

Supporting Information

Interfacial electric fields catalyze Ullmann coupling reactions on gold surfaces

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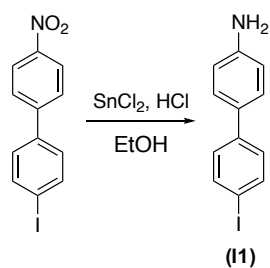
General Synthetic Information and Instrumentation

All reactions were performed open to atmosphere with magnetic stirring, unless otherwise noted. Reagents were purchased from Sigma-Aldrich, TCI, Alfa-Aesar and Acros. All solvents and reagents were directly used as purchased without any further purification. All final products were dried in vacuo prior to reporting yields. The syntheses of **I2**, **D1** and **Au2** have already been reported.¹⁻² **D3** was purchased from TCI. **I5** was purchased from Acros.

¹H, ¹⁹F and ¹³C NMR spectra were recorded on Bruker DRX400 and DMX500 spectrometers in deuterated solvent and at frequencies as noted. Data for ¹H NMR are reported as follows: chemical shift (δ , in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J, in Hz), and integration (b = broad). Data for ¹³C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (High-Res MS) was performed at the Columbia University mass spectrometry facility using a XEVO G2-XS Waters® equipped with a QTOF detector with multiple inlet and ionization capabilities including electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric solids analysis probe (ASAP). The base peaks were usually obtained as [M]⁺ or [M+H]⁺ ions.

Secondary electron images (SEI) were collected using a Zeiss Sigma VP scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Energy dispersive X-ray spectra (EDX) were collected using an accelerating voltage of 12 kV and a Bruker XFlash 6|30 detector. Elemental compositions were approximated by integrating peaks in the EDX spectra using the Bruker ESPRIT2 software. Reported compositions are the averages and standard deviations calculated for elemental compositions determined for 3-10 sites on the same sample region.

Synthesis and Characterization

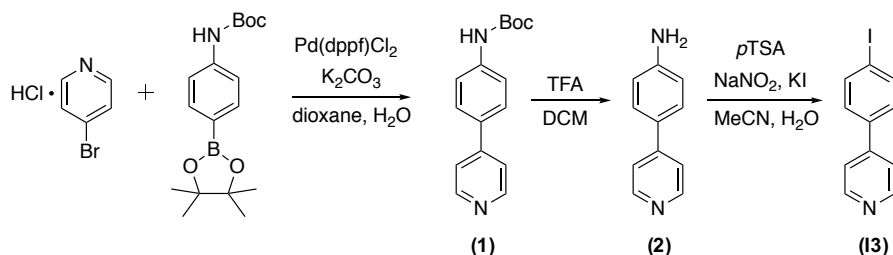


Scheme 1: Synthesis of **I1**.

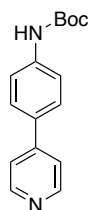
I1. An oven-dried 50 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with 4-iodo-4'-nitrobiphenyl (310 mg, 0.95 mmol), SnCl₂•2H₂O (1.27 g, 5.6 mmol) and ethanol (8 mL). The

solution was sparged with N₂ for 20 minutes. Concentrated aqueous HCl (1 mL) was then added and the solution was refluxed overnight. The mixture was cooled to room temperature and then poured into 10 mL of ice cold water. The solution was basified by careful addition of 2 M aqueous NaOH until the pH reached ~10. The aqueous solution was then extracted with DCM (3 x 25 mL), washed with brine (50 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation, and the crude mixture was recrystallized in hot ethanol to afford a white powder. Yield: 155 mg, 55%.

This compound has been reported previously.³ ¹H NMR (400 MHz, DMSO) δ 7.69 (d, J = 8.5 Hz, 2H), 7.64 – 7.00 (m, 4H), 6.63 (d, J = 8.5 Hz, 2H), 5.27 (s, 2H).



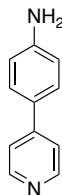
Scheme 2: Synthesis of **I3**.



1. A 100 mL three-necked round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with 4-bromopyridine hydrochloride salt (307 mg, 1.58 mmol), (4-tert-butoxycarbonylamino)phenylboronic acid pinacol ester (557 mg, 1.74 mmol), K₂CO₃ (815 mg, 5.8 mmol), and Pd(dppf)Cl₂ DCM adduct (53 mg, 0.07 mmol). A separate 50 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with dioxane (9 mL) and water (1 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 36 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was extracted with ethyl acetate (2 x 50 mL), washed with water (50 mL) and brine (50 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using basified silica gel flash column chromatography,

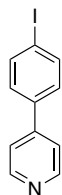
eluting with EtOAc/hexanes buffered with Et₃N to afford a white crystalline solid. Yield: 370 mg, 87%.

This compound has been reported previously.⁴ ¹H NMR (400 MHz, DMSO) δ 9.54 (s, 1H), 8.58 (d, J = 6.2 Hz, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 6.2 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 1.49 (s, 9H).



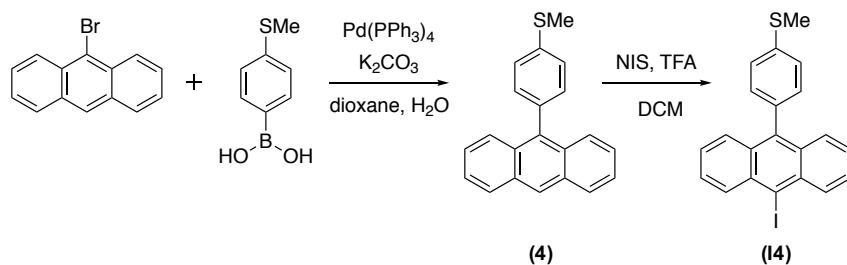
2. A 25 mL round bottom flask equipped with a Teflon coated stir bar was charged with **1** (360 mg, 1.33 mmol) and dissolved in DCM (10 mL). Trifluoroacetic acid (3 mL) was added, and the was stirred at room temperature for one hour, then diluted with DCM (50 mL) and washed with 1 M aqueous NaOH (50 mL), brine (50 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation to afford a pale yellow solid. Yield: 210 mg, 93%.

This compound has been reported previously.⁴ ¹H NMR (400 MHz, DMSO) δ 8.48 (d, J = 5.1 Hz, 2H), 7.76 – 7.16 (m, 4H), 6.67 (d, J = 8.5 Hz, 2H), 5.61 (s, 2H).

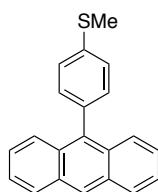


I3. A 25 mL round bottom flask equipped with a Teflon coated stir bar was charged with **2** (112 mg, .66 mmol) and dissolved in acetonitrile (8 mL) and water (0.5 mL). *p*-Toluenesulfonic acid monohydrate (380 mg, 2 mmol) was added and the resulting suspension was allowed to stir for 5 minutes and placed in a room temperature water bath. A separate solution of NaNO₂ (92 mg, 1.33 mmol) and potassium iodide (276 mg, 1.66 mmol) in water (3 mL) was added slowly, resulting in a viscous, dark brown mixture. The reaction was stirred overnight then quenched with saturated NaHCO₃, extracted into DCM (3 x 50 mL), washed with brine (100 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation and the residue was purified using basified silica gel flash column chromatography, eluting with DCM/hexanes to afford a beige solid. Yield: 130 mg, 70%.

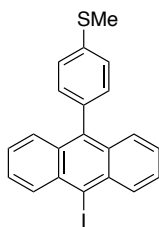
This compound has been reported previously.⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 6.4 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 6.2 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H).



Scheme 3: Synthesis of **14**.

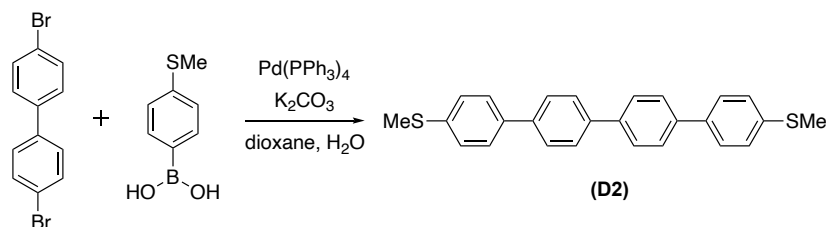


4. A 100 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with 9-bromoanthracene (257 mg, 1 mmol), (4-thiomethoxyphenyl)boronic acid (193 mg, 1.15 mmol), K₂CO₃ (657 mg, 4.7 mmol), and Pd(PPh₃)₄ (40 mg, 0.035 mmol). A separate 50 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with dioxane (8 mL), and water (2 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was extracted with ethyl acetate (2 x 50 mL), washed with water (50 mL) and brine (50 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with DCM/hexanes to afford a beige solid. Yield: 198 mg, 66%. ¹H NMR (500 MHz, CDCl₃) δ 8.50 (s, 1H), 8.11 – 7.99 (m, 2H), 7.69 (dd, *J* = 8.9, 1.0 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.40 – 7.32 (m, 4H), 2.62 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 137.73, 136.38, 135.41, 131.72, 131.38, 130.28, 128.37, 126.74, 126.63, 126.33, 125.39, 125.12, 15.79. High-Res MS (ESI⁺): calculated *m/z* for [M+H]⁺ 300.0973, found 300.0997.



I4. A 25 mL round bottom flask equipped with a Teflon coated stir bar was charged with **4** (31 mg, 0.1 mmol) and dissolved in DCM (0.8 mL). 5 drops of TFA were added and N-iodosuccinamide (30 mg, 0.13 mmol) was added in portions. The suspension was allowed to stir for 18 h and then was quenched with saturated NaHCO₃, extracted with DCM (2 x 25 mL), washed with brine (50 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with DCM/hexanes to afford a yellow solid. Yield: 21.6 mg, 50%.

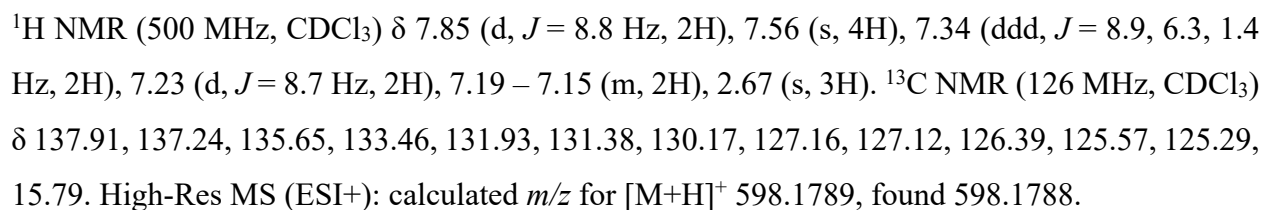
¹H NMR (500 MHz, CDCl₃) δ 8.57 (d, *J* = 8.8 Hz, 2H), 7.70 – 7.60 (m, 2H), 7.57 (ddd, *J* = 8.9, 6.5, 1.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.37 (ddd, *J* = 8.8, 6.5, 1.2 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 2.62 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 138.50, 138.24, 134.96, 133.71, 133.52, 131.53, 131.09, 127.55, 127.49, 126.28, 125.64, 105.73, 15.70. High-Res MS (ESI⁺): calculated *m/z* for [M+H]⁺ 425.9939, found 425.9936.



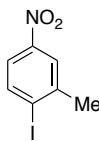
Scheme 3: Synthesis of **D2**.

D2. A 100 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with 4,4'-diiodobiphenyl (243 mg, 0.6 mmol), (4-thiomethoxyphenyl)boronic acid (242 mg, 1.44 mmol), K₂CO₃ (414 mg, 3 mmol), and Pd(PPh₃)₄ (42 mg, 0.04 mmol). A separate 50 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with dioxane (12 mL) and water (2.5 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the solution was filtered, and the resulting beige solid was washed with DCM, MeOH and acetone.

High-Res MS (ASAP+): calculated m/z for $[M+H]^+$ 399.1241, found 399.1239.

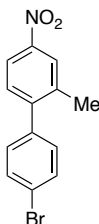


Scheme 5: Synthesis of **B1**.



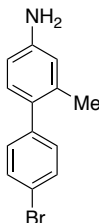
5. A 25 mL round bottom flask equipped with a Teflon coated stir bar was charged with 2-methyl-4-nitro-benzenamine (500 mg, 3.29 mmol) and dissolved in acetonitrile (25 mL) and water (2 mL). *p*-Toluenesulfonic acid monohydrate (1.9 g, 10 mmol) was added and the resulting suspension was allowed to stir for 5 minutes and placed in a room temperature water bath. A separate solution of NaNO₂ (460 mg, 6.7 mmol) and potassium iodide (1.38 g, 8.3 mmol) in water (3 mL) was added slowly, resulting in a viscous, dark brown mixture. The reaction was stirred overnight then quenched with saturated NaHCO₃, extracted into DCM (3 x 50 mL), washed with brine (100 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation and the residue was purified using silica gel flash column chromatography, eluting with DCM/hexanes to afford a beige solid. Yield: 680 mg, 79%

This compound has been reported previously.⁶ ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 2.7 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.67 (m, 1H), 2.55 (s, 3H).



