Type II Anion Relay Chemistry: Conformational Constraints to Achieve Effective [1,5]-Vinyl Brook Rearrangements

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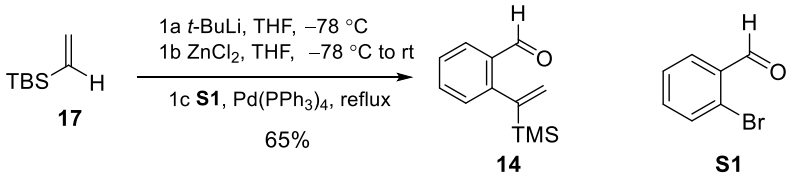
I. Materials and methods

Reactions were performed in either flame- or oven-dried glassware under a nitrogen atmosphere with anhydrous solvents, unless noted otherwise. Anhydrous diethyl ether (Et_2O) and tetrahydrofuran (THF) were obtained from a solvent purification system. Hexamethylphosphoramide (HMPA) and trimethylsilyl chloride (TMSCl) was freshly purified prior to use by distillation over calcium hydride and stored in calcium hydride under nitrogen atmosphere. Commercial lithium reagents were titrated with 2,2-diphenylacetic acid before use. All other commercially available reagents were used as received, unless otherwise noted. Reactions were magnetically stirred unless stated otherwise and monitored by thin-layer chromatography (TLC) with 0.25 mm precoated silica gel plates. Silica gel chromatography was performed utilizing ACS grade solvents and silica gel (particle size 40-63 μm). Medium pressure liquid chromatography was conducted by using a medium-pressure pump equipped with a high-pressure glass column (350 mm × 35 mm or 350 mm × 10 mm) packed with silica gel (standard grade, porosity 60 Å, particle size 32−63 μm). ^{1}H NMR spectra (500 MHz field strength) and ^{13}C NMR spectra (125 MHz field strength) were recorded on a 500 MHz spectrometer. Chemical shifts are reported relative to chloroform (δ 7.26) and benzene (δ 7.16) for ^{1}H NMR spectra and chloroform (δ 77.16) and benzene (δ 128.06) for ^{13}C spectra. The following abbreviations are used to describe multiplicities in 1H NMR spectra: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), t (triplet), td (triplet of doublets), m (multiplet), q (quartet), and app (apparent). Infrared spectra were obtained using a FT/IR plus spectrometer. High-resolution mass spectra (HRMS) were measured on a LC-TOF mass spectrometer. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Single crystal X-ray structures were determined on a detector employing graphite-monochromated Mo-Ka radiation (l=0.71073Å) at a temperature of 143(1) K.

II. Experiment Section



Preparation of phenyl linchpin **14**

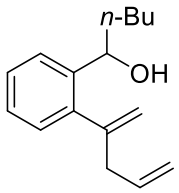
2-(1-(Trimethylsilyl)vinyl)benzaldehyde (14). To a solution of (1-bromovinyl)trimethylsilane (**17**) (1.94 g, 10.8 mmol) in THF (20 mL) was added *tert*-BuLi (16.5 mL, 21.6 mmol) dropwise at −78 °C. The resulting solution was stirred at −78 °C for 30 min before the addition of a $ZnCl_2$ solution (27.4 mL, freshly prepared from flame-dried $ZnCl_2$ solid, 1 M in THF). The reaction mixture was then warmed to −20 °C and stirred for another 30 min. The cooling bath was removed and a solution of $Pd(PPh_3)_4$ (416 mg, 0.36 mmol) and 2-bromobenzaldehyde (**S1**, 1.34 g, 7.2 mmol) in THF (20 mL) was added at room temperature. The resulting mixture was stirred vigorously for 12 hours at reflux temperature before it was cooled to room temperature. The reaction mixture was then quenched with a saturated aqueous solution of NH_4Cl (20 mL), and extracted with Et_2O (4 × 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography on silica gel (2:1 CH_2Cl_2/hexanes) to provide a pale-yellow oil (0.96 g, 65%).

IR (neat) 3057, 2956, 2843, 2747, 1694, 1597, 1475, 1389, 1250, 1194, 841, 773 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.34 (dd, *J* = 8.5, 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 5.91 (d, *J* = 3.0 Hz, 1H), 5.72 (d, *J* = 3.0 Hz, 1H), 0.12 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 151.4, 149.4, 133.5, 133.0, 130.7, 128.9, 127.7, 126.6, -1.6.

HRMS (CI^+) *m*/*z* 189.0737 [$(M-Me)^+$; calcd for $C_{11}H_{13}OSi$ 189.0736].



Three-component coupling of linchpin **14** via ARC/alkylation. Example:

1-(2-(Penta-1,4-dien-2-yl)phenyl)pentan-1-ol (15a).

General procedures

Condition a: To a solution of linchpin **14** (50 mg, 0.245 mmol) in Et_2O (0.5 mL) at –78 °C was added *n*-BuLi (200 µL, 2.4 M, 0.48 mmol). After 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA/THF (1 mL, 1:1) via cannula at room temperature. The resulting mixture was stirred for 2 h, followed by the addition of allyl bromide (41 uL, 0.48 mmol). The resulting reaction mixture was stirred for another 2 h, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (2:1 CH_2Cl_2/hexanes) afforded compound **15a** (41 mg, 73%) as a colorless oil.

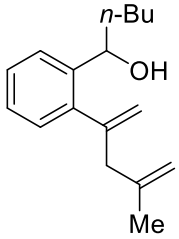
Condition b: To a solution of linchpin **14** (50 mg, 0.245 mmol) in THF (0.5 mL) at –78 °C was added *n*-BuLi (110 µL, 2.4 M, 0.26 mmol). After 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA (0.5 mL) via cannula at room temperature, followed by the addition of *t*-BuOK (240 uL, 1 M in THF). The resulting mixture was stirred for 30 min, followed by the addition of allyl bromide (41 uL, 0.48 mmol). The resulting reaction mixture was stirred for 2 h, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (2:1 CH_2Cl_2/hexanes) afforded compound **15a** (42 mg, 74%) as a colorless oil.

IR(neat) 3367 (br), 3077, 2956, 2931, 2859, 1638, 1430, 1045, 997, 910, 761 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 (ddd, *J* = 8.3, 7.6, 1.5 Hz, 1H), 7.23 (ddd, *J* = 8.3, 7.5, 1.4 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.90-5.79 (m, 1H), 5.24 (q, *J* = 1.6 Hz, 1H), 5.10 – 5.02 (m, 2H), 4.92-4.90 (m, 1H), 4.88 – 4.83 (m, 1H), 3.11 – 2.99 (m, 2H), 1.85 – 1.76 (m, 1H), 1.73-1.65 (m, 2 H), 1.47 – 1.40 (m, 1H), 1.37 – 1.25 (m, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 141.9, 141.7, 135.5, 128.6, 127.7, 127.1, 125.8, 117.0, 115.5, 70.7, 43.5, 38.6, 28.6, 22.7, 14.2.

HRMS (ES^+) *m*/*z* 213.1637 [$(M-OH)^+$; calcd for $C_{16}H_{21}$ 213.1643].



1-(2-(4-Methylpenta-1,4-dien-2-yl)phenyl)pentan-1-ol (15b).

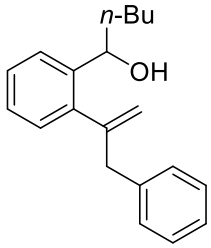
Colorless oil (condition a: 41 mg, 68%; condition b: 43 mg, 73%).

IR (neat) 3367 (br), 3077, 2956, 2931, 2859, 1638, 1430, 1045, 997, 910, 761 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 1H), 7.30 (dd, *J* = 8.6, 7.7 Hz, 1H), 7.21 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 5.26 (s, 1H), 4.95 (s, 1H), 4.89 – 4.84 (m, 1H), 4.82 (s, 1H), 4.65 (s, 1H), 3.03 (s, 2H), 1.86 – 1.78 (m, 1H), 1.77 (s, 3H), 1.73 – 1.64 (m, 2H), 1.49 – 1.40 (m, 1H), 1.39 – 1.24 (m, 3H), 0.89 (t, *J* = 8.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 142.6, 142.0, 141.7, 128.6, 127.6, 127.1, 125.8, 116.4, 113.7, 70.6, 47.9, 38.5, 28.6, 22.8, 22.3, 14.2.

HRMS (ES^+) *m*/*z* 267.1722 [$(M+Na)^+$; calcd for $C_{17}H_{24}ONa$ 267.1725].



1-(2-(3-Phenylprop-1-en-2-yl)phenyl)pentan-1-ol (15c).

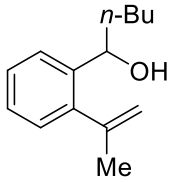
Colorless oil (condition a: 48 mg, 70%; condition b: 50 mg, 73%).

IR (neat) 3389 (br), 3062, 3027, 2955, 2930, 2858, 1637, 1601, 1494, 1453, 1044, 905, 762, 731, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.26 – 7.17 (m, 4H), 7.11 – 7.05 (m, 1H), 5.24 (s, 1H), 4.88 (s, 1H), 4.65 – 4. 59 (m, 1H), 3.67 (d, *J* = 14.6 Hz, 1H), 3.63 (d, *J* = 14.6 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.54 – 1.46 (m, 1H), 1.39 – 1.25 (m, 3H), 1.21 – 1.12 (m, 1H), 1.06 (d, *J* = 3.3 Hz, 1H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 142.3, 140.9, 138.7, 129.5, 128.4, 128.3, 127.6, 127.0, 126.5, 125.9, 116.0, 70.5, 46.3, 38.3, 28.5, 22.7, 14.2.

HRMS (ES^+) *m*/*z* 263.1806 [$(M\text{-}OH)^+$; calcd for $C_{20}H_{23}$ 263.1800].



1-(2-(Prop-1-en-2-yl)phenyl)pentan-1-ol (15d).

Colorless oil (condition b: 38 mg, 77%).

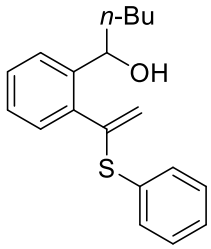
IR (neat) 3359 (br), 3075, 2957, 2859, 1640, 1374, 1300, 1046, 1004, 900, 761 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 8.2, 7.8 Hz, 1H), 7.23 (dd, *J* = 8.2, 7.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 1H), 4.94 – 4.88 (m, 1H), 4.84 (s, 1H), 2.07 (s, 3H), 1.85 – 1.74 (m, 2H), 1.73 – 1.66 (m, 1H), 1.49 – 1.40 (m, 1H), 1.38 – 1.24 (m, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 142.7, 141.6, 128.1, 127.5, 127.2, 125.8, 115.7,

70.7, 38.8, 28.5, 25.9, 22.7, 14.2.

HRMS (ES^+) *m*/*z* 227.1401 [$(M+Na)^+$; calcd for $C_{14}H_{20}ONa$ 227.1412].



1-(2-(1-(Phenylthio)vinyl)phenyl)pentan-1-ol (15e).

Pale-yellow oil (condition a: 44 mg, 61%; condition b: 40 mg, 56%).

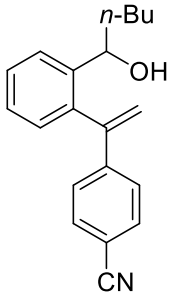
IR (neat) 3073, 2959, 1766, 1716, 1466, 1285, 1023, 743, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 3H), 7.38 – 7.29 (m, 4H), 7.26 – 7.20 (m, 2H), 5.15 – 5.11 (m, 1H), 5.11 (s, 1H), 5.05 (s, 1H), 1.86 – 1.79 (m, 1H), 1.78 (d, *J* = 3.2 Hz, 1H), 1.75 – 1.71 (m, 1H), 1.50 – 1.42 (m, 1H), 1.38 – 1.28 (m, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 143.0, 137.9, 135.1, 131.9, 129.8, 129.5, 129.1, 128.9, 127.2, 126.0, 113.4, 70.4, 38.2, 28.6, 22.8, 14.2.

HRMS (ES^+) *m*/*z* 297.1319 [$(M-H)^+$; calcd for $C_{19}H_{21}OS$ 297.1313].

Three-component coupling of linchpin **15** via ARC/CCR.



4-(1-(2-(1-Hydroxypentyl)phenyl)vinyl)benzonitrile (16a).

General procedures

Condition a: To a solution of linchpin **14** (50 mg, 0.245 mmol) in Et_2O (0.5 mL) at

–78 °C was added *n*-BuLi (200 µL, 2.4 M, 0.48 mmol). After 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA/THF (1 mL, 1:1) via cannula at room temperature. The resulting mixture was stirred for 2 h, followed by the addition of a pre-mixed solution of 4-iodobenzonitrile (110 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 µmol) in THF (0.5 mL). The resulting reaction mixture was stirred overnight, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (1:1:0.0125 CH_2Cl_2 /hexanes/MeOH) afforded compound **16a**.

Condition b: To a solution of linchpin **14** (50 mg, 0.245 mmol) in THF (0.5 mL) at –78 °C was added *n*-BuLi (110 µL, 2.4 M, 0.26 mmol). After 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA (0.5 mL) via cannula at room temperature, followed by the addition of *t*-BuOK (240 uL, 1 M in THF). The resulting mixture was stirred for 30 min, followed by the addition of a pre-mixed solution of 4-iodobenzonitrile (110 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 µmol) in THF (0.5 mL). The resulting reaction mixture was stirred overnight, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (1:1:0.0125 CH_2Cl_2/hexanes /MeOH) afforded compound **16a**.

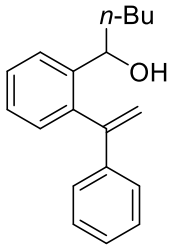
Pale-yellow amorphous solid (condition a: 51 mg, 72%; condition b: 50 mg, 70%).

IR (neat) 3447 (br), 3061, 2955, 2845, 2228, 1604, 1504, 1403, 1016, 915, 850, 766 cm^{-1}.

^1H NMR (500 MHz,$CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 3H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 (dd, *J* = 7.5, 7.5, 1H), 7.18 (d, *J* = 7.6, 1H), 5.92 (s, 1H), 5.39 (s, 1H), 4.52 (dd, *J* = 8.3, 4.8 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.57 – 1.45 (m, 2H), 1.24 – 1.10 (m, 3H), 1.10 – 1.02 (m, 1H), 0.79 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 145.3, 142.9, 138.6, 132.5, 130.3, 128.9, 127.7, 127.1, 126.2, 118.9, 118.9, 111.5, 70.8, 38.4, 28.3, 22.5, 14.1.

HRMS (ES^-) *m*/*z* 290.1550 [$(M-H)^-$; calcd for $C_{20}H_{20}NO$ 290.1545].



1-(2-(1-Phenylvinyl)phenyl)pentan-1-ol (16b).

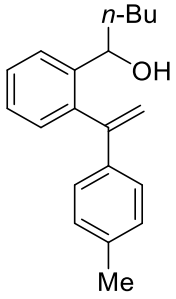
Pale-yellow oil (condition a: 50 mg, 77%; condition b: 46 mg, 71%).

IR (neat) 3390 (br), 3058, 2955, 2858, 1615, 1494, 1444, 1322, 1028, 903, 760, 710 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.33 – 7.16 (m, 7H), 5.79 (d, *J* = 1.3 Hz, 1H), 5.20 (d, *J* = 1.4 Hz, 1H), 4.63 – 4.47 (m, 1H), 1.66 – 1.55 (m, 2H), 1.53 – 1.45 (m, 1H), 1.29 – 1.09 (m, 3H), 1.09 – 0.99 (m, 1H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 143.0, 141.0, 140.1, 130.3, 128.6, 128.3, 128.0, 127.4, 126.5, 125.9, 115.8, 70.7, 38.1, 28.3, 22.5, 14.1.

HRMS (CI^+) *m*/*z* 266.1674 [$(M)^+$; calcd for $C_{19}H_{22}O$ 266.1671].



1-(2-(1-(P-tolyl)vinyl)phenyl)pentan-1-ol (16c).

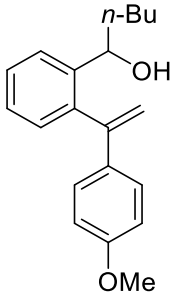
Pale-yellow oil (condition a: 50 mg, 73%; condition b:54 mg, 78%).

IR (neat) 3390 (br), 2929, 2858, 1510, 1447, 1040, 900, 827, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.30 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.77 (d, *J* = 1.5 Hz, 1H), 5.16 (d, *J* = 1.5 Hz, 1H), 4.63 (dd, *J* = 8.2, 4.9 Hz, 1H), 2.34 (s, 3H), 1.73 – 1.59 (m, 2H), 1.58 – 1.47 (m, 1H), 1.29 – 1.23 (m, 1H), 1.23 – 1.21 (m, 2H), 1.11 – 1.03 (m, 1H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 143.0, 140.3, 138.2, 137.9, 130.3, 129.3, 128.2, 127.3, 126.4, 125.9, 114.9, 70.7, 38.0, 28.3, 22.5, 21.2, 14.0.

HRMS (CI^+) *m*/*z* 263.1794 [$(M\text{-}OH)^+$; calcd for $C_{20}H_{23}$ 263.1800].



1-(2-(1-(4-Methoxyphenyl)vinyl)phenyl)pentan-1-ol (16d).

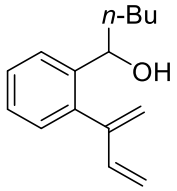
Pale-yellow oil (condition a: 52 mg, 72%; condition b: 55 mg; 76%).

IR (neat) 3420 (br), 2954, 2931, 1607, 1510, 1249, 1180, 1035, 837, 761 cm-1.

^{1}H NMR (500 MHz, CDCl3) δ 7.56 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (ddd, J = 7.4, 7.4, 1.4 Hz, 1H), 7.23 – 7.17 (m, 3H), 6.86 – 6.76 (m, 2H), 5.71 (d, J = 1.4 Hz, 1H), 5.10 (d, J = 1.3 Hz, 1H), 4.63 (dt, J = 8.4, 4.4 Hz, 1H), 3.79 (s, 3H), 1.68 – 1.61 (m, 1H), 1.55 – 1.49 (m, 2H), 1.29 – 1.13 (m, 3H), 1.12 – 1.04 (m, 1H), 0.79 (t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 159.6, 148.0, 143.0, 140.4, 133.7, 130.2, 128.2, 127.8, 127.4, 125.9, 113.93, 113.86, 70.7, 55.4, 38.1, 28.3, 22.5, 14.1.

HRMS (CI^+) m/z 279.1736 [$(M\text{-}OH)^+$; calcd for $C_{20}H_{23}O$ 279.1749].



1-(2-(Buta-1,3-dien-2-yl)phenyl)pentan-1-ol (16e).

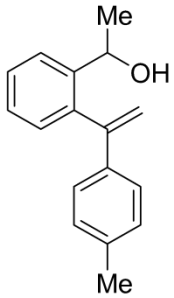
Three equivalents of vinyl bromide were added for optimal yield. Pale-yellow oil (condition a: 40 mg, 75%; condition b: 42 mg; 78%).

