

SUPPLEMENTARY INFORMATION

Sulphated alumina tungstic acid (SATA): A highly efficient and novel heterogeneous mesostructured catalyst for the synthesis of Pyrazole Carbonitrile Derivatives and evaluation of green metrics

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(I) General Information:

Melting points of all the synthesized compounds taken in a Riechert Thermover instrument and are uncorrected. The IR spectra were recorded on Perkin Elmer RXI spectrometer using KBr pellets, ^1H NMR, ^{13}C NMR spectra recorded on a Bruker DRX-400 spectrometer using tetramethylsilane (TMS) as an internal standard and $\text{DMSO-d}_6/\text{CDCl}_3$ as solvent. Mass spectra were recorded on Micromass Quattro II (ESI) spectrometer. Elemental analyses (C, H and N) were conducted using the Elemental vario EL III elemental analyser and their results were found to be in agreement with the calculated values. TGA data was obtained with DSC-60 Shimadzu instrument and the analysis was performed in the temperature range of 0–600 °C at a constant heating rate of 20°C/min in the nitrogen atmosphere. X-ray diffractograms (XRD) of the catalyst were recorded in the 2θ range of 20–80° with scan rate of 4°/min on a Rigaku Miniflex X-ray diffractometer with Ni-filtered Cu K $_{\alpha}$ radiation at a wavelength of 1.54060 Å. The SEM and EDX characterization of the catalyst were performed on QUANTA 200 FEG from FEI Netherlands. TEM analysis was performed on JEM-2100 F Model (ACC. Voltage: 200 kV) electron microscope. BET surface area of the sample was measured from the nitrogen adsorption/desorption isotherms obtained by using a Quantachrome Autosorb 1C BET analyzer at 77 K temperature. Prior to gas adsorption, the sample was degassed for 3 h at 423 K. All reagents were purchased from Merck, Aldrich and were used without further purification. The purity of compounds was checked by thin layer chromatography (TLC) on glass plates coated with silica gel G254 (E. Merck) using chloroform–methanol (3:1) mixture as mobile phase and visualized by iodine vapours and alcoholic ferric chloride.

(II) Spectral data of novel compounds:

1. 5-(4-chlorophenyl)-3-oxo-1-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile:

White solid; Yield: 94%, m.p.170-172°C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm^{-1}):, 3433, 2959, 2223, 1726, ^1H NMR (400 MHz, CDCl_3): δ 3.97 (s, 1H, NH), 6.90 (s, 1H, ArH), 7.26 (s, 1H, ArH), 7.47 (d, J = 4Hz, 2H, ArH), 7.92 (d, J = 4Hz, 2H, ArH), 8.22 (d, J = 8Hz, 2H, ArH) ppm. ^{13}C NMR (400MHz, CDCl_3): 53.38, 103.18, 115.23, 120.35, 122.15, 130.15, 132.33, 139.63, 144.36, 151.28, 153.85, 162.97, 165.52, 174.25, 182.61 ppm. Anal. Found ($\text{C}_{16}\text{H}_{10}\text{ClN}_3\text{O}$); Calcd: C, 64.98; H, 3.41; N, 14.21. Found: C, 64.96; H, 3.43; N, 14.23 ESI-MS m/z ($\text{C}_{16}\text{H}_{10}\text{ClN}_3\text{O} + \text{H}^+$); Calcd: 296.0585; Found: 296.0671.

2. 5-(3-nitrophenyl)-3-oxo-1-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile

Yellow solid; Yield: 94%, m.p.172-174°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}):, 3309, 2955, 2226, 1729, ^1H NMR (400 MHz, CDCl_3): δ 4.38 (s, 1H, NH), 7.21(d, J = 4 Hz, 1H, ArH), 7.65-7.75 (m, 3H, ArH), 8.28-8.42 (m, 3H, ArH), 8.66 (s, 1H, ArH) ppm. ^{13}C NMR (400MHz, CDCl_3): 66.34, 113.04, 119.86, 124.26, 125.42, 129.23, 130.13, 134.84, 137.60, 144.15, 154.12, 162.50, 164.99, 176.52, 179.80 ppm. Anal. Found ($\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_3$); Calcd: C, 62.74; H, 3.29; N, 18.29. Found: C, 62.76; H, 3.27; N, 18.31 ESI-MS m/z ($\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_3 + \text{H}^+$): 307.0826; Found: 307.0877.

3. 5-(4-nitrophenyl)-3-oxo-1-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile

Yellow solid; Yield: 94%, m.p.172-174°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}):, 3301, 2944, 2225, 1721, ^1H NMR (400 MHz, CDCl_3): δ 4.45 (s, 1H, NH), 7.81 (d, J = 8Hz, 2H, ArH), 8.11-8.27 (m, 5H, ArH), 8.37 (d, J = 4Hz, 2H, ArH) ppm. ^{13}C NMR (400MHz, CDCl_3): 63.34, 107.55, 112.68, 126.17, 130.89, 131.28, 137.07, 144.01, 149.87, 152.04, 160.79, 173.50, 182.23 ppm. Anal. Found ($\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_3$); Calcd: C, 62.74; H, 3.29; N, 18.29. Found: C, 62.76; H, 3.27; N, 18.31 ESI-MS m/z ($\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_3 + \text{H}^+$): 307.0826; Found: 307.1067.

4. 5-(3-chlorophenyl)-3-oxo-1-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile

White solid; Yield: 92%, m.p.170-172°C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3430, 2925, 2219, 1724, ^1H NMR (400 MHz, CDCl_3): δ 3.90 (s, 1H, NH), 6.88 (d, J = 8Hz, 2H, ArH), 7.46-7.73 (m, 7H, ArH) ppm. ^{13}C NMR (400MHz, CDCl_3): 55.26, 112.22, 113.98, 119.78, 121.79, 127.29, 129.31, 131.05, 131.89, 137.68, 144.31, 146.12, 146.65, 160.00, 168.06, 169.79, 180.49 ppm. Anal. Found ($\text{C}_{16}\text{H}_{10}\text{ClN}_3\text{O}$); Calcd: C, 64.98; H, 3.41; N, 14.21. Found: C, 64.97; H, 3.42; N, 14.23. ESI-MS m/z ($\text{C}_{16}\text{H}_{10}\text{ClN}_3\text{O} + \text{H}^+$); Calcd: 296.0585; Found: 296.0594.

5. 5-(4-bromophenyl)-3-oxo-1-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile

Brown solid; Yield: 94%, m.p.164-166°C; Rf Value: 0.42 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3322, 2959, 2218, 1720, ^1H NMR (400 MHz, CDCl_3): δ 4.40 (s, 1H, NH), 7.28 (s, 1H, ArH), 7.51 (d, J = 8Hz, 2H, ArH), 7.71 (d, J = 8Hz, 2H, ArH), 7.96 (d, J = 8Hz, 2H, ArH), 8.24 (d, J = 4Hz, 2H, ArH), ppm. ^{13}C NMR (400MHz, CDCl_3): 55.55, 98.16, 115.24, 116.37, 123.60, 124.31, 125.48, 133.83, 142.19, 146.56, 154.29, 155.29, 162.96, 164.76, 171.68, 175.03, 180.42 ppm. Anal. Found ($\text{C}_{16}\text{H}_{10}\text{BrN}_3\text{O}$); Calcd: C, 56.48; H, 2.96; N, 12.35. Found: C, 56.46; H, 2.98; N, 12.37. ESI-MS m/z ($\text{C}_{16}\text{H}_{10}\text{BrN}_3\text{O} + \text{H}^+$): Calcd: 340.0800; Found: 340.0854.

6. 5-(4-methoxyphenyl)-3-oxo-1-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile

Violet solid; Yield: 92%, m.p.106-108°C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3314, 2953, 2215, 1718, ^1H NMR (400 MHz, CDCl_3): δ 3.88 (s, 3H, CH_3), δ 4.22 (s, 1H, NH), 6.94 (d, J = 4Hz, 2H, ArH), δ 7.30-7.84 (m, 9H, ArH) ppm. ^{13}C NMR (400MHz, CDCl_3): 52.99, 58.80, 98.85, 108.69, 114.19, 116.37, 123.95, 126.52, 133.83, 138.20, 151.28, 153.85, 163.33, 165.91, 170.27, 179.68, 188.10 ppm. Anal. Found ($\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2$); Calcd: C, 70.08; H, 4.50; N, 14.41; Found: C, 70.10; H, 4.52; N, 14.39. ESI-MS m/z ($\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2 + \text{H}^+$): Calcd: 292.1081; Found: 292.1074.

7. 5-(4-chlorophenyl)-3-oxo-2,3-dihydro-1H-pyrazole-4-carbonitrile

White solid; Yield: 94%, m.p.170-172°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3433, 2958, 2222, 1726, ^1H NMR (400 MHz, CDCl_3): δ 3.96 (d, J = 4 Hz, 1H, NH^a), δ 4.36 (d, J = 4 Hz, 1H, NH^b), 7.43 (d, J = 4Hz, 2H, ArH), 7.95 (d, J = 8Hz, 2H, ArH) ppm. ^{13}C NMR (400MHz, CDCl_3): 53.66, 63.14, 103.19, 114.85, 129.47, 132.27, 140.01, 154.25, 152.22, 171.70 ppm. Anal. Found ($\text{C}_{10}\text{H}_6\text{ClN}_3\text{O}$); Calcd: C,

54.69; H, 2.75; N, 19.13; Found: C, 54.71; H, 2.73; N, 19.15. ESI-MS m/z ($C_{10}H_6ClN_3O + H^+$); Calcd: 220.0272; Found: 220.0252.

8. 5-(3-nitrophenyl)-3-oxo-2,3-dihydro-1H-pyrazole-4-carbonitrile

yellow solid; Yield: 92%, m.p. 172-174°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3428, 2965, 2220, 1724, 1H NMR (400 MHz, $CDCl_3$): δ 4.03 (d, 1H, $J = 4$ Hz, NH^a), δ 4.46 (d, $J = 4$ Hz, 1H, NH^b), 7.31 (s, 1H, ArH), 7.71 (s, 1H, ArH), 8.37 (d, $J = 8$ Hz, 1H, ArH), 8.75 (s, 1H, ArH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 63.20, 106.82, 114.78, 126.22, 127.29, 130.58, 132.65, 134.94, 148.97, 151.77, 161.68 ppm. Anal. Found ($C_{10}H_6N_4O_3$); Calcd: C, 52.18; H, 2.63; N, 24.34; Found: C, 52.16; H, 2.61; N, 24.35. ESI-MS m/z ($C_{10}H_6N_4O_3 + H^+$); Calcd: 231.0513; Found: 231.0535.