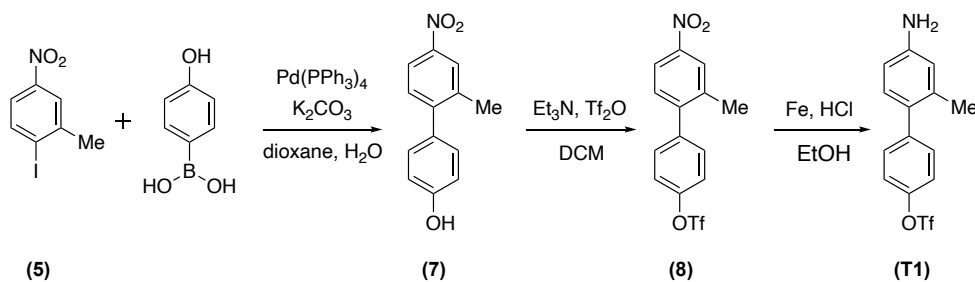
6. A 100 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with **5** (263 mg, 1 mmol), 4-bromophenylboronic acid (201 mg, 1 mmol), K₂CO₃ (700 mg, 5.1 mmol), and Pd(PPh₃)₄ (30 mg, 0.03 mmol). A separate 50 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with dioxane (8 mL), and water (2 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 8 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was dissolved in ethyl acetate (50 mL), washed water (50 mL) and brine (50 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with DCM/hexanes to afford a white solid. Yield: 254 mg, 87%.

^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 2.4 Hz, 1H), 8.09 (dd, J = 8.3, 2.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.22, 138.60, 137.22, 131.71, 130.50, 130.37, 125.28, 122.38, 121.04, 20.59.

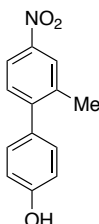


B1. An oven-dried 50 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N_2 atmosphere was charged with **6** (125 mg, 0.43 mmol), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (600 mg, 2.6 mmol) and ethanol (8 mL). The solution was sparged with N_2 for 20 minutes. Concentrated aqueous HCl (1 mL) was then added and the solution was refluxed overnight. The mixture was cooled to room temperature and then poured into 10 mL of ice cold water. The solution was basified by careful addition of 2 M aqueous NaOH until the pH reached ~ 10 . The aqueous solution was then extracted with DCM (3 x 25 mL), washed with brine (50 mL) and dried with Na_2SO_4 . The solvent was removed via rotary evaporation to afford a reddish brown oil. Yield: 112 mg, 99%

^1H NMR (500 MHz, DMSO) δ 7.54 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.51 – 6.38 (m, 2H), 5.10 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 148.67, 141.64, 135.35, 131.72, 131.32, 130.65, 128.03, 119.50, 116.08, 112.28, 20.85. High-Res MS (ESI $^+$): calculated m/z for $[\text{M}+\text{H}]^+$ 262.0231, found 262.0253.

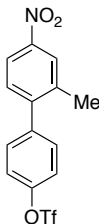


Scheme 6: Synthesis of **T1**.



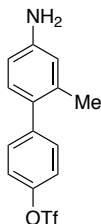
7. A 100 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with **5** (100 mg, 0.38 mmol), 4-hydroxyphenylboronic acid (68 mg, 0.5 mmol), K₂CO₃ (262 mg, 1.9 mmol), and Pd(PPh₃)₄ (12 mg, 0.01 mmol). A separate 50 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with dioxane (6 mL), and water (2 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was dissolved in DCM (50 mL), washed water (50 mL) and brine (50 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with EtOAc/hexanes to afford a white solid. Yield: 32 mg, 37%.

¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.20 (dd, *J* = 8.4, 1.5 Hz, 2H), 6.96 – 6.89 (m, 2H), 5.17 (s, 1H), 2.37 (s, 2H).



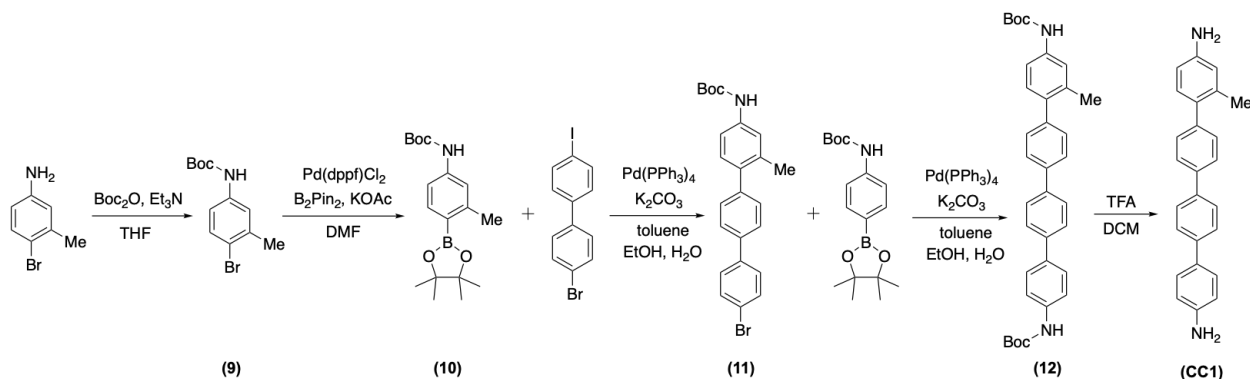
8. A 50 mL oven dried three-necked round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with **7** (31 mg, 0.14 mmol) and anhydrous DCM (2 mL). Anhydrous Et₃N was added (0.03 mL, 0.21 mmol), followed by triflic anhydride (0.30 mL, 0.18 mmol). The solution was allowed to stir for 18 h and was quenched with water, then diluted with DCM (30 mL), washed with water (30 mL) and brine (30 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with EtOAc/hexanes to afford a white solid. Yield: 40 mg, 80%.

¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.67 – 6.44 (m, 2H), 3.70 (s, 2H), 2.19 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -71.95. ¹³C NMR (126 MHz, CDCl₃) δ 148.11, 146.15, 142.51, 136.31, 131.15, 130.79, 130.42, 120.82, 120.09, 116.85, 112.70, 20.50.

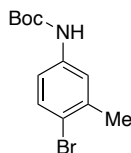


T1. An oven-dried 25 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with **8** (30 mg, 0.08 mmol) and ethanol (2.5 mL). The solution was sparged with N₂ for 20 minutes. Fe powder (27 mg, 0.5 mmol) was added. Concentrated aqueous HCl (1 mL) was then added slowly and the solution was refluxed overnight. The mixture was cooled to room temperature and then poured into 10 mL of ice cold water. The solution was basified by careful addition of 1M aqueous NaOH until the pH reached ~6. The aqueous solution was then extracted with DCM (3 x 25 mL), washed with brine (50 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation to afford a reddish brown oil. Yield: 25 mg, 91%.

¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.31 (m, 4H), 2.53 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -71.87. ¹³C NMR (126 MHz, CDCl₃) δ 148.82, 141.04, 138.91, 135.90, 128.52, 127.48, 126.83, 121.70, 120.06, 15.66. High-Res MS (ESI⁺): calculated *m/z* for [M+H]⁺ 332.0568, found 332.0580.



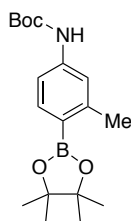
Scheme 7: Synthesis of CC1.



9. A 50 mL three-neck round bottom flask under N₂ atmosphere was charged with 4-bromo-3-methylaniline (1.93g, 10.4 mmol) and degassed THF (65). Triethylamine (2.5 mL, 18 mmol) was

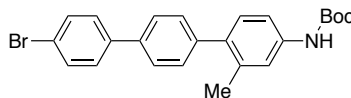
added, followed by di-tertbutyl-dicarbonate (3 mL, 13 mmol) and the reaction mixture was then refluxed for 18 h. The solvent was removed via rotary evaporation, and the residue was purified using silica gel flash column chromatography, eluting with Et₂O/hexanes. The resulting mixture of 292 and excess boc anhydride was then dissolved in DCM (100 mL) and imidazole (2.7 g, 39mmol) was added. The solution was allowed to stir for 2 h then washed with 1% HCl w/w (2 x 100 mL), water (100 mL) and brine (100 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation to afford a white solid. Yield: 2.1 g, 71%.

This compound has been reported previously.⁷ ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.6 Hz, 1H), 7.32 (s, 1H), 7.02 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.39 (s, 1H), 2.36 (s, 3H), 1.51 (s, 9H).



10. An oven-dried 25 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with **9** (342 mg, 1.2 mmol), diboron pinacol ester (360 mg, 1.42 mmol), Pd(dppf)Cl₂ DCM adduct (26 mg, 0.03 mmol), potassium acetate (360 mg, 3.67 mmol) and dry degassed DMF (5 mL). The solution was stirred at 80 degrees for 18 h, allowed to cool to room temperature and partitioned between DCM (50 mL) and water (50 mL). The organic layer was washed with water (5 x 50 mL) and brine (2 x 50 mL) to remove the DMF, then dried with Na₂SO₄. The solvent was removed via rotary evaporation, and the residue was purified using silica gel flash column chromatography eluting with DCM/hexanes to afford a colorless oil that solidifies under vacuum to a fluffy white solid. Yield: 277 mg, 69%.

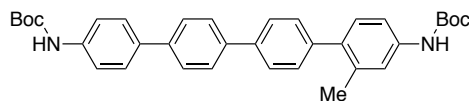
¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.11 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.47 (s, 1H), 2.51 (s, 3H), 1.51 (s, 9H), 1.32 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 152.45, 146.46, 140.60, 137.12, 119.08, 114.34, 83.23, 80.58, 28.34, 24.89, 22.36. High-Res MS (ESI⁺): calculated *m/z* for [M+Na]⁺ 356.2012, found 356.2029.



11. A 100 mL three-neck round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with 4-bromo-4'-iodobiphenyl (200 mg,

0.56 mmol), **10** (140 mg, 0.35 mmol), K₂CO₃ (350 mg, 2.5 mmol), and Pd(PPh₃)₄ (12 mg, 0.01 mmol). A separate 25 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with toluene (8 mL), ethanol (2.5 mL) and water (2.5 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was extracted with DCM (2 x 50 mL), washed with water (50 mL) and brine (50 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with DCM/hexanes to afford a white solid. Yield: 146 mg, 95%.

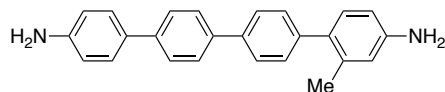
¹H NMR (500 MHz, DMSO) δ 9.33 (s, 1H), 7.72 – 7.66 (m, 2H), 7.65 (d, *J* = 3.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 2.21 (s, 3H), 1.46 (s, 9H). ¹³C NMR (126 MHz, DMSO) δ 153.27, 141.09, 139.46, 139.26, 137.48, 135.44, 134.94, 132.32, 130.23, 129.17, 127.07, 126.83, 121.34, 120.27, 116.42, 79.51, 28.61, 21.03. High-Res MS (ESI+): calculated *m/z* for [M+Na]⁺ 462.0871, found 462.0874.



12. A 50 mL three-necked round bottom flask fitted with a reflux condenser and equipped with a Teflon coated stir bar under N₂ atmosphere was charged with **11** (75 mg, 0.17 mmol), (4-tert-butoxycarbonylamino)phenylboronic acid pinacol ester (65 mg, 0.2 mmol), K₂CO₃ (250 mg, 1.78 mmol), and Pd(PPh₃)₄ (6 mg, 0.005 mmol). A separate 25 mL round bottom flask equipped with a Teflon stir bar under N₂ atmosphere was charged with toluene (8 mL), ethanol (2 mL) and water (2 mL) and sparged with N₂ for 20 min. The solution was then added to the mixture of solids resulting in a bright yellow cloudy solution. The reaction mixture was refluxed for 48 h. After cooling to room temperature, the solvent was removed via rotary evaporation. The solid residue was extracted with DCM (2 x 50 mL), washed with water (50 mL) and brine (50 mL), dried with Na₂SO₄ and the solvent was removed via rotary evaporation. The residue was purified using silica gel flash column chromatography, eluting with EtOAc/hexanes to afford a pale orange solid. Yield: 40 mg, 43%.

¹H NMR (500 MHz, CDCl₃) δ 7.76 – 7.65 (m, 6H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.37 (s, 1H), 7.24 (s, 2H), 6.57 (s, 1H), 6.51 (s, 1H), 2.35 (s, 3H), 1.57 (s, 9H), 1.57 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 152.86, 152.79, 139.50, 139.40, 140.56,

138.96, 137.76, 137.43, 136.43, 136.29, 135.39, 130.40, 129.78, 127.51, 127.39, 127.11, 126.63, 120.4, 118.86, 116.14, 29.71, 28.37, 20.76. High-Res MS (ESI+): calculated m/z for $[M+Na]^+$ 573.2729, found 573.2750.



CC1. A 6 dram vial equipped with a Teflon coated stir bar was charged with **12** (15 mg, 0.03 mmol) and dissolved in DCM (2 mL). TFA was added (0.25 mL) and the solution was allowed to stir for 4 h then diluted with DCM (5 mL), washed with 2M NaOH (2 x 10 mL) and brine (10 mL) and dried with Na₂SO₄. The solvent was removed via rotary evaporation to afford a beige solid. Yield: 9 mg, 99%.

¹H NMR (400 MHz, DMSO) δ 7.80 – 7.61 (m, 6H), 7.43 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 7.9 Hz, 2H), 6.49 (d, J = 13.1 Hz, 2H), 5.23 (s, 2H), 5.05 (s, 2H), 2.19 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 148.98, 148.40, 141.33, 140.00, 137.63, 137.51, 135.43, 131.79, 130.74, 130.12, 128.98, 127.51, 127.22, 126.37, 126.21, 116.14, 114.72, High-Res MS (ESI+): calculated m/z for $[M+H]^+$ 350.1783, found 350.1778.

2. STM-BJ Methods.

Conductance measurements were made using a custom-built scanning tunneling microscope that has been described in detail before.⁸ Conductance measurements were performed in dilute solutions (100 μ M) of the molecules in propylene carbonate (PC) and when used with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. The insulated tips used with PC were created by driving a mechanically cut gold tip through Apiezon wax.⁹ One-dimensional (1D) conductance histograms are constructed using logarithmic bins (100/decade), and two-dimensional (2D) histograms use logarithmic bins along the conductance axis (100/decade) and linear bins (1000/nm) along the displacement axis. For all measurements reported here, the Au substrate was a 100 nm Au layer thermally evaporated on Ted Pella, #16208 AFM specimen disc.

