

Supporting Information

Ni-Catalyzed Coupling of Butadiene, Aldimines and Arylboronic Acids to Homoallylic Amines under Base-Free Conditions

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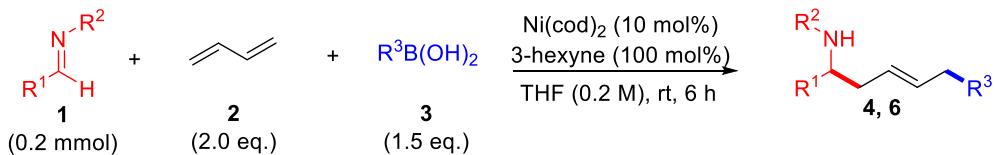
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1. General Information

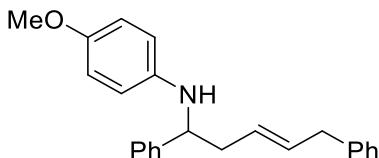
All reactions were conducted under a nitrogen atmosphere in oven-dried glassware with a standard drybox or vacuum-line techniques unless otherwise indicated. Reaction solvents, including methanol, tetrahydrofuran, toluene, cyclohexane, etc., were purchased from Energy Chemical Co. Ltd. or J&K Chemical Co. Ltd. and used as received. Bis(1,5-cyclooctadiene)nickel was purchased from Strem Chemicals Inc. and stored in the fridge (-20°C) of the glovebox. Chemicals were used as received from the suppliers. All new compounds were characterized by NMR spectroscopy, high-resolution mass spectroscopy. NMR spectra were recorded on a Bruker 400 MHz spectrometer and were calibrated using residual solvent as an internal reference (CDCl_3 : 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). EI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier. ESI-HRMS spectra were obtained on a Thermo Fisher Scientific LTQ FT Ultra or an Agilent Technologies 6224 TOF LC/MS. FI-HRMS spectra were obtained on a JEOL-AccuTOF-GCv4G-GTC MS.

2. Coupling of Butadiene, Aldimine, and Organoboronic Acids



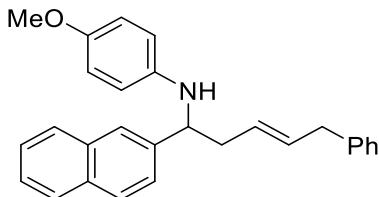
General Procedure (GP): In a nitrogen-filled glovebox, aldimine (0.2 mmol) and Ni(cod)₂ (5.5 mg, 0.02 mmol) were dissolved in THF (0.7 mL) in an 8 ml vial equipped with a magnetic stirrer bar. Then butadiene (3 M in toluene, 134 μ L, 0.4 mmol), 3-hexyne (23 μ L, 0.2 mmol), and organoboronic acid (1 M in THF, 300 μ L, 0.3 mmol) were added successively. The vial was sealed, taken out of the glovebox, and stirred at ambient temperature for 6 h. The resulting mixture was then filtered through a silica gel pad eluting with EtOAc and concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography (silica gel) to give the corresponding homoallylic amines.

(E)-N-(1,5-Diphenylpent-3-en-1-yl)-4-methoxyaniline (4a)



Yellow oil, 69.2 mg, yield 99%. **IR (neat, cm⁻¹)** 1509, 1235, 1033, 970, 817, 747, 698; **¹H NMR (400 MHz, CDCl₃)** δ : 7.39 – 7.25 (m, 6H), 7.26 – 7.15 (m, 2H), 7.17 – 7.10 (m, 2H), 6.71 – 6.62 (m, 2H), 6.45 – 6.35 (m, 2H), 5.81 – 5.64 (m, 1H), 5.55 – 5.38 (m, 1H), 4.26 (dd, *J* = 8.2, 5.1 Hz, 1H), 3.93 (br, 1H), 3.67 (s, 3H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.61 – 2.50 (m, 1H), 2.48 – 2.35 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ : 152.1, 144.1, 141.9, 140.6, 133.3, 128.7, 128.6, 128.6, 127.7, 127.0, 126.5, 126.2, 114.9, 114.7, 58.5, 55.9, 42.3, 39.2; **HRMS (ESI)** calculated for C₂₄H₂₆NO [M+H]⁺ *m/z* 344.2009, found 344.2014.

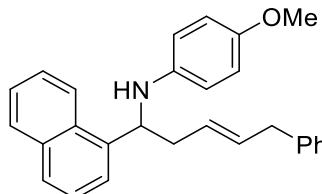
(E)-4-Methoxy-N-(1-(naphthalen-2-yl)-5-phenylpent-3-en-1-yl)aniline (4b)



Yellow oil, 72.1 mg, yield 92%. **IR (neat, cm⁻¹)** 1508, 1235, 1034, 816, 745, 698, 477; **¹H NMR (400 MHz, CDCl₃)** δ : 7.87 – 7.70 (m, 4H), 7.50 – 7.37 (m, 3H), 7.27 – 7.14 (m, 3H), 7.12 – 7.07 (m, 2H), 6.68 – 6.59 (m, 2H), 6.48 – 6.39 (m, 2H), 5.80 – 5.65 (m, 1H), 5.56 – 5.42 (m, 1H), 4.41 (dd, *J* = 8.1, 5.1 Hz, 1H), 4.01 (br, 1H), 3.64 (s, 3H), 3.32 (d, *J* = 6.9 Hz, 2H), 2.71 – 2.56 (m, 1H), 2.55 – 2.41

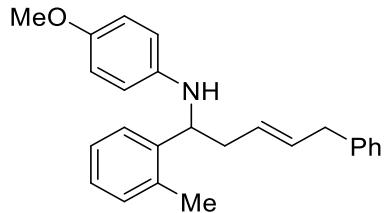
(m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 141.8, 141.6, 140.5, 133.6, 133.4, 132.9, 128.6, 128.6, 128.5, 128.0, 127.8, 127.6, 126.2, 126.1, 125.6, 125.1, 124.9, 114.9, 114.8, 58.7, 55.8, 42.2, 39.2. **HRMS (ESI)** calculated for C₂₈H₂₈NO [M+H]⁺ *m/z* 394.2165, found 394.2159.

(E)-4-Methoxy-N-(1-(naphthalen-1-yl)-5-phenylpent-3-en-1-yl)aniline (4c)



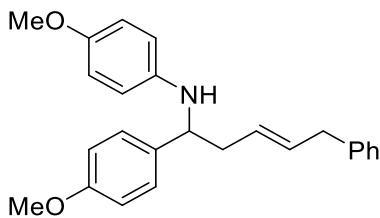
Yellow oil, 59.4 mg, yield 76%. **IR (neat, cm⁻¹)** 1509, 1235, 1035, 970, 907, 799, 729, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 8.18 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.43 – 7.36 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.12 (m, 3H), 6.66 – 6.59 (m, 2H), 6.39 – 6.33 (m, 2H), 5.84 – 5.71 (m, 1H), 5.62 – 5.50 (m, 1H), 5.10 (t, *J* = 6.1 Hz, 1H), 3.65 (s, 3H), 3.36 (d, *J* = 6.8 Hz, 2H), 2.85 – 2.74 (m, 1H), 2.55 – 2.43 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 141.7, 140.6, 138.6, 134.3, 133.4, 130.8, 129.4, 128.6, 128.6, 127.9, 127.5, 126.3, 126.2, 126.0, 125.5, 123.4, 122.6, 114.9, 114.6, 55.9, 54.2, 40.7, 39.3. **HRMS (ESI)** calculated for C₂₈H₂₈NO [M+H]⁺ *m/z* 394.2165, found 394.2156.

(E)-4-Methoxy-N-(5-phenyl-1-(o-tolyl)pent-3-en-1-yl)aniline (4d)



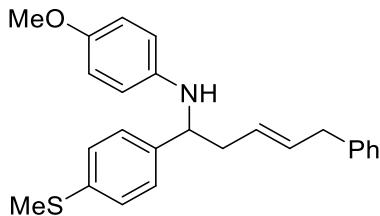
Yellow oil, 62.1 mg, yield 87%. **IR (neat, cm⁻¹)** 1509, 1235, 1035, 971, 817, 749, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.42 – 7.37 (m, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.10 (m, 6H), 6.69 – 6.62 (m, 2H), 6.36 – 6.29 (m, 2H), 5.81 – 5.67 (m, 1H), 5.56 – 5.43 (m, 1H), 4.47 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.66 (s, 3H), 3.35 (d, *J* = 6.8 Hz, 2H), 2.58 – 2.46 (m, 1H), 2.42 (s, 3H), 2.38 – 2.28 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.0, 141.9, 141.6, 140.6, 134.6, 133.2, 130.7, 128.6, 128.6, 127.9, 126.7, 126.6, 126.2, 125.6, 114.9, 114.4, 55.9, 54.6, 40.3, 39.2, 19.3. **HRMS (ESI)** calculated for C₂₅H₂₈NO [M+H]⁺ *m/z* 358.2165, found 358.2158.

(E)-4-Methoxy-N-(1-(4-methoxyphenyl)-5-phenylpent-3-en-1-yl)aniline (4e)



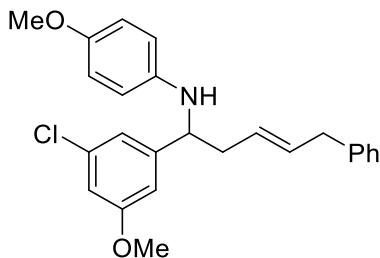
Yellow oil, 58.5 mg, yield 78%. **IR (neat, cm⁻¹)** 1508, 1237, 1174, 1033, 819, 699; **¹H NMR (400 MHz, CDCl₃)** δ: 7.36 – 7.24 (m, 5H), 7.21 – 7.15 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 5.80 – 5.67 (m, 1H), 5.56 – 5.45 (m, 1H), 4.26 (dd, *J* = 8.0, 5.3 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.62 – 2.50 (m, 1H), 2.51 – 2.39 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 158.6, 152.1, 141.9, 140.6, 136.0, 133.2, 128.6, 127.8, 127.5, 126.2, 114.8, 114.1, 57.9, 55.9, 55.4, 42.4, 39.2. **HRMS (ESI)** calculated for C₂₅H₂₈NO₂ [M+H]⁺ *m/z* 374.2115, found 374.2113.

(E)-4-Methoxy-N-(1-(4-(methylthio)phenyl)-5-phenylpent-3-en-1-yl)aniline (4f)



Yellow oil, 62.9 mg, yield 81%. **IR (neat, cm⁻¹)** 1509, 1235, 1034, 969, 816, 729, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.32 – 7.23 (m, 4H), 7.23 – 7.17 (m, 3H), 7.15 – 7.10 (m, 2H), 6.67 (d, *J* = 6.7 Hz, 2H), 6.39 (d, *J* = 7.3 Hz, 2H), 5.77 – 5.64 (m, 1H), 5.52 – 5.40 (m, 1H), 4.22 (t, *J* = 6.4 Hz, 1H), 3.67 (s, 3H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.56 – 2.46 (m, 1H), 2.47 – 2.34 (m, 4H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 141.7, 141.1, 140.5, 136.6, 133.4, 128.6, 128.6, 127.5, 127.0, 127.0, 127.0, 126.2, 114.8, 114.7, 58.0, 55.8, 42.2, 39.2, 16.1. **HRMS (ESI)** calculated for C₂₅H₂₇NONaS [M+Na]⁺ *m/z* 412.1706, found 412.1703.

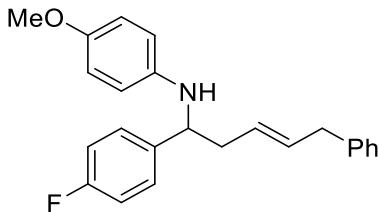
(E)-N-(1-(3-Chloro-5-methoxyphenyl)-5-phenylpent-3-en-1-yl)-4-methoxyaniline (4g)



Yellow oil, 66.3 mg, yield 82%. **IR (neat, cm⁻¹)** 1576, 1510, 1459, 1235, 1048, 907, 818, 730, 697; **¹H NMR (400 MHz, CDCl₃)** δ: 7.35 – 7.24 (m, 2H), 7.25 – 7.18 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 2H),

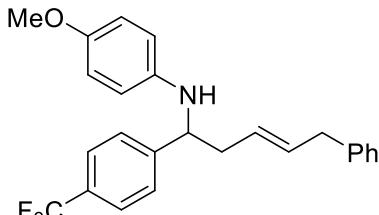
6.95 (s, 1H), 6.80 (s, 1H), 6.75 (s, 1H), 6.72 – 6.65 (m, 2H), 6.43 – 6.36 (m, 2H), 5.78 – 5.66 (m, 1H), 5.51 – 5.38 (m, 1H), 4.16 (t, J = 6.1 Hz, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 3.34 (d, J = 6.8 Hz, 2H), 2.56 – 2.47 (m, 1H), 2.44 – 2.32 (m, 1H); **^{13}C NMR (101 MHz, CDCl_3)** δ : 160.7, 152.3, 147.7, 141.5, 140.4, 135.1, 133.7, 128.6, 128.6, 127.2, 126.3, 119.0, 114.9, 114.7, 112.6, 111.0, 58.3, 55.9, 55.6, 42.1, 39.2. **HRMS (ESI)** calculated for $\text{C}_{25}\text{H}_{27}\text{NO}_2\text{Cl} [\text{M}+\text{H}]^+$ m/z 408.1725, found 408.1712.

(E)-N-(1-(4-Fluorophenyl)-5-phenylpent-3-en-1-yl)-4-methoxyaniline (4h)



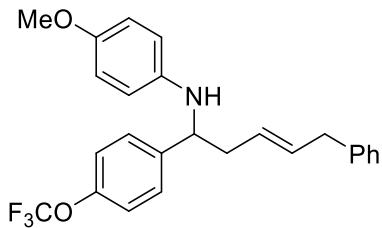
Yellow oil, 69.8 mg, yield 97%. **IR (neat, cm⁻¹)** 1507, 1234, 1035, 970, 817, 733, 698, 518; **^1H NMR (400 MHz, CDCl_3)** δ : 7.32 – 7.24 (m, 4H), 7.22 – 7.18 (m, 1H), 7.13 (d, J = 7.5 Hz, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.67 (d, J = 6.7 Hz, 2H), 6.38 (d, J = 6.7 Hz, 2H), 5.77 – 5.64 (m, 1H), 5.52 – 5.38 (m, 1H), 4.28 – 4.19 (m, 1H), 3.68 (s, 3H), 3.34 (d, J = 6.8 Hz, 2H), 2.57 – 2.45 (m, 1H), 2.46 – 2.33 (m, 1H); **^{13}C NMR (101 MHz, CDCl_3)** δ : 161.9 (d, J = 244.5 Hz), 152.2, 141.6, 140.5, 139.7 (d, J = 3.0 Hz), 133.5, 128.6, 128.6, 127.9 (d, J = 7.9 Hz), 127.4, 126.2, 115.5 (d, J = 21.4 Hz), 114.8, 114.8, 57.8, 55.9, 42.4, 39.2; **^{19}F NMR (377 MHz, CDCl_3)** δ : -116.19. **HRMS (ESI)** calculated for $\text{C}_{24}\text{H}_{25}\text{NOF} [\text{M}+\text{H}]^+$ m/z 362.1915, found 362.1908.

(E)-4-Methoxy-N-(5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-3-en-1-yl)aniline (4i)



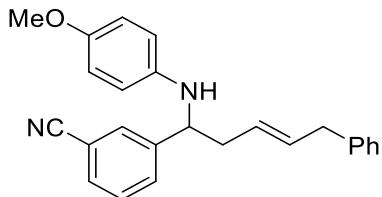
Yellow oil, 63.4 mg, yield 77%. **IR (neat, cm⁻¹)** 1511, 1323, 1237, 1161, 1113, 1065, 818, 732, 698; **^1H NMR (400 MHz, CDCl_3)** δ : 7.55 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.35 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 7.13 (d, J = 7.5 Hz, 2H), 6.71 – 6.64 (m, 2H), 6.39 – 6.33 (m, 2H), 5.79 – 5.66 (m, 1H), 5.51 – 5.38 (m, 1H), 4.31 (t, J = 6.7 Hz, 1H), 3.68 (s, 3H), 3.34 (d, J = 6.9 Hz, 2H), 2.61 – 2.49 (m, 1H), 2.48 – 2.35 (m, 1H); **^{13}C NMR (101 MHz, CDCl_3)** δ : 152.4, 148.4, 141.3, 140.4, 134.0, 129.3 (q, J = 32.3 Hz), 128.7, 128.6, 127.0, 126.9, 126.3, 125.7 (q, J = 3.7 Hz), 124.4 (q, J = 273.7 Hz), 114.9, 114.8, 58.2, 55.8, 42.1, 39.2; **^{19}F NMR (377 MHz, CDCl_3)** δ : -62.23. **HRMS (ESI)** calculated for $\text{C}_{25}\text{H}_{25}\text{NOF}_3 [\text{M}+\text{H}]^+$ m/z 412.1883, found 412.1885.

(E)-4-Methoxy-N-(5-phenyl-1-(4-(trifluoromethoxy)phenyl)pent-3-en-1-yl)aniline (4j)



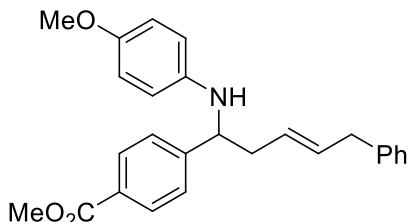
Yellow oil, 73.2 mg, yield 86%. **IR (neat, cm⁻¹)** 1509, 1220, 1158, 1036, 817, 732, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.38 – 7.33 (m, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.18 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 4H), 6.71 – 6.65 (m, 2H), 6.40 – 6.34 (m, 2H), 5.79 – 5.66 (m, 1H), 5.52 – 5.38 (m, 1H), 4.26 (t, *J* = 6.1 Hz, 1H), 3.68 (s, 3H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.58 – 2.47 (m, 1H), 2.46 – 2.33 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.3, 148.2 (d, *J* = 2.0 Hz), 142.8, 141.5, 140.5, 133.8, 128.6, 128.6, 127.8, 127.2, 126.3, 121.2, 120.6 (q, *J* = 256.6 Hz), 114.9, 114.7, 57.9, 55.8, 42.3, 39.2; **¹⁹F NMR (377 MHz, CDCl₃)** δ: -57.76. **HRMS (ESI)** calculated for C₂₅H₂₅NO₂F₃ [M+H]⁺ *m/z* 428.1832, found 428.1836.

(E)-3-(1-((4-Methoxyphenyl)amino)-5-phenylpent-3-en-1-yl)benzonitrile (4k)



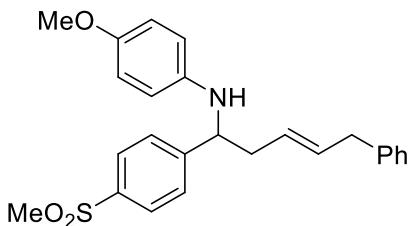
Yellow oil, 65.7 mg, yield 89%. **IR (neat, cm⁻¹)** 1511, 1239, 1032, 972, 908, 821, 730, 695; **¹H NMR (400 MHz, CDCl₃)** δ: 7.64 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.71 – 6.64 (m, 2H), 6.38 – 6.31 (m, 2H), 5.78 – 5.67 (m, 1H), 5.47 – 5.35 (m, 1H), 4.27 (t, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.58 – 2.47 (m, 1H), 2.46 – 2.33 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.4, 145.9, 141.0, 140.2, 134.3, 131.1, 130.8, 130.2, 129.5, 128.6, 128.5, 126.5, 126.3, 119.1, 114.9, 114.7, 112.7, 57.9, 55.8, 42.0, 39.1. **HRMS (ESI)** calculated for C₂₅H₂₅N₂O [M+H]⁺ *m/z* 369.1961, found 369.1953.

Methyl (E)-4-(1-((4-Methoxyphenyl)amino)-5-phenylpent-3-en-1-yl)benzoate (4l)



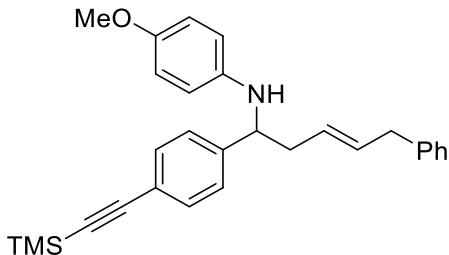
Yellow oil, 75.9 mg, yield 95%. **IR (neat, cm⁻¹)** 1755, 1508, 1192, 1035, 911, 818, 699; **¹H NMR (400 MHz, CDCl₃)** δ: 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 8.9 Hz, 2H), 5.78 – 5.66 (m, 1H), 5.52 – 5.41 (m, 1H), 4.25 (dd, *J* = 8.2, 4.9 Hz, 1H), 3.90 (br, 1H), 3.67 (s, 3H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.58 – 2.49 (m, 1H), 2.45 – 2.32 (m, 1H), 2.26 (s, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ: 169.5, 152.1, 149.6, 141.6, 141.6, 140.5, 133.5, 128.6, 128.6, 127.5, 127.4, 126.2, 121.6, 114.8, 114.7, 57.9, 55.8, 42.2, 39.2, 21.2. **HRMS (ESI)** calculated for C₂₆H₂₇NO₃Na [M+Na]⁺ *m/z* 424.1883, found 424.1886.

(E)-4-Methoxy-N-(1-(4-(methylsulfonyl)phenyl)-5-phenylpent-3-en-1-yl)aniline (4m)



Yellow oil, 75.7 mg, yield 90%. **IR (neat, cm⁻¹)** 1511, 1304, 1235, 1146, 819, 727, 699, 550; **¹H NMR (400 MHz, CDCl₃)** δ: 7.87 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 6.71 – 6.64 (m, 2H), 6.38 – 6.32 (m, 2H), 5.81 – 5.67 (m, 1H), 5.51 – 5.38 (m, 1H), 4.34 (dd, *J* = 8.1, 5.0 Hz, 1H), 3.68 (s, 3H), 3.35 (d, *J* = 6.8 Hz, 2H), 3.03 (s, 3H), 2.60 – 2.51 (m, 1H), 2.47 – 2.36 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.4, 150.9, 141.0, 140.3, 139.2, 134.3, 128.6, 128.6, 127.9, 127.5, 126.6, 126.3, 114.9, 114.8, 58.2, 55.8, 44.6, 42.0, 39.2. **HRMS (ESI)** calculated for C₂₅H₂₈NO₃S [M+H]⁺ *m/z* 422.1784, found 422.1771.

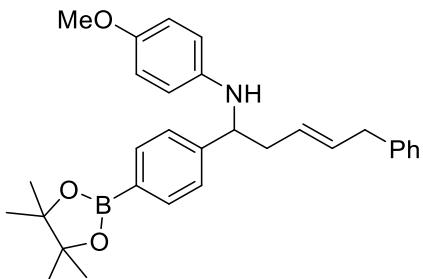
(E)-4-Methoxy-N-(5-phenyl-1-(4-((trimethylsilyl)ethynyl)phenyl)pent-3-en-1-yl)aniline (4n)



Yellow oil, 77.7 mg, yield 89%. **IR (neat, cm⁻¹)** 1510, 1237, 862, 840, 730, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.44 – 7.38 (m, 2H), 7.33 – 7.22 (m, 4H), 7.22 – 7.17 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.68 – 6.62 (m, 2H), 6.39 – 6.32 (m, 2H), 5.75 – 5.63 (m, 1H), 5.50 – 5.36 (m, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 3.67 (s, 3H), 3.32 (d, *J* = 6.8 Hz, 2H), 2.56 – 2.45 (m, 1H), 2.46 – 2.33 (m, 1H), 0.24 (s, 9H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.2, 144.8, 141.5, 140.5, 133.6, 132.4, 128.6, 128.6, 127.3, 126.4,

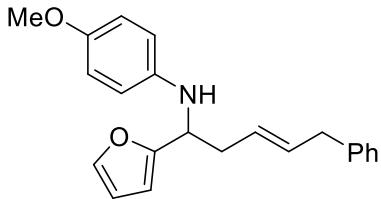
126.2, 121.7, 114.8, 105.3, 93.9, 58.4, 55.8, 42.1, 39.2, 0.1. **HRMS (ESI)** calculated for C₂₉H₃₄NOSi [M+H]⁺ *m/z* 440.2404, found 440.2409.

(E)-4-Methoxy-N-(5-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-3-en-1-yl)aniline (4o)



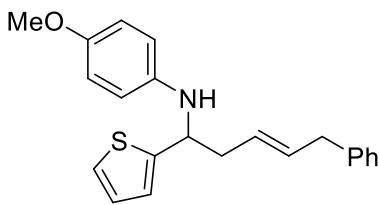
Yellow oil, 66.8 mg, yield 71%. **IR (neat, cm⁻¹)** 1510, 1357, 1237, 1142, 1087, 819, 731, 658; **¹H NMR (400 MHz, CDCl₃)** δ: 7.77 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 8.9 Hz, 2H), 5.77 – 5.64 (m, 1H), 5.52 – 5.40 (m, 1H), 4.27 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.67 (s, 3H), 3.33 (d, *J* = 6.9 Hz, 2H), 2.60 – 2.49 (m, 1H), 2.48 – 2.36 (m, 1H), 1.33 (s, 12H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 147.5, 141.7, 140.6, 135.2, 133.4, 128.6, 128.6, 127.6, 126.2, 125.9, 114.8, 114.8, 83.8, 58.6, 55.9, 42.2, 39.2, 25.0, 25.0. **HRMS (ESI)** calculated for C₃₀H₃₇BNO₃ [M+H]⁺ *m/z* 470.2861, found 470.2864.

(E)-N-(1-(Furan-2-yl)-5-phenylpent-3-en-1-yl)-4-methoxyaniline (4p)



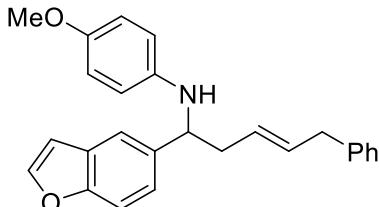
Yellow oil, 45.4 mg, yield 68%. **IR (neat, cm⁻¹)** 1510, 1235, 1035, 970, 817, 730, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.35 – 7.10 (m, 6H), 6.75 – 6.70 (m, 2H), 6.55 – 6.50 (m, 2H), 6.27 (d, *J* = 2.2 Hz, 1H), 6.13 (s, 1H), 5.76 – 5.63 (m, 1H), 5.53 – 5.40 (m, 1H), 4.43 (t, *J* = 6.5 Hz, 1H), 3.71 (s, 3H), 3.33 (d, *J* = 6.9 Hz, 2H), 2.70 – 2.54 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ: 156.3, 152.5, 141.5, 141.4, 140.6, 133.3, 128.6, 128.6, 127.0, 126.2, 115.2, 114.9, 110.2, 106.2, 55.8, 52.9, 39.2, 38.2. **HRMS (ESI)** calculated for C₂₂H₂₄NO₂ [M+H]⁺ *m/z* 334.1802, found 334.1804.

(E)-4-Methoxy-N-(5-phenyl-1-(thiophen-2-yl)pent-3-en-1-yl)aniline (4q)



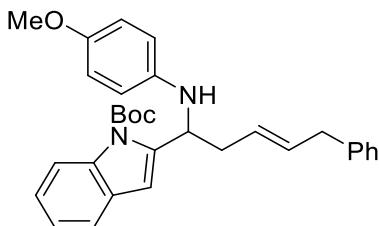
Yellow oil, 63.9 mg, yield 91%. **IR (neat, cm⁻¹)** 1509, 1234, 1035, 818, 731, 696; **¹H NMR (400 MHz, CDCl₃)** δ: 7.31 – 7.24 (m, 2H), 7.22 – 7.11 (m, 4H), 6.96 – 6.89 (m, 2H), 6.74 – 6.67 (m, 2H), 6.53 – 6.48 (m, 2H), 5.79 – 5.66 (m, 1H), 5.57 – 5.44 (m, 1H), 4.58 (t, *J* = 6.2 Hz, 1H), 3.69 (s, 3H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.68 – 2.53 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ: ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 149.4, 141.4, 140.5, 133.7, 128.6, 127.1, 126.9, 126.2, 123.8, 123.4, 115.2, 114.8, 55.8, 54.9, 42.2, 39.2. **HRMS (ESI)** calculated for C₂₂H₂₄NOS [M+H]⁺ *m/z* 350.1573, found 350.1566.

(E)-N-(1-(Benzofuran-5-yl)-5-phenylpent-3-en-1-yl)-4-methoxyaniline (4r)



Yellow oil, 69.0 mg, yield 90%. **IR (neat, cm⁻¹)** 1509, 1235, 1032, 816, 736, 699; **¹H NMR (400 MHz, CDCl₃)** δ: 7.57 (d, *J* = 2.1 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.22 – 7.16 (m, 1H), 7.14 – 7.07 (m, 2H), 6.70 – 6.63 (m, 3H), 6.45 – 6.40 (m, 2H), 5.77 – 5.64 (m, 1H), 5.54 – 5.43 (m, 1H), 4.35 (dd, *J* = 8.1, 5.2 Hz, 1H), 3.66 (s, 3H), 3.33 (d, *J* = 6.9 Hz, 2H), 2.62 – 2.53 (m, 1H), 2.51 – 2.41 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 154.3, 152.0, 145.3, 141.9, 140.6, 138.7, 133.2, 128.6, 127.8, 127.7, 126.2, 122.9, 118.8, 114.8, 114.8, 111.5, 106.8, 58.5, 55.8, 42.8, 39.2. **HRMS (ESI)** calculated for C₂₆H₂₆NO₂ [M+H]⁺ *m/z* 384.1958, found 384.1950.

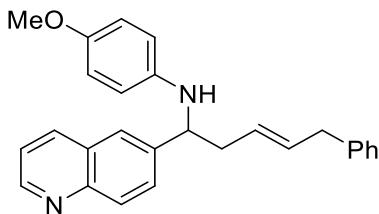
tert-Butyl (E)-2-((4-Methoxyphenyl)amino)-5-phenylpent-3-en-1-yl-1*H*-indole-1-carboxylate (4s)



Yellow oil, 77.3 mg, yield 80%. **IR (neat, cm⁻¹)** 1727, 1511, 1452, 1324, 1236, 1157, 907, 816, 729, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 8.09 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.12

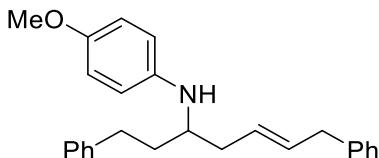
(m, 7H), 6.74 – 6.68 (m, 2H), 6.56 – 6.47 (m, 3H), 5.80 – 5.67 (m, 1H), 5.58 – 5.46 (m, 1H), 5.23 (t, J = 5.9 Hz, 1H), 3.68 (s, 3H), 3.34 (d, J = 6.8 Hz, 2H), 2.81 – 2.69 (m, 1H), 2.55 – 2.43 (m, 1H), 1.70 (s, 9H); **^{13}C NMR (101 MHz, CDCl_3)** δ : 152.1, 150.7, 143.5, 141.4, 140.6, 137.3, 133.4, 129.2, 128.6, 128.5, 127.3, 126.2, 123.7, 122.9, 120.5, 115.8, 114.9, 114.7, 108.4, 84.4, 55.9, 52.5, 39.4, 39.3, 28.4. **HRMS (ESI)** calculated for $\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}_3$ [M+H] $^+$ m/z 483.2642, found 483.2641.

(E)-4-Methoxy-N-(5-phenyl-1-(quinolin-6-yl)pent-3-en-1-yl)aniline (4t)



Yellow oil, 71.8 mg, yield 93%. **IR (neat, cm $^{-1}$)** 1510, 1235, 1033, 907, 818, 727, 699; **^1H NMR (400 MHz, CDCl_3)** δ : 8.89 (dd, J = 3.8, 2.0 Hz, 1H), 8.18 – 8.08 (m, 2H), 7.79 (s, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.25 (d, J = 7.1 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.12 (d, J = 7.4 Hz, 2H), 6.69 – 6.63 (m, 2H), 6.46 – 6.40 (m, 2H), 5.80 – 5.68 (m, 1H), 5.55 – 5.43 (m, 1H), 4.45 (t, J = 6.2 Hz, 1H), 3.66 (s, 3H), 3.34 (d, J = 6.9 Hz, 2H), 2.70 – 2.58 (m, 1H), 2.56 – 2.44 (m, 1H); **^{13}C NMR (101 MHz, CDCl_3)** δ : 152.2, 149.8, 147.5, 142.7, 141.6, 140.4, 136.6, 133.8, 130.9, 129.6, 128.8, 128.6, 128.5, 127.9, 127.2, 126.3, 124.9, 121.3, 114.9, 58.4, 55.8, 42.2, 39.2. **HRMS (ESI)** calculated for $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}$ [M+H] $^+$ m/z 395.2118, found 395.2111.

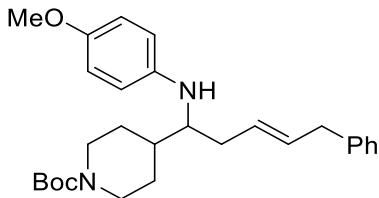
(E)-N-(1,7-diphenylhept-5-en-3-yl)-4-methoxyaniline (4u)



The corresponding aldimine was in-situ formed: aldehyde (0.2 mmol), *p*-anisidine (27.1 mg, 0.22 mmol), and 4 Å MS were stirred in THF (0.7 mL) in ambient temperature overnight, then 4 Å MS was filtered to afford the aldimine solution in THF, which was used in the coupling reaction.

Yellow oil, 54.2 mg, yield 73%. **IR (neat, cm $^{-1}$)** 1509, 1233, 1036, 817, 732, 697; **^1H NMR (400 MHz, CDCl_3)** δ : 7.32 – 7.22 (m, 4H), 7.21 – 7.12 (m, 6H), 6.77 – 6.72 (m, 2H), 6.50 – 6.45 (m, 2H), 5.67 – 5.58 (m, 1H), 5.54 – 5.45 (m, 1H), 3.73 (s, 3H), 3.39 – 3.28 (m, 3H), 2.79 – 2.66 (m, 2H), 2.33 – 2.22 (m, 2H), 1.89 – 1.72 (m, 2H); **^{13}C NMR (101 MHz, CDCl_3)** δ : 152.0, 142.2, 142.0, 140.8, 132.6, 128.6, 128.6, 128.5, 128.5, 127.5, 126.1, 125.9, 115.1, 114.9, 56.0, 53.3, 39.3, 37.3, 36.3, 32.5. **HRMS (ESI)** calculated for $\text{C}_{26}\text{H}_{30}\text{NO}$ [M+H] $^+$ m/z 372.2322, found 372.2323.