9. 5-(4-nitrophenyl)-3-oxo-2,3-dihydro-1H-pyrazole-4-carbonitrile

yellow solid; Yield: 94%, m.p. 172-174°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}): 2928, 2208, 1640, 1580, 1510, 1340, 1248, 1H NMR (400 MHz, $CDCl_3$): δ 3.95 (d, $J = 4$ Hz, 1H, NH^a), δ 4.40 (d, $J = 4$ Hz, 1H, NH^b), 7.23 (s, 1H, ArH), 8.10-8.36 (m, 4H, ArH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 63.20, 115.00, 126.03, 127.49, 130.38, 133.11, 134.42, 147.90, 151.97, 161.68 ppm. Anal. Found ($C_{10}H_6N_4O_3$); Calcd: C, 52.18; H, 2.63; N, 24.34. Found: C, 52.17; H, 2.61; N, 24.35. ESI-MS m/z ($C_{10}H_6N_4O_3 + H^+$); Calcd: 231.0513; Found: 231.0563.

10. 5-(3-chlorophenyl)-3-oxo-2,3-dihydro-1H-pyrazole-4-carbonitrile

White solid; Yield: 92%, m.p. 172-174°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3424, 2945, 2225, 1722, 1H NMR (400 MHz, $CDCl_3$): δ 4.02 (d, $J = 4$ Hz, 1H, NH^a), δ 4.46 (d, $J = 4$ Hz, 1H, NH^b), 8.34-8.57 (m, 3H, ArH), 8.75 (s, 1H, ArH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 64.00, 114.54, 126.03, 126.49, 130.58, 132.09, 135.26, 148.44, 153.02, 160.93 ppm. Anal. Found ($C_{10}H_6ClN_3O$); Calcd: C, 54.69; H, 2.75; N, 19.13; Found: C, 54.71; H, 2.73; N, 19.15. ESI-MS m/z ($C_{10}H_6ClN_3O + H^+$); Calcd: 220.0272; Found: 220.0262.

11. 5-(4-bromophenyl)-3-oxo-2,3-dihydro-1H-pyrazole-4-carbonitrile

Brown solid; Yield: 92%, m.p. 162-164°C; Rf Value: 0.38 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3432, 2928, 2220, 1720, 1H NMR (400 MHz, $CDCl_3$): δ 3.96 (d, $J = 4$ Hz, 1H, NH^a), δ 4.46 (d, $J = 4$ Hz, 1H, NH^b), 7.57 (d, $J = 4$ Hz, 2H, ArH), 7.87 (d, $J = 4$ Hz, 2H, ArH), 8.20 (s, 1H, ArH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 63.47, 114.78,

125.75, 127.29, 130.11, 133.11, 135. 26,148.44, 151.97, 161.68 ppm. Anal. Found ($C_{10}H_6BrN_3O$); Calcd: C, 45.48; H, 2.29; N, 15.91; Found: C, 45.50; H, 2.27; N, 15.89. ESI-MS m/z ($C_{10}H_6BrN_3O + H^+$); Calcd: 263.9767; Found: 263.9786.

12. 5-(4-methoxyphenyl)-3-oxo-2,3-dihydro-1H-pyrazole-4-carbonitrile

Violet solid; Yield: 94%, m.p.106-108°C; Rf Value: 0.40 (10% methanol in chloroform); IR (KBr, cm^{-1}): 3435, 2999, 2221, 1725, 1H NMR (400 MHz, $CDCl_3$): δ 3.97 (s 3H, OCH₃), δ 4.38 (d, J = 8 Hz, 1H, NH^a), δ 4.72 (d, J = 4 Hz, 1H, NH^b), 7.71 (s, 1H, ArH), 8.31 (d, J = 8Hz, 2H, ArH), 8.68 (s, 1H, ArH) ppm. ^{13}C NMR (400MHz, $CDCl_3$): 52.99, 55.85, 99.58, 113.82, 117.05, 123.95, 127.28, 133.08, 154.22, 163.33, 185.55 ppm. Anal. Found ($C_{11}H_9N_3O_2$); Calcd: C, 61.39; H, 4.22; N, 19.41; Found: C, 61.41; H, 4.21; N, 19.43. ESI-MS m/z ($C_{11}H_9N_3O_2 + H^+$): Calcd: 216.0768; Found: 216.0773.

III. Materials used for green metrics calculations

A. Formula used for calculations:

The following formulae were used for evaluating green chemistry metrics such as atom economy (AE), carbon efficiency (CE), reaction mass efficiency (RME), overall efficiency (OE), process mass intensity (PMI) solvent intensity (SI) and E-factor.^{1,2}

1. % **Atom Economy (AE)** = (Mol Wt. of desired product/ Mol Wt. of all reactants) $\times$ 100

2. % **Carbon Efficiency (CE)** = (Amount of carbon in the product)/ Total no of carbon present in reactant) $\times$ 100

3. % **Reaction Mass Efficiency (RME)** = (Mass of isolated product)/ Total mass of reactants) $\times$ 100

4. % **Overall Efficiency (OE)** = (RME/AE) $\times$ 100

5. % **Process Mass Intensity (PMI)** = (Total mass of input materials in a process)/ Mass of product) $\times$ 100

6. **Solvent Intensity (SI)** = (Total mass of input solvents in a process)/ Mass of product)

7. **E-Factor** = PMI-1

B. Details of reactants and products used for metric calculations:

a) **Reactants:** Ethylcyanoacetate, Molecular Weight = 113.11g/mol, weight used = 0.113 g;
Phenylhydrazine, Molecular weight = 108.14 g/mol, weight used = 0.108g;
Hydrazinehydrate, Molecular weight = 32.04 g/mol;

Weight of different aromatic aldehydes: 4-Cholorobenzaldehyde = 0.140g, 3-Cholorobenzaldehyde = 0.140g, 4-Nitrobenzaldehyde = 0.151g, 3-Nitrobenzaldehyde = 0.151g, 4-Bromobenzaldehyde = 0.185g, 4-Methoxybenzaldehyde = 0.136g.

b). Products:

Compounds	4a	4b	4c	4d	4e	4f	4g
Molecular Formula	C ₁₆ H ₁₀ Cl N ₃ O	C ₁₆ H ₁₀ N ₄ O ₃	C ₁₆ H ₁₀ N ₄ O ₃	C ₁₆ H ₁₀ Cl N ₃ O	C ₁₆ H ₁₀ Br N ₃ O	C ₁₇ H ₁₃ N ₃ O ₂	C ₁₀ H ₆ Cl N ₃ O
Molecular Weight (g/mol)	295.72	306.28	306.28	295.72	340.18	290.31	219.62
Weight (g)	0.278	0.288	0.288	0.273	0.320	0.268	0.207
Yield (%)	94	94	94	92	94	92	94

Compounds	4h	4i	4j	4k	4l
Molecular Formula	C ₁₀ H ₆ N ₄ O ₃	C ₁₀ H ₆ N ₄ O ₃	C ₁₀ H ₆ ClN ₃ O	C ₁₀ H ₆ BrN ₃ O	C ₁₁ H ₉ N ₃ O ₂
Molecular Weight (g/mol)	230.18	230.18	219.62	264.08	215.21
Weight (g)	0.212	0.217	0.203	0.243	0.203
%Yield	92	94	92	92	94

