Supporting Information for:

On the Mechanism of the Reactions of Alcohols with *o*-Benzynes

Patrick H. Willoughby‡, Dawen Niu‡, Tao Wang, Moriana K. Haj, Christopher J. Cramer, and Thomas R. Hoye*

‡These authors contributed equally to the work
*To whom correspondence should be addressed. email: hoye@umn.edu

Department of Chemistry, Supercomputing Institute, and Chemical Theory Center
University of Minnesota
207 Pleasant St. SE
Minneapolis, MN 55455

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I. General Experimental Protocols

"^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 500 (500 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 "3]

High-resolution mass spectrometry (HRMS) measurements were performed on a Bruker BioTOF II (ESI-TOF) instrument, using electrospray ionization (ESI) and PEG or PPG as the internal standard and calibrant. Samples were introduced as methanolic solutions.

"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."[3]

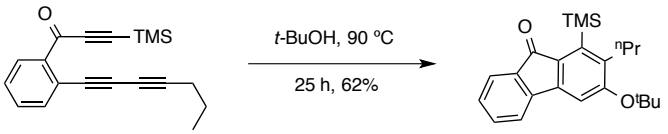
"MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of Silasorb silica gel (18–32 μm, 60 Å pore size), a Waters HPLC pump, a Waters R401 differential refractive index detector, and a Gilson 116 UV detector. Flash chromatography was performed using E. Merck silica 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."[3]

Reactions needing anhydrous conditions were performed under argon or nitrogen glassware that had been dried in an oven or flame-dried. Piperidine for the solvent in cross-coupling reactions was deoxygenated by a freeze-pump-thaw cycle or by purging with N_2 immediately prior to use. Anhydrous THF was obtained by being passed through a column containing 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."[3]

II. Preparation procedures and characterization data for each new compound

3-(*tert*-Butoxy)-2-propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (11)



9 *11*

A solution of triynone **9**[3] (17 mg, 0.058 mmol) in *tert*-butanol (6 mL) was heated at 90 ºC. After 25 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give the fluorenone **11** (13 mg, 0.036 mmol, 62%) as a clear amber oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.40 (ddd, *J* = 7.3, 7.3, 1.1 Hz, *H6*), 7.38 (ddd, *J* = 7.3, 1.5, 0.8 Hz, *H5*), 7.22 (ddd, *J* = 7.2, 7.2, 1.4 Hz, *H7*), 7.15 (s, 1H, *H4*), 2.72 (br t, *J* = 8.1 Hz, 2H, $CH_2CH_2CH_3$), 1.54 [s, 9H, $(CH_3)_3$], 1.45 (br sext, *J* = 8.3 Hz, 2H, $CH_2CH_2CH_3$), 0.96 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), and 0.43 [s, 9H, $(CH_3)_3Si$].

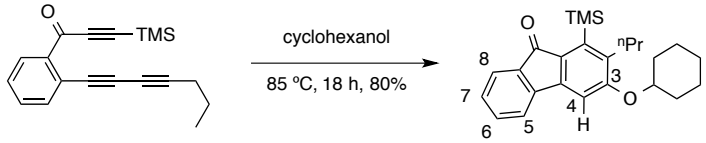
^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 159.5, 145.1, 143.7, 143.4, 142.4, 134.8, 133.9, 132.6, 128.7, 123.5, 118.9, 111.0, 79.7, 31.9, 29.5, 25.5, 14.4, and 2.8.

IR (neat): 2974, 2957, 2900, 2871, 1707, 1582, 1239, 1166, 847, and 756 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{30}NaO_2Si^+$ [M+Na^+] requires 389.1907; found 389.1877.

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

3-(Cyclohexyloxy)-2-propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (13)



9 *13*

A solution of triynone **9**[3] (13 mg, 0.045 mmol) in cyclohexanol (2 mL) was heated at 85 ºC. After 18 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 12:1) to give the fluorenone **13** (14 mg, 0.036 mmol, 80%) as a golden yellow oil.

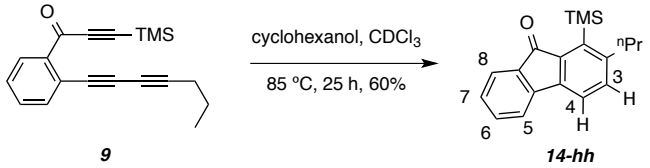
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.52 (ddd, *J* = 7.2, 0.9, 0.9 Hz, 1H, *H8*), 7.40 (m, 2H, *H5* and *H6*), 7.22 (nfom, 1H, *H7*), 6.96 (s, 1H, *H4*), 4.50 (tt, *J* = 3.4, 7.8 Hz, 1H, C*H*OAr), 2.75 (br t, *J* = 8.2 Hz, 2H, ArCH_2), 1.99–1.93 (m, 2H, CH_2), 1.85–1.77 (m, 2H, CH_2), 1.73–1.65 (m, 2H, CH_2), 1.60–1.45 (m, 6H), and 0.98 (t, *J* = 7.4 Hz, 3H, CH_3), and 0.44 [s, 9H, $(CH_3)_3Si$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.1, 160.3, 146.3, 143.6, 143.4, 139.2, 135.0, 133.8, 131.3, 128.8, 123.4, 119.0, 104.6, 74.9, 31.7, 31.4, 25.8, 25.3, 23.5, 14.5, and 2.8 ppm.

IR (neat): 2935, 2861, 1704, 1607, 1582, 1553, 1486, 1234, 1203, 1134, and 846 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{25}H_{32}NaO_2Si^+$ [M+Na^+] requires 415.2064; found 415.2033.

2-Propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (14-hh)



9 ***14-hh***

A solution of triynone **9**[3] (18 mg, 0.062 mmol) and cyclohexanol (10 mg, 0.10 mmol) in $CDCl_3$ (7.5 mL) was heated at 85 ºC. After 25 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 19:1) to give the fluorenone **14-hh** (11 mg, 0.037 mmol, 60%) as a golden yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.43 (m, 2H, *H5* and *H6*), 7.42 (d, *J* = 7.6 Hz, 1H, *H4*), 7.23 (nfom, 1H, *H7*), 7.21 (d, *J* = 7.6 Hz, 1H, *H3*), 2.73 (br t, *J* = 8.0 Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 1.54 (br sext, *J* = 7 Hz, 2H, C*H*$_2$CH$_3$), 0.97 (t, *J* = 7.3 Hz, CH$_2$C*H*$_3$), and 0.43 (s, 9H, SiC*H*$_3$).

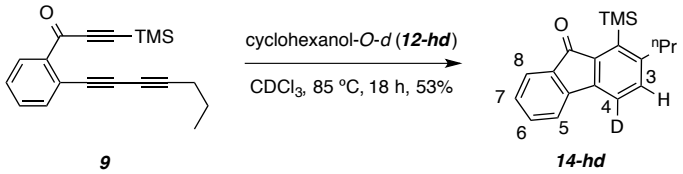
^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 150.7, 144.2, 143.2, 141.0, 140.4, 135.4, 134.5, 134.0, 128.6, 124.0, 120.8, 119.5, 39.0, 27.1, 14.0, and 2.5.

IR (neat): 2955, 2935, 2875, 1713, 1606, 1248, 968, 861, and 846 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{22}NaOSi^+$ [M+Na$^+$] requires 317.1332; found 317.1358.

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

2-Propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one-4-*d* (14-hd)



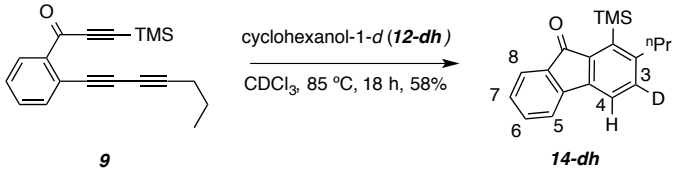
9 ***14-hd***

A solution of triynone **9**[3] (17 mg, 0.058 mmol) and cyclohexanol-*O*-*d* (**12-hd**, 9 mg, 0.09 mmol) in $CDCl_3$ (6 mL) was heated at 85 ºC. After 18 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 19:1) to give the mono-deuterated fluorenone **14-hd** (9 mg, 0.031 mmol, 53%) as a golden yellow oil.

Cyclohexanol-*O*-*d* was prepared by treating cyclohexanol in methanol-d_4 and concentrating the mixture on a rotary evaporator. This procedure was repeated several times. ^{1}H NMR analysis suggested ca. 95% deuterium incorporation.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.44 (m, 2H, *H5* and *H6*), 7.22 (s, 1H, *H3*), 7.23 (nfom, 1H, *H7*), 2.73 (br t, 8.0 Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 1.54 (br sext, 2H, C*H*$_2$CH$_3$), 0.97 (t, *J* = 7.3 Hz, 3H, CH$_3$), and 0.43 (s, 9H, SiC*H*$_3$).

2-Propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one-3-*d* (14-dh)

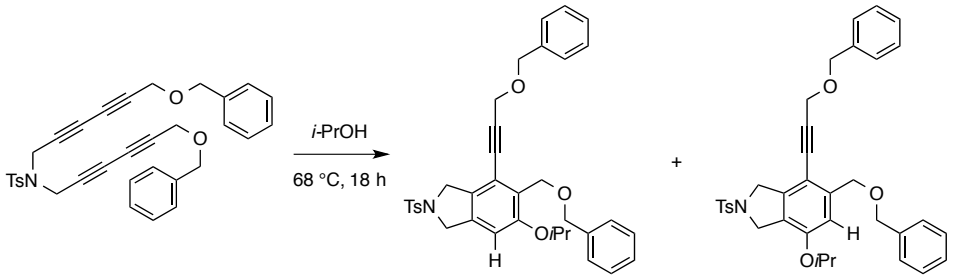


9 *14-dh*

A solution of triynone **9**[3] (12 mg, 0.041 mmol) and cyclohexanol-1-*d*[4] (**12-dh**, 6 mg, 0.06 mmol) in $CDCl_3$ (4 mL) was heated at 90 ºC. After 18 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 19:1) to give the mono-deuterated fluorenone **14-dh** (7 mg, 0.023 mmol, 58%) as a golden yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.44 (m, 2H, *H5* and *H6*), 7.42 (s, 1H, *H4*), 7.23 (nfom, 1H, *H7*), 2.73 (br t, 8.0 Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 1.54 (br sext, 2H, CH$_2$C*H*$_2$CH$_3$), 0.97 (t, *J* = 7.3 Hz, 3H, CH$_3$), and 0.43 (s, 9H, SiC*H*$_3$).

5-((Benzyloxy)methyl)-4-(3-(benzyloxy)prop-1-yn-1-yl)-6-isopropoxy-2-tosylisoindoline (27a) and 5-((benzyloxy)methyl)-4-(3-(benzyloxy)prop-1-yn-1-yl)-7-isopropoxy-2-tosylisoindoline (27b)



24 *27a* (2.6:1 by ^{1}H NMR) *27b*

A solution of tetrayne **24** (20 mg, 0.038 mmol) in *i*-PrOH (4 mL) was heated at 68 ºC. After 18 h the mixture was concentrated and the crude material was purified by MPLC (hexanes:EtOAc 5:1) to give, in order of elution, the isoindolines **27b** (5 mg, 0.008 mmol, 22%) and **27a** (15 mg, 0.024 mmol, 66%). The location of the *i*-propoxy substituent in **27a** was established by combined interpretation of its HSQC and HMBC data.

Characterization data for **27a**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H, Ar$_{Ts}$*H*$_o$), 7.38–7.26 (m, 11H, Ar*H*), 7.23 (tt, *J* = 7.2, 1.5 Hz, 1H, Ph*H*$_p$), 6.68 (s, 1H, *H7*), 4.650 (s, 2H, OC*H*$_2$), 4.646 (s, 2H, OC*H*$_2$), 4.62 (t, *J* = 2.5 Hz, 2H, NC*H*$_2$), 4.61 (t, *J* = 2.5 Hz, 2H, NC*H*$_2$), 4.56 (s, 2H, OC*H*$_2$), 4.47 (septet, *J* = 6.1 Hz, 1H, C*H*OAr), 4.40 (s, 2H, OC*H*$_2$), 2.40 (s, 3H, ArC*H*$_3$), and 1.29 [d, *J* = 6.1 Hz, 6H, CH(C*H*$_3$)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1, 143.9, 138.9, 137.5, 137.0, 133.8, 131.0, 130.1, 129.2, 128.7, 128.39, 128.36, 128.2, 127.9, 127.7, 127.6, 120.2, 108.6, 93.3, 81.9, 72.8, 71.7, 71.6, 64.9, 58.0, 54.7, 54.0, 22.2, and 21.7 ppm.

IR (neat): 3062, 3032, 2978, 2930, 2855, 2219, 1720 (weak), 1598, 1496, 1454, 1384, 1347, 1305, 1294, 1164, 1096, 1069, 1027, and 940.

HRMS (ESI-TOF): Calcd for $C_{36}H_{37}NNaO_3S^+$ [M+Na$^+$] requires 618.2285; found 618.2344.

Characterization data for **27b**

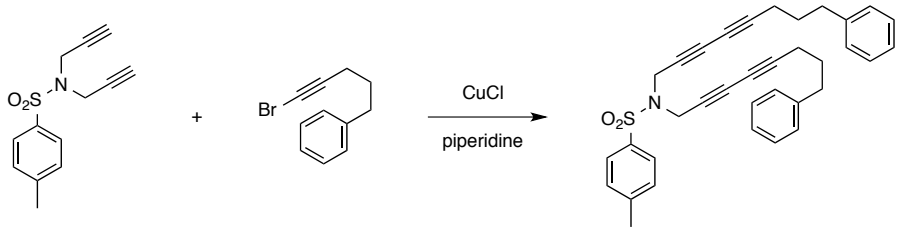
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.3 Hz, 2H, $Ar_{Ts}H_o$), 7.38–7.25 (m, 12H, Ar*H*), 6.89 (s, 1H, *H6*), 4.67 (t, *J* = 2.2 Hz, 2H, NCH_2), 4.66 (s, 2H, OCH_2), 4.62 (s, 2H, OCH_2), 4.57 (septet, *J* = 6.1 Hz, 1H, C*H*OAr), 4.56 (s, 2H, OCH_2), 4.56 (br s, 2H, NCH_2), 4.39 (s, 2H, OCH_2), 2.40 (s, 3H, $ArCH_3$), and 1.30 [d, *J* = 6.1 Hz, 6H, $CH(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 143.8, 142.6, 141.2, 138.3, 137.5, 134.0, 130.1, 128.7, 128.6, 128.4, 128.2, 127.9, 127.8, 124.6, 110.9, 107.8, 92.3, 81.1, 74.6, 72.7, 71.8, 70.7, 70.2, 58.1, 54.7, 52.7, 22.2, and 21.7.

IR (neat): 3030, 2978, 2923, 2853, 2220, 1607, 1494, 1454, 1350, 1322, 1164, 1096, 1072, and 816 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{36}H_{37}NNaO_3S^+$ [$M+Na^+$] requires 618.2285; found 618.2296.

4-Methyl-*N*,*N*-bis(8-phenylocta-2,4-diyn-1-yl)benzenesulfonamide (30)



30

A solution of 4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide[5] (247 mg, 1.0 mmol) and (5-bromopent-4-yn-1-yl)benzene[6] (888 mg, 4.0 mmol) in piperidine (3 mL) was deoxygenated (three freeze-pump-thaw cycles). The solution was cooled to 0 °C and CuCl (20 mg, 0.2 mmol) was added. After 1 h saturated aqueous NH_4Cl was added and the resulting mixture was extracted with EtOAc. The combined extracts were washed (brine), dried (Na_2SO_4), and concentrated. The crude material was then purified using flash chromatography on silica gel (hexanes:EtOAc 12:1 to 5:1) to give the tetrayne **30** (360 mg, 0.62 mmol, 62%) as a colorless oil.

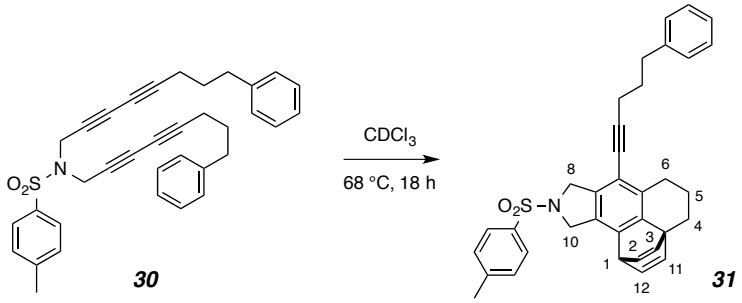
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.2 Hz, 2H, $SO_2Ar H_o$), 7.32 (d, *J* = 8.2 Hz, 2H, $SO_2Ar H_m$), 7.29 (dd, *J* = 7.5, 7.5 Hz, 4H, ArH_m), 7.20 (dd, *J* = 7.4, 7.4 Hz, 2H, ArH_p), 7.17 (d, *J* = 7.4 Hz, ArH_o), 4.20 (s, 4H, NCH_2), 2.70 (t, *J* = 7.6 Hz, 4H, $ArCH_2$), 2.38 (s, 3H, $ArCH_3$), 2.24 (t, *J* = 7.0 Hz, 4H, $C{\equiv}CCH_2$), and 1.83 (tt, *J* = 7.5, 7.5 Hz, 4H, $CH_2CH_2CH_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 141.2, 134.9, 129.9, 128.73, 128.69, 128.6, 126.3, 80.6, 71.1, 68.3, 65.0, 37.5, 34.8, 29.8, 21.8, and 18.7.

IR (neat): 3027, 2935, 2860, 2257, 1599, 1496, 1454, 1353, 1328, 1163, 1092, and 890 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{35}H_{33}NNaO_2S^+$ [$M+Na^+$] requires 554.2124; found 554.2166.

Authentic sample of 7-(5-Phenylpent-1-yn-1-yl)-9-tosyl-4,5,6,8,9,10-hexahydro-1H-1,3a-ethenonaphtho[1,8-ef]isoindole (31).



A solution of tetrayne **30** (20 mg, 0.038 mmol) in $CDCl_3$ (2 mL) was heated at 68 °C. After 18 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 5:1) to give the fluorenone isoindoline **31** (15 mg, 0.028 mmol, 75%) as a pale yellow oil.

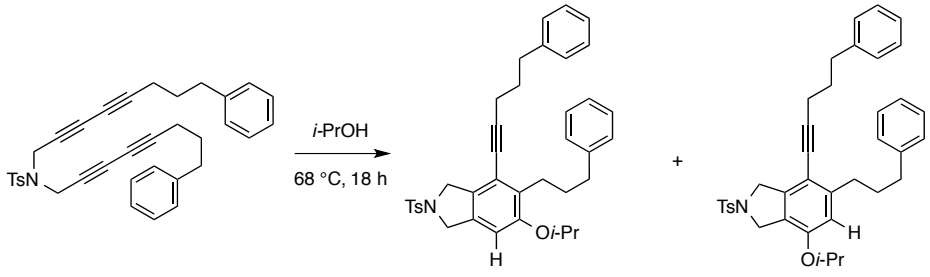
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.3 Hz, 2H, $Ar_{Ts}H_o$), 7.30 (t, *J* = 7.5 Hz, 2H, PhH_m), 7.28 (d, *J* = 8.5 Hz, 2H, $Ar_{Ts}H_m$), 7.23–7.20 (m, 3H, PhH_oH_p), 6.79 (dd, *J* = 6.0, 6.0 Hz, 2H, *H2* and *H12*), 6.58 (dd, *J* = 6.5, 1.4 Hz, 2H, *H3* and *H11*), 4.73 (tt, *J* = 5.8, 1.5 Hz, 1H, *H1*), 4.65 (t, *J* = 1.7 Hz, 2H, NCH_2), 4.57 (t, *J* = 1.8 Hz, 2H, NCH_2), 2.77 (t, *J* = 7.5 Hz, 2H, $ArCH_2$), 2.74 (t, *J* = 6.0 Hz, 2H, $ArCH_2$), 2.45–2.42 (m, 2H, CH_2), 2.44 (t, *J* = 7.0 Hz, 2H, $C{\equiv}CCH_2$), 2.39 (s, 3H, $ArCH_3$), and 1.93–1.86 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 145.3, 143.8, 141.8, 141.6, 139.5, 134.7, 134.3, 133.8, 130.0, 128.8, 128.6, 127.8, 126.6, 126.2, 113.1, 97.4, 76.8, 54.4, 52.8, 52.0, 46.2, 35.0, 31.3, 30.8, 27.2, 21.8, 21.7, and 19.3.

IR (neat): 3063, 3027, 2930, 2857, 2256, 1598, 1496, 1452, 1435, 1346, 1164, 1097, 1062, 909, and 815 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{35}H_{33}NNaO_2S^+$ [$M+Na^+$] requires 554.2124; found 554.2148.

6-Isopropoxy-4-(5-phenylpent-1-yn-1-yl)-5-(3-phenylpropyl)-2-tosylisoindoline (32a) and 7-Isopropoxy-4-(5-phenylpent-1-yn-1-yl)-5-(3-phenylpropyl)-2-tosylisoindoline (32b)



A solution of tetrayne **30** (20 mg, 0.038 mmol) in *i*-PrOH (4 mL) was heated at 68 ºC. After 18 h the mixture was concentrated and the crude material was purified by MPLC (hexanes:EtOAc 5:1) to give, in order of elution, the isoindolines **32b** (ca. 2 mg, ~70% purity) and **32a** (17 mg, 0.028 mmol, 75%) in order of elution. The location of the *i*-propoxy substituent in **32a** was established by an NOE experiment.

Characterization data for **32a**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.3 Hz, 2H, $ArTsH_o$), 7.31 (t, *J* = 7.5 Hz, 2H, PhH_m), 7.28 (d, *J* = 8.5 Hz, 2H, $Ar_{Ts}H_m$), 7.24–7.19 (m, 5H, Ar*H*), 7.16–7.11 (m, 3H, Ar*H*), 6.56 (s, 1H, *H7*), 4.58

(overlapping br s, 4H, NCH_2), 4.42 (septet, J = 6.1 Hz, 1H, CHOAr), 2.78 (overlapping t, J = 7.5 Hz, 4H, ArCH_2), 2.65 (t, J = 7.7 Hz, 2H, ArCH_2), 2.42 (t, J = 7.0 Hz, 2H, C≡CCH_2), 2.38 (s, 3H, ArCH_3), 1.89 (tt, J = 7.7, 7.7 Hz, 2H, CH_2), 1.82 (tt, J = 7.8, 7.8 Hz, 2H, CH_2), and 1.25 [d, J = 6.0 Hz, 6H, CH(CH_3)$_2$].

^{13}C NMR (125 MHz, CD_3CN): δ 156.6, 145.1, 143.4, 142.7, 135.2, 134.4, 134.0, 130.8, 130.6, 129.4, 129.33, 129.26, 129.1, 128.4, 126.9, 126.5, 119.9, 108.0, 98.7, 77.4, 71.1, 55.4, 54.7, 36.6, 35.4, 31.8, 31.3, 28.7, 22.1, 21.4, and 19.4.

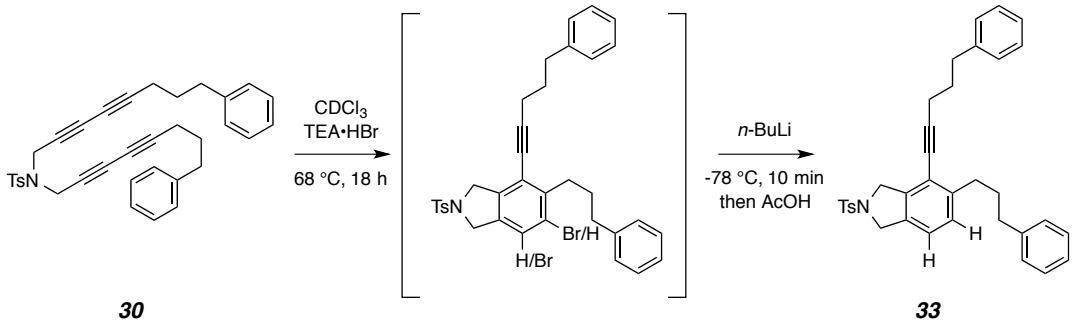
IR (neat) 3059, 3026, 2975, 2859, 2226, 1597, 1495, 1455, 1347, 1293, 1163, 1114, 1098, and 815 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{38}H_{41}NNaO_3S^+$ [M+Na$^+$] requires 614.2699; found 614.2747.