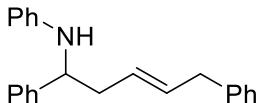
tert-Butyl (E)-4-(1-((4-Methoxyphenyl)amino)-5-phenylpent-3-en-1-yl)piperidine-1-carboxylate (4v)



The corresponding aldimine was in-situ formed: aldehyde (0.2 mmol), *p*-anisidine (27.1 mg, 0.22 mmol), and 4 Å MS were stirred in THF (0.7 mL) in ambient temperature overnight, then 4 Å MS was filtered to afford the aldimine solution in THF, which was used in the coupling reaction.

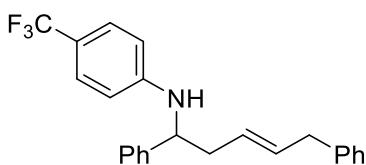
Yellow oil, 71.9 mg, yield 80%. **IR (neat, cm⁻¹)** 1677, 1510, 1425, 1234, 1166, 907, 728; **¹H NMR (400 MHz, CDCl₃)** δ: 7.31 – 7.22 (m, 2H), 7.20 – 7.16 (m, 1H), 7.13 – 7.06 (m, 2H), 6.78 – 6.72 (m, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 5.67 – 5.55 (m, 1H), 5.52 – 5.42 (m, 1H), 4.14 (br, 2H), 3.73 (s, 3H), 3.31 (d, *J* = 6.7 Hz, 2H), 3.16 (q, *J* = 5.9 Hz, 1H), 2.62 (t, *J* = 12.9 Hz, 2H), 2.37 – 2.26 (m, 1H), 2.21 – 2.09 (m, 1H), 1.79 (dt, *J* = 13.1, 2.8 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.45 (s, 9H), 1.33 – 1.18 (m, 2H); **¹³C NMR (101 MHz, CDCl₃)** δ: 154.9, 151.8, 142.5, 140.7, 132.4, 128.5, 128.5, 127.7, 126.1, 115.0, 114.6, 79.4, 58.2, 55.9, 44.1, 40.1, 39.2, 34.6, 28.7, 28.6. **HRMS (ESI)** calculated for C₂₈H₃₉N₂O₃ [M+H]⁺ *m/z* 451.2955, found 451.2952.

(E)-N-(1,5-Diphenylpent-3-en-1-yl)aniline (4w)



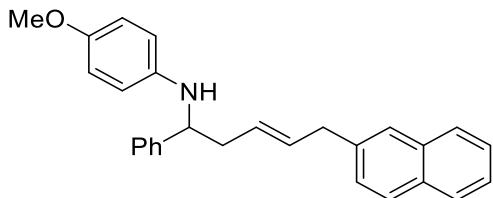
Yellow oil, 59.4 mg, yield 95%. **IR (neat, cm⁻¹)** 1600, 1500, 1314, 970, 745, 694; **¹H NMR (400 MHz, CDCl₃)** δ: 7.38 – 7.26 (m, 6H), 7.25 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 7.10 – 7.03 (m, 2H), 6.68 – 6.58 (m, 1H), 6.49 – 6.39 (m, 2H), 5.78 – 5.67 (m, 1H), 5.54 – 5.41 (m, 1H), 4.34 (dd, *J* = 8.1, 5.1 Hz, 1H), 4.15 (br, 1H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.63 – 2.51 (m, 1H), 2.50 – 2.39 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 147.5, 143.8, 140.6, 133.4, 129.2, 128.7, 128.6, 128.6, 127.6, 127.0, 126.4, 126.2, 117.4, 113.6, 57.6, 42.2, 39.2. **HRMS (ESI)** calculated for C₂₃H₂₄N [M+H]⁺ *m/z* 314.1903, found 314.1912.

(E)-N-(1,5-Diphenylpent-3-en-1-yl)-4-(trifluoromethyl)aniline (4x)



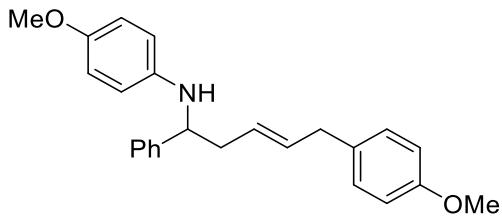
Yellow oil, 65.9 mg, yield 86%. **IR (neat, cm⁻¹)** 1615, 1318, 1104, 1062, 823, 732, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.34 – 7.19 (m, 10H), 7.17 – 7.11 (m, 2H), 6.43 (d, *J* = 8.5 Hz, 2H), 5.81 – 5.68 (m, 1H), 5.52 – 5.39 (m, 1H), 4.45 (br, 1H), 4.38 (dd, *J* = 8.0, 5.1 Hz, 1H), 3.35 (d, *J* = 6.9 Hz, 2H), 2.64 – 2.55 (m, 1H), 2.51 – 2.41 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 149.9, 142.8, 140.5, 133.9, 128.9, 128.7, 128.6, 127.4, 127.0, 126.5 (q, *J* = 3.8 Hz), 126.3, 126.3, 125.1 (q, *J* = 270.7 Hz), 119.0 (q, *J* = 32.6 Hz), 112.8, 57.2, 42.0, 39.2; **¹⁹F NMR (377 MHz, CDCl₃)** δ: -60.93. **HRMS (FI)** calculated for C₂₄H₂₂NF₃ [M]⁺ *m/z* 381.1699, found 381.1703.

(E)-4-Methoxy-N-(5-(naphthalen-2-yl)-1-phenylpent-3-en-1-yl)aniline (6a)



Following the GP, the reaction was performed using 5.0 equiv of butadiene, and 20 mol% Ni(cod)₂. The title compound was obtained as yellow oil in 71% yield (55.6 mg). **IR (neat, cm⁻¹)** 1509, 1235, 907, 816, 730, 700, 475; **¹H NMR (400 MHz, CDCl₃)** δ: 7.83 – 7.72 (m, 3H), 7.58 (s, 1H), 7.48 – 7.39 (m, 2H), 7.37 – 7.25 (m, 5H), 7.23 – 7.19 (m, 1H), 6.69 – 6.61 (m, 2H), 6.43 – 6.36 (m, 2H), 5.87 – 5.69 (m, 1H), 5.61 – 5.47 (m, 1H), 4.27 (dd, *J* = 8.2, 5.1 Hz, 1H), 3.67 (s, 3H), 3.49 (d, *J* = 6.8 Hz, 2H), 2.63 – 2.51 (m, 1H), 2.48 – 2.39 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.0, 144.1, 141.8, 138.1, 133.8, 133.1, 132.2, 128.7, 128.2, 128.0, 127.8, 127.6, 127.4, 127.0, 126.6, 126.5, 126.1, 125.4, 114.8, 114.8, 58.5, 55.9, 42.3, 39.4. **HRMS (ESI)** calculated for C₂₈H₂₈NO [M+H]⁺ *m/z* 394.2165, found 394.2161.

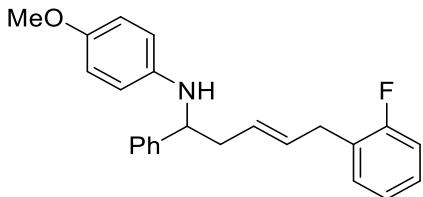
(E)-4-Methoxy-N-(5-(4-methoxyphenyl)-1-phenylpent-3-en-1-yl)aniline (6b)



Yellow oil, 68.8 mg, yield 93%. **IR (neat, cm⁻¹)** 1509, 1236, 1176, 1033, 817, 730, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.36 – 7.27 (m, 4H), 7.23 – 7.19 (m, 1H), 7.07 – 7.01 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.40 (d, *J* = 8.9 Hz, 2H), 5.75 – 5.62 (m, 1H), 5.51 – 5.38 (m, 1H), 4.25 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.27 (d, *J* = 6.9 Hz, 2H), 2.60 – 2.48 (m, 1H), 2.46 – 2.37 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 158.1, 152.0, 144.1, 141.9, 133.7, 132.6,

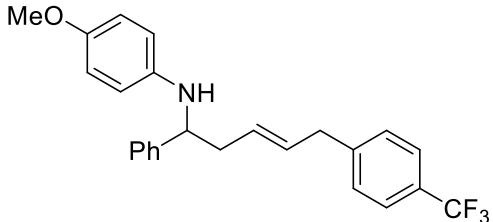
129.5, 128.7, 127.4, 127.0, 126.5, 114.8, 114.7, 114.0, 58.5, 55.8, 55.4, 42.3, 38.3. **HRMS (ESI)** calculated for C₂₅H₂₈NO₂ [M+H]⁺ *m/z* 374.2115, found 374.2112.

(E)-N-(5-(2-Fluorophenyl)-1-phenylpent-3-en-1-yl)-4-methoxyaniline (6c)



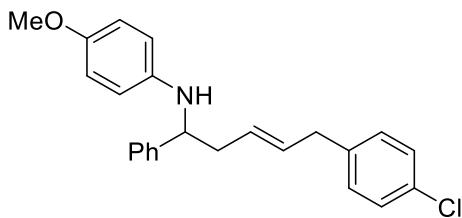
Yellow oil, 73.2 mg, yield 60%. **IR (neat, cm⁻¹)** 1510, 1453, 1231, 1034, 908, 818, 754, 730, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.34 – 7.26 (m, 4H), 7.23 – 7.16 (m, 2H), 7.16 – 7.07 (m, 1H), 7.08 – 6.96 (m, 2H), 6.70 – 6.62 (m, 2H), 6.44 – 6.36 (m, 2H), 5.76 – 5.63 (m, 1H), 5.52 – 5.41 (m, 1H), 4.26 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.67 (s, 3H), 3.37 (d, *J* = 6.7 Hz, 2H), 2.60 – 2.48 (m, 1H), 2.47 – 2.37 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 161.1 (d, *J* = 245.3 Hz), 152.1, 144.0, 141.8, 131.7 (d, *J* = 1.0 Hz), 130.7 (d, *J* = 4.8 Hz), 128.7, 128.1, 128.0, 127.9, 127.5 (d, *J* = 15.8 Hz), 127.0, 126.5, 124.2 (d, *J* = 3.6 Hz), 115.4 (d, *J* = 22.0 Hz), 114.8 (d, *J* = 3.4 Hz), 58.4, 55.9, 42.2, 32.2 (d, *J* = 2.9 Hz). **¹⁹F NMR (377 MHz, CDCl₃)** δ: -118.43. **HRMS (ESI)** calculated for C₂₄H₂₅NOF [M+H]⁺ *m/z* 362.1915, found 362.1913.

(E)-4-Methoxy-N-(1-phenyl-5-(4-(trifluoromethyl)phenyl)pent-3-en-1-yl)aniline (6d)



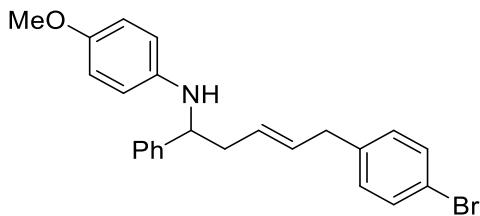
Following the GP, the reaction was performed using 5.0 equiv of butadiene, and 20 mol% Ni(cod)₂. The title compound was obtained as yellow oil in 70% yield (57.4 mg). **IR (neat, cm⁻¹)** 1510, 1323, 1236, 1161, 1110, 1064, 817, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.56 – 7.49 (m, 2H), 7.35 – 7.28 (m, 4H), 7.25 – 7.20 (m, 3H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.40 (d, *J* = 8.9 Hz, 2H), 5.73 – 5.61 (m, 1H), 5.57 – 5.43 (m, 1H), 4.28 (dd, *J* = 7.9, 5.4 Hz, 1H), 3.68 (s, 3H), 3.38 (d, *J* = 6.8 Hz, 2H), 2.62 – 2.50 (m, 1H), 2.50 – 2.41 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 144.7, 143.9, 141.7, 132.0, 128.9, 128.8, 128.7, 128.6 (q, *J* = 32.3 Hz), 127.1, 126.5, 125.5 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 272.7 Hz), 114.9, 114.8, 58.5, 55.9, 42.2, 39.0; **¹⁹F NMR (377 MHz, CDCl₃)** δ: -62.28. **HRMS (ESI)** calculated for C₂₅H₂₅NOF₃ [M+H]⁺ *m/z* 412.1883, found 412.1997.

(E)-N-(5-(4-Chlorophenyl)-1-phenylpent-3-en-1-yl)-4-methoxyaniline (6e)



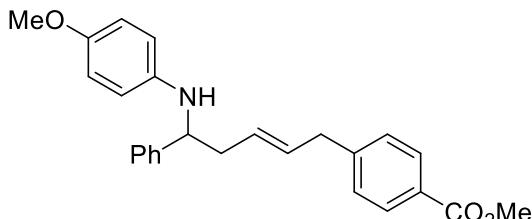
Yellow oil, 58.3 mg, yield 78%. **IR (neat, cm⁻¹)** 1510, 1235, 1035, 816, 731, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.35 – 7.28 (m, 4H), 7.26 – 7.20 (m, 3H), 7.07 – 7.00 (m, 2H), 6.70 – 6.64 (m, 2H), 6.43 – 6.38 (m, 2H), 5.71 – 5.58 (m, 1H), 5.53 – 5.40 (m, 1H), 4.26 (dd, *J* = 8.0, 5.3 Hz, 1H), 3.68 (s, 3H), 3.29 (d, *J* = 6.8 Hz, 2H), 2.59 – 2.50 (m, 1H), 2.48 – 2.39 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 143.9, 141.7, 139.0, 132.6, 131.9, 129.9, 128.7, 128.7, 128.3, 127.0, 126.5, 114.9, 114.7, 58.5, 55.9, 42.2, 38.5. **HRMS (ESI)** calculated for C₂₄H₂₅NOCl [M+H]⁺ *m/z* 378.1619, found 378.1624.

(E)-N-(5-(4-Bromophenyl)-1-phenylpent-3-en-1-yl)-4-methoxyaniline (6f)



Following the GP, the reaction was performed using 5.0 equiv of butadiene, and 20 mol% Ni(cod)₂. The title compound was obtained as yellow oil in 60% yield (50.8 mg). **IR (neat, cm⁻¹)** 1509, 1235, 1069, 816, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.41 – 7.36 (m, 2H), 7.35 – 7.29 (m, 4H), 7.24 – 7.20 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 8.9 Hz, 2H), 5.72 – 5.59 (m, 1H), 5.53 – 5.40 (m, 1H), 4.27 (dd, *J* = 8.0, 5.3 Hz, 1H), 3.69 (s, 3H), 3.28 (d, *J* = 6.7 Hz, 2H), 2.61 – 2.49 (m, 1H), 2.48 – 2.40 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.1, 144.0, 141.8, 139.6, 132.5, 131.6, 130.4, 128.7, 128.3, 127.1, 126.5, 120.0, 114.9, 114.8, 58.5, 55.9, 42.2, 38.6. **HRMS (ESI)** calculated for C₂₄H₂₅NOBr [M+H]⁺ *m/z* 422.1114, found 422.1113.

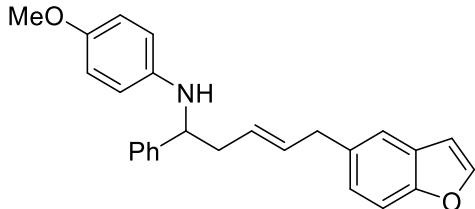
Methyl (E)-4-(5-((4-Methoxyphenyl)amino)-5-phenylpent-2-en-1-yl)benzoate (6g)



Following the GP, the reaction was performed using 5.0 equiv of butadiene, and 20 mol% Ni(cod)₂. The title compound was obtained as yellow oil in 55% yield (44.4 mg). **IR (neat, cm⁻¹)** 1714, 1510,

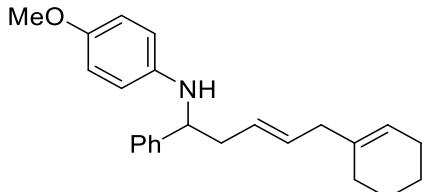
1277, 1235, 1177, 1107, 818, 710, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.95 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.24 – 7.16 (m, 3H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 8.9 Hz, 2H), 5.74 – 5.61 (m, 1H), 5.56 – 5.43 (m, 1H), 4.28 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.91 (s, 3H), 3.68 (s, 3H), 3.38 (d, *J* = 6.8 Hz, 2H), 2.62 – 2.50 (m, 1H), 2.50 – 2.41 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 167.2, 152.1, 146.0, 143.9, 141.7, 132.0, 129.9, 128.7, 128.7, 128.6, 128.2, 127.1, 126.5, 114.9, 114.7, 58.5, 55.9, 52.2, 42.2, 39.2. **HRMS (ESI)** calculated for C₂₆H₂₈NO₃ [M+H]⁺ *m/z* 402.2074, found 402.2062.

(E)-N-(5-(Benzofuran-5-yl)-1-phenylpent-3-en-1-yl)-4-methoxyaniline (6h)



Following the GP, the reaction was performed using 5.0 equiv of butadiene, and 20 mol% Ni(cod)₂. The title compound was obtained as yellow oil in 73% yield (56.3 mg). **IR (neat, cm⁻¹)** 1510, 1465, 1235, 1031, 907, 817, 731, 700; **¹H NMR (400 MHz, CDCl₃)** δ: 7.59 (d, *J* = 2.2 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.36 – 7.27 (m, 5H), 7.24 – 7.19 (m, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.71 – 6.63 (m, 3H), 6.39 (d, *J* = 8.9 Hz, 2H), 5.81 – 5.68 (m, 1H), 5.56 – 5.43 (m, 1H), 4.27 (dd, *J* = 8.2, 5.0 Hz, 1H), 3.67 (s, 3H), 3.42 (d, *J* = 6.9 Hz, 2H), 2.62 – 2.50 (m, 1H), 2.47 – 2.38 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 153.8, 152.0, 145.3, 144.1, 141.9, 135.1, 133.9, 128.7, 127.8, 127.0, 127.0, 126.5, 125.1, 120.7, 114.9, 114.7, 111.3, 106.5, 58.5, 55.9, 42.3, 39.1. **HRMS (ESI)** calculated for C₂₆H₂₆NO₂ [M+H]⁺ *m/z* 384.1958, found 384.1951.

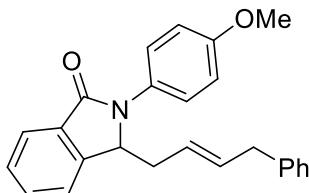
(E)-N-(5-(Cyclohex-1-en-1-yl)-1-phenylpent-3-en-1-yl)-4-methoxyaniline (6i)



Following the GP, the reaction was performed using 5.0 equiv of butadiene, and 20 mol% Ni(cod)₂. The title compound was obtained as yellow oil in 79% yield (54.9 mg). **IR (neat, cm⁻¹)** 1510, 1235, 1067, 817, 732, 699; **¹H NMR (400 MHz, CDCl₃)** δ: 7.38 – 7.26 (m, 4H), 7.24 – 7.18 (m, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.42 (d, *J* = 8.9 Hz, 2H), 5.62 – 5.49 (m, 1H), 5.44 – 5.30 (m, 2H), 4.24 (dd, *J* = 8.2, 5.0 Hz, 1H), 3.67 (s, 3H), 2.67 – 2.48 (m, 3H), 2.47 – 2.32 (m, 1H), 2.04 – 1.95 (m, 2H), 1.92 – 1.81 (m, 2H), 1.65 – 1.51 (m, 4H); **¹³C NMR (101 MHz, CDCl₃)** δ: 152.0, 144.2, 141.9, 136.7, 132.7,

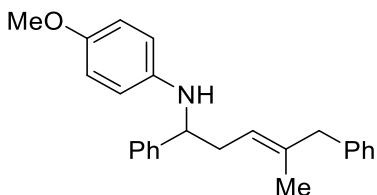
128.6, 127.4, 126.9, 126.5, 121.9, 114.8, 114.7, 58.4, 55.9, 42.4, 41.4, 28.5, 25.4, 23.1, 22.6. **HRMS (ESI)** calculated for C₂₄H₃₀NO [M+H]⁺ *m/z* 348.2322, found 348.2312.

(E)-2-(4-Methoxyphenyl)-3-(4-phenylbut-2-en-1-yl)isoindolin-1-one (8)



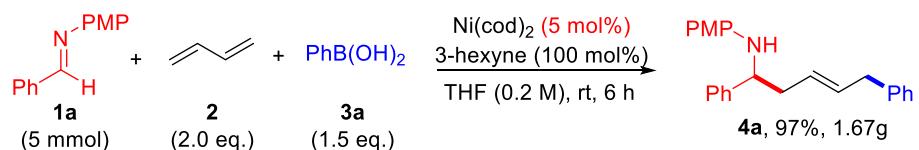
The corresponding aldimine was in-situ formed: aldehyde (0.2 mmol), *p*-anisidine (27.1 mg, 0.22 mmol), and 4Å MS were stirred in THF (0.7 mL) in ambient temperature overnight, then 4Å MS was filtered to afford the aldimine solution in THF, which was used in the coupling reaction. The title compound was obtained as yellow oil in 51% yield (37.8 mg). **IR (neat, cm⁻¹)** 1683, 1511, 1385, 1244, 828, 727, 694; **¹H NMR (400 MHz, CDCl₃)** δ: 7.93 (d, *J* = 6.9 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.17 – 7.13 (m, 1H), 6.97 – 6.87 (m, 4H), 5.43 – 5.30 (m, 1H), 5.16 (dd, *J* = 5.9, 3.3 Hz, 1H), 5.08 – 4.95 (m, 1H), 3.82 (s, 3H), 3.13 (d, *J* = 6.9 Hz, 2H), 2.72 – 2.64 (m, 1H), 2.59 – 2.50 (m, 1H); **¹³C NMR (101 MHz, CDCl₃)** δ: 167.4, 157.5, 144.4, 140.1, 134.3, 132.8, 131.8, 130.0, 128.5, 128.4, 128.4, 126.1, 125.7, 124.1, 123.6, 122.5, 114.5, 61.0, 55.6, 39.0, 34.4. **HRMS (ESI)** calculated for C₂₅H₂₄NO₂ [M+H]⁺ *m/z* 370.1802, found 370.1807.

(E)-4-Methoxy-N-(4-methyl-1,5-diphenylpent-3-en-1-yl)aniline (9)



Following the GP, the reaction was performed using 2.0 equiv of isopropene. The title compound was obtained as yellow oil in 87% yield (62.4 mg) (regioselectivity 4/1). **IR (neat, cm⁻¹)** 1510, 1236, 1034, 817, 732, 698; **¹H NMR (400 MHz, CDCl₃)** δ: 7.47 – 7.17 (m, 10H), 6.73 (t, *J* = 9.6 Hz, 2H), 6.53 – 6.38 (m, 2H), 5.59 (t, *J* = 7.5 Hz, 0.19H), 5.37 (t, *J* = 7.5 Hz, 0.81H), 4.42 – 4.30 (m, 1H), 3.75 (s, 3H), 3.55 – 3.30 (m, 2H), 2.64 – 2.37 (m, 2H), 1.83 (s, 0.6H), 1.59 (s, 2.4H); **¹³C NMR (101 MHz, CDCl₃)** (major) δ: 152.0, 144.2, 141.9, 140.1, 138.5, 128.9, 128.6, 128.4, 126.9, 126.5, 126.2, 122.3, 114.8, 114.8, 59.2, 55.9, 46.5, 37.7, 16.2. **HRMS (ESI)** calculated for C₂₅H₂₈NO [M+H]⁺ *m/z* 358.2165, found 358.2160.

3. Gram-Scale Reaction



In a nitrogen-filled glovebox, $\text{Ni}(\text{cod})_2$ (69 mg, 0.25 mmol) was charged to a 100 ml tube equipped with a magnetic stirrer bar, followed by the addition of THF (25 mL). Then aldimine **1a** (1.06 g, 5.0 mmol), butadiene **2** (3 M in toluene, 3.3 mL, 10.0 mmol), 3-hexyne (570 μL , 5 mmol) and phenylboronic acid **3a** (915 mg, 7.5 mmol) were added successively. The vial was sealed, taken out of the glovebox, and stirred at ambient temperature for 6 h. The resulting mixture was then filtered through a silica gel pad, eluting with EtOAc and concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography (silica gel, hexane/EtOAc = 20/1) to give the corresponding homoallylic alcohol **4a** as a yellow oil (1.67 g, 97% yield).

