When Cobalt-Mediated [2+2+2] Cycloaddition Reaction Dares Go Astray: Synthesis of Unprecedented Cobalt(III)-Complexes.

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General experimental

^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded using an internal deuterium lock at ambient temperatures on the following instruments: Bruker AC400 (400 MHz) and Bruker AC300 (300 MHz). The internal references of ^{1}H 7.26 was used for the residual protons in $CDCl_3$. Data are presented as follows: chemical shift (in ppm), integration, interpretation, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quintet = quin, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, br = broad) and coupling constant (*J* in Hz). ^{13}C NMR spectra were recorded on a Bruker AC400 (101 MHz) and a Bruker AC300 (75 MHz) spectrometers with complete proton decoupling. Chemical shifts were reported in ppm from the internal solvent signal (peak at 77.16 ppm in the case of $CDCl_3$. ^{59}Co NMR spectra were measured on a Bruker AC 500 (119 MHz). ^{59}Co chemical shifts are given relative to $K_3[Co(CN)_6]$ in D_2O (^{59}Co = 0 ppm) used as external reference.

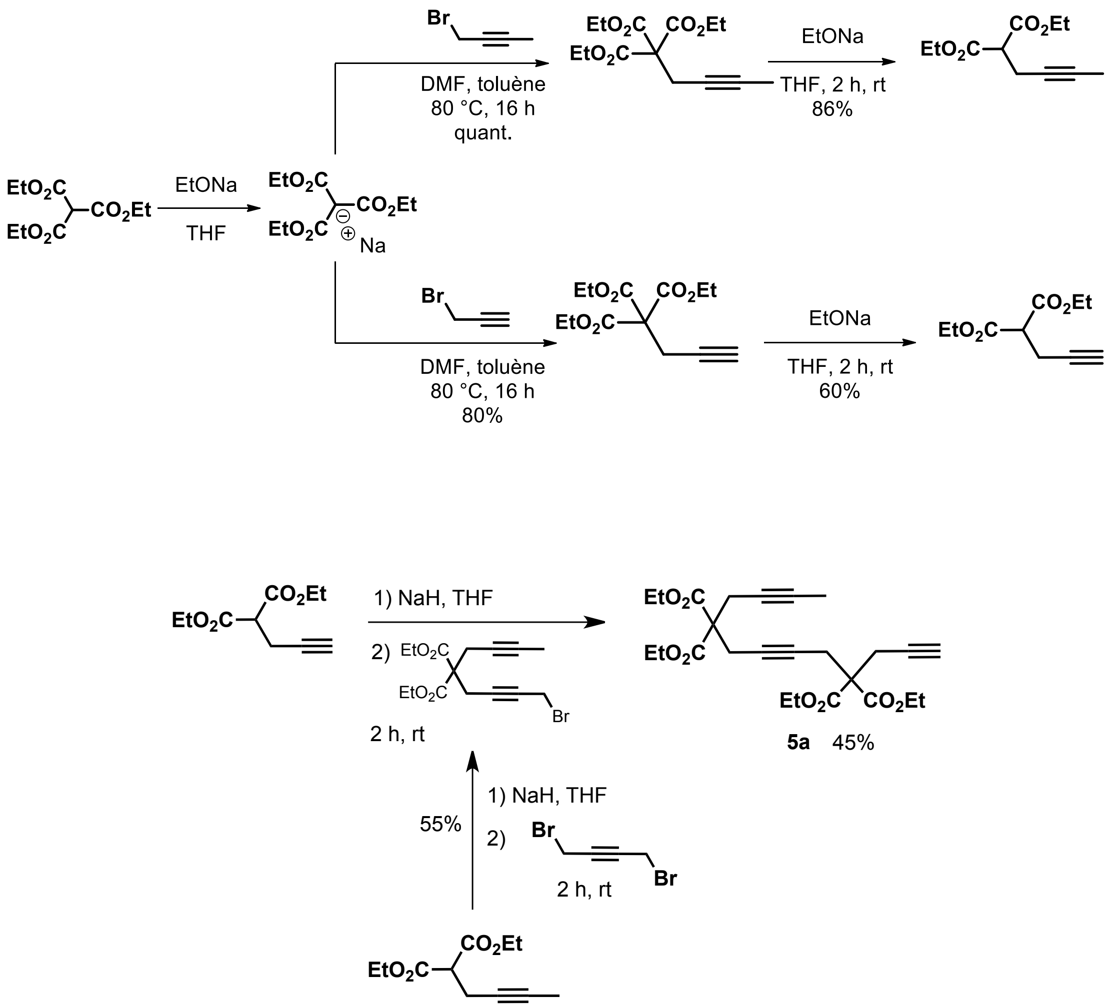
Infra-red spectra were recorded on a Bruker VERTEX70 Fourier transform infraredspectrometer fitted with a single reflection diamond ATR Bruker A222 accessory. The measurements were done for pure samples. For each individual spectrum, about 30 scans were averaged at 4 cm^{-1} resolution. The diamond crystal without sample served as reference.

All the system was purged with dry air. The identification of peaks was done with the standard method proposed in OPUS 6.0 software. Wavelengths of maximum absorbance (max) are quoted in cm^{-1}.

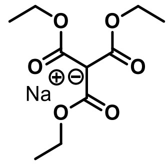
High resolution MS experiments were performed with a QSTAR Elite mass spectrometer (Applied Biosystems SCIEX) or a SYNAPT G2 HDMS mass spectrometer (Waters) equipped with an electrospray ionization source operated in the positive ion mode. In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight (oa-TOF) mass analyzer.

Analytical thin layer chromatography (TLC) was carried out on Merck® Kieselgel 60 F254 plates and achieved under a 254 nM UV light, visualized with a $KMnO_4$ solution or anisaldehyde solution.

Synthesis of Triynes 5



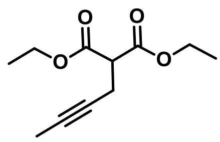
Scheme S1. Synthesis of Triyne 5a



Sodium ethoxide solution was prepared in a flame-dried flask under a flow of argon gas using sodium metal (1 g, 43.1 mmol) and dry ethanol (21.5 mL) and was added slowly to a solution of triethyl methane carboxylate (10 g, 43.1 mmol) in THF (94 mL) at 0 °C. The reaction mixture was stirred at 0 °C until the precipication of the product as a white solid. The solvent was removed *in vacuo* and the salt was washed with dry petroluem ether and dried under high vaccum to get the crude product in 94% yield (10.2 g) without further purification.[1]

Aspect: white solid

[1] Sylvester, K.; Chirik, P. *J. Am. Chem. Soc.*, **2009**, *131*, 8772–8774



To a solution of sodium 1,3-diethoxy-2-(ethoxycarbonyl)-1,3-dioxopropan-2-ide (1 equiv., 2 g, 7.87 mmol) in toluene (16 mL) and DMF (16 mL) was added 1-bromobut-2-yne (1 equiv., 7.87 mmol). The reaction mixture was heated at 80 °C for 16 hours. Then the mixture was cooled dowm and quenched with water. The aqueous layer was extracted with toluene. The combined organic layers were washed with water then with a saturated aqueous solution of Na_2CO_3, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was pure enough to be use directly in the next step. The crude was obtained with quantitative yield.

To a suspension of EtONa (1 equiv., 0.306 g, 4.5 mmol) in THF (7.18 mL) was added dropwise a solution of triethyl but-2-yn-1-ylmethanetricarboxylate (1 equiv., 1.28 g, 4.5 mmol) in THF (4.8 mL). The reaction mixture was stirred for 2 hours at room temperature. The mixture was quenched with a solution of HCl 1N and and diluted with Et_2O. The organic layer was washed with water, a saturated aqueous solution of $NaHCO_3$ and brine then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography on silica gel (PE/Et_2O 3:1).

Yield: 86% (825 mg)

Aspect: limpid oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.28 (t, J = 7.1 Hz, 6H, 2 x CH_3), 1.75 (t, J = 2.6 Hz, 3H, CH_3), 2.72 (dq, J = 7.7 and 2.6 Hz, 2H, CH_2), 3.50 (t, J = 7.7, Hz, 1H, CH), 4.22 (q, J = 7.1 Hz, 4H, 2 x CH_2).

^{1}H NMR in agreement with previouly reported data[2]

[2] Bennacer, B.; FuJiwara, M.; Lee, S.; OJima, I. *J. Am. Chem. Soc.*, **2005**, *127,* 17756–17767

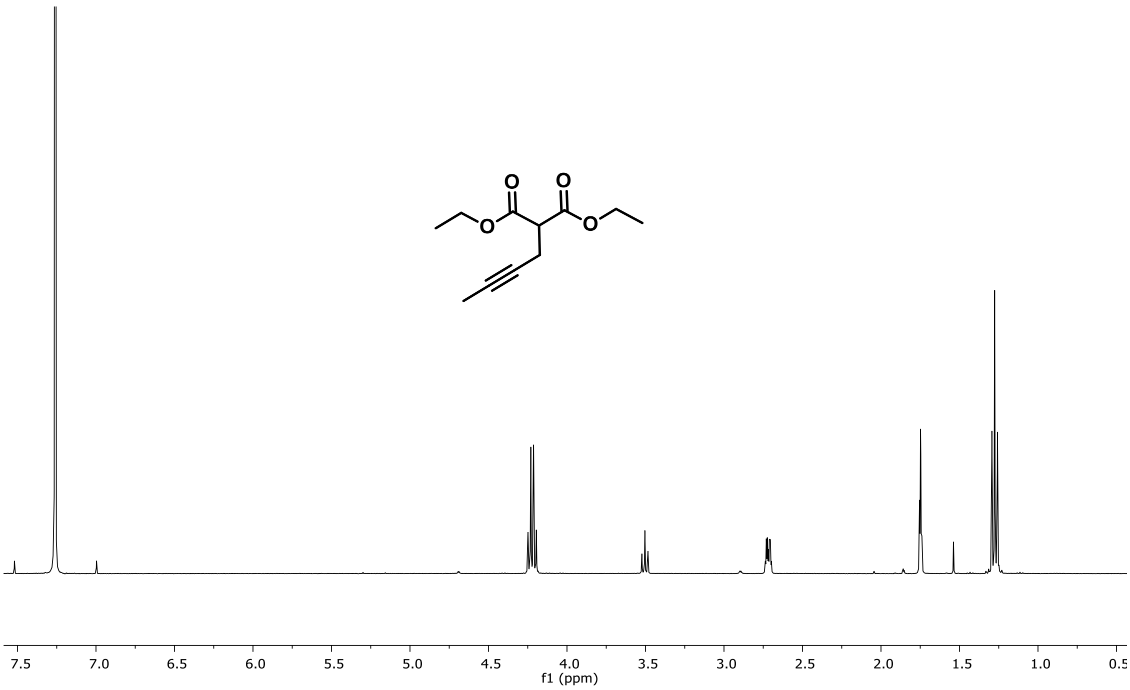
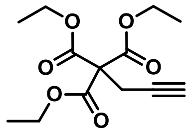


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum



To a solution of sodium 1,3-diethoxy-2-(ethoxycarbonyl)-1,3-dioxopropan-2-ide (1 equiv., 1.5 g, 5.9 mmol) in toluene (12 mL) and DMF (12 mL) was added 3-bromopropyne (1 equiv., 0.877 g, 0.636 mL, 5.9 mmol). The reaction mixture was stirred at 80 °C for 16 hours. Then the mixture was cooled dowm and quenched with water. The aqueous layer was extracted with toluene. The combined organic layers were washed with water then with a saturated aqueous solution of Na_2CO_3, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was pure enough to be use directly in the next step.

Yield: 80% (1.27 g)

Aspect: yellowish oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.30 (t, J = 7.1 Hz, 9H, 3 x CH_3), 2.05 (t, J = 2.7 Hz, 1H, CH), 3.02 (d, J = 2.7 Hz, 2H, CH_2), 4.29 (q, J = 7.1 Hz, 6H, 3 x CH_2).

^{1}H NMR in agreement with previouly reported data [3]

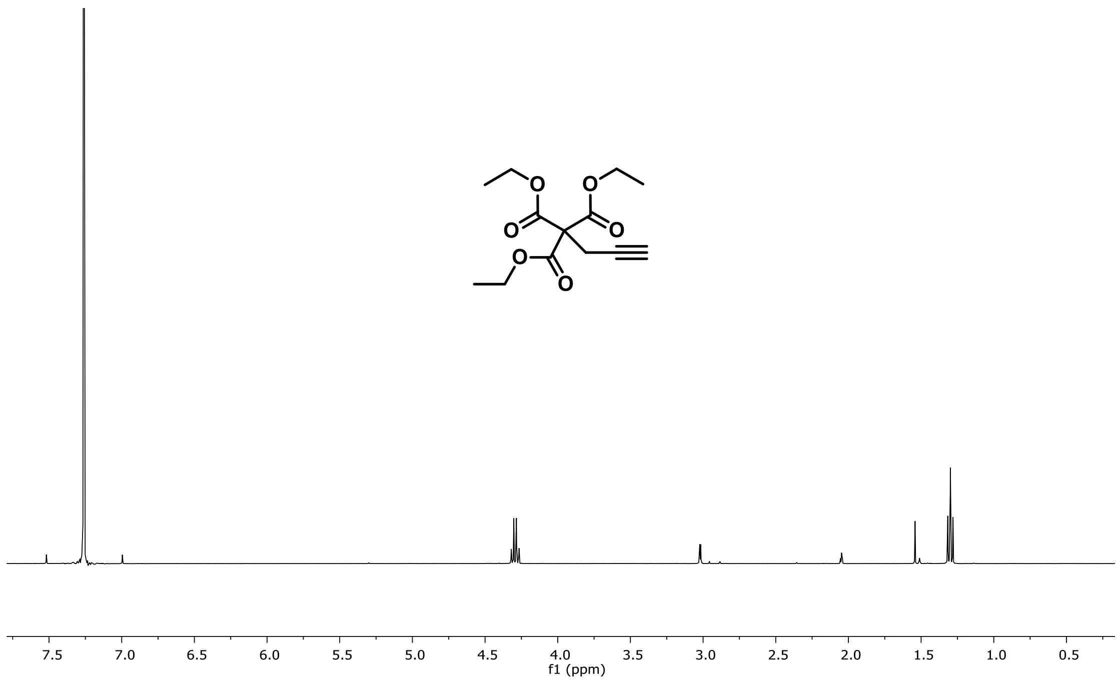
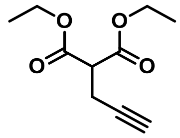


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[3] Aldegunde, M. J.; FandiÇo, R. G.; Castedo, L.; Granja, J. R. *Chem. Eur. J.*, **2007**, *13*, 5135–5150



To a suspension of EtONa (1 equiv., 0.306 g, 4.5 mmol) in THF (7.2 mL) was added dropwise a solution of triethyl but-2-yn-1-ylmethanetricarboxylate (1 equiv., 1.28 g, 4.5 mmol) in THF (4.8 mL). The mixture reaction was stirred for 2 hours at room temperature. The mixture was quenched with a solution of HCl 1N and diluted with Et_2O. The organic layer was washed with water, a saturated aqueous solution of $NaHCO_3$ and brine then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography on silica gel (PE/Et_2O 3:1).

Yield: 60% (539 mg)

Aspect: Colorless oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.28 (t, *J* = 7.1 Hz, 6H, 2 x CH_3), 2.01 (t, *J* = 2.7 Hz, 1H, CH), 2.78 (dd, *J* = 7.7 and 2.7 Hz, 2H, CH_2), 3.56 (t, *J* = 7.7 Hz, 1H, CH), 4.23 (q, *J* = 7.1 Hz, 4H, 2 x CH_2).

^{1}H NMR in agreement with previouly reported data[4]

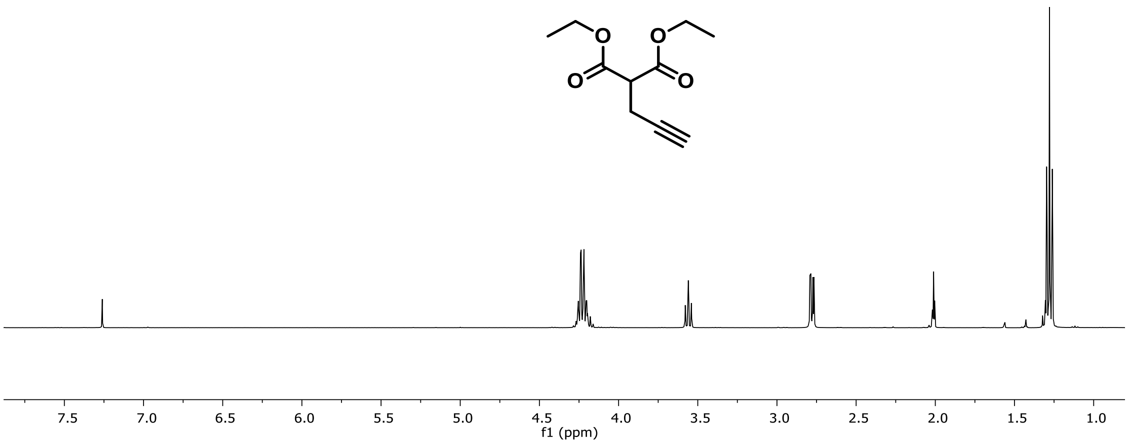
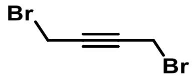


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[4] Wu, Z.; Minhas, G.; Wen, D.; Jiang, H.; Chen, K.; Zimniak, P.; Zheng, J. *J. Med. Chem.*, **2004**, *47*, 3282



To a flame dried round bottom flask was added but-2-yne-1,4-diol (20.0 g, 232.4 mmol), pyridine (3.32mL, 41.2 mmol) and Et_2O (300 mL). After cooling to 0 °C, PBr_3 (17.52 mL, 186 mmol) was added via syringe. The reaction mixture was stirred at 0 °C for 30 minutes and refluxed for 4 hours. The mixture was quenched with water. The aqueous layer was extracted with Et_2O. The combined organic layers washed were with saturated aqueous solution of $NaHCO_3$, brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Distillation (84 °C/0.05 torr) afforded the product.

Yield: 48% (23.6 g)

Aspect: Colorless oil

^{1}H NMR: (400 MHz, Chloroform-*d*) δ 3.96 (s, 4H, CH_2).

^{1}H NMR in agreement with previouly reported data [5]

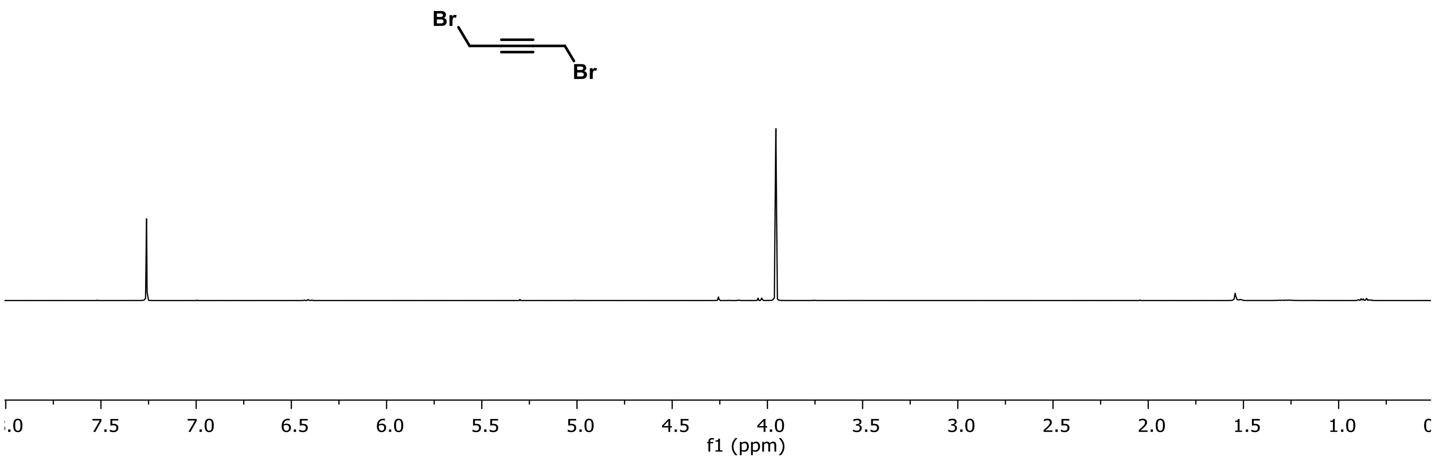
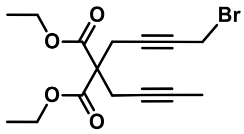


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[5] Iafe, R.; Kuo, J.; Hochstatter, D.; Saga, T.; Turner, J.; Merlic, C. *Org. Lett.* **2013**, *15*, 582



To a solution of NaH 60% dispersion in oil (1.1 equiv., 412 mg, 10.36 mmol) in THF (8.5 mL) cooled down to 0 °C was added dropwise diethyl 2-(but-2-yn-1-yl)malonate (1 equiv., 2 g, 9.42 mmol). The reaction mixture was allowed to warm up to room temperature and stirred for 30 minutes. Then 1,4-dibromobut-2-yne (1.2 equiv., 2.4 g, 11.30 mmol) was added dropwise at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 2 hours. The mixture was diluted in Et_2O and quenched with water then an aqueous solution of HCl (2M). The aqueous layer was extracted with diethylether. The combined organic layers were washed with water and brine then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography on silica gel (PE/Et_2O 3:1).

Yield: 64% (2.08 g)

Aspect: Colorless oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.27 (t, *J* = 7.1 Hz, 6H, 2 x CH_3), 1.75 (t, *J* = 2.7 Hz, 3H, CH_3), 2.88 (q, *J* = 2.7 Hz, 2H,CH_2), 3.02 (t, *J* = 2.4 Hz, 2H, CH_2), 3.86 (t, *J* = 2.4 Hz, 2H, CH_2), 4.22 (q, *J* = 7.1 Hz, 4H, CH_2).

^{1}H NMR in agreement with previouly reported data2

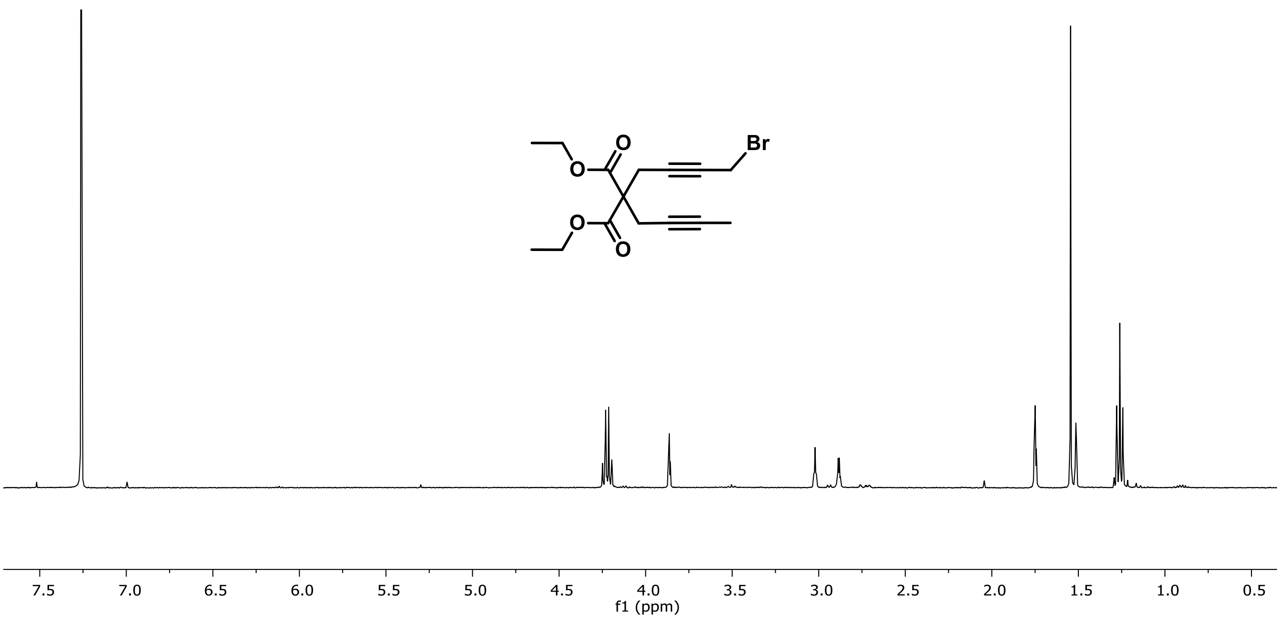
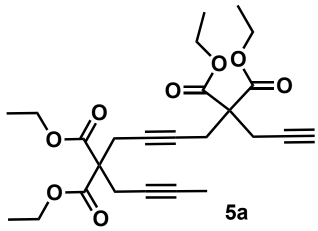


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum



5a

To a solution of NaH 60% dispersion in oil (1.1 equiv., 256 mg, 6.4 mmol) in THF (7 mL) was added 1,3-diethyl 2-(prop-2-yn-1-yl)propanedioate (1 equiv., 1.29 g, 5.8 mmol) at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred 30 minutes. Then diethyl 2-(4-bromobut-2-yn-1-yl)-2-(but-2-yn-1-yl)malonate (1 equiv., 2 g, 5.8 mmol) was added dropwise at 0 °C. The mixture reaction was allowed to warm up to room temperature and stirred 2 hours. The mixture was diluted in Et_2O and quenched with water then an aqueous solution of HCl (1M). The aqueous layer was extracted with Et_2O. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography on silica gel (PE/EtOAc 95:5 to 8:2)

Yield: 45% (1.2 g)

Aspect: white paste

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.24 (t, *J* = 7.1, 6H, 2 x CH_3), 1.25 (t, *J* = 7.1, 6H, 2 x CH_3), 1.74 (t, *J* = 2.6 Hz, 3H, CH_3), 1.99 (t, *J* = 2.6 Hz, 1H, CH), 2.85 (br q, *J* = 2.6 Hz, 2H, CH_2), 2.89 -2.92 (m, 2H, CH_2), 2.92 – 2.95 (m, 4H, 2 x CH_2), 4.21 (q, *J* = 7.1, 8H, 4 x CH_2).

^{1}H NMR in agreement with previouly reported data[6]

[6] Ojima, I.; Vu, A.; McCullagh, J.; Kinoshita, A. *J. Am. Chem. Soc*. **1999**, *121*, 3230-3231

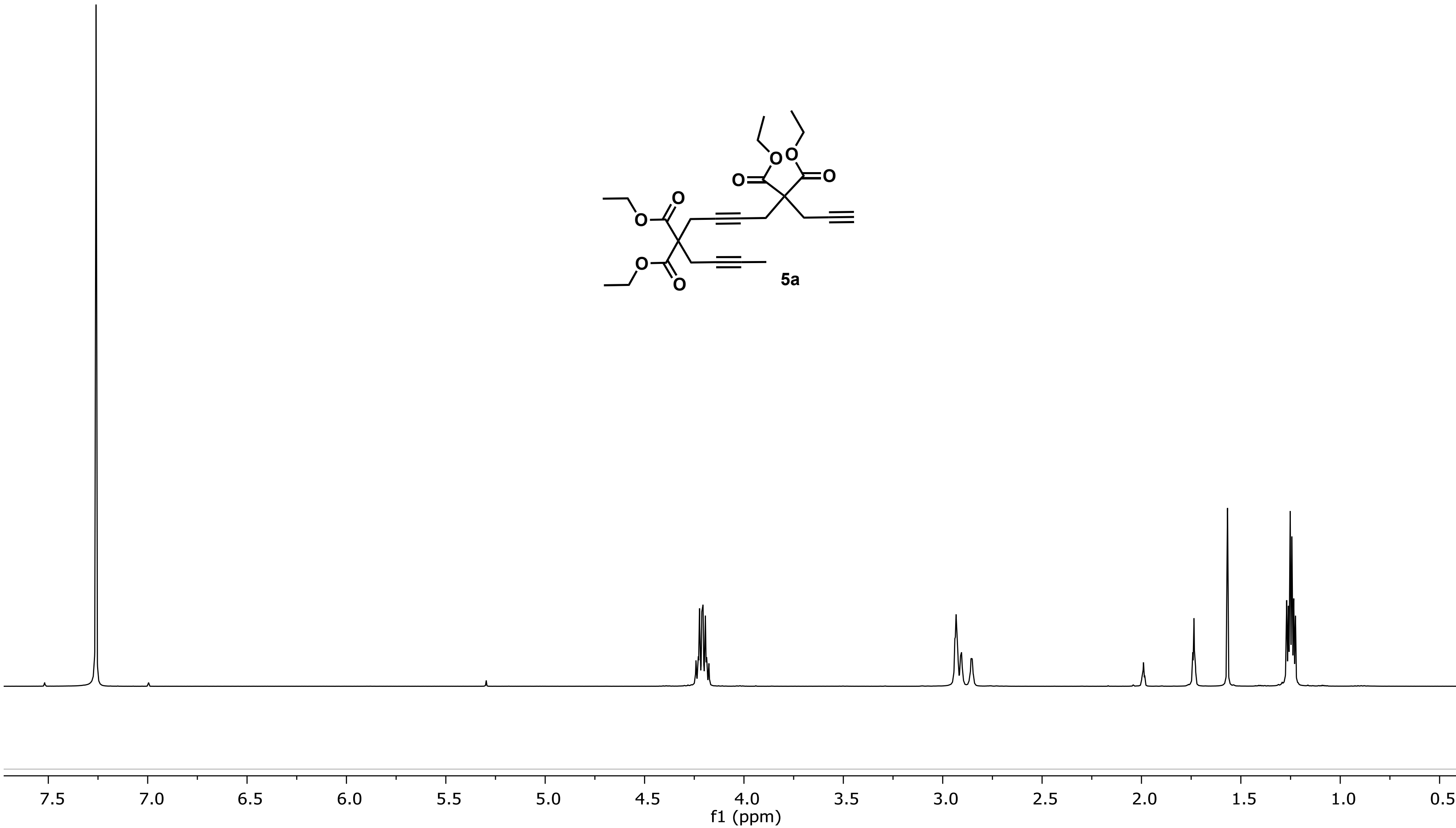


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5a

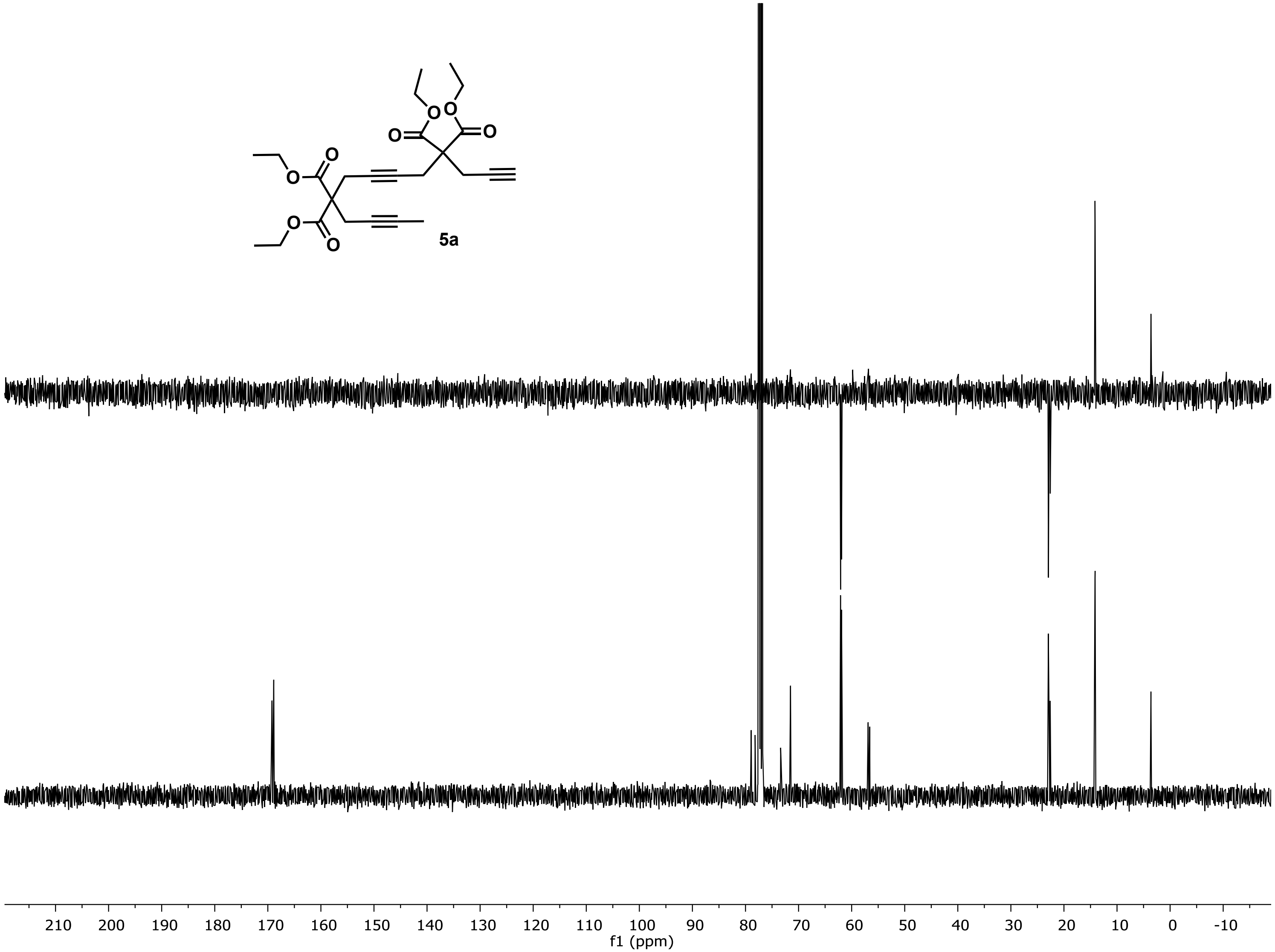
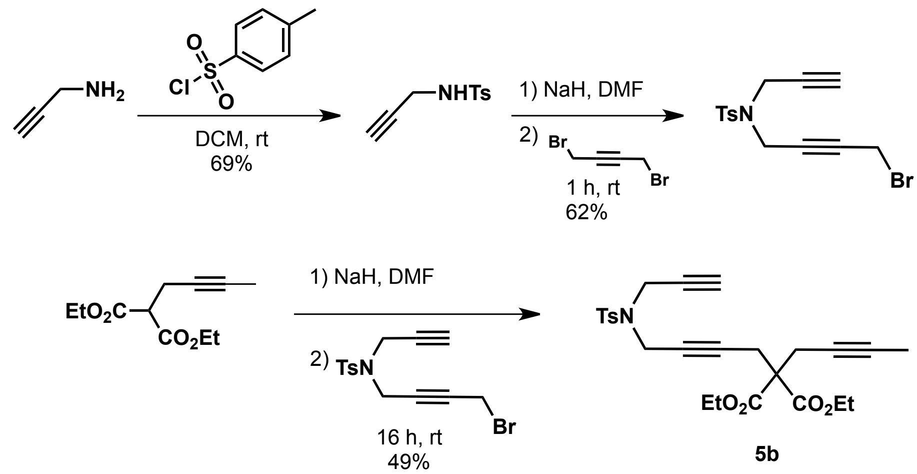
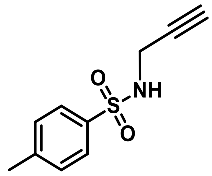


Figure S7. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 5a



Scheme S2. Synthesis of triyne with five-membered aza tether 5b



To a solution of propargylamine (1.5 equiv., 864 mg, 15.7 mmol) in DCM (64 mL) was added tosyl chloride (1 equiv., 2 g, 10.48 mmol) in portion. The reaction mixture was stirred for 16 hours and room temperature. The mixture was quenched with water. The aqueous layer was extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by chromatography (PE/AcOEt 9:1 to 1:1)

Yield: 69% (1.5 g)

Aspect: white solid

^{1}H NMR (400 MHz, Chloroform-d) δ 2.11 (t, 1H, *J* = 2.4 Hz, CH), 2.44 (s, 3H, CH_3), 3.84 (br dd, *J* = 6.1 and 2.4 Hz, 2H, CH_2), 4.49 (t, 1H, *J* = 6.1 Hz, 1H, NH), 7.32 (d, *J* = 8.2 Hz, 2H, CH), 7.77 (d, *J* = 8.2 Hz, 2H, CH).

^{1}H NMR in agreement with previouly reported data[7]

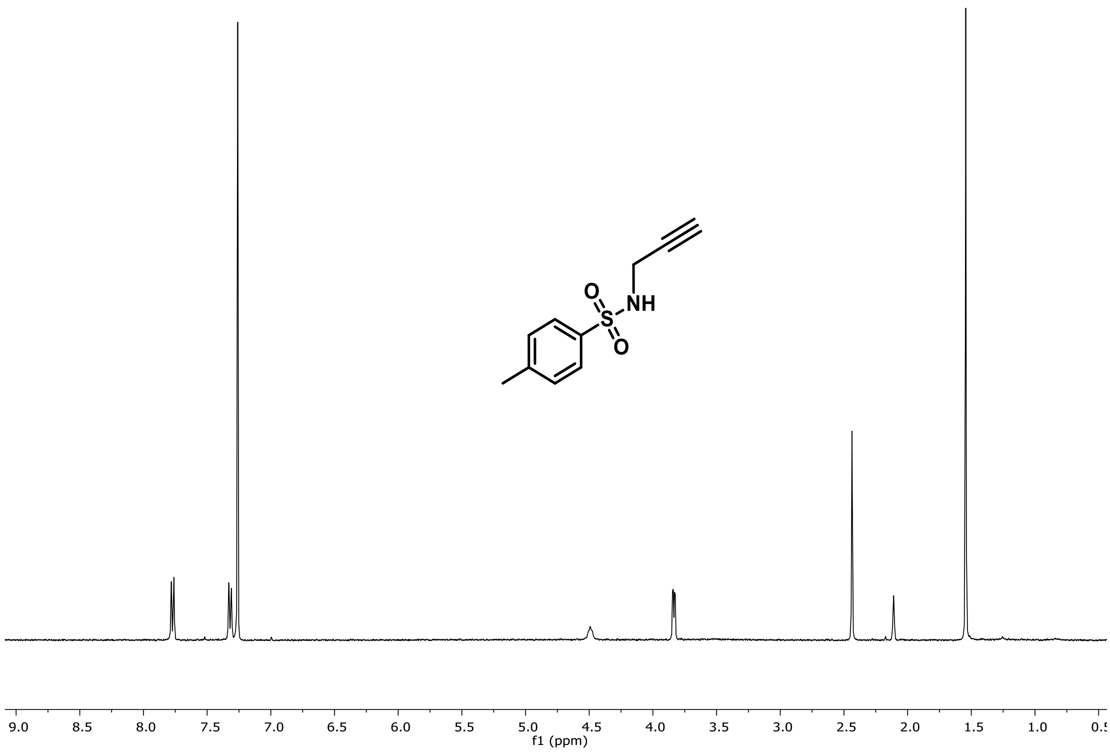
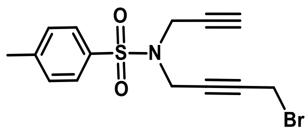


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[7] Song, H.; Liu, Y.; Wang, Q. *Org. Lett.*, **2013**, *15*, 3274–3277



To a suspension of NaH 60% dispersion in oil (1.2 equiv., 0.227 g, 5.67 mmol) in DMF (10 mL) was added dropwise 4-methyl-N-(prop-2-yn-1-yl)benzene-1-sulfonamide (1 equiv., 0.988 g, 4.72 mmol) in DMF (10 mL). The reaction mixture was stirred 1 hour at room temperature after a solution of 1,4-dibromobut-2-yne (0.5 equiv., 0.5 g, 2.36 mmol) in DMF (10 mL) was added. The mixture was stirred 16 hours at room temperature. The mixture was quenched with water. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by chromatography (PE/AcOEt 9:1 to 1:1)

Yield: 62% (998 mg)

Aspect: yellow oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.17 (br t, *J* = 2.0 Hz, 1H, CH), 2.45 (s, 3H, CH_3), 3.71 (t, *J* = 2.0 Hz, 2H, CH_2), 4.12 (d, *J* = 2.3 Hz, 2H, CH_2), 4.23 (d, *J* = 2.3 Hz, 2H, CH_2), 7.32 (d, *J* = 8.2 Hz, 2H, CH_2), 7.72 (d, *J* = 8.2 Hz, 2H, CH_2).

^{1}H NMR in agreement with previouly reported data[8]

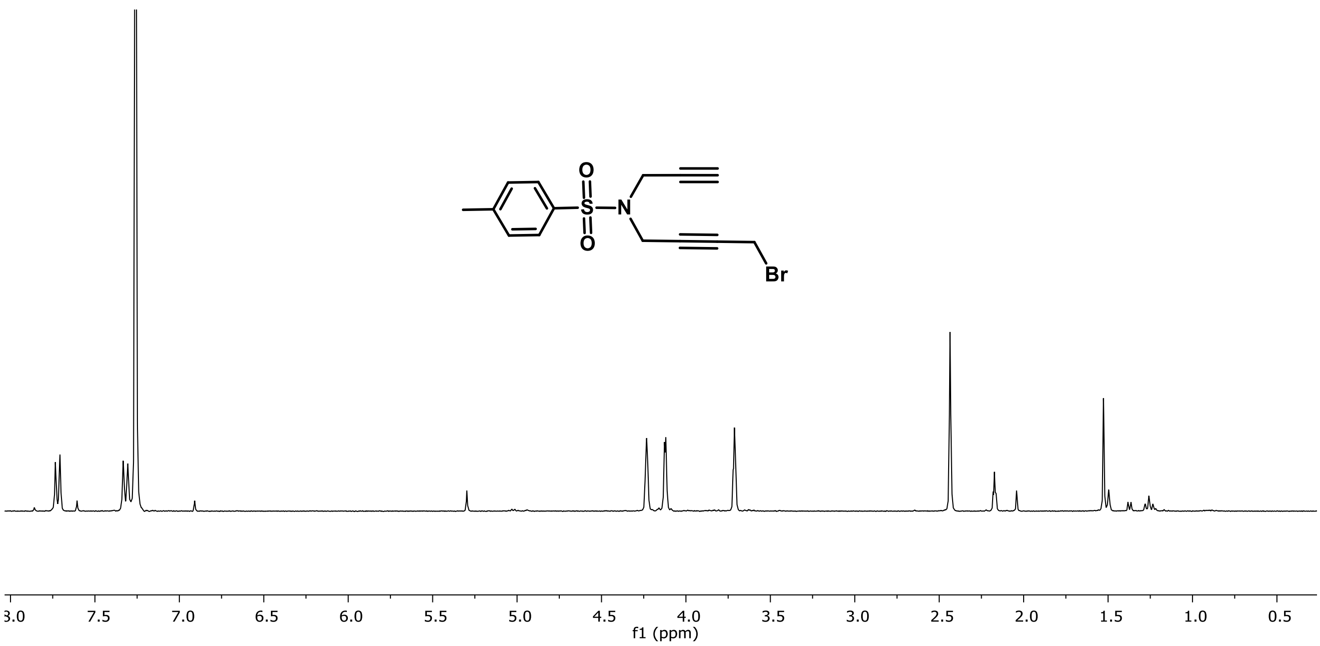
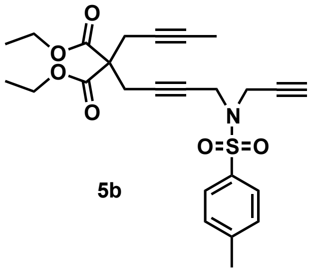


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[8] Kaloko, J.; Teng, Y.; Ojima, I. *Chem. Commun.*, **2009**,*0*, 4569-4571



5b

To a solution of NaH 60% dispersion in oil (1.5 equiv., 83 mg, 2.1 mmol) in DMF (7 mL) was added dropwise 1,3-diethyl 2-(prop-2-yn-1-yl)propanedioate (1 equiv., 297 mg, 1.4 mmol) at 0 °C. The reaction mixture was allowed to warm up to room temperatre and after 30 minutes then N-(4-bromobut-2-yn-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (1 equiv., 0.48 g, 1.4 mmol) was added dropwise to the mixture at 0 °C. The reaction mixture was allowed to warm up to room temperature stirred for 16 hours at room temperature. The mixture was quenched with water. The aqueous layer was extracted with Et_2O. The combined organic phases were washed with an aqueous solution of HCl (2M), water and brine then dried over $MgSO_4$ filtered and concentrated *in vacuo*. The crude was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Aspect: white solid

Yield: 49% (329 mg)

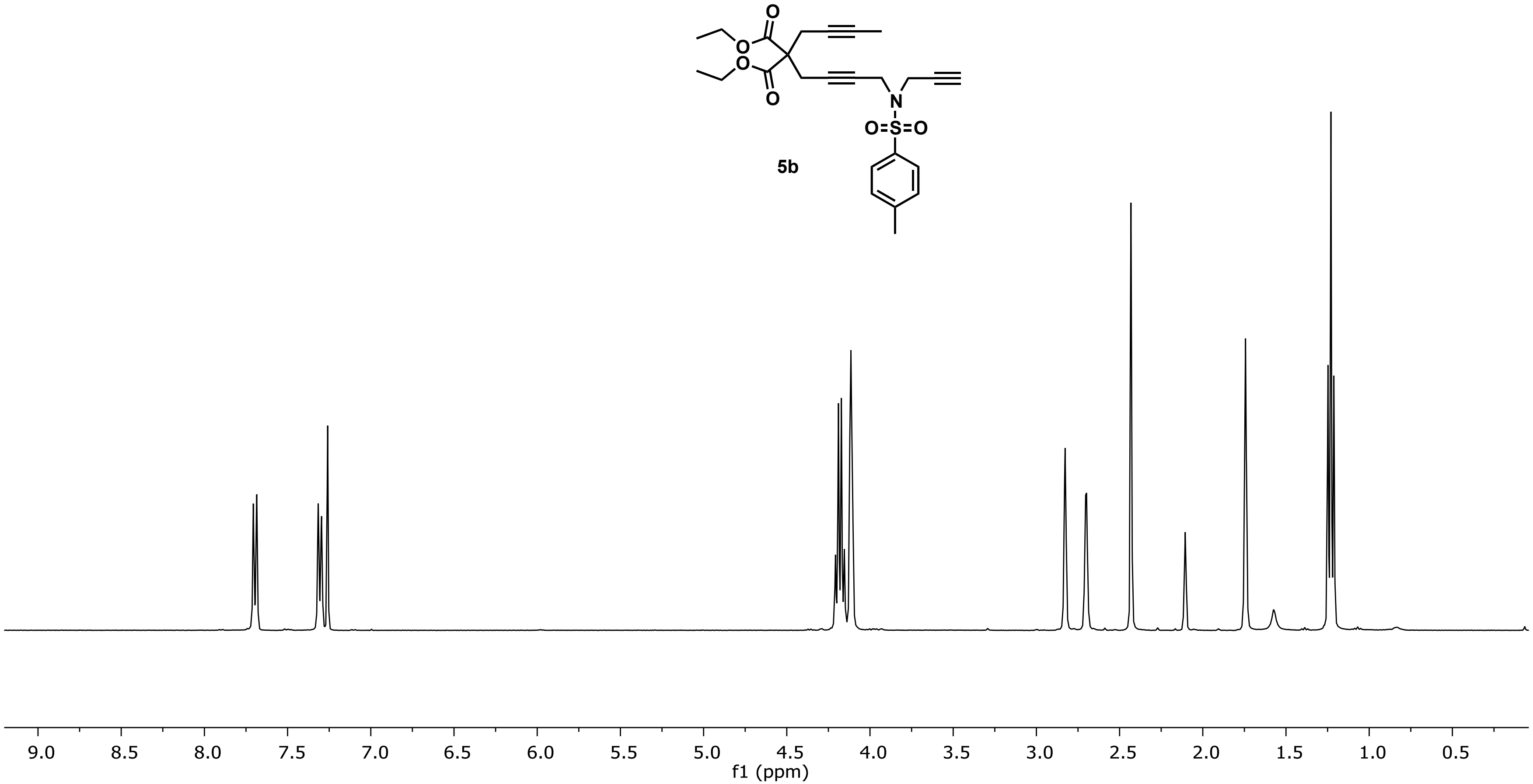
^{1}H NMR (400 MHz, Chloroform-d) δ 1.23 (td, J = 7.1 Hz, 6H, 2 x CH_3), 1.75 (m, 3H, CH_3,), 2.11 (m, 1H, CH), 2.43 (s, 3H, CH_3), 2.71 (m, 2H, CH_2), 2.83 (m, 2H, CH_2), 4.10 (m, 4H, CH_2), 4.18 (q, J = 7.1 Hz, 4H, CH_2), 7.31 (d, J= 8.1 Hz, 2H, 2 x CH), 7.69 (d, J= 8.1 Hz, 2H, 2 x CH).

^{13}C NMR (101 MHz, CDCl3) δ 3.6 (CH_3), 14.2 (2 x CH_3), 21.7 (CH_3), 22.9 (CH_2), 23.0 (CH_2), 36.1 (CH_2), 36.7 (CH_2), 56.7 (C), 62.0 (CH_2), 73.2 (C), 73.9 (CH), 75.6 (C), 76.5 (C,),79.2 (C), 81.0 (C), 128.0 (2 x C), 129.7 (2 x C), 135.5 (C), 144.0 (C), 169.1 (C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{25}H_{30}NO_6S^+$ 472.1788, found 472.1788

IR (neat): 3257, 2978, 2360, 1737, 1201, 1157, 1091, 1064, 1045, 889, 752 cm^{-1}

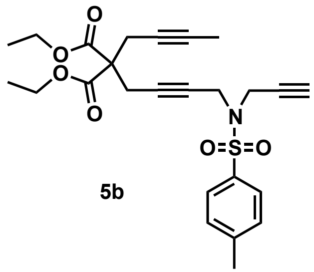
Mp: 70 °C



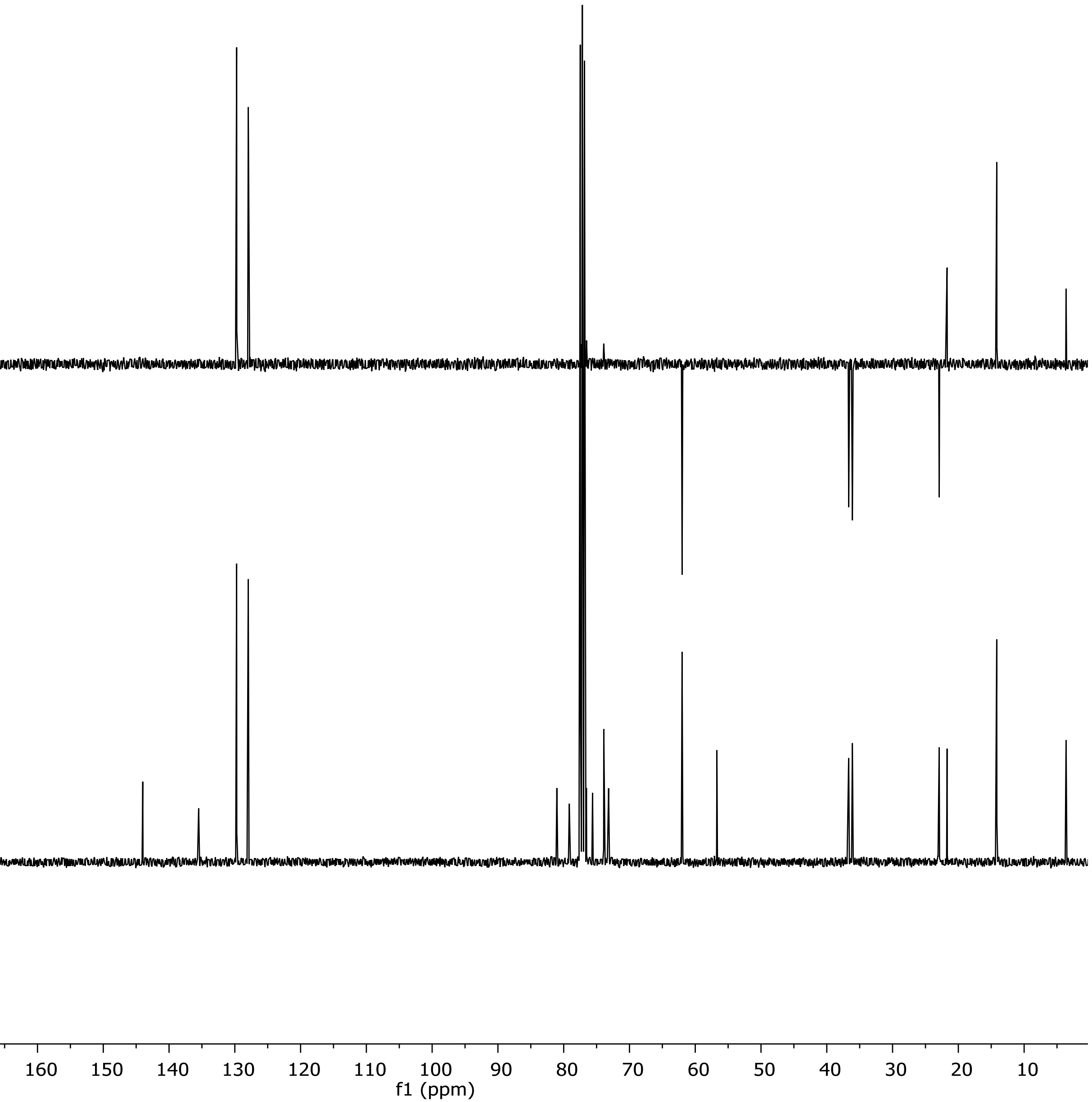
5b

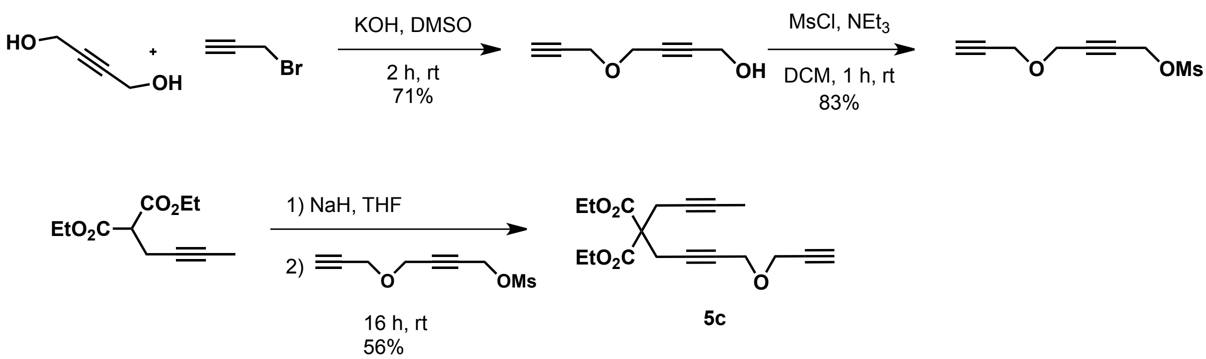
Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5b

Figure S11. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 5b

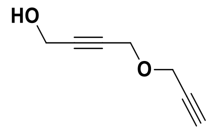


5b





Scheme S3. Synthesis of triyne with five-membered tetrahydrofuran tether 5c



To a suspension of KOH (3 equiv., 7.07 g, 126 mmol) in DMSO (91 mL) was added 3-bromopropyne (1 equiv., 5 g, 3.62 mL, 42 mmol) and 2-butyne-1,4-diol (2.95 equiv., 10.7 g, 123 mmol). The reaction mixture was stirred for 2 hours at room temperature. The mixture was quenched with water then with an aqueous solution of HCl (6M). The aqueous layer was extracted with DCM. The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated *in vacuo.* The crude was purified by flash chromatography on silica gel (PE/EtOAc 3:1).

Yield: 71% (3.7 g)

Aspect: Yellow oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1,74 (t, J = 5.2 Hz, 1H, OH), 2.45 (t, J = 2.4 Hz, 1H, CH), 4.25 (d, J = 2.4 Hz, 2H, CH_2), 4.28 – 4.34 (m, 4H, CH_2).