Characterization data for **32b**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H, Ar$_{Ts}H_o$), 7.31 (t, J = 7.5 Hz, 2H, PhH_m), 7.30–7.13 (m, 10H, ArH), 6.51 (s, 1H, *H6*), 4.63 (t, J = 1.8 Hz, 2H, NCH_2), 4.54 (t, J = 2.0 Hz, 2H, NCH_2), 4.50 (septet, J = 6.1 Hz, 1H, CHOAr), 2.77 (t, J = 7.4 Hz, 2H, ArCH_2), 2.74 (t, J = 7.9 Hz, 2H, ArCH_2), 2.64 (t, J = 7.8 Hz, 2H, ArCH_2), 2.41 (t, J = 7.0 Hz, 2H, C≡CCH_2), 2.39 (s, 3H, ArCH_3), 1.95–1.85 (m, 4H, CH_2), and 1.28 [d, J = 6.0 Hz, 6H, CH(CH_3)$_2$].

Authentic sample of 4-(5-phenylpent-1-yn-1-yl)-5-(3-phenylpropyl)-2-tosylisoindoline (33)



30 ***33***

A solution of tetrayne **30** (20 mg, 0.038 mmol) and Et_3N•HBr (70 mg, 0.38 mmol) in $CDCl_3$ (1.5 mL) was heated at 68 ºC. After 18 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give two bromoarenes as an inseparable mixture (ca. 1.5:1 ratio). *n*-BuLi (2.5 M in hexanes, 20 mL, 0.05 mmol) was added to a stirred solution of these bromoarenes (ca. 20 mg) in THF (0.4 mL) at -78 °C. The resulting dark solution was kept at this temperature for 10 min, when an excess of AcOH in THF was slowly added. The mixture was warmed to room temperature and partitioned between EtOAc and saturated NH_4Cl. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated to give **33** (12 mg, 0.022 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H, Ar$_{Ts}H_o$), 7.31 (t, J = 7.6 Hz, 2H, PhH_m), 7.29 (d, J = 8.7 Hz, 2H, Ar$_{Ts}H_m$), 7.26–7.21 (m, 5H, ArH), 7.17–7.13 (m, 3H, ArH), 7.05 (d, J = 7.8 Hz, *H6* or *H7*), 6.98 (d, J = 7.8 Hz, *H7* or *H6*), 4.65 (t, J = 2.0 Hz, 2H, NCH_2), 4.61 (t, J = 2.2 Hz, 2H, NCH_2), 2.78 (t, J = 7.6 Hz, 2H, ArCH_2), 2.76 (t, J = 7.9 Hz, 2H, ArCH_2), 2.64 (t, J = 7.8 Hz, 2H, ArCH_2), 2.44 (t, J = 7.0 Hz, 2H, C≡CCH_2), 2.39 (s, 3H, ArCH_3), and 1.96–1.88 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.81, 143.80, 142.3, 141.6, 139.2, 134.0, 133.5, 130.0, 128.8, 128.7, 128.6, 128.51, 128.48, 127.8, 126.3, 125.9, 121.6, 118.6, 98.6, 76.7, 54.42, 54.40, 35.8, 35.1, 34.0, 32.4, 30.7, 21.7, and 19.3.

IR (neat): 3062, 3028, 2928, 2857, 2225, 1599, 1496, 1453, 1348, 1164, 1098, 1063, and 815 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{35}H_{35}NNaO_2S^+$ [M+Na$^+$] requires 556.2281; found 556.2260.

III. HDDA cyclization of triyne 9 in the presence of varying concentrations of *i*-PrOH or EtOH.

Triyne **9** (3 mg, 0.01 mmol) and varying amounts of *i*-PrOH and ethanol were dissolved in varying amounts of $CDCl_3$ to produce a series of reaction mixtures differing in the initial concentration of alcohol from 0.01–6.5 M (cf. Table S2) and with a constant triyne concentration of 0.01 M. Each solution was heated at 85 °C (bath temperature) for 20 h. The ratio of products **14-hh**/**13** resulting from each individual reaction was determined by integrating appropriately resolved resonances in the ^{1}H NMR spectrum of each product mixture. A representative ^{1}H NMR spectrum for the reaction of **9** with each of *i*-PrOH and EtOH is shown on the following two pages.

Graph S1: Graph of the effect of alcohol [isopropanol (blue) or ethanol (red)] concentration on the branching ratio of (i) dihydrogen transfer vs. (ii) alcohol addition to form products **14-hh** and **13**, respectively.

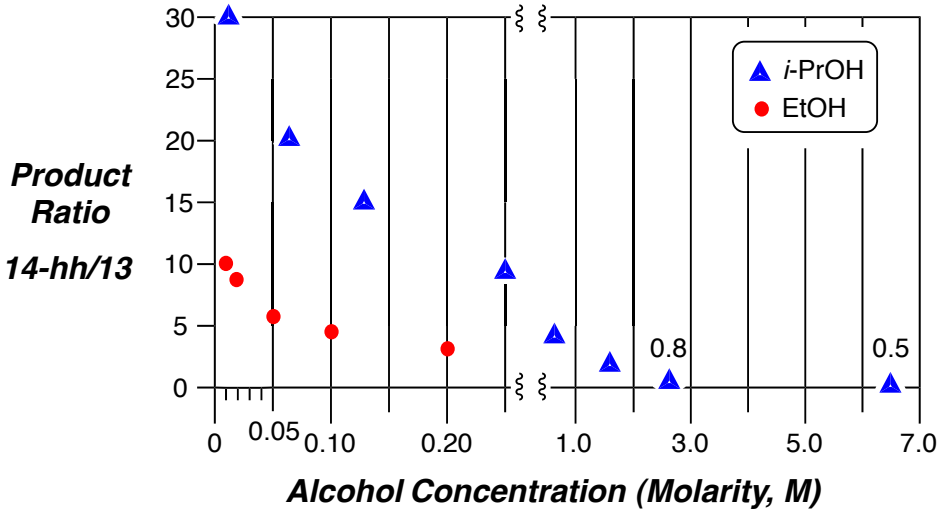
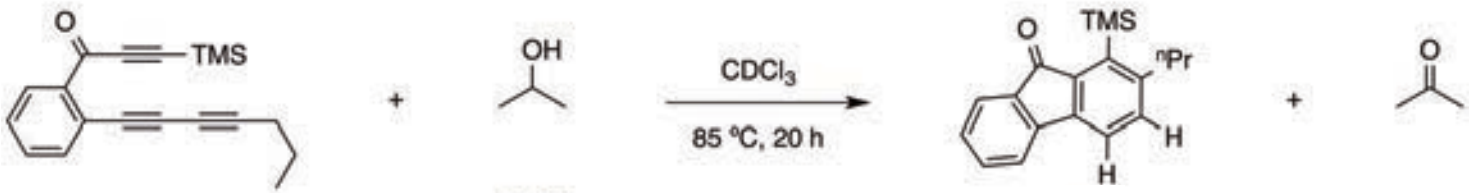


Table S1: Tabular version of the data plotted above in Graph S1. In the case of isopropanol, the amount of acetone, the co-product formed as a result of the dihydrogen transfer, is also given.

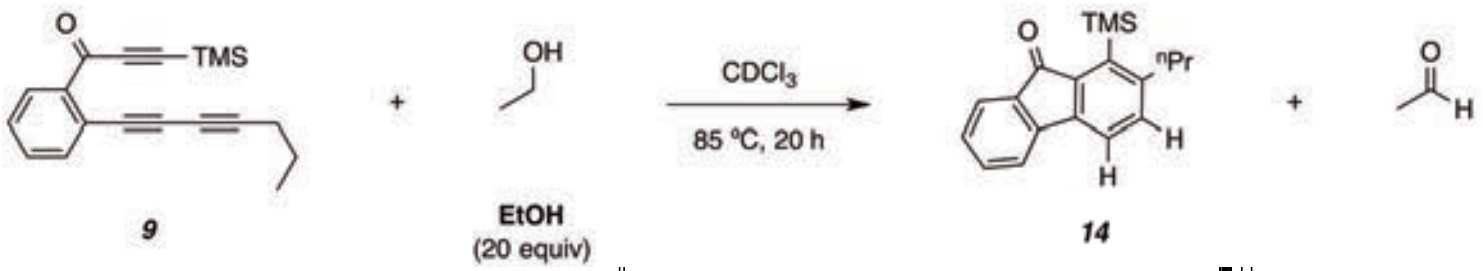
Isopropanol					**Ethanol**			
		Product Ratios					Product Ratios	
[*i*-PrOH] M	equiv *i*-PrOH	***14-hh*** : ***13***$_{i\text{-Pr}}$		Ace-tone	[EtOH] M	equiv EtOH	***14-hh*** : ***13***$_{Et}$	
0.013	1.3	30	~1	30	0.01	1	10	1
0.062	6.2	20	1	20	0.02	2	7.8	1
0.13	13	15	1	13	0.05	5	5.7	1
0.25	25	9.3	1	8.7	0.10	10	4.8	1
0.76	80	4.3	1	-	0.20	20	3.0	1
1.4	160	1.7	1	-				
2.6	320	1	1.2	-				
6.5	650	1	2.2	-				

A representitative ^{1}H NMR spectrum (500 MHz) of the reaction between ***9*** and *iso*-propanol from which the product ratios of alcohol addition vs. H_2-transfer were deduced

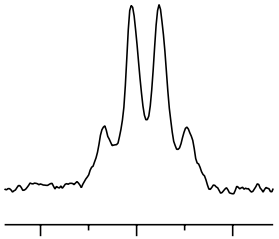


9 + ***i*-PrOH** (10 equiv) → ***14*** + acetone

A representitative ^{1}H NMR spectrum (500 MHz) of the reaction between ***9*** and ethanol from which the product ratios of alcohol addition vs. H_2-transfer were deduced



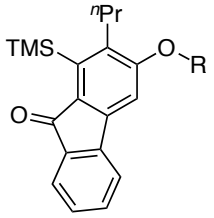
9 + **EtOH** (20 equiv) → ***14*** +



IV. Reaction of 20 with cyclooctanol (Figure 5b) and reaction of 9 with alcohols 23a-k in $CDCl_3$ (Figure 5c)

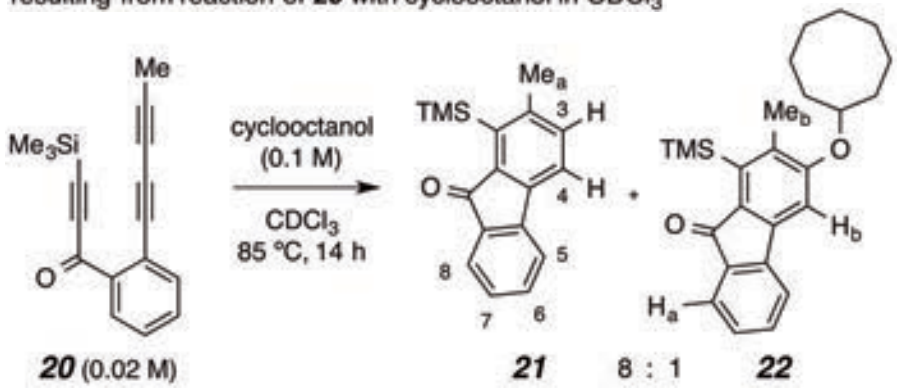
Solutions containing triyne **20** (5 mg, 0.02 mmol) and cyclooctanol (0.1 mmol) in 2 mL of $CDCl_3$ or triyne **9** (3 mg, 0.01 mmol) and one of the alcohols **23a**–**k** [0.1 mmol (or 0.02 mmol in the case of the cyclopropyl carbinol **23e** and 0.2 mmol in the case of ethanol (**2j**)] in $CDCl_3$ (total reaction volume = 1 mL) were each heated at 85 °C (bath temperature). After 20 h (ca. 5 half-lives) a ^{1}H NMR spectrum of each reaction mixture was acquired, and the feasibility of the alcohol to undergo the dihydrogen transfer reaction was determined by observing the presence of reduced benzenoid **14**. The ^{1}H NMR spectra corresponding to the reduction by cyclooctanol and by **23a–k** are shown on the following pages S14–S25. In the cases where stable ketone byproducts are formed, there is excellent correlation between the integrated intensity of resonances in **14** vis-à-vis those in the ketone. For the primary alcohols and methanol, where aldehydes or formaldehyde were formed, the parent byproduct could be observed but secondary reactions of those aldehydes made for a less robust quantitative correlation.

The alkoxyarene addition products showed the following diagnostic molecular ions during GCMS (electron impact) analysis:

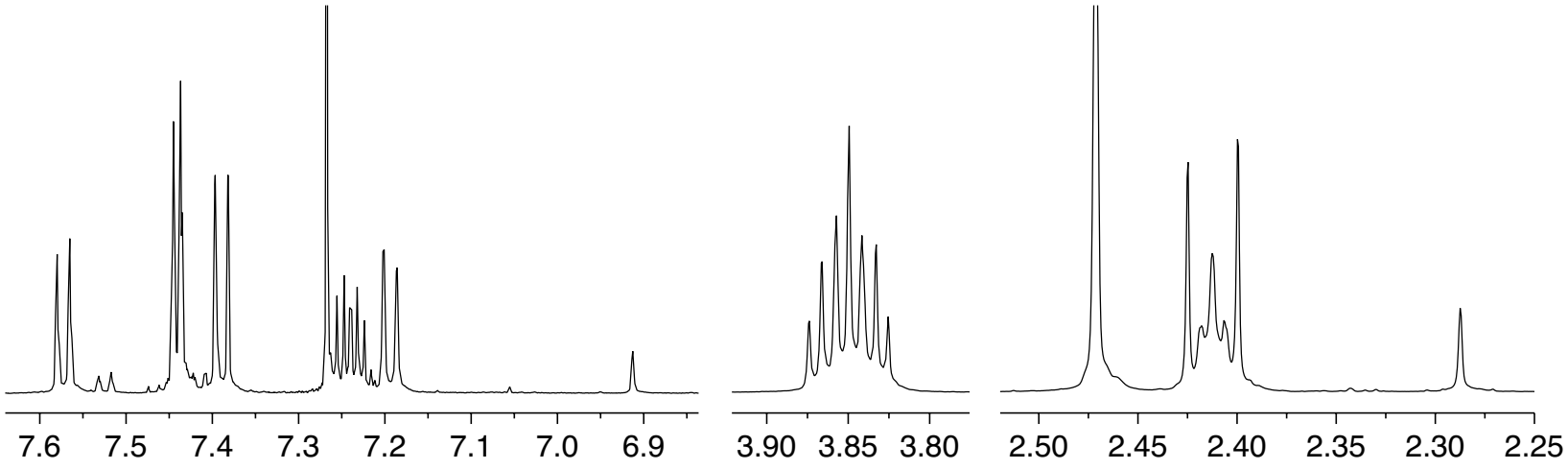


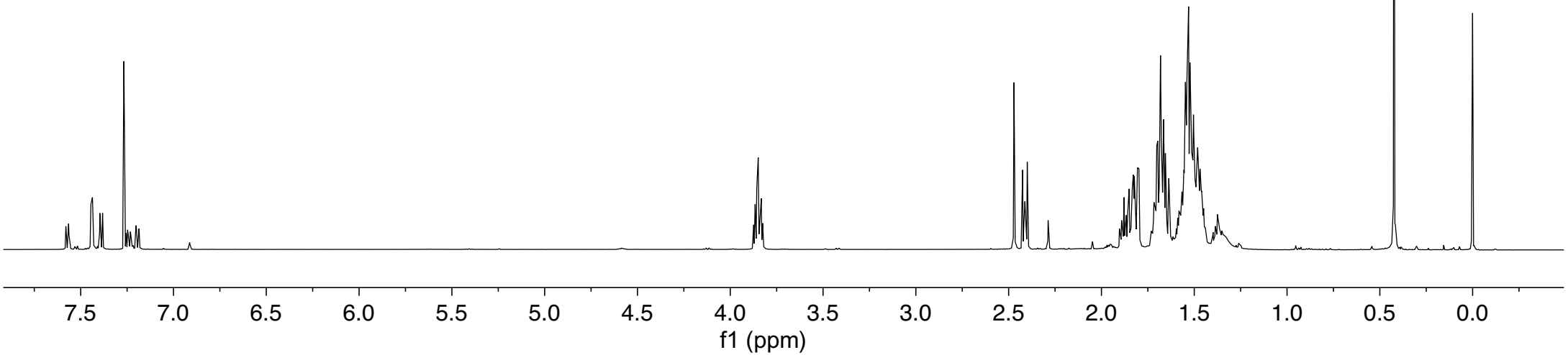
alkoxy-arene	***R***	***M⁺ (m/z)***
a	2,4-dimethyl-3-pentyl	408
b	bornyl	446
c	fenchyl	not observed
d	2-hydroxycyclohexyl	408
e	(cyclopropyl)benzyl	-
f	isobutyl	366
g	PMB	not observed
h	allyl	350
i	but-3-yn-1-yl	362
j	ethyl	see ***S2***
k	methyl	see ***S1***

^{1}H NMR spectrum (500 MHz) of the product mixture resulting from reaction of ***20*** with cyclooctanol in $CDCl_3$

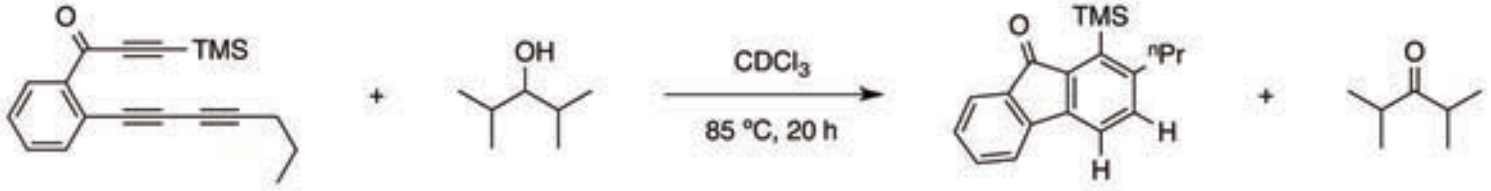


20 (0.02 M) ***21*** 8 : 1 ***22***

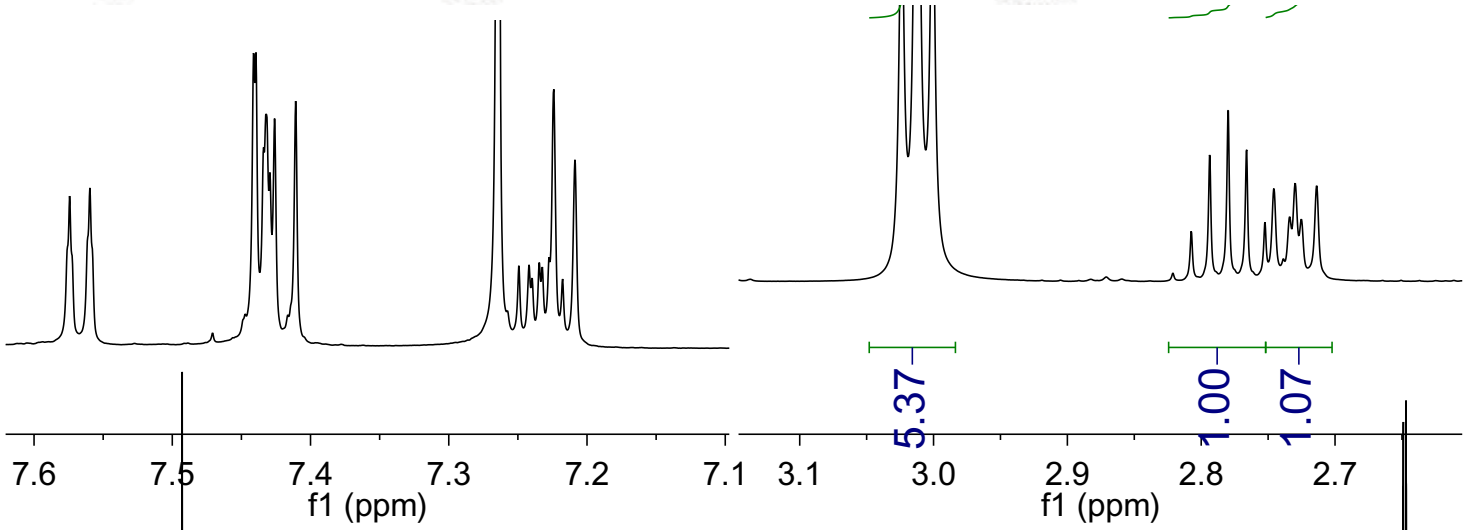




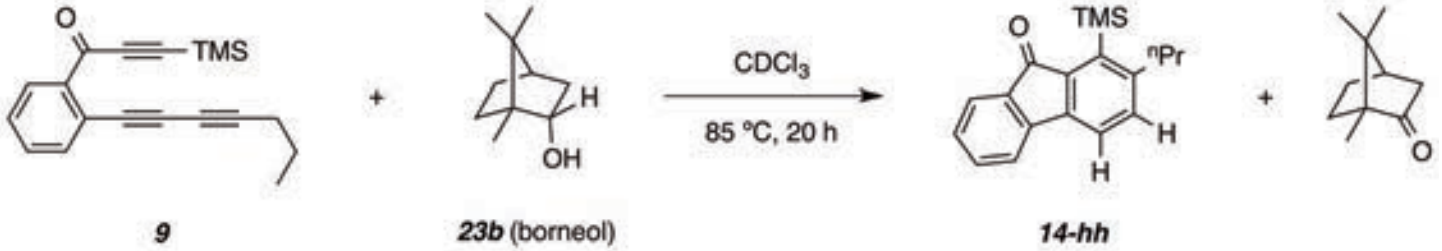
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with 2,4-dimethylpentan-3-ol (***23a***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



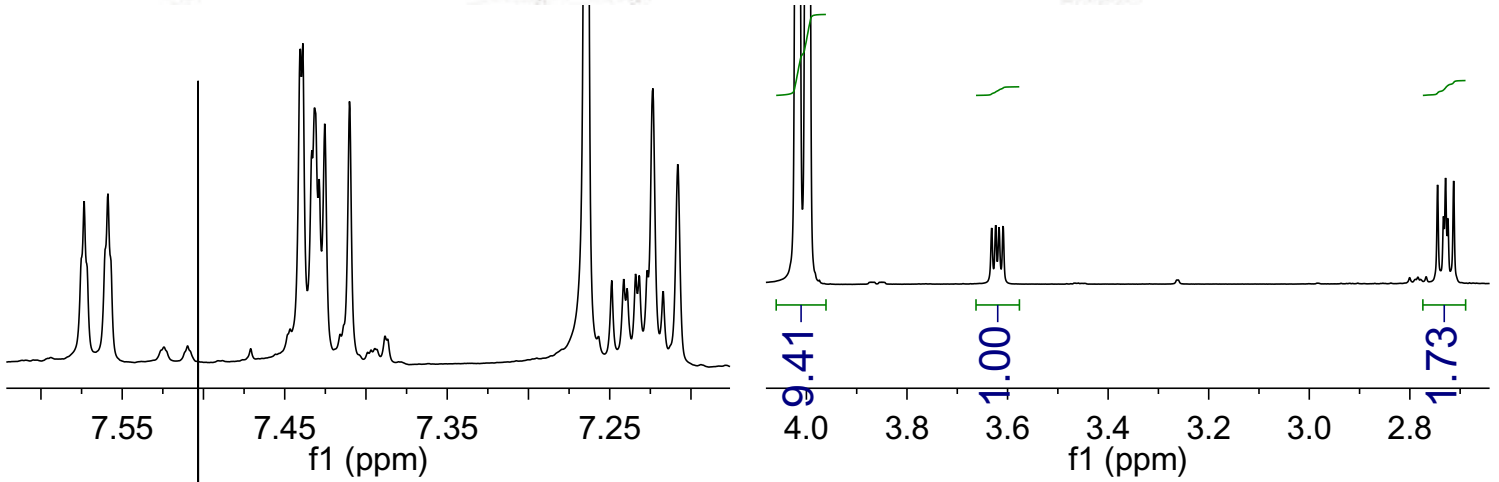
9 ***23a*** ***14-hh***



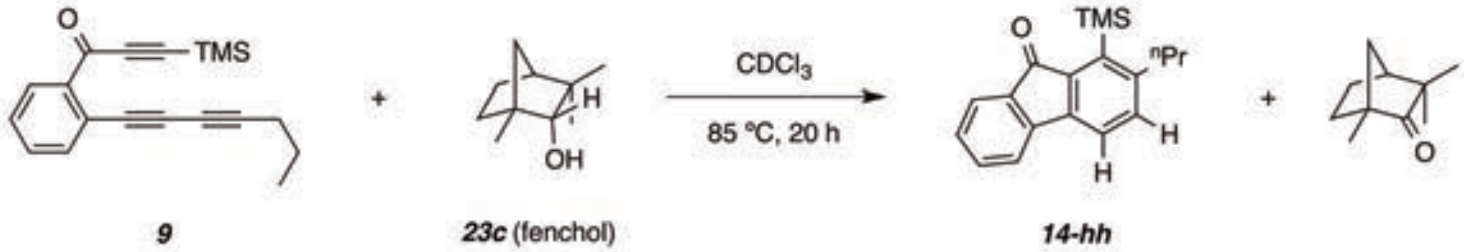
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with borneol (***23b***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