IR (neat) 3403 (br), 2955, 2930, 2870, 1749, 1466, 1379, 999, 761 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.36 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H), 7.28-7.24 (m, 1H), 7.07 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.67 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.43 (dd, *J* = 2.0, 0.8 Hz, 1H), 5.16 (d, *J* = 10.6 Hz, 1H), 5.09 (s, 1H), 4.77 – 4.68 (m, 2H), 1.80 – 1.70 (m, 1H), 1.69 – 1.61 (m, 2H), 1.4-1.18 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 142.9, 140.0, 137.8, 129.8, 128.1, 127.2, 125.6, 119.3, 117.6, 70.8, 38.3, 28.4, 22.7, 14.1.

HRMS (ES^+) *m/z* 199.1493 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{19}$ 199.1487].



1-(2-(1-(P-tolyl)vinyl)phenyl)ethan-1-ol (16f).

Pale-yellow oil (condition a: 41 mg, 70%; condition b: 40 mg, 69%).

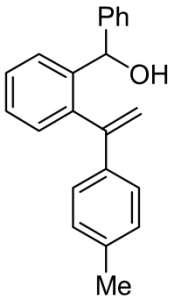
IR (neat) 3367(br), 2971, 1616, 1510, 1446, 1118, 1068, 1003, 900, 827, 761 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.31 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 5.79 (s, 1H), 5.17 (s, 1H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.34 (s, 3H), 1.77 –

1.55 (m, 1H), 1.30 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 143.8, 139.9, 138.01, 137.96, 130.2, 129.3, 128.3, 127.4, 126.4, 125.4, 114.8, 66.8, 24.4, 21.3.

HRMS (CI^+) *m*/*z* 221.1326 [$(M\text{-}OH)^+$; calcd for $C_{17}H_{17}$ 221.1330].



Phenyl(2-(1-(p-tolyl)vinyl)phenyl)methanol (16g).

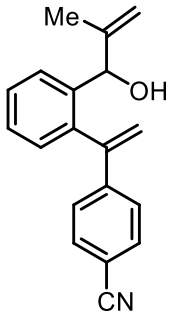
Pale-yellow oil (condition a: 46 mg, 63%; condition b: 42 mg, 57%;).

IR (neat) 3414 (br), 3026, 1510, 1447, 1183, 1017, 903, 827, 761, 736, 700 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H), 7.31 (ddd, *J* = 7.4, 7.4, 1.5 Hz, 1H), 7.27 – 7.17 (m, 8H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.84 (d, *J* = 3.6 Hz, 1H), 5.79 (d, *J* = 1.3 Hz, 1H), 5.13 (d, *J* = 1.3 Hz, 1H), 2.35 (s, 3H), 1.95 (d, *J* = 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 143.7, 141.9, 140.9, 138.1, 138.0, 130.4, 129.4, 128.3, 128.2, 127.7, 127.6, 127.2, 126.6, 115.4, 72.4, 21.3.

HRMS (CI^+) *m*/*z* 283.1487 [$(M\text{-}OH)^+$; calcd for $C_{22}H_{19}$ 283.1487].



4-(1-(2-(1-Hydroxy-2-methylallyl)phenyl)vinyl)benzonitrile (**16h)**

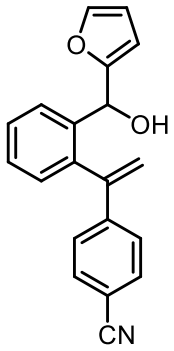
To a solution of 2-bromopropene (24 uL, 0.27 mmol) in THF (0.5 mL) was added dropwise *t*-BuLi (370 uL, 1.48 M in hexanes, 0.55 mmol) at -78 ^{o}C. The reaction mixture was stirred for 30 minutes, followed by the addition of linchpin **14** (50 mg, 0.245 mmol) in THF (0.2 mL). After 30 minutes, the reaction mixture was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA (0.5 mL) via cannula at room temperature, followed by the addition of *t*-BuOK (240 uL,1 M in THF). The resulting suspension was stirred at room temperature for 30 minutes, followed by the addition of a pre-mixed solution of 4-iodobenzonitrile (110 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 µmol) in THF (0.5 mL). The resulting reaction mixture was stirred overnight, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (1:10 EtOAc/toluene) afforded compound **16h** (46 mg, 69%) as a pale-yellow oil.

IR (neat) 3446 (br), 3061, 2227, 1604, 1402, 1046, 906, 849,764 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 5.95 (s, 1H), 5.42 (s, 1H), 5.06 (s, 1H), 5.00 (d, *J* = 3.9 Hz, 1H), 4.90 (s, 1H), 1.65 (d, *J* = 4.1 Hz, 1H), 1.47 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 146.3, 145.2, 139.9, 139.7, 132.4, 130.4, 128.8, 128.1, 127.3, 127.1, 119.1, 118.9, 111.5, 111.3, 73.7, 19.4.

HRMS (ES^+) *m*/*z* 258.1293 [$(M\text{-}OH)^+$; calcd for $C_{19}H_{16}N$ 258.1283].



4-(1-(2-(Furan-2-yl(hydroxy)methyl)phenyl)vinyl)benzonitrile (**16i**)

To a solution of furan (20 uL, 0.27 mmol) in THF (0.5 mL) was added dropwise *n*-BuLi (110 uL, 2.5 M in hexanes, 0.27 mmol) at -78 ^{o}C. After addition, the reaction mixture was warmed up to 0 ^{o}C and stirred for another hour. The resulting solution was then cooling down to -78 ^{o}C, followed by the addition of linchpin **14** (50 mg, 0.245 mmol) in THF (0.2 mL). After 30 minutes, the reaction mixture was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA (0.5 mL) via cannula at room temperature. After addition of *t*-BuOK (240 uL,1 M in THF), the resulting suspension was heated to 60 ^{o}C and stirred for another 45 minutes. The resulting mixture was then cooled down to room temperature, followed by the addition of a pre-mixed solution of 4-iodobenzonitrile (110 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 μmol) in THF (0.5 mL). The resulting reaction mixture was stirred overnight, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (1:10 EtOAc/hexanes) afforded compound **16i** (41 mg, 57%) as brown solid.

Note: The tri-component adduct **16i** should be quickly isolated and purified due to its instablitiy.

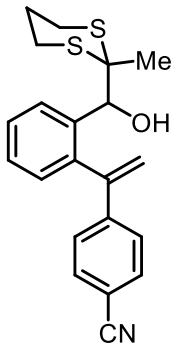
IR (neat) 3446 (br), 3074, 2227, 1604, 1503, 1404, 1149, 1011, 924, 848, 740 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.47 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.38 (dd, *J* = 8.7, 7.5 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.27

(m, 1H), 7.19 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.26 – 6.19 (m, 1H), 5.93 – 5.86 (m, 2H), 5.72 (d, *J* = 4.1 Hz, 1H), 5.32 (s, 1H), 2.15 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 146.4, 144.7, 142.4, 139.0, 138.9, 132.3, 130.2, 128.7, 128.4, 127.5, 127.3, 119.2, 118.9, 111.4, 110.3, 108.0, 67.0.

HRMS (ES^-) *m*/*z* 300.1033 [$(M-H)^-$; calcd for $C_{20}H_{14}NO$ 300.1025].



4-(1-(2-(Hydroxy(2-methyl-1,3-dithian-2-yl)methyl)phenyl)vinyl)benzonitrile (**16j**)

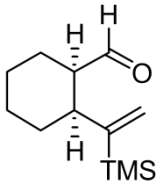
To a solution of 2-methyl-1,3-dithiane (33 uL, 0.27 mmol) in THF (0.5 mL) was added dropwise *n*-BuLi (110 uL, 2.5 M in hexanes, 0.27 mmol) at room temperature. The reaction mixture was stirred for another 10 minutes before cooling down to 0 ^oC, followed by the addition of linchpin **14** (50 mg, 0.245 mmol) in THF (0.2 mL). The resulting solution was then warmed up to room temperature and stirred for another 30 minutes before it was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in HMPA (0.5 mL) via cannula at room temperature. *t*-BuOK (240 uL,1 M in THF) was then added. The resulting mixture was stirred for 30 min, followed by the addition of a pre-mixed solution of 4-iodobenzonitrile (110 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 μmol) in THF (0.5 mL). The resulting reaction mixture was stirred overnight, followed by the addition of 1 N HCl (2 mL). After 1 hour, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (1:15 EtOAc/toluene) afforded compound **16j** (48 mg, 53%) as a pale-yellow solid.

IR (neat) 3467 (br), 3061, 2923, 2226, 1603, 1374, 1027, 911, 849, 762 cm^{-1}.

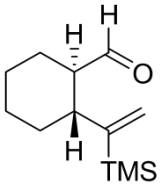
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.31 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.04 (s, 1H), 5.56 (s, 1H), 4.95 (s, 1H), 2.97 (s, 1H), 2.89 (t, *J* = 12.8 Hz, 1H), 2.71 (dd, *J* = 14.2, 13.1 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.48 – 2.38 (m, 1H), 2.03 – 1.94 (m, 1H), 1.88 – 1.74 (m, 1H), 1.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 144.8, 141.2, 136.8, 132.4, 130.7, 129.1, 128.3, 127.6, 127.2, 119.6, 118.9, 111.6,71.7, 54.7, 28.0, 26.1, 24.3, 23.8.

HRMS (ES^+) *m*/*z* 368.1155 [$(M+H)^+$; calcd for $C_{21}H_{22}NOS_2$ 368.1143].



(19)

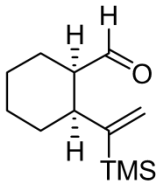


(20)

Synthesis of cyclohexyl linchpin **19** and **20**.

To a vigorously stirred suspension of magnesium turnings (2.11 g, 87.9 mmol) in THF (9 mL) was added a few drops of (1-bromovinyl)trimethylsilane (8.74 g, 48.8 mmol) solution in THF (9 mL), followed by the addition of a few iodine crystals. After the reaction was initiated, another 9 mL THF was added, followed by the addition of the remaining (1-bromovinyl)trimethylsilane solution. The reaction mixture was stirred under reflux for another hour. After cooling to room temperature, the freshly prepared Grignard reagent was diluted with 9 mL THF and slowly cannulated into a suspension of CuBr·DMS (3.40 g, 16.5 mmol) in THF (20 mL) and dimethyl sulfide (20 mL) at –50 °C, followed by the addition of HMPA (17 mL, 97.7 mmol). To this mixture was then added dropwise a THF (20 mL) solution of cyclohex-1-ene-1-carbaldehyde (3.54 g, 32.1 mmol) and TMSCl (8.3 mL, 65.4 mmol). The resulting mixture was stirred for 1h before addition of 1 N HCl (40 mL). After warming up to room temperature, the reaction

mixture was extracted with Et_2O (3×50 mL) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude residue was purified by column chromatography with silica gel (1:4 CH_2Cl_2/hexanes to 100% CH_2Cl_2) to yield both *cis*-linchpin and *trans*-linchpin as colorless oils (*cis*:*trans* 1:1, 4.25 g, 63%). Note: Both linchpins can be easily oxidized to the corresponding acids. Samples are stored under N_2 atmosphere in a freezer (−20 °C) unless they are used immediately.



***Cis*-2-(1-(trimethylsilyl)vinyl)cyclohexane-1-carbaldehyde (19).**

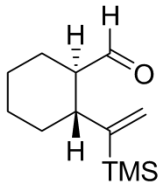
Colorless oil.

IR (neat) 3054, 2934, 2857, 2740, 1718, 1449, 1249,927, 837, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 9.76 (d, *J* = 1.1 Hz, 1H), 5.64 (dd, *J* = 2.2, 1.7 Hz, 1H), 5.56 (dd, *J* = 2.0, 1.1 Hz, 1H), 2.64 – 2.53 (m, 2H), 2.22 – 2.08 (m, 1H), 1.85 – 1.80 (m, 1H), 1.75 – 1.70 (m, 1H), 1.64 – 1.57 (m, 1H), 1.56 – 1.51 (m, 1H), 1.51 – 1.45 (m, 1H), 1.40 – 1.32 (m, 2H), 0.12 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 153.6, 125.2, 49.1, 43.0, 28.2, 27.0, 26.1, 22.6, -0.7.

HRMS (CI^+) *m*/*z* 195.1197 [$(M-CH_3)^+$; calcd for $C_{11}H_{19}OSi$ 195.1205].



***Trans*-2-(1-(trimethylsilyl)vinyl)cyclohexane-1-carbaldehyde (20).**

Colorless oil.

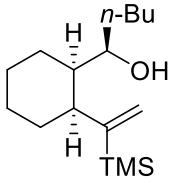
IR (neat) 2931, 2855, 2707, 1726, 1447, 1249, 929, 838, 759, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 9.44 (d, *J* = 3.5 Hz, 1H), 5.70 – 5.63 (m, 1H), 5.46. (d, *J* =

1.9 Hz, 1H), 2.59 – 2.43 (m, 1H), 2.30 (ddd, *J* = 12.6, 11.7, 3.3 Hz, 1 H), 1.89 – 1.73 (m, 4H), 1.37 – 1.21 (m, 3H), 1.17 – 1.08 (m, 1H), 0.10 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 154.9, 125.4, 54.3, 43.7, 34.5, 26.9, 26.4, 25.0, -1.1.

HRMS (ES^+) *m*/*z* 195.1206 [$(M\text{-}CH_3)^+$; calcd for $C_{11}H_{19}OSi$ 195.1205].



Intermediate 21.

To a solution of linchpin **19** (50 mg, 0.24 mmol) in freshly degassed THF (0.5 mL, freeze-pump-thaw three cycles) at −78 °C was added *n*-BuLi (110 µL, 2.4 M, 0.26 mmol). After stirring for 30 min, the reaction mixture was quenched with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:20 EtOAc/hexanes) to give intermediate **21**.

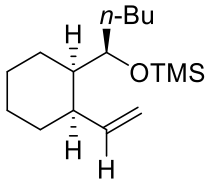
Colorless oil (55 mg, 86%).

IR (neat) 3375 (br), 2929, 2856, 1450, 1408, 1248, 925, 856, 836, 756, 687 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (s, 1H), 5.56 (d, *J* = 2.3 Hz, 1H), 3.73 – 3.66 (m, 1H), 2.63 – 2.47 (m, 1H), 1.89 – 1.79 (m, 1H), 1.79 – 1.69 (m, 2H), 1.67 – 1.55 (m, 3H), 1.49 – 1.18 (m, 10H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.09 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 125.7, 73.7, 44.1, 42.2, 35.7, 29.6, 28.5, 25.4, 24.9, 23.3, 22.9, 14.3, -0.9.

HRMS (CI^+) *m*/*z* 253.1988 [$(M\text{-}CH_3)^+$; calcd for $C_{15}H_{29}OSi$ 253.1988].



Intermediate 22.

To a solution of linchpin **19** (50 mg, 0.24 mmol) in freshly degassed THF (0.5 mL, freeze-pump-thaw three cycles) at −78 °C was added *n*-BuLi (110 µL, 2.4 M, 0.26 mmol). After stirring for 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in freshly distilled HMPA (0.5 mL) via cannula at room temperature, followed by the addition of *t*-BuOK (240 uL, 1 M in THF). The resulting mixture was stirred at 60 °C for 45 min. The reaction mixture was then quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (hexanes to 1:33 EtOAc/hexanes, buffered with 5% Et_3N) to give intermediate **22**.

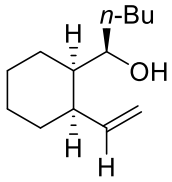
Colorless oil (47 mg, 73%).

IR (neat) 3073, 2927, 2860, 1450, 1250, 1105, 1064, 953, 912, 839, 750, 684 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 6.11 – 6.01 (m, 1H), 5.03 (s, 1H), 5.02 – 4.98 (m, 1H), 3.39 – 3.32 (m, 1H), 2.44 – 2.35 (m, 1H), 1.81 (t, *J* = 14.6 Hz, 2H), 1.65 (d, *J* = 13.0 Hz, 1H), 1.49 – 1.37 (m, 5H), 1.33 – 1.17 (m, 6H), 1.16 – 1.06 (m, 1H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.09 (s, 9H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 115.5, 75.0, 45.2, 40.7, 34.0, 33.4, 26.6, 26.4, 24.9, 23.2, 21.3, 14.3, 0.8.

HRMS (CI^+) *m*/*z* 268.2215 [$(M)^+$; calcd for $C_{16}H_{32}OSi$ 268.2222].



Byproduct 23.

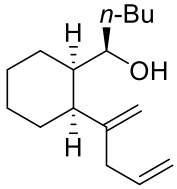
IR (neat) 3343 (br), 3072, 2925, 2859, 1450, 1129, 1041, 996, 912 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (ddd, *J* = 16.7, 10.2, 9.9 Hz, 1H), 5.11 (dd, *J* = 17.2, 2.3 Hz, 1H), 5.05 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.45 – 3.38 (m, 1H), 2.48 – 2.41 (m, 1H), 1.84 (d, *J* = 12.6 Hz, 1H), 1.77 (d, *J* = 13.1 Hz, 1H), 1.65 (d, *J* = 13.2 Hz, 1H), 1.63 – 1.57 (m, 1H), 1.54 – 1.25 (m, 11H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 115.8, 74.9, 46.7, 42.8, 34.0, 33.6, 28.0, 26.6, 22.9, 22.7, 21.4, 14.3.

HRMS (CI^+) *m*/*z* 196.1819 [$(M)^+$; calcd for $C_{13}H_{24}O$ 196.1827].

Three-component coupling of linchpin **19** via ARC/alkylation. Example:



Adduct 24a.

General procedures.

Condition a: To a solution of linchpin **19** (50 mg, 0.24 mmol) in freshly degassed THF (0.5 mL, three freeze-pump-thaw cycles) at −78 °C was added *n*-BuLi (200 μL, 2.4 M, 0.48 mmol). After stirring for 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in freshly distilled HMPA/THF (1 mL, 1:1) via cannula at room temperature. The resulting mixture was stirred at 60 °C for 45 min, followed by the addition of allyl bromide (41 uL, 0.48 mmol). The resulting mixture was stirred for 2 h before addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic

layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:20 EtOAc /hexanes) to give compound **24a**.

Condition b: To a solution of linchpin **19** (50 mg, 0.24 mmol) in freshly degassed THF (0.5 mL, three freeze-pump-thaw cycles) at –78 °C was added *n*-BuLi (110 µL, 0.26 mmol). After stirring for 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in freshly distilled HMPA (0.5 mL) via cannula at room temperature, followed by the addition of *t*-BuOK (240 uL, 1 M in THF). The resulting mixture was stirred at 60 °C for 45 min, followed by the addition of allyl bromide (41 uL, 0.48 mmol). The resulting mixture was stirred for 2 h before addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:20 EtOAc /hexanes) to give compound **24a**.

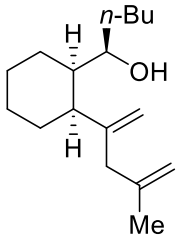
Colorless oil (condition a: 35 mg, 63%; condition b: 35 mg, 63%).

IR (neat) 3365 (br), 3078, 2926, 2853, 1640, 1450, 1383, 996, 911, 894 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.74 (m, 1H), 5.06 (t, *J* = 1.3 Hz, 1H), 5.05 – 5.02 (m, 1H), 4.94 (s, 1H), 4.93 (s, 1H), 3.72 – 3.67 (m, 1H), 2.77 (qd, *J* = 15.5, 7.0 Hz, 2H), 2.28 – 2.23 (m, 1H), 1.92 – 1.84 (m, 1H), 1.79 – 1.67 (m, 4H), 1.57 – 1.51 (m, 2H), 1.45 – 1.24 (m, 9H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 136.7, 116.5, 111.6, 73.0, 43.8, 42.3, 41.9, 36.0, 28.6, 28.4, 25.7, 24.6, 24.4, 22.9, 14.2.