^{1}H NMR in agreement with previouly reported data[9]

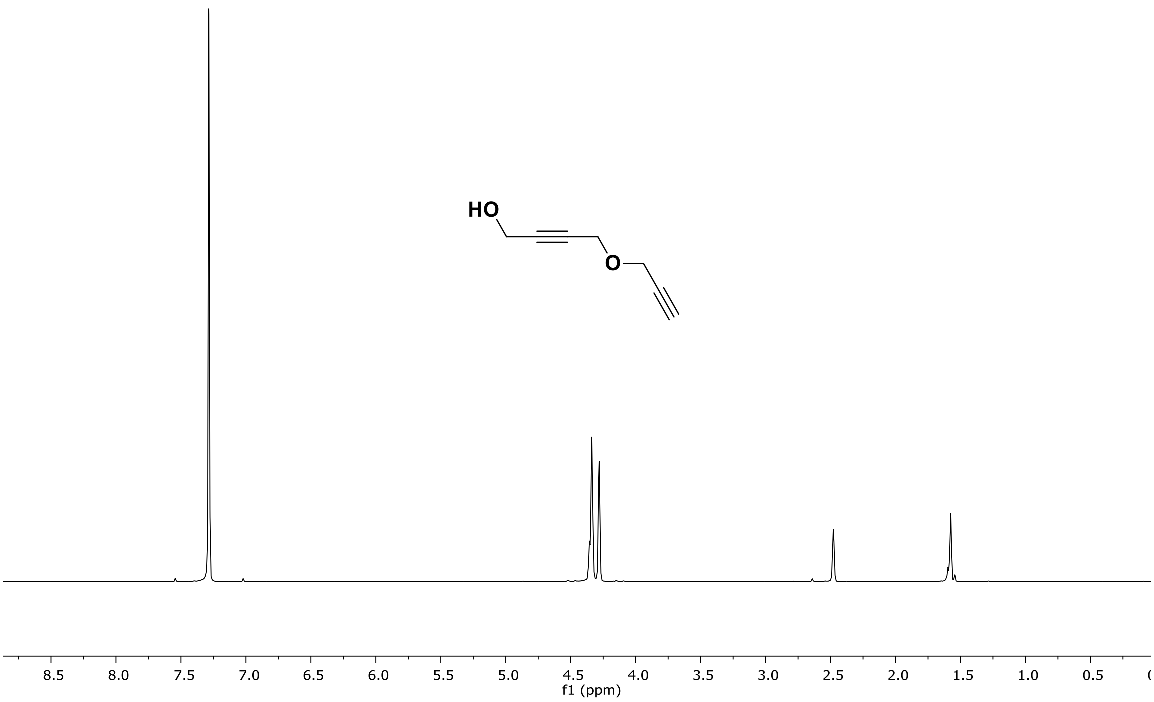
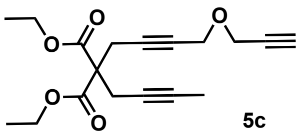


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[9] Nicolaus, N.; Strauss, S.; Neudörfl, J.; Prokop, A.; Schmalz, *Org. Lett.*, **2009**, *11*, 341–344



5c

To a solution of 4-(prop-2-yn-1-yloxy)but-2-yn-1-ol (1 equiv., 1 g, 8.06 mmol) and NEt_3 (1.45 equiv., 1.18 g, 1.62 mL, 11.7 mmol) in DCM (51 mL) was added dropwise MsCl (1.3 equiv., 1.2 g, 0.811 mL, 10.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 hour. The mixture was quenched with water. The aqueous phase was extracted with DCM. The organics layers were washed with water, dried over $MgSO_4$, filtered and concentrated *in vacuo.* Due to the relative instability of the compound, it was directly engaged in the next step without further purification. The crude was obtained in 83% yield.

To a solution of NaH (1.1 equiv., 282 mg, 7.07 mmol) in THF (12.6 mL) was added dropwise a solution of 1,3-dimethyl 2-(but-2-yn-1-yl)propanedioate (1 equiv., 1184 mg, 6.43 mmol) in THF (6.3 mL) at 0 °C.The reaction mixture was allowed to room temperature after 30 min 4-(prop-2-yn-1-yloxy)but-2-yn-1-yl methanesulfonate (1 equiv., 1,3 g, 6.43 mmol) was added. The reaction mixture was stirred 16 hours at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography (PE/AcOEt 95:5).

Yield: 56% (1.15 g)

Aspect: yellow pale oil

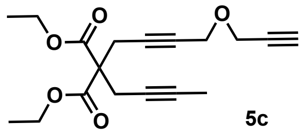
^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.26 (t, J = 7.1 Hz, 6H, 2 x CH_3), 1.75 (t, J = 2.6 Hz, 3H, CH_3), 2.43 (t, J = 2.4 Hz, 1H, CH), 2.90 (q, J = 2.6 Hz, 2H, CH_2), 3.01 (t, J = 2.1 Hz, 2H, CH_2), 4.18 – 4.26 (m, 8H, 4 x CH_2).

^{13}C NMR (101 MHz, Chloroform-d) δ 3.6 (CH_3), 14.2 (2 x CH_3), 23.1 (CH_2), 23.2 (CH_2), 56.3 (CH_2), 56.9 (C), 57.0 (CH_2), 62.0 (CH_2), 73.2 (C), 74.9 (CH), 78.3 (C), 79.2 (C), 79.3 (C), 82.1 (C), 169.2 (2 x C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{18}H_{23}O_5^+$ 319.1540, found 319.1536

IR (neat): 3279, 2983, 1728, 1286, 1193, 1068, 1047, 856 cm^{-1}

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5c



5c

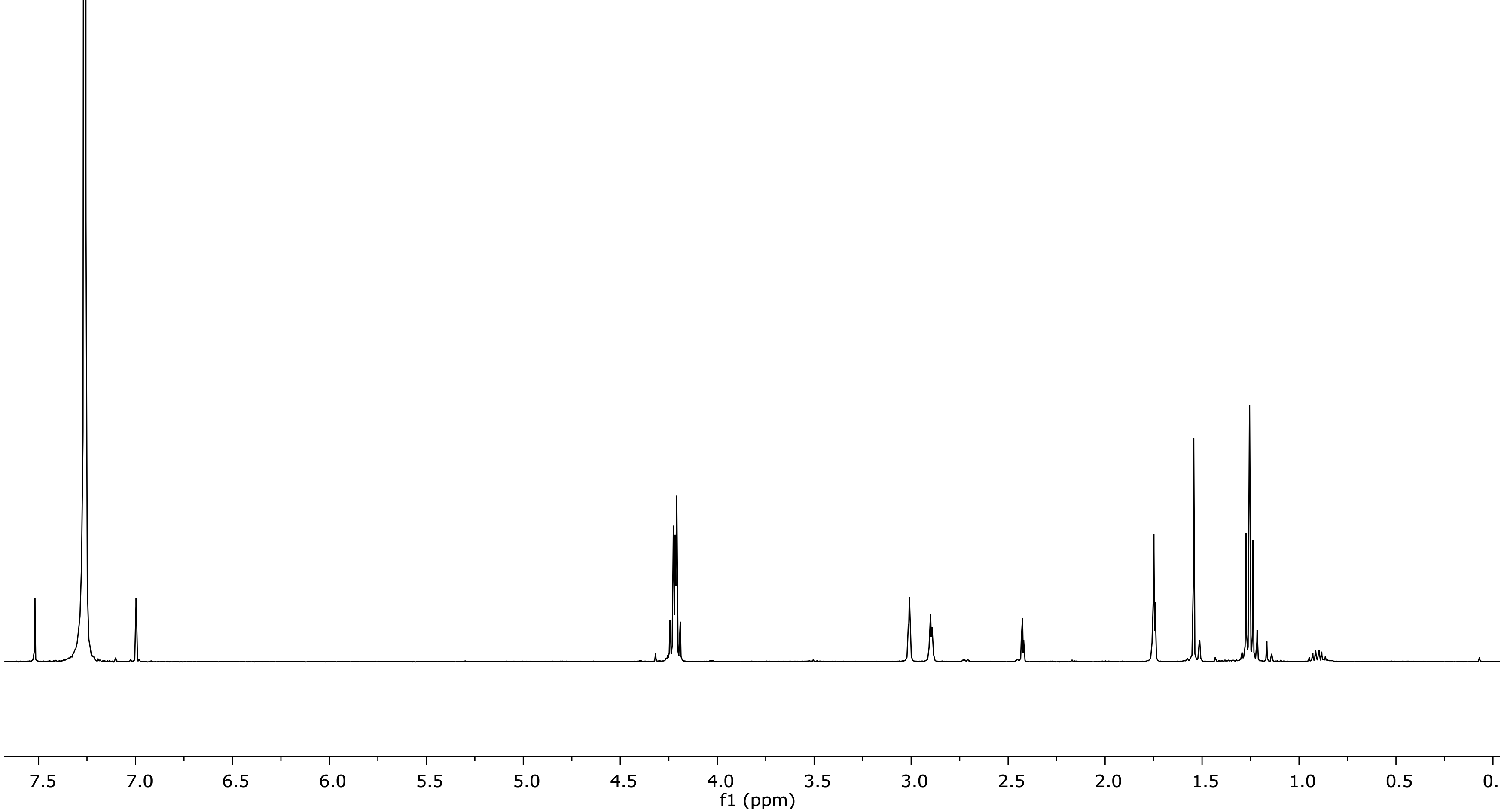
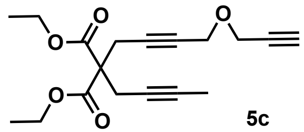
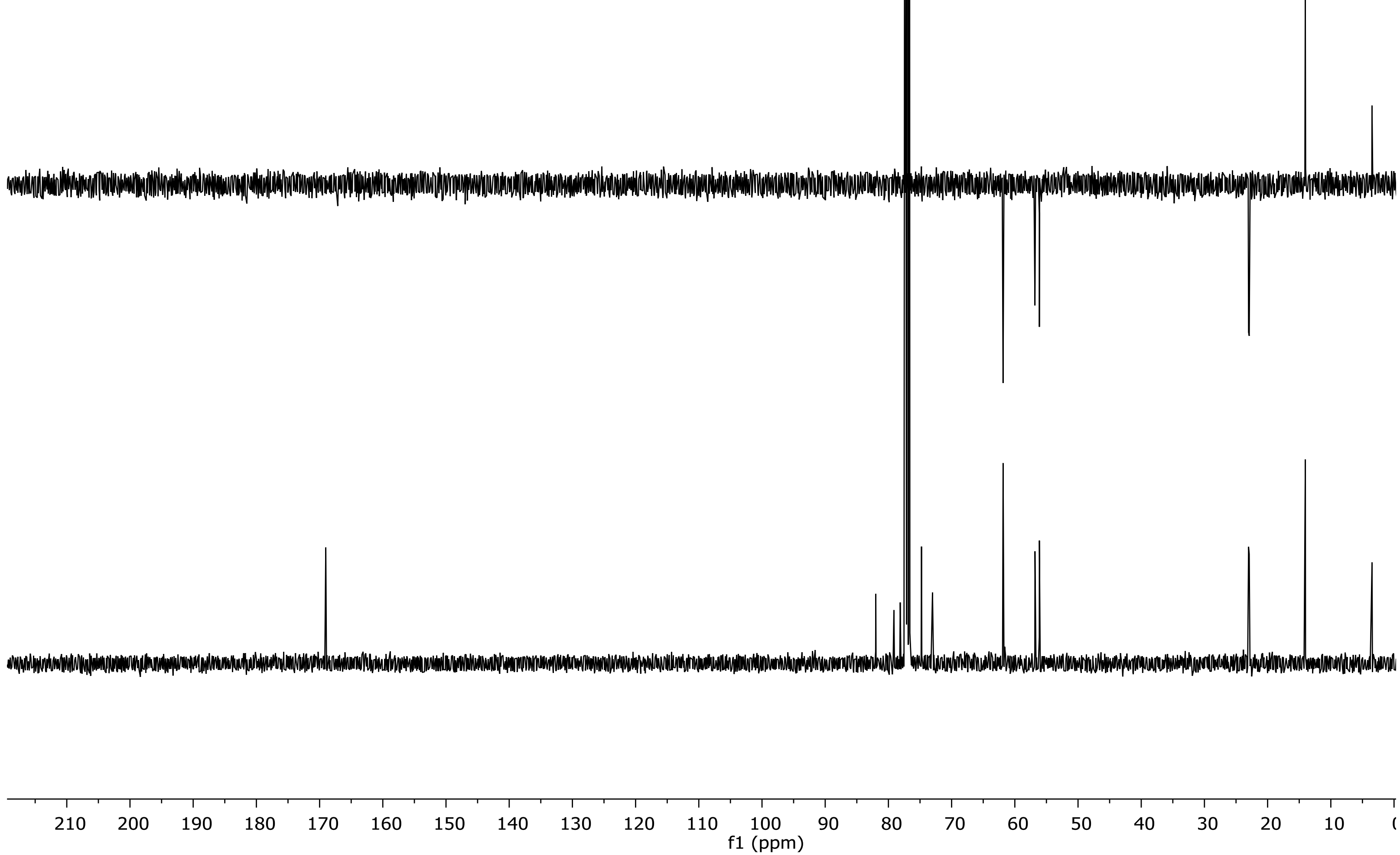
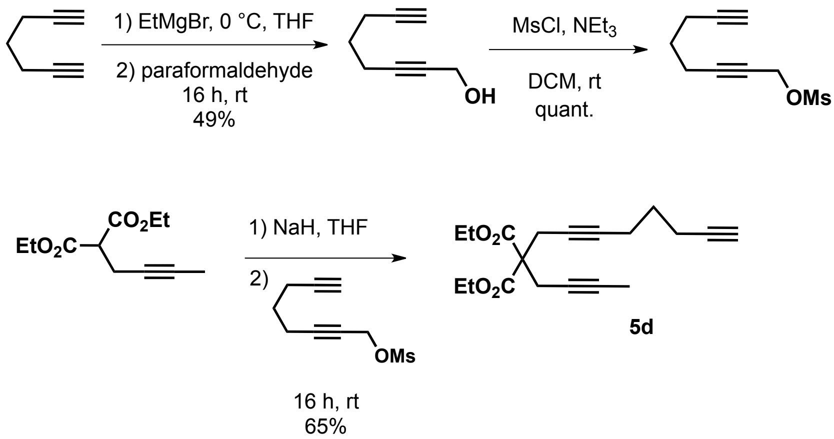


Figure S14. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 5c

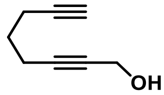


5c





Scheme S4. Synthesis of triyne with five-membered all carbon tether 2d



To a solution of 1,6-heptadiyne (1 equiv., 2 g, 21.7 mmol) in THF (100 mL) at 0 °C was added ethyl magnesiumbromide (1.05 equiv., 3 M, 7.6 mL, 22.8 mmol) over 5 minutes. After 2 hours, paraformaldehyde (1.05 equiv., 2.05 g, 22.8 mmol) was added in one portion. The mixture was stirred at 50 °C for 21 hours. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl then with an aqueous solution of HCl (10% aq). The aqueous layer was extracted with Et_2O. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purifed by flash chromatography on silica gel (PE/Et_2O 7:3).

Yield: 49% (1.31 g)

Aspect: colorless oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.45 (t, *J* = 6.0 Hz, 1H, OH), 1.74 (qt, *J* = 7.0 Hz, 2H, CH_2), 1.96 (t, *J* = 2.6 Hz, 1H, CH), 2.31 (td, *J* = 7.0 and 2.6 Hz, 2H, CH_2), 2.36 (tt, *J* = 7.0 and 2.1 Hz, 2H, CH_2), 4.25 (dt, *J* = 6.0 and 2.1 Hz, 2H, CH_2).

^{1}H NMR in agreement with previouly reported data.[10]

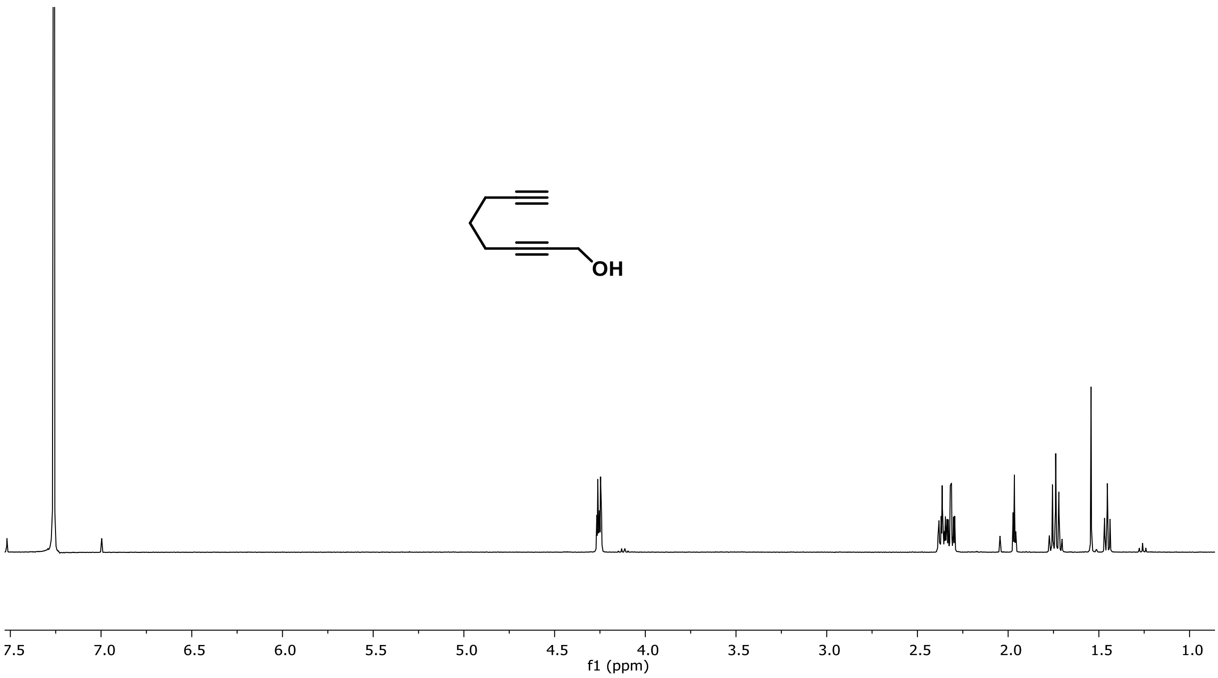
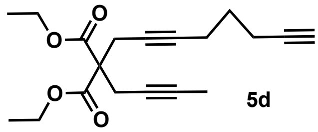


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum

[10] Robinson, J.; Sakai, T.; Okano, K.; Kitawaki, T.; Danheiser, R. *J. Am. Chem. Soc* **2010,** *132*, 11039-11041



5d

To a solution of octa-2,7-diyn-1-ol (1 equiv., 1.3 g, 6.55 mmol) and NEt_3 (1.45 equiv., 1.56 g, 15.4 mmol) in DCM (67mL) was added dropwise MsCl (1.3 equiv., 1.58 mg, 13.8 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 1 hour. The reaction mixture was quenched with water. The aqueous layer was extracted with DCM. The combined organics layers were washed with water, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Due to the relative instability of the compound, it was directly engaged in the next step without further purification. The crude was obtained in quantitative yield.

To a solution de NaH 60% dispersion in oil (1.1 equiv., 0.371 g, 9.26 mmol) in THF (16.6 mL) was added dropwise a solution of 1,3-diethyl 2-(but-2-yn-1-yl)propanedioate (1 equiv., 1.79 g, 8.42 mmol) in THF (8.3 mL). The mixture was allowed to warm up to room temperature and after 30 min octa-2,7-diyn-1-yl methanesulfonate (1.2 equiv., 2.02 g, 10.1 mmol) was added. The reaction mixture was stirred for 16 hours at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo.* The crude was purified by flash chromatography on silica gel (PE/AcOEt 95:5).

Yield: 65% (1.73g)

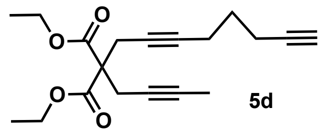
Aspect: colorless oil

^{1}H NMR (300 MHz, Chloroform-d) δ 1.24 (t, *J* = 7.1 Hz, 6H, 2 x CH_3), 1.65 (p, *J* = 7.0 Hz, 2H, CH_2), 1.73 (t, *J* = 2.6 Hz, 3H, CH_3), 1.92 (t, *J* = 2.6 Hz, 1H, CH), 2.20-2.29 (m, 4H, 2 x CH_2), 2.87 (br q, 2H, *J* = 2.6 Hz, CH_2), 2.90 (br t, *J* = 2.6 Hz, 2H, CH_2), 4.19 (q, *J* = 7.1 Hz, 4H, 2 x CH_2).

^{13}C NMR (75 MHz, Chloroform-d) δ 3.6 (CH_3), 14.2 (2 x CH_3), 17.5 (CH_2), 17.9 (CH_2), 23.0_2 (CH_2), 23.0_4 (CH_2), 27.9 (CH_2), 57.1 (C), 61.8 (CH_2), 68.8 (CH), 73.4 (C), 75.3 (C), 78.9 (C), 82.4 (C), 83.7 (C), 169.4 (2 x C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{19}H_{25}O_4^+$ 317.1747, found 317.1747

IR (neat): 3282, 2968, 1732, 1286, 1190, 1072, 1053 cm^{-1}



5d

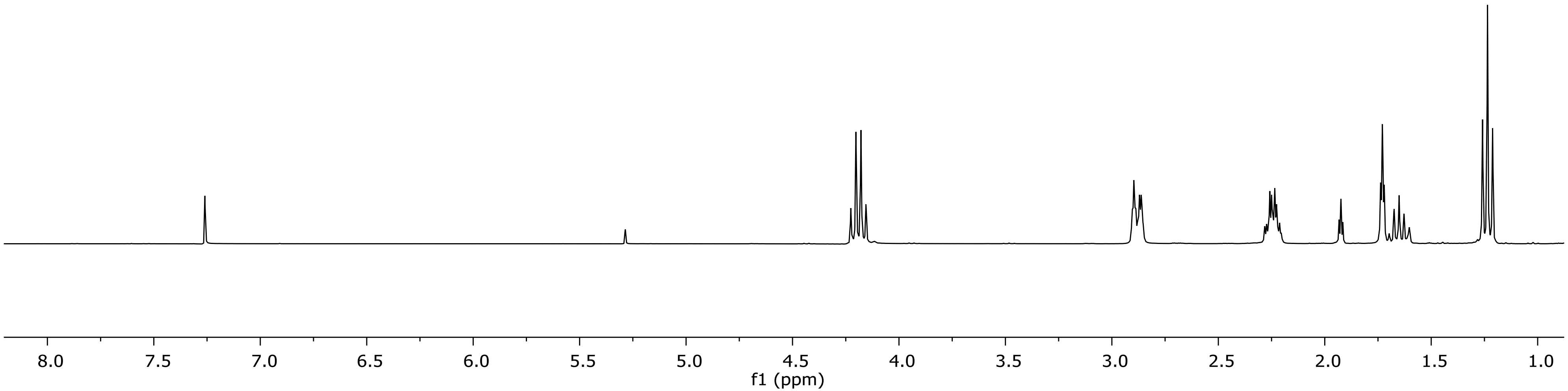
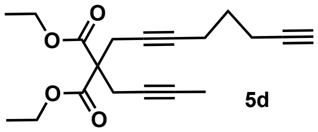
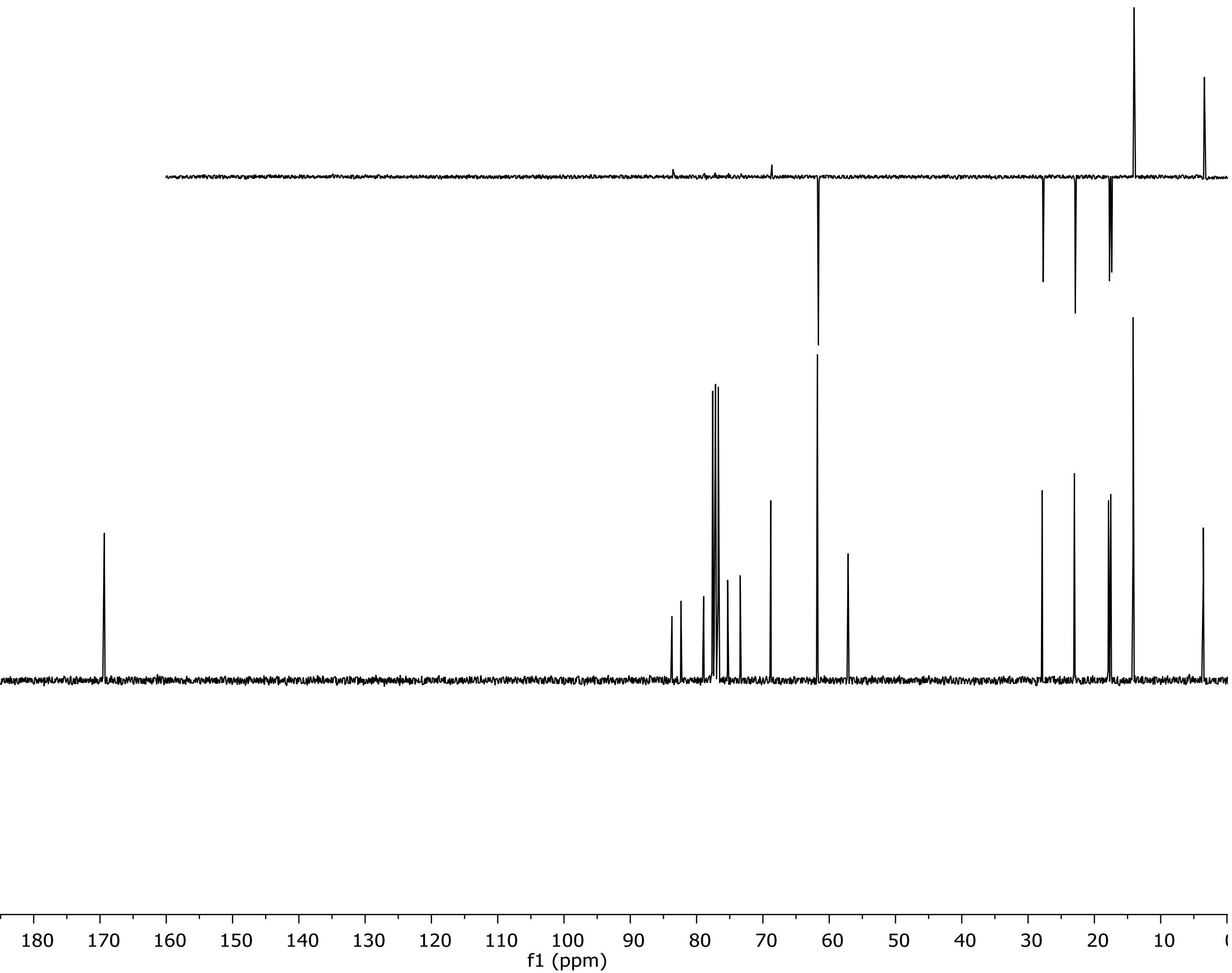


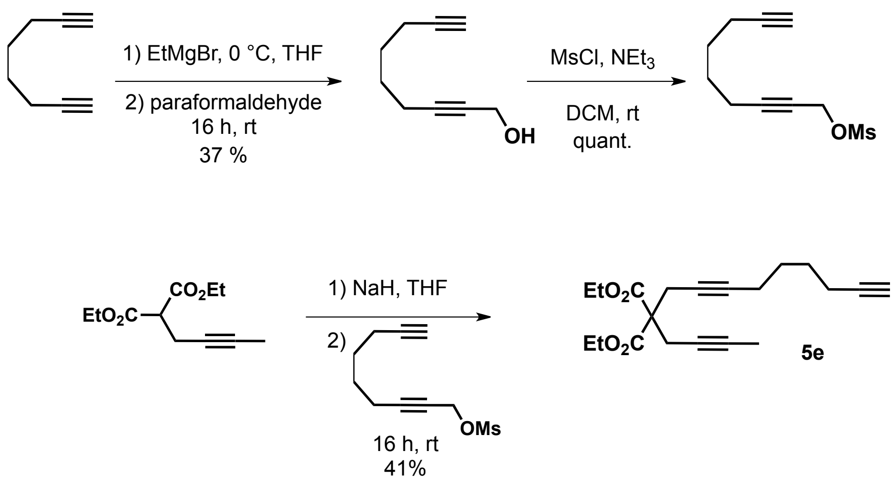
Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5d

Figure S17. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 5d

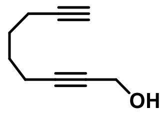


5d





Scheme S5. Synthesis of triyne with six-membered all carbon tether 5e



To a solution of 1,7-octadiyne (1 equiv., 0.72 g, 0.9 mL, 6.78 mmol) in THF (31.5 mL) at 0 °C was added ethylmagnesiumbromide (1.05 equiv., 3 M, 2.37 mL, 7.12 mmol) over 5 minutes. Then after 2 hours, paraformaldehyde (1.05 equiv., 0.641 g, 7.12 mmol) was added in one portion to the mixture. The mixture reaction was stirred at 50 °C for 21 hours. The mixture was quenched with a saturated aqueous solution of NH_4Cl then with an aqueous solution of HCl (10% aq). The aqueous layer was extracted with Et_2O. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purifed by flash chromatography on silica gel (PE/Et_2O 7:3).

Yield: 37% (341 mg)

Aspect: colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 1.47 (t, J = 6.0 Hz, 1H, CH), 1.61–1.70 (m, 4H, 2 x CH_2), 1.95 (t, J = 2.7 Hz, 1H, CH), 2.23 (m, 4H, 2 x CH_2), 4.25 (dt, J = 6.0 and 2.2 Hz, 2H, CH_2).

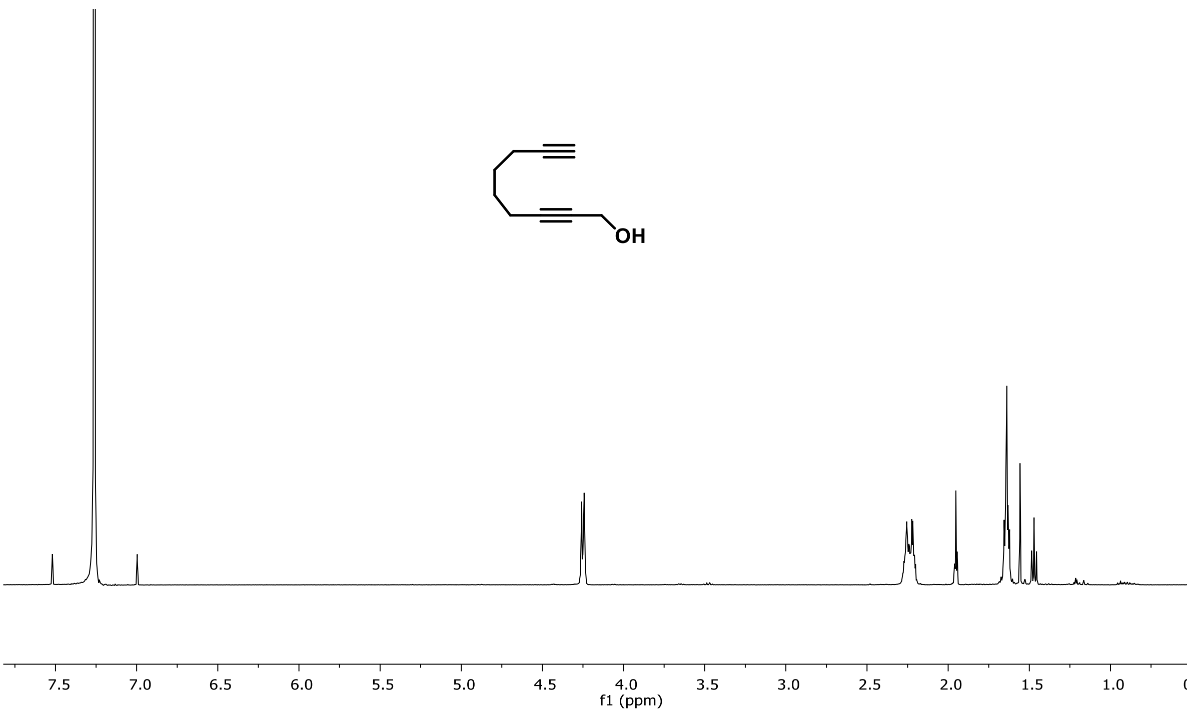
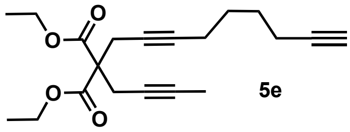


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum



5e

To a solution of nona-2,8-diyn-1-ol (1 equiv., 400 mg, 2.94 mmol), previously prepared, and NEt_3 (1.45 equiv., 430 mg, 4.26 mmol) in DCM (18.5 mL) was added dropwise MsCl (1.3 equiv., 437 mg, 3.82 mmol) at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 1 hour. The mixture was quenched with water. The aqueous layer was extracted with DCM. The combined organics layers were washed with water and dried over $MgSO_4$, filtered and concentrated *in vacuo*. Due to the relative instability of the compound, it was directly engaged in the next step without further purification. The crude was obtained with a quantitative yield. To a solution of NaH 60% dispersion in oil (1.1 equiv., 77 mg, 1.92 mmol) in THF (3.4 mL) was added dropwise a solution of 1,3-diethyl 2-(but-2-yn-1-yl)propanedioate (1 equiv., 371 mg, 1.75 mmol) in THF (1.7 mL). The reaction mixture was allowed to warm to room temperature and after 30 minutes nona-2,8-diyn-1-yl methanesulfonate (1.2 equiv., 450 g, 2.1 mmol) was added. The mixture was stirred for 16 hours at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo.* The crude was purified by flash chromatography on silica gel (PE/AcOEt 95:5).

Yield: 41% (238 mg) *with the presence of 30% of starting material*

Aspect: colorless oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.24 (t, *J* = 7.1 Hz, 6H, 2 x CH_3), 1.54 – 1.61 (m, 4H, 2 x CH_2), 1.74 (t, *J* = 2.5 Hz, 3H, CH_3), 1.93 (t, *J* = 2.6 Hz, 1H, CH), 2.11–2.21 (m, 4H, 2x CH_2), 2.88 (br q, *J* = 2.5 Hz, 2H, CH_2), 2.90 (t, *J* = 2.6 Hz, 2H, CH_2), 4.20 (q, *J* = 7.1 Hz, 4H, 2 x CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 3.6 (CH_3), 14.2 (2 x CH_3), 18.1 (CH_2), 18.3 (CH_2), 23.0 (2 x CH_2), 27.5 (CH_2), 27.9 (CH_2), 57.1 (C), 61.7 (CH_2), 61.8 (CH_2), 68.5 (CH), 73.4 (C), 74.8 (C), 78.9 (C), 83.0 (C), 84.3 (C), 169.4 (2 x C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{20}H_{27}O_4$ 331.1904, found 331.1902

IR (neat): 2943, 2873, 1747, 1448, 1359, 1327, 1168, 1132, 1112, 1062, 1028, 977, 935, 800, 711 cm^{-1}

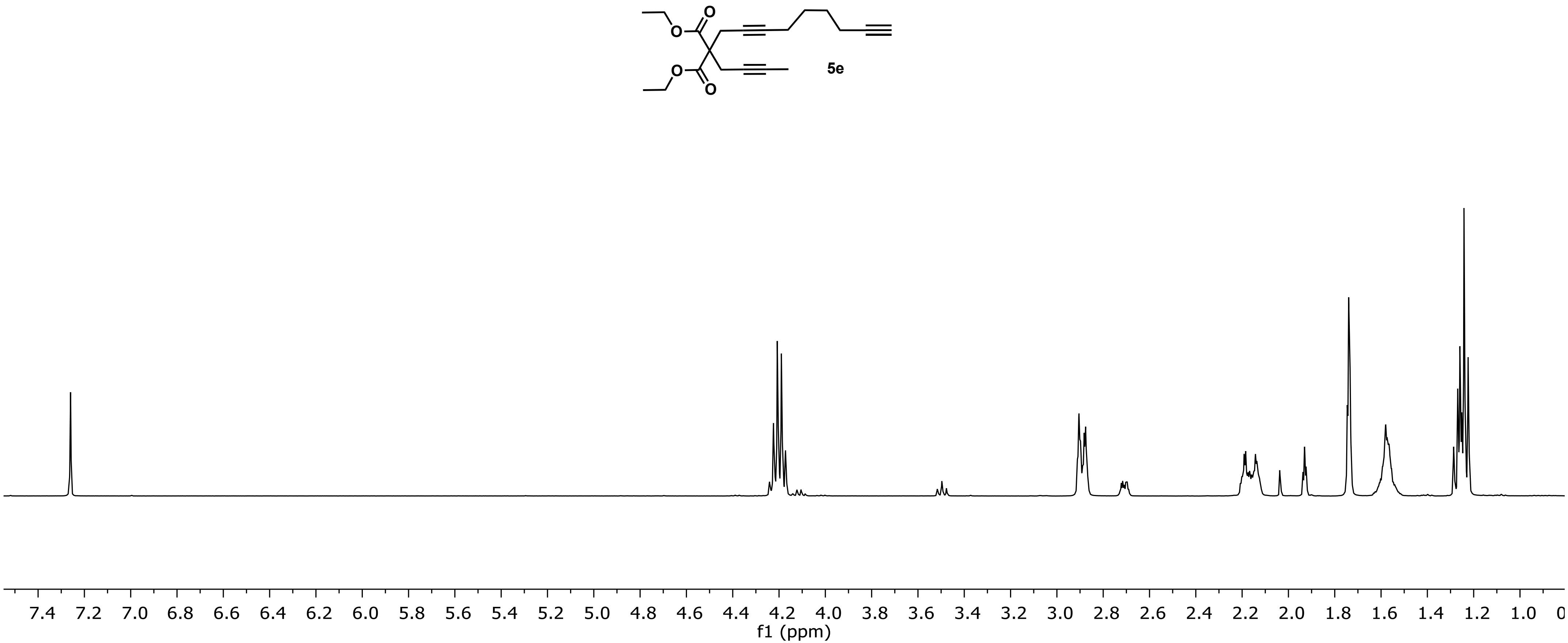
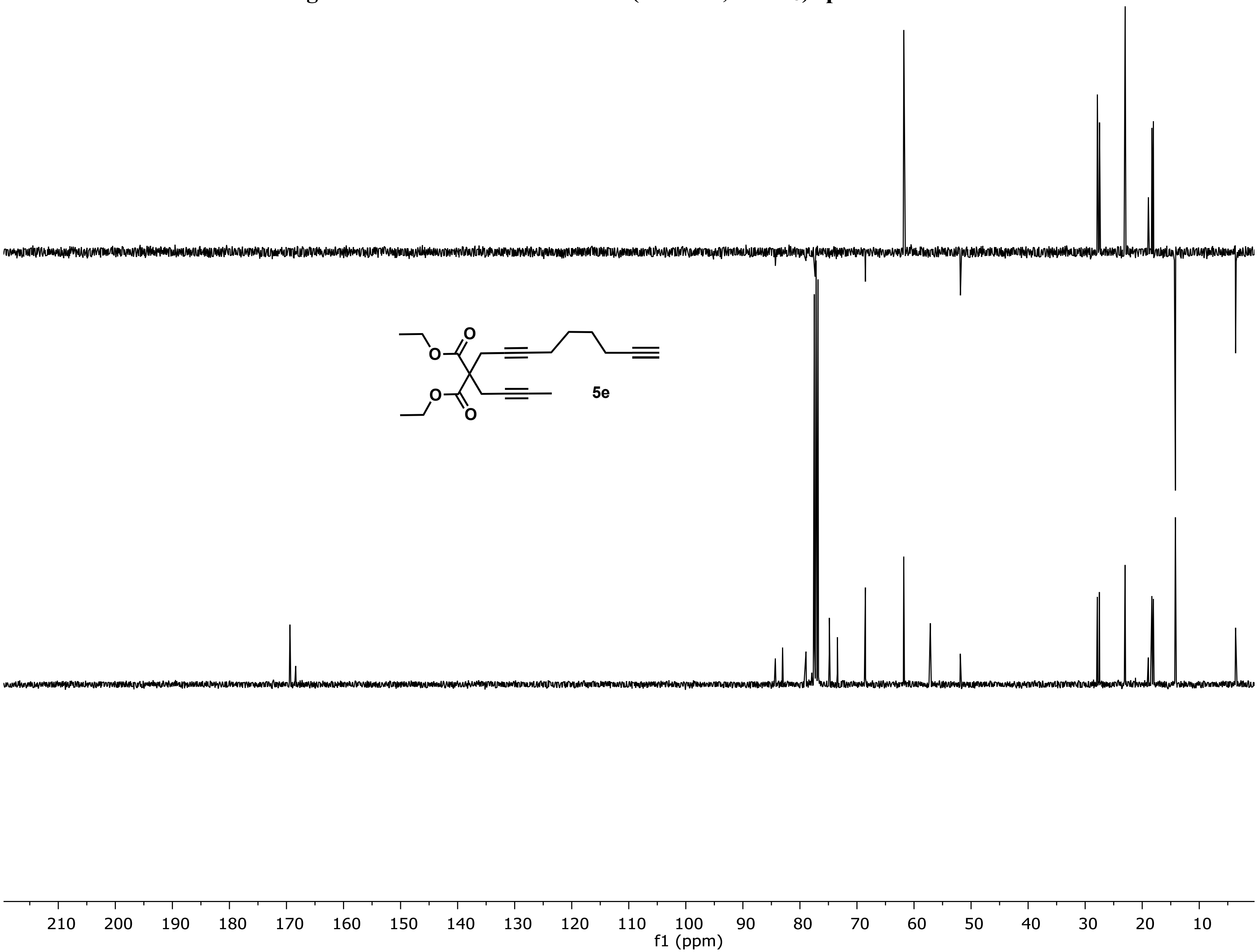
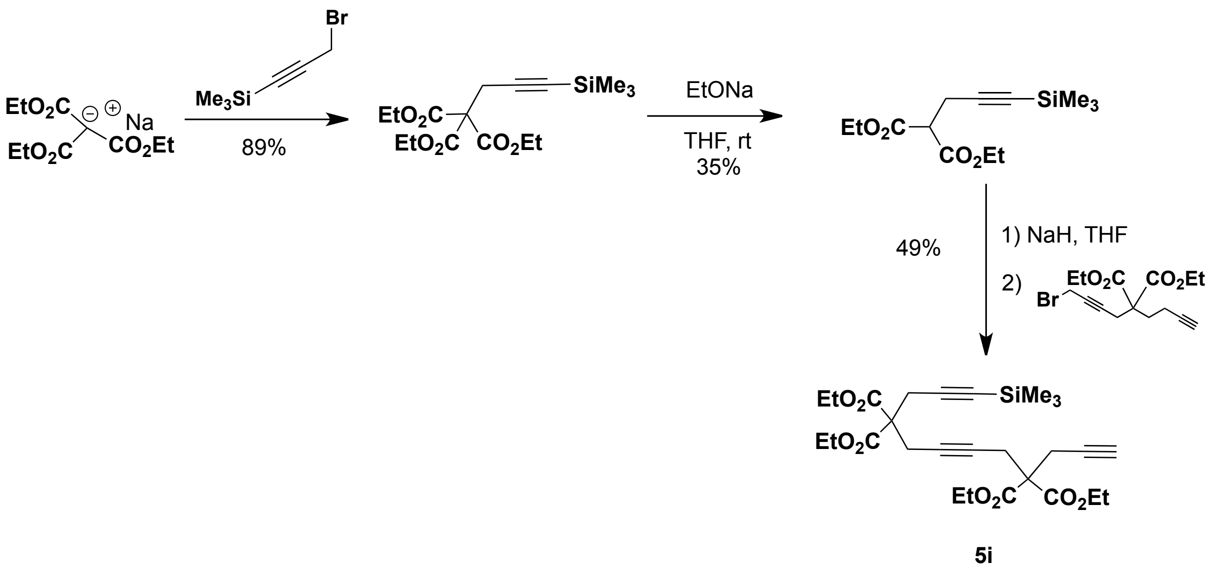


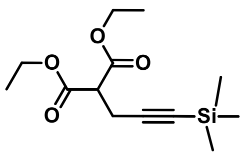
Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5e

Figure S20. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 5e





Scheme S6. Synthesis of triyne with six-membered all carbon tether 5i



To a solution of sodium 1,3-diethoxy-2-(ethoxycarbonyl)-1,3-dioxopropan-2-ide (1equiv., 2.5g, 9.93 mmol) in toluene (20 ml) and DMF (20 mL) was added 3-(trimethylsilyl)propargyl bromide (1equiv., 1.88g, 1.39mL, 9.83 mmol). The mixture was strirred at 80 °C for 16 hours. he mixture was cooled dowm at room temperature and quenched with water. The aqueous layer was extracted with toluene. The combined organic layers were washed with water then with a saturated aqueous solution of Na_2CO_3, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was quite pure to be use directly in the next step. The crude was obtained in 89% yield.

To a suspension of EtONa (1 equiv., 0.596 g, 8.76 mmol) in THF (9.3 mL) was added dropwise a solution of triethyl 4-(trimethylsilyl)but-3-yne-1,1,1-tricarboxylate (1 equiv., 3 g, 8.76 mmol) in THF (14 mL). The reaction mixture was stirred for 4 hours at room temperature. The mixture was quenched with an aqueous solution of HCl (1N). The aqueous layer was extracted with Et_2O. The combined organic layers were washed with water, a saturated aqueous solution of $NaHCO_3$ and brine then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatograpy on silica gel (PE/Et_2O 3:1).

Yield: 35% (820 mg)

Aspect: colorless oil

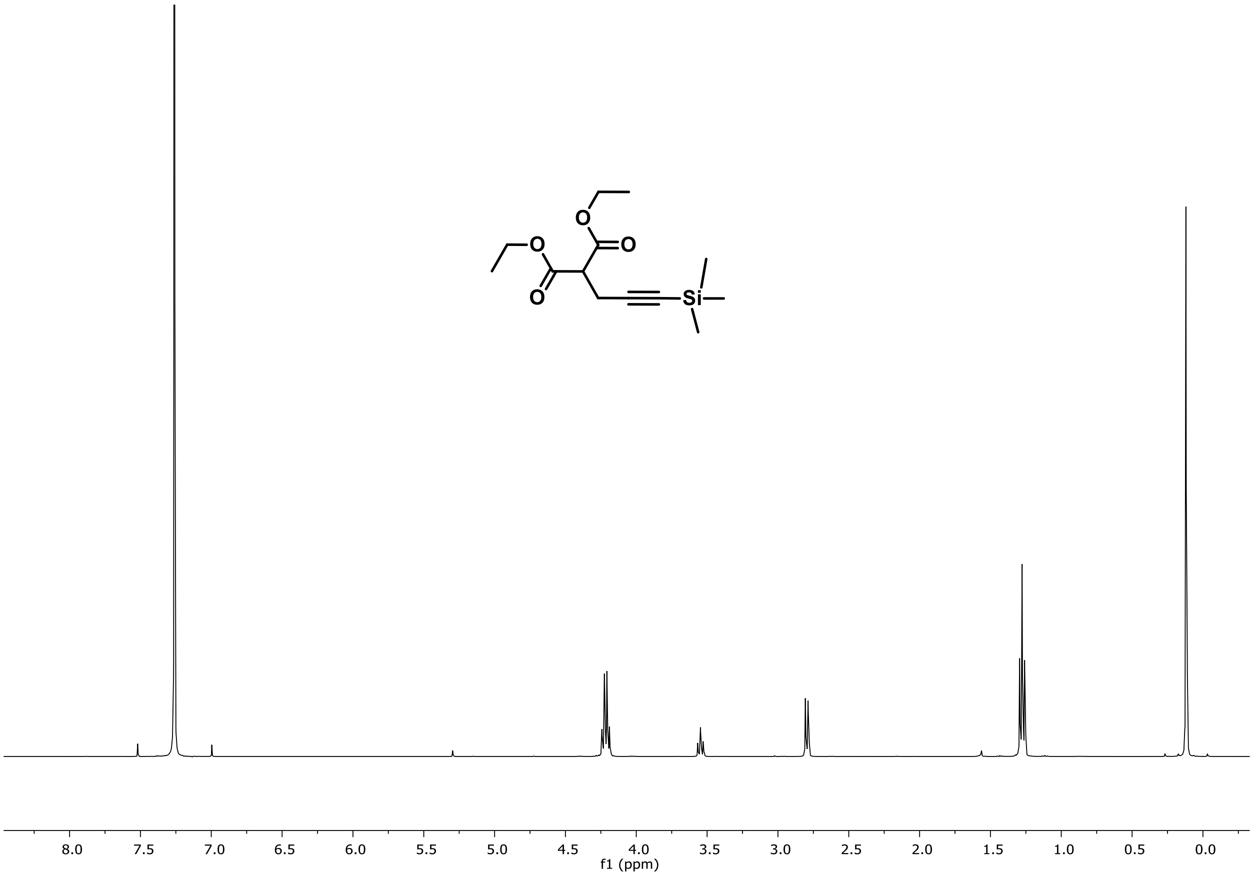
^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.12 (s, 9H, 3 x CH_3), 1.28 (t, J = 7.1 Hz, 6H, 2 x CH_3), 2.80 (d, J = 7.8 Hz, 2H, CH_2), 3.55 (t, J = 7.8 Hz, 1H, CH), 4.22 (q, J = 7.1 Hz, 4H, 2 x CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 0.1 (3 x CH_3), 14.2 (2 x CH_3), 20.0 (CH_2), 51.6 (CH,), 61.8 (2 x CH_2), 87.1 (C), 102.4 (C), 168.1 (C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{13}H_{23}O_4Si$ 271.1360, found 271.1360

IR (neat): 2968, 14722, 1249, 1149, 1022, 846, 750 cm^{-1}

Figure S21.¹H NMR (400 MHz, CDCl$_3$) spectrum



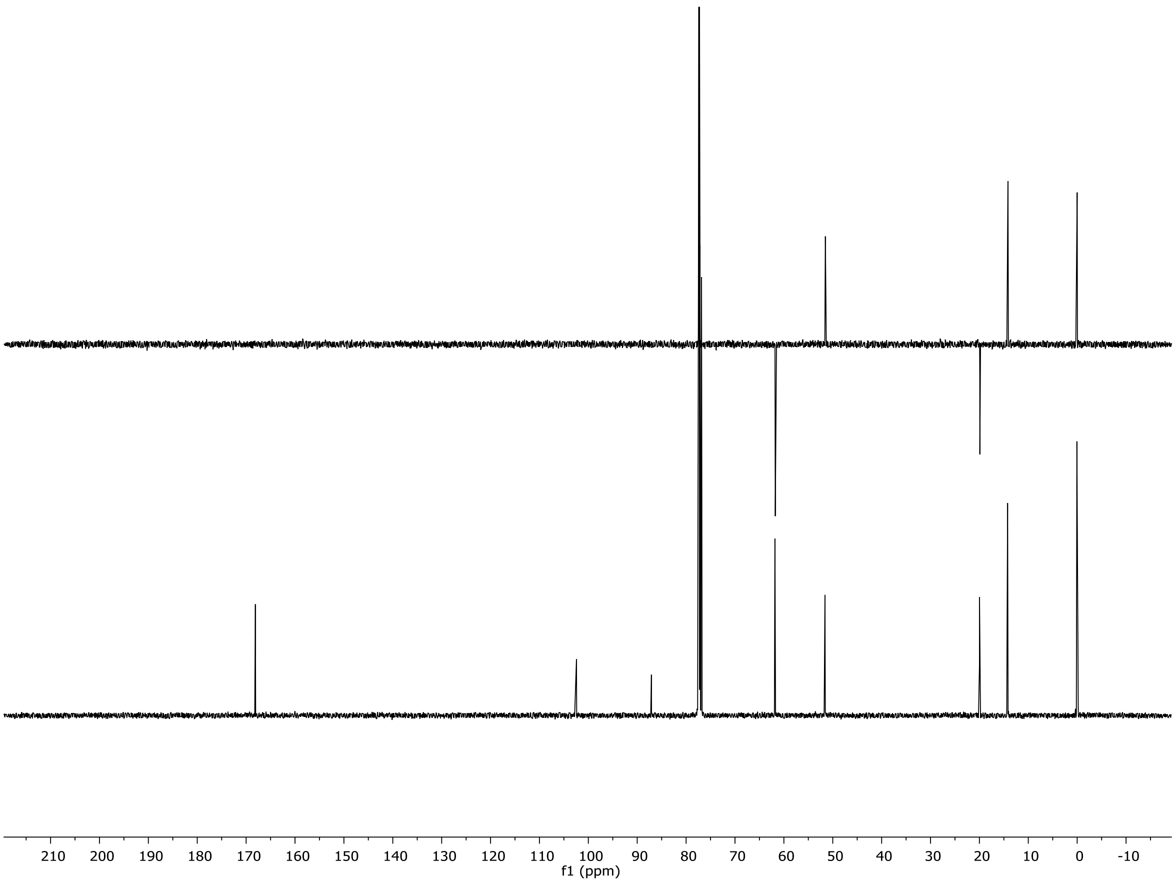
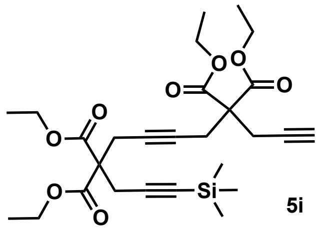


Figure S22. ¹³C NMR and DEPT (101 MHz, CDCl$_3$) spectra



5i

To a solution of NaH 60% dispersion in oil (1.5 equiv., 91.1 mg, 2.28 mmol) in THF (1.8 mL) was added dropwise to a solution of diethyl 2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (1 equiv., 410 mg, 1.52 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 min. Then, diethyl 2-(4-bromobut-2-yn-1-yl)-2-(but-2-yn-1-yl)malonate (1 equiv., 500mg, 1.52 mmol) was added dropwise at 0 °C. The mixture was stirred for 2 hours at room temperature. The mixture was quenched with an aqueous solution of HCl (1N). The aqueous phase was extracted with Et_2O. The combined organic layers were washed with water and brine then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography (PE/AcOEt 95:5 to 9:1).

Yield: 49% (387 mg)

Aspect: colorless oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.12 (s, 9H, 3 x CH_3), 1.25 (br t, *J* = 7.1 Hz, 12H, 4 x CH_3), 1.99 (t, *J* = 2.6 Hz, 1H, CH), 2.90- 2.96 (m, 8H, 4 x CH_2), 4.16-4.26 (m, 8H, 4 x CH_2).

^{13}C NMR (101 MHz, Chloroform-d) δ 0.1 (3 x CH_3), 14.2 (4 x CH_3), 22.6 (CH_2), 22.8$_9$ (CH_2), 22.9$_3$ (CH_2), 23.9 (CH_2), 56.6 (C), 56.8 (C), 62.0 (2 x CH_2), 62.1 (2 x CH_2), 71.5 (CH), 77.6 (C), 78.0 (C), 78.8 (C), 88.1 (C), 101.7 (C), 168.9 (4 x C).

