Supplementary Information for:

The hexadehydro-Diels–Alder reaction: triynes to *o*-benyznes to benzenoids

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General Experimental Protocols

^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 500 (500 MHz), Varian Inova 300 (300 MHz), Varian VXR 300 (300 MHz), and Bruker Avance 500 (500 MHz) spectrometers. ^{1}H NMR chemical shifts in $CDCl_3$ are referenced to TMS (δ 0.00 ppm). Non-first order multiplets are identified as "nfom". ^{13}C NMR chemical shifts in $CDCl_3$ are referenced to chloroform (δ 77.16 ppm). A spurious spike at *ca.* 5 ppm is sometimes present in the copies of the ^{1}H NMR spectra that were processed using iNMR software. TMS is present in some ^{13}C NMR samples (δ ca. 0.0 ppm). The following format is used to report resonances: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment, e.g., CH_aH_b. Some complex structures are numbered in order to simplify proton assignment numbering and naming. Coupling constant analysis was guided by methods we have described elsewhere.[1,2]

Infrared spectra were recorded on a Midac Corporation Prospect 4000 FT-IR spectrometer. The most intense and/or diagnostic peaks are reported, and all spectra were collected in attenuated total reflectance (ATR) mode as thin films on a germanium window.

High-resolution mass spectrometry (HRMS) measurements were made on one of two instruments. Chemical ionization mass spectrometry was performed on a Finnigan MAT 95 (CIMS) mass spectrometer. Samples were introduced via capillary gas chromatography using an oven temperature profile of 25- 320 ºC ramped at 50 ºC/min. Electrospray ionization (ESI) mass spectrometry was performed on a Bruker BioTOF II (ESI-TOF) instrument using PEG or PPG as an internal standard/calibrant. Samples were introduced as solutions in methanol or acetonitrile.

MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of Silasorb silica gel (18-32 μm, 60 Å pore size), a Waters HPLC pump, a Waters R401 differential refractive index detector, and a Gilson 116 UV detector. Flash chromatography was performed using E. Merck silica gel (230-400 mesh). Thin layer chromatography was performed on glass or plastic backed plates of silica gel and visualized by UV detection and/or a solution of ceric ammonium molybdate, anisaldehyde, potassium permanganate, or phosphomolybdic acid.

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame or oven dried glassware. Piperidine, diisopropylamine and triethylamine for cross-coupling reactions were deaerated by a freeze-pump-thaw cycle and then stored in a Schlenk flask or by direct purging with N_2 gas immediately prior to use. Anhydrous THF, diethyl ether, toluene, and methylene chloride were taken immediately prior to use after being passed through a column of activated alumina. Reported (external) reaction temperatures are the temperature of the heating bath. HDDA reactions, including those that were carried out at temperatures above the boiling point of the solvent, were typically performed in a screw-capped vial or culture tube fitted with an inert, Teflon®-lined cap. Those carried out in deuterated solvents were often performed directly in a capped 5 mm NMR sample tube.

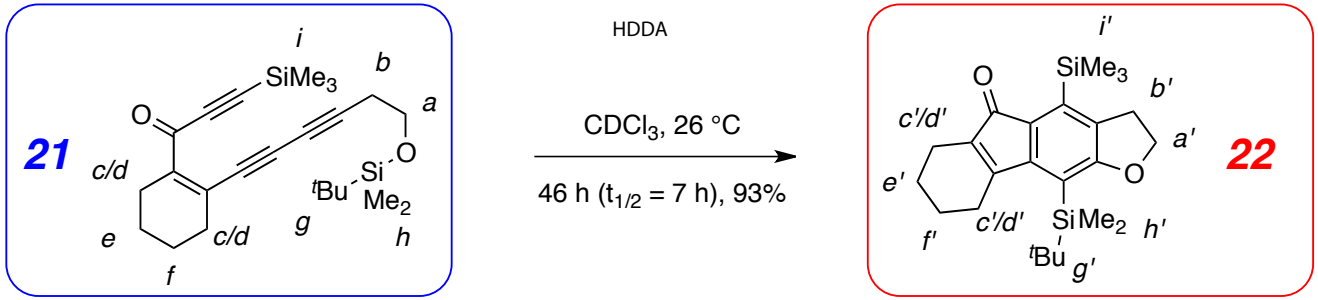
A. General Procedure A: Alkyne Bromination

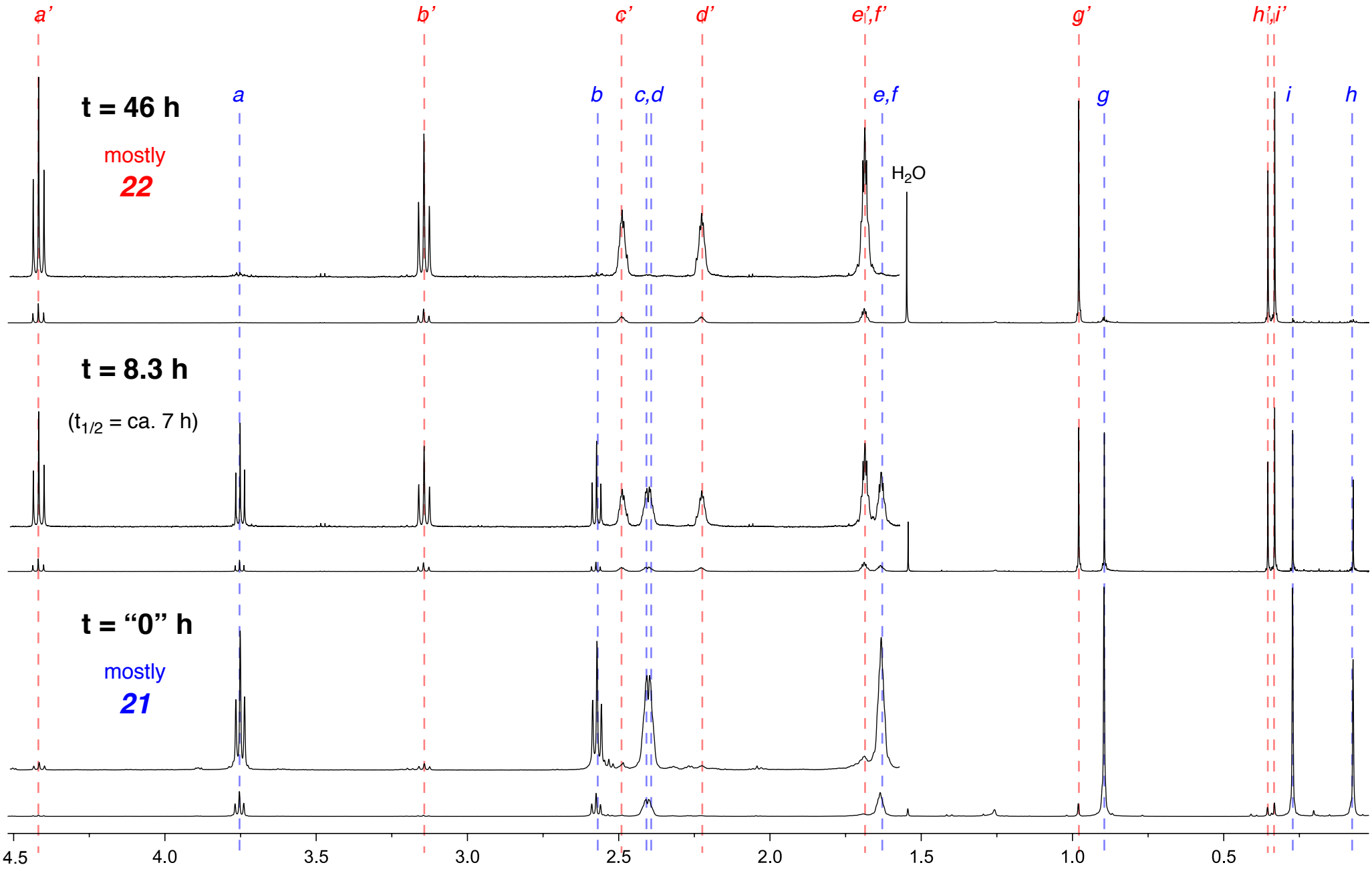
Powdered $AgNO_3$ (0.1 equiv) was added to a stirred solution of alkyne (1.0 equiv) and *N*-bromosuccinimide (NBS, 1.1 equiv) in acetone (0.1 M) at rt. After 1 h the slurry was either i) filtered through Celite® (acetone eluent) and concentrated or ii) partitioned between Et_2O and water, further extracted with Et_2O, washed with brine, dried ($MgSO_4$), and concentrated. The crude material was typically purified by flash chromatography.

B. General Procedure B: Cadiot–Chodkiewicz Alkyne Cross-Coupling

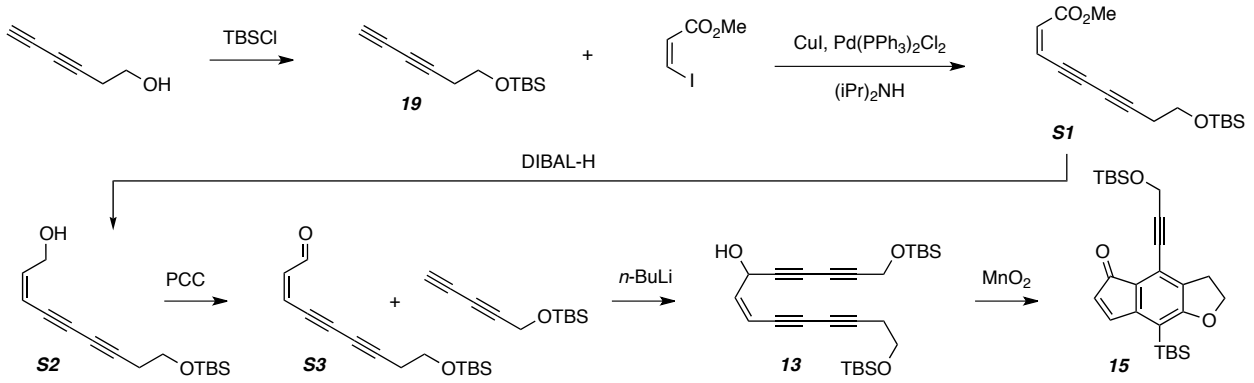
CuCl (0.05 equiv) was added to a stirred solution of alkyne (partner A, 1.0 equiv) and 1-bromoalkyne (partner B, 1.5 equiv) in freshly deaerated piperidine (0.3 M) at 0 ºC and under an inert atmosphere. After 1 h the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with EtOAc or Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The crude material was typically purified by flash chromatography.

Fig. S1 An example of HDDA reaction monitoring by in situ ^{1}H NMR analysis: **21** to **22** (cf. Fig. 2B of manuscript) at *t* = 0, 8, and 46 h.

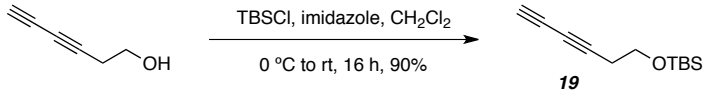




Synthesis of indenone 15 (Fig. 2A of manuscript)



tert-Butyl(hexa-3,5-diyn-1-yloxy)dimethylsilane (19)



TBSCl (2.19 g, 14.6 mmol) was added to a stirred solution of hexa-3,5-diyn-1-ol[3] (665 mg, 7.1 mmol) and imidazole (1.20 g, 17.6 mmol) in CH_2Cl_2 (45 mL) at 0 ºC. After 15 minutes the ice bath was removed and the reaction mixture was allowed to warm to room temperature. After 12 h the reaction mixture was filtered through a plug of silica gel (EtOAc eluent) and concentrated. Purification by flash chromatography (hexanes:EtOAc 15:1) gave the diyne **19** (1.33 g, 6.4 mmol, 90%) as a clear colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (t, J = 6.9 Hz, 2H, SiOCH_2), 2.47 (dt, J = 1.2, 6.9 Hz, 2H, ≡CCH_2), 1.97 (t, J = 1.2 Hz, 1H, ≡CH), 0.90 [s, 9H, C(CH_3)$_3$], and 0.08 [s, 6H, Si(CH_3)$_2$].

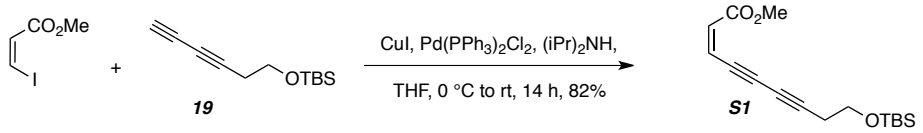
^{13}C NMR (125 MHz, $CDCl_3$): δ 75.6, 68.5, 65.9, 64.9, 61.3, 26.0, 23.6, 18.4, and -5.2.

IR (neat): 3308, 2956, 2931, 2859, 2228, 1471, 1256, 1108, 839, and 779 cm^{-1}.

HRMS (CIMS): Calcd for $C_{12}H_{21}OSi^+$ [M+H$^+$] requires 209.1356; found 209.1372.

TLC: R_f 0.6 (9:1 Hex/EtOAc).

(*Z*)-Methyl 9-((*tert*-Butyldimethylsilyl)oxy)nona-2-en-4,6-diynoate (S1)



CuI (25 mg, 0.13 mmol) and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) were added to a stirred solution of (*Z*)-methyl 3-iodoacrylate[4] (220 mg, 1.04 mmol), diyne **19** (180 mg, 0.87 mmol), and freshly deaerated diisopropylamine (3.0 mL, 21 mmol) and THF (5 mL) at 0 °C under N_2 atmosphere. After 1 h the ice-bath was removed and the reaction mixture was allowed to warm to rt. After 14 h the reaction mixture was diluted in Et_2O and washed with satd. aq. NH_4Cl. The aqueous phase was extracted with Et_2O and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 9:1) gave the diyne **S1** (207 mg, 0.71 mmol, 82%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.22 (d, *J* = 11.4 Hz, 1H, *H2*), 6.16 (dt, *J* = 11.4, 1.1 Hz, 1H, *H3*), 3.78 (s, 3H, OC*H*$_3$), 3.77 (t, *J* = 7.0 Hz, 2H, C*H*$_2$O), 2.58 (dt, *J* = 1.1, 7.0 Hz, 2H, ≡CC*H*$_2$), 0.90 [s, 9H, C(C*H*$_3$)$_3$], and 0.08 [s, 6H, Si(C*H*$_3$)$_2$].

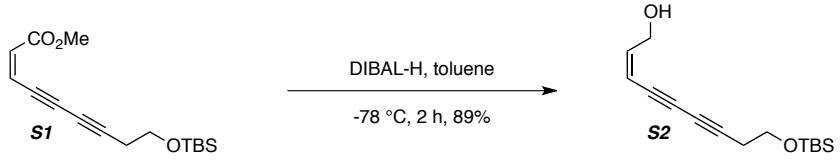
^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9, 131.1, 122.4, 87.0, 86.4, 71.2, 66.2, 61.3, 51.8, 26.0, 24.4, 18.4, and -5.2.

IR (neat): 2931, 2857, 2231, 1727, 1607, 1438, 1256, 1212, 1171, 1105, 909, 839, and 778cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{16}H_{24}NaO_3Si^+$ [M+Na$^+$] requires 315.1387; found 315.1388.

TLC: R_f 0.5 (9:1 Hex/EtOAc).

(*Z*)-9-((*tert*-Butyldimethylsilyl)oxy)nona-2-en-4,6-diyn-1-ol (S2)



DIBAL-H (1.3 mL, 1.5 M in toluene, 2.0 mmol) was added to a stirred solution of ester **S1** (180 mg, 0.62 mmol) in toluene (3 mL) at -78 °C. After 2 h the reaction mixture was diluted with ether and washed with satd. aq. NH_4Cl. The aqueous phase was extracted with Et_2O and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 3:1) gave the allylic alcohol **S2** (145 mg, 0.55 mmol, 89%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.22 (dt, *J* = 11.0, 6.4 Hz, 1H, *H2*), 5.60 (dtt, *J* = 11.0, 1.4, 1.4 Hz, 1H, *H3*), 4.42 (br d, *J* = 6.0 Hz, 2H, C*H*$_2$OH), 3.76 (t, *J* = 7.0 Hz, 2H, C*H*$_2$OSi), 2.55 (dt, *J* = 1.2, 7.0 Hz, 2H, ≡CC*H*$_2$), 1.84 (br s, 1H, O*H*), 0.90 [s, 9H, C(C*H*$_3$)$_3$], and 0.08 [s, 6H, SiC*H*$_3$)$_2$].

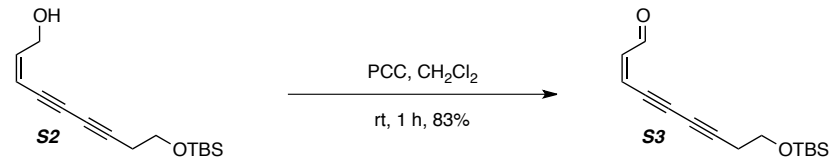
^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 109.7, 83.1, 80.0, 70.8, 66.0, 61.5, 61.2, 26.0, 24.1, 18.4, and -5.2.

IR (neat): 3362, 2953, 2930, 2858, 2236, 1470, 1255, 1106, 1028, 909, 839, and 779 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{15}H_{24}NaO_2Si^+$ [M+Na$^+$] requires 287.1438; found 287.1463.

TLC: R_f 0.4 (3:1 Hex/EtOAc).

(*Z*)-9-((*tert*-Butyldimethylsilyl)oxy)nona-2-en-4,6-diynal (S3)



PCC (130 mg, 0.60 mmol) was added to a stirred solution of endiynol **S2** (80 mg, 0.30 mmol) in CH_2Cl_2 (2 mL) at room temperature. After 1 h the reaction mixture was filtered through a plug of silica gel (CH_2Cl_2 eluent) and concentrated. Purification by flash chromatography (hexanes:EtOAc 9:1) gave aldehyde **S3** (66 mg, 0.25 mmol, 83%) as a clear yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.1 (d, *J* = 8.2 Hz, 1H, C*H*O), 6.65 (dt, *J*= 10.8, 1.2 Hz,1H, *H3*), 6.40 (dd, *J*= 8.2, 10.9 Hz,1H, *H2*), 3.79 (t, *J* = 6.8 Hz, 2H, C*H*$_2$O), 2.60 (dt, *J* = 1.2, 6.6 Hz, 2H, ≡CC*H*$_2$), 0.91 [s, 9H, C(C*H*$_3$)$_3$], and 0.09 [s, 6H, Si(C*H*$_3$)$_2$].

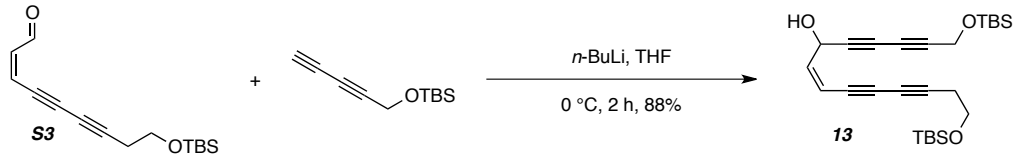
^{13}C NMR (75 MHz, $CDCl_3$): δ 191.5, 140.9, 127.9, 87.6, 69.3, 65.7, 61.2, 60.8, 26.0, 24.3, 18.5, and -5.2.

IR (neat): 2953, 2930, 2857, 2360, 2231, 1683, 1469, 1255, 1108, 909, 839, and 779 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{15}H_{22}NaO_2Si^+$ [M+Na^+] requires 285.1281; found 285.1297.

TLC: R_f 0.5 (9:1 Hex/EtOAc).

(*Z*)-2,2,3,3,20,20,21,21-Octamethyl-4,19-dioxa-3,20-disiladocosa-11-en-6,8,13,15-tetrayn-10-ol (13)



n-BuLi (0.24 mL, 2.5 M in hexanes, 0.60 mmol) was added to a stirred solution of *tert*-butyldimethyl(penta-2,4-diyn-1-yloxy)silane[5] (118 mg, 0.61 mmol) in THF (2 mL) under N_2 and at 0 ºC. After 1 h a solution of aldehyde **S3** (78 mg, 0.30 mmol) in THF (3 mL) was added dropwise. After 1 h satd. aq. NH_4Cl was added and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 6:1) gave the propargylic alcohol **13** (120 mg, 0.26 mmol, 88%) as a clear yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.65 (dd, *J*= 8.8, 10.6 Hz, 1H, =C(*H*)CHOH), 5.67 (dddd, *J*= 1.0, 1.0, 1.0, 10.6 Hz, 1H, =C(*H*)C≡), 5.44 (br dd, *J* = 3.3, 8.7 Hz, 1H, C*H*OH), 4.38 (br s, 2H, ≡CCH_2OSi), 3.77 (t, *J* = 7.0 Hz, 2H, CH_2CH_2OSi), 2.56 (dt, *J* = 1.1, 7.0 Hz, 2H, ≡CCH_2), 2.13 (br d, *J* =4.5 Hz, O*H*), 0.90 [s, 18H, C(CH_3)$_3$], 0.12 [s, 6H, Si(CH_3)$_2$], and 0.08 [s, 6H, Si(CH_3)$_2$].

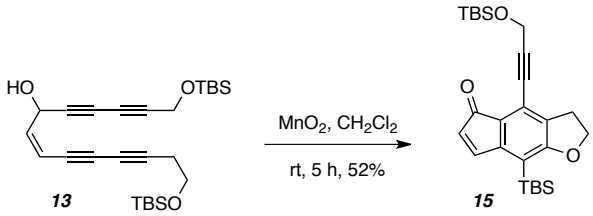
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.4, 111.5, 84.0, 81.3, 79.3, 70.3, 69.8, 68.8, 66.0, 65.9, 61.4, 60.8, 52.2, 26.0, 25.9, 24.2, 18.5, 18.4, -5.1, and -5.2.

IR (neat): 3402, 2954, 2930, 2857, 2236, 1468, 1364, 1256, 1093, 838, and 780 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{41}O_3Si_2^+$ [M+H^+] requires 455.2589; found 455.2570.

TLC: R_f 0.4 (6:1 Hex/EtOAc).

8-(*tert*-Butyldimethylsilyl)-4-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-2*H*-indeno[5,6-*b*]furan-5(3*H*)-one (15)



MnO_2 (195 mg, 2.2 mmol) was added to a solution of alcohol **13** (40 mg, 0.088 mmol) in CH_2Cl_2 (1 mL) and this black heterogeneous mixture was vigorously stirred at room temperature. After 5 h the reaction mixture was filtered through a plug of silica gel (CH_2Cl_2 eluent). Purification by flash chromatography (hexanes:EtOAc 9:1) gave the tricyclic indenone **15** (21 mg, 0.046 mmol, 52%) as a golden yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 6.1 Hz, 1H, *H3*), 5.83 (d, *J* = 6.1 Hz, 1H, *H2*), 4.64 (s, 2H, CH_2OSi), 4.58 (t, *J* = 9.0 Hz, 2H, ArOCH_2), 3.17 (t, *J* = 9.0 Hz, 2H, ArCH_2), 0.94 [s, 9H, C(CH_3)$_3$], 0.90 [s, 9H, C(CH_3)$_3$], 0.36 [s, 6H, C_{Ar}Si(CH_3)$_2$], and 0.19 [s, 6H, CH_2Si(CH_3)$_2$].

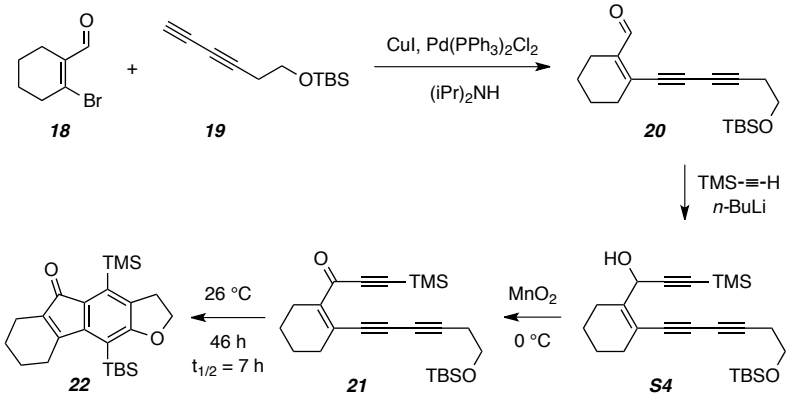
^{13}C NMR (125 MHz, $CDCl_3$): δ 195.7, 169.5, 154.2, 148.0, 127.5, 122.4, 117.6, 116.4, 97.0, 80.4, 79.5, 71.6, 52.6, 28.7, 26.6, 26.0, 18.5, 17.9, -2.3, and -4.9.

IR (neat): 2954, 2927, 2855, 1704, 1595, 1534, 1461, 1384, 1326, 1252, 1121, 1085, 836, and 780 cm^{-1}.

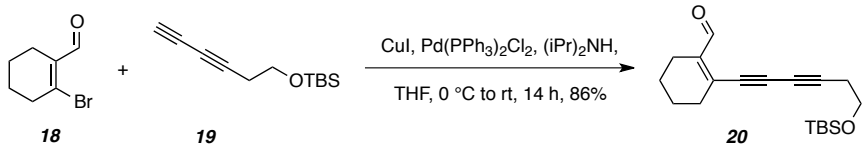
HRMS (ESI-TOF): Calcd for $C_{26}H_{39}O_3Si_2^+$ [M+H$^+$] requires 455.2432; found 455.2463.

TLC: R_f 0.4 (19:1 Hex/EtOAc).

Synthesis of indenone 22 (Figure 2B of manuscript)



2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)cyclohex-1-enecarboxaldehyde (20)



CuI (29 mg, 0.15 mmol) and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) were added to a stirred solution of 2-bromo-1-cyclohexene-1-carboxaldehyde[6] (**18**, 188 mg, 0.99 mmol), diyne **19** (250 mg, 1.20 mmol), and freshly deaerated diisopropylamine (3.0 mL, 21 mmol) in THF (5 mL) at 0 ºC and under an atmosphere of N_2. After 1 h the ice-bath was removed and the reaction mixture was allowed to warm to rt. After 14 h the reaction mixture was diluted in Et_2O and washed with satd. aq. NH_4Cl. The aqueous phase was extracted with Et_2O and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by MPLC (hexanes:EtOAc 15:1) gave the diyne **20** (269 mg, 0.85 mmol, 86%) as a clear brown oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.11 (s, 1H, C*H*O), 3.78 (t, *J* = 6.9 Hz, 2H, OSiCH_2), 2.58 (t, *J* = 6.9 Hz, 1H, ≡CCH_2), 2.40 (nfom, 2H, =C-CH_2), 2.27 (nfom, 2H, =C-CH_2), 1.65 [nfom, 4H, $CH_2(CH_2)_2CH_2$], 0.90 [s, 9H, $C(CH_3)_3$], and 0.08 [s, 6H, $Si(CH_3)_2$].

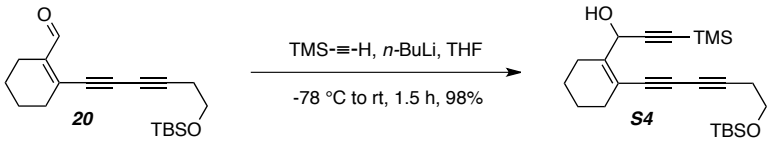
^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3, 146.3, 138.8, 85.7, 83.5, 71.7, 65.9, 61.3, 32.2, 26.0, 24.3, 22.4, 21.9, 21.0, 18.5, and -5.2.

IR (neat): 2933, 2858, 2232, 1677, 1255, 1220, 1108, 839, and 779 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{28}NaO_2Si^+$ [M+Na^+] requires 339.1751; found 339.1774.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

1-(2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)cyclohex-1-en-1-yl)-3-(trimethylsilyl)prop-2-yn-1-ol (S4)



n-BuLi (800 µL, 2.5 M in hexanes, 2.0 mmol) was added to a stirred solution of ethynyltrimethylsilane (350 µL, 2.5 mmol) in THF (2.3 mL) at -78 ºC. After 1 h a solution of diyne **20** (399 mg, 1.26 mmol) in THF (1.7 mL) was added and the reaction mixture was allowed to warm to rt. After 30 min satd. aq. NH_4Cl was added and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The crude product triynol **S4** (508 mg, 1.23 mmol, 98%) was a clear red oil and used directly in the next reaction.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.58 (d, J = 4.2 Hz, 1H, C*H*OH), 3.76 (t, J = 7.1 Hz, 2H, SiOCH_2), 2.55 (t, J = 7.1 Hz, 2H, ≡CCH_2), 2.33 (nfom, 2H, =C-CH_2), 2.19 (nfom, 2H, =C-CH_2), 1.94 (d, J = 4.5 Hz, 1H, O*H*), 1.64 (nfom, 4H, $CH_2(CH_2)_2CH_2$), 0.90 [s, 9H, SiC(CH_3)$_3$], 0.18 [s, 9H, Si(CH_3)$_3$], and 0.08 [s, 6H, Si(CH_3)$_2$C].

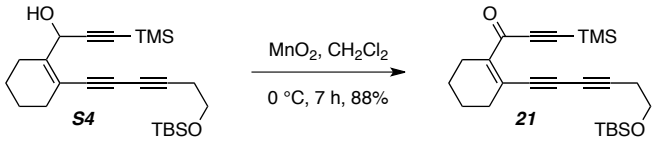
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 117.9, 104.1, 90.7, 82.5, 78.3, 73.7, 66.3, 64.7, 61.6, 30.0, 26.0, 24.2, 23.7, 22.2, 21.9, 18.5, 0.0, and -5.2.

IR (neat): 3409, 2933, 2859, 2171, 1251, 1106, 842, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{24}H_{38}NaO_2Si_2^+$ [M+Na$^+$] requires 437.2303; found: 437.2306.

TLC: R_f 0.3 (9:1 Hex/EtOAc).

1-(2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)cyclohex-1-en-1-yl)-3-(trimethylsilyl)prop-2-yn-1-one (21)



MnO_2 (267 mg, 3.07 mmol) was added in two portions to a stirred solution of alcohol **S4** (41 mg, 0.099 mmol) in CH_2Cl_2 (0.5 mL) at 0 ºC. After 7 h the reaction mixture was filtered through Celite® (Et_2O eluent) and concentrated at 0 ºC to give ketone **21** (36 mg, 0.087 mmol, 88%) as a clear amber oil. Because of the high reactivity of this ketone (toward conversion to **22**) at ambient temperature this sample was characterized without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (t, J = 7.2 Hz, 2H, SiOCH_2), 2.57 (t, J = 7.2 Hz, 2H, ≡CCH_2), 2.37-2.44 (m, 4H, =C-CH_2), 1.61-1.66 (m, 4H, $CH_2(CH_2)_2CH_2$), 0.90 [s, 9H, SiC(CH_3)$_3$], 0.27 [s, 9H, Si(CH_3)$_3$], and 0.07 [s, 6H, Si(CH_3)$_2$C].

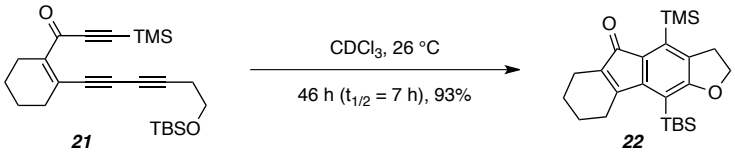
^{13}C NMR (125 MHz, $CDCl_3$): δ 177.4, 144.4, 131.4, 102.4, 101.4, 85.8, 85.3, 74.3, 67.1, 61.5, 33.4, 26.0, 25.6, 24.3, 21.9, 21.6, 18.4, -0.4, and -5.2.

IR (neat): 2953, 2933, 2859, 2228, 2151, 1612, 1250, 1106, and 844 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{24}H_{36}NaO_2Si_2^+$ [M+Na$^+$] requires 435.2146; found 435.2154.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

10-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)-6,7,8,9-tetrahydro-2*H*-fluoreno[3,2-*b*]furan-5(3*H*)-one (22)



A solution of ketone **21** (29 mg, 0.070 mmol) in $CDCl_3$ (2 mL) was kept at 26 ºC (external bath temperature). After 46 h the reaction mixture was concentrated and purified by flash chromatography (hexanes:EtOAc 15:1) to give the benzenoid **22** (27 mg, 0.066 mmol, 93%) as a clear amber oil. Reaction progress was monitored by ^{1}H NMR spectroscopy, and the spectral data for a series of time points are presented in Fig. S1 (page 6).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.42 (t, *J* = 8.9 Hz, 2H, OC*H*$_2$), 3.15 (t, *J* = 8.9 Hz, 2H, OCH$_2$C*H*$_2$), 2.49 (nfom, 2H, =C-C*H*$_2$), 2.23 (nfom, 2H, =C-C*H*$_2$), 1.69 (nfom, 4H, CH$_2$(C*H*$_2$)$_2$CH$_2$), 0.98 [s, 9H, SiC(C*H*$_3$)$_3$], 0.36 [s, 6H, Si(C*H*$_3$)$_2$C], and 0.33 [s, 9H, Si(C*H*$_3$)$_3$].

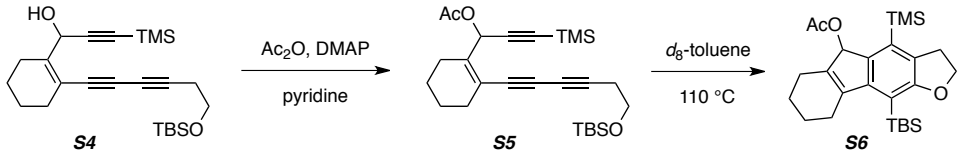
^{13}C NMR (125 MHz, $CDCl_3$): δ 198.2, 169.1, 157.6, 154.9, 136.2, 133.9, 130.6, 128.2, 115.7, 70.2, 31.3, 28.1, 27.5, 23.2, 21.5, 20.2, 18.9, 1.6, and 1.5.

IR (neat): 2929, 2856, 1737, 1370, 1301, 1255, 1225, 1015, 838, 810, and 760 cm^{-1}.

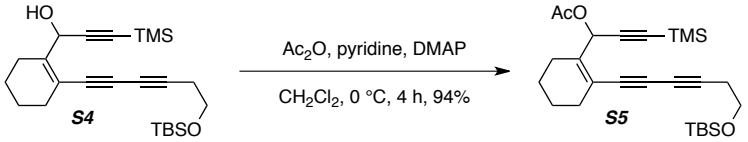
HRMS (ESI-TOF): Calcd for $C_{24}H_{36}NaO_2Si_2^+$ [M+Na$^+$] requires 435.2146; found 435.2126.

TLC: R_f 0.6 (9:1 Hex/EtOAc).

Synthesis of indenoacetate S6 (Fig. 3, entry 1 of manuscript)



1-(2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)cyclohex-1-en-1-yl)-3-(trimethylsilyl)prop-2-yn-1-yl acetate (S5)



Acetic anhydride (26 mg, 0.25 mmol) was added to a stirred solution of alcohol **S4** (21 mg, 0.051 mmol), pyridine (0.50 mL, 6.2 mmol), and DMAP (1 mg, 0.008 mmol) in CH_2Cl_2 (2 mL) at 0 ºC. After 4 h the reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The crude material was passed through a plug of silica gel with (hexanes:EtOAc 19:1 eluent) to give the acetate **S5** (22 mg, 0.048 mmol, 94%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.46 (s, 1H, C*H*OAc), 3.76 (t, *J* = 7.2 Hz, 2H, SiOCH_2), 2.55 (t, *J* = 7.2 Hz, 2H, ≡CCH_2), 2.39 [br d, *J*= 19 Hz, 1H,CH_aH$_b$C(CHOAc)=C], 2.20 [m, 3H, CH_aH$_b$C(CHOAc)=C and CH_2C=], 2.08 [s, 3H, C(=O)CH_3], 1.63 (nfom, 4H, CH_2(CH_2)$_2$CH_2), 0.90 [s, 9H, SiC(CH_3)$_3$], 0.17 [s, 9H, Si(CH_3)$_3$], and 0.08 [s, 6H, Si(CH_3)$_2$C].

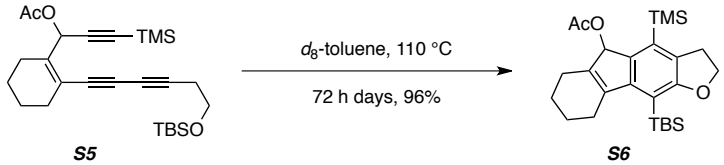
^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 142.6, 119.6, 100.9, 91.2, 82.7, 80.4, 78.9, 73.1, 66.2, 61.6, 30.1, 26.0, 24.4, 24.2, 22.0, 21.9, 21.2, 18.5, -0.1, and -5.2.

IR (neat): 2933, 2859, 2177, 1750, 1251, 1223, 1108, 1019, 947, 843, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{40}NaO_3Si_2^+$ [M+Na$^+$] requires 479.2408; found 479.2390.

TLC: R_f 0.5 (9:1 Hex/EtOAc).

10-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)-3,5,6,7,8,9-hexahydro-2*H*-fluoreno[3,2-*b*]furan-5-yl acetate (S6, entry 1, Fig. 3 of manuscript)



A solution of triyne **S5** (28 mg, 0.061 mmol) in d_8-toluene (0.6 mL) was heated at 110 ºC (external bath temperature) in a sealed tube. After 72 h the solvent was evaporated and the crude residue was purified by flash chromatography (hexanes:EtOAc 49:1) to give the benzenoid **S6** (27 mg, 0.059 mmol, 96%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.08 (d, *J* = 1.4 Hz, 1H, C*H*OAc), 4.47 (ddd, *J* =5.6 ,8.4, 10.0 Hz, 1H,OCH_aH$_b$), 4.30 (ddd, *J* = 9.0, 9.0, 9.0 Hz, 1H, OCH$_a$$H_b$), 3.27 (ddd, *J* = 9.7, 9.7, 15.1 Hz, 1H, ArCH_aH$_b$), 3.05 (ddd, *J* = 5.6, 9.4, 15.1 Hz, 1H, ArCH$_a$$H_b$), 2.49 [br d, *J* = 16.5 Hz, 1H,

$CH_aH_bC(CHOAc)=C$], 2.36–2.47 [m, 3H, $CH_aH_bC(CHOAc)=C$ and $CH_2C=$], 2.15 [s, 3H, $C(=O)CH_3$], 1.5–1.8 [m, 4H, $CH_2(CH_2)_2CH_2$], 0.99 [s, 9H, $SiC(CH_3)_3$], 0.344 [s, 6H, $Si(CH_3)$], 0.340 [s, 6H, $Si(CH_3)_2C$], and 0.33 [s, 9H, $Si(CH_3)_3$].

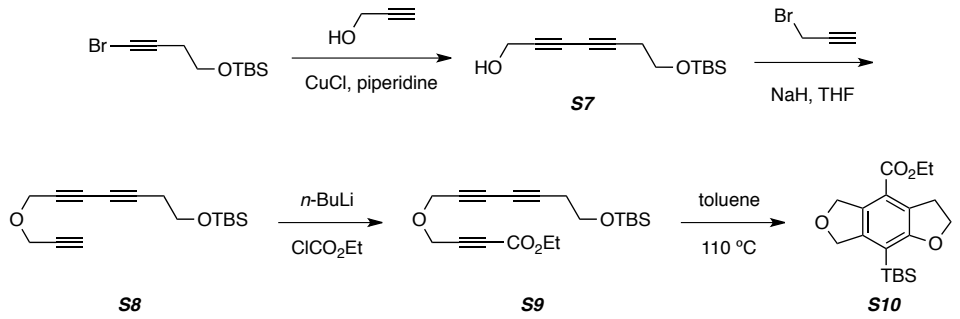
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 166.6, 151.3, 141.6, 141.5, 139.5, 132.8, 127.5, 113.4, 78.6, 69.7, 31.7, 28.4, 26.9, 25.5, 23.2, 22.5, 22.0, 19.1, 1.8, 1.4, and 1.2.

IR (neat): 2929, 2856, 1737, 1370, 1301, 1255, 1225, 1015, 838, and 810 cm^{-1}.

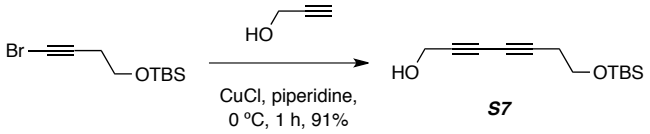
HRMS (ESI-TOF): Calcd for $C_{26}H_{40}NaO_3Si_2^+$ [$M+Na^+$] requires 479.2408; found 479.2414.

TLC: R_f 0.52 (9:1 Hex/EtOAc).

Synthesis of benzodifuran S10 (Fig. 3, entry 2 of manuscript)



7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-ol (S7)



Diyne **S7** was prepared following general procedure B from ((4-bromobut-3-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane[7] (1.00 g, 3.82 mmol), propargyl alcohol (260 mg, 4.6 mmol), CuCl (40 mg, 0.40 mmol), and piperidine (4 mL). Purification by flash chromatography (hexanes:EtOAc 5:1) gave the diyne **S7** (828 mg, 3.48 mmol, 91%) as a pale yellow oil.

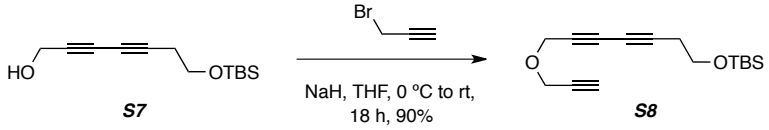
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.32 (dt, *J* = 6.3, 1.1 Hz, 2H, C*H*$_2$OH), 3.74 (t, *J* = 6.9 Hz, 2H, C*H*$_2$OSi), 2.50 (dt, *J* = 6.9, 1.1 Hz, 2H, C≡CC*H*$_2$CH$_2$), 1.55 (t, *J* = 6.3 Hz, 1H, CH$_2$O*H*), 0.90 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.08 [s, 6H, Si(C*H*$_3$)$_2$].