HRMS (ES^+) *m*/*z* 237.2228 [$(M+H)^+$; calcd for $C_{16}H_{29}O$ 237.2218].



Adduct 24b.

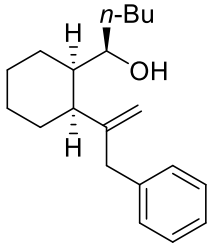
Colorless oil (condition a: 32 mg, 54%; condition b: 40 mg, 67%).

IR (neat) 3365 (br), 3075, 2927, 2855, 16335, 1450, 1384, 1011, 892, 668 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (s, 1H), 4.95 (s, 1H), 4.82 (s, 1H), 4.73 (s, 1H), 3.73 – 3.68 (m, 1H), 2.73 (s, 2H), 2.27 – 2.20 (m, 1H), 1.92 – 1.86 (m, 1H), 1.81 – 1.75 (m, 1H), 1.68 (s, 3H), 1.56 – 1.46 (m, 5H), 1.45 – 1.37 (m, 5H), 1.34 – 1.24 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 143.8, 112.9, 112.4, 73.0, 46.5, 43.0, 42.0, 36.1, 28.7, 28.5, 25.7, 24.58, 24.55, 22.9, 22.0, 14.3.

HRMS (CI^+) *m*/*z* 233.2261 [$(M\text{-}OH)^+$; calcd for $C_{17}H_{29}$ 233.2269].



Adduct 24c.

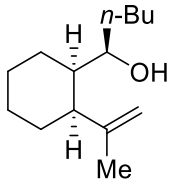
Colorless oil (condition a: 45 mg, 66%; condition b: 48 mg, 71%).

IR (neat) 3366 (br), 3027, 2927, 2855, 1639, 1494, 1451, 895, 746, 700 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.2, 7.3 Hz, 2H), 7.21 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 2H), 5.01 (s, 1H), 4.87 (s, 1H), 3.76 – 3.64 (m, 1H), 3.37 (d, *J* = 15.0 Hz, 1H), 3.30 (d, *J* = 15.0 Hz, 1H), 2.24 – 2.19 (m, 1H), 1.90 – 1.83 (m, 1H), 1.81 – 1.74 (m, 1H), 1.70 – 1.66 (m, 2H), 1.55 – 1.46 (m, 3H), 1.40 – 1.23 (m, 9H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 139.8, 129.3, 128.4, 126.3, 112.9, 73.0, 44.2, 43.1, 42.5, 36.0, 28.8, 28.5, 25.6, 24.6, 24.3, 22.8, 14.3.

HRMS (ES^+) *m*/*z* 287.2368 [$(M+H)^+$; calcd for $C_{20}H_{31}O$ 287.2375].



Adduct 24d.

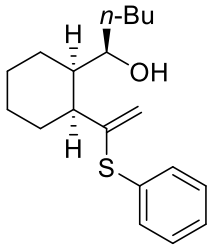
Colorless oil (condition b: 33 mg, 65%).

IR(neat) 3371 (br), 2929, 2856, 1643, 1451, 1375, 1248, 1047, 1009, 888 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (s, 1H), 4.82 (s, 1H), 3.77 – 3.60 (m, 1H), 2.22 (dt, *J* = 8.4, 4.6 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.77 (s, 3H), 1.75 – 1.63 (m, 4H), 1.60 – 1.52 (m, 2H), 1.47 – 1.36 (m, 6H), 1.35 – 1.24 (m, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 111.4, 73.1, 45.5, 42.6, 35.9, 28.7, 28.5, 25.6, 24.7, 24.48, 24.47, 22.9, 14.3.

HRMS (ES^+) *m*/*z* 211.2065 [$(M+H)^+$; calcd for $C_{14}H_{27}O$ 211.2062].



Adduct 24e.

Three equivalents of diphenyl disulfide were added for optimal yield. Pale-yellow oil. (condition a: 32 mg, 45%; condition b: 38 mg, 53%).

IR (neat) 3408 (br), 2928, 2856, 1709, 1583, 1447, 1378, 1082, 1022, 908, 747, 691 cm^{-1}.

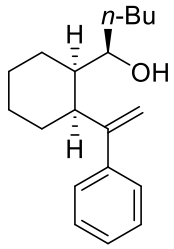
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.31 (m, 3H), 5.25 (s, 1H), 4.81 (s, 1H), 3.85 – 3.78 (m, 1H), 2.49 – 2.44 (m, 1H), 2.00 – 1.93 (m, 1H), 1.90 – 1.81

(m, 2H), 1.77 – 1.70 (m, 2H), 1.63 – 1.59 (m, 1H), 1.48 – 1.32 (m, 9H), 0.93 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 134.3, 132.9, 129.4, 128.4, 111.6, 73.0, 45.2, 42.7, 36.2, 29.4, 28.5, 25.3, 24.5, 22.9, 14.3.

HRMS (ES^+) m/z 327.1755 [$(M+Na)^+$; calcd for $C_{19}H_{28}OSNa$ 327.1759].

Three-component coupling of linchpin **19** via ARC/CCR.



Adduct 25b.

General procedures.

Condition a: To a solution of linchpin **19** (50 mg, 0.24 mmol) in freshly degassed THF (0.5 mL, three freeze-pump-thaw cycles) at −78 °C was added *n*-BuLi (200 µL, 2.4 M, 0.48 mmol). After stirring for 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (98 mg, 0.48 mmol) in freshly distilled HMPA/THF (1 mL, 1:1) via cannula at room temperature. The resulting mixture was stirred at 60 °C for 45 min before the addition of a pre-mixed solution of iodobenzene (98 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 µmol) in THF (0.5 mL). The resulting mixture was stirred overnight, followed by the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:20 EtOAc /hexanes) to give compound **25b**.

Condition b: To a solution of linchpin **19** (50 mg, 0.24 mmol) in freshly degassed THF (0.5 mL, three freeze-pump-thaw cycles) at −78 °C was added *n*-BuLi (110 µL, 0.26 mmol). After stirring for 30 min, the resulting solution was transferred to a suspension of

CuBr·DMS (98 mg, 0.48 mmol) in freshly distilled HMPA (0.5 mL) via cannula at room temperature, followed by the addition of *t*-BuOK (240 uL, 1 M in THF). The resulting mixture was stirred at 60 ºC for 45 min before the addition of a pre-mixed solution of iodobenzene (98 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 μmol) in THF (0.5 mL). The resulting mixture was stirred overnight before the addition of 1 N HCl (1 mL). After 10 minutes, the reaction mixture was diluted with H_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:20 EtOAc/hexanes) to give compound **25b**.

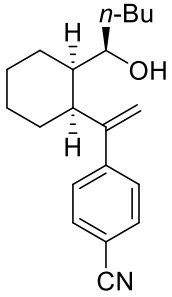
Pale-yellow oil (condition a: 40 mg, 61%; condition b: 38 mg, 57%)

IR (neat) 3364 (br), 3078, 2928, 2856, 1640, 1450, 1383, 996, 912, 894, 745 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 5.30 (s, 1H), 5.18 (s, 1H), 3.77 – 3.72 (m, 1H), 2.93 – 2.83 (m, 1H), 1.94 – 1.80 (m, 3H), 1.76 – 1.65 (m, 2H), 1.60 – 1.56 (m, 1H), 1.50 – 1.43 (m, 2H), 1.35 – 1.28 (m, 2H), 1.25 – 1.14 (m, 4H), 1.11 – 1.04 (m, 1H), 0.80 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 143.2, 128.4, 127.4, 126.8, 113.4, 72.7, 43.4, 41.2, 36.1, 28.3, 28.2, 26.0, 25.3, 24.2, 22.7, 14.2.

HRMS (CI^+) *m*/*z* 272.2133[$(M+H)^+$; calcd for $C_{19}H_{28}O$ 272.2140].



Adduct 25a.

Following the general procedure, the reaction mixture is treated with 1N HCl to hydrolyze TMS silyl ether. Unfortunately, compound **25a** has very close polarity to

impurities. To simplify purification, before addition of 1N HCl, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL), filtered through Celite, rinsed and extracted with hexanes (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (hexanes to 1:40 EtOAc /hexanes, buffered with 1% Et_3N) to give TMS protected product, which was submitted into 1N HCl/THF (2 mL, 1:1). After 10 minutes, the reaction mixture was diluted with Et_2O (5 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to give the clean adduct **25 a**.

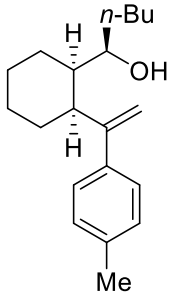
Pale-yellow oil (condition a: 35 mg, 49%; condition b: 38 mg, 53%).

IR (neat) 3433 (br), 2928, 2857, 2228, 1604, 1502, 1451, 1402, 1014, 907, 847, 745 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.38 (s, 1H), 5.31 (s, 1H), 3.74 – 3.62 (m, 1H), 2.94 – 2.83 (m, 1H), 1.92 – 1.80 (m, 3H), 1.74 – 1.64 (m, 2H), 1.54 – 1.42 (m, 4H), 1.31 – 1.24 (m, 2H), 1.22 – 1.13 (m, 4H), 1.08 – 1.01 (m, 1H), 0.80 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 147.8, 132.3, 127.5, 119.0, 116.0, 111.0, 72.5, 43.3, 41.0, 36.2, 28.2, 28.1, 26.0, 25.2, 24.0, 22.6, 14.1.

HRMS (ES^-) *m*/*z* 296.2017 [$(M-H)^-$; calcd for $C_{20}H_{26}NO$ 296.2014].



Adduct 25c.

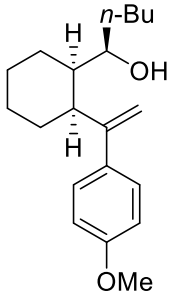
Pale-yellow oil (37 mg, 54%; 40 mg, 59%).

IR (neat) 3482 (br), 2929, 2857, 1622, 1511, 1451, 1079, 1017, 895, 823, 730 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.27 (s, 1H), 5.13 (s, 1H), 3.78 – 3.69 (m, 1H), 2.96 – 2.83 (m, 1H), 2.34 (s, 3H), 1.96 – 1.76 (m, 3H), 1.76 – 1.65 (m, 2H), 1.61 – 1.42 (m, 4H), 1.36 – 1.26 (m, 2H), 1.20 (dd, *J* = 11.2, 5.2 Hz, 4H), 1.12 – 1.03 (m, 1H), 0.80 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 140.2, 137.1, 129.1, 126.6, 112.7, 72.7, 43.4, 41.2, 36.1, 28.32, 28.28, 26.1, 25.3, 24.2, 22.7, 21.2, 14.2.

HRMS (ES^+) *m*/*z* 287.2371 [$(M+H)^+$; calcd for $C_{20}H_{31}O$ 287.2375].



Adduct 25d. Pale-yellow oil (condition a: 40 mg, 55%; condition b: 45 mg, 62%).

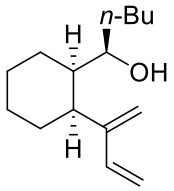
Adduct 25e. Pale-yellow oil (condition b: 40 mg, 55%).

IR (neat) 3421 (br), 2928, 2855, 1608, 1510, 1463, 1246, 1178, 1036,893, 835, 741 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.24 (s, 1H), 5.10 (s, 1H), 3.81 (s, 3H), 3.74 – 3.68 (m, 1H), 2.89 – 2.83 (m, 1H), 1.94 – 1.89 (m, 1H), 1.88 – 1.79 (m, 2H), 1.75 – 1.65 (m, 2H), 1.56 – 1.41 (m, 3H), 1.33 – 1.27 (m, 2H), 1.24 – 1.05 (m, 5H), 0.81 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 151.9, 135.5, 127.8, 113.8, 112.1, 72.6, 55.4, 43.5, 41.1, 36.1, 28.3, 28.3, 26.1, 25.4, 24.2, 22.7, 14.2.

HRMS (ES^+) *m*/*z* 303.2324[$(M+H)^+$; calcd for $C_{20}H_{31}O_2$ 303.2324].



Adduct 25f.

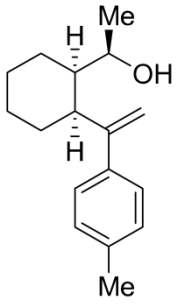
Three equivalents of vinyl bromide were added for optimal yield. Pale-yellow oil (condition b: 36 mg, 68%).

IR (neat) 3359 (br), 3087, 2929, 2856, 1804, 1593, 1450, 990, 896 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.29 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.24 (d, *J* = 17.6 Hz, 1H), 5.17 (s, 1H), 5.12 (s, 1H), 5.03 (d, *J* = 10.9 Hz, 1H), 3.69 – 3.55 (m, 1H), 2.76 – 2.61 (m, 1H), 1.90 – 1.77 (m, 2H), 1.77 – 1.62 (m, 4H), 1.56 – 1.46 (m, 1H), 1.44 – 1.21 (m, 9H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 140.1, 116.2, 112.9, 72.8, 42.4, 39.1, 36.1, 28.8, 28.2, 26.0, 24.6, 24.5, 22.8, 14.2.

HRMS (CI^+) *m*/*z* 222.1982 [M^+; calcd for $C_{15}H_{26}O$ 222.1984].



Adduct 25g.

Pale-yellow oil (condition a: 32 mg, 55%; condition b: 30 mg, 51%).

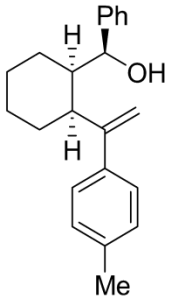
IR (neat) 3366 (br), 2926, 2853, 1622, 1511, 1449, 1384, 1089, 1065, 1040, 928, 895, 824 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz , 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.27 (s, 1H), 5.13 (s, 1H), 4.06 – 3.94 (m, 1H), 2.98 – 2.73 (m, 1H), 2.34 (s, 3H), 2.00 – 1.88 (m, 1H), 1.85 - 1.77 (m, 2H), 1.77 – 1.65 (m, 2H), 1.61 – 1.53 (m, 3H), 1.50 - 1.39 (m, 2H),

1.08 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 140.3, 137.1, 129.1, 126.6, 112.9, 68.7, 43.7, 43.0, 28.3, 26.1, 24.9, 24.1, 23.0, 21.2.

HRMS (ES^+) *m*/*z* 245.1905[$(M+H)^+$; calcd for $C_{17}H_{25}O$ 245.1905].



Adduct 25h.

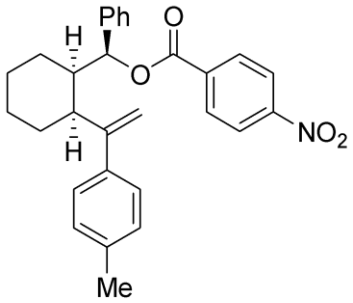
Pale-yellow oil (condition a: 46 mg, 63%; condition b: 38 mg, 52%)

IR (neat) 3432 (br), 3027, 2927, 2853, 1623, 1511, 1450, 1384, 1019, 897, 826, 762, 732, 702 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 3H), 7.13 – 7.04 (m, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.30 (s, 1H), 5.25 (s, 1H), 4.99 – 4.94 (m, 1H), 2.74 – 2.67 (m, 1H), 2.33 (s, 3H), 1.94 – 1.76 (m, 5H), 1.66 (d, *J* = 2.0 Hz, 1H), 1.63 - 1.56 (m, 2H), 1.47 – 1.39 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 144.9, 140.5, 137.0, 129.0, 128.2, 127.1, 126.8, 126.5, 113.4, 75.6, 44.0, 42.7, 28.5, 25.4, 24.7, 24.4, 21.2.

HRMS (ES^+) *m*/*z* 307.2066 [$(M+H)^+$; calcd for $C_{22}H_{27}O$ 307.2062].



Derivative 26.

To the three-component adduct **25h** (33 mg, 0.11 mmol) in pyridine (0.4 mL) was added 4-nitrobenzoyl chloride (23 mg, 0.12 mmol). The reaction mixture was stirred at room temperature for 2 hours before addition of 1N HCl (1 mL). The reaction mixture was extracted with hexanes (3×3 mL), washed with 1N HCl (2×3 mL), and brine (6 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:20 EtOAc/hexanes) to give compound **26**.

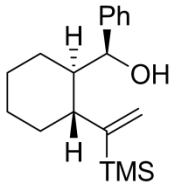
Colorless crystal (45 mg, 91%, m.p. 113-114 ^oC).

IR (neat) 2925, 1726, 1528, 1345, 1272, 1100, 826, 719 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.9 Hz, 2H), 8.25 (d, *J* = 8.9 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.14 – 7.06 (m, 4H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.28 (d, *J* = 6.8 Hz, 1H), 5.30 (s, 1H), 5.14 (s, 1H), 2.80 – 2.73 (m, 1H), 2.35 (s, 3H), 2.31 – 2.26 (m, 1H), 1.94 – 1.80 (m, 3H), 1.73 – 1.65 (m, 1H), 1.64 – 1.56 (m, 3H), 1.51 – 1.45 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 150.7, 150.5, 140.1, 140.0, 137.2, 136.0, 130.8, 129.1, 128.5, 127.9, 126.8, 126.83, 123.81, 114.0, 79.2, 42.7, 41.8, 28.1, 25.7, 24.4, 24.0, 21.2.

HRMS (ES^+) *m*/*z* 456.2178 [$(M+H)^+$; calcd for $C_{29}H_{30}NO_4$ 456.2175].



Alcohol S2. To a solution of *trans*-TMS linchpin **20** (30 mg, 0.14 mmol) in THF (0.4 mL) at – 78 ^oC was added PhLi (94 µL, 0.16 mmol, 1.7 M in dibutyl ether) dropwise. After 30 min, the reaction mixture was quenched with H_2O (2 mL), diluted with Et_2O (2 mL) and extract with Et_2O (3×3 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash

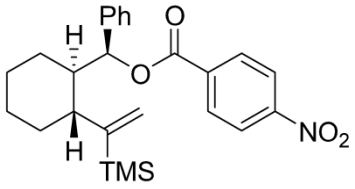
chromatography (1:20 EtOAc /hexanes) to give compound **S2** as a colorless oil (34 mg, 85%).

IR (neat) 3417 (br), 2927, 2852, 1450, 1248, 1018, 924, 836, 758, 701 cm^{-1}.

^1H NMR (500 MHz, C_6D_6) δ 7.30 (d, *J* = 7.3 Hz, 2H), 7.24 – 7.20 (m, 2H), 7.14 – 7.08 (m, 1H), 5.76 (d, *J* = 2.6 Hz, 1H), 5.59 (d, *J* = 2.6 Hz, 1H), 4.88 (d, *J* = 4.4 Hz, 1H), 2.48 (td, *J* = 11.3, 3.5 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.76 – 1.66 (m, 1H), 1.64 – 1.57 (m, 2H), 1.52 – 1.45 (m, 1H), 1.45 - 1.37 (m, 1H), 1.22 – 1.12 (m, 2H), 1.08 – 1.02 (m, 1H), 1.00 – 0.94 (m, 1H), 0.19 (s, 9H).