HRMS (ESI+): $[M+NH_4]^+$, calcd for $C_{27}H_{42}NO_8Si^+$ 536.2674, found 536.2675

IR (neat): 2972, 1739, 1290, 1213, 1193, 1055, 1028, 848 cm^{-1}

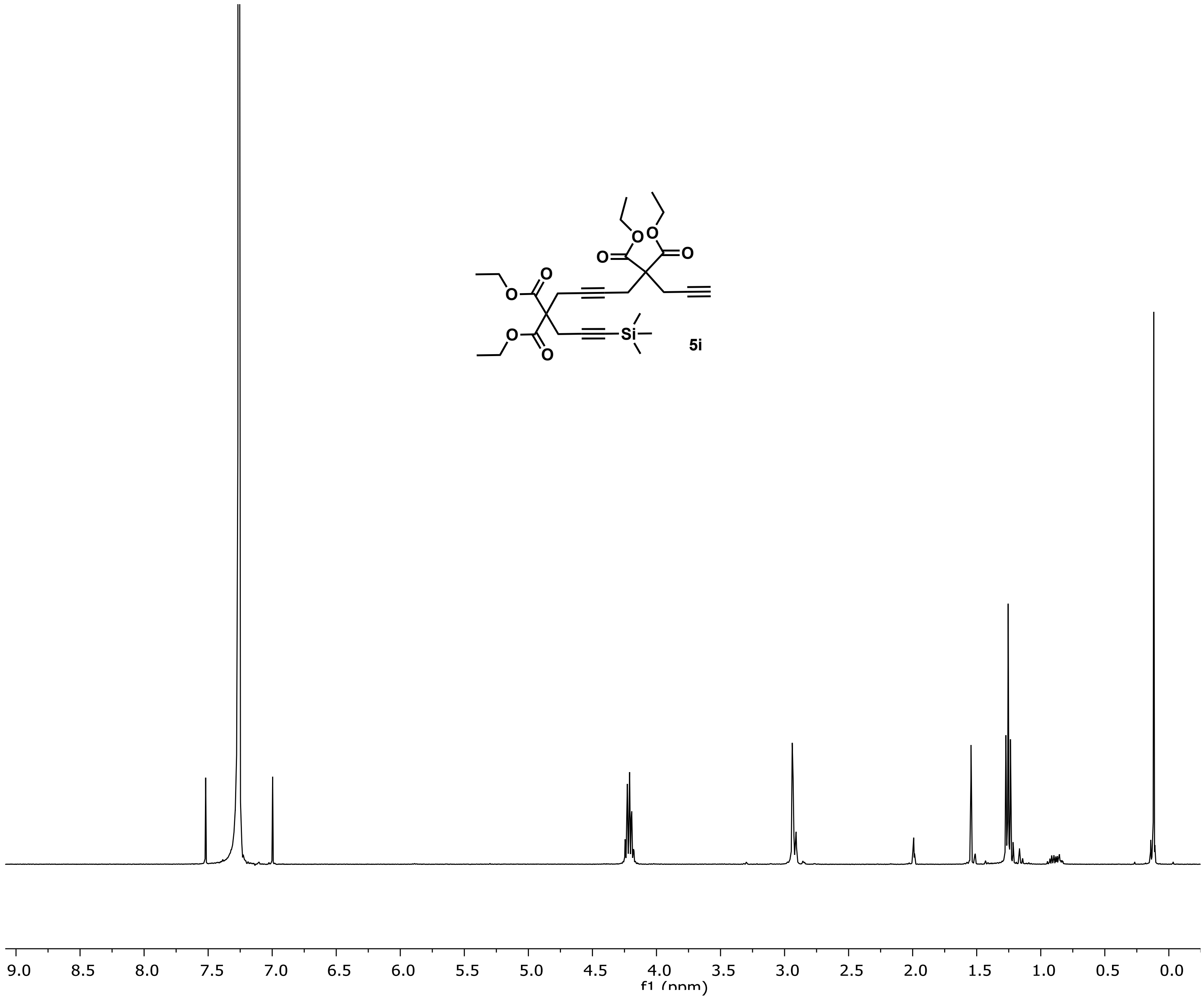


Figure S23. ^{1}H **NMR (400 MHz,** $CDCl_3$**) spectrum of 5i**

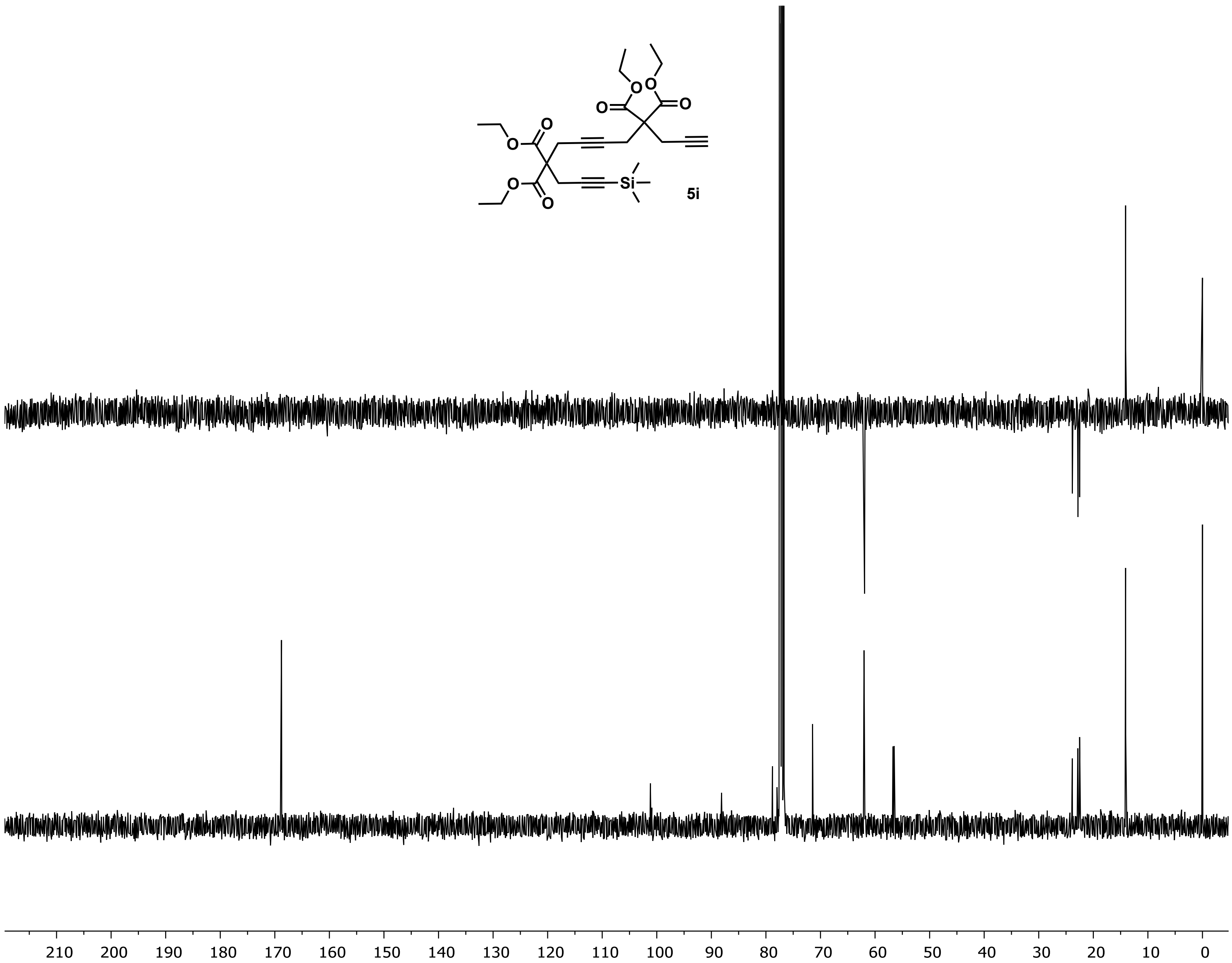
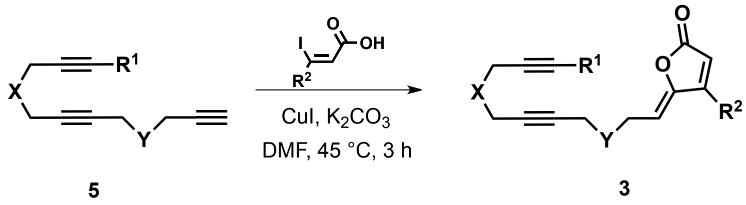


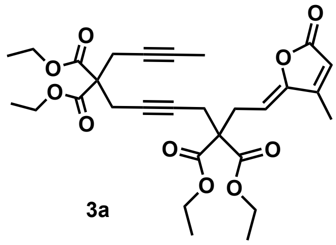
Figure S24. ^{13}C **NMR and DEPT (101 MHz, $CDCl_3$) spectra of 5i**

General procedure for the synthesis of γ-alkylidenebutenolides 3



Scheme S7. Synthesis of γ-alkylidenebutenolides 3

(*Z*)-3-Substituted-3-iodoprop-2-enoic acid (1 equiv.) was dissolved in DMF (0.25 M, dried over CaH_2) in oven-dried-Schlenck tube. K_2CO_3 (2 equiv.) was then added to the solution and the suspension was stirred for 10 min under Argon. The mixture was then degassed at -78 °C for 2x10 min and was backfilled with argon. After reaching room temperature, the triyne **5** (1 equiv.) and CuI (1 equiv.) were respectively added. The mixture was then rapidly degassed and was backfilled with argon. The sealed Schlenck tube was placed in the preheated oil bath (45 °C) and was stirred for 3 hours. The reaction mixture was cooled to 0 °C, was quenched with the addition of aqueous saturated solution of NH_4Cl and was stirred for 15 min. The crude mixture was filtered through a pad of Celite®. The aqueous phase was extracted with ethyl acetate and the combined organic layers were washed with brine. The organic phase was dried over Na_2SO_4 and was evaporated under reduced pressure. The crude product was then purified by flash chromatography on silica gel.



3a

According to the general procedure starting from 1 g (2.17 mmol) of triyne (**5a**) in DMF (8.6 ml). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 80% (949 mg)

Aspect: colorless oil

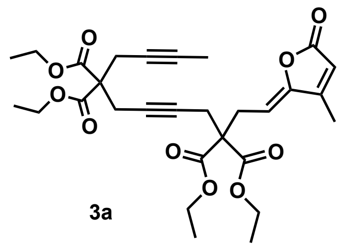
^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.24 (br t, *J*=7.1 Hz, 12H, 4 x CH_3), 1.73 (t, *J* = 2.5 Hz, 3H, CH_3), 2.13 (br s, 3H, CH_3), 2.79 (t, *J* = 2.3 Hz, 2H, CH_2), 2.88 (q, *J* = 2.5 Hz, 2H, CH_2), 2.91 (t, *J* = 2.3 Hz, 2H, CH_2), 3.05 (d, *J* = 8.1 Hz, 2H, CH_2), 4.19 (br q, *J* = 7.1, 8H, 4 x CH_2), 5.29 (t, *J* = 8.1 Hz ,1H, CH), 5.91 (br s, 1H, CH).

^{13}C NMR (101 MHz, Chloroform-d) δ 3.6 (CH_3), 11.9 (CH_3), 14.1 (2 x CH_3), 14.2 (2 x CH_3), 22.9 (CH_2), 23.0 (CH_2), 24.0 (CH_2), 29.6 (CH_2), 56.9 (C), 57.1 (C), 61.9 (2xCH_2), 62.0 (2xCH_2), 73.3 (C), 78.6 (C), 79.1 (C), 106.4 (CH, C12), 117.0 (CH), 152.7 (C), 154.5 (C), 169.1 (C), 169.2 (2 x C), 169.7 (2 x C).

One acetylenic carbon is under $CDCl_3$

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{29}H_{40}NO_{10}^+$ 562.2647, found 562.2646

IR (neat): 2987, 1770, 1720, 1284, 1195, 1093, 1043, 852 cm^{-1}



3a

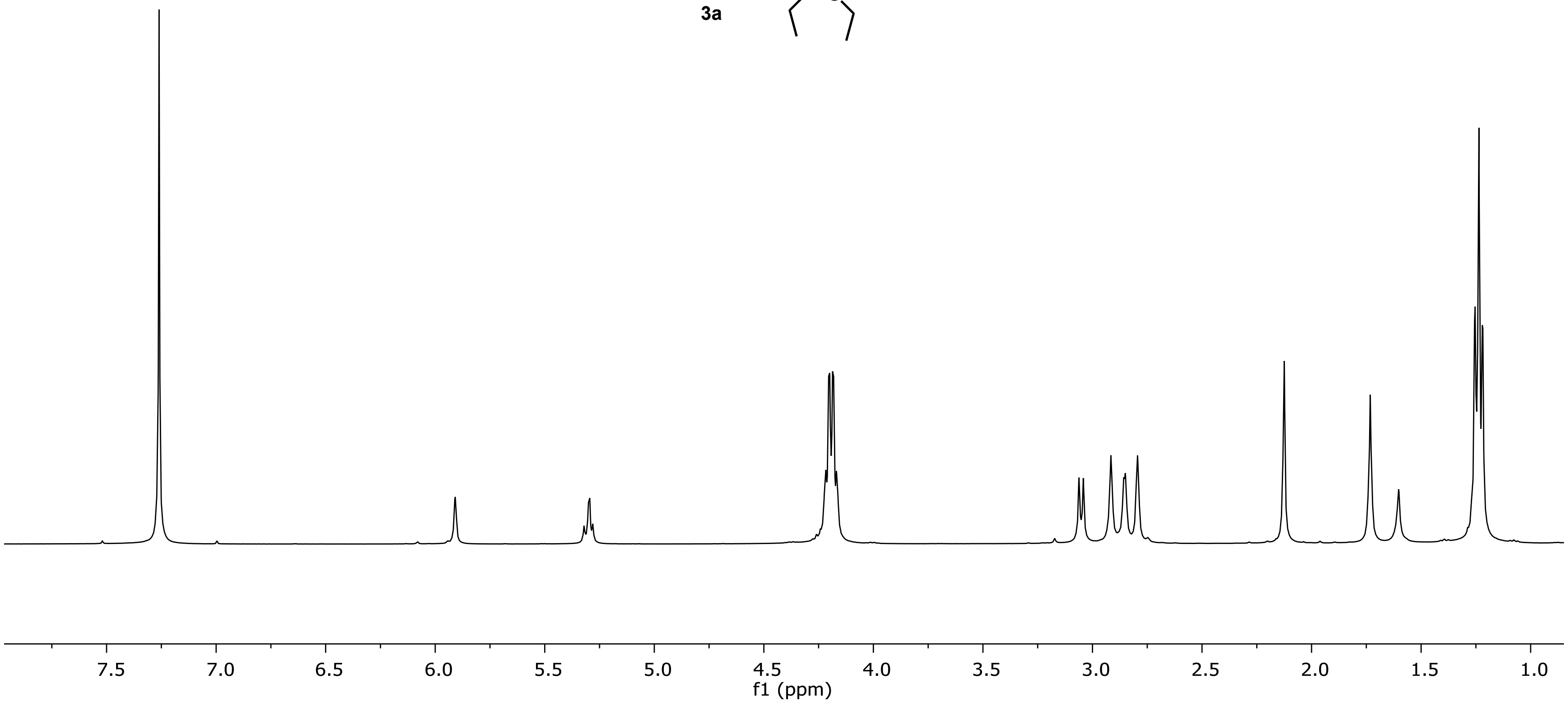
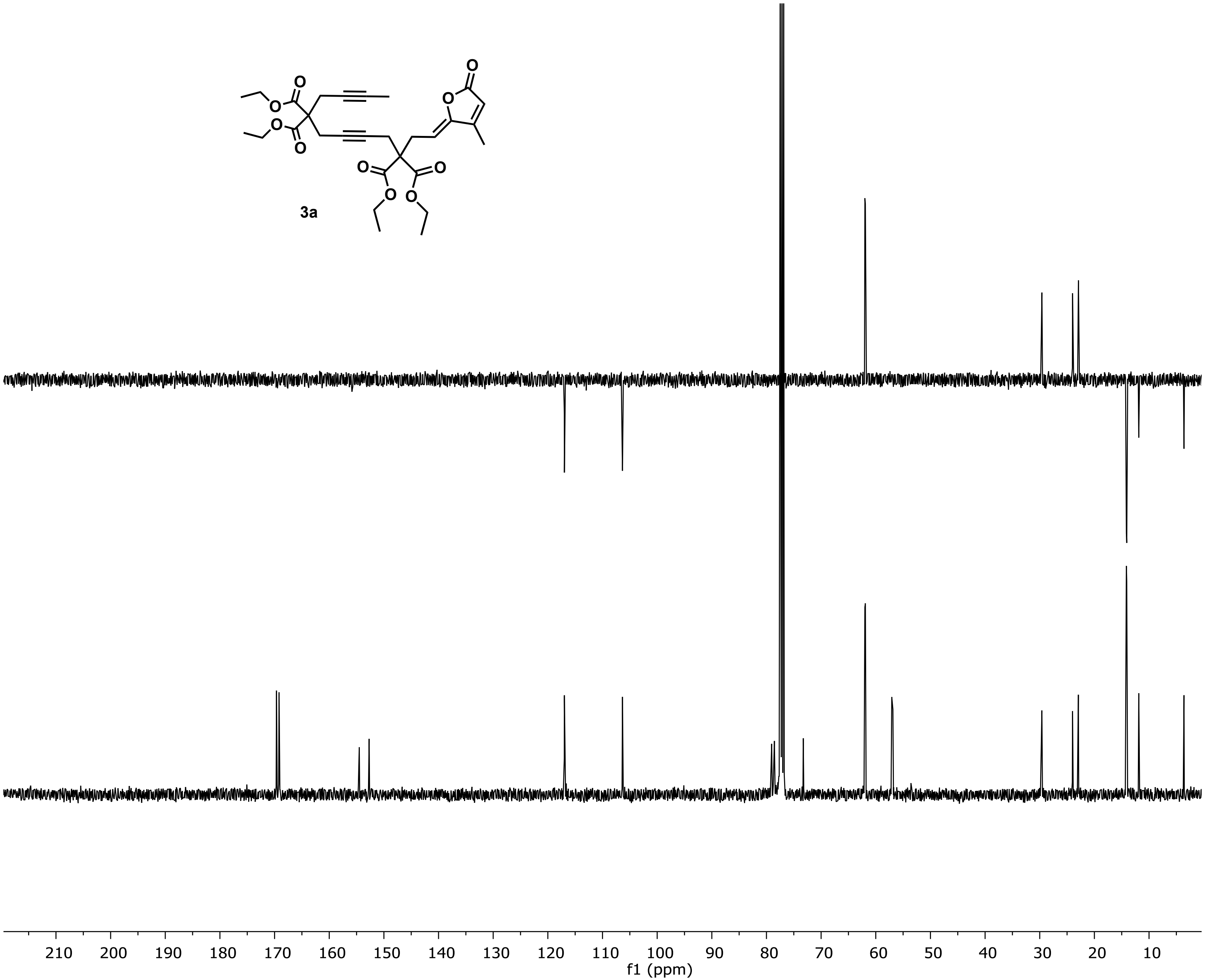
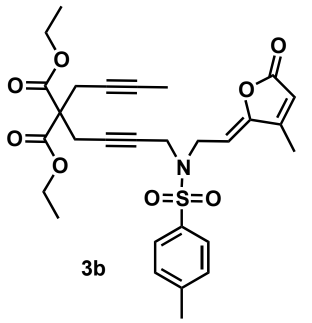


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a

Figure S26. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 3a





3b

According to the general procedure starting from 300 mg (0.63mmol) of triyne (**5b**) in DMF (2.5 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 40% (142 mg)

Aspect: orange solid

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.23 (t, J = 7.1 Hz, 6H, 3 x CH_3), 1.75 (t, J = 2.5 Hz, 3H, CH_3), 2.13 (br d, J = 1.4 Hz, 3H CH_3), 2.45 (s, 3H, CH_3), 2.66 (q, J = 2.5 Hz, 2H, CH_2), 2.78 (t, J = 2.2 Hz, 2H, CH_2), 4.06 (t, J = 2.2 Hz, 2H, CH_2), 4.08 (d, J = 7 Hz, 2H, CH_2), 4.12-4.24 (m, 4H, 2 x CH_2), 5.34 (br t, J= 7 Hz,1H, CH), 5.96 (br s, 1H, CH), 7.34 (d, J = 8.0 Hz, 2H, CH), 7.72 (d, J = 8.0 Hz, 2H, CH).

^{13}C NMR (101 MHz, Chloroform-d) δ 3.7 (CH_3), 11.9 (CH_3), 14.2 (2 x CH_3), 21.7 (CH_3,), 22.9 (CH_2), 23.0 (CH_2), 38.2 (CH_2), 43.0 (CH_2), 56.6 (C), 62.0 (2 x CH_2), 73.2 (C), 76.0 (C), 79.1 (C), 81.0 (C), 106.8 (CH), 117.6 (CH), 127.8 (2 x C), 129.9 (2 x C), 135.7 (C), 144.0 (C), 152.1 (C), 154.7 (C), 168.6 (C), 169.0 (2 x C).

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{29}H_{37}N_2O_8S^+$ 573.2265, found 573.2265

IR (neat): 2979, 1770, 1733, 1342, 1288, 1203, 1155, 1089, 1049, 914, 738, 655, 549 cm^{-1}

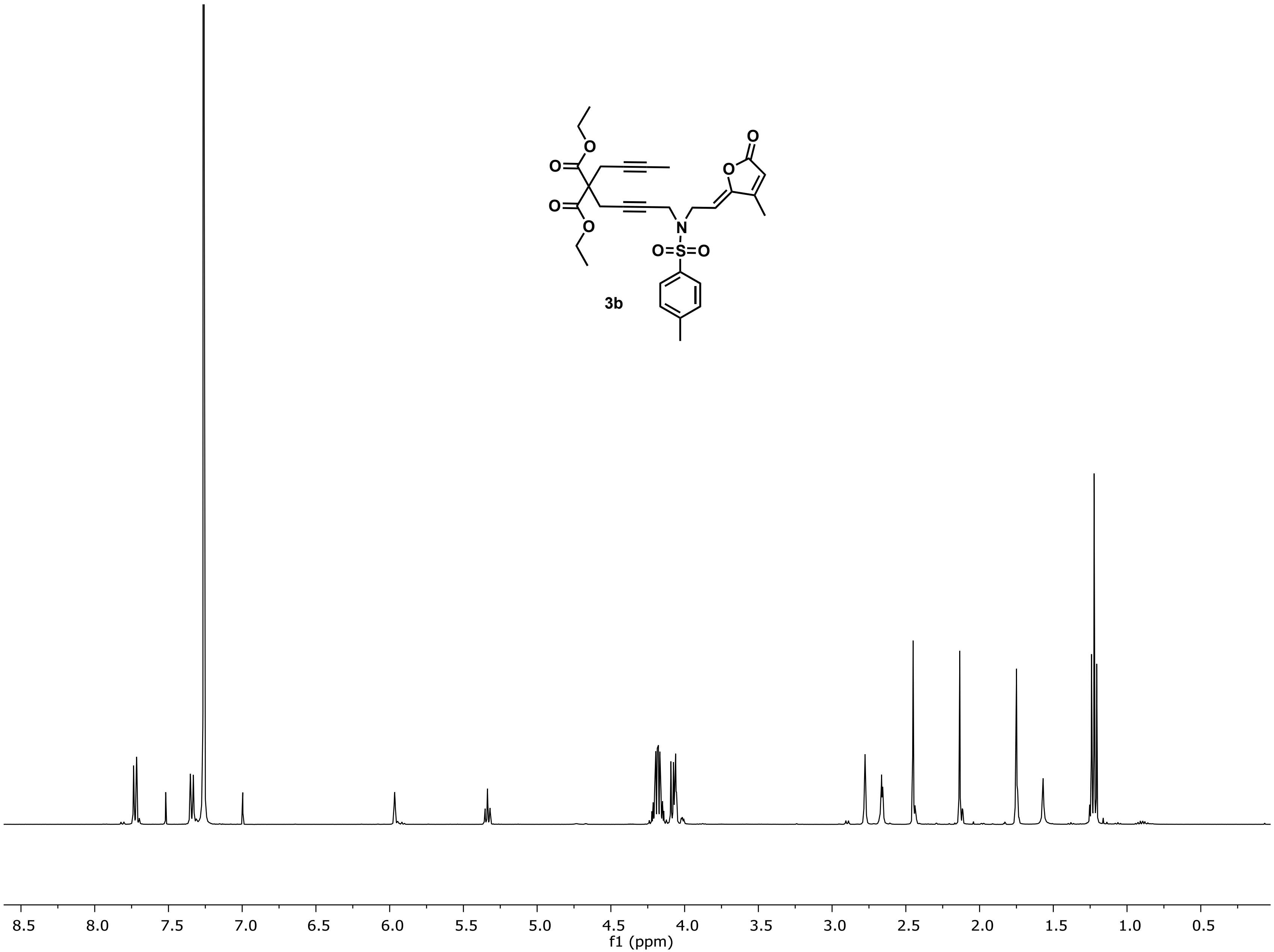


Figure S27. [1]H NMR (300 MHz, $CDCl_3$) spectrum of 3b.

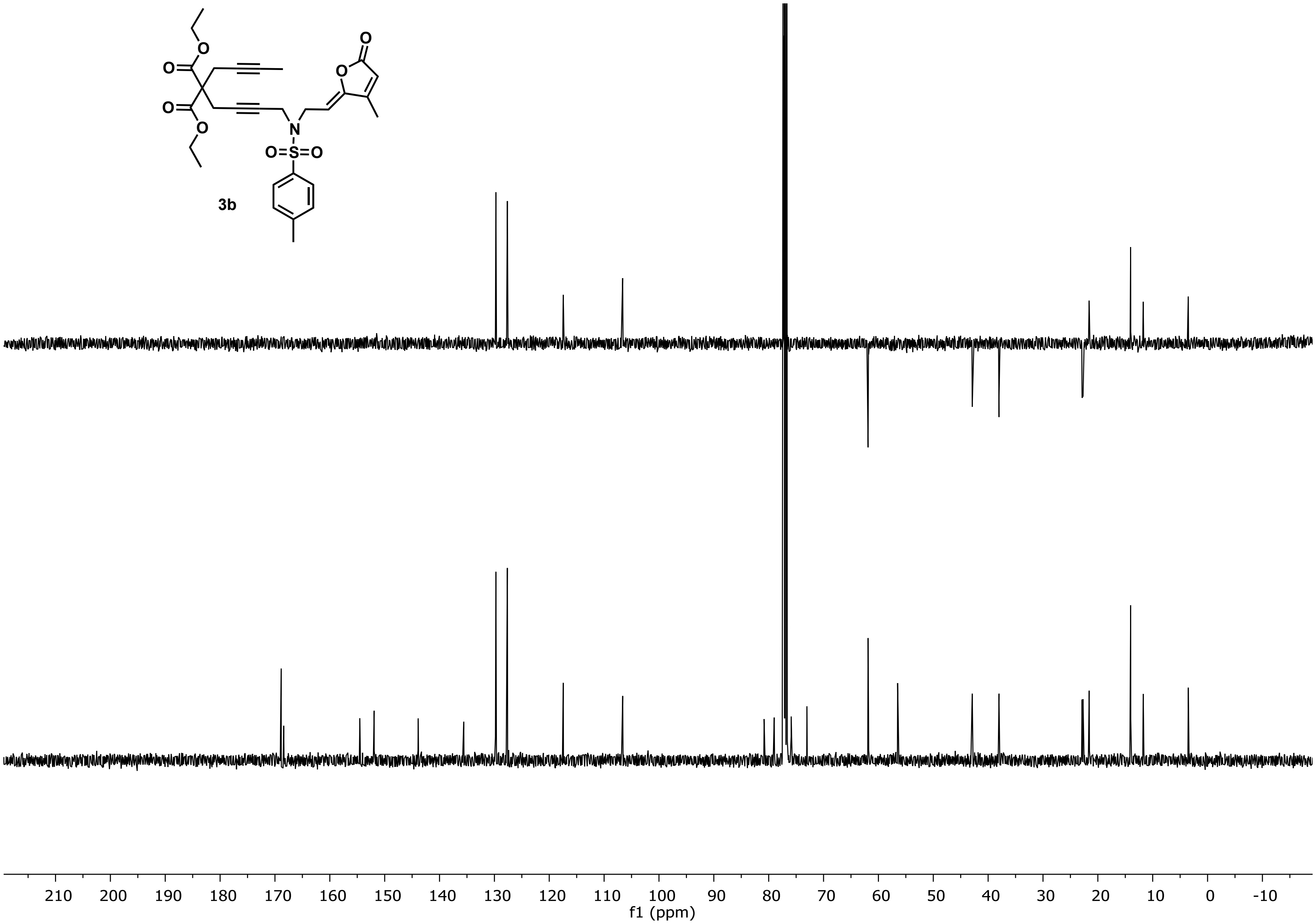
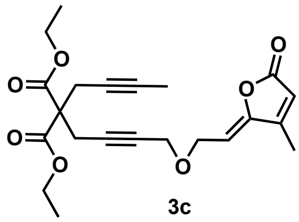


Figure S28. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 3b



3c

According to the general procedure starting from 200 mg (0.62 mmol) of triyne (**5c**) in DMF (2.5 mL). The product was purified by flash chromatography (PE/Et_2O 9:1 to 8:2).

Yield: 65% (164 mg)

Aspect: yellowish oil

^{1}H NMR (400 MHz, Chloroform-d) δ 1.25 (t, *J* = 7.1, 6H, 2 x CH_3), 1.75 (t, *J* = 2.6 Hz, 3H, CH_3), 2.16 (d, *J* = 1.4 Hz, 3H, CH_3), 2.90 (q, *J* = 2.6 Hz, 2H, CH_2), 3.02 (t, *J* = 2.1 Hz, 2H, CH_2), 4.15 (t, *J* = 2.1 Hz, 2H, CH_2), 4.22 (q, *J* = 7.1 Hz, 4H, 2 x CH_2), 4.36 (d, *J* = 6.8 Hz, 2H, CH_2), 5.41 (br t, *J* = 6.8 Hz, 1H, CH), 5.98 (br s, 1H, CH_2).

^{13}C NMR (101 MHz, Chloroform-d) δ 3.6 (CH_3), 11.9 (CH_3), 14.2 (2 x CH_3), 23.0 (CH_2), 23.1 (CH_2), 56.9 (C), 58.6 (CH_2), 62.0 (2 x CH_2), 63.9 (CH_2), 73.2 (C), 78.7 (C), 79.3 (C), 82.0 (C), 107.6 (CH), 117.6 (CH), 151.6 (C), 154.7 (C), 168.7 (C), 169.2 (2 x C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{22}H_{27}O_7^+$ 403.1751, found 403.1750

IR (neat): 2979, 1782, 1729, 1288, 1193, 1078, 1051, 1010 cm^{-1}

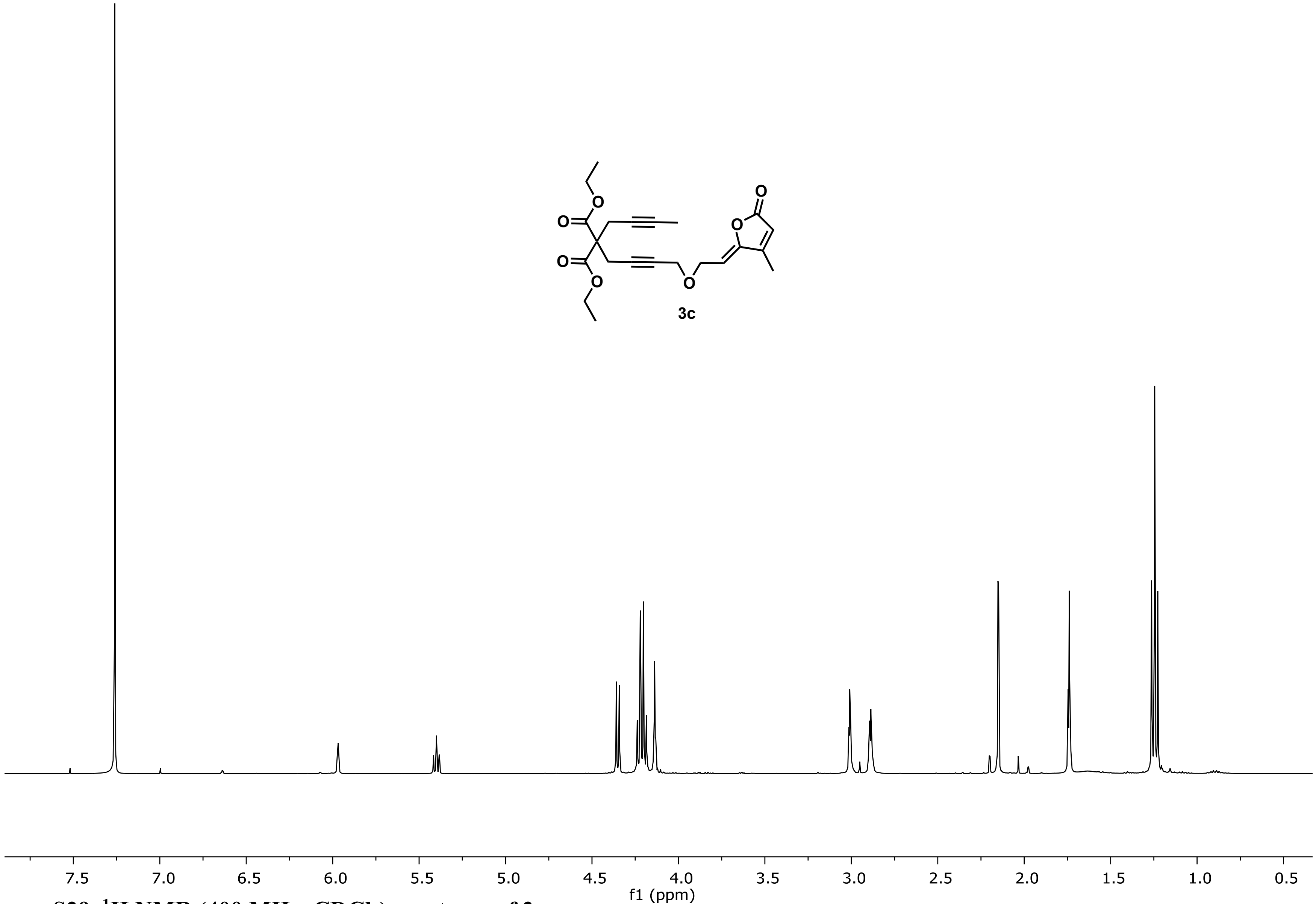
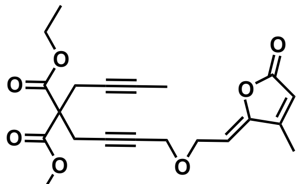


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c.



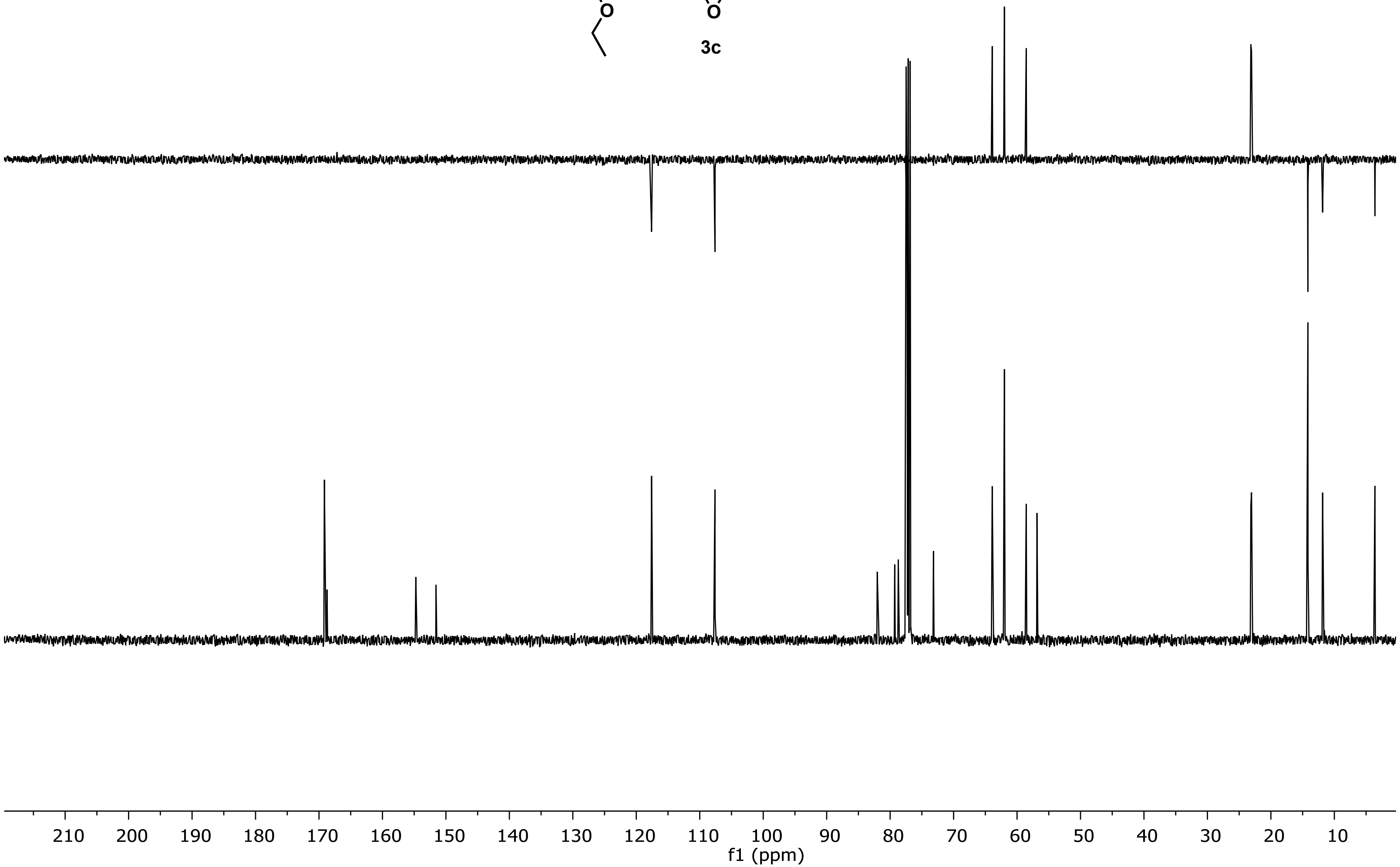
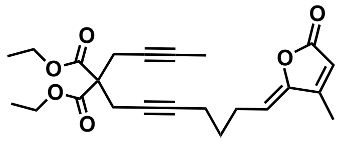


Figure S30. [13]C NMR and DEPT (101 MHz, CDCl$_3$) spectra of 3c



3d

According to the general procedure starting from 400 mg (0.86 mmol) of triyne (**5d**) in DMF (8.5 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: quant (472 mg)

Aspect: yellowish oil

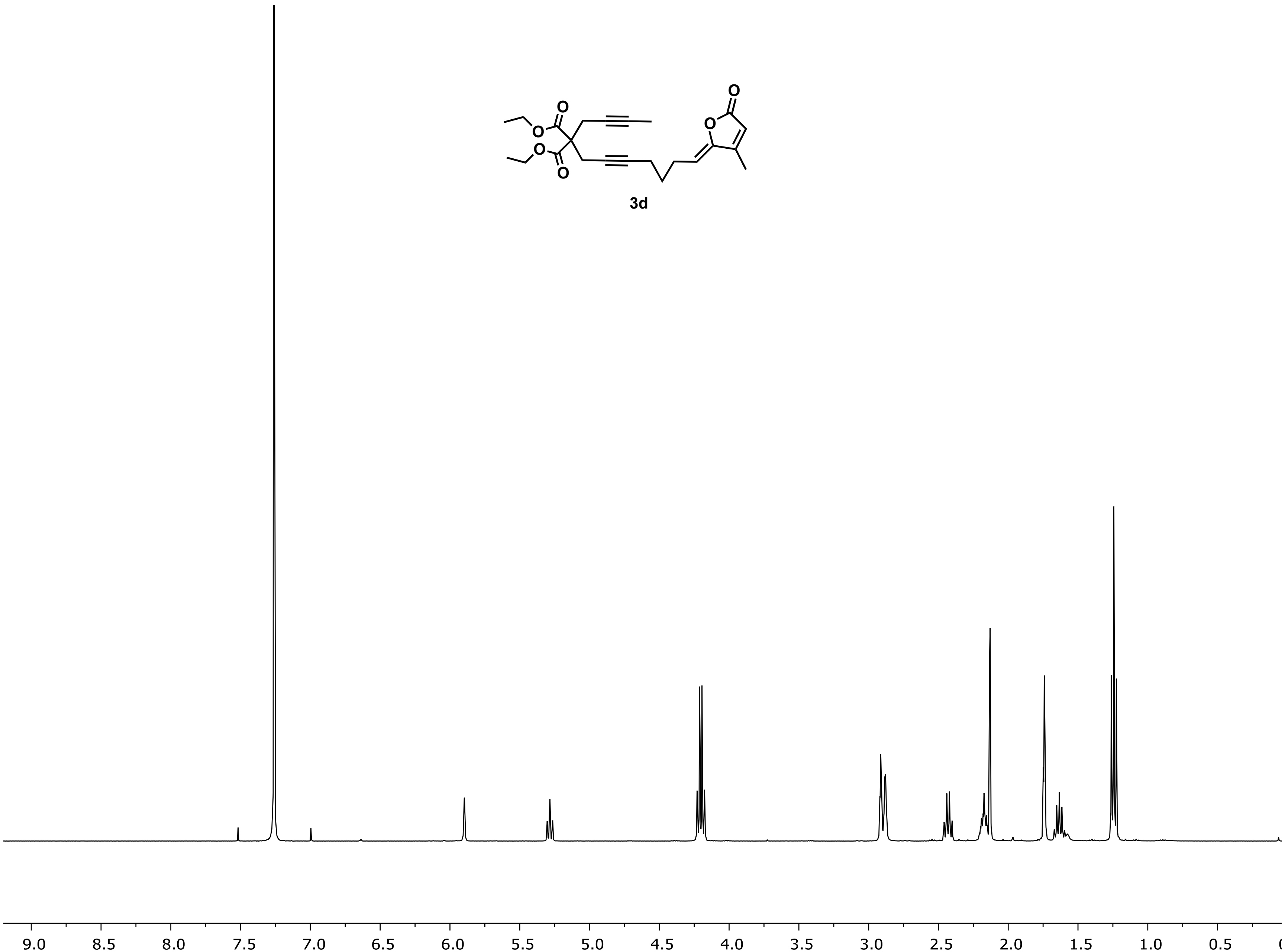
^{1}H NMR (400 MHz, Chloroform-d) δ 1.24 (t, *J* = 7.1 Hz, 6H, 2 x CH_3), 1.59-1,68 (m, 2H, CH_2), 1.74 (t, *J* = 2.5 Hz, 3H, CH_3), 2.13 (br d, *J* = 1.4 Hz, 3H, CH_3), 2.20 (tt, *J* = 7.2 and 2.4 Hz, 2H, CH_2), 2.43 (q, *J* = 7.8 Hz, 2H, CH_2), 2.88 (br q, *J* = 2.5 Hz, 2H, CH_2), 2.91 (bt, *J* = 2.4 Hz, 2H, CH_2), 4.20 (q, *J* = 7.1 Hz, 4H, 2 x CH_2), 5.28 (t, *J* = 7,8 Hz,1H, CH), 5.90 (br q, *J* = 1.4 Hz, 1H, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 3.6 (CH_3), 11.9 (CH_3), 14.2 (2 x CH_3), 18.6 (CH_2) , 23.0 (2 x CH_2), 25.5 (CH_2), 28.4 (CH_2), 57.1 (C), 61.8 (2 x CH_2) 73.4 (C), 75.3 (C), 79.0 (C), 82.7 (C), 112.0 (CH), 116.4 (CH), 151.3 (C), 154.6 (C), 169.4 (2 x C), 169.5 (C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{23}H_{29}O_6^+$ 401.1959, found 401.1958

IR (neat): 2983, 1770, 1720, 1432, 1284, 1199, 1065, 1049, 910, 852 cm^{-1}

Figure S29. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 3d**



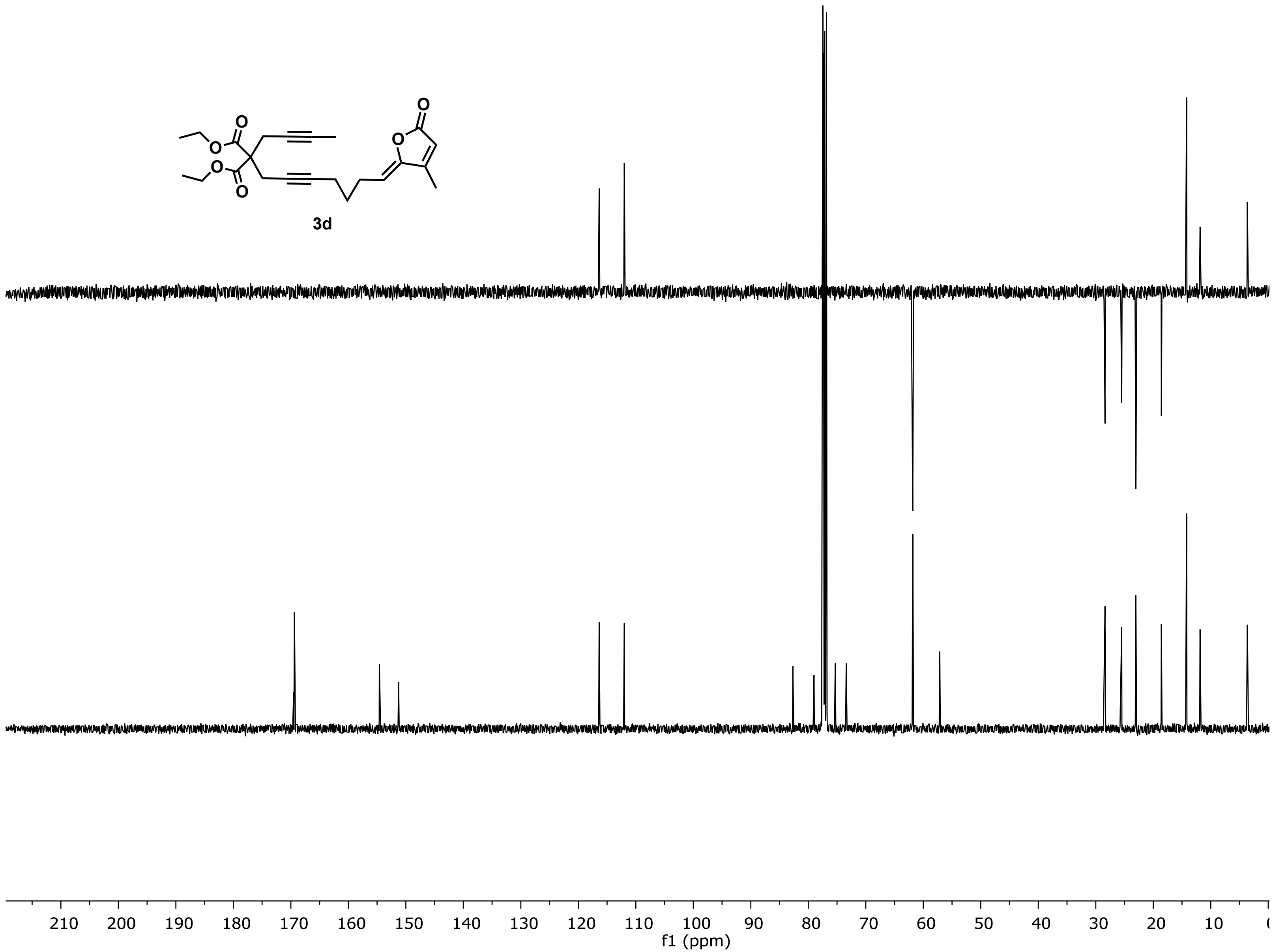
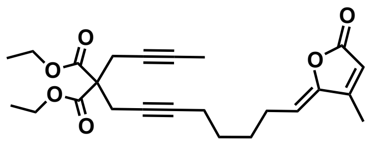


Figure S32. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 3d



3e

According to the general procedure starting from 200 mg (0.61 mmol) of triyne (**5e**) in DMF (2.4 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 76% (190 mg)

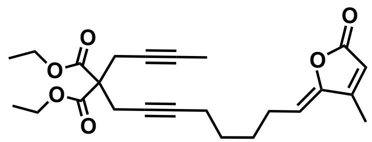
Aspect: colorless oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.23 (t, J = 7.1 Hz, 6H, 2 x CH_3), 1.42 – 1.60 (m, 4H, 2 x CH_2), 1.73 (t, J = 2.5 Hz, 3H, CH_3), 2.13 (br d, J = 1.4 Hz, 3H, CH_3) 2.10 – 2.17 (m, 2H, CH_2), 2.37 (q, J = 7.3 Hz, 2H, CH_2), 2.87 (br q, J = 2.5 Hz, 2H, CH_2), 2.89 (br t, J = 2.3 Hz, 2H, CH_2), 4.18 (q, J = 7.1 Hz, 4H, 2 x CH_2), 5.29 (t, J = 7.3 Hz, 1H, CH), 5.88 (br q, J = 1.4 Hz ,1H, CH).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 3.6 (CH_3), 11.8 (CH_3), 14.2 (2 x CH_3), 18.5 (CH_2), 23.0 (2x CH_2), 25.8 (CH_2), 28.1 (CH_2), 28.5 (CH_2), 57.2 (C), 61.8 (2 x CH_2), 73.4 (C), 74.9 (C), 78.9 (C), 83.1 (C), 112.8 (CH), 116.2 (CH), 151.0 (C), 154.6 (C), 169.4 (C), 169.6 (C).

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{24}H_{34}NO_6^+$ 432.2381, found 432.2376

IR (neat): 2931, 2347, 1735, 1282, 1190, 1047 cm^{-1}



3e

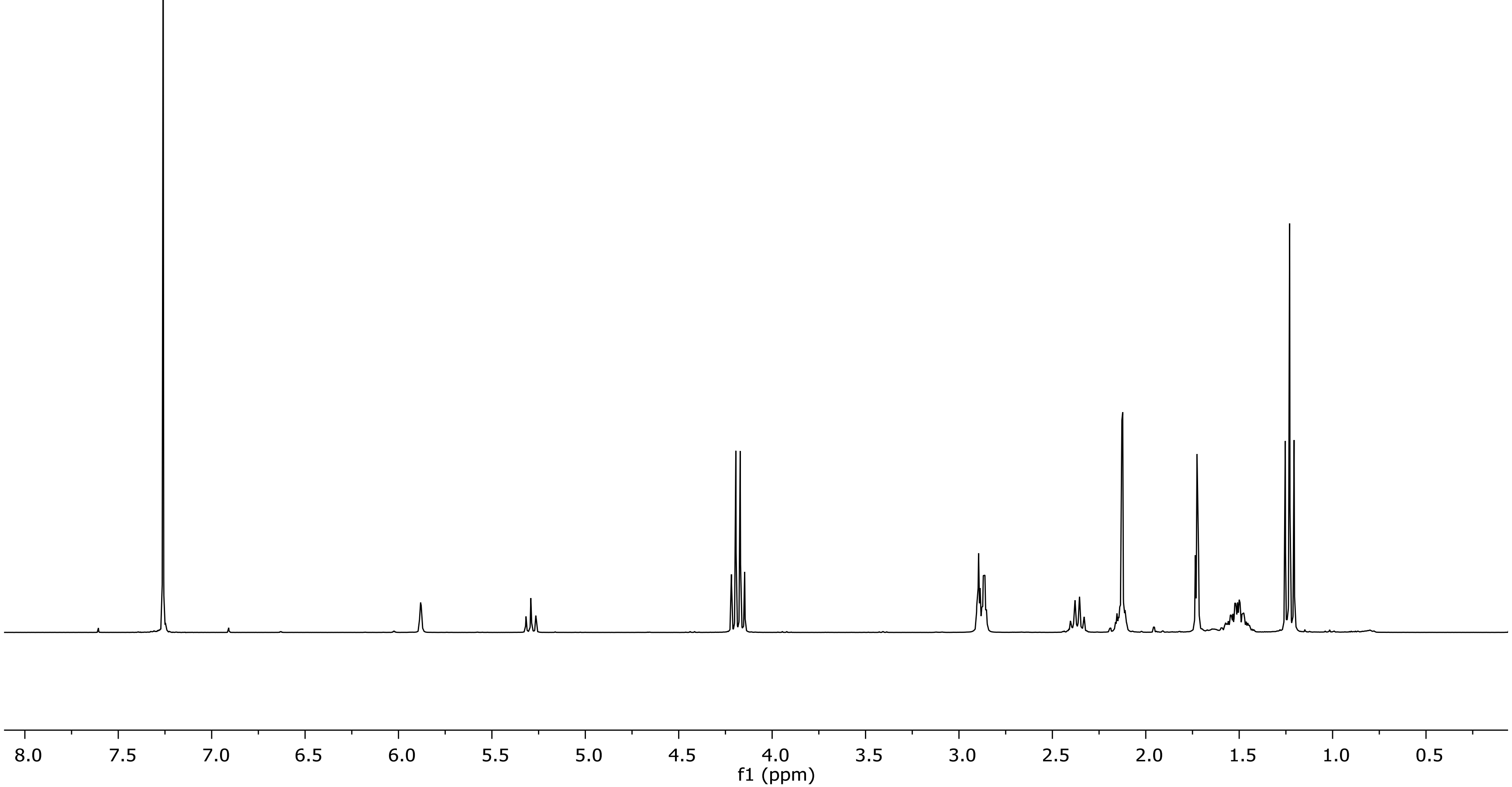
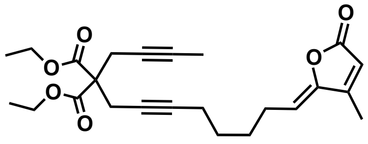


Figure S33. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 3e



3e

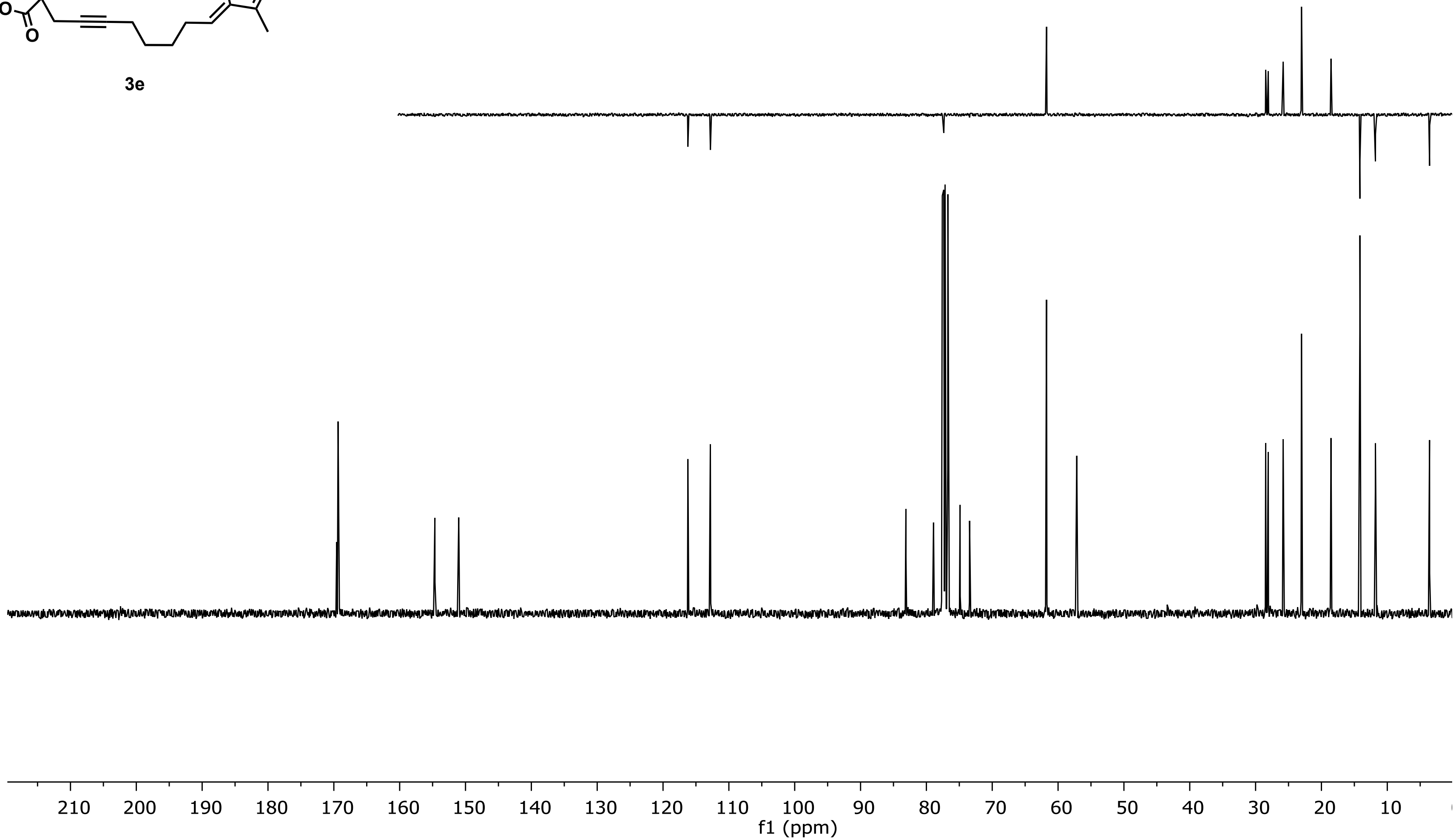
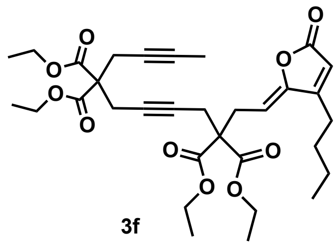


Figure S34. ^{13}**C NMR and DEPT (75 MHz, CDCl$_3$) spectra of 3e**



3f

According to the general procedure starting from 200 mg (0.43 mmol) of triyne (**5a**) in DMF (1.7 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 55% (140 mg)

Aspect: yellow pale oil

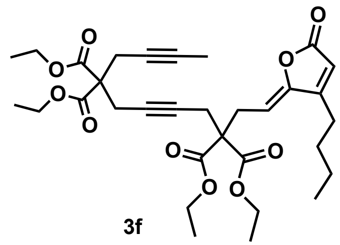
^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.95 (t, *J* = 7.4 Hz, 3H, CH_3), 1.24 (t, *J* = 7.1 Hz, 12H, 4 x CH_3), 1.34 – 1.47 (m, 2H, CH_2), 1.53 – 1.64 (m, 2H, CH_2), 1.74 (t, *J* = 2.5 Hz, 3H, CH_3), 2.43 (br dd, *J* = 7.7 and 7.5 Hz, 2H, CH_2), 2.79 (br t, *J* = 2.3 Hz, 2H, CH_2), 2.86 (br q, *J* = 2.5 Hz, 2H, CH_2), 2.92 (t, *J* = 2.3 Hz, 2H, CH_2), 3.06 (d, *J* = 8.0 Hz, 2H, CH_2), 4.14 – 4.26 (m, 8H, 4 x CH_2), 5.31 (t, *J* = 8.0 Hz, 1H, CH), 5.90 (br s, 1H, CH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 3.6 (CH_3), 13.9 (CH_3), 14.1 (2 x CH_3), 14.2 (2 x CH_3), 22.4 (CH_2), 22.9 (CH_2), 23.0 (CH_2), 24.0 (CH_2), 25.8 (CH_2), 29.6 (CH_2), 30.2 (CH_2), 56.9 (C), 57.1 (C), 61.9 (2 x CH_2), 62.0 (2 x CH_2), 73.3 (C), 78.5 (C), 79.0 (C), 106.2 (C), 115.7 (C), 152.2 (C), 159.4 (C), 169.2 (2 x C), 169.3 (C), 169.7 (2 x C).

