SUPPORTING INFORMATION

Molybdenum Nitride Complexes with Ph_3SiO-Ligands Are Exceedingly Practical and Tolerant Precatalysts for Alkyne Metathesis and Efficient Nitrogen Transfer Agents

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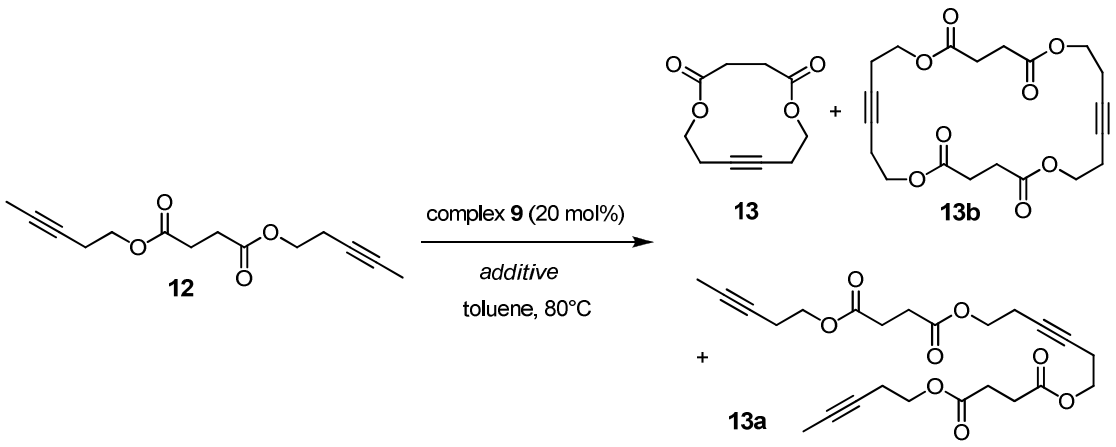
Screening of Additives



Additives (4 equiv. relative to **9**) that led to ***no or only marginal (< 5%) conversion*** after 8-18 h reaction time:

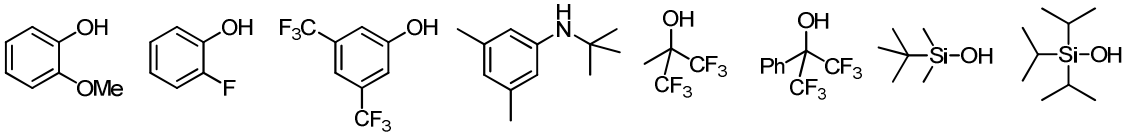
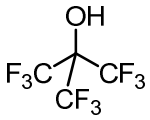
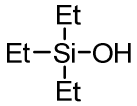
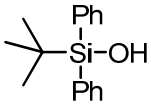
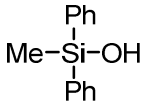
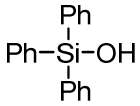
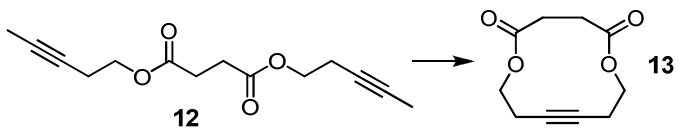


Table S-1. Additives that induced metathesis activity in the reaction of diyne **12** (isolated yields, unless stated otherwise)

Additive	t (h)	13	13a	13b
	18	19% [a]	traces	traces
	18	---	15%	---
	18	4%	24%	traces
	5	57%	4% [a]	22%
	1.5	83%	3% [a]	traces

[a] determined by NMR of the crude mixture

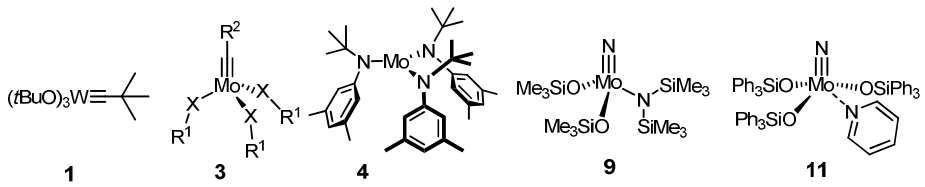
Table S-2. Optimization of the RCAM Reaction of Diyne **12**.[a]



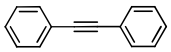
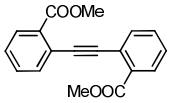
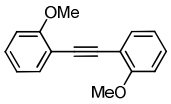
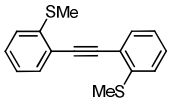
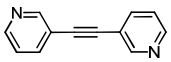
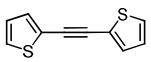
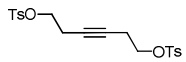
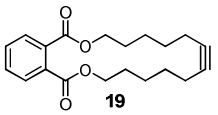
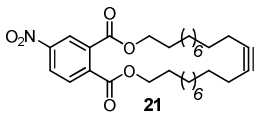
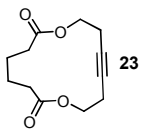
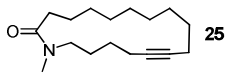
Entry	[Mo]	Additive	t (h)	Yield [b]
1	**9** (20%)	---	10	0%
2	**9** (20%)	Ph_3SiOH (80%)	1.2	83%
3	**9** (20%)	Ph_3SiOH (60%)	1.2	82%
4	**9** (20%)	Ph_3SiOH (40%)	1.2	84%
5	**9** (20%)	Ph_3SiOH (30%)	1.2	81%
6	**9** (20%)	Ph_3SiOH (20%)	1.2	< 10%
7	**9** (10%)	Ph_3SiOH (20%)	5	78%[c]
8	**11** (20%)	---	2	79%
9	**11** (10%)	---	4	75%[d]
10	**11** (5%)	---	18	74%[d]
11	**11** (2%)	---	65	74%

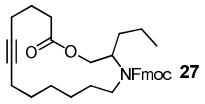
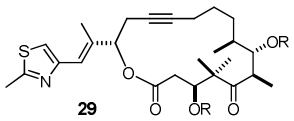
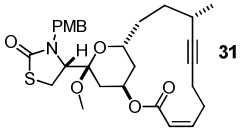
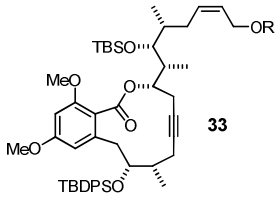
[a] All reactions were carried out in toluene at 80 °C on a 80-100 mg scale unless stated otherwise; small amounts (< 5%) of the acyclic and the cyclic dimer derived from **12** were also detected in the crude mixtures; [b] isolated yields; [c] 600 mg scale; [d] 300 mg scale.

Table S-2. Comparison of the New and the Established Alkyne Metathesis Precatalysts



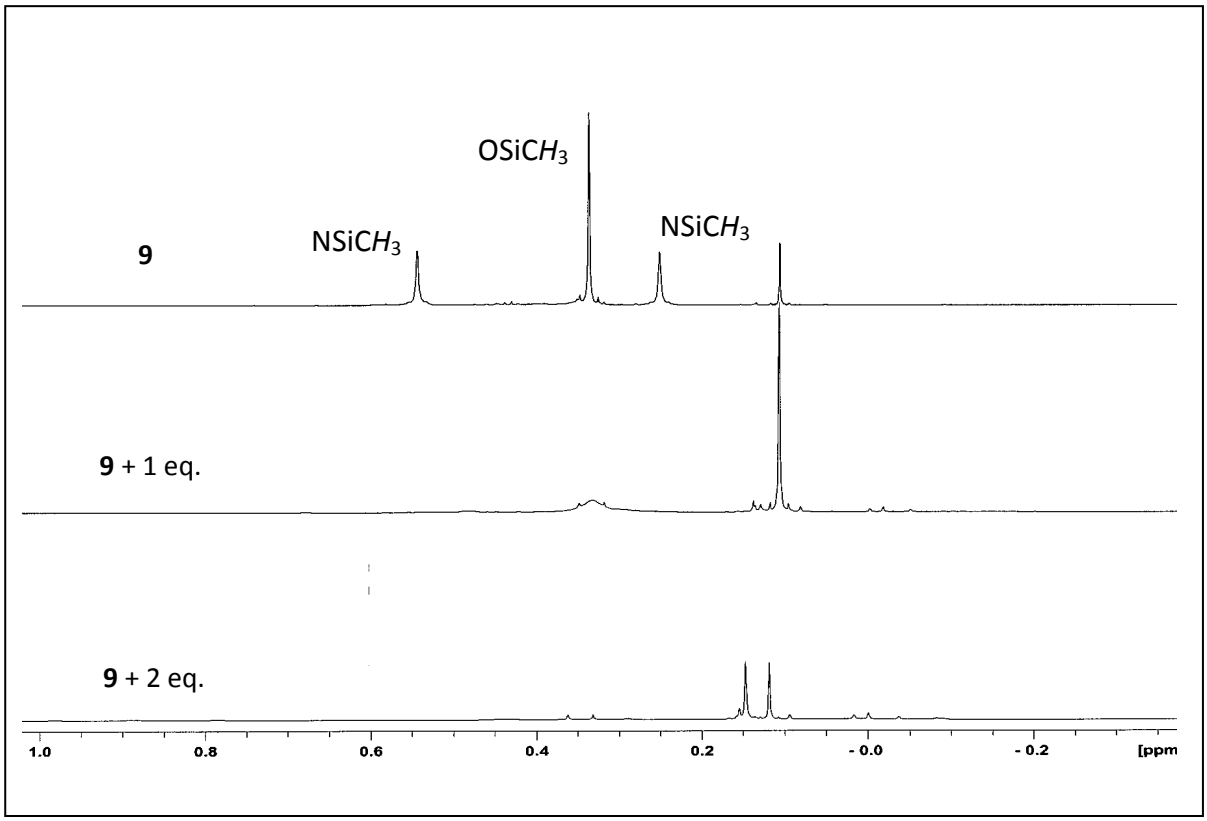
1 **3** **4** **9** **11**

Product	9/2 Ph_3SiOH[a]	11[b]	other catalysts	ref
	67%	84% 76%[c] 79%[d]	$Mo(CO)_6$/*p*-ClC_6H_4OH: 52% $Mo(CO)_6$/*o*-FC_6H_4OH:[f] 69%	1 4
		70%	**4**:[h] 76% $Mo(CO)_6$/*p*-ClC_6H_4OH:[i] 0%	2 3
	64%	59%	**4**:[h] 68% $Mo(CO)_6$/*p*-ClC_6H_4OH:[i] 0% $Mo(CO)_6$/*o*-FC_6H_4OH:[f] 71%	2 3 4
	64%	67%		
		68%[e]	$Mo(CO)_6$/*p*-ClC_6H_4OH:[i] 0%	3
	49%	61%	**4**:[h] 0% $Mo(CO)_6$/*p*-ClC_6H_4OH:[i] 0% **3**/*o*-$F_3CC_6H_4OH$:[j] < 5%	2 3 5
		81%[e]	**3**:[k] 86%	6
	79%			
	82%		**4**:[h] 69%	8
	73%	87%	$Mo(CO)_6$/*o*-FC_6H_4OH:[f] 83% $Mo(CO)_6$/*o*-FC_6H_4OH:[g] 36% **1**:[l] 79% **4**:[h] 81%	4 4 7 8
		54%	**4**:[h] 72%	8

 **27**	79%	**1**:[l] 69%	7
 **29**	61%	**4**:[h] 80%	8
 **31**	42%	**4**:[h] 41%	9
 **33**	81%	**4**:[h] 87% **1**:[m] ---	10

[a] complex **9** (20 mol%), Ph_3SiOH (40 mol%), toluene, 80°C; [b] complex **11** (20 mol%), toluene, 80°C; [c] complex **11** (2 mol%), toluene, 80°C; [d] performed in dry air; [e] at reflux temperature; [f] $Mo(CO)_6$ (5 mol%)/*o*-FC_6H_4OH (100 mol%), chlorobenzene, reflux; [g] in benzene at reflux; [h] complex **4** (10 mol%), toluene/CH_2Cl_2, 80°C; [i] $Mo(CO)_6$ (5 mol%)/*p*-ClC_6H_4OH (30 mol%), 1,2-dichlorobenzene, 140°C, 12-16h; [j] **3** (X = N(tBu), R^1 = mesityl, R^2 = Et) (10 mol%)/*o*-$F_3CC_6H_4OH$ (10 mol%), 1,2,4-triclorobenzene, 30°C, vacuum (1 mm Hg); if instead of 2-propynylthiophene, however, 2-butynylthiophene was used as the substrate, a yield of up to 69% of the desired product was obtained, cf. ref. 5; [k] **3** (XR^1 = O-adamantyl, $R^2 = CH_2SiMe_3$) (10 mol%), toluene, 25°C; [l] complex **1** (5 mol%), chlorobenzene, 80°C; [m] complex **1** (10 mol%), toluene, results only in the cleavage of the THP group of the substrate.

NMR Studies



Scheme S-1. Aliphatic region of the ^{1}H NMR spectrum (300 MHz) of complex **9** in [D_8]-toluene at −20°C compared with the spectra recorded after addition of 1 or 2 equivalents of Ph_3SiOH. Variable temperature measurements allowed the barrier to rotation about the Mo–N bond in **9** to be estimated as 14.7 ± 0.5 kcal·mol^{-1}.

Experimental Procedures and Data of the Products

General. Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O, 1,4-dioxane (Mg/anthracene), CH_2Cl_2, DME, MeCN (CaH_2), hexane, toluene (Na/K), MeOH (Mg). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400, DPX 600 and AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual ^{1}H: $\delta_H \equiv 5.32$ ppm; [D_8]-toluene: $\delta_C \equiv 20.7$ ppm; residual $D_5C_6CD_2H$: $\delta_H \equiv 2.09$ ppm). IR: Magna IR750 (Nicolet) or Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Melting points: Büchi melting point apparatus B-540 (corrected).

Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

Preparation of the Catalysts

[$(Me_3SiO)_2((Me_3Si)_2N)Mo{\equiv}N$] (9). Me_3SiCl (24 mL, 189 mmol) was added to a suspension of Na_2MoO_4 (9.80 g, 47.2 mmol) in DME (300 mL) under Ar and the mixture was vigorously stirred under reflux for 16 h. After evaporation of the solvents, the light blue residue was suspended in hexane (200 mL). A solution of freshly prepared $LiN(SiMe_3)_2$ (15.92 g, 95.2 mmol) in hexane (80 mL) was added to a suspension of the resulting fine powder and the mixture was stirred at room temperature for 2 h. For work-up, the suspension was filtered through a pad of Celite under Ar, the filtrate was evaporated and the residue purified by distillation in high vacuum to give complex **9** as a pale yellow liquid (13.6 g, 64%). B. p. = 57-58 °C ($1.8\cdot10^{-2}$ mbar); ^{1}H NMR (300 MHz, [D_8]-toluene, −20 °C): δ = 0.54 (s, 9H), 0.34 (s, 18H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, [D_8]-toluene, −20 °C): δ = 4.4, 2.5, 1.2; IR (film): $\tilde{\nu}$ = 1056 (Mo≡N) cm^{-1}. The spectroscopic data are in agreement with those reported in the literature.[11]

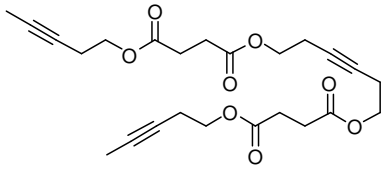
[(Pyridine)($Ph_3SiO)_3Mo{\equiv}N$] (11). Ph_3SiOH (6.27 g, 22.69 mmol) was added to a solution of complex **9** (3.39 g, 7.56 mmol) in toluene (110 mL) and the resulting mixture stirred at 80°C for 30 min. After reaching ambient temperature, pyridine (3.05 mL, 37.8 mmol) was introduced and the resulting solution was stirred for 18 h. The solvent was evaporated and the resulting yellow foam was recrystallized from hot toluene (80°C) to give compound **11** as a yellow powder (6.76 g, 81%, co-crystallizes with toluene in a 1:1 ratio, cf. Scheme S-2). M. p. = 189–191°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.04 (d, *J* = 5.0 Hz, 2H), 7.60–7.36 (m, 17H), 7.34–6.98 (m, 29H), 6.60 (br s, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 150.1 (2xCH), 138.4 (CH), 136.6 (9xC), 135.8 (18xCH), 129.7 (9xCH) 127.9 (18xCH), 124.9 (2xCH); IR (ATR): $\tilde{\nu}$ = 3066, 3048, 3024, 3009, 2998, 1608, 1588, 1484, 1448, 1427, 1113, 989, 890, 857, 835, 738, 708, 696 cm^{-1}; MS (EI) *m/z* (%): 937 [M^+ – pyridine]; HRMS (EI): *m/z*: calcd for $C_{54}H_{45}MoNO_3Si_3$: 937.1762; found: 937.1781.

Alkyne Metathesis Reactions

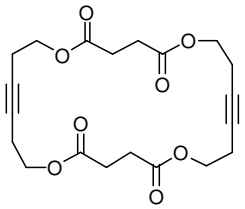
1,6-Dioxacyclododec-9-yne-2,5-dione (13). Representative Procedure for Alkyne Metathesis using a Catalyst Generated *in situ* from Complex 9 and Ph_3SiOH. Triphenylsilanol (134.3 mg, 0.486 mmol) was added to a solution of complex **9** (109.0 mg, 0.243 mmol) in toluene (4 mL) and the resulting mixture was stirred for 30 min at ambient temperature. A solution of diyne **12** (608 mg, 2.43 mmol) in toluene (117 mL) was then added and the solution stirred at 80°C for 1.2 h. For work up, the mixture was filtered through a pad of silica, the filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 4:1 → 1:1) to give cycloalkyne **13** as a colorless solid (370 mg, 78%). Two additional fractions were collected which contained the acyclic dimer **13a** (7.1 mg, 2%) and the cyclic dimer **13b** (20.2 mg, 4%) as colorless solids each. Analytical and spectroscopic data of compound **13**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.21–4.14 (m, 4H), 2.61 (s, 4H), 2.44–2.37 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 171.9 (2xC), 79.0 (2xC),

61.6 (2xCH_2), 30.2 (2xCH_2), 19.7 (2xCH_2); IR (film): $\tilde{\nu}$ = 2965, 2915, 2840, 1729, 1458, 1421, 1383, 1353, 1336, 1267, 1251, 1158, 1053, 1030, 1000, 952, 837 cm^{-1}; MS (EI) *m/z* (%): 166 (1), 101 (14), 78 (100), 66 (59), 65 (16), 55 (7), 40 (12), 28 (7); HRMS (ESI): *m/z*: calcd for $C_{10}H_{12}O_4$ + Na: 219.0628; found: 219.0627. The recorded analytical and spectral data agree with those published in the literature.[7]

Acyclic Dimer 13a. M. p. = 145–146°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.15–4.09 (m, 8H), 2.61 (s, 8H), 2.50–2.44 (m, 8H), 1.76 (t, *J* = 2.6 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 172.9 (4xC), 77.7 (2xC), 77.4 (2xC), 74.9 (2xC), 63.4 (2xCH_2), 63.1 (2xCH_2), 29.3 (4xCH_2), 19.5 (4xCH_2), 3.5 (2xCH_3); IR (film): $\tilde{\nu}$ = 2967, 2933, 2918, 2855, 1729, 1450, 1432, 1415, 1388, 1314, 1285, 1235, 1142, 1071, 1036, 1005, 889, 871, 806 cm^{-1}; MS (EI) *m/z* (%): 263 (11), 167 (16), 144 (17), 132 (16), 129 (22), 117 (14), 97 (12), 79 (18), 78 (37), 77 (15), 67 (100), 66 (23), 65 (14), 41 (13); HRMS (ESI): *m/z*: calcd for $C_{24}H_{30}O_8$ + Na: 469.1833; found: 469.1836.

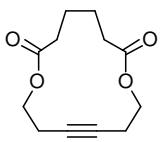


Cyclic Dimer 13b. M. p. = 83–84°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.17–4.12 (m, 8H), 2.63 (s, 8H), 2.50–2.46 (m, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 172.1 (4xC), 77.8 (4xC), 63.0 (4xCH_2), 29.6 (4xCH_2), 19.6 (4xCH_2); IR (film): $\tilde{\nu}$ = 2965, 2932, 2910, 2853, 1730, 1456, 1432, 1408, 1387, 1355, 1333, 1249, 1267, 1219, 1210, 1193, 1154, 1086, 1007, 990, 973, 837, 830 cm^{-1}; MS (EI) *m/z* (%): 392 [M^+] (3), 174 (8), 156 (22), 101 (12), 96 (14), 79 (32), 78 (100), 77 (36), 66 (28), 65 (13), 55 (13); HRMS (ESI): *m/z*: calcd for $C_{20}H_{24}O_8$ + Na: 415.1363; found: 415.1368; elemental analysis (%) calcd for $C_{20}H_{24}O_8$: C 61.22, H 6.16; found: C 61.36, H 6.29.

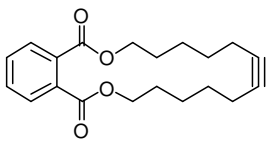


Representative Procedure for the Use of Adduct 11 as Precatalyst in RCAM Reactions: Diyne **12** (325.4 mg, 1.3 mmol) was added to a solution of complex **11** (72.0 mg, 65.0 µmol) in toluene (65 mL) and the resulting mixture was stirred at 80°C for 18 h. The solution was cooled to room temperature and filtered through a short pad of silica, the filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 9:1) to give cycloalkyne **13** as a colorless solid (189.0 mg, 74%).

1,8-Dioxacyclotetradec-11-yn-2,7-dione (23). Prepared analogously as a colorless solid (76 mg, 87%). M. p. = 109–110°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.13–4.06 (m, 4H), 2.53–2.47 (m, 4H), 2.39–2.30 (m, 4H), 1.76–1.67 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 173.2 (2xC), 78.2 (2xC), 62.8 (2xCH_2), 35.2 (2xCH_2), 25.4 (2xCH_2), 19.4 (2xCH_2); IR (film) $\tilde{\nu}$ = 2995, 2954, 2937, 2918, 2901, 2872, 1721, 1458, 1425, 1384, 1341, 1272, 1236, 1167, 1140, 1080, 1065, 1021, 981, 931, 843, 824, 699 cm^{-1}; MS (EI) *m/z* (%): 129 (3), 111 (8), 78 (100), 66 (20), 55 (15), 41 (8); HRMS (ESI): *m/z*: calcd for $C_{12}H_{16}O_4$ + Na: 247.0941; found: 247.0938. The recorded analytical and spectral data agree with those published in the literature.[7]



Cycloalkyne 19. Prepared analogously as a colorless oil (123 mg, 79%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.72 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.55 (dd, *J* = 5.7, 3.3 Hz, 2H), 4.32 (t, *J* = 6.0 Hz, 4H), 2.21–2.14 (m, 4H), 1.82–1.73 (m, 4H), 1.60–1.47 (m, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 168.0 (2xC), 132.8 (2xC), 131.3 (2xCH), 129.1 (2xCH), 80.9 (2xC), 66.7 (2xCH_2), 28.7 (2xCH_2), 28.5 (2xCH_2), 26.3 (2xCH_2), 18.9 (2xCH_2); IR (film): $\tilde{\nu}$ = 2928, 2859, 1720, 1600, 1579, 1488, 1460, 1447, 1433, 1385, 1269, 1122, 1070, 1039, 957, 734, 703 cm^{-1}; MS (EI) *m/z* (%): 328 [M^+] (8), 180 (9), 162 (30), 149 (100), 133 (17),



122 (18), 121 (26), 119 (14), 108 (43), 107 (18), 105 (15), 95 (11), 94 (24), 93 (44), 91 (29), 81 (19), 80 (28), 79 (34), 77 (13), 67 (19), 55 (13); HRMS (ESI): *m/z*: calcd for $C_{20}H_{24}O_4$ + Na: 351.1567; found: 351.1567; elemental analysis (%) calcd for $C_{20}H_{24}O_4$: C 73.15, H 7.37; found: C 73.26, H 7.28.