^{13}C NMR (125 MHz, C_6D_6) δ 156.9, 145.5, 128.2, 126.7, 125.9, 124.3, 72.6, 48.7, 36.5, 27.2, 26.6, 23.5, -0.8.

HRMS (ES^+) *m/z* 311.1805 [$(M+Na)^+$; calcd for $C_{18}H_{28}OSiNa$ 311.1807].



Derivative 27. Following the procedure for **26**, derivative **27** was prepared from **S2** (19 mg, 0.066 mmol) and isolated as a white solid.

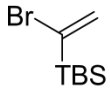
Colorless crystal (29 mg, near quant., m.p. 93-94 °C).

IR (neat) 2930, 2856, 1730, 1607, 1529, 1347, 1280, 1101, 840, 720, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.13 (s, 1H), 5.73 (s, 1H), 5.60 (s, 1H), 2.31 (td, *J* = 11.4, 3.4 Hz, 1H), 1.96 (t, *J* = 11.2 Hz, 1H), 1.86 – 1.71 (m, 4H), 1.56 – 1.47 (m, 1H), 1.36 – 1.24 (m, 1H), 1.22 - 1.09 (m, 2H), 0.05 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 155.5, 150.7, 140.3, 136.1, 130.8, 128.4, 127.3, 125.3, 123.9, 77.4, 46.9, 36.2, 26.9, 26.4, 24.9, -0.8.

HRMS (ES^+) *m/z* 460.1917 [$(M+Na)^+$; calcd for $C_{25}H_{31}NO_4NaSi$ 460.1920].



(1-Bromovinyl)(tert-butyl)dimethylsilane (29). To neat *tert*-butyldimethyl(vinyl)silane (6.73 mL, 35 mmol) was added dropwise liquid Br_2 (2.1 mL, 41 mmol) at –78 °C. After addition, the mixture was warmed to room temperature and stirred for 2 h. The flask was then fitted with a water-cooled condenser, and Et_2NH (19.9 mL, 193 mmol) was cautiously added with continued stirring. After the addition was completed, the reaction mixture was heated at reflux for 12 hours, during which time a precipitate of diethylamine hydrochloride formed. The salts were separated from the cooled suspension by filtration and washed with Et_2O (3×30 mL). The ether filtrate was carefully washed, first with 10 mL portions of 10% hydrochloric acid until the aqueous layer remains acidic (pH ca. 2), then with water (30 mL) and brine (30 mL). The ether solution was dried with anhydrous Na_2SO_4, concentrated, and purified by flash chromatography (hexanes) to give compound **29**.

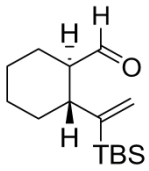
Colorless oil (5.35g, 69%)

IR (neat) 2930, 2858, 1469, 1252, 913, 827, 776 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 6.39 (d, *J* = 1.8 Hz, 1H), 6.21 (d, *J* = 1.8 Hz, 1H), 0.96 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 131.7, 26.9, 17.1, -5.7.

HRMS (CI^+) *m*/*z* 220.0273 [$(M)^+$; calcd for $C_8H_{17}BrSi$ 220.0283].



***Trans*-TBS linchpin 31**: To a vigorously stirred mixture of magnesium turnings (197 mg, 8.2 mmol) in THF (1.3 mL) was added a few drops of (1-Bromovinyl) tert-

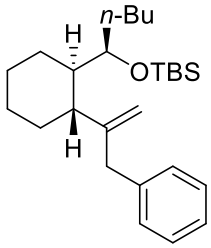
butyldimethylsilane (1.5 g, 6.8 mmol) in THF (1.3 mL). After the reaction initiation (iodine crystals were added), another 1.3 mL THF was added followed by the addition of the remaining (1-Bromovinyl)trimethylsilane solution. The reaction mixture was heated to reflux and kept for another hour. After cooling to room temperature, freshly prepared Grignard reagent was diluted with 1.3 mL THF and slowly cannulated into a suspension of CuBr·DMS (467 mg, 2.3 mmol) in THF (2.8 mL) and dimethyl sulfide (2.8 mL), followed by the addition of HMPA (2.4 mL, 13.8 mmol) at –78 ^{o}C. Then to this mixture was added dropwise a THF (3 mL) solution of cyclohex-1-ene-1-carbaldehyde (485 mg, 4.4 mmol) and TMSCl (1.1 mL, 8.7 mmol) via syringe pump over 30 minutes. After another hour, the reaction mixture was warmed up to room temperature and quenched with 1 N HCl (10 mL) and extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude residue was then dissolved in MeOH (30 mL) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (1 mL, 6.7 mmol) was added. After stirring for 1 hour, the reaction mixture was directly concentrated and purified by column chromatography with silica gel (hexanes to 2:1 CH_2Cl_2/hexanes) to afford compound **31** as colorless oil (800 mg, 72 %) over two steps.

IR (neat) 2929, 2856, 2705, 1725, 1250, 824, 768 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J* = 3.5 Hz, 1H), 5.80 (dd, *J* = 1.8, 0.9 Hz, 1H), 5.51 (d, *J* = 1.7 Hz, 1H), 2.50 (tt, *J* = 11.4, 3.4 Hz, 1H), 2.26 (td, *J* = 11.4, 3.2 Hz, 1H), 1.94 – 1.72 (m, 4H), 1.48 – 1.20 (m, 3H), 1.14 – 0.98 (m, 1H), 0.87 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 152.6, 127.3, 55.1, 43.4, 34.8, 27.1, 26.9, 26.5, 25.0, 17.3, -5.4, -5.5.

HRMS (ES^+) *m/z* 253.1983 [$(M+H)^+$; calcd for $C_{15}H_{29}OSi$ 253.1988].



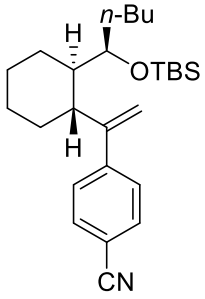
Adduct 32. To a solution of linchpin **31** (50 mg, 0.20 mmol) in freshly degassed Et_2O (0.5 mL, degassed by three freeze-pump-thaw cycles) at −78 °C was added *n*-BuLi (86 µL, 0.22 mmol, 2.5 M in hexanes). After stirring for 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (82 mg, 0.40 mmol) and *t*-BuOK (23 mg, 0.20 mmol) in freshly distilled HMPA (1 mL) in a microwave vial (2 - 5 mL) via cannula at room temperature. The reaction mixture was purged under a positive pressure of N_2 and then on high vacuum to remove Et_2O. After the vial was refilled with N_2, the resulting mixture was microwaved (Biotage: "high" level of absorption setting) at 100 ^oC for 5 min, followed by the addition of benzyl bromide (48 uL, 0.40 mmol). The resulting reaction mixture was stirred for 2 h at room temperature. then quenched with a saturated aqueous solution of NH_4Cl (3 mL) and extracted with Et_2O (3×5 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (hexanes) to give compound **32** as a colorless oil 38 mg in 48% yield.

IR (neat) 3074, 2929, 2855, 1462, 1253, 1078, 900, 836, 773 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 2H), 4.85 (s, 1H), 4.42 (s, 1H), 3.79 (dd, *J* = 9.4, 5.0 Hz, 1H), 3.30 (d, *J* = 16.4 Hz, 1H), 3.22 (d, *J* = 16.4 Hz, 1H), 2.20 (t, *J* = 11.4 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.70 – 1.64 (m, 3H), 1.52 – 1.40 (m, 3H), 1.34 – 1.26 (m, 4H), 1.22 – 1.11 (m, 4H), 0.93 - 0.97 (m, 3H), 0.90 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 140.1, 129.8, 128.3, 126.0, 112.3, 72.3, 47.7, 42.9, 40.2, 35.3, 34.4, 28.5, 26.8, 26.5, 26.3, 23.8, 23.2, 18.5, 14.3, -3.0, -4.2.

HRMS (CI^+) *m*/*z* 401.3252 [$(M+H)^+$; calcd for $C_{26}H_{45}OSi$ 401.3240].



Adduct 33. To a solution of linchpin **27** (50 mg, 0.20 mmol) in freshly degassed Et_2O (0.5 mL, degassed by three freeze-pump-thaw cycles) at –78 °C was added *n*-BuLi (86 µL, 0.22 mmol, 2.5 M in hexanes). After stirring for 30 min, the resulting solution was transferred to a suspension of CuBr·DMS (82 mg, 0.40 mmol) and *t*-BuOK (23 mg, 0.20 mmol) in freshly distilled HMPA (1 mL) in a microwave vial (2 - 5 mL) via cannula at room temperature. The reaction mixture was purged under a positive pressure of N_2 and then on high vacuum to remove Et_2O. After the vial was refilled with N_2, the resulting mixture was microwaved (Biotage: "high" level of absorption setting) at 100 °C for 5 min. A pre-mixed solution of $Pd(PPh_3)_4$ (12 mg, 10 µmol) and 4-iodobenzonitrile (92 mg, 0.40 mmol) in THF (0.5 mL) was then added. The resulting mixture was stirred at room temperature overnight before addition of a saturated aqueous solution of NH_4Cl (3 mL). The mixture was extracted with Et_2O (3×5 mL) and the combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by flash chromatography (1:25 EtOAc/hexanes) to give compound **33** as a colorless oil 50 mg in 61% yield.

IR (neat) 2930, 2855, 2228, 1605, 1462, 1252, 1085, 856, 773 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 5.41 (s, 1H), 5.16 (s, 1H), 3.73 (dd, *J* = 9.6, 4.7 Hz, 1H), 2.56 – 2.44 (m, 1H), 1.99 (d, *J* = 11.3 Hz, 1H), 1.85 - 1.77 (m, 1H), 1.76 - 1.65 (m, 2H), 1.56 – 1.46 (m, 2H), 1.37 – 1.31 (m, 1H), 1.30 - 1.19 (m, 5H), 1.18 – 1.08 (m, 1H), 1.07- 0.96 (m, 1H), 0.89 – 0.85 (m, 4H), 0.77 (s, 9H), -0.09 (s, 3H), -0.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 148.3, 132.2, 127.3, 119.2, 115.2, 110.7, 72.0, 44.8,

44.4, 37.1, 35.0, 28.2, 26.9, 26.3, 26.1, 23.9, 23.0, 18.3, 14.2, -3.1, -4.8.

HRMS (ES^+) *m*/*z* 412.3025[$(M+H)^+$; calcd for $C_{26}H_{42}NOSi$ 412.3036].

III. Computational Details

(a) Computational methods

All DFT calculations were performed with the Gaussian 09[1].Geometry optimizations were carried out at the M06 level of theory[2].The SDD basis set[3] was used for Cu, Br, and I, and the 6-31G(d) basis set[4] for the other atoms(keyword 5D was used in the calculations).The vibrational frequencies were computed at the same level to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. A quasiharmonic correction was applied duringthe entropy calculation by setting all positive frequencies that are lessthan 100 cm^{-1} to 100 cm^{-1}[5].The single-point energies and solvent effects in tetrahydrofuran (THF) were computed at the M06/6-311+G(d,p)[SDD, for Cu, Br, and I] level using the gas-phase optimized structures. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the CPCM model[6],where UFF radii were used.The frontier molecular orbitals (FMOs) and their energies werecomputed at the HF/6-311+G(d,p)[SDD, for Cu, Br, and I] level using the M06-2X/6-31G(d)[SDD, for Cu, Br, and I]geometries.

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; *Gaussian 09, revision D.01*; Gaussian Inc.: Wallingford, CT, 2013.

[2] (a) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.***2008**, *41*, 157.

[3] (a) Szentpaly, L. V.; Fuentealba, P.; Preuss, H.; Stoll, H. *Chem. Phys. Lett.***1982**, *93*, 555. (b) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.***1987**, *86*, 866. (c) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.***1989**, *91*, 1762.

[4] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio MolecularOrbital Theory*; Wiley: New York, 1986.

[5] (a) Zhao, Y.; Truhlar, D. G. *Phys. Chem. Chem. Phys.***2008**, *10*, 2813. (b) Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B***2011**, *115*, 14556.

[6] (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669. (c) Takano, Y.; Houk, K. N. *J. Chem. Theory Comput.***2005**, *1*, 70.

(b)Coordinates and energies of stationary points

A

G_{sol} = -687.041269 Hartree

C	-2.806075	-0.177045	1.447783
H	-2.205635	-0.120988	2.367920
H	-3.442391	-1.070632	1.492946
H	-3.462933	0.704943	1.407373
C	-1.928133	-0.227798	0.199638
C	-1.089753	1.023370	0.118851
H	-1.700010	1.941475	0.103082
C	0.244782	1.123992	0.022508
C	0.891544	2.481219	-0.081530
H	1.611283	2.657035	0.732904
H	1.462112	2.595821	-1.016214
H	0.146691	3.289523	-0.044350
O	-2.676808	-0.363156	-0.937817
Li	-3.357154	-0.177037	-2.393773
Si	1.365283	-0.394953	-0.007814
C	3.147489	0.162397	-0.299293
H	3.504392	0.839459	0.488492
H	3.814958	-0.710611	-0.309268
H	3.267394	0.677751	-1.261977
C	0.891601	-1.548731	-1.427356
H	-0.194778	-1.698043	-1.480182
H	1.217869	-1.118546	-2.384668
H	1.374222	-2.530364	-1.322589
C	1.344461	-1.316460	1.640241
H	0.344327	-1.684269	1.903046
H	2.025721	-2.178683	1.611237
H	1.678919	-0.656151	2.451962
H	-1.245664	-1.097691	0.328496
C	-1.802346	3.574908	-0.082579
H	-2.846727	3.617529	0.257898
H	-1.708419	4.175194	-0.995599
H	-1.162409	4.027376	0.688326
C	-1.351072	2.149718	-0.353153
H	-2.038434	1.715691	-1.113468
C	-1.449116	1.304363	0.910308
H	-1.307924	1.863186	1.848629
C	-1.672098	-0.049917	0.987656
C	-1.782984	-0.692041	2.352692
H	-2.822762	-1.001900	2.546366
H	-1.166424	-1.596421	2.435646
H	-1.487467	-0.001532	3.154983
C	-4.031265	-0.984642	-0.703952
H	-4.411164	-1.696022	-1.449802
H	-4.568756	-1.168843	0.236272
H	-4.287597	0.027978	-1.042501
C	-1.268544	-0.855960	-2.090337
H	-1.254572	0.199941	-2.385272
H	-0.227654	-1.204574	-2.032192
H	-1.763539	-1.428723	-2.888246
C	-1.770951	-2.944308	0.054048
H	-2.343333	-3.266054	0.933781
H	-1.995928	-3.642165	-0.763794
H	-0.700615	-3.044788	0.286747
Si	-2.171878	-1.183586	-0.471602
O	-0.038236	2.096633	-0.783209
Li	1.552281	1.822229	-1.317157
Cu	0.366704	0.326761	0.490023
I	2.684621	-0.410079	-0.067113

Ac

G_{sol} = -895.938339 Hartree

Ap

G_{sol} = -895.948494 Hartree

C	-2.916897	2.083311	0.861396
H	-2.770738	2.969099	1.491816
H	-3.520353	1.364198	1.430588
H	-3.485231	2.385412	-0.029337
C	-1.572478	1.520934	0.454816
C	-0.708893	2.563080	-0.201264
H	-1.269075	3.386721	-0.675020
C	0.641560	2.561693	-0.208971
C	1.348954	3.707658	-0.875872
H	1.984158	4.237398	-0.151773
H	2.031717	3.357561	-1.664083
H	0.658309	4.444679	-1.320550
O	-1.747799	0.406303	-0.478245
H	-1.043891	1.113738	1.333895
C	-2.243400	-1.582363	1.605131
H	-2.633820	-0.895695	2.367320
H	-2.694064	-2.566989	1.788422
H	-1.159103	-1.680492	1.756474
C	-4.444964	-0.768818	-0.443726
H	-4.942090	-0.196955	0.348970
H	-4.610620	-0.242672	-1.393079
H	-4.948613	-1.742706	-0.514644
C	-1.921866	-2.213263	-1.407940
H	-0.852830	-2.413172	-1.238234
H	-2.437379	-3.181346	-1.355461
H	-2.053886	-1.835442	-2.431957
Si	-2.612897	-1.019146	-0.139434
Cu	1.644631	1.025876	0.353714
I	2.030780	-1.420169	0.016636
Li	-0.035760	0.266471	-1.268726

B

G_{sol} = -687.041467 Hartree

C	0.756613	-0.368551	-3.430179
H	1.462968	0.415657	-3.745146
H	-0.240034	0.086774	-3.343749
H	0.727133	-1.134682	-4.216039
C	1.241813	-0.983499	-2.121319
H	0.477348	-1.735805	-1.805209
C	1.305364	0.086426	-1.014335
H	2.035330	0.849893	-1.339885
H	1.740356	-0.409458	-0.129492
C	-0.004066	0.730679	-0.650446
C	-0.201661	2.039563	-0.851809
H	0.572070	2.676674	-1.292201
H	-1.133252	2.544961	-0.590093
C	-2.422958	-1.174645	-1.198384
H	-1.830459	-1.884437	-1.790028
H	-3.247814	-1.729390	-0.729343
H	-2.861763	-0.445870	-1.893407
C	-0.632704	-1.595245	1.266185
H	-1.420900	-2.179287	1.760633
H	0.008255	-2.297667	0.716624
H	-0.022406	-1.127025	2.050141
C	-2.539518	0.807771	1.107223
H	-1.993961	1.391735	1.859637
H	-3.082235	1.512841	0.463460
H	-3.290473	0.200580	1.631254
Si	-1.384532	-0.304762	0.114981
O	2.461643	-1.573274	-2.276642
Li	3.955204	-2.143185	-2.485389

Bc

G_{sol} = -895.949807 Hartree

C	2.02082	-0.10361	-0.7414
C	1.56364	-0.03945	-2.03749
C	2.22834	-1.4445	-0.07088
H	1.53317	-1.55162	0.7794
H	2.00276	-2.25877	-0.78237
C	3.67609	-1.61465	0.41517
H	3.82023	-0.91125	1.26784
C	3.90941	-3.0221	0.93725
H	3.76247	-3.74844	0.12499

H	4.93841	-3.12696	1.30508
H	3.22463	-3.27521	1.75865
O	4.55586	-1.30895	-0.61127
Li	6.00313	-1.19683	-1.54079
Si	2.22305	1.50455	0.27062
C	1.41454	1.23052	1.94857
H	1.94514	0.4663	2.53243
H	1.42757	2.16017	2.53335
H	0.36818	0.91293	1.84938
C	4.02963	1.98341	0.50241
H	4.51443	2.18946	-0.46302
H	4.08459	2.90428	1.10115
H	4.61657	1.2103	1.01322
C	1.38023	2.90703	-0.65544
H	1.42824	3.82771	-0.05821
H	1.88888	3.1124	-1.60789
H	0.32353	2.70005	-0.8679
H	1.2967	-0.94653	-2.58958
H	1.27067	0.89924	-2.50957
I	5.52077	0.469	-3.6553
Cu	3.67431	-0.06406	-1.99286

Bp

G_{sol} = -895.949383 Hartree

C	1.8729	1.33804	-0.4178
C	2.30493	1.75934	-1.62575
C	0.84776	2.18992	0.29273
H	1.30048	2.63788	1.19236
H	0.49899	3.02946	-0.34097
C	-0.36171	1.39386	0.76457
H	-0.02522	0.67105	1.52953
C	-1.45045	2.28608	1.31927
H	-1.85155	2.93154	0.52593
H	-2.28121	1.71114	1.74975
H	-1.04784	2.92707	2.11377
H	1.99658	2.72167	-2.06058
H	3.05264	1.20702	-2.20152
O	-0.86247	0.6266	-0.35551
Si	-2.02648	-0.60789	-0.21963
Cu	2.27702	-0.41626	0.26003
C	-1.49198	-1.74818	-1.61987
H	-1.4331	-1.22494	-2.58869
H	-0.53045	-2.24433	-1.40234
H	-2.218	-2.55853	-1.76505
C	-1.89898	-1.45892	1.43518
H	-2.16766	-0.80732	2.27638
H	-2.5782	-2.32173	1.46006
H	-0.87964	-1.83821	1.60082
C	-3.73022	0.08029	-0.57144
H	-4.46424	-0.73355	-0.64518
H	-4.07619	0.76695	0.21077
H	-3.7412	0.62526	-1.5243
Li	0.53075	-0.01192	-1.51778
I	2.10755	-2.84421	0.60508

BrCuBr$^-$

G_{sol} = -224.401805 Hartree

Cu	-0.31317	0.22678	0.
Br	1.97897	0.22678	0.
Br	-2.60532	0.22678	0.