One acetylenic carbon is under $CDCl_3$

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{32}H_{46}NO_{10}^+$ 604.3116, found 604.3123

IR (neat): 2949, 1734,1300, 1201, 1049 cm^{-1}



3f

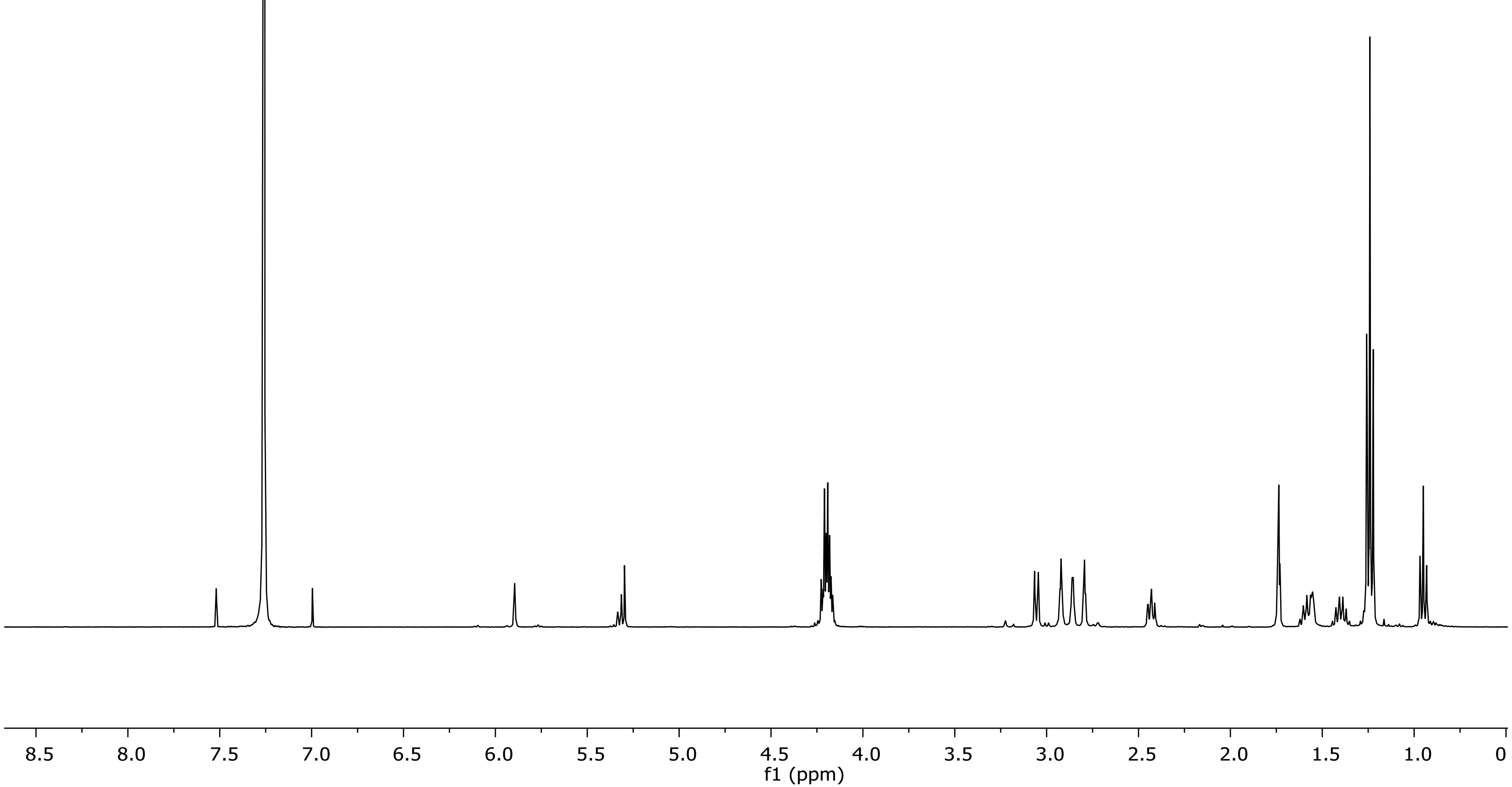


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3f

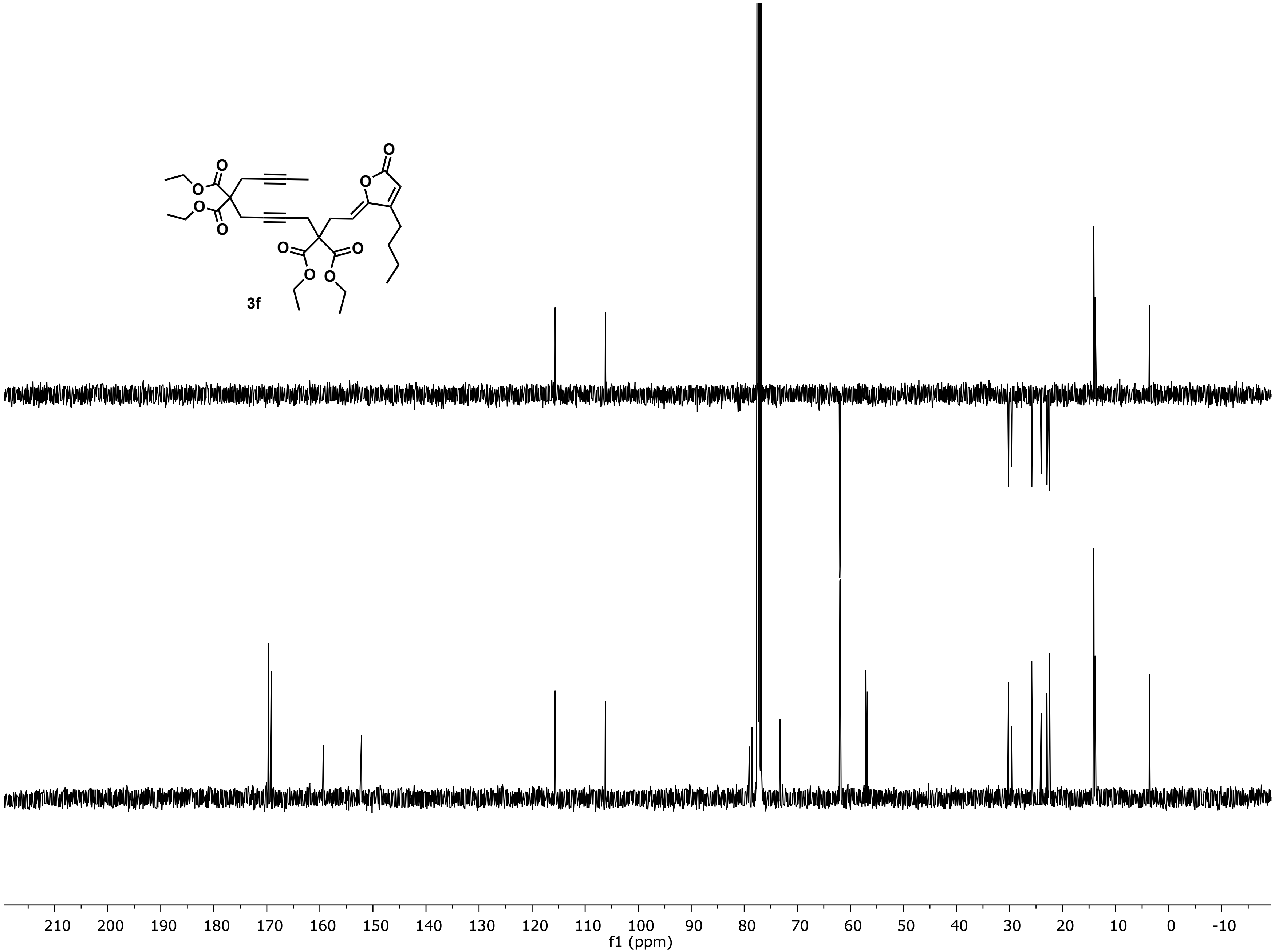
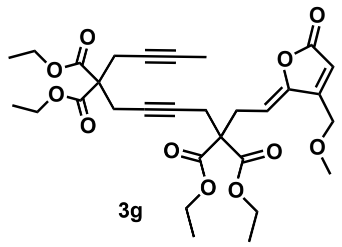


Figure S36. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 3f



3g

According to the general procedure starting from 300 mg (0.65 mmol) of triyne (**5a**) in DMF (2.3 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 37% (146 mg)

Aspect: yellow pale oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.24 (br t, J = 7.1 Hz, 12H, 4 x CH_3), 1.73 (t, J = 2.5 Hz, 3H, CH_3), 2.79 (t, J = 2.3 Hz, 2H, CH_2), 2.85 (q, J = 2.5 Hz, 2H, CH_2), 2.93 (t, J = 2.3 Hz, 2H, CH_2), 3.05 (d, J = 8.0 Hz, 2H, CH_2), 3.43 (s, 3H, CH_3), 4.19 (q, J = 7.1 Hz, 4H, 2 x CH_2), 4.20 (q, J = 7.1 Hz, 4H, 2 x CH_2), 4.35 (br d, J = 1.5 Hz, 2H, CH_2), 5.30 (t, J = 8.0 Hz, 1H, CH), 6.12 (t, J = 1.5 Hz, 1H, CH).

^{13}C NMR (75 MHz, Chloroform-d) δ 3.6 (CH_3), 14.1 (2 x CH_3), 14.2 (2 x CH_3), 22.9 (CH_2,), 23.0 (CH_2), 24.0 (CH_2) 29.6 (CH_2), 56.9 (C), 57.1 (C), 59.2 (CH_3), 61.9 (2 x CH_2), 62.0 (2 x CH_2), 66.5 (CH_2), 73.3 (C), 77.5 (C), 78.6 (C), 79.1 (C), 107.4 (CH), 116.7 (CH), 149.9 (CH), 155.2 (CH), 168.5 (C), 169.2 (2 x C), 169.6 (2 x C).

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{30}H_{42}NO_{11}^+$ 592.2752, found 592.2750

IR (neat): 2987, 1778, 1726, 1284, 1097, 1068, 1045, 1022, 854, 734, 698 cm^{-1}

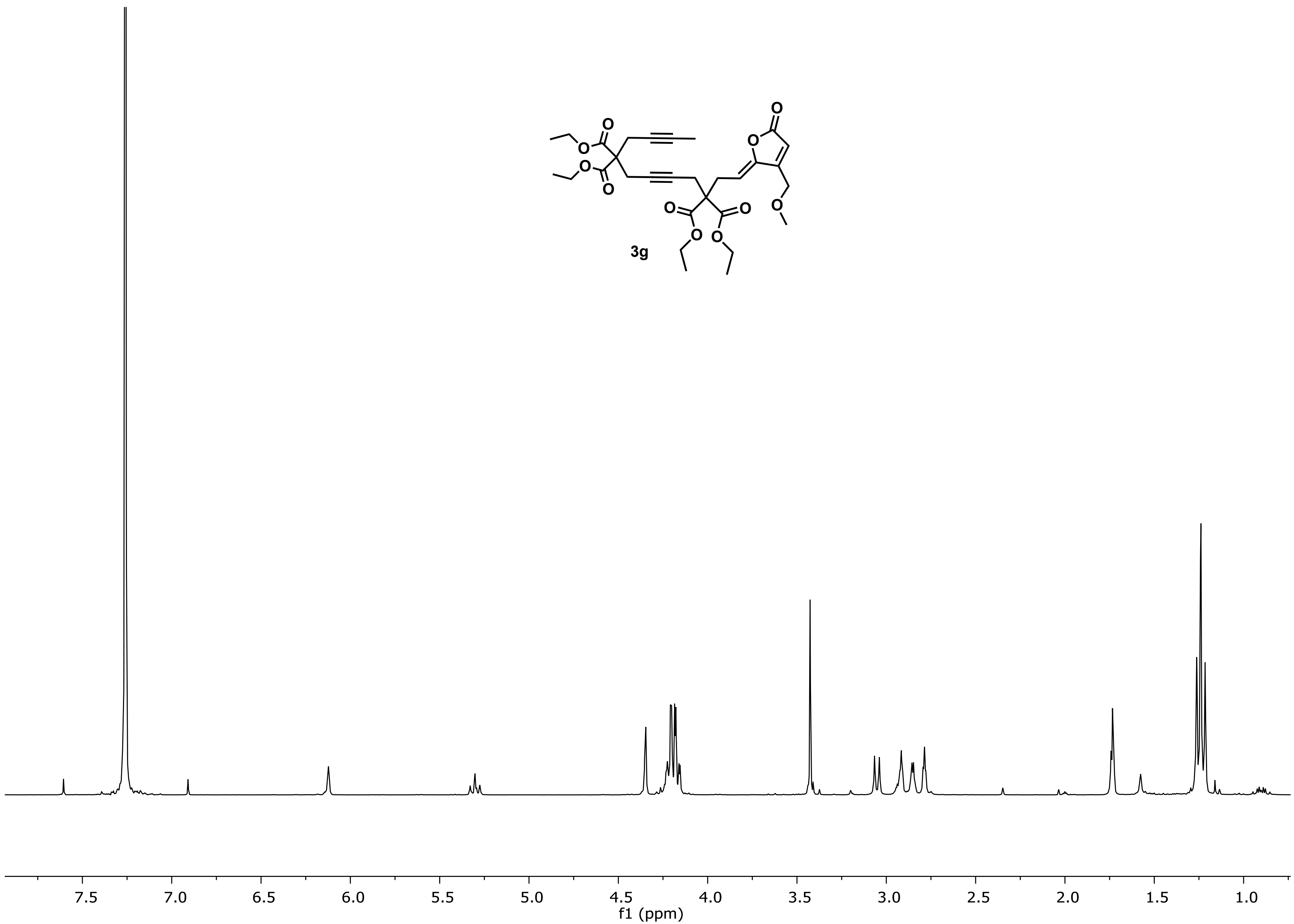


Figure S37. [1]H NMR (300 MHz, $CDCl_3$) spectrum of 3g

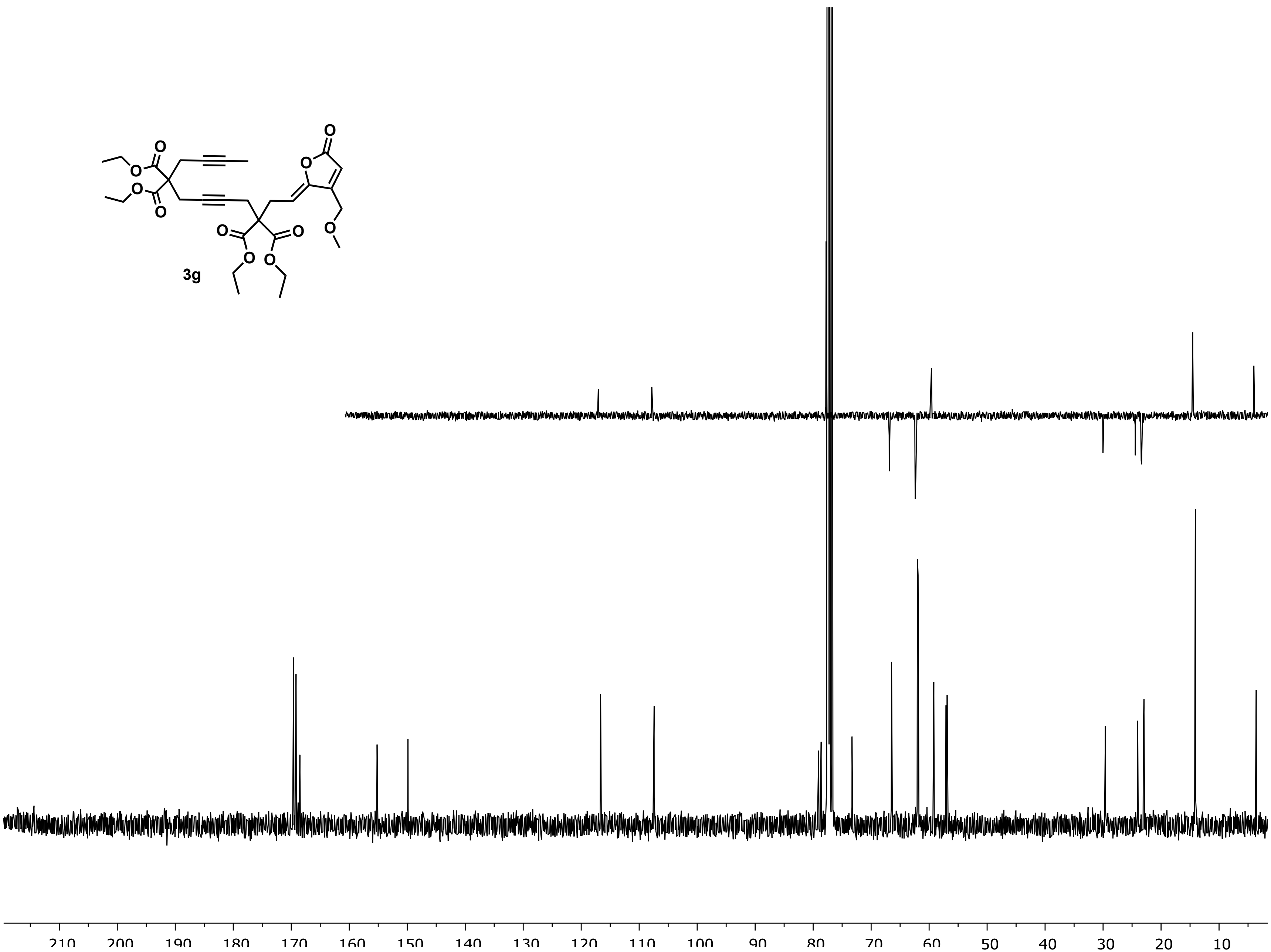
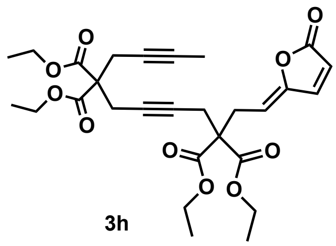


Figure S38. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 3g



3h

According to the general procedure starting from 200 mg (0.43mmol) of triyne (**5a**) in DMF (1.7 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 90% (207 mg) (1:0.6 mixture of *Z*:*E* diastereomers)

Aspect: yellowish oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.26 (br t, J = 7.1 Hz, 12H, 4 x CH_3), 1.76 (t, J = 2.5 Hz, 3H, CH_3), 2.82 (t, J = 2.3 Hz, 2H, CH_2), 2.87 (q, J = 2.5 Hz, 2H, CH_2), 2.94 (t, J = 2.3 Hz, 2H, CH_2), 3.10 (d, J = 8.0 Hz, 2H, CH_2), 4.21 (q, J = 7.1 Hz, 4H, CH_2), 4.22 (q, J = 7.0 Hz, 4H, CH_2), 5.35 (t, J = 8.0 Hz, 1H, CH), 6.18 (d, J = 5.5 Hz, 1H, CH), 7.35 (d, J = 5.5 Hz, 1H, CH).

^{13}C NMR (75 MHz, Chloroform-d) δ 3.6 (CH_3), 14.1 (2 x CH_3), 14.2 (2 x CH_3), 23.9$_5$ (CH_2,), 23.0 (CH_2), 24.0 (CH_2), 29.9 (CH_2), 56.9 (C), 57.1 (C), 61.9 (2 x CH_2), 62.0 (CH_2), 73.3 (CH_2), 77.5 (CH_2), 78.6 (CH_2), 79.1 (CH_2), 110.8 (CH), 120.1 (CH), 143.5 (CH), 151.6 (C) 169.2 (2 x C), 169.6 (3 x C).

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{28}H_{38}NO_{10}^+$ 548.2490, found 548.2486

IR (neat): 2978, 1782, 1730, 1286, 1201, 1053 cm^{-1}

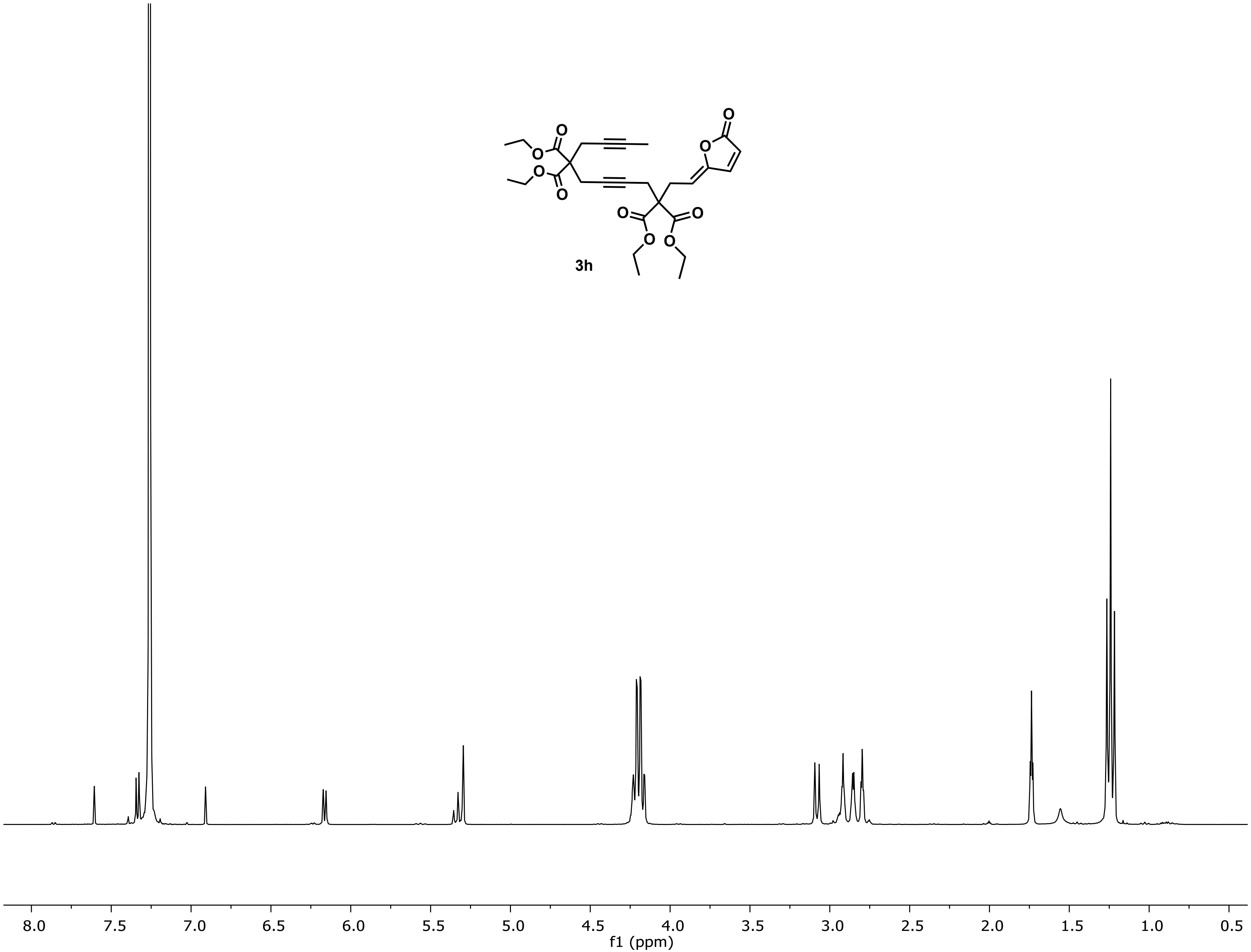


Figure S39. [1]H NMR (300 MHz, $CDCl_3$) spectrum of 3h

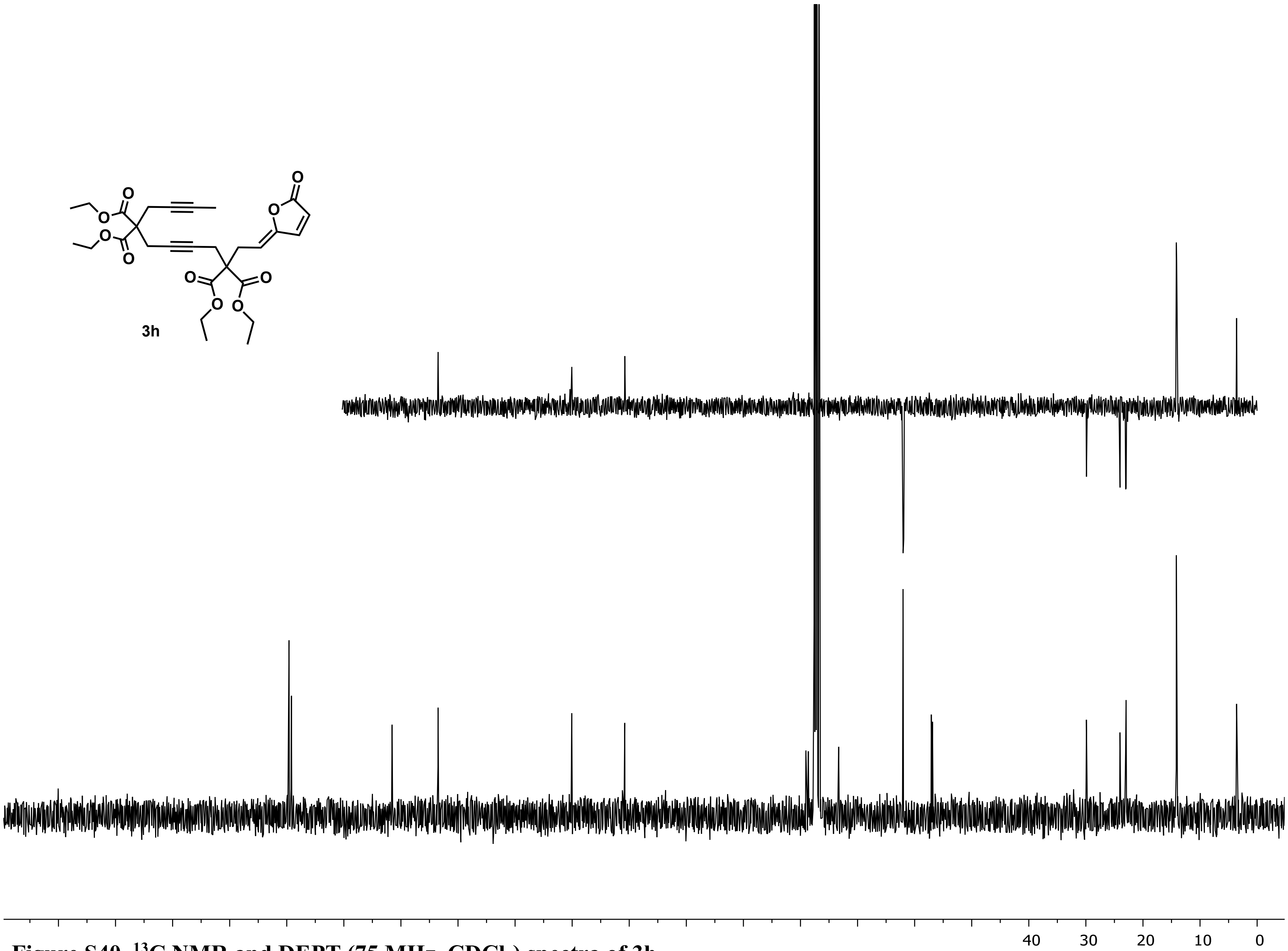
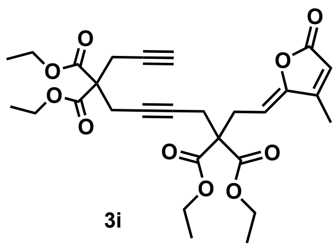


Figure S40. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 3h



3i

According to the general procedure starting from 300 mg (0.57 mmol) of triyne (**5i**) in DMF (2.3 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 34% (103 mg) *the low yield could be explained by the formation of the dilactone.*

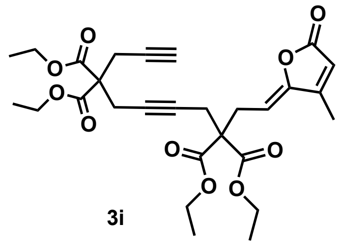
Aspect: colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 1.24 (t, *J* = 7.0 Hz, 6H, 2 x CH_3), 1.25 (t, *J* = 7.0 Hz, 6H, 2 x CH_3), 2.00 (t, *J* = 2.6 Hz, 1H, CH), 2.13 (br d, *J* = 1.2 Hz, 3H, CH_3), 2.80 (t, *J* = 2.3 Hz, 2H, CH_2), 2.93-2.96 (m, 4H, 2 x CH_2), 3.05 (d, *J* = 8.0 Hz, 2H, CH_2), 4.19 (q, *J* = 7.0 Hz, 4H, 2 x CH_2), 4.21 (q, *J* = 7.0 Hz, 4H, 2 x CH_2), 5.29 (t, *J* = 8.0 Hz, 1H, CH), 5.91 (br s, 1H, CH).

^{13}C NMR (101 MHz, Chloroform-d) δ 11.9 (CH_3), 14.1 (2 x CH_3), 14.2 (2 x CH_3), 22.7 (CH_2), 22.9 (CH_2), 24.0 (CH_2), 29.6 (CH_2), 56.5 (C), 57.1 (C), 62.0 (2 x CH), 62.1 (2 x CH_2), 71.7 (CH) , 77.8 (C), 78.2 (C), 78.8 (C), 106.3 (CH), 117.0 (CH), 152.7 (C), 154.5 (C), 168.8 (2 x C), 169.1 (C), 169.6 (2 x C)

HRMS (ESI+): $[M+NH_4]^+$ calcd for $C_{28}H_{38}NO_{10}^+$ 548.2490, found 548.2486

IR (neat): 2985, 1728, 1288, 1190, 1055, 1028, 848 cm^{-1}



3i

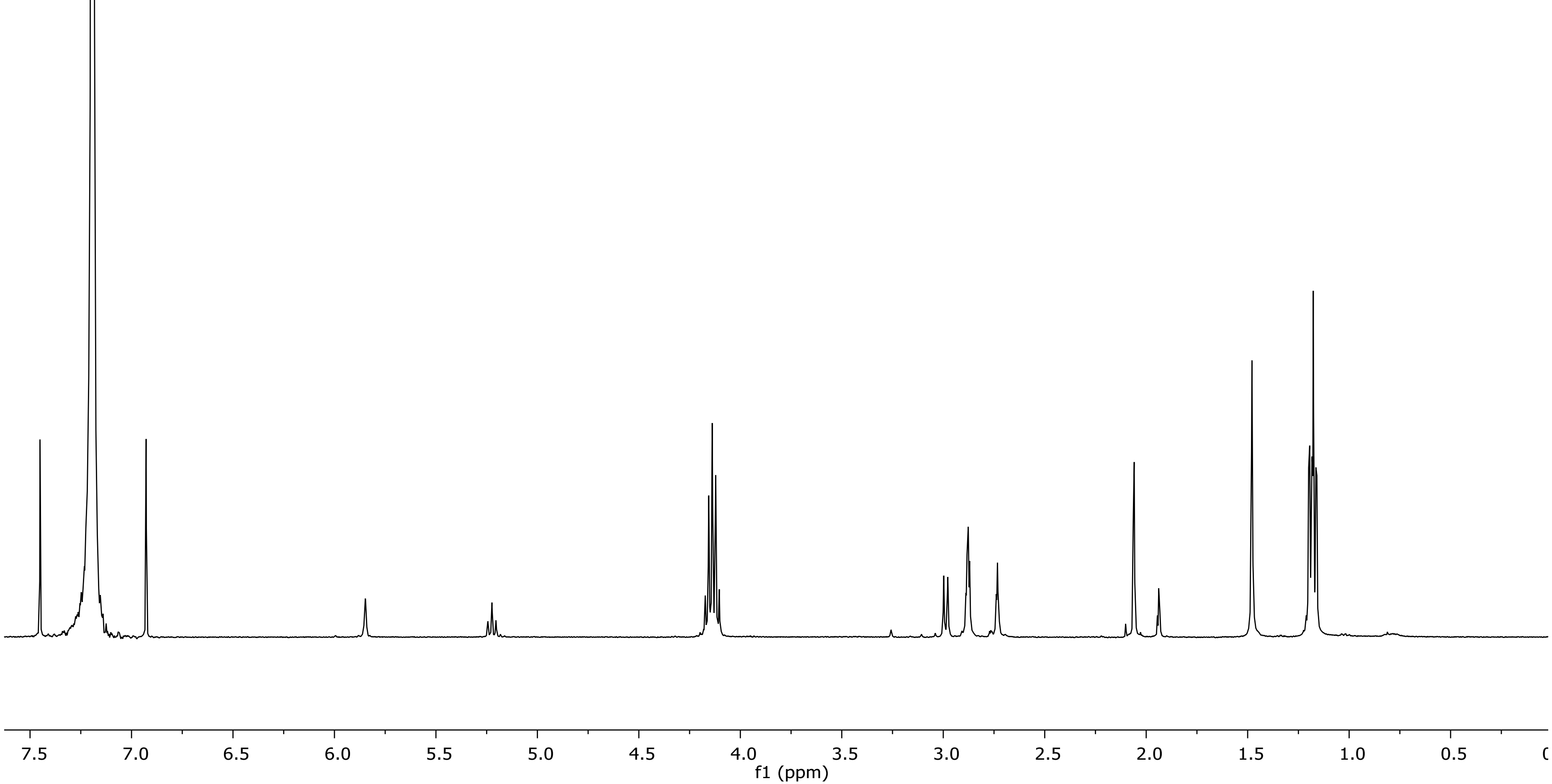


Figure S41. [1]H NMR (400 MHz, $CDCl_3$) spectrum of 3i

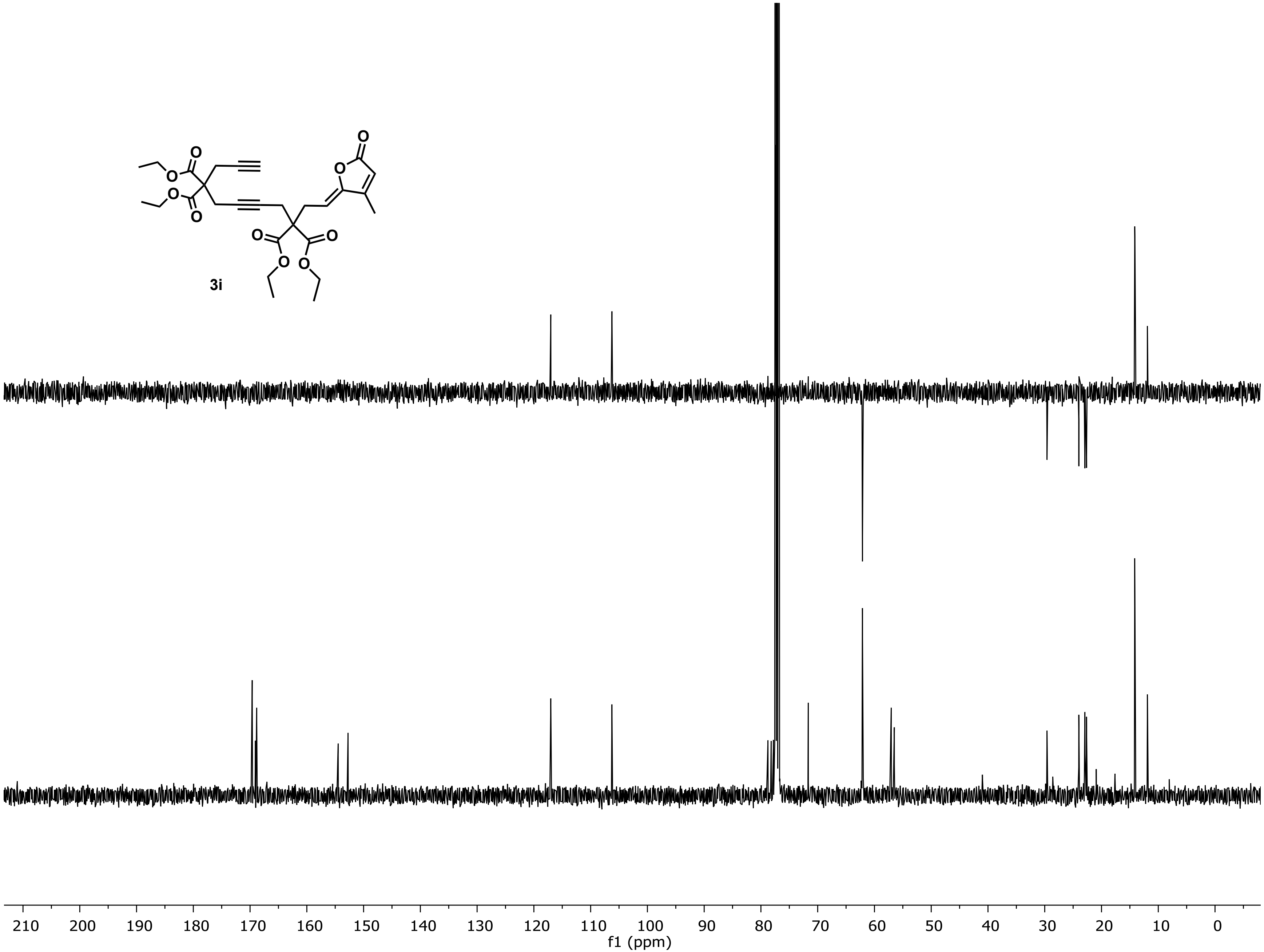
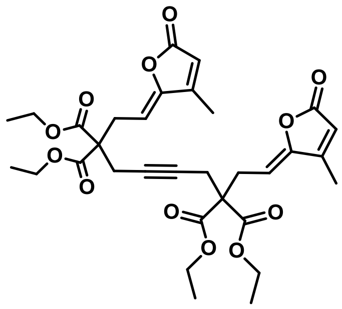


Figure S42. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 3i.

dilactone



Yield: 14% (50 mg)

Aspect: colorless oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.16 – 1.31 (m, 8H, 2 x CH_3), 2.13 (br s Hz, 3H, CH_3), 2.81 (s, 2H, CH_2), 3.07 (d, *J* = 8.0 Hz, 2H, CH_2), 4.20 (q, *J* = 7.1 Hz, 4H, 2 x CH_2), 5.28 (t, *J* = 8.0 Hz, 1H, CH), 5.91 (s, 1H, CH).

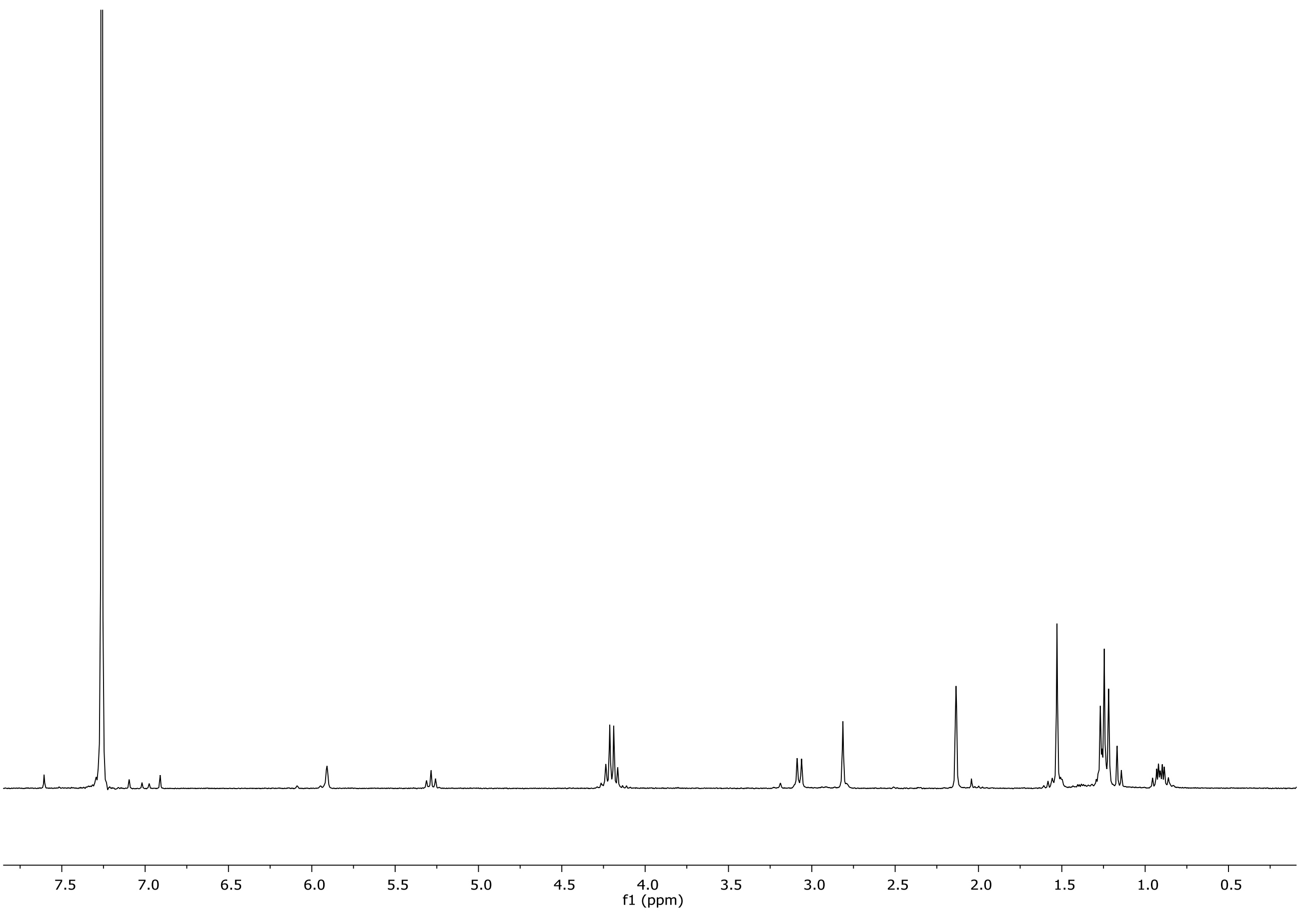
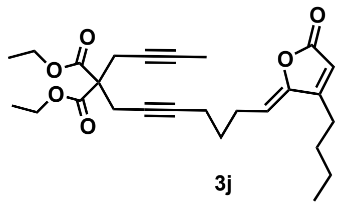


Figure S43. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum



3j

According to the general procedure starting from 200 mg (0.63 mmol) of triyne (**5d**) in DMF (1.7 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 41% (116 mg)

Aspect: colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 0.96 (t, J = 7.3 Hz, 3H, CH_3), 1.25 (t, J = 7.1 Hz, 6H, 2 x CH_3), 1.40 (sex, J = 7.3 Hz, 2H, CH_2), 1.56-1.67 (m, 4H, 2 x CH_2), 1.75 (t, J = 2.5 Hz, 3H, CH_3), 2.17 (tt, J = 7.1 and 2.3 Hz, 2H, CH_2), 2.41 – 2.46 (m, 4H, CH_2), 2.89 (br q, J = 2.5 Hz, 2H, CH_2), 2.92 (br t, J = 2.3 Hz, 2H,CH_2), 4.21 (q, J = 7.1 Hz, 4H, CH_2), 5.30 (t, J = 7.8 Hz, 1H, CH), 5.89 (br s, 1H, CH).

^{13}C NMR (75 MHz, Chloroform-d) δ 3.6 (CH_3), 13.8 (CH_3), 14.2 (2 x CH_3), 18.6 (CH_2), 22.5 (CH_2), 23.0 (CH_2), 23.1 (CH_2), 25.5 (CH_2), 25.8 (CH_2), 28.5 (CH_2), 30.3 (CH_2), 57.2 (C), 61.8 (2 x CH_2), 73.4 (C), 75.3 (C), 79.0 (C), 82.7 (C), 111.8 (CH), 115.1 (CH), 150.8 (C), 159.4 (C), 169.4 (2 x C), 169.7 (C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{26}H_{35}O_6^+$ 443.2428, found 443.2427

IR (neat): 2949, 1734,1300, 1201, 1049 cm^{-1}

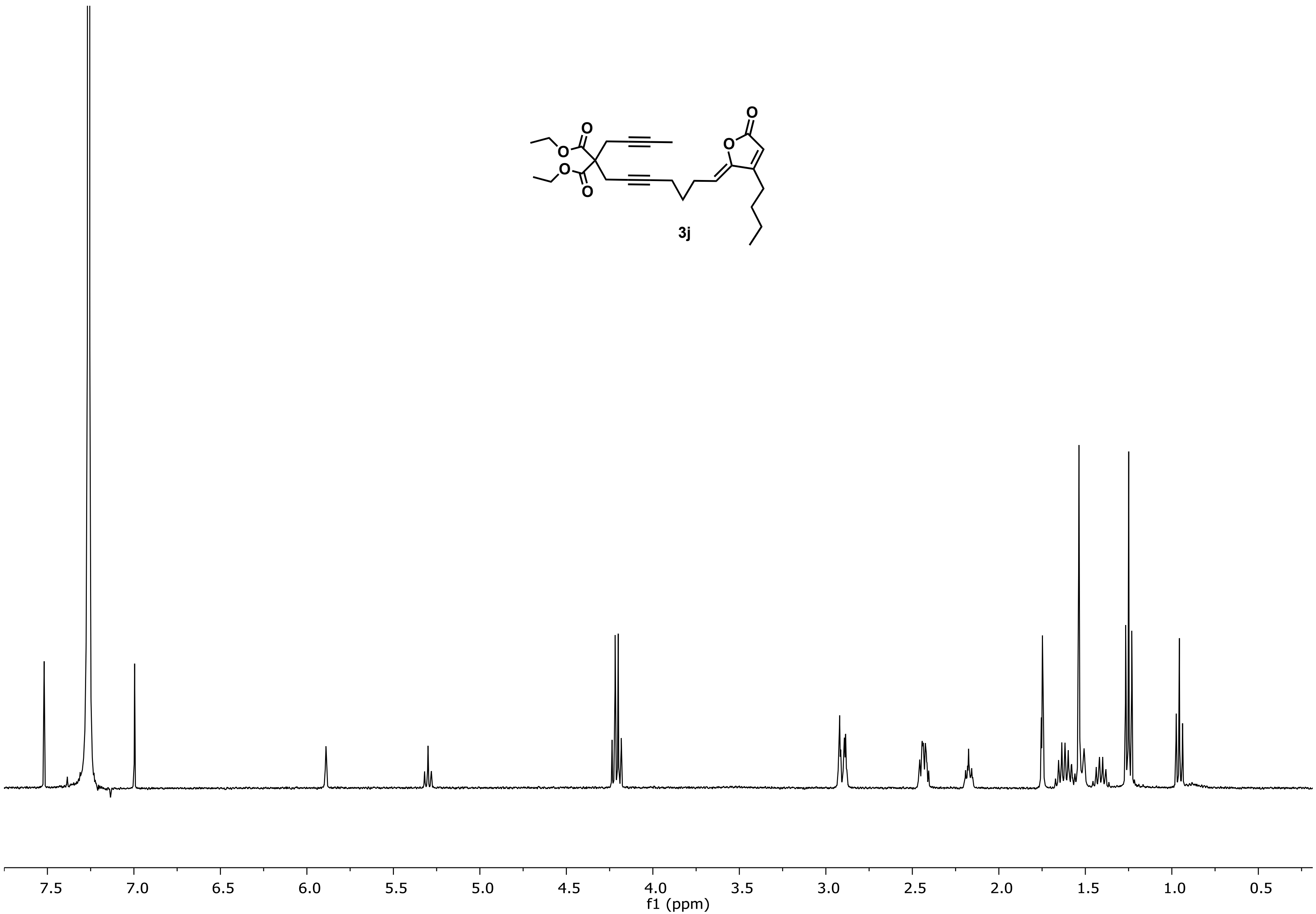


Figure S44. **^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3j**

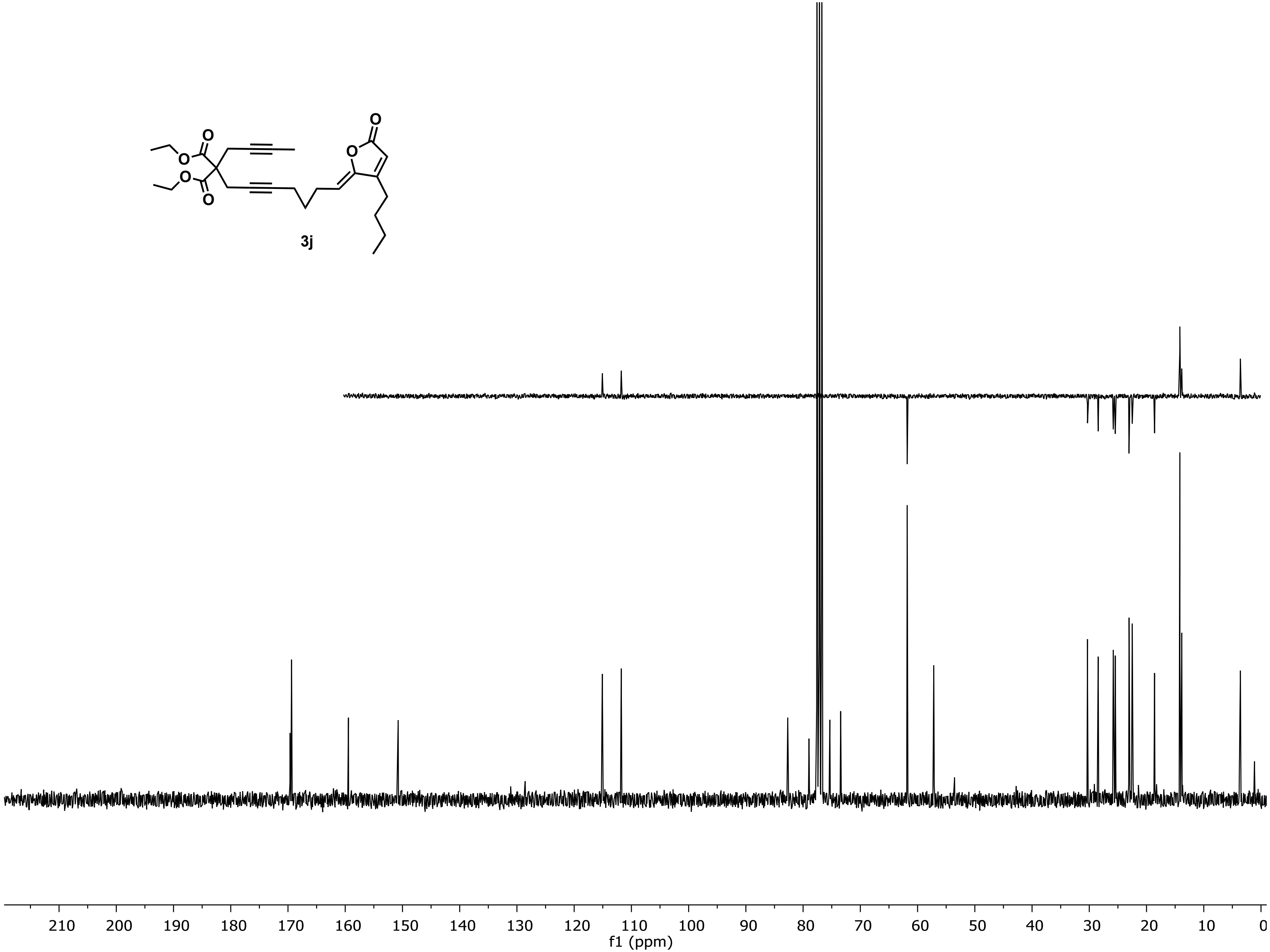
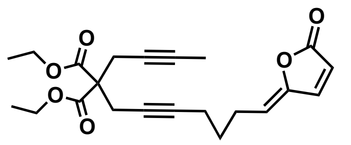


Figure S45. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 3j



3k

According to the general procedure starting from 200 mg (0.63 mmol) of triyne (**5d**) in DMF (1.7 mL). The product was purified by flash chromatography (PE/AcOEt 9:1 to 8:2).