Cycloalkyne 21. Prepared analogously as a white solid (49 mg, 82%). M. p. = 81–82°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 2.2 Hz, 1H), 8.37 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 4.35–4.30 (m, 4H), 2.15 (br s, 4H), 1.74 (sext, *J* = 7.1 Hz, 4H), 1.45–1.29 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3 (C), 165.2 (C), 148.8 (C), 138.2 (C), 133.2 (C), 130.1 (CH), 125.8 (CH), 124.4 (CH), 80.6 (2xC), 66.7 (2xCH_2), 29.6 (2xCH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (2xCH_2), 29.1 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 28.4 (CH_2), 28.4 (CH_2), 28.4 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 18.5 (2xCH_2); IR (film): $\tilde{\nu}$ = 3108, 3077, 3046, 2918, 2851, 1741, 1720, 1613, 1548, 1532, 1468, 1354, 1298, 1272, 1241, 1136, 1061, 997, 962, 932, 861, 835, 733, 725 cm^{-1}; MS (EI) *m/z* (%): 496 (19), 195 (37), 194 (32), 192 (33), 191 (11), 180 (13), 179 (19), 178 (69), 177 (15), 164 (22), 149 (22), 148 (11), 136 (12), 135 (30), 123 (12), 122 (14), 121 (43), 111 (23), 110 (16), 109 (29), 108 (14), 107 (29), 105 (11), 97 (15), 96 (28), 95 (64), 94 (26), 93 (46), 91 (19), 83 (38), 82 (30), 81 (84), 80 (42), 79 (54), 69 (92), 68 (25), 67 (84), 57 (20), 56 (11), 55 (100), 54 (24), 43 (30), 41 (61); HRMS (ESI): *m/z*: calcd for $C_{30}H_{43}NO_6$ + Na: 536.2982; found: 536.2989. The recorded analytical and spectral data agree with those published in the literature.[8]

Compound 25. Prepared analogously as a colorless oil (60 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, rotamers): *δ* = 3.43 (t, *J* = 7.0 Hz, 1H), 3.27 (*J* = 7.6 Hz, 1H), 2.99 (s, 1H), 2.91 (s, 2H), 2.32–2.36 (m, 2H), 2.15–2.23 (m, 4H), 1.56–1.77 (m, 4H), 1.28–1.52 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$, rotamers): *δ* = 173.0, 172.7, 80.9, 79.6, 49.8, 46.6, 35.3, 33.4, 33.0, 31.1, 29.4, 28.6, 28.5, 28.0, 28.0, 27.9, 27.9, 27.7, 27.5, 27.4, 27.1, 26.8, 26.8, 26.6, 26.2, 25.0, 23.9, 18.9, 18.7, 18.5, 18.4; IR (film) $\tilde{\nu}$ = 2926, 2855, 1643, 1459, 1437, 1401, 1333, 1273, 1170, 1091 cm^{-1}; MS (EI): *m/z* (%): 263 (20) [M^+], 262 (15), 248 (20), 124 (17), 111 (23), 110 (14), 93 (10), 91 (10), 86 (16), 81 (10), 79 (19), 73 (13), 70 (86), 67 (16), 58 (18), 57 (17), 55 (27), 44 (100), 41 (29), 40 (16); HRMS (ESI): calcd for [$C_{17}H_{29}NO$ + Na^+]: 286.2141; found: 286.2139. The recorded analytical and spectral data agree with those published in the literature.[8]

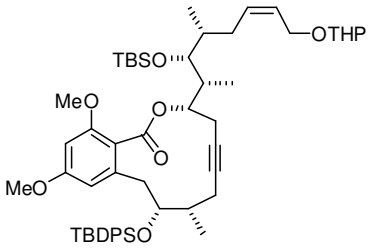
Cycloalkyne 27. Prepared analogously as a colorless oil (14.3 mg, 79%). ^{1}H NMR (rotamers, 400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.4 Hz, 2H), 7.61–7.53 (m, 2H), 7.42–7.28 (m, 4H), 4.72–4.49 (m, 2H), 4.34–4.24 (m, 2H), 3.88–3.79 (m, 1.5H), 3.41 (br s, 0.5H), 3.02–2.91 (m, 1H), 2.65–2.40 (m, 2H), 2.28–2.15 (m, 3H), 2.13–2.01 (m, 1H), 1.83–1.70 (m, 2H), 1.64–0.77 (m, 14.5H), 0.70 (br s, 1.5H); ^{13}C NMR (rotamers, 150 MHz, $CDCl_3$): δ = 173.3 (C), 173.2 (C), 156.8 (C), 156.4 (C), 144.1 (C), 144.0 (C), 143.9 (C), 141.4 (C), 141.3 (C), 127.6 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 124.6 (CH), 119.9 (CH), 119.8 (CH), 82.7 (C), 79.6 (C), 79.4 (C), 66.5 (CH_2), 66.2 (CH_2), 63.4 (CH_2), 47.5 (CH), 47.3 (CH), 34.9 (CH_2), 34.6 (CH_2), 34.5 (CH_2), 32.4 (CH_2), 32.3 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 23.5 (CH_2), 23.4 (CH_2), 19.5 (CH_2), 18.2 (CH_2), 17.7 (CH_2), 14.0 (CH_3), 13.8 (CH_3); IR (film): $\tilde{\nu}$ = 3065, 3043, 3020, 2931, 2859, 1734, 1688, 1450, 1410, 1386, 1328, 1312, 1292, 1268, 1241, 1222, 1155, 1135, 1054, 1010, 758, 737 cm^{-1}; MS (EI) *m/z* (%): 236 (3), 180 (4), 179 (36), 178 (100), 165 (2); HRMS (ESI): *m/z*: calcd for $C_{32}H_{39}NO_4$ + Na:

524.2771; found: 524.2776. The recorded analytical and spectral data agree with those published in the literature.[7]

Cycloalkyne 29. Prepared analogously as an amorphous solid (11.2 mg, 61%). $[\alpha]_D^{20}$ = –18.5 (c = 0.6 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.96 (s, 1H), 6.55 (br s, 1H), 5.33 (dd, *J* = 7.3, 3.1 Hz, 1H), 4.70 (dd, *J* = 6.4, 5.0 Hz, 1H), 3.93 (dd, *J* = 6.8, 1.9 Hz, 1H), 3.24 (quin, *J* = 6.9 Hz, 1H), 2.78 (dq, *J* = 17.2, 2.8 Hz, 1H), 2.71 (s, 3H), 2.69–2.63 (m, 2H), 2.57 (dd, *J* = 15.3, 5.0 Hz, 1H), 2.27–2.21 (m, 1H), 2.18 (d, *J* = 1.2 Hz, 3H), 2.13–2.07 (m, 1H), 1.78–1.71 (m, 1H), 1.59–1.53 (m, 1H), 1.30–1.20 (m, 2H), 1.41–1.34 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.14 (s, 3H), 1.10 (s, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.91 (s, 9H), 0.86 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 216.7 (C), 170.1 (C), 164.9 (C), 152.3 (C), 136.9 (C), 120.4 (CH), 116.8 (CH), 82.2 (C), 78.0 (CH), 76.7 (CH), 76.3 (C), 72.6 (CH), 54.5 (C), 44.4 (CH), 41.6 (CH_2), 38.9 (CH), 29.5 (CH_2), 26.2 (3xCH_3), 26.1 (3xCH_3), 25.9 (CH_2), 24.1 (CH_2), 20.9 (CH_3), 20.5 (CH_3), 19.3 (C), 18.6 (CH_3), 18.5 (CH_2), 18.3 (C), 17.0 (2xCH_3), 15.0 (CH_3), –3.2 (CH_3), –3.7 (CH_3), –4.0 (CH_3), –4.1 (CH_3); IR (film): $\tilde{\nu}$ = 2952, 2929, 2894, 2856, 1739, 1702, 1505, 1472, 1463, 1385, 1361, 1254, 1182, 1152, 1097, 1085, 1039, 1018, 1007, 988, 836, 775 cm^{-1}; MS (EI) *m/z* (%): 703 [M$^+$] (5), 648 (23), 647 (47), 646 (97), 604 (11), 446 (14), 445 (33), 444 (100), 402 (22), 344 (15), 270 (38), 195 (12), 185 (18), 178 (12), 151 (21), 143 (13), 115 (13), 101 (12), 75 (45), 73 (51); HRMS (ESI): *m/z*: calcd for $C_{38}H_{65}NO_5SSi_2$ + Na: 726.4014; found: 726.4015. The recorded analytical and spectral data agree with those published in the literature.[8]

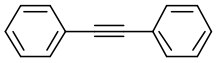
Cycloalkyne 31. Prepared analogously as a colorless solid (5 mg, 42%). $[\alpha]_D^{20}$ = +46.1 (c = 0.2 in $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.23 (m, 2H), 6.87 (m, 2H), 6.27–6.18 (m, 1H), 5.75 (d, *J* = 11.8 Hz, 1H), 5.30–5.25 (m, 1H), 5.00 (d, *J* = 14.3 Hz, 1H), 4.97–4.88 (m, 1H), 4.33 (d, *J* = 14.3 Hz, 1H), 3.84 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.79 (s, 3H), 3.44–3.33 (m, 1H), 3.30–3.20 (m, 2H), 3.14 (s, 3H), 2.56–2.46 (m, 1H), 2.44–2.38 (m, 1H), 2.36–2.30 (m, 1H), 2.21–2.05 (m, 3H), 1.94 (dd, *J* = 15.1, 4.2 Hz, 1H), 1.88–1.73 (m, 3H), 1.45–1.31 (m, 2H), 1.13 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 172.9 (C), 166.3 (C), 159.4 (C), 146.5 (CH), 130.3 (2xCH), 129.2 (C), 122.9 (CH), 114.1 (2xCH), 102.2 (C), 86.2 (C), 80.9 (C), 67.5 (CH_3), 65.6 (CH_3), 59.4 (CH), 55.5 (CH), 47.7 (CH), 47.6 (CH_2), 34.4 (CH_2), 33.9 (CH_2), 31.1 (CH_2), 30.2 (CH_2), 28.6 (CH_2), 26.9 (CH), 25.7 (CH_2), 22.3 (CH_3), 19.4 (CH_2); IR (film): $\tilde{\nu}$ = 3029, 3006, 2962, 2920, 2908, 2856, 1692, 1666, 1608, 1511, 1450, 1404, 1359, 1325, 1295, 1246, 1212, 1196, 1174, 1120, 1110, 1081, 1050, 1031, 1016, 971, 850, 834, 758, 660 cm^{-1}; MS (EI) *m/z* (%): 292 (18), 291 (91), 273 (24), 259 (11), 241 (23), 213 (16), 199 (27), 189 (25), 171 (10), 149 (14), 145 (12), 121 (100), 91 (12); HRMS (ESI): *m/z*: calcd for $C_{28}H_{35}NO_6S$ + Na: 536.2077; found: 536.2078. The recorded analytical and spectral data agree with those published in the literature.[9]

Cycloalkyne 33. Prepared analogously as a colorless amorphous solid (15.3 mg, 81%). $[\alpha]_D^{20}$ = –27.6 (c = 0.9 in $CHCl_3$); ^{1}H NMR (two diastreomers at the THP acetal, 400 MHz, $CDCl_3$): δ = 7.75–7.67 (m, 2H), 7.62–7.54 (m, 2H), 7.42–7.27 (m, 6H), 6.39 (d, *J* = 2.8 Hz, 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 5.67–5.52 (m, 2H), 5.52–5.41 (m, 1H), 4.66–4.59 (m, 1H), 4.28–4.18 (m, 1H), 4.09–3.94 (m, 2H), 3.93–3.81 (m, 2H), 3.75 (s, 3H), 3.60 (s, 3H), 3.54–3.45 (m, 2H), 2.55–2.41 (m, 3H), 2.25–2.14 (m, 1H), 1.91–1.65 (m,



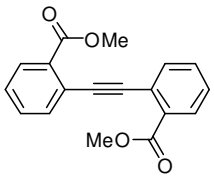
8H), 1.65–1.44 (m, 5H), 1.00–0.84 (m, 26H), 0.05 (s, 6H); ^{13}C NMR (two diastreomers at the THP acetal, 75 MHz, $CDCl_3$): δ = 167.1 (C), 160.5 (C), 157.5 (C), 139.0 (C), 136.0 (2xCH), 135.8 (2xCH), 134.5 (C), 134.0 (C), 132.4 (CH), 129.5 (CH), 129.4 (CH), 127.5 (2xCH), 127.4 (2xCH), 127.0 and 126.9 (CH), 118.1 (C), 107.5 (CH), 97.9 and 97.8 (CH), 97.0 (CH), 79.0 (C), 77.2 (CH), 76.4 (CH), 76.3 (CH), 74.5 (C), 62.8 (CH_2), 62.2 and 62.1 (CH_2), 55.7 (CH_3), 55.3 (CH_3), 40.7 and 40.7 (CH), 38.9 (CH_2), 37.9 (CH), 36.0 (CH), 30.7 and 30.6 (CH_2), 30.1 and 30.1 (CH_2), 26.8 (3xCH_3), 26.2 (3xCH_3), 25.5 and 25.5 (CH_2), 23.7 (CH_2), 22.2 (CH_2), 19.5 (CH_2), 19.4 (C), 18.4 (C), 16.9 (CH_3), 16.9 (CH_3), 11.3 (CH_3), –3.8 (CH_3), –3.7 (CH_3); IR (film): $\tilde{\nu}$ = 3052, 2961, 2928, 2857, 1729, 1604, 1588, 1463, 1427, 1342, 1264, 1202, 1158, 1104, 1079, 1050, 1025, 908, 835 cm^{-1}; MS (EI) *m/z* (%): 855 (14), 854 (30), 853 (46), 769 (11), 642 (14), 641 (28), 528 (11), 527 (26), 243 (11), 225 (19), 199 (13), 135 (13), 85 (100), 73 (24); HRMS (ESI): *m/z*: calcd for $C_{54}H_{78}O_8Si_2$ + Na: 933.5132; found: 933.5127; elemental analysis (%) calcd for $C_{54}H_{78}O_8Si_2$: C 71.17, H 8.63; found: C 71.06, H 8.62.

Representative Procedure for Intermolecular Alkyne Metathesis Reactions: Diphenylacetylene. 1-



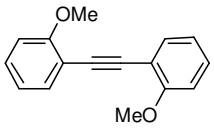
Phenyl-1-propyne (113.8 mg, 980 µmol) was added to a solution of complex **11** (21.7 mg, 19.6 µmol) in toluene (4.9 mL) and the resulting mixture was stirred at 80°C for 24 h. The solution was cooled to room temperature and filtered through a short pad of silica, the filtrate was evaporated and the residue purified by flash chromatography (hexanes). Residual 1-phenyl-1-propyne was removed under high vacuum to give pure diphenylacetylene as a white solid (66.5 mg, 76%). The analytical and spectroscopic data are identical to those of a commercial sample.

Dimethyl 2,2'-(ethyne-1,2-diyl)dibenzoate. Prepared analogously as a yellow solid (44 mg, 70%). M.



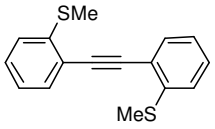
p. = 83–84°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–8.00 (m, 2H), 7.73 (ddd, *J* = 7.7, 1.2, 0.4 Hz, 2H), 7.51 (dt, *J* = 7.6, 1.4 Hz, 2H), 7.39 (dt, *J* = 7.7, 1.3 Hz, 2H), 3.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 134.3, 131.8, 131.7, 130.4, 128.1, 123.8, 93.1, 52.2; IR (ATR) $\tilde{\nu}$ = 2950, 1725, 1714, 1595, 1567, 1491, 1448, 1431, 1292, 1250, 1189, 1128, 1077, 1041, 963, 755, 699 cm^{-1}; MS (EI) *m/z* (%): 294 (11) [M^+], 280 (18), 279 (100), 265 (5), 264 (24), 248 (20), 220 (16), 176 (5), 163 (8), 132 (10), 102 (7), 88 (9); HRMS (ESI): *m/z*: calcd for $C_{18}H_{14}O_4$ + Na: 317.0784; found: 317.0785. The recorded analytical and spectral data agree with those published in the literature.[2]

1,2-Bis(2-methoxyphenyl)ethyne. Prepared analogously at reflux temperature as a colorless solid (39

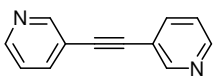


mg, 59%). M. p. = 126–127°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.49 (ddd, *J* = 7.3, 1.6, 0.5 Hz, 2H), 7.33 (ddd, *J* = 7.9, 7.7, 1.9 Hz, 2H), 6.95 (td *J* = 7.9, 1.0 Hz, 4H), 3.92 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 160.3 (2xC), 133.7 (2xCH), 130.1 (2xCH), 120.8 (2xCH), 113.0 (2xC), 111.3 (2xCH), 90.1 (2xC), 56.2 (2xCH_3); IR (film): $\tilde{\nu}$ = 3105, 3033, 2998, 2963, 2937, 2833, 1945, 1903, 1863, 1598, 1574, 1498, 1464, 1456, 1432, 1274, 1241, 1184, 1162, 1115, 1047, 1020, 937, 750 cm^{-1}; MS (EI) *m/z* (%): 238 [M^+] (100), 237 (32), 223 (23), 221 (15), 207 (10), 195 (5), 178 (8), 165 (14), 152 (9), 131 (19), 111 (6), 97 (3), 89 (3); HRMS (ESI): *m/z*: calcd for $C_{16}H_{14}O_2$ + Na: 261.0886; found: 261.0884. The recorded analytical and spectral data agree with those published in the literature.[12]

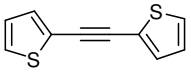
1,2-Bis(2-(methylthio)phenyl)ethyne. Prepared analogously as a colorless solid (72 mg, 67%). M. p. = 123–124°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.52 (ddd, *J* = 7.9, 1.5, 0.5 Hz, 2H), 7.34 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 2H), 7.22 (dd, *J* = 8.1, 0.7 Hz, 2H), 7.14 (td, *J* = 7.4, 1.2, Hz, 2H), 2.52 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 142.2 (2xC), 132.8 (2xCH), 129.4 (2xCH), 124.6 (2xCH), 124.5 (2xCH), 121.4 (2xC), 93.4 (2xC), 15.3 ($2xCH_3$); IR (film): $\tilde{\nu}$ = 3086, 3053, 3011, 2915, 2854, 2830, 1954, 1909, 1868, 1827, 1781, 1584, 1555, 1470, 1432, 1279, 1245, 1125, 1074, 1036, 972, 954 cm^{-1}; MS (EI) *m/z* (%): 270 [M$^+$] (16), 255 (53), 241 (17), 240 (100), 221 (19), 208 (6), 195 (5), 163 (5), 120 (15); HRMS (EI): *m/z*: calcd for $C_{16}H_{14}S_2$: 270.0537; found: 270.0535. The recorded analytical and spectral data agree with those published in the literature.[13]



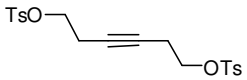
1,2-Di(pyridine-3-yl)ethyne. Prepared analogously at reflux temperature as a pale yellow solid (40.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.79 (br s, 2H); 8.58 (d, *J* = 4.0 Hz, 2H), 7.83 (dt, *J* = 7.8, 1.8 Hz, 2H), 7.31 (dd, *J* = 7.8, 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 149.2, 138.7, 123.3, 119.9, 89.3; IR (film): 3029, 2924, 1987, 1952, 1916 1881, 1771, 1727, 1558, 1480, 1410, 1328, 1295, 1254, 1187, 1127, 1097, 1040, 1018, 959, 926, 882, 850, 809, 701 cm^{-1}; MS (EI) *m/z* (%): 180 (100) [M$^+$], 153 (7), 152 (6), 127 (11), 126 (5), 100 (6), 99(5), 76 (5), 74 (12), 63 (5); HRMS (EI): *m/z*: calcd for $C_{12}H_8N_2$ [M$^+$]: 180.0687, found: 180.0686. The recorded analytical and spectral data agree with those published in the literature.[14]



1,2-Di(thiophene-2-yl)ethyne. Prepared analogously as a colorless solid (53 mg, 61%). M. p. = 98–99°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.35 (dd, *J* = 5.2, 1.1 Hz, 2H), 7.29 (dd, *J* = 3.6, 1.1 Hz, 2H), 7.04 (dd, *J* = 5.2, 3.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 132.5 (2xCH), 128.2 (2xCH), 127.6 (2xCH), 123.1 (2xC), 86.4 (2xC); IR (film): $\tilde{\nu}$ = 3100, 3082, 1791, 1723, 1651, 1596, 1432, 1406, 1195, 1098, 1040, 1028, 849, 824, 692 cm^{-1}; MS (EI) *m/z* (%): 192 (9), 191 (13), 190 (100), 158 (8), 145 (13), 114 (9), 95 (8), 69 (6), 45 (5); HRMS (EI): *m/z*: calcd for $C_{10}H_6S_2$: 189.9911; found: 189.9912. The recorded analytical and spectral data agree with those published in the literature.[5]



Hex-3-yne-1,6-diyl bis(4-methylbenzenesulfonate). Prepared analogously as a colorless solid (108 mg, 81%). M. p. = 83-84°C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.77–7.80 (m, 4H), 7.34–7.36 (m, 4H), 4.01 (t, *J* = 7.0 Hz, 4H), 2.44–2.47 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 145.0, 132.9, 129.9, 127.9, 76.8, 67.7, 21.6, 19.6; IR (film): $\tilde{\nu}$ = 2955, 2920, 1597, 1453, 1352, 1293, 1190, 1170, 1096, 969, 898, 841, 813, 761, 662 cm^{-1}; MS (EI): *m/z* (%): 423 (5), 422 (21) [*M*$^+$], 251 (11), 250 (10), 186 (6), 156 (8), 155 (86), 139 (21), 92 (9), 91 (100), 90 (7), 79 (10), 78 (62), 77 (9), 66 (7), 65 (47); HRMS (ESI): calcd (*m/z*) for [$C_{20}H_{22}O_6S_2$ + Na$^+$]: 445.0750; found: 445.0750. The recorded analytical and spectral data agree with those published in the literature.[6]



Total Synthesis of Gallicynoic Acid I

(*R*)-(*tert*-Butyldimethyl(oct-2-yn-4-yloxy)silane (14). TBSCl (362 mg, 2.40 mmol), imidazole (164 mg, 2.40 mmol) and DMAP (45 mg, 0.36 mmol) were added to a solution of (*R*)-oct-2-yn-4-ol (309 mg, 1.98 mmol)[15] in DMF (10 mL) and $CHCl_3$ (2 mL) and the mixture was stirred for 48 h before the reaction was quenched with aq. sat. NH_4Cl (50 mL). The aqueous layer was extracted with hexanes (3 x 25 mL), the combined organic phases were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/toluene, 10:1) to give the title compound as a colorless syrup (525 mg, quant.). $[\alpha]_D^{20}$ = +41.5 (*c* = 1.03 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.29 (tq, *J* = 6.4, 2.1 Hz, 1H), 1.82 (d, *J* = 2.1 Hz, 3H), 1.58–1.66 (m, 2H), 1.25–1.44 (m, 4H), 0.86-0.93 (m, 12H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 81.2, 79.7, 63.2, 38.7, 27.5, 25.9, 22.4, 18.3, 14.1, 3.5, −4.5, −5.0; IR (film) $\tilde{\nu}$ = 2957, 2930, 2858, 1463, 1342, 1250, 1077, 1005, 937, 834, 775 cm^{-1}; MS (EI): *m/z* (%): 240 (<1) [M^+], 184 (16), 183 (100), 143 (20), 127 (14), 97 (63), 75 (49), 73 (22); HRMS (ESI): *m/z*: calcd for [$C_{14}H_{28}OSi + Na^+$]: 263.1802; found: 263.1799; elemental analysis (%) calcd for $C_{14}H_{28}OSi$: C 69.93, H 11.74; found: C 69.86, H 11.83.

Representative Procedure for Alkyne Cross Metathesis: 6-(*tert*-Butyldimethylsilyloxy)dec-4-ynoic acid methylester (16). A mixture containing complex **9** (7.4 mg, 0.017 mmol), Ph_3SiOH (9.2 mg, 0.033 mmol) and molecular sieves (4 Å, ca. 20 mg) in toluene (0.5 mL) was stirred for 30 min at ambient temperature before a solution of compound **14** (20 mg, 0.083 mmol) and compound **15** (16.5 mg, 0.083 mmol)[16] in toluene (3.7 mL) was added. The mixture was stirred at 80°C for 3 h. After reaching ambient temperature, the mixture was filtered through a short pad of silica, the filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 15:1) to give product **16** as a colorless oil (19.8 mg, 76%); the product contained traces (ca. 5%) of triphenylsilanol which was removed after the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.29 (t, *J* = 6.5 Hz, 1H), 3.69 (s, 3H), 2.52 (s, 4H), 1.64–1.57 (m, 2H), 1.39–1.28 (m, 4H), 0.90 (t, *J* = 5.0 Hz, 3H), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.4 (C), 82.9 (C), 82.1 (C), 63.1 (CH), 51.7 (CH_3), 38.6 (CH_2), 33.5 (CH_2), 27.5 (CH_2), 25.8 (3xCH_3), 22.3 (CH_2), 18.3 (C), 14.7 (CH_2), 14.0 (CH_3), −4.5 (CH_3), −5.0 (CH_3); IR (film) $\tilde{\nu}$ = 2955, 2930, 2858, 1742, 1463, 1437, 1361, 1250, 1198, 1165, 1079, 1004, 937, 834, 776 cm^{-1}; MS (EI) *m/z* (%): 256 (16), 255 (84), 170 (14), 169 (100), 139 (32), 89 (33), 75 (22), 73 (26); HRMS (ESI): *m/z*: calcd for $C_{17}H_{32}O_3Si$ + Na: 335.2013; found: 335.2013.

(*R*)-Gallicynoic Acid I (17). LiOH (18 mg, 0.75 mmol) was added to a suspension of compound **16** (45 mg *ca*. 114 µmol) in MeOH/1,4-dioxane/H_2O (7 mL, 4:2:1 *v/v/v*) and the resulting mixture was vigorously stirred for 3 h. For work up, the mixture was diluted with EtOAc (20 mL) and the organic phase washed with aq. HCl (0.5 M, 50 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL), the combined organic phases were dried over Na_2SO_4 and the solvent was evaporated. The residue was dissolved in THF (4 mL) and treated with TBAF in THF (1 M, 0.58 mL) at 0°C. The mixture was then stirred at ambient temperature for 16 h before it was diluted with EtOAc (20 mL) and washed with

aq. HCl (0.5 M, 20 mL). After extraction of the aqueous layer with EtOAc (2 x 20 mL), the combined organic phases were dried (Na_2SO_4) and evaporated, and the crude product purified by flash chromatography (hexanes/EtOAc/HOAc, 400:200:1 → 200:100:1) to give the title compound as a yellowish wax (12.8 mg, 61%). The optical purity of the product (95% ee) was determined via HPLC by comparison with a racemic sample prepared by the same route (250 mm *Chiralcel* OD-H, ∅ 4.6 mm, *n*-heptane/2-propanol/trifluoroacetic acid = 95:5:0.1 (*v*/*v*), 0.5 mL · min^{-1}, 2.2 MPa, 298 K, RI; t_R = 24.4 min (major), t_R = 26.5 min (minor)). $[\alpha]_D^{27}$ = +8.1 (*c* = 0.75, acetone; ref.[17]: $[\alpha]_D^{27}$ = +11.1); ^{1}H NMR (400 MHz, CD_3OD): δ = 4.24 (t, *J* = 6.6 Hz, 1H), 2.48–2.49 (m, 4H), 1.54–1.68 (m, 2H), 1.30–1.45 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ = 175.7, 83.8, 83.1, 62.9, 38.9, 34.5, 28.6, 23.5, 15.4, 14.4; IR (ATR) $\tilde{\nu}$ = 3395, 2956, 2930, 2859, 1686, 1430, 1291, 1214, 1148, 1052, 996 cm^{-1}; MS (EI): *m/z* (%): 183 (<1) [M^+−H], 151 (5), 128 (8), 127 (100), 110 (7), 109 (98), 99 (12), 96 (9), 95 (5), 82 (6), 81 (19), 57 (12), 55 (16), 53 (28), 43 (15), 41 (18), 39 (12), 29 (17), 27 (14); HRMS (CI): calcd for [$C_{10}H_{16}O_3$ + H^+]: 185.1178; found: 185.1176. The recorded analytical and spectral data agree with those published in the literature.[17]

Nitrogen Transfer Reactions

Oxidative Conversion of 4-Methoxybenzaldehyde to 4-Methoxybenzonitrile: A 5 mL microwave vial was charged with a solution of **9** (1.0 g, 2.23 mmol) in CH_3CN (5 mL), 4-methoxybenzaldehyde (276 mg, 2.03 mmol), Me_3SiCl (243 mg, 2.23 mmol) and DABCO (250 mg, 2.23 mmol), and sealed under argon. This mixture was exposed to microwave irradiation (Smith Creator reactor, Personal Chemistry, Konstanz) while stirring for 2 h at 160 °C (13 bar). After reaching ambient temperature, the mixture was diluted with EtOAc (40 mL), the organic layer was washed with aq. HCl (1 M, 50 mL), aq. sat. $NaHCO_3$ (50 mL) and brine (50 mL), dried over Na_2SO_4 and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 9:1) gave 4-methoxybenzonitrile as a white solid (197 mg, 73%). This nitrile was identical in all regards with a commercial sample.

Representative Procedure for the Conversion of Acyl Chlorides to Nitriles. 4-Methoxybenzoyl chloride (370 mg, 2.17 mmol) was added to a solution of complex **9** (972 mg, 2.17 mmol) in CH_3CN (10 mL) under Ar and the resulting mixture stirred at ambient temperature for 16 h before EtOAc (40 mL) was added. The organic layer was successively washed with aq. HCl (1 M, 50 mL), sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexane/EtOAc, 9:1) to give 4-methoxybenzonitrile as a white solid (269 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H). This nitrile and all other nitriles prepared by this method were identical in all regards to authentic commercial samples. Characteristic data are compiled below:

Benzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.53 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H); **4-Chlorobenzonitrile:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H); **2,4,6-Trimethylbenzonitrile:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 3H), 2.46 (s, 6H), 2.31 (s, 3H); **3-(Trifluoromethyl)benzonitrile:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.85-7.82 (m, 2H), 7.63 (t, *J* = 7.9 Hz, 1H); **2-Nitrobenzonitrile:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37-8.32 (m, 1H), 7.96-7-91 (m,

1H), 7.87-7.82 (m, 2H); **1-Adamantanecarbonitrile:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (br, 9H), 1.74 (br, 6H).

Crystal Structure Determination

Definitions:

$R_{int} = \Sigma \mid F_o^2 - F_o^2(\text{mean}) \mid / \Sigma [F_o^2]$; $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$

$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{½}$

X-ray Crystal Structure Analysis of 11·C_7H_8: $[C_{59}H_{50}MoN_2O_3Si_3,]\cdot[C_7H_8]$, M_r = 1107.35 g · mol^{-1}, light yellow prism, crystal size 0.22 x 0.12 x 0.10 mm^3, triclinic, space group *P1̄*, a = 13.0697(2) Å, b = 13.5755(3) Å, c = 18.2169(3) Å, α = 87.206(1)°, β = 77.527(1)°, γ = 64.003(1)°, V = 2832.69(9) Å^3, T = 100 K, Z = 2, D_{calc} = 1.298 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.343 mm^{-1}, Gaussian absorption correction (T_{min} = 0.86, T_{max} = 0.94), Enraf-Nonius KappaCCD diffractometer, 2.91 < θ < 31.59, 86247 measured reflections, 18892 independent reflections (R_{int} = 0.054), 14883 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0586 [$I > 2\sigma(I)$], wR_2 = 0.1565, 677 parameters, S = 1.048. The structure contains disordered toluene solute. Disordered atoms were refined with isotropic atomic displacement parameters. Hydrogen atoms were not included on disordered atoms, otherwise H atoms riding. Residual electron density +4.4 / −1.6 e Å^{-3} (0.91/0.68 Å from Mo1). **CCDC 726076**.