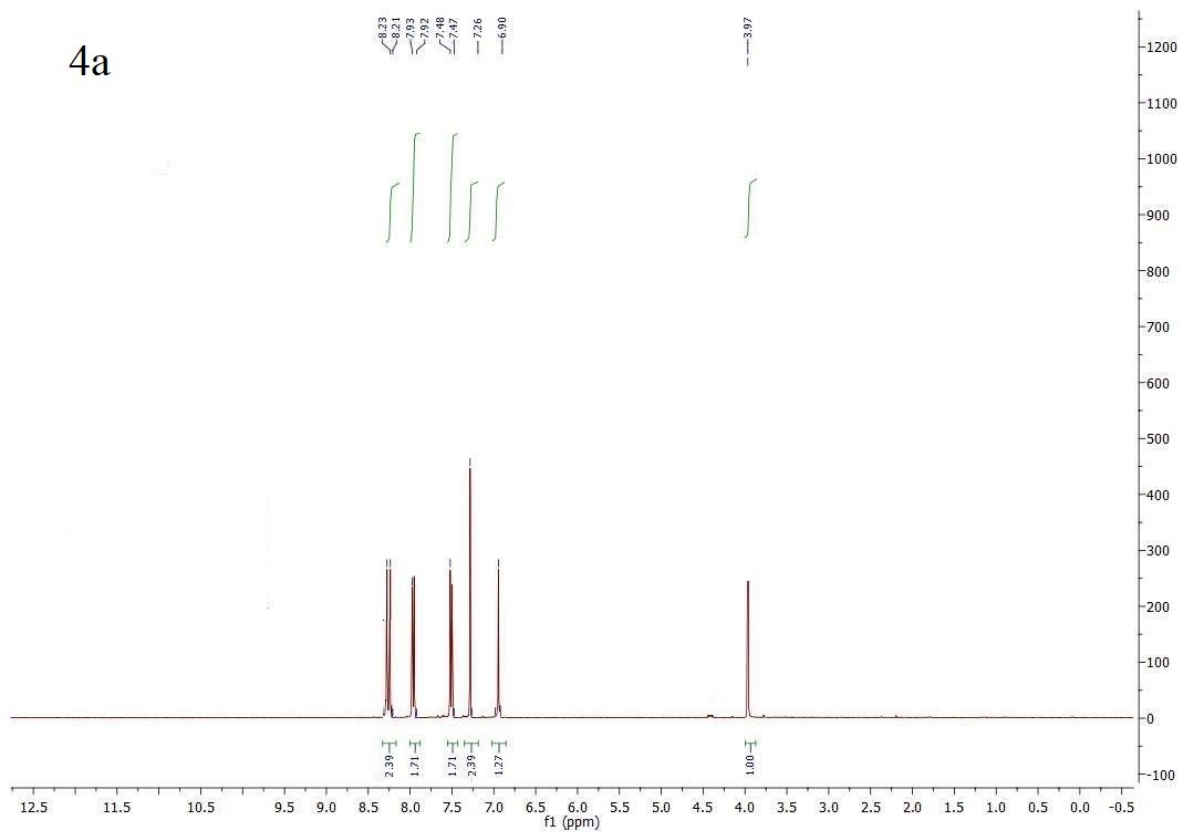


Figure S1. ^1H NMR Spectrum of compound 4a

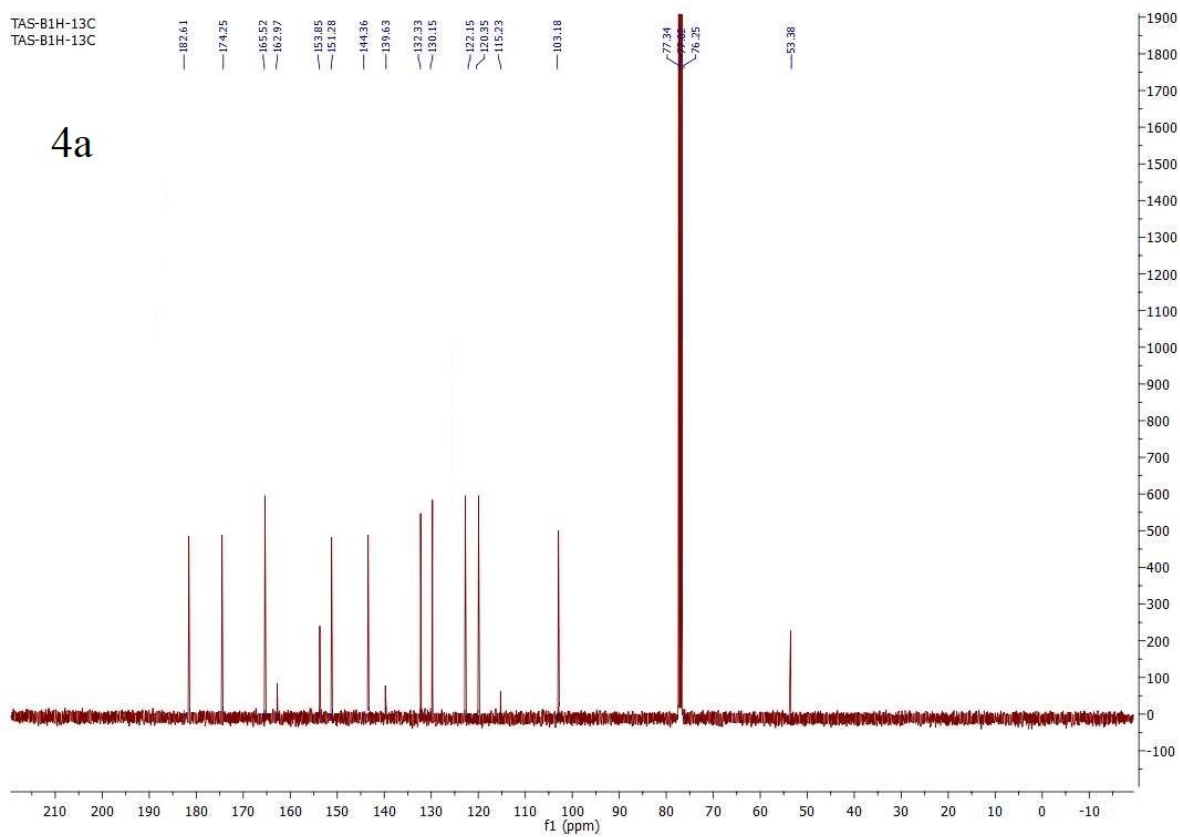


Figure S2. ^{13}C NMR Spectrum of compound 4a

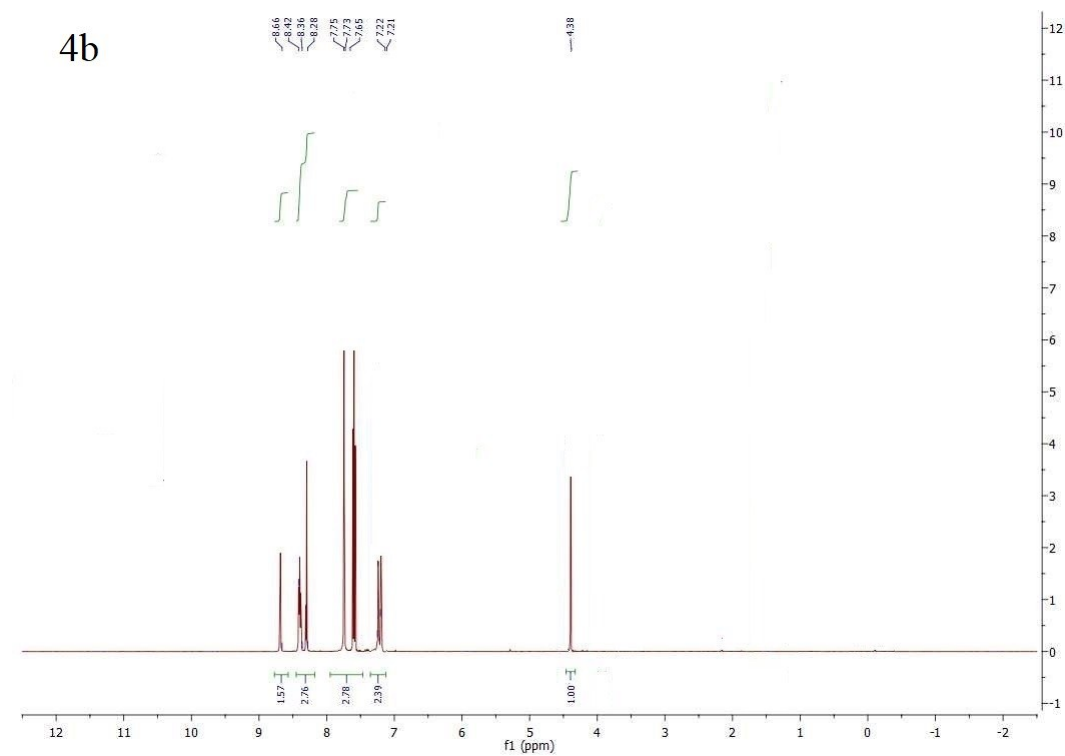


Figure S3. ^1H NMR Spectrum of compound 4b

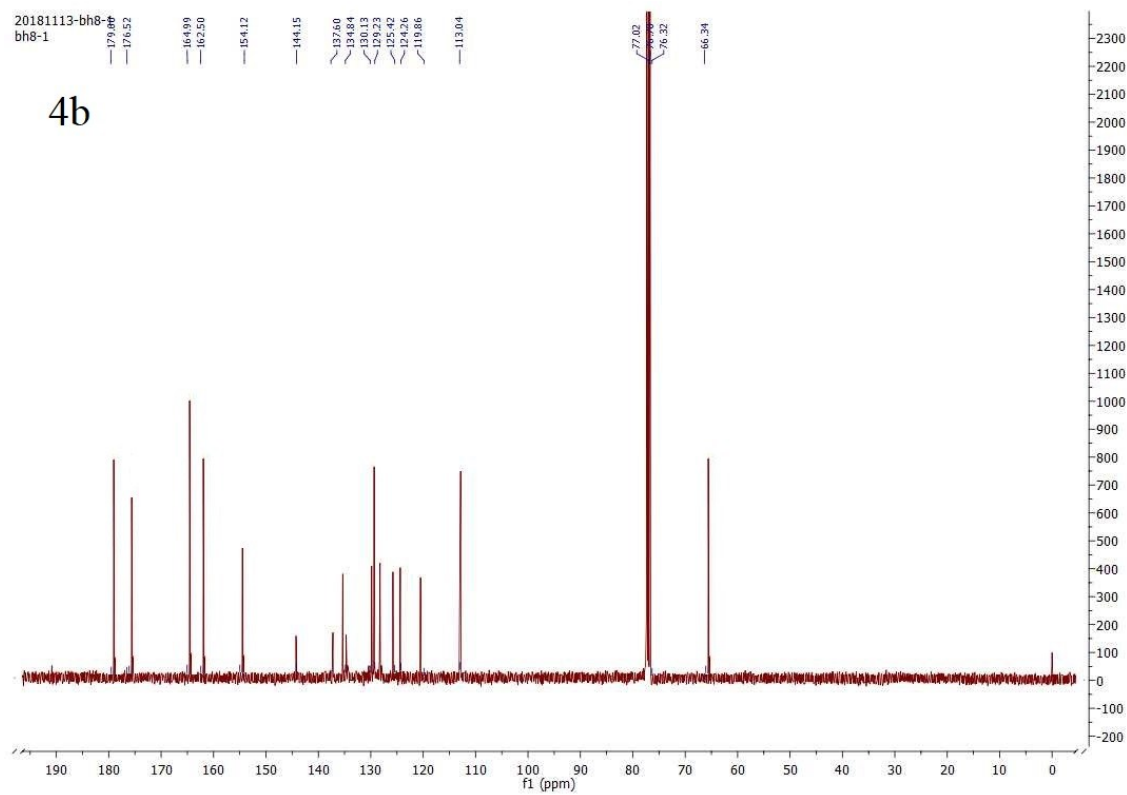


Figure S4. ^{13}C NMR Spectrum of compound 4b