4. NMR Spectra

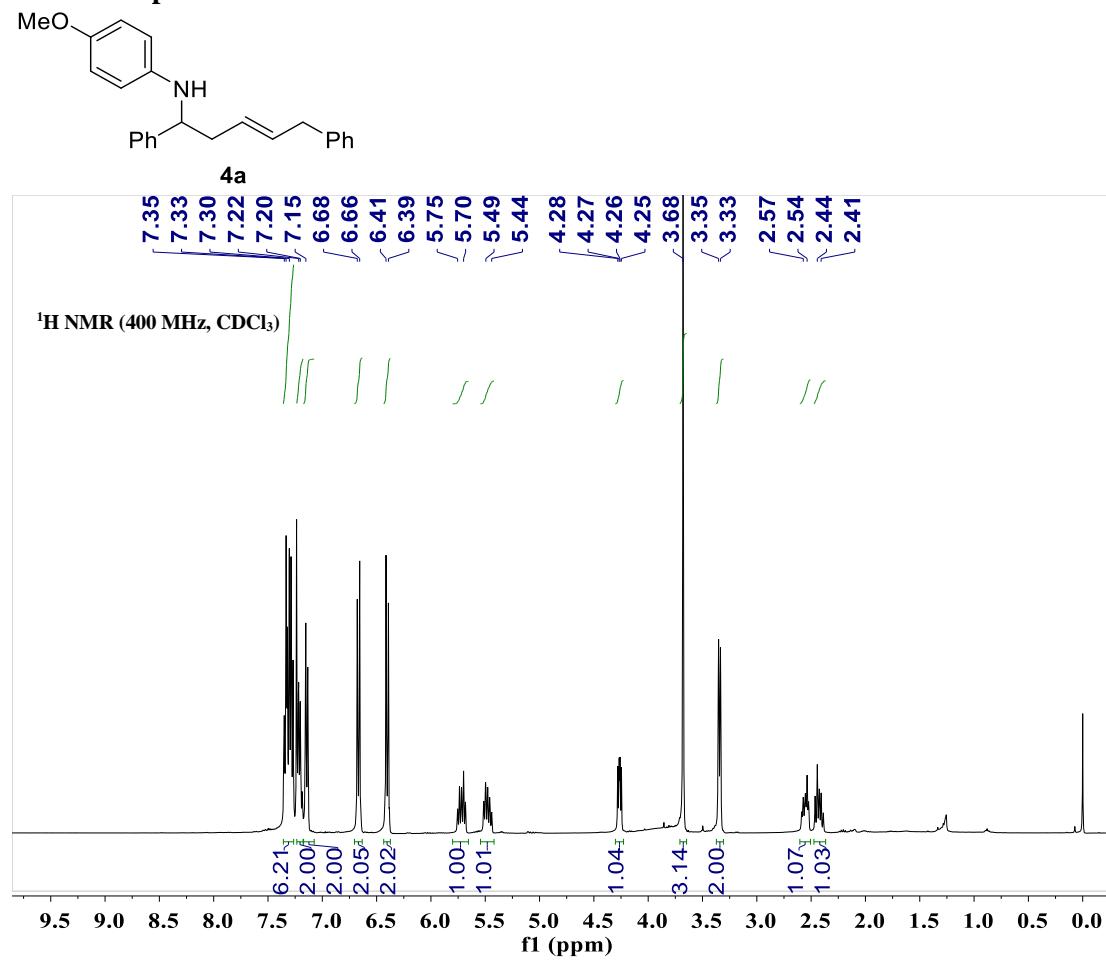


Figure S1

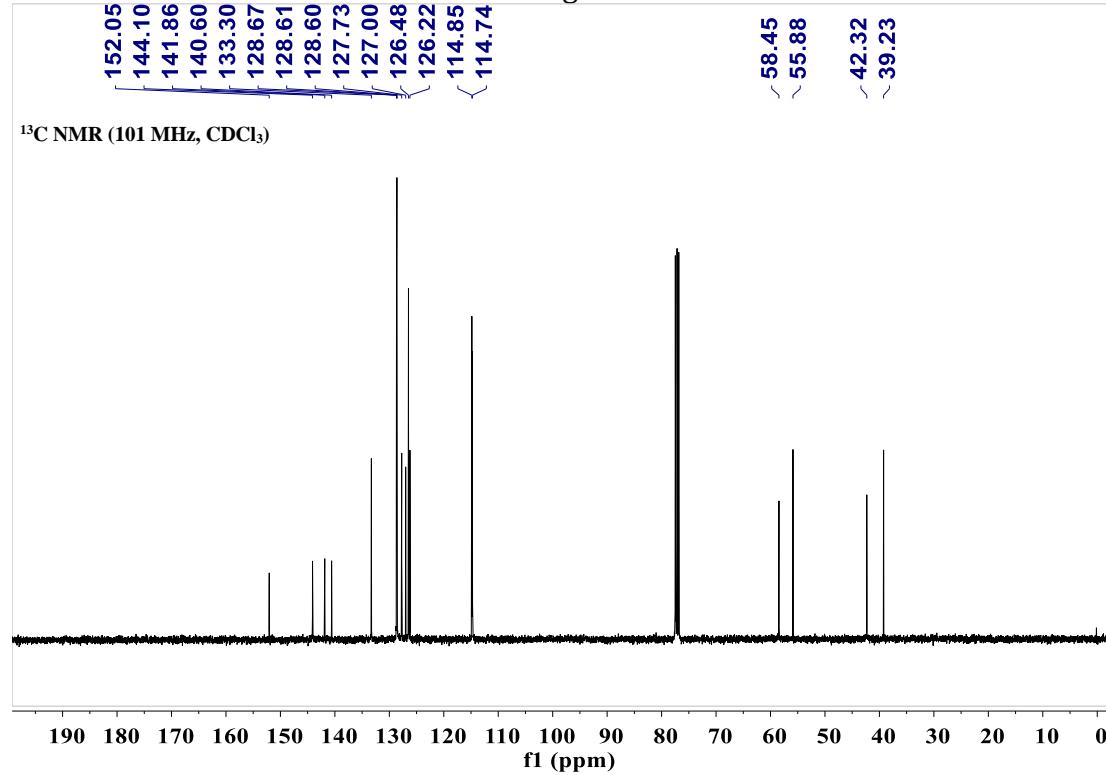


Figure S2

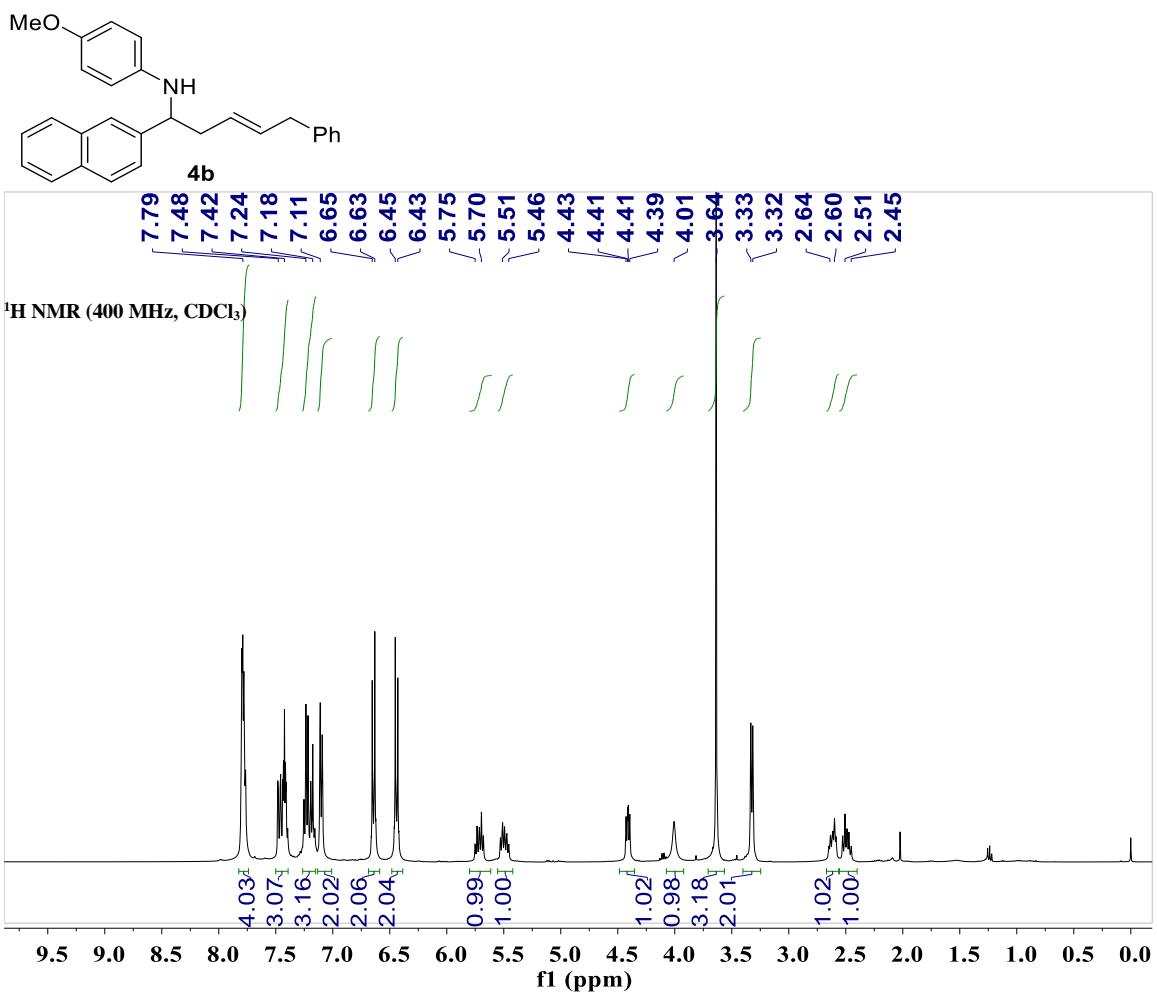


Figure S3

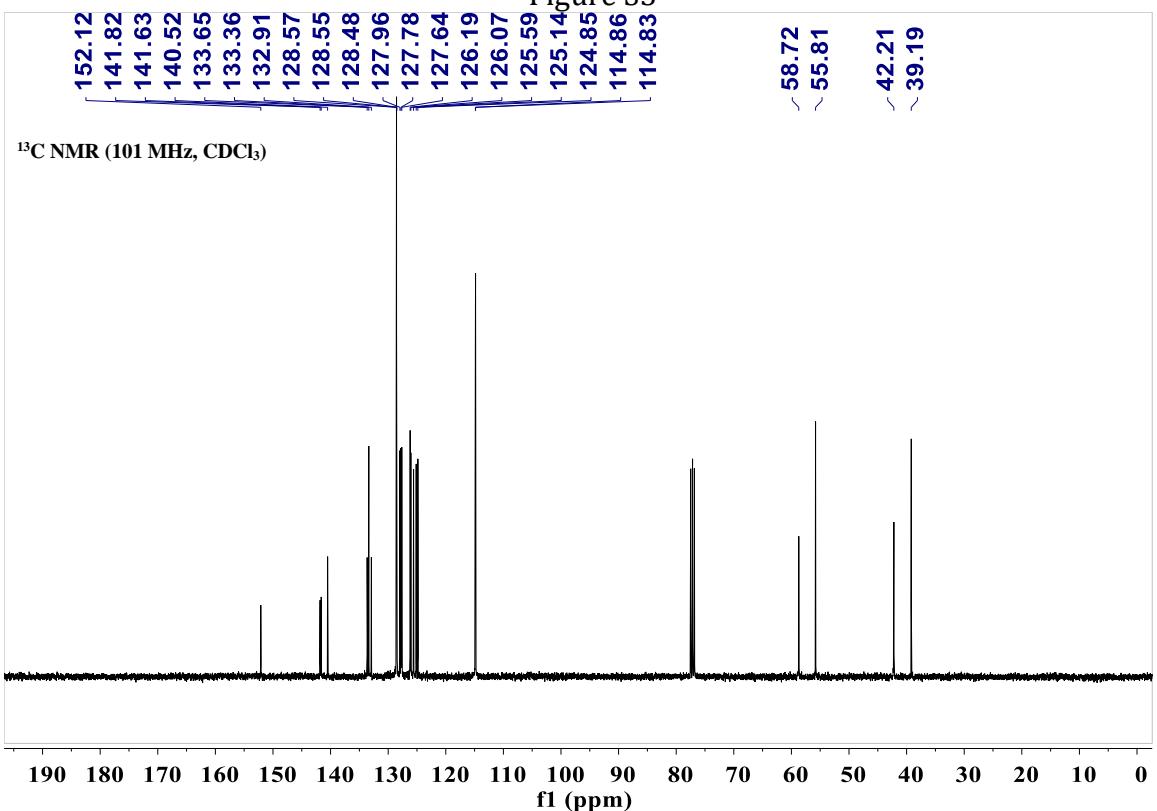


Figure S4

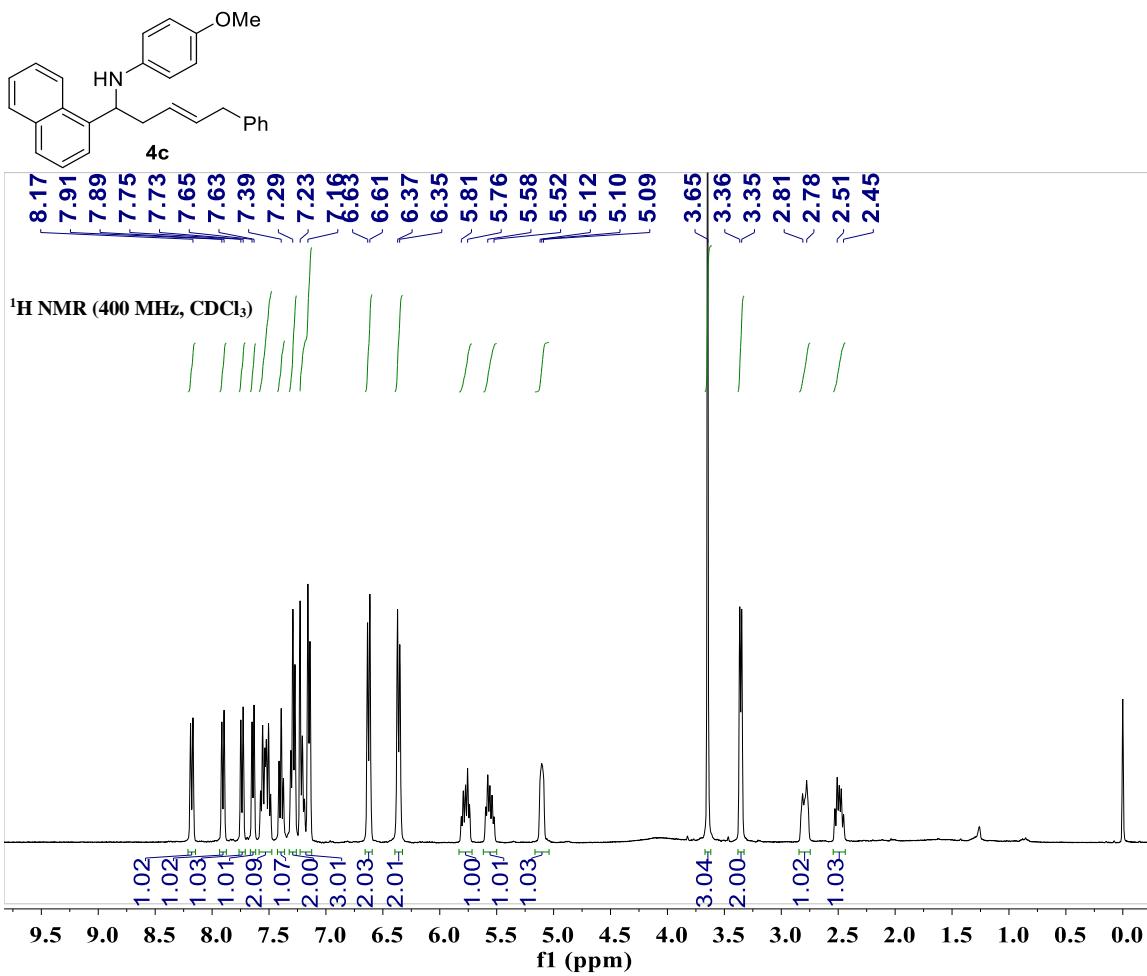


Figure S5

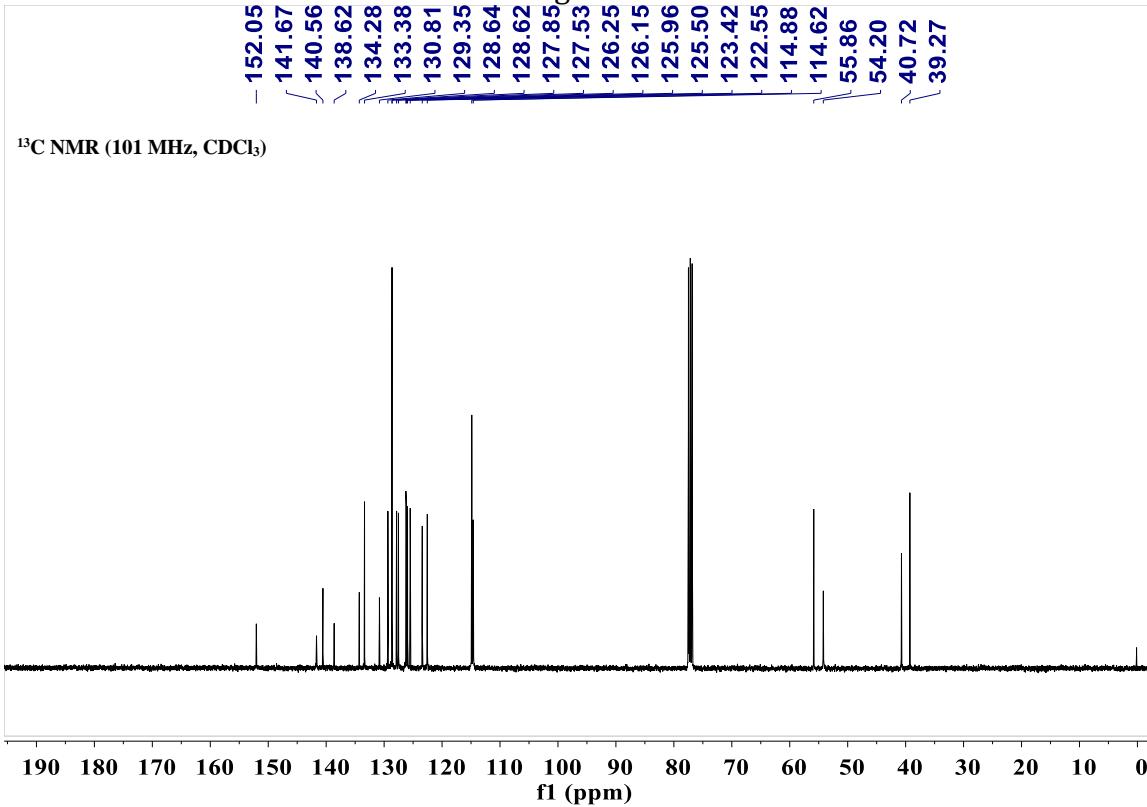


Figure S6

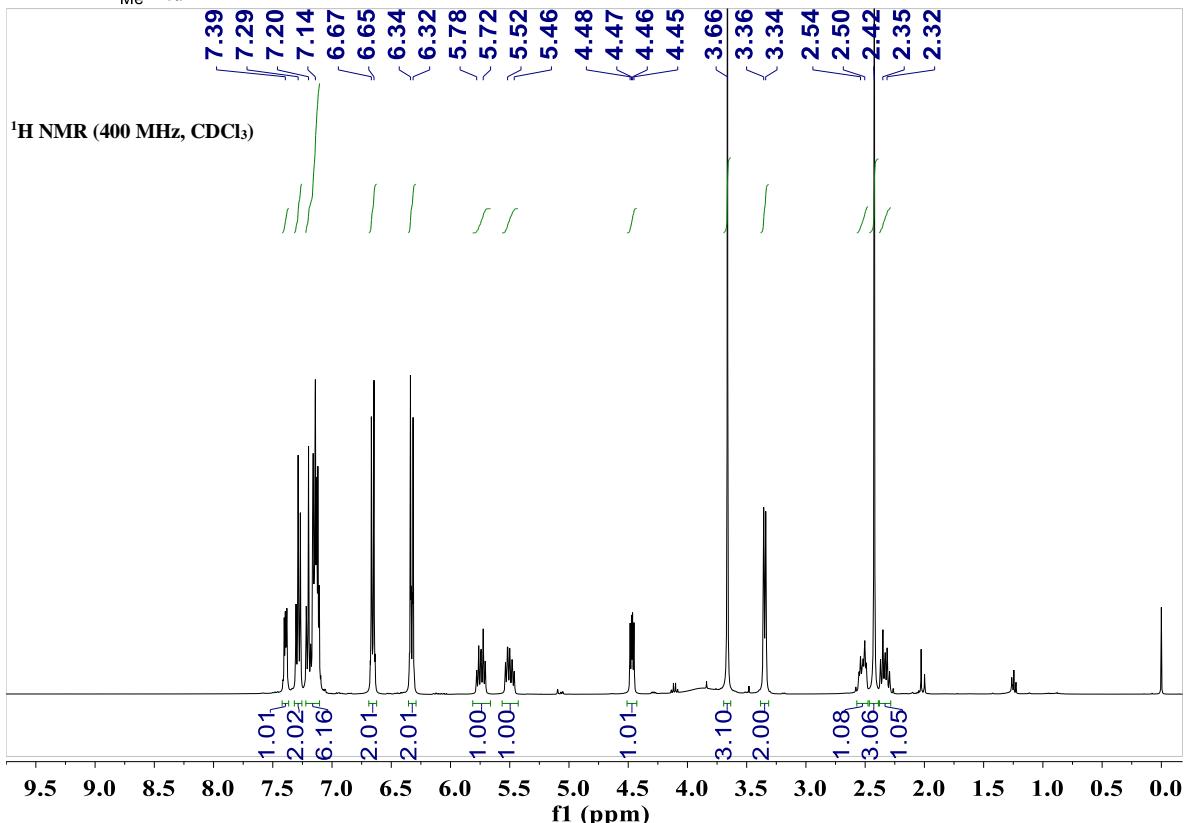
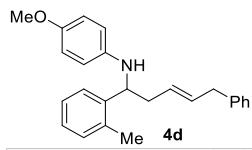


Figure S7

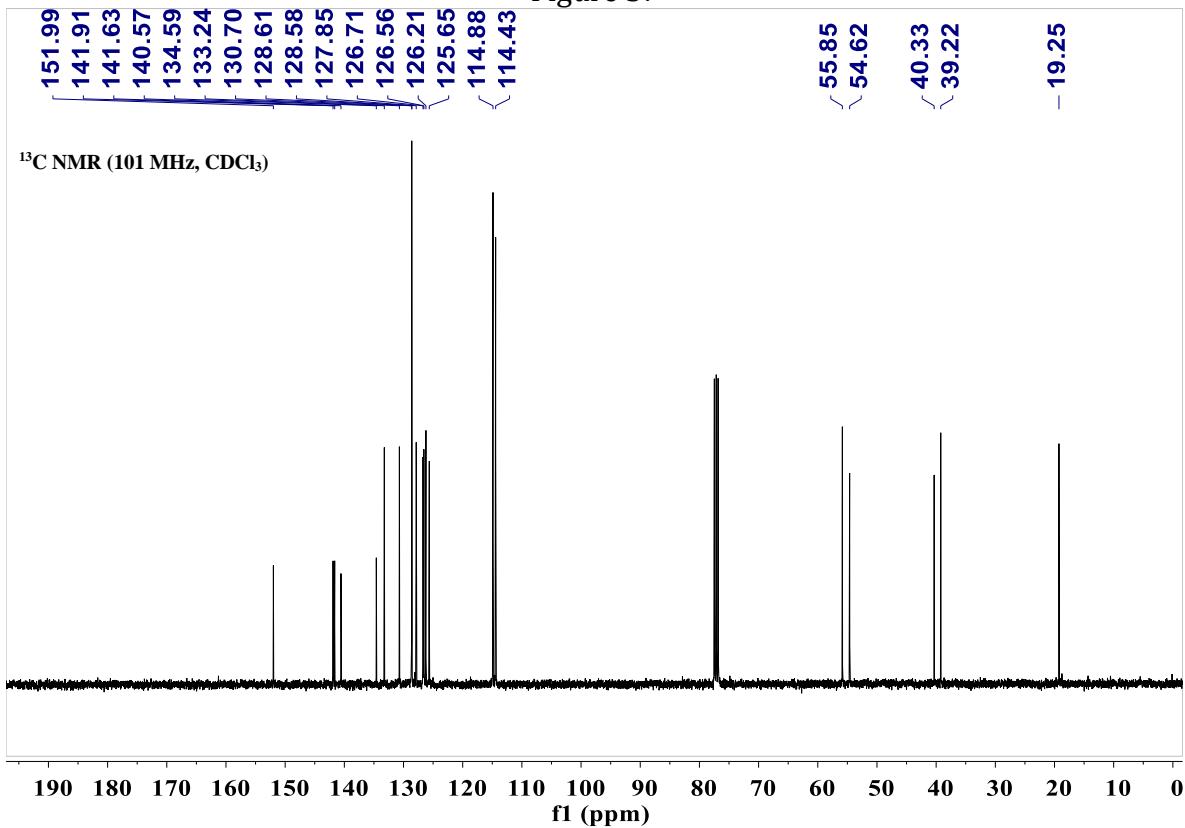


Figure S8

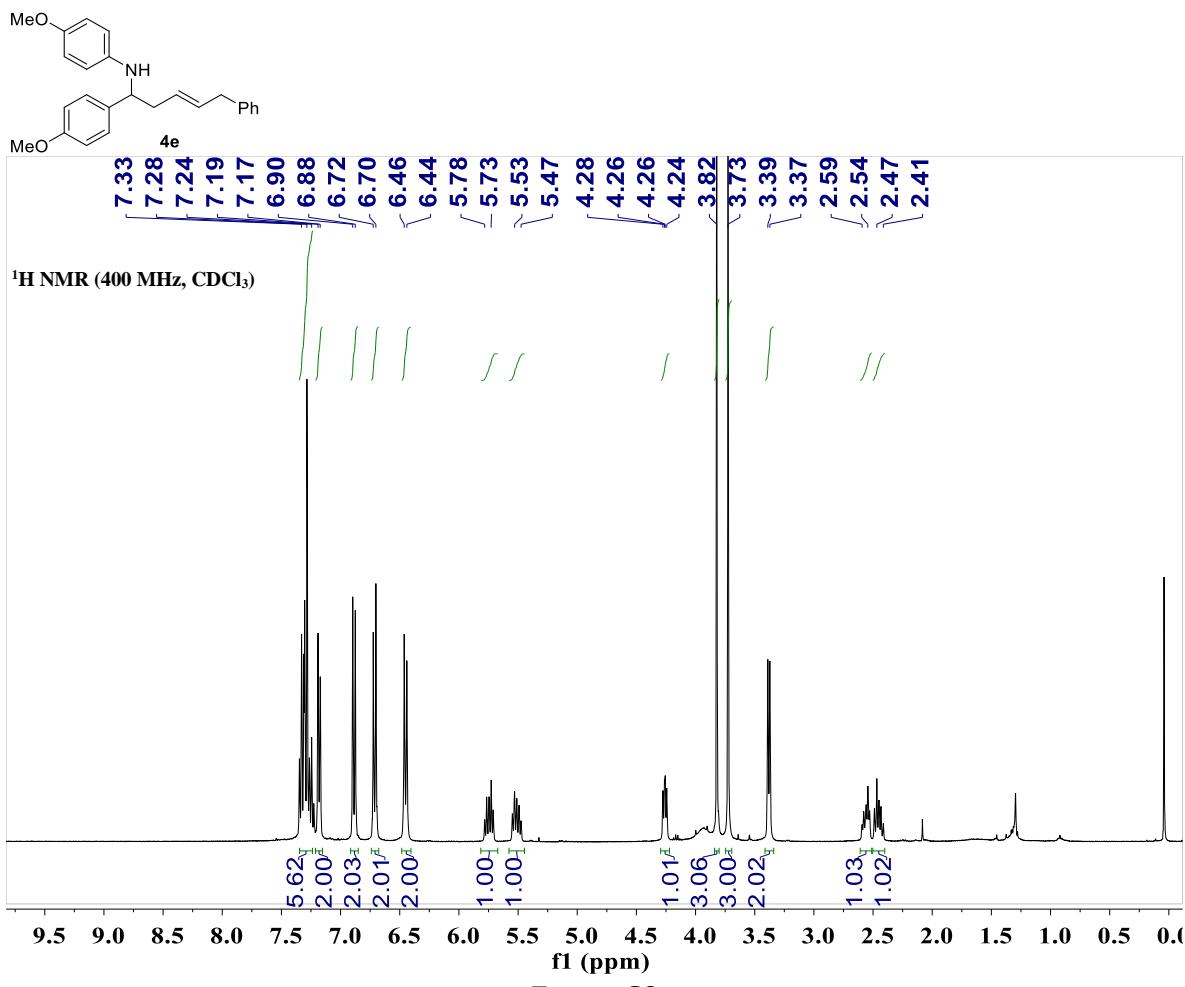


Figure S9

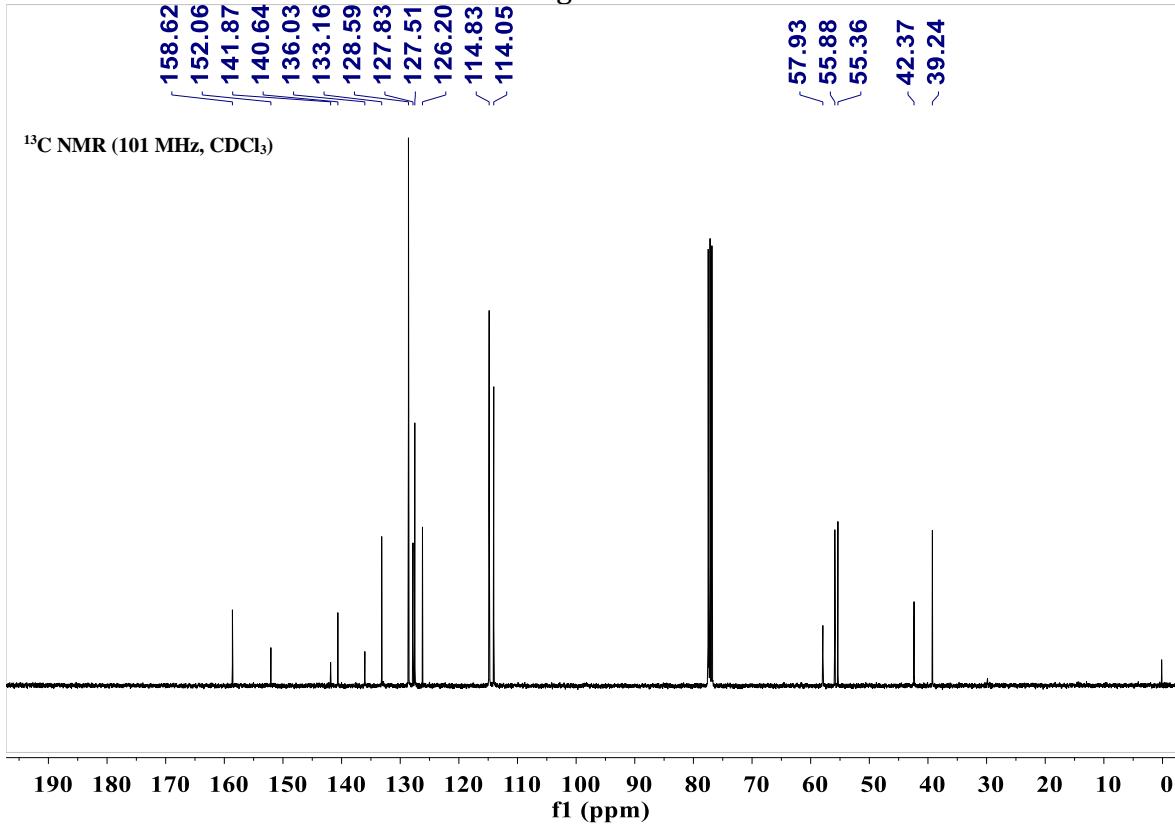


Figure S10

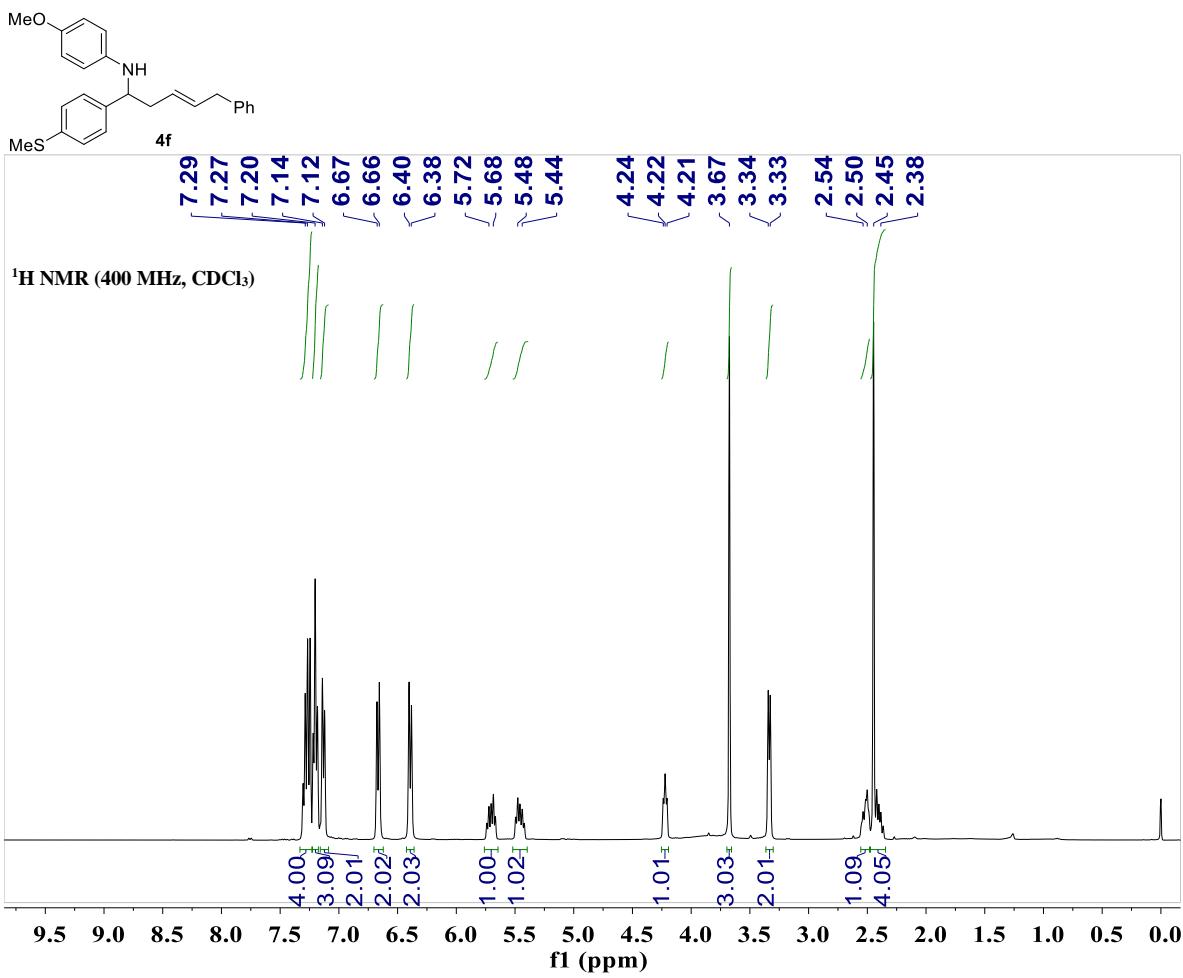


Figure S11

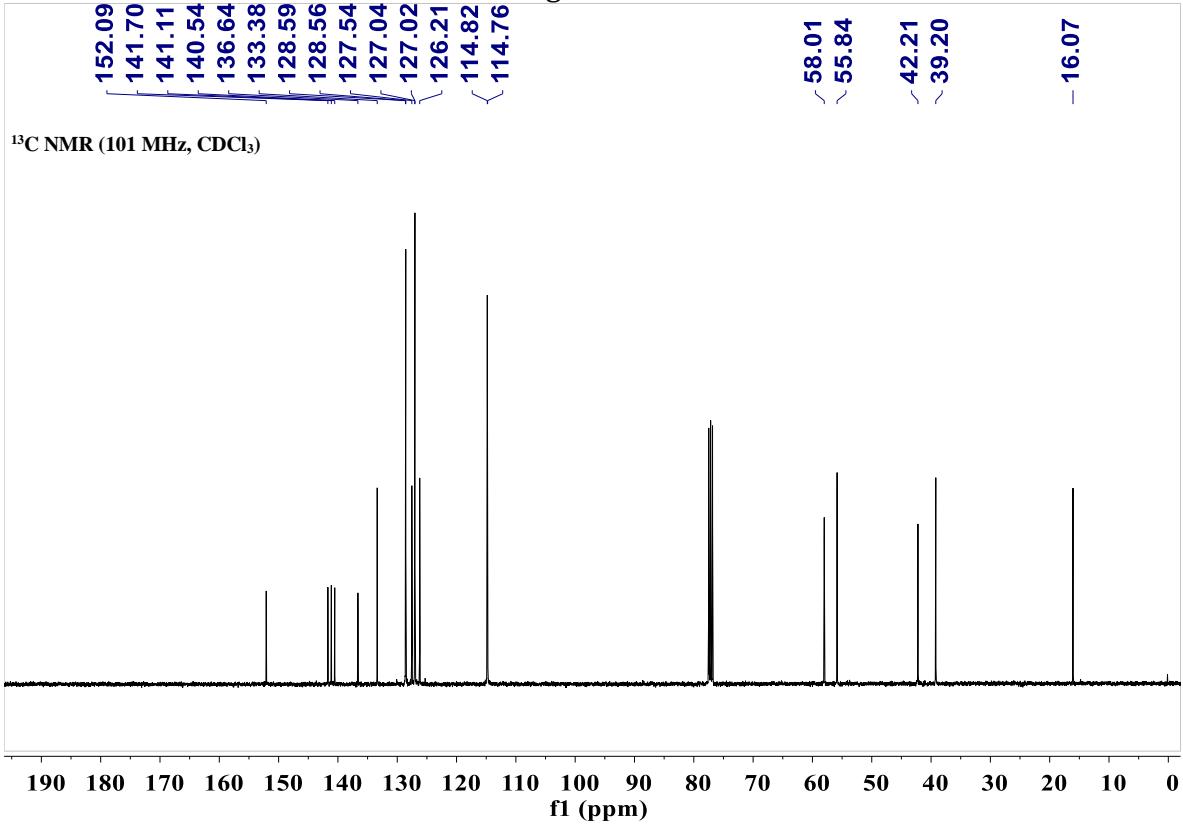


Figure S12

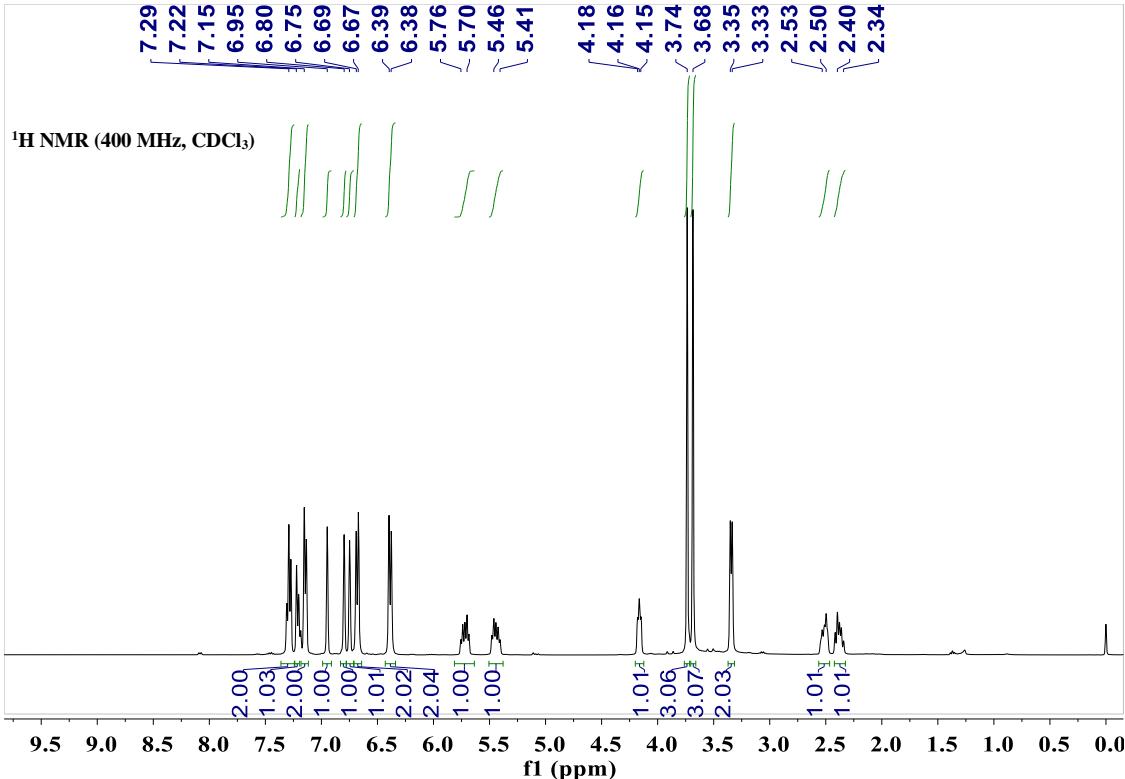
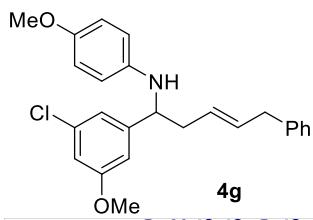