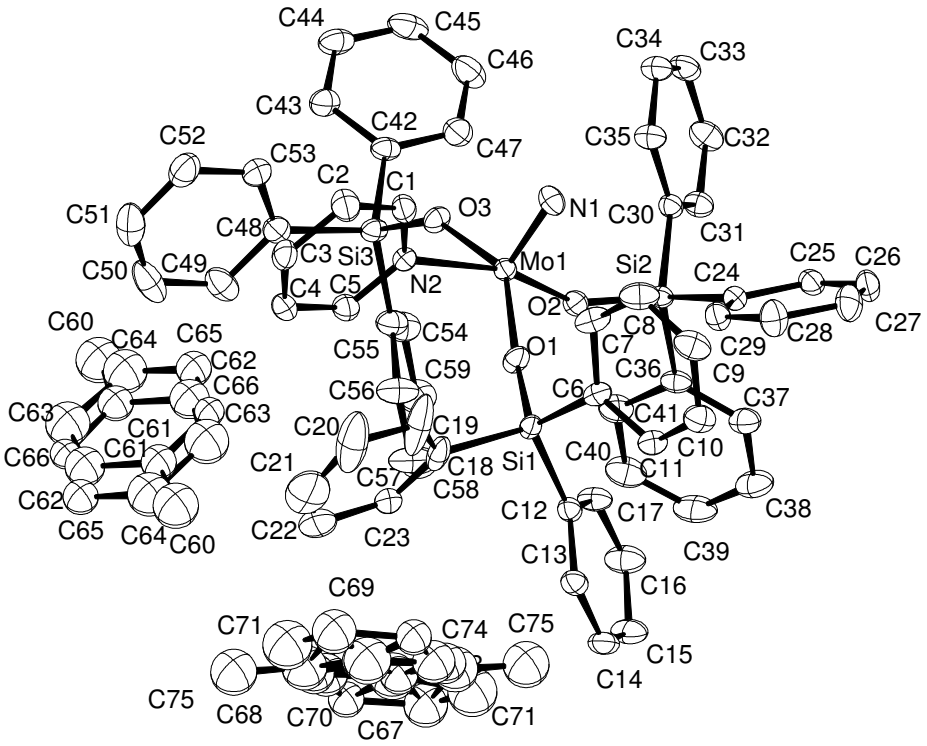
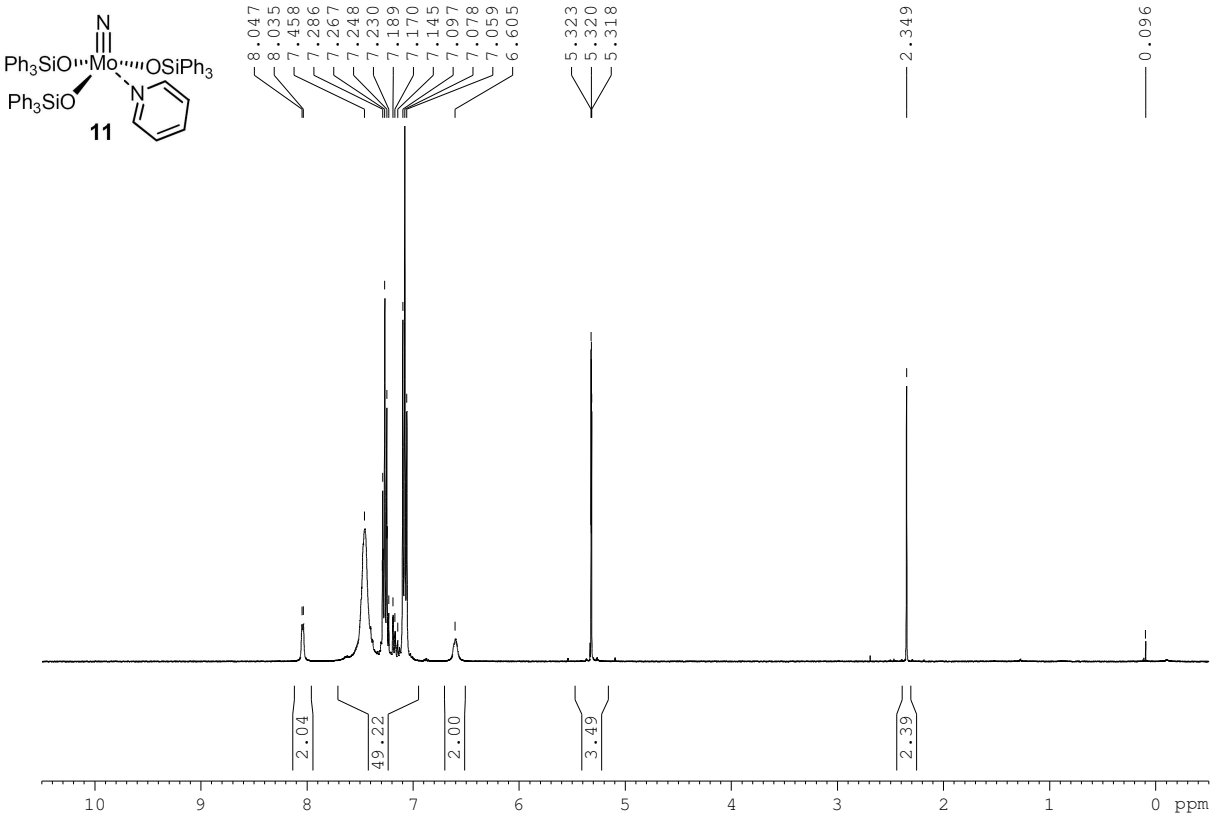


Figure S-2. Molecular structure of **11**·C_7H_8, showing the disordered solute toluene about the centers of symmetry in the crystal.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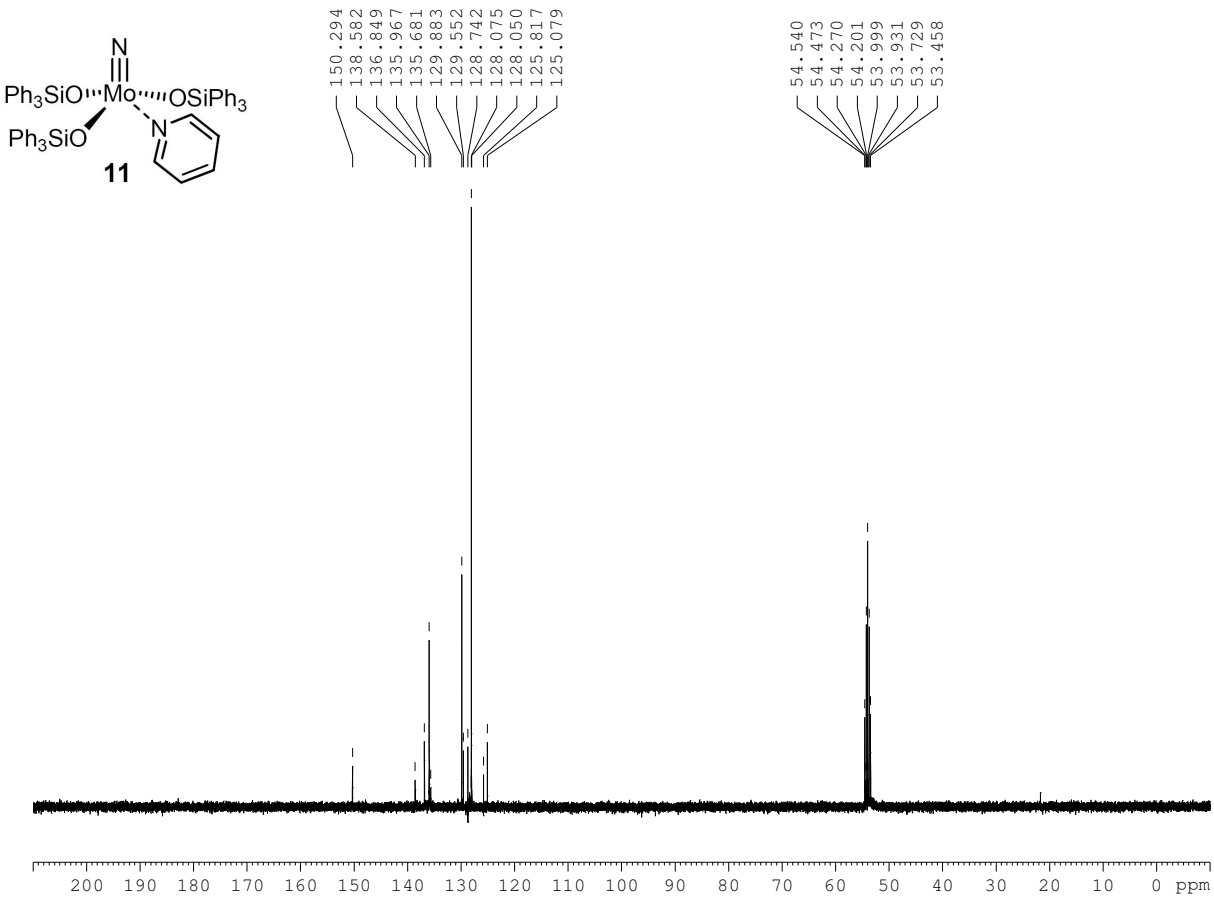
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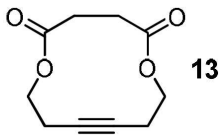
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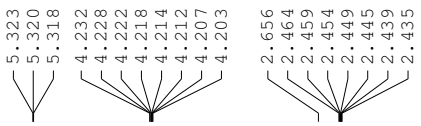
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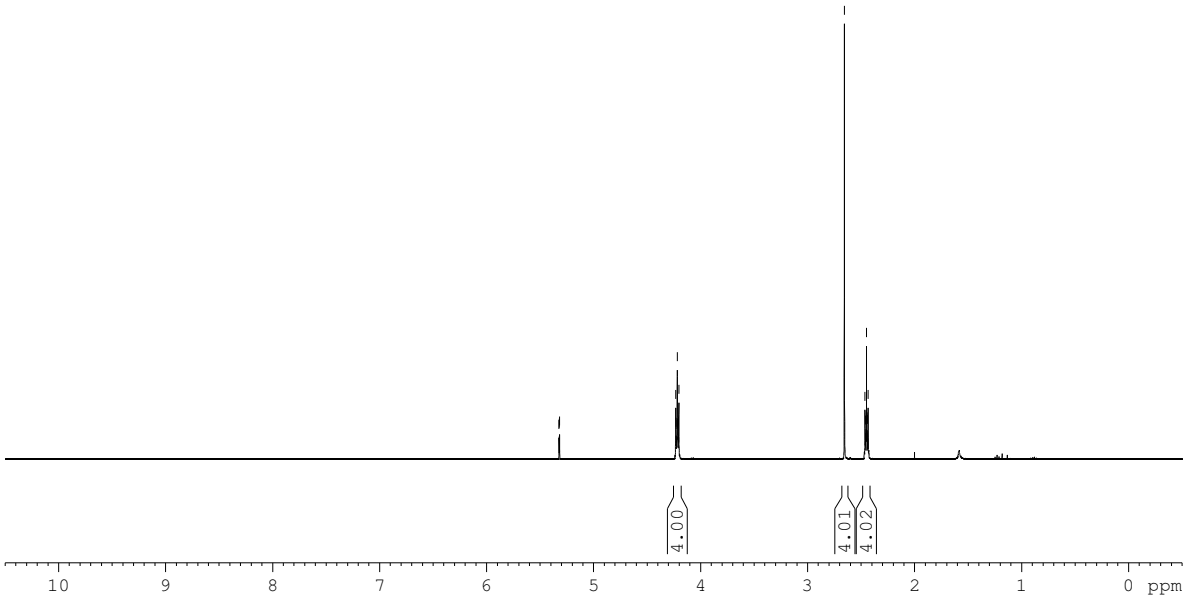
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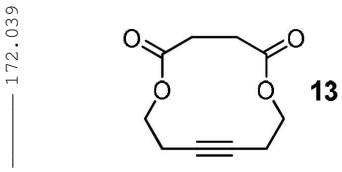
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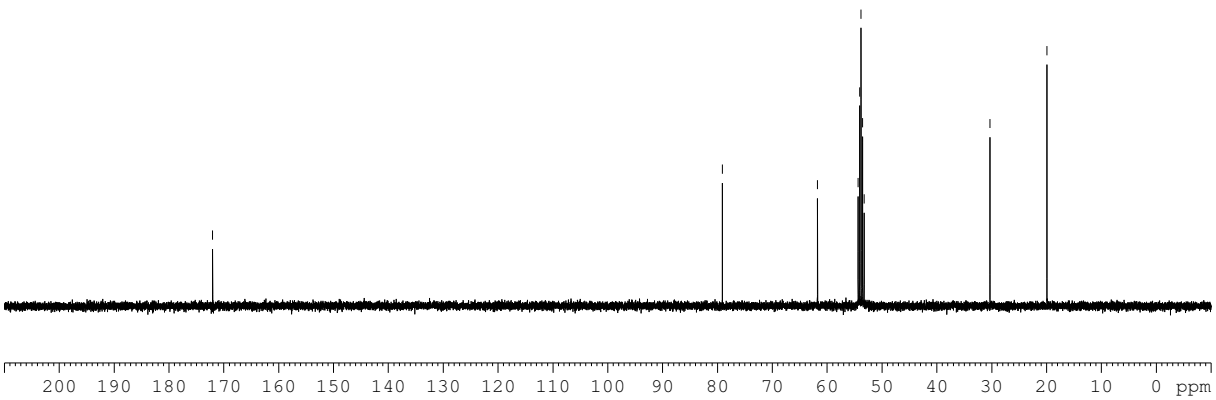
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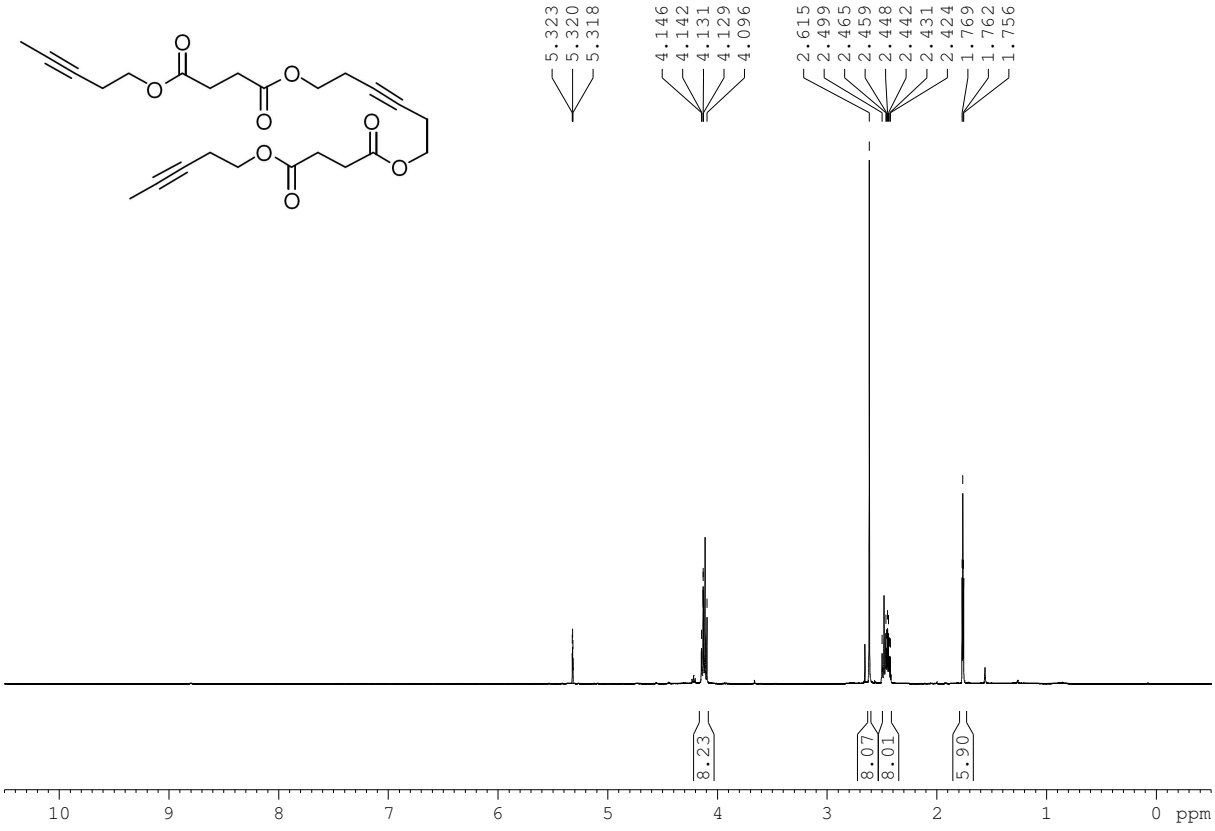
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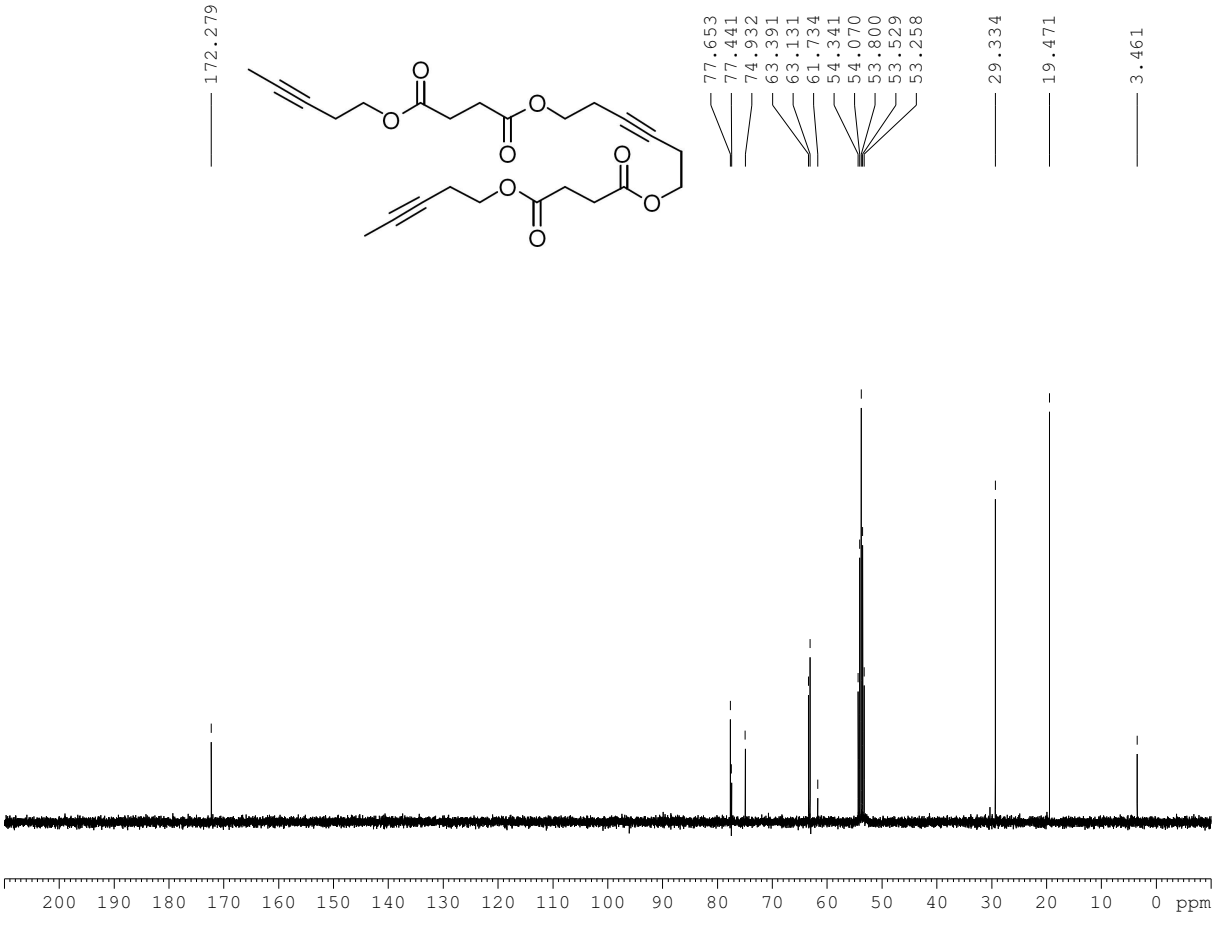
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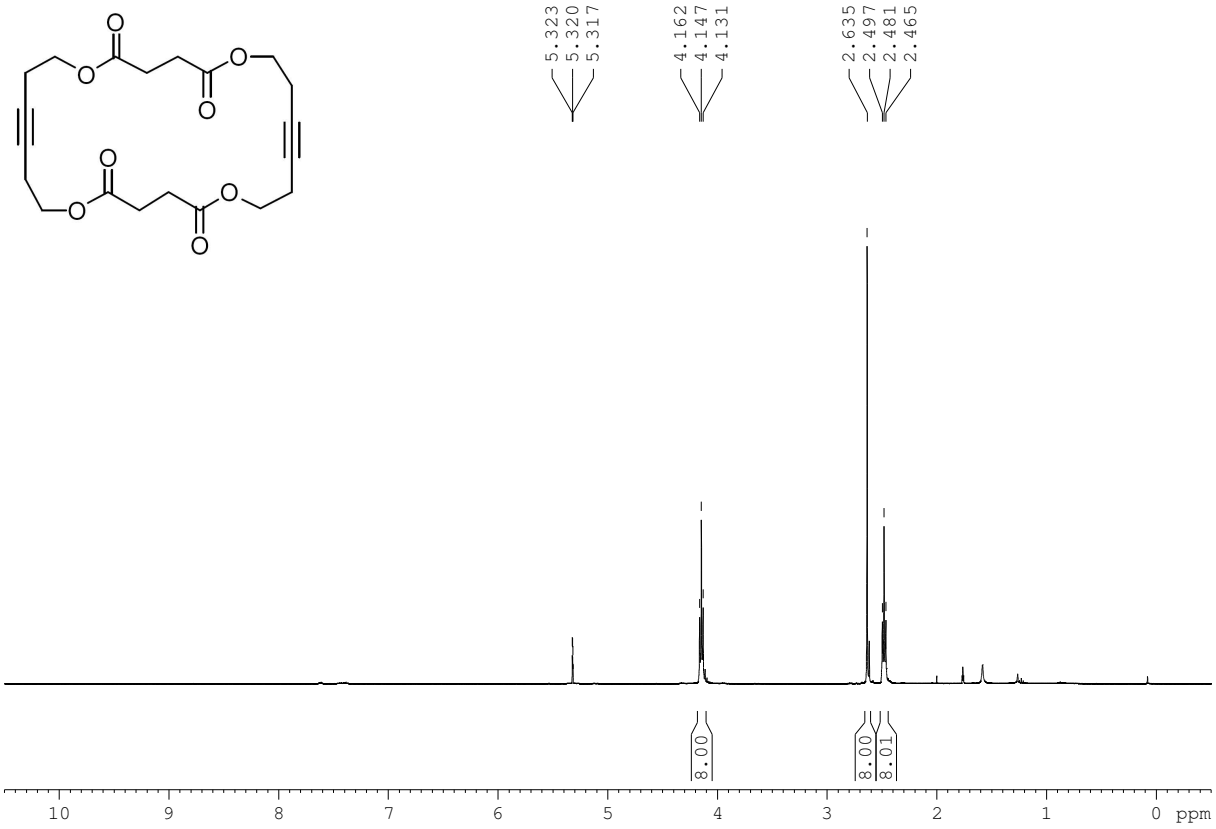
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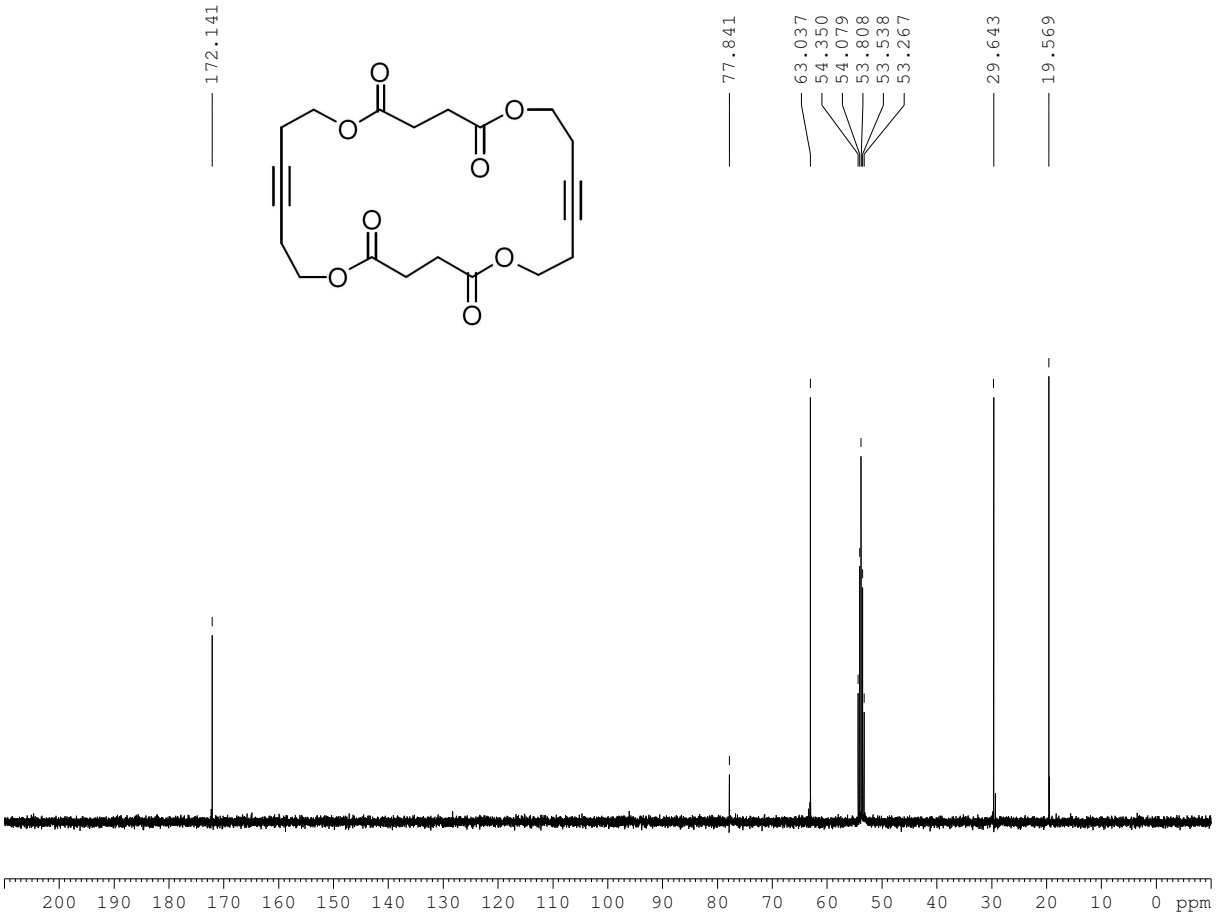
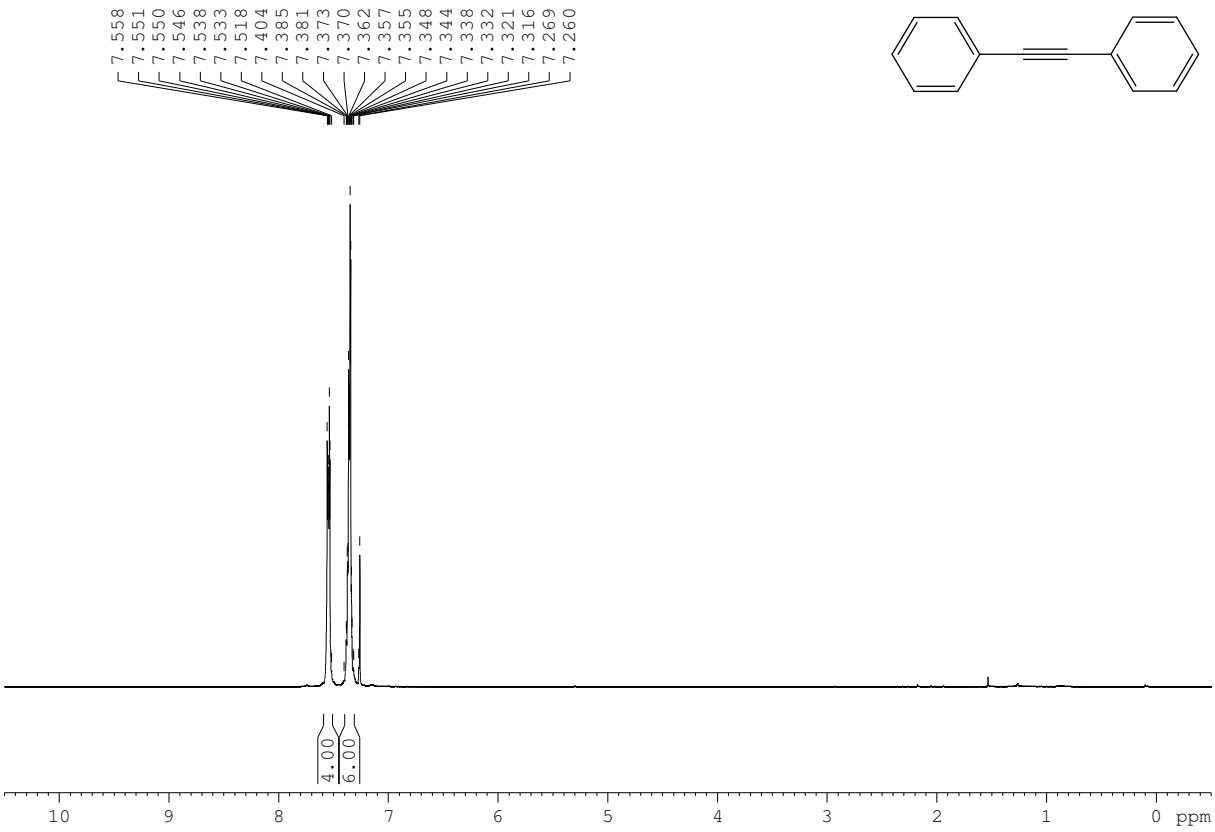
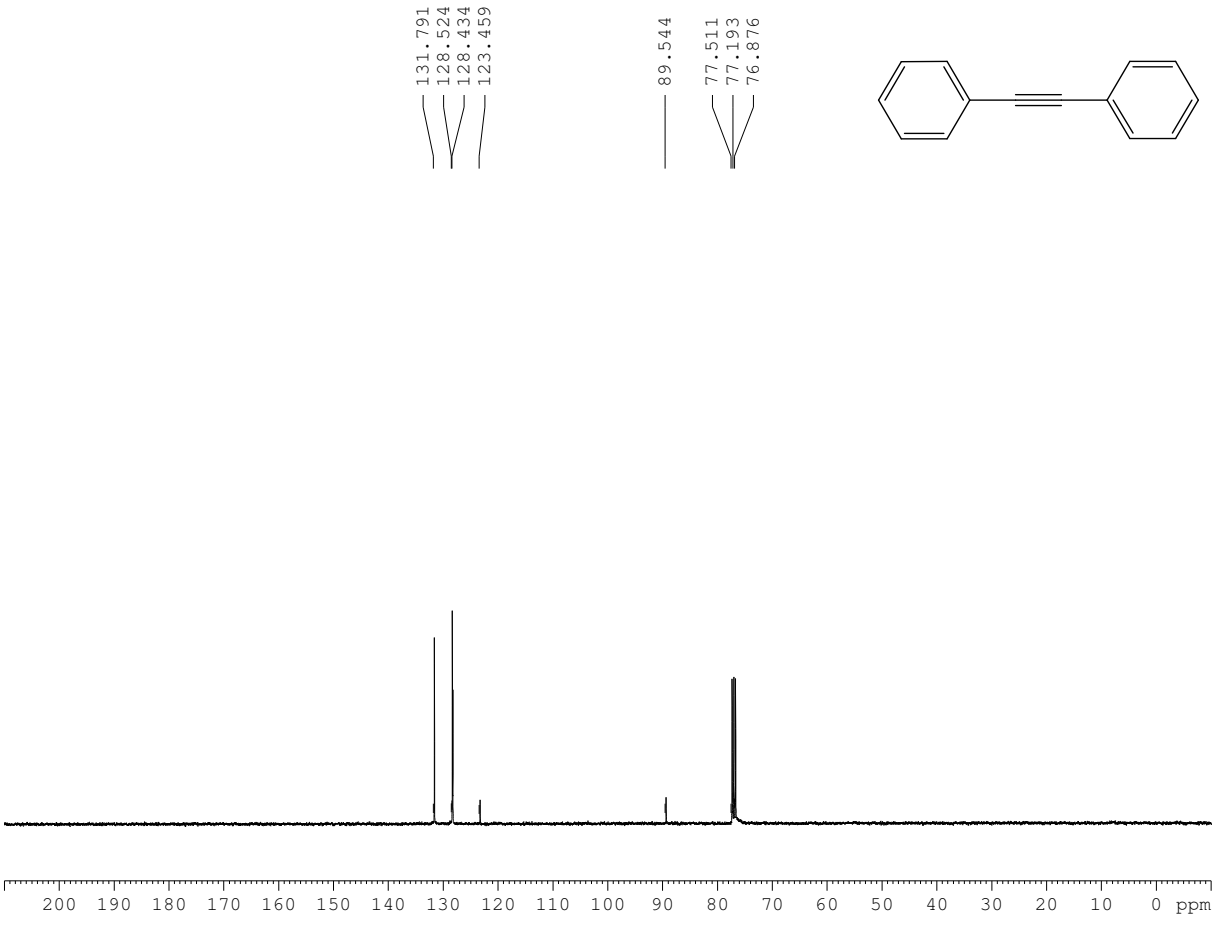
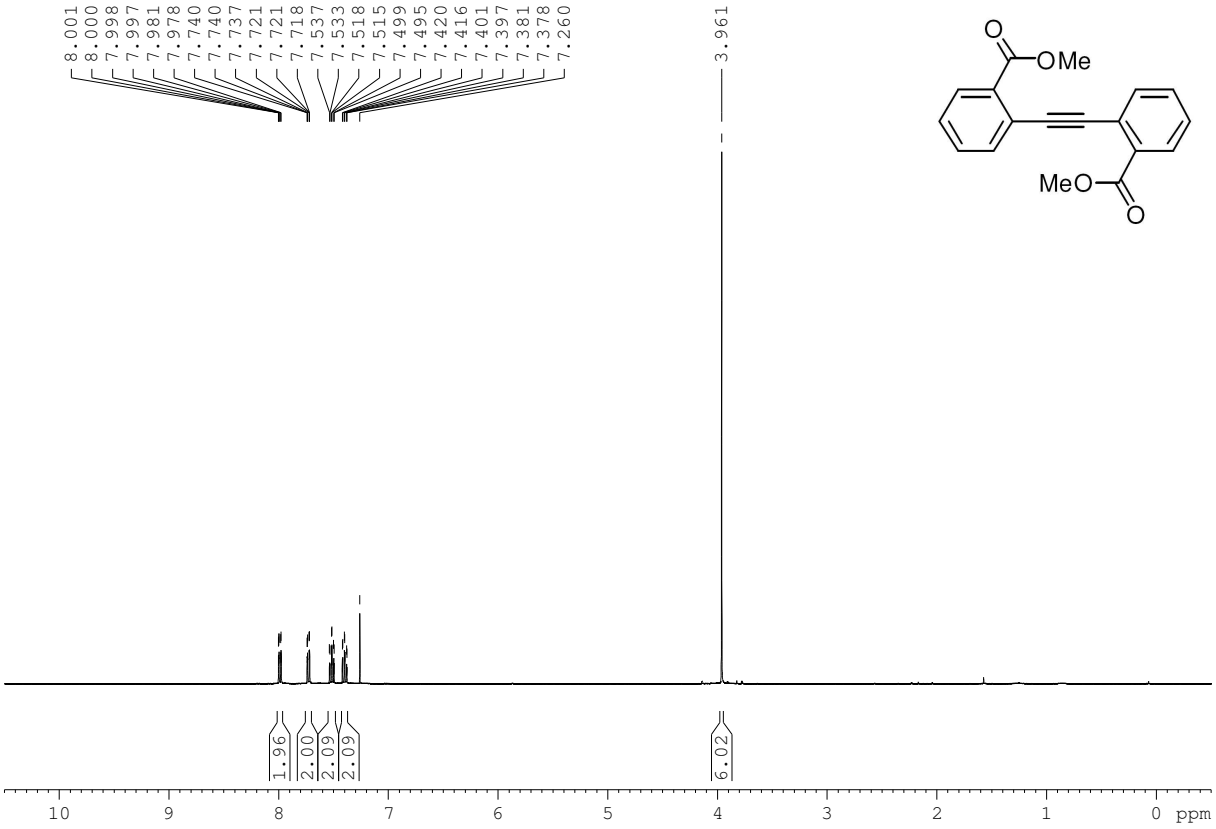