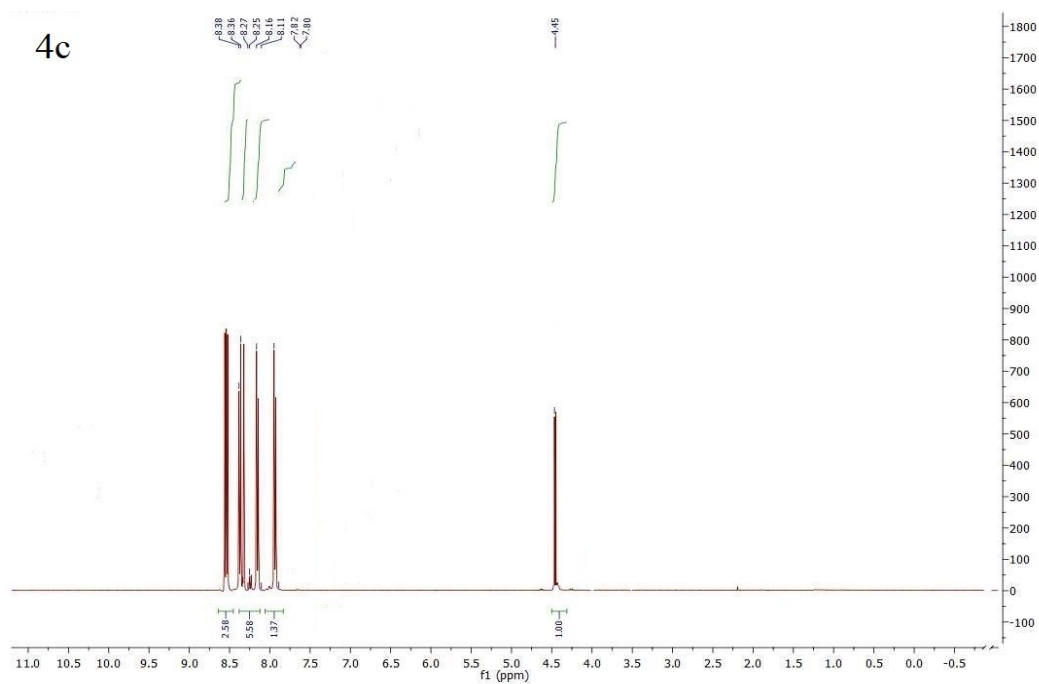


Figure S5. ^1H NMR Spectrum of compound 4c

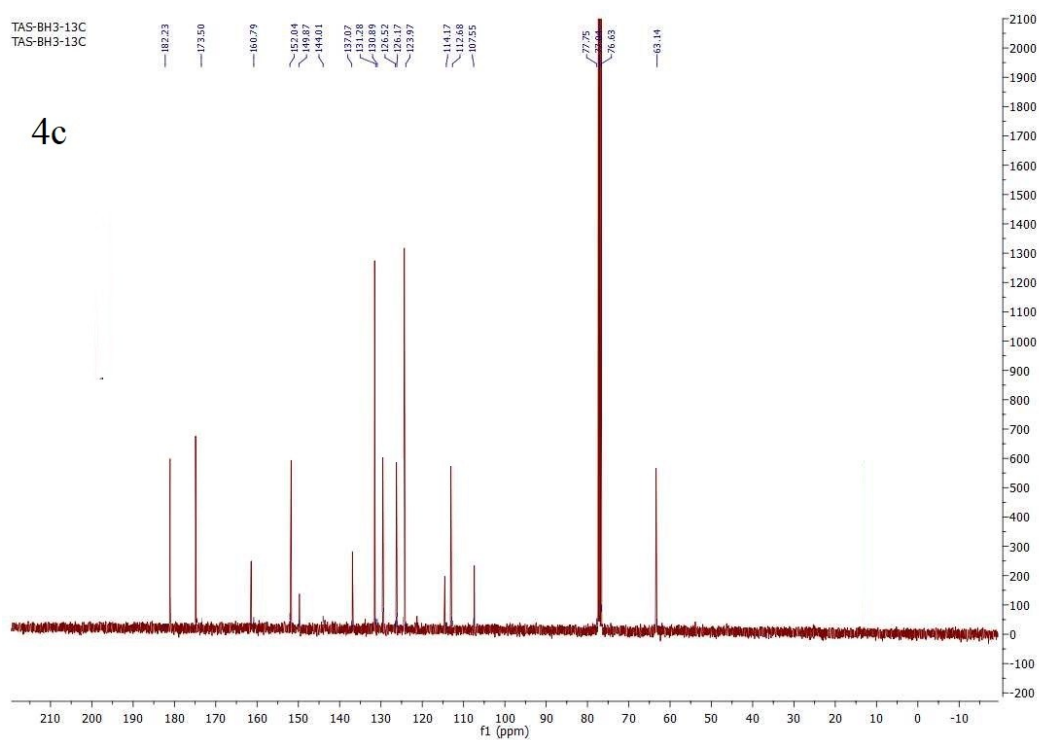


Figure S6. ^{13}C NMR Spectrum of compound 4c

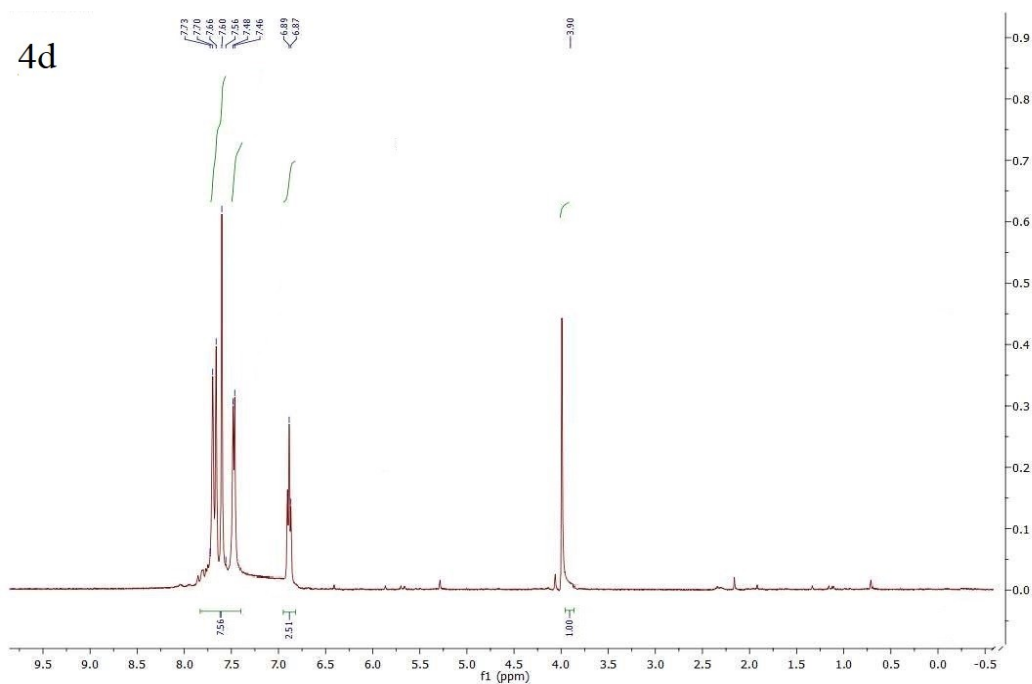


Figure S7. ^1H NMR Spectrum of compound 4d

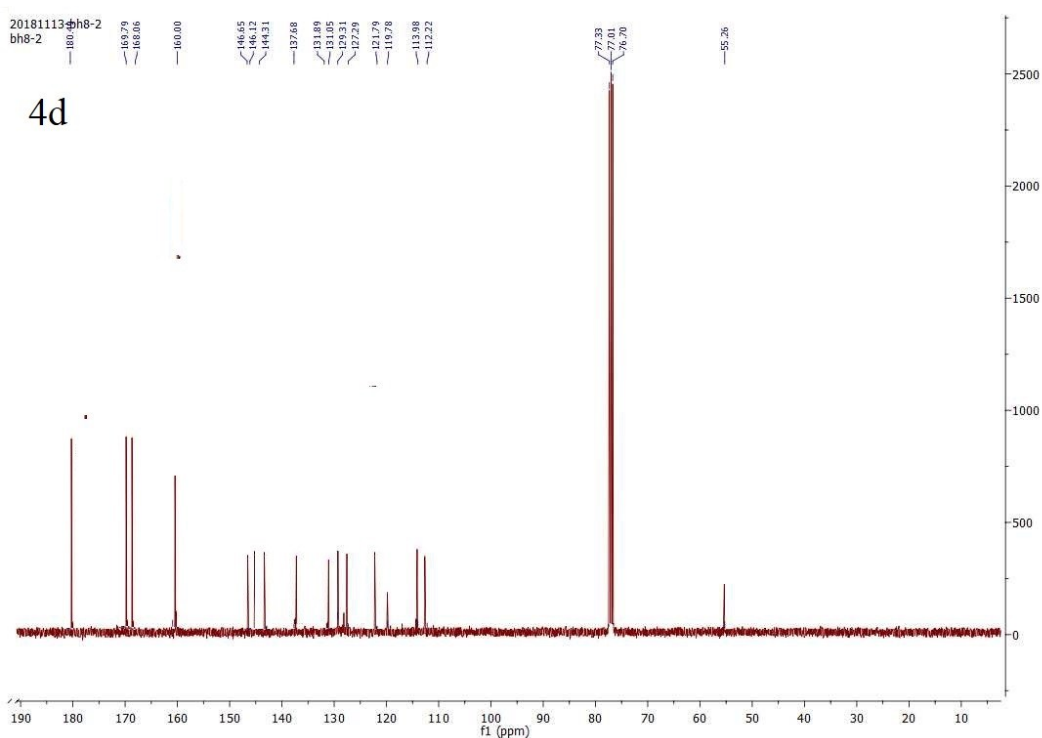


Figure S8. ^{13}C NMR Spectrum of compound 4d

