Electronic Supplementary Information for:

Selective Synthesis of Unsymmetric Dibenzo[*a*,*e*]pentalenes by Rhodium-Catalysed Stitching Reaction

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1. General

General: All reactions were carried out using glove boxes or standard Schlenk techniques under argon purified by passing through a hot column packed with BASF catalyst R3-11. Thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel impregnated with a fluorescent indicator (Merck, #1.15685.0001).

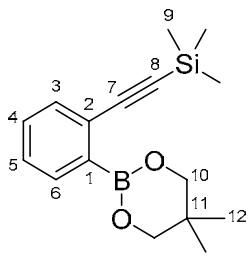
Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER Ascend500 spectrometer (^{1}H: 500 MHz and ^{13}C: 126 MHz) at ambient temperature unless otherwise noted. Chemical shift values for protons were referenced to the residual proton resonance of chloroform-*d* (δ: 7.26). Chemical shift values for carbons were referenced to the carbon resonance of chloroform-*d* (δ: 77.16). Elemental analyses were performed at One-stop Sharing Facility Center for Future Drug Discoveries, Graduate School of Pharmaceutical Sciences, The University of Tokyo or the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo. High resolution electrospray-ionisation (ESI) mass spectra were recorded on a JEOL JMS-T100LP AccuTOF LC-plus instrument. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer equipped with an attenuated total reflection (ATR) system. Melting points and decomposition points were recorded on an OptiMelt MPA-100 apparatus. Ultraviolet(UV)/visible absorption spectra were recorded on a Shimadzu UV-3150 spectrometer. Cyclic voltammograms were recorded on a BAS ALS electrochemical analyser 619Ep. Preparative gel permeation chromatography (GPC) was carried out with a JAI LC-9260 II NEXT system equipped with two JAIGEL-2HR column (Japan Analytical Industry Co., Ltd.; 20 mm i.d. × 600 mm). X-ray crystallographic analyses of single crystals were performed on a Rigaku VariMax with Saturn diffractometer. A single crystal was mounted with mineral oil on a loop-type mount and transferred to the goniometer. The radiation was performed with graphite-monochromated Mo Kα (α = 0.71075 Å) at 50 kV and 24 mA. The structures were solved by the direct method with (SHELXT 2014)[1] and refined by full-matrix least-squares techniques against F^2 (SHELXL 2014).[1] The intensities were corrected for Lorentz and polarisation effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

(1) G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 2014.

Materials: Anhydrous toluene, THF, and dichloromethane were purchased from Kanto Chemical Co. Inc. (Kanto) and purified by the method of Pangborn *et al.*[2] Diisopropylamine (Wako Pure Chemical Industries, Ltd. (Wako)), triethylamine (Tokyo Chemical Industry, Co., Ltd. (TCI)), and dipropylamine (TCI) were used after distillation over KOH under argon. Anhydrous 1,4-dioxane (Wako) was used after degassing by purging argon prior to use. The following compounds were purchased from commercial suppliers and used as received: 2,2-dimethyl-1,3-propanediol (TCI), molecular sieves 4A (MS4A) (Nacalai Tesque; powder), magnesium sulfate (Kanto), butyllithium (Kanto; 1.60–1.63 M solution in hexane), triisopropyl borate (TCI), *tert*-butyl(ethynyl)dimethylsilane (TCI), copper(I) iodide (Kanto), ethynyltrimethylsilane (TCI), 1,2,4,5-tetrabromobenzene (TCI), 1,5-cyclooctadiene (TCI), and cesium carbonate (Kanto), and tetrabutylammonium hexafluorophosphate (Wako). The following compounds were prepared by literature procedures: 2-[(trimethylsilyl)ethynyl]phenylboronic acid,[3] [(2-bromophenyl)ethynyl](*tert*-butyl)dimethylsilane,[4] 2-[(triisopropylsilyl)ethynyl]phenylboronic acid,[5] 2,3-dibromonaphthalene,[6] dichloridobis(triphenylphosphane)palladium,[7] 4-bromo-3-iodo-*N*,*N*-dimethylaniline,[8] 2-bromo-3-iodothiophene,[9] 3-bromo-2-iodothiophene,[10] 1-bromo-2-iodo-4-nitrobenzene,[11] and di-μ-hydroxidobis[(1,5-cyclooctadiene)rhodium] ([Rh(OH)(cod)]$_2$).[12]

2. Synthesis of Substrates

2-[(Trimethylsilyl)ethynyl]phenylboronic acid neopentylglycol ester (1a)



A mixture of 2-[(trimethylsilyl)ethynyl]phenylboronic acid (510 mg, 2.34 mmol), 2,2-dimethyl-1,3-propanediol (244 mg, 2.34 mmol), and MS4A (480 mg) in toluene (18 mL) was refluxed for 1 h. After cooled to room temperature, the mixture was passed through a pad of magnesium sulfate with hexane and concentrated under vacuum. The residue was dissolved in pentane, filtered through a PTFE membrane (pore size: 0.20 μm), and concentrated under vacuum to afford compound **1a** as a colorless solid (668 mg, 2.34 mmol, 100% yield); mp 41–43 °C; IR (neat) cm^{-1} 3053, 2959, 2898, 2156, 1558, 1476, 1436, 1413, 1302, 1247, 1133, 1092, 839, 755, 646; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.67–7.65 (m, 1H, H6), 7.49–7.48 (m, 1H, H3), 7.32–7.29 (m, 1H, H4), 7.29–7.25 (m, 1H, H5), 3.79 (s, 4H, H10), 1.06 (s, 6H, H12), 0.25 (s, 9H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 134.1 (1C, C6), 133.2 (1C, C3), 129.7 (1C, C4), 127.7 (1C, C5), 127.0 (1C, C2), 106.4 (1C, C7), 95.3 (1C, C8), 72.5 (2C, C10), 31.9 (1C, C11), 22.1 (2C, C12), 0.2 (3C, C9); HRMS (ESI) *m/z* calcd for $C_{16}H_{23}BNaO_2Si$ $[M+Na]^+$ 309.1453, found 309.1452.

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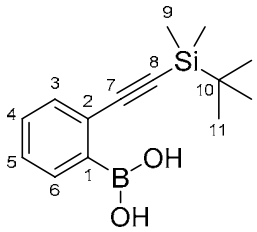
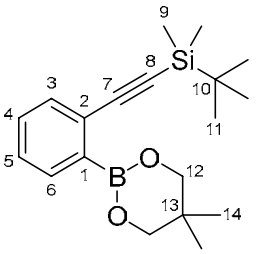
(2) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
(3) A. Kondoh, T. Aoki and M. Terada, *Chem. Eur. J.*, 2015, **21**, 12577.
(4) D. Arican and R. Brückner, *Org. Lett.*, 2013, **15**, 2582.
(5) A. Jančařík, J. Rybáček, K. Cocq, J. Vacek Chocholoušová, J. Vacek, R. Pohl, L. Bednárová, P. Fiedler, I. Císařová, I. G. Stará and I. Starý, *Angew. Chem. Int. Ed.*, 2013, **52**, 9970.
(6) H. Hart, A. Bashir-Hashemi, J. Luo and M. A. Meador, *Tetrahedron*, 1986, **42**, 1641.
(7) H. Oskooie, M. M. Heravi and F. K. Behbahani, *Molecules*, 2007, **12**, 1438.
(8) M. Rickhaus, L. M. Bannwart, M. Neuburger, H. Gsellinger, K. Zimmermann, D. Häussinger and M. Mayor, *Angew. Chem. Int. Ed.*, 2014, **53**, 14587.
(9) M. Sonoda, S. Kinoshita, T. Luu, H. Fukuda, K. Miki, R. Umeda and Y. Tobe, *Synth. Commun.*, 2009, **39**, 3315.
(10) A. C. J. Heinrich, B. Thiedemann, P. J. Gates and A. Staubitz, *Org. Lett.*, 2013, **15**, 4666.
(11) T. Kowada, S. Yamaguchi, H. Fujinaga and K. Ohe, *Tetrahedron*, 2011, **67**, 3105.
(12) R. Uson, L. A. Oro and J. A. Cabeza, *Inorg. Synth.* 1985, **23**, 126.

2-[(*tert*-Butyldimethylsilyl)ethynyl]phenylboronic acid



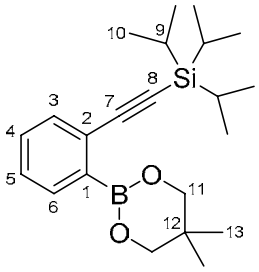
To a solution of [(2-bromophenyl)ethynyl](*tert*-butyl)dimethylsilane (2.33 g, 7.89 mmol) in THF (60 mL) was slowly added butyllithium (6.00 mL, 9.78 mmol; 1.63 M solution in hexane) over 10 min at −78 °C. After the mixture was stirred for 30 min at −78 °C, triisopropyl borate (3.80 mL, 16 mmol) was then added and the mixture was stirred for 30 min at −78 °C and for 7 h at room temperature. The reaction was quenched with 1 M hydrochloric acid and extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/diethyl ether (gradient from 95:5 to 0:100) to afford 2-[(*tert*-butyldimethylsilyl)ethynyl]phenylboronic acid as a colorless solid (1.83 g, 7.03 mmol; 89% yield); R_f = 0.34 (hexane/diethyl ether; 4:1); mp 60–62 °C; IR (neat) cm^{-1} 3480, 3397, 3218, 3062, 2950, 2928, 2857, 2142, 1472, 1442, 1401, 1363, 1334, 1250, 1076, 1048, 1020, 835, 777, 754, 743, 599, 547; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.99–7.97 (m, 1H, H6), 7.53–7.51 (m, 1H, H3), 7.43–7.37 (m, 2H, H4 and H5), 5.78 (s, 2H, HO), 1.01 (s, 9H, H11), 0.24 (s, 6H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 135.7 (1C, C6), 133.0 (1C, C3), 130.8 (1C, C4), 128.7 (1C, C5), 126.8 (1C, C2), 107.4 (1C, C7), 97.5 (1C, C8), 26.2 (3C, C11), 16.8 (1C, C10), −4.6 (2C, C9).

2-[(*tert*-Butyldimethylsilyl)ethynyl]phenylboronic acid neopentylglycol ester (1b)



To a solution of 2-[(*tert*-butyldimethylsilyl)ethynyl]phenylboronic acid (472 mg, 1.81 mmol) and 2,2-dimethyl-1,3-propanediol (189 mg, 1.81 mmol) in dichloromethane (6.0 mL) was added magnesium sulfate (654 mg, 5.43 mmol) and the mixture was stirred for 30 min at room temperature. The reaction mixture was then concentrated under vacuum. The residue was dissolved in pentane, filtered through a PTFE membrane (pore size: 0.20 μm), and concentrated under vacuum to afford compound **1b** as a colorless viscous oil (514 mg, 1.79 mmol, 100% yield); IR (neat) cm^{-1} 2955, 2926, 2885, 2854, 2156, 1478, 1438, 1415, 1377, 1336, 1305, 1257, 1246, 1216, 1134, 1094, 849, 835, 804, 773, 760, 714; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.68–7.67 (m, 1H, H6), 7.51–7.49 (m, 1H, H3), 7.32–7.29 (m, 1H, H4), 7.28–7.25 (m, 1H, H5), 3.77 (s, 4H, H12), 1.05 (s, 6H, H14), 1.01 (s, 9H, H11), 0.18 (s, 6H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 134.2 (1C, C6), 133.6 (1C, C3), 129.7 (1C, C4), 127.6 (1C, C5), 127.2 (1C, C2), 107.0 (1C, C7), 93.7 (1C, C8), 72.5 (2C, C12), 31.9 (1C, C13), 26.3 (3C, C11), 22.1 (2C, C14), 16.9 (1C, C10), −4.3 (2C, C9); HRMS (ESI) *m/z* calcd for $C_{19}H_{29}BNaO_2Si$ $[M+Na]^+$ 351.1922, found 351.1917.

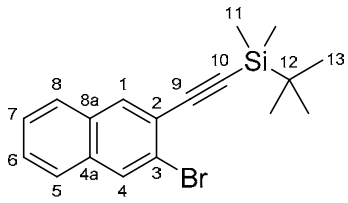
2-[(Triisopropylsilyl)ethynyl]phenylboronic acid neopentylglycol ester (1c)



A mixture of 2-[(triisopropylsilyl)ethynyl]phenylboronic acid (419 mg, 1.39 mmol), 2,2-dimethyl-1,3-propanediol (145 mg, 1.39 mmol), and MS4A (307 mg) in toluene (10 mL) was refluxed for 1 h. After cooled to room temperature, this was passed through a pad of magnesium sulfate with hexane and concentrated under vacuum. The residue was dissolved in pentane, filtered through a PTFE membrane (pore size: 0.20 μm), and concentrated under vacuum to afford compound **1c** as a colorless viscous oil (514 mg, 1.39 mmol, 100% yield); IR (neat) cm^{-1} 2955, 2939, 2889, 2863, 2154, 1339, 1312, 1305, 1287, 1258, 1212, 1136, 1094, 995, 883, 836, 760, 715, 668; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.70–7.69 (m, 1H, H6), 7.53–7.51 (m, 1H, H3), 7.33–7.29 (m, 1H, H4), 7.28–7.25 (m, 1H, H5), 3.76 (s, 4H, H11),

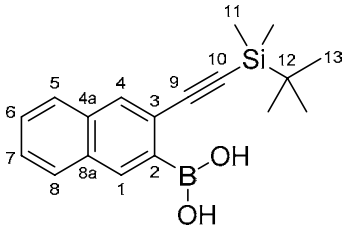
1.18–1.12 (m, 21H, H9 and H10), 1.04 (s, 6H, H13); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 134.3 (1C, C6), 134.1 (1C, C3), 129.7 (1C, C4), 127.6 (1C, C2), 127.5 (1C, C5), 108.4 (1C, C7), 91.8 (1C, C8), 72.5 (2C, C11), 31.9 (1C, C12), 22.1 (2C, C13), 18.8 (6C, C10), 11.6 (3C, C9); HRMS (ESI) *m/z* calcd for $C_{22}H_{35}BNaO_2Si$ $[M+Na]^+$ 393.2392, found 393.2399.

[(3-Bromonaphthalen-2-yl)ethynyl](*tert*-butyl)dimethylsilane



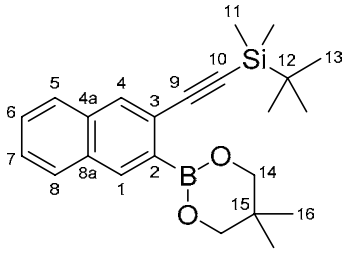
To a mixture of 2,3-dibromonaphthalene (1.14 g, 4.00 mmol), dichloridobis(triphenylphosphane)palladium (141 mg, 200 μmol), and copper(I) iodide (38.1 mg, 200 μmol) in triethylamine (40 mL) was added *tert*-butyl(ethynyl)dimethylsilane (830 μL, 4.44 mmol), and the mixture was stirred for 2 h at 90 °C. The mixture was then concentrated under vacuum. The residue was suspended in hexane, then passed through a pad of Celite and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with chloroform to afford [(3-bromonaphthalen-2-yl)ethynyl](*tert*-butyl)dimethylsilane as a white solid (798 mg, 2.31 mmol, 58% yield); R_f = 0.32 (hexane); mp 78–80 °C; IR (neat) cm^{-1} 3056, 2952, 2925, 2881, 2853, 2154, 1580, 1489, 1471, 1462, 1444, 1423, 1387, 1361, 1317, 1267, 1245, 1237, 1210, 1174, 1146, 1132, 1007, 991, 948, 941, 907, 895, 885, 826, 810, 771, 739, 674, 626, 595, 576, 526, 472, 457; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 8.07 (s, 1H, H4), 8.04 (s, 1H, H1), 7.76–7.74 (m, 1H, H8), 7.73–7.70 (m, 1H, H5), 7.51–7.47 (m, 2H, H6 and H7), 1.05 (s, 9H, H13), 0.24 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 133.8 (2C, C1 and C4a), 131.8 (1C, C8a), 131.1 (1C, C4), 127.8 (1C, C6), 127.7 (1C, C8), 126.9 (2C, C5 and C7), 122.8 (1C, C2), 122.1 (1C, C3), 104.0 (1C, C9), 97.9 (1C, C10), 26.3 (3C, C13), 17.0 (1C, C12), −4.5 (2C, C11); Anal. calcd for C, 62.60; H, 6.13, found C, 62.33; H, 6.15.

3-[(*tert*-Butyldimethylsilyl)ethynyl]naphthalene-2-ylboronic acid



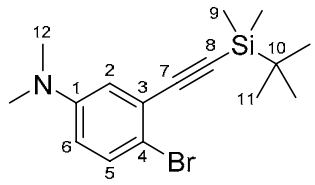
To a solution of [(3-bromonaphthalen-2-yl)ethynyl](*tert*-butyl)-dimethylsilane (691 mg, 2.00 mmol) in THF (15 mL) was slowly added butyllithium (1.50 mL, 2.40 mmol; 1.60 M solution in hexane) over 5 min at −78 °C, and the mixture was stirred for 30 min at −78 °C. Triisopropyl borate (0.920 mL, 4.0 mmol) was then added to it and the mixture was stirred for 30 min at room temperature. The reaction was quenched with 1 M hydrochloric acid and extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/diethyl ether (gradient from 93:7 to 54:46) to afford 3-[(*tert*-butyldimethylsilyl)ethynyl]naphthalene-2-ylboronic acid as a colorless solid (546 mg, 1.76 mmol; 88% yield); R_f = 0.32 (hexane/diethyl ether; 7:3); mp 80–82 °C; IR (neat) cm^{-1} 3408, 3057, 2951, 2929, 2856, 2137, 1456, 1394, 1332, 1293, 1250, 1210, 1173, 1074, 1004, 888, 824, 774, 743, 677, 475; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 8.53 (s, 1H, H1), 8.05 (s, 1H, H4), 7.90–7.88 (m, 1H, H8), 7.80–7.78 (m, 1H, H5), 7.57–7.51 (m, 2H, H6 and H7), 5.88 (s, 2H, HO), 1.05 (s, 9H, H13), 0.27 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 137.6 (1C, C1), 134.1 (1C, C4a), 133.3 (1C, C4), 132.7 (1C, C8a), 128.9 (1C, C8), 128.1 (1C, C6), 127.5 (1C, C5), 127.3 (1C, C7), 122.5 (1C, C3), 107.9 (1C, C9), 97.0 (1C, C10), 26.3 (3C, C13), 16.9 (1C, C12), −4.5 (2C, C11).

3-[(*tert*-Butyldimethylsilyl)ethynyl]naphthalene-2-ylboronic acid neopentylglycol ester (1d)



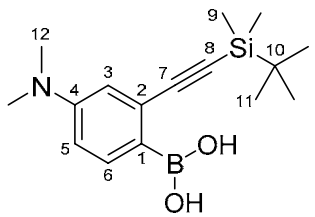
To a solution of 3-[(*tert*-butyldimethylsilyl)ethynyl]naphthalene-2-ylboronic acid (413 mg, 1.33 mmol) and 2,2-dimethyl-1,3-propanediol (140 mg, 1.33 mmol) in dichloromethane (20 mL) was added magnesium sulfate (481 mg, 4.00 mmol) and the mixture was stirred for 3 h at room temperature. The reaction mixture was then concentrated under vacuum. The residue was dissolved in pentane, filtered through a PTFE membrane (pore size: 0.20 μm), and concentrated under vacuum to afford compound **1d** as a colorless viscous oil (500 mg, 1.32 mmol, 99% yield); IR (neat) cm^{-1} 3054, 2954, 2926, 2884, 2855, 2150, 1583, 1476, 1456, 1439, 1416, 1476, 1336, 1322, 1288, 1248, 1218, 1202, 1171, 1138, 1095, 1025, 1007, 953, 906, 891, 825, 813, 773, 746, 721, 702, 675, 631, 586, 476; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 8.22 (s, 1H, H1), 8.03 (s, 1H, H4), 7.82–7.80 (m, 1H, H8), 7.75–7.74 (m, 1H, H5), 7.49–7.43 (m, 2H, H6 and H7), 3.83 (s, 4H, H14), 1.08 (s, 6H, H16), 1.04 (s, 9H, H13), 0.22 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 135.5 (1C, C1), 133.8 (1C, C4a), 133.6 (1C, C4), 132.4 (1C, C8a), 128.4 (1C, C8), 127.5 (1C, C5), 127.2 (1C, C6), 126.6 (1C, C7), 123.6 (1C, C3), 107.3 (1C, C9), 93.4 (1C, C10), 72.6 (2C, C14), 32.0 (1C, C15), 26.4 (3C, C13), 22.2 (2C, C16), 17.0 (1C, C12), –4.2 (2C, C11); HRMS (ESI) *m/z* calcd for $C_{23}H_{31}BNaO_2Si$ $[M+Na]^+$ 401.2079, found 401.2093.

4-Bromo-3-[(*tert*-butyldimethylsilyl)ethynyl]-*N,N*-dimethylaniline



To a mixture of 4-bromo-3-iodo-*N,N*-dimethylaniline (652 mg, 2.00 mmol), dichloridobis(triphenylphosphane)palladium (42.1 mg, 60.0 μmol), and copper(I) iodide (22.9 mg, 120 μmol) in THF (4.0 mL) and triethylamine (0.84 mL) was added *tert*-butyl(ethynyl)dimethylsilane (400 μL, 2.14 mmol), and the mixture was stirred for 3.5 h at 60 °C. The reaction was quenched with 1 M aqueous ammonium chloride solution and extracted with diethyl ether. The organic layer was washed with water and then brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/dichloromethane (gradient from 95:5 to 75:25) to afford 4-bromo-3-[(*tert*-butyldimethylsilyl)ethynyl]-*N,N*-dimethylaniline as a colorless solid (572 mg, 1.69 mmol, 85% yield); R_f = 0.29 (hexane/dichloromethane; 9:1); mp 72–74 °C; IR (neat) cm^{-1} 2951, 2926, 2853, 2156, 1589, 1495, 1447, 1372, 1245, 1161, 890, 834, 822, 801, 772, 731, 677, 628, 601; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.34 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H5), 6.82 (d, $^4J_{HH}$ = 3.1 Hz, 1H, H2), 6.53 (dd, $^3J_{HH}$= 8.9 Hz, $^4J_{HH}$ = 3.1 Hz, 1H, H6), 2.92 (s, 6H, H12), 1.02 (s, 9H, H11), 0.20 (s, 6H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 149.4 (1C, C1), 132.6 (1C, C5), 125.2 (1C, C3), 117.2 (1C, C2), 114.5 (1C, C6), 112.1 (1C, C4), 104.8 (1C, C7), 96.5 (1C, C8), 40.6 (2C, C12), 26.3 (3C, C11), 17.0 (1C, C10), –4.5 (2C, C9); Anal. calcd for $C_{16}H_{24}BrNSi$: C, 56.80; H, 7.15; N, 4.14, found C, 56.68; H, 6.96; N, 4.15.

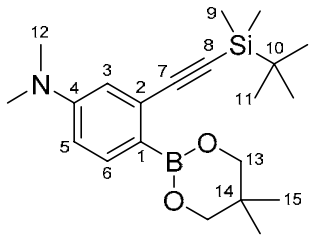
2-[(*tert*-Butyldimethylsilyl)ethynyl]-4-(dimethylamino)phenylboronic acid



To a solution of 4-bromo-3-[(*tert*-butyldimethylsilyl)ethynyl]-*N,N*-dimethylaniline (406 mg, 1.20 mmol) and triisopropyl borate (330 μL, 1.4 mmol) in toluene (4.0 mL) and THF (1.0 mL) was slowly added butyllithium (900 μL, 1.44 mmol; 1.60 M solution in hexane) over 1 h at –78 °C, and the mixture was stirred for 30 min at room temperature. The reaction was quenched with 1 M ammonium chloride solution and

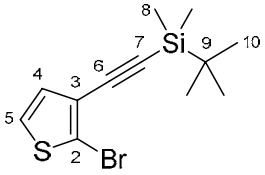
extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/diethyl ether (gradient from 93:7 to 0:100) to afford 2-[(*tert*-butyldimethylsilyl)ethynyl]-4-(dimethylamino)phenylboronic acid as a colorless solid (137 mg, 0.452 mmol; 38% yield); R_f = 0.21 (hexane/diethyl ether; 7:3); mp 96–98 °C; IR (neat) cm^{-1} 3501, 3382, 2948, 2929, 2858, 2139, 1590, 1539, 1387, 1361, 1332, 1248, 1100, 1069, 1024, 975, 889, 837, 825, 809, 774, 750, 678, 635, 611; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.80 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H6), 6.79 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H3), 6.70 (dd, $^3J_{HH}$= 8.5 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, H5), 5.54 (s, 2H, HO), 3.00 (s, 6H, H12), 1.01 (s, 9H, H11), 0.23 (s, 6H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 151.8 (1C, C4), 137.0 (1C, C6), 127.8 (1C, C2), 115.9 (1C, C3), 112.4 (1C, C5), 108.5 (1C, C7), 95.7 (1C, C8), 40.1 (2C, C12), 26.3 (3C, C11), 16.8 (1C, C10), –4.5 (2C, C9).

2-[(*tert*-Butyldimethylsilyl)ethynyl]-4-(dimethylamino)phenylboronic acid neopentylglycol ester (1e)



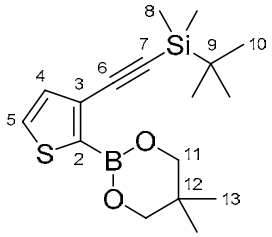
To a solution of 2-[(*tert*-butyldimethylsilyl)ethynyl]-4-(dimethylamino)phenylboronic acid (121 mg, 400 μmol) and 2,2-dimethyl-1,3-propanediol (41.7 mg, 400 μmol) in dichloromethane (4 mL) was added magnesium sulfate (144 mg, 1.20 mmol) and the mixture was stirred for 30 min at room temperature. The mixture was then concentrated under vacuum. The residue was dissolved in pentane, filtered through a PTFE membrane (pore size: 0.20 μm), and concentrated under vacuum to afford compound **1e** as a colorless solid (146 mg, 392 μmol, 98% yield); mp 124–126 °C; IR (neat) cm^{-1} 2953, 2926, 2855, 2154, 1587, 1539, 1476, 1363, 1333, 1307, 1244, 1163, 1147, 981, 888, 849, 823, 808, 770, 702, 648, 619; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H6), 6.83 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H3), 6.63, (dd, $^3J_{HH}$= 8.5 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, H5), 3.73 (s, 4H, H13), 2.96 (s, 6H, H12), 1.014 (s, 6H, H15), 1.008 (s, 9H, H11), 0.18 (s, 6H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 151.3 (1C, C4), 136.0 (1C, C6), 128.4 (1C, C2), 117.2 (1C, C3), 111.9 (1C, C5), 108.1 (1C, C7), 92.2 (1C, C8), 72.4 (2C, C13), 40.3 (2C, C12), 31.9 (1C, C14), 26.4 (3C, C11), 22.2 (2C, C15), 17.0 (1C, C10), –4.2 (2C, C9); HRMS (ESI) *m/z* calcd for $C_{21}H_{34}BNNaO_2Si$ $[M+Na]^+$ 394.2344 found 394.2350.

2-Bromo-3-[(*tert*-butyldimethylsilyl)ethynyl]thiophene



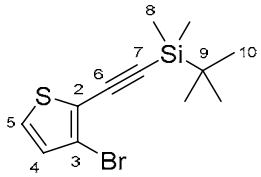
To a mixture of 2-bromo-3-iodothiophene (1.73 g, 6.00 mmol), dichloridobis(triphenylphosphane)palladium (140 mg, 200 μmol), and copper(I) iodide (80.0 mg, 420 μmol) in THF (60 mL) and diisopropylamine (60 mL) was added *tert*-butyl(ethynyl)dimethylsilane (1.20 mL, 6.42 mmol), and the mixture was stirred for 1 h at room temperature. The mixture was then concentrated under vacuum. The residue was suspended in hexane, then passed through a pad of Celite and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford 2-bromo-3-[(*tert*-butyldimethylsilyl)ethynyl]thiophene as a colorless oil (1.66 g, 5.50 mmol, 92% yield); R_f = 0.41 (hexane); IR (neat) cm^{-1} 2953, 2925, 2882, 2856, 2155, 1472, 1405, 1363, 1350, 1256, 1248, 1223, 1004, 965, 838, 833, 822, 810, 775, 713, 671, 633, 622; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.16 (d, $^3J_{HH}$ = 5.8 Hz, 1H, H5), 6.96 (d, $^3J_{HH}$ = 5.8 Hz, 1H, H4), 1.01 (s, 9H, H10), 0.19 (s, 6H, H8); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 130.1 (1C, C4), 125.7 (1C, C5), 124.8 (1C, C2), 118.1 (1C, C3), 98.8 (1C, C6), 97.4 (1C, C7), 26.3 (3C, C10), 16.8 (1C, C9), –4.5 (2C, C8); HRMS (ESI) *m/z* calcd for $C_{12}H_{17}AgBrSSi$ $[M+Ag]^+$ 406.9049, found 406.9043.

3-[(*tert*-Butyldimethylsilyl)ethynyl]thiophene-2-ylboronic acid neopentylglycol ester (1f)



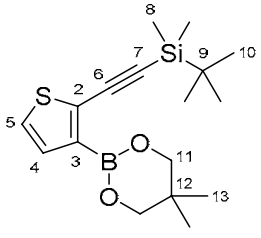
To a solution of 2-bromo-3-[(*tert*-butyldimethylsilyl)ethynyl]thiophene (603 mg, 2.00 mmol) in THF (15 mL) was slowly added butyllithium (1.60 mL, 2.58 mmol; 1.61 M solution in hexane) over 5 min at −78 °C, and the mixture was stirred for 30 min at −78 °C. Triisopropyl borate (0.920 mL, 4.0 mmol) was then added to it and the mixture was stirred for 1 h at room temperature. The reaction was quenched with 1 M hydrochloric acid and extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/diethyl ether (gradient from 95:5 to 20:80). The resulting boronic acid and 2,2-dimethyl-1,3-propanediol (208 mg, 2.00 mmol) were dissolved in dichloromethane (7.5 mL), and to the solution was added magnesium sulfate (722 mg, 6.00 mmol). After stirring for 5 h at room temperature, the reaction mixture was concentrated under vacuum. The residue was purified by GPC with chloroform to afford compound **1f** as a yellow green oil (371 mg, 1.11 mmol, 56% yield); IR (neat) cm^{-1} 2954, 2931, 2883, 2854, 2147, 1505, 1476, 1419, 1362, 1284, 1250, 1223, 1203, 1113, 1078, 1023, 1007, 959, 836, 824, 811, 775, 737, 716, 702, 673, 626; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.41 (d, $^3J_{HH}$ = 4.8 Hz, 1H, H5), 7.19 (d, $^3J_{HH}$ = 4.8 Hz, 1H, H4), 3.75 (s, 4H, H11), 1.03 (s, 6H, H13), 1.01 (s, 9H, H10), 0.18 (s, 6H, H8); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 132.8 (1C, C4), 130.1 (1C, C5), 129.3 (1C, C3), 101.8 (1C, C6), 94.1 (1C, C7), 72.5 (1C, C11), 32.1 (1C, C12), 26.2 (3C, C10), 22.1 (2C, C13), 16.9 (1C, C9), –4.4 (2C, C8); HRMS (ESI) *m/z* calcd for $C_{17}H_{27}BNaO_2SSi$ $[M+Na]^+$ 357.1486, found 357.1490.

3-Bromo-2-[(*tert*-butyldimethylsilyl)ethynyl]thiophene



To a mixture of 3-bromo-2-iodothiophene (1.16 g, 4.00 mmol), dichloridobis(triphenylphosphane)palladium (98.3 mg, 140 μmol), and copper(I) iodide (49.5 mg, 260 μmol) in THF (40 mL) and diisopropylamine (40 mL) was added *tert*-butyl(ethynyl)dimethylsilane (0.80 mL, 4.3 mmol), and the mixture was stirred for 12 h at room temperature. The mixture was then concentrated under vacuum. The residue was suspended in hexane, then passed through a pad of Celite and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford 3-bromo-2-[(*tert*-butyldimethylsilyl)ethynyl]thiophene as a colorless oil (1.02 g, 3.40 mmol, 85% yield); R_f = 0.41 (hexane); IR (neat) cm^{-1} 2951, 2928, 2882, 2855, 2148, 1363, 1347, 1249, 1174, 1147, 1079, 1006, 938, 865, 839, 825, 815, 775, 748, 710, 680, 634, 609; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.17 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H5), 6.94 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H4), 1.01 (s, 9H, H10), 0.20 (s, 6H, H8); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 130.1 (1C, C4), 127.0 (1C, C5), 121.1 (1C, C2), 117.0 (1C, C3), 102.1 (1C, C7), 96.3 (1C, C6), 26.3 (3C, C10), 16.9 (1C, C9), –4.6 (2C, C8); HRMS (ESI) *m/z* calcd for $C_{12}H_{17}AgBrSSi$ $[M+Ag]^+$ 406.9049, found 406.9051.

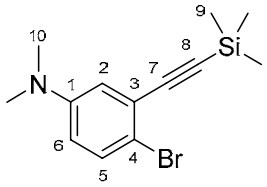
2-[(*tert*-Butyldimethylsilyl)ethynyl]thiophene-3-ylboronic acid neopentylglycol ester (1g)



To a solution of 3-bromo-2-[(*tert*-butyldimethylsilyl)ethynyl]thiophene (603 mg, 2.00 mmol) and triisopropyl borate (0.550 mL, 2.4 mmol) in THF (15 mL) was slowly added butyllithium (1.50 mL, 2.42 mmol; 1.61 M solution in hexane) over 40 min at −78 °C, and the mixture was stirred for 20 min at room temperature. The reaction was quenched with 1 M aqueous ammonium chloride solution and extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum.