3. Computational Details.

DFT calculations were performed with Quantum Espresso¹⁰, using the optB86b-vdW functional¹¹ and the projector augmented wave method for the treatment of core electrons. The clean Au(111)

surface was modeled by four 5x5 layers and the rough surface was modeled by three 5x5 layers and one Au adatom using 15 Å of vacuum, a Au lattice constant of 4.140 Å, a 2x2x1 k -point sampling of the Brillouin zone, and a 500 eV kinetic energy cutoff. For the clean surface, the two uppermost layers of the slabs were relaxed, while for the rough surface, the adatom and the uppermost layer were relaxed. Reaction paths were found with the climbing image nudged elastic band method.¹² The electric field was modeled using a sawtooth potential¹⁰ and dipole corrections¹³, using a correcting dipole length of 0.89 Å in the direction of the field.

4. Additional Data.

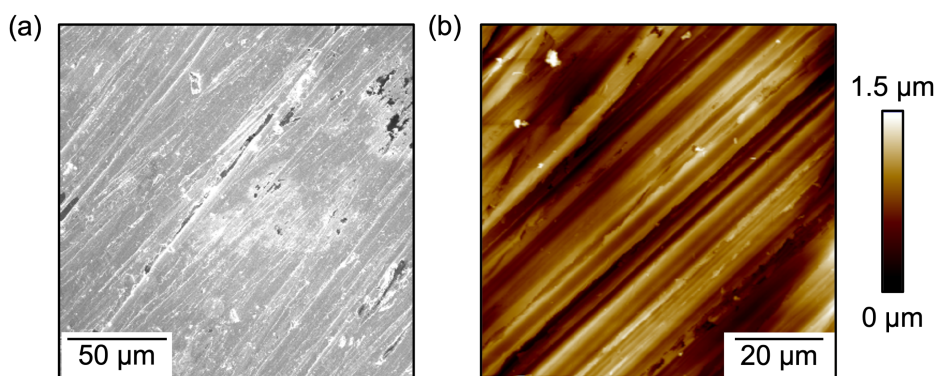


Figure S1. (a) SEM image of Au-coated Steel AFM substrate. (b) AFM image of the same substrate showing features that are under 100 nm high.

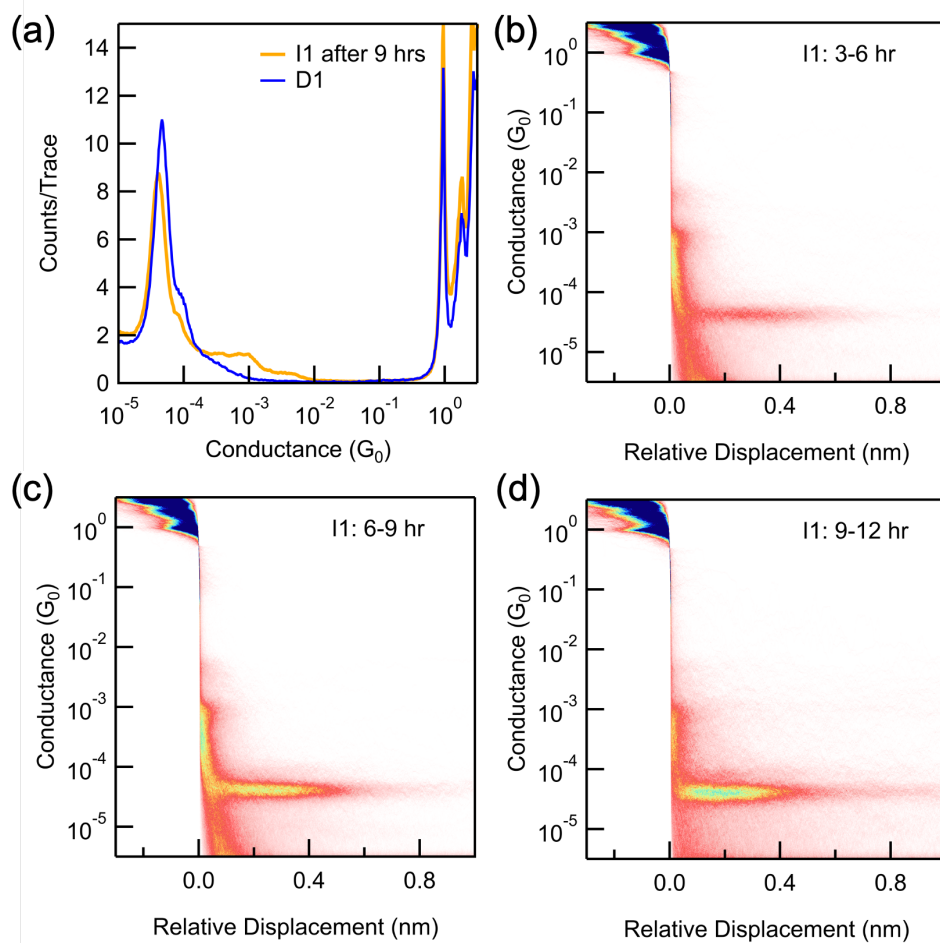


Figure S2. (a) 1D histograms of **I1** after 9 h of measurements and **D1** synthesized ex-situ. (b-d) 2D histograms for data shown in Figure 1b.

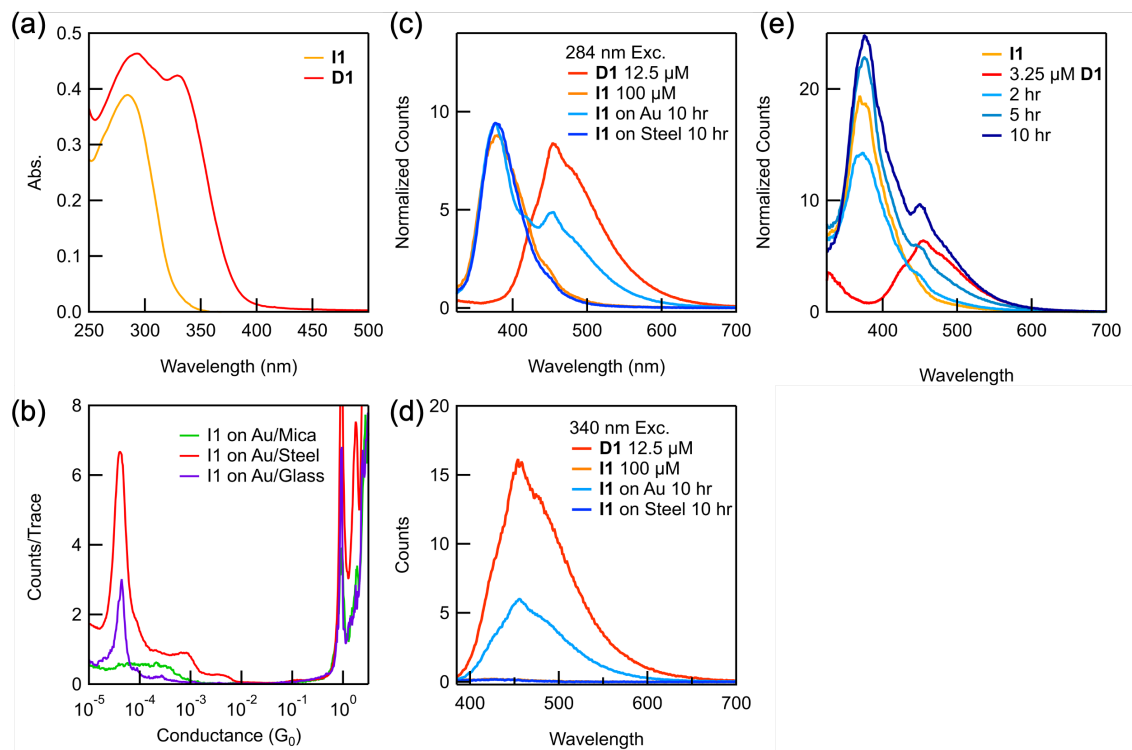


Figure S3. (a) Electronic absorption spectra of **I1** and **D1**. (b) 1D conductance histograms from measurements of solutions of **I1** on different substrates. Note that no peak is seen for measurements of Au on Mica. (c-d) Emission spectra ($\lambda_{ex} = 284$ nm (c) or 340 nm (d)) of solutions of **I1** on steel (no Au coating) compared with stock solutions of **I1** and **D1** and a solution placed on an Au-coated steel substrate. (e) Figure 2a without normalizing the peak heights.

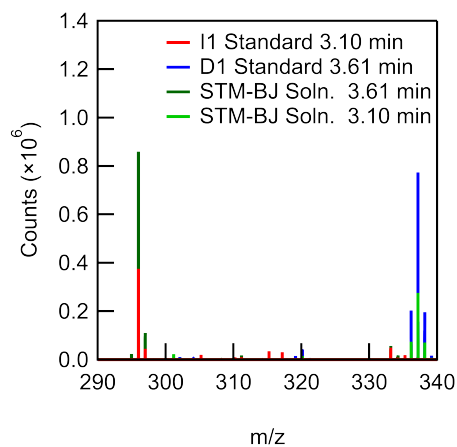


Figure S4. Mass spectra from the **D1** standard (blue), **I1** standard (red) and solution subject to STM-BJ measurements for 12 hours (green) taken from the chromatograms shown in Figure 2c at 3.10 and 3.61 minutes as indicated in the legend. Peak heights do not indicate absolute concentrations as no internal standard was used for these measurements.

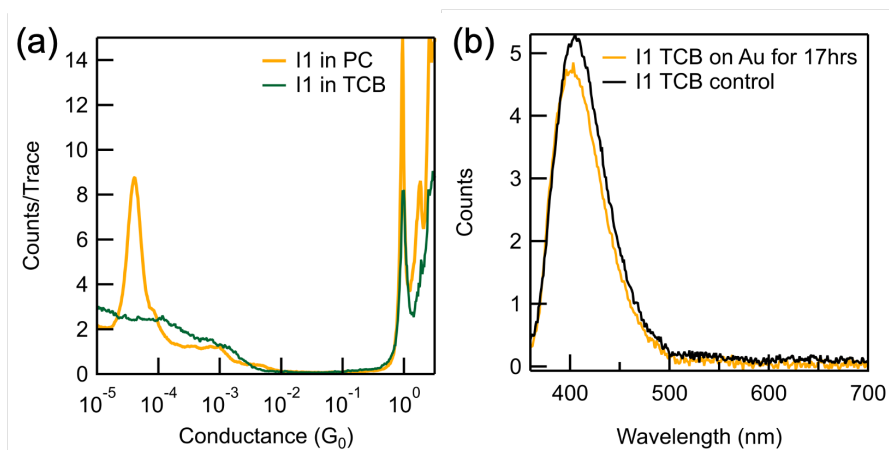


Figure S5. (a) 1D histograms of **I1** measured from a TCB solution (100 μM , green) and a PC solution (100 μM). **D1** is not formed in TCB. (b) Emission spectra ($\lambda_{\text{ex}} = 284 \text{ nm}$) of a TCB solution of **I1** placed on an Au substrate for 17 h along with the stock solution. No evidence of **D1** is seen.

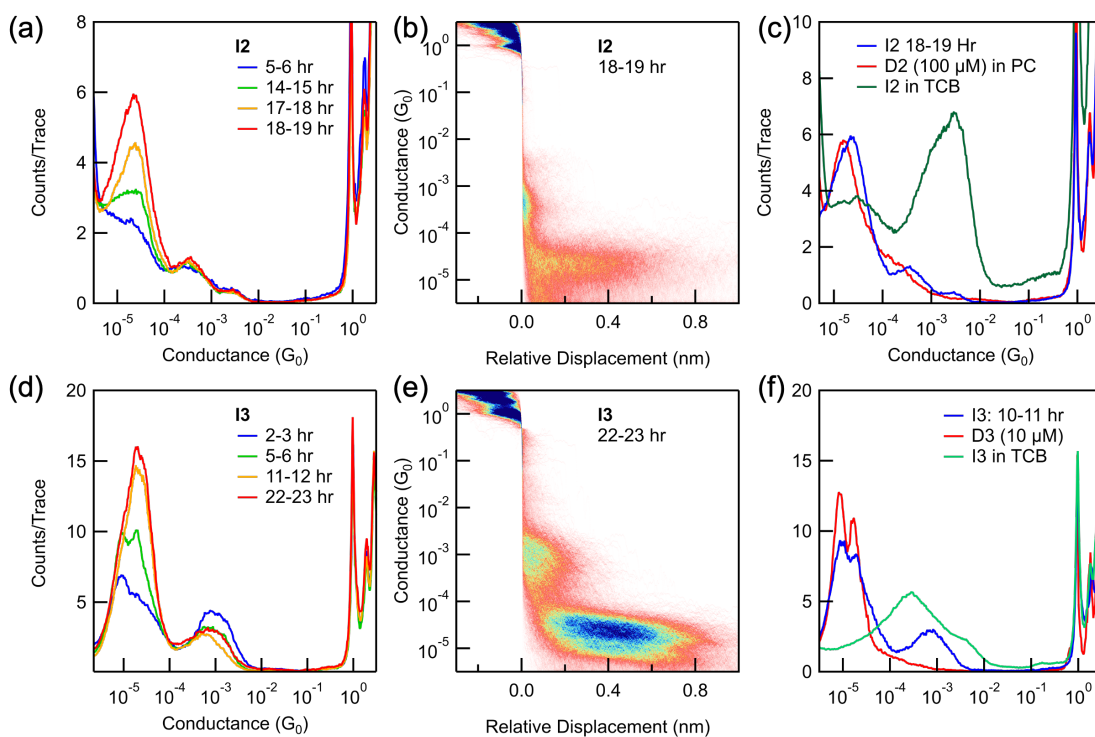


Figure S6. (a) 1D histograms of **I2** measured from PC solution (100 μM) as a function of time. A clear peak grows around $2 \times 10^{-5} G_0$ corresponding to **D2**. (b) 2D histogram corresponding to the data collected from 18-19 h. (c) 1D conductance histograms for **I2** in PC after 18 h, **D2** in PC and **I2** in TCB. (d-f) Analogous figures for **I3** measurements.