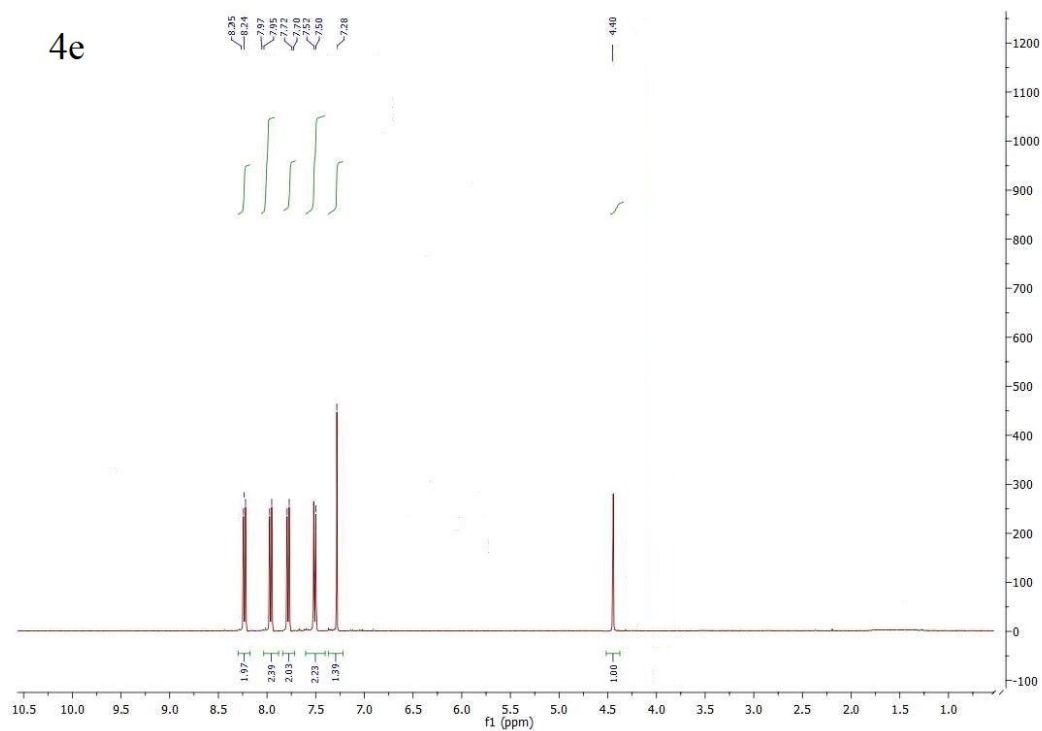


Figure S9. ^1H NMR Spectrum of compound 4e

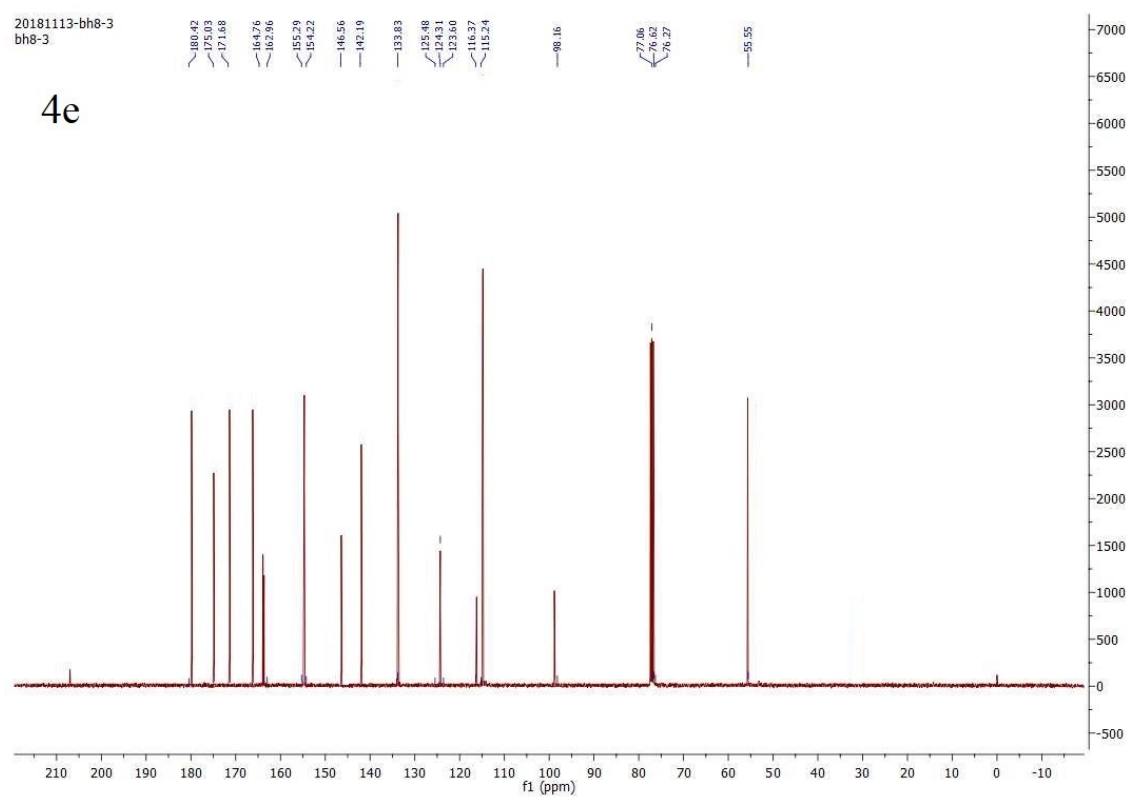


Figure S10. ^{13}C NMR Spectrum of compound 4e

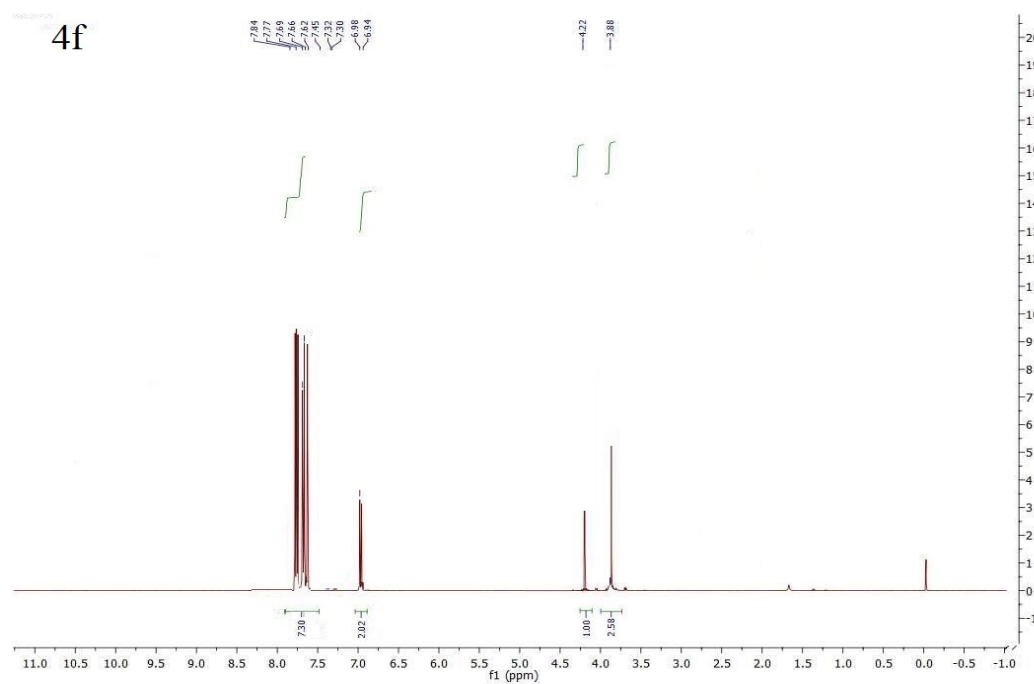


Figure S11. ^1H NMR Spectrum of compound 4f

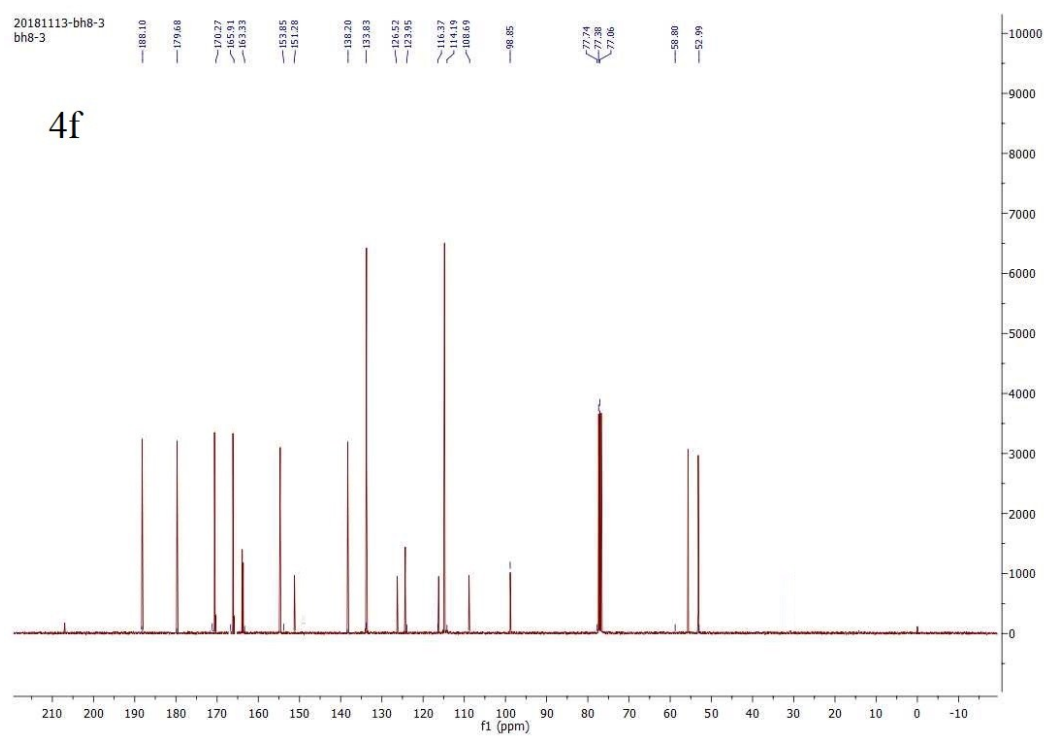


Figure S12. ^{13}C NMR Spectrum of compound 4f

