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Supporting Information

A phosphorus-based olefin linked fully conjugated polymeric ligand for palladium-catalysed *trans*-selective dicarbofunctionalization of internal alkynes

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Section SM-I: General Information

All the reactions were performed in oven-dried glassware under an inert atmosphere. Solvents were dried under the standard protocol and were degassed and stored over activated molecular sieves (4 Å). The chemicals were purchased from Sigma Aldrich, Avra Synthesis, TCI, Alfa Aesar, Spectrochem, BLDpharm, and Combi-Blocks, and used without further purification unless otherwise mentioned. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F254/ 0.25 mm) were used. Visualization was accomplished by UV light (254 nm and 365 nm). Thermal reactions have been performed under oil-bath, the reaction temperatures are disclosed as the bath temperature surrounding the vessel unless otherwise mentioned.

Nuclear magnetic resonance (NMR) spectra were collected using BRUKER (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 471 MHz, ^{31}P: 162 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz, ^{31}P: 130 MHz) instrument. NMR data was taken in the ppm unit and referenced against the TMS residual peaks. Coupling constants (*J*) are reported in Hertz (Hz). Coupling patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sep (septet), dd (doublet of doublet), ddd (doublet of doublet of doublet), td (triplet of doublet), dt (doublet of triplet), tt (triplet of triplet) or m (multiplet).

Gas Chromatography-Mass Spectrometry (GC-MS) was performed on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an HP-5 ms capillary column (30 m × 0.25 mm × 0.25 µm, J&W Scientific) with helium as the carrier gas.

High-resolution electrospray ionization mass spectrometry (ESI-HRMS) was performed in Bruker microTOF-Q II Spectrometer. The samples were prepared simply by dissolving solid or liquid substrates in MeOH or CH_3CN (10^{-3} to 10^{-5} M).

Powder X-ray diffraction (PXRD) data were collected by using a XEUSS system using a Genix micro source from Xenocs operated at 50 kV and 0.6 mA. The Cu Kα radiation (λ = 1.54 Å) was collimated with FOX2D mirror and two pairs of scattering less slits from Xenocs. The 2D patterns were recorded on a Mar345 image plate and processed using Fit2D software. All the measurements have been made in the transmission mode. The sample to detector distance calibrated with silver behenate standard is 220.8 mm for PXRD measurement.

Single Crystal X-Ray Diffraction (SCXRD) data for the crystal was collected at 100 K or 113 K on Rigaku (dual, Cu/Mo at zero, Eos) diffractometer using monochromatic CuKα (λ = 1.54184) and MoKα (λ = 0.71073), respectively. Structures were solved by Using Olex2 in the Superflip structure solution program by charge flipping and refined with the least squares minimization SHELXL refinement program.

Fourier transform infrared (FT-IR) spectra of the solid samples were recorded on a Bruker Optics ALPHA II spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory. All the data have been reported in the wavenumber (cm^{-1}) scale.

Nitrogen adsorption experiments (0 to 1 bar) were performed using Quantachrome Quadrasorb automatic and Autosorb iQ instrument. The nitrogen adsorption isotherms were collected at 77 K using a liquid nitrogen bath. Before performing gas adsorption experiments, PKPOP and Pd@PKPOP were degassed at 120 °C for 12 hrs under vacuum. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) model applied between p/p^o values of 0.05 and 0.3 for microporous and mesoporous PKPOP. Corresponding pore size distributions were calculated using the non-localized density functional theory (NLDFT).

Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TG50 and SDT Q600 TG-DTA analyzer under N_2 atmosphere from 30 °C to 900 °C along with a ramp rate of 10 °C min^{-1}. Before carrying out the TGA, the samples were activated at 100°C for 30 minutes to eliminate the water from the samples.

Field Emission Scanning Electron Microscopy (FESEM) images were obtained using Zeiss SUPRA 55 VP FESEM operating at 10 kV using tungsten filament as the electron source. The samples were sputtered with gold (nano-sized film) before the imaging using an SCD 040 Balzers Union sputterer to avoid charging during FESEM analyses. The samples were prepared simply by putting a drop of dispersed samples (PKPOP and Pd@PKPOP) in isopropanol on a clean piece of silicon wafer. Elemental mapping of the PKPOP and Pd@PKPOP were also recorded using FESEM with energy dispersive X-ray analysis (EDAX). In these cases, samples were prepared by solid sample coating on a non-porous and conductive adhesive carbon strip.

Transmission Electron Microscopy (TEM) images were obtained using UHR FEGTEM, DST-FIST facility of IISER Kolkata at an accelerating voltage of 200 kV. The samples were prepared by direct drop casting (dispersed in isopropanol) onto copper grids TEM Window (TED PELLA, INC. 200 mesh).

Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) analysis by the Thermo Scientific instrument (Model no. ThermoiCAP-7400) with Qtegra software. Analytical wavelength for metals detection was selected based on intensity counts and background interference. Operating condition for ICP-OES are given as follow- [Power-1150, Coolant Flow-12 L/min, Auxiliary Flow-0.50 L/min, Nebulizer Flow-0.50 L/min, Additional Flow-0 L/min, Nebulizer gas pressure-210 kPa, Plasma torch- Quartz, Spray chamber- Cyclonic, Carrier gas- Argon].

X-ray Photoelectron Spectroscopy (XPS) analysis was carried out using Thermo Scientific's K-Alpha+ spectrometer. The pass energy for the survey scan and the high-resolution scan was maintained at 100 eV and 50 eV, respectively, where the angle between the analyzer and sample surface was 90°. In the case of deconvoluted spectra, first, the spectra were analyzed and fitted by Fityk 1.3.1 software.

Dynamic Light Scattering (DLS) measurement was carried out using Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., UK) equipped with a He-Ne laser (wavelength: 633 nm). First, 0.5 mg PKPOP was dispersed into 5.0 mL 2-isopropanol for 2 h. Thereafter, 200.0 uL was taken out and further diluted into 1.0 mL fresh 2-isopropanol. It was further dispersed for another 2 hr. 20 uL of the solution was taken into a quartz cuvette and filled with 0.8 mL 2-isopropanol to carry out the experiment for the determination of the size of hollow spheres.

Section SM-II: Synthesis of Building Block

Synthesis of 4,4',4"-phosphanetriyltribenzaldehyde **(BB1)**

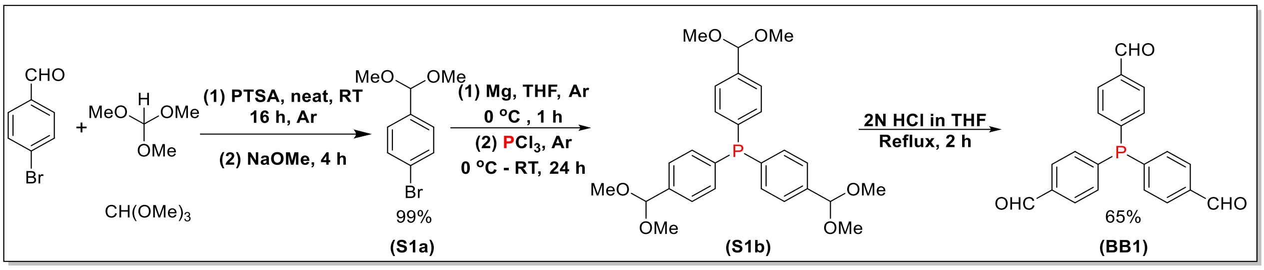


Figure S1: Schematic protocol for the synthesis of 4,4',4"-phosphanetriyltribenzaldehyde **(BB1)**

(BB1) was synthesized by following a reported procedure with some modification[1]. 4-bromobenzaldehyde (18.50 g, 100.0 mmol) was taken in 250 mL oven-dried RB charged with a magnetic bar. The reactant was dried over a high vacuum for 5 min before adding trimethoxymethane (10.62 g, 100.1 mmol) to give a turbid solution. Dried *p*-toluenesulphonic acid (PTSA) (0.86 g, 5.0 mmol) was added as a catalyst, making the solution clear with a small amount of heat liberation. The solution was capped tightly and kept for stirring for 16 h at room temperature. After confirming from TLC monitoring, sodium methoxide NaOMe (0.32g, 6.0 mmol) was added and allowed to stir for another 4 h to quench the acid. The whole solution was directly transferred to the column chromatography. Hexane:ethylacetate (99:1) mixture was used as eluent to purify the product. After removing the solvent under reduced pressure, the colorless oily compound **S1a** was obtained with 99% yield.

Oven-dried Mg turnings (0.53 g, 22.0 mmol) were taken in oven-dried Schleck RB, equipped with a magnetic stir bar. The whole set up was flame dried under an inert atmosphere. After cooling to rt, 25 mL of anhydrous THF was poured into the RB. A pinch of molecular iodine was added that turned the color of the solution brown. Under stirring conditions, **S1a** (4.62 g, 20 mmol) was added slowly. After the addition was completed, the set up was capped with rubber septa and allowed to stir at 40 °C in a water bath under inert conditions. The solution was observed carefully, and once it started becoming colorless, it was removed from the water bath and continued stirring further at room temperature for 1 h. Further, the whole set up was kept under an ice bath, and freshly distilled PCl_3 (0.69 g, 5.0 mmol) was added dropwise and continued stirring for 1 h under the ice bath. Then-after, the reaction was allowed to stir at room temperature for 24 h. The reaction mixture was quenched with saturated NH_4Cl solution under an ice bath. The quenched reaction mixture was filtered with a cotton pad, and the reaction mixture was concentrated under reduced pressure. Further, ethyl acetate (3 x 20 mL) was used to extract the organic phase from the aqueous phase. The organic layer was washed with fresh distilled H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude compound **(S1b)** was diluted with 20 mL of 2 N HCl in THF (v/v) and was refluxed for 2 h. The mixture was allowed to attain room temperature, and a saturated solution of Na_2CO_3 was added slowly to neutralize HCl with vigorous stirring under an ice bath. The reaction mixture was extracted with ethyl acetate (3 x 20 mL), washed with brine, and dried over anhydrous Na_2SO_4. The organic layer was concentrated through rotary evaporator, and a free-flowing slurry was made using 240-400 mesh silica gel, and a column was packed to purify the compound. The column was drained using ethyl acetate: hexane (10:90) to obtain the off-white desired product **BB1** in 65% yield (4.5 g, 13.0 mmol). The purity of the compound was checked with NMR and found to be matched with the reported value in the literature.[1] **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.01 (s, 3H), 7.86 (d, *J* = 8.0 Hz, 6H), 7.46 (t, *J* = 7.9 Hz, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 191.7, 143.2 (d, *J* = 14.7 Hz), 136.9, 134.3 (d, *J* = 20.4 Hz), 129.8 (d, *J* = 7.4 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ -3.38.

Section SM-III: Synthesis of monomers and their characterizations

Synthesis of **PKMONO**

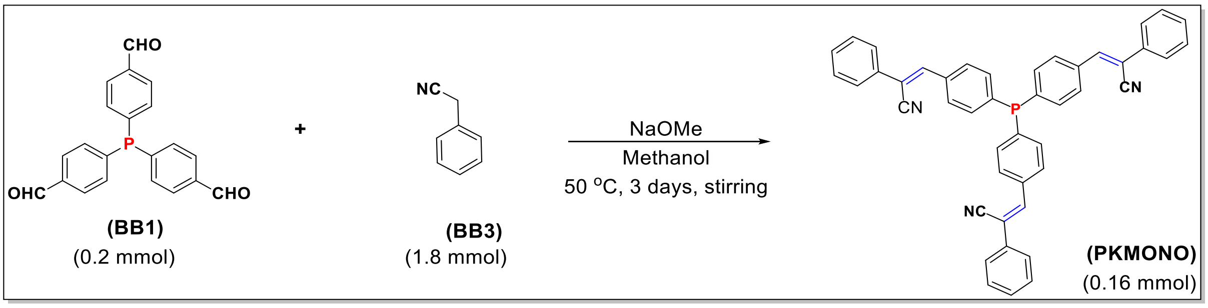


Figure S2: Schematic protocol for the synthesis of **PKMONO**

In a 16 mL reaction tube, 4-formyl(triphenyl)phosphine (**BB1**, 0.20 mmol, 69.2 mg) and 2-phenylacetonitrile (**BB3**, 1.80 mmol, 210.6 mg, 206.5 uL) were taken and dissolved in 5.0 mL methanol. Sodium methoxide (0.60 mmol, 32.4 mg) was then added. The solution was degassed for 0.5 h by passing nitrogen, thereafter capped tightly. It was allowed to stir for 3 days at 50 °C. The light greenish color precipitate was filtered and washed thoroughly with methanol. The collected precipitate was dried under vacuum overnight to get 80% yield (103.0 mg, 0.16 mmol). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.83 (d, *J* = 8.2 Hz, 6H), 7.62 (dd, *J* = 7.3, 2.0 Hz, 6H), 7.47 (s, 3H), 7.40 – 7.32 (m, 15H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.3, 139.4 (d, *J* = 13.4 Hz), 134.6, 134.4, 134.3 (d, *J* = 20.0 Hz), 129.6, 129.5 (d, *J* = 7.2 Hz), 129.3, 126.2, 117.9, 112.8. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -4.91.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.08 (s, 3H), 8.00 (d, *J* = 7.8 Hz, 6H), 7.78 (d, *J* = 7.6 Hz, 6H), 7.55 – 7.52 (m, 6H), 7.50 – 7.45 (m, 9H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 142.0, 138.7 (d, *J* = 13.7 Hz), 134.5, 133.8 (d, *J* = 19.5 Hz), 133.6, 129.42, 129.36, 129.2, 125.8, 117.7, 111.2. **^{31}P NMR (203 MHz, DMSO-*d*$_6$)** δ -6.08. **IR(ATR/cm^{-1})** 3060.9, 3025.8, 2962.7, 2927.7, 2850.5, 2213.6, 1588.2, 1546.1, 1497.0, 1447.9, 1398.8, 1356.7, 1314.7, 1251.6, 1188.4, 1160.4, 1118.3, 1097.3, 1090.3, 1076.2, 1034.6, 1013.1, 900.9, 816.7, 753.6, 683.5, 641.4, 627.4. **HRMS (ESI)** m/z calcd. for $C_{45}H_{31}N_3P$ ([M+H]$^+$) 644.2250, found m/z 644.2277

Synthesis of (*Z*)-2,3-diphenylacrylonitrile **(BB5)**

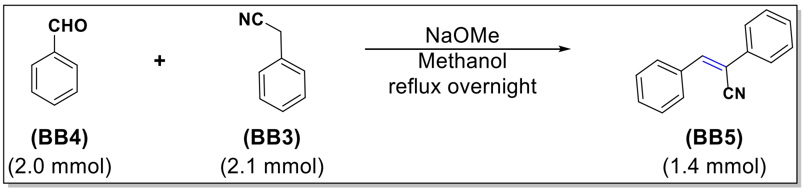


Figure S3: Schematic protocol for the synthesis of (*Z*)-2,3-diphenylacrylonitrile **(BB5)**

A 16 mL reaction tube was charged with benzaldehyde (2.0 mmol, 212.2 mg, 204.0 uL) **(BB4)**, and 2-phenylacetonitrile (2.1 mmol, 245.7 mg, 240.9 uL) **(BB3)** has been taken and dissolved in 2.0 mL methanol. Further, sodium methoxide (0.80 mmol, 43.2 mg) was added and capped tightly. It was allowed to reflux overnight. The clear solution was kept aside to attain RT where the product (*Z*)-2,3-diphenylacrylonitrile **(BB5)** was precipitated. The solid product was filtered and washed with cold ethanol and water. It was vacuum dried to get 70% yield (287.1 mg, 1.4 mmol). The purity of the compound was checked with NMR and found to be matched with the reported values.[2] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 7.39 – 7.26 (m, 6H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.3, 134.6, 133.8, 130.6, 129.4, 129.3, 129.2, 129.0, 126.1, 118.1, 111.8.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.05 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.58 – 7.45 (m, 6H).**^{13}C NMR (126 MHz, DMSO-d_6)** δ 142.9, 133.73, 133.69, 130.5, 129.2, 129.12, 129.06, 128.9, 125.7, 117.8, 110.4. **IR(ATR/cm^{-1})** 3036.4, 2216.9, 1601.3, 1482.7, 1445.9, 1349.3, 1247.2, 1011.7, 982.25, 929.0, 903.0, 749.3, 684.8, 629.0, 574.0.

Section SM-IV: Synthesis and characterization of PKPOP

Synthesis of **PKPOP**

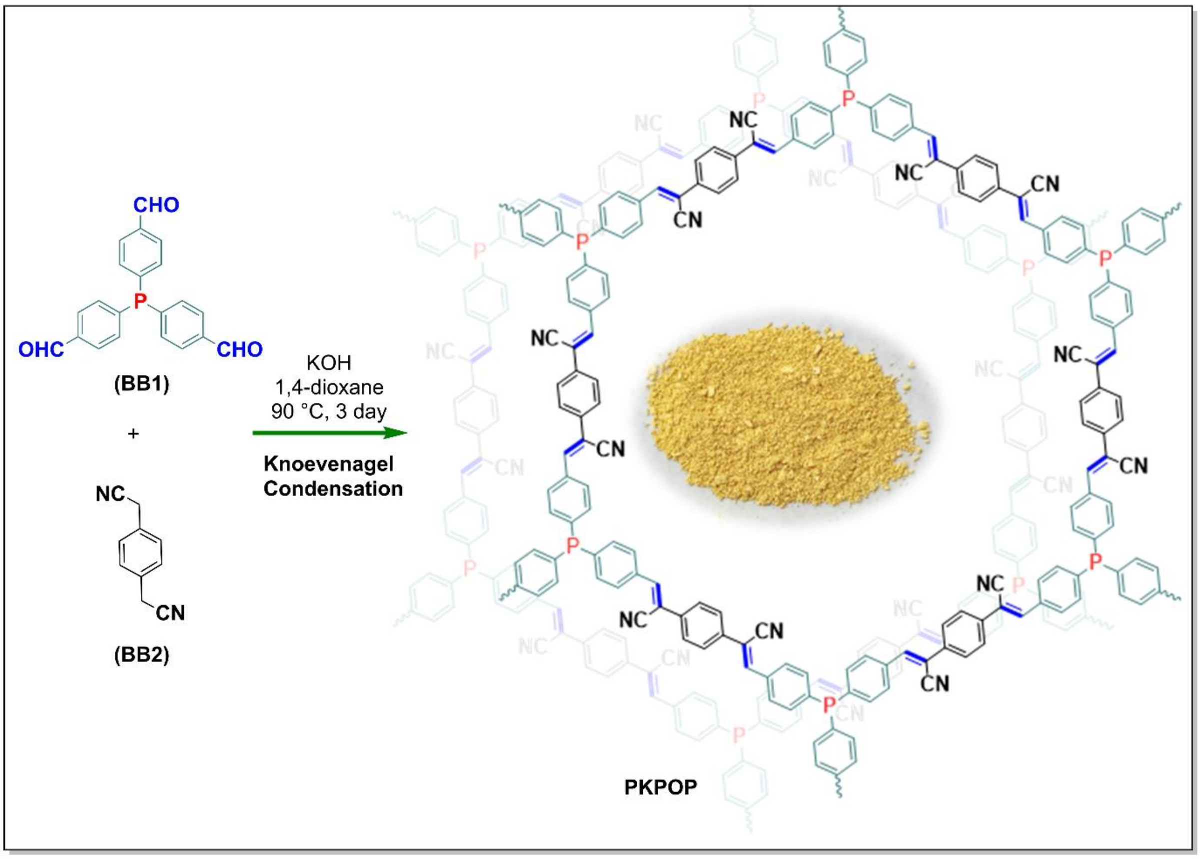


Figure S4: Schematic protocol for the synthesis of **PKPOP**

In a 16 mL reaction tube, 4-formyl(triphenyl)phosphine (**BB1**, 0.036 mmol, 8.3 mg) and phenyl-1,4-diacetonitrile (**BB2**, 0.048 mmol, 5.7 mg) were taken and degassed using Schleck line. Under inert conditions, pre-degassed 1,4-dioxane (three times freeze-pump- thaw cycle) (0.9 mL) was poured into the reaction tube. 4M aq. KOH solution (0.1 mL) was then added. The reaction was capped under an inert condition and sonicated for 5 min. Thereafter, it was kept in a pre-heated oil bath at 90 ^oC for 3 days without stirring. This reaction was kept in multiple batches. After completion of the reaction, a greenish color precipitate (ppt.) was obtained and was filtered using general filter paper and sequentially washed with dimethylformamide (DMF), methanol, acetone, 1M aq. HCl solution, H_2O, acetone, and methanol. Upon washing with 1M aq. HCl solution, the color of the ppt. changed to bright yellow. Further, it was stirred for 2 days in the DMF solution at 140 ^oC, collected after centrifugation, and further washed with refluxing methanol for 1 day. Finally, it was centrifuged and dried under high vacuum at 120 ^oC for 12 h to obtain bright yellow color solid in 95% yield. The material is named **PKPOP**.

Characterization of **PKPOP**

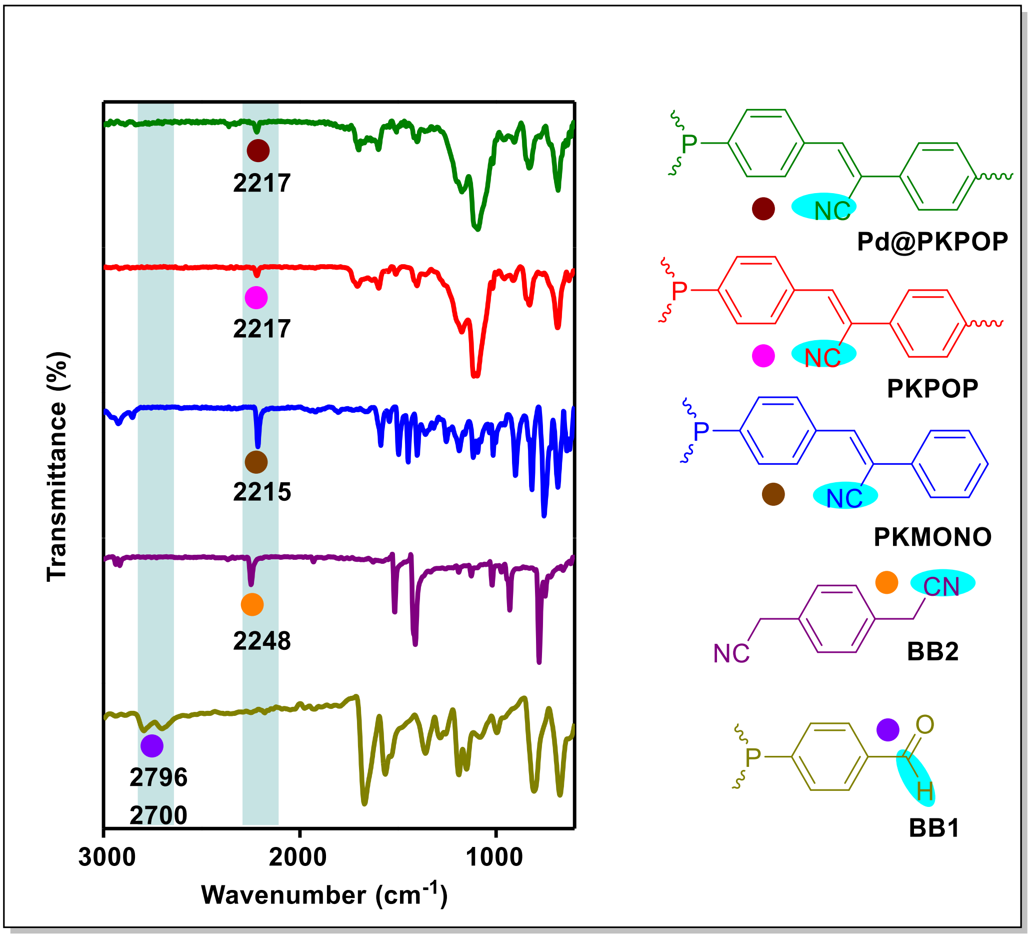


Figure S5: FT-IR spectrum of 4-formyl(triphenyl)phosphine **(BB1)**, phenyl-1,4-diacetonitrile **(BB2), PKMONO, PKPOP** and **Pd@PKPOP**. The corresponding wavenumbers related to different functional groups in monomer as well as in polymer have been depicted schematically.

The Fourier-Transform Infrared (FT-IR) spectroscopy confirmed the formation of **PKPOP**. The disappearance of the formyl C-H band of 4-formyl(triphenyl)phosphine at 2700 cm^{-1} and 2796 cm^{-1}, authenticated the elimination of water molecules. Shifting of the CN band stretching towards a lower frequency (2248 cm^{-1} in phenyl-1,4-diacetonitrile to 2217 cm^{-1} in **PKPOP**) corroborated the fully conjugative effect in the PKPOP due to partial conversion of the hybridization from sp to sp^2.

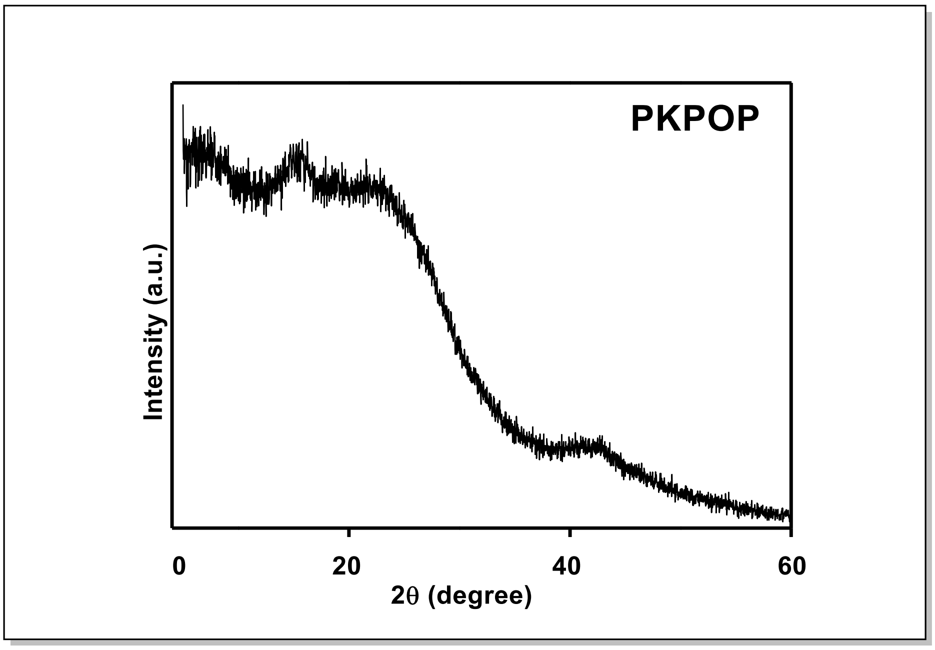


Figure S6: PXRD spectra of **PKPOP**. A broad peak from 20° to 40° indicates the π-π-stacked amorphous nature of the material.

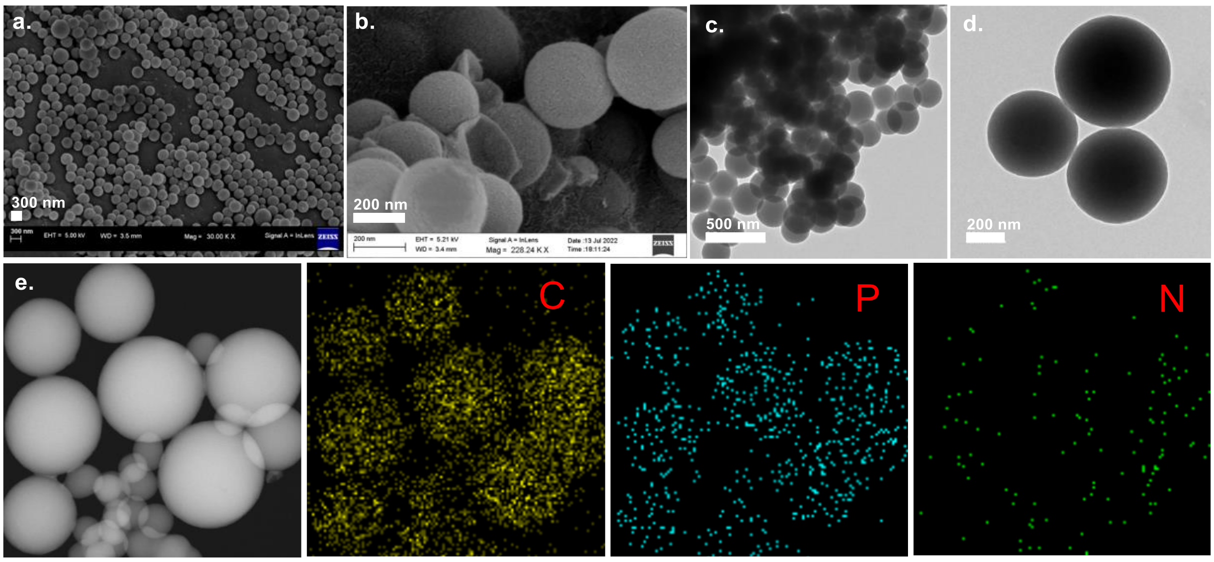


Figure S7: FESEM images of **PKPOP**. (a) low magnification, (b) high magnification. TEM images of **PKPOP**. (c) low magnification, (d) high magnification. (e) EDAX shows the elemental mapping of elements present in **PKPOP**.

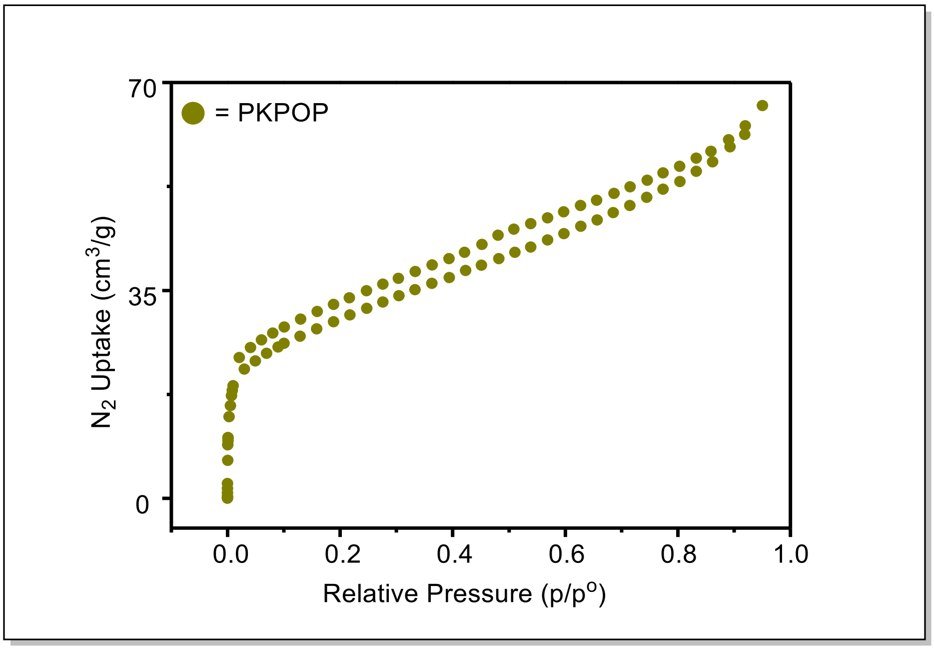


Figure S8: BET isotherm of **PKPOP**. Steep rise of curve at low pressure of Type II curve shows the filling of micropores and formation of monolayers afterwards. BET surface area measured was 108 m^2/g

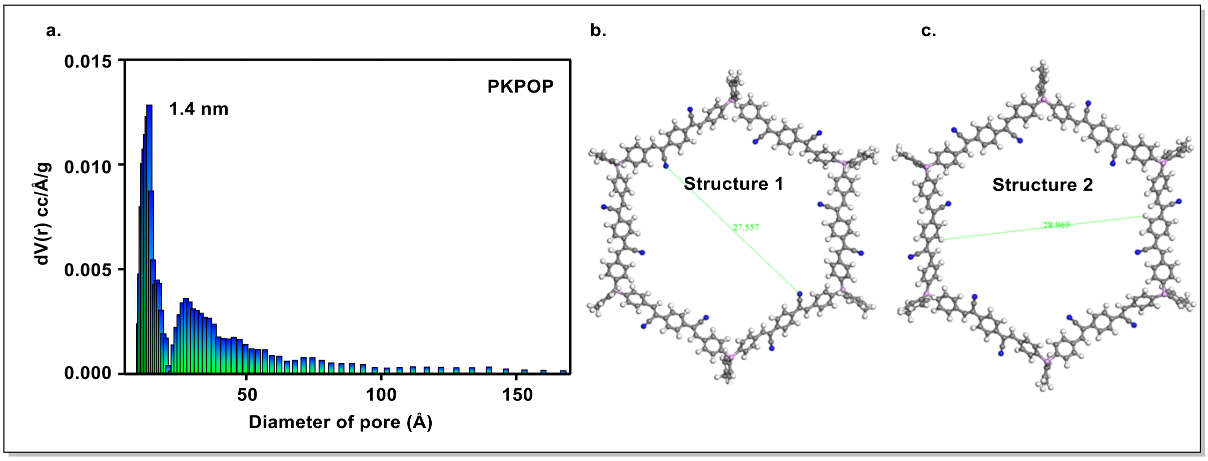


Figure S9: (a) Pore size distribution of **PKPOP** shows micropores having average diameter of 1.4 nm; (b, c) Upon optimization of energy and hexagonal geometry using Force Field method in Material Studio software, we found the pore size of 2.8 nm (CN to CN) (Structure 1) and 2.9 nm (H to H) (Structure 2). The decrement in the experimental pore size value shows that major part of **PKPOP** comprises of distorted or broken hexagonal structure

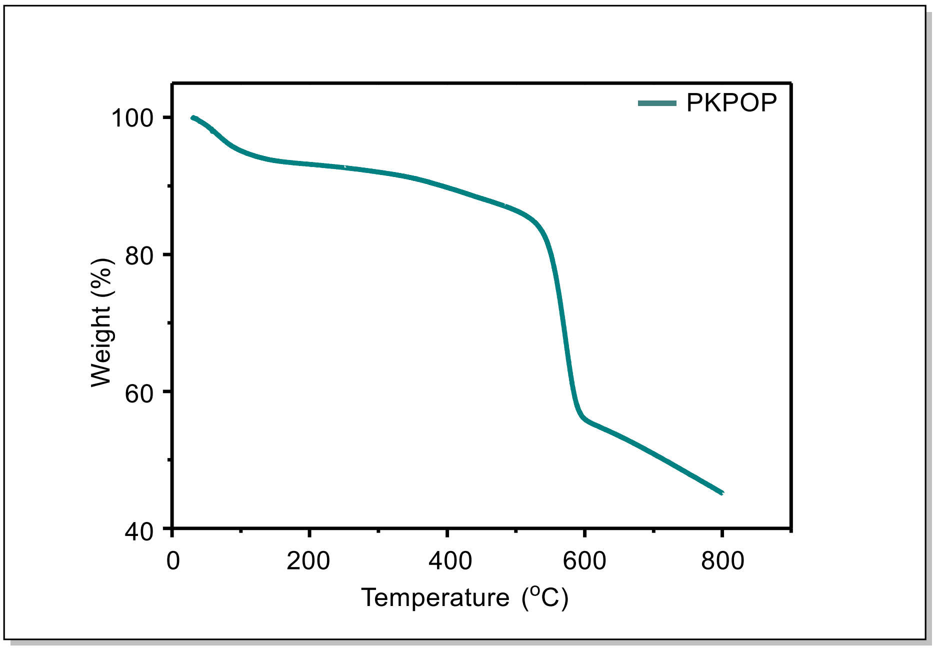


Figure S10: TGA curve showing thermal stability of **PKPOP** upto 500 °C

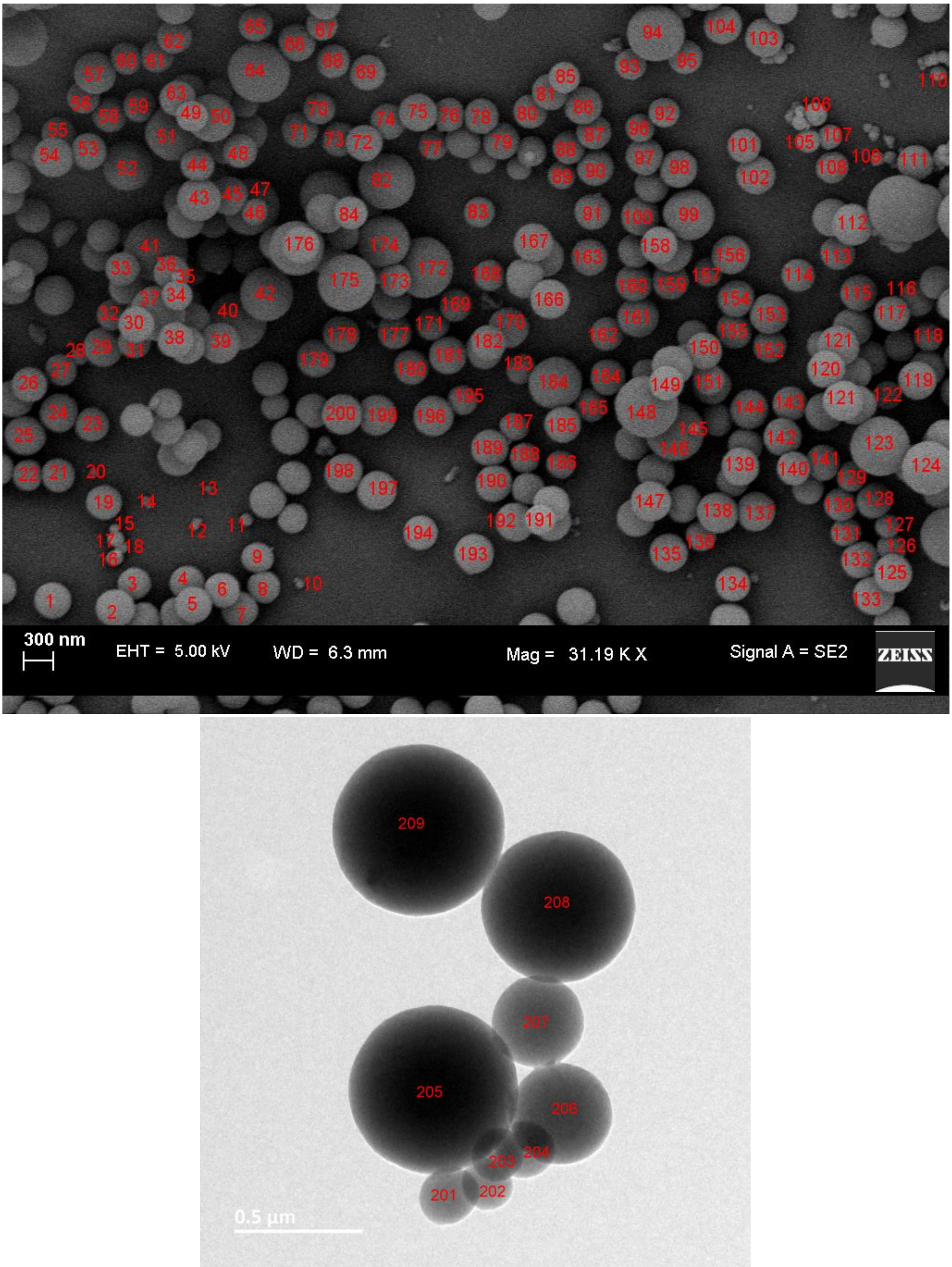


Figure S11: FESEM image and TEM image for the random measurement of the size of the spheres by measuring the diameter using Image J software

S. No.	Label	Length (nm)	Round off	S. No.	Label	Length (nm)	Round off
1	3D-R_02	409.158	410	**49**	3D-R_02	328.666	330
2	3D-R_02	434.851	430	**50**	3D-R_02	514.692	510
3	3D-R_02	365.685	370	**51**	3D-R_02	585.539	590
4	3D-R_02	384.199	380	**52**	3D-R_02	546.898	550
5	3D-R_02	392.204	390	**53**	3D-R_02	407.992	410
6	3D-R_02	395.909	400	**54**	3D-R_02	429.542	430
7	3D-R_02	393.172	390	**55**	3D-R_02	392.221	390
8	3D-R_02	367.147	370	**56**	3D-R_02	383.916	380
9	3D-R_02	366.006	370	**57**	3D-R_02	496.05	500
10	3D-R_02	102.104	100	**58**	3D-R_02	383.528	380
11	3D-R_02	150.472	150	**59**	3D-R_02	364.3	360
12	3D-R_02	100.698	100	**60**	3D-R_02	362.492	360
13	3D-R_02	77.218	80	**61**	3D-R_02	358.849	360
14	3D-R_02	132.043	130	**62**	3D-R_02	368.361	370
15	3D-R_02	114.765	110	**63**	3D-R_02	395.745	400
16	3D-R_02	193.742	190	**64**	3D-R_02	681.879	680
17	3D-R_02	196.316	200	**65**	3D-R_02	381.844	380
18	3D-R_02	157.161	160	**66**	3D-R_02	415.309	420
19	3D-R_02	393.641	390	**67**	3D-R_02	345.437	350
20	3D-R_02	108.09	110	**68**	3D-R_02	381.454	380
21	3D-R_02	369.478	370	**69**	3D-R_02	394.49	390
22	3D-R_02	347.137	350	**70**	3D-R_02	338.916	340
23	3D-R_02	382.882	380	**71**	3D-R_02	396.496	400
24	3D-R_02	408.477	410	**72**	3D-R_02	406.225	410
25	3D-R_02	463.16	460	**73**	3D-R_02	367.417	370
26	3D-R_02	380.413	380	**74**	3D-R_02	390.543	390
27	3D-R_02	354.373	350	**75**	3D-R_02	418.994	420
28	3D-R_02	195.557	200	**76**	3D-R_02	366.201	370
29	3D-R_02	432.626	430	**77**	3D-R_02	314.322	310
30	3D-R_02	390.812	390	**78**	3D-R_02	373.175	370
31	3D-R_02	345.553	350	**79**	3D-R_02	398.99	400
32	3D-R_02	333.31	330	**80**	3D-R_02	356.04	360
33	3D-R_02	366.877	370	**81**	3D-R_02	392.095	390
34	3D-R_02	332.993	330	**82**	3D-R_02	607.484	610
35	3D-R_02	132.324	130	**83**	3D-R_02	331.033	330
36	3D-R_02	380.486	380	**84**	3D-R_02	370.608	370
37	3D-R_02	592.714	590	**85**	3D-R_02	325.139	330
38	3D-R_02	387.236	390	**86**	3D-R_02	428.328	430
39	3D-R_02	445.25	450	**87**	3D-R_02	378.551	380
40	3D-R_02	637.358	640	**88**	3D-R_02	371.043	370
41	3D-R_02	682.978	680	**89**	3D-R_02	302.751	300
42	3D-R_02	588.901	590	**90**	3D-R_02	388.41	390
43	3D-R_02	459.061	460	**91**	3D-R_02	380.511	380
44	3D-R_02	370.106	370	**92**	3D-R_02	328.364	330
45	3D-R_02	414.742	410	**93**	3D-R_02	338.623	340
46	3D-R_02	295.289	300	**94**	3D-R_02	639.145	640
47	3D-R_02	595.531	600	**95**	3D-R_02	358.676	360
48	3D-R_02	378.191	380	**96**	3D-R_02	321.342	320

S. No.	Label	Length (nm)	Round off	S. No.	Label	Length (nm)	Round off
97	3D-R_02	409.78	410	**145**	3D-R_02	127.269	130
98	3D-R_02	418.016	420	**146**	3D-R_02	628.348	630
99	3D-R_02	560.731	560	**147**	3D-R_02	447.575	450
100	3D-R_02	416.263	420	**148**	3D-R_02	692.182	690
101	3D-R_02	362.97	360	**149**	3D-R_02	390.321	390
102	3D-R_02	413.304	410	**150**	3D-R_02	403.93	400
103	3D-R_02	419.112	420	**151**	3D-R_02	329.72	330
104	3D-R_02	416.977	420	**152**	3D-R_02	373.972	370
105	3D-R_02	254.72	250	**153**	3D-R_02	442.226	440
106	3D-R_02	250.598	250	**154**	3D-R_02	405.798	410
107	3D-R_02	285.035	290	**155**	3D-R_02	414.203	410
108	3D-R_02	360.331	360	**156**	3D-R_02	404.084	400
109	3D-R_02	150.121	150	**157**	3D-R_02	315.11	320
110	3D-R_02	179.252	180	**158**	3D-R_02	392.221	390
111	3D-R_02	371.043	370	**159**	3D-R_02	407.505	410
112	3D-R_02	435.503	440	**160**	3D-R_02	404.911	400
113	3D-R_02	388.506	390	**161**	3D-R_02	453.518	450
114	3D-R_02	362.492	360	**162**	3D-R_02	368.932	370
115	3D-R_02	399.114	400	**163**	3D-R_02	399.114	400
116	3D-R_02	388.538	390	**164**	3D-R_02	401.344	400
117	3D-R_02	391.557	390	**165**	3D-R_02	351.414	350
118	3D-R_02	302.874	300	**166**	3D-R_02	431.615	430
119	3D-R_02	412.554	410	**167**	3D-R_02	412.554	410
120	3D-R_02	388.666	390	**168**	3D-R_02	333.31	330
121	3D-R_02	450.254	450	**169**	3D-R_02	354.399	350
122	3D-R_02	418.283	420	**170**	3D-R_02	448.267	450
123	3D-R_02	300.779	300	**171**	3D-R_02	341.974	340
124	3D-R_02	639.281	640	**172**	3D-R_02	662.908	660
125	3D-R_02	573.215	570	**173**	3D-R_02	359.504	360
126	3D-R_02	395.495	400	**174**	3D-R_02	559.912	560
127	3D-R_02	309.353	310	**175**	3D-R_02	641.314	640
128	3D-R_02	257.045	260	**176**	3D-R_02	383.399	380
129	3D-R_02	379.891	380	**177**	3D-R_02	372.077	370
130	3D-R_02	322.459	320	**178**	3D-R_02	422.764	420
131	3D-R_02	340.339	340	**179**	3D-R_02	420.176	420
132	3D-R_02	421.236	420	**180**	3D-R_02	371.711	370
133	3D-R_02	456.624	460	**181**	3D-R_02	406.347	410
134	3D-R_02	358.572	360	**182**	3D-R_02	377.009	380
135	3D-R_02	410.022	410	**183**	3D-R_02	347.726	350
136	3D-R_02	348.011	350	**184**	3D-R_02	608.198	610
137	3D-R_02	427.546	430	**185**	3D-R_02	406.469	410
138	3D-R_02	438.679	440	**186**	3D-R_02	304.099	300
139	3D-R_02	424.403	420	**187**	3D-R_02	321.342	320
140	3D-R_02	347.833	350	**188**	3D-R_02	336.603	340
141	3D-R_02	392.221	390	**189**	3D-R_02	424.403	420
142	3D-R_02	405.278	410	**190**	3D-R_02	423.028	420
143	3D-R_02	381.454	380	**191**	3D-R_02	320.725	320
144	3D-R_02	435.56	440	**192**	3D-R_02	418.728	420

S. No.	Label	Length (nm)	Round off	S. No.	Label	Length (nm)	Round off
193	3D-R_02	407.961	410	**204**	Grid.21622	224.608	220
194	3D-R_02	382.914	380	**205**	Grid.21622	665.931	670
195	3D-R_02	312.542	310	**206**	Grid.21622	397.215	400
196	3D-R_02	429.772	430	**207**	Grid.21622	355.347	360
197	3D-R_02	439.977	440	**208**	Grid.21622	599.505	600
198	3D-R_02	436.81	440	**209**	Grid.21622	676.075	680
199	3D-R_02	454.447	450	Round-off has been done in Microsoft Excel using the formula **=MROUND(XX,10)**, in the multiple of 10.			
200	3D-R_02	443.15	440				
201	Grid.21622	240.589	240				
202	Grid.21622	203.864	200				
203	Grid.21622	205.122	210				

Table ST1: Representation of the diameter size of spheres in the tabular form. Measured in Image J software and calculated using Microsoft excel 16.0.

Round off size(nm)	Freq.	Round off size(nm)	Freq.	Round off size(nm)	Freq.	Round off size(nm)	Freq.
50	**0**	240	**1**	430	**7**	620	**0**
60	**0**	250	**2**	440	**7**	630	**1**
70	**0**	260	**1**	450	**6**	640	**4**
80	**1**	270	**0**	460	**3**	650	**0**
90	**0**	280	**0**	470	**0**	660	**1**
100	**2**	290	**1**	480	**0**	670	**1**
110	**2**	300	**5**	490	**0**	680	**3**
120	**0**	310	**3**	500	**1**	690	**1**
130	**3**	320	**5**	510	**1**	700	**0**
140	**0**	330	**8**	520	**0**	Mean = **387.65 nm** (without round-off) Mean = **387.70 nm** (with round-off) **72.25 %** of spheres have 320-450 nm size	
150	**2**	340	**5**	530	**0**		
160	**1**	350	**9**	540	**0**		
170	**0**	360	**11**	550	**1**		
180	**1**	370	**17**	560	**2**		
190	**1**	380	**16**	570	**1**		
200	**3**	390	**17**	580	**0**		
210	**1**	400	**12**	590	**3**		
220	**1**	410	**17**	600	**2**		
230	**0**	420	**14**	610	**2**		

Table ST2 : Representation of rounded-off size and frequency in the tabular form. Refined using Microsoft Excel 16.0

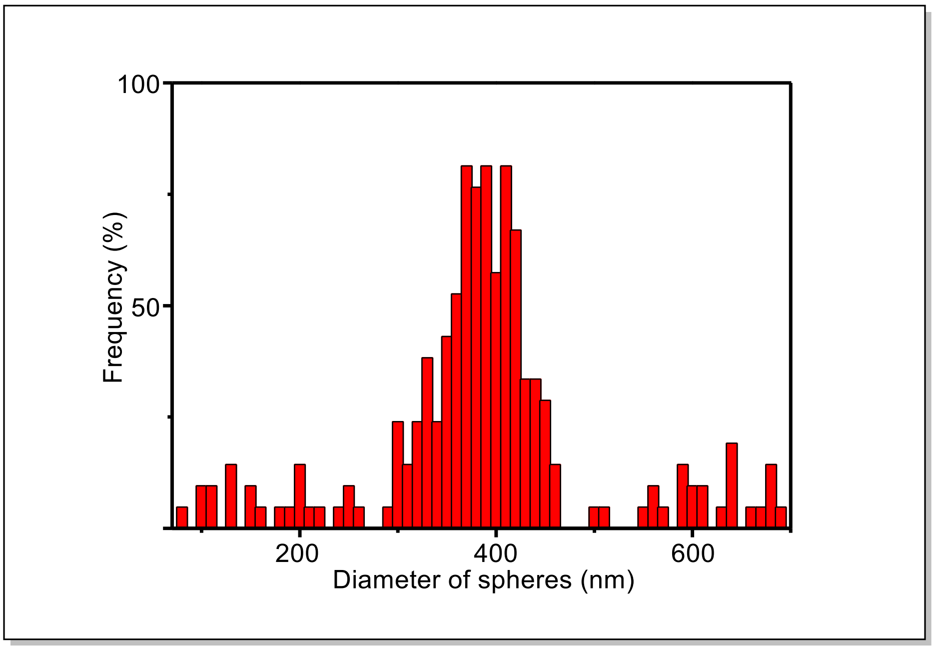


Figure S12: Graphical representation of measured diameter of spheres using Image J software showing average diameter of 387.7 nm

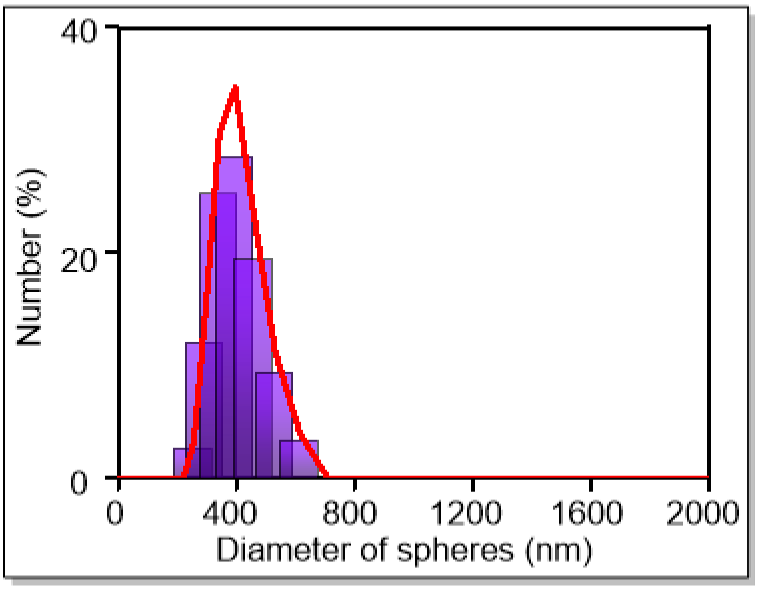


Figure S13 : DLS spectra for the measured diameter of spheres. The average size of spheres is 398.5 nm, whereas 72.80 % of spheres fall in 340 - 460 nm range

Section SM-V: Synthesis and characterization of Pd@PKPOP

Synthesis of **Pd@PKPOP**

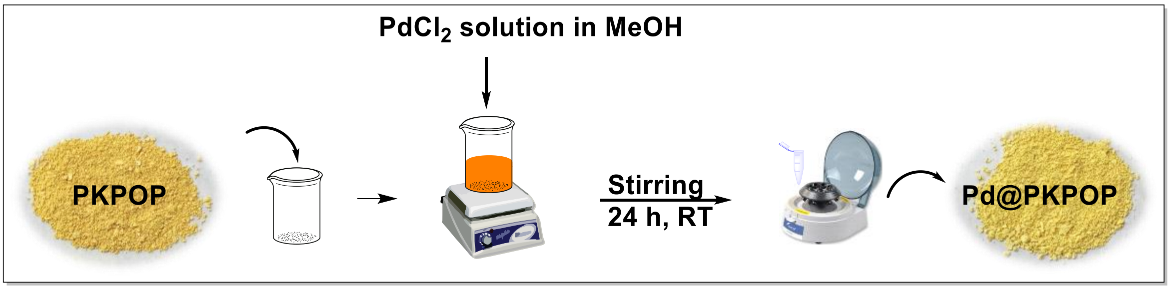


Figure S14: Schematic post-metalation of **PKPOP** to obtain **Pd@PKPOP**

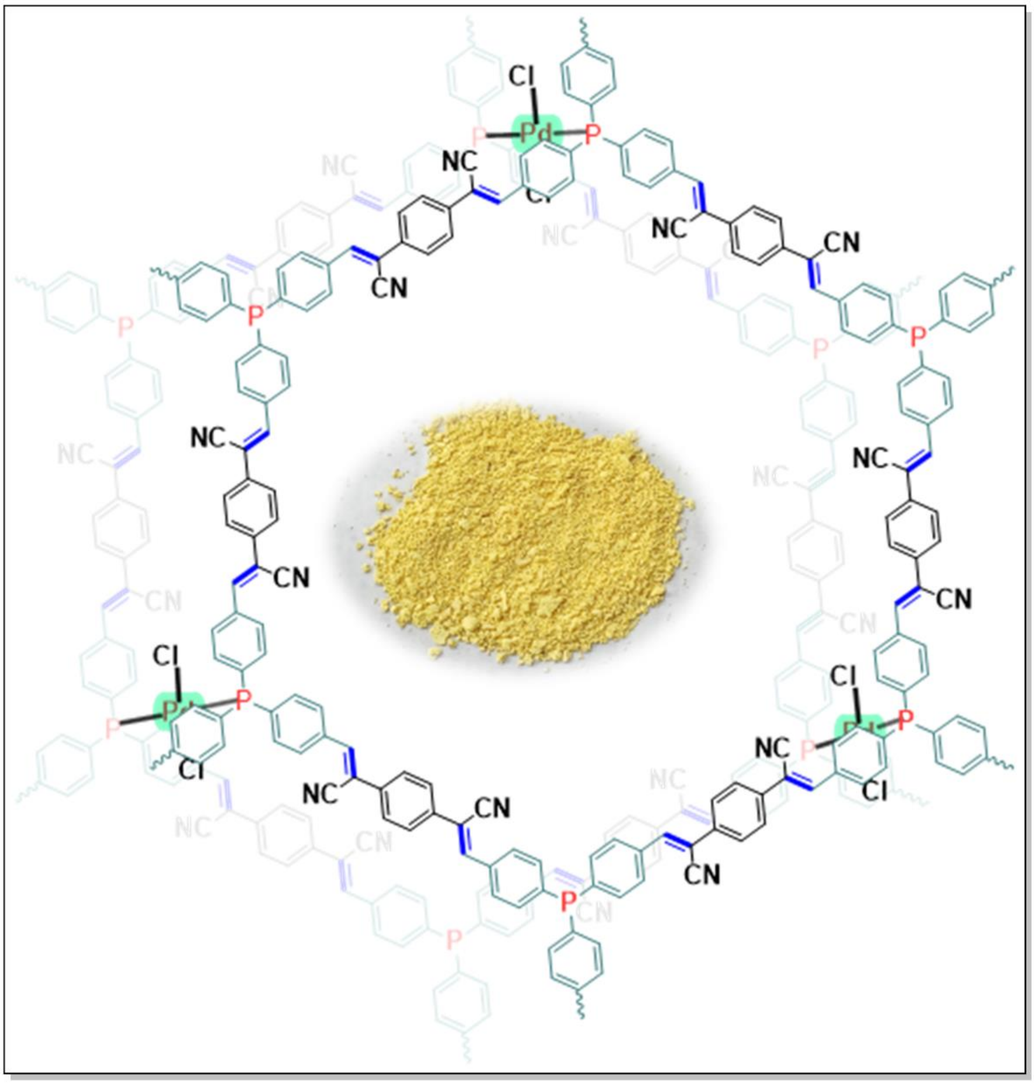


Figure S15: Plausible structure of **Pd@PKPOP**

Methanol (5 mL) was taken in a clean reaction tube with a magnetic stir bar. 94 mg **PKPOP** was suspended into it and stirred for 2 h at RT. A pre-formed solution of 6.0 mg $PdCl_2$ in 5.0 mL methanol was mixed with the suspension and allowed to stir for 24 h at RT. Further, it was centrifuged and washed with fresh methanol five times to ensure the removal of extra unsupported $PdCl_2$. It was dried under vacuum at 120 °C for 12 h to obtain **Pd@PKPOP**. A similar procedure has been applied for the metalation of **PKPOP** with other variations of $PdCl_2$ loading like 2 wt%, 4 wt%, and 8 wt%.

Characterization of **Pd@PKPOP**

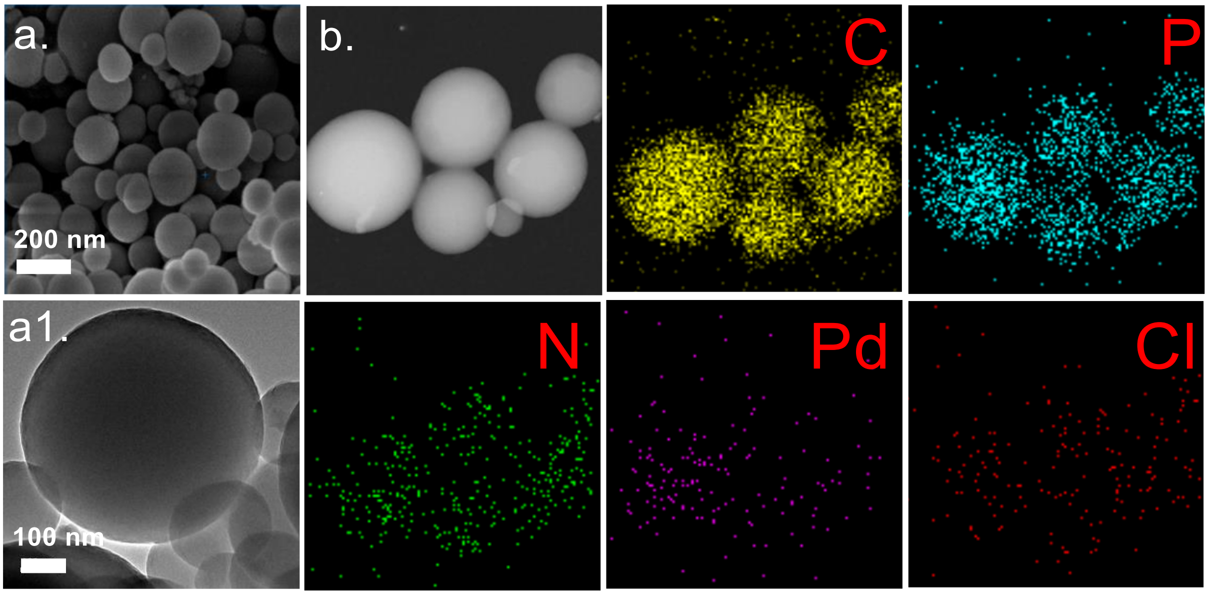


Figure S16: (a) FESEM image of **Pd@PKPOP**; (a1) TEM image of **Pd@PKPOP**; (b) EDAX shows the presence of C, P, N, Pd, and Cl through elemental mapping of **Pd@PKPOP**

Quantifying the Amount of Pd in different catalysts

2 mg of the catalyst has been digested in 2 mL aqua regia solution for 30 h. It was diluted with 8 mL Milli-Q water. 1 mL aliquot was again taken and diluted with 2% concentrated HNO_3 (9 mL). 2 ml of the final solution was filtered with 0.2 µm syringe filter, and measurement was carried out on ICP-OES. Commercially available Pd (1000 ppm Pd in 10% HCl) solution has been used as standard. After calculation, we got the following result.

Catalysts	Expt. Found Pd (wt %)	Theoretically $PdCl_2$ taken (wt %)
Pd@PKPOP	1.12	2
Pd@PKPOP	1.89	4
Pd@PKPOP	2.70	6
Pd@PKPOP	3.52	8

Table ST3: Quantity of Pd in different catalysts quantified by ICP-OES. Wt% was calculated with respect to **PKPOP**. So, 2.0 mg 6 wt% **Pd@PKPOP** contains 0.054 mg (0.5074×10^{-3} mmol) Pd

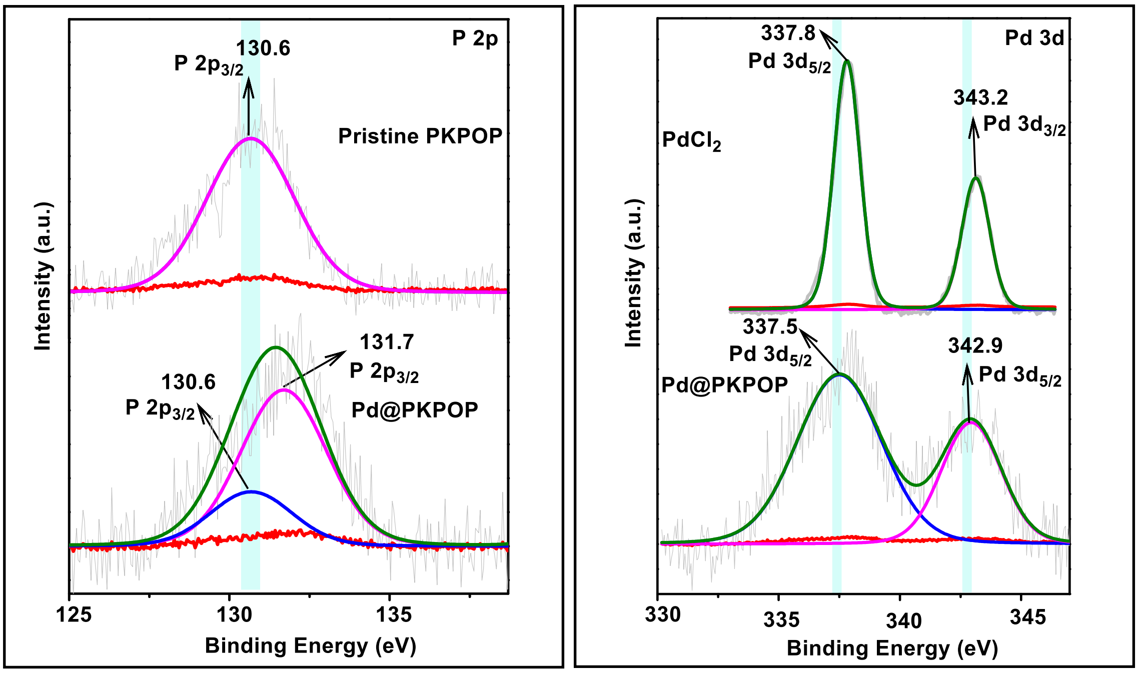


Figure S17: XPS spectra for **PKPOP** and **Pd@PKPOP**. (a) P in pristine **PKPOP** has 130.6 eV for P $2p_{3/2}$ while 131.7 eV for P $2p_{3/2}$ after metalation. Some unmetalated P has been left out in the **Pd@PKPOP**. (b) In $PdCl_2$, Pd $3d_{5/2}$ and Pd $3d_{3/2}$ have 337.8 eV and 343.2 eV, respectively. Interaction with P has been reflected by shifting the binding energy towards the lower side for Pd(II). **Pd@PKPOP** has Pd $3d_{5/2}$, and Pd $3d_{3/2}$ has 337.5 eV and 342.9 eV, respectively

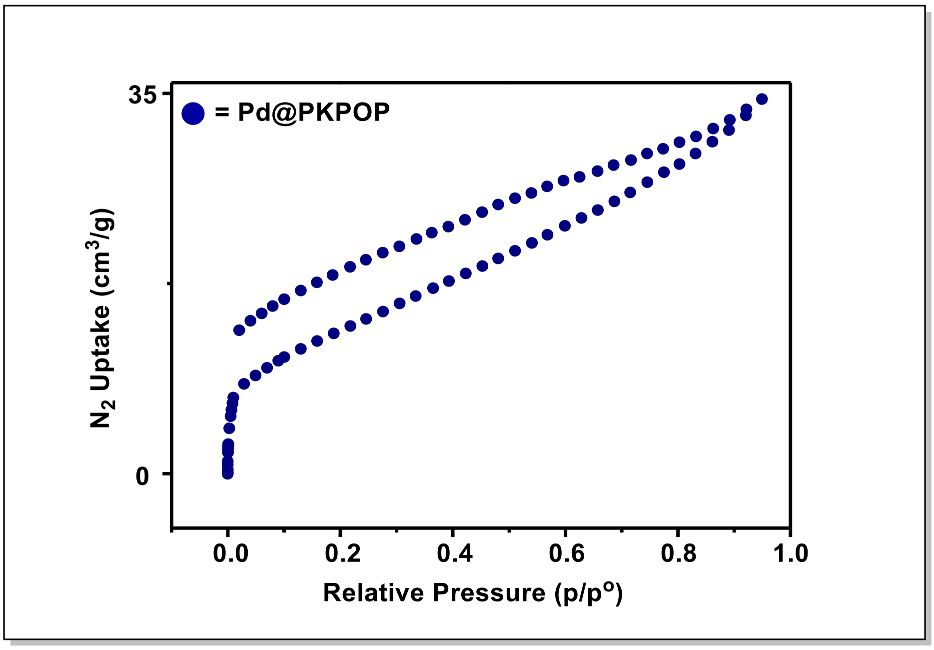


Figure S18: BET isotherm of **Pd@PKPOP**. Steep rise of curve at low pressure of Type II curve shows the filling of micropores (similar to **PKPOP**) and formation of monolayers afterwards. BET surface area measured was 49 m^2/g

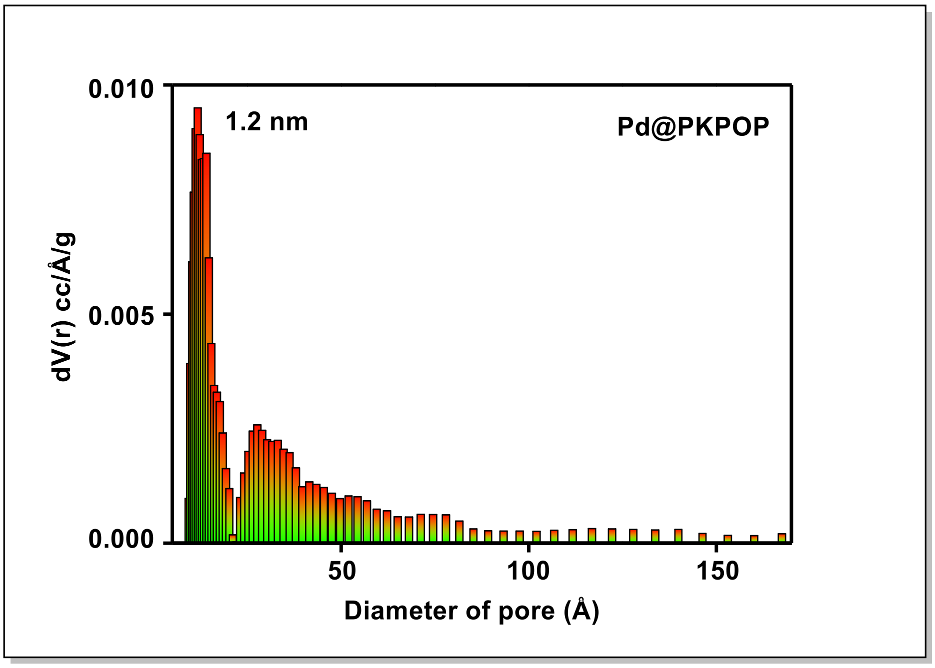


Figure S19: Pore size distribution spectra of **Pd@PKPOP** shows micropores having average diameter of 1.2 nm

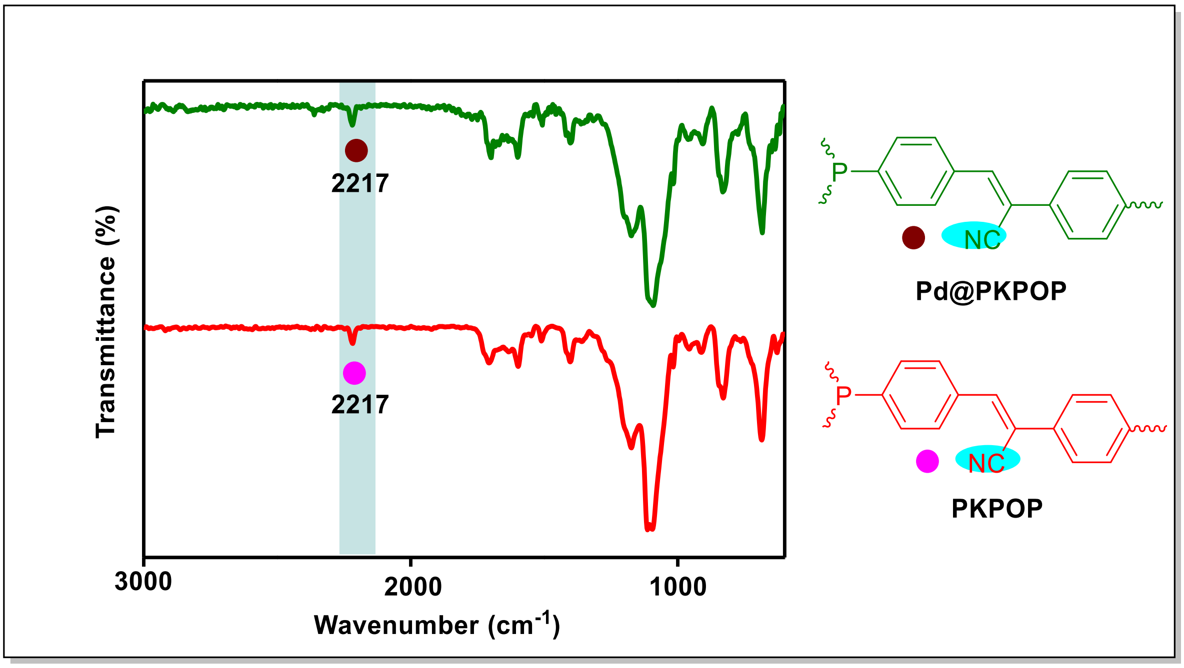


Figure S20: FTIR analysis of **Pd@PKPOP** showing unaltered olefinic C-N stretching frequency

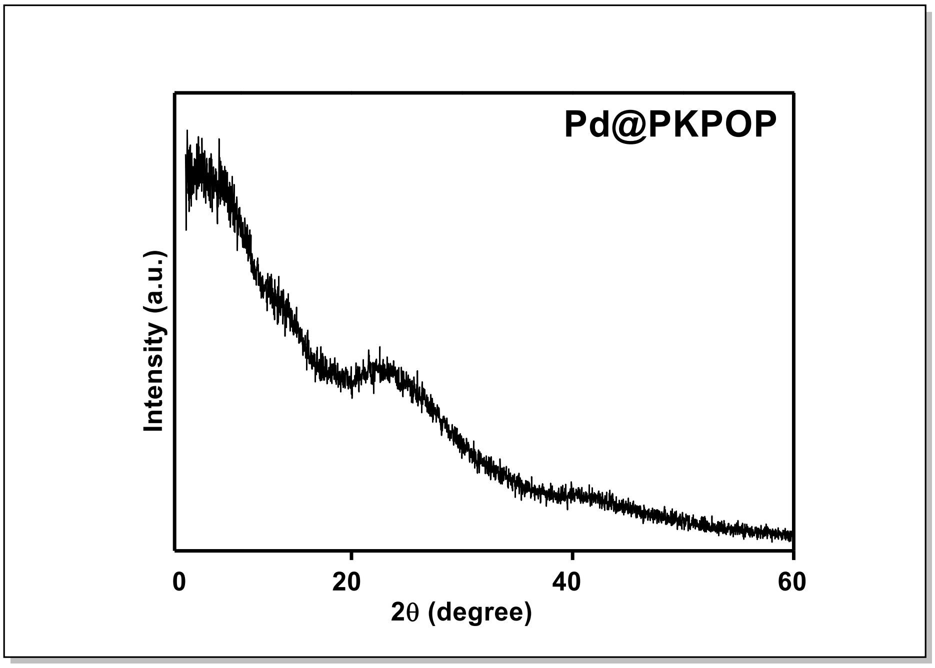
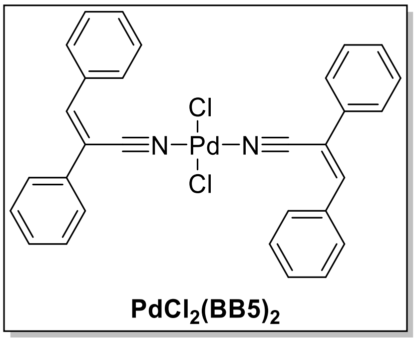


Figure S21: PXRD analysis of **Pd@PKPOP** having broad peak between 20° to 40° showing similar stacking as **PKPOP**

Section SM-VI: Synthesis of homogeneous metal complexes and their characterizations

Synthesis of Bis-((*Z*)-2,3-diphenylacrylonitrile)Palladium dichloride, **$PdCl_2(BB5)_2$**



Method 1:- A 16 mL reaction tube was charged with (*Z*)-2,3-diphenylacrylonitrile **(BB5)** (0.2 mmol, 41.0 mg), methanol (3.0 mL) and $PdCl_2$ (0.1 mmol, 17.7 mg). The whole solution was allowed to stir for 12 h at room temperature. A dull green-colored precipitate was filtered out and washed thoroughly with methanol. It was vacuum dried to get 82% yield.

Method 2:- A 16 mL reaction tube was charged with (*Z*)-2,3-diphenylacrylonitrile **(BB5)** (0.2 mmol, 41.0 mg), chloroform (3.0 mL) and $PdCl_2$ (0.1 mmol, 17.7 mg). The whole solution was allowed to stir for 12 h at room temperature. A yellow-colored solution formed, which on concentration, gave yellow color powder. Further, it was washed with methanol and vacuum dried to get 77% yield with its retained yellow color.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 4H), 7.67 – 7.63 (m, 2H), 7.63 – 7.58 (m, 2H), 7.58 – 7.56 (m, 2H), 7.49 – 7.47 (m, 2H), 7.47 – 7.43 (m, 2H), 7.42 – 7.40 (m, 2H), 7.40 – 7.38 (m, 2H), 7.38 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.1, 142.4, 134.6, 133.9, 132.8, 132.6, 132.2, 130.7, 130.1, 129.9, 129.59, 129.56, 129.42, 129.36, 129.2, 129.1, 126.2, 126.1, 126.0, 122.2, 118.1, 111.9, 108.8. mp = 162-164 ^{o}C. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.06 (s, 2H), 7.95 (d, *J* = 7.5 Hz, 4H), 7.79 (s, 4H), 7.57 – 7.45 (m, 12H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 143.5, 134.3, 134.2, 131.1, 129.8, 129.7, 129.6, 129.4, 126.3, 118.4, 110.9. **IR(ATR/cm^{-1})** 3059.6, 3022.3, 2277.4, 1590.3, 1566.3, 1492.9, 1447.1, 1353.3, 1314.8, 1253.4, 1241.4, 1206.5, 1188.4, 1180.0, 1155.9, 1106.6, 1080.1, 1029.6, 1006.7, 986,3, 934.5, 899.6, 843.1, 827.4, 797.3, 761.2, 749.2, 689.0, 621.7.

Synthesis of **$PdCl_2(PKMONO)_2$**

A 16 mL reaction tube was charged with **PKMONO** (0.05 mmol, 32.2 mg), chloroform (2.0 mL), and $PdCl_2$ (0.025 mmol, 4.4 mg). The whole solution was allowed to stir for 24 h at room temperature. A yellow-colored solution was concentrated to get a solid product, which was washed thoroughly with methanol. Further, it was vacuum dried to get 85% yield with retained yellow color.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.1 Hz, 12H), 7.82 – 7.79 (m, 12H), 7.62 (d, *J* = 7.9 Hz, 12H), 7.49 (s, 6H), 7.42 – 7.33 (m, 18H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 140.8, 136.3, 135.6, 134.3, 131.0, 129.8, 129.3, 129.2, 126.4, 117.8, 114.0.**^{31}P NMR (203 MHz, CDCl$_3$)** δ 23.80. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.12 (s, 6H), 8.11 – 8.04 (m, 12H), 7.95 – 7.87 (m, 12H), 7.81 – 7.77 (m, 12H), 7.54 – 7.50 (m, 12H), 7.49 – 7.42 (m, 6H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 141.6, 136.2, 135.0, 133.5, 132.1, 129.7, 129.3, 129.0, 126.0, 117.6, 112.3. **^{31}P NMR (203 MHz, DMSO-*d*$_6$)** δ 23.79. **IR(ATR/cm^{-1})** 3059.3, 3030.5, 2213.6, 1593.2, 1544.1, 1494.9, 1445.8,1396.6, 1354.2, 1313.6, 1261.0, 1189.8, 1094.9, 1018.6, 903.4, 811.9, 759.3, 684.7, 638.9, 625.4, 611.9.

Synthesis of **$(PdCl_2)_4(PKMONO)_2$**

Method 1:- A 16 mL reaction tube was charged with **PKMONO** (0.1 mmol, 64.3 mg), methanol (3.0 mL), and $PdCl_2$ (0.2 mmol, 35.4 mg). The whole solution was allowed to stir for 24 h at room temperature. A light green colored precipitate was filtered out and washed thoroughly with methanol. It was vacuum dried to get 91% yield.

Method 2:- A 16 mL reaction tube was charged with **PKMONO** (0.1 mmol, 64.3 mg), chloroform (3.0 mL), and $PdCl_2$ (0.2 mmol, 35.4 mg). The whole solution was allowed to stir for 24 h at room temperature. A yellow-colored precipitate was filtered out and thoroughly washed with chloroform and methanol. Further, it was vacuum dried to get 84% yield with retained yellow color.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.96 – 7.87 (m, 12H), 7.82 – 7.72 (m, 12H), 7.67 – 7.59 (m, 12H), 7.52 – 7.47 (m, 6H), 7.41 – 7.36 (m, 12H), 7.33 – 7.28 (m, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 140.8, 135.6, 135.5, 132.7, 129.5, 129.4, 129.34, 129.32, 126.4, 117.8, 114.0. **^{31}P NMR (203 MHz, CDCl$_3$)** δ 22.99. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.12 (s, 6H), 8.06 (dd, *J* = 8.5, 2.3 Hz, 12H), 7.90 (dd, *J* = 11.9, 8.4 Hz, 12H), 7.80 (d, *J* = 7.9 Hz, 12H), 7.54 (t, *J* = 7.6 Hz, 12H), 7.48 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 141.5, 136.5, 135.3 (d, *J* = 10.9 Hz), 133.5, 130.6, 129.8, 129.3, 128.8 (d, *J* = 12.3 Hz), 126.0, 117.5, 112.6. **^{31}P NMR (203 MHz, DMSO-*d*$_6$)** δ 30.68. **IR(ATR/cm^{-1})** 3057.6, 3032.2, 2213.5, 1594.9, 1545.8, 1496.6, 1445.8, 1400.0, 1355.9, 1250.8, 1193.2, 1101.7, 1008.5, 901.7, 815.3, 755.9, 686.4, 637.3

Synthesis of **$Pd(0)(PKMONO)_4$**

A 16 mL reaction tube was charged with **PKMONO** (0.1 mmol, 64.3 mg), anhydrous DMSO (0.3 mL), and $Pd(OAc)_2$ (0.025 mmol, 5.6 mg). It was capped under Ar and continuously stirred at 150 ^oC. After 2 h, L-ascorbic acid (0.1 mmol, 17.6 mg) in 50 uL anhydrous DMSO was poured through a syringe under Ar, keeping continuous stirring at 150 ^oC. It was allowed to stir for another 15 min and kept to attain room temperature. Unlike $Pd(0)(PPh_3)_4$, it did not form a precipitate. The yield was not quantified. The solution was found to be dark yellowish-brown. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.09 – 8.05 (m, 36H), 7.86 – 7.82 (m, 24H), 7.77 – 7.74 (m, 24H), 7.52 – 7.48 (m, 24H), 7.46 – 7.41 (m, 12H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 141.7, 137.7 (d, *J* = 2.8 Hz), 133.5, 132.34 (d, *J* = 10.1 Hz), 130.1, 129.6, 129.4, 129.3, 126.3, 117.7, 113.3. **^{31}P NMR (202 MHz, DMSO-d_6)** δ 25.05. **IR(ATR/cm^{-1} in DMSO-d_6 solvent)** 2250.8, 1054.2, 1022.0,1006.8, 991.5,825.4, 757.6.

NMR analysis of **$[Pd(0)(PKMONO)_n]$** and **$[Pd(0)(OAc)(PKMONO)_n]^-$**

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.89 (s, 12H), 7.80 (d, *J* = 8.5 Hz, 24H), 7.64 – 7.58 (m, 24H), 7.40 – 7.32 (m, 60H).**^{13}C NMR (126 MHz, DMSO-d_6)** δ 142.1, 134.1, 133.8, 133.3, 129.7, 129.6, 128.3, 127.9, 126.0, 116.9, 111.4. **^{31}P NMR (202 MHz, DMSO-d_6)** δ 8.63.

Attempted synthesis of **Tetrakis-((*Z*)-2,3-diphenylacrylonitrile)Palladium(0)**

Method 1:- A 16 mL reaction tube was charged with **BB5** (0.1 mmol, 20.5 mg), anhydrous DMSO (0.3 mL), and $PdCl_2$ (0.025 mmol, 4.4 mg). It was capped under Ar and continuously stirred at 150 ^oC. After 2 h, L-ascorbic acid (0.1 mmol, 17.6 mg) in 50 uL anhydrous DMSO was poured through a syringe under Ar, continuously stirring at 150 ^oC. It was allowed to stir for another 15 min and kept to attain room temperature. A transparent clear solution was observed, and along with it, some settled black particles were at the bottom of the reaction tube. It seemed **BB5** could not stabilize Pd(0) through this method.

Method 2:- A 16 mL reaction tube was charged with **BB5** (0.1 mmol, 20.5 mg), methanol (0.5 mL), and Na_2OAc (0.2 mmol, 16.4 mg) under Ar. It was capped and allowed to stir at 50 ^oC for 1 h. Further, freshly prepared methanolic solution of Na_2PdCl_4 (0.025 mmol, 7.3 mg) was poured slowly using a syringe on continuous stirring condition at 50 ^oC. It was allowed for another 2 h to stir. Finally, after attaining room temperature, a similar transparent solution with settled black particles at the bottom of the reaction tube, like method 1 was observed. Through this method, also it seemed **BB5** was unable to stabilize Pd(0), resulting in the formation of black Pd nanoparticles.

Synthesis of **Sodium tetrachloropalladate (Na_2PdCl_4)**

A 16 mL reaction tube was charged with $PdCl_2$ (0.1 mmol, 17.7 mg), NaCl (0.25 mmol, 14.6 mg), and anhydrous methanol (2 mL). It was allowed to stir at rt overnight. The dark yellow solution formed was filtered out with a syringe filter and kept aside for use.

NMR analysis of different homogeneous metal complexes in DMSO-*d*6 and $CDCl_3$ solvent

We have compared the ^{1}H NMR spectra of **PKMONO**, **$PdCl_2(PKMONO)_2$**, **$(PdCl_2)_4(PKMONO)_2$** and **$Pd(0)(PKMONO)_4$** using DMSO-d_6 as NMR solvent (Figure S22). In **$PdCl_2(PKMONO)_2$**, the ortho-protons near to P shifted downfield with splitting (orange ball), showing Pd binding with P. Similar peak patterns can be seen even after using excess Pd in **$(PdCl_2)_4(PKMONO)_2$** while in case of **$Pd(0)(PKMONO)_4$**, spectra shifted upfield maintaining similar peak positions with respect to each other except overlapping of olefinic proton (blue ball) and ortho-protons of benzylic nitrile (pink ball). Moreover, the other broad peaks (asterisks) hinted the presence of equilibrium between the probable complexes, **[Pd(0)(PKMONO)$_n$]** and **[Pd(0)(OAc)(PKMONO)$_n$]$^-$**. [3] Concurrently, the ^{1}H NMR spectra of **BB5** and **PdCl$_2$(BB5)$_2$** displayed exactly the same spectra with exact peak positions in DMSO-*d*$_6$ (Figure S22A). Here, it can be concluded, Pd-P binding took place and same was depicted by ^{1}H NMR in DMSO-*d*$_6$ while Pd-olefinic CN binding cannot be depicted as probably Pd-olefinic CN binding affinity might be overcome by DMSO-*d*$_6$.

