CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Recent Advances in "Formal" Ruthenium-Catalyzed [2+2+2] Cycloaddition Reactions of Diynes to Alkenes

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Supporting Information

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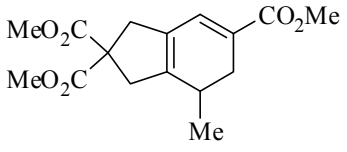
I. General methods

All reactions were performed under an atmosphere of dry argon in flamed dried glassware unless otherwise indicated. Dry DMF (Fluka) was used as received. All other solvents and reagents were used as received, unless otherwise noted. ^{1}H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solutions. Flash chromatography was performed with a silica gel column eluted with mixed solvents (hexane/ethyl acetate).

II. Preparation of starting materials and catalyst

- 1,6-Diynes **1a**,[1] **7'a**, **7''a**,[2] **7b**,[3] and **10** were prepared following published procedures or with appropriate modifications.
- 1,6-Diyne **7a** was prepared in 86% yield by reaction of the sodium salt of the dimethyl 2-(prop-2-ynyl)malonate (generated by treatment of dimethyl 2-(prop-2-ynyl)malonate with sodium hydride in THF) with 1-bromobut-2-yne.
- 1,6-Diyne **7c**[4] was prepared in two steps in 70% overall yield. First, dimethyl 2-(3-phenylprop-2-ynyl)malonate was prepared by Sonogashira reaction of dimethyl 2-(prop-2-ynyl)malonate with iodobenzene, $PdCl_2(PPh_3)$ and CuI in THF/Et_3N at r.t. Second, alkylation of dimethyl 2-(3-phenylprop-2-ynyl)malonate with 3-bromoprop-1-yne in THF using sodium hydride as base.
- Catalyst $[Cp^*Ru(CH_3CN)_3]PF_6$ was also prepared following published procedures.[5]

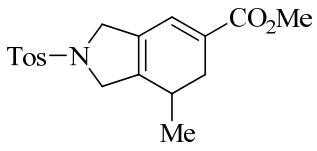
*III. "Formal" Ru(II)-catalyzed [2+2+2] cycloaddition of unsymmetrical 1,6-diynes **7** with alkenes **2**: procedures and spectral data of the products*



8aa

Trimethyl 7-methyl-1,3,6,7-tetrahydro-2*H*-indene-2,2,5-tricarboxylate (8aa)
Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 129 mg (0.14 mL, 1.5 mmol, 3 eq.) of methyl acrylate **2a**, and 111 mg (0.5 mmol, 1 eq.) of diyne **7a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8aa** (139 mg, 0.45 mmol) was obtained as a yellow oil in 90% yield.
^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 6.94 (s, 1H), 3.75 (s, 6H), 3.74 (s, 3H), 3.13 (s, 4H), 2.66 (dd, *J*= 16.8, 8.1 Hz, 1H), 2.54-2.44 (m, 1H), 2.63 (dd, *J*= 16.8, 10.4 Hz, 1H), 1.04 (d, *J*=7.0 Hz, 3H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 172.2 (2×CO), 167.8 (CO), 145.9 (C), 131.2 (CH), 129.6 (C), 126.3 (C), 58.5 (C), 52.9 (2×CH_3), 51.6 (CH_3), 41.6 (CH_2), 41.0 (CH_2), 30.5 (CH_2), 29.3 (CH), 17.8 (CH_3). MS, *m/z* (% relative intensity): 309 (M^+ +1, 100), 308 (61), 307 (60), 289 (22), 278 (51), 277 (99), 275 (56), 251 (27), 250 (54), 249 (96), 248 (54), 247 (53), 217 (46), 191 (21), 189 (41). HRMS calculated for $C_{16}H_{21}O_6$: 309.1338; found: 309.1340.

[1] Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, *124*, 5025.
[2] Chang, H-T.; Jeganmohan, M.; Cheng, C-H. *Org. Lett.* **2007**, *9*, 505.
[3] Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763.
[4] Yamamoto, Y.; Ogawa, R.; Itoh, K. *Chem. Commun*. **2000**, *7*, 549.
[5] a) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544. b) Schrenk, J. L.; McNair, A. M.; McCormick, F. B. Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501.

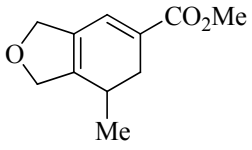


8´aa

Methyl 7-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1*H*-isoindole-5-carboxylate (8´aa)

Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 129 mg (0.14 mL, 1.5 mmol, 3 eq.) of methyl acrylate **2a**, and 130 mg (0.5 mmol, 1 eq.) of diyne **7´a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8´aa** (104 mg, 0.30 mmol) was obtained as a yellow oil in 60% yield.

^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): 7.74 (d, *J*= 8.3 Hz, 2H), 7.32 (d, *J*= 8.3 Hz, 2H), 6.85 (s, 1H), 4.30-4.08 (m, 4H), 3.74 (s, 3H), 2.65 (dd, *J*= 16.8, 8.5 Hz, 1H), 2.56-2.43 (m, 1H), 2.43 (s, 3H), 2.21 (dd, *J*= 16.8, 10.8 Hz, 1H), 0.99 (d, *J*=6.9 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 167.2 (CO), 143.6 (C), 142.1 (C), 134.0 (C), 129.8 (2×CH), 128.0 (CH), 127.8 (C), 127.7 (C), 127.3 (2×CH), 55.1 (CH_2), 54.6 (CH_2), 51.7 (CH_3), 30.3 (CH_2), 27.7 (CH), 21.5 (CH_3), 17.7 (CH_3). MS, *m/z* (% relative intensity): 348 (M^+ +1, 100), 347 (5), 316 (7), 192 (19), 125 (7).

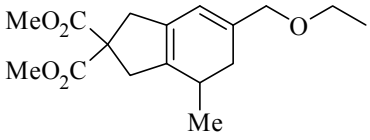


8´´aa

Methyl 7-methyl-1,3,6,7-tetrahydro-2-benzofuran-5-carboxylate (8´´aa)

Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 129 mg (0.14 mL, 1.5 mmol, 3 eq.) of methyl acrylate **2a**, and 54 mg (0.5 mmol, 1 eq.) of diyne **7´´a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (9:1) as eluent, **8´´aa** (48 mg, 0.25 mmol) was obtained as a yellow oil in 50% yield.

^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): 6.99 (s, 1H), 4.74-4.67 (m, 4H), 3.77 (s, 3H), 2.76 (dd, *J*= 16.6, 8.8 Hz, 1H), 2.67-2.58 (m, 1H), 2.34 (dd, *J*= 16.6, 10.7 Hz, 1H), 1.06 (d, *J*=6.9 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 167.5 (CO), 144.4 (C), 129.5 (C), 127.8 (CH), 127.1 (C), 75.4 (CH_2), 75.0 (CH_2), 51.7 (CH_3), 30.8 (CH_2), 27.3 (CH), 18.0 (CH_3). MS, *m/z* (% relative intensity): 195 (M^+ +1, 100), 194 (5), 193 (32), 177 (15), 165 (46), 163 (48), 135 (11), 107 (19).



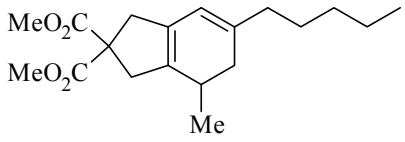
8ab

Dimethyl 6-(ethoxymethyl)-4-methyl-1,3,4,5-tetrahydro-2*H*-indene-2,2-dicarboxylate (8ab):

Following conditions B, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 431 mg (0.57 mL, 5 mmol, 10 eq.) of ethyl allyl ether **2b**, and 111 mg (0.5 mmol, 1 eq.) of diyne **7a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8ab** (108 mg, 0.35 mmol) was obtained as a pale yellow oil in 70% yield.

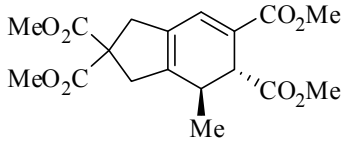
^{1}H-NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.81 (s, 1H), 3.93 (s, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3.45 (q, *J*= 7.0 Hz, 2H), 3.15-2.94 (m, 4H), 2.49-2.41 (m, 1H), 2.33 (dd, *J*= 16.6, 8.7 Hz, 1H), 1.95 (dd, *J*= 16.6, 8.3 Hz, 1H), 1.20 (t, *J*= 7.0 Hz, 3H), 1.00 (d, *J*=6.9 Hz, 3H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 172.6 (2×CO), 136.9 (C), 135.1 (C), 129.3 (C), 118.7 (CH), 73.7 (CH_2), 65.4 (CH_2), 58.6 (C),

52.8 (2×CH_3), 41.4 (CH_2), 41.3 (CH_2), 33.6 (CH_2), 29.1 (CH), 18.8 (CH_3), 15.3 (CH_3). MS, m/z (% relative intensity): 309 (M^++1, 89), 308 (100), 307 (32), 264 (31), 263 (95), 249 (68), 248 (20), 203 (50). HRMS calculated for $C_{17}H_{25}O_5$: 309.1691; found: 309.1702.



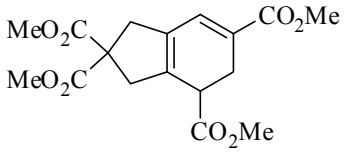
8ac

Dimethyl 4-methyl-6-pentyl-1,3,4,5-tetrahydro-2*H*-indene-2,2-dicarboxylate (8ac):
Following conditions A, 25 mg (10% mol) of [Cp*Ru(CH_3CN)$_3$]PF_6, 8 mg (10% mol) of Et_4NCl, 152 mg (0.22 mL, 1.5 mmol, 3 eq.) of 1-heptene **2c**, and 111 mg (0.5 mmol, 1 eq.) of diyne **7a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (9:1) as eluent, **8ac** (111 mg, 0.35 mmol) was obtained as a colorless oil in 69% yield.
^{1}H-NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.56 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.13-2.93 (m, 4H), 2.43-2.35 (m, 1H), 2.25 (dd, *J*= 16.7, 9.0 Hz, 1H), 2.04 (t, *J*= 7.5 Hz, 2H), 1.89 (dd, *J*= 16.7, 10.2 Hz, 1H), 1.43-1.25 (m, 6H), 0.99 (d, *J*= 6.9 Hz, 3H), 0.89 (t, *J*=7.2 Hz, 3H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 172.8 (2×CO), 139.4 (C), 134.2 (C), 130.2 (C), 116.3 (CH), 58.4 (C), 52.6 (2×CH_3), 41.6 (CH_2), 41.2 (CH_2), 37.1 (CH_2), 36.4 (CH_2), 31.5 (CH_2), 29.3 (CH), 27.2 (CH_2), 22.5 (CH_2), 18.1 (CH_3), 14.0 (CH_3). MS, m/z (% relative intensity): 321 (M^++1, 99), 320 (100), 319 (88), 318 (24), 317 (27), 289 (40), 287 (49), 275 (20), 263 (38), 262 (81), 261 (99), 260 (73), 259 (93), 258 (22), 245 (31), 201 (25), 189 (21). HRMS calculated for $C_{19}H_{29}O_4$: 321.2066; found: 321.2069.



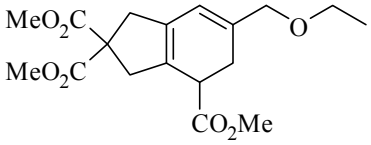
8ad

Tetramethyl 4-methyl-1,3,4,5-tetrahydro-2*H*-indene-2,2,5,6-tetracarboxylate (8ad):
Following conditions A, 25 mg (10% mol) of [Cp*Ru(CH_3CN)$_3$]PF_6, 8 mg (10% mol) of Et_4NCl, 225 mg (0.19 mL, 1.5 mmol, 3 eq.) of dimethyl maleate **2d**, and 111 mg (0.5 mmol, 1 eq.) of diyne **7a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (7:3) as eluent, **8ad** (128 mg, 0.35 mmol) was obtained as a pale yellow oil in 70% yield.
^{1}H-NMR ($CDCl_3$, 250 MHz), δ (ppm): 7.10 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H), 3.55 (d, *J*= 2.8 Hz, 1H), 3.26-2.96 (m, 5H), 1.03 (d, *J*= 7.3 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 173.2 (CO), 172.1 (CO), 171.7 (CO), 167.2 (CO), 145.7 (C), 132.7 (CH), 128.7 (C), 123.2 (C), 58.7 (C), 53.0 (CH_3), 52.9 (CH_3), 52.3 (CH_3), 51.9 (CH_3), 46.1 (CH), 41.8 (CH_2), 40.6 (CH_2), 32.4 (CH), 17.0 (CH_3). MS, m/z (% relative intensity): 367 (M^++1, 100), 366 (66), 337 (22), 336 (51), 335 (96), 334 (26), 307(69), 274 (48), 247 (25). HRMS calculated for $C_{18}H_{23}O_8$: 367.1391; found: 367.1393.



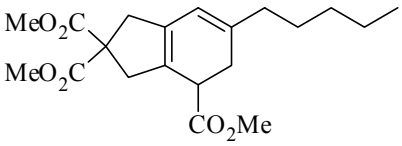
8ba

Tetramethyl 1,3,4,5-tetrahydro-2*H*-indene-2,2,4,6-tetracarboxylate (8ba):
Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 129 mg (0.14 mL, 1.5 mmol, 3 eq.) of methyl acrylate **2a**, and 133 mg (0.5 mmol, 1 eq.) of diyne **7b** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8ba** (119 mg, 0.34 mmol) was obtained as a yellow oil in 68% yield.
^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): 6.96 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.40-2.98 (m, 6H), 2.79-2.58 (m, 1H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 172.4 (CO), 172.0 (CO), 171.7 (CO), 166.9 (CO), 136.2 (C), 132.6 (C), 130.5 (CH), 126.7 (C), 58.4 (C), 53.0 (CH_3), 52.9 (CH_3), 52.1 (CH_3), 51.8 (CH_3), 42.4 (CH_2), 40.8 (CH_2), 40.6 (CH), 25.4 (CH_2). MS (ESI-TOF) *m/z (%)*: 375 (M^+ +Na, 100), 372 (30), 321 (18), 261 (10). HRMS calculated for $C_{17}H_{20}NaO_8$: 375.1050; found: 375.1060.



8bb

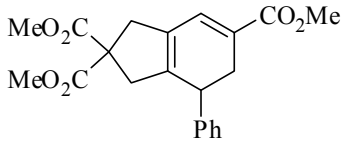
Trimethyl 6-(ethoxymethyl)-1,3,4,5-tetrahydro-2*H*-indene-2,2,4-tricarboxylate (8bb):
Following conditions B, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 431 mg (0.57 mL, 5 mmol, 10 eq.) of ethyl allyl ether **2b**, and 133 mg (0.5 mmol, 1 eq.) of diyne **7b** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8bb** (124 mg, 0.35 mmol) was obtained as a pale yellow oil in 70% yield.
^{1}H-NMR ($CDCl_3$, 500 MHz), δ (ppm): 5.85 (s, 1H), 3.97 (s, 2H), 3.74 (s, 6H), 3.69 (s, 3H), 3.48-3.44 (m, 2H), 3.22-3.00 (m, 5H), 2.69-2.64 (m, 1H), 2.48-2.42 (m, 1H), 1.21 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$), δ (ppm): 173.3 (CO), 172.4 (CO), 172.2 (CO), 135.5 (C), 132.6 (C), 127.6 (C), 118.2 (CH), 73.2 (CH_2), 65.5 (CH_2), 58.5 (C), 52.9 (CH_3), 52.8 (CH_3), 51.9 (CH_3), 42.1 (CH_2), 41.2 (CH_2), 40.4 (CH), 27.8 (CH_2), 15.1 (CH_3). MS, m/z (% relative intensity): 353 (M^++1, 41), 352 (31), 351 (98), 349 (33), 339 (29), 337 (67), 335 (23), 323 (55), 322 (27), 321 (100), 320 (47), 319 (99), 311 (21), 309 (60), 308 (23), 307 (99), 306 (51), 305 (99), 291 (62), 289 (31), 277 (33), 275 (70), 263 (31), 261 (56), 249 (25), 247 (37). HRMS calculated for $C_{18}H_{25}O_7$: 353.1600; found: 353.1599.



8bc

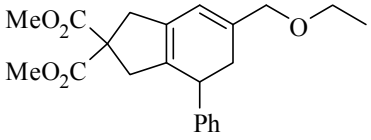
Trimethyl 6-pentyl-1,3,4,5-tetrahydro-2*H*-indene-2,2,4-tricarboxylate (8bc):
Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 152 mg (0.22 mL, 1.5 mmol, 3 eq.) of 1-heptene **2c**, and 133 mg (0.5 mmol, 1 eq.) of diyne **7b** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8bc** (114 mg, 0.31 mmol) was obtained as a pale yellow oil in 63% yield.
^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): 5.60 (s, 1H), 3.74 (s, 6H), 3.69 (s, 3H), 3.44-2.98 (m, 5H), 2.67-2.57 (m, 1H), 2.41-2.28 (m, 1H), 2.17-2.05 (m, 2H), 1.35-1.23 (m, 6H), 0.89 (t, *J*= 7.1 Hz, 3H). ^{13}C-NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 173.7 (CO), 172.6 (CO), 172.3 (CO), 139.7 (C), 133.2 (C),

125.1 (C), 116.1 (CH) , 58.4 (C), 52.8 (2×CH_3), 51.8 (CH_3), 42.0 (CH_2), 41.4 (CH_2), 40.7 (CH), 36.8 (CH_2), 31.5 (CH_2), 30.5 (CH_2), 27.0 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MS (ESI-TOF) *m/z (%)*: 387 (M^+ +Na, 100), 384 (21), 365 (M^+ +1, 37), 333 (70), 305 (24). HRMS calculated for $C_{20}H_{29}O_6$: 365.1959; found: 365.1961.



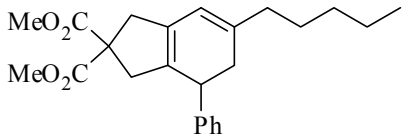
8ca

Trimethyl 7-phenyl-1,3,6,7-tetrahydro-2*H*-indene-2,2,5-tricarboxylate (8ca):
Following conditions A, 25 mg (10% mol) of [Cp*Ru(CH_3CN)$_3$]PF_6, 8 mg (10% mol) of Et_4NCl, 129 mg (0.14 mL, 1.5 mmol, 3 eq.) of methyl acrylate **2a**, and 142 mg (0.5 mmol, 1 eq.) of diyne **7c** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (7:3) as eluent, **8ca** (73 mg, 0.20 mmol) was obtained as a yellow oil in 40% yield.
^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): 7.44-7.14 (m, 5H), 7.05 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.70 (s, 3H), 3.42-2.89 (m, 6H), 2.76-2.65 (m, 1H). ^{13}C-NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 172.1 (2×CO), 167.4 (CO), 142.6 (C), 142.3 (C), 140.8 (C), 131.6 (C), 131.1 (CH), 128.6 (2×CH), 127.6 (2×CH), 126.8 (CH), 58.4 (C), 52.9 (CH_3), 52.8 (CH_3), 51.6 (CH_3), 42.2 (CH_2), 41.2 (CH), 41.0 (CH_2), 31.7 (CH_2). MS, m/z (% relative intensity): 371 (M^++1, 67), 369 (23), 339 (51), 331 (73), 295 (86), 293 (32), 285 (40), 263 (36), 261 (22), 253 (23), 235 (77), 225 (100), 147 (57). HRMS calculated for $C_{21}H_{23}O_6$: 371.1495; found: 371.1495.



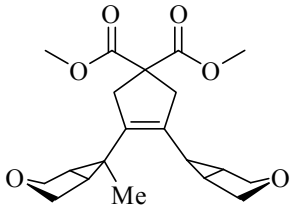
8cb

Dimethyl 6-(ethoxymethyl)-4-phenyl-1,3,4,5-tetrahydro-2*H*-indene-2,2-dicarboxylate (8cb):
Following conditions B, 25 mg (10% mol) of [Cp*Ru(CH_3CN)$_3$]PF_6, 8 mg (10% mol) of Et_4NCl, 431 mg (0.57 mL, 5 mmol, 10 eq.) of ethyl allyl ether **2b**, and 142 mg (0.5 mmol, 1 eq.) of diyne **7c** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8cb** (144 mg, 0.39 mmol) was obtained as a pale yellow oil in 78% yield.
^{1}H-NMR ($CDCl_3$, 250 MHz), δ (ppm): 7.37-7.16 (m, 5H), 5.93 (s, 1H), 3.90 (s, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 3.62-3.53 (m, 1H), 3.35 (q, *J*= 7.0 Hz, 2H), 3.17-3.13 (m, 2H), 2.87 (s, 2H), 2.71-2.60 (m, 1H), 2.41-2.31 (m, 1H), 1.11 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 172.5 (2×CO), 143.5 (C), 135.0 (C), 133.7 (C), 131.6 (C), 128.4 (2×CH), 127.6 (2×CH), 126.4 (CH), 118.7 (CH), 73.4 (CH_2), 65.3 (CH_2), 58.4 (C), 52.8 (CH_3), 52.7 (CH_3), 41.8 (CH_2), 41.4 (CH_2), 41.0 (CH), 34.7 (CH_2), 15.1 (CH_3). MS, m/z (% relative intensity): 371 (M^++1, 67), 370 (80), 369 (28), 339 (30), 327 (22), 326 (71), 325 (100), 323 (29), 312 (35), 311 (91), 293 (59), 265 (88), 264 (23), 205 (22). HRMS calculated for $C_{22}H_{27}O_5$: 371.1858; found: 371.1860.