Cc

G_{sol} = -924.311820 Hartree

C	2.04327	-0.10947	-0.73345
C	1.57966	-0.033	-2.02425
C	2.22899	-1.45629	-0.06874
H	1.47928	-1.58143	0.73257
H	2.05837	-2.26205	-0.8053
C	3.6463	-1.61533	0.49671
H	3.73064	-0.91915	1.36737
C	3.86164	-3.02378	1.02993
H	3.76048	-3.7494	0.20962
H	4.87338	-3.12093	1.4441

H	3.1397	-3.28463	1.81714
O	4.56529	-1.29108	-0.47382
Li	5.81388	-0.99476	-1.58282
Si	2.23033	1.48254	0.29917
C	1.36263	1.20955	1.94863
H	1.87409	0.45619	2.56189
H	1.3372	2.14432	2.52527
H	0.32544	0.87863	1.80449
C	4.0355	1.9431	0.58321
H	4.49221	2.31616	-0.34488
H	4.10557	2.742	1.3352
H	4.63184	1.0876	0.92389
C	1.40575	2.90285	-0.62097
H	1.47854	3.82347	-0.02581
H	1.89806	3.09871	-1.58384
H	0.34162	2.71274	-0.81284
H	1.31879	-0.93552	-2.58651
H	1.27801	0.90911	-2.48462
Cu	3.68654	0.03064	-2.01728
C	5.25358	0.3777	-3.18761
H	6.09566	0.92715	-2.71837
H	5.69073	-0.48458	-3.7318
H	4.91386	1.04563	-3.98891

Cp

G_{sol} = -924.315879 Hartree

C	-1.74314	-1.46399	-0.49243
C	-2.28654	-1.7937	-1.68524
C	-0.62301	-2.34996	0.00869
H	-0.97884	-2.94297	0.86762
H	-0.2815	-3.07685	-0.75659
C	0.57271	-1.55046	0.50562
H	0.25424	-0.98269	1.39654
C	1.76719	-2.41894	0.82984
H	2.1425	-2.90352	-0.08162
H	2.58836	-1.84127	1.276
H	1.48514	-3.20203	1.54526
H	-2.00583	-2.70056	-2.24384
H	-3.10625	-1.21689	-2.12525
O	0.93096	-0.58155	-0.51327
Si	1.86144	0.79976	-0.1863
Cu	-2.13834	0.21741	0.43669
C	1.14734	2.02203	-1.43029
H	1.16177	1.62736	-2.45919
H	0.12055	2.32064	-1.16227
H	1.73488	2.94881	-1.4567
C	1.5717	1.38731	1.56052
H	1.96374	0.69429	2.31623
H	2.06129	2.3577	1.71799
H	0.49414	1.52034	1.73902
C	3.66365	0.4747	-0.57018
H	4.24627	1.4031	-0.49842
H	4.11225	-0.25004	0.12047
H	3.78297	0.08369	-1.58882
C	-2.36211	1.94633	1.23578
H	-3.41426	2.26713	1.17469
H	-2.09766	1.91664	2.30659
H	-1.76101	2.75463	0.78495
Li	-0.60909	-0.00156	-1.52331

CuBr

G_{sol} = -210.807207 Hartree

Br	-2.44012	0.36649	-0.12536
Cu	-4.6539	0.36649	-0.12536

CuI

G_{sol} = -208.851716 Hartree

I	-1.26615	0.55789	-0.11077
Cu	-3.64474	0.55789	-0.11077

D

G_{sol} = -726.303854 Hartree

C -2.855047 -0.400613 0.310183
H -2.814603 -0.641995 1.401423
C -1.398866 -0.274084 -0.154002
H -1.399756 -0.045417 -1.234794
H -0.891313 -1.247523 -0.032701
C -0.635970 0.812030 0.596175
H -1.243734 1.731304 0.583394
H -0.555388 0.506268 1.655738
C 0.737783 1.092888 0.045969
C 1.048196 2.306977 -0.423805
H 0.322056 3.126450 -0.426637
H 2.033223 2.551908 -0.824994
C -3.520038 -1.582587 -0.389220
H -4.561833 -1.679473 -0.056427
H -3.527505 -1.409913 -1.476114
H -3.002425 -2.533097 -0.192497
C 1.803933 -1.420081 -1.462244
H 2.623869 -2.149690 -1.518258
H 0.859902 -1.976830 -1.412285
H 1.802350 -0.846367 -2.398813
C 3.758851 0.491722 -0.124387
H 3.906787 0.988379 -1.092821
H 3.941879 1.232552 0.664676
H 4.527034 -0.288892 -0.037472
C 1.935658 -1.263386 1.615830
H 2.715621 -2.036187 1.646924
H 2.072664 -0.616279 2.492578
H 0.965601 -1.767052 1.721772
Si 2.041018 -0.272209 0.015697
O -3.552784 0.752333 0.091097
Li -4.391136 2.105637 -0.166072

Dc

G_{sol} = -963.573633 Hartree

C 2.174047 -1.303475 -0.164627
H 2.785680 -1.074109 -1.070470
C 0.920481 -2.019843 -0.670596
H 0.315473 -2.324368 0.201155
H 1.233273 -2.951844 -1.167905
C 0.068765 -1.213903 -1.649884
H 0.712579 -0.836094 -2.464951
H -0.647468 -1.904036 -2.129206
C -0.732388 -0.072897 -1.060308
C -0.840502 1.127134 -1.741129
H -0.317778 1.284227 -2.691099
H -1.598876 1.873472 -1.502579
C 2.985864 -2.245607 0.714775
H 3.904874 -1.751747 1.058767
H 2.397986 -2.519178 1.604044
H 3.269449 -3.167678 0.187838
C -3.247802 0.913562 0.439261
H -3.939010 0.711108 1.269011
H -2.812003 1.907509 0.612808
H -3.838072 0.954841 -0.485398
C -2.727755 -2.096154 0.097629
H -3.232890 -2.131072 -0.877057
H -2.001975 -2.919408 0.129321
H -3.483177 -2.290796 0.871361
C -1.058278 -0.408703 2.068538
H -1.748704 -0.772914 2.843097
H -0.149715 -1.022303 2.080401
H -0.761165 0.615302 2.339878
Si -1.917504 -0.418521 0.390471
O 1.888752 -0.141627 0.531920
Li 2.473323 1.337841 1.195408
Cu 0.574104 1.277491 -0.248625
C 1.332179 2.991755 0.500157
H 2.360598 3.284493 0.201772
H 1.264720 3.142725 1.598536
H 0.704578 3.792203 0.089733

Dp

G_{sol} = -963.574806 Hartree

C -1.675123 -2.093258 -1.940738

H	-1.623251	-3.185050	-2.035100
H	-1.150441	-1.654908	-2.801673
H	-2.729066	-1.792535	-1.993504
C	-1.026519	-1.637628	-0.651642
H	-1.548844	-2.092675	0.210962
C	0.447687	-1.991617	-0.580782
H	0.968501	-1.428590	-1.377754
H	0.550637	-3.049979	-0.863805
C	1.126039	-1.727931	0.776416
H	1.313745	-2.696043	1.278833
H	0.406708	-1.194221	1.421392
C	2.393693	-0.903273	0.674005
C	3.527146	-1.437388	1.151070
H	4.482616	-0.909382	1.119428
H	3.565062	-2.439515	1.604750
O	-1.179641	-0.198194	-0.551536
C	-2.004141	2.347746	0.137694
H	-2.727393	2.973119	0.676763
H	-1.007293	2.673851	0.473706
H	-2.114930	2.591181	-0.929741
C	-4.036609	-0.005554	0.055779
H	-4.280253	0.234526	-0.987065
H	-4.181124	-1.085003	0.197870
H	-4.766975	0.505899	0.696862
C	-1.887301	0.139838	2.276431
H	-0.865415	0.465638	2.515109
H	-2.575792	0.667016	2.950927
H	-1.959105	-0.931432	2.503614
Si	-2.299005	0.529209	0.497246
Cu	2.222044	0.814141	-0.158342
Li	0.138350	1.083149	-1.096899
C	1.753956	2.480514	-1.123507
H	1.137826	3.236273	-0.601504
H	2.753995	2.934242	-1.195655
H	1.406717	2.465977	-2.179301

E

G_{sol} = -878.615574 Hartree

C	-2.37049	1.14951	1.23644
C	-1.6492	1.03659	0.04619
C	-0.94678	2.14926	-0.4607
C	-1.01165	3.34384	0.25581
C	-1.73443	3.45172	1.44259
C	-2.4187	2.35029	1.93823
H	-2.90896	0.27485	1.6081
H	-0.48706	4.22076	-0.12158
H	-1.76222	4.40127	1.97606
H	-2.99083	2.42203	2.86232
C	-0.12016	1.97833	-1.73539
H	-0.83626	1.60388	-2.5059
C	0.43398	3.29062	-2.27651
H	0.97391	3.08313	-3.20829
H	-0.35113	4.03075	-2.48828
H	1.15259	3.7277	-1.56821
C	-1.61008	-0.29079	-0.62042
C	-2.50862	-0.63568	-1.54895
H	-2.51093	-1.62208	-2.0212
H	-3.28158	0.05617	-1.89215
C	0.87306	-0.76994	1.19351
H	1.09693	0.28999	1.00037
H	0.39375	-0.78933	2.1816
H	1.80706	-1.34662	1.29735
C	-1.13541	-3.01165	0.75687
H	-0.39685	-3.7517	1.09425
H	-1.71253	-2.6884	1.63409
H	-1.82974	-3.51664	0.07184
C	0.657	-2.17597	-1.57909
H	1.66103	-2.55798	-1.32644
H	0.12392	-3.02475	-2.02816
H	0.72854	-1.40464	-2.36011
Si	-0.31536	-1.53547	-0.07429
O	0.88141	1.06977	-1.52955
Li	1.95245	-0.05666	-1.00485

Ec

G_{sol} = -1115.897317 Hartree

C	3.44583	1.3611	-1.94785
C	2.46586	0.37935	-1.85613
C	1.64739	0.26123	-0.72784
C	1.82456	1.16209	0.3488
C	2.81258	2.13925	0.23553
C	3.61931	2.24674	-0.89438
H	4.07174	1.42466	-2.8368
H	2.33199	-0.33277	-2.67111
H	2.96328	2.84587	1.04966
H	4.38138	3.02308	-0.94451
C	0.62827	-0.82838	-0.71599
C	-0.21555	-0.98108	-1.81351
H	-0.16125	-0.30446	-2.67194
H	-0.7826	-1.8984	-1.98061
Si	0.7765	-2.30077	0.49362
C	0.52281	-3.88802	-0.49371
H	1.18492	-3.93249	-1.36821
H	0.74224	-4.75924	0.13935
H	-0.51181	-3.99541	-0.84633
C	2.51429	-2.34378	1.21542
H	2.65479	-3.26254	1.80128
H	3.26361	-2.33993	0.41201
H	2.73026	-1.49042	1.86974
C	-0.54568	-2.27119	1.8364
H	-1.54278	-2.38472	1.38559
H	-0.39957	-3.11149	2.53003
H	-0.55043	-1.33847	2.41343
C	0.92927	1.0632	1.58123
H	1.13177	0.06484	2.03159
C	1.25488	2.08104	2.66434
H	2.28712	1.99923	3.03031
H	1.09107	3.10422	2.29678
H	0.57931	1.91371	3.51225
O	-0.41619	1.15118	1.25353
Li	-2.01179	1.77044	1.11239
Cu	-1.12657	0.09165	-0.3395
C	-3.03235	0.72886	-0.45334
H	-3.20196	1.78695	-0.74229
H	-3.49297	0.16015	-1.26993
H	-3.68997	0.52296	0.41706

Ep

G_{sol} = -1115.906710 Hartree

C	-0.21965	3.51813	-1.60045
C	0.72593	2.72397	-0.96359
C	0.36481	1.78621	0.01498
C	-1.00772	1.65774	0.34044
C	-1.94365	2.46526	-0.30466
C	-1.56313	3.39251	-1.26967
H	0.09632	4.24154	-2.35098
H	1.78336	2.83558	-1.20138
H	-3.00052	2.37223	-0.05776
H	-2.31442	4.01367	-1.75417
C	1.42241	0.9944	0.67591
C	2.28552	0.32019	-0.11911
H	2.22458	0.32447	-1.21823
H	3.14376	-0.22354	0.29202
C	-1.43046	0.63654	1.36985
H	-0.85829	0.83532	2.29411
C	-2.90153	0.59988	1.71732
H	-3.22322	1.55414	2.15108
H	-3.52955	0.39798	0.83765
H	-3.08447	-0.19149	2.45377
O	-0.99369	-0.69821	0.98698
Cu	1.64922	1.00792	2.63094
Si	-1.5028	-1.60032	-0.35589
C	-3.10915	-2.48471	0.02437
H	-3.3261	-3.23315	-0.75
H	-3.0512	-3.00824	0.98765
H	-3.96287	-1.79693	0.06796
C	-0.09207	-2.84066	-0.47115
H	0.03851	-3.40187	0.46707
H	-0.27946	-3.58671	-1.25418

H	0.85759	-2.34823	-0.73408
C	-1.62575	-0.58397	-1.91764
H	-2.44977	0.13898	-1.87736
H	-0.70393	-0.01605	-2.10311
H	-1.80051	-1.249	-2.77508
Li	0.83843	-0.96364	1.40449
C	1.89366	0.91226	4.52397
H	1.81602	-0.09852	4.95326
H	2.89492	1.29416	4.78029
H	1.15656	1.54297	5.04575

F

G_{sol} = -882.173283 Hartree

C	3.01361	-0.73517	-1.79826
C	1.62335	-0.11159	-1.8273
C	0.65819	-0.84514	-0.89417
C	1.19724	-0.94402	0.55507
C	2.61022	-1.53643	0.53567
C	3.57003	-0.78765	-0.38135
H	1.69167	0.94041	-1.51767
H	1.22222	-0.12844	-2.85303
H	2.95694	-1.76317	-2.19873
H	3.69305	-0.18318	-2.46576
H	0.55981	-1.68312	1.07888
H	3.01358	-1.59022	1.55733
H	2.54004	-2.5818	0.18371
H	3.70095	0.23479	0.00268
H	4.55776	-1.27308	-0.37585
H	0.62978	-1.89399	-1.25849
C	1.0302	0.35652	1.37884
H	-0.07101	0.53428	1.38552
O	1.67838	1.4513	0.87269
Li	2.21481	2.94266	0.53708
C	1.43368	0.13213	2.83648
H	2.5265	0.04044	2.91802
H	1.13242	1.0014	3.43653
H	0.9755	-0.76596	3.27929
C	-0.77183	-0.34815	-0.94117
C	-1.1194	0.79898	-1.53814
H	-0.39195	1.4648	-2.00831
H	-2.15597	1.13643	-1.58842
Si	-2.13818	-1.42105	-0.19376
C	-2.33596	-1.16685	1.66517
H	-3.19869	-1.73942	2.0348
H	-1.4514	-1.4851	2.23181
H	-2.51203	-0.10736	1.89586
C	-1.75908	-3.23745	-0.53442
H	-1.64825	-3.4292	-1.61018
H	-0.83527	-3.56658	-0.03971
H	-2.57541	-3.87335	-0.16517
C	-3.79285	-0.99607	-0.99283
H	-4.56436	-1.69584	-0.64251
H	-4.13079	0.01608	-0.73298
H	-3.74829	-1.06535	-2.08736

Fc

G_{sol} = -1119.435776 Hartree

C	-4.6203	-0.74252	-0.07782
C	-3.40594	-1.46864	0.48071
C	-2.10605	-0.64712	0.44248
C	-2.27971	0.80605	0.97784
C	-3.55375	1.43057	0.39437
C	-4.80608	0.59835	0.61159
H	-3.62155	-1.75419	1.52352
H	-3.25882	-2.40441	-0.07803
H	-4.48758	-0.57103	-1.16057
H	-5.51089	-1.37859	0.02978
H	-1.45828	1.39524	0.53788
H	-3.68138	2.45179	0.77692
H	-3.40798	1.53963	-0.6954
H	-4.97607	0.44381	1.69019
H	-5.68946	1.12187	0.21769
H	-1.85891	-0.51554	-0.6324
C	-2.07239	0.96948	2.51208

H	-0.96882	1.04401	2.63945
O	-2.53665	-0.08099	3.28315
Li	-2.95279	-0.97196	4.68729
C	-2.61941	2.28982	3.03982
H	-3.71823	2.30332	3.0137
H	-2.30851	2.4148	4.08571
H	-2.24736	3.15407	2.46992
C	-0.92759	-1.40269	1.06398
C	-0.94956	-2.78099	1.2475
H	-1.78438	-3.41722	0.94592
H	-0.0365	-3.33224	1.48289
Si	0.82961	-0.66778	1.24674
C	1.34475	-0.64651	3.06159
H	2.36356	-0.24551	3.16297
H	0.67602	-0.03476	3.68283
H	1.3449	-1.66399	3.47853
C	1.06189	1.04551	0.49153
H	0.64881	1.10842	-0.52445
H	0.62033	1.85139	1.09089
H	2.1411	1.24328	0.41702
C	2.03254	-1.79995	0.33101
H	3.0456	-1.37523	0.37001
H	2.08189	-2.80509	0.76927
H	1.75637	-1.90996	-0.72617
C	-2.08758	-2.92958	4.62111
H	-1.60213	-3.90626	4.50334
H	-1.6971	-2.55448	5.59036
H	-3.15523	-3.18539	4.78378
Cu	-1.60745	-1.89544	2.95529

