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SUPPORTING INFORMATION

Exploring C-C Bond Formation Reactions for Expanding Azulene Derivatives Linked at the 2- and/or 6-positions

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Apparatus

A Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz and an Agilent DD2 500 MHz were used to perform all NMR analyses. All peaks are reported on a ppm scale (δ), identified as m (multiplet), s (singlet), d (doublet), t (triplet) and dd (doublet of doublets). They are reported relatively to the residual solvent peak. The coupling constant (*J*) values are reported in hertz (Hz). HRMS (high-resolution mass spectroscopy) analyses were achieved on an Agilent 6210 TOF-LCMS instrument utilizing an ESI and APPI ion source (Agilent Technologies, Toronto, Canada). Absorption properties of the compounds were measured in a 1 cm path length quartz cells using a Cary 7000 spectrophotometer (Varian diode-array apparatus). A Solartron 1287 potentiostat was used to perform cyclic voltammetry. Platinum wires were used as electrodes at a scan rate of 50 mV s^{-1}. Ag/Ag^{+} (0.01 M $AgNO_3$ in dichloromethane) in an anhydrous and nitrogen-purged solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dry dichloromethane was used as the reference electrode. Microwave reactions were carried out in a Monowave 300 (Anton Paar) microwave synthesis reactor. Luzchem photochemical reactor equipped with 16 x 7.2 W low-pressure lamps (λ = 300 or 400 nm) was used to perform photochemical reactions in quartz standard reaction vessels or in quartz UV cells.

Chemicals

Chemical reagents were used as received and were ordered from Sigma–Aldrich Co. Canada, Oakwood Products Inc and A2B chem. Compounds **4** to **11** and **13** were synthesized as previously reported.[1–4]

Experimental Section

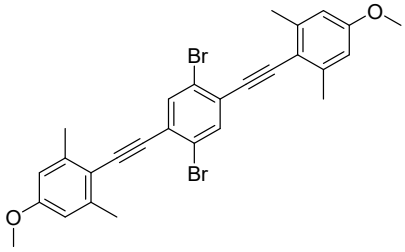
Table S1. Conditions and results of the different cyclization reactions used on azulene at positions 1 and 5.

Molecules	Type of reaction	Conditions	Yields
14	Photochemistry (Mallory)	0.002M in benzene, 1 eq I_2, 25 eq PPO, hν 300 nm, 96 h	No conversion[a)]
		0.002M in toluene, 2 eq I_2, hν 400 nm, 48 h	45% (**14**) Degradation
15		0.002M in benzene, 1 eq I_2, 25 eq PPO, hν 300 nm, 96 h	No conversion [a)]
		0.002M in toluene, 2 eq I_2, hν 400 nm, 48 h	5% (**15**) Degradation
16	Photochemistry/ Metal catalysis (CDHC)	0.002M in cyclohexane, hν 300 nm, 24 h	No conversion [a)b)]
		0.016M in DMF, 0.1 eq thioxanthone, hν 365 nm, 24 h	No conversion [a)b)]
		0.001M in decalin, hν 300 nm, 100 °C, 24 h	Degradation
		0.1 eq $PdCl_2(PCy_3)_2$, 6 eq DBU, DMF, 160 °C, 36 h	Trace
		0.8 eq $PdCl_2(PCy_3)_2$, 6 eq DBU, DMF, 190 °C, 6 h, microwave	21% (**24**)
17		0.002M in cyclohexane, hν 300 nm, 24 h	No conversion [a)b)]

		0.016M in DMF, 0.1 eq thioxanthone, hν 365 nm, 24 h	No conversion [a)b)]
		0.001M in decalin, hν 300 nm, 100 °C, 24 h	Degradation
		0.1 eq $PdCl_2(PCy_3)_2$, 6 eq DBU, DMF, 160 °C, 36 h	Trace
		0.8 eq $PdCl_2(PCy_3)_2$, 6 eq DBU, DMF, 190 °C, 6 h, microwave	8% (**25**)
18	Oxydant (Scholl)	5 eq DDQ, 5 eq $Sc(OTf)_3$, toluene, 50 °C, 24 h	Degradation
		1 eq DDQ, DCM/MSA 9/1, 0 °C, 2 h	No reaction
		5 eq $FeCl_3$, DCM, 0 °C, 1 h	30% (**26**) 12% (**18**)
19		5 eq DDQ, 5 eq $Sc(OTf)_3$, toluene, 50 °C, 24 h	Degradation
		1 eq DDQ, DCM/MSA 9/1, 0 °C, 2 h	No reaction
		5 eq $FeCl_3$, DCM, 0 °C, 1 h	Oligomere
20	Acid/Metal catalysis (Benzannulation)	2.2 eq TFA, DCM, 0 °C to rt, 1 h	5% (**27**)
		2.2 eq MSA, DCM, 0 °C to rt, 1 h	55% (**27**)
		0.02 eq $InCl_3$, 0.06 eq $AgNTf_2$, toluene, 100 °C, 24 h	79% (**27**)
		0.02 eq $PtCl_2$, toluene, 110 °C, 24 h	70% (**27**)
21		TFA	Degradation
		2.2 eq MSA, DCM, 0 °C to rt, 1 h	29% (**28**)
		0.02 eq $InCl_3$, 0.06 eq $AgNTf_2$, toluene, 100	Degradation

		°C, 24 h	
		10% $[RhCl_2(p\text{-cymene})]_2$, toluene, 100 °C, 24 h	No reaction
		0.02 eq $PtCl_2$, toluene, 110 °C, 24 h	36% (**28**)

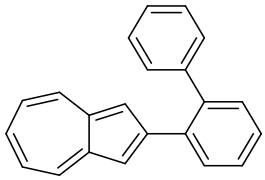
[a] Trace of product was identified in MS but was not observed in NMR spectroscopy and not isolated.
[b] Trace of dehalogenation compound was observed in MS but was not observed by NMR spectroscopy and was isolated.



Compound 12: A mixture consisting of **13** (0.758 g, 4.74 mmol), 1,4-dibromo-2,5-diiodobenzene (1.154 g, 2.37 mmol), $Pd(PPh_3)_2Cl_2$ (273 mg, 0.2 mmol), and CuI (90 mg, 0.4 mmol) was added to the dry and degassed flask filled with THF (30 mL) and triethylamine (10 mL). The reaction mixture was warm up to 60 °C and stirred for 48 hours. Afterward, the mixture was cooled to room temperature, and filtered through the pad of silica. The residue was diluted with AcOEt (50 mL). The mixture was subjected to washing with water and brine. The organic phase was dried using MgSO4, filtered, and evaporated under reduced pressure. The remaining residue was purified using silica gel column chromatography with a hexanes/DCM (9/1 to 5/5) solvent system. This purification process yielded the product (0.250 g, 19%) as a pale-yellow solid.

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.74 (s, 2H), 6.64 (s, 4H), 3.81 (s, 6H), 2.54 (s, 12H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 159.8, 142.8, 135.7, 126.6, 122.9, 114.5, 112.6, 94.9, 93.8, 55.2, 21.6.

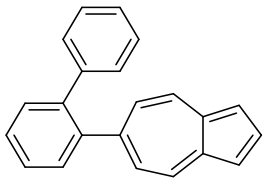


Compound 14: 2-Iodoazulene (200 mg, 0.79 mmol), 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (242 mg, 0.86 mmol), tris(dibenzylideneacetone) dipalladium(0) (36 mg, 0.04 mmol), lithium hydroxide monohydrate (264 mg, 6.3 mmol), SPhos (65 mg, 0.16 mmol) and a nitrogen-purged mixture of THF/H_2O (4/1 mL) were added to a screw-capped pressure vessel under nitrogen. The mixture was purged three times with nitrogen and heated at 70 °C for 24 h. After cooling at room temperature, the reaction mixture was extracted with ethyl acetate and the combined organic layers were washed with NH_4Cl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a blue solid (204 mg, 92 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.12 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.51–7.42 (m, 2H), 7.30–7.22 (m, 2H), 7.13–7.04 (m, 2H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 151.0, 142.1, 141.5, 140.3, 136.4, 136.3, 136.0, 131.6, 131.0, 130.0, 128.1, 127.9, 127.8, 126.9, 123.3, 118.5.

HRMS (ESI+): $C_{22}H_{16}$ $[M+H]^+$ 280.1247; found, 280.1247.

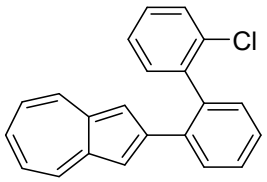


Compound 15: The procedure for the synthesis of compound **14** was followed with 6-bromoazulene (200 mg, 0.96 mmol), 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (298 mg, 1.06 mmol), tris(dibenzylideneacetone) dipalladium(0) (44 mg, 0.05 mmol), lithium hydroxide monohydrate (324 mg, 7.7 mmol) and SPhos (79 mg, 0.2 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a purple solid (247 mg, 89 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.18 (d, *J* = 10.5 Hz, 2H), 7.86 (t, *J* = 3.7 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.33 (d, *J* = 3.7 Hz, 2H), 7.17 (dt, *J* = 5.1, 2.5 Hz, 5H), 7.09 (d, *J* = 10.4 Hz, 2H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 151.5, 144.0, 140.9, 140.5, 138.9, 136.7, 135.3, 130.9, 130.7, 129.9, 128.1, 128.0, 127.4, 126.6, 125.8, 118.0.

HRMS (ESI+): $C_{22}H_{16}$ $[M+H]^+$ 280.1247; found, 280.1247.

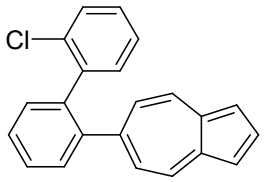


Compound 16: The procedure for the synthesis of compound **14** was followed with 2-iodoazulene (200 mg, 0.79 mmol), 2-(2'-chloro-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (272 mg, 0.86 mmol), tris(dibenzylideneacetone) dipalladium(0) (36 mg, 0.04 mmol), lithium hydroxide monohydrate (264 mg, 6.3 mmol) and SPhos (65 mg, 0.16 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a blue solid (220 mg, 89 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.12 (dd, *J* = 10.0, 0.9 Hz, 1H), 7.86 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.50 – 7.43 (m, 1H), 7.40 (dddd, *J* = 7.6, 2.7, 1.4, 0.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.21 (ddd, *J* = 7.7, 7.0, 1.3 Hz, 1H), 7.11 – 7.05 (m, 1H).

^{13}C NMR (126 MHz, $cdcl_3$) δ 150.3, 141.1, 140.3, 138.7, 136.7, 136.5, 136.2, 133.8, 132.2, 131.2, 130.9, 129.6, 128.7, 128.4, 127.5, 126.7, 123.3, 117.8.

HRMS (ESI+): $C_{22}H_{15}Cl$ $[M+H]^+$ 314.0857; found, 314.0857.

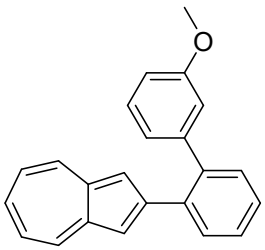


Compound 17: The procedure for the synthesis of compound **14** was followed with 6-bromoazulene (200 mg, 0.96 mmol), 2-(2'-chloro-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (334 mg, 1.06 mmol), tris(dibenzylideneacetone) dipalladium(0) (44 mg, 0.05 mmol), lithium hydroxide monohydrate (324 mg, 7.7 mmol) and SPhos (79 mg, 0.19 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a blue solid (147 mg, 65 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.20 (d, *J* = 10.5 Hz, 1H), 7.88 (t, *J* = 3.7 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.44 (dd, *J* = 6.2, 2.3 Hz, 1H), 7.34 (d, *J* = 3.7 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.09 – 7.03 (m, 1H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 150.7, 144.9, 139.9, 139.0, 137.9, 136.8, 135.2, 133.3, 132.2, 131.0, 130.3, 129.5, 128.5, 128.1, 127.4, 126.3, 125.3, 118.0.

HRMS (ESI+): $C_{22}H_{15}Cl$ $[M+H]^+$ 314.0857; found, 314.0857.

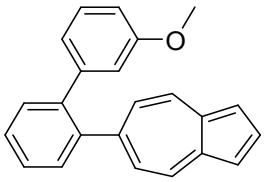


Compound 18: The procedure for the synthesis of compound **14** was followed with 2-iodoazulene (100 mg, 0.4 mmol), 2-(3'-methoxy-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (122 mg, 0.4 mmol), tris(dibenzylideneacetone) dipalladium(0) (18 mg, 0.02 mmol), lithium hydroxide monohydrate (132 mg, 3.1 mmol) and SPhos (32 mg, 0.08 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a purple solid (103 mg, 84 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.13 (d, *J* = 9.1 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.13 (s, 1H), 7.08 (t, *J* = 9.8 Hz, 1H), 6.84 – 6.78 (m, 1H), 3.62 (s, 2H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 159.4, 150.9, 143.5, 141.3, 140.3, 136.4, 136.3, 136.0, 131.5, 130.9, 129.1, 127.8, 123.2, 122.7, 118.4, 115.3, 112.9, 55.2.

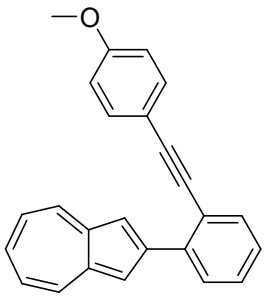
HRMS (ESI+): $C_{23}H_{18}O$ $[M+H]^+$ 310.1352; found, 310.1352.



Compound 19: The procedure for the synthesis of compound **14** was followed with 6-bromoazulene (200 mg, 0.96 mmol), 2-(3'-methoxy-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (300 mg, 0.96 mmol), tris(dibenzylideneacetone) dipalladium(0) (44 mg, 0.05 mmol), lithium hydroxide monohydrate (324 mg, 7.7 mmol) and SPhos (79 mg, 0.19 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a purple solid (280 mg, 93 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.20 (d, *J* = 10.5 Hz, 1H), 7.86 (t, *J* = 3.7 Hz, 1H), 7.53 – 7.43 (m, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.08 (dd, *J* = 17.8, 9.5 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.70 (ddd, *J* = 8.3, 2.4, 1.0 Hz, 1H), 3.55 (s, 1H).

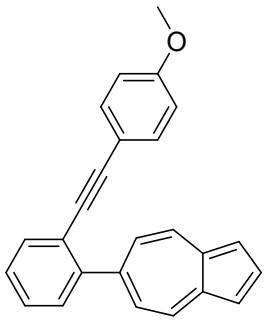
^{13}C NMR (101 MHz, chloroform-*d*) δ 159.3, 151.6, 144.3, 142.5, 140.5, 139.1, 136.9, 135.5, 131.0, 130.7, 129.2, 128.1, 127.6, 125.8, 122.7, 118.2, 115.5, 112.7, 55.2. HRMS (ESI+): $C_{23}H_{18}O$ $[M+H]^+$ 310.1352; found, 310.1352.



Compound 20: The procedure for the synthesis of compound **14** was followed with 2-(azulen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (276 mg, 1.1 mmol), 1-bromo-2-((4-methoxyphenyl)ethynyl)benzene (122 mg, 1.1 mmol), tris(dibenzylideneacetone) dipalladium(0) (50 mg, 0.05 mmol), lithium hydroxide monohydrate (365 mg, 8.7 mmol) and SPhos (89 mg, 0.22 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a blue solid (167 mg, 46 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.35 (d, *J* = 9.4 Hz, 1H), 7.95 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 9.8 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.34 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.18 (t, *J* = 9.8 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 3.83 (s, 1H).

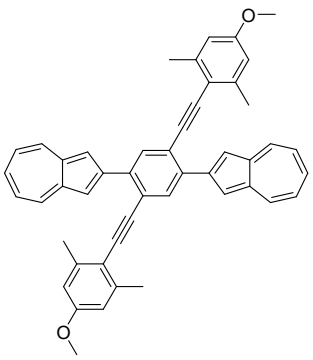
^{13}C NMR (101 MHz, chloroform-*d*) δ 159.6, 149.5, 140.4, 138.5, 136.7, 136.3, 133.5, 132.8, 130.3, 128.3, 127.4, 123.4, 122.2, 117.9, 115.8, 114.0, 92.5, 89.1, 55.3. HRMS (ESI+): $C_{25}H_{18}O$ $[M+H]^+$ 334.1352; found, 334.1352.



Compound 21: The procedure for the synthesis of compound **14** was followed with 2-(azulen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (325 mg, 1.27 mmol), 1-bromo-2-((4-methoxyphenyl)ethynyl)benzene (367 mg, 1.27 mmol), tris(dibenzylideneacetone) dipalladium(0) (59 mg, 0.06 mmol), lithium hydroxide monohydrate (429 mg, 10 mmol) and SPhos (105 mg, 0.25 mmol). The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a purple solid (376 mg, 88 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.42 (d, *J* = 10.5 Hz, 1H), 7.94 (t, *J* = 3.7 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.50 – 7.35 (m, 2H), 7.16 (d, *J* = 8.9 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 1H), 3.76 (s, 1H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 159.6, 150.2, 147.1, 139.4, 137.0, 135.4, 132.9, 132.6, 129.8, 128.0, 127.6, 125.2, 122.2, 118.1, 115.2, 113.9, 93.2, 87.5, 55.3. HRMS (ESI+): $C_{25}H_{18}O$ $[M+H]^+$ 334.1352; found, 335.1422.

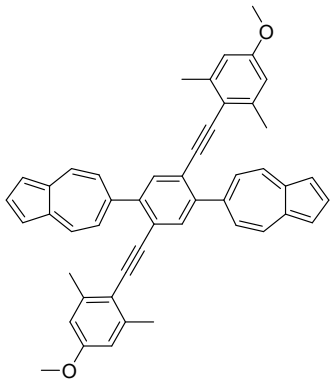


Compound 22: The procedure for the synthesis of compound **14** was followed with 2-(azulen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (267 mg, 1.05 mmol), 2,2'-((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(5-methoxy-1,3-dimethylbenzene) (290 mg, 0.52 mmol), tris(dibenzylideneacetone) dipalladium(0) (24 mg, 0.03 mmol), lithium hydroxide monohydrate (176 mg, 4.2 mmol) and SPhos (43 mg, 0.10 mmol). After cooling to room temperature, the reaction mixture was washed with NH4Cl, and the product precipitated upon the addition of ethyl acetate for extraction. The combined organic layers containing the crude product were filtered to afford the desired compound as a green solid. (291 mg, 86 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.34 (d, *J* = 9.1 Hz, 1H), 8.10 (s, 1H), 7.98 (s, 1H), 7.57 (t, *J* = 9.9 Hz, 1H), 7.19 (t, *J* = 9.8 Hz, 1H), 6.60 (s, 1H), 3.79 (s, 1H), 2.44 (s, 2H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 159.2, 148.6, 142.5, 140.4, 137.0, 136.9, 136.5, 135.6, 123.5, 122.6, 117.8, 115.6, 112.5, 96.7, 92.2, 55.2, 21.5.

HRMS (ESI+): $C_{48}H_{38}O_2$ $[M+H]^+$ 646.2867; found, 646.2866.

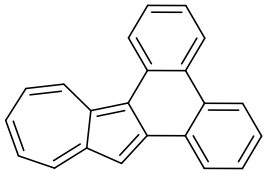


Compound 23: The procedure for the synthesis of compound **14** was followed with 2-(azulen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (156 mg, 0.61 mmol), 2,2'-((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(5-methoxy-1,3-dimethylbenzene) (290 mg, 0.30 mmol), tris(dibenzylideneacetone) dipalladium(0) (14 mg, 0.02 mmol), lithium hydroxide monohydrate (103 mg, 2.5 mmol) and SPhos (25 mg, 0.06 mmol). After cooling to room temperature, the reaction mixture was washed with NH4Cl, and the product precipitated upon the addition of ethyl acetate for extraction. The combined organic layers containing the crude product were filtered to afford the desired compound as a green solid. (166 mg, 83 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.42 (d, *J* = 10.0 Hz, 1H), 7.96 (t, *J* = 3.6 Hz, 1H), 7.71 (s, 1H), 7.45 (t, *J* = 6.8 Hz, 1H), 6.45 (s, 1H), 3.71 (s, 1H), 2.05 (s, 1H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 159.2, 149.4, 146.0, 142.3, 139.5, 137.3, 135.7, 133.3, 124.7, 122.2, 118.4, 115.0, 112.3, 95.1, 93.0, 55.0, 21.0.

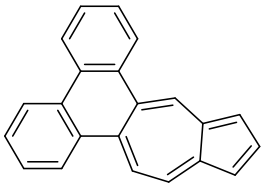
HRMS (ESI+): $C_{48}H_{38}O_2$ $[M+H]^+$ 646.2867; found, 646.2866.



Compound 24: 2-([1,1'-biphenyl]-2-yl)azulene (33 mg, 0.1 mmol), $PdCl_2(PCy_3)_2$ (62 mg, 0.08 mmol), DBU (0.094 mL, 0.6 mmol) and nitrogen-purged DMF (5 mL) were added to a vial adapted for the microwave reactor under nitrogen. The mixture was heated at 190 °C for 6 h. After cooling to room temperature, the reaction was extracted with Et_2O and the combined organic layers were washed with brine, water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 3/1 as the eluent) to afford the desired compound as a green solid (6 mg, 21 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 9.40 (d, *J* = 9.4 Hz, 1H), 8.99 (d, *J* = 8.2 Hz, 1H), 8.80 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 7.4 Hz, 1H), 8.62 (d, *J* = 7.3 Hz, 1H), 8.51 (d, *J* = 10.1 Hz, 1H), 8.14 (s, 1H), 7.78 – 7.70 (m, 3H), 7.70 – 7.65 (m, 1H), 7.64 – 7.59 (m, 1H), 7.43 (t, *J* = 9.9 Hz, 1H), 7.27 (t, *J* = 9.6 Hz, 2H).

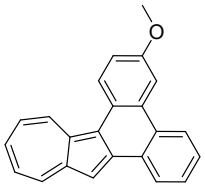
^{13}C NMR (101 MHz, chloroform-*d*) δ 142.8 (s), 141.0 (s), 138.0 (s), 136.8 (s), 136.5 (s), 134.6 (s), 131.3 (s), 130.6 (s), 129.1 (s), 128.1 (s), 128.0 (s), 127.6 (s), 126.9 (s), 125.7 (s), 124.6 (s), 124.6 (s), 124.4 (s), 124.2 (s), 123.6 (s), 123.5 (s), 120.7 (s), 112.4 (s). HRMS (ESI+): $C_{22}H_{14}$ $[M+H]^+$ 278.1096; found, 278.1096.



Compound 25: 2-([1,1'-biphenyl]-2-yl)azulene (74 mg, 0.24 mmol), $PdCl_2(PCy_3)_2$ (138 mg, 0.19 mmol), DBU (0.213 mL, 1.44 mmol) and nitrogen-purged DMF (5 mL) were added to a vial adapted for the microwave reactor under nitrogen. The mixture was heated at 190 °C for 6 h. After cooling down to room temperature, the reaction mixture was extracted with Et_2O and the combined organic layers were washed with brine, water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 4/1 as the eluent) to afford the desired compound as a blue solid (5 mg, 8 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.17 (d, *J* = 10.5 Hz, 1H), 7.85 (t, *J* = 3.7 Hz, 1H), 7.51 (dddd, *J* = 13.9, 9.0, 6.3, 3.2 Hz, 2H), 7.41 (ddd, *J* = 7.0, 4.4, 3.4 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.10 (d, *J* = 10.5 Hz, 2H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 150.72 (s), 144.8 (s), 139.8 (s), 139.0 (s), 137.9 (s), 136.8 (s), 135.4 (s), 135.2 (s), 132.2 (s), 131.0 (s), 130.3 (s), 129.9 (s), 129.4 (s), 129.0 (s), 128.5 (s), 128.0 (s), 127.4 (s), 126.3 (s), 125.8 (s), 125.3 (s), 118.0 (s), 117.9 (s). HRMS (APPI+): $C_{22}H_{14}$ $[M+H]^+$ 278.1096; found, 278.1096.

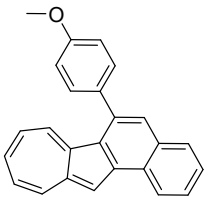


Compound 26: 2-(3'-methoxy-[1,1'-biphenyl]-2-yl)azulene (50 mg, 0.16 mmol), $FeCl_3$ (131 mg, 0.8 mmol) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen, cooled to 0 °C for and stirred for 1 h. After warming at room temperature, the reaction was quenched with MeOH, extracted with dichloromethane and the combined organic layers were washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by

column chromatography (silica gel, hexanes/dichloromethane 5/5 as the eluent) to afford the desired compound as a blue solid (15 mg, 30 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.19 (d, J = 9.4 Hz, 1H), 7.39 (t, J = 9.8 Hz, 1H), 7.29 (s, 1H), 7.12 (td, J = 7.5, 1.3 Hz, 2H), 7.06 (t, J = 9.6 Hz, 1H), 6.96 (dd, J = 7.6, 1.1 Hz, 1H), 6.90 (td, J = 7.5, 1.3 Hz, 1H), 6.64 (t, J = 9.7 Hz, 1H), 6.62 (dd, J = 7.7, 1.2 Hz, 1H), 6.45 (t, J = 7.9 Hz, 1H), 6.09 (d, J = 6.3 Hz, 1H), 5.92 (s, 1H), 5.87 (d, J = 7.6 Hz, 1H), 3.33 (s, 3H). The extra peak for a proton couldn't be identified. The mass spectrometry and the ^{13}C NMR analysis confirm the structure of the expected product.