172.141
77.841
63.037
54.350
54.079
53.808
53.538
53.267
29.643
19.569
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.558
7.551
7.550
7.546
7.538
7.533
7.518
7.404
7.385
7.381
7.373
7.370
7.362
7.357
7.355
7.348
7.344
7.338
7.332
7.321
7.316
7.269
7.260
4.00
6.00
10
9
8
7
6
5
4
3
2
1
0 ppm


131.791
128.524
128.434
123.459
89.544
77.511
77.193
76.876
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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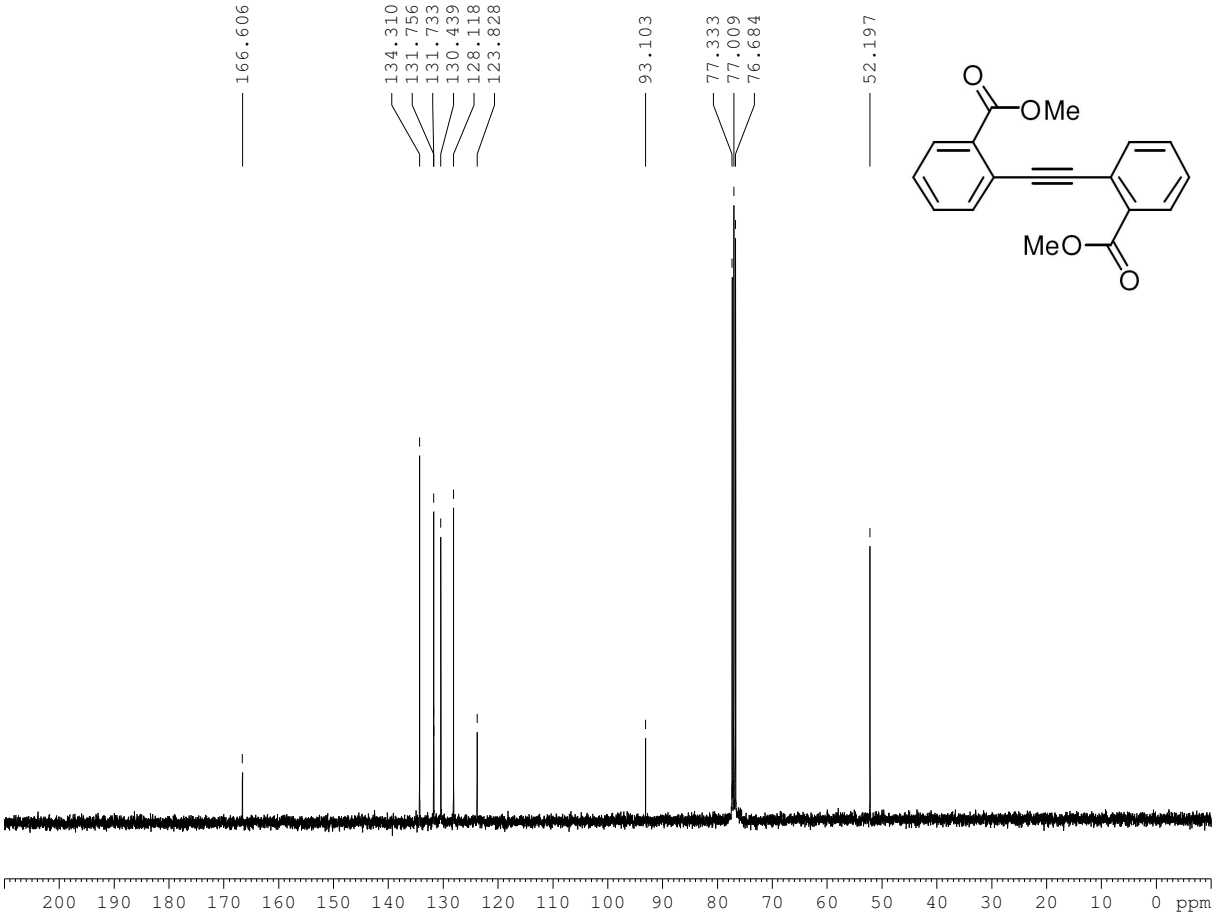
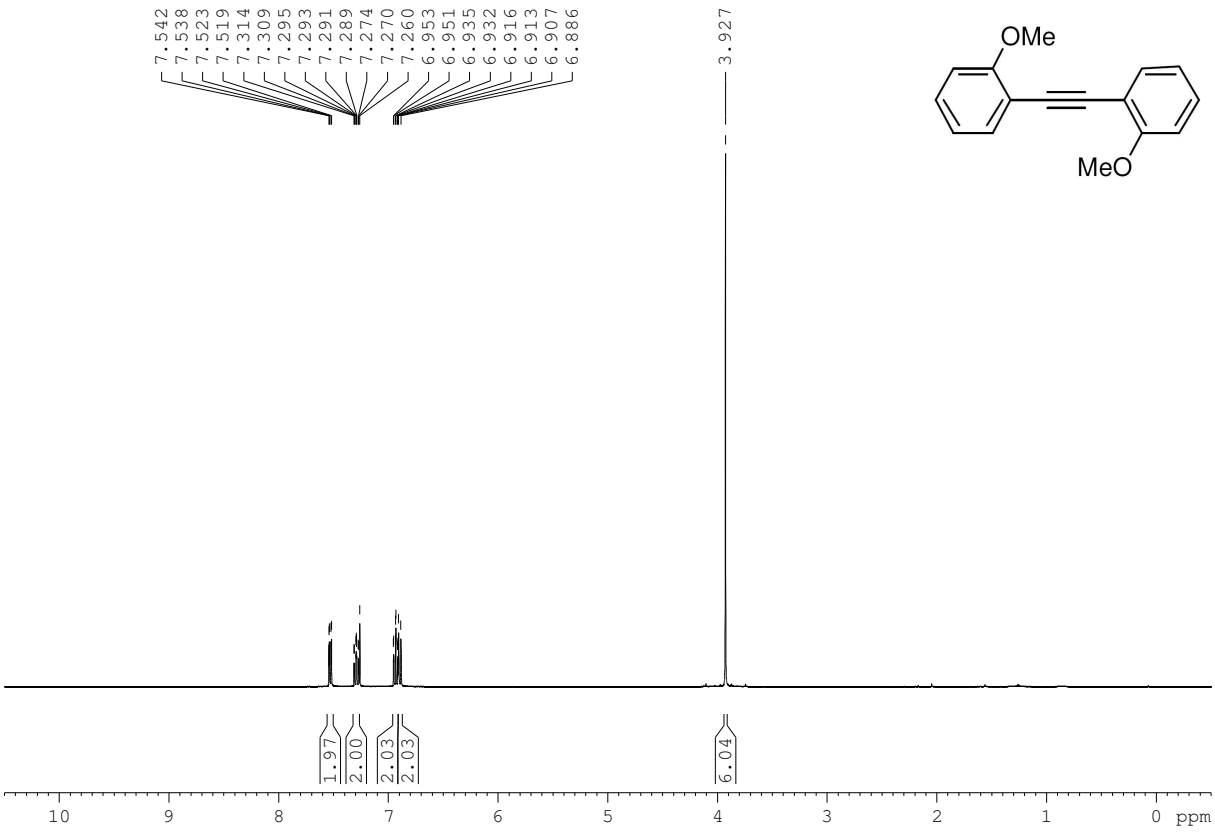
8.000
7.998
7.997
7.981
7.978
7.740
7.740
7.737
7.721
7.721
7.718
7.537
7.533
7.518
7.515
7.499
7.495
7.420
7.416
7.401
7.397
7.381
7.378
7.260
3.961
OMe
MeO
O
1.96
2.00
2.09
2.09
6.02
10 9 8 7 6 5 4 3 2 1 0 ppm


166.606
134.310
131.756
131.733
130.439
128.118
123.828
93.103
77.333
77.009
76.684
52.197
OMe
MeO
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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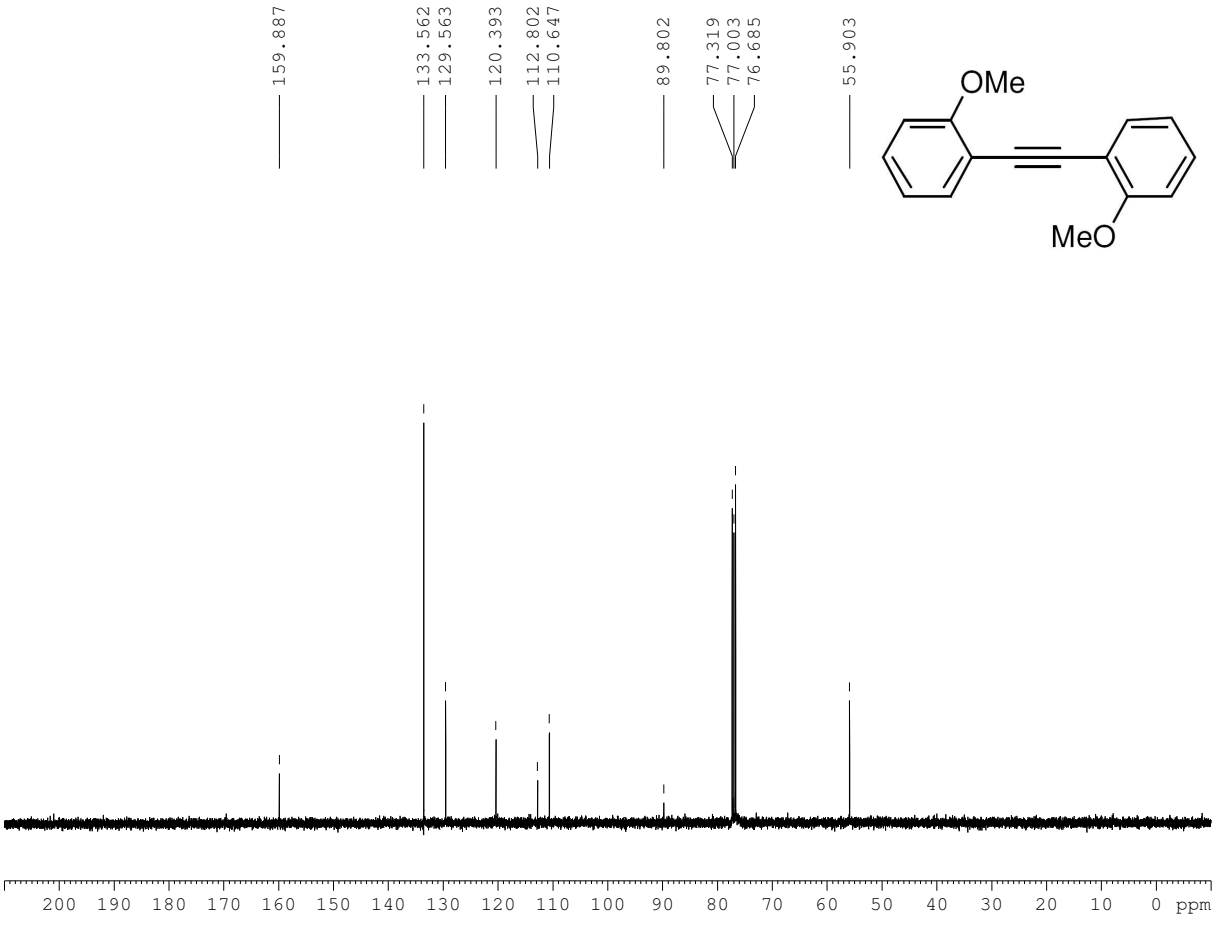
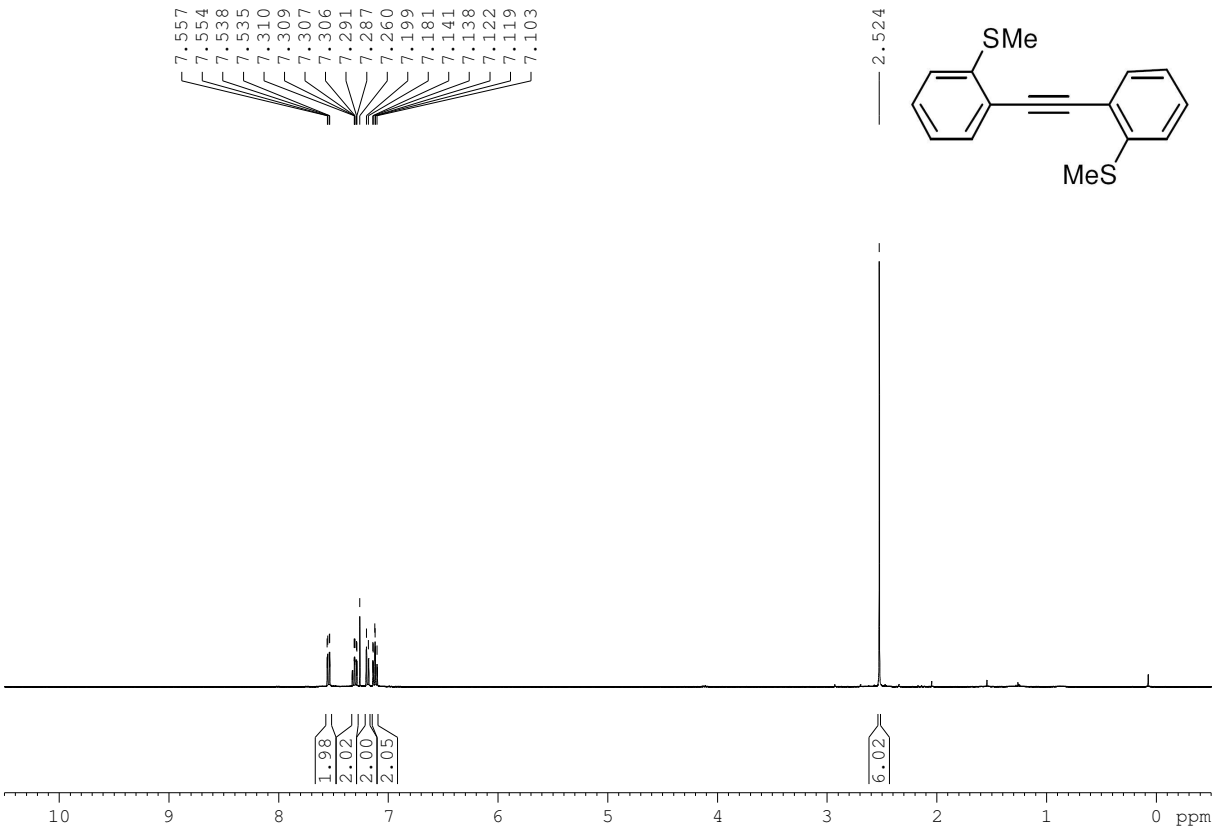
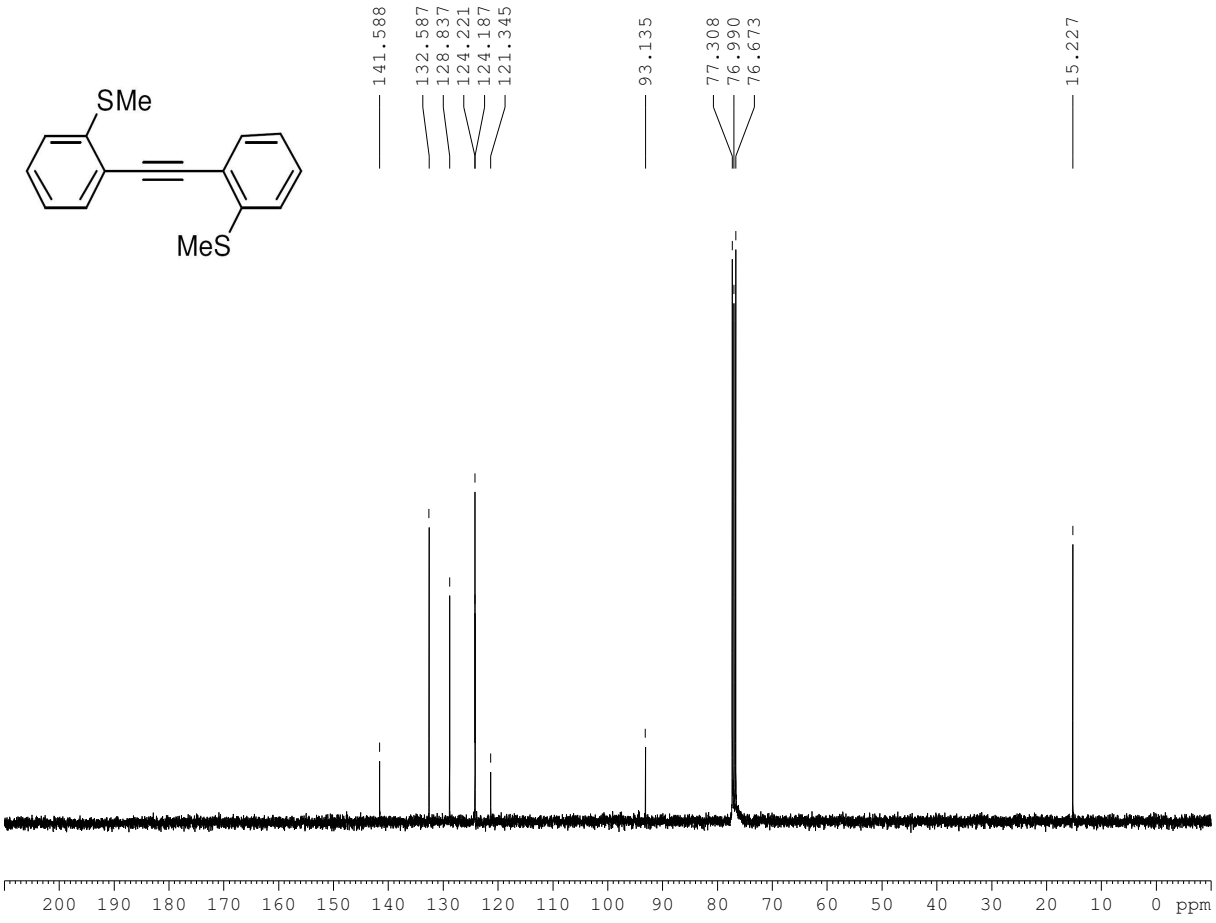
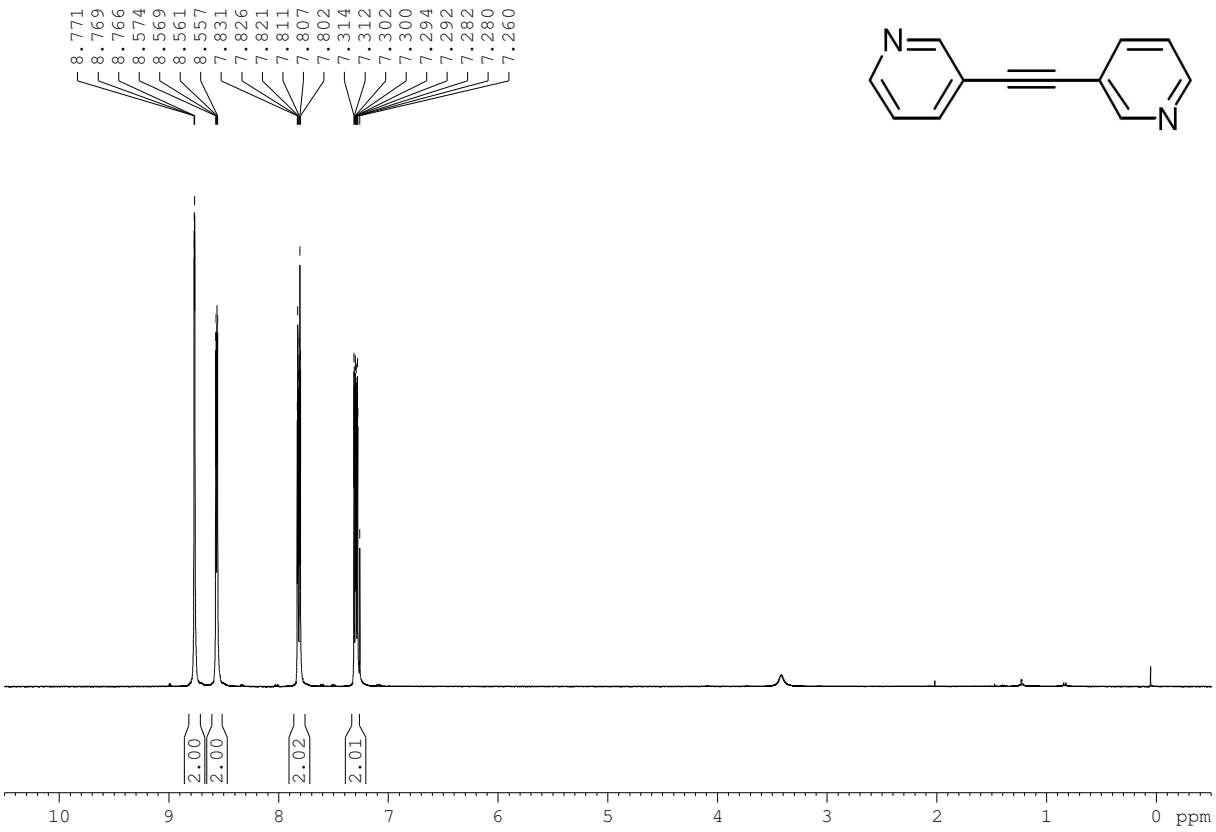
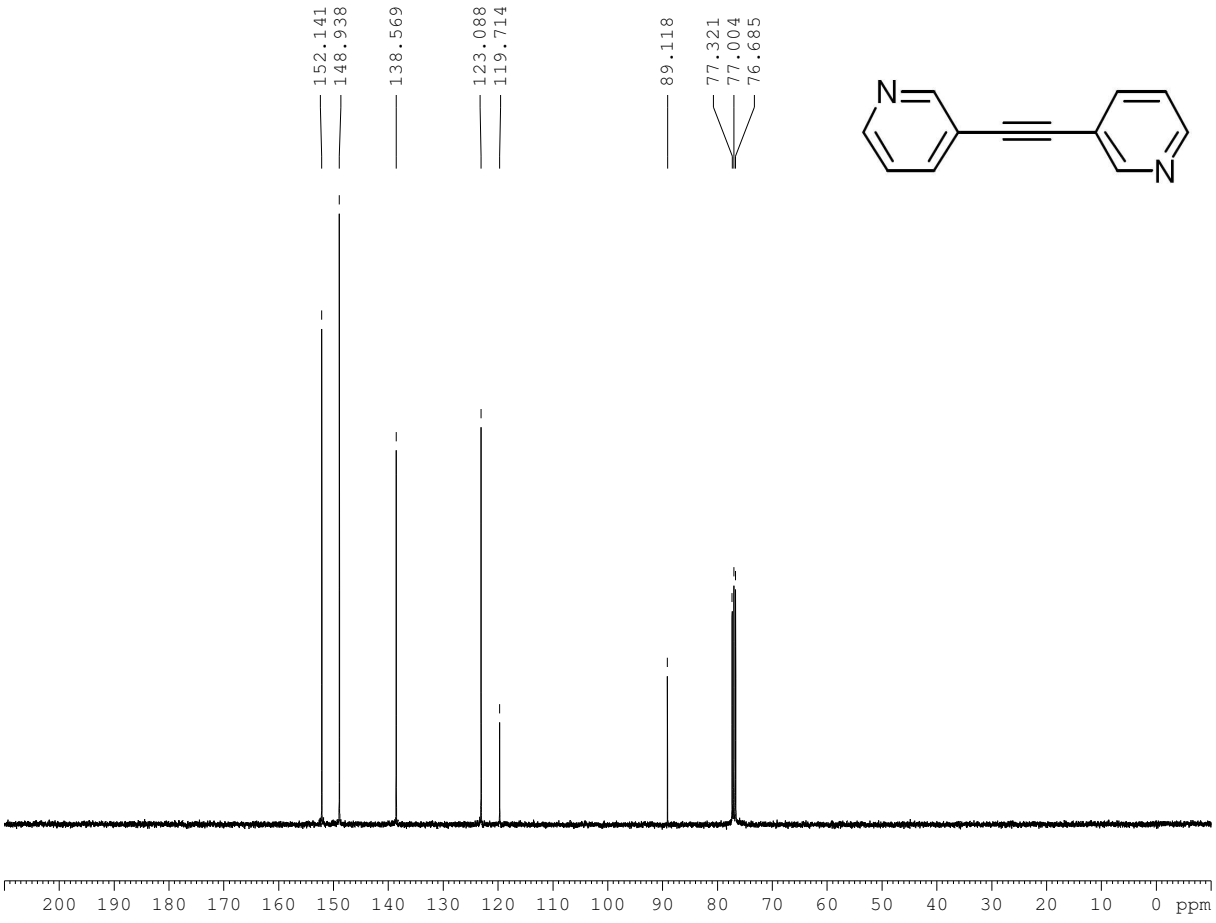
7.538
7.523
7.519
7.314
7.309
7.295
7.293
7.291
7.289
7.274
7.270
7.260
6.953
6.951
6.935
6.932
6.916
6.913
6.907
6.886
3.927
OMe
MeO
1.97
2.00
2.03
2.03
6.04
10
9
8
7
6
5
4
3
2
1
0 ppm