Yield: 67% (163 mg) (1:0.4 mixture of *Z*:*E* diastereomers)

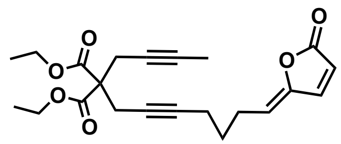
Aspect: yellow pale oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.24 (br t, *J* = 7.1, 6H, 2 x CH_3), 1.64 (quin, *J* = 7.3 Hz, 2H, CH_2), 1.74 (t, *J* = 2.4 Hz, 3H, CH_3), 2.18 (tt, *J* = 7.3 and 2.4 Hz, 2H, CH_2), 2.46 (q, *J* = 7.7 Hz, 2H, CH_2), 2.88 (br q, *J* = 2.4 Hz, 2H CH_2), 2.91 (br t, *J* = 2.4 Hz, 2H, CH_2), 4.20 (q, *J* = 7.1, 4H, 2 x CH_2), 5.30 (t, *J* = 7.7 Hz, 1H, CH_3), 6.15 (d, *J* = 5.4 Hz, 1H, CH), 7.33 (d, *J* = 5.4 Hz, 1H, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 3.6 (CH_3) 14.2 (2 x CH_3), 18.6 (CH_2), 23.0$_2$ (CH_2), 23.0$_4$ (CH_2), 25.7 (CH_2), 28.3 (CH_2), 57.1 (C), 61.8 (2 x CH_2), 73.4 (C), 75.4 (C), 79.0 (C), 82.6 (C), 116.5 (CH), 119.4 (CH), 143.7 (CH), 150.2 (C), 169.4 (2 x C), 170.1 (C)

HRMS (ESI+): $[M+H]^+$ calcd for $C_{22}H_{27}O_6{}^+$ 387.1802, found 387.1802

IR (neat): 2858, 1780, 1731, 1675, 1297, 1197, 1087, 1058 cm^{-1}



3k

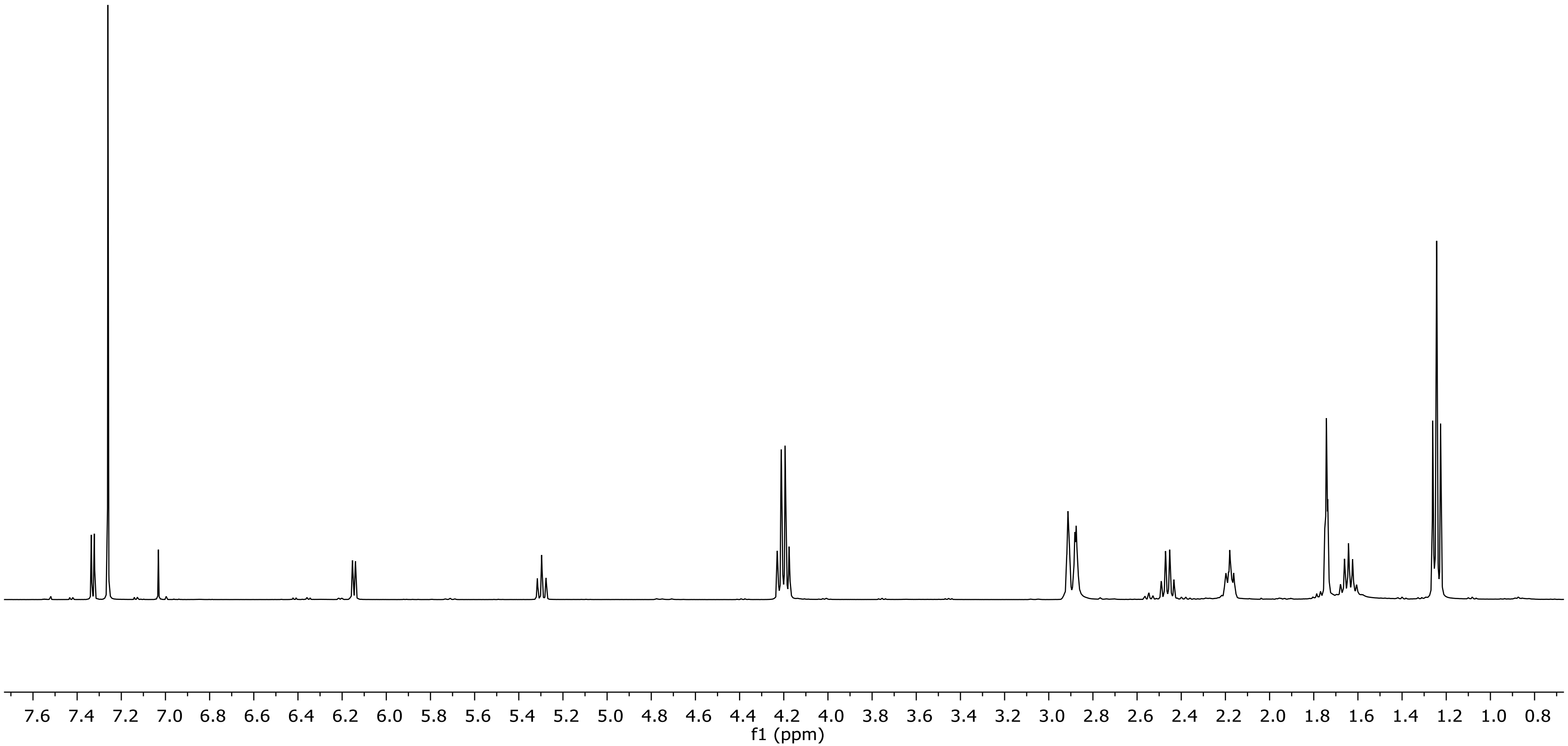


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k

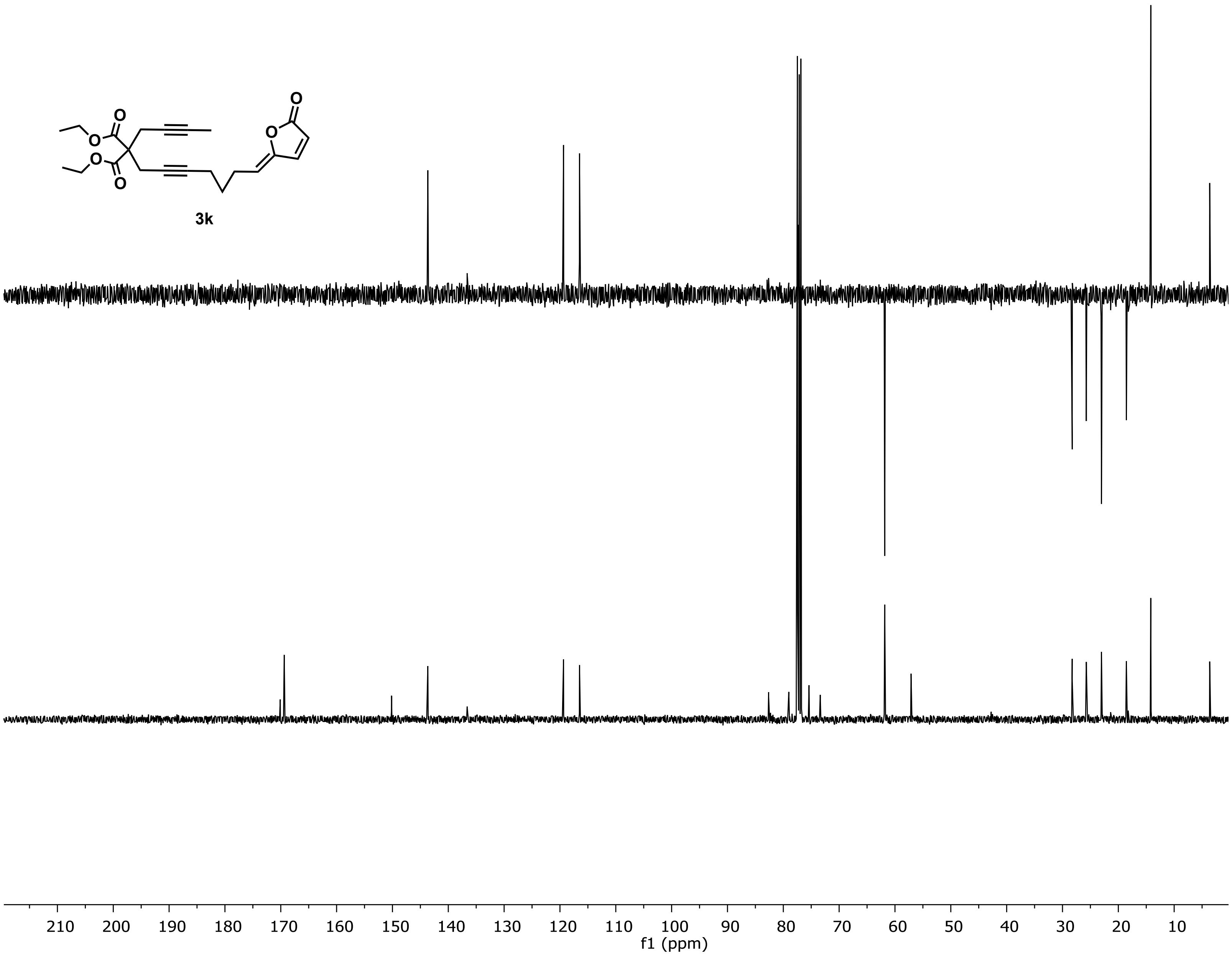
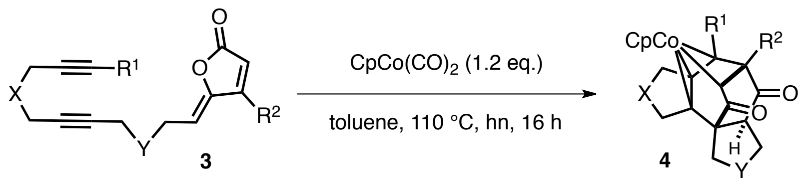


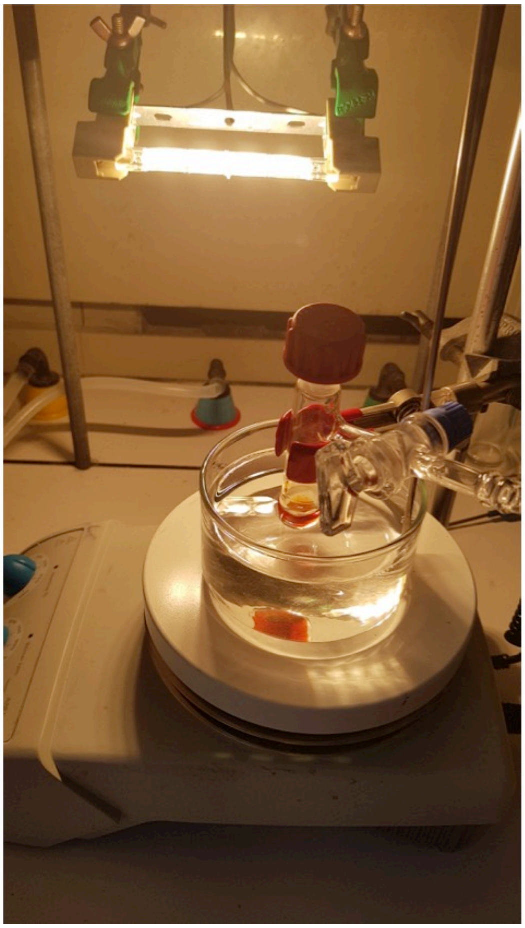
Figure S47. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 3k

General procedure for the synthesis of Co(III)-complexes 4

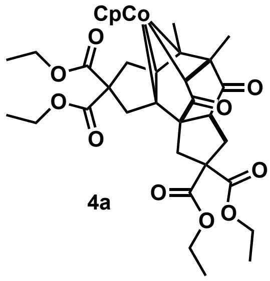


Scheme S7. synthesis of Co(III)-complexes 4

The diyne/γ-alkylidenebutenolides **3** (1 equiv.) was charged in a Schlenck tube under inert atmosphere. Dry toluene (0.043 mol/L) was then added and the solution was degassed twice at -78 °C. Dicarbonylcyclopentadienylcobalt (1.2 equiv.) was added to the solution and the Schlenck tube was sealed. The mixture was heated at 110 °C under irradiation (halogene lamp, 400 W) for16 hours then concentrated *in vacuo* and purified by flash chromatography on silica gel.



Characterisation, UV-Vis spectroscopie and electrochemical studies of Co(III)-complexe 4a



4a

According to the general procedure starting from 50 mg (0.092 mmol) of lactone (**3a**) in toluene (2.1 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 71% (44 mg)

Aspect: orange solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.21 – 1.27 (m, 9H, 3 x CH_3), 1.31 (q, J = 7.2 Hz, 6H, 2 x CH_3), 1.50 (s, 3H, CH_3), 2.04 – 2.08 (m, 2H, CH_2), 2.09 (s, 1H,CH), 2.42 (br dd, J = 11 and 10 Hz, 1H, CH), 3.04 (d, J = 13.6 Hz, 1H, CH_2), 3.25 (d, J = 16.8 Hz, 1H, CH_2), 3.27 (d, J = 13.6 Hz, 1H, CH_2), 3.40 (d, J = 16.8 Hz, 1H, CH_2), 3.47 (d, J = 17.3 Hz, 1H, CH_2), 3.63 (d, J = 17.3 Hz, 1H, CH_2), 4.10 – 4.38 (m, 8H, 4 x CH_2), 4.69 (s, 5H, Cp).

^{13}C NMR (100 MHz, Chloroform-d) δ 10.3 (CH), 14.1 (CH_3), 14,1$_6$ (CH_3), 14.1$_8$ (CH_3), 14.20 (CH_3), 18.5 (CH_3), 19.2 (CH_3), 33.6 (CH_2), 35.6 (CH_2), 41.5 (CH_2), 45.6 (CH_2), 47.4 (C), 53.0 (C), 54.0 (C), 57.9 (C), 58.1 (C), 58.2 (CH), 61.8 (CH_2), 62.0 (CH_2), 62.3 (CH_2), 62.6 (CH_2), 72.7 (C), 86.6 (5 x CH, Cp), 103.1 (C), 170.9 (C), 171.3 (C), 172.2 (C), 172.32 (C), 180.12 (C), 204.5 (C).

^{59}Co NMR[11] (119 MHz, Chloroform-d): 11238.10 ppm

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{34}H_{42}O_{10}Co^+$ 669.2104, found 669.2104

IR (neat): 2980, 1714, 1691, 1629, 1452, 1369, 1257, 1188, 1097, 1060, 839 cm^{-1}

Mp: 96 °C

[11] S. C. F. Au-Yeung, D. R. Eaton, *Can. J. Chem*. **1983**, *61*, 2431-2441.

X-RAY: the product was crystallized by diffusion from DCM to pentane

CCDC 1853760 contains the supplementary crystallographic data for this paper. Even if one "ethyl" moiety was found to be disordered, the structure of **4a** was established without ambiguity

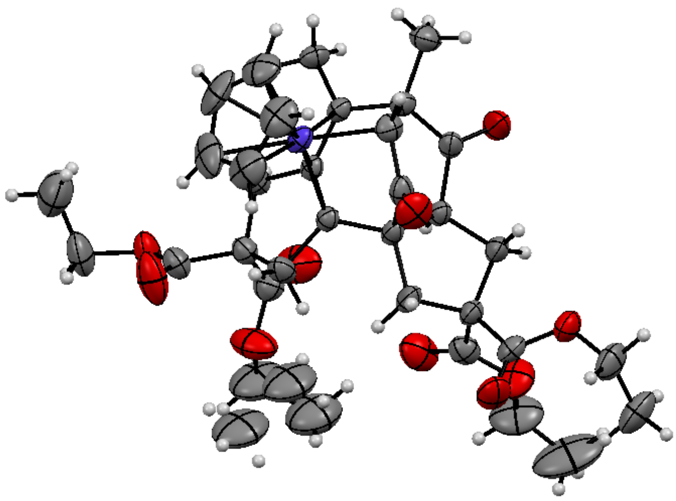


Figure S48. Crystallographically-derived molecular structure of polycyclic cobalt(III) complex 4a.

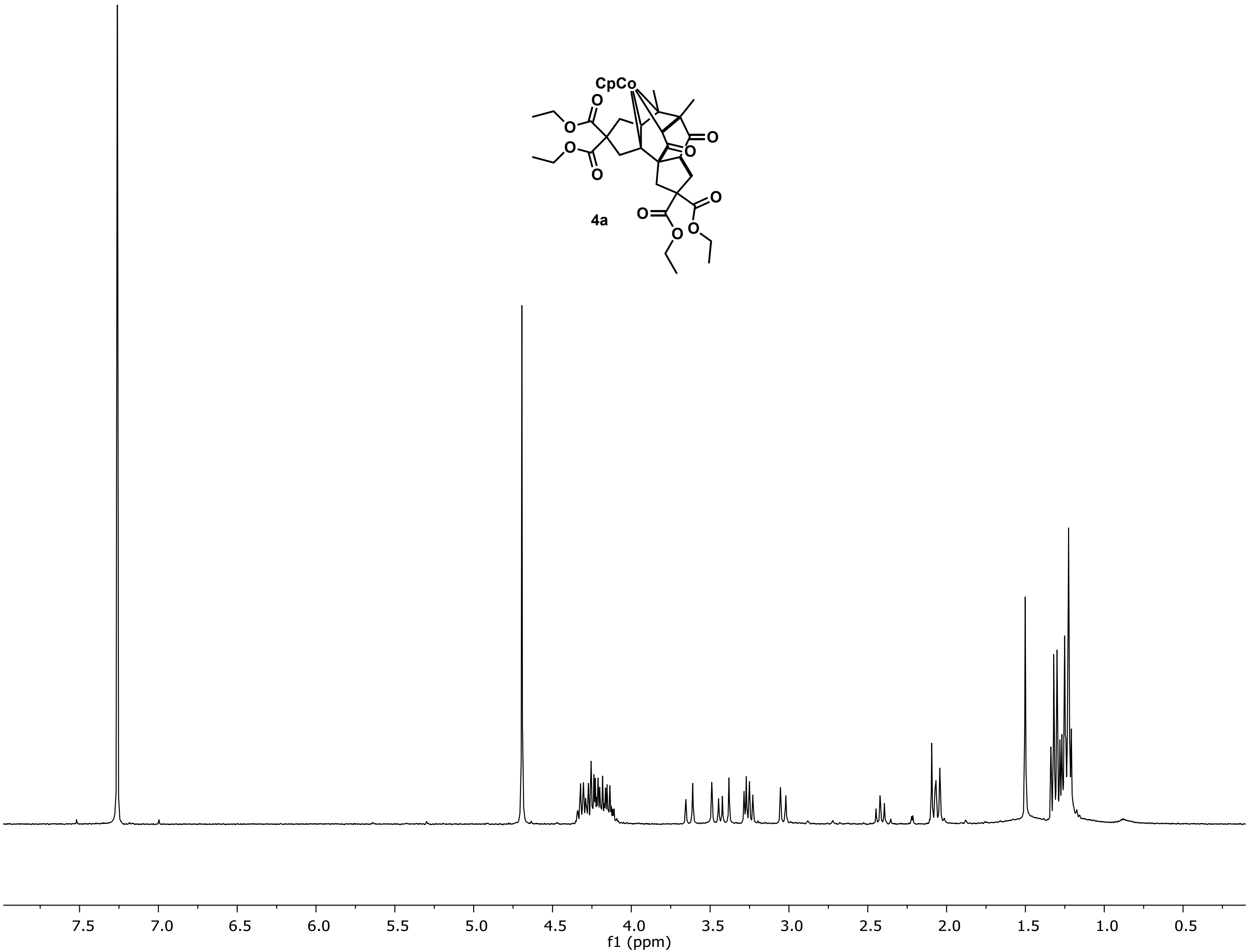


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a

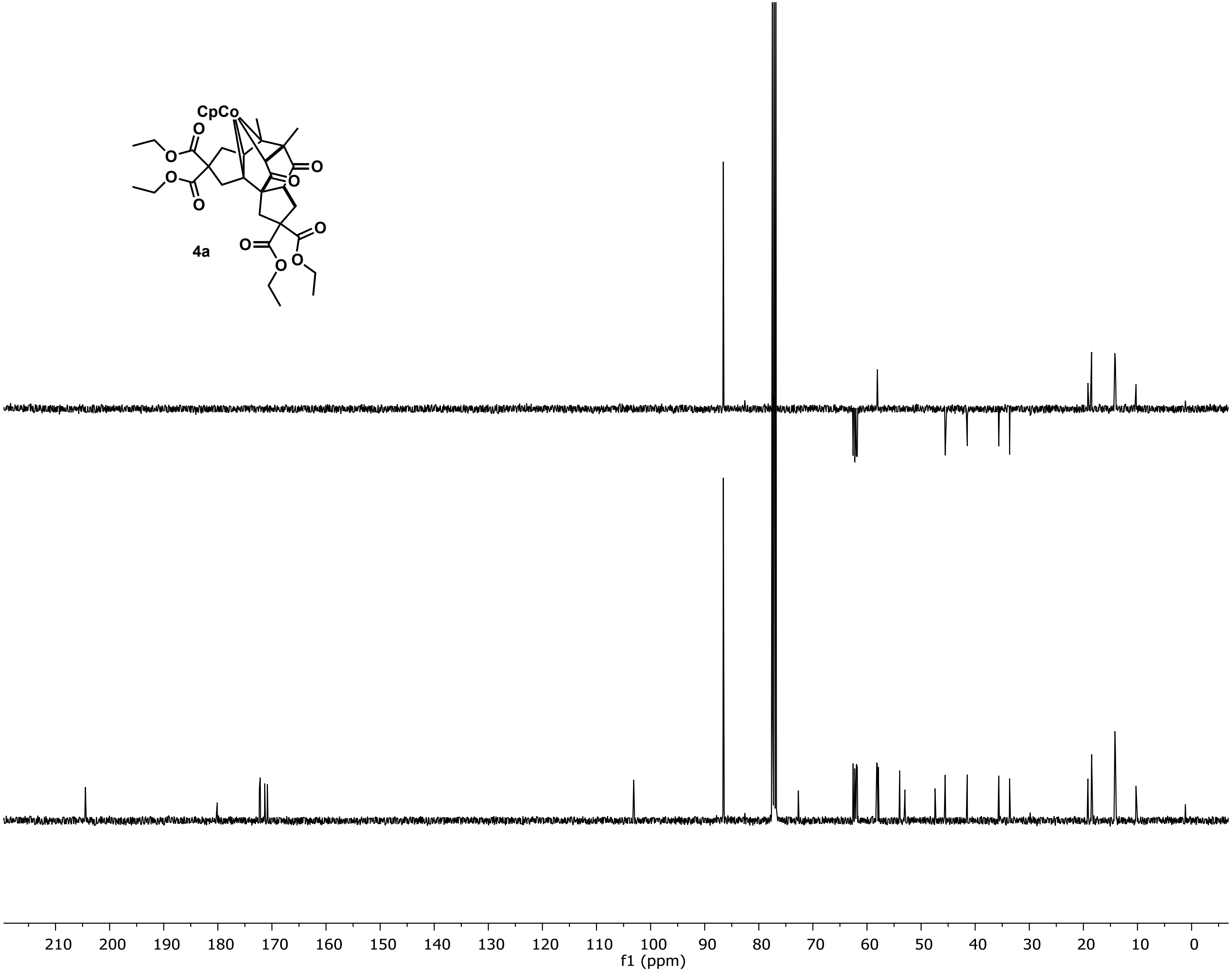


Figure S50. ^{13}**C NMR and DEPT (100 MHz, CDCl$_3$) spectra of 4a**

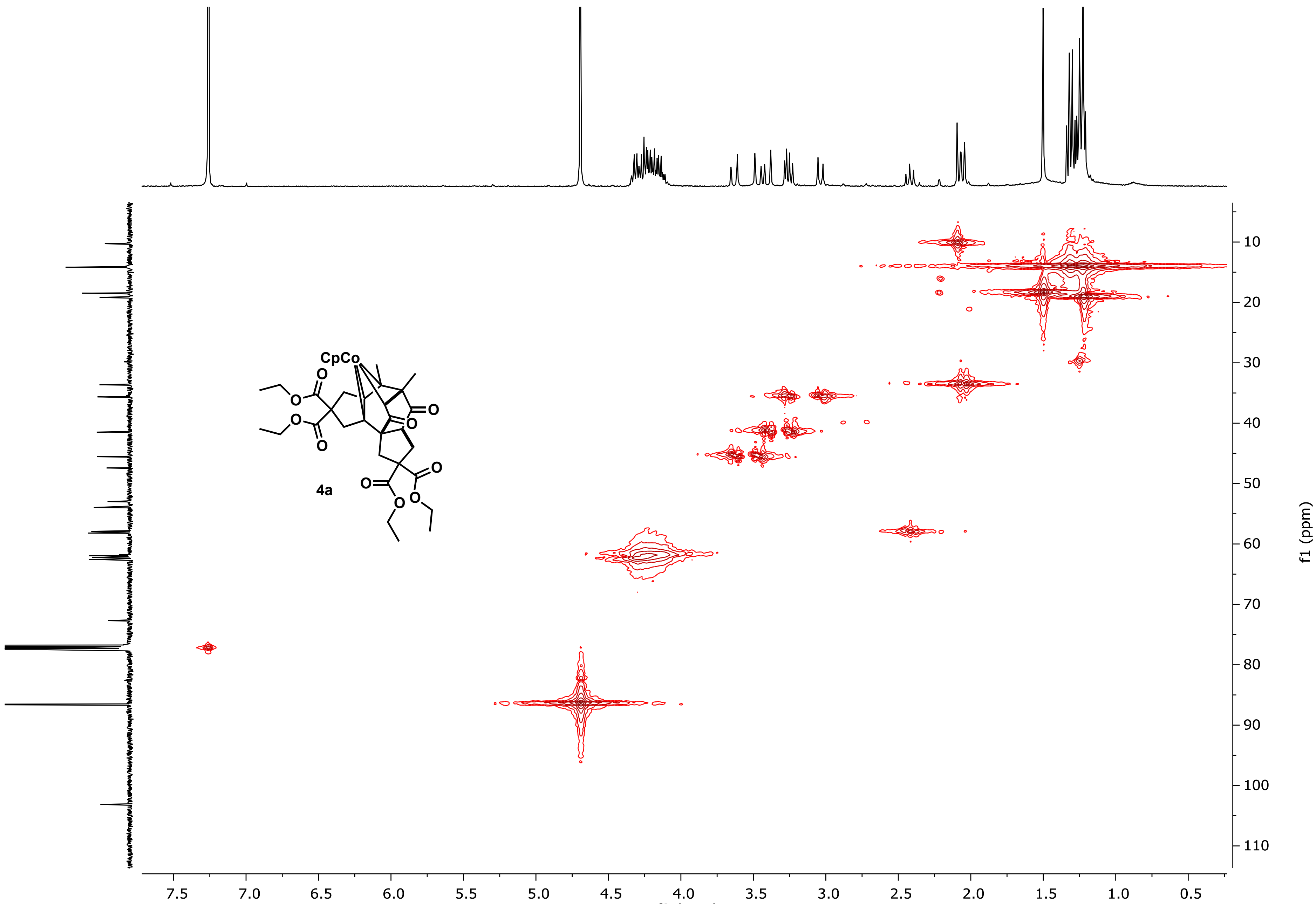


Figure S51. HMQC ($CDCl_3$) spectrum of 4a

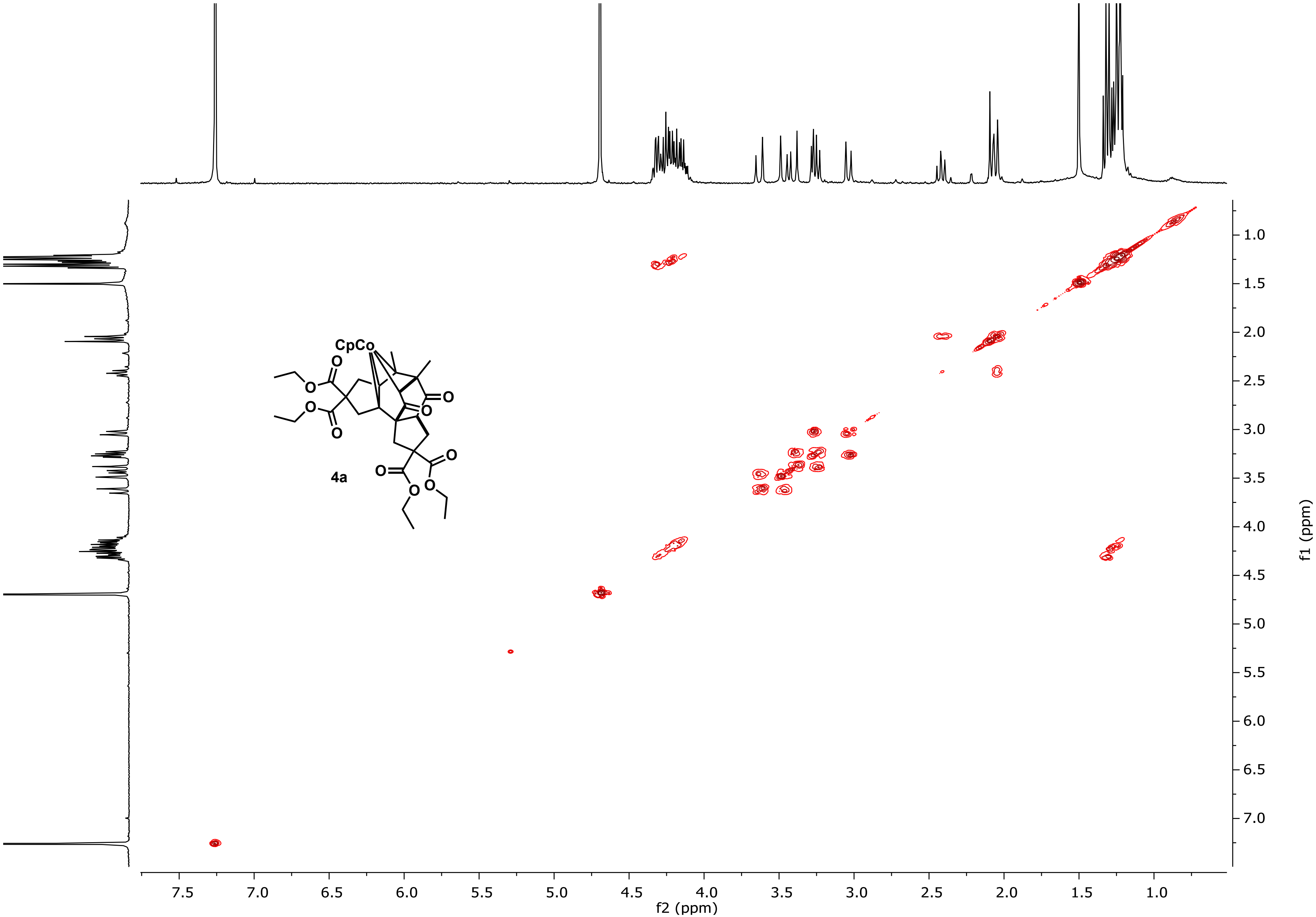


Figure S52. COSY ($CDCl_3$) spectrum of 4a

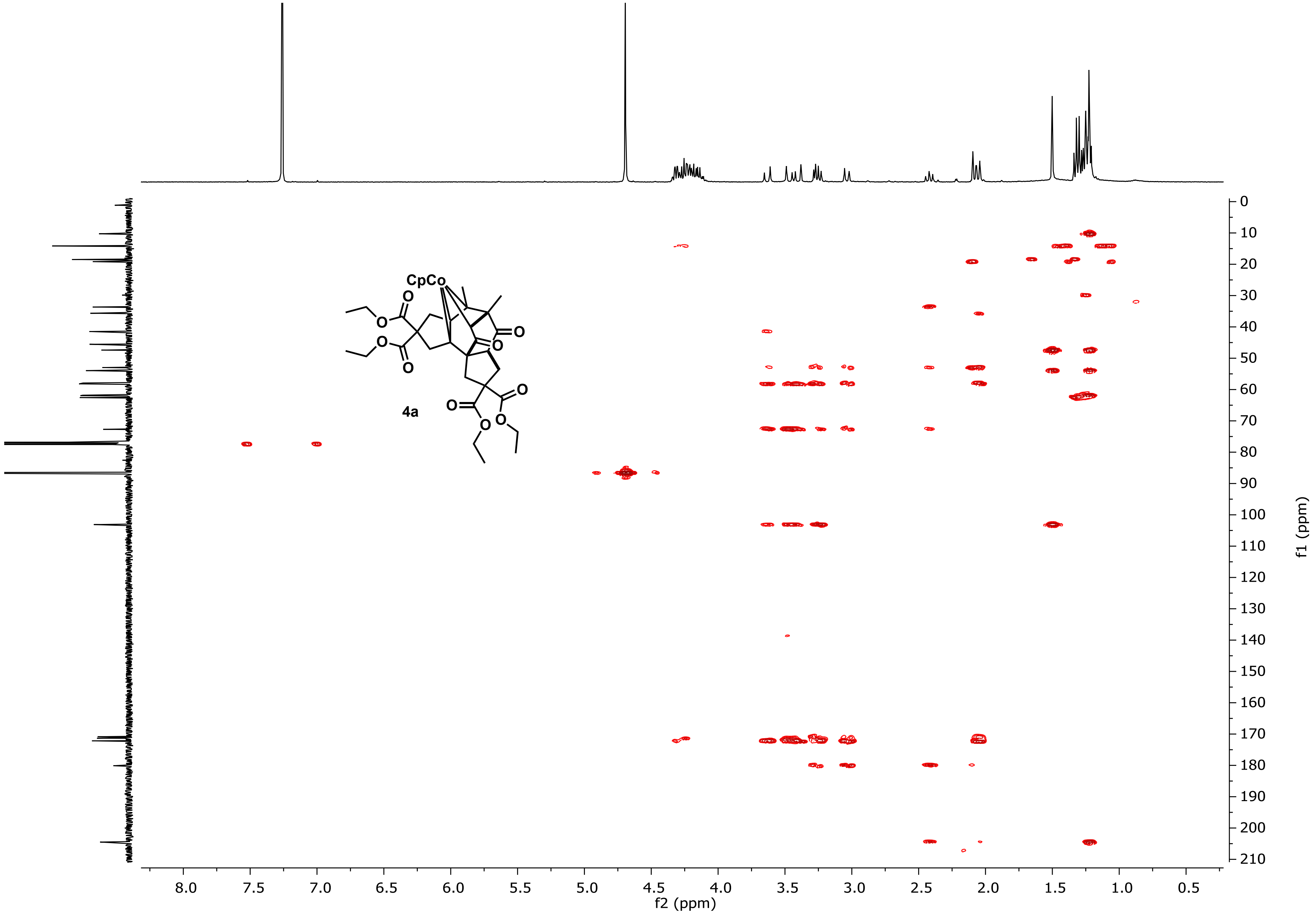


Figure S53. HMBC ($CDCl_3$) spectrum of 4a

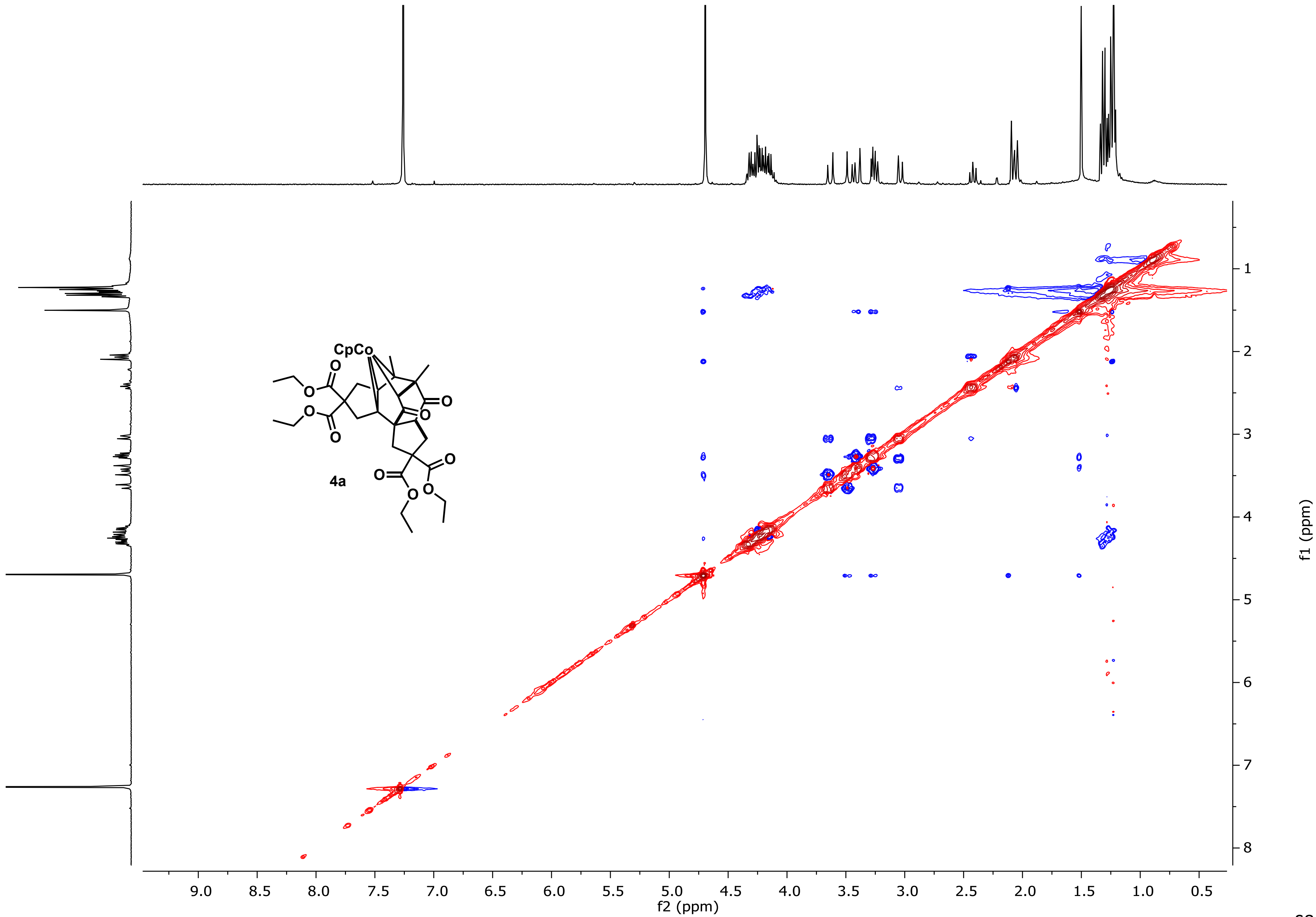


Figure S54. NOESY(CDCl$_3$) spectrum of 4a

The oxidation state of the cobalt(III) complex **4a** was confirmed by ^{59}Co NMR spectroscopy with a chemical shift of 11238 ppm.

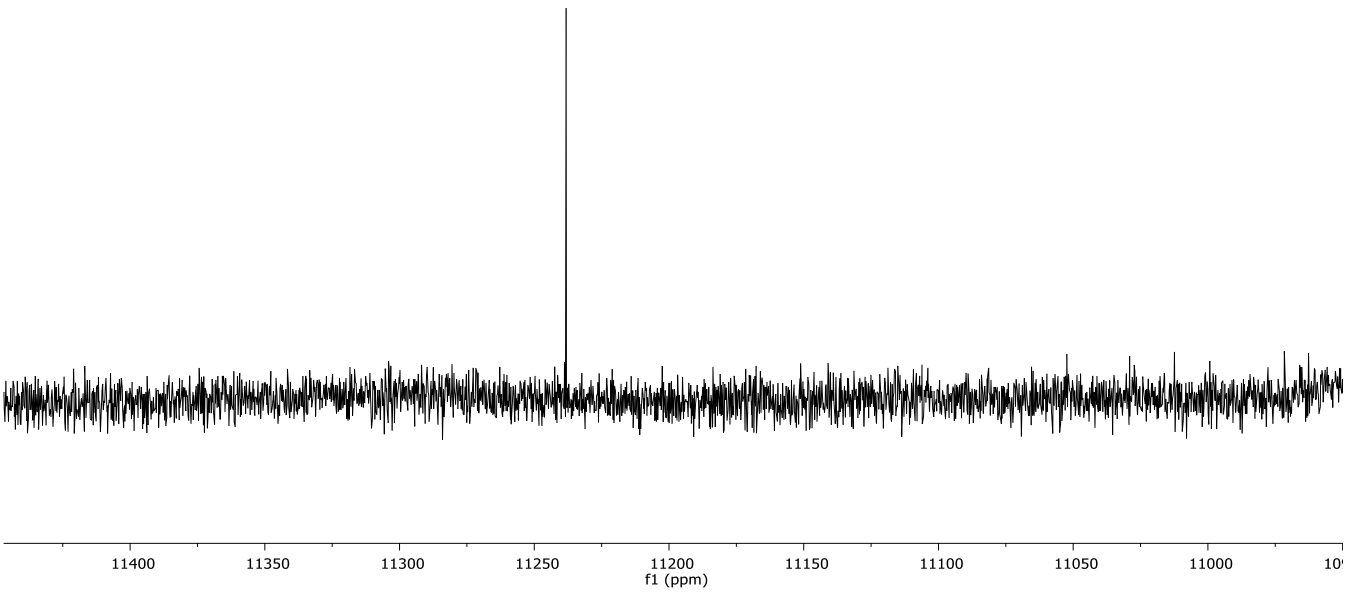


Figure S55. ^{59}Co NMR (119 M, $CDCl_3$) spectrum of 4a

UV-Vis absorption spectrum of **4a** revealed three distinct absorption maxima: two highly intense peaks at 275 and 300 nm and another less intense peak at 439 nm characteristic of the orange color of the complex **4a**.

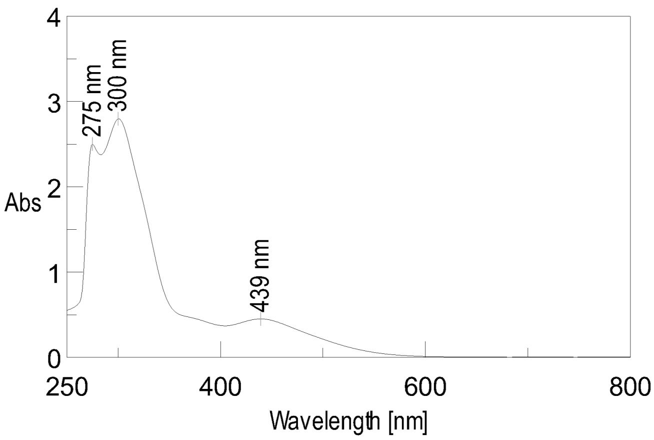


Figure S56. UV-Vis absorption spectrum of 4a

Cyclic Voltammetry

Electrochemical experiments

All electrochemical experiments were performed at room temperature using a Multipotentiostat (Autolab PGSTAT 30; Eco Chemie) controlled by GPES 4.9 software.

A homemade 0.5 mm Au disc was used as working electrode (WE), a Pt wire was used as counter electrode (CE) and commercial saturated calomel electrode (SCE) was used as the reference electrode.

All measurements were performed under argon.

Results:

The electrochemical behaviour of complex **4a** was investigated by cyclic voltammetry in 0.1M $TBABF_4$ in DMF using at a gold disk working electrode. As seen in Figure bellow, a single irreversible oxidation peak is observable at 1.05 V vs. SCE. This established that the corresponding cation **4a**$^+$ was chemically unstable over the range of scan rates investigated (voltammetric responses were recorded at different concentrations, 2 and 4 mM, and different scan rates, 0.1, 0.5 and 1 V s^{-1}). The resulting peak current intensity was proportional to the concentration (see Table 1) and to the square root of the scan rate over the experimental range investigated, indicating that the wave was controlled by the same kinetic factor. The peak potential shifted towards positive potentials upon increasing the scan rate (v) with a slope of 60 mV/$\log_{10}$v and was independent of the concentrations. This established that the rate-determining step of **4a** oxidation was the electron uptake from **4a**.[12] This evidences that the molecular and electronic structure of the complex experiences a strong reorganization upon its one-electron oxidation. Note that it is then impossible to infer anything about either the thermodynamics of the electron transfer step or about the follow-up reactions that give rise to the chemical irreversibility of the oxidation wave.

[12] Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.*, **1973**, *48*, 113-145.

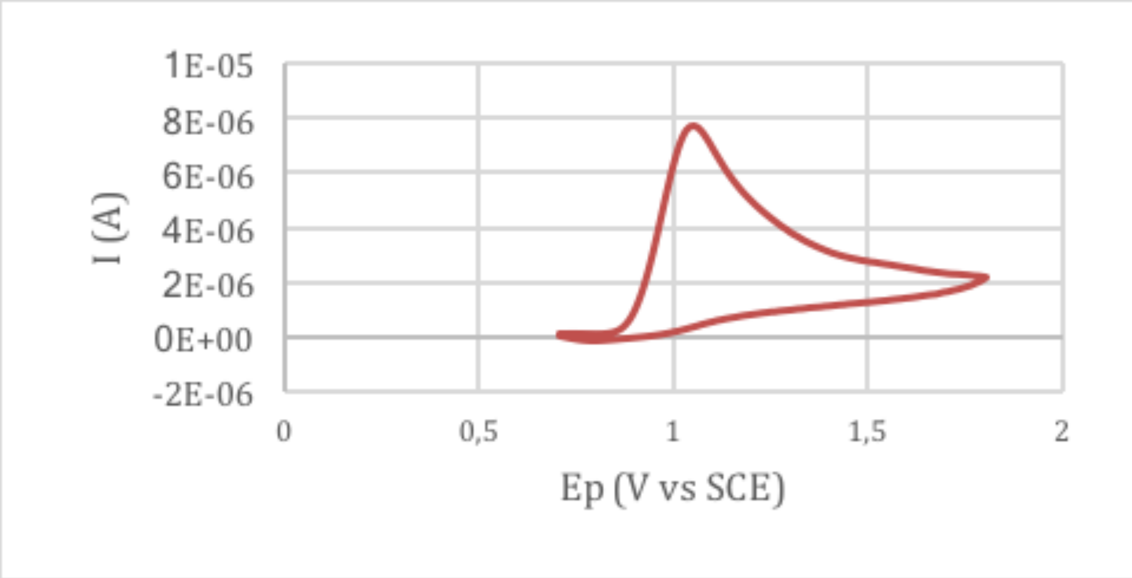
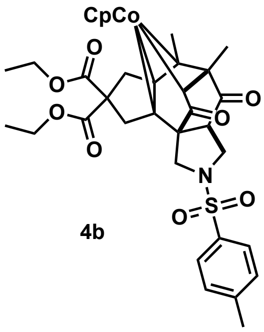


Figure S57. Cyclic voltammetry of 4mM of **4a** in 0.1M $TBABF_4$ in DMF at a 0.5 mm Au disc WE. Scan rate: 500 mV s^{-1}.

Table 1: Ep and Ip values after subtracting the blank. The experiments were performed in DMF 0.1 M $TBABF_4$ using an Au 0.5 mm disc WE.

	2 mM		4 mM	
Scan rate (V s^{-1})	Ep (V vs SCE)	Ip (µA)	E p (V vs SCE)	Ip (µA)
0.1	1.010	1.62	1.015	3.30
0.5	1.035	4.22	1.050	7.71
1	1.070	4.13	1.075	10.4

Characterisation of Co(III)-complexe 4b-4k



4b

According to the general procedure starting from 15 mg (0.027 mmol) of lactone (**3b**) in toluene (0.65 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield 55% (10 mg)

Aspect: orange solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.18 (s, 3H, CH_3), 1.31 (br t, *J* = 7.1 Hz, 3H, CH_3), 1.33 (br t, *J* = 7.1 Hz, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.01 (s, 1H, CH), 2.39 (m, 4H, CH_3 and CH_2), 2.70 (dd, *J* = 11.2 and 8.6 Hz, 1H, CH), 3.30 (d, *J* = 16.9 Hz, 1H, CH_2), 3.35 (d, *J* = 16.9 Hz, 1H, CH_2), 3.37 (d, *J* = 16.9 Hz, 1H, CH_2), 3.46 (d, *J* = 16.9 Hz, 1H, CH_2), 3.54 (br t, J = 9 Hz, 1H, CH_2), 3.98 (d, *J* = 9.5 Hz, 1H, CH_2), 4.22 – 4.30 (m, 4H, 2 x CH_2), 4.41 (d, *J* = 9.5 Hz, 1H, CH_2), 4.70 (s, 5H, Cp), 7.29 (d, *J*= 8.1 Hz, 2H, 2 x CH), 7.73 (d, *J*= 8.1 Hz, 2H, 2 x CH).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 10.3 (CH), 14.2_1 (CH_3), 14.2_3 (CH_3), 18.7 (CH_3), 19.0 (CH_3), 21.8 (CH_3), 41.3 (CH_2), 45.7 (CH_2), 46.6 (CH_2), 47.9 (CH_2), 49.2 (C), 51.7 (C), 54.0 (CH), 57.0 (C) , 58.7 (C), 62.4 (CH_2), 62.8 (CH_2), 70.2 (C), 86.8 (5 x CH), 103.4 (C), 127.8 (2 x CH), 129.7 (2 x CH), 134.4 (C), 143.5 (C), 170.9 (C), 172.2 (C), 178.8 (C), 202.0 (C).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{34}H_{39}NO_8SCo^+$ 680.1723, found 680.1731

IR (neat): 2923, 1722, 1702, 1257, 1159, 1093, 1049, 1008, 806, 740, 655, 549 cm^{-1}

Mp: 160 °C

X-RAY: the product was crystallized from acetonitrile

CCDC 1853762 contains the supplementary crystallographic data for this paper

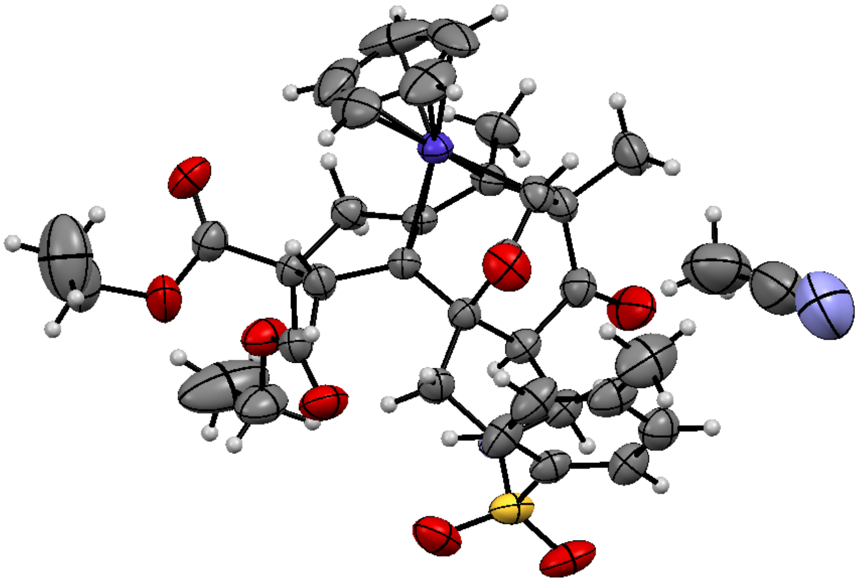


Figure S58. Crystallographically-derived molecular structure of polycyclic cobalt(III) complex 4b.

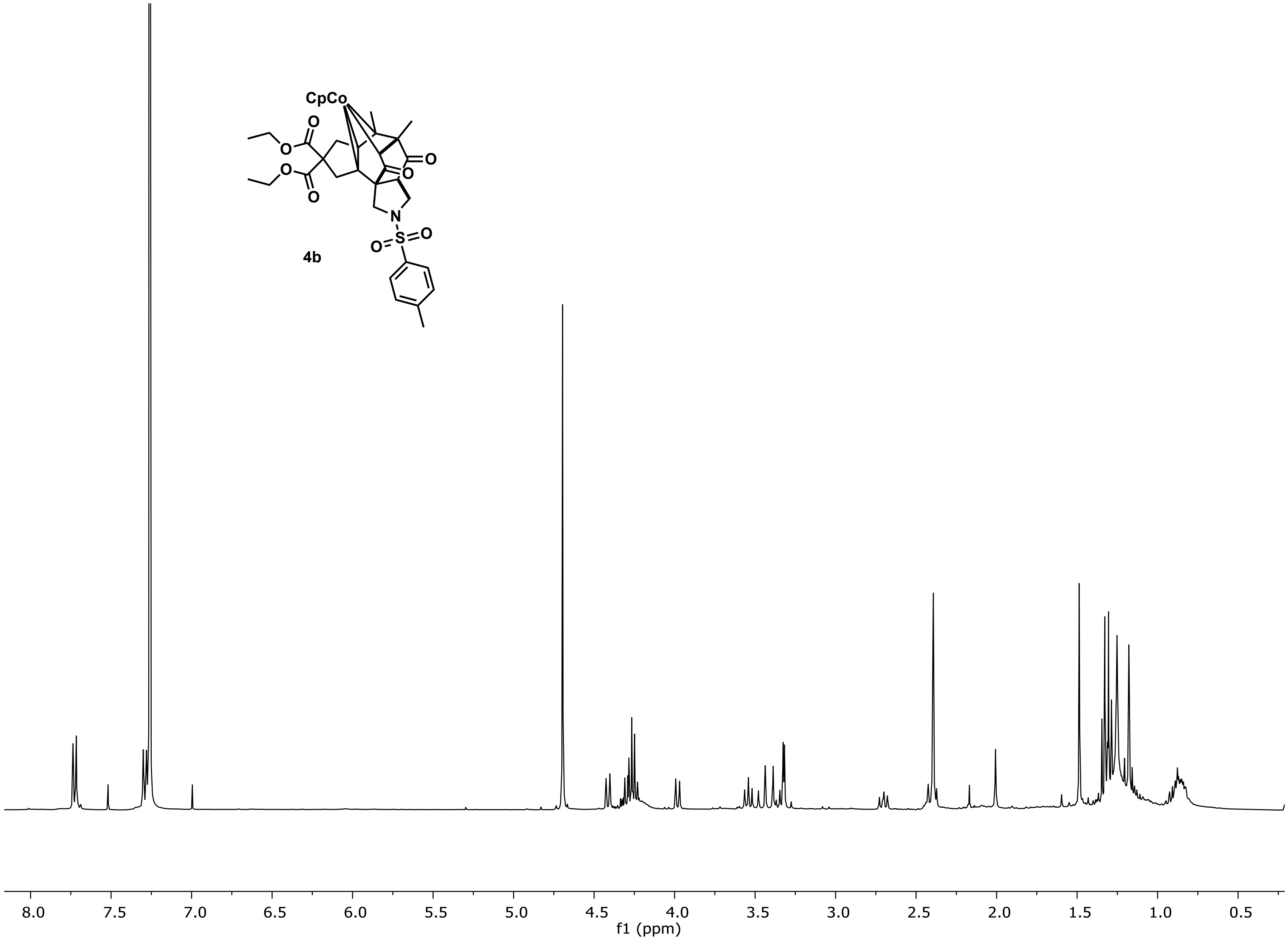


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4b

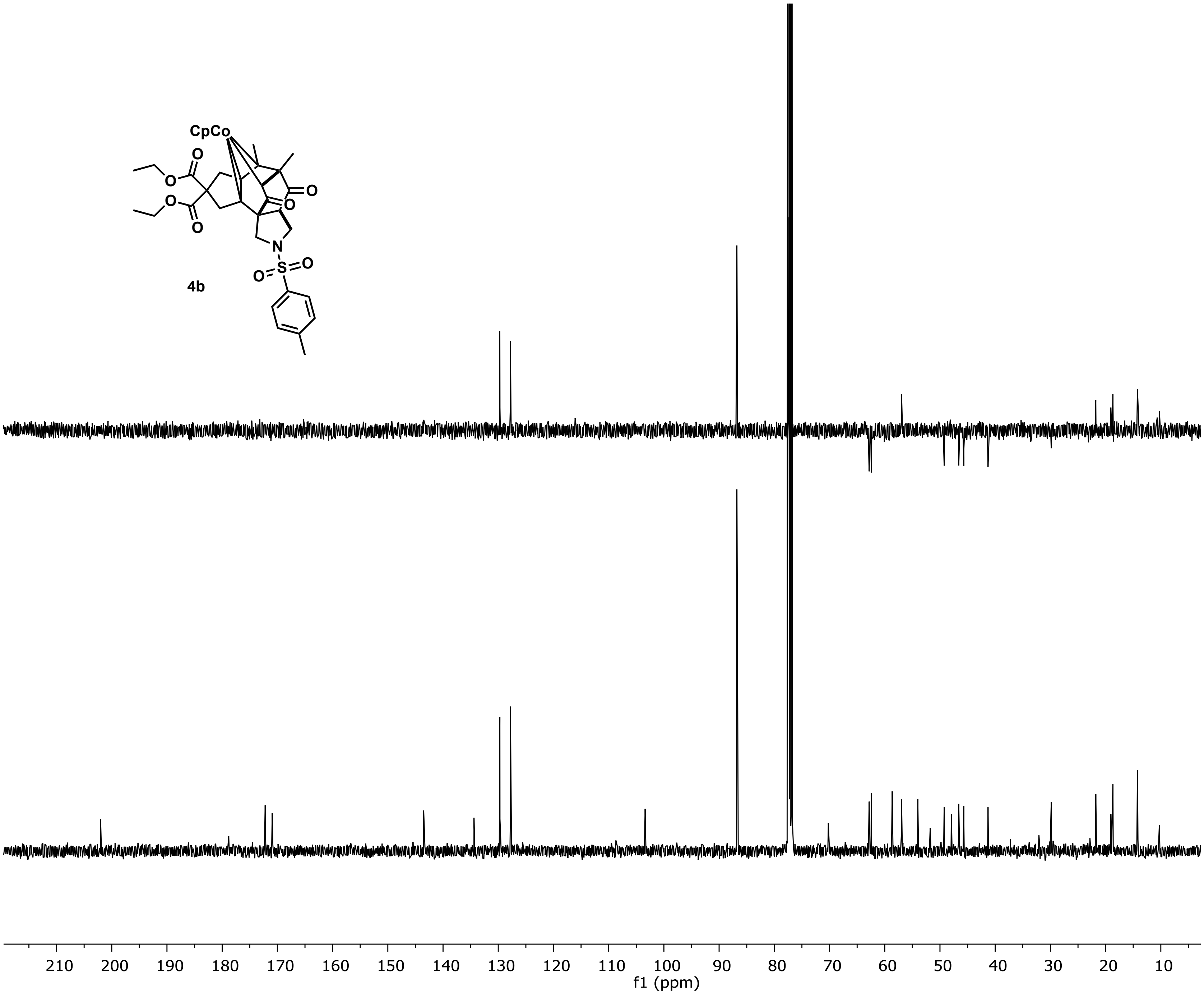
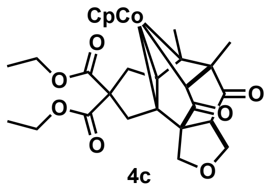


Figure S60. ^{13}C NMR and DEPT (100 MHz, $CDCl_3$) spectra of 4b



4c

According to the general procedure starting from 20 mg (0.05 mmol) of lactone (**3c**) in toluene (1.2 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 66% (17.3 mg)

Aspect: orange oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.24 (s, 3H, CH_3), 1.30 (br t, *J* = 7.1 Hz, 3H, CH_3), 1.31 (br t, *J* = 7.1 Hz, 3H, CH_3), 1.52 (s, 3H CH_3), 2.16 (s, 1H, CH), 2.75 (t, *J* = 10.0 Hz, 1H,CH_2), 3.27 – 3.43 (m, 5H, 2 x CH_2 and CH_2), 3.90 (br t, *J* = 9.3 Hz, 1H, CH_2), 4.15 (d, *J* = 7.9 Hz, 1H, CH_2), 4.18 - 4.30 (m, 4H, 2 x CH_2), 4.75 (s, 5H, Cp), 4.89 (d, *J* = 7.9 Hz, 1H, CH_2).

