Supporting Information

Recyclable Amberlyst-15-catalyzed three-component reaction in water to synthesize diarylmethyl sulfones

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1. General Information

All reactions were carried out under air atmosphere in dried glassware. The glassware used was dried in an electric oven at 120 ℃. Chemicals were purchased from Aladdin, Adamas, Aldrich, Alfa Aesar, and Kelong Chemical Co. and used as received. Petroleum ether refers to the fraction boiling in the 60–90 ℃ range. Unless otherwise stated, there is no further purification for the commercial supplier's chemicals.

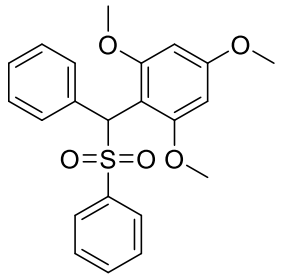
Melting points were determined using a Shanghai Jingke SGW X-4 microscope melting point apparatus. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{31}P NMR (162 MHz) spectra were determined on a Bruker Avance III 400 MHz instrument or on an Agilent Technologies 400MHz instrument. ^{1}H NMR data are reported in δ units (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), DMSO (2.50 ppm) or acetone (2.05 ppm) in the deuterated solvent, unless otherwise stated. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. ^{13}C NMR spectra were determined on a Bruker Avance III 101 MHz instrument. ^{13}C NMR spectra are reported in (ppm) relative to deuterochloroform (77.2 ppm), DMSO-d_6 (39.5 ppm) or acetone-d_6 (206.7 ppm for C=O), and all were obtained with ^{1}H decoupling. High-resolution mass spectra are recorded on a Shimadzu LCMS-IT-TOF instrument in the ESI mode.

2. General procedure for the synthesis of compounds 4

To a 25 mL glass test tube equipped a stir bar were added the corresponding aldehyde **1** (1.5 mmol), sulfinate **2** (1 mmol), Aryl-H **3** (1 mmol), Amberlyst-15 wet ion exchange resin (50% weight percentage according to **3**) and 1 mL water. The test tube was stirred in an oil bath preheated at 60 ℃. After 6 hours, reaction progress was checked by TLC and confirmed reaction was completed. Then, the reaction mixture was cooled to room temperature. Then added water (10 mL) to reaction mixture, and the ion exchange resin was filtered and washed with ethyl acetate (5 mL) for three times. The filtrate was extracted with ethyl acetate (10 mL) for three times, and the combined organic layer was dried over anhydrous $MgSO_4$, and then adsorbed on some silica gel under reduced pressure on a rotary evaporator. The silica gel adsorbing the sample was transferred to a silica gel column. After purified by the silica gel column chromatography (Petroleum ether : Ethyl acetate = 5 : 1 used as eluents), the desired product **4** was obtained.

3. Spectral data of the synthesized compounds

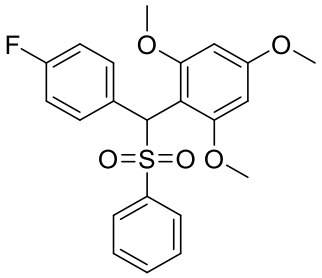
1. *1,3,5-trimethoxy-2-(phenyl(phenylsulfonyl)methyl)benzene* **4aaa**



4aaa

Yield: 88%; white solid; Mp: 106-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.63(m, 2H), 7.61-7.49 (m, 3H), 7.45-7.24 (m, 5H), 6.21 (s, 1H), 6.06 (s, 2H), 3.80(s, 3H), 3.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.72, 141.02, 134.19, 132.64, 130.18, 128.67, 128.15, 127.91, 127.64, 104.12, 91.00, 67.77, 55.59, 55.30. HRMS (ESI): calculated for $C_{22}H_{22}O_5SNa$ $[M + Na]^+$ = 421.1086, found $C_{22}H_{22}O_5SNa[M + Na]^+$ = 421.1079.

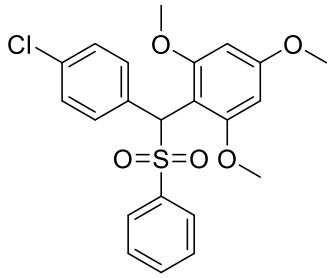
2. 2-((4-fluorophenyl)(phenylsulfonyl)methyl)-1,3,5-trimethoxybenzene **4baa**



4baa

Yield: 90%; white solid; Mp: 87-88 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) : δ 7.70 – 7.60 (m, 1H), 7.59 – 7.45 (m, 6H), 7.20 – 7.08 (m, 2H), 6.18 (s, 2H), 6.09 (s, 1H), 3.76 (s, 3H), 3.62 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d6) : δ 167.99, 166.74, 165.56, 145.29, 138.48, 137.31, 137.23, 135.31, 135.28, 133.86, 133.23, 120.07, 119.85, 108.10, 96.41, 71.66, 60.88, 60.50.HRMS (ESI): calculated for $C_{22}H_{21}FO_5SNa[M + Na]^+$ = 439.0991, found $C_{22}H_{21}FO_5SNa$ $[M + Na]^+$ = 439.0992.

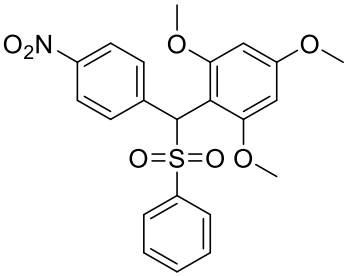
3. *2-((4-chlorophenyl)(phenylsulfonyl)methyl)-1,3,5-trimethoxybenzene* **4caa**



4caa

Yield: 91%; white solid; Mp: 118-119 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 7.71-7.62(m, 2H), 7.59-7.49 (m, 3H), 7.46-7.22 (m, 4H), 6.14 (s, 1H), 6.05 (s, 2H), 3.80(s, 3H), 3.64 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.91, 140.66, 133.51, 132.81, 131.54, 128.64, 128.26, 128.03, 103.50, 91.00, 66.83, 55.59, 55.31. HRMS (ESI): calculated for $C_{22}H_{21}ClO_5SNa$ $[M + Na]^+$ = 455.0696, found $C_{22}H_{21}ClO_5SNa$ $[M + Na]^+$ = 455.0696.