Fp

G_{sol} = -1119.451284 Hartree

C	2.7034	2.84887	-0.10119
C	2.57056	1.34313	0.08924
C	1.36528	0.98003	0.96299
C	0.03578	1.58105	0.42859
C	0.22162	3.08618	0.17128
C	1.42989	3.44404	-0.68846
H	2.49796	0.84293	-0.88947
H	3.47608	0.93515	0.5628
H	2.89741	3.32044	0.87789
H	3.56886	3.08356	-0.7366
H	-0.68175	1.49924	1.26524
H	-0.70146	3.51193	-0.25642
H	0.35294	3.5717	1.15242
H	1.29472	3.08157	-1.71987
H	1.51372	4.53789	-0.76322
H	1.51272	1.52251	1.92216
C	-0.7098	0.89152	-0.73047
H	-1.48983	1.61159	-1.04777
O	-1.40471	-0.28096	-0.23048
Li	-0.39376	-1.61582	0.64405
C	0.04355	0.45657	-1.96938
H	0.77336	-0.33263	-1.73508
H	-0.67008	0.0518	-2.70006
H	0.57258	1.29404	-2.43777
C	1.30678	-0.50604	1.26384
C	0.92653	-0.85551	2.51329
H	0.71083	-0.12274	3.30728
H	0.88391	-1.90234	2.84031
Si	-3.07648	-0.28868	0.00703
C	-3.31635	-1.96818	0.80992
H	-4.37342	-2.1765	1.01787
H	-2.95402	-2.78189	0.16445
H	-2.79484	-2.02538	1.77896
C	-3.93408	-0.14764	-1.6489
H	-3.66261	0.78522	-2.16121
H	-3.65709	-0.98152	-2.3066
H	-5.02617	-0.15294	-1.53783
C	-3.56261	1.09543	1.16856
H	-4.64269	1.08304	1.36587
H	-3.04376	0.9929	2.1315
H	-3.31503	2.08442	0.75944
C	2.39965	-3.25262	-1.25537
H	3.49425	-3.2194	-1.38693

H	2.14923	-4.26547	-0.90398
H	1.95092	-3.13191	-2.25409
Cu	1.89808	-1.8747	-0.02622

G

G_{sol} = -882.181018 Hartree

C	2.99348	-0.84582	0.20381
C	3.82154	0.23778	-0.4768
C	3.13165	0.74965	-1.73404
C	1.7259	1.23769	-1.41183
C	0.88891	0.14108	-0.7421
C	1.57879	-0.37361	0.53558
H	3.7201	1.55108	-2.20451
H	3.95809	1.0809	0.22323
H	4.8293	-0.13584	-0.71221
H	2.92439	-1.72885	-0.4547
H	3.50268	-1.18076	1.11943
H	1.79988	2.11148	-0.73846
H	1.21302	1.59029	-2.32052
H	0.85792	-0.71743	-1.44088
H	1.66991	0.47489	1.23982
H	3.06826	-0.068	-2.47308
C	0.72824	-1.45489	1.23738
O	0.53043	-2.55016	0.44792
Li	0.29319	-3.85046	-0.47526
C	1.32092	-1.85045	2.58868
H	0.62235	-2.51391	3.11541
H	2.26124	-2.40404	2.45492
H	1.51789	-0.97718	3.23
H	-0.2466	-0.95727	1.46362
C	-0.53418	0.59974	-0.52343
C	-1.53381	-0.03974	-1.14383
H	-1.34477	-0.90317	-1.79039
H	-2.5821	0.24717	-1.04109
Si	-1.00593	2.11606	0.50859
C	-2.74348	1.85984	1.19646
H	-2.9976	2.67301	1.89031
H	-3.51102	1.84699	0.4116
H	-2.81093	0.91226	1.74803
C	-1.02158	3.65017	-0.5917
H	-1.66591	3.49036	-1.46695
H	-1.41018	4.51875	-0.0416
H	-0.01933	3.90712	-0.95907
C	0.12695	2.44976	1.98023
H	1.16054	2.67621	1.68744
H	-0.25809	3.32205	2.52853
H	0.15077	1.60384	2.68056

Gc

G_{sol} = -1119.446083 Hartree

C	-3.78067	-0.63495	2.82791
C	-2.60559	-1.05957	3.70673
C	-1.29994	-0.38755	3.29959
C	-1.45604	1.12597	3.20028
C	-2.61586	1.48054	2.26096
C	-3.92947	0.88778	2.80937
H	-0.49782	-0.64945	4.0047
H	-2.83753	-0.78632	4.75088
H	-2.49176	-2.15336	3.69342
H	-3.64165	-0.99981	1.79475
H	-4.69624	-1.1103	3.2063
H	-1.64339	1.55503	4.20144
H	-0.52634	1.58542	2.83067
H	-2.40792	0.94191	1.31445
H	-4.02722	1.20144	3.86678
H	-0.98573	-0.77152	2.31398
C	-5.19254	1.42826	2.09585
O	-5.04646	1.54286	0.72556
Li	-5.39008	1.69495	-0.94079
C	-6.43898	0.6221	2.43288
H	-7.32628	1.13723	2.04193
H	-6.3969	-0.37285	1.96798
H	-6.56875	0.49335	3.51815
H	-5.36496	2.44017	2.52713

C	-2.63341	2.96127	1.91417
C	-1.80663	3.39627	0.88664
H	-1.13189	2.708	0.3643
H	-1.59901	4.45474	0.71463
Si	-3.33518	4.34615	3.02082
C	-4.64396	5.30273	2.06071
H	-5.04456	6.13203	2.66034
H	-4.21746	5.72888	1.14123
H	-5.48426	4.65789	1.76697
C	-1.90844	5.5076	3.44222
H	-1.48963	5.99965	2.5547
H	-2.24152	6.29503	4.13258
H	-1.09377	4.95492	3.93134
C	-4.03441	3.76506	4.67322
H	-3.29867	3.18062	5.24207
H	-4.27744	4.65354	5.27422
H	-4.9485	3.16549	4.58276
C	-4.07337	3.13027	-1.8478
H	-3.91639	2.2572	-2.51419
H	-3.36989	3.88021	-2.22986
H	-5.07026	3.5504	-2.09704
Cu	-3.62491	2.91329	0.10339

Gp

G_{sol} = -1119.456000 Hartree

C	-0.44943	2.86949	0.9046
C	0.11122	4.01789	0.07856
C	1.573	3.76775	-0.2616
C	1.72048	2.44248	-0.9923
C	1.18261	1.25672	-0.17895
C	-0.29246	1.50805	0.2144
H	1.97641	4.59056	-0.86876
H	-0.46759	4.11038	-0.85663
H	-0.01327	4.96677	0.61945
H	0.07209	2.84817	1.87769
H	-1.51468	3.04624	1.12929
H	1.18189	2.50263	-1.95276
H	2.77214	2.24304	-1.24428
H	1.7558	1.24679	0.76801
H	-0.88196	1.5411	-0.7218
H	2.16557	3.74469	0.66913
C	-0.94783	0.43882	1.10238
O	-1.29422	-0.74521	0.34795
Li	0.08432	-1.68721	-0.53857
C	-0.13941	-0.00805	2.30125
H	-0.73681	-0.68428	2.92621
H	0.76814	-0.54519	1.98661
H	0.1655	0.84685	2.91722
H	-1.89777	0.87484	1.46894
C	1.42579	-0.06649	-0.9019
C	0.97438	-0.19939	-2.16946
H	0.45699	0.5872	-2.7401
H	1.16183	-1.11292	-2.74888
Si	-2.86001	-1.02174	-0.22295
C	-2.57482	-2.48678	-1.36176
H	-3.51325	-2.8544	-1.79574
H	-1.92824	-2.21039	-2.20948
H	-2.12184	-3.33763	-0.83051
C	-3.48251	0.46497	-1.1712
H	-4.4897	0.27926	-1.56745
H	-3.53864	1.36362	-0.54187
H	-2.82335	0.69078	-2.02069
C	-3.964	-1.44143	1.22707
H	-3.95701	-0.63861	1.97683
H	-5.006	-1.58988	0.91542
H	-3.62549	-2.36027	1.72274
C	3.33281	-2.91329	0.90965
H	3.90773	-3.5267	0.19825
H	2.67922	-3.59635	1.47428
H	4.04994	-2.48851	1.6315
Cu	2.42737	-1.48786	0.01172

ICuI$^-$

G_{sol} = -220.485482 Hartree

Cu -1.3747 -0.49474 -0.10819
I 1.08895 -0.49474 -0.10819
I -3.83834 -0.49474 -0.10819

Li^+

G_{sol} = -7.472842 Hartree

Li -1.82105 1.21053 0.

MeCu

G_{sol} = -237.237824 Hartree

Cu -1.61676 1.11231 -0.57562
C -3.49513 1.11231 -0.57562
H -3.83989 1.60063 0.34278
H -3.83989 1.66351 -1.45771
H -3.83989 0.0728 -0.61192

MeLi

G_{sol} = -47.405685 Hartree

C -0.94383 0.45864 0.
H -0.60862 1.03461 0.87993
H -0.60862 1.03461 -0.87993
H -2.04553 0.5266 0.
Li -0.28906 -1.39341 0.

TSA

G_{sol} = -895.912962 Hartree

C -1.433869 -0.855938 1.204344
C -1.907576 -0.918539 2.632511
C -1.929891 -1.712399 0.296185
C -1.638591 -1.518470 -1.164382
H -0.844253 -2.225075 -1.477704
C -2.866917 -1.777276 -2.020170
H -3.705404 -1.143681 -1.704218
H -2.653091 -1.566490 -3.074987
H -3.180462 -2.826370 -1.933058
O -1.147324 -0.206557 -1.364123
Si -1.536387 1.104227 -0.118865
C -3.398609 1.334638 -0.318814
H -3.978997 0.702840 0.366679
H -3.648837 2.381586 -0.094507
H -3.726456 1.119687 -1.344075
C -1.119822 2.107543 1.470129
H -0.036352 2.118097 1.670087
H -1.434595 3.153599 1.323294
H -1.618484 1.725249 2.368948
C -0.674758 2.365307 -1.320022
H -1.169938 3.332044 -1.153015
H 0.387430 2.558374 -1.088606
H -0.789965 2.157727 -2.397282
H -2.386117 -1.883360 2.863182
H -1.098887 -0.757831 3.357515
Cu 0.428117 -0.394703 0.814687
I 2.672814 -0.070251 -0.209730
Li 0.535248 0.339620 -1.891064
H -2.654835 -0.133567 2.826181
H -2.632808 -2.517950 0.552959

TSB

G_{sol} = -895.902193 Hartree

C 1.55799 0.75851 -1.19572
C 1.86101 0.67134 -2.50346
C 2.16672 1.83703 -0.34189
H 3.26427 1.74492 -0.36648
H 1.93254 2.8411 -0.72988
C 1.67438 1.72273 1.1156
H 2.51619 1.93868 1.79564
C 0.54966 2.69807 1.41057
H -0.27503 2.57577 0.69037
H 0.15083 2.5493 2.4263
H 0.90037 3.73647 1.34633
O 1.23204 0.40474 1.39561

Li	-0.46927	-0.10448	1.92256
Si	1.65975	-1.03286	0.33372
C	3.53843	-1.07216	0.49364
H	3.91777	-0.39077	1.26555
H	3.84194	-2.09405	0.76405
H	4.02479	-0.83022	-0.46035
C	0.84658	-2.14797	1.70242
H	-0.20477	-2.40792	1.48537
H	1.37339	-3.11187	1.67784
H	0.93435	-1.78428	2.73914
C	1.31254	-2.28334	-1.08744
H	1.67398	-3.27361	-0.76538
H	0.24262	-2.39653	-1.32279
H	1.84157	-2.01209	-2.00901
H	2.53353	1.38025	-3.00434
H	1.4579	-0.11272	-3.14607
Cu	-0.29922	0.22647	-0.8751
I	-2.55772	-0.15656	0.10358

TSC

G_{sol} = -924.270640 Hartree

C	-0.1733	0.81252	-1.33325
C	0.18187	0.88192	-2.62738
C	-0.5376	2.08018	-0.6023
H	0.2287	2.85313	-0.77763
H	-1.48269	2.49694	-0.98677
C	-0.6812	1.8384	0.91646
H	-0.22808	2.68615	1.45844
C	-2.13515	1.71873	1.33763
H	-2.64209	0.93086	0.75644
H	-2.2169	1.48346	2.41018
H	-2.67849	2.65696	1.16512
O	0.00071	0.66301	1.32853
Li	-0.90701	-0.9259	1.76533
Si	1.33641	-0.11145	0.36574
C	2.61446	1.27442	0.33449
H	2.44406	2.02971	1.112
H	3.611	0.83689	0.49227
H	2.63049	1.7739	-0.64289
C	1.61826	-1.29989	1.86572
H	1.11239	-2.27362	1.73977
H	2.68796	-1.55165	1.89211
H	1.37041	-0.8797	2.85195
C	1.99894	-1.33255	-0.96173
H	2.96326	-1.72842	-0.6014
H	1.33947	-2.19466	-1.14075
H	2.16904	-0.82556	-1.91887
H	0.19861	1.82377	-3.19339
H	0.47105	-0.00213	-3.1988
Cu	-0.95468	-0.86532	-0.66683
C	-1.86065	-2.29966	0.31942
H	-2.69074	-2.01811	1.0009
H	-2.35955	-2.88617	-0.46504
H	-1.23359	-3.03801	0.85527

TSD

G_{sol} = -963.526726 Hartree

C	-0.998884	-1.649310	2.126683
H	-0.667569	-2.399732	2.857779
H	-1.992564	-1.239208	2.306124
C	-0.232034	-1.282626	1.084900
C	1.105240	-1.975889	0.931839
H	1.001830	-2.767749	0.167334
H	1.381297	-2.495249	1.867519
C	2.250798	-1.075126	0.492897
H	3.160560	-1.683757	0.372882
H	2.484486	-0.322106	1.260704
C	1.987395	-0.375373	-0.828143
H	1.629500	-1.149884	-1.542105
C	3.249614	0.255779	-1.387442
H	4.023925	-0.500805	-1.571216
H	3.046216	0.775793	-2.332967
H	3.646412	0.994739	-0.677267
C	-0.586024	2.675875	-0.616873

H	0.176870	2.968739	-1.355329
H	-1.564676	2.557910	-1.115645
H	-0.719029	3.548816	0.037541
C	-1.837962	1.303398	1.490639
H	-2.684904	0.837182	0.965964
H	-1.772394	0.866940	2.493891
H	-2.072632	2.374055	1.600658
C	1.052020	1.736447	1.903835
H	0.638030	2.639293	2.377486
H	1.153616	0.977247	2.690267
H	2.049410	1.977912	1.515512
Si	-0.150606	1.182023	0.559984
O	0.996247	0.644457	-0.761448
Li	-0.281490	0.816154	-2.116196
Cu	-1.219738	-0.861050	-0.562309
C	-1.981162	-0.537381	-2.339820
H	-1.347653	-0.768957	-3.221128
H	-2.800383	-1.266288	-2.410493
H	-2.468974	0.438379	-2.531255

TSE

G_{sol} = -1115.860260 Hartree

C	-3.81773	-0.84213	-0.69325
C	-2.52736	-1.00628	-1.1709
C	-1.38983	-0.57648	-0.45575
C	-1.62412	0.09484	0.76939
C	-2.92802	0.24636	1.24338
C	-4.02641	-0.22389	0.5361
H	-4.66426	-1.18862	-1.28499
H	-2.37414	-1.45689	-2.15111
H	-3.08556	0.77321	2.18796
H	-5.03269	-0.08089	0.92591
C	-0.0664	-0.63981	-1.09362
C	0.21369	-1.72299	-1.89494
H	-0.46757	-2.57533	-2.06071
H	1.07432	-1.71149	-2.58085
Si	0.81861	1.88289	-0.51951
C	2.3817	1.32398	-1.41331
H	2.12428	0.84242	-2.36442
H	3.04826	2.17637	-1.60953
H	2.96216	0.57557	-0.84972
C	-0.69146	2.29523	-1.56261
H	-1.62157	2.22581	-0.9826
H	-0.59978	3.33333	-1.91276
H	-0.7946	1.62814	-2.42516
C	1.27313	3.56815	0.23678
H	1.47692	4.31954	-0.54009
H	0.45073	3.9556	0.85696
H	2.16426	3.5087	0.87881
C	-0.54821	0.71002	1.64351
H	-0.95649	1.65708	2.04555
C	-0.21016	-0.19838	2.81744
H	-1.0915	-0.38109	3.44287
H	0.13225	-1.18173	2.45558
H	0.56305	0.25667	3.4576
O	0.67397	1.02535	0.98937
Cu	1.43571	-1.81691	-0.23813
C	2.82842	-2.11848	1.10633
H	3.75131	-1.50448	1.06623
H	2.53077	-2.19407	2.16994
H	3.17741	-3.12874	0.85134
Li	2.05889	-0.15315	1.34584

TSF

G_{sol} = -1119.395002 Hartree

C	3.62041	-0.09582	-0.67828
C	2.29425	0.64113	-0.54223
C	1.11115	-0.23561	-0.9855
C	1.06444	-1.59309	-0.24008
C	2.44034	-2.2777	-0.2518
C	3.61725	-1.38311	0.13407
H	2.16118	0.97686	0.50119
H	2.30404	1.55524	-1.15464
H	3.78576	-0.33587	-1.74263

H	4.45332	0.55169	-0.36913
H	0.41383	-2.23849	-0.85523
H	2.41401	-3.17871	0.38269
H	2.62184	-2.63867	-1.2776
H	3.58605	-1.12598	1.20344
H	4.55597	-1.93546	-0.01647
H	1.34978	-0.5099	-2.03628
C	0.39567	-1.64936	1.14928
H	0.23908	-2.72747	1.353
O	-0.88185	-1.01909	1.16387
Li	-0.86238	0.84309	1.41112
C	1.15913	-1.0866	2.33581
H	1.43064	-0.02802	2.1974
H	0.53074	-1.17021	3.23253
H	2.08483	-1.64012	2.52934
C	-0.22876	0.50001	-1.00191
C	-0.36565	1.46693	-1.97223
H	0.38981	1.6658	-2.75088
H	-1.34548	1.92008	-2.18681
Si	-2.02145	-1.02915	-0.16448
C	-3.18015	0.44475	0.11067
H	-4.17541	0.1596	-0.2608
H	-3.32752	0.63021	1.18949
H	-2.89434	1.38792	-0.37139
C	-3.08255	-2.45204	0.55027
H	-2.49044	-3.37609	0.64228
H	-3.45922	-2.21243	1.55502
H	-3.94832	-2.68578	-0.08757
C	-1.86556	-1.71077	-1.93246
H	-2.87517	-1.60302	-2.36148
H	-1.15873	-1.22526	-2.60971
H	-1.66056	-2.7904	-1.90009
C	-0.35701	3.07841	1.69044
H	-0.22694	4.16881	1.63794
H	-1.33189	2.94621	2.19975
H	0.42775	2.7296	2.38636
Cu	-0.20955	2.42785	-0.13962