^{13}C NMR (126 MHz, chloroform-*d*) δ 158.1 (s), 151.3 (s), 143.1 (s), 140.3 (s), 140.2 (s), 137.9 (s), 136.4 (s), 136.2 (s), 135.9 (s), 135.0 (s), 131.5 (s), 129.8 (s), 127.4 (s), 127.1 (s), 126.7 (s), 124.2 (s), 123.0 (s), 122.5 (s), 121.4 (s), 119.3 (s), 113.4 (s), 112.0 (s), 54.5 (s). HRMS (APPI+): $C_{23}H_{16}O$ $[M+H]^+$ 308.1196; found, 308.1196.



Compound 27. Method A (MSA as the Bronsted acid). 2-(2-((4-methoxyphenyl)ethynyl)phenyl)azulene (42 mg, 0.13 mmol) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cool down to 0 °C before methanesulfonic acid (MSA) (0.018 mL, 0.28 mmol) was added dropwise. Mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with $NaHCO_3$, extracted with dichloromethane and the combined organic layers were washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography

(silica gel, hexanes/dichloromethane 7/3 as the eluent) to afford the desired compound as a green solid (23 mg, 55 %).

Method B (TFA as the Bronsted acid).: 2-(2-((4-methoxyphenyl)ethynyl)phenyl)azulene (42 mg, 0.13 mmol) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cooled to 0 °C before TFA (0.021 mL, 0.28 mmol) was added dropwise. The mixture was allowed to warm at room temperature and stirred for 1 h. The reaction was quenched with $NaHCO_3$, extracted with dichloromethane and combined organic layers were washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 7/3 as the eluent) to afford the desired compound as a green solid (2 mg, 5 %).

Method C ($InCl_3$ as the catalyst): 2-(2-((4-methoxyphenyl)ethynyl)phenyl)azulene (42 mg, 0.13 mmol), $InCl_3$ (5 mg, 0.02 mmol), $AgNTf_2$ (3 mg, 0.008 mmol) and nitrogen-purged toluene (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen, warm to 100 °C and stirred for 16 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 7/3 as the eluent) to afford the desired compound as a green solid (33 mg, 79 %).

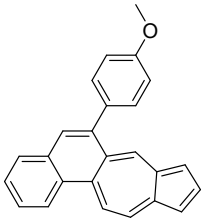
Method D ($PtCl_2$ as the catalyst): 2-(2-((4-methoxyphenyl)ethynyl)phenyl)azulene (119 mg, 0.35 mmol), $PtCl_2$ (19 mg, 0.07 mmol) and nitrogen-purged toluene (20 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen, warmed to 110

°C and stirred for 16 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 4/1 as the eluent) to afford the desired compound as a green solid (83 mg, 70 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.65 (dd, *J* = 6.2, 3.1 Hz, 1H), 8.40 (d, *J* = 10.1 Hz, 1H), 8.17 (s, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.00 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.57 – 7.52 (m, 1H), 7.48 – 7.39 (m, 1H), 7.11 (dd, *J* = 12.5, 5.9 Hz, 1H), 6.97 – 6.90 (m, 1H), 3.96 (s, 1H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 159.1, 142.2, 142.2, 139.9, 138.6, 137.1, 136.7, 136.0, 135.9, 134.6, 133.9, 133.0, 130.3, 128.1, 127.2, 126.8, 126.1, 125.6, 124.8, 124.8, 124.7, 124.4, 123.3, 114.1, 112.8, 55.4.

HRMS (ESI+): $C_{25}H_{18}O$ $[M+H]^+$ 334.1253; found, 334.1352.



Compound 28. Method A (MSA as the Bronsted acid): 6-(2-((4-methoxyphenyl)ethynyl)phenyl)azulene (41 mg, 0.12 mmol) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cooled to 0 °C before MSA (0.02 mL, 0.28 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with $NaHCO_3$, extracted with dichloromethane and the combined organic layers were washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure.

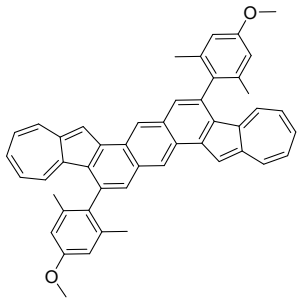
The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 2/8 as the eluent) to afford the desired compound as a green solid (12 mg, 29 %).

Method B ($PtCl_2$ as the catalyst). 6-(2-((4-methoxyphenyl)ethynyl)phenyl)azulene (50 mg, 0.15 mmol), $PtCl_2$ (8 mg, 0.03 mmol) and nitrogen-purged toluene (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen, warmed to 100 °C and stirred for 16 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 4/1 as the eluent) to afford the desired compound as a green solid (18 mg, 36 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.95 (s, 1H), 8.87 (d, *J* = 9.5 Hz, 1H), 8.59 (d, *J* = 11.7 Hz, 1H), 8.31 (d, *J* = 11.6 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.81 (s, 1H), 7.76 – 7.65 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.40 (s, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 3.96 (s, 1H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 159.1 (s), 142.8 (s), 140.5 (s), 139.0 (s), 137.0 (s), 135.5 (s), 134.8 (s), 134.6 (s), 133.5 (s), 132.0 (s), 131.4 (s), 131.4 (s), 128.8 (s), 128.6 (s), 128.2 (s), 128.0 (s), 126.8 (s), 124.9 (s), 120.6 (s), 120.0 (s), 118.7 (s), 113.9 (s), 55.4 (s).

HRMS (ESI+): $C_{25}H_{18}O$ $[M+H]^+$ 334.1253; found, 334.1352.

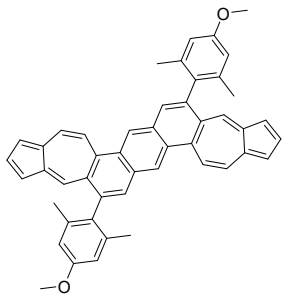


Compound AzuPAH-1. Method A (MSA as the Bronsted acid): 2,2'-(2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)-1,4-phenylene)diazulene (40 mg, 0.06 mmol) and nitrogen-purged

dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cool to 0 °C. MSA (0.021 mL, 0.32 mmol) was added dropwise and the mixture was allowed to warm at room temperature for 24 h. The reaction was quenched with a solution of $NaHCO_3$ and the precipitate was filtered, rinse with water and dried to provide the desired compound as a green powder. (30 mg, 75 %).

Method B ($InCl_3$ as the catalyst): 2,2'-(2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)-1,4-phenylene)diazulene (50 mg, 0.08 mmol), $InCl_3$ (7 mg, 0.003 mmol), $AgNTf_2$ (3.6 mg, 0.009 mmol) and nitrogen-purged toluene (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and warm to 100 °C for 16 h. The reaction was filtered, rinse with water and dried to provide the desired compound as a green solid (41 mg, 82 %).

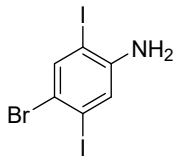
Method C ($PtCl_2$ as the catalyst): 2,2'-(2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)-1,4-phenylene)diazulene (31 mg, 0.05 mmol), $PtCl_2$ (2 mg, 0.008 mmol) and nitrogen-purged toluene (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen, warm to 100 °C and stirred for 48 h. The reaction mixture was cooled to room temperature and filtered, rinse with water and dried to afford the desired compound as a green solid (11 mg, 36 %). The ^{13}C NMR spectrum could not be obtained due to its low solubility.
^1H NMR (400 MHz, chloroform-*d*) δ 9.32 (s, 1H), 8.53 (d, *J* = 10.6 Hz, 1H), 8.43 (s, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.77 (s, 1H), 7.51 (d, *J* = 6.6 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.03 – 6.94 (m, 1H), 6.88 (s, 1H), 3.97 (s, 1H), 2.05 (s, 2H). HRMS (APPI+): $C_{48}H_{38}O_2$ $[M+H]^+$ 646.2866; found, 647.2936.



Compound AzuPAH-2: Method A (MSA as the Bronsted acid): 6,6'-(2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)-1,4-phenylene)diazulene (29 mg, 0.05 mmol) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cool to 0 °C. MSA (0.012 mL, 0.18 mmol) was added dropwise and the mixture was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with a solution of $NaHCO_3$ and the precipitate was filtered, rinse with water and dried to provide the desired compound as a green powder (2.5 mg, 9 %).

Method B ($PtCl_2$ as the catalyst): 6,6'-(2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)-1,4-phenylene)diazulene (30 mg, 0.05 mmol), $PtCl_2$ (2 mg, 0.008 mmol) and nitrogen-purged toluene (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and warm to 100 °C for 48 h. The reaction mixture was filtered, rinse with water and dried to afford the desired compound as a green solid (20 mg, 67 %). The ^{13}C NMR spectrum could not be obtained due to its low solubility.

^1H NMR (400 MHz, chloroform-*d*) δ 9.37 (s, 1H), 8.84 (d, *J* = 11.7 Hz, 1H), 8.63 (s, 1H), 8.46 (d, *J* = 11.2 Hz, 1H), 7.95 (s, 1H), 7.87 – 7.79 (m, 1H), 7.46 (s, 1H), 6.86 (s, 1H), 3.96 (s, 1H), 2.05 (s, 1H). HRMS (APPI+): $C_{48}H_{38}O_2$ $[M+H]^+$ 646.2866; found, 647.2943.

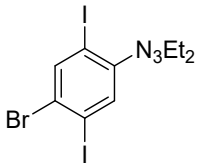


Compound 29: 4-bromo-3-iodoaniline (2.00 g, 6.7 mmol) and nitrogen-purged acetonitrile (20 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and *N*-iodosuccinimide (1.66 g, 7.4 mmol), trimethylsilyl chloride (0.09 mL, 0.68 mmol) were added. The reaction mixture was stirred for 24 h at room temperature before it was extracted with ethyl acetate. The combined organic layers were washed with a solution of $Na_2S_2O_3$, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 10/1 as the eluent) to afford the desired compound as a brown solid (1.30 g, 44 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79, 7.22.

^{13}C NMR (101 MHz, chloroform-*d*) δ 146.8, 140.6, 124.5, 117.4, 101.1, 83.7.

HRMS (APPI+): $C_6H_4BrI_2N$ $[M+H]^+$ 422.7611; found, 422.7611.



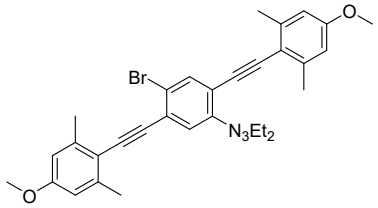
Compound 30: 4-bromo-2,5-diiodoaniline (1.125 g, 2.65 mmol) and nitrogen-purged THF (50 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cool to -5 °C before boron trifluoride etherate (0.655 mL, 5.3 mmol) was added slowly, followed by *tert*-butyl nitrite (0.631 mL, 5.3 mmol). The reaction mixture was stirred at -5 °C for 1.5 h and diethylamine (2.20 mL, 21 mmol) and K_2CO_3 (2.57 g, 18 mmol) were added. The reaction mixture was stirred for 2 h at 0 °C and poured in water. The resulting mixture was

extracted with ethyl acetate and the combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 9/1 as the eluent) to afford the desired compound as an off-white solid (1.046 g, 78 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 8.02 (s, 1H), 7.78 (s, 1H), 3.80 (dq, *J* = 13.9, 7.1 Hz, 4H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 150.1, 141.0, 128.0, 125.3, 101.0, 96.3, 49.6, 42.5, 14.5, 10.9.

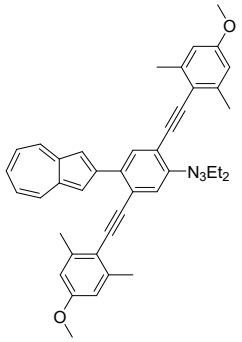
HRMS (APPI+): $C_{10}H_{12}BrI_2N_3$ $[M+H]^+$ 506.8299; found, 506.8298.



Compound 31: (Z)-1-(4-bromo-2,5-diiodophenyl)-3,3-diethyltriaz-1-ene (**30**) (100 mg, 0.2 mmol), 2-ethynyl-5-methoxy-1,3-dimethylbenzene (73 mg, 0.45 mmol), bis(triphenylphosphine)palladium(II) dichloride (14 mg, 0.02 mmol), copper(I) iodide (2 mg, 0.01 mmol) and a nitrogen-purged mixture of toluene and triethylamine 1/1 (8 mL) were added to a screw-capped pressure vessel under nitrogen. The mixture was purged three times with nitrogen, heated to 90 °C and stirred for 24 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and the combined organic layers were washed with brine, water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 8/2 as the eluent) to afford the desired compound as a yellow solid (69 mg, 61 %).

^{1}H NMR (500 MHz, chloroform-*d*) δ 7.75 (s, 1H), 7.63 (s, 1H), 6.63 (d, *J* = 4.4 Hz, 4H), 3.84 (d, *J* = 6.7 Hz, 4H), 3.81 (s, 3H), 3.80 (s, 3H), 2.56 (s, 5H), 2.53 (s, 6H), 1.28 (t, *J* = 28.6 Hz, 9H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 159.4, 159.1, 150.4, 142.6, 142.1, 135.9, 125.6, 120.9, 119.9, 119.6, 115.8, 115.2, 112.5, 112.4, 95.4, 93.8, 93.5, 92.6, 55.2, 55.2, 49.0, 41.3, 29.8, 21.7, 21.5, 19.2, 14.5, 11.2.

HRMS (ESI+): $C_{32}H_{34}BrN_3O_2$ $[M+H]^+$ 571.1828; found, 572.1861.

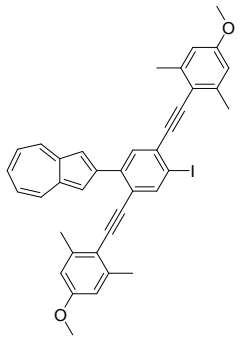


Compound 32: 2-(azulen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**31**) (329 mg, 1.29 mmol), 1-(4-bromo-2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)phenyl)-3,3-diethyltriaz-1-ene (741 mg, 1.29 mmol), tris(dibenzylideneacetone) dipalladium(0) (59 mg, 0.06 mmol), lithium hydroxide monohydrate (434 mg, 10 mmol), SPhos (106 mg, 0.26 mmol) and a nitrogen-purged mixture of THF and H_2O 4/1 (20 mL) were added to a screw-capped pressure vessel under nitrogen. The mixture was purged three times with nitrogen, heated to 70 °C and stirred for 24 h. After cooling to room temperature, the reaction was extracted with ethyl acetate and the combined organic layers were washed with NH_4Cl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 8/2 as the eluent) to afford the desired compound as a green solid (629 mg, 91 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 8.29 (d, J = 9.2 Hz, 1H), 7.95 (d, J = 6.4 Hz, 1H), 7.81 (s, 1H), 7.52 (t, J = 9.9 Hz, 1H), 7.16 (t, J = 9.8 Hz, 1H), 6.64 (s, 1H), 6.59 (s, 1H), 3.88 (d, J = 6.5 Hz, 1H), 3.81 (s, 1H), 3.79 (s, 1H), 2.57 (s, 1H), 2.43 (s, 1H), 1.31 (d, J = 38.2 Hz, 1H).

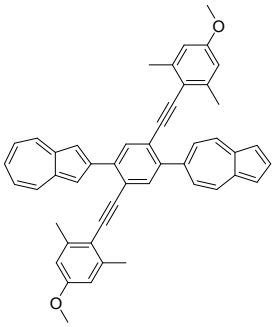
^{13}C NMR (101 MHz, chloroform-*d*) δ 159.0, 158.9, 150.4, 149.1, 142.4, 142.0, 140.3, 136.3, 135.9, 134.8, 134.4, 123.3, 122.7, 122.1, 119.1, 117.6, 116.2, 115.8, 112.4, 112.3, 97.2, 95.0, 92.4, 91.4, 77.3, 77.0, 76.7, 55.1, 49.0, 41.3, 21.5, 21.5, 14.4, 11.2.

HRMS (ESI+): $C_{42}H_{41}N_3O_2$ $[M+H]^+$ 619.3193; found, 619.3041.



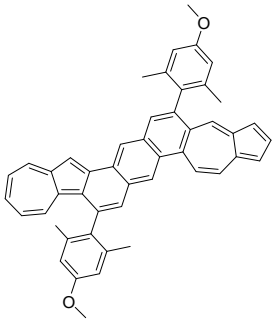
Compound 33. (E)-1-(4-(azulen-2-yl)-2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)phenyl)-3,3-diethyltriaz-1-ene (**32**) (364 mg, 0.59 mmol) and nitrogen-purged methyl iodide (6 mL, 96 mmol) were added to a screw-capped pressure vessel under nitrogen. The mixture was purged three times with nitrogen, heated to 120 °C and stirred for 4 h. After cooling to room temperature, the solvent was removed under reduced pressure and the crude product was used without further purification.

HRMS (APPI+): $C_{38}H_{31}IO_2$ $[M+H]^+$ 646.1362; found, 647.1433.



Compound 34. 2-(4-iodo-2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)phenyl)azulene (**33**) (453 mg, 0.7 mmol), 2-(azulen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (162 mg, 0.6 mmol), tris(dibenzylideneacetone) dipalladium(0) (32 mg, 0.04 mmol), lithium hydroxide monohydrate (235 mg, 5.6 mmol), SPhos (58 mg, 0.14 mmol) and a nitrogen-purged mixture of THF/H_2O 4/1 (25 mL) were added to a screw-capped pressure vessel under nitrogen. The mixture was purged three times with nitrogen, heated to 70 °C and stirred for 24 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and the combined organic layers were washed with NH_4Cl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was used without further purification.

HRMS (APPI+): $C_{48}H_{38}O_2$ $[M+H]^+$ 646.2866; found, 646.2863.



Compound AzuPAH-3: Method A (MSA as the Bronsted acid): 2-(4-(azulen-6-yl)-2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)phenyl)azulene (**34**) (30 mg, 0.05 mmol) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The

mixture was purged three times with nitrogen and cool to 0 °C. MSA (0.013 mL, 0.2 mmol) was added dropwise and the mixture was warm to room temperature and stirred for 24 h. The reaction mixture was quenched with a solution of $NaHCO_3$, extracted with dichloromethane, and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 5/5 as the eluent) to afford the desired compound as a green solid (2 mg, 7 %).

Method B ($PtCl_2$ as the catalyst): 2-(4-(azulen-6-yl)-2,5-bis((4-methoxy-2,6-dimethylphenyl)ethynyl)phenyl)azulene (**34**) (30 mg, 0.05 mmol), $PtCl_2$ (2 mg, 0.008 mmol) and nitrogen-purged toluene (20 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen, warm to 110 °C and stirred for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, hexanes/dichloromethane 5/5 as the eluent) to afford the desired compound as a green solid (15 mg, 50 %).

^{1}H NMR (400 MHz, chloroform-*d*) δ 9.54 (s, 1H), 9.17 (s, 1H), 8.92 (d, *J* = 11.7 Hz, 1H), 8.65 (s, 1H), 8.54 (d, *J* = 10.2 Hz, 1H), 8.46 (d, *J* = 11.5 Hz, 1H), 8.39 (s, 1H), 7.96 (s, 1H), 7.85 – 7.69 (m, 3H), 7.53 (t, *J* = 9.8 Hz, 1H), 7.45 (s, 1H), 7.21 (t, 3H), 7.00 (t, *J* = 10.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 4H), 3.97 (d, *J* = 3.4 Hz, 6H), 2.05 (s, 13H).

^{13}C NMR (126 MHz, chloroform-*d*) δ 158.8 (s), 142.1 (s), 141.0 (s), 140.4 (s), 140.2 (s), 139.8 (s), 138.5 (s), 138.1 (s), 138.0 (s), 137.7 (s), 137.1 (s), 136.8 (s), 136.6 (s), 136.0 (s), 135.1 (s), 133.7 (s), 133.6 (s), 133.2 (s), 132.9 (s), 132.2 (s), 131.9 (s), 131.6 (s), 131.5 (s), 130.7 (s), 129.5 (s), 129.0 (s), 128.4 (s), 127.4 (s), 125.8 (s), 125.6 (s), 125.1 (s), 124.9 (s), 124.8 (s), 124.7 (s),

124.0 (s), 123.5 (s), 123.3 (s), 122.1 (s), 120.6 (s), 119.3 (s), 113.2 (s), 113.0 (s), 55.3 (s), 21.0 (s), 20.6 (s).

HRMS (ESI+): $C_{48}H_{38}O_2$ $[M+H]^+$ 646.2866; found, 646.2866.

NMR Spectroscopy

Compound 12:

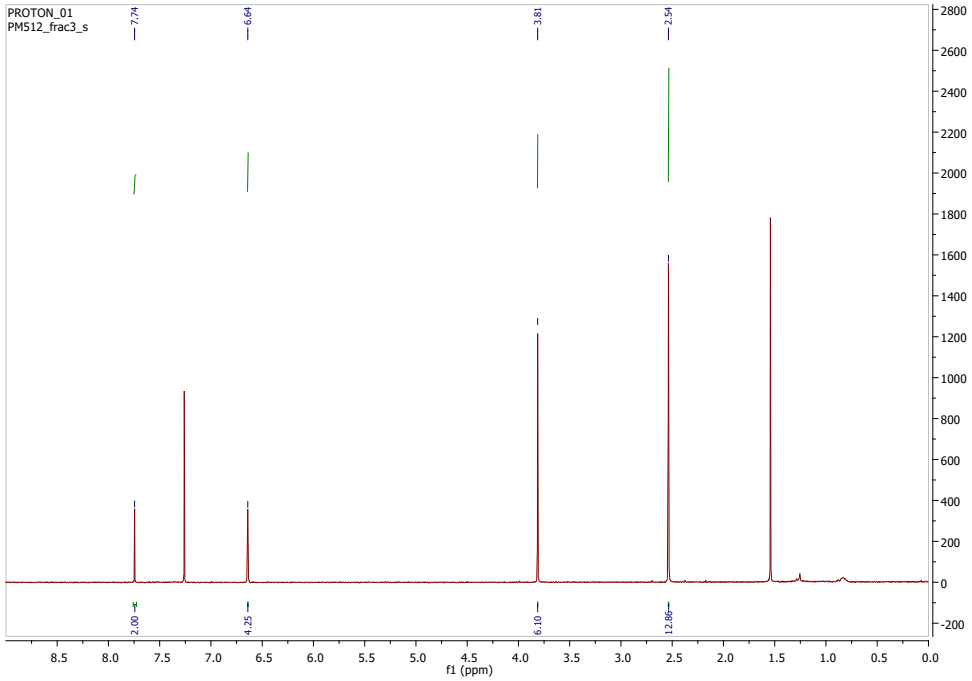


Fig. S1. ^{1}H NMR spectrum of compound **12** in $CDCl_3$ at 400 MHz

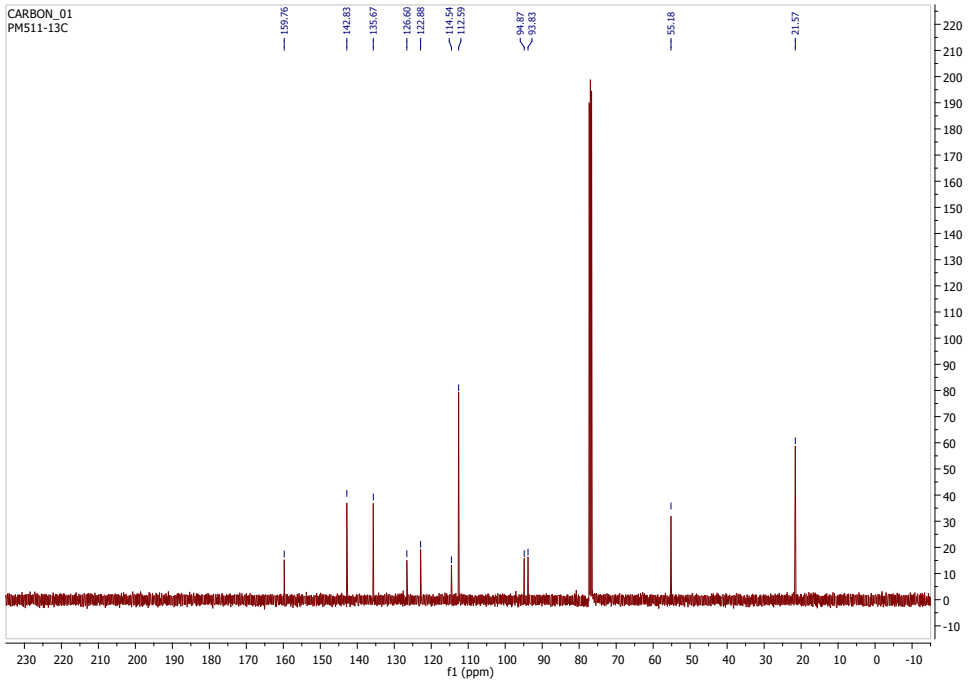


Fig. S2: ^{13}C NMR spectrum of compound **12** in $CDCl_3$ at 400 MHz

Compound 14:

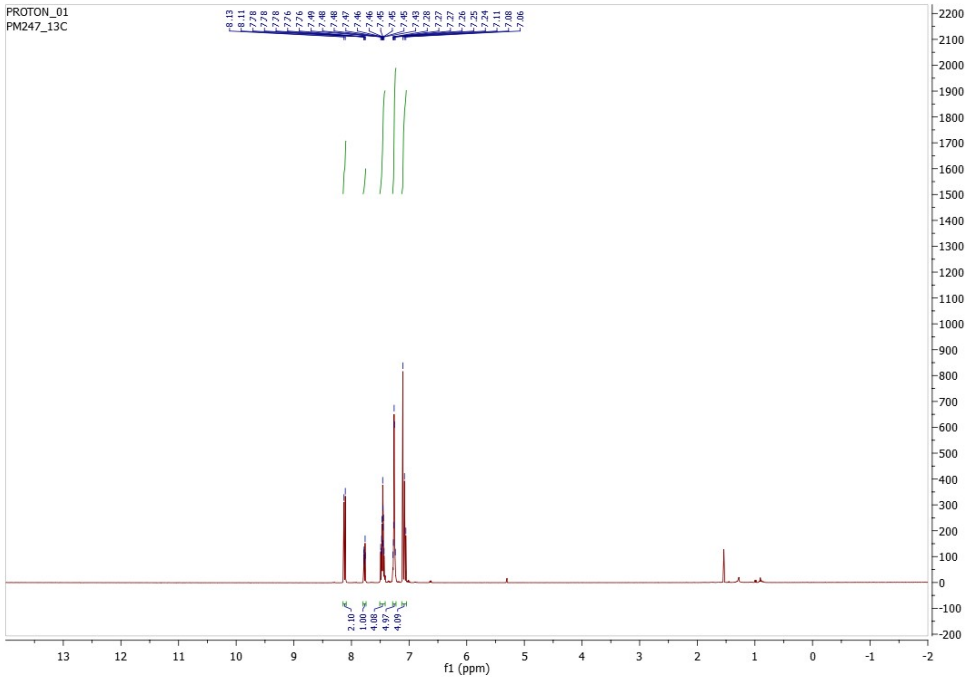


Fig. S3. ^{1}H NMR spectrum of compound **14** in $CDCl_3$ at 400 MHz

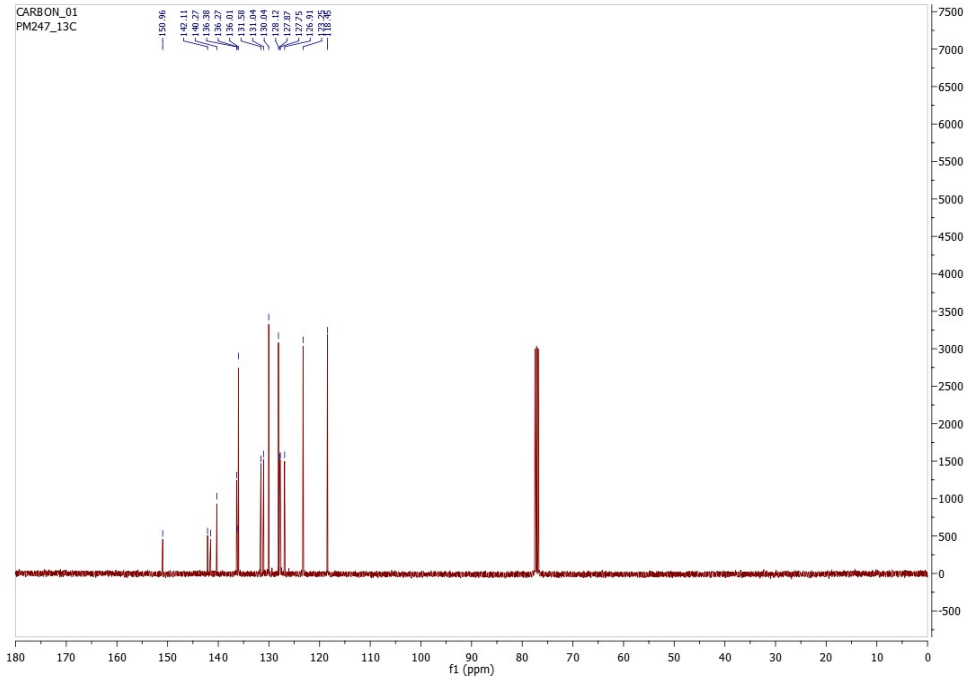


Fig. S4: ^{13}C NMR spectrum of compound **14** in $CDCl_3$ at 400 MHz

Compound 15:

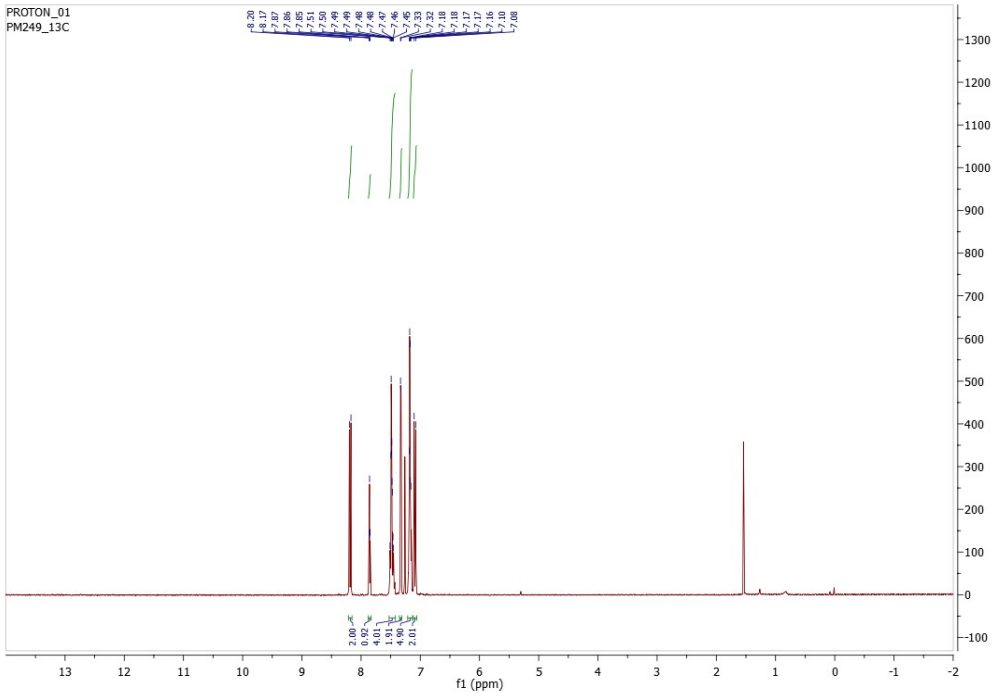


Fig. S5: ^{1}H NMR spectrum of compound **15** in $CDCl_3$ at 400 MHz

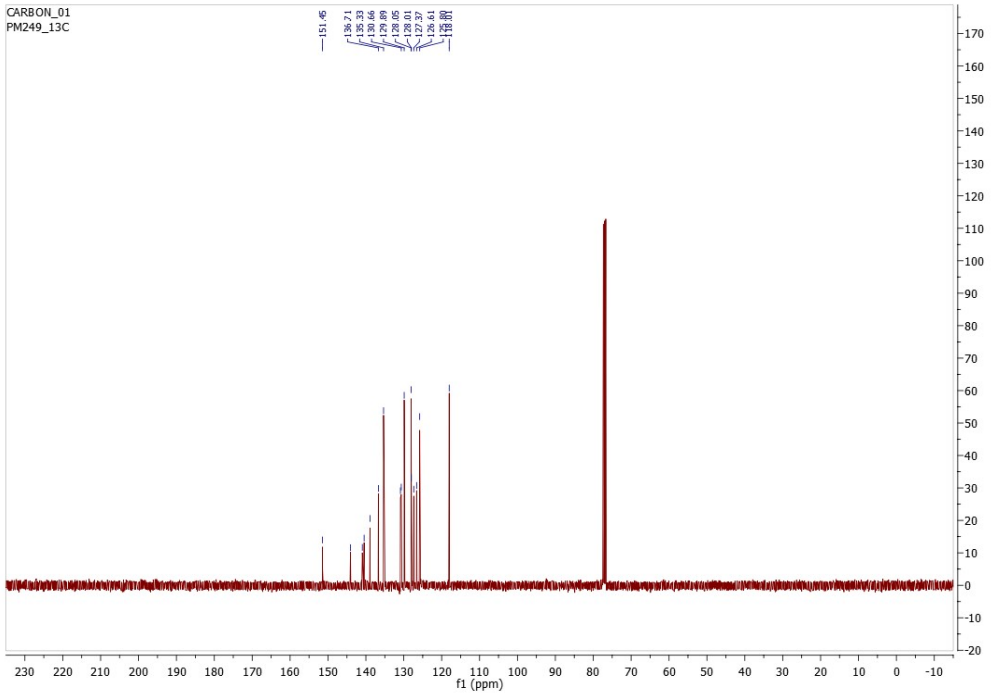


Fig. S6: ^{13}C NMR spectrum of compound **15** in $CDCl_3$ at 400 MHz

Compound 16:

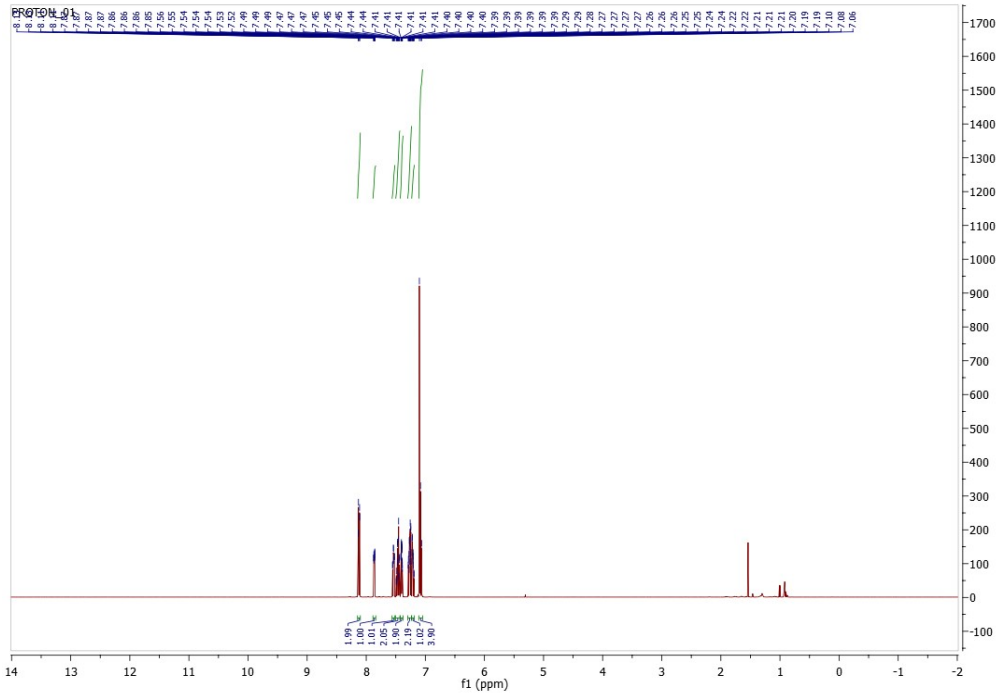


Fig. S7: ^{1}H NMR spectrum of compound **16** in $CDCl_3$ at 400 MHz

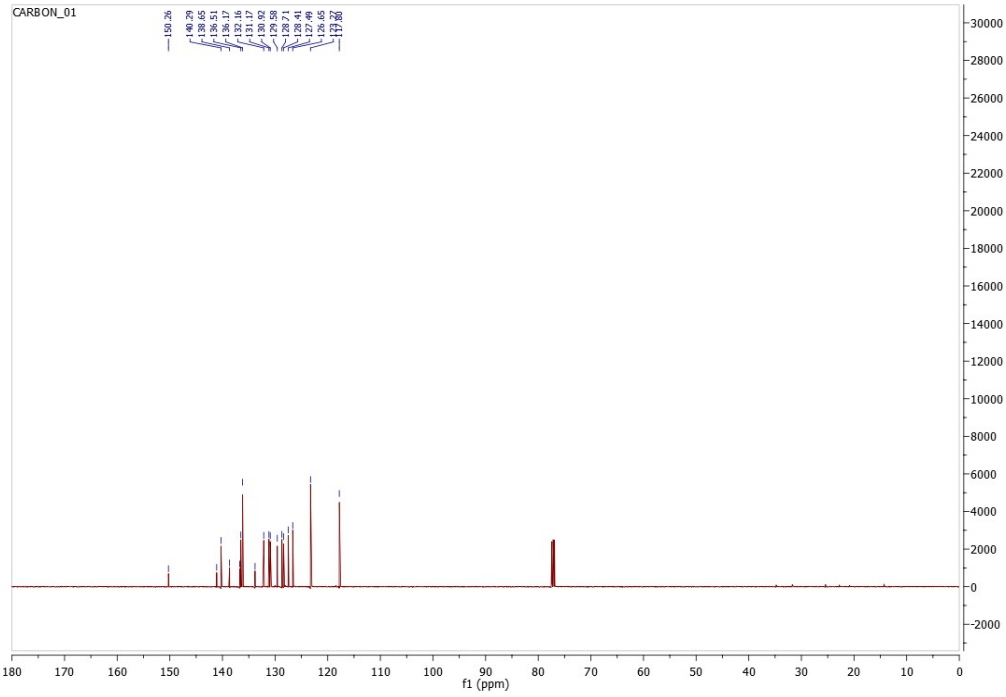


Fig. S8: ^{13}C NMR spectrum of compound **16** in $CDCl_3$ at 400 MHz

Compound 17:

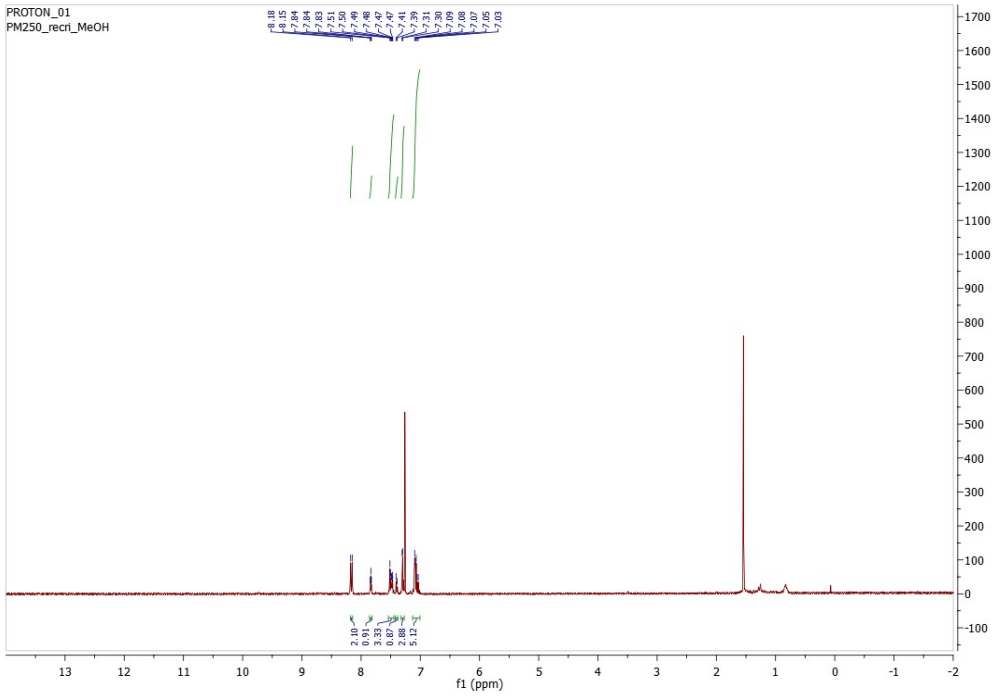


Fig. S9: ^{1}H NMR spectrum of compound **17** in $CDCl_3$ at 400 MHz

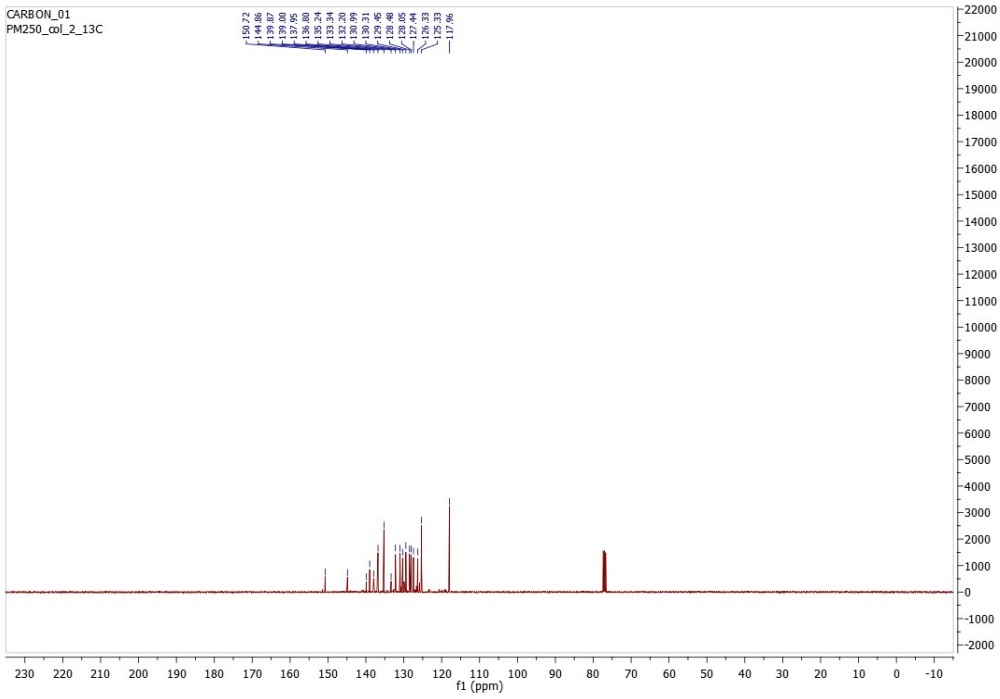


Fig. S10: ^{13}C NMR spectrum of compound **17** in $CDCl_3$ at 400 MHz

Compound 18:

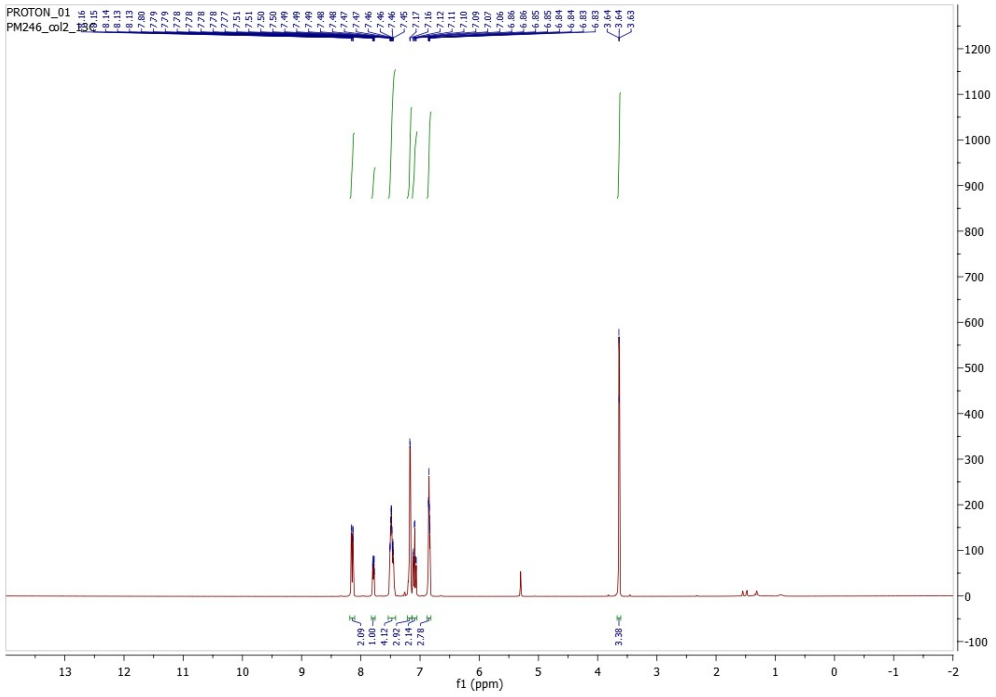


Fig. S11: ^{1}H NMR spectrum of compound **18** in $CDCl_3$ at 400 MHz

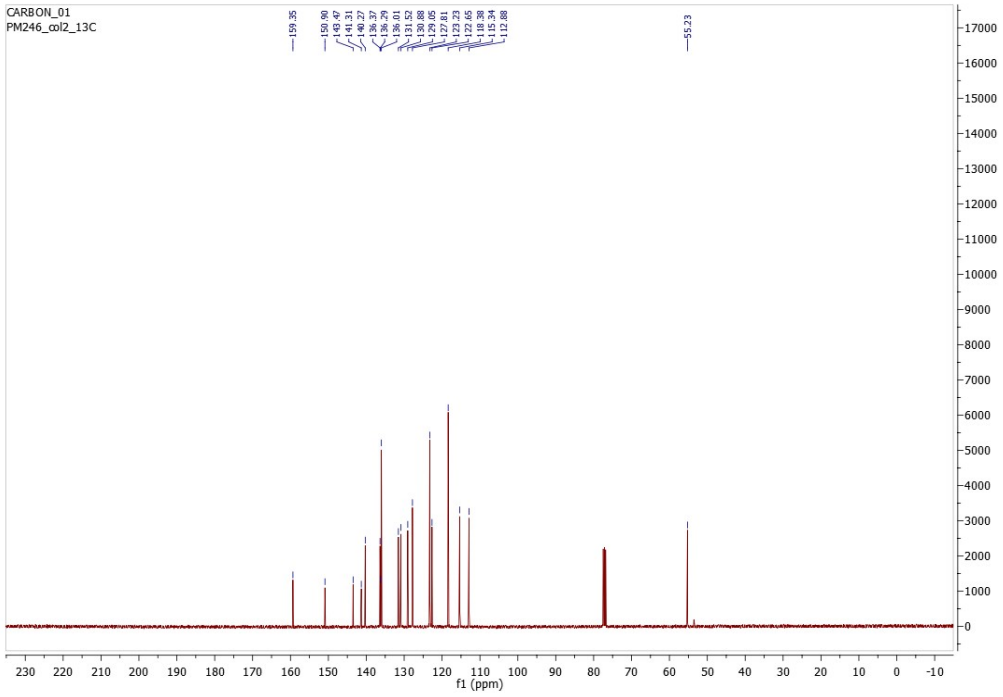


Fig. S12: ^{13}C NMR spectrum of compound **18** in $CDCl_3$ at 400 MHz

Compound 19:

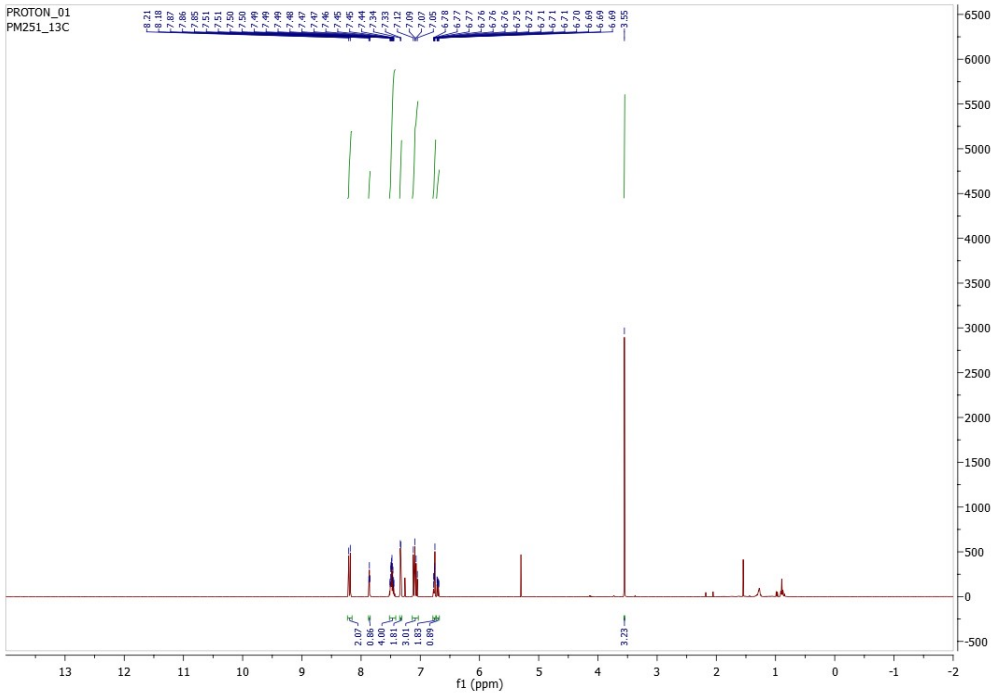


Fig. S13: ^{1}H NMR spectrum of compound **19** in $CDCl_3$ at 400 MHz

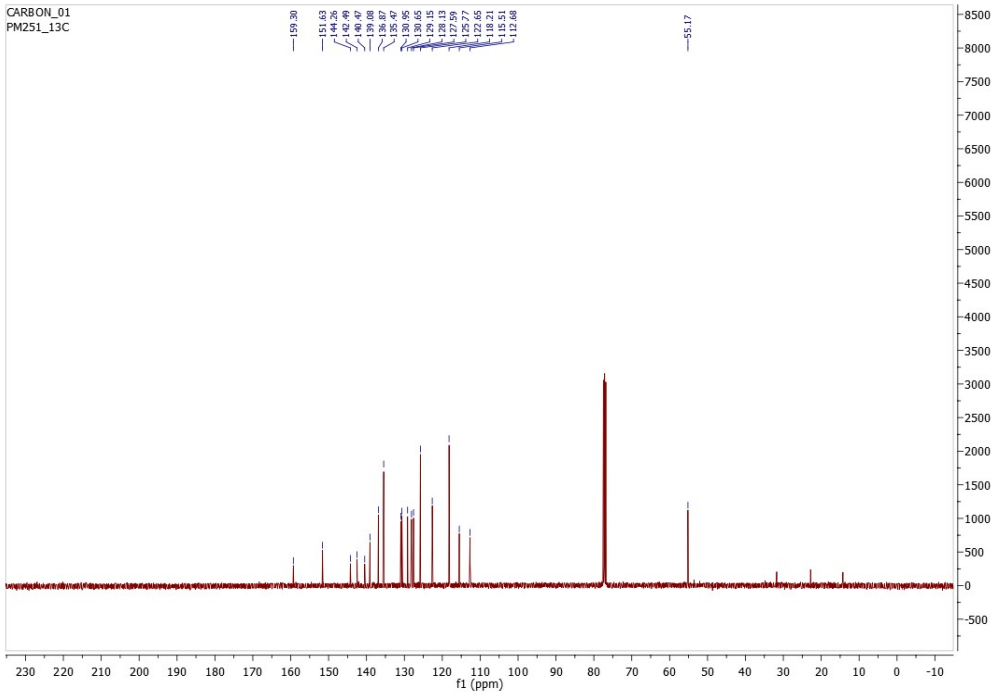


Fig. S14: ^{13}C NMR spectrum of compound **19** in $CDCl_3$ at 400 MHz

Compound 20:

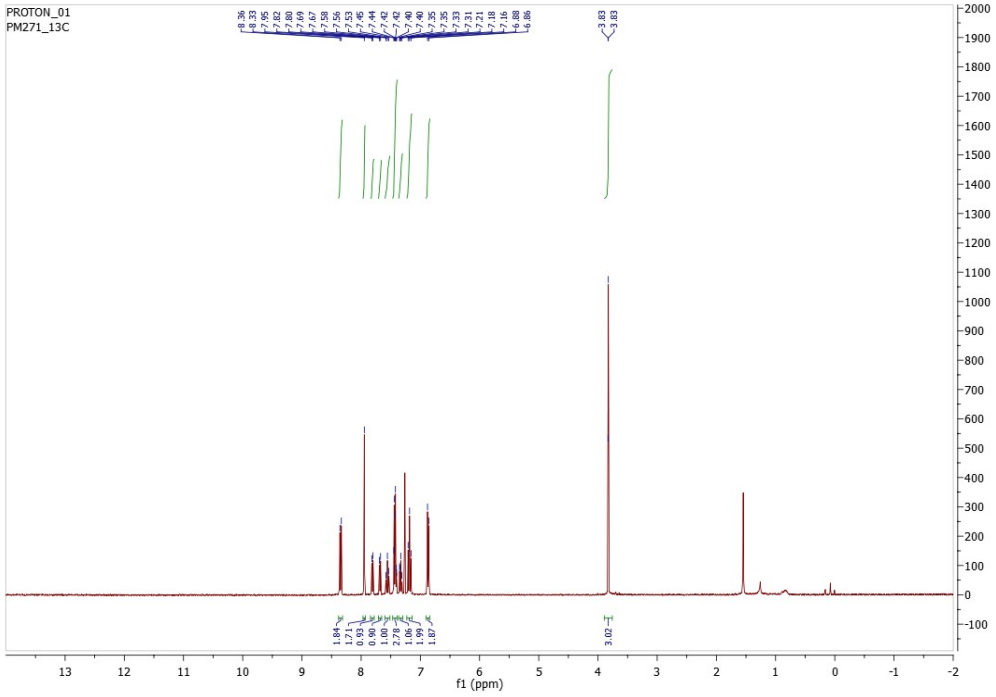


Fig. S15: ^{1}H NMR spectrum of compound **20** in $CDCl_3$ at 400 MHz

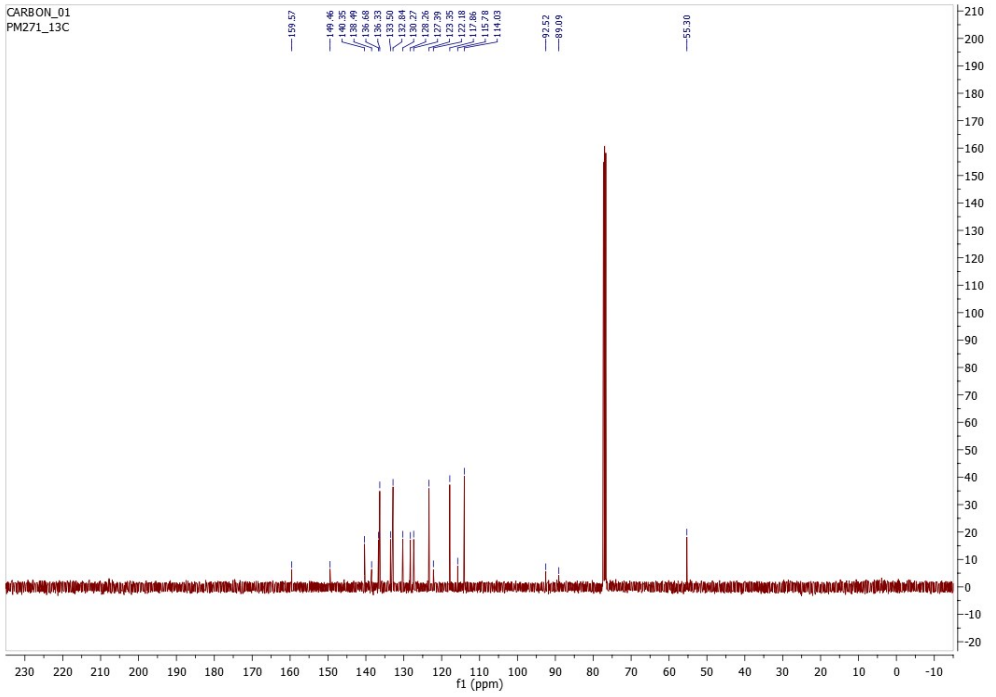


Fig. S16: ^{13}C NMR spectrum of compound **20** in $CDCl_3$ at 400 MHz

Compound 21:

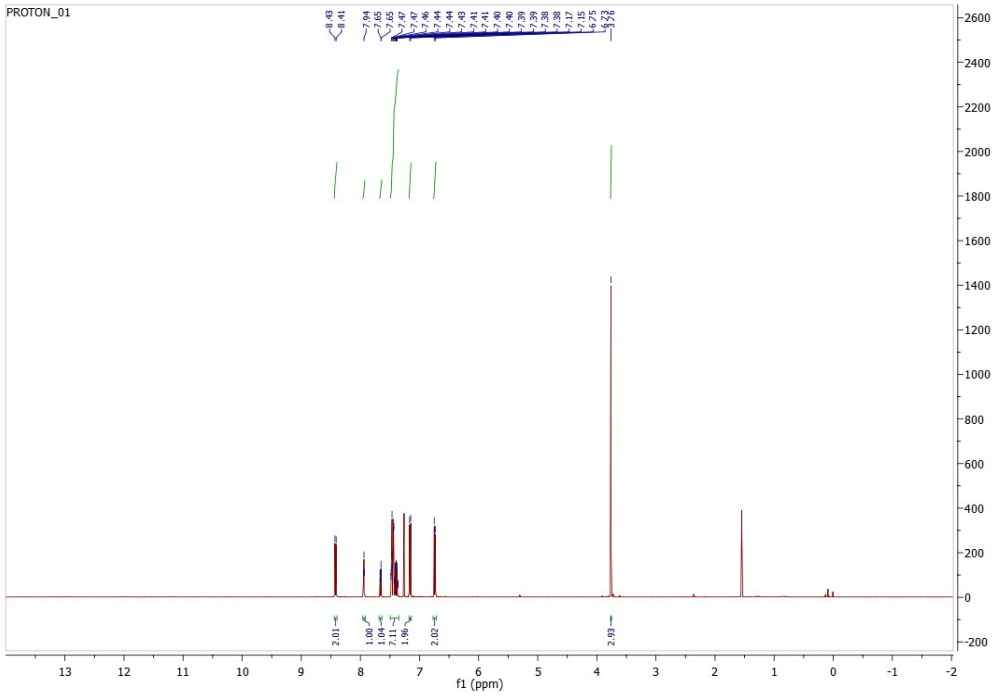


Fig. S17: ^{1}H NMR spectrum of compound **21** in $CDCl_3$ at 400 MHz

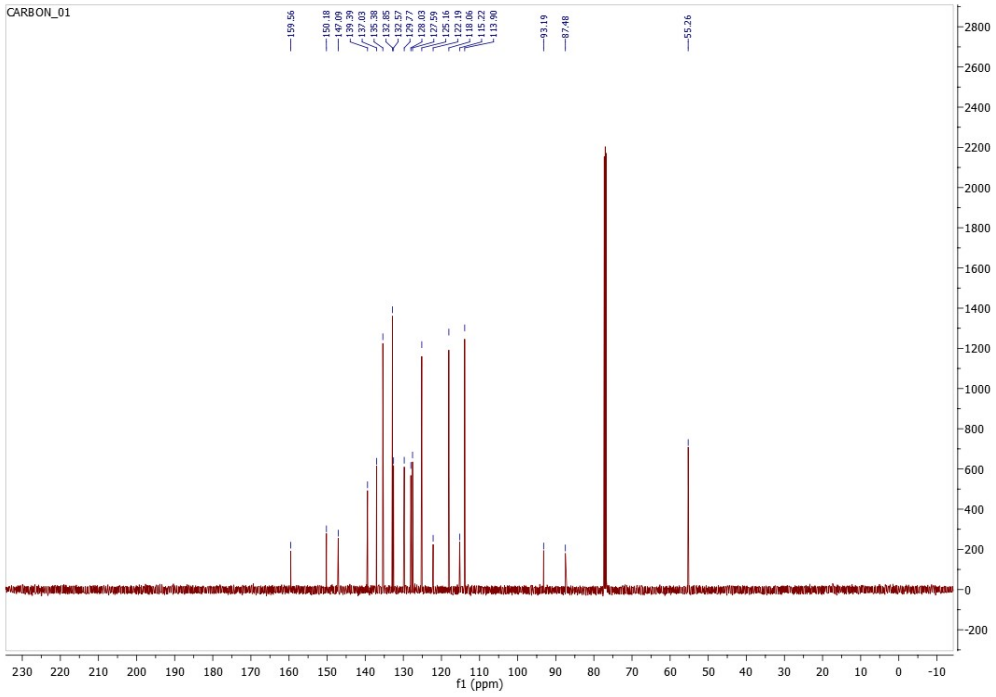


Fig. S18: ^{13}C NMR spectrum of compound **21** in $CDCl_3$ at 400 MHz

Compound 22:

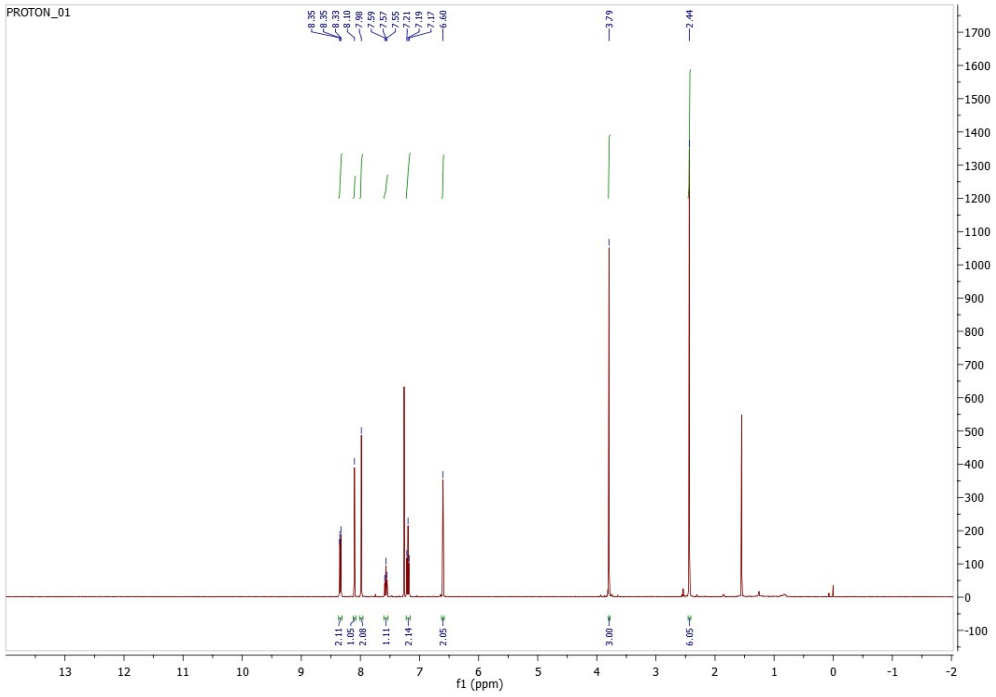


Fig. S19: ^{1}H NMR spectrum of compound **22** in $CDCl_3$ at 400 MHz

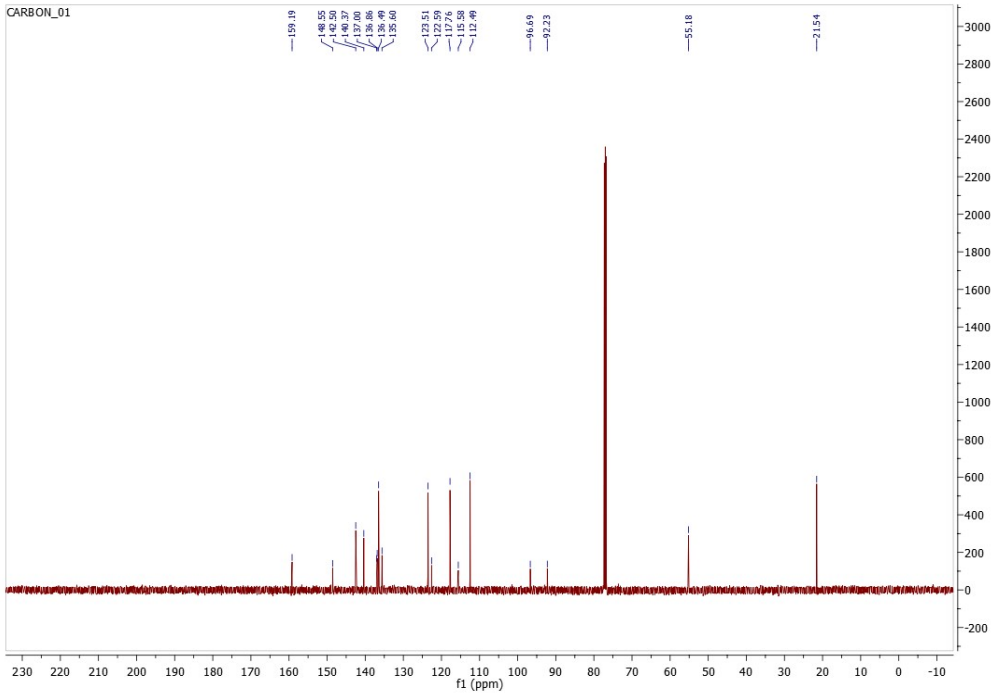


Fig. S20: ^{13}C NMR spectrum of compound **22** in $CDCl_3$ at 400 MHz

Compound 23:

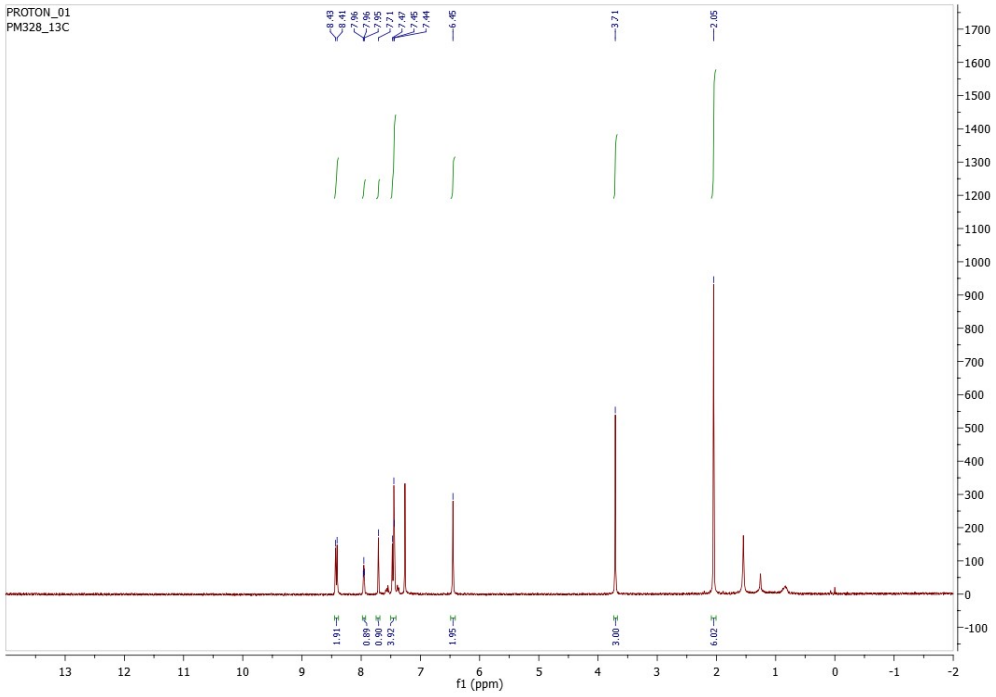


Fig. S21: ^{1}H NMR spectrum of compound **23** in $CDCl_3$ at 400 MHz

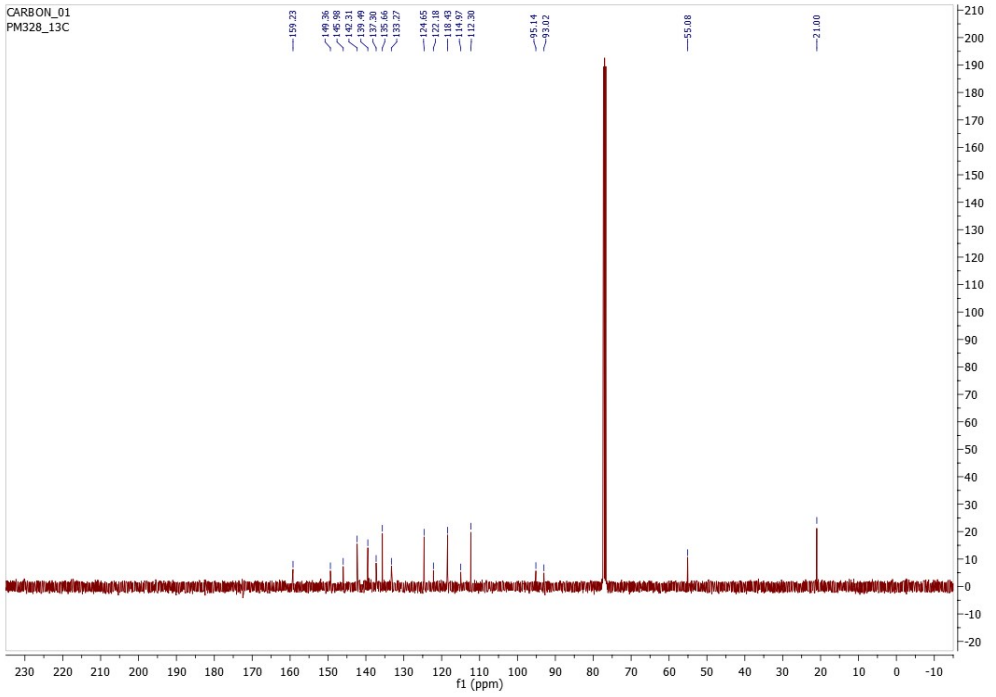


Fig. S22: ^{13}C NMR spectrum of compound **23** in $CDCl_3$ at 400 MHz

Compound 24:

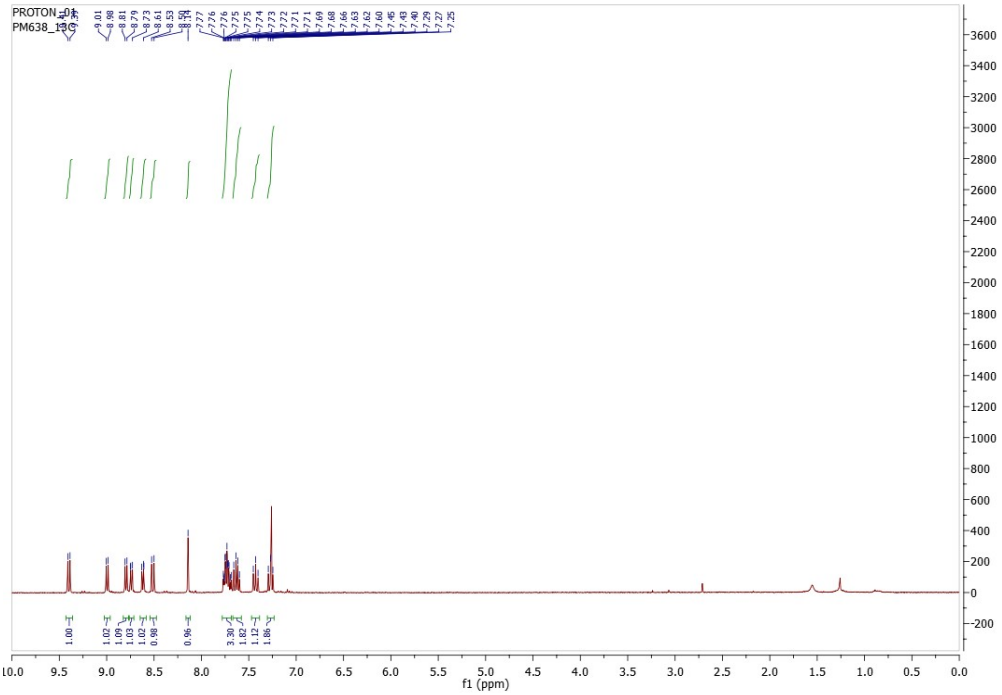


Fig. S23: ^{1}H NMR spectrum of compound **24** in $CDCl_3$ at 400 MHz

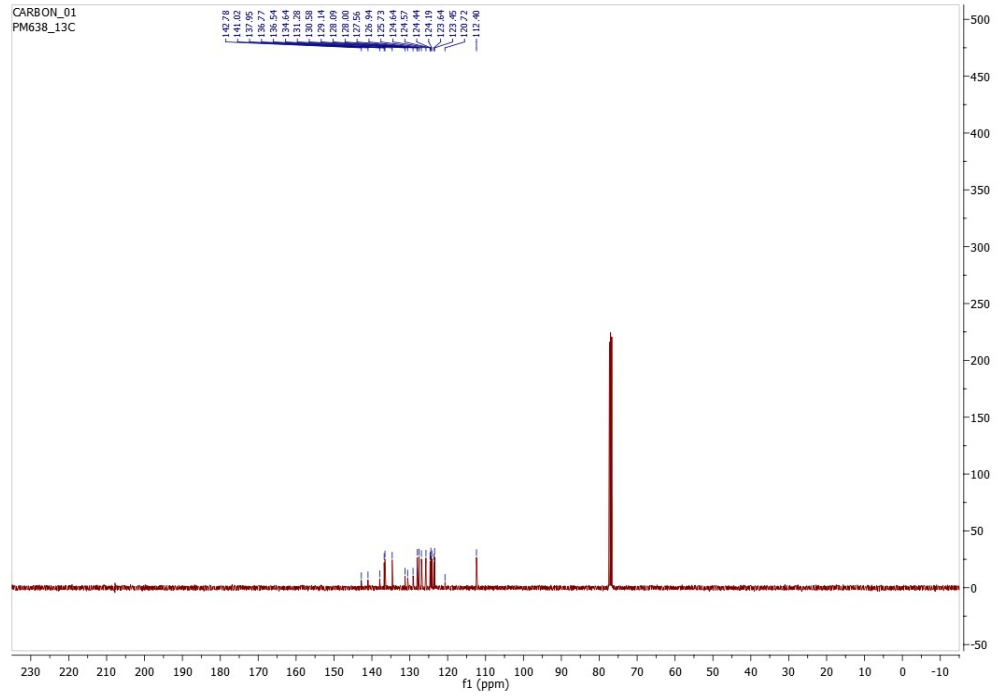


Fig. S24: ^{13}C NMR spectrum of compound **24** in $CDCl_3$ at 400 MHz

Compound 25:

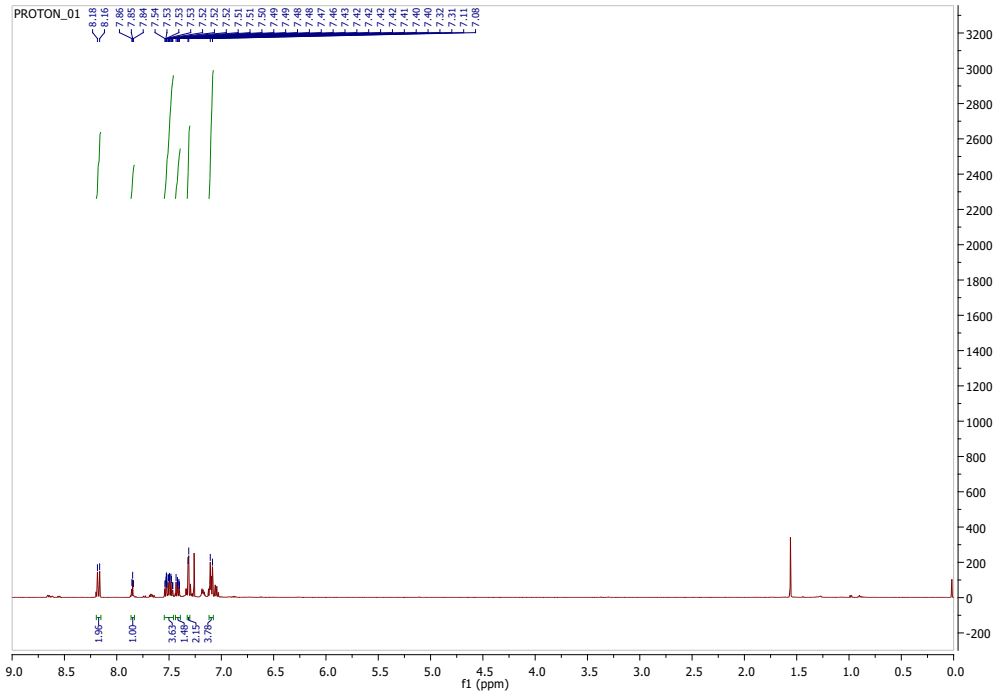


Fig. S25: ^{1}H NMR spectrum of compound **25** in $CDCl_3$ at 500 MHz

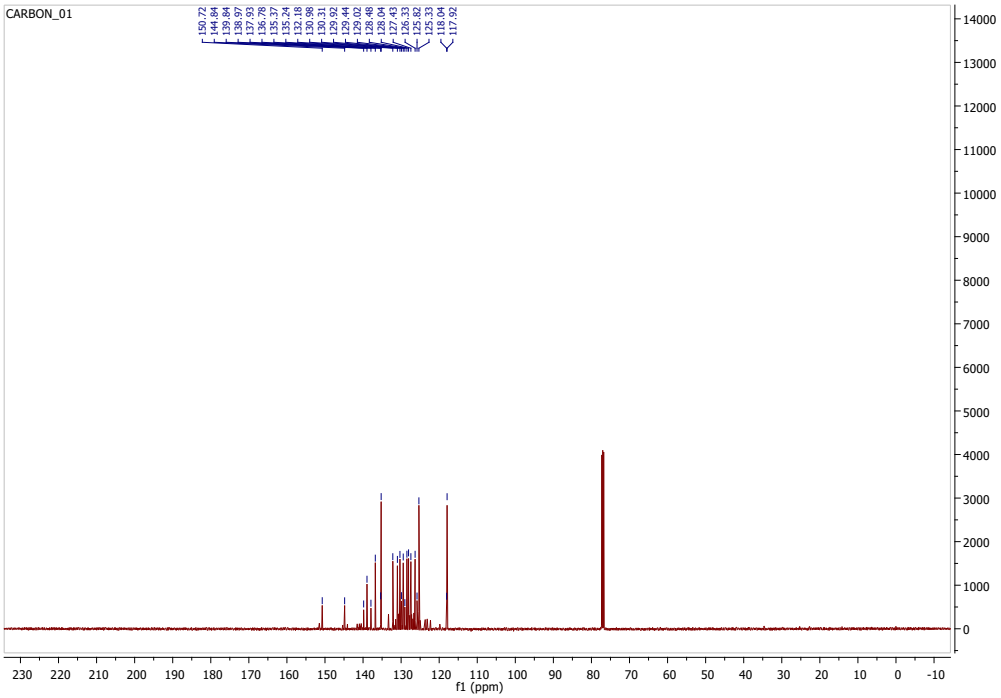


Fig. S26: ^{13}C NMR spectrum of compound **25** in $CDCl_3$ at 500 MHz

Compound 26:

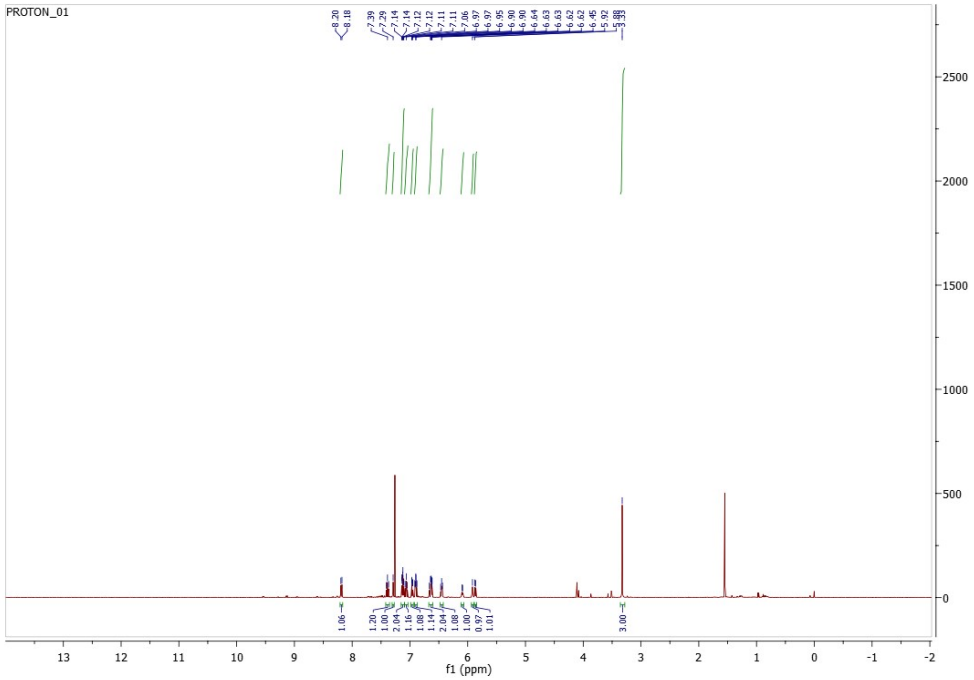


Fig. S27: ^{1}H NMR spectrum of compound **26** in $CDCl_3$ at 400 MHz

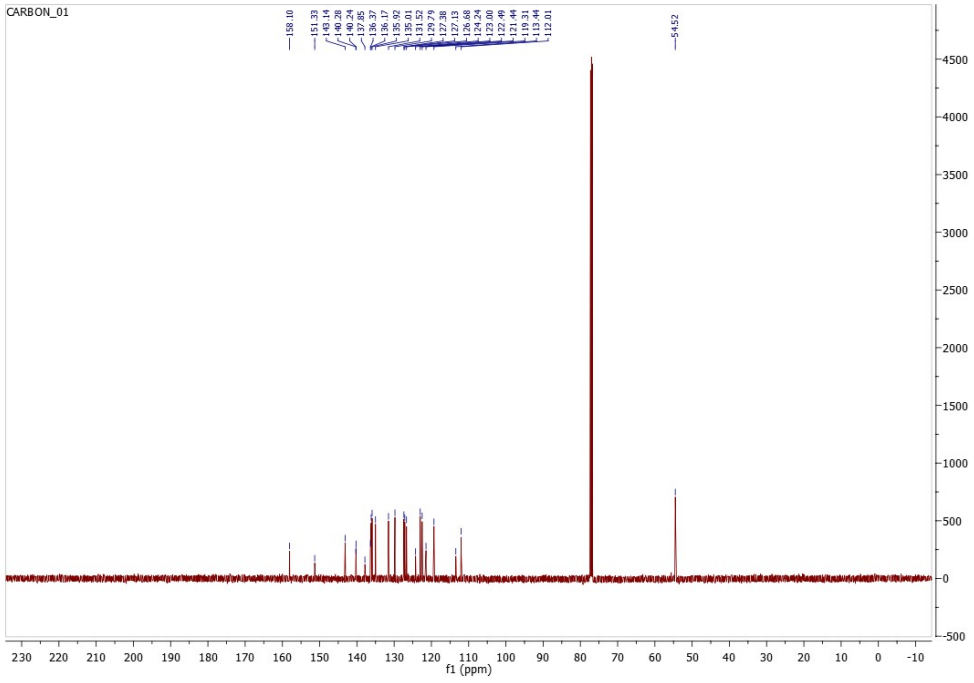


Fig. S28: ^{13}C NMR spectrum of compound **26** in $CDCl_3$ at 400 MHz

Compound 27:

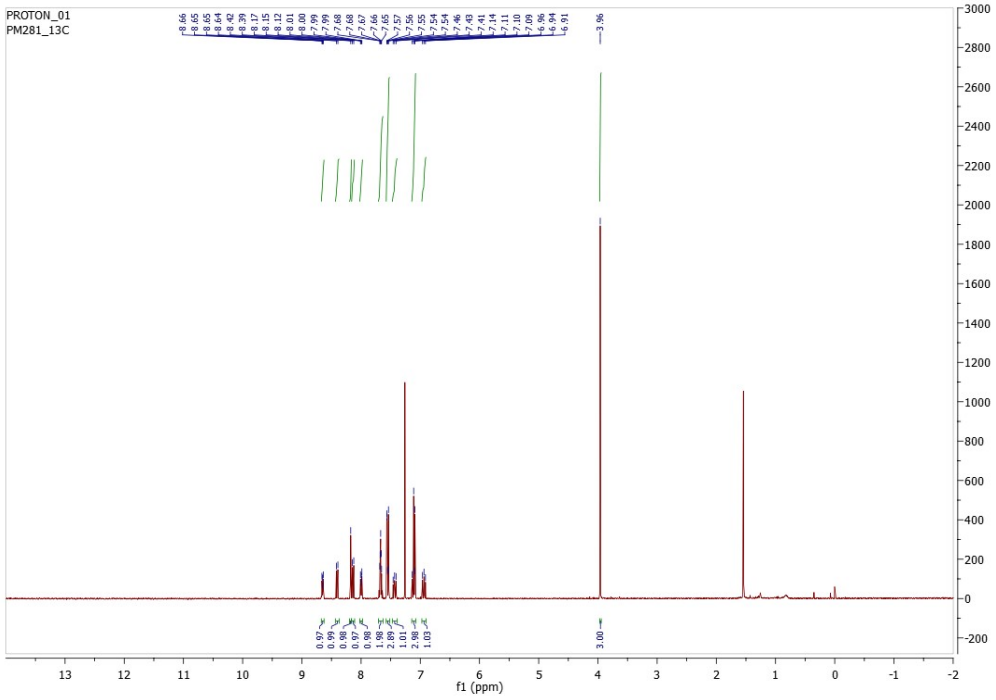


Fig. S29: ^{1}H NMR spectrum of compound **27** in $CDCl_3$ at 400 MHz

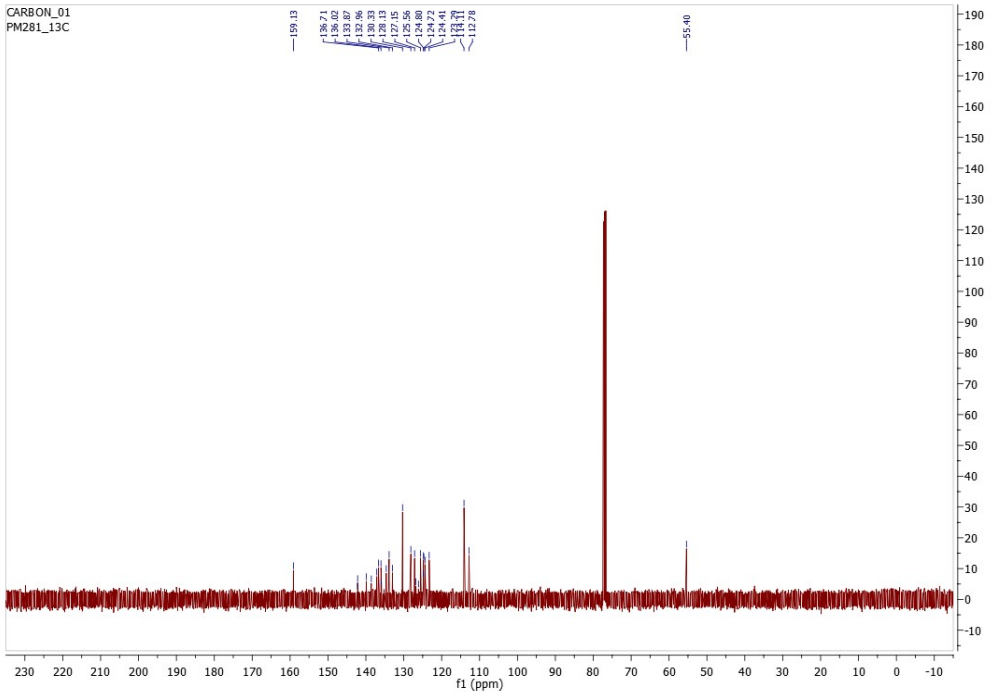


Fig. S30: ^{13}C NMR spectrum of compound **27** in $CDCl_3$ at 400 MHz

Compound 28:

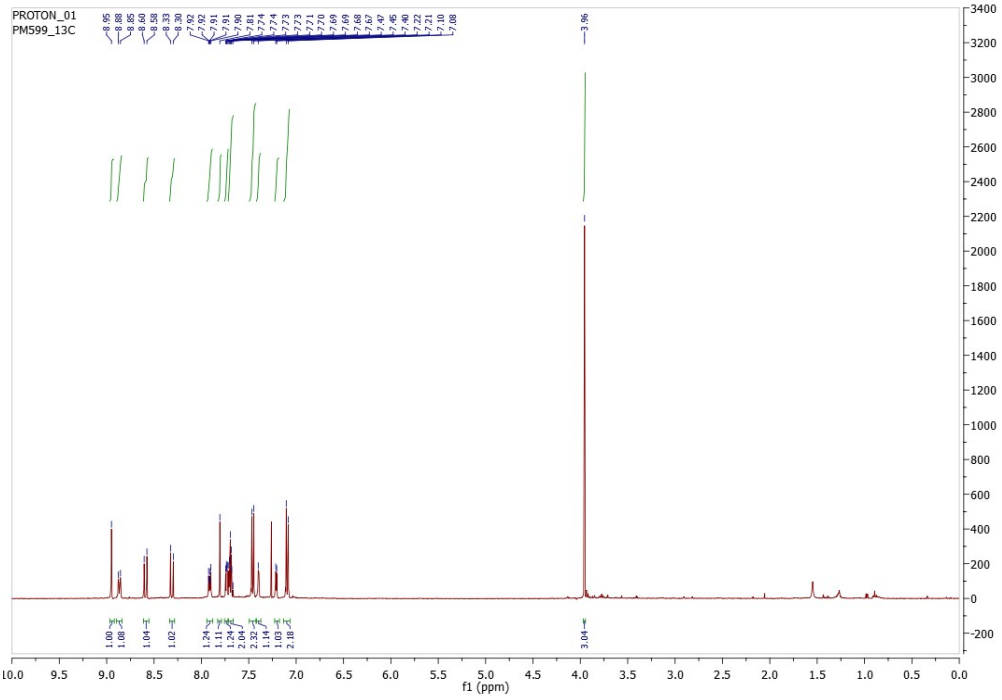


Fig. S31: ^{1}H NMR spectrum of compound **28** in $CDCl_3$ at 400 MHz

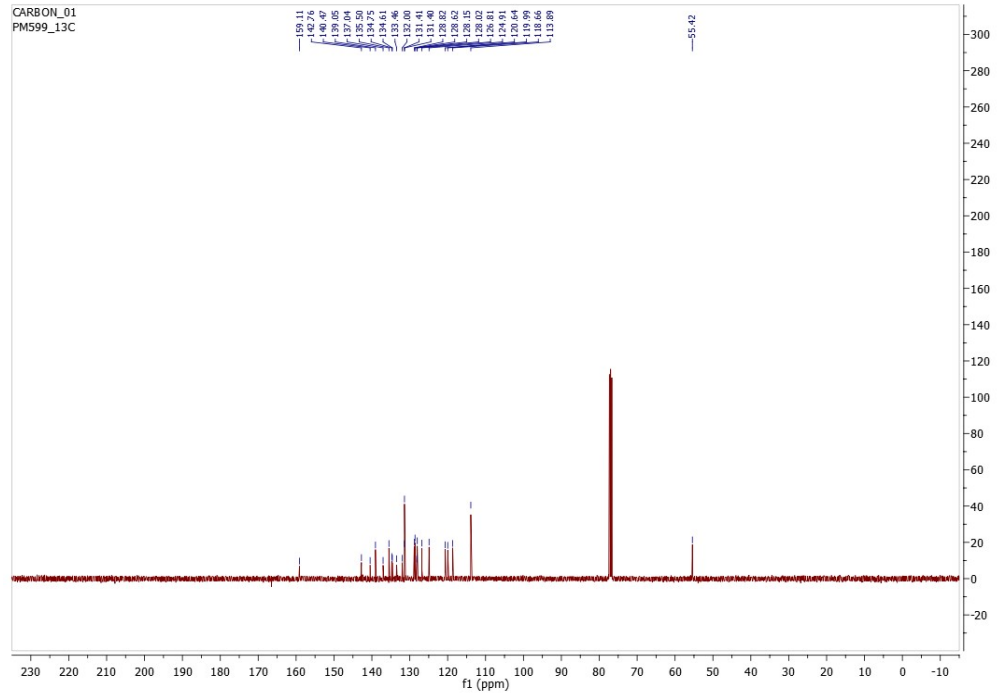


Fig. S32: ^{13}C NMR spectrum of compound **28** in $CDCl_3$ at 400 MHz

Compound 1:

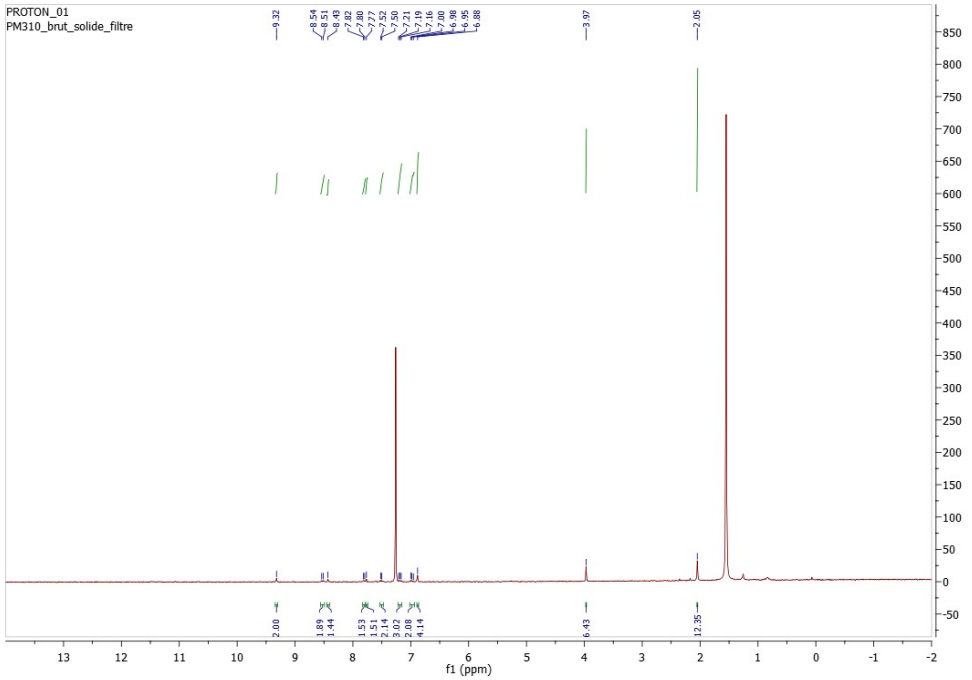


Fig. S33: ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at 400 MHz

Compound 2:

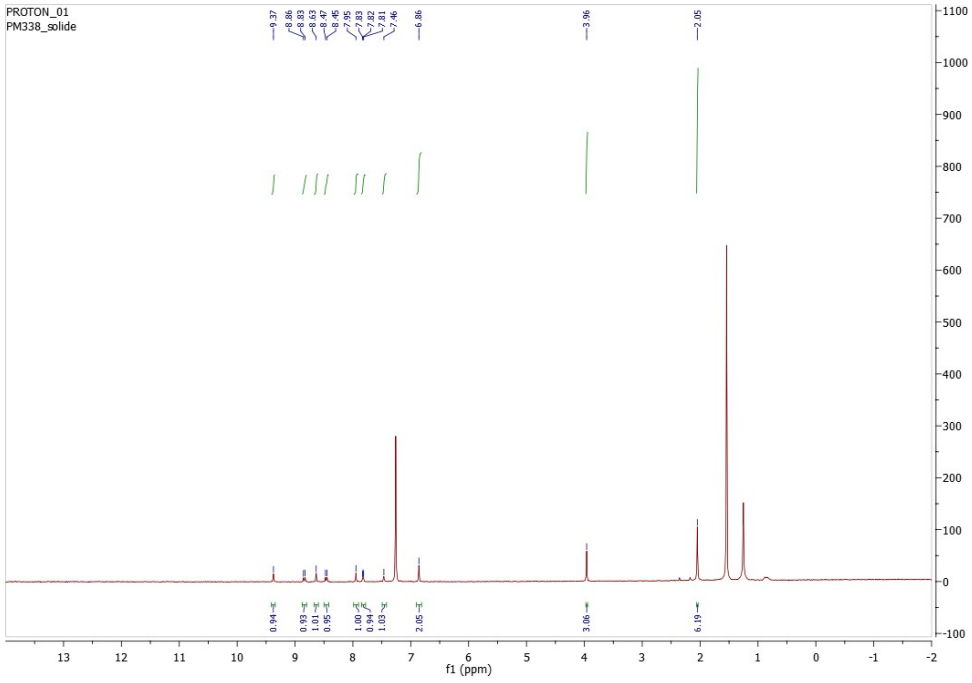


Fig. S34: ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at 400 MHz

Compound 29:

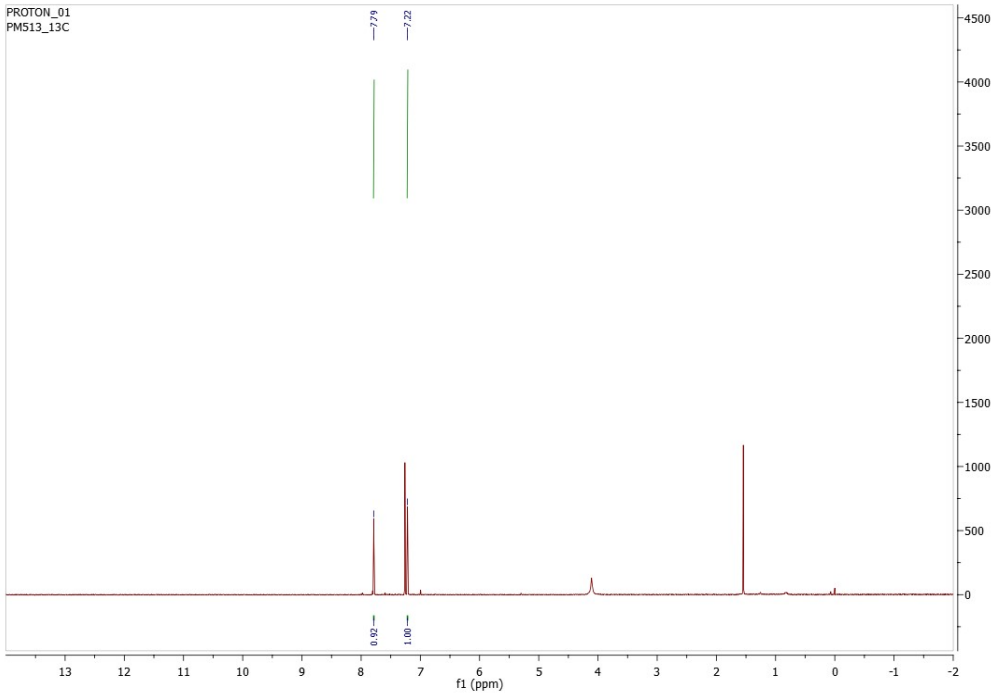


Fig. S35: ^{1}H NMR spectrum of compound **29** in $CDCl_3$ at 400 MHz

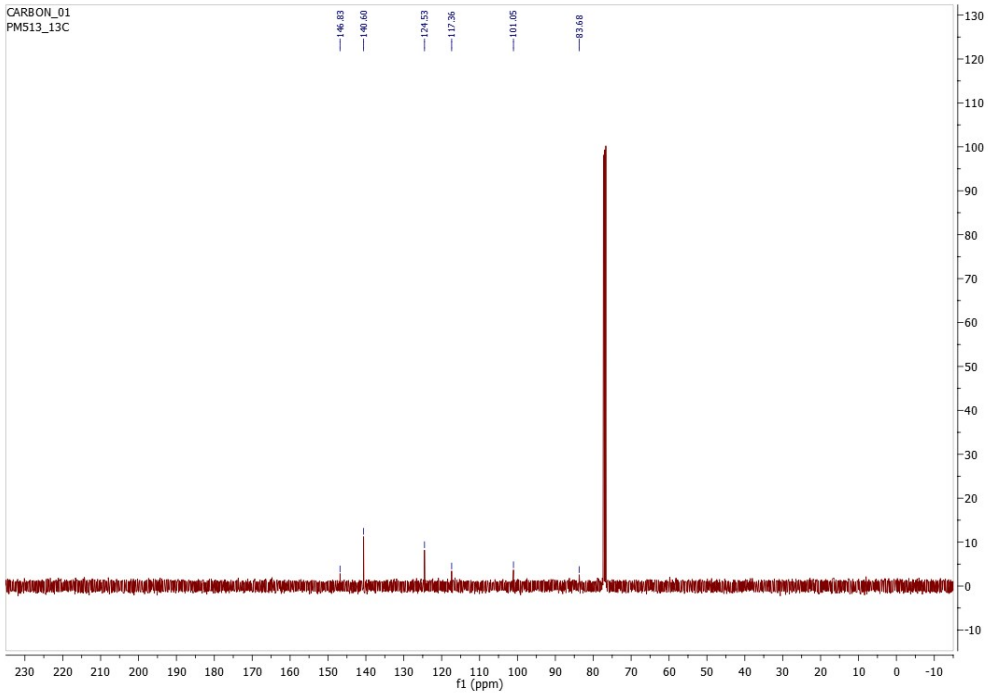


Fig. S36: ^{13}C NMR spectrum of compound **29** in $CDCl_3$ at 400 MHz

Compound 30:

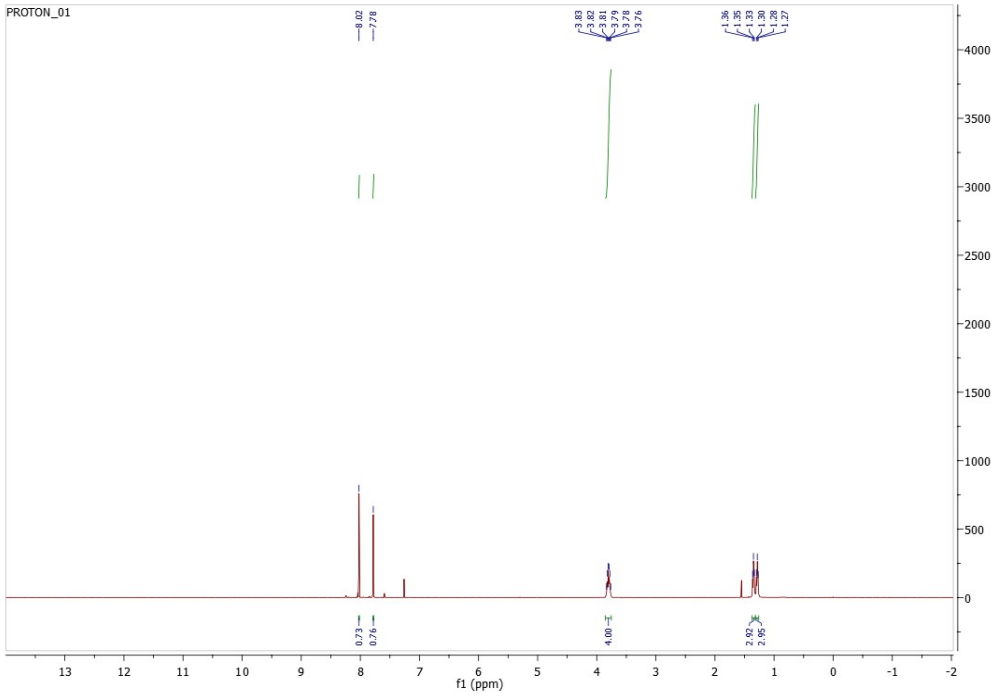


Fig. S37: ^{1}H NMR spectrum of compound **30** in $CDCl_3$ at 400 MHz

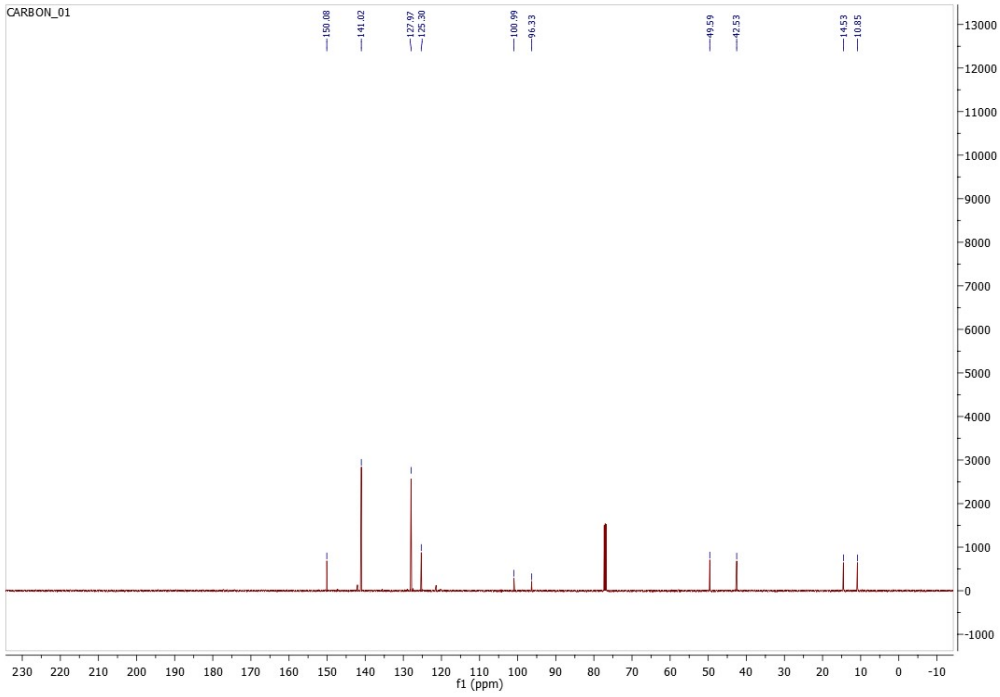


Fig. S38: ^{13}C NMR spectrum of compound **30** in $CDCl_3$ at 400 MHz

Compound 31:

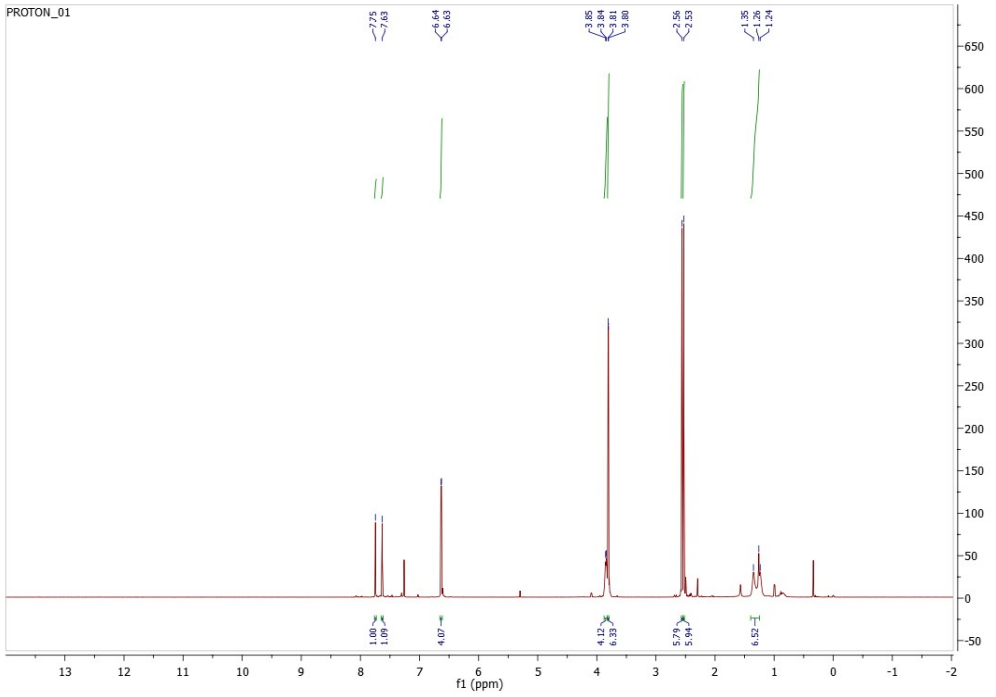


Fig. S39: ^{1}H NMR spectrum of compound **31** in $CDCl_3$ at 400 MHz

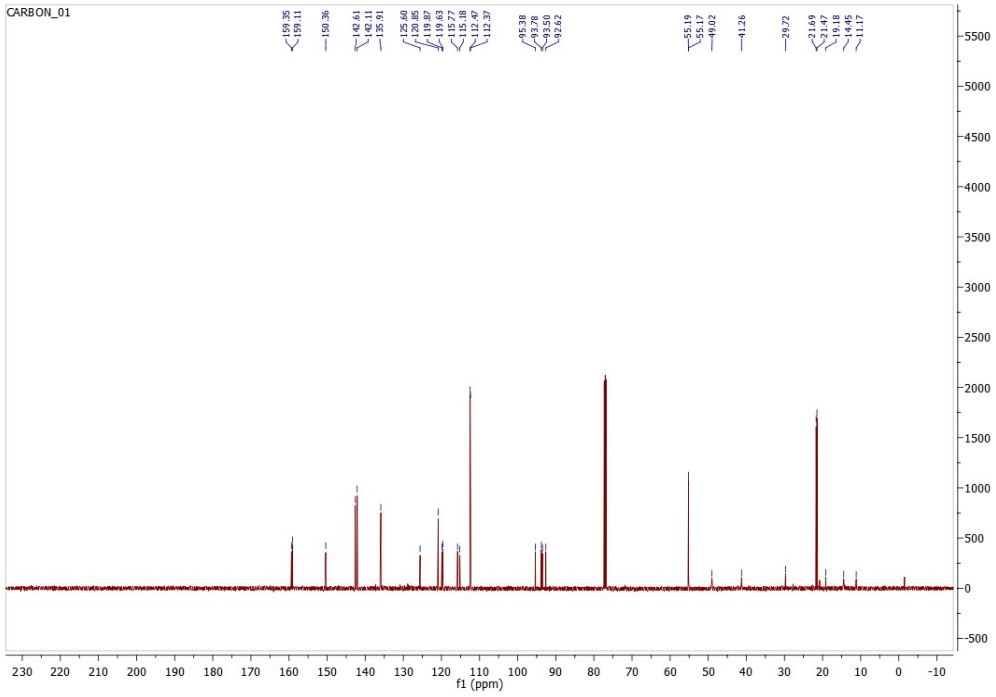


Fig. S40: ^{13}C NMR spectrum of compound **31** in $CDCl_3$ at 400 MHz

Compound 32:

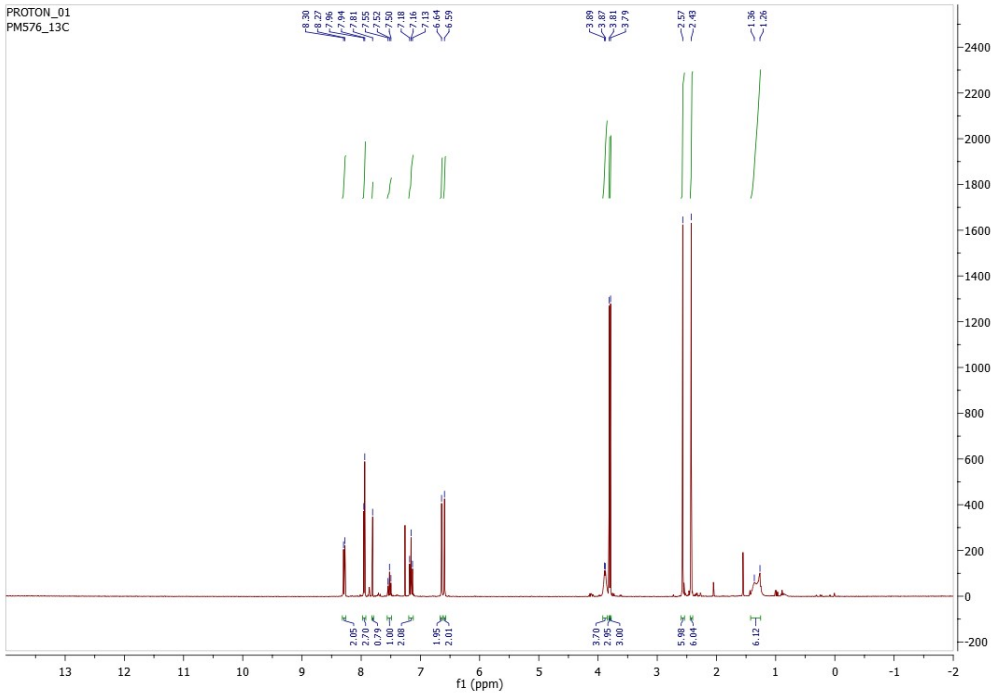


Fig. S41: ^{1}H NMR spectrum of compound **32** in $CDCl_3$ at 400 MHz

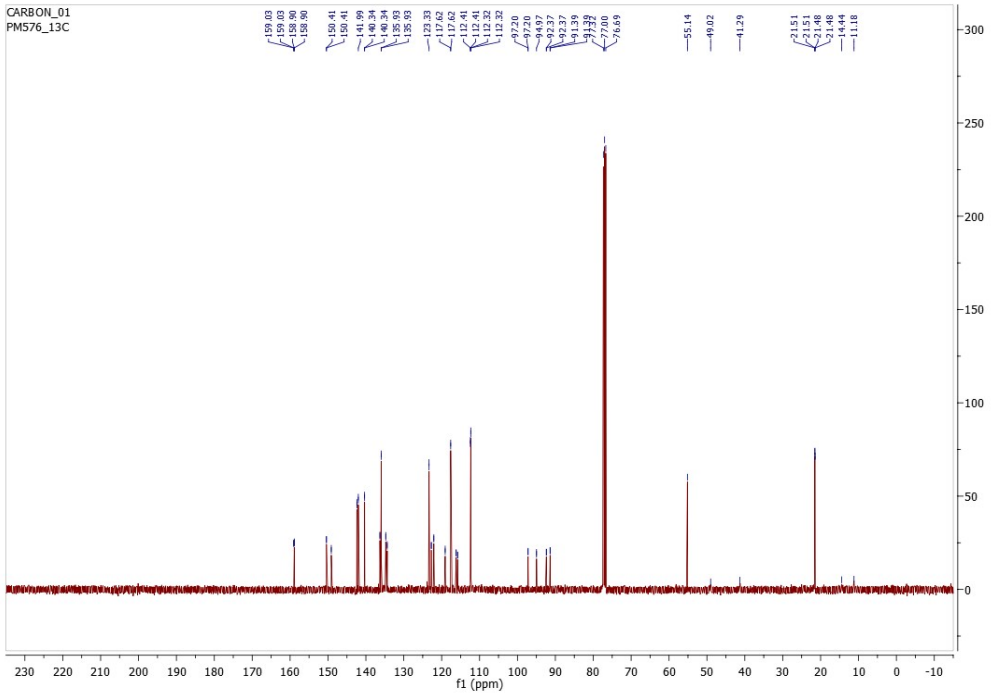


Fig. S42: ^{13}C NMR spectrum of compound **32** in $CDCl_3$ at 400 MHz

Compound 3:

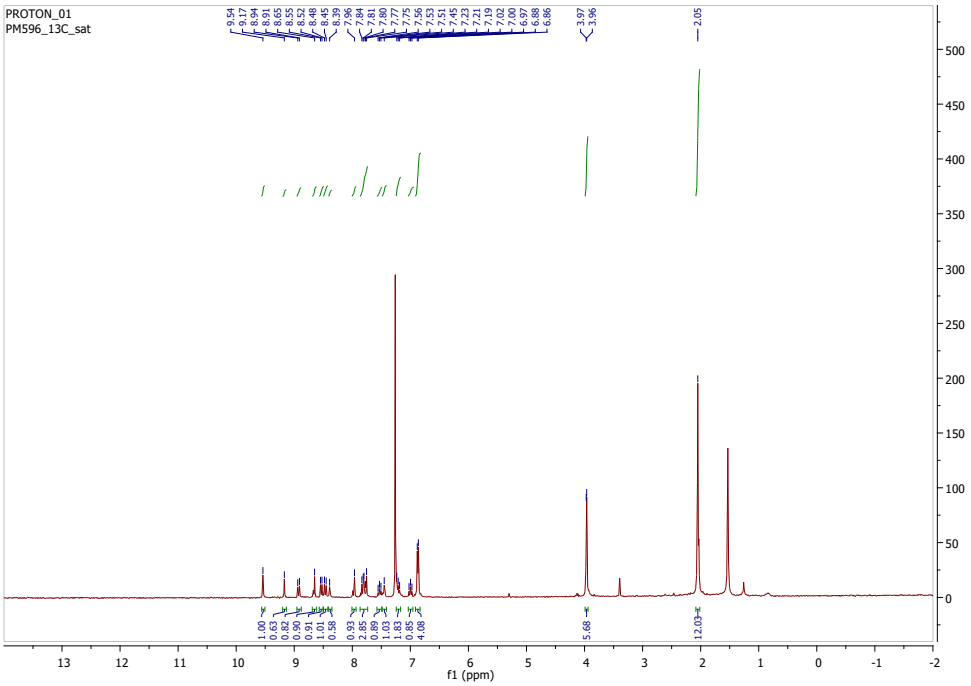


Fig. S43: ^{1}H NMR spectrum of compound **3** in $CDCl_3$ at 400 MHz

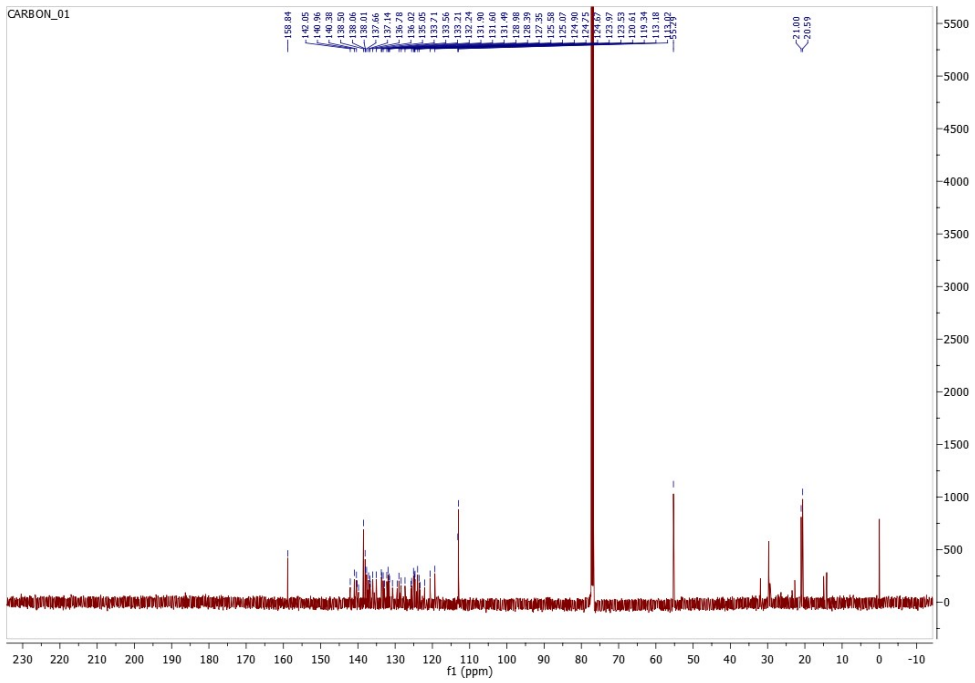


Fig. S44: ^{13}C NMR spectrum of compound **3** in $CDCl_3$ at 400 MHz

Acid Titration

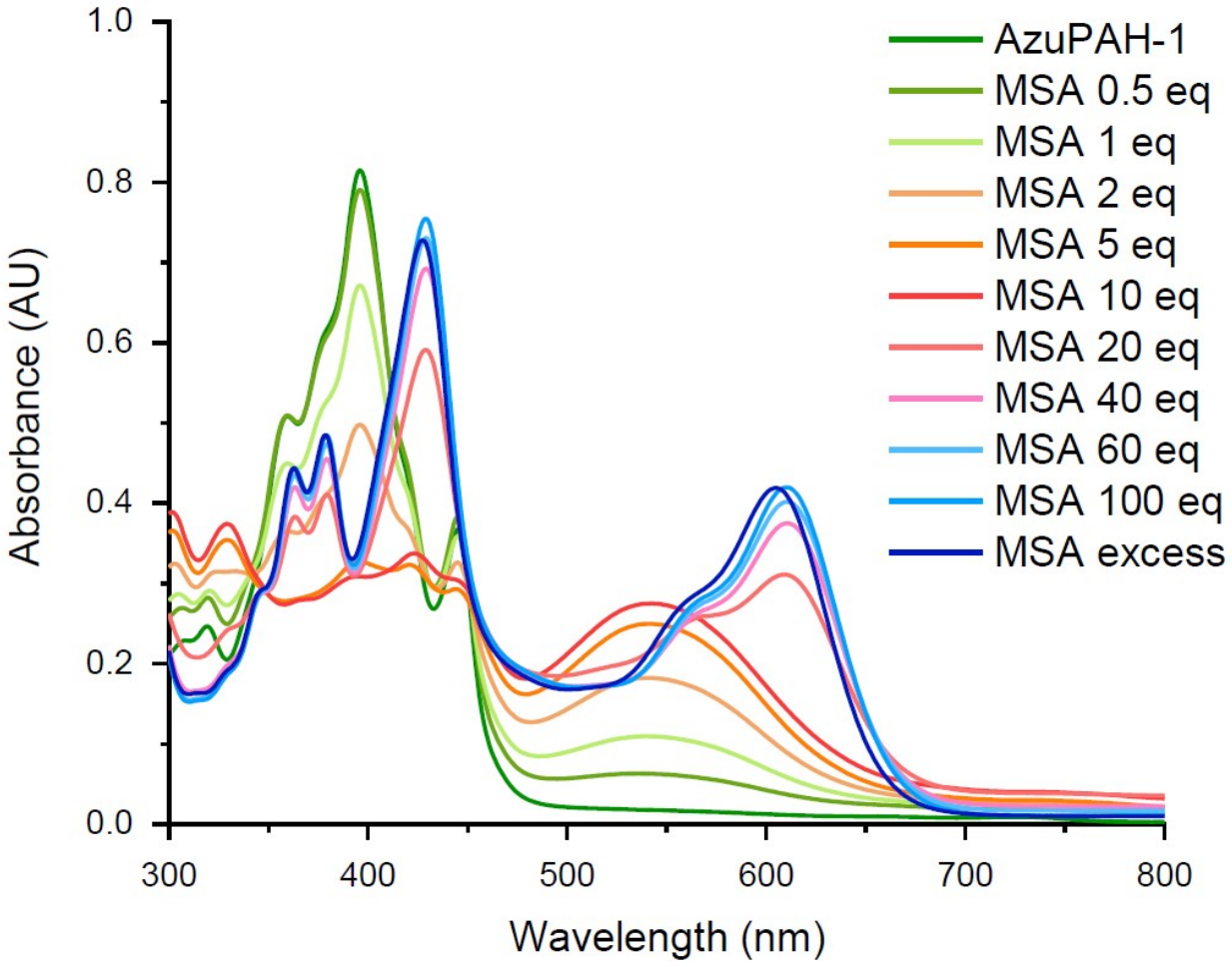


Fig. S45: UV-visible absorption spectra of compound **1** in solution of CH_2Cl_2 upon addition of various amount of MSA.

