtyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (3a) and (*P*,a*R*)-13-methoxy-3-methyl-14-(1-naphtyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (4a).



(*P*,a*S*)-**3a** (*P*,a*R*)-**4a**

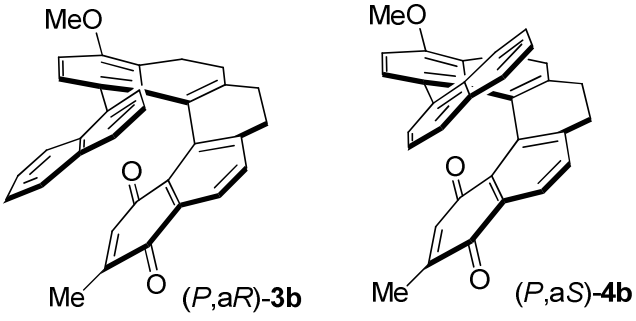
(2) Carreño, M. C.; García Ruano, J. L.; Urbano, A. *Synthesis*, **1992**, 651-653.

Compounds (*P*,a*S*)-**3a** and (*P*,a*R*)-**4a** were obtained, as a 50:50 mixture, from 3-vinyltetrahydrophenanthrene **1a** (40 mg) following method F (12 h at –27 ºC and 3 h at room temperature, eluent CH_2Cl_2) as a red solid, in 68% overall yield. Analytic amounts of both diastereoisomers could be obtained after preparative HPLC (Column C18, 250 x 4.6 mm, 5 μm; H_2O/CH_3CN 20/80; R_t (*P*,a*S*)-**3a**: 14.93 min, R_t (*P*,a*R*)-**4a**: 16.96 min):

Diastereoisomer (*P*,a*S*)-**3a**: m.p. 220-221 ºC; $\{[\alpha]_D^{20} = +936$ (c = 0.012 in $CHCl_3$), 99% *ee* (Chiral HPLC: Daicel Chiralpak OD, hexane/2-propanol 98:2; 1.0 mL min^{-1}, 254 nm, $R_t = 33.0$ min, $T = 25$ ºC}; ^{1}H NMR δ 1.77 (d, $J = 1.3$ Hz, 3H), 2.27-2.40 (m, 3H), 2.50-2.63 (m, 3H), 2.87 (dd, $J = 4.6$ and 13.4 Hz, 1H), 3.02 (ddd, $J = 5.5$, 14.2 and 14.6 Hz, 1H), 3.53 (s, 3H), 6.06 (q, $J = 1.3$ Hz, 1H), 6.74 (d, $J = 7.0$ Hz, 1H), 6.81-6.87 (m, 2H), 7.09 (d, $J = 7.6$, 1H), 7.18-7.28 (m, 3H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 7.9$ Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR δ 15.7, 29.4, 29.8, 29.9, 30.2, 55.5, 107.3, 122.0, 124.0, 125.1, 125.4, 125.5. 126.5, 126.7, 127.2, 127.4, 128.2, 128.5, 129.8, 130.7, 130.8, 131.2, 132.5, 133.0, 135.9, 136.0, 136.6, 137.4, 142.9, 144.8, 148.8, 155.8, 184.5, 185.3; MS (EI): *m/z* (%) 241 (5), 451 (6), 482 (M^+, 100); HRMS (EI) calcd for $C_{34}H_{26}O_3$ (M^+) 482.1881, found 482.1881.

Diastereoisomer (*P*,a*R*)-**4a**: m.p. 203-205ºC; $\{[\alpha]_D^{20} = +977$ (c = 0.009 in $CHCl_3$), 98% *ee* (Chiral HPLC: Daicel Chiralpak OD, hexane/2-propanol 95:5; 0.8 mL min^{-1}, 254 nm, $R_t = 20.8$ min, $T = 25$ ºC)}; ^{1}H NMR δ 2.11 (d, $J = 1.5$ Hz, 3H), 2.14-2.26 (m, 4H), 2.35 (dd, $J = 5.6$ and 17.2 Hz, 1H), 2.60 (ddd, $J = 5.0$, 16.3 and 16.5 Hz, 1H), 2.86 (ddd, $J = 1.7$, 4.9 and 13.8 Hz, 1H), 3.00 (ddd, $J = 5.5$, 13.9 and 14.6 Hz, 1H), 3.59 (s, 3H), 6.53 (q, $J = 1.5$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 6.90 (d, $J = 8.3$ Hz, 1H), 6.96 (dd, $J = 7.1$ and 8.1 Hz), 7.08-7.13 (m, 2H), 7.17-7.22 (m, 1H), 7.25-7.28 (m, 3H), 7.39 (d, $J = 8.2$ Hz, 1H), 7.45 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR δ 15.9, 28.4, 29.1, 29.6, 30.4, 55.9, 108.5, 122.2, 123.3, 123.5, 125.2, 125.8, 125.9, 126.7, 127.1, 128.0, 128.3, 128.6, 129.5, 130.1, 130.2, 131.0, 132.2, 133.3, 133.7, 135.4 (2C), 136.4, 144.6, 144.8, 148.3, 155.9, 184.4, 186.0; MS (EI): *m/z* (%) 175 (5), 241 (5), 451 (6), 482 (M^+, 100); HRMS (EI) calcd for $C_{34}H_{26}O_3$ (M^+) 482.1881, found 482.1881.

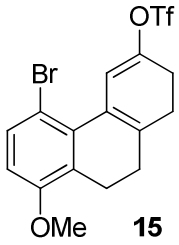
(*P*,a*R*)-11-methoxy-3-methyl-14-(1-naphtyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (3b) and (*P*,a*S*)-11-Methoxy-3-methyl-14-(1-naphthyl)-7,8,9,10-tetrahydro-[5]-helicenequinone (4b)



Compounds (*P*,*a*R)-**3b** and (*P*,*a*S)-**4b** were obtained, as an unseparable 20:80 mixture, from 3-vinyltetrahydrophenanthrene **1b** (40 mg) following method F (12 h at –27 ºC and 3 h at –10 ºC, eluent hexane/CH_2Cl_2 3:1) as a red solid, in 74% overall yield: m.p. 220-221 ºC; $[\alpha]_D^{20}$ = + 1434 (c = 0.009 in $CHCl_3$); MS (EI): *m/z* (%) 391 (12), 482 (M^+, 100); HRMS (EI) calcd for $C_{34}H_{26}O_3$ (M^+) 482.1881, found 482.1875.

The following data correspond to the major diastereoisomer (*P*,*a*S)-**4b** and were obtained from the mixture: 93% *ee* (Chiral HPLC: Daicel Chiralpak IB, hexane/2-propanol 95:5; 0.6 mL min^{-1}, 254 nm, R_t = 19.1 min, *T* = 25 ºC); ^{1}H NMR δ 2.10 (d, *J* = 1.4 Hz, 3H), 2.17-2.25 (m, 3H), 2.37-2.51 (m, 3H), 2.55-2.62 (m, 2H), 3.51 (dd, *J* = 4.2 and 10.2 Hz, 1H), 3.96 (s, 3H), 6.47 (q, *J* = 1.4 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.95-7.07 (m, 3H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.21-7.29 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ 15.9, 21.0, 28.5, 28.9, 29.5, 55.5, 108.7, 123.4, 124.0, 125.3, 125.5, 125.8 (2C), 126.5, 127.0, 127.4, 127.8, 128.2, 128.7, 129.9, 130.4, 130.8, 131.9, 132.8, 133.7, 135.2, 136.3, 142.0, 144.8, 144.9, 147.5, 155.4, 184.2, 186.0.

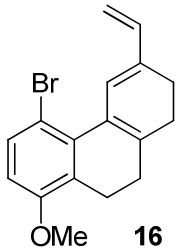
5-Bromo-1,2,9,10-tetrahydro-8-methoxyphenanthren-3-yl-trifluoromethanesulfonate (15).



15

Compound **15** was obtained from tetrahydrophenanthrenone **12b** (128 mg) following method D as a pale yellow oil, in 90% yield: ^{1}H NMR δ 2.16 (dd, *J* = 6.1 and 7.0 Hz, 2H), 2.62 (br s, 4H), 2.68 (dd, *J* = 6.1 and 7.0 Hz, 2H), 3.80 (s, 3H), 6.65 (d, *J* = 8.7 Hz, 1H), 6.73 (s, 1H), 7.37 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR δ 21.6, 25.5, 27.3, 30.3, 55.7, 110.2, 111.0, 117.6, 118.6 (q, *J* = 320 Hz), 125.1, 128.2, 132.3, 134.4, 139.4, 144.2, 155.2; MS (EI): *m/z* (%) 196 (100), 224 (78), 436 (M^+ – 2, 89), 438 [(M^+ – 2) + 2, 89). HRMS (EI) calcd for $C_{16}H_{14}O_4BrF_3S$ (M^+ – 2) 435.9592, found 435.9574.

5-Bromo-8-methoxy-3-vinyl-1,2,9,10-tetrahydrophenanthrene (16).

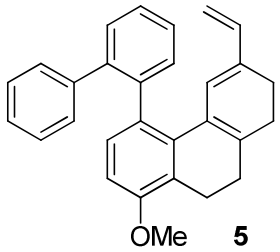


16

Compound **16** was obtained from enol triflate **15** (116 mg) following method E (50 min, eluent hexane in neutral Al_2O_3 deactivated with 10% of water) as a colourless oil, in 56% yield: ^{1}H NMR δ

2.20 (dd, J = 7.4 and 7.7 Hz, 2H), 2.40-2.41 (m, 4H), 2.67 (dd, J = 7.4 and 7.7 Hz, 2H), 3.81, (s, 3H), 5.04 (d, J = 10.8 Hz, 1H), 5.23 (d, J = 17.4 Hz, 1H), 6.58 (dd, J = 10.8 and 17.4 Hz, 1H), 6.61-6.64 (m, 2H), 7.38 (d, J = 8.9 Hz, 1H); ^{13}C NMR δ 21.0, 21.7, 27.9, 29.5, 55.8, 110.5, 110.6 (2C), 127.5, 128.2, 128.5, 131.1, 132.1, 135.6, 138.8, 140.8, 155.1. MS (EI): *m/z* (%) 165 (87), 194 (95), 316 (M^+, 100), 318 (M^+ + 2, 85).

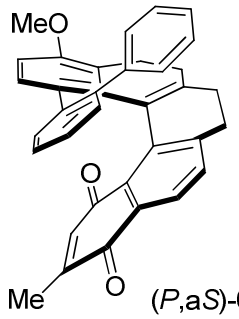
5-(2-Biphenyl)-8-methoxy-3-vinyl-1,2,9,10-tetrahydrophenanthrene (5)



5

A mixture of bromo tetrahydrophenanthrene **16** (46 mg, 0.14 mmol), 2-biphenyl boronic acid (70 mg, 0.33 mmol), $Ba(OH)_2 \cdot 8H_2O$ (102 mg, 0.32 mmol) and $Pd(PPh_3)_4$ (13 mg, 8% mol) in DME (3.5 mL), under argon, was heated at 90 ºC for 1 h. The reaction mixture was filtered with celite and washed with water. After workup and flash chromatography (hexane/CH_2Cl_2 10:1 in Al_2O_3 deactivated with 10% of water), pure compound **5** was obtained as a colourless oil, in 62% yield: ^{1}H NMR δ 1.55-1.66 (m, 1H), 1.80 (ddd, J = 4.7, 5.0 and 16.1 Hz, 1H), 2.04-2.27 (m, 5H), 2.82 (ddd, J = 4.2, 4.3 and 15.7 Hz, 1H), 3.85 (s, 3H), 4.80 (d, J = 10.6 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 5.27 (s, 1H), 5.81 (dd, J = 10.6 and 17.2 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 6.84-6.88 (m, 2H), 7.07-7.09 (m, 3H), 7.13 (d, J = 8.6 Hz, 1H), 7.27-7.29 (m, 1H), 7.34-7.37 (m, 2H), 7.42-7.45 (m, 1H); ^{13}C NMR δ 20.8, 20.9, 27.9, 28.8, 55.6, 108.6, 109.6, 125.5, 125.9, 127.1, 127.4, 127.5, 127.8 (2C), 129.7 (2C), 130.1, 130.3, 130.6, 131.1, 135.0, 138.3, 139.1, 141.3, 141.4 (2C), 155.0; MS (EI): *m/z* (%) 165 (13), 239 (7), 315 (6), 359 (7), 390 (M^+, 100); HRMS (EI) calcd for $C_{29}H_{26}O$ (M^+) 390.1983, found 390.1985.

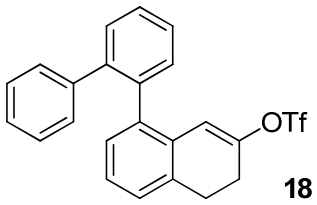
(*P*,a*S*)-14-(2-Biphenyl)-11-methoxy-3-methyl-7,8,9,10-tetrahydro-[5]-helicenequinone (6)



(*P*,a*S*)-**6**

Compound (*P*,a*S*)-**6** was obtained from 3-vinyltetrahydrophenanthrene **5** (43 mg) following method F (12 h at –27 ºC, 5 h at –10 ºC; eluent hexane/CH_2Cl_2/EtOAc 6:2:1) as a red solid, in 75% yield: m.p. 229-230 ºC; $\{[\alpha]_D^{20} = +1970$ (c = 0.01 in $CHCl_3$), 95% *ee* (Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min^{-1}, 254 nm, $R_t = 9.6$ min, $T = 25$ ºC)$\}$; ^{1}H NMR δ 1.82-1.88 (m, 2H), 2.02 (dd, *J* = 5.0 and 16.8 Hz, 1H), 2.11 (d, *J* = 1.4 Hz, 3H), 2.17-2.41 (m, 4H), 3.25 (ddd, *J* = 1.5, 5.1 and 15.2 Hz, 1H), 3.95 (s, 3H), 6.48 (q, *J* = 1.4 Hz, 1H), 6.77-6.80 (m, 2H), 6.88-6.94 (m, 4H), 6.97-7.00 (m, 3H), 7.05-7.07 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR δ 15.9, 20.9, 28.4, 28.7, 29.0, 55.4, 108.6, 123.9, 125.9, 126.1, 126.2, 127.4, 127.6, 128.6, 128.7, 129.5, 129.6, 130.1, 130.5, 130.6, 130.7, 132.4, 134.5, 134.8, 136.4, 138.3, 139.6, 142.0, 144.7, 145.7, 147.6, 155.0, 184.6, 186.1; MS (EI): *m/z* (%) 165 (13), 189 (6), 239 (6), 477 (6), 508 (M^+, 100); HRMS (EI) calcd for $C_{36}H_{28}O_3$ (M^+) 508.2038, found 508.2016.

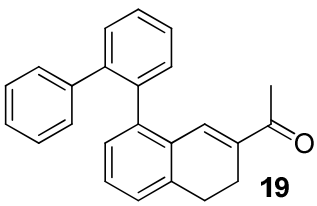
8-(2-Biphenyl)-3,4-dihydronaphtalen-2-trifluoromethanesulfonate (18).



18

To a solution of 8-(2-biphenyl)-2-tetralone (**17**)[3] (64 mg, 0.21 mmol) and N-phenyl-bis(trifluoromethanesulfonimide) (82 g, 0.23 mmol) in dry THF (2.1 mL) was slowly added a solution of KHMDS 0.5M in THF (0.46 mL, 0.23 mmol) at –78 ºC, under argon. The mixture was stirred for 80 min and quenched with H_2O at –78 ºC. After warming to room temperature, workup and flash chromatography (eluent EtOAc/hexane 1:5), compound **18** was obtained as a colorless oil, in 98% yield: ^{1}H NMR δ 2.46 (ddd, *J* = 7.9, 9.1 and 16.9 Hz, 1H), 2.53 (ddd, *J* = 7.3, 8.2 and 16.9 Hz, 1H), 2.96 (m, 2H), 6.19 (s, 1H), 6.97-7.17 (m, 8H), 7.26-7.29 (m, 1H), 7.38-7.48 (m 3H); ^{13}C NMR δ 26.1, 29.1, 117.0, 126.3, 126.5, 127.3, 127.5, 128.2, 128.5, 129.4, 129.5, 130.2, 131.0, 132.0, 133.2, 135.6, 138.0, 139.7, 141.0, 141.5, 149.9; MS (EI): m/z (%) 239 (37), 279 (100), 297 (79), 430 (M^+, 36); HRMS (EI) calcd. for $C_{23}H_{17}O_3F_3S$ (M^+) 430.0850, found 430.0850.

2-Acetyl-8-(2-biphenyl)-3,4-dihydronaphthalene (19)

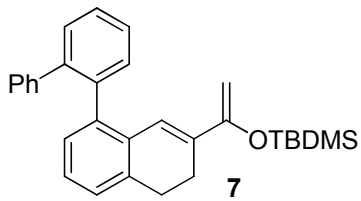


19

(3) M. C. Carreño, M. González-López, A. Latorre, A. Urbano, *J. Org. Chem.* **2006**, *71*, 4956-4964.

To a mixture of enol triflate **18** (255 mg, 0.59 mmol), LiCl (123 mg, 2.9 mmol) and $Pd(PPh_3)_4$ (34 mg, 5% mol) in THF (5.9 mL), under argon, (1-ethoxyvinyl)-tributylstannane (166 μL, 0.65 mmol) was added. The reaction mixture was heated at 90 ºC for 1.5 h, filtered with celite and washed with water. The solvent was evaporated and the residue was charged in a flash column chromatography for 1 h to provoke the hydrolysis of the vinyl ether. Then, the residue was eluted with a mixture of EtOAc/hexane 1:6, to obtain pure compound **19** as a white solid, in 62% yield: m.p. 140-141ºC; ^{1}H NMR δ 2.03-2.16 (m, 1H), 2.16 (s, 3H), 2.40-2.50 (m, 1H), 2.68 (dd, *J* = 6.1 and 7.4 Hz, 2H), 7.01-7.06 (m, 3H), 7.07-7.13 (m, 5H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.35-7.38 (m, 1H), 7.42-7.50 (m, 3H); ^{13}C NMR δ 20.4, 25.2, 28.1, 126.7, 127.4, 127.8, 128.3, 129.1, 129.4, 129.5, 130.0, 130.5, 131.2, 135.5, 137.9 (2C), 138.3, 140.8, 140.9, 141.6, 198.5; MS (EI): m/z (%) 203 (25), 252 (31), 265 (50), 281 (82), 324 (M^+, 100); HRMS (EI) calcd. for $C_{24}H_{20}O$ (M+) 324.1514, found 324.1519.