^{13}C NMR (75 MHz, Chloroform-d) δ 11.3 (CH), 14.2 (2 x CH_3), 18.8 (CH_3), 19.1 (CH_3), 41.1 (CH_2), 45.3 (CH_2), 47.9 (C), 52.1 (C), 54.7 (C), 58.9 (C), 59.0 (CH), 62.4 (CH_2), 62.7 (CH_2), 66. 7 (CH_2), 69.2 (CH_2), 69.8 (C), 86.8 (5 x CH, Cp), 104.0 (C), 171.0 (C), 172.5 (C), 179.8 (C), 203.0 (C).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{27}H_{32}O_7Co^+$ 527.1475, found 527.1473

IR (neat): 2976, 2927, 1724, 1703, 1647, 1253, 1184, 1087, 1060 cm^{-1}

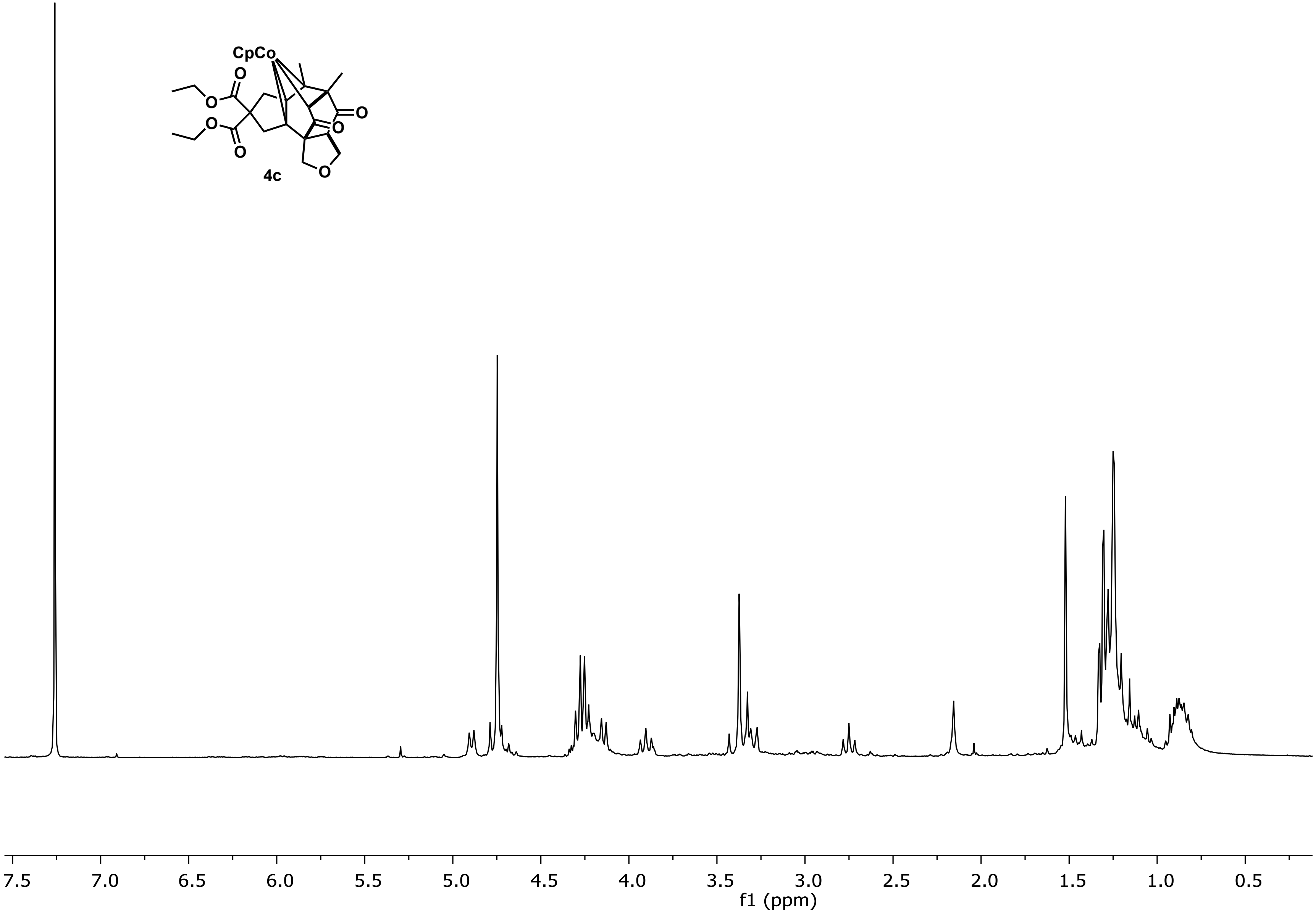


Figure S61. [1]**H NMR (300 MHz, $CDCl_3$) spectrum of 4c**

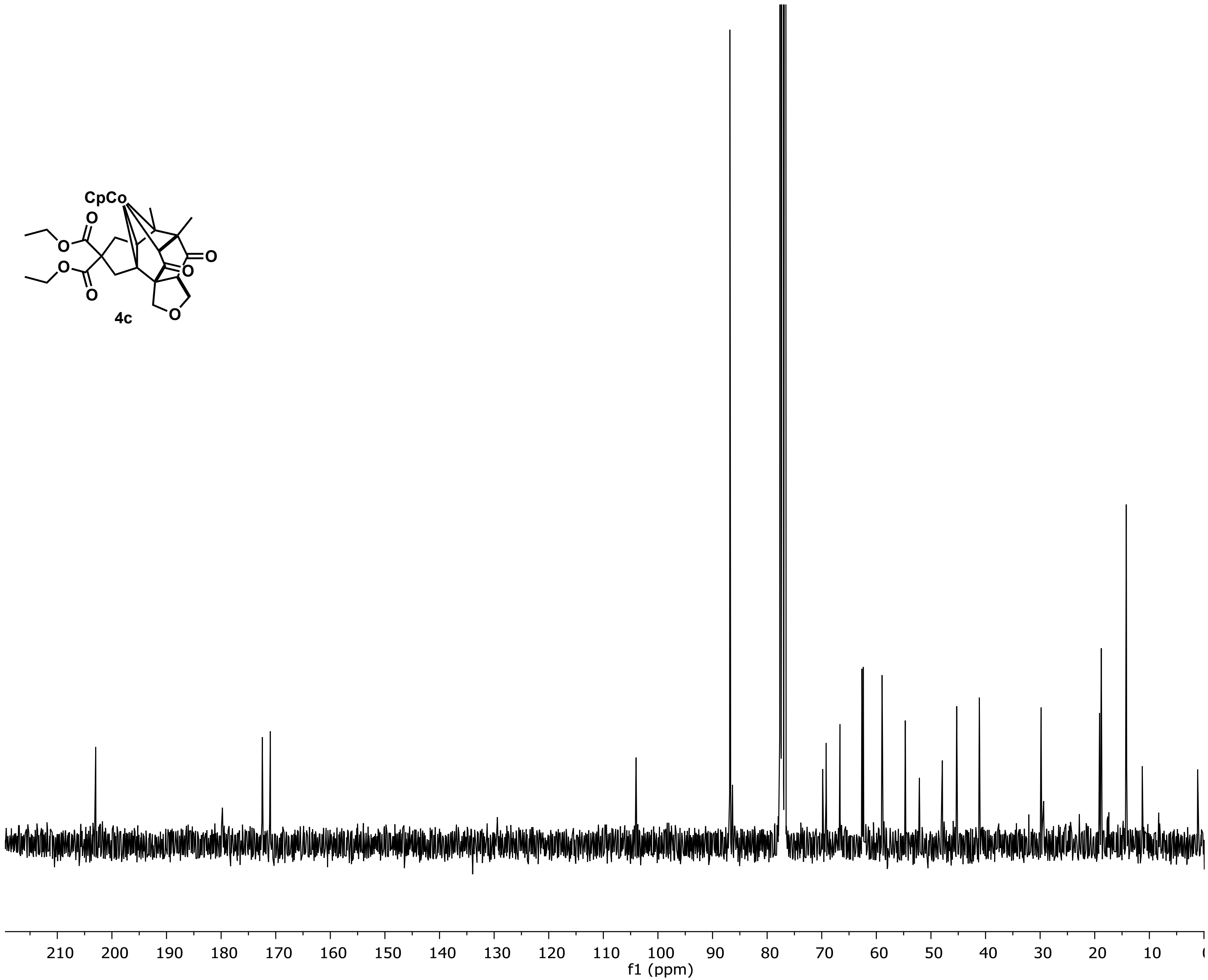


Figure S62. ^{13}C NMR (75 MHz, CDCl$_3$) spectrum of 4c

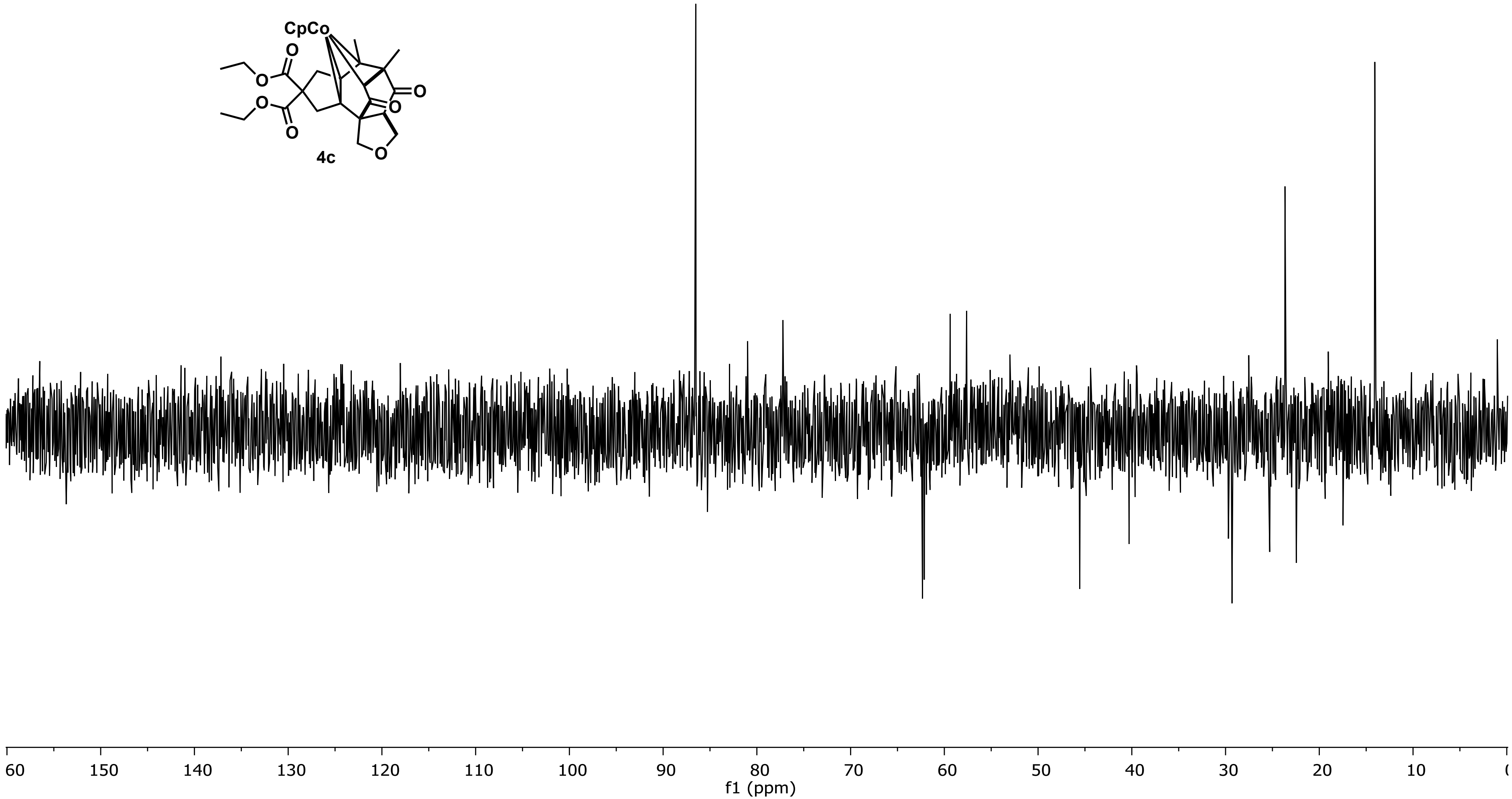
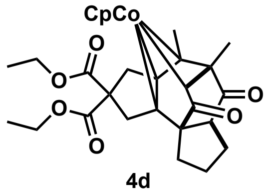


Figure S63. DEPT (75 MHz, $CDCl_3$) spectrum of 4c



4d

According to the general procedure starting from 50 mg (0.125 mmol) of lactone (**3d**) in toluene (2.9 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 55% (36 mg)

Aspect: orange solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.22 (s, 3H, CH_3), 1.23-1.27 (m, 1H, CH_2), 1.30 (t, J = 7.1 Hz, 3H, CH_3), 1.31 (t, J = 7.1 Hz, 3H, CH_3), 1.50 (s, 3H ,CH_3), 1.65-1.75 (m, 2H, CH_2), 1.77-1.83 (m, 1H, CH_2) , 1.95-2.07 (m, 1H, CH_2), 2.09 (s, 1H, CH), 2.27 (br dd, J = 10.8 and 9.4 Hz, 1H), 2.66 (br dt, J = 11.4 and 5.5 Hz, 1H, CH_2), 3.25 (d, J = 16.8 Hz, 1H, CH_2), 3.34 (d, J = 17.1 Hz, 1H, CH_2), 3.40 (d, J = 16.8 Hz, 1H, CH_2), 3.54 (d, J = 17.1 Hz, 1H, CH_2), 4.18 – 4.38 (m, 4H, 2 x CH_2), 4.70 (s, 5H, Cp)

^{13}C NMR (100 MHz, Chloroform-d) δ 11.3 (CH), 14.2 (2x CH_3), 18.5 (CH_3), 19.2 (CH_3), 22.4 (CH_2), 25.7 (CH_2), 29.1 (CH_2), 41.4 (CH_2), 45.8 (CH_2), 47.3 (C), 53.4 (C), 54.3 (C), 58.5 (C), 59.8 (CH), 62.3 (CH_2), 62.4 (CH_2), 73.2 (C), 86.6 (5 x CH), 103.3 (C), 171.3 (C), 172.6 (C), 181.8 (C), 206.6 (C).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{28}H_{34}O_6Co^+$ 525.1682, found 525.1682

IR (neat): 2983, 2964, 2931, 1718, 1693, 1635, 1263, 1186, 1080, 1014 cm^{-1}

Mp: 170 °C

X-ray: the product was crystallized from EtOH

CCDC 1853766 contains the supplementary crystallographic data for this paper

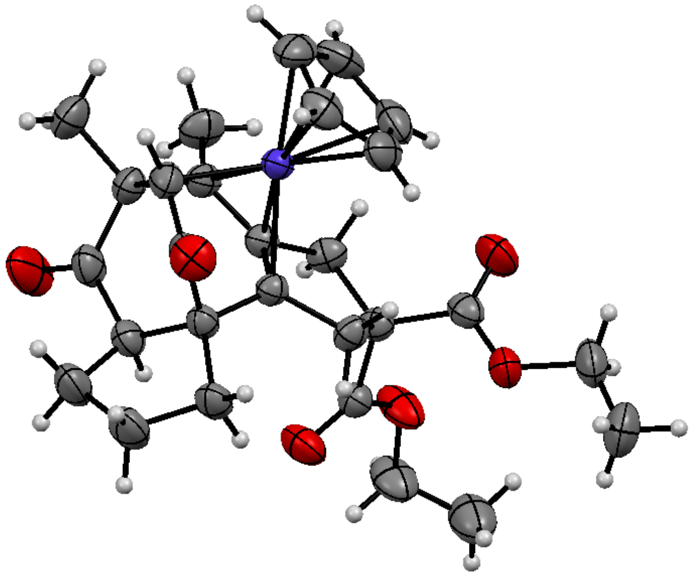


Figure S64. Crystallographically-derived molecular structure of polycyclic cobalt(III) complex 4d.

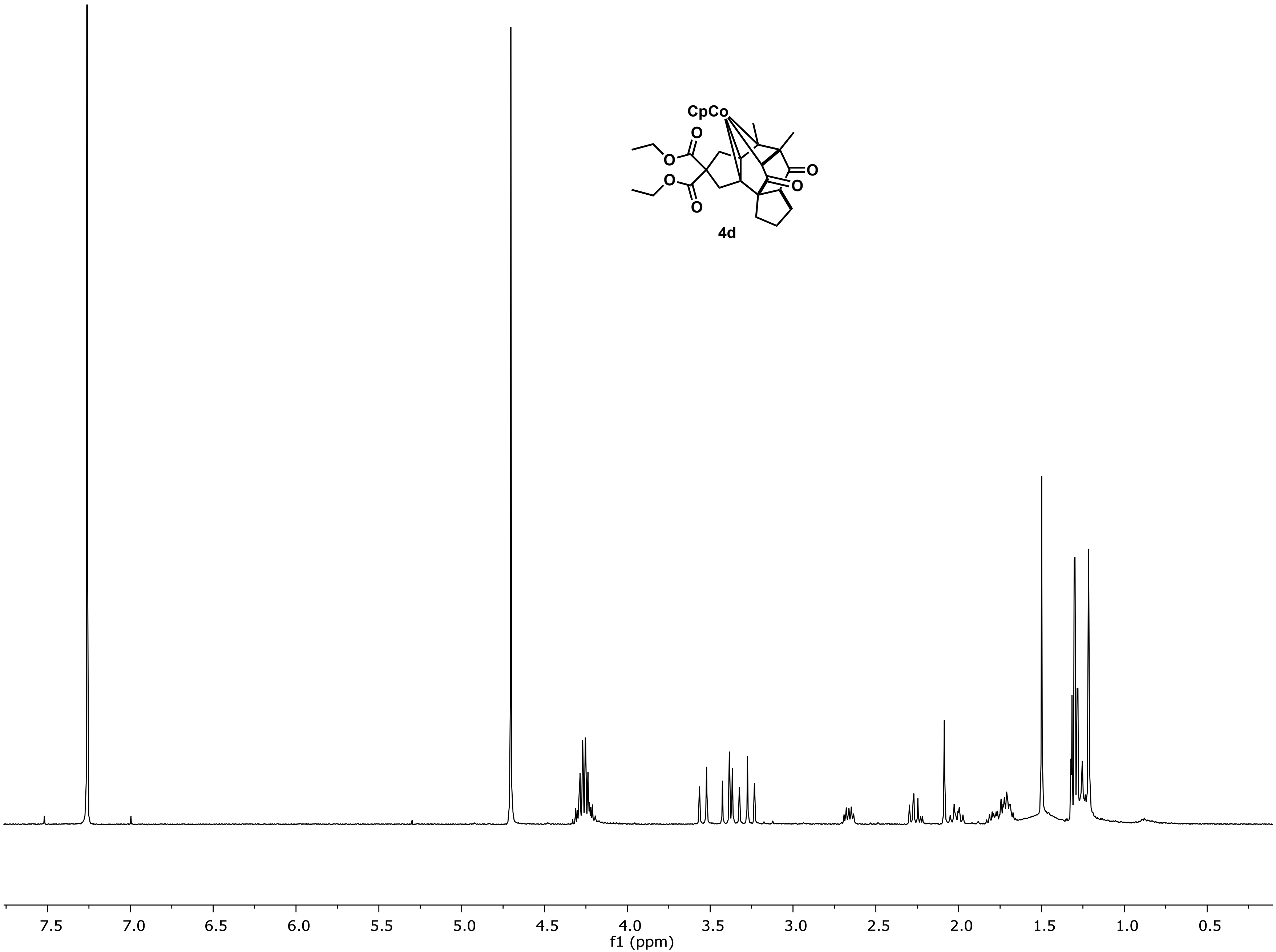


Figure S65. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 4d**

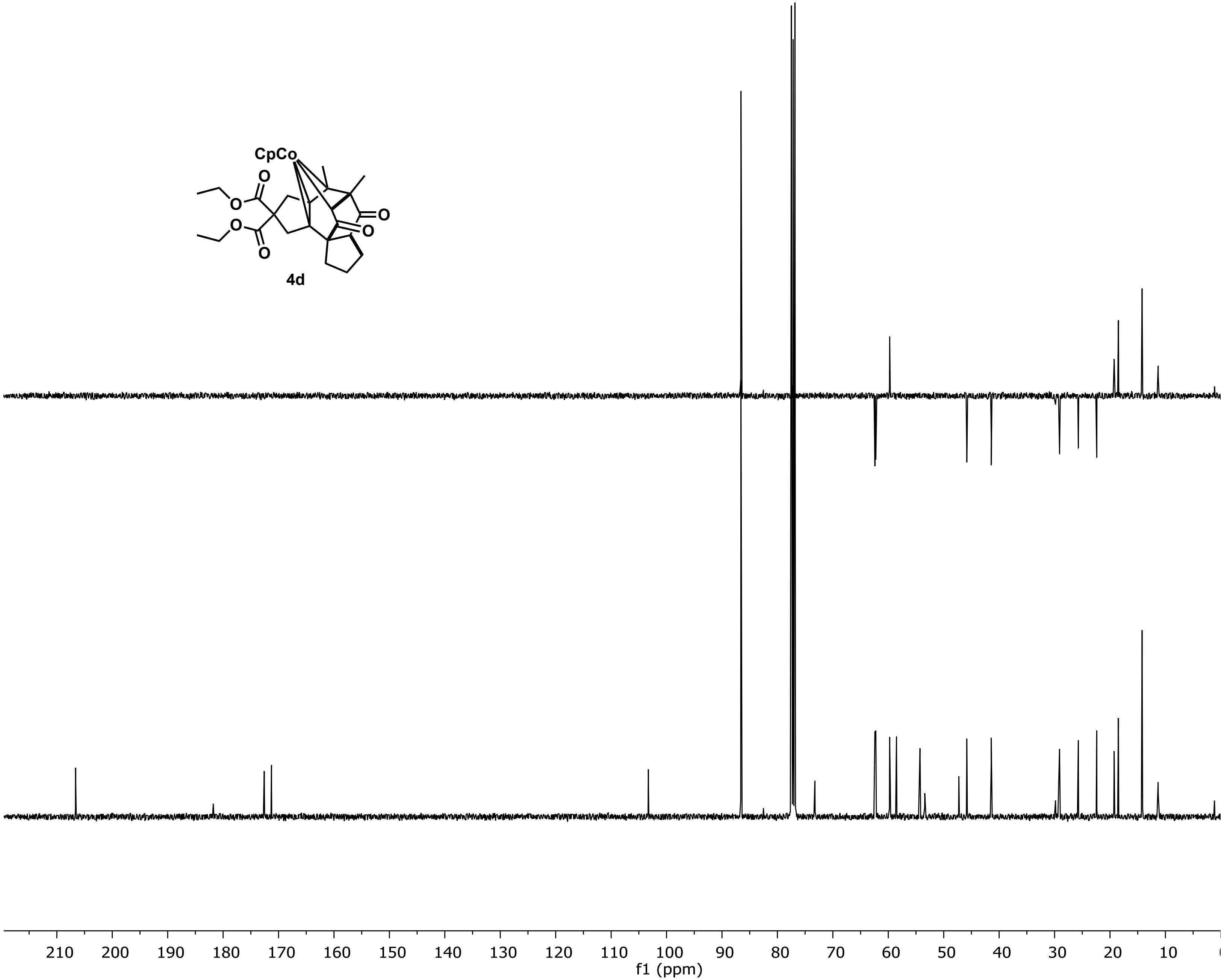
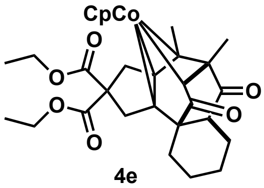


Figure S66. ^{13}C NMR and DEPT (100 MHz, $CDCl_3$) spectra of 4d



4e

According to the general procedure Starting from 30 mg (0.072 mmol) of lactone (**3e**) in toluene (1.7 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 29% (11 mg) or 72% based on recovery material

Aspect: orange oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.74 – 1.05 (m, 1H, C*H*$_2$), 1.16 (s, 3H, CH$_3$), 1.17-125 m, 1H, C*H*$_2$), 1.29 (br t, *J* = 7.1 Hz, 3H, CH$_3$), 1.30 (br t, *J* = 7.2 Hz, 3H, CH$_3$), 1.35-1.46 (m, 1H, C*H*$_2$), 1.51 (s, 3H, CH$_3$), 1.60 – 1.75 (m, 2H, 2 x C*H*$_2$), 1.78 – 1.93 (m, 2H, 2 x C*H*$_2$), 2.03 (dd, *J* = 13.2 and 4.0 Hz, 1H, CH), 2.26 (s, 1H, CH), 2.54 (br d, *J* = 10.8 Hz, 1H, C*H*$_2$), 3.20 (d, *J* = 16.8 Hz, 1H, C*H*$_2$), 3.29 (d, *J* = 17.2 Hz, 1H, C*H*$_2$), 3.37 (d, *J* = 16.8 Hz, 1H, C*H*$_2$), 3.68 (d, *J* = 17.2 Hz, 1H, C*H*$_2$), 4.14-4.33 (m, 4H, 2 x CH$_2$) 4.70 (s, 5H, Cp).

^{13}C NMR (75 MHz, Chloroform-d) δ 12.4 (CH), 14.2 (CH$_3$), 14.3 (CH$_3$), 17.7 (CH$_3$), 18.9 (CH$_3$), 23.4 (CH$_2$), 25.8 (CH$_2$), 27.1 (CH$_2$), 30.7 (CH$_2$), 41.2 (CH$_2$), 45.1 (CH$_2$), 46.0 (C), 46.9 (C), 52.2 (C), 56.5 (CH), 58.0 (C), 62.3 (CH$_2$), 62.4 (CH$_2$), 86.9 (5 x CH), 102.6 (C), 171.4 (C), 172.4 (C), 179.9 (C), 207.1 (C).

One quaternary carbon is under CDCl$_3$

HRMS (ESI-MS): [M+H]$^+$ calcd for $C_{29}H_{36}O_6Co^+$ 539.1838, found 539.1837

IR (neat): 2924, 1724, 1691, 1627, 1253, 1197, 1099, 1066, 1045, 1008 cm^{-1}

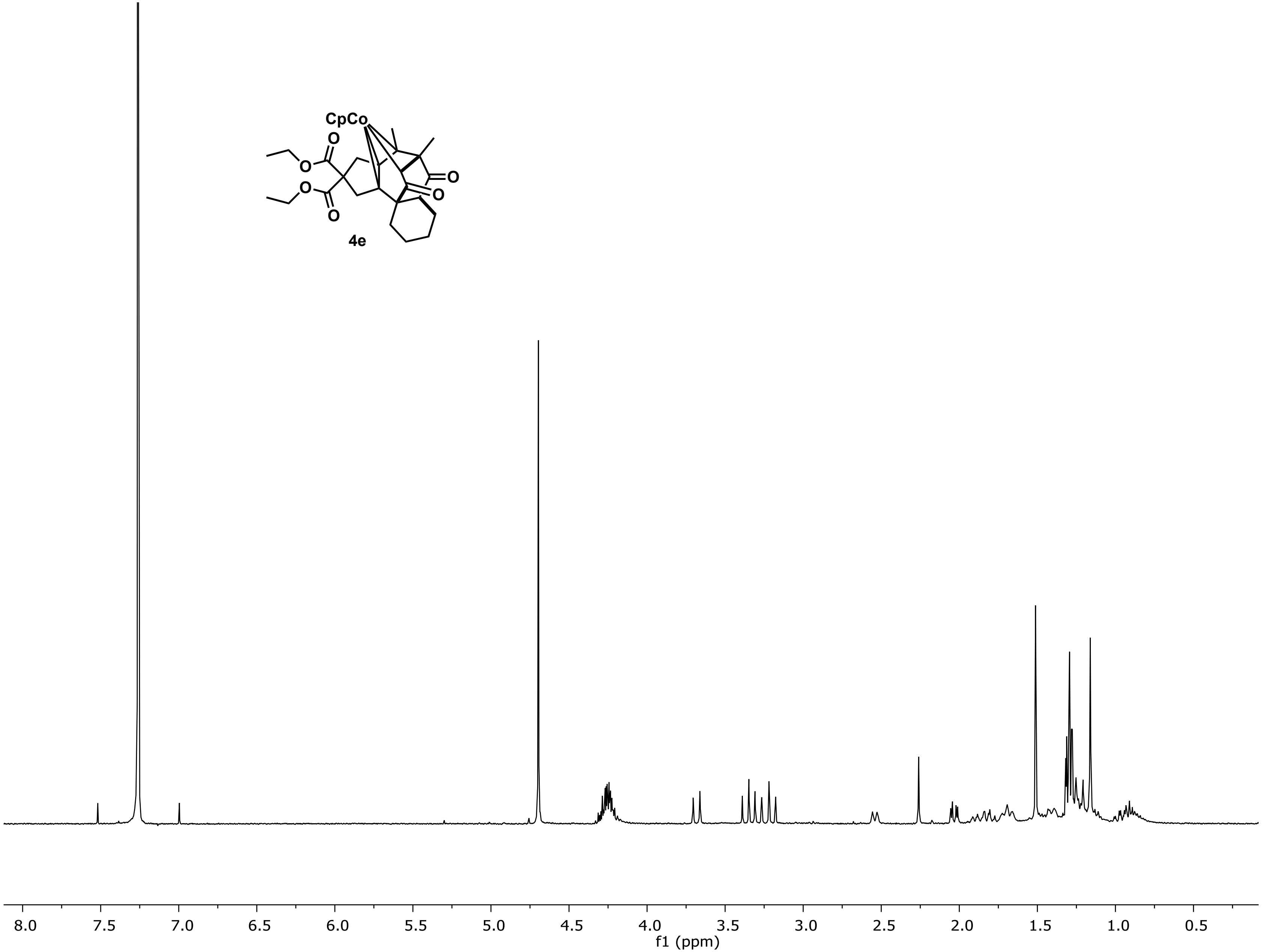


Figure S67. **[1]H NMR (400 MHz, $CDCl_3$) spectrum of 4e**

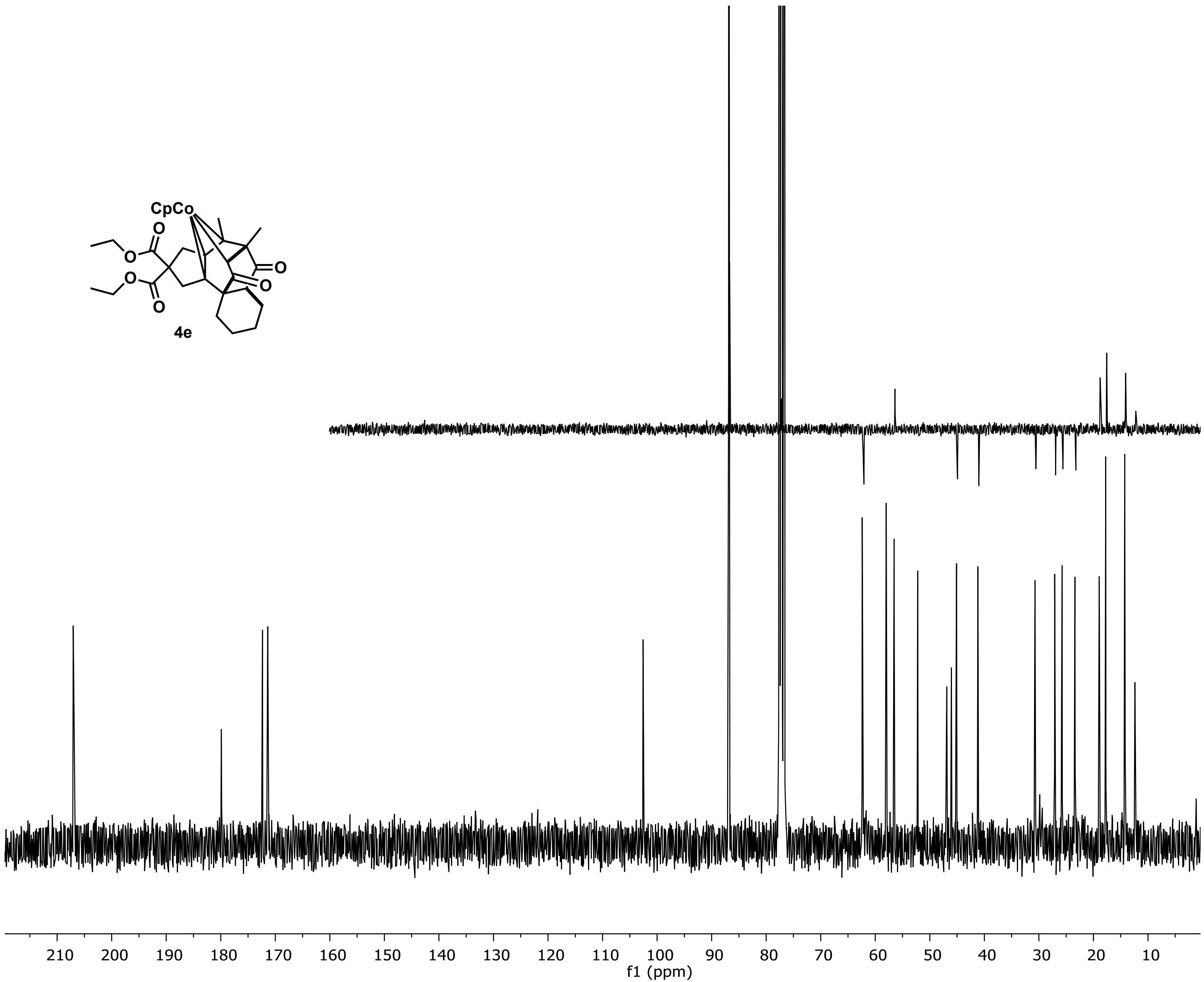
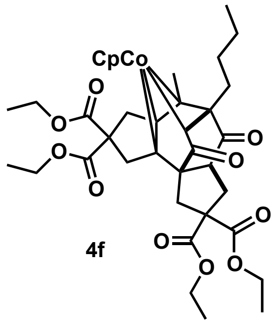


Figure S68. [13]C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 4e



4f

According to the general procedure starting from 30 mg (0.051 mmol) of lactone (**3f**) in toluene (1.2 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 48% (16 mg)

Aspect: orange oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 0.86-0.94 (m, 1H, C*H*$_2$), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3), 1.18 – 1.38 (m, 15H, 4 x CH_3 and CH_2 and C*H*$_2$), 1.40-1.44 (m, 1H, C*H*$_2$), 1.49 (s, 3H, CH_3), 1.86 – 2.05 (m, 3H, CH_2 and C*H*$_2$), 2.38 (s, 1H,CH), 2.44 (dd, *J* = 13.1, 8.3 Hz, 1H, CH), 2.98 (d, *J* = 13.4 Hz, 1H, C*H*$_2$), 3.25 (d, *J* = 13.4 Hz, 1H, C*H*$_2$), 3.26 (d, *J* = 16.6 Hz, 1H, C*H*$_2$), 3.33 (d, *J* = 16.6 Hz, 1H, C*H*$_2$), 3.38 (d, *J* = 17.2 Hz, 1H, C*H*$_2$), 3.57 (d, *J* = 17.2 Hz, 1H, C*H*$_2$), 4.05 – 4.38 (m, 8H, 4 x CH_2), 4.69 (s, 5H, Cp).

^{13}C NMR (75 MHz, Chloroform-d) δ 8.5 (CH), 14.0$_8$ (CH_3), 14.1$_3$ (CH_3), 14.1$_7$ (CH_3), 14.1$_8$ (CH_3), 14.1$_9$ (CH_3), 18.1 (CH_3), 23.7 (CH_2), 26.6 (CH_2), 31.7 (CH_2), 32.8 (CH_2), 35.5 (CH_2), 41.4 (CH_2), 45.5 (CH_2), 47.3 (C), 53.3 (C), 57.7 (C), 58.0 (C), 58.1 (CH), 58.4 (C), 61.8 (CH_2), 62.0 (CH_2), 62.2 (CH_2), 62.6 (CH_2), 72.2 (C), 86.8 (5 x CH), 102.7 (C), 170.8 (C), 171.3 (C), 172.1 (C), 172.3 (C), 179.7 (C), 203.5 (C).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{37}H_{48}O_{10}Co^+$ 711.2574, found 711.2578

IR (neat): 2958, 1732, 1685, 1253, 1190, 1161, 1091 cm^{-1}

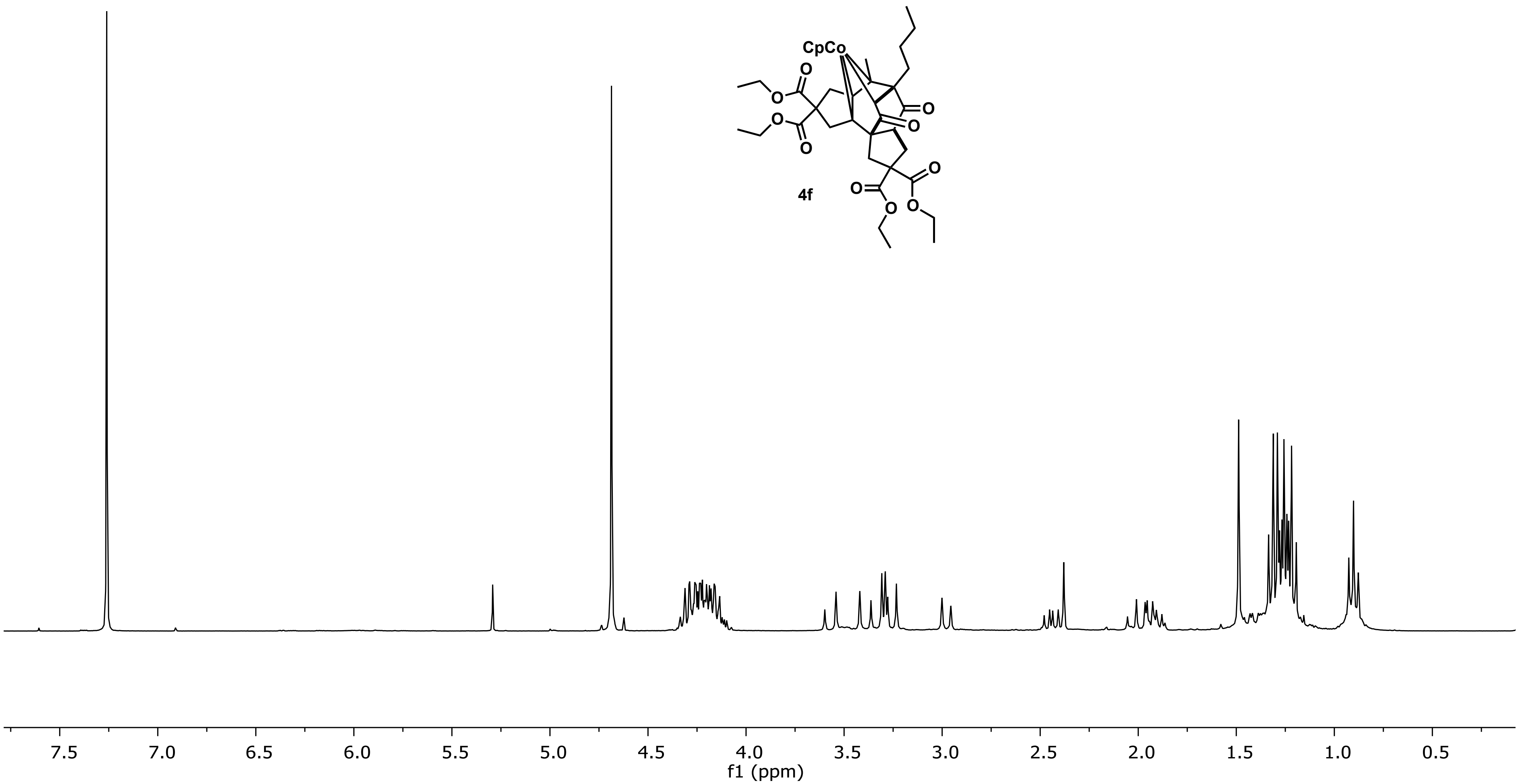


Figure S69. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4f

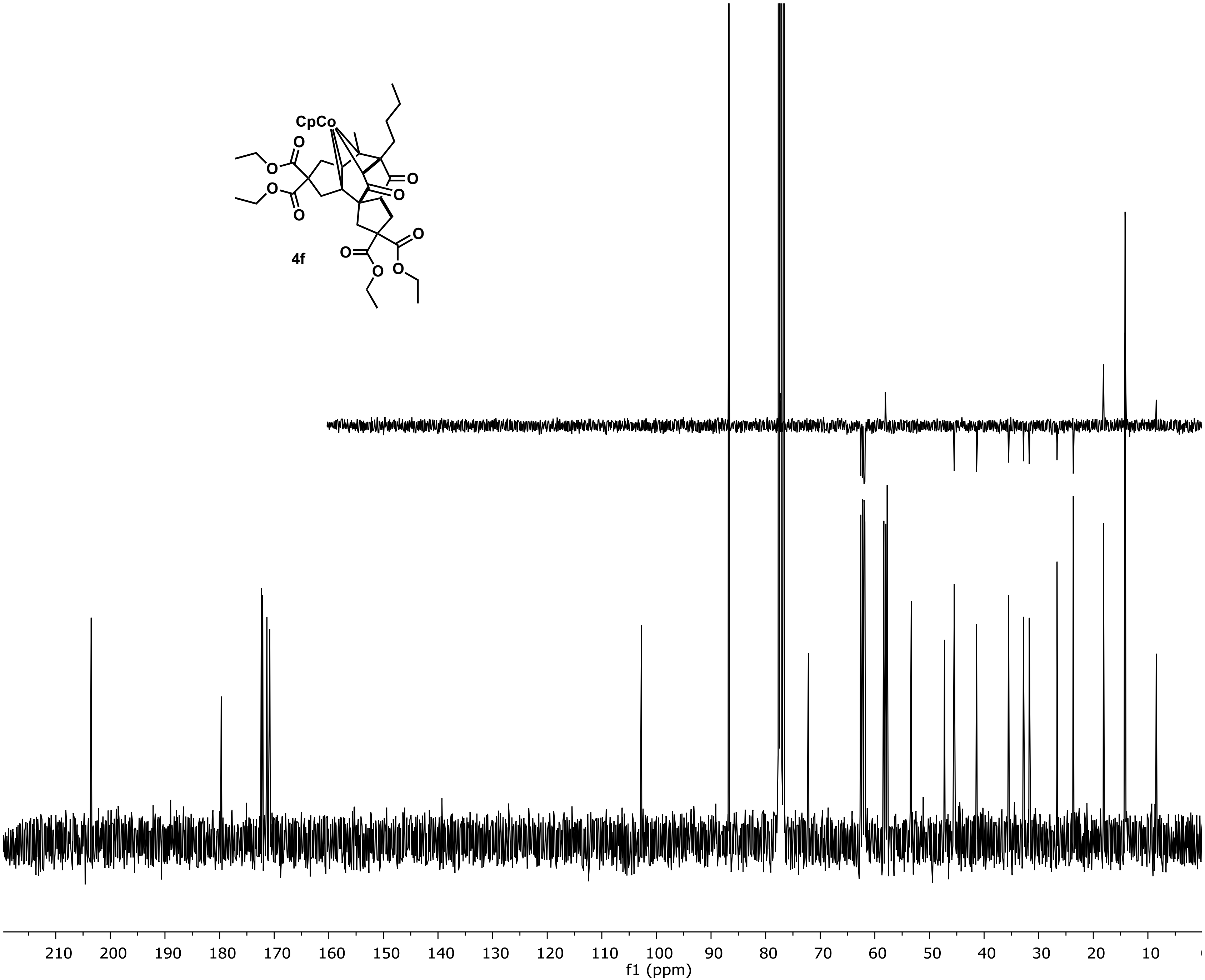
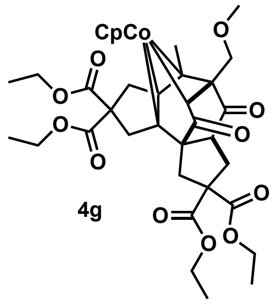


Figure S70. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 4f



4g

According to the general procedure starting from 50 mg (0.087 mmol) of lactone (**3g**) in toluene (2 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 46% (28 mg)

Aspect: orange oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.20 – 1.33 (m, 12H, 4 x CH_3) 1.54 (s, 3H, CH_3), 1.96 – 2.10 (m, 2H, CH_2), 2.42 (dd, J = 12.8, 8.5 Hz, 1H, CH), 2.59 (s, 1H, CH), 3.00 (d, J = 13.5 Hz, 1H, CH_2), 3.23 – 3.30 (m, 2H, 2 x CH_2), 3.36 - 3.47 (m, 3H, 3 x CH_2), 3.43 (s, 3H, CH_3), 3.58 – 3.63 (m, 2H, 2 x CH_2), 4.09 – 4.34 (m, 8H, 4xCH_2), 4.68 (s, 5H, Cp).

^{13}C NMR (101 MHz, Chloroform-d) δ 5.6 (CH), 14.1 (CH_3), 14.1$_8$ (CH_3), 14.1$_9$ (CH_3), 14.2$_1$ (CH_3), 17.8 (CH_3), 33.3 (CH_2), 35.5 (CH_2), 41.3 (CH_2), 44.5 (C), 45.5 (CH_2), 52.6 (C), 57.5 (C), 57.9 (C), 58.2 (C), 58.3 (CH), 59.6 (CH_3), 61.8 (CH_2), 62.0 (CH_2), 62.2 (CH_2), 62.6 (C), 71.7 (CH_2), 71.8 (C), 87.0 (5 x CH), 102.6 (C), 170.8 (C), 171.3 (C), 172.2 (C), 172.4 (C), 180.1 (C), 203.1 (C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{35}H_{44}O_{11}Co^+$ 699.2210, found 699.2208

IR (neat): 2976, 2910, 1734, 1242, 1188, 1101, 1068, 798 cm^{-1}

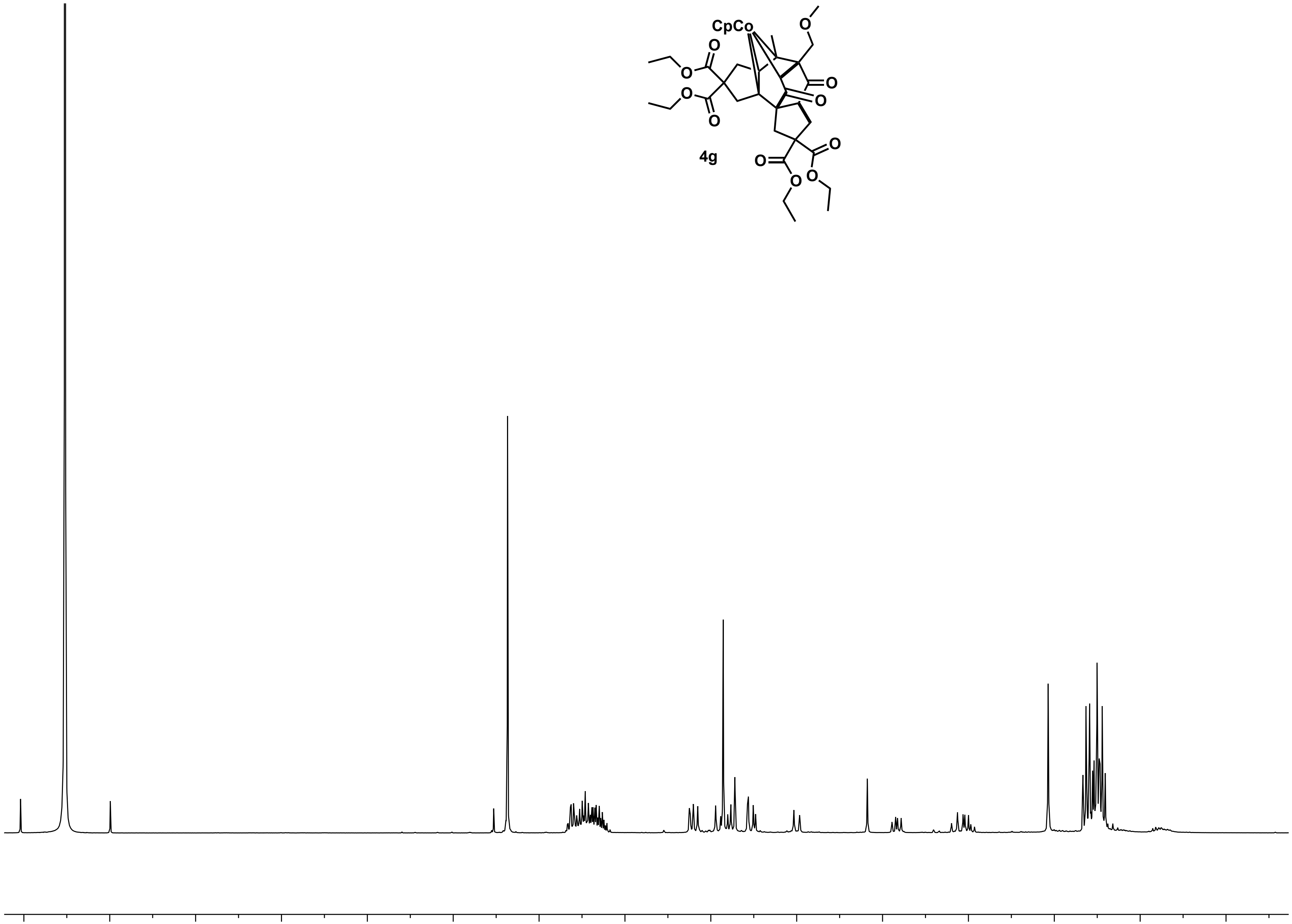


Figure S71. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 4g**

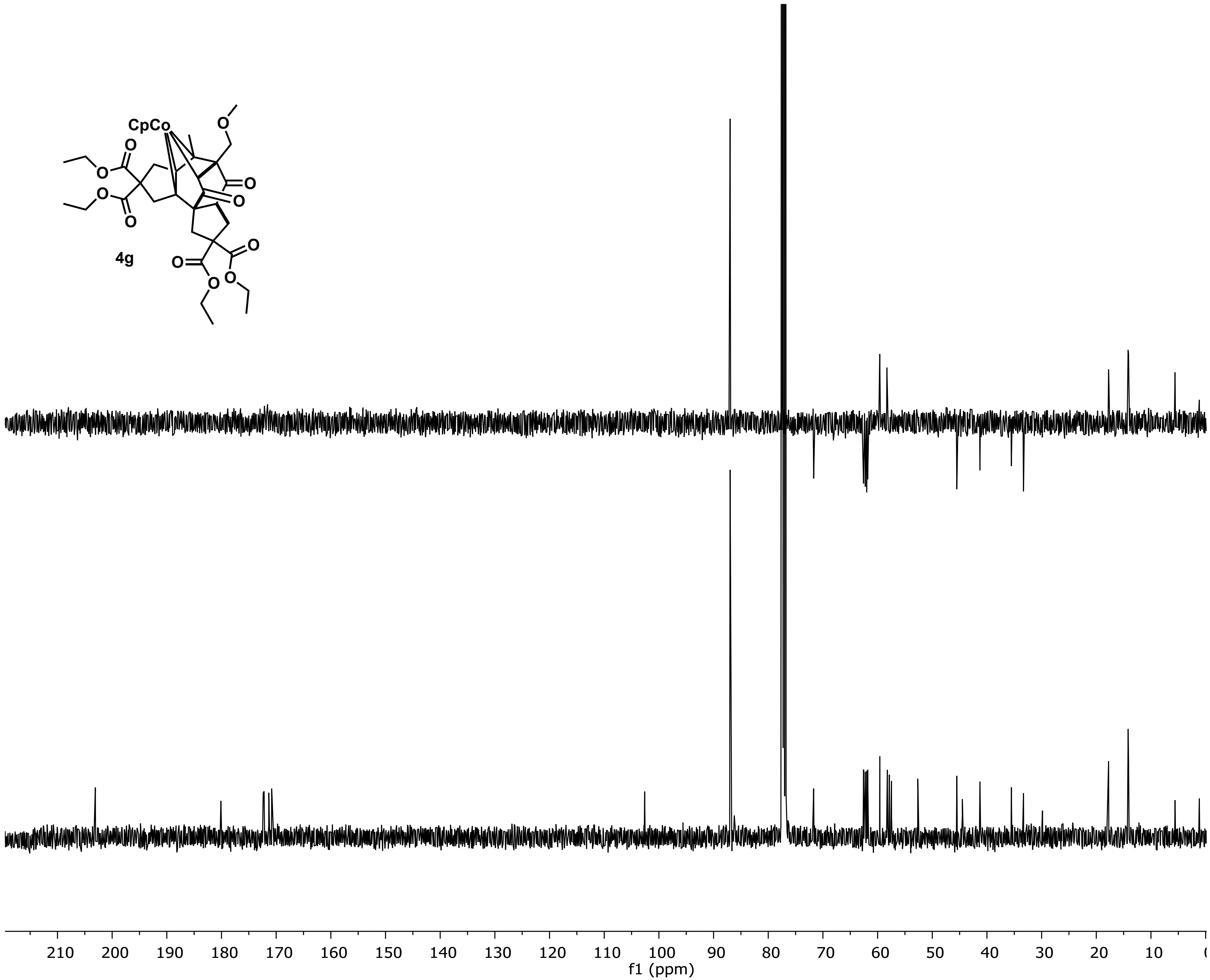
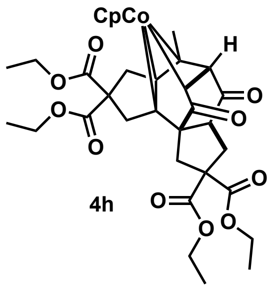


Figure S72. ^{13}**C NMR and DEPT (101 MHz, CDCl$_3$) spectra of 4g**



4h

According to the general procedure starting from 30 mg (0.057 mmol) of lactone (**3h**) in toluene (1.3 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 40% (15 mg)

Aspect: orange oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.22 (t, *J*= 7.1 Hz, 3H, CH_3), 1.25 (t, *J*= 7.1 Hz, 3H, CH_3), 1.30 (t, *J*= 7.1 Hz, 3H, CH_3), 1.32 (t, *J*= 7.1 Hz, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.06 – 2.10 (m, 2H, CH_2), 2.37 (br dd, *J* = 11 and 10 Hz, 1H, CH), 2.53 (d, *J* = 8.6 Hz, 1H, CH), 2.94 (d, *J* = 8.6 Hz, 1H, CH), 3.04 (d, *J* = 13.8 Hz, 1H, CH_2), 3.24 (d, *J* = 16.8 Hz, 1H, CH_2), 3.30 (d, *J* = 13.8 Hz, 1H, CH_2), 3.44 (d, *J* = 16.8 Hz, 1H, CH_2), 3.48 (d, *J* = 17.5 Hz, 1H, CH_2), 3.62 (d, *J* = 17.5 Hz, 1H, CH_2), 4.07 – 4.37 (m, 8H, 4 x CH_2), 4.68 (s, 5H, Cp).