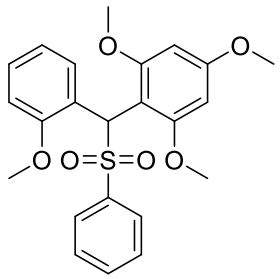
4. *1,3,5-trimethoxy-2-((4-nitrophenyl)(phenylsulfonyl)methyl)benzene* **4daa**



4daa

Yield: 90%; white solid; Mp: 130-131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.06 (d, J = 8.9 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 6.14 (s, 1H), 5.93 (s, 2H), 3.71 (s, 3H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.34, 146.96, 142.16, 140.09, 133.15, 130.79, 128.72, 128.35, 122.91, 102.55, 90.89, 66.33, 55.56, 55.34. HRMS (ESI): calculated for $C_{22}H_{21}NO_7SNa$ $[M + Na]^+$ = 466.0936, found $C_{22}H_{21}NO_7SNa$ $[M + Na]^+$ = 466.0911.

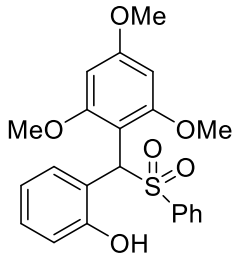
5. *1,3,5-trimethoxy-2-((2-methoxyphenyl)(phenylsulfonyl)methyl)benzene* **4eaa**



4eaa

Yield: 70%; white solid; Mp: 150-151 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.22 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.53 – 7.44 (m, 1H), 7.41 – 7.32 (m, 2H), 7.20 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.70 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.62 (s, 1H), 6.01 (s, 2H), 3.76 (s, 3H), 3.60 (s, 6H), 3.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): 161.50, 156.88, 141.53, 132.36, 132.32, 128.75, 128.73, 127.98, 122.59, 119.99, 110.25, 104.01, 91.22, 59.89, 55.72, 55.36, 55.22.HRMS (ESI): calculated for $C_{23}H_{24}O_6SNa$ $[M + Na]^+$ = 451.1191, found $C_{23}H_{24}O_6SNa$[M + Na]$^+$ = 451.1193.

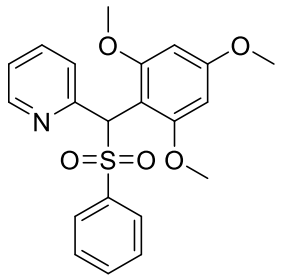
6. *2-((phenylsulfonyl)(2,4,6-trimethoxyphenyl)methyl)phenol* **4faa**



4faa

Yield: 75%; white solid; Mp: 116-117 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.3 (bs, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.55 (td, *J* = 21.3, 19.1, 7.4 Hz, 4H), 7.32 (d, *J* = 6.2 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 6.11 (s, 2H), 3.73 (s, 3H), 3.52 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 161.70, 155.61, 148.72, 141.20, 133.42, 132.66, 128.90, 128.90, 128.86, 128.60, 128.11, 125.94, 120.57, 118.23, 115.05, 103.40, 91.75, 59.70, 56.10, 55.71.HRMS (ESI): calculated for $C_{23}H_{24}O_6SNa$ $[M + Na]^+$ m/z = 437.1035, found $C_{23}H_{24}O_6SNa$ $[M + Na]^+$ m/z = 437.1036.

7. *2-((phenylsulfonyl)(2,4,6-trimethoxyphenyl)methyl)pyridine* **4gaa**

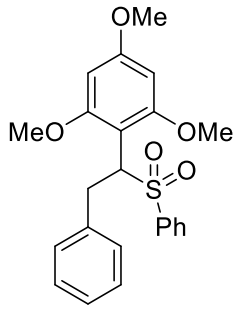


4gaa

Yield: 75%; white solid; Mp: 130-131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.46 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 8.07 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.75 – 7.62 (m, 3H), 7.56 – 7.46 (m, 1H), 7.38 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.14 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 6.35 (s, 1H), 5.98 (s, 2H), 3.75 (s, 3H), 3.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.09, 154.76, 148.64, 140.75, 135.73, 132.81, 128.97,

128.11, 125.09, 122.18, 102.75, 90.98, 68.64, 55.54, 55.27. HRMS (ESI): calculated for $C_{21}H_{21}NO_5SNa[M + Na]^+$ = 422.1038, found $C_{21}H_{21}NO_5SNa$ $[M + Na]^+$ = 422.1039.

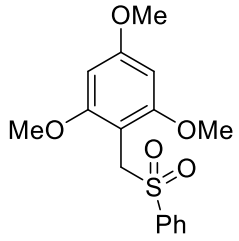
8. *1,3,5-trimethoxy-2-(2-phenyl-1-(phenylsulfonyl)ethyl)benzene* **4haa**



4haa

Yield: 70%; color less liquid; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.78 – 7.66 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.01 (m, 5H), 6.00 (d, *J* = 2.3 Hz, 1H), 5.81 (d, *J* = 2.3 Hz, 1H), 5.27 (dd, *J* = 11.6, 4.7 Hz, 1H), 3.89 (dd, *J* = 13.6, 11.6 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 4H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.59, 160.78, 159.85, 139.83, 138.45, 132.71, 128.93, 128.67, 128.11, 128.03, 126.06, 100.92, 91.02, 90.34, 63.97, 55.74, 55.26, 55.14, 31.65. HRMS (ESI): calculated for $C_{23}H_{24}O_5SNa$ $[M + Na]^+$ = 435.1242, found $C_{22}H_{21}FO_5SNa$ $[M + Na]^+$ = 435.1242.