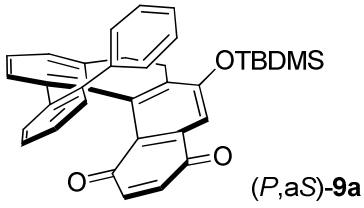
8-(2-Biphenyl)-2-[1-(*tert*-butyldimethylsilyloxy)vinyl]-3,4-dihydronaphthalene (7)



7

To a solution of methyl ketone **19** (35 mg, 0.1 mmol) in THF (2.1 mL) was slowly added a solution of KHMDS 0.5M in THF (0.24 mL, 0.12 mmol) at –78 ºC, under argon, and the mixture stirred for 10 min. Then, TBDMSOTf (0.26 mL, 0.12 mmol) was added and the mixture was stirred for 1.5 h and quenched with H_2O at –78 ºC. After warming to room temperature, workup and flash chromatography (hexane in Al_2O_3 deactivated with 10% of water), compound **7** was obtained as a colorless oil, in 85% yield: ^{1}H NMR δ 0.05 (s, 3H), 0.07 (s, 3H), 0.73 (s, 9H), 2.22 (ddd, *J* = 8.0, 8.2 and 15.2 Hz, 1H), 2.37 (ddd, *J* = 7.7, 8.0 and 15.2 Hz, 1H), 2.78 (m, 2H), 4.33 (d, *J* = 0.9 Hz, 1H), 4.54 (d, *J* = 0.9 Hz, 1H), 6.75 (s, 1H), 6,83 (dd, *J* = 1.7 and 7.2 Hz, 1H), 6.92-6.98 (m, 2H), 7.03-7.06 (m, 2H), 7.08-7.12 (m, 3H), 7.27-7.30 (m,1H), 7.32-7.37 (m, 1H), 7.38-7.41 (m, 2H); ^{13}C NMR δ –4.8, –4.7, 18.0, 23.5, 25.7, 28.7, 92.1, 122.6, 125.8, 126.1, 126.2, 127.0, 127.4, 127.5, 128.5, 128.9, 129.5, 130.0, 131.1, 132.0, 132.6, 134.8, 135.7, 139.3, 141.4, 156.0; MS (EI): m/z (%) 371 (100), 382 (53), 397 (64), 415 (75), 438 (M^+, 59); HRMS (EI) calcd. for $C_{30}H_{34}O$ (M^+) 438.2378, found 438.2371.

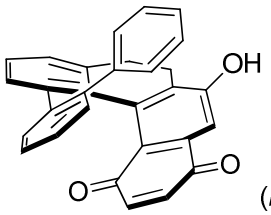
(*P*,a*S*)-12-(2-Biphenyl)-6-(*tert*-butyldimethylsilyloxy)-7,8-dihydro-[4]-helicenequinone (9a)



(*P*,a*S*)-**9a**

Compound (*P*,a*S*)-**9a** was obtained following method F (18 h, –27 ºC, eluent hexane/CH_2Cl_2 1:3) from diene **7** and (S*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**8**)[2] (0.18 mmol, 44 mg, 2 equiv) as an orange solid, in 76% yield: m.p. 183-184 ºC; $[\alpha]_D^{20}$ = +748 (c = 0.033 in $CHCl_3$), 85% *ee* (Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min^{-1}, 254 nm, R_t = 7.9 min, *T* = 25 ºC)}; ^{1}H NMR (500 MHz) δ 0.27 (s, 3H), 0.43 (s, 3H), 1.03 (s, 3H), 1.22 (dd, *J* = 4.6 and 15.4 Hz, 1H), 2.73 (td, *J* = 4.41 and 15.8 Hz, 1H), 6.28 and 6.39 (AB system, *J* = 10.4 Hz, 2H), 6.31-6.33 (m, 2H), 6.84-6.87 (m, 2H), 6.96-7.00 (m, 2H), 7.12 (s, 1H), 7.22-7.24 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.36-7.41 (m, 3H); ^{13}C NMR δ –4.4, –3.8, 18.3, 22.3, 25.6, 29.4, 112.4, 125.9, 126.6, 127.0, 127.3, 127.4, 127.5, 128.3, 128.4, 129.6, 130.9, 131.4, 132.4, 134.9, 135.1, 136.9, 139.6, 139.7, 140.3 (2C), 140.5, 140.9, 155.4, 185.0, 185.9; MS (EI): *m/z* (%) 333 (12), 389 (100), 485 (39), 542 (M^+, 75); HRMS (EI) calcd for $C_{36}H_{34}O_3Si$ (M^+) 542.2277, found 542.2254.

(*P*,a*S*)-12-(2-Biphenyl)-6-hydroxy-7,8-dihydro-[4]-helicenequinone (9b)



(*P*,a*S*)-**9b**

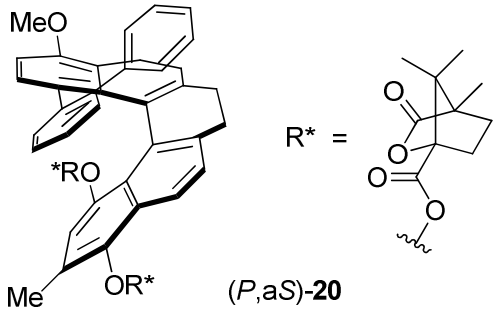
To a solution of OTBDMS derivative (*P*,a*S*)-**9a** (13.5 mg, 0.025 mmol) in THF (2 mL), a solution of TBAF 1M in THF (0.05 mL, 0.05 mmol) was added at 0 ºC. The reaction was stirred 1 h and quenched with NH_4Cl. After workup and flash chromatography (CH_2Cl_2), compound (*P*,a*S*)-**9b** was obtained as an orange solid, in 75% yield: m.p. 226-228 ºC; $[\alpha]_D^{20}$ = +1034 (c = 0.014 in $CHCl_3$); ^{1}H NMR δ 1.25 (dd, *J* = 5.1 and 15.5 Hz, 1H), 2.26 (dd, *J* = 4.6 and 15.5 Hz, 1H), 2.58-2.71 (m, 2H), 5.85 (s, 1H), 6.30 and 6.41 (AB system, *J* = 10.1 Hz, 2H), 6.31-6.33 (m, 1H), 6.87-6.92 (m, 2H), 6.97-7.04 (m, 2H), 7.20-7.26 (m, 2H), 7.21 (s, 1H), 7.30-7.32 (m, 1H), 7.37 (dd, *J* = 7.1 and 7.6 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.41-7.44 (m, 1H); ^{13}C NMR δ 21.6, 29.2, 110.5, 126.0, 126.5, 126.9, 127.3, 127.4, 127.5, 128.4, 128.5, 129.5, 131.0, 131.6, 132.0, 134.8, 135.0, 135.4, 137.3, 139.4, 140.2, 140.3, 140.5, 140.6, 140.9, 155.6, 185.2, 185.7; MS (FAB): *m/z* (%) 136 (68), 154 (100), 307 (19), 429 (M^+ + 1, 8); HRMS (FAB) calcd for $C_{30}H_{21}O_3$ (M^+ + 1) 429.1491, found 429.1481.

General synthesis of bis-(–)-camphanates. Method G.

Et_3N (195 μL) and CH_2Cl_2 (3 mL) were added to a mixture of the corresponding helicenequinone (0.066 mmol), activated Zn (56 mg, 0.85 mmol), (–)-camphanoyl chloride (72 mg, 0.33 mmol) and

DMAP (3.8 mg, 0.033mmol), under argon. The mixture was refluxed for the time indicated in each case. Filtration through celite, aided by several ethyl acetate washes, removed remaining Zn. The organic solution was washed with saturated aqueous $NaHCO_3$, 2% HCl and water. After workup and flash chromatography, the corresponding pure bis-(–)-camphanate was obtained.

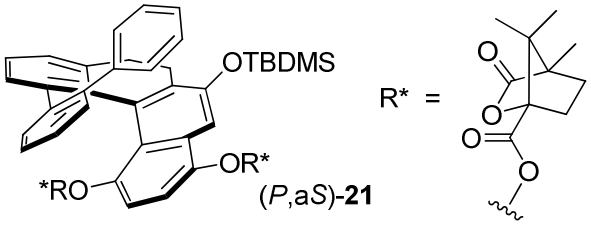
(*P*,a*S*)-14-(2-Biphenyl)-11-methoxy-7,8,9,10-tetrahydro-[5]-helicene-bis-(-)-camphanoyl-hydroquinone (20).



(*P*,a*S*)-**20**

Compound (*P*,a*S*)-**20** was obtained from helicenequinone (*P*,a*S*)-**6** (16 mg) following method G (45 min, eluent hexane/EtOAc 2:1) as a pale brown solid, in 78% yield; m.p. 200-202 ºC; $[\alpha]_D^{20} = +355$ (c = 0.12 in $CHCl_3$); ^{1}H NMR (500 MHz) δ 0.80 (s, 3H), 1.00 (3H), 1.05 (3H), 1.23 (3H), 1.26 (s, 3H), 1.59-1.68 (m, 2H), 1.74 (m, 5H), 2.03-2.12 (m, 3H), 2.16-2.39 (m, 3H), 2.26 (s, 3H), 2.58 (dt, *J* = 5.5 and 15.6 Hz, 1H), 2.67 (ddd, *J* = 4.2, 10.7 and 15.0 Hz, 1H), 3.06 (dd, *J* = 5.3 and 15.0 Hz, 1H), 3.88 (s, 3H), 6.59-6.60 (m, 4H), 6.73-6-77 (m, 3H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 7.01 (m, 3H), 7.06-7.08 (m, 2H); ^{13}C NMR δ 9.8, 9.9, 16.7, 16.9, 17.0, 17.1, 17.2, 20.2, 28.6, 28.7, 28.8, 28.9, 29.0, 31.6, 54.4, 54.8, 55.1, 55.2, 56.2, 90.9, 91.2, 108.0, 118.3, 119.2, 123.6, 123.8, 125.6, 127.7, 126.8, 127.2, 127.3, 128.5, 129.1, 129.3, 129.5, 129.6, 130.5, 132.3, 135.9, 136.8, 138.0, 140.1, 140.6, 141.7, 143.1, 145.3, 154.8, 165.0, 178.1, 178.2; MS (MALDI): *m/z* (%) 673 (100), 870 (M^+, 34); HRMS (MALDI) calcd for $C_{56}H_{54}O_9$ (M^+) 870.3815, found 870.3762.

(*P*,a*S*)-12-(2-Biphenyl)-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydro-[4]-helicene-bis(–)-camphanoyl-hydroquinone (21)



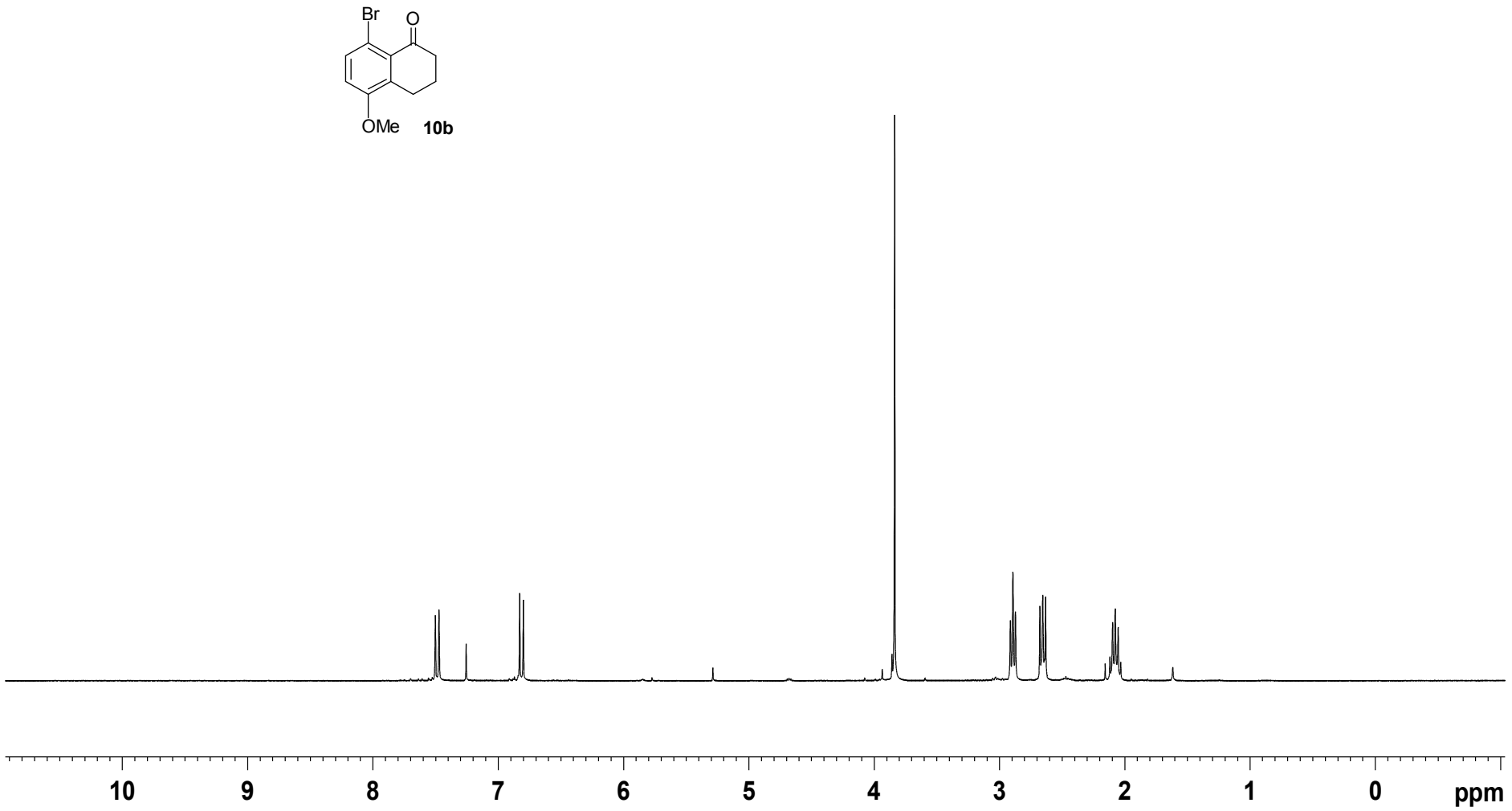
(*P*,a*S*)-**21**

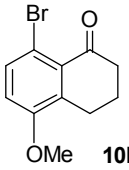
Compound (*P*,a*S*)-**21** was obtained from helicenequinone (*P*,a*S*)-**9a** (59 mg) following method G (50 min, eluent hex/EtOAc 3:1) as a yellow solid, in 72% yield: m.p. 194-195ºC; $[\alpha]_D^{20}$ = +252 (c = 0.16 in $CHCl_3$); ^{1}H NMR (500 MHz) δ 0.23 (s, 3H), 0.44 (s, 3H), 0.65 (s, 3H), 1.03 (s, 9H), 1.06 (s, 3H), 1.10 (s, 3H), 1.22 (s, 6H), 1.23 (s, 3H), 1.34 (dt, *J* = 4.4 and 16.0 Hz, 1H), 1.46 (ddd, *J* = 4.2, 9.3 and 13.7 Hz, 1H), 1.60 (ddd, *J* = 3.9, 9.1 and 13.2 Hz, 1H), 1.83-1.88 (m, 2H), 2.03-2.09 (m, 2H), 2.32 (ddd, *J* = 4.6, 9.3 and 13.4 Hz, 1H), 2.39 (dt, *J* = 4.2 and 14.3 Hz, 1H), 2.56-2.72 (m, 3H), 6.13-6.15 (m, 2H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.78-6.82 (m, 3H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 7.03, (dd, *J* = 7.6 and 7.7 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.24-7.27 (m, 1H), 7.36 (dd, *J* = 7.4 and 7.6 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR δ –4.7, –3.7, 9.6, 9.8, 16.5, 17.0, 17.1, 17.2, 18.2, 23.1, 25.6, 29.1, 29.2, 29.6, 29.8, 31.3, 54.1, 54.5, 54.6, 54.9, 90.7, 90.9, 105.2, 114.6, 116.0, 122.2, 125.5, 125.7, 126.7, 127.1, 127.2, 127.5, 128.1, 129.3, 130.9, 131.0, 133.4, 137.6, 139.5, 139.7, 140.0 (2C), 141.1, 142.6, 143.1, 151.7, 165.0, 166.0, 177.7, 177.8; MS (EI): *m/z* (%) 904 (M^+, 100), 905 (M^+ + 1, 65); HRMS (MALDI) calcd for $C_{56}H_{60}O_9Si$ (M^+) 904.4038, found 904.4001.

X-Ray Crystallography

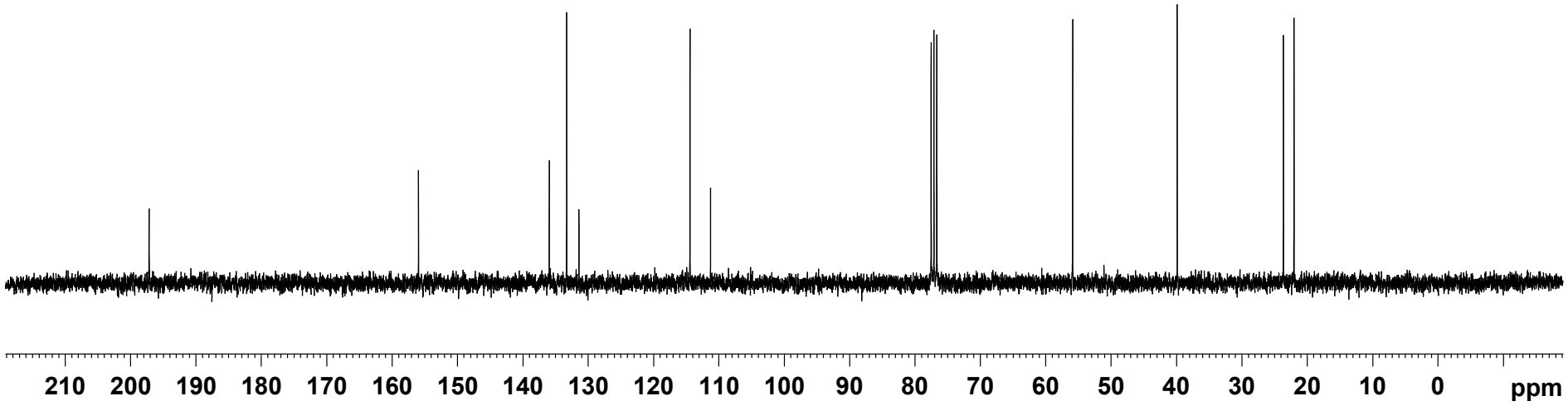
Crystal data for (*P*,a*R*)-**4a**: $C_{34}H_{26}O_3$, *M* = 482.55, triclinic, *a* = 10.1039(6), *b* = 11.6511(7), *c* = 11.8095(7) Å, α = 116.0420(10), β = 90.402(3), γ = 95.849(4)º, *U* = 1240.50(13) Å^3, *T* = 100(2) K, space group *P*1, *Z* = 2, 22716 measured and 22716 independent reflections (R_{int} = 0.000), R_1 = 0.0584, wR_2 = 0.1639, Flack *x* parameter = –0.5(6).

Crystal data for (*P*,a*S*)-**6**: $C_{36}H_{28}O_3$, *M* = 508.58, orthorhombic, *a* = 7.6471(4), *b* = 15.5793(9), *c* = 21.7870(13) Å, *U* = 2595.60(3) Å^3, *T* = 100(2) K, space group $P2_12_12_1$, *Z* = 4, 106248 measured and 5503 independent reflections (R_{int} = 0.0507), R_1 = 0.0308, wR_2 = 0.0854, Flack *x* parameter = –0.1(9).