Figure S13

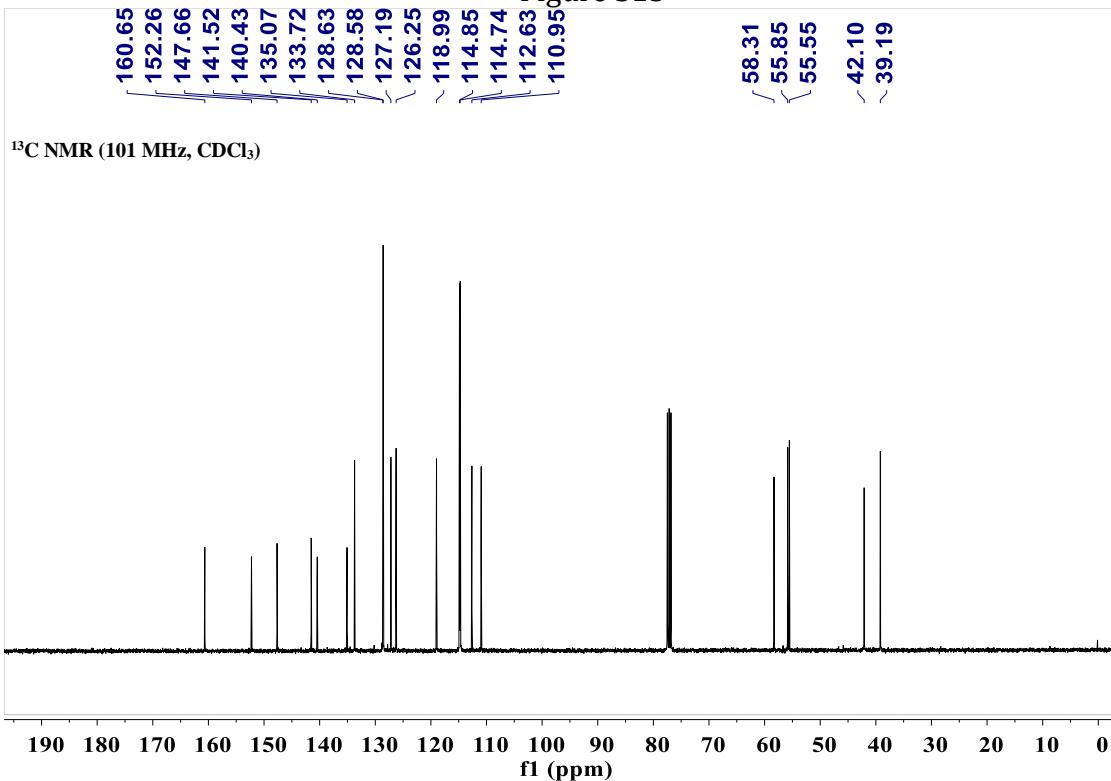


Figure S14

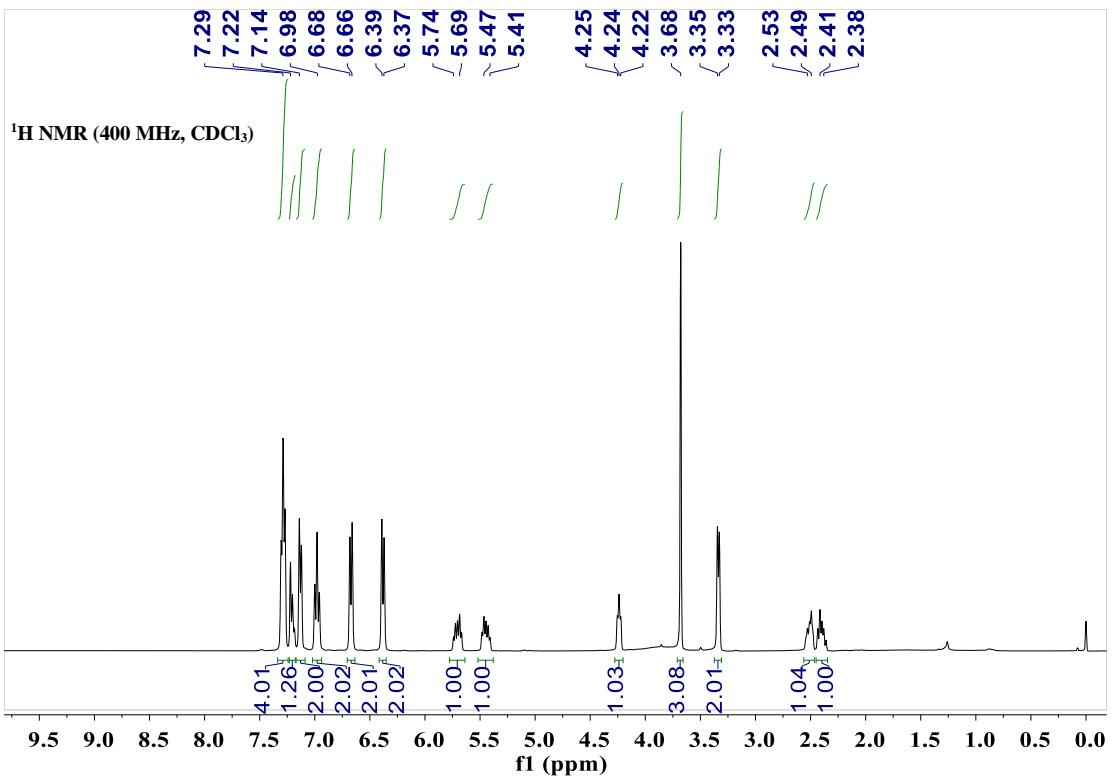
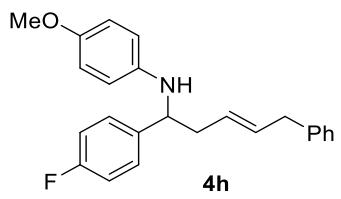


Figure S15

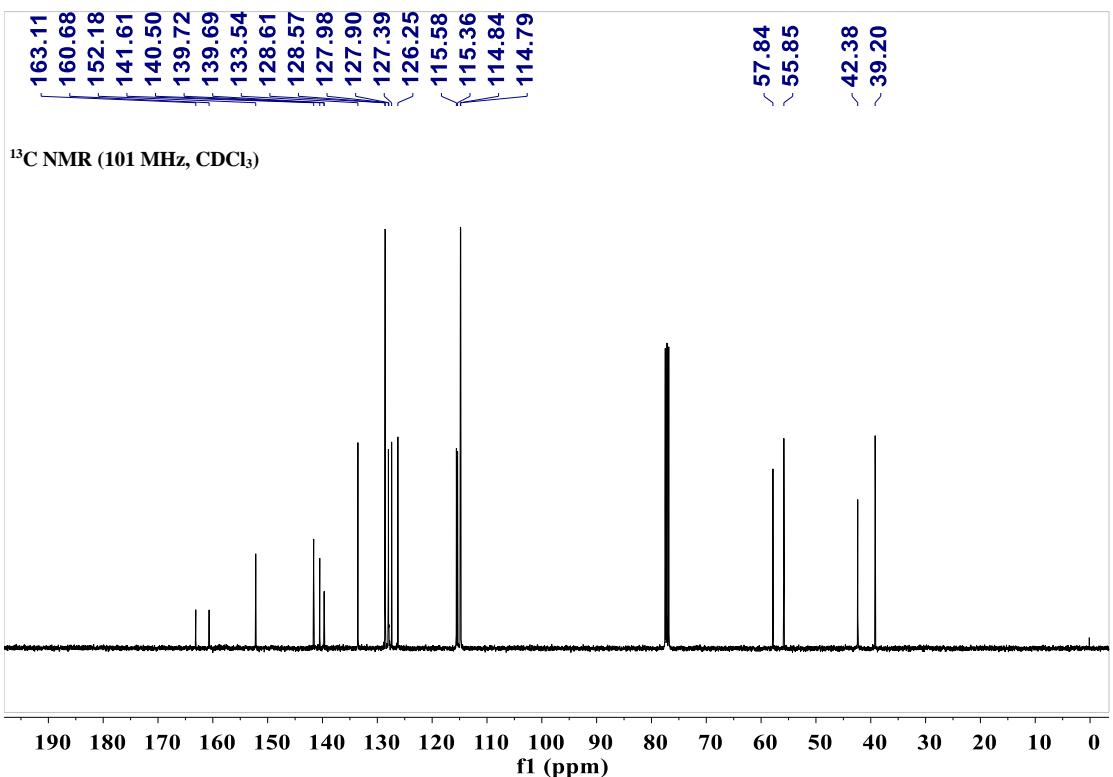


Figure S16

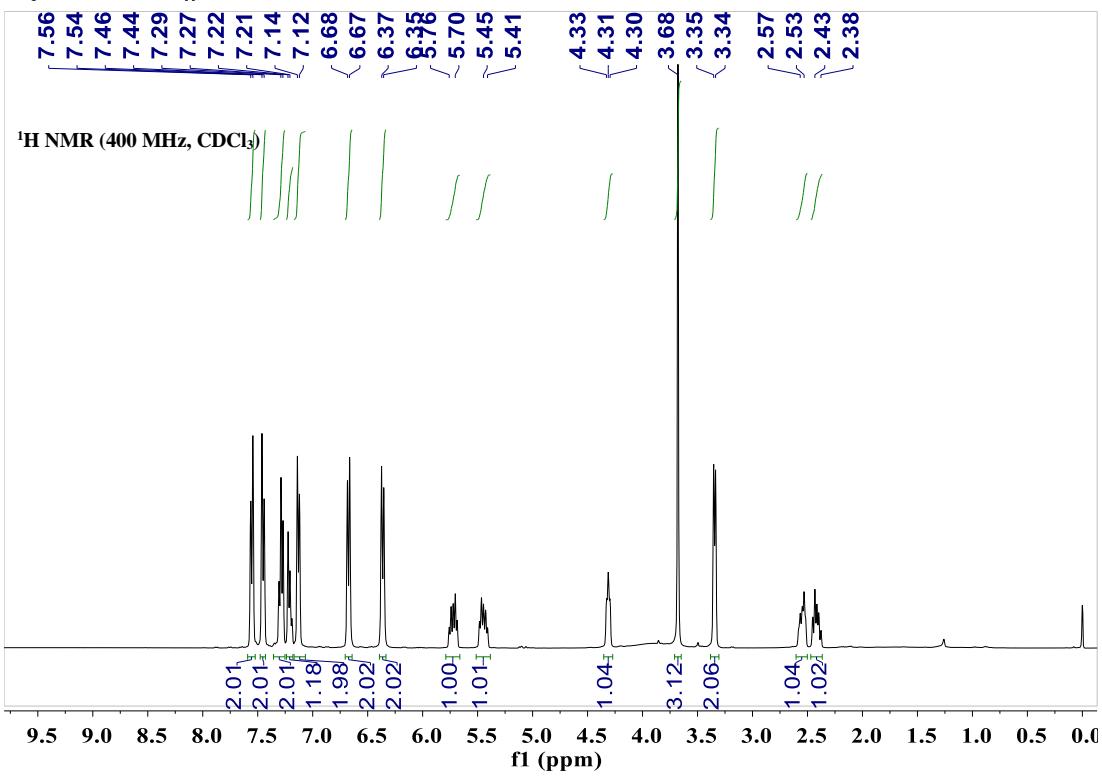
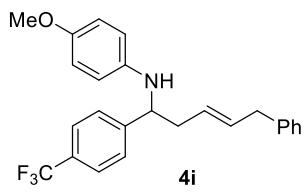


Figure S17

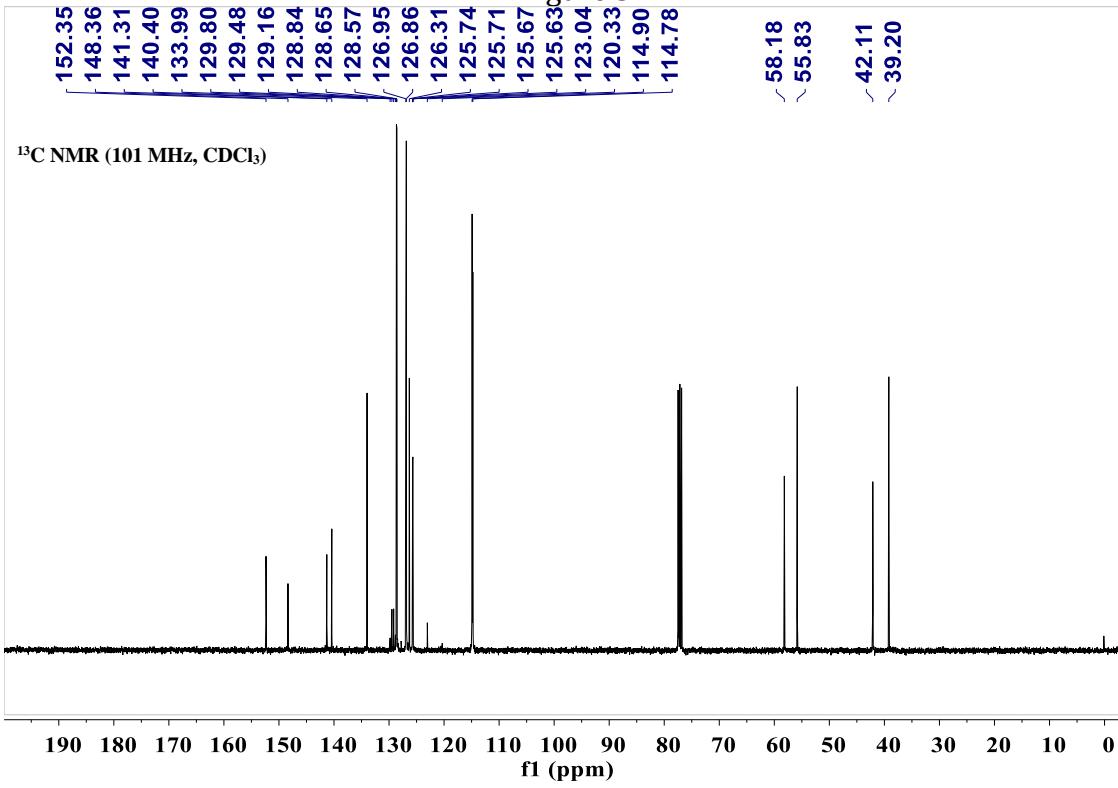


Figure S18

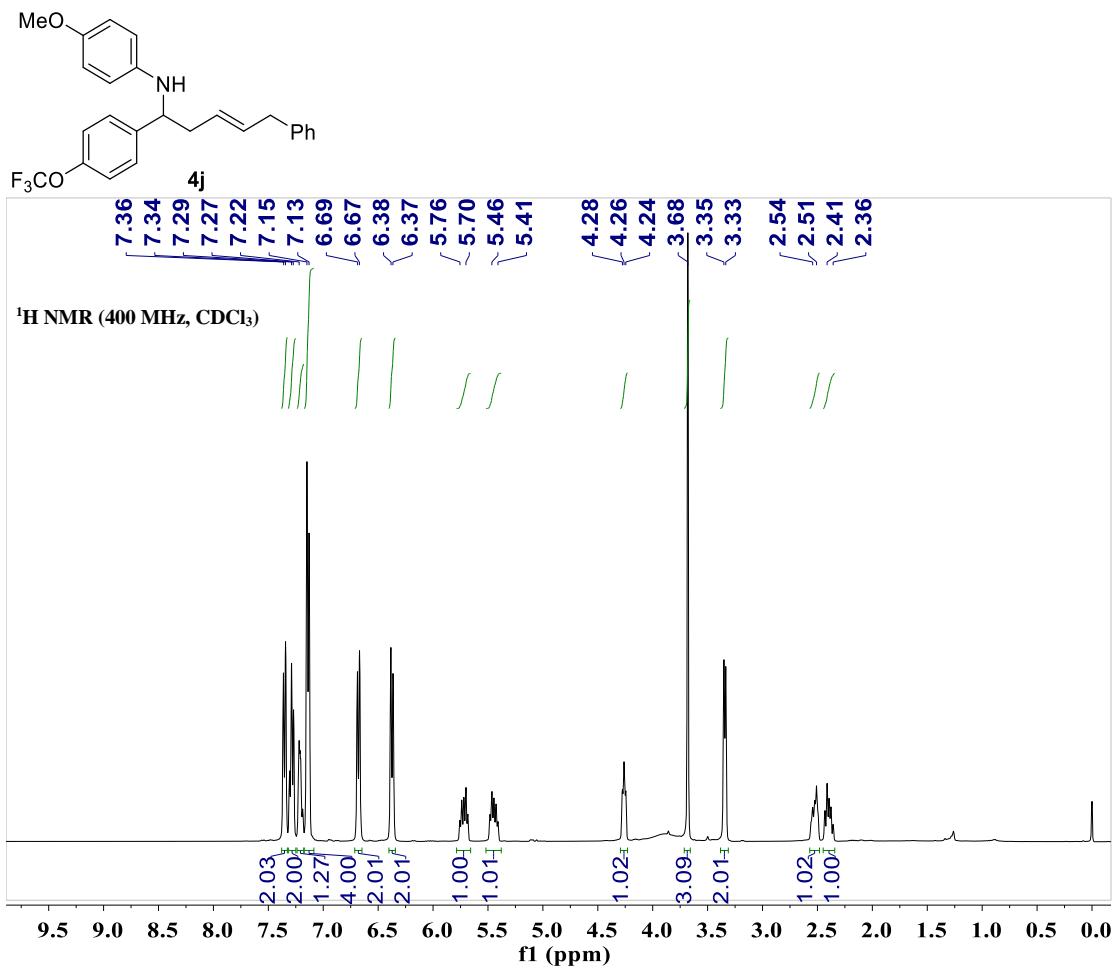


Figure S19

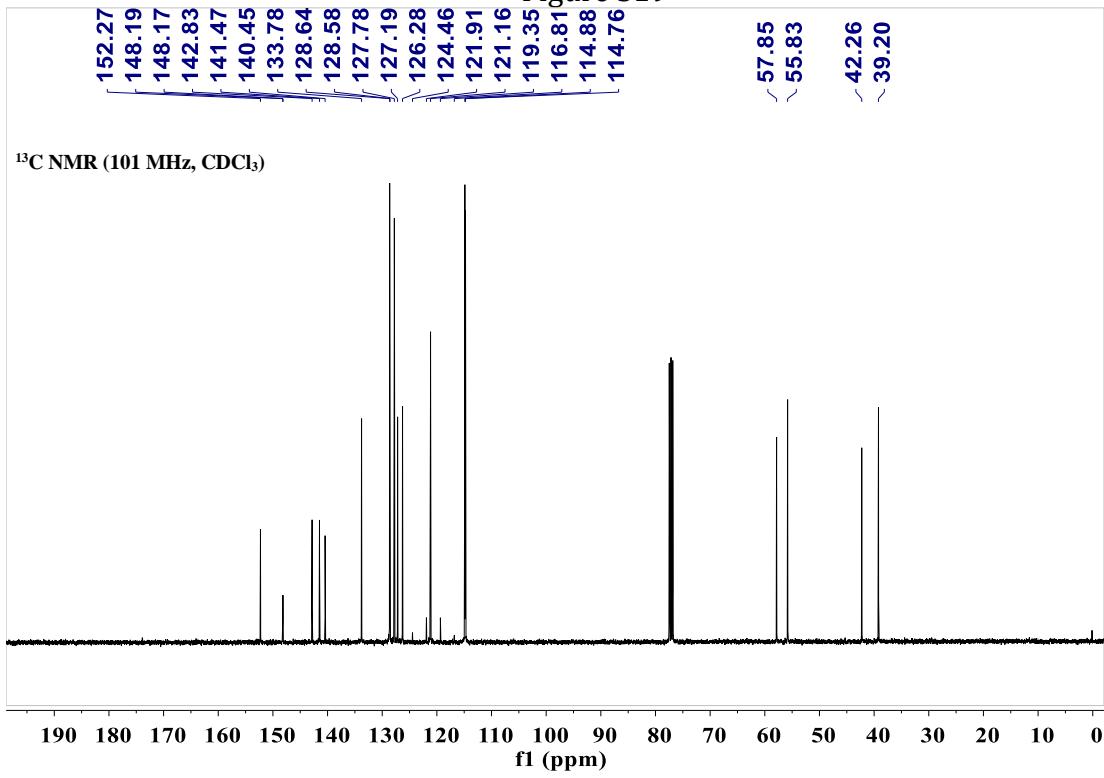


Figure S20

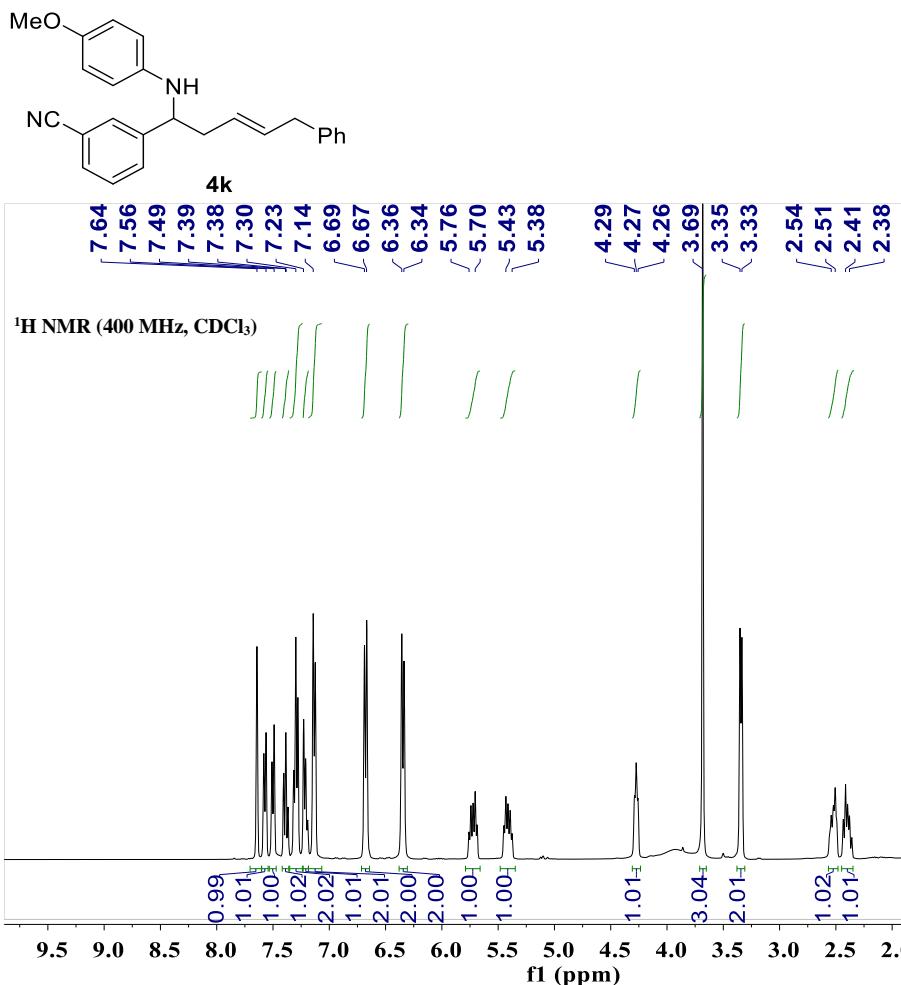


Figure S21

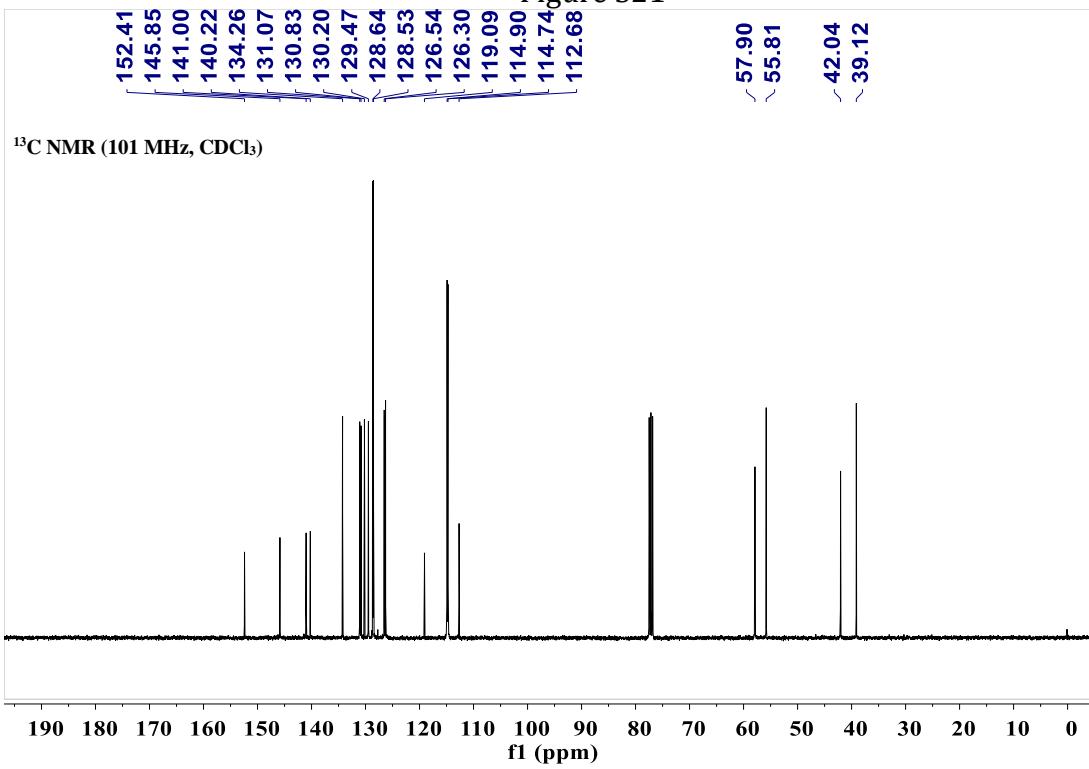


Figure S22

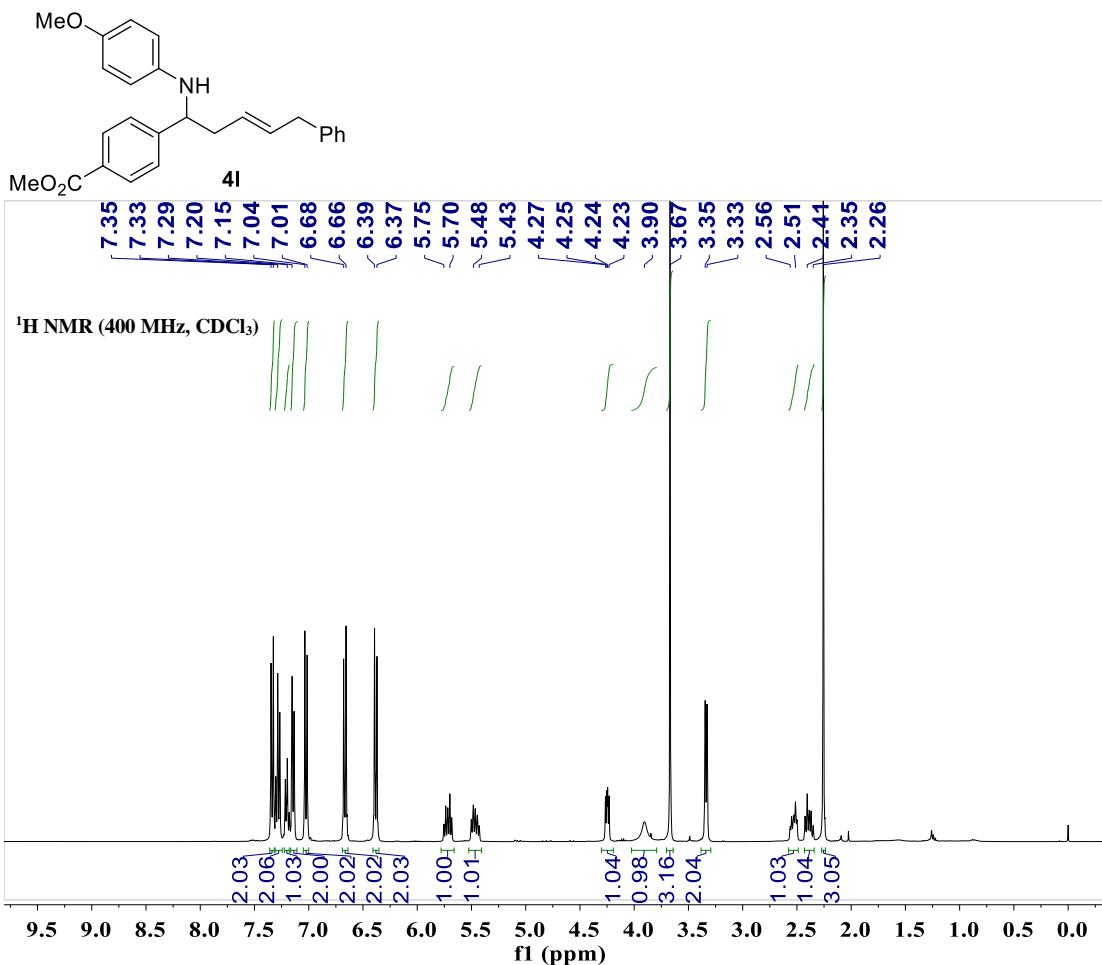


Figure S23

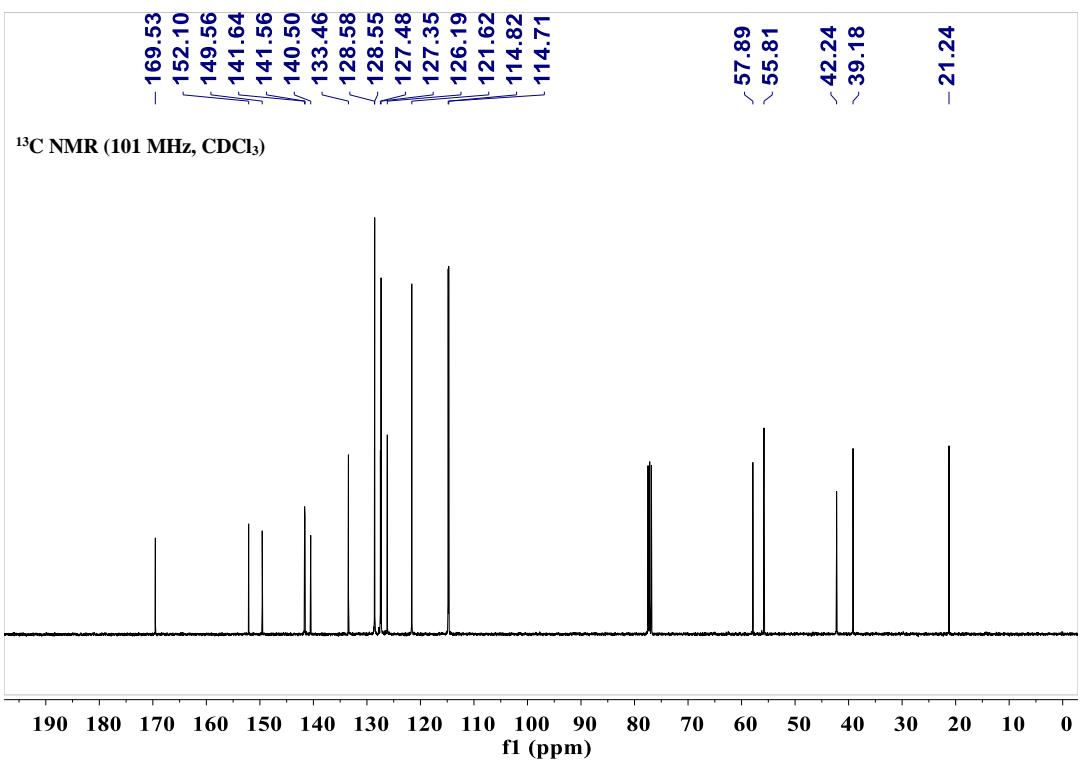


Figure S24

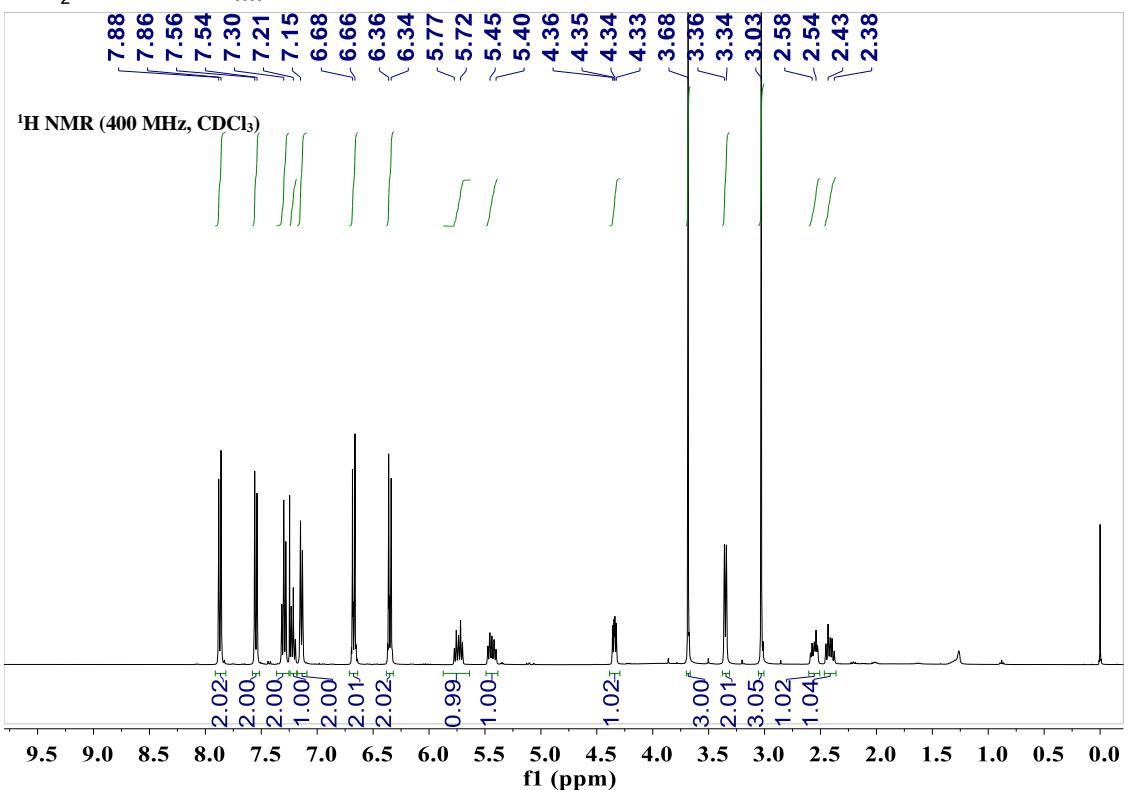
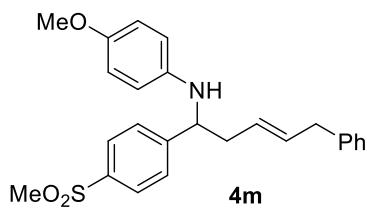