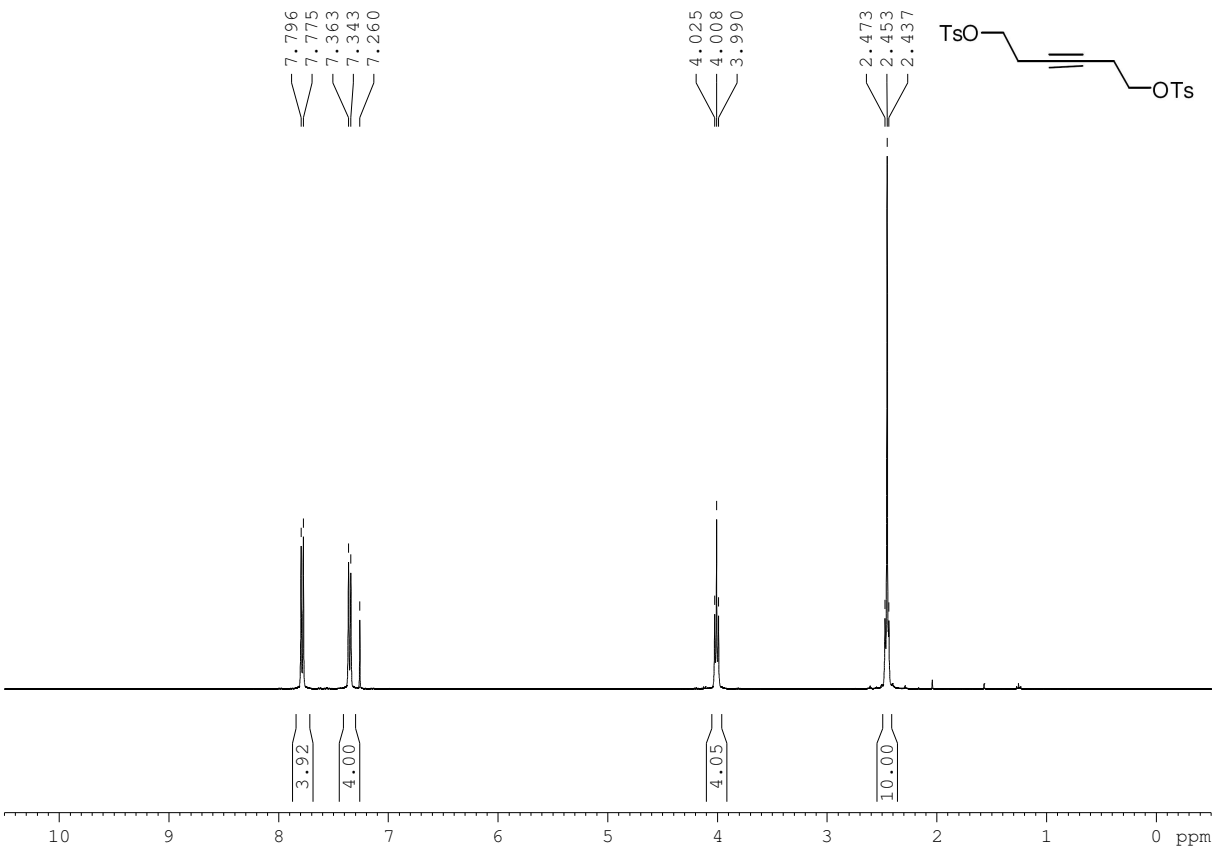

159.887
133.562
129.563
120.393
112.802
110.647
89.802
77.319
77.003
76.685
55.903
OMe
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

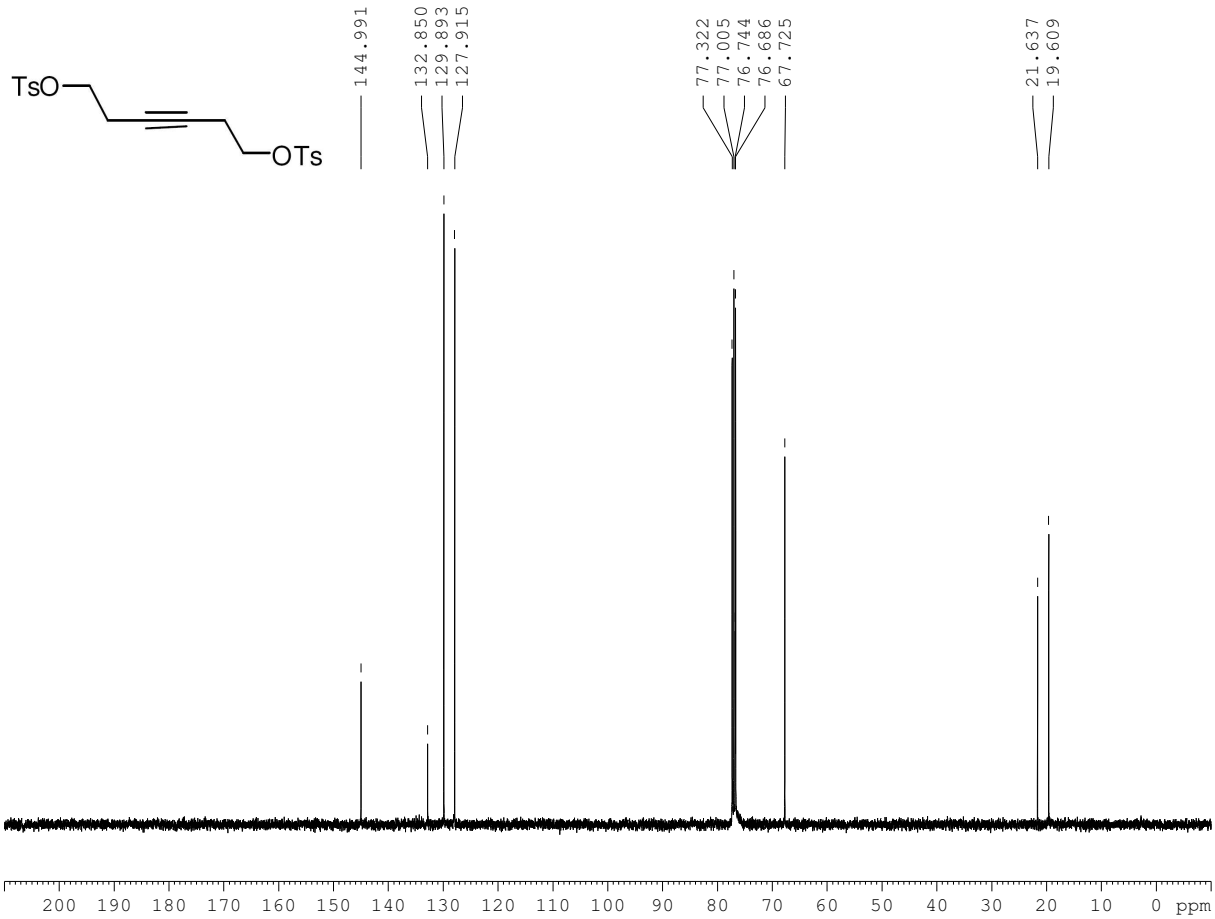

7.557
7.554
7.538
7.535
7.310
7.309
7.307
7.306
7.291
7.287
7.260
7.199
7.181
7.141
7.138
7.122
7.119
7.103
2.524
SMe
MeS
1.98
2.02
2.00
2.05
6.02
10
9
8
7
6
5
4
3
2
1
0 ppm

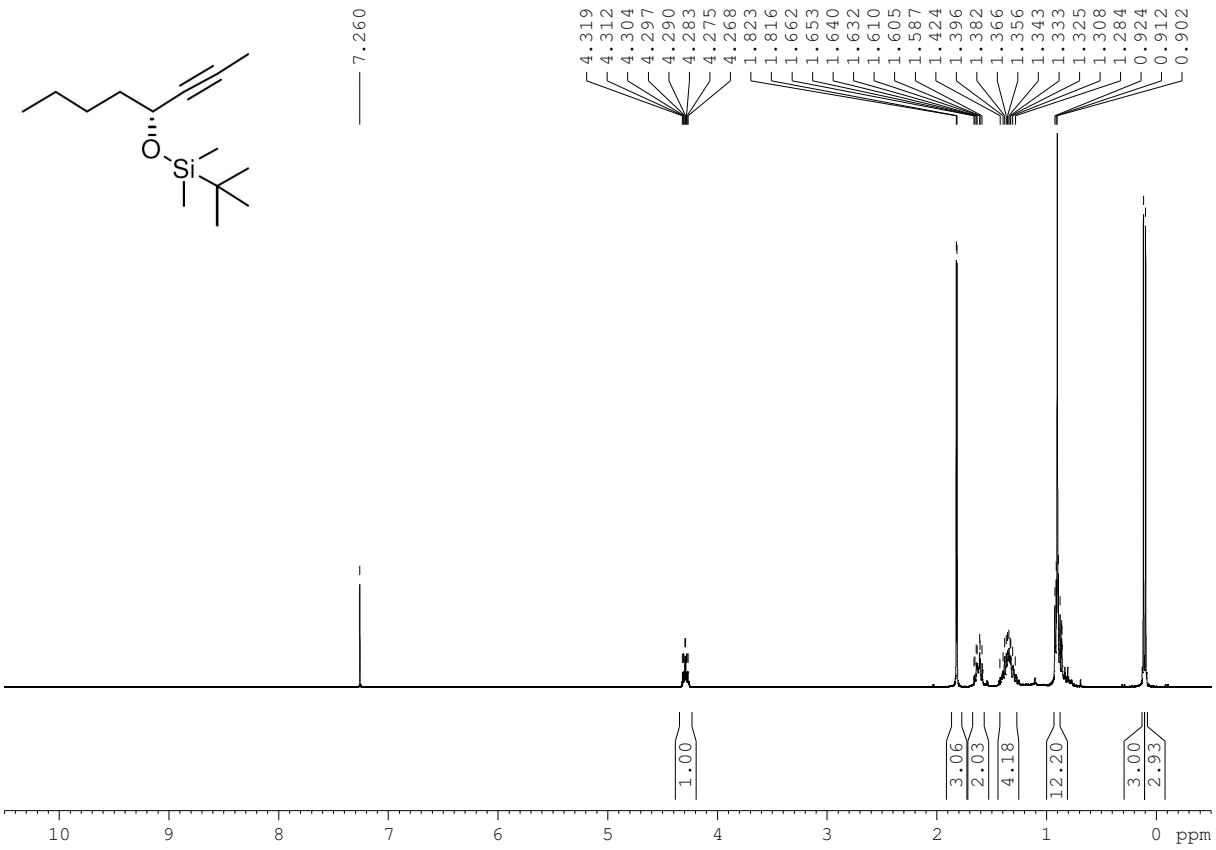

SMe
MeS
141.588
132.587
128.837
124.221
124.187
121.345
93.135
77.308
76.990
76.673
15.227
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

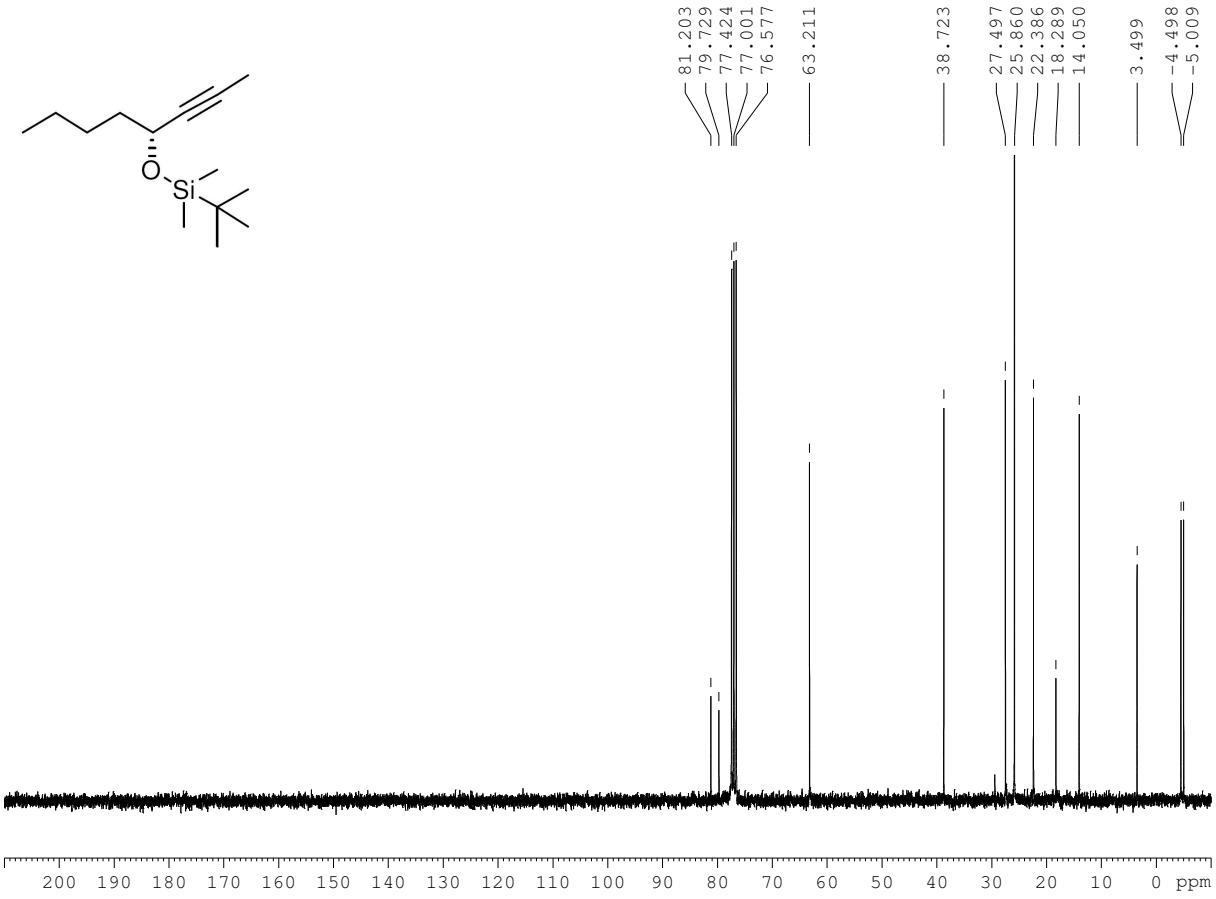

8.771
8.769
8.766
8.574
8.569
8.561
8.557
7.831
7.826
7.821
7.811
7.807
7.802
7.314
7.312
7.302
7.300
7.294
7.292
7.282
7.280
7.260
N
N
2.00
2.00
2.02
2.01
10
9
8
7
6
5
4
3
2
1
0 ppm

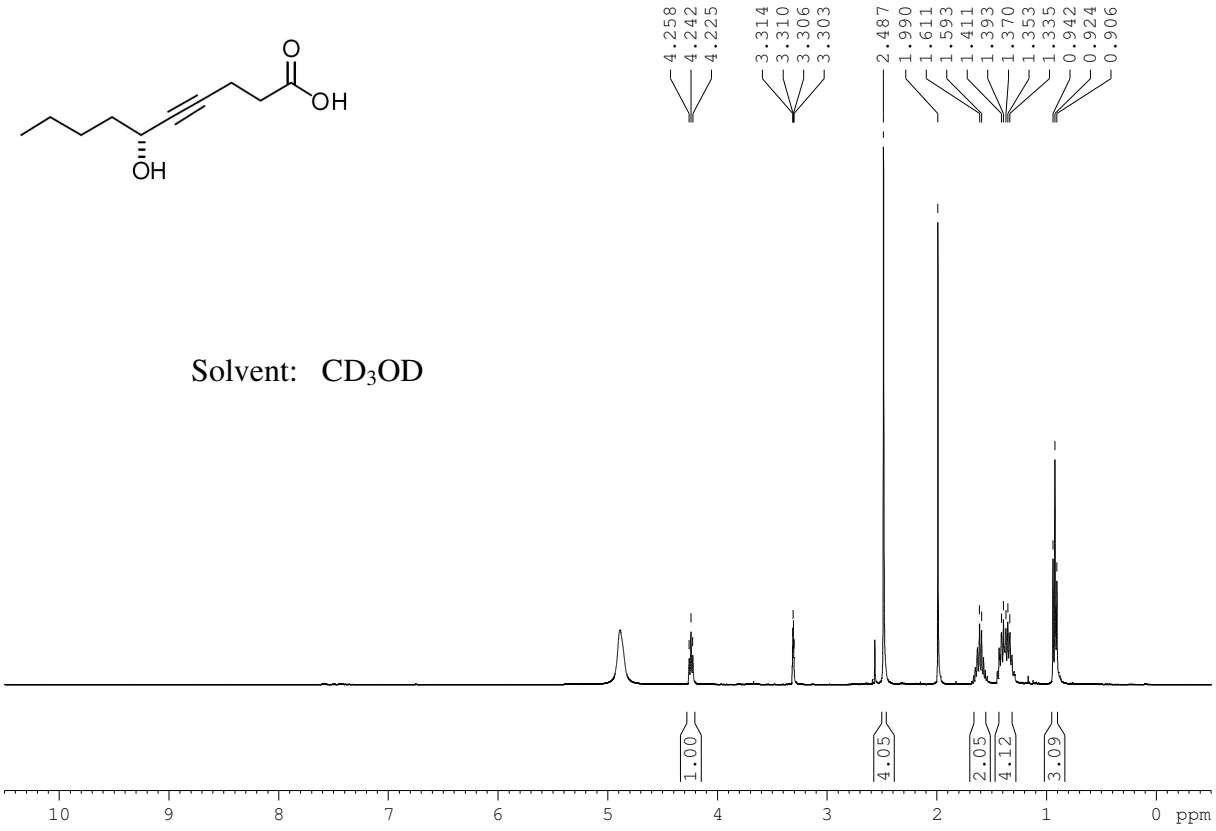

152.141
148.938
138.569
123.088
119.714
89.118
77.321
77.004
76.685
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.796
7.775
7.363
7.343
7.260
4.025
4.008
3.990
2.473
2.453
2.437
TsO
OTs
3.92
4.00
4.05
10.00
10
9
8
7
6
5
4
3
2
1
0 ppm

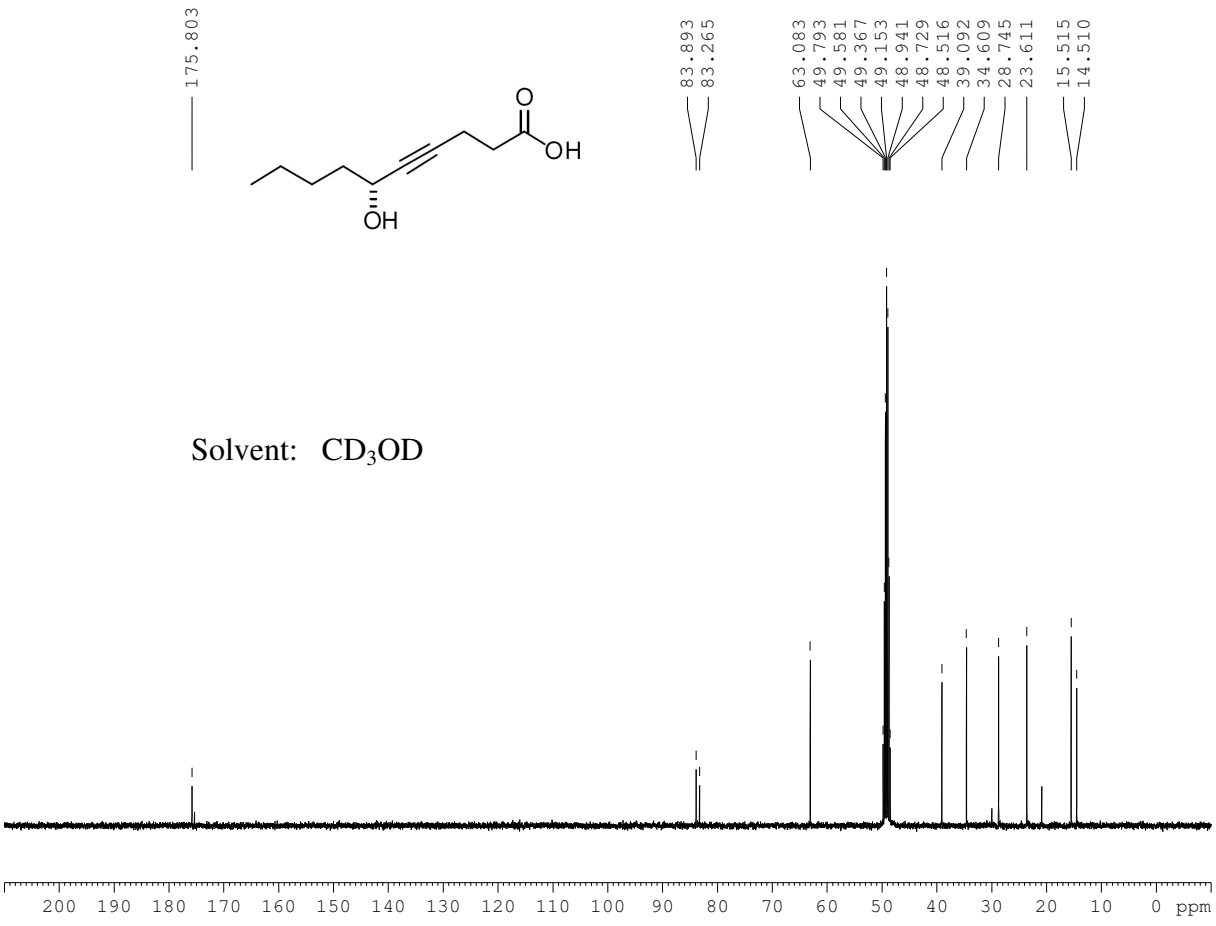

TsO
OTs
144.991
132.850
129.893
127.915
77.322
77.005
76.744
76.686
67.725
21.637
19.609
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
4.319
4.312
4.304
4.297
4.290
4.283
4.275
4.268
1.823
1.816
1.662
1.653
1.640
1.632
1.610
1.605
1.587
1.424
1.396
1.382
1.366
1.356
1.343
1.333
1.325
1.308
1.284
0.924
0.912
0.902
1.00
3.06
2.03
4.18
12.20
3.00
2.93
10
9
8
7
6
5
4
3
2
1
0 ppm