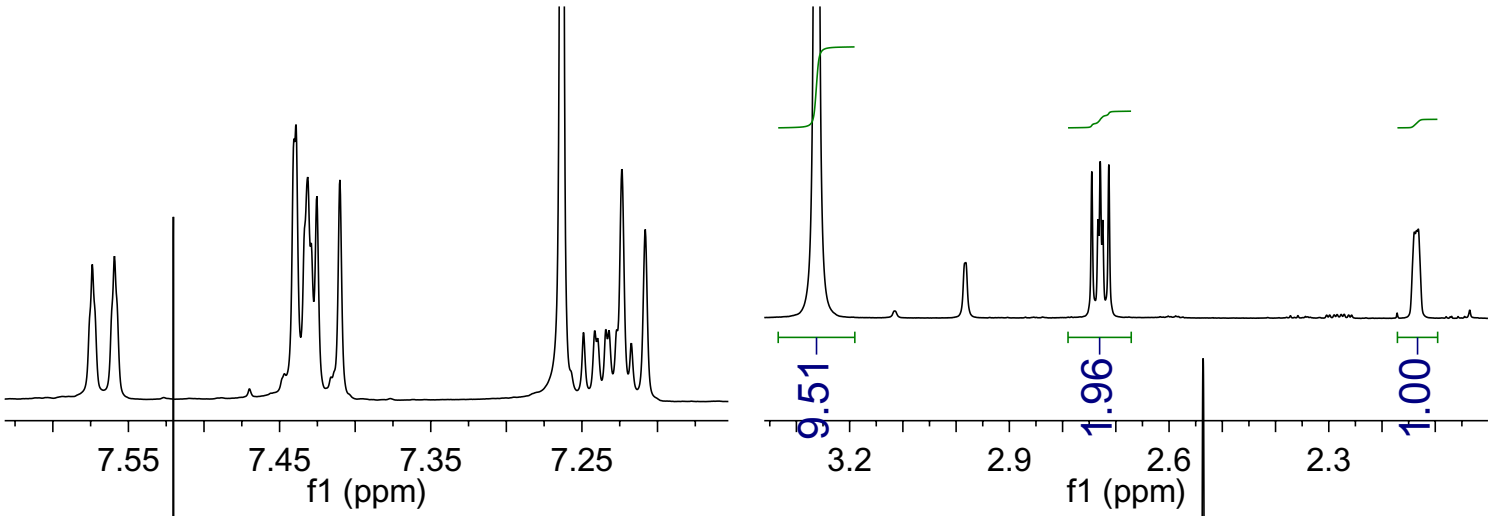
9 ***23b*** (borneol) ***14-hh***



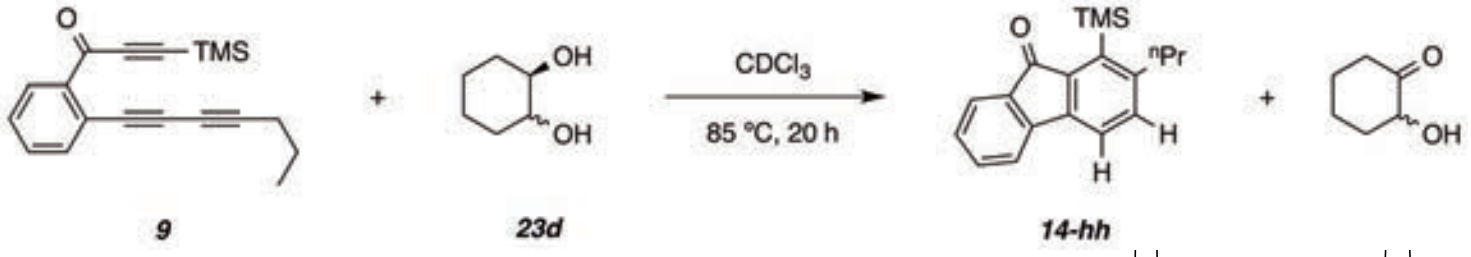
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with fenchol (***23c***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



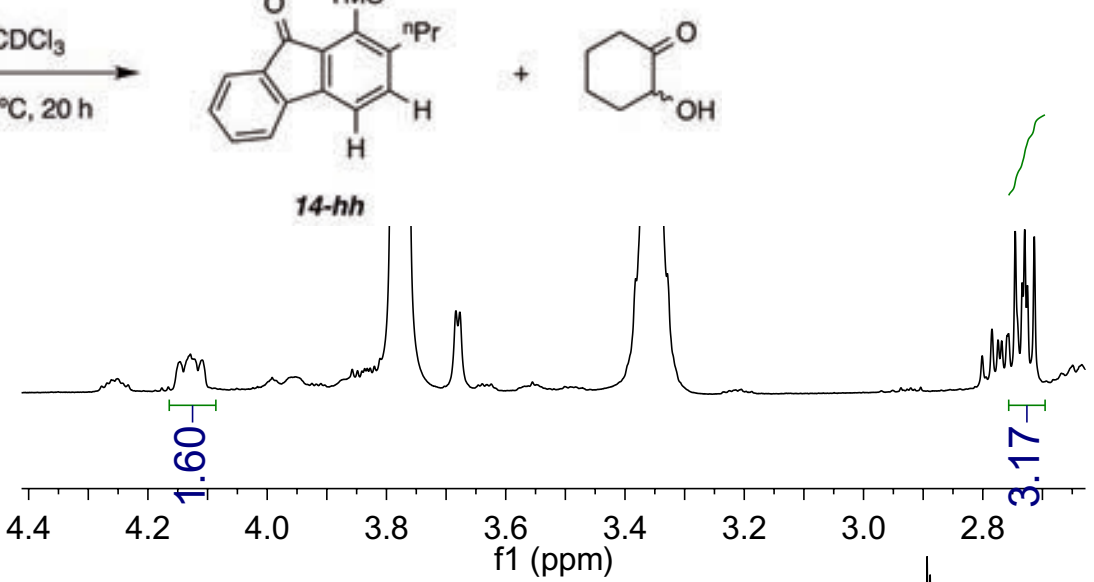
9 ***23c*** (fenchol) ***14-hh***

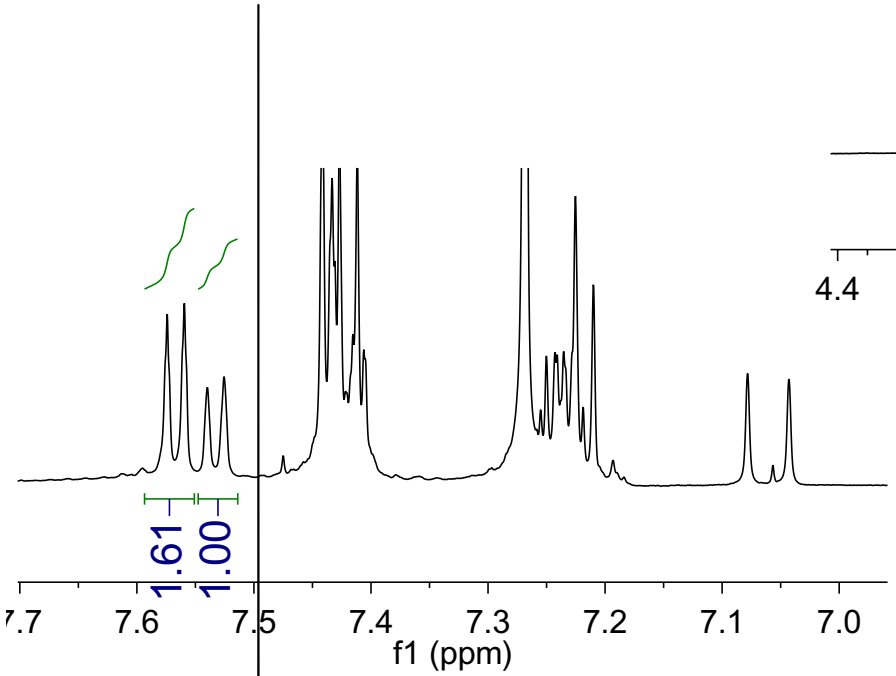


^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with 1,2-cyclohexanediol (***23d***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms

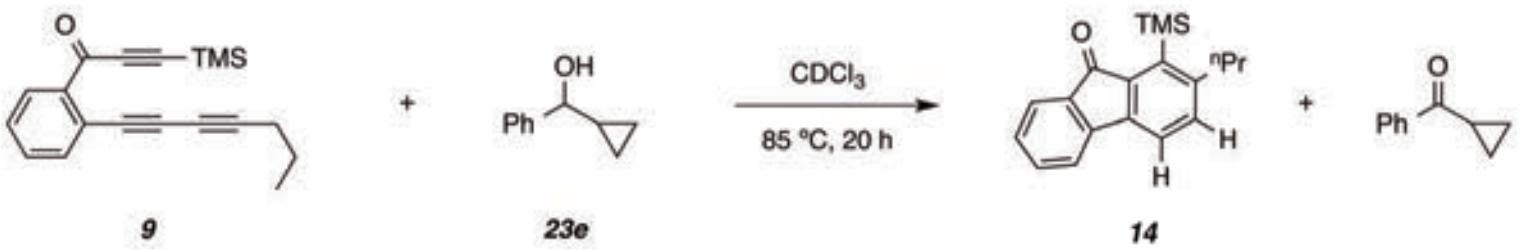


9 ***23d*** ***14-hh***



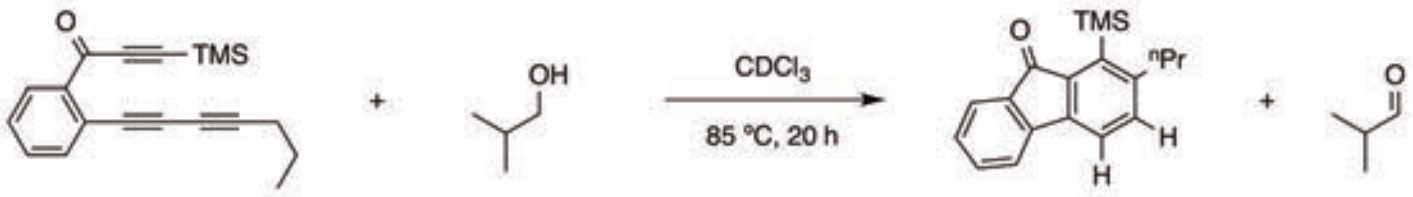


^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with cyclopropyl(phenyl)methanol (***23e***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms

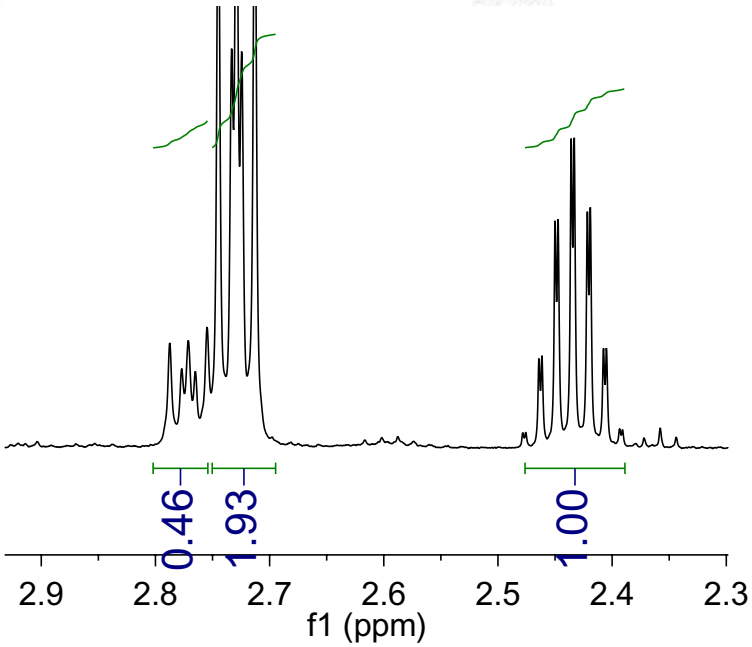


9 ***23e*** ***14***

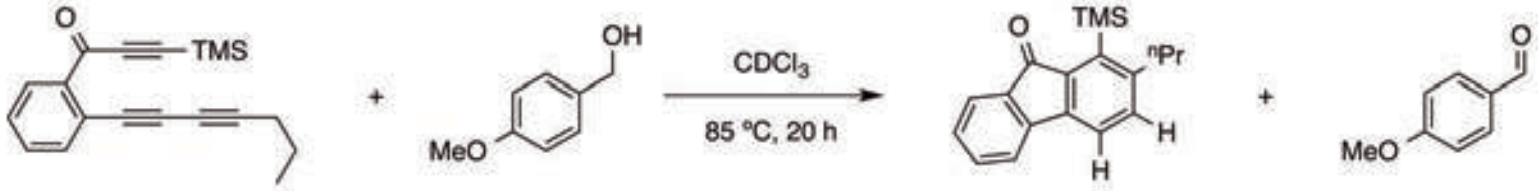
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with isobutanol (***23f***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



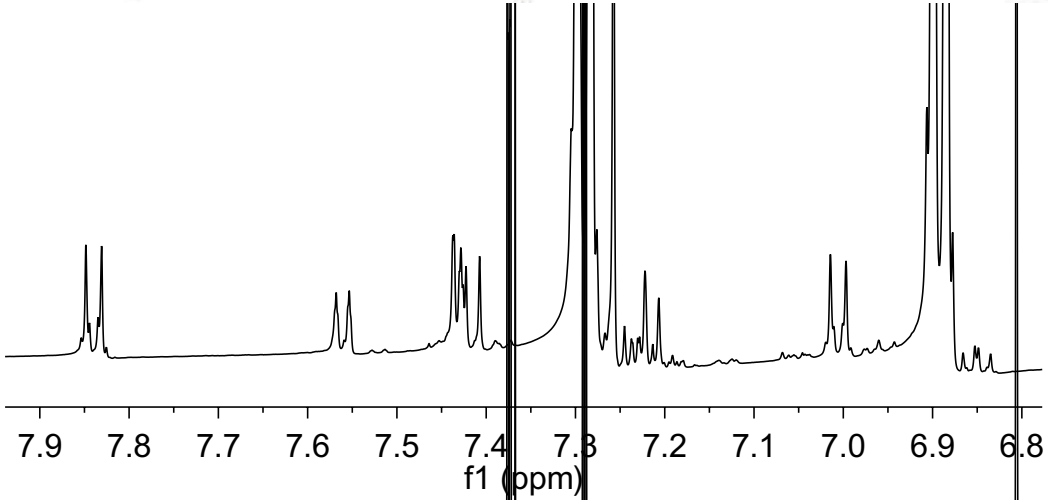
9 ***23f*** ***14-hh***



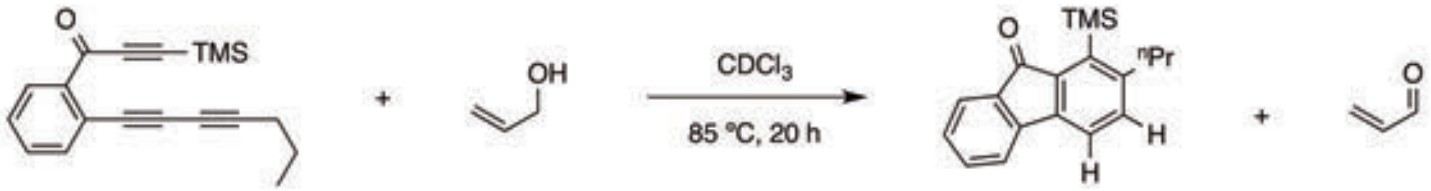
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with 4-methoxybenzyl alcohol (***23g***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



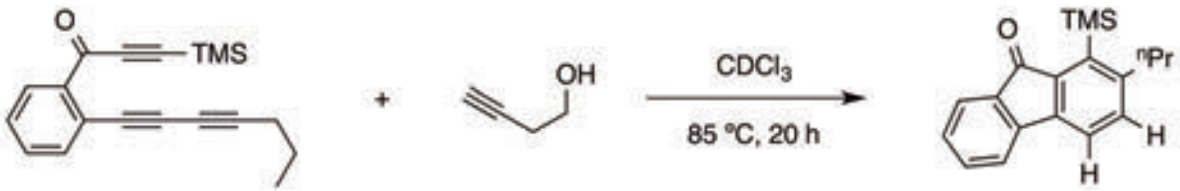
9 ***23g*** ***14-hh***



^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with allyl alcohol (***23h***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms

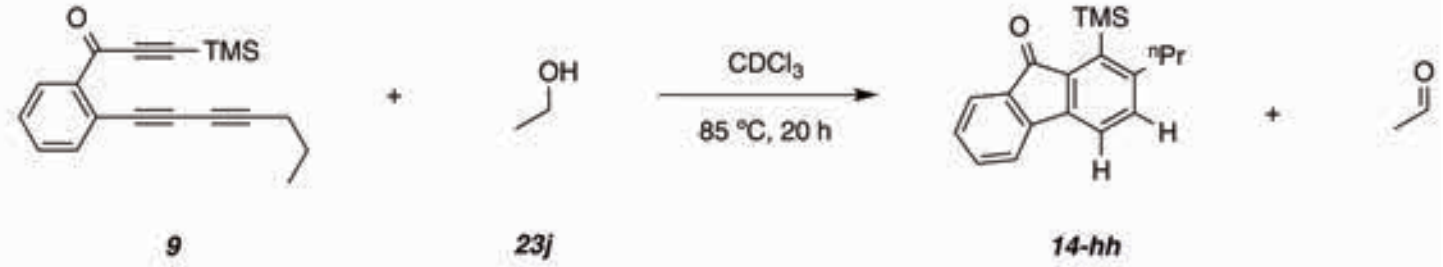


^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with bu-3-yn-1-ol (***23i***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms

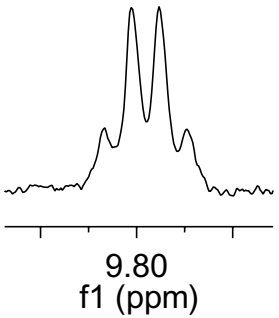


9 ***23i*** ***14-hh***

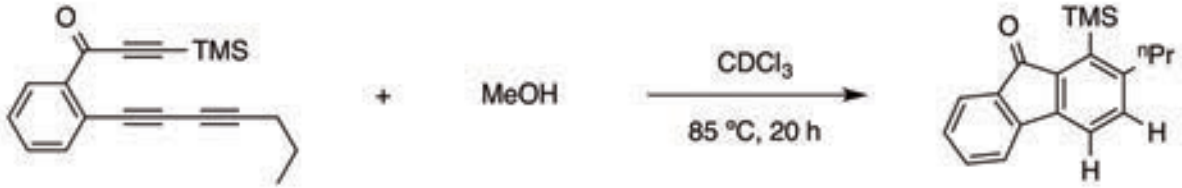
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with ethanol (***23j***)
in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



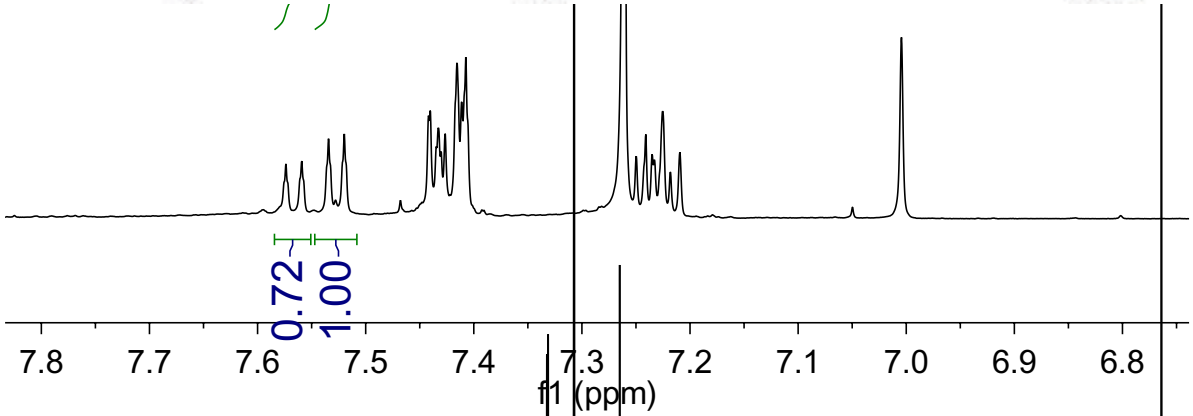
9 ***23j*** ***14-hh***



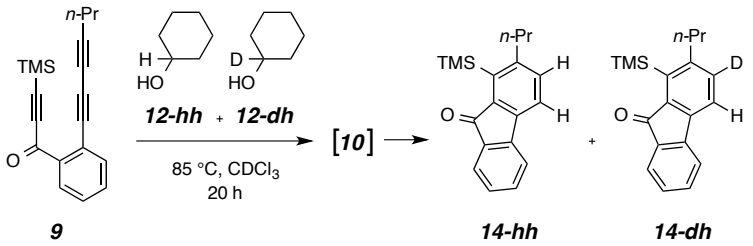
^{1}H NMR spectrum (500 MHz) of reaction of ***9*** with methanol (***23k***) in $CDCl_3$ demonstrating the ability of this alcohol to transfer two hydrogen atoms



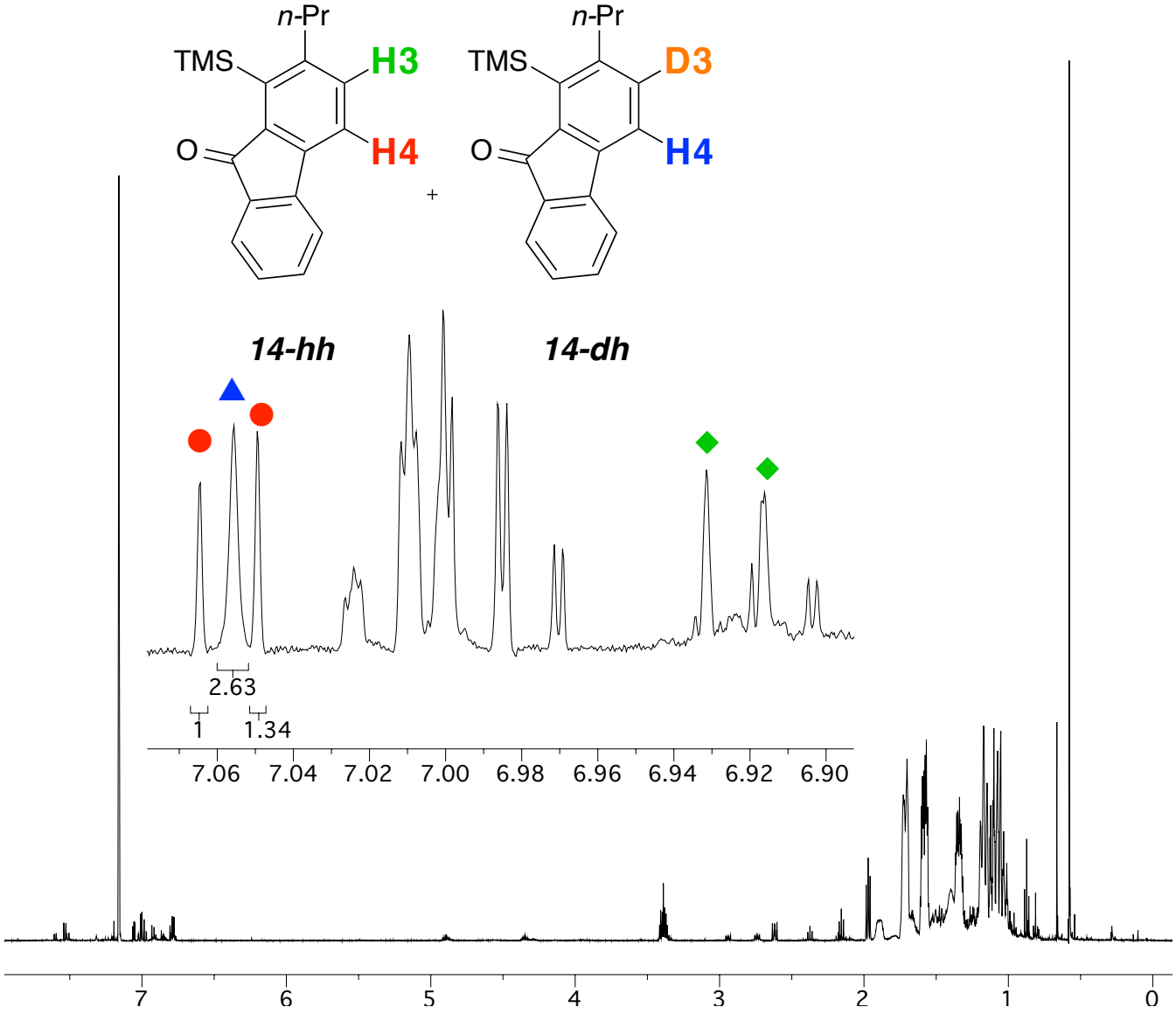
9 ***23k*** ***14-hh***



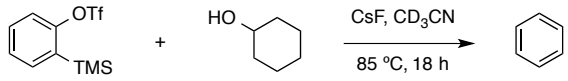
V. Kinetic isotope effect for the reduction of benzyne 10 by cyclohexanol.