Simultaneously, downfield shift of β-olefinic C (blue ball) (Figure S23) in ^{13}C NMR spectra in DMSO-*d*6, slightly upfield shift of α-olefinic C (pink ball) and no shift in nitrile C (cyan ball) of **PdCl$_2$(PKMONO)$_2$**, in comparison with **PKMONO** has observed because of purely Pd(II)-P binding. Further slight downfield shift in β-olefinic C (blue ball) of **(PdCl$_2$)$_4$(PKMONO)$_2$** gave hint of interaction between Pd(II) and olefin which can also be sensed via ^{1}H NMR in DMSO-*d*6 (Figure S22) as the separation between olefinic proton (blue ball) and ortho-protons of benzyl nitrile (pink ball) increased. Pd(0)-P binding was also well observed via downfield shift of β-olefinic C (blue ball) of **Pd(0)(PKMONO)$_4$** (Figure S23). Conclusion can be drawn here as Pd(0) as well as Pd(II) were stabilized by P. On the other hand, olefin also helped to stabalize Pd(II).

Similar downfield shift was observed for ortho-protons near to P (orange ball) of **PdCl$_2$(PKMONO)$_2$** (fully soluble in CDCl$_3$) and **(PdCl$_2$)$_4$(PKMONO)$_2$** (slightly soluble in CDCl$_3$) in ^{1}H NMR spectra in CDCl$_3$ (Figure S24) with respect to **PKMONO**. But olefinic proton (blue ball) and meta-protons near to P (maroon ball) of **(PdCl$_2$)$_4$(PKMONO)$_2$** splitted much like **PdCl$_2$(BB5)$_2$** while corresponding protons of **PdCl$_2$(PKMONO)$_2$** remained unsplitted. As a conclusion, both P as well as CN could stabilize Pd (II). Concomitantly, ^{31}P NMR in DMSO-*d*$_6$ has also presented different chemical environment of P in various complexes (Figure S25).

In short, Pd(II) has been stabalized by P, olefin and CN of **PKMONO** (Figure S22, S23 and S24) homogeneously which can be extended to stabalize heterogeneously too.[4] Similarly, Pd(0) has been stabalized by P of **PKMONO** (Figure S22 and S23) as well as olefinic compounds [5] homogeneously which guided to envision that P, olefin and CN stabalized Pd nanoparticles in extended form of **PKMONO** i.e **PKPOP** heterogeneously.[6,7,8]

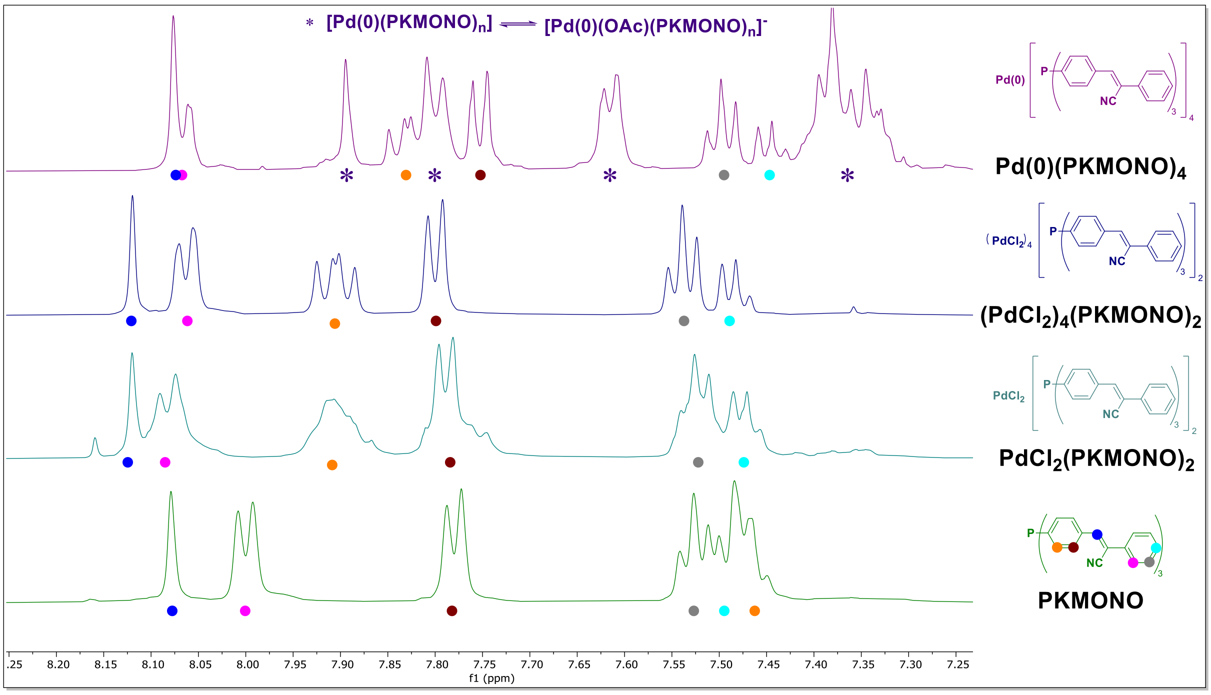


Figure S22: ^{1}H NMR in DMSO-*d*$_6$

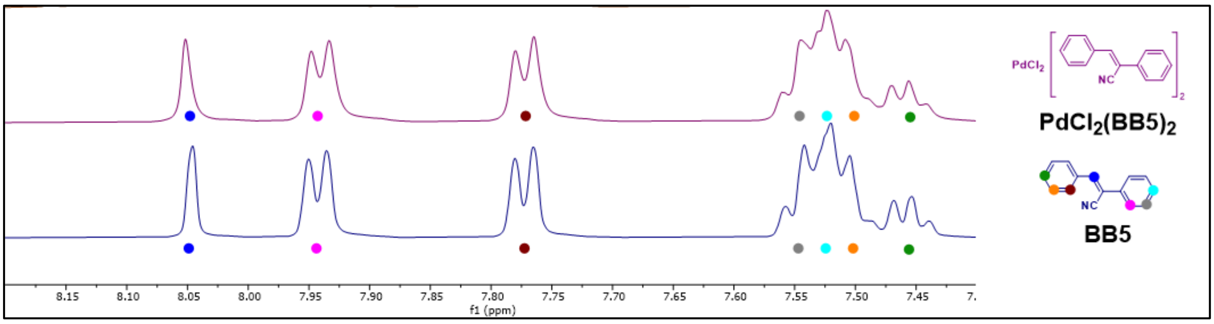


Figure S22A: ^{1}H NMR in DMSO-*d*$_6$

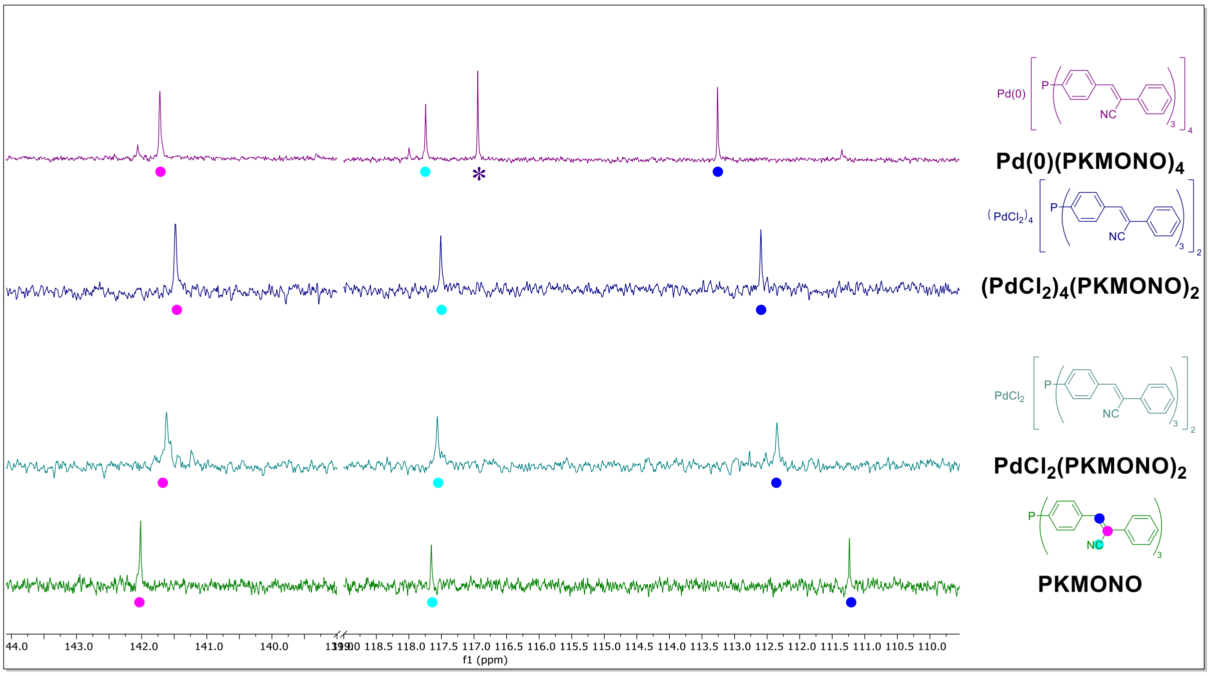


Figure S23: ^{13}C NMR in DMSO-d_6

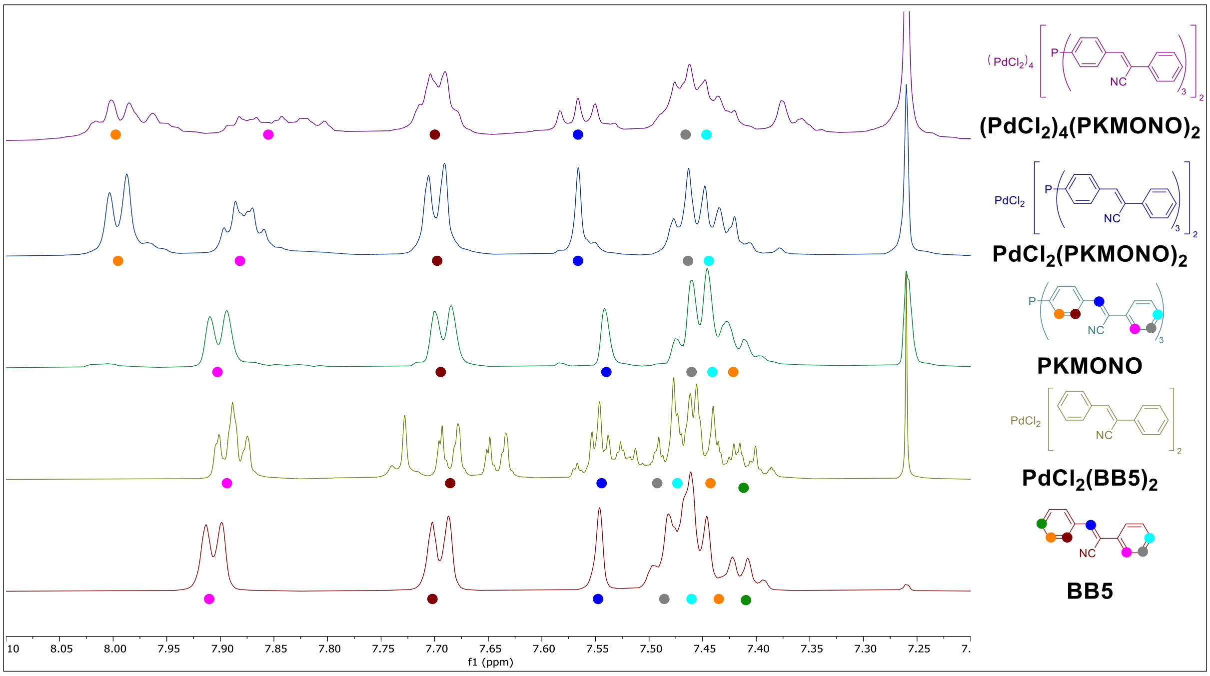


Figure S24: ^{1}H NMR in CDCl$_3$

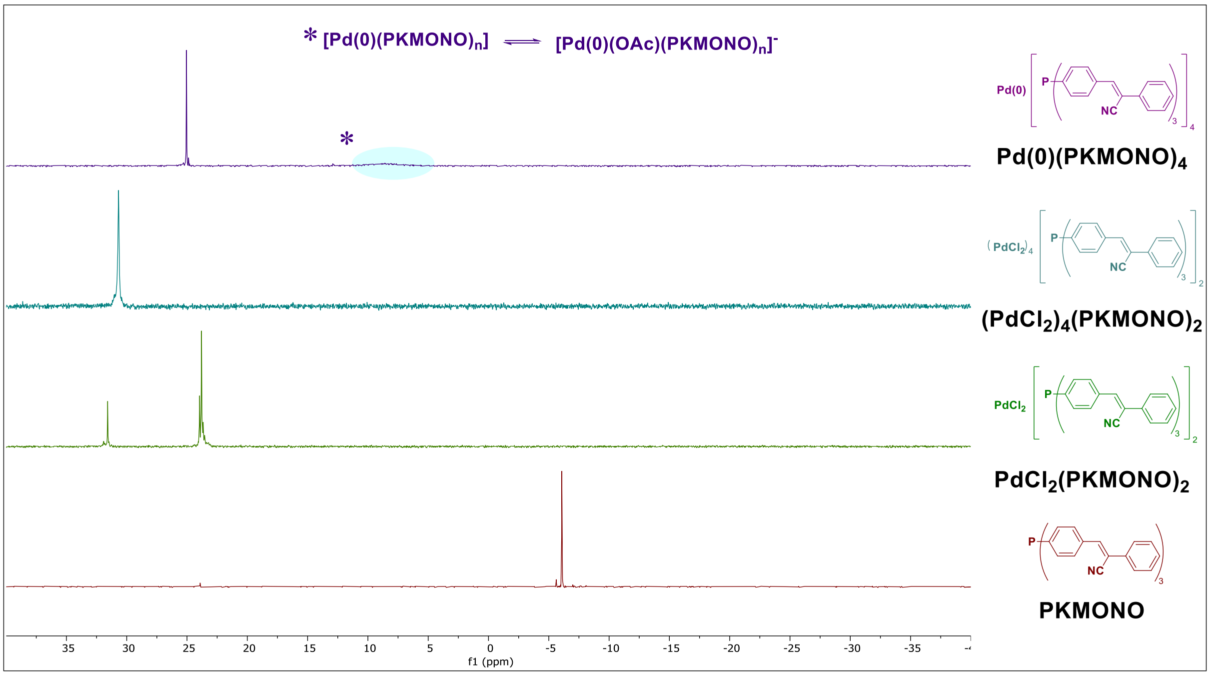


Figure S25: ^{31}P NMR in DMSO-d_6

Section SM-VII: Synthetic protocol for the formation of reactants

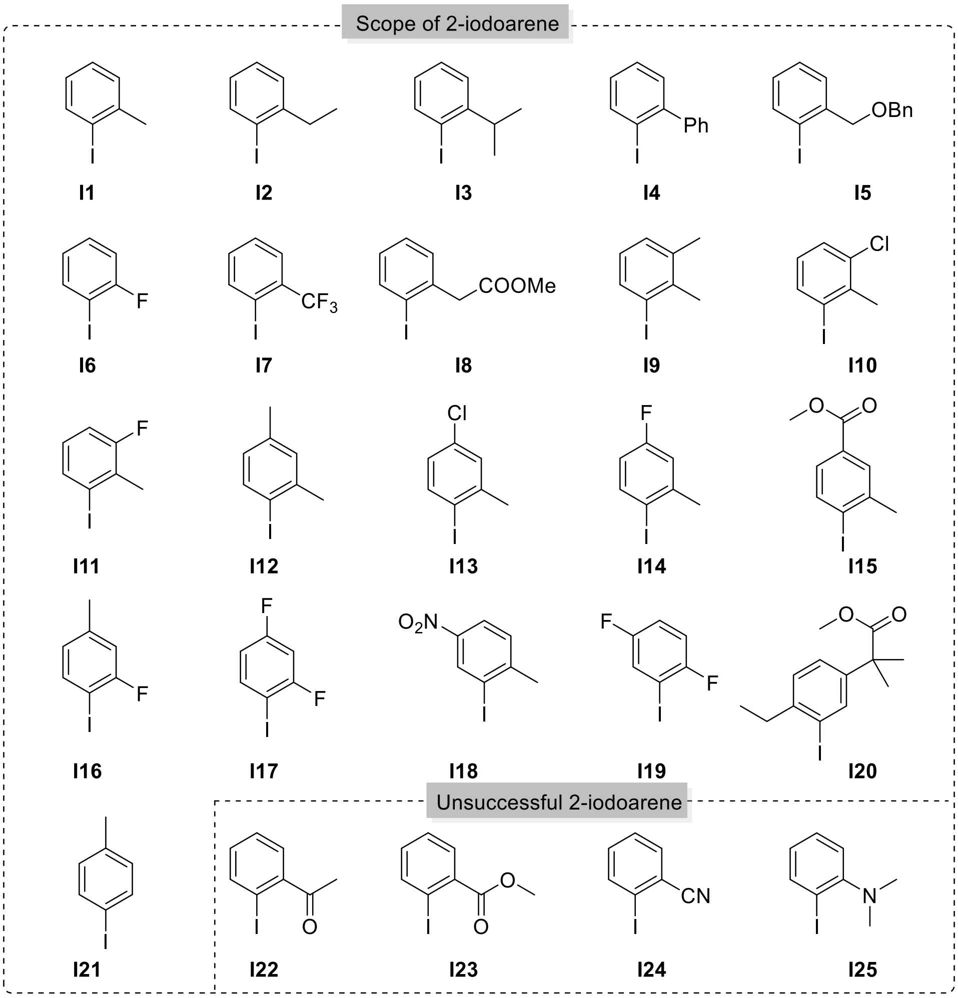


Figure S26: Iodoarenes used in this study. Except for **I20**, all are commercially available

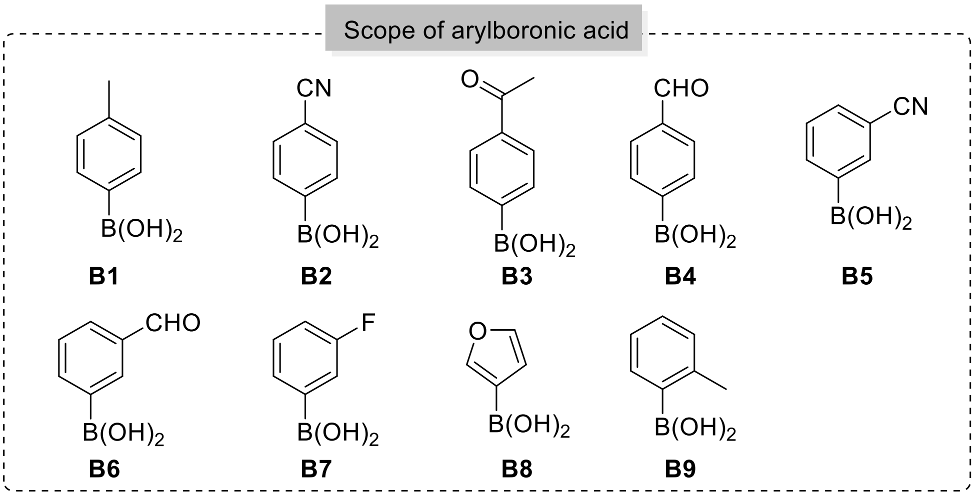


Figure S27: Boronic acids used in this study. All are commercially available

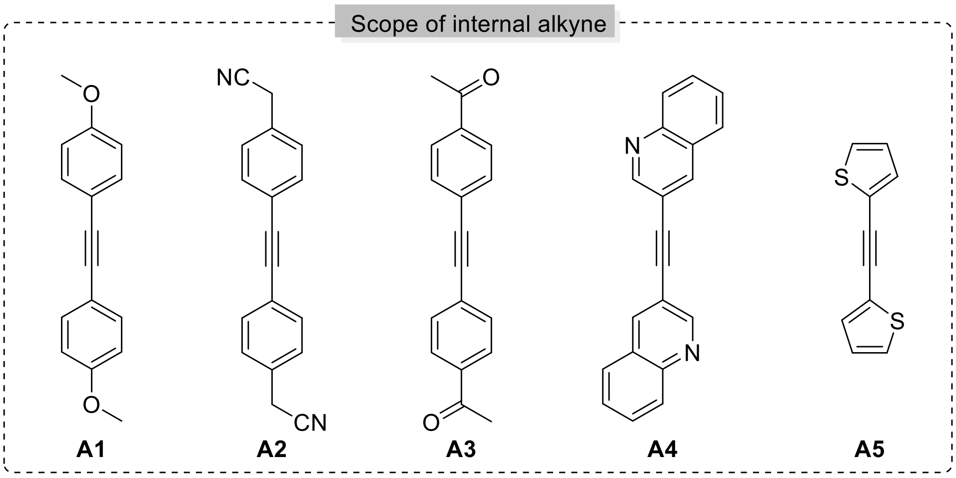
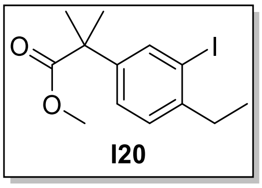


Figure S28: Internal alkynes used in this study. Except for **A2**, all are reported in the literature



I20

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68 (s, 1H), 7.16 (d, *J* = 9.2 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 3.57 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.46 (s, 6H), 1.11 (t, *J* = 7.6 Hz, 3H**). ^{13}C NMR (126 MHz, CDCl$_3$)** δ 176.8, 145.0, 144.2, 136.6, 128.3, 126.1, 100.8, 52.4, 45.9, 33.8, 26.6, 14.5. **IR(ATR/cm^{-1})** 2968.8, 2949.3, 2932.5, 2872.7, 2840.3, 1728.6, 1598.0, 1546.1, 1484.9, 1470.9, 1461.2, 1433.0, 1386.2, 1368.4, 1253.2, 1189.6, 1144.2, 1103.9, 1061.0, 1027.3, 1014.3, 988.3, 927.3, 879.2, 849.3, 828.6, 803.9, 774.0, 715.6, 664.9, 628.6, 611.7. **HRMS (ESI)** m/z calcd. for $C_{13}H_{18}IO_2$ ($[M+H]^+$) 333.0346, found m/z 333.0354.

Synthesis of internal alkynes

General Procedure A: The reported procedure was followed with some modifications.[9] Corresponding aryl halide (5.0 mmol) was taken into 50 mL two neck RB with magnetic stirring bar under argon atmosphere. It was vacuumed for 5 min and filled back with argon. 10 mL pre-degassed triethylamine (Et_3N) was added and charged with $PdCl_2(PPh_3)_2$ (5.0 mol%) along with CuI (1.0 mol %) under inert atmosphere. The whole solution was again degassed for 5 min. Lastly, corresponding aryl acetylene (5.1 mmol) was added and stoppered tightly. Further, it was allowed to run at rt for 12 h. Thereafter, Et_3N was neutralized via slow addition of 1M aqueous HCl solution under stirring mode. The neutralized reaction mixture was extracted using DCM (3 × 10 mL). The extracted organic layer underwent washing with brine solution (10 mL) followed by drying using anhydrous Na_2SO_4. Furthermore, the solvent was evaporated under reduced pressure, and a slurry was prepared. The slurry was packed into a column, and the corresponding compound was purified using ethyl acetate and hexane as eluent. Finally, the solvent was reduced to get desired internal aryl alkynes.

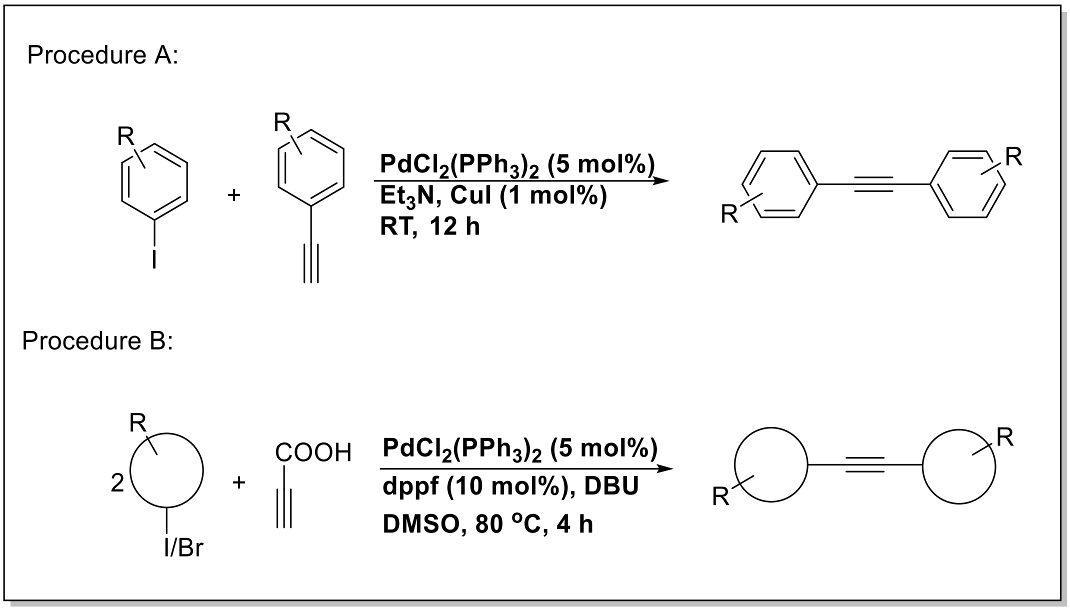
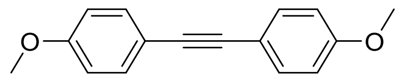


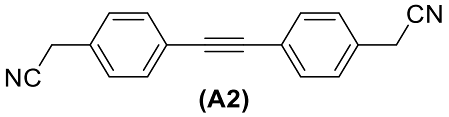
Figure S29: Schematic protocol for the synthesis of internal alkynes

General Procedure B: This procedure was followed according to the reported literature with some modifications.[10] Aryl halide (4.0 mmol) was introduced into 25 ml two neck RB equipped with magnetic bead followed by $PdCl_2(PPh_3)_2$ (5.0 mol%), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (10.0 mol%), DMSO (2.0 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (4.0 mmol) under inert atmosphere. It was stirred for a minute, and then after, propiolic acid (2.0 mmol) was charged, followed by capping the RB tightly. After stirring at 80 °C for 4h, the reaction mixture was allowed to attain room temperature. Further, the reaction mixture was extracted using brine solution and ethyl acetate (5 x 4 mL). The organic layer was washed with fresh distilled water (4.0 mL) and dried using anhydrous Na_2SO_4. A slurry was prepared after evaporating the solvent under a rotary evaporator. The slurry was charged into the column afterward, and the product was eluted using ethyl acetate and hexane as eluent. Finally, the desired compound was obtained after evaporating the solvent under reduced pressure.



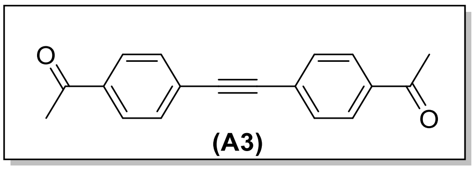
(A1)

1,2-bis(4-methoxyphenyl)ethyne **(A1)** has been synthesized following general procedure A. It is a colorless solid compound with 84% yield (1000.1 mg, 4.2 mmol). The NMR was found to be matched with reported value in literature.[10] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 9.2 Hz, 4H), 6.79 (d, *J* = 8.5 Hz, 4H), 3.74 (s, 6H) **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.5, 133.0, 115.8, 114.1, 88.1, 55.4.



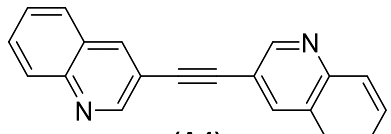
(A2)

2,2'-(ethyne-1,2-diylbis(4,1-phenylene))diacetonitrile **(A2)** has been synthesized following general procedure B. It is a yellowish solid compound with 70% yield (358.6 mg, 1.4 mmol). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.47 (d, *J* = 7.9 Hz, 4H), 7.25 (d, *J* = 7.9 Hz, 4H), 3.70 (s, 4H).**^{13}C NMR (126 MHz, CDCl$_3$)** δ 132.4, 130.2, 128.1, 123.1, 117.5, 89.4, 23.7. **IR(ATR/cm^{-1})** 2943.8, 2917.8, 2244.6, 1511.5, 1410.2, 1186.6, 1103.4, 1020.2, 921.5,833.3, 796.7, 708.3 **HRMS (ESI)** m/z calcd. for $C_{18}H_{12}N_2Na$ ($[M+Na]^+$) 279.0893, found m/z 279.0923.



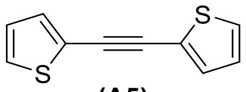
(A3)

1,1'-(ethyne-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) **(A3)** has been synthesized following general procedure B. It is a colorless solid compound with 68% yield (356.4 mg, 1.4 mmol). The NMR was found to be matched with reported value in literature. [10] **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 8.1 Hz, 4H), 7.63 (d, *J* = 8.1 Hz, 4H), 2.62 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 197.4, 136.8, 132.0, 128.5, 127.6, 91.8, 26.8.



(A4)

1,2-di(quinolin-3-yl)ethyne **(A4)** has been synthesized following general procedure B. It is a yellowish solid compound with 72% yield (403.4 mg, 1.4 mmol). The NMR was found to be matched with reported value in literature. [11] **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.05 (d, *J* = 2.1 Hz, 2H), 8.37 (d, *J* = 2.1 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.75 (t, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H).**^{13}C NMR (126 MHz, CDCl$_3$)** δ 151.9, 147.0, 138.7, 130.5, 129.5, 127.7, 127.5, 127.2, 116.8, 89.9.



(A5)

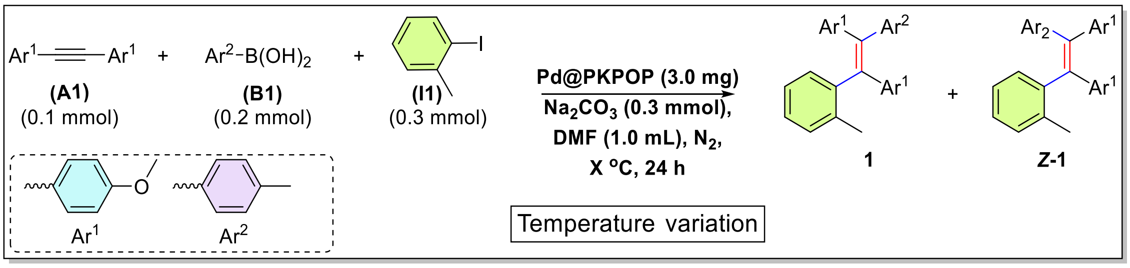
1,2-di(thiophen-2-yl)ethyne **(A5)** has been synthesized following general procedure B. It is a colorless solid compound with 74% yield (281.2 mg, 1.5 mmol). The NMR was found to be matched with reported value in literature. [10] **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.23 (d, *J* = 5.6 Hz, 2H), 7.21 (d, *J* = 3.8 Hz, 2H), 6.97 – 6.92 (m, 2H).**^{13}C NMR (126 MHz, CDCl$_3$)** δ 132.2, 127.7, 127.3, 123.0, 86.3.

Section SM-VIII: Catalytic activity of Pd@PKPOP

General procedure for optimization of reaction condition

To a 16 mL culture tube equipped with a magnetic stirrer bar, the required amount of **Pd@PKPOP**, 1,2-bis(4-methoxyphenyl)ethyne **(A1)**, *p*-tolylboronic acid **(B1)**, 1-iodo-2-methylbenzene **(I1)** Na_2CO_3 and 1,3,5-trimethoxybenzene as internal standard were taken under inert atmosphere, followed by dried DMF was added. Thereafter, it was capped tightly and kept in an ambient pre-heated oil bath at 250 rpm stirring. After stirring for the speculated time, it was kept to attain rt. 2 mL brine solution, and 5 mL ethyl acetate was poured into the same culture tube. The mixture was shaken well and allowed the layer to be separated. 2 mL aliquot of separated ethyl acetate was dried under anhydrous Na_2SO_4. The ethyl acetate was well evaporated, and the residue was dissolved into 0.5 mL $CDCl_3$ solvent. Further, it was transferred into an NMR tube, and the product was quantified through ^{1}H NMR analysis. 1,2-bis(4-methoxyphenyl)ethyne **A1** was treated as limiting reagent.

Table ST4: Temperature variation



Entry	Temperature (°C)	Yield (%)^a **(1 + *Z*-1)**	Selectivity **(1 : *Z*-1)**
1	90	70	87 : 13
2	100	90	88 : 12
3	**110**	**96 (91)^b**	**90 : 10**
4	120	94	89 : 11
5	130	91	89 : 11
6	140	91	88 : 12
7	150	73	88 : 12

Reaction conditions: **A1** (0.1 mmol), **B1** (0.2 mmol), **I1** (0.3 mmol), DMF (1.0 mL), Na_2CO_3 (0.3 mmol), **Pd@PKPOP** (3.0 mg, 2.7 wt% Pd), 24 h, N_2. ^{a}Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^{b}Isolated yield

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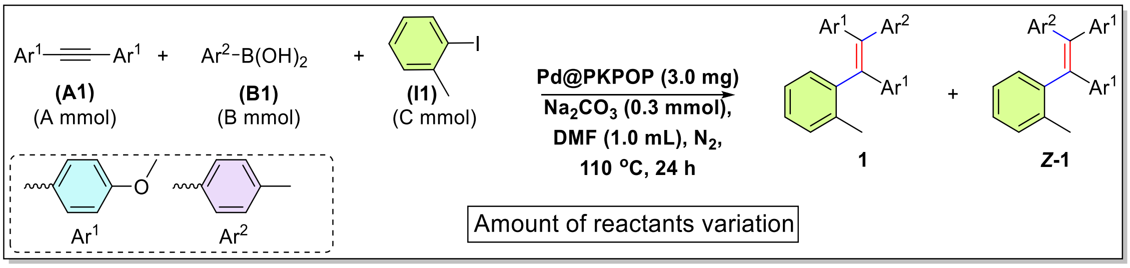
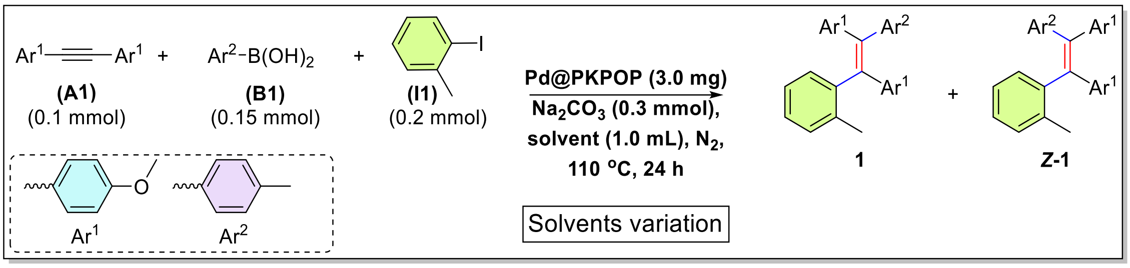
Table ST5: Amount of reactants variation



Entry	Amount of reactants (10^{-1} mmol)	Yield (%)^a **(1 + *Z*-1)**	Selectivity **(1 : *Z*-1)**
1	1:2:3	96	90 : 10
2	**1:1.5:2**	**96 (91)^b**	**90 : 10**
3	1:1.2:1.5	88	89 : 11
4	1:1.1:1.2	81	89 : 11

Reaction conditions: DMF (1.0 mL), Na_2CO_3 (0.3 mmol), **Pd@PKPOP** (3.0 mg, 2.7 wt% Pd), 110 °C, 24 h, N_2. ^{a}Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^{b}Isolated yield

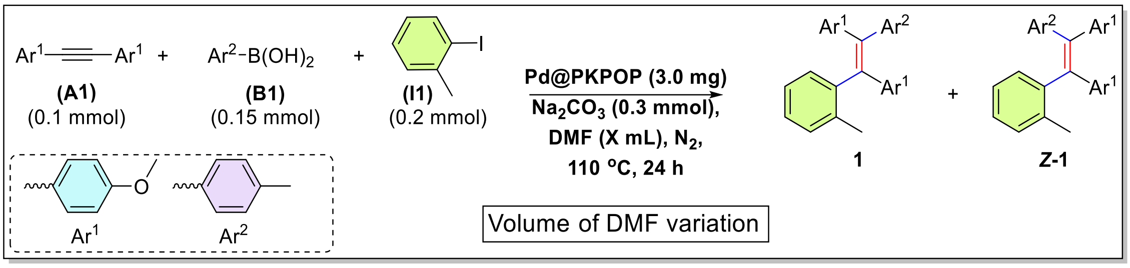
Table ST6: Solvents variation



Entry	Solvent (1.0 mL)	Yield (%)[a] **(1 + *Z*-1)**	Selectivity **(1 : *Z*-1)**
1	Tetrahydrofuran (THF)	trace	-
2	*ter*-Amylalcohol (^{t}AmOH)	trace	-
3	**DMF**	**96 (91)[b]**	**90 : 10**
4	Toluene	trace	-
5	Acetonitrile (MeCN)	10	85 : 15
6	Water (H_2O)	10	100 : 0
7	1,2-dichloroethane (DCE)	trace	-
8	Dimethylsulphoxide (DMSO)	80	78 : 22
9	Chlorobenzene (PhCl)	trace	-
10	Benzene	trace	-
11	1,4-dioxane	20	95 : 05

Reaction conditions: **A1** (0.1 mmol), **B1** (0.15 mmol), **I1** (0.2 mmol), Na_2CO_3 (0.3 mmol), **Pd@PKPOP** (3.0 mg, 2.7 wt% Pd), 110 °C, 24 h, N_2. [a]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield

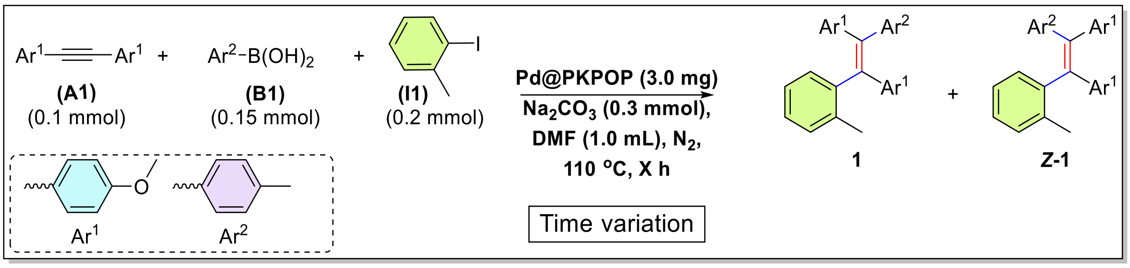
Table ST7: Volume of DMF variation



Entry	Volume of DMF (mL)	Yield (%)[a] **(1 + *Z*-1)**	Selectivity **(1 : *Z*-1)**
1	0.1	83	86 : 14
2	0.25	84	86 : 14
3	0.5	92	89 : 11
4	**1.0**	**96 (91)[b]**	**90 : 10**
5	1.5	92	90 : 10

Reaction conditions: **A1** (0.1 mmol), **B1** (0.15 mmol), **I1** (0.2 mmol), Na_2CO_3 (0.3 mmol), **Pd@PKPOP** (3.0 mg, 2.7 wt% Pd), 110 °C, 24 h, N_2. [a]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield

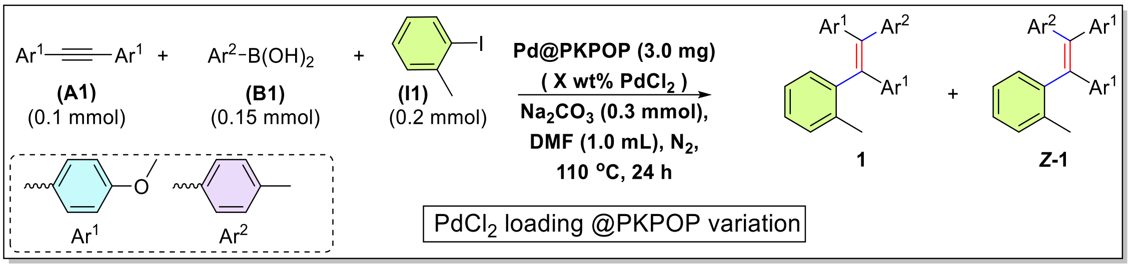
Table ST8: Time variation



Entry	Time (h)	Yield (%)[a] (**1 + *Z*-1**)	Selectivity (**1 : *Z*-1**)
1	16	72	89 : 11
2	20	81	89 : 11
3	**24**	**96 (91)[b]**	**90 : 10**
4	36	95	90 : 10
5	48	95	90 : 10

Reaction conditions: **A1** (0.1 mmol), **B1** (0.15 mmol), **I1** (0.2 mmol), Na_2CO_3 (0.3 mmol), **Pd@PKPOP** (3.0 mg, 2.7 wt% Pd), N_2. [a]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield

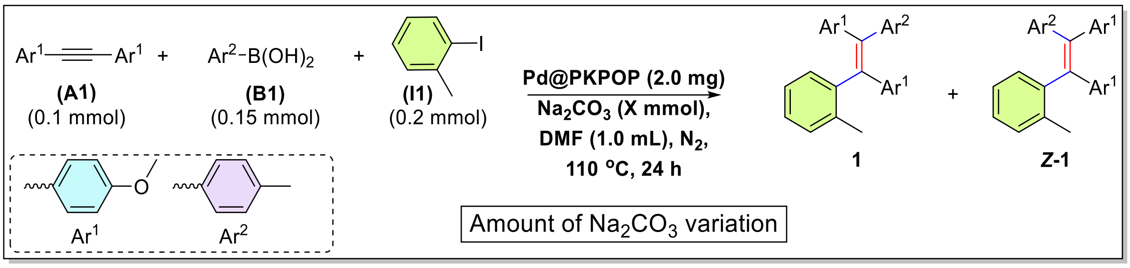
Table ST9: PdCl$_2$ loading at PKPOP variation



Entry	Theoretical loading of PdCl$_2$ over **PKPOP** (wt%)	Yield (%)[a] (**1 + *Z*-1**)	Selectivity (**1 : *Z*-1**)
1	2	46	89 : 11
2	4	81	89 : 11
3	6	96	90 : 10
4	8	96	90 : 10
5[c]	**6**	**96 (91)[b]**	**90 : 10**
6[d]	6	71	90 : 10

Reaction conditions: **A1** (0.1 mmol), **B1** (0.15 mmol), **I1** (0.2 mmol), Na_2CO_3 (0.3 mmol), **Pd@PKPOP** (3.0 mg), 110 °C, 24 h, N_2. [a]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield. [c]**Pd@PKPOP** (2.0 mg), [d]**Pd@PKPOP** (1.5 mg)

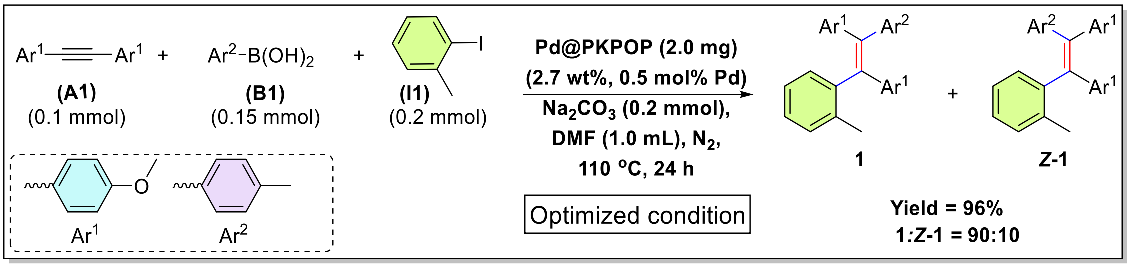
Table ST10: Amount of Na_2CO_3 variation



Entry	Amount of Na_2CO_3 (mmol)	Yield (%)[a] **(1 + *Z*-1)**	Selectivity **(1 : *Z*-1)**
1	0.05	72	90 : 10
2	0.10	81	90 : 10
3	0.15	87	90 : 10
4	**0.20**	**96 (91)[b]**	**90 : 10**
5	0.30	96	90 : 10

Reaction conditions: **A1** (0.1 mmol), **B1** (0.15 mmol), **I1** (0.2 mmol), **Pd@PKPOP** (2.0 mg, 2.7 wt% Pd), 110 °C, 24 h, N_2. [a]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield

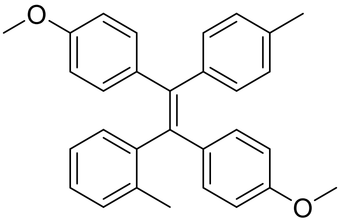
Table S11: Final optimized condition



General procedure for palladium-catalyzed *trans*-selective dicarbofunctionalization of internal alkynes via **Pd@PKPOP**

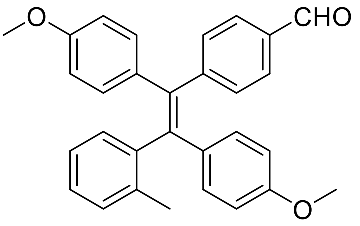
To a 16 mL culture tube equipped with a magnetic stirrer bar, **Pd@PKPOP** (2.0 mg, 0.5 mol% Pd), diarylacetylene **Ax** (0.1 mmol), aryl boronic acid **Bx** (0.15 mmol), aryl halide **Ix** (0.2 mmol) and Na_2CO_3 (0.2 mmol) were taken under inert atmosphere. Dried DMF (1.0 mL) was then added, and the tube was capped tightly and kept in a pre-heated (110 °C) oil bath at 250 rpm stirring speed. After 24 h, the oil bath was removed, and the mixture was allowed to attain rt. The reaction mixture was transferred into a centrifuge tube, and the catalyst was centrifuged. The mother liquor was added to brine (5 mL) and then extracted using ethyl acetate (3 x 2 mL). The organic layer was washed with distilled water (5mL) and dried over anhydrous Na_2SO_4. Further, the organic layer was evaporated under reduced pressure, and a slurry was prepared. The slurry was packed into a silica gel column and eluted using ethyl acetate and hexane as eluent. The final product was obtained after reducing the eluent under the rota-evaporator. The major product *E* has been given w.r.t internal alkyne.

Note:- The general reaction time was 24 h unless explicitly stated.



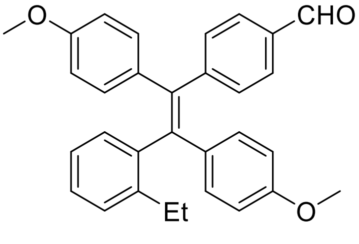
(1)

(*Z*)-4,4'-(1-(o-tolyl)-2-(p-tolyl)ethene-1,2-diyl)bis(methoxybenzene) **(1)** has been obtained as a colorless solid in 91% yield. **R_f =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 38.2 mg, 0.091 mmol, **Selectivity** = 90 : 10. The NMR data was found to be matched with the reported literature value.[12] **^{1}H NMR (500 MHz, CDCl$_3$)** δ 6.98 – 6.90 (m, 4H), 6.90 – 6.85 (m, 4H), 6.80 – 6.75 (m, 4H), 6.50 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 6.9 Hz, 2H), 3.62 (s, 3H), 3.60 (s, 3H), 2.19 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 158.0, 157.8, 143.7, 141.0, 140.2, 138.4, 136.7, 136.6, 136.0, 135.8, 131.9 1, 131.88, 131.5, 130.2, 128.6, 126.7, 125.5, 113.1, 112.8, 55.17, 55.17, 21.3, 20.3.



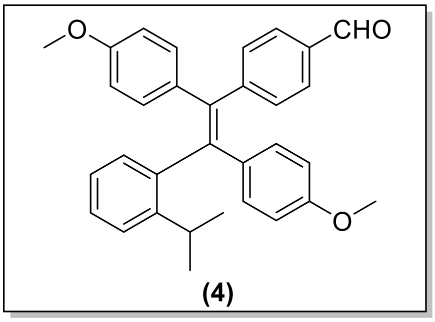
(2)

(*Z*)-4-(1,2-bis(4-methoxyphenyl)-2-(o-tolyl)vinyl)benzaldehyde **(2)** has been obtained as a light yellowish green solid in 91% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 39.4 mg, 0.091 mmol, **Selectivity** = 92 : 8. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.83 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.98 – 6.90 (m, 4H), 6.76 (d, *J* = 3.1 Hz, 2H), 6.74 (d, *J* = 3.1 Hz, 2H), 6.50 (d, *J* = 2.4 Hz, 2H), 6.48 (d, *J* = 2.4 Hz, 2H), 3.60 (s, 3H), 3.59 (s, 3H), 1.99 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 192.0, 158.4, 158.3, 151.0, 142.9, 140.9, 139.1, 136.5, 135.4, 134.8, 134.4, 132.2, 132.0, 131.9, 131.6, 130.3, 129.4, 127.1, 125.7, 113.3, 113.1, 55.1, 20.3. **IR (ATR/cm^{-1})** 3011.4, 2975.0, 2941.0, 2915.2, 2839.8, 2730.6, 1698.7, 1594.7, 1508.9, 1451.8, 1246.6, 1173.6, 1022.9, 809.7 **HRMS (ESI)** m/z calcd. for $C_{30}H_{26}NaO_3$ ([M+Na]$^+$) 457.1774, found m/z 457.1797.



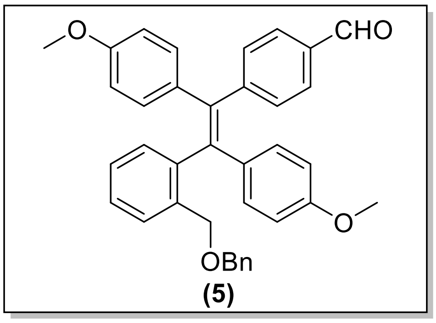
(3)

(*Z*)-4-(2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(3)** has been obtained as a light yellowish green solid compound in 92% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 41.5 mg, 0.092 mmol, **Selectivity** = 94 : 6. **mp** = 146-148 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.84 (s, 1H), 7.57 (d, 2H), 7.17 (d, *J* = 10.4 Hz, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.03 (d, 1H), 6.97 – 6.93 (m, 1H), 6.93 – 6.88 (m, 1H), 6.76 (d, 2H), 6.73 (d, 2H), 6.50 (d, 2H), 6.48 (d, 2H), 3.61 (s, 3H), 3.60 (s, 3H), 2.52 – 2.44 (m, 1H), 2.38 – 2.30 (m, 1H), 0.87 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.0, 158.4, 158.2, 151.1, 142.3, 141.0, 138.9, 135.3, 135.1, 134.4, 132.2, 132.1, 131.9, 131.7, 129.4, 128.5, 127.3, 125.5, 113.3, 113.1, 55.2, 55.1, 26.0, 14.4. **IR (ATR/cm^{-1})** 2964.6, 2930.8, 2839.8, 2730.6, 1693.5, 1597.3, 1506.3, 1243.8, 1171.0, 1022.9, 833.1, 812.3, 760.3 **HRMS (ESI)** m/z calcd. for $C_{31}H_{28}NaO_3$ ([M+Na]$^+$) 471.1931, found m/z 471.1928.



(4)

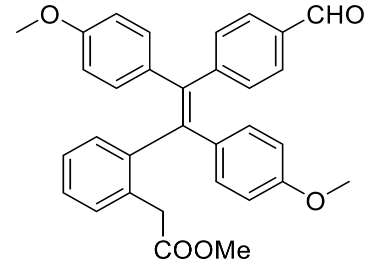
(*Z*)-4-(2-(2-isopropylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(4)** has been obtained as an orange solid in 71% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 32.7 mg, 0.071 mmol, **Selectivity** = 95 : 5. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.09 (m, 2H), 6.97 – 6.92 (m, 2H), 6.78 (d, *J* = 2.4 Hz, 2H), 6.76 (d, *J* = 3.1 Hz, 2H), 6.52 (d, *J* = 4.3 Hz, 2H), 6.50 (d, *J* = 3.7 Hz, 2H), 3.63 (s, 3H), 3.62 (s, 3H), 3.11 (h, *J* = 6.7 Hz, 1H), 0.88 (d, *J* = 7.3 Hz, 3H), 0.72 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.1, 158.4, 158.3, 151.1, 147.2, 141.7, 141.1, 138.9, 135.6, 135.3, 134.4, 132.3, 132.2, 131.6, 129.4, 127.6, 126.1, 125.5, 113.3, 113.2, 55.2, 30.2, 24.7, 23.2. **IR (ATR/cm^{-1})** 2954.2, 2930.8, 2839.8, 2735.9, 1698.7, 1599.9, 1508.9, 1454.9, 1290.6, 1241.2, 1171.0, 1030.7, 833.1, 807.1, 757.7 **HRMS (ESI)** m/z calcd. for $C_{32}H_{30}NaO_3$ ([M+Na]$^+$) 485.2087, found m/z 485.2089.



(5)

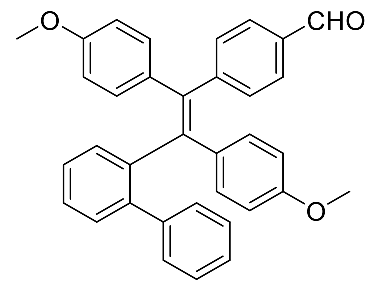
(*Z*)-4-(2-(2-((benzyloxy)methyl)phenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(5)** has been obtained as a light green solid in 78% yield. **R_f =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 42.0 mg, 0.078 mmol, **Selectivity** = 89 : 11. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 2.3 Hz, 3H), 7.22 – 7.20 (m, 1H), 7.18 (s, 1H), 7.14 – 7.11 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 2.1 Hz, 2H), 6.48 (d, *J* = 2.1 Hz, 2H), 4.40 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 4.29 (d, *J* = 11.9 Hz, 1H), 4.04 (d, *J* = 11.9 Hz, 1H), 3.64 (s, 3H), 3.62 (s, 3H). **^{13}C**

NMR (126 MHz, $CDCl_3$) δ 192.1, 158.5, 158.4, 150.9, 142.3, 140.1, 139.3, 138.5, 136.7, 135.1, 134.7, 134.4, 132.23, 132.17, 132.0, 129.4, 128.6, 128.5, 127.9, 127.7, 127.5, 127.4, 113.3, 113.2, 72.8, 70.5, 55.23, 55.18. **IR(ATR/cm^{-1})** 2962.0, 2925.6, 2852.8, 2733.2, 1693.5, 1602.5, 1501.1, 1456.4, 1243.8, 1173.6, 1106.0, 1069.7,1028.1, 822.7, 796.7, 713.7, 697.9 **HRMS (ESI)** m/z calcd. for $C_{37}H_{32}NaO_4$ ($[M+Na]^+$) 563.2193, found m/z 563.2184.



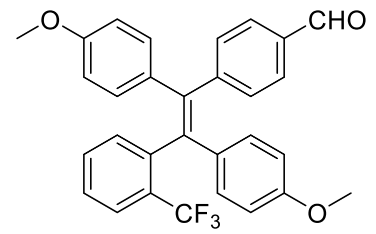
(6)

methyl (*Z*)-2-(2-(2-(4-formylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)phenyl)acetate **(6)** has been obtained as a yellow solid in 91% yield. **R_f =** 0.2, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 45.0 mg, 0.091 mmol, **Selectivity** = 89 : 11. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 2.4 Hz, 2H), 7.08 – 7.01 (m, 4H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 2.1 Hz, 2H), 6.50 (d, *J* = 2.3 Hz, 2H), 3.63 (s, 3H), 3.62 (s, 3H), 3.52 (d, *J* = 16.0 Hz, 1H), 3.52 (s, 3H), 3.18 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.0, 172.2, 158.5, 158.4, 150.8, 143.1, 140.0, 139.6, 134.9, 134.8, 134.5, 132.7, 132.4, 132.3, 132.2, 132.1, 130.6, 129.4, 127.5, 127.1, 113.4, 113.2, 55.18, 55.16, 51.9, 38.7. **IR(ATR/cm^{-1})** 3003.6, 2959.4, 2928.2, 2342.4, 2738.4, 1735.1, 1690.9, 1690.9, 1602.5, 1503.7, 1290.6, 1246.4, 1207.4, 1171.0, 1028.1, 822.7, 799.3, 752.5 **HRMS (ESI)** m/z calcd. for $C_{32}H_{28}NaO_5$ ($[M+Na]^+$) 515.1829, found m/z 515.1823.



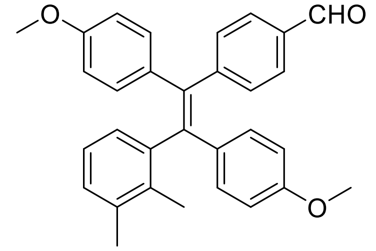
(7)

(*Z*)-4-(2-([1,1'-biphenyl]-2-yl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(7)** has been obtained as a yellowish green solid in 72% yield. **R_f =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 35.8 mg, 0.072 mmol, **Selectivity** = 90 : 10. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.79 (s, 1H), 7.50 (d, *J* = 10.1 Hz, 2H), 7.19 – 7.12 (m, 3H), 7.11 – 7.08 (m, 2H), 7.07 – 7.05 (m, 2H), 7.03 – 7.01 (m, 2H), 7.01 – 6.99 (m, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 8.9 Hz, 2H), 6.35 (d, *J* = 8.9 Hz, 2H), 6.23 (d, *J* = 6.7 Hz, 2H), 3.63 (s, 3H), 3.62 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.0, 158.4, 158.1, 151.5, 142.1, 141.9, 141.5, 139.3, 138.6, 135.9, 135.1, 134.2, 132.8, 132.3, 131.9, 130.5, 129.3, 128.8, 127.7, 127.6, 127.1, 126.5, 113.2, 112.8, 55.24, 55.22. **IR(ATR/cm^{-1})** 3011.4, 2959.4, 2933.4, 2837.2 2811.2, 2727.5, 1696.1, 1599.9, 1507.7, 1446.6, 1243.8, 1176.8, 1033.3, 835.7, 812.3, 714.3, 700.5 **HRMS (ESI)** m/z calcd. for $C_{35}H_{28}NaO_3$ ($[M+Na]^+$) 519.1931, found m/z 519.1925



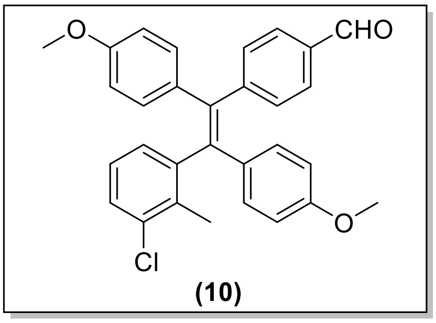
(8)

(*Z*)-4-(1,2-bis(4-methoxyphenyl)-2-(2-(trifluoromethyl)phenyl)vinyl)benzaldehyde **(8)** has been obtained as a light yellow solid in 34% yield. **Reaction time** = 60 h, **R_f =** 0.2, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 16.7 mg, 0.034 mmol, **Selectivity** = 87 : 13. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.96 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.58 (m, 1H), 7.41 – 7.37 (m, 1H), 7.33 – 7.30 (m, 1H), 7.30 – 7.29 (m, 1H), 7.27 (d, *J* = 6.4 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 1.4 Hz, 2H), 6.60 (d, *J* = 1.4 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 191.9, 158.5, 158.3, 150.5, 141.7 (q, *J* = 0.8 Hz), 139.6, 138.9, 134.7, 134.4, 133.9, 133.7, 132.1, 132.0, 131.7 (q, *J* = 6.5 Hz), 131.3, 129.3, 129.2, 127.1, 126.91 (q, *J* = 4.8 Hz), 124.16 (q, *J* = 272.1 Hz), 113.1, 55.08, 55.06. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -58.7. **IR(ATR/cm^{-1})** 2956.8, 2920.4, 2847.6, 2741.0, 1701.3, 1602.5, 1506.3, 1456.9, 1308.8, 1246.4, 1171.0, 1124.2, 1106.0, 1125.4, 827.9, 814.9, 775.9 **HRMS (ESI)** m/z calcd. for $C_{30}H_{23}F_3NaO_3$ ([M+Na]$^+$) 511.1492, found m/z 511.1487.



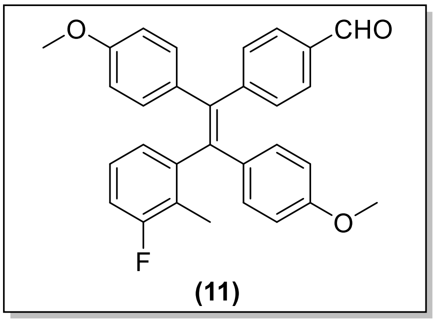
(9)

(*Z*)-4-(2-(2,3-dimethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(9)** has been obtained as a light yellowish green solid in 93% yield **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5:99.5), **Amount** = 42.0 mg, 0.093 mmol, **Selectivity** = 97 : 3. **mp** = 140-142 ^{o}C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.59 (d, *J* = 6.6 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.82 (m, 3H), 6.76 (d, *J* = 6.6 Hz, 2H), 6.74 (d, *J* = 6.4 Hz, 2H), 6.52 (d, *J* = 2.7 Hz, 2H), 6.50 (d, *J* = 2.6 Hz, 2H), 3.64 (s, 3H), 3.63 (s, 3H), 2.10 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.1, 158.3, 158.2, 151.1, 143.0, 141.5, 138.9, 137.0, 135.6, 135.2, 135.0, 134.4, 132.3, 132.0, 131.8, 129.4, 129.3, 128.6, 125.2, 113.3, 113.1, 55.23, 55.20, 20.6, 16.8. **IR (ATR/cm^{-1})** 2969.8, 2941.2, 2834.6, 2735.8, 1703.9, 1597.3, 1506.3, 1462.2, 1251.6, 1168.4, 1022.9, 825.3, 791.5, 708.3. **HRMS (ESI)** m/z calcd. for $C_{31}H_{28}NaO_3$ ([M+Na]$^+$) 471.1931, found m/z 471.1926.



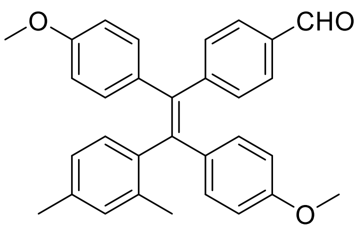
(10)

(*Z*)-4-(2-(3-chloro-2-methylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(10)** has been obtained as an orange solid in 90% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 42.0 mg, 0.090 mmol, **Selectivity** = 90 : 10. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.86 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.11 (dd, *J* = 6.8, 2.5 Hz, 1H), 6.90 – 6.88 (m, 2H), 6.75 (d, *J* = 3.4 Hz, 2H), 6.73 (d, *J* = 3.4 Hz, 2H), 6.54 (d, *J* = 3.2 Hz, 2H), 6.52 (d, *J* = 3.4 Hz, 2H), 3.64 (s, 3H), 3.64 (s, 3H), 2.08 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.0, 158.5, 158.5, 150.5, 145.0, 140.3, 139.8, 135.3, 135.0, 134.8, 134.6, 134.3, 132.2, 131.9, 131.8, 130.2, 129.5, 128.0, 126.5, 113.5, 113.3, 55.24, 55.22, 17.6. **IR (ATR/cm^{-1})** 2951.6, 2928.2, 2834.6, 2738.4, 1701.2, 1602.5, 1514.1, 1462.2, 1246.4, 1171.0, 1028.1, 817.5, 786.3, 726.5, 697.9. **HRMS (ESI)** m/z calcd. for $C_{30}H_{25}ClNaO_3$ ([M+Na]$^+$) 491.1384, found m/z 491.1376.



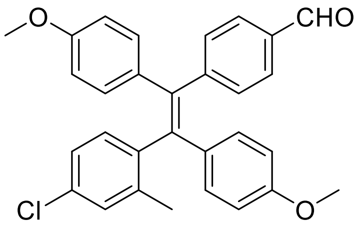
(11)

(*Z*)-4-(2-(3-fluoro-2-methylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(11)** has been obtained as a light yellowish green solid in 92% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 41.8 mg, 0.092 mmol, **Selectivity** = 91 : 9. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.86 (s, 1H), 7.60 (d, *J* = 10.1 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 6.91 (td, *J* = 7.5, 5.3 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 2.0 Hz, 2H), 6.74 (d, *J* = 1.8 Hz, 2H), 6.53 (d, *J* = 8.2 Hz, 4H), 3.65 (s, 3H), 3.65 (s, 3H), 1.92 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.0, 161.7 (d, *J* = 244.0 Hz), 158.5, 158.5, 150.6, 145.3 (d, *J* = 4.5 Hz), 139.9, 139.6 (d, *J* = 2.3 Hz), 135.1, 134.6, 134.5, 132.2, 131.9, 131.8, 129.5, 127.2 (d, *J* = 3.1 Hz), 126.5 (d, *J* = 9.0 Hz), 124.0 (d, *J* = 16.6 Hz), 113.6 (d, *J* = 24.8 Hz), 113.5, 113.3, 55.2, 55.2, 12.0 (d, *J* = 5.0 Hz). **^{19}F NMR (471 MHz, CDCl$_3$)** δ -116.2. **IR (ATR/cm^{-1})** 2964.6, 2930.8, 2839.8, 2741.0, 2738.4, 1709.1, 1597.3, 1501.1, 1457.0, 1236.0, 1176.2, 1025.5, 830.5, 781.1, 708.3. **HRMS (ESI)** m/z calcd. for $C_{30}H_{25}FNaO_3$ ([M+Na]$^+$) 475.1680, found m/z 475.1676.



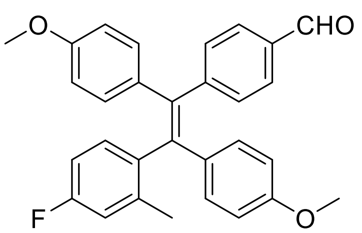
(12)

(*Z*)-4-(2-(2,4-dimethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(12)** has been obtained as a light yellowish green solid in 92% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 41.2 mg, 0.092 mmol, **Selectivity** = 91 : 9. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 3.1 Hz, 2H), 6.77 – 6.75 (m, 2H), 6.74 (d, 2H), 6.52 (d, *J* = 5.0 Hz, 2H), 6.50 (d, *J* = 2.0 Hz, 2H), 3.64 (s, 6H), 2.18 (s, 3H), 1.95 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.1, 158.3, 158.2, 151.3, 141.1, 140.0, 139.0, 136.7, 136.3, 135.7, 135.2, 134.4, 132.3, 132.0, 131.9, 131.5, 131.1, 129.4, 126.5, 113.3, 113.1, 55.23, 55.20, 21.3, 20.2. **IR(ATR/cm^{-1})** 2951.6, 2925.6, 2842.4, 2730.6, 1698.7, 1599.9, 1519.3, 1454.3, 1295.8, 1214.8, 1171.0, 1035.9, 833.1, 794.1. **HRMS (ESI)** m/z calcd. for $C_{31}H_{28}NaO_3$ ($[M+Na]^+$) 471.1931, found m/z 471.1937.



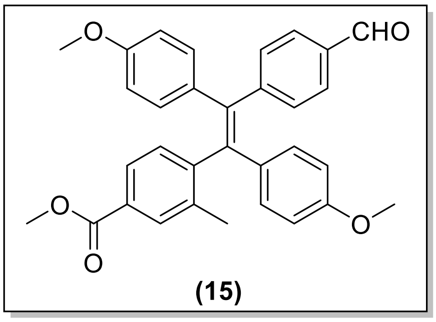
(13)

(*Z*)-4-(2-(4-chloro-2-methylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(13)** has been obtained as an orange solid in 81% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 38.0 mg, 0.081 mmol, **Selectivity** = 91 : 9. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.97 (dt, *J* = 4.9, 2.1 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 1H), 6.76 (d, *J* = 5.5 Hz, 2H), 6.74 (d, *J* = 4.9 Hz, 2H), 6.55 (d, *J* = 5.5 Hz, 2H), 6.53 (d, *J* = 4.9 Hz, 2H), 3.65 (s, 6H), 1.96 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.0, 158.6, 158.6, 150.5, 144.6, 140.0, 139.4, 135.0, 134.9, 134.6, 132.2, 131.9, 131.8, 131.7, 131.2, 131.1, 129.4, 129.1, 113.5, 113.3, 55.21, 55.19, 19.7. **IR(ATR/cm^{-1})** 3050.4, 2954.2, 2936.0, 2834.6, 2741.0, 1701.3, 1599.9, 1511.5, 1290.6 1241.2, 1171.0, 1030.7, 830.5, 736.9. **HRMS (ESI)** m/z calcd. for $C_{30}H_{25}ClNaO_3$ ($[M+Na]^+$) 491.1384, found m/z 491.1391.



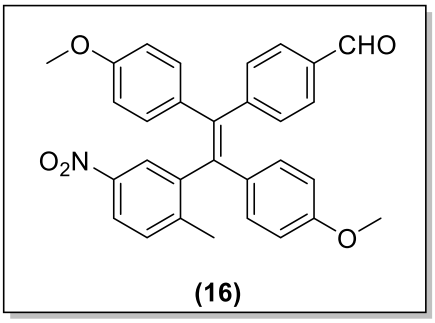
(14)

(*Z*)-4-(2-(4-fluoro-2-methylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(14)** has been obtained as a light green solid in 84% yield. **R*f* =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 38.0 mg, 0.084 mmol, **Selectivity** = 92 : 8 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.87 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.91 (dd, *J* = 8.1, 5.8 Hz, 1H), 6.77 (d, *J* = 5.8 Hz, 2H), 6.75 (d, *J* = 5.8 Hz, 2H), 6.72 – 6.68 (m, 2H), 6.54 (d, *J* = 4.3 Hz, 2H), 6.53 (d, *J* = 4.4 Hz, 2H), 3.65 (s, 6H), 1.96 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.0, 161.0 (d, *J* = 243.9 Hz), 158.59, 158.57, 150.6, 144.6 (d, *J* = 7.5 Hz), 139.8, 135.0, 134.6, 134.25, 132.23 (d, *J* = 2.9 Hz), 132.20, 132.0, 131.9, 131.8, 131.6 (d, *J* = 8.1 Hz), 129.5, 118.0 (d, *J* = 20.8 Hz), 114.0 (d, *J* = 20.8 Hz), 113.5, 113.3, 55.3, 55.2, 19.5. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -118.3. **IR(ATR/cm^{-1})** 2969.8, 2907.4, 2837.2, 2730.7, 1696.1, 1599.9, 1293.2, 1249.0, 1168.4, 1025.5, 827.9, 783.7. **HRMS (ESI)** m/z calcd. for $C_{30}H_{25}FNaO_3$ ($[M+Na]^+$) 475.1680, found m/z 475.1659.



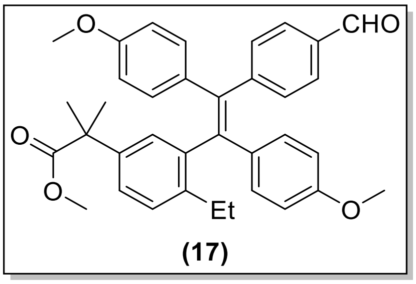
(15)

methyl (*Z*)-4-(2-(4-formylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)-3-methylbenzoate **(15)** has been obtained as a yellow solid in 67% yield. **R*f* =** 0.3, **Eluent** = EtOAc : hexane (1 : 99), **Amount** = 33.0 mg, 0.067 mmol, **Selectivity** = 88 : 12 **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.86 (s, 1H), 7.68 – 7.61 (m, 2H), 7.61 – 7.58 (m, 2H), 7.18 (d, *J* = 4.3 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.74 (d, 2H), 6.72 (d, 2H), 6.52 (d, *J* = 6.1 Hz, 2H), 6.50 (d, *J* = 6.7 Hz, 2H), 3.80 (s, 3H), 3.64 (s, 3H), 3.63 (s, 3H), 2.04 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 192.0, 167.3, 158.6, 150.4, 148.1, 140.0, 137.0, 134.9, 134.6, 134.1, 132.2, 132.0, 131.9, 131.7, 129.5, 128.7, 126.9, 113.5, 113.3, 55.2, 52.1, 20.3. **IR(ATR/cm^{-1})** 2951.6, 2920.4, 2837.2, 2738.4, 1693.5, 1599.9, 1506.3, 1438.7, 1293.4, 1249.0, 1163.2, 1106.0, 1038.5, 827.9, 786.3. **HRMS (ESI)** m/z calcd. for $C_{32}H_{28}NaO_5$ ($[M+Na]^+$) 515.1829, found m/z 515.1832.



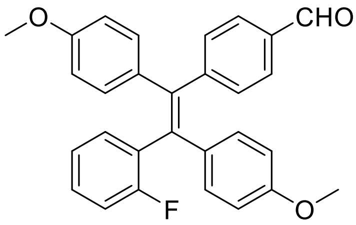
(16)

(*Z*)-4-(1,2-bis(4-methoxyphenyl)-2-(2-methyl-5-nitrophenyl)vinyl)benzaldehyde **(16)** has been obtained as an orange solid in 44% yield. **R*f* =** 0.2, **Eluent** = EtOAc : hexane (1 : 99), **Amount** = 21.0 mg, 0.044 mmol, **Selectivity** = 87 : 13 **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.87 (s, 1H), 7.90 – 7.84 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.19 (dd, 2H), 7.13 (s, 1H), 6.75 (d, *J* = 2.4 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 2H), 6.55 (d, *J* = 7.3 Hz, 2H), 6.52 (d, 2H), 3.66 (s, 3H), 3.63 (s, 3H), 2.11 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 192.0, 158.8, 149.9, 146.3, 144.8, 144.4, 141.1, 138.6, 134.8, 134.4, 133.4, 132.1, 131.9, 131.8, 131.3, 129.5, 126.7, 122.0, 113.8, 113.6, 55.3, 20.6. **IR (ATR/cm^{-1})** 2951.6, 2928.2, 2839.8, 2741.0, 1696.1, 1599.9, 1508.9, 1345.3, 1241.2, 1171.0, 1030.7, 827.9, 807.1, 736.9. **HRMS (ESI)** m/z calcd. for $C_{30}H_{25}NNaO_5$ ([M+Na]$^+$) 502.1625, found m/z 502.1679.



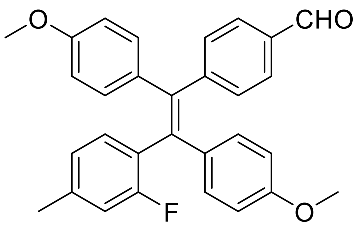
(17)

methyl (*Z*)-2-(4-ethyl-3-(2-(4-formylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)phenyl)-2-methylpropanoate **(17)** has been obtained as a yellow solid in 85% yield. **R$_f$ =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 46.5 mg, 0.085 mmol, **Selectivity** = 95 : 5 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.86 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 6.3 Hz, 2H), 7.03 – 7.00 (m, 2H), 6.87 (s, 1H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 3.64 (s, 3H), 3.61 (s, 3H), 3.45 (s, 3H), 2.38 – 2.30 (m, 2H), 1.32 (s, 3H), 1.29 (s, 3H), 0.85 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.1, 177.4, 158.4, 158.3, 150.8, 142.2, 141.8, 141.5, 141.1, 139.1, 135.5, 134.6, 134.4, 132.2, 132.0, 131.9, 129.7, 129.4, 128.5, 124.2, 113.3, 113.2, 55.2, 52.1, 46.0, 26.6, 26.3, 25.8, 14.3. **IR (ATR/cm^{-1})** 2964.6, 2928.2, 2855.4, 2735.9, 1729.9, 1698.7, 1602.5, 1506.3, 1464.8, 1288.0, 1243.8, 1176.2, 1150.2, 1025.5, 820.1, 773.3. **HRMS (ESI)** m/z calcd. for $C_{36}H_{36}NaO_5$ ([M+Na]$^+$) 571.2455, found m/z 571.2460.



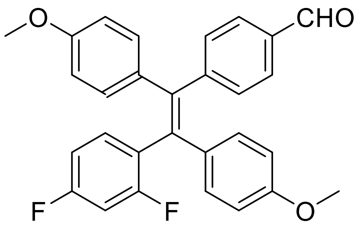
(18)

(*Z*)-4-(2-(2-fluorophenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(18)** has been obtained as light green solid compound in 53% yield. **Reaction time** = 48 h, **R$_f$ =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 23.3 mg, 0.053 mmol, **Selectivity** = 88 : 12. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.85 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.04 (m, 1H), 7.02 – 6.97 (m, 1H), 6.90 – 6.87 (m, 1H), 6.84 (d, *J* = 2.3 Hz, 2H), 6.83 (d, *J* = 2.9 Hz, 2H), 6.82 – 6.78 (m, 1H), 6.56 (d, *J* = 3.2 Hz, 2H), 6.55 (d, *J* = 3.2 Hz, 2H), 3.65 (s, 3H), 3.65 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.1, 160.3 (d, *J* = 247.7 Hz), 158.62, 158.59, 150.3, 141.1, 135.3 (d, *J* = 14.7 Hz), 134.5 (d, *J* = 8.2 Hz), 132.9 (d, *J* = 4.1 Hz), 132.1, 131.9, 131.84, 131.81, 131.3 (d, *J* = 8.2 Hz), 129.4, 129.0 (d, *J* = 8.2 Hz), 123.9 (d, *J* = 4.1 Hz), 115.8 (d, *J* = 22.1 Hz), 113.5, 113.3, 55.2. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -113.3. **IR (ATR/cm^{-1})** 3081.5, 3011.3, 2972.4, 2837.2, 2733.2, 1696.4, 1602.5, 1506.3, 1454.4, 1243.8, 1171.0, 1022.9, 822.7, 757.7 **HRMS (ESI)** m/z calcd. for $C_{29}H_{23}FNaO_3$ ([M+Na]$^+$) 461.1523, found m/z 461.1522.



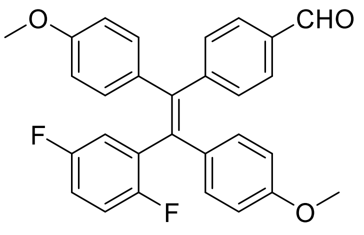
(19)

(*Z*)-4-(2-(2-fluoro-4-methylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(19)** has been obtained as a light yellowish green solid in 75% yield. **Reaction time** = 48 h, **R_f =** 0.4, **eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 34.0 mg, 0.075 mmol, **Selectivity** = 82 : 18 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.83 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.87 (dd, *J* = 7.0, 1.8 Hz, 1H), 6.84 (d, *J* = 5.5 Hz, 2H), 6.82 (d, *J* = 5.6 Hz, 2H), 6.68 (dd, *J* = 7.8, 2.4 Hz, 1H), 6.61 (d, *J* = 8.9 Hz, 1H), 6.56 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.1, 160.13 (d, *J* = 247.3 Hz), 158.6, 158.5, 150.6, 140.8, 139.5 (d, *J* = 7.8 Hz), 135.48 (d, *J* = 3.2 Hz), 134.7, 134.4, 132.1, 131.9, 131.8, 131.3, 129.3, 128.31 (d, *J* = 15.2 Hz), 124.67 (d, *J* = 2.8 Hz), 116.30 (d, *J* = 21.6 Hz), 113.4, 113.3, 55.2, 21.2(d, *J* = 1.3 Hz). **^{19}F NMR (471 MHz, CDCl$_3$)** δ -114.2. **IR (ATR/cm^{-1})** 2954.2, 2923.0, 2850.2, 2733.2, 1698.7, 1597.3, 1503.7, 1457.0, 1301.0, 1246.4, 1173.6, 1103.4, 1028.1, 830.5, 794.1. **HRMS (ESI)** m/z calcd. for $C_{30}H_{25}FNaO_3$ ([M+Na]$^+$) 475.1680, found m/z 475.1678.



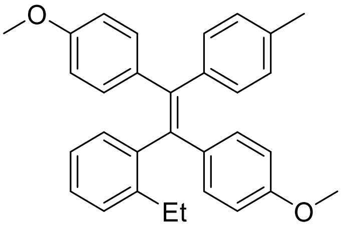
(20)

(*Z*)-4-(2-(2,4-difluorophenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(20)** has been obtained as a yellow solid in 67% yield. **Reaction time** = 48 h, **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 30.5 mg, 0.067 mmol, **Selectivity** = 78 : 22 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.85 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.97 – 6.93 (m, 1H), 6.83 (d, *J* = 2.1 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 2H), 6.62 – 6.60 (m, 1H), 6.59 (d, *J* = 2.4 Hz, 2H), 6.57 (d, *J* = 2.4 Hz, 2H), 6.55 – 6.54 (m, 1H), 3.67 (s, 3H), 3.66 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.0, 162.3 (dd, *J* = 248.2 Hz), 158.74, 158.70, 158.3 (dd, *J* = 253.3 Hz), 150.1, 141.5, 135.1, 134.6, 134.5, 134.2, 133.6 (dd, *J* = 9.5, 5.1 Hz), 132.0, 131.9, 131.8, 129.4, 127.6 (t, *J* = 18.9 Hz), 113.5, 113.4, 111.3 (dd, *J* = 21.0, 3.6 Hz), 104.2 (t, *J* = 25.7 Hz), 55.2. **^{19}F NMR (471 MHz, CDCl$_3$)** δ 111.6 (d, *J* = 7.8 Hz), 109.2 (d, *J* = 8.7 Hz). **IR (ATR/cm^{-1})** 2962.0, 2928.2, 2858.0, 2735.9, 1696.1, 1605.1, 1501.1, 1459.5, 1293.2, 1238.6, 1171.0, 1139.8, 1178.8, 1028.1, 960.5, 827.9, 791.5, 768.1, 744.7. **HRMS (ESI)** m/z calcd. for $C_{29}H_{22}F_2NaO_3$ ([M+Na]$^+$) 479.1429, found m/z 479.1422.



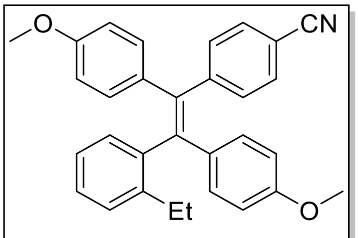
(21)

(*Z*)-4-(2-(2,5-difluorophenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(21)** has been obtained as a yellow solid in 47% yield. **Reaction time** = 48 h, **R_f =** 0.3, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 21.5 mg, 0.047 mmol, **Selectivity** = 80 : 20 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.86 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 6.6 Hz, 2H), 6.77 – 6.74 (m, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 3.67 (s, 3H), 3.66 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.0, 159.6 (dd, *J* = 243.2, 3.8 Hz), 158.9, 158.8, 156.3 (dd, *J* = 245.2, 3.3 Hz), 149.9, 141.9, 134.7, 133.8, 132.5, 132.0, 131.9, 131.8, 131.2, 129.4, 118.9 (dd, *J* = 23.8, 3.9 Hz), 116.7 (dd, *J* = 25.0, 9.0 Hz), 115.5 (dd, *J* = 23.9, 8.8 Hz), 114.0 (d, *J* = 3.4 Hz), 113.94, 113.92, 113.6, 113.5, 55.3. **^{19}F NMR (471 MHz, $CDCl_3$)** δ 101.0 (d, *J* = 17.3 Hz), 100.8 (d, *J* = 17.3 Hz). **IR (ATR/cm^{-1})** 2964.6, 2928.2, 2855.4, 2735.8, 1696.1, 1602.5, 1514.1, 1485.5, 1457.0, 1296.8, 1249.0, 1168.4, 1030.7, 820.1, 757.7, 734.3, 713.5. **HRMS (ESI)** m/z calcd. for $C_{29}H_{22}F_2NaO_3$ ([M+Na]$^+$) 479.1429, found m/z 479.1427.



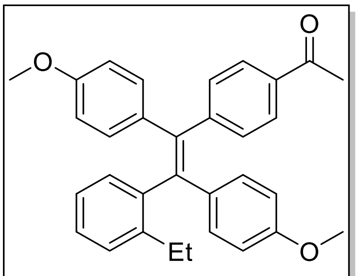
(22)

(*Z*)-4,4'-(1-(2-ethylphenyl)-2-(p-tolyl)ethene-1,2-diyl)bis(methoxybenzene) **(22)** has been obtained as a yellow solid in 96% yield. **R_f =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 41.5 mg, 0.096 mmol, **Selectivity** = 91 : 9. The NMR data was found to be matched with the reported literature value.[12] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.01 (d, *J* = 3.7 Hz, 2H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.92 – 6.85 (m, 5H), 6.79 (d, *J* = 7.3 Hz, 2H), 6.77 (d, *J* = 7.3 Hz, 2H), 6.50 (d, *J* = 8.9 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 2H), 3.61 (s, 3H), 3.58 (s, 3H), 2.49 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.33 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.19 (s, 3H), 0.86 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.9, 157.8, 143.1, 142.4, 141.1, 139.9, 138.4, 136.5, 136.1, 136.0, 132.01, 131.96, 131.9, 131.5, 128.6, 128.3, 126.9, 125.4, 113.0, 112.8, 55.2, 55.1, 26.0, 21.3, 14.5. **IR(ATR/cm^{-1})** 2959.4, 2928.2, 2873.6, 2842.4, 1607.7, 1508.9, 1467.3, 1298.4, 1246.4, 1176.2, 1111.2, 1025.5, 833.1, 812.3, 752.5.



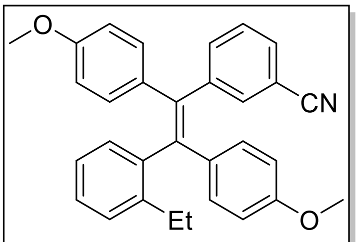
(23)

(Z)-4-(2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzonitrile **(23)** has been obtained as a light green solid in 88% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (1 : 99), **Amount** = 39.0 mg, 0.088 mmol, **Selectivity** = 94 : 6 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.34 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 7.06 – 7.02 (m, 2H), 6.95 – 6.91 (m, 2H), 6.75 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 8.9 Hz, 2H), 6.52 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 8.9 Hz, 2H), 3.64 (s, 3H), 3.61 (s, 3H), 2.46 (dq, J = 15.1, 7.6 Hz, 1H), 2.32 (dq, J = 15.0, 7.6 Hz, 1H), 0.86 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 158.5, 158.3, 149.3, 142.3, 142.1, 141.4, 138.3, 135.0, 134.8, 132.3, 132.1, 131.9, 131.7, 131.6, 128.5, 127.4, 125.6, 119.2, 113.4, 113.2, 109.8, 55.22, 55.16, 26.0, 14.4. **IR (ATR/cm^{-1})** 2959.4, 2928.2, 2839.8, 2223.8, 1605.1, 1511.5, 1462.2, 1246.4, 1241.2, 1173.6, 1160.0, 1022.9, 827.9, 749.9. **HRMS (ESI)** m/z calcd. for $C_{31}H_{27}NNaO_2$ ([M+Na]$^+$) 468.1934, found m/z 468.1924.