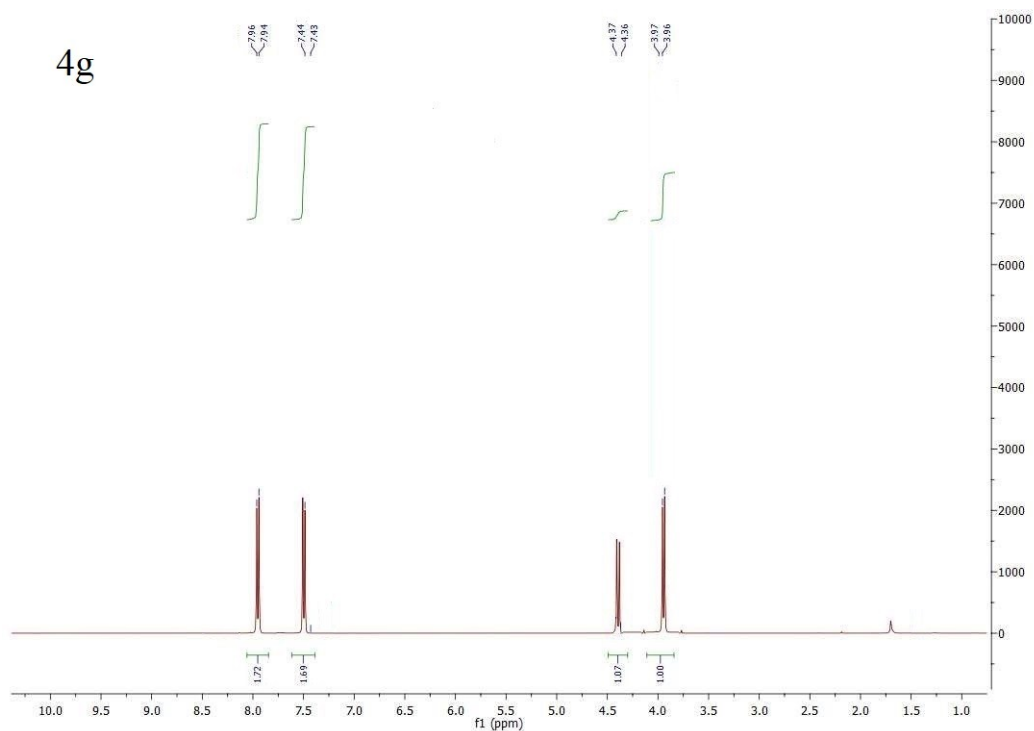


Figure S13. ^1H NMR Spectrum of compound 4g

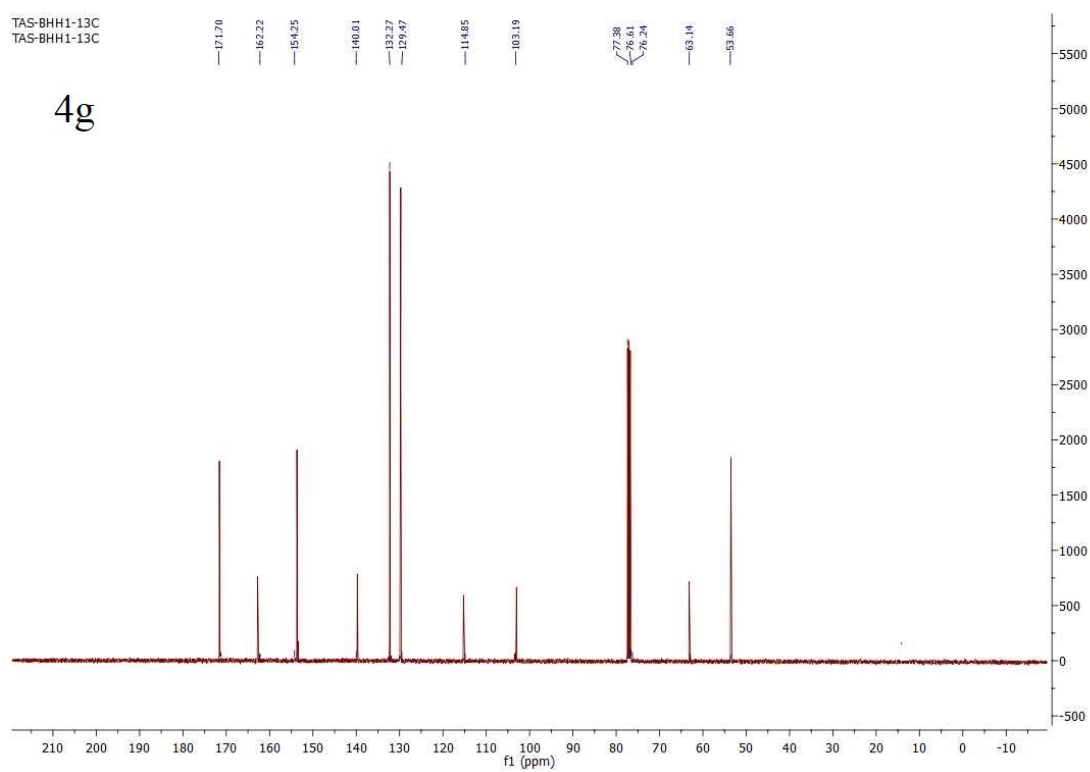


Figure S14. ^{13}C NMR Spectrum of compound 4g

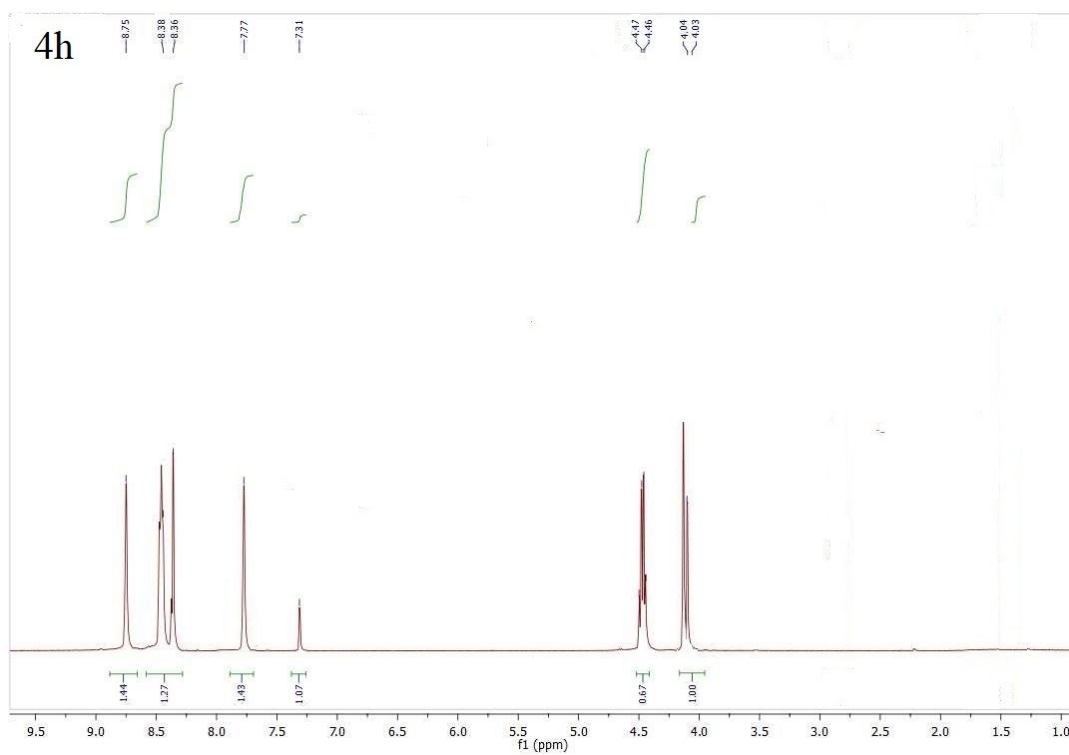


Figure S15. ^1H NMR Spectrum of compound 4h

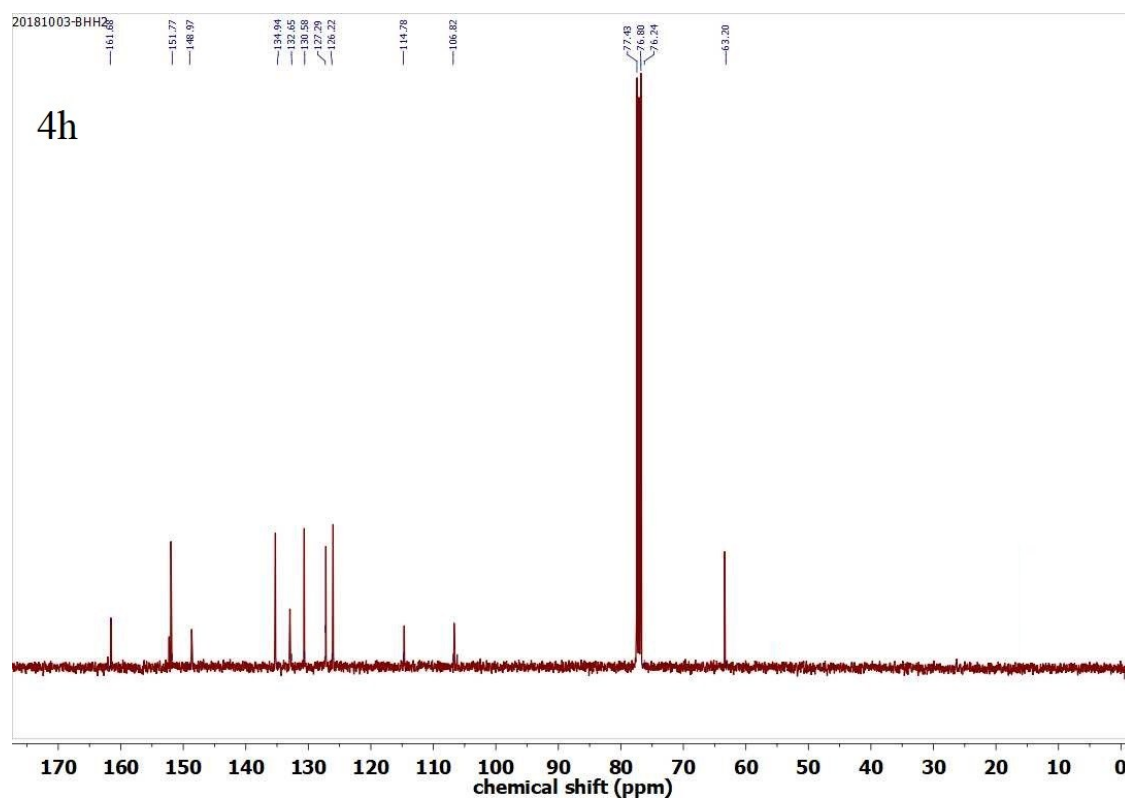


Figure S16. ^{13}C NMR Spectrum of compound 4h