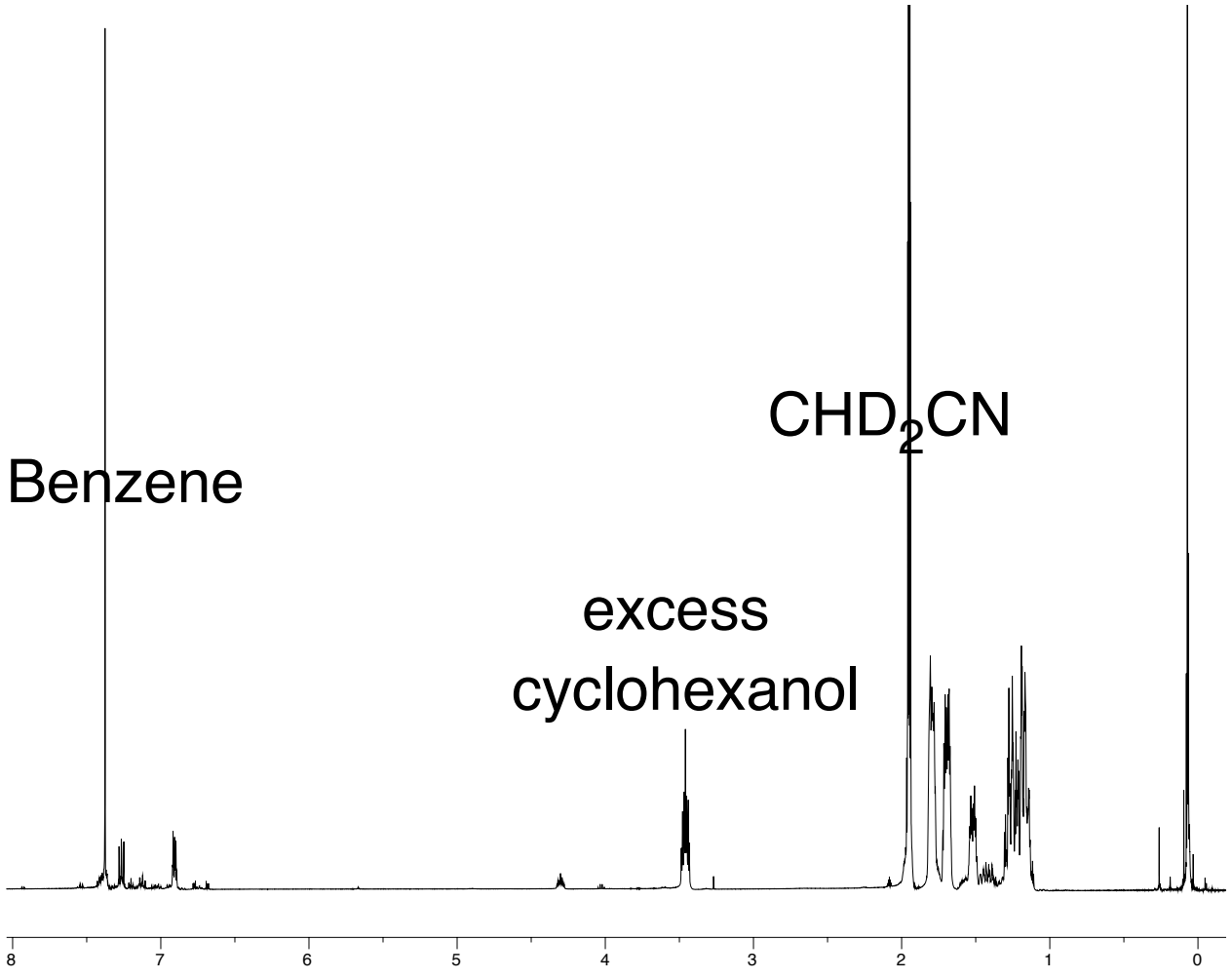
In a glass vial was added 25.4 mg of 1-*d*-cyclohexanol (**12-dh**) and 11.4 mg of cyclohexanol (**12-hh**). Triyne **9**[3] (5.3 mg) and 1.8 mL of dry $CDCl_3$ were added. The vial containing the resulting homogenous solution was sealed with a Teflon-lined cap and heated to 85 °C for 20 h. The reaction mixture was then concentrated and redissovled in C_6D_6 and directly subjected to NMR analysis. The spectrum is shown below. This experiment was done a second time and gave essentially the same result. The choice of deuterobenzene as the NMR solvent was based on the superior resolution of key resonances for the newly introduced hydrogen atoms at C3 and C4.



VI. Reaction of 2-trimethylsilylphenyl triflate with cyclohexanol in the presence of cesium fluoride produces benzene.



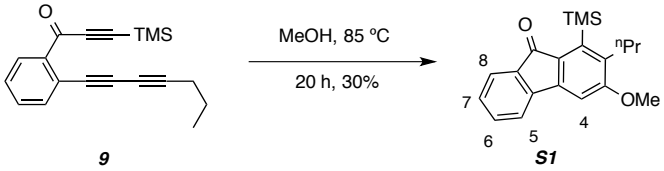
A solution of 2-trimethylsilylphenyl triflate (20 mg, 0.067 mmol), cesium fluoride (52 mg, 0.34 mmol), and cyclohexanol (50 µL, 0.47 mmol) in CD_3CN (1 mL) was heated at 85 ºC. After 18 h, the mixture was cooled to room temperature and ^{1}H NMR data in CD_3CN were acquired. The ^{1}H NMR spectrum of the reaction mixture is shown below.



VII. Competition alcohol trapping reactions of 9 with ca. equimolar mixtures of MeOH vs. EtOH, EtOH vs. *i*-PrOH, and *i*-PrOH vs. *t*-BuOH

General Procedure: Triynone **9**[3] (3.2 mg, 0.011 mmol) was added to 1.1 mL an ca. equimolar solution of alcohol^{fast} and alcohol^{slow}. The precise ratio of the two alcohols was determined by ^{1}H NMR analysis of an aliquot of the stock solution of the alcohol mixture. The final concentration was 0.01 M in **9**. The mixture was sealed with a Teflon-lined cap and heated at 85 ºC (bath temperature). After 20 h, the reaction solution was concentrated to dryness, and the product ratio, adjusted slightly for the precise ratio of alcohols used, was determined from ^{1}H NMR analysis of the resulting reaction mixtures in $CDCl_3$. Characterization data for each of the relevant new compounds is listed below.

3-Methoxy-2-propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (S1)



9 *S1*

A solution of triynone **9**[3] (21 mg, 0.072 mmol) in methanol (7 mL) was heated at 85 ºC. After 20 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give the methoxyfluorenone **S1** (7 mg, 0.02 mmol, 30%).

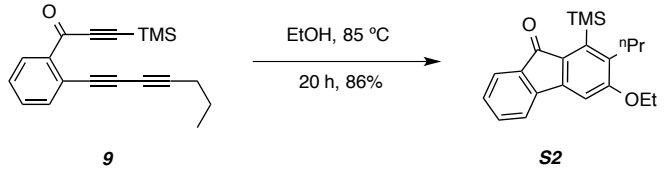
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.40–7.42 (m, 2H, *H5* and *H6*), 7.23 (nfom, 1H, *H7*), 7.10 (s, 1H, *H4*), 3.94 (s, 3H, OCH_3), 2.74 (br t, *J* = 8.1 Hz, 2H, $CH_2CH_2CH_3$), 1.46 (br sext, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 0.97 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), and 0.44 [s, 9H, $(CH_3)_3Si$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.2, 162.1, 146.4, 143.5, 143.1, 138.6, 134.8, 133.9, 131.9, 128.9, 123.5, 119.0, 103.2, 55.8, 30.9, 25.2, 14.2, and 2.7.

IR (neat): 2957, 1706, 1583, 1235, 1133, and 847 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{20}H_{24}NaO_2Si^+$ [M+Na$^+$] requires 347.1438; found 347.1437.

3-Ethoxy-2-propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (S2)



9 *S2*

A solution of triynone **9**[3] (21 mg, 0.072 mmol) in ethanol (7 mL) was heated at 85 ºC. After 20 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give the ethoxyfluorenone **S2** (21 mg, 0.062 mmol, 86%).

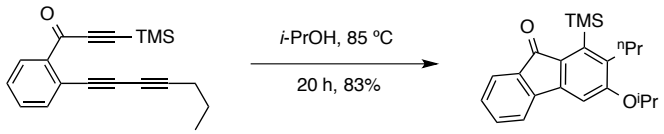
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.40 (ddd, *J* = 7.4, 7.4, 1.1 Hz, *H6*), 7.38 (ddd, *J* = 7.0, 1.7, 0.8 Hz, *H5*), 7.22 (ddd, *J* = 7.3, 7.0, 2.1 Hz, *H7*), 6.97 (s, 1H, *H4*), 4.16 (q, *J* = 7.0 Hz, 2H, OCH_2CH_3), 2.76 (br t, *J* = 8.0 Hz, 2H, $CH_2CH_2CH_3$), 1.481 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3), 1.478 (br sext, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 0.96 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), and 0.44 [s, 9H, $(CH_3)_3Si$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.2, 161.4, 146.4, 143.5, 143.1, 138.7, 134.8, 133.8, 131.6, 128.8, 123.4, 118.9, 103.8, 64.1, 31.0, 25.2, 14.9, 14.3, and 2.8.

IR (neat): 2956, 1704, 1583, 1234, 1134, and 847 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{26}NaO_2Si^+$ [M+Na^+] requires 361.1594; found 361.1591.

3-Isopropoxy-2-propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (S3)



9 ***S3***

A solution of triynone **9**[3] (21 mg, 0.072 mmol) in isopropanol (7 mL) was heated at 85 ºC. After 20 h the mixture was concentrated and the crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give the *iso*-propoxyfluorenone **S3** (21 mg, 0.060 mmol, 83%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.40 (ddd, *J* = 7.4, 7.4, 1.1 Hz, *H6*), 7.39 (dd, *J* = 7.4, 1.0 Hz, *H5*), 7.22 (nfom, 1H, *H7*), 6.97 (s, 1H, *H4*), 4.72 (sept, *J* = 6.0 Hz, 1H, OC*H*), 2.73 (br t, *J* = 8.1 Hz, 2H, $CH_2CH_2CH_3$), 1.47 (br sext, *J* = 8.3 Hz, 2H, $CH_2CH_2CH_3$), 1.41 [d, *J* = 6.0 Hz, 6H, $CH(CH_3)_2$], 0.96 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), and 0.44 [s, 9H, $(CH_3)_3Si$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.1, 160.3, 146.2, 143.5, 143.4, 139.2, 134.9, 133.8, 131.3, 128.8, 123.4, 118.9, 104.6, 70.1, 31.2, 25.2, 22.3 (2x), 14.3, and 2.8.

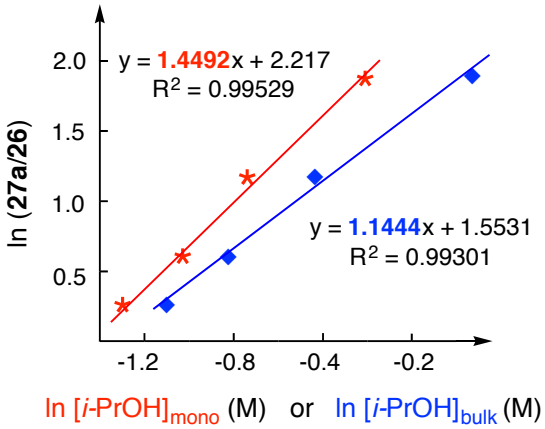
IR (neat): 2957, 2870, 1704, 1581, 1234, 1110, and 847 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{28}NaO_2Si^+$ [M+Na^+] requires 375.1751; found 375.1746.

VIII. Procedure used for competition (internal clock) reactions of substrate 24 or 30 in the presence of a fixed molar ratio of isopropanol, but at varying overall concentrations.

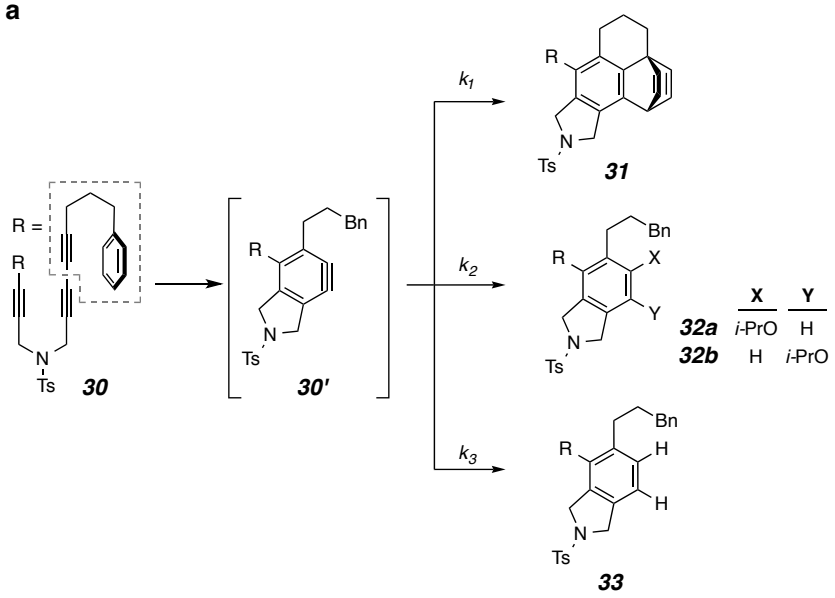
Triyne **24** (or **30**) (10 mg), containing a tethered aromatic ring capable of undergoing a competitive intramolecular Diels–Alder reaction, and *i*-PrOH (100 μL, 70 molar equiv) were dissolved in varying amounts of $CDCl_3$ to produce a series of reaction mixtures differing in the initial concentration of triyne from 5–20 mM. Each solution was heated at 68 °C (bath temperature) for 18 h, concentrated, and redissolved in $CDCl_3$ (0.7 mL). The ratio of products **27a**/**26** (or **32a**/**31**) resulting from each individual reaction was determined by integrating appropriately resolved resonances in the ^{1}H NMR spectrum of each crude product mixture. A representative ^{1}H NMR spectrum (for the reaction of **30** with *i*-PrOH) is shown on the following page.

Graph S2: The slope of a log-log plot of the ratio of alcohol addition product (**27a**) to IMDA product (**26**) for the reaction of **24** and *i*-PrOH gives the kinetic order of the alcohol in the addition reaction.



Graph S3: This is merely a slight variant of Figure 8 in the manuscript that has been reproduced for discussion of the derivations for the kinetic order of alcohol in the formation of products **32a** and **33**.

a

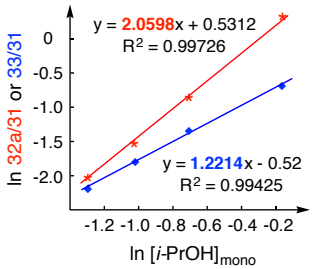


X	Y
i-PrO	H
H	*i*-PrO

b

[*i*-PrOH] (bulk) (M)	[*i*-PrOH] (monomer) (M)	*32a* / *31*	*33* / *31*
1.31	0.83	1.2	0.46
0.66	0.49	0.37	0.26
0.44	0.35	0.19	0.17
0.33	0.28	0.13	0.12

c



The kinetic order of the alcohol formation during formation of **32a** and **33** was determined as follows. The Diels–Alder adduct **31** results from unimolecular (i.e., first order) cycloaddition within the benzyne **30'**. On the other hand, reaction between **30'** and the alcohol trapping agent is intermolecular and the rate of that trapping event should be, therefore, dependent on the concentration alcohol. In the formation of product **32a**, resulting from *addition* of *i*-PrOH to **30'**, the ratio of rates for the formation of **32a** and **31** can be expressed as eq 1, which can be rewritten as eq 2. Because the alcohol is present in large excess (70 equiv), its concentration remains essentially constant throughout the duration of the reaction and eq 2 can, therefore, be approximated by eq 3, which can further be expressed as eq 4. The product ratio of **32a** to **31** was measured at a series of different concentrations of alcohol and the results are given in Graph S3 (panel b). Following eq 4 the slope of the plot of ln[**32a**]/[**31**] vs. ln[alcohol]$_{mono}$ gives *n*, the order of dependence on alcohol.

For ***32a***

$$\frac{d[\mathbf{32a}]}{d[\mathbf{31}]} = \frac{k_2 \cdot [\mathbf{30'}] \cdot [i\text{-PrOH}]_{mono}^{\,n} \cdot dt}{k_1 \cdot [\mathbf{30'}] \cdot dt} \qquad \text{(eq 1)}$$

$$\frac{[\mathbf{32a}]}{[\mathbf{31}]} = \frac{\int k_2 \cdot [\mathbf{30'}] \cdot [i\text{-PrOH}]_{mono}^{\,n} \cdot dt}{\int k_1 \cdot [\mathbf{30'}] \cdot dt} \qquad \text{(eq 2)}$$

$$\frac{[\mathbf{32a}]}{[\mathbf{31}]} \approx \frac{k_2}{k_1} \cdot [i\text{-PrOH}]_{mono}^{\,n} \qquad \text{(eq 3)}$$

$$\ln\frac{[\mathbf{32a}]}{[\mathbf{31}]} \approx n \cdot \ln[i\text{-PrOH}]_{mono} + \ln\frac{k_2}{k_1} \qquad \text{(eq 4)}$$

"Alcohols are known to form aggregates in chlorinated solvents. The enthalpy and entropy change associated with dimerization of monomeric *iso*-propanol [i.e., *i*-PrOH(monomer) + *i*-PrOH(monomer) ⟶

i-PrOH(dimer)] in CCl_4 has been determined to be -5.7±0.9 kcal/mol and -19.5±3.0 cal/mol, respectively. Assuming that these values would be similar to those for its dimerization in $CDCl_3$, we estimated the free energy change in the dimerization process of iso-propanol at 68 °C to be $\Delta G = \Delta H - T\bullet\Delta S = +0.95$ kcal•mol^{-1}. Applying $\Delta G = -R\bullet T\bullet \ln K_{eq}$, the equilibrium constant for the dimerization is deduced to be 0.35; that is, $[i\text{-PrOH}]_{dimer} = 0.35\bullet\{[i\text{-PrOH}]_{mono}\}^2$."[7] The presence of *i*-PrOH trimers and higher oligomers is ignored for simplicity; therefore, the corresponding $[i\text{-PrOH}]_{mono}$ (panel b) could be deduced at different $[i\text{-PrOH}]_{bulk}$ using eq 5 and eq 6 shown below. A plot of ln[**32a**]/[**31**] against $\ln[i\text{-PrOH}]_{mono}$ gave a line with a slope of 2.0598, which corresponds to the order of dependence on $[i\text{-PrOH}]_{mono}$ for the formation of **32a**.

$$2\bullet[i\text{-PrOH}]_{dimer} + [i\text{-PrOH}]_{mono} = [i\text{-PrOH}]_{bulk} \quad \text{(eq 5)}$$

$$[i\text{-PrOH}]_{dimer} = 0.35\bullet([i\text{-PrOH}]_{mono})^2 \quad \text{(eq 6)}$$

In the *redox* process between aryne and alcohol, the ratio of rates for the formation of **33** and **31** can be expressed as eq 7, which can be rewritten as eq 8. Because alcohol is present in large excess (70 equiv), its concentration remains essentially constant throughout the duration of the reaction and eq 8 can be approximated by eq 9, which can further be expressed as eq 10. The product ratio of **33** to **31** was measured at a series of different concentrations of alcohol and these results are also given in Graph S3 (panel b). Following eq 10 the slope of the plot of ln[**33**]/[**31**] vs. $\ln[\text{alcohol}]_{mono}$ gives *n*, the order of dependence on alcohol. As shown in Graph S3 (panel c), the plot of ln[**33**]/[**31**] *vs.* $\ln[\text{alcohol}]_{mono}$ gave a line with a slope of 1.2214, which is the order of dependence on $[i\text{-PrOH}]_{mono}$ for the formation of **31**.