Br
O
OMe
10b
10
9
8
7
6
5
4
3
2
1
0
ppm


Br
O
OMe

10b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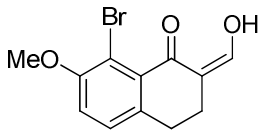
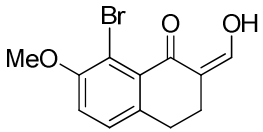


11a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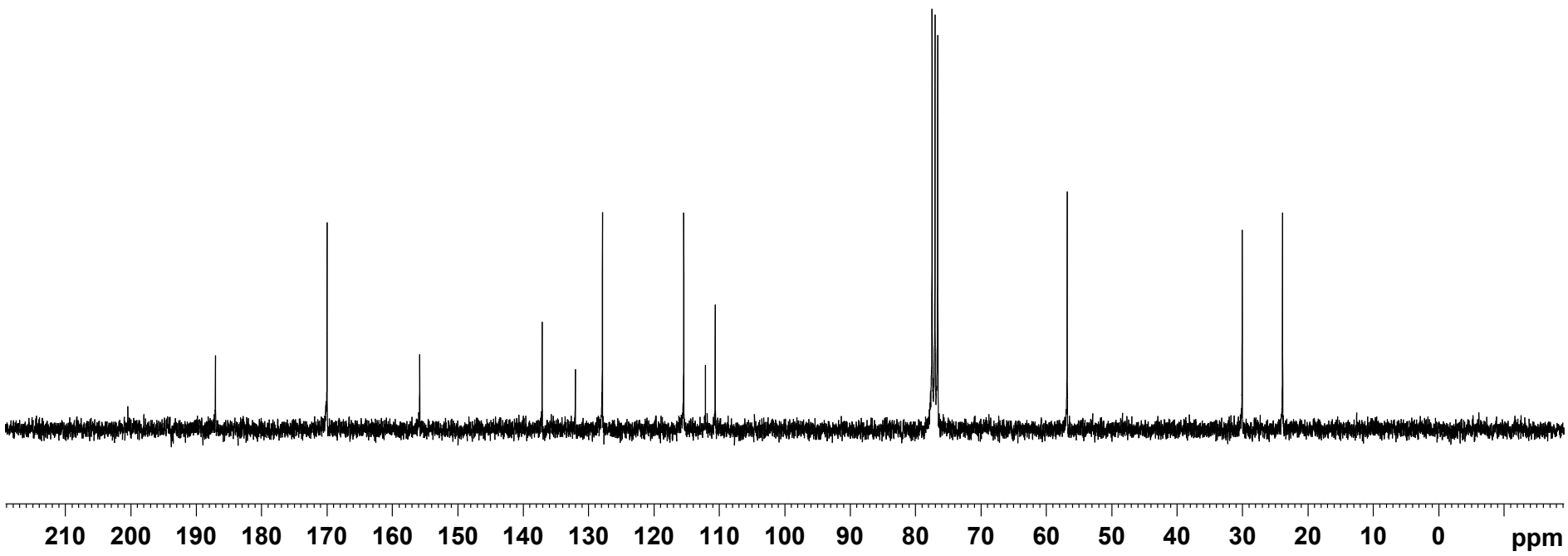
O
OH
MeO

11a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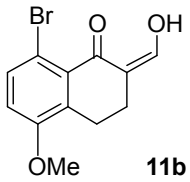

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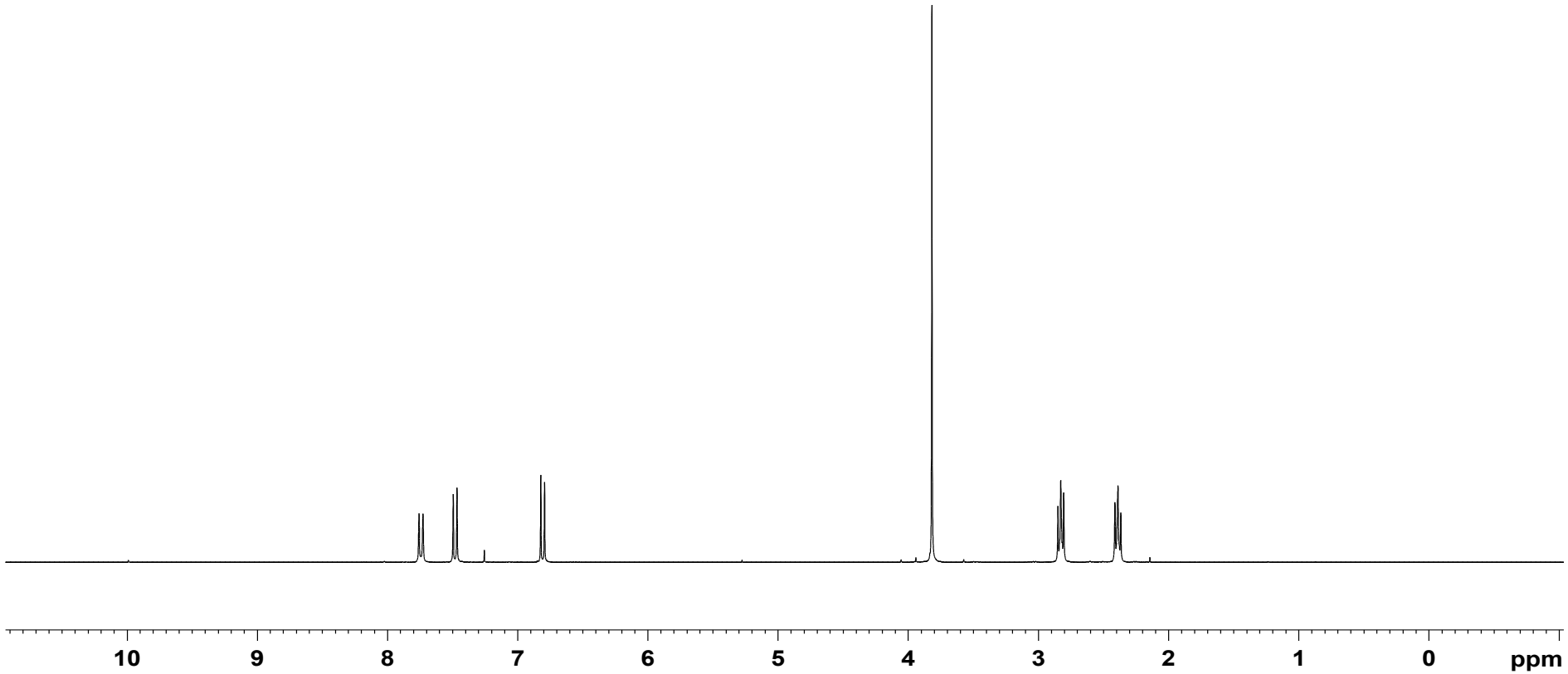
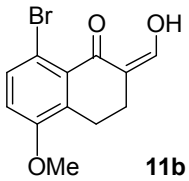
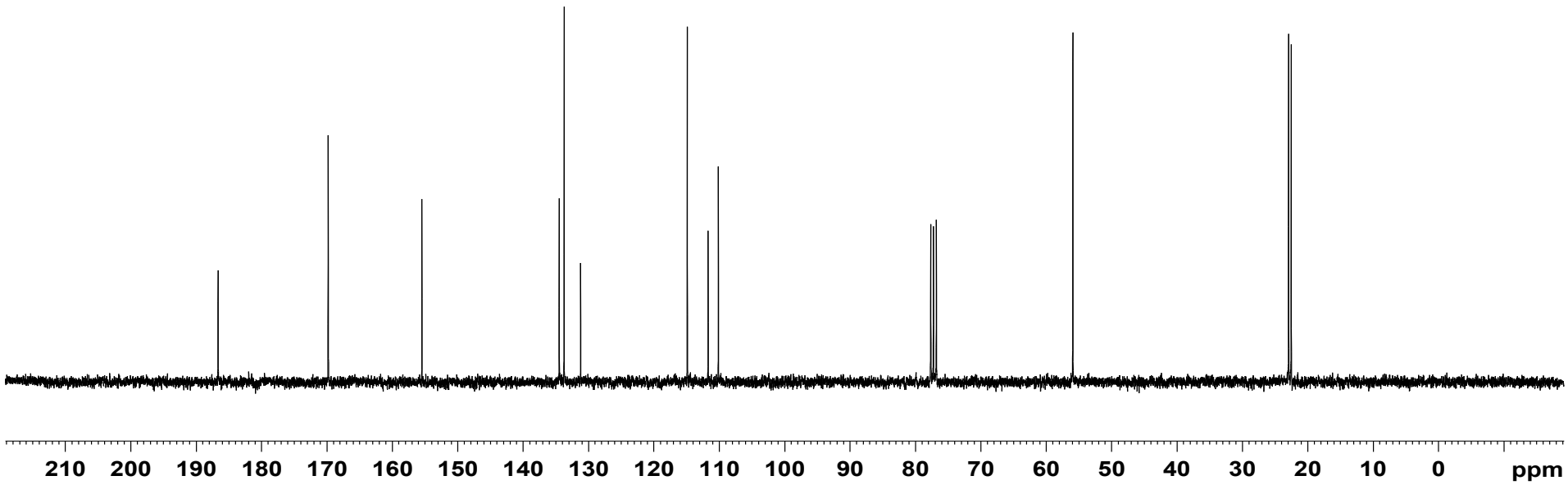



Br
O
OH
OMe

11b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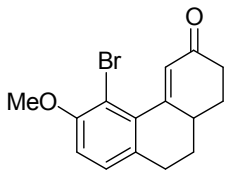

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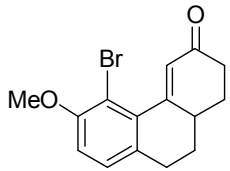

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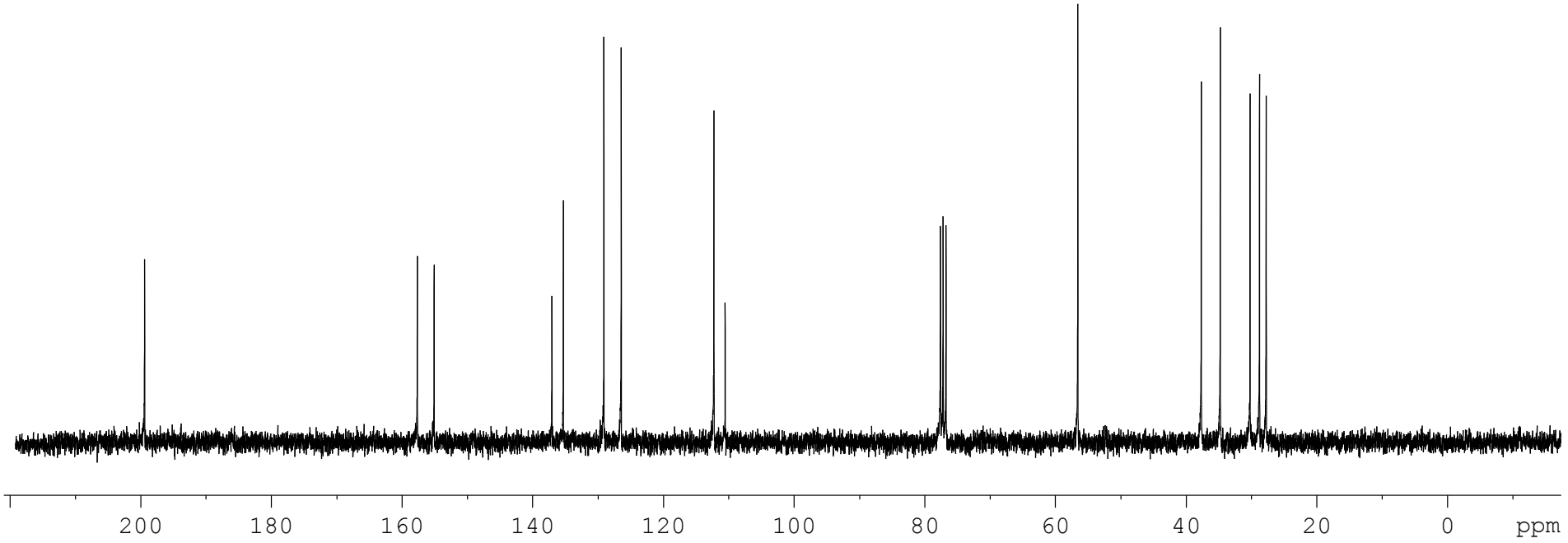

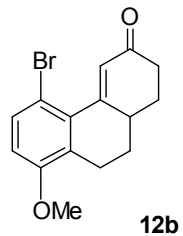

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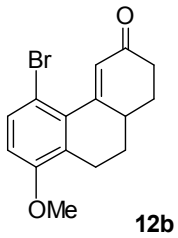
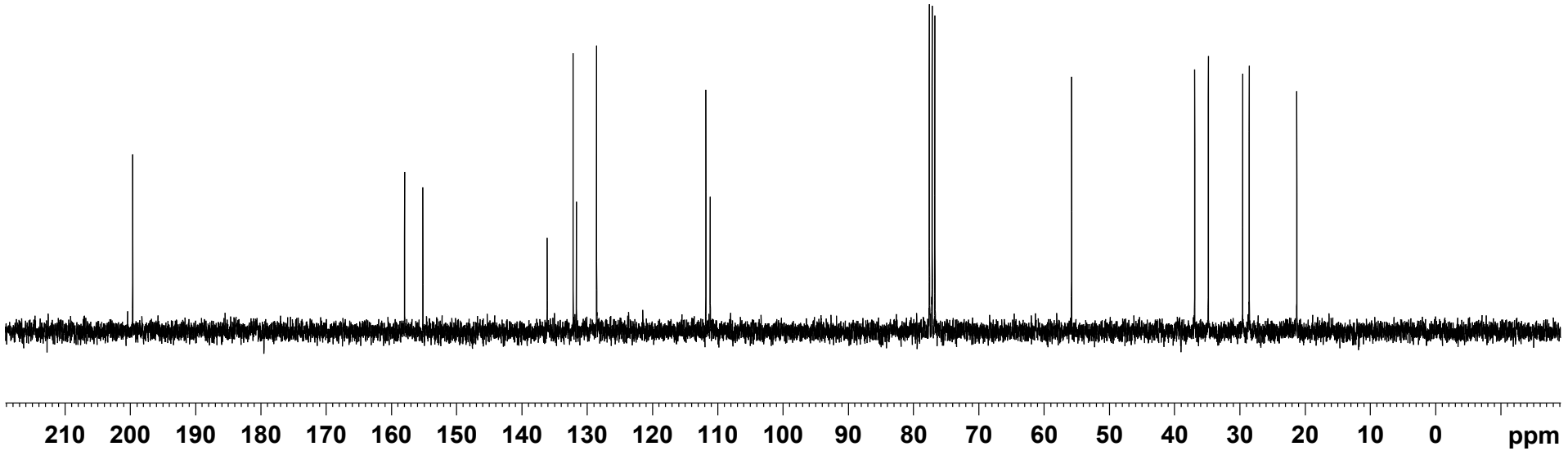

O
Br
OMe

12b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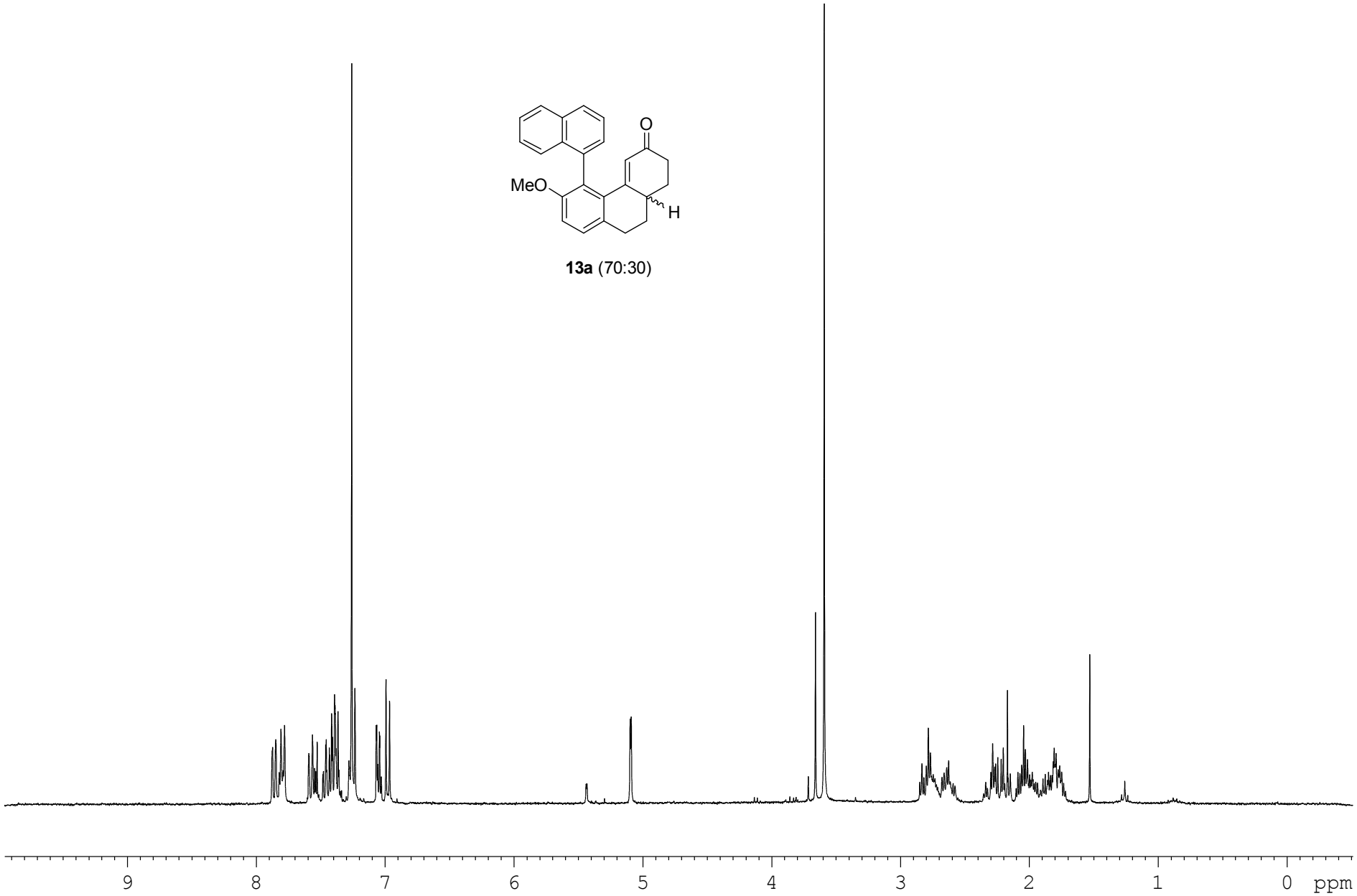
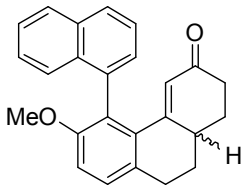