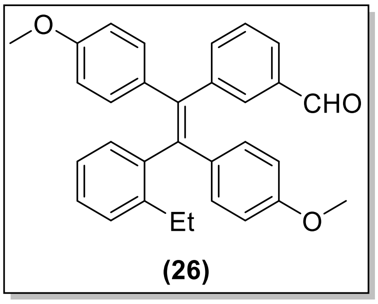
(24)

(Z)-1-(4-(2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)phenyl)ethan-1-one **(24)** has been obtained as an orange solid in 93% yield. **R_f =** 0.3, **Eluent** = EtOAc : hexane (1 : 99), **Amount** = 43.0 mg, 0.093 mmol, **Selectivity** = 93 : 7 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.67 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.98 – 6.92 (m, 2H), 6.77 (d, J = 8.9 Hz, 2H), 6.74 (d, J = 9.0 Hz, 2H), 6.51 (d, J = 7.0 Hz, 2H), 6.49 (d, J = 6.9 Hz, 2H), 3.63 (s, 3H), 3.61 (s, 3H), 2.48 (dq, J = 15.0, 7.5 Hz, 1H), 2.47 (s, 3H), 2.33 (dq, J = 15.0, 7.5 Hz, 1H), 0.87 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 198.0, 158.3, 158.2, 149.6, 142.5, 142.4, 140.6, 139.0, 135.6, 135.3, 135.0, 132.1, 131.9, 131.8, 131.7, 128.4, 128.1, 127.3, 125.5, 113.3, 113.1, 55.20, 55.15, 26.7, 26.0, 14.5. **IR (ATR/cm^{-1})** 2964.6, 2933.4, 2876.2, 2837.2, 1680.5, 1599.9, 1508.9, 1464.8, 1241.2, 1176.2, 1108.8, 1030.8, 952.7, 825.3, 729.1, 643.4. **HRMS (ESI)** m/z calcd. for $C_{32}H_{30}NaO_3$ ([M+Na]$^+$) 485.2087, found m/z 485.2087.



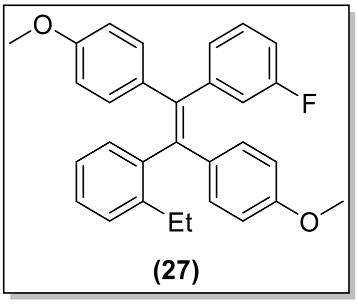
(25)

(*E*)-3-(2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzonitrile **(25)** has been obtained as a light yellow solid in 86% yield. **R_f = 0.3**, **Eluent** = EtOAc : hexane (1 : 99), **Amount** = 38.2 mg, 0.086 mmol, **Selectivity** = 88 : 12 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 – 7.31 (m, 2H), 7.25 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.16 (d, 1H), 7.07 – 7.04 (m, 2H), 6.96 – 6.92 (m, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.55 – 6.48 (m, 4H), 3.65 (s, 3H), 3.63 (s, 3H), 2.48 (dq, *J* = 14.8, 7.5 Hz, 1H), 2.33 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.87 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.3, 158.2, 145.4, 142.2, 142.1, 140.9, 137.6, 136.0, 135.0, 134.9, 134.7, 132.0, 131.8, 131.5, 129.9, 128.6, 128.4, 127.3, 125.5, 118.9, 113.3, 113.1, 112.0, 55.13, 55.08, 25.9, 14.3. **IR (ATR/cm^{-1})** 2956.8, 2928.2, 2873.6, 2234.1, 1605.1, 1506.3, 1464.8, 1246.4, 1171.0, 1030.7, 830.5, 799.3, 734.3, 690.1. **HRMS (ESI)** m/z calcd. for $C_{31}H_{27}NNaO_2$ ([M+Na]$^+$) 468.1934, found m/z 468.1932.



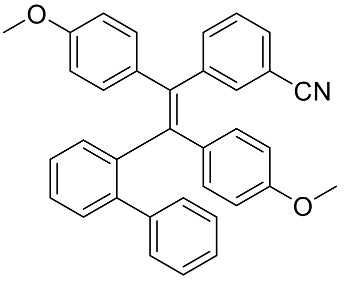
(26)

(*E*)-3-(2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(26)** has been obtained as a light yellowish green solid in 82% yield. **R_f = 0.3**, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 37.0 mg, 0.082 mmol, **Selectivity** = 95 : 5 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.78 (s, 1H), 7.59 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.52 (t, *J* = 1.7 Hz, 1H), 7.30 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.06 (dd, *J* = 5.9, 1.8 Hz, 2H), 6.98 – 6.92 (m, 2H), 6.77 (d, *J* = 3.2 Hz, 2H), 6.76 (d, *J* = 2.0 Hz, 2H), 6.51 (d, *J* = 1.8 Hz, 2H), 6.50 (s, 2H), 3.63 (s, 6H), 2.49 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.35 (dq, *J* = 15.1, 7.6 Hz, 1H), 0.88 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.6, 158.23, 158.18, 145.3, 142.45, 142.37, 140.4, 138.6, 137.8, 136.4, 135.5, 135.2, 133.4, 132.1, 131.9, 131.7, 128.7, 128.5, 127.4, 125.6, 113.3, 113.1, 55.22, 55.19, 26.0, 14.4. **IR (ATR/cm^{-1})** 2962.0, 2933.4, 2834.6, 2725.5, 1696.1, 1602.5, 1508.9, 1459.6, 1290.6, 1241.2, 1171.0, 1113.8, 1033.3, 835.7, 794.1, 768.1, 752.5. **HRMS (ESI)** m/z calcd. for $C_{31}H_{28}NaO_3$ ([M+Na]$^+$) 471.1931, found m/z 471.1930.



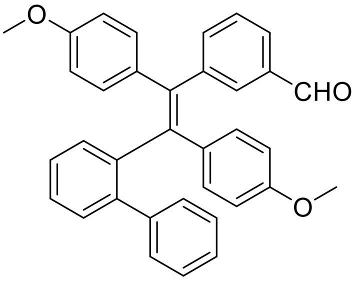
(27)

(*E*)-4,4'-(1-(2-ethylphenyl)-2-(3-fluorophenyl)ethene-1,2-diyl)bis(methoxybenzene) **(27)** has been obtained as a light yellow solid in 86% yield. **R_f = 0.3**, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 37.7 mg, 0.086 mmol, **Selectivity** = 96 : 4 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.17 – 7.12 (m, 3H), 7.09 – 7.03 (m, 2H), 6.94 – 6.88 (m, 5H), 6.88 – 6.83 (m, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 2.61 (dq, *J* = 15.1, 7.6 Hz, 1H), 2.46 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.00 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.6 (d, *J* = 245.4 Hz), 158.15, 158.13, 146.3 (d, *J* = 7.4 Hz), 142.6, 142.4, 139.8, 138.6 (d, *J* = 1.8 Hz), 135.7, 135.4, 131.94, 131.89, 131.8, 129.2 (d, *J* = 8.3 Hz), 128.4, 127.3 (d, *J* = 2.8 Hz), 127.2, 125.5, 118.2 (d, *J* = 21.1 Hz), 113.3 (d, *J* = 21.1 Hz), 113.2, 113.0, 55.2, 55.1, 26.0, 14.5. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -114.0. **IR (ATR/cm^{-1})** 2959.4, 2930.8, 2876.2, 2839.8, 1610.3, 1508.9, 1459.5, 1295.8, 1243.8, 1171.0, 1111.2, 1035.8, 830.5, 791.5, 744.2, 684.9. **HRMS (ESI)** m/z calcd. for $C_{30}H_{27}FNaO_2$ ([M+Na]$^+$) 461.1893, found m/z 461.1883.



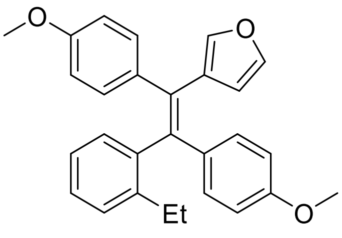
(28)

(*E*)-3-(2-([1,1'-biphenyl]-2-yl)-1,2-bis(4-methoxyphenyl)vinyl)benzonitrile **(28)** has been obtained as off colorless solid in 72% yield. **R$_f$ =** 0.3, **Eluent** = EtOAc : hexane (1 : 99), **Amount** = 35.5 mg, 0.072 mmol, **Selectivity** = 88 : 12 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.28 – 7.25 (m, 1H), 7.17 – 7.14 (m, 3H), 7.11 – 7.06 (m, 7H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 6.38 (d, *J* = 8.9 Hz, 2H), 6.22 (d, *J* = 8.9 Hz, 2H), 3.67 (s, 3H), 3.65 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 158.4, 158.2, 146.0, 142.1, 141.7, 141.5, 139.3, 137.4, 135.8, 135.6, 134.80, 134.78, 132.8, 132.7, 132.3, 130.5, 129.9, 128.8, 128.6, 127.73, 127.67, 127.2, 126.6, 119.1, 113.4, 112.9, 112.0, 55.31, 55.29. **IR (ATR/cm^{-1})** 3060.7, 3042.6, 3027.0, 2951.6, 2907.4, 2829.4, 2221.2, 1602.5, 1508.9, 1446.6, 1295.8, 1241.2, 1173.6, 1038.5, 838.3, 739.5, 697.9. **HRMS (ESI)** m/z calcd. for $C_{35}H_{27}NO_2$ ([M]$^+$) 493.2042, found m/z 493.2015.



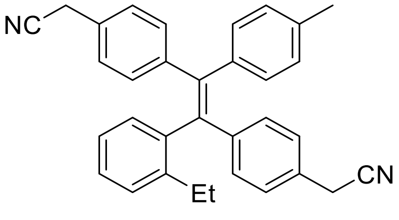
(29)

(*E*)-3-(2-([1,1'-biphenyl]-2-yl)-1,2-bis(4-methoxyphenyl)vinyl)benzaldehyde **(29)** has been obtained as a light yellow solid in 70% yield. **R$_f$ =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 34.7 mg, 0.070 mmol, **Selectivity** = 90 : 10 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.73 (s, 1H), 7.53 – 7.51 (m, 1H), 7.37 (s, 1H), 7.17 – 7.14 (m, 4H), 7.12 – 7.06 (m, 5H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 6.37 (d, *J* = 9.5 Hz, 2H), 6.27 (d, *J* = 8.9 Hz, 2H), 3.65 (s, 3H), 3.64 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.5, 158.1, 145.7, 142.1, 142.0, 141.6, 138.7, 138.3, 137.4, 136.3, 136.0, 135.2, 133.2, 132.80, 132.78, 132.3, 130.5, 128.9, 128.5, 127.7, 127.5, 127.2, 127.1, 126.5, 113.2, 112.9, 55.29, 55.25. **IR (ATR/cm^{-1})** 3055.5, 3026.9, 2954.2, 2938.6, 2910.0, 2834.6, 2730.6, 1693.5, 1599.9, 1503.7, 1467.3, 1285.4, 1238.6, 1173.6, 1028.8, 908.5, 835.7, 729.1, 695.3. **HRMS (ESI)** m/z calcd. for $C_{35}H_{28}NaO_3$ ([M+Na]$^+$) 519.1931, found m/z 519.1962.



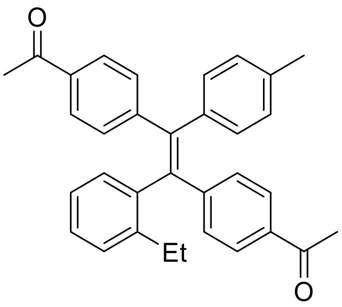
(30)

(*E*)-3-(2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)furan **(30)** has been obtained as off colorless solid in 77% yield. **R_f =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 31.6 mg, 0.077 mmol, **Selectivity** = 98 : 2 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 (d, *J* = 1.5 Hz, 1H), 7.13 (d, *J* = 1.7 Hz, 1H), 7.02 – 6.97 (m, 3H), 6.94 – 6.85 (m, 5H), 6.65 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 5.81 (s, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.48 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.33 (dq, *J* = 15.0, 7.6 Hz, 1H), 0.84 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.4, 158.2, 143.4, 142.7, 142.3, 141.9, 139.0, 136.0, 135.4, 131.74, 131.72, 131.5, 130.8, 128.3, 128.1, 126.9, 125.3, 113.4, 112.9, 112.6, 55.3, 55.2, 26.1, 14.5. **IR (ATR/cm^{-1})** 2964.8, 2928.2, 2967.4, 2834.6, 1599.9, 1503.7, 1459.5, 1288.0, 1236.0, 1173.6, 1150.0, 1030.7, 835.7, 791.5, 778.5, 747.3 **HRMS (ESI)** m/z calcd. for $C_{28}H_{26}NaO_3$ ($[M+Na]^+$) 433.1774, found m/z 433.1831.



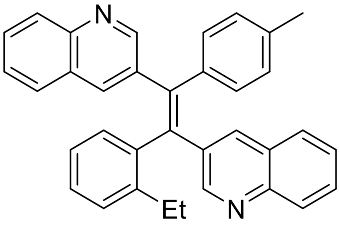
(31)

(*Z*)-2,2'-((1-(2-ethylphenyl)-2-(p-tolyl)ethene-1,2-diyl)bis(4,1-phenylene))diacetonitrile **(31)** has been obtained as a yellow solid in 72% yield. **R_f =** 0.2, **Eluent** = EtOAc : hexane (5 : 95), **Amount** = 32.5 mg, 0.072 mmol, **Selectivity** = 99 : 1 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.08 – 7.02 (m, 2H), 6.95 – 6.82 (m, 14H), 3.55 (s, 2H), 3.51 (s, 2H), 2.45 (dq, *J* = 15.1, 7.6 Hz, 1H), 2.33 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.22 (s, 3H), 0.85 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.5, 143.0, 142.3, 142.0, 141.1, 139.8, 139.5, 136.8, 131.7, 131.4, 131.3, 131.2, 128.9, 128.5, 127.9, 127.7, 127.5, 127.3, 127.1, 125.6, 118.0, 117.9, 26.0, 23.4, 23.3, 21.3, 14.4. **IR (ATR/cm^{-1})** 3019.2, 2964.6, 2871.0, 2254.9, 1677.9, 1599.9, 1511.5, 1415.4, 1256.8, 1178.8, 1116.4, 1020.3, 913.7, 817.5, 721.3. **HRMS (ESI)** m/z calcd. for $C_{33}H_{28}N_2Na$ ($[M+Na]^+$) 475.2145, found m/z 475.2155.



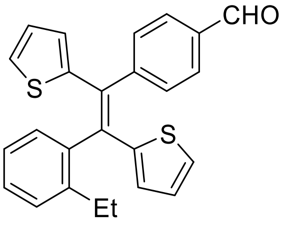
(32)

(*Z*)-1,1'-((1-(2-ethylphenyl)-2-(p-tolyl)ethene-1,2-diyl)bis(4,1-phenylene))bis(ethan-1-one) **(32)** has been obtained as a yellow solid in 67% yield. **R_f =** 0.2, **Eluent** = EtOAc : hexane (5 : 95), **Amount** = 30.7 mg, 0.067 mmol, **Selectivity** = 99 : 1 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 – 7.56 (m, 4H), 7.08 – 7.04 (m, 2H), 7.01 – 6.96 (m, 4H), 6.93 – 6.89 (m, 4H), 6.84 (d, *J* = 8.1 Hz, 2H), 2.53 – 2.39 (m, 1H), 2.43 (d, *J* = 12.8 Hz, 6H), 2.40 – 2.29 (m, 1H), 2.23 (s, 3H), 0.85 (t, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.9, 197.8, 148.5, 148.1, 142.4, 142.2, 141.4, 140.5, 139.3, 137.3, 135.3, 135.1, 131.8, 131.3, 131.0, 130.9, 129.1, 128.7, 127.93, 127.91, 127.7, 125.8, 26.7, 26.6, 26.1, 21.4, 14.4. **IR (ATR/cm^{-1})** 2964.6, 2925.6, 2855.4, 1677.9, 1602.5, 1506.3, 1399.8, 1358.2, 1256.8, 1178.8, 1116.4, 1017.7, 955.3, 825.3, 782.3, 782.5, 703.1. **HRMS (ESI)** m/z calcd. for $C_{33}H_{30}NaO_2$ ($[M+Na]^+$) 481.2138, found m/z 481.2152.



(33)

(*E*)-3,3'-(1-(2-ethylphenyl)-2-(p-tolyl)ethene-1,2-diyl)diquinoline **(33)** has been obtained as a light yellow solid in 65% yield. **R_f =** 0.2, **Eluent** = EtOAc : hexane (5 : 95), **Amount** = 31.0 mg, 0.065 mmol, **Selectivity** = 99 : 1 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 8.47 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.57 (t, *J* = 1.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.38 (t, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.09 (m, 2H), 7.11 – 7.05 (m, 1H), 7.01 (t, *J* = 1.7 Hz, 1H), 6.83 (s, 4H), 2.54 – 2.40 (m, 2H), 2.18 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.1, 152.7, 146.9, 146.4, 142.3, 141.6, 140.1, 139.5, 138.5, 138.3, 137.3, 137.2, 136.2, 136.0, 131.9, 130.7, 129.8, 129.6, 129.4, 129.2, 128.72, 127.70, 127.96, 128.93, 127.90, 127.85, 127.8, 127.0, 126.9, 126.0, 26.2, 21.3, 14.4. **IR (ATR/cm^{-1})** 3058.2, 3021.8, 2964.6, 2925.6, 2855.4, 1716.9, 1576.9, 1490.8, 1459.6, 1020.3, 788.3, 744.7. **HRMS (ESI)** m/z calcd. for $C_{35}H_{28}N_2Na$ ($[M]^+$) 477.2325, found m/z 477.2328.



(34)

(*E*)-4-(2-(2-ethylphenyl)-1,2-di(thiophen-2-yl)vinyl)benzaldehyde **(34)** has been obtained as a yellowish green solid in 87% yield. **R_f =** 0.4, **Eluent** = EtOAc : hexane (0.5 : 99.5), **Amount** = 34.8 mg, 0.087 mmol, **Selectivity** = 80 : 20 **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.04 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.37 (dt, *J* = 8.5, 4.3 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 4.1 Hz, 2H), 6.98 (dd, *J* = 7.8, 5.0 Hz, 2H), 6.63 (dt, *J* = 9.8, 4.4 Hz, 2H), 6.22 (dd, *J* = 13.7, 3.9 Hz, 2H), 2.61 – 2.46 (m, *J* = 7.7 Hz, 2H), 1.03 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.1, 148.6, 145.0, 144.6, 143.3, 140.2, 136.1, 132.4, 132.1, 132.0, 131.1, 130.5, 129.9, 129.14, 119.10, 129.0, 127.6, 127.2, 126.9, 126.2, 125.9, 25.7, 14.2.

IR (ATR/cm^{-1}) 3107.6, 3071.1, 3091.2, 2964.6, 2923.0, 2876.2, 2837.2, 2730.7, 1693.5, 1602.5, 1566.1, 1386.7, 1204.8, 1163.2, 817.5, 744.7, 700.5. **HRMS (ESI)** m/z calcd. for $C_{25}H_{21}OS_2$ ($[M+H]^+$) 401.1028 found m/z 401.1011.

Section SM-IX: Practical usability of Pd@PKPOP

General procedure for the scale-up reaction

To a 100 mL Schlenk tube equipped with a magnetic stirrer bar, **Pd@PKPOP** (60.0 mg, 0.5 mol% Pd), 1,2-bis(4-methoxyphenyl)ethyne **A1** (715 mg, 3.0 mmol), 4-formylphenylboronic acid **B4** (675 mg, 4.5 mmol), 2-ethyliodobenzene **I2** (1392 mg, 6.0 mmol) and Na_2CO_3 (636 mg, 6.0 mmol) were taken under inert atmosphere. Dried DMF (30.0 mL) was then added, and the tube was stoppered tightly and kept in a pre-heated (110 ^oC) oil bath at 250 ppm stirring. After 24 h, the oil bath was removed, and the mixture was cooled to rt. The reaction mixture was transferred into a centrifuge tube, and the catalyst was centrifuged. The mother liquor was then mixed with brine (150 mL) and extracted using ethyl acetate (3 x 60 mL). The organic layer was washed with distilled water (150 mL) and dried over anhydrous Na_2SO_4. Further, the organic layer was evaporated under reduced pressure, and a slurry was made. The slurry was packed into a silica gel column and eluted using ethyl acetate and hexane (0.5 : 99.5). The final product was obtained after reducing the eluent under a rota-evaporator. Finally, it was crystallized in the ethyl acetate and hexane solution mixture to get 1.20 g of the light yellowish-green solid product with 89% yield and 92 : 08 selectivity.

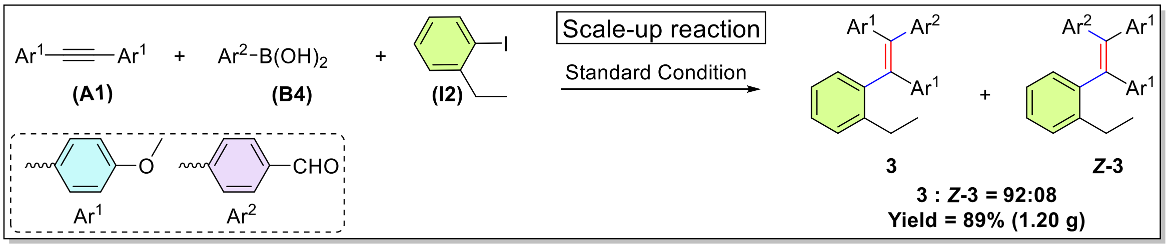


Figure S30: Scale-up reaction

General procedure for recyclability test

To a 16 mL culture tube equipped with magnetic stirrer bar, **Pd@PKPOP** (2.0 mg), 1,2-bis(4-methoxyphenyl)ethyne **A1** (0.1 mmol), 4-formylphenylboronic acid **B4** (0.15 mmol), 2-ethyliodobenzene **I2** (0.2 mmol), Na_2CO_3 (0.2 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) were taken under inert atmosphere. Dried DMF (1.0 mL) was then added, and the tube was stoppered tightly and kept in a pre-heated (110 ^oC) oil bath at 250 ppm stirring. After 24 h, the oil bath was removed, and the mixture was cooled to rt. The reaction mixture was transferred into a centrifuge tube, and the catalyst was centrifuged. The mother liquor was taken out using a syringe under an inert atmosphere. The reaction mixture was analyzed using ^1H NMR to obtain yield and selectivity by following the initially described standard workup and NMR sample preparation procedure. The fresh batch of reactants, internal standard, base, and solvent were transferred into the same culture tube used above, maintaining an inert atmosphere. Again, the reaction was run for another 24 h. The above protocols were repeated for 7 times to get the recyclability result.

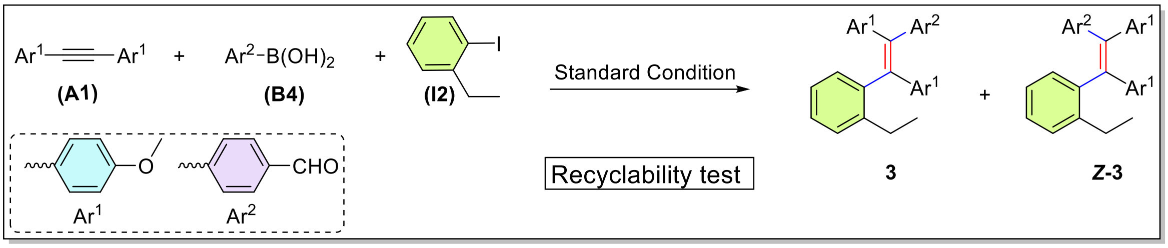


Figure S31: Schematic protocol for recyclability test

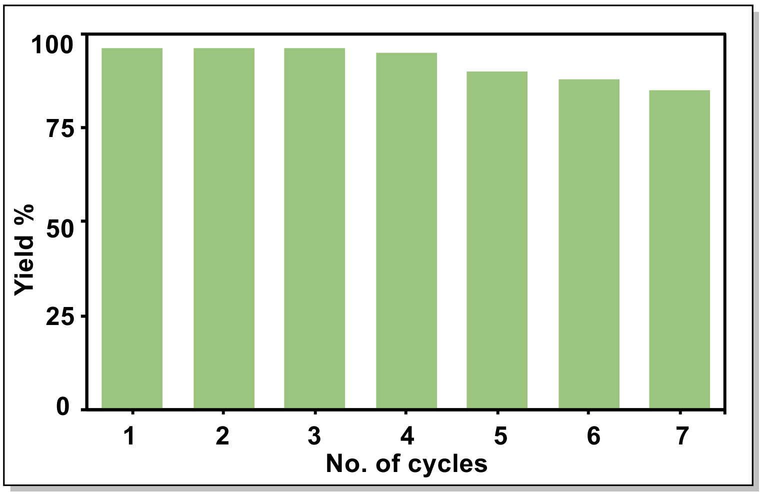


Figure S32: Recyclability test graph shows that **Pd@PKPOP** maintains high activity up to 7th cycle

General procedure for calculating turnover number (TON) and turnover frequency (TOF)

To a 16 mL culture tube equipped with magnetic stirrer bar, **Pd@PKPOP** (0.5 mg, 0.025 mol% Pd), 1,2-bis(4-methoxyphenyl)ethyne **A1** (0.5 mmol), 4-formylphenylboronic acid **B4** (0.75 mmol), 2-ethyliodobenzene **I2** (1.0 mmol), Na_2CO_3 (1.0 mmol) and 1,3,5-trimethoxybenzene as internal standard (0.5 mmol) were taken under inert atmosphere. Dried DMF (5.0 mL) was then added, and the tube was stoppered tightly and kept in a pre-heated (110 °C) oil bath at 250 ppm stirring. After 60 h, the oil bath was removed, and the mixture was cooled to rt. 1 mL aliquot was taken into 5 mL glass vial and mixed with 1 mL H_2O and 2 mL ethyl acetate. It was shaken well and kept for the layer to be separated. 1 mL aliquot of separated ethyl acetate was dried under anhydrous Na_2SO_4. The ethyl acetate was evaporated. ^{1}H NMR analysis determines 65% yield of the product.

Calculation of **TON**

$$\begin{aligned} \text{TON} &= \text{mol of desired product/ mol of Pd used} \\ &= (0.3250 \text{ mmol product}) /(0.1269 \times 10^{-3} \text{ mmol Pd}) \\ &= 2561 \\ &> 2500 \end{aligned}$$

Calculation of **TOF**

$$\begin{aligned} \text{TOF} &= \text{TON/time} \\ &= 2561/60 \text{ h} \\ &= 42.7 \end{aligned}$$

Quantifying the amount of Pd in Pd@PKPOP after catalysis

2 mg catalyst has been digested in 2 mL piranha solution for 30 h. It was diluted with 8 mL Milli-Q water. 1 mL aliquot was again taken and diluted with 9 mL 2% concentrated HNO_3 . 2 ml of the final solution was filtered with 0.2 µm syringe filter, and measurement was carried out on ICP-OES. Commercially available Pd (1000 ppm Pd in 10% HCl) solution has been used as standard. After calculation, we got the following result.

Catalysts	Expt. Found Pd (wt %)	Theoretically $PdCl_2$ taken (wt %)
Pd@PKPOP	2.70	6
Pd@PKPOP (1st cycle)	2.41	-
Pd@PKPOP (7th cycle)	0.28	-

Table ST12 : Quantity of Pd in different catalysts quantified by ICP-OES. Wt % was calculated with respect to **PKPOP**. So, 2.0 mg 6 wt % **Pd@PKPOP** contains 0.054 mg Pd (0.5074×10^{-3} mmol)

General procedure for hot filtration test

To a 16 mL culture tube equipped with magnetic stirrer bar, **Pd@PKPOP** (2.0 mg, 0.5 mol% Pd), 1,2-bis(4-methoxyphenyl)ethyne **A1** (0.1 mmol), 4-formylphenylboronic acid **B4** (0.15 mmol), 2-ethyliodobenzene **I2** (0.2 mmol), Na_2CO_3 (0.2 mmol) and 1,3,5-trimethoxybenzene as internal standard (0.1 mmol) were taken under inert atmosphere. Dried DMF (1.0 mL) was then added, and the tube was stoppered tightly and kept in a pre-heated (110 °C) oil bath at 250 ppm stirring.

After 12 h, 0.5 mL reaction mixture was taken out via a syringe and filtered through 0.2 µm syringe filter into a new 16 mL culture tube equipped with a magnetic bar under an inert atmosphere. This changed reaction setup was again allowed to run for another 12 h at 110 °C.

100 µL aliquot was taken from both batches and analyzed through GCMS according to the workup and sample preparation procedure described.

Note: A GCMS calibration was made by taking an equal amount of the product **3** and 1,3,5-trimethoxybenzene. After optimal dilution, 3 batches were measured, and the ratio of average retention time of internal standard with the product was calculated.

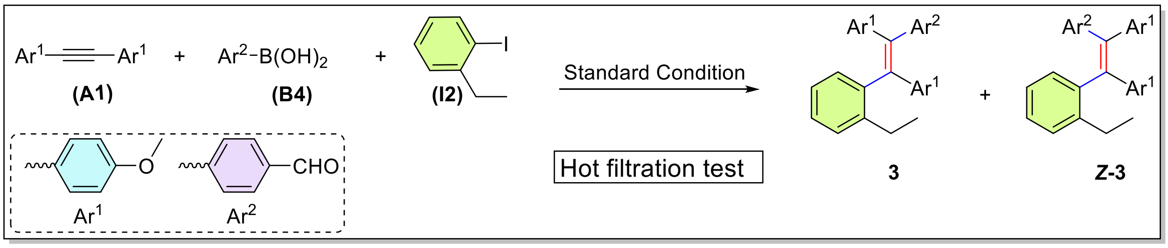


Figure S33: Schematic protocol for hot filtration test

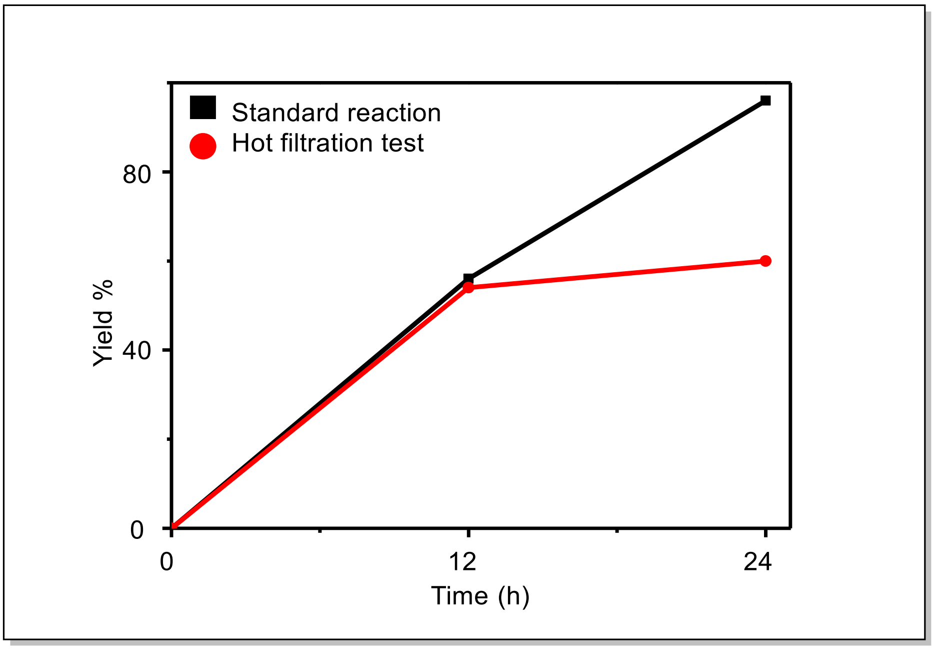


Figure S34: Hot filtration test to probe the heterogeneity showing yield obtained in 12 h up to 54% and after filtering catalyst, 6% yield obtained in next 12 h

Section SM-X: Characterization of Pd@PKPOP after catalysis

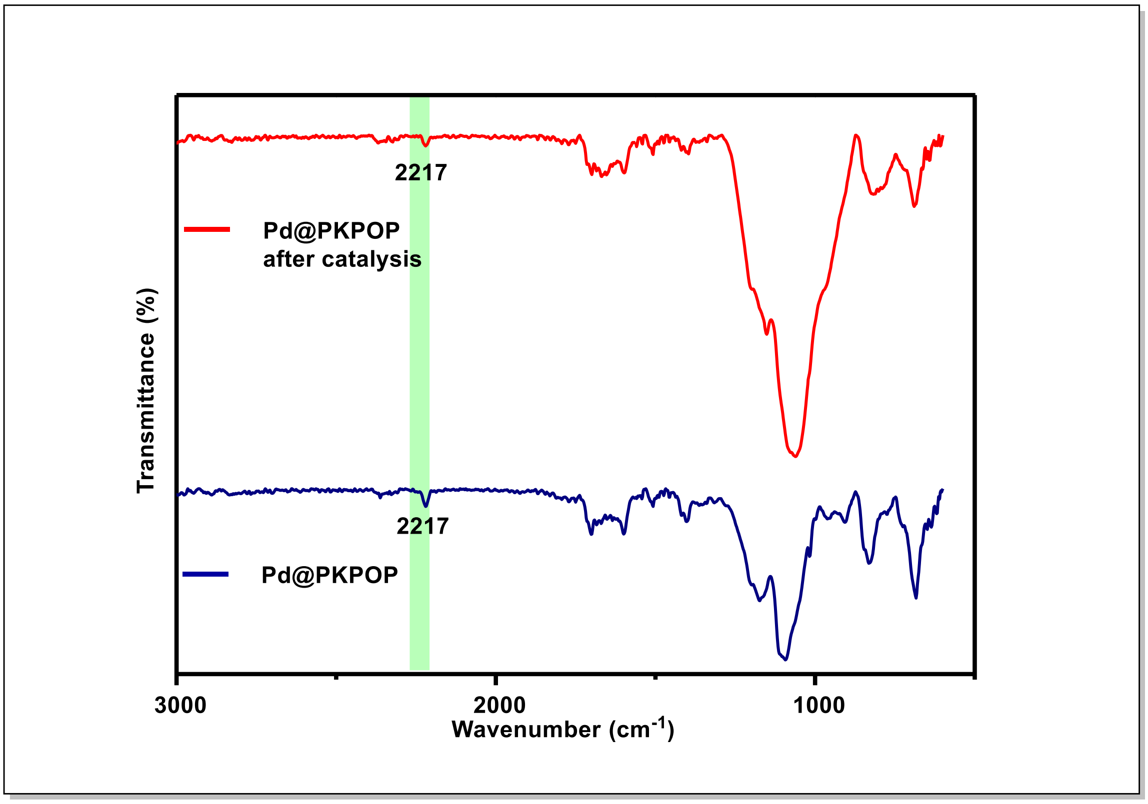


Figure S35: FT-IR spectra of **Pd@PKPOP** before and after catalysis

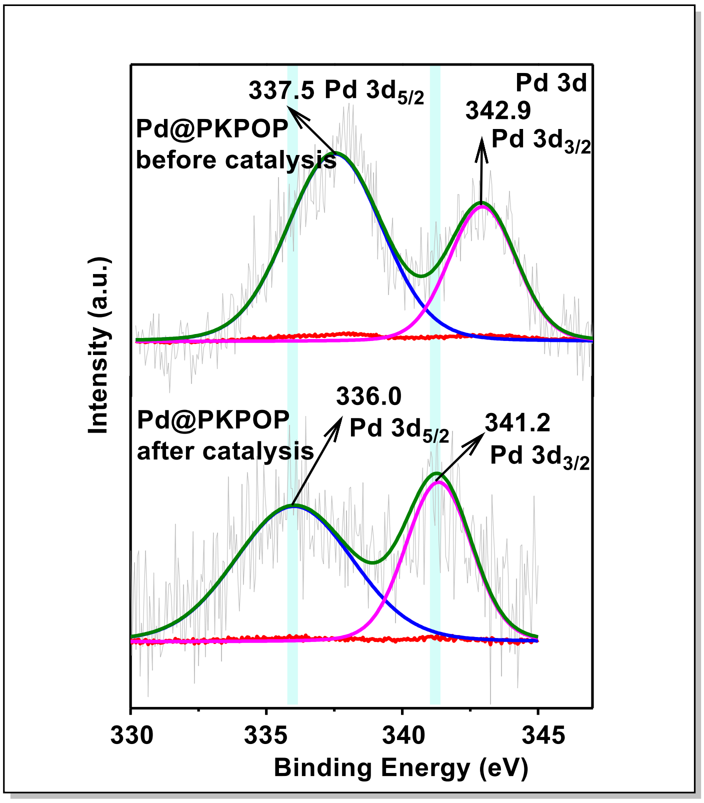


Figure S36: Comparative Pd (3$d_{5/2}$) and (3$d_{3/2}$) XPS spectra of **Pd@PKPOP** before and after catalysis. Pd(0) in the form of nanoparticles is deconvoluted after catalysis

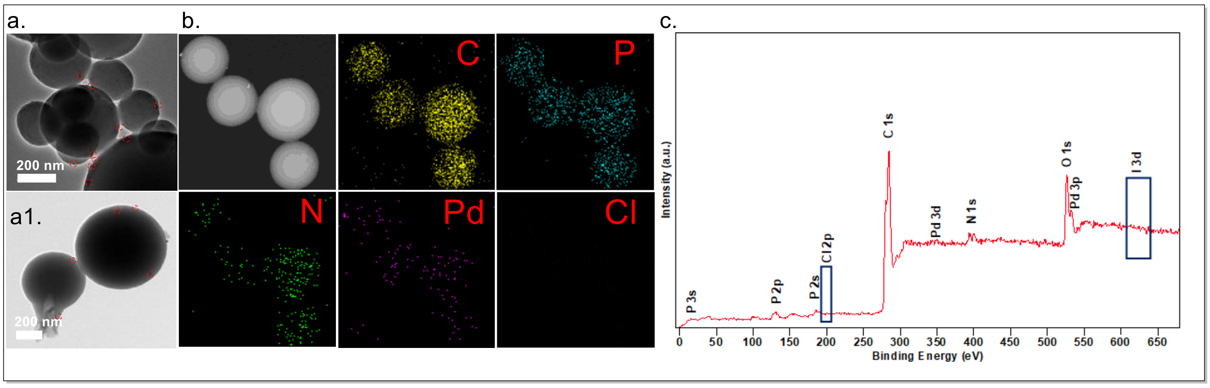


Figure S37: (a.)TEM image of **Pd@PKPOP** after catalysis (1st cycle) with unchanged morphology containing Pd nanoparticles; (a1.) TEM images with burst morphology (after 7th cycle); (b.) Elemental analysis of **Pd@PKPOP** after catalysis through EDAX. Cl is absent after catalysis; (c.) XPS analysis also supported the absence of counter anion like Cl and I after catalysis

Section SM-XI: Controlled experiments and mechanistic investigations

General procedure for kinetic study

To a 16 mL culture tube equipped with magnetic stirrer bar, **Pd@PKPOP** (2.0 mg, 0.5 mol% Pd), 1,2-bis(4-methoxyphenyl)ethyne **A1** (0.1 mmol), 4-formylphenylboronic acid **B4** (0.15 mmol), 2-ethyliodobenzene **I2** (0.2 mmol), Na_2CO_3 (0.2 mmol) and 1,3,5-trimethoxybenzene as internal standard (0.1 mmol) were taken under inert atmosphere. Dried DMF (1.0 mL) was then added, and the tube was capped with rubber septa, fitted with an argon-filled balloon, and kept in a pre-heated (110 ^{o}C) oil bath at 250 ppm stirring. After respective times (1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 10 h, 15 h, 20 h, 25 h, and 30 h.), 90 µL of aliquot was taken into a vial and mixed it with 1 mL brine and 1 mL ethyl acetate. After working up via shaking, 100 µL aliquot of the organic phase was passed through Na_2SO_4 and celite pad and mixed with 0.9 mL fresh ethyl acetate to make 1 mL GCMS samples and analyzed.

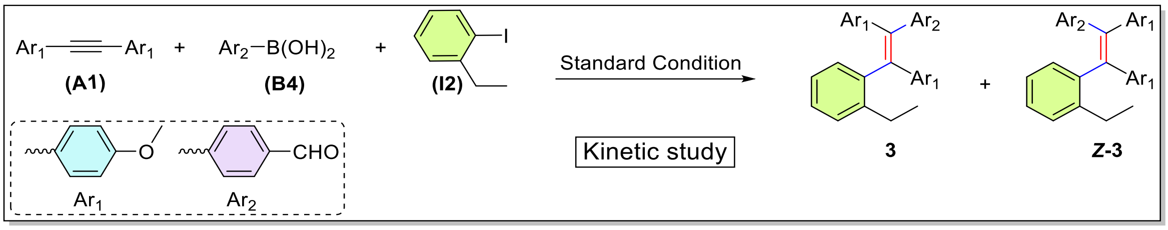


Figure S38: Schematic protocol for the kinetic study

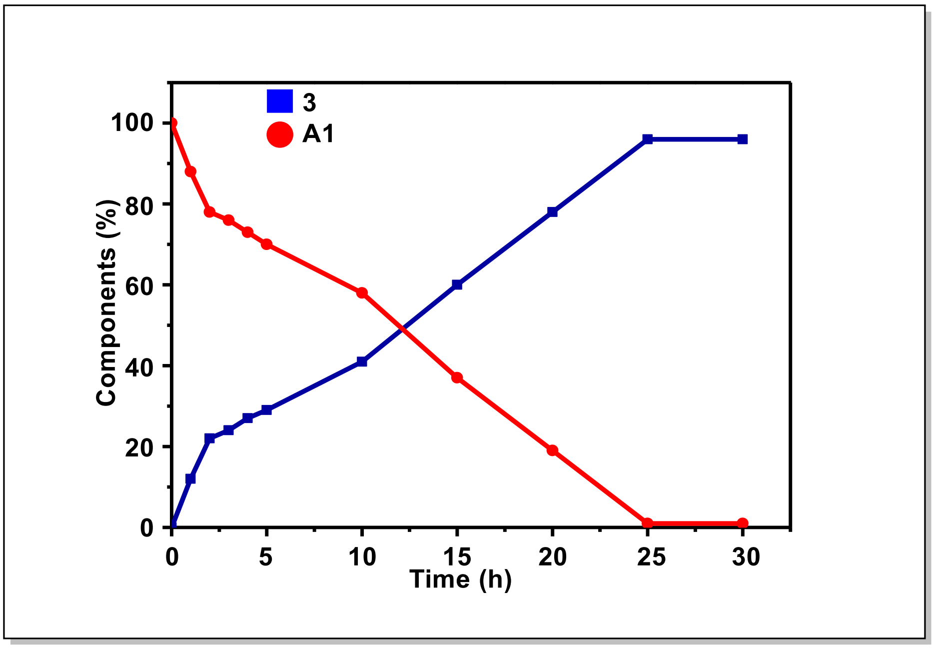


Figure S39: In the kinetic investigation, the blue line shows the formation of the product, and the red line shows the conversion of the internal alkynes against time

<u>General procedure for comparative kinetic analysis with different catalysts</u>

To six 16 mL culture tubes equipped with magnetic stirrer bar, **Pd@PKPOP** (2.0 mg), Pd@KAPs(Ph-PPh_3) (2.0 mg), Pd@Phos-polymer (2.0 mg), 5% Pd/C (1.1 mg), $PdCl_2$ (0.09 mg) and $PdCl_2(PPh_3)_2$ (0.36 mg) were taken seperately. 1,2-bis(4-methoxyphenyl)ethyne **A1** (0.1 mmol), 4-formylphenylboronic acid **B4** (0.15 mmol), 2-ethyliodobenzene **I2** (0.2 mmol), Na_2CO_3(0.2 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) were then subsequently introduced under inert atmosphere. Dried DMF (1.0 mL) was then added, and the tube was capped with rubber septa, fitted with an argon-filled balloon, and kept in a pre-heated (110 ^{o}C) oil bath at 250 ppm stirring. After respective times (2 h, 3 h, 4 h, 8 h, 12 h, 24 h and 30 h.), 100 μL of aliquot was taken into a vial and mixed with 1 mL brine and 1 mL ethyl acetate. After working up via shaking, 100 μL aliquot of the organic phase was passed through Na_2SO_4 and celite pad and mixed with 0.9 mL fresh ethyl acetate to make 1 mL GCMS samples and analyzed.

Note:- Solution of 5.0 mg $PdCl_2$ was made into 2.0 mL dry DMF. 36.0 μL of the solution was taken and used as the catalyst.

Note:- Solution of 5.0 mg $PdCl_2(PPh_3)_2$ was made into 1.0 mL dry DMF. 72.0 μL of the solution was taken out and used as the catalyst.

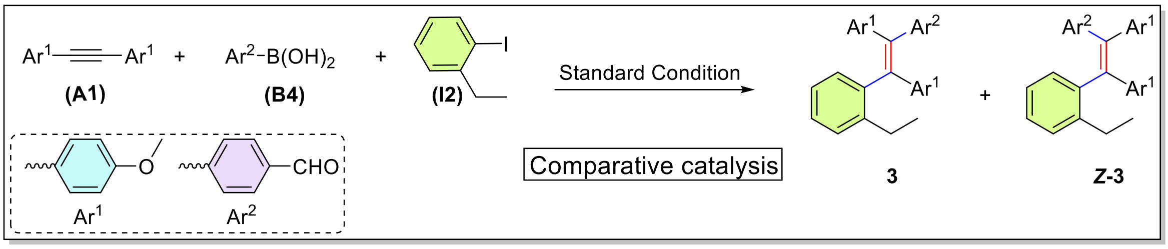


Figure S40: Schematic protocol for comparative catalysis

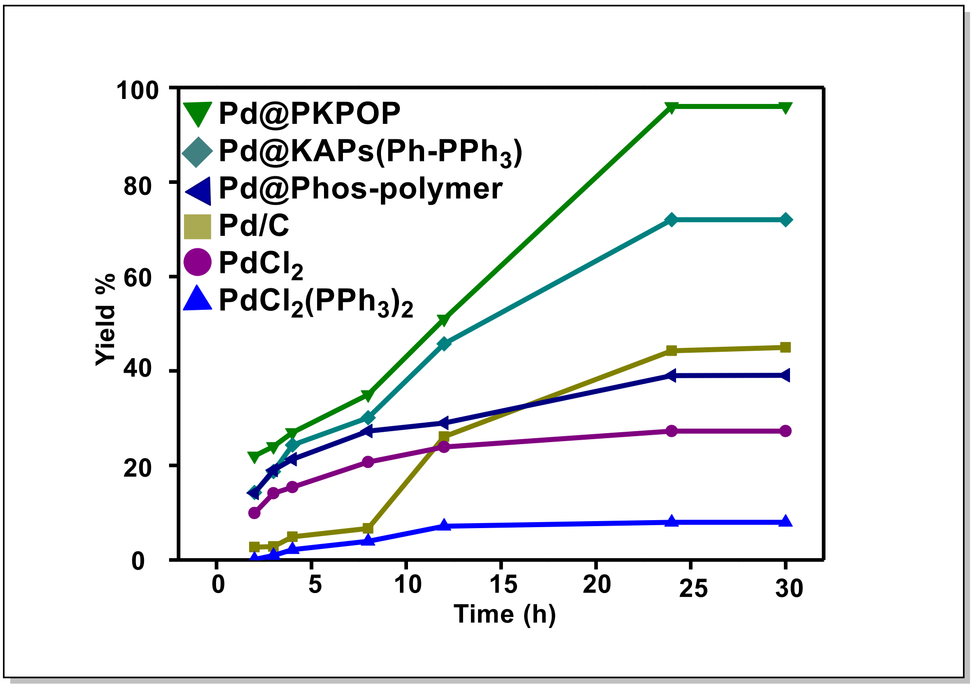


Figure S41: Comparative rate of product formation in different heterogeneous and homogeneous catalysts

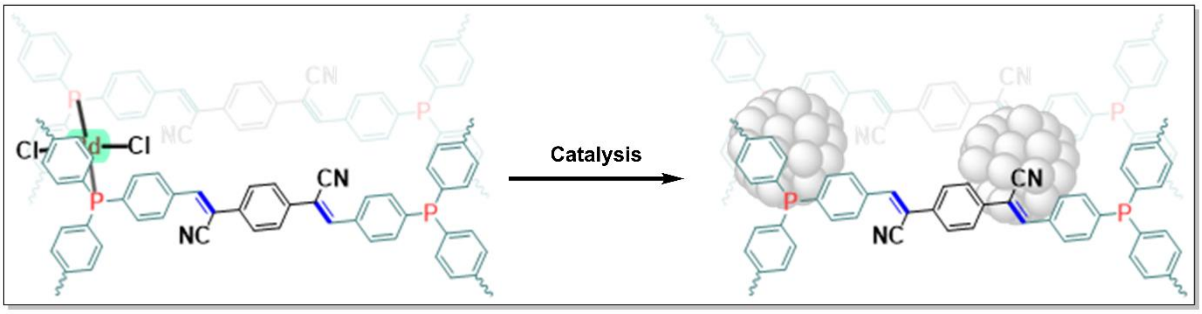


Figure S42: Plausible active sites to stabilize Pd(0) formed during the catalysis

Controlled experiments to determine *trans*-selective product

We performed some controlled reactions to get insight into the selectivity and the choice of substituents at different reactants. Under optimized conditions, when we reacted 4-methyliodobenzene (**I21**) instead of 2-methyl iodobenzene (**I1**), we found **35 : *Z*-35** = 55 : 45 selectivity **(A)**. On the other hand, when 2-methylphenylboronic acid (**B9**) was reacted instead of 4-methylphenylboronic acid (**B1**), the reaction still gave **36 : *Z*-36** = 55 : 45 selectivity **(B)**. This result suggested that 2-methyliodobenzene plays a vital role in stereoselectivity and that *trans*-metalation with aryl boronic acid took place after the *Z* to *E* isomerization of the palladium(II) intermediate.

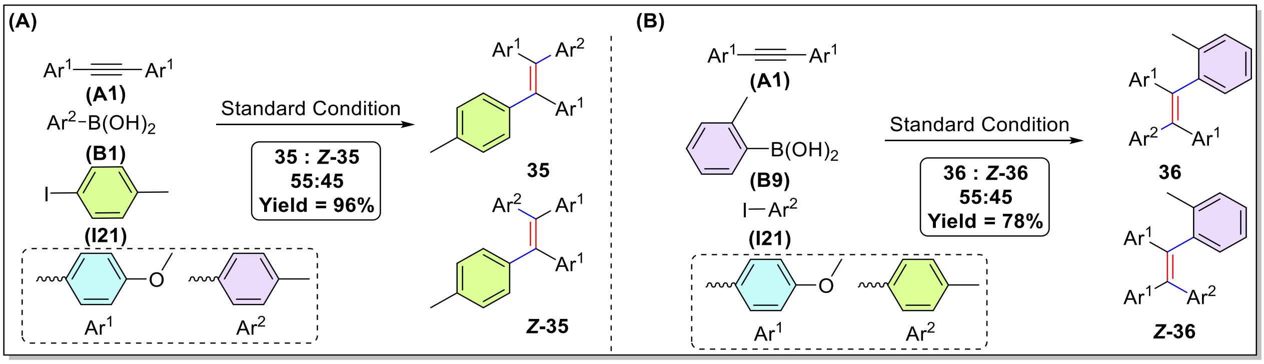


Figure S43: Controlled experiments to determine *trans*- selective product

Proposed mechanism

Eventually, we assume the possible pathway of the reaction mechanism based on the previous report and our experimental observations. Pd(II) pre-catalyst is reduced to Pd(0) under the reaction conditions with the aid of base and ligand. The oxidative addition with aryl iodide gives complex **II**, which undergoes carbopalladation diarylacetylene to form complex **III**. In this complex, steric hindrance between Ar^3 and **PKPOP** ligand pushes isomerization to form complex **IV**. Bulkier *ortho*-substituent facilitates the isomerization and thereby yield higher *trans*-selective product. At this stage, arylboronic acid, in collaboration with Na_2CO_3, undergoes *trans*-metalation to form complex **V**. Finally, reductive elimination expels the product and regenerates the catalyst.

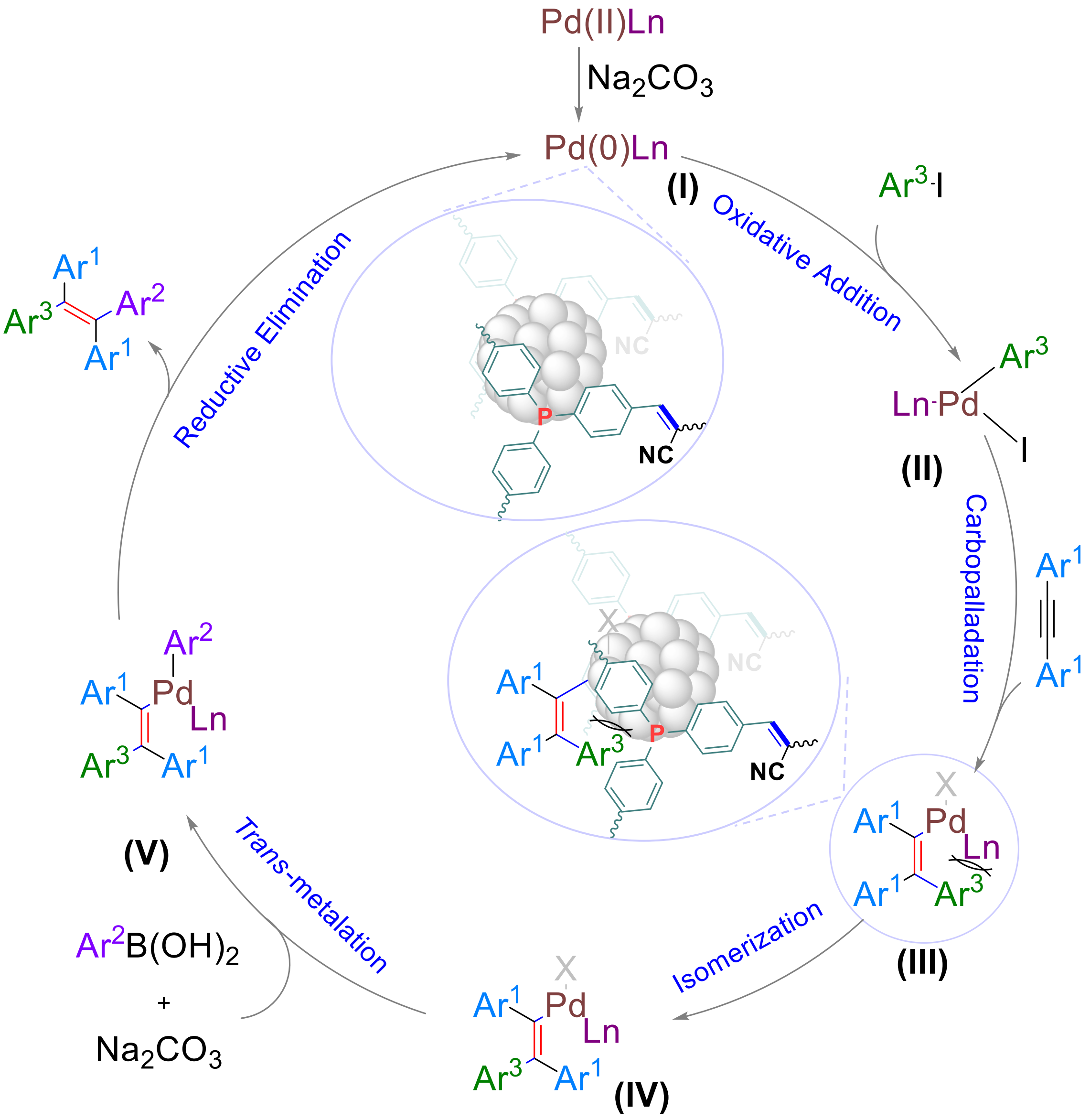


Figure S44: Plausible catalytic cycle

Section SM-XII : Molecular structure and crystal data

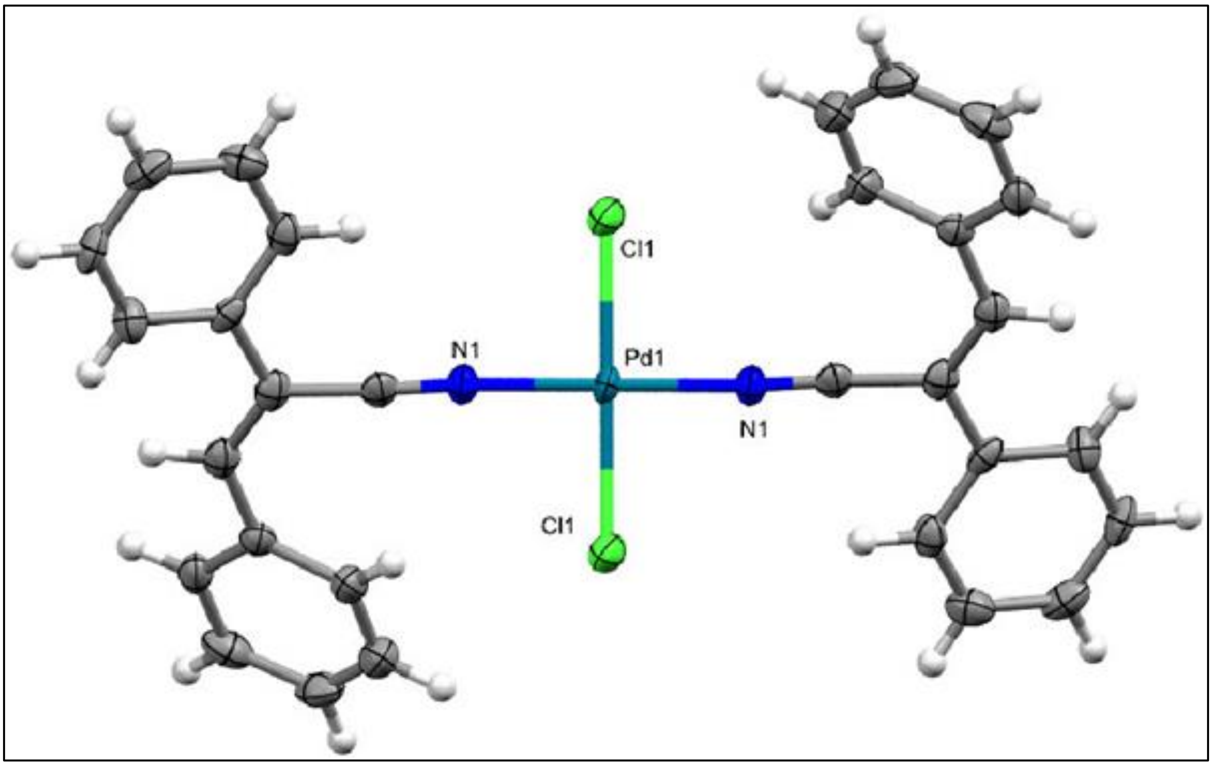


Figure S45: Molecular structure for compound **$PdCl_2(BB5)_2$**. Crystallization procedure: 10.0 mg solid compound was taken in a glass vial and dissolved in 0.5 mL $CHCl_3$ and kept at ambient temperature (20 ^oC) for crystalization. **CCDC No.-2265650**

Crystal data and structure refinement for $PdCl_2(BB5)_2$

Identification code	PKA730_Pd_auto_1
Empirical formula	$C_{30}H_{22}Cl_2N_2Pd$
Formula weight	587.79
Temperature/K	99.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.6299(2)
b/Å	8.9441(2)
c/Å	10.0875(2)
α/°	97.816(2)
β/°	106.126(2)
γ/°	102.556(2)
Volume/Å^3	631.18(3)
Z	1
ρ_{calc}g/cm^3	1.546
μ/mm^{-1}	0.969
F(000)	296.0
Crystal size/mm^3	0.1 × 0.1 × 0.02
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.298 to 53.98
Index ranges	$-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$
Reflections collected	10383
Independent reflections	2627 [R_{int} = 0.0568, R_{sigma} = 0.0559]
Data/restraints/parameters	2627/0/160
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.0826
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.0883
Largest diff. peak/hole / e Å^{-3}	1.09/-0.53

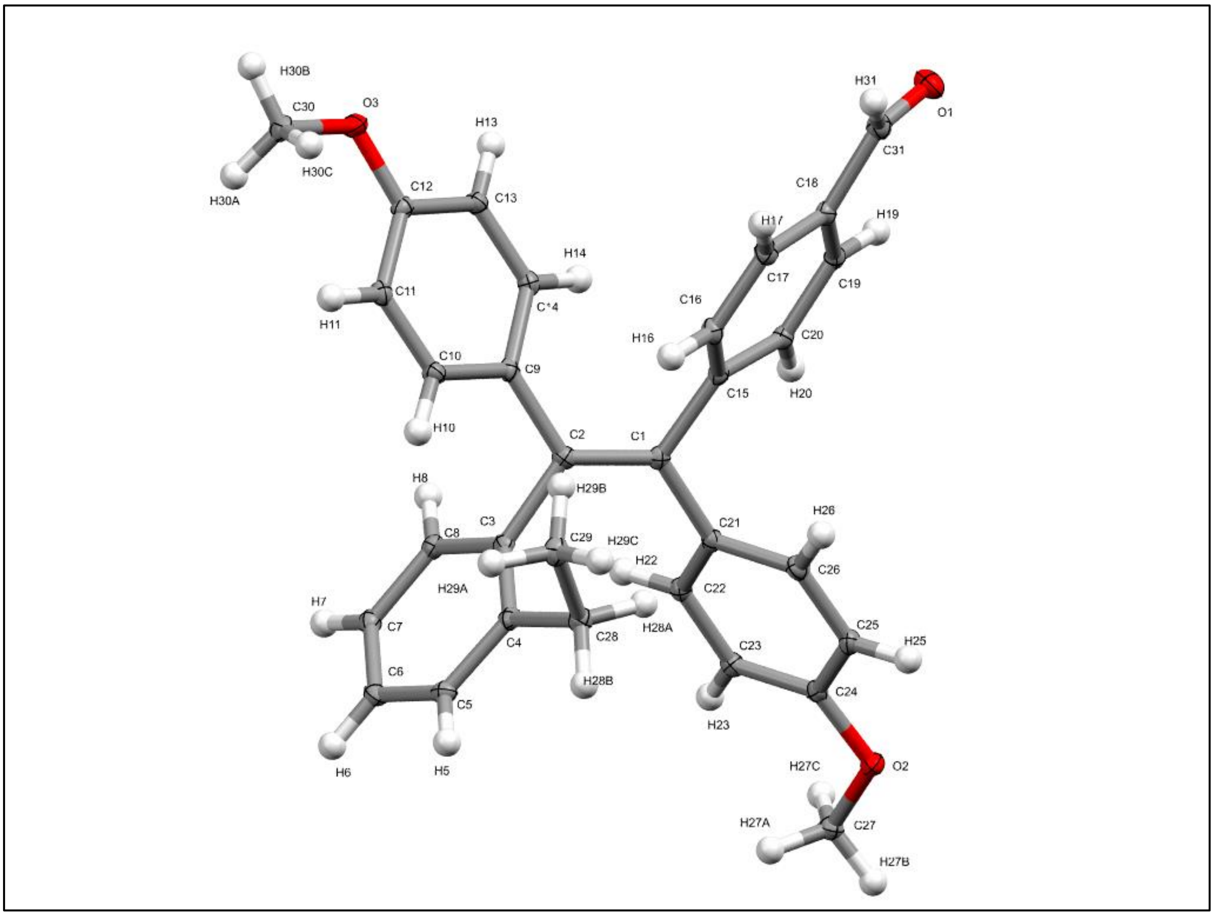


Figure S46: Molecular structure for compound **3**. Crystallization procedure: 10.0 mg solid compound was taken in a glass vial and dispersed in 0.5 mL ethyl acetate: hexane (0.5 : 99.5). It was dissolved on reflux and kept at ambient temperature (20 °C) for crystalization. **CCDC No.-2221369**

Crystal data and structure refinement for compound 3

Identification code	PK-CHOOME_auto_1
Empirical formula	$C_{31}H_{28}O_3$

Formula weight	448.53
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.2216(2)
b/Å	15.1257(3)
c/Å	14.4955(3)
α/°	90
β/°	108.837(2)
γ/°	90
Volume/Å^3	2328.61(8)
Z	4
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	0.639
F(000)	952.0
Crystal size/mm^3	0.1 × 0.1 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.702 to 136.27
Index ranges	$-13 \leq h \leq 12, -18 \leq k \leq 17, -17 \leq l \leq 17$
Reflections collected	16598
Independent reflections	4212 [R_{int} = 0.0912, R_{sigma} = 0.0471]
Data/restraints/parameters	4212/0/310
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.1582
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.1626
Largest diff. peak/hole / e Å^{-3}	0.41/-0.37

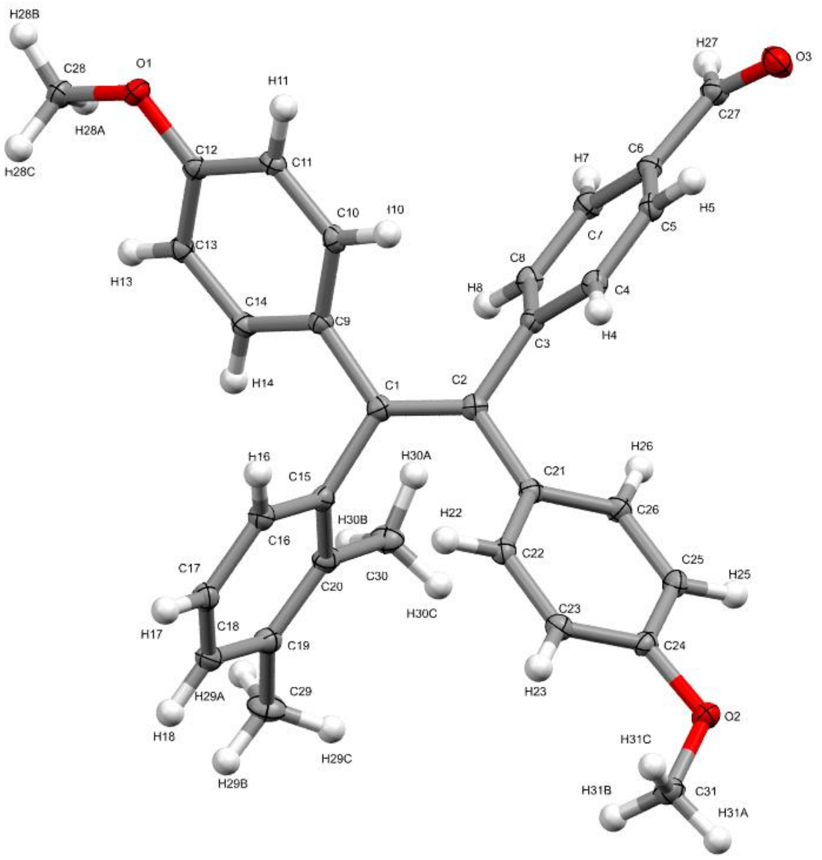


Figure S47: Molecular structure for compound **9**. Crystallization procedure: 10.0 mg solid compound was taken in a glass vial and dispersed in 0.5 mL ethyl acetate: hexane (0.5 : 99.5). It was dissolved on reflux and kept at ambient temperature (20 ^{o}C) for crystalization. **CCDC No.-2232806**

Crystal data and structure refinement for compound 9

Identification code	PKA_538A_auto_1
Empirical formula	C31H28O3
Formula weight	448.53
Temperature/K	113(18)
Crystal system	monoclinic
Space group	P21/n
a/Å	10.9595(4)
b/Å	15.8984(5)
c/Å	14.7337(5)
α/°	90
β/°	111.118(4)
γ/°	90
Volume/Å3	2394.77(15)
Z	4
ρcalcg/cm3	1.244
μ/mm-1	0.079

F(000)	952.0
Crystal size/mm3	0.5 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.918 to 54.134
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 19, -18 ≤ l ≤ 18
Reflections collected	29857
Independent reflections	5010 [Rint = 0.0387, Rsigma = 0.0297]
Data/restraints/parameters	5010/0/311
Goodness-of-fit on F2	1.047
Final R indexes [I>=2σ (I)]	R1 = 0.0428, wR2 = 0.1101
Final R indexes [all data]	R1 = 0.0540, wR2 = 0.1177
Largest diff. peak/hole / e Å-3	0.29/-0.21

Section SM-XIII: Synthesis, characterizations and catalytic activity of other polymeric ligands for dicarbofunctionalization reaction

Synthesis of **KAPs(Ph-PPh$_3$), Pd@KAPs(Ph-PPh$_3$)** and their preliminary characterizations

In a 16 mL culture tube equipped with a magnetic bar, anhydrous ferric chloride ($FeCl_3$)(975 mg, 6.0 mmol), triphenylphosphine (525 mg, 2.0 mmol), dimethoxymethane (456 mg, 6.0 mmol) and benzene (156 mg, 2.0 mmol) were taken under inert atmosphere. Further, 2.0 mL dichloroethane was poured, and it was capped tightly. Initially, the solution was stirred at rt for 5 min and then at 45 ^oC for 5 h. Finally, it was stirred at 80 ^oC for 67 h for a complete reaction. The resulting precipitate was filtered and washed with methanol multiple times before soxhleting it for another 24 h in methanol. At last, it was dried at 60 ^oC under vacuum for 24 h to get dark maroon colored powder (**KAPs(Ph-PPh$_3$)**) in quantitative yield.

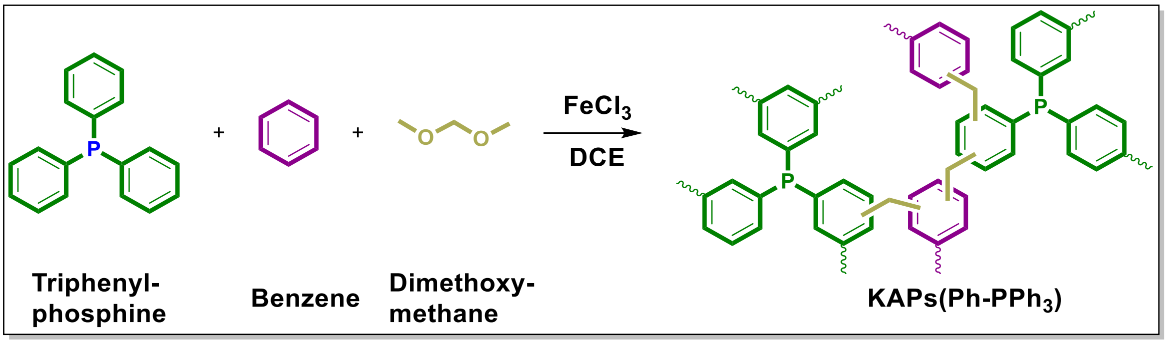


Figure S48: Schematic protocol for the synthesis of **KAPs(Ph-PPh$_3$)**

Methanol (2.5 mL) was taken in a clean reaction tube with a magnetic stir bar. 47 mg **KAPs(Ph-PPh$_3$)** was suspended into it and stirred for 2 h at rt. A pre-formed solution of 3.0 mg $PdCl_2$ in 2.5 mL methanol was mixed with the suspension and allowed to stir for 24 h at rt. Further, it was centrifuged and washed with fresh methanol five times to ensure the removal of extra unsupported $PdCl_2$. It was dried under vacuum at 60 ^oC for 12 h to obtain **Pd@KAPs(Ph-PPh$_3$)**.

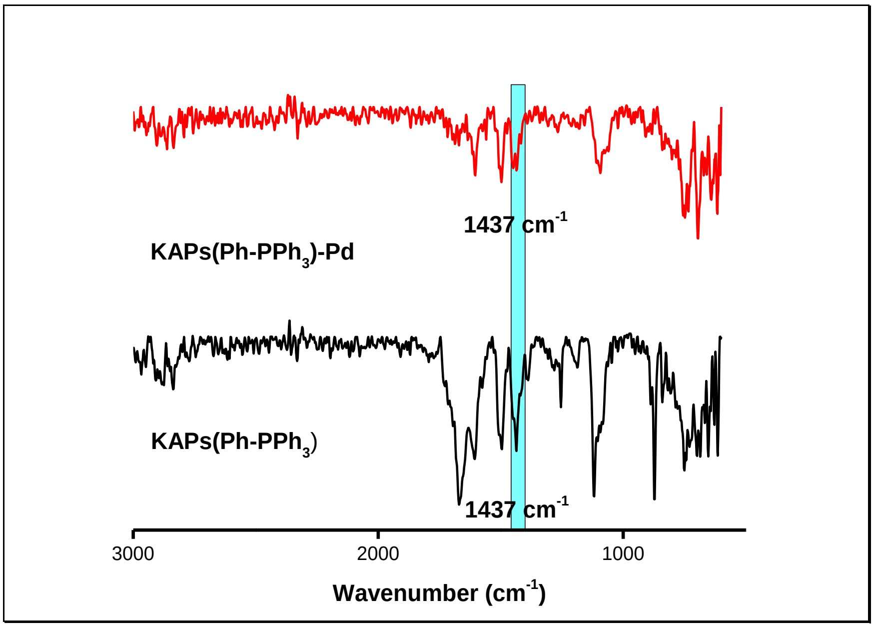


Figure S49: The bands in the FTIR spectrum around 1600–1450, 1250–950, and 900–650 cm^{-1} can be assigned to benzene skeleton stretching, C–H out-of-plane bending, and in-plane bending vibrations of the benzene ring, respectively. The peaks at 1437 cm^{-1} correspond to the vibrations of the P–CH_2 bond and data matching with the literature[13]

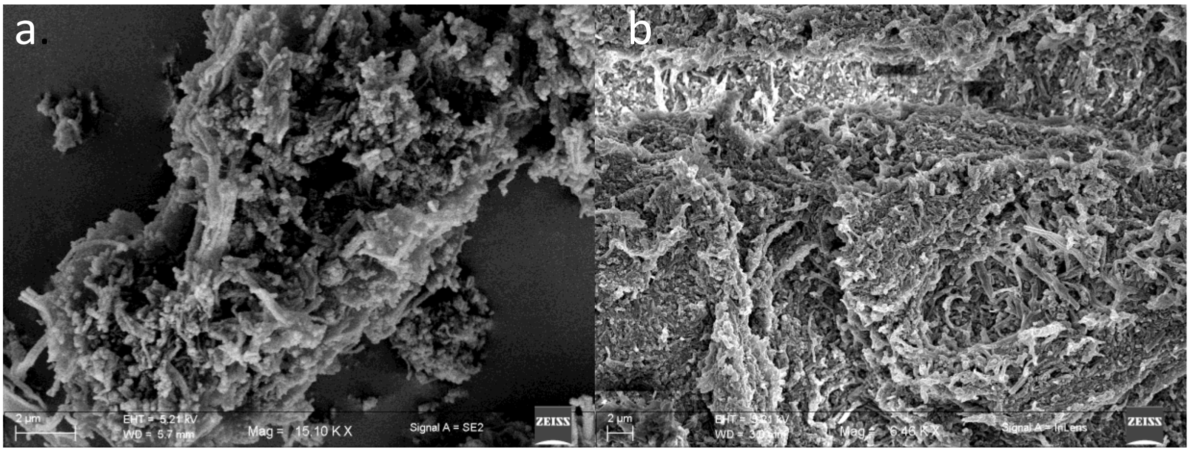


Figure S50: (a) FESEM image of **KAPs(Ph-PPh$_3$)** and (b) FESEM image of **Pd@KAPs(Ph-PPh$_3$)**. The scale is 2 µm unless otherwise stated. Also, the morphology is similar to the report in literature[13]

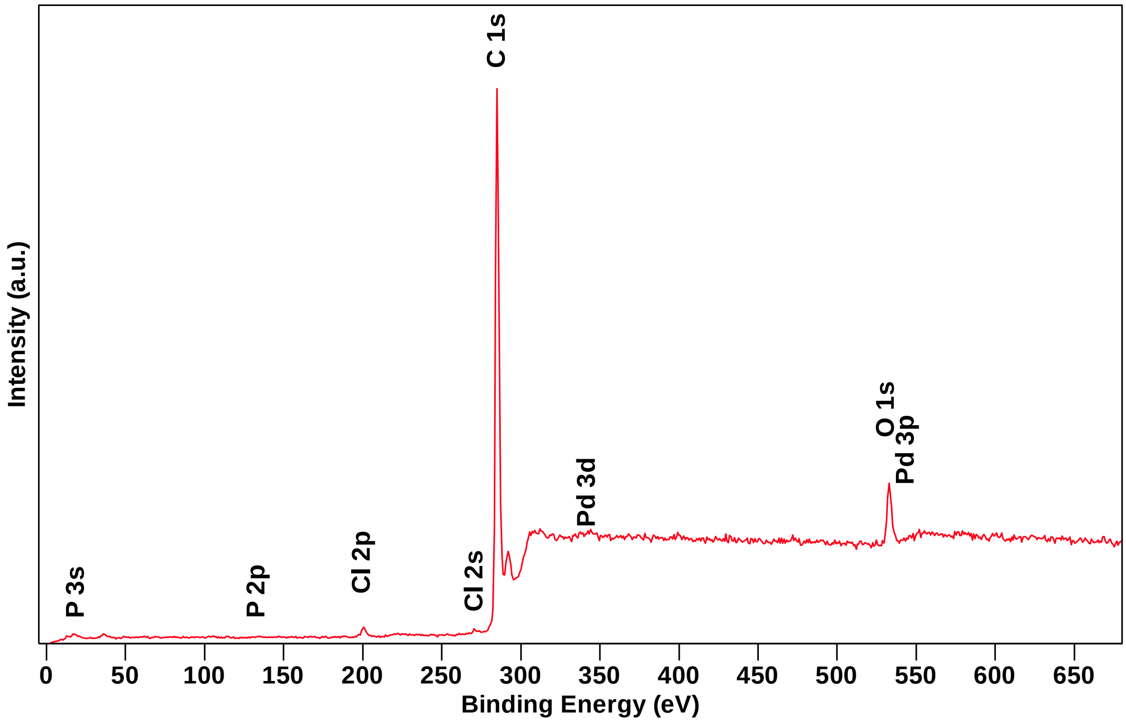


Figure S51: XPS spectrum of **Pd@KAPs(Ph-PPh$_3$)** showing elemental constituency after metalation and data matching with literature[13]

Synthesis of **Phos-polymer**, **Pd@Phos-polymer,** and their preliminary characterizations

In a 16 mL reaction tube, **BB1** (104 mg, 0.30 mmol), 1,4-diaminobenzene (48.6 mg, 0.45 mmol), 6M acetic acid (0.6 mL), 1,4-dioxane (1.5 mL), and mesitylene (0.5 mL) were added and was degassed three times through freeze–pump–thaw technique, and capped under inert condition. The mixture was allowed to attain rt before keeping it at 120 °C for 72h. The yellow-colored precipitate was filtered and washed with DMF and THF multiple times and dried under vacuum at 60 °C to yield the **Phos-polymer** in a quantitative amount.

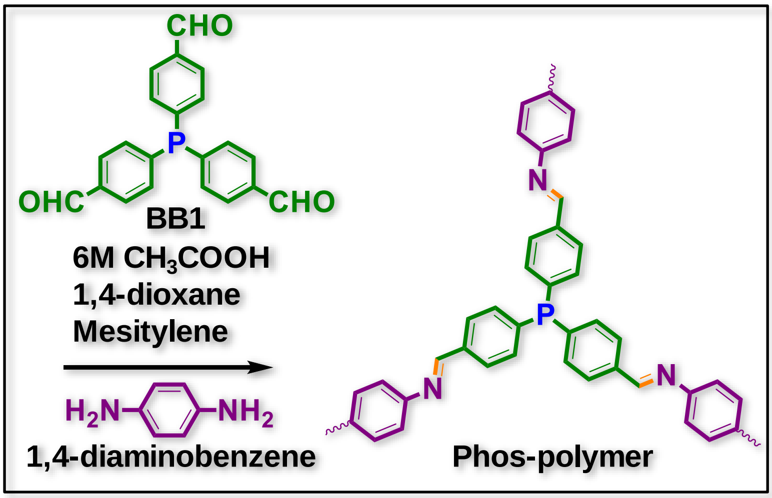


Figure S52: Schematic protocol for the synthesis of **Phos-polymer**

Methanol (2.5 mL) was taken in a clean reaction tube with a magnetic stir bar. 47 mg **Phos-polymer** was suspended into it and stirred for 2 h at rt. A pre-formed solution of 3.0 mg $PdCl_2$ in 2.5 mL methanol was mixed with the suspension and allowed to stir for 24 h at rt. Further, it was centrifuged and washed with fresh methanol five times to ensure the removal of extra unsupported $PdCl_2$. It was dried under vacuum at 60 ^{o}C for 12 h to obtain **Pd@Phos-polymer**.