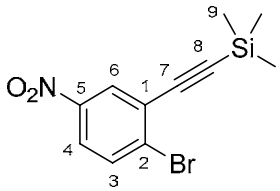
The residue and 2,2-dimethyl-1,3-propanediol (208 mg, 2.00 mmol) were dissolved in dichloromethane (7.5 mL), and magnesium sulfate (722 mg, 6.00 mmol) was added to the solution. After stirring for 30 min at room temperature, the reaction mixture was concentrated under vacuum. The residue was purified by GPC with chloroform to afford compound **1g** as a pale brown oil (438 mg, 1.31 mmol, 66% yield); IR (neat) cm^{-1} 2955, 2927, 2883, 2855, 2144, 1362, 1290, 1250, 1152, 1079, 1050, 995, 862, 837, 826, 813, 774, 695, 678, 637, 503; ^1H NMR (500 MHz, $CDCl_3$, rt) δ 7.20 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H4), 7.15 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H5), 3.73 (s, 4H, H11), 1.02 (s, 6H, H13), 1.01 (s, 9H, H10), 0.18 (s, 6H, H8); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 132.6 (1C, C4), 131.0 (1C, C2), 126.1 (1C, C5), 99.4 (1C, C6), 98.9 (1C, C7), 72.4 (2C, C11), 32.0 (1C, C12), 26.2 (3C, C10), 22.1 (2C, C13), 17.0 (1C, C9), –4.5 (2C, C8); HRMS (ESI) *m/z* calcd for $C_{17}H_{27}BNaO_2SSi$ $[M+Na]^+$ 357.1486, found 357.1498.

4-Bromo-3-[(trimethylsilyl)ethynyl]-*N*,*N*-dimethylaniline (2c)



To a mixture of 4-bromo-3-iodo-*N*,*N*-dimethylaniline (326 mg, 1.00 mmol), dichloridobis(triphenylphosphane)palladium (21.1 mg, 30.0 μmol), and copper(I) iodide (11.4 mg, 60.0 μmol) in THF (2.0 mL) and triethylamine (0.42 mL) was added ethynyltrimethylsilane (150 μL, 1.1 mmol), and the mixture was stirred for 3.5 h at 60 °C. The reaction was quenched with a saturated aqueous ammonium chloride solution and extracted with diethyl ether. The organic layer was washed with water and then brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/dichloromethane (gradient from 98:2 to 80:20) to afford compound **2c** as a colorless solid (243 mg, 0.821 mmol, 82% yield); R_f = 0.25 (hexane/dichloromethane; 9:1); mp 69–71 °C; IR (neat) cm^{-1} 2957, 2897, 2805, 2163, 1590, 1489, 1444, 1363, 1247, 1158, 1031, 974, 891, 833, 797, 757, 730, 650, 595; ^1H NMR (500 MHz, $CDCl_3$, rt) δ 7.34 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H5), 6.81 (d, $^4J_{HH}$ = 3.1 Hz, 1H, H2), 6.53 (dd, $^3J_{HH}$= 8.9 Hz, $^4J_{HH}$ = 3.1 Hz, 1H, H6), 2.92 (s, 6H, H10), 0.27 (s, 9H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 149.4 (1C, C1), 132.6 (1C, C5), 125.1 (1C, C3), 117.1 (1C, C2), 114.5 (1C, C6), 111.9 (1C, C4), 104.2 (1C, C7), 98.1 (1C, C8), 40.6 (2C, C10), 0.1 (3C, C9); Anal. calcd for $C_{13}H_{18}BrNSi$: C, 52.70; H, 6.12; N, 4.73, found C, 52.50; H, 6.06; N, 4.65.

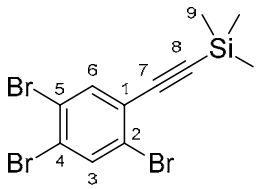
[(2-Bromo-5-nitrophenyl)ethynyl]trimethylsilane (2d)



To a mixture of 1-bromo-2-iodo-4-nitrobenzene (328 mg, 1.00 mmol), dichloridobis(triphenylphosphane)palladium (35.1 mg, 50.0 μmol), and copper(I) iodide (9.5 mg, 50 μmol) in dipropylamine (10 mL) was added ethynyltrimethylsilane (170 μL, 1.2 mmol), and the mixture was stirred for 2 h at room temperature. The mixture was then concentrated under vacuum. The residue was suspended in hexane, then passed through a pad of Celite and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/dichloromethane (gradient from 95:5 to 81:19) and further purified by recrystallisation from hexane to afford [(2-bromo-5-nitrophenyl)ethynyl]trimethylsilane as a colorless solid (167 mg, 0.560 mmol, 56% yield); R_f = 0.36 (hexane/dichloromethane; 4:1); mp 94–96 °C; IR (neat) cm^{-1} 3103, 2957, 1521, 1346, 1248, 1035, 840, 827, 815, 759, 737, 698, 643; ^1H NMR (500 MHz, $CDCl_3$, rt) δ 8.32 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H6), 7.99 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, H4), 7.76 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H3), 0.30 (s, 9H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 146.9 (1C, C5), 133.5 (1C, C3), 133.1 (1C, C2), 128.2 (1C, C6), 127.1 (1C, C1), 123.9 (1C, C4), 103.4 (1C, C8), 100.8 (1C,

C7), −0.2 (3C, C9); Anal. calcd for $C_{11}H_{12}BrNO_2Si$: C, 44.30; H, 4.06; N, 4.70, found C, 44.27; H, 4.11; N, 4.67.

[(2,4,5-Tribromophenyl)ethynyl]trimethylsilane (2e)



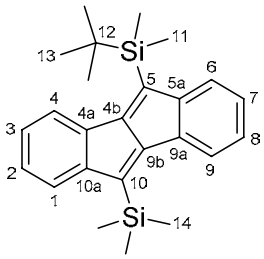
To a mixture of 1,2,4,5-tetrabromobenzene (787 mg, 2.00 mmol), dichloridobis(triphenylphosphane)palladium (70.1 mg, 100 μmol), and copper(I) iodide (19.0 mg, 100 μmol) in triethylamine (20 mL) was added ethynyltrimethylsilane (0.33 mL, 2.3 mmol), and the mixture was stirred for 2 h at 90 °C. The mixture was then concentrated under vacuum. The residue was suspended in hexane, then passed through a pad of Celite and concentrated under vacuum. The residue was chromatographed on silica gel with hexane and further purified by GPC with chloroform to afford [(2,4,5-tribromophenyl)ethynyl]trimethylsilane as a colorless solid (313 mg, 0.76 mmol, 38% yield); R_f = 0.50 (hexane); mp 83–85 °C; IR (neat) cm^{-1} 3082, 2958, 2894, 2160, 1436, 1318, 1248, 1114, 1047, 886, 837, 763, 719, 658, 580; ^1H NMR (500 MHz, $CDCl_3$, rt) δ 7.83 (s, 1H, H3), 7.71 (s, 1H, H6), 0.27 (s, 9H, H9); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 137.4 (1C, C6), 136.5 (1C, C3), 126.0 (1C), 125.5 (1C), 124.7 (1C), 123.4 (1C), 102.5 (1C, C8), 100.9 (1C, C7), −0.2 (3C, C9); HRMS (ESI) *m/z* calcd for $C_{11}H_{11}AgBr_3Si$ $[M+Ag]^+$ 514.7226, found 514.7212.

3. Catalytic Reactions

General Procedure for Table 1, Entries 1–5

To a mixture of di-μ-hydroxidobis[(1,5-cyclooctadiene)rhodium] (1.9 mg, 8.3 μmol Rh), cesium carbonate (48.9 mg, 150 μmol), and compound **2a** (25.3 mg, 100 μmmol) in 1,4-dioxane/water (0.50 mL; 50/1) was added a solution of 1,5-cyclooctadiene (5,2 μL, 42 μmol) and compound **1** (100 μmol) in 1,4-dioxane/water (0.50 mL; 50/1). The reaction mixture was stirred for 16 h at the given temperature and this was directly passed through a pad of silica gel with dichloromethane. After removal of the solvent under vacuum, NMR yield was determined by ^1H NMR against an internal standard (dibromomethane). All ^1H NMR signals for **3aa** in entry 1 were in good agreement with those reported by Kawase *et al.*[13] **3ba** was isolated in entry 5. **3ca** was obtained with inseparable side-product **4ca** in entry 3.

Table 1, Entry 5; 5-(*tert*-butyldimethylsilyl)-10-(trimethylsilyl)dibenzo[*a*,*e*]pentalene (3ba)



The residue was chromatographed on silica gel with hexane and further purified by recrystallisation from dichloromethane/methanol to afford compound **3ba** as a reddish brown solid (30.2 mg, 77.7 μmol; 78% yield); R_f = 0.26 (hexane); mp 158–160 °C; IR (neat) cm^{-1} 2951, 2923, 2851, 1424, 1249, 1101, 964, 830, 802, 741, 684; ^1H NMR (500 MHz, $CDCl_3$, rt) δ 7.24–7.22 (m, 1H, H4), 7.16–7.15 (m, 1H, H9), 7.04–7.01 (m, 2H, H1 and H6), 6.86–6.78 (m, 4H, H2, H3, H7 and H8), 1.02 (s, 9H, H13), 0.42 (s, 9H, H14), 0.41 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 160.0 (1C, C4b), 158.9 (1C, C9b), 155.9 (1C, C5a), 155.5 (1C, C10a), 141.4 (1C, C10), 140.5 (1C, C5), 136.1 (1C, C4a), 135.7 (1C, C9a), 128.2 (1C, C2), 128.0 (1C, C7), 126.5 (1C, C3), 126.4 (1C, C8), 125.3 (1C, C6), 124.5 (1C, C1), 124.0 (1C, C4), 123.5 (1C, C9), 27.2 (3C, C13), 19.1 (1C, C12), 0.4 (3C, C14), −2.2 (2C, C11); Anal. calcd for $C_{25}H_{32}Si_2$: C, 77.25; H, 8.30, found C, 76.97; H, 8.29.

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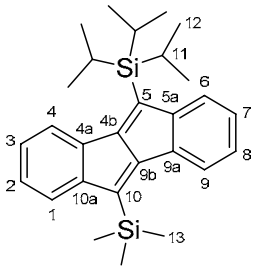
(13) T. Kawase, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata and T. Kubo, *Chem. Eur. J.*, 2009, **15**, 2653.

Table 1, Entry 3; 5-(triisopropylsilyl)-10-(trimethylsilyl)dibenzo[*a,e*]pentalene (3ca)



The residue was purified by silica gel preparative TLC with hexane and further purified by GPC with chloroform to afford compound **3ca** as a reddish brown solid with inseparable side-product (15.5 mg); R_f = 0.31 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26–7.25 (m, 1H, H4), 7.17–7.15 (m, 1H, H9), 7.14–7.12 (m, 1H, H6), 7.05–7.03 (m, 1H, H1), 6.86–6.79 (m, 4H, H2, H3, H7 and H8), 1.64 (sept, $^3J_{HH}$ = 7.3 Hz, 3H, H11), 1.20 (d, $^3J_{HH}$ = 7.3 Hz, 18H, H12), 0.43 (s, 9H, H13); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 160.3 (1C, C4b), 159.3 (1C, C9b), 156.0 (1C, C5a), 155.6 (1C, C10a), 141.7 (1C, C5), 140.4 (1C, C10), 136.6 (1C, C4a), 135.8 (1C, C9a), 128.0 (1C, C2), 127.9 (1C, C7), 126.44 (1C, C3), 126.39 (1C, C8), 125.2 (1C, C6), 124.4 (1C, C1), 124.0 (1C, C4), 123.3 (1C, C9), 19.5 (6C, C12), 13.5 (3C, C11), 0.5 (3C, C13); HRMS (ESI) *m/z* calcd for $C_{28}H_{38}NaSi_2$ $[M+Na]^+$ 453.2404, found 453.2398.

Table 1, Entry 6; Large Scale Synthesis of 3ba

To a mixture of di-μ-hydroxidobis[(1,5-cyclooctadiene)rhodium] (9.6 mg, 42 μmol Rh), cesium carbonate (244 mg, 0.750 mmol), and compound **2a** (127 mg, 0.500 mmol) in 1,4-dioxane/water (2.5 mL; 50/1) was added a solution of 1,5-cyclooctadiene (26 μL, 0.21 mmol) and compound **1b** (164 mg, 0.500 mmol) in 1,4-dioxane/water (2.5 mL; 50/1). The reaction mixture was stirred for 16 h at 40 °C and this was directly passed through a pad of silica gel with dichloromethane. After removal of the solvent under vacuum, NMR yield was determined by ^{1}H NMR against an internal standard (dibromomethane). The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to give a reddish brown solid. The filtrate was purified by silica gel preparative TLC with hexane/toluene (9:1) and further purified by recrystallisation from dichloromethane/methanol. These solids were combined to afford compound **3ba** as a reddish brown solid (150 mg, 0.387 mmol; 77% yield).

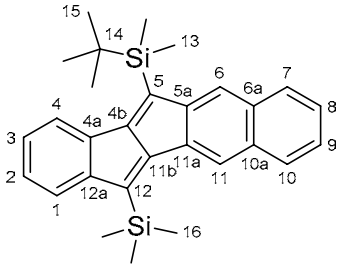
Use of Arylboronic Acid or Pinacol Arylboronate instead of Neopentyl Glycol Arylboronate

To a mixture of di-μ-hydroxidobis[(1,5-cyclooctadiene)rhodium] (1.9 mg, 8.3 μmol Rh), cesium carbonate (48.9 mg, 150 μmol), and compound **2a** (25.3 mg, 100 μmmol) in 1,4-dioxane/water (0.50 mL; 50/1) was added a solution of 1,5-cyclooctadiene (5,2 μL, 42 μmol) and 2-[(*tert*-butyldimethylsilyl)ethynyl]phenylboronic acid or 2-[(*tert*-butyldimethylsilyl)ethynyl]phenylboronic acid pinacol ester (100 μmol) in 1,4-dioxane/water (0.50 mL; 50/1). After stirring for 16 h at 40 °C, the reaction mixture was directly passed through a pad of silica gel with dichloromethane. After removal of volatile matters under vacuum, NMR yields were determined to be 79% and 90%, respectively, by ^{1}H NMR analyses against an internal standard (dibromomethane).

General Procedure for Schemes 3 and 4

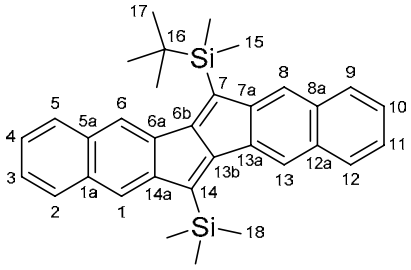
To a mixture of di-μ-hydroxidobis[(1,5-cyclooctadiene)rhodium] (1.9 mg, 8.3 μmol Rh), cesium carbonate (48.9 mg, 150 μmol), and compound **2** (100 μmol) in 1,4-dioxane/water (0.50 mL; 50/1) was added a solution of 1,5-cyclooctadiene (5,2 μL, 42 μmol) and compound **1** (100 μmol) in 1,4-dioxane/water (0.50 mL; 50/1). The reaction mixture was stirred for 16 h at 40 °C or 32 h at 60 °C and this was directly passed through a pad of silica gel with dichloromethane. After removal of the solvent under vacuum, NMR yield was determined by ^{1}H NMR against an internal standard (dibromomethane).

5-(*tert*-Butyldimethylsilyl)-12-(trimethylsilyl)benzo[*a*]naphtho[2,3-*e*]pentalene (3bb)



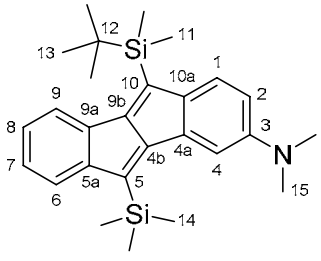
The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to give a reddish brown solid. The filtrate was purified by silica gel preparative TLC with hexane/dichloromethane (9:1) and further purified by recrystallisation from dichloromethane/methanol. These solids were combined to afford compound **3bb** as a reddish brown solid (32.5 mg, 74.1 μmol; 74% yield); R_f = 0.23 (hexane); mp 172–174 °C; IR (neat) cm^{-1} 2945, 2926, 2853, 1419, 1363, 1339, 1248, 1147, 1025, 1008, 961, 943, 936, 882, 834, 807, 785, 775, 765, 757, 742, 728, 711, 683, 673, 634, 615; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.59–7.53 (m, 2H, H7 and H10), 7.57 (s, 1H, H11), 7.45–7.43 (m, 1H, H4), 7.43 (s, 1H, H6), 7.30–7.27 (m, 2H, H8 and H9), 7.20–7.18 (m, 1H, H1), 6.98–6.95 (m, 1H, H2), 6.91–6.88 (m, 1H, H3), 1.06 (s, 9H, H15), 0.52 (s, 6H, H13), 0.50 (s, 9H, H16); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 162.4 (1C, C4b), 157.0 (1C, C11b), 155.8 (1C, C12a), 153.7 (1C, C5a), 140.9 (1C, C5), 137.4 (1C, C12), 135.1 (1C, C4a), 134.0 (1C, C10a), 133.8 (1C, C11a), 133.2 (1C, C6a), 128.94 (1C, C7), 128.86 (1C, C10), 128.5 (1C, C2), 126.5 (2C, C8 and C9), 125.8 (1C, C3), 124.5 (1C, C4), 124.3 (1C, C6), 124.2 (1C, C1), 122.6 (1C, C11), 27.3 (3C, C15), 19.2 (1C, C14), 0.4 (3C, C16), −1.9 (2C, C13); Anal. calcd for $C_{29}H_{34}Si_2$: C, 79.39; H, 7.81, found C, 79.09; H, 7.98.

7-(*tert*-Butyldimethylsilyl)-14-(trimethylsilyl)dinaphtho[2,3-*a*:2',3'-*e*]pentalene (3db)



The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **3db** as a reddish brown solid (31.0 mg, 63.4 μmol; 63% yield); R_f = 0.18 (hexane); mp 224–226 °C; IR (neat) cm^{-1} 3061, 2947, 2923, 2851, 1419, 1254, 1249, 1153, 1025, 1007, 952, 931, 880, 858, 833, 801, 775, 748, 714, 677, 626, 617; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.89 (s, 1H, H6), 7.78 (s, 1H, H13), 7.67–7.61 (m, 4H, H2, H5, H9 and H12), 7.58 (s, 1H, H1), 7.56 (s, 1H, H8), 7.35–7.30 (m, 4H, H3, H4, H10 and H11), 1.11 (s, 9H, H17), 0.60 (s, 15H, H15 and H18); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 160.7 (1C, C6b), 159.7 (1C, C13b), 153.8 (1C, C7a), 153.2 (1C, C14a), 138.0 (1C, C14), 136.8 (1C, C7), 134.2 (1C, C1a), 134.1 (1C, C8a), 133.5 (1C, C6a), 133.3 (1C, C13a), 132.7 (2C, C5a and C12a), 129.2 (1C, C5), 129.0 (1C, C12), 128.9 (1C, C9), 128.7 (1C, C2), 126.8 (1C, C3), 126.6 (1C, C10), 126.2 (2C, C4 and C11), 124.0 (1C, C6), 123.8 (1C, C8), 123.4 (1C, C13), 122.8 (1C, C1), 27.4 (3C, C17), 19.5 (1C, C16), 0.6 (3C, C18), −1.9 (2C, C15); Anal. calcd for $C_{33}H_{36}Si_2$: C, 81.09; H, 7.42, found C, 81.21; H, 7.53.

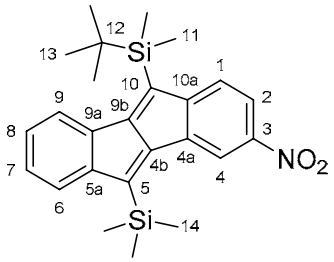
10-(*tert*-Butyldimethylsilyl)-3-(dimethylamino)-5-(trimethylsilyl)dibenzo[*a*,*e*]pentalene (3bc)



The residue was purified by silica gel preparative TLC with carbon disulfide and further purified by reprecipitation from dichloromethane/methanol. The precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **3bc** as a green solid (15.8 mg, 36.6 μmmol; 37% yield); R_f = 0.37 (hexane/dichloromethane; 7:3); mp 160–162 °C; IR (neat) cm^{-1} 2949,

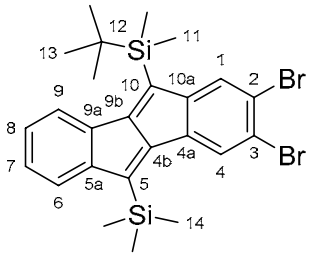
2925, 2891, 2853, 2798, 1609, 1489, 1469, 1435, 1423, 1353, 1252, 1108, 1073, 1006, 979, 950, 832, 803, 771, 719, 690, 679, 663, 641, 627, 576; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.21–7.17 (m, 1H, H9), 7.06–7.02 (m, 1H, H6), 6.85 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, H1), 6.82–6.76 (m, 2H, H7 and H8), 6.76 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, H4), 6.10 (dd, $^{3}J_{HH}$= 8.5 Hz, $^{4}J_{HH}$ = 2.4 Hz, 1H, H2), 2.93 (s, 6H, H15), 1.01 (s, 9H, H13), 0.43 (s, 9H, H14), 0.38 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 159.2 (1C, C4b), 156.7 (1C, C9b), 154.9 (1C, C5a), 149.7 (1C, C3), 144.5 (1C, C10a), 142.6 (1C, C10), 139.2 (1C, C5), 137.7 (1C, C4a), 136.4 (1C, C9a), 127.0 (1C, C7), 126.1 (1C, C8), 126.0 (1C, C1), 124.3 (1C, C6), 123.2 (1C, C9), 110.7 (1C, C4), 109.6 (1C, C2), 40.8 (2C, C15), 27.2 (3C, C13), 19.0 (1C, C12), 0.3 (3C, C14), −2.3 (2C, C11); HRMS (ESI) *m/z* calcd for $C_{27}H_{38}NSi_2$ $[M+H]^+$ 432.2537, found 432.2558.

10-(*tert*-Butyldimethylsilyl)-3-nitro-5-(trimethylsilyl)dibenzo[*a*,*e*]pentalene (3bd)



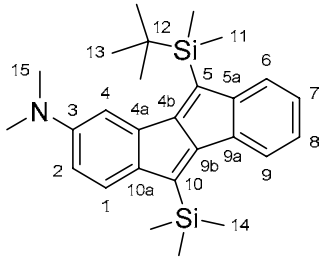
The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **3bd** as a brown solid (28.2 mg, 65.0 μmol; 65% yield); R_f = 0.41 (hexane/dichloromethane; 7:3); mp 214–216 °C; IR (neat) cm^{-1} 2950, 2923, 2853, 1508, 1415, 1325, 1246, 1159, 977, 897, 838, 735; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.99 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, H4), 7.79 (dd, $^{3}J_{HH}$= 8.5 Hz, $^{4}J_{HH}$ = 2.4 Hz, 1H, H2), 7.28–7.26 (m, 1H, H9), 7.13 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, H1), 7.09–7.07 (m, 1H, H6), 6.93–6.90 (m, 1H, H7), 6.88–6.85 (m, 1H, H8), 1.02 (s, 9H, H13), 0.47 (s, 9H, H14), 0.43 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 164.4 (1C, C9b), 162.0 (1C, C10a), 156.2 (1C, C4b), 155.1 (1C, C5a), 146.6 (1C, C3), 146.5 (1C, C5), 138.6 (1C, C10), 136.6 (1C, C4a), 135.6 (1C, C9a), 129.3 (1C, C7), 127.5 (1C, C8), 125.4 (1C, C6), 124.7 (1C, C9), 124.3 (1C, C1), 123.8 (1C, C2), 117.4 (1C, C4), 27.1 (3C, C13), 19.3 (1C, C12), 0.5 (3C, C14), −2.3 (2C, C11); Anal. calcd for $C_{25}H_{31}NO_2Si_2$: C, 69.24; H, 7.21; N, 3.23, found C, 69.35; H, 7.27; N, 3.20.

2,3-Dibromo-10-(*tert*-butyldimethylsilyl)-5-(trimethylsilyl)dibenzo[*a*,*e*]pentalene (3be)



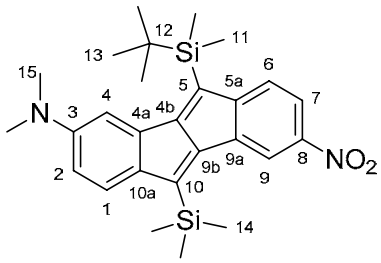
The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **3be** as a brown solid (40.5 mg, 74.1 μmol; 74% yield); R_f = 0.43 (hexane); mp 160–162 °C; IR (neat) cm^{-1} 2948, 2925, 2851, 1419, 1361, 1339, 1249, 1097, 877, 834, 808, 773, 715, 689, 622; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.35 (s, 1H, H4), 7.24–7.23 (m, 1H, H9), 7.23 (s, 1H, H1), 7.07–7.05 (m, 1H, H6), 6.90–6.87 (m, 1H, H7), 6.86–6.83 (m, 1H, H8), 1.01 (s, 9H, H13), 0.42 (s, 9H, H14), 0.40 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 161.1 (1C, C9b), 156.5 (1C, C4b), 156.3 (1C, C10a), 155.0 (1C, C5a), 144.3 (1C, C5), 138.9 (1C, C10), 136.4 (1C, C4a), 135.6 (1C, C9a), 129.5 (1C, C1), 128.8 (1C, C7), 127.5 (1C, C4), 127.1 (1C, C8), 125.0 (1C, C6), 124.4 (1C, C9), 123.4 (1C, C2), 122.0 (1C, C3), 27.1 (3C, C13), 19.2 (1C, C12), 0.4 (3C, C14), −2.4 (2C, C11); Anal. calcd for $C_{25}H_{30}Br_2Si_2$: C, 54.95; H, 5.53, found C, 54.95; H, 5.51.

5-(*tert*-Butyldimethylsilyl)-3-(dimethylamino)-10-(trimethylsilyl)dibenzo[*a*,*e*]pentalene (3ea)



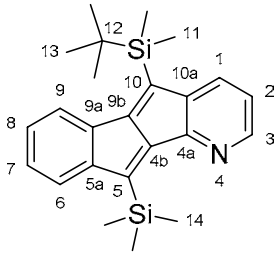
The residue was purified by silica gel preparative TLC with hexane/dichloromethane (7:3) and further purified by reprecipitation from dichloromethane/methanol. The precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **3ea** as a green solid (14.6 mg, 33.8 μmol; 34% yield); R_f = 0.37 (hexane/dichlromethane; 7:3); mp 139–141 °C; IR (neat) cm^{-1} 3080, 3054, 2953, 2924, 2886, 2850, 2799, 1611, 1591, 1569, 1516, 1490, 1456, 1436, 1358, 1328, 1305, 1284, 1249, 1168, 1146, 1109, 1074, 1064, 1009, 978, 965, 951, 931, 921, 870, 831, 806, 791, 773, 757, 742, 717, 689, 676, 629, 590, 574, 540; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.13–7.10 (m, 1H, H9), 7.04–7.00 (m, 1H, H6), 6.87 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H1), 6.83 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H4), 6.82–6.78 (m, 2H, H7 and H8), 6.09 (dd, $^3J_{HH}$= 8.2 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, H2), 2.94 (s, 6H, H15), 1.02 (s, 9H, H13), 0.42 (s, 6H, H11), 0.39 (s, 9H, H14); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 160.3 (1C, C4b), 155.7 (1C, C9b), 155.4 (1C, C5a), 149.8 (1C, C3), 143.9 (1C, C10a), 143.7 (1C, C10), 138.2 (1C, C4a), 138.1 (1C, C5), 136.0 (1C, C9a), 126.8 (1C, C7), 126.1 (1C, C8), 125.14 (1C, C1), 125.09 (1C, C6), 122.6 (1C, C9), 111.4 (1C, C4), 109.6 (1C, C2), 40.9 (2C, C15), 27.2 (3C, C13), 19.6 (1C, C12), 0.4 (3C, C14), –2.4 (2C, C11); HRMS (ESI) *m/z* calcd for $C_{27}H_{38}NSi_2$ $[M+H]^+$ 432.2537, found 432.2556.

5-(*tert*-Butyldimethylsilyl)-3-(dimethylamino)-8-nitro-10-(trimethylsilyl)dibenzo[*a*,*e*]pentalene (3ed)



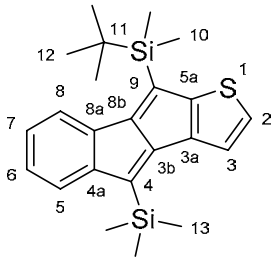
The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol. The precipitate was purified by silica gel preparative TLC with hexane/dichloromethane (7:3) and further purified by reprecipitation from dichloromethane/methanol. The precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **3ed** as a green solid (17.2 mg, 36.1 μmol; 36% yield); R_f = 0.32 (hexane/dichloromethane; 7:3); mp 184–186 °C; IR (neat) cm^{-1} 2949, 2925, 2892, 2853, 2809, 1609, 1589, 1507, 1430, 1363, 1329, 1296, 1241, 1149, 1124, 1102, 1086, 1061, 1006, 985, 967, 952, 890, 857, 832, 820, 807, 794, 772, 752, 734, 720, 691, 668, 625, 613, 581, 534; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.93 (d, $^4J_{HH}$ = 2.1 Hz, 1H, H9), 7.71 (dd, $^3J_{HH}$= 8.5 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, H7), 7.10 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H6), 6.89 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H1), 6.84 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H4), 6.09 (dd, $^3J_{HH}$= 8.2 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, H2), 2.97 (s, 6H, H15), 1.02 (s, 9H, H13), 0.44 (s, 15H, H11 and H14); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 164.7 (1C, C4b), 161.3 (1C, C5a), 152.7 (1C, C9b), 150.3 (1C, C3), 149.5 (1C, C10), 146.4 (1C, C8), 143.0 (1C, C10a), 138.0 (1C, C4a), 136.8 (1C, C5a), 136.2 (1C, C5), 126.5 (1C, C1), 124.1 (1C, C6), 122.2 (1C, C7), 116.6 (1C, C9), 111.9 (1C, C4), 109.9 (1C, C2), 40.8 (2C, C15), 27.1 (3C, C13), 19.8 (1C, C12), 0.5 (3C, C14), –2.4 (2C, C11); Anal. calcd for $C_{27}H_{36}N_2O_2Si_2$: C, 68.02; H, 7.61; N, 5.88, found C, 68.08; H, 7.61; N, 5.82.

10-(*tert*-Butyldimethylsilyl)-5-(trimethylsilyl)benzo[*a*]pyrido[2,3-*e*]pentalene (3bf)



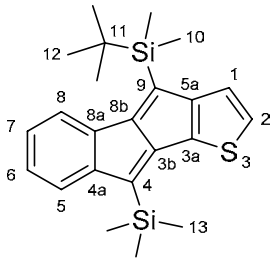
The residue was purified by silica gel preparative TLC with hexane/dichloromethane (9:1) to afford compound **3bf** as a brown solid (31.4 mg, 80.6 μmol; 81% yield); R_f = 0.14 (hexane); mp 139–141 °C; IR (neat) cm^{-1} 2951, 2927, 2854, 1381, 1242, 969, 840, 767, 752, 711; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.94 (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H3), 7.25–7.24 (m, 1H, H9), 7.18 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H1), 7.13–7.11 (m, 1H, H6), 6.90–6.84 (m, 2H, H7 and H8), 6.64 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H2), 1.00 (s, 9H, H13), 0.46 (s, 9H, H14), 0.39 (s, 6H, H11); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 159.1 (1C, C9b), 158.0 (1C, C4a), 157.2 (1C, C4b), 155.1 (1C, C5a), 149.8 (1C, C10a), 147.5 (1C, C5), 145.8 (1C, C3), 137.9 (1C, C10), 136.4(1C, C9a), 130.2 (1C, C1), 128.6 (1C, C7), 127.3 (1C, C8), 125.5 (1C, C6), 124.1 (1C, C9), 121.0 (1C, C2), 27.0 (3C, C13), 19.2 (1C, C12), 0.1 (3C, C14), –2.7 (2C, C11); Anal. calcd for $C_{24}H_{31}NSi_2$: C, 73.97; H, 8.02; N, 3.59, found C, 73.84; H, 8.03; N, 3.64.

9-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)benzo[*a*]thieno[3,2-*e*]pentalene (3bg)



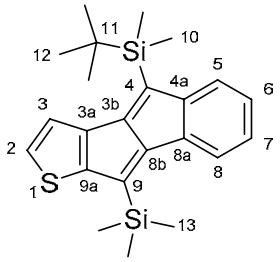
The residue was chromatographed on silica gel with hexane to afford compound **3bg** as a green solid (7.7 mg, 20 μmol; 20% yield); R_f = 0.38 (hexane); mp 108–110 °C; IR (neat) cm^{-1} 3094, 3062, 2952, 2928, 2896, 2855, 1454, 1419, 1360, 1249, 1242, 1205, 1103, 1026, 1001, 907, 839, 827, 805, 784, 765, 760, 753, 718, 692, 676, 664, 654, 642, 618, 579; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 6.85–6.83 (m, 1H, H8), 6.77 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H2), 6.75–6.74 (m, 1H, H5), 6.71 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H3), 6.65–6.61 (m, 2H, H6 and H7), 0.99 (s, 9H, H12), 0.321 (s, 9H, H13), 0.316 (s, 6H, H10); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 159.5 (1C, C9a), 159.0 (1C, C8b), 155.0 (1C, C3b), 154.6 (1C, C4a), 143.1 (1C, C4), 138.8 (1C, C3a), 137.9 (1C, C8a), 134.6 (1C, C9), 127.7 (1C, C6), 127.2 (1C, C7), 126.4 (1C, C2), 124.8 (1C, C5), 122.4(1C, C8), 122.1 (1C, C3), 27.0 (3C, C12), 19.0 (1C, C11), 0.0 (3C, C13), –3.8 (2C, C10); HRMS (ESI) *m/z* calcd for $C_{23}H_{30}SSi_2$ $[M]^+$ 394.1601, found 394.1600.

9-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)benzo[*a*]thieno[2,3-*e*]pentalene (3bh)



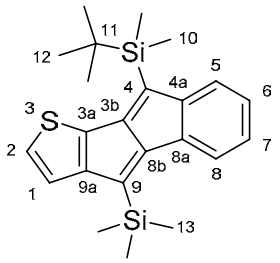
The residue was chromatographed on silica gel with hexane to afford compound **3bh** as a green solid (8.9 mg, 23 μmol; 23% yield); R_f = 0.38 (hexane); mp 108–110 °C; IR (neat) cm^{-1} 3092, 3060, 2953, 2896, 2855, 1430, 1243, 1183, 1102, 1019, 1009, 953, 925, 910, 828, 804, 774, 761, 745, 724, 708, 666, 644, 620, 578, 507; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 6.88 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H2), 6.87–6.83 (m, 1H, H8), 6.74–6.70 (m, 1H, H5), 6.67–6.63 (m, 2H, H6 and H7), 6.57 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H1), 0.98 (s, 9H, H12), 0.33 (s, 9H, H13), 0.30 (s, 6H, H10); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 162.5 (1C, C9a), 161.5 (1C, C8b), 154.7 (1C, C4a), 154.1 (1C, C3b), 142.8 (1C, C4), 137.5 (1C, C8a), 136.3 (1C, C9), 133.8 (1C, C3a), 128.4 (1C, C2), 127.8 (1C, C6), 127.4 (1C, C7), 124.4 (1C, C5), 123.3 (1C, C1), 122.2 (1C, C8), 26.9 (3C, C12), 18.9 (1C, C11), –0.5 (3C, C13), –3.4 (2C, C10); Anal. calcd for $C_{23}H_{30}SSi_2$: C, 69.99; H, 7.66, found C, 69.83; H, 7.50.

