Supporting Information for

**Metal-mediated Efficient Synthesis, Structural Characterization and Skeletal
Rearrangement of Octa-substituted Semibullvalenes**

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Contents

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2. Crystallographic data, and lists of bond lengths and angles for **4b**, **4e**;
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1. Experimental details and characterization data for all new compounds

General Methods. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether and toluene were refluxed and distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. *t*-BuLi was obtained from Acros Organics. ¹H and ¹³C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in CDCl₃ unless stated otherwise. HR-MS were recorded at instrument ZAB-HS (1-2000u, 1000-10000, 10 – 10 C/ug.)

A typical procedure for the CuCl-mediated synthesis of 4: To a 10mL solution of diiodide (1.0mmol) in toluene at 0°C was added *t*-BuLi (4.0mmol, 1.5M in pentane). After this reaction mixture was stirred at room temperature for 1h, CuCl (198mg, 2.0mmol) was added at 0°C and the reaction mixture was kept at 50°C for 4h. The above reaction mixture was quenched with 3M aqueous HCl and extracted with petroleum ether. The extract was washed in turn with saturated aqueous NaHCO₃, water and brine and dried over MgSO₄. The solvent was then evaporated in vacuo to give yellow oil, which was distilled in Büchi glass oven to get rid of the low-boiling-point components. The residue thereafter was purified by column chromatograph (silica gel, hexane) to afford title products **4**. When **1d** was used, the oil obtained after evaporated in vacuo was directly purified by column chromatograph without any predistillation.

4a: Colorless liquid, 80% yield (132 mg); ¹H NMR (CDCl₃, Me₄Si): δ0.75-0.83 (m, 12H), 0.96 (t, *J* = 7.2, 12H), 1.63 (q, *J* = 7.2, 4H), 1.90-1.98 (m, 8H), 2.05 (q, *J* = 7.5, 4H); ¹³C NMR (CDCl₃, Me₄Si): δ11.54 (2 CH₃), 12.90 (2 CH₃), 14.50 (4 CH₃), 19.70 (2 CH₂), 19.82 (4 CH₂), 19.98 (2 CH₂), 66.17 (2 quart C), 101.69 (4 quart C), 132.00 (2 quart C). HRMS calcd. for C₂₄H₄₀ 328.3130, found 328.3129.

4b: Colorless crystal, 85% yield (187 mg), m. p. 110-111 °C; ^1H NMR (CDCl_3 , Me_4Si): δ 0.79-0.95 (m, 24H), 1.00-1.51 (m, 16H), 1.71-2.19 (m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 14.96 (2 CH_3), 15.04 (4 CH_3), 15.20 (2 CH_3), 20.30 (2 CH_2), 21.71 (2 CH_2), 23.31 (4 CH_2), 29.90 (4 CH_2), 30.11 (2 CH_2), 30.37 (2 CH_2), 65.69 (2 quart C), 100.68 (4 quart C), 131.32 (2 quart C). HRMS calcd. for $\text{C}_{32}\text{H}_{56}$ 440.4382, found 440.4392. Anal. Calcd for $\text{C}_{32}\text{H}_{56}$: C, 87.19%; H, 12.81%. Found: C, 87.19%, H, 12.71%.

4c: Colorless liquid, 88% yield (242 mg); ^1H NMR (CDCl_3 , Me_4Si): δ 0.84-0.94 (m, 24H), 1.02-1.50 (m, 32H), 1.74-2.17 (m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 13.96 (2 CH_3), 14.05 (4 CH_3), 14.17 (2 CH_3), 23.46 (2 CH_2), 23.62 (4 CH_2), 23.87 (2 CH_2), 27.12 (4 CH_2), 27.35 (2 CH_2), 27.53 (2 CH_2), 29.15 (2 CH_2), 30.73 (2 CH_2), 32.11 (4 CH_2), 65.69 (2 quart C), 100.68 (4 quart C), 131.32 (2 quart C). HRMS calcd. for $\text{C}_{40}\text{H}_{72}$ 552.5634, found 552.5627.

4d: Colorless liquid, 74% yield (245 mg); ^1H NMR (CDCl_3 , Me_4Si): δ 0.83-0.92 (m, 24H), 1.01-1.54 (m, 48H), 1.76-2.20 (m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 14.07 (2 CH_3), 14.14 (6 CH_3), 22.48 (2 CH_2), 22.57 (4 CH_2), 22.61 (2 CH_2), 26.60 (2 CH_2), 27.45 (4 CH_2), 27.71 (2 CH_2), 28.14 (2 CH_2), 29.37 (2 CH_2), 29.63 (4 CH_2), 32.70 (2 CH_2), 32.84 (4 CH_2), 33.14 (2 CH_2), 65.56 (2 quart C), 100.49 (4 quart C), 131.17 (2 quart C). HRMS calcd. for $\text{C}_{48}\text{H}_{88}$ 664.6686, found 664.6871.

A typical procedure for the transformation between 4 and 5: Semibuvallene **4** could be totally transformed into NMR-pure **5** as yellow oil after heated neatly in Büchi glass oven at 140-160°C for 4h. This transformation could also be taken in high-boiling-point solvent such as decahydronaphthalene at the same temperature. Further purification by column chromatograph (silica gel, hexane) gave **5** as colorless solid or oil.