8cc

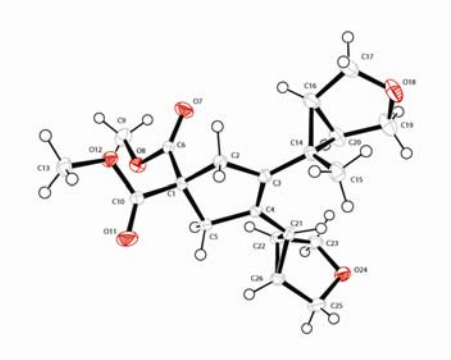
Dimethyl 6-pentyl-4-phenyl-1,3,4,5-tetrahydro-2*H*-indene-2,2-dicarboxylate (8cc):
Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 152 mg (0.22 mL, 1.5 mmol, 3 eq.) of 1-heptene **2c**, and 142 mg (0.5 mmol, 1 eq.) of diyne **7c** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **8cc** (89 mg, 0.23 mmol) was obtained as a pale yellow oil in 47% yield.
^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): 7.33-7.16 (m, 5H), 5.68 (s, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.58-3.48 (m, 1H), 3.20-3.11 (m, 2H), 2.85 (s, 2H), 2.63-2.53 (m, 1H), 2.34-2.23 (m, 1H), 2.04-1.98 (m, 2H), 1.35-1.20 (m, 6H), 0.84 (t, *J*= 7.1 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 172.6 (2×CO), 143.9 (C), 139.3 (C), 132.2 (C), 131.2 (C), 128.4 (2×CH), 127.6 (2×CH), 126.3 (CH), 116.5 (CH), 58.4 (C), 52.8 (CH_3), 52.7 (CH_3), 41.8 (CH_2), 41.6 (CH_2), 41.4 (CH), 37.5 (CH_2), 36.9 (CH_2), 31.4 (CH_2), 27.0 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MS, m/z (% relative intensity): 383 (M^++1, 100), 382 (93), 381 (61), 351 (60), 325 (46), 324 (64), 323 (96), 322 (29), 321 (36), 307 (31), 247 (40). HRMS calculated for $C_{24}H_{31}O_4$: 371.2222; found: 383.2218.



9

Dimethyl 3-(6-methyl-3-oxabicyclo[3.1.0]hex-6-yl)-4-(3-oxabicyclo[3.1.0]hex-6-yl)cyclopent-3-ene-1,1-dicarboxylate (9):
Following conditions A, but using acetone as solvent, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 108 mg (0.11 mL, 1.5 mmol, 3 eq.) of 2,5-dihydrofuran **5a**, and 111 mg (0.5 mmol, 1 eq.) of diyne **7a** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, the product **9** (115 mg, 0.32 mmol) was obtained as a white solid in 64% yield.
^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.93-3.85 (m, 8H), 3.72 (s, 6H), 2.95 (s, 2H), 2.72 (s, 2H), 1.76-1.57 (m, 4H), 1.58 (t, *J*= 3.7 Hz, 1H), 1.07 (s, 3H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 172.3 (2×CO), 136.7 (C), 131.9 (C), 69.7 (2×CH_2), 68.0 (2×CH_2), 57.1 (C), 52.8 (2×CH_3), 42.5 (CH_2), 41.0 (CH_2), 28.6 (2×CH), 23.7 (2×CH), 22.6 (C), 19.7 (CH), 10.3 (CH_3). MS, m/z (% relative intensity): 363 (M^++1, 78), 362 (64), 361 (44), 345 (35), 333 (100), 303 (36), 293 (21), 273 (35). HRMS calculated for $C_{20}H_{27}O_6$: 363.1808; found: 363.1808.

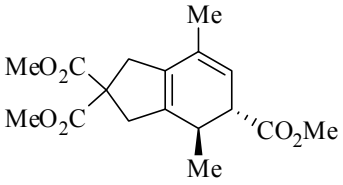
Crystal data and structure refinement for **9**.



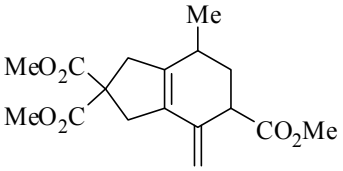
9

Empirical formula	$C_{20}\ H_{26}\ O_6$	
Formula weight	362.41	
Temperature	100(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 12.9730(7) Å	α= 90°.
	b = 13.2543(7) Å	β= 105.213(2)°.
	c = 22.5810(11) Å	γ = 90°.
Volume	3746.7(3) $Å^3$	
Z	8	
Density (calculated)	1.285 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	1552	
Crystal size	0.58 x 0.37 x 0.36 mm^3	
Theta range for data collection	1.87 to 26.02°.	
Index ranges	-16<=h<=15, 0<=k<=16, 0<=l<=27	
Reflections collected	30146	
Independent reflections	3695 [R(int) = 0.0314]	
Completeness to theta = 26.02°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9669 and 0.9474	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3695 / 0 / 238	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.0994	
R indices (all data)	R1 = 0.0505, wR2 = 0.1030	
Largest diff. peak and hole	0.258 and -0.222 $e.Å^{-3}$	

*IV. "Formal" Ru(II)-catalyzed [2+2+2] cycloaddition of disubstituted 1,6-diyne **10** with acyclic alkenes: procedures and spectral data of the products*



11a



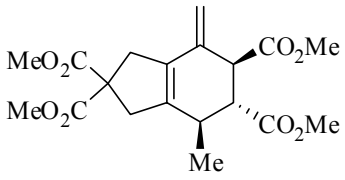
12a

Trimethyl 4,7-dimethyl-1,3,4,5-tetrahydro-2*H*-indene-2,2,5-tricarboxylate (11a) and Trimethyl 7-methyl-4-methylene-1,3,4,5,6,7-hexahydro-2*H*-indene-2,2,5-tricarboxylate (12a):

Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 129 mg (0.14 mL, 1.5 mmol, 3 eq.) of methyl acrylate **2a**, and 118 mg (0.5 mmol, 1 eq.) of diyne **10** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, a mixture of **11a** and **12a** (88 mg, 0.27 mmol, 55%) was obtained as a pale yellow oil in a 1.25:1 relationship.

11a: ^{1}H-NMR ($CDCl_3$, 250 MHz), δ (ppm): 5.32 (s, 1H), 3.75 (s, 6H), 3.70 (s, 3H), 3.24-3.01 (m, 5H), 2.87-2.71 (m, 1H), 1.77 (s, 3H), 1.03 (d, J= 6.9 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 174.7 (2×CO), 172.3 (CO), 136.9 (C), 131.3 (C), 130.7 (C), 117.0 (CH), 58.1 (C), 52.9 (2×CH_3), 51.9 (CH_3), 49.1 (CH), 41.6 (CH_2), 40.1 (CH_2), 31.3 (CH), 19.0 (CH_3), 17.8 (CH_3). MS (ESI-TOF) *m/z* (%): 345 (M^+ +Na, 33), 245 (95), 177 (24), 149 (15), 102 (100). HRMS calculated for $C_{17}H_{22}NaO_6$: 345.1309; found: 345.1308.

12a: ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 4.81 (s, 1H), 4.75 (s, 1H), 3.74 (s, 6H), 3.68 (s, 3H), 3.24-3.05 (m, 5H), 2.83-2.74 (m, 2H), 0.93 (d, J= 6.9 Hz, 3H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 174.2 (2×CO), 172.5 (CO), 144.9 (C), 141.4 (C), 138.9 (C), 108.7 (CH_2), 57.6 (C), 52.9 (2×CH_3), 51.5 (CH_3), 44.3 (CH), 42.7 (CH_2), 39.6 (CH_2), 32.1 (CH), 27.6 (CH_2), 13.6 (CH_3).

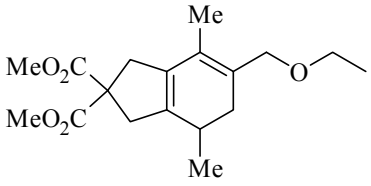


12d

Tetramethyl 4-methyl-7-methylene-4,5,6,7-tetrahydro-1H-indene-2,2,5,6(3H)-tetracarboxylate (12d):

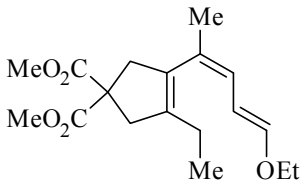
Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 225 mg (0.19 mL, 1.5 mmol, 3 eq.) of dimethyl maleate **2d**, and 118 mg (0.5 mmol, 1 eq.) of diyne **10** were used. Once the slow addition finished, the reaction was heated for 15 hours. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (8:2) as eluent, **12d** (80 mg, 0.21 mmol) was obtained as a pale yellow oil in 42% yield.

^{1}H-NMR ($CDCl_3$, 250 MHz), δ (ppm): 4.92 (s, 1H), 4.79 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.70-3.62 (m, 1H), 3.29-3.01 (m, 4H), 2.78 (dd, *J*= 11.5, 9.8 Hz, 1H), 2.67-2.58 (m, 1H), 1.10 (d, *J*= 6.9 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 174.3 (2×CO), 172.8 (CO), 172.2 (CO), 139.9 (C), 136.9 (C), 131.2 (C), 109.6 (CH_2), 57.6 (C), 53.0 (2×CH_3), 52.0 (2×CH_3), 51.1 (CH), 49.4 (CH), 42.0 (CH_2), 40.0 (CH_2), 33.9 (CH), 17.3 (CH_3). MS (ESI-TOF) *m/z* (%): 403 (M^+ +Na, 100), 400 (22), 394 (11), 381 (M^+ +1, 7), 349 (31), 321 (13). HRMS calculated for $C_{19}H_{25}O_8$: 381.1544; found: 381.1549.



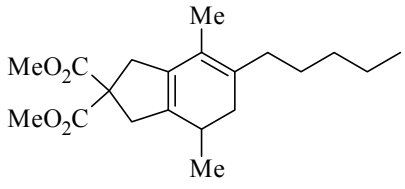
11b

Dimethyl 6-(ethoxymethyl)-4,7-dimethyl-1,3,4,5-tetrahydro-2*H*-indene-2,2-dicarboxylate (11b):
Following conditions B, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 431 mg (0.57 mL, 5 mmol, 10 eq.) of ethyl allyl ether **2b**, and 118 mg (0.5 mmol, 1 eq.) of diyne **10** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (9:1) as eluent, **11b** (104 mg, 0.32 mmol) was obtained as a colorless oil in 65% yield.
^{1}H-NMR ($CDCl_3$, 500 MHz), δ (ppm): 4.04 (d, *J*=11.5 Hz, 1H), 3.98 (d, *J*= 11.5 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.44 (q, *J*= 7.0 Hz, 2H), 3.18-2.93 (m, 4H), 2.40-2.34 (m, 1H), 2.04-1.95 (m, 1H), 1.77 (s, 3H), 1.72 (d, *J*= 15.4 Hz, 1H), 1.20 (t, *J*= 7.0 Hz, 3H), 0.99 (d, *J*= 6.6 Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$), δ (ppm):172.7 (2×CO), 137.5 (C), 132.2 (C), 127.3 (C), 127.0 (C), 69.5 (CH_2), 64.9 (CH_2), 58.2 (C), 52.8 (2×CH_3), 41.6 (CH_2), 40.7 (CH_2), 35.4 (CH_2), 29.0 (CH), 18.0 (CH_3), 15.3 (CH_3), 14.2 (CH_3). MS, m/z (% relative intensity): 323 (M^++1, 93), 322 (100), 321 (69), 279 (26), 278 (85), 277 (99), 275 (25), 263 (66), 217 (81), 203 (25). HRMS calculated for $C_{18}H_{27}O_5$: 323.1858; found: 323.1852.



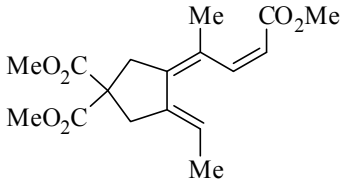
13

Dimethyl 3-[(1*Z*,3*E*)-4-ethoxy-1-methylbuta-1,3-dien-1-yl]-4-ethylcyclopent-3-ene-1,1-dicarboxylate (13):
Following conditions B, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 431 mg (0.57 mL, 5 mmol, 10 eq.) of ethyl allyl ether **2b**, and 118 mg (0.5 mmol, 1 eq.) of diyne **10** were used. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (9:1) as eluent, **13** (19 mg, 0.06 mmol) was obtained as a pale yellow oil in 12% yield.
^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm): 6.47 (d, *J*= 12.5 Hz, 1H), 5.77 (d, *J*= 11.0 Hz, 1H), 5.40 (dd, *J*= 12.5, 11.0 Hz, 1H), 3.74 (s, 6H), 3.73 (q, *J*= 7.0 Hz, 2H), 3.03 (s, 4H), 1.96 (q, *J*= 7.5 Hz, 2H), 1.75 (s, 3H), 1.26 (t, *J*= 7.0 Hz, 3H), 0.95 (t, *J*= 7.5 Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$), δ (ppm): 172.7 (2×CO), 149.1 (CH), 136.1 (C), 132.5 (C), 128.8 (C), 123.3 (CH), 104.9 (CH), 65.2 (CH_2), 57.8 (C), 52.7 (2×CH_3), 43.3 (CH_2), 42.6 (CH_2), 22.6 (CH_3), 22.0 (CH_2), 14.7 (CH_3), 12.2 (CH_3). MS, m/z (% relative intensity): 323 (M^++1, 16), 321 (31), 309 (54), 297 (38), 295 (38), 293 (77), 281 (91), 279 (71), 277 (39), 269 (77), 267 (39), 265 (42), 263 (51), 255 (36), 253 (56), 251 (82), 249 (65), 237 (100), 233 (42), 227 (35), 223 (41), 221 (50), 219 (34), 217 (43), 206 (55), 203 (57), 195 (32), 193 (35), 191 (30), 177 (44), 167 (35), 145 (36), 103 (41), 95 (49). HRMS calculated for $C_{18}H_{27}O_5$: 323.1858; found: 323.1852.



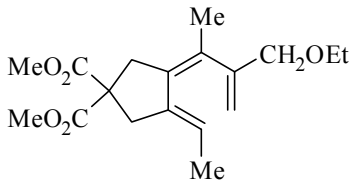
11c

Dimethyl 4,7-dimethyl-6-pentyl-1,3,4,5-tetrehydro-2*H*-indene-2,2-dicarboxylate (11c):
Following conditions A, 25 mg (10% mol) of $[Cp^*Ru(CH_3CN)_3]PF_6$, 8 mg (10% mol) of Et_4NCl, 108 mg (0.11 mL, 1.5 mmol, 3 eq.) of 1-heptene **2c**, and 118 mg (0.5 mmol, 1 eq.) of diyne **10** were used. Once the slow addition finished, the reaction was heated for 15 hours. After workup and column chromatography of the residue on silica gel using hexane/ ethyl acetate (9:1) as eluent, **11c** (51 mg, 0.15 mmol) was obtained as a pale yellow oil in 31% yield.
^{1}H-NMR ($CDCl_3$, 250 MHz), δ (ppm): 3.74 (s, 3H), 3.72 (s, 3H), 3.12-2.93 (m, 4H), 2.29-1.61 (m, 5H), 1.69 (s, 3H), 1.36-1.14 (m, 6H), 0.95 (d, *J*= 6.2 Hz, 3H), 0.87 (t, *J*= 7.1 Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$), δ (ppm):172.4 (2×CO), 129.8 (C), 129.1 (C), 127.0 (C), 121.3 (C), 58.8 (C), 52.7 (2×CH_3), 39.2 (CH), 37.3 (CH_2), 36.9 (CH_2), 34.3 (CH_2), 32.1 (CH_2), 31.3 (CH_2), 26.4 (CH_2), 22.6 (CH_2), 19.6 (CH_3), 17.9 (CH_3), 14.1 (CH_3). MS, m/z (% relative intensity): 335 (M^++1, 100), 334 (93), 333 (56), 332 (99), 331 (98), 317 (20), 303 (21), 302 (22), 301 (92), 291 (30), 289 (40), 275 (99), 274 (84), 273 (89), 272 (93), 271 (38), 263 (30), 215 (53), 203 (21), 157 (22). HRMS calculated for $C_{20}H_{31}O_4$: 335.2222; found: 335.2218.



14

Dimethyl (3*E*,4*Z*)-3-ethylidene-4-[(2*Z*)-4-methoxy-1-methyl-4-oxobut-2-en-1-ylidene]cyclopentane-1,1-dicarboxylate (14)
In a 10 mL round-bottomed flask was prepared, under argon, a solution of $[Cp^*Ru(CH_3CN)_3]PF_6$ (25 mg, 10% mol) and Et_4NCl (8 mg, 10% mol) in DMF (1 mL) and stirred for 10 minutes at room temperature and then the alkene **2a** (430 mg, 0.45 mL, 5 mmol, 10eq) was added. The solution was stirred for another 10 minutes and then, the diyne **10** (118 mg, 0.5 mmol, 1 eq) was also added. After stirring for 1 h at room temperature, the crude solution was charged directly to a column chromatography on silica gel and eluted using ethyl ether/hexane (6:4). After evaporation of the eluent under vacuum in a rotavapor keeping the bath at room temperature, the hexatriene **14** (56 mg, 0.17 mmol) was isolated as a pale yellow oil in 35% yield.
^{1}H-NMR ($CDCl_3$, 250 MHz), δ (ppm): 6.88 (d, *J*= 12.1 Hz, 1H), 5.73 (d, *J*= 12.1 Hz, 1H), 5.58-5.50 (m, 1H), 3.74 (s, 6H), 3.71 (s, 3H), 3.09-2.99 (m, 4H), 1.93 (s, 3H), 1.78 (d, *J*= 7.5 Hz, 3H). ^{13}C-NMR, DEPT (63 MHz, $CDCl_3$), δ (ppm): 171.9 (2×CO), 166.7 (CO), 146.3 (CH), 140.4 (C), 137.8 (C), 126.4 (CH), 122.0 (C), 117.5 (CH), 56.9 (C), 52.9 (2×CH_3), 51.2 (CH_3), 39.2 (CH_2), 37.5 (CH_2), 20.3 (CH_3), 15.6 (CH_3). MS (ESI-TOF) *m/z* (%): 345 (M^+ +Na, 100), 323 (M^+ +1, 19), 321 (21), 291 (6), 263 (13), 261 (14), 102 (13). HRMS calculated for $C_{17}H_{23}O_6$: 323.1489; found: 323.1478.



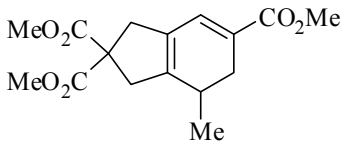
15

Dimethyl (3*Z*,4*E*)-3-[2-(ethoxymethyl)-1-methylprop-2-en-1-ylidene]-4-ethylidenecyclopentane-1,1-dicarboxylate (15):

In a 10 mL round-bottomed flask was prepared, under argon, a solution of $[Cp^*Ru(CH_3CN)_3]PF_6$ (25 mg, 10% mol) and Et_4NCl (8 mg, 10% mol) in DMF (1 mL) and stirred for 10 minutes at room temperature and then the alkene **2b** (453 mg, 0.60 mL, 5 mmol, 10eq) was added. The solution was stirred for another 10 minutes and then, the diyne **10** (118 mg, 0.5 mmol, 1 eq) was also added. After stirring for 2 h at room temperature, the crude solution was charged directly to a column chromatography on silica gel and eluted using ethyl ether/hexane (6:4). After evaporation of the eluent under vacuum in a rotavapor keeping the bath at room temperature, the hexatriene **15** (80 mg, 0.25 mmol) was isolated as a pale yellow oil in 49% yield.

^{1}H-NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.95-5.90 (m, 1H), 5.24 (s, 1H), 4.98 (s, 1H), 3.94 (s, 2H), 3.74 (s, 6H), 3.49 (q, *J*= 7.0 Hz, 2H), 2.99-2.93 (m, 4H), 1.85 (s, 3H), 1.64 (d, *J*= 6.8 Hz, 3H), 1.21 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 172.1 (2×CO), 149.2 (C), 136.4 (C), 131.7 (C), 128.4 (C), 120.4 (CH), 111.8 (CH_2), 70.3 (CH_2), 65.8 (CH_2), 56.7 (C), 52.7 (2×CH_3), 39.6 (CH_2), 37.9 (CH_2), 23.4 (CH_3), 15.2 (CH_3), 15.1 (CH_3). MS (ESI-TOF) *m/z* (%): 345 (M^+ +Na, 100), 342 (30), 323 (M^+ +1, 11), 277 (12). HRMS calculated for $C_{18}H_{27}O_5$: 323.1853; found: 323.1852.