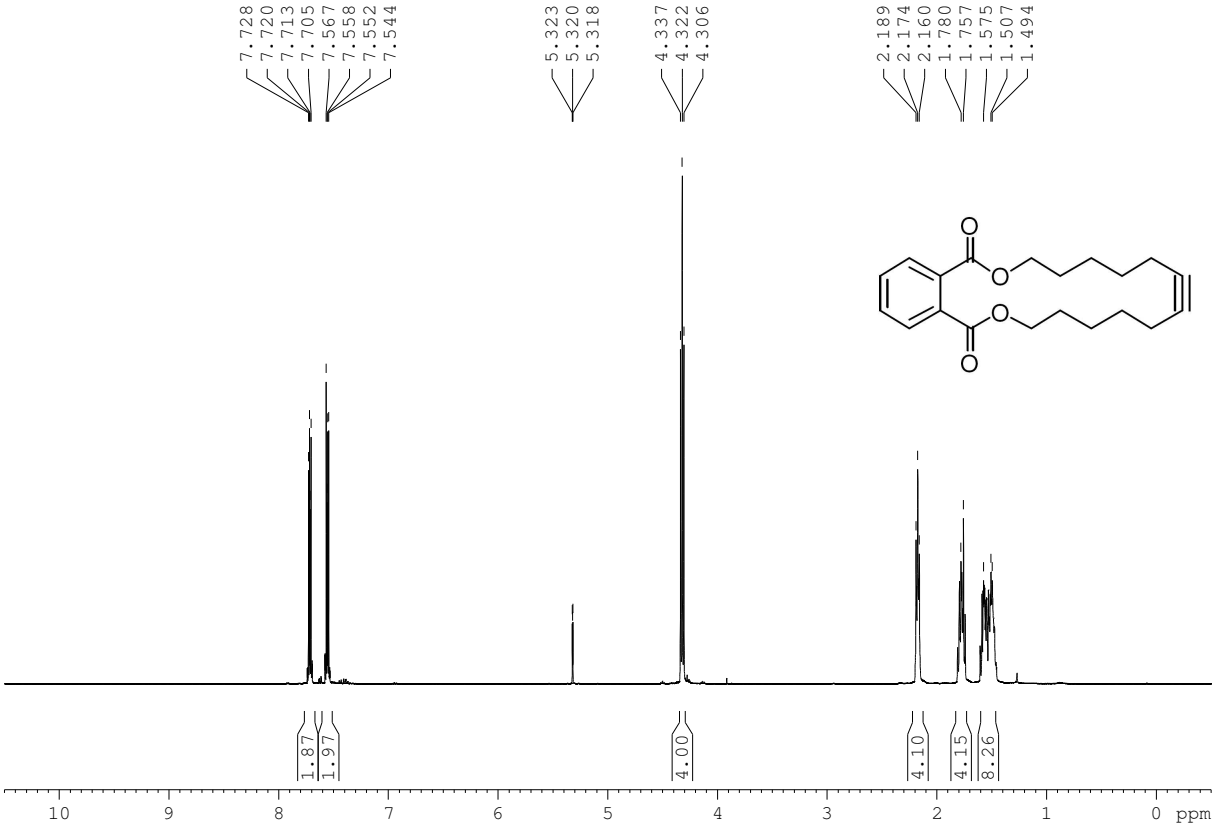

81.203
79.729
77.424
77.001
76.577
63.211
38.723
27.497
25.860
22.386
18.289
14.050
3.499
-4.498
-5.009
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

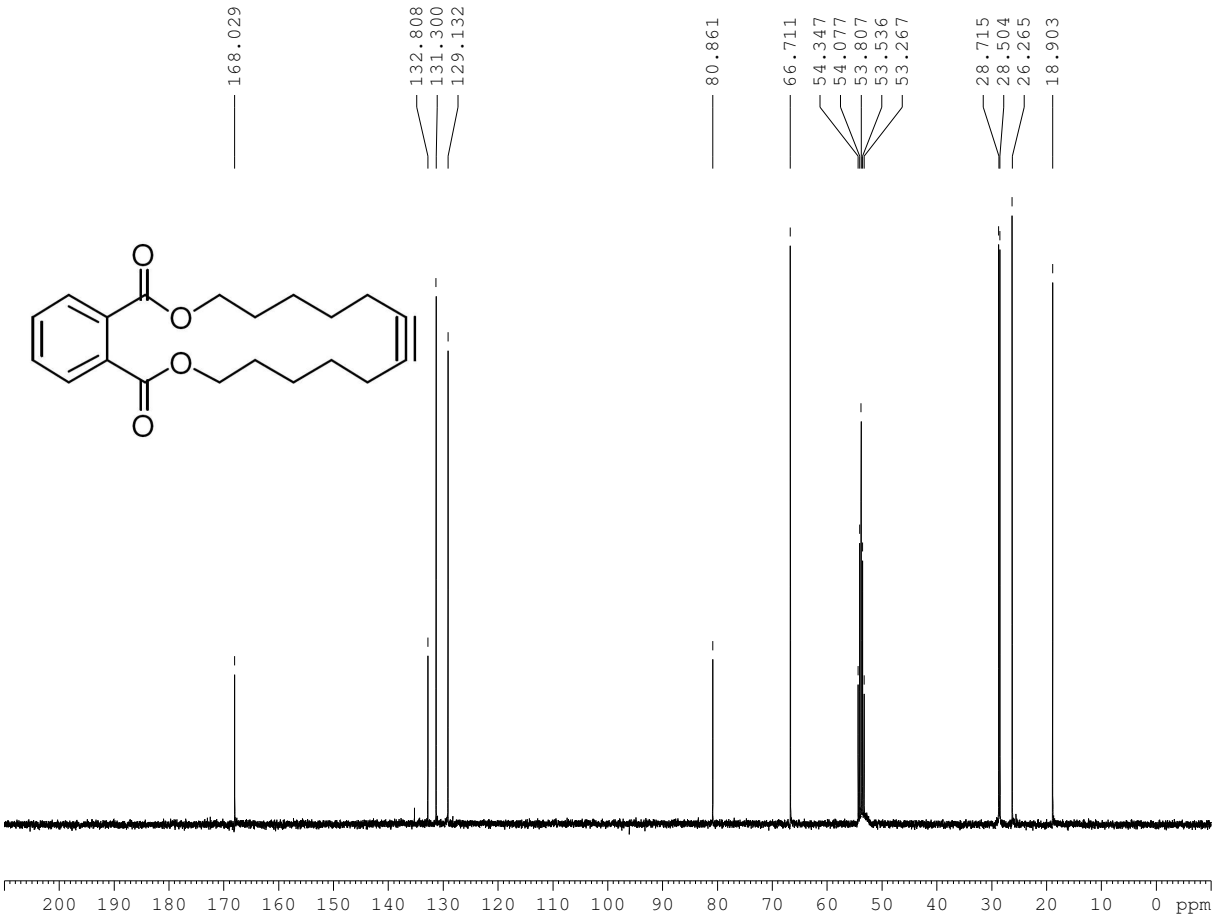


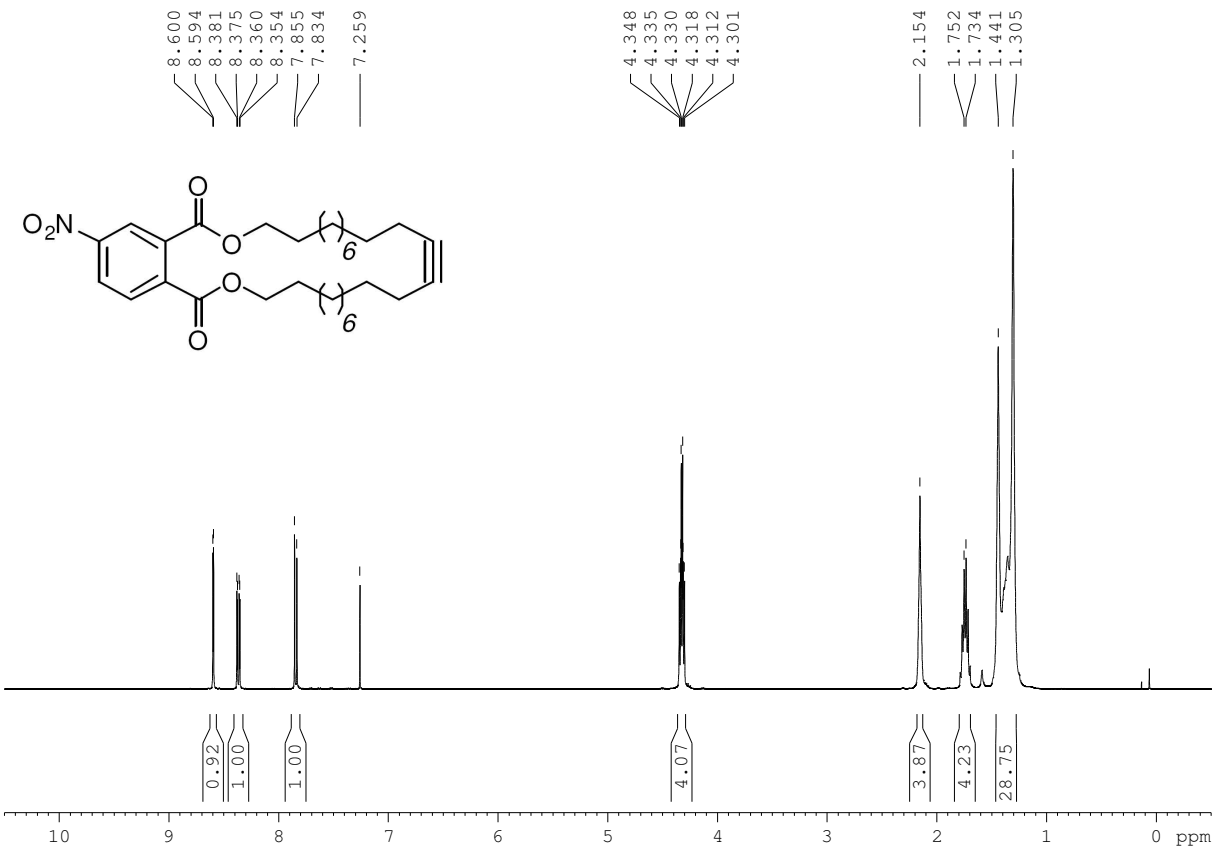
Solvent: CD_3OD

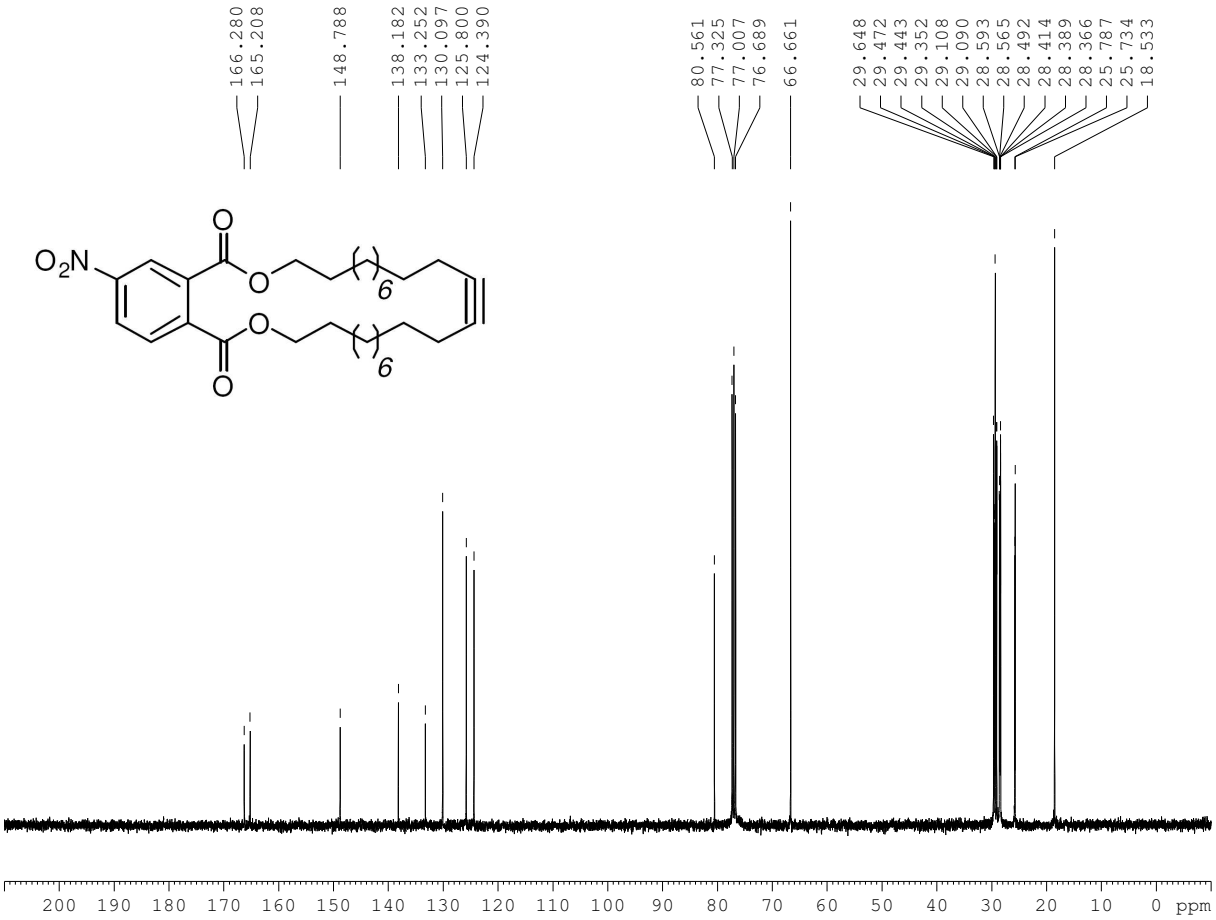


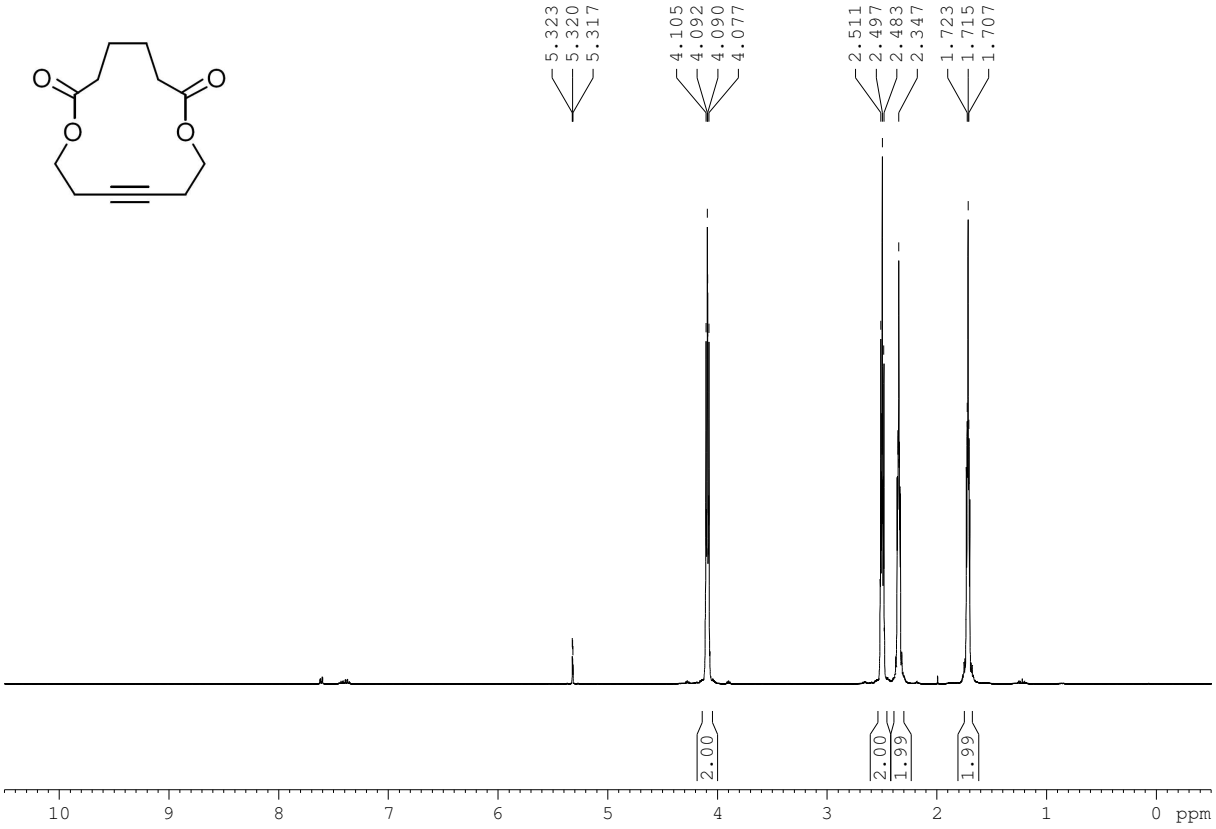
Solvent: CD_3OD

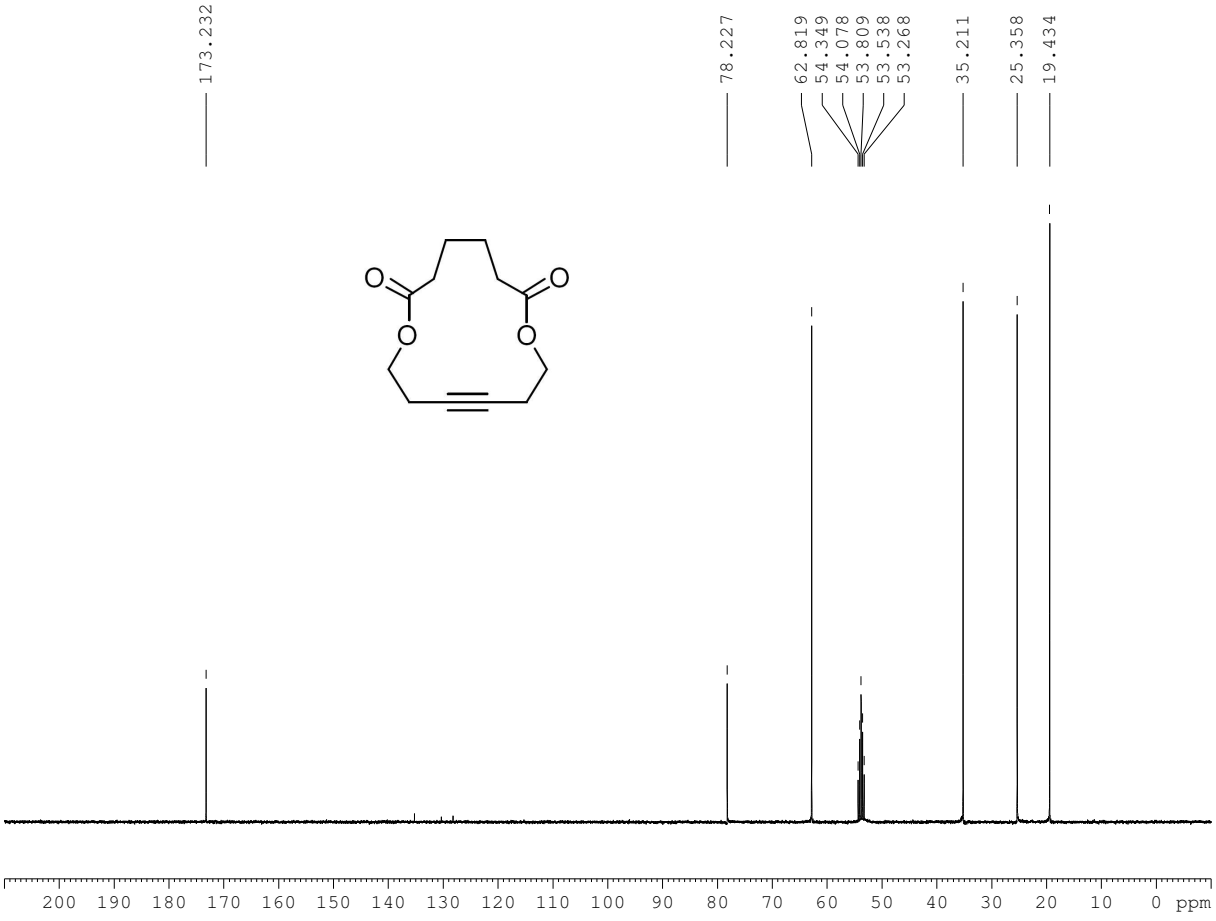

7.728
7.720
7.713
7.705
7.567
7.558
7.552
7.544
5.323
5.320
5.318
4.337
4.322
4.306
2.189
2.174
2.160
1.780
1.757
1.575
1.507
1.494
1.87
1.97
4.00
4.10
4.15
8.26
10 9 8 7 6 5 4 3 2 1 0 ppm

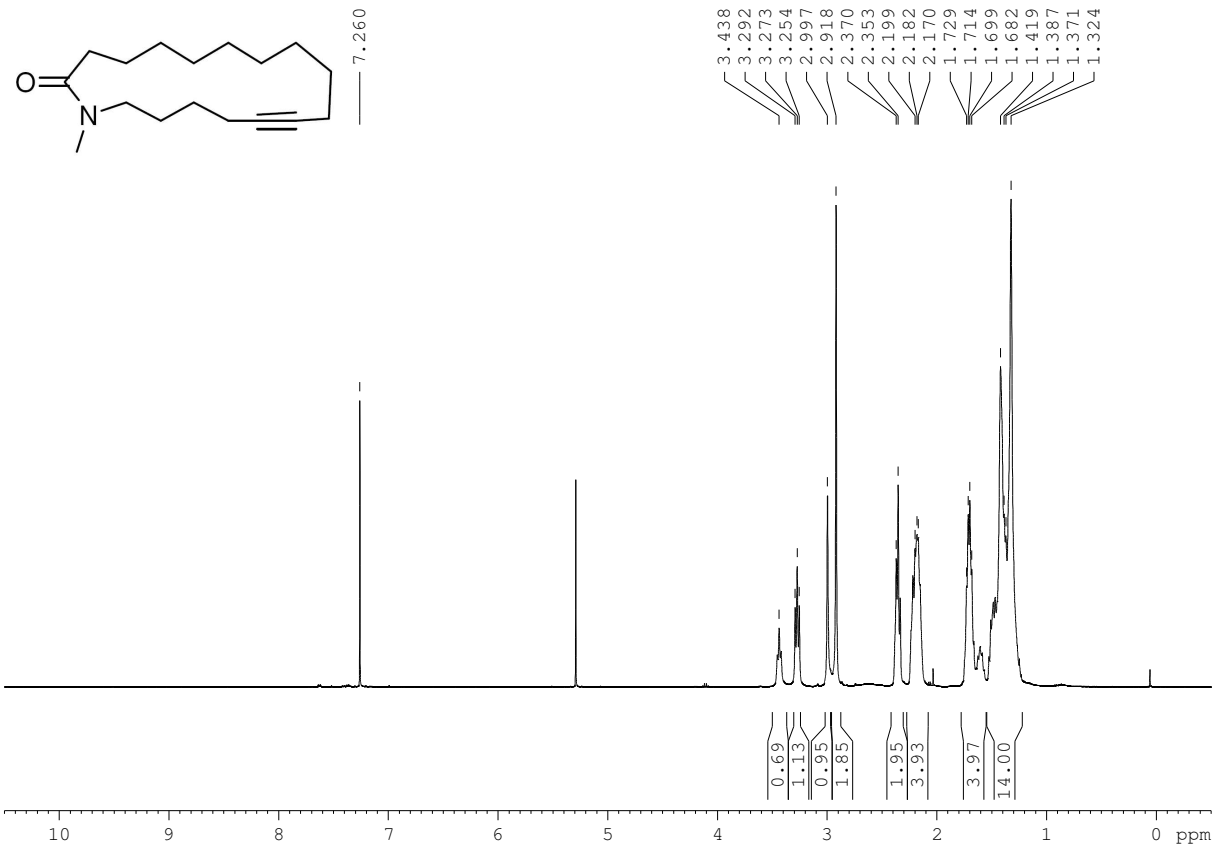

168.029
132.808
131.300
129.132
80.861
66.711
54.347
54.077
53.807
53.536
53.267
28.715
28.504
26.265
18.903
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

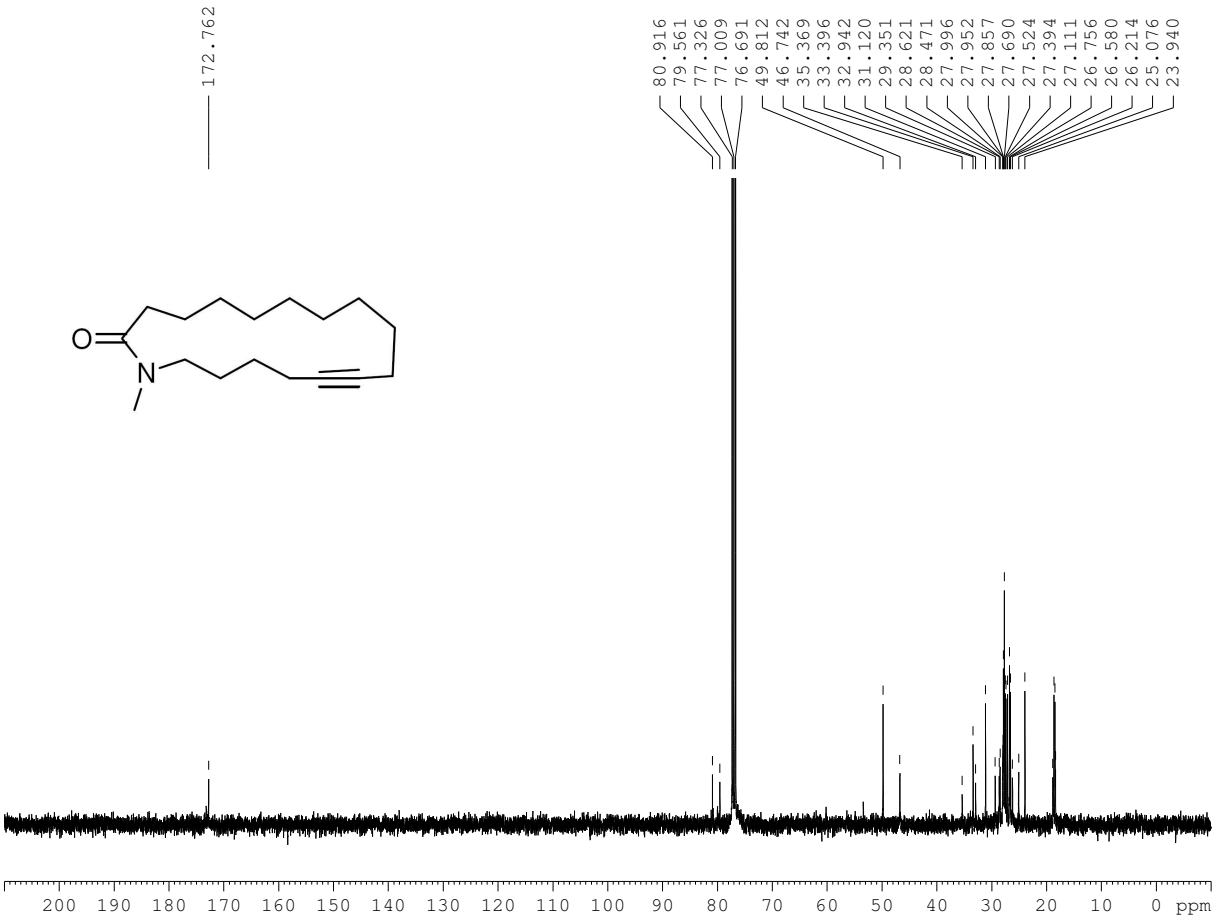

8.600
8.594
8.381
8.375
8.360
8.354
7.855
7.834
7.259
4.348
4.335
4.330
4.318
4.312
4.301
2.154
1.752
1.734
1.441
1.305
O2N
O
O
O
O
6
6
0.92
1.00
1.00
4.07
3.87
4.23
28.75
10
9
8
7
6
5
4
3
2
1
0 ppm