5a: Colorless solid; ^1H NMR (CDCl_3 , Me_4Si): δ 0.94 (t, $J = 7.5$, 24H), 1.97-2.11(m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 14.22 (8 CH_3), 23.54 (8 CH_2), 138.32 (8 quart C). HRMS calcd. for $\text{C}_{24}\text{H}_{40}$ 328.3130, found 328.3133.

5b: Colorless oil; ^1H NMR (CDCl_3 , Me_4Si): δ 0.87 (t, $J = 7.2$, 24H), 1.20-1.42 (m, 16H), 1.86-2.02 (m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 14.89 (8 CH_3), 22.89 (8 CH_2), 33.58 (8 CH_2), 137.69 (8 quart C). HRMS calcd. for $\text{C}_{32}\text{H}_{56}$ 440.4379, found 440.4382.

5c: Colorless oil; ^1H NMR (CDCl_3 , Me_4Si): δ 0.89 (t, $J = 6.4$, 24H), 1.18-1.39 (m, 32H), 1.92-2.00 (m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 14.01 (8 CH_3), 23.45 (8 CH_2), 30.89 (8 CH_2), 31.89 (8 CH_2), 137.64 (8 quart C). HRMS calcd. for $\text{C}_{40}\text{H}_{72}$ 552.5634, found 552.5639.

The analytical data of **5a**, **5b** and **5c** are identical with the report values.¹

5d: Colorless oil; ^1H NMR (CDCl_3 , Me_4Si): δ 0.89 (t, $J = 6.9$, 24H), 1.22-1.33 (m, 48H), 1.87-2.08 (m, 16H); ^{13}C NMR (CDCl_3 , Me_4Si): δ 14.18 (8 CH_3), 22.62 (8 CH_2), 29.40 (8 CH_2), 31.22 (8 CH_2), 32.66 (8 CH_2), 137.64 (8 quart C). HRMS calcd. for $\text{C}_{48}\text{H}_{88}$ 664.6886, found 664.6884.

A typical procedure for the CuCl-mediated synthesis of 4e and 6 and relative transformation: To a 10mL solution of corresponding diiodide (1.0mmol) in diethyl ether at -78°C was added $t\text{-BuLi}$ (4.0mmol, 1.5M in pentane). This reaction mixture was stirred at -78°C for 30min and 0°C for 10min. CuCl (198mg, 2.0mmol) was then added and the reaction mixture was maintained at 0°C for 4h. The above reaction mixture was quenched with 3M aqueous HCl or saturated aqueous NaHCO_3 and extracted with diethyl ether. The extract was washed in turn with saturated aqueous NaHCO_3 (if quenched with aqueous HCl), water and brine and dried over MgSO_4 . The solvent was then evaporated in vacuo to give yellow oil which was purified by column chromatograph (silica gel, hexane) to afford **4e** (if quenched with aqueous NaHCO_3) or **6**.

(if quenched with aqueous HCl). When **4e** was stirred in 12MHCl for 2h, **6** was obtained quantitatively after usual work-up.

4e: Colorless crystal, 44% yield (102mg), m. p.189-191 °C; ¹H NMR (CDCl₃, Me₄Si): δ 1.20 (s, 6H), 1.31 (s, 6H), 6.86-7.22 (m, 20H); ¹³C NMR (CDCl₃, Me₄Si): δ 12.80 (2 CH₃), 13.68 (2 CH₃), 64.27 (2 quart C), 98.78 (2 quart C), 104.57 (2 quart C), 125.62 (2 CH), 126.23 (2 CH), 127.55 (4 CH), 127.73 (4 CH), 129.25 (4 CH), 131.73 (4 CH), 134.99 (2 quart C), 137.48 (2 quart C), 138.25 (2 quart C). HRMS calcd. for C₃₆H₃₂ 464.2504, found 464.2509. CCDC 226885.

6: Colorless crystal, 45% yield (104mg), m. p.196-198 °C; ¹H NMR (CDCl₃, Me₄Si): δ 1.45-1.54 (m, 9H), 3.99 (s, 1H), 4.63 (d, *J* = 2.4 Hz, 1H), 4.77 (d, *J* = 2.4 Hz, 1H), 6.21-7.25 (m, 20H); ¹³C NMR (CDCl₃, Me₄Si): δ 13.46 (1 CH₃), 19.71 (1 CH₃), 23.93 (1 CH₃), 58.31 (1 quart C), 67.71 (1 CH), 69.57 (1 quart C), 107.12 (1 CH₂), 125.83 (1 CH), 126.28 (1 CH), 126.34 (2 CH), 126.62 (2 CH), 127.11 (2 CH), 127.15 (2 CH), 127.78 (2 CH), 127.84 (2 CH), 128.78 (2 CH), 129.42 (2 CH), 129.94 (2 CH), 134.90 (1 quart C), 137.82 (1 quart C), 137.96 (1 quart C), 138.05 (1 quart C), 139.93 (1 quart C), 141.03 (1 quart C), 141.62 (1 quart C), 150.28 (1 quart C), 157.91 (1 quart C). HRMS calcd. for C₃₆H₃₂ 464.2504, found 464.2503. Anal. Calcd for C₃₆H₃₂: C, 93.06%; H, 6.90%. Found: C, 92.82%, H, 6.92%. CCDC: 213834.