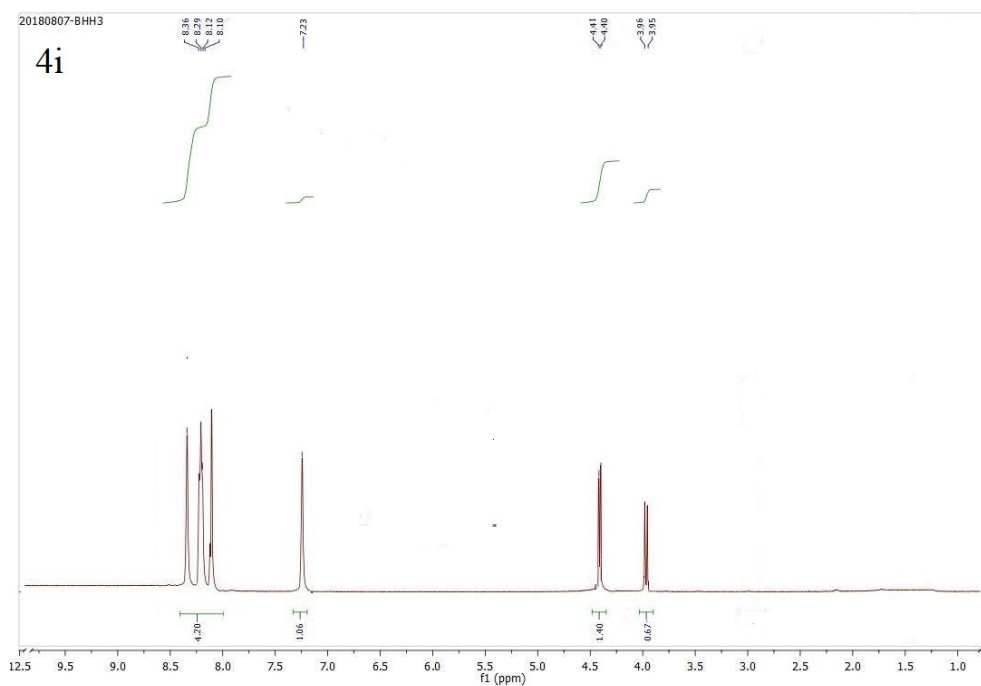


Figure S17. ^1H NMR Spectrum of compound 4i

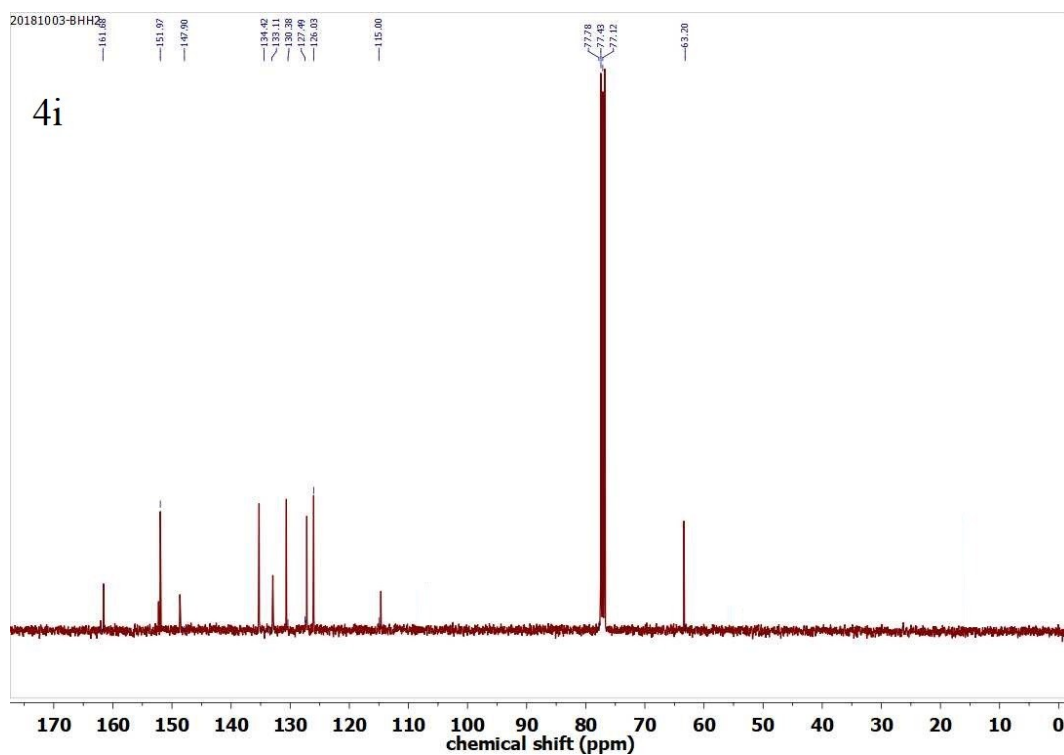


Figure S18. ^{13}C NMR Spectrum of compound 4i

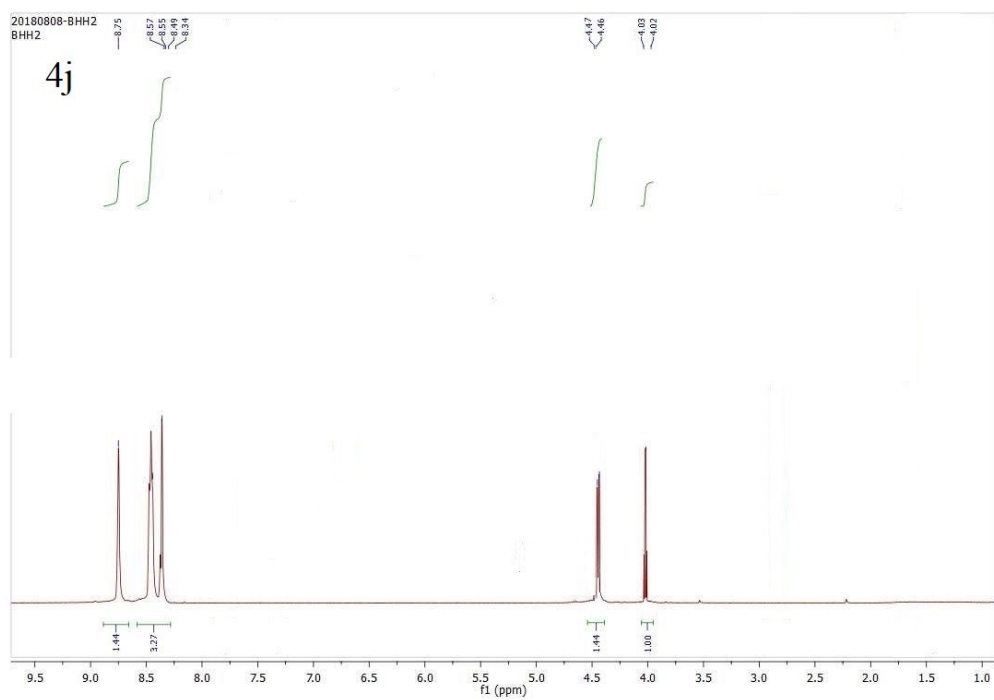


Figure S19. ^1H NMR Spectrum of compound 4j

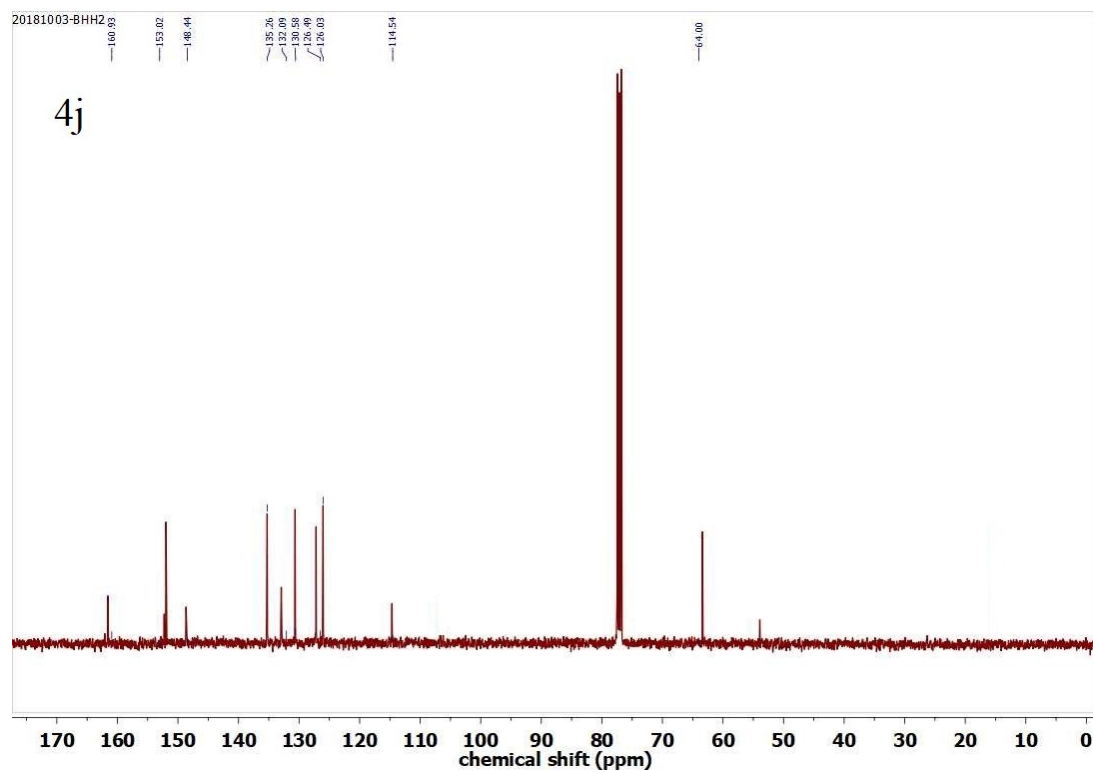


Figure S20. ^{13}C NMR Spectrum of compound 4j