V. Spectra of new compounds



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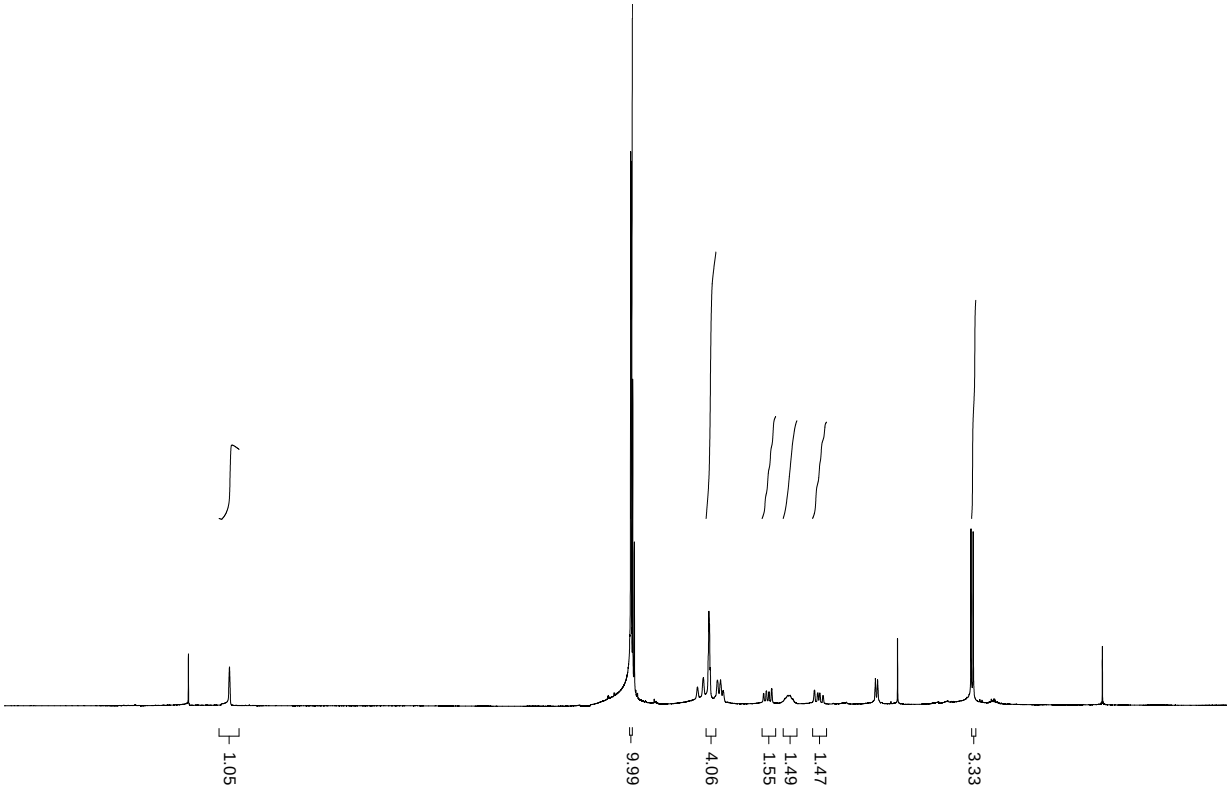

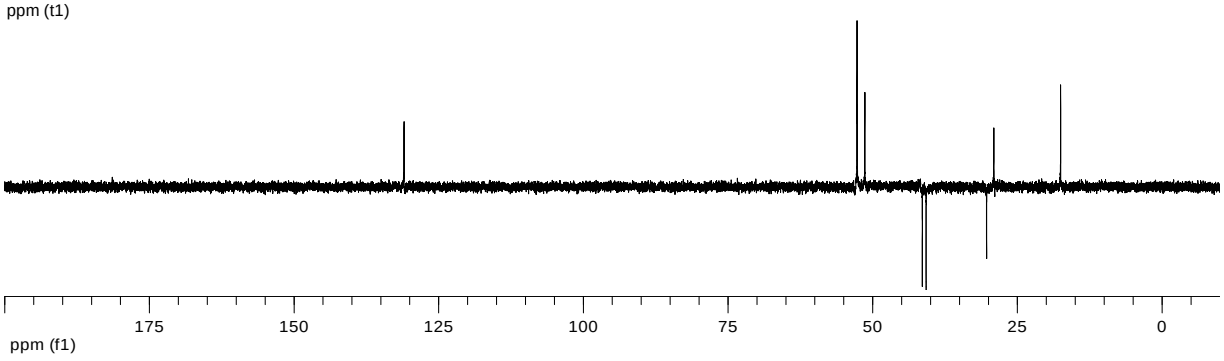

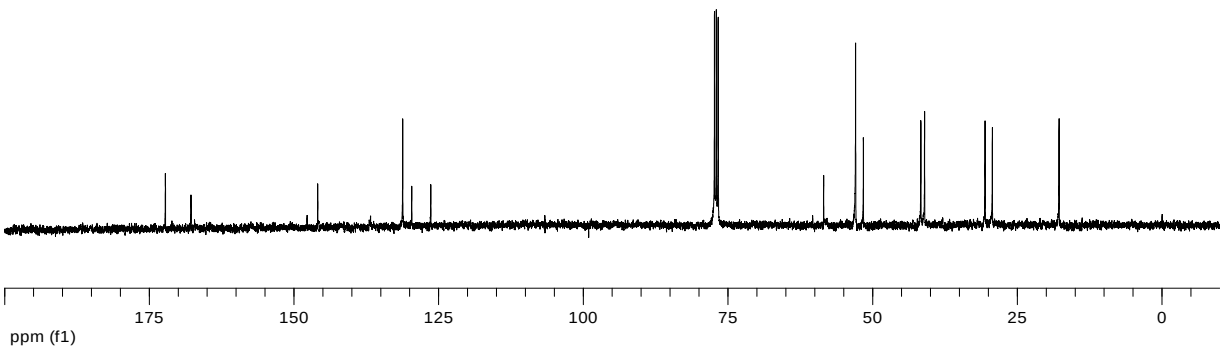

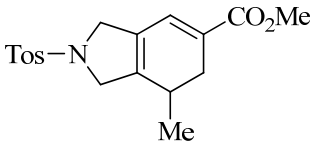
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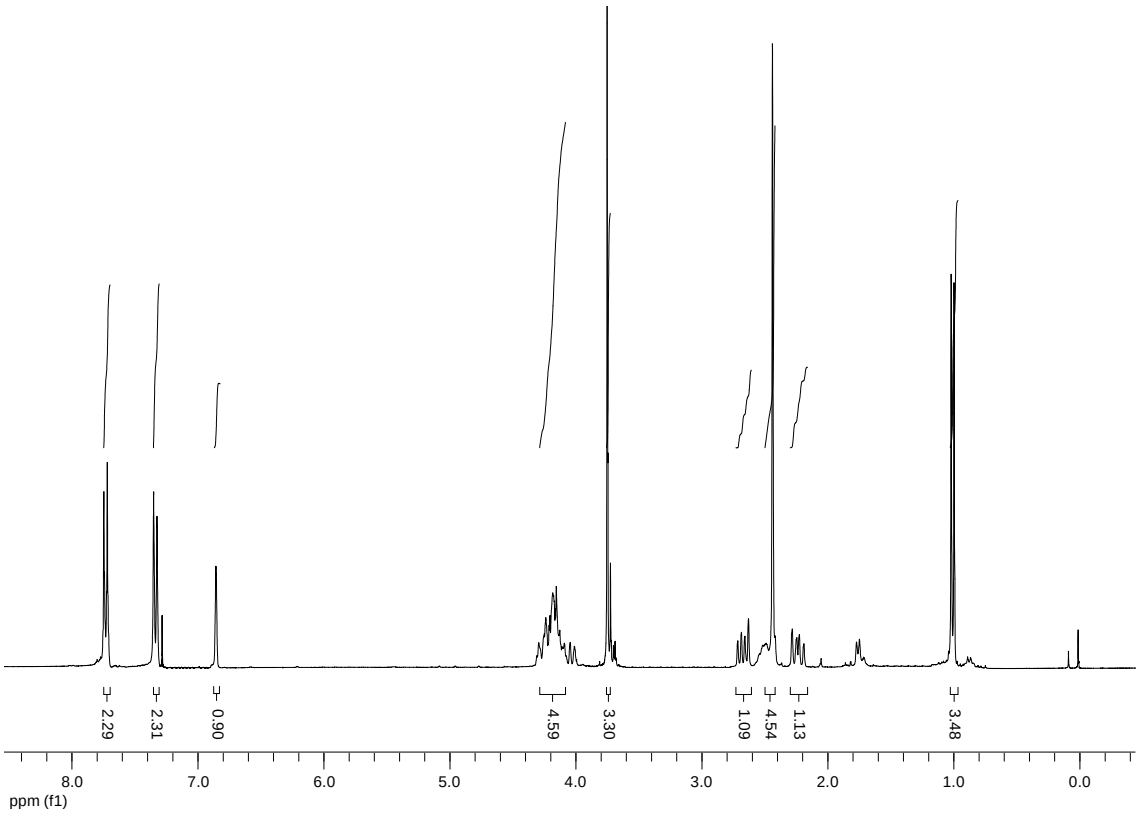
Tos−N
Me

8′aa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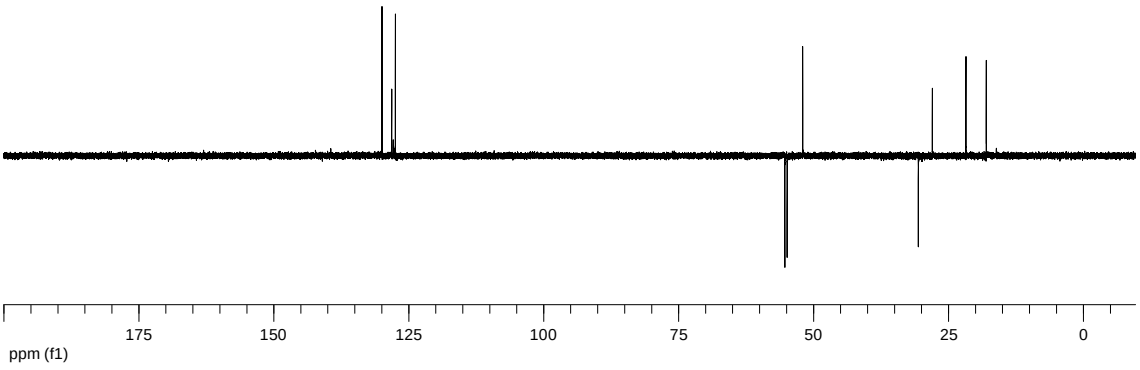
0.0
ppm (f1)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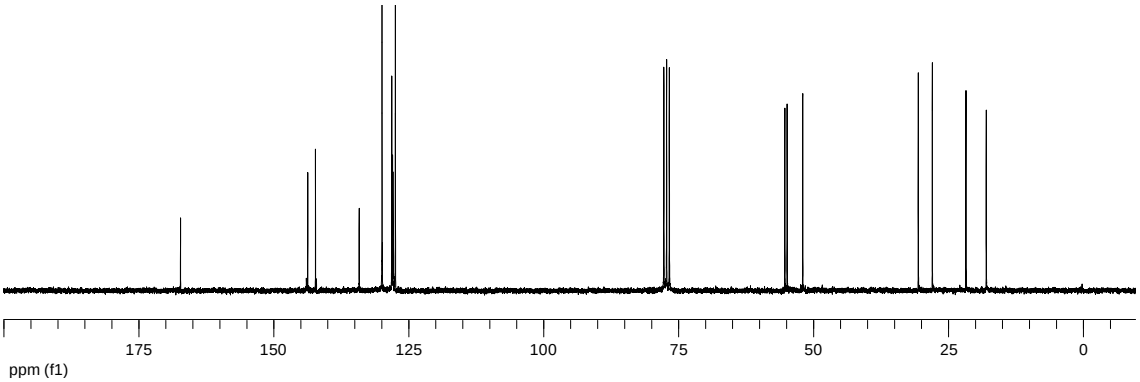
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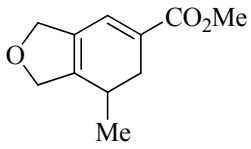
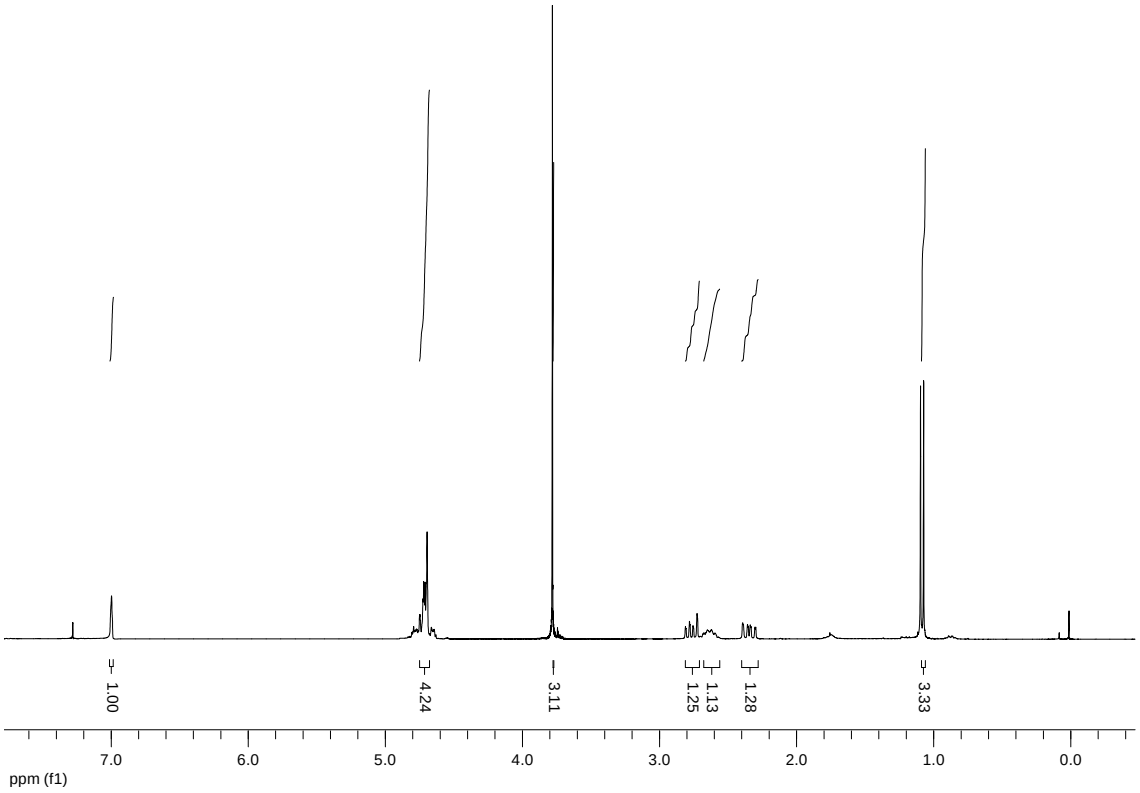

CO2Me
O
Me

8´´aa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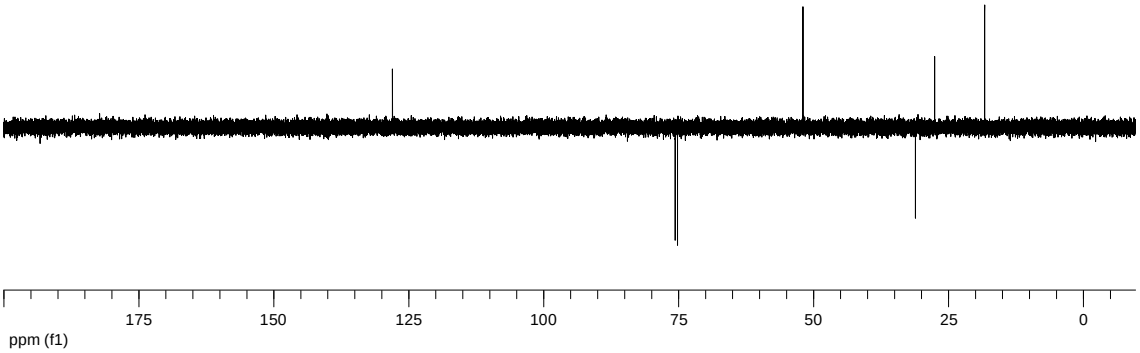
ppm (f1)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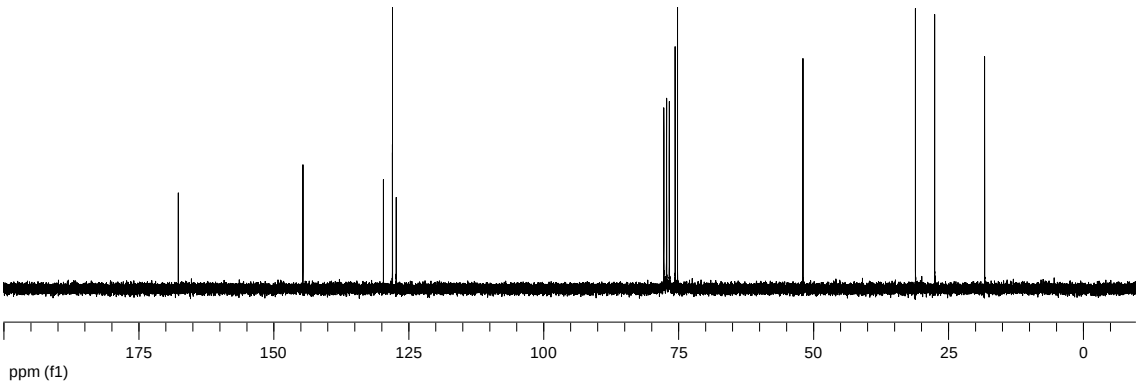
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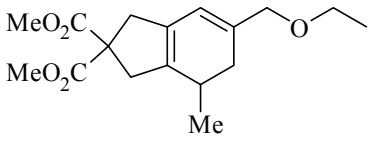
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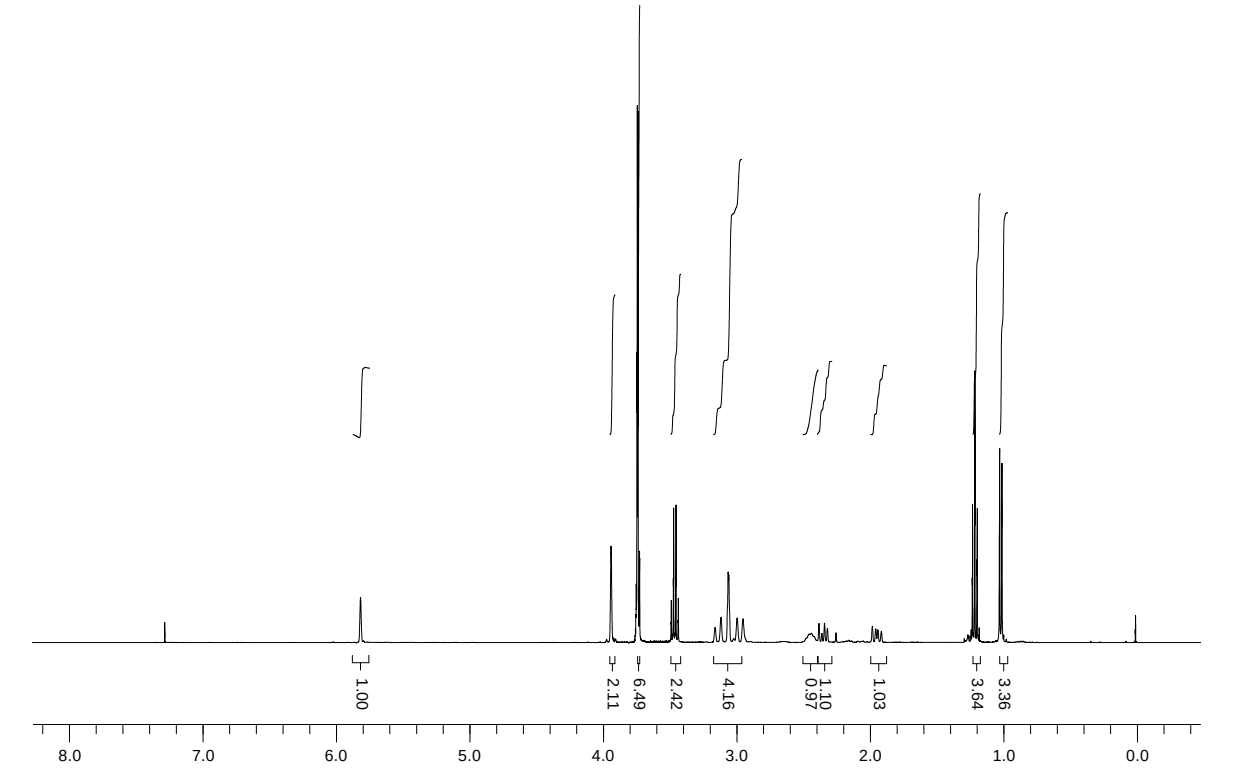
MeO2C
O
Me