Figure S25

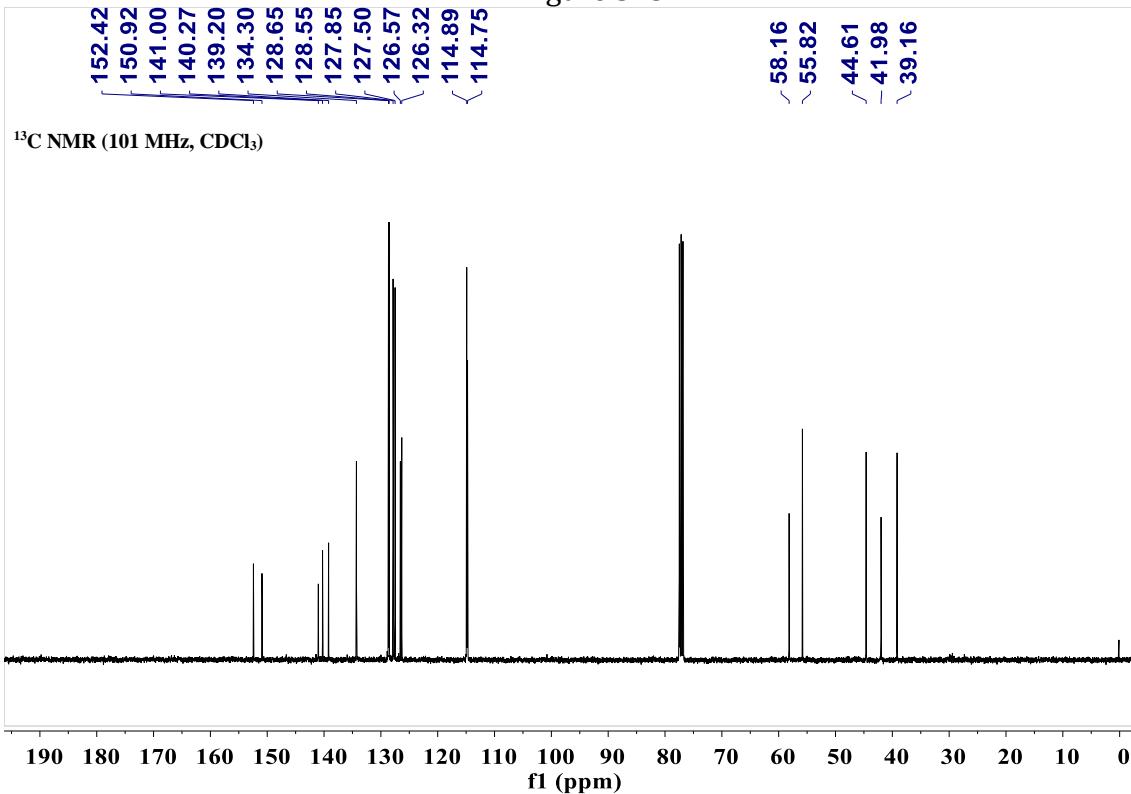


Figure S26

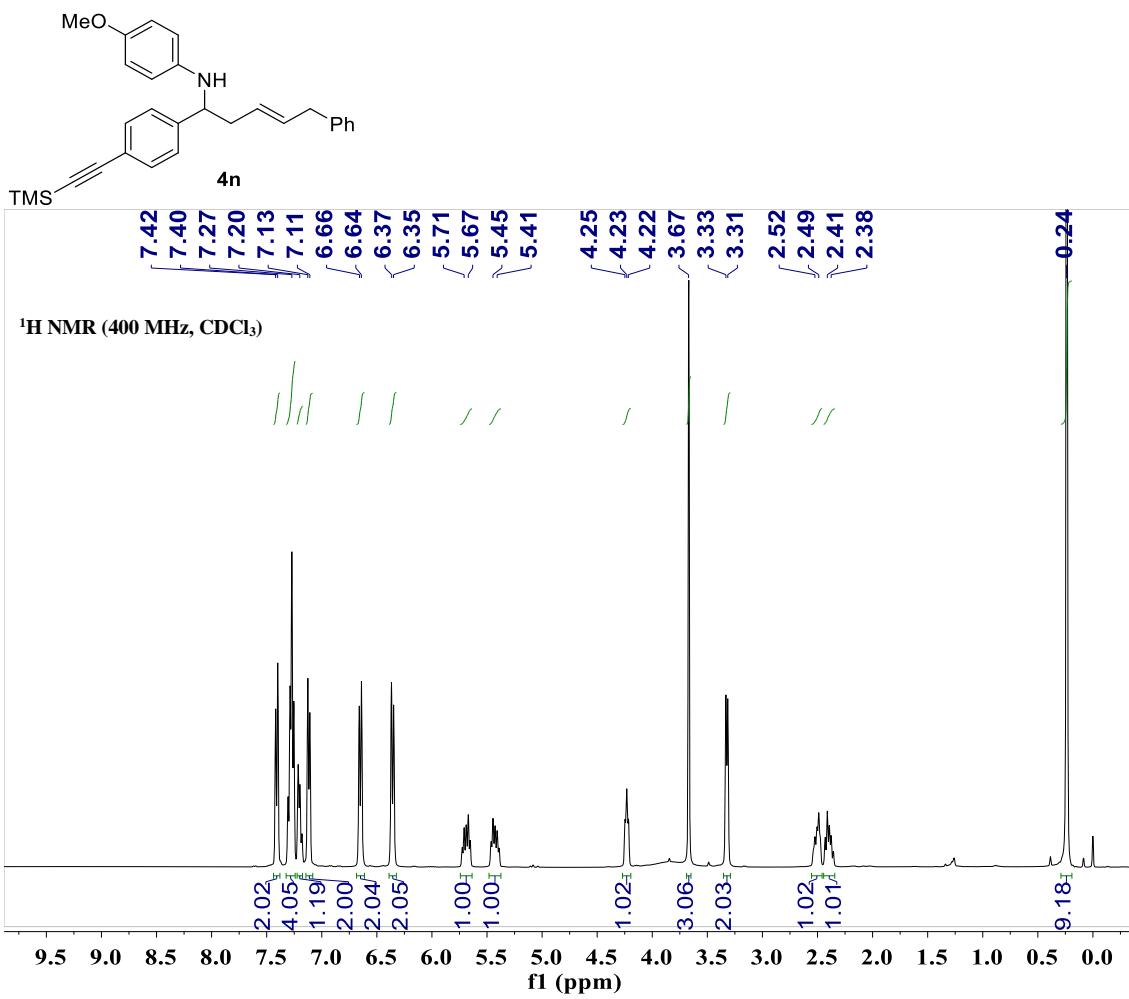


Figure S27

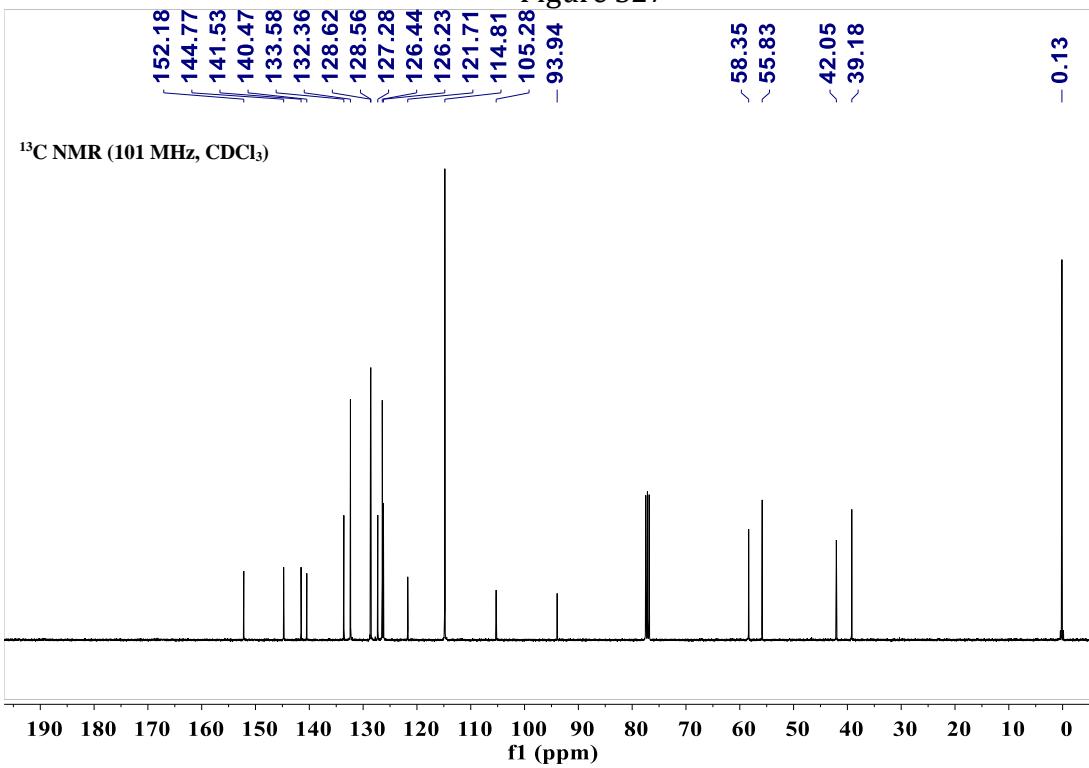


Figure S28

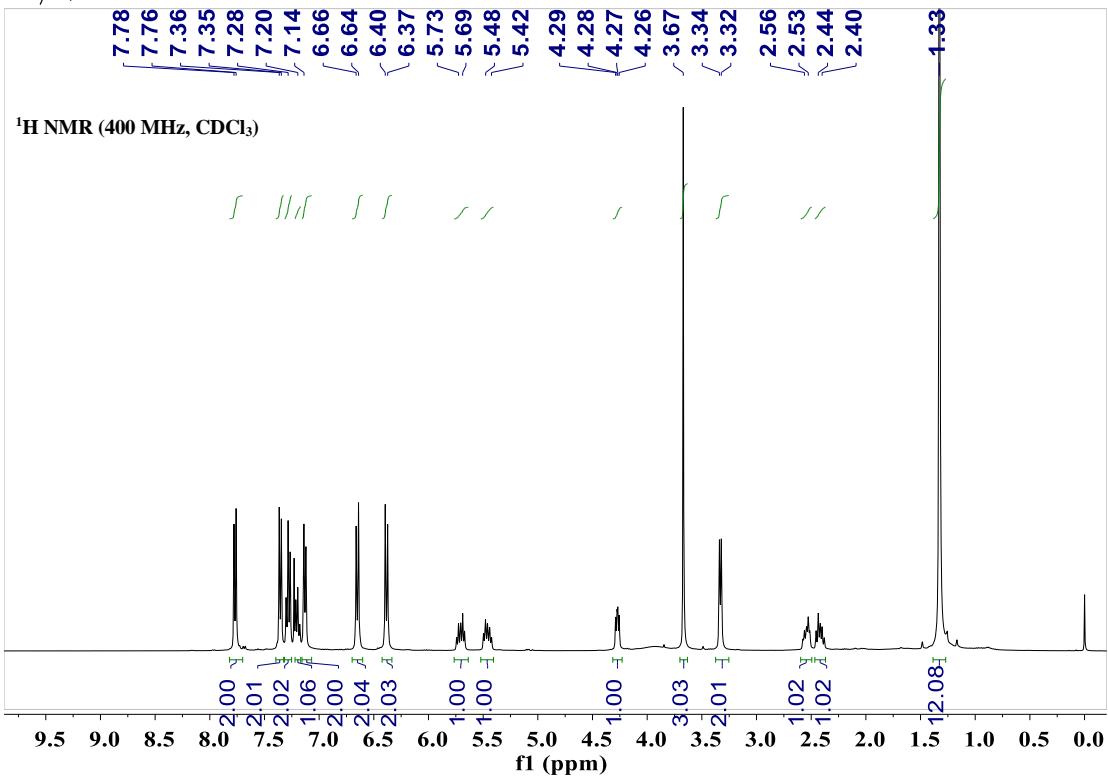
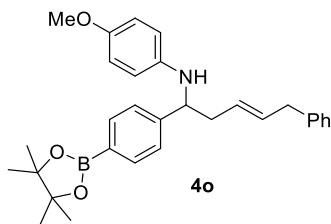


Figure S29

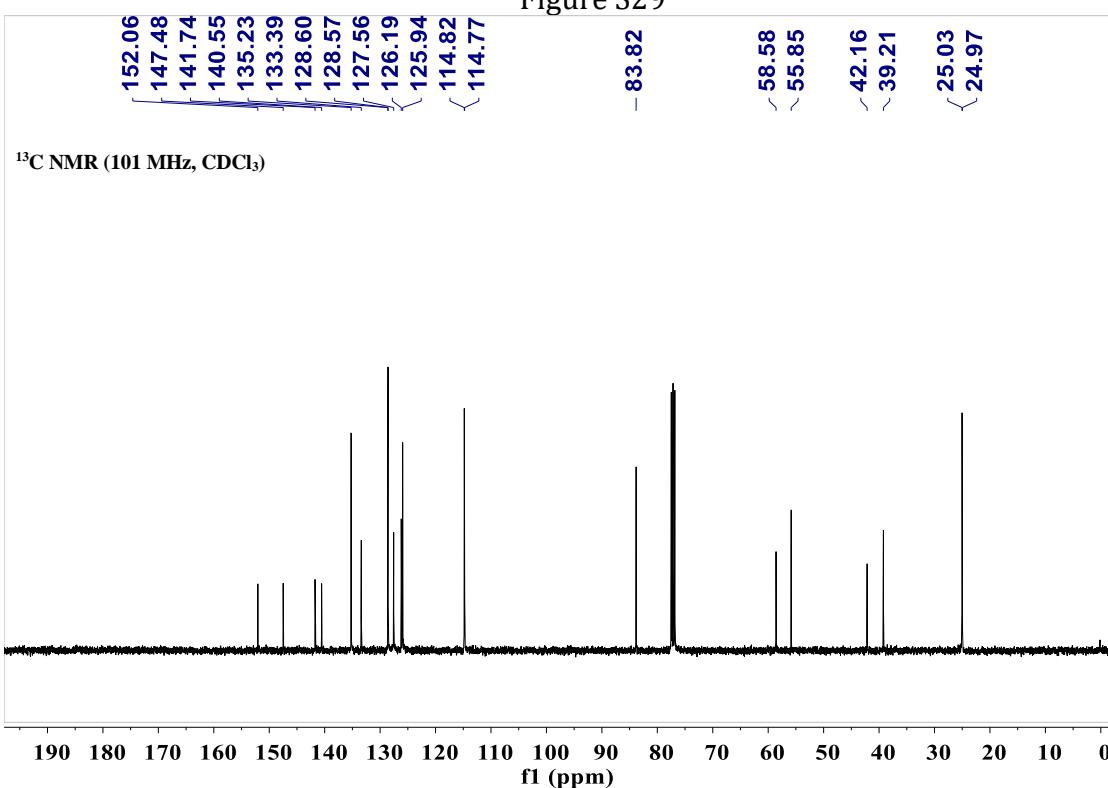


Figure S30

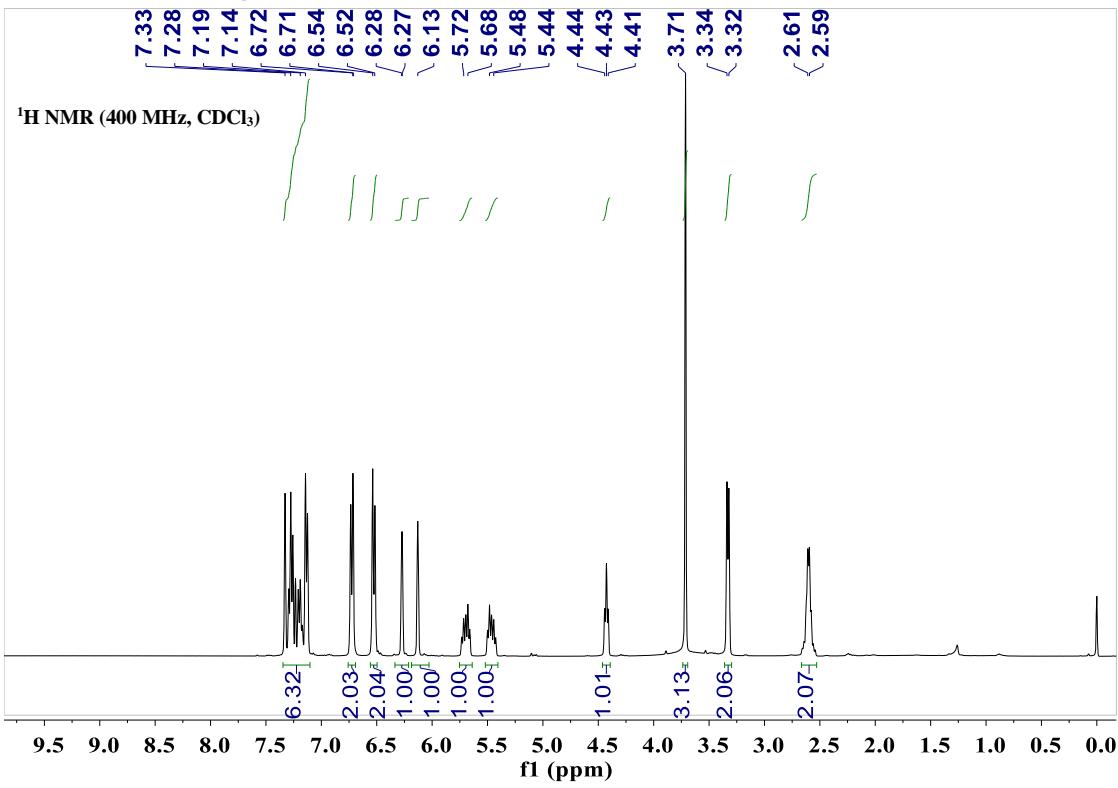
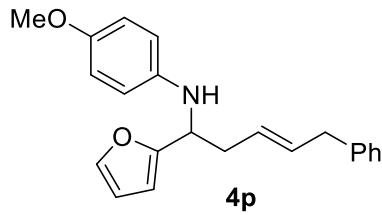


Figure S31

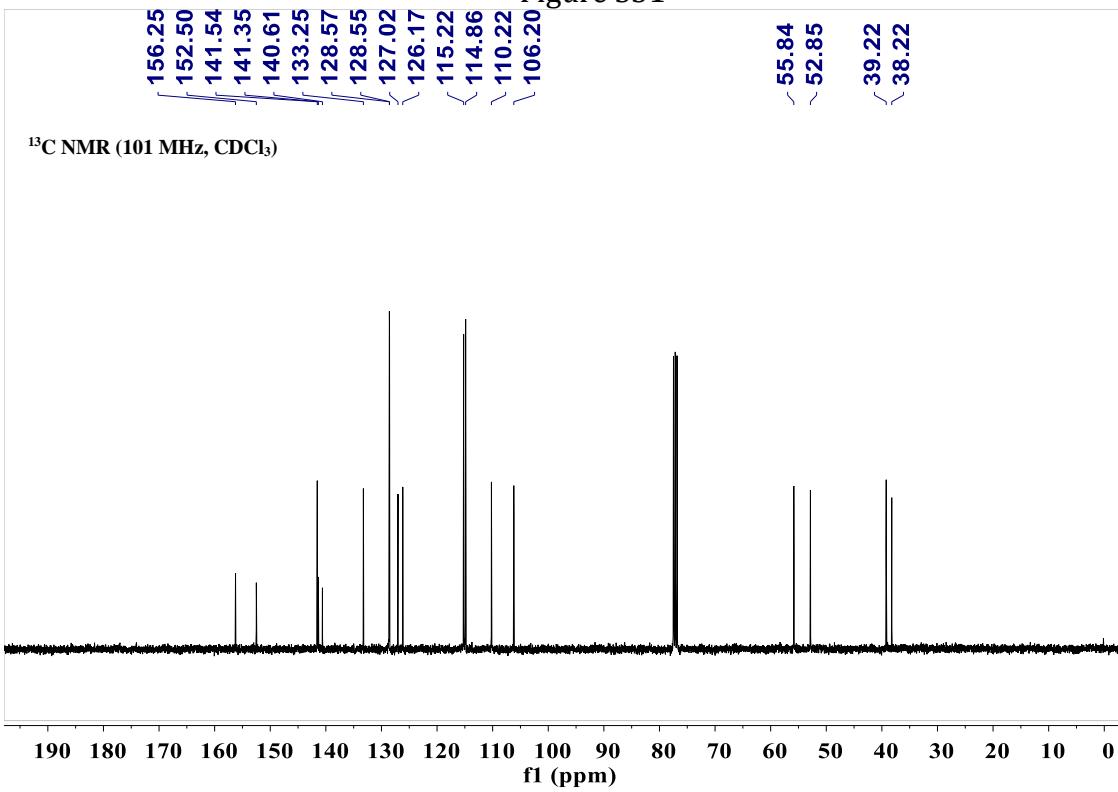


Figure S32

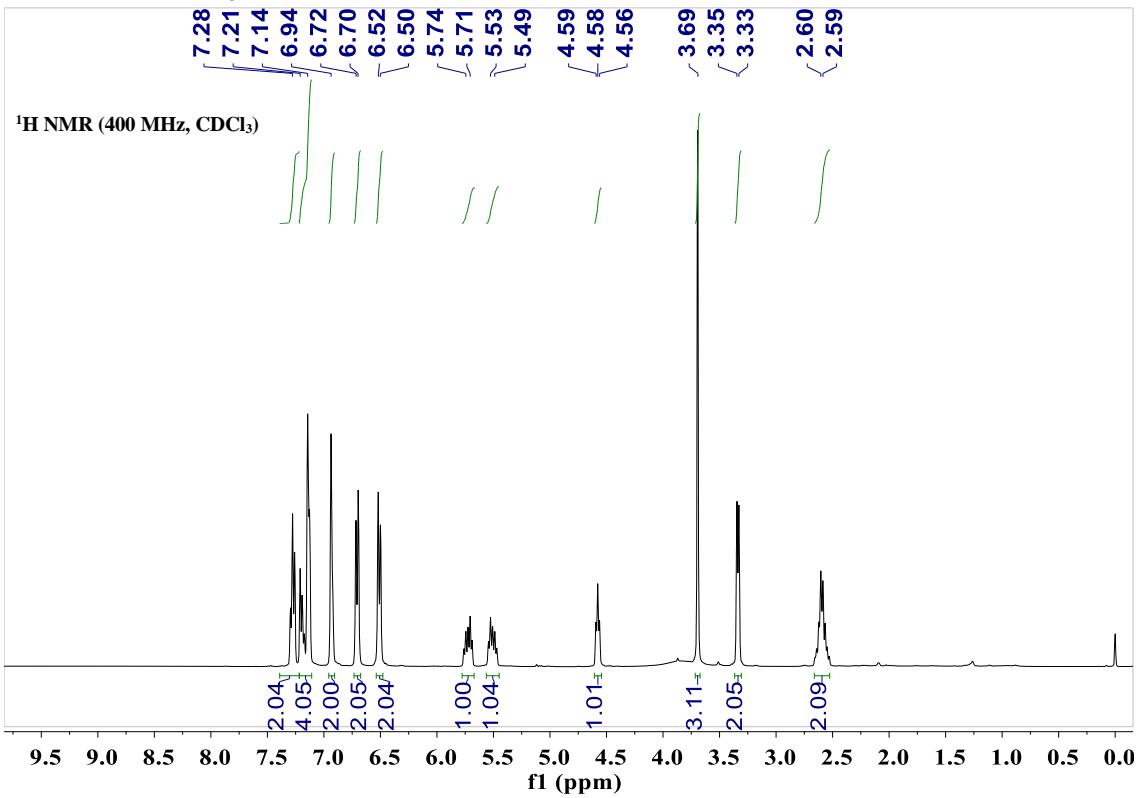
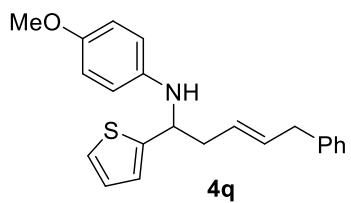


Figure S33

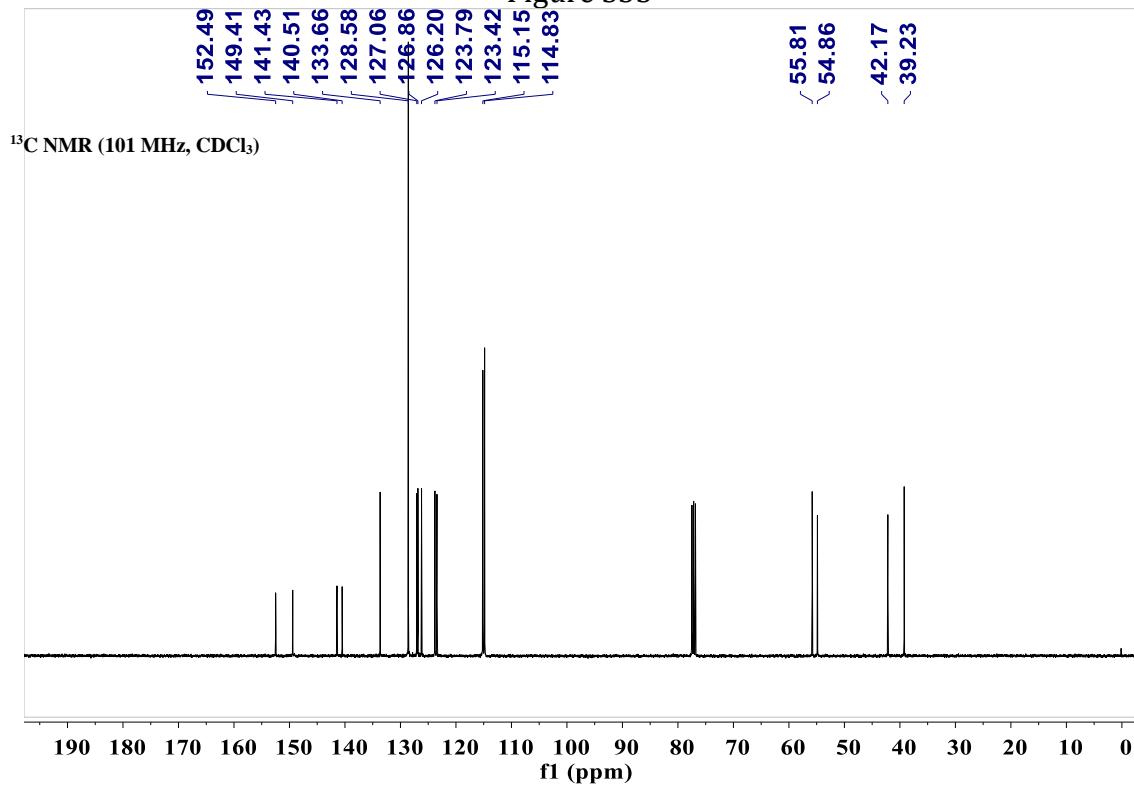


Figure S34

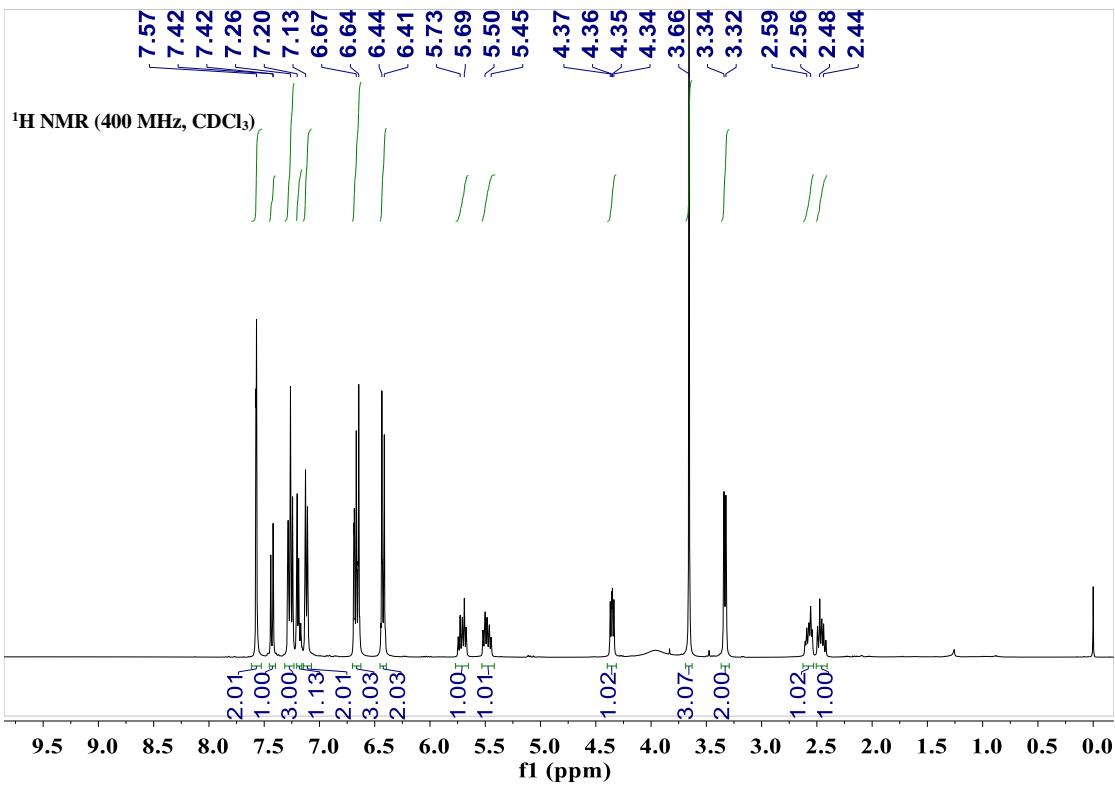
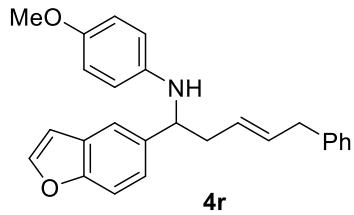


Figure S35

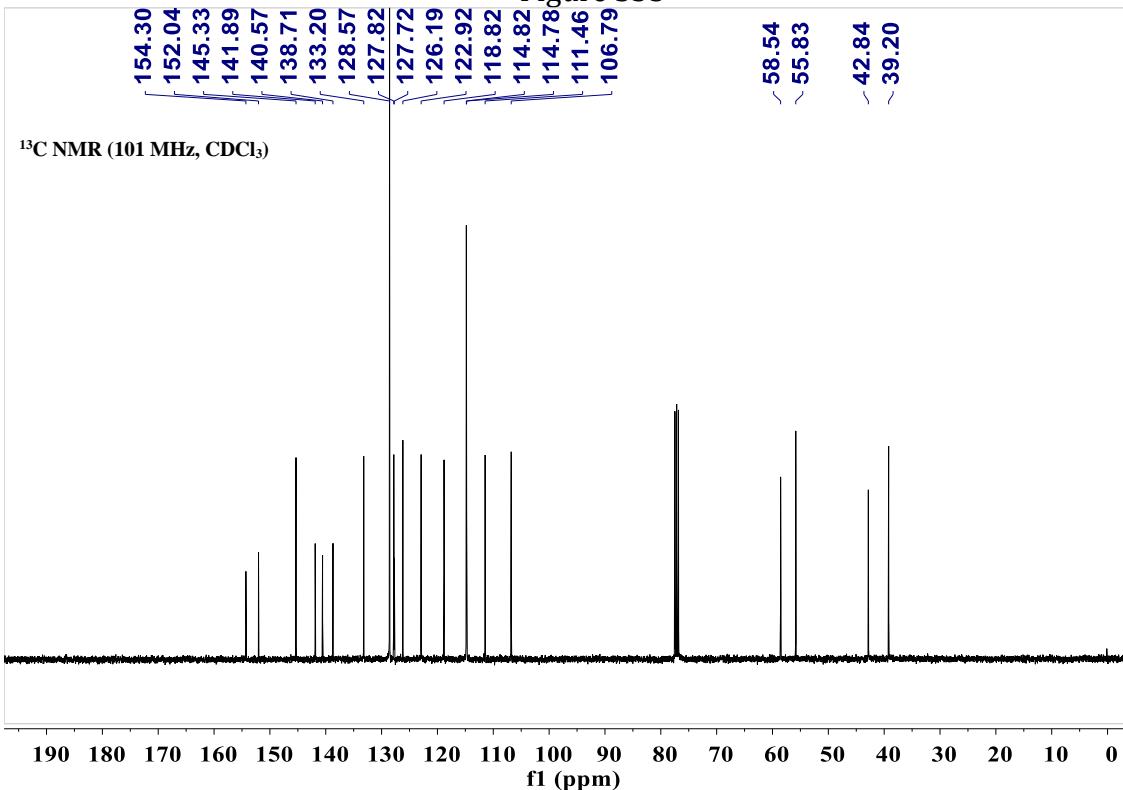


Figure S36

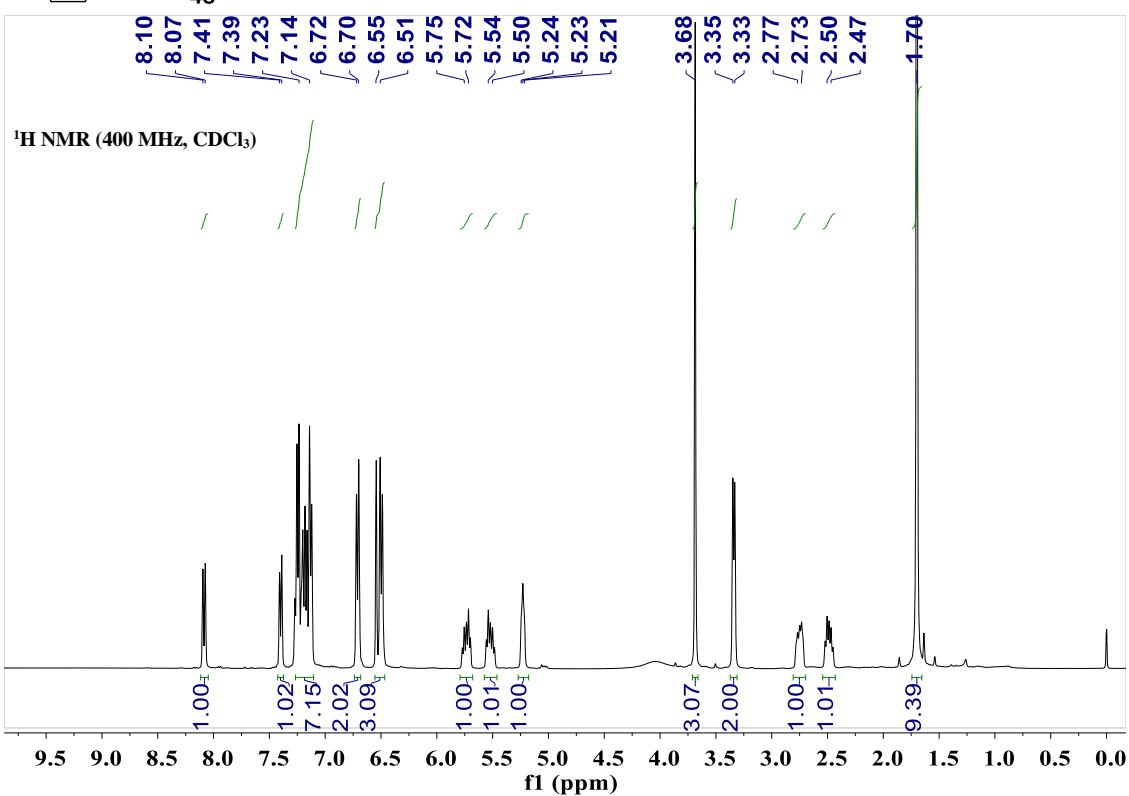
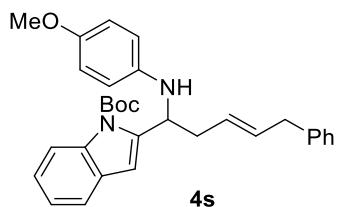