^{13}C NMR (500 MHz, $CDCl_3$): δ 78.9, 73.9, 70.9, 65.6, 61.4, 51.7, 26.0, 23.9, 18.5, and -5.2.

IR (neat): 3450, 2953, 2930, 2857, 2359, 2258, 1470, 1387, 1255, 1106, 913, 838, 778, and 746 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{13}H_{22}NaO_2Si^+$ [M+Na$^+$] requires 261.1281; found 261.1301.

tert-Butyldimethyl((7-(prop-2-yn-1-yloxy)hepta-3,5-diyn-1-yl)oxy)silane (S8)



A solution of diyne **S7** (200 mg, 0.84 mmol) in THF (2 mL) was added to a stirred suspension of NaH (67 mg, 60% suspension in mineral oil, 1.68 mmol) in THF (10 mL) at 0 ºC. The reaction mixture was allowed to warm to rt over 1 h and propargyl bromide (0.19 mL, 80 wt. % in toluene, 1.71 mmol) was added. After 18 h the mixture was cooled to 0 ºC, water was added, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 20:1) gave the triyne **S8** (210 mg, 0.76 mmol, 90%) as a clear yellow oil.

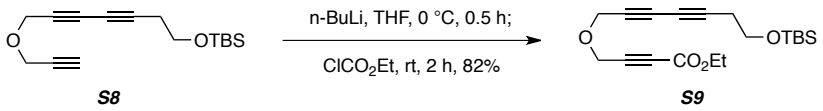
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.32 (t, *J* = 1.1 Hz, 2H, C≡CC≡CC*H*$_2$O), 4.25 (d, *J* = 2.4 Hz, 2H, OC*H*$_2$C≡CH), 3.74 (t, *J* = 7.0 Hz, 2H, C*H*$_2$OSi), 2.50 (tt, *J* = 1.0, 7.0 Hz, C*H*$_2$CH$_2$OSi) 2.46 (t, *J* = 2.4 Hz, 1H, ≡C*H*), 0.90 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.08 [s, 6H, Si(C*H*$_3$)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 78.8, 78.6, 75.3, 72.0, 71.1, 65.6, 61.4, 57.1, 56.6, 26.0, 23.8, 18.4, and -5.2.

IR (neat): 3300, 2953, 2931, 2857, 2258, 1470, 1385, 1346, 1255, 1085, 839, and 779 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{16}H_{24}NaO_2Si^+$ [M+Na^+] requires 299.1438; found 299.1422.

Ethyl 4-((7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl)oxy)but-2-ynoate (S9)



S8 ***S9***

n-BuLi (0.25 mL, 2.5 M in hexanes, 0.62 mmol) was added to a stirred solution of triyne **S8** (170 mg, 0.62 mmol) in THF (5 mL) at 0 ºC. After 0.5 h ethyl chloroformate (0.24 mL, 2.5 mmol) was added and the resulting solution was allowed to come to room temperature. After 2 h satd. aq. NH_4Cl was added and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by MPLC (hexanes:EtOAc 7:1) gave the triyne **S9** (178 mg, 0.51 mmol, 82%) as a clear amber oil.

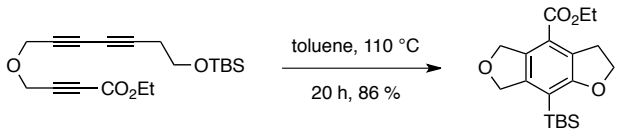
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.39 (s, 2H, CH_2C≡CCO$_2$Et), 4.33 (t, J = 1.0 Hz, 2H, C≡CC≡CCH_2O), 4.25 (q, J = 7.2 Hz, 2H, CH_2CH$_3$), 3.75 (t, J = 6.9 Hz, 2H, CH_2OSi), 2.50 (tt, J = 1.0, 6.9 Hz, ≡CCH_2CH$_2$) 1.32 (t, J = 7.2 Hz, 3H, CH$_2$CH_3), 0.90 [s, 9H, SiC(CH_3)$_3$], and 0.08 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 82.2, 79.0, 78.8, 72.6, 70.4, 65.5, 62.3, 61.4, 57.7, 56.2, 26.0, 23.8, 18.4, 14.1, and -5.2.

IR (neat): 2953, 2931, 2857, 2255, 1716, 1249, 1097, 1059, 839, and 780 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{28}NaO_4Si^+$ [M+Na^+] requires 371.1649; found 371.1679.

Ethyl 8-(*tert*-Butyldimethylsilyl)-2,3,5,7-tetrahydrobenzo[1,2-*b*:4,5-*c′*]difuran-4-carboxylate (S10, entry 2, Fig. 3 of manuscript)



S9 ***S10***

A solution of triyne **S9** (23 mg, 0.066 mmol) in toluene (3 mL) was heated at 110 ºC (external bath temperature) in a sealed tube. After 20 h the mixture was concentrated and purified by MPLC (hexanes:EtOAc 7:1) to give the tricyclic ester **S10** (20 mg, 0.057 mmol, 86%) as a clear yellow oil.

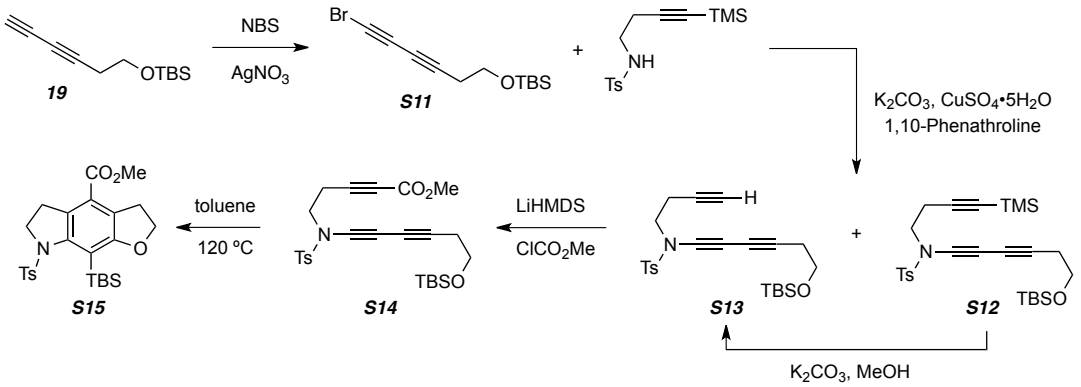
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.27 (br t, J = 2.2 Hz, 2H, OCH_2C$_{Ar}$=C$_{Ar}$CO), 5.06 (br s, 2H, OCH_2C$_{Ar}$=C$_{Ar}$Si), 4.53 (t, J = 8.8 Hz, 2H, CH$_2$CH_2O), 4.34 (q, J = 7.1 Hz, 2H, CH_2CH$_3$), 3.49 (br t, J = 8.8 Hz, 2H, CH_2CH$_2$O), 1.38 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 0.90 [s, 9H, SiC(CH_3)$_3$], and 0.31 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 166.3, 146.5, 132.0, 127.9, 122.1, 116.2, 74.7, 74.5, 71.2, 61.0, 31.0, 26.8, 18.6, 14.5, and -3.4.

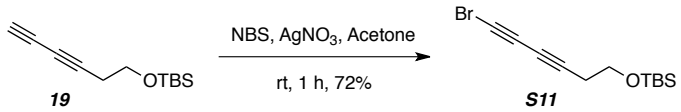
IR (neat): 2953, 2923, 2856, 1715, 1464, 1387, 1256, 1186, and 1038 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{28}NaO_4Si^+$ [M+Na^+] requires 371.1649; found 371.1674.

Synthesis of indoline S15 (Fig. 3, entry 3 of manuscript)



((6-Bromohexa-3,5-diyn-1-yl)oxy)*tert*-butyl)dimethylsilane (S11)



Bromoalkyne **S11** was prepared following general procedure A from diyne **19** (211 mg, 1.01 mmol), *N*-bromosuccinimide (NBS, 196 mg, 1.11 mmol), $AgNO_3$ (19 mg, 0.11 mmol), and acetone (10 mL). Purification by flash chromatography (hexanes:EtOAc 19:1) gave the bromodiyne **S11** (201 mg, 0.735 mmol, 72%) as a clear yellow oil.

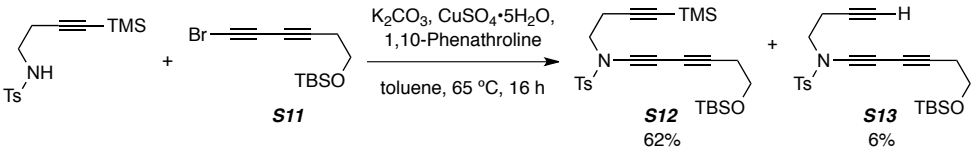
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (t, *J* = 6.8 Hz, 2H, OCH_2), 2.46 (t, *J* = 6.9 Hz, 2H, C≡CCH_2), 0.89 [s, 9H, SiC(CH_3)$_3$], and 0.07 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 74.5, 66.6, 65.8, 64.9, 61.4, 26.0, 23.7, 18.4, and -5.2.

IR (neat): 2953, 2930, 2857, 2224, 2144, 1469, 1386, 1255, 1107, 908, 836, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{12}H_{19}AgBrOSi^+$ [M+Ag$^+$] requires 392.9434; found 392.9435.

N-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)-4-methyl-*N*-(4-(trimethylsilyl)but-3-yn-1-yl)benzenesulfonamide (S12)



A solution of 4-methyl-*N*-(4-(trimethylsilyl)but-3-yn-1-yl)benzenesulfonamide[8] (200 mg, 0.680 mmol), **S11** (230 mg, 0.8 mmol), K_2CO_3 (190 mg, 1.4 mmol), $CuSO_4{\cdot}5H_2O$ (17 mg, 0.068 mmol), and 1,10-phenanthroline (22 mg, 0.14 mmol) in anhydrous toluene (1 mL) was heated to 65 ºC. After 16 h the reaction mixture was directly subjected to gradient flash chromatography (hexanes:EtOAc 12:1 to 5:1) to yield, in order of elution, the triynes **S12** (210 mg, 0.420 mmol, 62%) and **S13** (19 mg, 6%, 0.0378), each as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H, SO_2ArH_o), 7.36 (d, *J* = 8.2 Hz, 2H, SO_2ArH_m), 3.74 (t, *J* = 7.1 Hz, 2H, OCH_2), 3.49 (d, *J* = 7.7 Hz, 2H, NCH_2), 2.54 (t, *J* = 7.9 Hz, 2H, NCH$_2$CH_2),

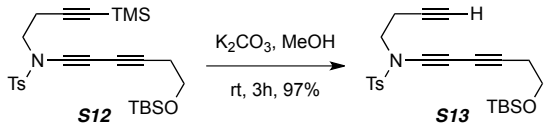
2.52 (t, J = 7.1 Hz, 2H, OCH_2CH_2), 2.46 (s, 3H, $ArCH_3$), 0.90 [s, 9H, $SiC(CH_3)_3$], 0.13 [s, 9H, $Si(CH_3)_3$], and 0.08 [s, 6H, $Si(CH_3)_2C$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 134.8, 130.1, 127.7, 101.7, 87.6, 81.4, 67.2, 65.6, 61.6, 59.0, 50.4, 26.0, 24.1, 21.8, 20.0, 18.5, 0.1, and -5.2.

IR (neat): 2955, 2930, 2857, 2253, 2228, 2179, 1598, 1469, 1376, 1252, 1172, 1105, and 842 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{39}NNaO_3SSi_2^+$ [M+Na^+] requires 524.2081; found 524.2088.

N-(But-3-yn-1-yl)-*N*-(6-((*tert*-butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)-4-methylbenzenesulfonamide (S13)



K_2CO_3 (62 mg, 0.44 mmol) was added to a stirred solution of **S12** (112 mg, 0.22 mmol) in MeOH (8 mL) at room temperature. After 3 h the reaction mixture was concentrated and purified by flash chromatography (hexanes:EtOAc 5:1) to yield **S13** (90 mg, 97%) as pale yellow oil.

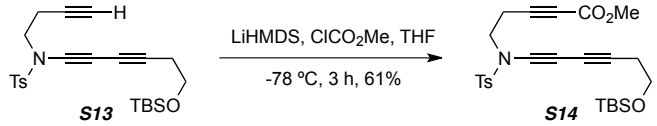
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H, SO_2ArH_o), 7.36 (d, J = 8.1 Hz, 2H, SO_2ArH_m), 3.74 (t, J = 7.1 Hz, 2H, OCH_2), 3.50 (t, J = 7.5 Hz, 2H, NCH_2), 2.52 (t, J = 7.0 Hz, 2H, OCH_2CH_2), 2.51 (td, J = 7.4, 2.7 Hz, 2H, NCH_2CH_2), 2.46 (s, 3H, $ArCH_3$), 1.97 (t, J = 2.6 Hz, 1H, C≡CH), 0.90 [s, 9H, $SiC(CH_3)_3$], and 0.08 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 145.3, 134.6, 130.1, 127.8, 81.5, 79.5, 70.9, 66.9, 65.5, 61.6, 59.2, 50.2, 26.0, 24.1, 21.8, 18.54, 18.47, and -5.1.

IR (neat): 3297, 2953, 2930, 2857, 2360, 2340, 2254, 2166, 1597, 1468, 1373, 1255, 1171, 1092, 903, and 839 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{31}NNaO_3SSi^+$ [M+Na^+] requires 452.1686; found 452.1687.

Methyl 5-(*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)-4-methylphenylsulfonamido)pent-2-ynoate (S14)



LiHMDS [0.15 mL, ca. 1.0 M in THF, 0.15 mmol, prepared by addition of *n*-BuLi (2.0 mL, 2.5 M in hexanes, 5.0 mmol) to a stirred solution of HMDS (1.0 mL, 4.8 mmol) in THF (2 mL) at -78 ºC] was added to a stirred solution of **S13** (43 mg, 0.10 mmol) in THF (1 mL) at -78 ºC. After 1 h methyl chloroformate was added at the same temperature. After an additional 2 h the reaction mixture was quenched with satd. aq. NH_4Cl, diluted with H_2O, and washed with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated. Purification by flash chromatography (hexanes:EtOAc 5:1) gave the ynoate **S14** (30 mg, 61%) as a pale yellow oil and recovered starting material **S13** (11 mg, 26%).

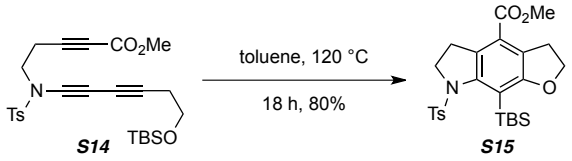
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H, SO_2ArH_o), 7.37 (d, J = 8.1 Hz, 2H, SO_2ArH_m), 3.76 (s, 3H, CO_2Me), 3.74 (t, J = 7.1 Hz, 2H, OCH_2), 3.55 (t, J = 7.5 Hz, 2H, NCH_2), 2.67 (t, J = 7.9 Hz, 2H, NCH_2CH_2), 2.53 (t, J = 7.0 Hz, 2H, OCH_2CH_2), 2.46 (s, 3H, $ArCH_3$), 0.90 [s, 9H, $SiC(CH_3)_3$], and 0.08 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8, 145.5, 134.4, 130.2, 127.8, 84.1, 81.8, 74.7, 66.5, 65.4, 61.6, 59.6, 52.9, 49.2, 26.0, 24.1, 21.9, 18.8, 18.5, and -5.1.

IR (neat): 2953, 2930, 2857, 2247, 2166, 1717, 1597, 1463, 1435, 1373, 1256, 1171, 1090, and 839 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{25}H_{33}NNaO_5SSi^+$ [M+Na^+] requires 510.1741; found 510.1779.

Methyl 8-(*tert*-Butyldimethylsilyl)-7-toluenesulfonyl -3,5,6,7-tetrahydro-2*H*-furo[3,2-f]indole-4-carboxylate (S15, entry 3, Fig. 3 of manuscript)



S14 ***S15***

A solution of **S14** (15 mg, 0.031 mmol) in toluene (3 mL) in a sealed vial was heated to 120 ºC (external bath temperature) in a sealed tube. After 18 h the reaction mixture was cooled and concentrated. Purification by flash chromatography (hexanes:EtOAc 5:1) gave the tricycle **S15** (12 mg, 0.025, 80%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.3 Hz, 2H, $SO_2Ar\mathit{H}_o$), 7.12 (d, *J* = 8.6 Hz, 2H, $SO_2Ar\mathit{H}_m$), 4.64 (ddd, *J* = 8.9, 8.9, 7.9 Hz, 1H, $OC\mathit{H}_aH_b$), 4.53 (ddd, *J* = 9.7, 8.7, 8.7 Hz, 1H, $OCH_a\mathit{H}_b$), 4.02 (ddd, *J* = 13.1, 8.0, 1.1 Hz, 1H, $NC\mathit{H}_aH_b$), 3.77 (s, 3H, $CO_2\mathit{Me}$), 3.71 (ddd, *J* = 13.2, 11.8, 8.5 Hz, 1H, $NCH_a\mathit{H}_b$), 3.46 (br t, *J* = 9 Hz, 2H, $OCH_2C\mathit{H}_2$), 2.60 (ddd, *J* = 16.9, 8.5, 1.0 Hz, 1H, $NCH_2C\mathit{H}_aH_b$), 2.37 (s, 3H, Ar*Me*), 1.74 (ddd, *J* = 16.9, 11.8, 8.0 Hz, 1H, $NCH_2CH_a\mathit{H}_b$), 0.95 [s, 9H, $SiC(C\mathit{H}_3)_3$], 0.54 (s, 3H, $SiC\mathit{H}_3$), and 0.41 (s, 3H, $SiC\mathit{H}_3$).

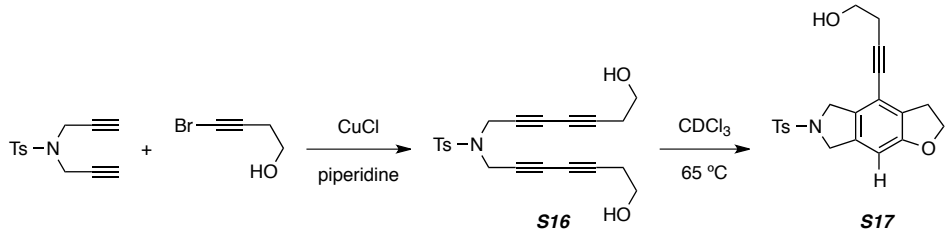
^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 166.1, 148.8, 144.1, 134.1, 131.0, 129.4, 128.2, 126.5, 123.0, 120.5, 70.9, 51.8, 51.7, 31.3, 29.1, 28.6, 21.7, 18.1, -0.9, and -1.9.

IR (neat): 2952, 2928, 2896, 2854, 1718, 1597, 1564, 1456, 1385, 1252, 1163, 1089, 1065, 1049, 1011, and 739 cm^{-1}.

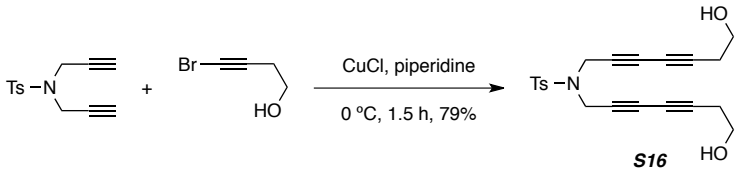
HRMS (ESI-TOF): Calcd for $C_{25}H_{33}NO_5SSi^+$ [M+H^+] requires 488.1921; found 488.1953.

mp: 144-147 ºC.

Synthesis of isoindoline S17 (Fig. 3, entry 4 of manuscript)



N,N-Bis(7-hydroxyhepta-2,4-diyn-1-yl)-4-methylbenzenesulfonamide (S16)



Tetrayne **S16** was prepared following **GP-2** from 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide[9] (247 mg, 1.0 mmol), 4-bromo-3-butyn-1-ol[10] (326 mg, 2.19 mmol), CuCl (20 mg, 0.20 mmol), and piperidine (2 mL). Purification by flash chromatography (EtOAc 100%) gave the tetrayne **S16** (302 mg, 0.79 mmol, 79%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H, $SO_2Ar\mathit{H}_o$), 7.34 (dd, J = 0.7, 8.6 Hz, 2H, $SO_2Ar\mathit{H}_m$), 4.18 (d, J = 0.6 Hz, 4H, $NC\mathit{H}_2$), 3.73 (t, J = 6.2 Hz, 4H, $C\mathit{H}_2OH$), 2.52 (t, J = 6.2 Hz, 4H, $C\mathit{H}_2CH_2OH$), 2.44 (s, 3H, $C\mathit{H}_3$), and 1.99 (br s, 2H, O*H*).

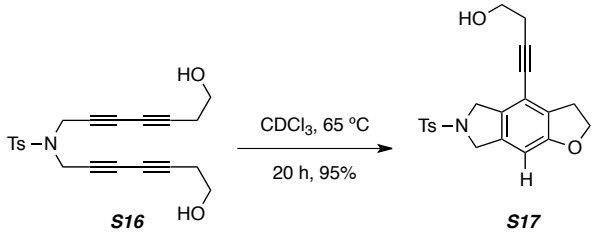
^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 134.6, 129.8, 127.9, 77.7, 70.8, 68.7, 65.9, 60.6, 37.4, 23.6, and 21.7.

IR (neat): 3349, 2943, 2888, 2258, 1597, 1420, 1348, 1160, 1045, and 750 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{21}NNaO_4S^+$ [$M+Na^+$] requires 406.1083; found 406.1072

TLC: R_f 0.4 (1:2 Hex/EtOAc).

4-(6-Toluenesulfonyl-3,5,6,7-tetrahydro-2*H*-furo[2,3-f]isoindol-4-yl)but-3-yn-1-ol (S17, entry 4, Fig. 3 of manuscript)



A solution of tetrayne **S16** (20 mg, 0.052 mmol) in $CDCl_3$ (0.6 mL) was heated at 65 ºC. After 20 h the reaction mixture was concentrated and the residue purified by flash chromatography (hexanes:EtOAc 1:1) to give the isoindole **S17** (19 mg, 0.050 mmol, 95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H, $SO_2Ar\mathit{H}_o$), 7.32 (d, J = 8.2 Hz, 2H, $SO_2Ar\mathit{H}_m$), 6.48 (s, 1H, Ar*H*), 4.57 (t, J = 8.7 Hz, 2H, $C\mathit{H}_2OAr$), 4.55 (s, 2H, $NC\mathit{H}_2$), 4.53 (s, 2H, $NC\mathit{H}_2$), 3.82

(br dt, J = 5, 5 Hz, 2H, CH_2OH), 3.17 (t, J = 8.7 Hz, 2H, CH_2CH$_2$OAr), 2.73 (t, J = 6.4 Hz, 2H, CH_2CH$_2$OH), 2.41 (s, 3H, CH_3), and 1.80 (br s, 1H, OH).

^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 143.8, 136.0, 134.0, 130.00, 129.98, 129.6, 127.7, 115.2, 103.6, 94.0, (77.0, a singlet with this chemical shift is observed in the spectrum in acetone), 71.9, 61.3, 54.3, 53.4, 29.5, 24.1, and 21.7.

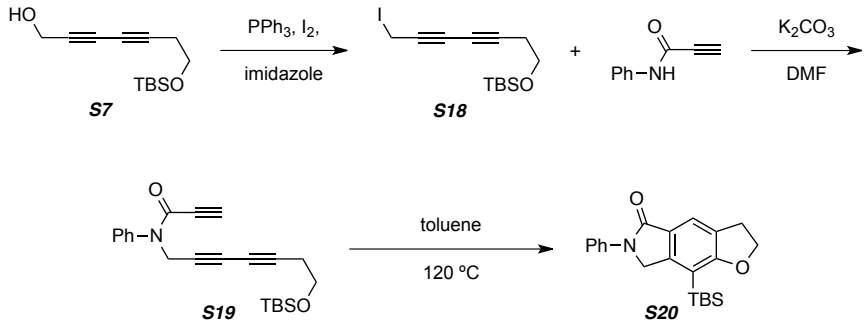
^{13}C NMR [125 MHz, $(CD_3)_2CO$]: 161.2, 144.6, 137.0, 134.9, 130.7, 130.5, 130.3, 128.5, 116.3, 104.1, 96.2, 77.0, 72.4, 61.5, 55.0, 54.0, (29.5, a singlet with this chemical shift is observed in the spectrum in chloroform), 24.5, and 21.4.

IR (neat): 3389, 2939, 2886, 2259, 1598, 1449, 1342, 1160, 1094, 1051, and 816 cm^{-1}.

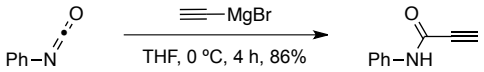
HRMS (ESI-TOF): Calcd for $C_{21}H_{21}NNaO_4S^+$ [M+Na$^+$] requires 406.1083; found 406.1059.

TLC: R_f 0.5 (1:1 Hex/EtOAc).

Synthesis of isoindolinone S20 (Fig. 3, entry 5 of manuscript)

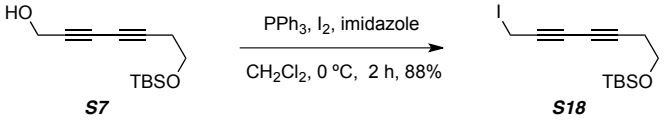


N-Phenylpropiolamide



Ethynylmagnesium bromide (16 mL, 0.5 M in THF, 8 mmol) was added to a stirred solution of phenyl isocyanate (480 mg, 4 mmol) in anhydrous THF (3 mL) under a N_2 atmosphere and at 0 ºC. After 4 h the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with ether. The organic extracts were washed with brine, dried (Na_2SO_4), and concentrated. Purification by flash chromatography (hexanes:EtOAc 7:3) gave *N*-phenylpropiolamide (508 mg, 3.44 mmol, 86%). The spectral data were consistent with reported values.[11]

tert-Butyl((7-iodohepta-3,5-diyn-1-yl)oxy)dimethylsilane (S18)



PPh_3 (120 mg, 0.46 mmol), I_2 (127 mg, 0.50 mmol), and imidazole (57 mg, 0.84 mmol) were sequentially added to a stirred solution of alcohol **S7** (100 mg, 0.42 mmol) in CH_2Cl_2 (2 mL) at 0 °C. After 2 h the reaction mixture was diluted with CH_2Cl_2 and washed with satd. aq. $Na_2S_2O_3$. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated. Purification by flash chromatography (hexanes:EtOAc 12:1) gave the iodide **S18** (128 mg, 0.37 mmol, 88%) as a pale yellow oil.

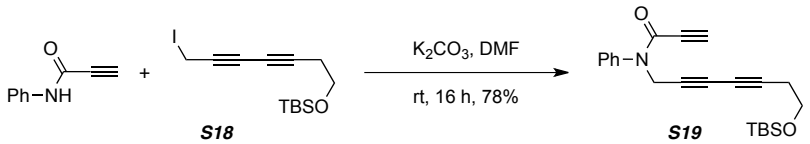
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.739 (t, J = 1.2 Hz, 2H, ICH_2), 3.737 (t, J = 7.0 Hz, 2H, SiOCH_2), 2.49 (tt, J = 7.0, 1.3 Hz, 2H, $SiCH_2CH_2$), 0.89 [s, 9H, $SiC(CH_3)_3$], and 0.07 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, C_6D_6): δ 80.9, 73.8, 71.4, 67.3, 61.9, 26.6, 24.5, 19.0, 4.7, and -18.5.

IR (neat): 2953, 2929, 2856, 2251, 1687, 1469, 1410, 1386, 1361, 1254, 1143, 1104, 1055, 1006, 909, and 838 cm^{-1}.

HRMS (CIMS): Calcd for $C_{13}H_{15}INOSi^+$ [M+NH_4^+] requires 366.0745; found 366.0773.

N-(7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl)-*N*-phenylpropiolamide (S19)



K_2CO_3 (40 mg, 0.29 mmol) was added to a stirred solution of *N*-phenylpropiolamide (23 mg, 0.16 mmol) and iodide **S18** (50 mg, 0.14 mmol) in DMF (1.4 mL) at rt. After 16 h the reaction mixture was concentrated and the residue was purified by flash chromatography (hexanes:EtOAc 5:1) to give the amide **S19** (41 mg, 0.11 mmol, 78%) as a pale yellow oil.

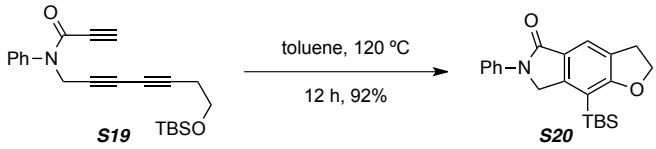
^{1}H NMR (500 MHz, $CDCl_3$, as an 8:1 mixture of rotamers): major rotamer: δ 7.47-7.39 (m, 3H, ArH_mH_p), 7.35 (dd, J = 7.9, 1.7 Hz, 2H, ArH_o), 4.58 (t, J = 1.1 Hz, 2H, ArNCH_2), 3.72 (t, J = 6.9 Hz, 2H, SiOCH_2), 2.83 (s, 1H, C≡CH), 2.46 (tt, J = 6.9, 1.2 Hz, 2H, SiOCH$_2$CH_2), 0.89 [s, 9H, SiC(CH_3)$_3$], and 0.06 [s, 6H, Si(CH_3)$_2$]. Minor rotamer: δ 4.75 (t, J = 1.1 Hz, ArNCH_2), 3.74 (br t, J = 7.0 Hz, SiOCH_2), 2.49 (br t, J = 7.0 Hz, SiOCH$_2$CH_2), and 0.07 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 140.5, 129.5, 129.0, 128.5, 80.5, 77.7, 75.8, 70.1, 69.6, 65.8, 61.4, 38.8, 26.0, 23.8, 18.4, and -5.2.

IR (neat): 3284, 2953, 2929, 2856, 2259, 2110, 1717, 1646, 1594, 1494, 1469, 1384, 1275, 1255, 1220, 1105, and 839.

HRMS (ESI-TOF): Calcd for $C_{22}H_{27}NNaO_2Si^+$ [M+Na$^+$] requires 388.1703; found 388.1736.

8-(*tert*-Butyldimethylsilyl)-6-phenyl-6,7-dihydro-2*H*-furo[2,3-f]isoindol-5(3*H*)-one (S20, entry 5, Fig. 3 of manuscript)



A solution of amide S19 (25 mg, 0.068 mmol) in toluene (2 mL) in a sealed vial was heated to 120 ºC (external bath temperature) in a sealed tube. After 12 h the reaction mixture was concentrated and the residue was purified by flash chromatography (hexanes:EtOAc 4:1) to give the amide **S20** as an (23 mg, 0.063 mmol, 92%) off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.8, 1.2 Hz, 2H, PhH_o), 7.71 (t, J = 1.3 Hz, 1H, ArH), 7.42 (dd, J = 8.7, 7.4 Hz, 2H, PhH_m), 7.15 (tt, J = 7.4, 1.2 Hz, 1H, ArH), 4.76 (s, 2H, ArCH_2N), 4.60 (t, J = 8.7, 2H, OCH_2), 3.25 (br t, J = 8.6 Hz, 2H, ArCH_2CH$_2$O), 0.92 [s, 9H, SiC(CH_3)$_3$], and 0.42 [s, 6H, Si(CH_3)$_2$].

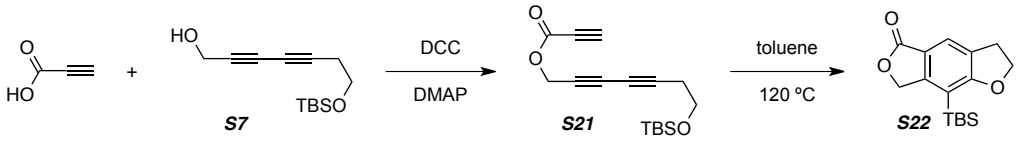
^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 167.7, 147.9, 140.0, 129.3, 127.5, 125.8, 124.0, 121.9, 119.2, 111.7, 71.4, 52.7, 29.0, 26.8, 18.7, and -3.3.

IR (neat): 2953, 2922, 2891, 2854, 1691, 1595, 1499, 1461, 1440, 1400, 1379, 1335, 1248, 1176, 1156, 1113, 889, and 838 cm^{-1}.

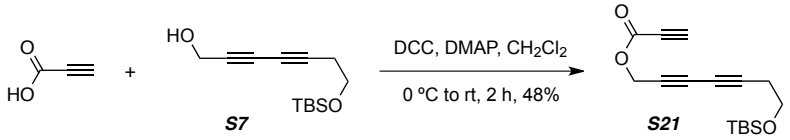
HRMS (ESI-TOF): Calcd for $C_{26}H_{27}O_2Si^+$ [M+H$^+$] requires 366.1884; found 366.1904.

mp: >225 ºC.

Synthesis of benzodifuranone S22 (Fig. 3, entry 6 of manuscript)



7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl Propiolate (S21)



DCC (110 mg, 0.55 mmol) was added to a stirred solution of propiolic acid (39 mg, 0.55 mmol), alcohol **S7** (119 mg, 0.50 mmol), and DMAP (6 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) at 0 ºC. After 2 h the mixture was passed through a plug of Celite® (EtOAc eluent) and concentrated. Purification by flash chromatography (hexanes:EtOAc 12:1) gave the ester **S21** (71 mg, 0.24 mmol, 48%) as a pale yellow oil.

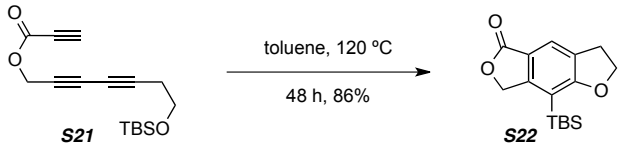
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.83 (t, J = 1.1 Hz, 2H, CO_2CH_2), 3.74 (t, J = 6.9 Hz, 2H, OCH_2), 2.94 (s, 1H, C≡C*H*), 2.50 (tt, J = 1.1, 6.9 Hz, 2H, OCH_2CH_2), 0.90 [s, 9H, $SiC(CH_3)_3$] and 0.07 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 79.9, 76.1, 74.0, 72.7, 68.1, 65.3, 61.3, 54.2, 26.0, 23.9, 18.4, and -5.2.

IR (neat): 3289, 2953, 2931, 2836, 2857, 2262, 2123, 1724, 1470, 1367, 1257, 1206, 1105, and 839cm^{-1}.

HRMS (CIMS): Calcd for $C_{16}H_{22}NaO_3Si^+$ [M+Na$^+$] requires 313.1230; found 313.1252.

8-(*tert*-Butyldimethylsilyl)-2,3-dihydrobenzo[1,2-b:4,5-c']difuran-5(7*H*)-one (S22, entry 6, Fig. 3 of manuscript)



A solution of triyne **S21** (29 mg, 0.10 mmol) in toluene (4 mL) was heated to 120 ºC (external bath temperature) in a sealed tube. After 48 h the reaction mixture was concentrated and purified by flash chromatography (hexanes:EtOAc 4:1) gave the tricycle **S22** (25 mg, 0.086, 86%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (t, J = 1.4 Hz, 1H, Ar*H*), 5.20 (s, 2H, $ArCH_2O$), 4.64 (t, J = 8.7 Hz, 2H, $ArCH_2CH_2$), 3.25 (dt, J = 8.7, 1.2 Hz, 2H, $ArCH_2CH_2$), 0.89 [s, 9H, $SiC(CH_3)_3$], and 0.33 [s, 6H, $Si(CH_3)_2$].

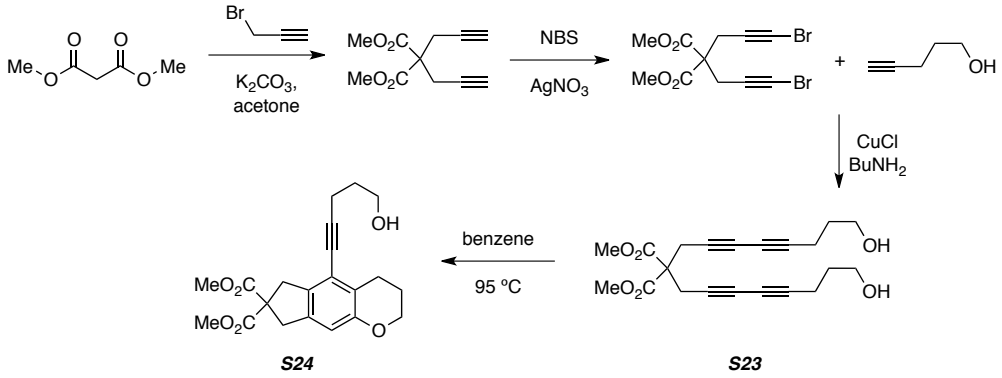
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 171.4, 155.3, 128.7, 123.2, 117.9, 111.4, 71.9, 71.2, 28.7, 26.7, 18.6, and 3.8.

IR (neat): 2949, 2927, 2902, 2855, 1747, 1589, 1459, 1400, 1360, 1325, 1259, 1099, 1023, 1013, 881, and 839 cm^{-1}.

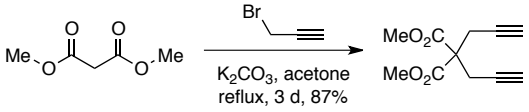
HRMS (CIMS): Calcd for $C_{16}H_{22}NaO_3Si^+$ [M+Na$^+$] requires 313.1230; found 313.1237.

mp: 167–169 ºC.

Synthesis of indane diester S24 (Fig. 3, entry 7 of manuscript)

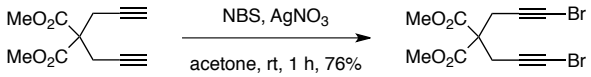


Dimethyl 2,2-Di(prop-2-yn-1-yl)malonate



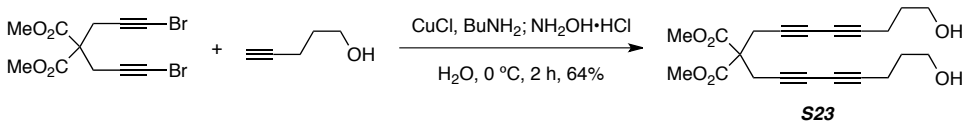
Propargyl bromide (7.8 mL, 80 wt. % in toluene, 70 mmol) was added to a stirred suspension of dimethyl malonate (2.00 mL, 17.5 mmol) and K_2CO_3 (5.32 g, 38.5 mmol) in acetone (30 mL) under a N_2 atmosphere and the mixture was brought to reflux (ca. 60 ºC). After 3 d the reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 3:1) gave the dimethyl 2,2-di(prop-2-yn-1-yl)malonate (3.15 g, 15.2 mmol, 87%) as a colorless oil which solidified upon standing. The spectral data were consistent with reported values.[12]

Dimethyl 2,2-Bis(3-bromoprop-2-yn-1-yl)malonate



Dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate was prepared following general procedure A from dimethyl 2,2-di(prop-2-yn-1-yl)malonate (1.2 g, 5.8 mmol), *N*-bromosuccinimide (2.26 g, 12.7 mmol), $AgNO_3$ (97 mg, 0.57 mmol), and acetone (40 mL). Purification by flash chromatography (hexanes:EtOAc 8:1) gave the known dibromodiyne[13] as a clear colorless oil (2.56 g, 12.6 mmol, 76%). The spectral data were consistent with reported values.

Dimethyl 2,2-Bis(8-hydroxyocta-2,4-diyn-1-yl)malonate (S23)



CuCl (40 mg, 0.4 mmol) was added to a 30% aqueous solution of butylamine (15 mL) at 0 ºC with stirring. Hydroxylamine hydrochloride was added until the solution was colorless (~10 mg) followed by a solution of pent-4-yn-1-ol (0.2 mL, 2.2 mmol) in dichloromethane (3 mL). A solution of dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate (320 mg, 0.88 mmol; 5 mL CH_2Cl_2) was added dropwise to the

yellow solution, and the resulting mixture allowed to come to rt. After 2 h water (10 mL) was added, the aqueous phase was extracted with CH_2Cl_2, and the combined organics were washed with satd. aq. NH_4Cl solution and brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 1:1) gave tetrayne **S23** (210 mg, 0.56 mmol, 64%) as a clear yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.77 (s, 6H, CO_2CH_3), 3.73 (t, J = 6.1 Hz, 4H, CH_2OH), 3.06 [s, 4H, $C(CO_2Me)_2CH_2C{\equiv}C$], 2.38 (t, J = 7.0 Hz, 4H, $C{\equiv}CCH_2CH_2$), 1.77 (tt, J = 7.0, 6.1 Hz, 4H, $CH_2CH_2CH_2$), and 1.37 (br s, 2H, CH_2OH).

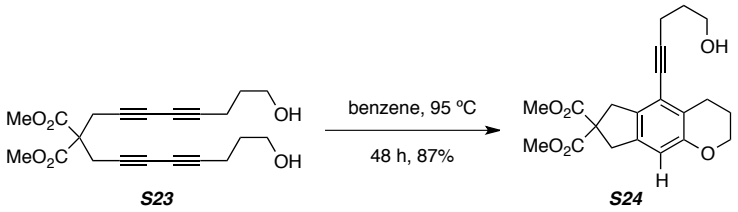
^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 78.1, 70.9, 68.7, 65.4, 61.4, 56.7, 53.4, 30.9, 23.9, and 15.8.

IR (neat): 3355, 2953, 2258, 1739, 1435, 1318, 1294, 1209, and 1055 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{24}NaO_6^+$ [M+Na^+] requires 395.1465; found 395.1461.

TLC: R_f 0.3 (1:2 Hex/EtOAc).