Reference:

- (1) Ubayama, H.; Sun, W.; Xi, Z.; Takahashi, T. *Chem. Commun.* **1998**, 1931-1932.

2. Crystallographic data, and lists of bond lengths and angles for 4b, 4e.

1) Crystal Data for 4b

Table 1. Crystal data and structure refinement for 4b.

Identification code	4b
Empirical formula	C ₃₂ H ₅₆
Formula weight	440.77
Temperature	293(2) K
Measurement device	Rigaku RAXIS RAPID IP
Measurement method	\W
Wavelength	0.71073 Å
Program for data collection	Rapid-AUTO (Rigaku,2000)
Program for cell refinement	Rapid-AUTO
Program for data reduction	CrystalStructure (Rigaku/MS,2000)
Program for structure solution	SHELXS-97,(Sheldrick,1997)
Program for structure refinement	SHELXL-97,(Sheldrick,1997)
Program for molecular graphics	Siemens SHELXTL V4.2,(Sheldrick,1990)
Program for publication material	SHELXL-97,(Sheldrick,1997)
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 35.708(7) Å alpha = 90 deg. b = 19.298(4) Å beta = 122.34(3) deg. c = 21.697(4) Å gamma = 90 deg.
Volume	12631(4) Å ³
Refls. No. for cell measurement	33632
Theta range for cell measurement	2.01 to 25.02 deg.
Z, Calculated density	16, 0.927 Mg/m ³
Absorption coefficient	0.051 mm ⁻¹
F(000)	3968
Crystal shape / Crystal colour	block / colourless
Crystal size	0.50 x 0.35 x 0.15 mm
Theta range for data collection	2.01 to 25.02 deg.
Limiting indices	-42<=h<=42, -22<=k<=22, -25<=l<=21
Reflections collected / unique	33652 / 10900 [R(int) = 0.0474]
Reflections with I>2sigma(I)	3870
Completeness to theta = 25.02	97.8 %
Decay correction (%)	0
Absorption correction	Empirical
Max. and min. transmission	0.992 and 0.975
Method for primary solution	direct
Method for secondary solution	difmap
Hydrogen addition / treatment	geom / contr
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10900 / 0 / 578
Goodness-of-fit on F ²	0.891
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0849
R indices (all data)	R1 = 0.1496, wR2 = 0.0956
Extinction coefficient	0.00091(3)
Largest diff. peak and hole	0.117 and -0.141 e.Å ⁻³
Max. and mean shift/sigma	0.001 and 0.000

Table 2. Bond lengths [Å] and angles [deg] for 4b.

C(1)-C(8)	1.507(3)
C(1)-C(2)	1.517(3)
C(1)-C(9)	1.534(2)
C(1)-C(5)	1.570(3)
C(2)-C(3)	1.408(3)
C(2)-C(12)	1.531(2)
C(2)-C(8)	1.931(3)
C(3)-C(4)	1.397(3)
C(3)-C(15)	1.516(3)
C(4)-C(18)	1.512(3)
C(4)-C(5)	1.524(3)
C(4)-C(6)	2.084(3)
C(5)-C(6)	1.504(3)
C(5)-C(21)	1.543(2)
C(6)-C(7)	1.386(3)
C(6)-C(24)	1.522(2)
C(7)-C(8)	1.423(3)
C(7)-C(27)	1.506(2)
C(8)-C(30)	1.518(3)
C(9)-C(10)	1.549(2)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.511(2)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(13)	1.525(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.518(3)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.531(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.518(3)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(19)	1.536(2)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(20)	1.522(3)

C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-C(22)	1.537(2)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.521(3)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-C(25)	1.538(3)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-C(26)	1.519(3)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-C(28)	1.535(3)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-C(29)	1.514(3)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(30)-C(31)	1.541(3)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-C(32)	1.521(3)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(33)-C(34)	1.510(3)
C(33)-C(40)	1.513(3)
C(33)-C(41)	1.537(2)
C(33)-C(37)	1.563(3)
C(34)-C(35)	1.395(3)
C(34)-C(44)	1.526(3)
C(34)-C(40)	1.999(3)
C(35)-C(36)	1.403(3)
C(35)-C(47)	1.518(2)
C(36)-C(50)	1.519(3)
C(36)-C(37)	1.520(3)
C(36)-C(38)	2.034(3)