4-(*tert*-Butyldimethylsilyl)-9-(trimethylsilyl)benzo[*a*]thieno[3,2-*e*]pentalene (3fa)



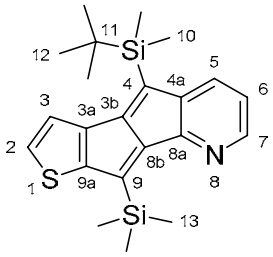
The residue was chromatographed on silica gel with hexane to afford compound **3fa** as a green solid (4.0 mg, 10 μmol; 10% yield); R_f = 0.36 (hexane); mp 124–126 °C; IR (neat) cm^{-1} 2952, 2926, 2892, 2853, 1361, 1249, 1103, 1082, 1025, 998, 906, 830, 806, 760, 721, 705, 681, 653, 641, 620, 576; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 6.76–6.73 (m, 2H, H5 and H8), 6.75 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H2), 6.71 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H3), 6.66–6.61 (m, 2H, H6 and H7), 0.97 (s, 9H, H12), 0.32 (s, 9H, H13), 0.31 (s, 6H, H10); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 158.8 (1C, C9a), 158.1 (1C, C8b), 156.7 (1C, C3b), 155.1 (1C, C4a), 142.4 (1C, C4), 139.3 (1C, C3a), 137.6 (1C, C8a), 135.7 (1C, C9), 127.6 (1C, C6), 127.2 (1C, C7), 126.1 (1C, C2), 125.6 (1C, C5), 122.8 (1C, C3), 121.9 (1C, C8), 27.0 (3C, C12), 18.5 (1C, C11), –0.6 (3C, C13), –3.3 (2C, C10); HRMS (ESI) *m/z* calcd for $C_{23}H_{30}SSi_2$ $[M]^+$ 394.1601, found 394.1616.

4-(*tert*-Butyldimethylsilyl)-9-(trimethylsilyl)benzo[*a*]thieno[2,3-*e*]pentalene (3ga)



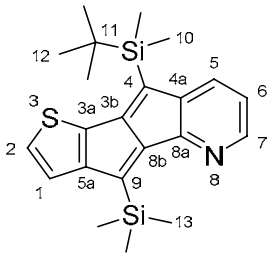
The residue was chromatographed on silica gel with hexane to afford compound **3ga** as a green solid with inseparable side-product (23.2 mg); R_f = 0.34 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 6.89 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H2), 6.76–6.75 (m, 1H, H8), 6.74–6.72 (m, 1H, H5), 6.67–6.62 (m, 2H, H6 and H7), 6.57 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H1), 0.98 (s, 9H, H12), 0.33 (s, 6H, H10), 0.31 (s, 9H, H13); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 161.9 (1C, C9a), 160.4 (1C, C8b), 155.9 (1C, C3b), 155.3 (1C, C4a), 142.1 (1C, C4), 137.3 (1C, C9), 137.2 (1C, C8a), 134.4 (1C, C3a), 128.6 (1C, C2), 127.6 (1C, C6), 127.3 (1C, C7), 125.4 (1C, C5), 122.5 (1C, C1), 121.9 (1C, C8), 27.0 (3C, C12), 19.0 (1C, C11), –0.3 (3C, C13), –4.0 (2C, C10); HRMS (ESI) *m/z* calcd for $C_{23}H_{30}SSi_2$ $[M]^+$ 394.1601, found 394.1608.

4-(*tert*-Butyldimethylsilyl)-9-(trimethylsilyl)pyrido[2,3-*a*]thieno[3',2'-*e*]pentalene (3ff)



The residue was purified by silica gel preparative TLC with hexane/dichloromethane (85:15) to afford compound **3ff** as a green solid (18.9 mg, 47.8 μmol; 48% yield); R_f = 0.38 (hexane/dichloromethane; 9:1); mp 120–122 °C; IR (neat) cm^{-1} 3090, 3048, 2948, 2928, 2895, 2854, 1377, 1362, 1240, 1196, 1162, 1129, 1102, 1088, 1036, 1007, 961, 940, 909, 832, 808, 778, 770, 761, 738, 725, 710, 679, 656, 645, 623, 592, 576; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.71 (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H7), 6.89 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H5), 6.83 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H2), 6.73 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H3), 6.41 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H6), 0.97 (s, 9H, H12), 0.36 (s, 9H, H13), 0.30 (s, 6H, H10); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 160.1 (1C, C8a), 158.6 (1C, C9a), 156.2 (1C, C8b), 155.7 (1C, C3b), 149.1 (1C, C4a), 146.1 (1C, C7), 141.8 (1C, C9), 140.4 (1C, C4), 140.3 (1C, C3a), 130.1 (1C, C5), 127.7 (1C, C2), 122.8 (1C, C3), 120.5 (1C, C6), 26.8 (3C, C12), 18.5 (1C, C11), –0.9 (3C, C13), –3.8 (2C, C10); Anal. calcd for $C_{22}H_{29}NSSi_2$: C, 66.78; H, 7.39; N, 3.54, found C, 66.51; H, 7.46; N, 3,56.

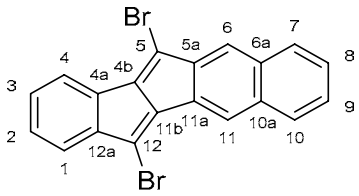
4-(*tert*-Butyldimethylsilyl)-9-(trimethylsilyl)pyrido[2,3-*a*]thieno[2',3'-*e*]pentalene (3gf)



The residue was purified by silica gel preparative TLC with hexane/dichloromethane (8:2) to afford compound **3gf** as a green solid (8.7 mg, 22 μmol; 22% yield); R_f = 0.38 (hexane/dichloromethane; 9:1); mp 40–42 °C; IR (neat) cm^{-1} 2950, 2925, 2896, 2855, 1379, 1243, 1192, 1157, 1101, 1086, 1035, 1006, 950, 915, 830, 806, 783, 764, 723, 678, 660, 644, 627, 610, 592, 576, 504; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.72 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H7), 6.93 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H2), 6.86 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H5), 6.63 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H1), 6.42 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H6), 0.97 (s, 9H, H12), 0.35 (s, 9H, H13), 0.32 (s, 6H, H10); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 161.9 (1C, C9a), 159.6 (1C, C8a), 158.6 (1C, C8b), 155.0 (1C, C3b), 149.3 (1C, C4a), 146.3 (1C, C7), 143.5 (1C, C9), 140.0 (1C, C4), 135.4 (1C, C3a), 129.9 (1C, C5), 129.2 (1C, C2), 122.9 (1C, C1), 120.6 (1C, C6), 26.9 (3C, C12), 19.1 (1C, C11), –0.6 (3C, C13), –4.5 (2C, C10); HRMS (ESI) *m/z* calcd for $C_{22}H_{30}NSSi_2$ $[M+H]^+$ 396.1632, found 396.1651.

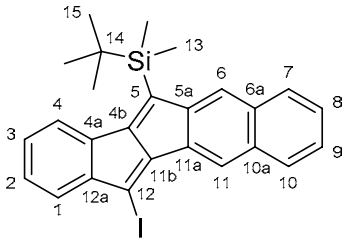
4. Desilylative Halogenations

Desilylative Bromination of Compound 3bb; 5,12-dibromobenzo[*a*]naphtho[2,3-*e*]pentalene (5)



To a solution of compound **3bb** (12.3 mg, 28.0 μmol) in diethyl ether (5 mL) was added bromine (0.030 mL, 0.580 mmol), and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated aqueous sodium bisulfite and this was extracted with dichloromethane. The organic layer was washed with saturated aqueous sodium bisulfite, water, and brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **5** as an orange solid (8.1 mg, 20 μmol; 71% yield); R_f = 0.32 (hexane); mp 215–217 °C; IR (neat) cm^{-1} 3048, 1609, 1569, 1456, 1423, 1405, 1338, 1264, 1241, 1219, 1204, 1184, 1156, 1145, 1124, 1096, 1079, 943, 926, 897, 878, 774, 756, 741, 721, 687, 619, 612, 517, 461, 437; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.80 (s, 1H, H11), 7.71–7.67 (m, 2H, H7 and H10), 7.56–7.54 (m, 1H, H4), 7.40 (s, 1H, H6), 7.40–7.38 (m, 2H, H8 and H9), 7.19–7.16 (m, 1H, H2), 7.11–7.08 (m, 2H, H1 and H3); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 147.9 (1C, C12a), 146.7 (1C, C4b), 145.2 (1C, C5a), 142.9 (1C, C11b), 134.2 (1C, C10a), 133.9 (1C, C6a), 132.0 (1C, C4a), 130.2 (1C, C11a), 129.44 (1C, C2), 129.36 (1C, C7), 129.2 (1C, C10), 128.0 (1C, C3), 127.5 (1C, C9), 127.3 (1C, C8), 122.7 (1C, C4), 121.9 (2C, C6 and C11), 121.8 (1C, C1), 120.7 (1C, C5), 116.2 (1C, C12); Anal. calcd for $C_{20}H_{10}Br_2$: C, 58.57; H, 2.46, found C, 58.30; H, 2.84.

Desilylative Iodination of Compound 3bb; 5-(*tert*-butyldimethylsilyl)-12-iodobenzo[*a*]naphtho[2,3-*e*]pentalene (6)



To a solution of compound **3bb** (132 mg, 0.300 mmol) in THF (10 mL) was added iodine (457 mg, 1.80 mmol), and the mixture was stirred for 30 min at 40 °C. After addition of saturated aqueous sodium bisulfite to the reaction mixture, the organic layer was washed with saturated aqueous sodium bisulfite, water, and brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The

residue was reprecipitated from dichloromethane/methanol and the precipitates that formed were collected by filtration with methanol and dried under vacuum to afford compound **6** as a brown solid (113 mg, 0.230 mmol; 77% yield); R_f = 0.30 (hexane); mp 162–164 °C (decomp); IR (neat) cm^{-1} 3062, 2949, 2924, 2897, 2881, 2851, 1616, 1459, 1417, 1360, 1347, 1258, 1248, 1241, 1221, 1187, 1151, 1115, 1073, 1023, 1006, 951, 936, 926, 880, 864, 832, 818, 806, 781, 769, 762, 750, 728, 705, 683, 667, 615, 610, 573, 468, 447; ^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.97 (s, 1H, H11), 7.68–7.66 (m, 1H, H10), 7.59–7.57 (m, 1H, H7), 7.48 (s, 1H, H6), 7.37–7.36 (m, 1H, H4), 7.33–7.32 (m, 2H, H8 and H9), 7.11–7.08 (m, 1H, H2), 7.00–6.97 (m, 1H, H3), 6.96–6.95 (m, 1H, H1), 1.05 (s, 9H, H15), 0.53 (s, 6H, H13); ^{13}C NMR (126 MHz, $CDCl_3$, rt) δ 160.1 (1C, C4b), 152.6 (1C, C5a), 151.6 (1C, C11b), 151.3 (1C, C12a), 141.3 (1C, C5), 134.6 (1C, C6a), 134.3 (1C, C4a), 133.2 (1C, C10a), 132.7 (1C, C11a), 129.4 (1C, C7), 129.0 (1C, C10), 128.8 (1C, C2), 127.5 (1C, C3), 126.9 (1C, C9), 126.8 (1C, C8), 125.0 (1C, C6), 124.0 (1C, C4), 123.5 (1C, C1), 120.6 (1C, C11), 90.6 (1C, C12), 27.2 (3C, C15), 19.0 (1C, C14), –2.1 (2C, C13); Anal. calcd for $C_{26}H_{25}ISi$: C, 63.41; H, 5.12, found C, 63.15; H, 5.17.

5. Theoretical Calculations

The computations were performed using workstation at Research Center for Computational Science, National Institutes of Natural Sciences, Okazaki, Japan. All the calculations were performed by using Gaussian 09 (revision D.1) program,[14] by B3LYP method[15] with 6-31G(d) basis sets[16] for structure optimisation, vibrational frequency, and time dependent calculations.

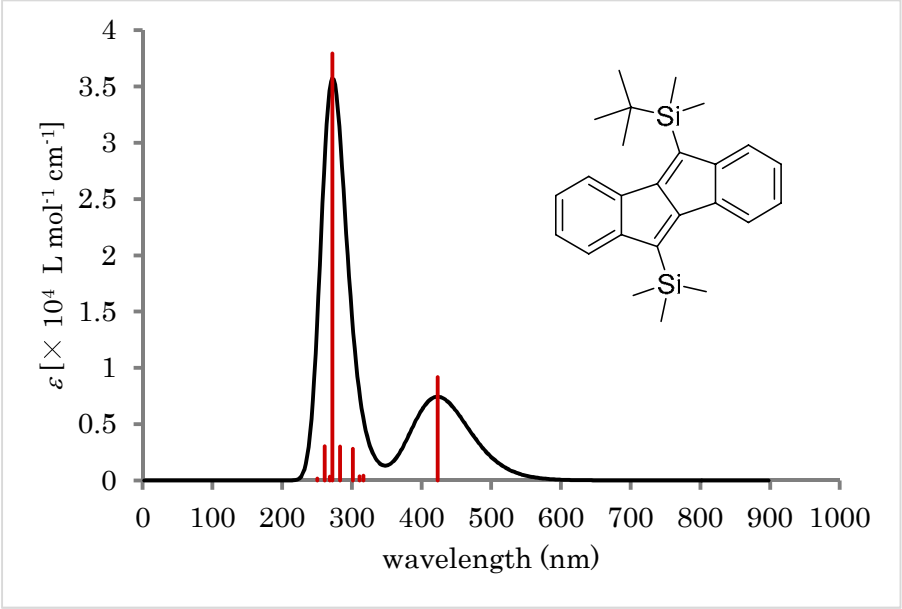


Fig. S1 Absorption spectrum of pentalene **3ba** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S1 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3ba** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
579.0	0	HOMO => LUMO (99.9%)
423.1	0.1836	HOMO−1 => LUMO (92.0%) HOMO => LUMO+1 (6.8%)
272.0	0.7589	HOMO−4 => LUMO (5.4%) HOMO−1 => LUMO (6.6%) HOMO => LUMO+1 (77.7%)

(14) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman,; J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

(15) (*a*) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*b*) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

(16) (*a*) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* 1971, **54**, 724; (*b*) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* 1972, **56**, 2257.

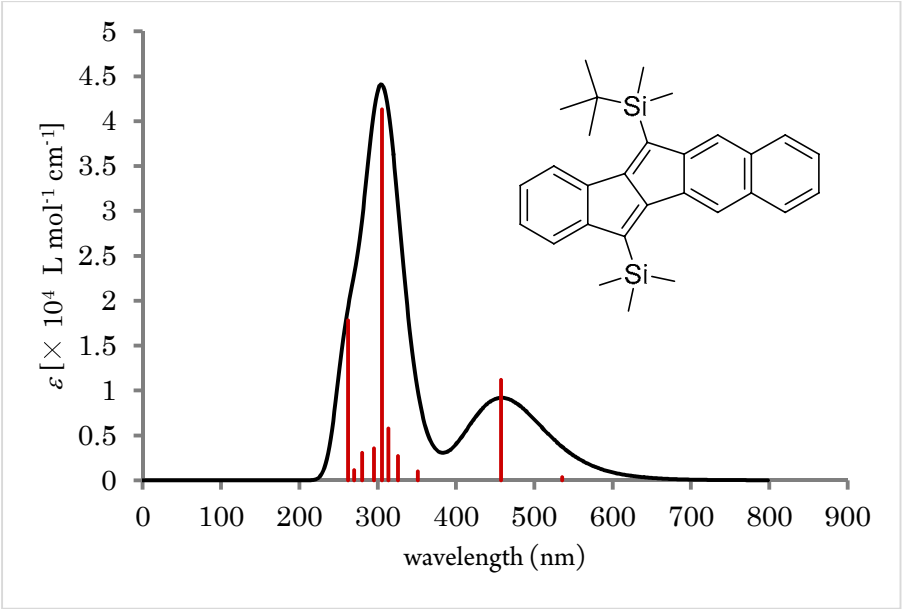


Fig. S2 Absorption spectrum of pentalene **3bb** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S2 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3bb** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
535.6	0.0074	HOMO−1 => LUMO (46.2%) HOMO => LUMO (53.3%)
457.6	0.2240	HOMO−1 => LUMO (49.2%) HOMO => LUMO (41.2%)
305.6	0.8261	HOMO−3 => LUMO (15.4%) HOMO−1 => LUMO+1 (59.1%) HOMO => LUMO+1 (8.6%)

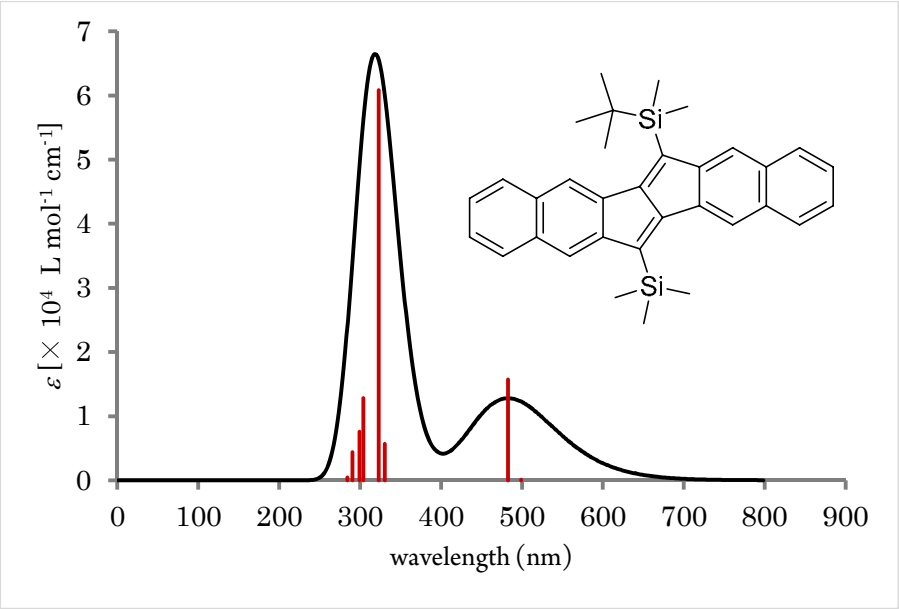


Fig. S3 Absorption spectrum of pentalene **3db** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S3 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3db** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
499.2	0.0016	HOMO−1 => LUMO (98.2%)
482.9	0.3145	HOMO−1 => LUMO+1 (8.1%) HOMO => LUMO (90.5%)
323.0	1.2166	HOMO−3 => LUMO (8.2%) HOMO−1 => LUMO+1 (73.1%) HOMO => LUMO (7.1%) HOMO => LUMO+2 (9.3%)

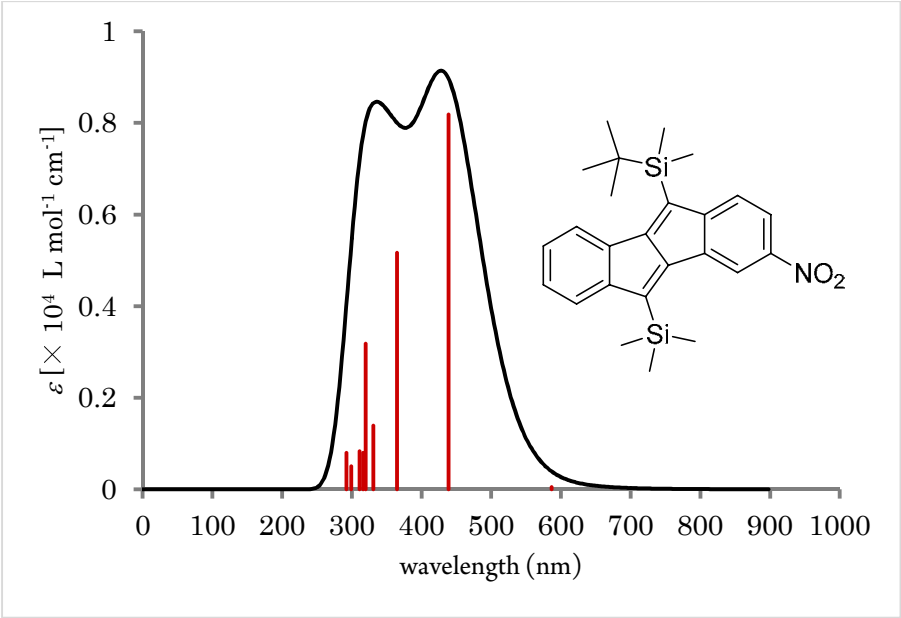


Fig. S4 Absorption spectrum of pentalene **3bd** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S4 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3bd** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
586.7	0.0012	HOMO => LUMO (98.4%)
438.6	0.2046	HOMO−1 => LUMO (90.8%)
364.8	0.1291	HOMO => LUMO+1 (90.3%)

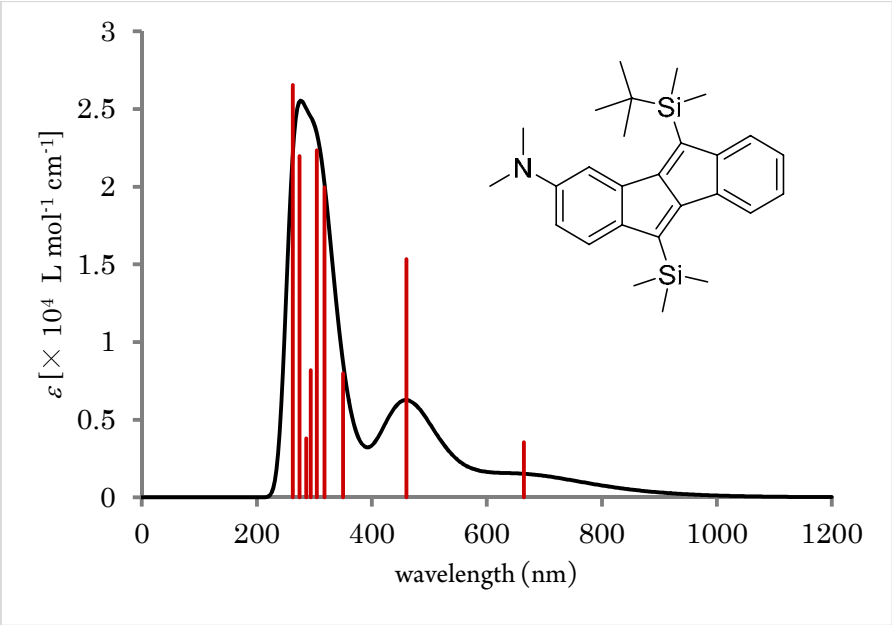


Fig. S5 Absorption spectrum of pentalene **3ea** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S5 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3ea** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
664.4	0.0355	HOMO−1 => LUMO (6.5%) HOMO => LUMO (92.9%)
459.9	0.1533	HOMO−1 => LUMO (88.4%) HOMO => LUMO (5.9%)
262.2	0.2654	HOMO−1 => LUMO+1 (11.8%) HOMO => LUMO+3 (71.8%)

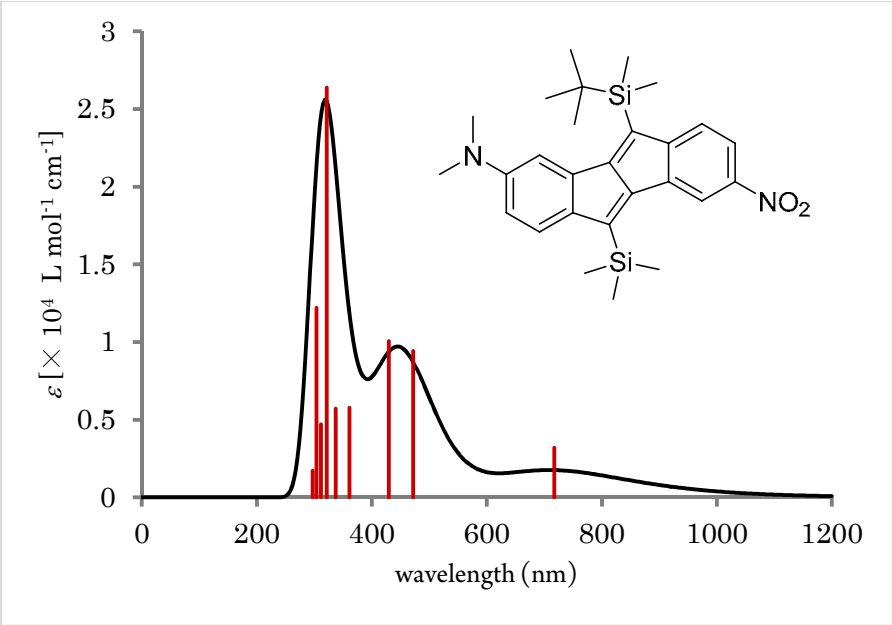


Fig. S6 Absorption spectrum of pentalene **3ed** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S6 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3ed** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
717.2	0.0426	HOMO => LUMO (94.7%)
471.5	0.1256	HOMO−1 => LUMO (75.4%) HOMO => LUMO+1 (16.1%)
429.3	0.1341	HOMO−1 => LUMO (15.2%) HOMO => LUMO+1 (82.2%)
321.7	0.3518	HOMO−4 => LUMO (16.0%) HOMO−3 => LUMO (9.1%) HOMO => LUMO+2 (60.5%)

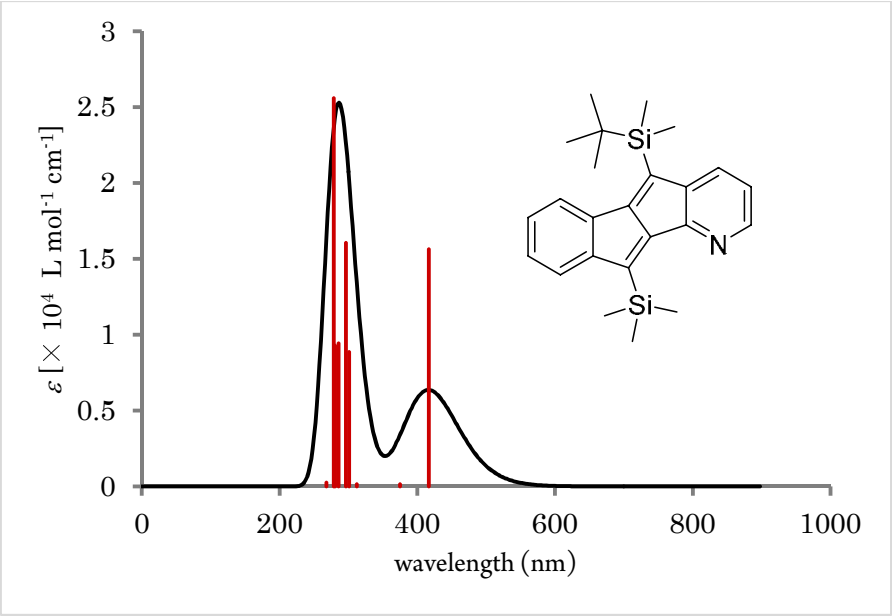


Fig. S7 Absorption spectrum of pentalene **3bf** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S7 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3bf** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
571.2	0.0000	HOMO => LUMO (99.8%)
416.5	0.1564	HOMO−1 => LUMO (90.7%) HOMO => LUMO+1 (7.4%)
296.5	0.1606	HOMO−5 => LUMO (34.3%) HOMO−4 => LUMO (22.5%) HOMO => LUMO+1 (30.1%)
278.5	0.2559	HOMO−7 => LUMO (10.8%) HOMO−6 => LUMO (5.0%) HOMO−5 => LUMO (37.0%) HOMO−1 => LUMO+1 (16.1%) HOMO => LUMO+1 (21.1%)

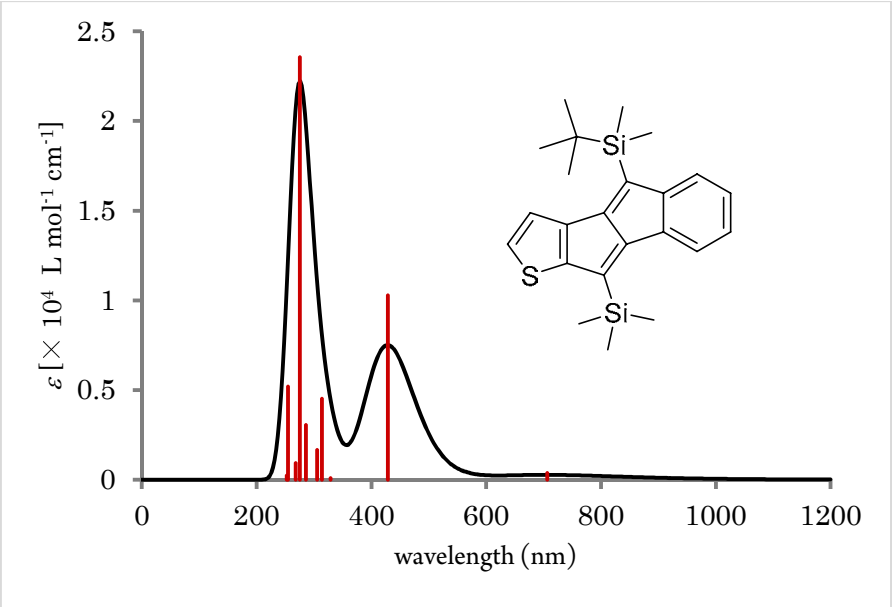


Fig. S8 Absorption spectrum of pentalene **3fa** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S8 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3fa** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
706.3	0.0066	HOMO => LUMO (99.0%)
428.3	0.1851	HOMO−1 => LUMO (92.6%)
275.4	0.4242	HOMO−6 => LUMO (5.9%) HOMO => LUMO+1 (76.9%)

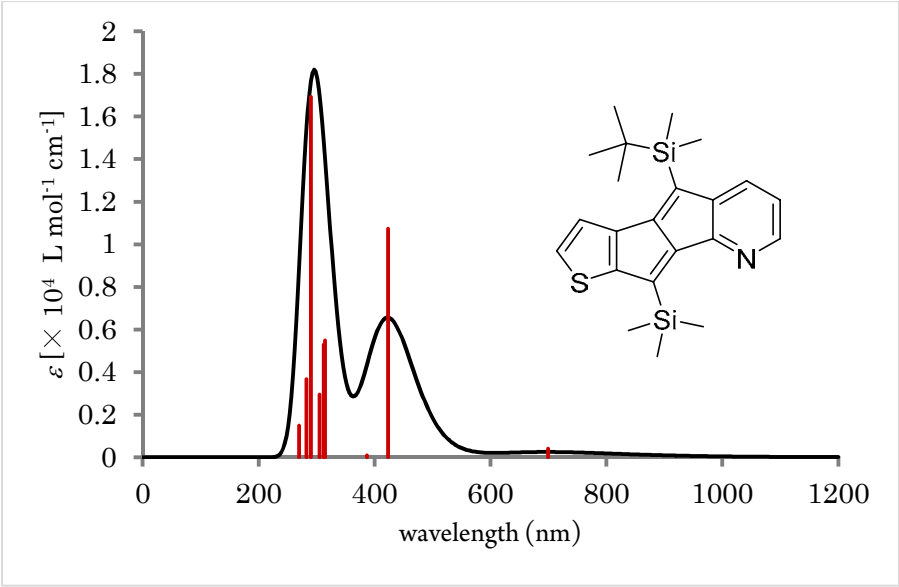


Fig. S9 Absorption spectrum of pentalene **3ff** obtained by TD-DFT calculation at the B3LYP/6-31G(d) level of theory.

Table S9 Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of compound **3ff** calculated at the B3LYP/6-31G(d) level of theory.

wavelength (nm)	Oscillator strengths(*f*)	Major Contributions
699.5	0.0061	HOMO => LUMO (99.2%)
423.2	0.1610	HOMO−1 => LUMO (91.3%) HOMO => LUMO+1 (5.3%)
290.2	0.2539	HOMO−8 => LUMO (13.4%) HOMO−7 => LUMO (9.0%) HOMO−5 => LUMO (21.5%) HOMO−3 => LUMO (6.0%) HOMO => LUMO+1 (33.4%)

6. ^{1}H and ^{13}C NMR Spectra

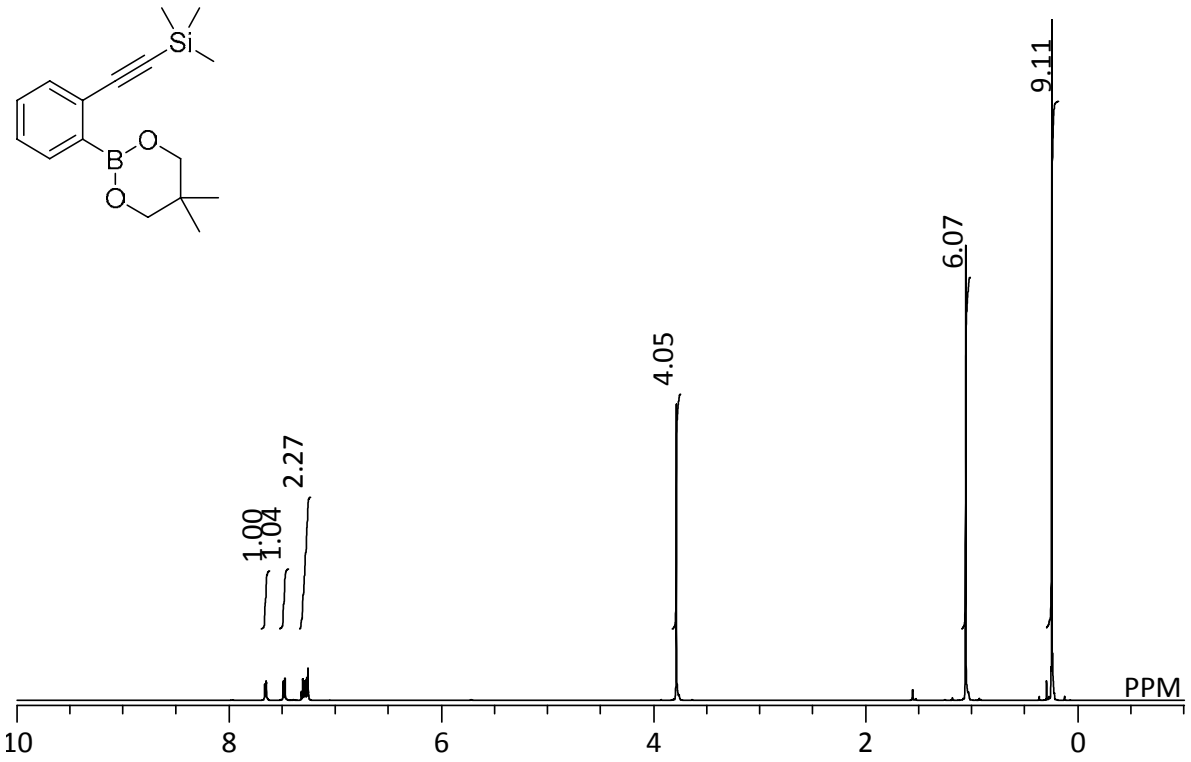


Fig. S10 ^{1}H NMR spectrum of **1a** (500 MHz, $CDCl_3$).