Dimethyl 5-(5-Hydroxypent-1-yn-1-yl)-3,4,6,8-tetrahydrocyclopenta[*g*]chromene-7,7(2*H*)-dicarboxylate (S23, entry 7, Fig. 3 of manuscript)



S23 ***S24***

A solution of tetrayne **S23** (23 mg, 0.062 mmol) in benzene (1 mL) was heated at 95 ºC (external bath temperature) in a sealed tube. After 48 h the mixture was concentrated and the crude material was purified by MPLC (hexanes:EtOAc 1:2) to give the tricycle **S24** (20 mg, 0.054 mmol, 87%) as an amber oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.59 (s, 1H, Ar*H*), 4.10 (br t, J = 5.1 Hz, 2H, CH_2OC), 3.84 (t, J = 6.2 Hz, 2H, CH_2OH), 3.75 (s, 6H, CO_2CH_3), 3.56 [s, 2H, $C(CO_2Me)_2CH_2C_{Ar}{=}C_{Ar}C{\equiv}C$], 3.52 [br s, 2H, $C(CO_2Me)_2CH_2C_{Ar}{=}C_{Ar}H$], 2.79 (br t, J = 6.6 Hz, 2H, $CCH_2CH_2CH_2OC$), 2.61 (t, J = 6.9 Hz, 2H, $CH_2CH_2CH_2OH$), 1.97 (br pent, J = 6.5 Hz, 2H, $CCH_2CH_2CH_2OC$), and 1.88 (tt, J = 6.9, 6.2 Hz, 2H, $CH_2CH_2CH_2OH$).

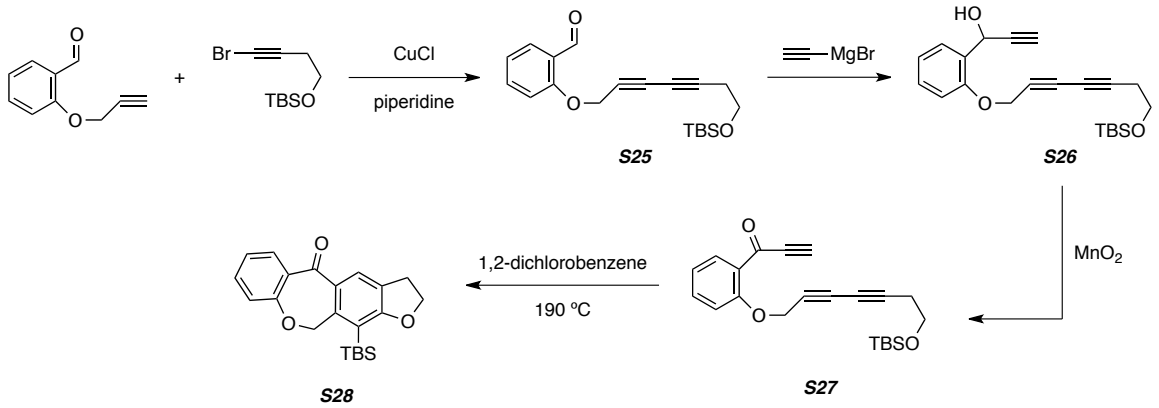
^{13}C NMR (500 MHz, $CDCl_3$): δ 172.3, 154.4, 138.3, 134.4, 122.6, 119.9, 112.4, 97.7, 77.5, 66.2, 61.9, 60.0, 53.1, 40.9, 40.2, 31.8, 24.0, 22.3, and 16.4.

IR (neat): 3458, 2951, 2876, 2229, 1734, 1604, 1587, 1436, 1341, 1253, 1199, 1174, 1160, 1132, 1104, and 1060 cm^{-1}.

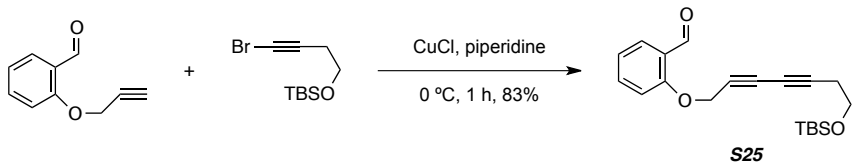
HRMS (ESI-TOF): Calcd for $C_{21}H_{24}O_6$ [M+Na^+] requires 395.1465; found 395.1495.

TLC: R_f 0.3 (1:1 Hex/EtOAc).

Synthesis of dibenzoxepinone S28 (Fig. 3, entry 8 of manuscript)



2-((7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl)oxy)benzaldehyde (S25)



CuCl (20 mg, 0.2 mmol) was added to a solution of 2-(prop-2-yn-1-yloxy)benzaldehyde[14] (320 mg, 2.0 mmol) and 4-*t*-butyldimethylsiloxy-1-butynyl bromide[7] (576 mg, 2.2 mmol) in freshly deaerated piperidine (4 mL) at 0 ºC. After 1 h the reaction mixture was partitioned between EtOAc and satd. aq. NH_4Cl. The aqueous phase was extracted twice with EtOAc and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 9:1) gave the diynal **S25** (569 mg, 1.66 mmol, 83%) as a pale red oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.47 (d, *J* = 0.7 Hz, 1H, C*H*O), 7.86 (dd, *J* = 1.8, 7.9 Hz, 1H, *H6*), 7.57 (ddd, *J* = 1.9, 7.4, 8.4 Hz, 1H, *H4*), 7.10 (br d, *J* = 7 Hz, 1H, *H3*), 7.09 (dddd, *J* = 0.9, 0.9, 7, 7 Hz, 1H, *H5*), 4.88 (t, *J* = 1.1 Hz, 2H, $C_{Ar}OCH_2$), 3.73 (t, *J* = 6.9 Hz, 2H, CH_2OSi), 2.49 (tt, *J* = 1.1, 7.0 Hz, 2H, ≡CCH_2CH_2), 0.88 [s, 9H, $SiC(CH_3)_3$], and 0.06 [s, 6H, $Si(CH_3)_2$].

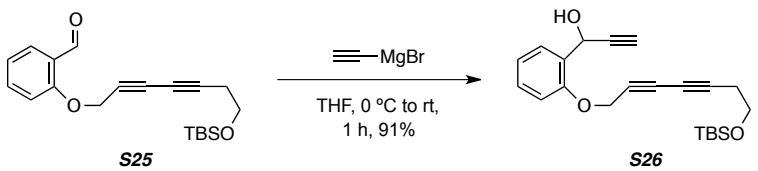
^{13}C NMR (125 MHz, $CDCl_3$): δ 189.6, 159.9, 135.9, 128.8, 125.6, 121.8, 113.3, 79.9, 73.2, 69.5, 65.3, 61.3, 57.1, 26.0, 23.8, 18.4, and -5.2.

IR (neat): 2953, 2930, 2857, 2259, 1691, 1599, 1480, 1460, 1288, 1255, 1217, 1105, 1012, 838, 778, and 759 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{20}H_{26}NaO_3Si^+$ [$M+Na^+$] requires 365.1543; found 365.1548.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

1-(2-((7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl)oxy)phenyl)prop-2-yn-1-ol (S26)



Ethynylmagnesium bromide (2 mL, 0.5 M in THF, 1 mmol) was added to a stirred solution of aldehyde **S25** (180 mg, 0.53 mmol) in anhydrous THF (3 mL) at 0 ºC and under an atmosphere of N_2. After 1 hour the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 6:1) gave the triynol **S26** (176 mg, 0.48 mmol, 91%) as a clear colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 1.7, 7.6 Hz, 1H, *H6*), 7.33 (ddd, *J* = 1.8, 7.5, 8.3 Hz, 1H, *H4*), 7.04 (ddd, *J* = 1.1, 7.5, 7.5 Hz, 1H, *H5*), 7.01 (dd, *J* = 1.1, 8.3 Hz, 1H, *H3*), 5.73 (dd, *J* = 2.3, 6.3 Hz, 1H, C*H*OH), 4.83 (t, *J* = 1.1 Hz, 2H, $C_{Ar}OCH_2$), 3.73 (t, *J* = 6.9 Hz, 2H, CH_2OSi), 2.83 (d, *J* = 6.3 Hz, 1H,O*H*), 2.62 (d, *J* = 2.3 Hz, 1H, ≡C*H*), 2.49 (tt, *J* = 1.0, 6.9 Hz, 2H, CH_2CH_2OSi), 0.89 [s, 9H, $SiC(CH_3)_3$], and 0.06 [s, 6H, $Si(CH_3)_2$].

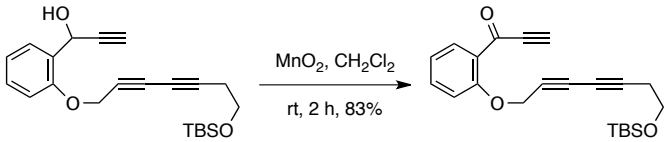
^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 129.9, 129.1, 128.2, 122.1, 112.6, 83.1, 79.6, 74.4, 72.7, 70.1, 65.5, 61.3, 60.8, 57.1, 26.0, 23.8, 18.4, and -5.2.

IR (neat): 3433, 3294, 2953, 2930, 2857, 2259, 2221, 1601, 1489, 1458, 1253, 1220, 1106, 1019, 943, 838, 780, and 754 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{28}NaO_3Si^+$ [M+Na^+] requires 391.1700; found 391.1691.

TLC: R_f 0.4 (4:1 Hex/EtOAc).

1-(2-((7-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl)oxy)phenyl)prop-2-yn-1-one (S27)



S26 ***S27***

MnO_2 (532 mg, 6.1 mmol) was added to a solution of alcohol **S26** (90 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) and the black heterogeneous mixture was vigorously stirred at rt. After 2 h the reaction mixture was filtered through a plug of silica gel (CH_2Cl_2 eluent) and concentrated. Purification by flash chromatography (hexanes:EtOAc 9:1) gave the triynone **S27** (74 mg, 0.20 mmol, 83%) as a clear yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 1.8, 7.8 Hz, 1H, *H6*), 7.56 (ddd, *J* = 1.8, 7.3, 8.4 Hz, 1H, *H4*), 7.12 (br d, *J* = 8.5 Hz, 1H, *H3*), 7.09 (br dd, *J* = 7.5, 7.5 Hz, 1H, *H5*), 4.88 (t, *J* = 1.0 Hz, 2H, $C_{Ar}OCH_2$), 3.73 (t, *J* = 7.9 Hz, 2H, CH_2OSi), 3.40 (s, 1H, ≡C*H*), 2.48 (tt, *J* = 1.0, 6.0 Hz, 2H, CH_2CH_2OSi), 0.88 [s, 9H, $SiC(CH_3)_3$], and 0.06 [s, 6H, $Si(CH_3)_2$].

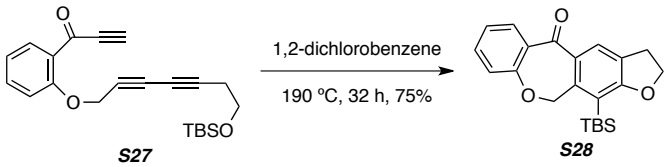
^{13}C NMR (125 MHz, $CDCl_3$): δ 175.9, 157.9, 135.3, 133.0, 126.8, 121.6, 114.4, 82.4, 79.8, 79.6, 73.1, 69.8, 65.5, 61.3, 57.3, 26.0, 23.8, 18.4, and -5.2.

IR (neat): 2953, 2929, 2856, 2258, 2093, 1654, 1597, 1483, 1453, 1292, 1256, 1220, 1105, 1009, 990, 839, 779, and 755 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{26}NaO_3Si^+$ [M+Na^+] requires 389.1543; found 389.1553.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

12-(*tert*-Butyldimethylsilyl)-2,3-dihydrobenzo[6,7]oxepino[4,3-f]benzofuran-5(11*H*)-one (S28, entry 8, Fig. 3 of manuscript)



S27 ***S28***

A solution of triynone **S27** (20 mg, 0.055 mmol) in 1,2-dichlorobenzene (3 mL) was heated to 195 ºC (external bath temperature) in a sealed tube. After 32 h the reaction mixture was directly subjected (or subjected directly) to flash chromatography (hexanes:EtOAc 9:1) to give the tetracycle **S28** (15 mg, 0.041 mmol, 75%) as a clear yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 1.8, 8.1 Hz, 1H, *H6*), 7.66 (t, *J* = 1.3, Hz, 1H, *H4*), 7.44 (ddd, *J* = 1.8, 6.9, 8.5 Hz, 1H, *H8*), 7.06 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1H, *H7*), 7.02 (dd, *J* = 1.3, 8.3 Hz, 1H, *H9*), 5.20 (s, 2H, OCH_2C_{Ar}), 4.54 (t, *J* = 8.8 Hz, 2H, CH_2CH_2O), 3.18 (t, *J* = 1.4, 8.8 Hz, 2H, CH_2CH_2O), 0.95 [s, 9H, $SiC(CH_3)_3$], and 0.48 [s, 6H, $Si(CH_3)_2$].

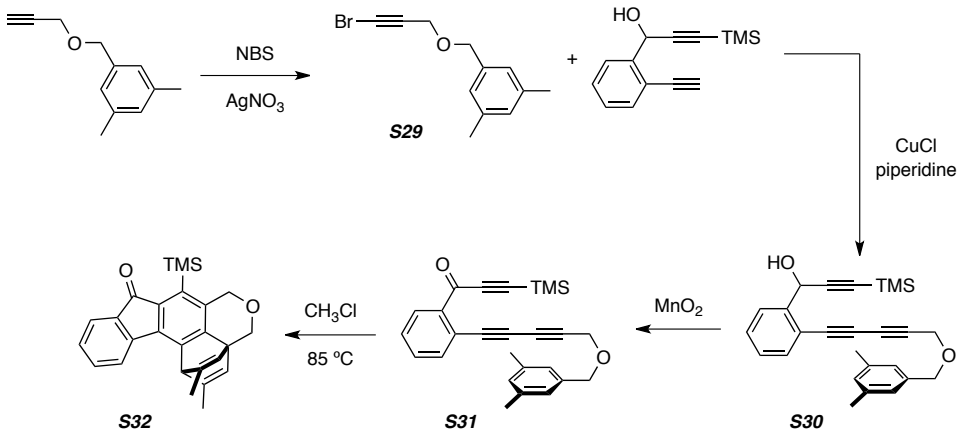
^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1, 170.0, 161.6, 141.8, 136.4, 135.0, 131.7, 127.3, 127.2, 125.6, 121.5, 120.2, 116.3, 72.3, 71.0, 29.0, 26.9, 18.2, and -1.1.

IR (neat): 2953, 2928, 2856, 1641, 1600, 1474, 1448, 1409, 1294, 1250, 1108, 1033, 1008, and 880 cm^{-1}.

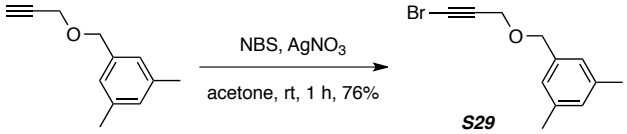
HRMS (ESI-TOF): Calcd for $C_{22}H_{27}O_3Si^+$ [$M+H^+$] requires 367.1724; found 367.1723.

TLC: R_f 0.5 (9:1 Hex/EtOAc).

Synthesis of fluorenone S32 (Fig. 3, entry 9 of manuscript)



1-(((3-Bromoprop-2-yn-1-yl)oxy)methyl)-3,5-dimethylbenzene (S29)



Bromoalkyne **S29** was prepared following general procedure A from 1,3-dimethyl-5-((prop-2-yn-1-yloxy)methyl)benzene (150 mg, 0.86 mmol), *N*-bromosuccinimide (NBS, 170 mg, 0.96 mmol), $AgNO_3$ (17 mg, 0.10 mmol), and acetone (10 mL). Purification by flash chromatography (hexanes:EtOAc 12:1) gave bromoalkyne **S29** (166 mg, 0.66 mmol, 76%) as a pale yellow oil.

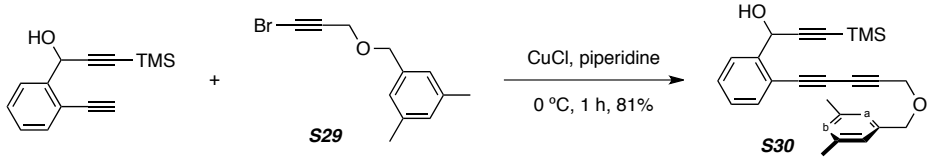
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (br s, 2H, Ar*H2,H6*), 6.94 (br s, 1H, Ar*H4*), 4.52 (s, 2H, OCH_2C≡C), 4.19 (t, *J* = 0.8 Hz, 2H, ArCH_2), and 2.31 [br s, 6H, Ar(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 137.2, 129.7, 126.1, 76.5, 72.0, 58.2, 46.1, and 21.4.

IR (neat): 3015, 2918, 2854, 2213, 1608, 1463, 1380, 1351, 1160, 1088, 1036, and 844 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{12}H_{13}NaOBr^+$ [M+Na$^+$] requires 275.0042; found 275.0066.

1-(2-(5-((3,5-Dimethylbenzyl)oxy)penta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S30)



Triyne **S30** was prepared following general procedure B from 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[15] (82 mg, 0.36 mmol), bromoalkyne **S29** (95 mg, 0.38 mmol), CuCl (4 mg, 0.04 mmol), and piperidine (1 mL). Purification by gradient flash chromatography (hexanes:EtOAc 12:1 to 8:1) gave the triyne **S30** (117 mg, 0.29 mmol, 81%) as a clear yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 7.8, 1.5 Hz, 1H, *H3*), 7.53 (dd, *J* = 7.7, 1.5 Hz, 1H, *H6*), 7.42 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H5*), 7.30 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H4*), 6.99 (br s, 2H,

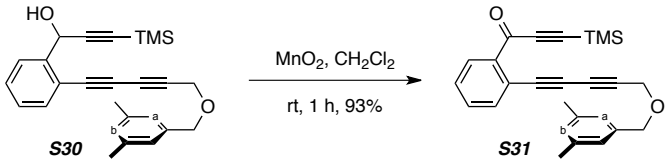
ArH_a), 6.95 (br s, 1H, ArH_b), 5.83 (d, J = 5.7 Hz, 1H, ArCH), 4.57 (br s, 2H, OCH_2C≡C), 4.33 (br s, 2H, ArCH_2), 2.42 (d, J = 5.7 Hz, 1H, OH), 2.33 [br s, 6H, Ar(CH_3)$_2$], and 0.20 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ143.7, 138.2, 137.1, 133.9, 130.0, 129.8, 128.5, 127.1, 126.2, 120.2, 104.1, 92.1, 80.6, 78.7, 75.3, 72.1, 71.0, 63.5, 57.9, 21.4, and 0.04.

IR (neat): 3417, 3017, 2957, 2920, 2856, 2237, 2173, 1607, 1450, 1351, 1250, 1085, 1056, 1040, 984, and 845 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{28}NaO_2Si^+$ [M+Na$^+$] requires 423.1751; found 423.1744.

1-(2-(5-((3,5-Dimethylbenzyl)oxy)penta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (S31)



MnO_2 (380 mg, 4.37 mmol) was added to a stirred solution of alcohol **S30** (117 mg, 0.29 mmol) in CH_2Cl_2 (3 mL) at room temperature. After 1 h the reaction mixture was filtered through a plug of Celite® (CH_2Cl_2) and concentrated to give the triyne **S31** (108 mg, 0.27 mmol, 93%) as a pale yellow oil.

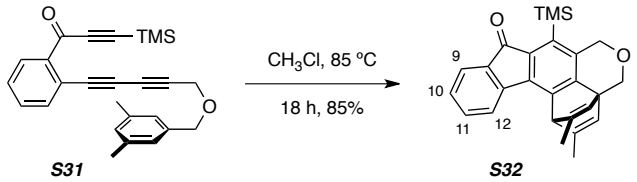
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.6, 1.7 Hz, 1H, *H6*), 7.64 (dd, J = 7.7, 1.4 Hz, 1H, *H3*), 7.52 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H, *H4*), 7.48 (ddd, J = 7.6, 7.6,1.4 Hz, 1H, *H5*), 6.99 (br s, 2H, ArH_a), 6.94 (br s, 1H, ArH_b), 4.56 (br s, 2H, OCH_2C≡C), 4.33 (br s, 2H, ArCH_2O), 2.32 [br s, 6H, Ar(CH_3)$_2$], and 0.31 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 139.2, 138.2, 137.1, 135.9, 132.7, 132.1, 129.8, 129.0, 126.2, 121.5, 101.6, 101.4, 81.2, 79.4, 76.2, 72.1, 71.5, 57.9, 21.4, and 0.6.

IR (neat): 2959, 2918, 2852, 2238, 2152, 1706, 1647, 1607, 1590, 1561, 1480, 1467, 1351, 1236, 1096, 1076, 1014, and 848 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{26}NaO_2Si^+$ [M+Na$^+$] requires 421.1594; found 421.1599.

(1*r*,3a*r*)-2,14-Dimethyl-7-(trimethylsilyl)-4,6-dihydro-1,3a-ethenobenzo[*de*]indeno[1,2-*g*]isochromen-8(1*H*)-one (S32, entry 9, Fig. 3 of manuscript)



A solution of ketone **S31** (20 mg, 0.050 mmol) in $CHCl_3$ (4 mL) was heated to 85 ºC (external bath temperature) in a sealed tube. After 16 h the reaction mixture was concentrated and purified by flash chromatography (hexanes:EtOAc 12:1) to give the polycyclic ketone **S32** (17 mg, 0.043, 85%) as a bright yellow oil.

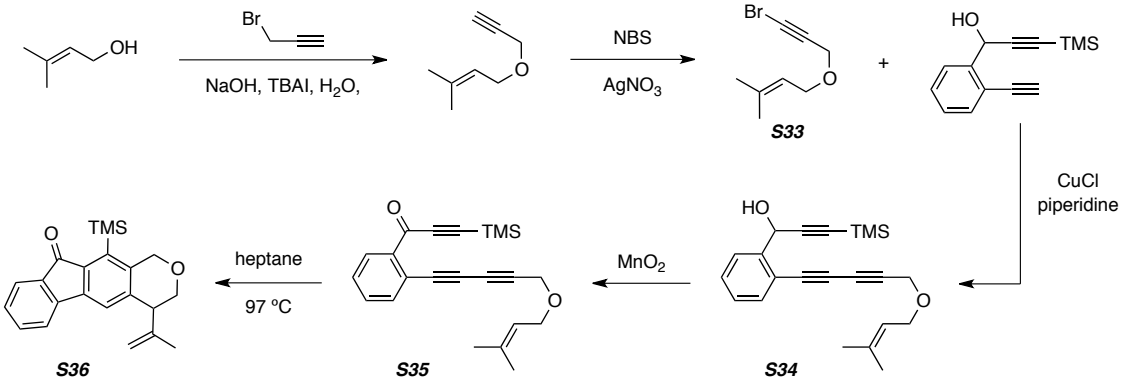
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 7.5 Hz, 1H, *H12*), 7.63 (d, J = 7.0 Hz, 1H, *H9*), 7.51 (dd, J = 7.5, 7.5 Hz, 1H, *H11*), 7.28 (dd, J = 7.5, 7.5 Hz, 1H, *H10*), 6.16 (br s, 2H, MeC=CH), 4.96 (s, 1H, HCR$_3$), 4.79 (br s, 2H, OCH_2C$_{Ar}$), 4.39 (br s, 2H, OCH_2CR$_3$), 1.99 (br s, 6H, CCH_3), and 0.36 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 149.8, 148.8, 144.6, 142.4, 136.3, 136.0, 135.5, 135.1, 135.0, 134.4, 133.7, 128.3, 124.2, 121.8, 71.2, 70.4, 56.2, 51.2, 20.0, and 2.3.

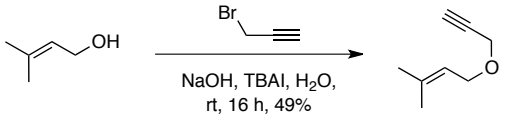
IR (neat): 2950, 2903, 2849, 1705, 1606, 1560, 1466, 1375, 1353, 1205, 1189, 1174, 1122, 1097, 995, and 942 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{26}NaO_2Si^+$ [M+Na^+] requires 421.1594; found 421.1559.

Synthesis of fluorenone S36 (Fig. 3, entry 10 of manuscript)

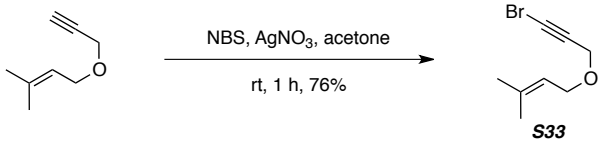


3-Methyl-1-(prop-2-yn-1-yloxy)but-2-ene



Propargyl bromide (3.00 mL, 26.9 mmol, 80 wt. % in toluene) was added dropwise to an aqueous (7.2 mL) solution of 3-methylbut-2-en-1-ol (2.95 mL, 34.2 mmol), tetra-*n*-butylammonium iodide (126 mg, 341 mmol), and sodium hydroxide (4.1 g, 103 mmol) at room temperature with stirring. After 16 h the reaction mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Purification by vacuum distillation gave the product ether as a clear colorless oil (2.07 g, 16.7 mmol, 49%). The spectra data were entirely consistent with literature values.[16]

1-((3-Bromoprop-2-yn-1-yl)oxy)-3-methylbut-2-ene (S33)



Bromoalkyne **S32** was prepared following general procedure A from 3-methyl-1-(prop-2-yn-1-yloxy)but-2-ene (2.07 g, 16.7 mmol), *N*-bromosuccinimide (NBS, 3.35 g, 18.8 mmol), $AgNO_3$ (312 mg, 1.84 mmol), and acetone (40 mL). Purification by flash chromatography (hexanes:EtOAc 9:1) gave the bromoalkyne **S33** (2.56 g, 12.6 mmol, 76%) as a clear colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (tqq, J = 7.1, 1.4, 1.4 Hz, 1H, =C*H*), 4.15 (s, 2H, OCH_2C≡), 4.05 (dqq, J = 7.1, 0.8, 0.8 Hz, 2H, OCH_2CH=), 1.76 (dt, J = 1.2, 1.2 Hz, 3H, CH_3), and 1.71 (br d, J = 1.5 Hz, 3H, CH_3).

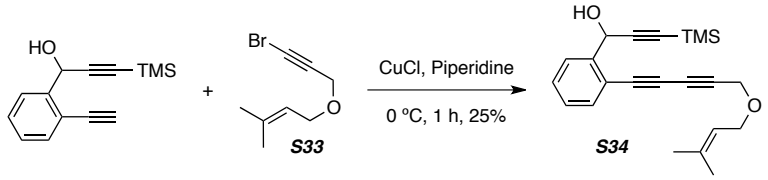
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 120.2, 76.7, 66.2, 57.9, 45.7, 25.9, and 18.2.

IR (neat): 2974, 2933, 2913, 2853, 2212, 1673, 1630, 1443, 1378, 1352, 1077, 1027, 1002, 925, and 897 cm^{-1}.

HRMS (CIMS): Calcd for $C_8H_{15}BrNO^+$ [M+NH_4^+] requires 220.0332; found 220.0348.

TLC: R_f 0.4 (19:1 Hex/EtOAc).

1-(2-(5-((3-Methylbut-2-en-1-yl)oxy)penta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S34)



Triyne **S34** was prepared following general procedure B from 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[15] (108 mg, 0.474 mmol), bromoalkyne **S33** (123 mg, 0.606 mmol), CuCl (3 mg, 0.03 mmol), and piperidine (1.0 mL). Purification by MPLC (hexanes:EtOAc 4:1) gave the triyne **S34** (42 mg, 0.12 mmol, 25%) as a clear yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 1.3, 7.8 Hz, 1H, *H3*), 7.52 (dd, *J* = 1.5, 7.7 Hz, 1H, *H6*), 7.42 (ddd, *J* = 1.5, 7.7, 7.7 Hz, 1H, *H4or5*), 7.30 (ddd, *J* = 1.4, 7.6, 7.6 Hz, 1H, *H4or5*), 5.82 [d, *J* = 4.9 Hz, 1H, C*H*(OH)], 5.35 [tqq, *J* = 7.1, 1.4, 1.4 Hz, 1H, $(CH_3)_2C{=}CH$], 4.29 (s, 2H, $OCH_2C{\equiv}$), 4.09 (dqq, *J* = 7.1, 0.8, 0.8 Hz, 2H, $OCH_2CH{=}$), 2.48 (d, *J* = 5.2 Hz, 1H, O*H*), 1.78 (dt, *J* = 1.2, 1.2 Hz, 3H, CCH_3), 1.73 (br d, *J* = 1.6 Hz, 3H, CCH_3), and 0.20 (s, 9H, $SiCH_3$).

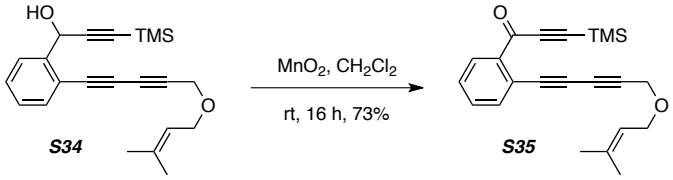
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 138.9, 133.8, 129.9, 128.5, 127.1, 120.2, 120.1, 104.1, 92.0, 80.9, 78.7, 75.1, 70.6, 66.4, 63.4, 57.6, 26.0, 18.3, and -0.1.

IR (neat): 3437, 2960, 2238, 2172, 1250, 1059, 845, and 760 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{26}NaO_2Si^+$ [M+Na^+] requires 373.1594; found 373.1604.

TLC: R_f 0.4 (4:1 Hex/EtOAc).

1-(2-(5-((3-Methylbut-2-en-1-yl)oxy)penta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (S35)



MnO_2 (230 mg, 2.64 mmol) was added to a solution of alcohol **S34** (37 mg, 0.11 mmol) in CH_2Cl_2 (0.25 mL). After 16 h the reaction mixture was filtered through a plug of Celite® (EtOAc eluent) and concentrated to give the ketone **S35** (28 mg, 0.080 mmol, 73%) as a clear amber oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 1.6, 7.7 Hz, 1H, *H6*), 7.63 (dd, *J* = 1.6, 7.6 Hz, 1H, *H3*), 7.52 (ddd, *J* = 1.6, 7.5, 7.5 Hz, 1H, *H4*), 7.48 (ddd, *J* = 1.5, 7.6, 7.6 Hz, 1H, *H5*), 5.34 (tqq, *J* = 7.1, 1.5, 1.5 Hz, 1H, $(CH_3)_2C{=}CH$), 4.29 (s, 2H, $OCH_2C{\equiv}$), 4.09 (br d, *J* = 7.1 Hz, 2H, $OCH_2CH{=}$), 1.77 (dt, *J* = 1.2, 1.2 Hz, 3H, CCH_3), 1.73 (d, *J* = 1.4 Hz, 3H, CCH_3), and 0.31 (s, 9H, $SiCH_3$).

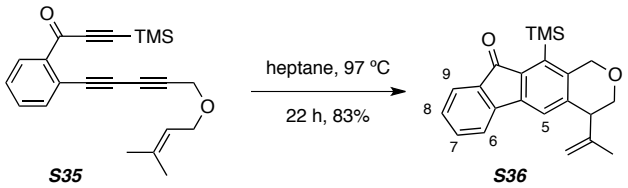
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.4, 139.1, 138.8, 135.9, 132.7, 132.1, 128.9, 121.5, 120.2, 101.6, 101.4, 81.6, 79.5, 76.0, 71.1, 66.4, 57.7, 26.0, 18.3, and -0.6.

IR (neat): 2965, 2931, 2872, 2152, 1649, 1236, 1067, 1015, 850, and 757 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{24}NaO_2Si^+$ [M+Na^+] requires 371.1438; found 371.1436.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

4-(Propen-2-yl)-11-(trimethylsilyl)-3,4-dihydroindeno[1,2-*g*]isochromen-10(1*H*)-one (S36, entry 10, Fig. 3 of manuscript)



S35 ***S36***

A solution of triynone **S35** (53 mg, 0.15 mmol) in heptane (4 mL) was heated at 97 ºC. After 16 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 15:1) to give the fluorenone **S36** (44 mg, 0.13 mmol, 83%) as a golden yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (ddd, *J* = 1.0, 1.0, 7.3 Hz, 1H, *H9*), 7.48 (ddd, *J* = 0.8, 1.5, 7.4 Hz, 1H, *H6*), 7.45 (ddd, *J* = 1.1, 7.2, 7.2 Hz, 1H, *H7*) 7.33 (d, *J* = 0.8 Hz, 1H, *H5*), 7.26 (ddd, *J* = 1.5, 7.2, 7.2 Hz, 1H, *H8*), 5.03 (br dq, *J* = 0.8, 1.5 Hz, 1H, =CH_aH$_b$), 4.91 (ddq, *J* = 0.8, 2.1, 0.8 Hz, 1H, =CH$_a$$H_b$), 4.90 (dd, *J* = 1.2, 15.2 Hz, C$_{Ar}$CH_aH$_b$O), 4.85 (dd, *J* = 1.2, 15.2 Hz, C$_{Ar}$CH$_a$$H_b$O), 3.97 (dd, *J* = 5.5, 11.3 Hz, OCH_aH$_b$CH), 3.84 (dd, *J* = 6.0, 11.3 Hz, OCH$_a$$H_b$CH), 3.63 (dddq, *J* = 0.8, 5.5, 6.0, 0.8 Hz, 1H, C*H*CH$_2$O), 1.73 (dd, *J* = 0.8, 1.5 Hz, 3H, CCH_3), and 0.43 (s, 9H, SiCH_3).

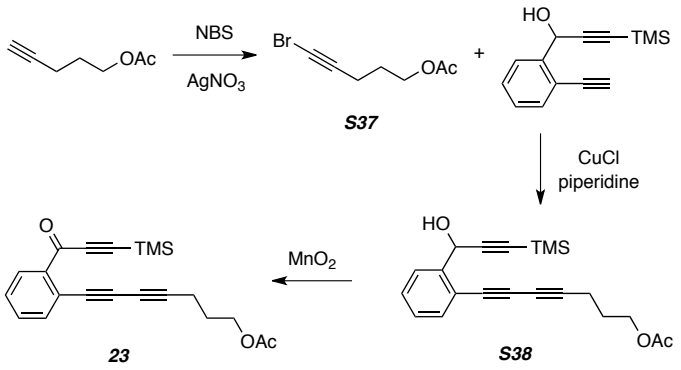
^{13}C NMR (125 MHz, $CDCl_3$): δ 195.1, 145.9, 144.0, 143.1, 142.2, 140.5, 139.0, 138.4, 134.6, 134.2, 128.9, 124.0, 122.1, 119.8, 115.5, 71.2, 68.3, 47.8, 20.3, and 2.7.

IR (neat): 2974, 2933, 2913, 2853, 2212, 1673, 1630, 1443, 1378, 1352, 1077, 1027, 1002, 925, and 897 cm^{-1}.

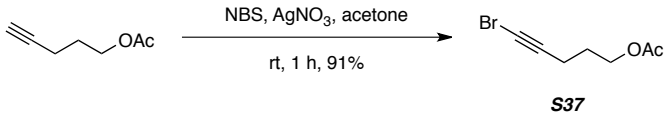
HRMS (CIMS): Calcd for $C_{22}H_{25}O_2Si^+$ [M+H$^+$] requires 349.1618; found 349.1629.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

Synthesis of triyne 23 (Figure 4A of manuscript)



5-Bromopent-4-yn-1-yl Acetate (S37)



5-Bromopent-4-yn-1-yl acetate was prepared following general procedure A from pent-4-yn-1-yl acetate[17] (780 mg, 6.19 mmol), *N*-bromosuccinimide (NBS, 1.24 g, 6.97 mmol), $AgNO_3$ (108 mg, 0.64 mmol), and acetone (40 mL). Purification by flash chromatography (hexanes:EtOAc 12:1) gave the bromoalkyne (1.30 g, 6.34 mmol, 91%) **S37** as a pale yellow oil.

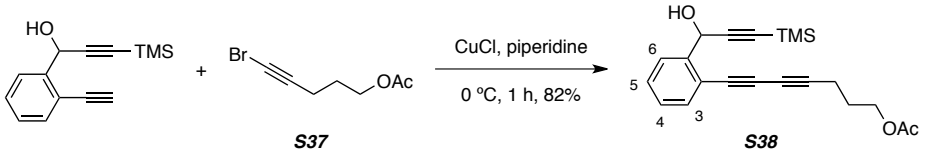
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.15 (t, *J* = 6.3 Hz, 2H, AcOCH_2), 2.32 (t, *J* = 7.0 Hz, 2H, C≡CCH_2), 2.06 (s, 3H, CH_3CO), and 1.85 (tt, *J* = 7.0, 6.3 Hz, 2H, CH_2CH$_2$O).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 79.0, 63.1, 38.8, 27.5, 21.0, and 16.7.

IR (neat): 2961, 2340, 1738, 1434, 1367, 1240, and 1044 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_7H_9AgBrO_2^+$ [M+Ag$^+$] requires 310.8831; found 310.8811.

7-(2-(1-Hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl Acetate (S38)



Triyne **S38** was prepared following general procedure B from 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[15] (200 mg, 0.88 mmol), bromoalkyne **S37** (200 mg, 0.98 mmol), CuCl (8 mg, 0.08 mmol), and piperidine (2.5 mL). Purification by flash chromatography (hexanes:EtOAc 5:1) gave the triyne **S38** (255 mg, 0.72 mmol, 82%) as a pale yellow oil. This compound is contaminated with ca. 15% bromoalkyne **S37** (^{1}H NMR), which can be removed chromatographically in the subsequent step.

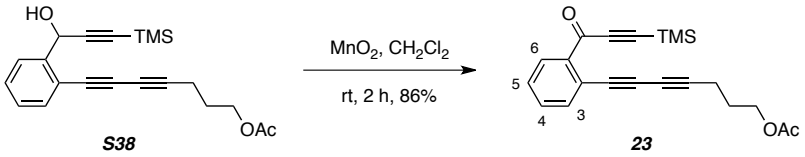
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar*H6*), 7.50 (dd, *J* = 7.7, 1.0 Hz, 1H, Ar*H3*), 7.40 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H, Ar*H4/H5*), 7.29 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, Ar*H4/H5*), 5.82 (d, *J* = 5.7 Hz, 1H, ArC*H*), 4.19 (t, *J* = 6.2 Hz, 2H, AcOCH_2), 2.51 (d, *J* = 5.8 Hz, 1H, O*H*), 2.49 (t, *J* = 7.3 Hz, 2H, C≡CCH_2), 2.08 (s, 3H, CH_3CO), 1.92 (tt, *J* = 7.0, 6.2 Hz, 2H, AcOCH$_2$CH_2), and 0.20 [s, 9H, Si(CH_3)$_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 143.5, 133.7, 129.6, 128.5, 127.1, 120.7, 104.2, 91.9, 84.6, 79.4, 72.3, 65.8, 63.5, 63.0, 27.4, 21.0, 16.7, and 0.05.

IR (neat): 3450, 2960, 2899, 2362, 2239, 2172, 1738, 1480, 1448, 1425, 1390, 1367, 1247, 1041, 984, 955, and 848 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{24}NaO_3Si^+$ [M+Na^+] requires 375.1392; found 375.1389.

7-(2-(3-(Trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl Acetate (23, Fig. 4A)



S38 *23*

MnO_2 (400 mg, 4.60 mmol) was added to a stirred solution of triyne **S38** (105 mg, 0.298 mmol) in CH_2Cl_2 (3 mL) at room temperature. After 2 h the reaction mixture was filtered through a plug of Celite® (CH_2Cl_2 eluent) and concentrated. Purification by flash chromatography (hexanes:EtOAc 12:1) gave the ketone **23** (90 mg, 0.26 mmol, 86%) as a clear amber oil.

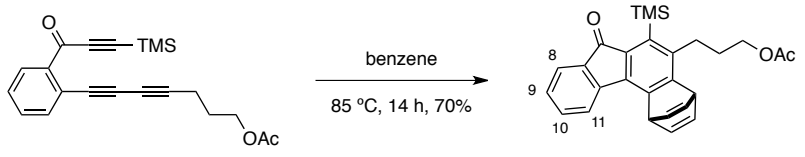
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.7 Hz, 1H, *H6*), 7.60 (d, *J* = 7.6 Hz, 1H, *H3*), 7.50 (dd, *J* = 7.5, 7.5 Hz, *H4*), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1H, *H5*), 4.18 (t, *J* = 6.2 Hz, 2H, AcOCH_2), 2.49 (t, *J* = 7.0 Hz, 2H, ArCH_2), 2.07 (s, 3H, CH_3CO), 1.91 (tt, *J* = 6.6, 6.6 Hz, 2H, $ArCH_2CH_2$), and 0.30 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 176.6, 171.1, 139.1, 135.8, 132.6, 132.0, 128.6, 122.0, 101.5, 101.4, 85.4, 80.4, 73.3, 66.4, 63.1, 27.5, 21.1, 16.8, and 0.6.

IR (neat): 2961, 2900, 2240, 2152, 1739, 1648, 1589, 1560, 1479, 1366, 1235, 1044, 1015, 955, and 850 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{22}NaO_3Si^+$ [M+Na^+] requires 373.1230; found 373.1206.

3-(7-Oxo-6-(trimethylsilyl)-4,7-dihydro-1*H*-1,4-ethenobenzo[*c*]fluoren-5-yl)propyl Acetate (25a, Fig. 4A of manuscript)



23 *25a*

A solution of triyne **23** (20 mg, 0.057 mmol) in benzene (5.5 mL) was heated at 85 ºC (external bath temperature) in a sealed tube. After 14 h the reaction mixture was concentrated and purified by flash chromatography (12:1) to give fluorenone **25a** (17 mg, 0.040 mmol, 70%) as a bright yellow oil.