Figure S37

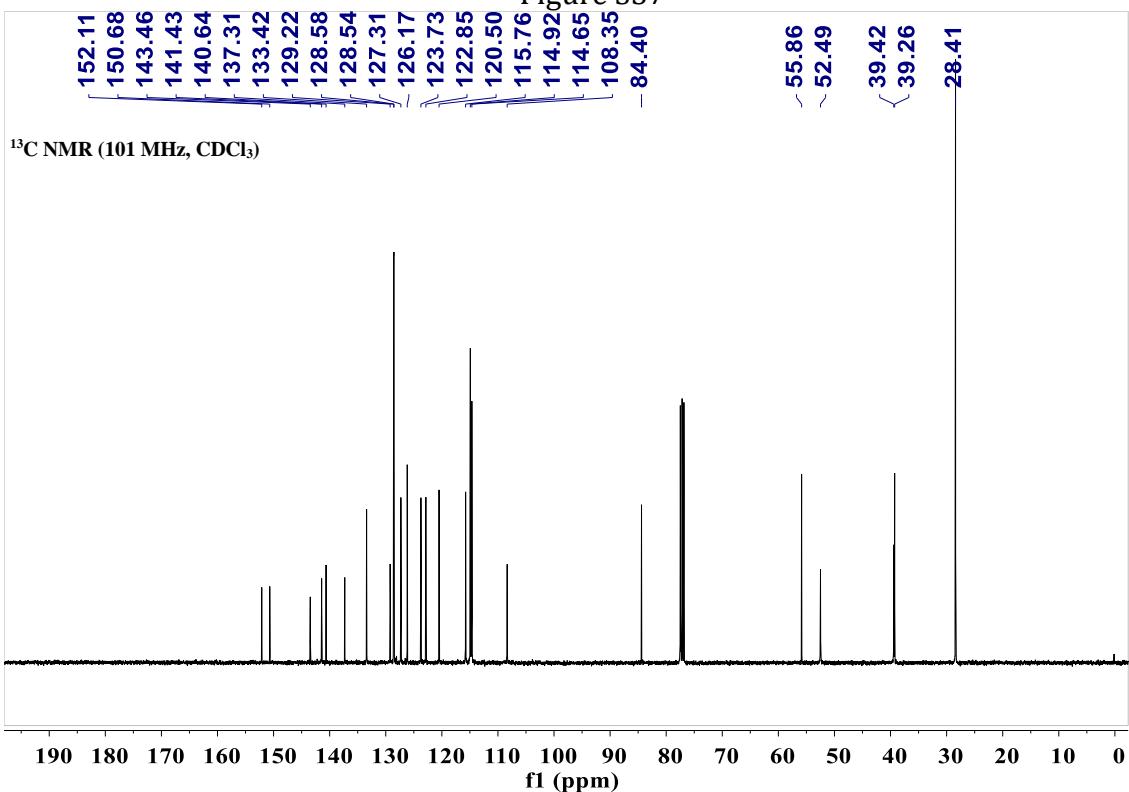


Figure S38

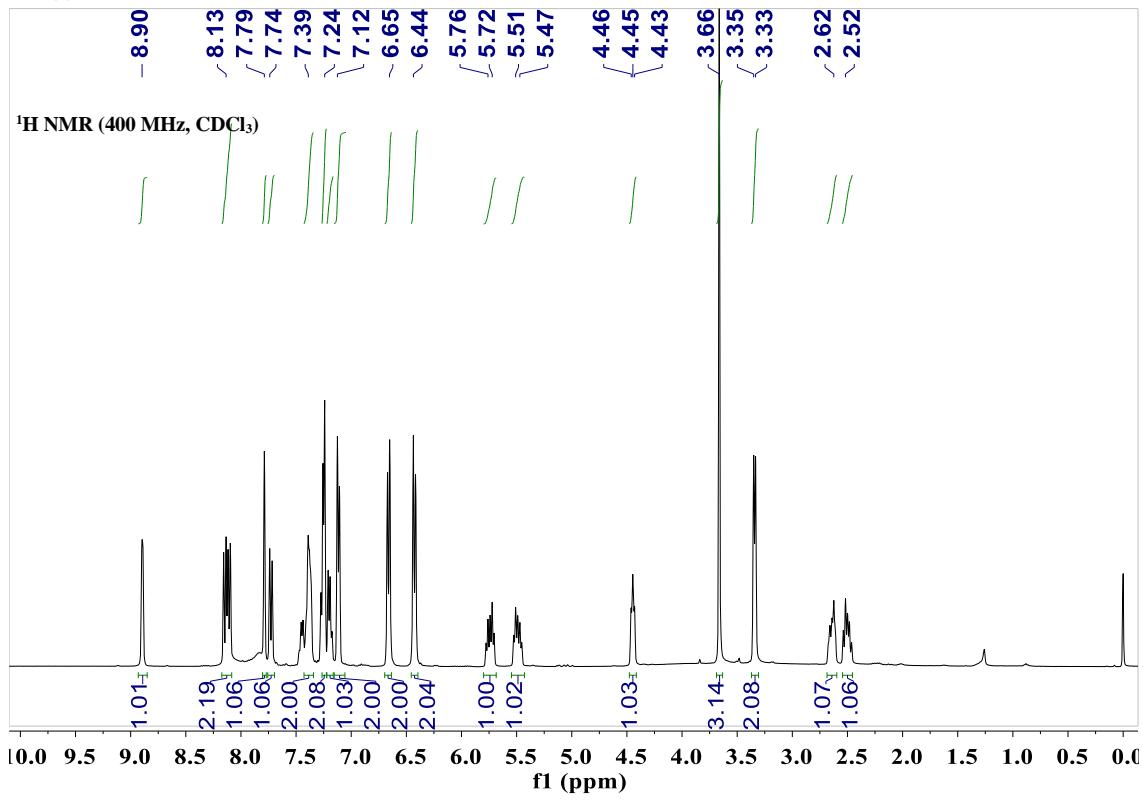
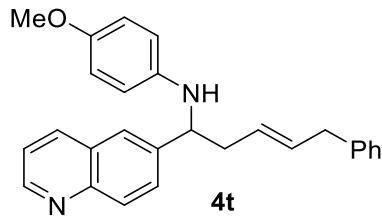


Figure S39

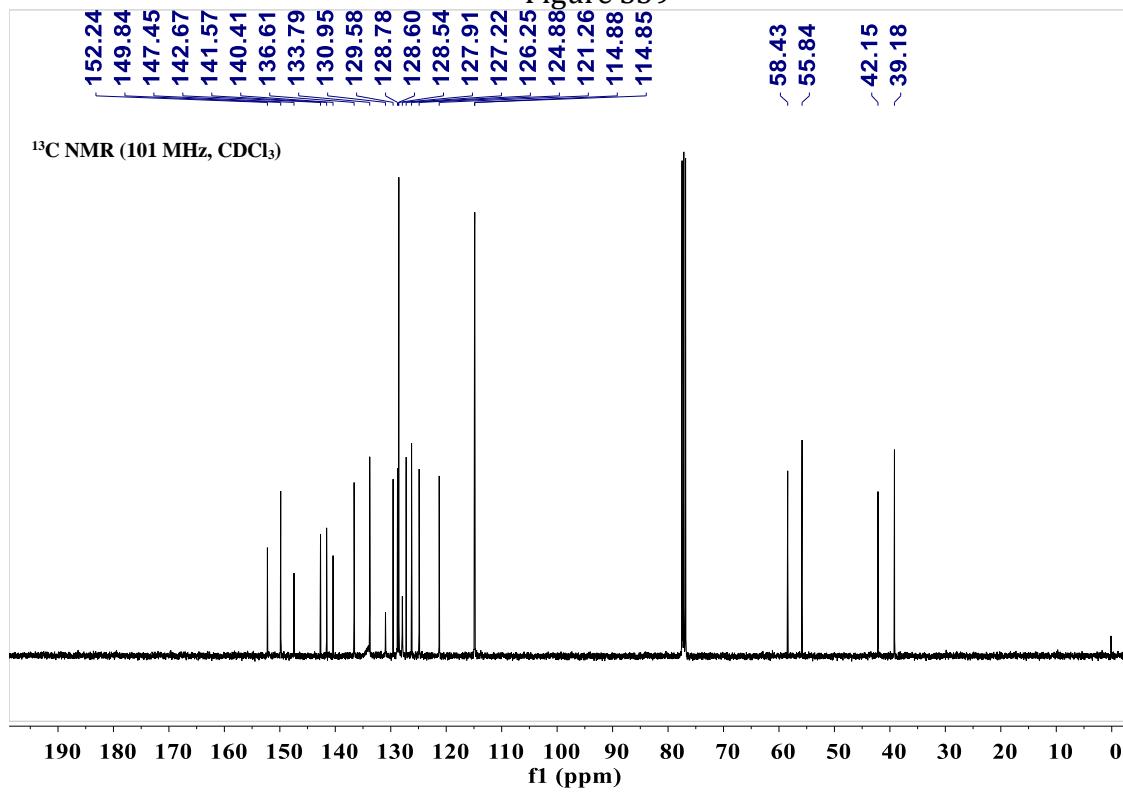


Figure S40

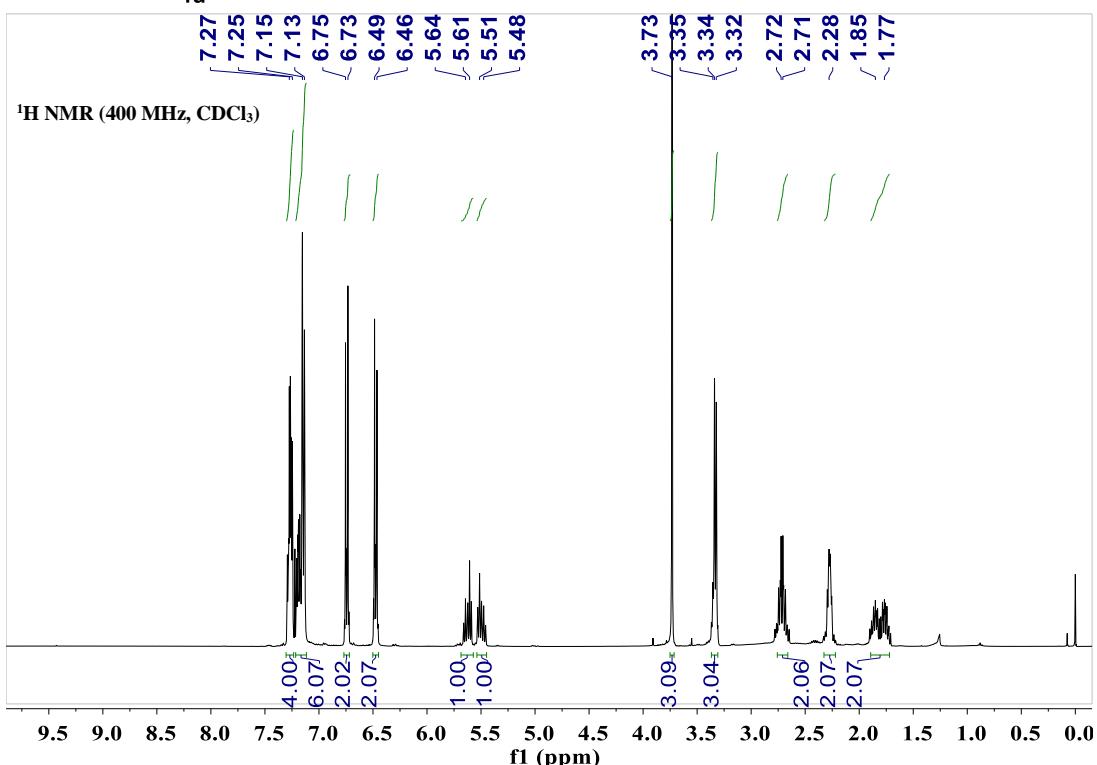
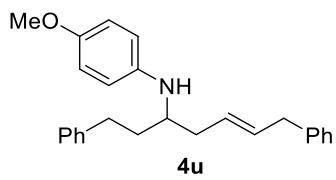


Figure S41

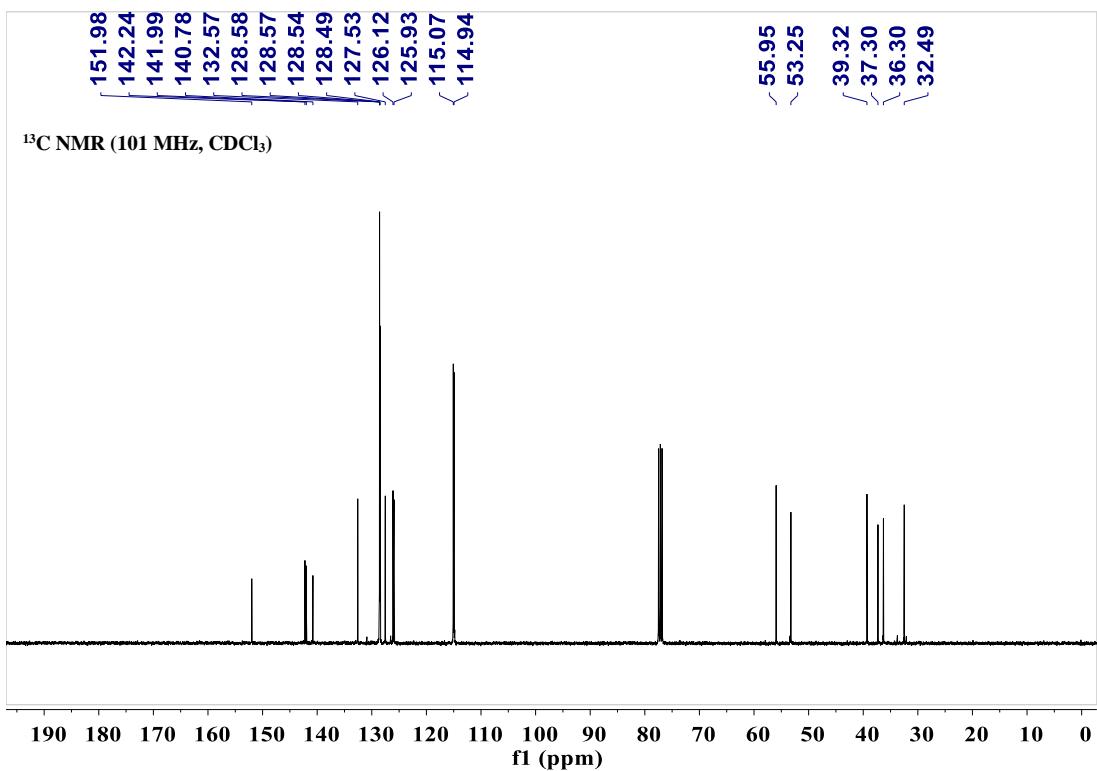


Figure S42

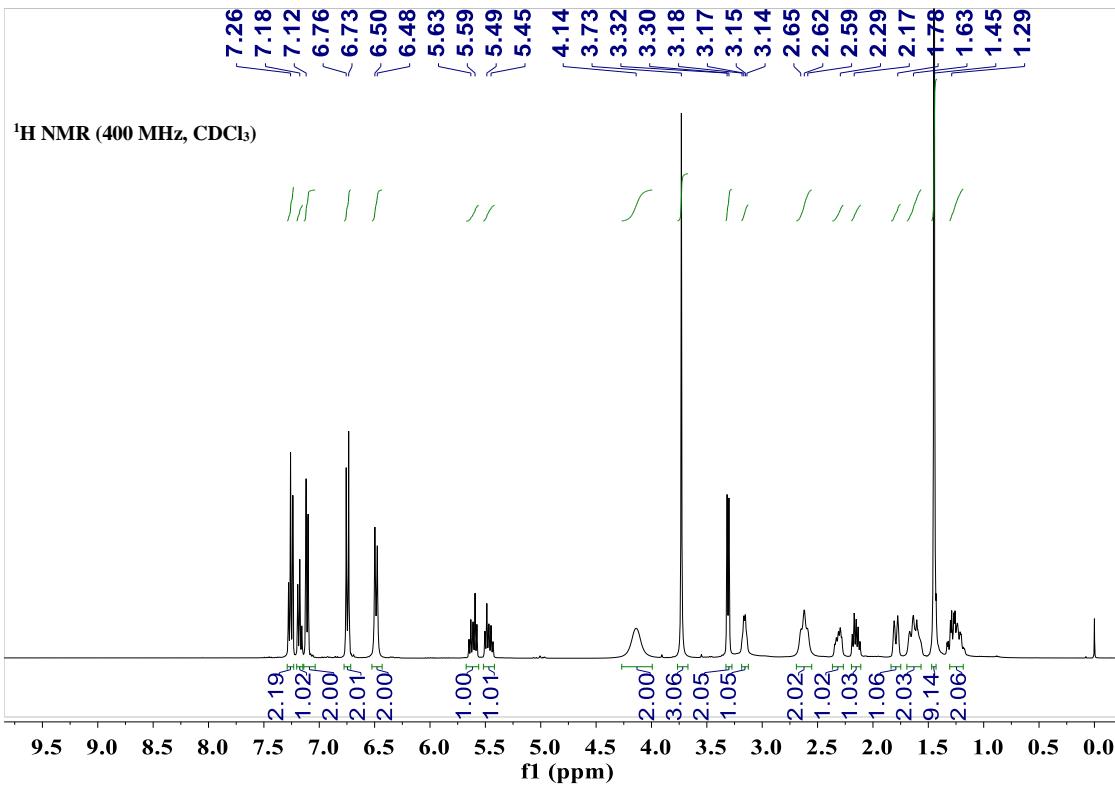
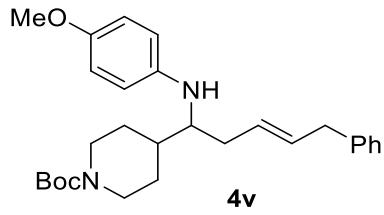


Figure S43

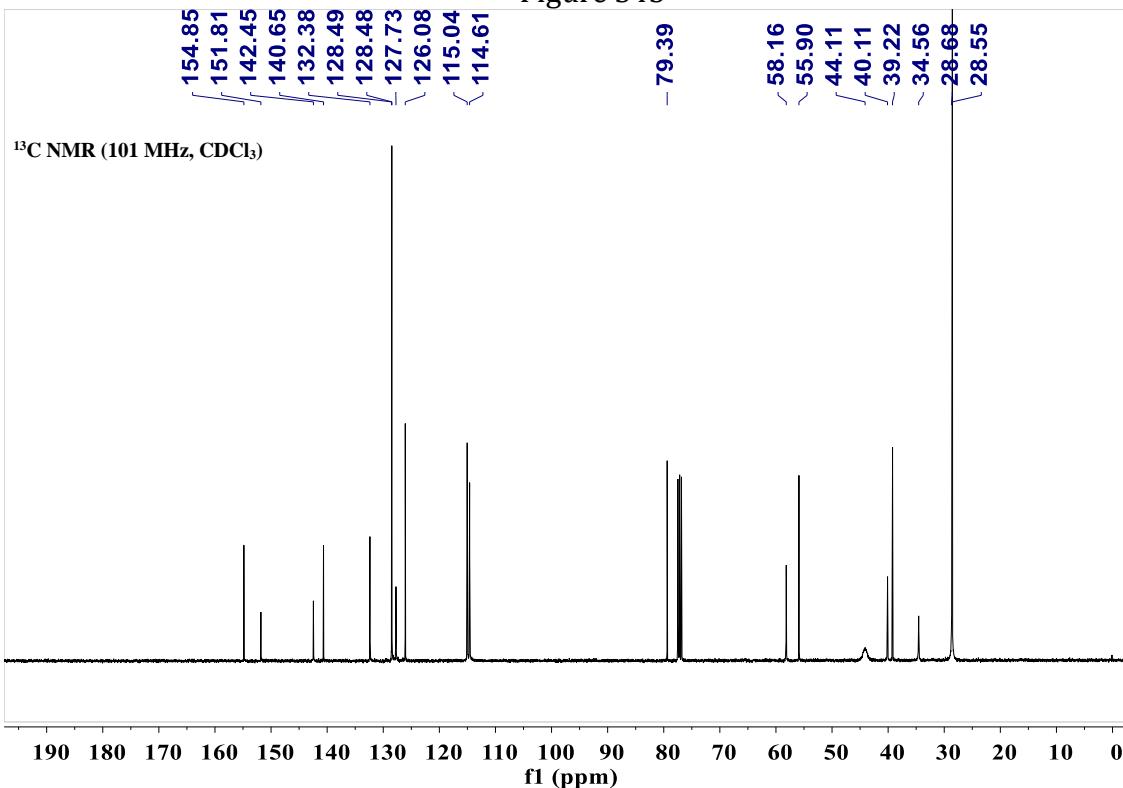


Figure S44

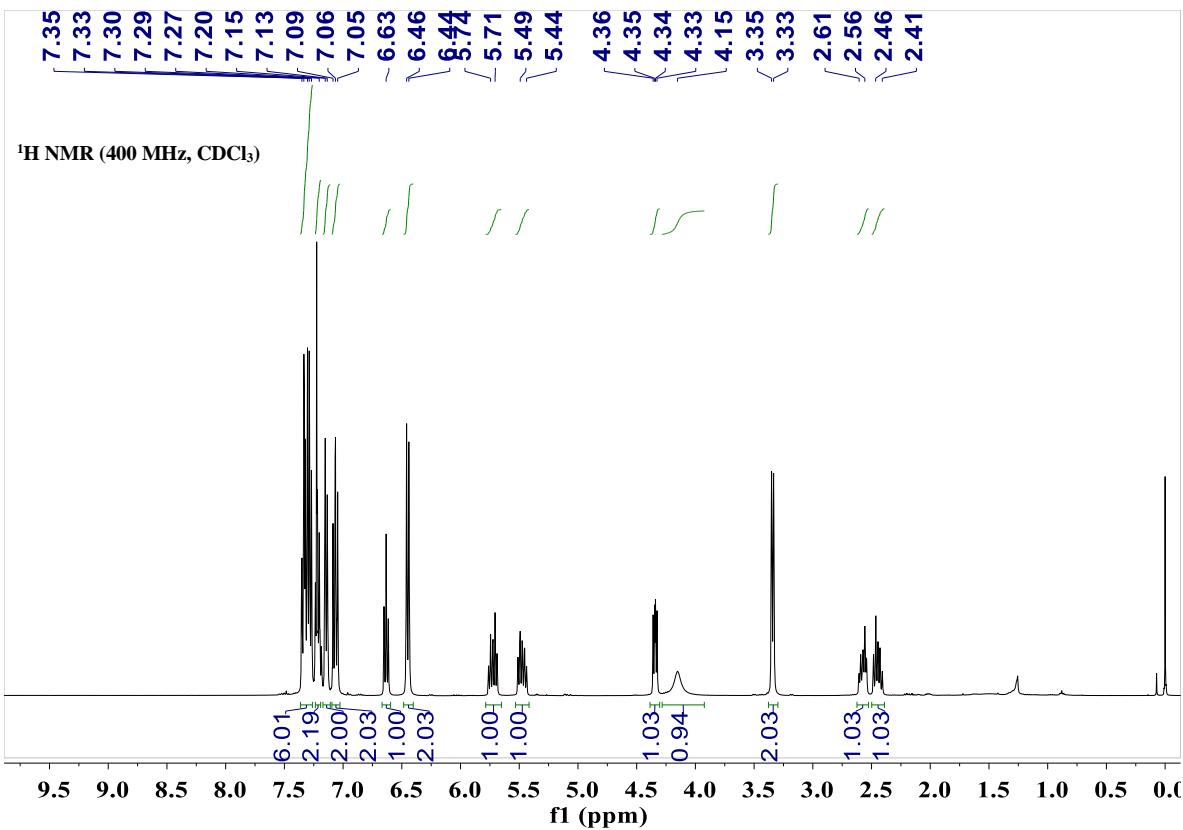
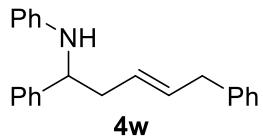


Figure S45

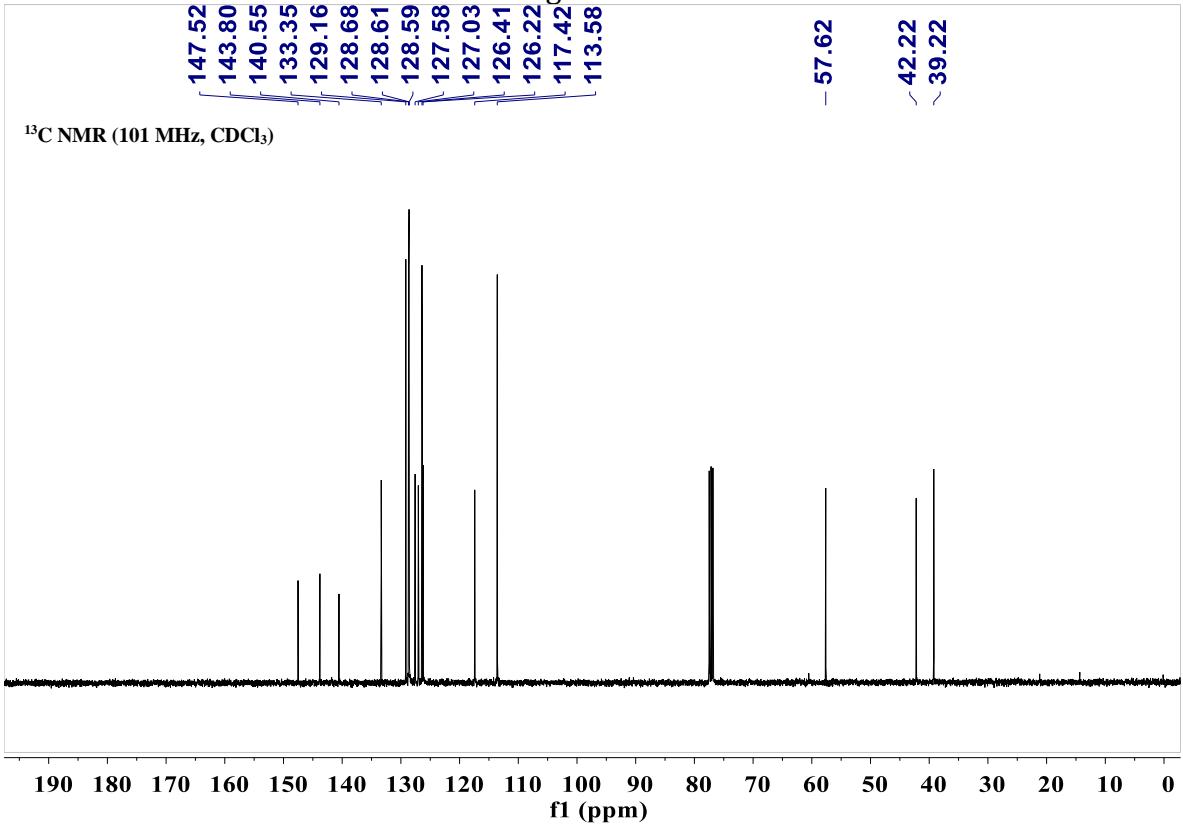


Figure S46

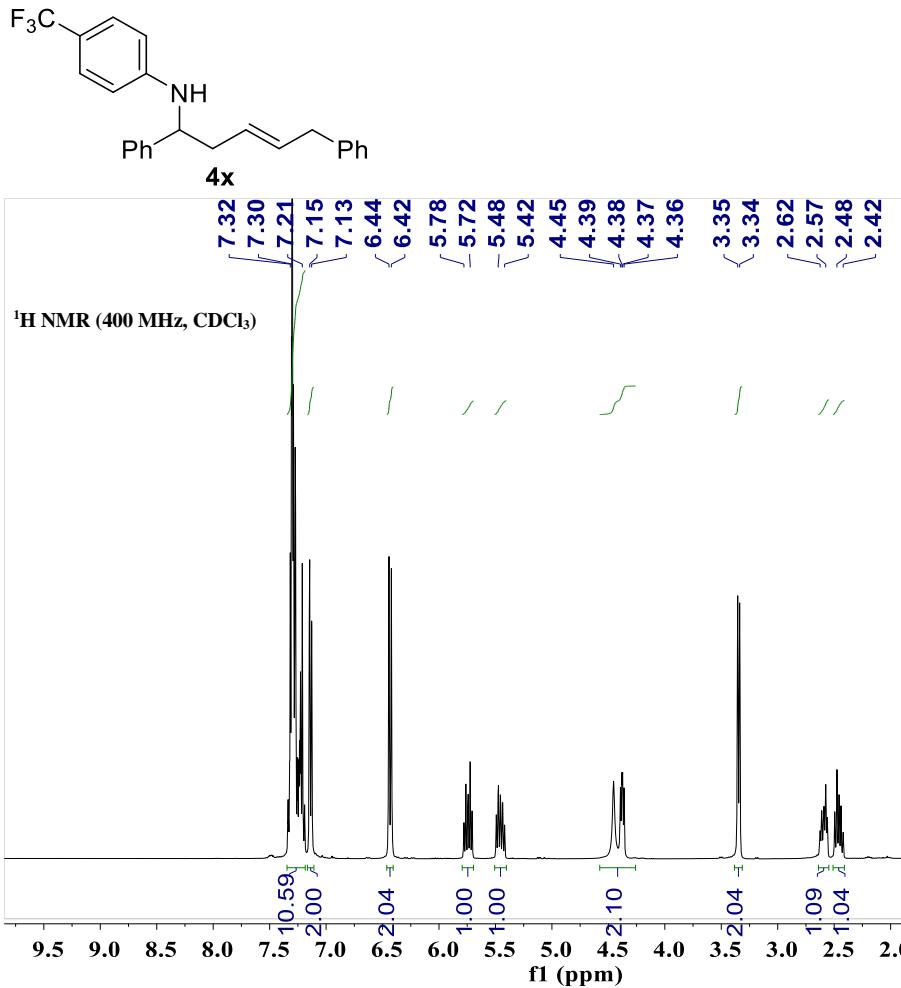


Figure S47

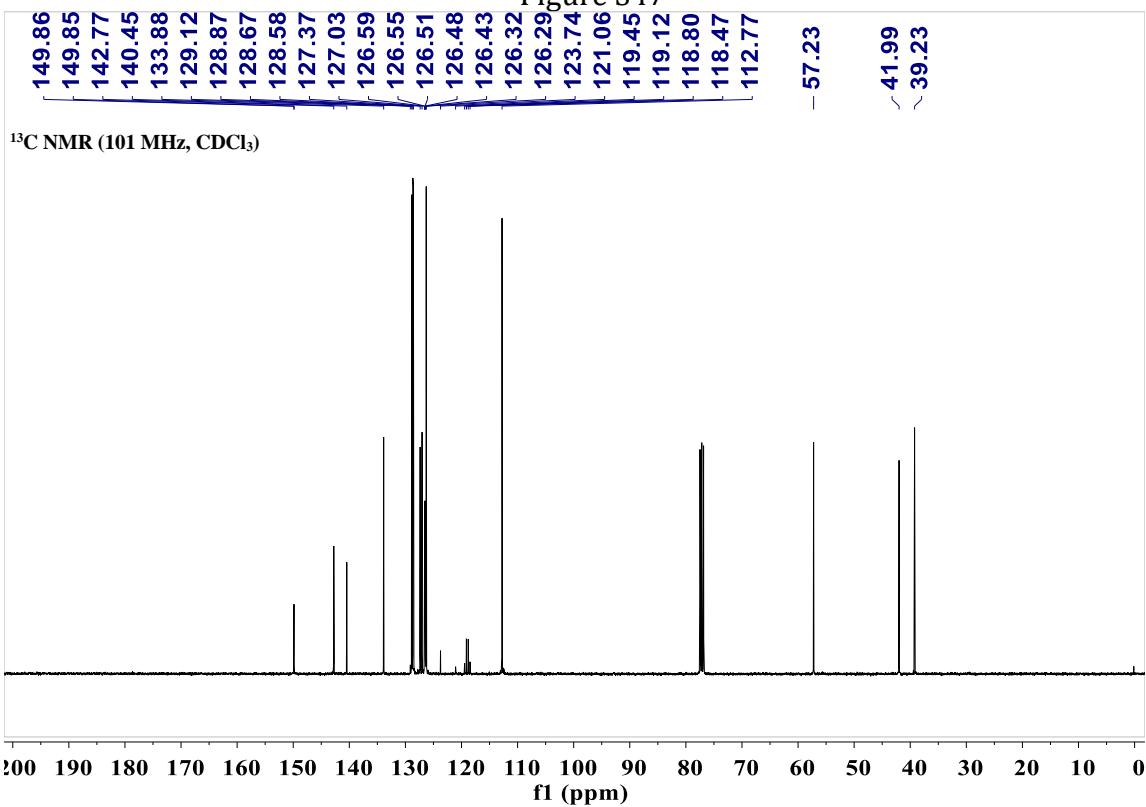


Figure S48

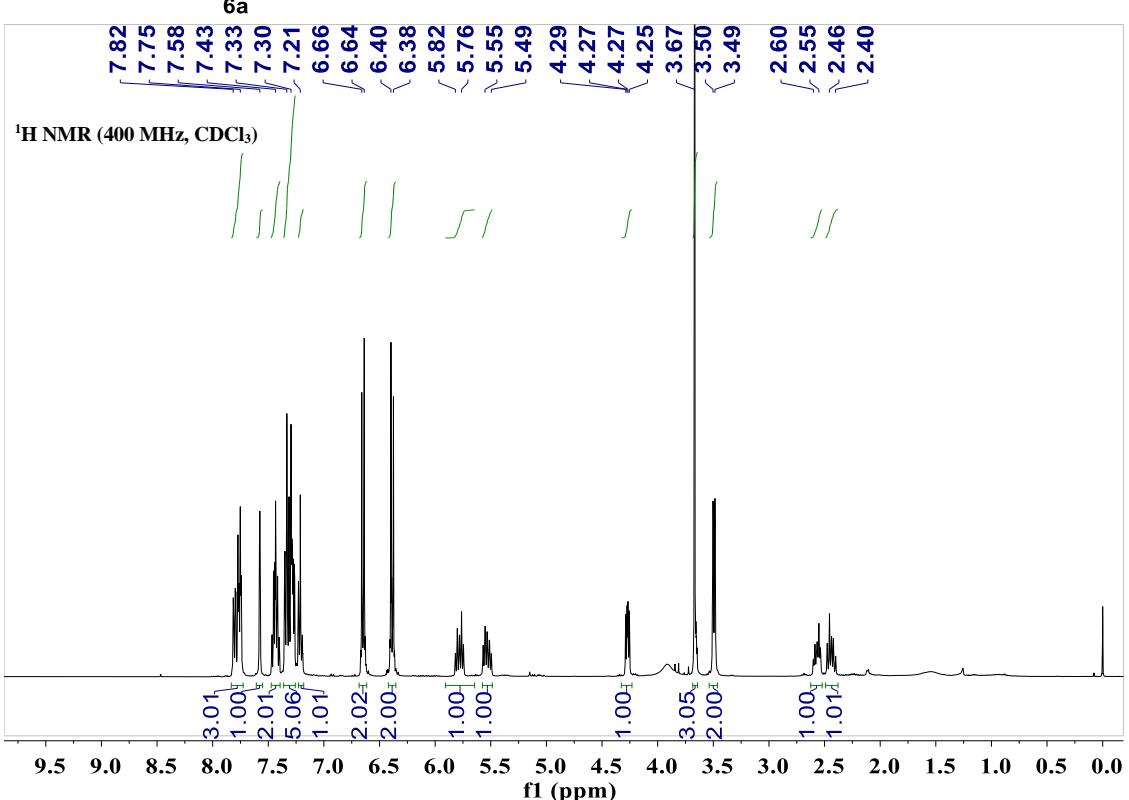
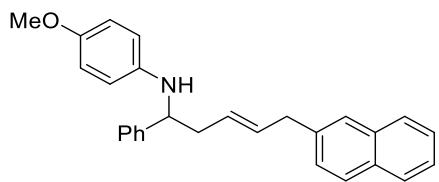