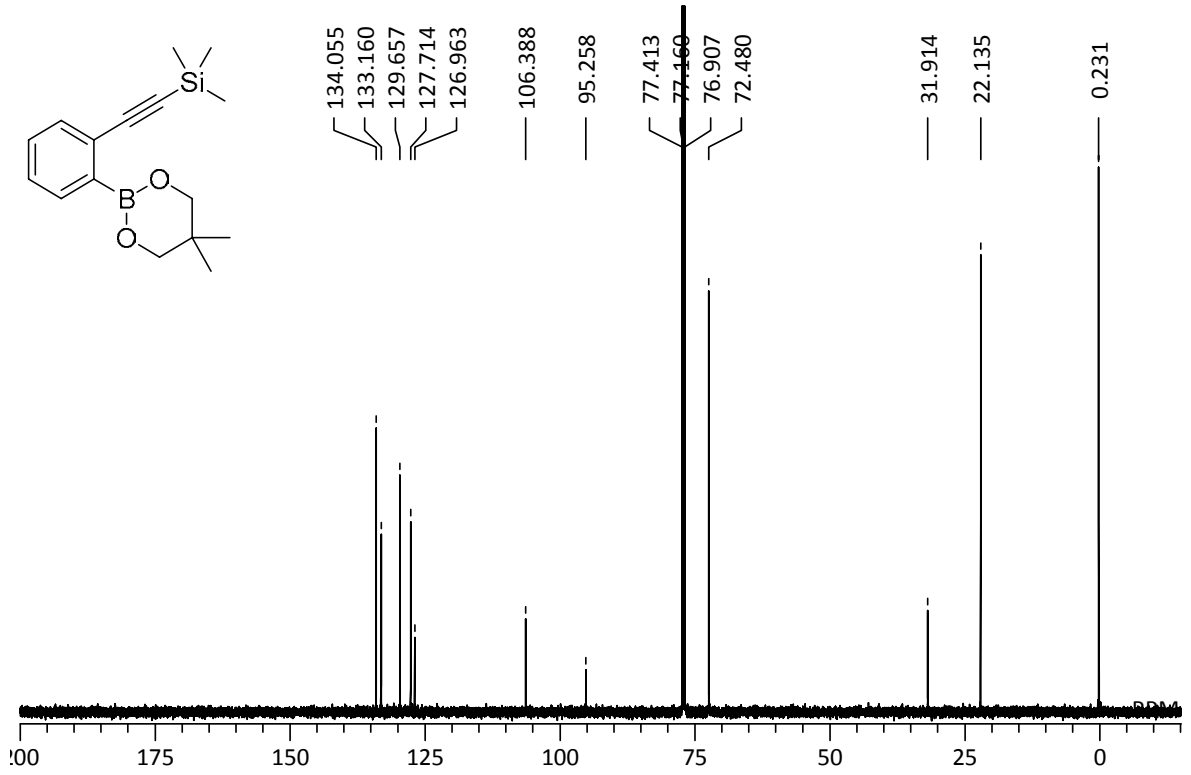


Fig. S11 ^{13}C NMR spectrum of **1a** (126 MHz, $CDCl_3$).

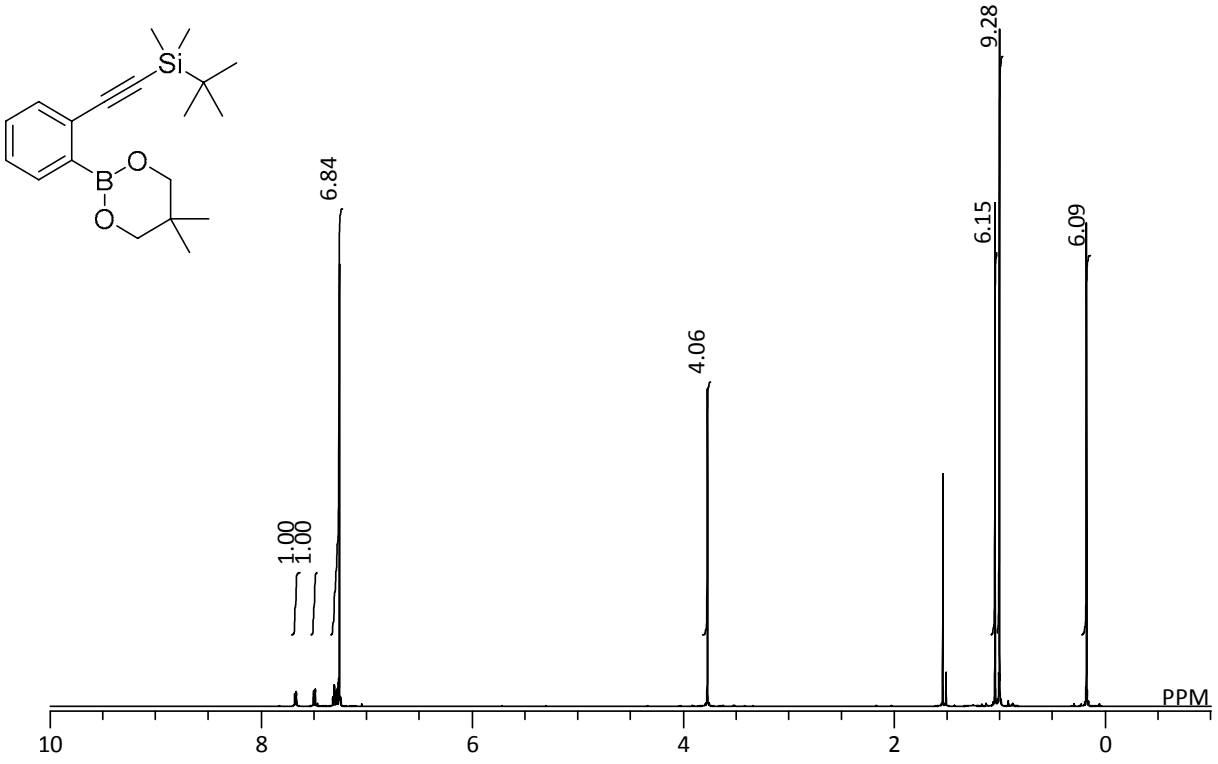


Fig. S12 ^{1}H NMR spectrum of **1b** (500 MHz, $CDCl_3$).

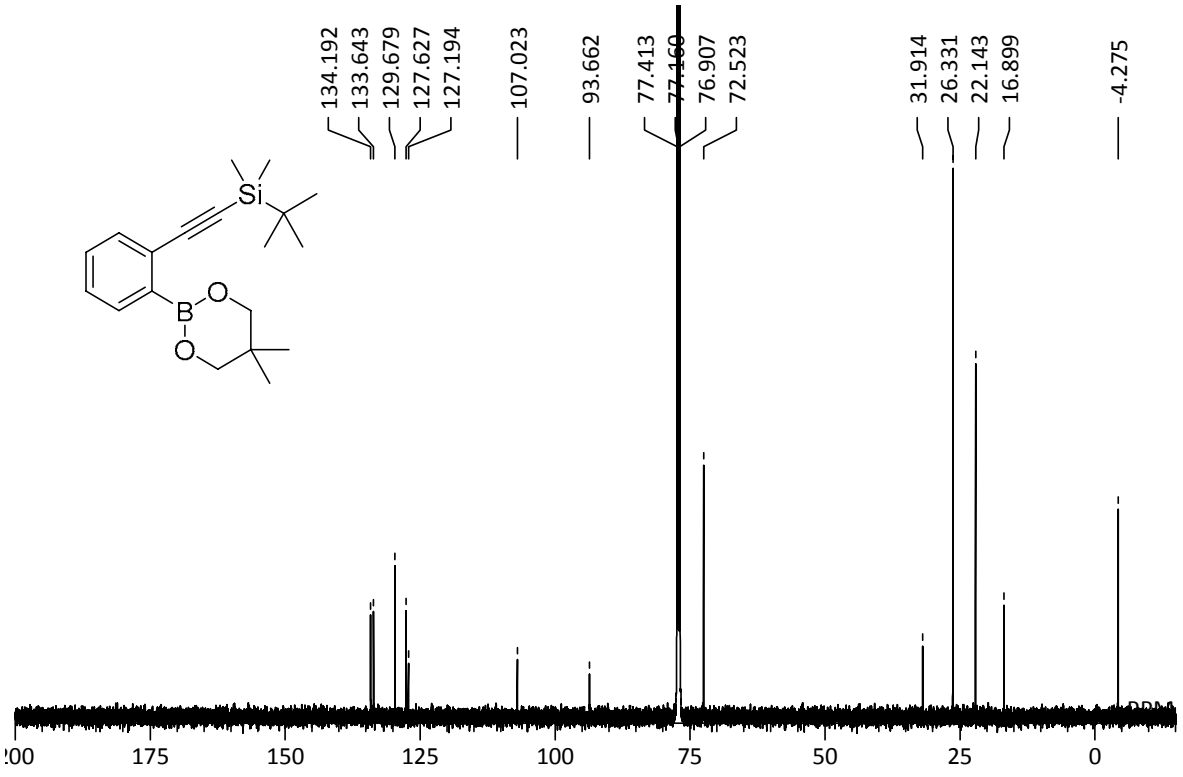


Fig. S13 ^{13}C NMR spectrum of **1b** (126 MHz, $CDCl_3$).

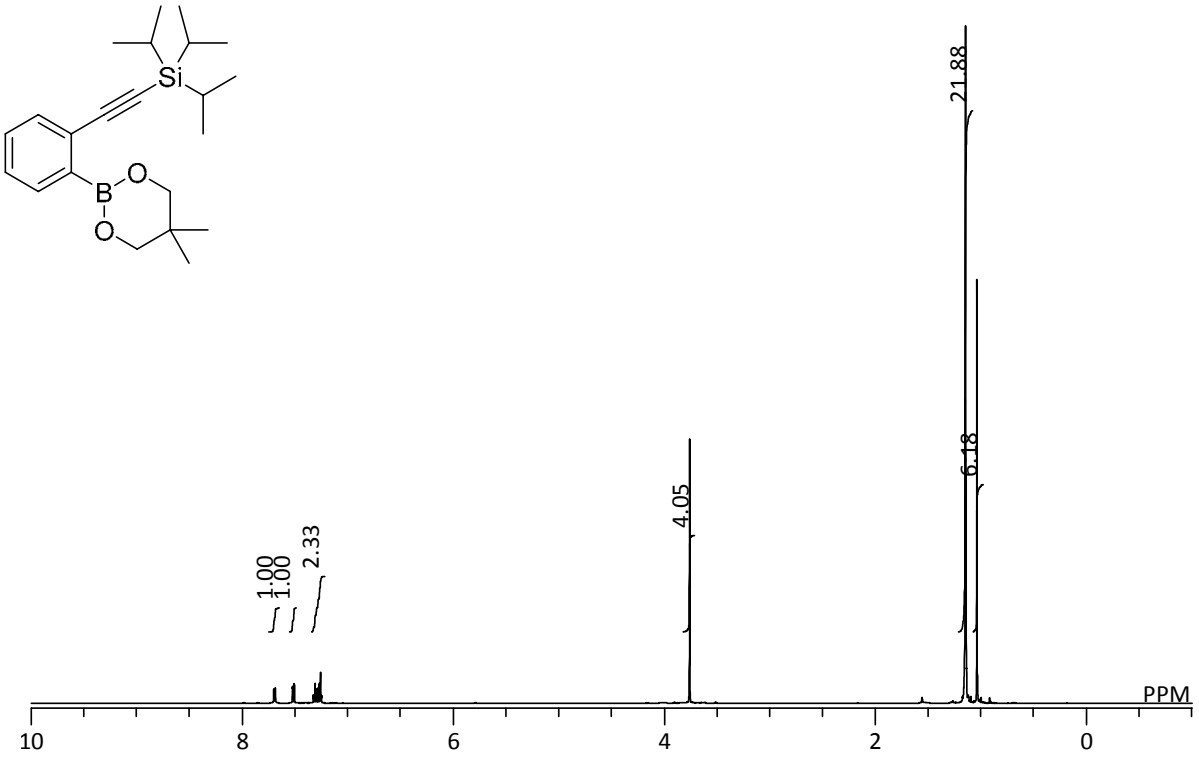


Fig. S14 ^{1}H NMR spectrum of **1c** (500 MHz, $CDCl_3$).

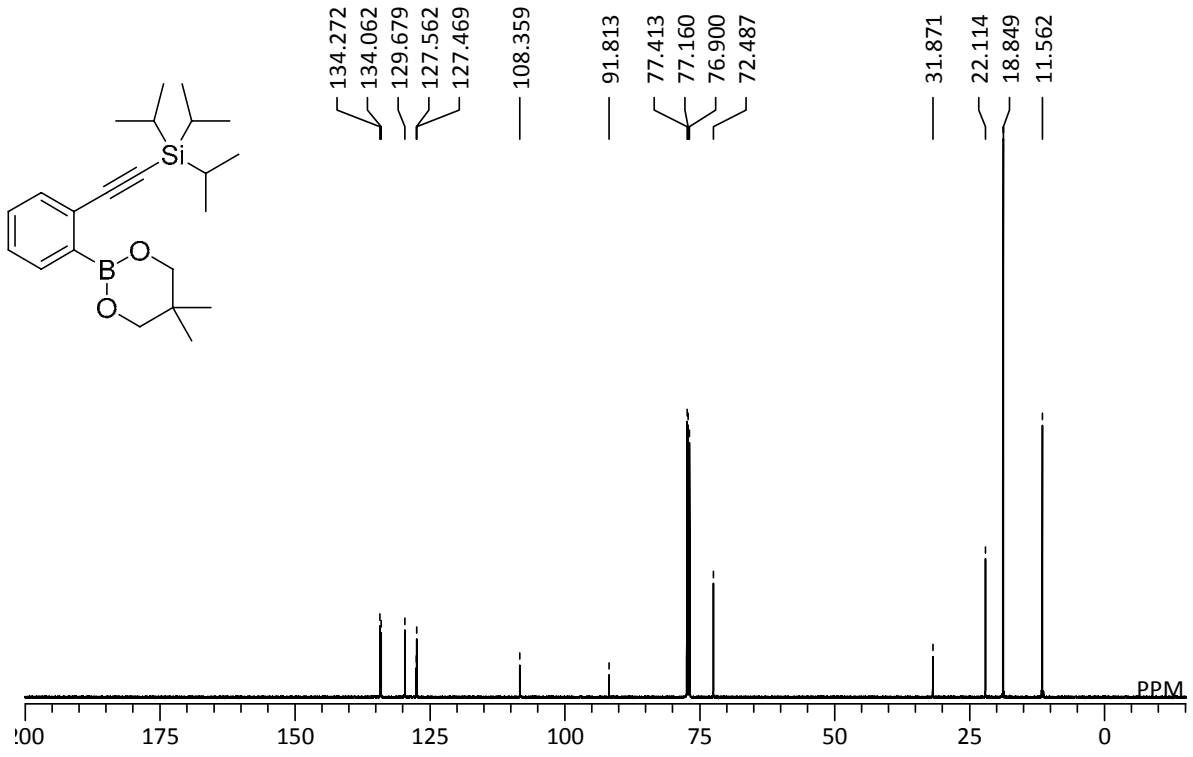


Fig. S15 ^{13}C NMR spectrum of **1c** (126 MHz, $CDCl_3$).

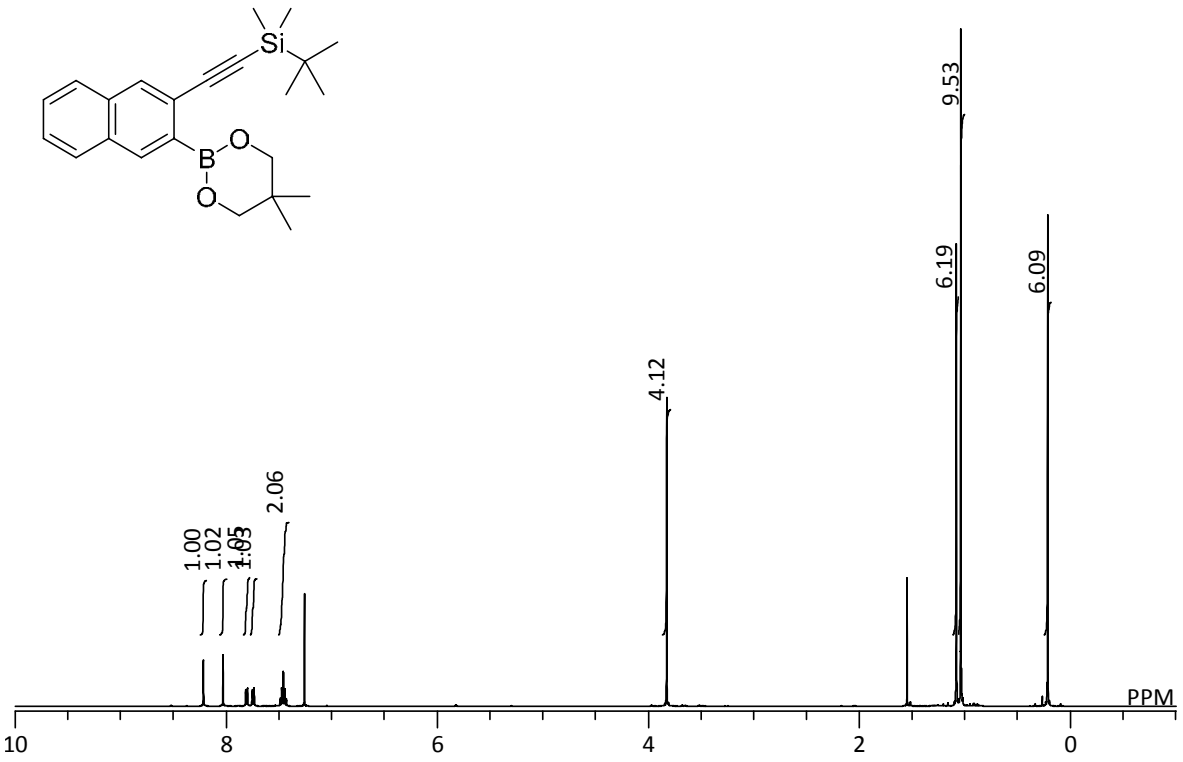


Fig. S16 ^{1}H NMR spectrum of **1d** (500 MHz, $CDCl_3$).

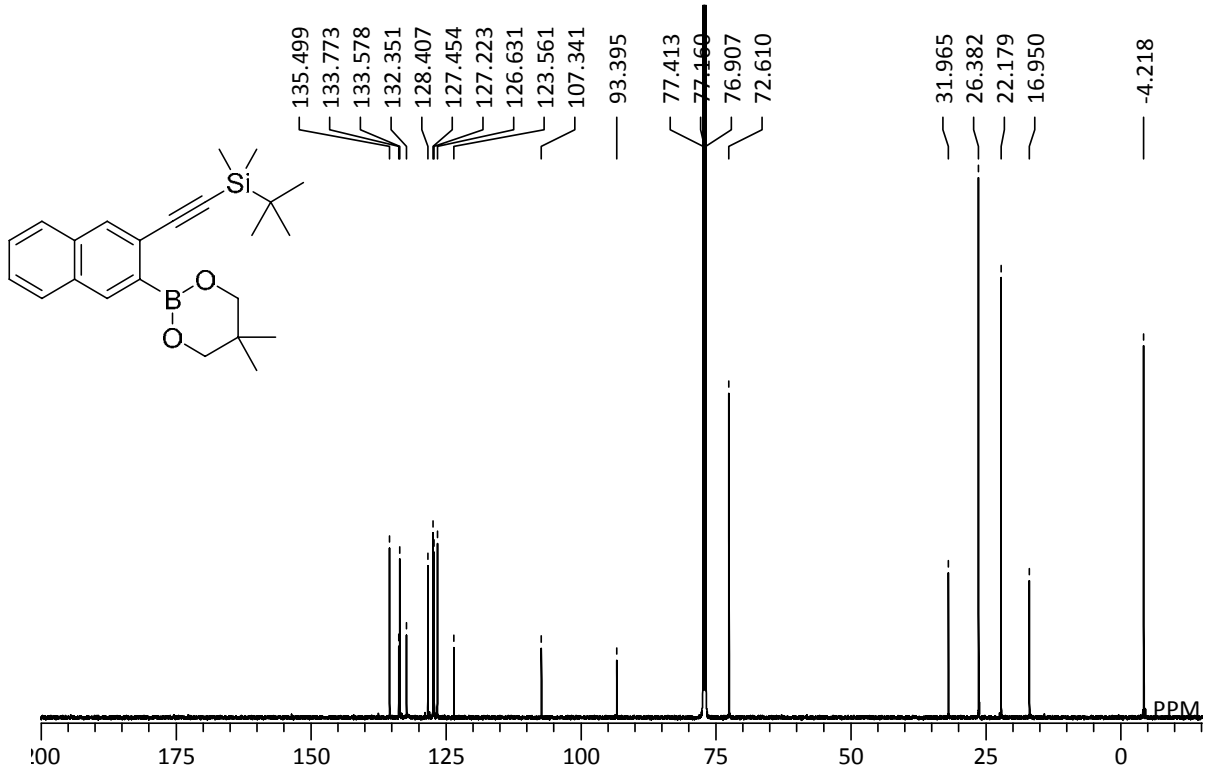


Fig. S17 ^{13}C NMR spectrum of **1d** (126 MHz, $CDCl_3$).

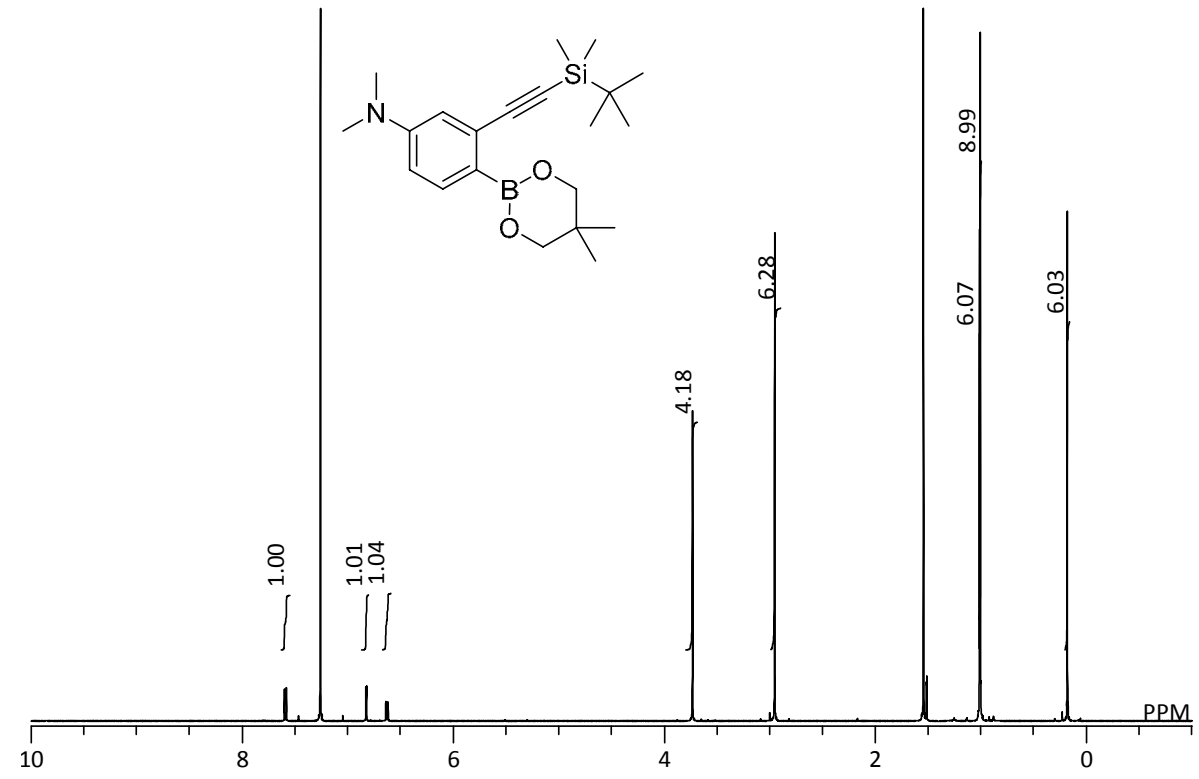


Fig. S18 ^{1}H NMR spectrum of **1e** (500 MHz, $CDCl_3$).

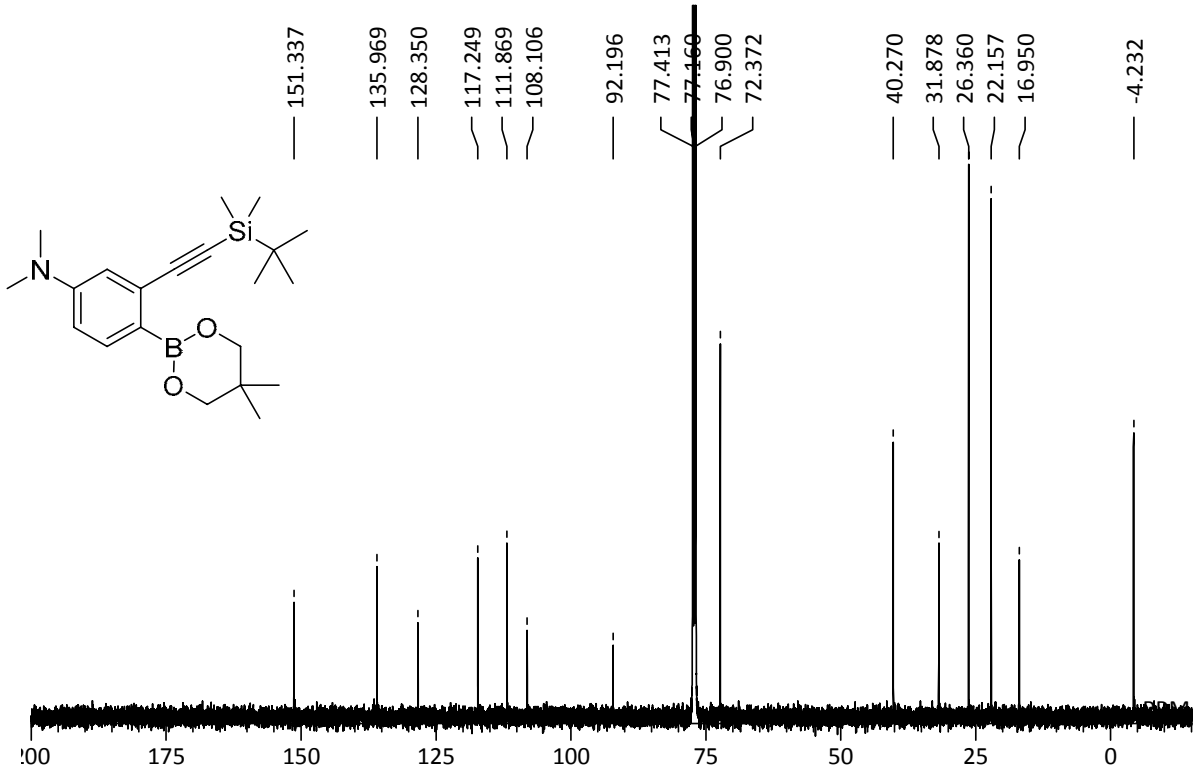


Fig. S19 ^{13}C NMR spectrum of **1e** (126 MHz, $CDCl_3$).

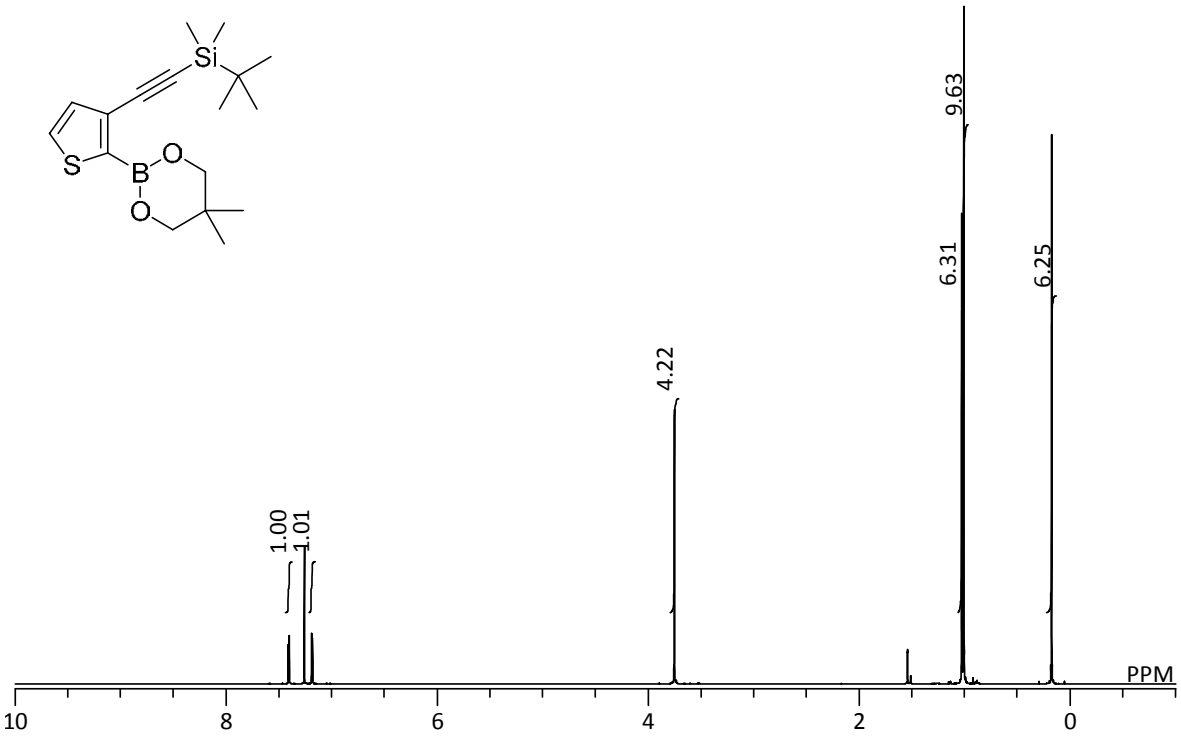


Fig. S20 ^{1}H NMR spectrum of **1f** (500 MHz, $CDCl_3$).

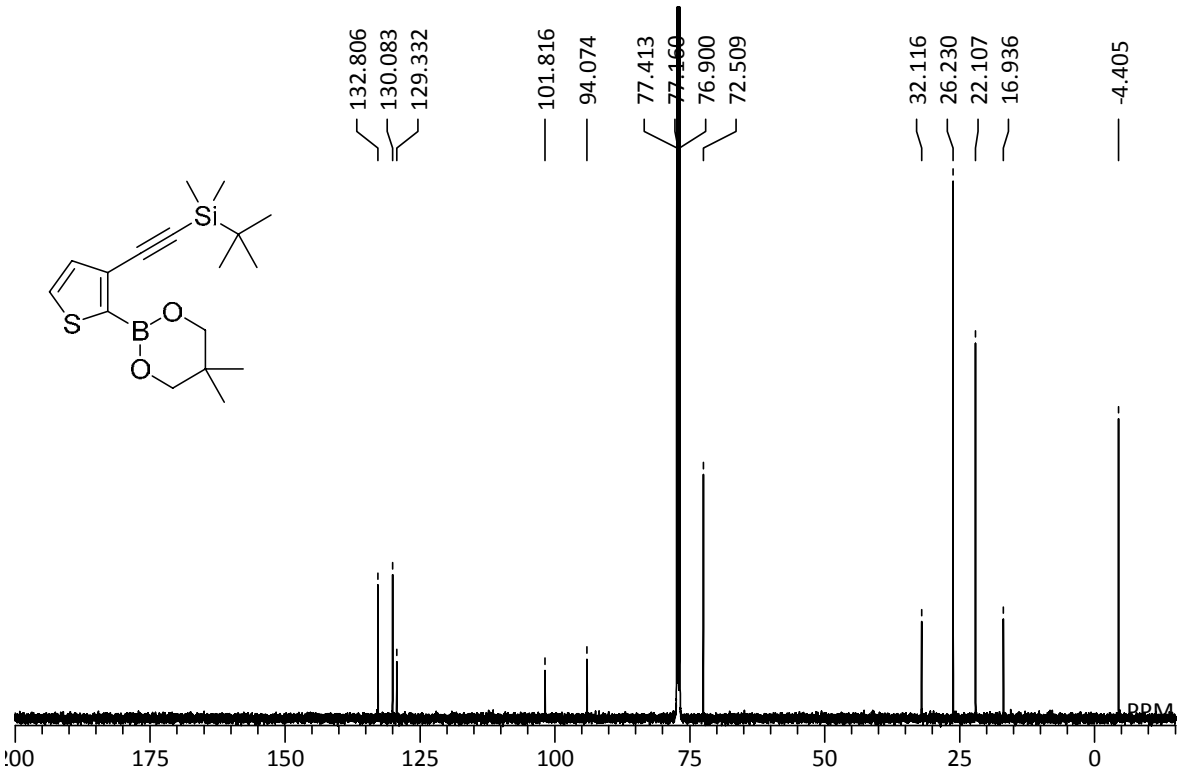


Fig. S21 ^{13}C NMR spectrum of **1f** (126 MHz, $CDCl_3$).