8ab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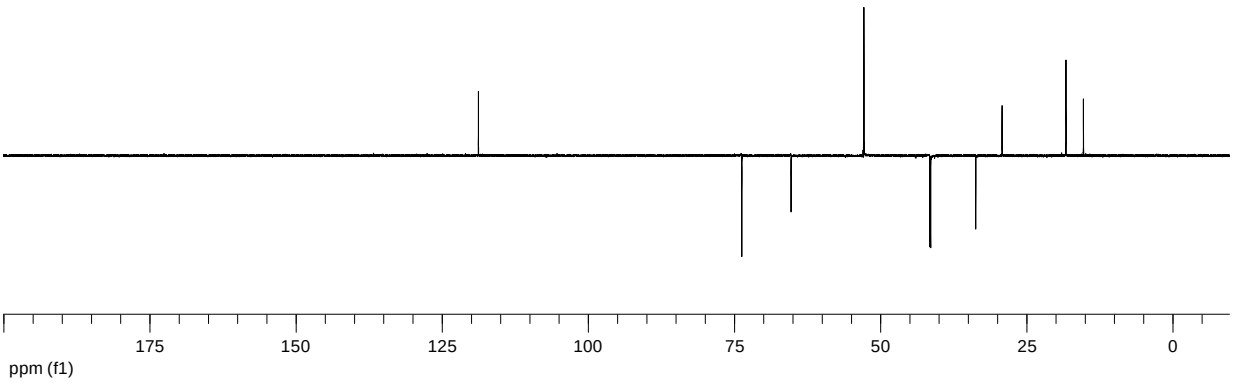
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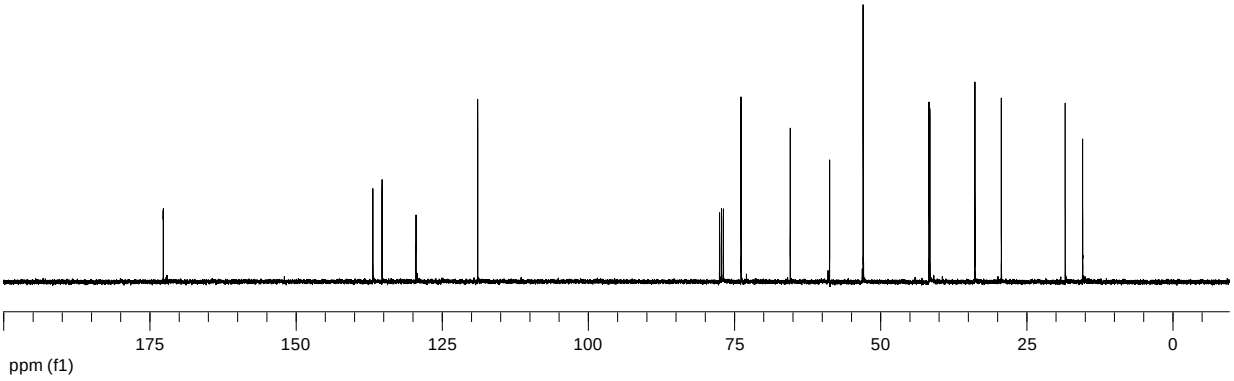
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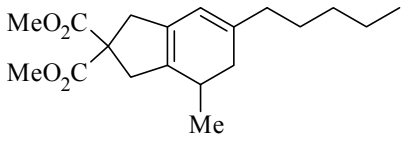
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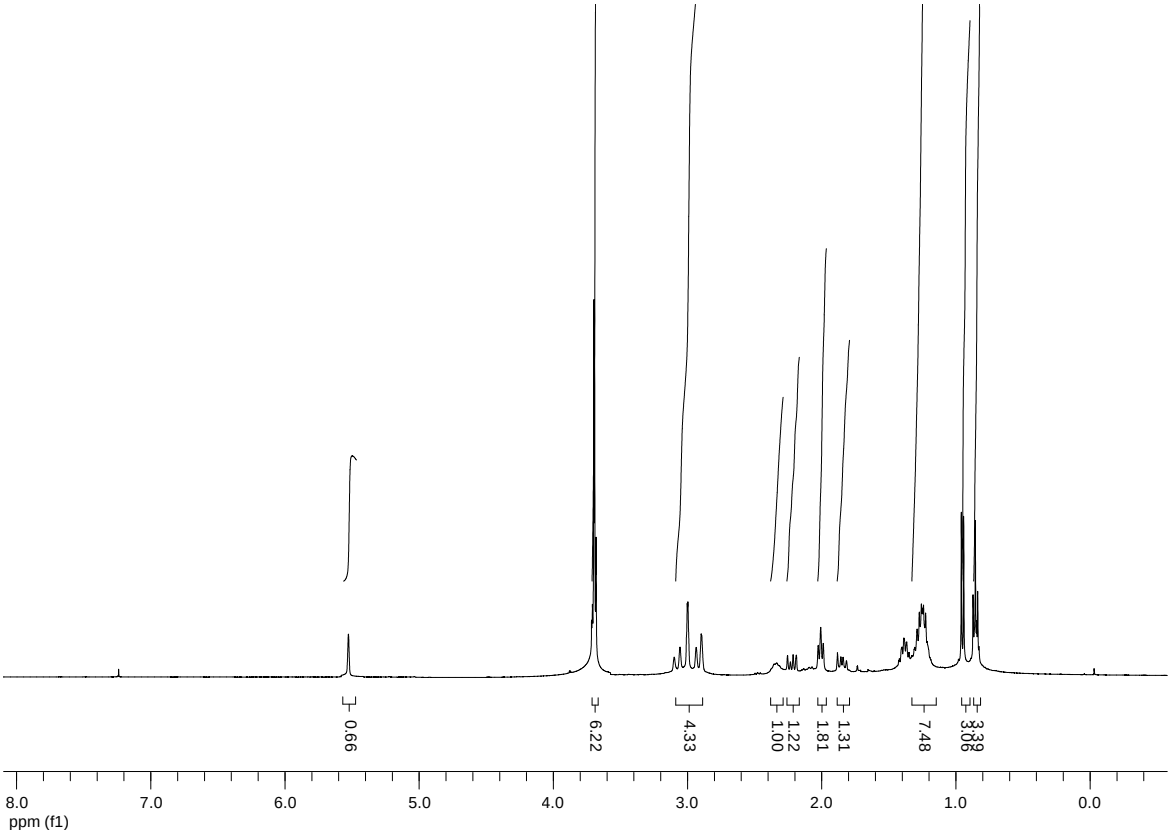
MeO2C
Me

8ac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4.0
3.0
2.0
1.0
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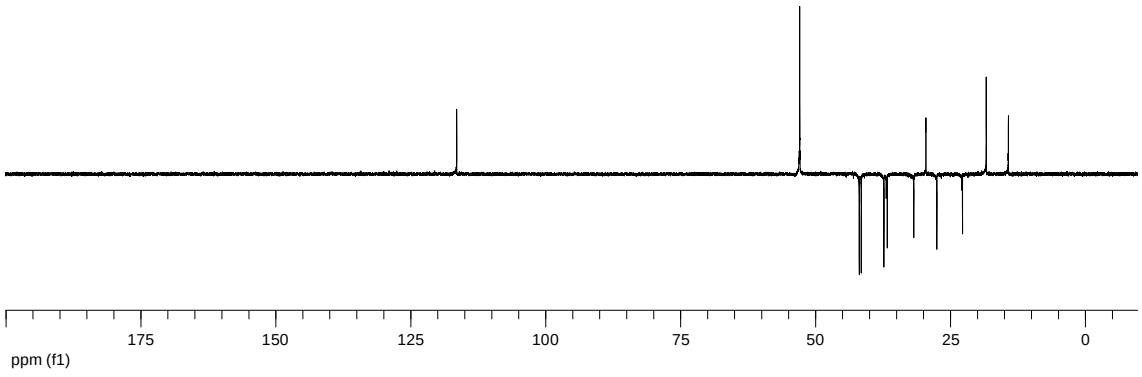
ppm (f1)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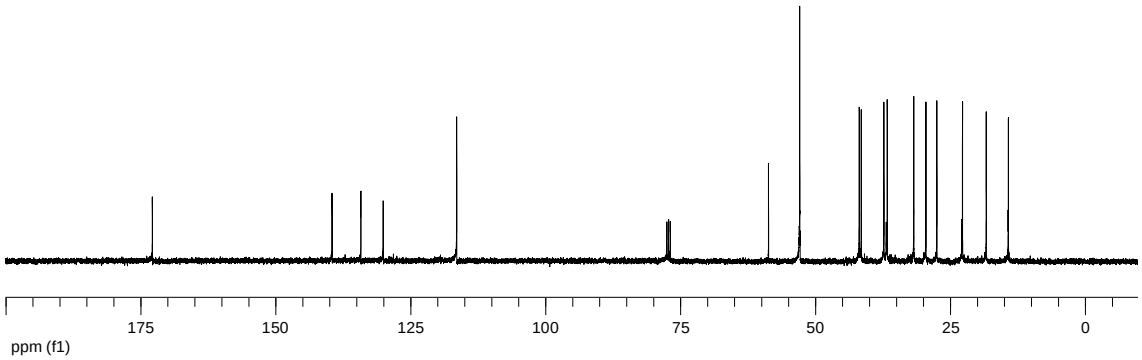
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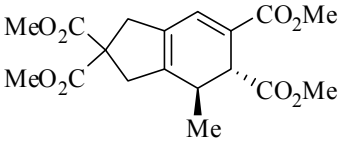
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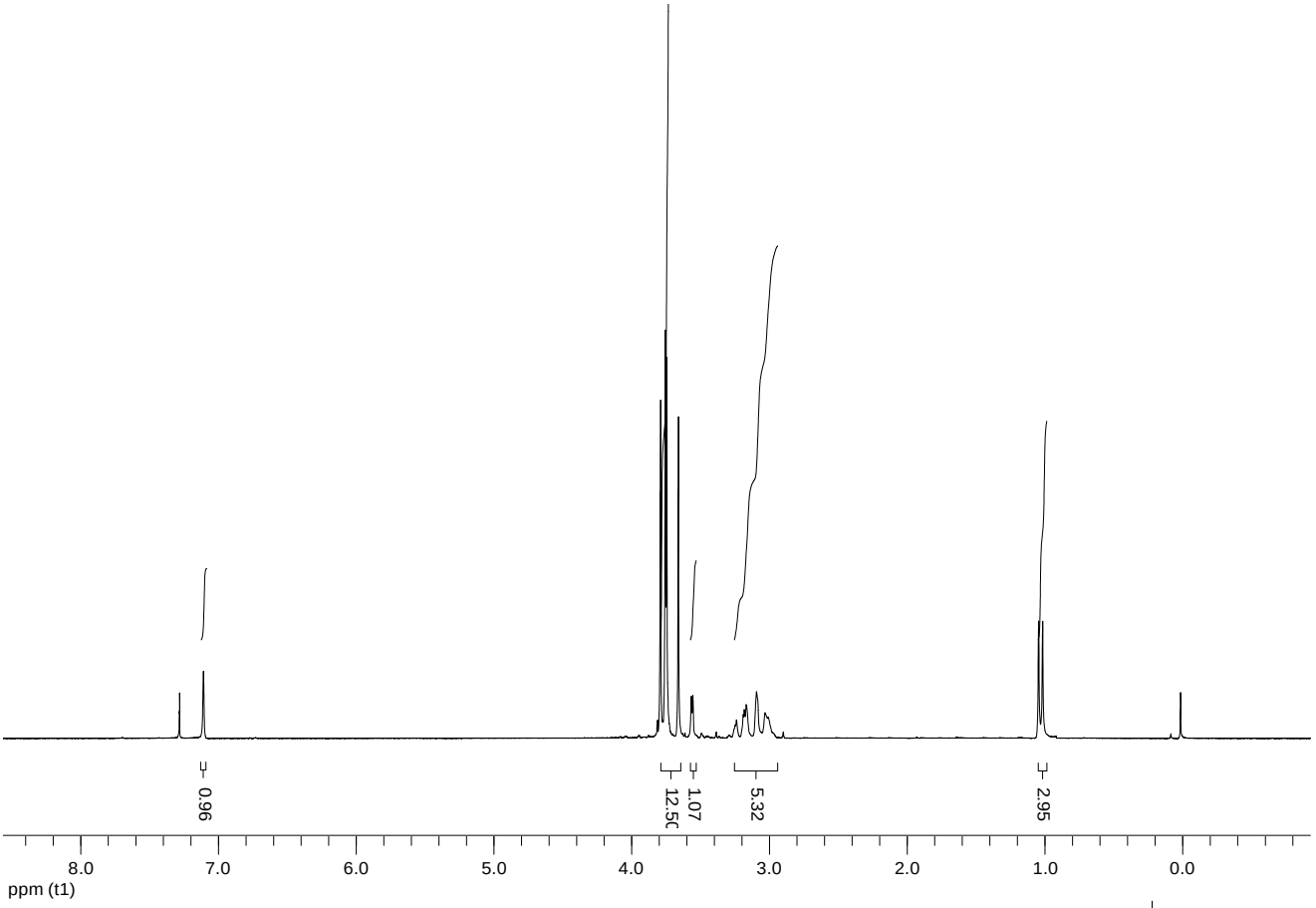
MeO2C
CO2Me
CO2Me
Me

8ad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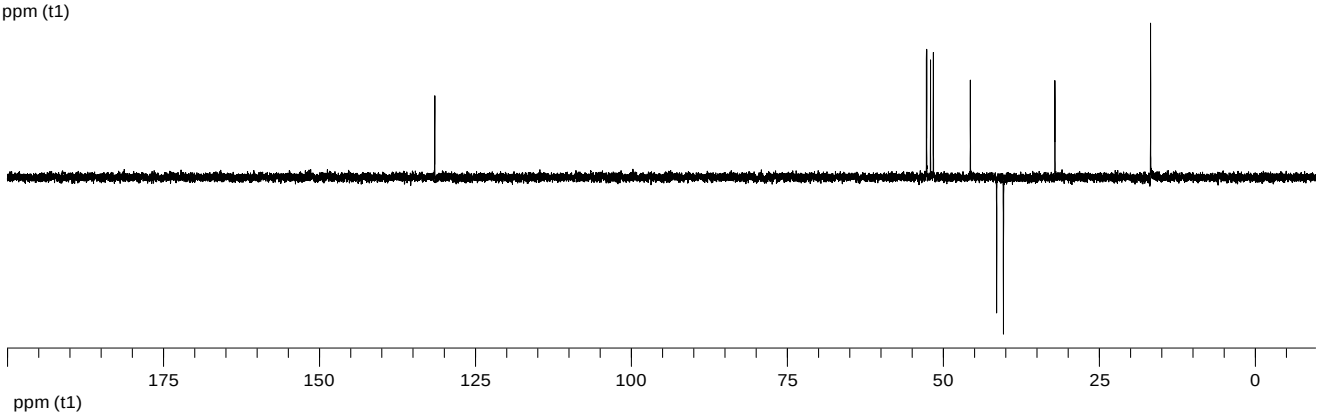
ppm (t1)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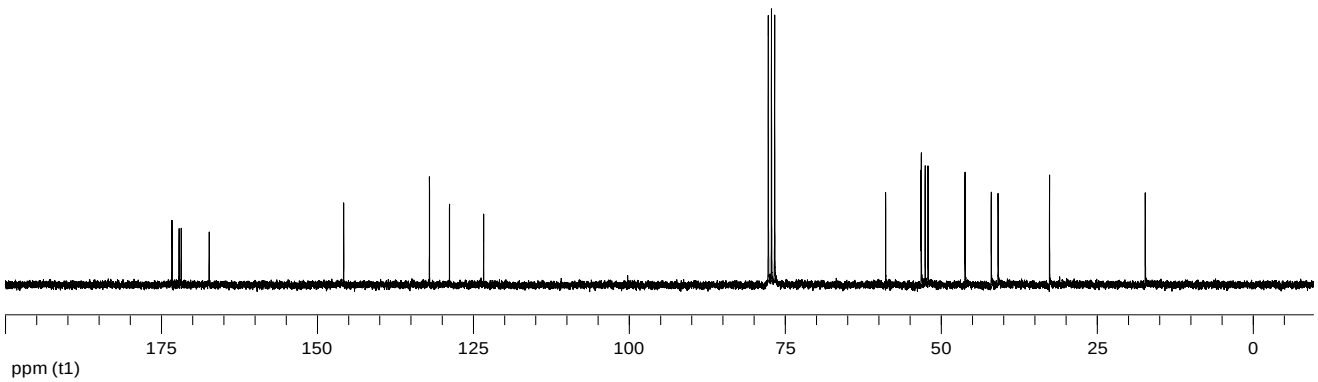
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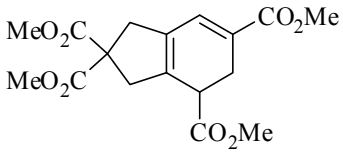
ppm (t1)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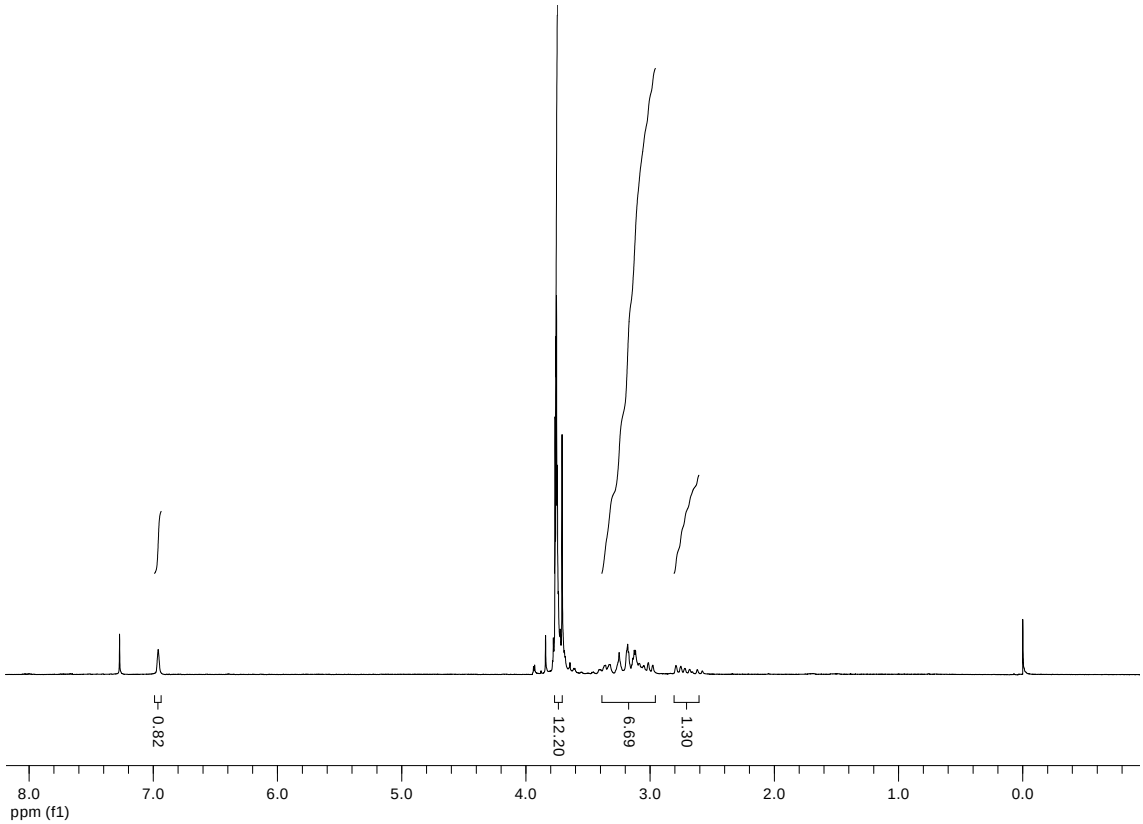
MeO2C
CO2Me
CO2Me

8ba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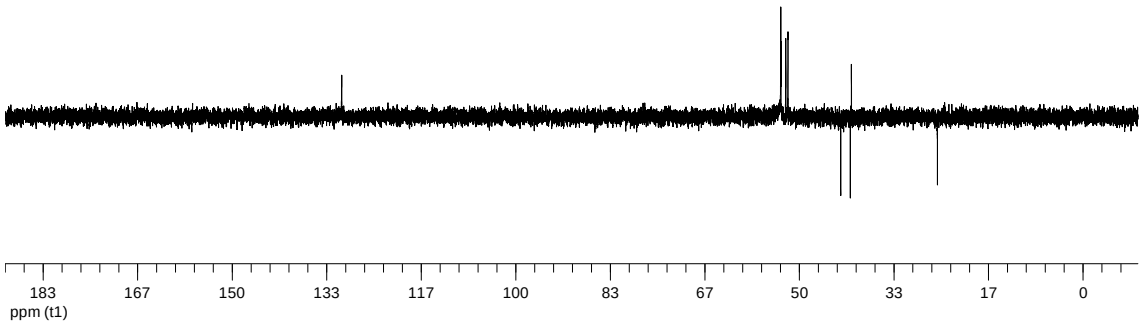
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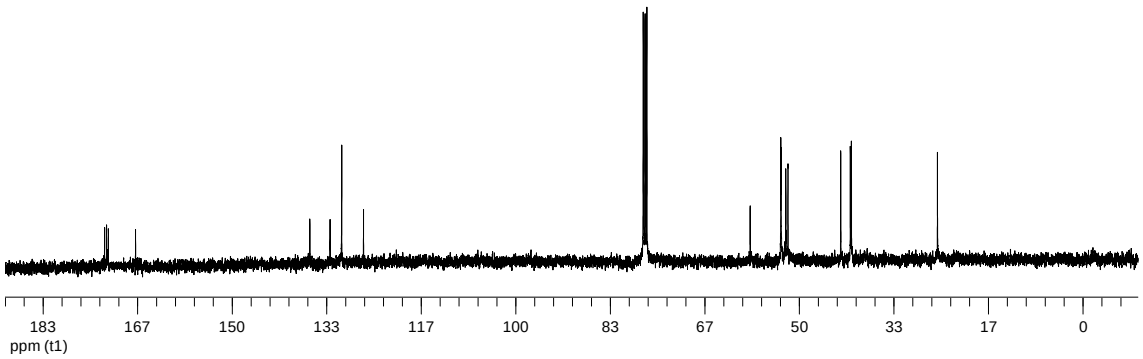
ppm (t1)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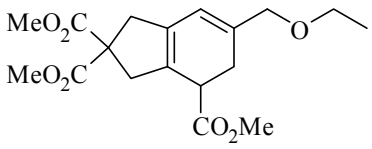
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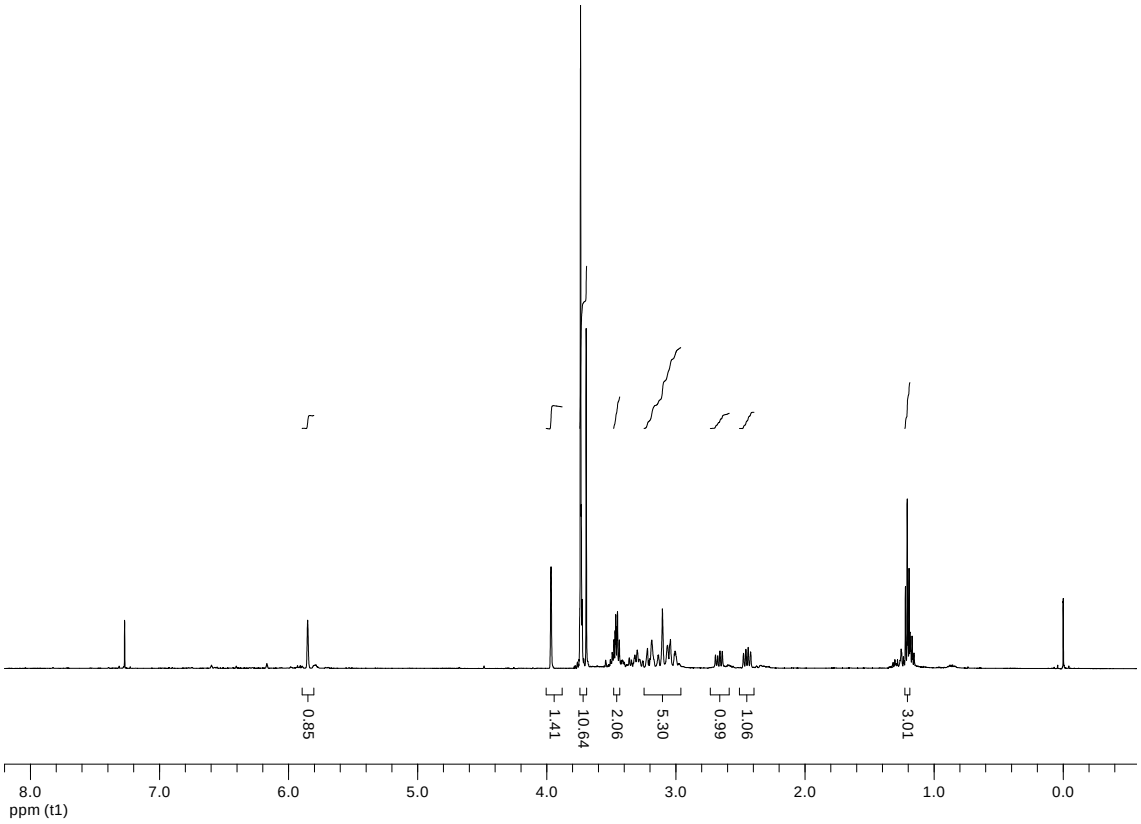
MeO2C
O
CO2Me