For ***33***

$$\frac{d[\mathbf{33}]}{d[\mathbf{31}]} = \frac{k_3\bullet[\mathbf{30'}]\bullet[i\text{-PrOH}]_{mono}^{\,n}\bullet dt}{k_1\bullet[\mathbf{30'}]\bullet dt} \quad \text{(eq 7)}$$

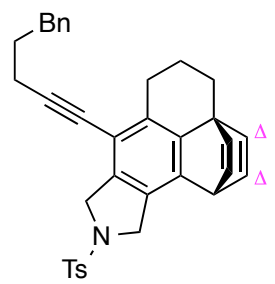
$$\frac{[\mathbf{33}]}{[\mathbf{31}]} = \frac{\int k_3\bullet[\mathbf{30'}]\bullet[i\text{-PrOH}]_{mono}^{\,n}\bullet dt}{\int k_1\bullet[\mathbf{30'}]\bullet dt} \quad \text{(eq 8)}$$

$$\frac{[\mathbf{33}]}{[\mathbf{31}]} \approx \frac{k_3}{k_1}\bullet[i\text{-PrOH}]_{mono}^{\,n} \quad \text{(eq 9)}$$

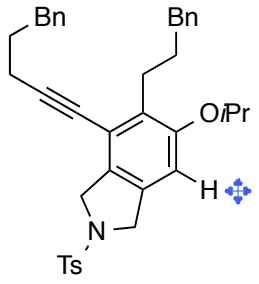
$$\ln\frac{[\mathbf{33}]}{[\mathbf{31}]} \approx n\bullet\ln[i\text{-PrOH}]_{mono} + \ln\frac{k_3}{k_1} \quad \text{(eq 10)}$$

A representative ^{1}H NMR spectrum (500 MHz) from which the branching ratios of internal clock (IMDA) vs. alcohol addition vs. H_2-transfer were deduced

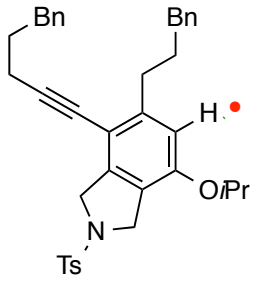
$CDCl_3$, 500 MHz



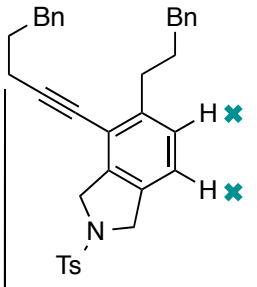
31



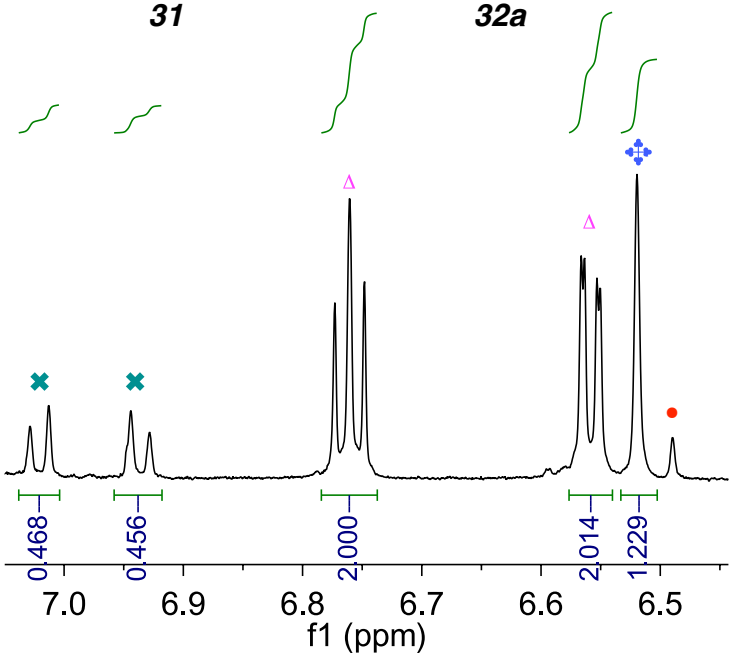
32a



32b



33



IX. Computational methods

DFT calculations were carried out with the Gaussian 09 software package.[8] All geometries were optimized using the M06-2X functional[9] and the triple-ζ split-valence 6-311+G(d,p) basis set. For structures shown in Figure 4, all geometry optimizations and frequency calculations were performed in the gas phase. In the studies of the alcohol trapping pathway (Figure 9), the SMD continuum solvation model was used during both the geometry optimization and frequency calculation with methanol as the solvent. The "grid=ultrafine" option was used to specify the integration grid applied during the numerical integrations. Harmonic vibrational frequency calculations for thermal corrections of the enthalpies were performed at 298 K. Starting geometries for the DFT calculations of all alcohol donors were found through Monte Carlo conformational searches performed with the OPLS_2005 force field in MacroModel version 9.9.[10] Each conformer was then subjected to geometry optimization using DFT. The optimized reactant and product geometries were checked and found to have no imaginary frequencies, and each of the optimized transition state structure geometries was found to have only one imaginary frequency. The value for the "Sum of electronic and thermal Free Energies=" was used to determine the free energy (G) of each of the two reactants ($G_{Benzyne}$ and $G_{Alcohol}$) and of the transition state structure (G_{TS}) for each reaction. The $\Delta G^{\ddagger}$ value was determined using the following equation:

$$\Delta G^{\ddagger} = G_{TS} - (G_{Benzyne} + G_{Alcohol})$$

where G is the free energy of the lowest energy geometry of the alcohol, benzyne, and transition state structure.

Table S2. The computed free energies for the reactant, product, and transition state structures from which the values of $\Delta G^{\ddagger}$ (cf. Figure 4 in the manuscript), the kinetic isotope effect, and ΔG_{RXN} (i.e. for dihydrogen transfer between *o*-benzyne and methanol) were determined. In cases where multiple conformations of a given transition state structure or reactant were found, only the lowest energy structure was used.

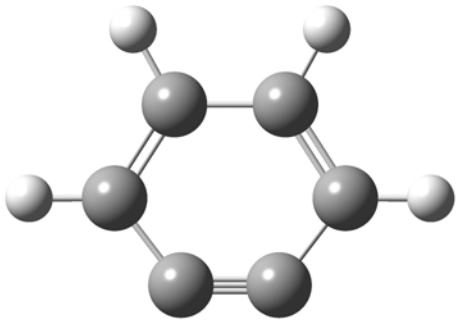
	Entry	Structure	Computed Free Energy G (kcal•mol^{-1})		
	1	*o*-Benzyne (**2**)	-144840.8		
	2	Methanol	-72587.2	$G_{Products} - G_{Reactants}$	ΔG_{rxn}
	3	Benzene	-145660.5		
	4	Formaldehyde	-71838.3	(G3 + G4) – (G1 + G2)	-70.8
Reactant and Product Structures	5	Cyclopentanol	-170436.4		
	6	Cyclohexanol (**12-hh**)	-195087.5		
	7	Cyclohexanol-1-*d* (**12-dh**)	-195089.7		
	8	Fluorynone **S4** (data from Ref 3)	-641139.6		
				$G_{TS} - G_{Reactants}$	$\Delta G^{\ddagger}$
	9	**2** + Methanol (**17‡**)	-217414.6	G9 – (G1 + G2)	13.4
	10	**2** + Cyclopentanol (**18a‡**)	-315264.4	G10 – (G1 + G5)	12.8
	11	**2** + Cyclopentanol (**18b‡**)	-315258.6	G11 – (G1 + G5)	18.6
	12	**S4** + ax-Cyclohexanol (**19‡**)	-836216.0	G12 – (G6 + G9)	11.1
Transition Structures	13	Alternative TS **S5‡** (**S4** + eq-Cylohexanol)	-836215.5	G13 – (G6 + G9)	11.6
	14	Regioisomeric TS **S6‡** (**S4** + eq-Cylohexanol)	-836212.3	G14 – (G6 + G9)	14.8
	15	KIE TS **S7‡** (**S4** + ax-**12-dh**)	-836217.8	G15 – (G7 + G9)	11.5

Kinetic Isotope Effect Determination

$$e^{\left(\Delta G^{\ddagger}_{D} / RT - \Delta G^{\ddagger}_{H} / RT\right)} = 1.97$$

Energies and geometries for all of the entries in Table S2 (Pages S36 – S55)

Computed energy and geometry of *o*-benzyne (2, gas phase, entry 1, Table S2)

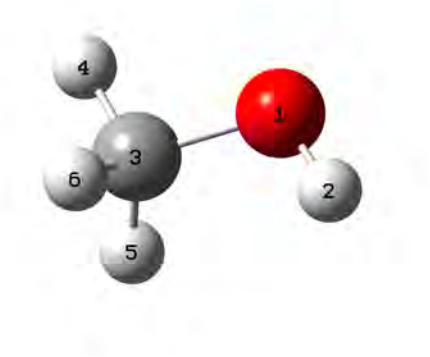


"Sum of electronic and thermal Free Energies[a] = -230.818447 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-1.459052	-0.132412	0.000018
C	-0.619665	-1.230665	-0.000010
C	0.619772	-1.230671	-0.000012
C	1.459048	-0.132316	0.000019
C	0.702178	1.051807	-0.000005
C	-0.702256	1.051763	-0.000003
H	-2.540326	-0.134912	0.000002
H	2.540323	-0.134729	0.000002
H	1.224618	2.002344	-0.000019
H	-1.224760	2.002265	-0.000024

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of the lowest energy conformation of methanol (entry 2, Table S2)

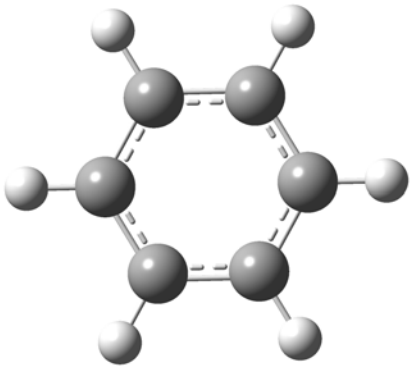


Sum of electronic and thermal Free Energies[a] = -115.675113 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
O	0.744587	0.122133	-0.000001
H	1.144787	-0.749098	0.000015
C	-0.662564	-0.020514	-0.000001
H	-1.081792	0.984558	-0.000311
H	-1.022133	-0.544994	-0.891349
H	-1.022177	-0.54445	0.891655

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

"Computed energy and geometry of benzene (entry 3, Table S2)

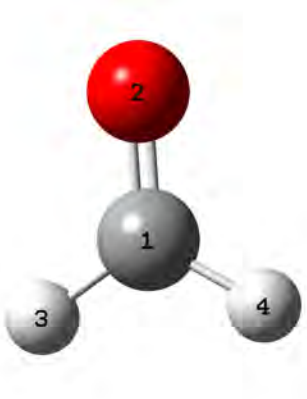


Sum of electronic and thermal Free Energies[a] = -232.124771 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-1.391337	-0.031931	0.000000
C	-0.667949	-1.220979	0.000009
C	0.723285	-1.188838	0.000001
C	1.391335	0.031992	0.000002
C	0.668002	1.220950	0.000001
C	-0.723336	1.188808	-0.000005
H	-2.474672	-0.056246	-0.000007
H	-1.188429	-2.171454	-0.000018
H	1.286545	-2.114684	-0.000021
H	2.474673	0.056165	-0.000012
H	1.188364	2.171490	0.000009
H	-1.286478	2.114725	0.000000

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of formaldehyde (entry 4, Table S2)



Sum of electronic and thermal Free Energies[a] = -114.481632 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.525528	-0.000001	0.000003
O	0.670999	-0.000006	-0.000009
H	-1.107368	0.939502	0.000007
H	-1.107461	-0.939446	0.000047

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

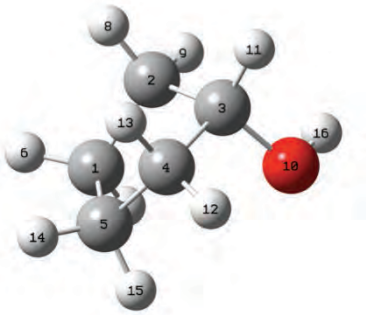
Computed energy and geometry for the benzyne + methanol TS (17‡, entry 9, Table S2)

Sum of electronic and thermal Free Energies[a] = -346.472271 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.088381	0.488354	0.000067
C	-0.061082	-0.787721	-0.00013
H	0.780258	2.511681	0.000416
C	0.909007	1.43811	0.000257
C	1.18545	-1.425138	-0.000168
C	2.295661	-0.577068	0.00002
C	2.164715	0.819529	0.000225
H	1.307387	-2.501553	-0.000336
H	3.291269	-1.007104	0.000002
H	3.053649	1.440243	0.000359
C	-2.669298	0.610833	-0.000013
H	-3.071069	1.059936	0.91288
H	-3.071048	1.060246	-0.912761
H	-1.708744	-1.077819	-0.000204
H	-1.533939	0.988119	0.000066
O	-2.683024	-0.734393	-0.000247

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cyclopentanol (entry 5, Table S2)

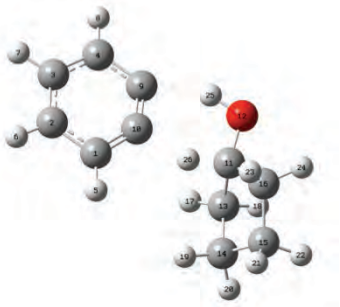


Sum of electronic and thermal Free Energies[a] = -271.607720 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-1.196007	0.818501	-0.355341
C	-0.010804	1.17988	0.561375
C	0.903364	-0.042465	0.478373
C	-0.081954	-1.203096	0.520278
C	-1.255683	-0.733792	-0.364346
H	-2.12618	1.267492	-0.004945
H	-1.016228	1.191037	-1.364419
H	-0.341957	1.300752	1.597314
H	0.495238	2.103987	0.268994
O	1.559574	-0.110263	-0.784739
H	1.639844	-0.081262	1.288556
H	0.378662	-2.127796	0.171234
H	-0.407924	-1.351279	1.553419
H	-2.210107	-1.110203	0.006021
H	-1.129681	-1.107911	-1.380423
H	2.088238	0.683122	-0.899867

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry for the *o*-benzyne + cyclopentanol TS (to cyclopentanone, 18a‡, entry 10, Table S2)



Sum of electronic and thermal Free Energies[a] = -502.405800 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.631431	1.397483	0.282804
C	3.026515	1.372344	0.160778
C	3.723053	0.174162	-0.057574
C	3.067404	-1.055806	-0.163177
H	1.069112	2.305196	0.454685
H	3.574875	2.304287	0.239597
H	4.80346	0.208392	-0.147846
H	3.624595	-1.96912	-0.335281
C	1.672549	-1.010608	-0.039614
C	1.129298	0.12133	0.16237
C	-1.35903	-0.661269	0.046777
O	-0.923976	-1.950231	0.037654
C	-1.919654	-0.096531	-1.256505
C	-2.600867	1.187202	-0.785372
C	-3.287818	0.768112	0.531265
C	-2.386848	-0.331121	1.140785
H	-1.145402	0.047383	-2.012745
H	-2.653951	-0.81	-1.646299
H	-1.841915	1.95266	-0.589121
H	-3.300772	1.60062	-1.512219
H	-3.437682	1.610997	1.206592
H	-4.274165	0.355341	0.307612
H	-1.896844	-0.017793	2.064101
H	-2.943384	-1.243004	1.364913
H	0.066105	-1.956799	-0.106218
H	-0.428423	0.021896	0.275778

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[b] Atomic Units = Hartrees

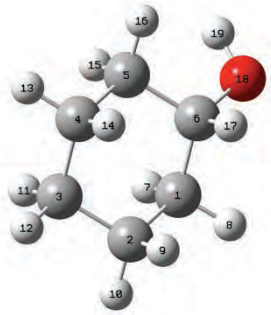
Computed energy and geometry for the *o*-benzyne + cyclopentanol TS (to 1-hydroxycyclopentene, 18b‡, entry 11, Table S2)

Sum of electronic and thermal Free Energies[a] = -502.396514 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.984986	-0.283662	0.013318
C	-1.257006	0.868459	-0.508671
C	-2.5835	1.31195	-0.51164
C	-3.531851	0.457871	0.055534
C	-3.170343	-0.782158	0.600733
C	-1.841013	-1.206749	0.594927
H	-2.89173	2.26524	-0.928028
H	-4.575339	0.756222	0.075478
H	-3.931841	-1.422426	1.031339
H	-1.53806	-2.162194	1.005732
C	1.66155	0.78438	-0.912202
C	1.526934	-0.619452	-0.452329
C	2.438076	1.504894	0.205885
C	2.259249	0.596874	1.435944
C	2.293152	-0.81272	0.837254
H	2.111263	0.860321	-1.903685
H	3.498929	1.562537	-0.054946
H	2.077717	2.519909	0.376858
H	3.02162	0.754222	2.199054
H	1.281113	0.777185	1.891484
H	3.317889	-1.103865	0.575697
H	1.869935	-1.590262	1.474688
O	1.600104	-1.66491	-1.337836
H	1.186355	-1.408361	-2.168281
H	0.299342	-0.620105	-0.02803
H	0.610399	1.212737	-0.997191

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cyclohexanol (12-hh, entry 6, Table S2)

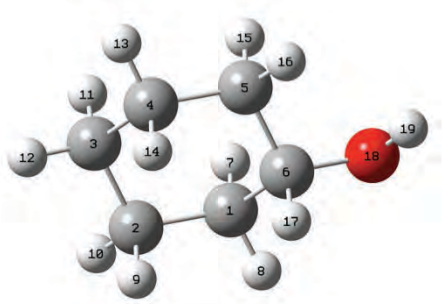


Sum of electronic and thermal Free Energies[a] = -310.891758 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.321841	-1.255719	-0.185760
C	-1.154028	-1.259381	0.221706
C	-1.866463	0.000038	-0.275496
C	-1.153963	1.259419	0.221705
C	0.321908	1.255679	-0.185757
C	1.032547	-0.000043	0.305844
H	0.410726	-1.280631	-1.278215
H	0.838794	-2.139146	0.198497
H	-1.229245	-1.305289	1.315463
H	-1.645671	-2.155906	-0.164195
H	-1.874229	0.000041	-1.371991
H	-2.910073	0.000067	0.050517
H	-1.645550	2.155969	-0.164210
H	-1.229187	1.305343	1.315460
H	0.410805	1.280602	-1.278208
H	0.838902	2.139081	0.198517
H	1.030032	-0.000045	1.405206
O	2.376079	-0.000010	-0.175456
H	2.985016	0.000040	0.563348

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cyclohexanol (12-dh, entry 7, Table S2)

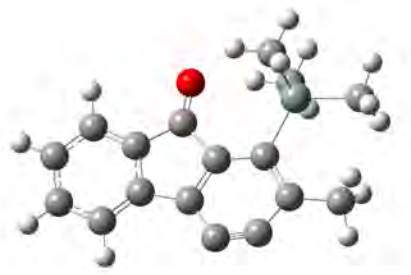


Sum of electronic and thermal Free Energies[a] = -310.895303 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.321841	-1.255719	-0.185760
C	-1.154028	-1.259381	0.221706
C	-1.866463	0.000038	-0.275496
C	-1.153963	1.259419	0.221705
C	0.321908	1.255679	-0.185757
C	1.032547	-0.000043	0.305844
H	0.410726	-1.280631	-1.278215
H	0.838794	-2.139146	0.198497
H	-1.229245	-1.305289	1.315463
H	-1.645671	-2.155906	-0.164195
H	-1.874229	0.000041	-1.371991
H	-2.910073	0.000067	0.050517
H	-1.645550	2.155969	-0.164210
H	-1.229187	1.305343	1.315460
H	0.410805	1.280602	-1.278208
H	0.838902	2.139081	0.198517
^{2}H	1.030032	-0.000045	1.405206
O	2.376079	-0.000010	-0.175456
H	2.985016	0.000040	0.563348

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry of fluorynone (S4, entry 8, Table S2)



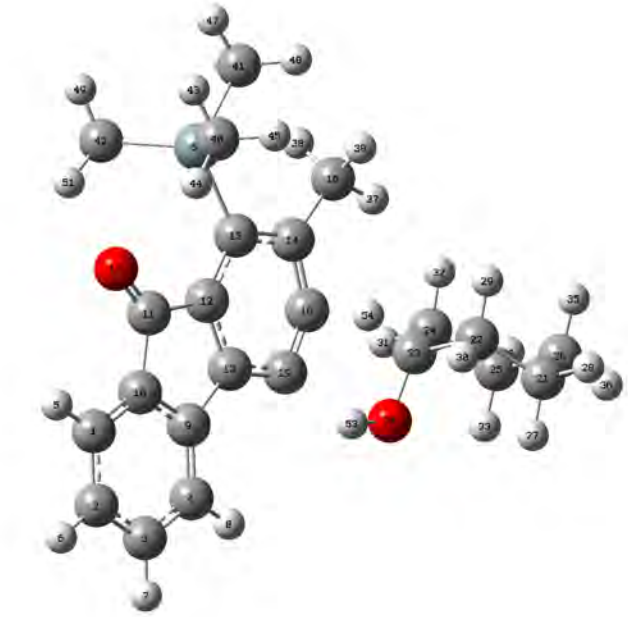
"Sum of electronic and thermal Free Energies[a] = -1021.720925 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-3.376586	-1.568926	0.000097
C	-4.662063	-1.019773	-0.000056
C	-4.840752	0.361839	-0.000211
C	-3.749231	1.236231	-0.000224
H	-3.214349	-2.640635	0.000236
H	-5.527599	-1.670916	-0.000050
H	-5.845969	0.766727	-0.000320
H	-3.892029	2.310480	-0.000332
C	-0.837833	-1.008104	0.000234
C	-2.304416	-0.699238	0.000066
C	-2.479968	0.686666	-0.000093
C	-0.121849	0.323846	-0.000073
C	-1.146687	1.312595	-0.000082
C	-0.655318	2.601049	-0.000016
C	0.575819	2.780441	0.000059
C	1.688362	1.973070	0.000020
C	1.261215	0.600346	-0.000126
C	3.100969	2.487509	0.000205
O	-0.355483	-2.113049	0.000702
C	2.288681	-1.856895	-1.587161
C	4.322963	-0.374847	-0.000942
C	2.289512	-1.855642	1.587784
H	3.647751	2.152402	0.881594
H	3.647737	2.152968	-0.881414
H	3.089526	3.576133	0.000552
H	2.976890	-2.707580	-1.581617
H	1.279030	-2.238808	-1.723083
H	2.548916	-1.228829	-2.443826

H	4.880949	-1.317754	-0.001166
H	4.632825	0.178075	-0.888607
H	4.633637	0.178116	0.886409
H	2.980000	-2.704485	1.584085
H	2.547035	-1.225858	2.444011
H	1.280667	-2.239973	1.722936
Si	2.504424	-0.879762	-0.000135

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry for the fluorynone S1 + ax-cyclohexanol TS (19‡, entry 12, Table S2)



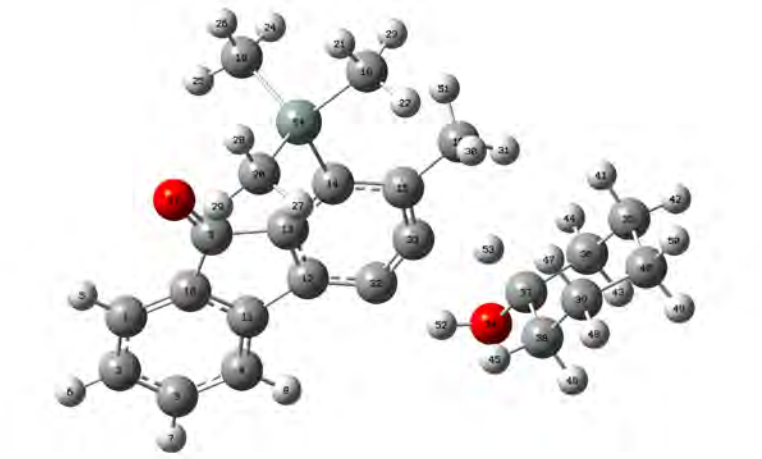
Sum of electronic and thermal Free Energies[a] = -1332.594960 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-4.097737	2.778689	-0.168398
C	-3.834679	4.149424	-0.102063
C	-2.529895	4.611449	0.060304
C	-1.451791	3.726652	0.160717
H	-5.104181	2.396143	-0.294533
H	-4.64832	4.860528	-0.177418
H	-2.348225	5.678816	0.109572
H	-0.438005	4.088807	0.286802
C	-1.717992	2.371095	0.094682
C	-3.027106	1.912008	-0.066771
C	-3.012284	0.415927	-0.106003
C	-1.567476	0.005106	0.060684
C	-0.819022	1.199584	0.167018
C	0.411895	-1.381264	0.216401
C	-1.008355	-1.288103	0.086097
C	1.239556	-2.636579	0.23652
O	-3.973759	-0.296867	-0.255445
C	0.960117	-0.12153	0.313267
C	0.565161	1.098604	0.297825
O	3.240376	1.692986	0.499561

C	5.226338	0.672781	-1.526074
C	3.841117	0.094525	-1.21438
C	3.490676	0.371519	0.243358
C	4.516677	-0.190058	1.218185
C	5.899397	0.390774	0.89218
C	6.279269	0.114562	-0.564554
H	5.180284	1.761531	-1.422913
H	5.496191	0.454054	-2.562234
H	3.841325	-0.988607	-1.386229
H	3.074532	0.536717	-1.856533
H	4.214444	0.058535	2.237317
H	4.545894	-1.281377	1.122595
H	5.873226	1.471126	1.065425
H	6.644759	-0.03096	1.571166
H	6.370443	-0.968638	-0.716063
H	7.258009	0.548294	-0.785281
H	2.293545	-2.383429	0.35843
H	0.954785	-3.294126	1.056982
H	1.132427	-3.193931	-0.694675
C	-2.969395	-2.859308	-1.732053
C	-1.264451	-4.481003	0.109785
C	-3.356931	-2.821597	1.412897
H	-3.659845	-3.7062	-1.789438
H	-3.527392	-1.951012	-1.951785
H	-2.206652	-3.002002	-2.502751
H	-0.794138	-4.636803	1.082437
H	-2.043011	-5.244751	0.00617
H	-0.52818	-4.667213	-0.672778
H	-3.974344	-3.724225	1.374243
H	-2.795703	-2.847431	2.35123
H	-4.01742	-1.956843	1.420505
Si	-2.165875	-2.827768	-0.038
H	2.264766	1.861401	0.357382
H	2.491564	-0.218154	0.453712