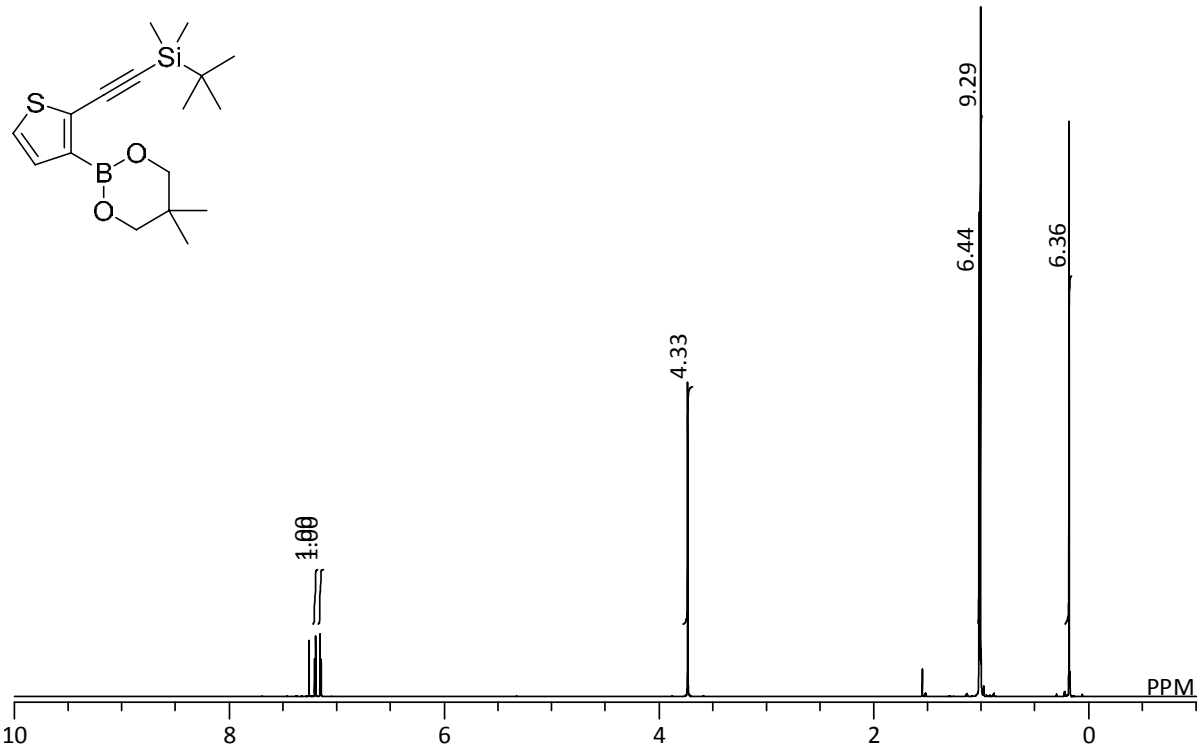


Fig. S22 ^{1}H NMR spectrum of **1g** (500 MHz, $CDCl_3$).

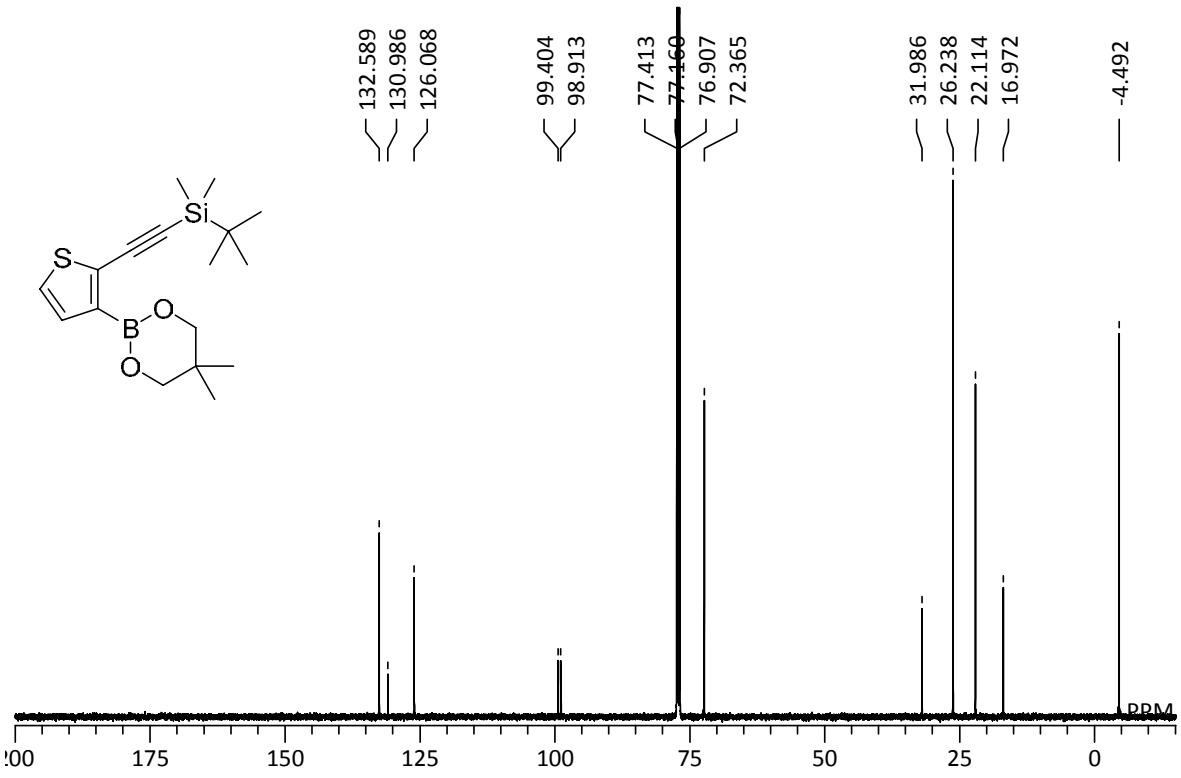


Fig. S23 ^{13}C NMR spectrum of **1g** (126 MHz, $CDCl_3$).

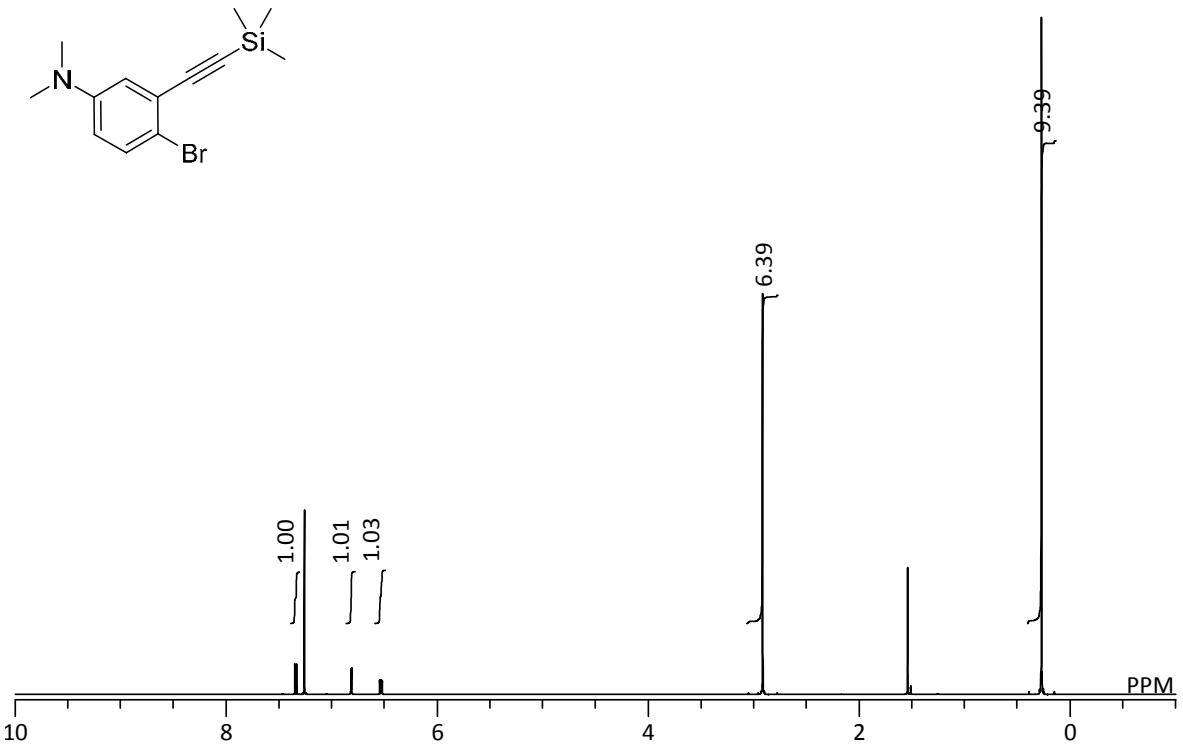


Fig. S24 ^{1}H NMR spectrum of **2c** (500 MHz, $CDCl_3$).

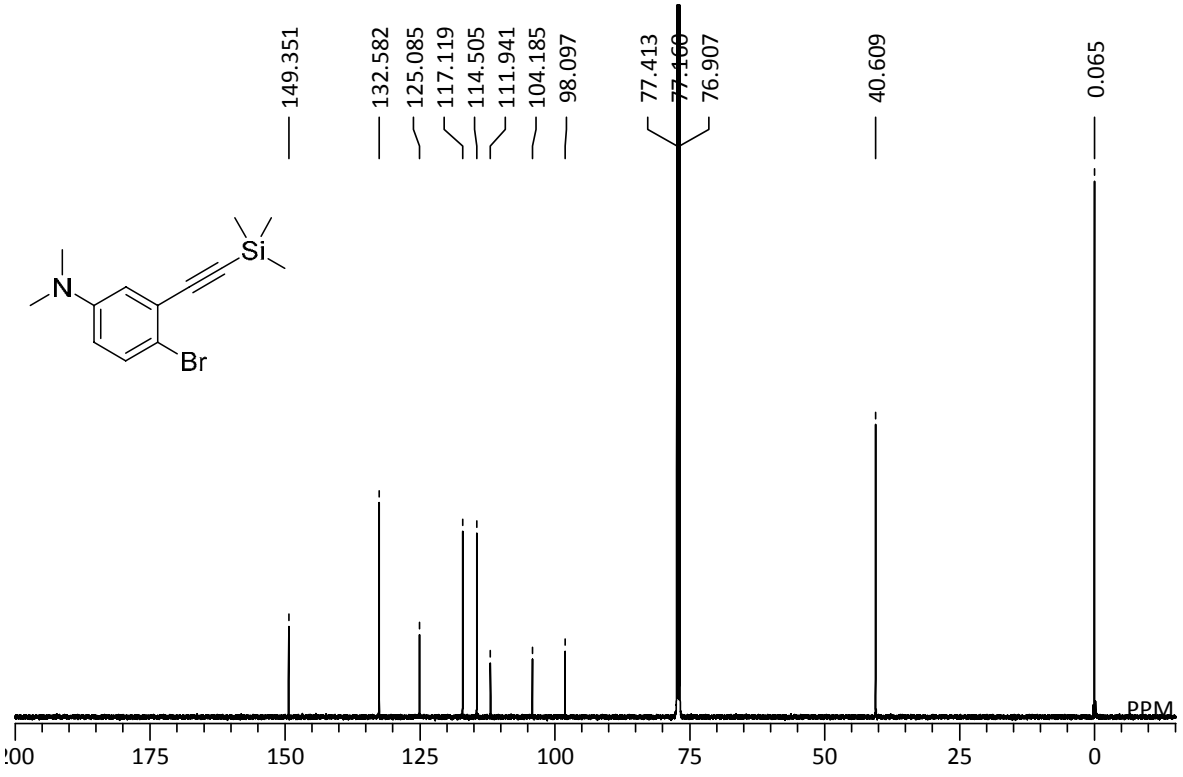


Fig. S25 ^{13}C NMR spectrum of **2c** (126 MHz, $CDCl_3$).

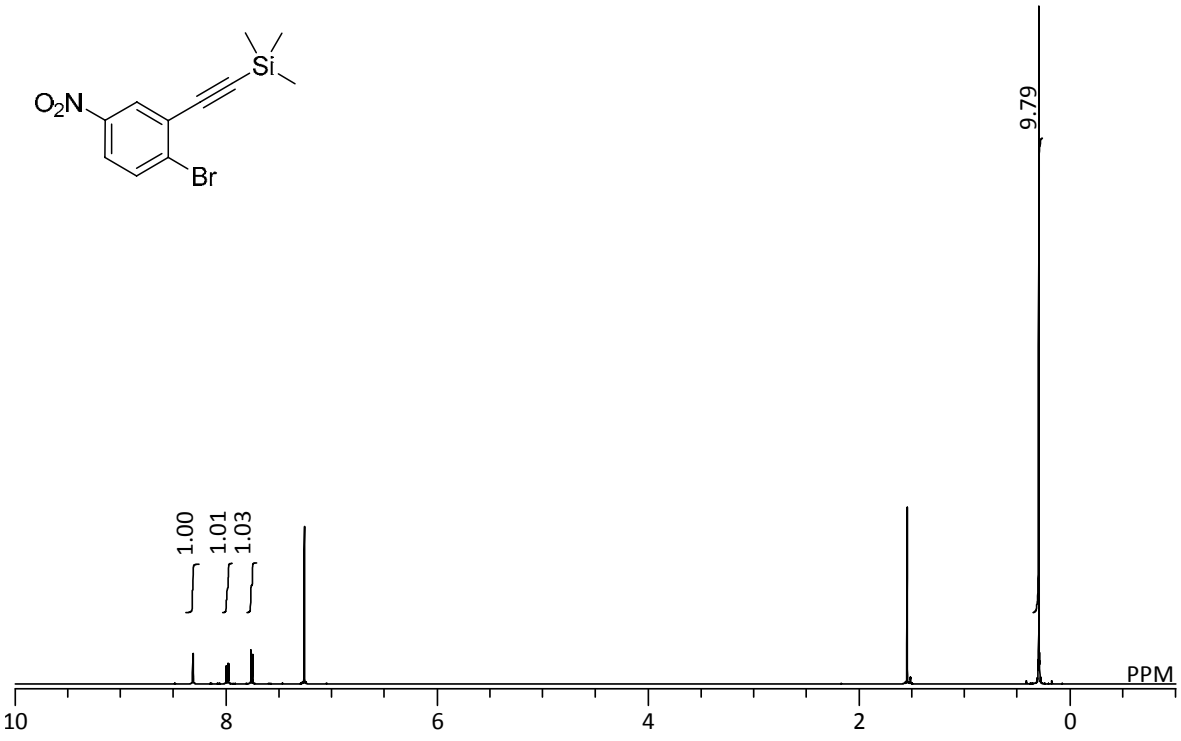


Fig. S26 ^{1}H NMR spectrum of **2d** (500 MHz, $CDCl_3$).

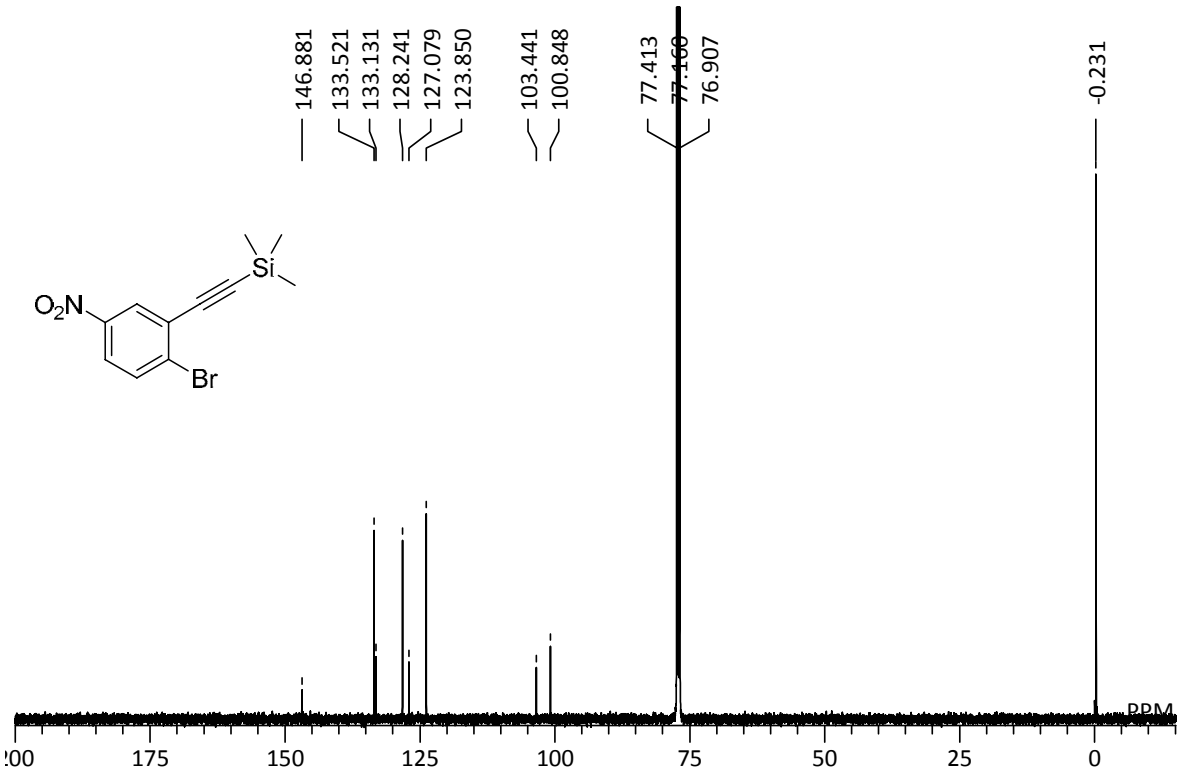


Fig. S27 ^{13}C NMR spectrum of **2d** (126 MHz, $CDCl_3$).

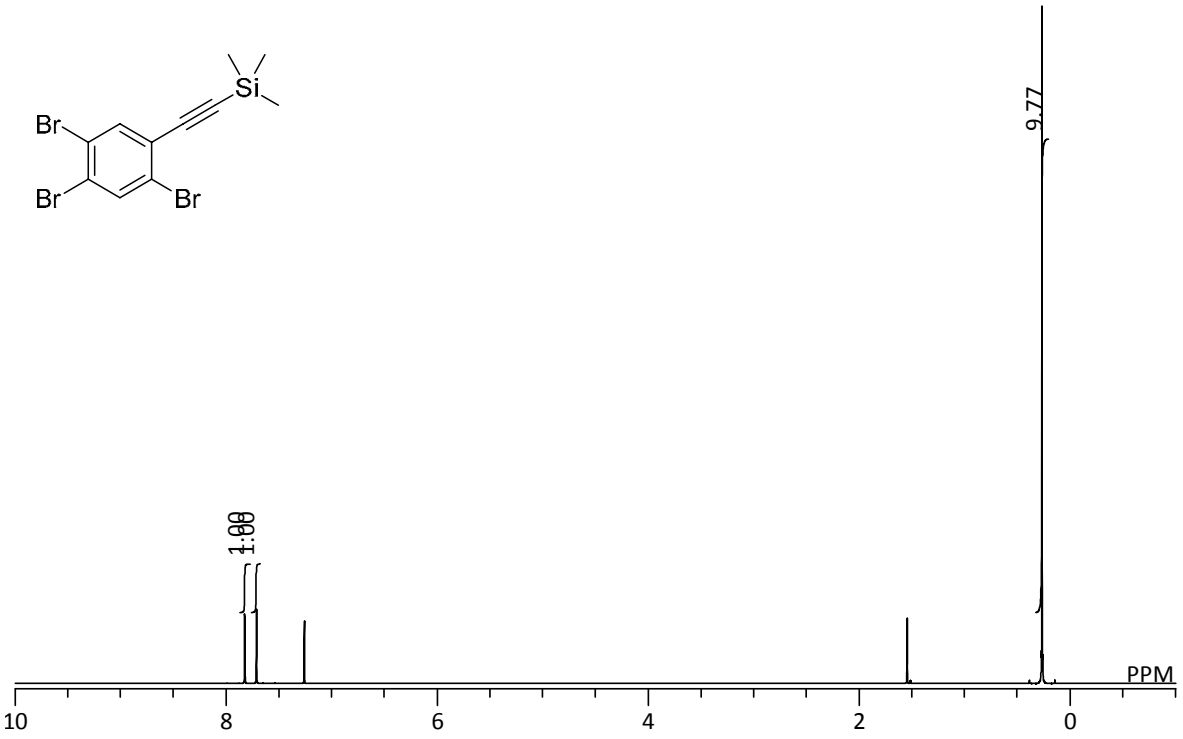


Fig. S28 ^{1}H NMR spectrum of **2e** (500 MHz, $CDCl_3$).

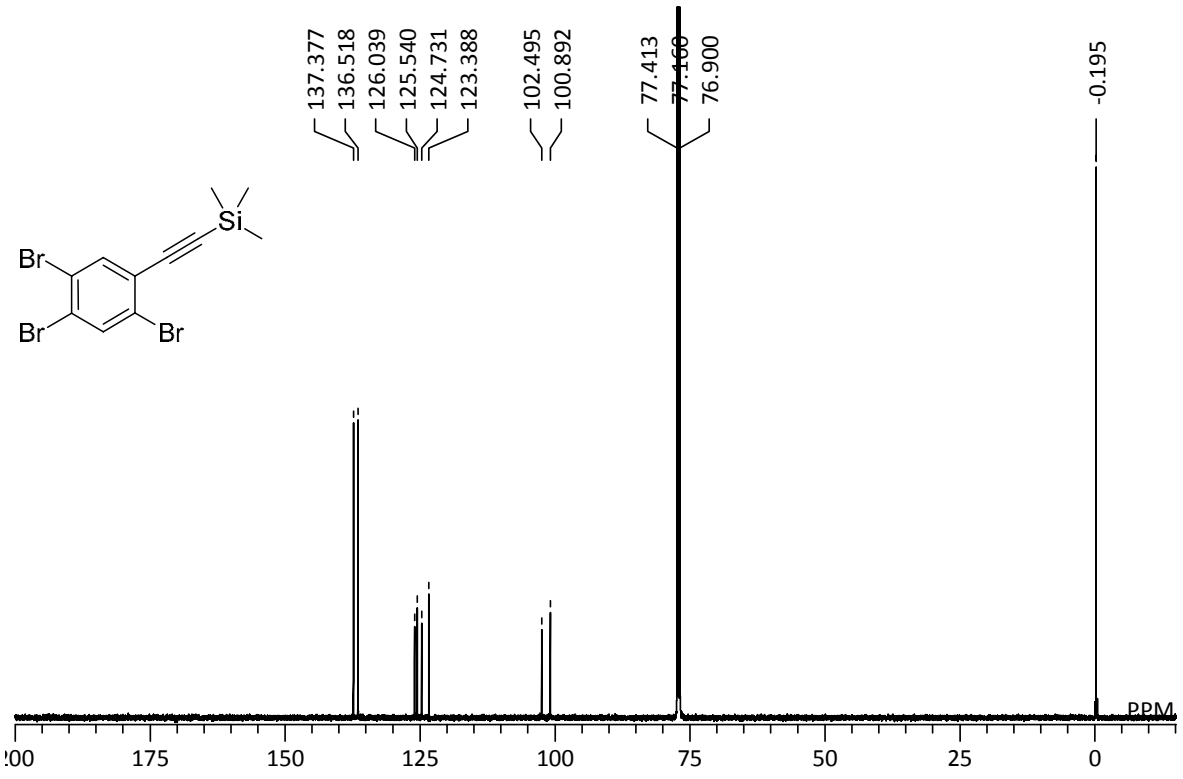


Fig. S29 ^{13}C NMR spectrum of **2e** (126 MHz, $CDCl_3$).

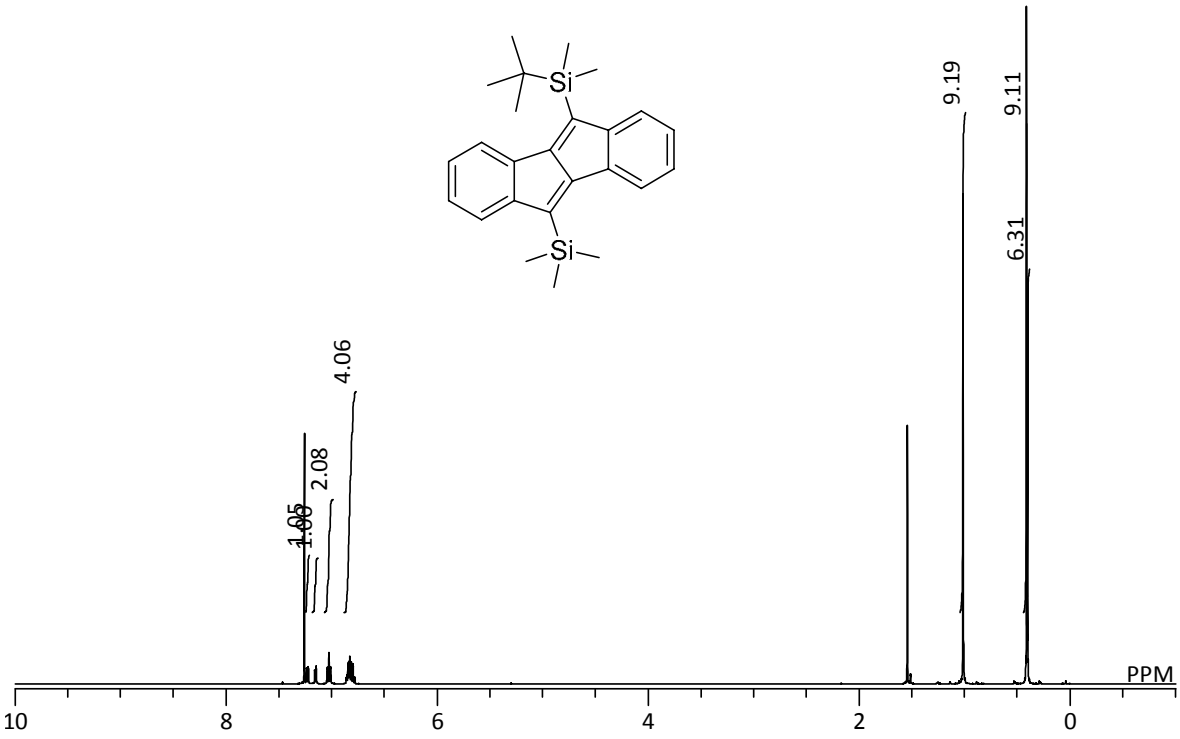


Fig. S30 ^{1}H NMR spectrum of **3ba** (500 MHz, $CDCl_3$).

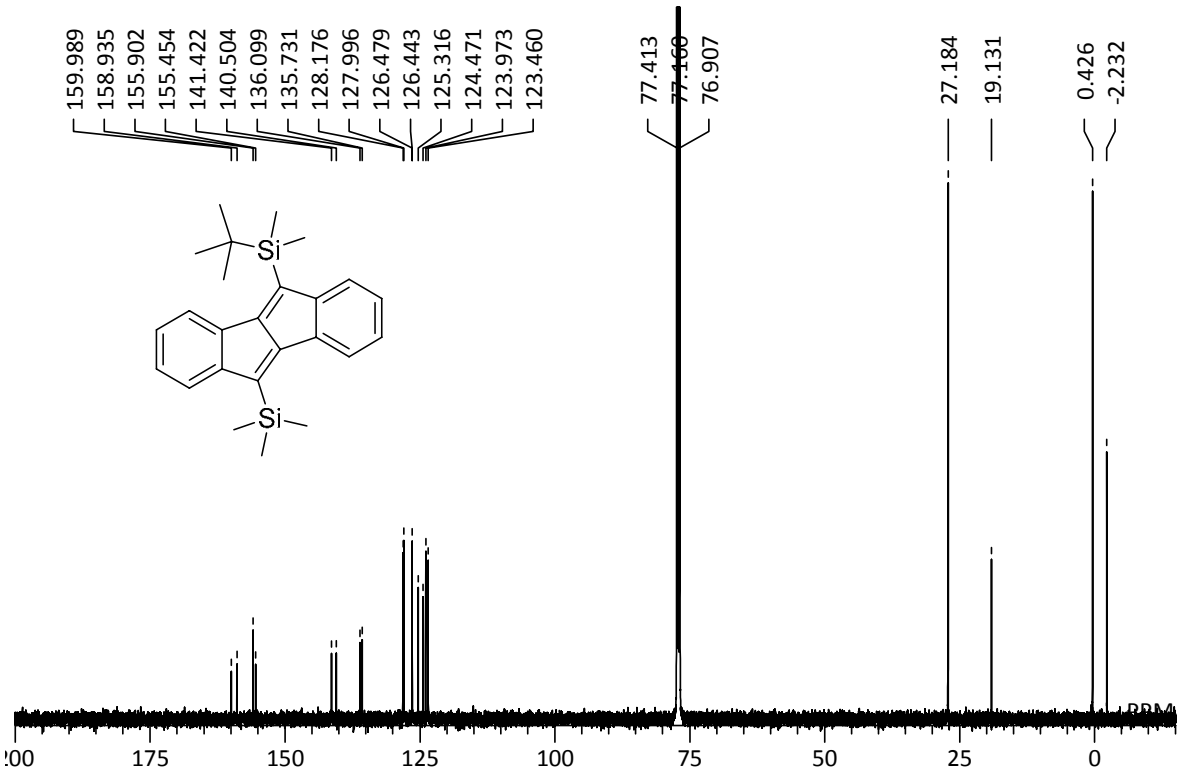


Fig. S31 ^{13}C NMR spectrum of **3ba** (126 MHz, $CDCl_3$).

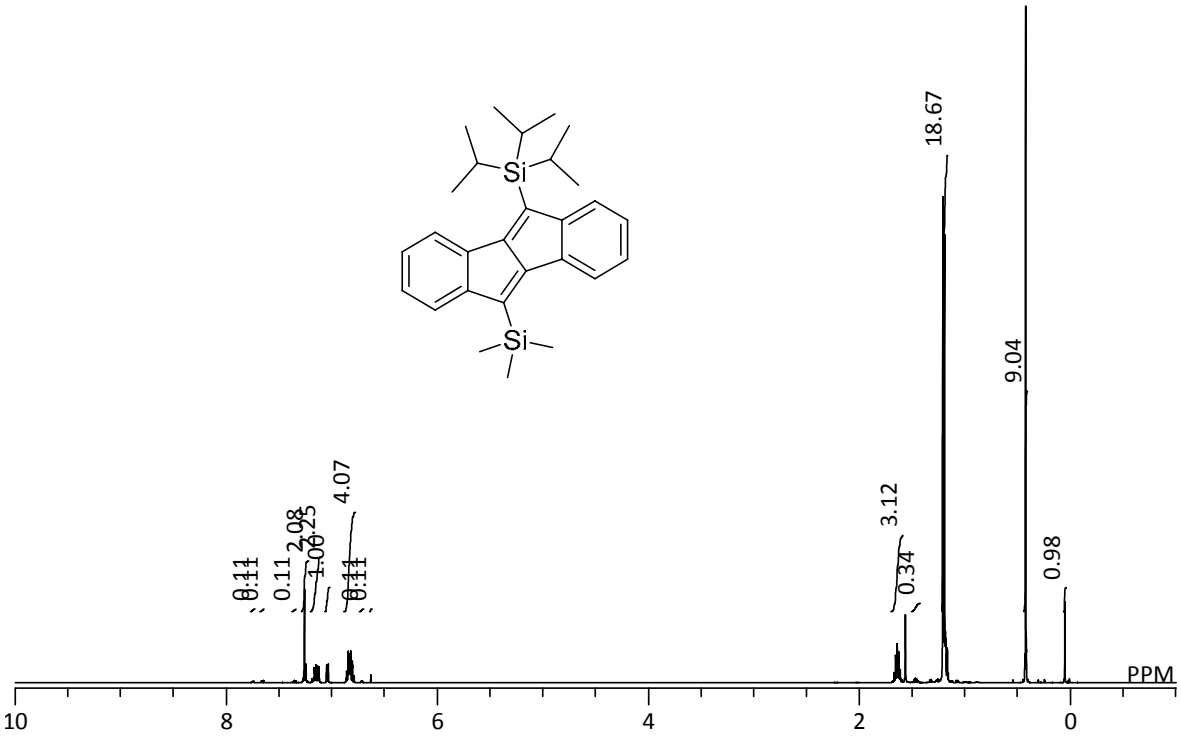


Fig. S32 ^{1}H NMR spectrum of **3ca** and inseparable side product **4ca** (500 MHz, $CDCl_3$).

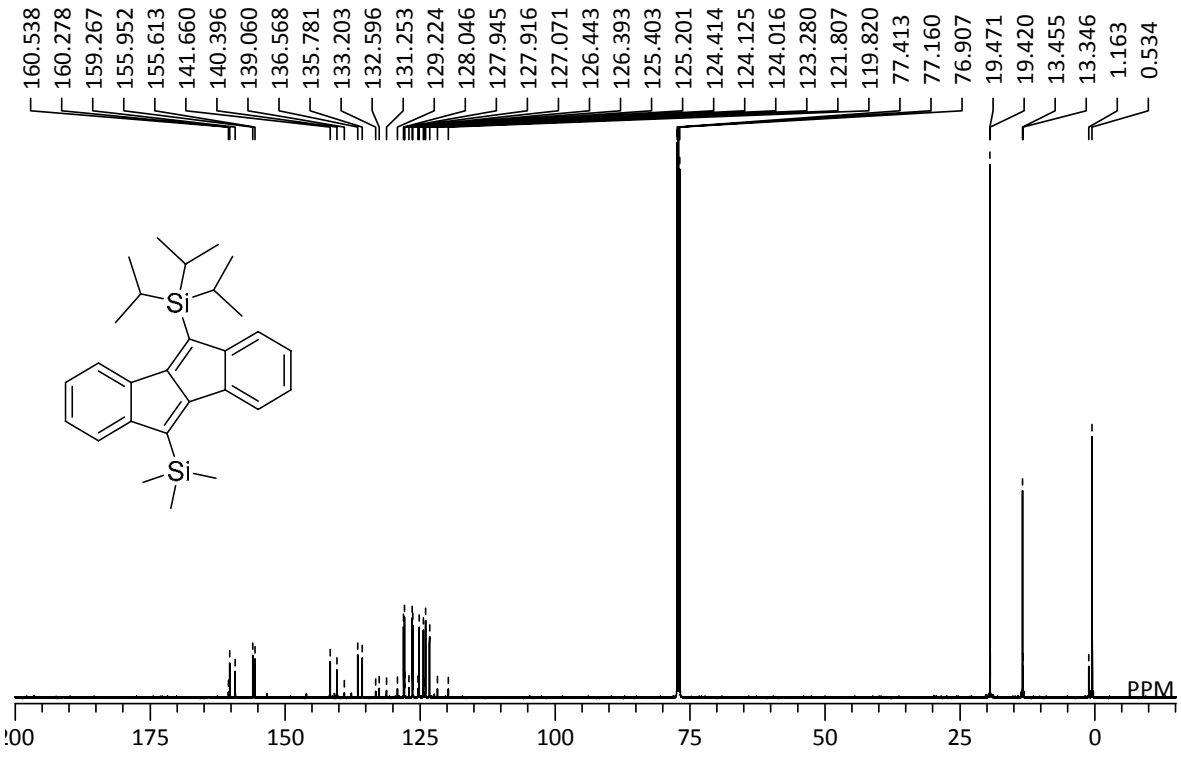


Fig. S33 ^{13}C NMR spectrum of **3ca** and inseparable side product **4ca** (126 MHz, $CDCl_3$).