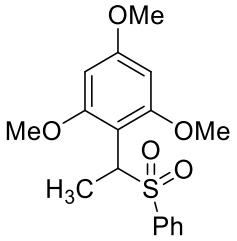
9. *1,3,5-trimethoxy-2-((phenylsulfonyl)methyl)benzene* **4iaa**[1]



4iaa

Yield: 82%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.73 – 7.63 (m, 2H), 7.59 – 7.47 (m, 1H), 7.46 – 7.36 (m, 2H), 5.96 (s, 2H), 4.48 (s, 2H), 3.76 (s, 3H), 3.46 (s, 6H). 13C NMR (101 MHz, $CDCl_3$) δ 161.88, 159.58, 140.16, 132.80, 128.63, 128.19, 98.11, 90.16, 55.38, 55.29, 51.65. HRMS (ESI): calculated for $C_{16}H_{18}O_5SNa$ $[M + Na]^+$ = 345.0773, found $C_{16}H_{18}O_5SNa$ $[M + Na]^+$ = 345.0772.

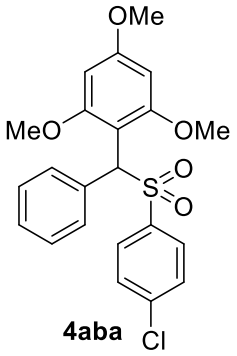
10. *1,3,5-trimethoxy-2-(1-(phenylsulfonyl)ethyl)benzene* **4jaa**



4jaa

Yield: 79%; white solid; Mp: 123-124 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.64 (m, 2H), 7.62 – 7.48 (m, 1H), 7.48 – 7.36 (m, 2H), 6.00 (dd, *J* = 36.1, 2.3 Hz, 2H), 5.06 (q, *J* = 7.3 Hz, 1H), 3.80 (s, 3H), 3.55 (d, *J* = 15.4 Hz, 6H), 1.84 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.54, 161.15, 159.23, 139.50, 132.62, 129.06, 128.04, 103.04, 91.08, 90.17, 57.86, 55.62, 55.24, 12.81. HRMS (ESI): calculated for $C_{17}H_{20}O_5SNa$[M + Na]$^+$ = 359.0929, found $C_{17}H_{20}O_5SNa$ [M + Na]$^+$ = 359.0921.

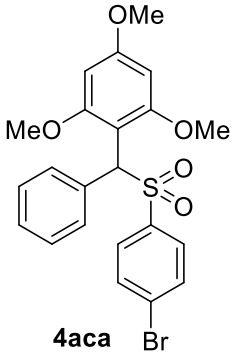
11. *2-(((4-chlorophenyl)sulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene* **4aba**



4aba

Yield: 90%; white solid; Mp: 125-126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.43 (m, 4H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 6.08 (s, 1H), 5.98 (s, 2H), 3.72 (s, 3H), 3.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.85, 139.54, 139.21, 133.89, 130.19, 130.15, 128.38, 128.00, 127.79, 103.82, 92.88, 91.02, 68.04, 55.57, 55.31. HRMS (ESI): calculated for $C_{22}H_{21}ClO_5SNa$ [M + Na]$^+$ = 455.0696, found $C_{22}H_{21}ClO_5SNa$ [M + Na]$^+$ = 455.0695.

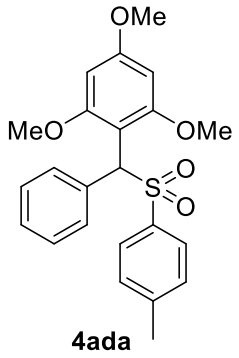
12. *2-(((4-bromophenyl)sulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene* **4aca**



4aca

Yield: 80%; white solid; Mp: 127-128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 4H), 7.53 – 7.45 (m, 2H), 7.35 – 7.24 (m, 3H), 6.17 (s, 1H), 6.08 (s, 2H), 3.81 (s, 3H), 3.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.90, 159.63, 140.10, 134.49, 131.42, 130.34, 130.19, 129.76, 129.02, 128.06, 127.86, 103.80, 92.91, 91.05, 68.08, 55.61, 55.36. HRMS (ESI): calculated for $C_{22}H_{21}BrO_5SNa$ $[M + Na]^+$ = 499.0191, found $C_{22}H_{21}BrO_5SNa$ $[M + Na]^+$ = 499.0149.

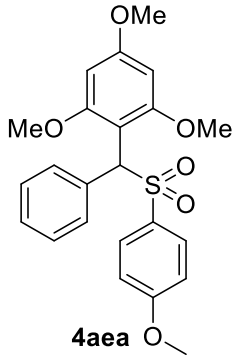
13. *1,3,5-trimethoxy-2-(phenyl(tosyl)methyl)benzene* **4ada**[2]



4ada

Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.50 (m, 4H), 7.33 – 7.25 (m, 3H), 7.20 (dd, *J* = 7.4, 1.3 Hz, 2H), 6.18 (s, 1H), 6.08 (s, 2H), 3.80 (s, 3H), 3.67 (s, 6H), 2.40 (s, 3H). 13C NMR (101 MHz, $CDCl_3$): δ 161.64, 143.35, 138.21, 134.40, 130.21, 128.80, 128.68, 127.88, 127.58, 104.34, 91.05, 67.80, 55.61, 55.30, 21.51. HRMS (ESI): calculated for $C_{23}H_{24}O_5SNa[M + Na]^+$ = 435.1242, found $C_{23}H_{24}O_5SNa$ $[M + Na]^+$ = 435.1228.

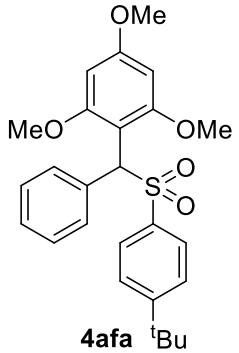
14. *1,3,5-trimethoxy-2-(((4-methoxyphenyl)sulfonyl)(phenyl)methyl)benzene* **4aea**



4aea

Yield: 75%; white solid; Mp: 120-121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.53 (m, 4H), 7.33 – 7.22 (m, 3H), 6.90 – 6.83 (m, 2H), 6.17 (s, 1H), 6.08 (s, 2H), 3.83 (d, *J* = 18.2 Hz, 6H), 3.68 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$): δ 162.95, 161.65, 161.53, 134.52, 134.50, 132.84, 130.83, 130.23, 129.76, 129.02, 127.91, 127.58, 113.36, 104.48, 92.91, 91.09, 67.94, 55.68, 55.57, 55.33. $C_{23}H_{24}O_6SNa[M + Na]^+$ = 451.1191, found $C_{23}H_{24}O_6SNa$ $[M + Na]^+$ = 451.1187.