C(37)-C(38)	1.503(3)
C(37)-C(53)	1.545(2)
C(38)-C(39)	1.399(3)
C(38)-C(56)	1.521(3)
C(39)-C(40)	1.402(3)
C(39)-C(59)	1.518(3)
C(40)-C(62)	1.531(3)
C(41)-C(42)	1.537(2)
C(41)-H(41A)	0.9700
C(41)-H(41B)	0.9700
C(42)-C(43)	1.509(2)
C(42)-H(42A)	0.9700
C(42)-H(42B)	0.9700
C(43)-H(43A)	0.9600
C(43)-H(43B)	0.9600
C(43)-H(43C)	0.9600
C(44)-C(45)	1.541(3)
C(44)-H(44A)	0.9700
C(44)-H(44B)	0.9700
C(45)-C(46)	1.516(3)
C(45)-H(45A)	0.9700
C(45)-H(45B)	0.9700
C(46)-H(46A)	0.9600
C(46)-H(46B)	0.9600
C(46)-H(46C)	0.9600
C(47)-C(48)	1.538(3)
C(47)-H(47A)	0.9700
C(47)-H(47B)	0.9700
C(48)-C(49)	1.525(3)
C(48)-H(48A)	0.9700
C(48)-H(48B)	0.9700
C(49)-H(49A)	0.9600
C(49)-H(49B)	0.9600
C(49)-H(49C)	0.9600
C(50)-C(51)	1.535(2)
C(50)-H(50A)	0.9700
C(50)-H(50B)	0.9700
C(51)-C(52)	1.532(2)
C(51)-H(51A)	0.9700
C(51)-H(51B)	0.9700
C(52)-H(52A)	0.9600
C(52)-H(52B)	0.9600
C(52)-H(52C)	0.9600
C(53)-C(54)	1.544(2)
C(53)-H(53A)	0.9700
C(53)-H(53B)	0.9700
C(54)-C(55)	1.524(3)
C(54)-H(54A)	0.9700
C(54)-H(54B)	0.9700
C(55)-H(55A)	0.9600
C(55)-H(55B)	0.9600
C(55)-H(55C)	0.9600
C(56)-C(57)	1.533(3)

C(56)-H(56A)	0.9700
C(56)-H(56B)	0.9700
C(57)-C(58)	1.525(3)
C(57)-H(57A)	0.9700
C(57)-H(57B)	0.9700
C(58)-H(58A)	0.9600
C(58)-H(58B)	0.9600
C(58)-H(58C)	0.9600
C(59)-C(60)	1.533(2)
C(59)-H(59A)	0.9700
C(59)-H(59B)	0.9700
C(60)-C(61)	1.528(3)
C(60)-H(60A)	0.9700
C(60)-H(60B)	0.9700
C(61)-H(61A)	0.9600
C(61)-H(61B)	0.9600
C(61)-H(61C)	0.9600
C(62)-C(63)	1.533(3)
C(62)-H(62A)	0.9700
C(62)-H(62B)	0.9700
C(63)-C(64)	1.528(3)
C(63)-H(63A)	0.9700
C(63)-H(63B)	0.9700
C(64)-H(64A)	0.9600
C(64)-H(64B)	0.9600
C(64)-H(64C)	0.9600
C(8)-C(1)-C(2)	79.37(17)
C(8)-C(1)-C(9)	118.17(18)
C(2)-C(1)-C(9)	122.94(18)
C(8)-C(1)-C(5)	104.21(16)
C(2)-C(1)-C(5)	104.25(17)
C(9)-C(1)-C(5)	119.94(18)
C(3)-C(2)-C(1)	110.73(19)
C(3)-C(2)-C(12)	121.6(2)
C(1)-C(2)-C(12)	123.6(2)
C(3)-C(2)-C(8)	112.04(17)
C(1)-C(2)-C(8)	50.09(12)
C(12)-C(2)-C(8)	118.15(17)
C(4)-C(3)-C(2)	110.27(19)
C(4)-C(3)-C(15)	126.0(2)
C(2)-C(3)-C(15)	123.6(2)
C(3)-C(4)-C(18)	124.1(2)
C(3)-C(4)-C(5)	111.17(19)
C(18)-C(4)-C(5)	123.6(2)
C(6)-C(5)-C(4)	86.99(16)
C(6)-C(5)-C(21)	121.69(18)
C(4)-C(5)-C(21)	116.81(18)
C(6)-C(5)-C(1)	103.86(16)
C(4)-C(5)-C(1)	103.58(17)
C(21)-C(5)-C(1)	118.50(17)
C(7)-C(6)-C(5)	111.00(19)
C(7)-C(6)-C(24)	124.5(2)
C(5)-C(6)-C(24)	123.16(19)

C(6)-C(7)-C(8)	110.62(19)
C(6)-C(7)-C(27)	124.2(2)
C(8)-C(7)-C(27)	125.1(2)
C(7)-C(8)-C(1)	109.57(19)
C(7)-C(8)-C(30)	121.4(2)
C(1)-C(8)-C(30)	124.3(2)
C(7)-C(8)-C(2)	116.93(18)
C(1)-C(8)-C(2)	50.54(12)
C(30)-C(8)-C(2)	114.43(19)
C(1)-C(9)-C(10)	113.98(16)
C(1)-C(9)-H(9A)	108.8
C(10)-C(9)-H(9A)	108.8
C(1)-C(9)-H(9B)	108.8
C(10)-C(9)-H(9B)	108.8
H(9A)-C(9)-H(9B)	107.7
C(11)-C(10)-C(9)	112.86(18)
C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10B)	109.0
C(9)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(13)-C(12)-C(2)	112.15(18)
C(13)-C(12)-H(12A)	109.2
C(2)-C(12)-H(12A)	109.2
C(13)-C(12)-H(12B)	109.2
C(2)-C(12)-H(12B)	109.2
H(12A)-C(12)-H(12B)	107.9
C(14)-C(13)-C(12)	114.1(2)
C(14)-C(13)-H(13A)	108.7
C(12)-C(13)-H(13A)	108.7
C(14)-C(13)-H(13B)	108.7
C(12)-C(13)-H(13B)	108.7
H(13A)-C(13)-H(13B)	107.6
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(3)-C(15)-C(16)	114.40(18)
C(3)-C(15)-H(15A)	108.7
C(16)-C(15)-H(15A)	108.7
C(3)-C(15)-H(15B)	108.7
C(16)-C(15)-H(15B)	108.7
H(15A)-C(15)-H(15B)	107.6
C(17)-C(16)-C(15)	113.9(2)
C(17)-C(16)-H(16A)	108.8