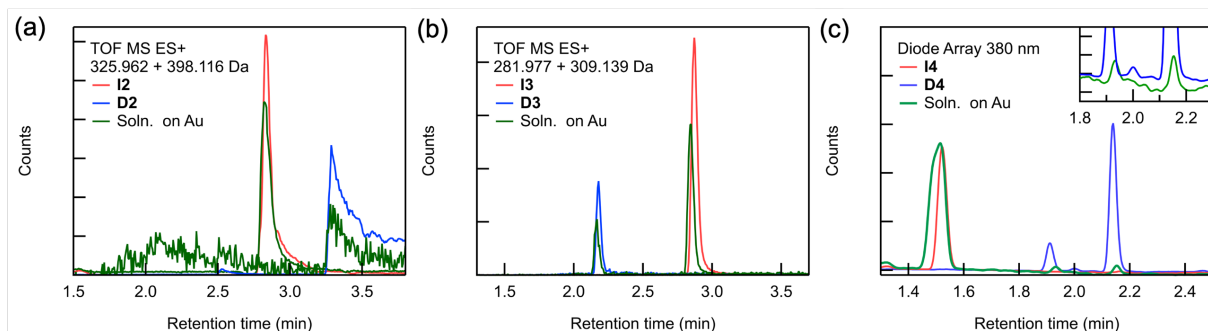


Figure S7. (a) LC-MS spectra for the **I2** standard (red), the **D2** standard (blue), and the solution subject to STM-BJ measurements for 12 h (green). A clear signal indicating formation of **D2** is seen in the green trace. (b) Analogous figure for **I3/D3** pair. (c) Electronic absorption spectroscopy for the **I4/D4** pair. Inset: relevant peaks expanded for clarity, demonstrating that both **I4** and **D4** are present in the experimental solution.

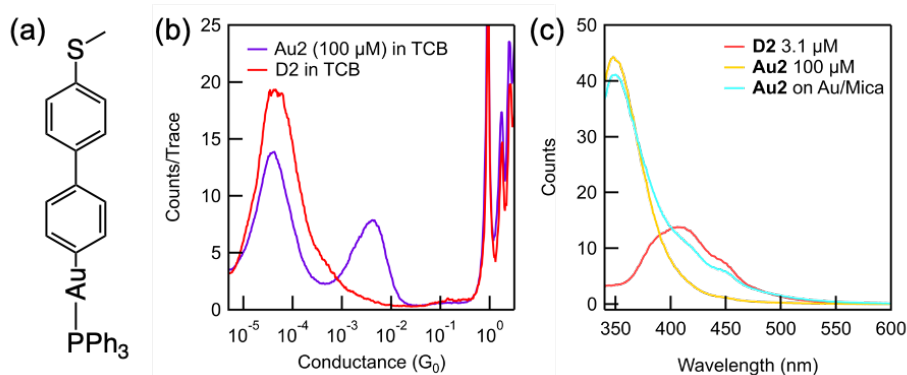


Figure S8. (a) Structure of **Au2**. (b) 1D histograms of a measurement of **Au2** and **D2** in TCB. (c) Emission spectra ($\lambda_{ex} = 284$ nm) of a **D2** standard (red), the solution of **Au2** and the solution of **Au2** placed on an Au/mica substrate. We have clear evidence of **D2** formed in the solution placed on Au/mica.

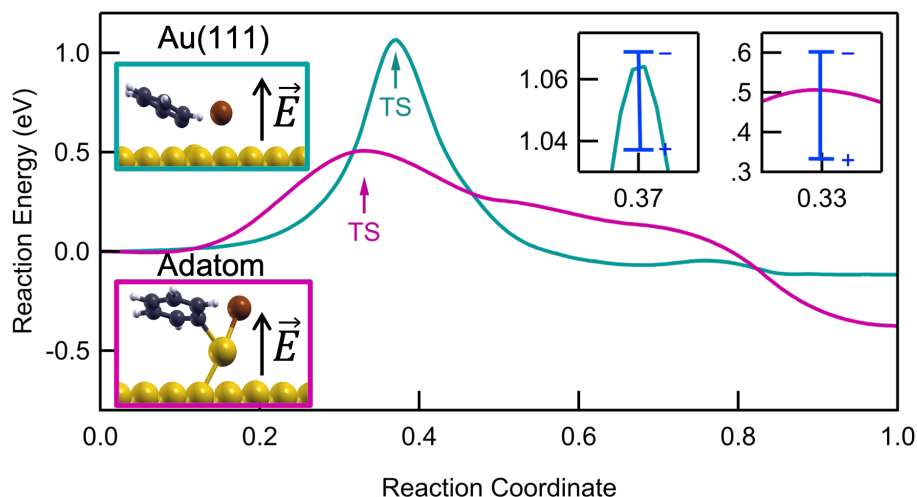


Figure S9. The reaction energy over the course of the dehalogenation process, from reactant (reaction coordinate = 0) to transition state (TS) to product (reaction coordinate = 1) of bromobenzene. The calculations are made on an Au(111) surface (green) and with an additional Au adatom (pink). The blue bars at the TS denote the change of the activation energy due to an applied electric field in the range of ± 3 V/nm (close-up shown in insets at right). Insets at left show the TS geometries and the black arrows indicate the direction of a positive electric field.