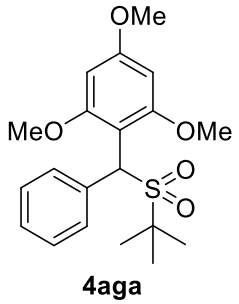
15. *2-(((4-(tert-butyl)phenyl)sulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene* **4afa**



4afa

Yield: 76%; white solid; Mp: 115-116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (ddt, *J* = 9.0, 4.3, 2.7 Hz, 4H), 7.44 – 7.37 (m, 2H), 7.35 – 7.23 (m, 3H), 6.19 (s, 1H), 6.05 (s, 2H), 3.80 (s, 3H), 3.63 (s, 6H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.71, 156.38, 138.10, 134.50, 134.44, 130.17, 129.76, 129.01, 128.55, 128.45, 127.87, 127.53, 125.59, 125.15, 104.34, 92.91, 91.02, 67.59, 55.60, 55.34, 55.32, 35.11, 31.12, 29.71. HRMS (ESI): calculated for $C_{26}H_{30}O_5SNa$[M + Na]$^+$ = 477.1712, found $C_{26}H_{30}O_5SNa$[M + Na]$^+$ = 477.1705.

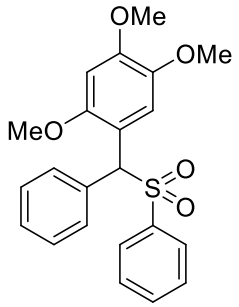
16. *2-((tert-butylsulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene* **4aga**



4aga

Yield: 75%; white solid; Mp: 112-113 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.70 (m, 2H), 7.26 – 7.11 (m, 3H), 6.30 (s, 1H), 6.05 (t, *J* = 1.9 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.70 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.35, 160.29, 157.84, 137.12, 130.36, 128.02, 127.51, 105.97, 91.71, 91.07, 62.36, 57.62, 56.18, 55.77, 55.31, 24.18. HRMS (ESI): calculated for $C_{20}H_{26}O_5SNa$ [M + Na]$^+$ = 401.1399, found $C_{20}H_{26}O_5SNa$ [M + Na]$^+$ = 401.1383.

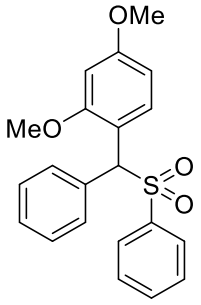
17. *1,2,4-trimethoxy-5-(phenyl(phenylsulfonyl)methyl)benzene* **4aab**[2]



4aab

Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.57 (m, 5H), 7.56 – 7.50 (m, 1H), 7.42 – 7.29 (m, 5H), 6.32 (s, 1H), 6.03 (s, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.64, 149.97, 143.14, 138.84, 133.34, 133.16, 129.99, 128.86, 128.61, 128.34, 128.33, 113.25, 112.74, 96.78, 66.32, 56.61, 56.33, 55.95. HRMS (ESI): calculated for $C_{22}H_{22}O_5SNa$[M + Na]$^+$ = 421.1086, found $C_{22}H_{22}O_5SNa$[M + Na]$^+$ = 421.1091.

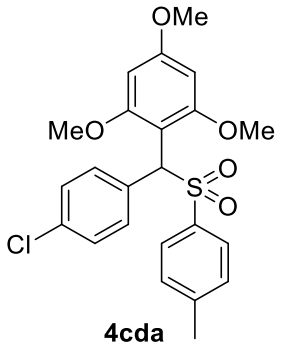
18. *2,4-dimethoxy-1-(phenyl(phenylsulfonyl)methyl)benzene* **4aac**



4aac

Yield: 69%; white solid; Mp: 111-112 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.40 (m, 1H), 7.34 – 7.21 (m, 4H), 7.19 (s, 1H), 6.49 (dd, J = 8.7, 2.5 Hz, 1H), 6.17 (d, J = 2.5 Hz, 1H), 5.90 (s, 1H), 3.71 (s, 3H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.95, 157.86, 138.92, 133.45, 133.09, 130.88, 130.10, 128.94, 128.53, 128.27, 128.25, 114.13, 109.99, 104.67, 98.24, 66.32, 55.37, 55.34.

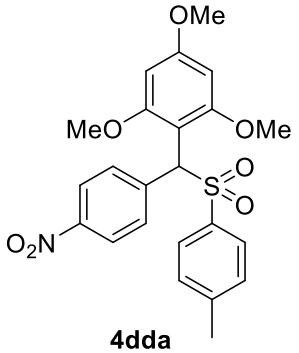
19. *2-((4-chlorophenyl)(tosyl)methyl)-1,3,5-trimethoxybenzene* **4cda**



4cda

Yield: 81%; white solid; Mp: 108-109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.47 (m, 4H), 7.31 – 7.17 (m, 4H), 6.11 (s, 1H), 6.06 (s, 2H), 3.81 (s, 3H), 3.76 – 3.54 (s, 6H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.81, 143.59, 137.87, 133.46, 133.01, 131.55, 128.90, 128.66, 128.01, 103.76, 91.02, 66.86, 55.61, 55.31, 21.52. HRMS (ESI): calculated for $C_{23}H_{23}ClO_5SNa$ [M + Na]$^+$ = 469.0852, found $C_{23}H_{23}ClO_5SNa$ [M + Na]$^+$ = 469.0830.