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry for the fluorynone S1 + eq-cyclohexanol TS (S5‡, entry 13, Table S2)



Sum of electronic and thermal Free Energies[a] = -1332.594198 A.U.[b]

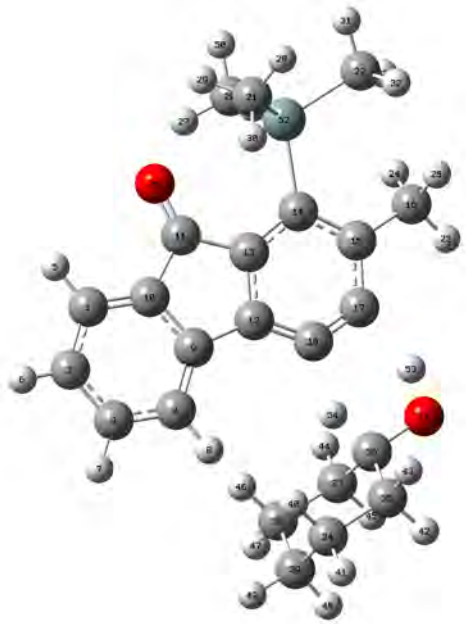
Atom Type	Cartesian Coordinates (x,y,z)		
C	0.403221	4.038002	-0.067409
C	-0.865723	4.611356	0.052050
C	-1.988880	3.803707	0.203399
C	-1.884458	2.409213	0.237280
H	1.294941	4.642961	-0.186069
H	-0.978666	5.688301	0.028803
H	-2.965889	4.263329	0.298132
H	-2.768890	1.797322	0.356581
C	-0.626643	1.843677	0.118988
C	0.497543	2.662139	-0.027043
C	1.718171	1.802222	-0.132849
C	-0.167209	0.439196	0.119199
C	1.248894	0.377644	0.024741
C	2.005898	-0.806687	-0.001826
C	1.301749	-2.046953	0.002438
C	1.957303	-3.397065	-0.128770
C	-0.088700	-1.934991	0.098064
C	-0.706523	-0.819699	0.159574
O	-2.451927	-3.133233	0.162421
C	4.533475	-0.194162	-1.684070
C	4.439109	0.543473	1.385638
C	4.798457	-2.277080	0.490582
H	1.192274	-4.156834	-0.280987

H	2.641791	-3.423620	-0.978520
H	2.525855	-3.661712	0.764398
O	2.836946	2.188034	-0.358927
H	4.101659	0.749746	-2.016714
H	5.163787	0.070000	2.052719
H	4.886482	1.443535	0.963108
H	3.584710	0.858519	1.988676
H	5.859370	-2.022875	0.588649
H	4.472867	-2.665198	1.458750
H	4.719635	-3.071918	-0.250544
C	-4.774881	-0.370214	1.115622
C	-4.087649	-1.732586	1.201680
C	-3.089977	-1.940057	0.070775
C	-3.657484	-1.656894	-1.314090
C	-4.328557	-0.285463	-1.378358
C	-5.376501	-0.130880	-0.272437
H	-4.043649	0.413980	1.342613
H	-5.550141	-0.296658	1.882400
H	-4.832193	-2.533866	1.116494
H	-3.576979	-1.869609	2.157539
H	-2.854781	-1.748957	-2.051098
H	-4.386589	-2.447507	-1.530231
H	-3.564020	0.493994	-1.276600
H	-4.787504	-0.140126	-2.359325
H	-6.179793	-0.858266	-0.440589
H	-5.833837	0.861244	-0.320177
H	5.622432	-0.090849	-1.680487
H	4.274985	-0.973447	-2.406457
Si	3.931512	-0.666241	0.028714
H	-1.446055	-2.976681	0.083286
H	-2.256942	-1.083225	0.226624

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the regioisomeric fluorynone S4 + eq-cyclohexanol TS (S6‡, entry 14, Table S2)



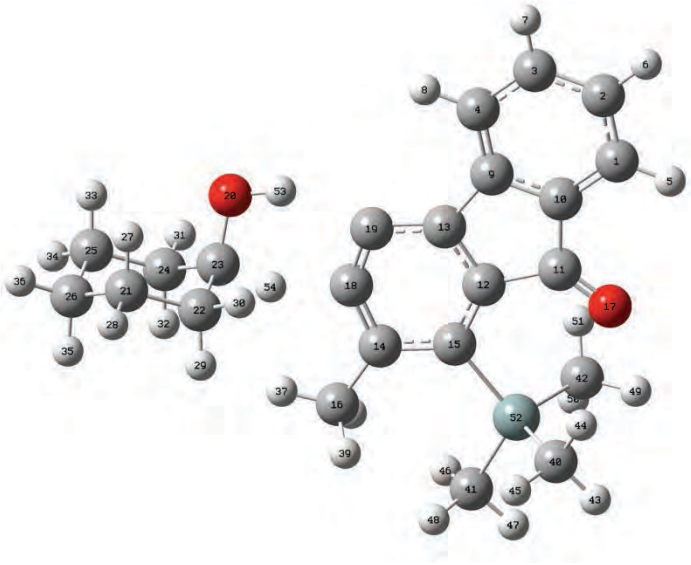
Sum of electronic and thermal Free Energies[a] = -1332.589072 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.403221	4.038002	-0.067409
C	-0.865723	4.611356	0.05205
C	-1.98888	3.803707	0.203399
C	-1.884458	2.409213	0.23728
H	1.294941	4.642961	-0.186069
H	-0.978666	5.688301	0.028803
H	-2.965889	4.263329	0.298132
H	-2.76889	1.797322	0.356581
C	-0.626643	1.843677	0.118988
C	0.497543	2.662139	-0.027043
C	1.718171	1.802222	-0.132849
C	-0.167209	0.439196	0.119199
C	1.248894	0.377644	0.024741
C	2.005898	-0.806687	-0.001826
C	1.301749	-2.046953	0.002438
C	1.957303	-3.397065	-0.12877
C	-0.0887	-1.934991	0.098064
C	-0.706523	-0.819699	0.159574

O	-2.451927	-3.133233	0.162421
C	4.533475	-0.194162	-1.68407
C	4.439109	0.543473	1.385638
C	4.798457	-2.27708	0.490582
H	1.192274	-4.156834	-0.280987
H	2.641791	-3.42362	-0.97852
H	2.525855	-3.661712	0.764398
O	2.836946	2.188034	-0.358927
H	4.101659	0.749746	-2.016714
H	5.163787	0.07	2.052719
H	4.886482	1.443535	0.963108
H	3.58471	0.858519	1.988676
H	5.85937	-2.022875	0.588649
H	4.472867	-2.665198	1.45875
H	4.719635	-3.071918	-0.250544
C	-4.774881	-0.370214	1.115622
C	-4.087649	-1.732586	1.20168
C	-3.089977	-1.940057	0.070775
C	-3.657484	-1.656894	-1.31409
C	-4.328557	-0.285463	-1.378358
C	-5.376501	-0.13088	-0.272437
H	-4.043649	0.41398	1.342613
H	-5.550141	-0.296658	1.8824
H	-4.832193	-2.533866	1.116494
H	-3.576979	-1.869609	2.157539
H	-2.854781	-1.748957	-2.051098
H	-4.386589	-2.447507	-1.530231
H	-3.56402	0.493994	-1.2766
H	-4.787504	-0.140126	-2.359325
H	-6.179793	-0.858266	-0.440589
H	-5.833837	0.861244	-0.320177
H	5.622432	-0.090849	-1.680487
H	4.274985	-0.973447	-2.406457
Si	3.931512	-0.666241	0.028714
H	-1.446055	-2.976681	0.083286
H	-2.256942	-1.083225	0.226624

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry for the fluorynone S4 + ax-cyclohexanol-1-*d* TS that was used in determining the kinetic isotope effect value (S7‡, entry 15, Table S2)



Sum of electronic and thermal Free Energies[a] = -1332.597971 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	4.098146	2.777955	0.169171
C	3.835469	4.148741	0.102407
C	2.530879	4.611057	-0.060690
C	1.452598	3.726512	-0.161433
H	5.104433	2.395179	0.295858
H	4.649251	4.859659	0.177988
H	2.349501	5.678460	-0.110286
H	0.438967	4.088898	-0.288099
C	1.718418	2.370901	-0.094971
C	3.027342	1.911525	0.067214
C	3.012129	0.415458	0.106712
C	1.567308	0.004972	-0.060599
C	0.819184	1.199593	-0.167525
C	-0.412286	-1.380926	-0.216986
C	1.007922	-1.288113	-0.086146
C	-1.240201	-2.636073	-0.236914
O	3.973354	-0.297560	0.256713
C	-0.960239	-0.121103	-0.314483
C	-0.564956	1.098973	-0.299101
O	-3.240081	1.693760	-0.499464

C	-5.225226	0.672638	1.526757
C	-3.840075	0.094668	1.214189
C	-3.490378	0.372269	-0.243605
C	-4.516774	-0.188916	-1.218218
C	-5.899404	0.391603	-0.891278
C	-6.278529	0.114661	0.565510
H	-5.179360	1.761435	1.424011
H	-5.494558	0.453468	2.562958
H	-3.840076	-0.988525	1.385644
H	-3.073235	0.536709	1.856141
H	-4.215033	0.060246	-2.237356
H	-4.545823	-1.280287	-1.123193
H	-5.873446	1.472038	-1.064037
H	-6.645035	-0.029911	-1.570102
H	-6.369407	-0.968627	0.716566
H	-7.257246	0.548096	0.786918
H	-2.294237	-2.382698	-0.357949
H	-0.956153	-3.293410	-1.057811
H	-1.132459	-3.193742	0.694007
C	2.968154	-2.860327	1.732232
C	1.263248	-4.481007	-0.111036
C	3.356474	-2.821577	-1.412563
H	3.658268	-3.707487	1.789618
H	3.526447	-1.952265	1.952201
H	2.205195	-3.002838	2.502748
H	0.792676	-4.635755	-1.083737
H	2.041641	-5.245042	-0.008307
H	0.527101	-4.667774	0.671509
H	3.973985	-3.724136	-1.373875
H	2.795493	-2.847353	-2.351047
H	4.016888	-1.956764	-1.419915
Si	2.165046	-2.828061	0.037962
H	-2.264520	1.862198	-0.356976
^{2}H	-2.491310	-0.217431	-0.454787

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees

Table S3. The computed free energies for the reactant, product, intermediate and transition state structures from which the values of $\Delta G^{‡}$ (cf. Figure 9 in the manuscript) and ΔG_{RXN} (i.e. for addition of methanol to *o*-benzyne) were determined. Calculations were performed using the SMD solvation model (methanol). Additionally, standard state corrections were applied (gas phase to 1 M solution), and the concentration of the methanol reactant was adjusted to 24.7 M. In cases where multiple conformations of a given transition state, intermediate, or reactant structure were found, only the geometry of lowest energy was used.

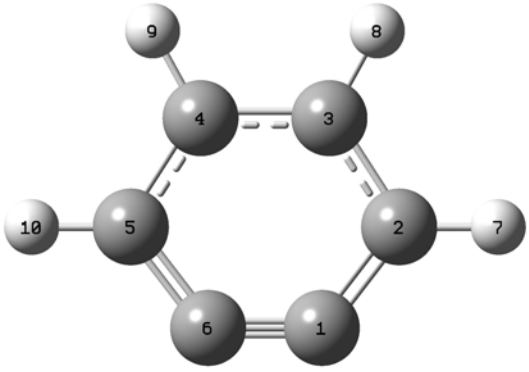
	Entry	Structure	Computed Free Energy G (kcal•mol^{-1})	Corrected Free Energy G (kcal•mol^{-1})		
	1	*o*-Benzyne (**2**)	-144845.1	-144843.2		
	2	Methanol	-72593.3	-72589.5[a]	$G_{Products}$[b] – $G_{Reactants}$[b]	ΔG_{rxn}
	3	Methanol Dimer (**34**)	-145181.7	-145179.8	(2 x G2) – G3	0.8
Reactant Product and Intermediate Structures	4	Zwitterion•Methanol (**38**)	-290028.6	-290026.7	G4 – (G1 + G3)	-3.7
	5	Zwitterion (**39**)	-217434.3	-217432.4	G5 + G2 – (G1 + G3)	1.0
	6	Anisole (**40**)	-217506.8	-217504.9	G6 + G2 – (G1 + G3)	-71.4
	7	Anisole•Methanol (**40•MeOH**)	-290094.3	-290092.4	G7 – (G1 + G3)	-69.4
					G_{TS}[b] – $G_{Reactants}$[b]	$\Delta G^{‡}$
	8	**2** + Methanol to Intermediate **39** (**37‡**)	-217427.1	-217425.2	G8 + G2 – (G1 + G3)	8.3
	9	1,3-Hydrogen Shift from Intermediate **39** (**41‡**)	-217430.2	-217428.3	G9 + G2 – (G1 + G3)	5.2
	10	**2** + Methanol Dimer to Intermediate **38** (**36‡**)	-290017.6	-290015.7	G10 – (G1 + G3)	7.3
	11	Rearrangement of **38** to **40•MeOH** (**42‡**)	-290028.3	-290026.4	G11 – (G1 + G3)	-3.4
Transition State Structures	12	Concerted Addition of **2** + Methanol Dimer to Product **40•MeOH** (**35‡**)	-290015.2	-290013.3	G12 – (G1 + G3)	9.7
					G_{TS-1}[b] – G_{TS-2}[b]	$\Delta\Delta G^{‡}$
	13	**2** + Methanol to Intermediate **39** (**37‡**) without Solvation Modeling	-217414.6	–	G13 – G9 (of Table S2)	-0.0
	14	**2** + Methanol to Intermediate **39** (**37‡**) with M06-2x/aug-cc-pVTZ and $CHCl_3$ Solvation (IEFPCM)	-217443.4	-217441.5	G14 – G15	-1.0
	15	**2** + Methanol via 2H-Transfer (**17‡**) with M06-2x/aug-cc-pVTZ and $CHCl_3$ Solvation (IEFPCM)	-217442.4	-217440.5		

[a] The concentration of methanol was also adjusted to 24.7 M (neat concentration)

[b] G# represents the value from the column "Corrected Free Energy" for Entry #

Energies and geometries for all of the entries in Table S3 (Pages S57 – S71)

Computed energy and geometry of *o*-benzyne (2, SMD-MeOH, entry 1, Table S3)

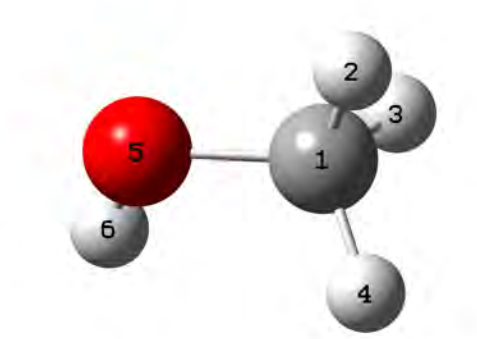


"Sum of electronic and thermal Free Energies[a] = -230.825373 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.619852	-1.229395	-0.000097
C	1.46399	-0.1319	0.000151
C	0.702906	1.050096	-0.000035
C	-0.702924	1.050086	-0.000036
C	-1.463992	-0.131923	0.000156
C	-0.619827	-1.229392	-0.000096
H	2.54578	-0.133741	0.000058
H	1.225887	2.00106	-0.000175
H	-1.225922	2.001041	-0.000187
H	-2.545781	-0.133784	0.00005

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of methanol (SMD-MeOH, entry 2, Table S3)

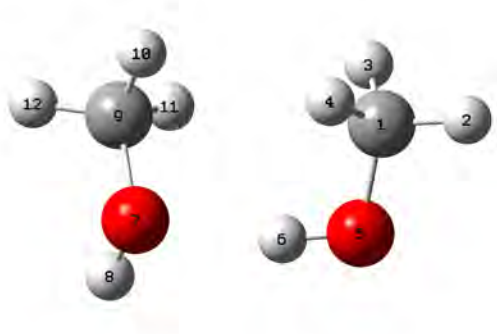


"Sum of electronic and thermal Free Energies[a] = -115.684827 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.668899	-0.01991	0.000007
H	1.093991	0.9835	-0.001203
H	1.013727	-0.551469	-0.891174
H	1.013919	-0.549492	0.892295
O	-0.748958	0.123931	0.00001
H	-1.143363	-0.754526	-0.000037

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of methanol dimer (34, SMD-MeOH, entry 3, Table S3)



"Sum of electronic and thermal Free Energies[a] = -231.361766 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.798512	0.590066	0.133295
H	2.883777	0.664265	0.053223
H	1.35038	1.336365	-0.530643
H	1.511811	0.812352	1.165999
O	1.426132	-0.730513	-0.238258
H	0.472062	-0.823927	-0.073228
O	-1.319354	-0.645029	0.294518
H	-1.810679	-1.318622	-0.189578
C	-1.749204	0.641566	-0.151986
H	-1.240118	1.383557	0.462173
H	-1.489408	0.802485	-1.20173
H	-2.827898	0.758068	-0.024143

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

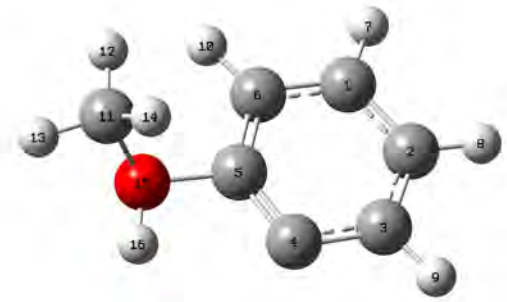
Computed energy and geometry of the intermediate zwitterion complexed with methanol (38, SMD-MeOH, entry 4, Table S3)

"Sum of electronic and thermal Free Energies[a] = -462.190021 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	2.626184	0.187325	-0.84804
C	2.84433	-0.828607	0.083908
C	1.815142	-1.234227	0.937519
C	0.519111	-0.664627	0.939847
C	0.411076	0.321907	-0.016936
C	1.370773	0.782718	-0.910008
H	3.415858	0.506984	-1.518561
H	3.819355	-1.303792	0.140428
H	2.046439	-2.035433	1.638927
H	1.146933	1.570642	-1.622103
C	-1.007459	2.199818	0.664366
H	-0.279852	2.92281	0.301783
H	-2.021575	2.566077	0.518464
H	-0.825049	1.94707	1.709226
O	-0.877136	1.003471	-0.14491
H	-1.69234	0.309815	0.065324
O	-2.732088	-0.517489	0.244782
H	-2.604953	-0.979545	1.0862
C	-2.835183	-1.478893	-0.824068
H	-2.919829	-0.910194	-1.74801
H	-1.946156	-2.110715	-0.852307
H	-3.72888	-2.08406	-0.677867

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of the zwitterion intermediate (39, SMD-MeOH, entry 5, Table S3)

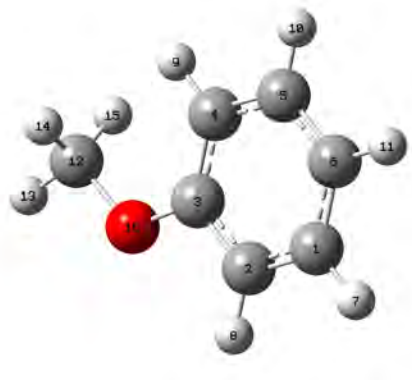


"Sum of electronic and thermal Free Energies[a] = -346.503683 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.514088	1.260609	-0.005828
C	2.289716	0.115475	0.187594
C	1.703304	-1.151945	0.150058
C	0.321212	-1.364141	-0.066067
C	-0.330165	-0.17478	-0.23573
C	0.148156	1.125407	-0.23429
H	1.964375	2.246328	0.011629
H	3.356144	0.217417	0.364405
H	2.360096	-2.007199	0.300858
H	-0.490096	1.985143	-0.406695
C	-2.687865	0.220756	0.544209
H	-2.541487	1.295914	0.565385
H	-3.696665	-0.032518	0.23062
H	-2.422078	-0.247273	1.490341
O	-1.792977	-0.29826	-0.496175
H	-1.93714	-1.260015	-0.62682

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of anisole (40, SMD-MeOH, entry 6, Table S3)



"Sum of electronic and thermal Free Energies[a] = -346.619102 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.85251	-0.991177	0.00981
C	0.501621	-1.302718	-0.002009
C	-0.450326	-0.278315	-0.013414
C	-0.044116	1.055389	-0.014579
C	1.320211	1.351163	-0.003227
C	2.272488	0.340355	0.009413
H	2.583083	-1.792489	0.020853
H	0.160697	-2.332036	-0.000069
H	-0.766175	1.861336	-0.024733
H	1.630966	2.390094	-0.004426
H	3.328791	0.58152	0.019433
C	-2.757819	0.327928	0.024768
H	-3.708371	-0.201452	0.042597
H	-2.6592	0.933781	0.929319
H	-2.714035	0.968546	-0.860079
O	-1.752897	-0.678131	-0.023433

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of anisole complexed with methanol (40•MeOH, SMD-MeOH, entry 7, Table S3)

"Sum of electronic and thermal Free Energies[a] = -462.294760 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-2.857576	0.5686	-0.221009
C	-3.064102	-0.798272	-0.086411
C	-1.972637	-1.633041	0.159766
C	-0.694816	-1.105459	0.269081
C	-0.499103	0.271192	0.131988
C	-1.578361	1.116791	-0.11435
H	-3.69618	1.228568	-0.413038
H	-4.061655	-1.212451	-0.171502
H	-2.118479	-2.701988	0.267394
H	-1.441138	2.184521	-0.223228
C	1.051626	2.096697	0.122265
H	0.531209	2.660434	0.900089
H	2.126795	2.212337	0.246913
H	0.755617	2.456836	-0.866002
O	0.792197	0.701451	0.253412
H	2.091734	-0.31178	-0.688824
O	2.906982	-0.802065	-0.87056
H	0.163918	-1.739804	0.461123
C	3.677316	-0.78398	0.325347
H	3.956895	0.23606	0.606783
H	3.13655	-1.247075	1.156584
H	4.587227	-1.355927	0.140839

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of TS for methanol adding to *o*-benzyne (37‡, SMD-MeOH, entry 8, Table S3)

"Sum of electronic and thermal Free Energies[a] = -346.492191 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.935835	1.044163	0.037483
C	2.431584	-0.26912	0.003583
C	1.579032	-1.378153	-0.032931
C	0.18845	-1.125668	-0.037609
C	-0.100868	0.104999	-0.005172
C	0.555136	1.302339	0.036794
H	2.623797	1.882217	0.066701
H	3.50565	-0.423471	0.007252
H	1.994474	-2.380947	-0.055773
H	0.125711	2.294538	0.066
C	-3.003745	-0.535339	0.086756
H	-2.886269	-0.912244	1.101954
H	-4.056989	-0.314576	-0.098643
H	-2.655556	-1.291635	-0.621254
O	-2.226404	0.656201	-0.013446
H	-2.352129	1.037187	-0.892103

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

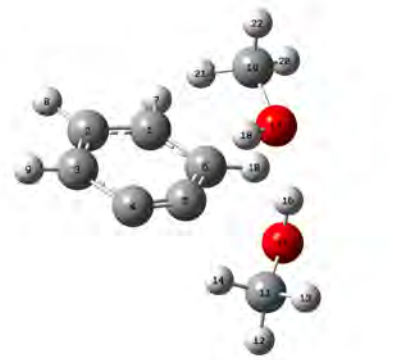
Computed energy and geometry of TS for 1,3-hydrogen shift from intermediate 39 (41‡, SMD-MeOH, entry 9, Table S3)

"Sum of electronic and thermal Free Energies[a] = -346.497103 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.594634	1.213883	0.026802
C	2.274092	0.004062	0.17988
C	1.599225	-1.223508	0.122383
C	0.213613	-1.264926	-0.08539
C	-0.359251	-0.023493	-0.235315
C	0.213878	1.227693	-0.195968
H	2.136804	2.151263	0.075881
H	3.345895	0.020825	0.350272
H	2.17567	-2.135948	0.2517
H	-0.343508	2.147868	-0.326619
C	-2.714217	0.194132	0.483907
H	-2.70925	1.279385	0.414016
H	-3.682041	-0.207981	0.196912
H	-2.420571	-0.13995	1.479678
O	-1.756073	-0.312607	-0.484735
H	-1.38625	-1.381667	-0.341753