^{13}C NMR (75 MHz, Chloroform-d) δ -0.52 (CH), 14.1 (CH_3), 14.1$_7$ (2 x CH_3), 14.$_{21}$ (CH_3), 23.8 (CH_3), 33.5 (CH_2), 35.7 (CH_2), 40.5 (CH_2), 41.5 (C), 45.5 (CH_2), 52.3 (C), 57.3 (CH,), 58.0 (CH), 58$_{.07}$ (C), 58.0$_9$ (C), 61.8 (CH_2), 61.9 (CH_2), 62.3 (CH_2), 62.6 (CH_2), 72.5 (C), 86.6 (5 x CH), 102.3 (C), 170.8 (C), 171.3 (C), 172.2 (C), 172.3 (C), 178.7 (C), 203.5 (C).

HRMS (ESI+): $[M+H]^+$ calcd for $C_{33}H_{40}O_{10}Co^+$ 655.1948, found 655.1952

IR (neat): 2975, 1728, 1703, 1635, 1257, 1184, 1157, 1095 cm^{-1}

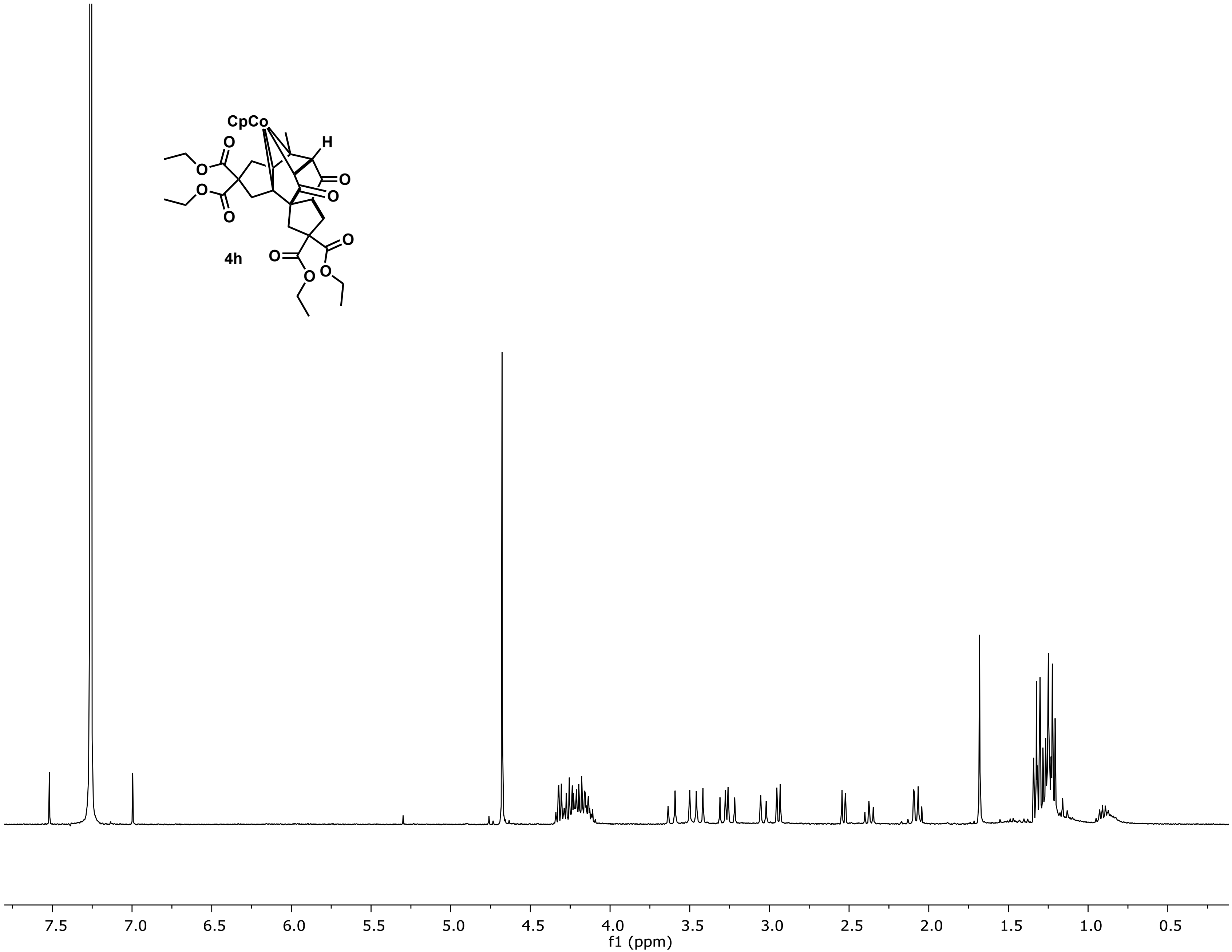


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4h

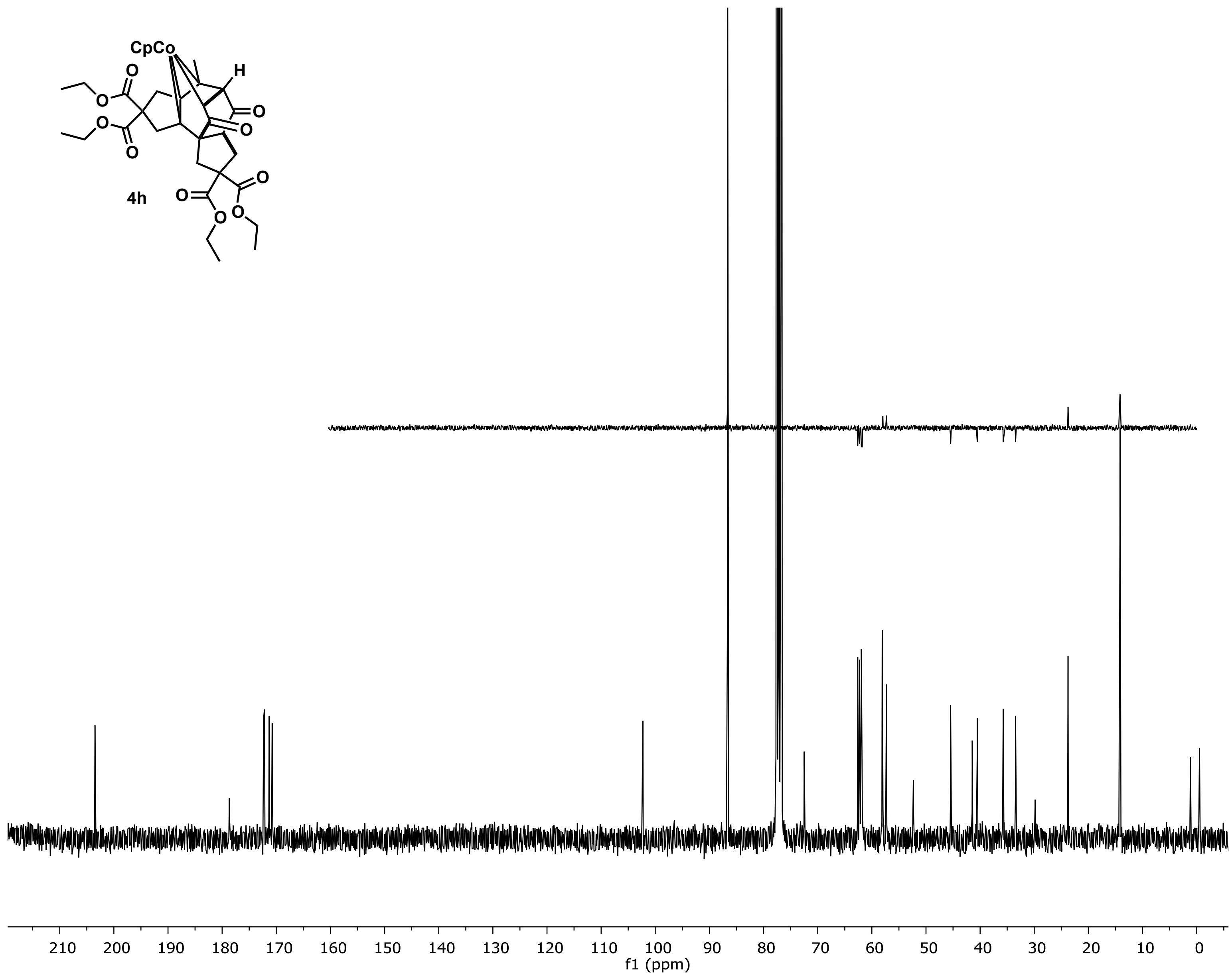
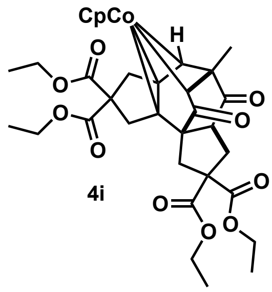


Figure S74. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 4h



4i

According to the general procedure starting from 20 mg (0.037 mmol) of lactone (**3i**) in toluene (0.9 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 43% (10.7 mg)

Aspect: orange oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.20 – 1.33 (m, 15H, 5 x CH_3) 1.99 – 2.17 (m, 3H, CH_2 and CH), 2.39 (br dd, J = 12.9, 8.0 Hz, 1H, CH), 3.00 – 3.04 (m, 2H, 2 x CH_2), 3.30 (d, J = 13.9 Hz, 1H, CH_2), 3.47 – 3.59 (m, 4H, CH_2 and CH_2 and CH), 4.09 – 4.33 (m, 8H, 4 x CH_2), 4.78 (s, 5H, Cp).

^{13}C NMR (101 MHz, Chloroform-d) δ 9.7 (CH), 14.1_1 (CH_3), 14.1_8 (2 x CH_3), 14.2 (CH_3), 20.8 (CH_3), 33.7_6 (CH_2), 33.7_9 (CH), 35.5 (CH_2), 41.5 (CH_2), 45.4 (CH_2), 50.3 (C), 53.0 (C), 58.0 (CH), 58.1 (C), 58.2 (C), 61.8 (CH_2), 62.0 (CH_2), 62.3 (CH_2), 62.6 (CH_2), 86.0 (5 x CH), 103.9 (C), 170.8 (C), 171.3 (C), 172.1 (C), 172.3 (C), 178.1 (C), 204.7 (C).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{33}H_{40}O_{10}Co^+$ 655.1948, found 655.1953

IR (neat): 2962, 1720, 1257, 1189, 1157, 1103 cm^{-1}

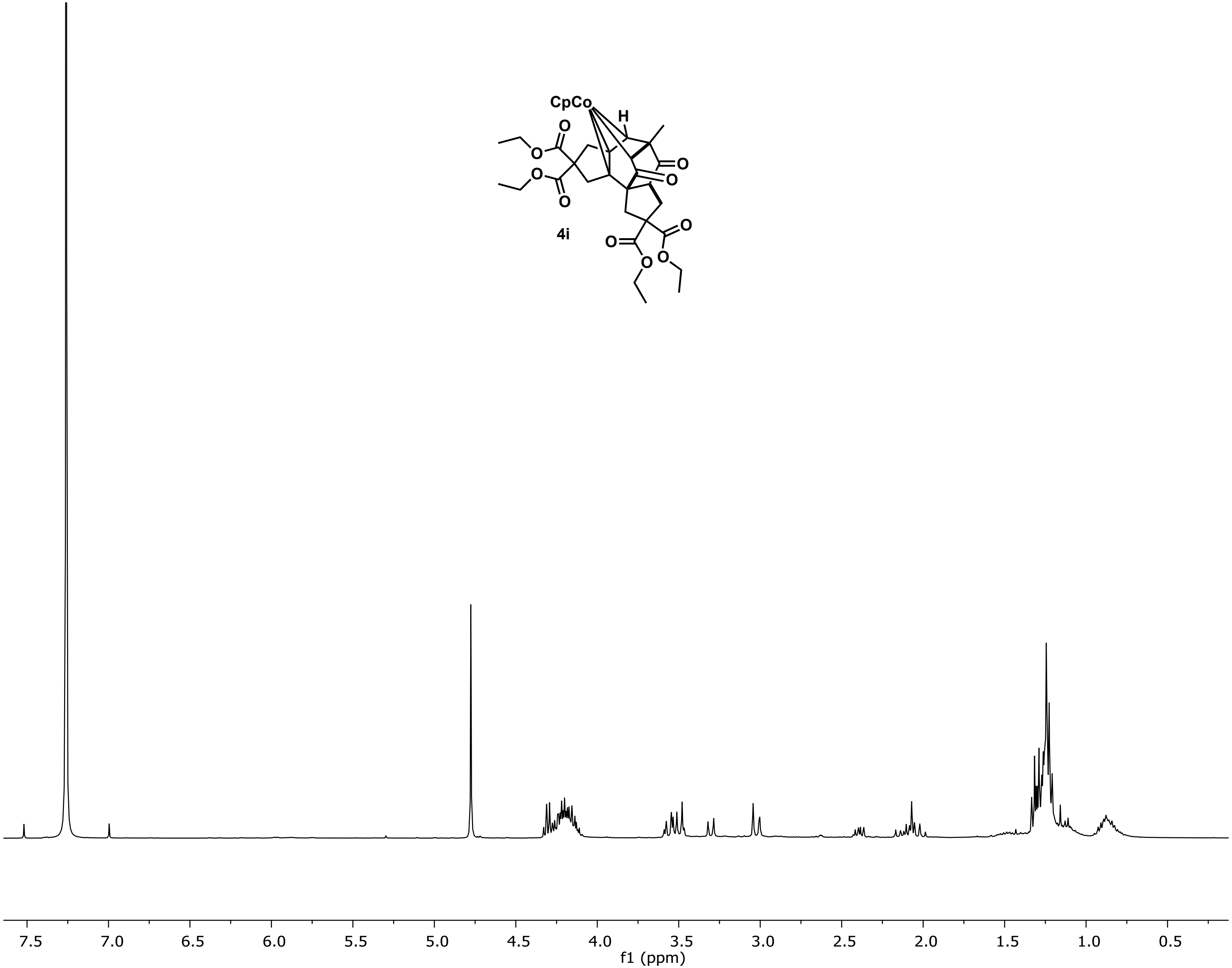


Figure S75. ^{1}H **NMR (400 MHz,** $CDCl_3$**) spectrum of 4i**

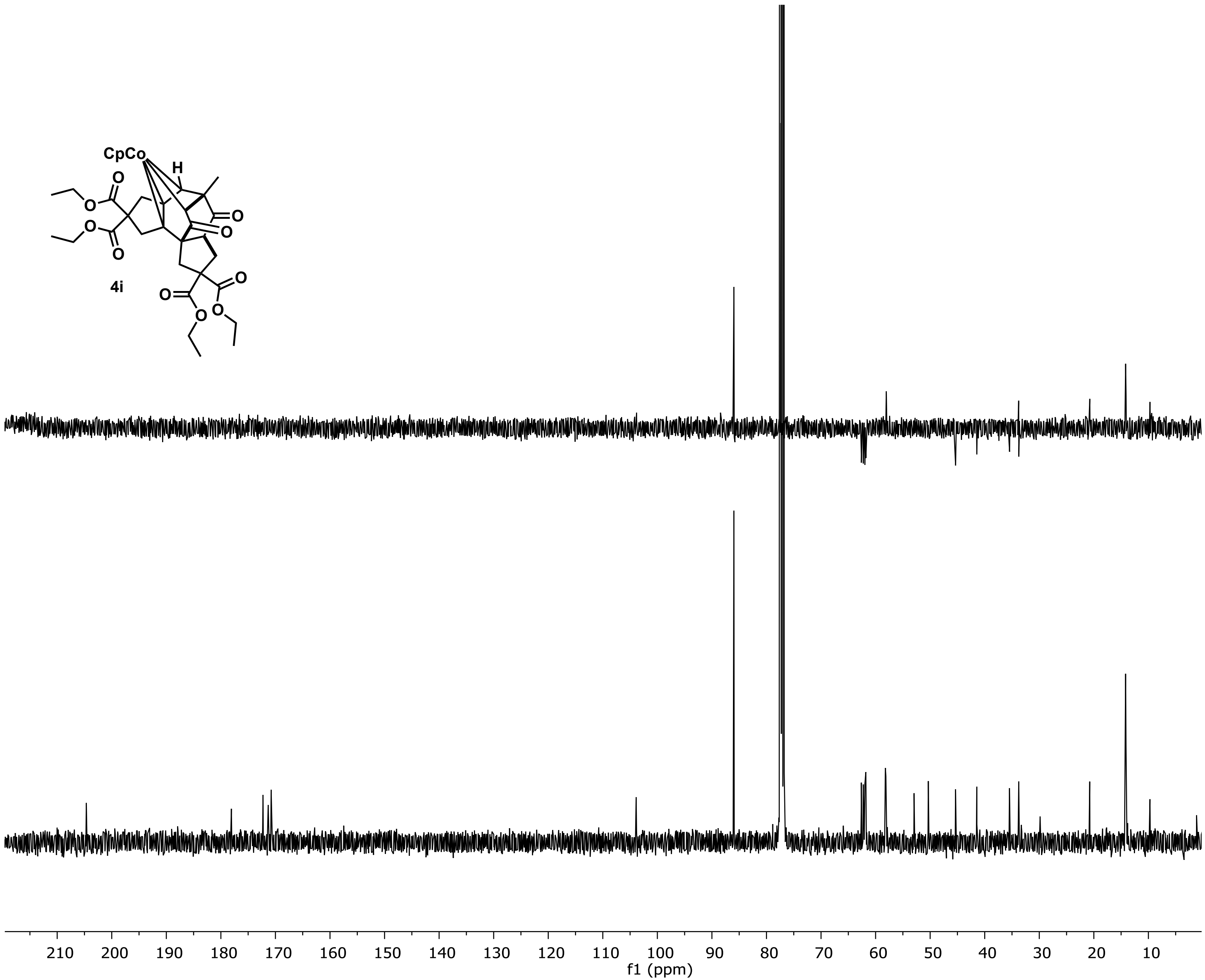
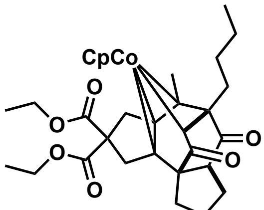


Figure S76. ^{13}C NMR and DEPT (101 MHz, $CDCl_3$) spectra of 4i



4j

According to the general procedure starting from 20 mg (0.05 mmol) of lactone (**3j**) in toluene (1.2 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 67% (19 mg)

Aspect: orange oil

^{1}H NMR (400 MHz, Chloroform-d) δ 0.89 (t, *J*= 7.3 Hz, 3H, CH_3), 1.09 – 1.31 (m, 9H, 2 x CH_3 and CH_2 and C*H*$_2$), 1.34-1.47 (m, 3H, CH_2 and C*H*$_2$), 1.49 (s, 3H, CH_3), 1.58 – 1.79 (m, 3H, CH_2 and C*H*$_2$), 1.85 – 2.07 (m, 2H, 2x *CH*$_2$), 2.29 (br dd, *J* = 12.4, 8.4 Hz, 1H, CH), 2.38 (s, 1H, CH), 2.62-2.68 (m, 1H, C*H*$_2$), 3.21 (d, *J* = 16.9 Hz, 1H, C*H*$_2$), 3.29 (d, *J* = 17.1 Hz, 1H, C*H*$_2$), 3.39 (d, *J* = 16.9 Hz, 1H, C*H*$_2$), 3.51 (d, *J* = 17.2 Hz, 1H, C*H*$_2$), 4.13 – 4.37 (m, 4H, 2 x CH_2), 4.69 (s, 5H, Cp).

^{13}C NMR (101 MHz, Chloroform-d) δ 9.4 (CH), 14.1$_9$ (CH_3), 14.2$_2$ (2 x CH_3), 18.1 (CH_3), 21.7 (CH_2), 23.7 (CH_2), 24.5 (CH_2), 26.7 (CH_2), 28.4 (CH_2), 31.7 (CH_2), 41.3 (CH_2), 45.7 (CH_2), 47.0 (C), 53.7 (C), 58.3 (C), 58.5(C), 59.8 (CH), 62.3 (CH_2), 62.4 (CH_2), 72.8 (C), 86.7 (5 x CH), 102.8 (C), 171.4 (C), 172.5 (C), 181.0 (C), 205.7 (C).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{31}H_{40}O_6Co^+$ 567.2151, found 567.2151

IR (neat): 2954, 2925, 1722, 1697, 1243, 1178, 1093, 1072, 1053, 1006 cm^{-1}

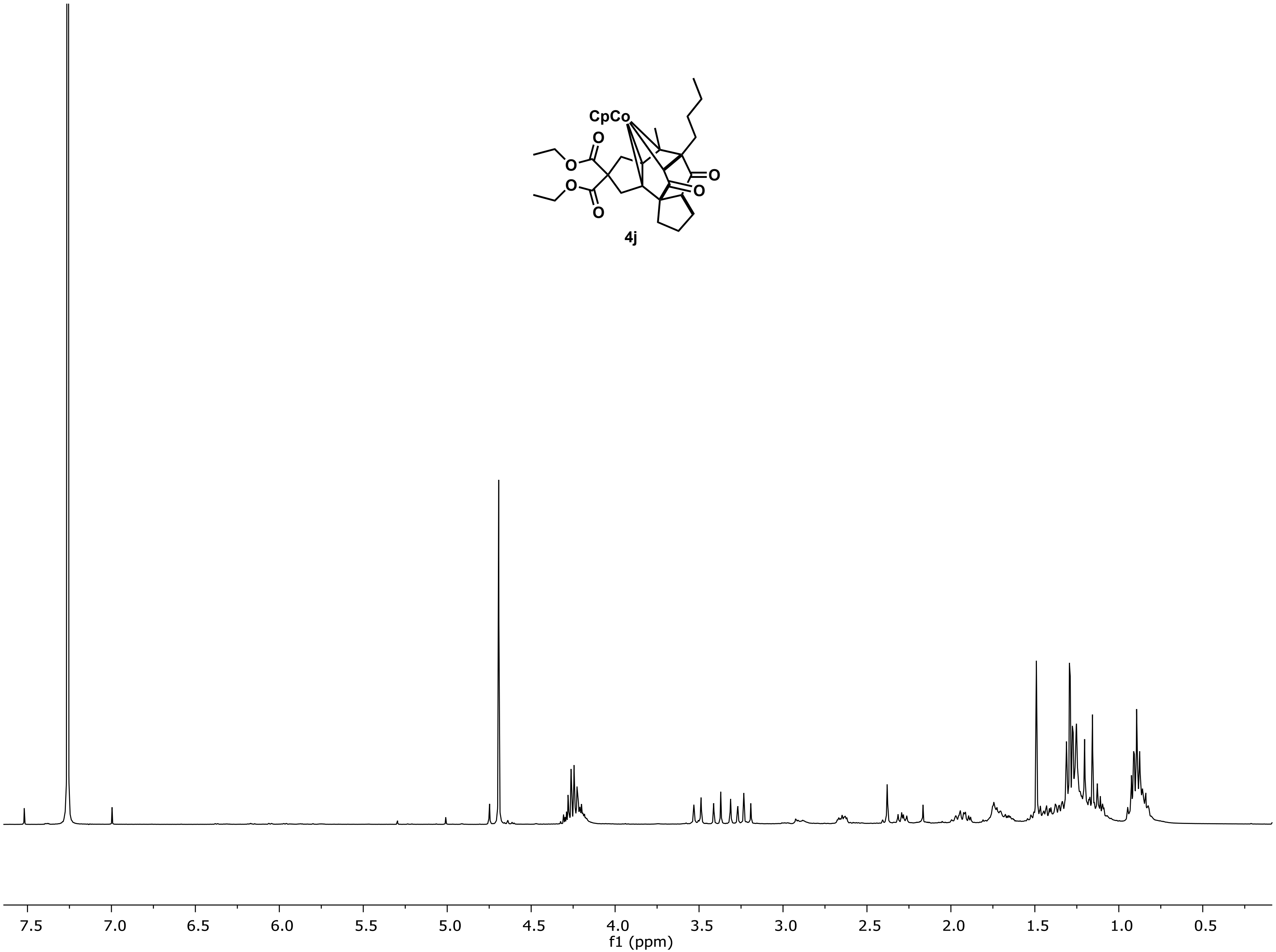
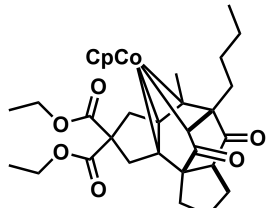


Figure S77. [1]**H NMR (400 MHz, CDCl₃) spectrum of 4j**



4j

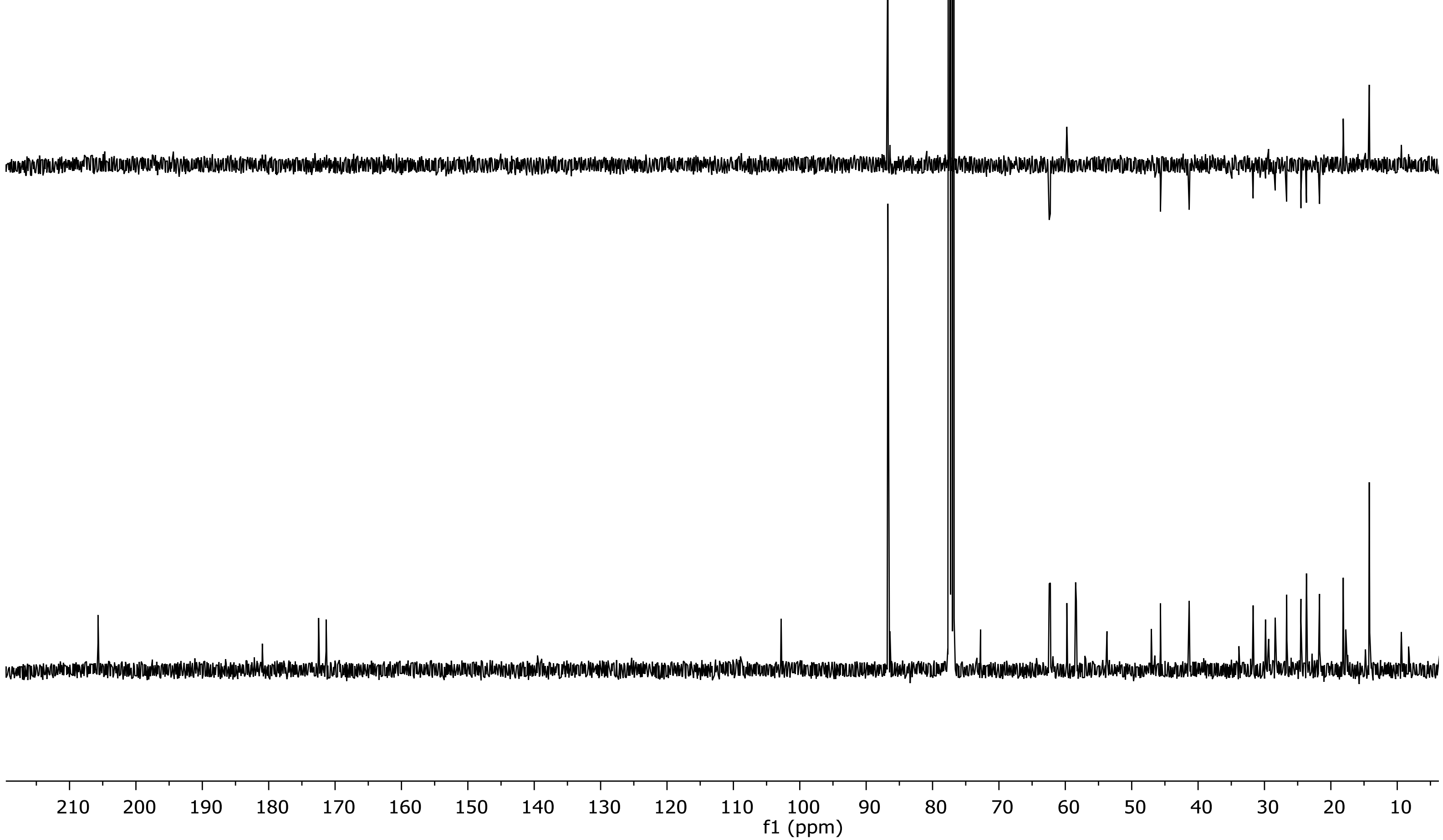
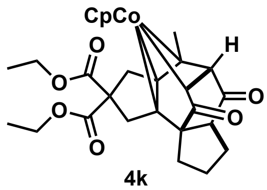


Figure S78. ^{13}C NMR and DEPT (101 MHz, CDCl$_3$) spectra of 4j



4k

According to the general procedure starting from 10 mg (0.025 mmol) of lactone (**3k**) in toluene (0.6 mL). The product was purified by flash chromatography (PE/AcOEt 7:3 to 1:1).

Yield: 39% (5 mg)

Aspect: orange oil

^{1}H NMR (400 MHz, Chloroform-d) 1.13 – 1.28 (m, 4H, 2 x C*H*$_2$ and CH$_2$), 1.30 (t, *J*= 7.1 Hz, 3H, CH$_3$), 1.31 (t, *J*= 7.1 Hz, 3H, CH$_3$), 1.68 (s, 3H, CH$_3$), 1.68 – 1.77 (m, 1H, C*H*$_2$), 2.15 – 2.27 (m, 1H, CH), 2.52 (d, *J*= 8.5 Hz, 1H, CH), 2.62-2.76 (m, 1H, C*H*$_2$), 2.93 (d, *J*= 8.5 Hz, 1H, CH), 3.28 (d, *J*= 16.5 Hz, 1H, C*H*$_2$), 3.35 (d, *J*= 17.5 Hz, 1H, C*H*$_2$), 3.41 (d, *J*= 16.5 Hz, 1H, C*H*$_2$), 3.51 (d, *J*= 17.5 Hz, 1H, C*H*$_2$), 4.22-4.31 (m, 4H, 2 x CH$_2$), 4.69 (s, 5H, Cp)

^{13}C NMR (75 MHz, Chloroform-d) δ 1.16 (CH), 14.2 (2 x CH$_3$), 22.6 (CH$_2$), 23.8 (CH$_3$), 25.4 (CH$_2$), 29.5 (CH$_2$), 40.4 (CH$_2$) , 41.3 (C), 45.7 (CH$_2$, C2 or C17), 52.7 (C, C12) 57.8 (CH, C14), 58.4 (C, C1), 59.5 (CH, C9), 62.3 (CH$_2$, C19 or C 21), 62.5 (CH$_2$, C19 or C 21), 72.9 (C, C15), 86.7 (5 x CH), 102.5 (C, C3), 171.3 (C, C17 or C18), 172.6 (C, C17 or C18), 180.4 (C, C13), 205.8 (C, C7).

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{27}H_{32}O_6Co^+$ 511.1525, found 511.1525

IR (neat): 2960, 2931, 1728, 1247, 1192, 1107, 1066 cm^{-1}

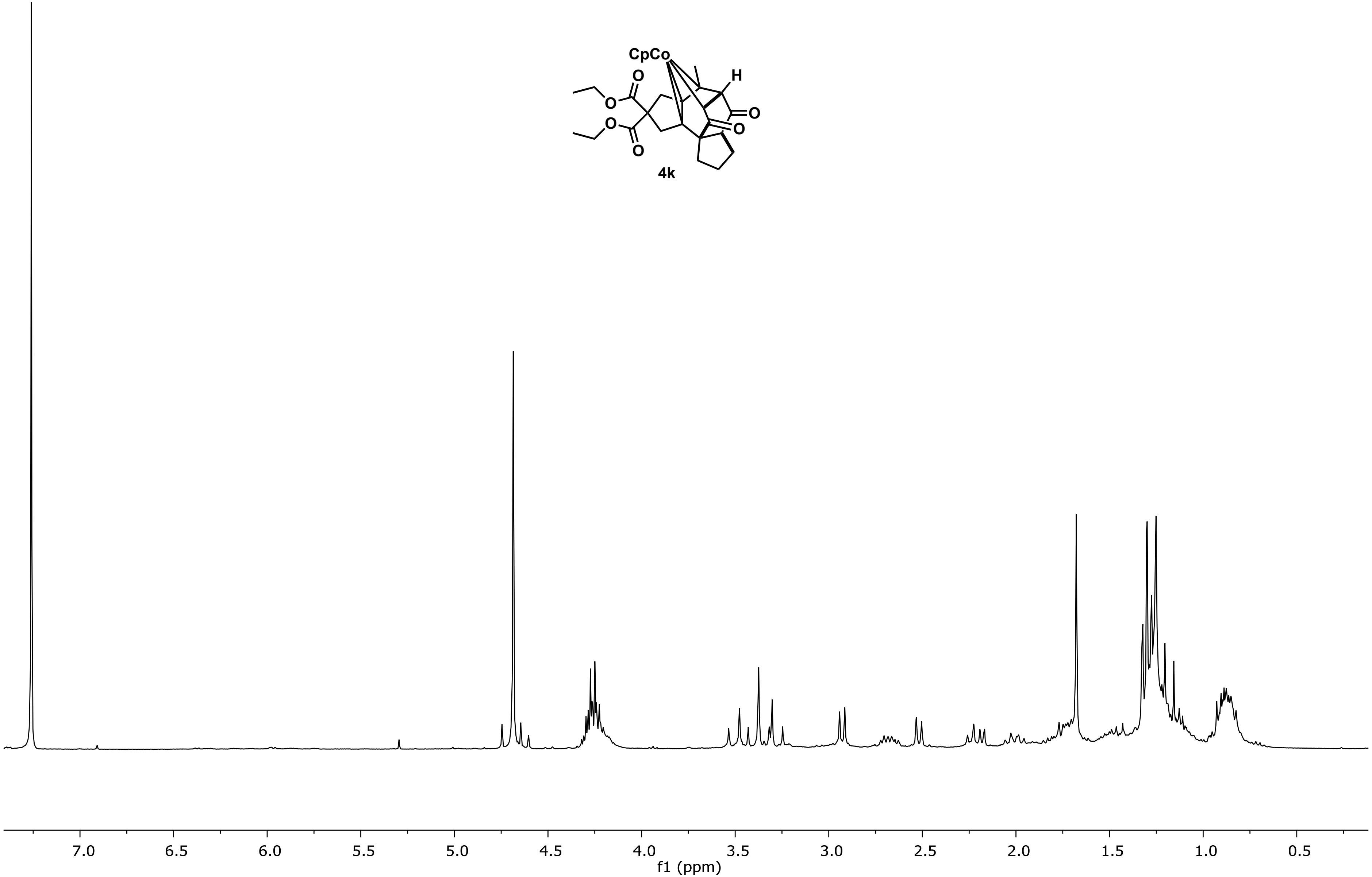


Figure S79. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 4k**

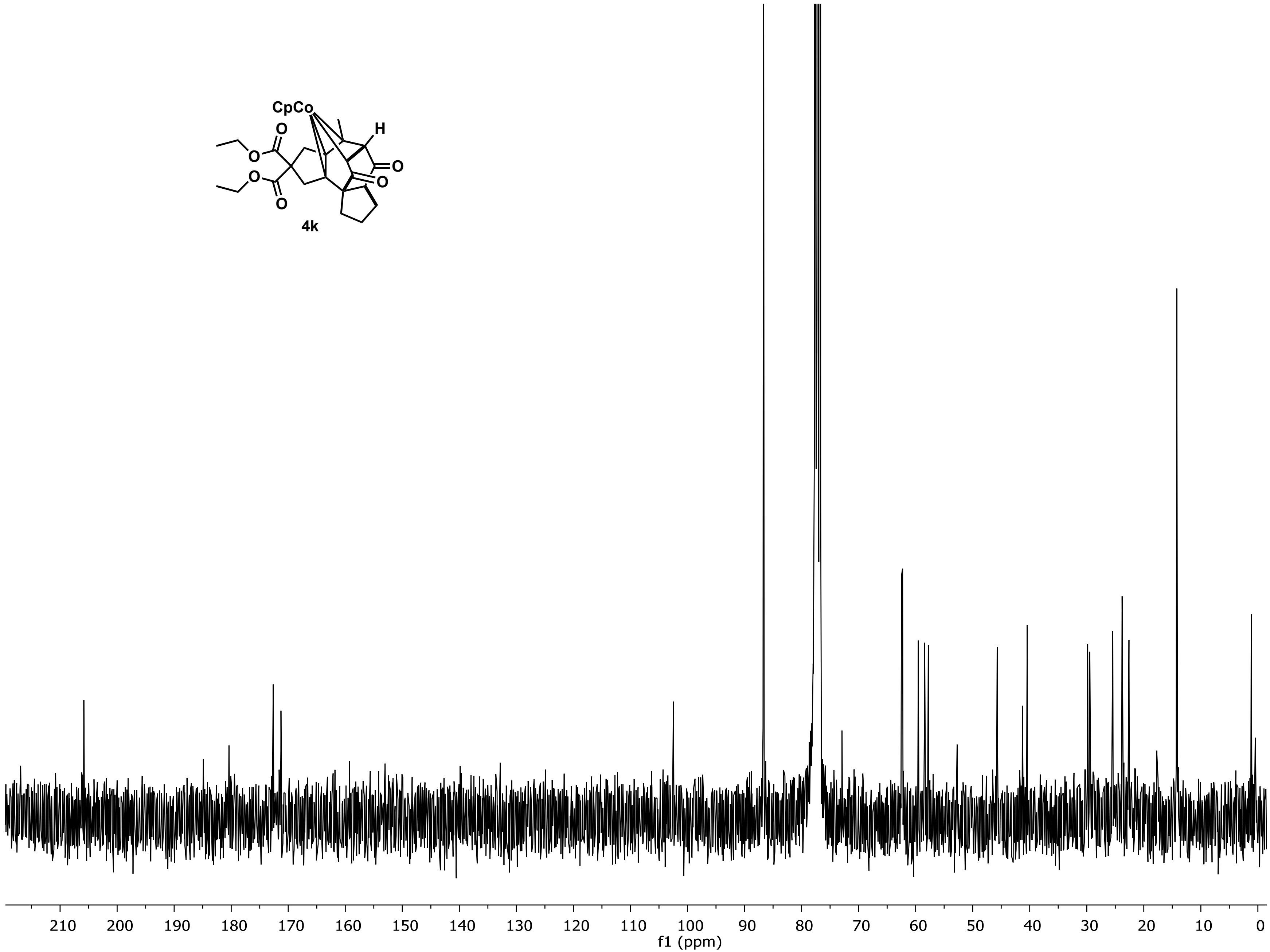


Figure S80. ^{13}C **NMR (75 MHz,** $CDCl_3$**) spectrum of 4k**

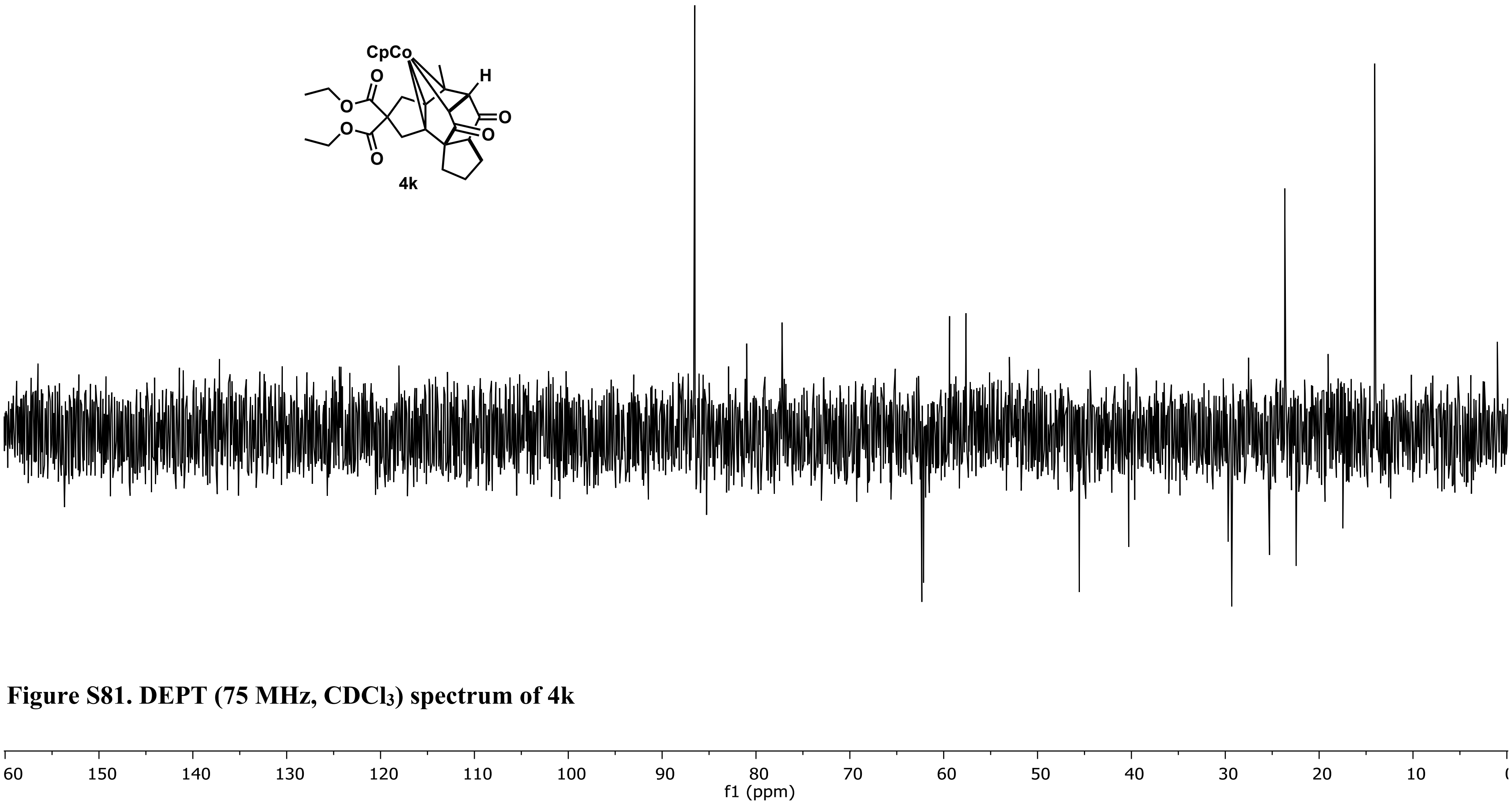
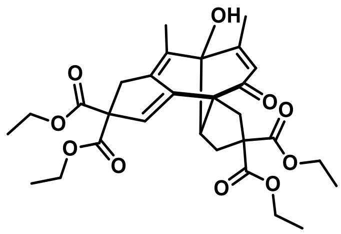


Figure S81. DEPT (75 MHz, $CDCl_3$) spectrum of 4k

General procedure for the synthesis of 6

Hydrogen chloride solution (4.0 M in dioxane) was added dropwise at room temperature to a solution of cobalt complex in dioxane (0.30 mol/L). The mixture was then stirred 2 to 4 hours at 80 °C. The solvent was removed under *vacuo,* the crude was purified by flash chromatography on silica gel (PE/EtOAc 8:2 to 6:4)



6a

According to the general procedure starting from 27 mg (0.040 mmol) of **4a** in dioxane 1.3 ml.

Yield: 55 % (12 mg)

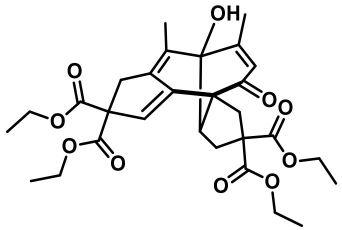
Aspect: white pale oil

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.19-1.28 (m, 12H, 4 x CH_3), 1.90 (br s, 3H, CH_3), 2.06 (br d, J = 1.4 Hz, 3H, CH_3), 2.31 – 2.43 (m, 2H, CH_2), 2.44 (d, J = 13.8 Hz, 1H, CH_2), 2.57 (dd, J = 11.6 and 7.8 Hz, 1H, CH), 3.02 (s, 2H, CH_2), 3.47 (d, J = 13.8 Hz, 1H, CH_2), 4.13 – 4.24 (m, 8H, 4x CH_2), 5.65 (br d, J = 1.4 Hz, 1H), 5.88 (br s, 1H).

^{13}C NMR (75 MHz, Chloroform-d) δ 13.5 (CH_3), 13.9 (4 x CH_3), 19.7 (CH_3), 33.9 (CH_2), 35.0 (CH_2), 38.8 (CH_2), 56.5 (CH), 57.6 (C), 58.9 (C), 61.8$_3$ (CH_2), 61.8$_4$ (CH_2), 61.8$_6$ (CH_2), 61.8$_9$ (CH_2), 65.0 (C), 76.2 (C), 122.5 (CH), 127.4 (CH), 133.6 (C), 137.1 (C), 143.3 (C), 164.0 (C), 169.8 (C), 170.4 (C), 171.2 (C), 172.3 (C), 194.2 (C).

HRMS (ESI-MS): $[M+Na]^+$ calcd for $C_{29}H_{36}O_{10}Na^+$ 567.2201, found 567.2215

IR (nujol): 2953, 2927, 2841, 1730, 1664, 1201, 1180, 1047, 997, 869 cm^{-1}



6a

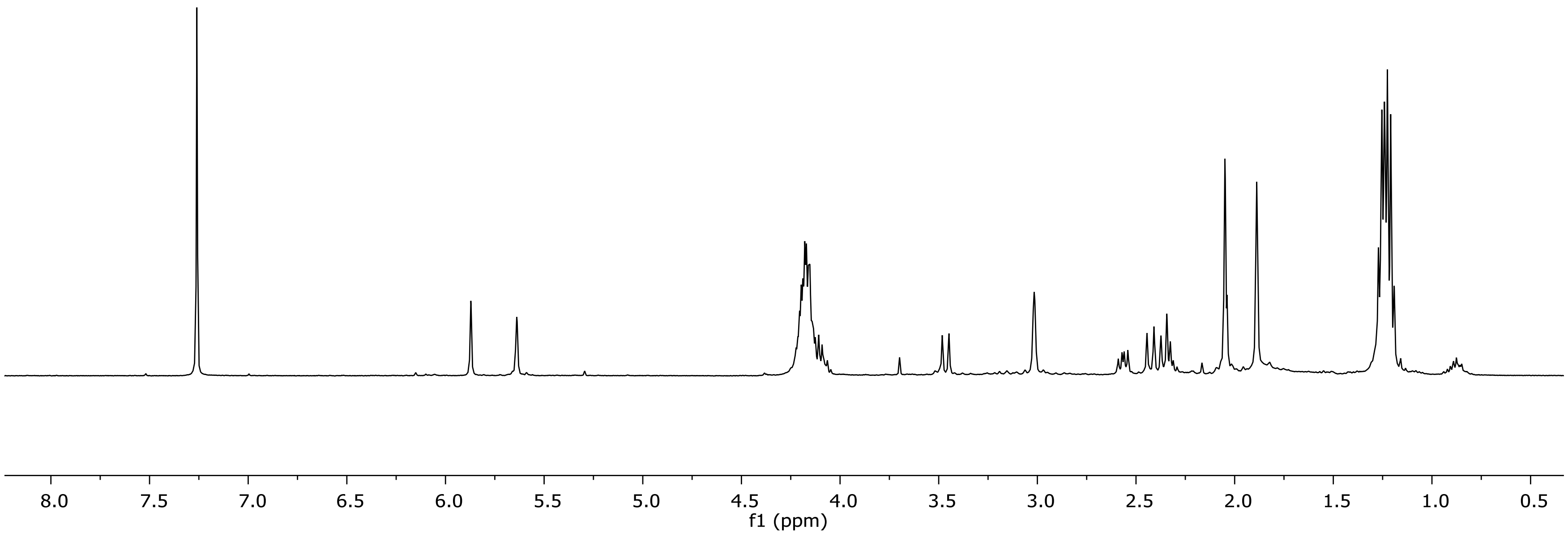
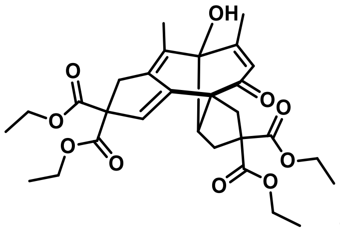


Figure S82. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 6a



6a

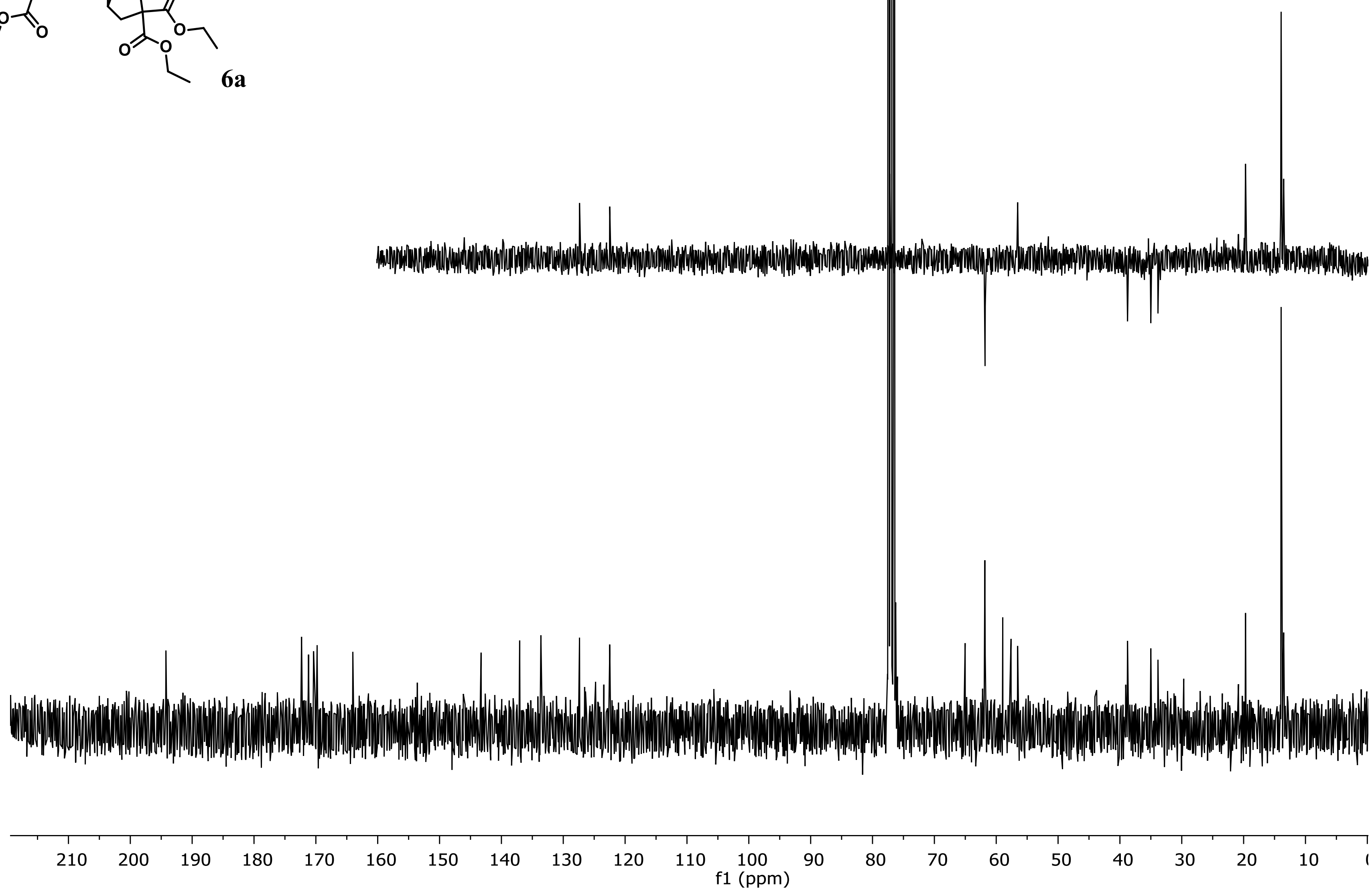
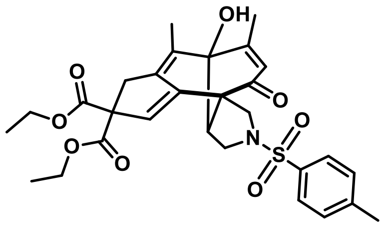


Figure S83. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 6a



6b

According to the general procedure starting from 30 mg (0.044 mmol) of **4b** in dioxane 1.5 ml

Yield: 53% (13 mg)

Aspect: white solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.21 (t, *J*= 7.1Hz, 3H, CH_3), 1.25 (t, *J*=7.1 Hz, 3H, CH_3), 1.86 (br s, 3H, CH_3), 2.01 (br s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.75 (dd, *J* = 11.1 and 7.6 Hz, 1H, CH), 2.97 (d, *J* = 17.3 Hz, 1H, C*H_2*) 3.03 (d, *J* = 17.3 Hz, 1H, C*H_2*), 3.12 (br dd, 1H, *J* = 11.1 and 9.5 Hz,C*H_2*), 3.25 (d, *J* = 9.3 Hz, 1H, C*H_2*), 3.67 (br dd, *J* = 9.50 and 7.6 Hz, 1H, C*H_2*), 4.05 -4.22 (m, 4H, 2 x CH_2), 4.41 (d, *J* = 9.3 Hz, 1H, C*H_2*), 5.49 (br s, 1H,CH), 5.81 (br s, 1H, CH), 7.30 (d, *J* = 8.1 Hz, 2H, 2 x CH), 7.68 (d, *J* = 8.1 Hz, 2H, 2 x CH).