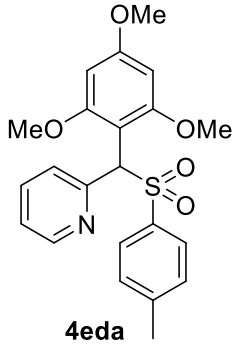
20. *1,3,5-trimethoxy-2-((4-nitrophenyl)(tosyl)methyl)benzene* **4dda**



4dda

Yield: 86%; white solid; Mp: 133-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.01 (m, 2H), 7.76 – 7.65 (m, 2H), 7.50 – 7.40 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.11 (s, 1H), 5.94 (s, 2H), 3.71 (s, 3H), 3.52 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.25, 146.93, 144.03, 142.37, 137.25, 130.83, 128.99, 128.72, 122.88, 102.76, 90.95, 66.39, 55.58, 55.35, 21.54. HRMS (ESI): calculated for $C_{23}H_{23}NO_7SNa$ $[M + Na]^+$ = 480.1093, found $C_{23}H_{23}NO_7SNa$ $[M + Na]^+$ = 469.1061.

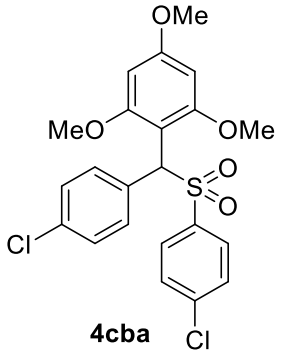
21. *2-(tosyl(2,4,6-trimethoxyphenyl)methyl)pyridine* **4eda**



4eda

Yield: 72%; white solid; Mp: 131-132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 8.08 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.66 (td, *J* = 7.8, 1.9 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.20 – 7.16 (m, 2H), 7.13 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.32 (s, 1H), 5.99 (s, 2H), 3.76 (s, 3H), 3.52 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.00, 154.92, 148.60, 143.55, 137.92, 135.72, 128.97, 128.76, 125.15, 122.14, 102.97, 91.02, 68.71, 55.55, 55.28, 21.51. HRMS (ESI): calculated for $C_{22}H_{23}NO_5SNa$ $[M + Na]^+$ = 436.1195, found $C_{22}H_{23}NO_5SNa$ $[M + Na]^+$ = 436.1194.

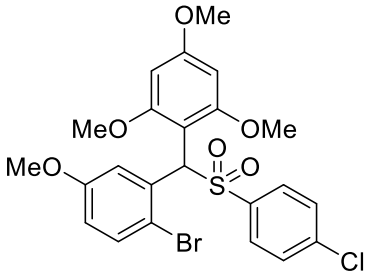
22. *2-((4-chlorophenyl)((4-chlorophenyl)sulfonyl)methyl)-1,3,5-trimethoxybenzene* **4cba**



4cba

Yield: 93%; white solid; Mp: 133-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.40 (m, 4H), 7.33 – 7.25 (m, 2H), 7.21 – 7.14 (m, 2H), 6.01 (s, 1H), 5.96 (s, 2H), 3.71 (s, 3H), 3.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.03, 139.47, 139.15, 133.70, 132.48, 131.48, 130.16, 129.32, 128.50, 128.13, 127.19, 103.18, 90.97, 67.04, 55.58, 55.34. HRMS (ESI): calculated for $C_{22}H_{20}Cl_2O_5SNa$ $[M + Na]^+$ m/z = 489.0306, found $C_{22}H_{20}Cl_2O_5SNa[M + Na]^+$ m/z = 489.0322.

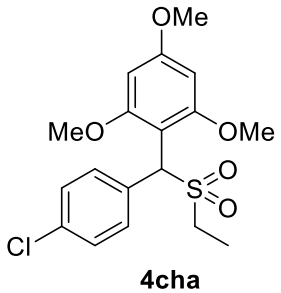
23. *2-((2-bromo-5-methoxyphenyl)((4-chlorophenyl)sulfonyl)methyl)-1,3,5-trimethoxybenzene* **4kba**



4kba

Yield: 71%; white solid; Mp: 161-162 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 3.1 Hz, 1H), 7.61 – 7.45 (m, 2H), 7.39 – 7.28 (m, 2H), 7.28 – 7.14 (m, 1H), 6.64 (dd, J = 8.8, 3.1 Hz, 1H), 6.27 (s, 1H), 5.96 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.06, 158.11, 139.59, 139.04, 134.64, 132.83, 130.49, 128.59, 118.51, 115.97, 115.54, 102.34, 91.05, 66.20, 55.57, 55.47, 55.28. HRMS (ESI): calculated for $C_{23}H_{22}BrClO_6SNa$ $[M + Na]^+$ m/z = 562.9907, found $C_{22}H_{20}Cl_2O_5SNa$ $[M + Na]^+$ m/z = 562.9906.

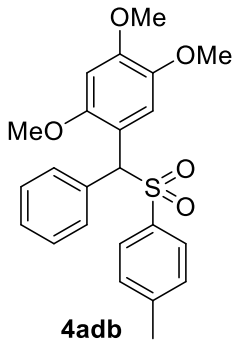
24. *2-((4-chlorophenyl)(ethylsulfonyl)methyl)-1,3,5-trimethoxybenzene* **4cha**



4cha

Yield: 75%; white solid; Mp: 88-89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.45 (m, 2H), 7.24 – 7.17 (m, 2H), 6.10 (s, 2H), 6.05 (s, 1H), 3.75 (s, 3H), 3.73 (s, 6H), 2.88 (ddq, *J* = 45.8, 13.7, 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.91, 133.80, 132.53, 131.11, 128.37, 103.49, 91.36, 65.15, 55.78, 55.36, 46.70, 6.14. HRMS (ESI): calculated for $C_{18}H_{21}ClO_5SNa$ $[M + Na]^+$ = 407.0696, found $C_{18}H_{21}ClO_5SNa$ $[M + Na]^+$ = 407.0676.