8bb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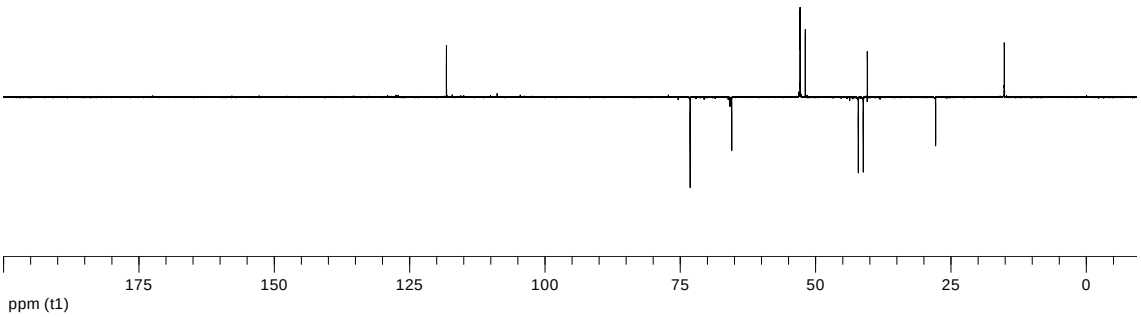
ppm (t1)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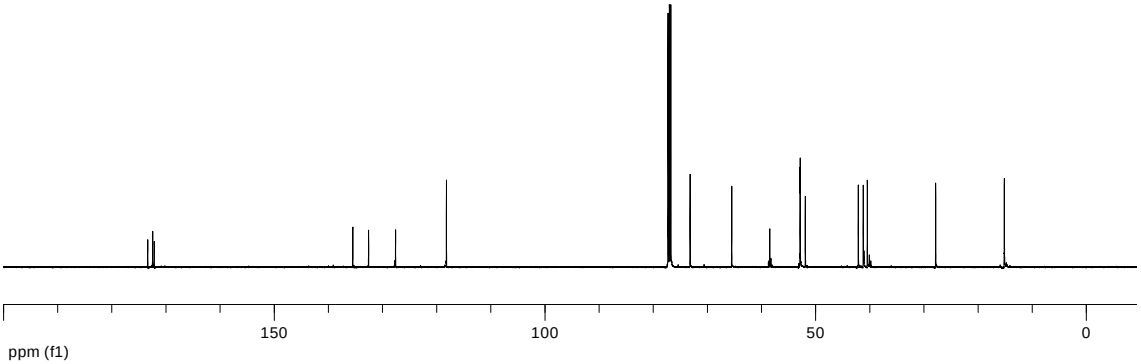
ppm (t1)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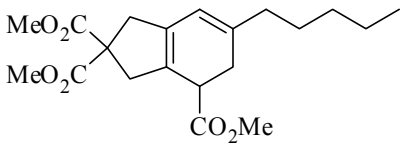
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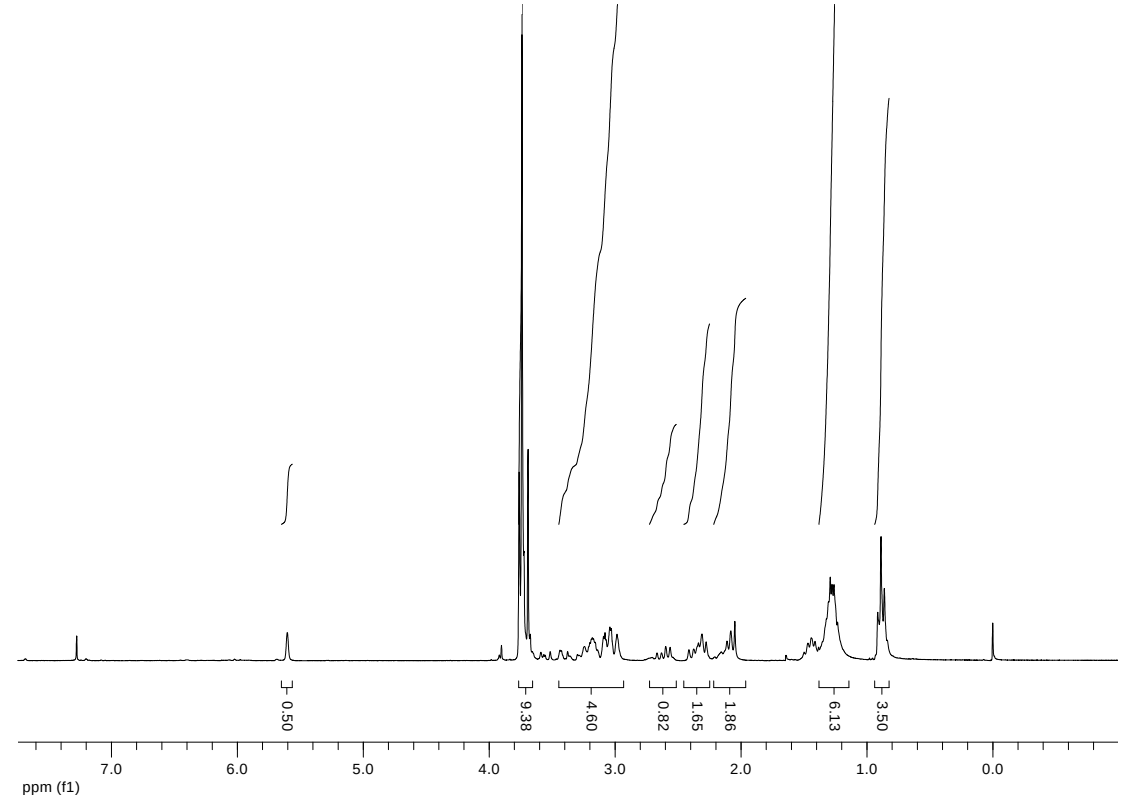
MeO2C
CO2Me

8bc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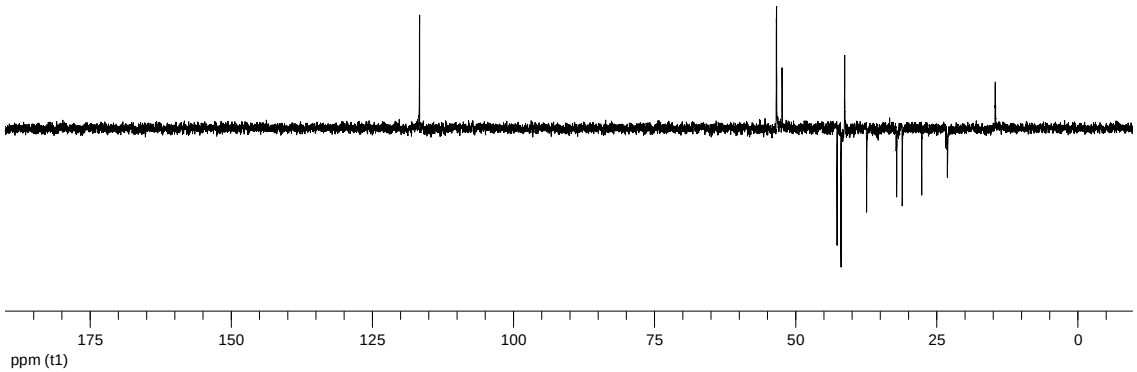
ppm (f1)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25
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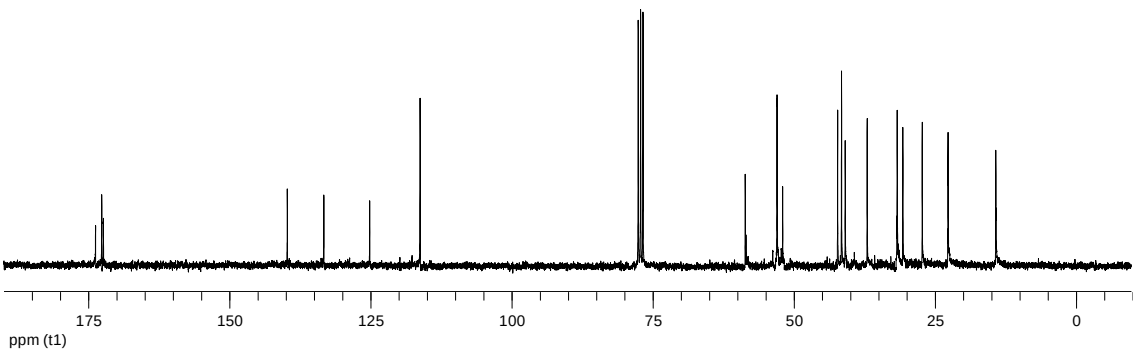
ppm (t1)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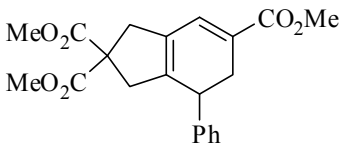
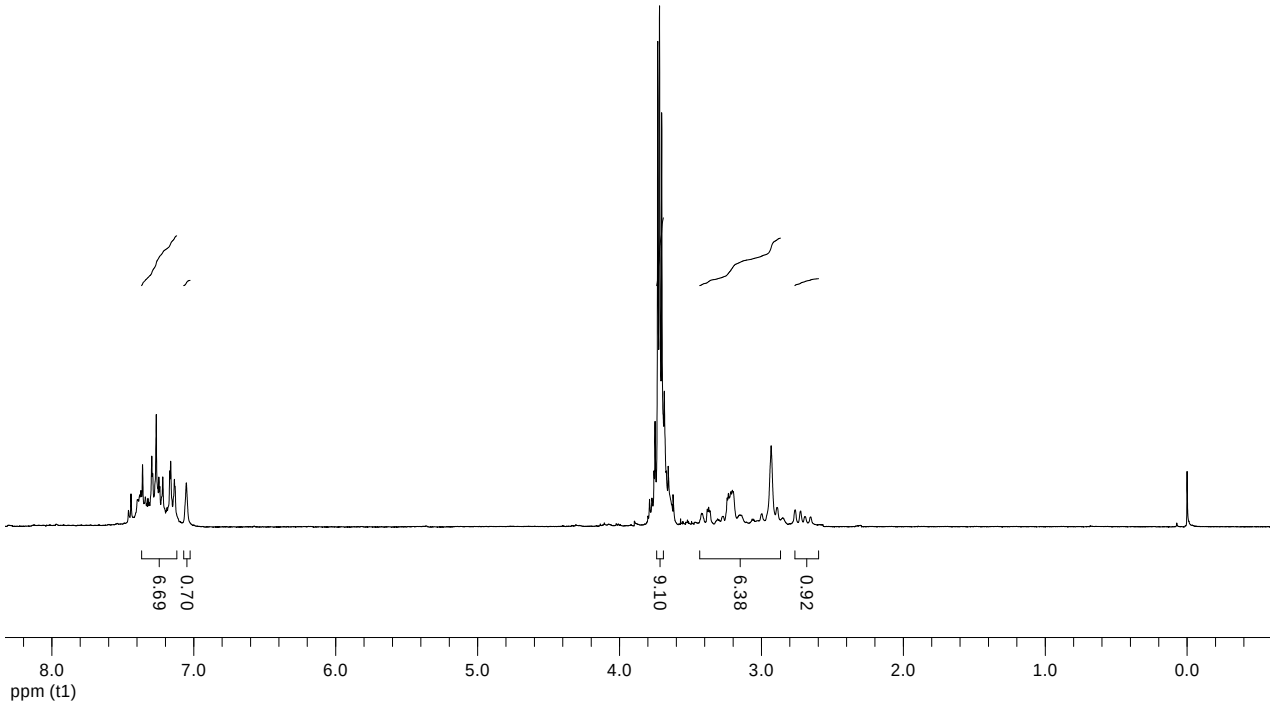
ppm (t1)


MeO2C
MeO2C
CO2Me
Ph

8ca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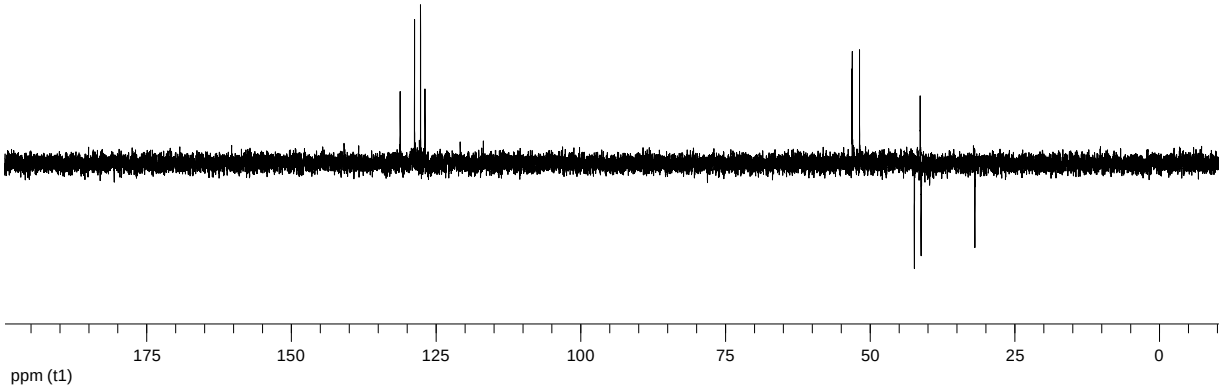
ppm (t1)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25
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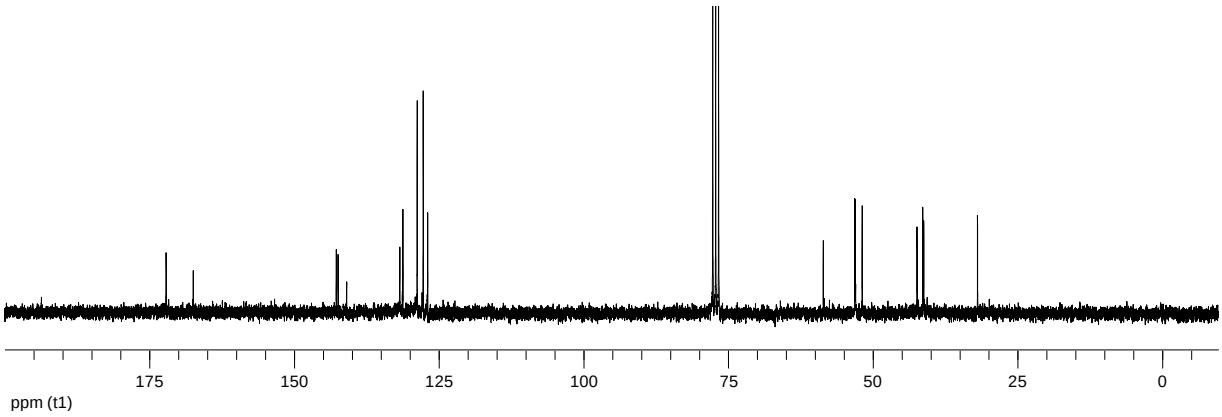
ppm (t1)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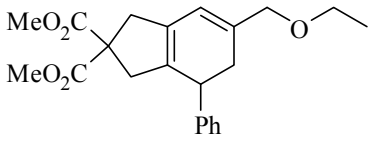
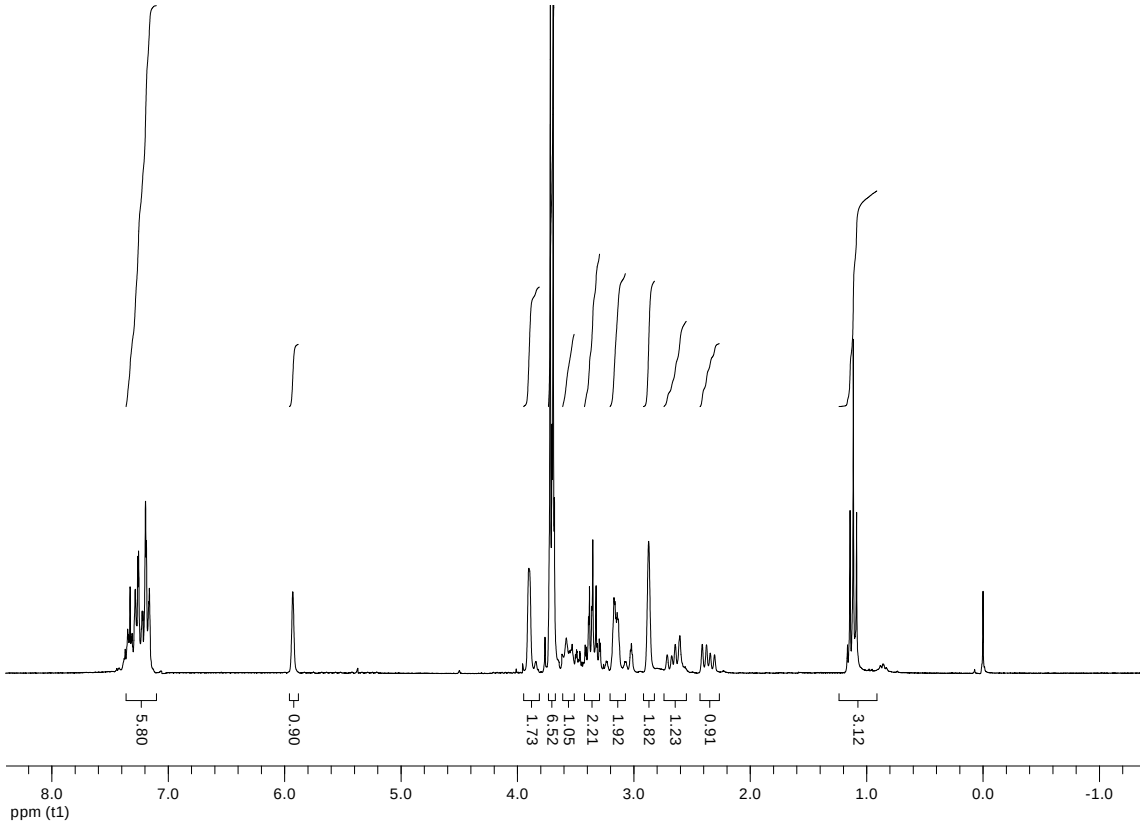
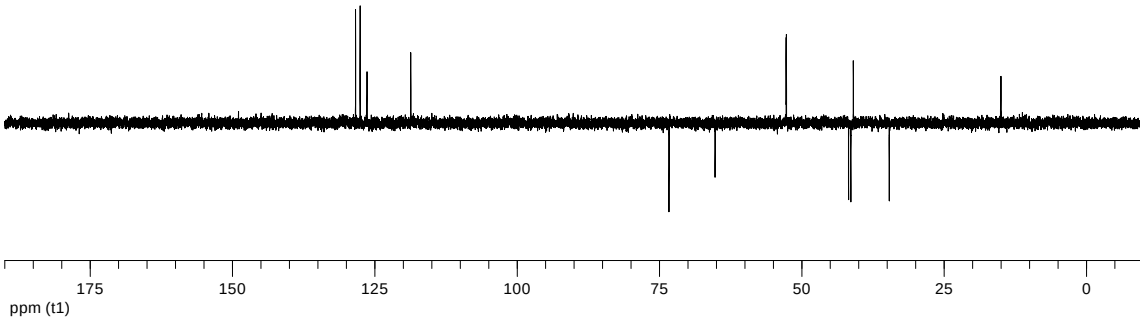
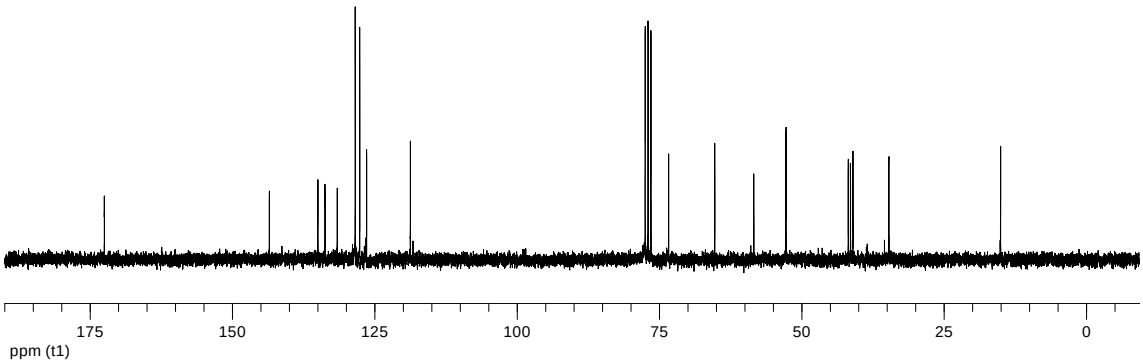
ppm (t1)