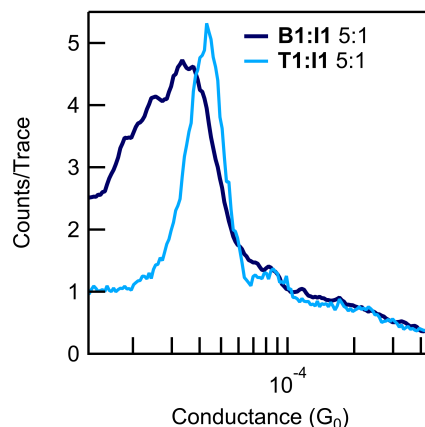
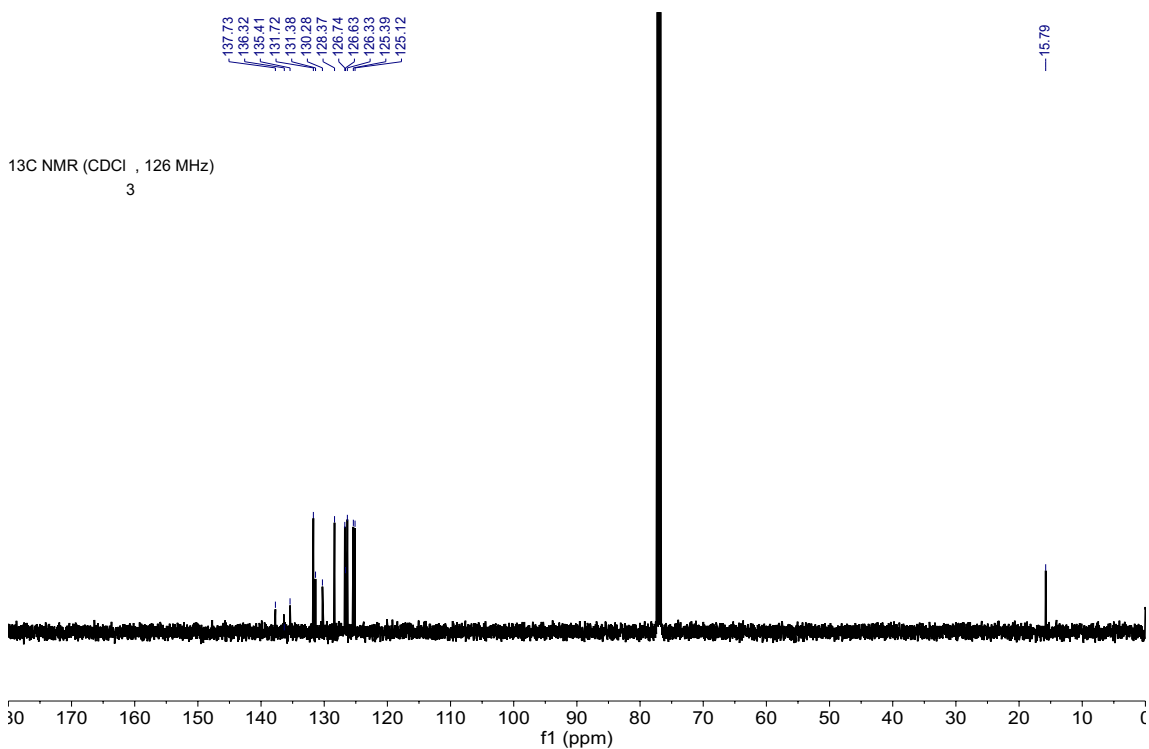
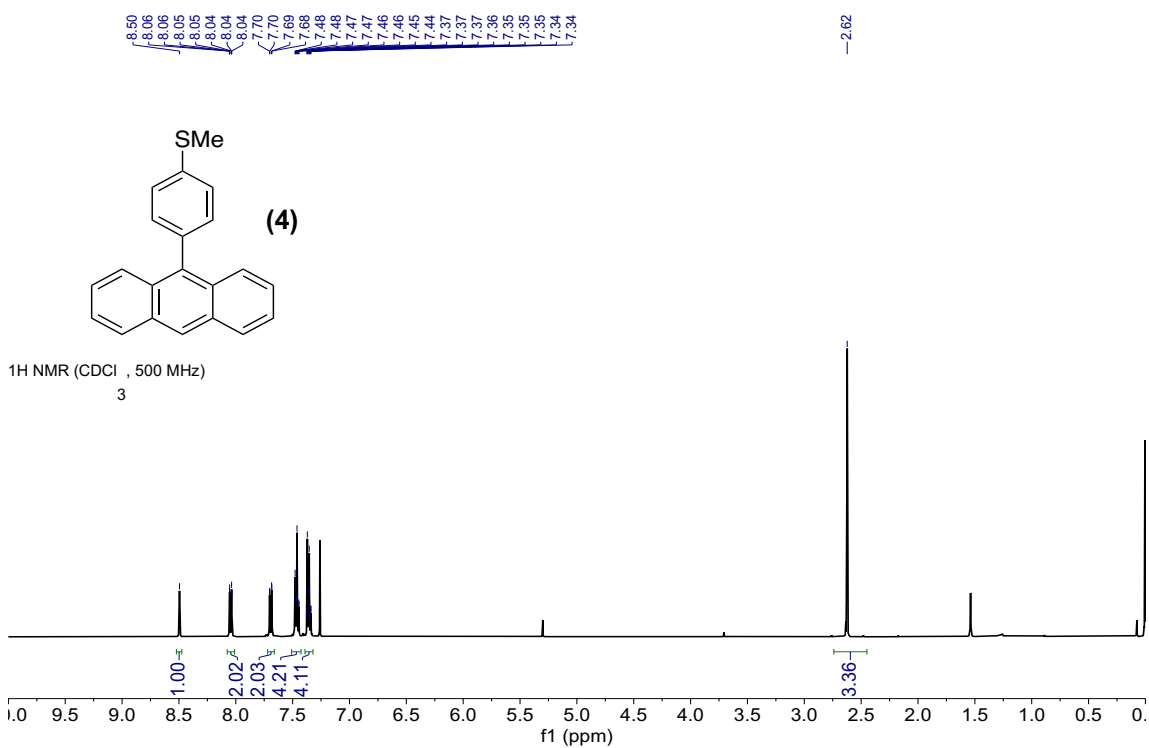
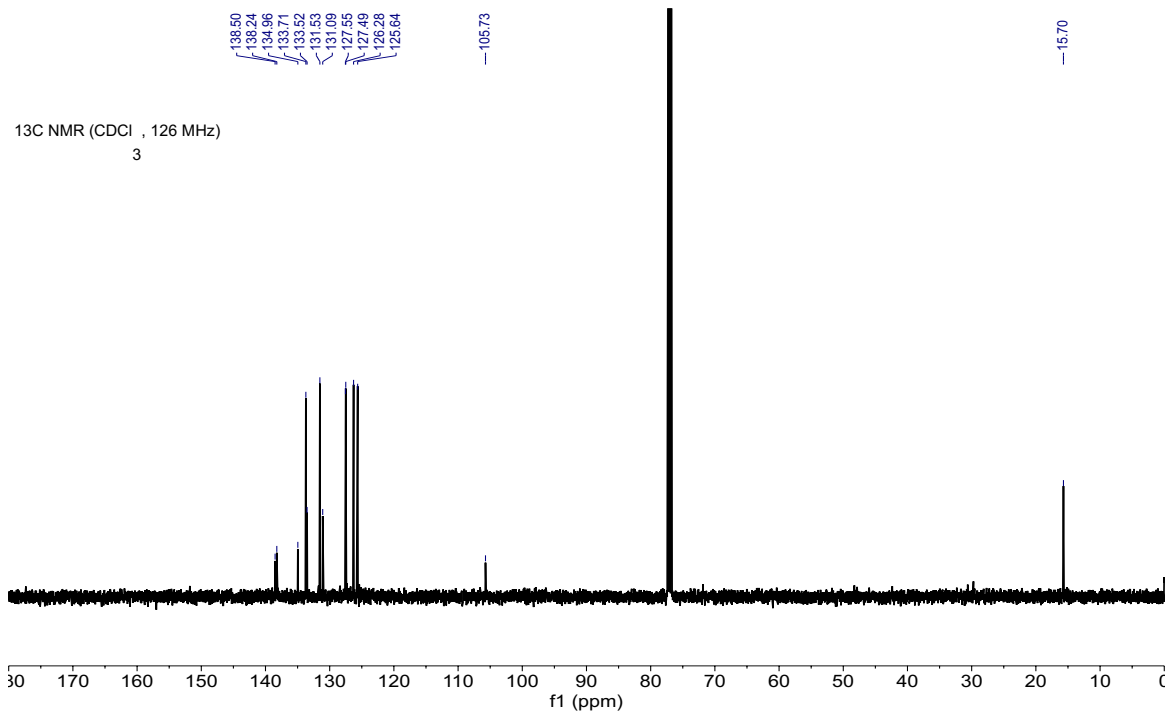
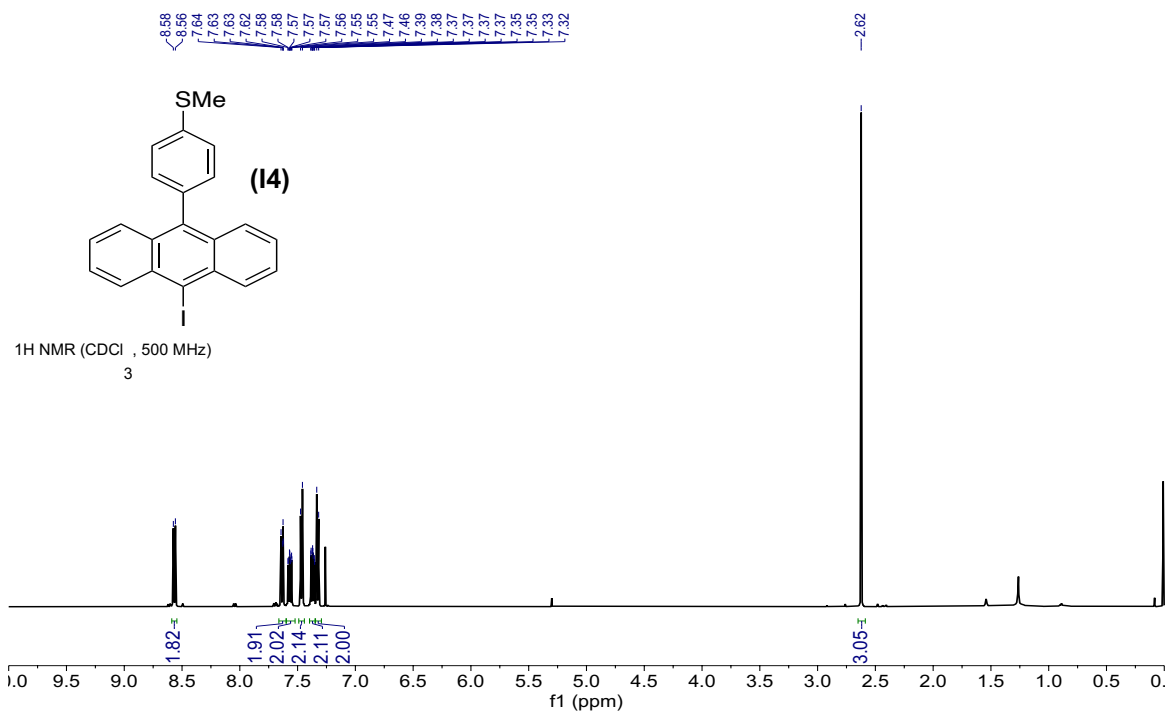
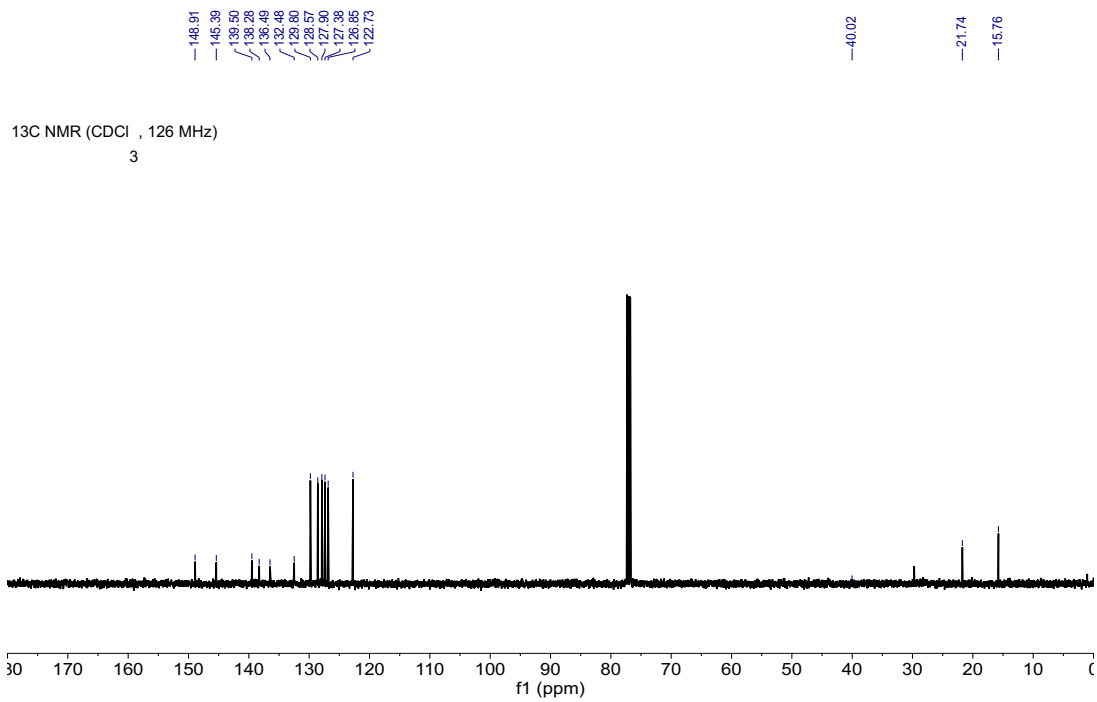
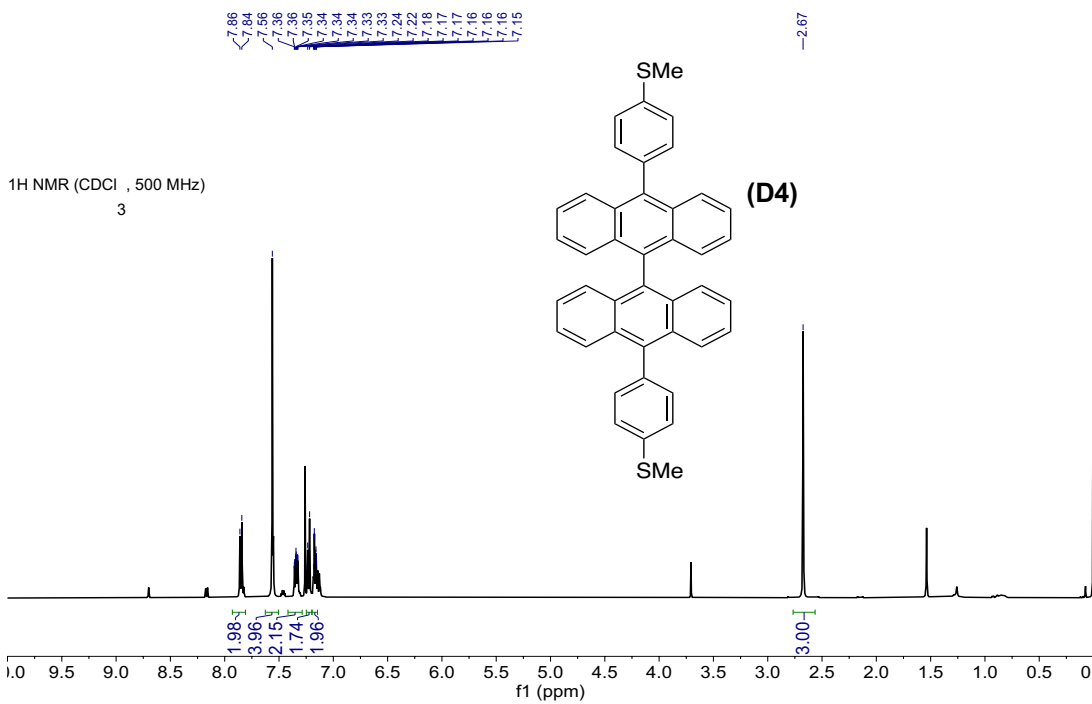


Figure S10. 1D histograms of a measurement of a mixture of **T1** and **I1** in a 5:1 ratio along with histogram for the **B1** and **I1** mixture. Solutions have a $100 \mu\text{M}$ concentration of molecules in PC with 100 mM Tetrabutyl Ammonium Perchlorate (TBAP) supporting electrolyte. The measurement with the **T1/I1** mixture was repeated six times and no second peak was ever observed similar to what was seen with the **B1/I1** mixture.

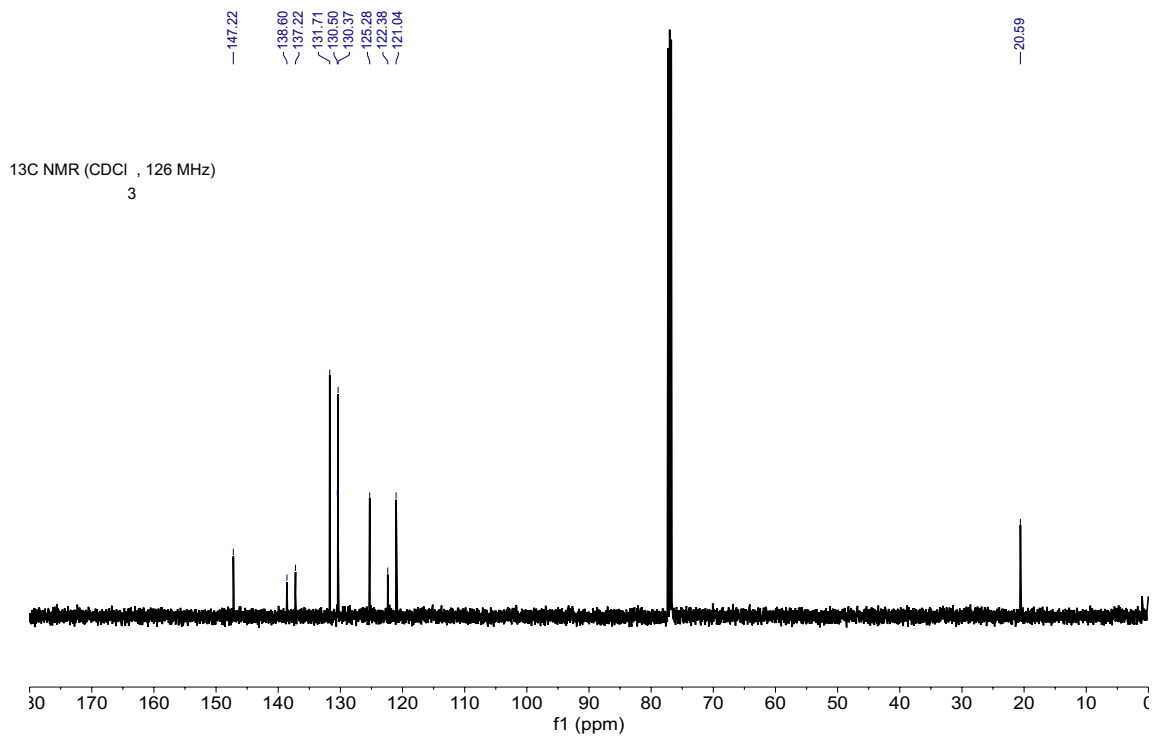
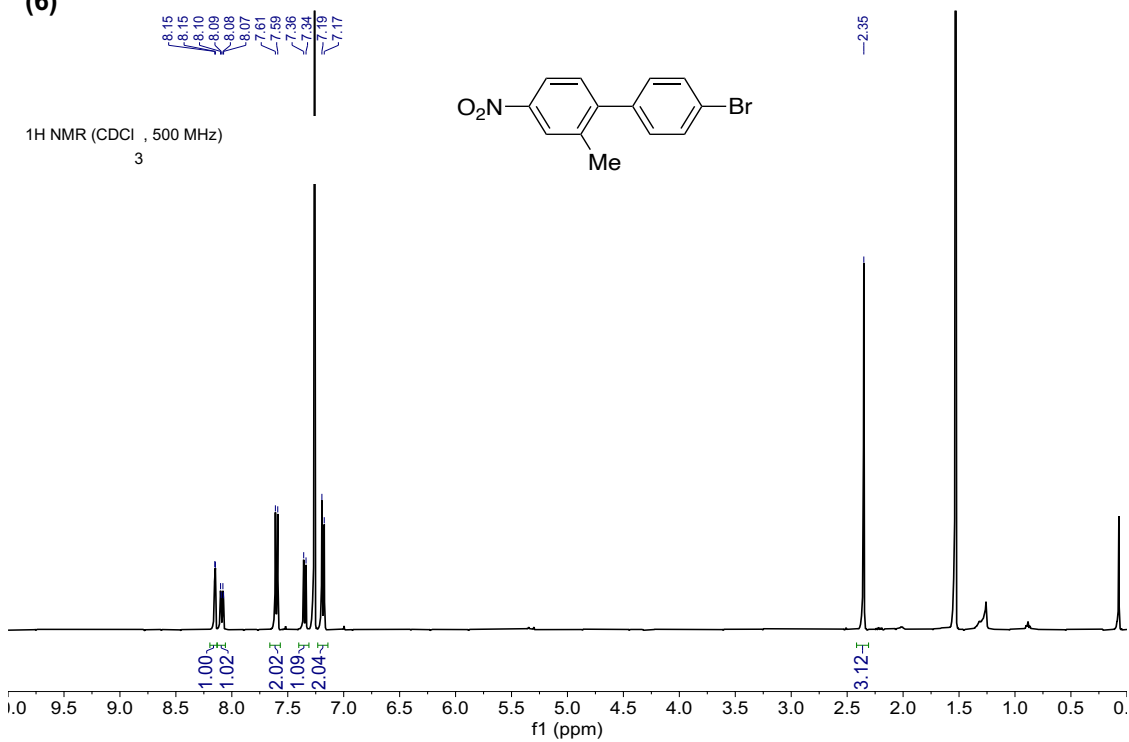
6. NMR Spectra.