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of TS for addition of methanol dimer to *o*-benzyne (36‡, SMD-MeOH, entry 10, Table S3)



"Sum of electronic and thermal Free Energies[a] = -462.172519 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-2.258428	-0.14238	1.032719
C	-2.772757	-0.015517	-0.26803
C	-2.005724	0.498523	-1.320954
C	-0.679965	0.870399	-1.01128
C	-0.35953	0.702953	0.196254
C	-0.939958	0.235673	1.340702
H	-2.884543	-0.540024	1.824363
H	-3.794858	-0.32617	-0.458798
H	-2.431656	0.586558	-2.315348
H	-0.501268	0.153661	2.325873
C	2.453219	1.740611	-0.235874
H	2.319746	2.785058	0.04665
H	3.521948	1.518141	-0.296058
H	1.995485	1.578527	-1.217943
O	1.828162	0.939247	0.75741
H	1.953446	0.005249	0.496406
O	1.956346	-1.566865	-0.367572
H	2.024028	-1.4404	-1.321068
C	0.859483	-2.440592	-0.095889
H	0.759227	-2.504057	0.987275
H	-0.07087	-2.054356	-0.521509
H	1.055214	-3.439271	-0.494428

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

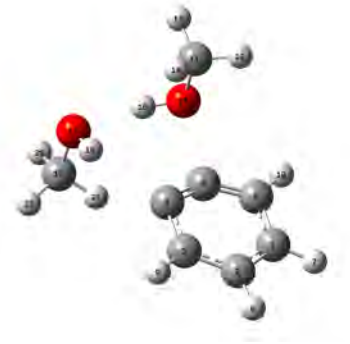
Computed energy and geometry of TS for 1,6-hydrogen shift from intermediate 38 (42‡, SMD-MeOH, entry 11, Table S3)

"Sum of electronic and thermal Free Energies[a] = -462.189450 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-2.618989	0.186784	0.843874
C	-2.830818	-0.831461	-0.086973
C	-1.797917	-1.234366	-0.93739
C	-0.503977	-0.660041	-0.937229
C	-0.401984	0.327944	0.018847
C	-1.365864	0.786726	0.908389
H	-3.411749	0.504886	1.511485
H	-3.803874	-1.310441	-0.145349
H	-2.024451	-2.037314	-1.638353
H	-1.146916	1.576926	1.619481
C	1.012013	2.208019	-0.664393
H	0.281841	2.930564	-0.306087
H	2.024906	2.577756	-0.518874
H	0.831864	1.950435	-1.708478
O	0.883843	1.014771	0.149679
H	1.696521	0.317087	-0.061717
O	2.703328	-0.543254	-0.258022
H	2.502554	-1.024135	-1.074728
C	2.811392	-1.478787	0.833275
H	2.966427	-0.890477	1.735406
H	1.89549	-2.065223	0.920485
H	3.666881	-2.131105	0.66307

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of TS for concerted addition of methanol dimer to *o*-benzyne to form product 40•MeOH (35‡, SMD-MeOH, entry 12, Table S3)

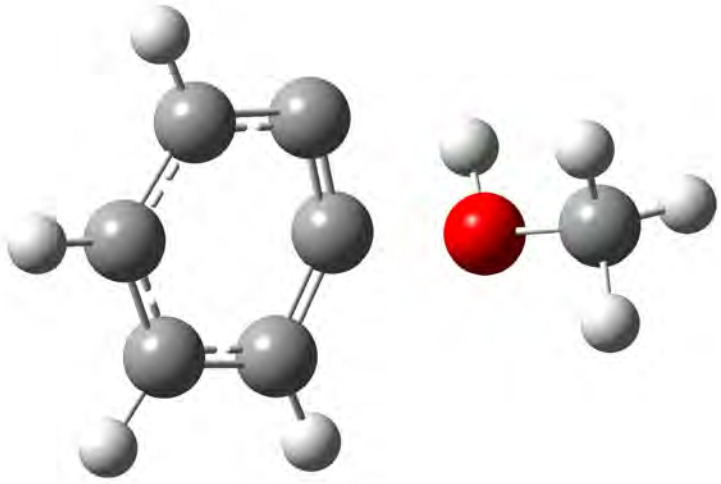


"Sum of electronic and thermal Free Energies[a] = -462.168576 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-2.737438	0.427598	0.627094
C	-2.90836	-0.705091	-0.185034
C	-1.834925	-1.311043	-0.848128
C	-0.5631	-0.723254	-0.662561
C	-0.575601	0.283585	0.096799
C	-1.473156	1.013813	0.817947
H	-3.593566	0.871229	1.123964
H	-3.904615	-1.118989	-0.300808
H	-1.996556	-2.185981	-1.469005
H	-1.291902	1.884872	1.431819
C	1.521471	2.230494	-0.782019
H	0.790479	3.036188	-0.707452
H	2.521817	2.662468	-0.872727
H	1.306329	1.634906	-1.674917
O	1.416339	1.43989	0.398535
H	1.987765	0.659393	0.277306
O	2.540675	-0.992431	-0.338976
H	1.708446	-1.090857	-0.827321
C	2.472369	-1.842498	0.80591
H	3.410561	-1.730166	1.348725
H	1.644526	-1.55624	1.462173
H	2.353047	-2.888128	0.511721

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.
[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of TS for methanol adding to *o*-benzyne (37‡, gas phase, entry 13, Table S3)



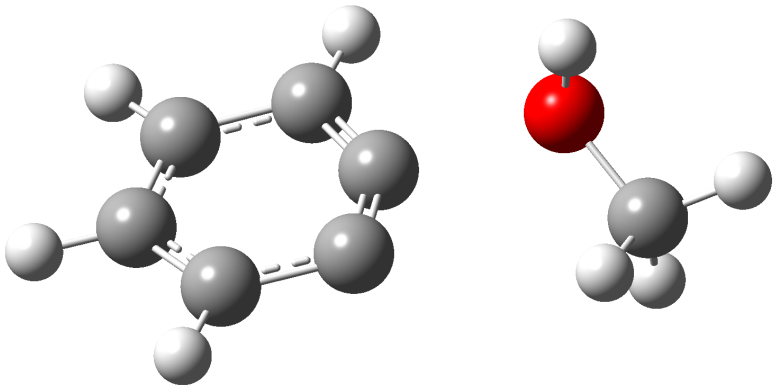
"Sum of electronic and thermal Free Energies[a] = -346.472248 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.749951	1.125983	0.14135
C	2.329541	-0.149734	0.194946
C	1.567085	-1.304335	0.007198
C	0.176587	-1.202101	-0.232186
C	-0.19656	0.032972	-0.249516
C	0.380522	1.267582	-0.102664
H	2.359474	2.010602	0.282976
H	3.394539	-0.234099	0.383521
H	2.059897	-2.271833	0.048535
H	-0.123406	2.221804	-0.170327
C	-2.752136	-0.175286	0.627094
H	-2.601686	0.606612	1.367948
H	-3.813226	-0.274372	0.399228
H	-2.336244	-1.118566	0.986315
O	-2.045365	0.24372	-0.550565
H	-2.106368	-0.460395	-1.210993

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[b] Atomic Units = Hartrees"[3]

Computed energy and geometry of TS for methanol adding to *o*-benzyne (37‡, IEFPCM-$CHCl_3$, entry 14, Table S3)[a]



"Sum of electronic and thermal Free Energies[b] = -346.518131 A.U.[c]

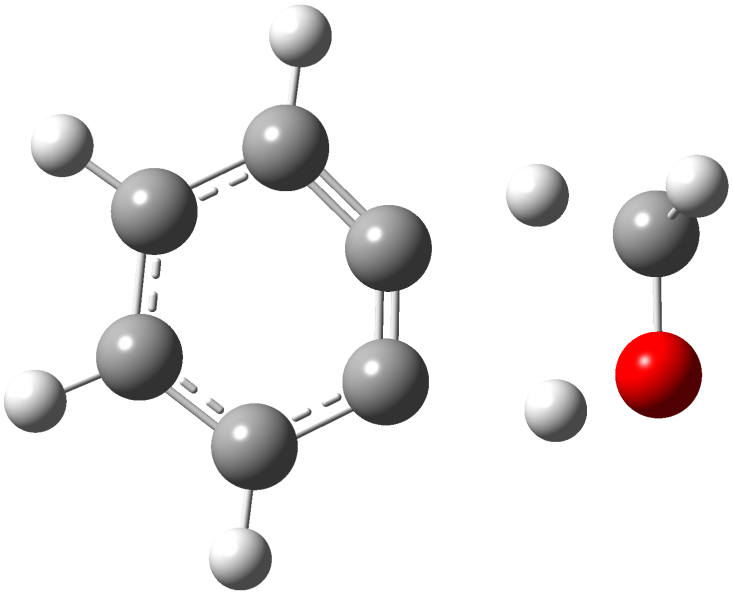
Atom Type	Cartesian Coordinates (x,y,z)		
C	1.884558	1.041872	0.126504
C	2.372313	-0.268782	0.077158
C	1.516476	-1.360175	-0.066685
C	0.127824	-1.129106	-0.16442
C	-0.156894	0.112108	-0.104824
C	0.513172	1.294082	0.031118
H	2.567373	1.872667	0.242851
H	3.439725	-0.43293	0.154909
H	1.935463	-2.35968	-0.100421
H	0.080747	2.282012	0.067923
C	-2.888733	-0.452391	0.326576
H	-2.89462	-0.287961	1.399755
H	-3.903226	-0.404589	-0.062379
H	-2.436171	-1.419805	0.106752
O	-2.098862	0.593097	-0.244942
H	-2.210681	0.579859	-1.202406

[a] The aug-cc-pVTZ basis set was used in this calculation

[b] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[c] Atomic Units = Hartrees"[3]

Computed energy and geometry for the benzyne + methanol TS (17‡, IEFPCM-$CHCl_3$, entry 15, Table S3)[a]



"Sum of electronic and thermal Free Energies[b] = -346.516574 A.U.[c]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-2.150111	0.827069	0
C	-0.891407	1.433833	0.000003
C	0.090525	0.474028	0.000008
C	0.064618	-0.801837	0.000007
C	-1.191259	-1.420815	0.000004
C	-2.291913	-0.565577	0
H	-3.031004	1.455132	-0.000003
H	-0.751058	2.503578	0.000004
H	-1.325283	-2.493845	0.000004
H	-3.288907	-0.986806	-0.000003
C	2.652066	0.613172	-0.000011
H	3.043958	1.067951	0.910885
O	2.6756	-0.734678	-0.000004
H	1.51674	0.98072	0.000009
H	1.69171	-1.076487	-0.000004
H	3.043924	1.067943	-0.910927

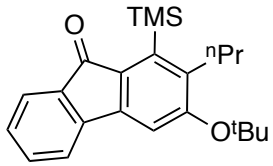
[a] The aug-cc-pVTZ basis set was used in this calculation

[b] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[c] Atomic Units = Hartrees"[3]

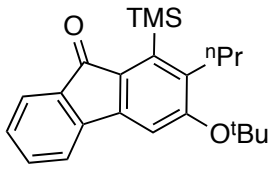
X. Copies of ^{1}H and ^{13}C NMR spectra of all new compounds

500 MHz, $CDCl_3$



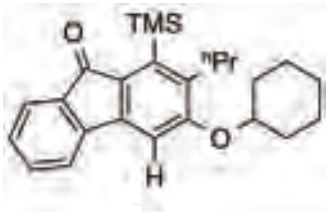
11

125 MHz, $CDCl_3$



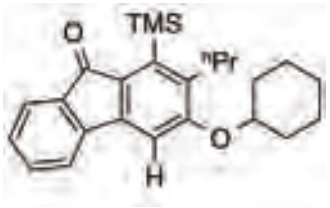
11

125 MHz, $CDCl_3$

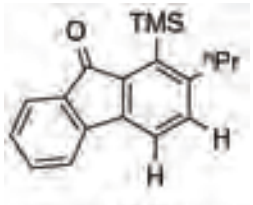


13

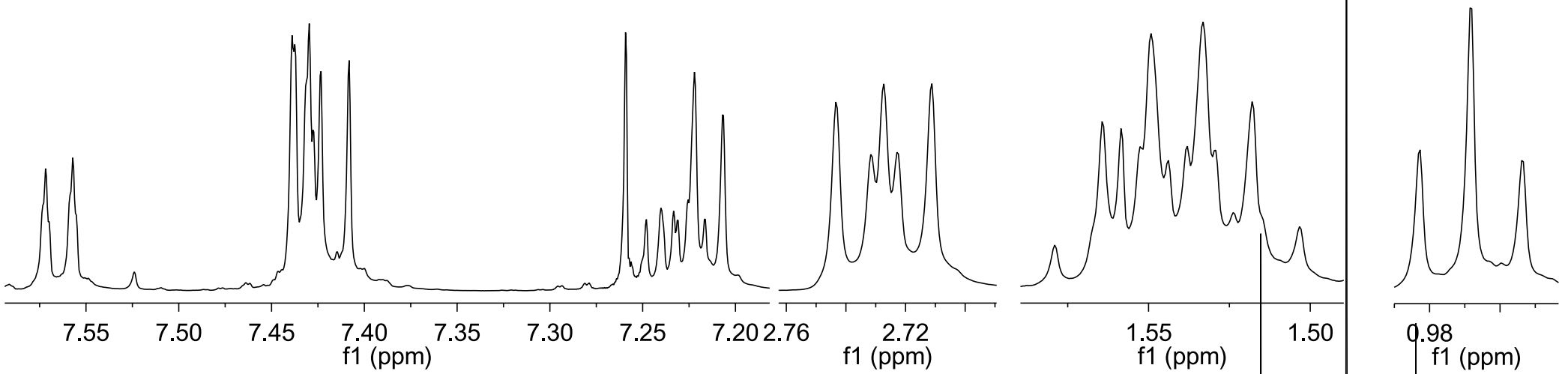
125 MHz, $CDCl_3$

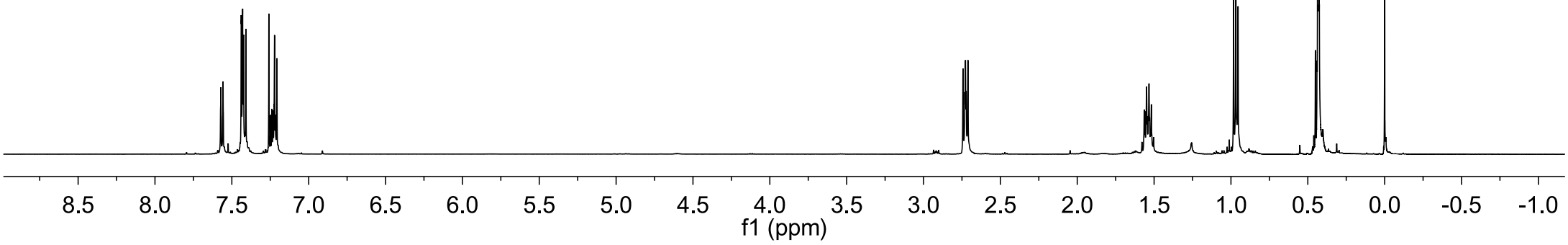


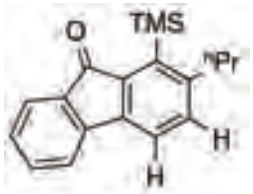
13



14-hh
($CDCl_3$, 500 MHz)

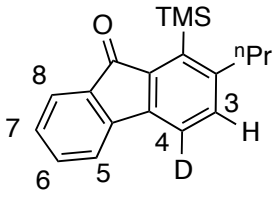




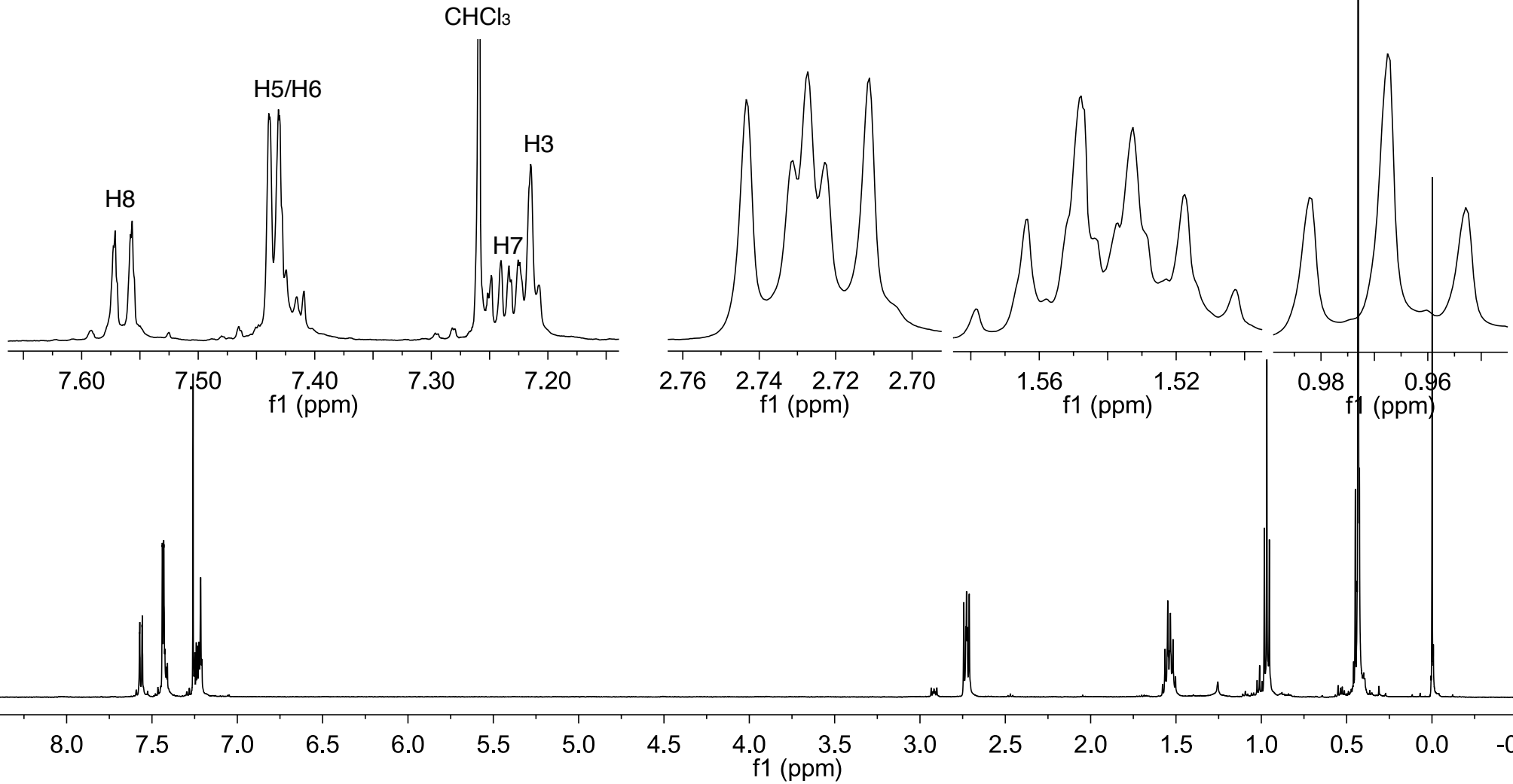


14-hh
($CDCl_3$, 125 MHz)