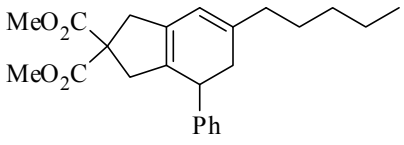

MeO2C
MeO2C
O
Ph

8cb

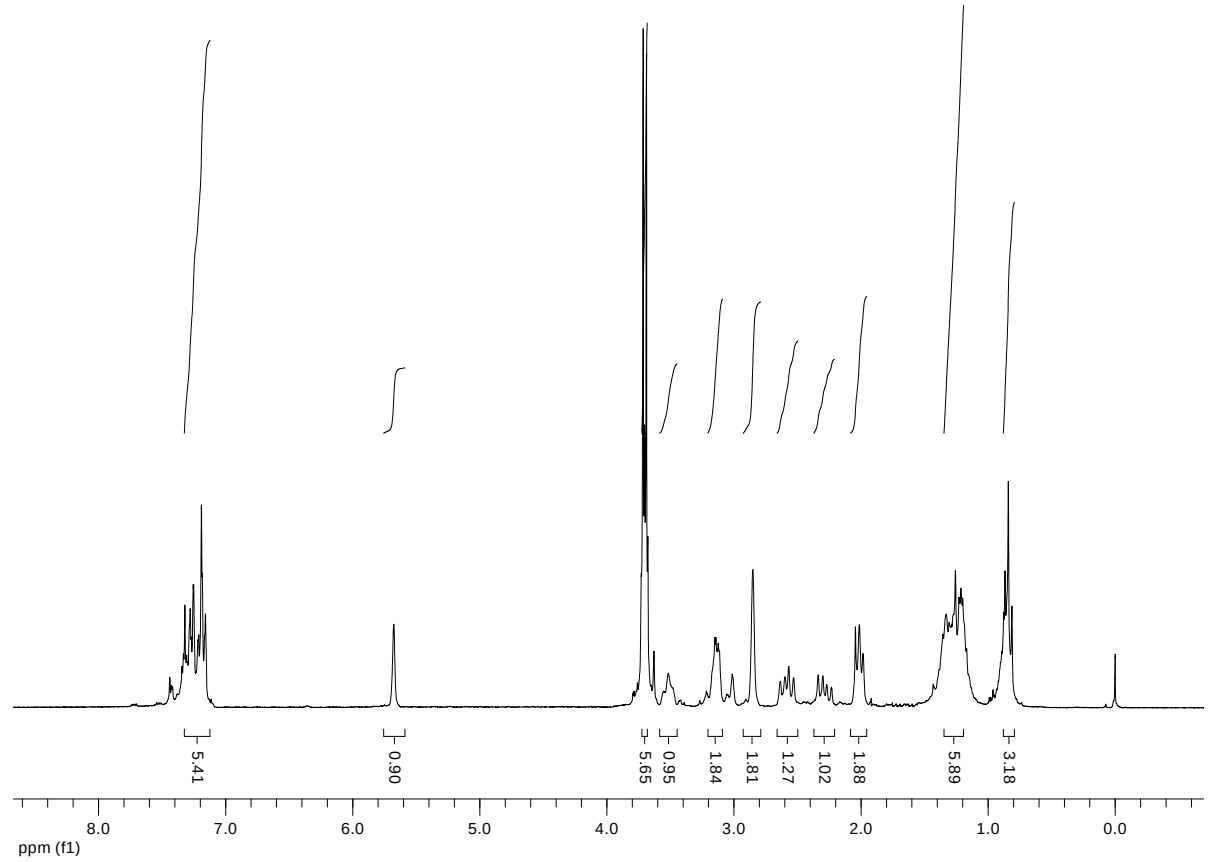

5.80
0.90
1.73
6.52
1.05
2.21
1.92
1.82
1.23
0.91
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

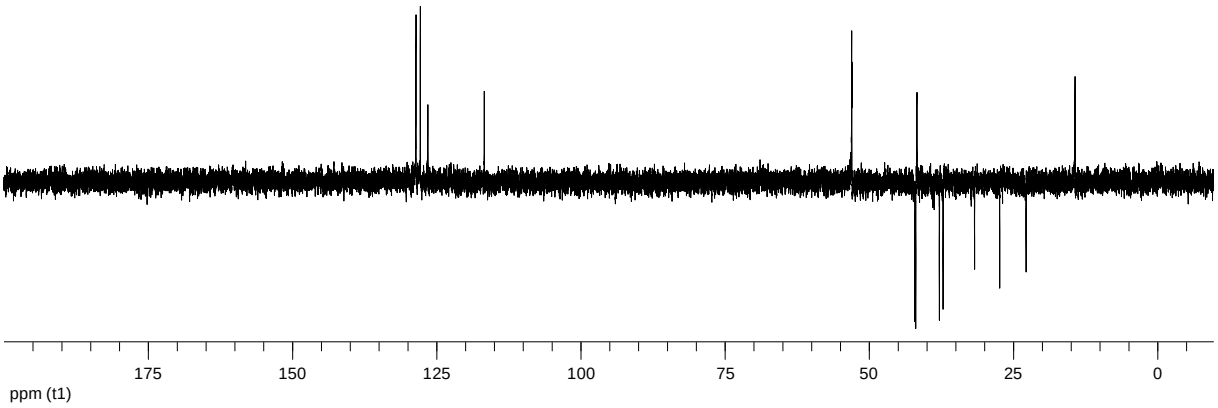

175
150
125
100
75
50
25
0
ppm (t1)

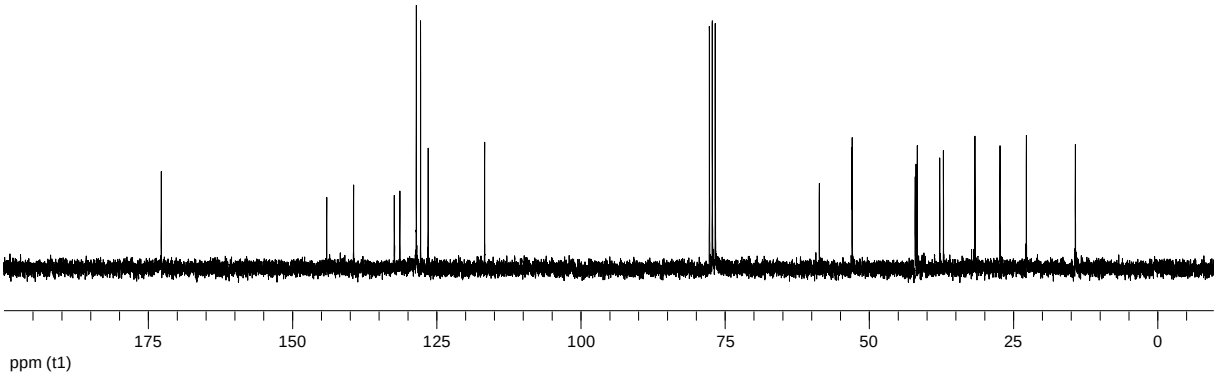

175
150
125
100
75
50
25
0
ppm (t1)

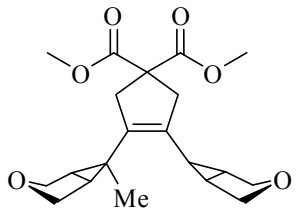

MeO2C
MeO2C
Ph

8cc

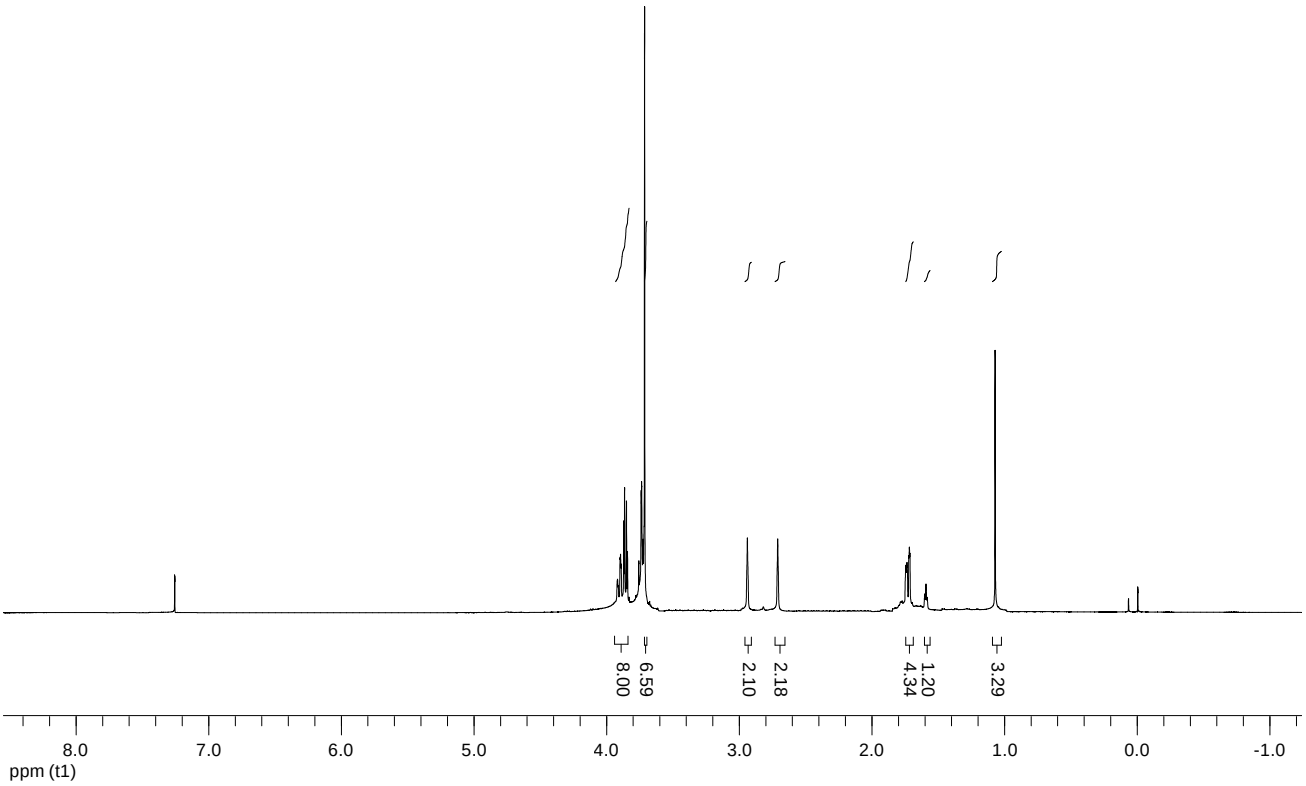

5.41
0.90
5.65
0.95
1.84
1.81
1.27
1.02
1.88
5.89
3.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

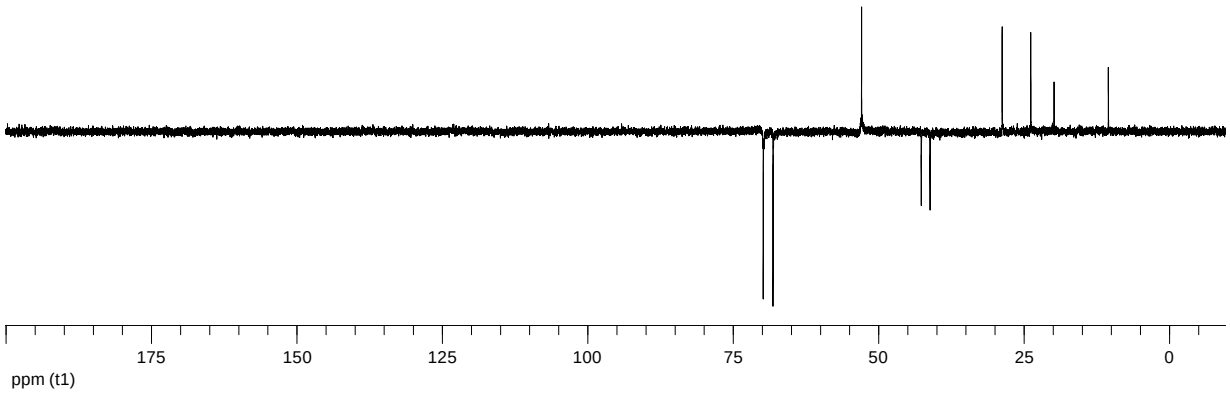

175
150
125
100
75
50
25
0
ppm (t1)

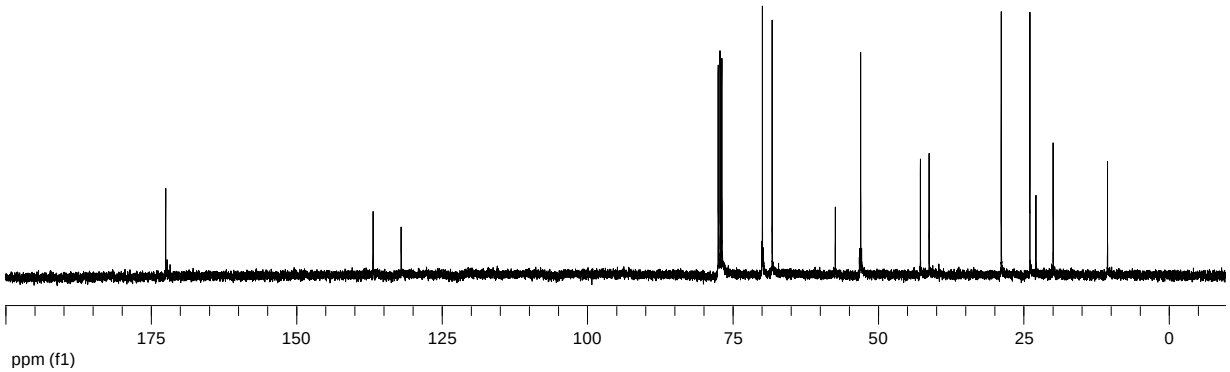

175
150
125
100
75
50
25
0
ppm (t1)

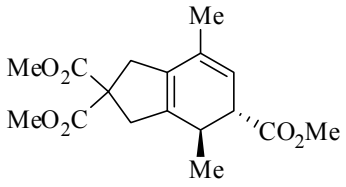

O
O
O
O
O
O
Me

9

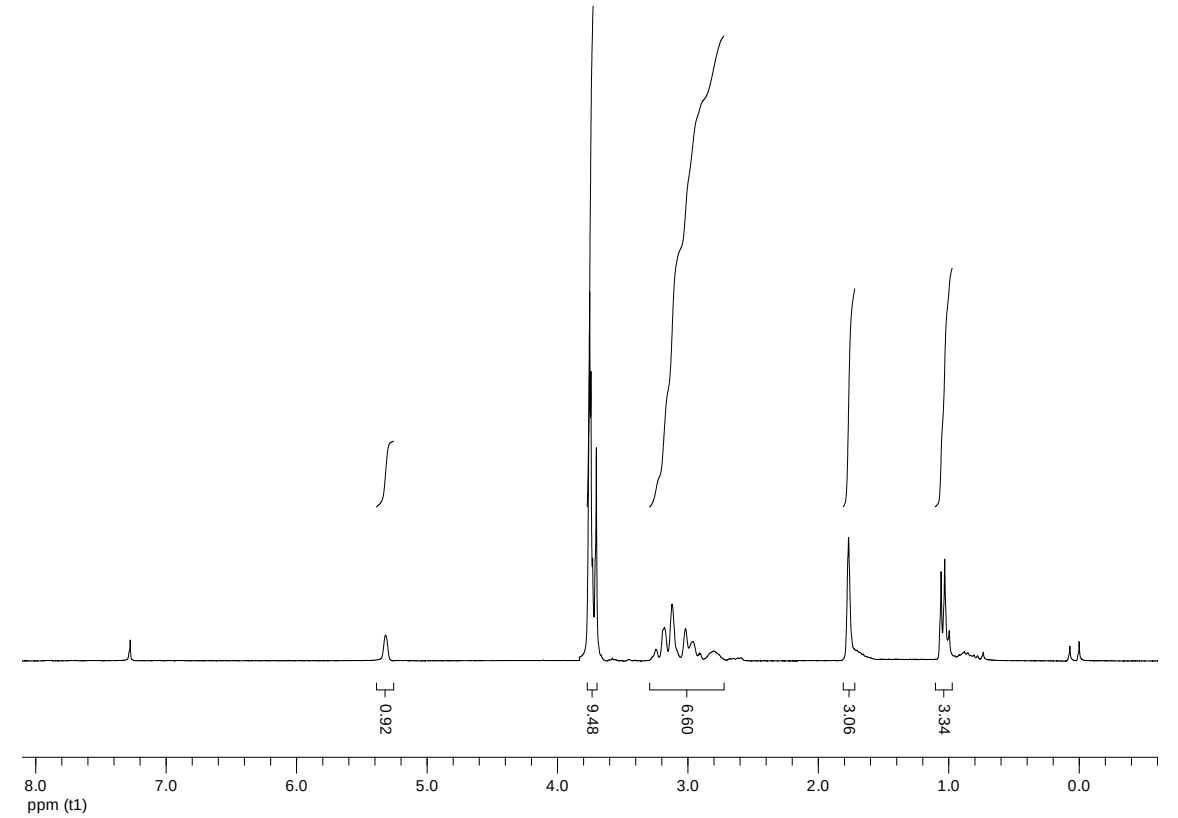

8.00
6.59
2.10
2.18
4.34
1.20
3.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

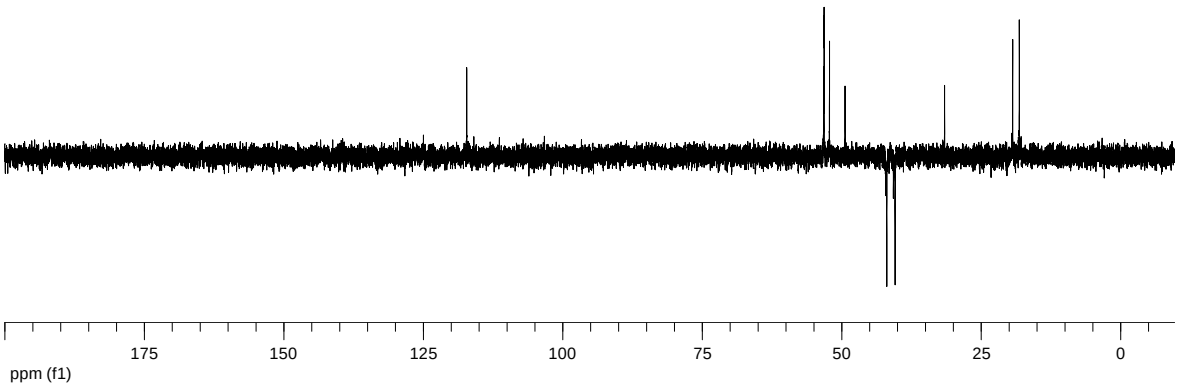

175
150
125
100
75
50
25
0
ppm (t1)

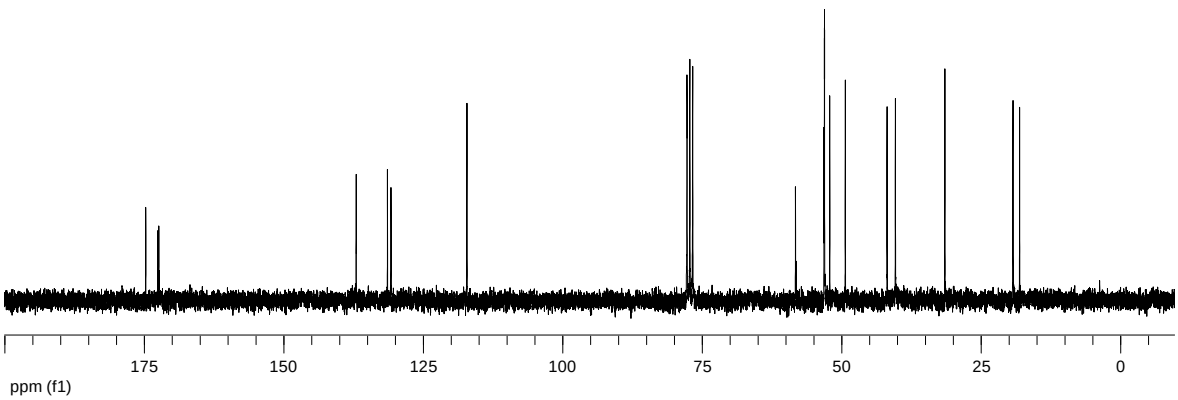

175
150
125
100
75
50
25
0
ppm (f1)