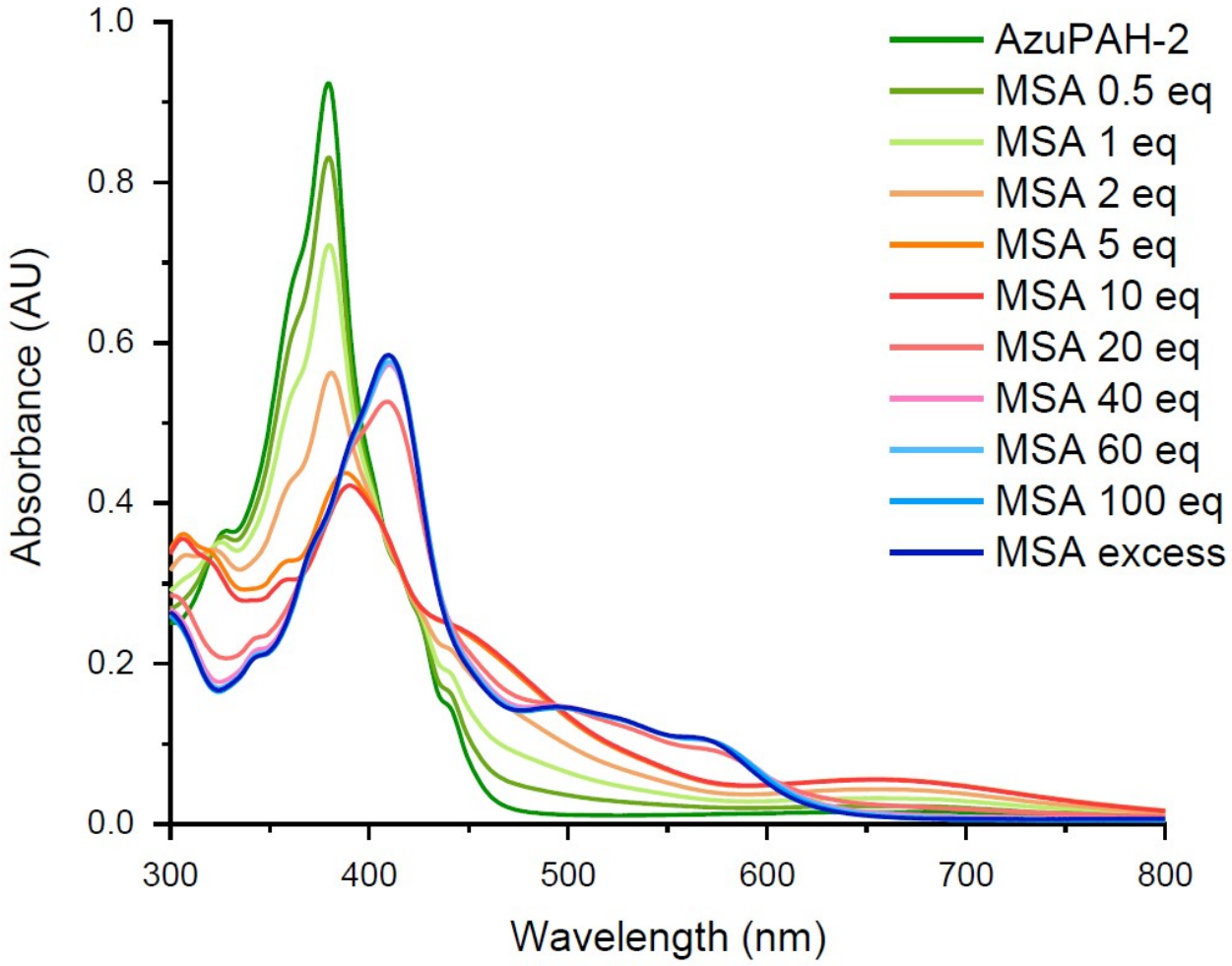


Fig. S46: UV-visible absorption spectra of compound **2** in solution of CH_2Cl_2 upon addition of various amount of MSA.

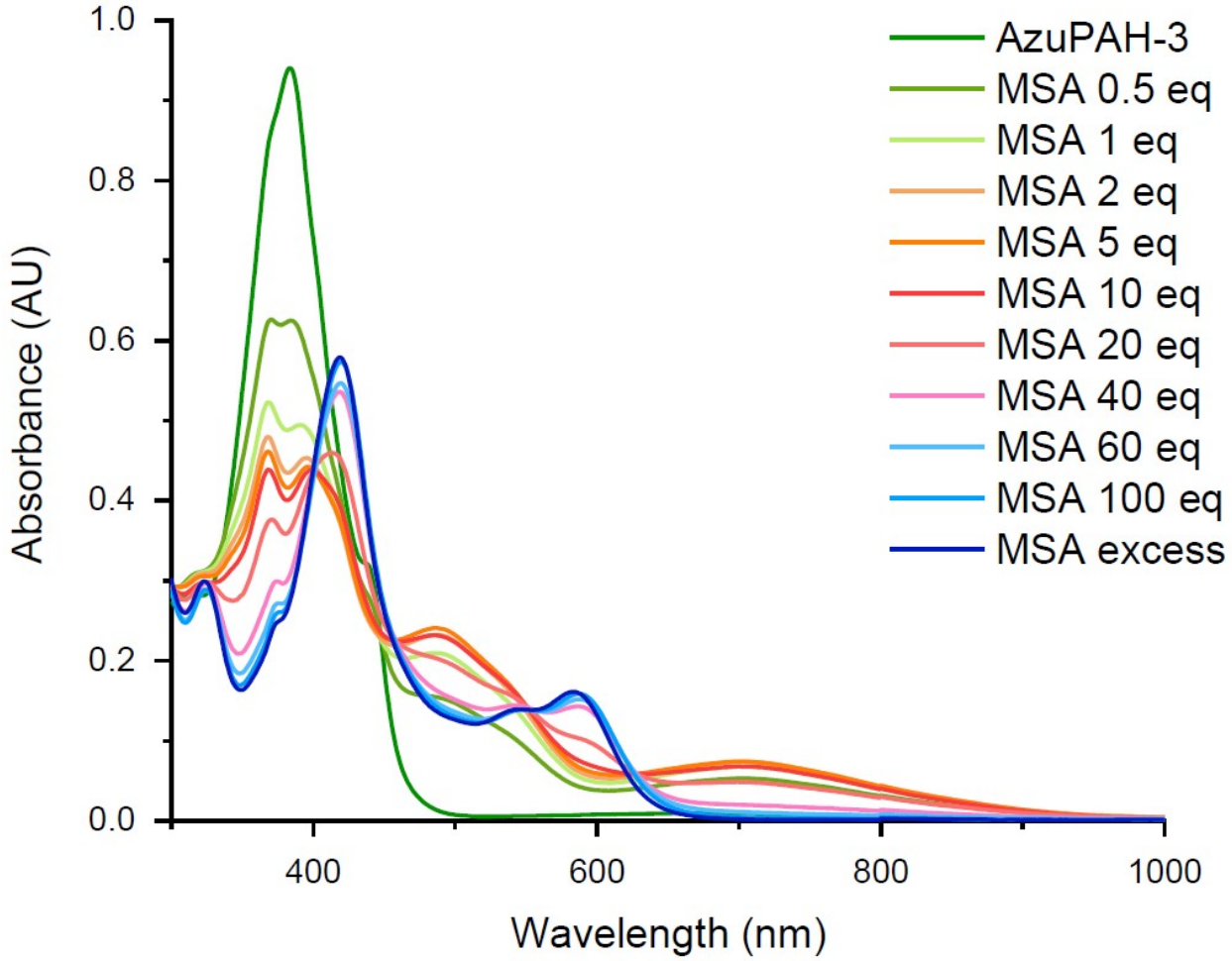


Fig. S47: UV-visible absorption spectra of compound **3** in solution of CH_2Cl_2 upon addition of various amount of MSA.

Cyclic Voltammetry

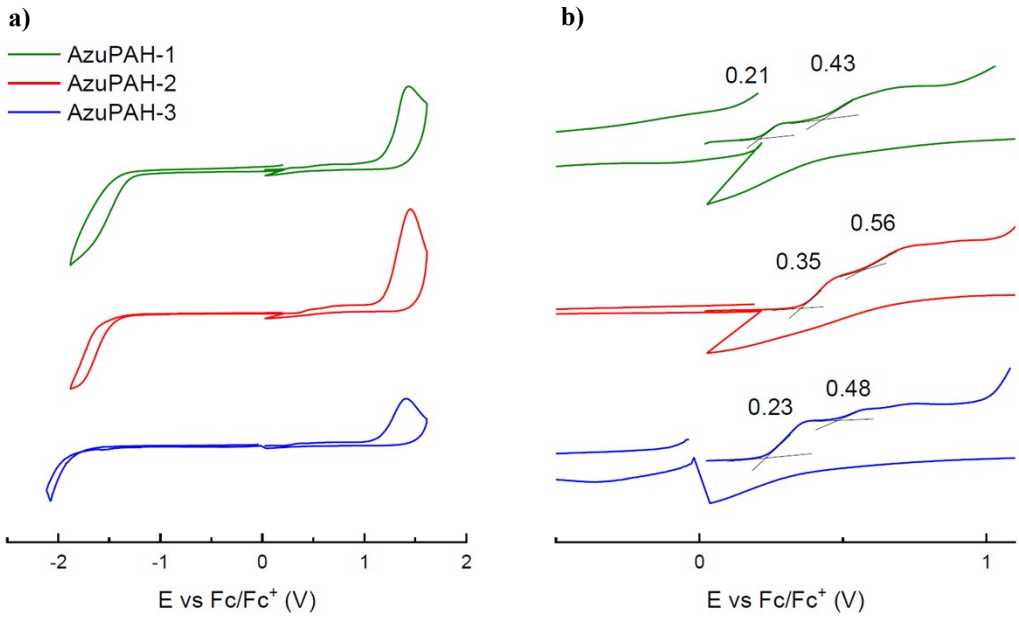


Fig. S48: Electrochemical properties of **AzuPAH-1-3**, a) Cyclic voltammetry of compounds AzuPAH-**1**, -**2** and -**3** in DCM solution with 0.1M $[Bu_4N][PF_6]$ as the electrolyte with a scan rate of 50 $mV \cdot s^{-1}$. b) Zoom of the oxidation states.

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[5] Electron correlation was partially taken into account using the M06-2X[6] functional and the double-ζ quality plus polarization functions def2-SVP[7] basis set for all atoms. All species were characterized by frequency calculations,[8] and have positive definite Hessian matrices. This level is denoted B3LYP-D3/def2-SVP, which was proven to provide good results for strongly related systems.[9,10] Calculations of the absorption spectrum were accomplished using time-

dependent density functional theory (TD-DFT)[11] at the B3LYP/def2-SVP level using the optimized geometries. The assignment of the excitation energies to the experimental bands was performed on the basis of the energy values and oscillator strengths. The B3LYP Hamiltonian was chosen because it was proven to provide reasonable UV-vis spectra for a variety of chromophores.[12] For the TD-DFT calculations, solvent effects (solvent = CH_2Cl_2) were taken into account by using the Polarizable Continuum Model (PCM).[13–15]

The aromaticity of the considered species has been assessed by the computation of the NICS[16] values computed using the gauge invariant atomic orbital (GIAO) method[17] at the B3LYP/def2-SVP level. Ring currents were computed by means of the the Anisotropy of the Induced Current Density (ACID) method.[18,19]

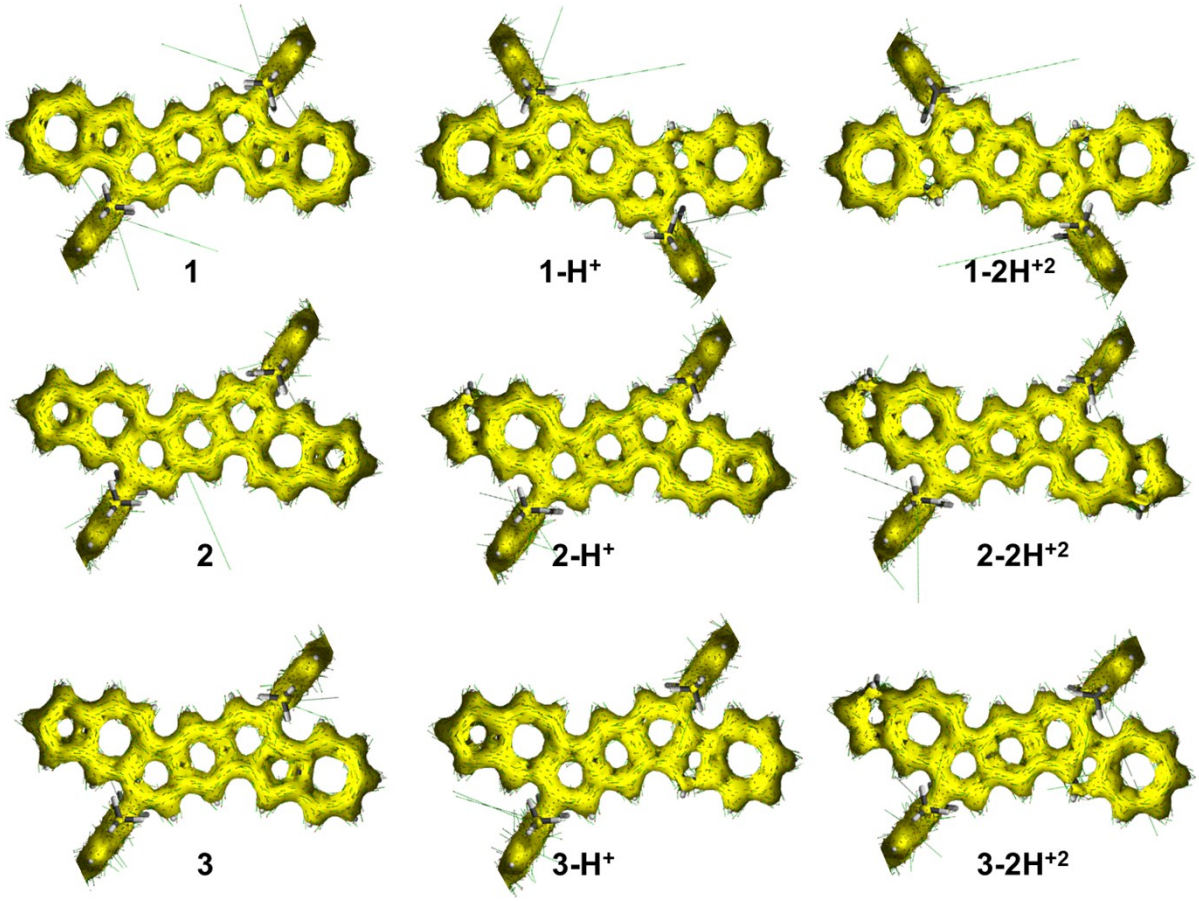


Figure S49. AICD plots for compounds **AzuPAH-1-3** (isosurface value of 0.04 a.u.)

Cartesian coordinates (in Å) of all the stationary points discussed in the text. All calculations have been performed at the M06-2X/def2-SVP level.

1

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C	-2.333670000	1.640380000	0.017008000
C	-1.135687000	0.840118000	0.009860000
C	-1.291657000	-0.582679000	-0.045320000
C	-2.612514000	-1.152529000	-0.090285000
C	-3.749487000	-0.392181000	-0.083568000
C	0.148379000	1.388938000	0.053782000
C	-0.148339000	-1.389064000	-0.053846000
C	1.135729000	-0.840245000	-0.009916000
C	1.291701000	0.582553000	0.045256000
C	2.612555000	1.152403000	0.090223000
H	2.702572000	2.240951000	0.131459000
C	3.749530000	0.392050000	0.083562000
C	3.614322000	-1.041319000	0.029088000
C	2.333710000	-1.640504000	-0.017058000
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H	-2.702533000	-2.241076000	-0.131555000
H	-0.270153000	-2.473351000	-0.095967000
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C	-5.704962000	-1.300397000	-1.374852000
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H	-5.741791000	-1.407475000	3.222337000
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H	-5.642222000	-1.122228000	-3.526568000
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C	5.704834000	1.300411000	1.374973000
C	7.005644000	1.998647000	-1.010521000
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H	7.497831000	2.261310000	-1.946385000
H	7.471586000	2.086901000	2.350474000
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H	4.857548000	0.044526000	-2.482828000
H	4.134558000	1.653216000	-2.488332000
H	5.742297000	1.406937000	-3.222220000
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H	5.641886000	1.122355000	3.526690000
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H	4.792832000	-0.180392000	2.648876000
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H	9.746256000	2.312347000	-1.446136000
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H	10.488132000	3.616532000	-0.468968000

1-H$^+$

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C	-3.737143000	0.412031000	0.074403000
C	0.166635000	-1.386871000	-0.055616000
C	-0.130864000	1.402378000	0.054073000
C	1.149984000	0.845214000	0.012574000
C	1.307565000	-0.585608000	-0.043041000
C	2.625303000	-1.158690000	-0.085005000
H	2.717007000	-2.246423000	-0.125952000
C	3.761318000	-0.394895000	-0.076822000

C	3.626898000	1.037212000	-0.023625000
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H	0.286090000	-2.472074000	-0.098700000
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H	-1.936634000	-3.509988000	-0.990805000
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C	-3.883835000	-3.343772000	-0.075805000
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C	-6.988645000	2.049143000	-0.982090000
C	-6.991903000	1.780874000	1.424281000
C	-7.633430000	2.200992000	0.249388000
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H	-4.736308000	0.258801000	-2.544243000
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H	-4.106841000	1.902997000	-2.435204000
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C	5.748999000	-1.401544000	1.068494000
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C	7.020058000	-1.988042000	1.018095000
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H	7.481249000	-2.083709000	-2.344363000
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H	4.866572000	-0.041226000	2.494570000
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H	5.760561000	-1.396344000	3.230472000
C	5.022357000	-0.907223000	-2.649319000
H	5.649182000	-1.130255000	-3.521335000
H	4.065423000	-1.437126000	-2.762099000
H	4.791567000	0.169295000	-2.651939000
O	8.853708000	-2.789338000	-0.353140000
C	9.563513000	-3.157493000	0.801683000
H	9.770054000	-2.284984000	1.443027000
H	9.014369000	-3.912005000	1.388302000
H	10.512424000	-3.586665000	0.463260000
H	-1.914970000	-3.575625000	0.778087000

1-2H^{2+}

C	3.590317000	1.011446000	0.002736000
C	2.334802000	1.601008000	-0.032843000
C	1.138294000	0.826838000	-0.017595000
C	1.287899000	-0.601449000	0.037181000
C	2.603218000	-1.175516000	0.079325000
C	3.746279000	-0.424082000	0.066386000
C	-0.140241000	1.398910000	-0.053699000
C	0.140252000	-1.398900000	0.053681000
C	-1.138283000	-0.826829000	0.017579000
C	-1.287888000	0.601460000	-0.037200000
C	-2.603209000	1.175525000	-0.079337000
H	-2.692956000	2.263254000	-0.129928000
C	-3.746268000	0.424089000	-0.066388000
C	-3.590303000	-1.011437000	-0.002757000
C	-2.334791000	-1.600998000	0.032822000
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H	2.692962000	-2.263244000	0.129928000
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C	2.446001000	3.088982000	-0.085875000
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H	5.957289000	6.104310000	-0.146614000
C	6.929186000	4.230605000	-0.086857000
H	7.884415000	4.760748000	-0.093987000
C	5.086363000	-1.075190000	0.128985000
C	5.717673000	-1.495418000	-1.051258000
C	5.730111000	-1.217481000	1.378317000
C	7.000625000	-2.052607000	-0.984962000

C	7.003381000	-1.769582000	1.421752000
C	7.648168000	-2.193659000	0.247971000
H	7.481256000	-2.377265000	-1.907057000
H	7.530800000	-1.898618000	2.367840000
C	5.036357000	-1.333189000	-2.387062000
H	4.724484000	-0.290678000	-2.555463000
H	5.699883000	-1.627732000	-3.208939000
H	4.127183000	-1.949261000	-2.446031000
C	5.054317000	-0.756430000	2.644291000
H	5.692159000	-0.931714000	3.518663000
H	4.817781000	0.319315000	2.604951000
H	4.102441000	-1.284569000	2.799890000
O	8.871169000	-2.713605000	0.403039000
C	9.560612000	-3.199256000	-0.727000000
H	8.997465000	-4.007742000	-1.218850000
H	9.753708000	-2.393778000	-1.453348000
H	10.514698000	-3.592881000	-0.363300000
C	-2.445993000	-3.088972000	0.085845000
H	-1.967507000	-3.582336000	-0.778166000
C	-4.604397000	-2.072124000	0.033235000
C	-3.930105000	-3.329872000	0.080418000
C	-4.449672000	-4.615016000	0.117622000
H	-3.710527000	-5.420823000	0.149486000
C	-6.000508000	-1.874455000	0.029419000
H	-6.340493000	-0.838071000	0.004018000
C	-7.010487000	-2.829579000	0.051536000
H	-8.025030000	-2.423570000	0.037967000
C	-5.790861000	-5.024905000	0.117424000
H	-5.957317000	-6.104270000	0.146562000
C	-6.929198000	-4.230557000	0.086756000
H	-7.884434000	-4.760689000	0.093871000
C	-5.086360000	1.075182000	-0.128961000
C	-5.717641000	1.495415000	1.051297000
C	-5.730152000	1.217439000	-1.378273000
C	-7.000598000	2.052593000	0.985033000
C	-7.003430000	1.769527000	-1.421676000
C	-7.648182000	2.193620000	-0.247882000
H	-7.481203000	2.377262000	1.907138000
H	-7.530881000	1.898538000	-2.367749000
C	-5.036277000	1.333219000	2.387080000
H	-4.724363000	0.290719000	2.555480000
H	-4.127120000	1.949321000	2.446013000
H	-5.699785000	1.627746000	3.208976000
C	-5.054398000	0.756364000	-2.644260000
H	-5.692271000	0.931624000	-3.518614000
H	-4.102530000	1.284504000	-2.799904000
H	-4.817857000	-0.319378000	-2.604902000
O	-8.871193000	2.713553000	-0.402921000
C	-9.560604000	3.199221000	0.727131000
H	-9.753674000	2.393755000	1.453499000
H	-8.997447000	4.007719000	1.218949000
H	-10.514704000	3.592834000	0.363452000
H	1.967501000	3.582345000	0.778128000
H	-1.985359000	-3.519695000	0.992057000

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C	3.623099000	-1.117725000	-0.139311000
C	2.349103000	-1.738879000	-0.250108000
C	1.150283000	-0.886082000	-0.216691000
C	1.285485000	0.534981000	-0.220485000
C	2.594954000	1.109621000	-0.174407000
C	3.713899000	0.341776000	-0.107453000
C	-0.157726000	-1.378923000	-0.140082000
C	0.160687000	1.367275000	-0.240238000
C	-1.148586000	0.871972000	-0.233411000
C	-1.282048000	-0.545813000	-0.134842000
C	-2.588259000	-1.114221000	-0.000921000
H	-2.681463000	-2.200158000	0.077674000
C	-3.704709000	-0.341992000	0.056249000
C	-3.616691000	1.112022000	-0.075754000
C	-2.348791000	1.722160000	-0.279023000
H	-0.355627000	-2.444286000	-0.042574000
H	2.689520000	2.198284000	-0.172533000
H	0.360512000	2.436626000	-0.223165000
C	2.116712000	-3.141942000	-0.418465000
H	1.078308000	-3.406516000	-0.598358000
C	4.882589000	-1.795784000	-0.058595000
C	2.948593000	-4.235363000	-0.425839000
C	5.036205000	1.038520000	-0.024002000
C	5.559509000	1.398633000	1.225355000
C	5.745174000	1.346627000	-1.204155000
C	6.786032000	2.072187000	1.297523000
C	6.960488000	2.015738000	-1.113057000
C	7.486512000	2.384415000	0.130901000
H	7.178074000	2.342430000	2.277410000
H	7.532578000	2.267765000	-2.007023000
C	4.815909000	1.050147000	2.489641000
H	4.607807000	-0.029568000	2.538091000
H	5.392295000	1.331934000	3.379908000
H	3.842458000	1.560314000	2.529437000
C	5.195658000	0.941226000	-2.547129000
H	5.880655000	1.224741000	-3.355809000
H	5.034930000	-0.146899000	-2.592868000
H	4.219687000	1.412817000	-2.732542000
O	8.672783000	3.031958000	0.108761000
C	9.243079000	3.421988000	1.328921000
H	8.589159000	4.121223000	1.876167000
H	9.453257000	2.552636000	1.973993000
H	10.185753000	3.926128000	1.089373000
C	-2.124897000	3.109675000	-0.553791000
H	-1.095106000	3.358896000	-0.795037000
C	-4.872302000	1.796344000	0.011515000
C	-2.957516000	4.201524000	-0.602047000
C	-5.022454000	-1.029671000	0.233802000
C	-5.758788000	-1.435342000	-0.887819000
C	-5.512398000	-1.283265000	1.532086000
C	-6.979391000	-2.100809000	-0.714251000
C	-6.726199000	-1.943975000	1.684938000
C	-7.463804000	-2.358651000	0.569611000
H	-7.538269000	-2.408018000	-1.597525000
H	-7.132562000	-2.152881000	2.675513000
C	-5.249420000	-1.145836000	-2.276793000

H	-5.074760000	-0.067760000	-2.414217000
H	-4.287204000	-1.646759000	-2.457260000
H	-5.964023000	-1.479996000	-3.039574000
C	-4.733694000	-0.826992000	2.738552000
H	-5.276503000	-1.048500000	3.665860000
H	-3.750523000	-1.317741000	2.782431000
H	-4.543784000	0.256481000	2.695811000
O	-8.628859000	-2.993773000	0.827183000
C	-9.409867000	-3.420731000	-0.256283000
H	-9.725489000	-2.572868000	-0.886796000
H	-8.868612000	-4.148399000	-0.883636000
H	-10.298153000	-3.903069000	0.166186000
C	-4.345209000	4.278628000	-0.378496000
C	-5.218105000	3.118404000	-0.089634000
H	-2.472542000	5.151071000	-0.847922000
H	-5.722860000	1.137306000	0.204666000
C	-6.546081000	3.631035000	0.045922000
H	-7.426174000	3.027838000	0.260443000
C	-5.151424000	5.402944000	-0.407762000
H	-4.812993000	6.419349000	-0.601663000
C	-6.495807000	4.998576000	-0.142890000
H	-7.350565000	5.673013000	-0.100214000
C	4.344723000	-4.298274000	-0.257164000
C	5.226733000	-3.121850000	-0.085769000
C	5.151273000	-5.422635000	-0.244932000
H	4.807016000	-6.449577000	-0.354896000
C	6.560528000	-3.625099000	0.025878000
H	7.448008000	-3.009440000	0.159119000
C	6.505077000	-5.002234000	-0.067365000
H	7.362463000	-5.672807000	-0.017198000
H	2.455438000	-5.199171000	-0.584533000
H	5.739093000	-1.125900000	0.054131000