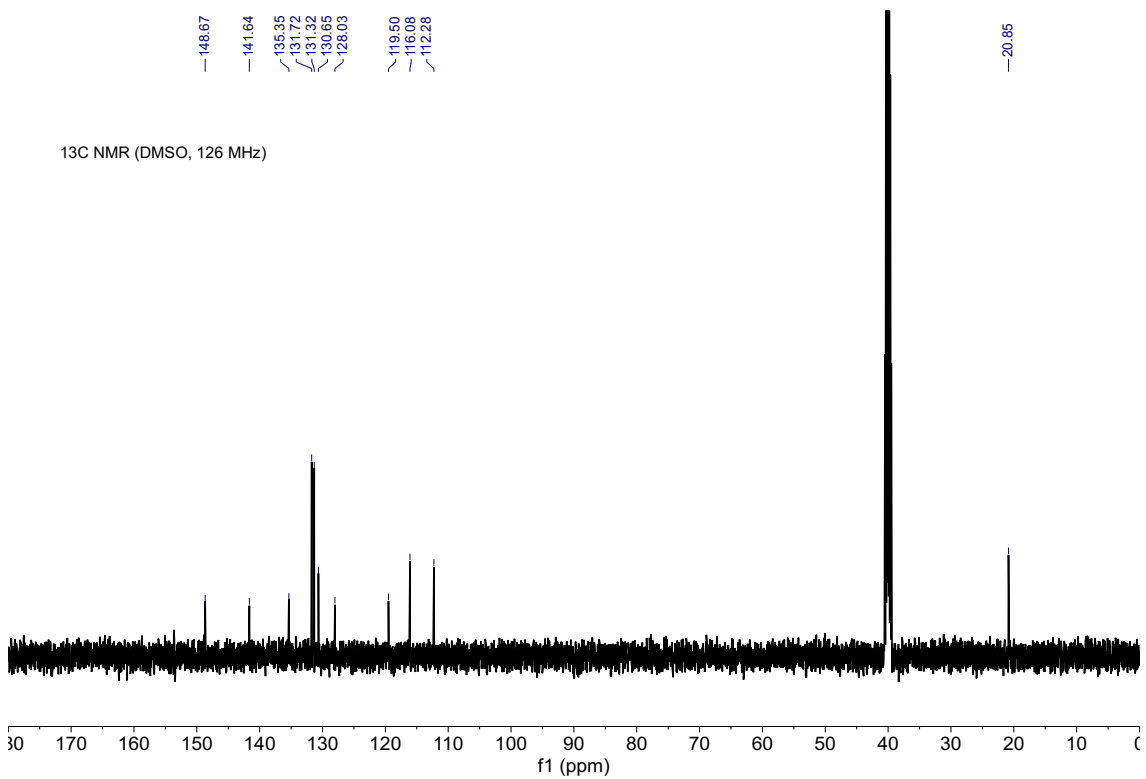
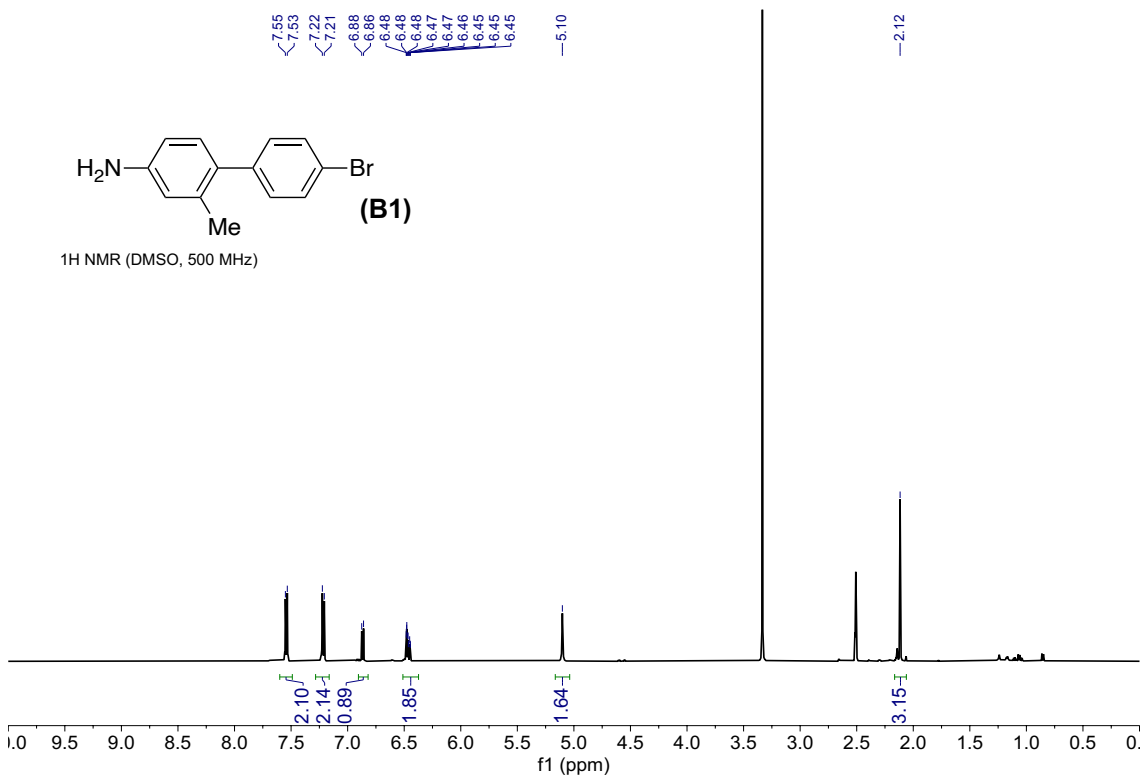




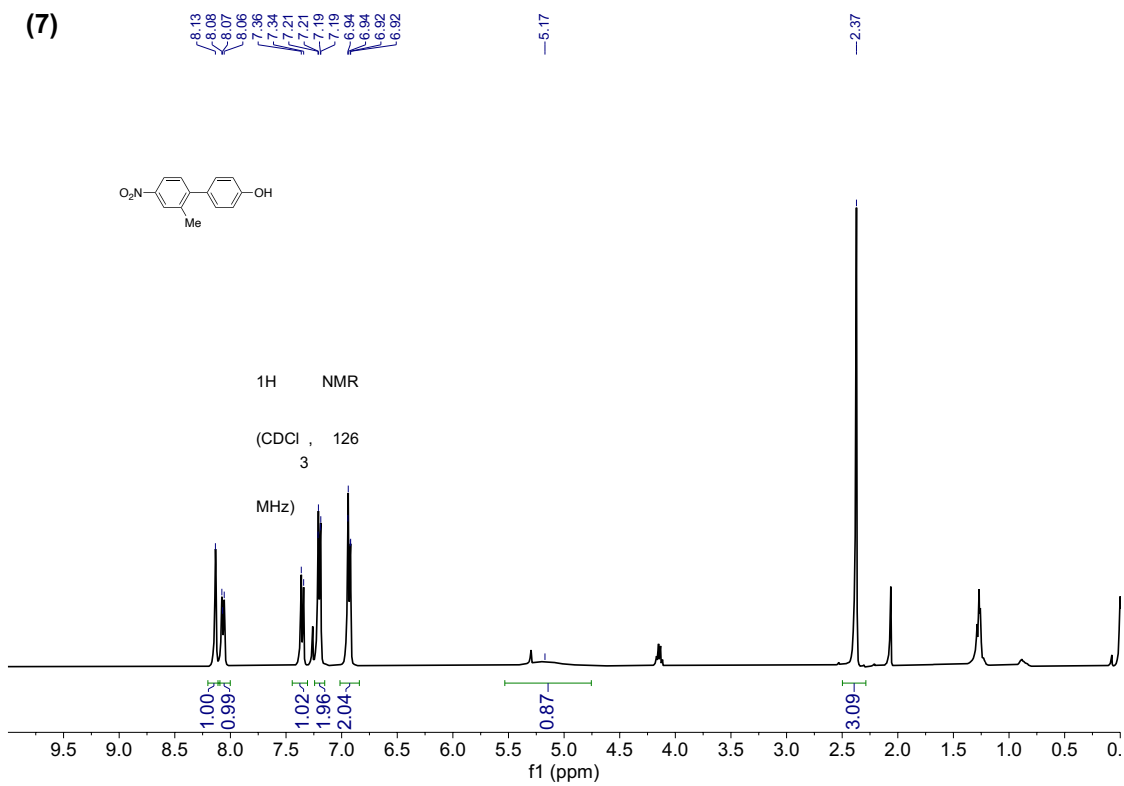


(6)

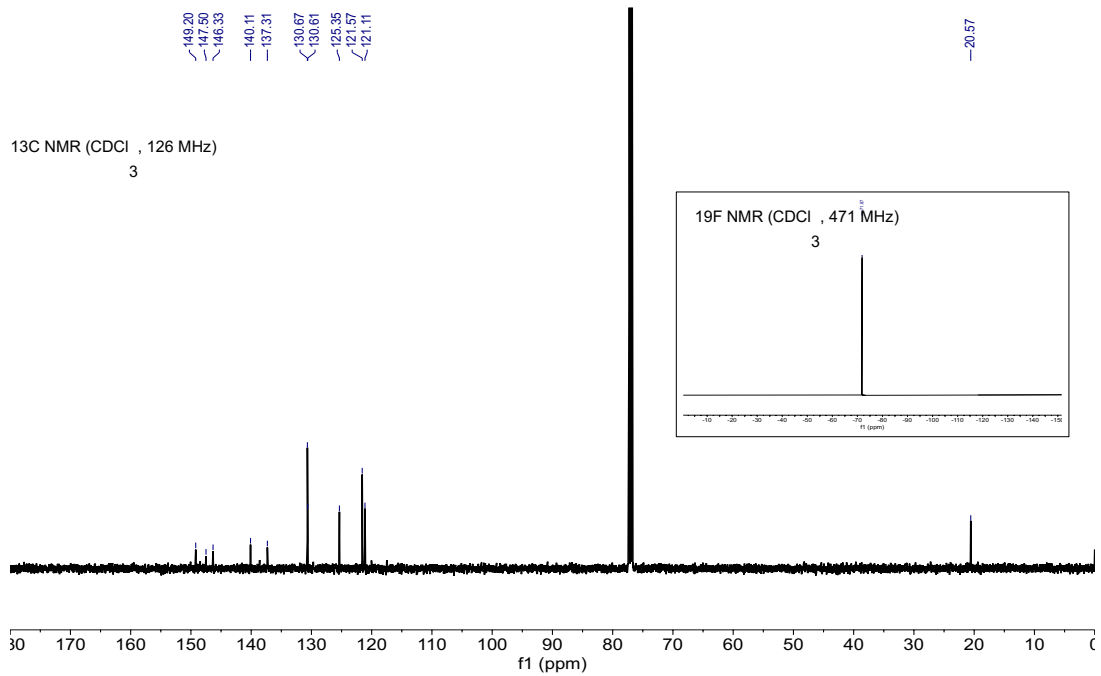
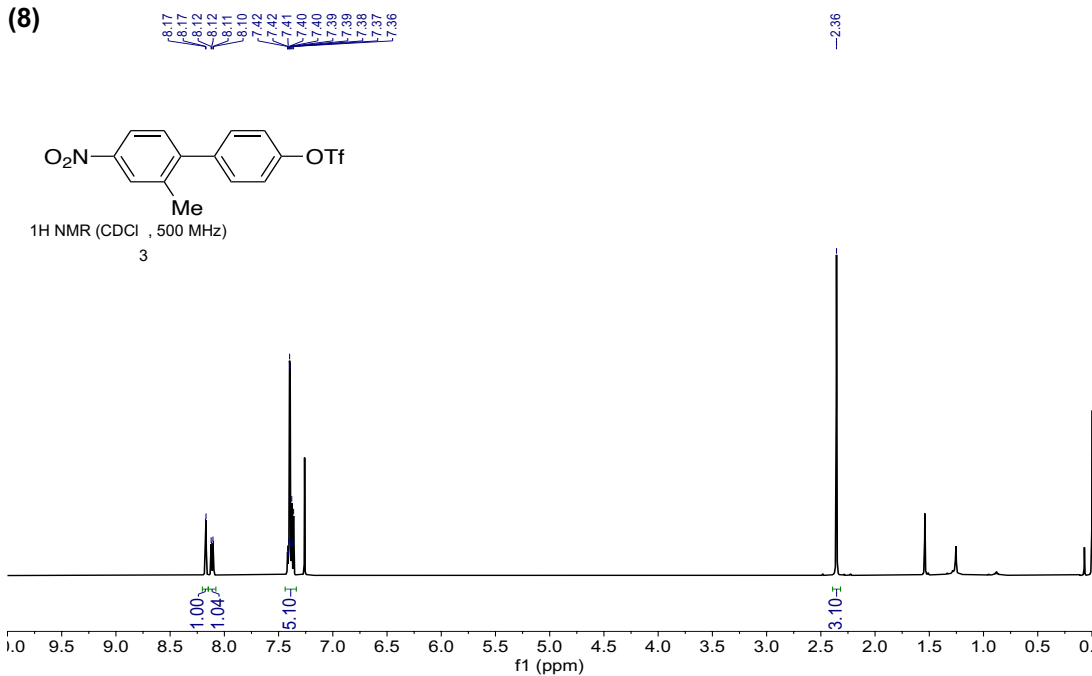