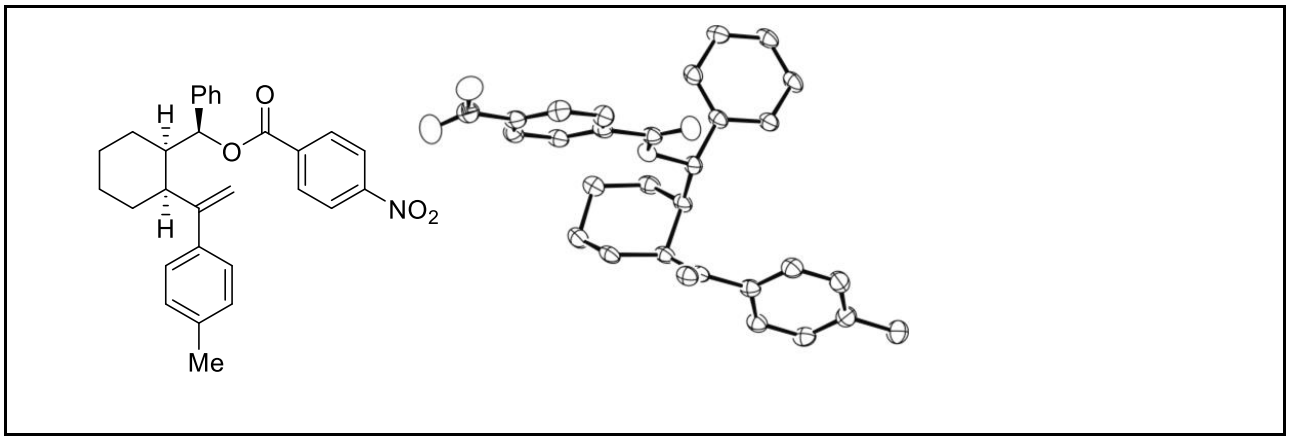
TSG

G_{sol} = -1119.398782 Hartree

C	3.05274	0.19015	1.20123
C	4.09307	-0.10954	0.13386
C	3.65039	-1.31004	-0.68894
C	2.27848	-1.07825	-1.30771
C	1.19348	-0.70587	-0.28569
C	1.67812	0.47399	0.59112
H	4.38493	-1.539	-1.47437
H	4.20987	0.76713	-0.52555
H	5.07442	-0.29068	0.59467
H	2.9845	-0.68426	1.87129
H	3.36287	1.04137	1.82869
H	2.34644	-0.26819	-2.0563
H	1.97245	-1.97759	-1.85891
H	1.09155	-1.57565	0.39744
H	1.81367	1.34512	-0.0784
H	3.60851	-2.19728	-0.03354
C	0.7115	0.93141	1.69222
O	-0.58455	1.26546	1.21069
Li	-1.71848	-0.23113	1.07137
C	0.51385	-0.07372	2.8165
H	-0.23986	0.30723	3.51863
H	0.17722	-1.05398	2.43883
H	1.43586	-0.24612	3.38335
H	1.15072	1.84759	2.13265
C	-0.19151	-0.445	-0.89589
C	-0.55392	-1.12091	-2.04013
H	0.09883	-1.77106	-2.63863
H	-1.48084	-0.84558	-2.567
Si	-0.97347	1.89817	-0.37211
C	-2.78695	1.40756	-0.64043
H	-3.2573	2.19033	-1.25255
H	-2.96082	0.44561	-1.14134
H	-3.34816	1.42113	0.31056
C	0.02654	2.15829	-1.9716
H	-0.60676	1.81287	-2.80167

H	0.23351	3.22835	-2.11305
H	0.96865	1.60823	-2.0575
C	-1.1353	3.70819	0.2077
H	-0.15524	4.10345	0.51887
H	-1.5052	4.36383	-0.59484
H	-1.81041	3.80686	1.06914
C	-2.641	-2.38378	1.12681
H	-3.15753	-3.32967	0.90949
H	-3.46083	-1.67804	1.36821
H	-2.08049	-2.56508	2.06052
Cu	-1.55957	-1.97655	-0.43723

X-ray Structure Determination of Compound 26



Compound 26, $C_{29}H_{29}NO_4$, crystallizes in the triclinic space group $P\bar{1}$ with a=9.4816(6)Å, b=10.0759(6)Å, c=13.0176(8)Å, α=83.550(3)°, β=89.861(3)°, γ=84.338(3)°, V=1229.70(13)Å^3, Z=2, and d_{calc}=1.230 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5 ° rotation frames with exposures of 10 seconds. A total of 3702 frames were collected with a crystal to detector distance of 37.6 mm, rotation widths of 0.5 ° and exposures of 15 seconds:

scan type	**2θ**	**ω**	**φ**	**χ**	Frames
ϕ	-15.50	258.48	-351.72	19.46	739
ω	-15.50	-82.24	18.69	41.79	142
ϕ	-23.00	-25.79	-280.64	73.66	658
ϕ	-23.00	315.83	-339.66	28.88	720
ϕ	19.50	59.55	-5.19	-26.26	721
ϕ	-18.00	-6.31	-48.02	-86.54	722

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 40564 reflections were measured over the ranges $3.148 \le 2\theta \le 51.002°$, $-11 \le h \le 11$, $-12 \le k \le 12$, $-15 \le l \le 15$ yielding 4518 unique reflections (R_{int} = 0.0561). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.4859, 0.7452). The structure was solved by direct methods - SHELXS-97 [4]. Refinement

was by full-matrix least squares based on F^2 using SHELXL-2014 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0341P)^2 + 1.7278P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0581 and wR2=0.1409 for 3648 observed reflections for which $F > 4\sigma(F)$ and R1=0.0711 and wR2=0.1474 and GOF =1.135 for all 4518 unique, non-zero reflections and 308 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.59 and -0.30 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

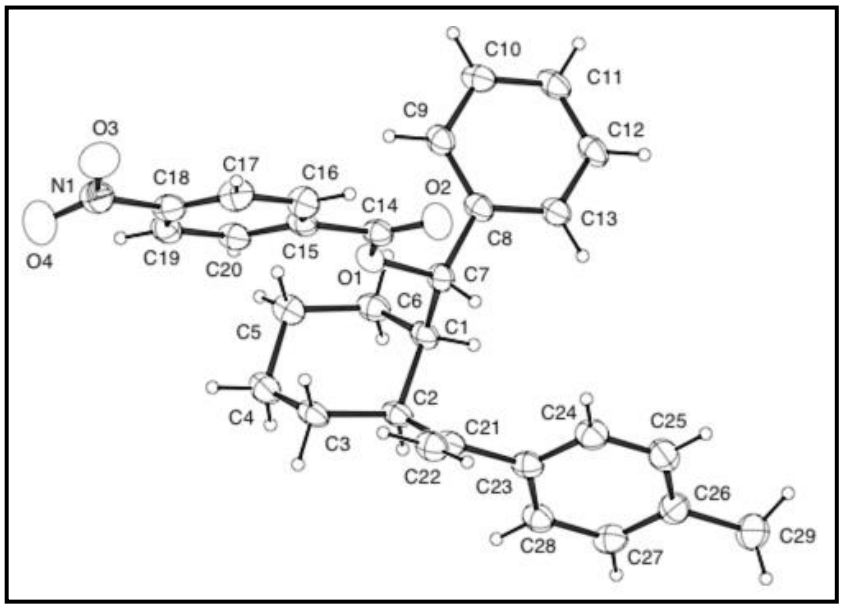


Figure 1. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 26

Empirical formula	$C_{29}H_{29}NO_4$
Formula weight	455.53
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	9.4816(6)Å
b	10.0759(6)Å
c	13.0176(8)Å
α	83.550(3) °
β	89.861(3) °
γ	84.338(3) °
Volume	1229.70(13)Å^3
Z	2
d_{calc}	1.230 g/cm^3
μ	0.082 mm^{-1}
F(000)	484.0
Crystal size, mm	0.28 × 0.26 × 0.03
2θ range for data collection	3.148 - 51.002 °
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	40564
Independent reflections	4518[R(int) = 0.0561]
Data/restraints/parameters	4518/0/308
Goodness-of-fit on F^2	1.135
Final R indexes [I>=2σ (I)]	R_1 = 0.0581, wR_2 = 0.1409
Final R indexes [all data]	R_1 = 0.0711, wR_2 = 0.1474
Largest diff. peak/hole	0.59/-0.30 eÅ^{-3}

Table 2 . Refined Positional Parameters for Compound 26

Atom	*x*	*y*	*z*	U(eq)
O1	0.82864(18)	0.74078(16)	0.18570(13)	0.0260(4)
O2	1.0591(2)	0.76740(19)	0.15338(15)	0.0357(5)
O3	1.2406(2)	0.2347(2)	0.52528(16)	0.0448(5)
O4	1.0256(3)	0.1805(2)	0.52527(18)	0.0526(6)
N1	1.1176(3)	0.2509(2)	0.49450(19)	0.0371(6)
C1	0.6365(3)	0.8297(2)	0.0638(2)	0.0264(6)
C2	0.6255(3)	0.6992(2)	0.0110(2)	0.0268(6)
C3	0.6175(3)	0.5760(2)	0.0904(2)	0.0287(6)
C4	0.4945(3)	0.5970(3)	0.1644(2)	0.0342(6)
C5	0.5058(3)	0.7218(3)	0.2206(2)	0.0317(6)
C6	0.5179(3)	0.8465(3)	0.1429(2)	0.0299(6)
C7	0.7862(3)	0.8462(2)	0.1017(2)	0.0258(5)
C8	0.7959(3)	0.9836(2)	0.1358(2)	0.0257(5)
C9	0.7923(3)	1.0081(3)	0.2390(2)	0.0282(6)
C10	0.7944(3)	1.1387(3)	0.2645(2)	0.0311(6)
C11	0.7971(3)	1.2444(3)	0.1878(2)	0.0316(6)
C12	0.8023(3)	1.2214(2)	0.0847(2)	0.0307(6)
C13	0.8034(3)	1.0913(3)	0.0589(2)	0.0282(6)
C14	0.9699(3)	0.7102(2)	0.1998(2)	0.0267(6)
C15	1.0025(3)	0.5903(2)	0.2790(2)	0.0264(6)
C16	1.1445(3)	0.5434(3)	0.2946(2)	0.0321(6)
C17	1.1832(3)	0.4306(3)	0.3643(2)	0.0338(6)
C18	1.0773(3)	0.3677(3)	0.4169(2)	0.0313(6)
C19	0.9349(3)	0.4118(3)	0.4027(2)	0.0317(6)
C20	0.8987(3)	0.5243(3)	0.3329(2)	0.0288(6)
C21	0.7383(3)	0.6860(2)	-0.0707(2)	0.0266(6)
C22	0.8513(3)	0.5963(3)	-0.0598(2)	0.0310(6)
C23	0.7210(3)	0.7865(3)	-0.1645(2)	0.0268(6)
C24	0.8295(3)	0.8649(3)	-0.1973(2)	0.0324(6)
C25	0.8141(3)	0.9565(3)	-0.2852(2)	0.0358(6)
C26	0.6909(3)	0.9721(3)	-0.3442(2)	0.0319(6)
C27	0.5831(3)	0.8942(3)	-0.3118(2)	0.0316(6)
C28	0.5963(3)	0.8033(3)	-0.2235(2)	0.0291(6)
C29	0.6736(3)	1.0714(3)	-0.4405(2)	0.0404(7)

Table 3 . Positional Parameters for Hydrogens in Compound 26

Atom	*x*	*y*	*z*	U(eq)
H1	0.615	0.9037	0.0089	0.035
H2	0.5345	0.7123	-0.0262	0.036
H3a	0.6057	0.4983	0.0547	0.038
H3b	0.7056	0.5585	0.1295	0.038
H4a	0.4941	0.5186	0.2149	0.045
H4b	0.4058	0.6072	0.126	0.045
H5a	0.4226	0.7364	0.263	0.042
H5b	0.5884	0.7072	0.2657	0.042
H6a	0.4284	0.869	0.106	0.04
H6b	0.5341	0.9213	0.1807	0.04
H7	0.8518	0.8356	0.0442	0.034
H9	0.7884	0.9373	0.291	0.038
H10	0.794	1.1545	0.3335	0.041
H11	0.7955	1.3316	0.2052	0.042
H12	0.805	1.2928	0.0331	0.041
H13	0.8091	1.0756	-0.0101	0.038
H16	1.214	0.5877	0.2583	0.043
H17	1.2779	0.3984	0.3751	0.045
H19	0.8656	0.3672	0.4389	0.042
H20	0.8037	0.5559	0.3221	0.038
H22a	0.9202	0.5959	-0.1107	0.041
H22b	0.8614	0.5341	-0.0012	0.041
H24	0.9137	0.8556	-0.1595	0.043
H25	0.8876	1.0082	-0.305	0.048
H27	0.4996	0.9032	-0.3505	0.042
H28	0.5216	0.7531	-0.2032	0.039
H29a	0.6941	1.0254	-0.5003	0.061
H29b	0.7378	1.1389	-0.4372	0.061
H29c	0.578	1.1131	-0.445	0.061

Table 4 . Refined Thermal Parameters (U's) for Compound 26

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

O1	0.0279(9)	0.0171(8)	0.0321(10)	-0.0001(7)	-0.0080(7)	-0.0005(7)
O2	0.030(1)	0.0333(11)	0.0421(11)	0.0055(9)	-0.0040(9)	-0.0045(9)
O3	0.0491(13)	0.0368(12)	0.0446(12)	-0.0022(9)	-0.0166(10)	0.0131(10)
O4	0.0600(15)	0.0364(12)	0.0570(15)	0.0131(11)	-0.0091(12)	-0.0032(11)
N1	0.0478(16)	0.0246(12)	0.0372(14)	-0.0036(10)	-0.0074(12)	0.0045(11)
C1	0.0315(14)	0.0152(12)	0.0316(14)	-0.0008(10)	-0.0074(11)	-0.0004(10)
C2	0.0286(13)	0.0182(12)	0.0333(14)	-0.0033(10)	-0.0109(11)	-0.0012(10)
C3	0.0313(14)	0.0175(12)	0.0377(15)	-0.0051(11)	-0.0092(11)	-0.0024(10)
C4	0.0356(15)	0.0258(14)	0.0413(16)	-0.0012(12)	-0.0069(12)	-0.0068(12)
C5	0.0303(14)	0.0289(14)	0.0365(15)	-0.0059(12)	-0.0019(11)	-0.0038(11)
C6	0.0297(14)	0.0237(13)	0.0364(15)	-0.0068(11)	-0.0079(11)	0.0008(11)
C7	0.0309(14)	0.0181(12)	0.0272(13)	0.0006(10)	-0.0063(10)	0.000(1)
C8	0.0248(13)	0.0181(12)	0.0338(14)	-0.0019(10)	-0.0059(10)	-0.0002(10)
C9	0.0294(14)	0.0213(13)	0.0330(14)	0.0003(11)	-0.0053(11)	-0.0016(11)
C10	0.0325(14)	0.0265(14)	0.0354(15)	-0.0090(11)	-0.0065(11)	-0.0015(11)
C11	0.0338(15)	0.0169(12)	0.0443(16)	-0.0057(11)	-0.0075(12)	-0.0008(11)
C12	0.0326(14)	0.0162(12)	0.0421(16)	0.0019(11)	-0.0093(12)	-0.0018(11)
C13	0.0293(14)	0.0228(13)	0.0325(14)	-0.0025(11)	-0.0076(11)	-0.0034(11)
C14	0.0291(14)	0.0211(12)	0.0298(14)	-0.0046(10)	-0.0065(11)	0.0000(11)
C15	0.0314(14)	0.0171(12)	0.0311(14)	-0.0065(10)	-0.0058(11)	0.0002(10)
C16	0.0306(14)	0.0293(14)	0.0355(15)	-0.0026(12)	-0.0038(12)	0.0009(12)
C17	0.0327(15)	0.0317(15)	0.0355(15)	-0.0052(12)	-0.0071(12)	0.0071(12)
C18	0.0427(16)	0.0199(13)	0.0302(14)	-0.0049(11)	-0.0113(12)	0.0050(11)
C19	0.0400(16)	0.0219(13)	0.0338(15)	-0.0047(11)	-0.0054(12)	-0.0042(12)
C20	0.0300(14)	0.0230(13)	0.0335(14)	-0.0063(11)	-0.0096(11)	0.0007(11)
C21	0.0284(13)	0.0200(12)	0.0321(14)	-0.0061(10)	-0.0089(11)	-0.0023(10)
C22	0.0325(14)	0.0228(13)	0.0371(15)	-0.0045(11)	-0.0068(12)	0.0016(11)
C23	0.0278(13)	0.0221(13)	0.0304(14)	-0.0069(10)	-0.0047(11)	0.0024(10)
C24	0.0291(14)	0.0321(15)	0.0355(15)	-0.0029(12)	-0.0084(11)	-0.0017(12)
C25	0.0382(16)	0.0309(15)	0.0388(16)	-0.0018(12)	-0.0014(13)	-0.0079(12)
C26	0.0377(15)	0.0263(14)	0.0305(14)	-0.0032(11)	-0.0006(12)	0.0018(12)
C27	0.0327(14)	0.0290(14)	0.0321(15)	-0.0053(11)	-0.0099(11)	0.0045(12)
C28	0.0297(14)	0.0233(13)	0.0342(15)	-0.0046(11)	-0.0044(11)	-0.0013(11)
C29	0.0490(18)	0.0317(15)	0.0380(16)	0.0024(13)	-0.0074(14)	0.0010(13)

Table 5 . Bond Distances in Compound 26, Å

O1-C7	1.464(3)	O1-C14	1.353(3)	O2-C14	1.195(3)
O3-N1	1.224(3)	O4-N1	1.217(3)	N1-C18	1.483(3)

C1-C2	1.563(3)	C1-C6	1.533(4)	C1-C7	1.534(3)
C2-C3	1.532(3)	C2-C21	1.513(4)	C3-C4	1.524(4)
C4-C5	1.537(4)	C5-C6	1.535(4)	C7-C8	1.512(3)
C8-C9	1.392(4)	C8-C13	1.398(4)	C9-C10	1.395(4)
C10-C11	1.378(4)	C11-C12	1.387(4)	C12-C13	1.388(4)
C14-C15	1.506(3)	C15-C16	1.390(4)	C15-C20	1.387(4)
C16-C17	1.392(4)	C17-C18	1.379(4)	C18-C19	1.385(4)
C19-C20	1.387(4)	C21-C22	1.328(4)	C21-C23	1.495(4)
C23-C24	1.395(4)	C23-C28	1.398(4)	C24-C25	1.385(4)
C25-C26	1.386(4)	C26-C27	1.386(4)	C26-C29	1.512(4)
C27-C28	1.386(4)				

Table 6 . Bond Angles in Compound 26, °

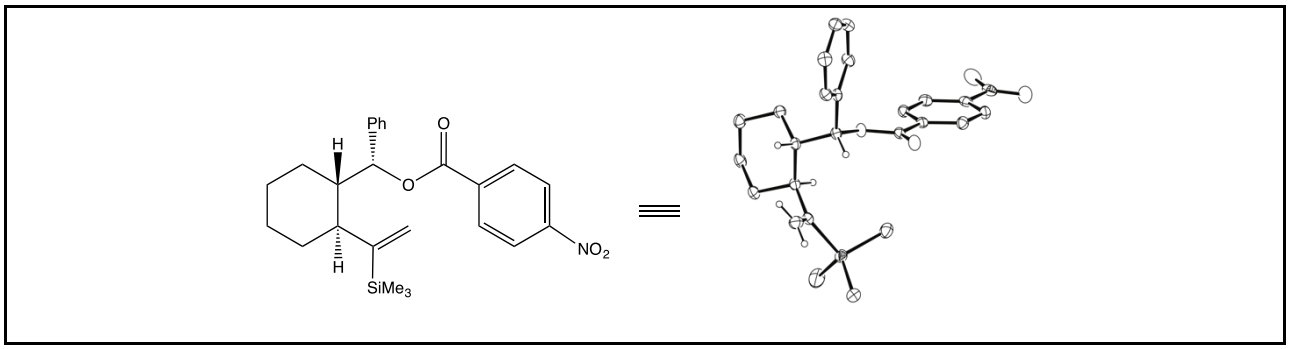
C14-O1-C7	115.7(2)	O3-N1-C18	117.3(3)	O4-N1-O3	124.7(2)
O4-N1-C18	118.0(2)	C6-C1-C2	110.3(2)	C6-C1-C7	115.8(2)
C7-C1-C2	114.1(2)	C3-C2-C1	111.9(2)	C21-C2-C1	110.4(2)
C21-C2-C3	115.8(2)	C4-C3-C2	111.4(2)	C3-C4-C5	111.4(2)
C6-C5-C4	110.9(2)	C1-C6-C5	114.2(2)	O1-C7-C1	109.7(2)
O1-C7-C8	110.8(2)	C8-C7-C1	111.8(2)	C9-C8-C7	123.2(2)
C9-C8-C13	119.1(2)	C13-C8-C7	117.7(2)	C8-C9-C10	120.1(2)
C11-C10-C9	120.2(3)	C10-C11-C12	120.3(2)	C11-C12-C13	119.8(2)
C12-C13-C8	120.5(3)	O1-C14-C15	111.6(2)	O2-C14-O1	125.0(2)
O2-C14-C15	123.4(2)	C16-C15-C14	116.8(2)	C20-C15-C14	123.3(2)
C20-C15-C16	119.9(2)	C15-C16-C17	120.3(3)	C18-C17-C16	118.3(3)
C17-C18-N1	118.7(2)	C17-C18-C19	122.7(2)	C19-C18-N1	118.5(3)
C18-C19-C20	118.1(3)	C19-C20-C15	120.7(3)	C22-C21-C2	123.5(2)
C22-C21-C23	120.4(2)	C23-C21-C2	116.0(2)	C24-C23-C21	121.3(2)
C24-C23-C28	117.7(2)	C28-C23-C21	121.0(2)	C25-C24-C23	121.2(3)
C24-C25-C26	121.1(3)	C25-C26-C27	117.9(3)	C25-C26-C29	121.3(3)
C27-C26-C29	120.8(3)	C28-C27-C26	121.8(2)	C27-C28-C23	120.4(3)

This report has been created with Olex2 [6], compiled on 2015.09.30 svn.r3233 for OlexSys.