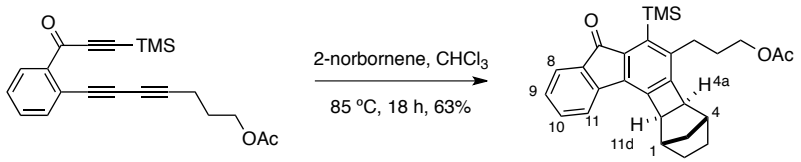
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (ddd, *J* = 7.7, 0.9, 0.9 Hz, 1H, *H11*), 7.60 (ddd, *J* = 7.3, 1.3, 0.7 Hz, 1H, *H8*), 7.49 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H10*), 7.25 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H, *H9*), 6.94 (ddd, *J* = 6.5, 6.5, 1.6 Hz, 2H, CH_a=CH_b), 6.88 (ddd, *J* = 6.0, 6.0, 1.6 Hz, 2H, CH_a=CH_b), 5.71 (dddd, *J* = 5.9, 5.9, 1.7, 1.7 Hz, 1H, C^{sp3}*H*CH=CHC^{sp3}H), 5.24 (dddd, *J* = 5.9, 5.9, 1.6, 1.6 Hz, 1H, C^{sp3}HCH=CHC^{sp3}*H*), 4.16 (t, *J* = 6.5 Hz, 2H, AcOCH_2), 3.05-3.01 (br t, *J* = 8.2 Hz, 2H, ArCH_2), 2.12 (s, 3H, CH_3CO), 1.83-1.76 (br tt, Σ_{Js} = 29 Hz, 2H, $ArCH_2CH_2$), and 0.41 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.5, 171.3, 152.1, 144.3, 143.0, 140.7, 139.1, 138.9, 138.4, 136.8, 135.3, 135.1, 134.2, 128.2, 124.1, 122.3, 64.0, 46.0, 45.2, 32.0, 28.4, 21.2, and 3.2.

IR (neat): 3065, 2951, 2897, 1738, 1705, 1607, 1586, 1550, 1467, 1387, 1365, 1326, 1301, 1244, 1043, and 857 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{27}H_{28}NaO_3Si^+$ [M+Na^+] requires 451.1700; found 451.1724.

3-((1*R**,4*S**,4aR*,11dS*)-7-Oxo-6-(trimethylsilyl)-2,3,4,4a,7,11d-hexahydro-1*H*-1,4-methanobenzo[3,4]cyclobuta[1,2-c]fluoren-5-yl)propyl Acetate (25b, Fig. 4A of manuscript)



23 *25b*

A solution of triyne **23** (20 mg, 0.057 mmol) and 2-norbornene (83 mg, 0.88 mmol) in ethanol-free $CHCl_3$ (5 mL) was heated at 85 ºC (external bath temperature) in a sealed tube. After 18 h the reaction mixture was concentrated and purified by flash chromatography (12:1) to give fluorenone **25b** (16 mg, 0.036 mmol, 63%) as a bright yellow oil, which is assigned as the endo adduct on the basis of comparative spectral data for the known exo and endo adducts of *o*-benzyne and norbornene.[18] No evidence was seen for the formation of a second diastereomer.

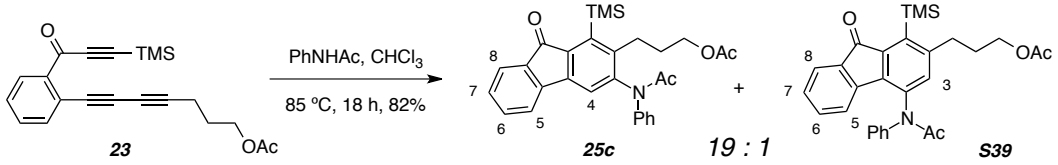
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.41 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H, *H10*), 7.32 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H, *H11*), 7.22 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1H, *H9*), 4.122 (dt, *J* = 11.0, 6.5 Hz, 1H, C$H_a$$H_b$OAc), 4.116 (dt, *J* = 11.0, 6.6 Hz, 1H, C$H_a$$H_b$OAc) 3.31 [dd, *J* = 4.0, 1.0 Hz, 1H, *H4a* (or H11d)], 3.29 [dd, *J* = 4.0, 1.0 Hz, 1H, *H11d* (or H4a)], 2.71 (br t, *J* = 8.0 Hz, 2H, ArCH_2), 2.47 (br s, 1H, *H1*), 2.37 (br s, 1H, *H4*), 2.08 (s, 3H, CCH_3), 1.88-1.72 (m, 2H, AcOCH_2CH_2), 1.72-1.62 (m, 2H), 1.31-1.22 (m, 2H), 1.10 (br s, 2H), and 0.42 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 195.4, 171.2, 152.4, 143.1, 142.0, 140.7, 140.4, 140.3, 137.5, 134.6, 134.3, 128.6, 124.0, 121.5, 64.2, 52.1, 48.6, 36.5, 35.9, 32.7, 32.0, 28.0, 27.8, 27.7, 21.1, and 2.7.

IR (neat): 2948, 2872, 1740, 1708, 1605, 1571, 1464, 1386, 1364, 1293, 1237, 1182, 1173, 1079, 1042, 997, 998, 950, and 917 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{28}H_{32}NaO_3Si^+$ [M+Na^+] requires 467.2013; found 467.2027.

3-(9-Oxo-3-(*N*-phenylacetamido)-1-(trimethylsilyl)-9*H*-fluoren-2-yl)propyl Acetate (25c, Fig. 4A of manuscript)



23 *25c* *19 : 1* *S39*

A solution of triyne **23** (20 mg, 0.057 mmol) and *N*-phenylacetamide (72 mg, 0.53 mmol) in $CHCl_3$ (5 mL) was heated at 85 ºC (external bath temperature) in a sealed tube. After 18 h the reaction mixture was concentrated and purified by flash chromatography (hexanes:EtOAc 5:1) to give the fluorenone **25c** (23 mg, 0.047 mmol, 82%) as a bright yellow oil. This sample contains ca. 5% of a second component to which we have tentatively assigned as the regioisomer having structure **S39** based on resonances in the ^{1}H NMR spectrum of the sample. The regioselectivity was substantiated by nOe analysis of the purified product mixture.

^{1}H NMR for 25c (500 MHz, $CDCl_3$): δ 7.56 (ddd, *J* = 7.3, 1.2, 1.2 Hz, 1H, *H8*), 7.47–7.41 (m, 2H, *H5* and *H6*), 7.35 (s, 1H, *H4*), 7.31–7.21 (m, 3H, PhH_m and *H7*), 7.05 (tt, *J* = 7.5, 1.3 Hz, 1H, PhH_p), 6.75 (dd, *J* = 8.4, 1.3 Hz, 2H, PhH_o), 4.17 (t, *J* = 6.4 Hz, 2H, OCH_2C), 2.86 (br t, *J* = 8.2 Hz, 2H, ArCH_2), 2.13 (s, 3H, CH_3CON), 2.08 (s, 3H, CH_3CO_2), 1.96–1.85 (m, Σ*J*s = 29.2 Hz, 2H, $ArCH_2CH_2$), and 0.46 (s, 9H, SiCH_3).

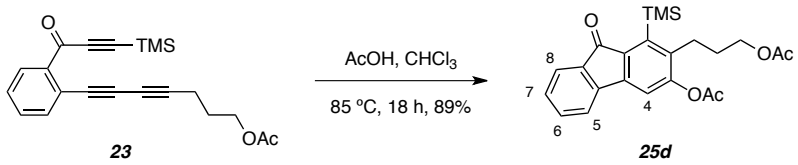
^{1}H NMR for S39 (500 MHz, $CDCl_3$): δ 7.13 (s, 1H, *H3*), 6.75 (br d, *J* = 8.1 Hz, 2H, PhH_o), 4.13 (t, *J* = 6.4 Hz, 2H, OCH_2C), 2.20 (s, 3H, CH_3CON), 2.07 (s, 3H, CH_3CO_2), and 0.43 (s, 9H, SiCH_3).

^{13}C NMR for 25c (125 MHz, $CDCl_3$): δ 194.4, 171.2, 161.1, 155.5, 148.1, 145.0, 144.1, 143.4, 140.4, 137.3, 134.5, 134.3, 129.2, 129.1, 123.9, 123.7, 120.8, 119.8, 116.6, 64.5, 31.1, 26.5, 21.2, 16.1, and 2.8.

IR (neat): 2950, 1738, 1711, 1685, 1591, 1487, 1467, 1368, 1295, 1224, 1164, 1120, 1039, and 858 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{29}H_{31}NNaO_4Si^+$ [M+Na^+] requires 508.1915; found 508.1882.

3-(3-Acetoxy-9-oxo-1-(trimethylsilyl)-9*H*-fluoren-2-yl)propyl Acetate (25d, Fig. 4A of manuscript)



23 ***25d***

A solution of triyne **23** (22 mg, 0.062 mmol) and acetic acid (0.2 mL, 3.5 mmol) in $CHCl_3$ (5 mL) was heated at 85 ºC (external bath temperature) in a sealed tube. After 18 h the reaction mixture was concentrated and purified by flash chromatography (hexanes:EtOAc 5:1) to give fluorenone **25d** (23 mg, 0.056 mmol 89%) as a bright yellow oil. The regioselectivity was substantiated by nOe analysis of the purified product mixture.

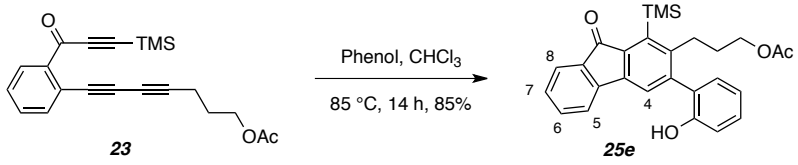
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (ddd, *J* = 7.2, 1.0, 1.0 Hz, 1H, *H8*), 7.46 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H, *H6*), 7.41 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H, *H5*), 7.28 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H, *H7*), 7.22 (s, 1H, *H4*), 4.11 (t, *J* = 6.4 Hz, 2H), 2.78 (m, 2H, ArCH_2), 2.39 (s, 3H, CH_3CO_2Ar), 2.08 (s, 3H, C$H_3CO_2CH_2$), 1.82-1.75 (br tt, Σ_{Js} = 29 Hz, 2H, $ArCH_2CH_2$), and 0.46 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 171.2, 169.4, 153.2, 145.2, 142.4, 143.1, 140.0, 137.8, 134.7, 134.1, 129.3, 124.1, 119.9, 115.9, 64.2, 31.0, 26.3, 21.18, 21.12, and 2.7.

IR (neat): 2949, 1759, 1739, 1713, 1605, 1591, 1467, 1387, 1366, 1295, 1243, 1201, 1159, 1118, 1039, 995, and 854 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{26}NaO_5Si^+$ [M+Na^+] requires 433.1441; found 433,1436.

3-(3-(2-Hydroxyphenyl)-9-oxo-1-(trimethylsilyl)-9*H*-fluoren-2-yl)propyl Acetate (25e, Fig. 4A of manuscript)



23 ***25e***

A solution of triyne **23** (21 mg, 0.06 mmol) and phenol (70 mg, 0.74 mmol) in $CHCl_3$ (5 mL) was heated at 85 ºC (external bath temperature) in a sealed tube. After 14 h the reaction mixture was

concentrated and purified by flash chromatography (hexanes:EtOAc 5:1) to give fluorenone **25e** (23 mg, 0.052, 86%) as a bright yellow oil. The regioselectivity was substantiated by nOe analysis of the purified product mixture.

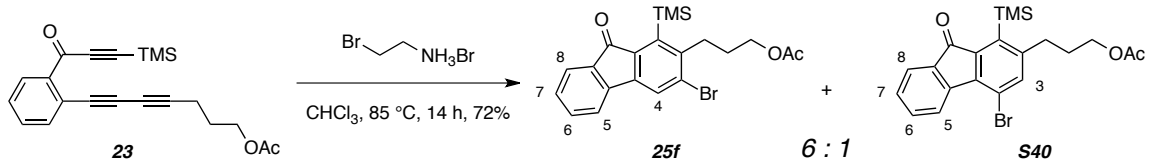
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H, *H8*), 7.46 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1H, *H6*), 7.41 (ddd, *J* = 7.5, 1.0, 1.0 Hz, 1H, *H5*), 7.40 (s, 1H, *H4*), 7.32 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H, *H4'*), 7.28 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H, *H7*), 7.15 (dd, 7.5, 1.7 Hz, 1H, *H6'*), 7.03 (ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, *H5'*), 7.01 (dd, *J* = 7.0, 1.3 Hz, 1H, *H3'*), 4.84 (s, 1H, O*H*), 3.83 (dt, *J* = 6.1, 11.0 Hz, 1H, AcOCH_aHb), 3.82 (dt, *J* = 6.0, 10.9 Hz, 1H, AcOCH$_a$*Hb*), 2.87 (ddd, *J* = 13.7, 11.1, 5.4 Hz, 1H, ArC*Ha*Hb), 2.65 (ddd, *J* = 13.7, 11.0, 5.5 Hz, 1H, ArCHa*Hb*), 1.87 (s, 3H, CH_3CO$_2$), 1.70-1.54 (m, 2H, ArCH$_2$CH_2), and 0.49 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 195.1, 171.1, 152.2, 148.5, 143.60, 143.59, 143.4, 142.0, 140.7, 134.8, 134.0, 130.2, 129.7, 129.2, 128.4, 124.2, 123.9, 121.0, 119.8, 115.9, 63.8, 32.1, 29.4, 21.0, and 2.9.

IR (neat): 3440, 2951, 1736, 1710, 1606, 1590, 1541, 1464, 1448, 1386, 1363, 1247, 1185, 1040, and 979 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{27}H_{28}NaO_4Si^+$ [M+Na$^+$] requires 467.1649; found 467.1647.

3-(3-Bromo-9-oxo-1-(trimethylsilyl)-9H-fluoren-2-yl)propyl acetate (25f, Fig. 4A of manuscript) and 3-(4-Bromo-9-oxo-1-(trimethylsilyl)-9H-fluoren-2-yl)propyl acetate (S40)



A solution of triyne **23** (18 mg, 0.051 mmol) and 2-bromoethylamine hydrobromide (the HBr source, 110 mg, 0.537 mmol) in THF:H_2O (5 mL, 19:1) was heated at 85 ºC (external bath temperature) in a sealed vial. After 18 h the reaction mixture was diluted with H_2O and extracted with EtOAc. The combined organic extracts were concentrated and purified by flash chromatography (hexanes: EtOAc 12:1) to give a mixture (6:1) of coeluting, regioisomeric fluorenones **25f** and **S40** (16 mg, 0.037 mmol, 72%) as a bright yellow oil. These were spectroscopically characterized as a mixture.

^{1}H NMR of 25f (500 MHz, $CDCl_3$): δ 7.76 (s, 1H, *H4*), 7.60 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H, *H8*), 7.48 (dd, *J* = 7.4, 7.4, 1.1 Hz, 1H, *H6*), 7.44 (d, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H5*), 7.30 (ddd, *J* = 7.3, 7.3, 7.3, 1.1 Hz, *H7*), 4.17 (t, *J* = 6.5 Hz, 2H, AcOCH_2), 3.09 (br t, *J* = 8.3 Hz, 2H, ArCH_2), 2.08 (s, 3H, CH_3CO$_2$), 1.90-1.80 (m, 2H, ArCH$_2$CH_2), and 0.46 (s, 9H, SiCH_3).

^{13}C NMR of 25f (125 MHz, $CDCl_3$): δ 194.4, 171.19, 147.0, 144.6, 144.2, 142.8, 139.5, 134.8, 134.0, 132.6, 129.5, 126.3, 124.3, 119.9, 64.1, 32.6, 30.6, 21.11, and 3.0

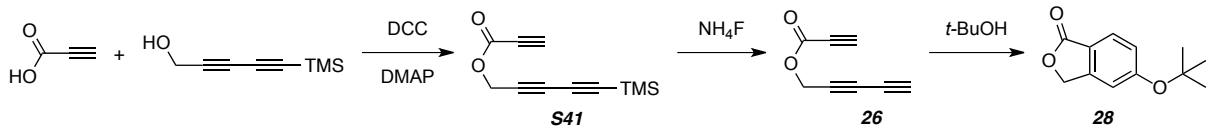
^{1}H NMR of S40 (500 MHz, $CDCl_3$): δ 8.32 (ddd, *J* = 7.7, 0.9, 0.9 Hz, 1H, *H5*), 7.63 (d, *J* = 7.3, 1.2, 0.8 Hz, 1H, *H8*), 7.51 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H, *H6*), 7.39 (s, 1H, *H3*), 7.32 (ddd, *J* = 7.5, 7.5, 0.8 Hz, 1H, *H7*), 4.12 (t, *J* = 6.4 Hz, 2H, AcOCH_2), 2.83 (br t, *J* = 8.2 Hz, 2H, ArCH_2), 2.08 (s, 3H, CH_3CO$_2$), 1.90-1.80 (m, 2H, ArCH$_2$CH_2), and 0.43 (s, 9H, SiCH_3).

^{13}C NMR of S40 (125 MHz, $CDCl_3$): δ 194.2, 171.15, 150.5, 143.4, 143.3, 141.4, 140.3, 134.7, 133.9, 129.2, 124.2, 123.2, 118.8, 63.7, 32.9, 32.1, 21.08, and 2.7 (one aromatic resonance is not detectable).

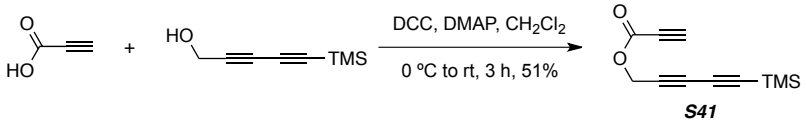
IR (neat): 2951, 1739, 1715, 1606, 1575, 1466, 1386, 1365, 1235, 1187, 1043, 974, 850, and 745 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{23}BrNaO_3Si^+$ [M+Na$^+$] requires 453.0492; found 453.0512.

Synthesis of phthalide 28 (Fig. 4B of manuscript)



5-(Trimethylsilyl)penta-2,4-diyn-1-yl Propiolate (S41)



The following agents were added in sequence to CH_2Cl_2 (1.5 mL) at 0 ºC: 5-trimethylsilyl-2,4-pentadiyn-1-ol[19] (750 mg, 4.92 mmol), propiolic acid (420 mg, 6.00 mmol), DCC (1.2 g, 5.8 mmol), and DMAP (60 mg, 0.49 mmol). The resulting homogeneous solution quickly became cloudy. After 3 h the resulting slurry was passed through a pad of Celite® (CH_2Cl_2) and concentrated. Purification by flash chromatography (hexanes:EtOAc 12:1) gave the ester **S41** (513 mg, 2.51 mmol, 51%) as a pale yellow oil.

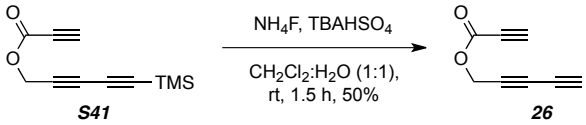
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.84 (s, 2H, C*H*$_2$O), 2.95 (s, 1H, *H*C≡C), and 0.20 (s, 9H, C*H*$_3$Si).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8, 89.2, 86.8, 76.2, 73.9, 72.6, 70.0, 54.0, and –0.4.

IR (neat): 3289, 2961, 2902, 2122, 1723, 1430, 1364, 1252, 1208, 966, 859, and 847 cm^{-1}.

HRMS (CIMS): Calcd for $C_{11}H_{16}NO_2Si^+$ [M+NH_4^+] requires 222.0945; found 222.0968.

Penta-2,4-diyn-1-yl Propiolate (26)



Tetra-*n*-butylammonium bisulfate ($TBAHSO_4$, 10 mg, 0.03 mmol) was added to a vigorously stirring solution of silyl alkyne **S41** (220 mg, 1.08 mmol) and NH_4F (2.5 mL, 45 wt. % in water, 30 mmol) in CH_2Cl_2 (5 mL) at room temperature. After 1.5 h the organic phase was separated from the biphasic reaction mixture and concentrated. Purification by flash chromatography (hexanes:EtOAc 12:1) gave the ester **26** (72 mg, 0.55 mmol, 50%) as a pale yellow oil.

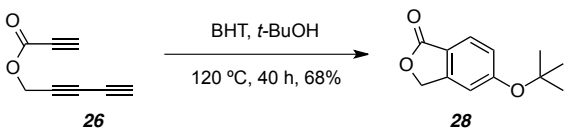
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.84 (d, *J* = 1.0 Hz, 2H, C*H*$_2$O), 2.97 (s, 1H, *H*C≡CC=O), and 2.24 (t, *J* = 1.0 Hz, 1H, *H*C≡CC≡C).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 76.4, 73.8, 71.9, 69.5, 68.8, 67.1, and 53.7.

IR (neat): 3289, 2123, 1720, 1432, 1367, 1209, and 966 cm^{-1}.

HRMS (CIMS): Calcd for $C_8H_8NO_2^+$ [M+NH_4^+] requires 150.0550; found 150.0564.

5-(*tert*-Butoxy)isobenzofuran-1(3*H*)-one (28, Fig. 4B)



A solution of ester **26** (15 mg, 0.11 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT, 2 mg, 0.009 mmol) in *t*-BuOH (9 mL) was heated to 120 ºC (external bath temperature) in a sealed tube. After 40 h the resulting solution was concentrated and purified by gradient flash chromatography (hexanes:EtOAc 12:1 to 5:1) to give the ester **28** (16 mg, 0.078 mmol, 68%) as a clear colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 0.4, 8.4 Hz, 1H, *H7*), 7.11 (ddt, *J* = 8.4, 2.0, 0.9 Hz, 1H, *H6*), 7.04 (ddt, *J* = 2.0, 0.9, 0.9 Hz, 2H, *H4*), 5.26 (dd, *J* = 0.8, 0.8 Hz, 2H, CH_2O), and 1.45 [s, 9H, $C(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 161.7, 148.6, 126.8, 124.1, 120.0, 115.2, 80.4, 69.2, and 29.0.

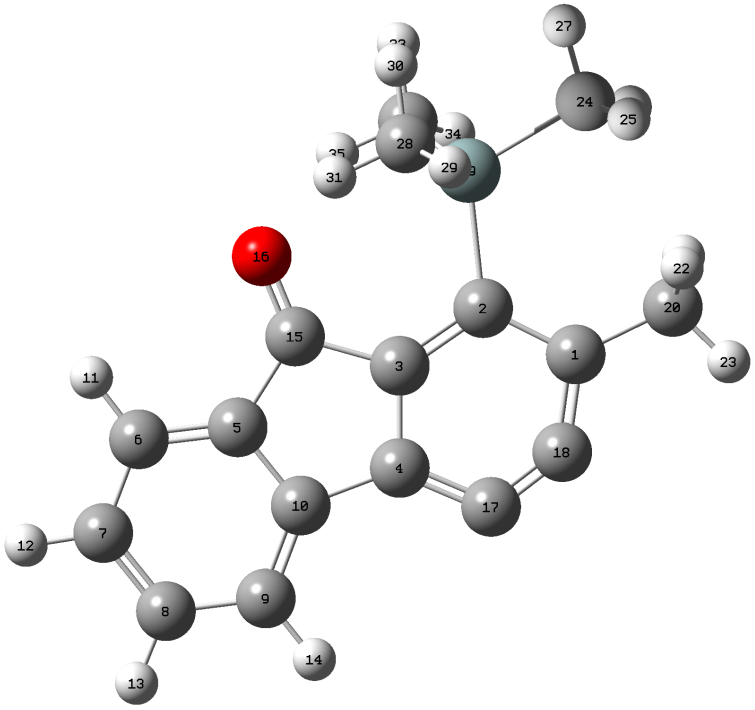
IR (neat): 2977, 2937, 2877, 1759, 1612, 1484, 1454, 1369, 1354, 1264, 1168, 1141, 1099, 1045, 1006, and 948 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{12}H_{14}NaO_3$ [$M+Na^+$] requires 229.0835; found 229.0859.

IV. Computational details for fluorenonyne 24 (R = CH_3)

Calculations were carried out in Gaussian 09[20] using M06-2X/6-31+G(d,p)[21] for geometry optimizations and frequency calculations. The optimized geometry was found to have no imaginary frequencies.

Optimized geometry of fluorenonyne 24 (R = CH_3)



Total Electronic Energy: `SCF Done: E(RM062X) = -1021.76985895 A.U.`[a]

[a] Atomic Units = Hartrees

Coordinates for optimized geometry of **24** (R = CH_3)

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	1.690386	1.977336	-0.000258
2	C	1.2624	0.602774	-0.000158
3	C	-0.12186	0.326038	-0.000031
4	C	-1.14924	1.315436	0.000142
5	C	-2.305505	-0.700459	-0.000143
6	C	-3.378661	-1.573123	-0.000251
7	C	-4.666616	-1.023565	-0.000102
8	C	-4.847252	0.360586	0.000151
9	C	-3.754875	1.237481	0.00026
10	C	-2.483313	0.687547	0.000105
11	H	-3.215238	-2.646641	-0.000449
12	H	-5.53335	-1.67636	-0.000181
13	H	-5.854817	0.765051	0.000267
14	H	-3.899142	2.313585	0.000461
15	C	-0.83808	-1.0052	-0.000257
16	O	-0.351486	-2.115683	-0.000537
17	C	-0.659874	2.605768	0.00018
18	C	0.577294	2.788264	0.000042
19	Si	2.505546	-0.877904	0.00014
20	C	3.104711	2.489669	-0.000678
21	H	3.653017	2.156017	0.88277
22	H	3.652975	2.15463	-0.883621
23	H	3.094569	3.580144	-0.001529
24	C	4.329368	-0.374376	0.000597
25	H	4.639615	0.179389	-0.888841
26	H	4.638956	0.180411	0.889618
27	H	4.886913	-1.319362	0.001349
28	C	2.29172	-1.863141	-1.586687
29	H	2.547082	-1.238863	-2.449627
30	H	2.985008	-2.711905	-1.575418
31	H	1.281059	-2.250974	-1.714636
32	C	2.290749	-1.862575	1.587209
33	H	2.982544	-2.712552	1.575919
34	H	2.547457	-1.238535	2.449917
35	H	1.279482	-2.248681	1.715612

V. Computational details for aryne 27-comp generation and trapping

To identify starting geometries for the DFT calculations, Monte Carlo conformational searches were carried out in MacroModel version 9.9[22]. DFT calculations were carried out in Gaussian 09[20] using M06-2X/6-31+G(d,p)[21] for geometry optimizations and frequency calculations. The optimized geometries were found to have no imaginary frequencies. The energy values corresponding to the "Sum of electronic and thermal Free Energies=" were used for the Boltzmann analysis of each family of conformers and as the $\Delta G_{M06\text{-}2X}$ values.

A total of six stable conformers (including two enantiomeric pairs) of the substrate triyne **26** were found (cf. **26-comp-a-d**). Only a single geometry was identified for aryne **27**. Four stable conformers (including one enantiomeric pair) of the product phthalide **28** were found (cf. **28-comp-a-c**). Full Boltzmann analysis was conducted with each of the six conformers of **26** and the aryne **27** to determine the equilibrium ratio of the two states (i.e., starting material and product). The Boltzmann analysis was carried out at 298 K by the following equation,

$$\begin{array}{c}\text{percentage}\\ \text{(mole fraction)}\\ \text{of the } i\text{th component}\\ \text{of } n \text{ species}\\ \text{in equilibrium}\end{array} = \frac{e^{\left(-\Delta E_i^* / RT\right)}}{\sum_{i=1}^{n} e^{\left(-\Delta E_i^* / RT\right)}}$$

where ΔE_i is the difference in free energy between the i^{th} component and the lowest energy component. Boltzmann analysis was also conducted on the aryne **27** (plus *tert*-butanol) and each of the four conformers of **28**.

Boltzmann Analysis to Determine $\Delta G_{M06\text{-}2X}$ for 26 to 27

Structure of each component *i*	Free Energy (rel to 27-comp) (kcal•mol^{-1})	mol fraction of each of the *i* components
27-comp	0.0	1.0
26-comp-a	56.8	$2.2\text{x}10^{-42}$
26-comp-b	55.8	$1.1\text{x}10^{-41}$
***ent*-26-comp-b**	55.8	$1.1\text{x}10^{-41}$
26-comp-c	51.2	$3.0\text{x}10^{-38}$
26-comp-d	51.4	$1.9\text{x}10^{-38}$
***ent*-26-comp-d**	51.4	$1.9\text{x}10^{-38}$

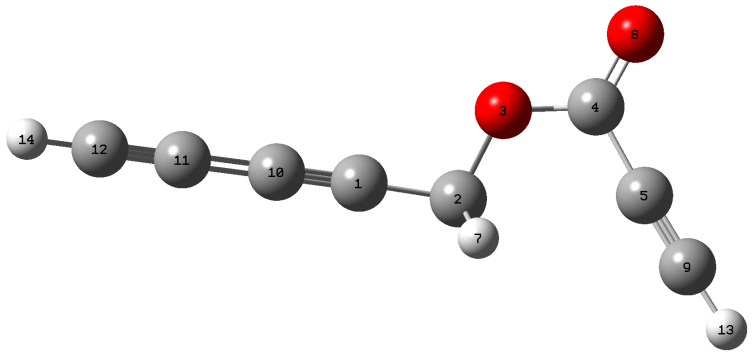
Equilibrium ratio of **27**/**26**:
[%**27-comp**/Σ(%**26-comp-a-d**)] = 1.5×10^{37},
which corresponds to a $\Delta G_{M06\text{-}2X}$ = -50.6 kcal•mol^{-1}.

Boltzmann Analysis to Determine $\Delta G_{M06\text{-}2X}$ for 27 to 28

Structure of each component *i*	Free Energy (rel to 28-comp-c) (kcal•mol^{-1})	mol fraction of each of the *i* components
27-comp + *tert*-butanol	72.0	5.6 x10^{-54}
28-comp-a	0.760	0.11
28-comp-b	0.834	0.097
28-comp-c	0.0	0.40
***ent*-28-comp-c**	0.0	0.40

Equilibrium ratio of **28**/**27**:
[Σ(%**28-comp-a-c**)/%(**27-comp + *tert*-butanol**)] = 1.8 x 10^{53},
which corresponds to a $\Delta G_{M06\text{-}2X}$ = -72.6 kcal•mol^{-1}.

Computed energies and geometry of conformer **26-comp-a**.

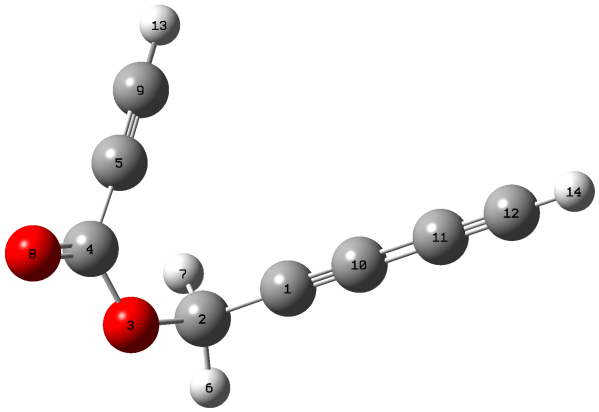


SCF Done: E(RM062X)[a] = -457.32014637 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -457.263860 A.U.[b]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	-1.330378	-0.374165	0.000053
2	C	0.110681	-0.599505	0.000086
3	O	0.764303	0.676623	0.000069
4	C	2.110197	0.728397	0.000006
5	C	2.815417	-0.554070	-0.000038
6	H	0.401232	-1.169518	-0.888790
7	H	0.401214	-1.169478	0.888994
8	O	2.685186	1.780395	-0.000044
9	C	3.440973	-1.584801	-0.000068
10	C	-2.529314	-0.215092	0.000013
11	C	-3.897267	-0.036261	-0.000011
12	C	-5.095672	0.120837	-0.000070
13	H	4.007666	-2.490939	-0.000075
14	H	-6.153839	0.261757	-0.000143

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

Computed energies and geometry of conformer **26-comp-b**.

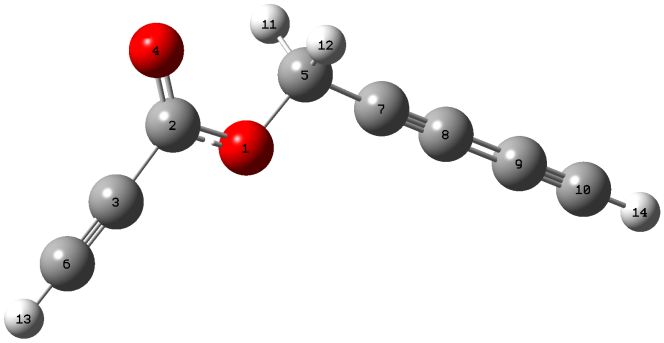


SCF Done: E(RM062X)[a] = -457.32215905 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -457.265396 A.U.[b,c]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	0.876586	-0.715053	-0.545004
2	C	-0.425875	-1.187842	-1.018120
3	O	-1.404360	-1.226789	0.024046
4	C	-1.965133	-0.082842	0.471172
5	C	-1.588454	1.150189	-0.217937
6	H	-0.348207	-2.221057	-1.360837
7	H	-0.774811	-0.566964	-1.849505
8	O	-2.745879	-0.103576	1.380360
9	C	-1.312505	2.196055	-0.750090
10	C	1.962854	-0.340698	-0.164597
11	C	3.198022	0.092227	0.271051
12	C	4.280463	0.471266	0.652834
13	H	-1.066966	3.127098	-1.213503
14	H	5.236146	0.804038	0.992748

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.
[c] This conformer is chiral and so its energy has been used twice in the Boltzmann analysis to account for its enantiomeric partner.

Computed energies and geometry of conformer **26-comp-c**.

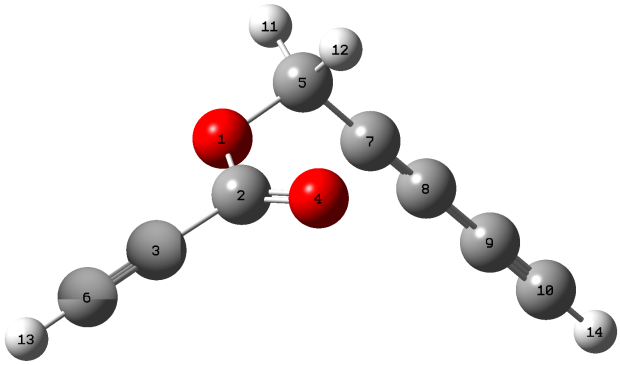


SCF Done: E(RM062X)[a] = -457.32971192 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -457.272831 A.U.[b]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	O	-0.826589	0.052971	0.000301
2	C	-2.115081	-0.320336	-0.000053
3	C	-2.996797	0.836372	-0.000026
4	O	-2.490236	-1.465777	-0.00036
5	C	0.099709	-1.044971	0.000240
6	C	-3.761608	1.766584	-0.000019
7	C	1.453599	-0.503563	0.000117
8	C	2.590968	-0.091598	0.000028
9	C	3.887812	0.379312	-0.000080
10	C	5.023940	0.792052	-0.000174
11	H	-0.074330	-1.665062	0.885082
12	H	-0.074491	-1.665115	-0.884529
13	H	-4.438960	2.592683	-0.000030
14	H	6.027130	1.156823	-0.000246

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

Computed energies and geometry of conformer **26-comp-d**.

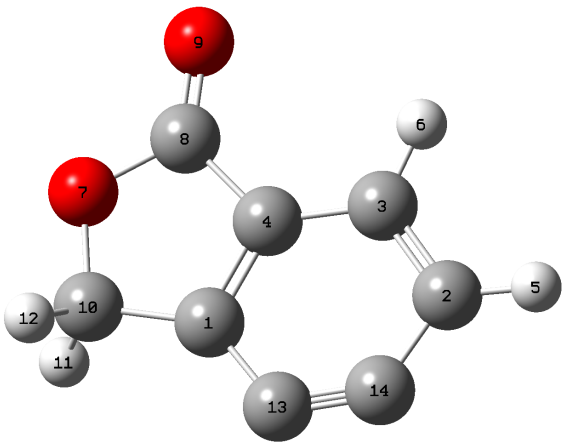


SCF Done: E(RM062X)[a] = -457.32970621 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -457.272414 A.U.[b,c]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	O	-1.144225	0.823289	-0.614533
2	C	-1.666743	0.042466	0.348947
3	C	-2.785924	-0.733671	-0.162130
4	O	-1.267807	-0.000602	1.483270
5	C	-0.015751	1.611665	-0.210366
6	C	-3.718358	-1.393078	-0.544482
7	C	1.212162	0.818059	-0.155572
8	C	2.238817	0.178423	-0.123093
9	C	3.409028	-0.551075	-0.082029
10	C	4.434776	-1.189656	-0.046039
11	H	0.067276	2.389830	-0.970350
12	H	-0.214302	2.064278	0.764941
13	H	-4.544399	-1.979557	-0.883419
14	H	5.339647	-1.754841	-0.012489

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.
[c] This conformer is chiral and so its energy has been used twice in the Boltzmann analysis to account for its enantiomeric partner.