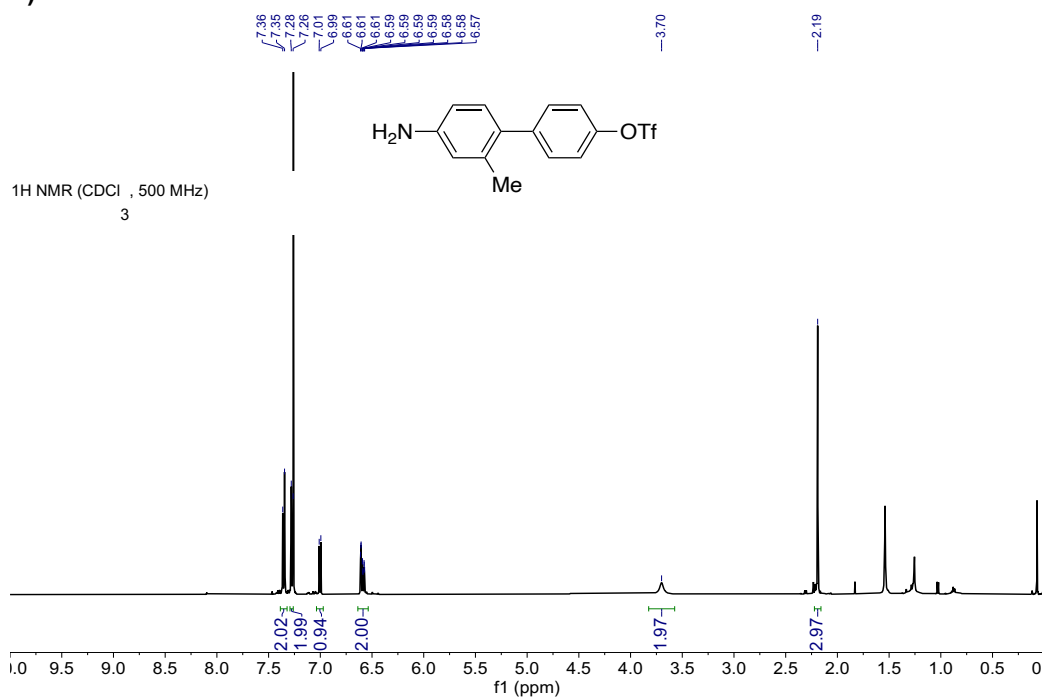
(7)



(8)

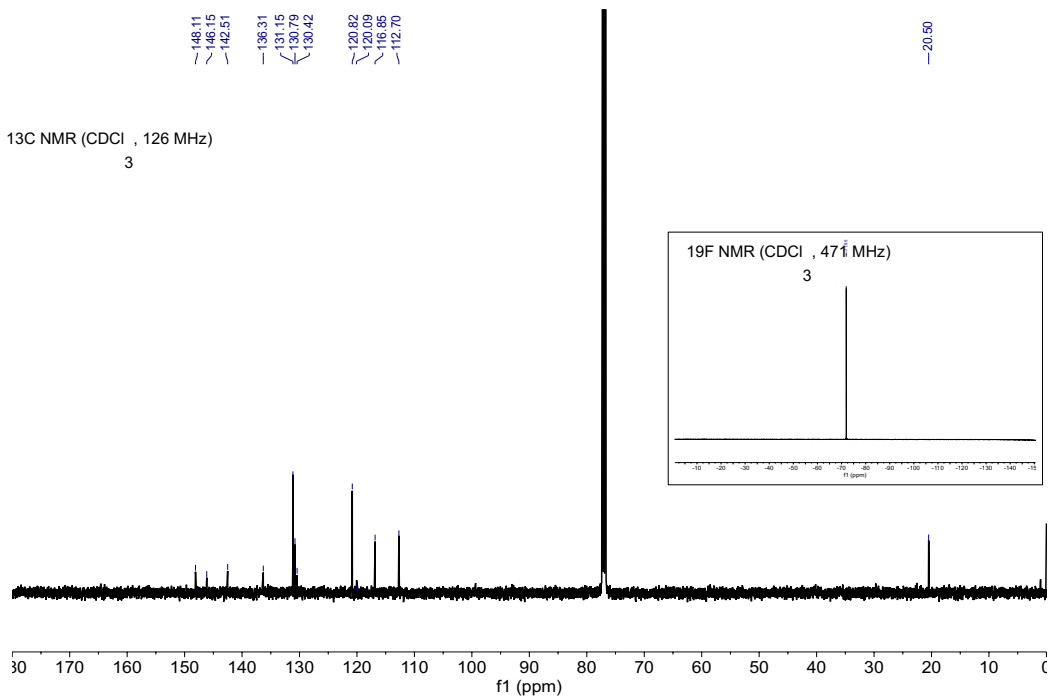


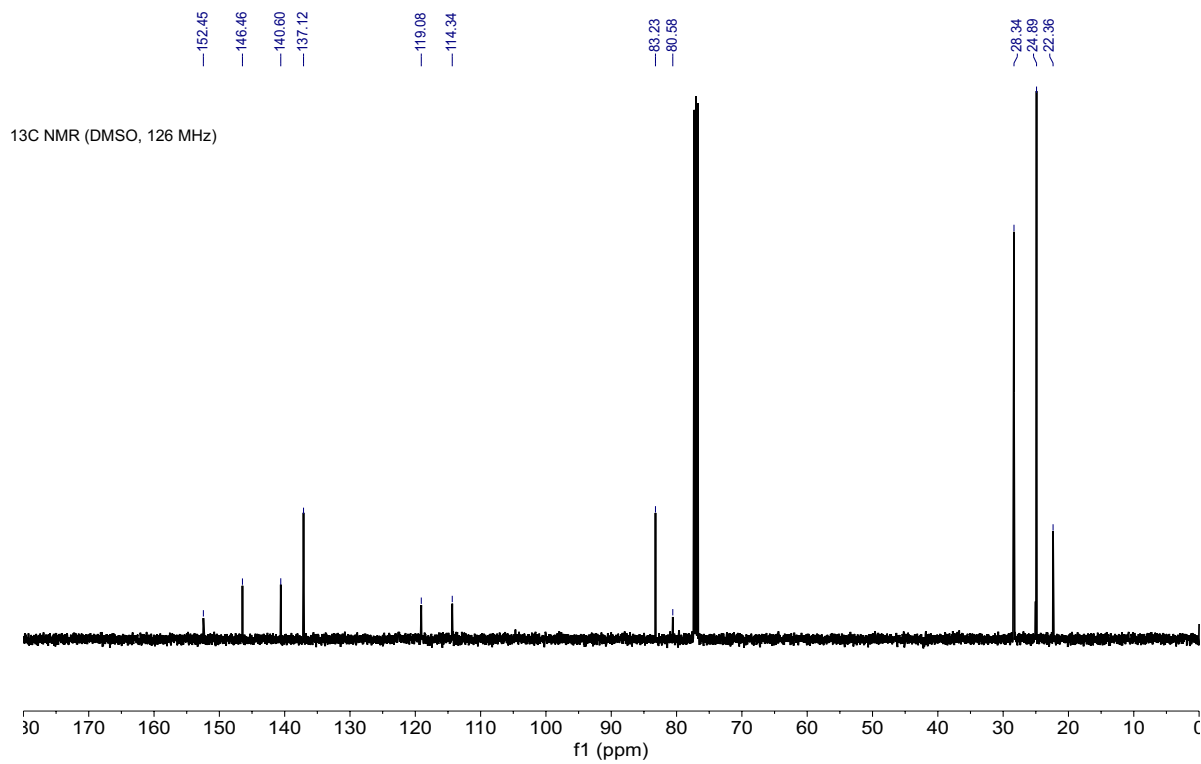
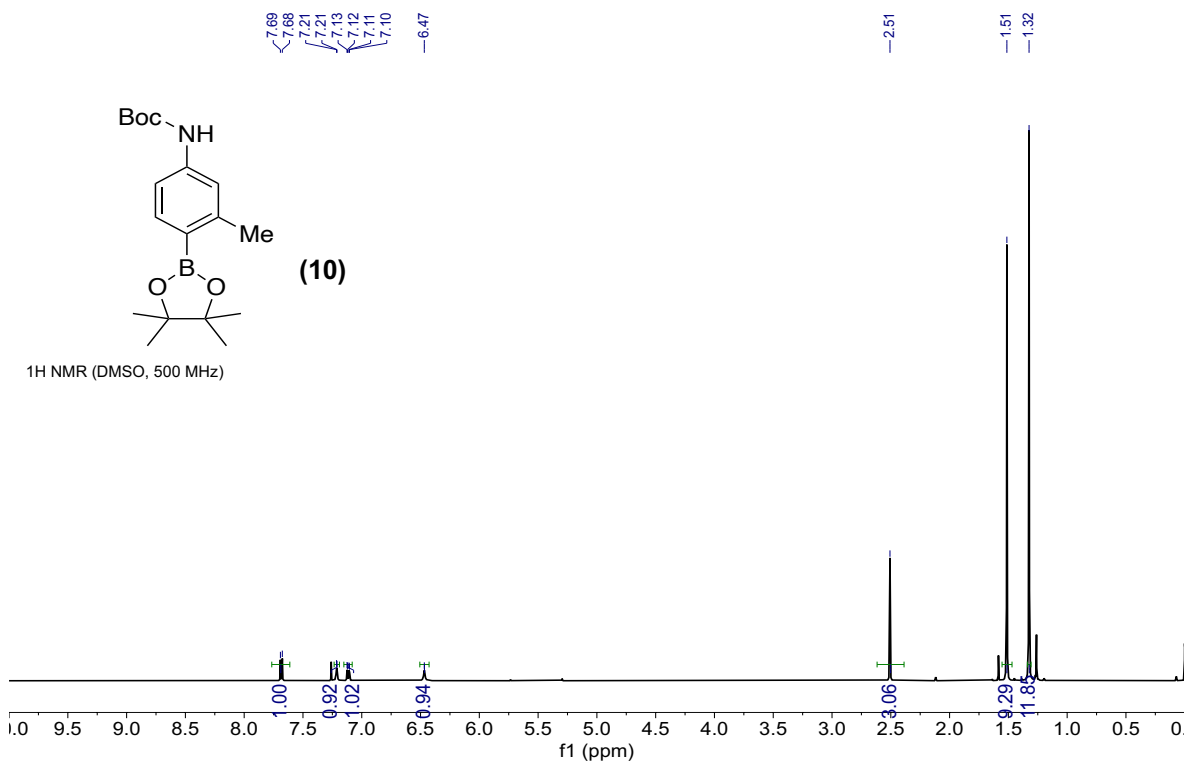
(T1)