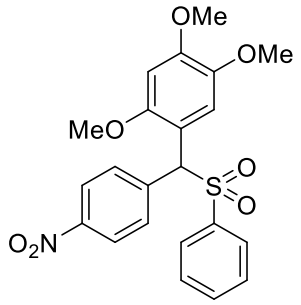
25. *1,2,4-trimethoxy-5-(phenyl(tosyl)methyl)benzene* **4adb**[2]



4adb

Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.54 (m, 3H), 7.54 – 7.48 (m, 2H), 7.36 – 7.28 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.33 (s, 1H), 5.98 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.52 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.66, 149.89, 144.00, 143.18, 135.98, 133.54, 130.01, 128.97, 128.88, 128.54, 128.25, 113.26, 97.03, 66.40, 56.61, 56.44, 55.97, 21.54. HRMS (ESI): calculated for $C_{23}H_{24}O_5SNa$ $[M + Na]^+$ = 435.1242, found $C_{23}H_{24}O_5SNa$ $[M + Na]^+$ = 435.1225.

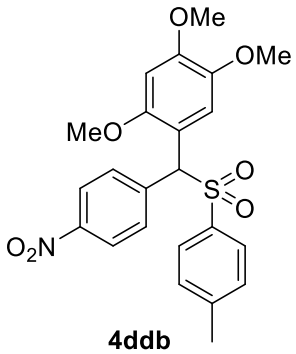
26. *1,2,4-trimethoxy-5-((4-nitrophenyl)(phenylsulfonyl)methyl)benzene* **4dab**



4dab

Yield: 89%; white solid; Mp: 160-161 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.12 (m, 2H), 7.83 – 7.71 (m, 2H), 7.68 – 7.58 (m, 2H), 7.59 – 7.49 (m, 1H), 7.43 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 6.27 (s, 1H), 6.08 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.66, 150.53, 147.60, 143.32, 140.85, 138.28, 133.65, 130.88, 128.82, 128.58, 123.64, 112.94, 111.31, 96.64, 65.69, 56.72, 56.15, 55.98. HRMS (ESI): calculated for $C_{22}H_{20}NO_7S$ $[M - H]^+$ = 442.0955, found $C_{22}H_{20}NO_7S$ $[M - H]^+$ = 442.0951.

27. *1,2,4-trimethoxy-5-((4-nitrophenyl)(tosyl)methyl)benzene* **4ddb**[2]

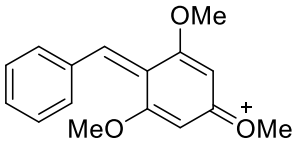


4ddb

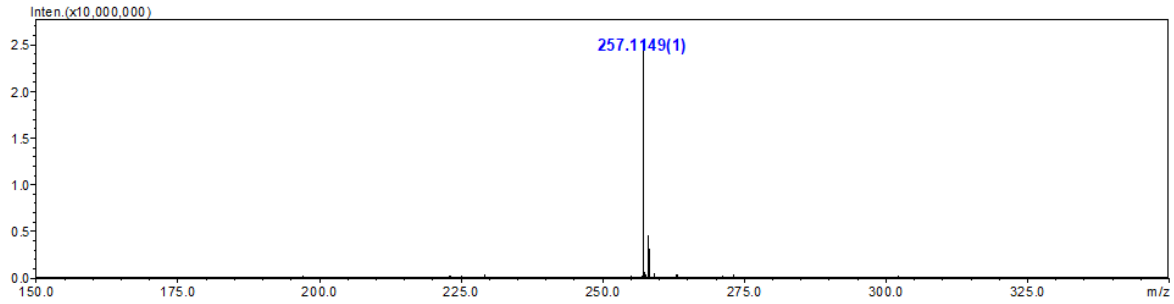
Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 – 8.09 (m, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.47 (s, 1H), 7.21 – 7.13 (m, 2H), 6.30 (s, 1H), 6.04 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.49 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.67, 150.42, 147.57, 144.68, 143.33, 141.06, 135.39, 130.89, 129.24, 128.84, 123.60, 112.87, 111.63, 96.81, 65.79, 56.70, 56.25, 55.99, 21.59. HRMS (ESI): calculated for $C_{23}H_{22}NO_7S$ [M - H]$^+$ = 456.1111, found $C_{22}H_{20}NO_7S$[M - H]$^+$ = 456.1114.

4. Trapping reaction intermediates C and D

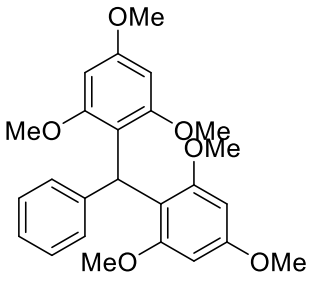
Reaction Intermediate **C**



HRMS (ESI): calculated for $C_{16}H_{17}O_3^+$[M]$^+$ = 257.1172, found $C_{16}H_{17}O_3^+$[M]$^+$ = 257.1149.