2-H$^+$

C	-3.620069000	1.069592000	-0.142077000
C	-2.327086000	1.707451000	-0.304266000
C	-1.120589000	0.875870000	-0.260002000
C	-1.253850000	-0.546459000	-0.262470000
C	-2.560284000	-1.122856000	-0.199919000
C	-3.702194000	-0.382010000	-0.109493000
C	0.175543000	1.385323000	-0.178958000
C	-0.127512000	-1.370675000	-0.290468000
C	1.180079000	-0.862520000	-0.291399000
C	1.308495000	0.556965000	-0.174111000
C	2.605089000	1.129302000	-0.021891000
H	2.700249000	2.213700000	0.066174000
C	3.721754000	0.351547000	0.047362000
C	3.638740000	-1.098072000	-0.101950000
C	2.377921000	-1.709897000	-0.347781000
H	0.363891000	2.452781000	-0.069212000
H	-2.643966000	-2.212964000	-0.200518000
H	-0.311531000	-2.442688000	-0.267847000
C	-2.139560000	3.075760000	-0.566257000
H	-1.112970000	3.347621000	-0.807064000
C	-4.852296000	1.743127000	-0.003510000
C	-3.003128000	4.173712000	-0.596461000

C	-5.018126000	-1.082350000	-0.001310000
C	-5.490886000	-1.490858000	1.254929000
C	-5.772670000	-1.340322000	-1.167165000
C	-6.718657000	-2.157086000	1.347856000
C	-6.988150000	-2.002008000	-1.052993000
C	-7.469625000	-2.416602000	0.197470000
H	-7.073320000	-2.469572000	2.329213000
H	-7.594901000	-2.221857000	-1.932290000
C	-4.689671000	-1.215520000	2.502754000
H	-4.431065000	-0.148872000	2.587220000
H	-5.246690000	-1.503846000	3.402450000
H	-3.740923000	-1.772537000	2.497396000
C	-5.264650000	-0.910135000	-2.519578000
H	-5.983837000	-1.161674000	-3.308163000
H	-5.084814000	0.175750000	-2.555678000
H	-4.308786000	-1.399714000	-2.757331000
O	-8.653795000	-3.048881000	0.194858000
C	-9.182359000	-3.509033000	1.415102000
H	-8.509343000	-4.239082000	1.892532000
H	-9.366268000	-2.675550000	2.112119000
H	-10.133463000	-3.996835000	1.179003000
C	2.157586000	-3.086226000	-0.671565000
H	1.137511000	-3.328157000	-0.958766000
C	4.896044000	-1.781113000	0.011607000
C	2.994784000	-4.175752000	-0.726960000
C	5.034007000	1.038955000	0.255540000
C	5.801835000	1.431135000	-0.849901000
C	5.484457000	1.300291000	1.566687000
C	7.018416000	2.093466000	-0.645830000
C	6.695212000	1.957344000	1.747852000
C	7.467396000	2.360691000	0.650195000
H	7.604899000	2.391122000	-1.514187000
H	7.075399000	2.171658000	2.747498000
C	5.333467000	1.128918000	-2.250816000
H	5.184070000	0.047294000	-2.392269000
H	4.369029000	1.614211000	-2.460938000
H	6.061877000	1.472977000	-2.995326000
C	4.671765000	0.854637000	2.755120000
H	5.194005000	1.074591000	3.694125000
H	3.692880000	1.355979000	2.777501000
H	4.474759000	-0.227788000	2.714717000
O	8.622169000	2.990665000	0.936188000
C	9.446547000	3.403431000	-0.124226000
H	9.777118000	2.546574000	-0.733584000
H	8.932379000	4.130144000	-0.774184000
H	10.321832000	3.881972000	0.327284000
C	4.372436000	-4.254563000	-0.459042000
C	5.238951000	-3.099524000	-0.108934000
H	2.521867000	-5.118284000	-1.017809000
H	5.737943000	-1.125193000	0.246205000
C	6.560276000	-3.619150000	0.056681000
H	7.434443000	-3.025068000	0.315589000
C	5.178904000	-5.375690000	-0.492151000
H	4.849745000	-6.386693000	-0.725744000
C	6.515358000	-4.980181000	-0.170321000
H	7.367180000	-5.657125000	-0.117801000
C	-4.360630000	4.202862000	-0.338251000

C	-5.194114000	3.091603000	-0.050349000
C	-5.207031000	5.444149000	-0.336543000
H	-5.172233000	5.953902000	-1.315554000
C	-6.554826000	3.591293000	0.146698000
H	-7.404009000	2.950690000	0.380992000
C	-6.573988000	4.928663000	-0.010777000
H	-7.451528000	5.567966000	0.078546000
H	-2.533419000	5.130755000	-0.838283000
H	-5.700052000	1.075622000	0.173749000
H	-4.843604000	6.179007000	0.403103000

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C	-3.648183000	1.064660000	-0.122920000
C	-2.363136000	1.706904000	-0.276411000
C	-1.149262000	0.871133000	-0.241993000
C	-1.281409000	-0.546483000	-0.240971000
C	-2.589368000	-1.133585000	-0.185793000
C	-3.728854000	-0.396738000	-0.099030000
C	0.148646000	1.386703000	-0.169426000
C	-0.151010000	-1.371889000	-0.265592000
C	1.147943000	-0.853888000	-0.264555000
C	1.278536000	0.560368000	-0.165504000
C	2.583391000	1.140847000	-0.027302000
H	2.663868000	2.228151000	0.047148000
C	3.720019000	0.398410000	0.047225000
C	3.642171000	-1.057730000	-0.080180000
C	2.363151000	-1.686832000	-0.316439000
H	0.334973000	2.454908000	-0.070568000
H	-2.671227000	-2.223307000	-0.192302000
H	-0.338941000	-2.444172000	-0.243952000
C	-2.174986000	3.078753000	-0.512633000
H	-1.148312000	3.365650000	-0.733696000
C	-4.887146000	1.724587000	0.010782000
C	-3.045457000	4.172667000	-0.542428000
C	-5.045445000	-1.095242000	-0.008298000
C	-5.532252000	-1.507970000	1.241777000
C	-5.787371000	-1.339772000	-1.186054000
C	-6.764120000	-2.167015000	1.316398000
C	-7.006305000	-1.995448000	-1.088366000
C	-7.504947000	-2.415912000	0.155314000
H	-7.133326000	-2.482323000	2.291445000
H	-7.605850000	-2.205862000	-1.974880000
C	-4.743619000	-1.244494000	2.500495000
H	-4.467537000	-0.182415000	2.590329000
H	-5.318741000	-1.520598000	3.392314000
H	-3.806567000	-1.821364000	2.512160000
C	-5.262592000	-0.904452000	-2.530749000
H	-5.982093000	-1.132713000	-3.325807000
H	-5.062021000	0.178311000	-2.557294000
H	-4.316873000	-1.412526000	-2.771438000
O	-8.687914000	-3.038113000	0.134477000
C	-9.245024000	-3.500746000	1.344622000
H	-8.587248000	-4.240267000	1.827629000
H	-9.433561000	-2.667774000	2.040188000
H	-10.195649000	-3.977187000	1.086375000

C	2.183785000	-3.039533000	-0.649896000
H	1.165265000	-3.309254000	-0.924103000
C	4.877420000	-1.726168000	0.045561000
C	3.055100000	-4.130814000	-0.721211000
C	5.030756000	1.087452000	0.239828000
C	5.781071000	1.486961000	-0.877166000
C	5.499981000	1.337111000	1.548920000
C	7.002918000	2.140660000	-0.685977000
C	6.716488000	1.983846000	1.715038000
C	7.475526000	2.393860000	0.606995000
H	7.575994000	2.449542000	-1.559244000
H	7.112081000	2.193988000	2.709535000
C	5.279699000	1.223880000	-2.275318000
H	5.043759000	0.159154000	-2.427633000
H	4.358228000	1.789240000	-2.480302000
H	6.026155000	1.513695000	-3.024381000
C	4.694515000	0.907162000	2.748634000
H	5.241483000	1.099922000	3.679022000
H	3.737229000	1.447327000	2.799454000
H	4.454979000	-0.167302000	2.711456000
O	8.629753000	3.010425000	0.880464000
C	9.440246000	3.459207000	-0.182761000
H	9.768548000	2.619108000	-0.814933000
H	8.909294000	4.198858000	-0.802333000
H	10.315896000	3.931674000	0.272663000
C	4.406982000	-4.167754000	-0.435588000
C	5.232033000	-3.069676000	-0.067059000
H	2.596415000	-5.076174000	-1.022810000
H	5.715202000	-1.061926000	0.275687000
C	6.586152000	-3.570732000	0.134871000
H	7.427280000	-2.942820000	0.425453000
C	5.258880000	-5.401330000	-0.481332000
H	4.881690000	-6.179726000	0.205894000
C	6.613189000	-4.899955000	-0.095083000
H	7.490937000	-5.541260000	-0.018619000
C	-4.406317000	4.191436000	-0.301291000
C	-5.240670000	3.072441000	-0.029104000
C	-5.259059000	5.425282000	-0.299035000
H	-5.217356000	5.943409000	-1.274122000
C	-6.601891000	3.559754000	0.158073000
H	-7.451159000	2.914689000	0.379034000
C	-6.624422000	4.900569000	0.009521000
H	-7.505979000	5.535524000	0.094630000
H	-2.578773000	5.135370000	-0.767024000
H	-5.730183000	1.047309000	0.174115000
H	-4.906880000	6.159795000	0.447235000
H	5.249778000	-5.858148000	-1.487419000

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C	-3.530602000	1.077357000	-0.086650000
C	-2.248380000	1.674115000	-0.093000000
C	-1.055971000	0.866255000	-0.096323000
C	-1.212801000	-0.554120000	-0.100735000
C	-2.536035000	-1.121850000	-0.088757000
C	-3.670003000	-0.357122000	-0.082252000

C	0.233867000	1.391694000	-0.077587000
C	-0.077040000	-1.370934000	-0.113260000
C	1.229804000	-0.857252000	-0.124436000
C	1.364182000	0.566688000	-0.078780000
C	2.670096000	1.144757000	-0.008629000
H	2.757696000	2.233550000	0.023122000
C	3.792594000	0.381634000	0.047614000
C	3.707595000	-1.076353000	-0.017332000
C	2.436908000	-1.700738000	-0.158005000
H	0.380160000	2.473223000	-0.049112000
H	-2.631033000	-2.210749000	-0.087036000
H	-0.261606000	-2.442585000	-0.089149000
C	-2.378820000	3.089637000	-0.094064000
H	-1.566179000	3.813842000	-0.099871000
C	-4.505212000	2.139044000	-0.084381000
C	-3.725277000	3.411990000	-0.089231000
C	-4.230914000	4.732582000	-0.089538000
H	-3.461890000	5.511117000	-0.093154000
C	-5.878388000	2.012588000	-0.080524000
H	-6.270050000	0.993882000	-0.078156000
C	-6.869963000	3.025097000	-0.080026000
H	-7.898523000	2.658285000	-0.078141000
C	-5.535992000	5.169975000	-0.086216000
H	-5.680431000	6.252357000	-0.087369000
C	-6.720521000	4.394976000	-0.082302000
H	-7.650421000	4.969934000	-0.081358000
C	-5.009117000	-1.017918000	-0.070247000
C	-5.630138000	-1.317246000	1.149853000
C	-5.660266000	-1.306597000	-1.287570000
C	-6.902310000	-1.904902000	1.155961000
C	-6.922940000	-1.888847000	-1.262418000
C	-7.549942000	-2.192080000	-0.047549000
H	-7.371455000	-2.128802000	2.113458000
H	-7.454350000	-2.122030000	-2.186193000
C	-4.947355000	-0.980728000	2.450656000
H	-4.706573000	0.092389000	2.496680000
H	-5.581381000	-1.233340000	3.310069000
H	-3.994604000	-1.520821000	2.547296000
C	-5.003877000	-0.957703000	-2.597671000
H	-5.652564000	-1.211483000	-3.445370000
H	-4.772631000	0.117726000	-2.641288000
H	-4.048621000	-1.489644000	-2.713125000
O	-8.776053000	-2.755774000	-0.133331000
C	-9.446022000	-3.079045000	1.055052000
H	-8.878386000	-3.810601000	1.653852000
H	-9.632517000	-2.183789000	1.671533000
H	-10.405920000	-3.520856000	0.765818000
C	2.221953000	-3.103599000	-0.356372000
H	1.189188000	-3.376546000	-0.551852000
C	4.969844000	-1.749027000	0.066366000
C	3.061777000	-4.190481000	-0.374361000
C	5.110448000	1.083243000	0.158021000
C	5.812223000	1.445023000	-1.000138000
C	5.635705000	1.394790000	1.429635000
C	7.033065000	2.123826000	-0.890121000
C	6.849123000	2.067819000	1.519607000
C	7.552077000	2.438367000	0.367146000

H	7.564587000	2.396128000	-1.801335000
H	7.282221000	2.320616000	2.488399000
C	5.265506000	1.093712000	-2.360302000
H	5.095447000	0.009652000	-2.446705000
H	4.294283000	1.579679000	-2.533106000
H	5.955167000	1.400227000	-3.156976000
C	4.894896000	0.985457000	2.676106000
H	5.460628000	1.252282000	3.577475000
H	3.908197000	1.468504000	2.725154000
H	4.714695000	-0.100478000	2.685687000
O	8.720427000	3.089966000	0.564447000
C	9.467213000	3.474373000	-0.558018000
H	9.770039000	2.602215000	-1.161164000
H	8.903709000	4.171852000	-1.200011000
H	10.364274000	3.978841000	-0.182403000
C	4.456268000	-4.249467000	-0.188696000
C	5.326081000	-3.071395000	0.018091000
H	2.576554000	-5.154021000	-0.557653000
H	5.820128000	-1.075892000	0.204135000
C	6.662370000	-3.566699000	0.139670000
H	7.542824000	-2.947212000	0.299443000
C	5.270517000	-5.368504000	-0.186808000
H	4.935190000	-6.395503000	-0.321354000
C	6.618621000	-4.942059000	0.018802000
H	7.480075000	-5.607450000	0.069172000

3-H$^+$

103
symmetry c1

C	9.156010000	-5.292483000	-0.052086000
C	7.886029000	-5.870961000	-0.077539000
C	6.704484000	-5.089929000	-0.085504000
C	6.859002000	-3.666702000	-0.074413000
C	8.177929000	-3.101340000	-0.045027000
C	9.318607000	-3.857295000	-0.035650000
C	5.412636000	-5.631633000	-0.080514000
C	5.718276000	-2.857168000	-0.093345000
C	4.417787000	-3.382313000	-0.128240000
C	4.283648000	-4.812695000	-0.082397000
C	2.978930000	-5.392647000	-0.007852000
H	2.886792000	-6.480616000	0.017340000
C	1.861502000	-4.623636000	0.071014000
C	1.947264000	-3.164252000	0.005972000
C	3.211777000	-2.538350000	-0.173843000
H	5.269900000	-6.714418000	-0.057970000
H	8.272007000	-2.012464000	-0.035924000
H	5.886947000	-1.783711000	-0.050794000
C	7.982513000	-7.359798000	-0.090916000
H	7.514988000	-7.806563000	-0.985434000
C	10.147250000	-6.356499000	-0.045046000
C	9.463384000	-7.616298000	-0.074212000
C	9.971193000	-8.900985000	-0.087683000
H	9.224804000	-9.700245000	-0.111658000
C	11.551020000	-6.176584000	-0.010257000
H	11.900202000	-5.143671000	0.020403000

C	12.546450000	-7.139018000	-0.012023000
H	13.564848000	-6.743716000	0.015122000
C	11.313481000	-9.325468000	-0.077417000
H	11.467811000	-10.406640000	-0.096740000
C	12.453904000	-8.544758000	-0.044792000
H	13.405280000	-9.081211000	-0.041840000
C	10.660982000	-3.206115000	-0.014711000
C	11.253456000	-2.862213000	1.209234000
C	11.343301000	-2.974096000	-1.229050000
C	12.533649000	-2.293769000	1.221860000
C	12.613797000	-2.412954000	-1.195476000
C	13.217122000	-2.066504000	0.023120000
H	12.981453000	-2.029059000	2.178988000
H	13.168792000	-2.217318000	-2.113952000
C	10.531026000	-3.117019000	2.508100000
H	10.228429000	-4.171839000	2.596999000
H	11.162381000	-2.866740000	3.369350000
H	9.610016000	-2.519672000	2.572267000
C	10.709460000	-3.351337000	-2.543133000
H	11.373463000	-3.117752000	-3.384002000
H	10.474302000	-4.427199000	-2.579008000
H	9.759940000	-2.817054000	-2.690910000
O	14.444766000	-1.528083000	-0.056660000
C	15.084507000	-1.115253000	1.126785000
H	14.495409000	-0.347031000	1.652538000
H	15.259399000	-1.965216000	1.806248000
H	16.047879000	-0.689368000	0.828720000
C	3.428336000	-1.145617000	-0.420955000
H	4.452194000	-0.881754000	-0.670630000
C	0.686612000	-2.492083000	0.125860000
C	2.587699000	-0.056998000	-0.439241000
C	0.543672000	-5.320301000	0.199700000
C	-0.187985000	-5.652048000	-0.949110000
C	0.049909000	-5.650524000	1.479296000
C	-1.410652000	-6.322595000	-0.820726000
C	-1.166121000	-6.314438000	1.585796000
C	-1.901767000	-6.657546000	0.443687000
H	-1.968352000	-6.572643000	-1.722454000
H	-1.578818000	-6.580971000	2.559674000
C	0.325955000	-5.276943000	-2.315975000
H	0.485667000	-4.190342000	-2.392751000
H	1.294242000	-5.756453000	-2.521373000
H	-0.380297000	-5.574902000	-3.100704000
C	0.822848000	-5.269431000	2.715676000
H	0.271144000	-5.540011000	3.624187000
H	1.801888000	-5.770164000	2.741679000
H	1.018752000	-4.186291000	2.739737000
O	-3.065756000	-7.300300000	0.658147000
C	-3.853417000	-7.656300000	-0.449246000
H	-4.164244000	-6.768650000	-1.024053000
H	-3.317050000	-8.348298000	-1.118972000
H	-4.743044000	-8.157195000	-0.053304000
C	1.204891000	0.005667000	-0.197654000
C	0.337179000	-1.169772000	0.070492000
H	3.064029000	0.900214000	-0.670631000
H	-0.157940000	-3.162268000	0.303911000
C	-0.989269000	-0.666396000	0.234058000

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H       -1.865824000     -1.277153000      0.440780000
C        0.393603000      1.124435000     -0.188510000
H        0.722562000      2.147800000     -0.360070000
C       -0.946405000      0.706067000      0.081613000
H       -1.803195000      1.375234000      0.151544000
H        7.495457000     -7.823475000      0.784585000
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3-2H^{2+}

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90
symmetry c1
C        3.517178000     -1.048751000     -0.079946000
C        2.260056000     -1.637532000     -0.106321000
C        1.071280000     -0.856955000     -0.116063000
C        1.220314000      0.564198000     -0.102763000
C        2.530974000      1.139414000     -0.073224000
C        3.675482000      0.384102000     -0.065229000
C       -0.220586000     -1.406116000     -0.116359000
C        0.070423000      1.373961000     -0.122872000
C       -1.216403000      0.835763000     -0.160305000
C       -1.348195000     -0.590940000     -0.121879000
C       -2.658065000     -1.176453000     -0.054197000
H       -2.736675000     -2.266368000     -0.039693000
C       -3.796660000     -0.440913000      0.031571000
C       -3.719489000      1.020862000     -0.018091000
C       -2.438937000      1.662954000     -0.210202000
H       -0.357564000     -2.489291000     -0.096065000
H        2.624460000      2.227998000     -0.065553000
H        0.237932000      2.448981000     -0.077748000
C        2.368591000     -3.126919000     -0.120249000
H        1.909971000     -3.580052000     -1.016420000
C        4.530531000     -2.114020000     -0.070238000
C        3.852834000     -3.369470000     -0.101228000
C        4.370373000     -4.657043000     -0.114415000
H        3.630019000     -5.461971000     -0.140632000
C        5.925279000     -1.918529000     -0.030300000
H        6.266257000     -0.882525000      0.002613000
C        6.934615000     -2.876028000     -0.029661000
H        7.949548000     -2.471929000      0.001326000
C        5.709925000     -5.068736000     -0.101464000
H        5.874933000     -6.148587000     -0.121369000
C        6.850506000     -4.275870000     -0.064719000
H        7.804449000     -4.808472000     -0.059873000
C        5.015611000      1.037572000     -0.051694000
C        5.608338000      1.393600000      1.169131000
C        5.696178000      1.249624000     -1.271383000
C        6.890070000      1.957005000      1.172750000
C        6.967545000      1.806737000     -1.245027000
C        7.574245000      2.167858000     -0.030283000
H        7.341007000      2.232089000      2.125450000
H        7.523020000      1.989459000     -2.165876000
C        4.886818000      1.157047000      2.472366000
H        4.573830000      0.106242000      2.574084000
H        5.523717000      1.407175000      3.329216000
H        3.974386000      1.767776000      2.537515000
C        5.060901000      0.857269000     -2.580777000
H        5.725060000      1.079828000     -3.424210000
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H	4.825580000	-0.219145000	-2.607396000
H	4.113410000	1.392957000	-2.737824000
O	8.798135000	2.699196000	-0.119069000
C	9.450751000	3.126339000	1.056094000
H	8.868241000	3.904882000	1.572929000
H	9.626563000	2.283562000	1.743361000
H	10.412931000	3.542837000	0.742869000
C	-2.267564000	3.025493000	-0.504084000
H	-1.250432000	3.308404000	-0.769223000
C	-4.956004000	1.680764000	0.131713000
C	-3.143577000	4.115352000	-0.542955000
C	-5.111628000	-1.138472000	0.153634000
C	-5.839660000	-1.464015000	-1.001347000
C	-5.609019000	-1.469563000	1.433791000
C	-7.066446000	-2.125059000	-0.877669000
C	-6.830137000	-2.121637000	1.533510000
C	-7.566439000	-2.458047000	0.386341000
H	-7.621374000	-2.376597000	-1.780571000
H	-7.246892000	-2.393025000	2.504247000
C	-5.308605000	-1.114906000	-2.369322000
H	-5.072195000	-0.042528000	-2.450356000
H	-4.381046000	-1.665020000	-2.587566000
H	-6.037701000	-1.359146000	-3.151063000
C	-4.828704000	-1.117975000	2.674902000
H	-5.395066000	-1.368540000	3.579607000
H	-3.872568000	-1.661270000	2.710696000
H	-4.587908000	-0.043755000	2.710437000
O	-8.727836000	-3.087484000	0.596328000
C	-9.515238000	-3.466371000	-0.510082000
H	-9.829039000	-2.587531000	-1.095310000
H	-8.971757000	-4.166572000	-1.163795000
H	-10.401132000	-3.964666000	-0.104641000
C	-4.494306000	4.140396000	-0.253288000
C	-5.314058000	3.027076000	0.076233000
H	-2.687611000	5.070720000	-0.815901000
H	-5.793380000	1.005772000	0.329354000
C	-6.669754000	3.515741000	0.299397000
H	-7.508008000	2.874438000	0.568255000
C	-5.350643000	5.372398000	-0.253536000
H	-5.346640000	5.864024000	-1.242962000
C	-6.702204000	4.852165000	0.117963000
H	-7.582149000	5.486857000	0.219743000
H	1.887818000	-3.598324000	0.754839000
H	-4.975352000	6.127382000	0.460106000

References

1 A. Ito, A. Ishii, T. Amaki, K. Fukuda, R. Yamasaki and I. Okamoto, *Tetrahedron Letters*, 2019, **60**, 1929–1933.

2 M. Zhao, A. G. Barrado, K. Sprenger, C. Golz, R. A. Mata and M. Alcarazo, *Org. Lett.*, 2020, **22**, 4932–4937.

3 S. Ito, T. Kubo, N. Morita, Y. Matsui, T. Watanabe, A. Ohta, K. Fujimori, T. Murafuji, Y. Sugihara and A. Tajiri, *Tetrahedron Letters*, 2004, **45**, 2891–2894.

4 J. Lee, B. Hong and A. Lee, *J. Org. Chem.*, 2019, **84**, 9297–9306.

5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. Nakatsuji, *Gaussian09, Revision D*.

6 Y. Zhao and D. G. Truhlar, *Theor Chem Account*, 2008, **120**, 215–241.

7 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

8 J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, 1972, **94**, 2625–2633.

9 Z. Zhou, J. M. Fernández-García, Y. Zhu, P. J. Evans, R. Rodríguez, J. Crassous, Z. Wei, I. Fernández, M. A. Petrukhina and N. Martín, *Angewandte Chemie*, 2022, **134**, e202115747.

10 Z. Zhou, Y. Zhu, J. M. Fernández-García, Z. Wei, I. Fernández, M. A. Petrukhina and N. Martín, *Chem. Commun.*, 2022, **58**, 5574–5577.

11 M. E. Casida, in *Theoretical and Computational Chemistry*, Elsevier, 1996, vol. 4, pp. 391–439.

12 A. Dreuw and M. Head-Gordon, *Chem. Rev.*, 2005, **105**, 4009–4037.

13 S. Miertuš, E. Scrocco and J. Tomasi, *Chemical Physics*, 1981, **55**, 117–129.

14 J. L. Pascual-ahuir, E. Silla and I. Tuñon, *J Comput Chem*, 1994, **15**, 1127–1138.

15 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

16 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. V. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.

17 K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260.

18 R. Herges and D. Geuenich, *J. Phys. Chem. A*, 2001, **105**, 3214–3220.

19 D. Geuenich, K. Hess, F. Köhler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758–3772.