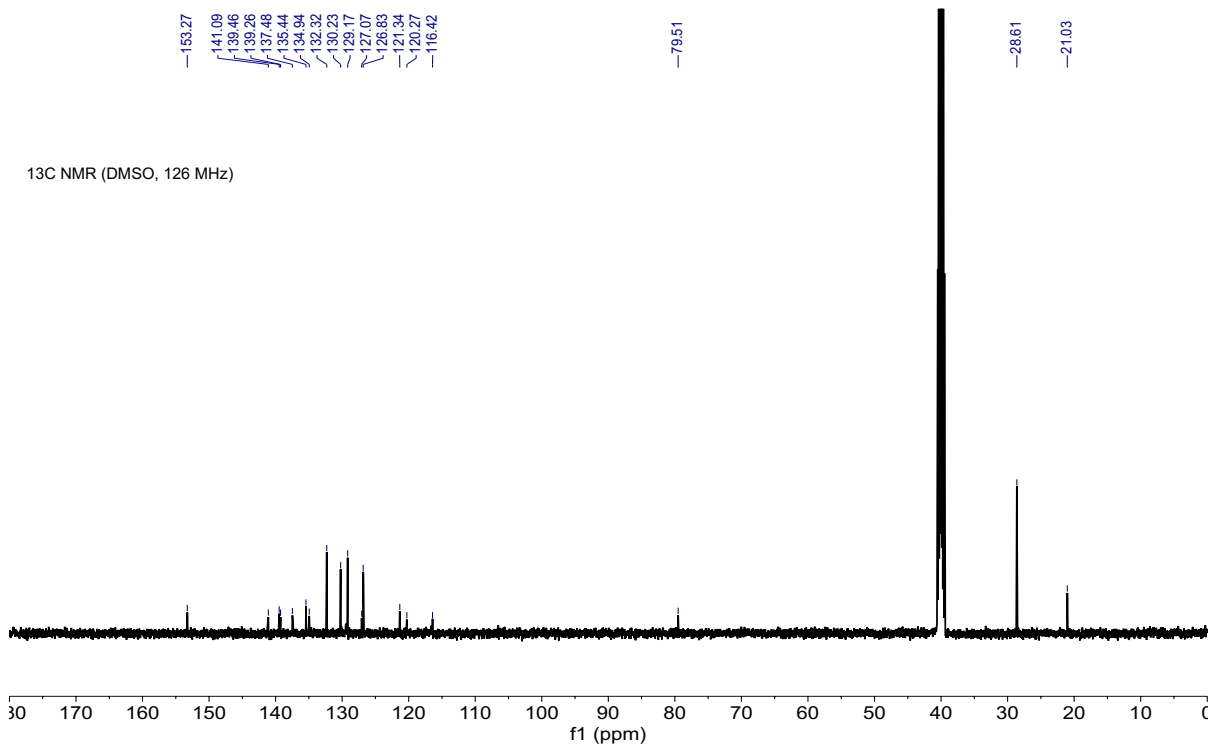
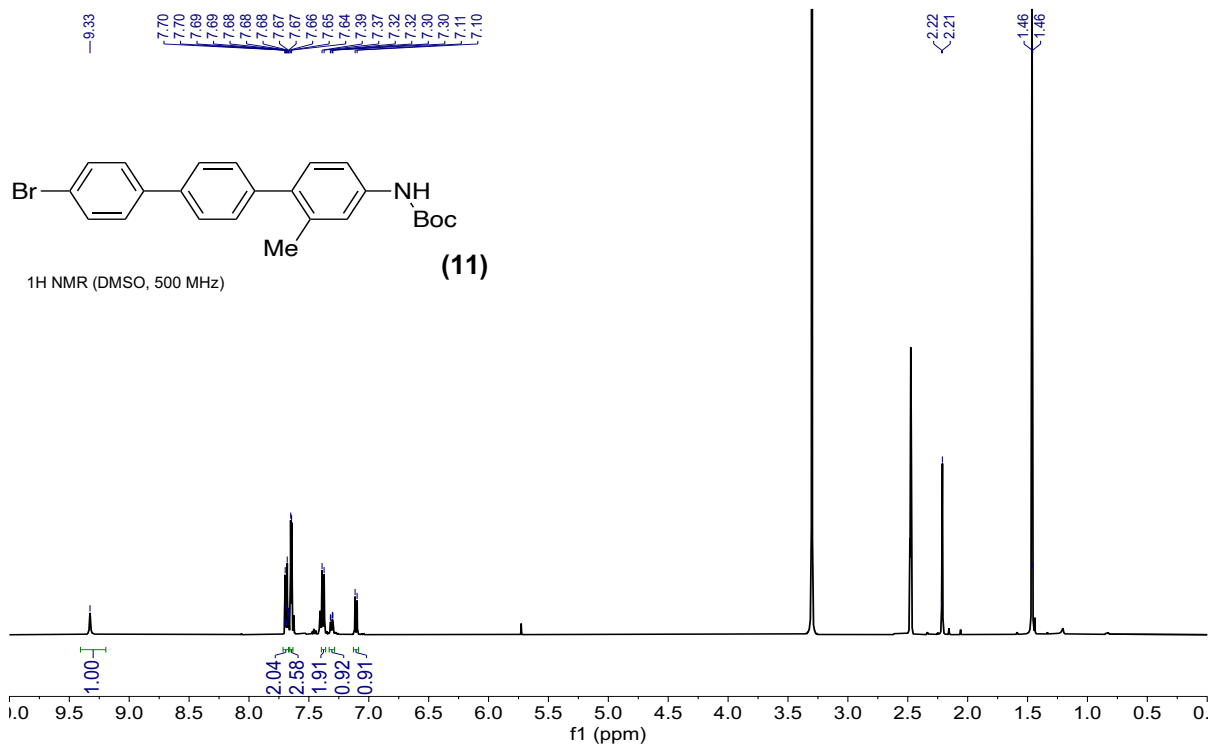


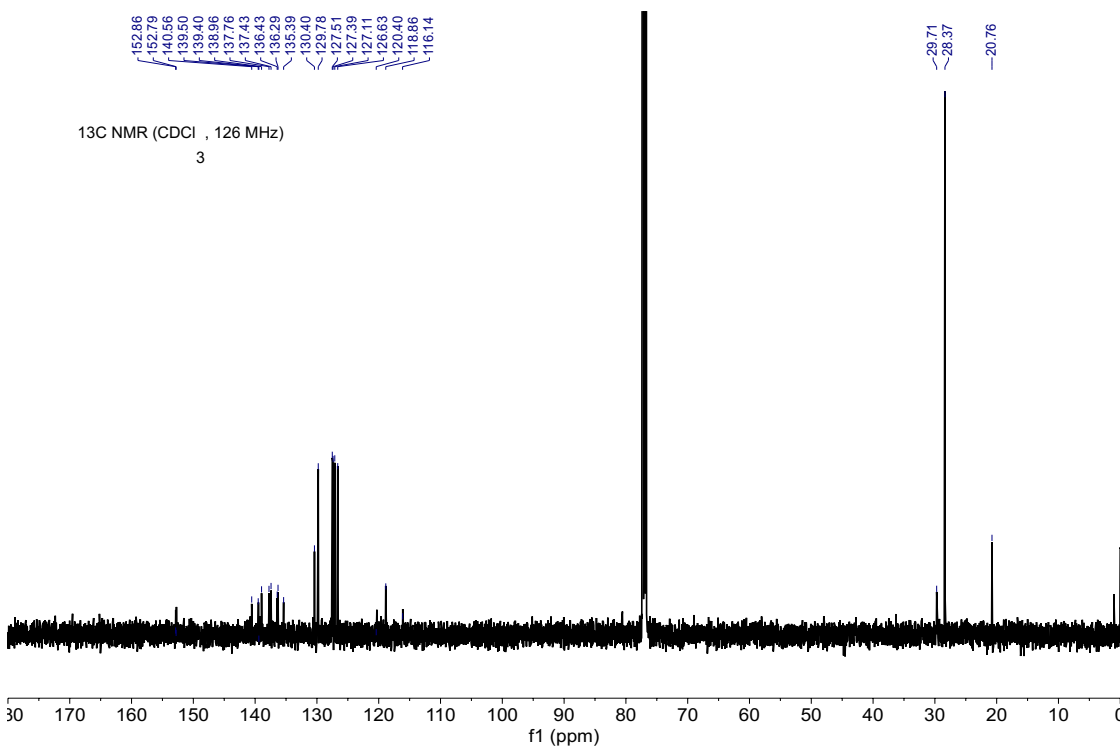
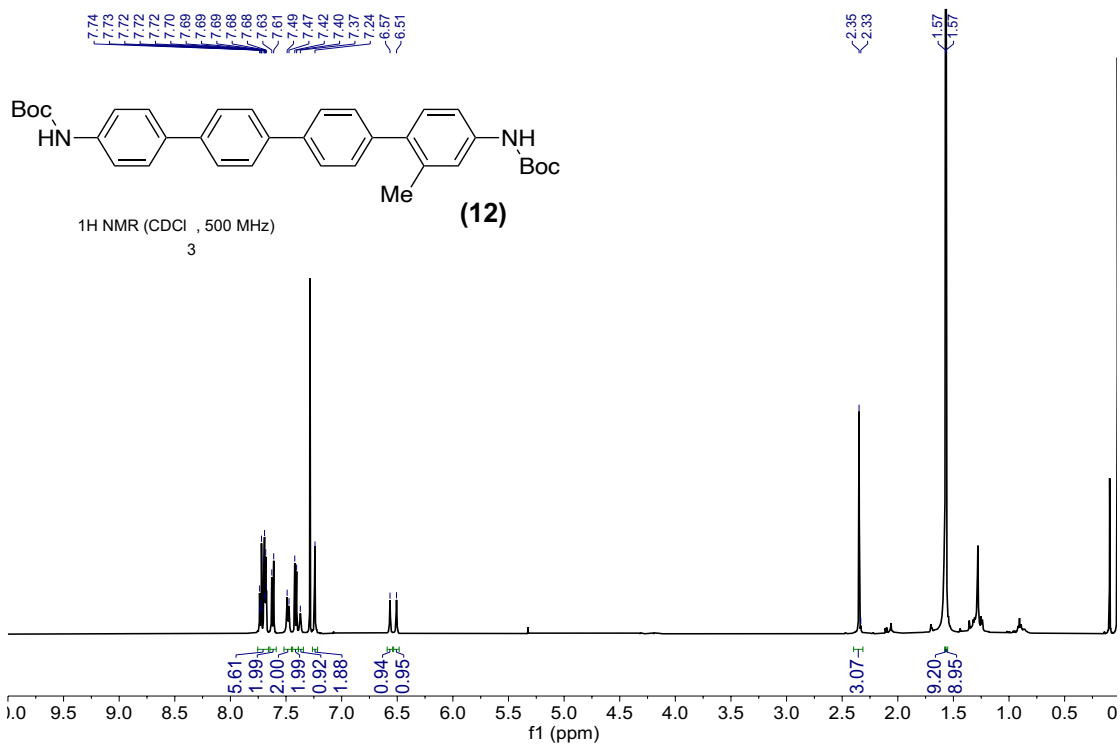
¹³C NMR (CDCl₃, 126 MHz)

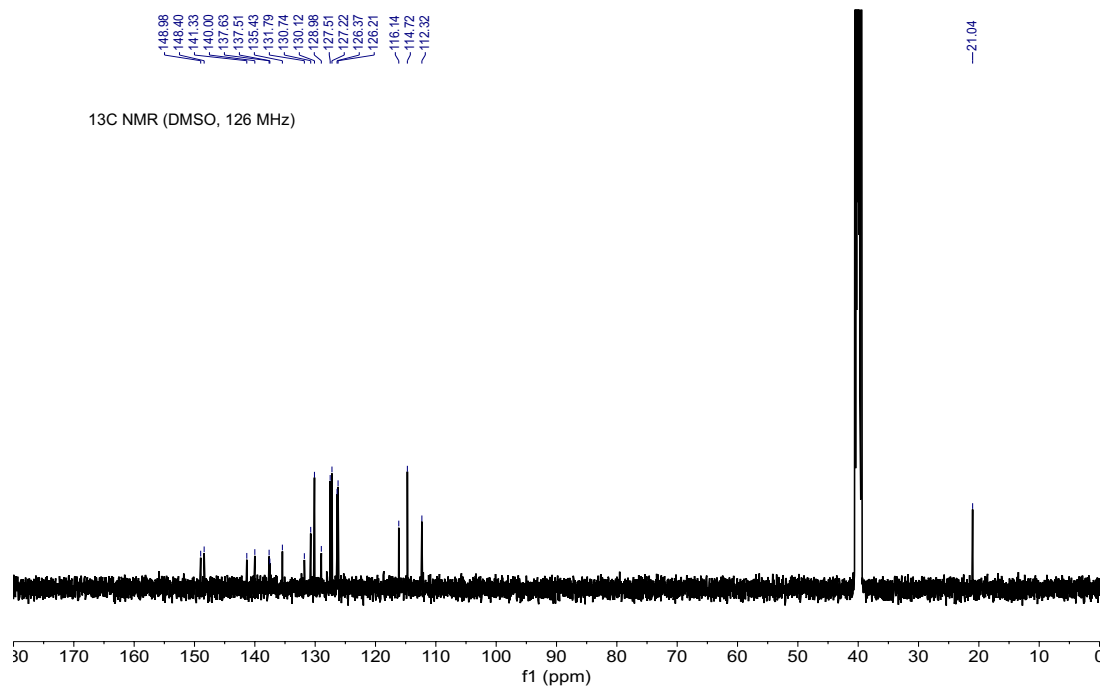
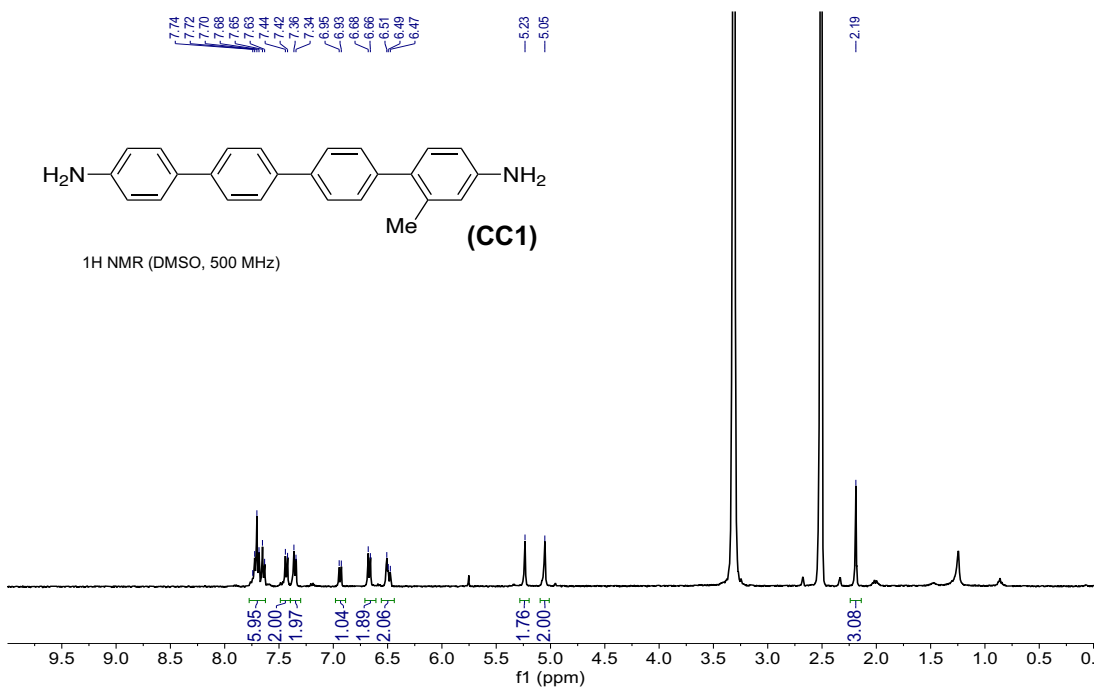
3











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