166.280
165.208
148.788
138.182
133.252
130.097
125.800
124.390
80.561
77.325
77.007
76.689
66.661
29.648
29.472
29.443
29.352
29.108
29.090
28.593
28.565
28.492
28.414
28.389
28.366
25.787
25.734
18.533
O2N
O
O
O
O
6
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


5.323
5.320
5.317
4.105
4.092
4.090
4.077
2.511
2.497
2.483
2.347
1.723
1.715
1.707
2.00
2.00
1.99
1.99
10
9
8
7
6
5
4
3
2
1
0 ppm


173.232
78.227
62.819
54.349
54.078
53.809
53.538
53.268
35.211
25.358
19.434
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
3.438
3.292
3.273
3.254
2.997
2.918
2.370
2.353
2.199
2.182
2.170
1.729
1.714
1.699
1.682
1.419
1.387
1.371
1.324
0.69
1.13
0.95
1.85
1.95
3.93
3.97
14.00
10 9 8 7 6 5 4 3 2 1 0 ppm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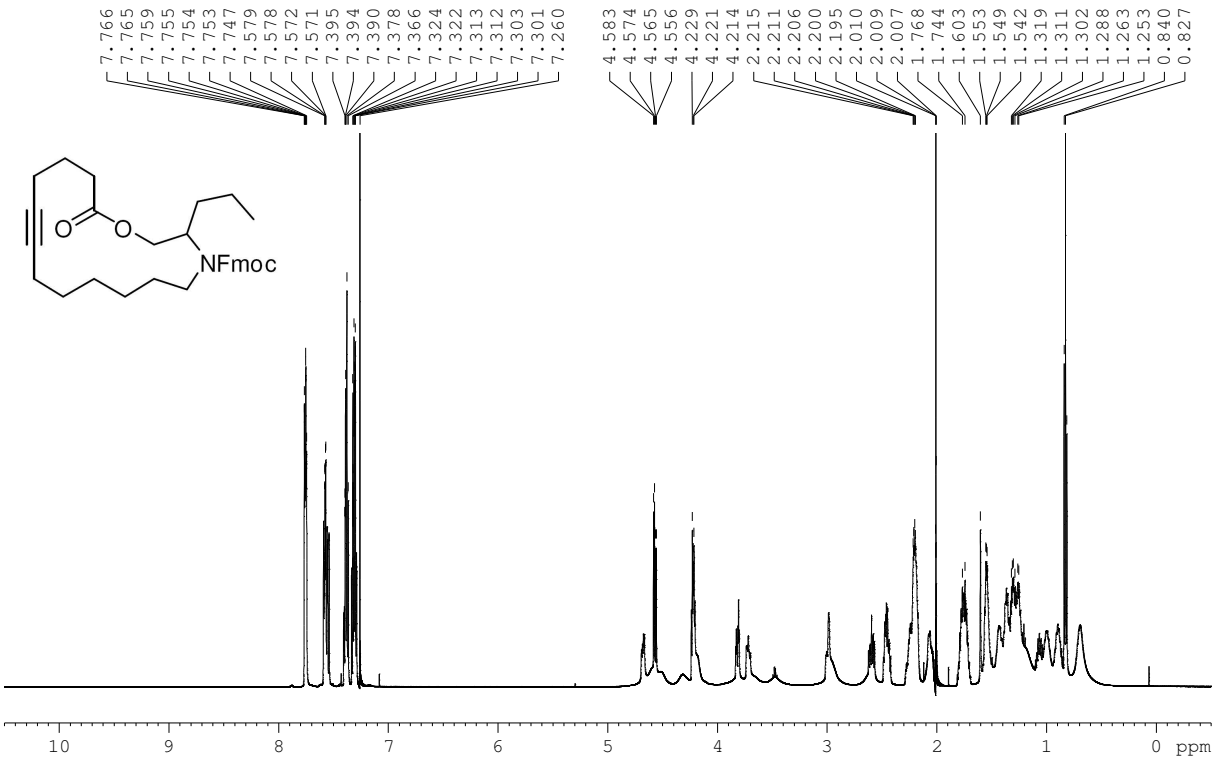
80.916
79.561
77.326
77.009
76.691
49.812
46.742
35.369
33.396
32.942
31.120
29.351
28.621
28.471
27.996
27.952
27.857
27.690
27.524
27.394
27.111
26.756
26.580
26.214
25.076
23.940
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.759
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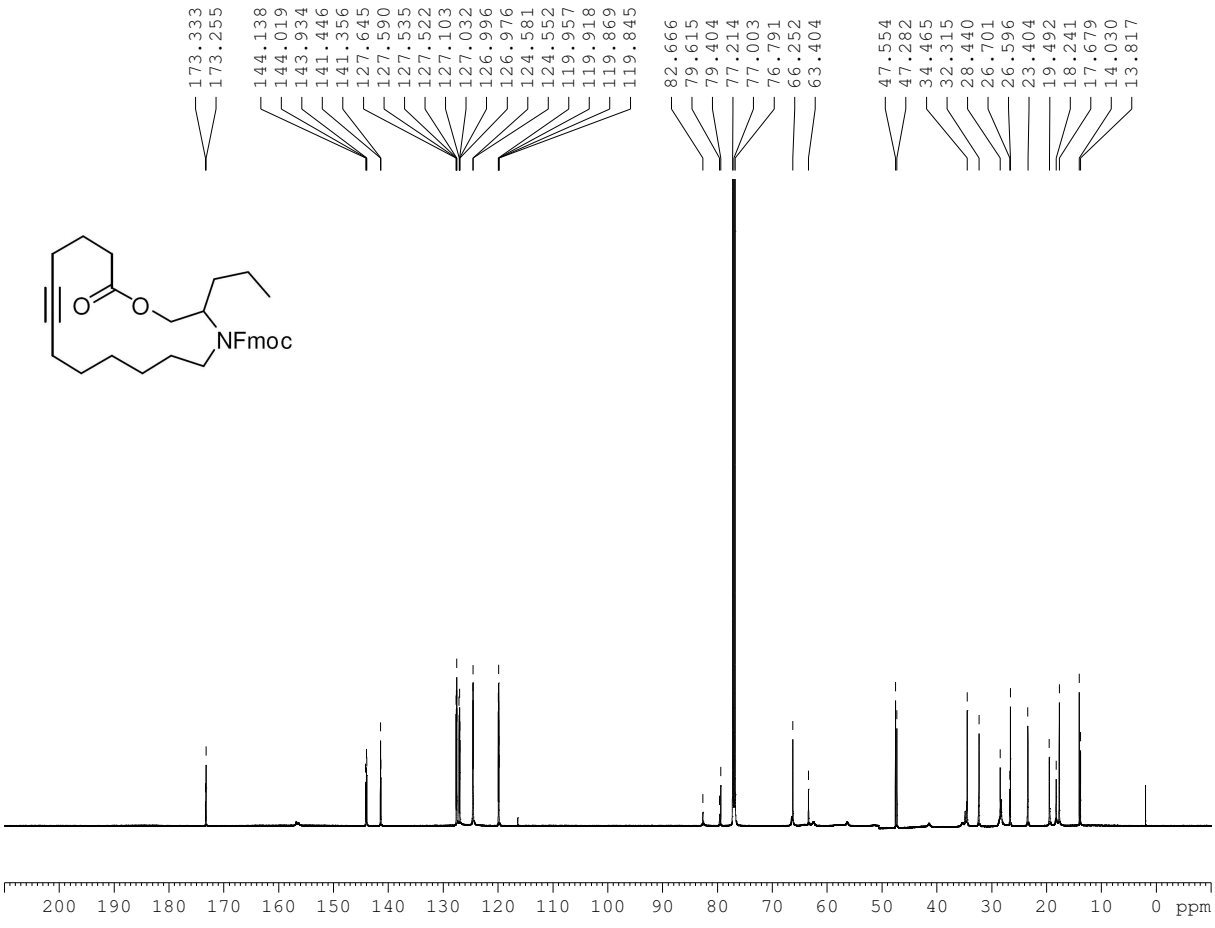
7.753
7.747
7.579
7.578
7.572
7.571
7.395
7.394
7.390
7.378
7.366
7.324
7.322
7.313
7.312
7.303
7.301
7.260
4.583
4.574
4.565
4.556
4.229
4.221
4.214
2.215
2.211
2.206
2.200
2.195
2.010
2.009
2.007
1.768
1.744
1.603
1.553
1.549
1.542
1.319
1.311
1.302
1.288
1.263
1.253
0.840
0.827
O
O
NFmoc
10
9
8
7
6
5
4
3
2
1
0 ppm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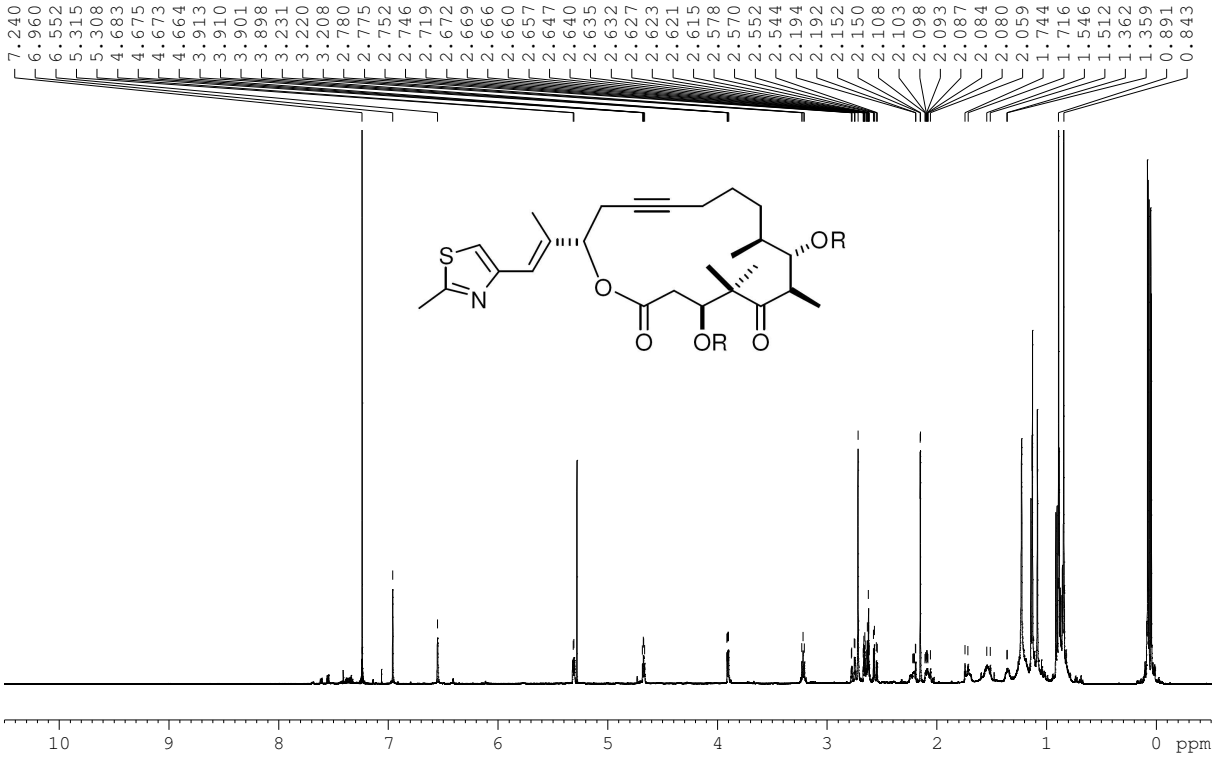
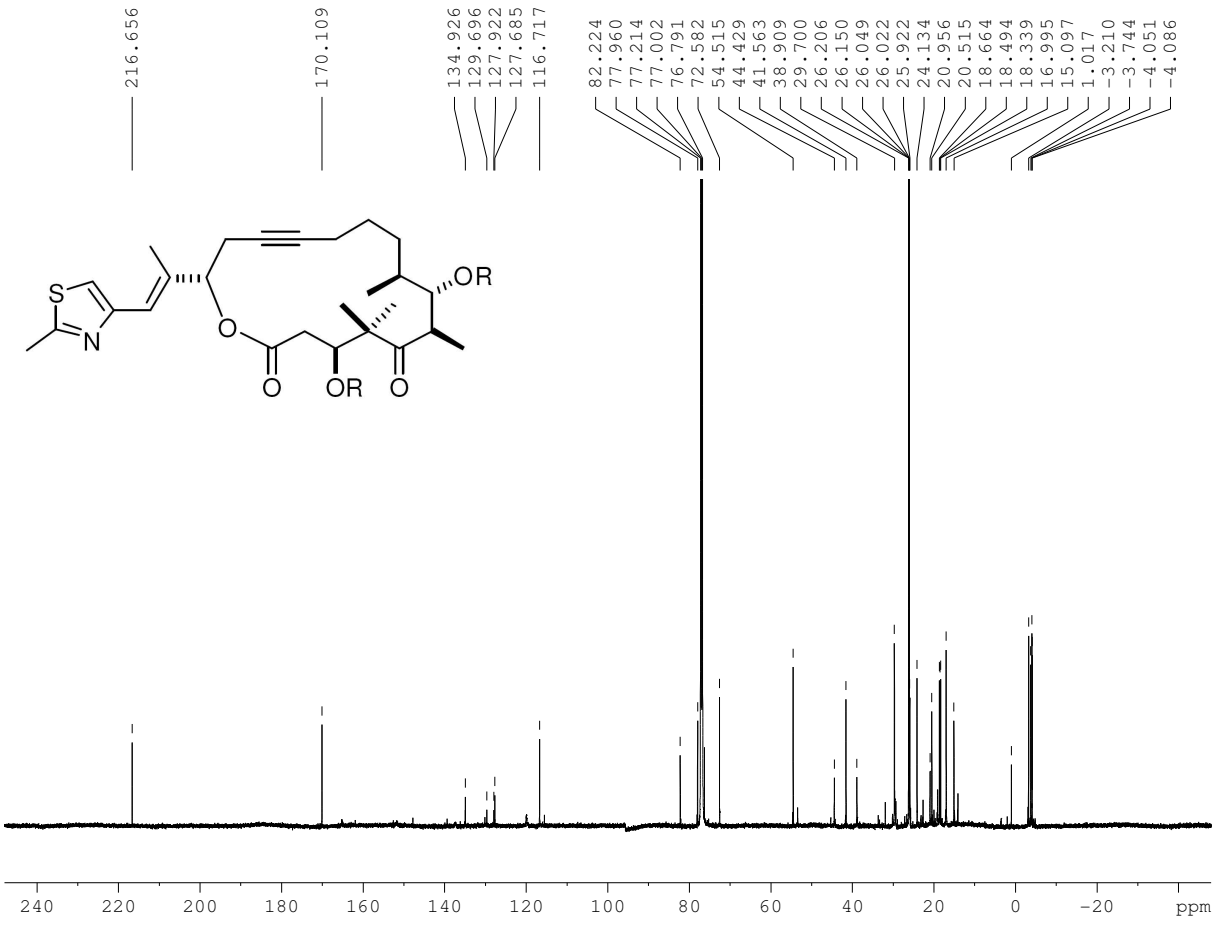
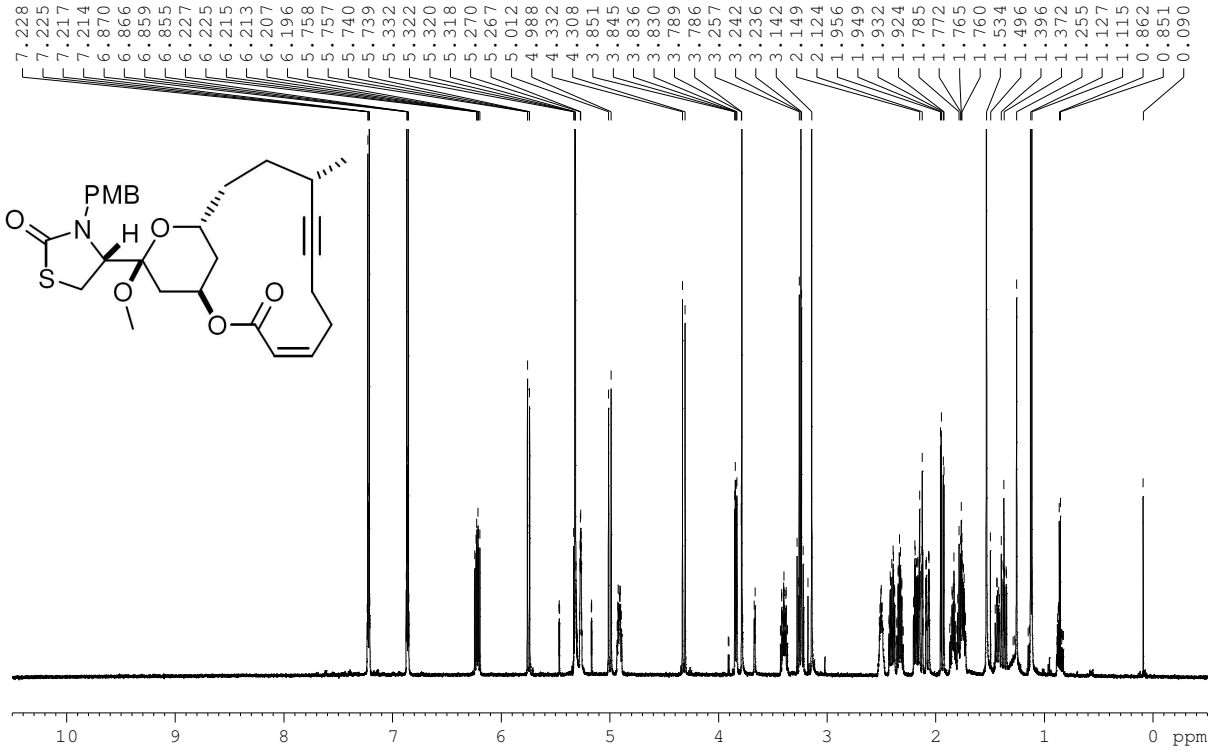
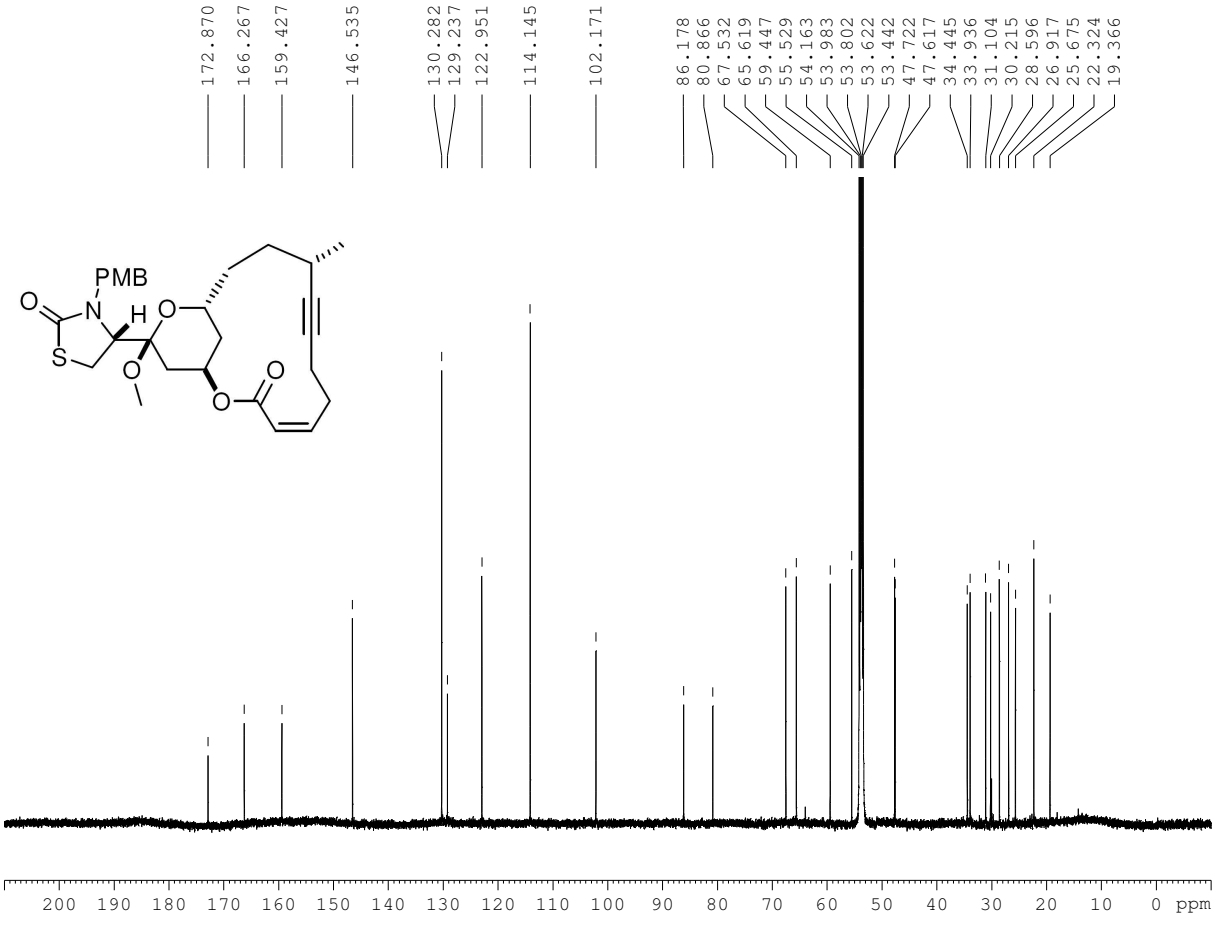
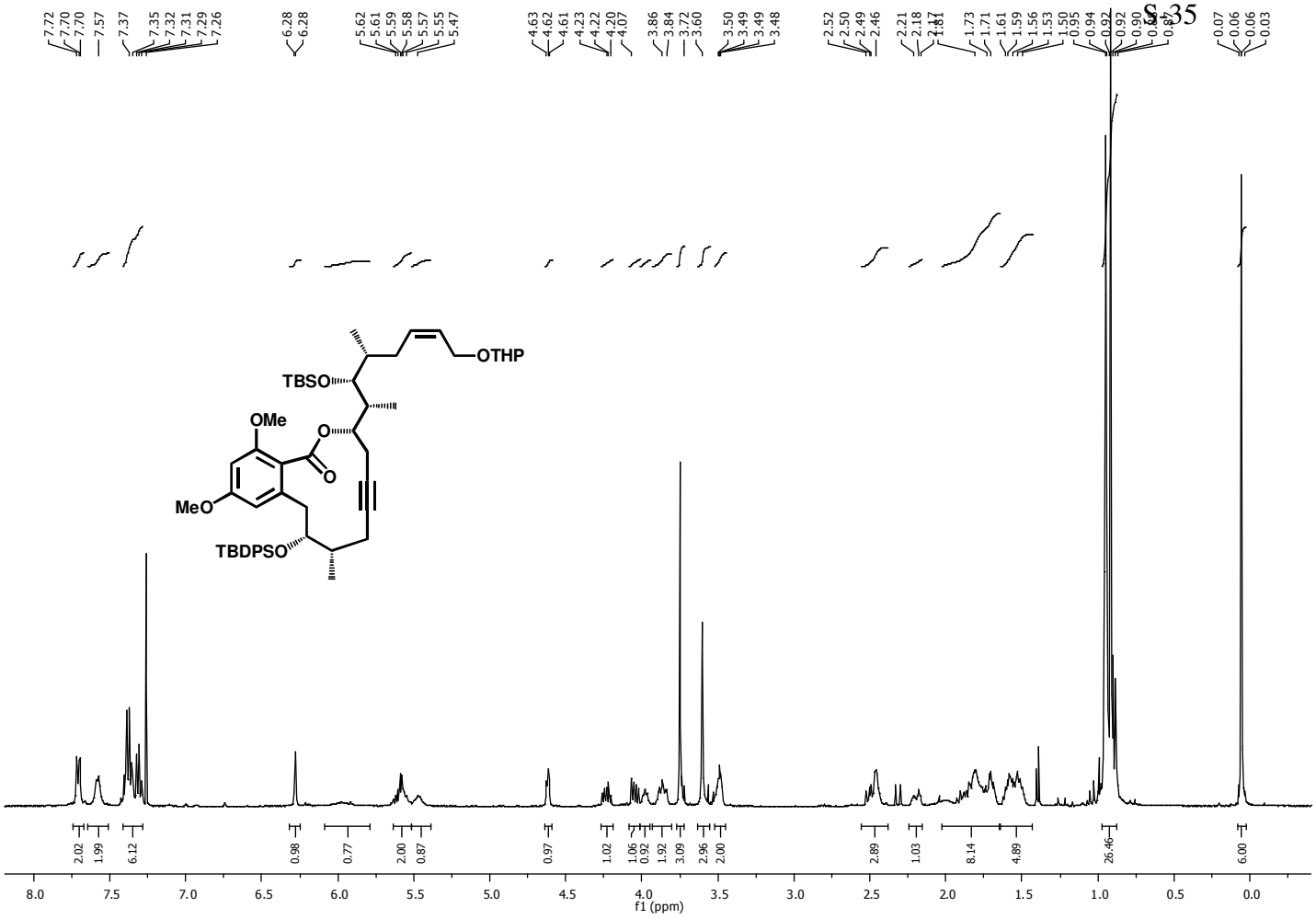
144.138
144.019
143.934
141.446
141.356
127.645
127.590
127.535
127.522
127.103
127.032
126.996
126.976
124.581
124.552
119.957
119.918
119.869
119.845
82.666
79.615
79.404
77.214
77.003
76.791
66.252
63.404
47.554
47.282
34.465
32.315
28.440
26.701
26.596
23.404
19.492
18.241
17.679
14.030
13.817
O
O
NFmoc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