Computed energies and geometry of phthalidyne **27-comp**

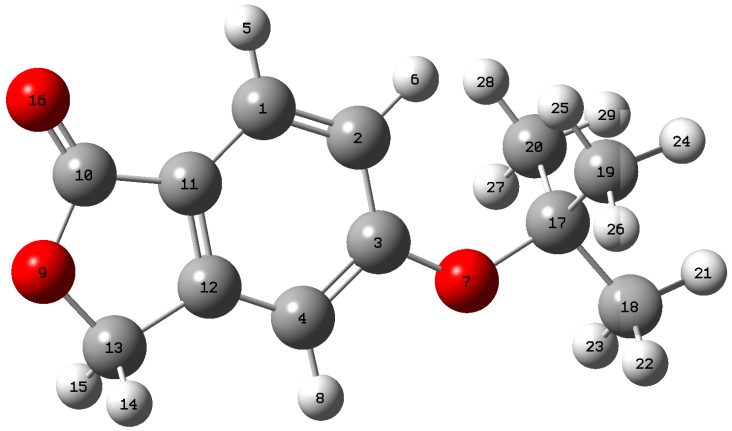


SCF Done: E(RM062X)[a] = -457.421000427 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -457.354360 A.U.[b]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	-0.203499	1.006256	-0.000567
2	C	-2.429086	-0.846300	0.000362
3	C	-1.096583	-1.299162	0.000158
4	C	-0.036961	-0.382278	-0.000389
5	H	-3.275962	-1.519894	0.001131
6	H	-0.882676	-2.363861	-0.000202
7	O	2.065715	0.558787	0.000610
8	C	1.424726	-0.648470	-0.000102
9	O	2.011276	-1.693712	-0.000320
10	C	1.147816	1.656842	0.000295
11	H	1.326688	2.263633	-0.891703
12	H	1.325278	2.263227	0.892881
13	C	-1.535693	1.380622	-0.000842
14	C	-2.455595	0.538540	0.000347

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

Computed energies and geometry of phthalide **28-comp-a**



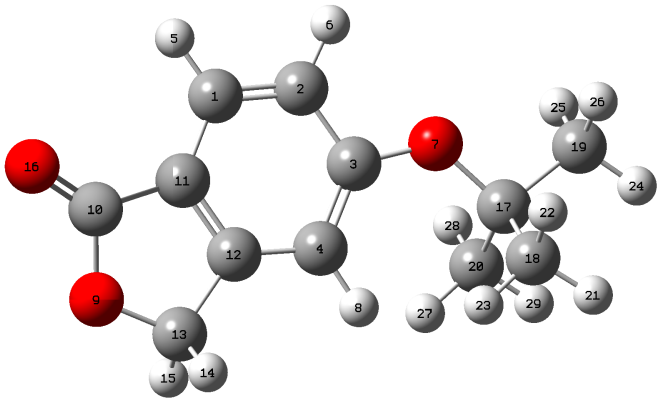
SCF Done: E(RM062X)[a] = -691.13488438 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -690.935672 A.U.[b]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	1.024545	-1.448621	-0.000301
2	C	-0.318542	-1.083017	-0.000799
3	C	-0.686907	0.277141	-0.001109
4	C	0.301189	1.278111	-0.000985
5	H	1.316982	-2.494005	-0.000053
6	H	-1.067972	-1.859557	-0.000992
7	O	-1.948166	0.765055	-0.001854
8	H	-0.014742	2.316201	-0.001254
9	O	3.951681	0.733714	0.000186
10	C	3.459485	-0.544078	0.000302
11	C	1.985864	-0.448717	-0.000178
12	C	1.627625	0.892356	-0.000547
13	C	2.897752	1.701803	-0.000320
14	H	3.000937	2.327188	0.891223
15	H	3.001467	2.326835	-0.892050
16	O	4.171571	-1.510638	0.000680
17	C	-3.163856	-0.019075	0.000419
18	C	-4.243096	1.062526	0.000860
19	C	-3.283441	-0.849464	1.279382
20	C	-3.286711	-0.851600	-1.276856
21	H	-5.236351	0.605929	0.002209
22	H	-4.142691	1.693652	0.887701

23	H	-4.144567	1.692457	-0.887040
24	H	-4.291310	-1.270457	1.339527
25	H	-2.574798	-1.676730	1.330752
26	H	-3.126345	-0.207738	2.150842
27	H	-3.132229	-0.211245	-2.149785
28	H	-2.577922	-1.678702	-1.328845
29	H	-4.294589	-1.273057	-1.333544

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

Computed energies and geometry of phthalide **28-comp-b**



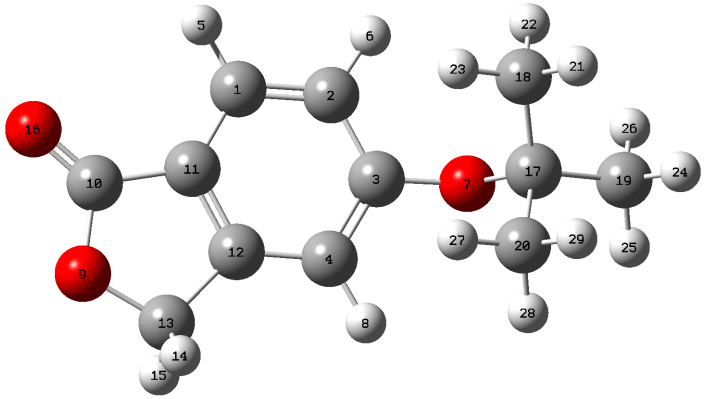
SCF Done: E(RM062X)[a] = -691.13501812 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -690.935554 A.U.[b]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	-1.453737	1.760783	0.000050
2	C	-0.072685	1.803325	0.000042
3	C	0.701120	0.618552	0.000076
4	C	0.073884	-0.634602	0.000078
5	H	-2.049658	2.667791	0.000084
6	H	0.464679	2.745188	0.000034
7	O	2.032180	0.853496	0.000043
8	H	0.632888	-1.559126	0.000019
9	O	-3.575047	-1.222151	-0.000204
10	C	-3.497772	0.146055	0.000381
11	C	-2.066169	0.507151	0.000138
12	C	-1.317321	-0.653326	0.000084
13	C	-2.274957	-1.815967	-0.000134
14	H	-2.179493	-2.443107	0.891504
15	H	-2.179291	-2.442867	-0.891920
16	O	-4.472110	0.847034	-0.000389
17	C	3.069382	-0.153854	0.000026
18	C	3.023230	-0.993372	1.277860
19	C	4.341102	0.692878	-0.000177
20	C	3.022974	-0.993597	-1.277651
21	H	3.928220	-1.604909	1.337490

22	H	2.994868	-0.334720	2.150323
23	H	2.165353	-1.664938	1.327384
24	H	5.224664	0.049178	-0.000165
25	H	4.367832	1.330759	-0.887426
26	H	4.367967	1.330977	0.886912
27	H	2.165173	-1.665287	-1.326821
28	H	2.994285	-0.335097	-2.150218
29	H	3.928027	-1.605026	-1.337430

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

Computed energies and geometry of phthalide **28-comp-c**



SCF Done: E(RM062X)[a] = -691.13668992 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -690.936883 A.U.[b,c]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	1.168789	-1.627371	-0.190269
2	C	-0.185308	-1.457945	-0.450028
3	C	-0.734000	-0.169632	-0.579236
4	C	0.067955	0.971351	-0.476475
5	H	1.613210	-2.612392	-0.089554
6	H	-0.844515	-2.310433	-0.572786
7	O	-2.056531	-0.035361	-0.899535
8	H	-0.377423	1.951605	-0.613776
9	O	3.703071	0.977825	0.197715
10	C	3.403066	-0.356537	0.191203
11	C	1.951650	-0.483259	-0.071915
12	C	1.419619	0.787787	-0.216463
13	C	2.542892	1.777074	-0.051096
14	H	2.396262	2.448551	0.800035
15	H	2.718122	2.372326	-0.952120
16	O	4.227743	-1.207841	0.377637
17	C	-3.035267	0.075111	0.172185
18	C	-3.015284	-1.176323	1.046087
19	C	-4.356872	0.193476	-0.574552
20	C	-2.769706	1.325353	1.007137
21	H	-3.813132	-1.115101	1.792005
22	H	-3.180672	-2.070300	0.437431

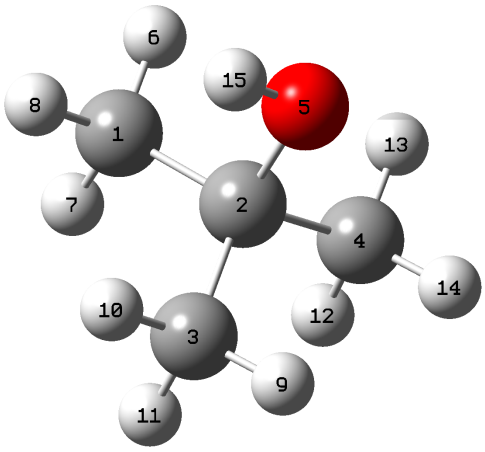
23	H	-2.064617	-1.280872	1.577144
24	H	-5.185461	0.284940	0.133194
25	H	-4.346006	1.074215	-1.222096
26	H	-4.518397	-0.691439	-1.195701
27	H	-1.817109	1.256599	1.540673
28	H	-2.756270	2.214487	0.369455
29	H	-3.563463	1.446329	1.750097

[a] Total electronic energy.

[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

[c] This conformer is chiral and so its energy has been used twice in the Boltzmann analysis to account for its enantiomeric partner.

Computed energies and geometry of *tert*-butanol



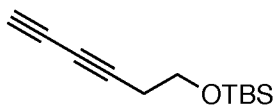
SCF Done: E(RM062X)[a] = -233.57558379 A.U. (Atomic Units = Hartrees)
Sum of electronic and thermal Free Energies = -233.467756 A.U.[b]

Atom #	Atom Type	Cartesian Coordinates (x,y,z)		
1	C	-0.682587	1.258466	-0.514106
2	C	0.005339	0.000000	0.015784
3	C	-0.682587	-1.258466	-0.514106
4	C	1.485602	0.000000	-0.344669
5	O	-0.027574	0.000000	1.445529
6	H	-0.202302	2.149750	-0.100742
7	H	-0.630700	1.304455	-1.606526
8	H	-1.740783	1.270730	-0.227281
9	H	-0.202301	-2.149750	-0.100743
10	H	-1.740782	-1.270731	-0.227281
11	H	-0.630700	-1.304455	-1.606526
12	H	1.618390	0.000000	-1.430583
13	H	1.971526	0.886897	0.071317
14	H	1.971527	-0.886896	0.071318
15	H	-0.947879	0.000000	1.735396

[a] Total electronic energy.
[b] Used for the $\Delta G_{M06\text{-}2X}$ calculation.

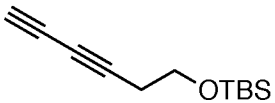
VI. Copies of ^{1}H and ^{13}C NMR spectra for each isolated compound

500 MHz, $CDCl_3$



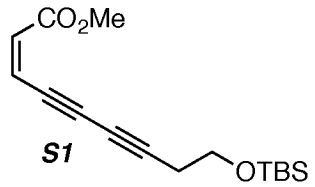
19

125 MHz, $CDCl_3$

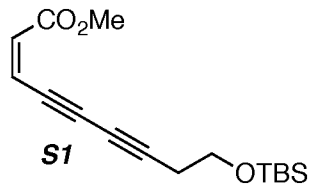


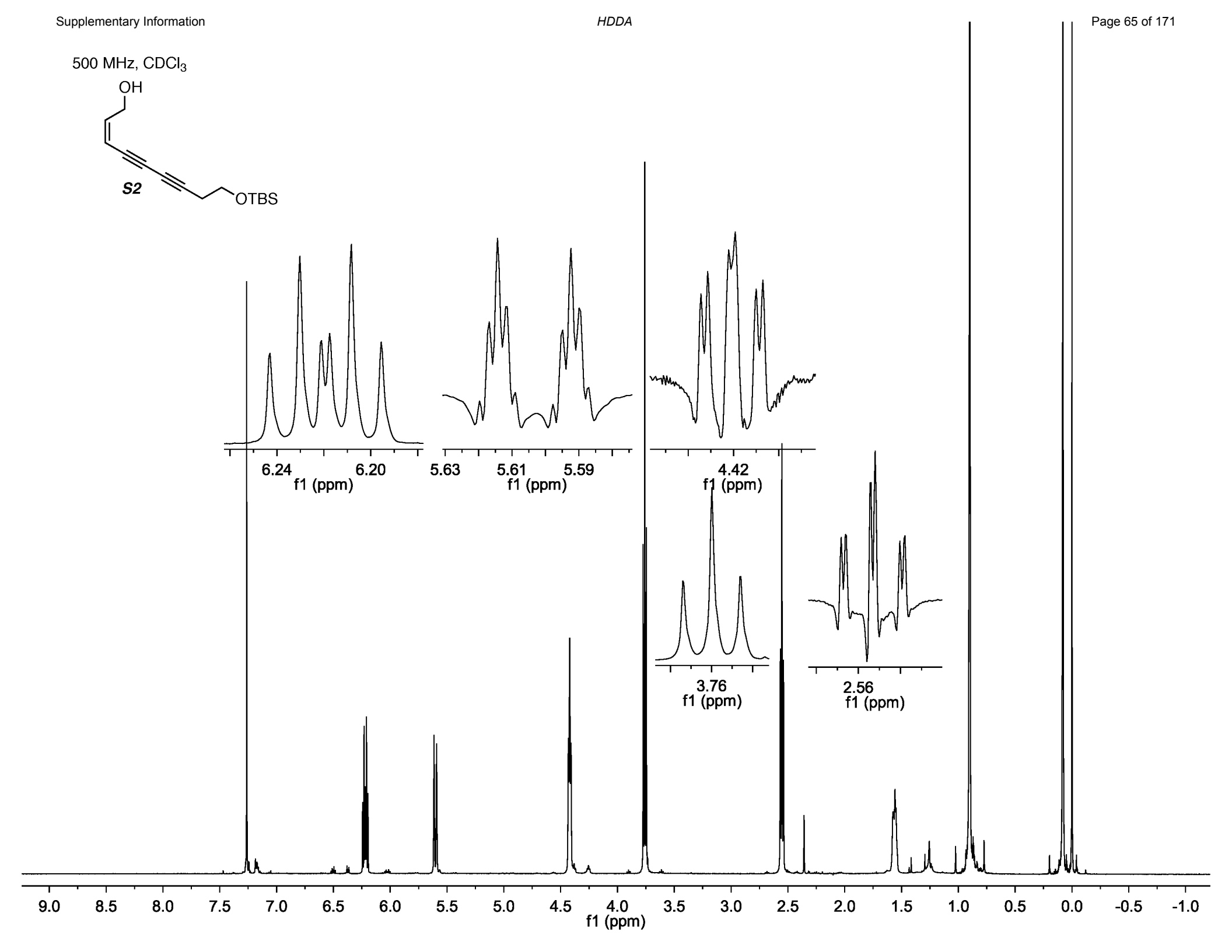
19

500 MHz, $CDCl_3$

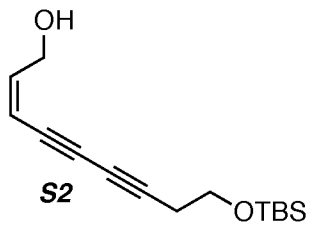


125 MHz, $CDCl_3$

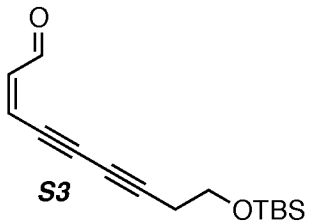



500 MHz, $CDCl_3$
OH
OTBS
S2
6.24
6.20
f1 (ppm)
5.63
5.61
5.59
f1 (ppm)
4.42
f1 (ppm)
3.76
f1 (ppm)
2.56
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