13a (70:30)



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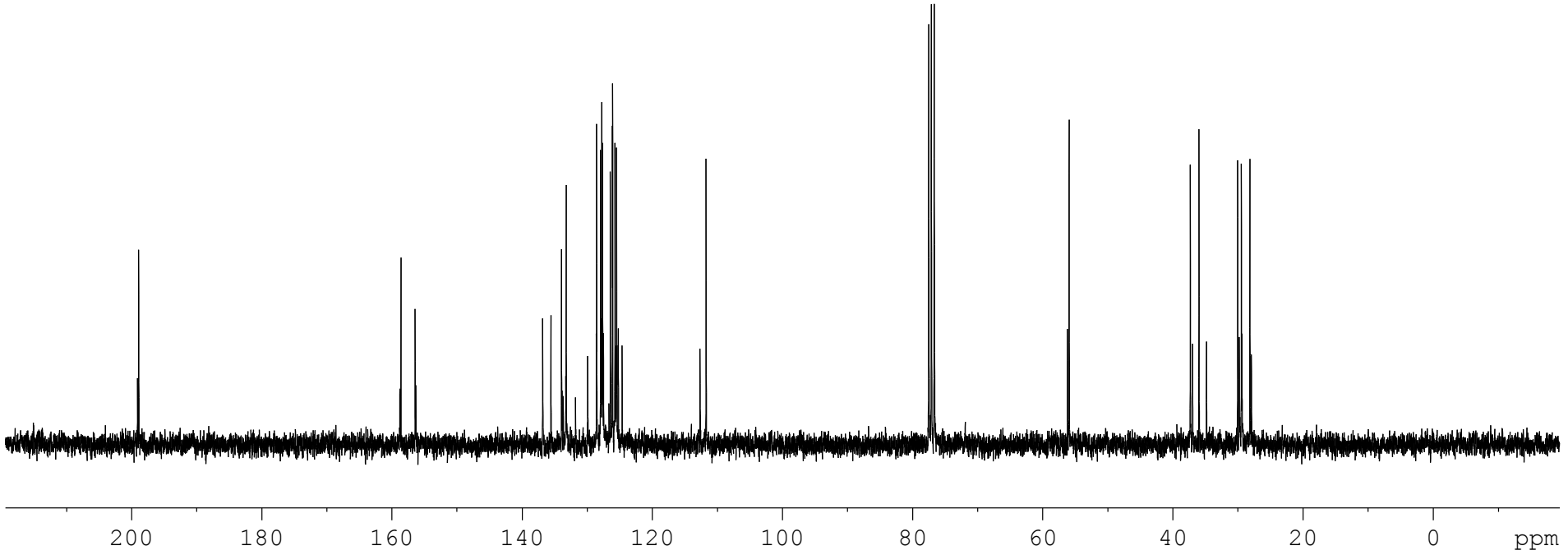

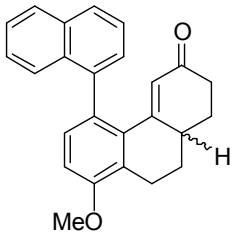

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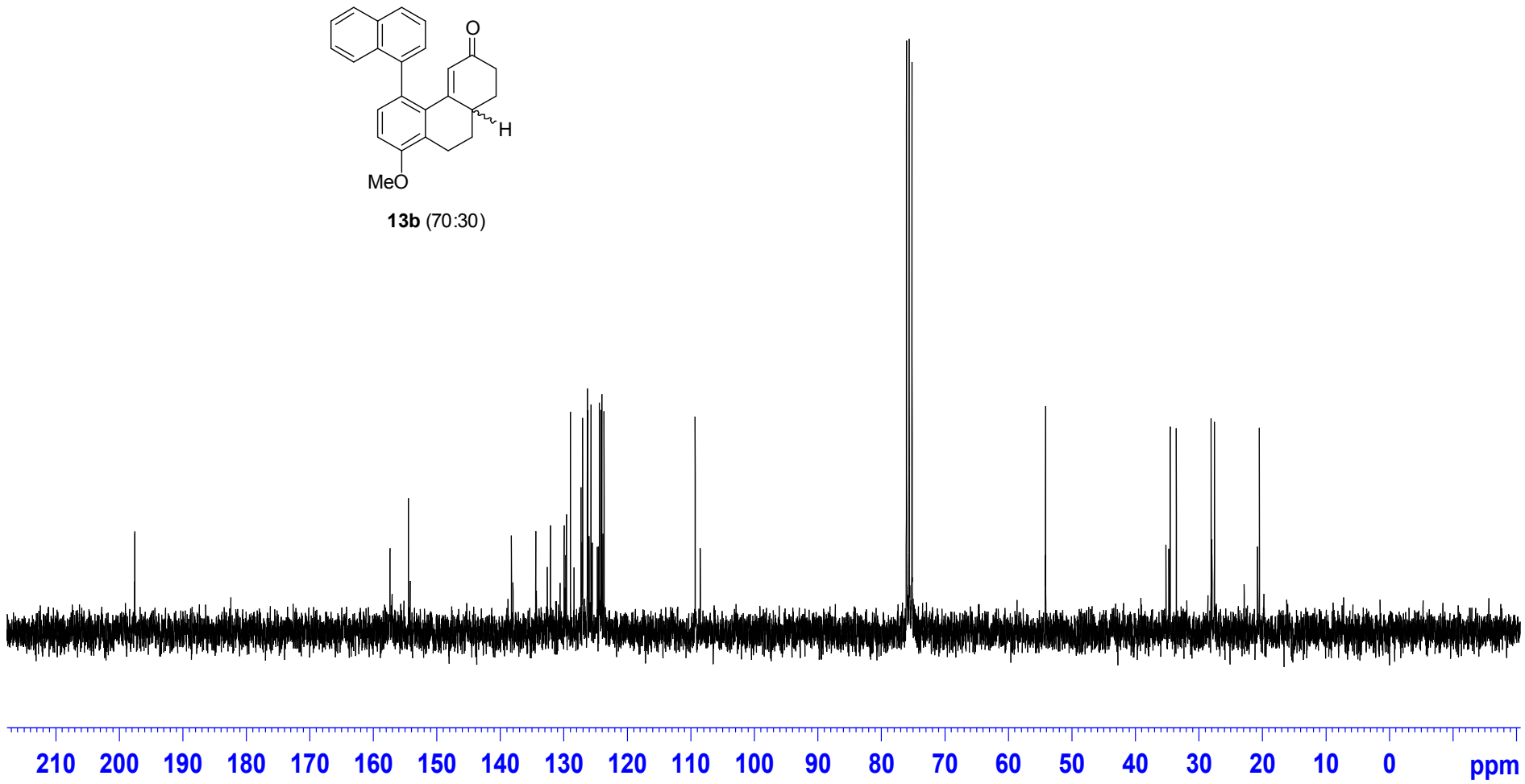
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H
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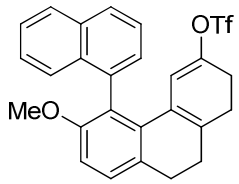
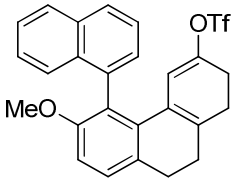
30
20
10
0
ppm

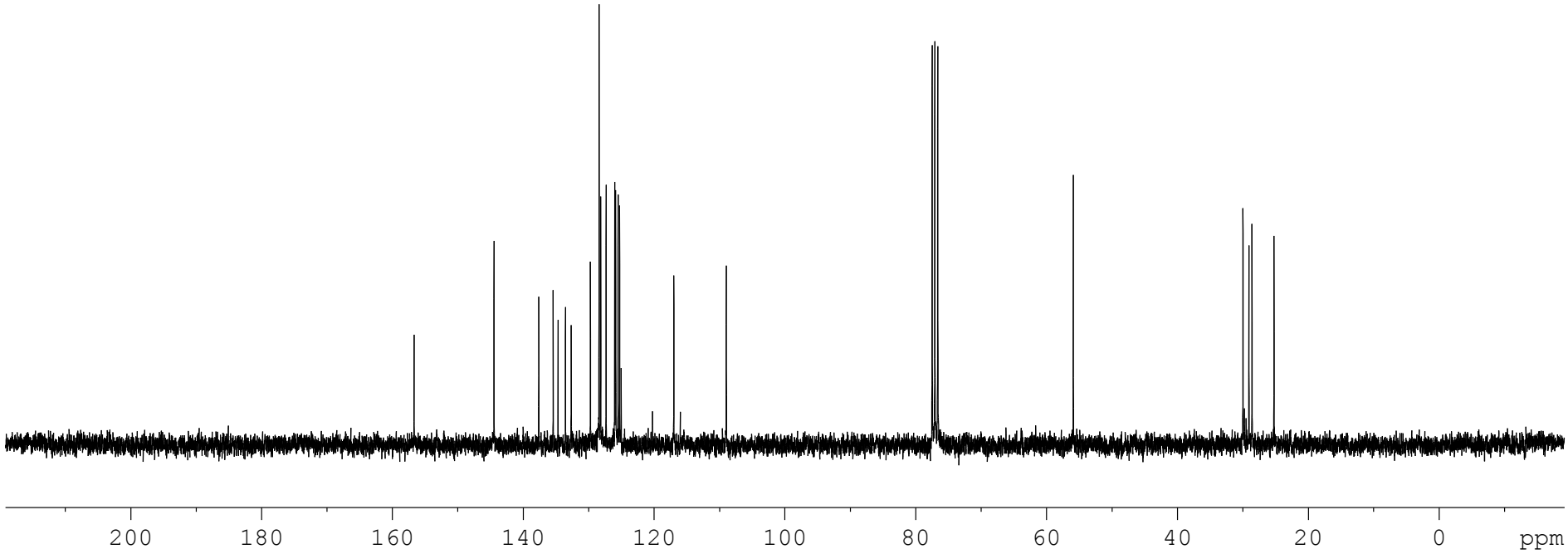
13b (70:30)