C(15)-C(16)-H(16A)	108.8
C(17)-C(16)-H(16B)	108.8
C(15)-C(16)-H(16B)	108.8
H(16A)-C(16)-H(16B)	107.7
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(4)-C(18)-C(19)	116.64(19)
C(4)-C(18)-H(18A)	108.1
C(19)-C(18)-H(18A)	108.1
C(4)-C(18)-H(18B)	108.1
C(19)-C(18)-H(18B)	108.1
H(18A)-C(18)-H(18B)	107.3
C(20)-C(19)-C(18)	112.7(2)
C(20)-C(19)-H(19A)	109.1
C(18)-C(19)-H(19A)	109.1
C(20)-C(19)-H(19B)	109.1
C(18)-C(19)-H(19B)	109.1
H(19A)-C(19)-H(19B)	107.8
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(5)	114.07(17)
C(22)-C(21)-H(21A)	108.7
C(5)-C(21)-H(21A)	108.7
C(22)-C(21)-H(21B)	108.7
C(5)-C(21)-H(21B)	108.7
H(21A)-C(21)-H(21B)	107.6
C(23)-C(22)-C(21)	112.82(19)
C(23)-C(22)-H(22A)	109.0
C(21)-C(22)-H(22A)	109.0
C(23)-C(22)-H(22B)	109.0
C(21)-C(22)-H(22B)	109.0
H(22A)-C(22)-H(22B)	107.8
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(6)-C(24)-C(25)	112.77(19)
C(6)-C(24)-H(24A)	109.0
C(25)-C(24)-H(24A)	109.0
C(6)-C(24)-H(24B)	109.0
C(25)-C(24)-H(24B)	109.0
H(24A)-C(24)-H(24B)	107.8
C(26)-C(25)-C(24)	113.1(2)

C(26)-C(25)-H(25A)	109.0
C(24)-C(25)-H(25A)	109.0
C(26)-C(25)-H(25B)	109.0
C(24)-C(25)-H(25B)	109.0
H(25A)-C(25)-H(25B)	107.8
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(7)-C(27)-C(28)	114.56(18)
C(7)-C(27)-H(27A)	108.6
C(28)-C(27)-H(27A)	108.6
C(7)-C(27)-H(27B)	108.6
C(28)-C(27)-H(27B)	108.6
H(27A)-C(27)-H(27B)	107.6
C(29)-C(28)-C(27)	113.1(2)
C(29)-C(28)-H(28A)	109.0
C(27)-C(28)-H(28A)	109.0
C(29)-C(28)-H(28B)	109.0
C(27)-C(28)-H(28B)	109.0
H(28A)-C(28)-H(28B)	107.8
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(8)-C(30)-C(31)	116.65(19)
C(8)-C(30)-H(30A)	108.1
C(31)-C(30)-H(30A)	108.1
C(8)-C(30)-H(30B)	108.1
C(31)-C(30)-H(30B)	108.1
H(30A)-C(30)-H(30B)	107.3
C(32)-C(31)-C(30)	111.66(19)
C(32)-C(31)-H(31A)	109.3
C(30)-C(31)-H(31A)	109.3
C(32)-C(31)-H(31B)	109.3
C(30)-C(31)-H(31B)	109.3
H(31A)-C(31)-H(31B)	107.9
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(34)-C(33)-C(40)	82.77(18)
C(34)-C(33)-C(41)	122.44(18)
C(40)-C(33)-C(41)	117.69(18)
C(34)-C(33)-C(37)	104.32(17)
C(40)-C(33)-C(37)	104.48(17)
C(41)-C(33)-C(37)	118.68(17)