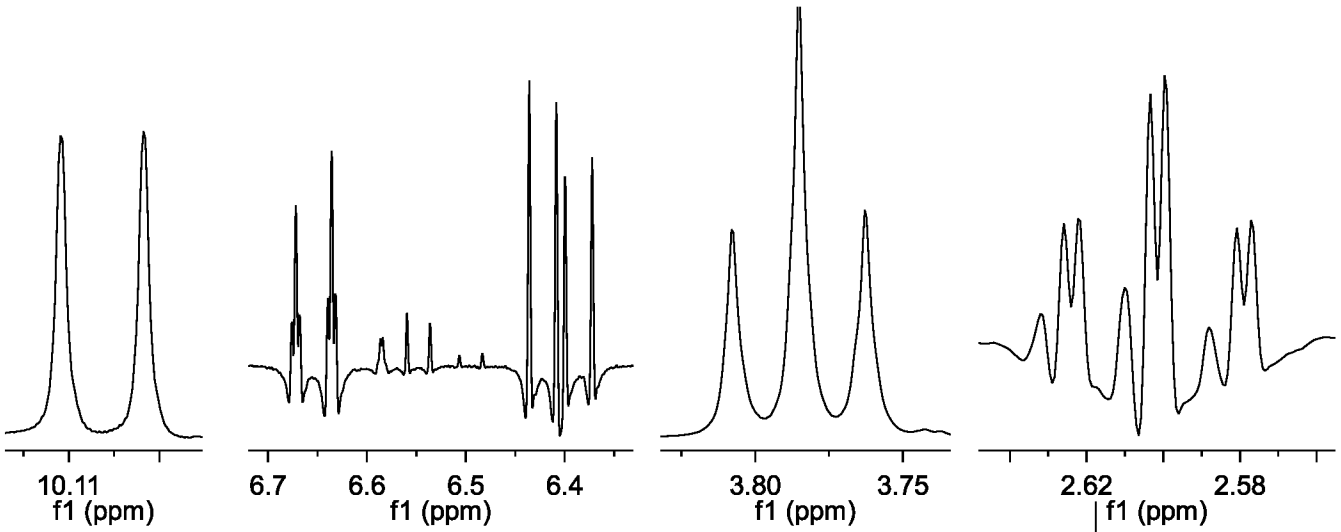
125 MHz, $CDCl_3$

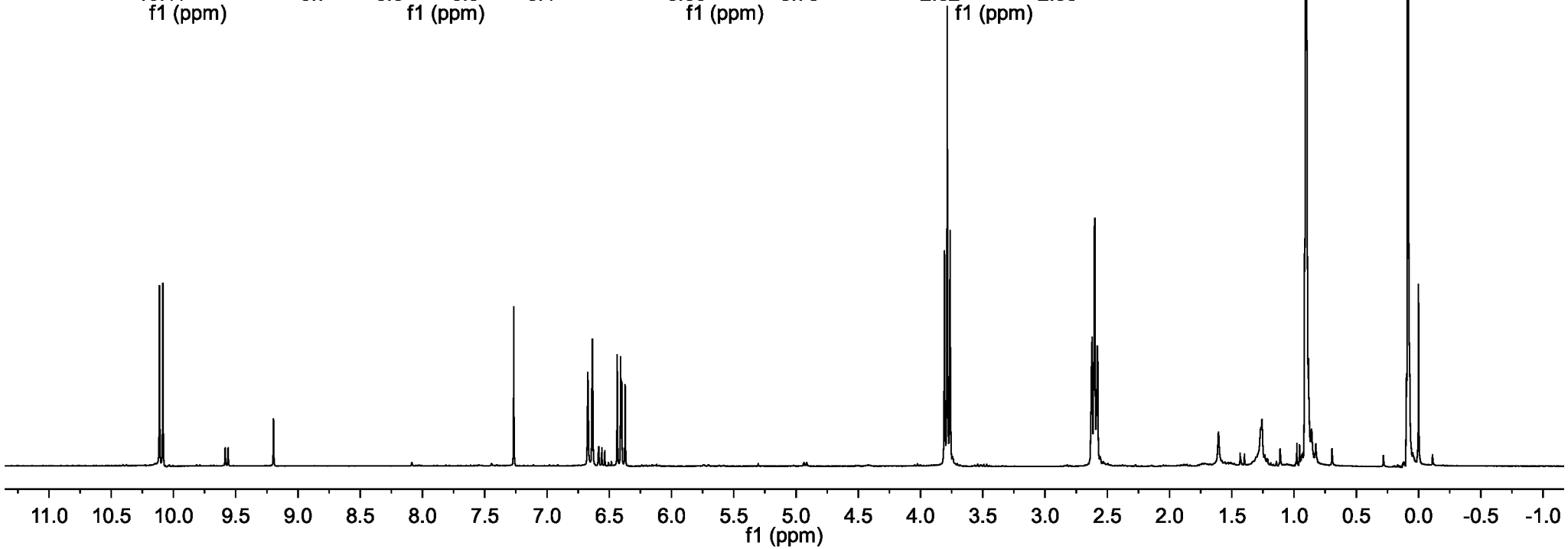


300 MHz, $CDCl_3$

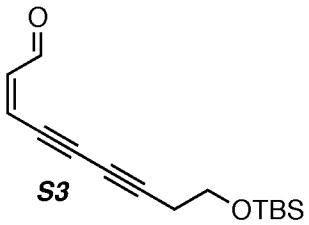


S3



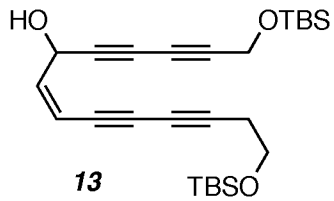


75 MHz, $CDCl_3$

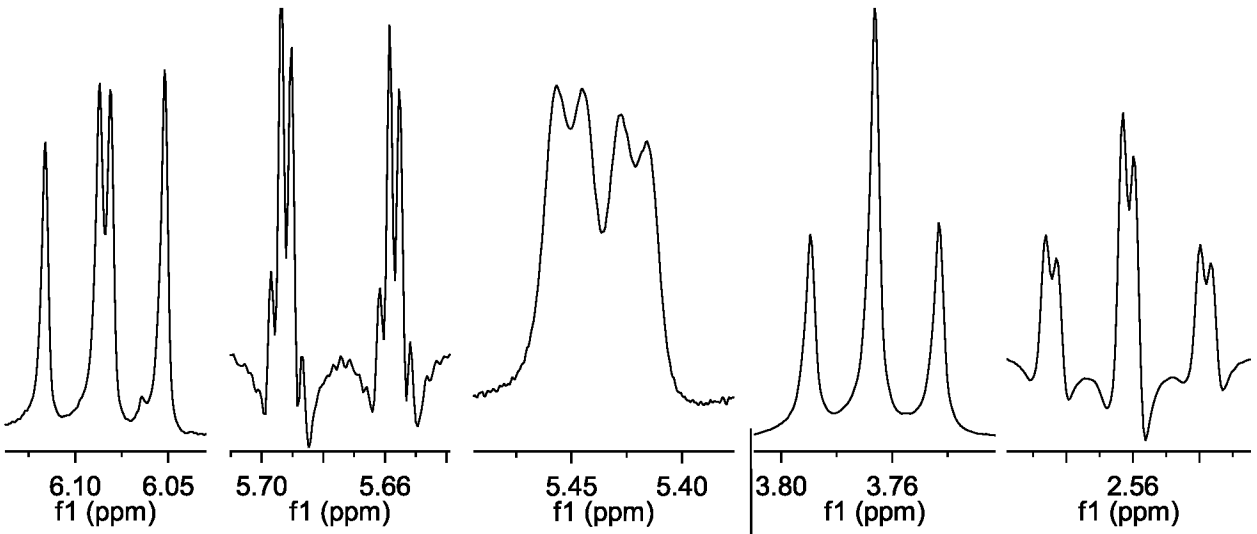


S3

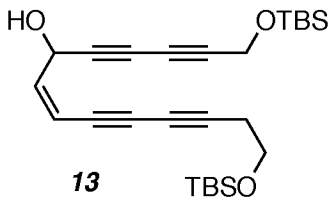
300 MHz, $CDCl_3$



13

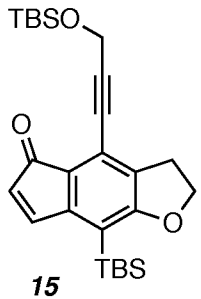


125 MHz, $CDCl_3$

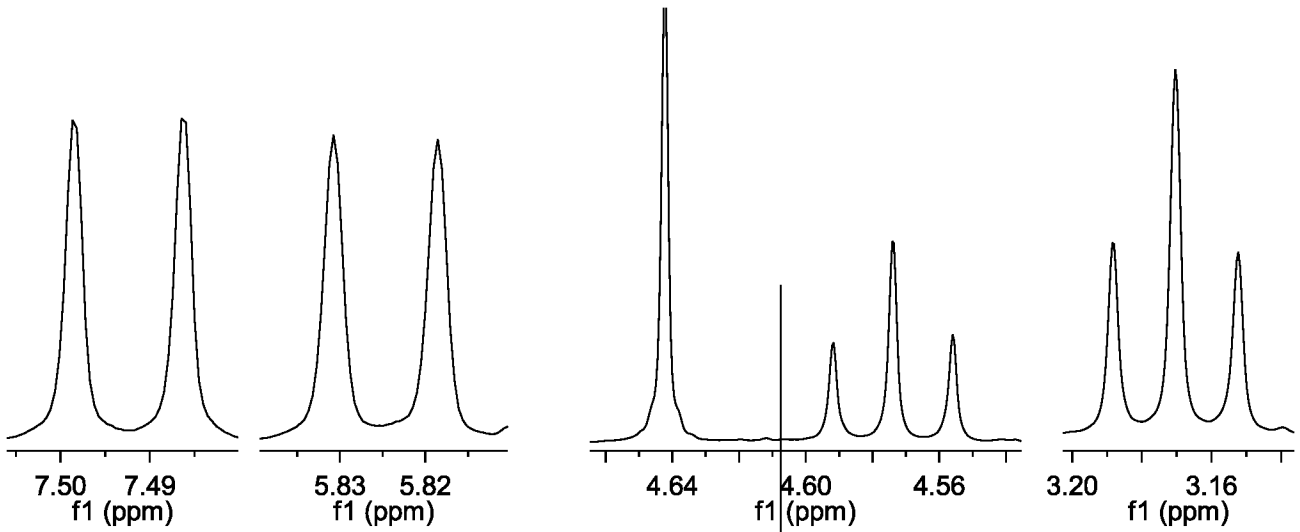


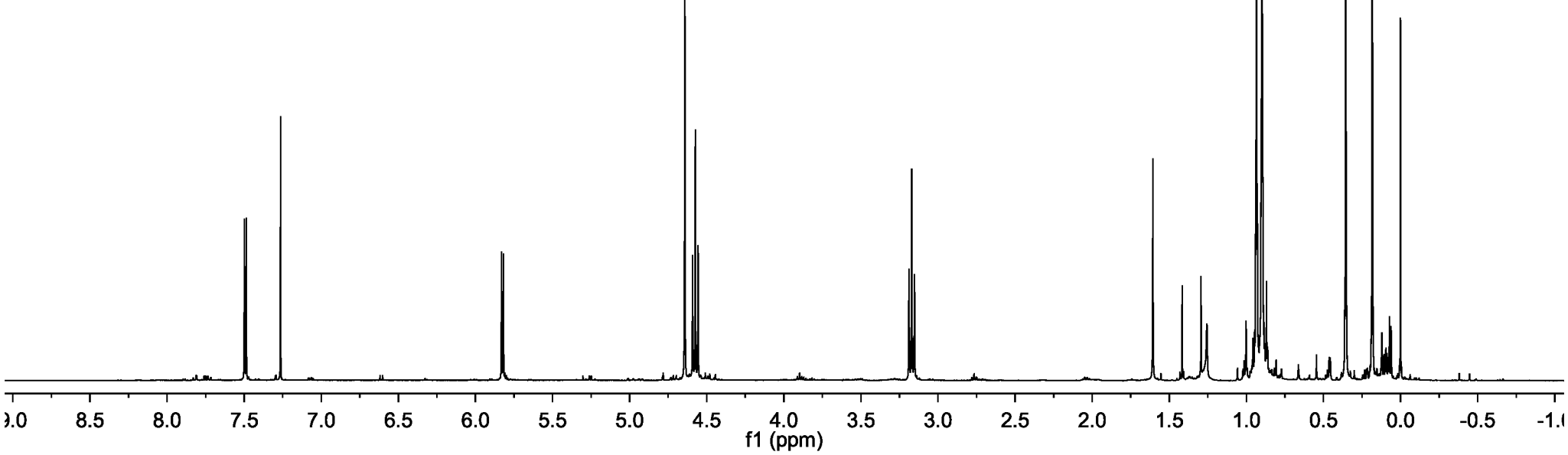
13

500 MHz, $CDCl_3$

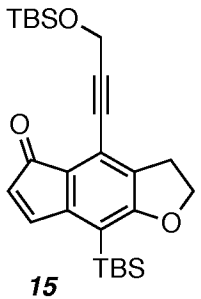


15



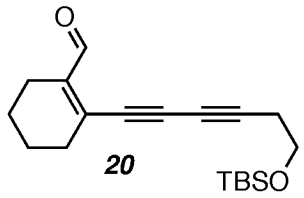


125 MHz, $CDCl_3$



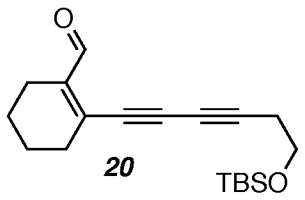
15

500 MHz, $CDCl_3$



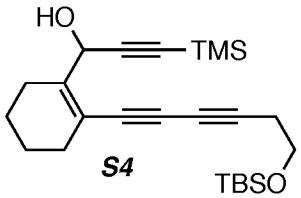
20

125 MHz, $CDCl_3$



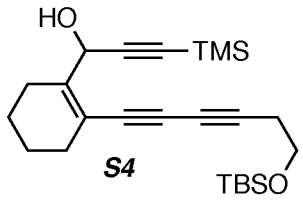
20

500 MHz, $CDCl_3$



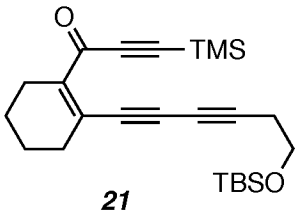
S4

125 MHz, $CDCl_3$

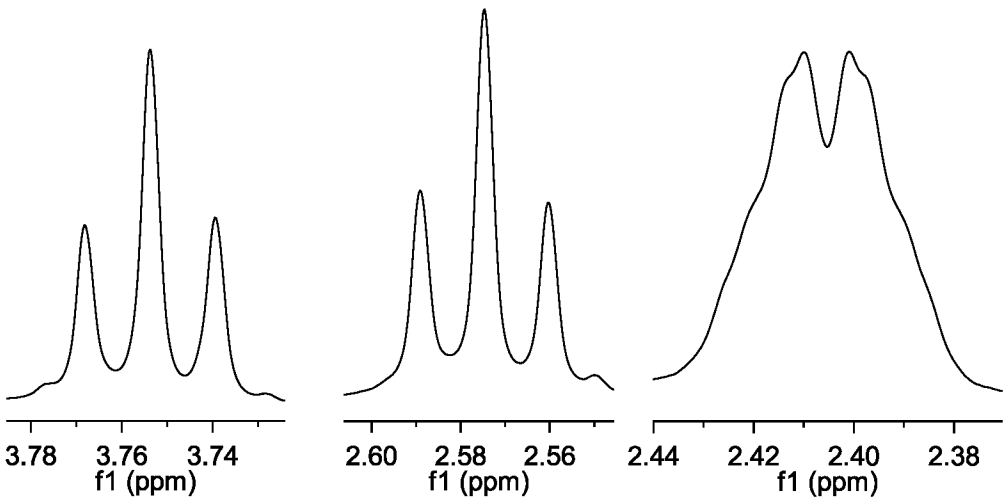


S4

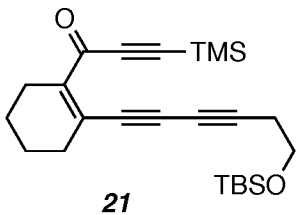
500 MHz, $CDCl_3$



21

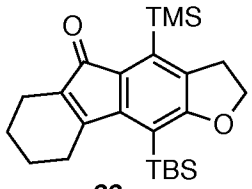


500 MHz, $CDCl_3$

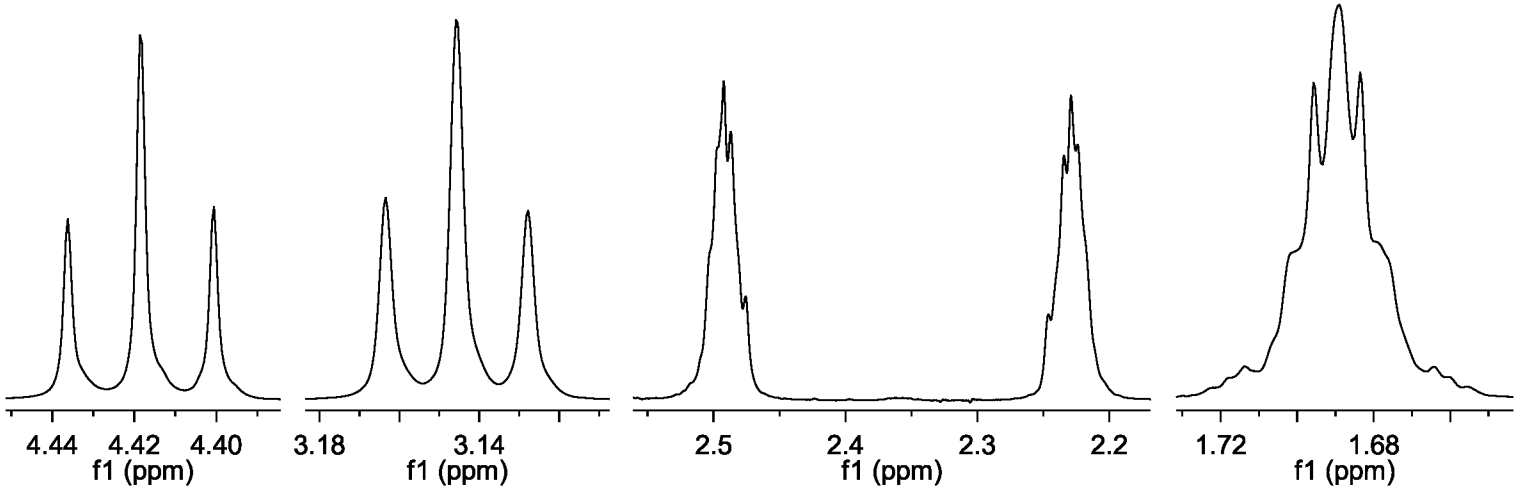


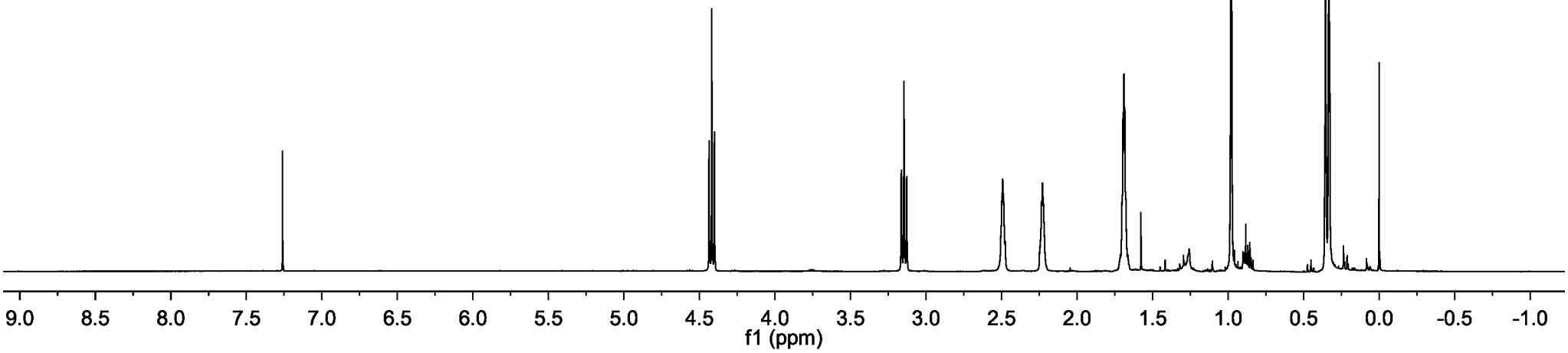
21

500 MHz, $CDCl_3$

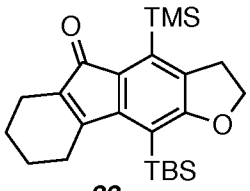


22



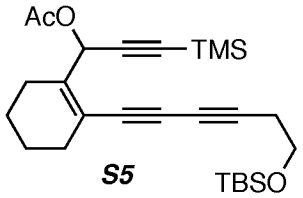


125 MHz, $CDCl_3$



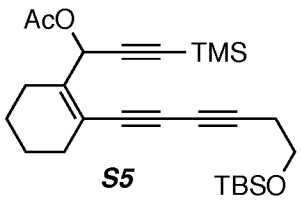
22

500 MHz, $CDCl_3$



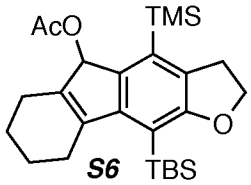
S5

125 MHz, $CDCl_3$

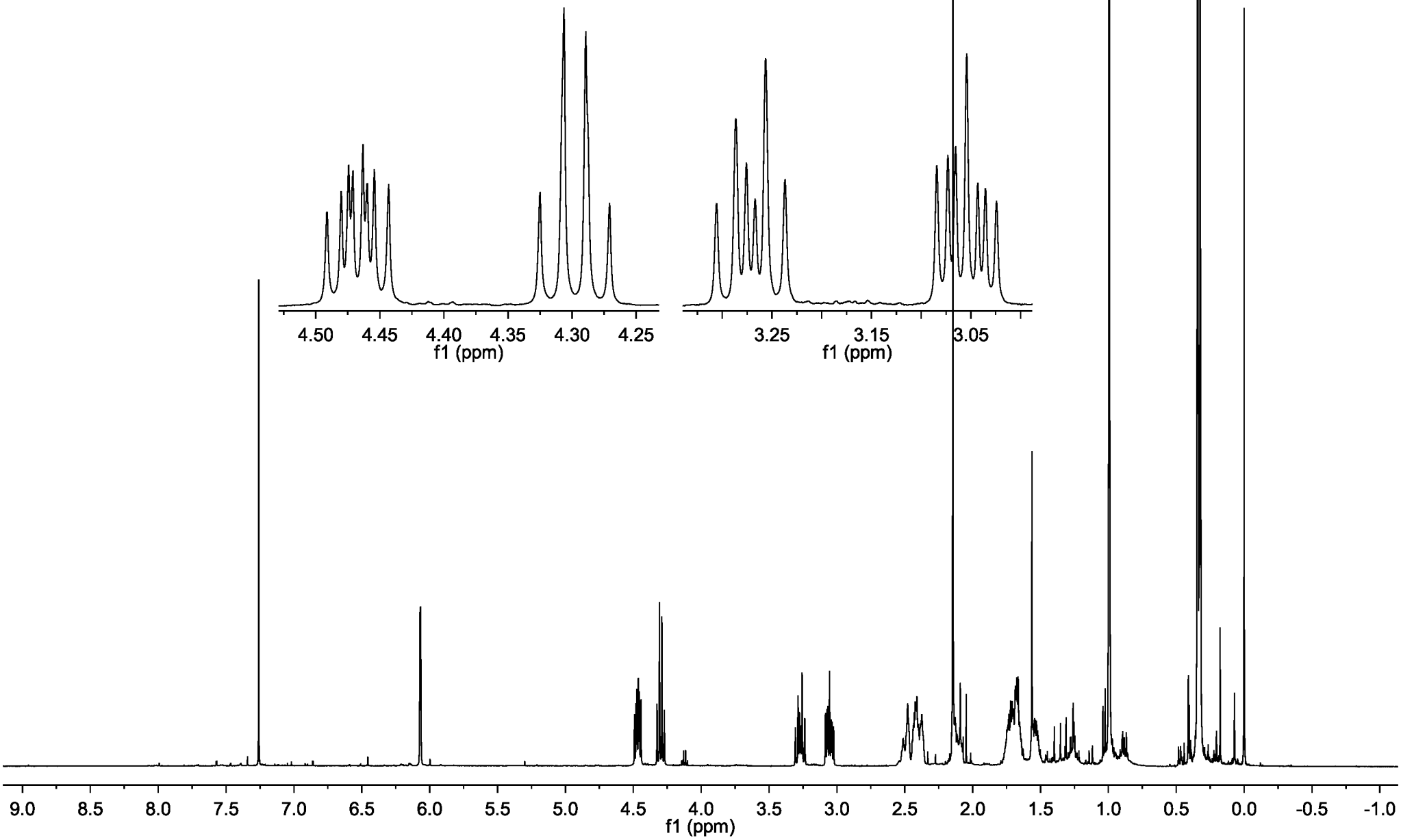


S5

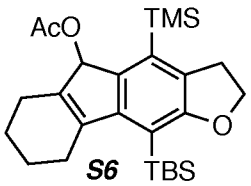
500 MHz, $CDCl_3$



S6

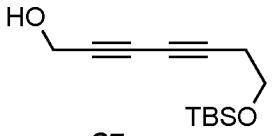


125 MHz, $CDCl_3$

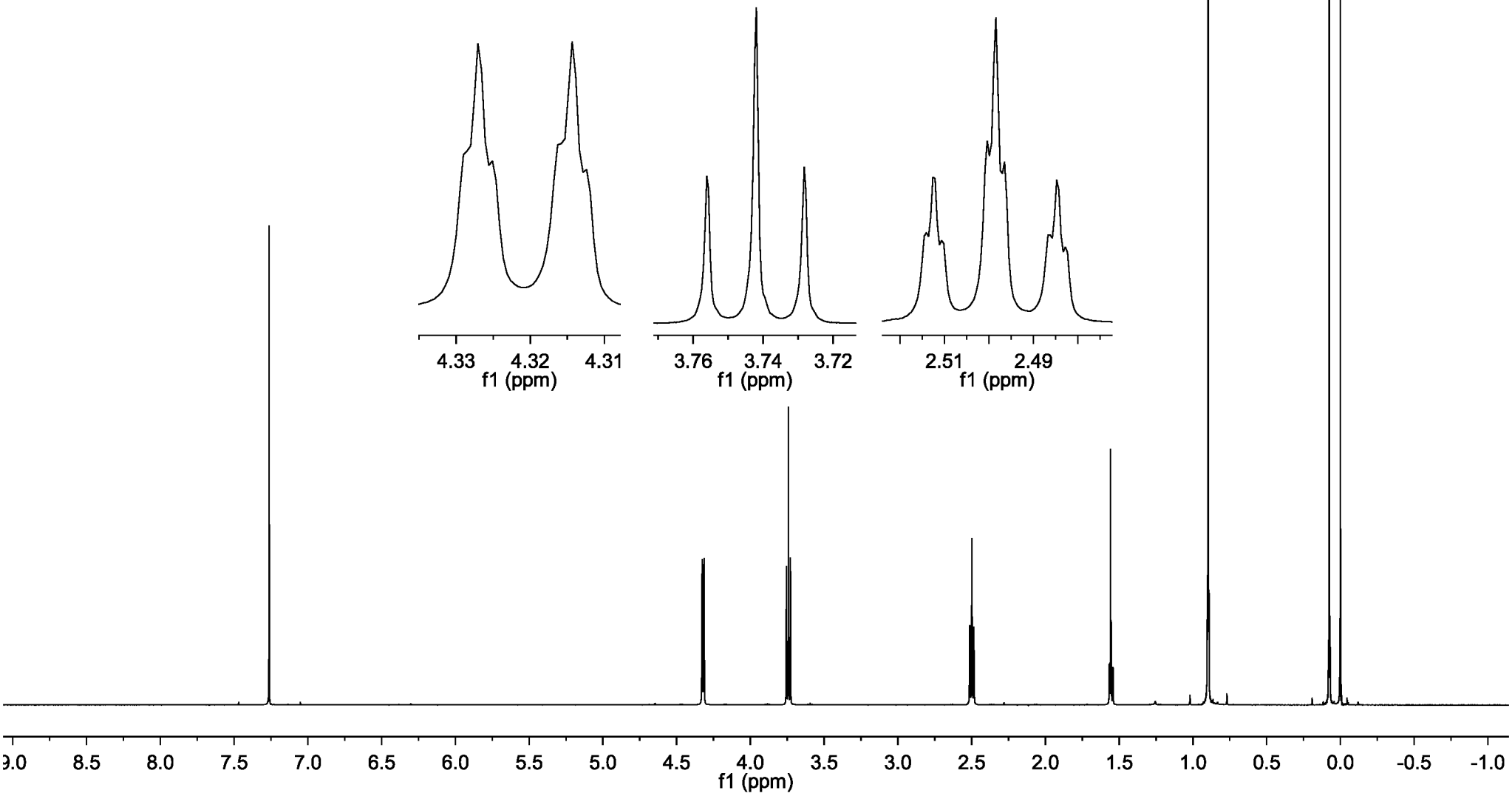


S6

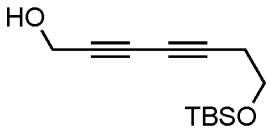
500 MHz, $CDCl_3$



S7

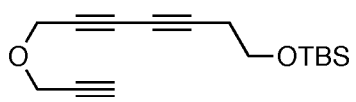


125 MHz, $CDCl_3$



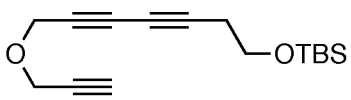
S7

500 MHz, $CDCl_3$

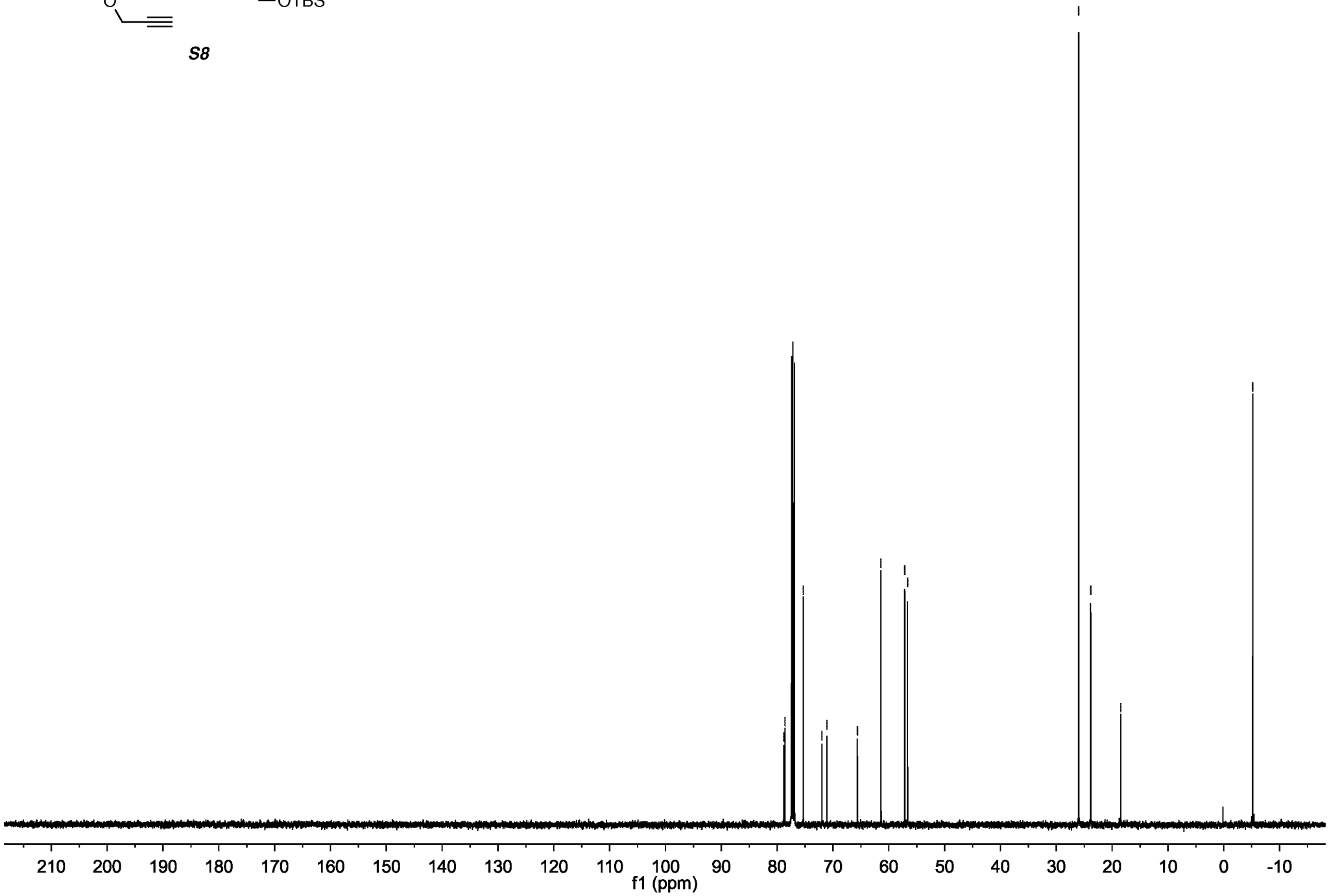


S8

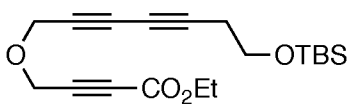
125 MHz, $CDCl_3$



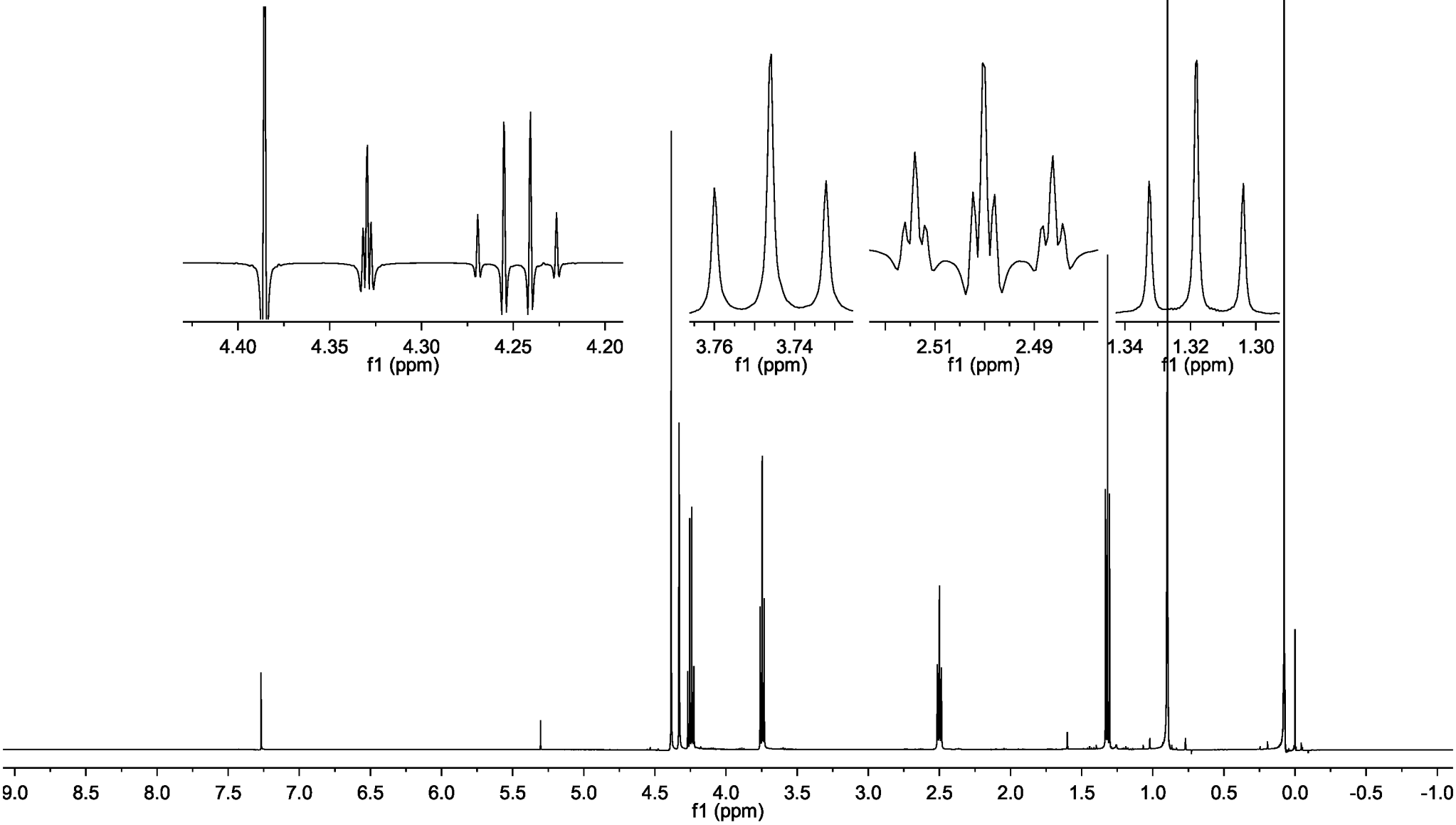
S8



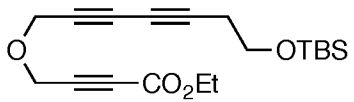
500 MHz, $CDCl_3$



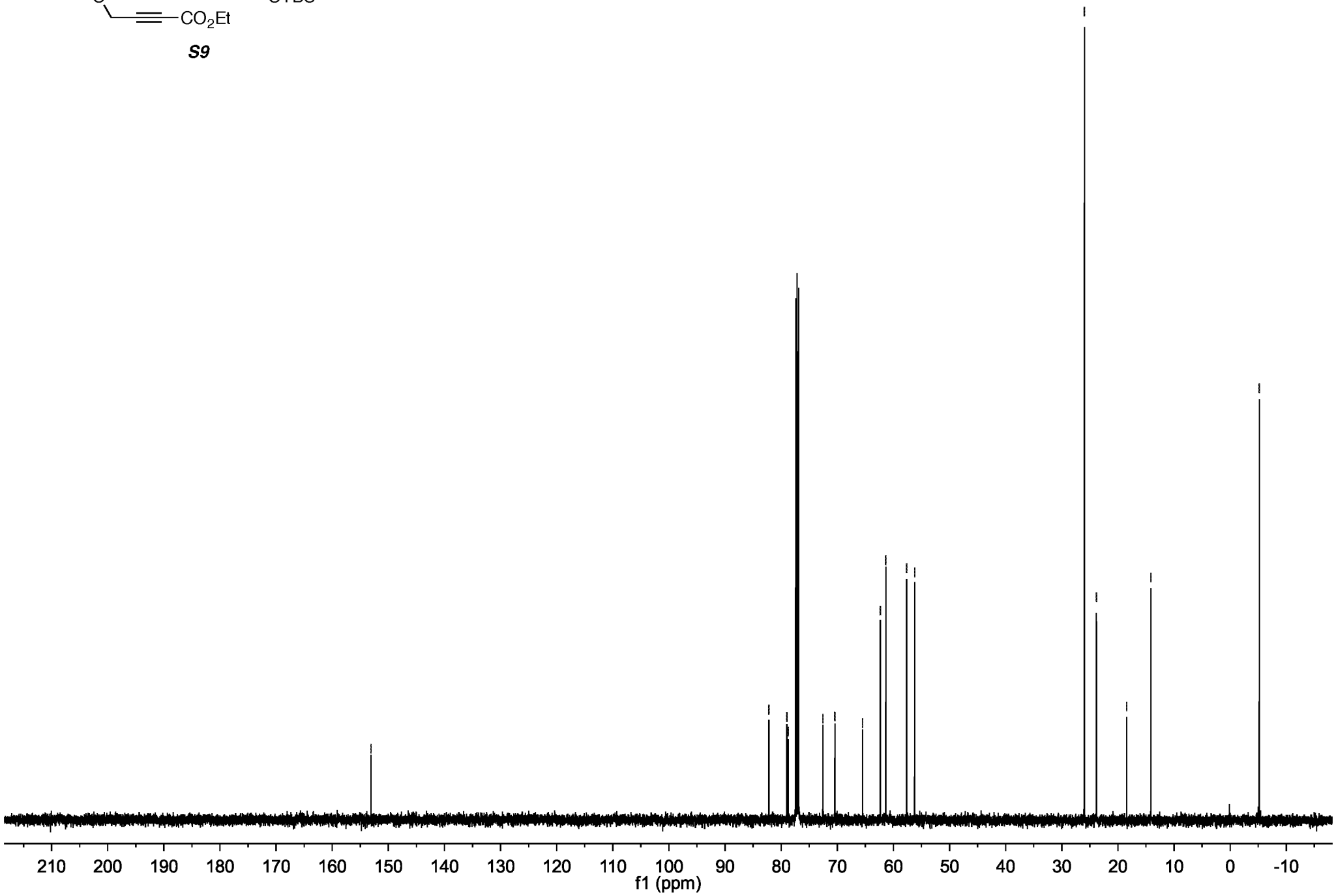
S9



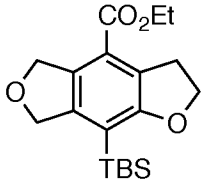
125 MHz, $CDCl_3$



S9

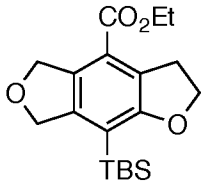


500 MHz, $CDCl_3$



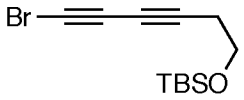
S10

125 MHz, $CDCl_3$

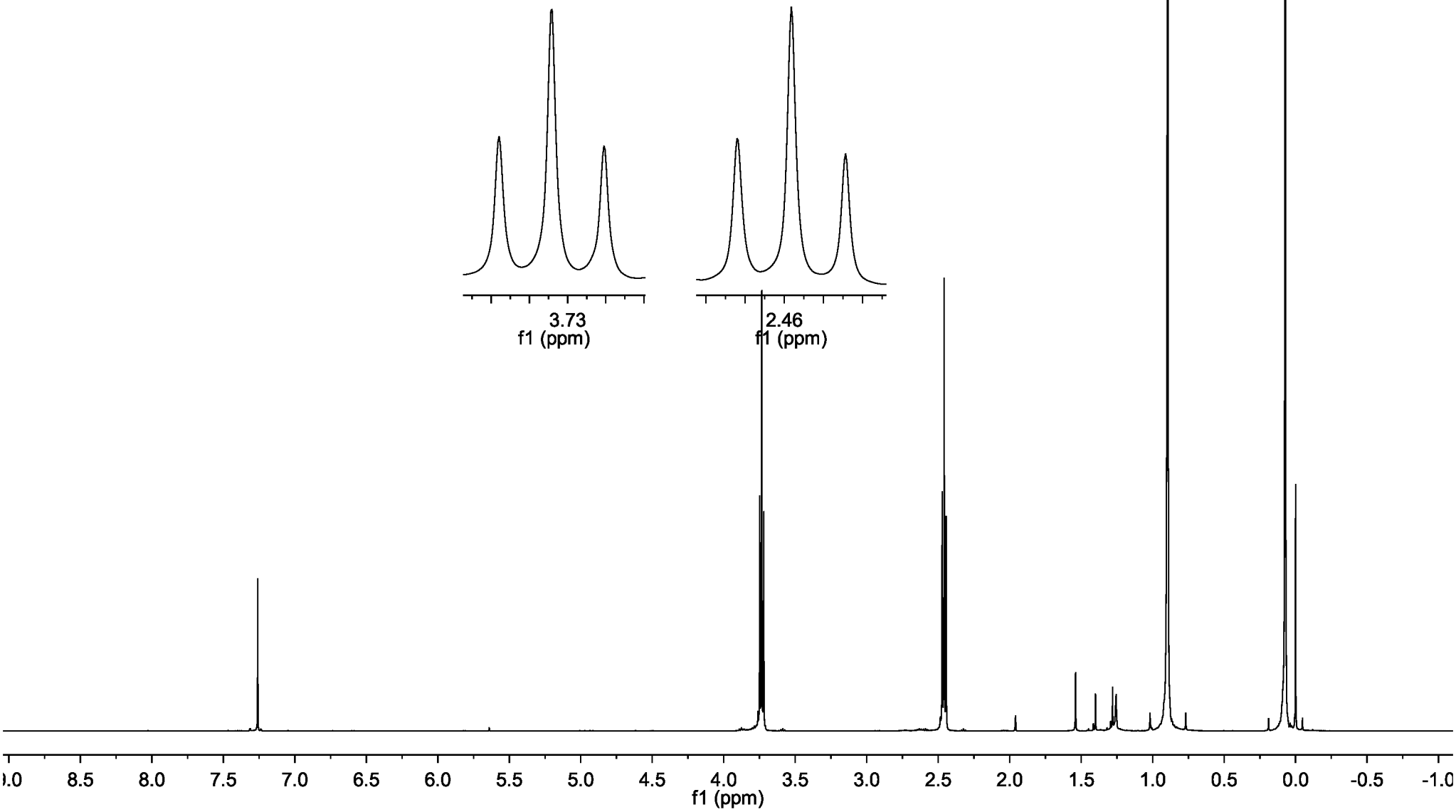


S10

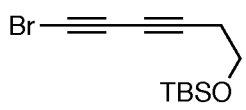
500 MHz, $CDCl_3$



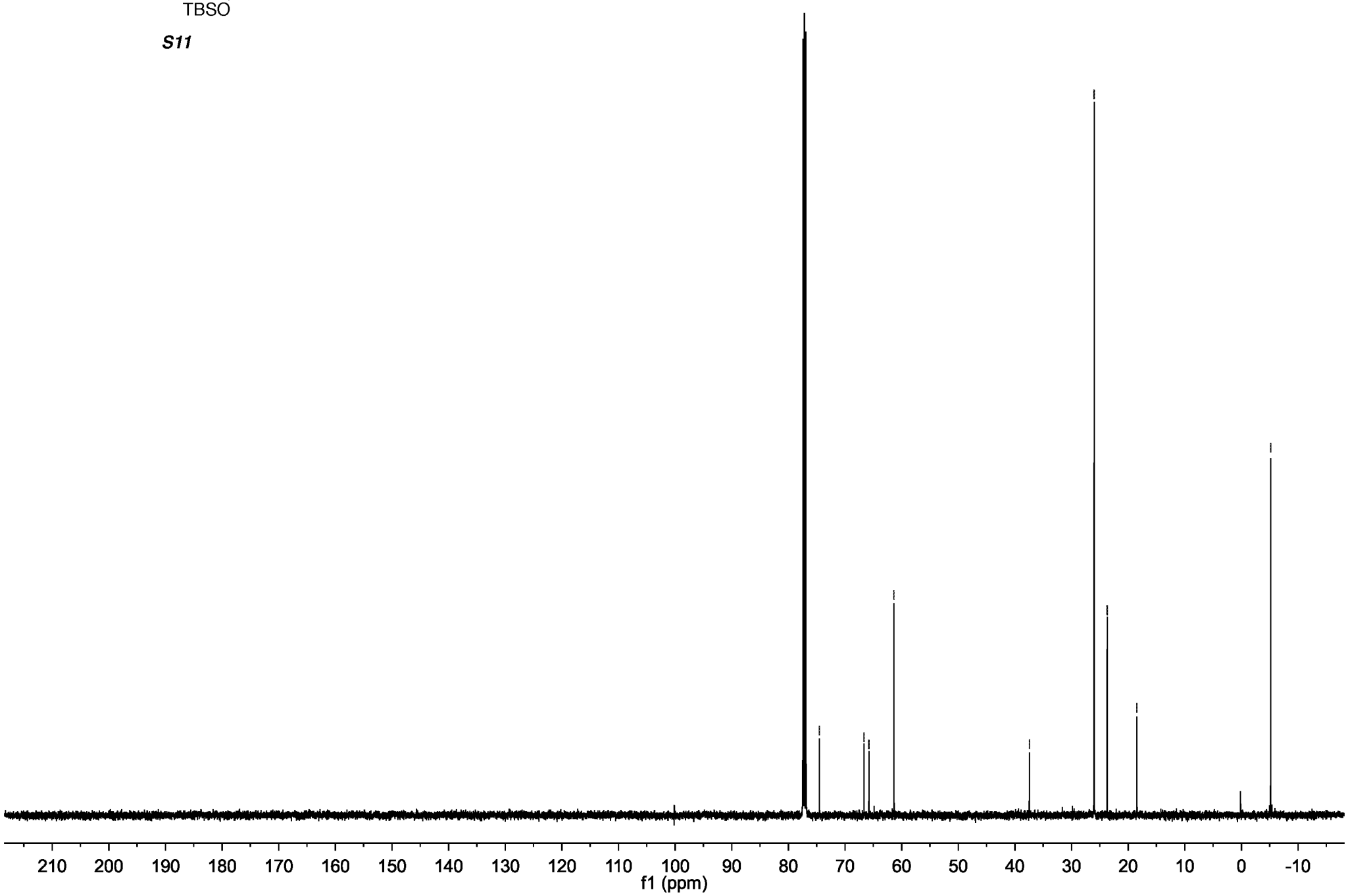
S11



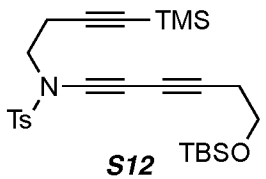
125 MHz, $CDCl_3$



S11

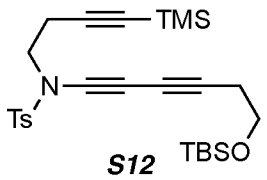


500 MHz, $CDCl_3$



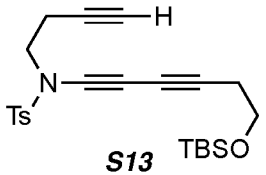
S12

125 MHz, $CDCl_3$



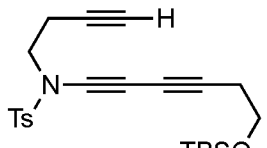
S12

500 MHz, $CDCl_3$



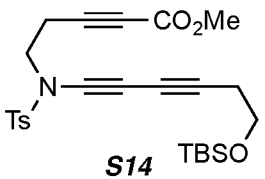
S13

125 MHz, $CDCl_3$



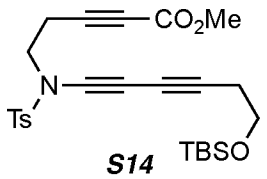
S13

500 MHz, $CDCl_3$



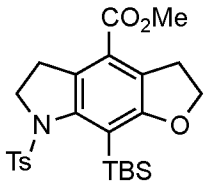
S14

125 MHz, $CDCl_3$



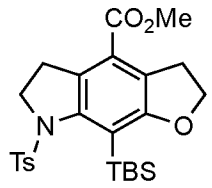
S14

500 MHz, $CDCl_3$



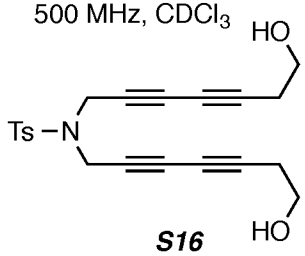
S15

125 MHz, $CDCl_3$



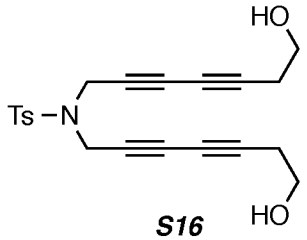
S15

500 MHz, $CDCl_3$



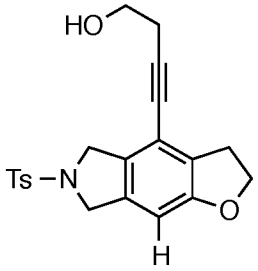
S16

75 MHz, $CDCl_3$

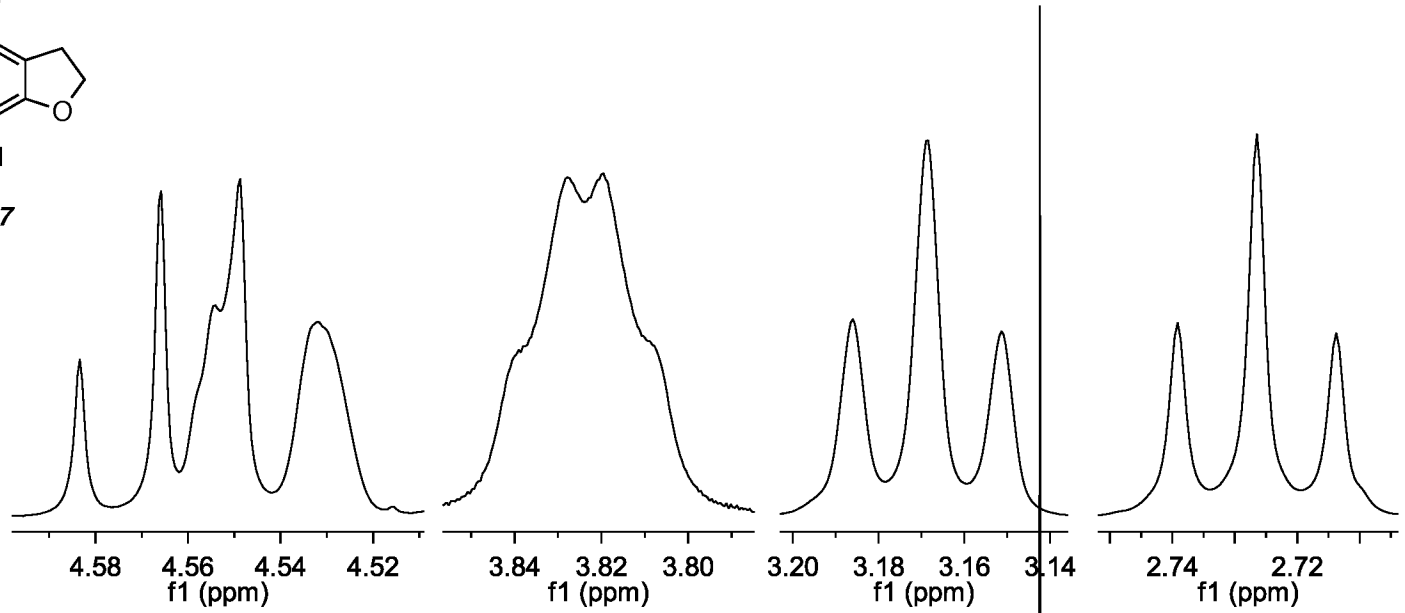


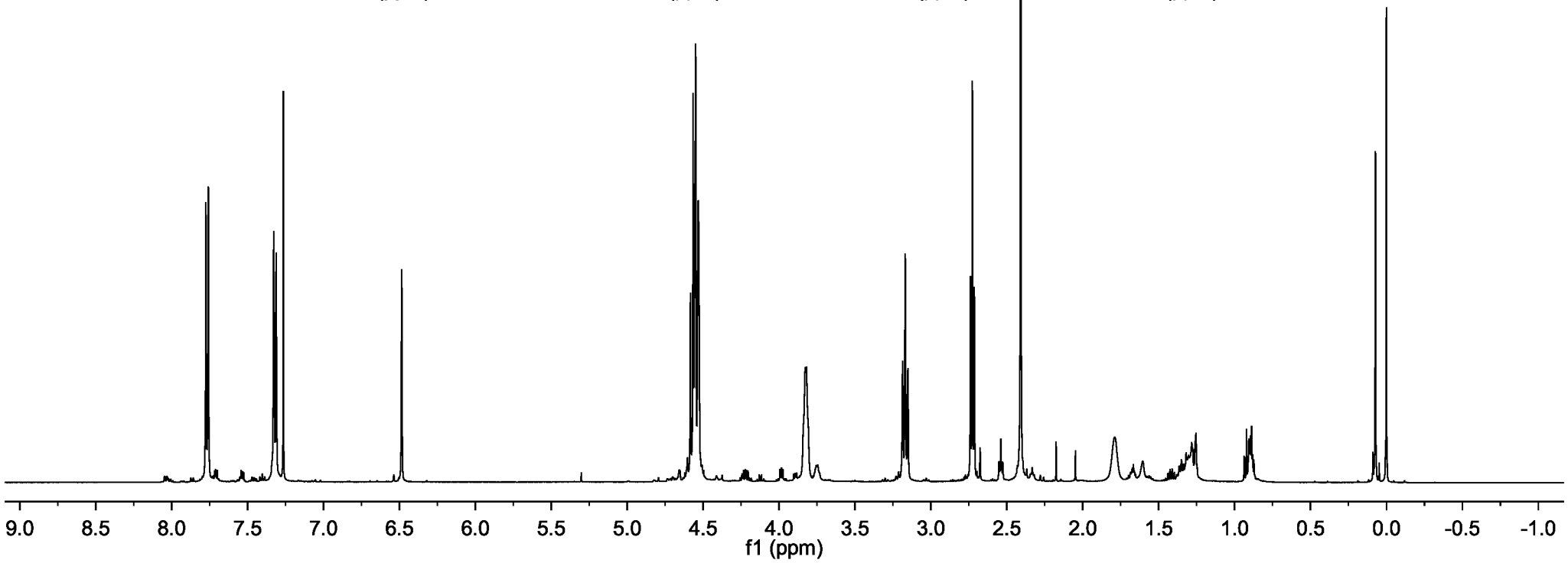
S16

500 MHz, $CDCl_3$

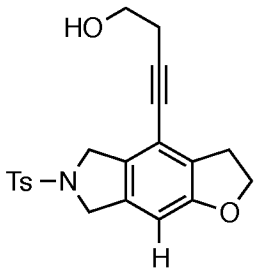