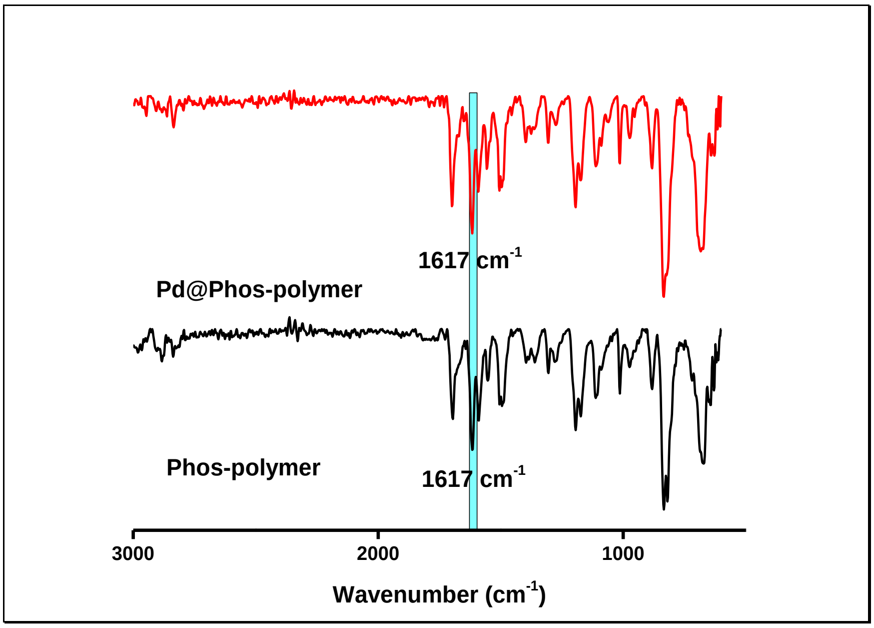


Figure S53: In the FT-IR spectrum, C=N stretching at ≈1617 cm^{-1} shows the formation of imine bonds, and remain intact even after metalation. This data is well matching with literature[14]

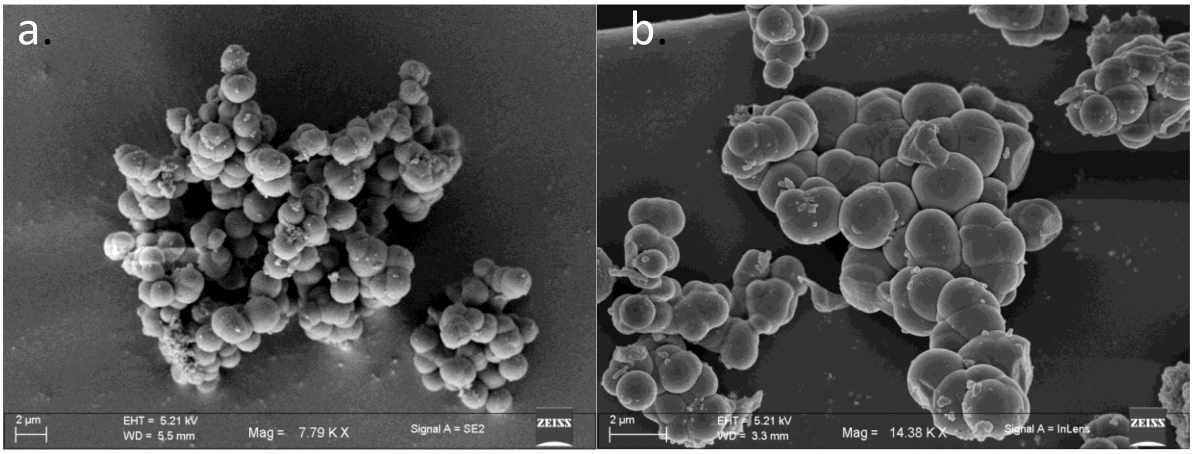


Figure S54: (a) FESEM image of **Phos-polymer** (b) FESEM image of **Pd@Phos-polymer**. The scale is 2 µm unless otherwise stated. Also, the morphology is similar to the report in literature[14]

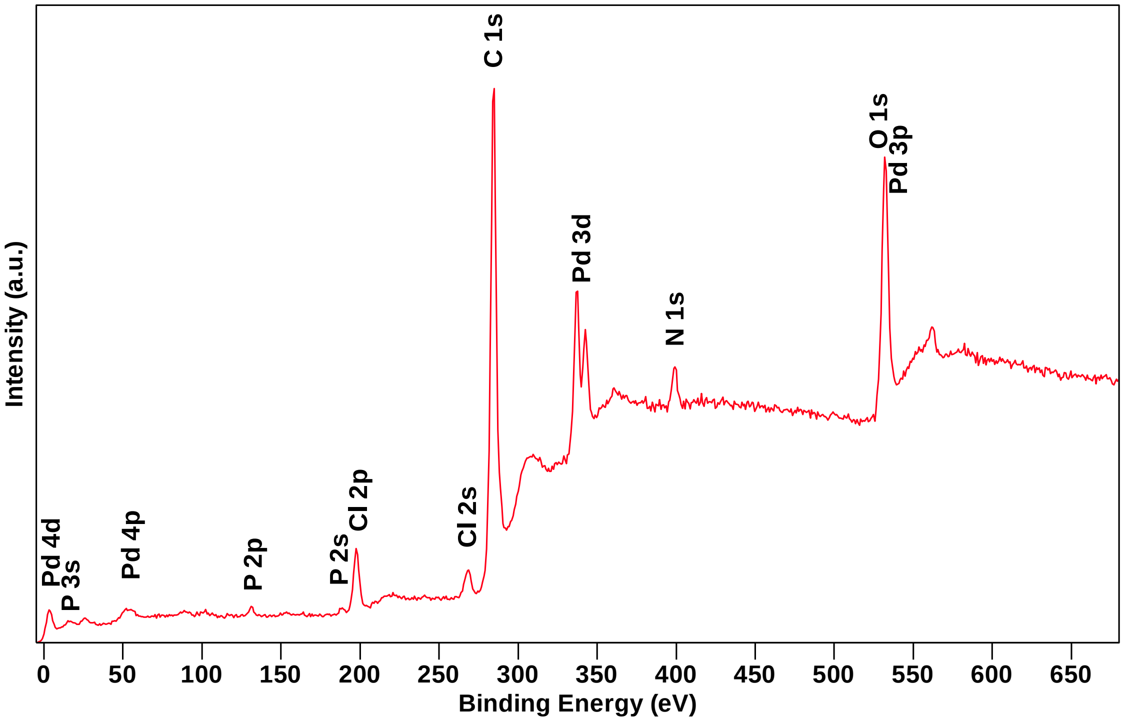


Figure S55: XPS spectrum of **Pd@Phos-polymer** showing elemental constituency after metalation and data is matching with literature[14]

Catalytic activity of **Pd@KAPs(Ph-PPh$_3$)** and **Pd@Phos-polymer**

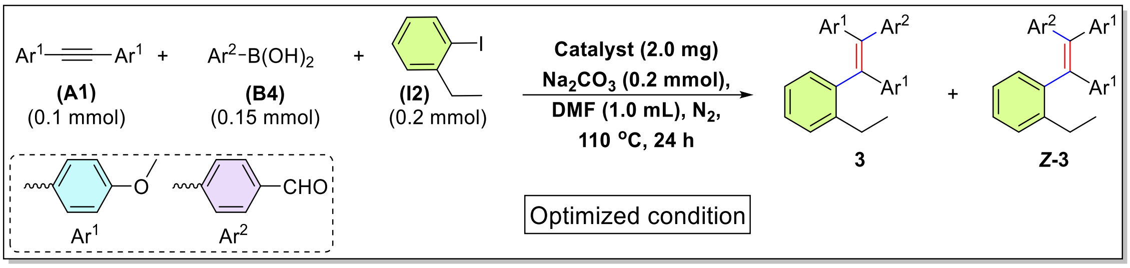
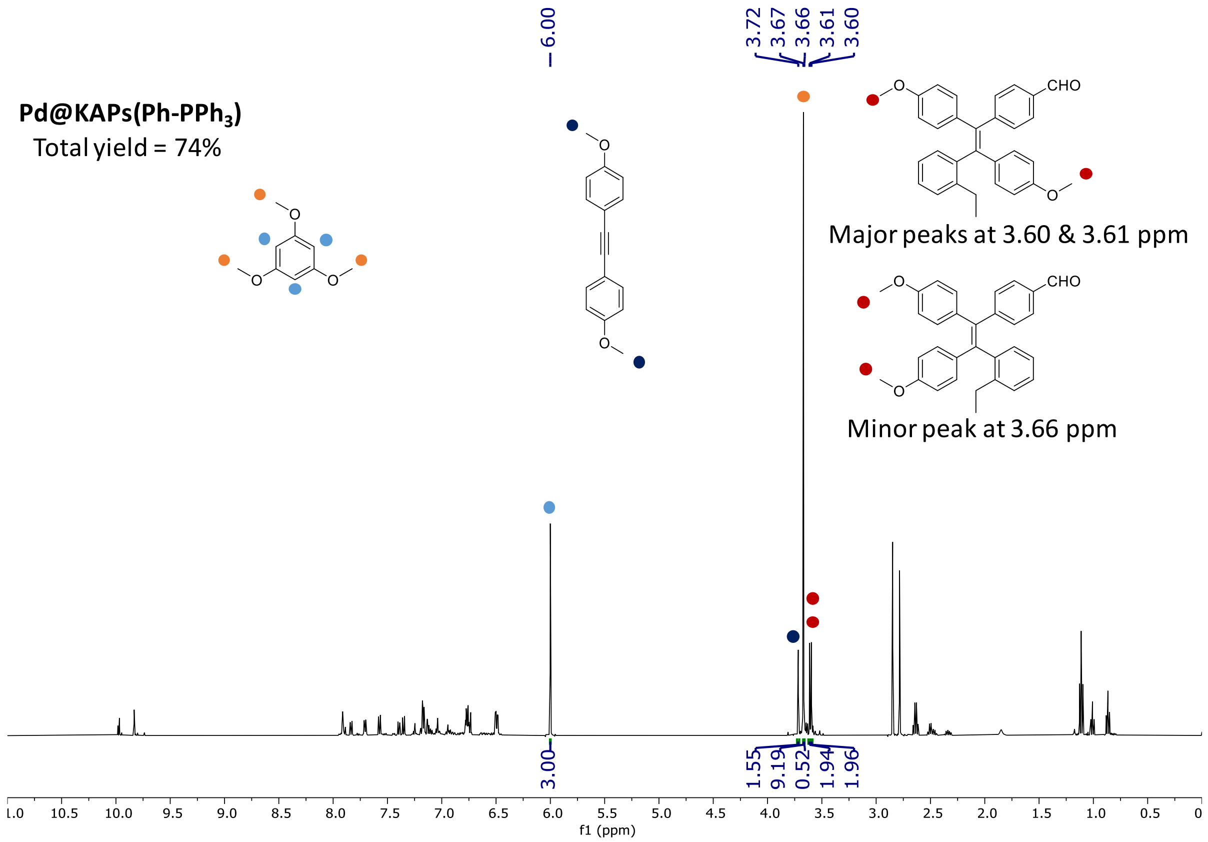
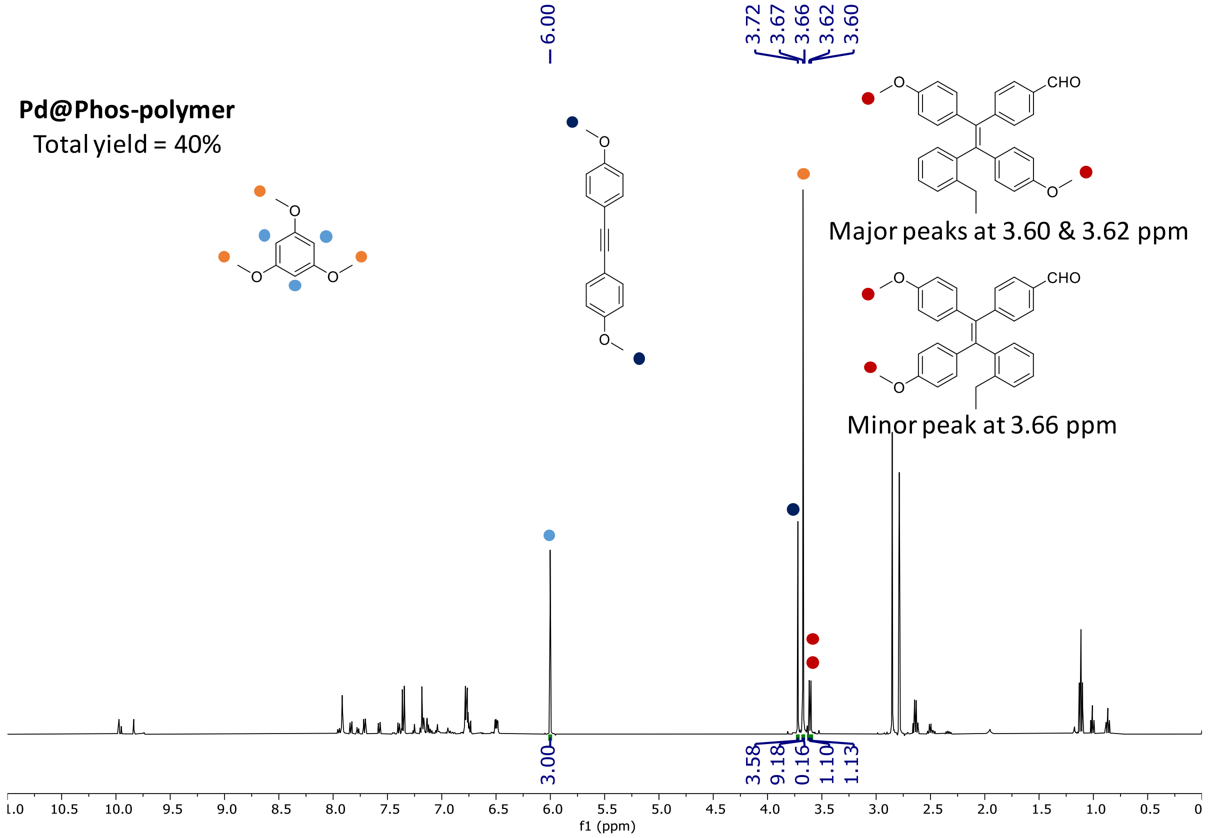


Figure S56 : Schematic protocol for checking catalytic activity of **Pd@KAPs(Ph-PPh$_3$)** and **Pd@Phos-polymer**

In two 16 mL culture tubes equipped with magnetic stirrer bars, **Pd@KAPs(Ph-PPh$_3$)** (2.0 mg) and **Pd@Phos-polymer** (2.0 mg) were taken separately. 1,2-bis(4-methoxyphenyl)ethyne **A1** (0.1 mmol), 4-formylphenylboronic acid **B4** (0.15 mmol), 2-ethyliodobenzene **I2** (0.2 mmol), Na_2CO_3(0.2 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) were then subsequently introduced under inert atmosphere. Dried DMF (1.0 mL) was then added, and the tube was capped tightly and kept in a pre-heated (110 °C) oil bath at 250 rpm stirring speed. After 24 h, the oil bath was removed, and the mixture was allowed to attain rt. The reaction mixture was transferred into a centrifuge tube, and the catalyst was centrifuged. The mother liquor was added to brine (5 mL) and then extracted using ethyl acetate (3 x 2 mL). The organic layer was washed with distilled water (5mL) and dried over anhydrous Na_2SO_4. Further, the organic layer was evaporated under reduced pressure, and NMR analysis of the crude sample was done in

$CDCl_3$ solvent. The quantification of the product has been given w.r.t internal alkyne. The crude ^{1}H NMR spectrum has been given below.





Section SM-XIV: References

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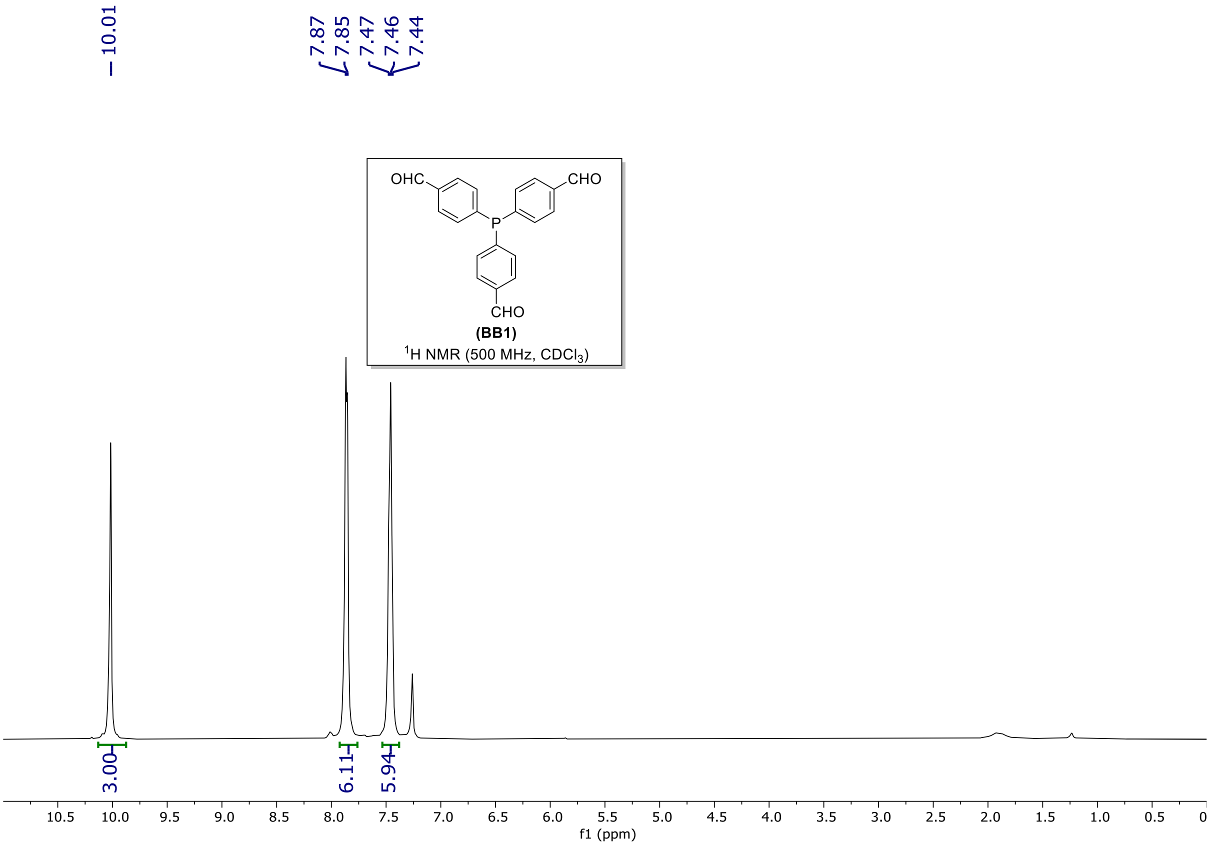
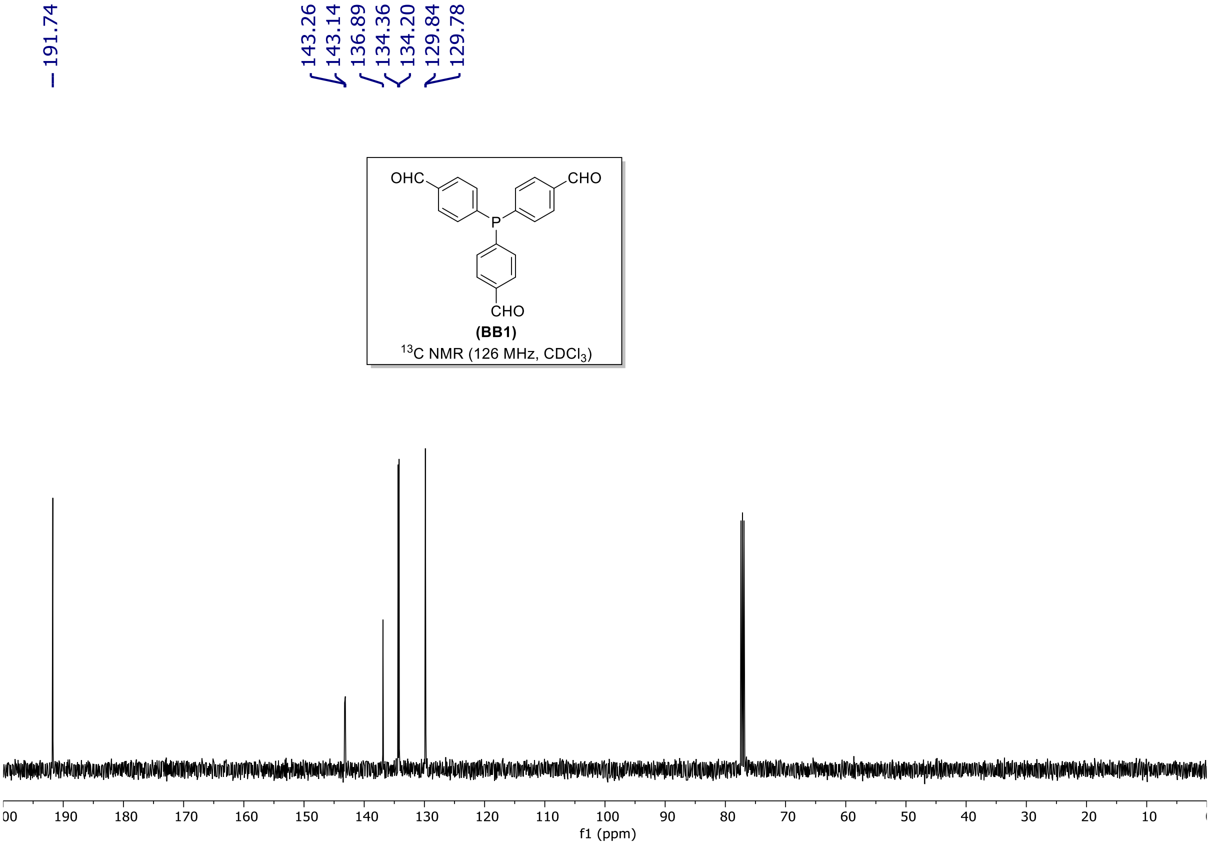
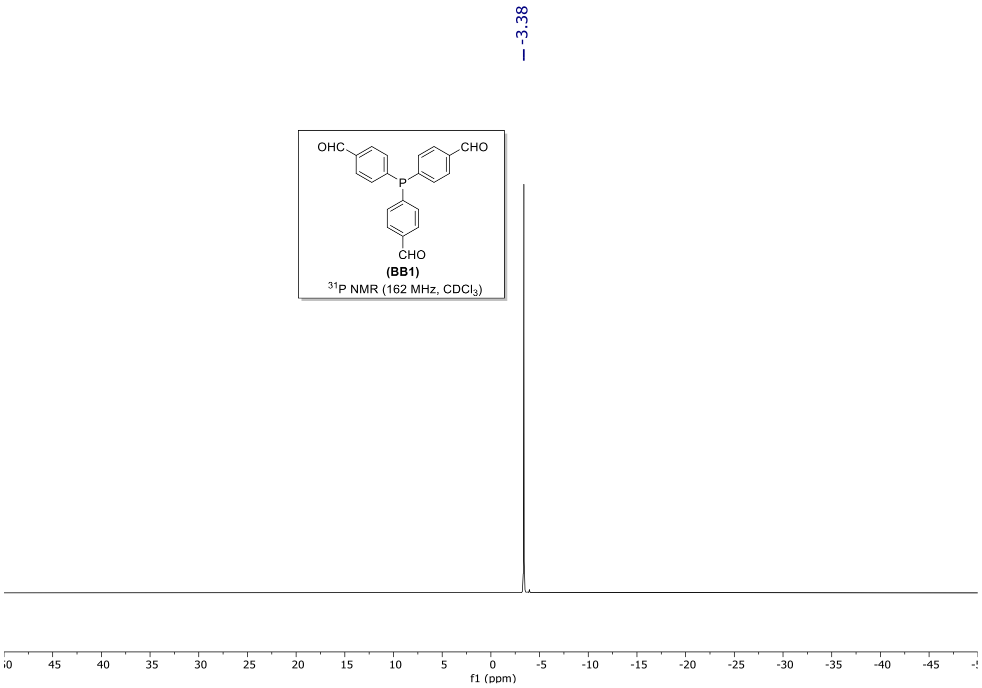
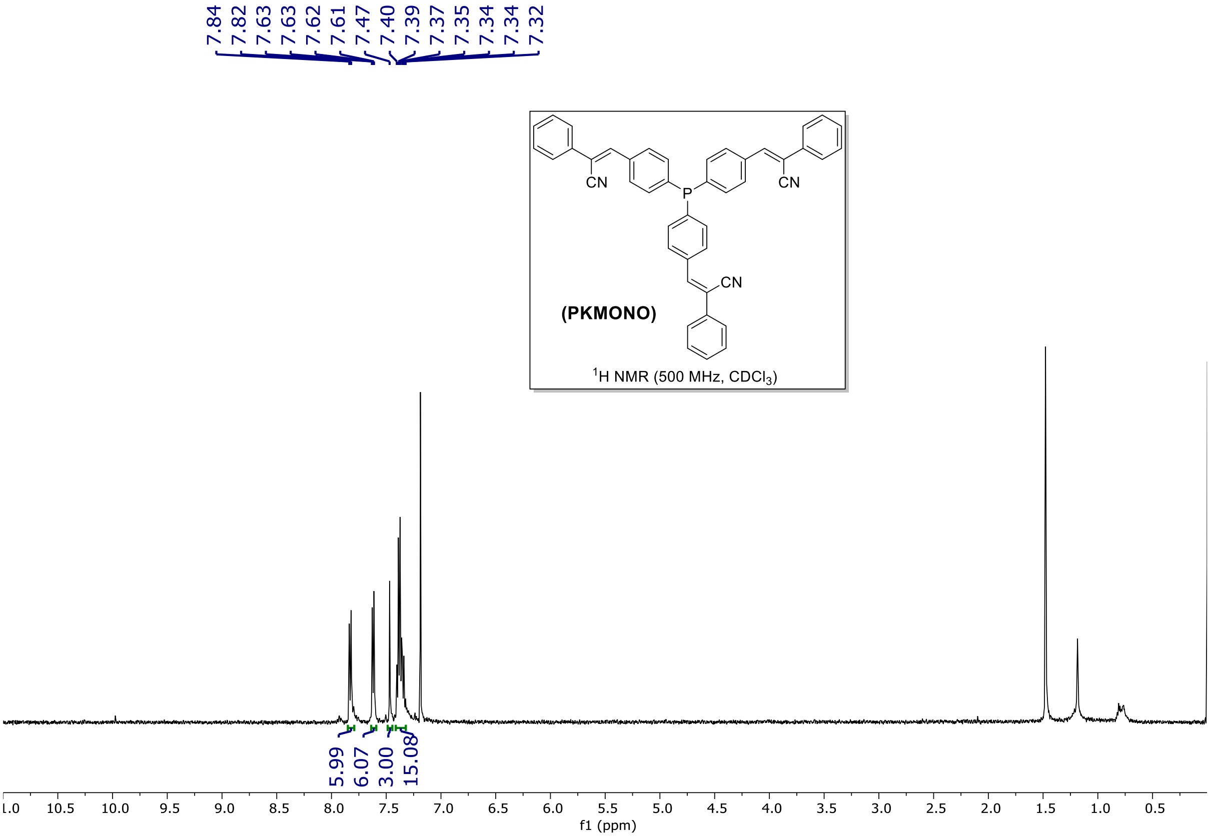
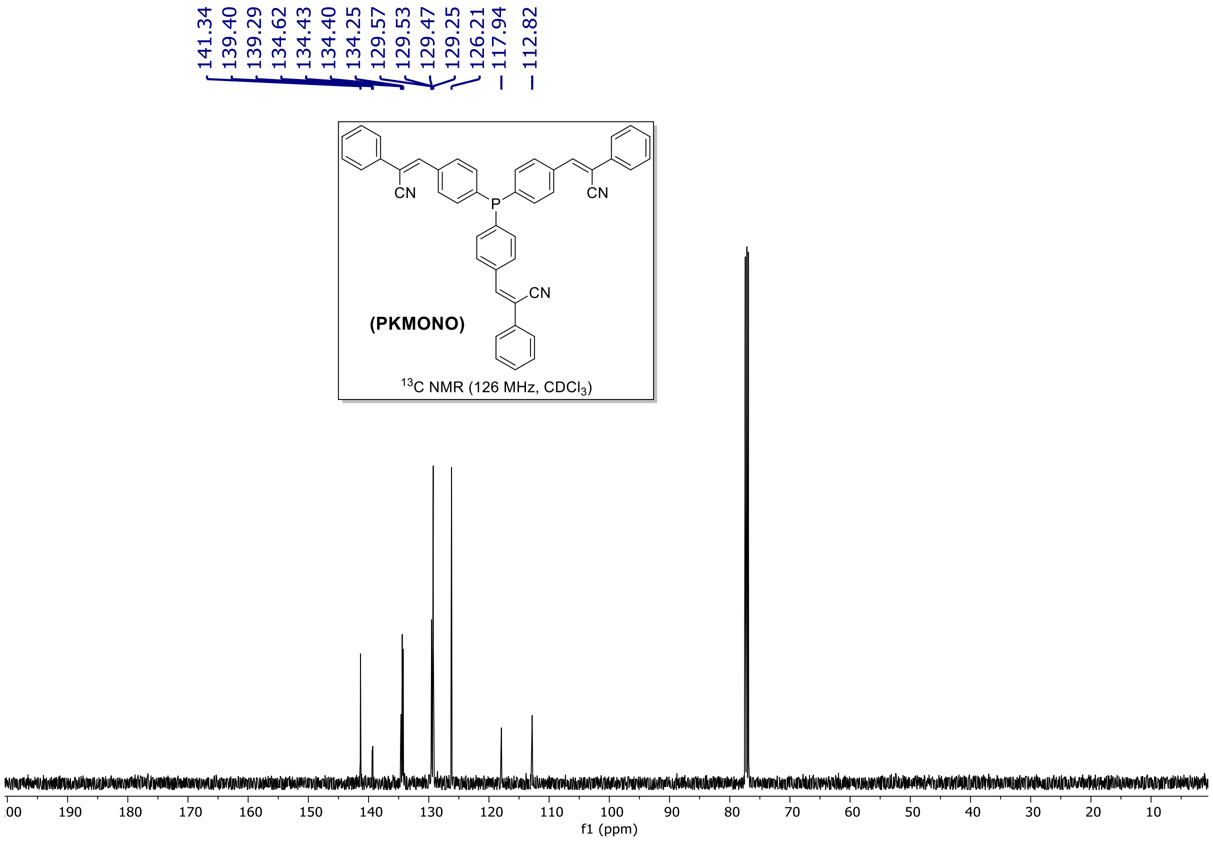
Section SM-XV: Copies of ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra

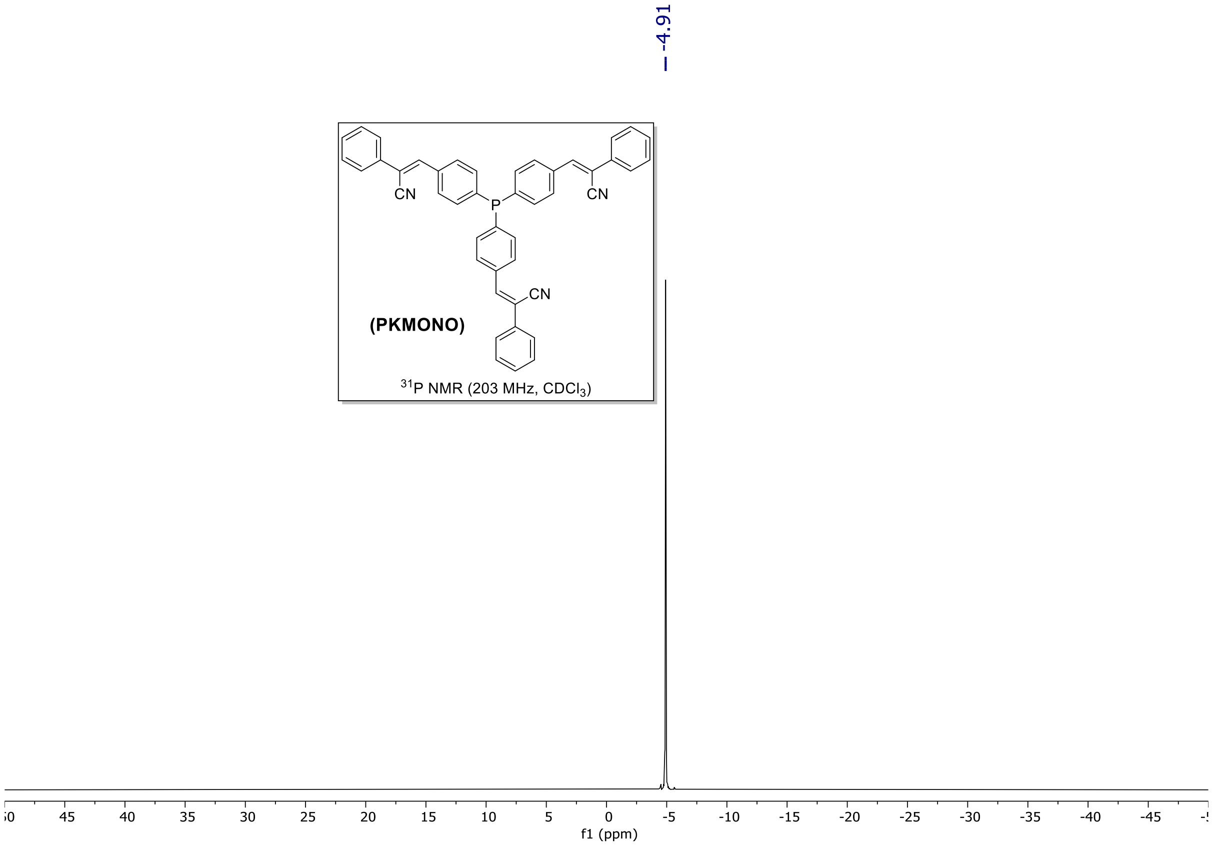


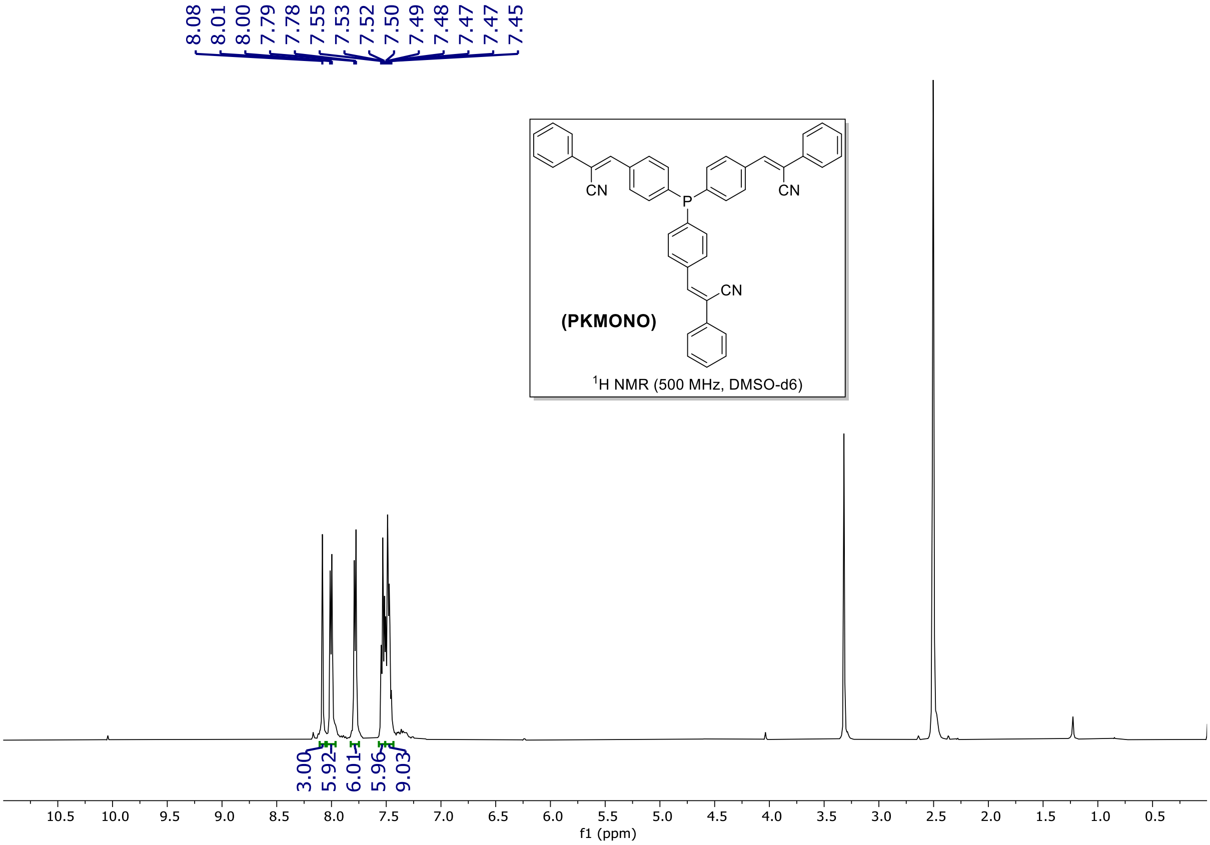


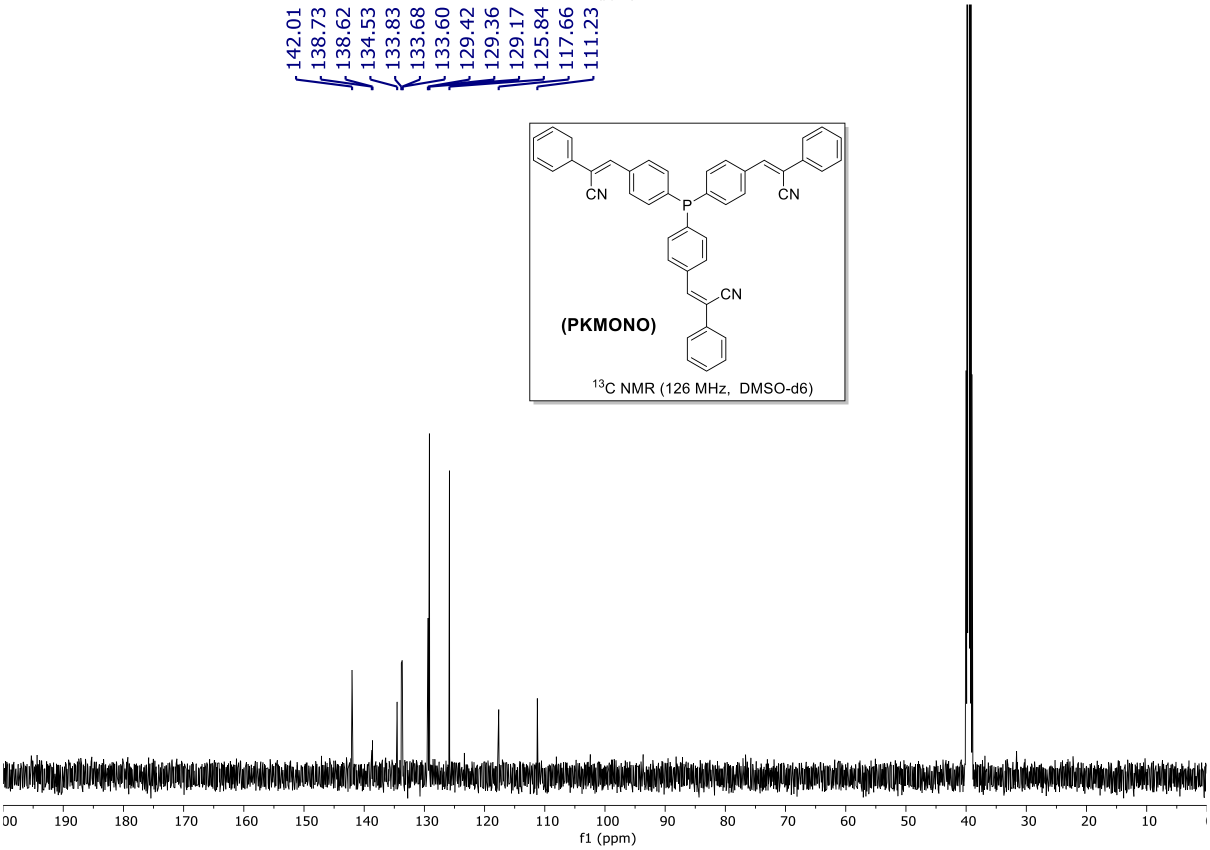

-3.38
OHC
CHO
P
CHO
(BB1)
^{31}P NMR (162 MHz, CDCl$_3$)
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

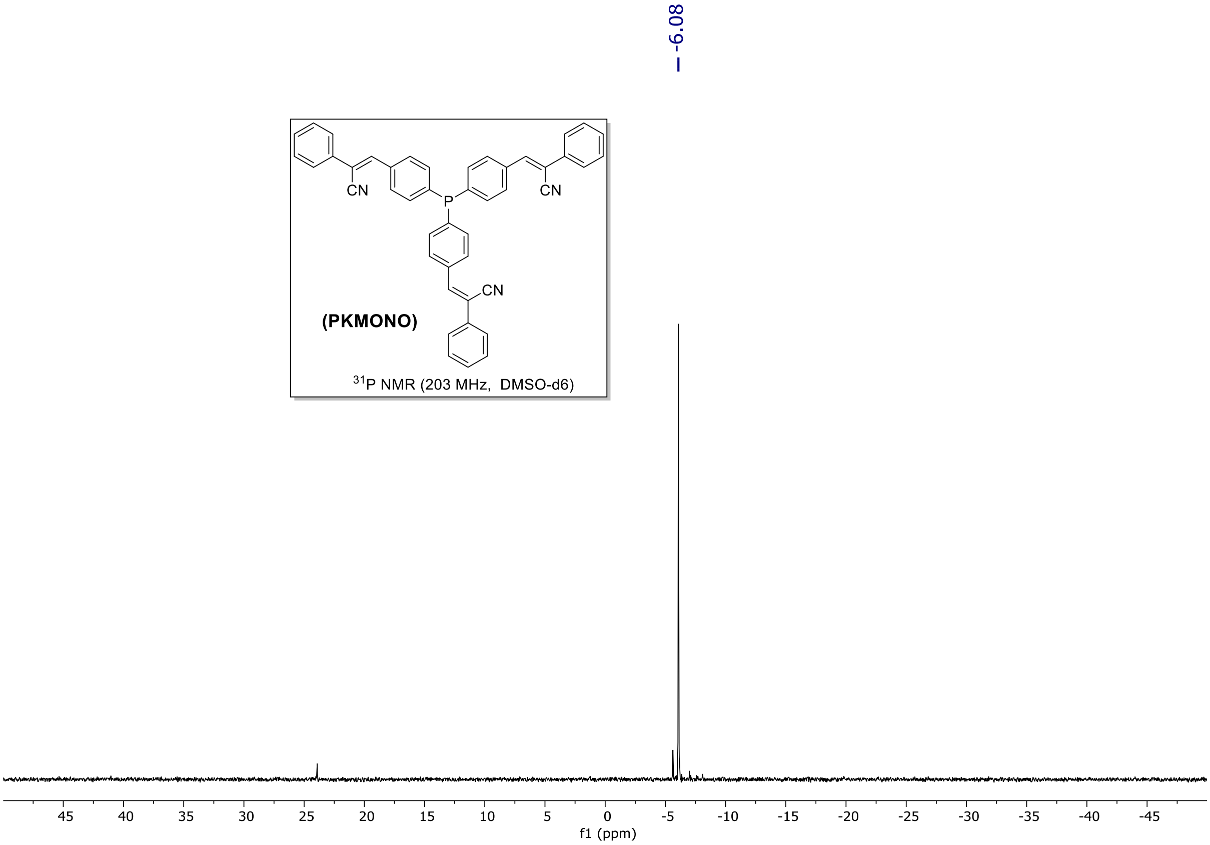

7.84 7.82 7.63 7.63 7.62 7.61 7.47 7.40 7.39 7.37 7.35 7.34 7.34 7.32
CN
P
CN
CN
(PKMONO)
^{1}H NMR (500 MHz, CDCl$_3$)
5.99 6.07 3.00 15.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

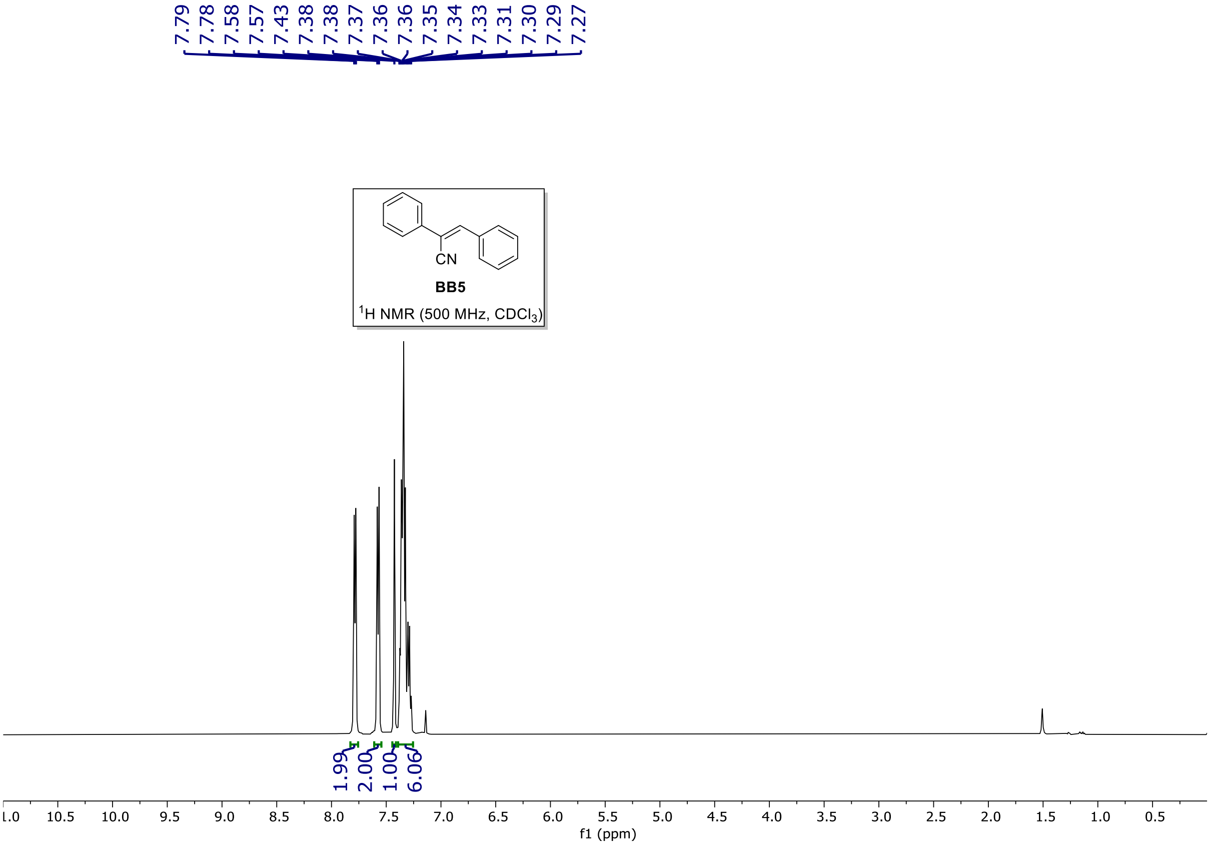

141.34
139.40
139.29
134.62
134.43
134.40
134.25
129.57
129.53
129.47
129.25
126.21
117.94
112.82
CN
P
CN
CN
(PKMONO)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

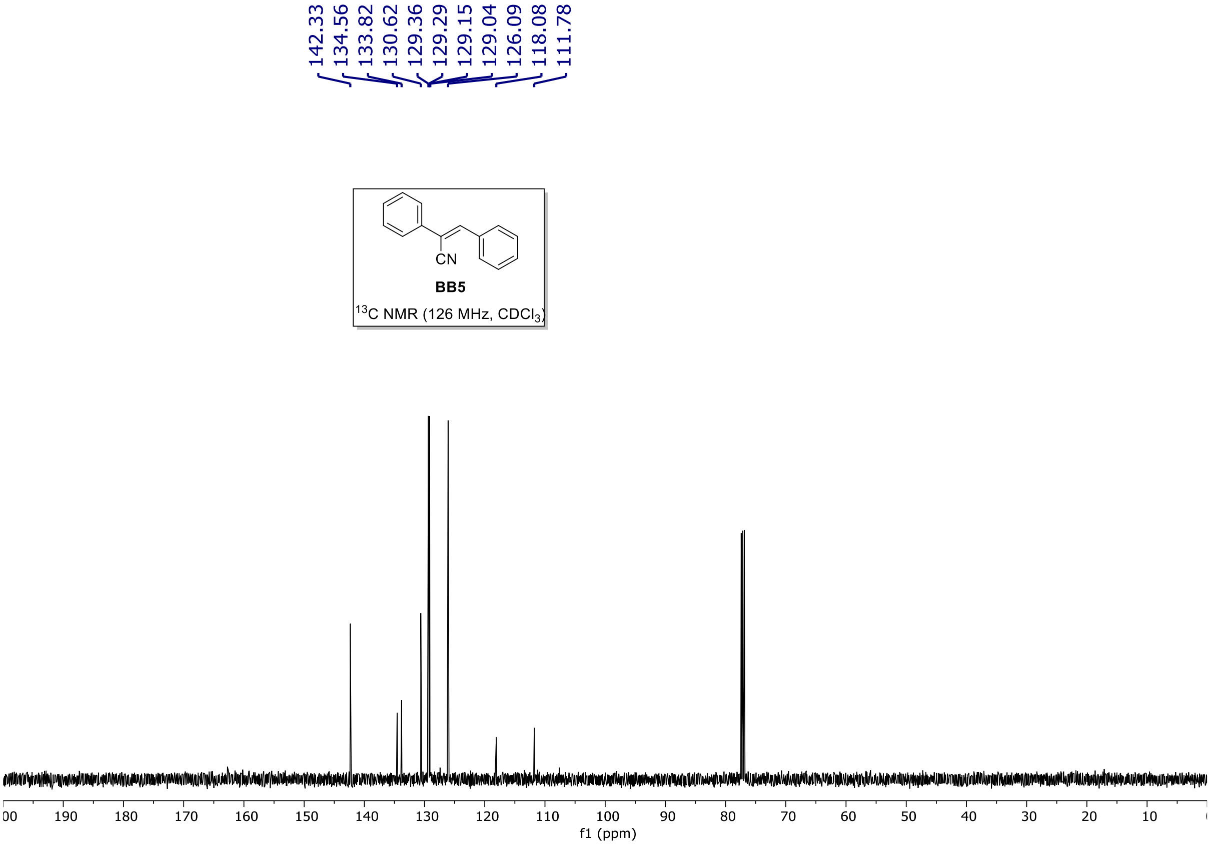

-4.91
CN
P
CN
CN
(PKMONO)
^{31}P NMR (203 MHz, CDCl$_3$)
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

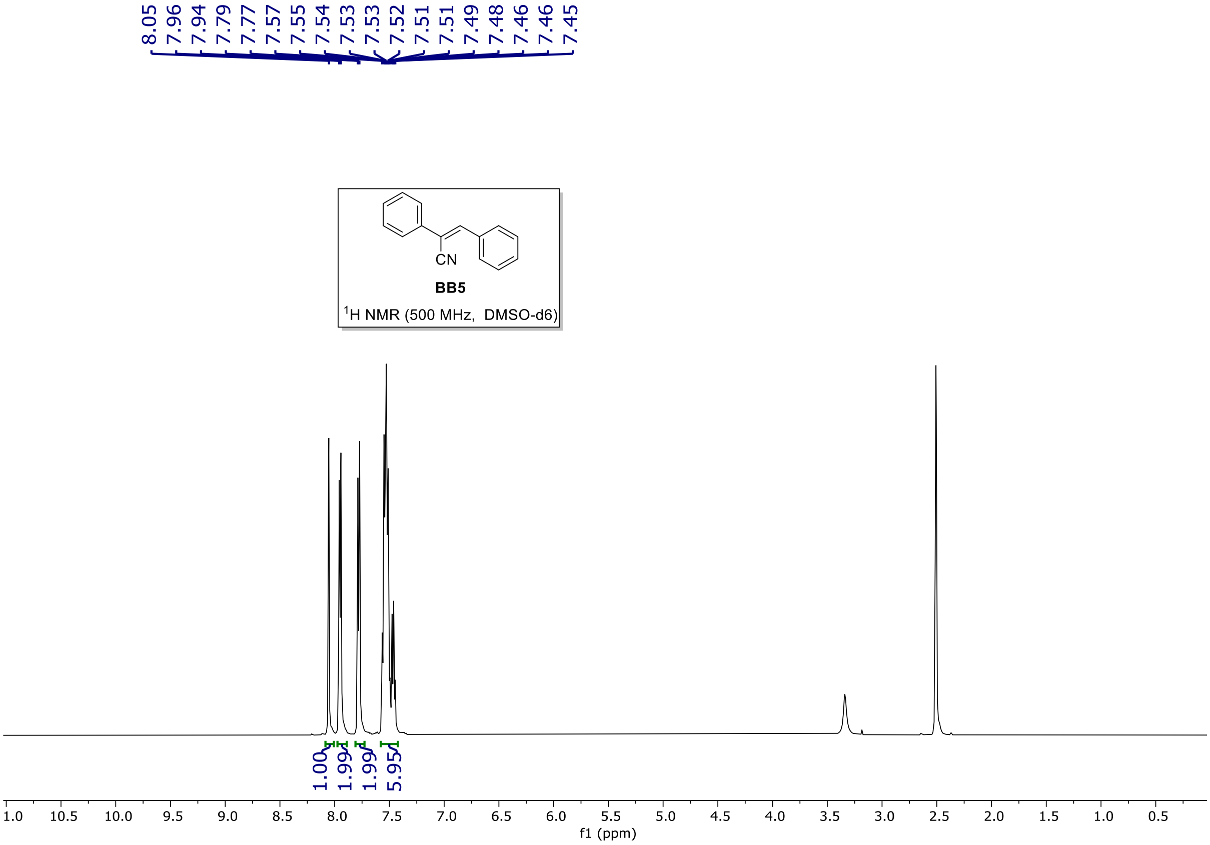

8.08
8.01
8.00
7.79
7.78
7.55
7.53
7.52
7.50
7.49
7.48
7.47
7.47
7.45
CN
P
CN
CN
(PKMONO)
^{1}H NMR (500 MHz, DMSO-d6)
3.00
5.92
6.01
5.96
9.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

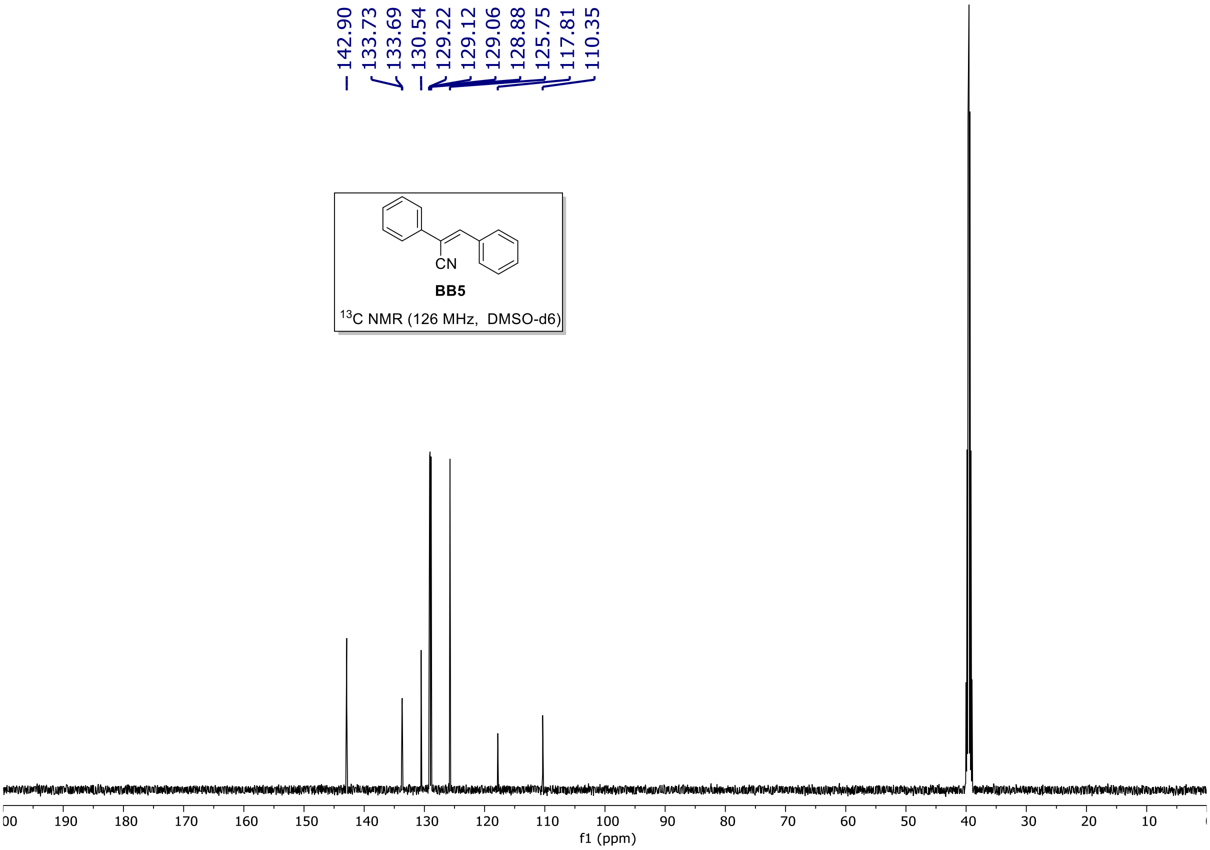

142.01
138.73
138.62
134.53
133.83
133.68
133.60
129.42
129.36
129.17
125.84
117.66
111.23
CN
P
CN
CN
(PKMONO)
^{13}C NMR (126 MHz, DMSO-d6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

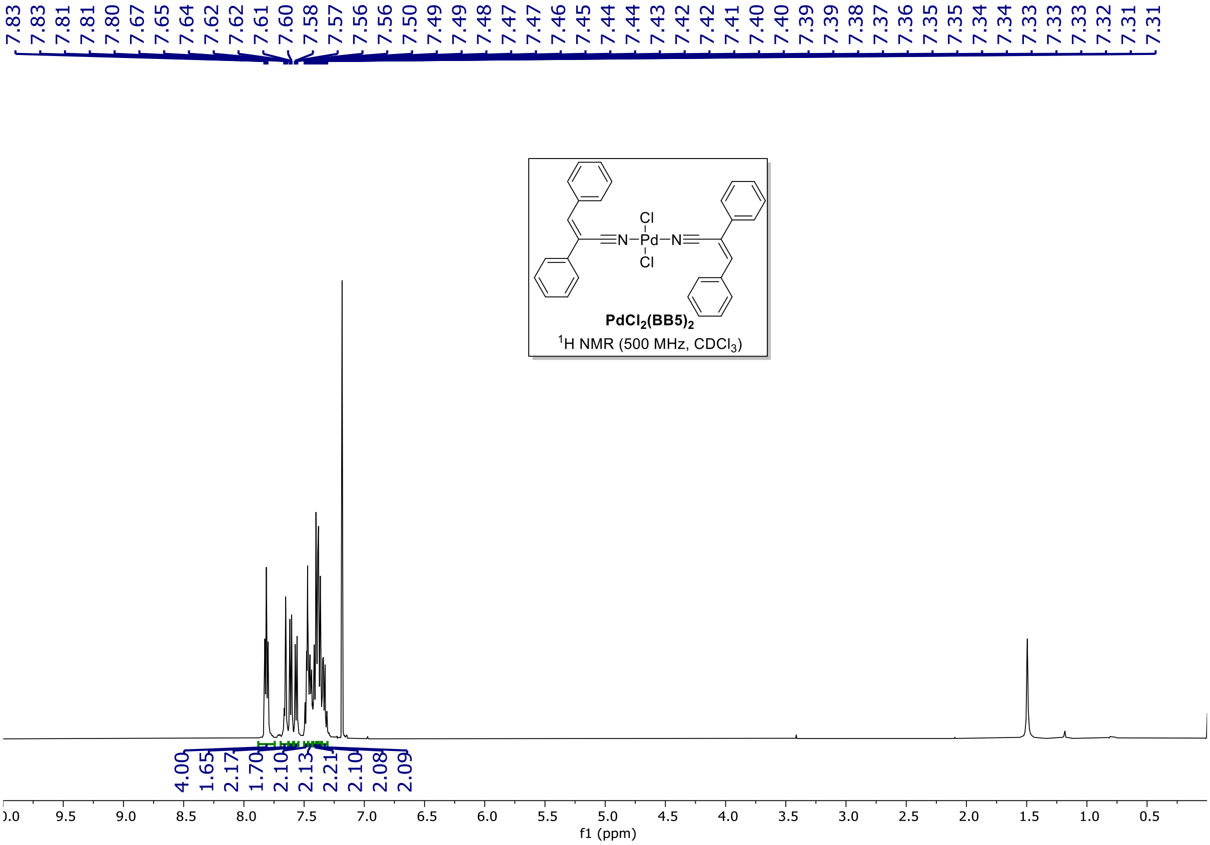

-6.08
CN
P
CN
CN
(PKMONO)
^{31}P NMR (203 MHz, DMSO-d6)
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

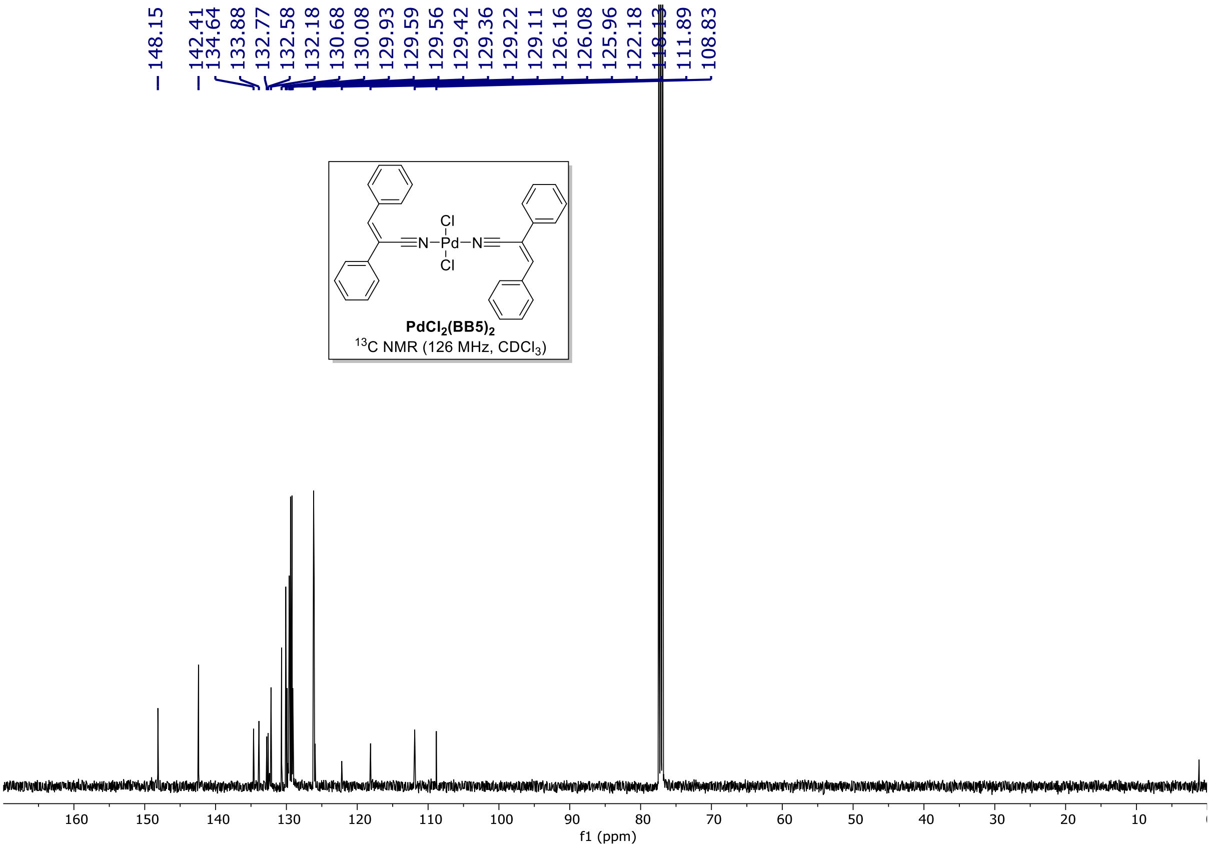

7.79
7.78
7.58
7.57
7.43
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.27
CN
BB5
^{1}H NMR (500 MHz, CDCl$_3$)
1.99
2.00
1.00
6.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

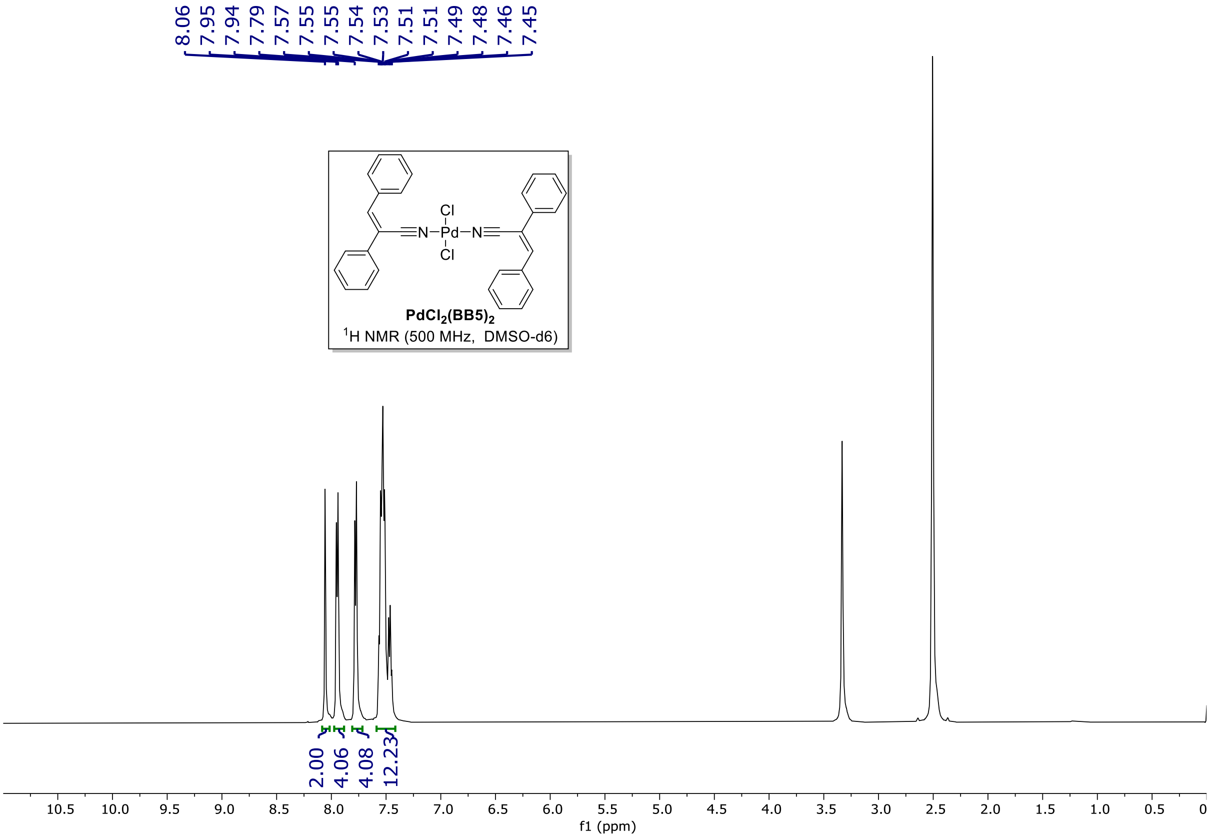

142.33
134.56
133.82
130.62
129.36
129.29
129.15
129.04
126.09
118.08
111.78
CN
BB5
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

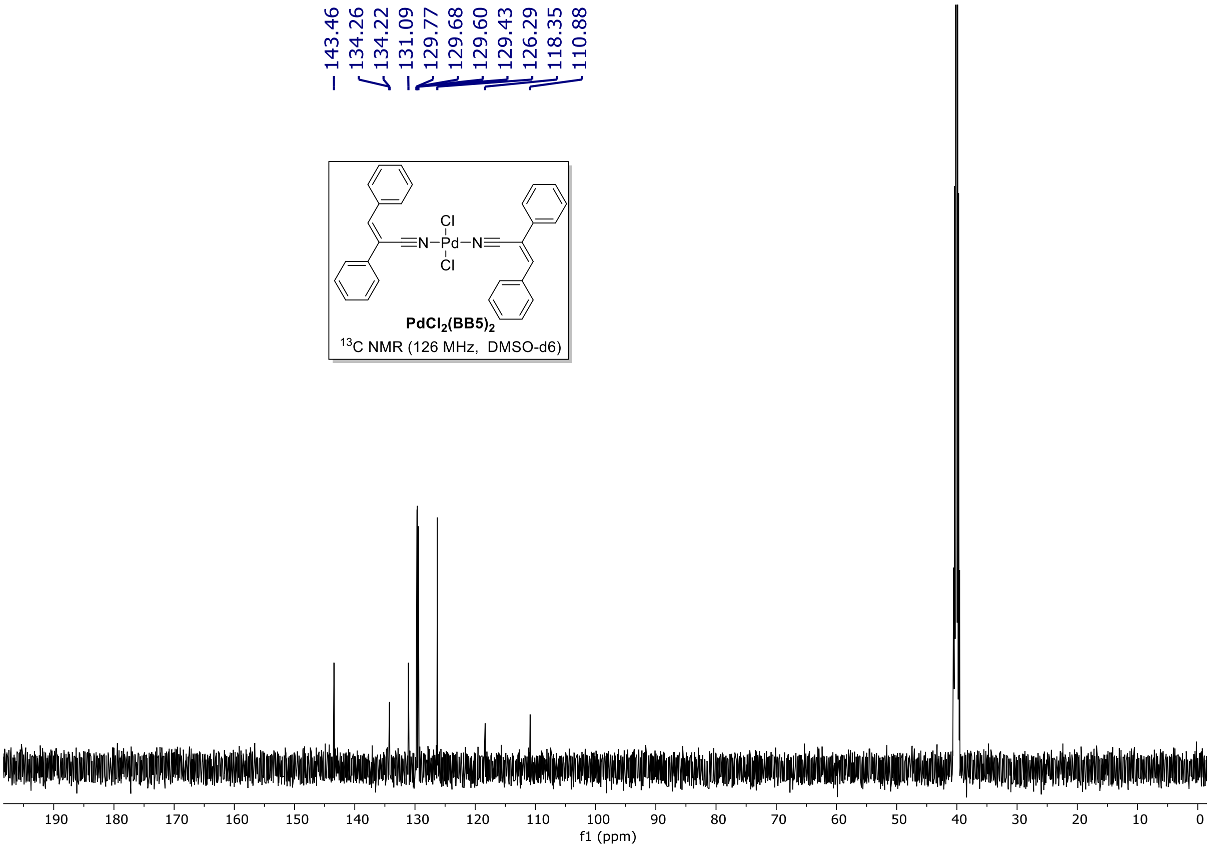

8.05
7.96
7.94
7.79
7.77
7.57
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.49
7.48
7.46
7.46
7.45
CN
BB5
^{1}H NMR (500 MHz, DMSO-d6)
1.00
1.99
1.99
5.95
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

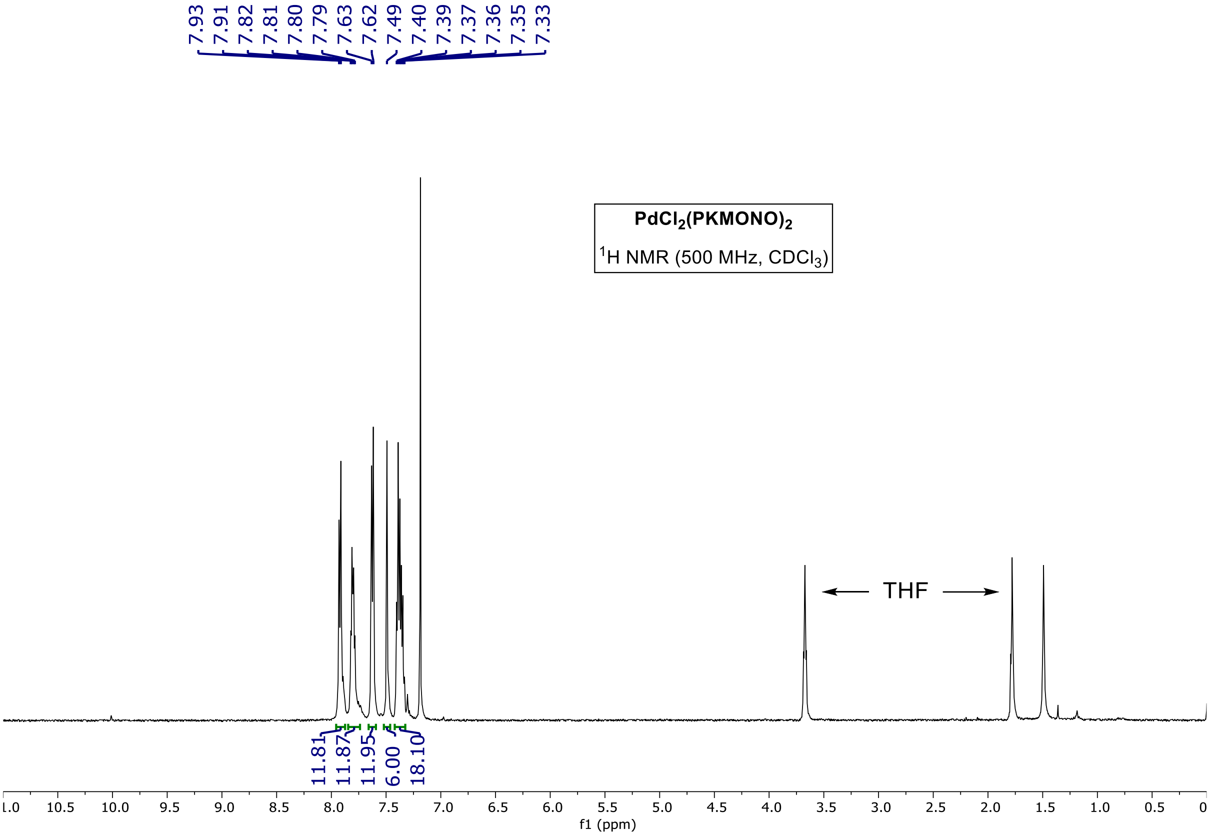

142.90
133.73
133.69
130.54
129.22
129.12
129.06
128.88
125.75
117.81
110.35
CN
BB5
^{13}C NMR (126 MHz, DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

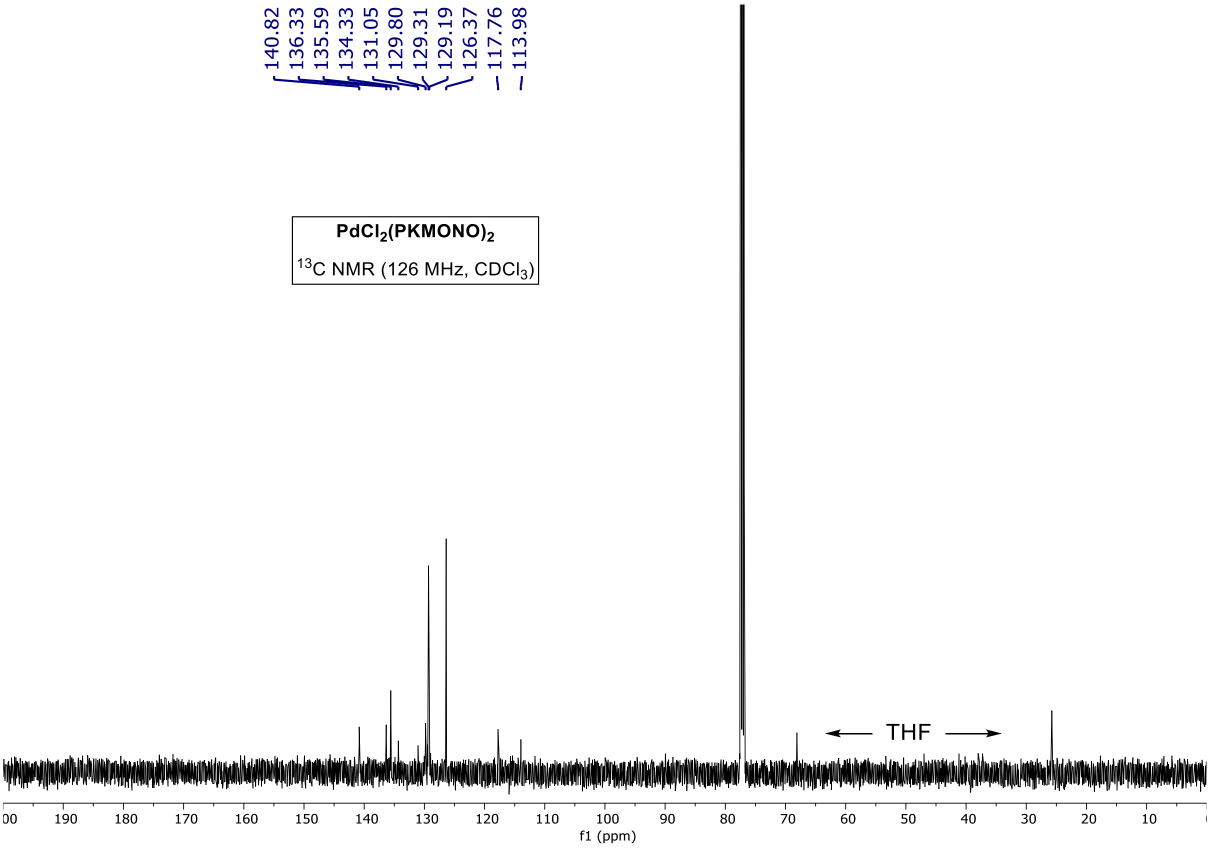

7.83 7.83 7.81 7.81 7.80 7.67 7.65 7.64 7.62 7.62 7.61 7.60 7.58 7.57 7.56 7.56 7.50 7.49 7.49 7.48 7.47 7.47 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31
Cl
N
Pd
N
Cl
PdCl$_2$(BB5)$_2$
^{1}H NMR (500 MHz, CDCl$_3$)
4.00
1.65
2.17
1.70
2.10
2.13
2.21
2.10
2.08
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


148.15
142.41
134.64
133.88
132.77
132.58
132.18
130.68
130.08
129.93
129.59
129.56
129.42
129.36
129.22
129.11
126.16
126.08
125.96
122.18
118.13
111.89
108.83
Cl
N
Pd
N
Cl
PdCl$_2$(BB5)$_2$
^{13}C NMR (126 MHz, CDCl$_3$)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.06
7.95
7.94
7.79
7.57
7.55
7.55
7.54
7.53
7.51
7.51
7.49
7.48
7.46
7.45
Cl
N
Pd
N
Cl
PdCl$_2$(BB5)$_2$
^{1}H NMR (500 MHz, DMSO-d6)
2.00
4.06
4.08
12.23
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

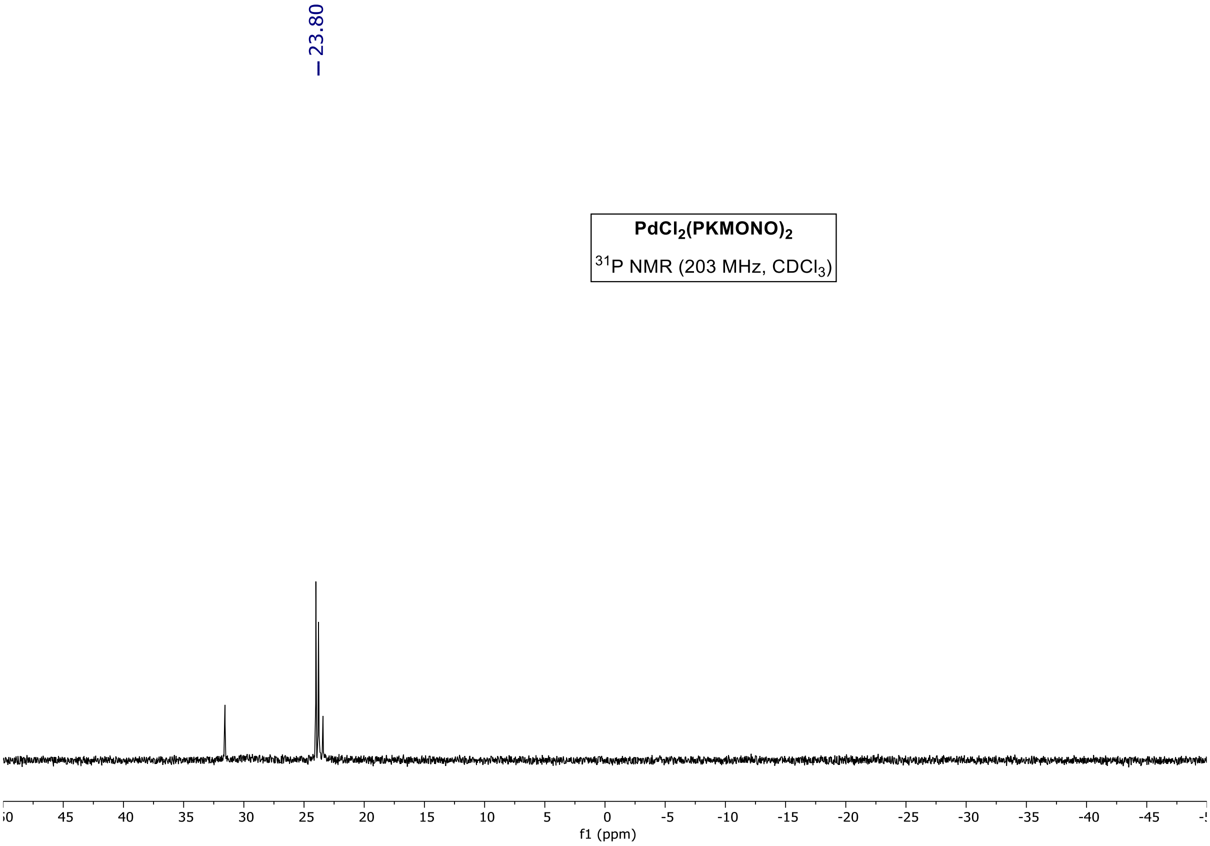

143.46
134.26
134.22
131.09
129.77
129.68
129.60
129.43
126.29
118.35
110.88
Cl
N
Pd
N
Cl
PdCl$_2$(BB5)$_2$
^{13}C NMR (126 MHz, DMSO-d6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.93
7.91
7.82
7.81
7.80
7.79
7.63
7.62
7.49
7.40
7.39
7.37
7.36
7.35
7.33
PdCl$_2$(PKMONO)$_2$
^{1}H NMR (500 MHz, CDCl$_3$)
THF
11.81
11.87
11.95
6.00
18.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



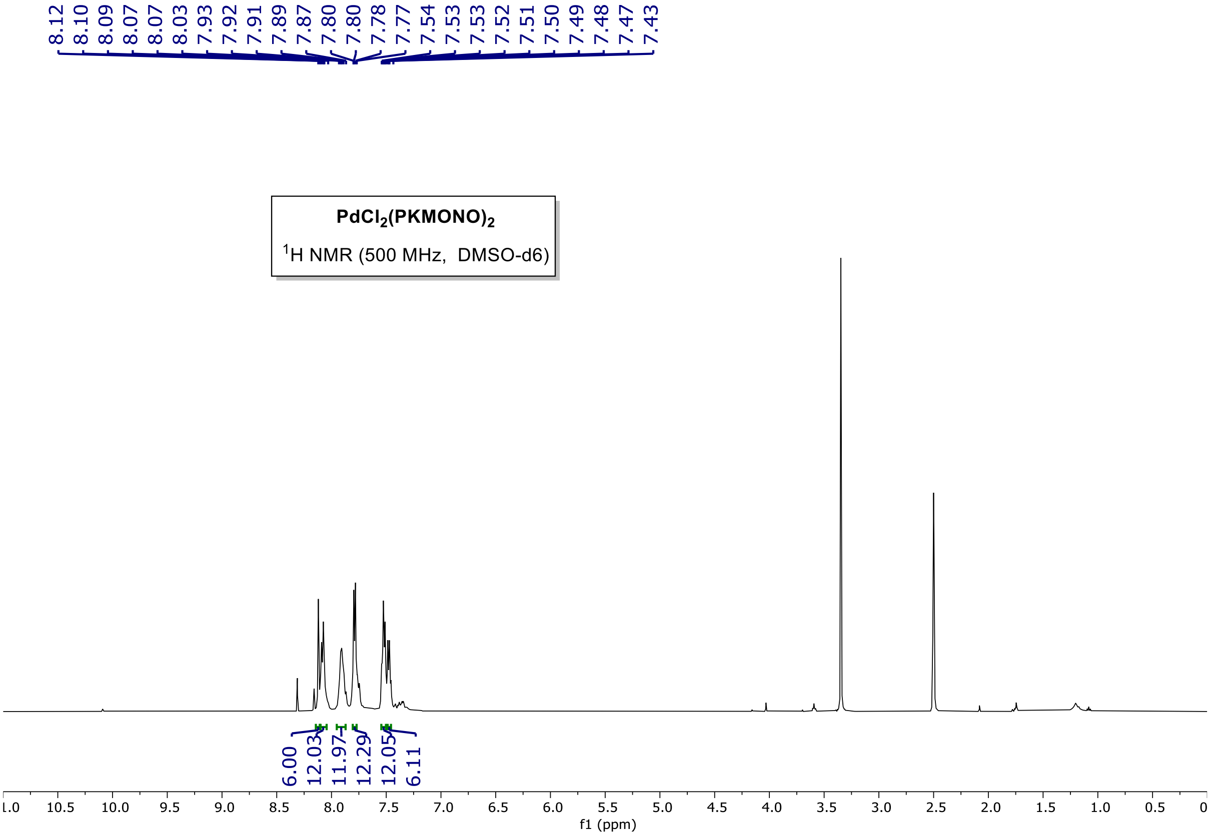
$PdCl_2(PKMONO)_2$

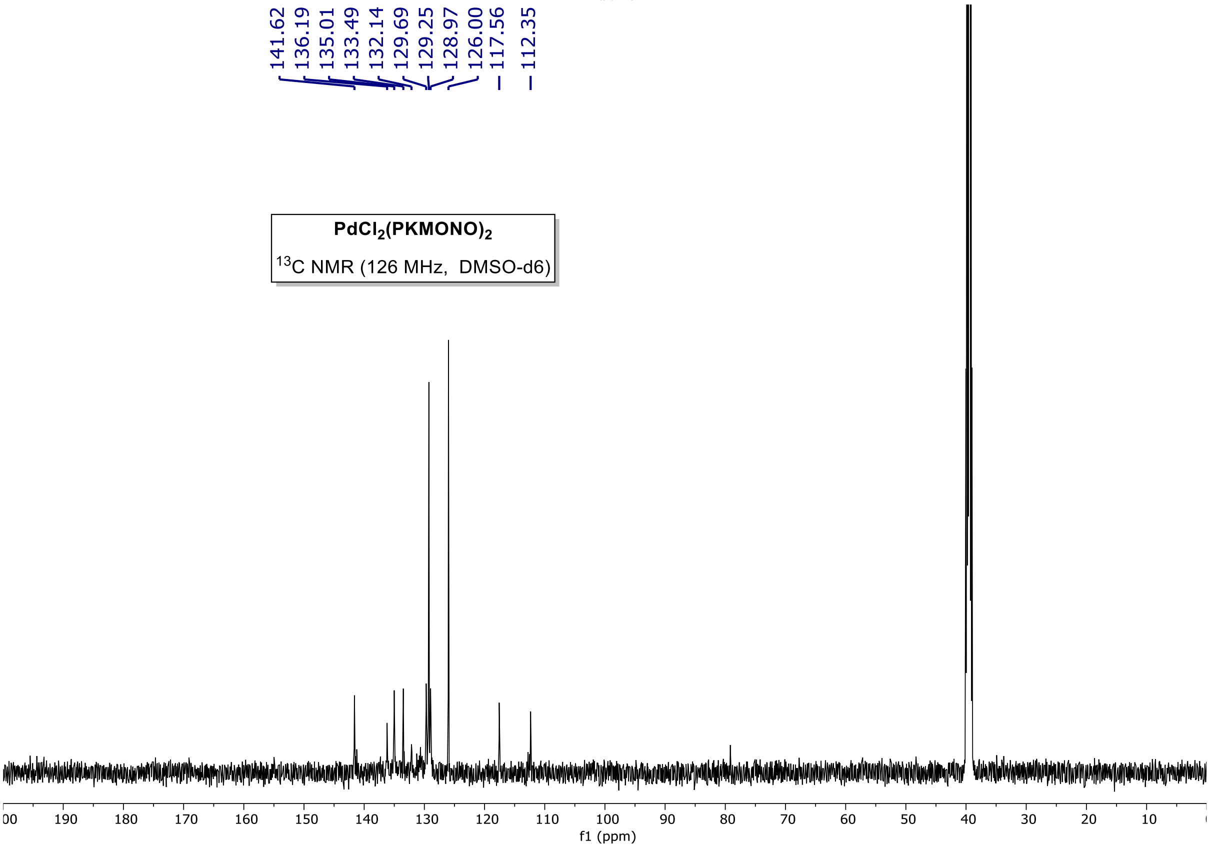
^{13}C NMR (126 MHz, $CDCl_3$)

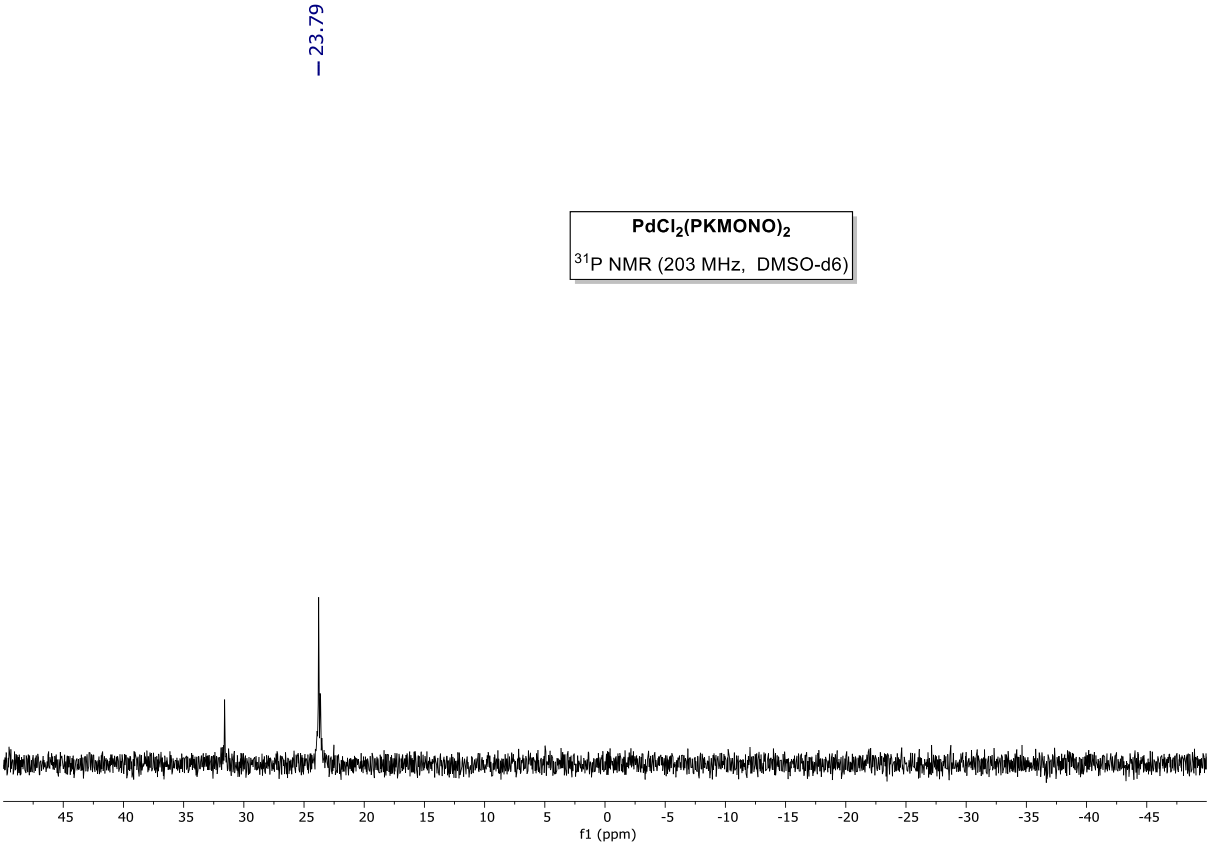


$PdCl_2(PKMONO)_2$

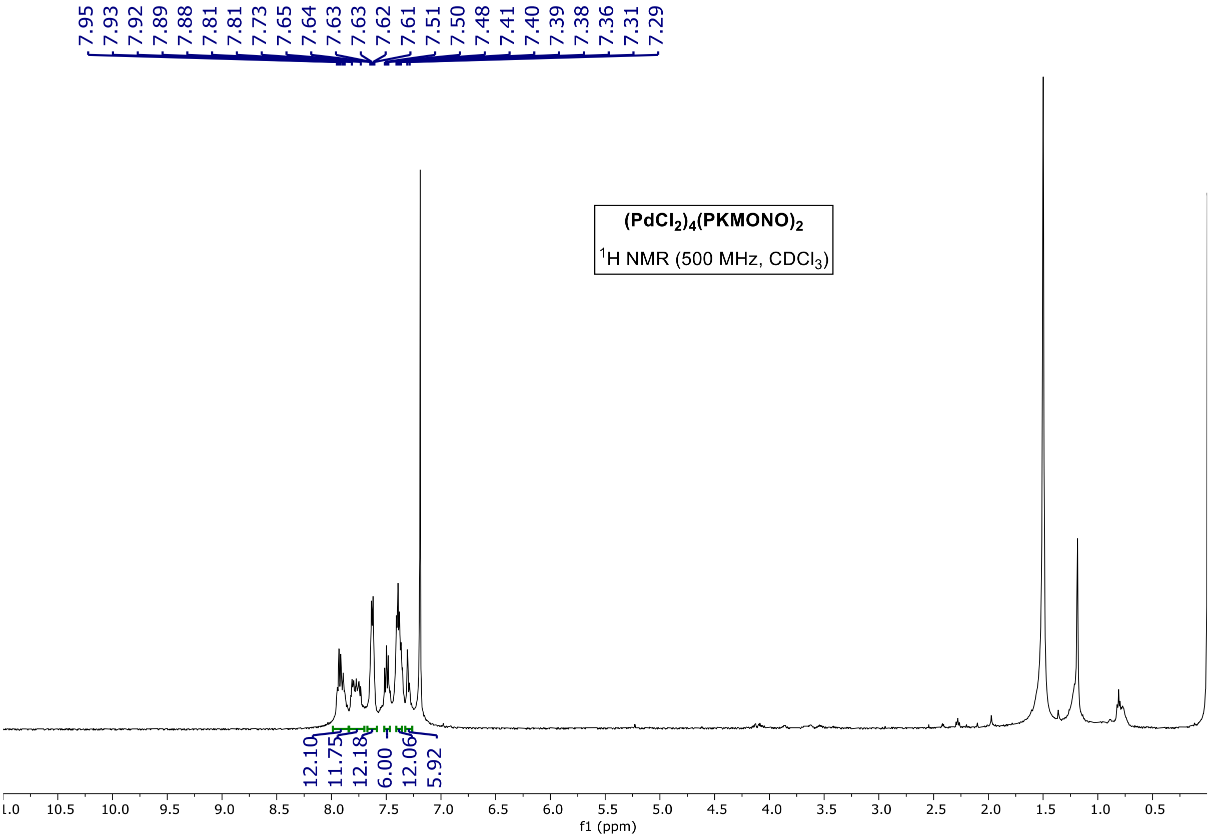
^{31}P NMR (203 MHz, $CDCl_3$)