C(35)-C(34)-C(33)	110.29(19)
C(35)-C(34)-C(44)	123.33(19)
C(33)-C(34)-C(44)	123.44(19)
C(35)-C(34)-C(40)	109.64(17)
C(33)-C(34)-C(40)	48.67(12)
C(44)-C(34)-C(40)	118.29(18)
C(34)-C(35)-C(36)	111.33(19)
C(34)-C(35)-C(47)	123.9(2)
C(36)-C(35)-C(47)	124.7(2)
C(35)-C(36)-C(50)	124.3(2)
C(35)-C(36)-C(37)	109.73(18)
C(50)-C(36)-C(37)	124.2(2)
C(35)-C(36)-C(38)	114.66(18)
C(50)-C(36)-C(38)	111.69(18)
C(37)-C(36)-C(38)	47.36(12)
C(38)-C(37)-C(36)	84.56(16)
C(38)-C(37)-C(53)	121.79(18)
C(36)-C(37)-C(53)	116.34(18)
C(38)-C(37)-C(33)	103.78(17)
C(36)-C(37)-C(33)	104.12(17)
C(53)-C(37)-C(33)	119.86(17)
C(39)-C(38)-C(37)	110.83(19)
C(39)-C(38)-C(56)	123.3(2)
C(37)-C(38)-C(56)	123.5(2)
C(39)-C(38)-C(36)	109.31(17)
C(37)-C(38)-C(36)	48.08(11)
C(56)-C(38)-C(36)	118.07(17)
C(38)-C(39)-C(40)	110.7(2)
C(38)-C(39)-C(59)	123.9(2)
C(40)-C(39)-C(59)	125.3(2)
C(39)-C(40)-C(33)	109.8(2)
C(39)-C(40)-C(62)	123.1(2)
C(33)-C(40)-C(62)	124.3(2)
C(39)-C(40)-C(34)	116.02(19)
C(33)-C(40)-C(34)	48.56(13)
C(62)-C(40)-C(34)	112.48(19)
C(33)-C(41)-C(42)	113.94(17)
C(33)-C(41)-H(41A)	108.8
C(42)-C(41)-H(41A)	108.8
C(33)-C(41)-H(41B)	108.8
C(42)-C(41)-H(41B)	108.8
H(41A)-C(41)-H(41B)	107.7
C(43)-C(42)-C(41)	112.67(17)
C(43)-C(42)-H(42A)	109.1
C(41)-C(42)-H(42A)	109.1
C(43)-C(42)-H(42B)	109.1
C(41)-C(42)-H(42B)	109.1
H(42A)-C(42)-H(42B)	107.8
C(42)-C(43)-H(43A)	109.5
C(42)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(42)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5

H(43B)-C(43)-H(43C)	109.5
C(34)-C(44)-C(45)	111.29(19)
C(34)-C(44)-H(44A)	109.4
C(45)-C(44)-H(44A)	109.4
C(34)-C(44)-H(44B)	109.4
C(45)-C(44)-H(44B)	109.4
H(44A)-C(44)-H(44B)	108.0
C(46)-C(45)-C(44)	113.7(2)
C(46)-C(45)-H(45A)	108.8
C(44)-C(45)-H(45A)	108.8
C(46)-C(45)-H(45B)	108.8
C(44)-C(45)-H(45B)	108.8
H(45A)-C(45)-H(45B)	107.7
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(35)-C(47)-C(48)	114.12(18)
C(35)-C(47)-H(47A)	108.7
C(48)-C(47)-H(47A)	108.7
C(35)-C(47)-H(47B)	108.7
C(48)-C(47)-H(47B)	108.7
H(47A)-C(47)-H(47B)	107.6
C(49)-C(48)-C(47)	113.61(19)
C(49)-C(48)-H(48A)	108.8
C(47)-C(48)-H(48A)	108.8
C(49)-C(48)-H(48B)	108.8
C(47)-C(48)-H(48B)	108.8
H(48A)-C(48)-H(48B)	107.7
C(48)-C(49)-H(49A)	109.5
C(48)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(48)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(36)-C(50)-C(51)	115.94(19)
C(36)-C(50)-H(50A)	108.3
C(51)-C(50)-H(50A)	108.3
C(36)-C(50)-H(50B)	108.3
C(51)-C(50)-H(50B)	108.3
H(50A)-C(50)-H(50B)	107.4
C(52)-C(51)-C(50)	112.57(18)
C(52)-C(51)-H(51A)	109.1
C(50)-C(51)-H(51A)	109.1
C(52)-C(51)-H(51B)	109.1
C(50)-C(51)-H(51B)	109.1
H(51A)-C(51)-H(51B)	107.8
C(51)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(51)-C(52)-H(52C)	109.5

H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(37)-C(53)-C(54)	113.96(17)
C(37)-C(53)-H(53A)	108.8
C(54)-C(53)-H(53A)	108.8
C(37)-C(53)-H(53B)	108.8
C(54)-C(53)-H(53B)	108.8
H(53A)-C(53)-H(53B)	107.7
C(55)-C(54)-C(53)	113.49(17)
C(55)-C(54)-H(54A)	108.9
C(53)-C(54)-H(54A)	108.9
C(55)-C(54)-H(54B)	108.9
C(53)-C(54)-H(54B)	108.9
H(54A)-C(54)-H(54B)	107.7
C(54)-C(55)-H(55A)	109.5
C(54)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(54)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(38)-C(56)-C(57)	112.29(18)
C(38)-C(56)-H(56A)	109.1
C(57)-C(56)-H(56A)	109.1
C(38)-C(56)-H(56B)	109.1
C(57)-C(56)-H(56B)	109.1
H(56A)-C(56)-H(56B)	107.9
C(58)-C(57)-C(56)	112.7(2)
C(58)-C(57)-H(57A)	109.1
C(56)-C(57)-H(57A)	109.1
C(58)-C(57)-H(57B)	109.1
C(56)-C(57)-H(57B)	109.1
H(57A)-C(57)-H(57B)	107.8
C(57)-C(58)-H(58A)	109.5
C(57)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5
C(57)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58C)	109.5
H(58B)-C(58)-H(58C)	109.5
C(39)-C(59)-C(60)	114.35(18)
C(39)-C(59)-H(59A)	108.7
C(60)-C(59)-H(59A)	108.7
C(39)-C(59)-H(59B)	108.7
C(60)-C(59)-H(59B)	108.7
H(59A)-C(59)-H(59B)	107.6
C(61)-C(60)-C(59)	113.9(2)
C(61)-C(60)-H(60A)	108.8
C(59)-C(60)-H(60A)	108.8
C(61)-C(60)-H(60B)	108.8
C(59)-C(60)-H(60B)	108.8
H(60A)-C(60)-H(60B)	107.7
C(60)-C(61)-H(61A)	109.5
C(60)-C(61)-H(61B)	109.5
H(61A)-C(61)-H(61B)	109.5