S17



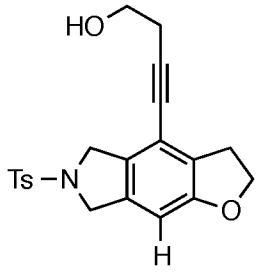


125 MHz, $CDCl_3$



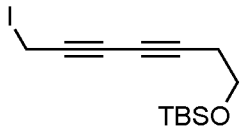
S17

125 MHz, acetone-d_6

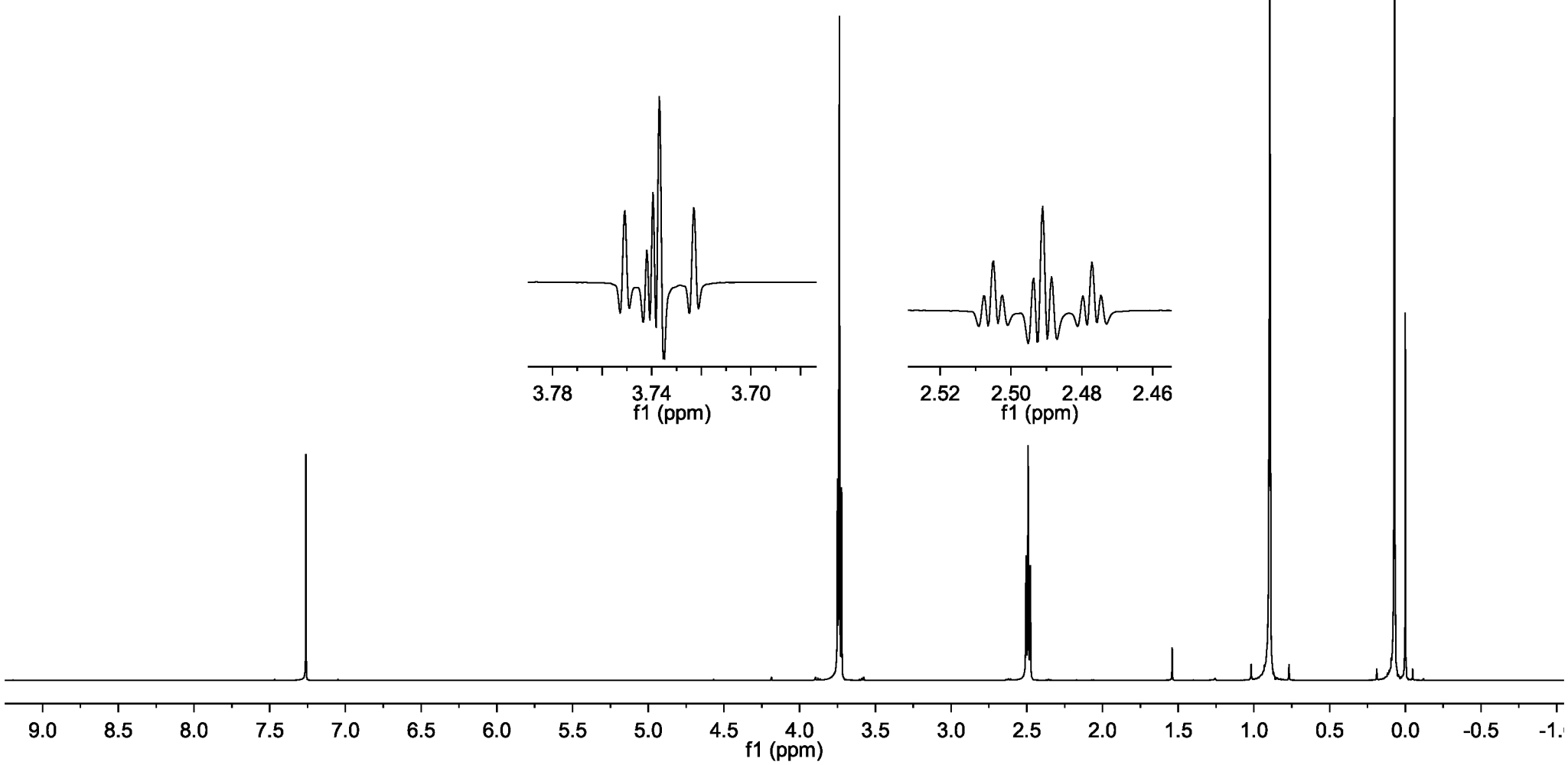


S17

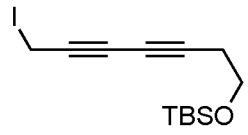
500 MHz, $CDCl_3$



S18

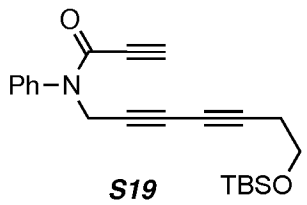


125 MHz, C_6D_6

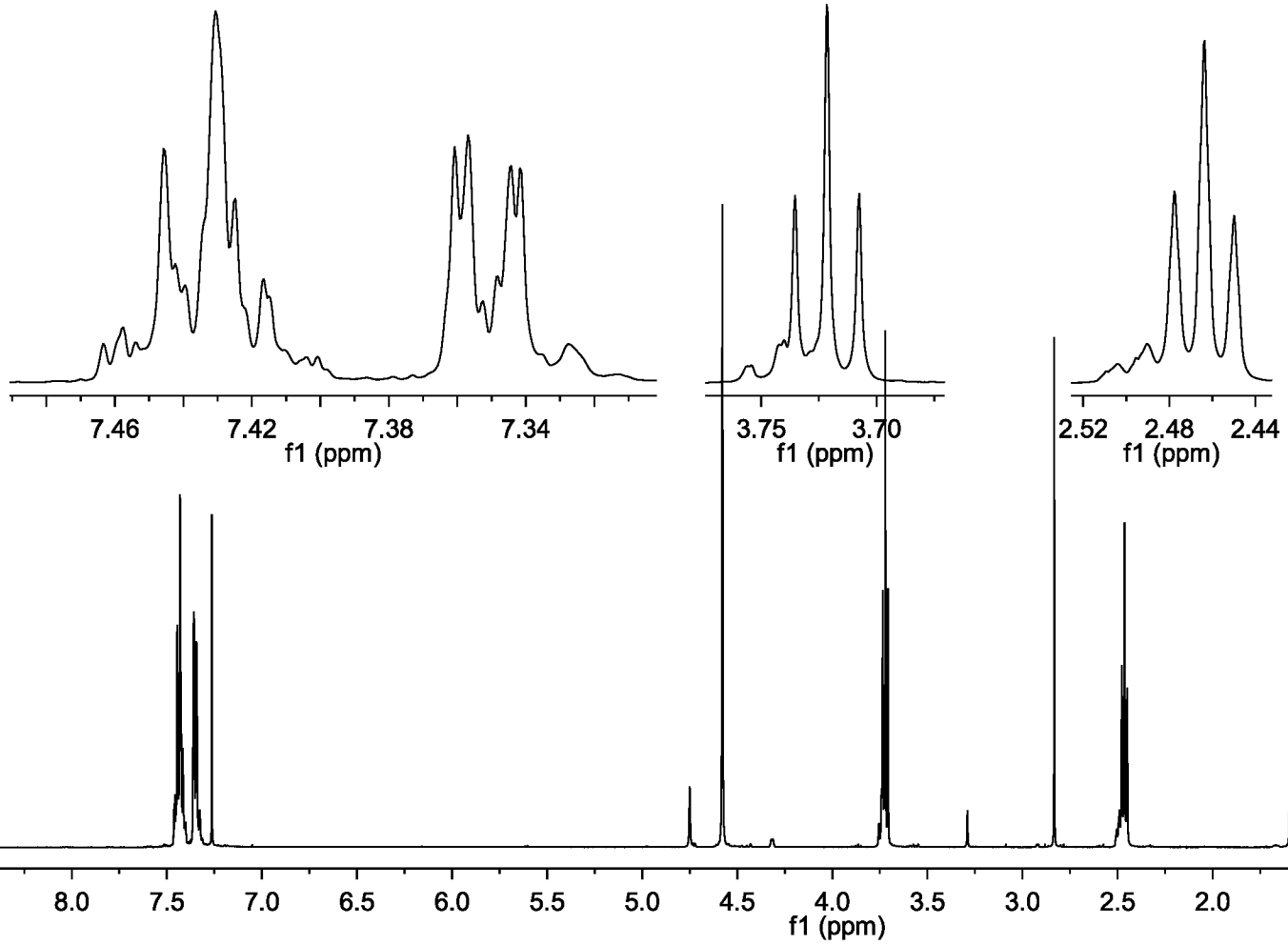


S18

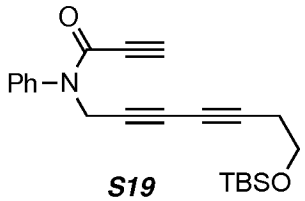
500 MHz, $CDCl_3$



S19

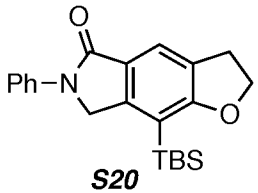


125 MHz, $CDCl_3$

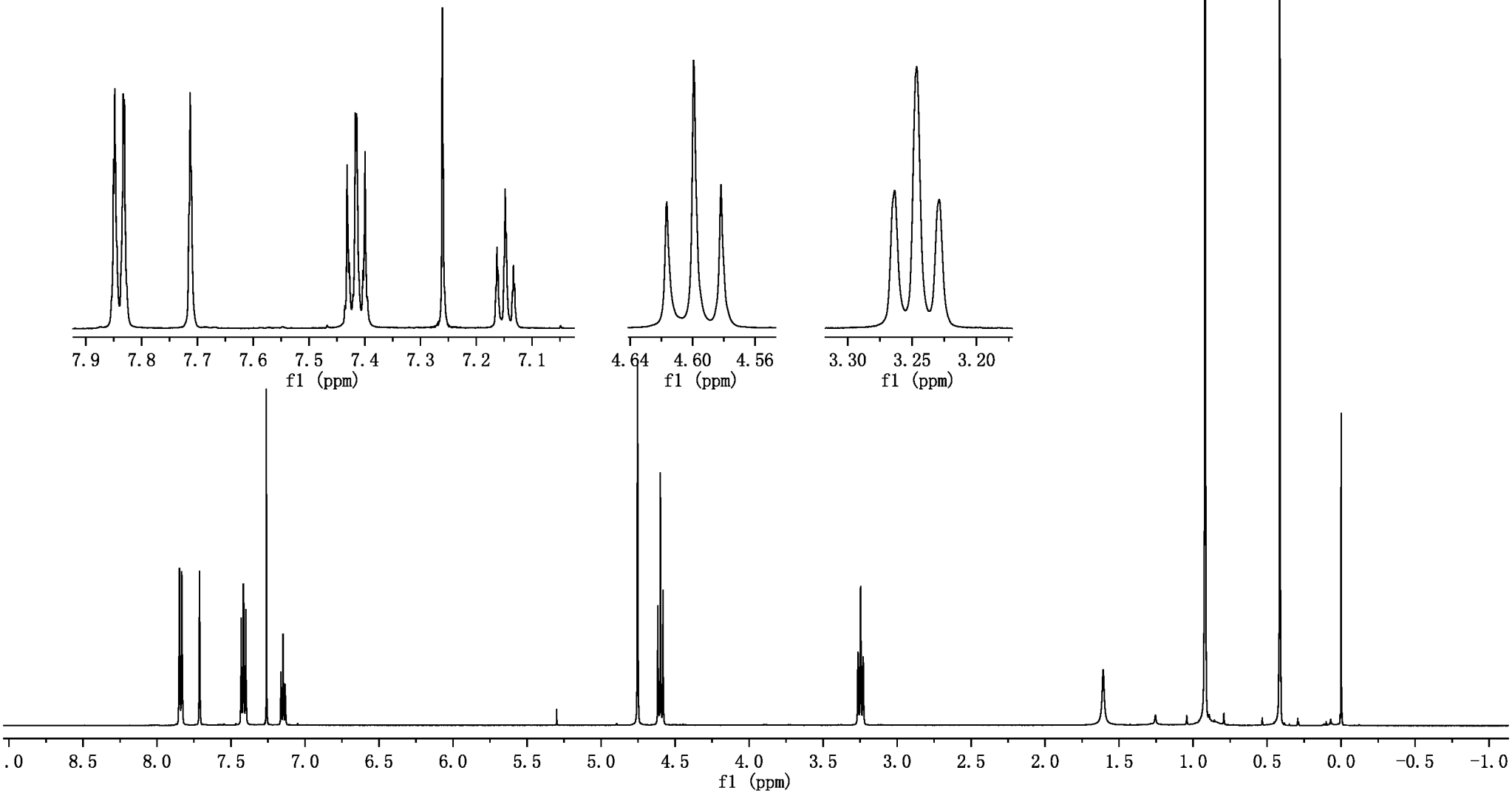


S19

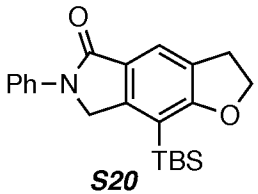
500 MHz, $CDCl_3$



S20

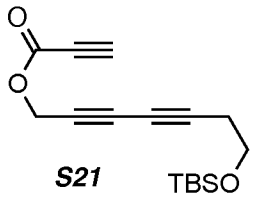


125 MHz, $CDCl_3$

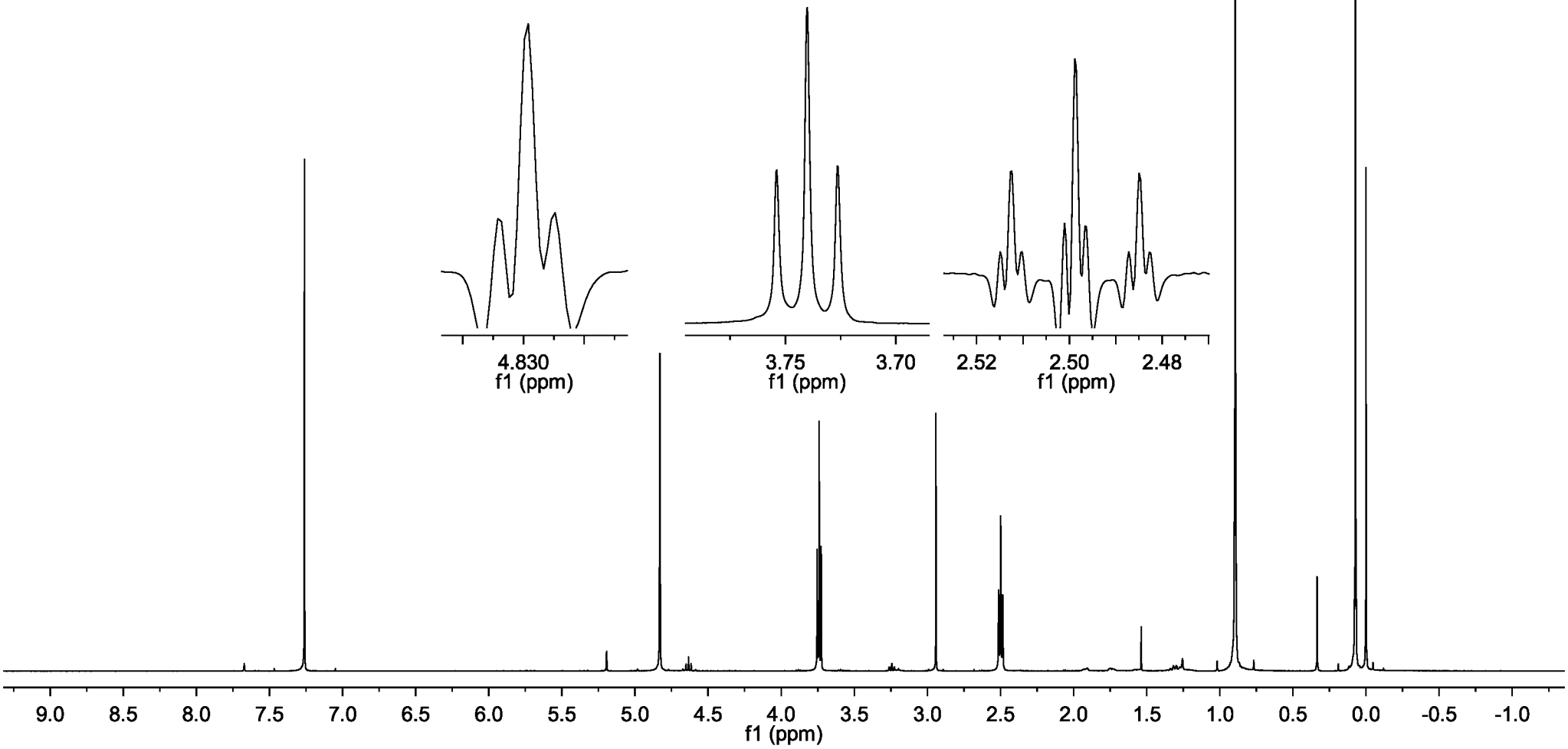


S20

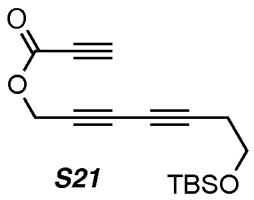
500 MHz, $CDCl_3$



S21

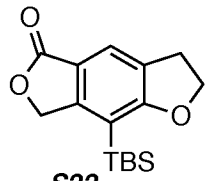


125 MHz, $CDCl_3$

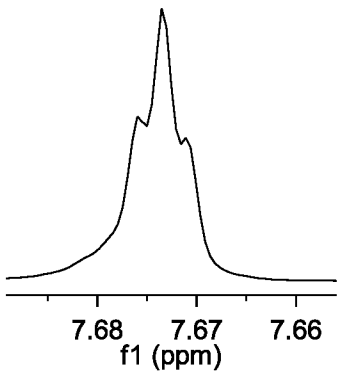


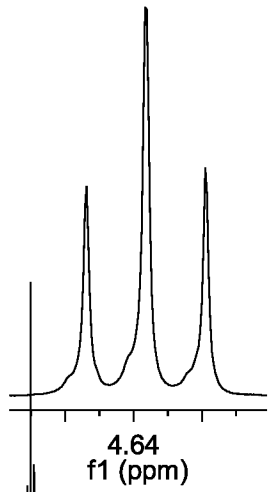
S21

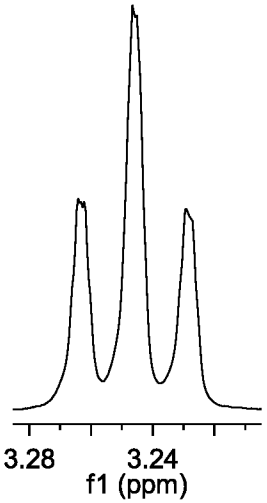
500 MHz, $CDCl_3$



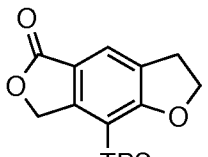
S22





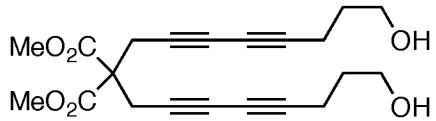


125 MHz, $CDCl_3$



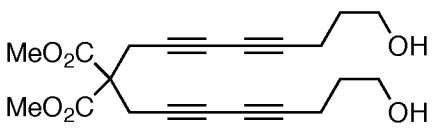
S22

500 MHz, $CDCl_3$

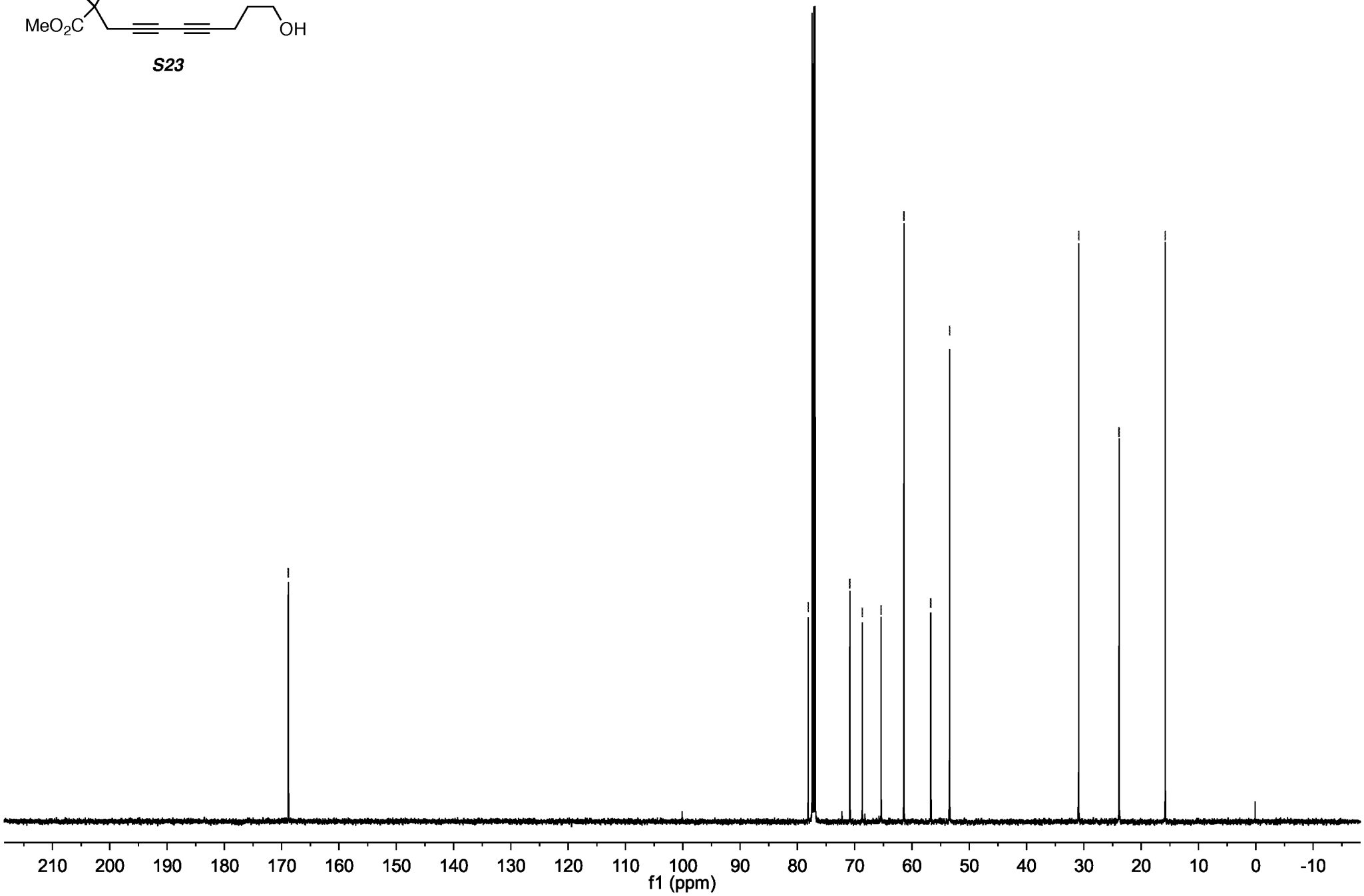


S23

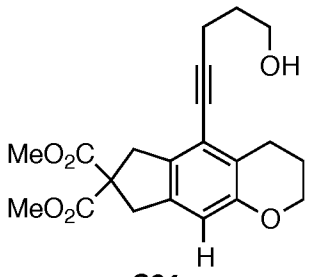
125 MHz, $CDCl_3$



S23

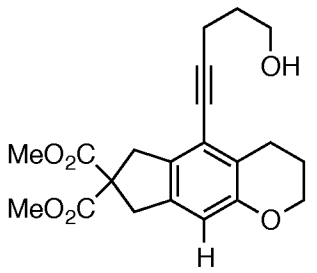


500 MHz, $CDCl_3$

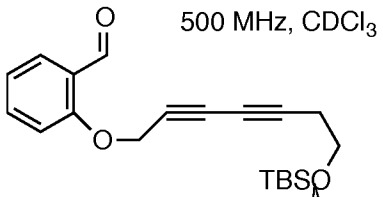


S24

125 MHz, $CDCl_3$

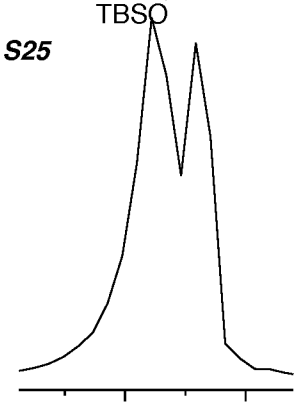


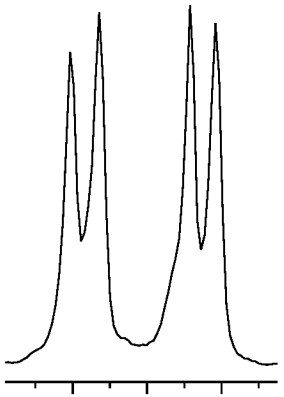
S24

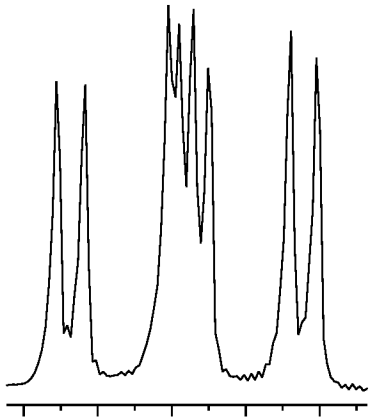


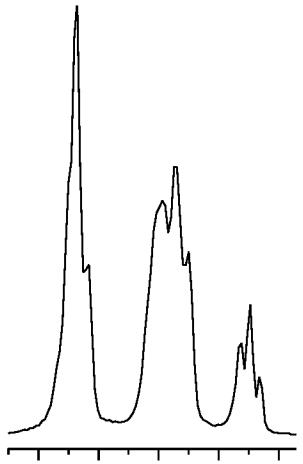
500 MHz, $CDCl_3$

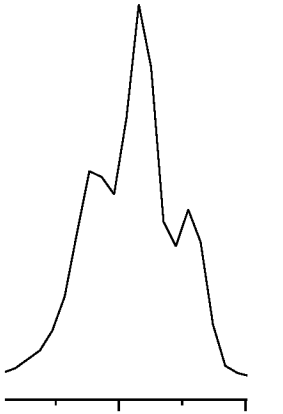
S25

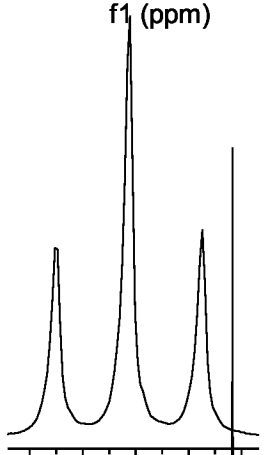


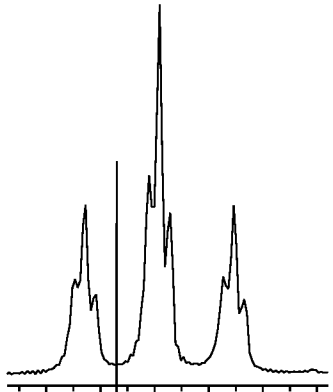




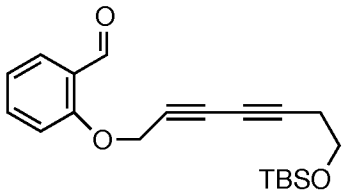






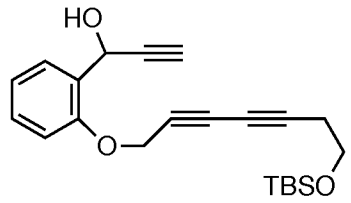


125 MHz, $CDCl_3$

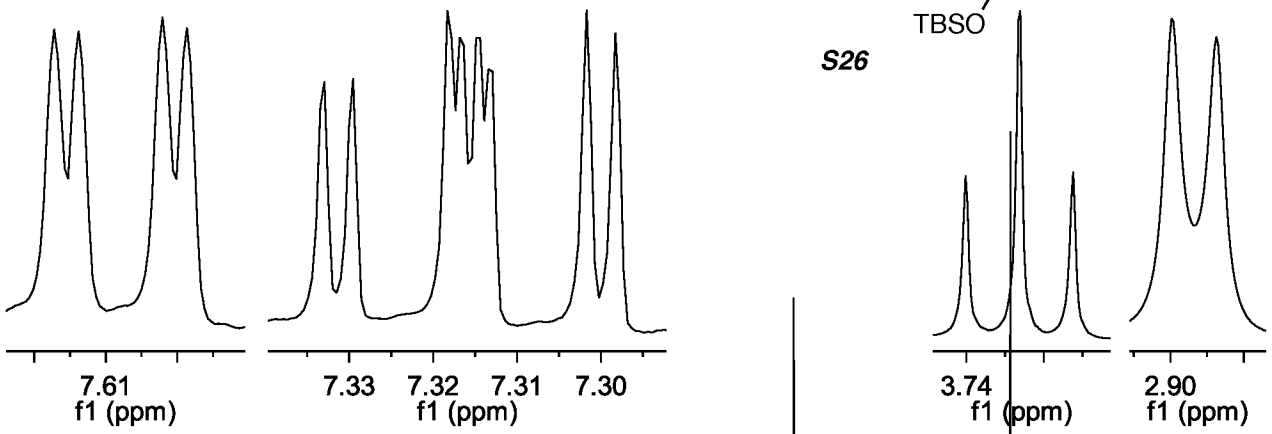


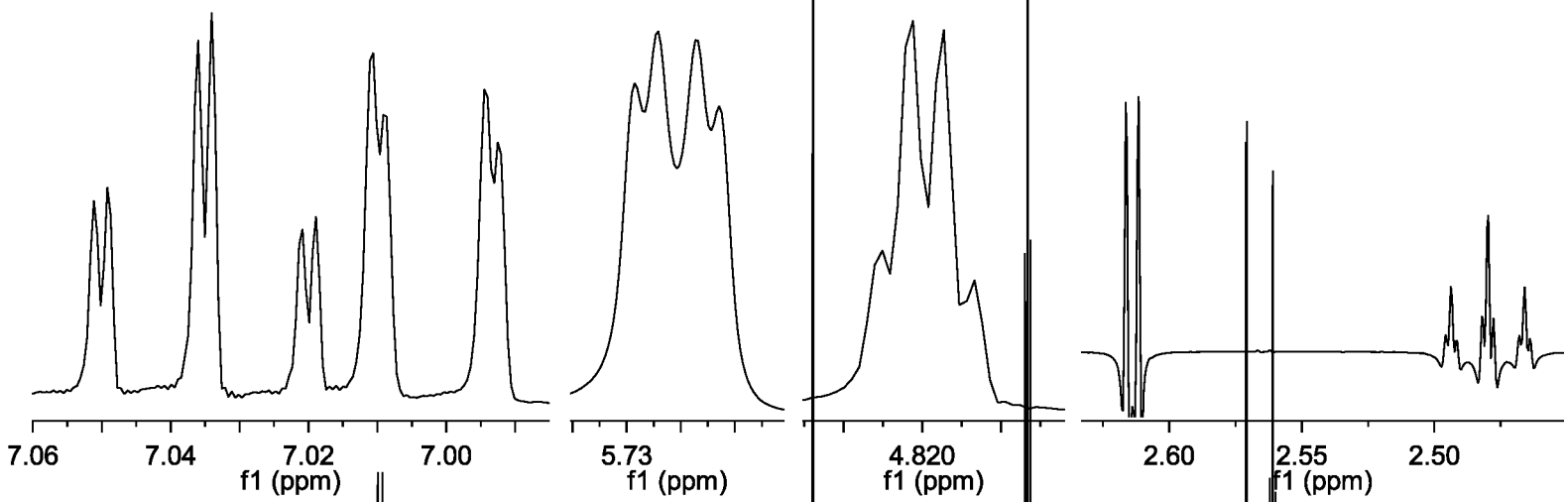
S25

500 MHz, $CDCl_3$

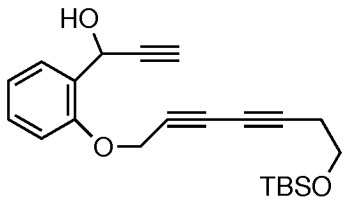


S26



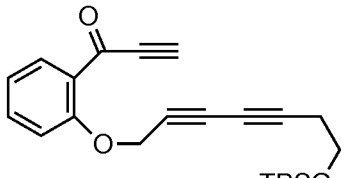


125 MHz, $CDCl_3$

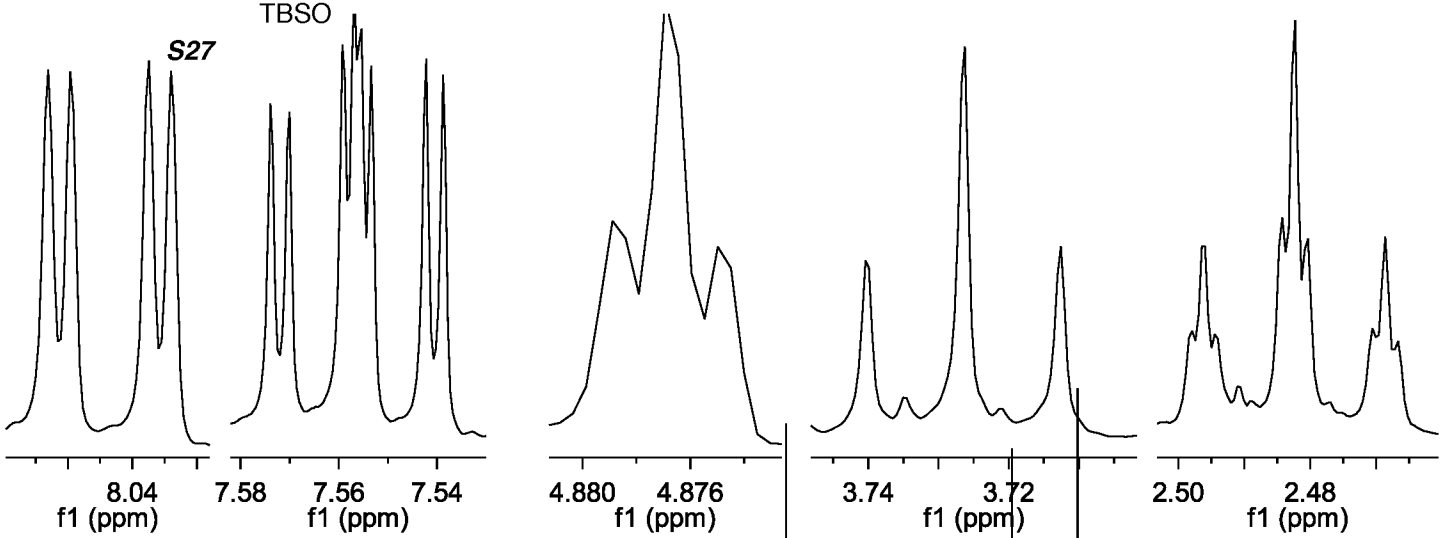


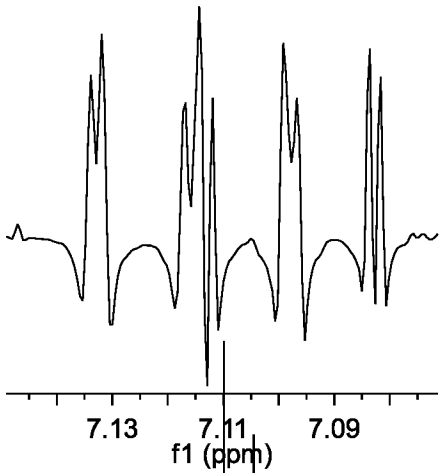
S26

500 MHz, $CDCl_3$

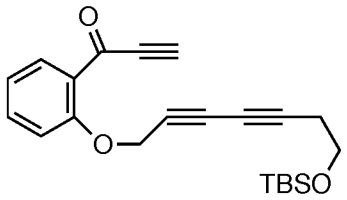


S27



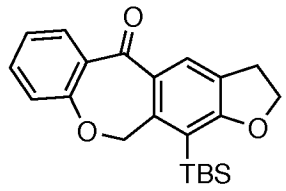


125 MHz, $CDCl_3$

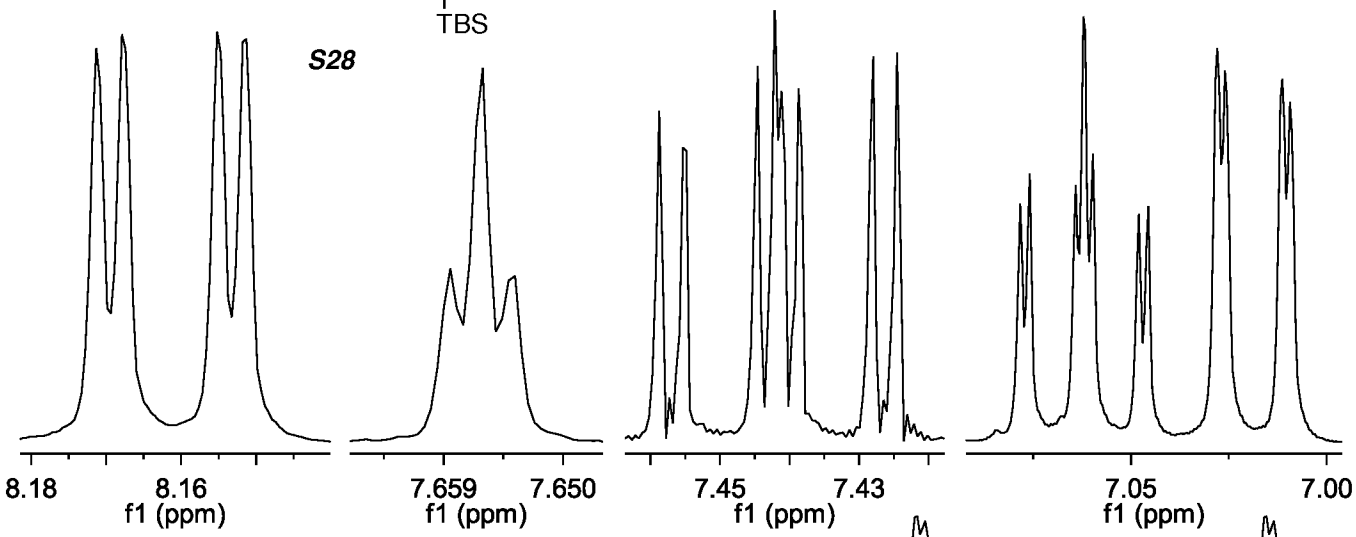


S27

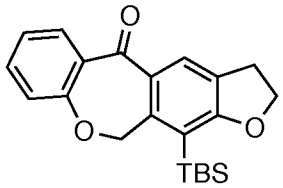
500 MHz, $CDCl_3$



S28

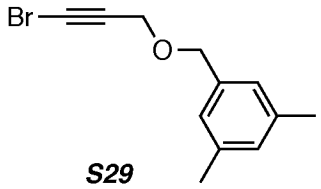


125 MHz, $CDCl_3$



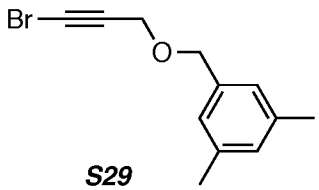
S28

500 MHz, $CDCl_3$

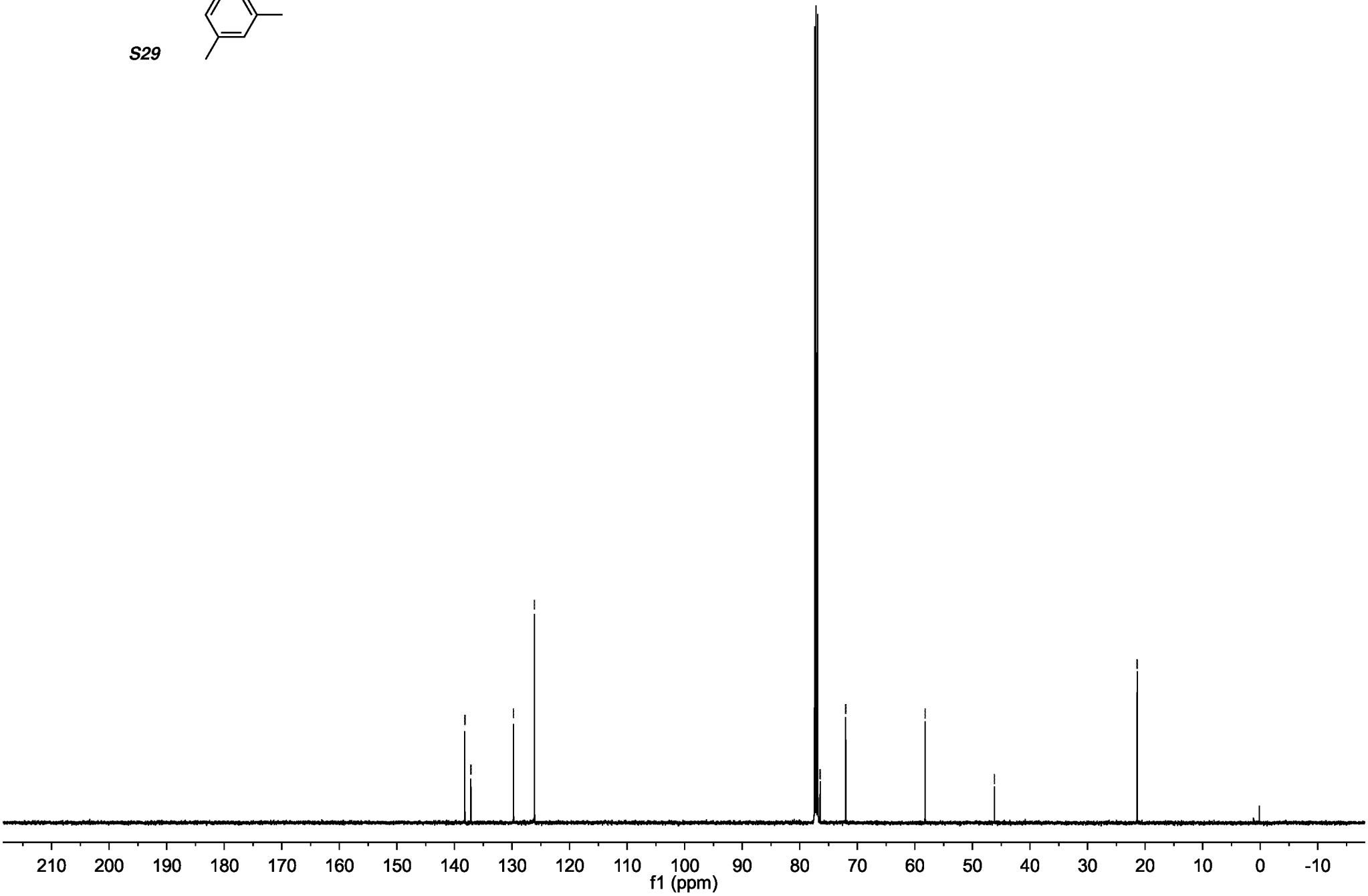


S29

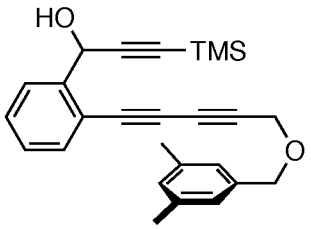
125 MHz, $CDCl_3$



S29

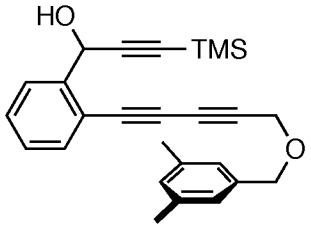


500 MHz, $CDCl_3$



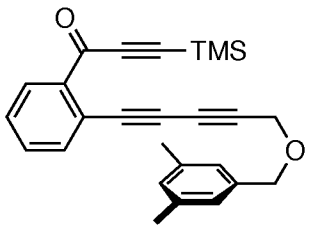
S30

125 MHz, $CDCl_3$



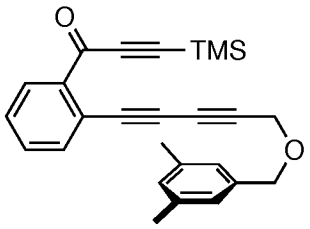
S30

500 MHz, $CDCl_3$



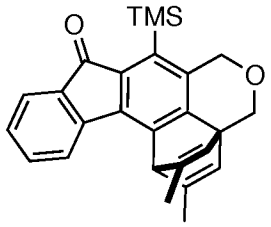
S31

125 MHz, $CDCl_3$

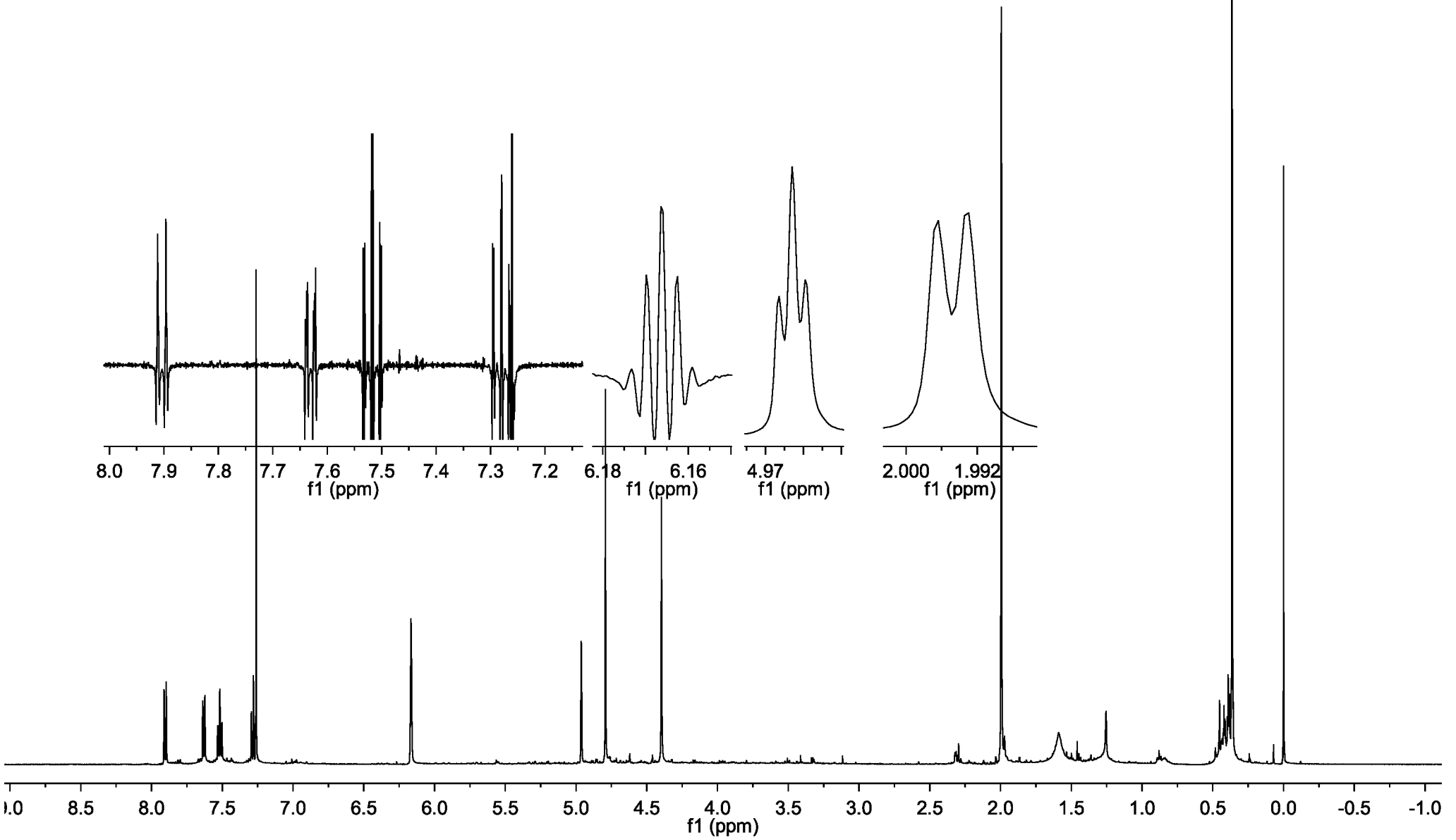


S31

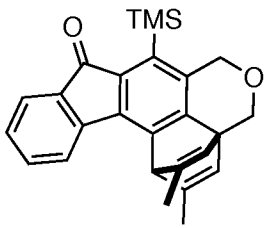
500 MHz, $CDCl_3$



S32

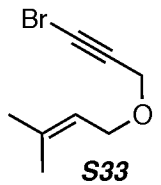


125 MHz, $CDCl_3$

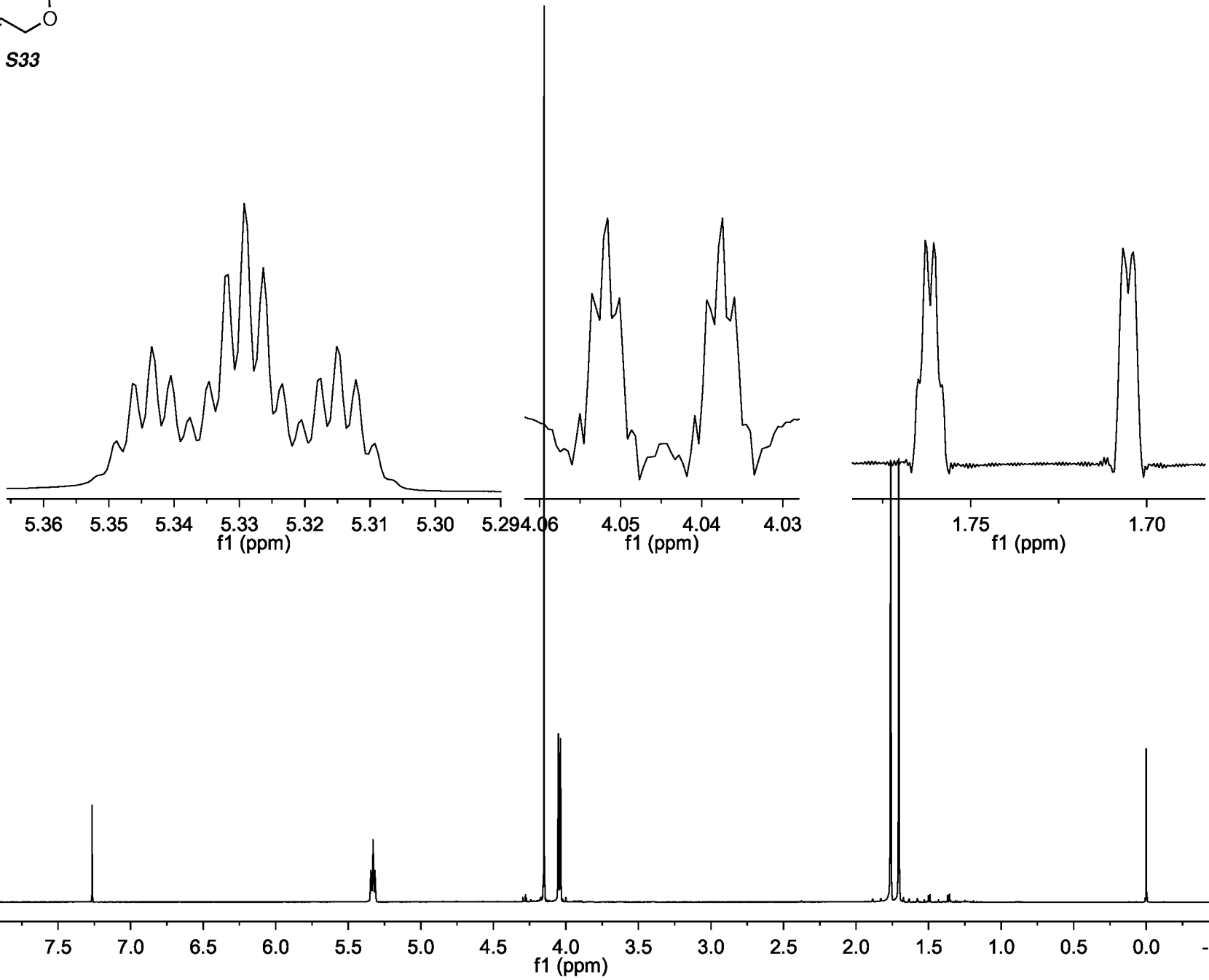


S32

500 MHz, $CDCl_3$



S33



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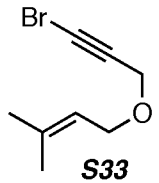
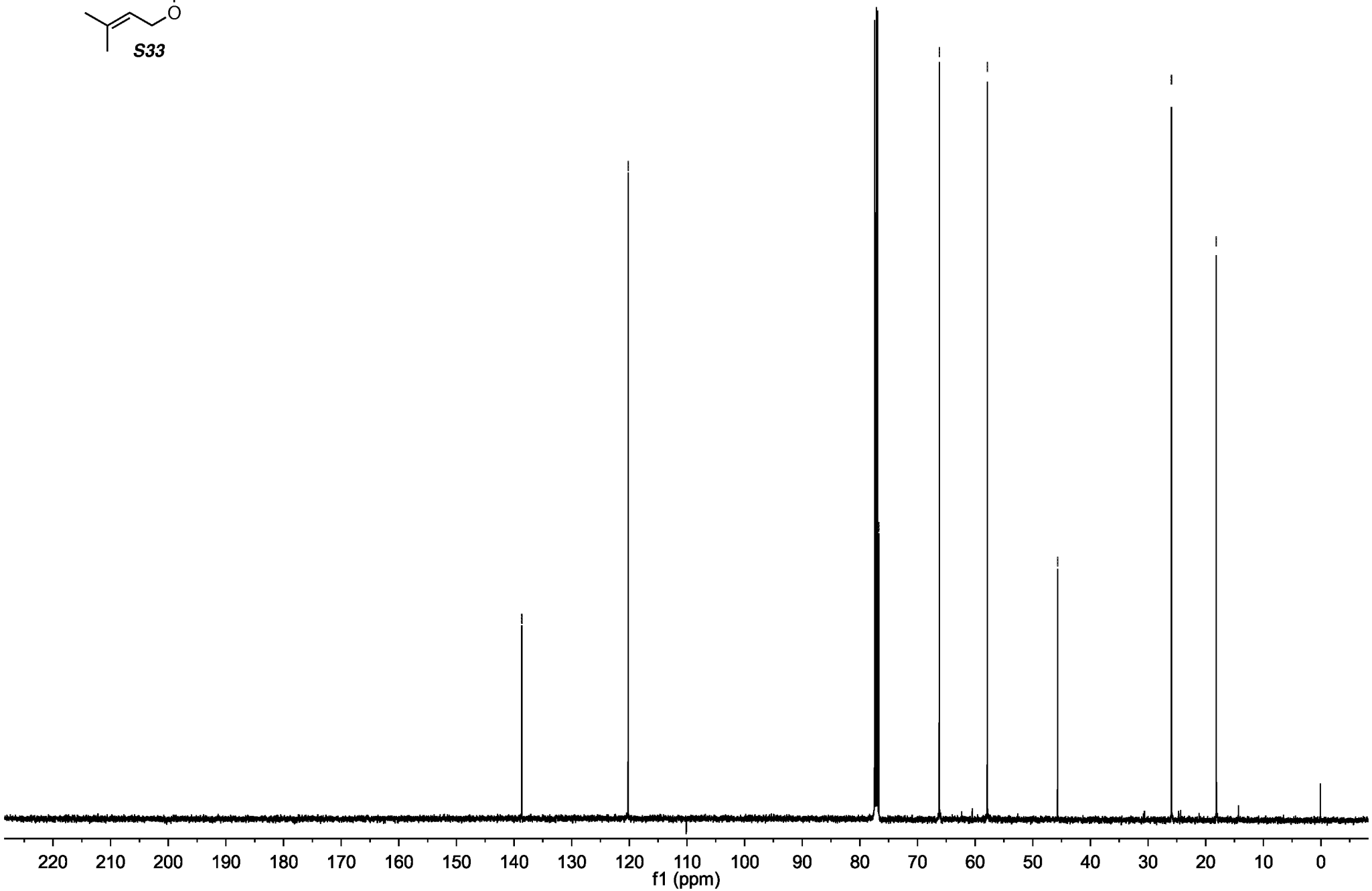