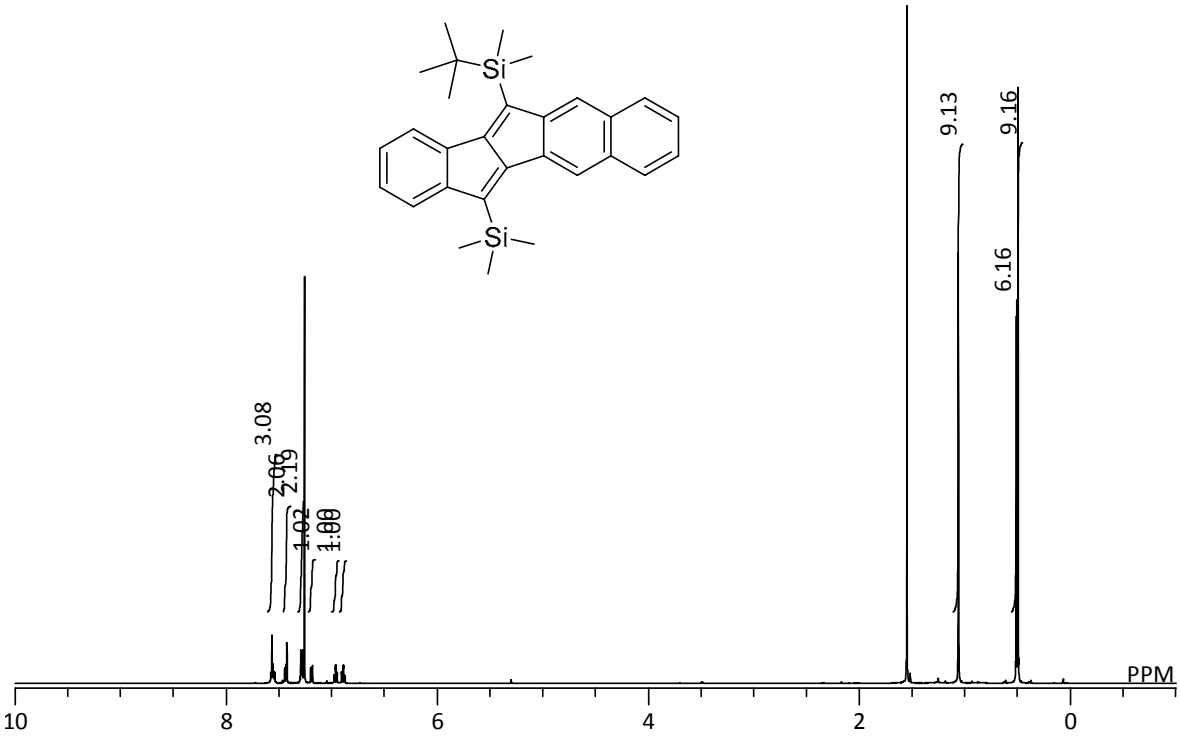


Fig. S34 ^{1}H NMR spectrum of **3bb** (500 MHz, $CDCl_3$).

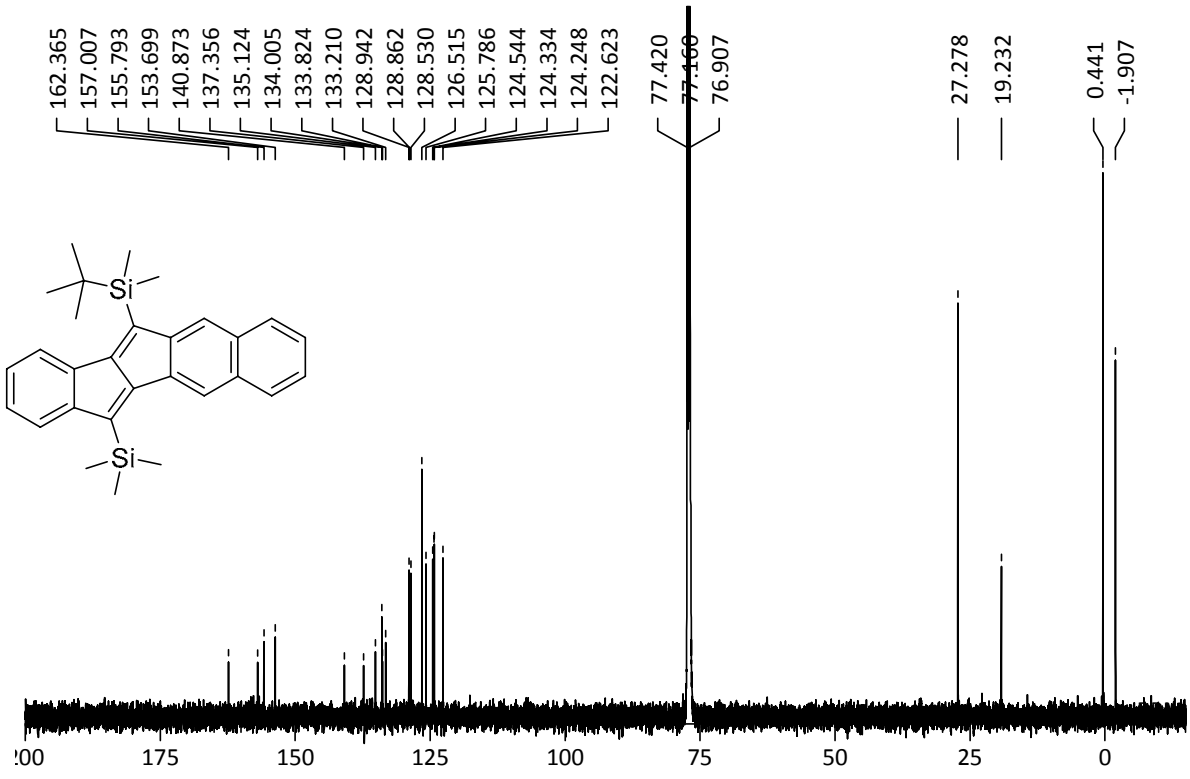


Fig. S35 ^{13}C NMR spectrum of **3bb** (126 MHz, $CDCl_3$).

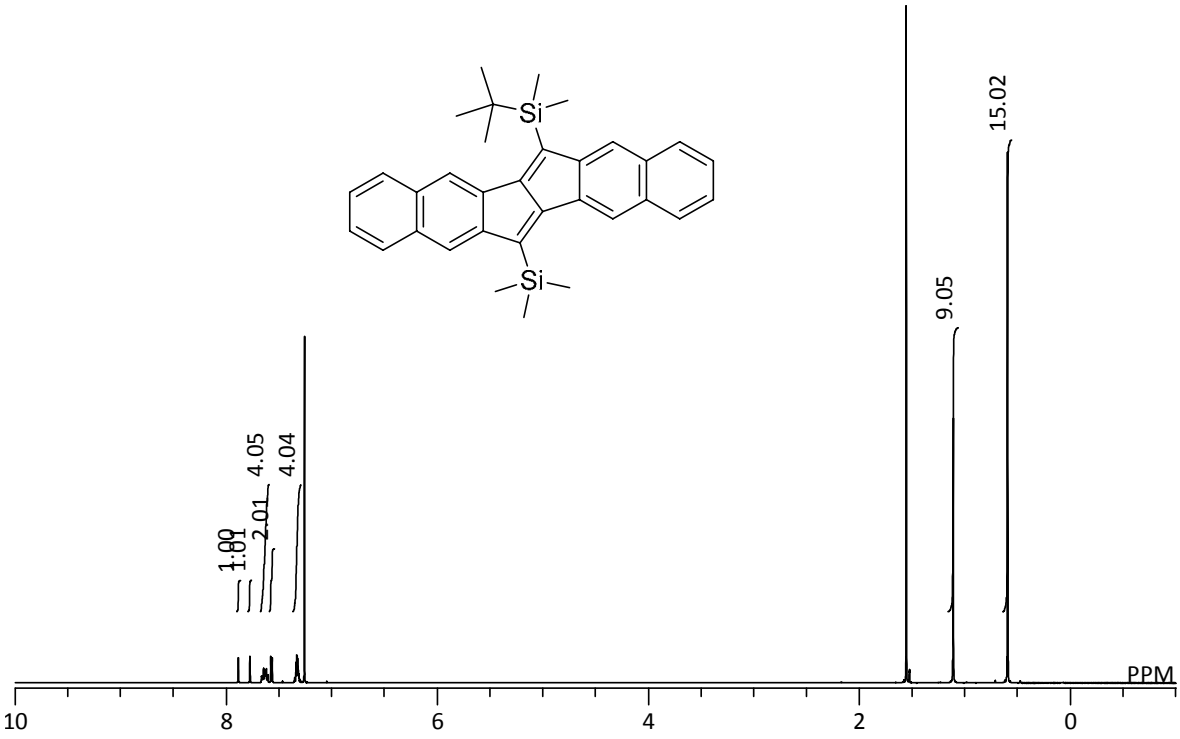


Fig. S36 ^{1}H NMR spectrum of **3db** (500 MHz, $CDCl_3$).

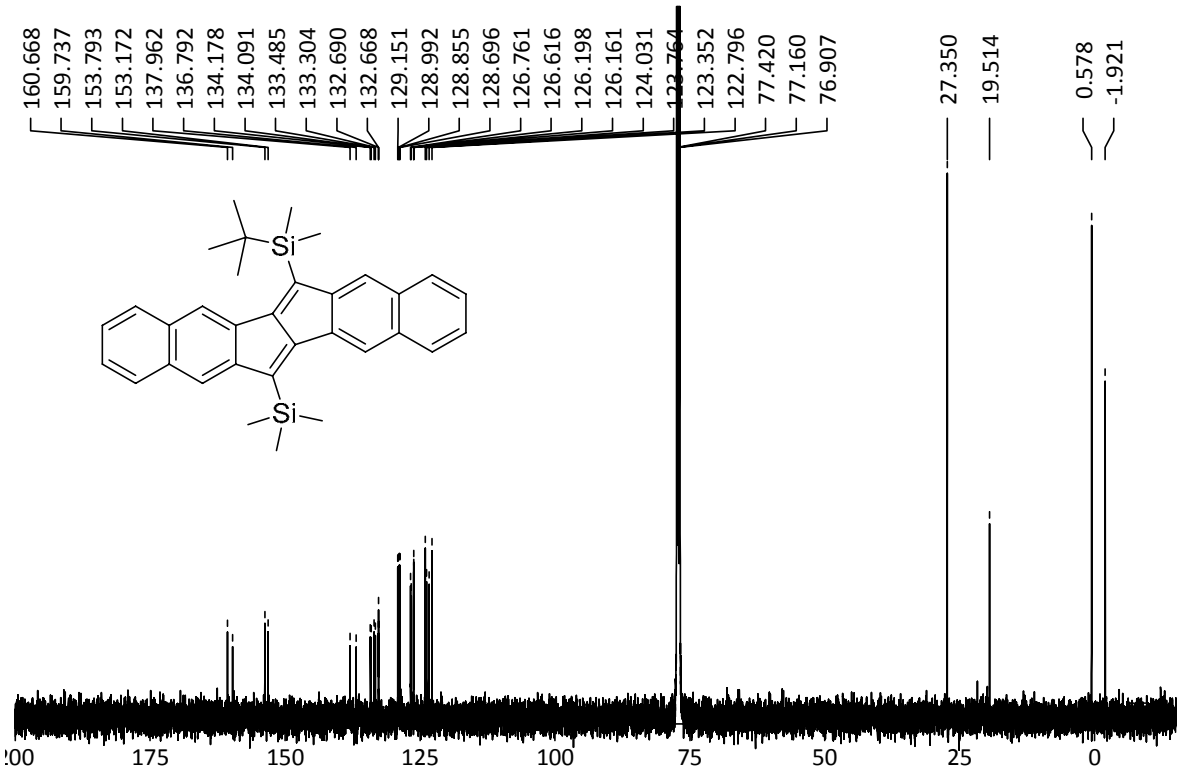


Fig. S37 ^{13}C NMR spectrum of **3db** (126 MHz, $CDCl_3$).

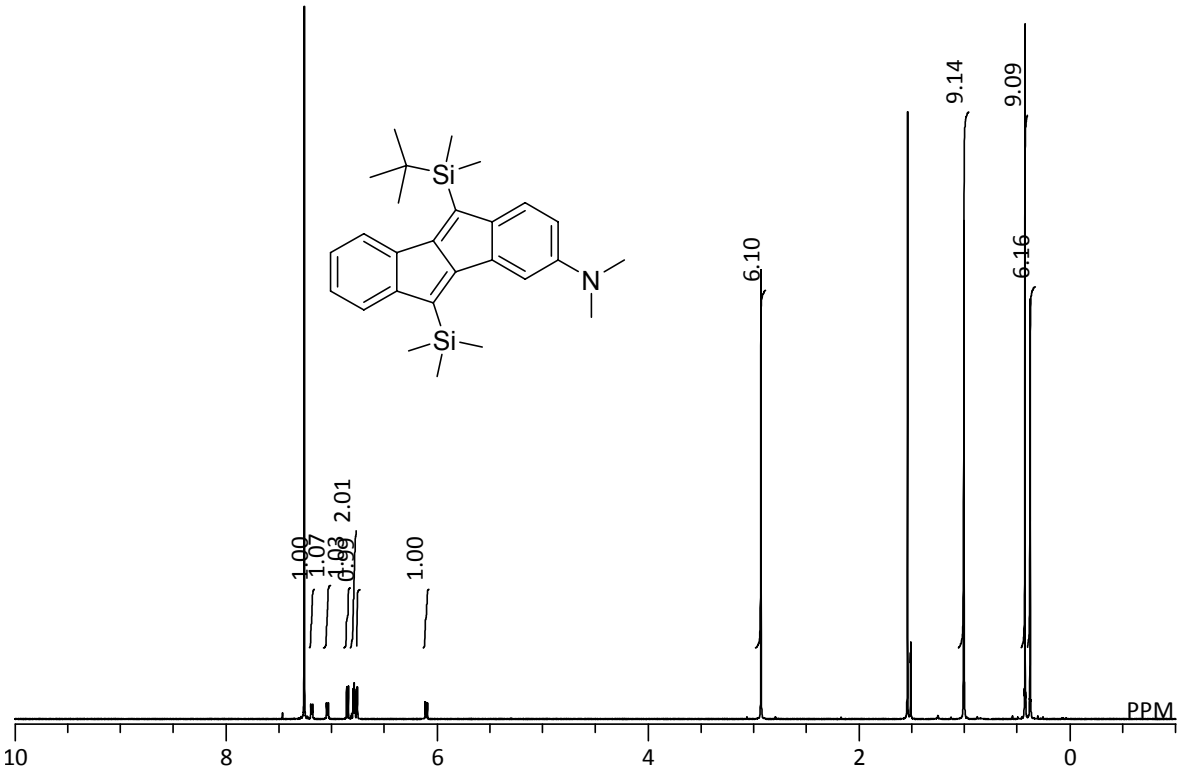


Fig. S38 ^{1}H NMR spectrum of **3bc** (500 MHz, $CDCl_3$).

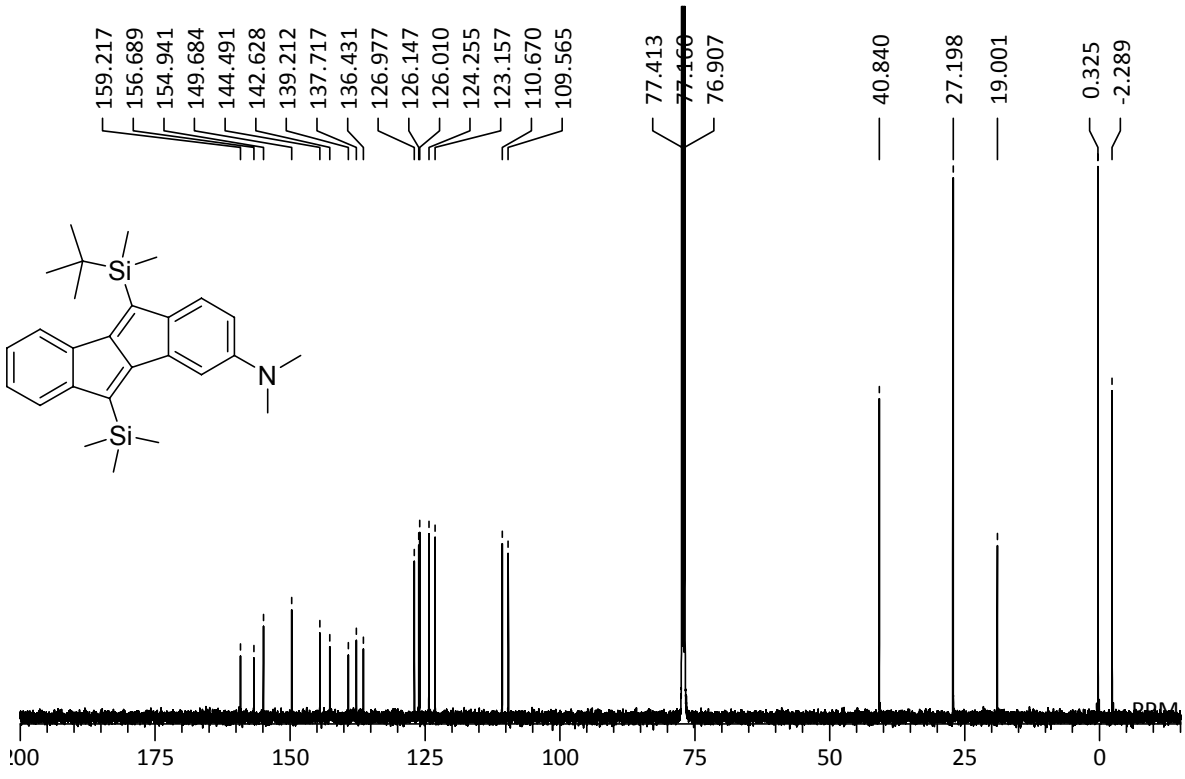


Fig. S39 ^{13}C NMR spectrum of **3bc** (126 MHz, $CDCl_3$).

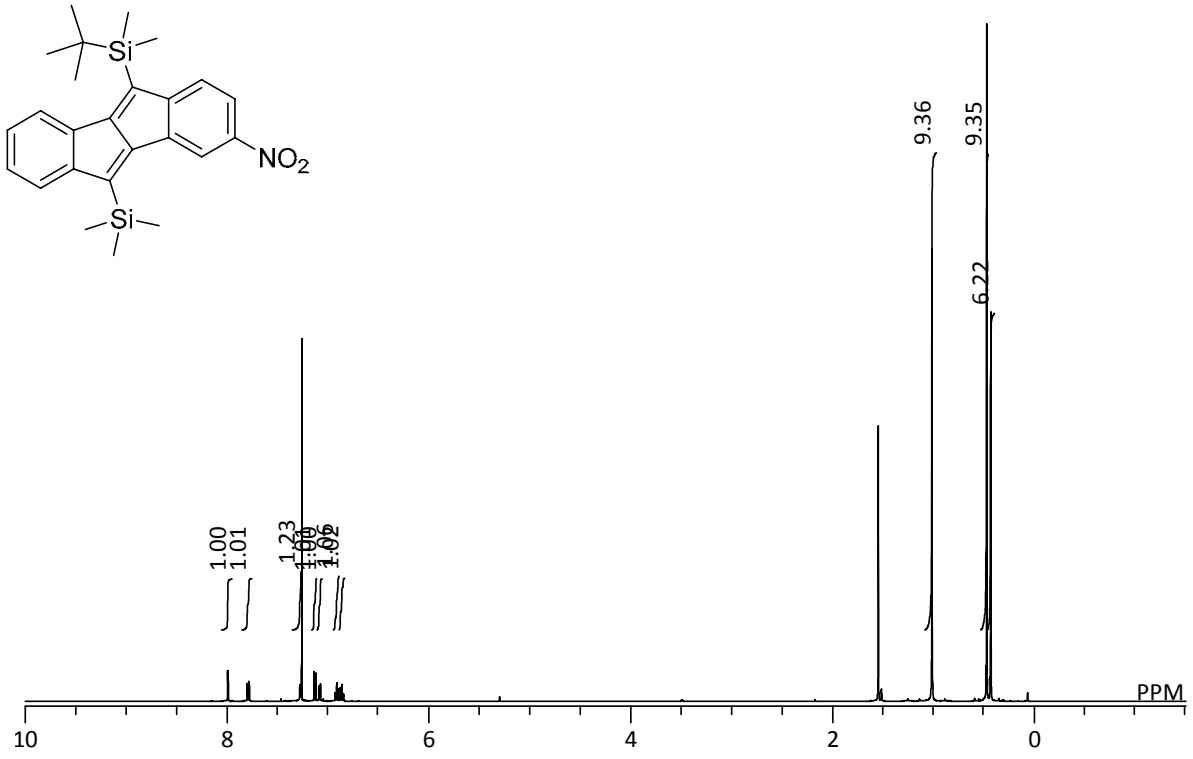


Fig. S40 ^{1}H NMR spectrum of **3bd** (500 MHz, $CDCl_3$).

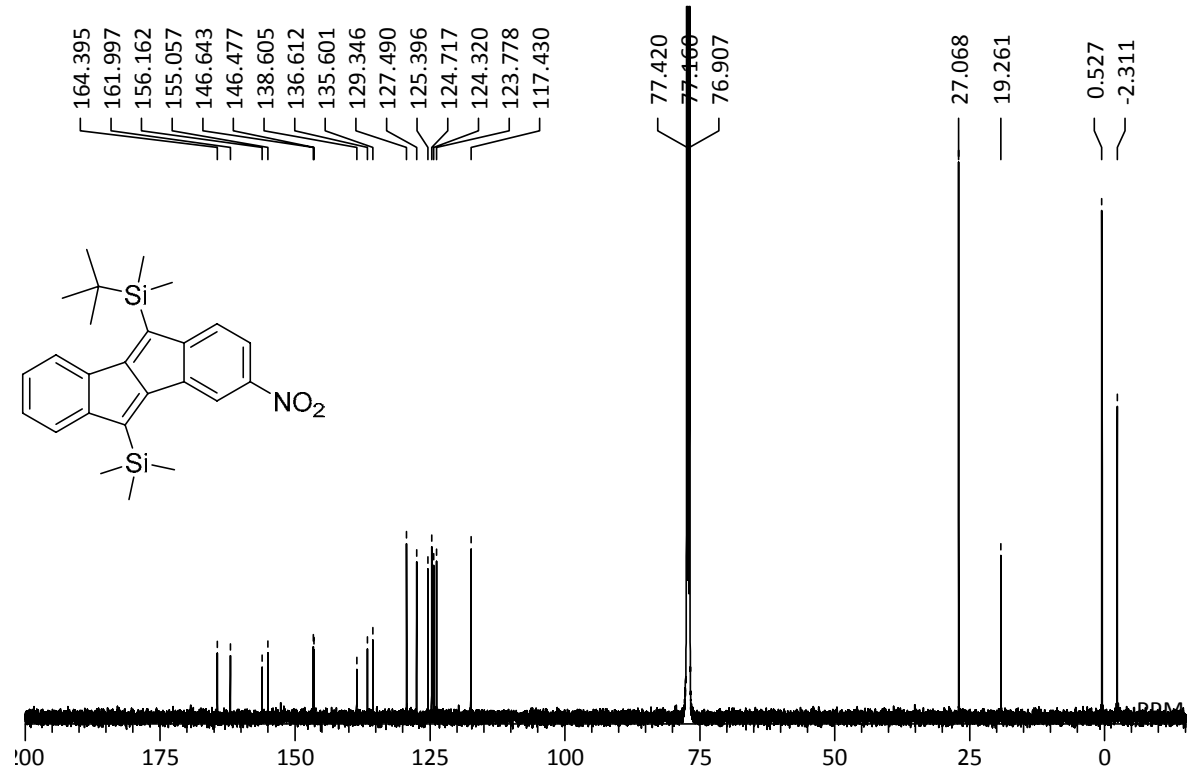


Fig. S41 ^{13}C NMR spectrum of **3bd** (126 MHz, $CDCl_3$).

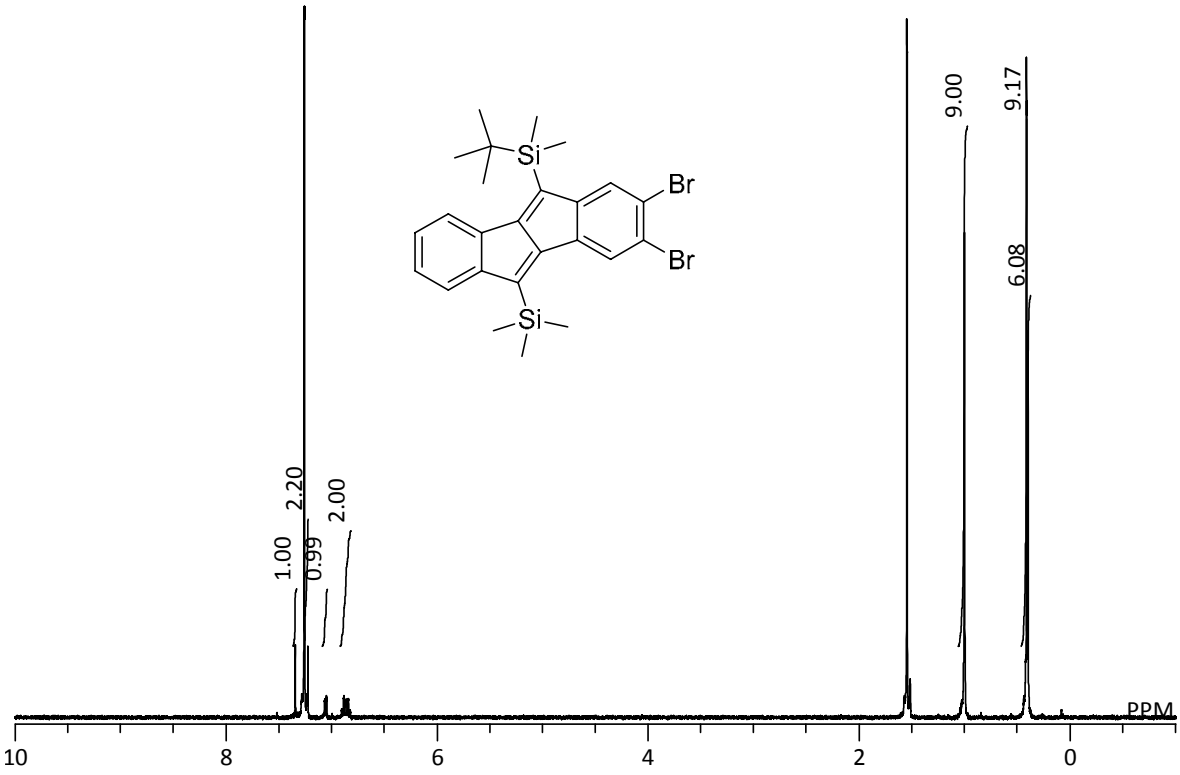


Fig. S42 ^{1}H NMR spectrum of **3be** (500 MHz, $CDCl_3$).

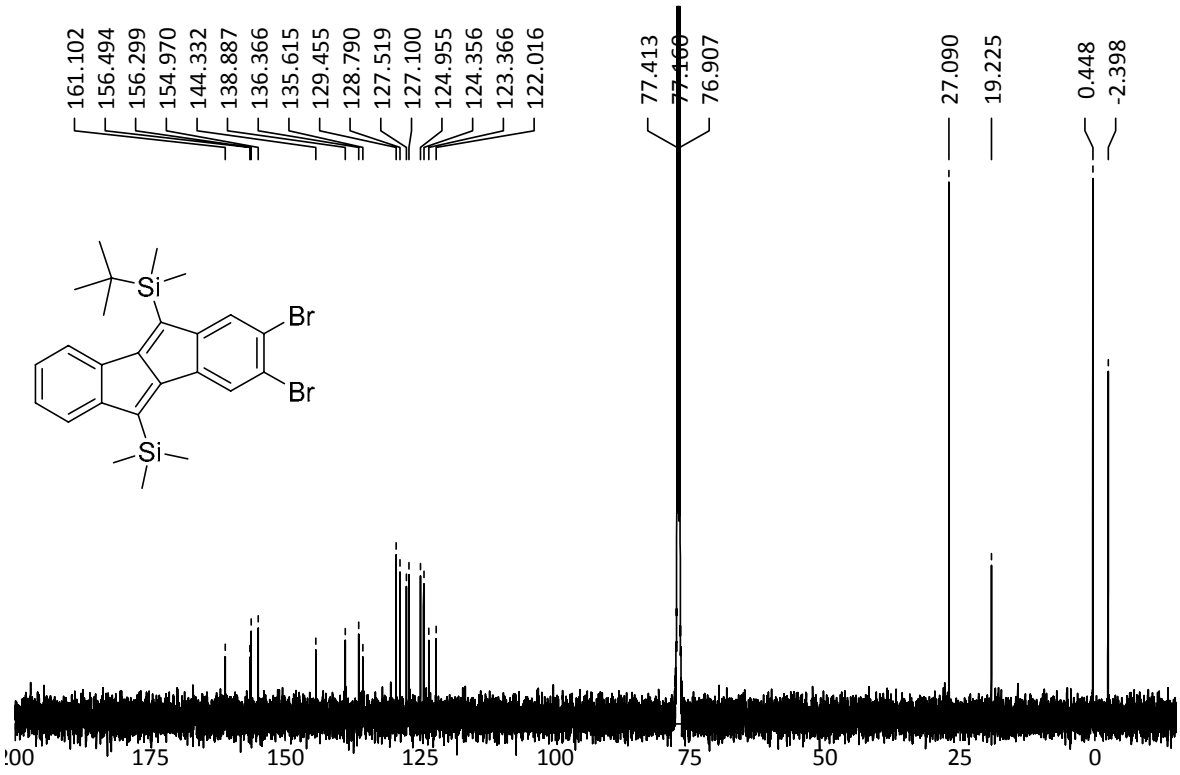


Fig. S43 ^{13}C NMR spectrum of **3be** (126 MHz, $CDCl_3$).

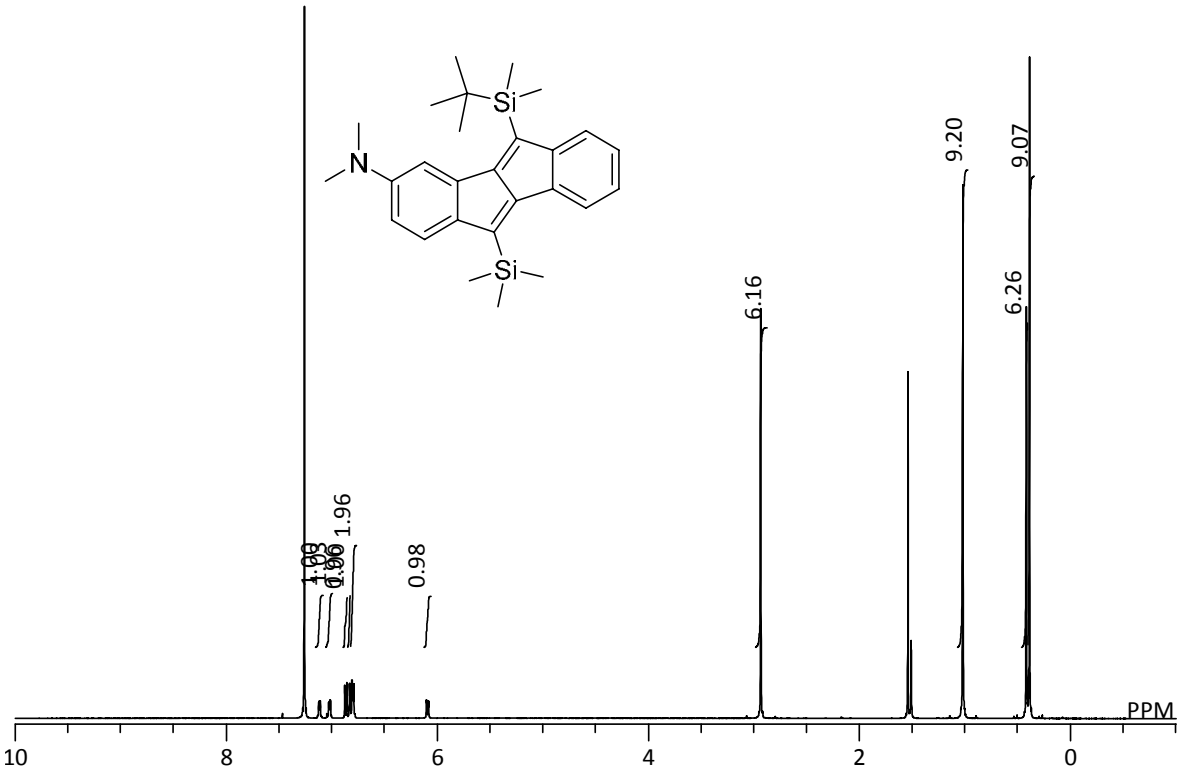


Fig. S44 ^{1}H NMR spectrum of **3ea** (500 MHz, $CDCl_3$).