Figure S49

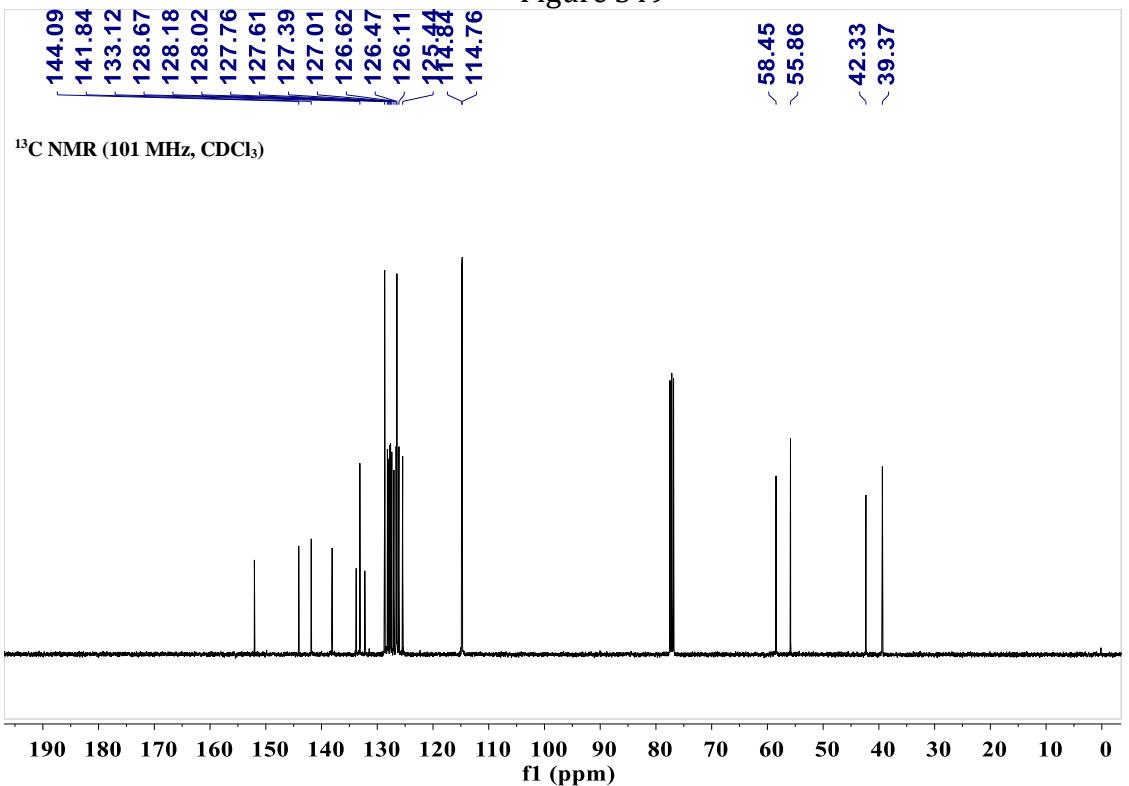


Figure S50

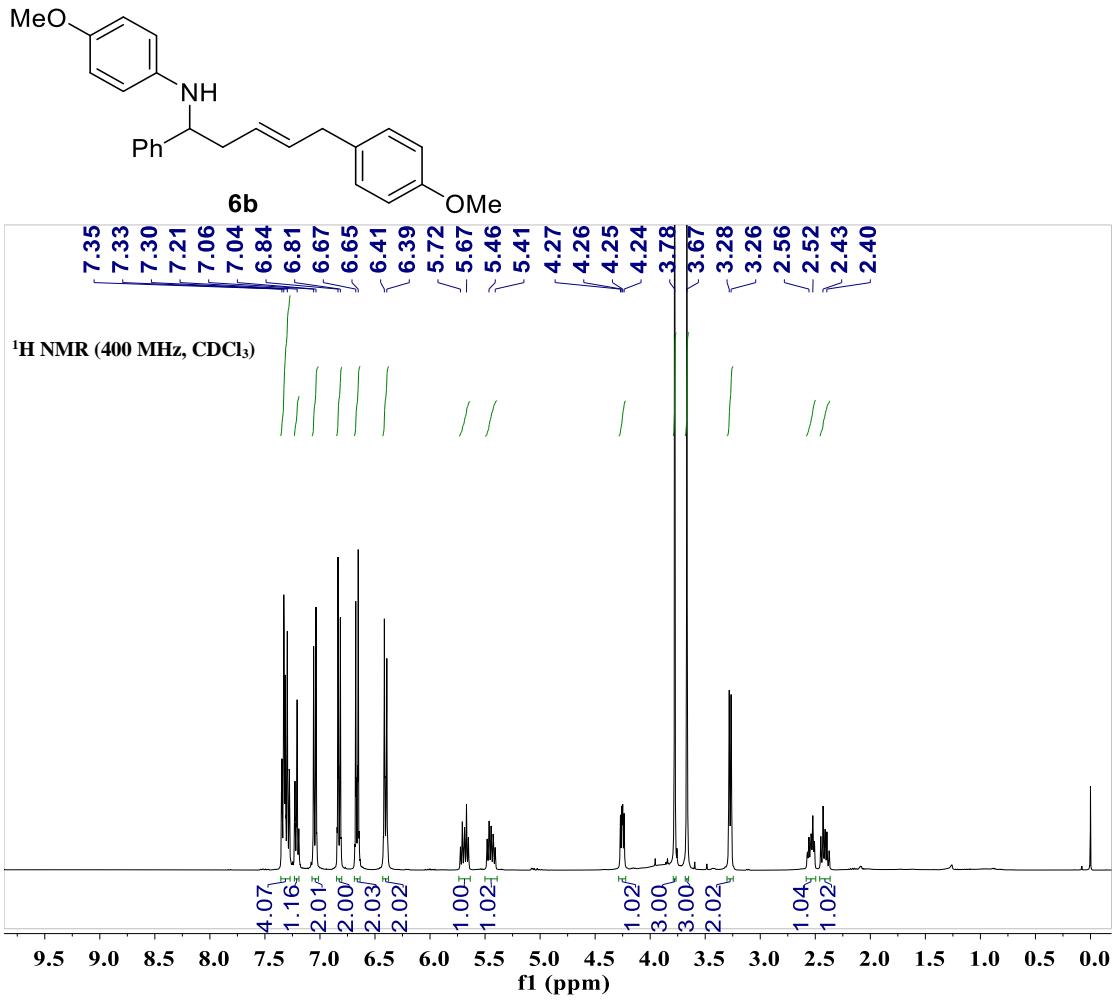


Figure S51

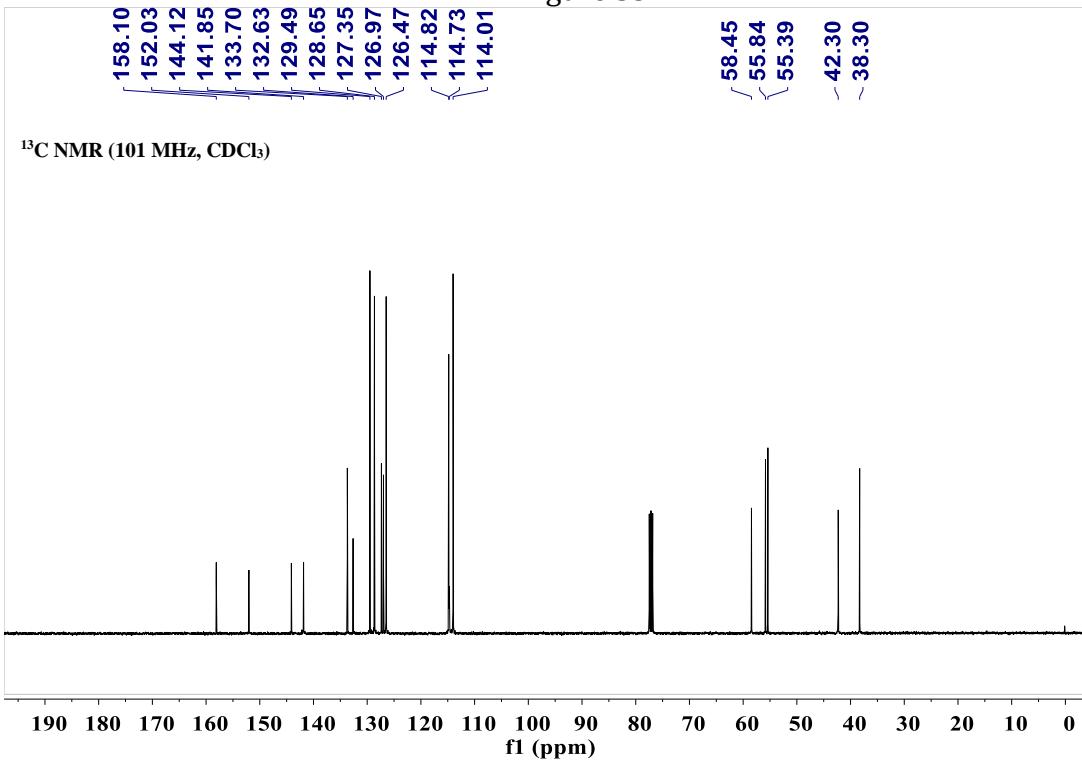


Figure S52

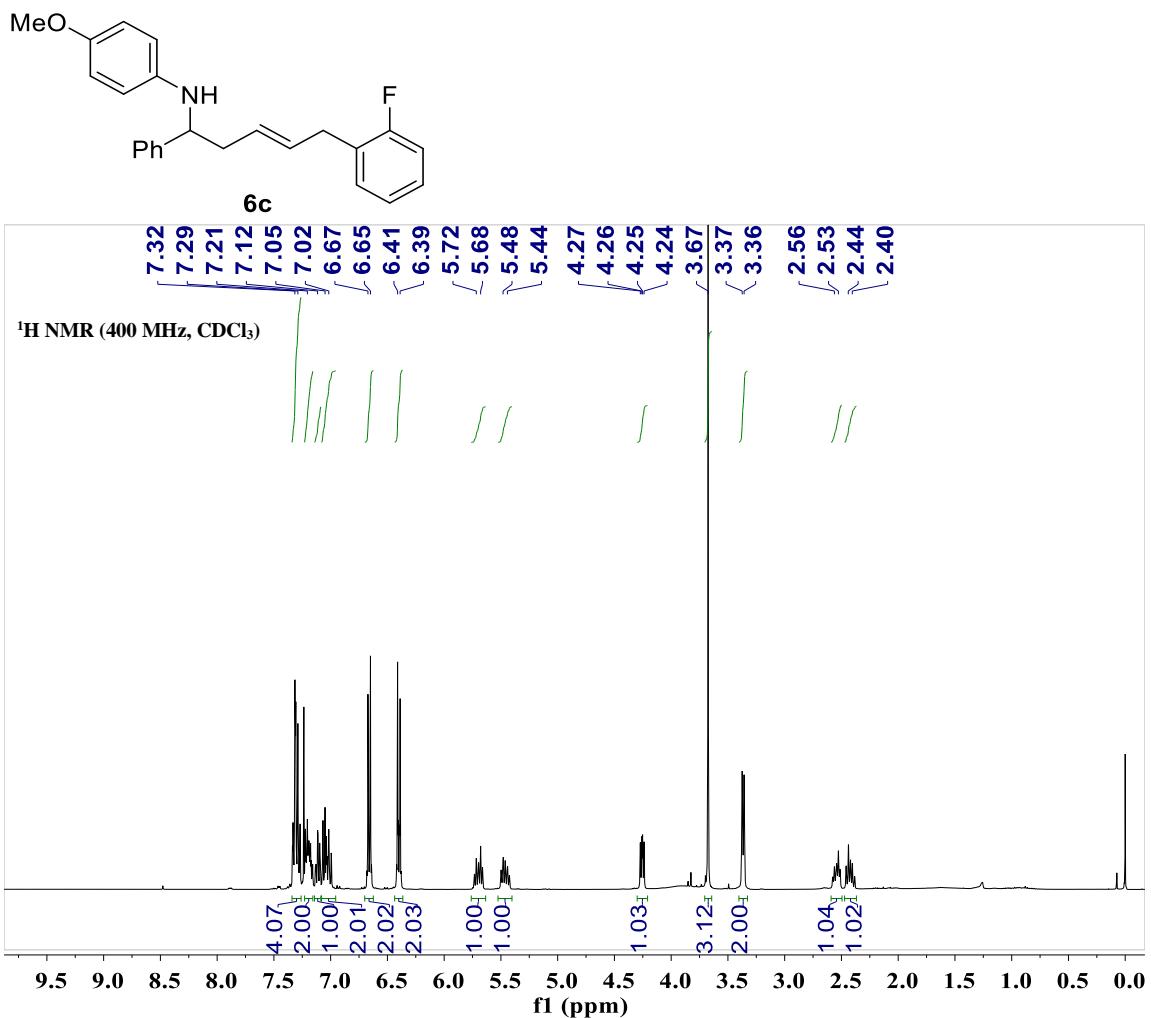


Figure S53

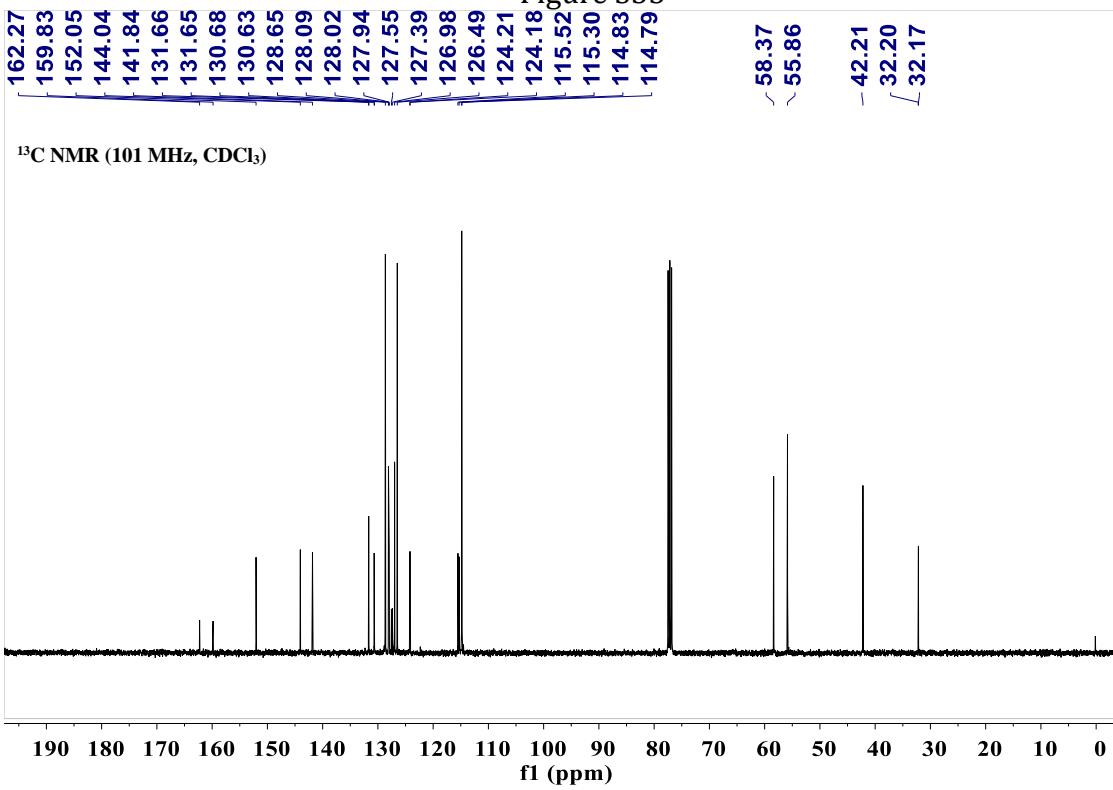


Figure S54

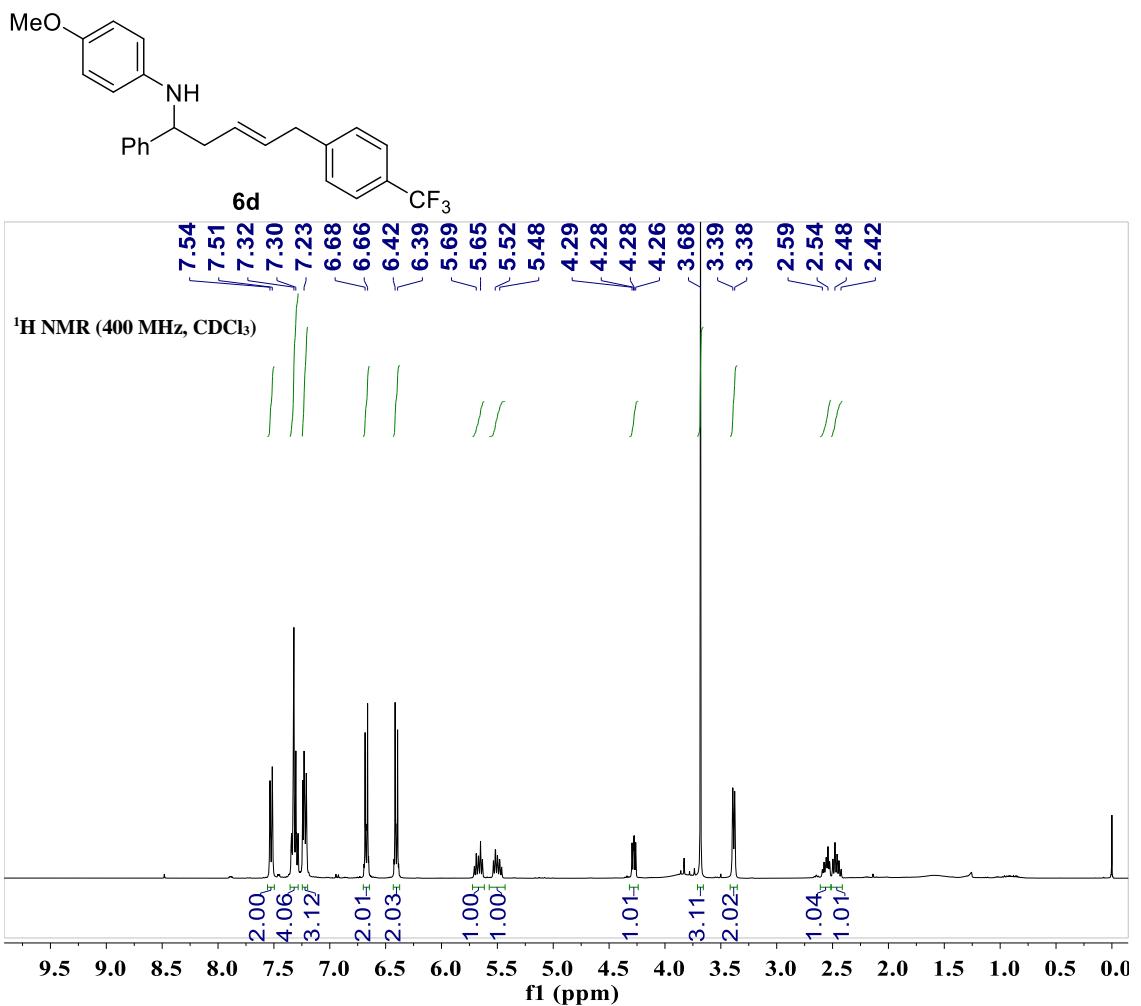


Figure S55

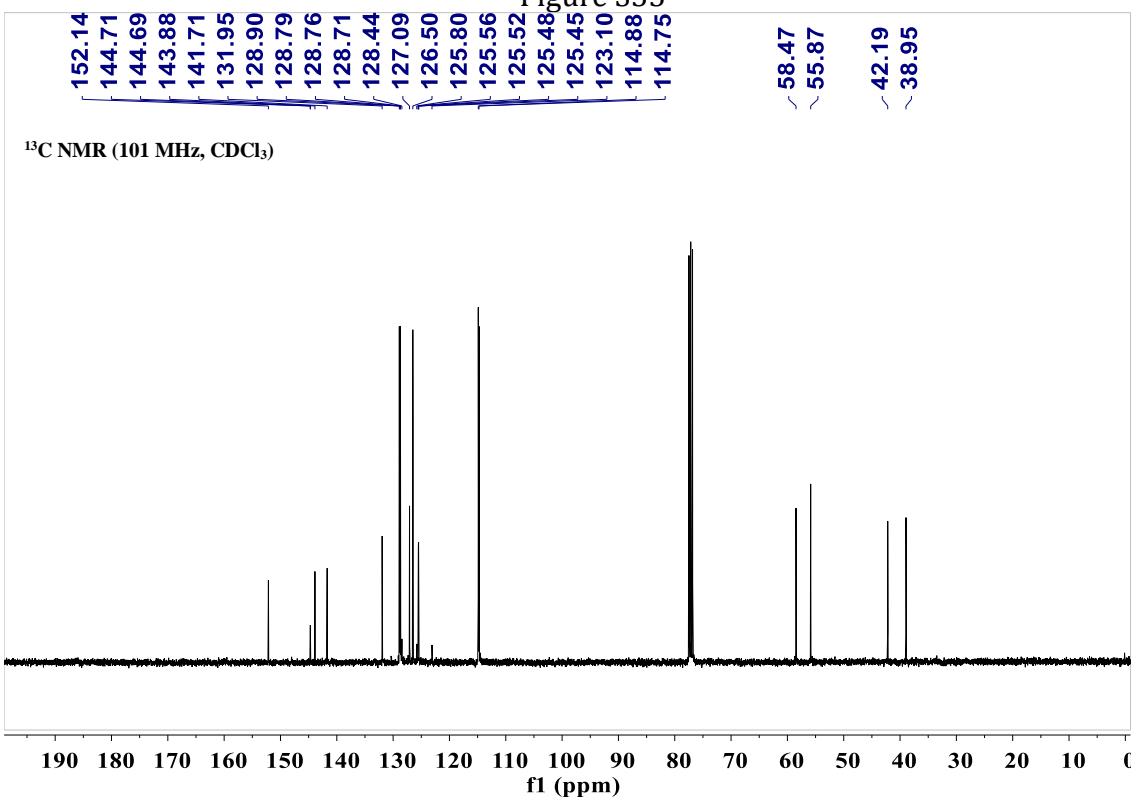


Figure S56

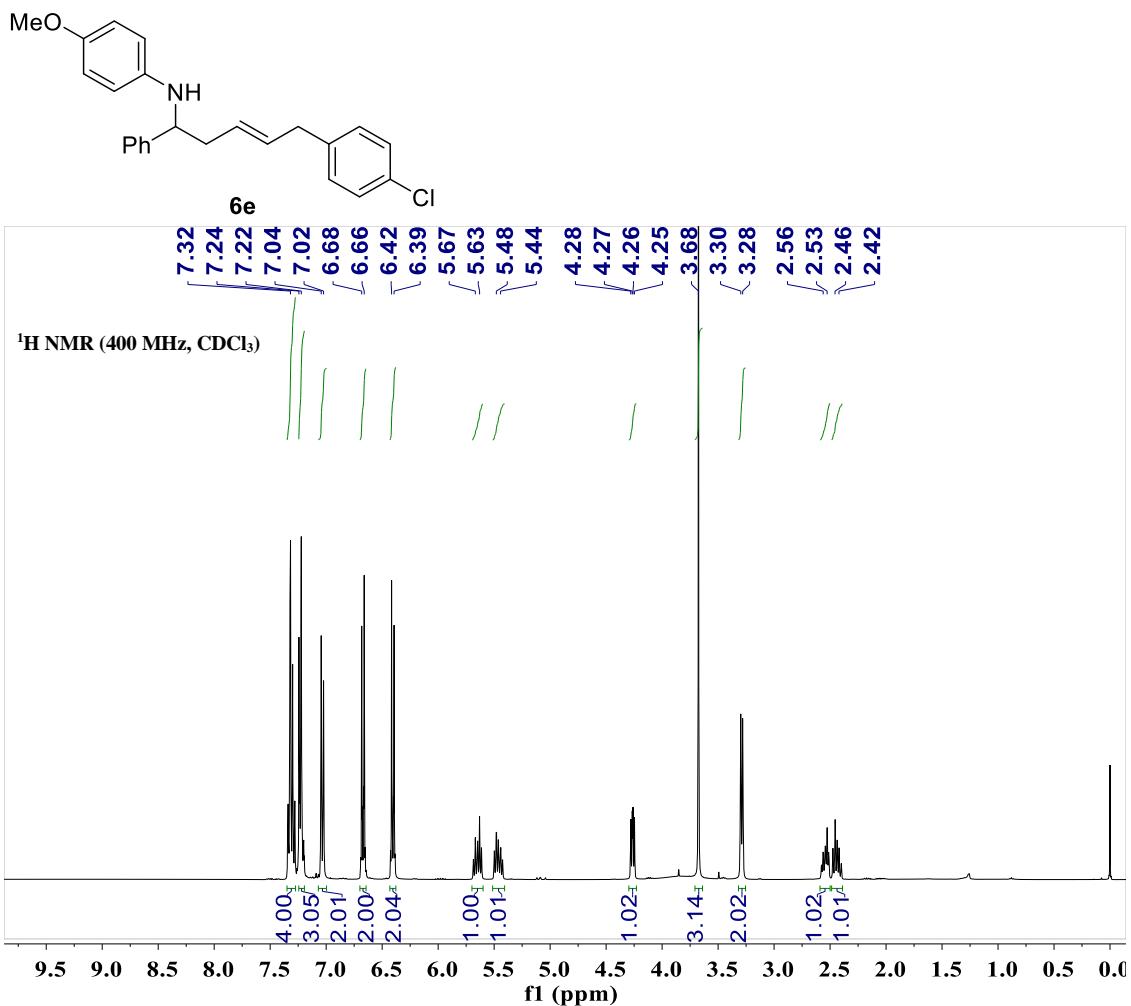


Figure S57

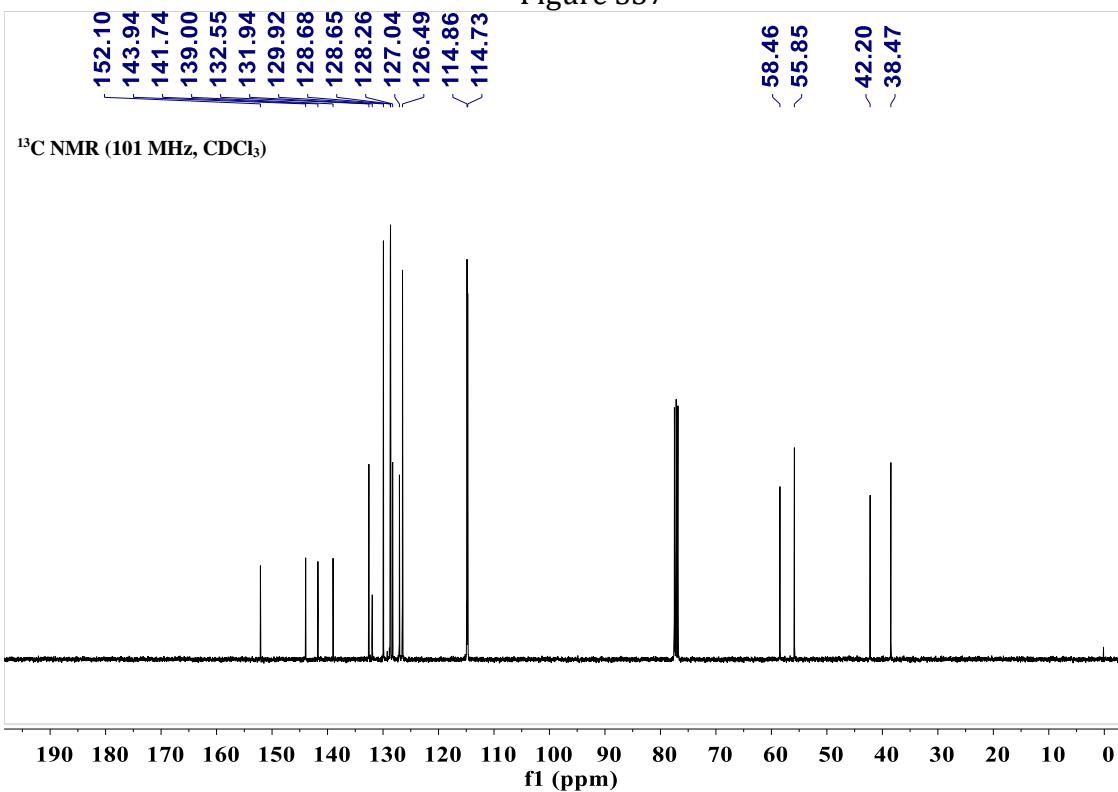


Figure S58

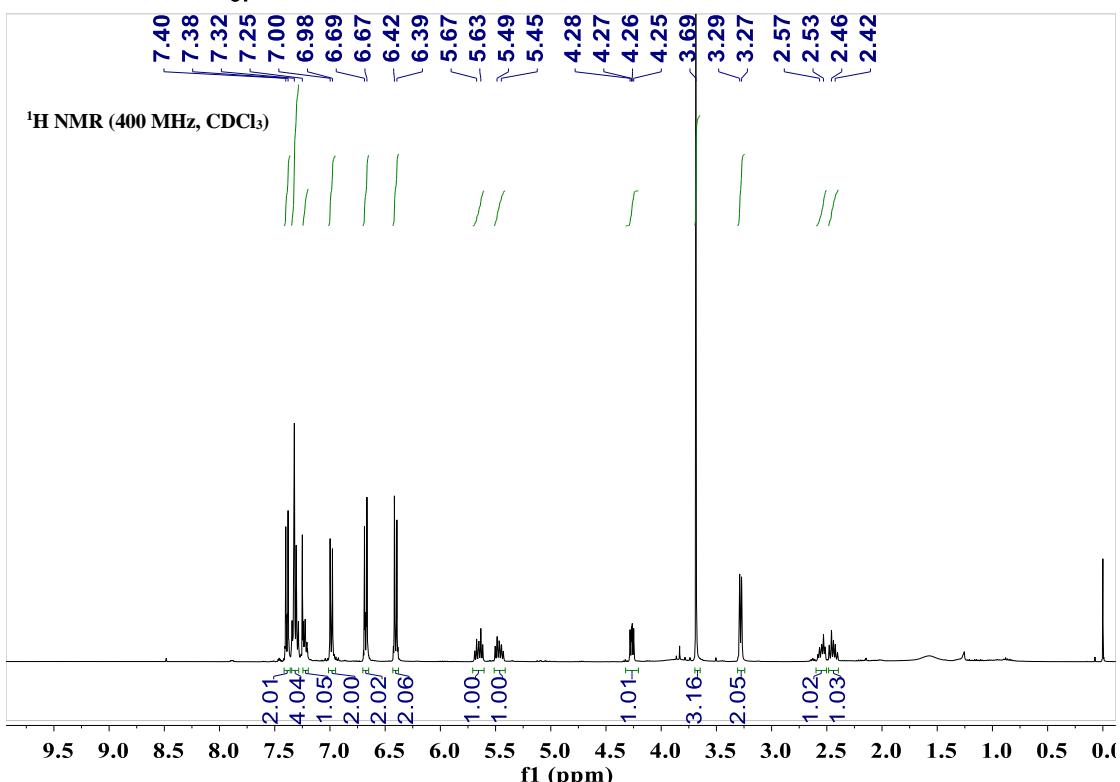
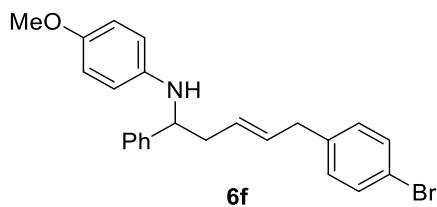