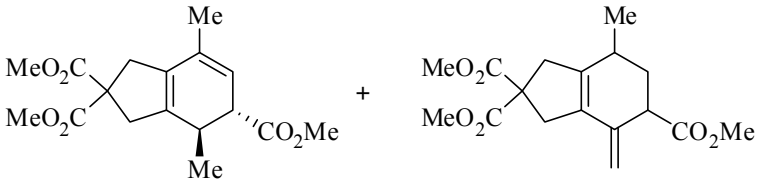

Me
MeO2C
MeO2C
CO2Me
Me

11a

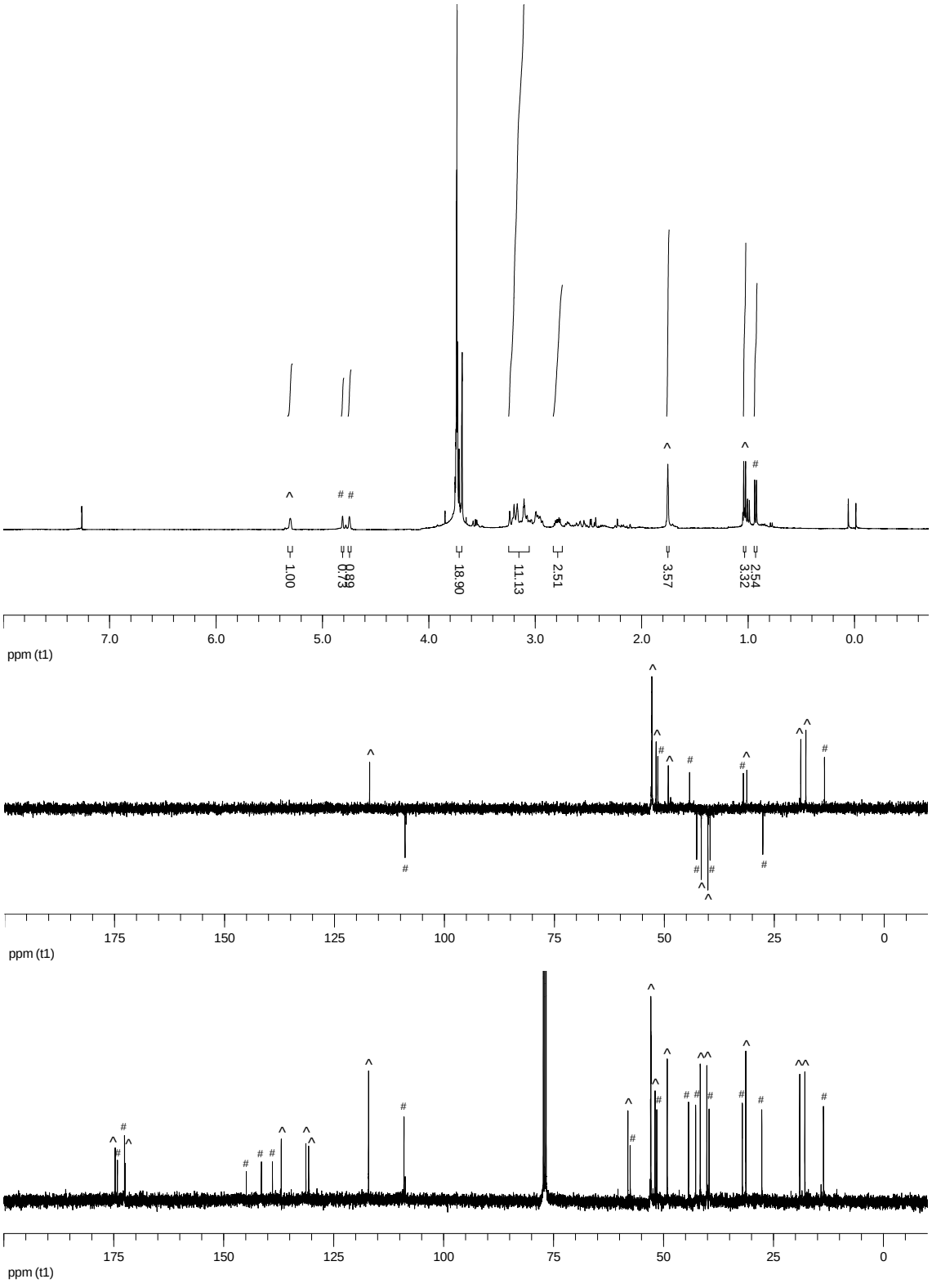

0.92
9.48
6.60
3.06
3.34
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

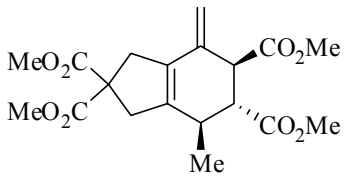

175
150
125
100
75
50
25
0
ppm (f1)


175
150
125
100
75
50
25
0
ppm (f1)

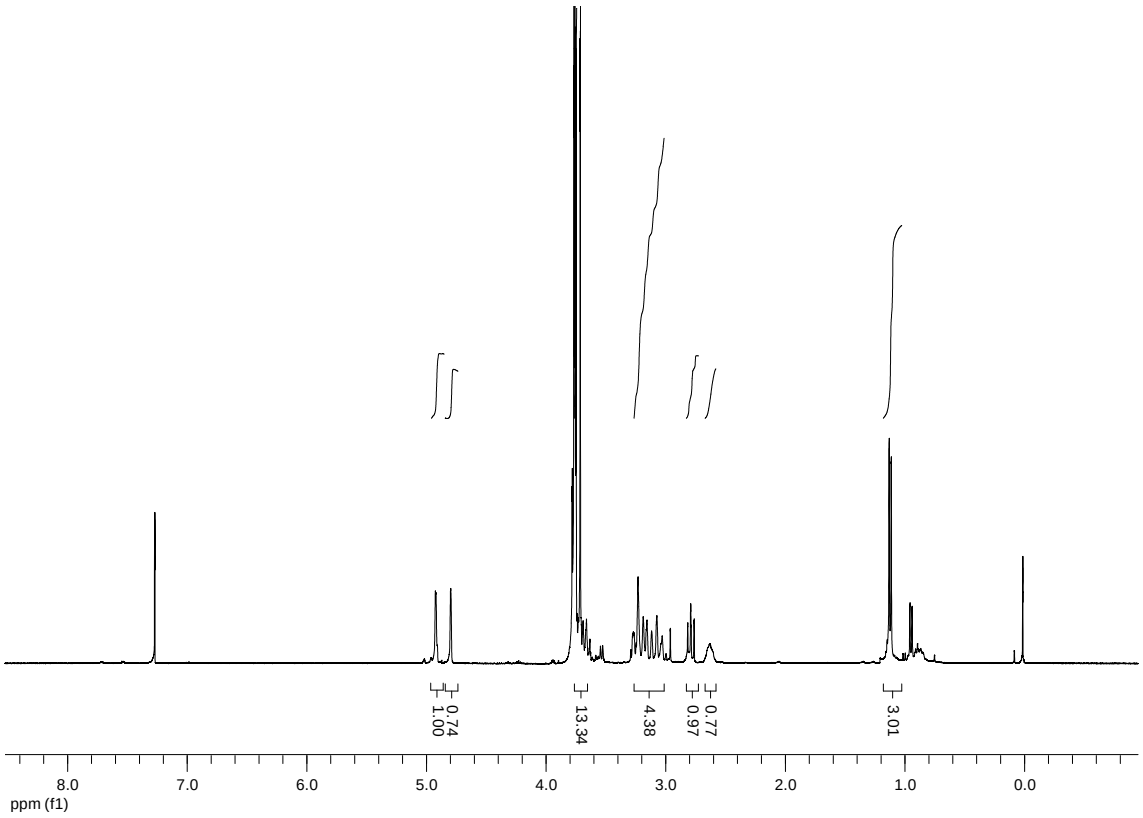

Me
MeO2C
MeO2C
CO2Me
Me
+
Me
MeO2C
MeO2C
CO2Me

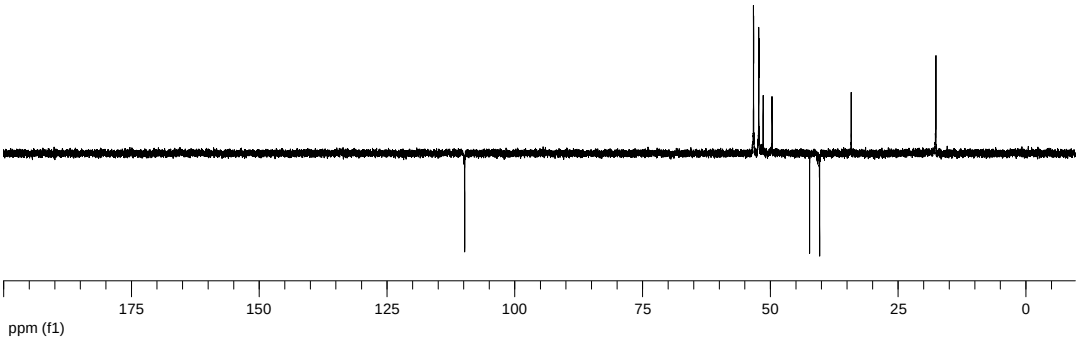
11a (^) **12a** (#)

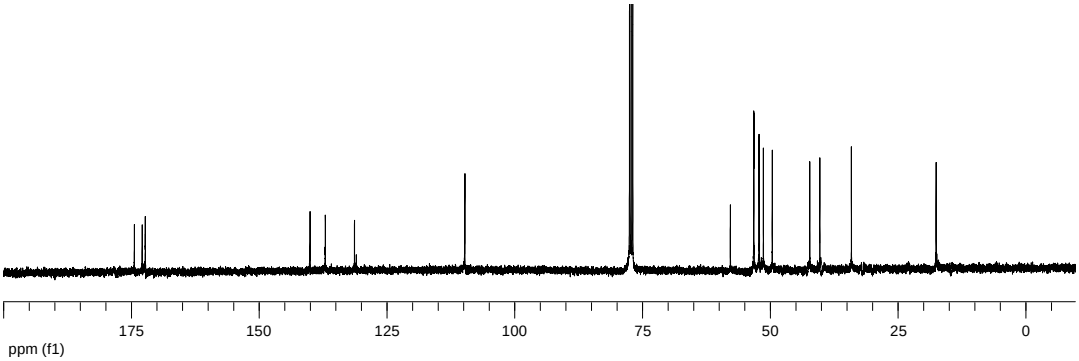

1.00
0.89
0.73
18.90
11.13
2.51
3.57
2.54
3.32
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
175
150
125
100
75
50
25
0
ppm (t1)
175
150
125
100
75
50
25
0
ppm (t1)

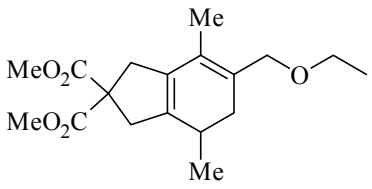

MeO2C
MeO2C
CO2Me
CO2Me
Me

12d

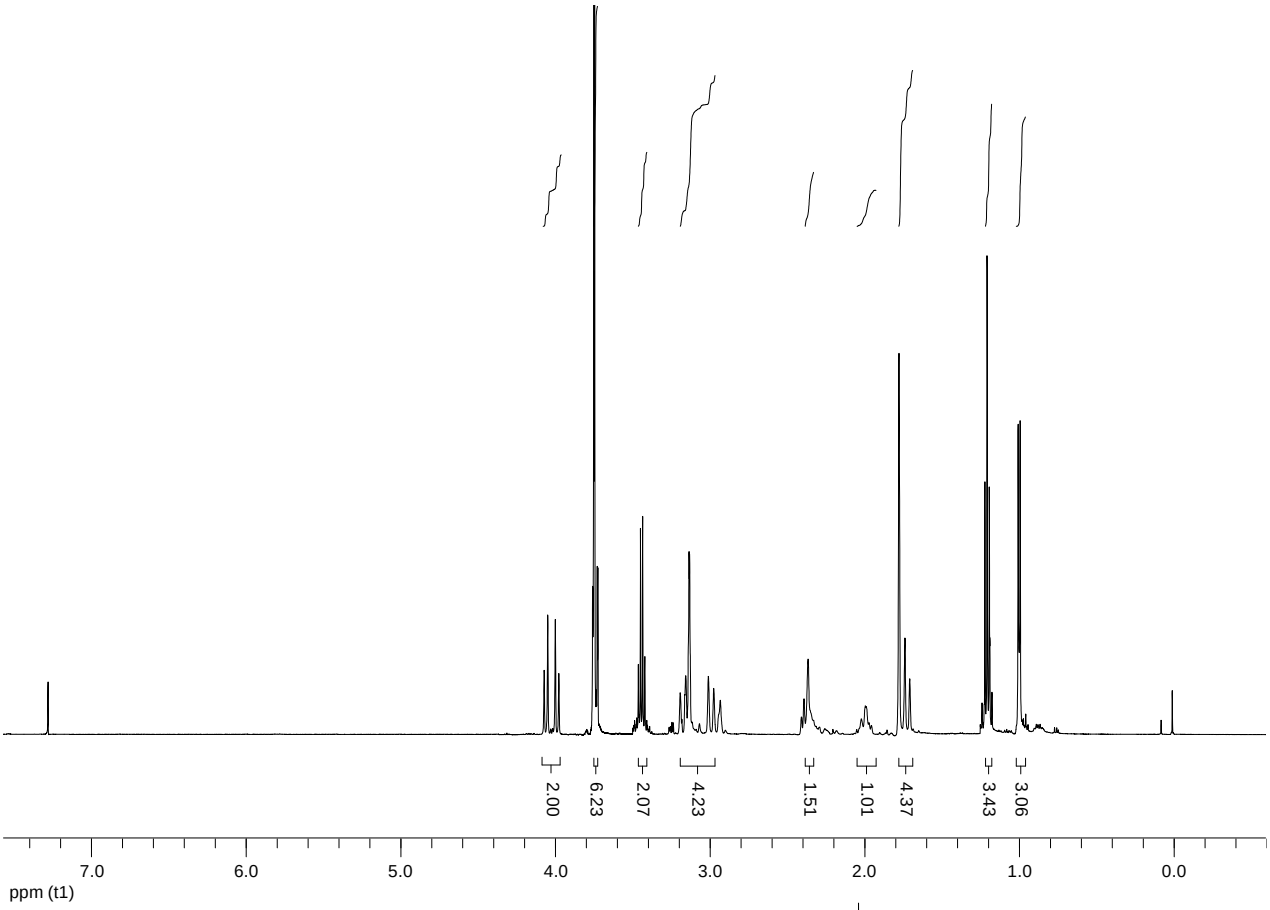

1.00
0.74
13.34
4.38
0.97
0.77
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

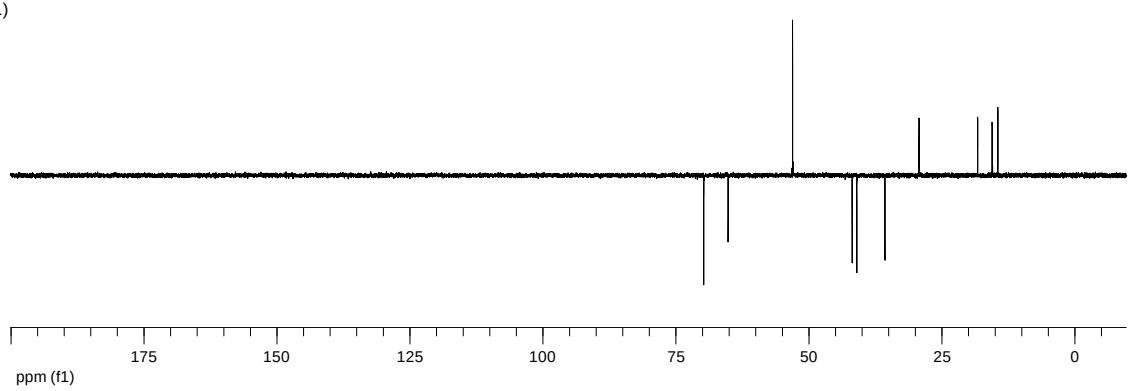

175
150
125
100
75
50
25
0
ppm (f1)

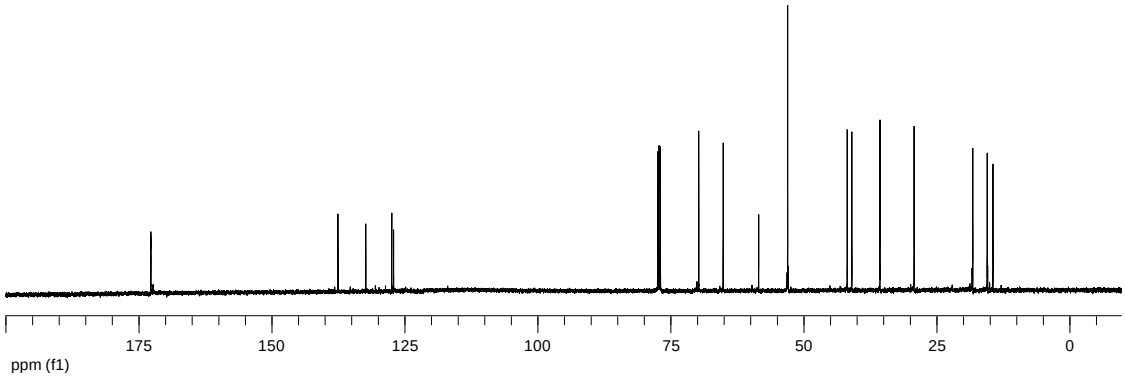

175
150
125
100
75
50
25
0
ppm (f1)

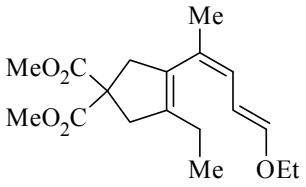

Me
MeO2C
MeO2C
O
Me

11b

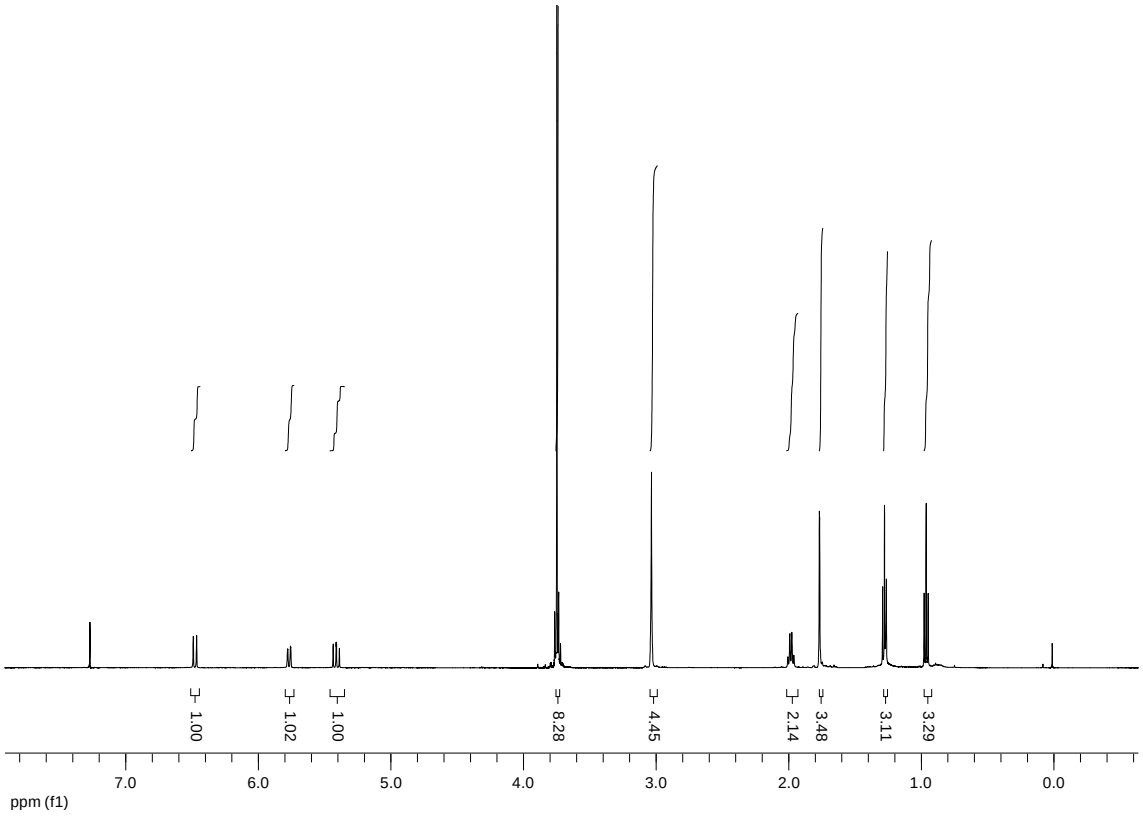

2.00
6.23
2.07
4.23
1.51
1.01
4.37
3.43
3.06
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