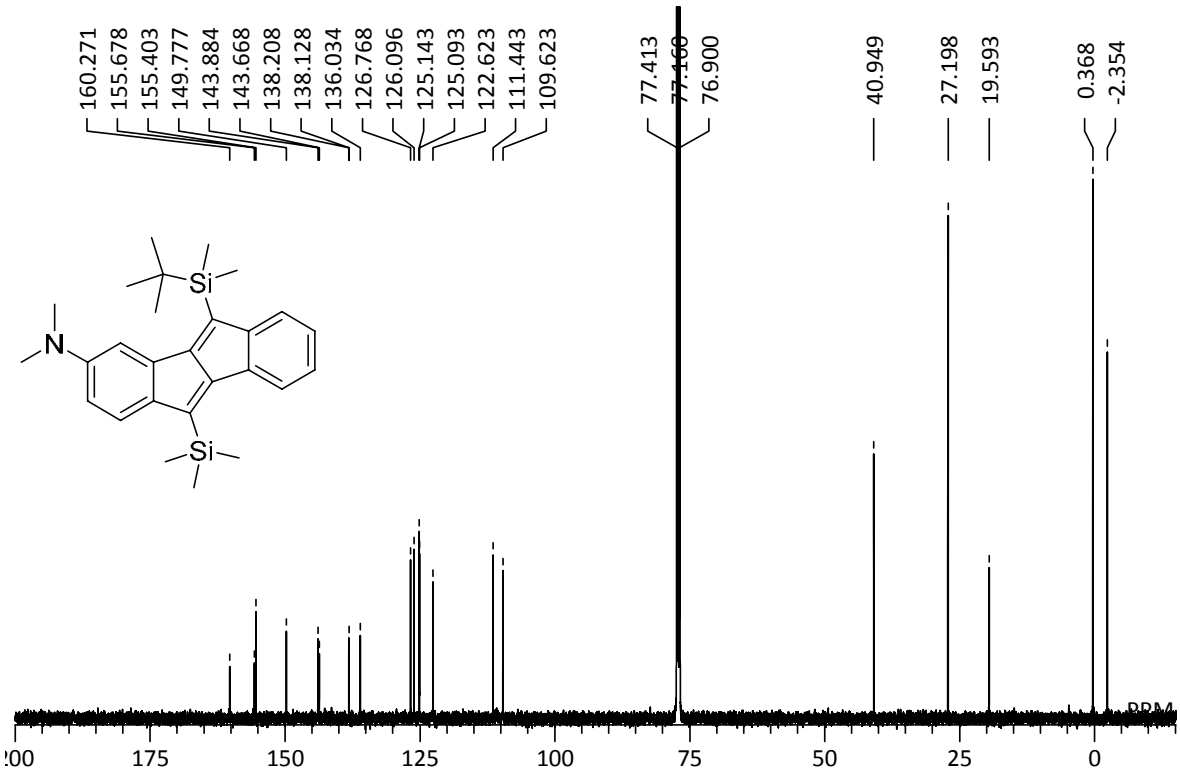


Fig. S45 ^{13}C NMR spectrum of **3ea** (126 MHz, $CDCl_3$).

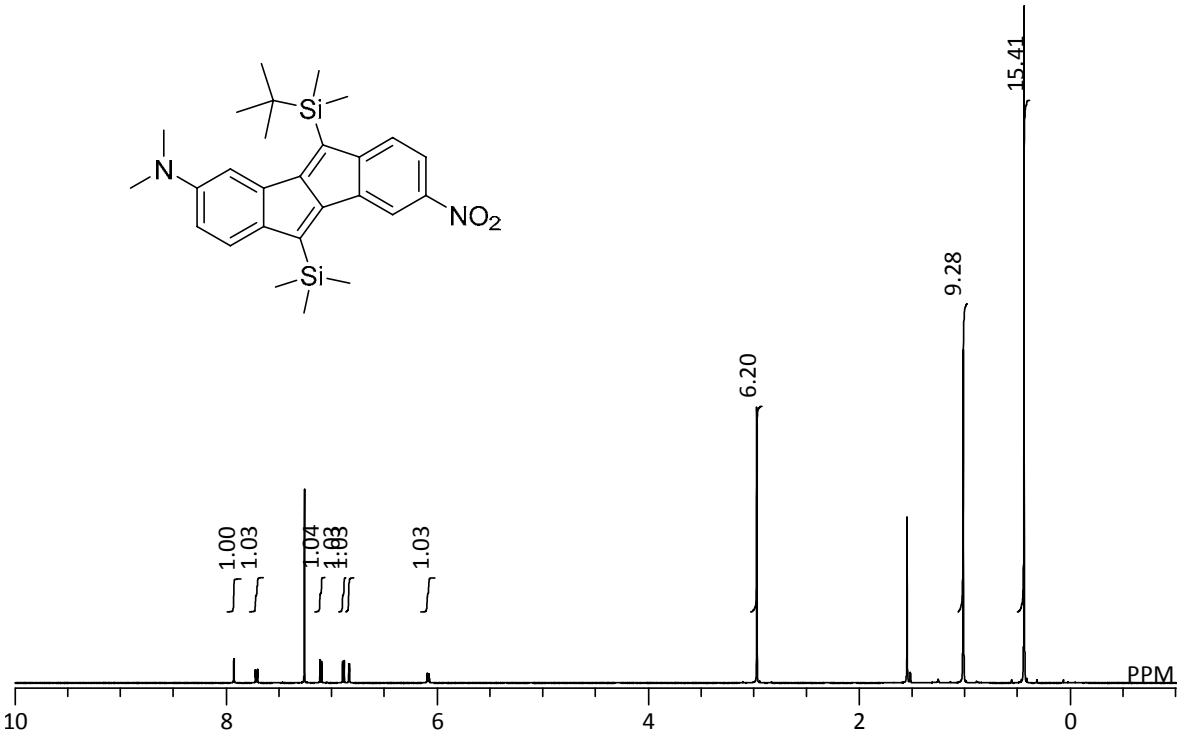


Fig. S46 ^{1}H NMR spectrum of **3ed** (500 MHz, $CDCl_3$).

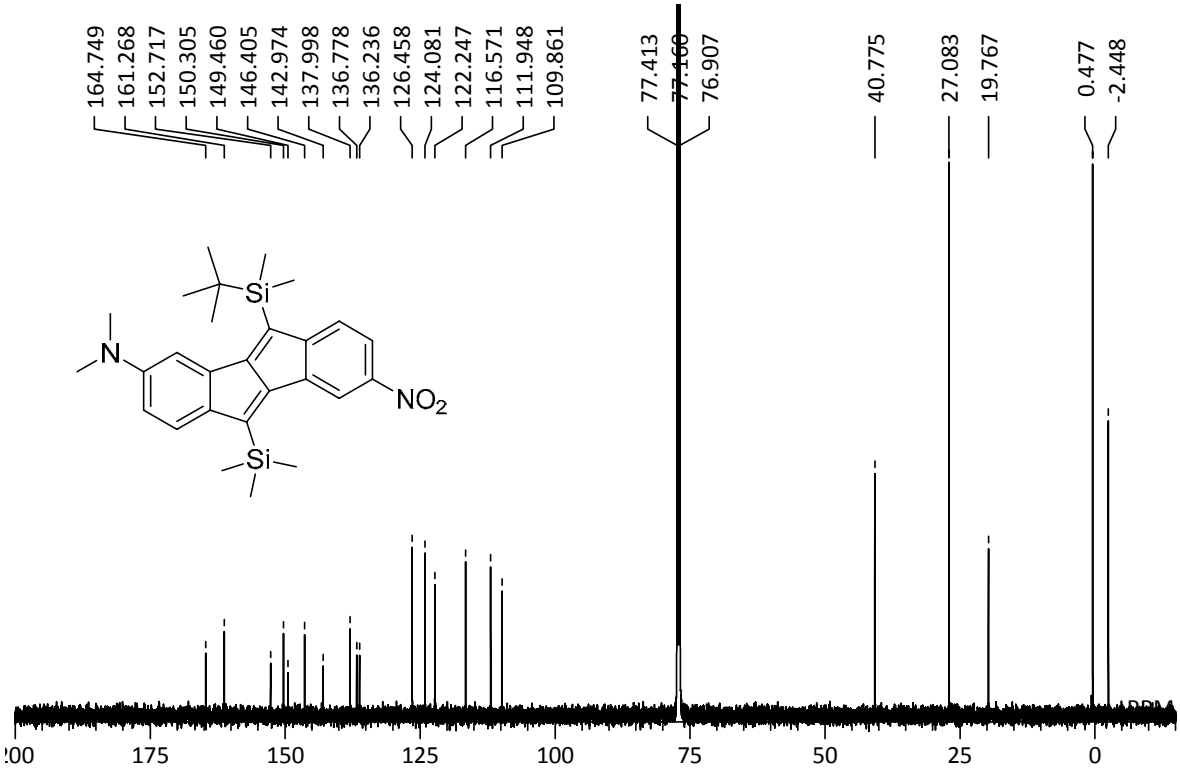


Fig. S47 ^{13}C NMR spectrum of **3ed** (126 MHz, $CDCl_3$).

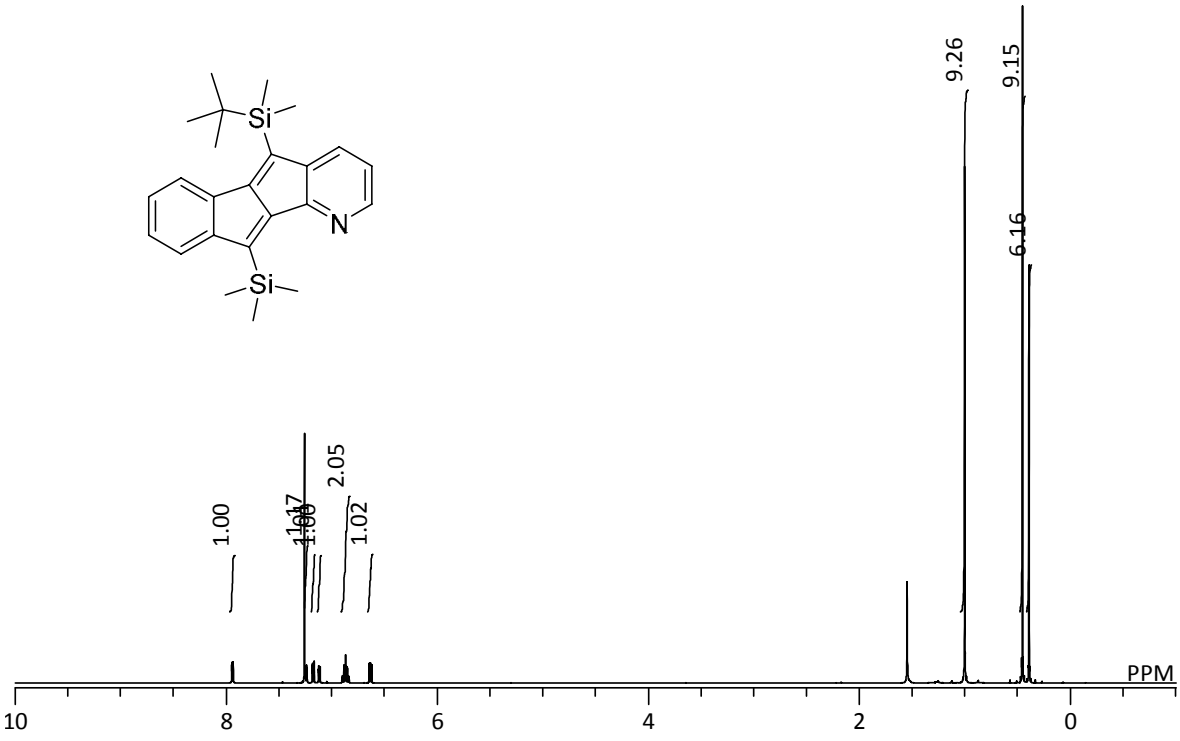


Fig. S48 ^{1}H NMR spectrum of **3bf** (500 MHz, $CDCl_3$).

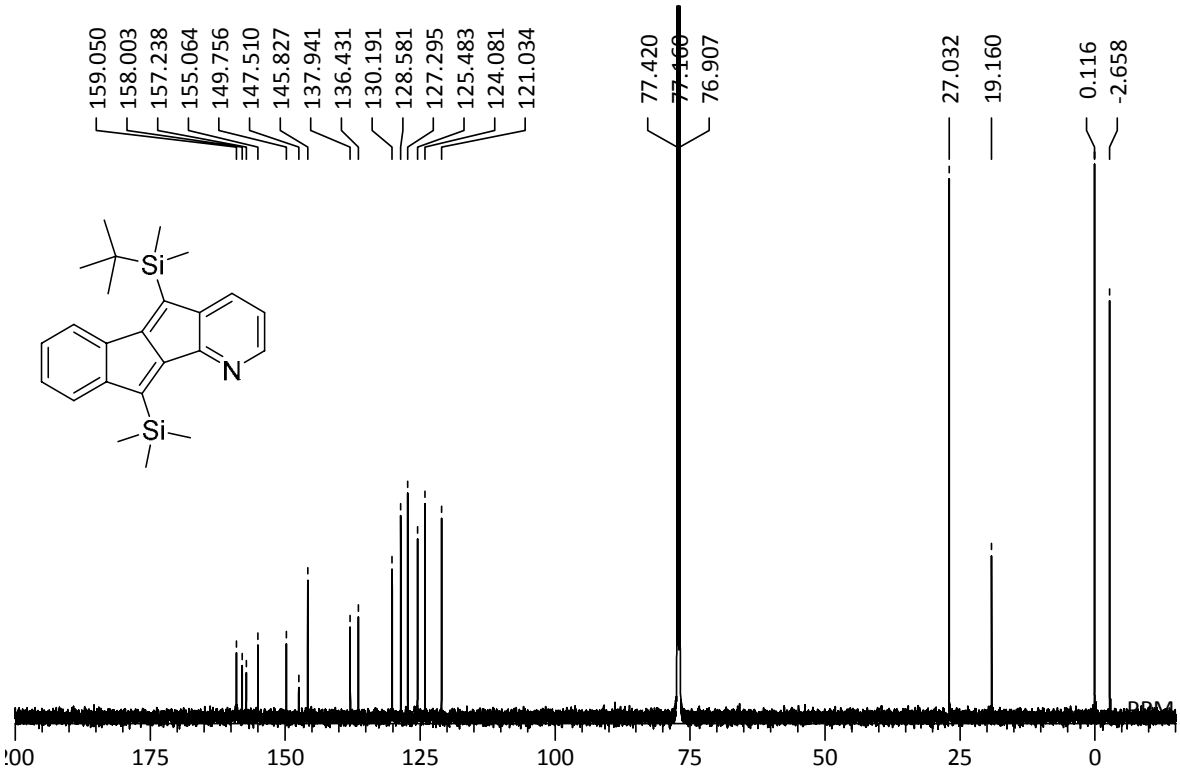


Fig. S49 ^{13}C NMR spectrum of **3bf** (126 MHz, $CDCl_3$).

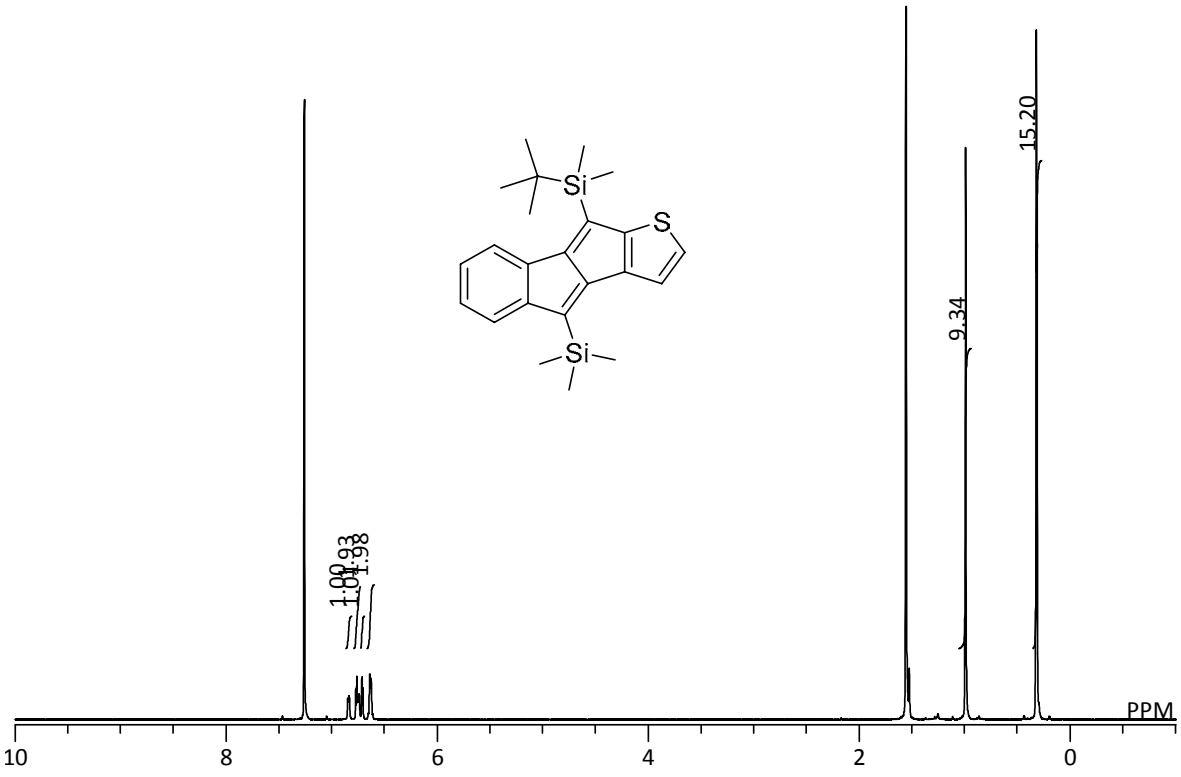


Fig. S50 ^{1}H NMR spectrum of **3bg** (500 MHz, $CDCl_3$).

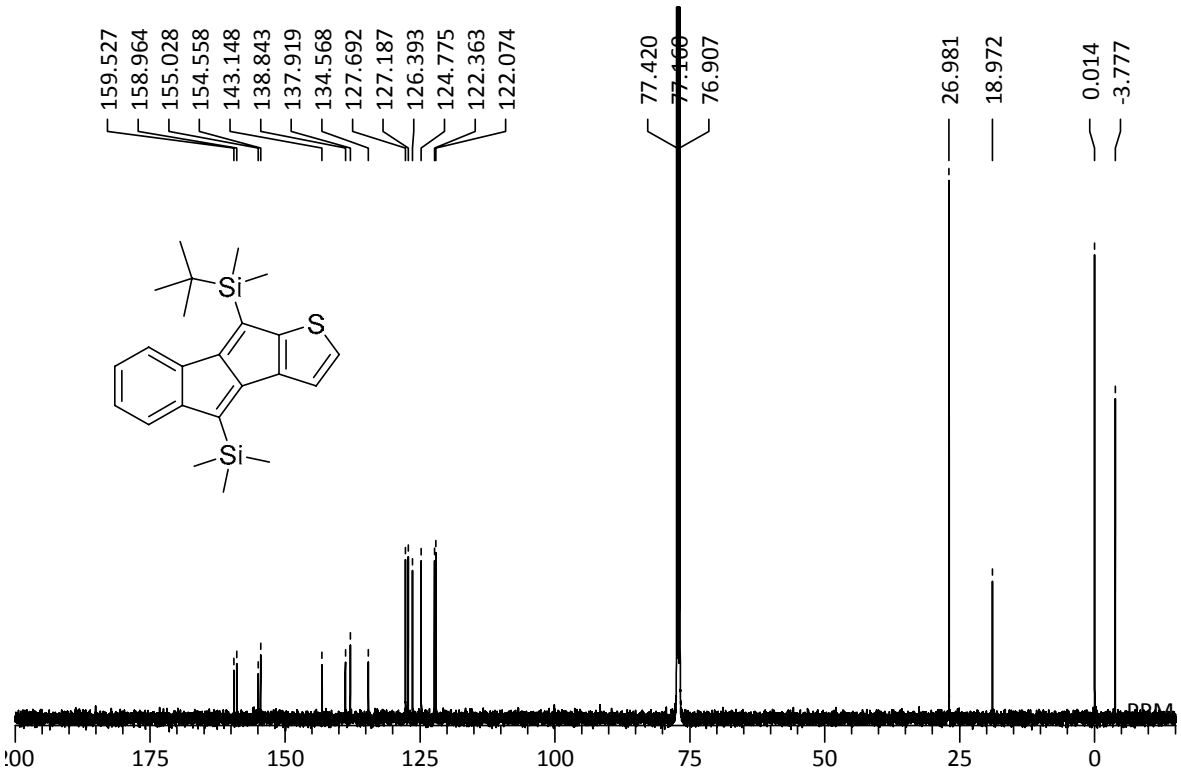


Fig. S51 ^{13}C NMR spectrum of **3bg** (126 MHz, $CDCl_3$).

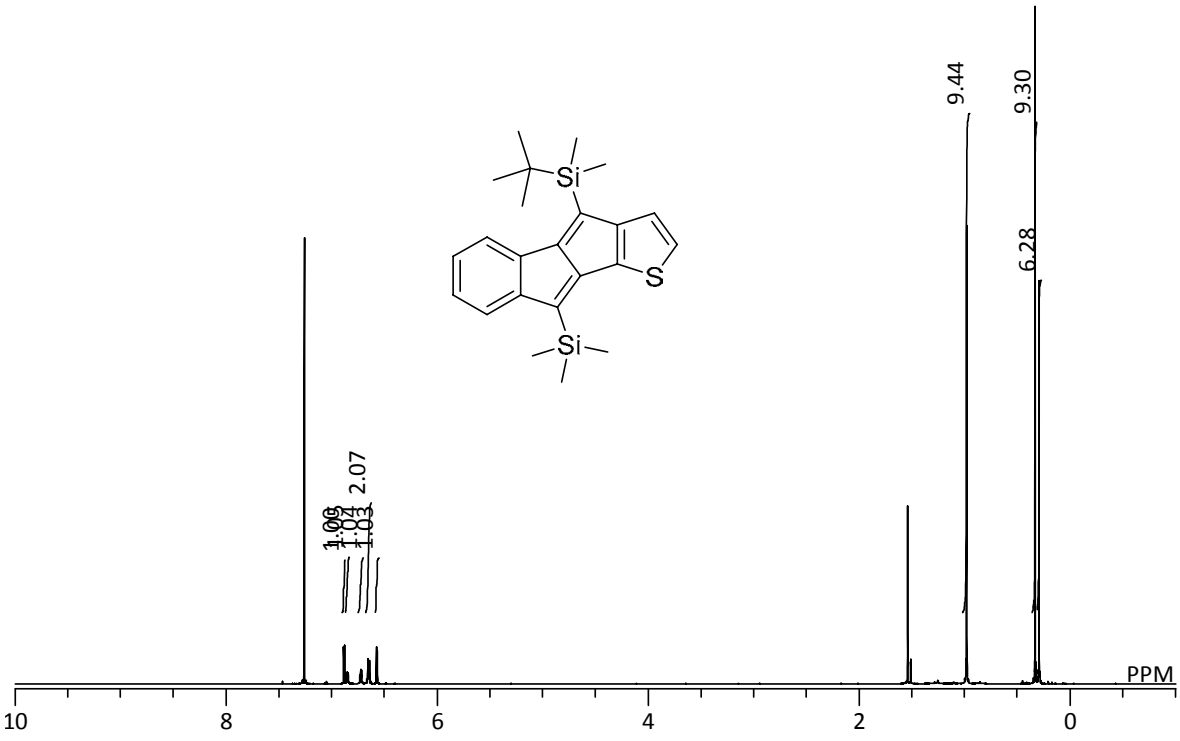


Fig. S52 ^{1}H NMR spectrum of **3bh** (500 MHz, $CDCl_3$).

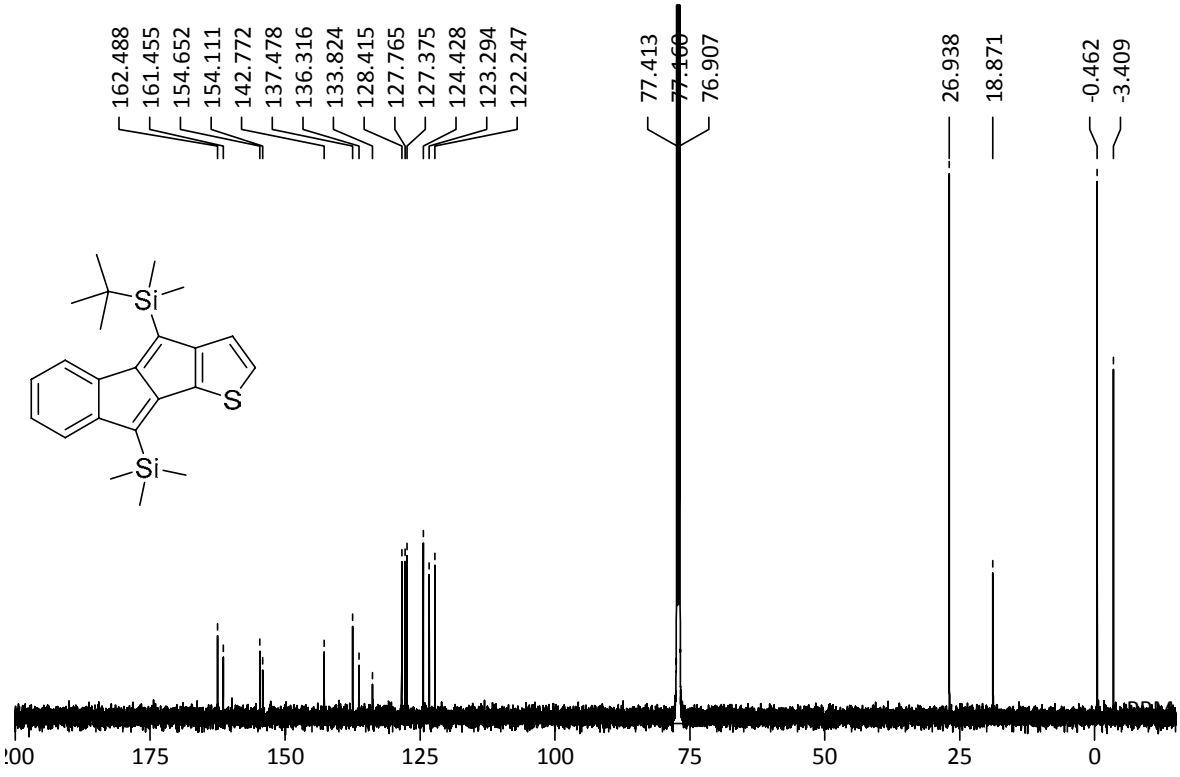


Fig. S53 ^{13}C NMR spectrum of **3bh** (126 MHz, $CDCl_3$).

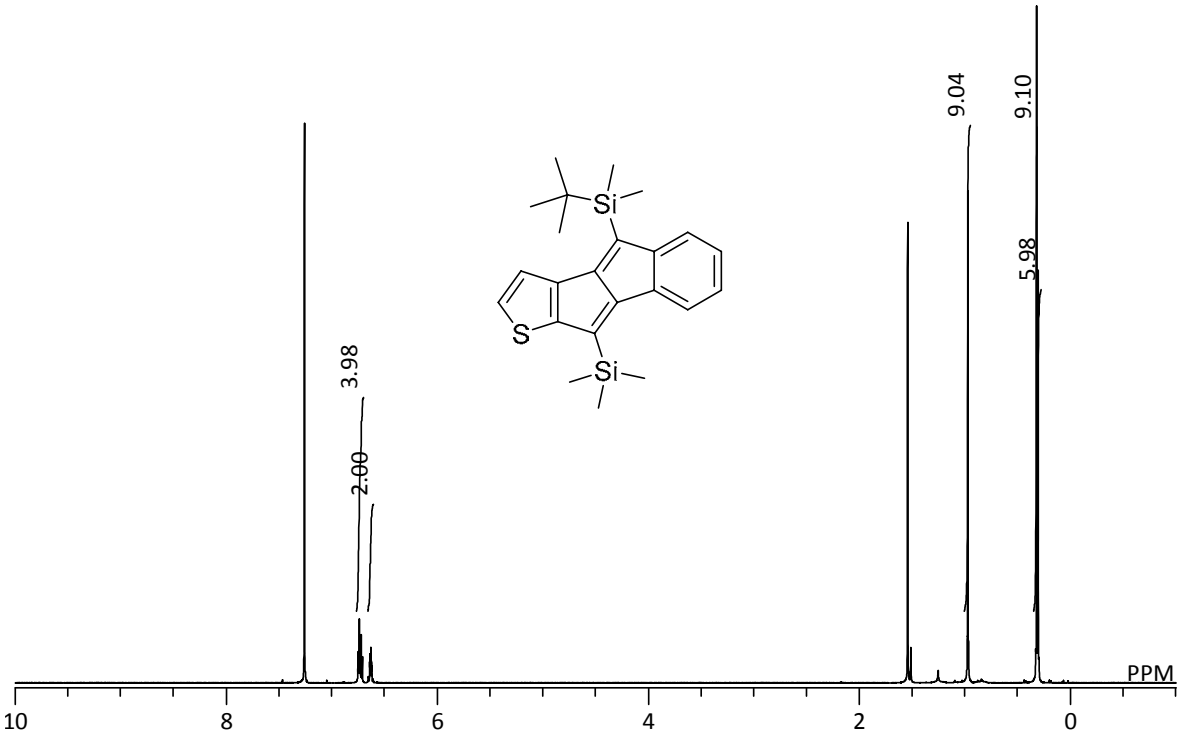


Fig. S54 ^{1}H NMR spectrum of **3fa** (500 MHz, $CDCl_3$).

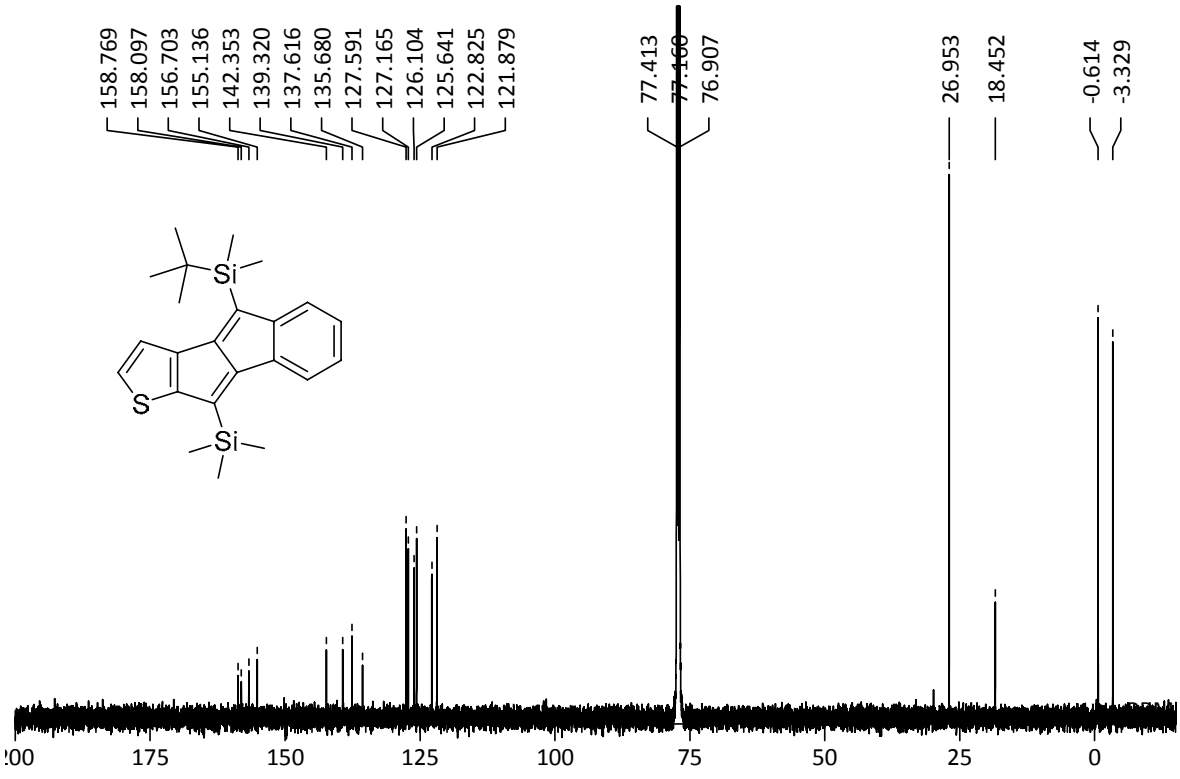


Fig. S55 ^{13}C NMR spectrum of **3fa** (126 MHz, $CDCl_3$).

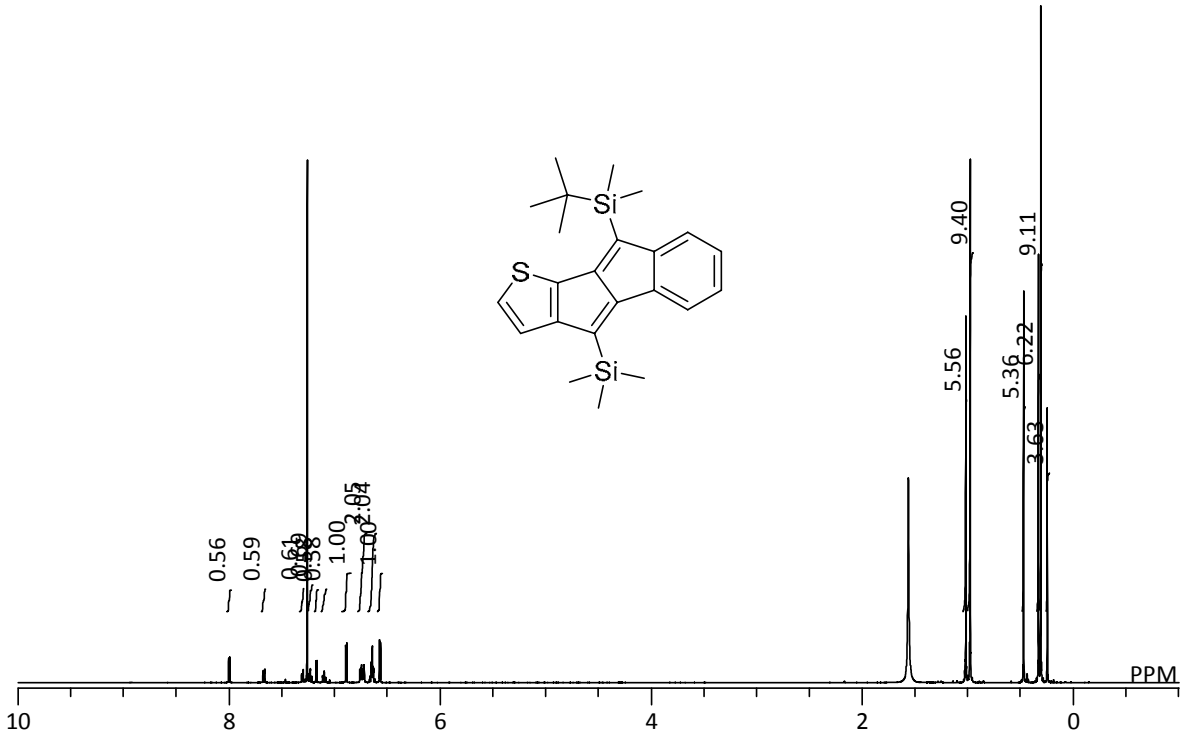


Fig. S56 ^{1}H NMR spectrum of **3ga** and inseparable side-product (500 MHz, $CDCl_3$).