C(60)-C(61)-H(61C)	109.5
H(61A)-C(61)-H(61C)	109.5
H(61B)-C(61)-H(61C)	109.5
C(40)-C(62)-C(63)	116.76(19)
C(40)-C(62)-H(62A)	108.1
C(63)-C(62)-H(62A)	108.1
C(40)-C(62)-H(62B)	108.1
C(63)-C(62)-H(62B)	108.1
H(62A)-C(62)-H(62B)	107.3
C(64)-C(63)-C(62)	112.90(19)
C(64)-C(63)-H(63A)	109.0
C(62)-C(63)-H(63A)	109.0
C(64)-C(63)-H(63B)	109.0
C(62)-C(63)-H(63B)	109.0
H(63A)-C(63)-H(63B)	107.8
C(63)-C(64)-H(64A)	109.5
C(63)-C(64)-H(64B)	109.5
H(64A)-C(64)-H(64B)	109.5
C(63)-C(64)-H(64C)	109.5
H(64A)-C(64)-H(64C)	109.5
H(64B)-C(64)-H(64C)	109.5

Symmetry transformations used to generate equivalent atoms:

2) Crystal Data for 4e

Table 1. Crystal data and structure refinement for 4e.

Identification code	4e
Empirical formula	C ₃₆ H ₃₂
Formula weight	464.62
Temperature	293(2) K
Measurement device	Rigaku RAXIS RAPID IP
Measurement method	Oscillation
Wavelength	0.71073 Å
Program for data collection	
Program for cell refinement	
Program for data reduction	
Program for structure solution	
Program for structure refinement	
Program for molecular graphics	
Program for publication material	
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.7357(19) Å alpha = 72.66(3) deg. b = 10.937(2) Å beta = 79.32(3) deg. c = 14.409(3) Å gamma = 66.81(3) deg.
Volume	1342.1(5) Å ³
Refls. No. for cell measurement	11772
Theta range for cell measurement	2.09 to 25 deg.
Z, Calculated density	2, 1.150 Mg/m ³
Absorption coefficient	0.065 mm ⁻¹
F(000)	496
Crystal shape / Crystal colour	Block / Colourless
Crystal size	0.40 x 0.30 x 0.15 mm
Theta range for data collection	2.09 to 25.00 deg.
Limiting indices	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -17 ≤ l ≤ 15
Reflections collected / unique	11772 / 4601 [R(int) = 0.0318]
Reflections with I > 2σ(I)	2441
Completeness to theta = 25.00	97.3 %
Decay correction (%)	?
Absorption correction	Empirical
Max. and min. transmission	0.990 and 0.974
Method for primary solution	direct
Method for secondary solution	difmap
Hydrogen addition / treatment	/
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4601 / 0 / 326
Goodness-of-fit on F ²	1.199
Final R indices [I > 2σ(I)]	R1 = 0.0651, wR2 = 0.1753
R indices (all data)	R1 = 0.1228, wR2 = 0.1905
Extinction coefficient	0.052(5)
Largest diff. peak and hole	0.178 and -0.144 e.Å ⁻³
Max. and mean shift/sigma	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [deg] for 4c.

C(1)-C(2)	1.530(5)
C(1)-C(5)	1.572(4)
C(1)-C(8)	1.487(5)
C(2)-C(3)	1.420(5)
C(2)-C(9)	1.488(4)
C(2)-C(8)	1.971(6)
C(3)-C(4)	1.407(4)
C(3)-C(15)	1.485(4)
C(4)-C(5)	1.490(5)
C(4)-C(33)	1.500(5)
C(4)-C(6)	2.018(6)
C(5)-C(34)	1.513(5)
C(5)-C(6)	1.515(5)
C(6)-C(7)	1.414(5)
C(6)-C(21)	1.484(5)
C(7)-C(8)	1.410(4)
C(7)-C(27)	1.484(4)
C(8)-C(35)	1.521(5)
C(1)-C(36)	1.514(4)
C(9)-C(10)	1.385(5)
C(9)-C(14)	1.396(5)
C(10)-C(11)	1.389(5)
C(11)-C(12)	1.369(5)
C(12)-C(13)	1.378(5)
C(13)-C(14)	1.399(5)
C(15)-C(16)	1.394(4)
C(15)-C(20)	1.402(4)
C(16)-C(17)	1.384(5)
C(17)-C(18)	1.386(5)
C(18)-C(19)	1.380(5)
C(19)-C(20)	1.391(5)
C(21)-C(26)	1.389(5)
C(21)-C(22)	1.407(5)
C(22)-C(23)	1.361(5)
C(23)-C(24)	1.383(5)
C(24)-C(25)	1.385(6)
C(25)-C(26)	1.376(5)
C(27)-C(32)	1.382(4)
C(27)-C(28)	1.399(5)
C(28)-C(29)	1.397(5)
C(29)-C(30)	1.389(6)
C(30)-C(31)	1.377(5)
C(31)-C(32)	1.405(5)
C(3)-C(2)-C(9)	124.1(3)
C(3)-C(2)-C(1)	109.6(3)
C(9)-C(2)-C(1)	123.9(3)
C(3)-C(2)-C(8)	111.7(3)
C(9)-C(2)-C(8)	115.1(3)
C(1)-C(2)-C(8)	48.3(2)