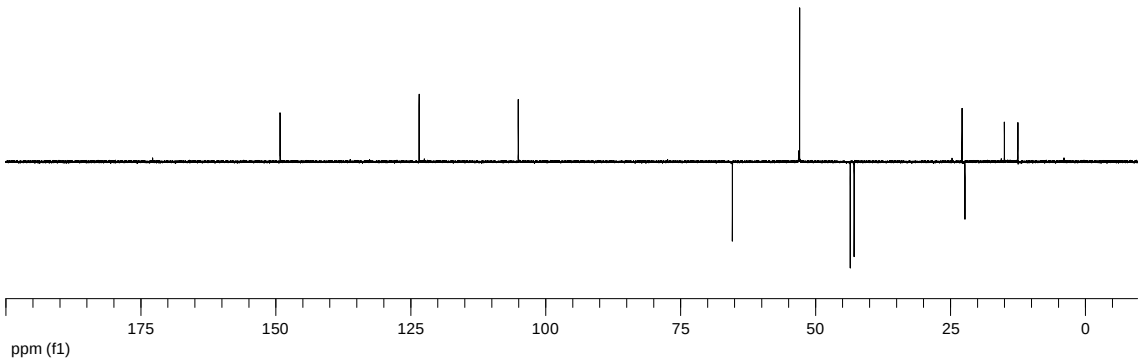

175
150
125
100
75
50
25
0
ppm (f1)

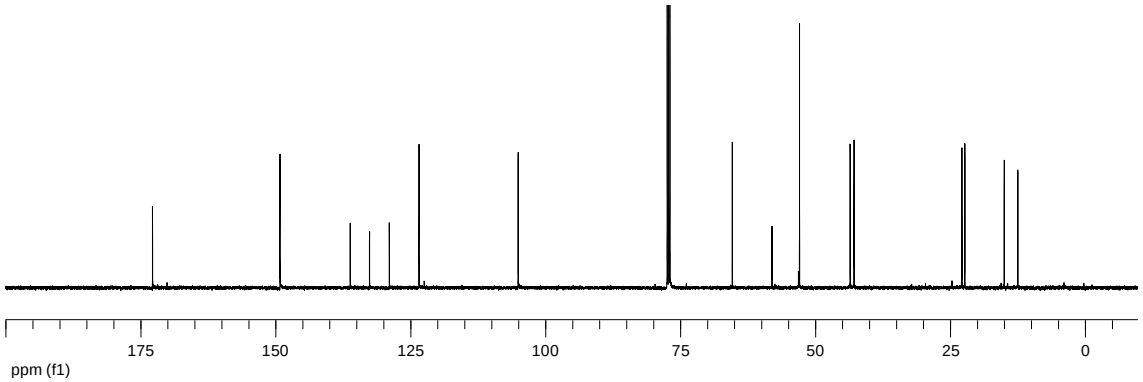

175
150
125
100
75
50
25
0
ppm (f1)

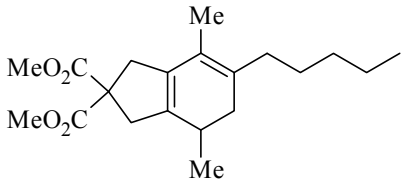

Me
MeO2C
MeO2C
Me
OEt

13

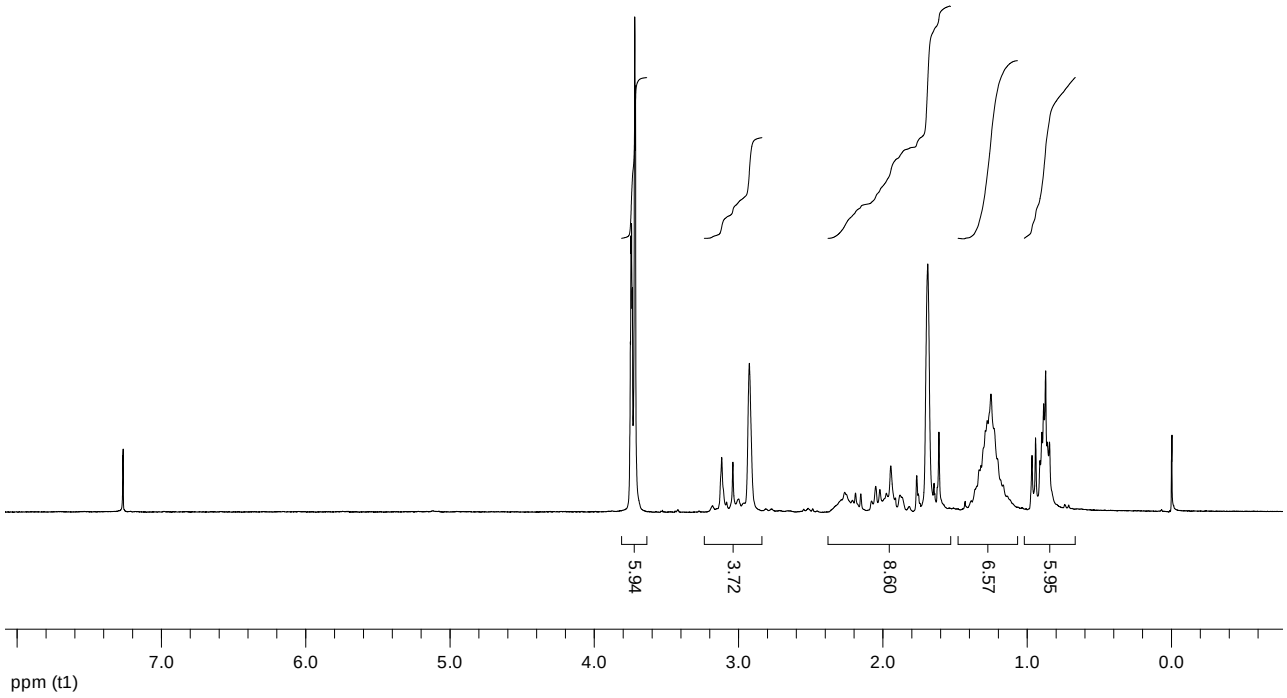

1.00
1.02
1.00
8.28
4.45
2.14
3.48
3.11
3.29
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

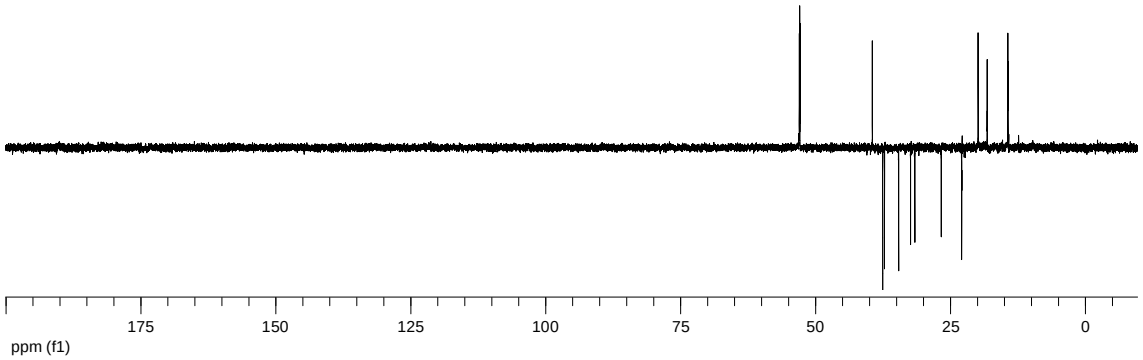

175
150
125
100
75
50
25
0
ppm (f1)

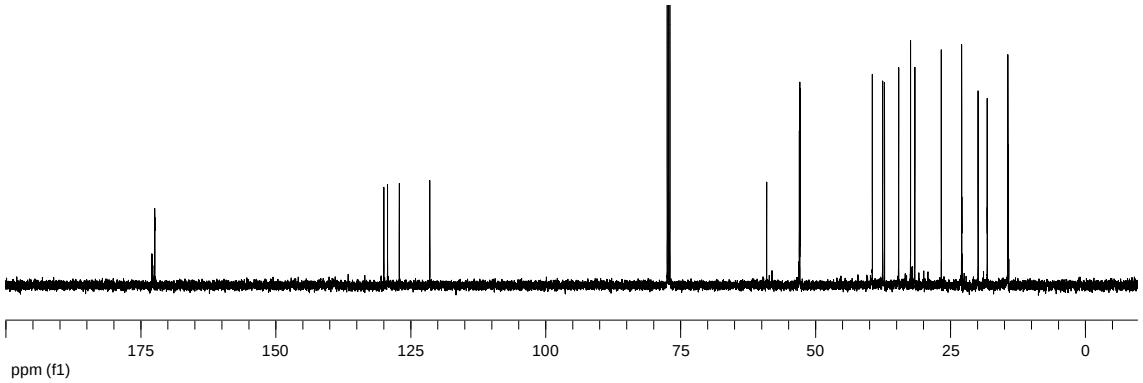

175
150
125
100
75
50
25
0
ppm (f1)

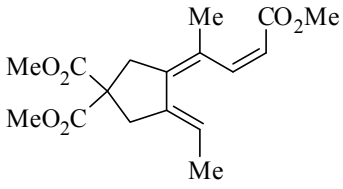

Me
MeO2C
MeO2C
Me

11c

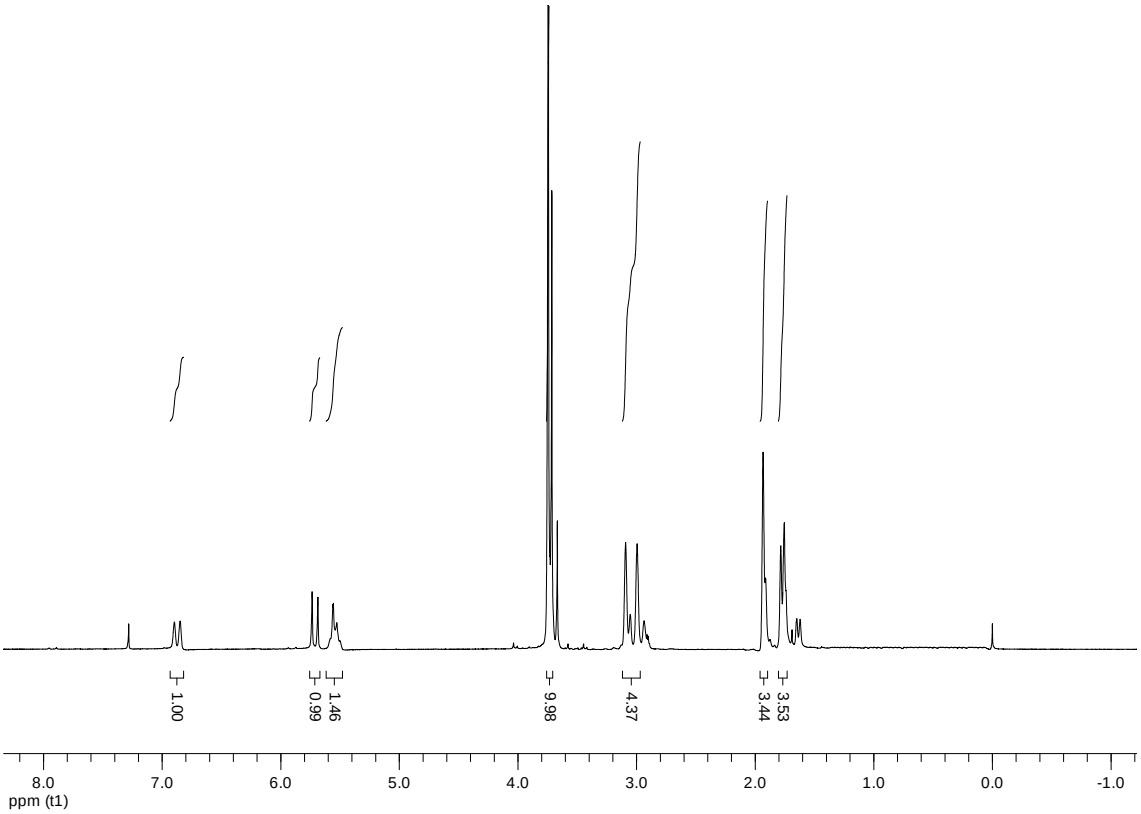

5.94
3.72
8.60
6.57
5.95
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

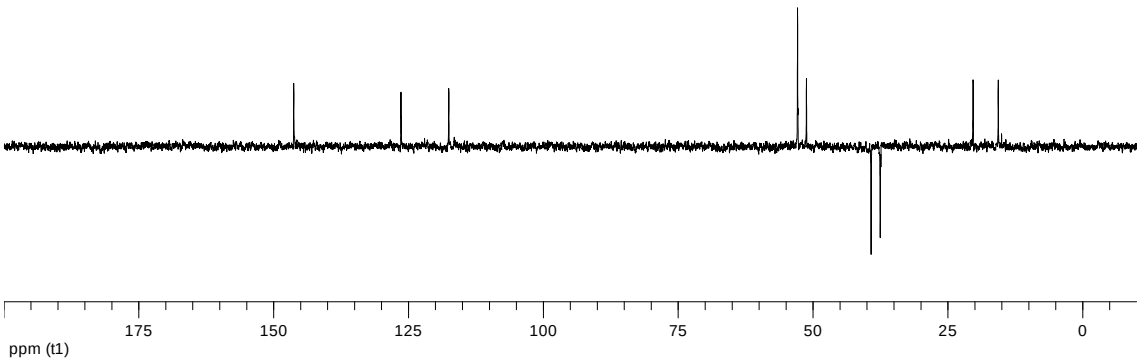

175
150
125
100
75
50
25
0
ppm (f1)

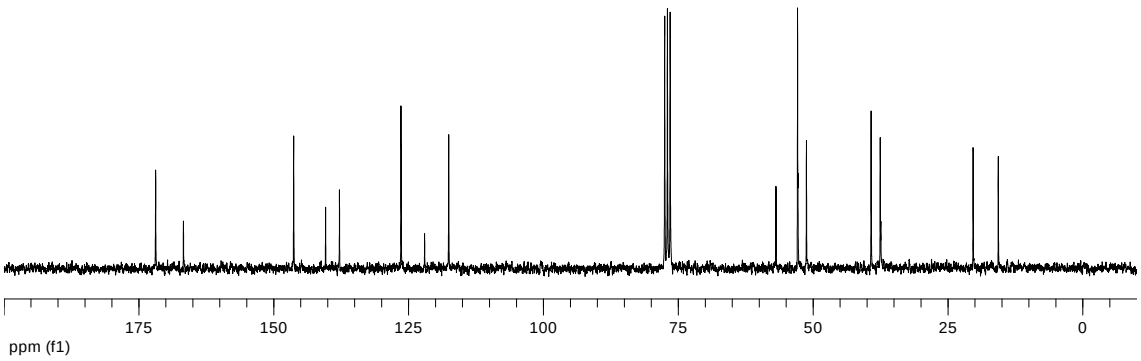

175
150
125
100
75
50
25
0
ppm (f1)

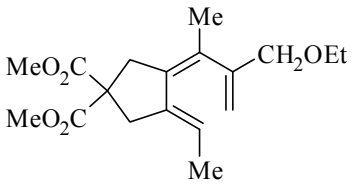

Me
CO2Me
MeO2C
MeO2C
Me

14

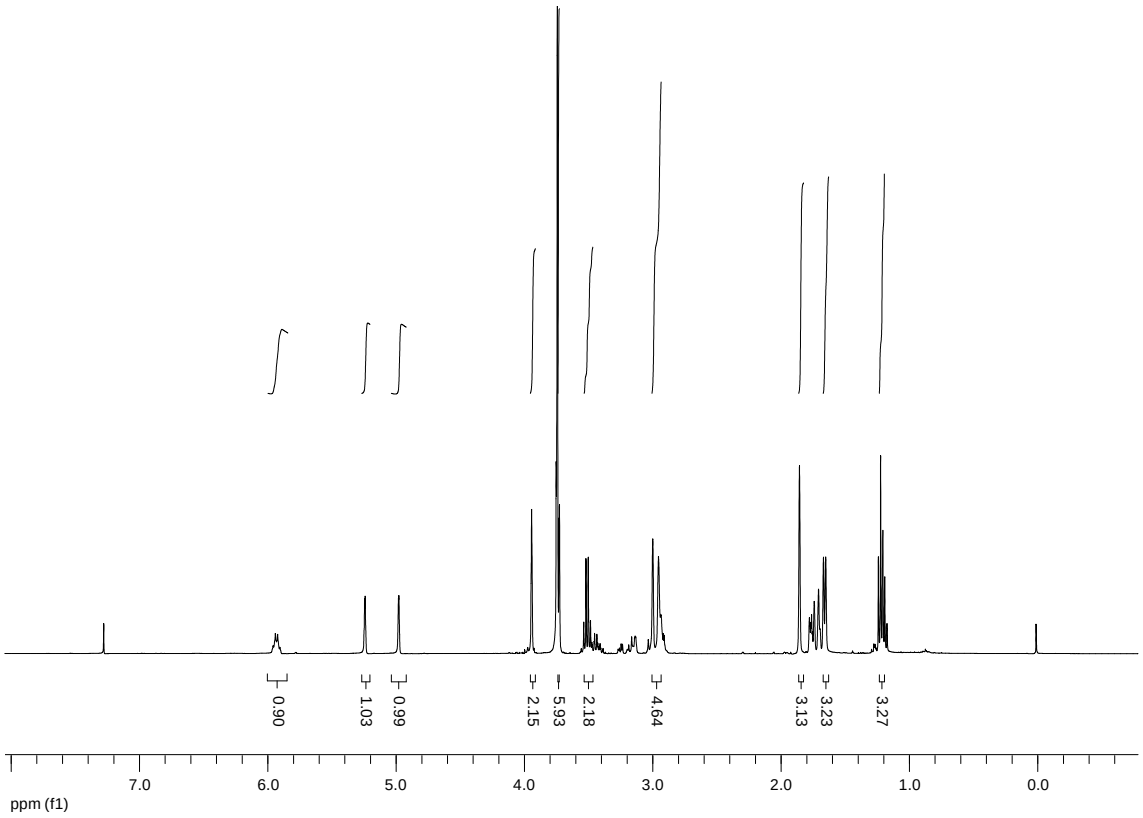

1.00
0.99
1.46
9.98
4.37
3.44
3.53
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

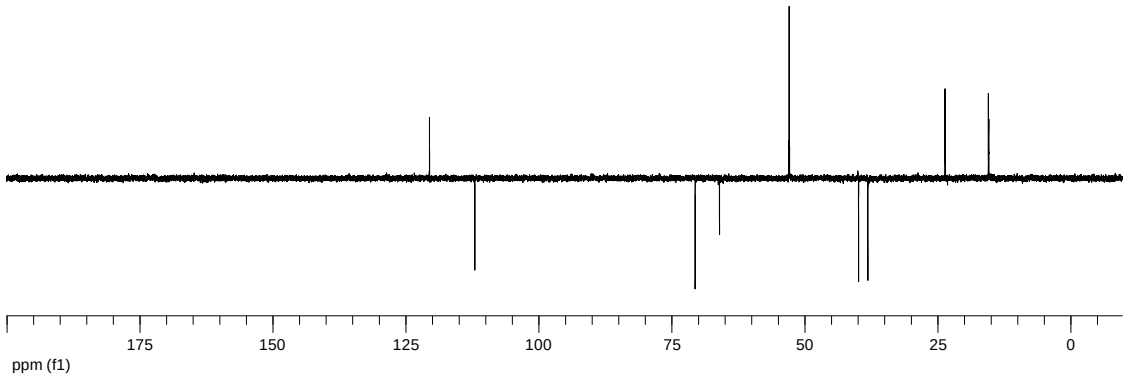

175
150
125
100
75
50
25
0
ppm (t1)

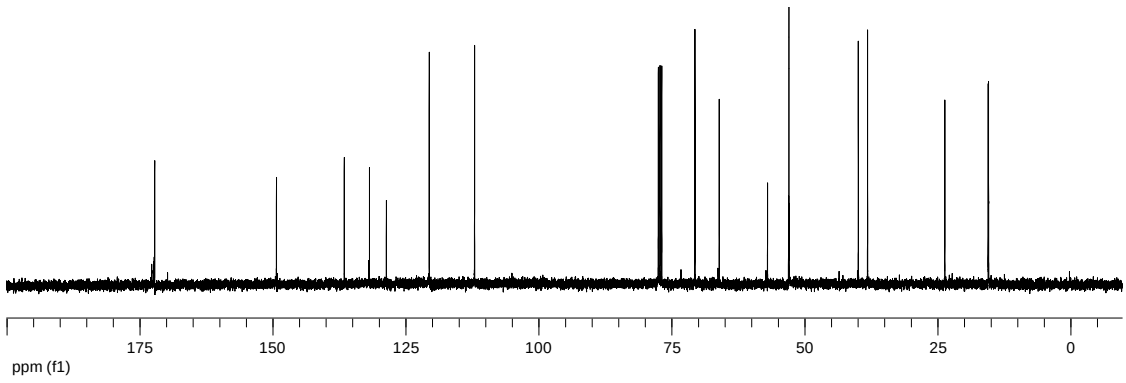

175
150
125
100
75
50
25
0
ppm (f1)


Me
CH2OEt
MeO2C
MeO2C
Me

15


0.90
1.03
0.99
2.15
5.93
2.18
4.64
3.13
3.23
3.27
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


175
150
125
100
75
50
25
0
ppm (f1)


175
150
125
100
75
50
25
0
ppm (f1)