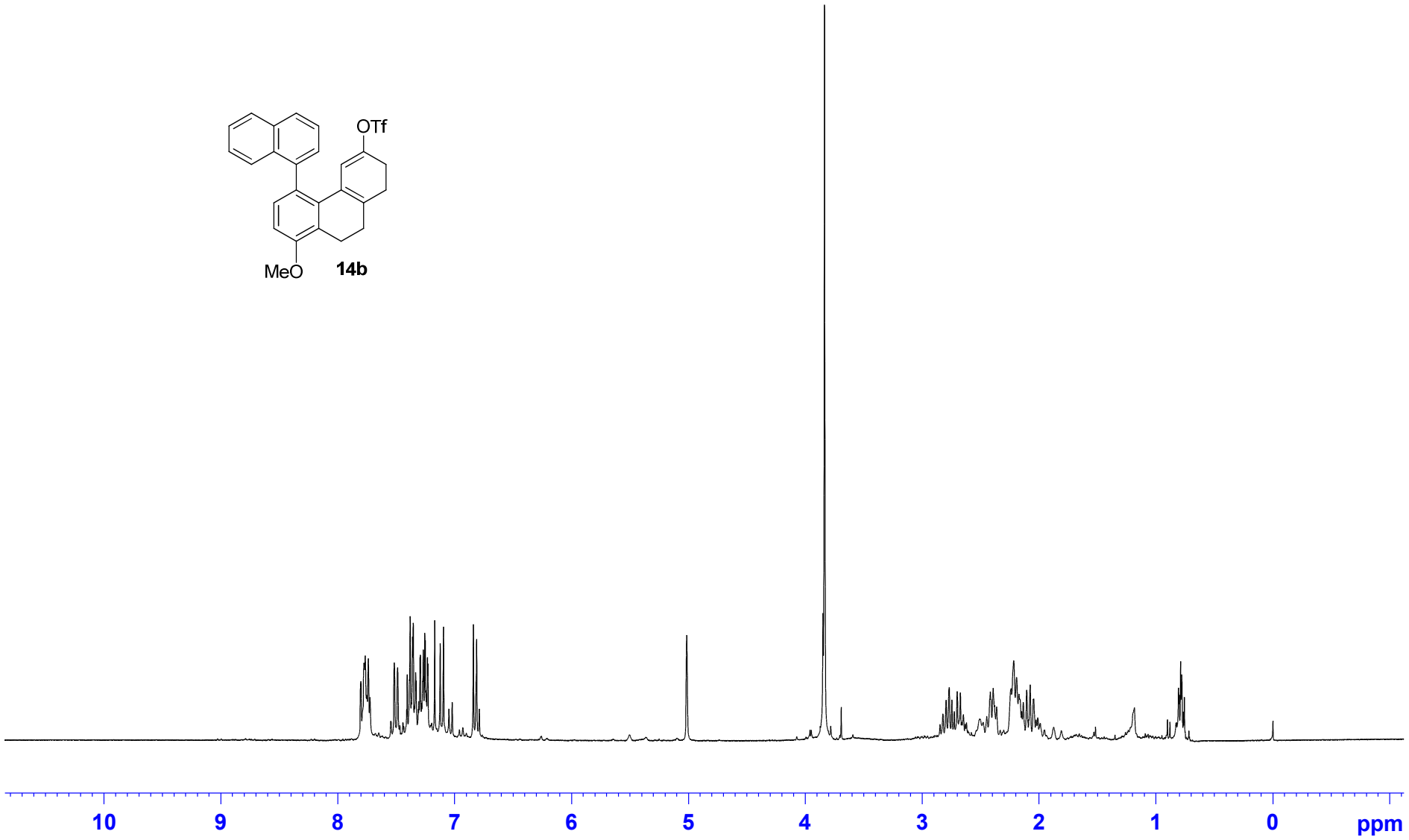


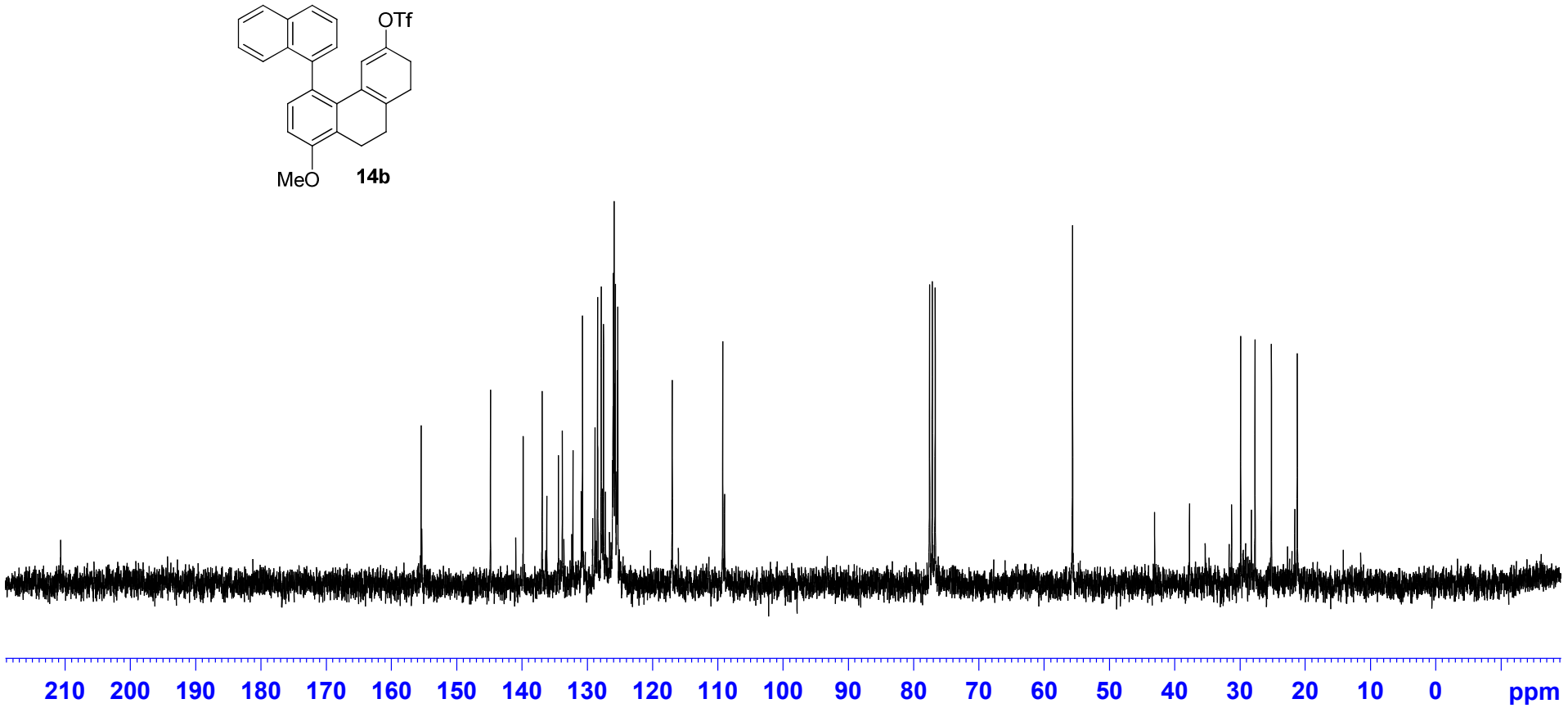
14a

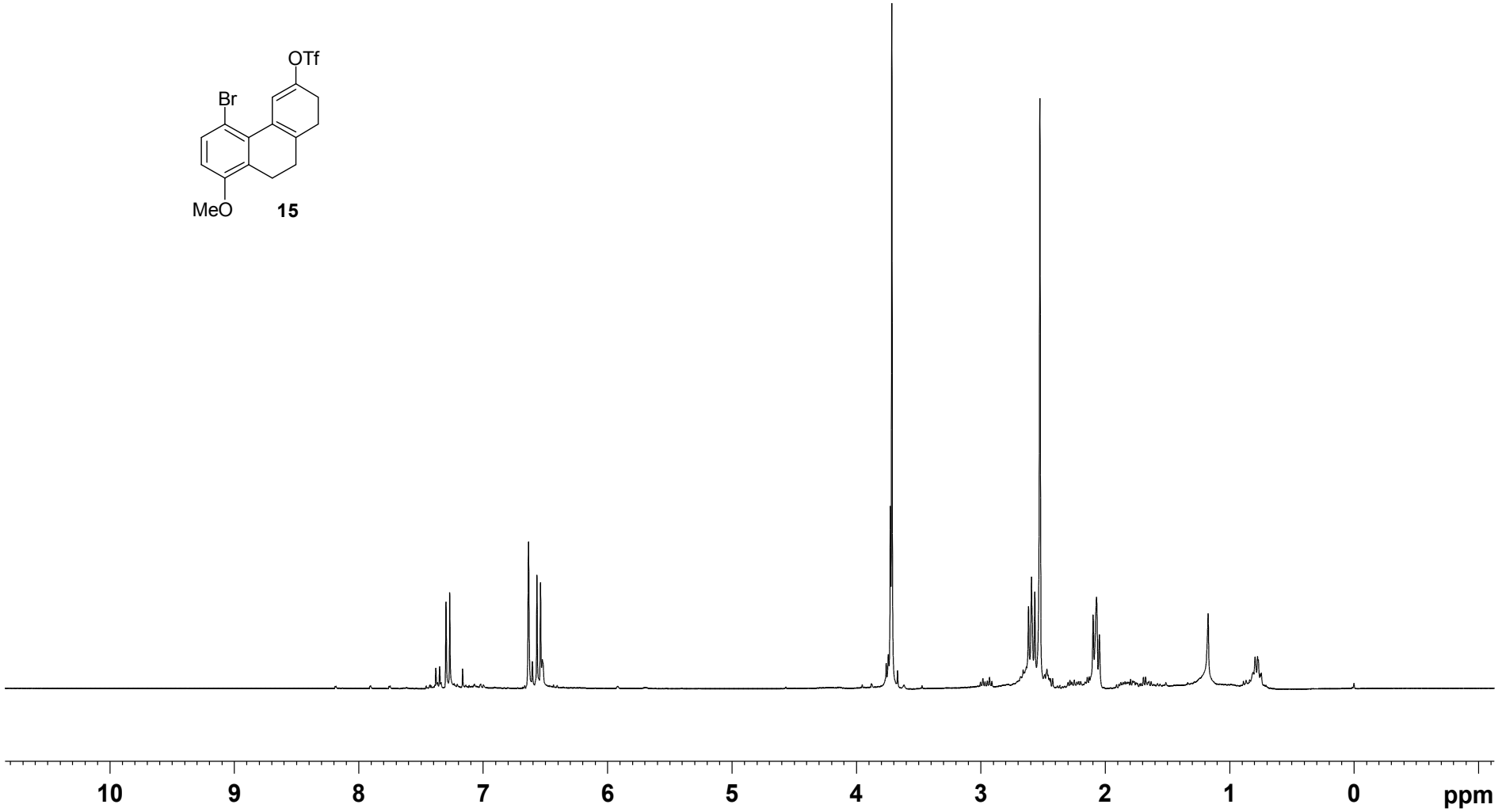


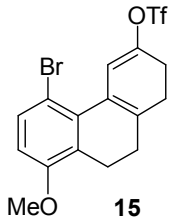
14a



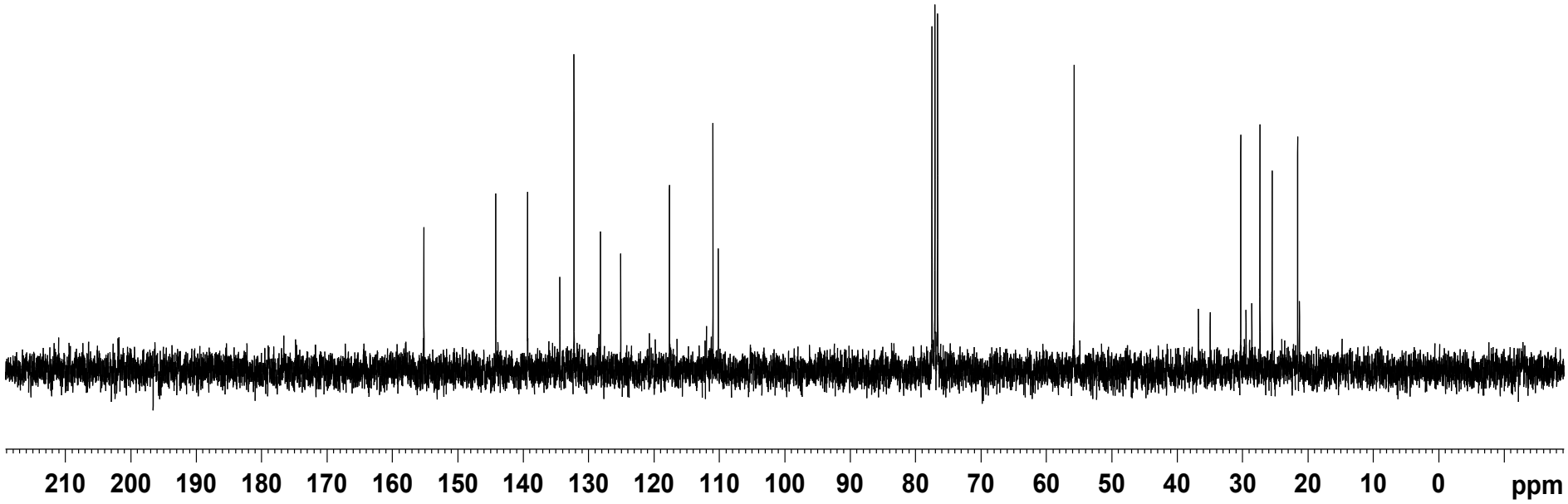

OTf
MeO
14b
10
9
8
7
6
5
4
3
2
1
0
ppm

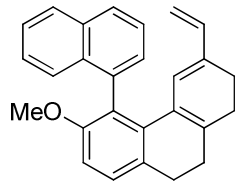

OTf
MeO
14b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OTf
Br
MeO
15
10
9
8
7
6
5
4
3
2
1
0
ppm