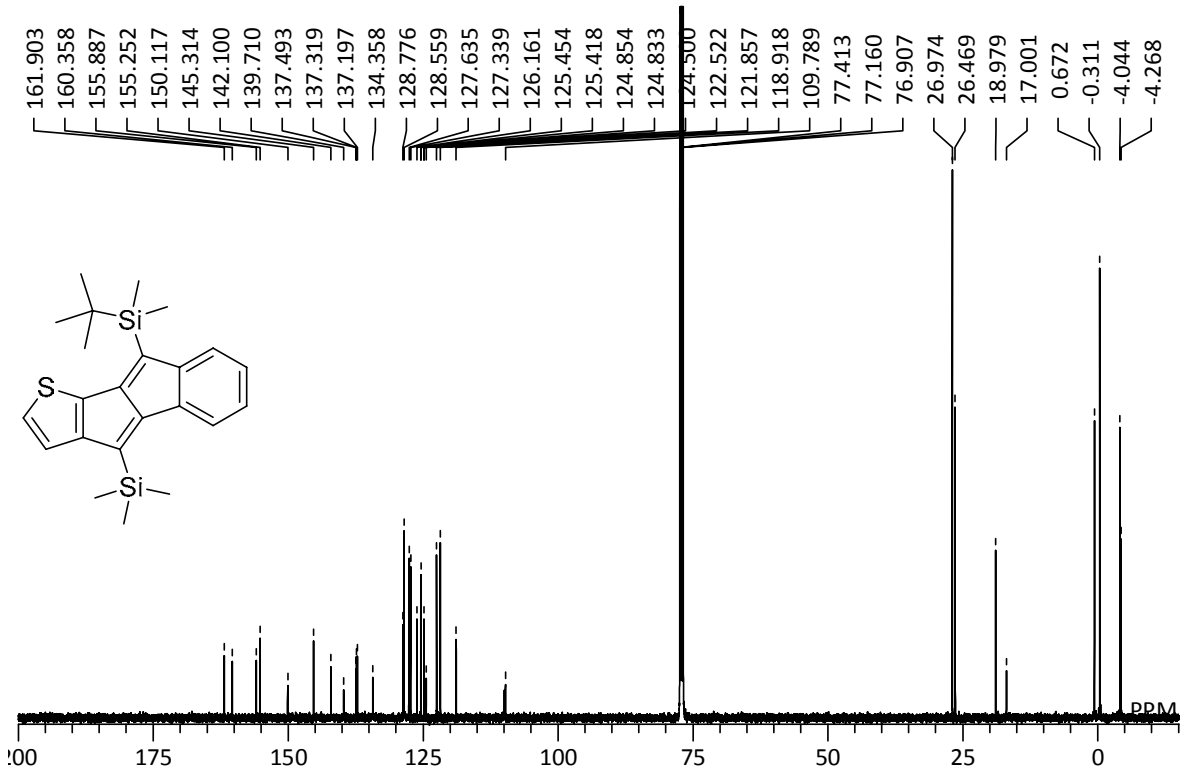


Fig. S57 ^{13}C NMR spectrum of **3ga** and inseparable side-product (126 MHz, $CDCl_3$).

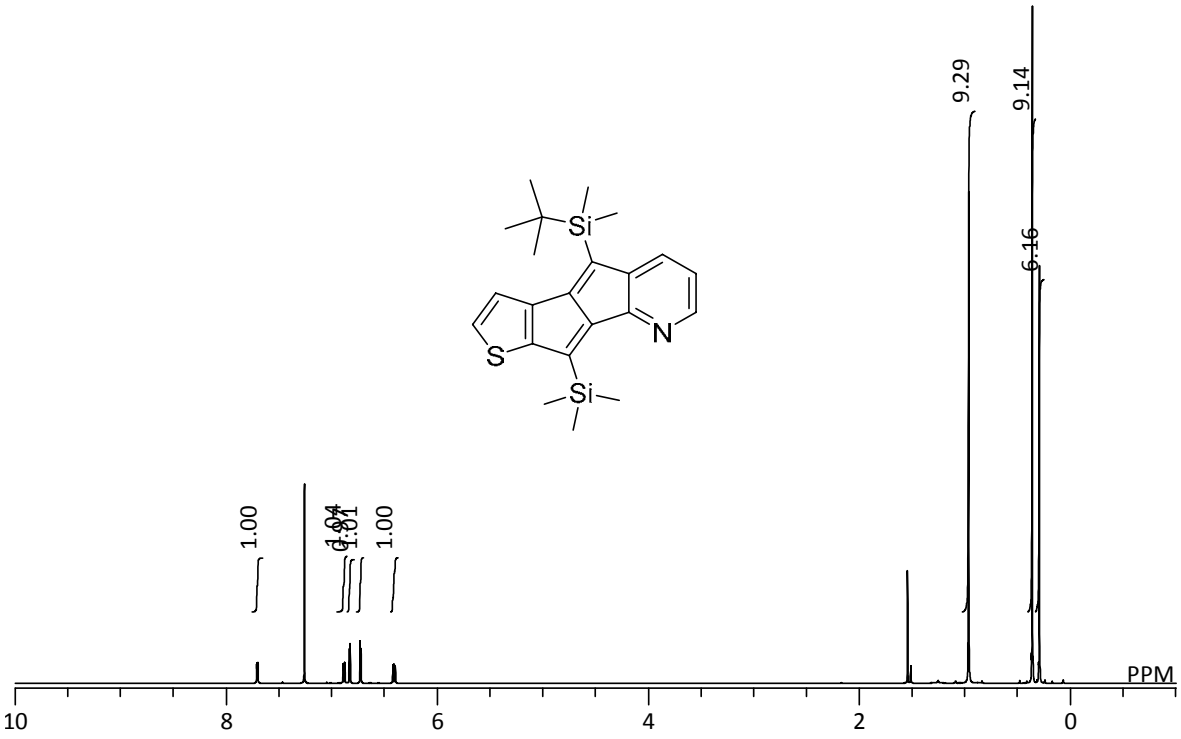


Fig. S58 ^{1}H NMR spectrum of **3ff** (500 MHz, $CDCl_3$).

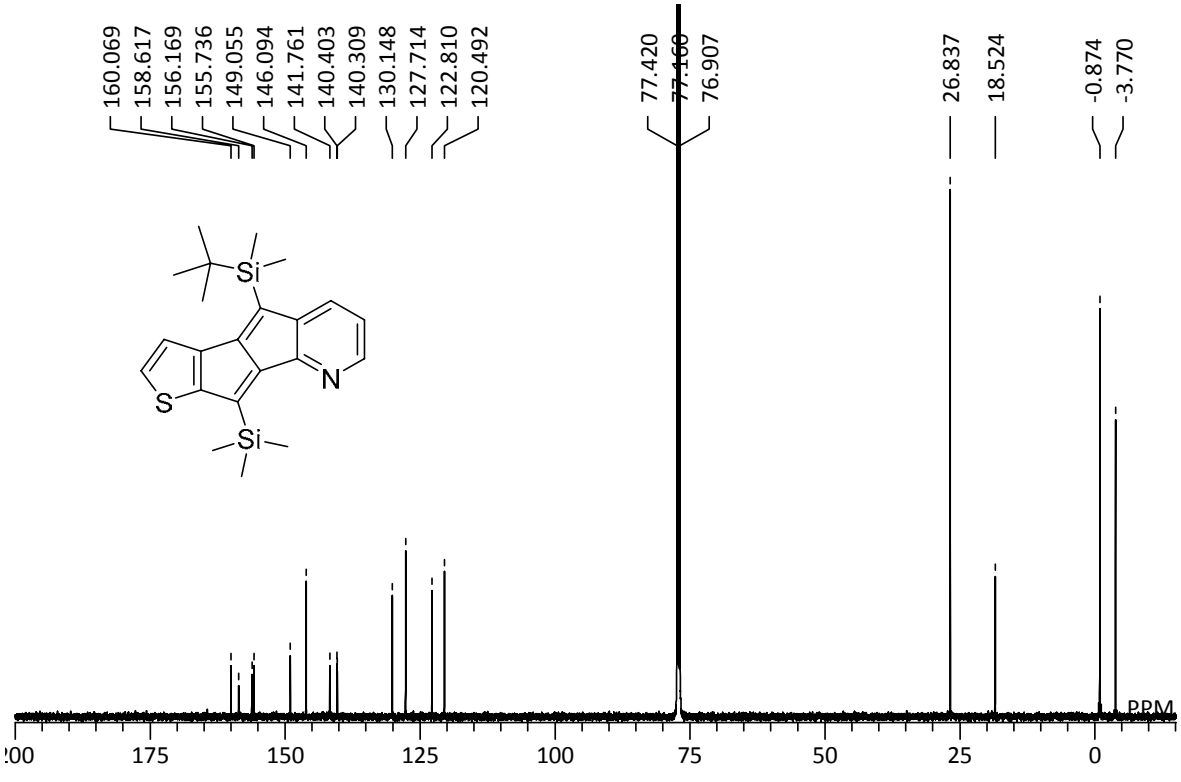


Fig. S59 ^{13}C NMR spectrum of **3ff** (126 MHz, $CDCl_3$).

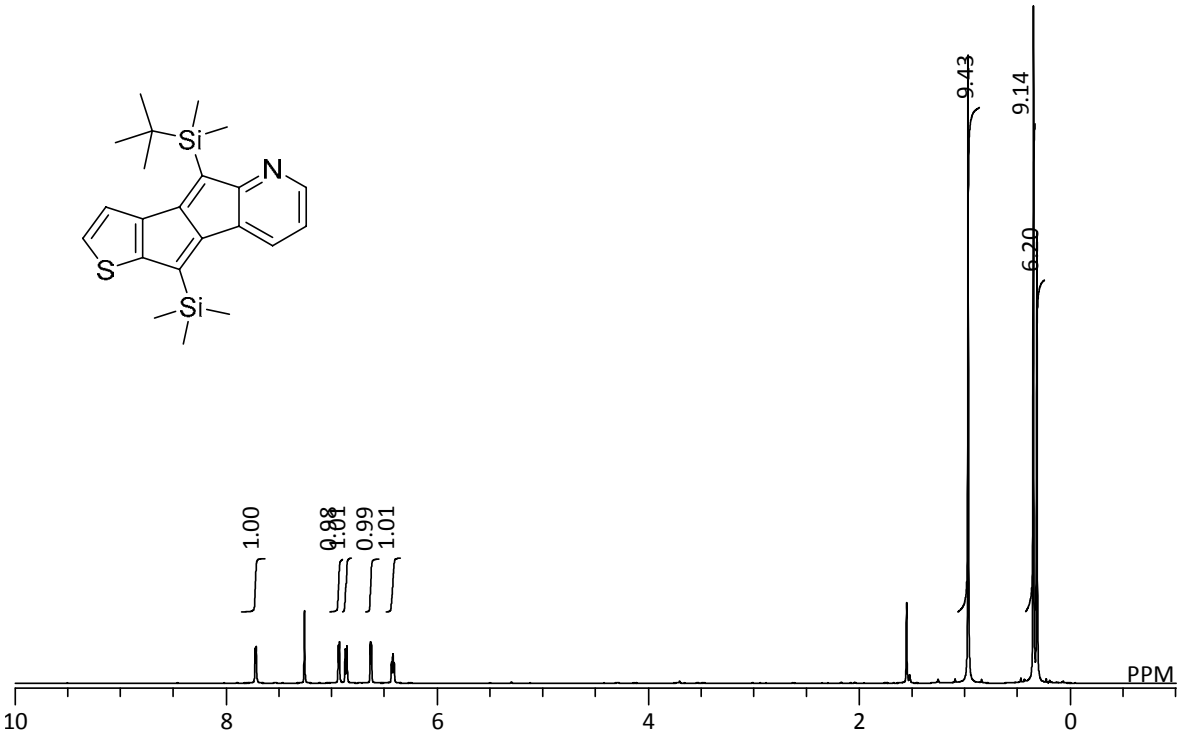


Fig. S60 ^{1}H NMR spectrum of **3gf** (500 MHz, $CDCl_3$).

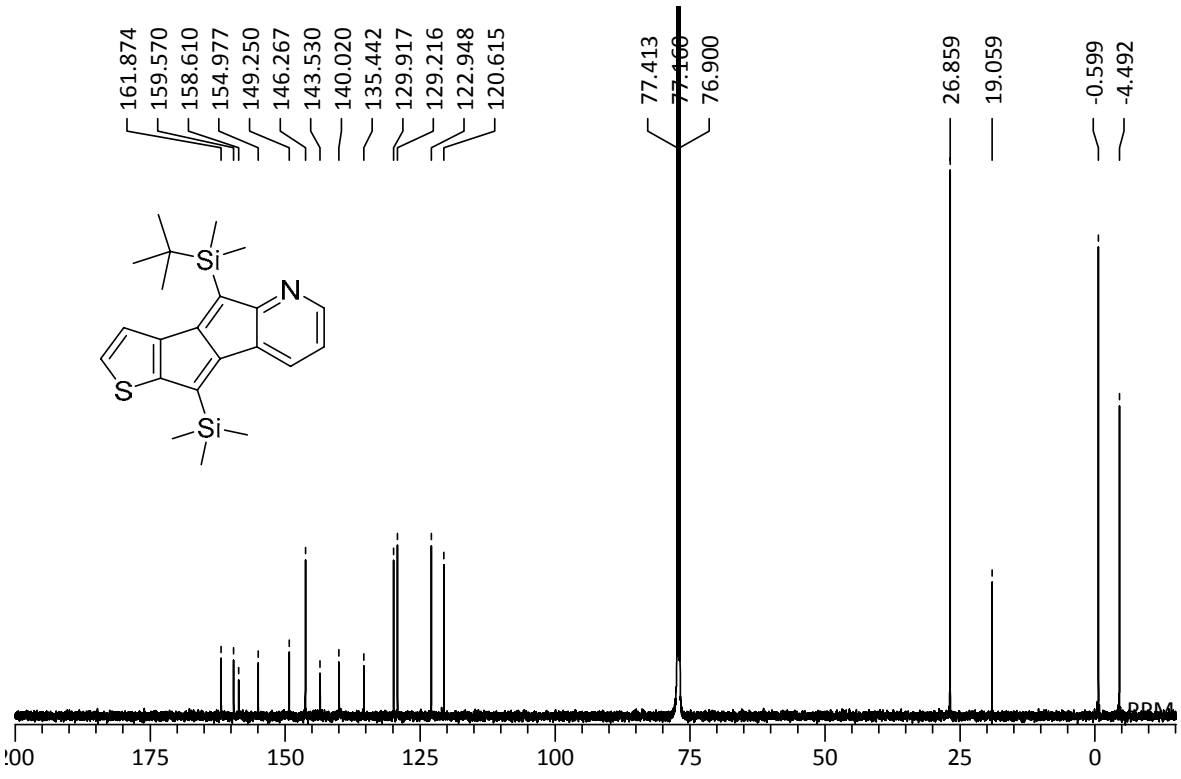


Fig. S61 ^{13}C NMR spectrum of **3gf** (126 MHz, $CDCl_3$).

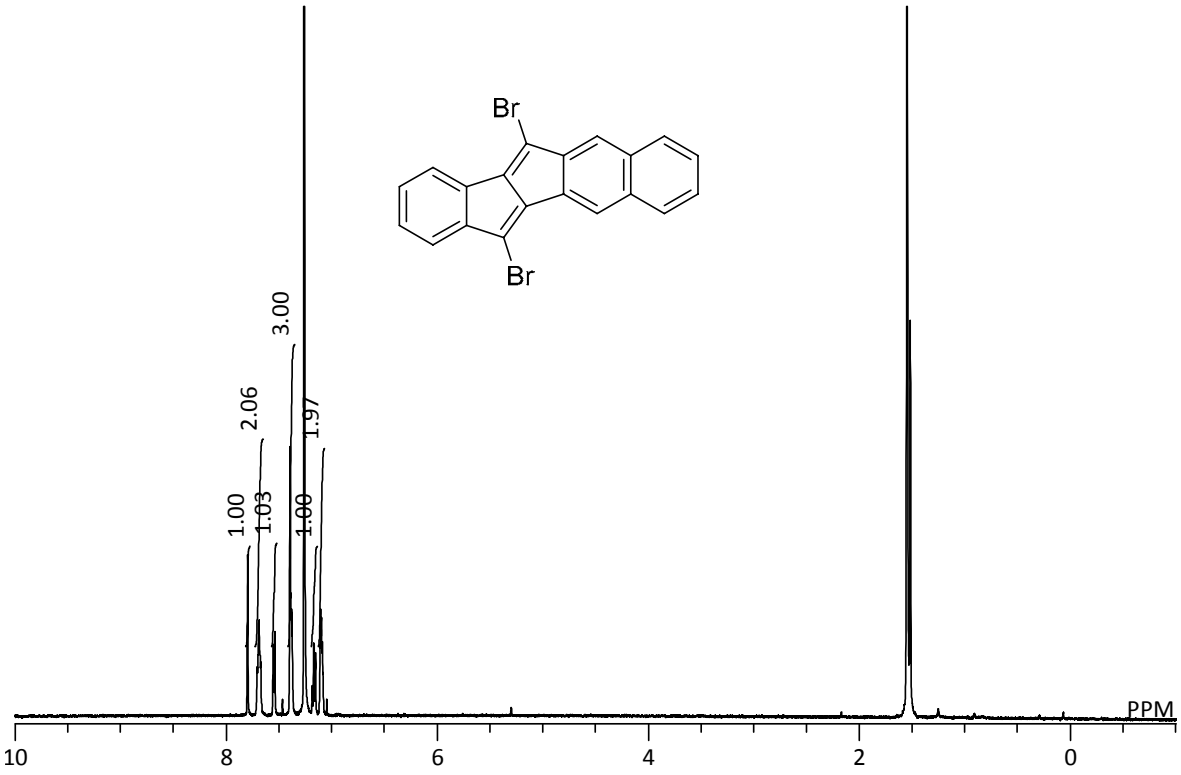


Fig. S62 ^{1}H NMR spectrum of **5** (500 MHz, $CDCl_3$).

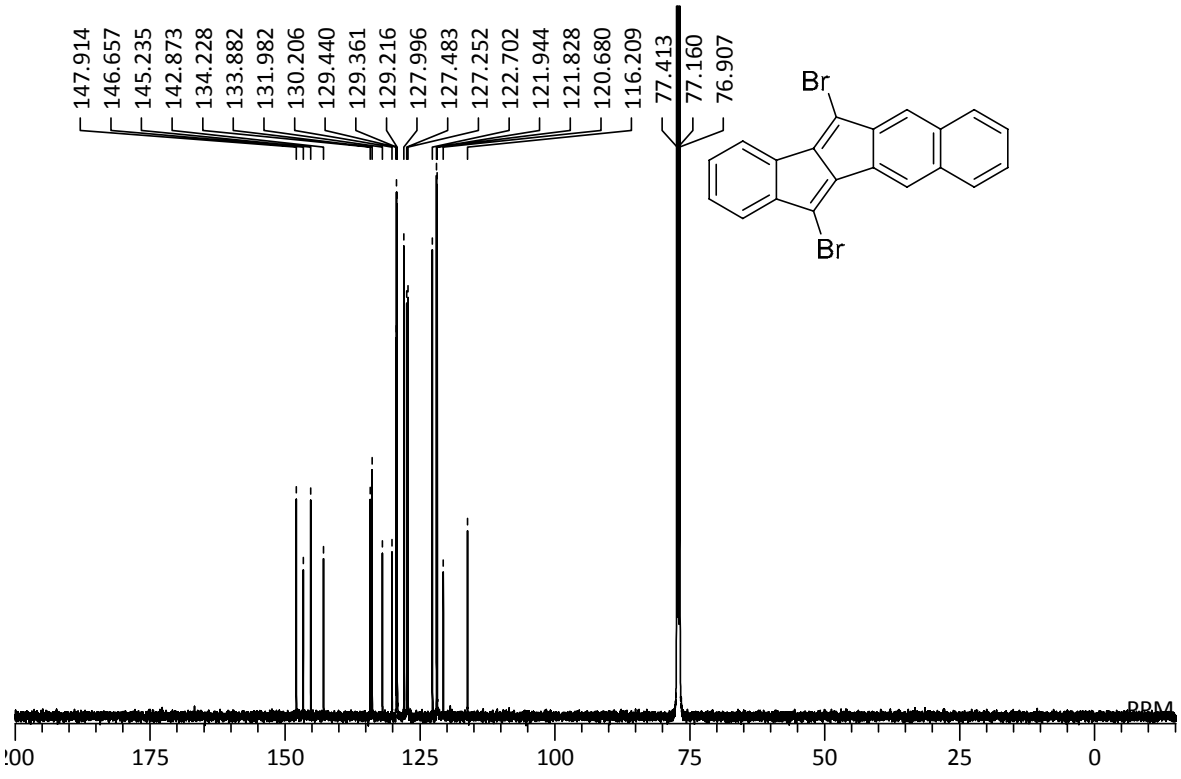


Fig. S63 ^{13}C NMR spectrum of **5** (126 MHz, $CDCl_3$).

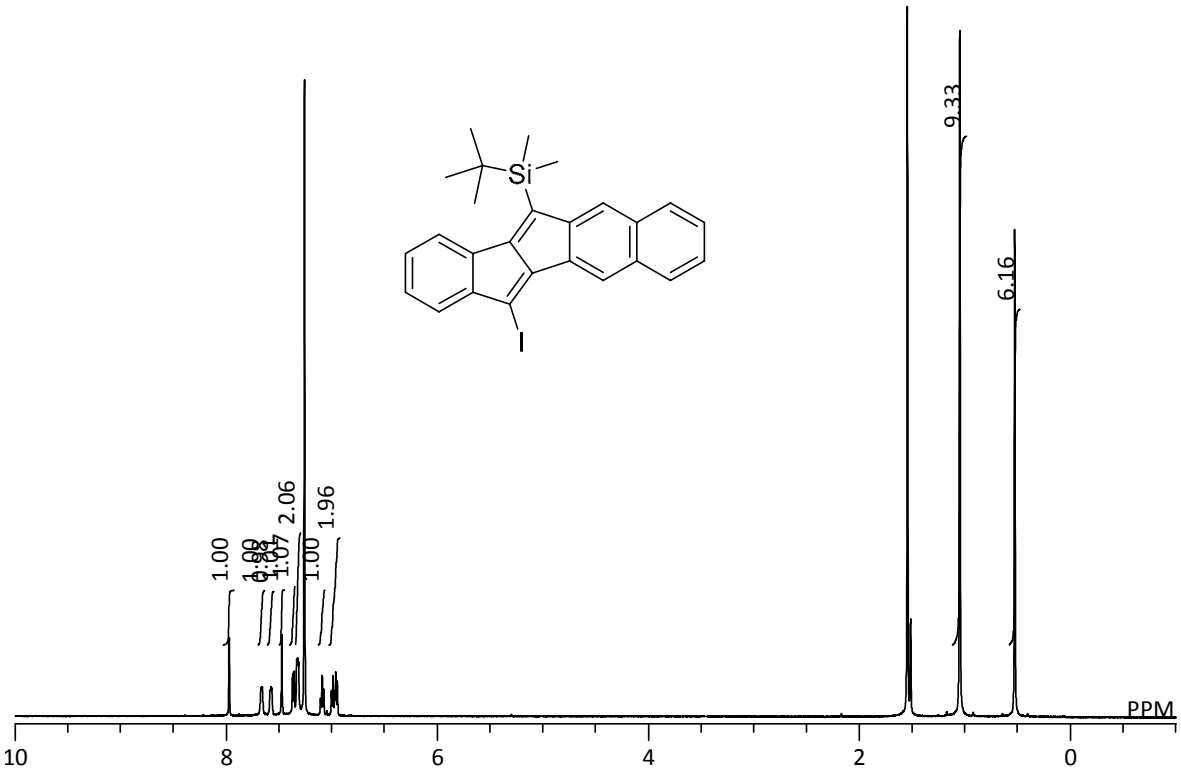


Fig. S64 ^{1}H NMR spectrum of **6** (500 MHz, $CDCl_3$).

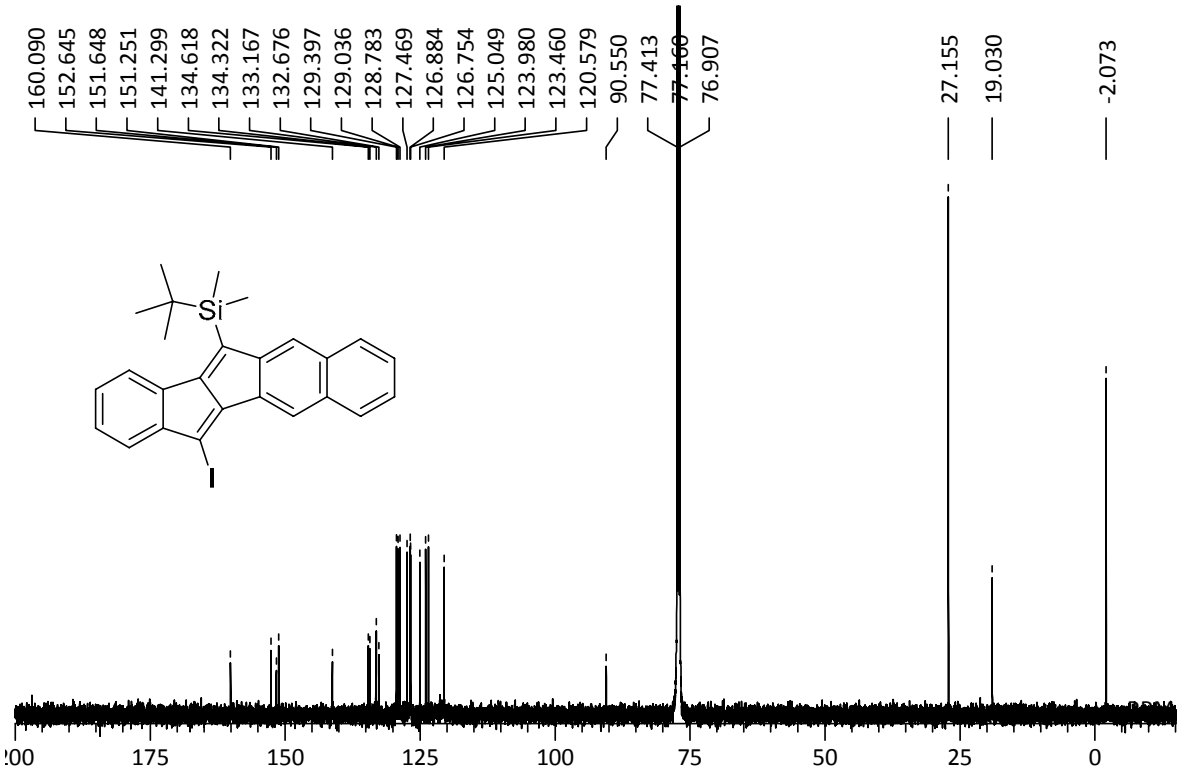


Fig. S65 ^{13}C NMR spectrum of **6** (126 MHz, $CDCl_3$).

7. X-ray Crystallographic Data

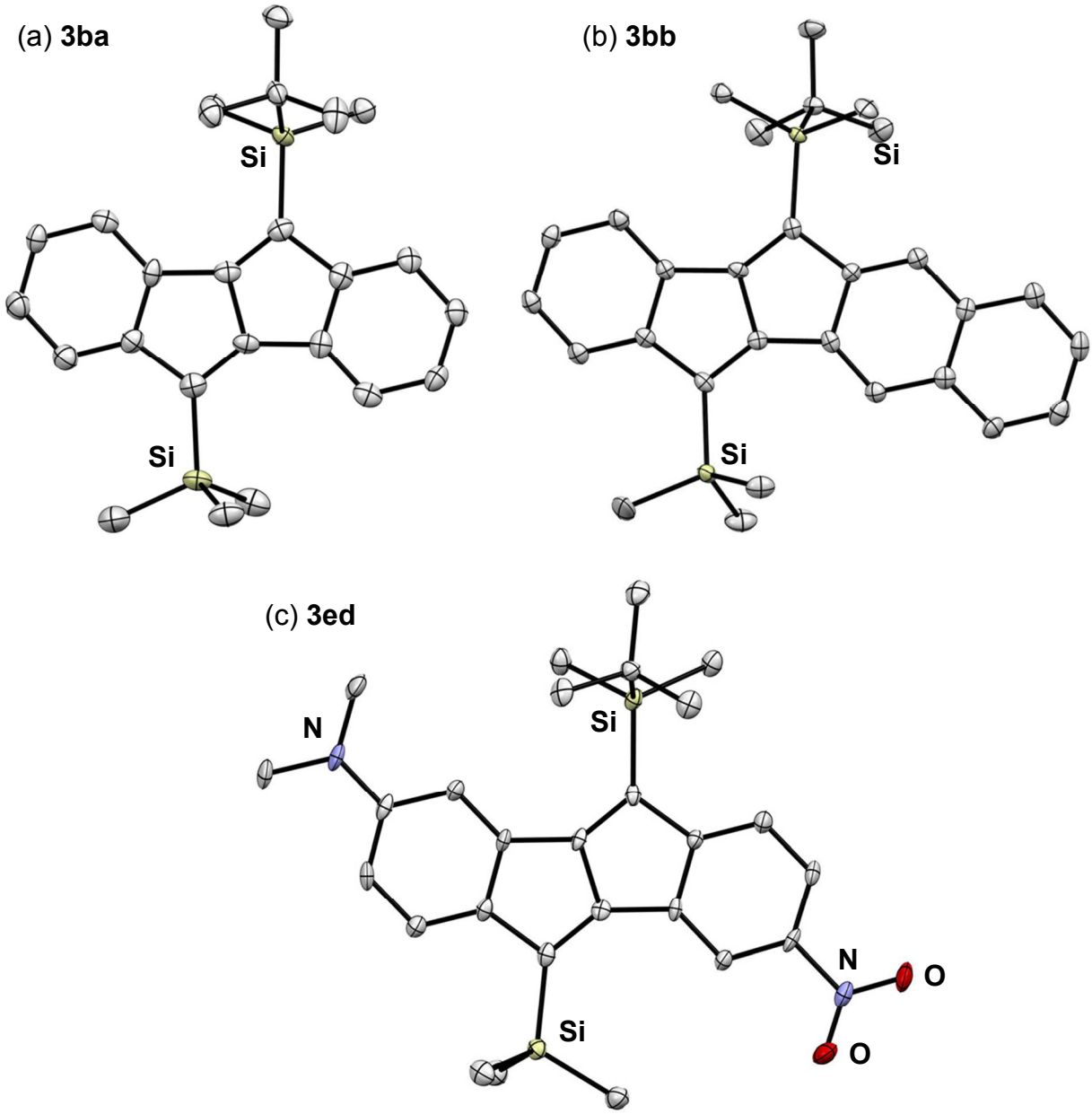


Fig. S66. X-ray structure of (a) **3ba** (b) **3bb** and (c) **3ed** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Table S10. Crystal data and structure refinement for **3ba**, **3bb**, and **3ed**.

Compound	**3ba**		**3bb**	
CCDC number	1511836		1511837	
Empirical formula	C25 H32 Si2		C29 H34 Si2	
Formula weight	388.68		438.74	
Temperature	93 K		93 K	
Wavelength	0.71075 Å		0.71075 Å	
Crystal system	Orthorhombic		Monoclinic	
Space group	*P*bca		$P2_1/c$	
Unit cell dimensions	a = 6.657(2) Å	α = 90°	a = 15.291(8) Å	α = 90°
	b = 34.537(13) Å	β = 90°	b = 11.701(6) Å	β = 93.057(7)°
	c = 19.811(8) Å	γ = 90°	c = 14.170(8) Å	γ = 90°
Volume	4555(3) Å^3		2532(2) Å^3	
Z	8		4	
Density (calculated)	1.134 Mg/m^3		1.151 Mg/m^3	
Absorption coefficient	0.163 mm^{-1}		0.154 mm^{-1}	
F(000)	1680		944	
Crystal size	0.30 x 0.15 x 0.03 mm^3		0.30 x 0.15 x 0.08 mm^3	
Theta range for data collection	1.564 to 25.496°		2.259 to 25.999°	
Index ranges	−8 <= h <= 8		−18 <= h <= 18	
	−40 <= k <= 41		−14 <= k <= 10	
	−22 <= l <= 23		−17 <= l <= 17	
Reflections collected	27767		17515	
Independent reflections	27767 [R(int) = 0.1158]		17515 [R(int) = 0.0924]	
Max. and min. transmission	1.000 and 0.751		1.000 and 0.336	
Data / restraints / parameters	4210 / 0 / 252		4952 / 0 / 288	
Goodness-of-fit on F^2	1.318		1.168	
Final R indices [I>2sigma(I)]	R_1 = 0.0987, wR_2 = 0.2249		R_1 = 0.0772, wR_2 = 0.1967	
R indices (all data)	R_1 = 0.1140, wR_2 = 0.2401		R_1 = 0.0922, wR_2 = 0.2171	
Max/min diff. peaks	0.457 and −0.591 e.Å^{-3}		0.580 and −0.603 e.Å^{-3}	

Compound	**3ed**	
CCDC Number	1511838	
Empirical formula	C27 H36 N2 O2 Si2	
Formula weight	476.76	
Temperature	93 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.221(3) Å	α = 110.915(10)°
	b = 11.790(5) Å	β = 93.663(16)°
	c = 16.389(9) Å	γ = 94.99(2)°
Volume	1291.6(10) Å	
Z	2	
Density (calculated)	1.226 Mg/m^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	512	
Crystal size	0.130 x 0.070 x 0.010 mm^3	
Theta range for data collection	1.855 to 25.997°	
Index ranges	−8 <= h <= 8	
	−14 <= k <= 11	
	−20 <= l <= 20	
Reflections collected	9281	
Independent reflections	9281 [R(int) = 0.0680]	
Max. and min. transmission	1.000 and 0.642	
Data / restraints / parameters	4927 / 0 / 308	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R_1 = 0.0765, wR_2 = 0.1805	
R indices (all data)	R_1 = 0.1298, wR_2 = 0.2282	
Max/min diff. peaks	0.843 and −0.590 e.Å^{-3}	