S33



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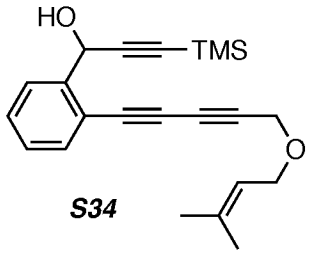
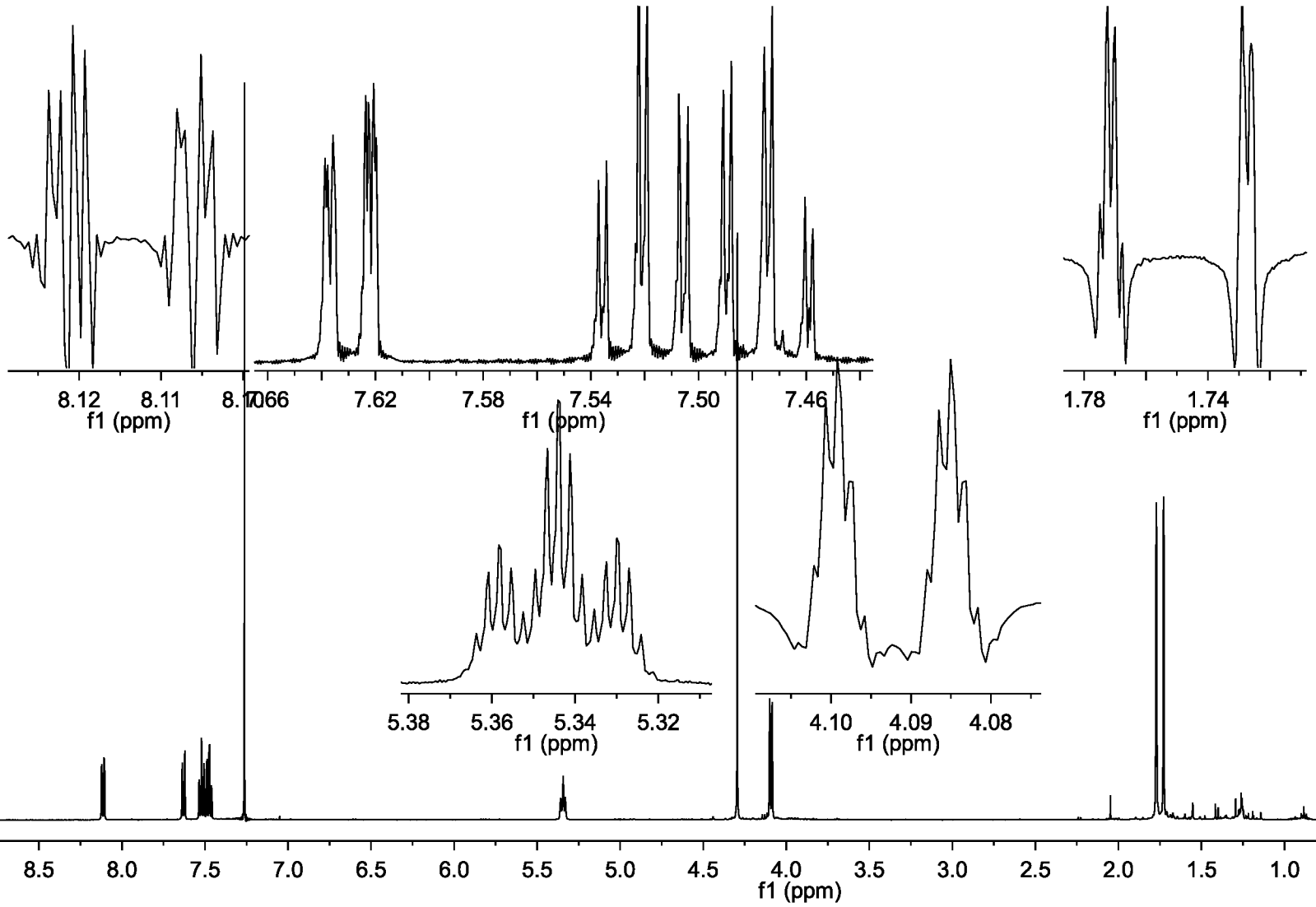


S34



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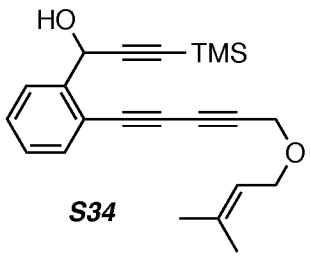
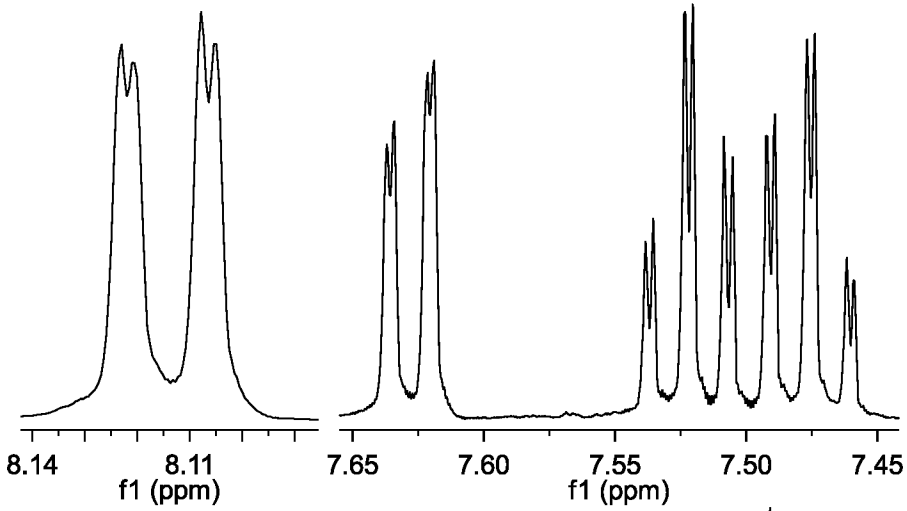
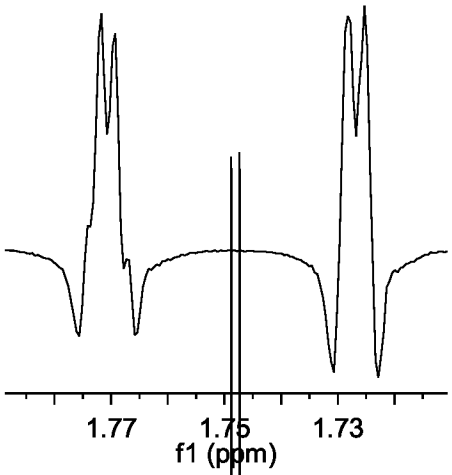
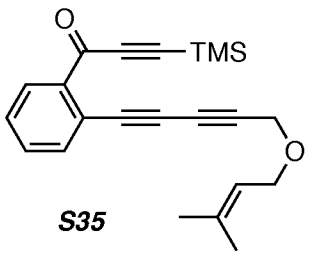


S34

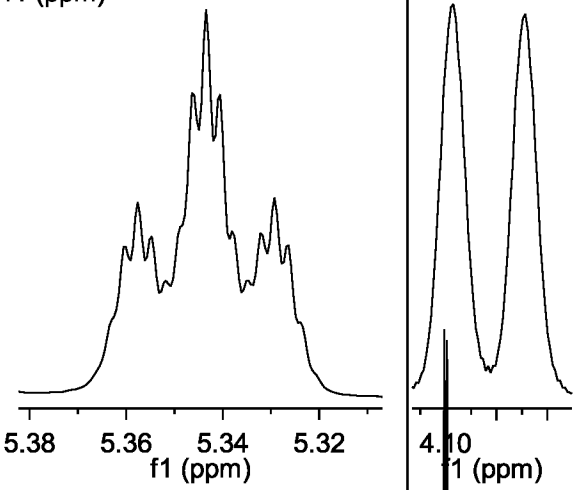
500 MHz, $CDCl_3$



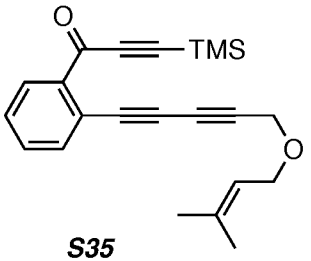




S35

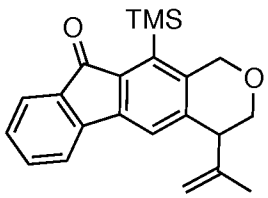


125 MHz, $CDCl_3$



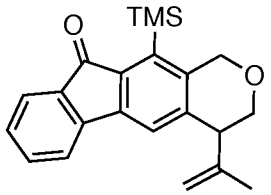
S35

500 MHz, $CDCl_3$



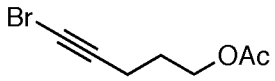
S36

125 MHz, $CDCl_3$

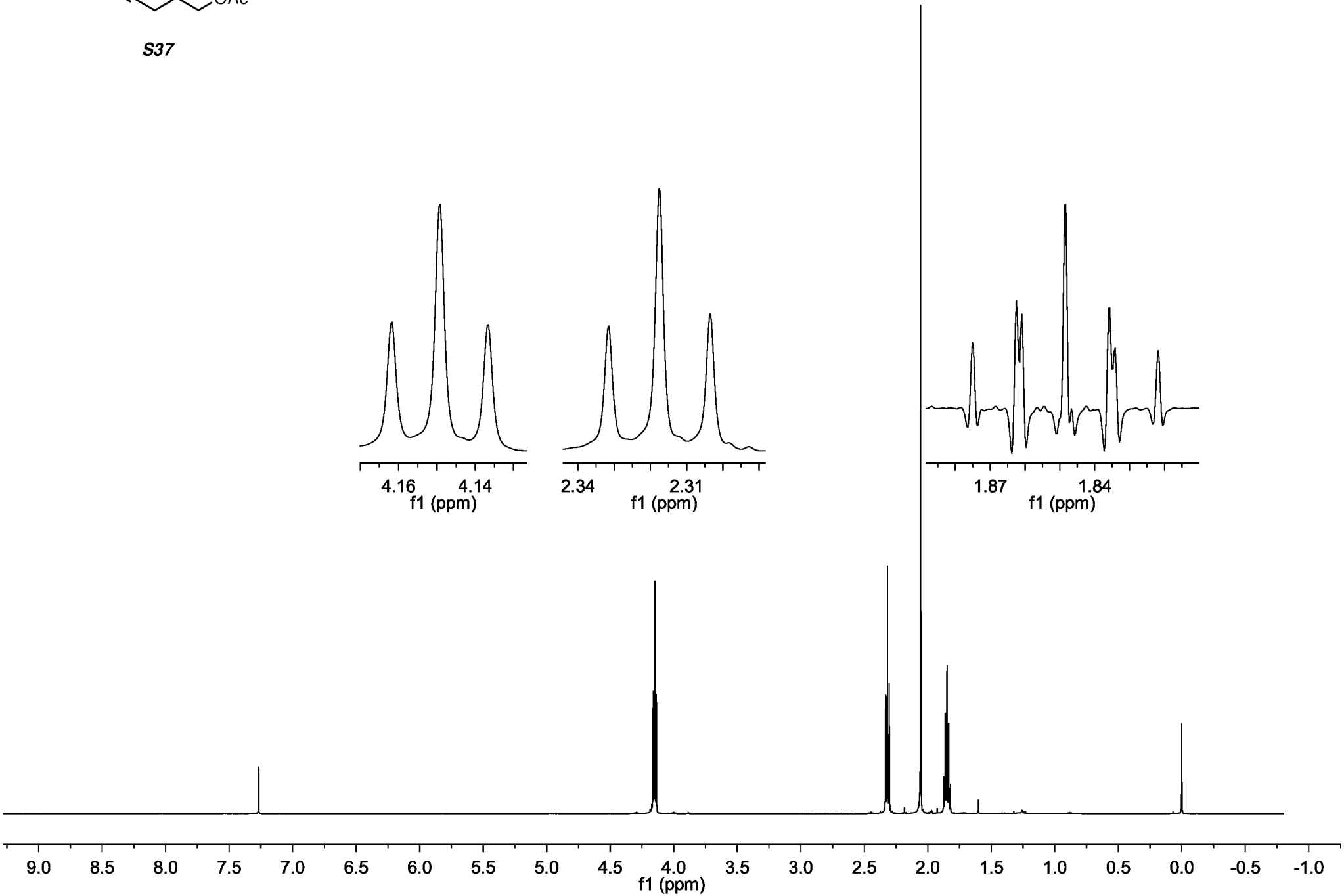


S36

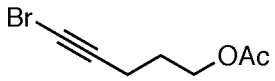
500 MHz, $CDCl_3$



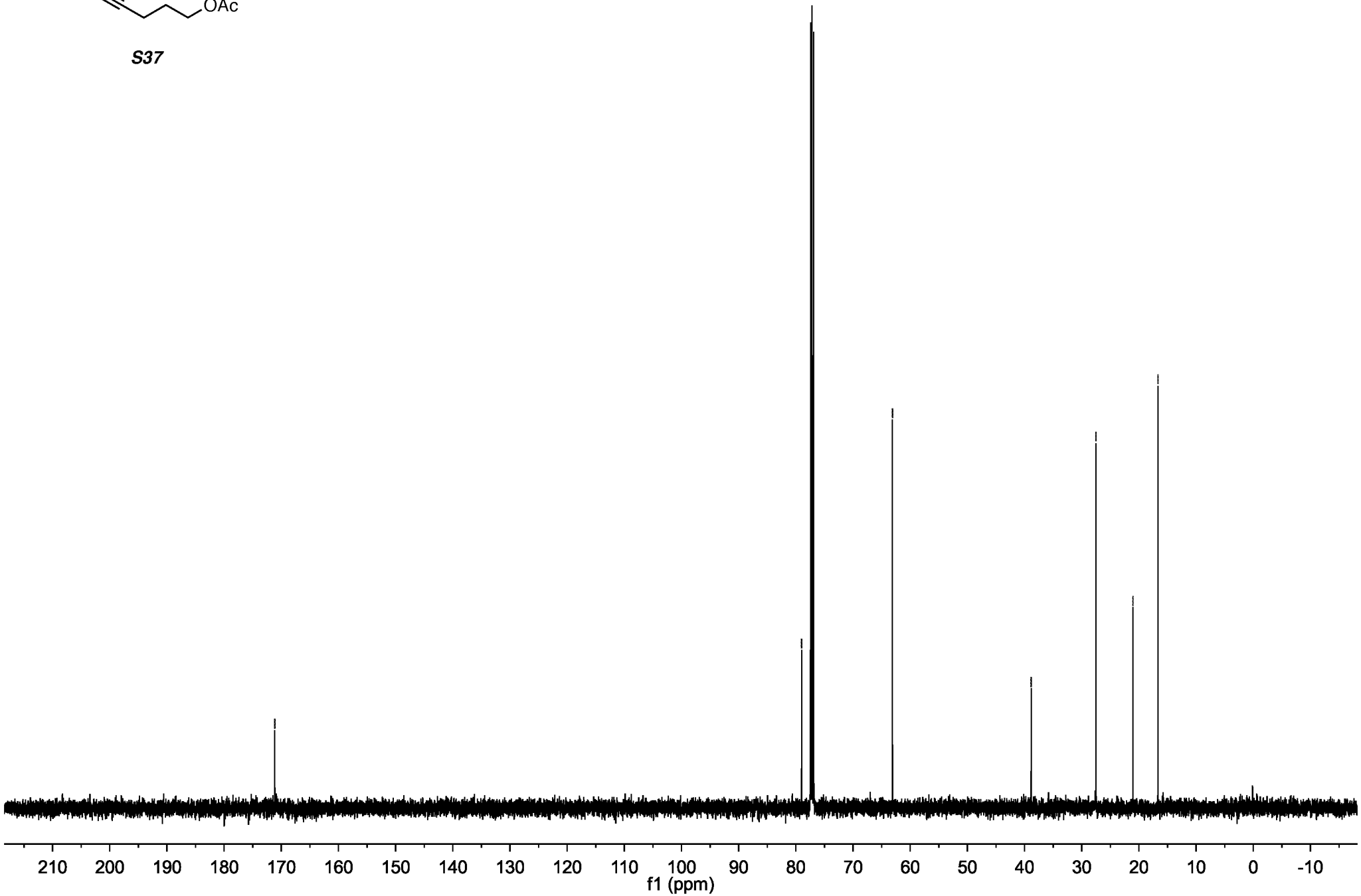
S37



125 MHz, $CDCl_3$



S37



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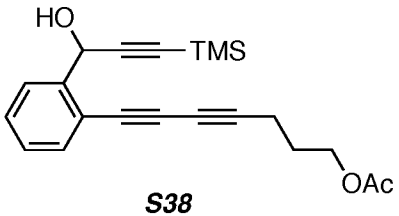
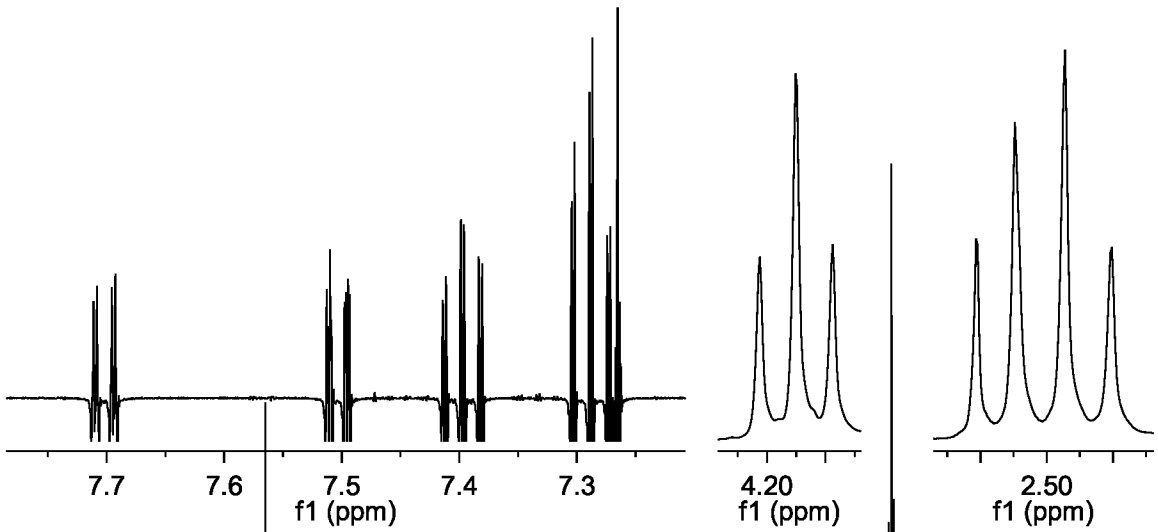
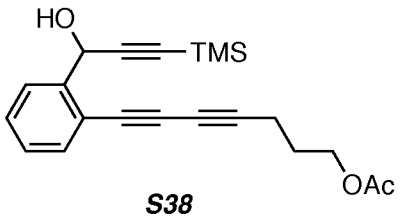


S38

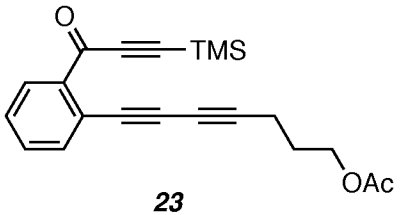


125 MHz, $CDCl_3$

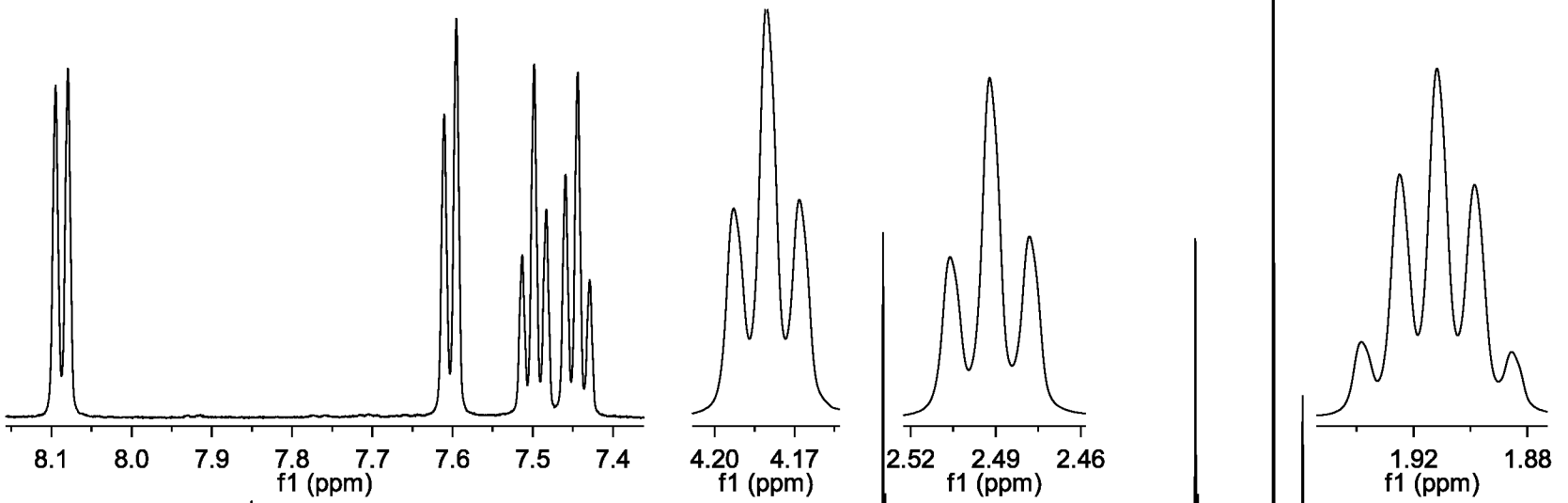


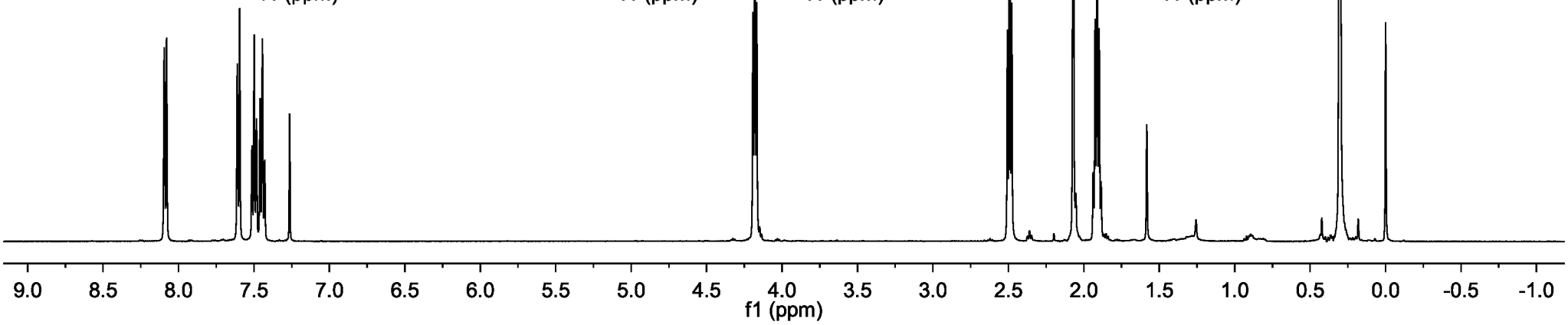
S38

500 MHz, $CDCl_3$

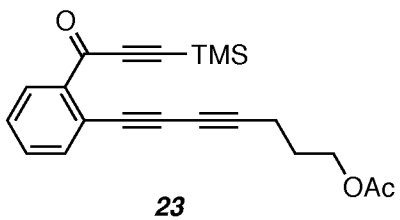


23



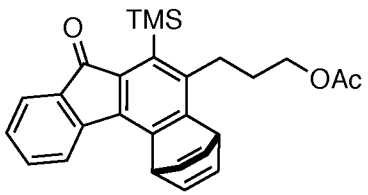


125 MHz, $CDCl_3$



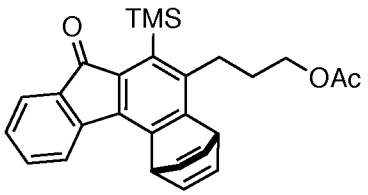
23

500 MHz, $CDCl_3$



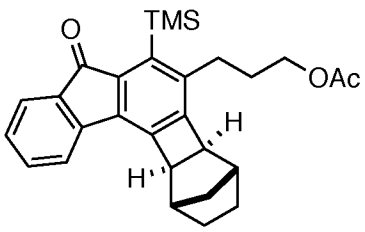
25a

125 MHz, $CDCl_3$



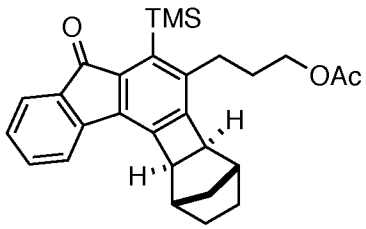
25a

500 MHz, $CDCl_3$



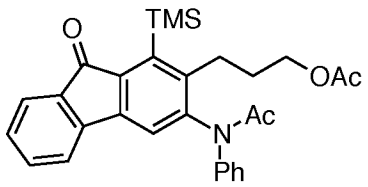
25b

125 MHz, $CDCl_3$



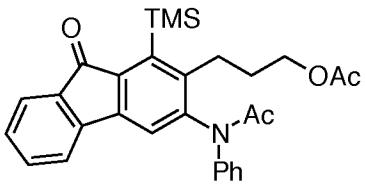
25b

500 MHz, $CDCl_3$



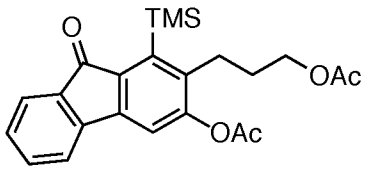
25c

125 MHz, $CDCl_3$



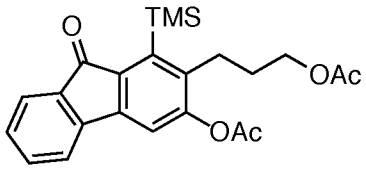
25c

500 MHz, $CDCl_3$



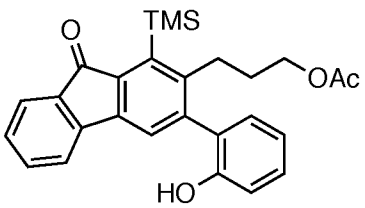
25d

125 MHz, $CDCl_3$



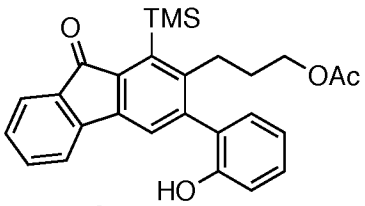
25d

500 MHz, $CDCl_3$

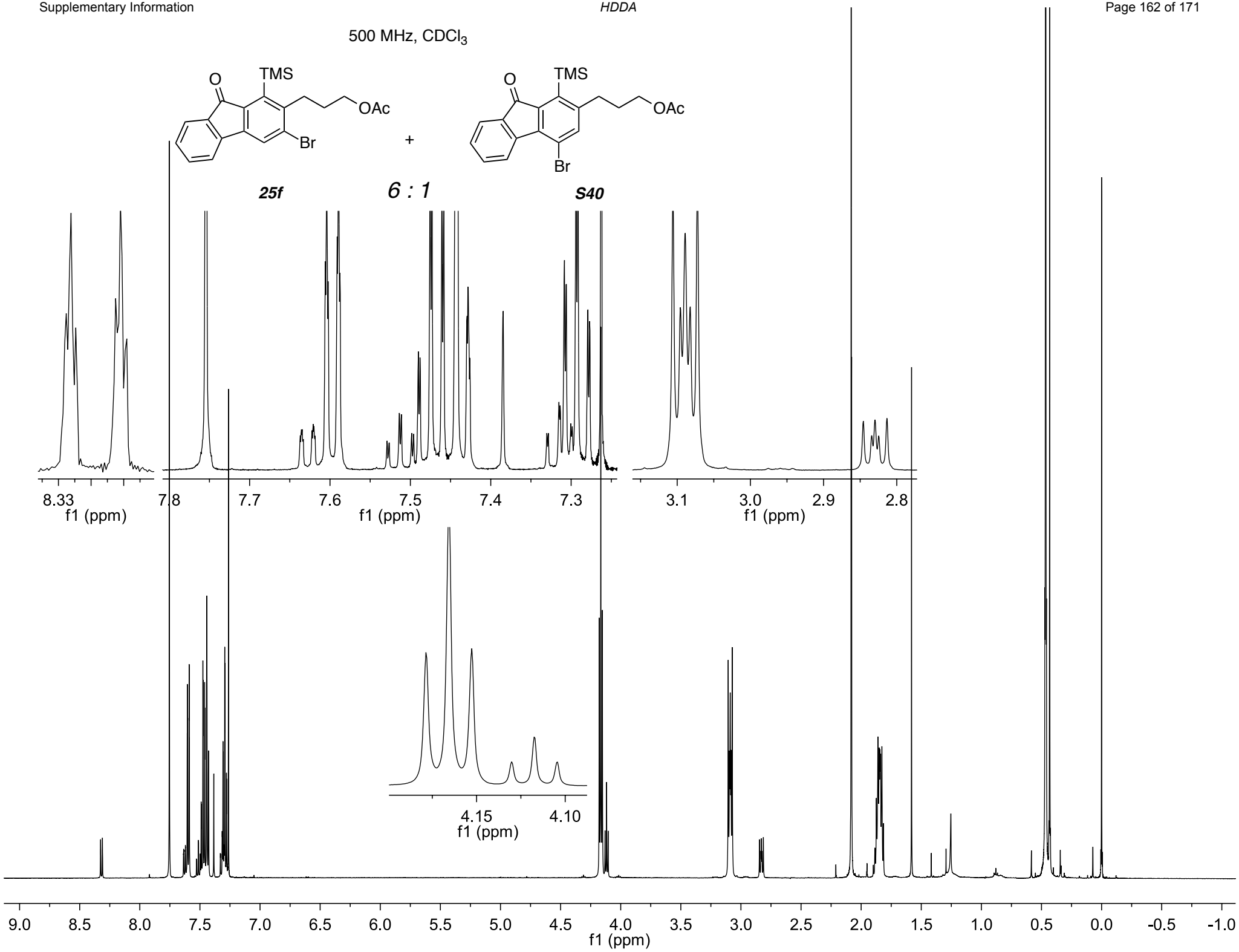


25e

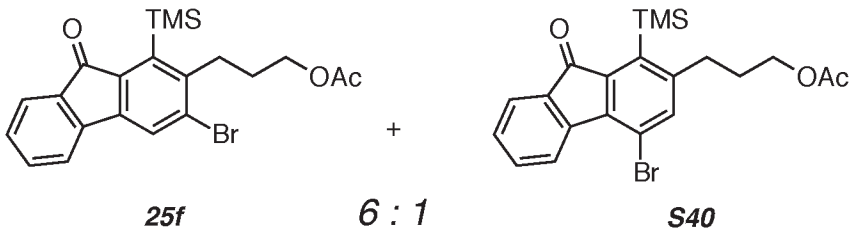
125 MHz, $CDCl_3$



25e

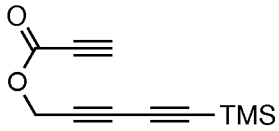

500 MHz, CDCl3
O
TMS
OAc
Br
+
O
TMS
OAc
Br
25f
6 : 1
S40
8.33
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
3.1
3.0
2.9
2.8
f1 (ppm)
4.15
4.10
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

125 MHz, $CDCl_3$



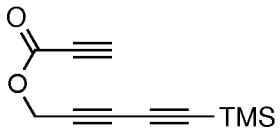
25f *6 : 1* ***S40***

500 MHz, $CDCl_3$



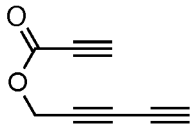
S41

125 MHz, $CDCl_3$

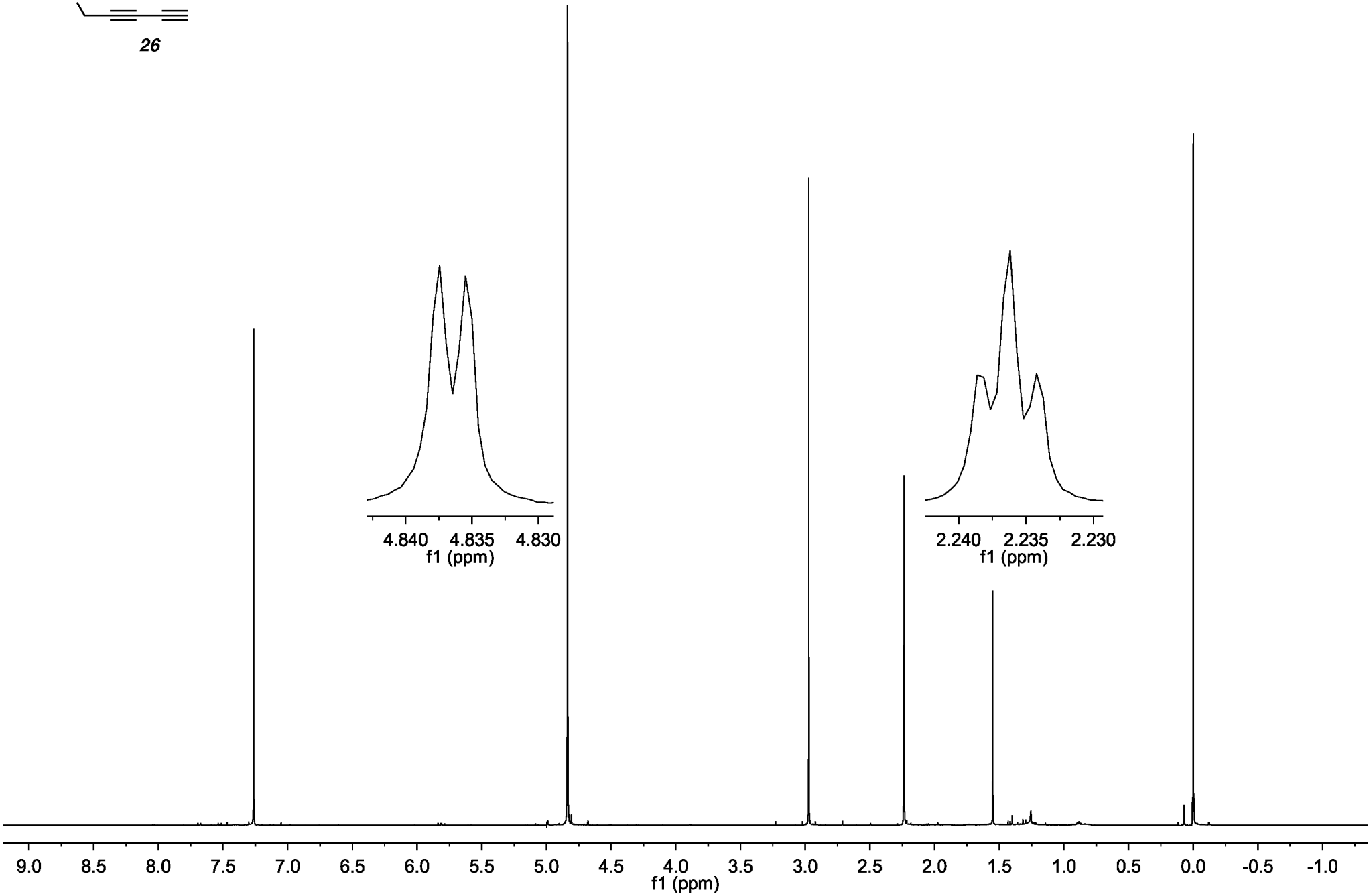


S41

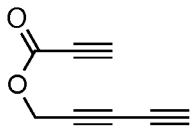
500 MHz, $CDCl_3$



26

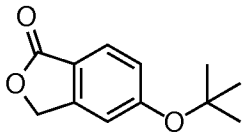


125 MHz, $CDCl_3$

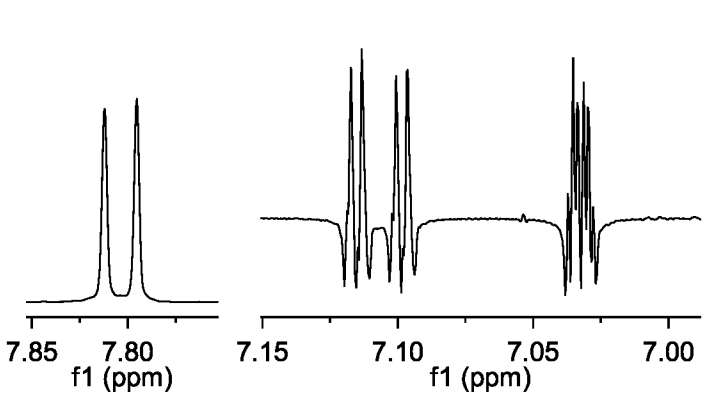


26

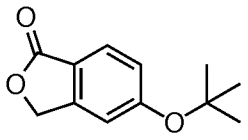
500 MHz, $CDCl_3$



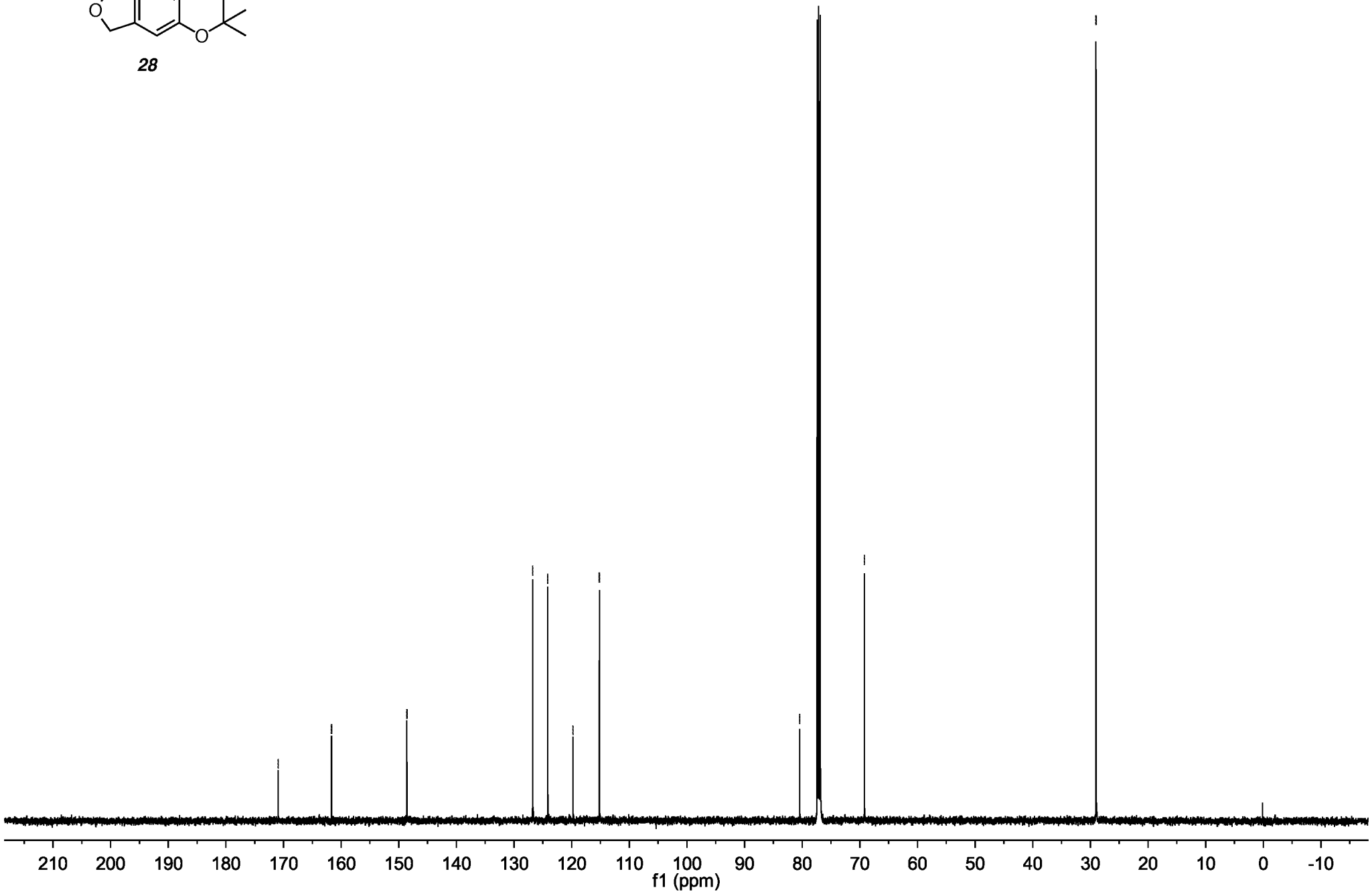
28



125 MHz, $CDCl_3$



28



VI. References for the Supplementary Information

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