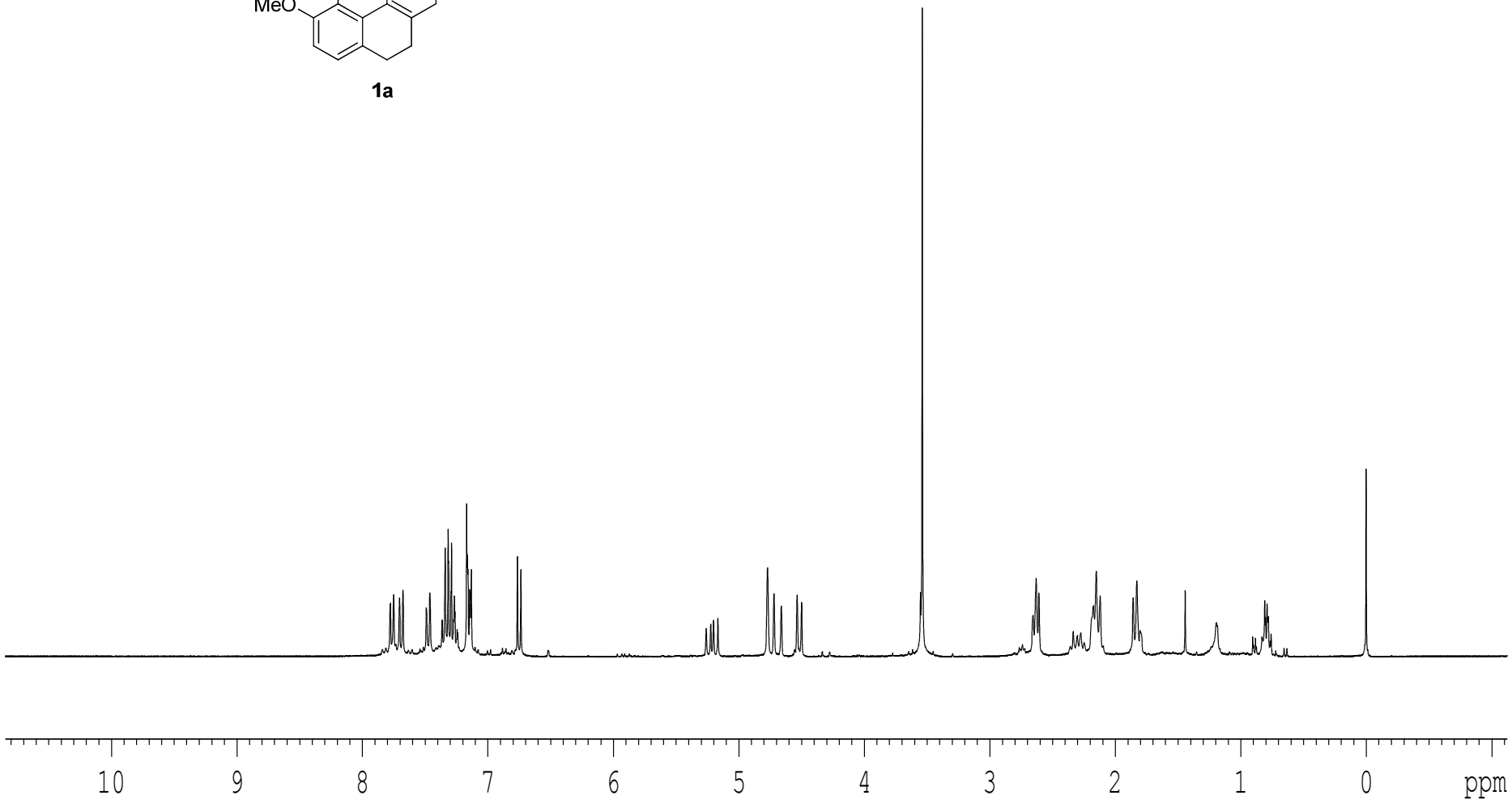

OTf
Br
MeO

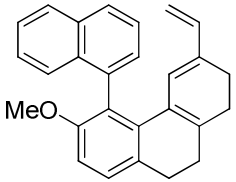
15


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

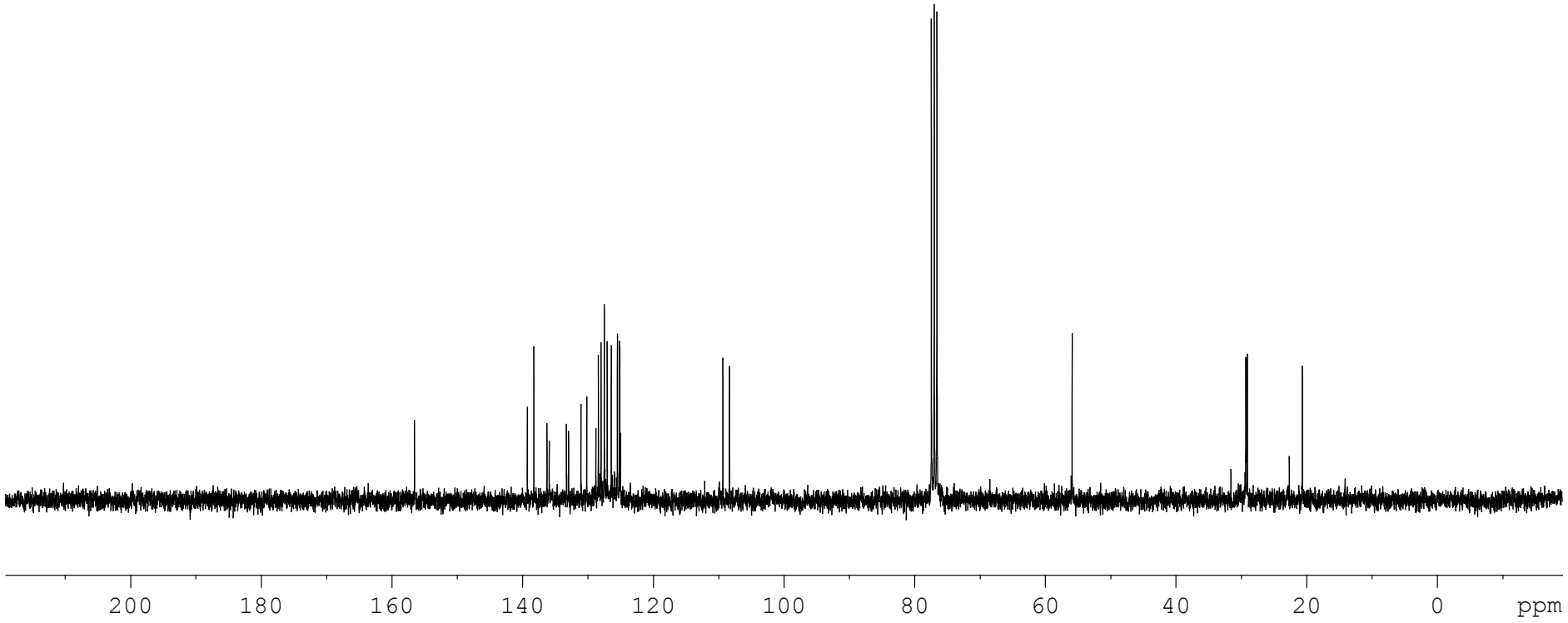


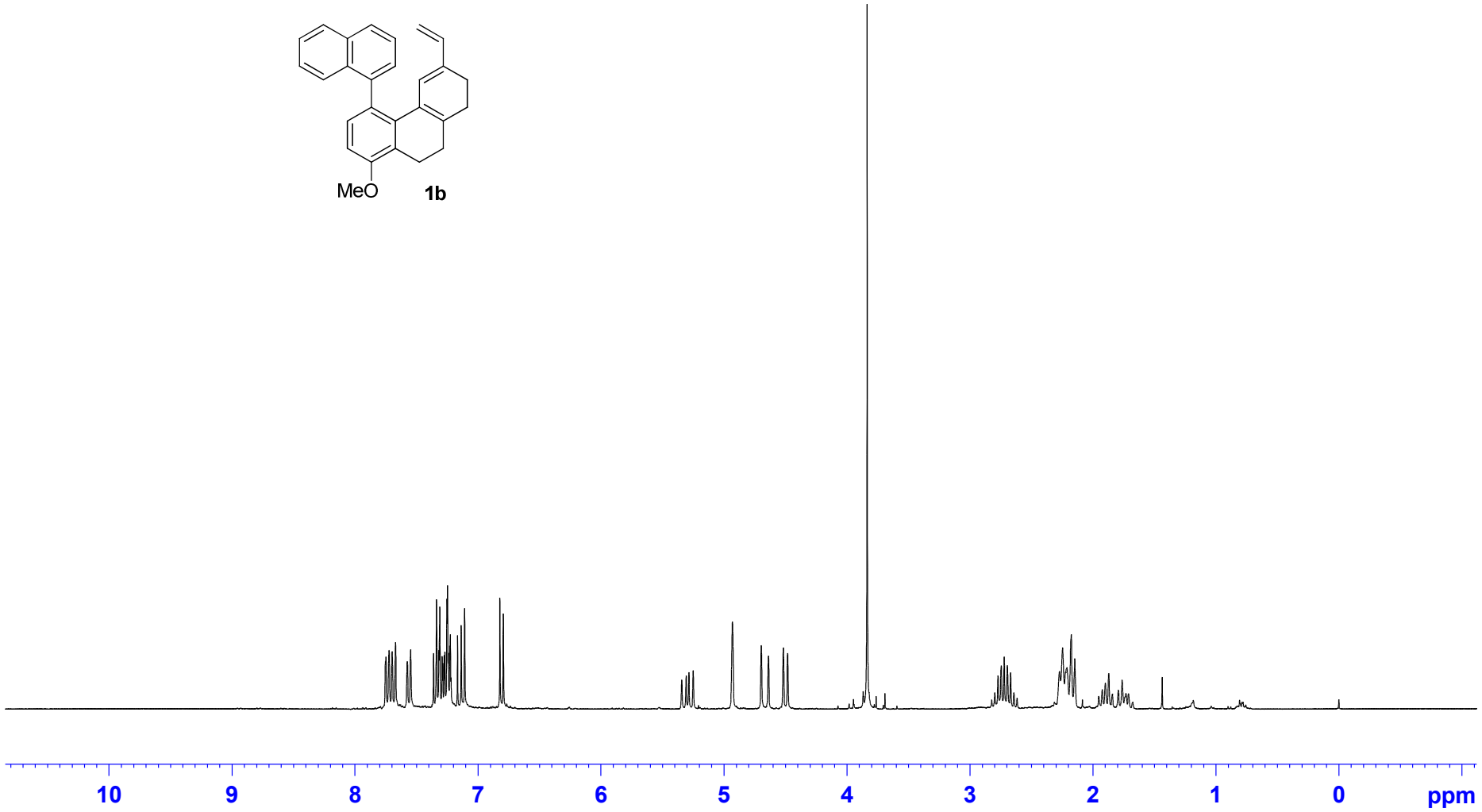
1a

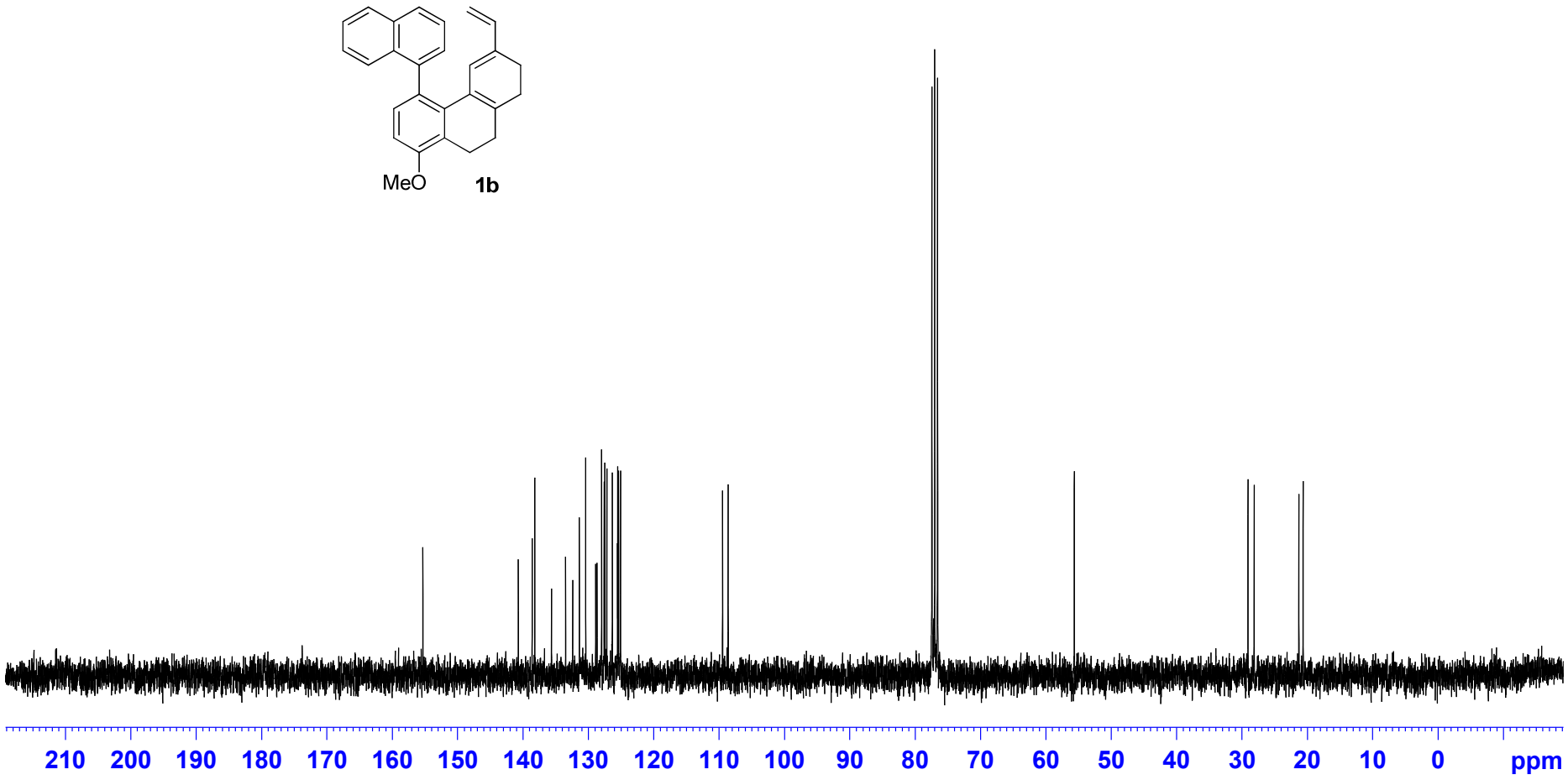


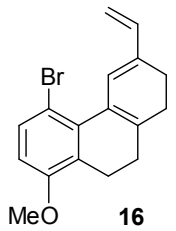


1a

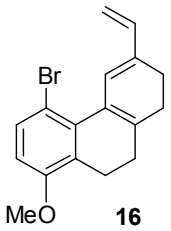



MeO
1b
10
9
8
7
6
5
4
3
2
1
0
ppm

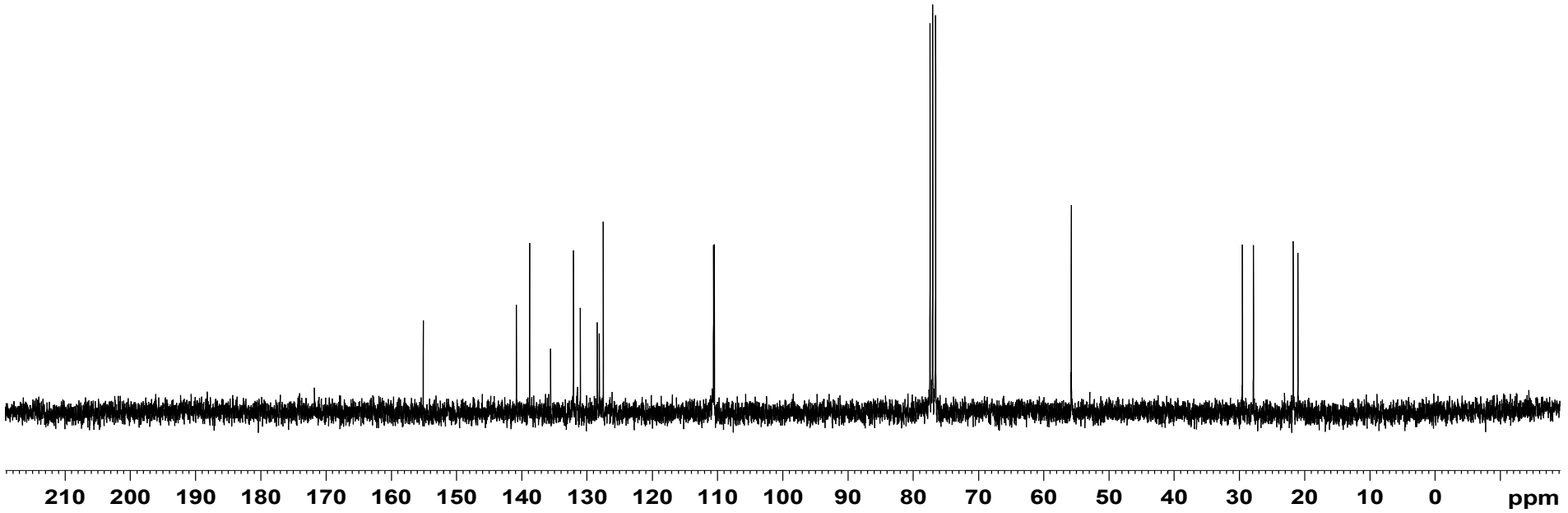

MeO
1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

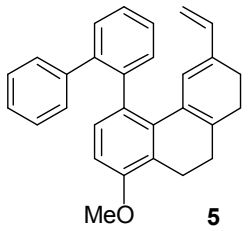


16

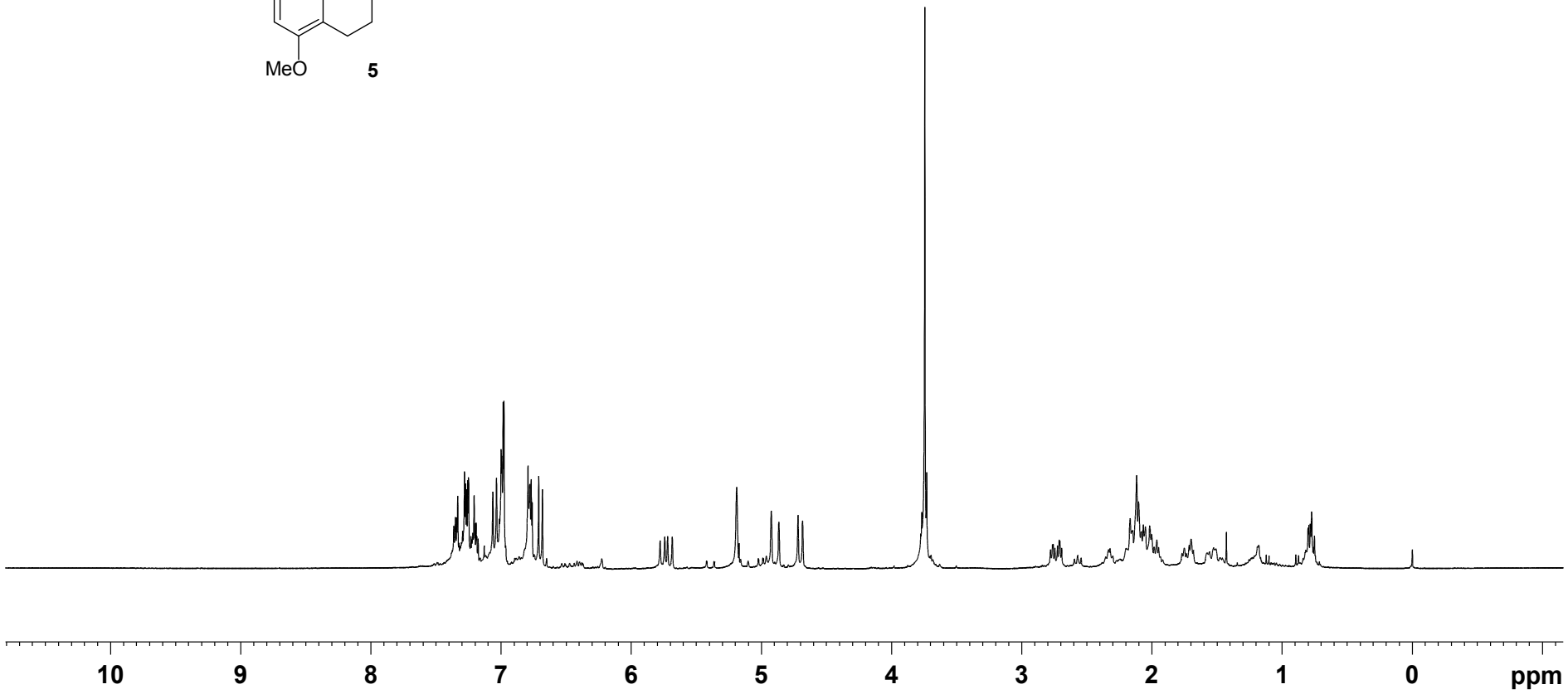

Br
MeO

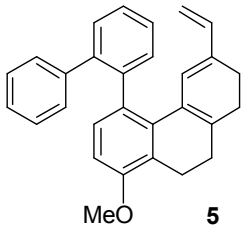
16


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

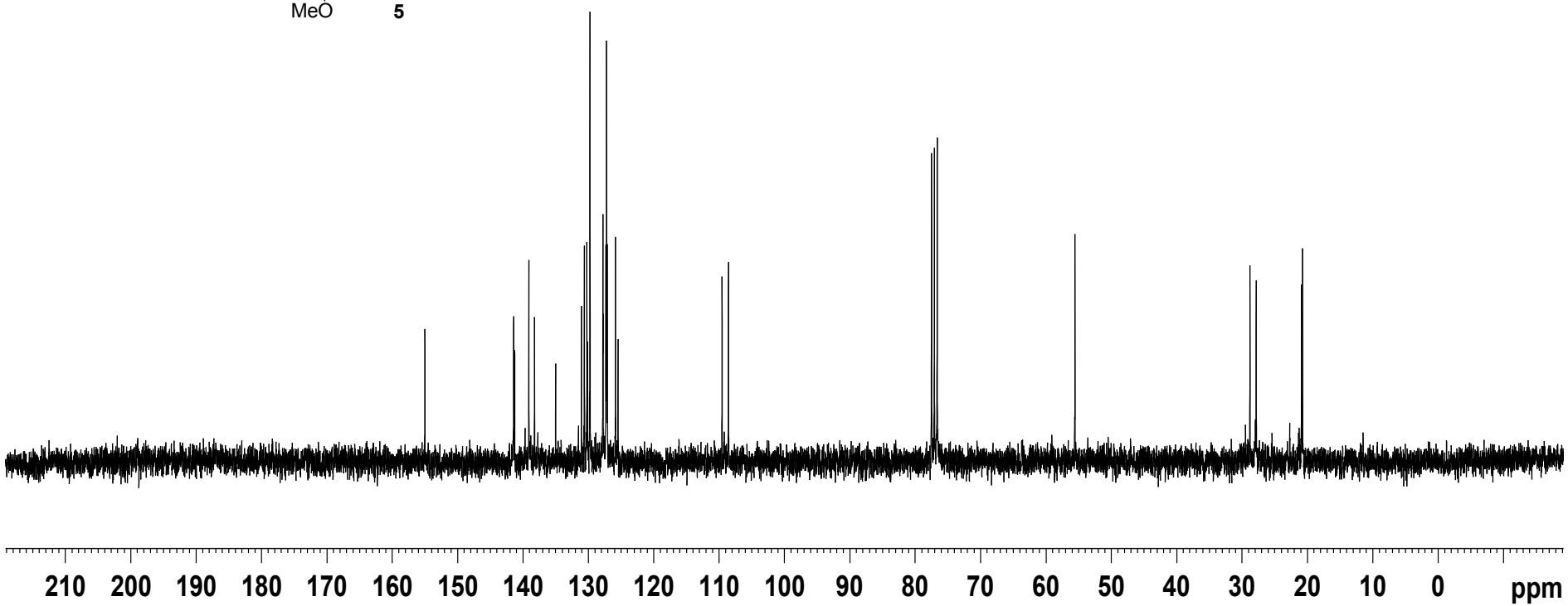


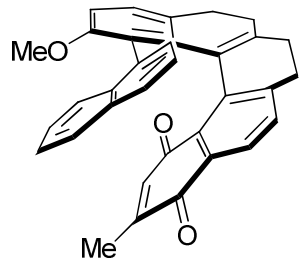
5



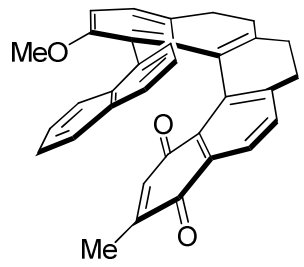

MeO

5

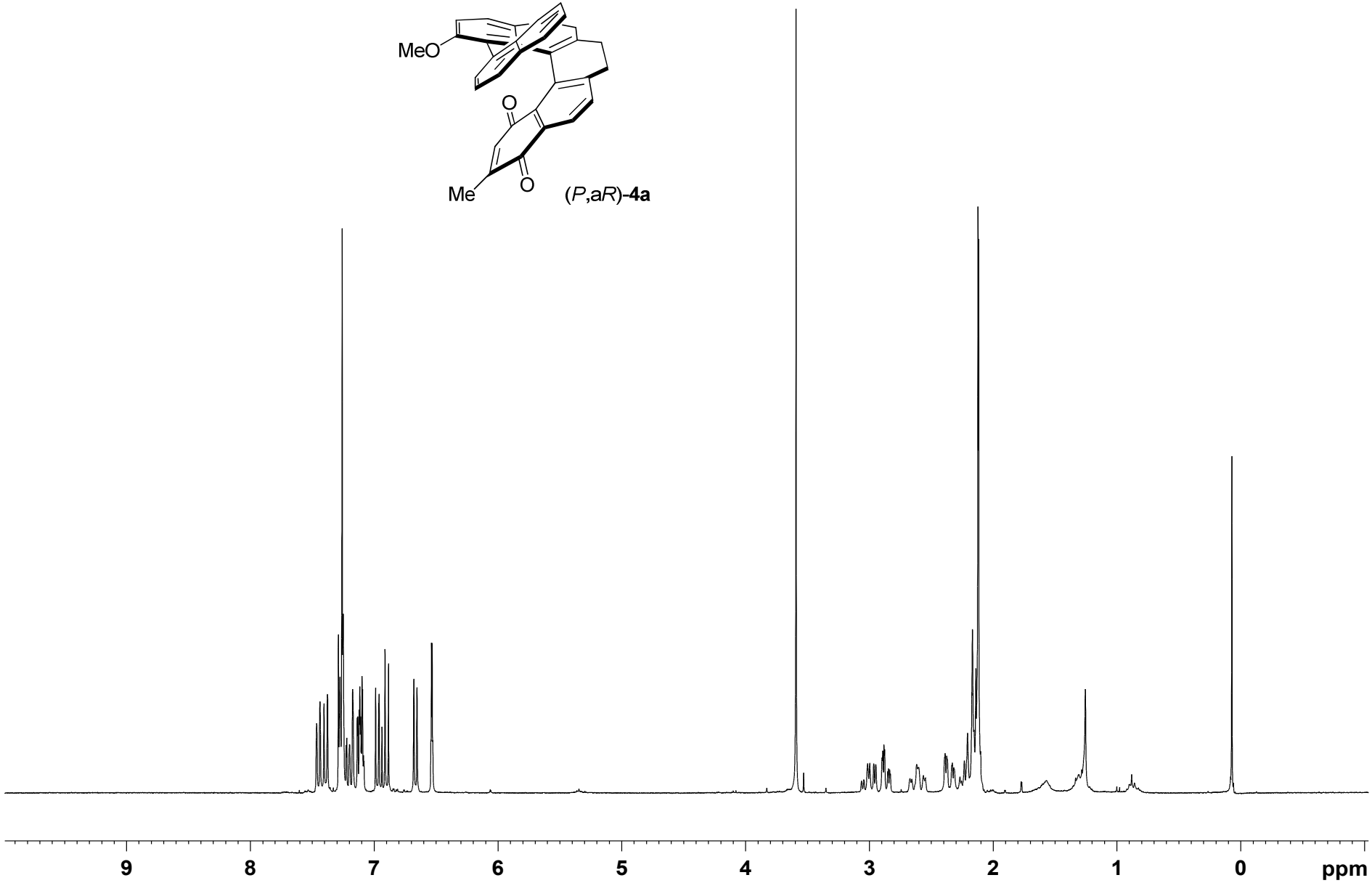

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

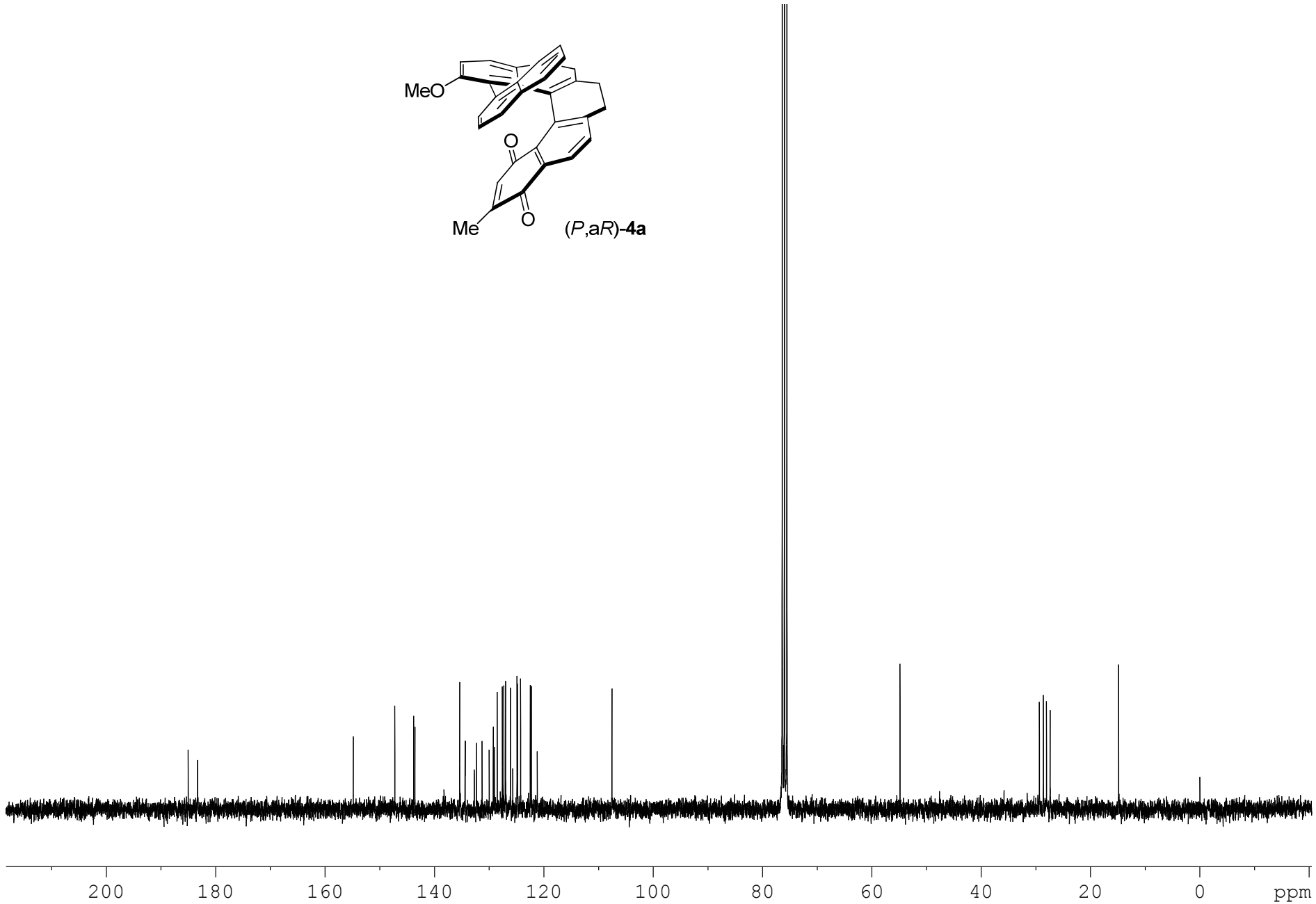


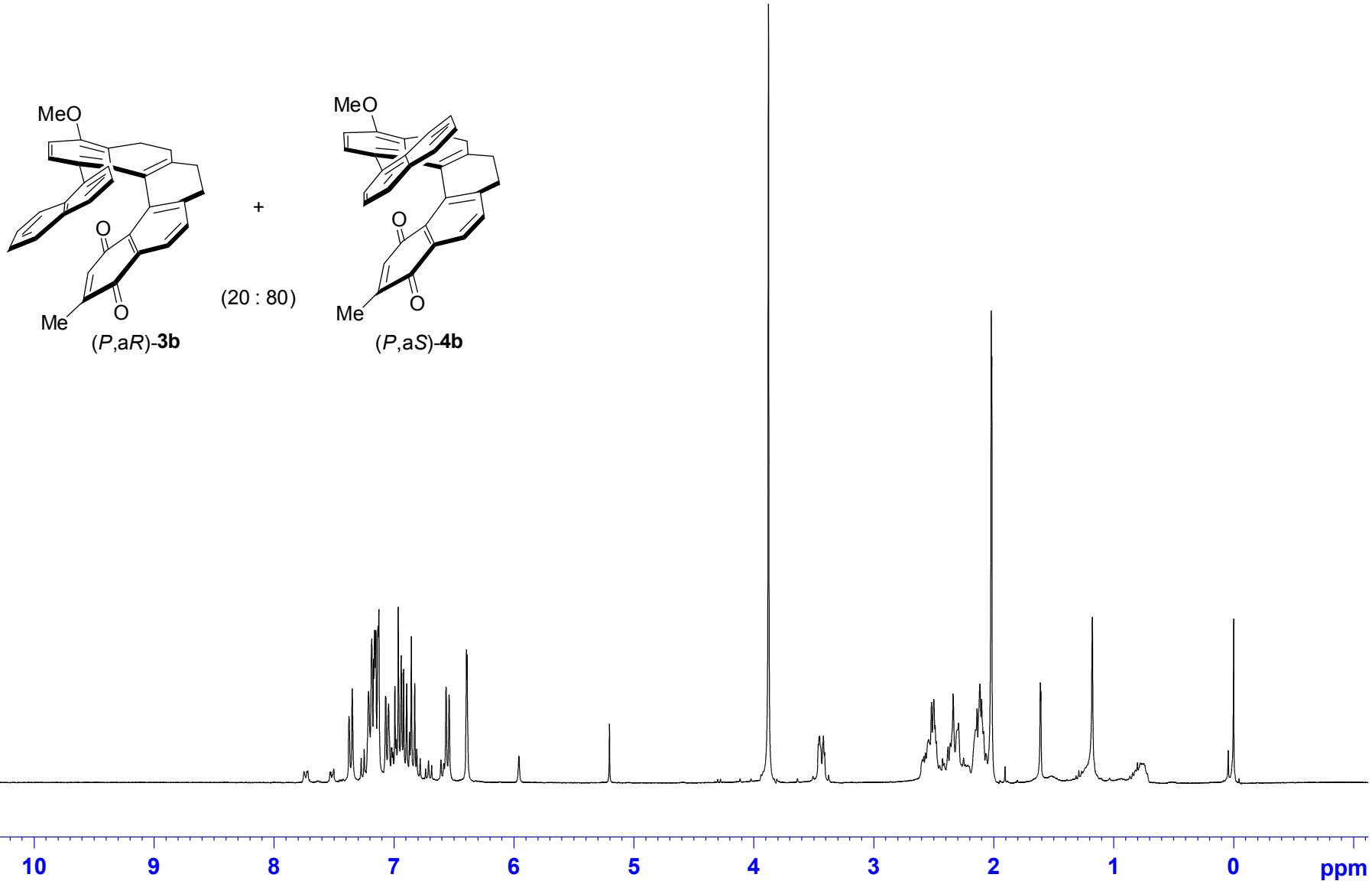