8.12
8.10
8.09
8.07
8.07
8.03
7.93
7.92
7.91
7.89
7.87
7.80
7.80
7.78
7.77
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.43
PdCl2(PKMONO)2
1H NMR (500 MHz, DMSO-d6)
6.00
12.03
11.97
12.29
12.05
6.11
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

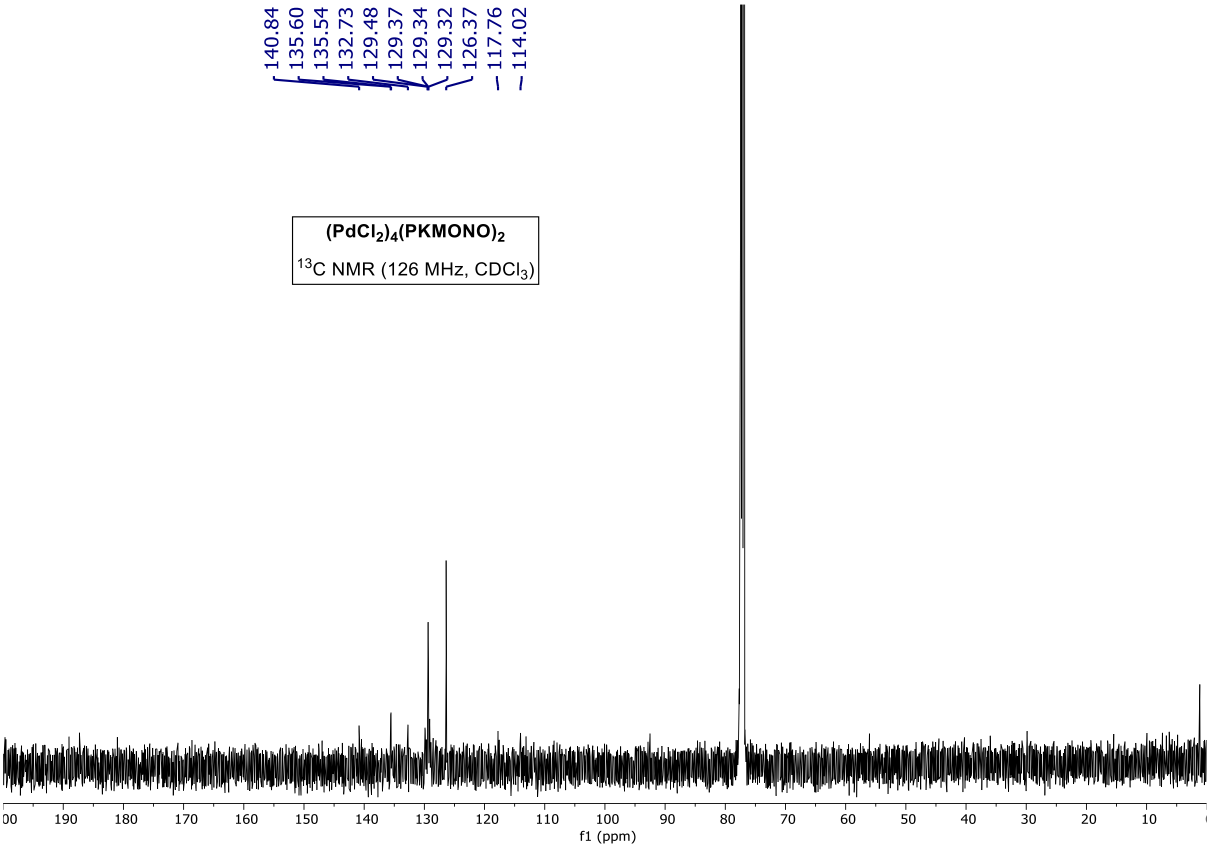

141.62
136.19
135.01
133.49
132.14
129.69
129.25
128.97
126.00
117.56
112.35
PdCl2(PKMONO)2
13C NMR (126 MHz, DMSO-d6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

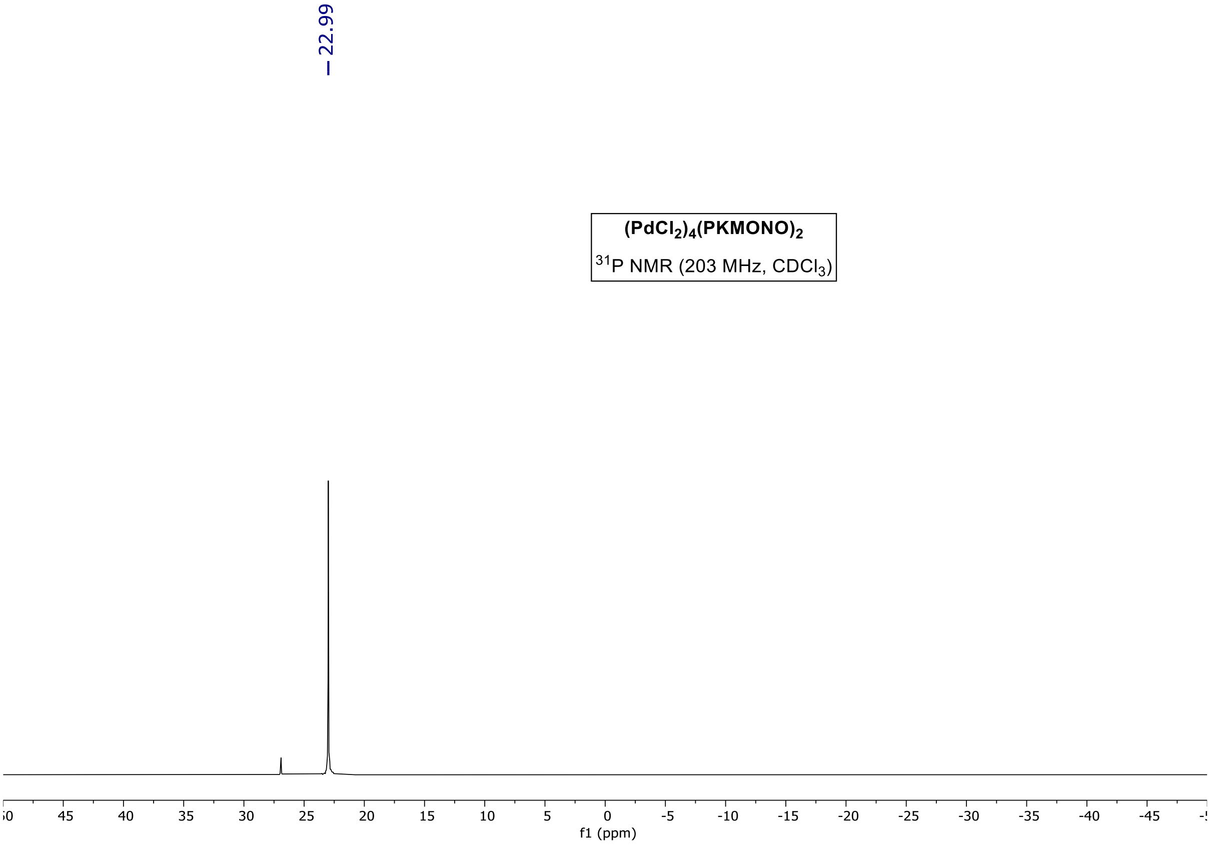

$PdCl_2(PKMONO)_2$

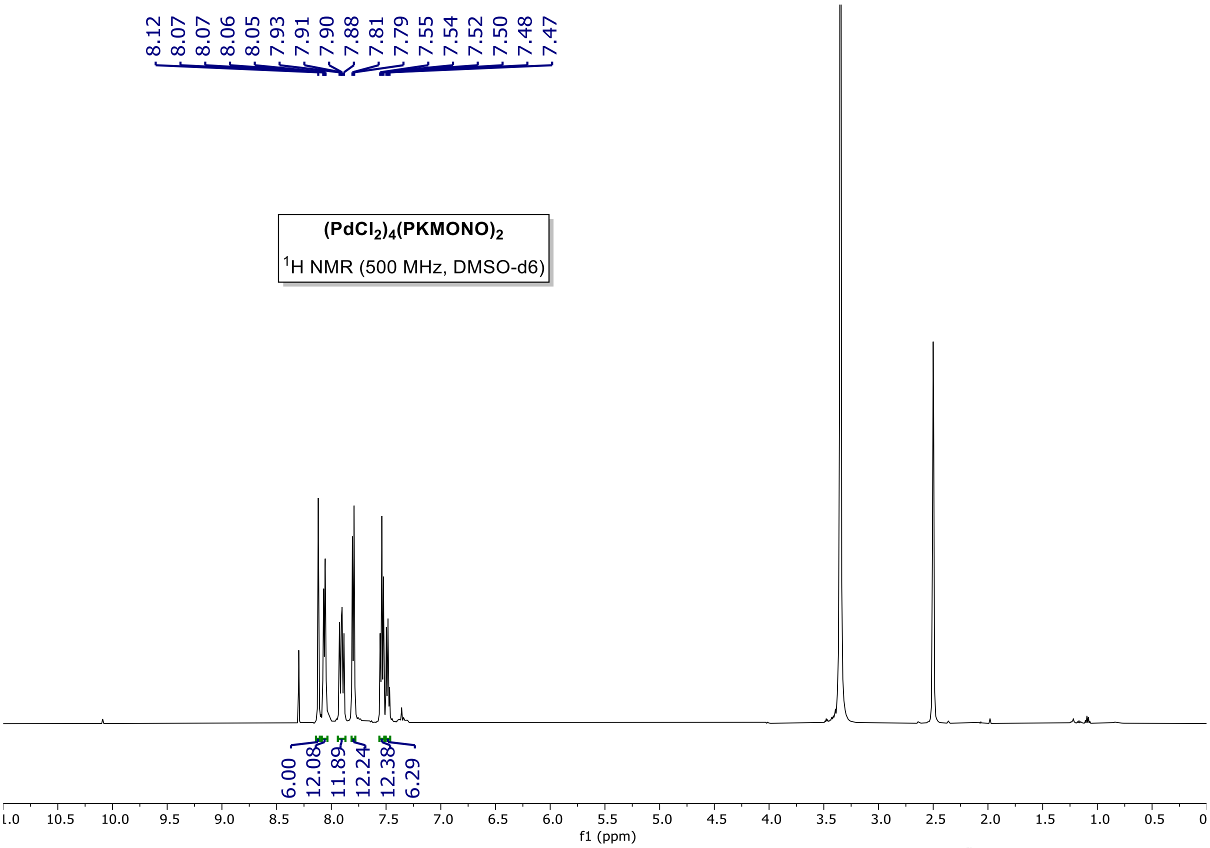
^{31}P NMR (203 MHz, DMSO-d6)


$(PdCl_2)_4(PKMONO)_2$

^1H NMR (500 MHz, $CDCl_3$)

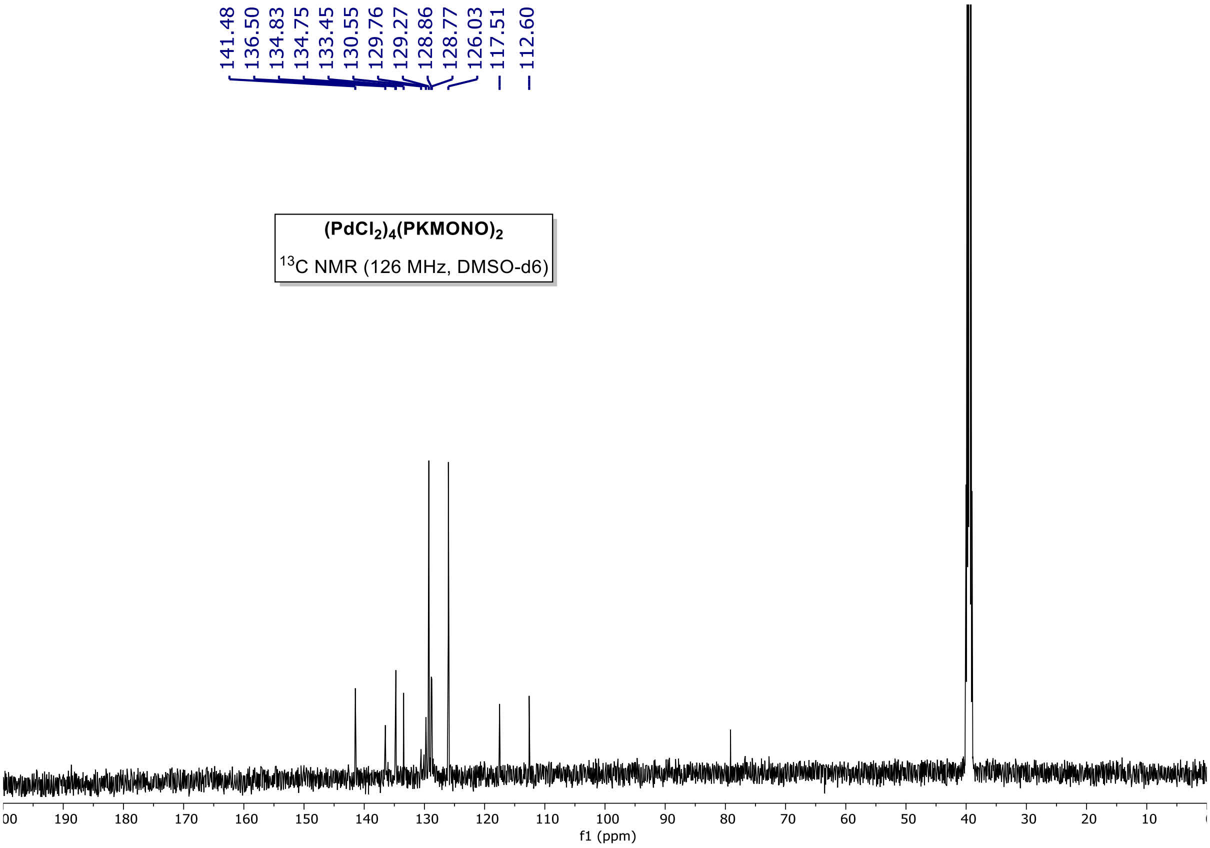

140.84
135.60
135.54
132.73
129.48
129.37
129.34
129.32
126.37
117.76
114.02
(PdCl2)4(PKMONO)2
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


22.99
(PdCl2)4(PKMONO)2
31P NMR (203 MHz, CDCl3)
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)



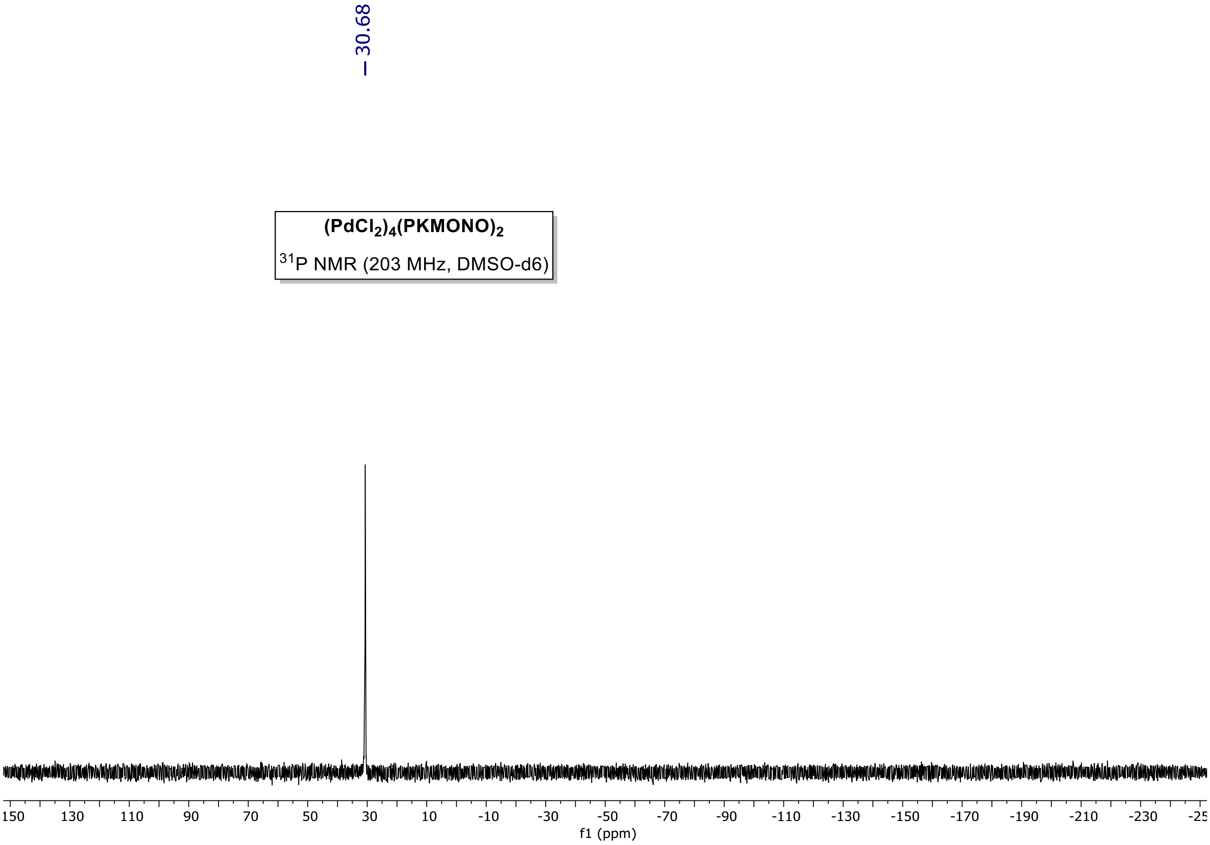
$(PdCl_2)_4(PKMONO)_2$

^1H NMR (500 MHz, DMSO-d6)



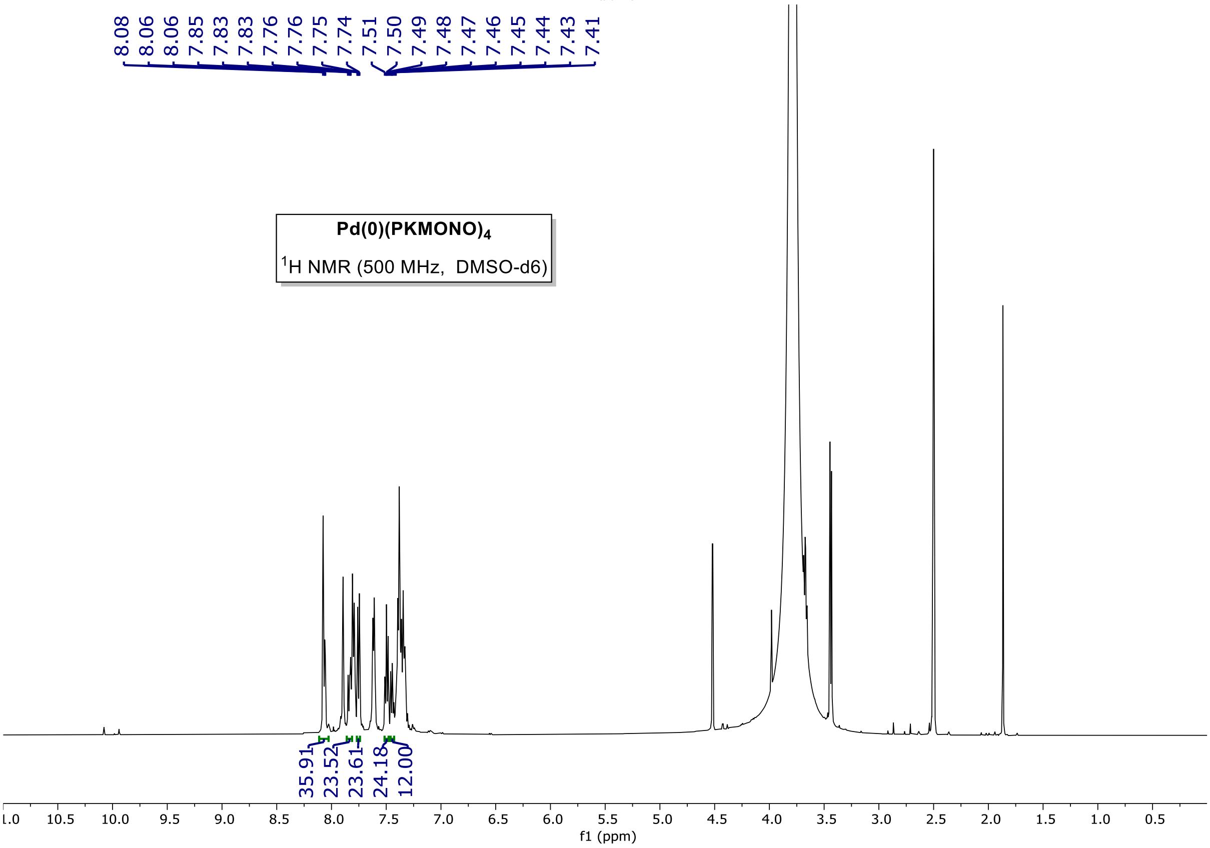
$(PdCl_2)_4(PKMONO)_2$

^{13}C NMR (126 MHz, DMSO-d6)



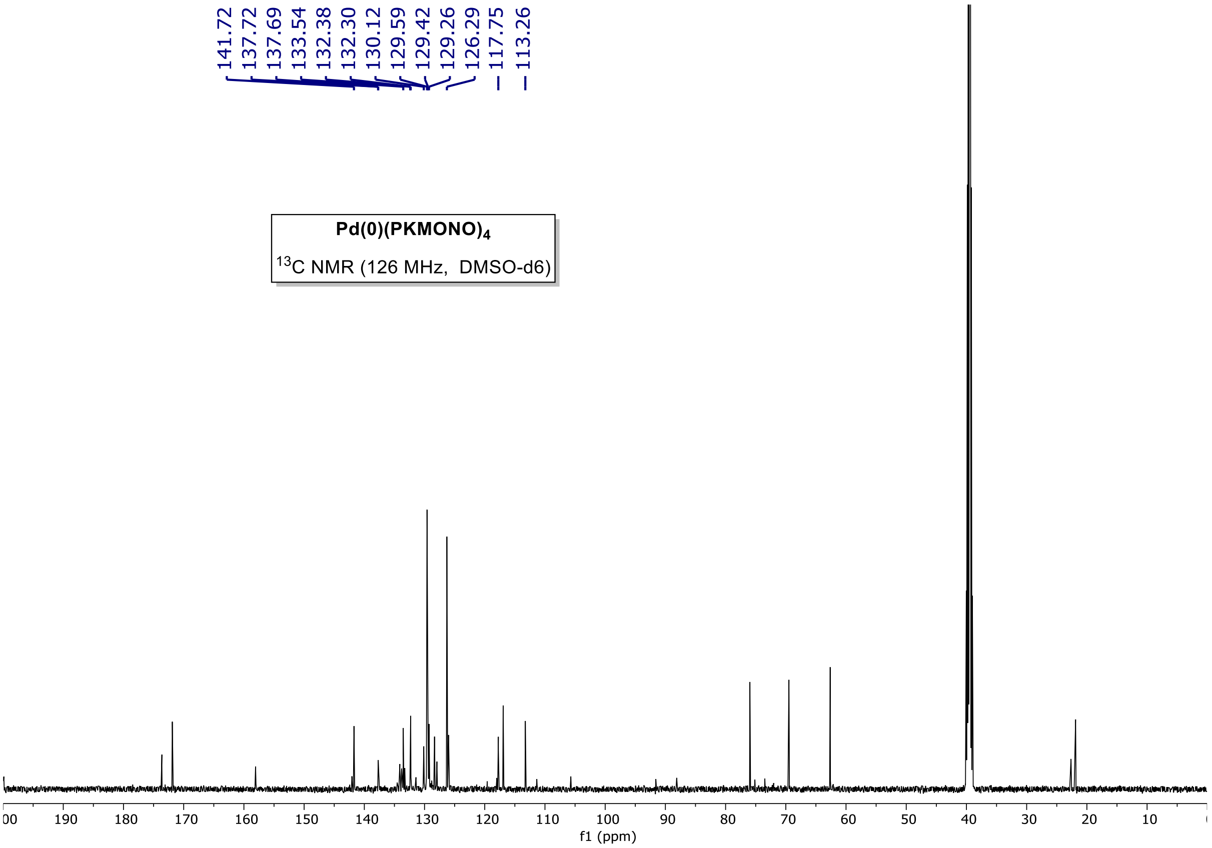
$(PdCl_2)_4(PKMONO)_2$

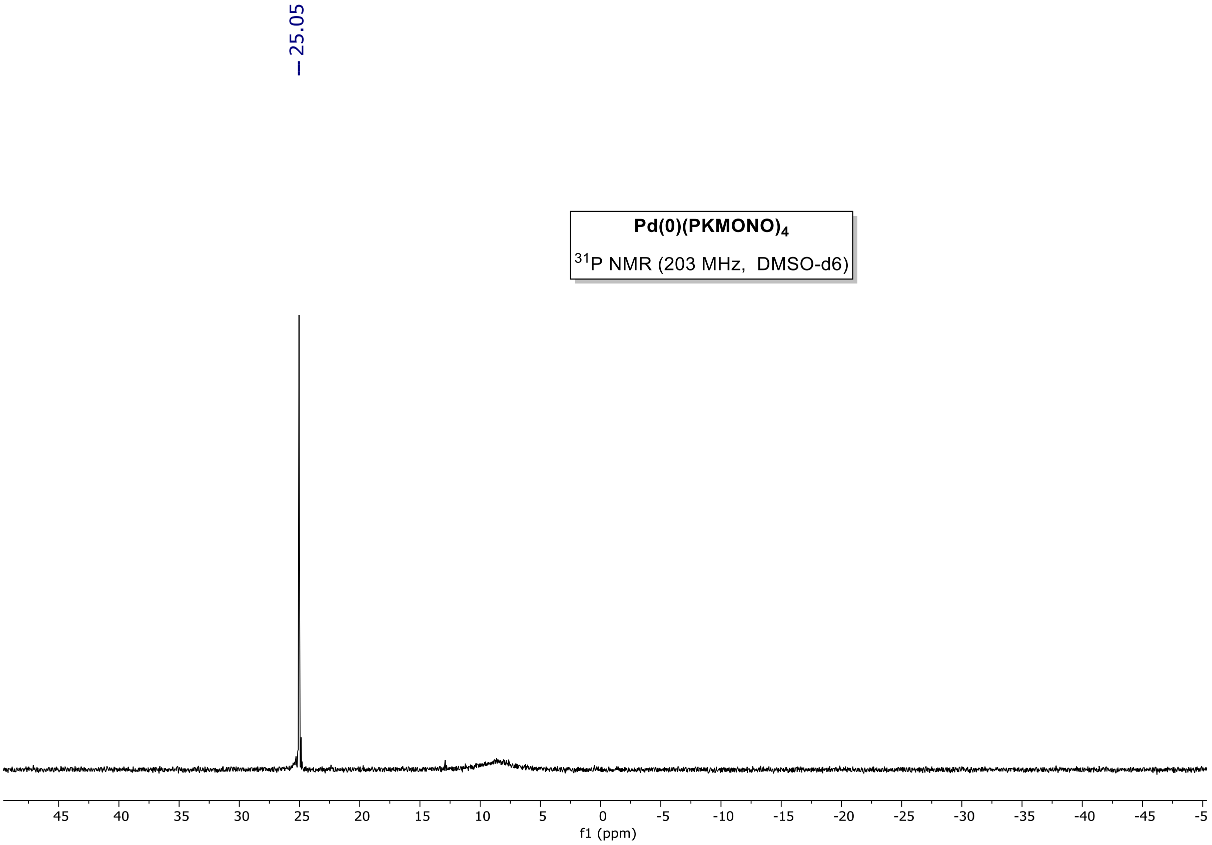
^{31}P NMR (203 MHz, DMSO-d6)

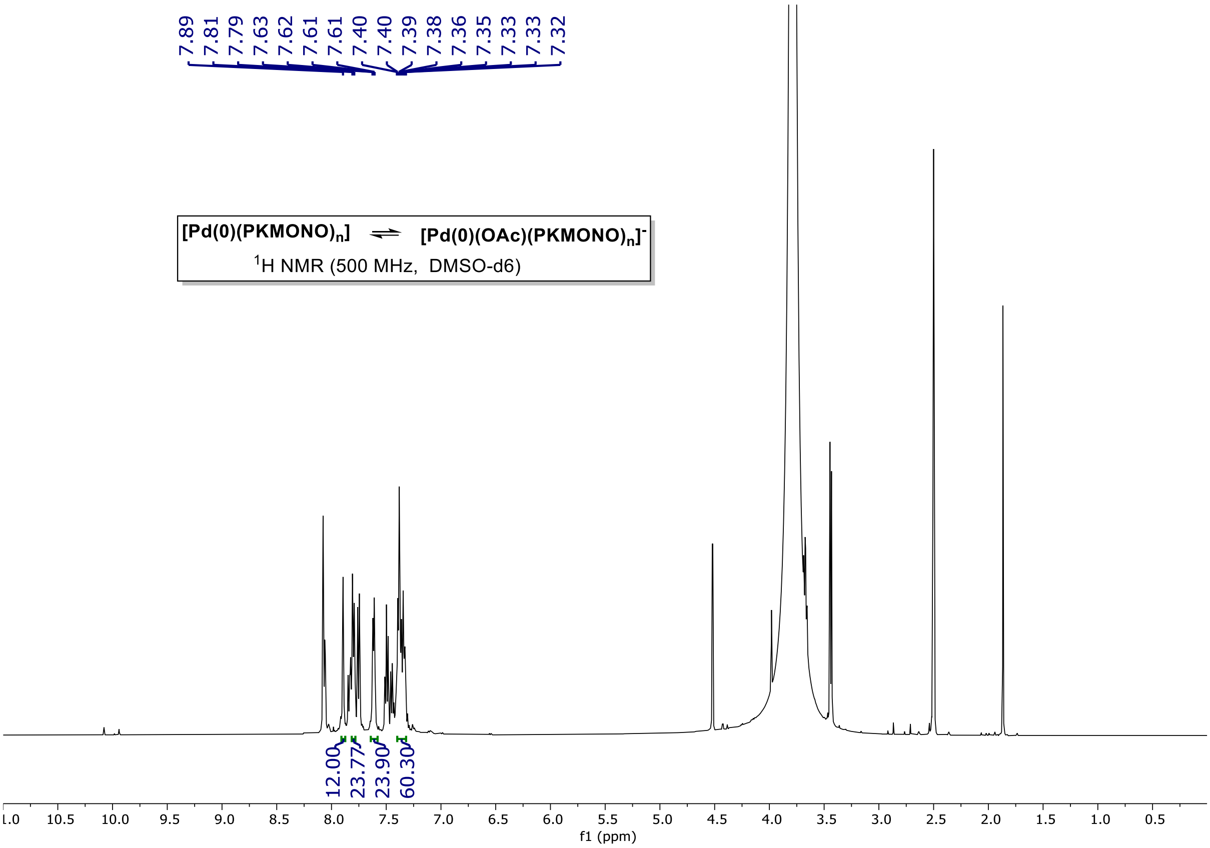


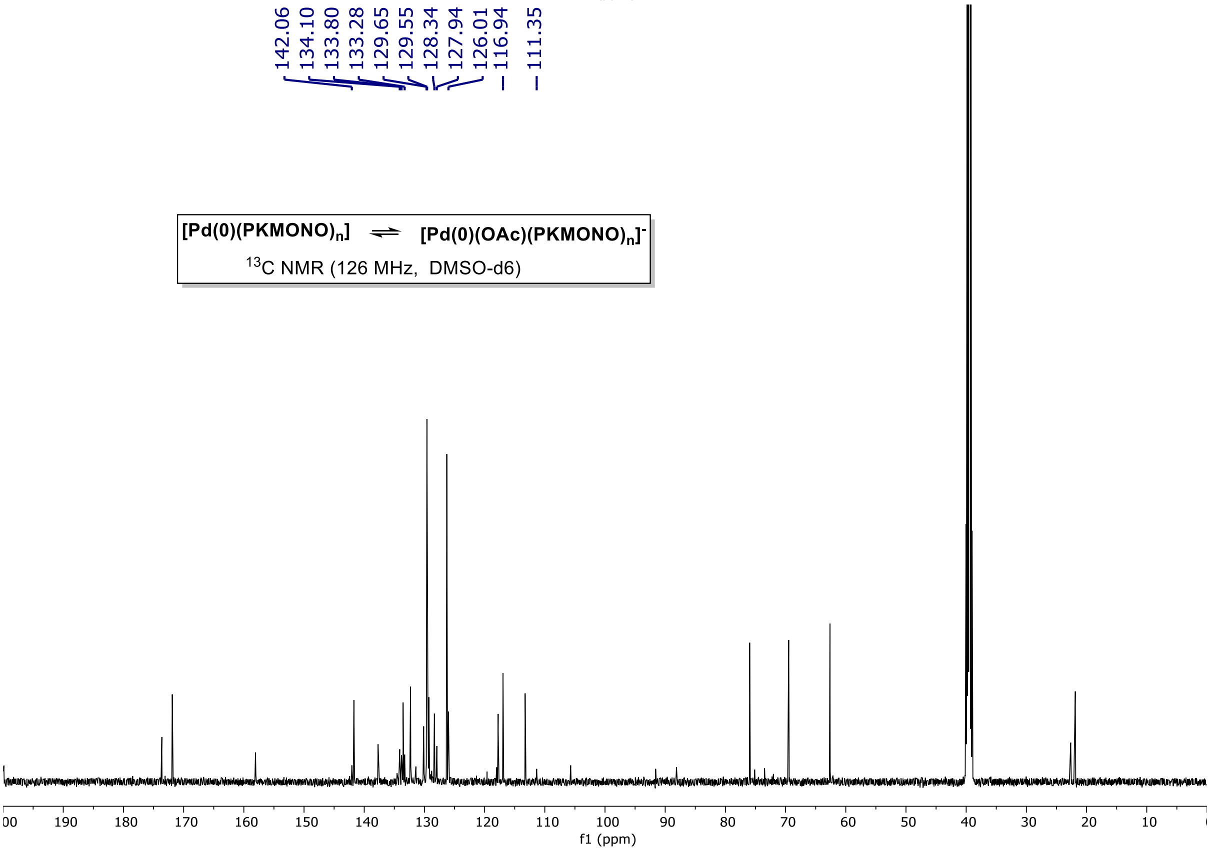
$Pd(0)(PKMONO)_4$

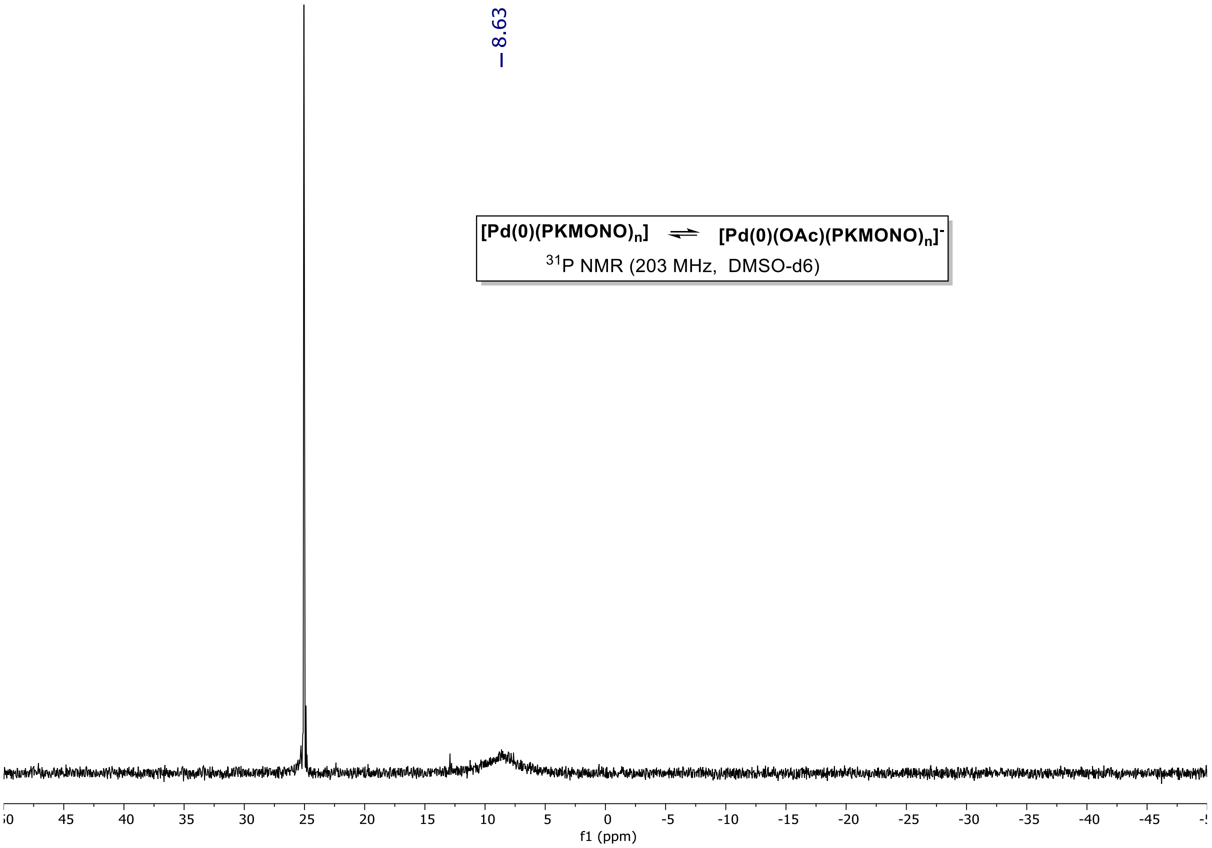
^1H NMR (500 MHz, DMSO-d6)


141.72
137.72
137.69
133.54
132.38
132.30
130.12
129.59
129.42
129.26
126.29
117.75
113.26
Pd(0)(PKMONO)$_4$
^{13}C NMR (126 MHz, DMSO-d6)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


25.05
Pd(0)(PKMONO)$_4$
^{31}P NMR (203 MHz, DMSO-d6)
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-5
f1 (ppm)

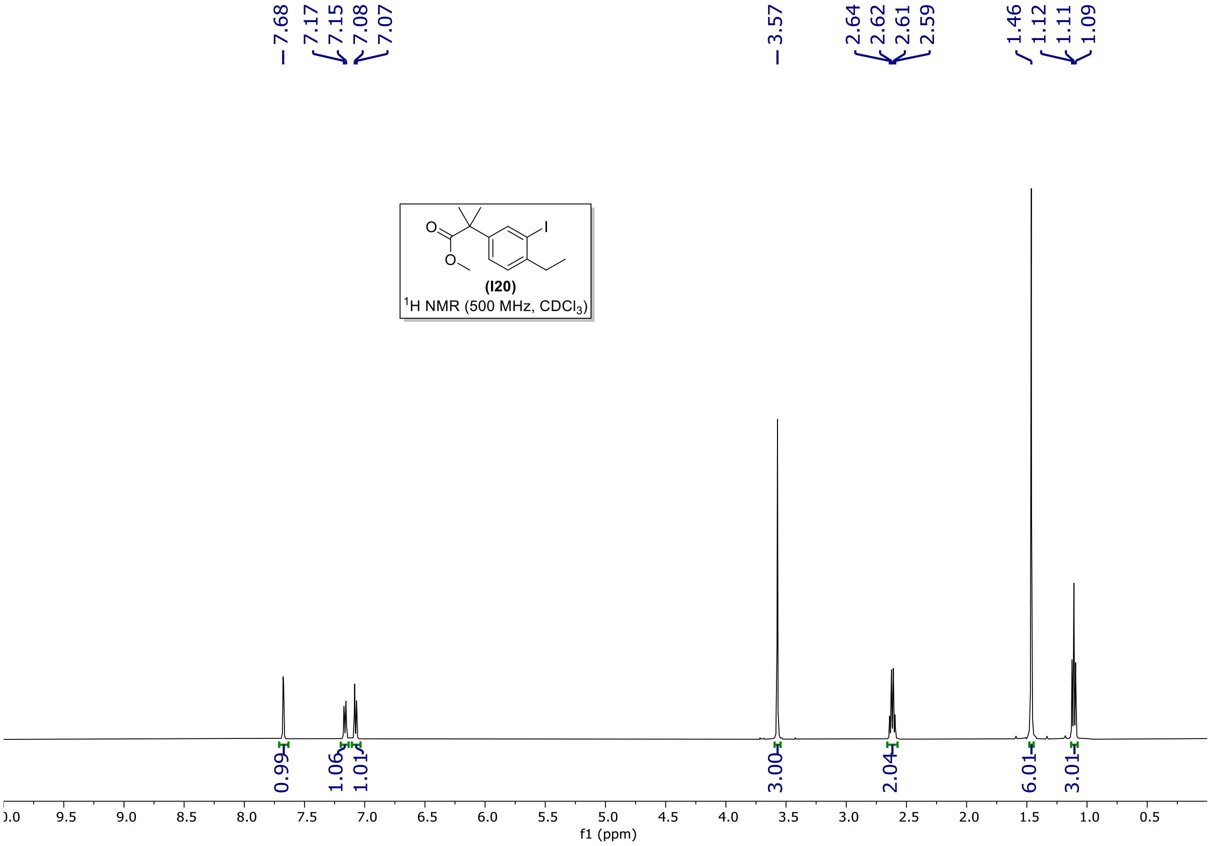

7.89
7.81
7.79
7.63
7.62
7.61
7.61
7.40
7.40
7.39
7.38
7.36
7.35
7.33
7.33
7.32
[Pd(0)(PKMONO)n] ⇌ [Pd(0)(OAc)(PKMONO)n]-
1H NMR (500 MHz, DMSO-d6)
12.00
23.77
23.90
60.30
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


142.06
134.10
133.80
133.28
129.65
129.55
128.34
127.94
126.01
116.94
111.35
[Pd(0)(PKMONO)n] ⇌ [Pd(0)(OAc)(PKMONO)n]-
13C NMR (126 MHz, DMSO-d6)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



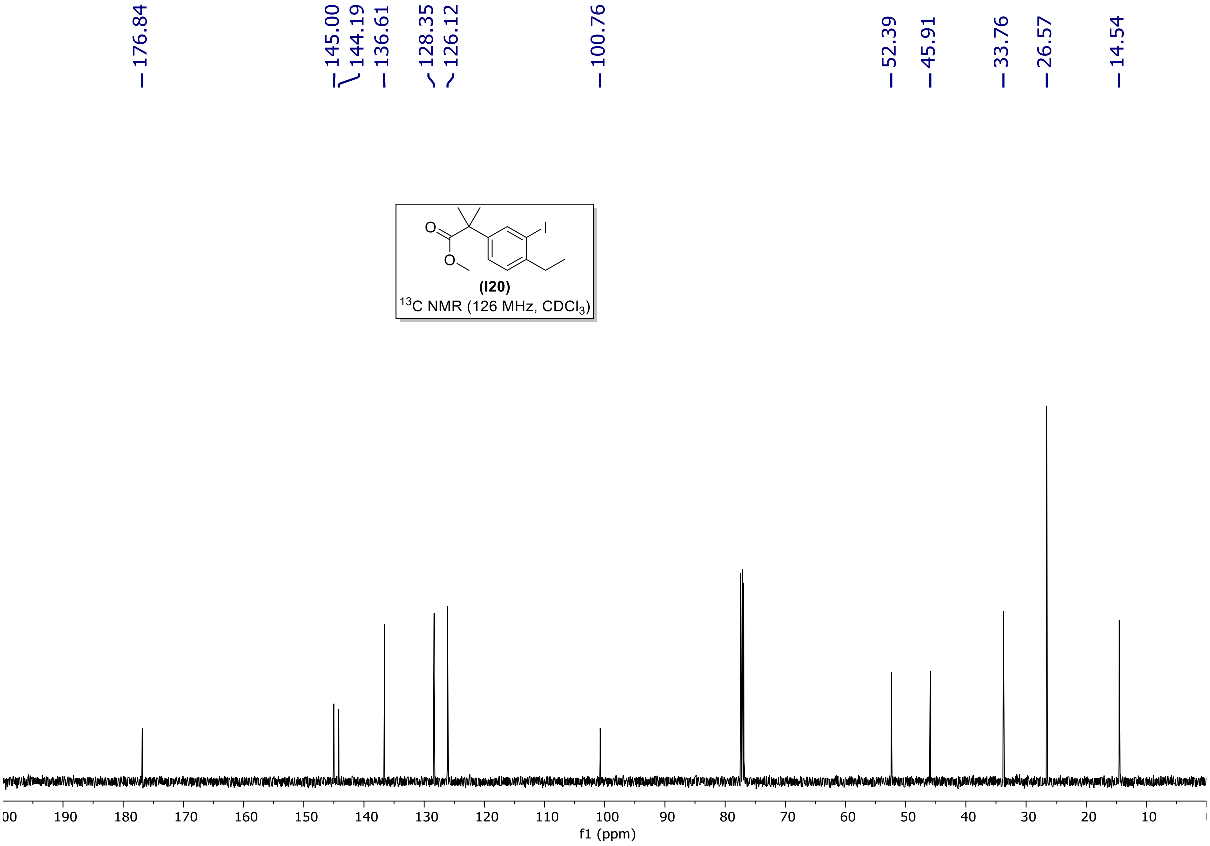
[Pd(0)(PKMONO)$_n$] ⇌ [Pd(0)(OAc)(PKMONO)$_n$]$^-$

^{31}P NMR (203 MHz, DMSO-d6)



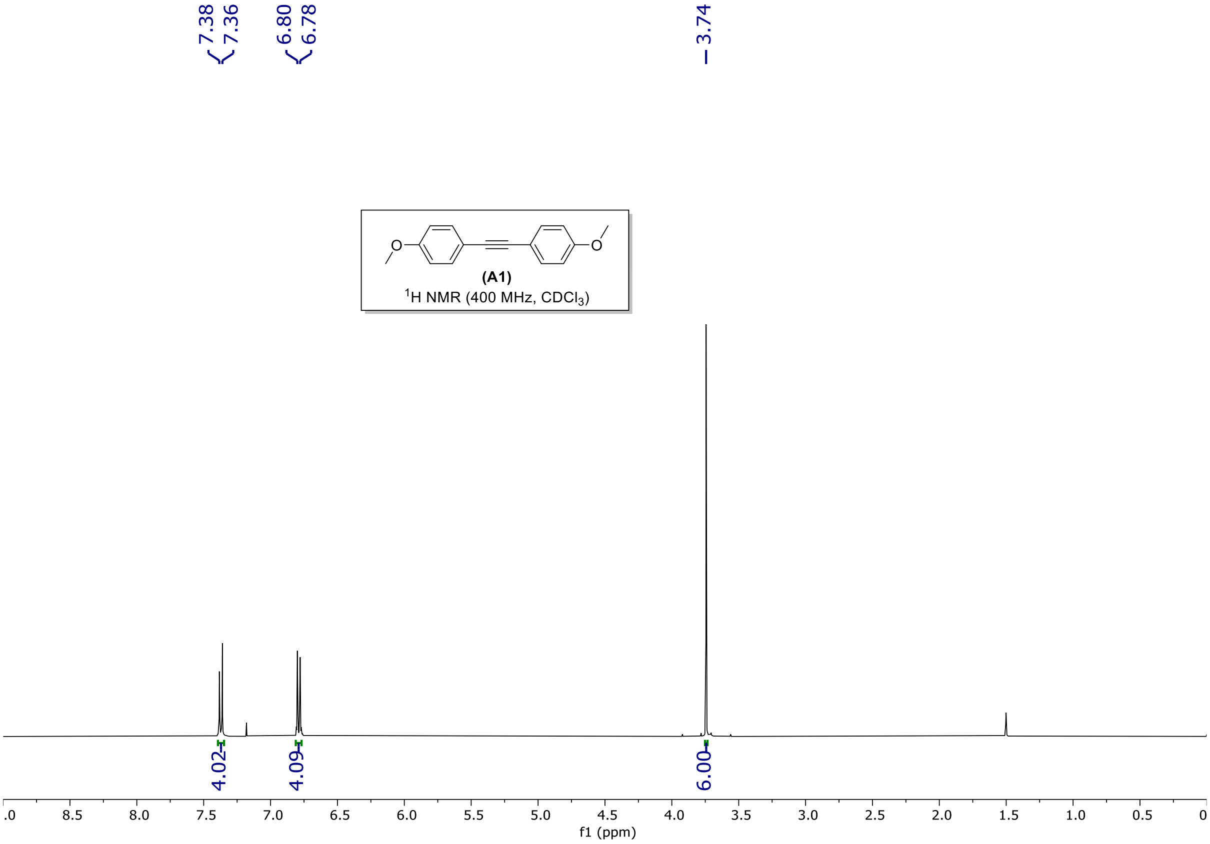
(I20)

^{1}H NMR (500 MHz, CDCl$_3$)



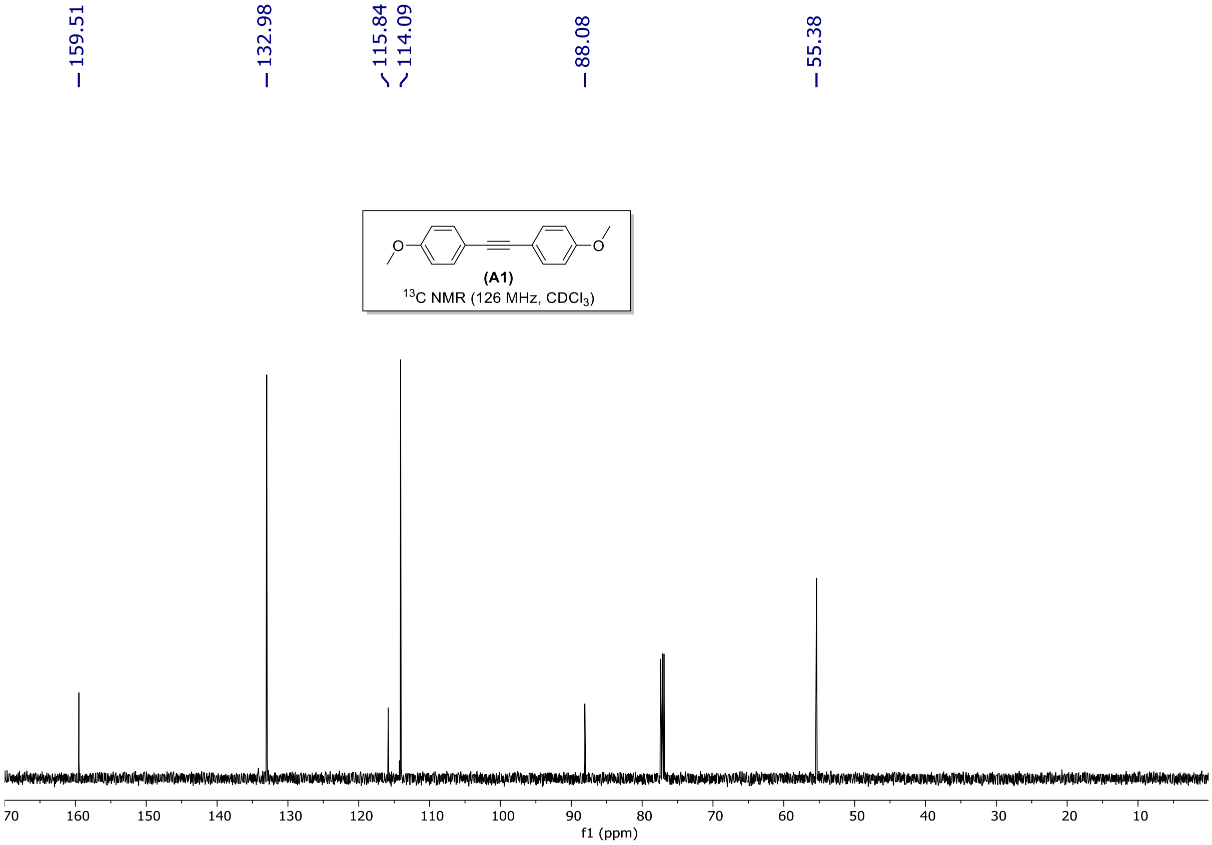
(I20)

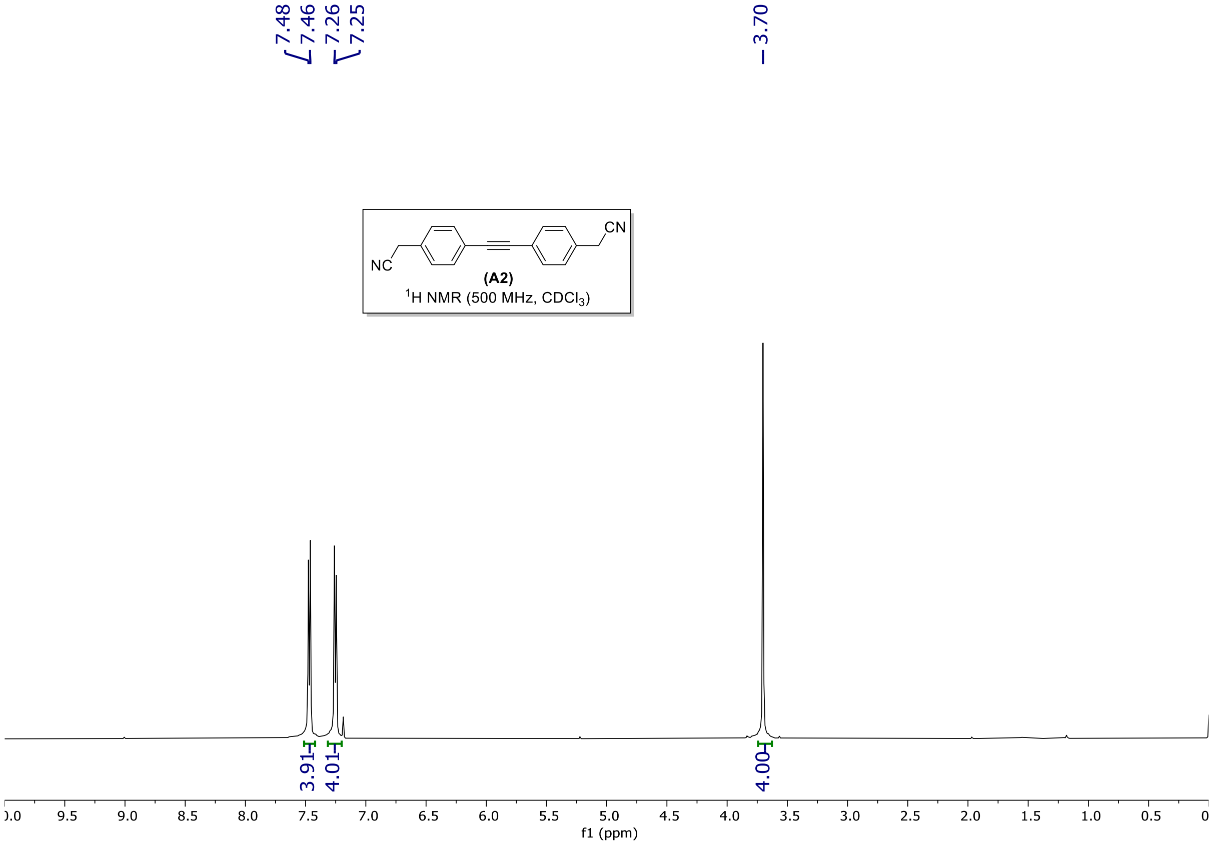
^{13}C NMR (126 MHz, CDCl$_3$)

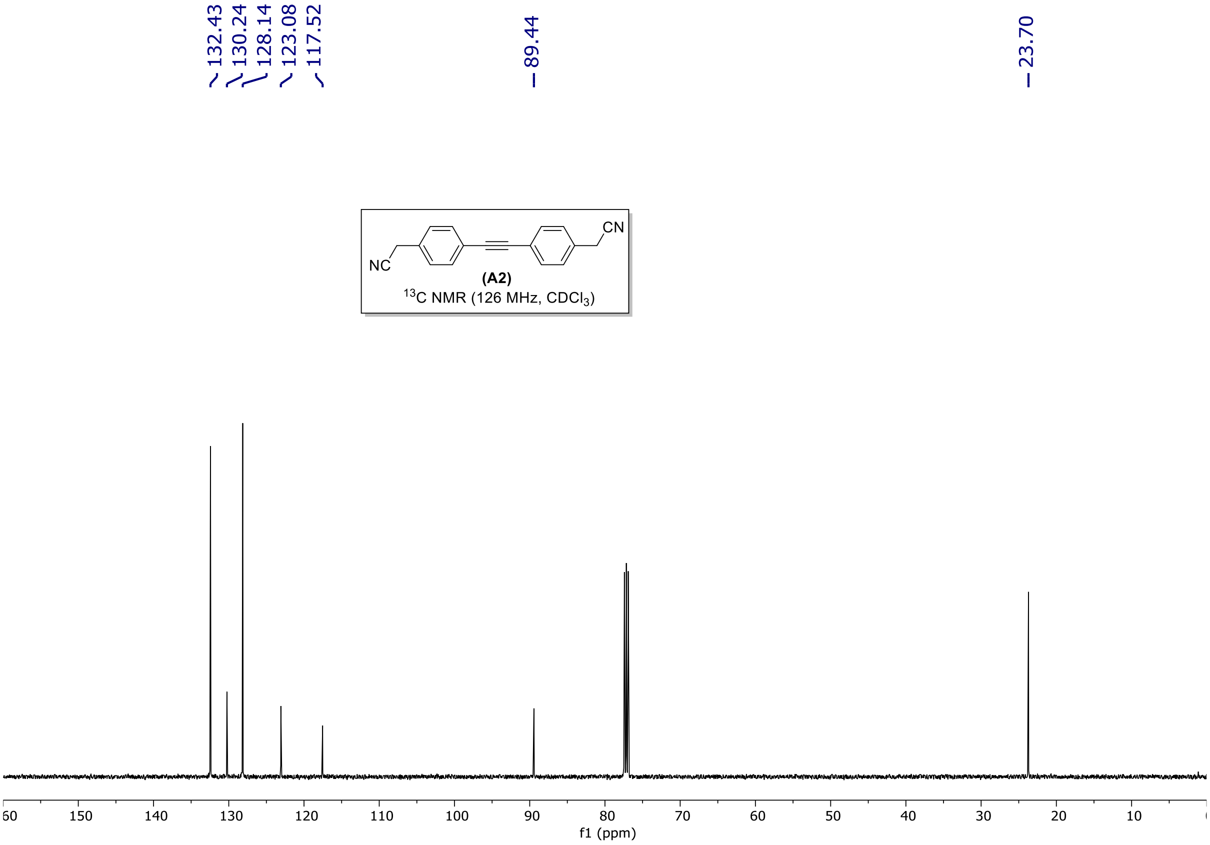


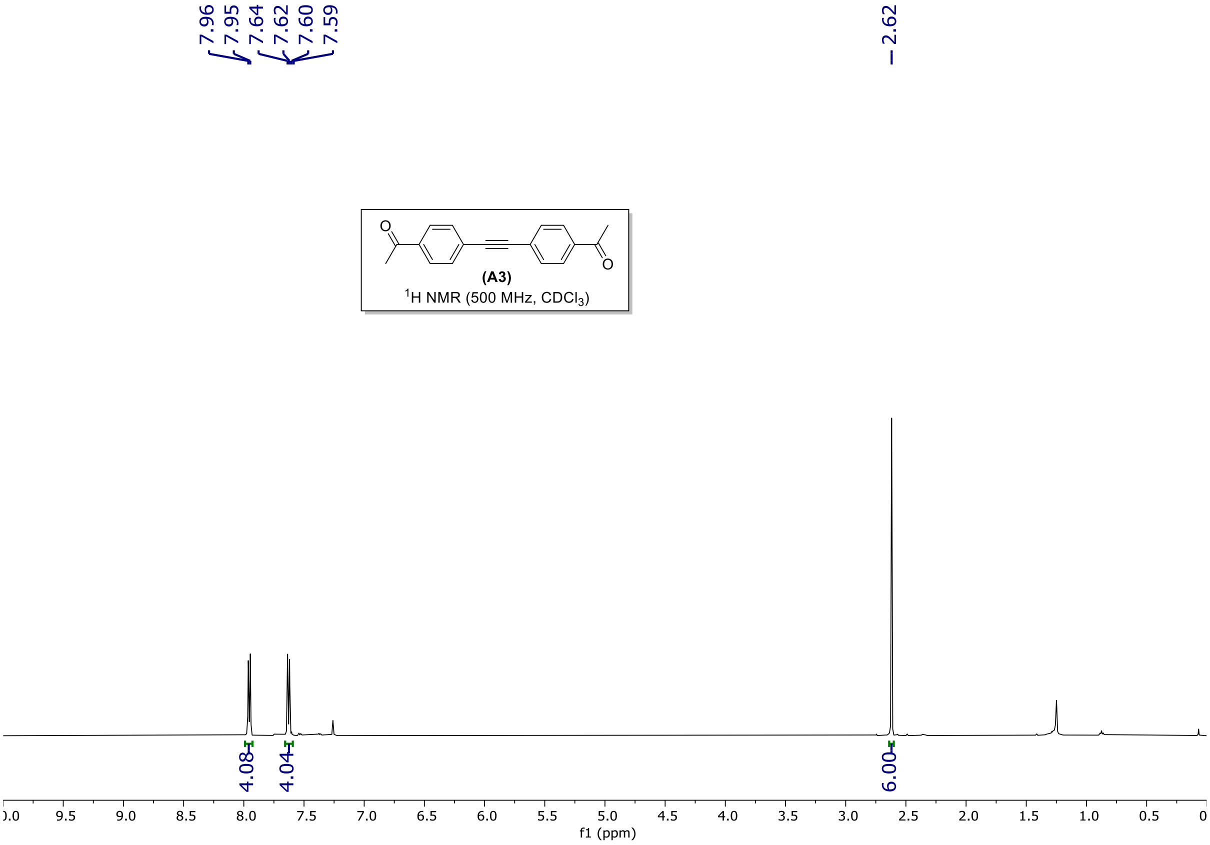
(A1)

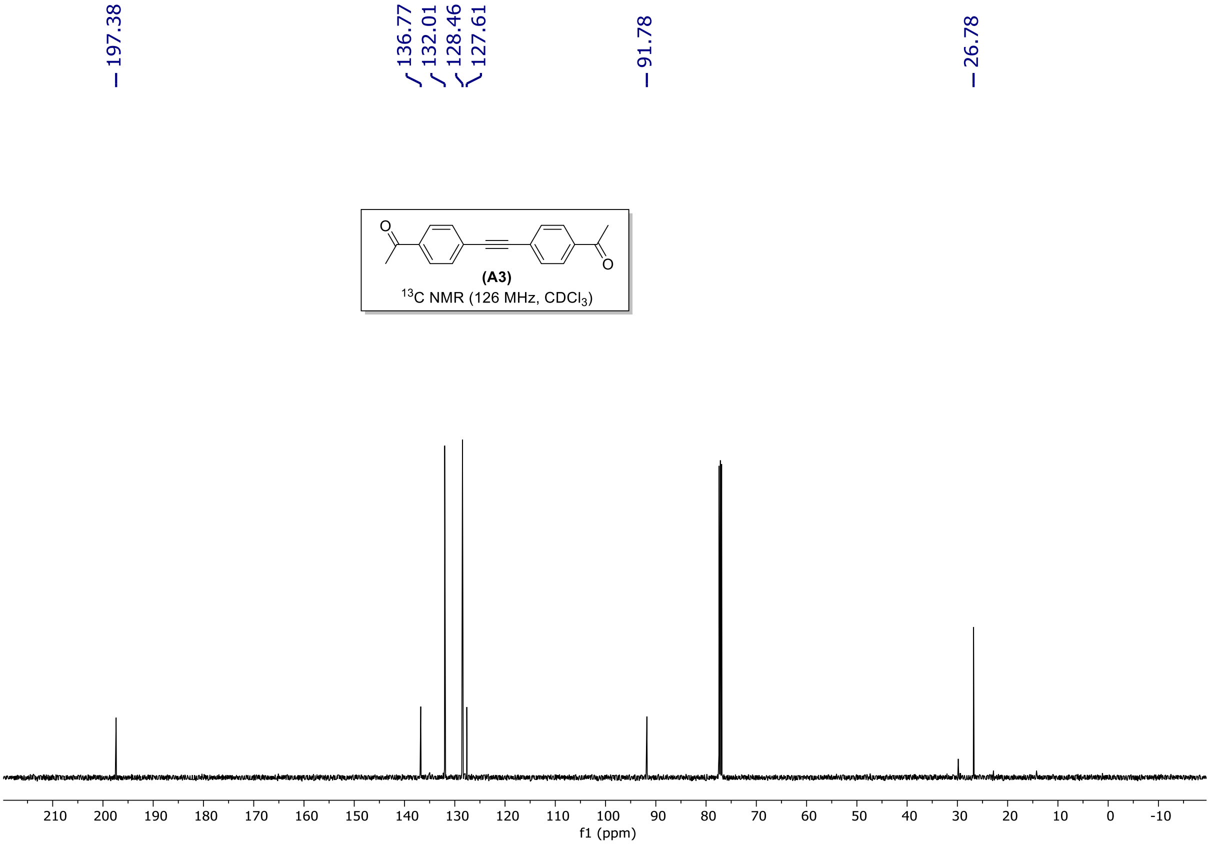
^{1}H NMR (400 MHz, CDCl$_3$)


159.51
132.98
115.84
114.09
88.08
55.38
(A1)
13C NMR (126 MHz, CDCl3)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

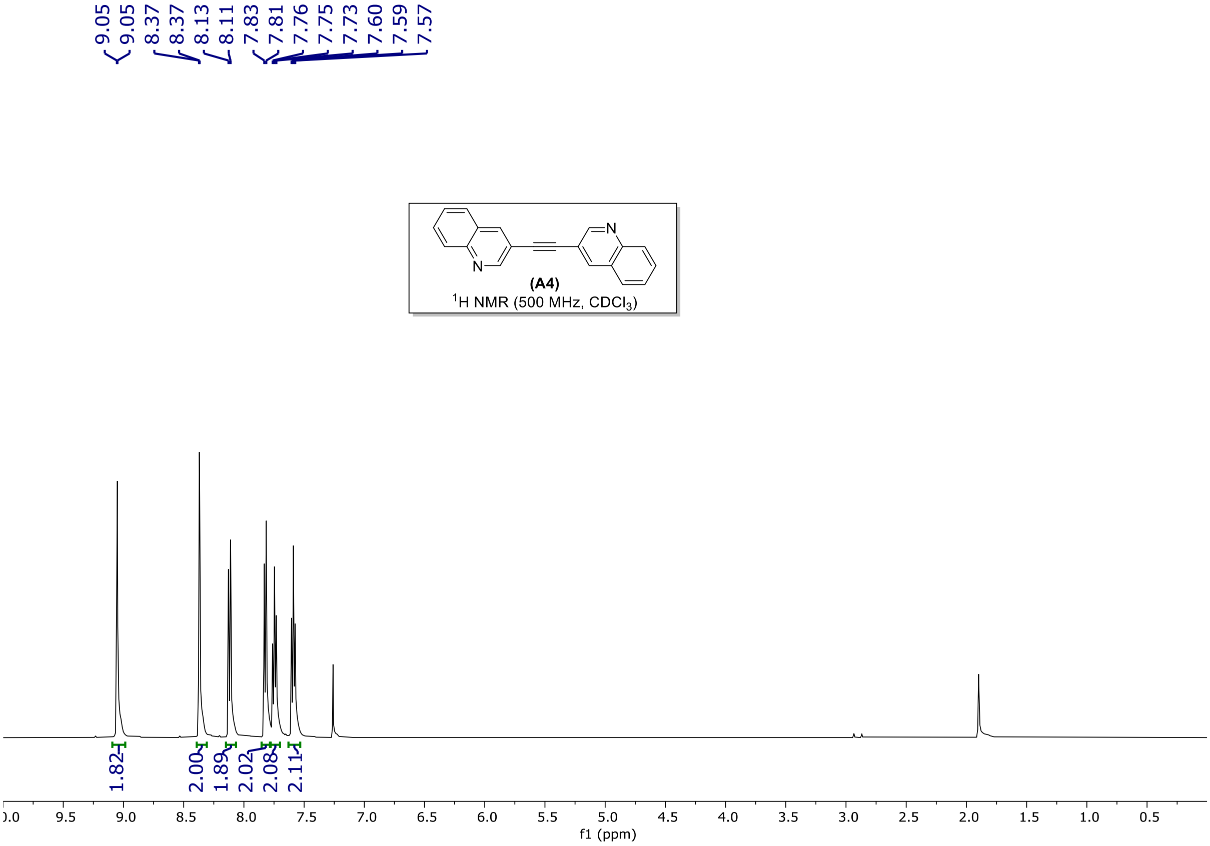

7.48
7.46
7.26
7.25
3.70
CN
NC
(A2)
1H NMR (500 MHz, CDCl3)
3.91
4.01
4.00
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


132.43
130.24
128.14
123.08
117.52
89.44
23.70
NC
CN
(A2)
^{13}C NMR (126 MHz, CDCl$_3$)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

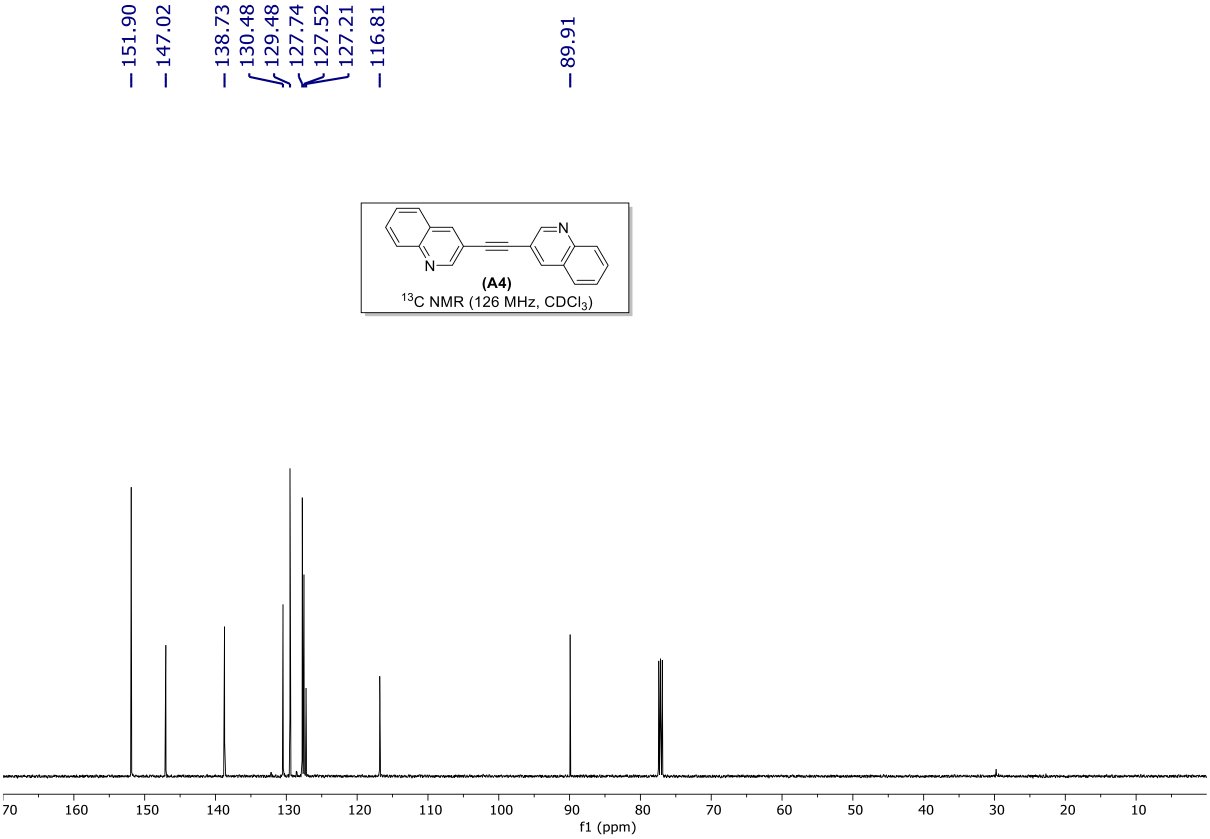

7.96
7.95
7.64
7.62
7.60
7.59
2.62
O
O
(A3)
^{1}H NMR (500 MHz, CDCl$_3$)
4.08
4.04
6.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

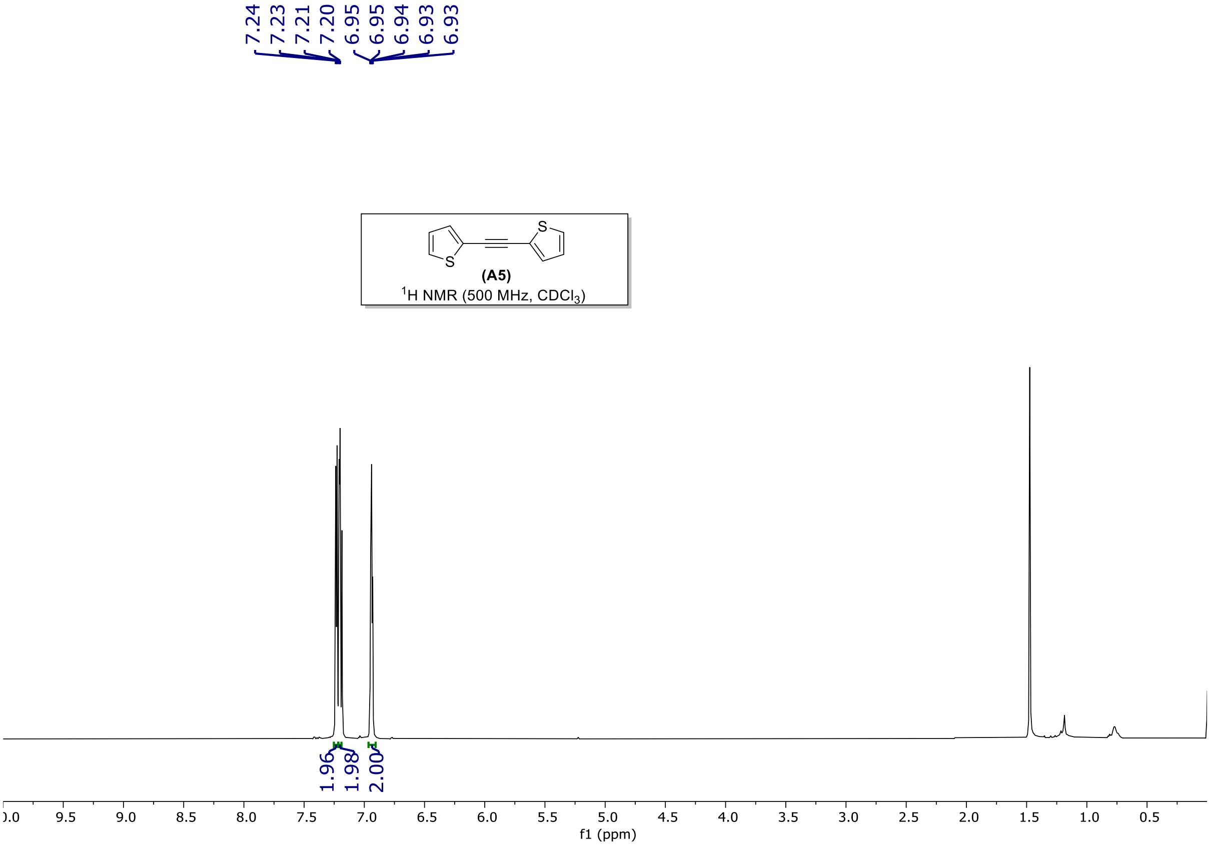

(A3)

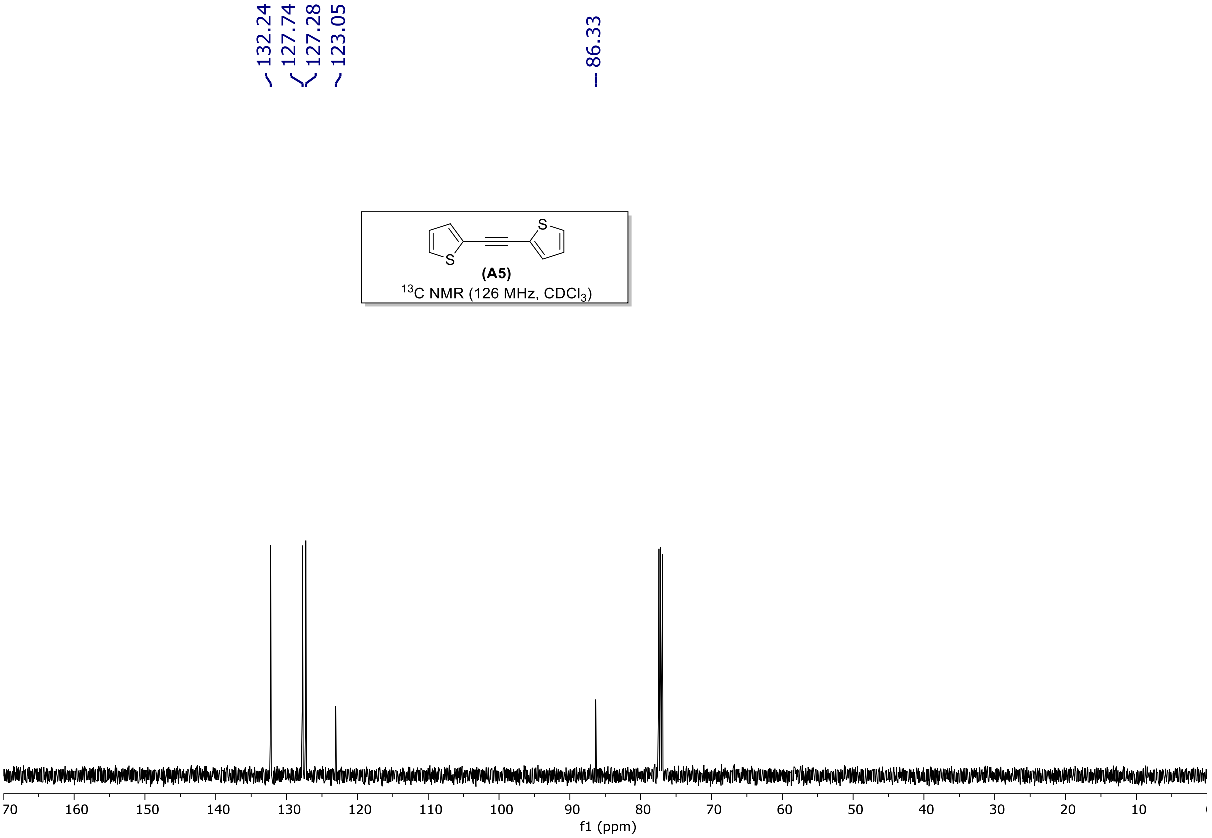
^{13}C NMR (126 MHz, CDCl$_3$)


(A4)

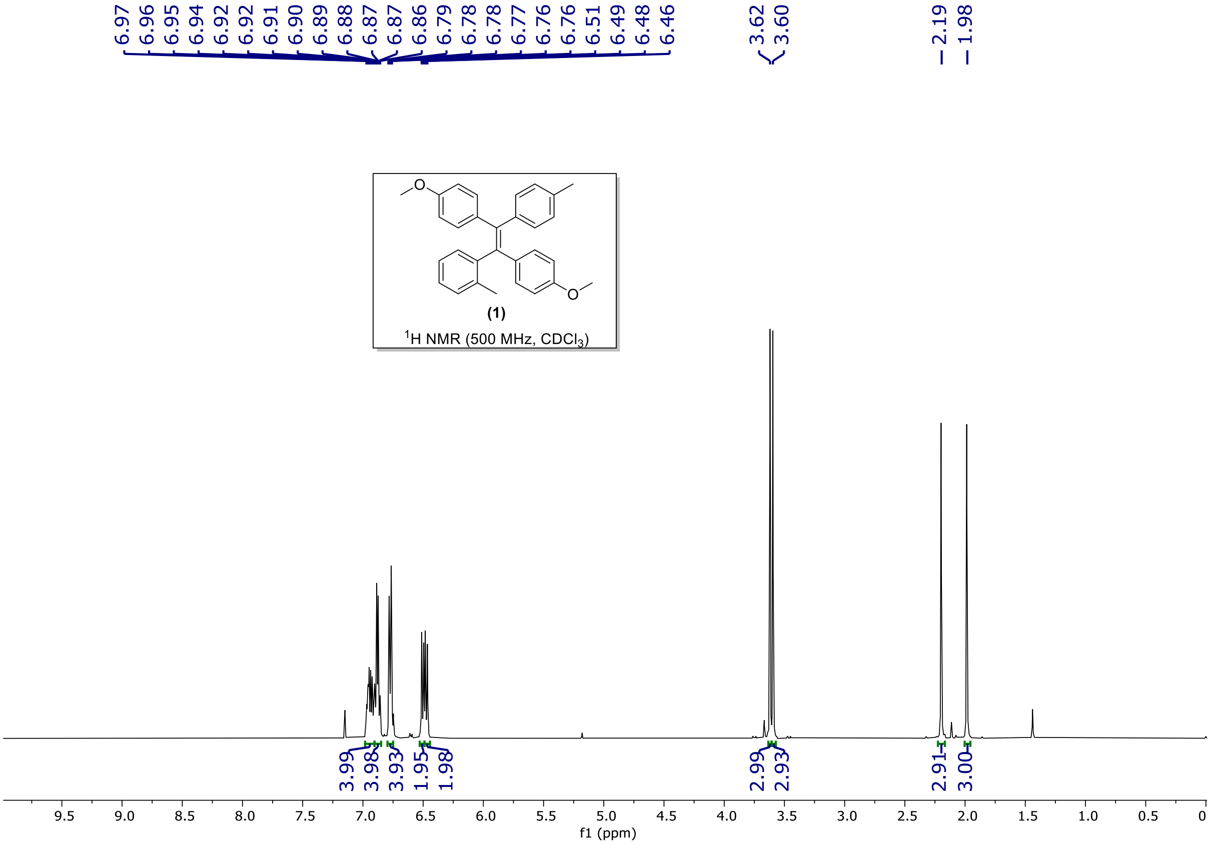
^{1}H NMR (500 MHz, CDCl$_3$)

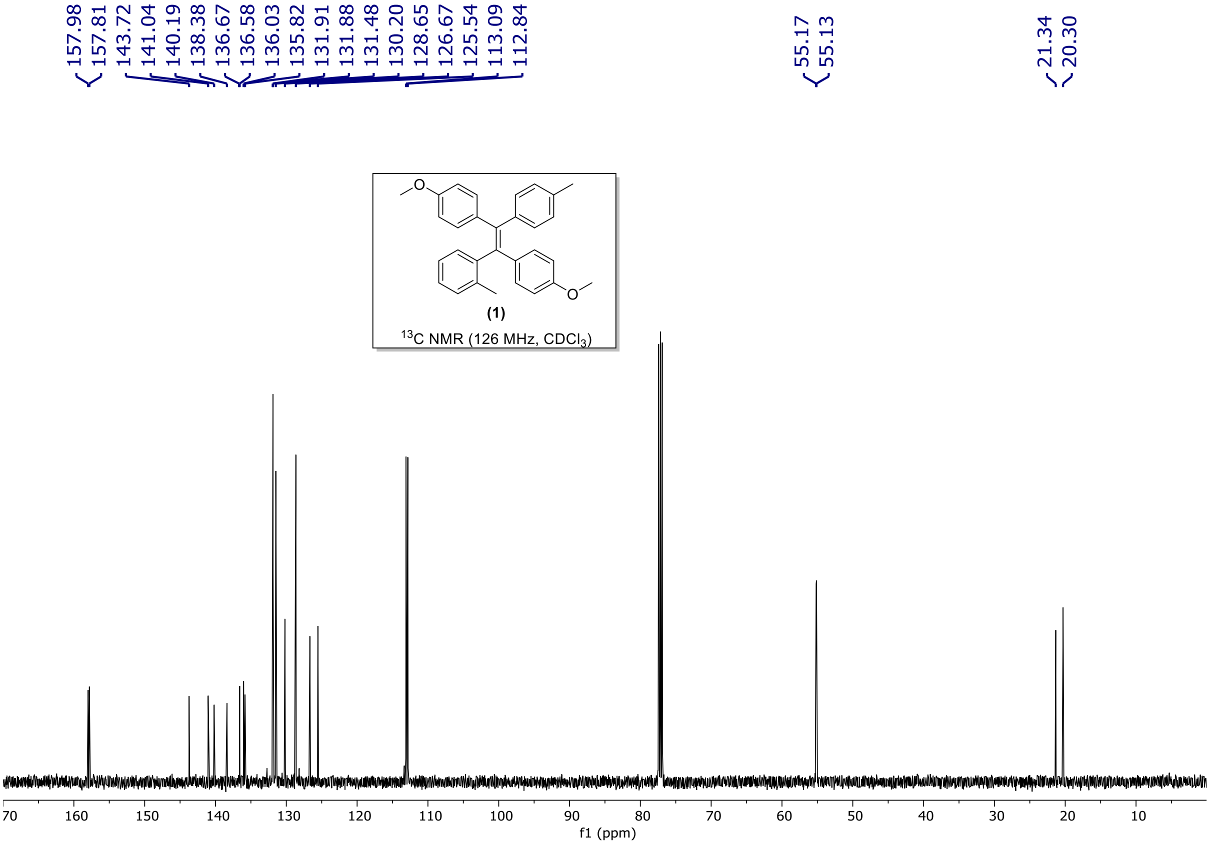

151.90
147.02
138.73
130.48
129.48
127.74
127.52
127.21
116.81
89.91
N
N
(A4)
13C NMR (126 MHz, CDCl3)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