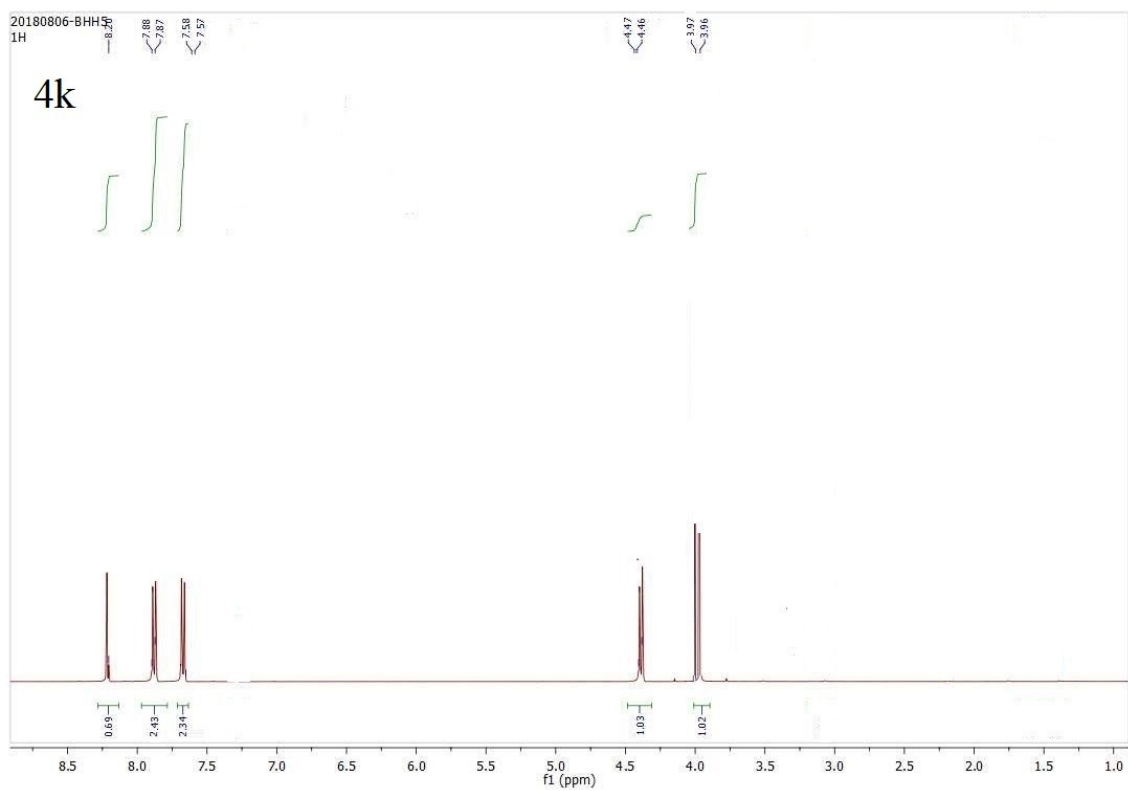


Figure S21. ^1H NMR Spectrum of compound 4k

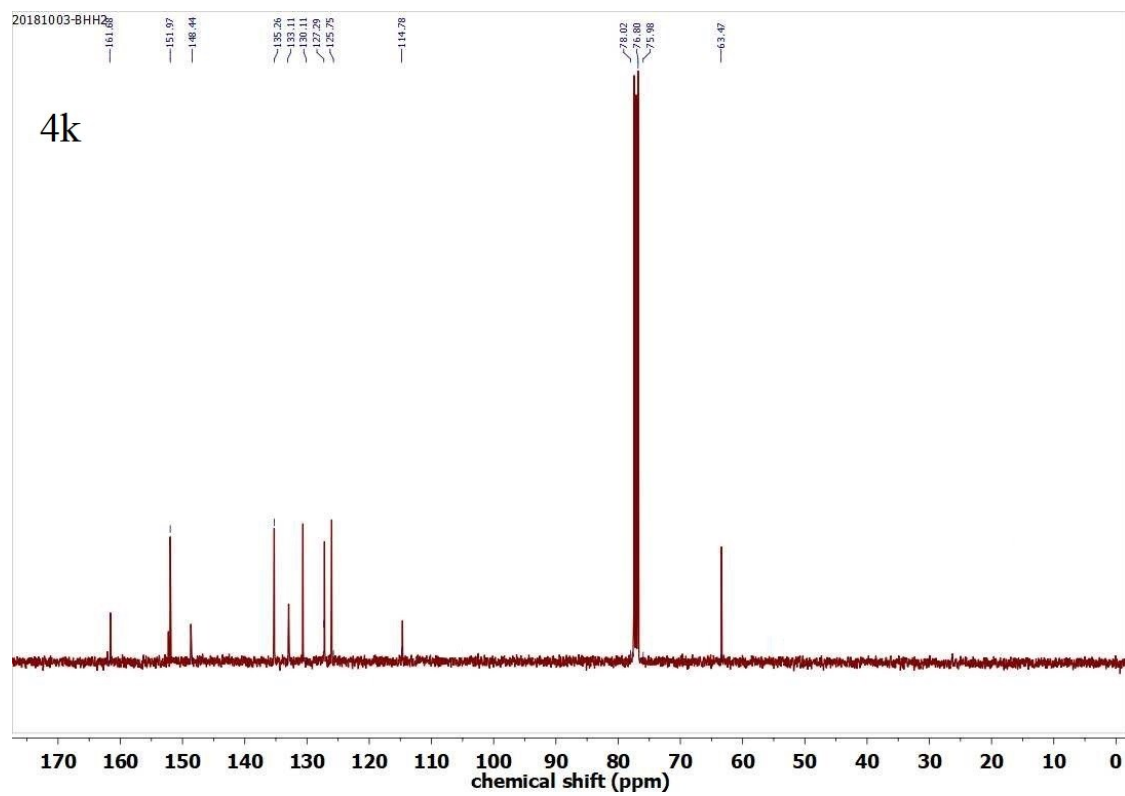


Figure S22. ^{13}C NMR Spectrum of compound 4k

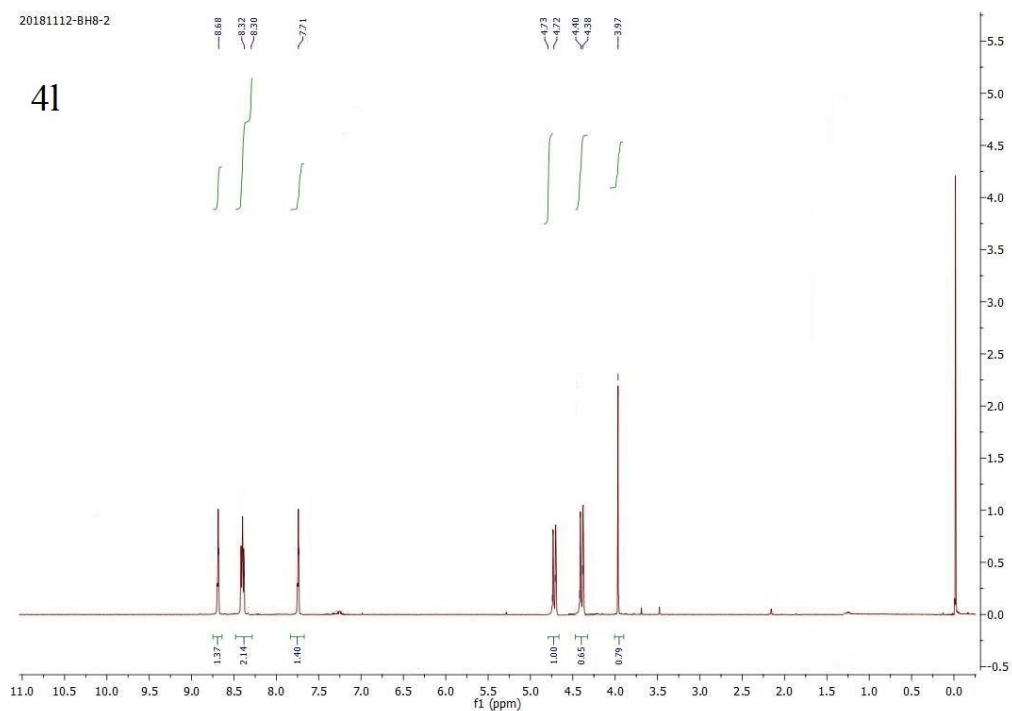


Figure S23. ^1H NMR Spectrum of compound 41

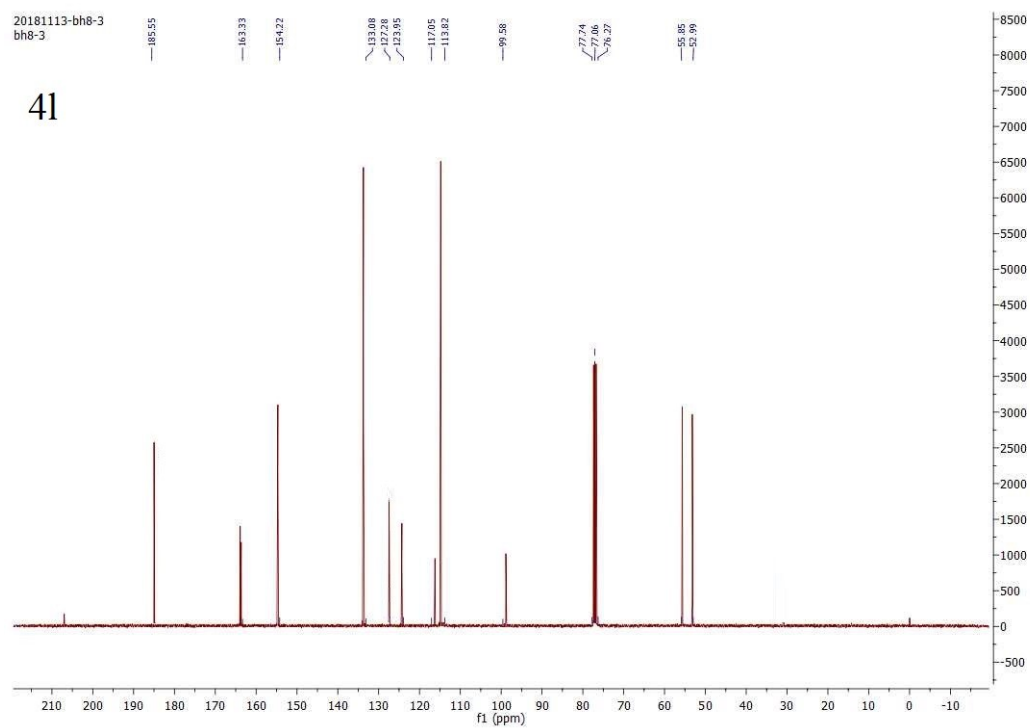


Figure S24. ^{13}C NMR Spectrum of compound 41