(*P*,a*S*)-**3a**

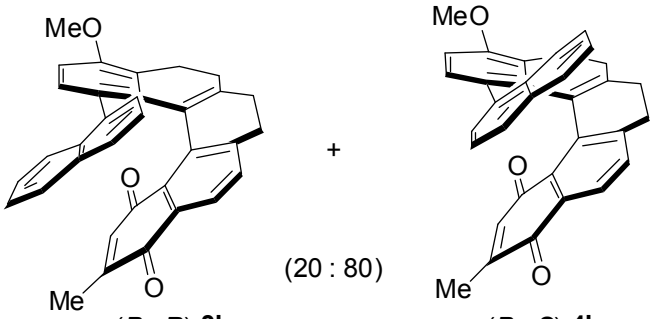


(*P*,a*S*)-**3a**


MeO
O
O
Me
(P,aR)-4a
9
8
7
6
5
4
3
2
1
0
ppm


MeO
O
O
Me
(P,aR)-4a
200
180
160
140
120
100
80
60
40
20
0
ppm


MeO
O
O
Me
(P,aR)-3b
+
(20 : 80)
MeO
O
O
Me
(P,aS)-4b
10
9
8
7
6
5
4
3
2
1
0
ppm

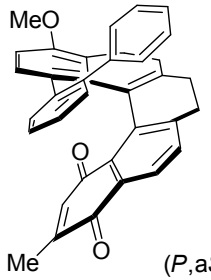


(*P*,a*R*)-**3b**

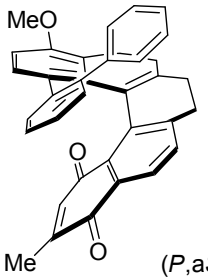
+

(20 : 80)

(*P*,a*S*)-**4b**

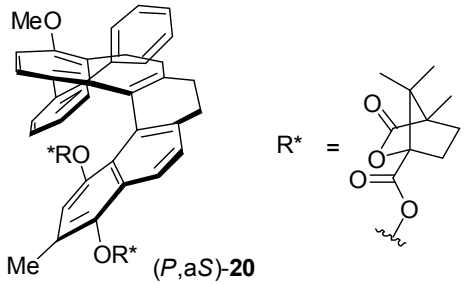


(*P*,a*S*)-**6**


MeO
O
O
Me

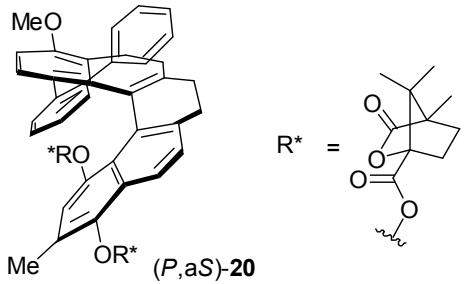
(*P*,a*S*)-**6**

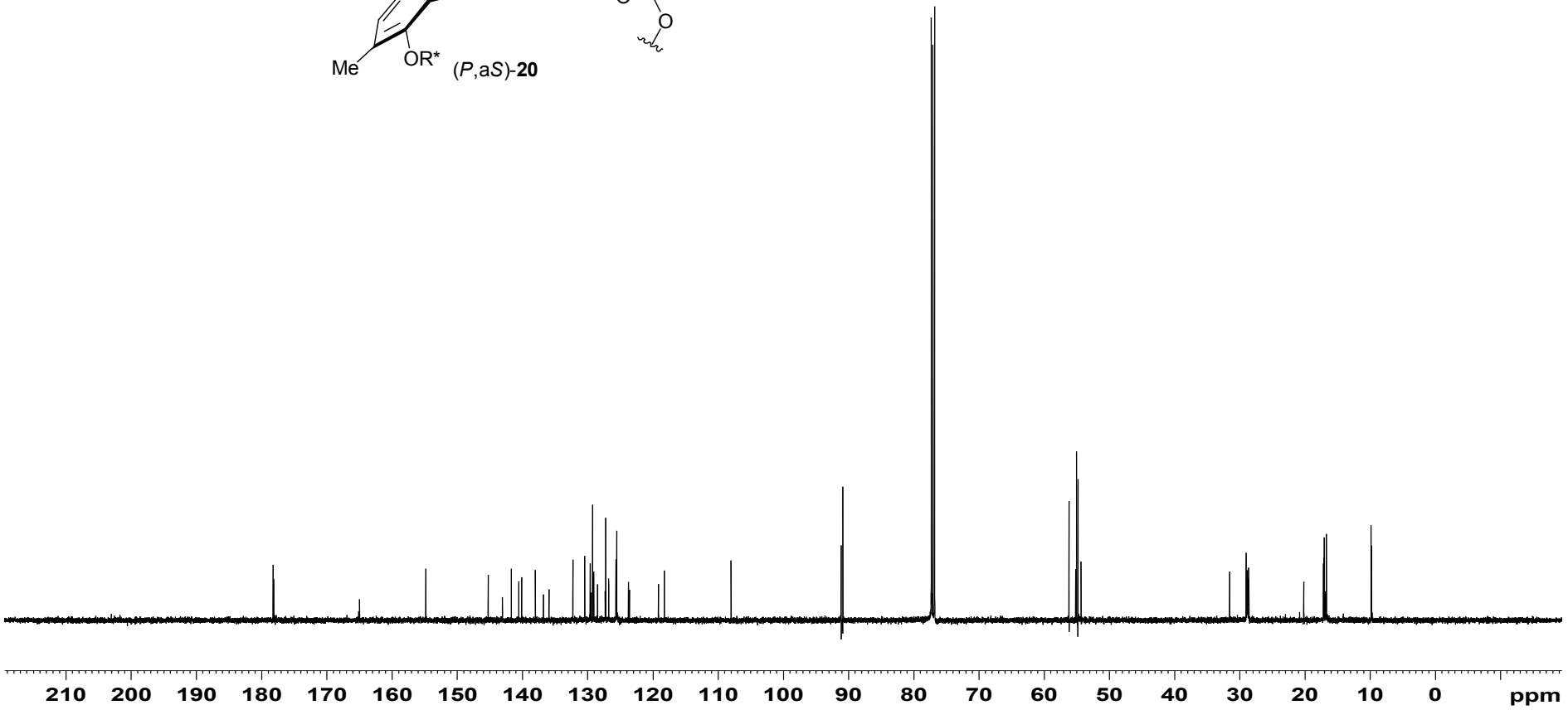
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

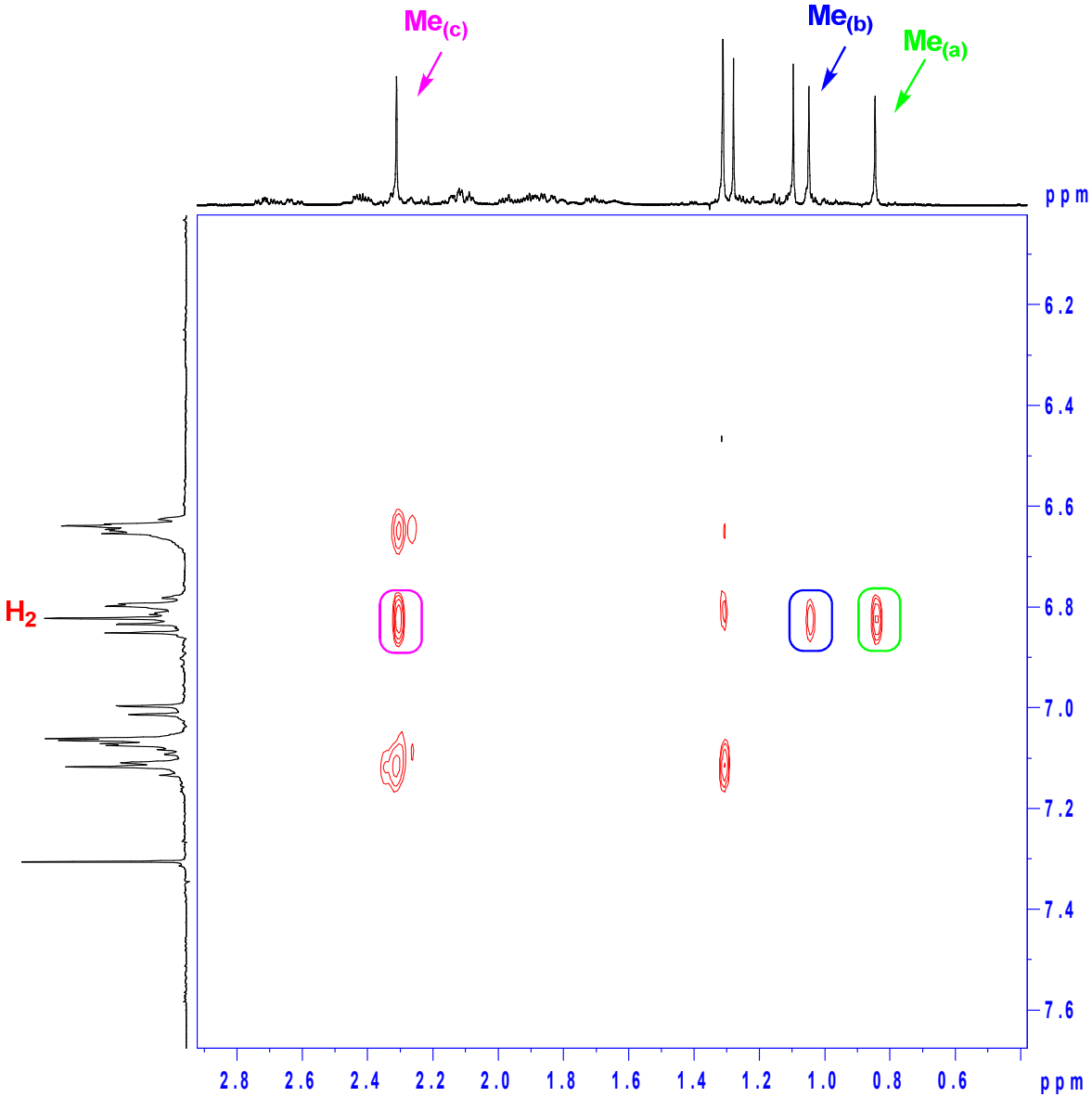


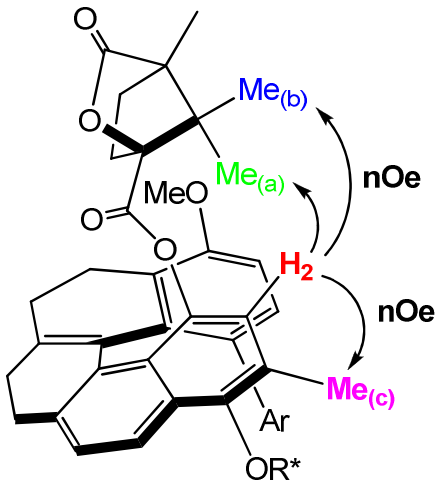
(*P*,a*S*)-**20**

R* =

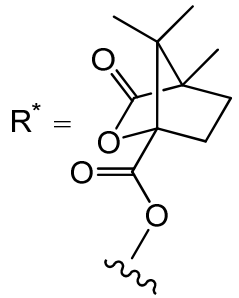

MeO
*RO
Me
OR*
(P,aS)-20
R* =
O
O
O
O

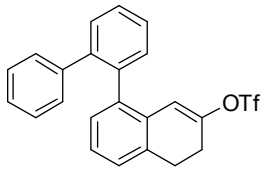

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Me(c)
Me(b)
Me(a)
H2
ppm
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
ppm