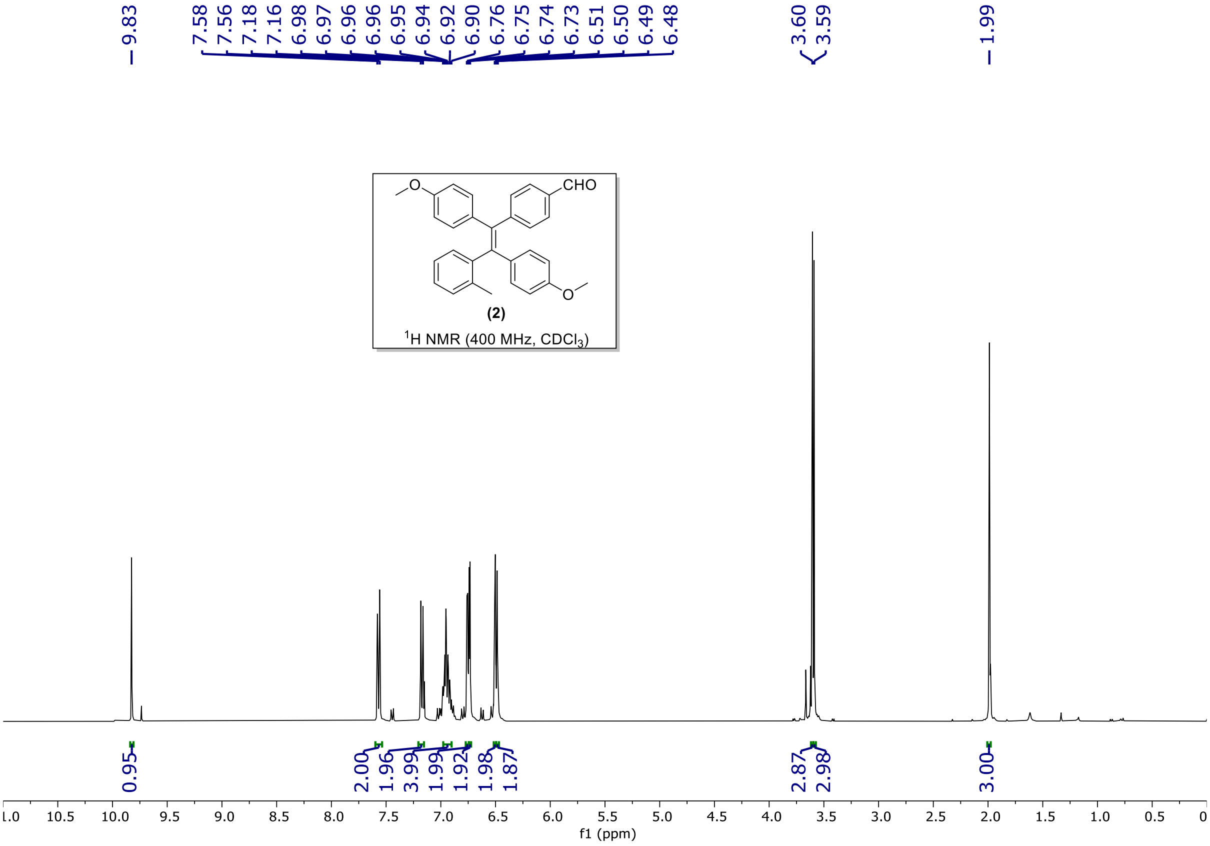

7.24
7.23
7.21
7.20
6.95
6.95
6.94
6.93
6.93
S
S
(A5)
1H NMR (500 MHz, CDCl3)
1.96
1.98
2.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

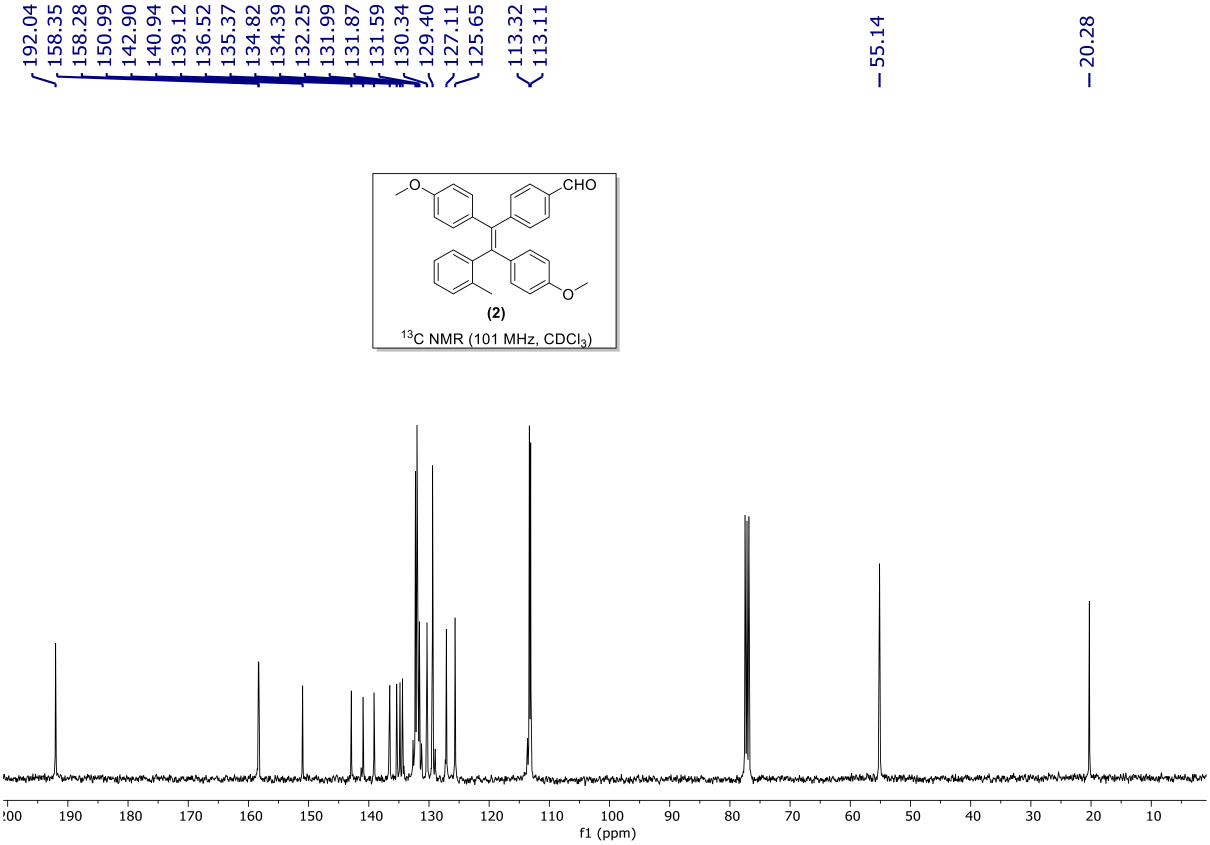


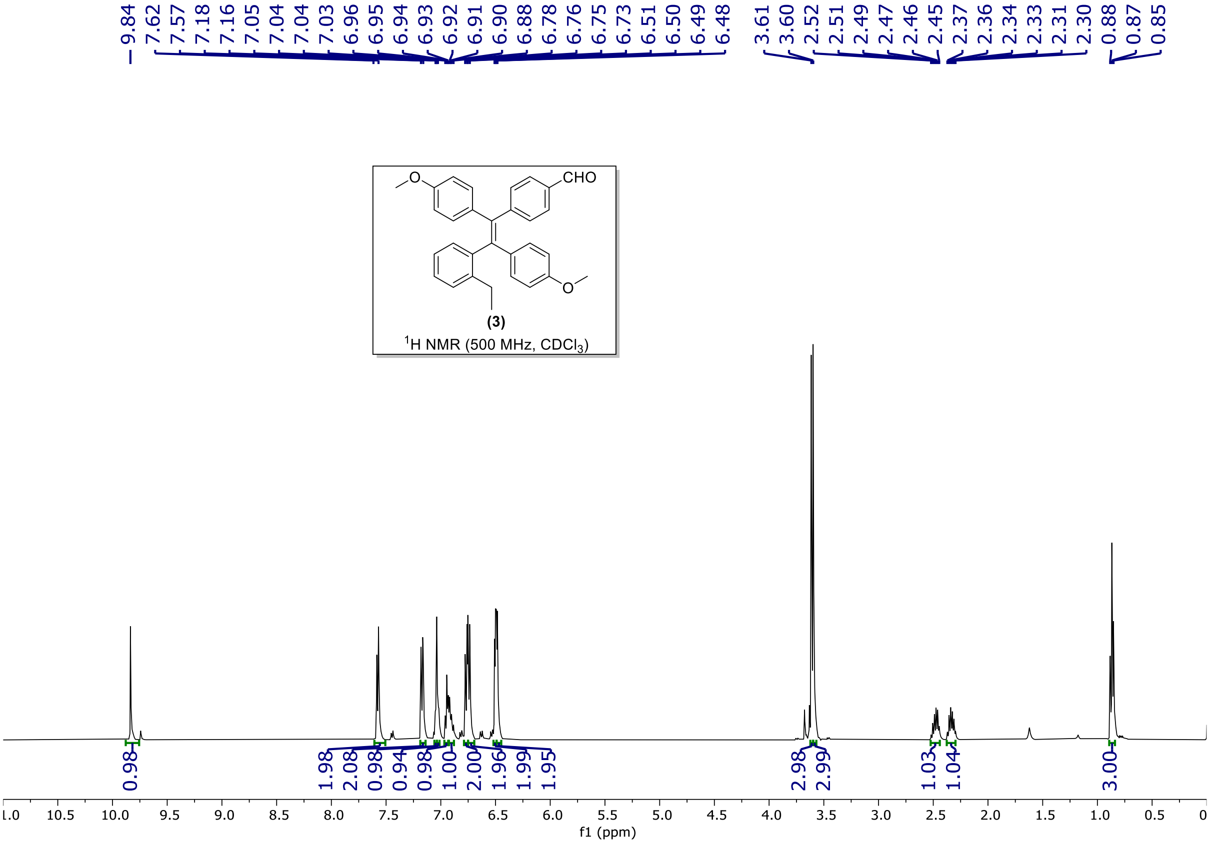
(A5)
^{13}C NMR (126 MHz, $CDCl_3$)


6.97
6.96
6.95
6.94
6.92
6.92
6.91
6.90
6.89
6.88
6.87
6.87
6.86
6.79
6.78
6.78
6.77
6.76
6.76
6.51
6.49
6.48
6.46
3.62
3.60
2.19
1.98
(1)
^{1}H NMR (500 MHz, CDCl$_3$)
3.99
3.98
3.93
1.95
1.98
2.99
2.93
2.91
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


157.98
157.81
143.72
141.04
140.19
138.38
136.67
136.58
136.03
135.82
131.91
131.88
131.48
130.20
128.65
126.67
125.54
113.09
112.84
55.17
55.13
21.34
20.30
(1)
^{13}C NMR (126 MHz, CDCl$_3$)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

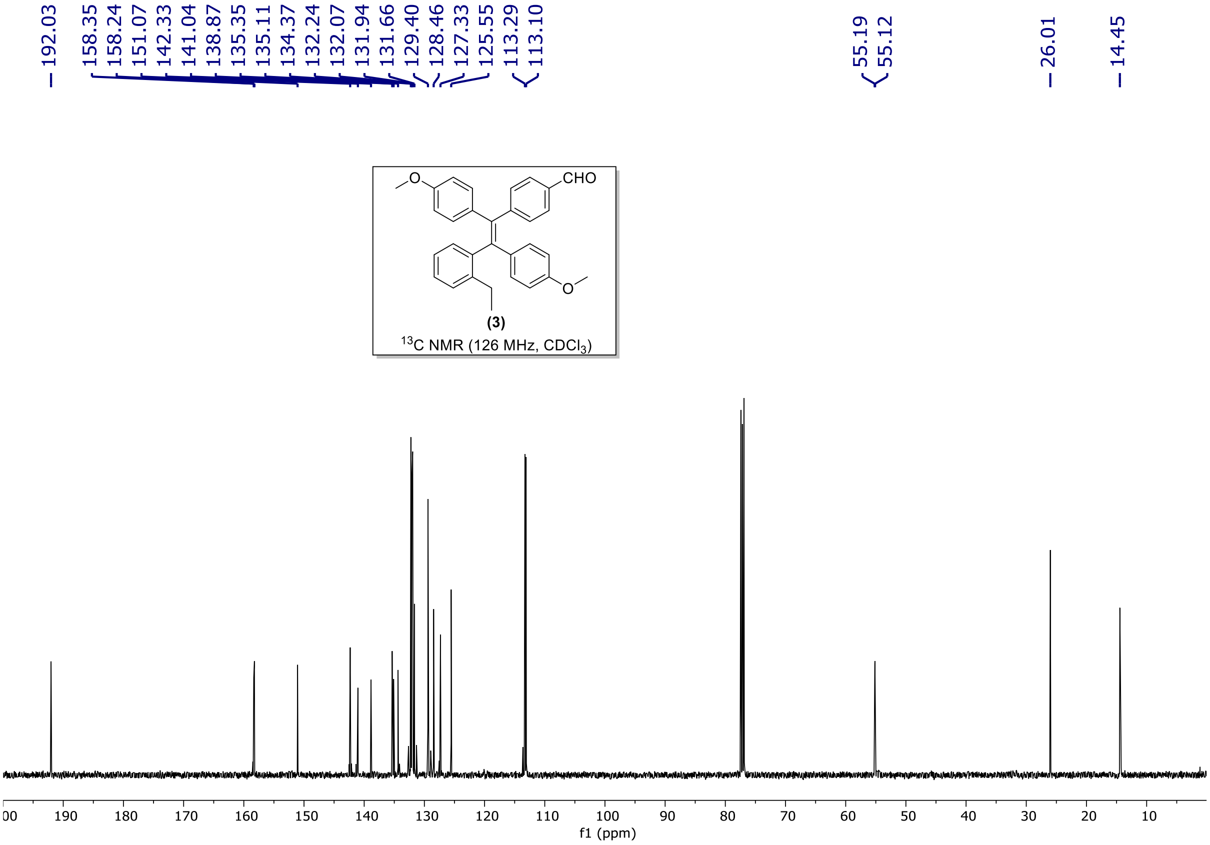

9.83
7.58
7.56
7.18
7.16
6.98
6.97
6.96
6.96
6.95
6.94
6.92
6.90
6.76
6.75
6.74
6.73
6.51
6.50
6.49
6.48
3.60
3.59
1.99
CHO
O
O
(2)
^{1}H NMR (400 MHz, CDCl$_3$)
0.95
2.00
1.96
3.99
1.99
1.92
1.98
1.87
2.87
2.98
3.00
f1 (ppm)


192.04
158.35
158.28
150.99
142.90
140.94
139.12
136.52
135.37
134.82
134.39
132.25
131.99
131.87
131.59
130.34
129.40
127.11
125.65
113.32
113.11
55.14
20.28
CHO
O
O
(2)
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)



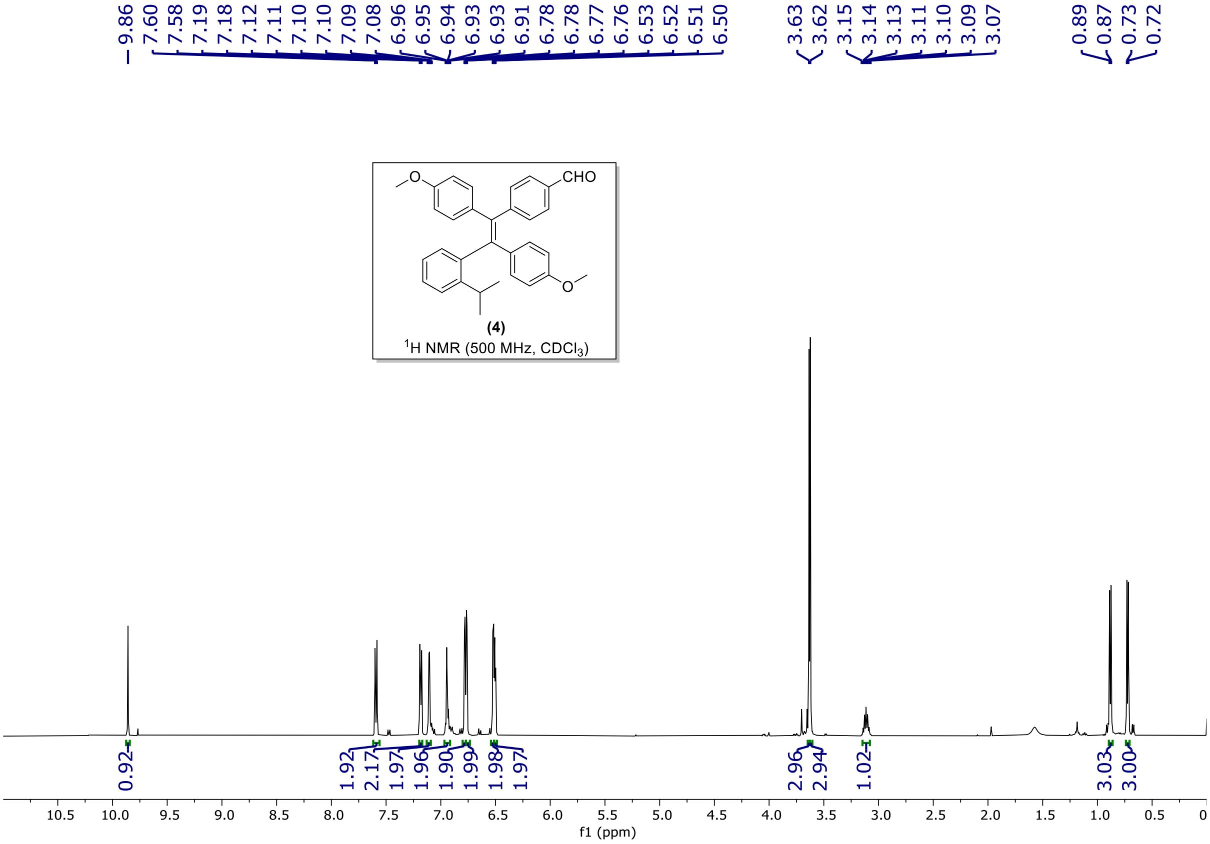
(3)

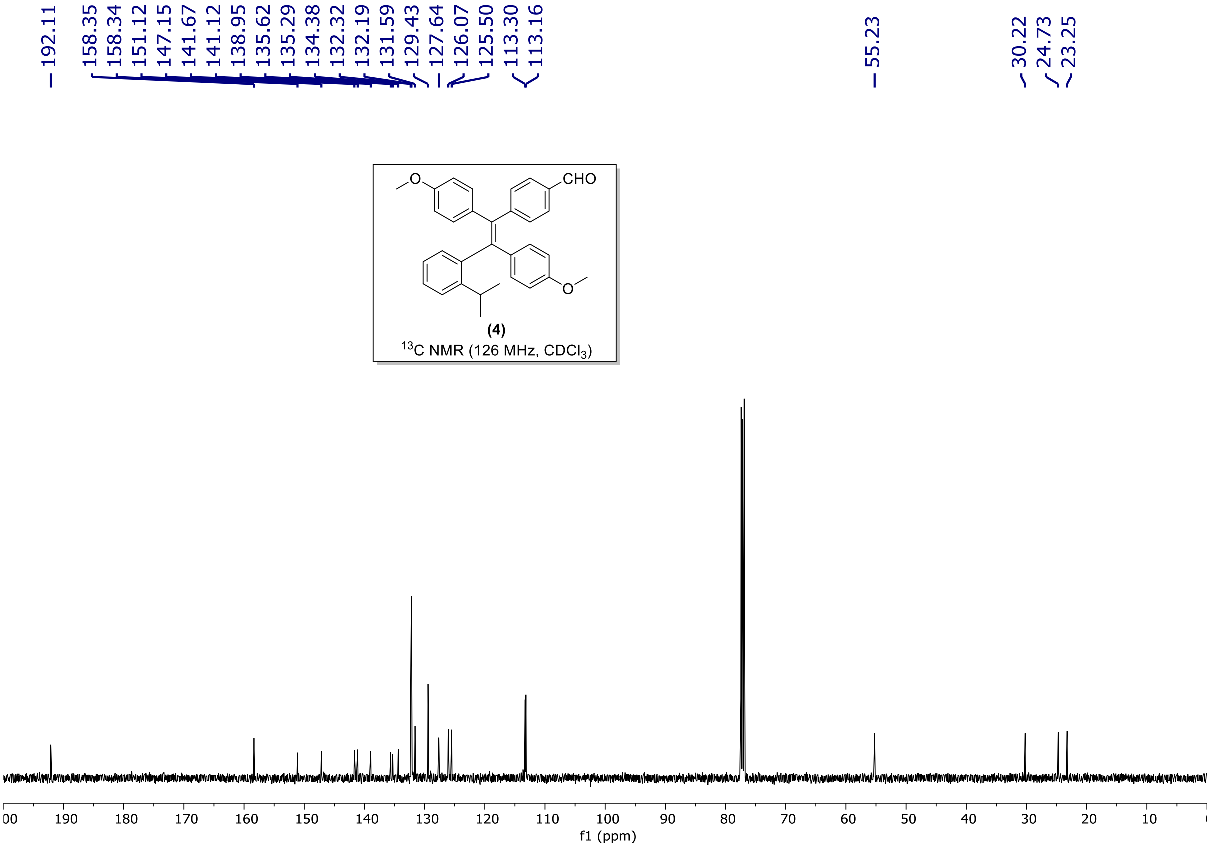
^{1}H NMR (500 MHz, CDCl$_3$)

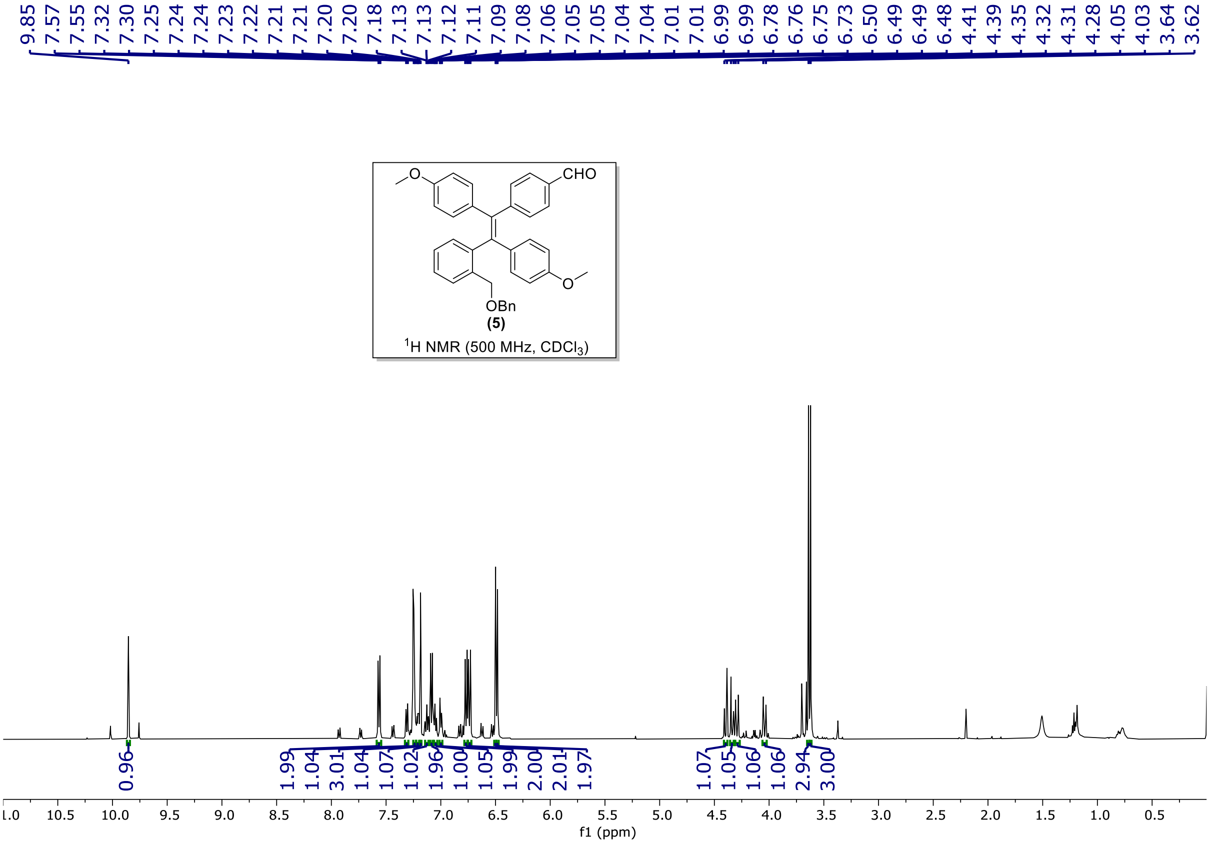


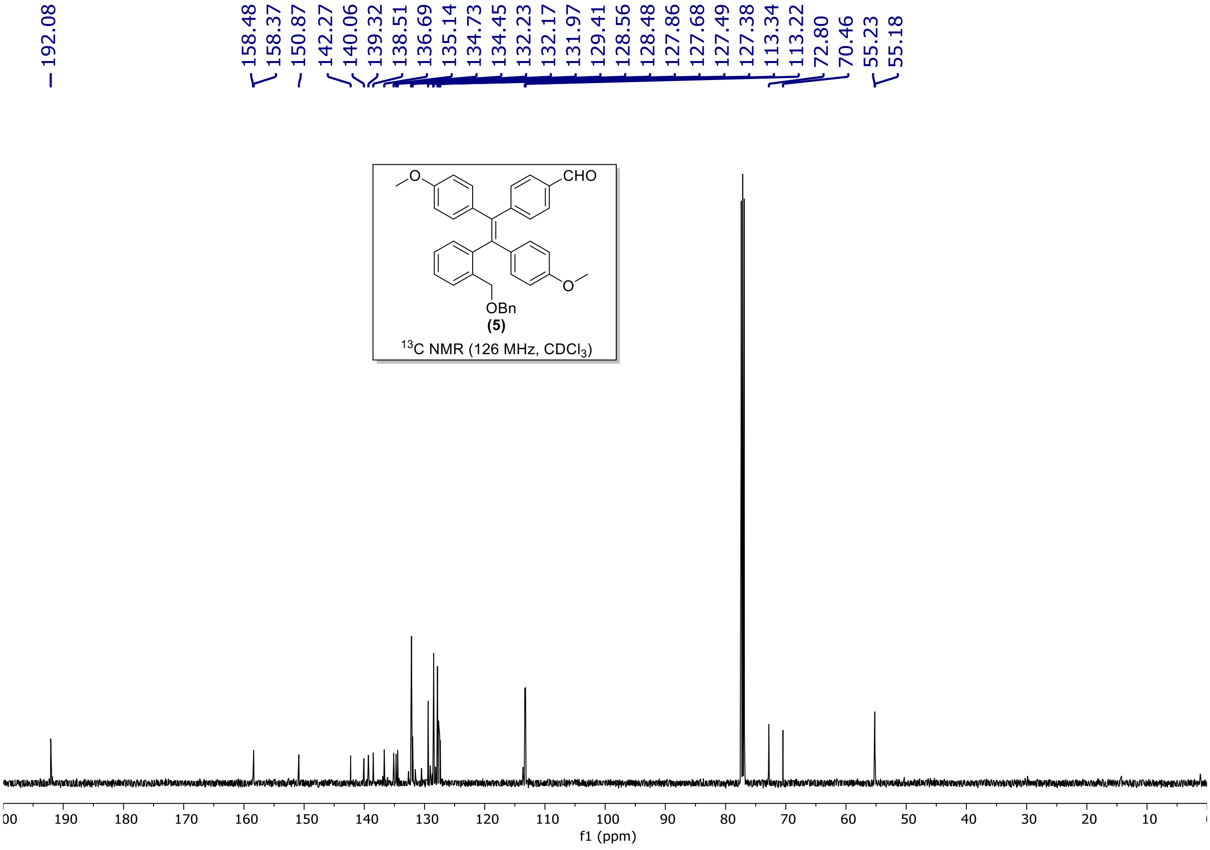
(3)

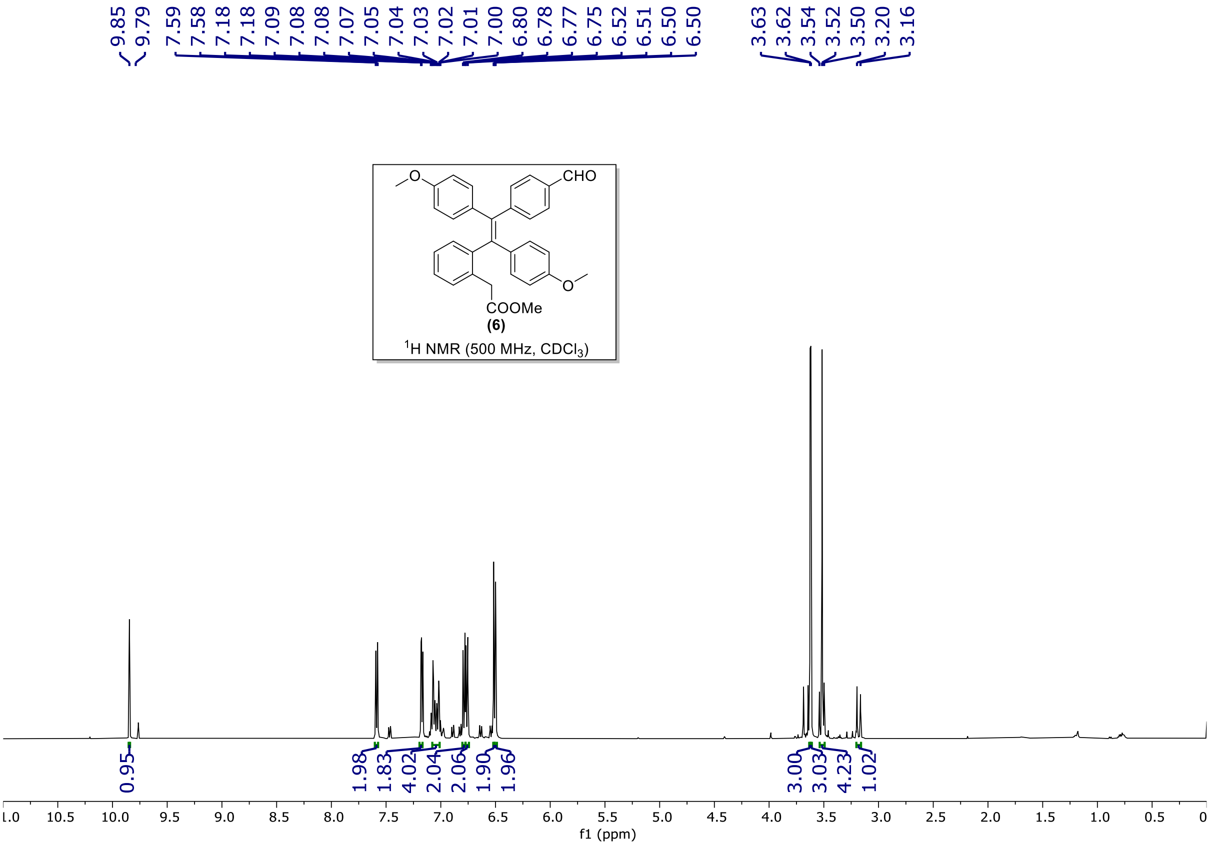
^{13}C NMR (126 MHz, CDCl$_3$)

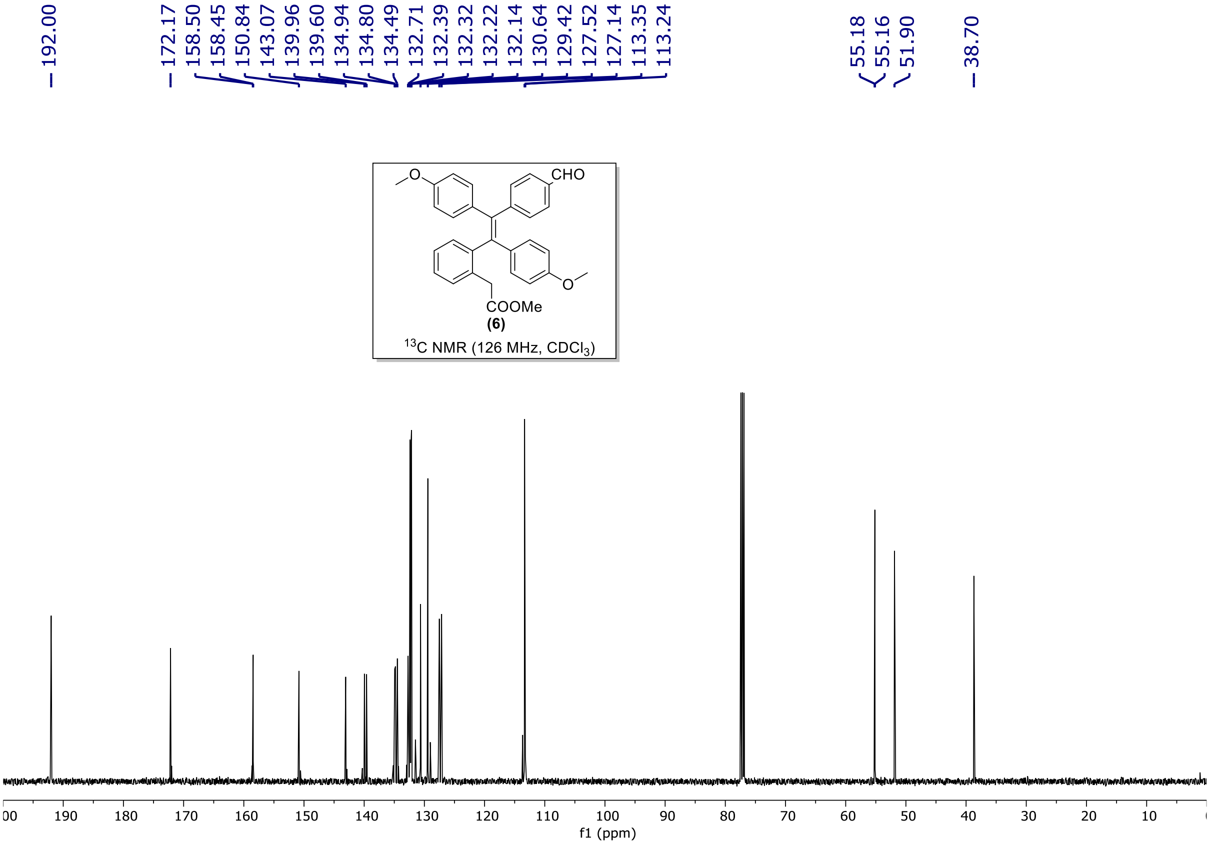

9.86
7.60
7.58
7.19
7.18
7.12
7.11
7.10
7.10
7.09
7.08
6.96
6.95
6.94
6.93
6.93
6.91
6.78
6.78
6.77
6.76
6.53
6.52
6.51
6.50
3.63
3.62
3.15
3.14
3.13
3.11
3.10
3.09
3.07
0.89
0.87
0.73
0.72
CHO
O
O
(4)
^{1}H NMR (500 MHz, CDCl$_3$)
0.92
1.92
2.17
1.97
1.96
1.90
1.99
1.98
1.97
2.96
2.94
1.02
3.03
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

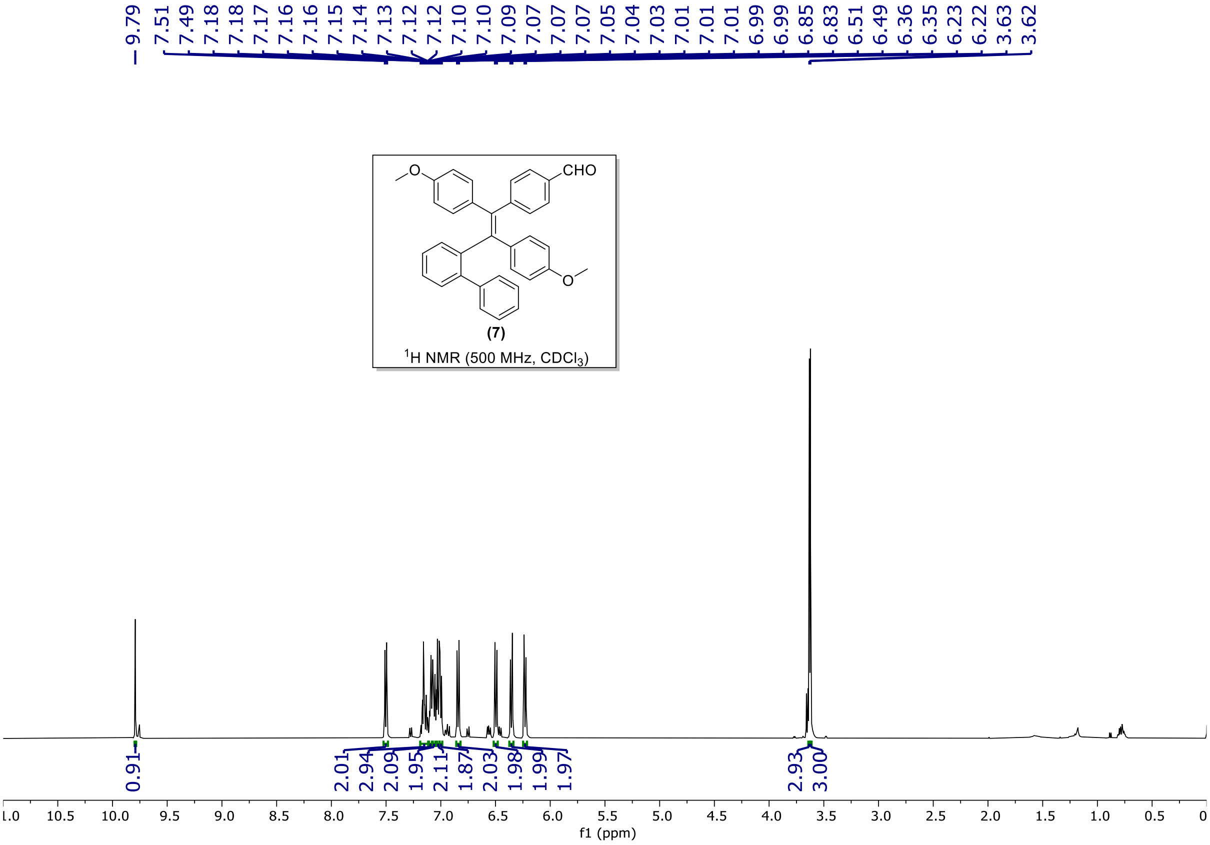

192.11
158.35
158.34
151.12
147.15
141.67
141.12
138.95
135.62
135.29
134.38
132.32
132.19
131.59
129.43
127.64
126.07
125.50
113.30
113.16
55.23
30.22
24.73
23.25
CHO
O
O
(4)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.85
7.57
7.55
7.32
7.30
7.25
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.20
7.18
7.13
7.13
7.12
7.11
7.09
7.08
7.06
7.05
7.05
7.04
7.04
7.04
7.01
7.01
6.99
6.99
6.78
6.76
6.75
6.73
6.50
6.49
6.49
6.48
4.41
4.39
4.35
4.32
4.31
4.28
4.05
4.03
3.64
3.62
O
CHO
O
OBn
(5)
^{1}H NMR (500 MHz, CDCl$_3$)
0.96
1.99
1.04
3.01
1.04
1.07
1.02
1.96
1.00
1.05
1.99
2.00
2.01
1.97
1.07
1.05
1.06
1.06
2.94
3.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


192.08
158.48
158.37
150.87
142.27
140.06
139.32
138.51
136.69
135.14
134.73
134.45
132.23
132.17
131.97
129.41
128.56
128.48
127.86
127.68
127.49
127.38
113.34
113.22
72.80
70.46
55.23
55.18
O
CHO
O
OBn
(5)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

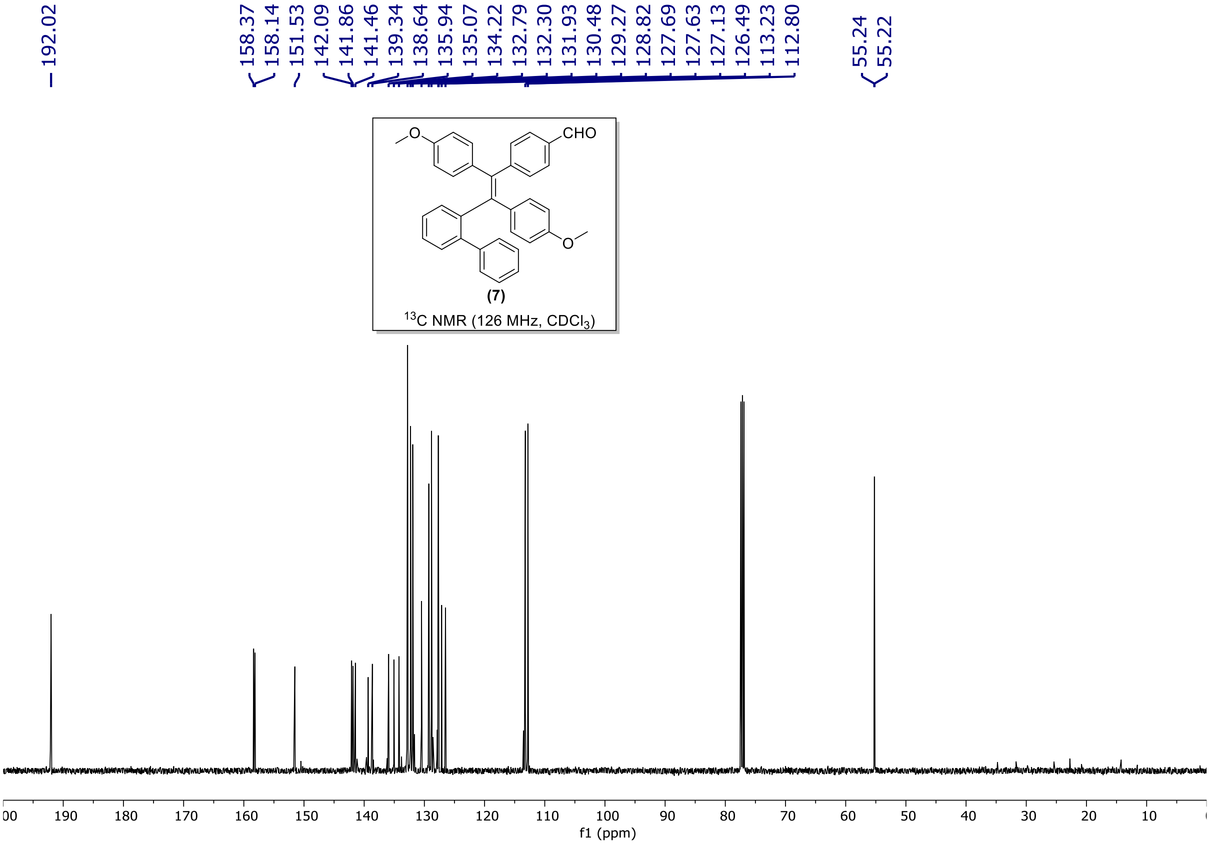

9.85
9.79
7.59
7.58
7.18
7.18
7.09
7.08
7.08
7.07
7.05
7.04
7.03
7.02
7.01
7.00
6.80
6.78
6.77
6.75
6.52
6.51
6.50
6.50
3.63
3.62
3.54
3.52
3.50
3.20
3.16
CHO
O
COOMe
(6)
^{1}H NMR (500 MHz, CDCl$_3$)
0.95
1.98
1.83
4.02
2.04
2.06
1.90
1.96
3.00
3.03
4.23
1.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


192.00
172.17
158.50
158.45
150.84
143.07
139.96
139.60
134.94
134.80
134.49
132.71
132.39
132.32
132.22
132.14
130.64
129.42
127.52
127.14
113.35
113.24
55.18
55.16
51.90
38.70
CHO
O
COOMe
(6)
^{13}C NMR (126 MHz, CDCl$_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



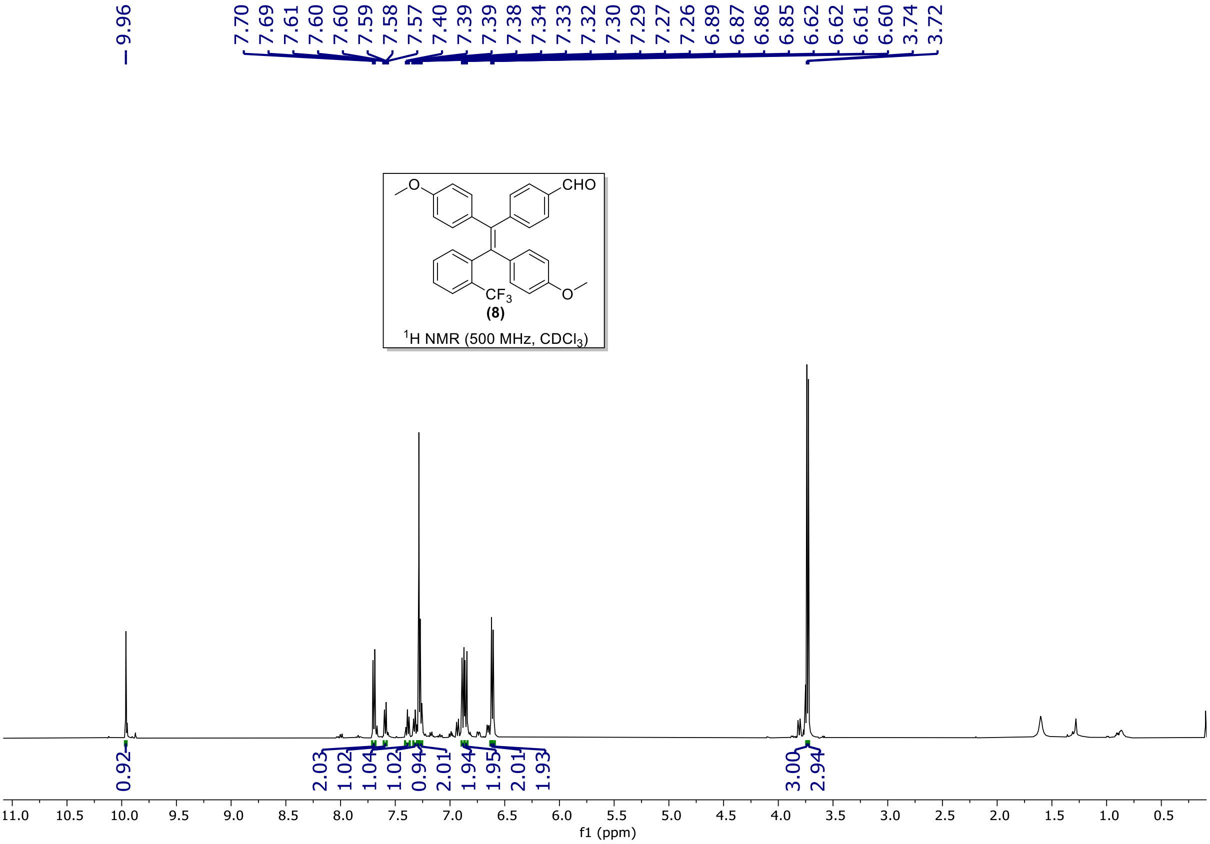
(7)

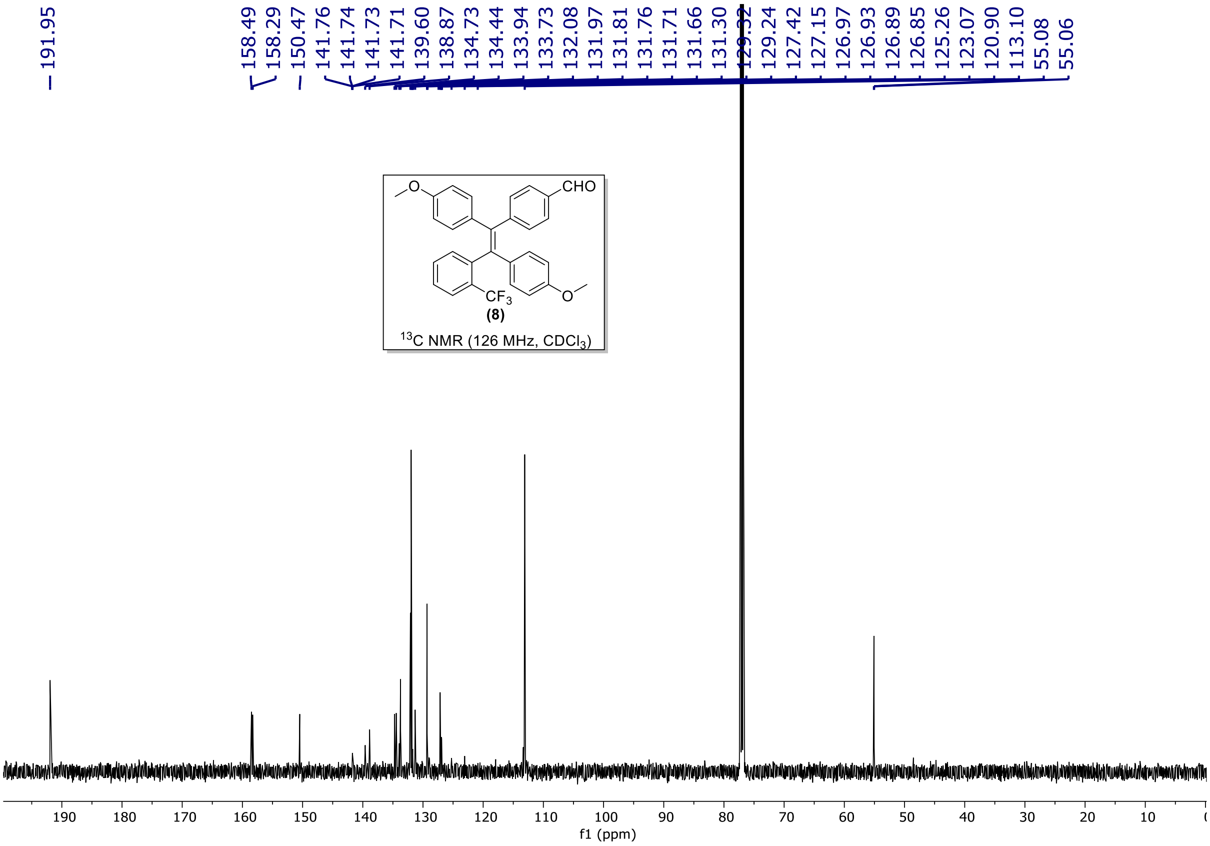
^1H NMR (500 MHz, $CDCl_3$)

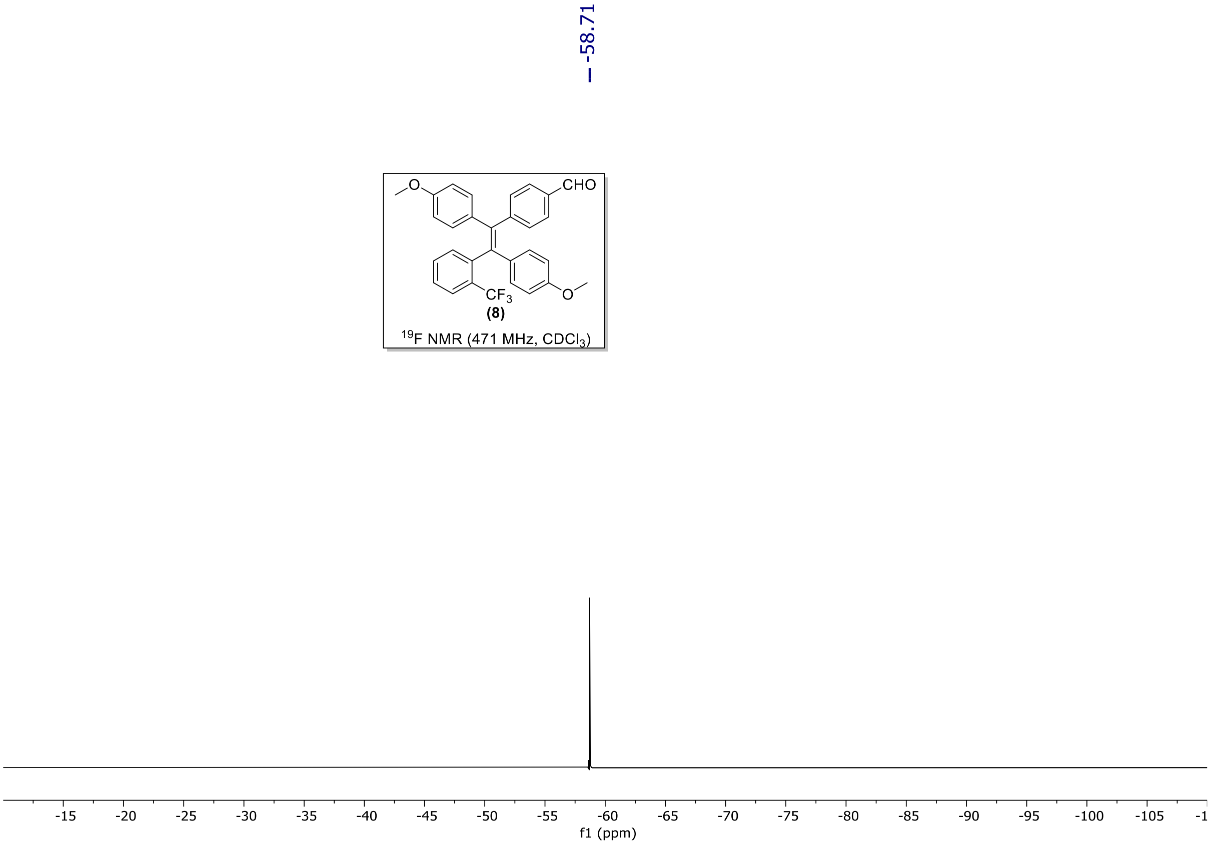


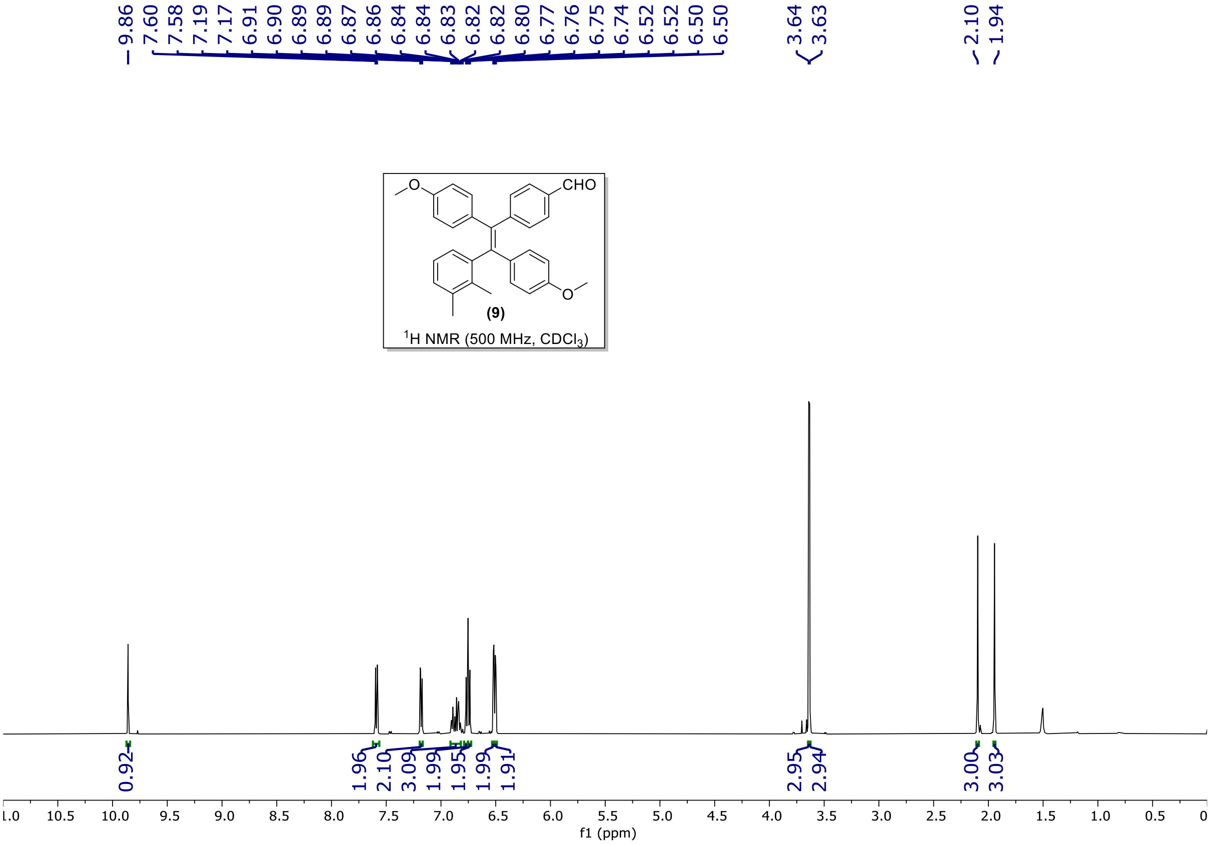
(7)

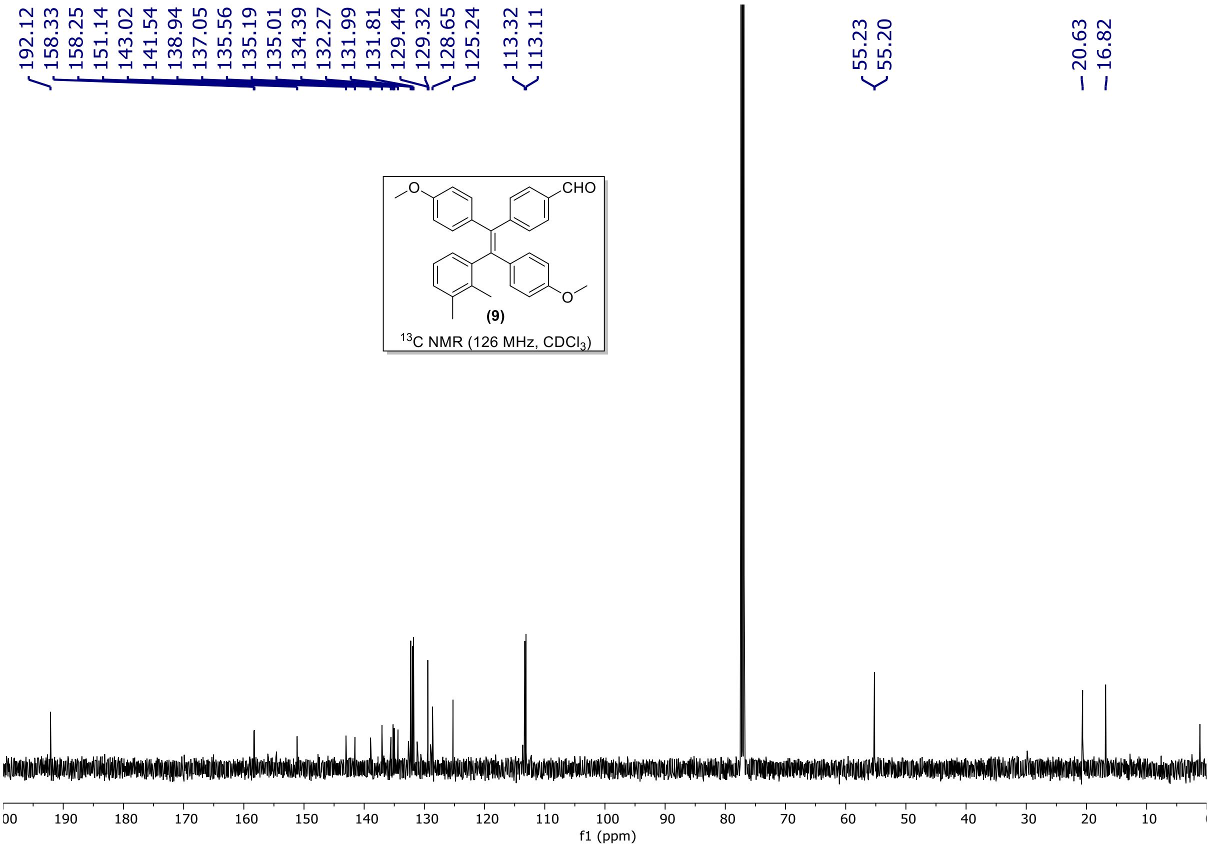
^{13}C NMR (126 MHz, $CDCl_3$)

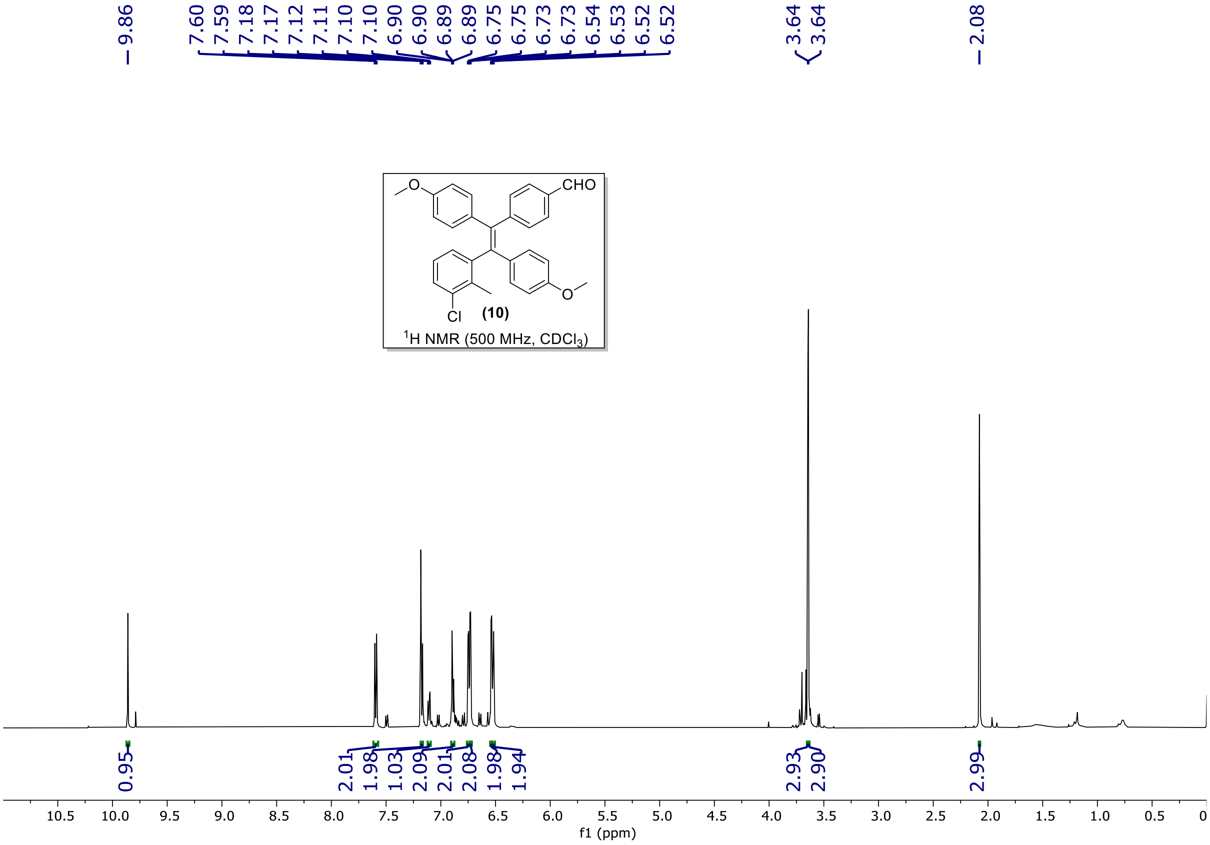

9.96
7.70
7.69
7.61
7.60
7.60
7.59
7.58
7.57
7.40
7.39
7.39
7.38
7.34
7.33
7.32
7.30
7.29
7.27
7.26
6.89
6.87
6.86
6.85
6.62
6.62
6.61
6.60
3.74
3.72
CHO
O
O
CF3
(8)
1H NMR (500 MHz, CDCl3)
0.92
2.03
1.02
1.04
1.02
0.94
2.01
1.94
1.95
2.01
1.93
3.00
2.94
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

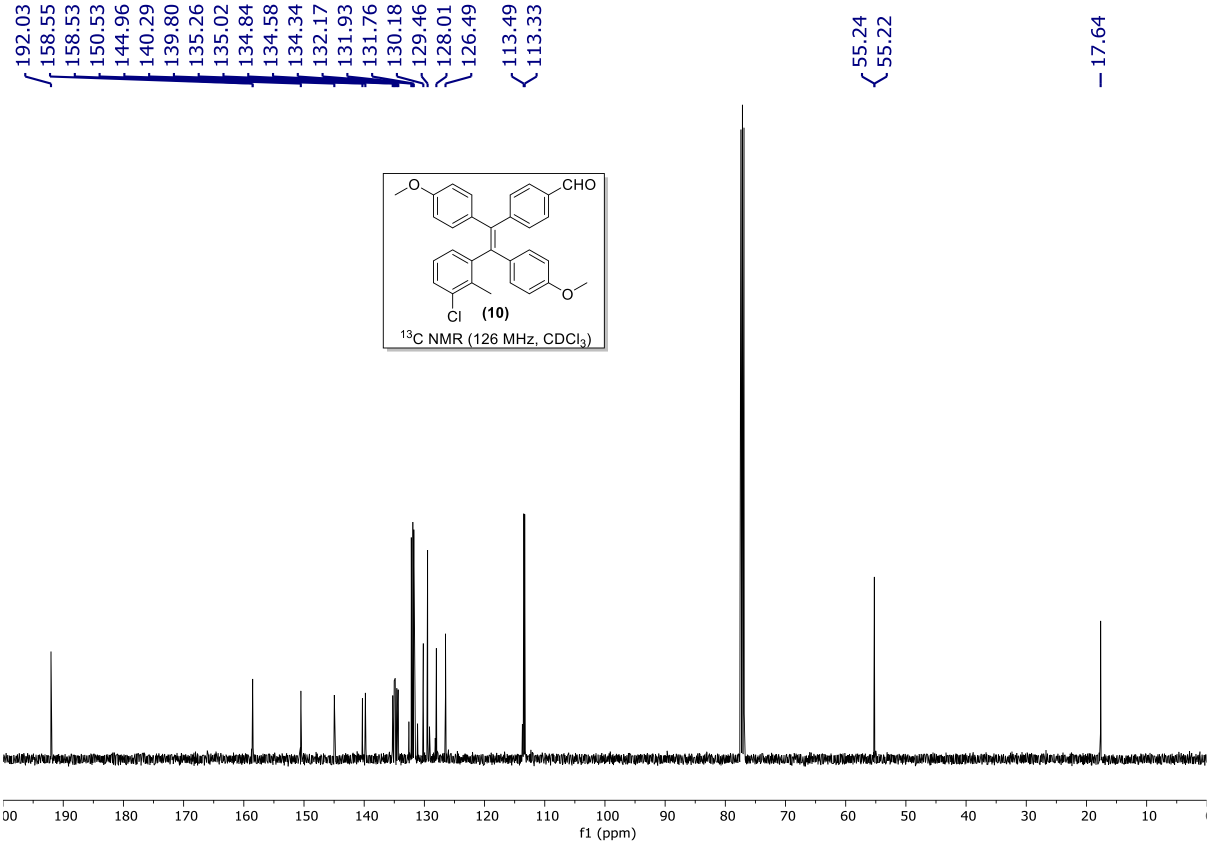

191.95
158.49
158.29
150.47
141.76
141.74
141.73
141.71
139.60
138.87
134.73
134.44
133.94
133.73
132.08
131.97
131.81
131.76
131.71
131.66
131.30
129.32
129.24
127.42
127.15
126.97
126.93
126.89
126.85
125.26
123.07
120.90
113.10
55.08
55.06
CHO
O
O
CF3
(8)
13C NMR (126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-58.71
CHO
O
CF3
(8)
^{19}F NMR (471 MHz, CDCl$_3$)
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105
f1 (ppm)


9.86
7.60 7.58 7.19 7.17 6.91 6.90 6.89 6.89 6.87 6.86 6.84 6.84 6.83 6.82 6.82 6.80 6.77 6.76 6.75 6.74 6.52 6.52 6.50 6.50
3.64 3.63
2.10 1.94
CHO
O
(9)
^{1}H NMR (500 MHz, CDCl$_3$)
0.92
1.96 2.10 3.09 1.99 1.95 1.99 1.91
2.95 2.94
3.00 3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

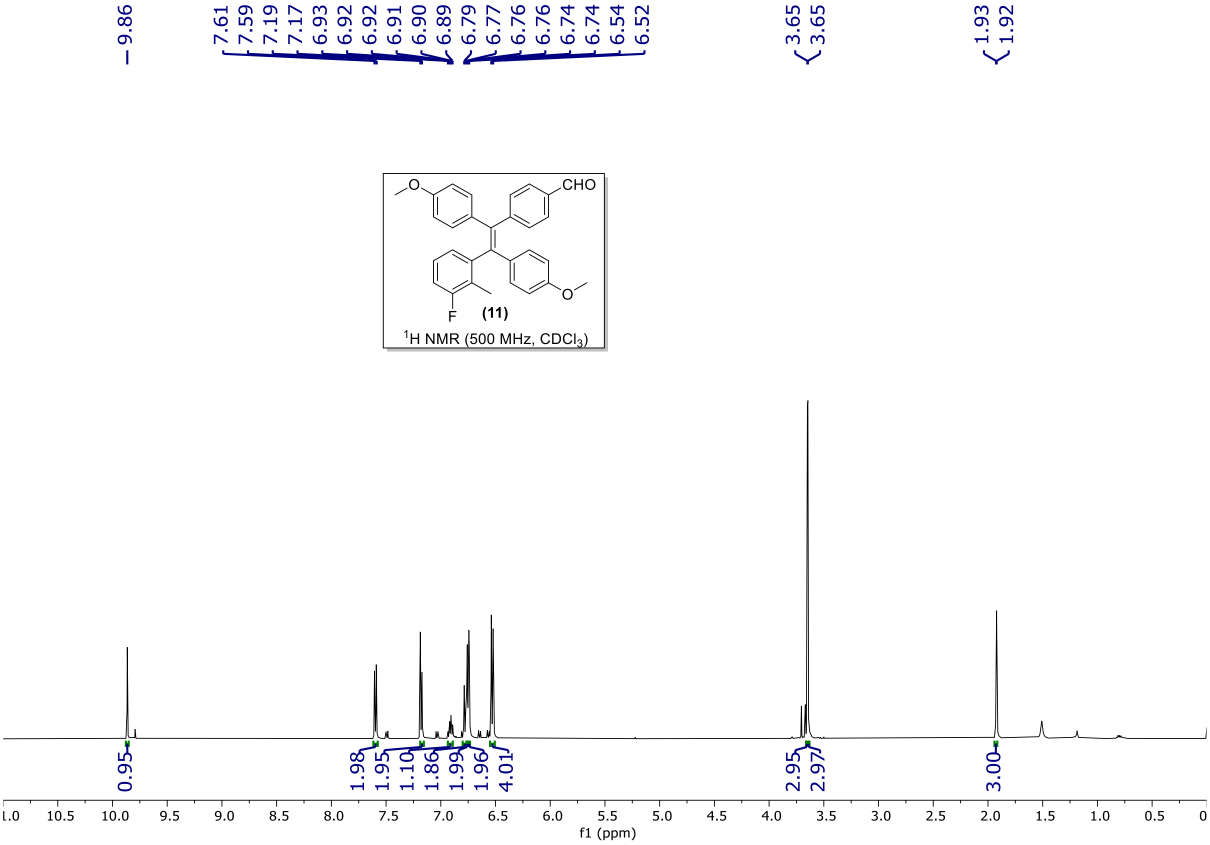

192.12
158.33
158.25
151.14
143.02
141.54
138.94
137.05
135.56
135.19
135.01
134.39
132.27
131.99
131.81
129.44
129.32
128.65
125.24
113.32
113.11
55.23
55.20
20.63
16.82
CHO
O
(9)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.86
7.60
7.59
7.18
7.17
7.12
7.11
7.10
7.10
6.90
6.90
6.89
6.89
6.75
6.75
6.73
6.73
6.54
6.53
6.52
6.52
3.64
3.64
2.08
CHO
O
Cl
(10)
^{1}H NMR (500 MHz, CDCl$_3$)
0.95
2.01
1.98
1.03
2.09
2.01
2.08
1.98
1.94
2.93
2.90
2.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



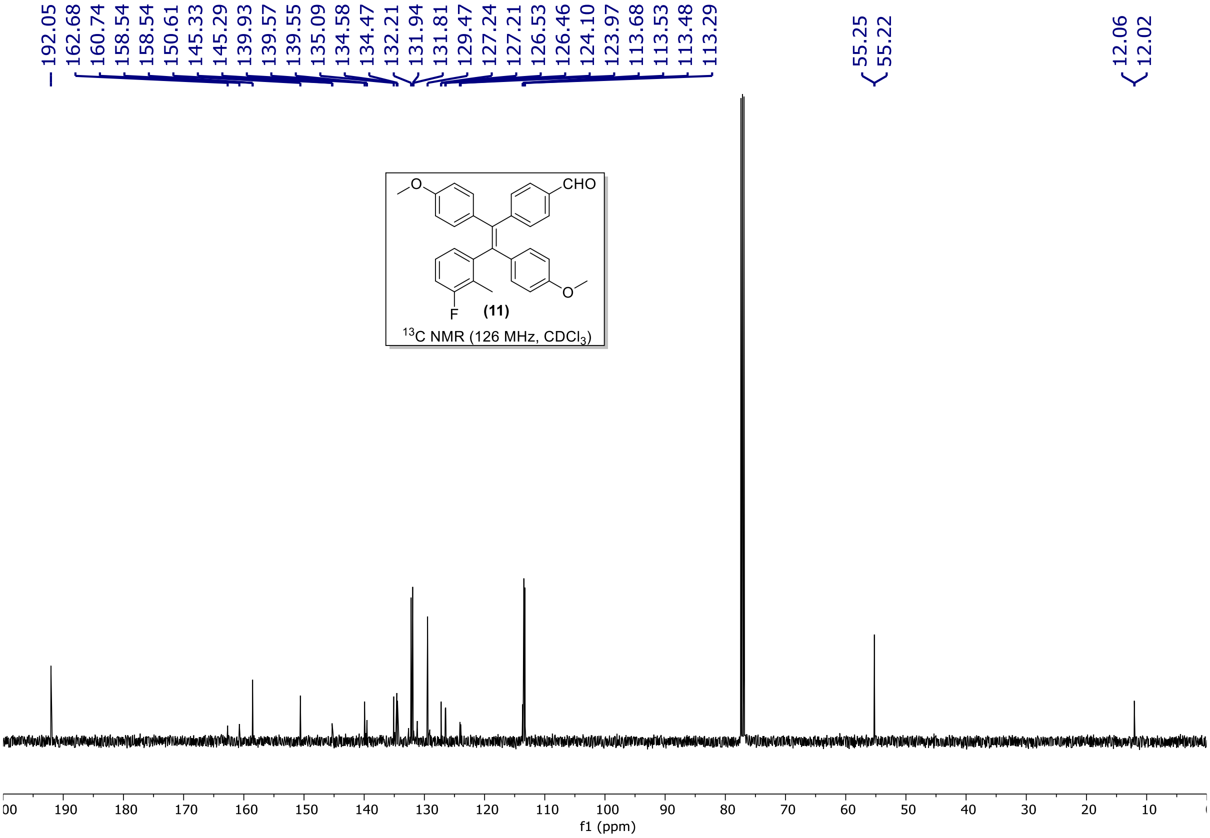
(10)

^{13}C NMR (126 MHz, CDCl$_3$)

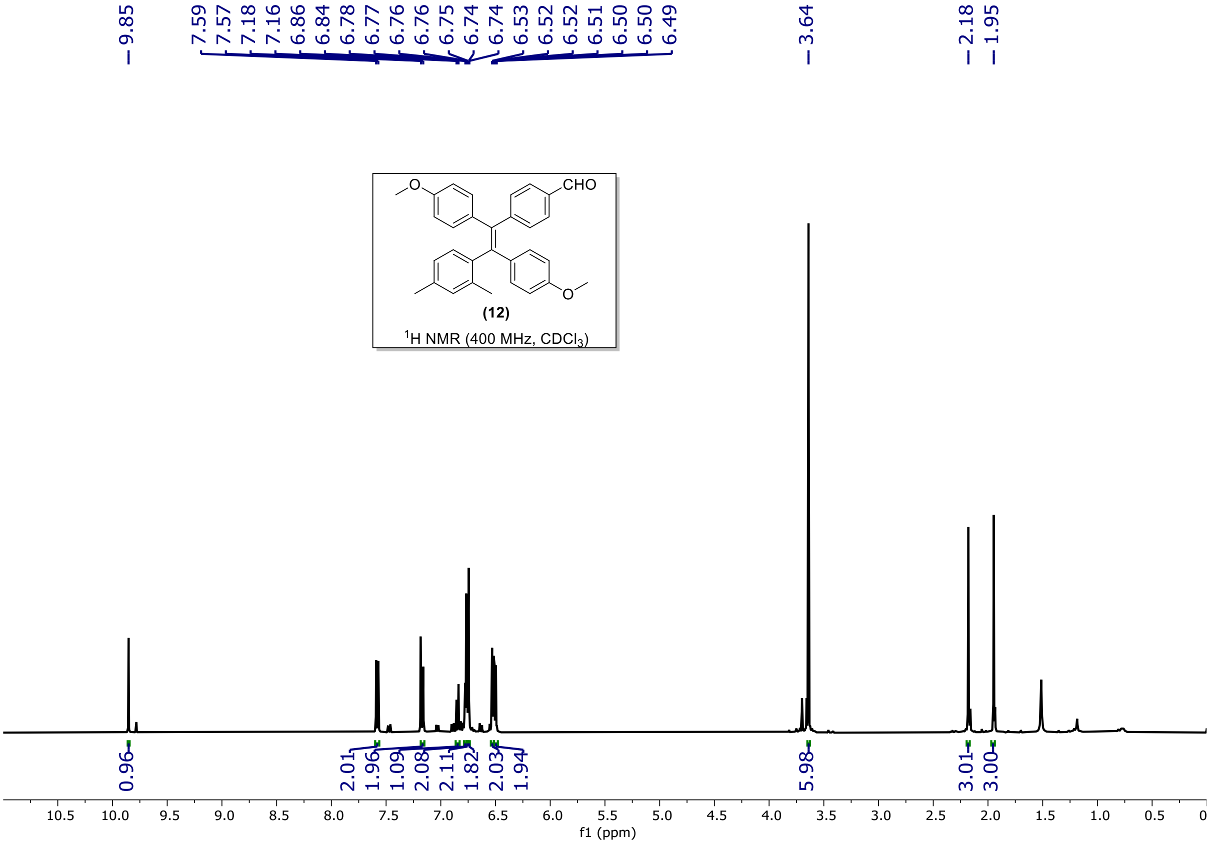


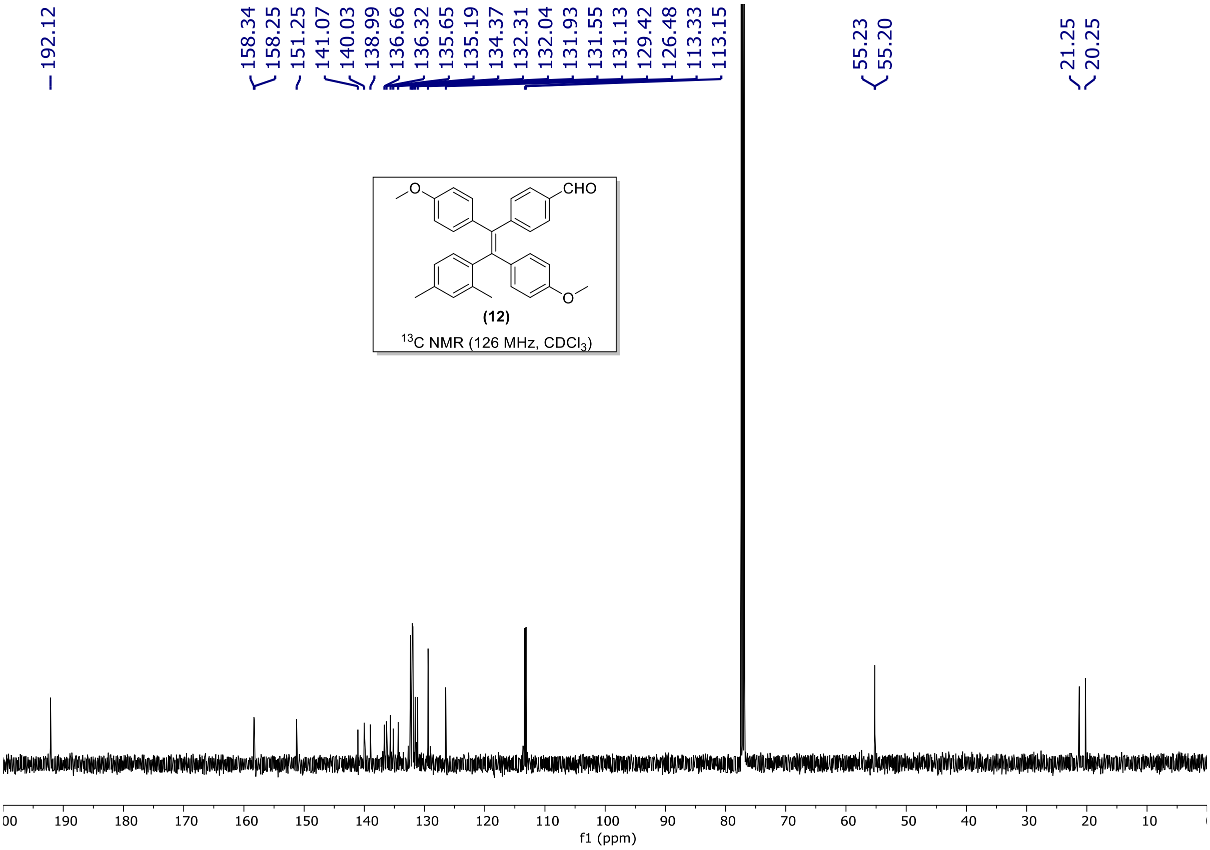
(11)

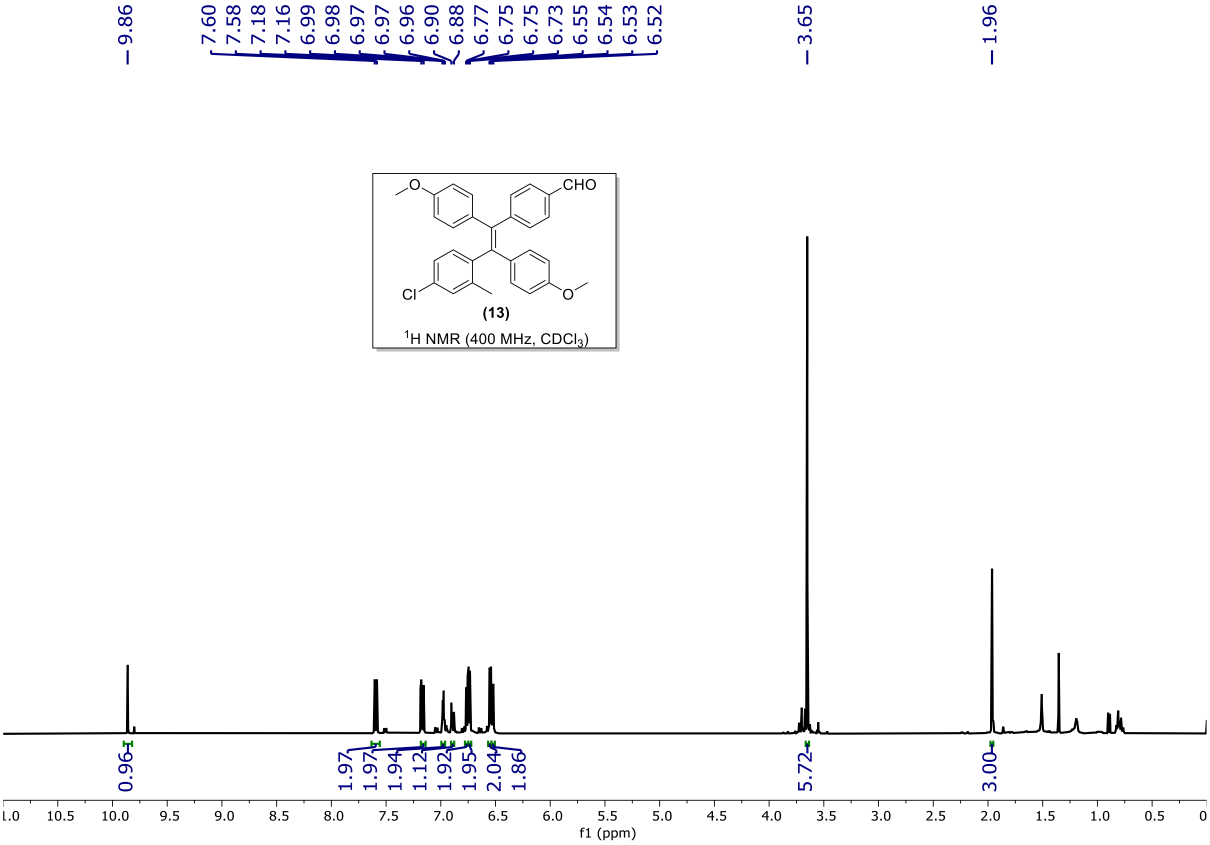
^{1}H NMR (500 MHz, CDCl$_3$)