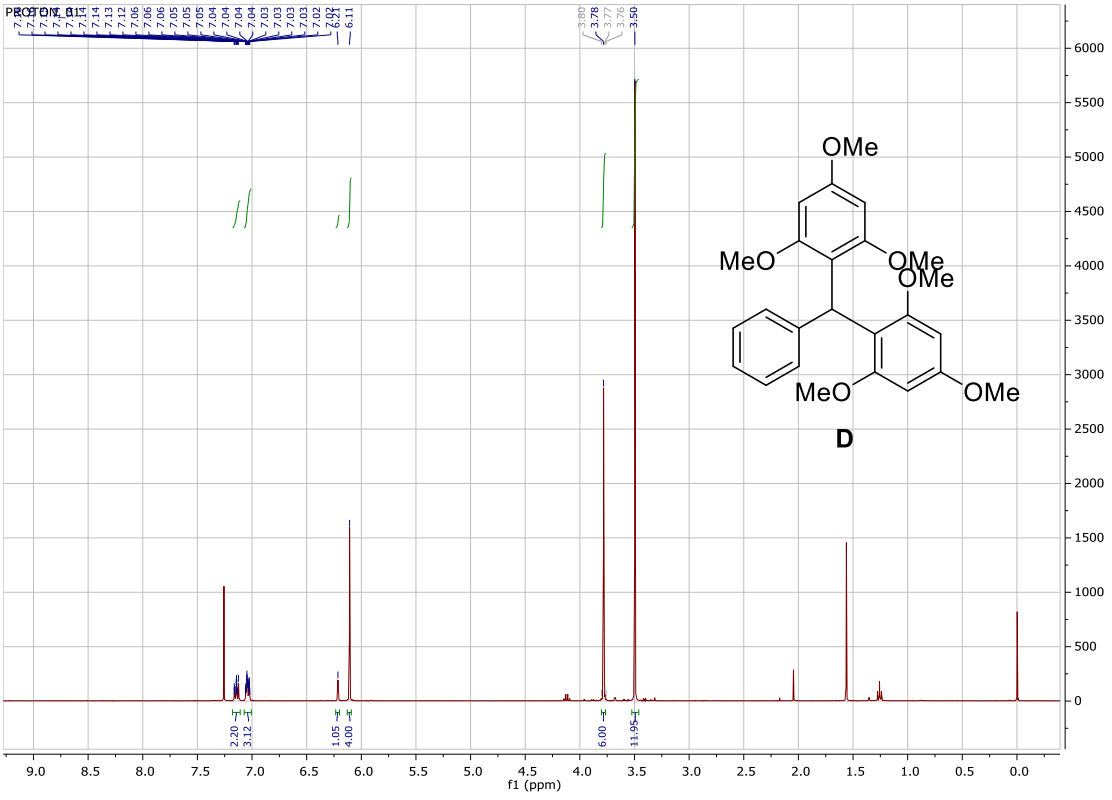
Reaction Intermediate **D**[2]



D

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 2H), 7.04 (dddd, J = 7.8, 3.8, 2.0, 1.2 Hz, 3H), 6.21 (s, 1H), 6.11 (s, 4H), 3.78 (s, 6H), 3.50 (s, 12H).

2,2'-(phenylmethylene)bis(1,3,5-trimethoxybenzene) **D**

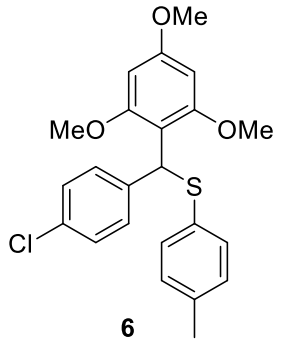


5. Procedure for the synthesis of compound 6

The compounds **4caa** (0.5 mmol) and 4-methylbenzenethiol **5** (0.55 mmol) were taken into DCM (2mL) solvent which was already added in 25mL dried glass reaction tube, then added $FeCl_3$(10 mol%) and stirred the reaction mixture for 1h at room temperature. The reaction was completed after 1h confirmed by the TLC. The reaction mixture was concentrated on a rotary evaporator. The

concentrated reaction mixture was extracted with ethyl acetate (3 × 5 mL) and dried over anhydrous $MgSO_4$. Then organic layer was adsorbed on some silica gel under reduced pressure on a rotary evaporator. After purified by column chromatography (Petroleum ether : Ethyl acetate = 10 : 1 used as eluents), white solid of product **6** was obtained in 84% yield.