C(4)-C(3)-C(2)	110.0(3)
C(4)-C(3)-C(15)	124.1(3)
C(2)-C(3)-C(15)	125.6(3)
C(3)-C(4)-C(5)	111.8(3)
C(3)-C(4)-C(33)	124.0(3)
C(5)-C(4)-C(33)	121.8(3)
C(3)-C(4)-C(6)	112.1(3)
C(5)-C(4)-C(6)	48.34(19)
C(33)-C(4)-C(6)	114.8(3)
C(4)-C(5)-C(34)	120.8(3)
C(4)-C(5)-C(6)	84.4(3)
C(34)-C(5)-C(6)	120.0(3)
C(4)-C(5)-C(1)	104.3(3)
C(34)-C(5)-C(1)	118.1(3)
C(6)-C(5)-C(1)	103.5(3)
C(7)-C(6)-C(21)	123.2(3)
C(7)-C(6)-C(5)	110.4(3)
C(21)-C(6)-C(5)	125.2(3)
C(7)-C(6)-C(4)	110.5(3)
C(21)-C(6)-C(4)	115.0(3)
C(5)-C(6)-C(4)	47.3(2)
C(8)-C(7)-C(6)	110.0(3)
C(8)-C(7)-C(27)	124.0(3)
C(6)-C(7)-C(27)	125.6(3)
C(7)-C(8)-C(1)	110.8(3)
C(7)-C(8)-C(35)	121.8(3)
C(1)-C(8)-C(35)	124.0(3)
C(7)-C(8)-C(2)	112.8(3)
C(1)-C(8)-C(2)	50.1(2)
C(35)-C(8)-C(2)	116.4(3)
C(8)-C(1)-C(36)	120.9(3)
C(8)-C(1)-C(2)	81.6(3)
C(36)-C(1)-C(2)	120.3(3)
C(8)-C(1)-C(5)	105.1(3)
C(36)-C(1)-C(5)	118.2(3)
C(2)-C(1)-C(5)	104.2(2)
C(10)-C(9)-C(14)	118.2(3)
C(10)-C(9)-C(2)	122.8(3)
C(14)-C(9)-C(2)	119.0(3)
C(9)-C(10)-C(11)	121.4(3)
C(12)-C(11)-C(10)	119.9(3)
C(11)-C(12)-C(13)	120.2(3)
C(12)-C(13)-C(14)	120.1(3)
C(9)-C(14)-C(13)	120.2(3)
C(16)-C(15)-C(20)	116.3(3)
C(16)-C(15)-C(3)	124.0(3)
C(20)-C(15)-C(3)	119.7(3)
C(17)-C(16)-C(15)	122.1(3)
C(18)-C(17)-C(16)	120.3(4)
C(19)-C(18)-C(17)	119.2(4)
C(18)-C(19)-C(20)	120.1(3)
C(19)-C(20)-C(15)	122.0(3)
C(26)-C(21)-C(22)	117.3(3)

C(26)-C(21)-C(6)	121.4(3)
C(22)-C(21)-C(6)	121.4(3)
C(23)-C(22)-C(21)	121.8(4)
C(22)-C(23)-C(24)	119.5(4)
C(23)-C(24)-C(25)	120.4(4)
C(26)-C(25)-C(24)	119.5(4)
C(25)-C(26)-C(21)	121.5(4)
C(32)-C(27)-C(28)	118.2(3)
C(32)-C(27)-C(7)	118.9(3)
C(28)-C(27)-C(7)	122.9(3)
C(29)-C(28)-C(27)	120.7(4)
C(30)-C(29)-C(28)	120.2(4)
C(31)-C(30)-C(29)	119.6(4)
C(30)-C(31)-C(32)	119.9(4)
C(27)-C(32)-C(31)	121.3(3)

Symmetry transformations used to generate equivalent atoms:

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

4a

expanded scale of ^1H NMR
(0.5-2.5ppm)

4b

expanded scale of ^1H NMR
(0.5-2.5ppm)

4b

DEPT 135

4d

expanded scale of ¹H NMR
(0.5-2.5ppm)

4e

expanded scale of ^1H NMR
(6.6-7.4ppm)

4e

DEPT-135

5a

expanded scale of ^1H NMR
(0.7-2.3ppm)

6

expanded scale of ^1H NMR
(1.4-1.6ppm)

6

expanded scale of ^1H NMR
(3.9-5.0ppm)