Reference

[1] APEX2 2014.11-0
[2] SAINT v8.34A
[3] SADABS v2014/5
[4] SHELXS-97
[5] SHELXL-2014/7
[6] Olex2 (Dolomanov et al., 2009)

X-ray Structure Determination of Compound 27



Compound 27, $C_{25}H_{31}NO_4Si$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=7.3090(5)Å, b=15.1112(11)Å, c=21.9523(16)Å, β=90.131(3)°, V=2424.6(3)Å^3, Z=4, and d_{calc}=1.199 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5 ° rotation frames with exposures of 10 seconds. A total of 3872 frames were collected with a crystal to detector distance of 37.5 mm, rotation widths of 0.5 ° and exposures of 10 seconds:

scan type	**2θ**	**ω**	**φ**	**χ**	Frames
ϕ	-23.00	315.83	12.48	28.88	727
ϕ	-23.00	334.21	38.95	73.66	739
ϕ	-15.50	258.48	8.28	19.46	739
ϕ	19.50	59.55	348.71	-26.26	739
ϕ	-23.00	123.37	310.10	-94.51	708
ϕ	-18.00	124.02	293.36	-95.28	220

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 72039 reflections were measured over the ranges $3.272 \le 2\theta \le 50.74°$, $-8 \le h \le 8$, $-18 \le k \le 18$, $-26 \le l \le 24$ yielding 4450 unique reflections (R_{int} = 0.0187). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.7262, 0.7452). The structure was solved by direct methods - SHELXS-97 [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0385P)^2 + 1.1817P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0301 and wR2=0.0797 for 4221 observed reflections for which $F > 4\sigma(F)$

and R1=0.0316 and wR2=0.0810 and GOF =1.030 for all 4450 unique, non-zero reflections and 283 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.30 and -0.27 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

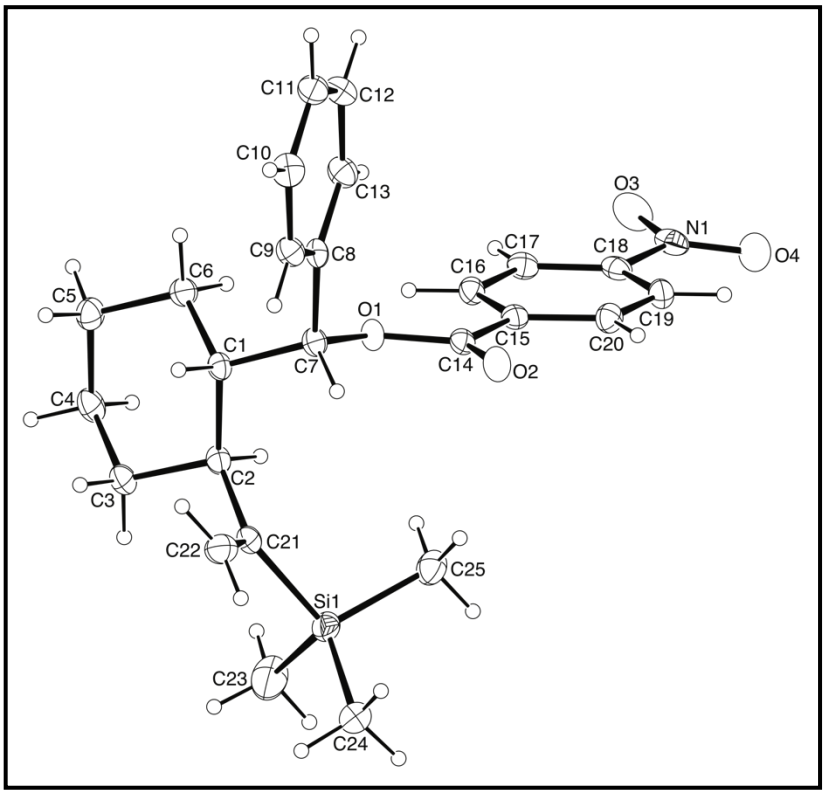


Figure 1. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 27

Empirical formula	$C_{25}H_{31}NO_4Si$
Formula weight	437.60
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a	7.3090(5)Å
b	15.1112(11)Å
c	21.9523(16)Å
β	90.131(3) °
Volume	2424.6(3)$Å^3$
Z	4
d_{calc}	1.199 g/cm^3
μ	0.126 mm^{-1}
F(000)	936.0
Crystal size, mm	0.38 × 0.25 × 0.2
2θ range for data collection	3.272 - 50.74 °
Index ranges	-8 ≤ h ≤ 8, -18 ≤ k ≤ 18, -26 ≤ l ≤ 24
Reflections collected	72039
Independent reflections	4450[R(int) = 0.0187]
Data/restraints/parameters	4450/0/283
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0797
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0810
Largest diff. peak/hole	0.30/-0.27 $eÅ^{-3}$

Table 2 . Refined Positional Parameters for Compound 27

Atom	*x*	*y*	*z*	U(eq)
C1	0.91840(15)	0.77229(7)	0.22710(5)	15.4(2)
C2	0.82918(15)	0.73327(7)	0.28495(5)	16.4(2)
C3	0.73501(16)	0.80711(8)	0.32198(5)	20.0(2)
C4	0.59398(16)	0.85745(8)	0.28419(5)	22.0(3)
C5	0.68415(16)	0.89776(8)	0.22821(5)	21.4(3)
C6	0.77882(16)	0.82663(8)	0.19045(5)	18.7(2)
C7	1.00622(15)	0.70016(7)	0.18727(5)	15.6(2)
C8	1.10465(15)	0.73676(7)	0.13195(5)	16.0(2)
C9	1.28151(15)	0.76973(8)	0.13817(5)	18.9(2)
C10	1.37153(16)	0.80738(8)	0.08885(6)	22.9(3)
C11	1.28604(17)	0.81177(8)	0.03243(5)	22.9(3)
C12	1.11118(17)	0.77782(8)	0.02561(5)	23.3(3)
C13	1.02085(16)	0.74081(8)	0.07499(5)	20.7(2)
C14	0.90051(15)	0.56221(7)	0.14790(5)	16.2(2)
C15	0.74098(15)	0.51688(7)	0.11863(5)	15.8(2)
C16	0.57030(15)	0.55746(8)	0.11347(5)	17.5(2)
C17	0.42723(16)	0.51424(8)	0.08433(5)	18.6(2)
C18	0.45999(16)	0.43052(8)	0.06126(5)	17.7(2)
C19	0.62764(16)	0.38863(8)	0.06567(5)	20.1(2)
C20	0.76940(16)	0.43274(8)	0.09457(5)	18.7(2)
C21	0.95841(16)	0.68110(8)	0.32640(5)	18.1(2)
C22	1.12565(17)	0.71073(8)	0.33980(5)	23.7(3)
C23	0.6601(2)	0.59547(10)	0.40570(8)	40.6(4)
C24	1.0490(2)	0.52162(9)	0.40854(6)	32.7(3)
C25	0.80887(18)	0.49900(8)	0.29534(6)	25.4(3)
N1	0.30911(14)	0.38349(7)	0.03034(4)	21.8(2)
O1	0.85599(10)	0.64361(5)	0.16728(3)	16.44(17)
O2	1.05062(11)	0.52973(5)	0.15300(4)	20.91(19)
O3	0.16568(12)	0.42341(7)	0.02162(4)	29.8(2)
O4	0.33585(13)	0.30634(6)	0.01486(4)	31.3(2)
Si1	0.87069(5)	0.57438(2)	0.35964(2)	21.94(10)

Table 3 . Positional Parameters for Hydrogens in Compound 27

Atom	*x*	*y*	*z*	U(eq)
H1	1.0159	0.8126	0.2402	20
H2	0.7332	0.6924	0.2715	22
H3a	0.6752	0.7812	0.3571	27
H3b	0.827	0.8482	0.3367	27
H4a	0.4972	0.8175	0.2716	29
H4b	0.5398	0.904	0.3087	29
H5a	0.7732	0.9417	0.2409	28
H5b	0.5922	0.9272	0.2035	28
H6a	0.8408	0.8546	0.1565	25
H6b	0.6869	0.787	0.1739	25
H7	1.0921	0.6654	0.2119	21
H9	1.3401	0.7665	0.1758	25
H10	1.4893	0.8297	0.0937	30
H11	1.3457	0.8373	-0.0006	30
H12	1.054	0.7798	-0.0122	31
H13	0.9032	0.7185	0.07	28
H16	0.5523	0.6137	0.1296	23
H17	0.3129	0.5407	0.0804	25
H19	0.6448	0.3323	0.0496	27
H20	0.8837	0.4061	0.0979	25
H22a	1.166	0.7643	0.3238	32
H22b	1.2019	0.6779	0.3651	32
H23a	0.5671	0.6208	0.3801	61
H23b	0.6884	0.6358	0.4382	61
H23c	0.6166	0.5407	0.4225	61
H24a	1.0063	0.4649	0.4222	49
H24b	1.0732	0.5587	0.4432	49
H24c	1.1593	0.5141	0.3855	49
H25a	0.9139	0.49	0.2699	38
H25b	0.7122	0.5251	0.2717	38
H25c	0.7687	0.4432	0.3113	38

Table 4 . Refined Thermal Parameters (U's) for Compound 27

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0154(5)	0.0144(5)	0.0164(5)	-0.0025(4)	0.0009(4)	-0.0018(4)
C2	0.0168(5)	0.0152(5)	0.0170(5)	-0.0027(4)	0.0023(4)	-0.0018(4)
C3	0.0220(6)	0.0202(6)	0.0177(5)	-0.0038(4)	0.0029(4)	0.0019(5)
C4	0.0205(6)	0.0243(6)	0.0214(6)	-0.0064(5)	0.0023(5)	0.0048(5)
C5	0.0205(6)	0.0196(6)	0.0239(6)	-0.0017(5)	-0.0004(5)	0.0042(5)
C6	0.0193(6)	0.0187(6)	0.0181(5)	-0.0002(4)	0.0012(4)	0.0018(5)
C7	0.0139(5)	0.0158(5)	0.0172(5)	-0.0026(4)	-0.0007(4)	-0.0021(4)
C8	0.0166(5)	0.0139(5)	0.0174(5)	-0.0034(4)	0.0019(4)	0.0015(4)
C9	0.0172(6)	0.0213(6)	0.0184(6)	-0.0022(4)	-0.0008(4)	0.0004(4)
C10	0.0174(6)	0.0250(6)	0.0262(6)	-0.0006(5)	0.0033(5)	-0.0026(5)
C11	0.0263(6)	0.0225(6)	0.0198(6)	0.0006(5)	0.0070(5)	0.0006(5)
C12	0.0280(6)	0.0259(6)	0.0161(6)	-0.0018(5)	-0.0012(5)	-0.0003(5)
C13	0.0194(6)	0.0230(6)	0.0197(6)	-0.0031(5)	-0.0007(5)	-0.0028(5)
C14	0.0184(6)	0.0157(5)	0.0145(5)	-0.0008(4)	0.0048(4)	-0.0007(4)
C15	0.0168(5)	0.0166(5)	0.0139(5)	0.0008(4)	0.0035(4)	-0.0021(4)
C16	0.0196(6)	0.0160(5)	0.0170(5)	-0.0011(4)	0.0046(4)	0.0000(4)
C17	0.0161(5)	0.0232(6)	0.0164(5)	0.0013(4)	0.0030(4)	0.0000(5)
C18	0.0193(6)	0.0217(6)	0.0122(5)	0.0012(4)	0.0010(4)	-0.0065(4)
C19	0.0259(6)	0.0160(6)	0.0186(6)	-0.0026(4)	0.0019(5)	-0.0019(5)
C20	0.0181(6)	0.0178(6)	0.0203(6)	-0.0007(4)	0.0021(4)	0.0016(4)
C21	0.0226(6)	0.0166(5)	0.0152(5)	-0.0024(4)	0.0041(4)	0.0015(4)
C22	0.0263(6)	0.0236(6)	0.0212(6)	0.0022(5)	-0.0021(5)	-0.0003(5)
C23	0.0469(9)	0.0283(7)	0.0468(9)	0.0015(6)	0.0270(7)	-0.0020(6)
C24	0.0521(9)	0.0218(6)	0.0240(6)	0.0020(5)	-0.0022(6)	0.0035(6)
C25	0.0274(6)	0.0188(6)	0.0300(7)	0.0008(5)	0.0028(5)	-0.0026(5)
N1	0.0234(5)	0.0280(6)	0.0139(5)	0.0005(4)	0.0008(4)	-0.0073(4)
O1	0.0146(4)	0.0143(4)	0.0205(4)	-0.0044(3)	0.0012(3)	-0.0017(3)
O2	0.0164(4)	0.0206(4)	0.0257(4)	-0.0051(3)	0.0010(3)	0.0018(3)
O3	0.0202(5)	0.0420(6)	0.0270(5)	-0.0059(4)	-0.0028(4)	-0.0024(4)
O4	0.0378(5)	0.0239(5)	0.0322(5)	-0.0050(4)	-0.0092(4)	-0.0076(4)
Si1	0.02778(19)	0.01685(17)	0.02122(18)	0.00114(12)	0.00727(13)	0.00048(13)

Table 5 . Bond Distances in Compound 27, Å

C1-C2	1.5457(15)	C1-C6	1.5358(15)	C1-C7	1.5386(15)
C2-C3	1.5435(15)	C2-C21	1.5289(16)	C3-C4	1.5250(16)
C4-C5	1.5228(17)	C5-C6	1.5245(16)	C7-C8	1.5172(15)
C7-O1	1.4581(13)	C8-C9	1.3918(16)	C8-C13	1.3924(16)
C9-C10	1.3901(17)	C10-C11	1.3875(18)	C11-C12	1.3850(18)
C12-C13	1.3882(17)	C14-C15	1.4962(15)	C14-O1	1.3418(14)
C14-O2	1.2069(14)	C15-C16	1.3944(16)	C15-C20	1.3925(16)
C16-C17	1.3877(16)	C17-C18	1.3839(17)	C18-C19	1.3824(17)
C18-N1	1.4759(14)	C19-C20	1.3847(17)	C21-C22	1.3340(17)
C21-Si1	1.8833(12)	C23-Si1	1.8712(14)	C24-Si1	1.8655(14)
C25-Si1	1.8684(13)	N1-O3	1.2242(14)	N1-O4	1.2301(14)

Table 6 . Bond Angles in Compound 27, °

C6-C1-C2	110.69(9)	C6-C1-C7	111.01(9)	C7-C1-C2	111.96(9)
C3-C2-C1	110.27(9)	C21-C2-C1	115.11(9)	C21-C2-C3	109.57(9)
C4-C3-C2	112.07(9)	C5-C4-C3	110.20(10)	C4-C5-C6	110.76(10)
C5-C6-C1	113.20(9)	C8-C7-C1	113.32(9)	O1-C7-C1	105.75(8)
O1-C7-C8	109.33(8)	C9-C8-C7	119.60(10)	C9-C8-C13	118.62(10)
C13-C8-C7	121.76(10)	C10-C9-C8	120.75(11)	C11-C10-C9	120.12(11)
C12-C11-C10	119.50(11)	C11-C12-C13	120.35(11)	C12-C13-C8	120.66(11)
O1-C14-C15	111.50(9)	O2-C14-C15	124.12(10)	O2-C14-O1	124.37(10)
C16-C15-C14	121.99(10)	C20-C15-C14	117.65(10)	C20-C15-C16	120.33(10)
C17-C16-C15	120.23(11)	C18-C17-C16	117.91(11)	C17-C18-N1	118.61(10)
C19-C18-C17	123.17(11)	C19-C18-N1	118.23(10)	C18-C19-C20	118.29(11)
C19-C20-C15	120.08(11)	C2-C21-Si1	117.50(8)	C22-C21-C2	121.51(11)
C22-C21-Si1	120.97(9)	O3-N1-C18	118.25(10)	O3-N1-O4	124.08(10)
O4-N1-C18	117.67(10)	C14-O1-C7	116.72(8)	C23-Si1-C21	110.17(6)
C24-Si1-C21	110.54(6)	C24-Si1-C23	109.65(7)	C24-Si1-C25	109.97(6)
C25-Si1-C21	108.14(5)	C25-Si1-C23	108.32(7)		

This report has been created with Olex2 [6], compiled on 2015.09.30 svn.r3233 for OlexSys.

Reference

[1] APEX2 2014.11-0
[2] SAINT v8.34A
[3] SADABS v2014/5
[4] SHELXS-97
[5] SHELXL-2014/7
[6] Olex2 (Dolomanov et al., 2009)