^{13}C NMR (75 MHz, Chloroform-d) δ 13.6 (CH_3) , 14.0$_8$ (CH_3), 14.1$_3$ (CH_3), 19.8 (CH_3), 21.7 (CH_3), 35.0 (CH_2), 47.7 (CH_2), 52.3 (CH_2), 55.6 (CH), 56.5 (C), 62.2 (2 x CH_3), 65.3 (C), 75.2 (C), 122.4 (CH), 127.5 (2 x CH), 128.0 (CH), 129.8 (2 x CH), 133.7 (C), 134.6 (C), 137.2 (C), 140.2 (C), 143.7 (C), 164.8 (C), 169.6 (C), 170.3 (C), 191.9 (C)

HRMS (ESI-MS): $[M+H]^+$ calcd for $C_{29}H_{34}NO_8S^+$ 556.2000 , found 556.2001

IR (nujol): 2983, 2922, 2360,1739, 1683, 1338, 1257, 1155, 1087, 1041, 661 cm^{-1}

Mp: 195 °C

RX: the product was crystallized from EtOAc

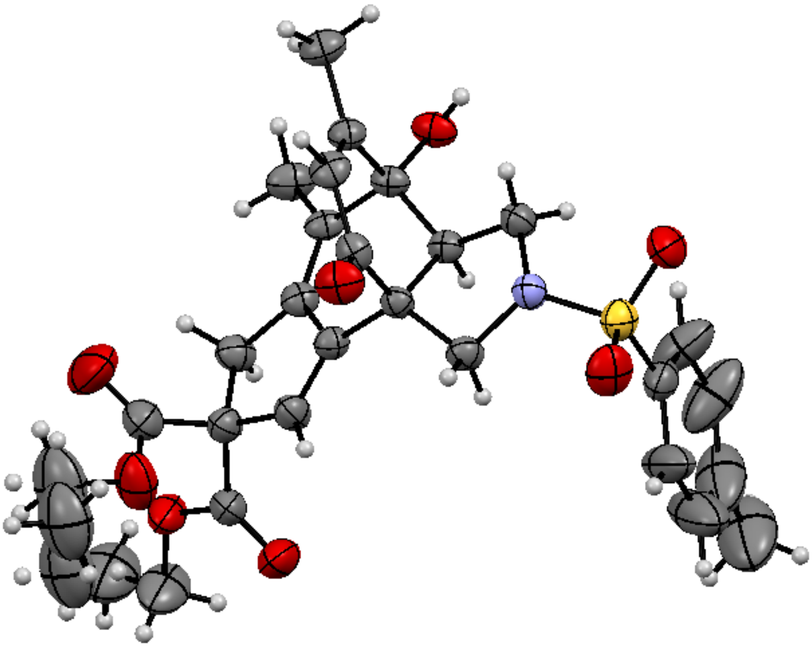
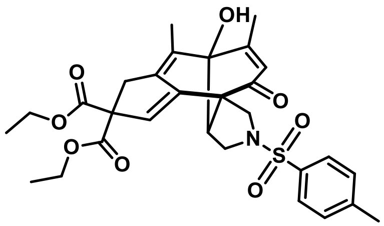


Figure S84. Crystallographically-derived molecular structure of polycyclic cobalt(III) complex 6b



6b

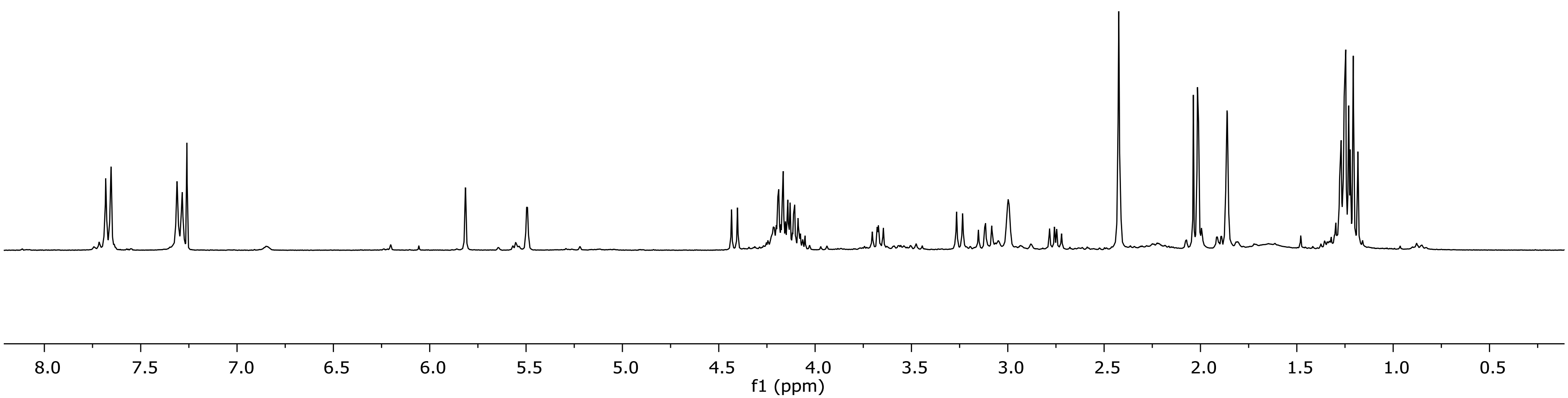
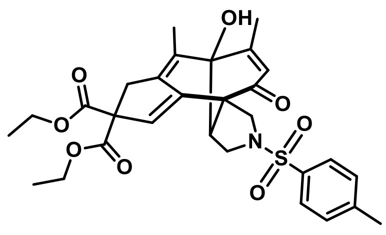


Figure S85. ^{1}**H NMR (400 MHz,** $CDCl_3$**) spectrum of 6b**



6b

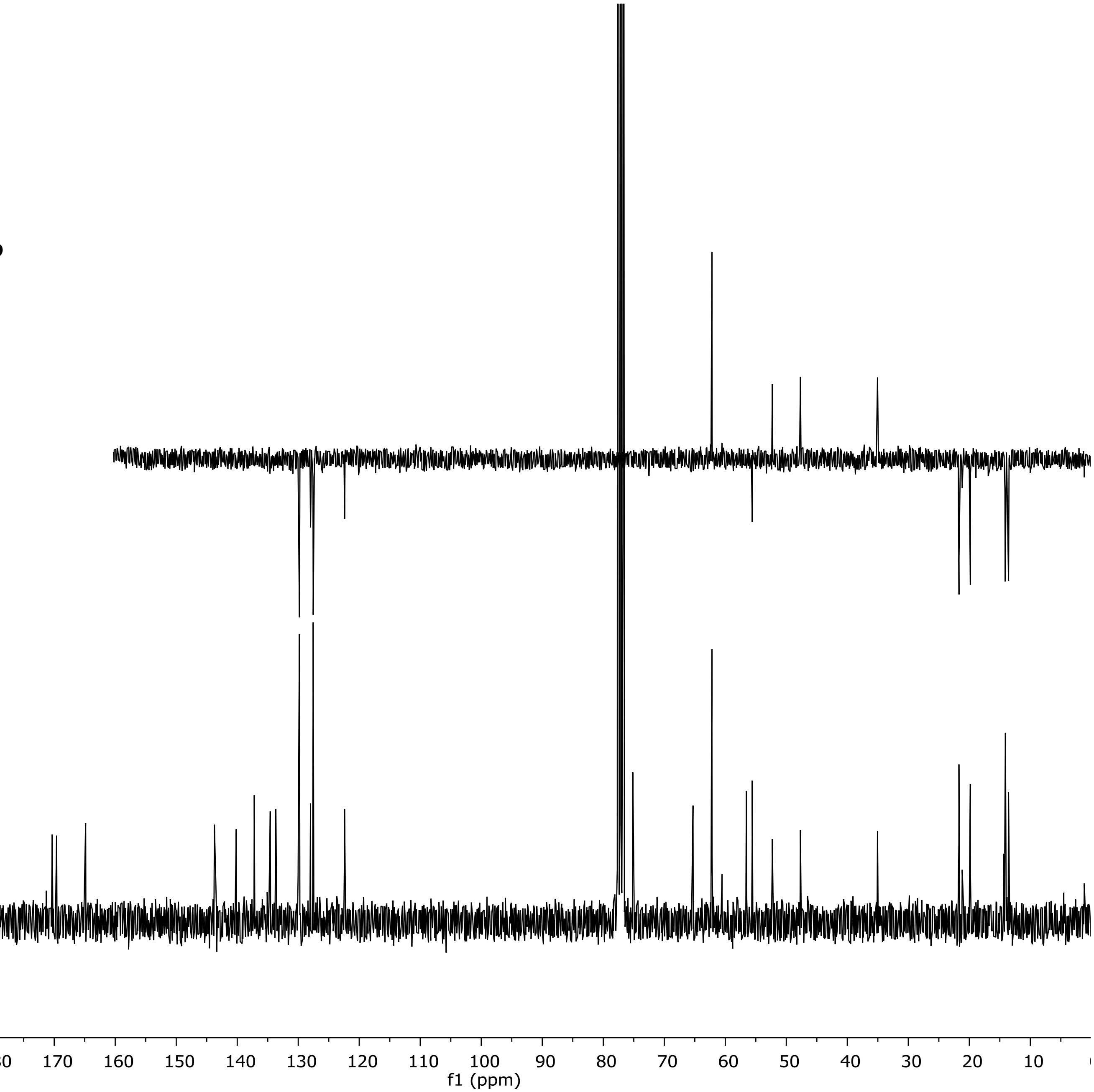


Figure S86. ^{13}C NMR and DEPT (75 MHz, $CDCl_3$) spectra of 6b

Computational Study

Optimizations were performed at the BP86-D3 level, using the def2-TZVP basis set and the appropriate auxiliary basis sets for the RI approximation technique, as indicated in the main article. Zero point energies and thermal correction to the Gibbs' free energy were obtained at the optimization level. Final electronic energies are obtained by single point calculations with the COSMO solvent model (epsilon=2.38). Energies and coordinates of the optimized structures are reported hereafter.

Table S2 : Energies of the computed structures, as described in the Computational Section.

	Energy (a.u.)	**ZPE (a.u)**	**Chemical Potential (kJ/mol)**	**Energy (a.u.) SP COSMO**	**Δ G (kcal/mol)**
I	-2843.281163735	0.4821988	985.35	-2843.2919086189	
Ts_{I-II}	-2843.270856817	0.4816156	985.45	-2843.2824526672	6.0
II	-2843.33191416	0.485638	1016.53	-2843.3424478641	-24.2
Ts_{II-III}	-2843.324780492	0.4851364	1017.12	-2843.3359426206	-20.0
III	-2843.335134364	0.4854242	1006.05	-2843.3470804314	-29.7
Ts_{III-IV}	-2843.306166354	0.4841015	1014.26	-2843.3192673257	-10.2
$Ts_{III-P1'}$	-2843.302812367	0.4833277	1006.47	-2843.3141543408	-8.9
IV	-2843.360470505	0.4875037	1028.1	-2843.3700802235	-38.8
Ts_{IV-V}	-2843.347268642	0.4867963	1027.99	-2843.3567943063	-30.5
V	-2843.352531304	0.4878563	1029.18	-2843.3621816225	-33.6
Ts_{V-P4}	-2843.338971129	0.4870875	1031.76	-2843.3490419955	-24.7
P4	-2843.390469693	0.4893769	1033.16	-2843.4022784728	-57.8
P1'	-2843.404862381	0.4889888	1031.66	-2843.4162201101	-66.9
Ts_{II-IV}	-2843.289760012	0.4832832	1020.07	-2843.3029562057	1.4

List of the coordinates

I
62
Energy = -2843.281163735

C	-0.1588178	-1.2689705	4.2306390
O	-1.3792800	-1.2337419	3.5083672
C	-1.7028017	0.0970957	3.2836706
C	-0.6918150	0.9449981	3.9015293
C	0.2281208	0.1232261	4.4687233
C	-2.7734143	0.4678955	2.5566326
C	-3.7078080	-0.4367766	1.8210009
C	-3.2574518	-0.5639590	0.3426629
C	-2.0729924	-1.5412162	0.1909724
C	-1.1896586	-1.2310941	-0.9395735
Co	0.3027010	-2.1615848	-1.8280339
C	-0.1448179	-2.8282665	-3.7996440
C	-0.9431748	-3.5053825	-2.8173452
C	-0.0754786	-4.2134847	-1.9279575
C	1.2629276	-3.9373367	-2.3483545
C	1.2179372	-3.0953111	-3.5098896
C	-0.7124581	2.4334058	3.8352718
O	0.3661691	-2.3194023	4.5158655
C	-0.6843484	-0.4349842	-1.7865734
C	-0.3419298	0.8872140	-2.3279606
C	1.0236277	1.3909562	-1.7492534
C	2.1403427	0.3255284	-1.9652762
C	1.7566196	-0.9272360	-1.3000554
C	1.5751339	-1.7385279	-0.3454961
C	1.8184717	-2.3268883	0.9787000
H	2.2574521	0.1826193	-3.0487315
H	3.0904617	0.7159224	-1.5731049
H	-1.1196666	1.6231671	-2.0706423
H	-0.2384631	0.8548971	-3.4238437
H	2.1679843	-4.2801110	-1.8548835
H	-0.3745734	-4.8315713	-1.0878823
H	-2.0262078	-3.4589866	-2.7462761
H	2.0786930	-2.7042633	-4.0437273
H	-0.5218107	-2.1943858	-4.5962203
H	-2.4384660	-2.5792218	0.1303634
H	-1.4456359	-1.5122577	1.0970118
H	-4.1006545	-0.8990458	-0.2800563
H	-2.9561311	0.4267833	-0.0293211
H	-4.7255470	-0.0186327	1.8598618
H	-3.7380023	-1.4321434	2.2884277
H	-2.8980195	1.5423911	2.4084127
H	1.1286375	0.3934685	5.0122215
H	-0.6899949	2.7544117	2.7824245
H	-1.6318985	2.8351953	4.2860502
H	0.1485682	2.8666471	4.3583263
H	2.0931201	-3.3893872	0.8948497

H	2.6249066	-1.8017039	1.5153455
H	0.9095158	-2.2881972	1.5975576
C	1.3947741	2.6602264	-2.5235336
C	0.8694727	1.7072233	-0.2510607
O	1.9598571	2.6673851	-3.5978123
O	-0.1760884	1.8252906	0.3554448
O	2.0917623	1.8599358	0.3171119
O	0.9598680	3.7776683	-1.8897374
C	1.2202491	5.0193610	-2.5875020
H	0.8092352	5.8042822	-1.9454005
H	2.2999514	5.1571996	-2.7316503
H	0.7256656	5.0178639	-3.5677378
C	2.0891560	2.1455606	1.7299631
H	1.5602890	1.3546562	2.2782363
H	3.1429455	2.1807188	2.0239475
H	1.6027903	3.1108764	1.9249452

II
62
Energy = -2843.331914160

C	1.2567422	1.9903155	-1.0743009
C	-1.2036910	2.1110263	-1.1330116
C	-0.7702378	0.6637666	-1.0526399
C	0.6790080	0.5902228	-1.0477846
C	-1.4366425	-0.4972159	-0.9063334
C	1.2384881	-0.6339495	-0.9401809
H	1.5284339	2.2988646	-2.0979664
H	2.1333313	2.1279924	-0.4294718
H	-2.1085172	2.3568179	-0.5640397
H	-1.3662127	2.4403571	-2.1717172
Co	-0.1410952	-2.0273523	-0.8307568
C	0.9098554	-3.5127137	-1.9170564
H	1.9379942	-3.7908560	-1.7107907
C	-0.2560405	-4.1507480	-1.3921724
H	-0.2573933	-4.9683138	-0.6813575
C	-1.4005130	-3.4782916	-1.8744299
H	-2.4310155	-3.7117716	-1.6289328
C	0.4744339	-2.4492567	-2.7711942
H	1.1017744	-1.7801944	-3.3490963
C	-0.9534064	-2.4118983	-2.7235005
H	-1.5801544	-1.7059198	-3.2572933
C	-2.9038275	-0.6910396	-0.7046876
H	-3.4474834	0.2216233	-1.0035146
H	-3.2833011	-1.5040793	-1.3455937
C	-3.2224528	-1.0229123	0.7690499
H	-4.2700325	-1.3421184	0.8794065
H	-3.0997554	-0.1035912	1.3657321
C	-2.2693737	-2.0914650	1.3179800
H	-2.4318797	-2.2139347	2.4035905
H	-2.4566684	-3.0729330	0.8613357
C	-0.8384641	-1.6810833	1.0815233

H	-0.6055323	-0.6487694	1.3611373
C	0.2654798	-2.5498482	1.2230904
C	1.5622286	-2.2198263	1.8289904
O	0.0541733	-3.9261834	1.3975039
C	2.1439816	-3.3899441	2.2018069
C	1.2344987	-4.4956517	1.9232070
H	3.1036248	-3.5297538	2.6906072
C	2.0269258	-0.8369318	2.1335200
H	1.7314554	-0.1129788	1.3661007
H	1.5570668	-0.5006333	3.0715127
H	3.1144544	-0.8047968	2.2736307
C	2.7037098	-0.9296565	-0.9957814
H	3.0073048	-1.2688309	-2.0007375
H	3.3039832	-0.0346447	-0.7603782
H	2.9929981	-1.7296564	-0.2994096
O	1.3265898	-5.6937755	2.0772644
C	0.0523862	2.8573073	-0.5866516
C	0.1657734	4.2852541	-1.1120359
O	-0.4500811	4.7493107	-2.0485909
O	1.1158221	4.9655104	-0.4183143
C	0.0040370	2.8555905	0.9463211
O	0.7366866	2.2321442	1.6872826
O	-1.0202105	3.6326065	1.3837344
C	1.3446443	6.3235914	-0.8607359
H	2.1237256	6.7174085	-0.2007317
H	1.6780586	6.3352332	-1.9069725
H	0.4232303	6.9145350	-0.7729246
C	-1.1725264	3.6944700	2.8198406
H	-0.2592011	4.0885600	3.2850877
H	-2.0190698	4.3656270	2.9946847
H	-1.3781208	2.6953848	3.2271468

III
62
Energy = -2843.335134364

C	1.5392384	2.0620664	0.0066863
C	-0.6348419	1.6487643	-1.1294281
C	-0.2435047	0.4251563	-0.3397021
C	1.1838484	0.5893445	-0.0246801
C	-1.0681592	-0.5455298	0.2135450
C	1.8349001	-0.5693752	-0.2263654
H	2.3188988	2.3058174	-0.7318705
H	1.8705733	2.4227225	0.9893437
H	-1.7068123	1.8716093	-1.1536931
H	-0.2656261	1.6102494	-2.1643207
Co	0.3578333	-1.6149478	-0.9559412
C	1.5004662	-2.5626193	-2.4013061
H	2.5350903	-2.8546744	-2.2535048
C	0.3542878	-3.3619293	-2.1048301
H	0.3727666	-4.3491052	-1.6540644
C	-0.8126557	-2.6173066	-2.4350258

H	-1.8346587	-2.9423601	-2.2761575
C	1.0351801	-1.3169469	-2.9520028
H	1.6532538	-0.4766447	-3.2520523
C	-0.3840709	-1.3540547	-2.9535626
H	-1.0370721	-0.5381352	-3.2497575
C	-2.5696857	-0.6185428	0.0996185
H	-3.0081680	0.1982572	-0.4888675
H	-2.8640760	-1.5712806	-0.3660421
C	-2.9907632	-0.6217020	1.5859496
H	-4.0213506	-0.9716807	1.7334523
H	-2.9250992	0.4044256	1.9817822
C	-1.9465074	-1.5274500	2.2810669
H	-1.7715121	-1.2329859	3.3238159
H	-2.2846496	-2.5713654	2.2762223
C	-0.6580870	-1.3842376	1.4228340
H	0.1563995	-0.8814922	1.9607719
C	-0.1026274	-2.6422073	0.7788464
C	0.9472189	-3.4490152	1.4107112
O	-1.1418992	-3.5629539	0.4272470
C	0.6045797	-4.7615989	1.3102359
C	-0.7088519	-4.8696966	0.6869851
H	1.1659587	-5.6275442	1.6500964
C	2.1220713	-2.8773975	2.1349274
H	2.2604340	-1.8157995	1.9053581
H	1.9645644	-2.9699670	3.2207627
H	3.0483497	-3.4173304	1.8947246
C	3.3068554	-0.7882260	-0.3177685
H	3.6432144	-0.6274700	-1.3570380
H	3.8657402	-0.0859615	0.3225441
H	3.5985094	-1.8122313	-0.0481951
O	-1.3927972	-5.8294579	0.3871403
C	0.1839043	2.7482489	-0.3783008
C	0.4440139	3.9629227	-1.2639221
O	0.3749735	3.9782249	-2.4755677
O	0.8320490	5.0211917	-0.5106176
C	-0.5841123	3.1478163	0.8913929
O	-0.2334324	2.9419188	2.0338258
O	-1.7624672	3.7336267	0.5571327
C	1.1572385	6.2200278	-1.2541398
H	1.4417207	6.9605028	-0.5004909
H	1.9883893	6.0278383	-1.9454462
H	0.2853499	6.5610156	-1.8277529
C	-2.5913818	4.1215395	1.6773910
H	-2.0591521	4.8378537	2.3170675
H	-3.4818854	4.5794960	1.2361138
H	-2.8619649	3.2405869	2.2748228

IV
62
Energy = -2843.360470505

C	1.5764839	-1.3641759	0.2637924

C	1.5275534	0.8384075	1.3562734
C	0.1297905	0.4021432	0.9959354
C	0.1497537	-0.8641848	0.3378016
C	-1.0815853	1.1333164	1.1410833
C	-1.0273057	-1.4398502	-0.2597480
H	1.8433976	-1.8549832	-0.6752763
H	1.7283687	-2.0902554	1.0799741
H	1.6965696	0.6672037	2.4313823
H	1.7357639	1.8919057	1.1377778
Co	-0.7261321	0.5157127	-0.8047891
C	0.1794987	1.8123298	-2.2184264
H	1.1430972	2.2982087	-2.1040507
C	-0.0688559	0.5349156	-2.7984473
H	0.6750079	-0.1359676	-3.2161494
C	-1.4799633	0.2711544	-2.7010755
H	-1.9844306	-0.6313788	-3.0302375
C	-1.0709684	2.3249065	-1.7544886
H	-1.2125297	3.2725787	-1.2452224
C	-2.1090337	1.3818956	-2.0647392
H	-3.1645464	1.4737501	-1.8298932
C	-1.0520498	2.6153549	1.4818978
H	-0.6535695	2.7462815	2.5070173
H	-0.4061914	3.1934596	0.8093497
C	-2.5296939	3.0161111	1.4541010
H	-2.8734834	3.0919461	0.4113397
H	-2.7327066	3.9759674	1.9479089
C	-3.2224988	1.8291401	2.1455879
H	-3.2029834	1.9673609	3.2363643
H	-4.2685968	1.7082384	1.8392961
C	-2.3771283	0.5850019	1.7792799
H	-2.1224897	0.0102485	2.6843476
C	-3.0421022	-0.3611243	0.8075791
C	-2.3607480	-1.7082032	0.5259718
O	-4.0998672	-0.0870103	0.2531024
C	-3.3462944	-2.5153727	-0.2800364
C	-4.4744291	-2.0640565	-0.8207469
H	-3.1600092	-3.5762266	-0.4466745
C	-2.0282249	-2.4634914	1.8377612
H	-1.2667210	-1.9313532	2.4235940
H	-2.9290219	-2.6058252	2.4511129
H	-1.6251751	-3.4556034	1.5906708
C	-0.7392887	-2.4989997	-1.3105007
H	0.1450798	-2.2367155	-1.9022329
H	-0.5583287	-3.4839363	-0.8441199
H	-1.5870304	-2.6170332	-1.9940967
O	-5.4874310	-1.9307353	-1.4053122
C	2.4533317	-0.1012986	0.5329259
C	2.9186720	0.6167447	-0.7424679
O	3.1813677	1.8027145	-0.7957126
C	3.6801377	-0.5135085	1.3587580
O	3.6236838	-0.8694845	2.5183250

O	3.0583376	-0.2252538	-1.7936395
O	4.8232770	-0.4740468	0.6367033
C	3.6109200	0.3772609	-2.9861394
H	2.9531181	1.1740818	-3.3566442
H	4.6014842	0.8000515	-2.7731503
H	3.6819741	-0.4350502	-3.7161909
C	6.0173145	-0.8769029	1.3508542
H	5.9239341	-1.9154516	1.6944331
H	6.8336488	-0.7763970	0.6294048
H	6.1798480	-0.2245161	2.2185016

V

62

Energy = -2843.352531304

C	-1.3946849	-1.2754255	0.7724248
C	0.9373031	-1.2308280	1.6030009
C	0.5742779	0.0878149	0.9754929
C	-0.7653974	0.0684273	0.4846245
C	1.3890570	1.2267083	0.7151835
C	-1.2970246	1.1594903	-0.3021633
H	-1.9726649	-1.6926744	-0.0562900
H	-2.0776896	-1.1585695	1.6305699
H	0.9317969	-1.1201993	2.6987228
H	1.9207033	-1.6116407	1.3037770
Co	0.5142366	0.4850764	-0.9788390
C	1.5690906	-0.9752999	-2.0977259
H	1.9928008	-1.8887946	-1.6931413
C	0.2546203	-0.8063011	-2.6234242
H	-0.5109692	-1.5723488	-2.6888760
C	0.1056452	0.5666324	-3.0036374
H	-0.7872503	1.0172092	-3.4226836
C	2.2234410	0.2922070	-2.1568970
H	3.2341952	0.4951654	-1.8202140
C	1.3290239	1.2535420	-2.7261413
H	1.5396372	2.2969707	-2.9281415
C	2.9062172	1.2075057	0.8193034
H	3.1942713	1.1246084	1.8834734
H	3.3703320	0.3595579	0.3029372
C	3.3304850	2.5959282	0.2629014
H	3.7114813	2.5090934	-0.7636734
H	4.1341592	3.0372268	0.8672678
C	2.0462454	3.4774569	0.2906292
H	2.2082903	4.4763069	0.7141327
H	1.6297696	3.5921205	-0.7188319
C	1.0637255	2.6409993	1.1429224
H	1.4048284	2.7403929	2.1941630
C	-0.3608126	3.1266688	1.2166524
C	-1.4683377	2.5840291	0.2715484
O	-0.6338105	4.0149044	2.0136214
C	-1.4701295	3.6652218	-0.8106089
C	-0.9778133	3.6066829	-2.0300297

H	-1.8440834	4.6509862	-0.5223052
C	-2.8130194	2.6588332	1.0389497
H	-2.8602316	1.8508394	1.7833178
H	-2.8908712	3.6166729	1.5660130
H	-3.6608239	2.5620504	0.3517189
C	-2.4886503	0.7597654	-1.1745457
H	-2.2727165	-0.1505057	-1.7438400
H	-3.3859518	0.5609846	-0.5666177
H	-2.7471249	1.5526572	-1.8875982
O	-0.5986510	3.6310238	-3.1430074
C	-0.2006413	-2.2048928	1.1759554
C	0.2940181	-3.1242478	0.0511792
O	1.4233641	-3.5721027	-0.0069498
C	-0.6431206	-3.0739899	2.3641097
O	-0.7649288	-2.6599678	3.4983450
O	-0.6705449	-3.4248370	-0.8497692
O	-0.9312104	-4.3417513	1.9886645
C	-0.2735400	-4.3719051	-1.8685640
H	0.5596874	-3.9721734	-2.4613756
H	0.0364591	-5.3180735	-1.4062117
H	-1.1603347	-4.5148888	-2.4938289
C	-1.3923774	-5.2087717	3.0535998
H	-2.3185120	-4.8145195	3.4919220
H	-1.5668023	-6.1799133	2.5808724
H	-0.6284422	-5.2871390	3.8379353

P4
62
Energy = -2843.390469693

C	1.4280694	-1.0242440	-0.7542499
C	1.1274322	1.3268456	-0.0368241
C	-0.1762497	0.5663579	0.1530595
C	-0.0133319	-0.7588013	-0.3660269
C	-1.1499425	0.8907998	1.2709653
C	-1.1116380	-1.6330014	-0.6097040
H	1.5639469	-1.1141697	-1.8406912
H	1.7963975	-1.9472935	-0.2875342
H	1.3671191	1.9899219	0.8019794
H	1.1307238	1.9473678	-0.9398424
Co	-1.2684269	0.1472210	-1.6196410
C	-0.0890264	0.8549452	-3.2187201
H	0.9948295	0.9376824	-3.2114560
C	-0.8523871	-0.2875171	-3.6113171
H	-0.4486853	-1.2346522	-3.9581004
C	-2.2408374	0.0105156	-3.4255829
H	-3.0761858	-0.6514732	-3.6300366
C	-1.0022487	1.8682911	-2.7855944
H	-0.7401552	2.8439969	-2.3883252
C	-2.3241899	1.3523814	-2.9098166
H	-3.2289109	1.8675873	-2.6004297
C	-0.8125004	2.0395804	2.2227627

H	0.2332601	1.9518745	2.5605982
H	-0.9490080	3.0196936	1.7467454
C	-1.7677731	1.8050489	3.4035995
H	-2.7653881	2.1724447	3.1256757
H	-1.4574005	2.3398593	4.3115672
C	-1.7924963	0.2706609	3.5972355
H	-1.0937003	-0.0424351	4.3840834
H	-2.7815658	-0.1076388	3.8863668
C	-1.3501273	-0.3208213	2.2310798
H	-0.3652826	-0.8112575	2.3428637
C	-2.2502745	-1.4114266	1.6766196
C	-2.4439998	-1.4071792	0.1433724
O	-2.7917530	-2.2322406	2.3977476
C	-2.8171403	0.0082875	-0.3407752
C	-2.4660409	1.1655637	0.4818675
H	-3.8024260	0.0804193	-0.8121330
C	-3.5304936	-2.4034816	-0.2519984
H	-3.2660728	-3.4298126	0.0299661
H	-4.4634822	-2.1503741	0.2671229
H	-3.7097592	-2.3580123	-1.3354409
C	-0.8501347	-2.9684044	-1.2545316
H	0.0552277	-2.9436197	-1.8731897
H	-0.7141954	-3.7480908	-0.4856896
H	-1.6833022	-3.2821000	-1.8945012
O	-3.0428862	2.2514425	0.4751265
C	2.1982408	0.2062347	-0.1936194
C	3.3144484	0.5823004	-1.1620113
O	3.2469554	1.4474173	-2.0126059
C	2.7220267	-0.1036175	1.2123728
O	2.3781589	-1.0460202	1.8974239
O	4.3719496	-0.2506772	-1.0125553
O	3.5560394	0.8760196	1.6362700
C	5.4671925	-0.0299659	-1.9339297
H	5.1290012	-0.1643229	-2.9698948
H	5.8649923	0.9863049	-1.8153303
H	6.2221882	-0.7769704	-1.6711127
C	4.0382240	0.7276613	2.9930073
H	4.5947413	-0.2126343	3.0998150
H	4.6909970	1.5887730	3.1648306
H	3.1972570	0.7287548	3.6990876

P1'
62
Energy = -2843.404862381

C	1.0188696	1.5732620	-0.6910704
C	0.1655607	1.5409788	-2.0103240
C	-1.1939616	0.8692471	-1.6198661
C	-0.8774296	0.1237275	-0.3560905
C	0.3831710	0.5225886	0.1800951
C	-1.5302280	-0.9038357	0.3708627
C	0.8335505	-0.1793484	1.3493449

H	2.0805498	1.4025793	-0.8962455
H	0.9270151	2.5607365	-0.2130346
H	-1.9545911	1.6386459	-1.4141972
H	-1.5588032	0.2354430	-2.4365597
Co	0.3725659	-1.4142662	-0.1866552
C	1.7637256	-2.0575342	-1.6246372
H	2.3568634	-1.4149164	-2.2657192
C	2.1245422	-2.4802240	-0.3068787
H	3.0348149	-2.2110611	0.2199503
C	1.0719047	-3.3068996	0.2177874
H	1.0517772	-3.7732471	1.1971490
C	0.4724172	-2.5855428	-1.9160043
H	-0.0967855	-2.4007427	-2.8214737
C	0.0493332	-3.3559828	-0.7774778
H	-0.9043602	-3.8659972	-0.6772219
C	-2.7593708	-1.6655966	-0.0728705
H	-3.5903888	-0.9636509	-0.2633441
H	-2.5923364	-2.2063219	-1.0133970
C	-3.0962722	-2.6002682	1.1288839
H	-3.1055427	-3.6591855	0.8372523
H	-4.0990025	-2.3726697	1.5174523
C	-2.0192652	-2.3247517	2.2081760
H	-2.3952901	-2.4355149	3.2331298
H	-1.1684443	-3.0065429	2.0900326
C	-1.5442724	-0.8966918	1.8922784
H	-2.3338501	-0.1973536	2.2351931
C	-0.1849770	-0.4513140	2.4784178
C	-0.3101443	0.7460232	3.4058728
O	0.3564502	-1.4954406	3.3357400
C	0.1058023	0.3974848	4.6342137
C	0.5309592	-1.0134520	4.6245991
H	0.1589843	1.0140949	5.5278981
C	-0.7664363	2.0708942	2.9043850
H	-0.0159661	2.4887288	2.2142018
H	-1.6977689	1.9820522	2.3250119
H	-0.9218146	2.7833961	3.7235468
C	2.2549337	0.0214784	1.8196593
H	2.9302386	0.1691494	0.9682447
H	2.3389816	0.9041989	2.4771881
H	2.6036191	-0.8456899	2.3934923
O	0.9733341	-1.7083101	5.5123233
C	-0.0688292	2.9409039	-2.5888947
O	-0.5949507	3.7716697	-1.6507310
C	-0.8872801	5.1100794	-2.1189038
H	-1.6180401	5.0779414	-2.9377082
H	-1.2968841	5.6376037	-1.2519342
H	0.0283027	5.5990535	-2.4767194
O	0.1522922	3.2769982	-3.7343998
C	0.8355145	0.7415714	-3.1438605
O	0.2599777	-0.0092991	-3.9031925
O	2.1549163	1.0328930	-3.2321202

C	2.8205607	0.4861436	-4.3949385
H	2.3753598	0.9033451	-5.3075576
H	3.8683186	0.7866696	-4.2989998
H	2.7280793	-0.6079306	-4.4193548

$Ts_{I\text{-}II}$
62
Energy = -2843.270856817

C	1.0926881	2.6512999	0.3542347
C	-1.3492507	2.6329262	0.2630532
C	-1.0448812	1.3439059	-0.4147475
C	0.8701649	1.3630668	-0.3554621
C	-1.5077752	0.1889537	-0.7728268
C	1.4098371	0.2446204	-0.7254622
H	1.1890767	3.4865940	-0.3578998
H	2.0051198	2.6017764	0.9613175
H	-2.2950448	2.5576673	0.8145682
H	-1.4136005	3.4618360	-0.4589649
Co	-0.0373557	0.5466614	-1.9678095
C	0.6767801	1.5228655	-3.7482339
H	1.3078853	2.4059253	-3.7571550
C	1.1286125	0.1737485	-3.6635757
H	2.1652263	-0.1464165	-3.6190953
C	-0.0173208	-0.6904655	-3.6179297
H	-0.0074161	-1.7747938	-3.5832089
C	-0.7505222	1.5074906	-3.7550877
H	-1.3996291	2.3774526	-3.7697547
C	-1.1776401	0.1493008	-3.6809328
H	-2.2079243	-0.1909615	-3.6356496
C	-2.5077090	-0.8610467	-0.4888624
H	-3.5308325	-0.4473238	-0.5422006
H	-2.4488760	-1.6529148	-1.2512351
C	-2.2825470	-1.4664258	0.9176058
H	-2.9251739	-2.3536358	1.0305155
H	-2.5848998	-0.7308222	1.6771717
C	-0.8101955	-1.8430133	1.1919764
H	-0.2408731	-0.8974376	1.2653137
H	-0.7305239	-2.3593798	2.1579486
C	-0.1802102	-2.6508461	0.1093551
H	-0.1243607	-2.1809394	-0.8771629
C	0.3953085	-3.8609073	0.2420036
C	1.0947114	-4.6436188	-0.7699087
O	0.4312350	-4.5428233	1.4485415
C	1.5423101	-5.7728139	-0.1657545
C	1.1417227	-5.7526109	1.2448233
H	2.1105304	-6.5902975	-0.5994085
C	1.2552494	-4.2085926	-2.1881989
H	0.2766168	-4.1568645	-2.6893964
H	1.6957799	-3.2015688	-2.2407149
H	1.8935782	-4.9020613	-2.7484079
C	2.5782769	-0.6340458	-0.5370062

H	3.1203742	-0.7797879	-1.4842605
H	3.2812624	-0.2174217	0.2028170
H	2.2714916	-1.6332104	-0.1877430
O	1.3180699	-6.5346890	2.1485610
C	-0.1656319	2.9155070	1.2254921
C	-0.1951907	4.3673724	1.6907996
O	-0.1184988	5.3164108	0.9347087
O	-0.3271390	4.4774101	3.0338826
C	-0.2647259	1.9288780	2.4030607
O	-1.2995967	1.4342515	2.8036194
O	0.9485523	1.6670721	2.9422513
C	-0.3807042	5.8337693	3.5381355
H	-1.2351904	6.3687042	3.1033623
H	-0.4935079	5.7352351	4.6219092
H	0.5436322	6.3707871	3.2877686
C	0.9309850	0.7370339	4.0506311
H	1.9741068	0.6410381	4.3669554
H	0.3077483	1.1262393	4.8663599
H	0.5321776	-0.2328692	3.7247710

$Ts_{II\text{-}III}$
62
Energy = -2843.324780492

C	1.5520646	1.9956619	-0.4196772
C	-0.7395535	2.0950363	-1.3190260
C	-0.3392698	0.6575536	-1.0995283
C	1.0292902	0.5955157	-0.6764607
C	-1.0506006	-0.5133531	-1.1179576
C	1.5775299	-0.6425955	-0.5457143
H	2.1734440	2.3605316	-1.2545553
H	2.1335456	2.0924074	0.5058286
H	-1.7903747	2.3227912	-1.1011077
H	-0.5307467	2.4451544	-2.3433645
Co	0.2984167	-2.0240476	-1.0042681
C	1.6943930	-3.2917798	-1.8974298
H	2.6922390	-3.4653549	-1.5095130
C	0.5374205	-4.0708949	-1.6130466
H	0.4939268	-4.9086695	-0.9256748
C	-0.5742618	-3.5135063	-2.2984900
H	-1.5972289	-3.8712622	-2.2492308
C	1.2993574	-2.2404290	-2.8002060
H	1.9401341	-1.4682436	-3.2126258
C	-0.0993180	-2.3790182	-3.0348122
H	-0.7001413	-1.7142276	-3.6469174
C	-2.4961012	-0.5968202	-1.5312971
H	-2.7723656	0.2727670	-2.1463003
H	-2.6806958	-1.4952778	-2.1414047
C	-3.3178300	-0.6834310	-0.2368270
H	-4.3668975	-0.9636480	-0.4111398
H	-3.3110816	0.2992759	0.2636180
C	-2.5793713	-1.7134627	0.6149438

H	-2.9131989	-1.7183504	1.6641957
H	-2.7439177	-2.7250970	0.2196463
C	-1.0868544	-1.4076039	0.5827150
H	-0.8009659	-0.5045097	1.1293880
C	-0.1791522	-2.5022079	0.9139011
C	0.8103736	-2.4503640	1.9977206
O	-0.7228180	-3.8129327	0.9222784
C	0.9507452	-3.7101910	2.4916654
C	0.0157243	-4.6020637	1.8209112
H	1.6000268	-4.0391180	3.2980079
C	1.4110393	-1.2048858	2.5666563
H	1.3111764	-0.3419427	1.9011399
H	0.8922610	-0.9565472	3.5056736
H	2.4721896	-1.3490162	2.8093289
C	3.0105702	-0.8998467	-0.2056708
H	3.6019240	-1.0713260	-1.1214131
H	3.4692845	-0.0465177	0.3219620
H	3.1277872	-1.7985184	0.4159603
O	-0.1965606	-5.7937934	1.9203735
C	0.2366398	2.8320026	-0.3482814
C	0.4818282	4.2838538	-0.7430999
O	0.1820078	4.7917756	-1.8032504
O	1.1498234	4.9303776	0.2472598
C	-0.3519437	2.7392619	1.0660072
O	0.0462844	2.0193121	1.9596454
O	-1.4428791	3.5381396	1.1746129
C	1.4753975	6.3122104	-0.0325311
H	1.9991076	6.6737870	0.8577133
H	2.1196419	6.3824064	-0.9190090
H	0.5596519	6.8917851	-0.2092829
C	-2.1121833	3.4926342	2.4560088
H	-1.4253204	3.7953217	3.2573142
H	-2.9476676	4.1943921	2.3731421
H	-2.4759462	2.4768990	2.6614953

$TS_{III\text{-}IV}$
62
Energy = -2843.306166354

C	1.8140746	0.8827455	1.2462587
C	1.8440367	-1.0335242	-0.2609467
C	0.5224397	-0.3032474	-0.4525887
C	0.4660500	0.7435290	0.5689122
C	-0.4119489	-0.6996962	-1.4341669
C	-0.7474769	1.1687803	1.0305037
H	1.7709507	0.4637839	2.2654940
H	2.1359152	1.9293161	1.3191010
H	2.2597157	-1.4395834	-1.1895617
H	1.7543469	-1.8661049	0.4510094
Co	-1.3762027	-0.6295722	0.4365764
C	-1.5627324	-1.3816179	2.4833079
H	-1.1319348	-0.8962295	3.3531196

C	-2.8111933	-1.0106476	1.8469792
H	-3.5079333	-0.2506331	2.1875697
C	-3.0100172	-1.8909298	0.7355902
H	-3.8615487	-1.8720590	0.0650735
C	-0.9704935	-2.4059611	1.7319971
H	0.0028765	-2.8532030	1.9093158
C	-1.8489708	-2.6992672	0.6234768
H	-1.6646361	-3.4370178	-0.1517921
C	-0.1423886	-1.9212695	-2.3091772
H	0.8711915	-1.8726790	-2.7384060
H	-0.1748792	-2.8481320	-1.7191939
C	-1.2256781	-1.8848732	-3.4099132
H	-1.5762576	-2.8862332	-3.6933243
H	-0.8174475	-1.4161725	-4.3185285
C	-2.3428134	-1.0077942	-2.8267158
H	-3.0137616	-0.5804966	-3.5816828
H	-2.9588638	-1.5876069	-2.1255290
C	-1.5838906	0.0747785	-2.0428846
H	-1.2384178	0.8605266	-2.7451902
C	-2.3137487	0.6478790	-0.8520755
C	-1.9801767	2.0339176	-0.3866104
O	-3.6948672	0.5046356	-0.8078825
C	-3.1677597	2.5536378	0.1298230
C	-4.2467762	1.6352638	-0.0720622
H	-3.3175823	3.5431158	0.5501871
C	-0.9517952	2.9215046	-1.0518287
H	-0.0371725	2.3851477	-1.3299940
H	-1.3937588	3.3692147	-1.9569846
H	-0.6675562	3.7443670	-0.3815393
C	-0.9945704	1.9079193	2.2935510
H	-0.5164557	1.4148781	3.1570729
H	-0.5953528	2.9341725	2.2319012
H	-2.0748406	1.9917634	2.4840467
O	-5.4310209	1.6349388	0.1937813
C	2.7685910	0.0441957	0.3621244
C	3.8774291	-0.5722159	1.2127369
O	3.8699465	-1.6973318	1.6681968
C	3.3581359	0.9223446	-0.7514991
O	3.1058051	2.0933360	-0.9419442
O	4.1876207	0.1881539	-1.5347565
O	4.8488092	0.3405968	1.4551671
C	4.8010628	0.9144245	-2.6260996
H	5.4015908	1.7478586	-2.2385145
H	5.4335142	0.1853533	-3.1416843
H	4.0320704	1.3114111	-3.3019175
C	5.9301399	-0.1190863	2.3014842
H	6.4339897	-0.9793472	1.8416205
H	6.6124422	0.7318267	2.3878827
H	5.5457601	-0.4128903	3.2870753

$TS_{IV\text{-}V}$

62
Energy = -2843.347268642

C	-1.1220502	-1.5682006	0.6544445
C	1.3440571	-1.5959909	0.5594362
C	0.8319024	-0.1821225	0.6260552
C	-0.5884977	-0.1511706	0.6682056
C	1.5631285	1.0386438	0.5706271
C	-1.3299449	1.0862809	0.5577632
H	-1.9909697	-1.7267684	0.0111946
H	-1.4137209	-1.8344015	1.6838929
H	1.7298027	-1.8846658	1.5502254
H	2.1411101	-1.7478783	-0.1772310
Co	0.1057563	0.8982313	-0.8797246
C	0.7537146	0.1603076	-2.7483754
H	1.3446871	-0.7388970	-2.8908544
C	-0.6703577	0.2377693	-2.7219075
H	-1.3632552	-0.5882499	-2.8420202
C	-1.0326995	1.5965351	-2.4555160
H	-2.0435028	1.9760400	-2.3566287
C	1.2616660	1.4739746	-2.4984955
H	2.3111563	1.7426674	-2.4386610
C	0.1615293	2.3752165	-2.3256160
H	0.2139719	3.4428293	-2.1434271
C	3.0301401	1.0220730	0.1665304
H	3.6132745	0.4756817	0.9340481
H	3.2110226	0.5179244	-0.7911567
C	3.4184342	2.5040850	0.1929896
H	3.0323965	2.9996520	-0.7108017
H	4.5040034	2.6684378	0.2255213
C	2.6943110	3.0527030	1.4386367
H	3.3549043	3.0348211	2.3155562
H	2.3581886	4.0897881	1.3212432
C	1.4796519	2.0985485	1.6639579
H	1.6325543	1.5685454	2.6283405
C	0.1874473	2.8366995	1.9326966
C	-1.2164958	2.2579415	1.5643882
O	0.2299721	3.8897611	2.5497868
C	-1.9917788	3.4875199	1.0841122
C	-2.0825849	3.9112013	-0.1569534
H	-2.2928658	4.2194149	1.8352212
C	-1.8094149	1.7974086	2.9274797
H	-1.2410173	0.9364076	3.3074790
H	-1.7542021	2.6114612	3.6623230
H	-2.8589286	1.4999774	2.8089652
C	-2.7729426	0.8441736	0.1042721
H	-2.8016113	0.1152334	-0.7134948
H	-3.3895899	0.4445332	0.9270985
H	-3.2644808	1.7565844	-0.2450043
O	-2.2433001	4.2995744	-1.2562329
C	0.0903375	-2.4535329	0.2178829
C	0.0957439	-2.8130097	-1.2747831

O	1.1029712	-2.9981516	-1.9296694
C	0.0901287	-3.7455569	1.0490406
O	0.2578881	-3.7691171	2.2514578
O	-1.1540374	-2.9577856	-1.7780227
O	-0.1423821	-4.8466708	0.2988516
C	-1.2029856	-3.4278435	-3.1451451
H	-0.6718879	-2.7353107	-3.8114793
H	-0.7391942	-4.4203138	-3.2193278
H	-2.2665093	-3.4744107	-3.3991647
C	-0.1668224	-6.0965940	1.0304812
H	-0.9649505	-6.0812505	1.7841512
H	-0.3548208	-6.8683924	0.2781932
H	0.7961510	-6.2638562	1.5301075

$Ts_{V\text{-}P4}$
62
Energy = -2843.338971129

C	-1.4279304	0.2512360	1.4186719
C	0.9823999	0.9169653	1.4210578
C	0.5082226	0.6060172	0.0286455
C	-0.8804873	0.2563755	0.0096410
C	1.1794053	0.6749948	-1.2337881
C	-1.5023928	-0.2617145	-1.1940948
H	-1.9561308	-0.6693620	1.6870901
H	-2.1448335	1.0780633	1.5399657
H	1.1787578	1.9994500	1.4984170
H	1.9011438	0.3959736	1.7133393
Co	0.2644350	-1.1664296	-0.7663793
C	0.2790578	-2.8070603	0.5692243
H	-0.1845691	-2.8087898	1.5497503
C	-0.3533799	-3.1739066	-0.6555980
H	-1.3782438	-3.5107330	-0.7669597
C	0.5834803	-3.0136095	-1.7196995
H	0.4175127	-3.2513015	-2.7625835
C	1.6142083	-2.4001489	0.2711157
H	2.3344213	-2.0285810	0.9920436
C	1.7936744	-2.5170271	-1.1436735
H	2.6895730	-2.2597525	-1.6993037
C	2.7048846	0.6760466	-1.3830432
H	3.2247815	0.6966198	-0.4137599
H	3.0218092	-0.2433486	-1.8922877
C	3.0404600	1.8774707	-2.2938731
H	3.9658106	1.7245495	-2.8658781
H	3.1673880	2.7933214	-1.6940847
C	1.7940549	2.0185742	-3.1833851
H	1.7033523	2.9939654	-3.6764628
H	1.7808012	1.2377506	-3.9572420
C	0.6686069	1.7864832	-2.1599936
H	0.6627881	2.6992124	-1.5289876
C	-0.7516902	1.7711657	-2.6791113
C	-1.5793748	0.4696282	-2.5742319

O	-1.1988893	2.7784752	-3.2083381
C	-0.9839025	-0.3426587	-3.7194443
C	0.2331179	-0.8691655	-3.7939926
H	-1.4608818	-0.2567871	-4.7015304
C	-3.0358083	0.8267523	-2.9424951
H	-3.4917608	1.4397911	-2.1541486
H	-3.0479856	1.4218823	-3.8626640
H	-3.6418805	-0.0726314	-3.0971808
C	-2.7273492	-1.1320670	-0.9446902
H	-2.5983542	-1.7479564	-0.0483945
H	-3.6405062	-0.5327887	-0.8036291
H	-2.8965265	-1.8069299	-1.7947599
O	1.2667436	-1.3339277	-4.1218376
C	-0.2016433	0.5010419	2.3501807
C	0.1748631	-0.7407053	3.1709298
O	1.2672575	-1.2659824	3.2260130
C	-0.4859531	1.6380852	3.3453572
O	-1.4198545	2.4095365	3.2986213
O	-0.9017707	-1.1784987	3.8732477
O	0.5037069	1.7018186	4.2700392
C	0.3765332	2.7730701	5.2357110
H	1.2416097	2.6702202	5.8977256
H	0.3864152	3.7470835	4.7290022
H	-0.5611150	2.6711402	5.7977553
C	-0.6522136	-2.3196556	4.7275994
H	-1.6079767	-2.5311773	5.2164831
H	-0.3203262	-3.1809857	4.1323400
H	0.1224538	-2.0790781	5.4675584

$Ts_{III\text{-}P1}$
62
Energy = -2843.302812367

C	1.5353541	1.7765172	-0.2391484
C	-0.8600493	1.8731349	-0.7961996
C	-0.5586958	0.5148518	-0.2003222
C	0.8940875	0.4228116	-0.0342787
C	-1.4781647	-0.4350624	0.3066575
C	1.3675037	-0.8470973	-0.1382292
H	2.0519656	1.8232734	-1.2126594
H	2.2565376	2.0418892	0.5447134
H	-1.8404781	2.2778540	-0.5176557
H	-0.7945038	1.8789309	-1.8929935
Co	-0.2946611	-1.3442739	-1.0362035
C	0.1241818	-2.9875640	-2.2851154
H	0.6852933	-3.8510836	-1.9424110
C	-1.2776277	-2.8017073	-2.1631307
H	-1.9881228	-3.4999857	-1.7333136
C	-1.5615602	-1.4899965	-2.6780440
H	-2.5411392	-1.0197550	-2.7105007
C	0.6755060	-1.8364004	-2.9752321
H	1.7285519	-1.6895563	-3.1969594

C	-0.3608752	-0.9381314	-3.2564050
H	-0.2659519	0.0392739	-3.7191011
C	-2.9928577	-0.3044696	0.2632460
H	-3.3131210	0.7344369	0.4437415
H	-3.3921523	-0.5845082	-0.7206293
C	-3.4947750	-1.2665939	1.3693974
H	-4.4456777	-1.7511746	1.1107098
H	-3.6581020	-0.7087806	2.3047767
C	-2.3496791	-2.2763351	1.5614223
H	-2.3887798	-2.8119131	2.5186693
H	-2.3510432	-3.0213687	0.7543151
C	-1.0985571	-1.3941677	1.4202657
H	-0.9472089	-0.8363633	2.3645454
C	0.2043898	-2.1078803	1.0336385
C	1.2600999	-2.1117863	2.0982036
O	0.0737438	-3.4721823	0.6480460
C	1.7695674	-3.3607032	2.1945302
C	1.0658176	-4.2463791	1.2712463
H	2.5479857	-3.7125176	2.8658246
C	1.5882004	-0.9364327	2.9577369
H	1.4641049	0.0164389	2.4265493
H	0.9117520	-0.9113637	3.8278183
H	2.6129101	-1.0053166	3.3453073
C	2.7633727	-1.3294584	-0.2939438
H	3.1874167	-0.9371646	-1.2332301
H	3.4125234	-0.9988733	0.5326061
H	2.8069595	-2.4259178	-0.3397032
O	1.2056738	-5.4198420	1.0017588
C	0.3133096	2.7394864	-0.2390213
C	0.5912238	3.9645913	-1.1048235
O	0.1907052	4.1353099	-2.2371697
O	1.4150936	4.8231666	-0.4521497
C	-0.0153603	3.1472865	1.2029894
O	0.5136601	2.7093412	2.2044097
O	-1.0342432	4.0424868	1.2169439
C	1.7839862	6.0074545	-1.1982461
H	2.4370004	6.5790340	-0.5317450
H	2.3132625	5.7303535	-2.1195220
H	0.8889973	6.5871461	-1.4600280
C	-1.4479389	4.4812101	2.5318837
H	-0.6106740	4.9625477	3.0543350
H	-2.2600817	5.1938766	2.3587383
H	-1.7983714	3.6278909	3.1276275

$Ts_{II\text{-}IV}$
62
Energy = -2843.289760012

C	1.1746997	2.0479141	0.6698175
C	-0.6230901	2.3277954	-1.0487997
C	-0.2693484	0.8748994	-0.8337670
C	0.6987204	0.7116450	0.1648516

C	-0.7006057	-0.2936407	-1.4467004
C	1.1282334	-0.6046020	0.5321553
H	2.1840811	2.2690328	0.2829354
H	1.2289434	2.1100648	1.7649210
H	-1.7023891	2.5305300	-1.0145297
H	-0.2585641	2.7028218	-2.0169611
Co	0.2820496	-1.8107621	-0.8674422
C	1.7312002	-3.3529226	-0.9331920
H	2.2443382	-3.7206572	-0.0507692
C	0.5195342	-3.8779732	-1.4668636
H	-0.0583992	-4.6793438	-1.0181574
C	0.1428830	-3.0985969	-2.5904455
H	-0.7472537	-3.2353969	-3.1957632
C	2.1176663	-2.2372067	-1.7478782
H	2.9960201	-1.6165560	-1.6127969
C	1.1329067	-2.0746980	-2.7653748
H	1.1288761	-1.2986712	-3.5245566
C	-1.8315017	-0.4207922	-2.4235552
H	-2.1512594	0.5686795	-2.7912995
H	-1.4869177	-0.9898817	-3.2999977
C	-3.0631534	-1.1510829	-1.8025744
H	-3.7220824	-1.5237327	-2.6000159
H	-3.6436852	-0.4065549	-1.2343680
C	-2.6693244	-2.2825970	-0.8247514
H	-3.5566189	-2.5642786	-0.2315853
H	-2.3263022	-3.1862891	-1.3410211
C	-1.6028617	-1.7188050	0.0656437
H	-1.8681940	-0.7171146	0.4150836
C	-0.6645030	-2.3146103	0.9422530
C	0.1893178	-1.4254809	1.8214999
O	-0.5763538	-3.6095803	1.2628059
C	0.9335406	-2.3951377	2.5878838
C	0.5560018	-3.7194163	2.3130370
H	1.6478167	-2.1643643	3.3712804
C	-0.4981393	-0.3331839	2.6345342
H	-1.0225687	0.3922343	1.9980226
H	-1.2113739	-0.7819152	3.3413547
H	0.2466152	0.2288028	3.2140106
C	2.5813748	-0.6870849	0.9510626
H	3.2501676	-0.2751197	0.1811005
H	2.7526994	-0.1132541	1.8795485
H	2.8648371	-1.7269531	1.1610852
O	0.8394467	-4.8360020	2.6803193
C	0.1327932	3.0691454	0.1035090
C	0.8609867	4.3201176	-0.3975217
O	1.0567190	4.6178107	-1.5567719
O	1.3257825	5.0343837	0.6583338
C	-0.8645404	3.4738508	1.1975774
O	-0.9285953	3.0115182	2.3171490
O	-1.7117399	4.4221705	0.7228134
C	2.0803155	6.2210810	0.3153733

H	2.3671611	6.6690627	1.2715654
H	2.9687379	5.9532759	-0.2717210
H	1.4591168	6.9120565	-0.2695842
C	-2.7084570	4.8818005	1.6657006
H	-2.2245949	5.3120040	2.5524556
H	-3.2866051	5.6410627	1.1302681
H	-3.3530371	4.0496673	1.9786149