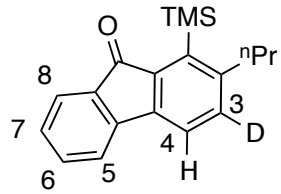
500 MHz, $CDCl_3$



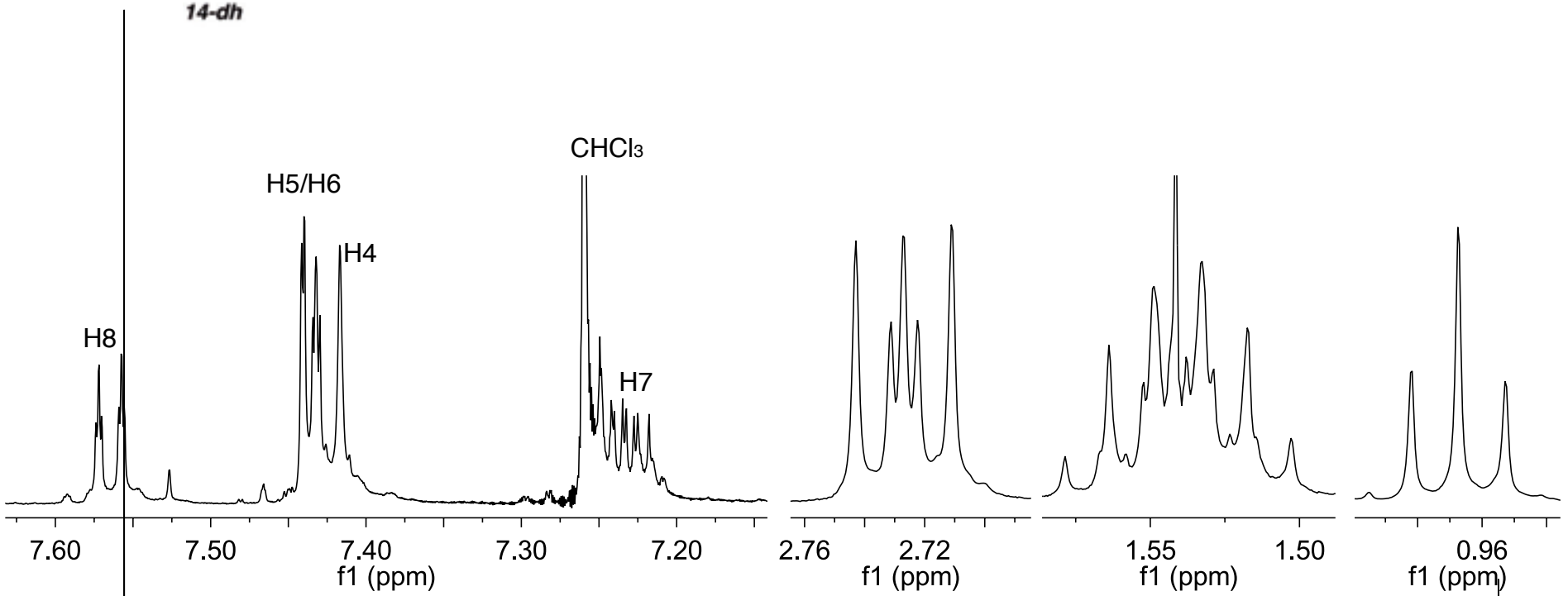
14-hd

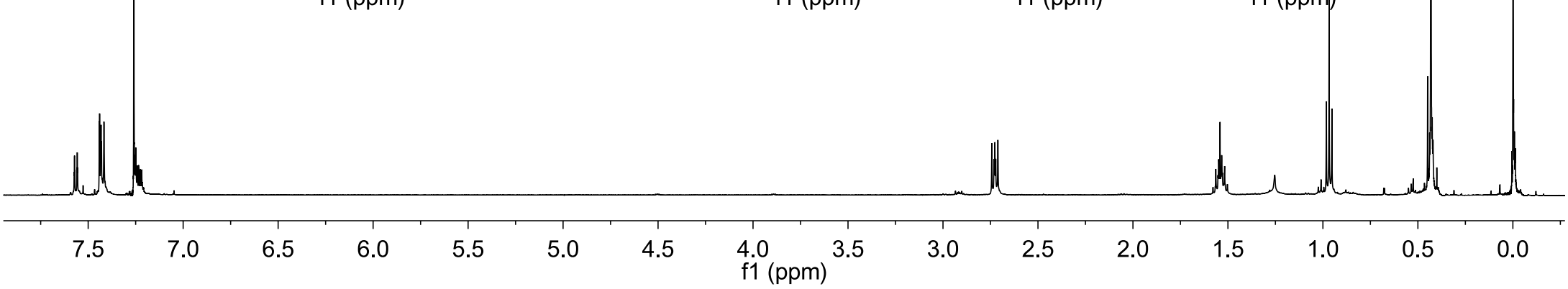


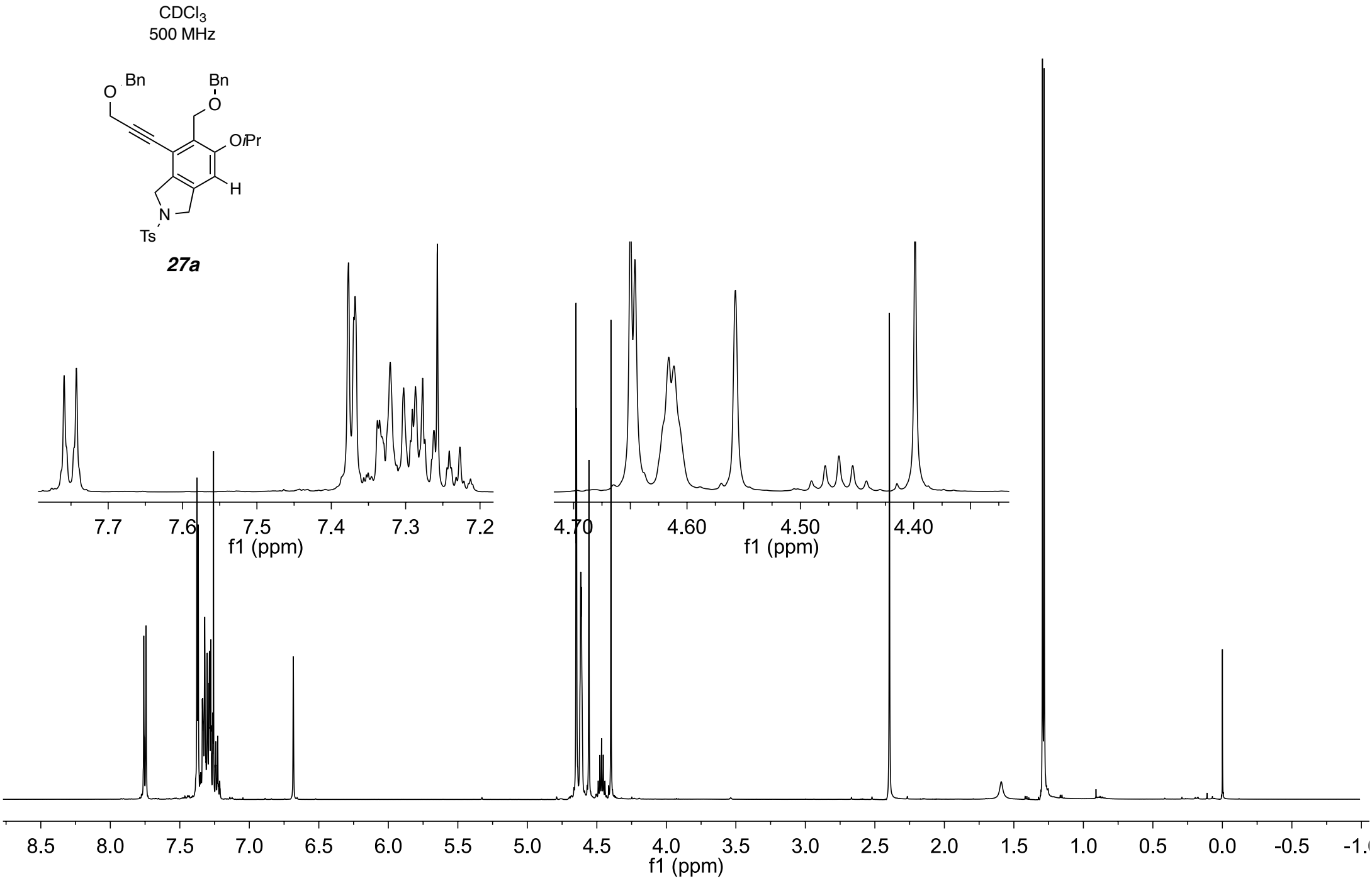
500 MHz, $CDCl_3$



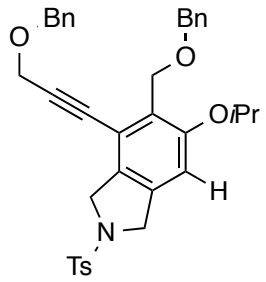
14-dh





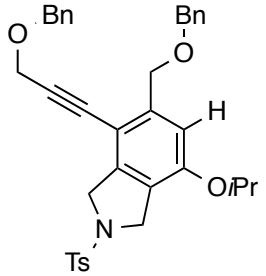

CDCl3
500 MHz
Bn
Bn
O
O
OiPr
H
N
Ts
27a
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
4.70
4.60
4.50
4.40
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

$CDCl_3$
125 MHz



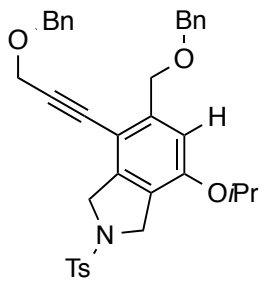
27a

$CDCl_3$
500 MHz

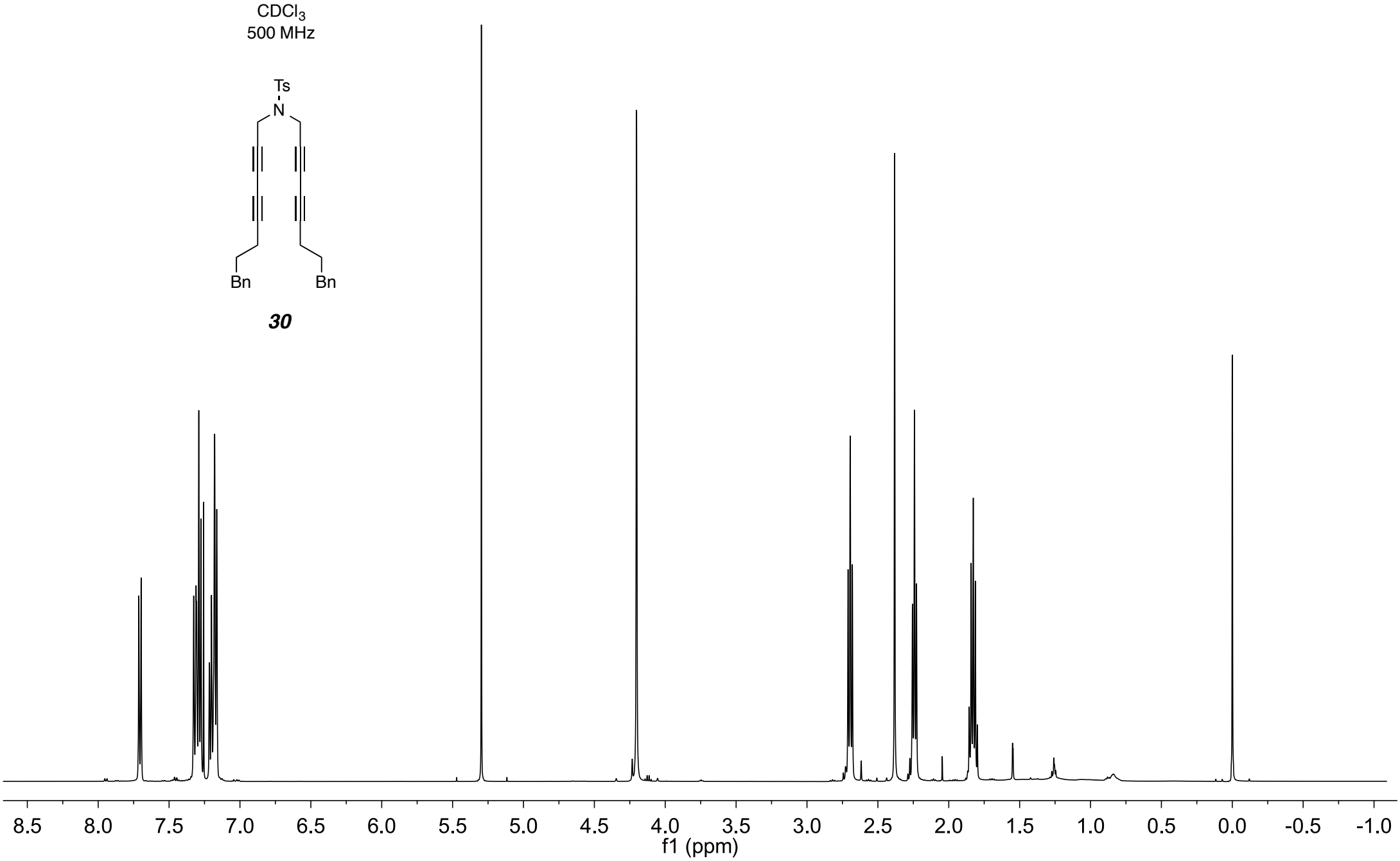


27b

$CDCl_3$
125 MHz

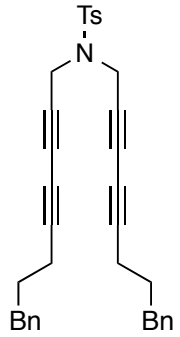


27b

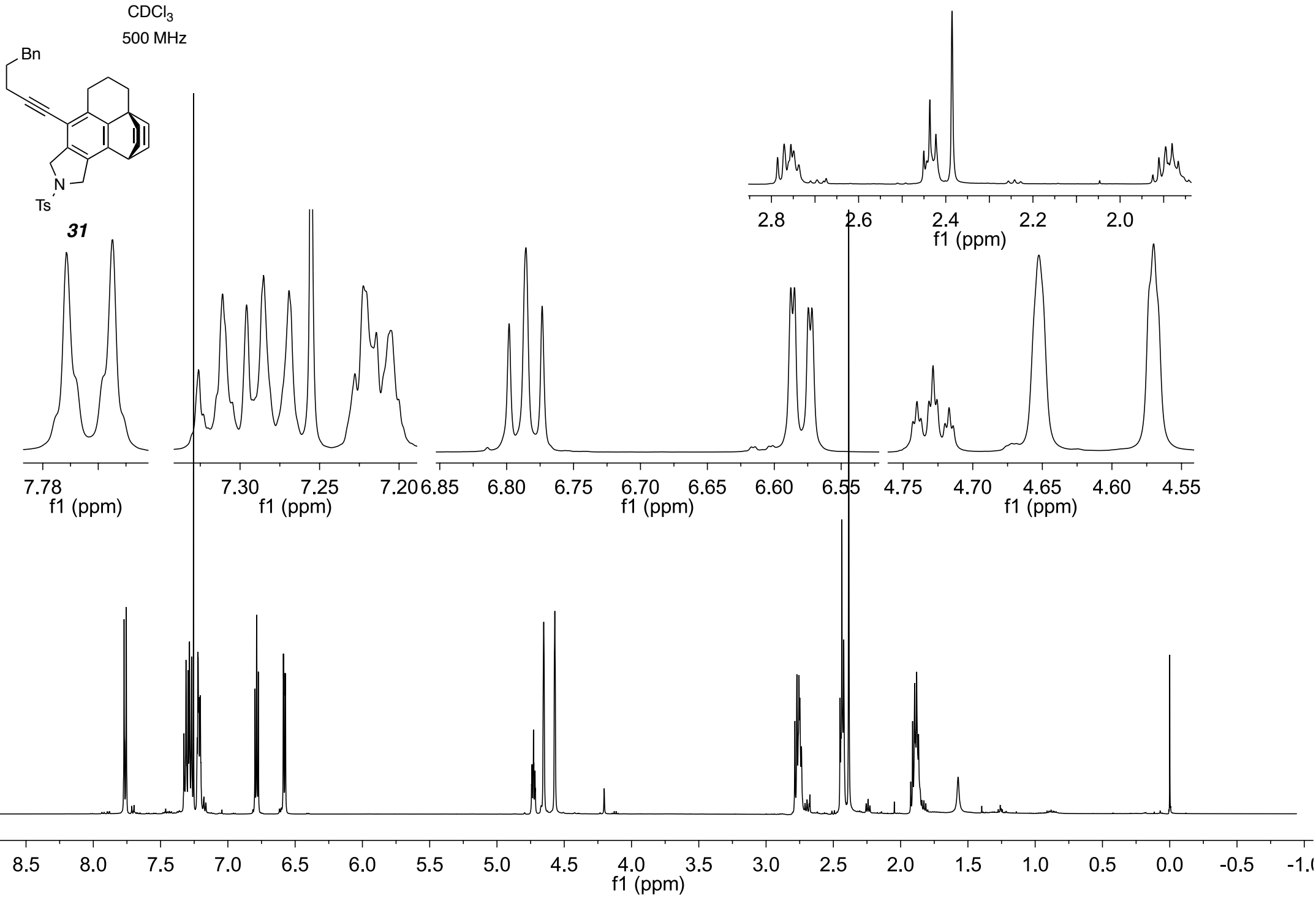

$CDCl_3$
500 MHz
Ts
N
Bn
Bn
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

30

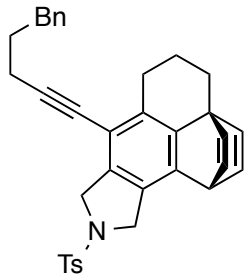
$CDCl_3$
125 MHz



30

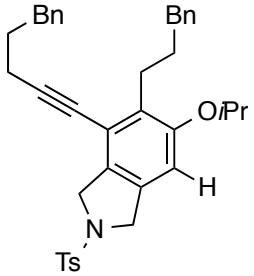

CDCl3
500 MHz
Bn
N
Ts
31
f1 (ppm)

$CDCl_3$
125 MHz

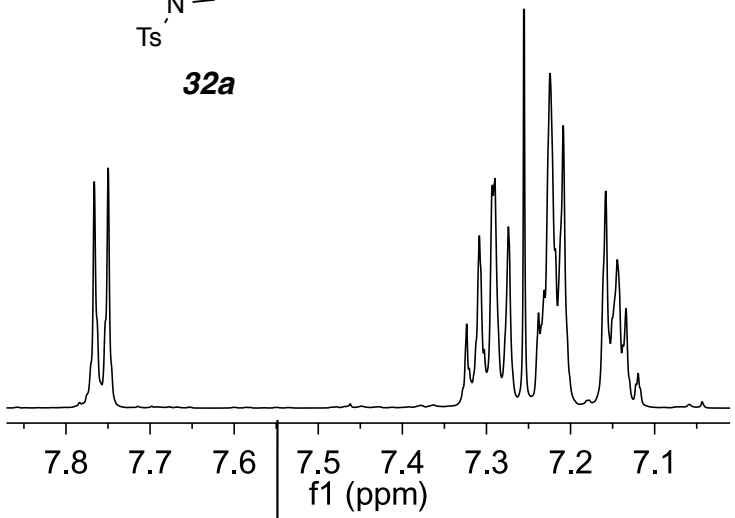


31

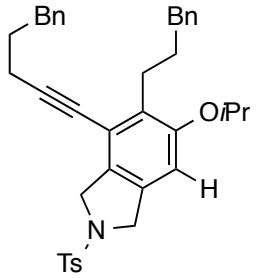
$CDCl_3$
500 MHz



32a

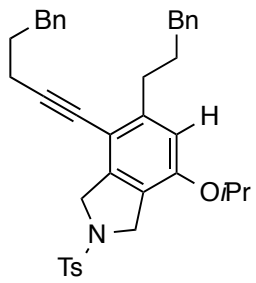


$CDCl_3$
125 MHz



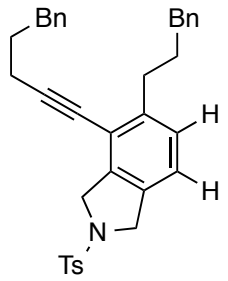
32a

$CDCl_3$
500 MHz



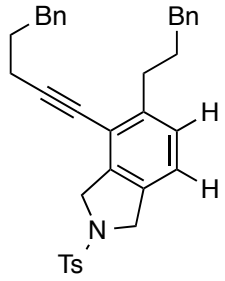
32b

$CDCl_3$
500 MHz

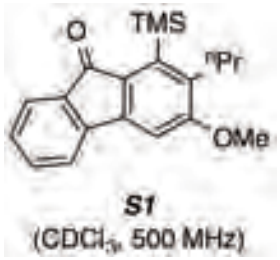


33

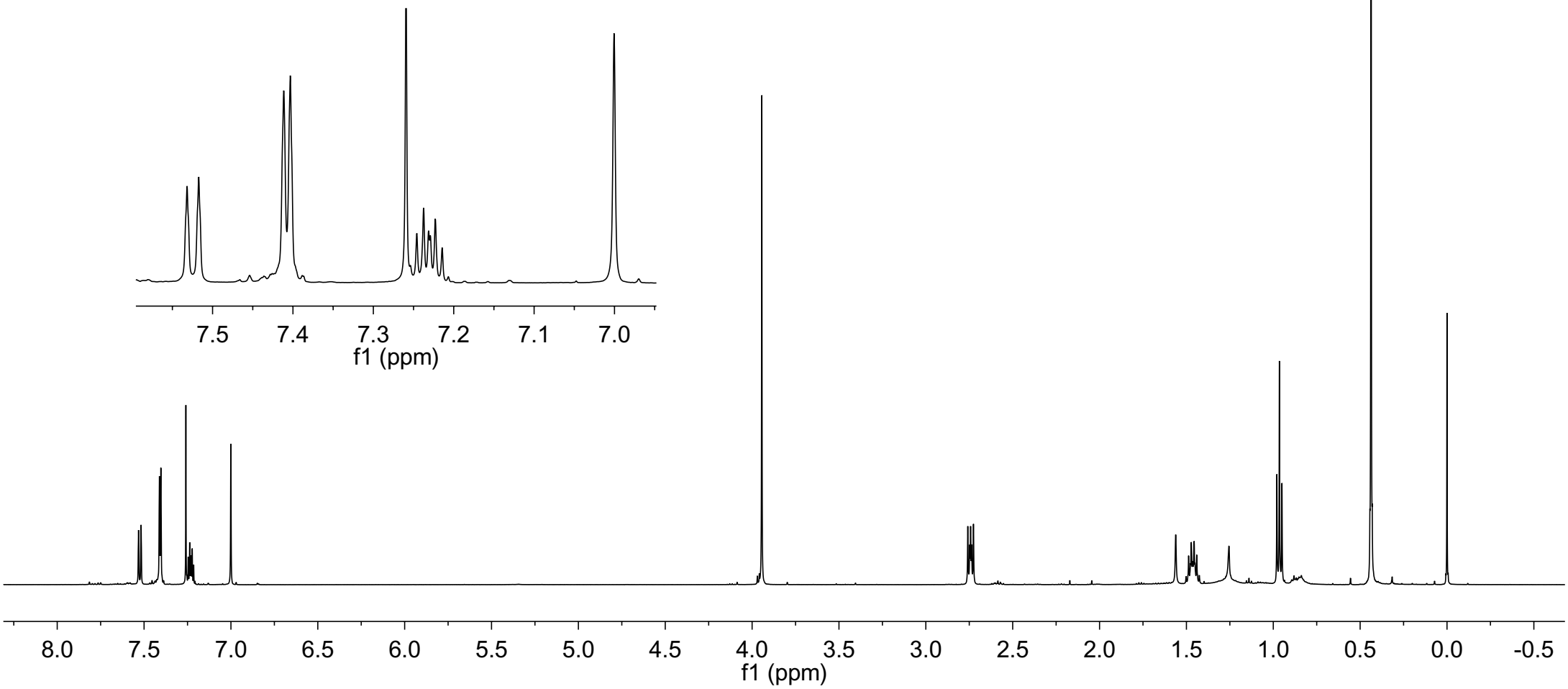
$CDCl_3$
125 MHz

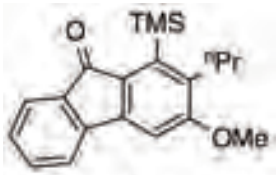


33

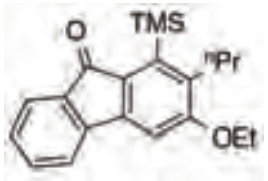


S1
($CDCl_3$, 500 MHz)

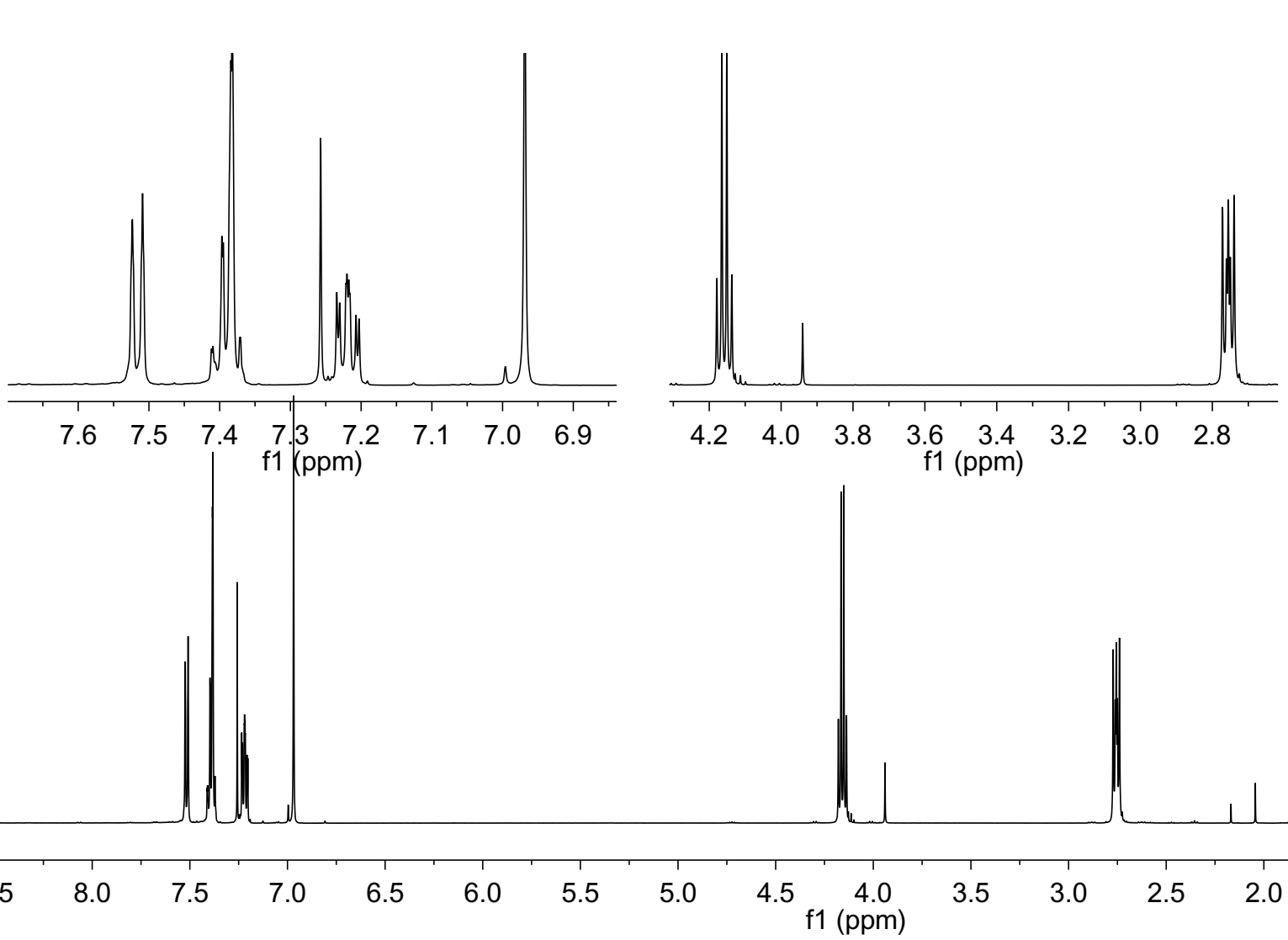


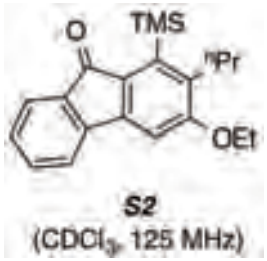


S1
($CDCl_3$, 125 MHz)

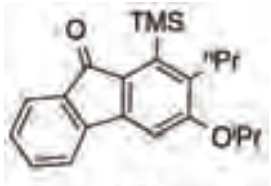


S2
($CDCl_3$, 500 MHz)

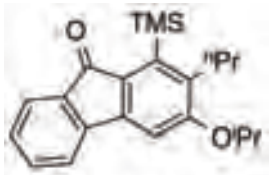




S2
($CDCl_3$, 125 MHz)



S3
($CDCl_3$, 500 MHz)



S3
($CDCl_3$, 125 MHz)

XI. References for the Supporting Information

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