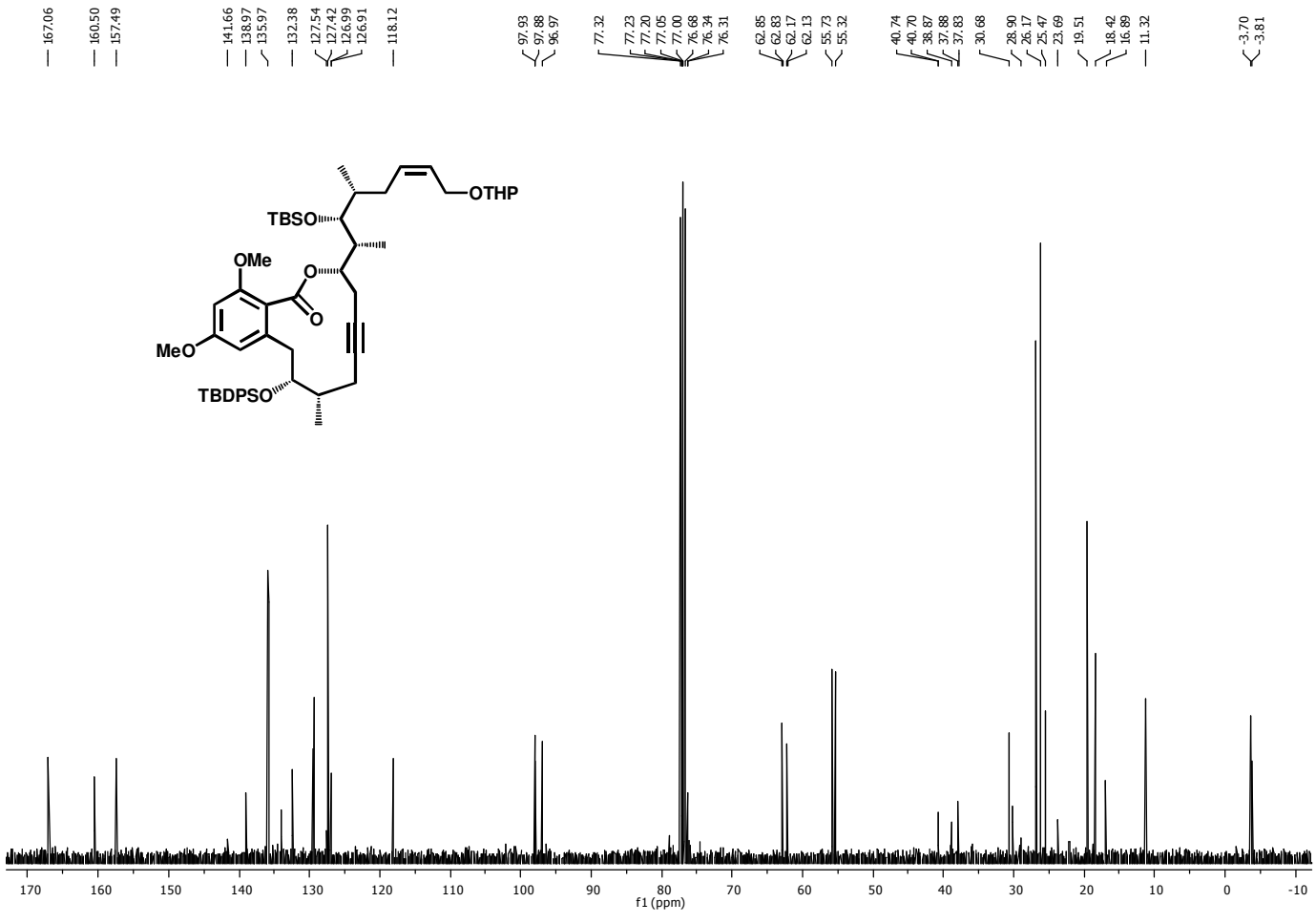

7.240
6.960
6.552
5.315
5.308
4.683
4.675
4.673
4.664
3.913
3.910
3.901
3.898
3.231
3.220
3.208
2.780
2.775
2.752
2.746
2.719
2.672
2.669
2.666
2.660
2.657
2.647
2.640
2.635
2.632
2.627
2.623
2.621
2.615
2.578
2.570
2.552
2.544
2.194
2.192
2.152
2.150
2.108
2.103
2.098
2.093
2.087
2.084
2.080
2.059
1.744
1.716
1.546
1.512
1.362
1.359
0.891
0.843
S
N
O
OR
O
OR
O
10
9
8
7
6
5
4
3
2
1
0
ppm

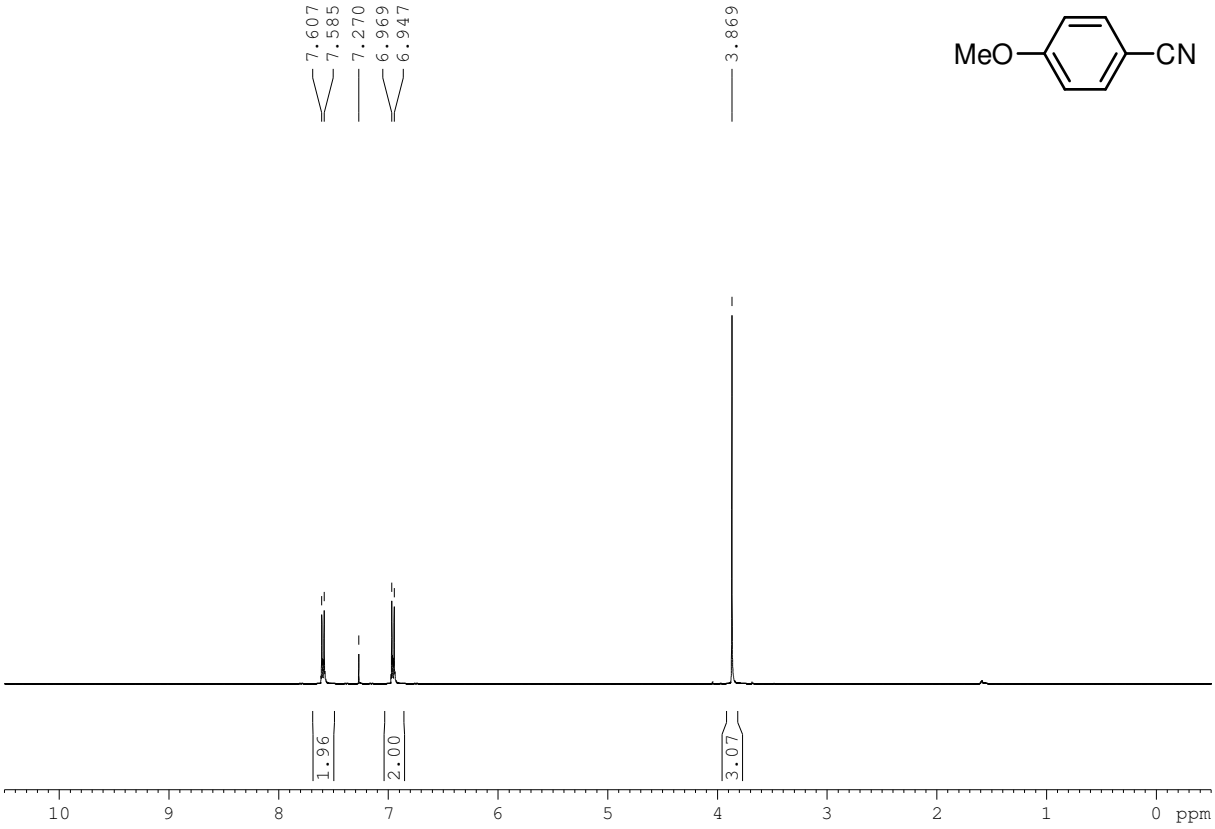

216.656
170.109
134.926
129.696
127.922
127.685
116.717
82.224
77.960
77.214
77.002
76.791
72.582
54.515
44.429
41.563
38.909
29.700
26.206
26.150
26.049
26.022
25.922
24.134
20.956
20.515
18.664
18.494
18.339
16.995
15.097
1.017
-3.210
-3.744
-4.051
-4.086
S
N
O
OR
O
OR
O
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

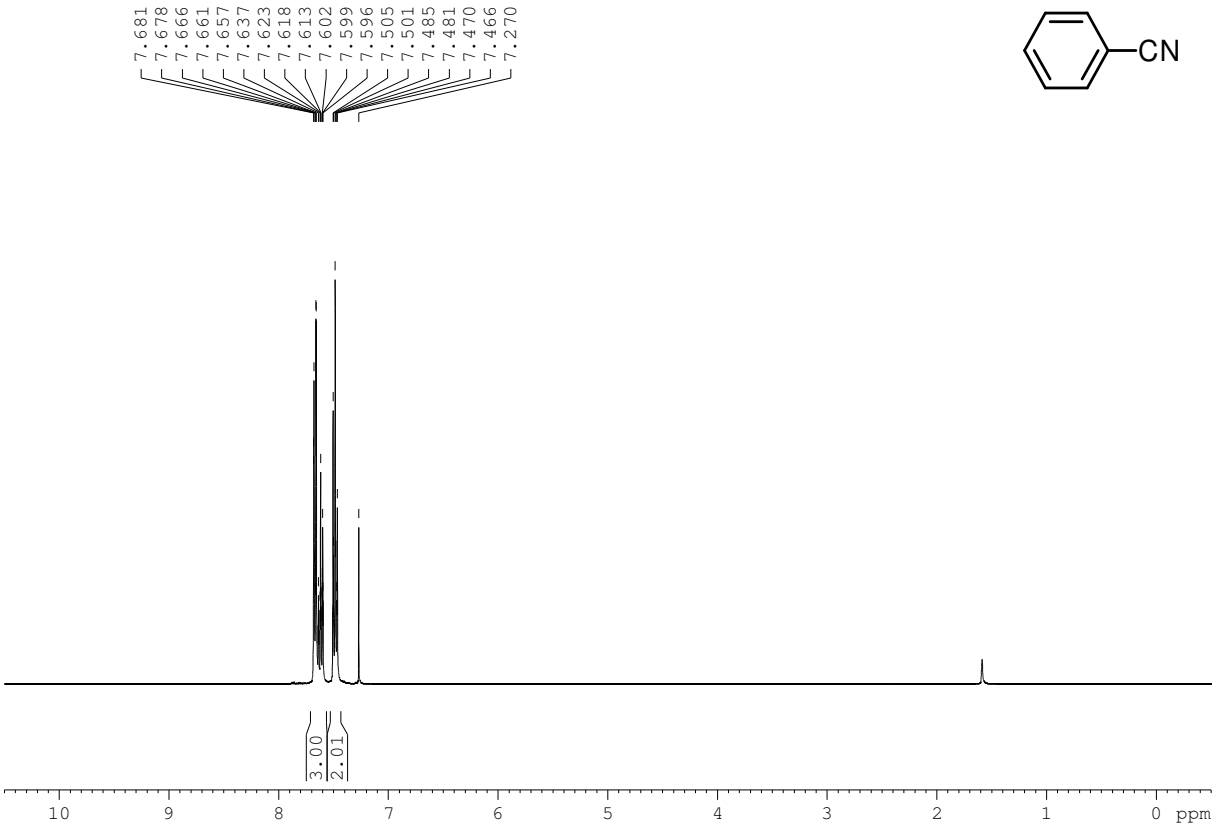

7.228
7.225
7.217
7.214
6.870
6.866
6.859
6.855
6.227
6.225
6.215
6.213
6.207
6.196
5.758
5.757
5.740
5.739
5.332
5.322
5.320
5.318
5.270
5.267
5.012
4.988
4.332
4.308
3.851
3.845
3.836
3.830
3.789
3.786
3.257
3.242
3.236
3.142
2.149
2.124
1.956
1.949
1.932
1.924
1.785
1.772
1.765
1.760
1.534
1.496
1.396
1.372
1.255
1.127
1.115
0.862
0.851
0.090
PMB
N
H
O
S
O
O
O
O
10
9
8
7
6
5
4
3
2
1
0 ppm

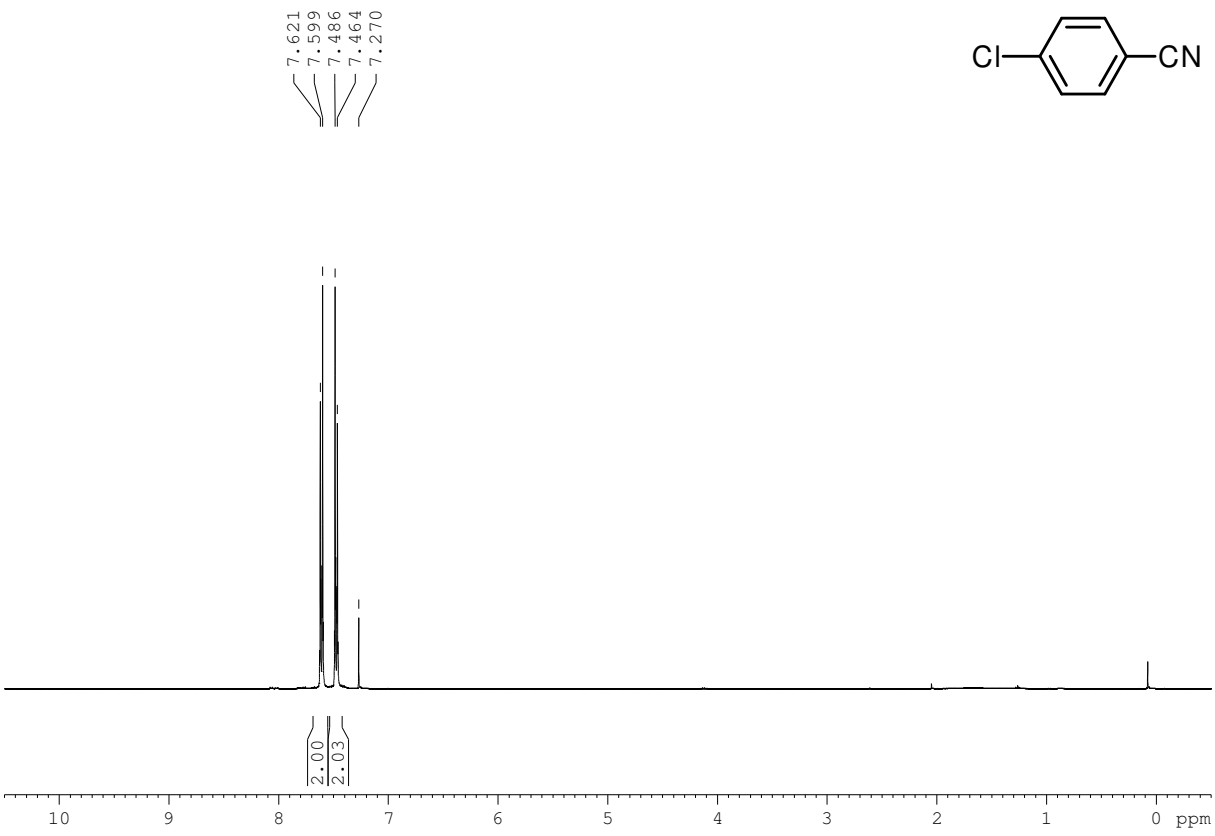

172.870
166.267
159.427
146.535
130.282
129.237
122.951
114.145
102.171
86.178
80.866
67.532
65.619
59.447
55.529
54.163
53.983
53.802
53.622
53.442
47.722
47.617
34.445
33.936
31.104
30.215
28.596
26.917
25.675
22.324
19.366
PMB
N
H
O
S
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

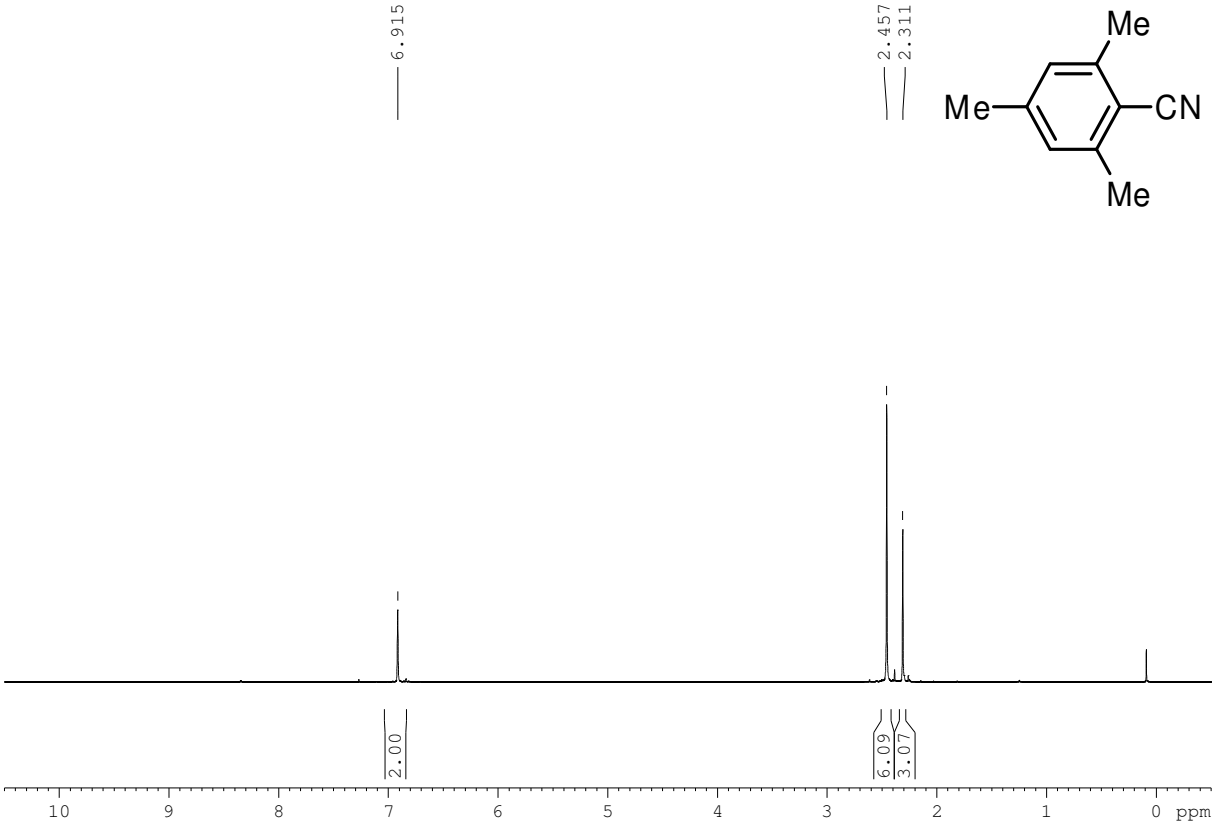

OTHP
TBSO
OMe
O
O
MeO
TBDPSO
f1 (ppm)

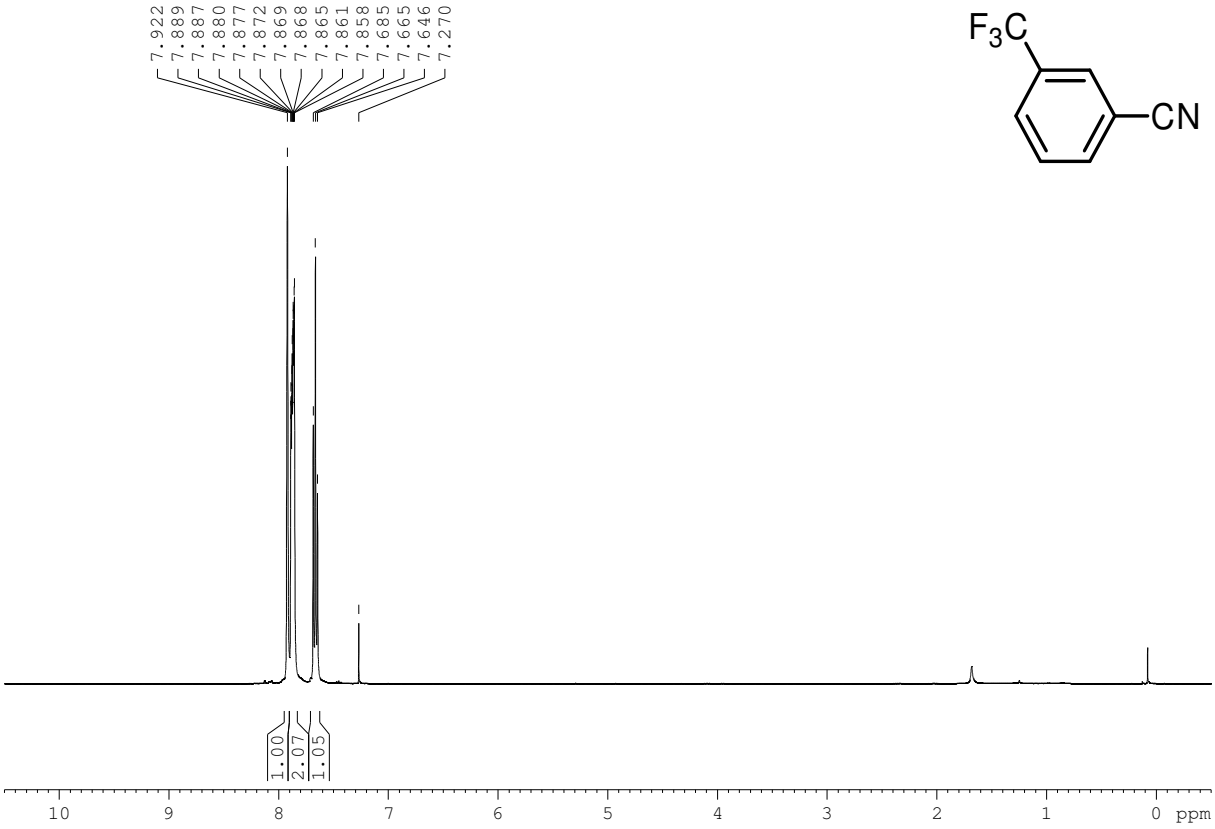

OTHP
TBSO
OMe
O
O
MeO
TBDPSO
f1 (ppm)

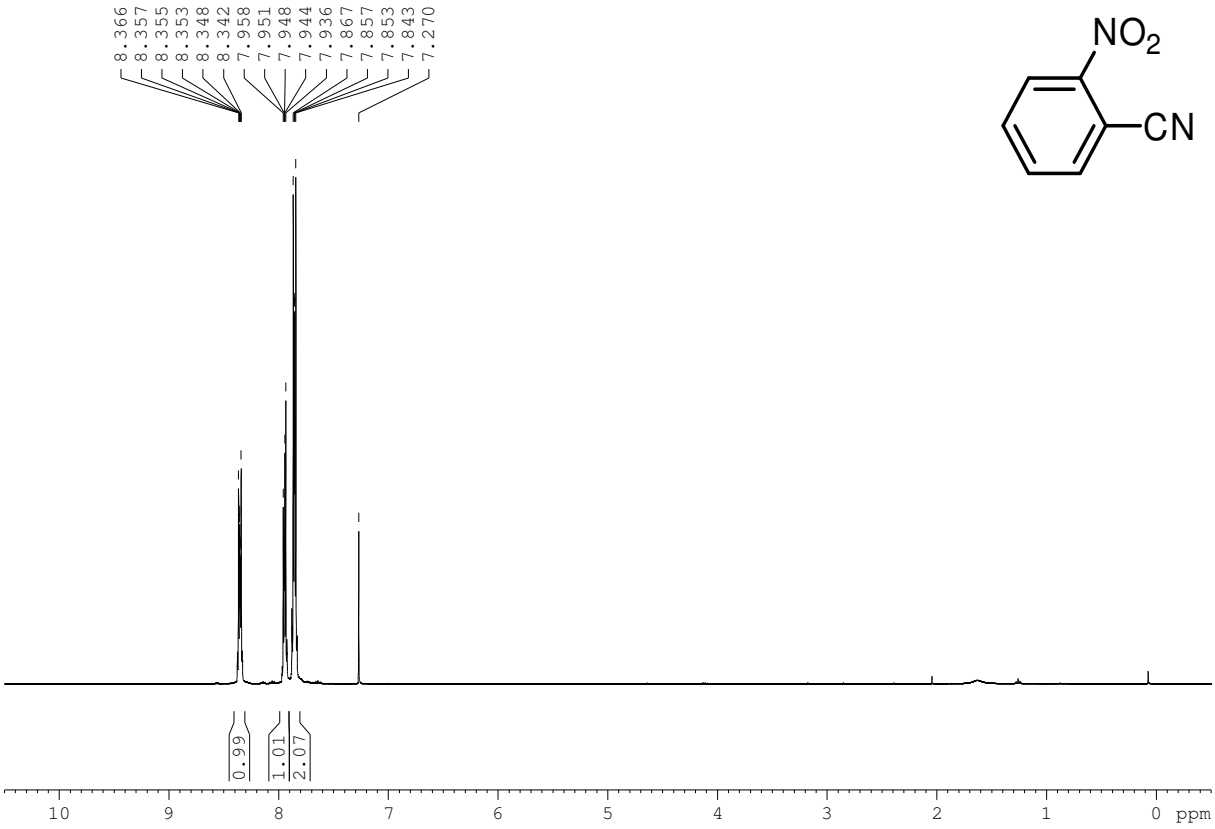

7.607
7.585
7.270
6.969
6.947
3.869
MeO
CN
1.96
2.00
3.07
10
9
8
7
6
5
4
3
2
1
0 ppm

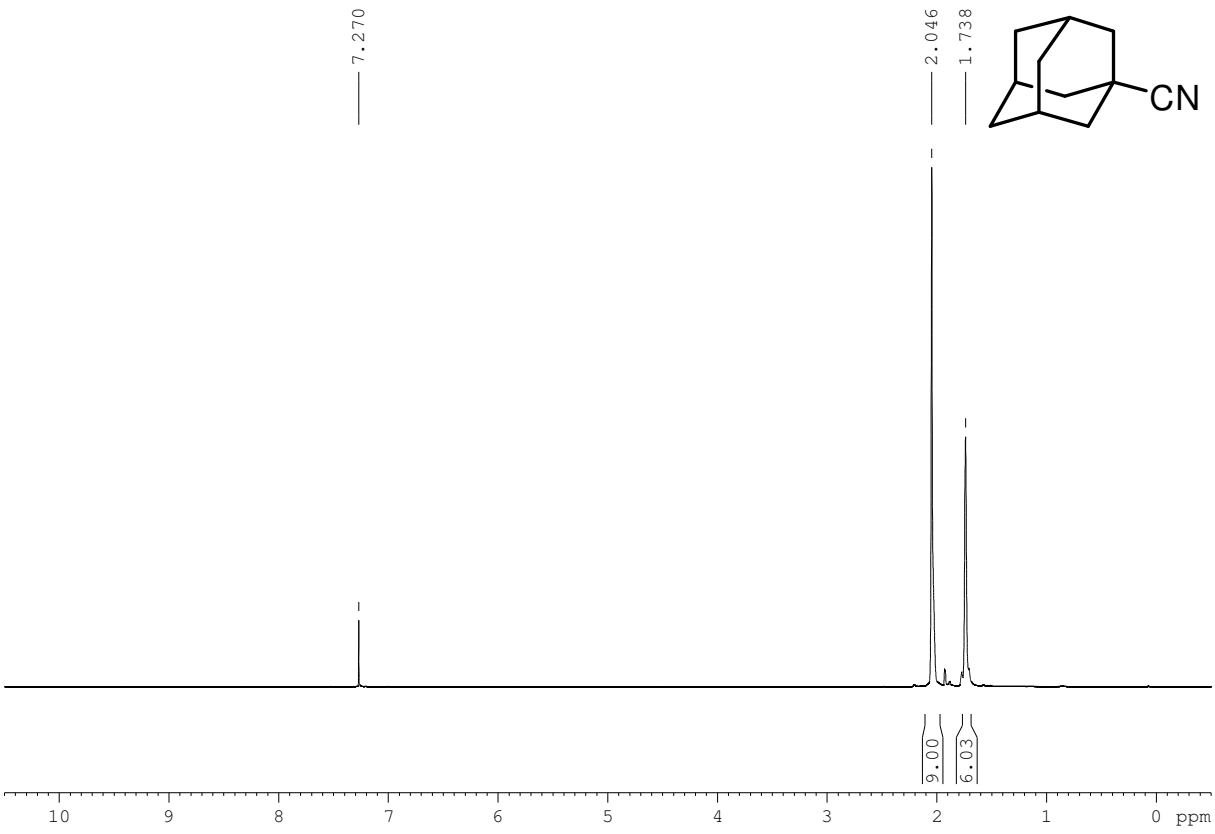

7.681
7.678
7.666
7.661
7.657
7.637
7.623
7.618
7.613
7.602
7.599
7.596
7.505
7.501
7.485
7.481
7.470
7.466
7.270
CN
3.00
2.01
10
9
8
7
6
5
4
3
2
1
0 ppm


7.621
7.599
7.486
7.464
7.270
Cl
CN
2.00
2.03
10
9
8
7
6
5
4
3
2
1
0 ppm


6.915
2.457
2.311
Me
Me
CN
Me
2.00
6.09
3.07
10
9
8
7
6
5
4
3
2
1
0 ppm


7.922
7.889
7.887
7.880
7.877
7.872
7.869
7.868
7.865
7.861
7.858
7.685
7.665
7.646
7.270
F3C
CN
1.00
2.07
1.05
10
9
8
7
6
5
4
3
2
1
0 ppm


8.366
8.357
8.355
8.353
8.348
8.342
7.958
7.951
7.948
7.944
7.936
7.867
7.857
7.853
7.843
7.270
NO2
CN
0.99
1.01
2.07
10
9
8
7
6
5
4
3
2
1
0 ppm


7.270
2.046
1.738
CN
9.00
6.03
10
9
8
7
6
5
4
3
2
1
0 ppm

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