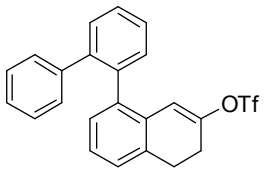

O
O
Me(b)
Me(a)
MeO
O
O
H2
nOe
nOe
Me(c)
Ar
OR*

(*P*,a*S*)-**20**

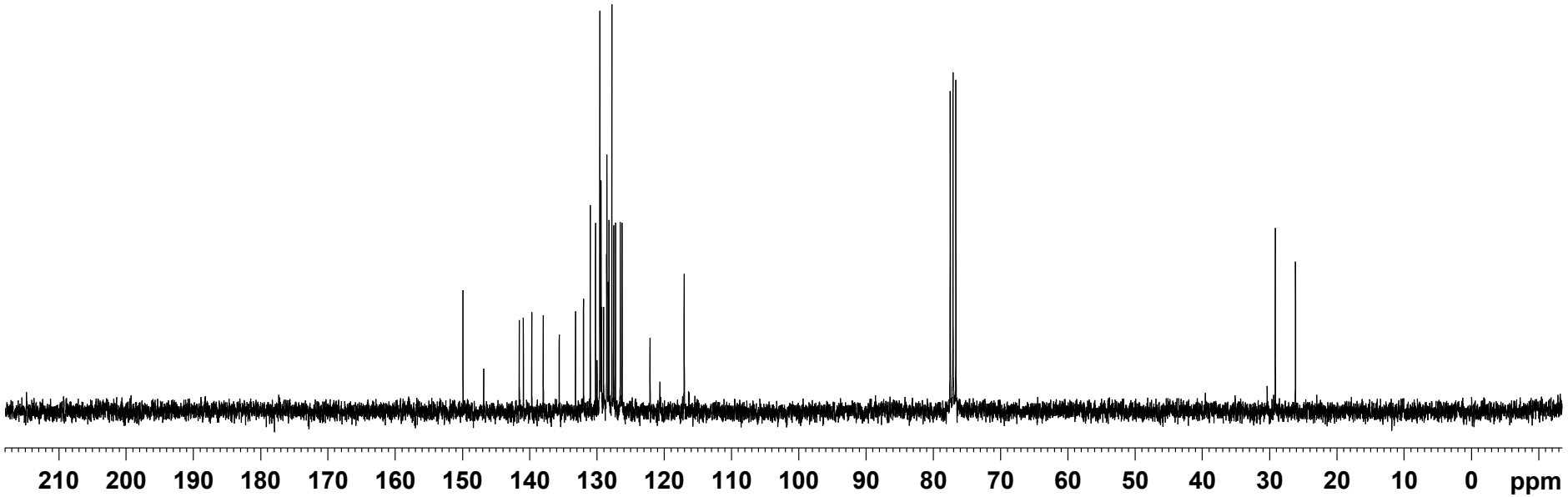

R* =
O
O
O
O

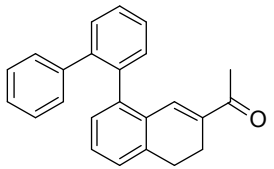


18

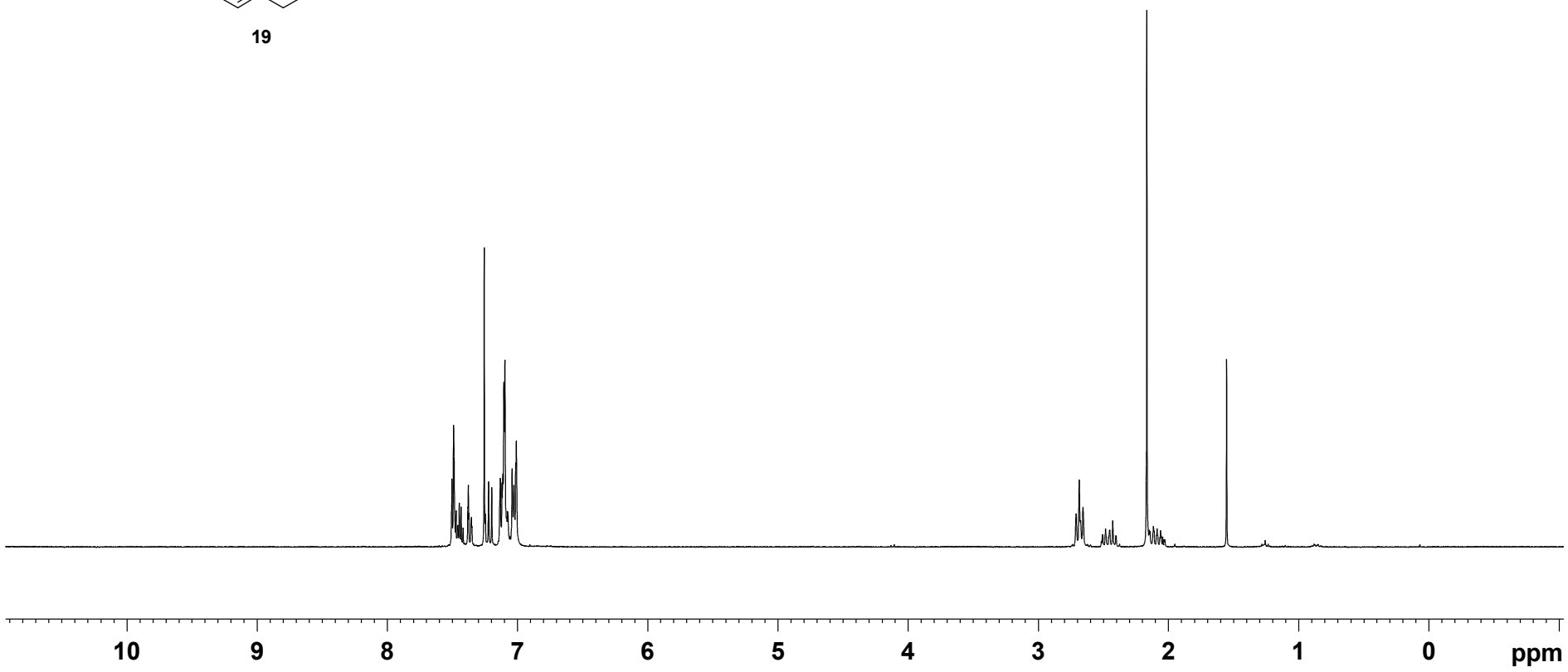

OTf

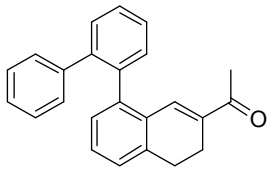
18


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



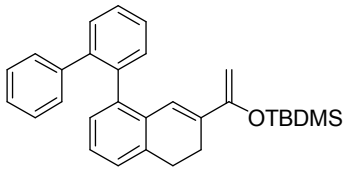
19



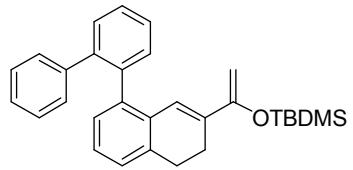

O

19

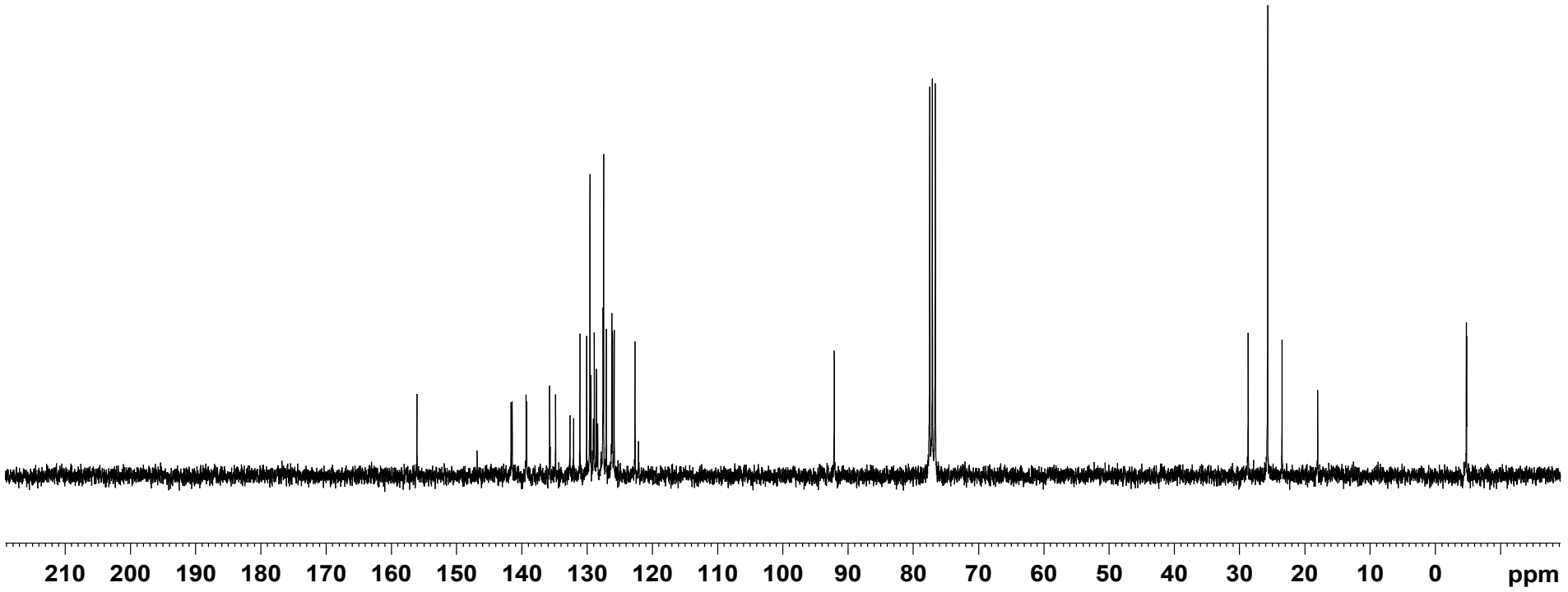
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

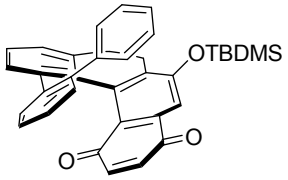


7

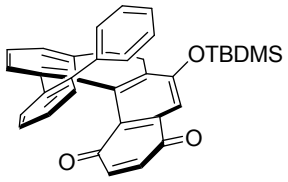

OTBDMS

7

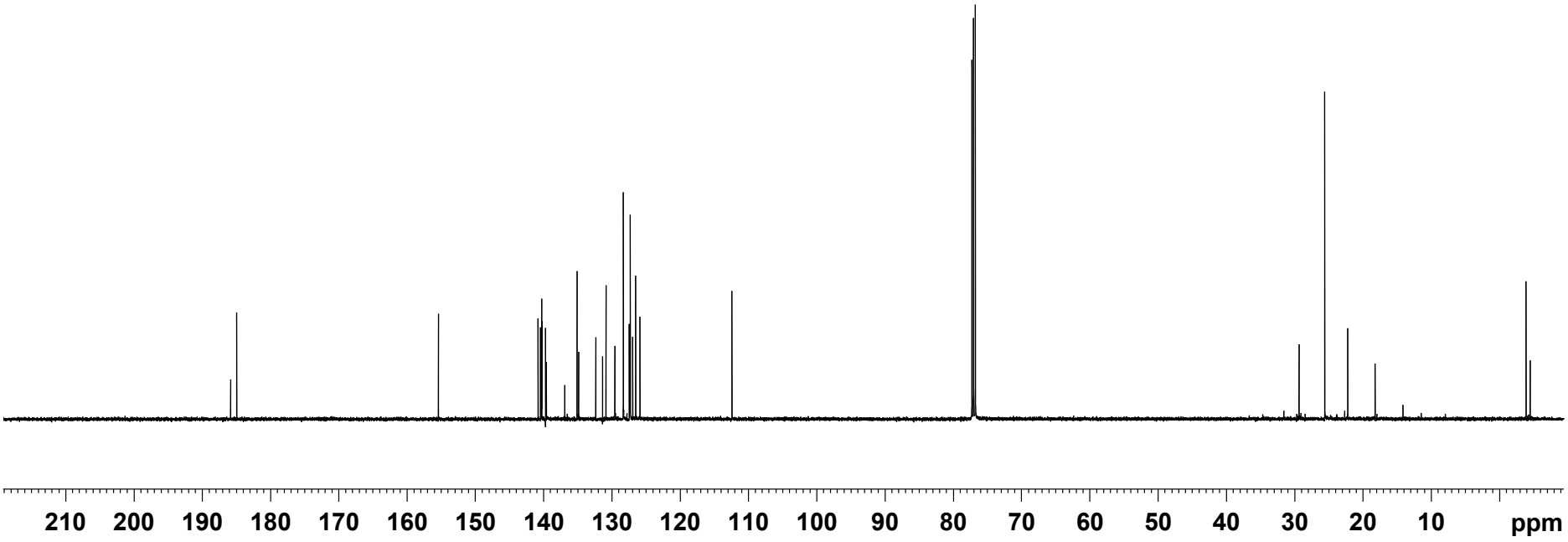

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

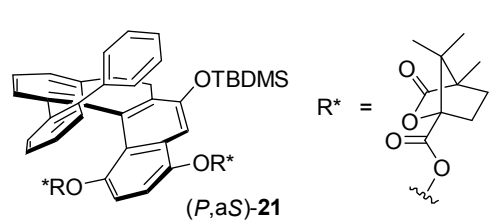


(*P*,a*S*)-**9a**

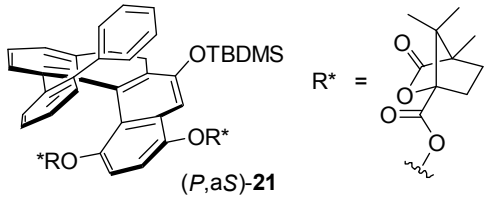

OTBDMS
O
O

(*P*,a*S*)-**9a**


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


OTBDMS
OR*
*RO
(P,aS)-21
R* =
O
O
O
O

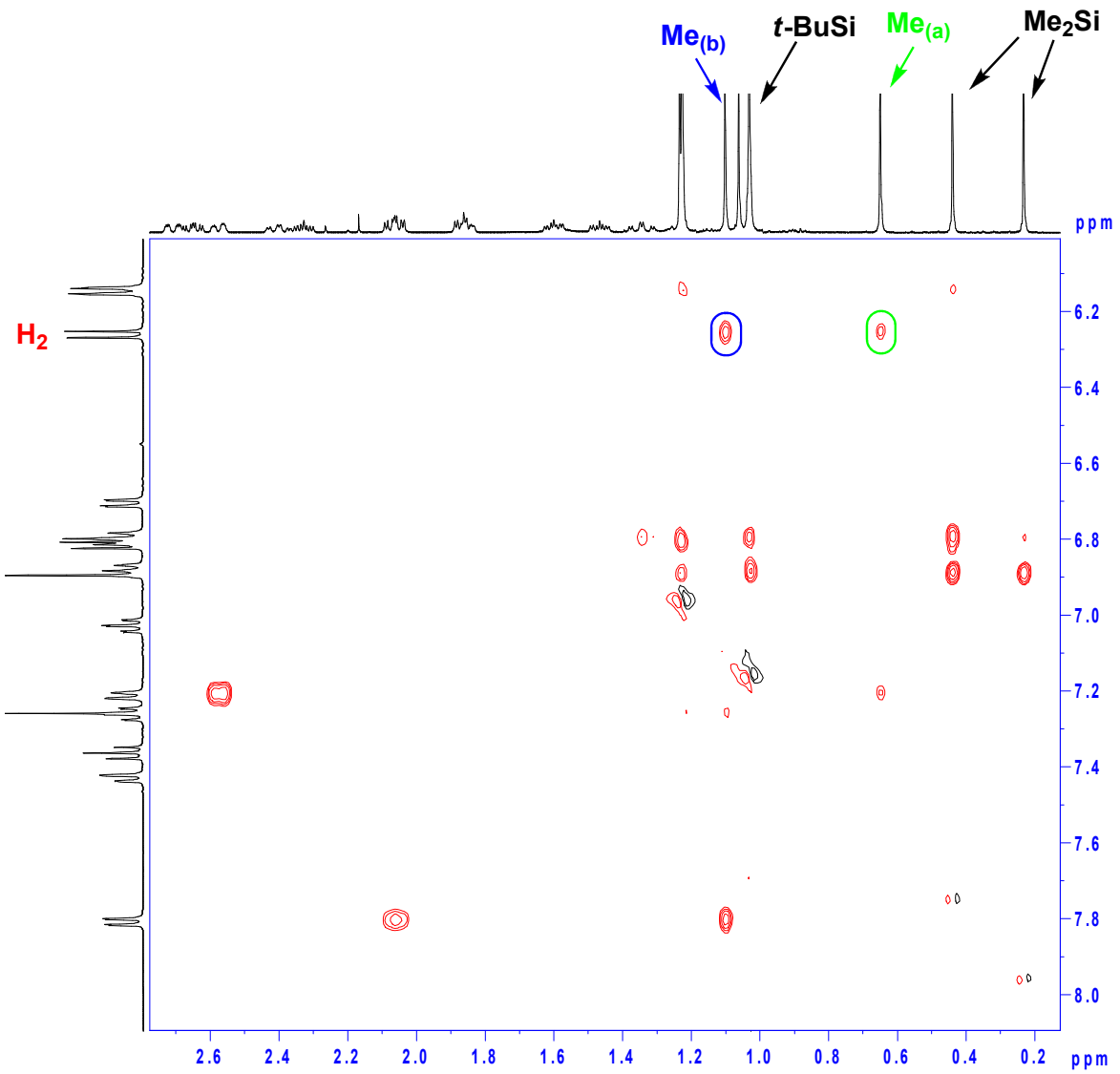
10
9
8
7
6
5
4
3
2
1
ppm

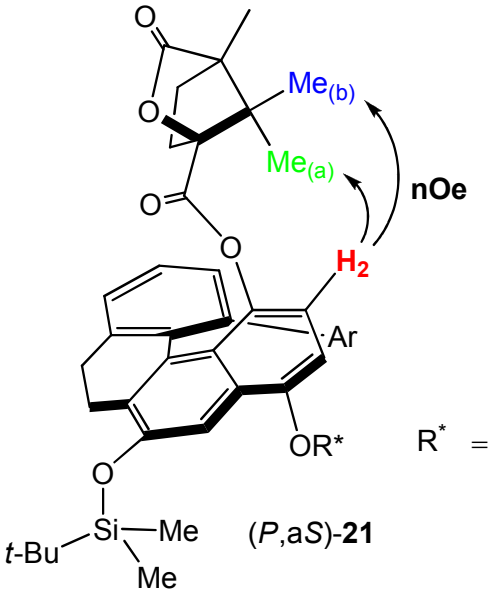

OTBDMS
OR*
*RO

(*P*,a*S*)-**21**

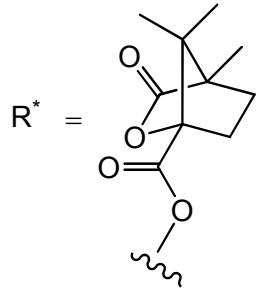
R* =

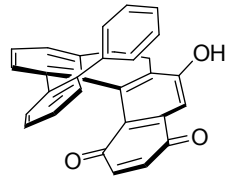
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Me(b)
t-BuSi
Me(a)
Me2Si
ppm
H2
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
ppm

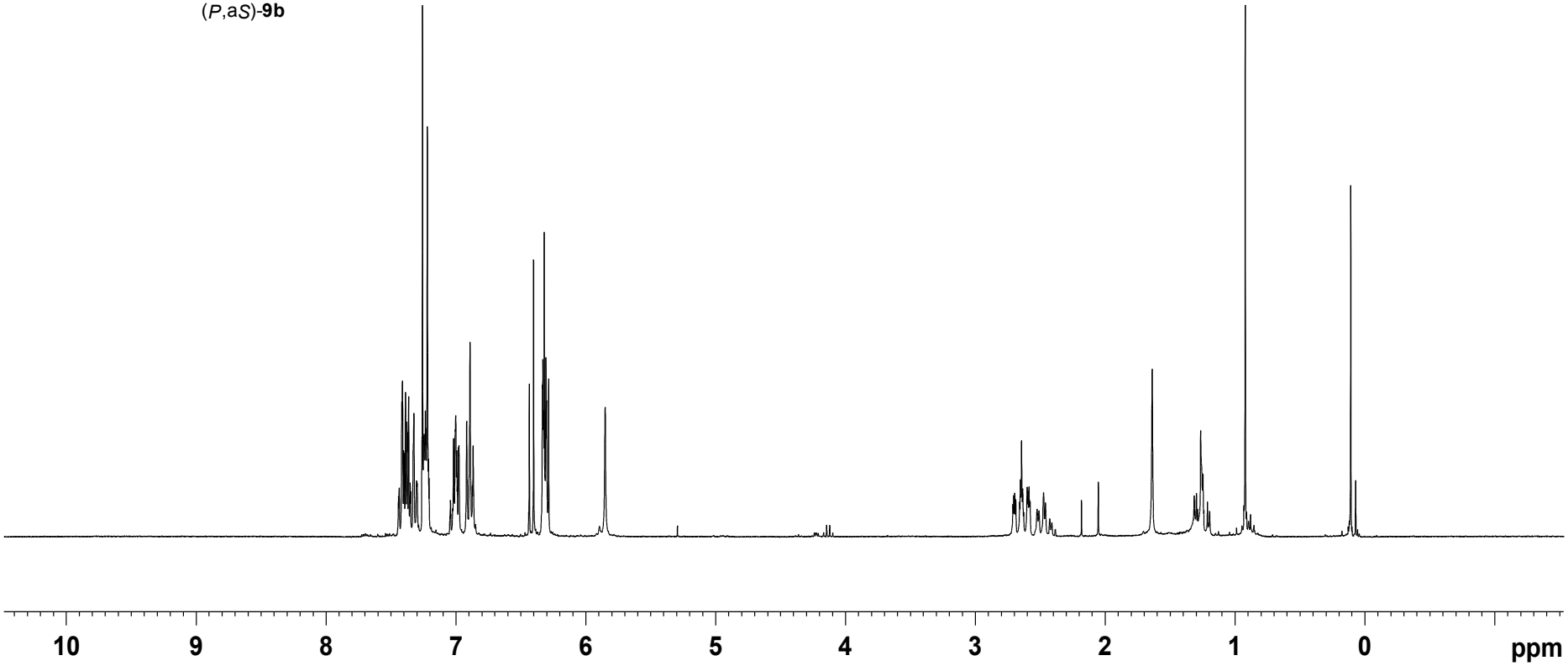

O
O
Me(b)
Me(a)
nOe
O
H2
Ar
OR*
O
Si
Me
t-Bu
Me

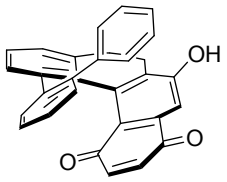
(*P*,a*S*)-**21**


R* =
O
O
O
O



(*P*,a*S*)-**9b**




OH
O
O

(*P*,a*S*)-**9b**

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