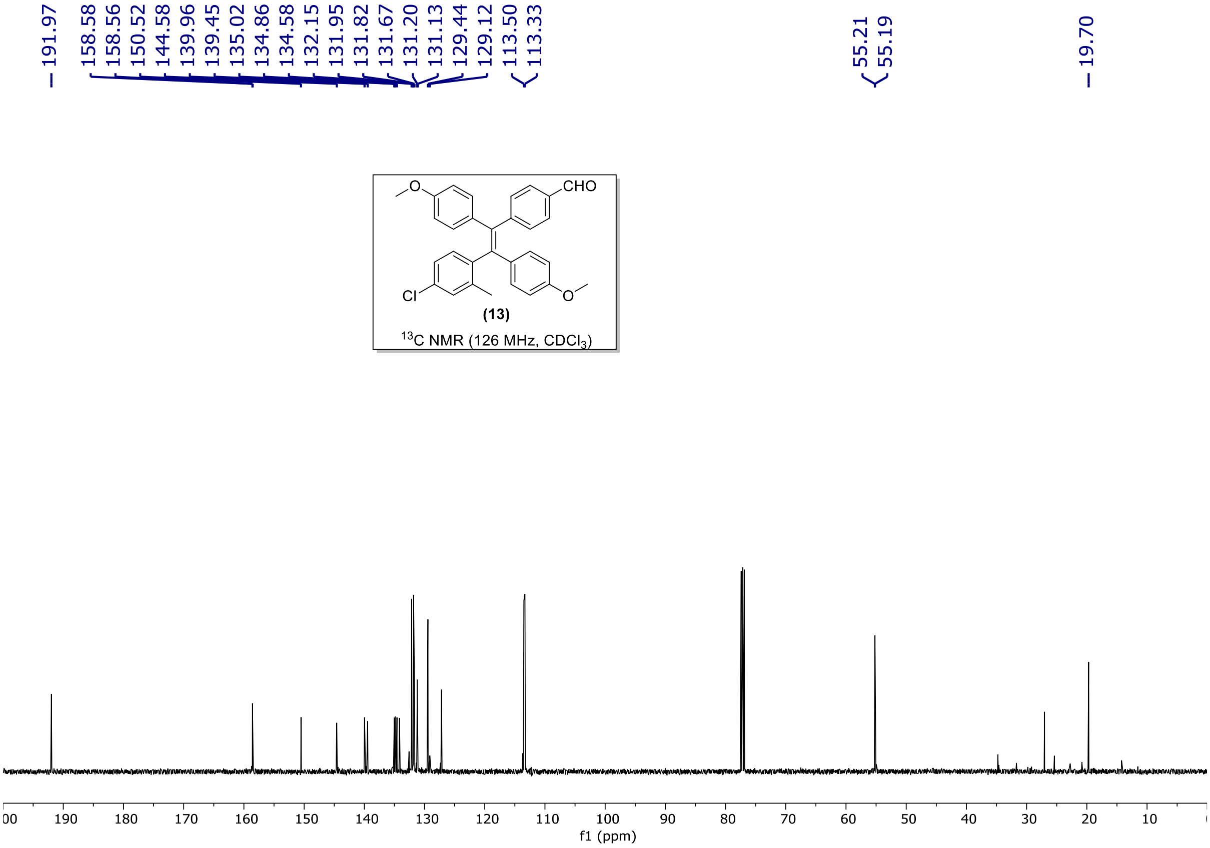

192.05
162.68
160.74
158.54
158.54
150.61
145.33
145.29
139.93
139.57
139.55
135.09
134.58
134.47
132.21
131.94
131.81
129.47
127.24
127.21
126.53
126.46
124.10
123.97
113.68
113.53
113.48
113.29
55.25
55.22
12.06
12.02
CHO
O
O
F
(11)
^{13}C NMR (126 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

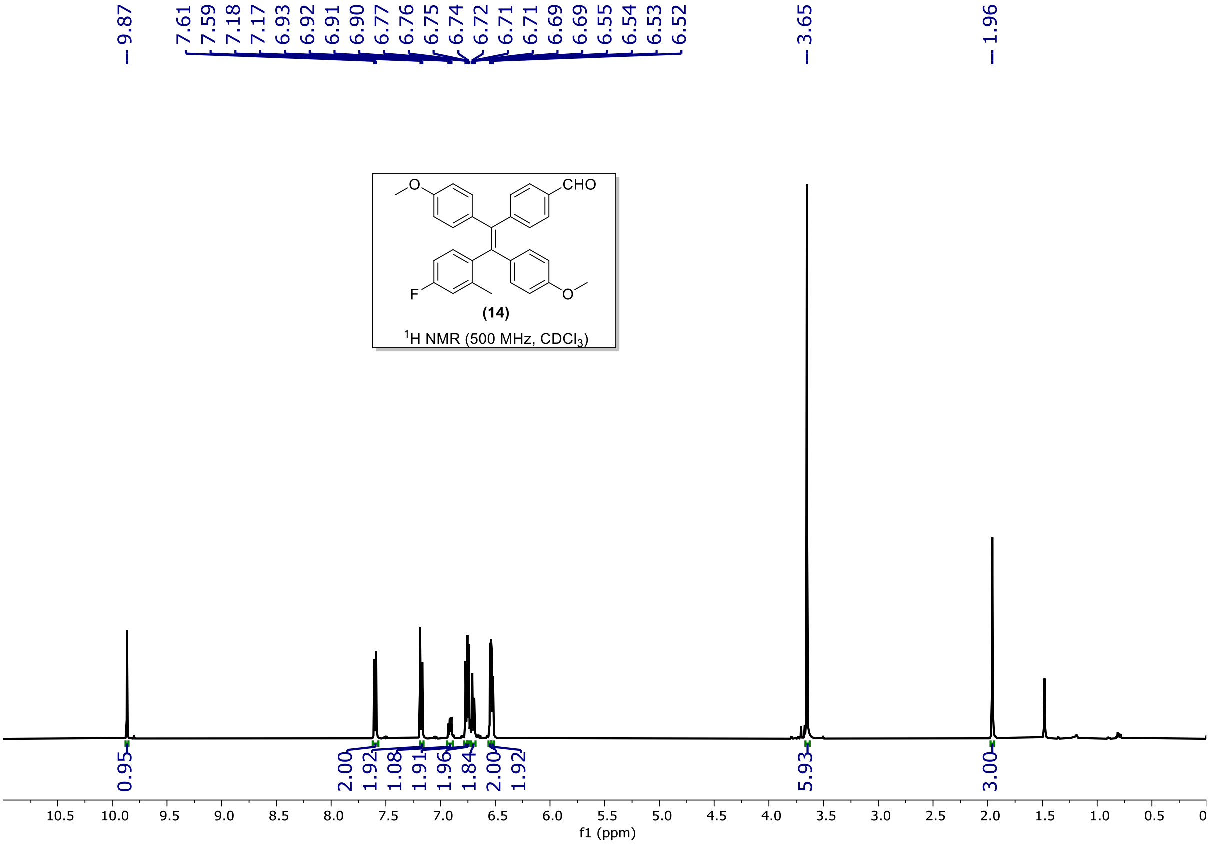

-116.16
CHO
O
O
F
(11)
^{19}F NMR (471 MHz, CDCl$_3$)
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
f1 (ppm)


9.85
7.59
7.57
7.18
7.16
6.86
6.84
6.78
6.77
6.76
6.76
6.75
6.74
6.74
6.53
6.52
6.52
6.51
6.50
6.50
6.49
3.64
2.18
1.95
CHO
O
O
(12)
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
2.01
1.96
1.09
2.08
2.11
1.82
2.03
1.94
5.98
3.01
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


192.12
158.34
158.25
151.25
141.07
140.03
138.99
136.66
136.32
135.65
135.19
134.37
132.31
132.04
131.93
131.55
131.13
129.42
126.48
113.33
113.15
55.23
55.20
21.25
20.25
CHO
O
O
(12)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

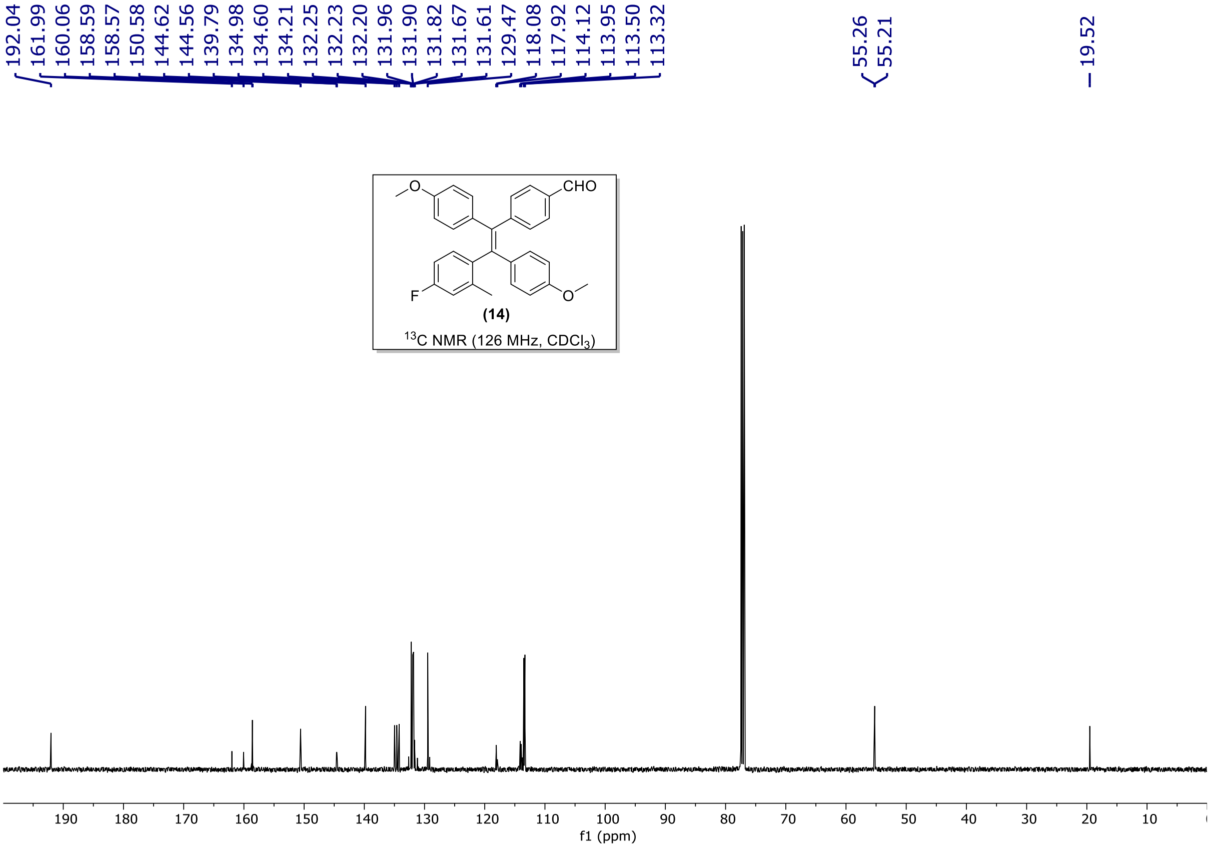

9.86
7.60
7.58
7.18
7.16
6.99
6.98
6.97
6.97
6.96
6.90
6.88
6.77
6.75
6.75
6.73
6.55
6.54
6.53
6.52
3.65
1.96
CHO
O
Cl
(13)
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
1.97
1.97
1.94
1.12
1.92
1.95
2.04
1.86
5.72
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


191.97
158.58
158.56
150.52
144.58
139.96
139.45
135.02
134.86
134.58
132.15
131.95
131.82
131.67
131.20
131.13
129.44
129.12
113.50
113.33
55.21
55.19
19.70
CHO
O
Cl
(13)
^{13}C NMR (126 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



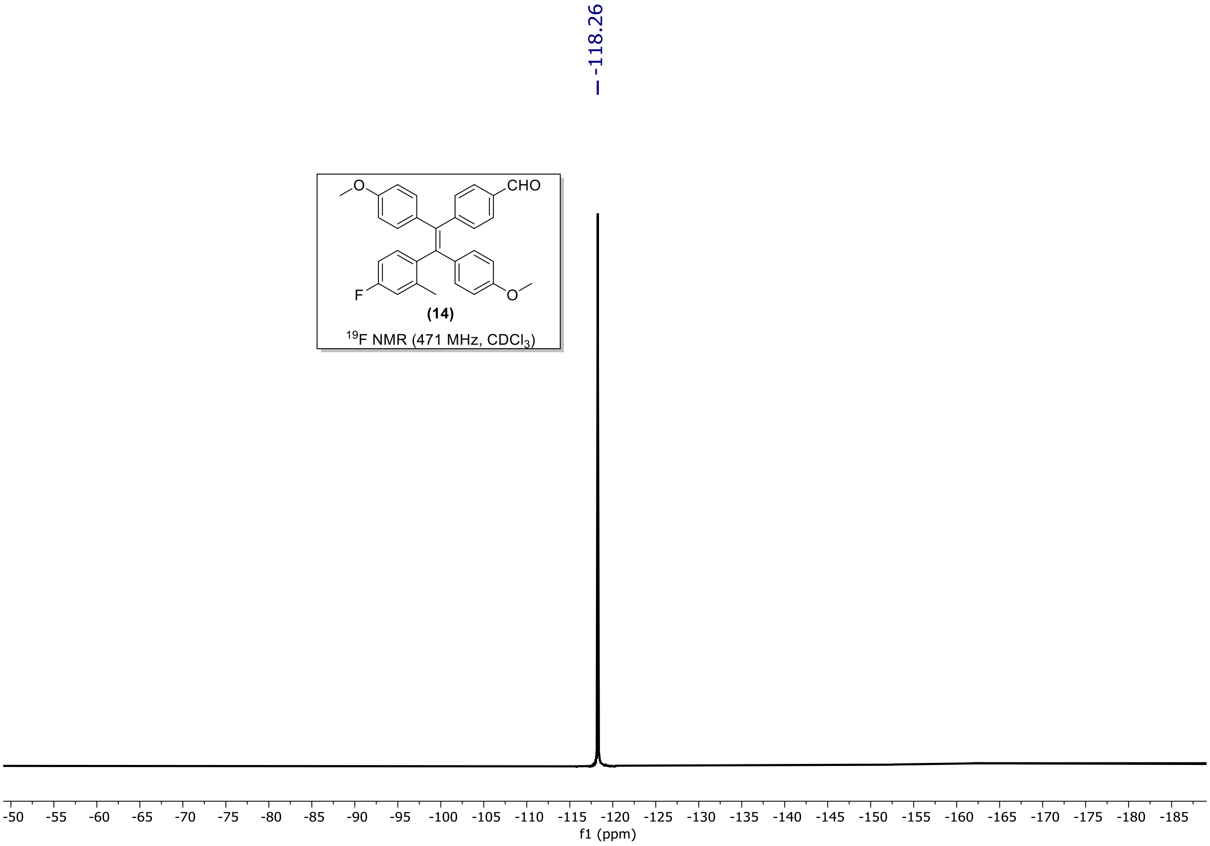
(14)

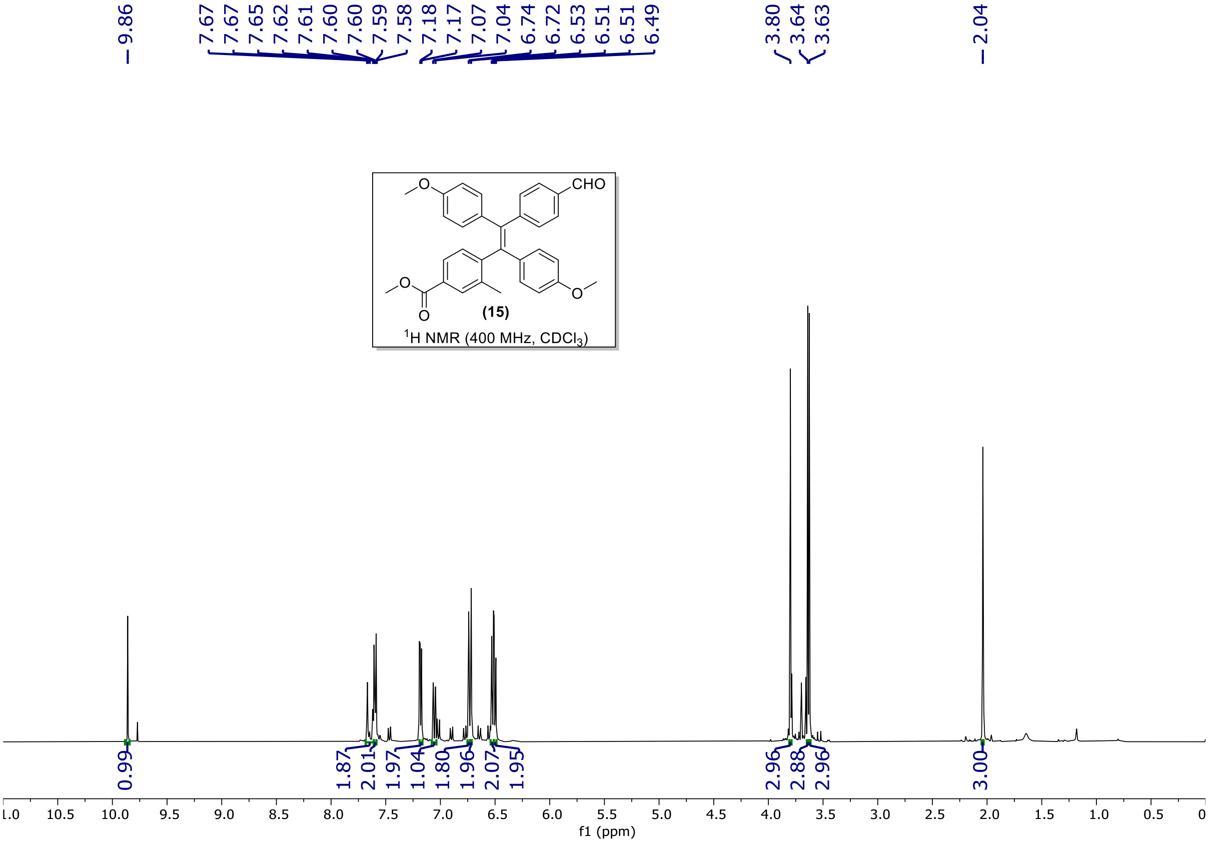
^1H NMR (500 MHz, $CDCl_3$)

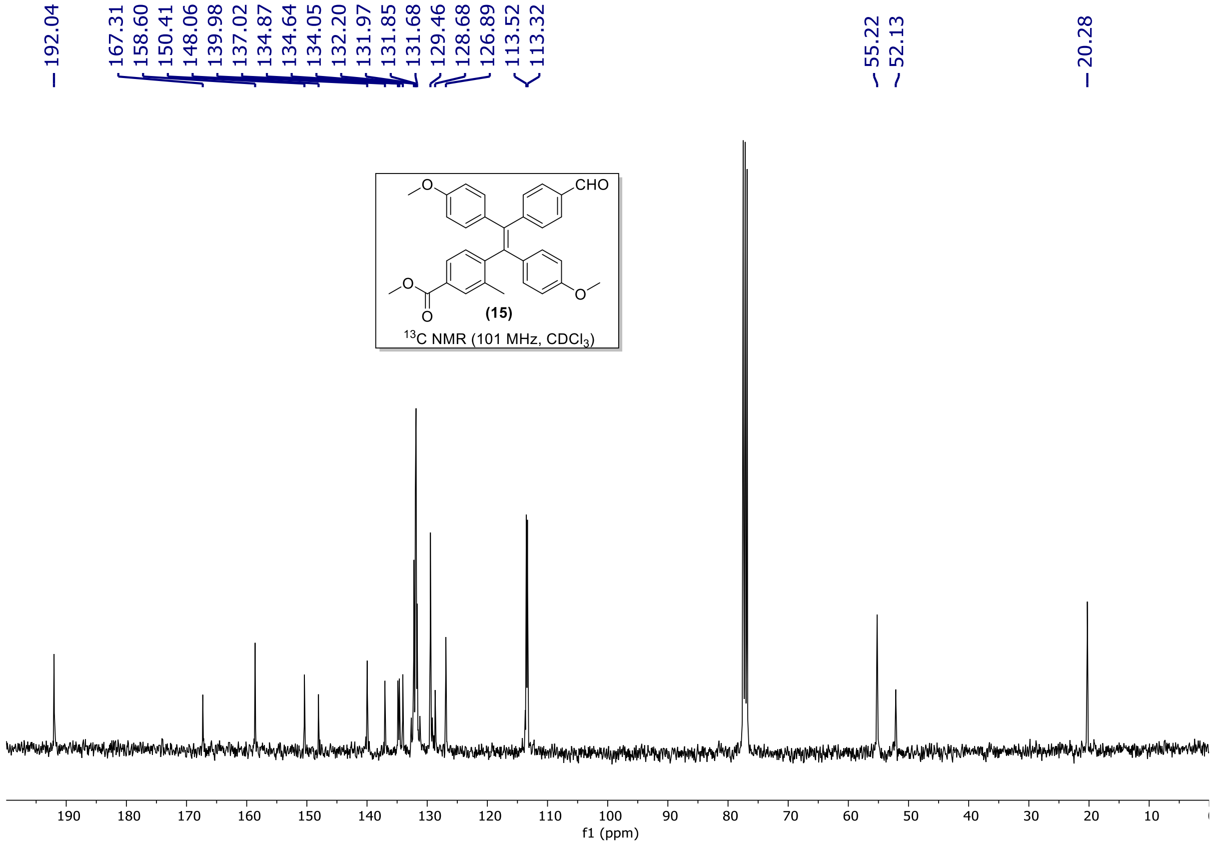


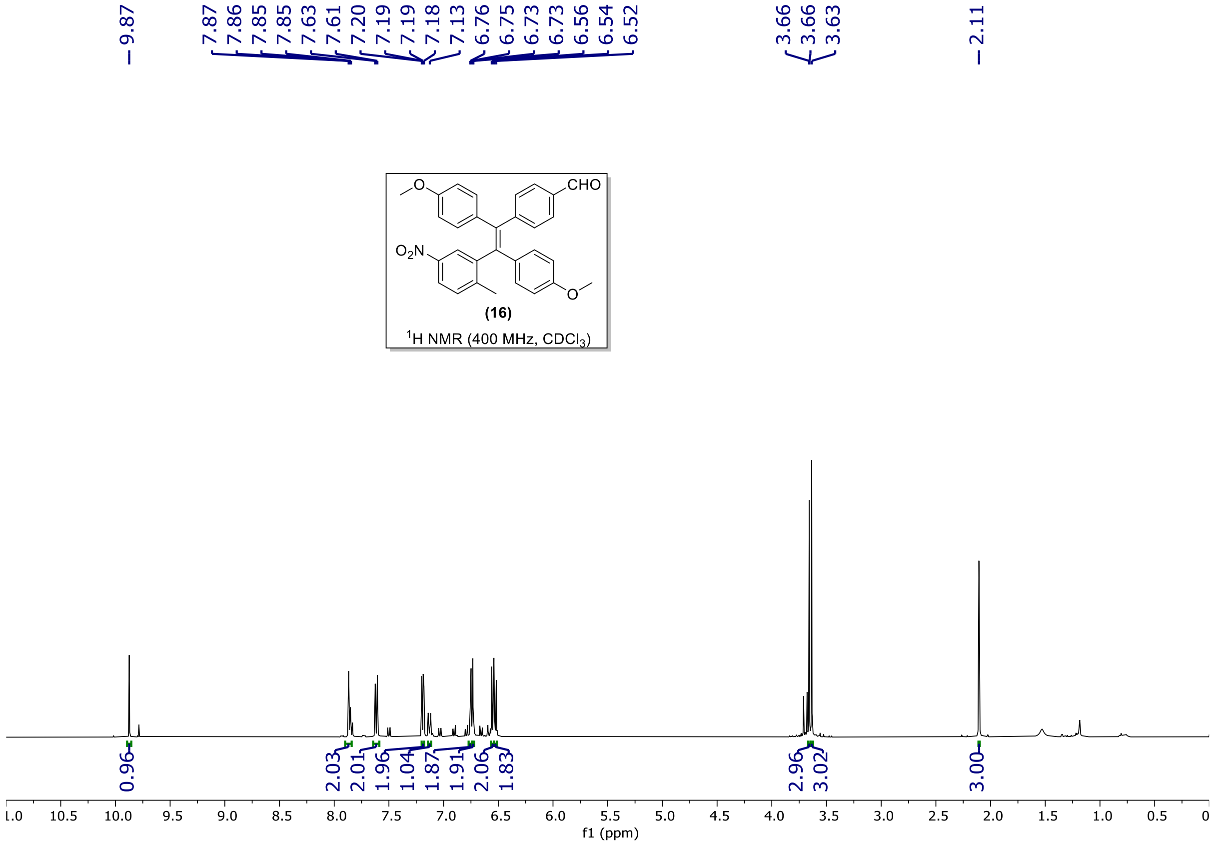
(14)

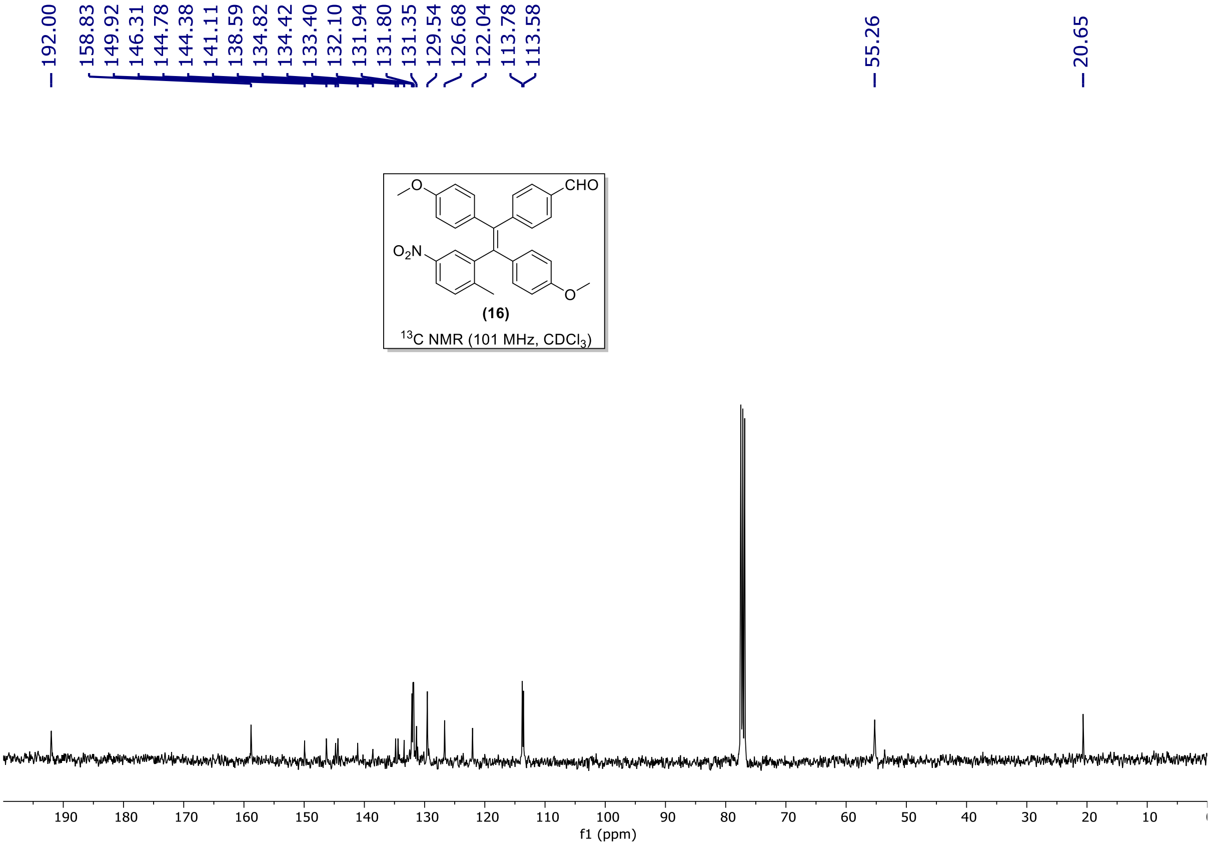
^{13}C NMR (126 MHz, $CDCl_3$)


-118.26
O
CHO
F
O
(14)
19F NMR (471 MHz, CDCl3)
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)


9.86
7.67
7.67
7.65
7.62
7.61
7.60
7.59
7.58
7.18
7.17
7.07
7.04
6.74
6.72
6.53
6.51
6.51
6.49
3.80
3.64
3.63
2.04
O
CHO
O
O
O
(15)
1H NMR (400 MHz, CDCl3)
0.99
1.87
2.01
1.97
1.04
1.80
1.96
2.07
1.95
2.96
2.88
2.96
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

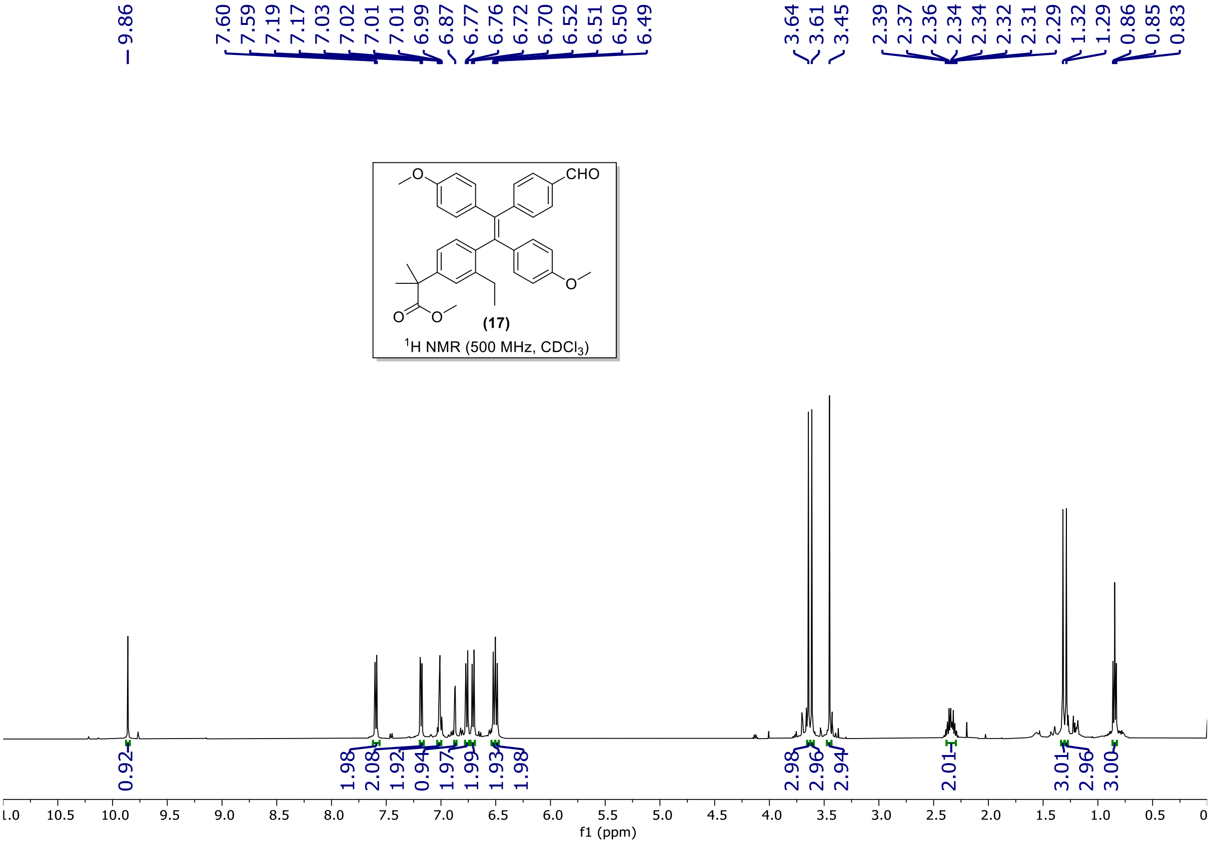

192.04
167.31
158.60
150.41
148.06
139.98
137.02
134.87
134.64
134.05
132.20
131.97
131.85
131.68
129.46
128.68
126.89
113.52
113.32
55.22
52.13
20.28
CHO
O
(15)
^{13}C NMR (101 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.87
7.87
7.86
7.85
7.85
7.63
7.61
7.20
7.19
7.19
7.18
7.13
6.76
6.75
6.73
6.73
6.56
6.54
6.52
3.66
3.66
3.63
2.11
CHO
O$_2$N
O
(16)
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
2.03
2.01
1.96
1.04
1.87
1.91
2.06
1.83
2.96
3.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



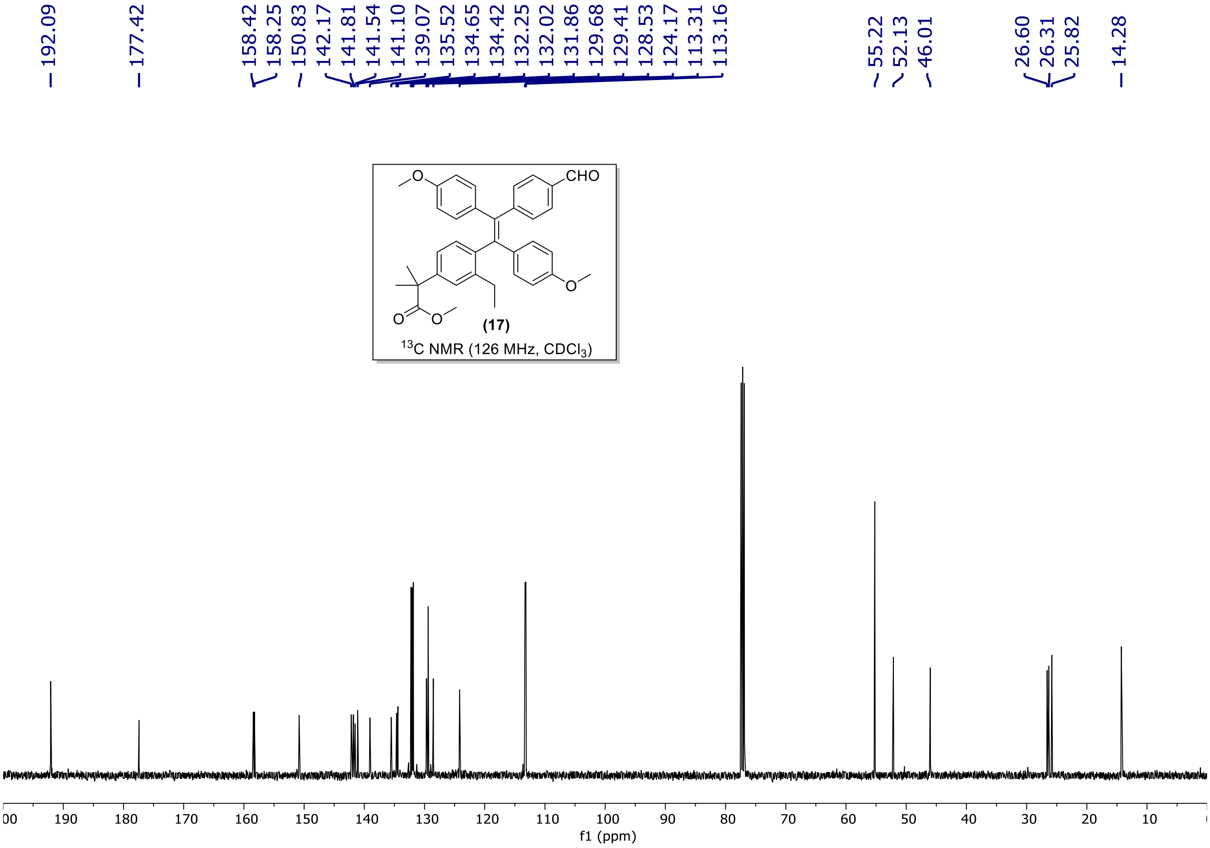
(16)

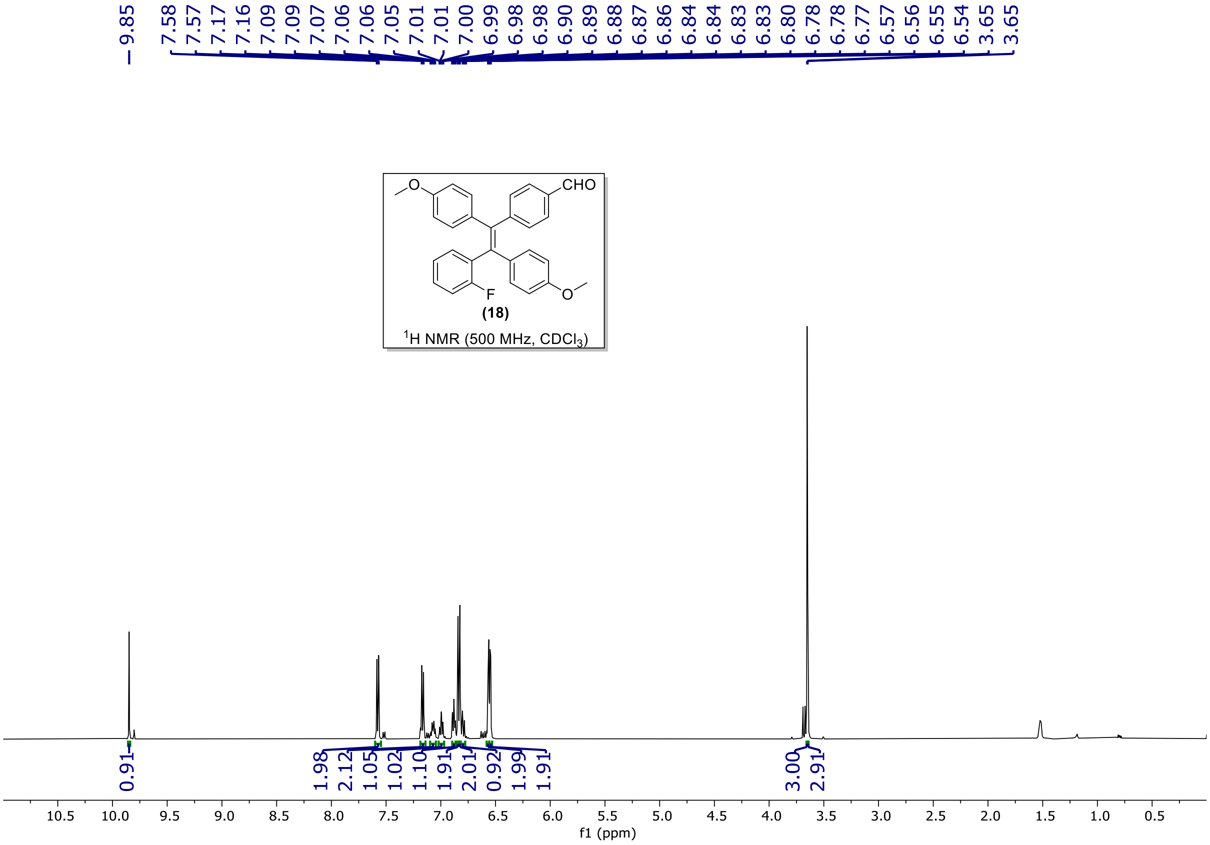
^{13}C NMR (101 MHz, $CDCl_3$)

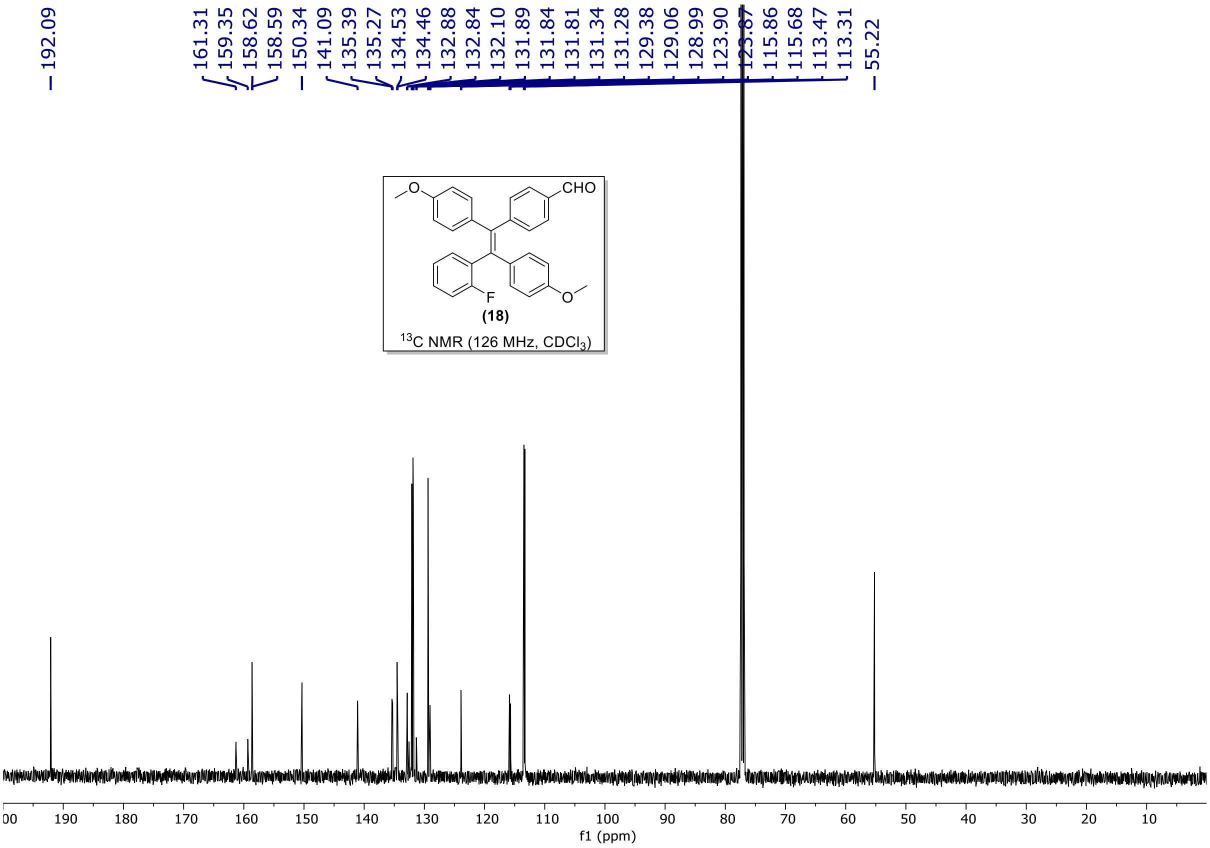


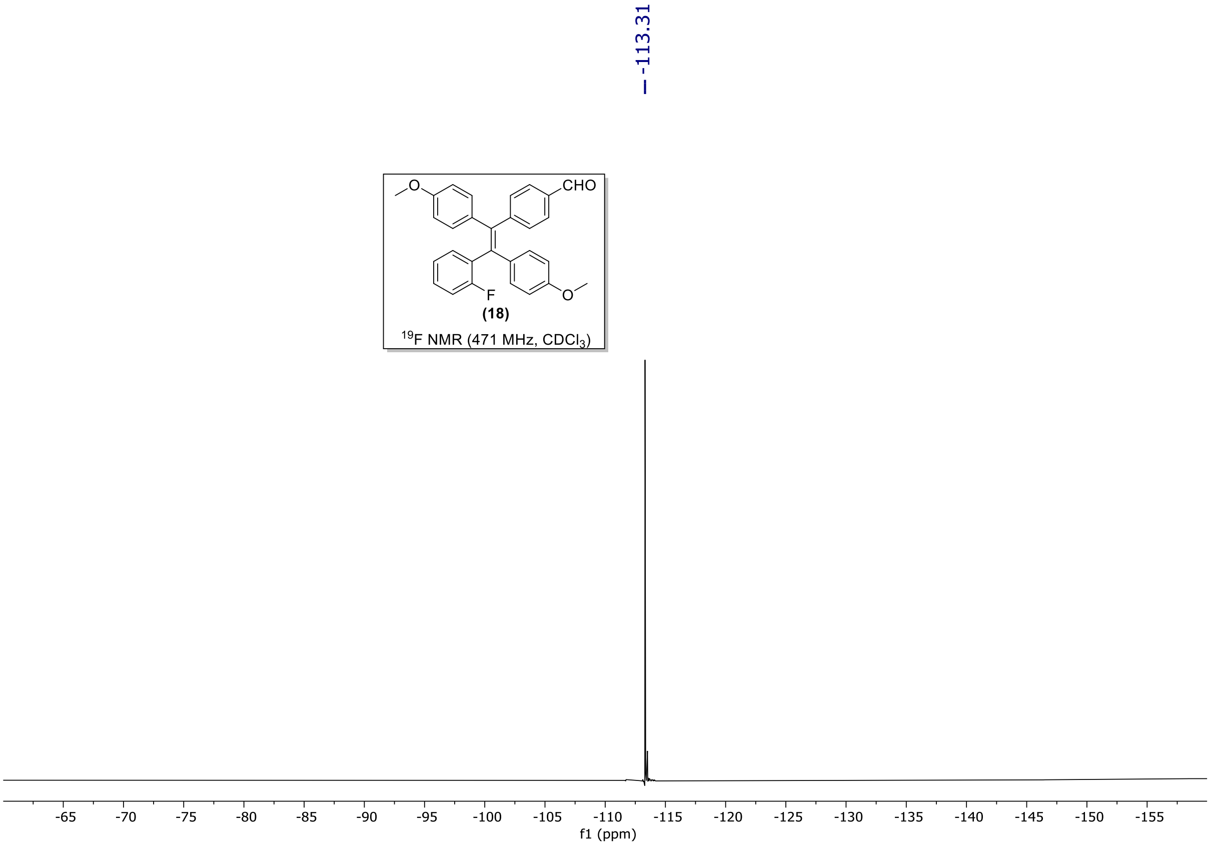
(17)

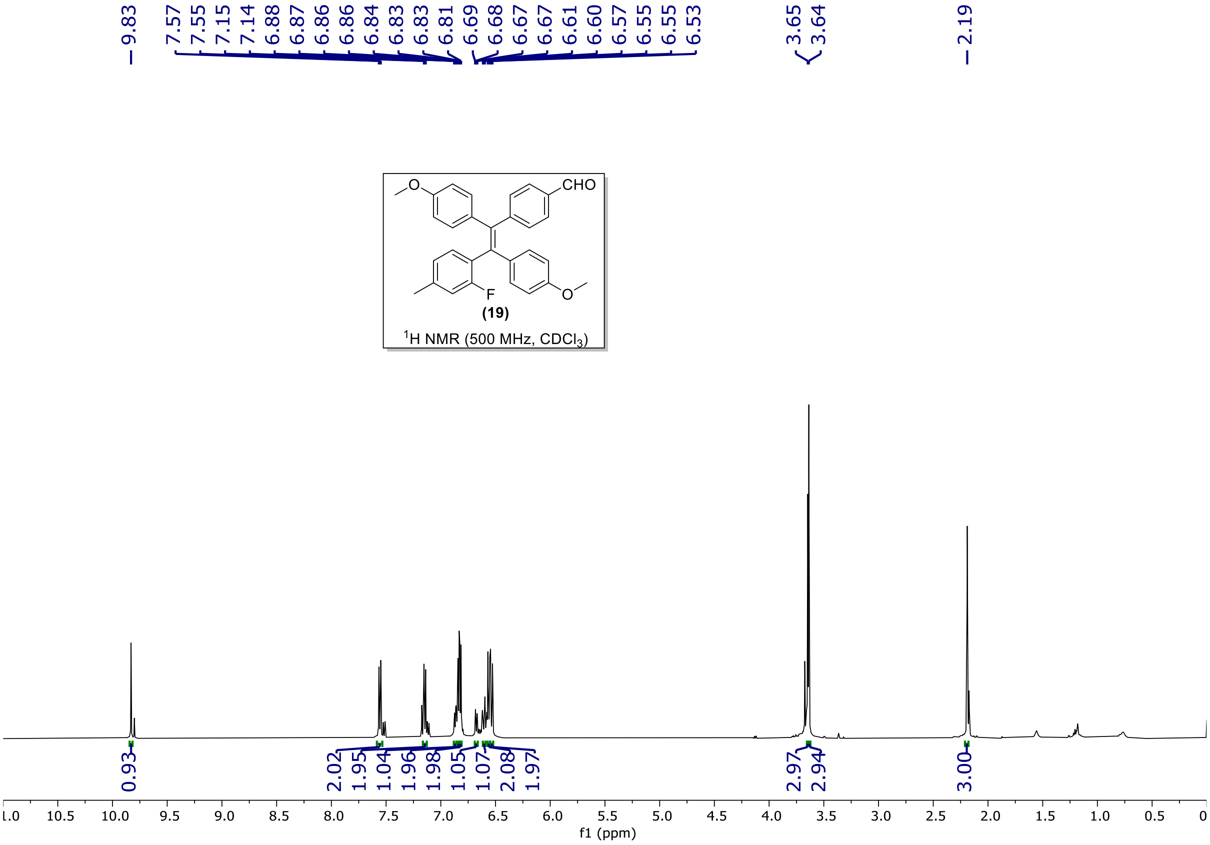
^{1}H NMR (500 MHz, $CDCl_3$)

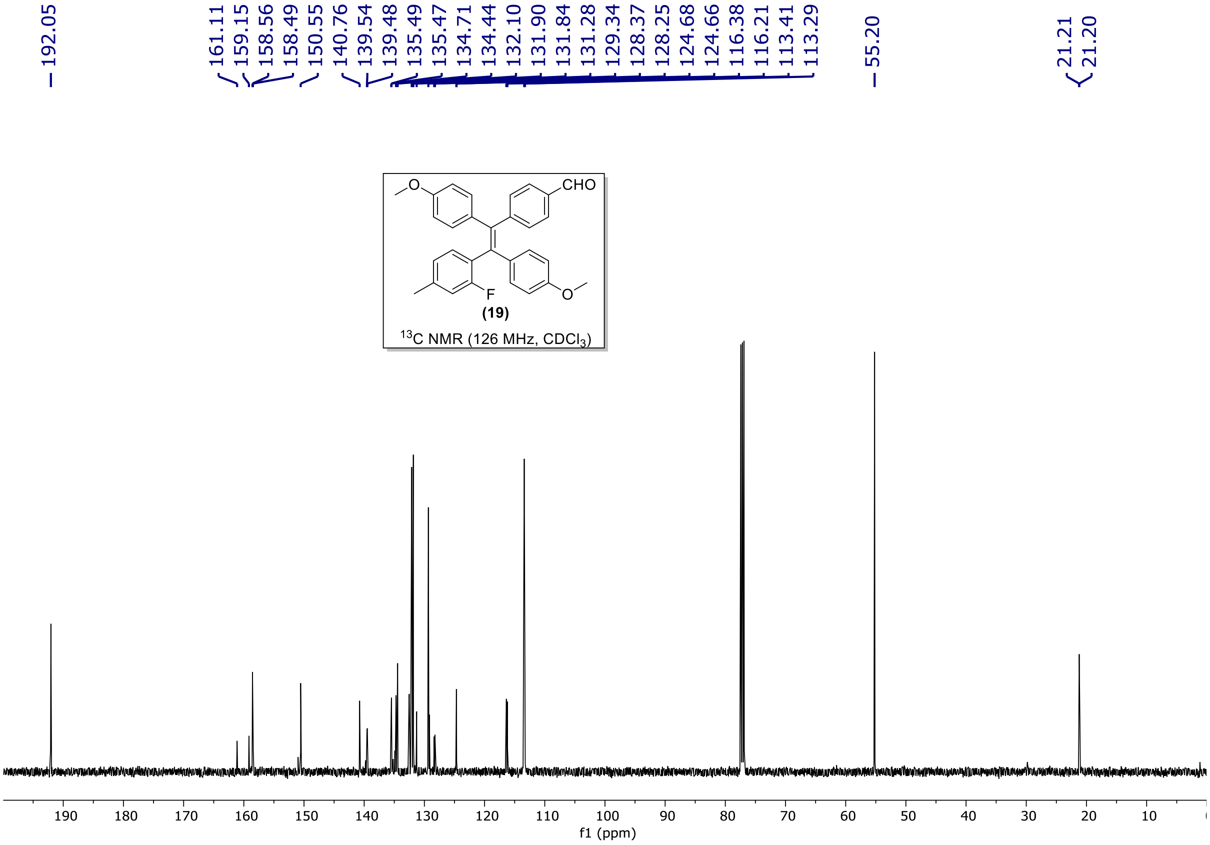

192.09
177.42
158.42
158.25
150.83
142.17
141.81
141.54
141.10
139.07
135.52
134.65
134.42
132.25
132.02
131.86
129.68
129.41
128.53
124.17
113.31
113.16
55.22
52.13
46.01
26.60
26.31
25.82
14.28
CHO
O
O
O
O
(17)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

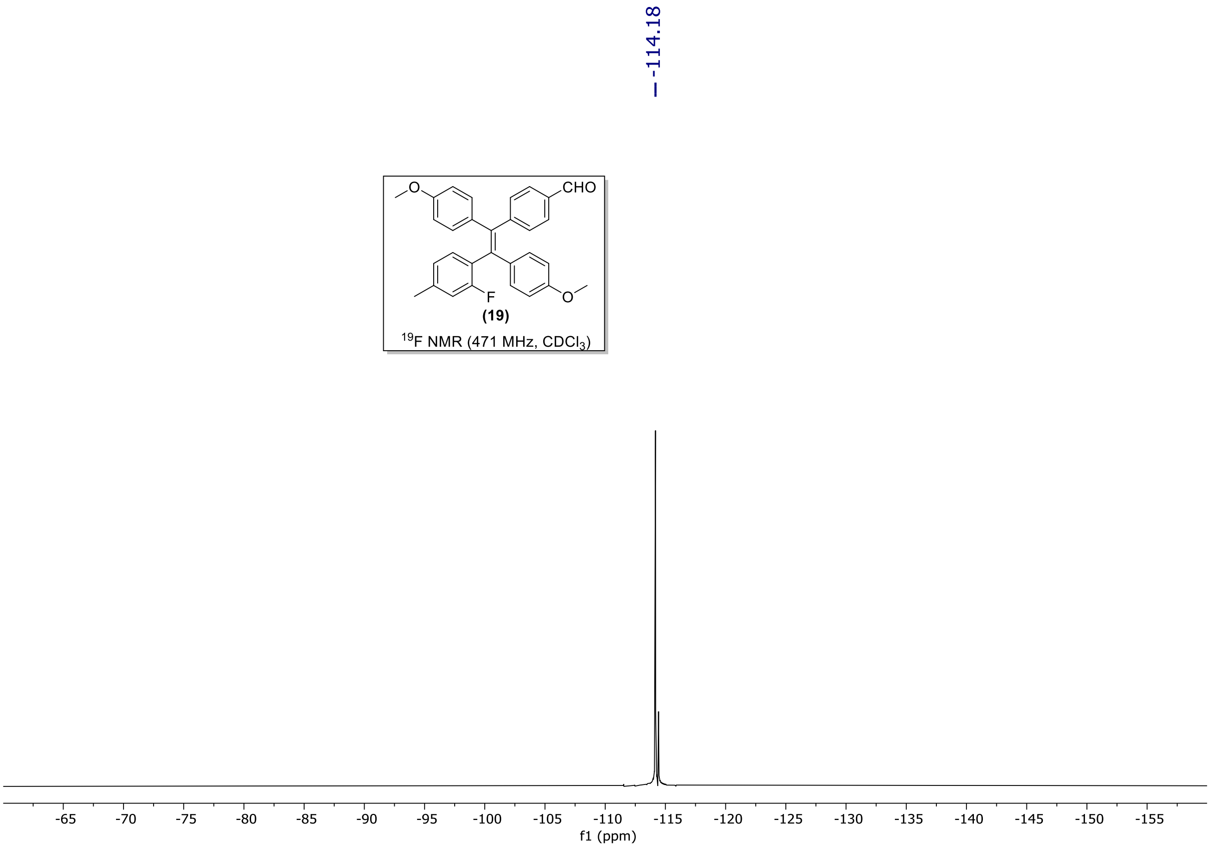

9.85
7.58
7.57
7.17
7.16
7.09
7.09
7.07
7.06
7.06
7.05
7.01
7.01
7.00
6.99
6.98
6.98
6.90
6.89
6.88
6.87
6.86
6.84
6.84
6.83
6.83
6.80
6.78
6.78
6.77
6.57
6.56
6.55
6.54
3.65
3.65
O
CHO
F
O
(18)
^{1}H NMR (500 MHz, CDCl$_3$)
0.91
1.98
2.12
1.05
1.02
1.10
1.91
2.01
0.92
1.99
1.91
3.00
2.91
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

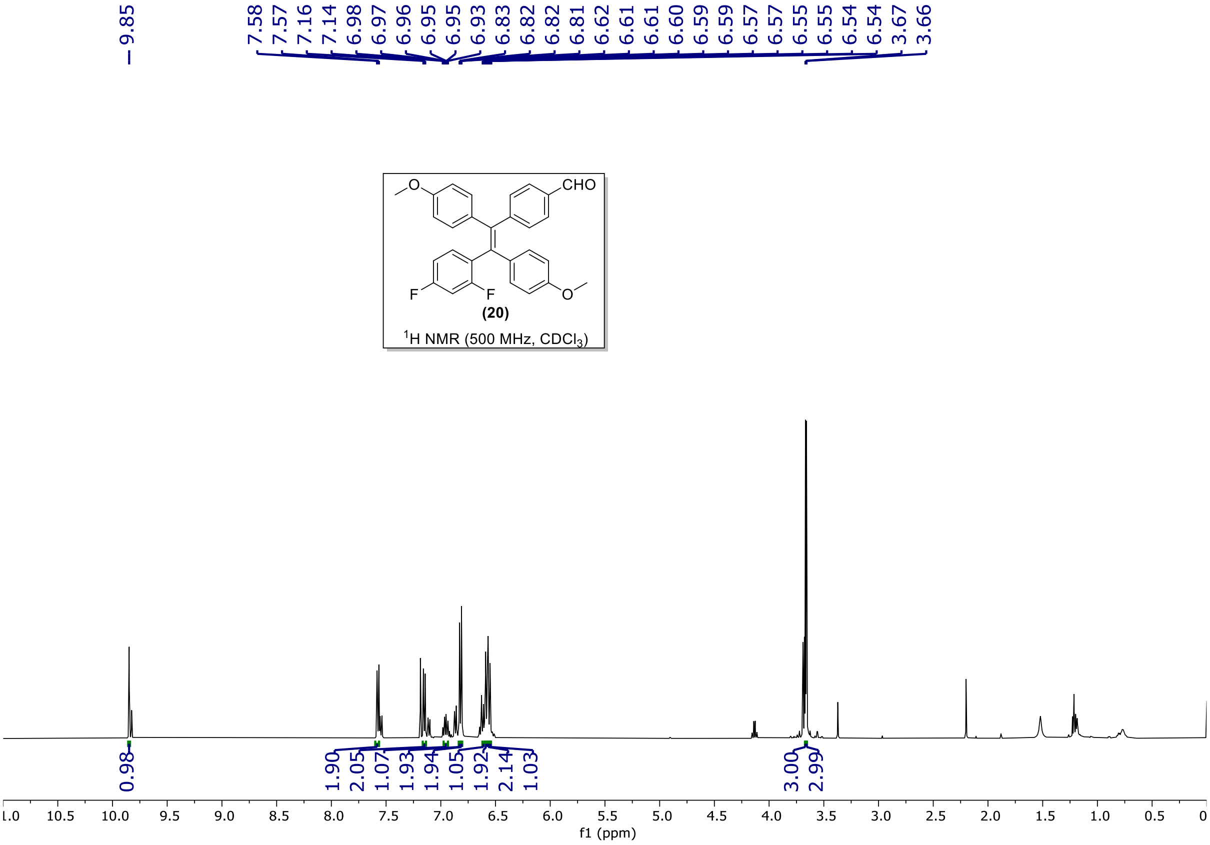

192.09
161.31
159.35
158.62
158.59
150.34
141.09
135.39
135.27
134.53
134.46
132.88
132.84
132.10
131.89
131.84
131.81
131.34
131.28
129.38
129.06
128.99
123.90
123.87
115.86
115.68
113.47
113.31
55.22
CHO
O
O
F
(18)
13C NMR (126 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

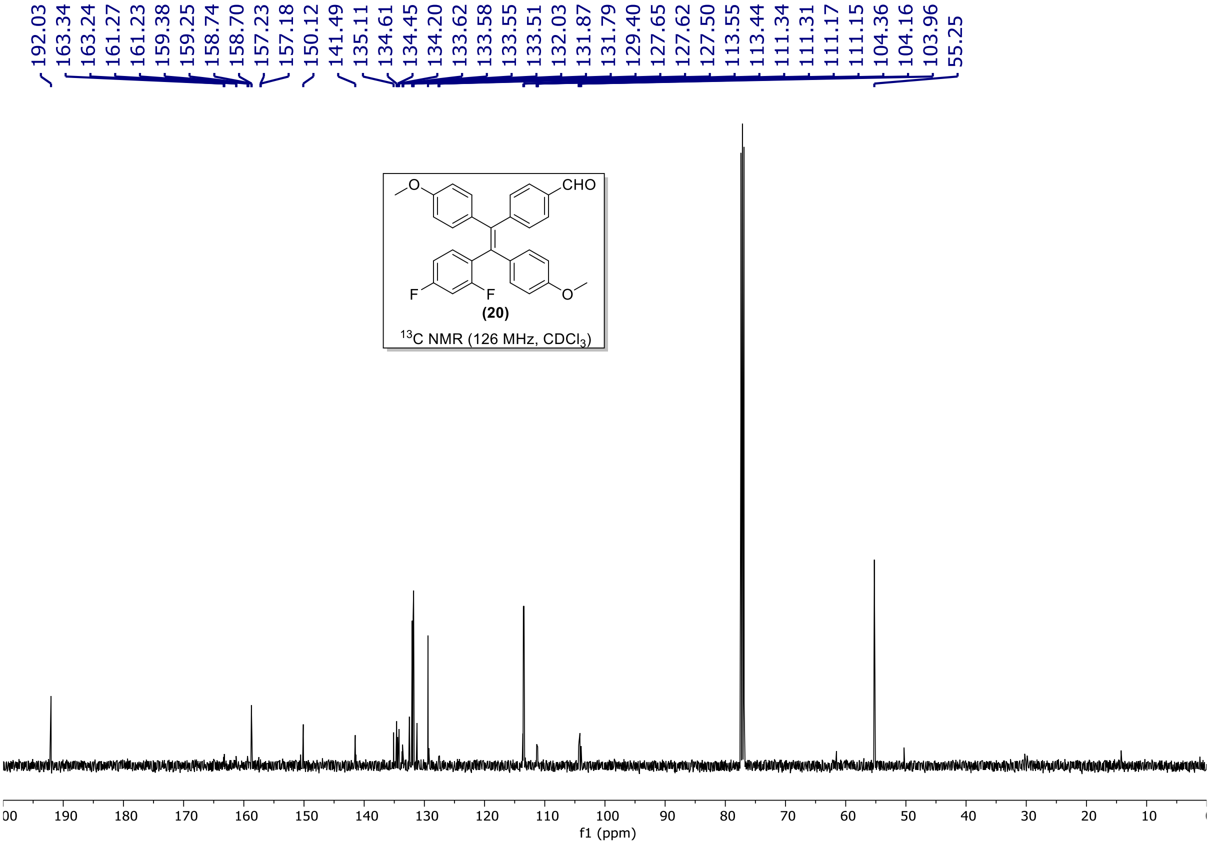

-113.31
CHO
O
O
F
(18)
19F NMR (471 MHz, CDCl3)
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

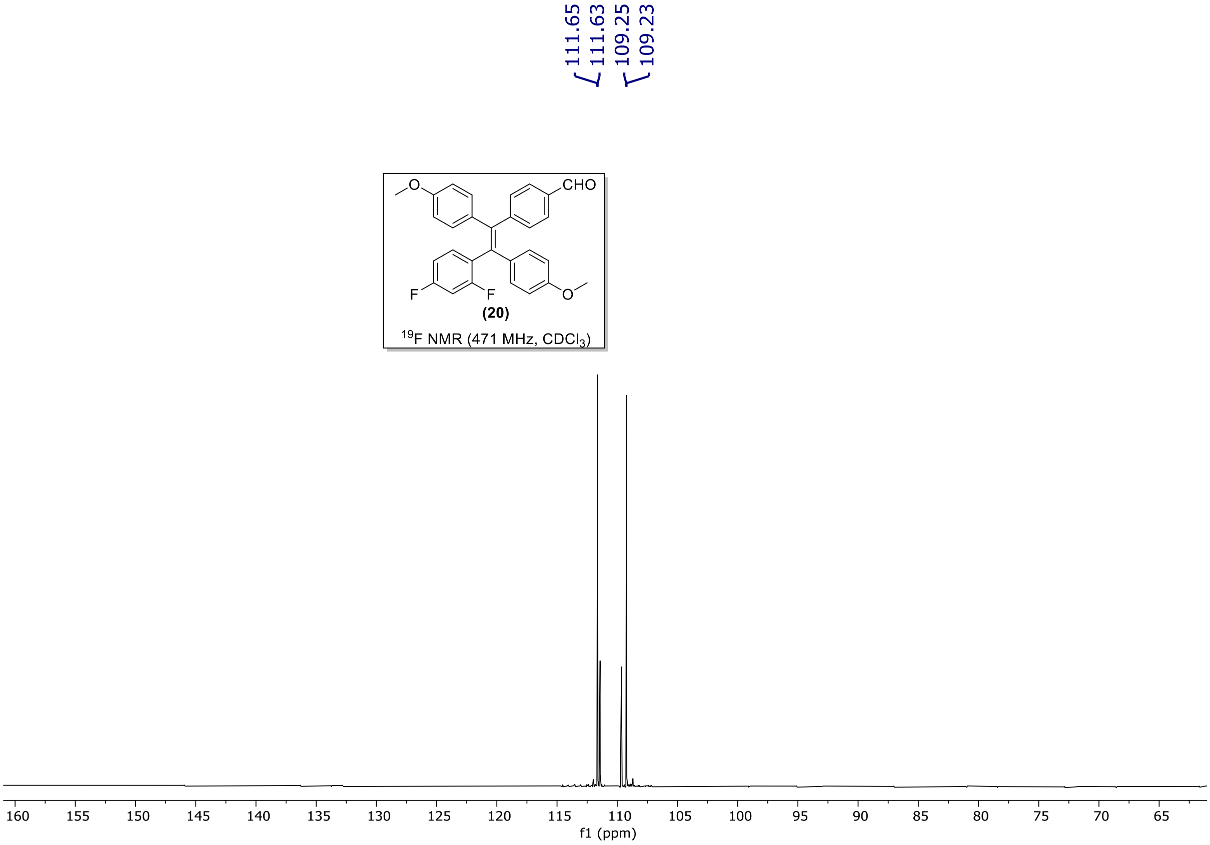

9.83
7.57
7.55
7.15
7.14
6.88
6.87
6.86
6.86
6.84
6.83
6.83
6.81
6.69
6.68
6.67
6.67
6.61
6.60
6.57
6.55
6.55
6.53
3.65
3.64
2.19
CHO
O
O
F
(19)
1H NMR (500 MHz, CDCl3)
0.93
2.02
1.95
1.04
1.96
1.98
1.05
1.07
2.08
1.97
2.97
2.94
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

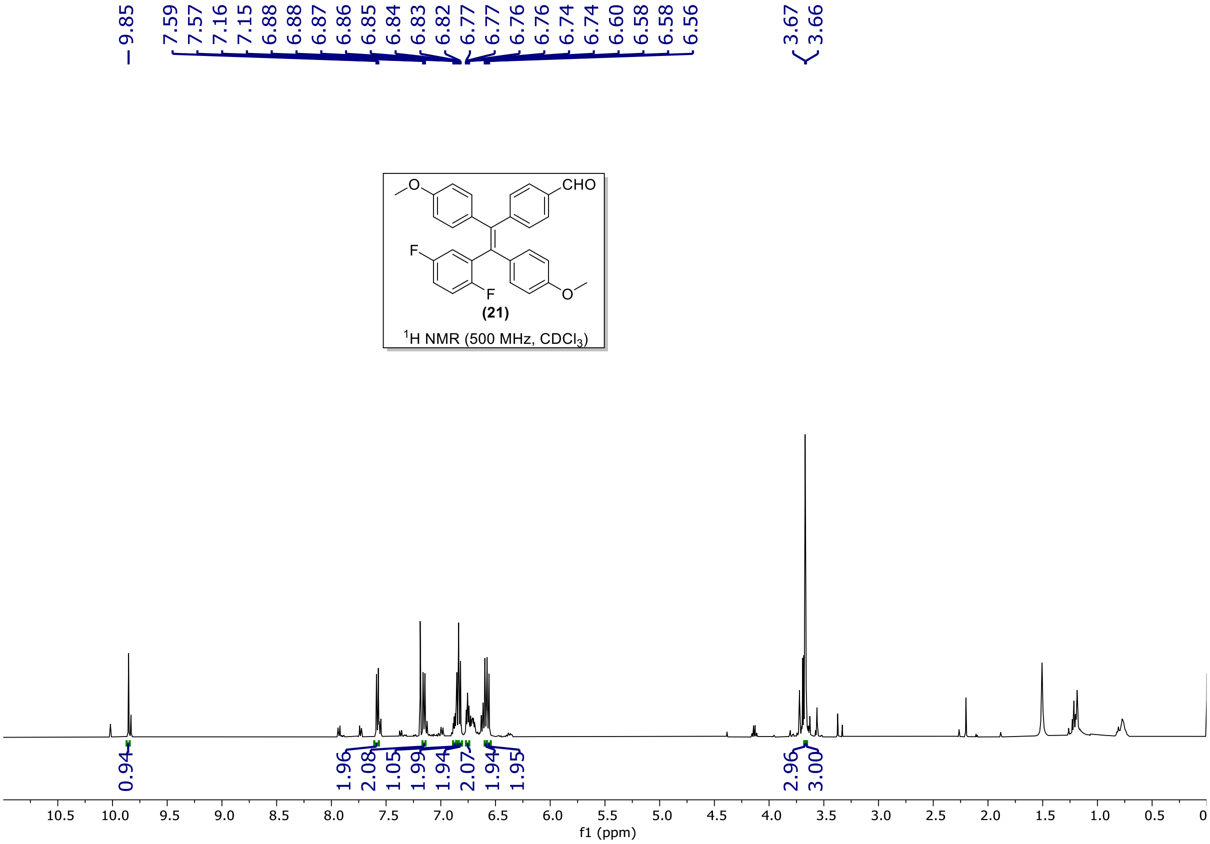

192.05
161.11
159.15
158.56
158.49
150.55
140.76
139.54
139.48
135.49
135.47
134.71
134.44
132.10
131.90
131.84
131.28
129.34
128.37
128.25
124.68
124.66
116.38
116.21
113.41
113.29
55.20
21.21
21.20
CHO
O
O
F
(19)
13C NMR (126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

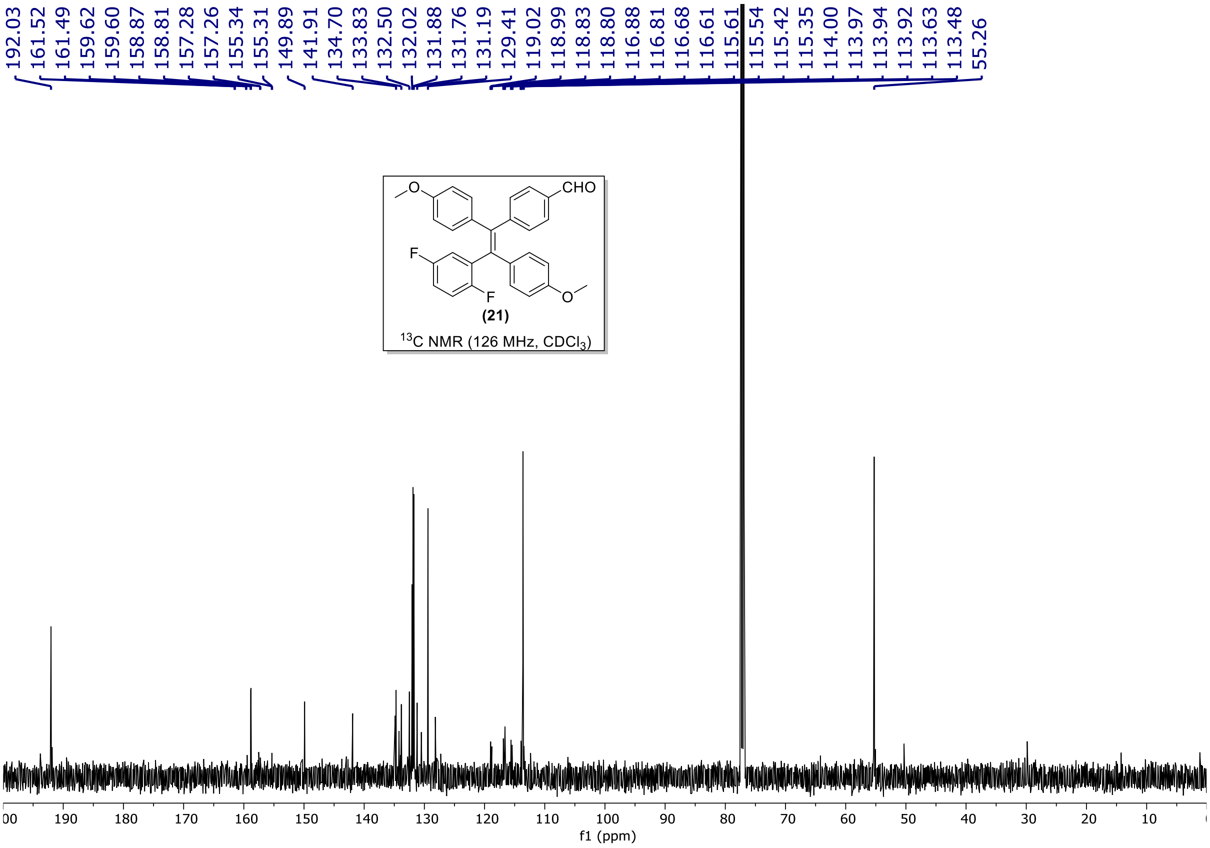

-114.18
CHO
O
F
(19)
^{19}F NMR (471 MHz, CDCl$_3$)
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

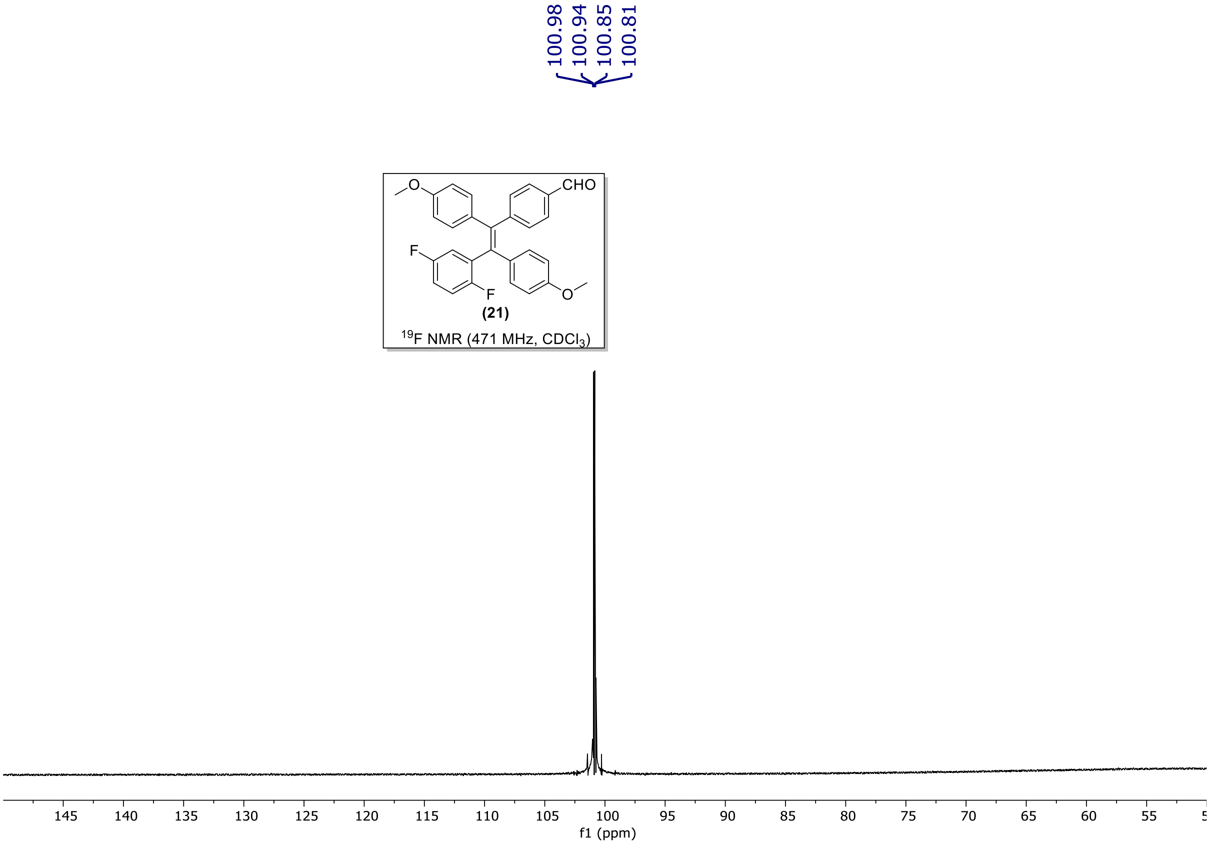

9.85
7.58
7.57
7.16
7.14
6.98
6.97
6.96
6.95
6.95
6.93
6.83
6.82
6.82
6.81
6.62
6.61
6.61
6.60
6.59
6.59
6.57
6.57
6.55
6.55
6.54
6.54
3.67
3.66
CHO
O
F
F
(20)
^{1}H NMR (500 MHz, CDCl$_3$)
0.98
1.90
2.05
1.07
1.93
1.94
1.05
1.92
2.14
1.03
3.00
2.99
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

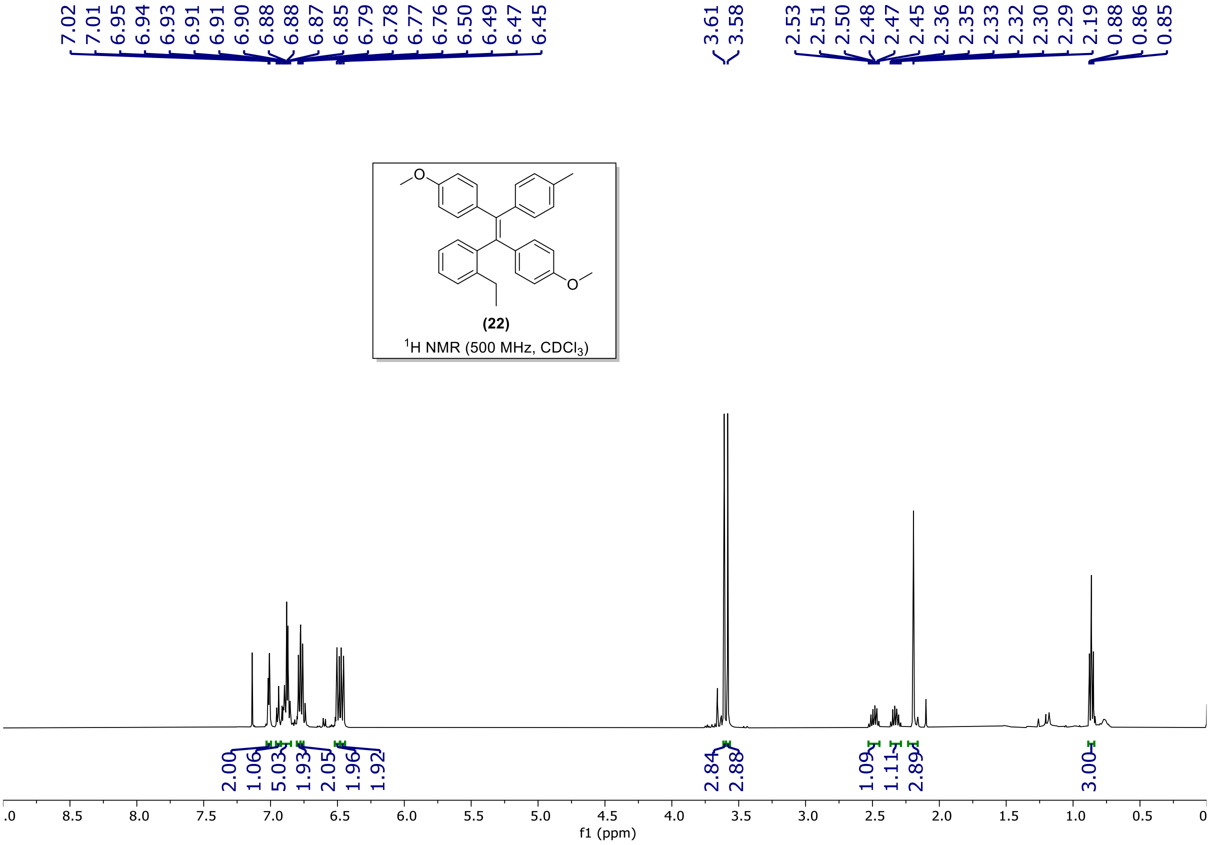

192.03
163.34
163.24
161.27
161.23
159.38
159.25
158.74
158.70
157.23
157.18
150.12
141.49
135.11
134.61
134.45
134.20
133.62
133.58
133.55
133.51
132.03
131.87
131.79
129.40
127.65
127.62
127.50
113.55
113.44
111.34
111.31
111.17
111.15
104.36
104.16
103.96
55.25
CHO
O
F
F
O
(20)
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

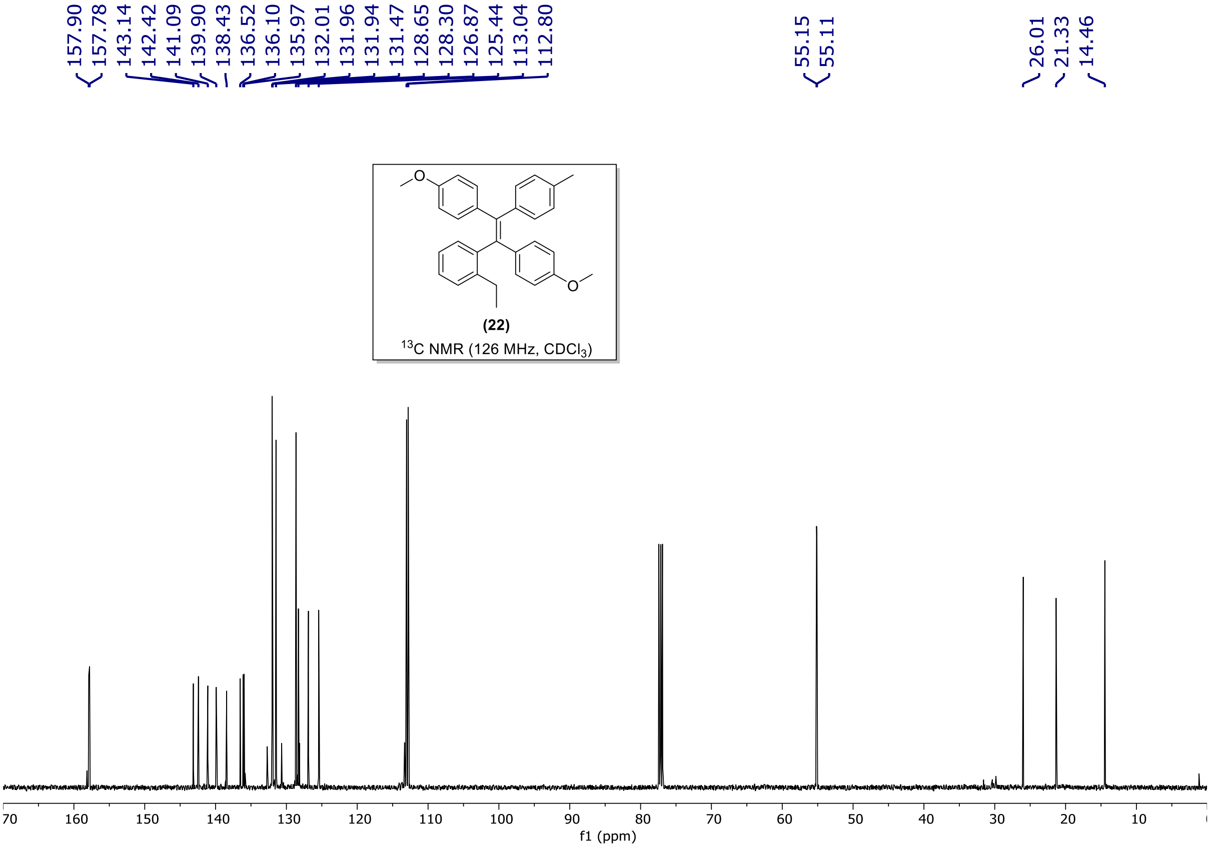

111.65
111.63
109.25
109.23
CHO
O
F
F
O
(20)
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65


9.85
7.59
7.57
7.16
7.15
6.88
6.88
6.87
6.86
6.85
6.84
6.83
6.82
6.77
6.77
6.76
6.76
6.74
6.74
6.60
6.58
6.58
6.56
3.67
3.66
O
CHO
F
F
O
(21)
^{1}H NMR (500 MHz, CDCl$_3$)
0.94
1.96
2.08
1.05
1.99
1.94
2.07
1.94
1.95
2.96
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


192.03
161.52
161.49
159.62
159.60
158.87
158.81
157.28
157.26
155.34
155.31
149.89
141.91
134.70
133.83
132.50
132.02
131.88
131.76
131.19
129.41
119.02
118.99
118.83
118.80
116.88
116.81
116.68
116.61
115.61
115.54
115.42
115.35
114.00
113.97
113.94
113.92
113.63
113.48
55.26
O
CHO
F
F
O
(21)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