Figure S59

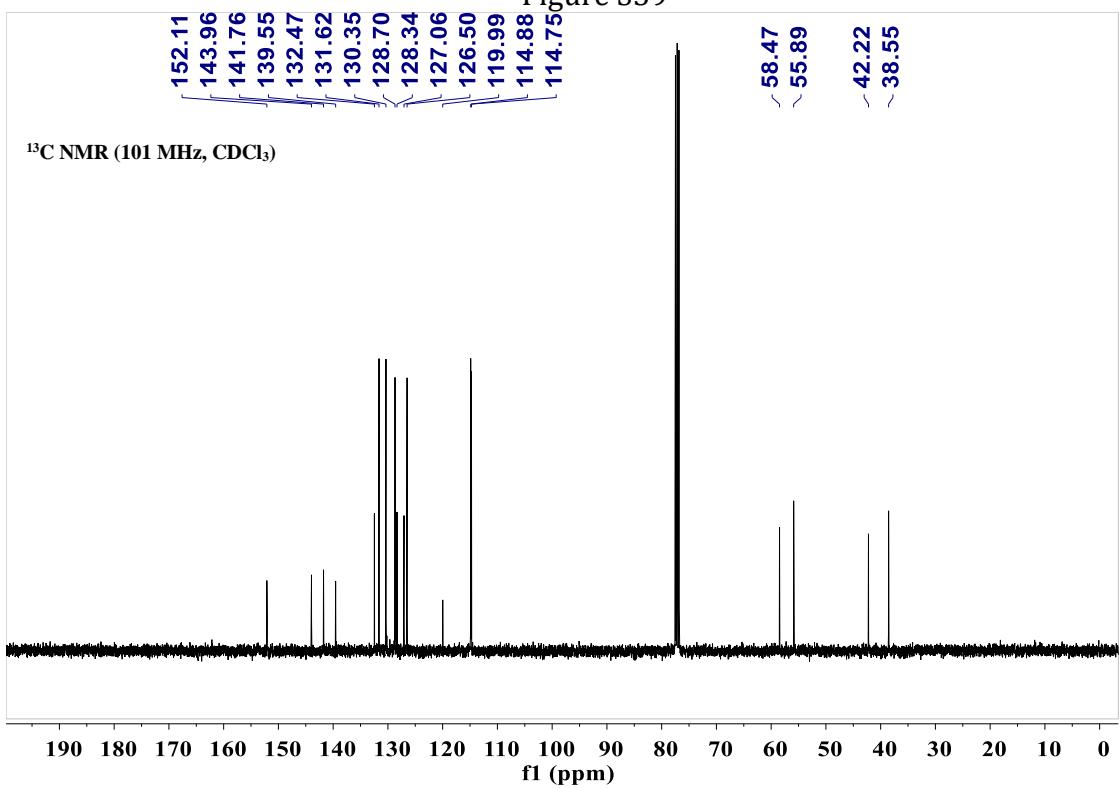


Figure S60

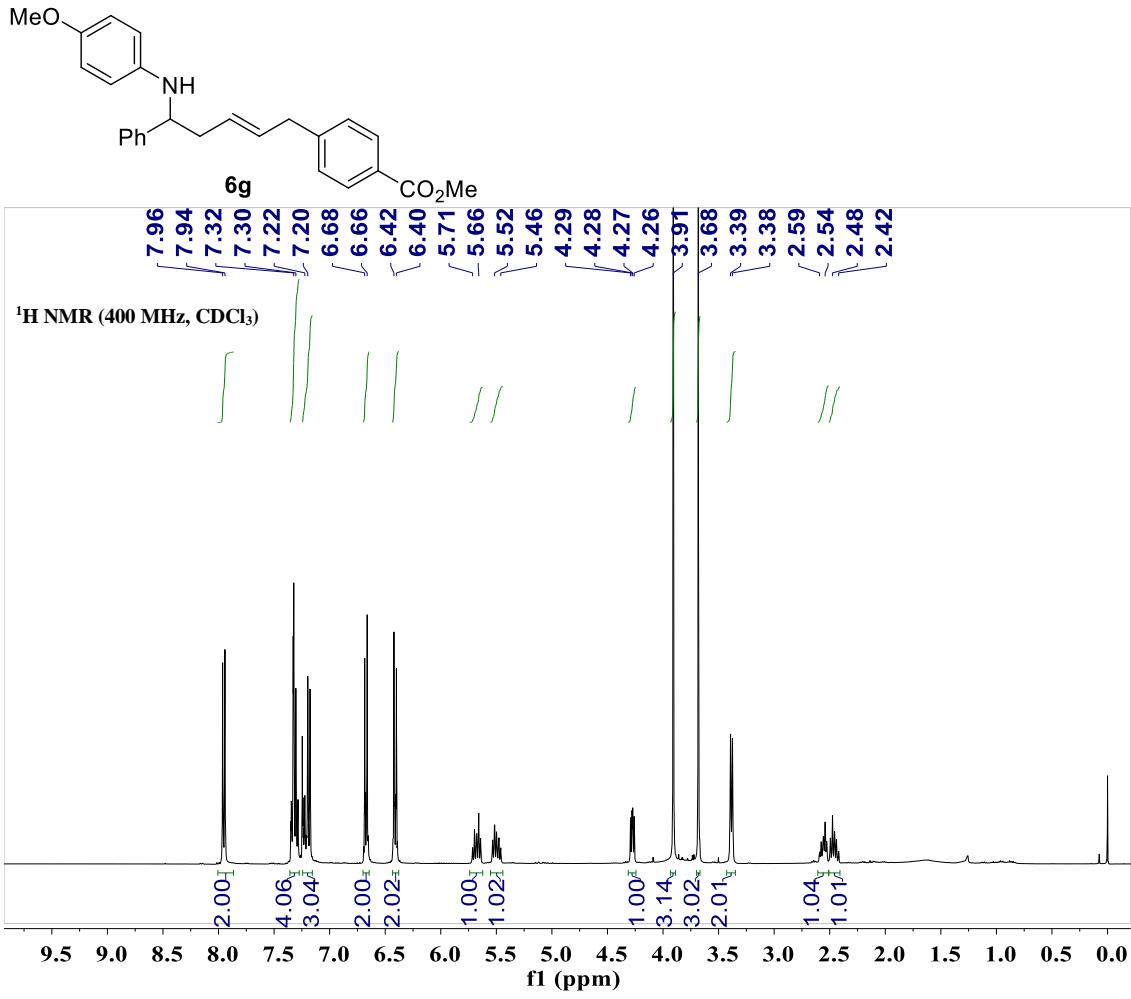


Figure S61

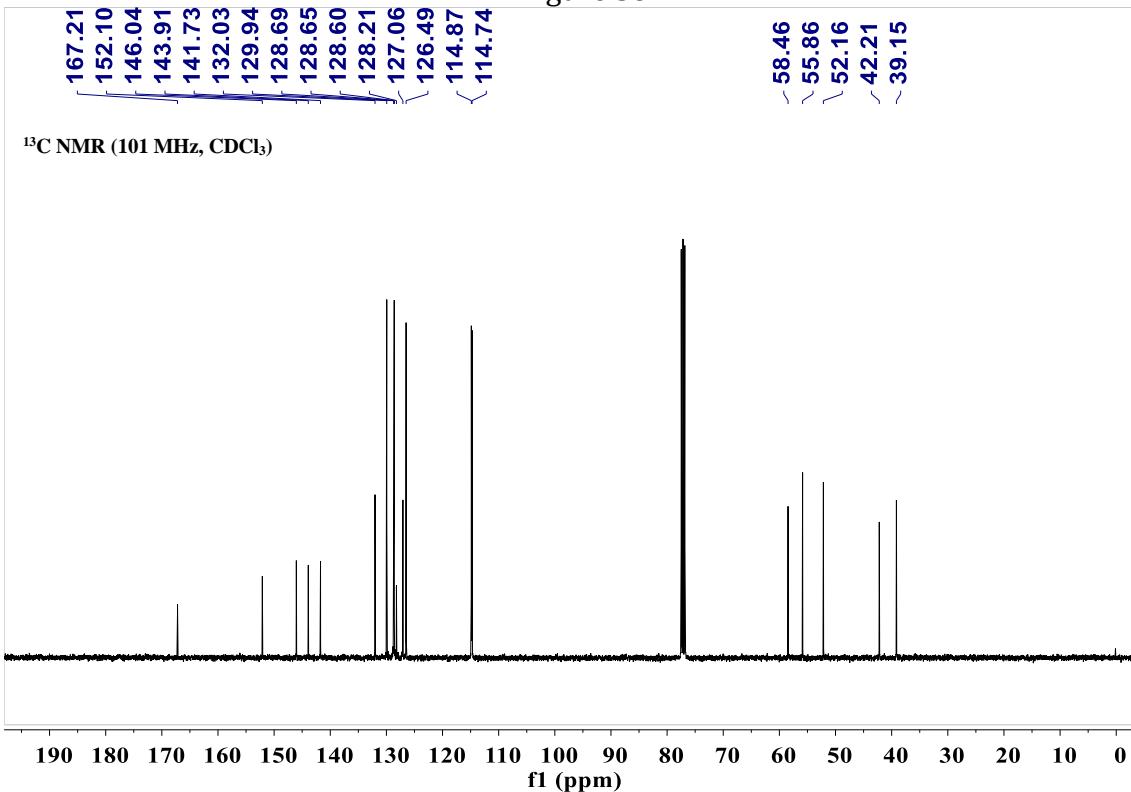


Figure S62

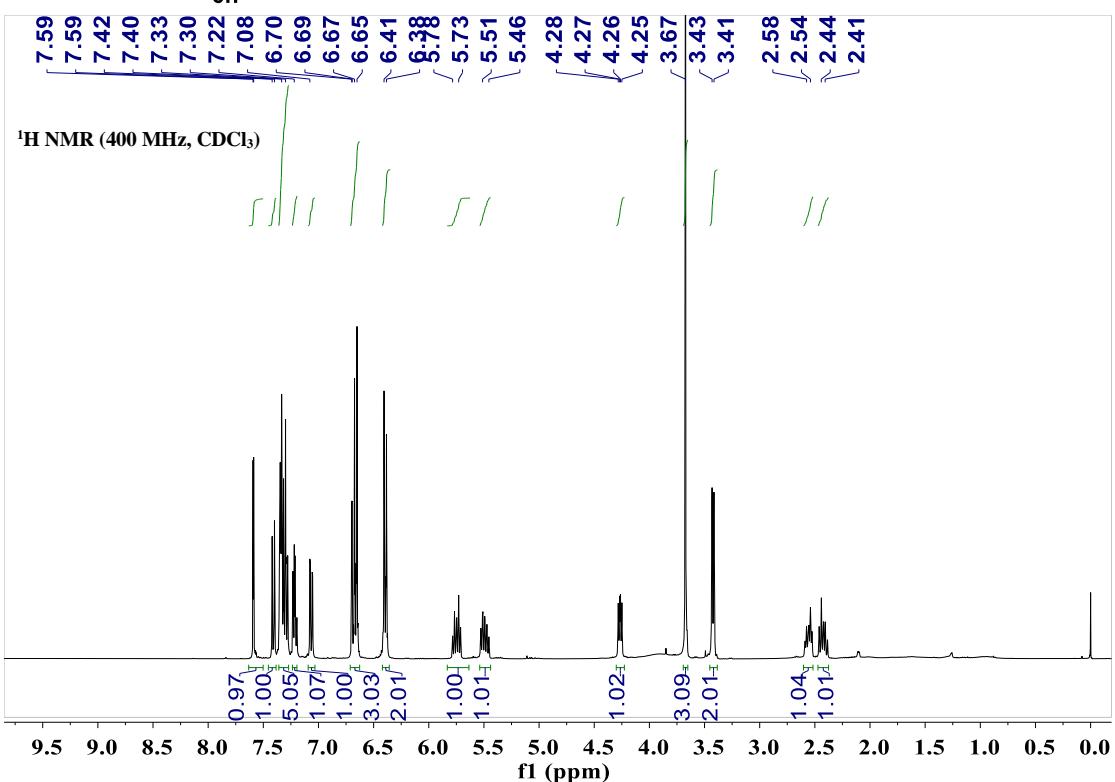
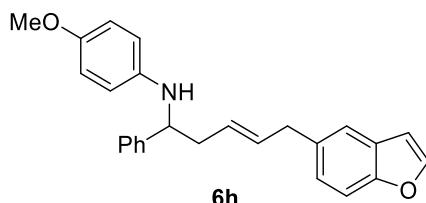


Figure S63

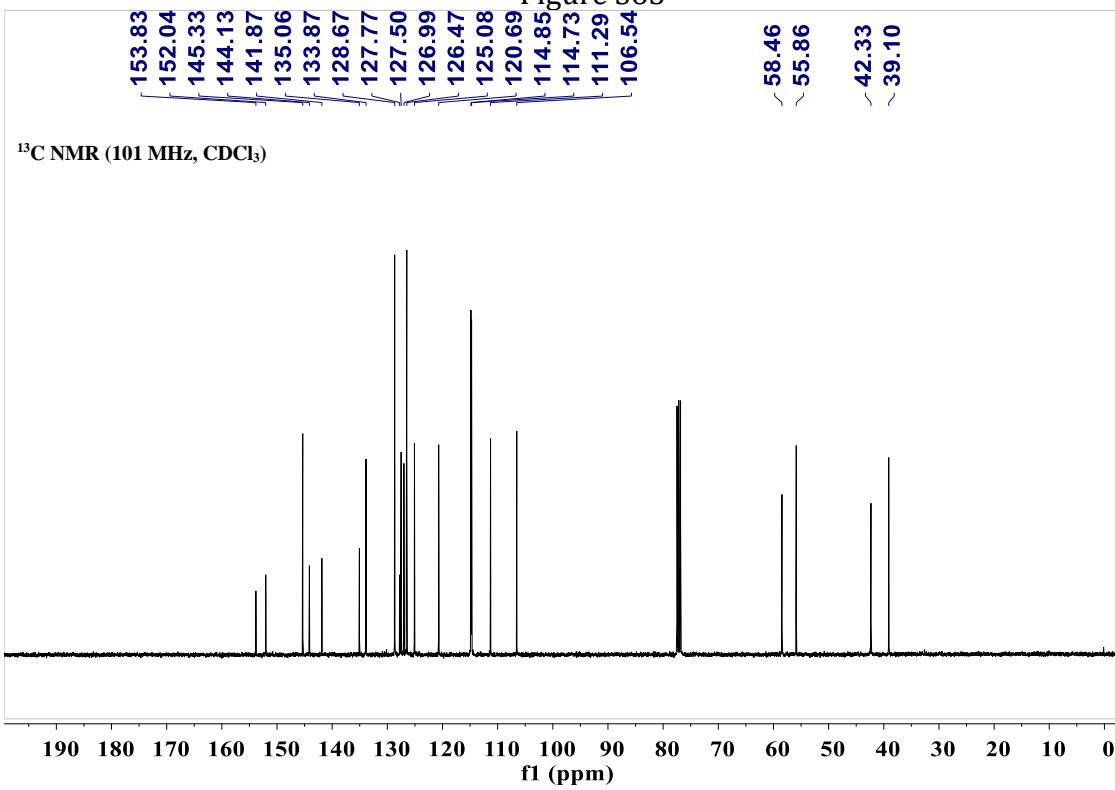
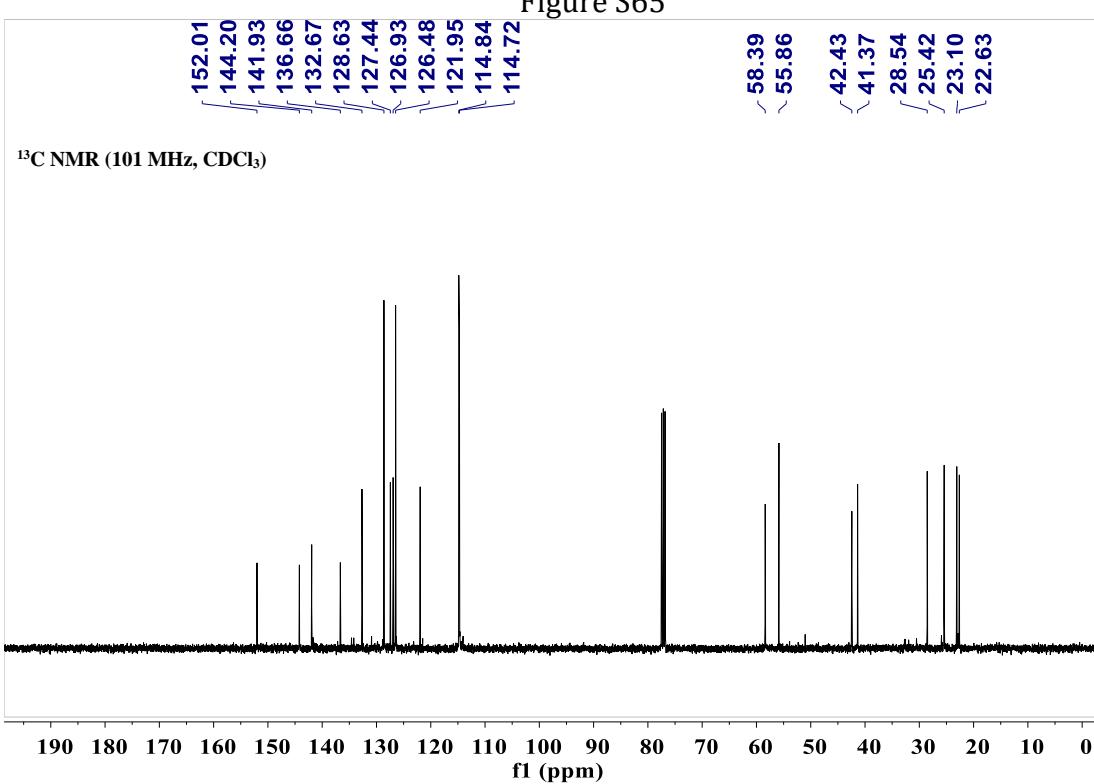
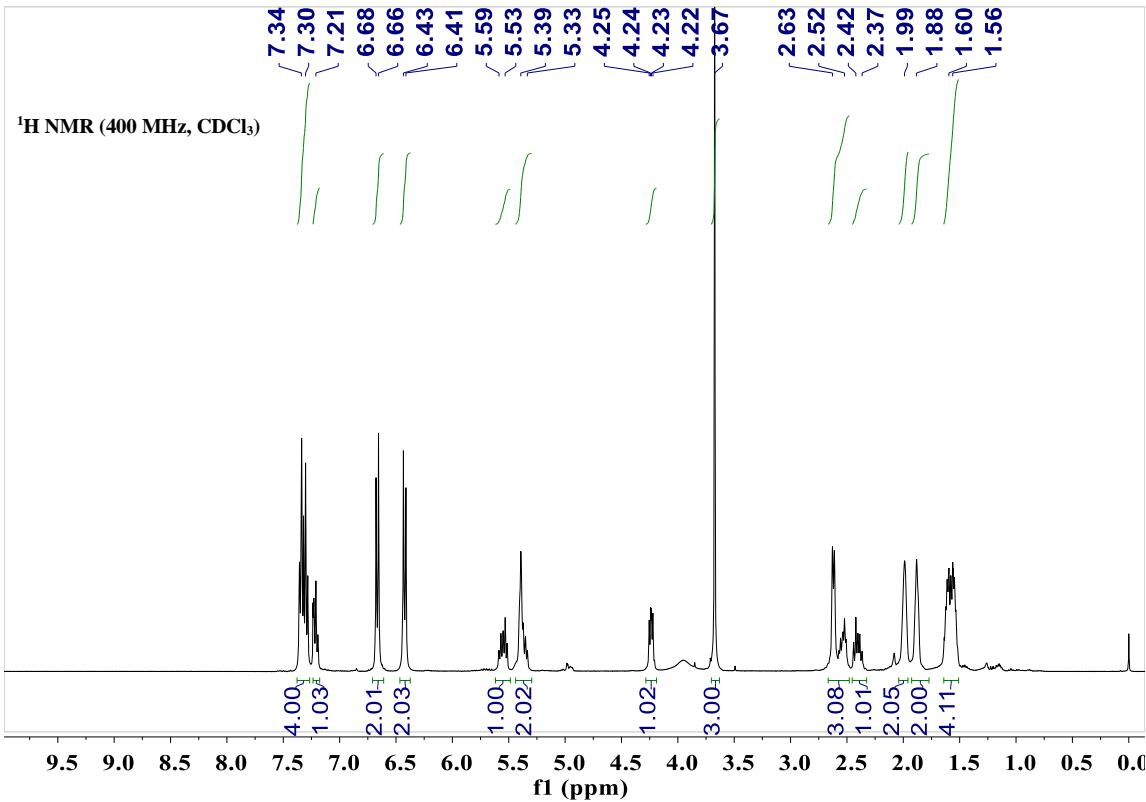
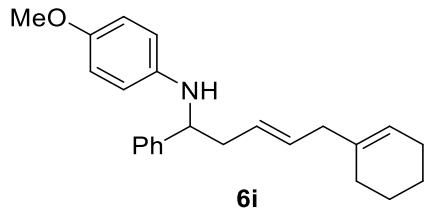


Figure S64



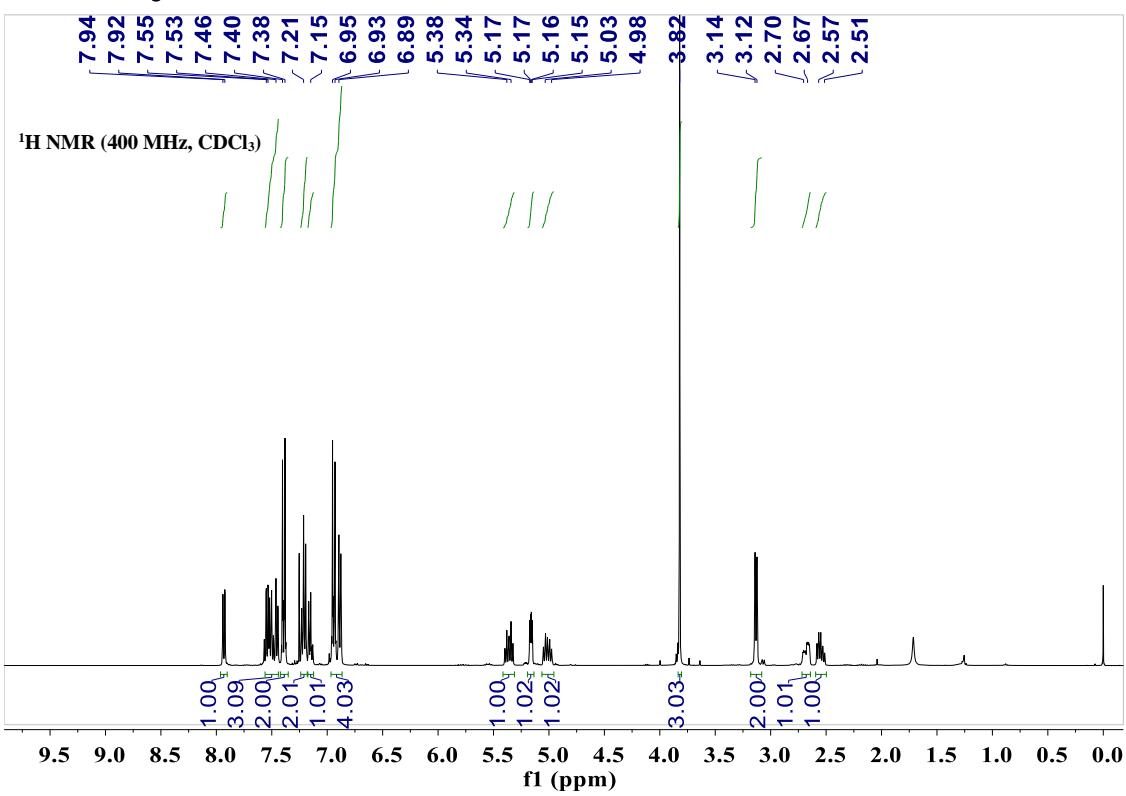
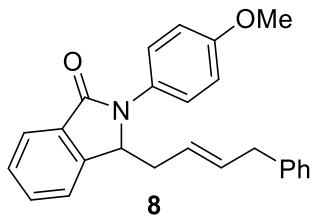


Figure S67

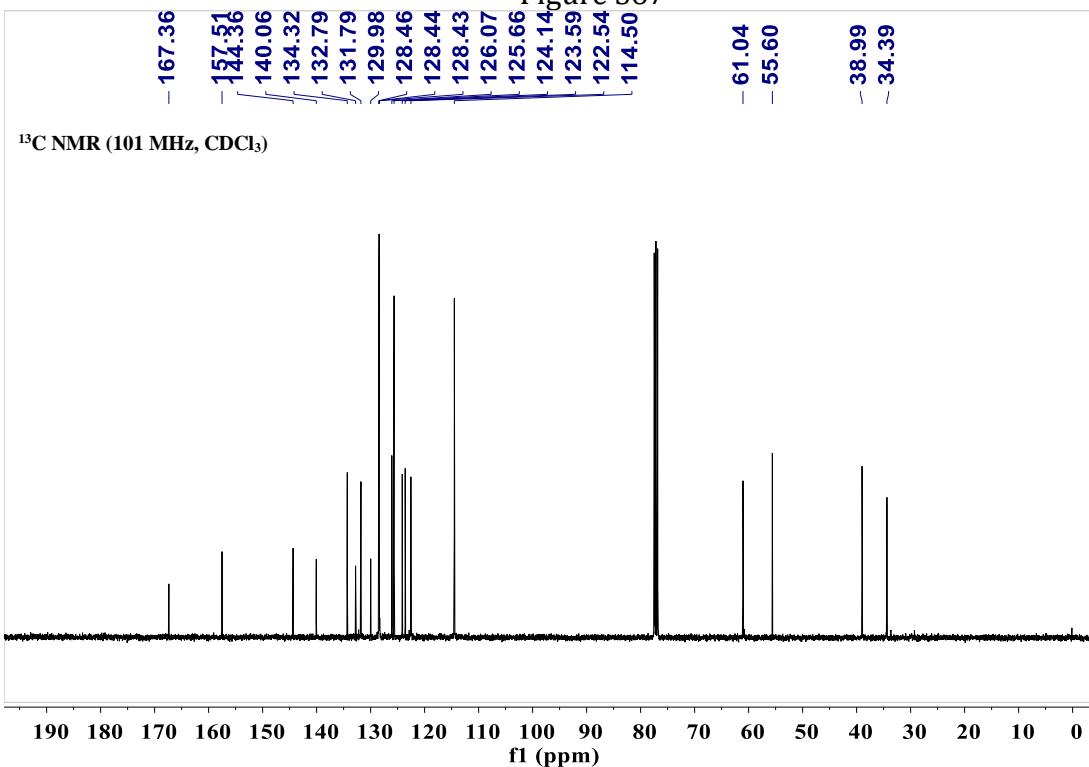


Figure S68

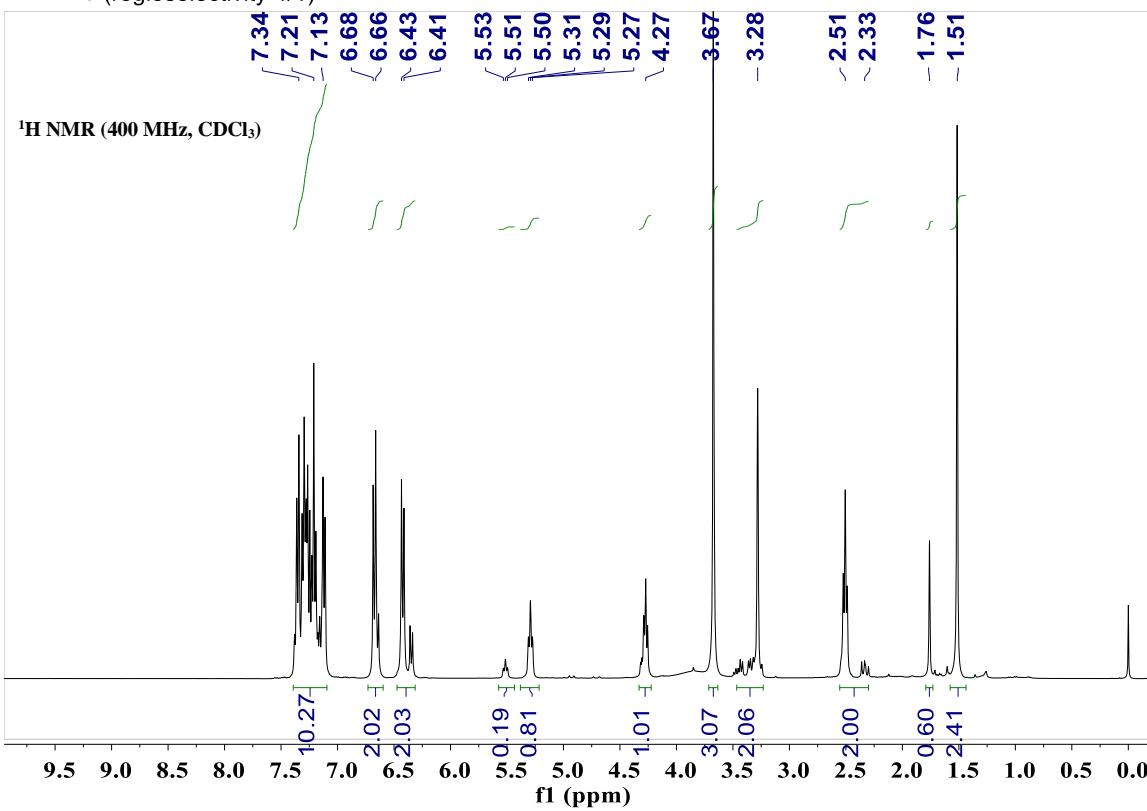
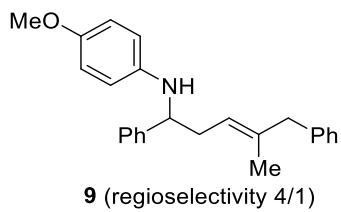


Figure S69

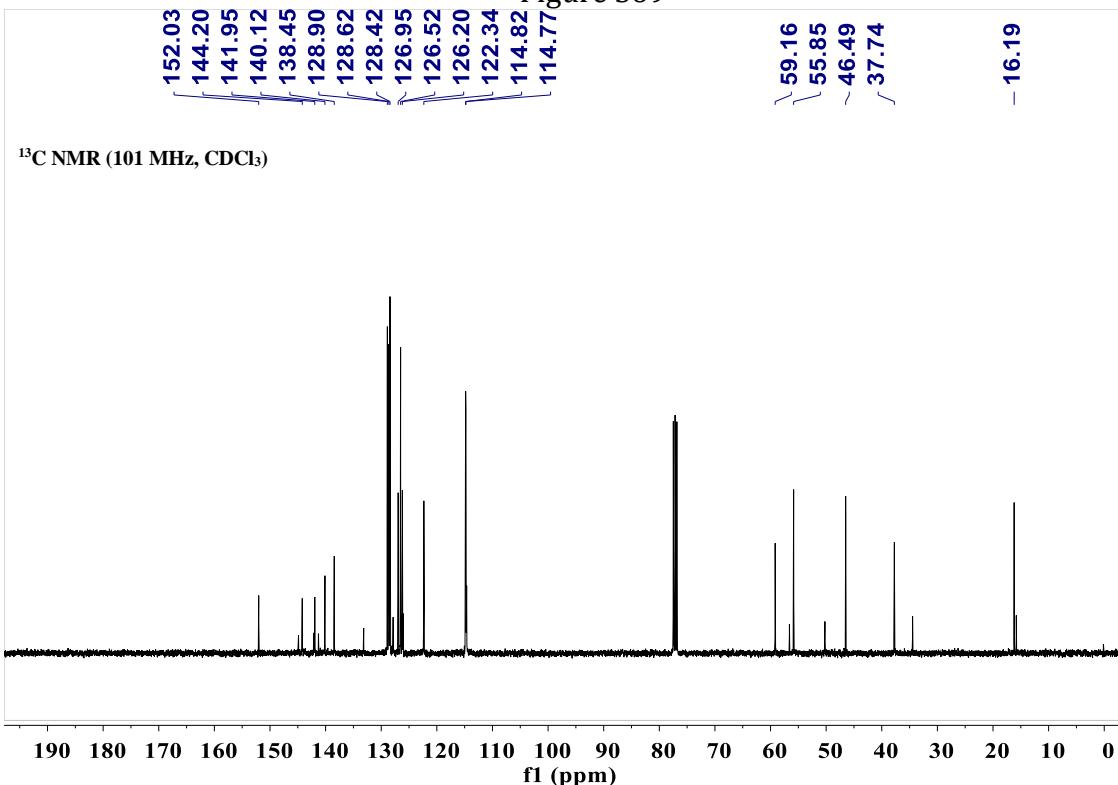


Figure S70