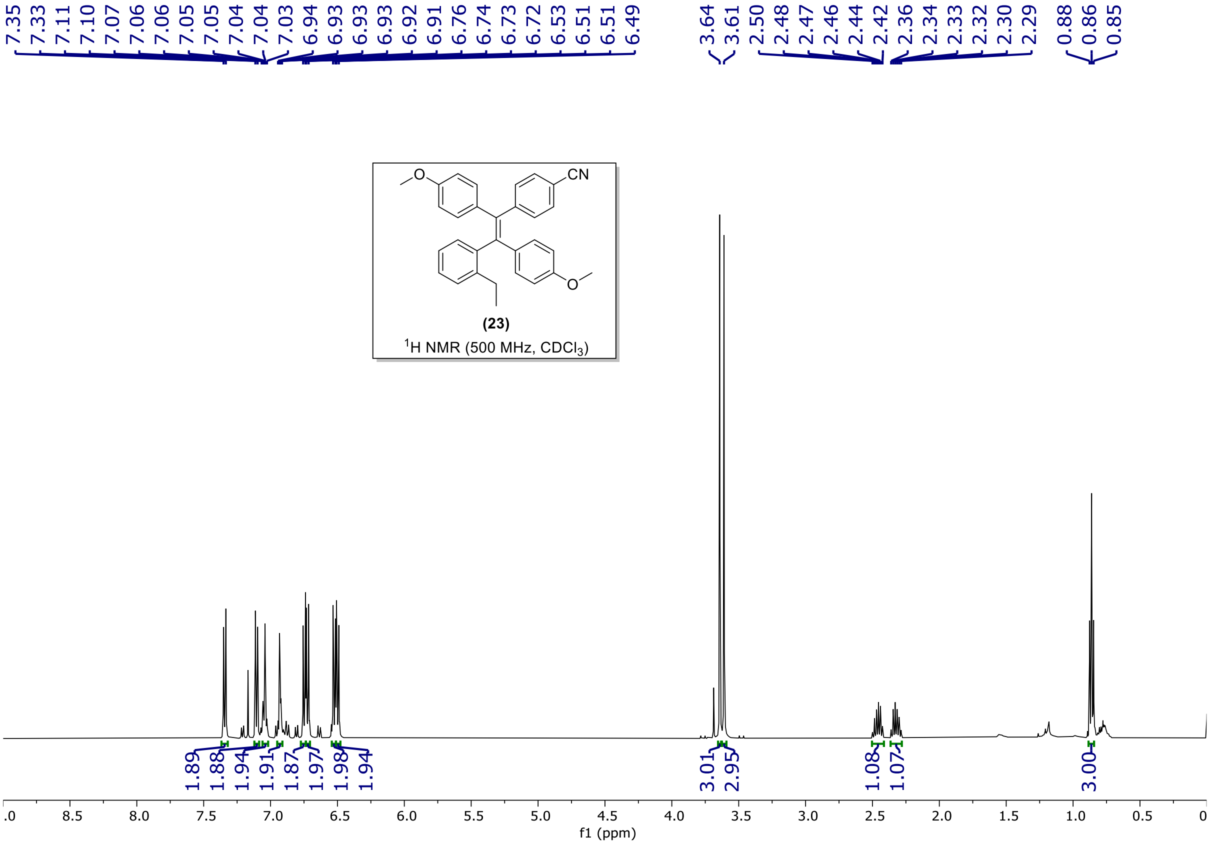

100.98
100.94
100.85
100.81
CHO
O
O
F
F
(21)
^{19}F NMR (471 MHz, CDCl$_3$)
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)


7.02
7.01
6.95
6.94
6.93
6.91
6.91
6.90
6.88
6.88
6.87
6.85
6.79
6.78
6.77
6.76
6.50
6.49
6.47
6.45
3.61
3.58
2.53
2.51
2.50
2.48
2.47
2.45
2.36
2.35
2.33
2.32
2.30
2.29
2.19
0.88
0.86
0.85
O
O
(22)
^{1}H NMR (500 MHz, CDCl$_3$)
2.00
1.06
5.03
1.93
2.05
1.96
1.92
2.84
2.88
1.09
1.11
2.89
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



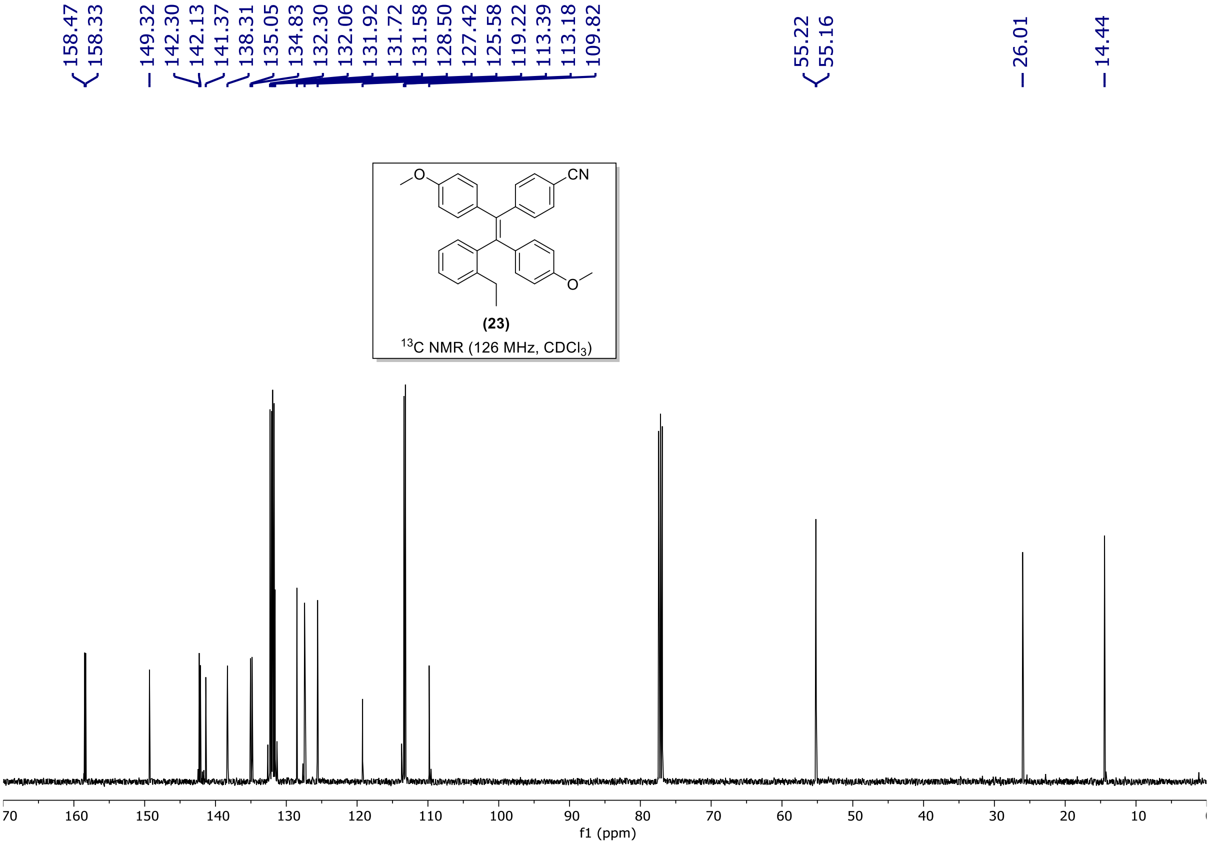
(22)

^{13}C NMR (126 MHz, $CDCl_3$)



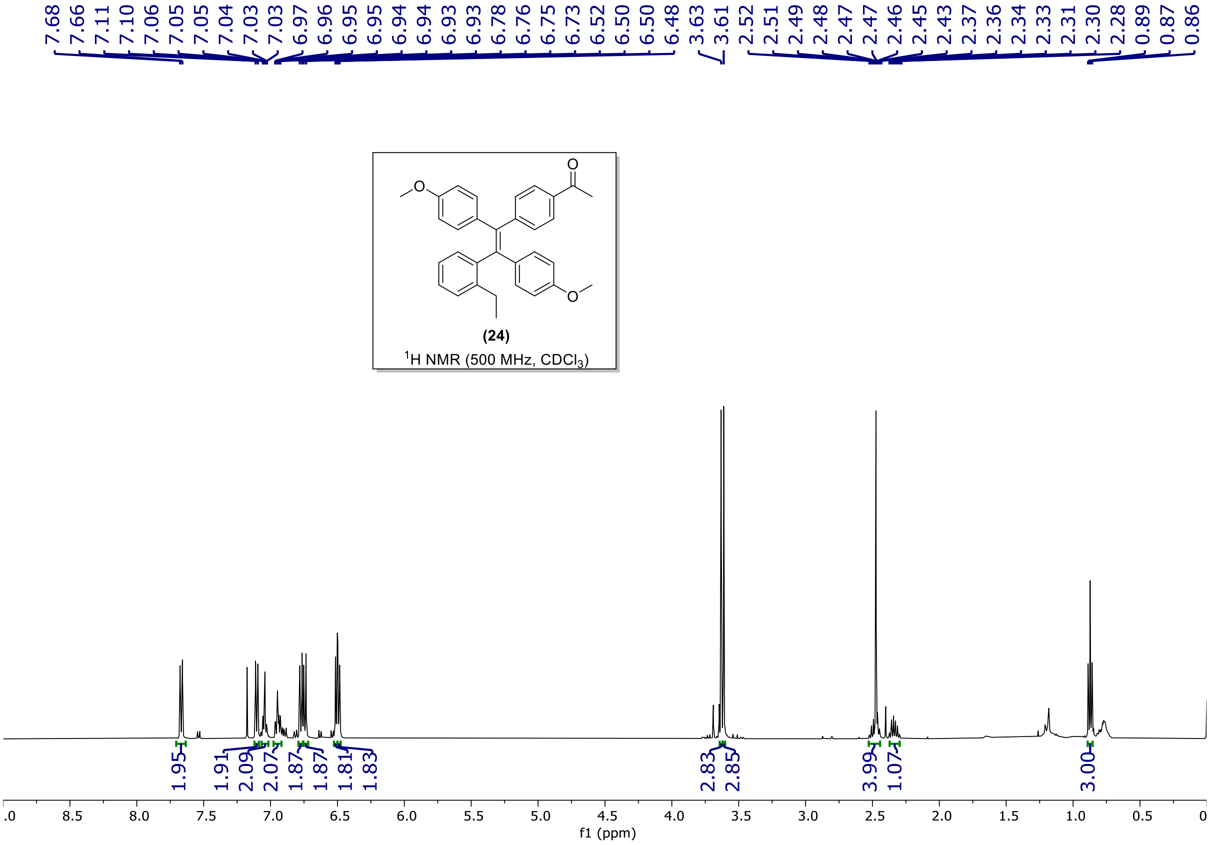
(23)

^{1}H NMR (500 MHz, $CDCl_3$)



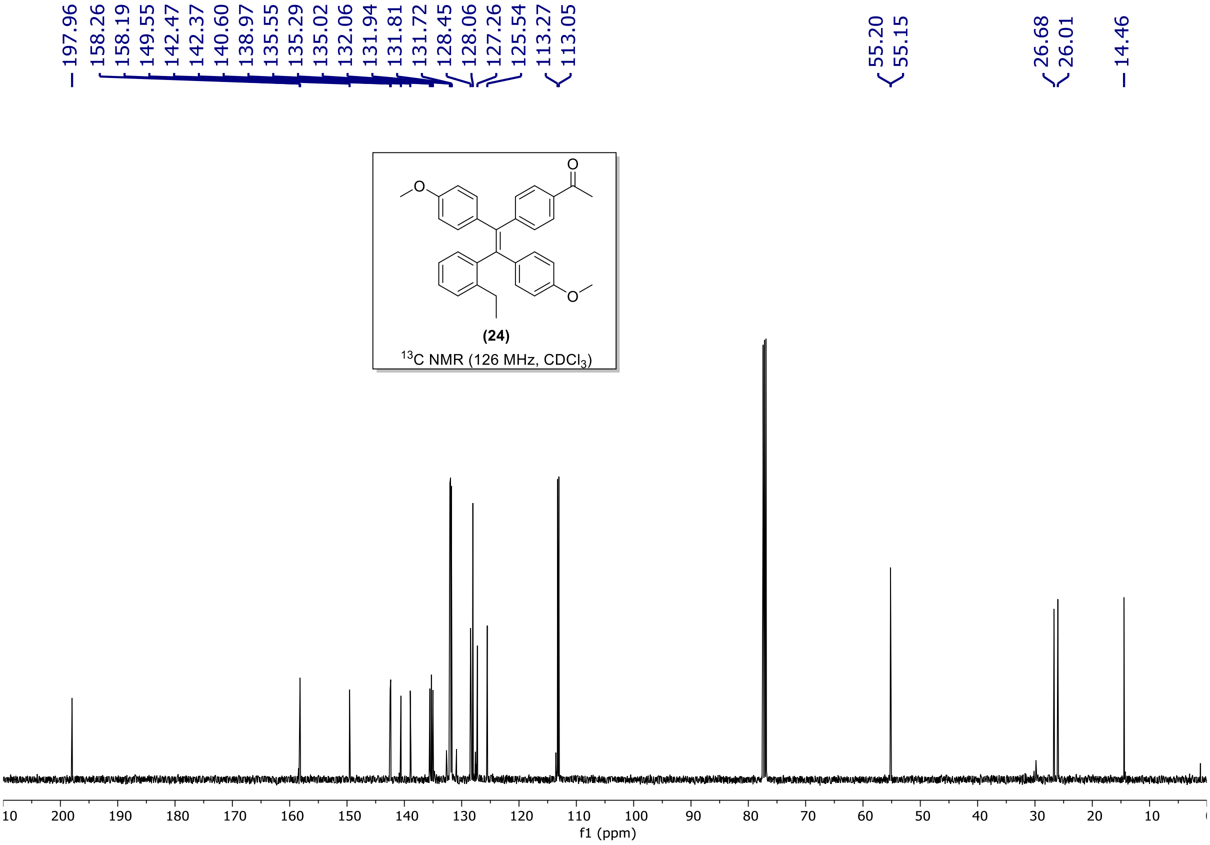
(23)

^{13}C NMR (126 MHz, CDCl$_3$)



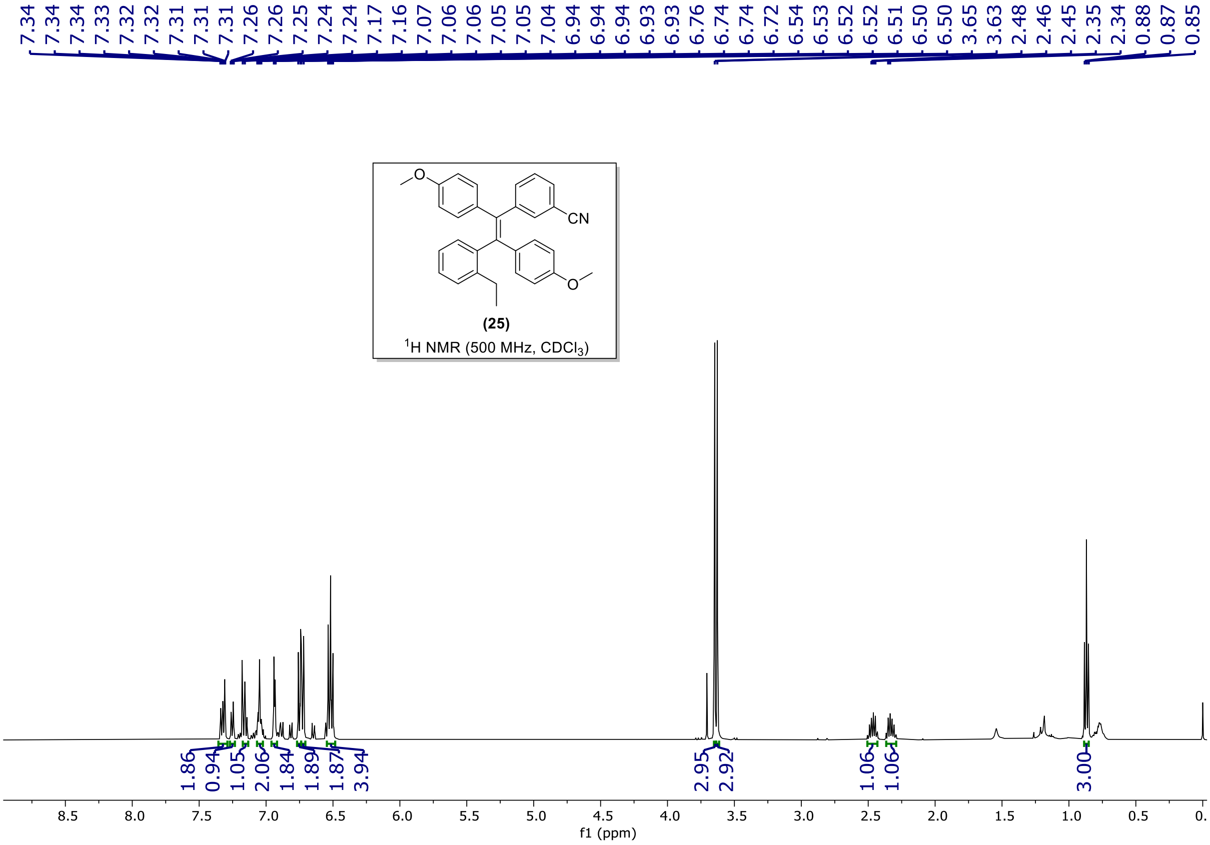
(24)

^{1}H NMR (500 MHz, CDCl$_3$)



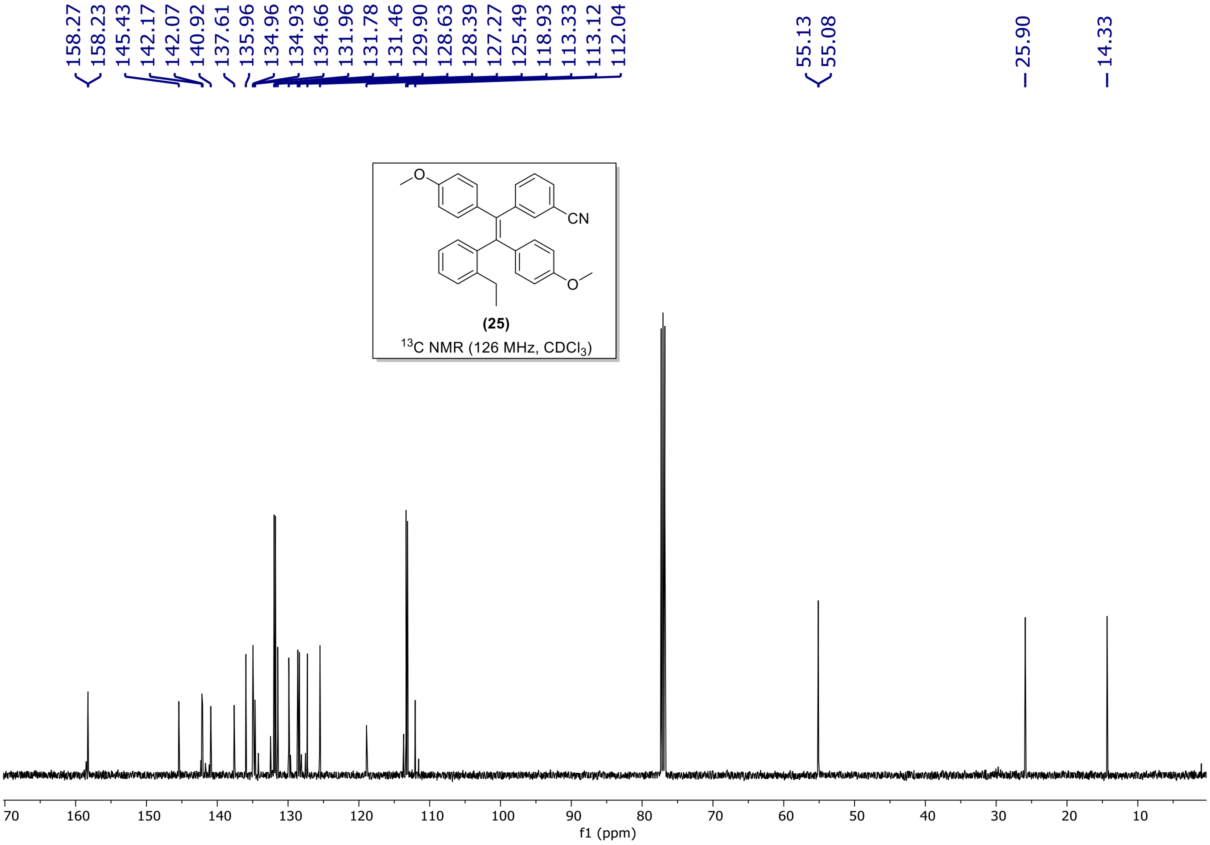
(24)

^{13}C NMR (126 MHz, $CDCl_3$)



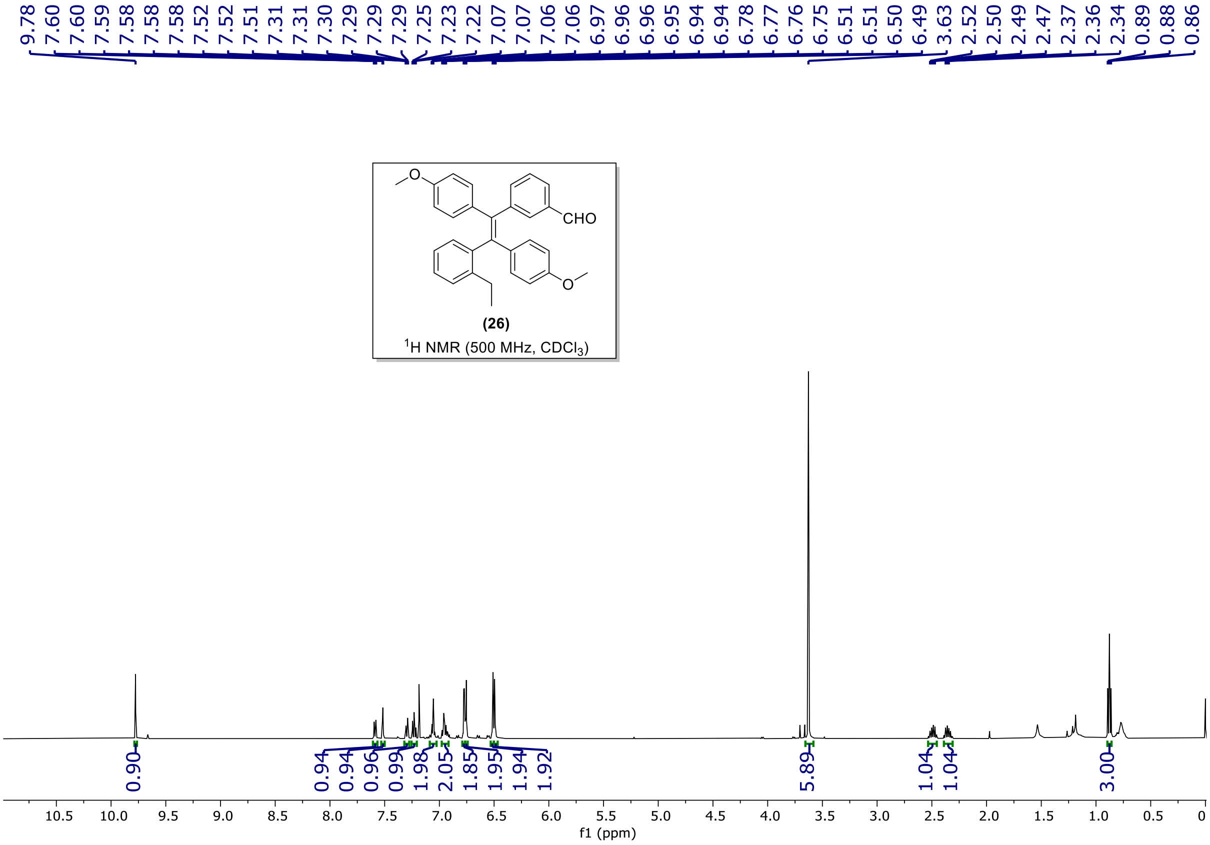
(25)

^{1}H NMR (500 MHz, $CDCl_3$)



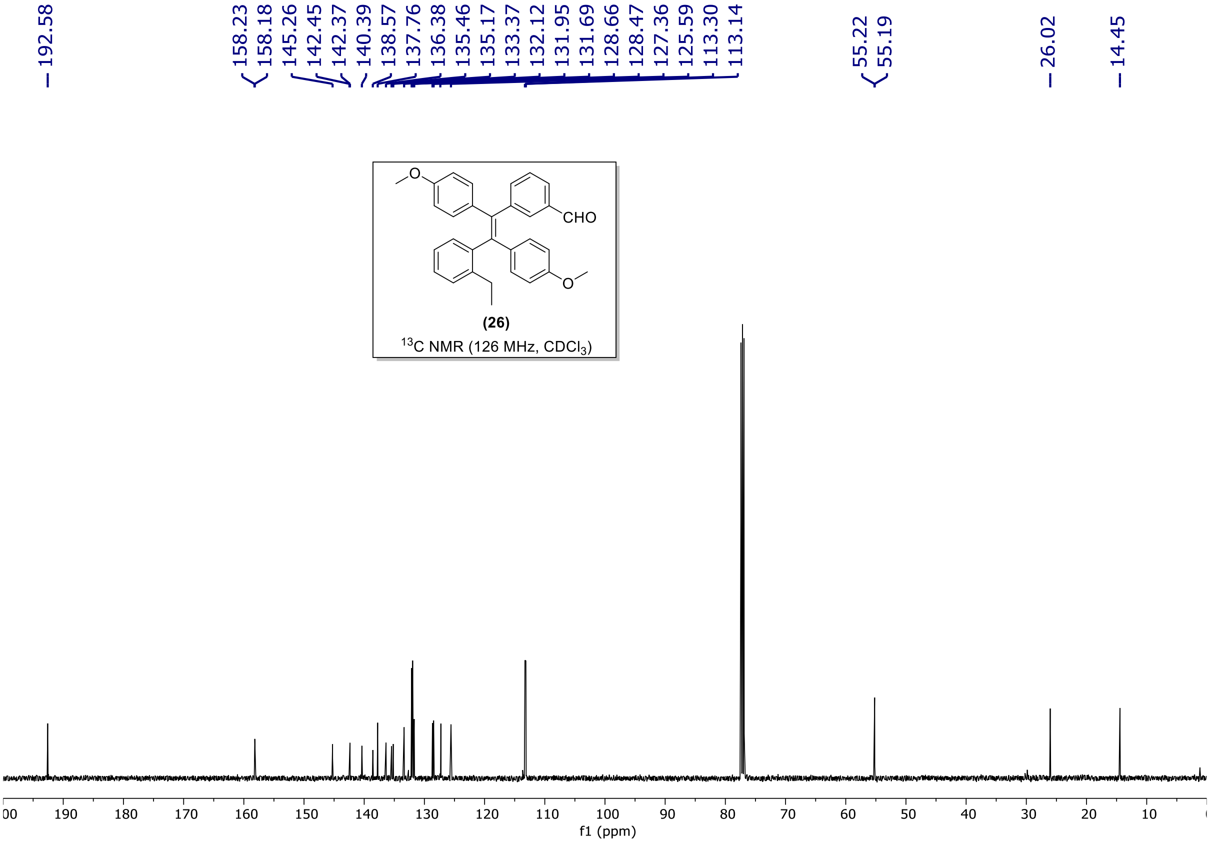
(25)

^{13}C NMR (126 MHz, $CDCl_3$)



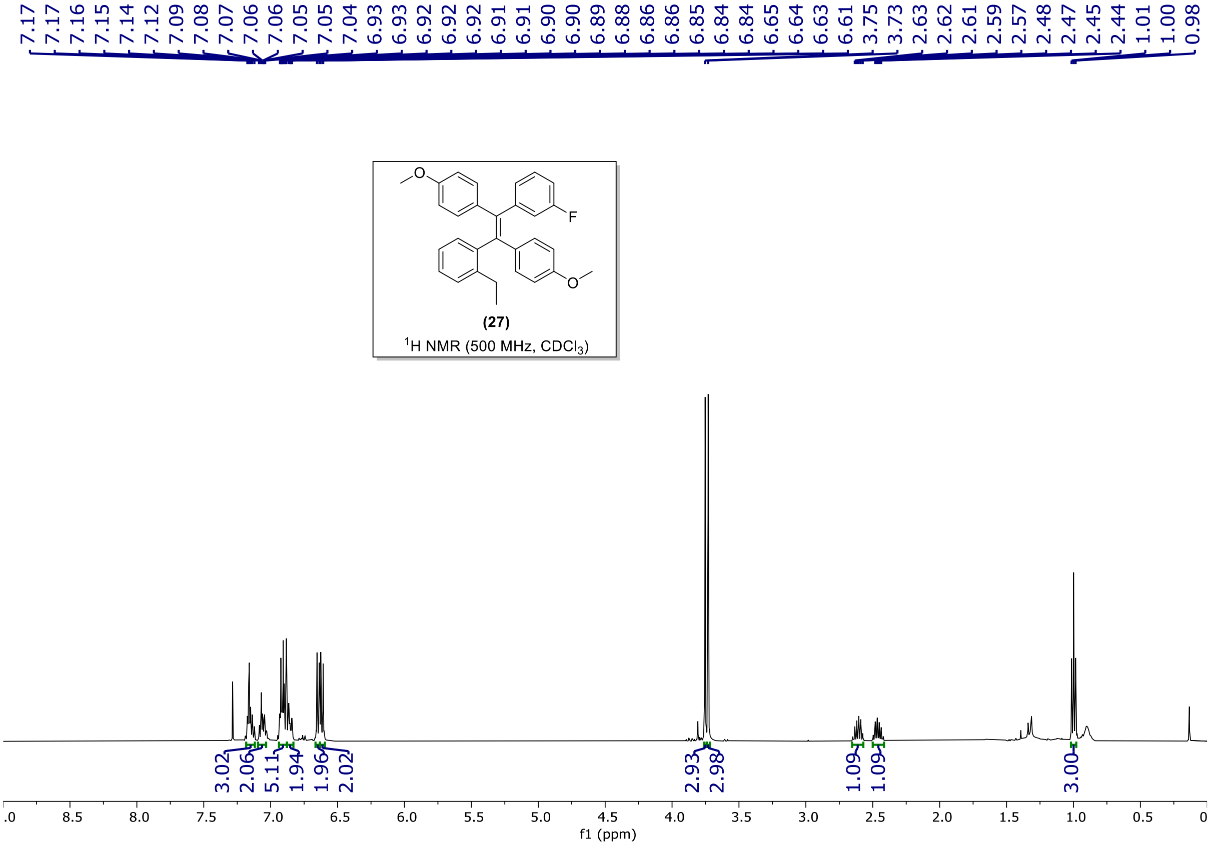
(26)

^{1}H NMR (500 MHz, $CDCl_3$)



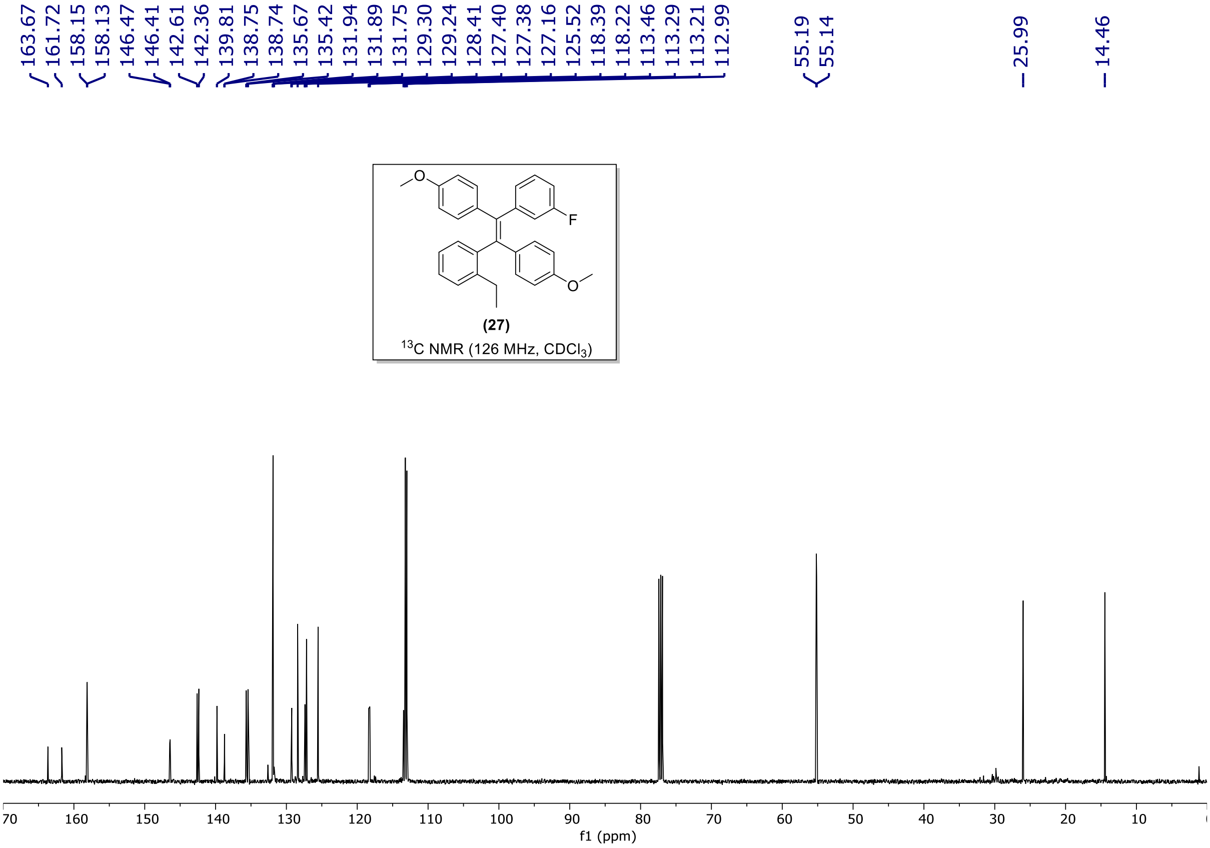
(26)

^{13}C NMR (126 MHz, $CDCl_3$)

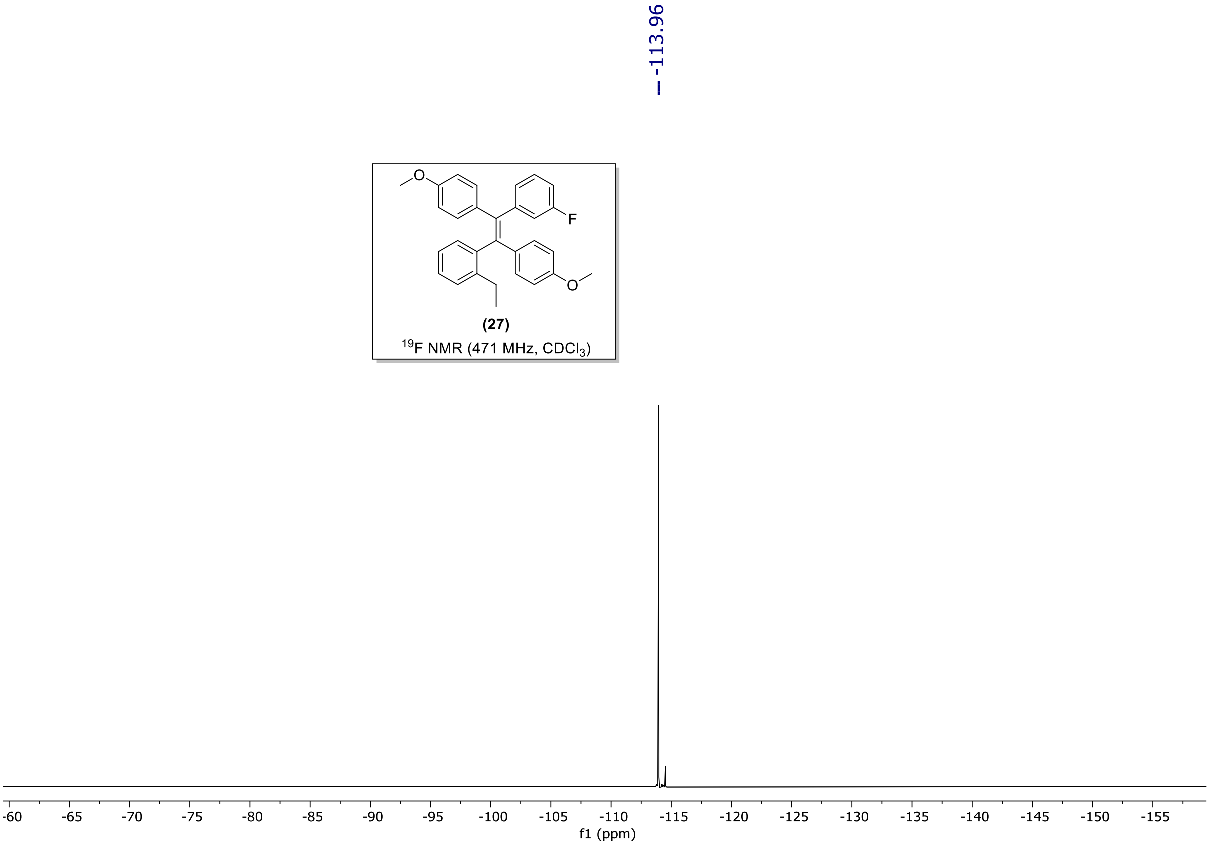


(27)

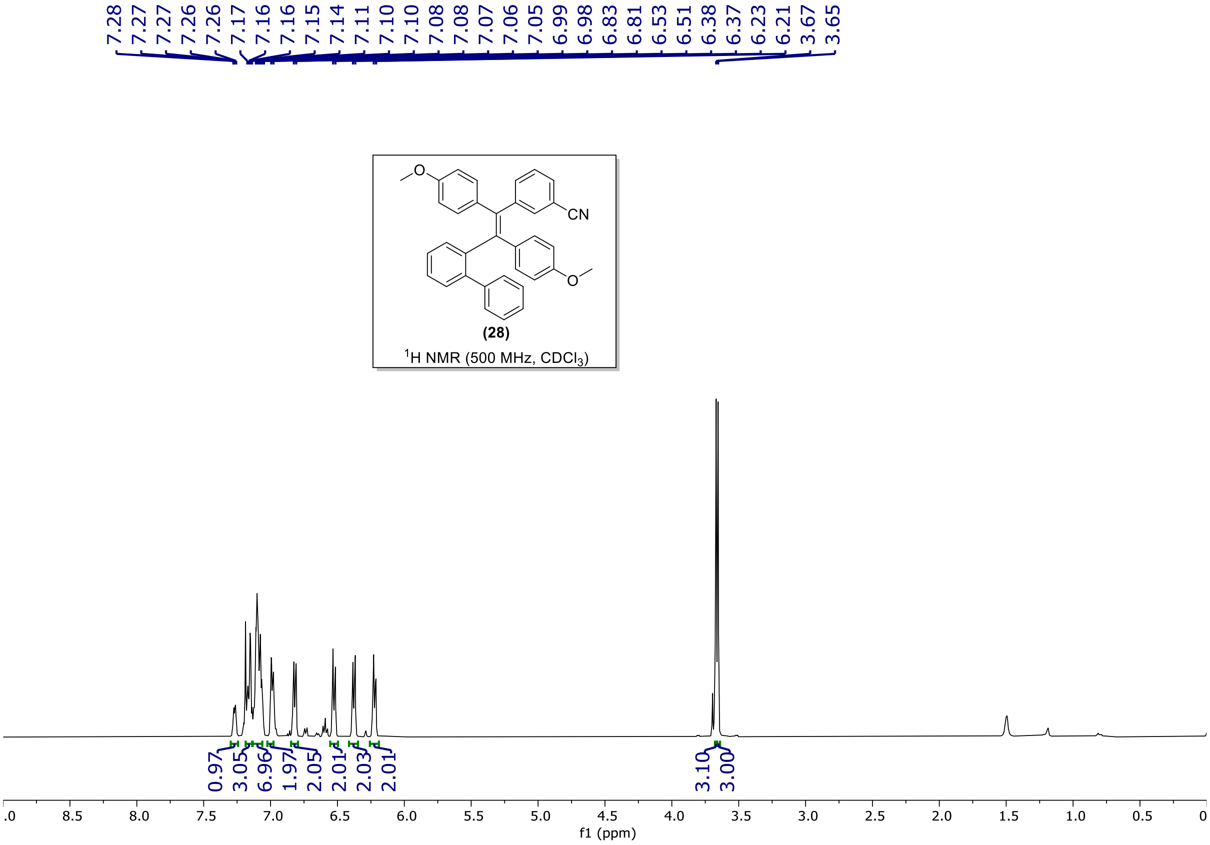
^{1}H NMR (500 MHz, $CDCl_3$)


(27)

^{13}C NMR (126 MHz, $CDCl_3$)

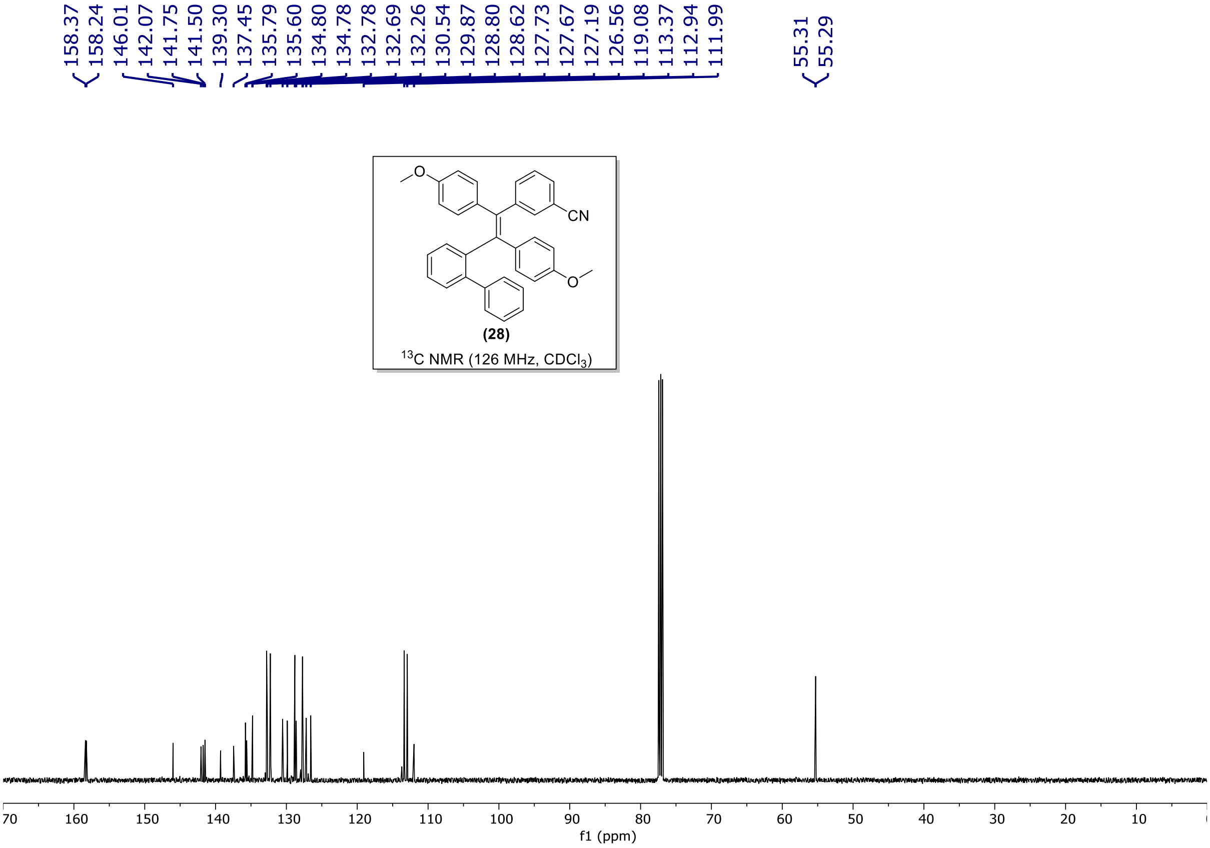

(27)

^{19}F NMR (471 MHz, $CDCl_3$)



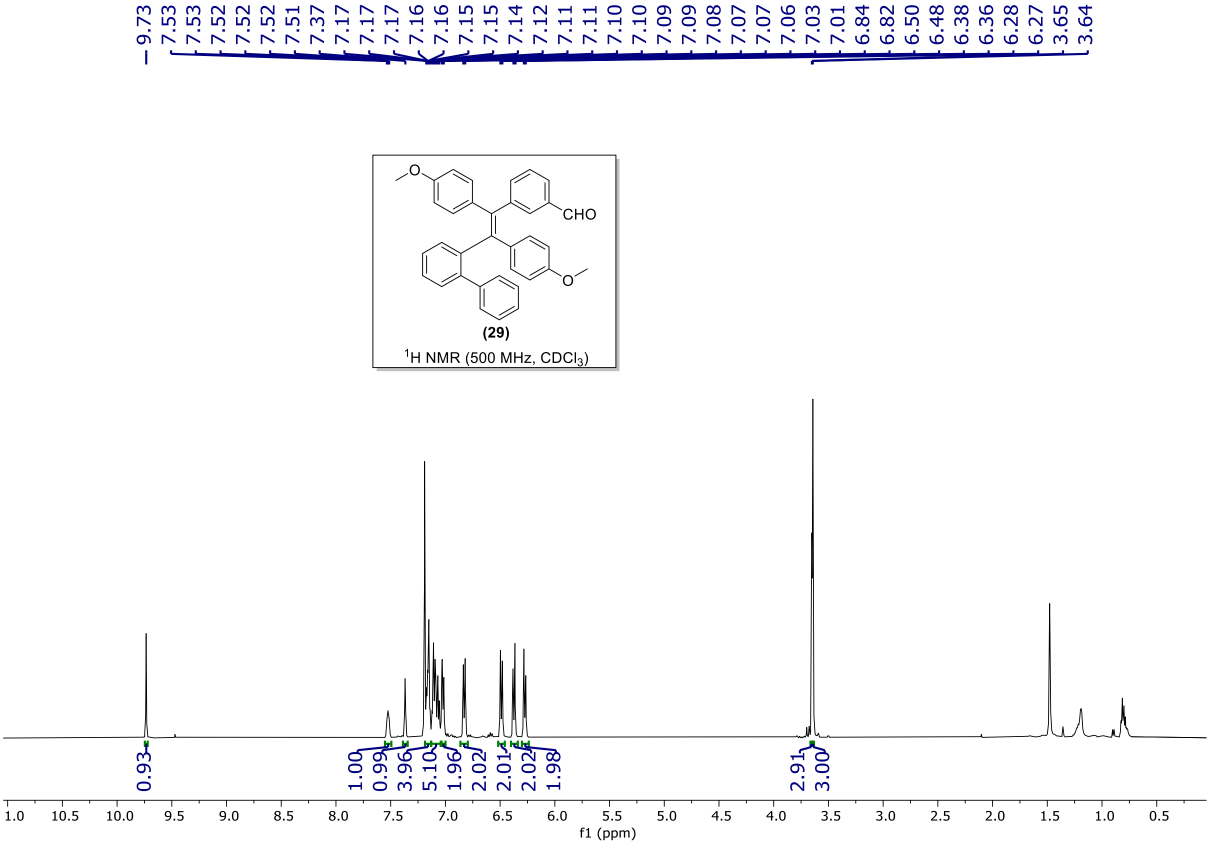
(28)

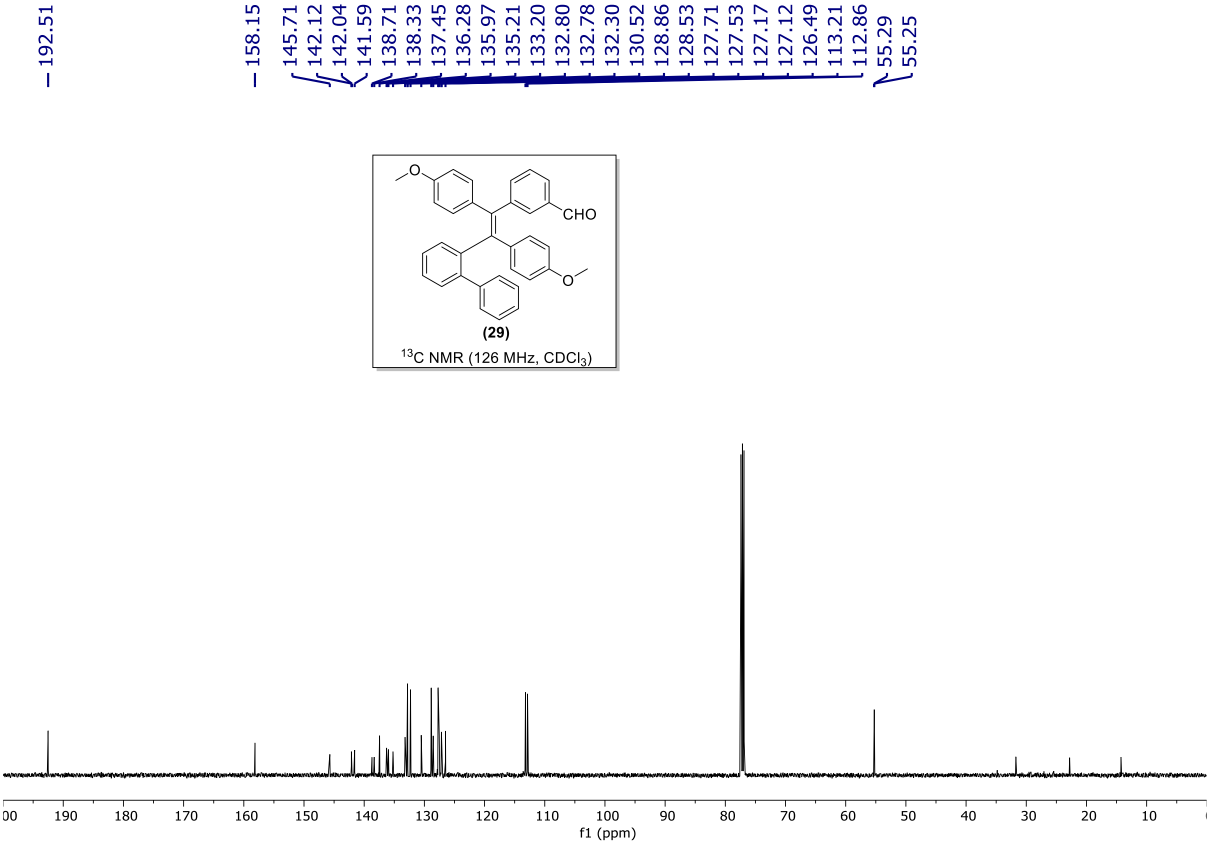
^{1}H NMR (500 MHz, $CDCl_3$)

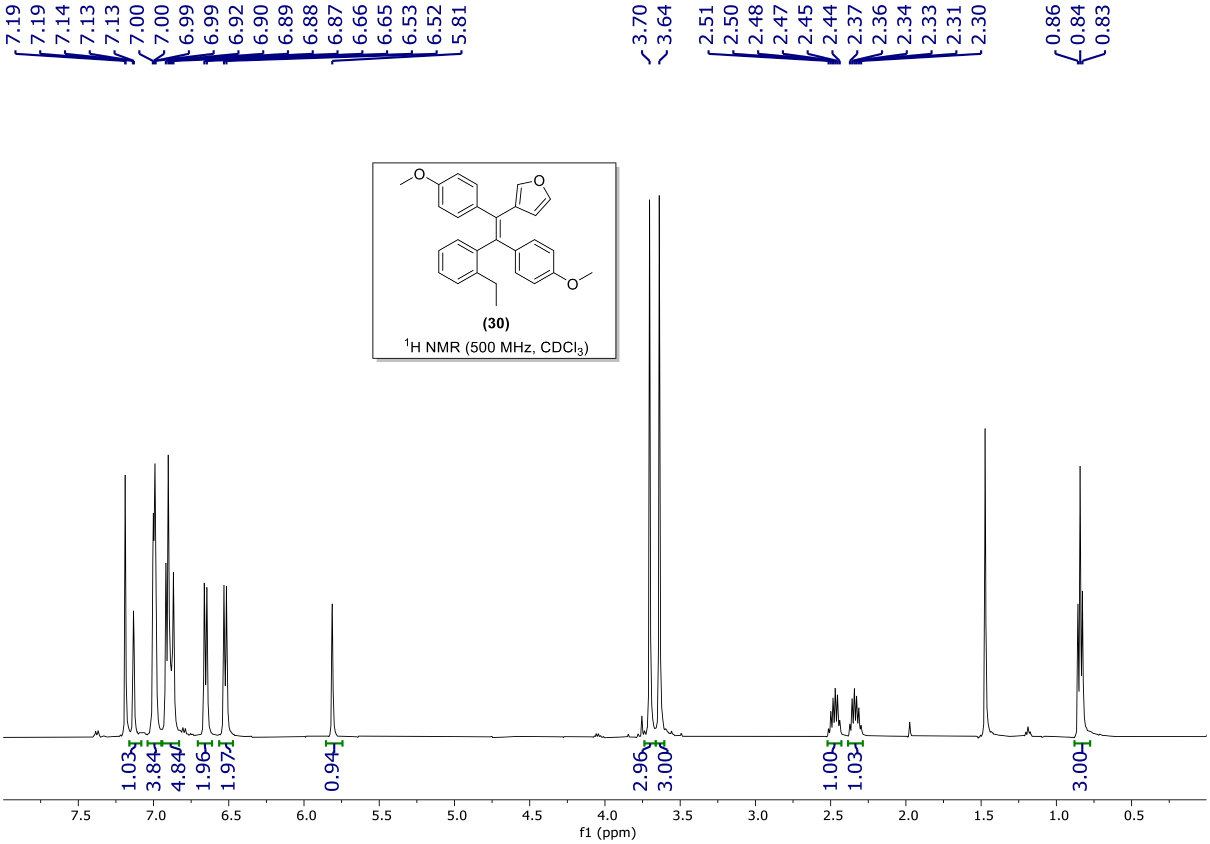


(28)

^{13}C NMR (126 MHz, $CDCl_3$)

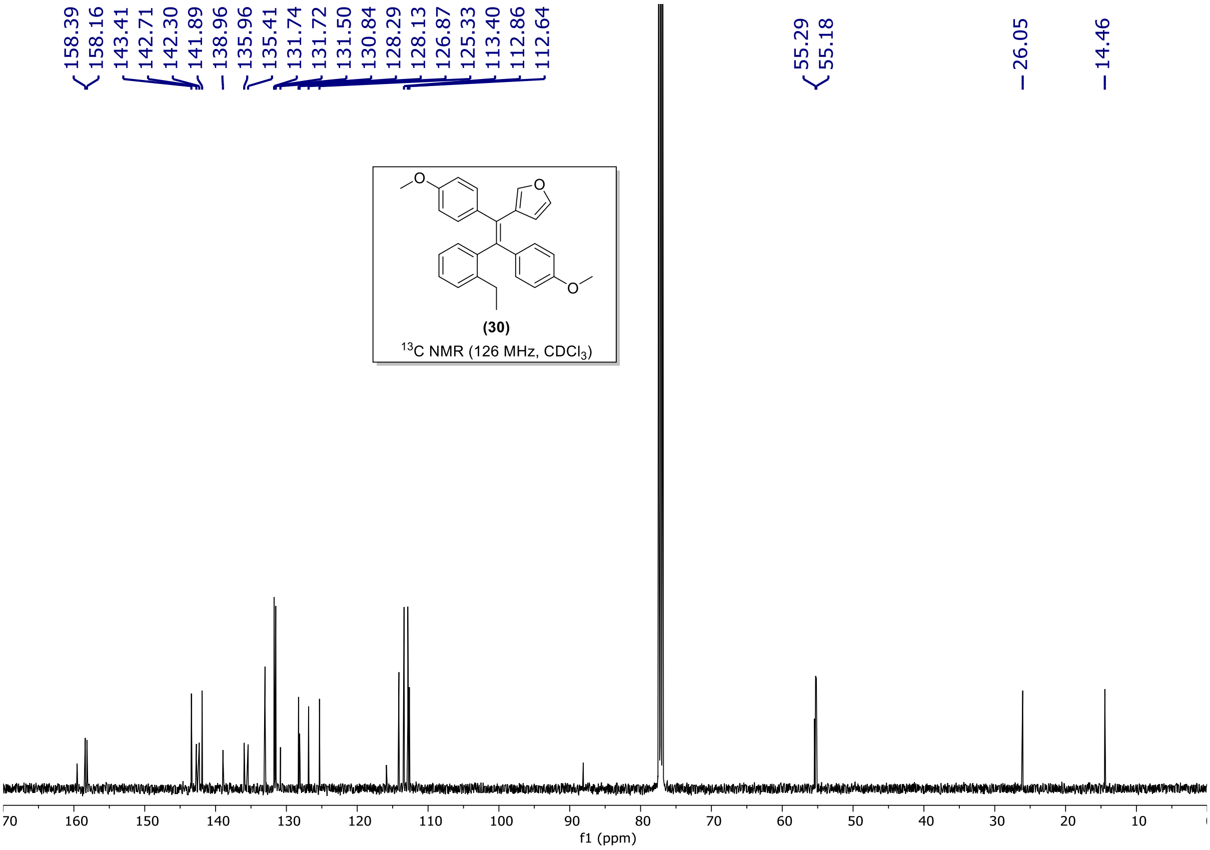

9.73
7.53
7.53
7.52
7.52
7.52
7.51
7.37
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.07
7.07
7.06
7.03
7.01
6.84
6.82
6.50
6.48
6.38
6.36
6.28
6.27
3.65
3.64
O
CHO
O
(29)
^{1}H NMR (500 MHz, CDCl$_3$)
0.93
1.00
0.99
3.96
5.10
1.96
2.02
2.01
2.02
1.98
2.91
3.00
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


192.51
158.15
145.71
142.12
142.04
141.59
138.71
138.33
137.45
136.28
135.97
135.21
133.20
132.80
132.78
132.30
130.52
128.86
128.53
127.71
127.53
127.17
127.12
126.49
113.21
112.86
55.29
55.25
O
CHO
O
(29)
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



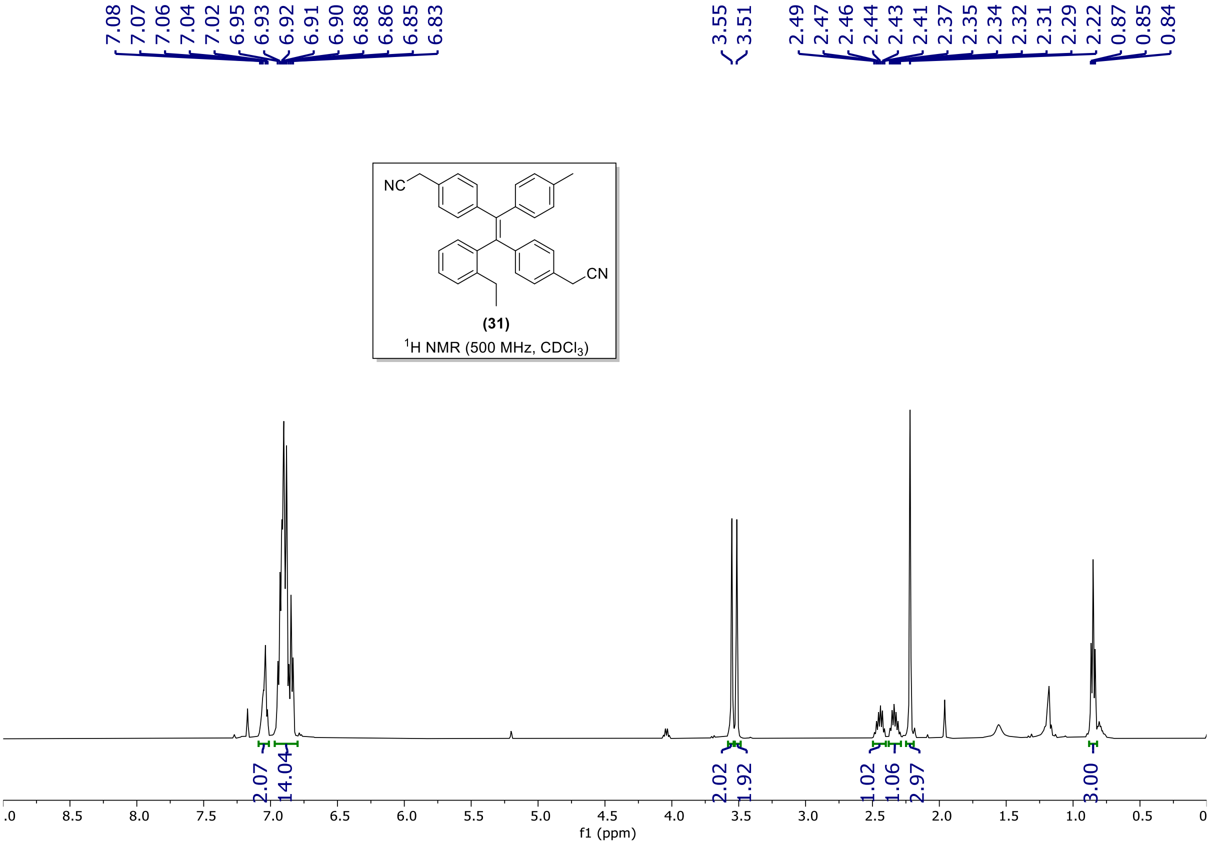
(30)

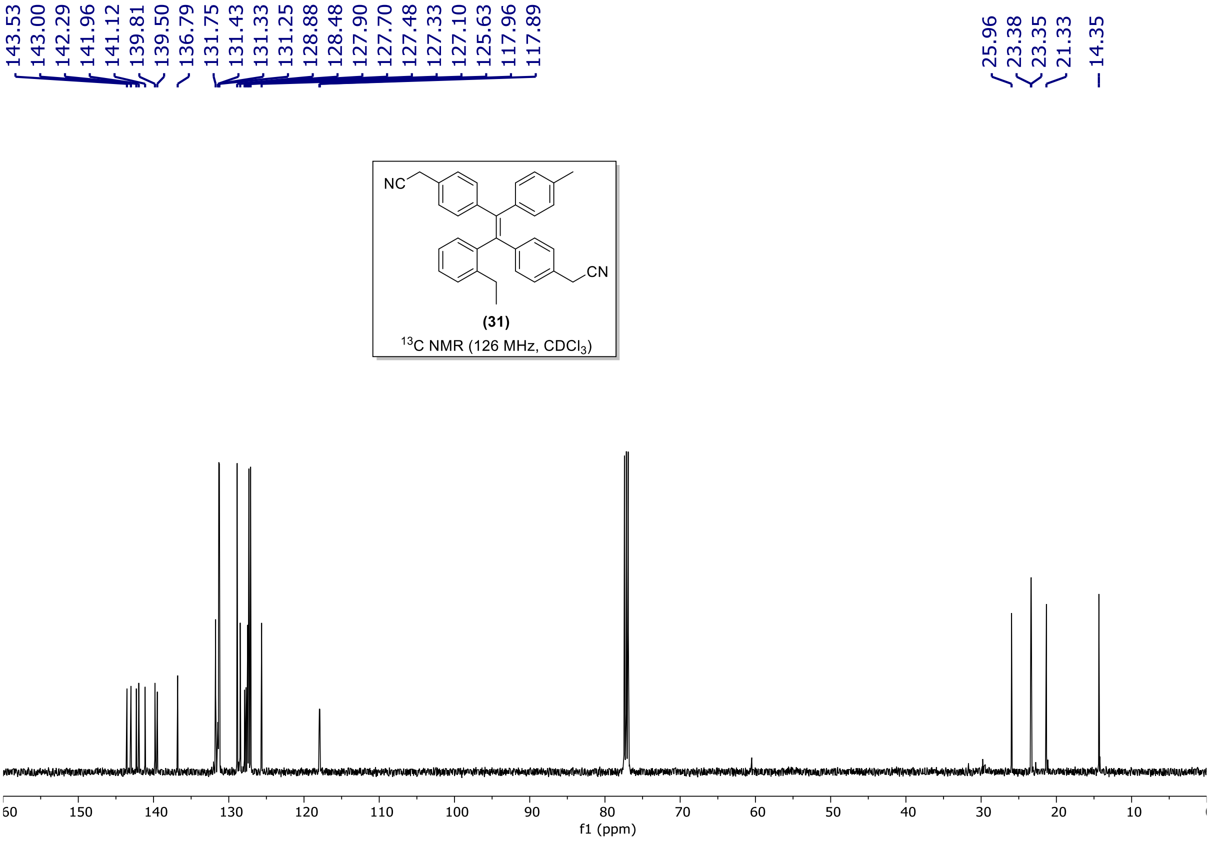
^{1}H NMR (500 MHz, CDCl$_3$)

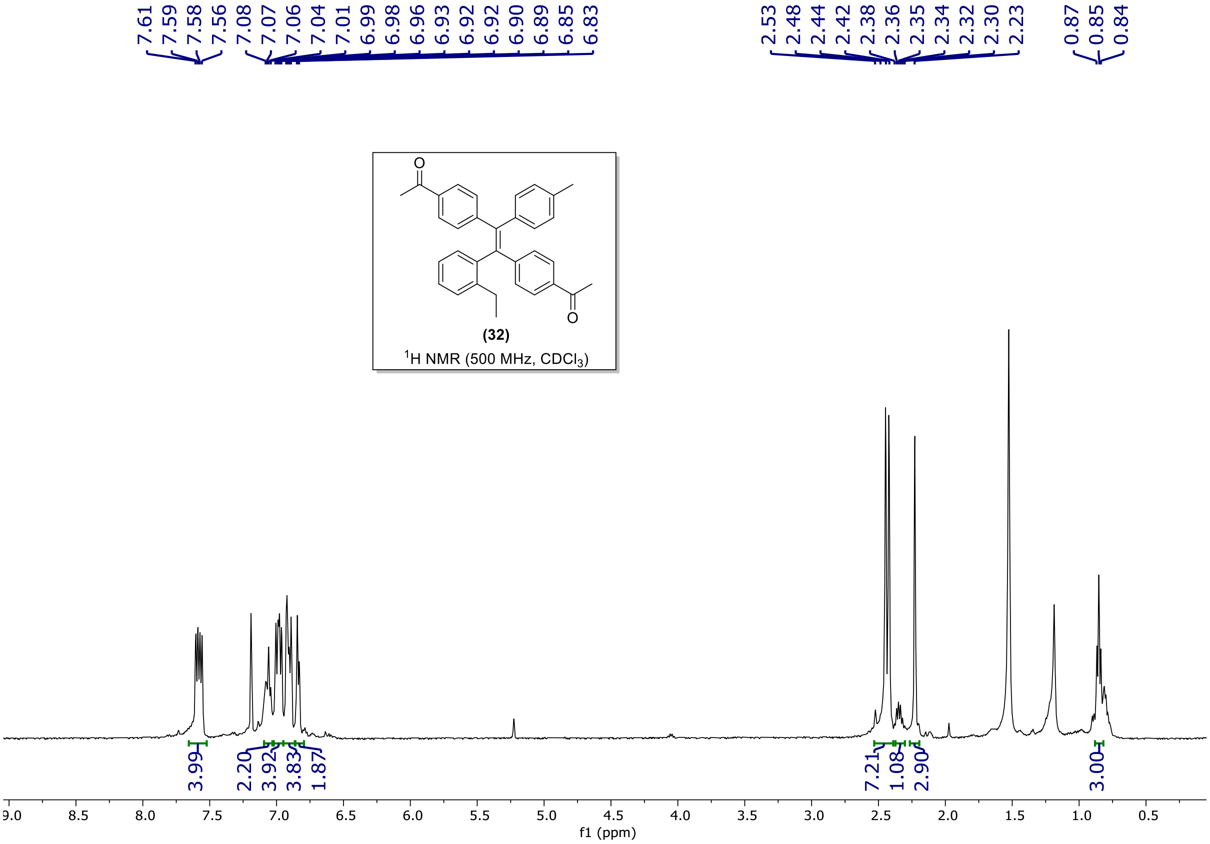


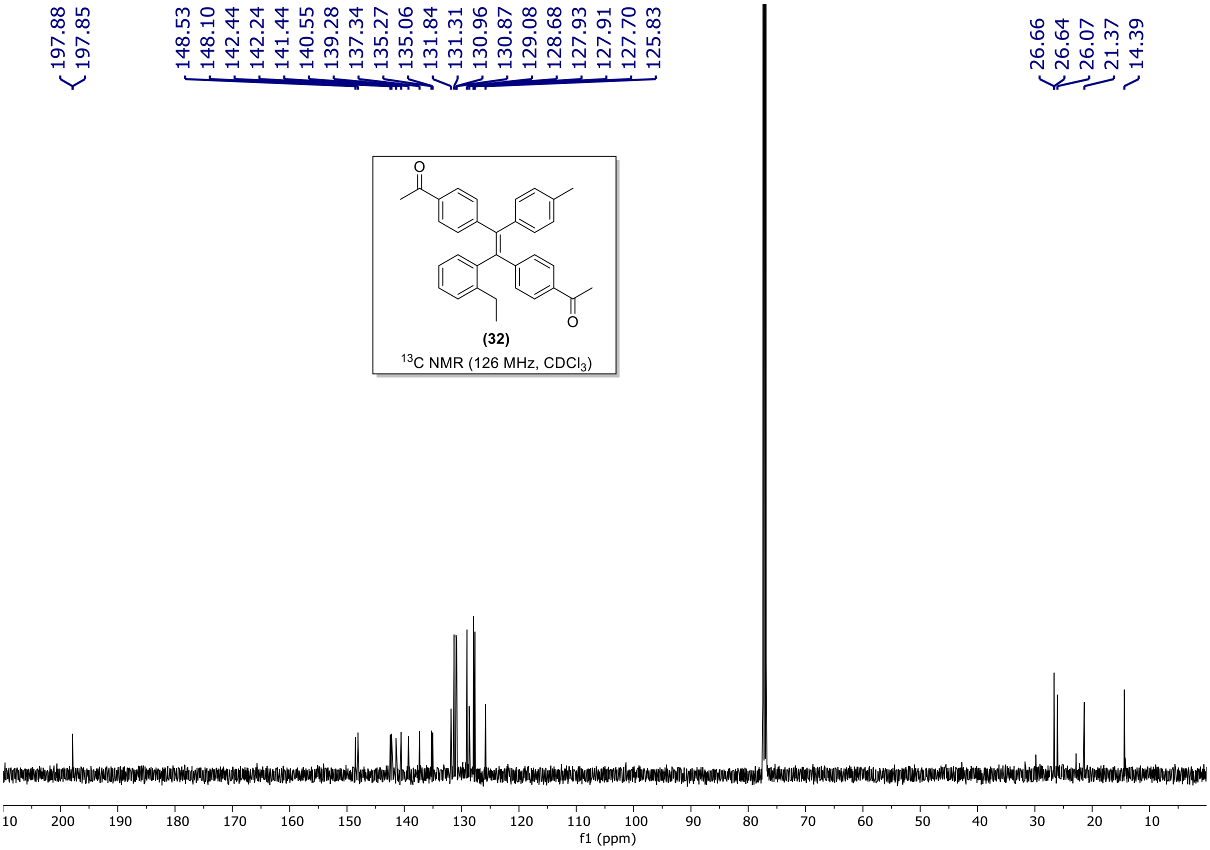
(30)

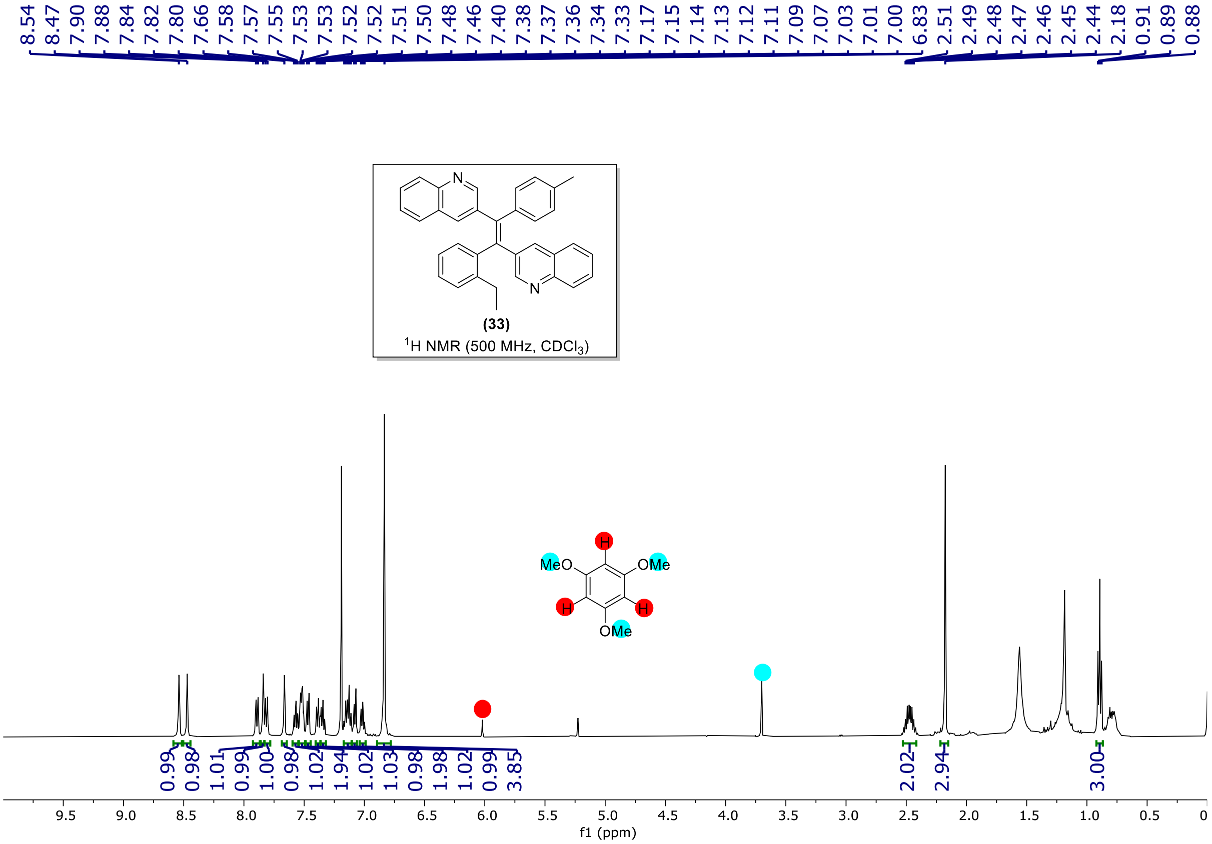
^{13}C NMR (126 MHz, CDCl$_3$)

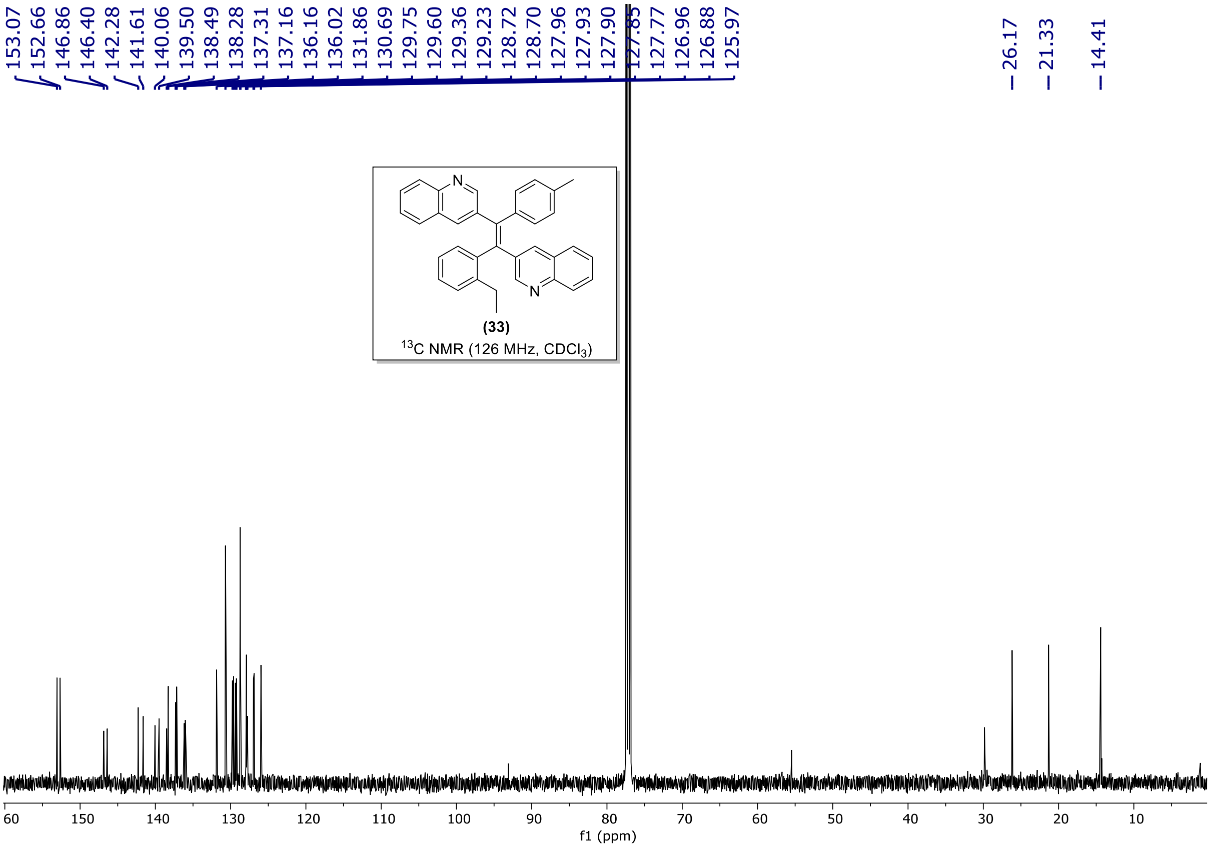

7.08
7.07
7.06
7.04
7.02
6.95
6.93
6.92
6.91
6.90
6.88
6.86
6.85
6.83
3.55
3.51
2.49
2.47
2.46
2.44
2.43
2.41
2.37
2.35
2.34
2.32
2.31
2.29
2.22
0.87
0.85
0.84
NC
CN
(31)
^{1}H NMR (500 MHz, CDCl$_3$)
2.07
14.04
2.02
1.92
1.02
1.06
2.97
3.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

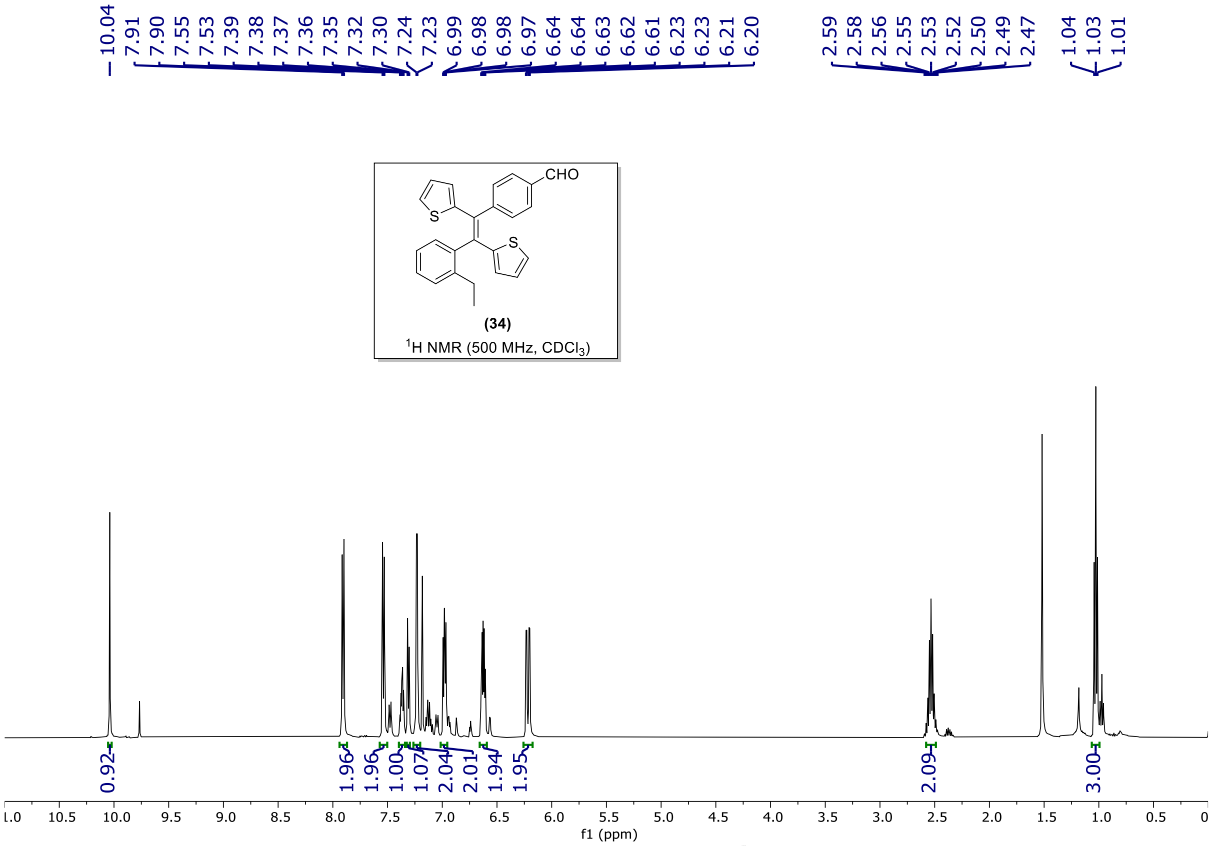

143.53
143.00
142.29
141.96
141.12
139.81
139.50
136.79
131.75
131.43
131.33
131.25
128.88
128.48
127.90
127.70
127.48
127.33
127.10
125.63
117.96
117.89
25.96
23.38
23.35
21.33
14.35
NC
CN
(31)
^{13}C NMR (126 MHz, CDCl$_3$)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.61
7.59
7.58
7.56
7.08
7.07
7.06
7.04
7.01
6.99
6.98
6.96
6.93
6.92
6.92
6.90
6.89
6.85
6.83
2.53
2.48
2.44
2.42
2.38
2.36
2.35
2.34
2.32
2.30
2.23
0.87
0.85
0.84
(32)
¹H NMR (500 MHz, CDCl₃)
3.99
2.20
3.92
3.83
1.87
7.21
1.08
2.90
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

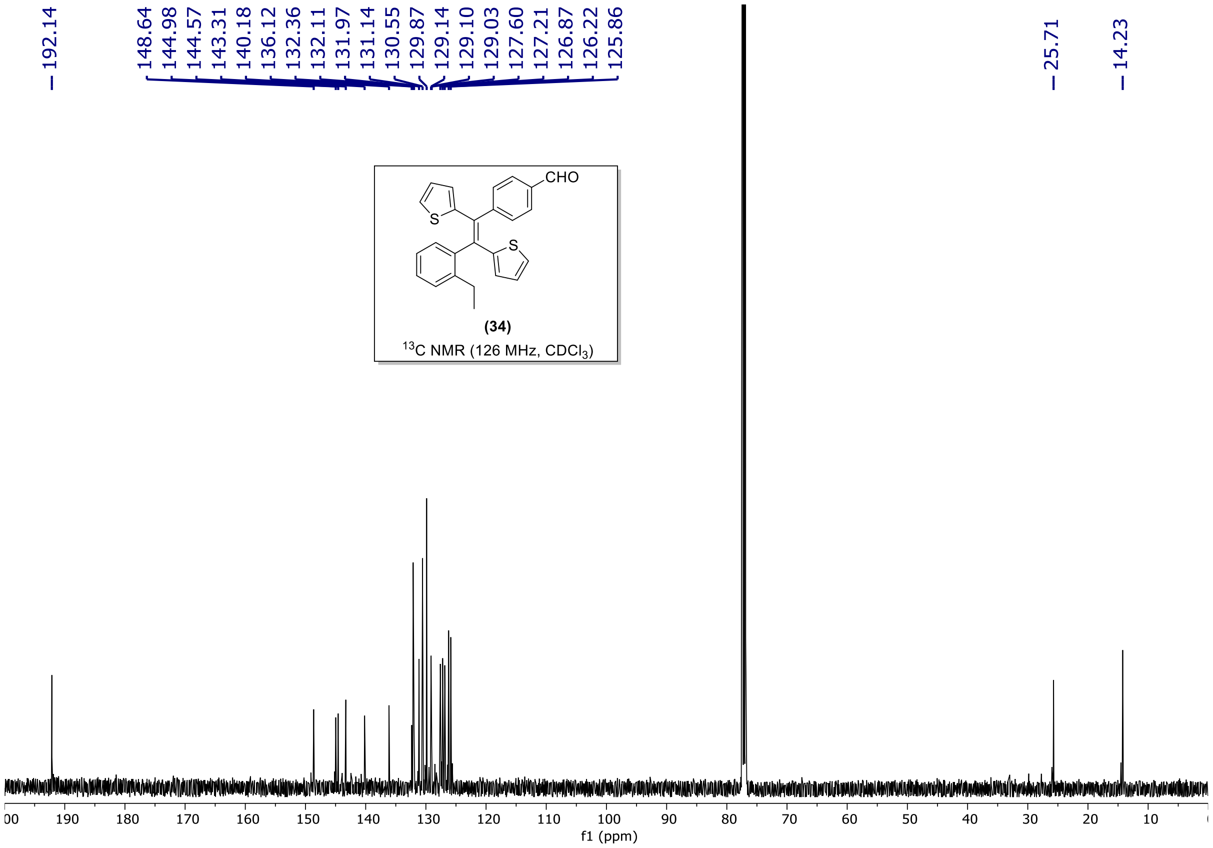

197.88
197.85
148.53
148.10
142.44
142.24
141.44
140.55
139.28
137.34
135.27
135.06
131.84
131.31
130.96
130.87
129.08
128.68
127.93
127.91
127.70
125.83
26.66
26.64
26.07
21.37
14.39
(32)
¹³C NMR (126 MHz, CDCl₃)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.54
8.47
7.90
7.88
7.84
7.82
7.80
7.66
7.58
7.57
7.55
7.53
7.53
7.52
7.52
7.51
7.50
7.48
7.46
7.40
7.38
7.37
7.36
7.34
7.33
7.17
7.15
7.14
7.13
7.12
7.11
7.09
7.07
7.03
7.01
7.00
6.83
2.51
2.49
2.48
2.47
2.46
2.45
2.44
2.18
0.91
0.89
0.88
N
N
(33)
¹H NMR (500 MHz, CDCl₃)
MeO
OMe
OMe
H
H
H
0.99
0.98
1.01
0.99
1.00
0.98
1.02
1.94
1.02
1.03
0.98
1.98
1.02
0.99
3.85
2.02
2.94
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


153.07
152.66
146.86
146.40
142.28
141.61
140.06
139.50
138.49
138.28
137.31
137.16
136.16
136.02
131.86
130.69
129.75
129.60
129.36
129.23
128.72
128.70
127.96
127.93
127.90
127.85
127.77
126.96
126.88
125.97
26.17
21.33
14.41
N
N
(33)
¹³C NMR (126 MHz, CDCl₃)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


(34)

^{1}H NMR (500 MHz, $CDCl_3$)


(34)

^{13}C NMR (126 MHz, $CDCl_3$)