28. *((4-chlorophenyl)(2,4,6-trimethoxyphenyl)methyl)(p-tolyl)sulfane* **6**

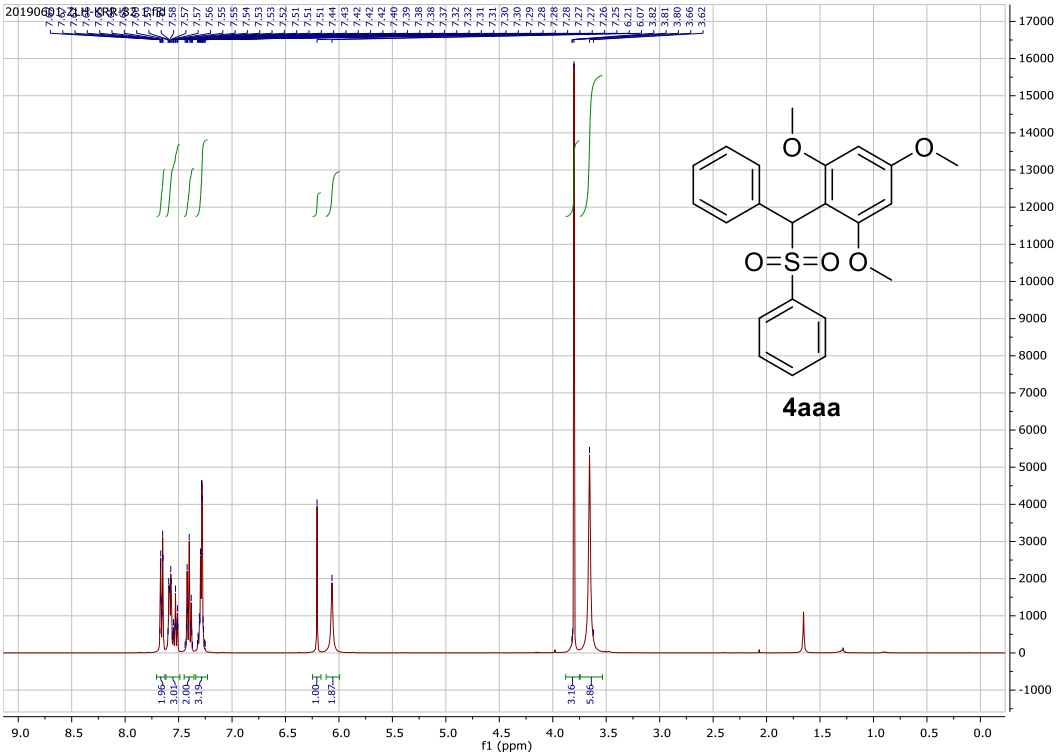


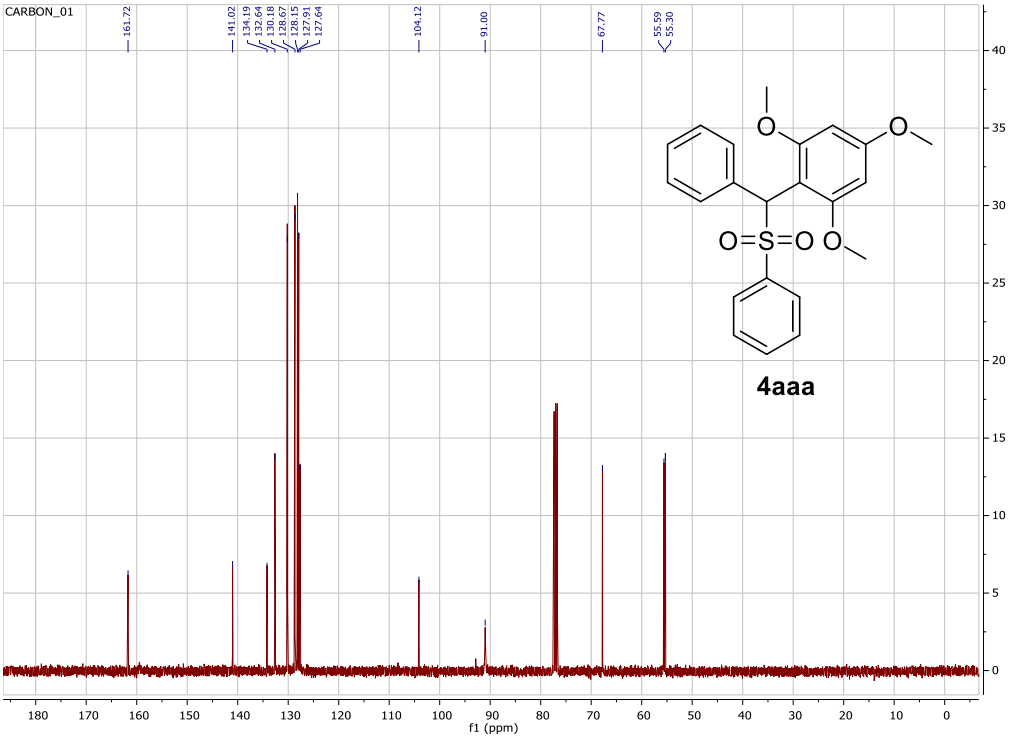
6

Yield: 84%; white solid; Mp: 120-121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.33 (m, 2H), 7.20 – 7.07 (m, 5H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.04 (s, 2H), 5.89 (s, 1H), 3.72 (s, 3H), 3.66 (s, 6H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, CDCl3): δ 160.60, 141.30, 135.97, 134.86, 131.56, 130.29, 129.75, 129.44, 129.23, 128.52, 127.69, 111.85, 91.29, 55.82, 55.30, 47.10, 20.98. HRMS (ESI): calculated for $C_{23}H_{23}ClKO_3S$ $[M + K]^+$ = 453.0693, found $C_{23}H_{23}ClNaO_3S$ $[M + K]^+$ = 453.0917.

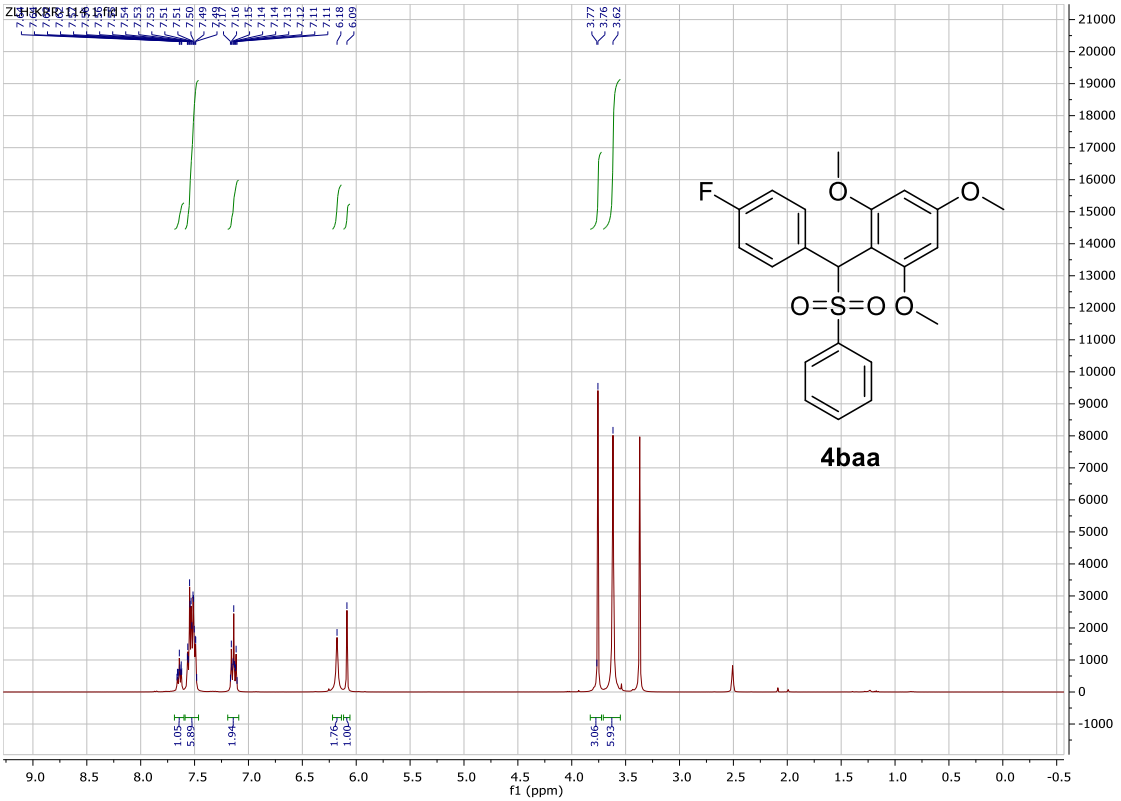
6. ^{1}HNMR & ^{13}CNMR spectra of the products 4 and 6

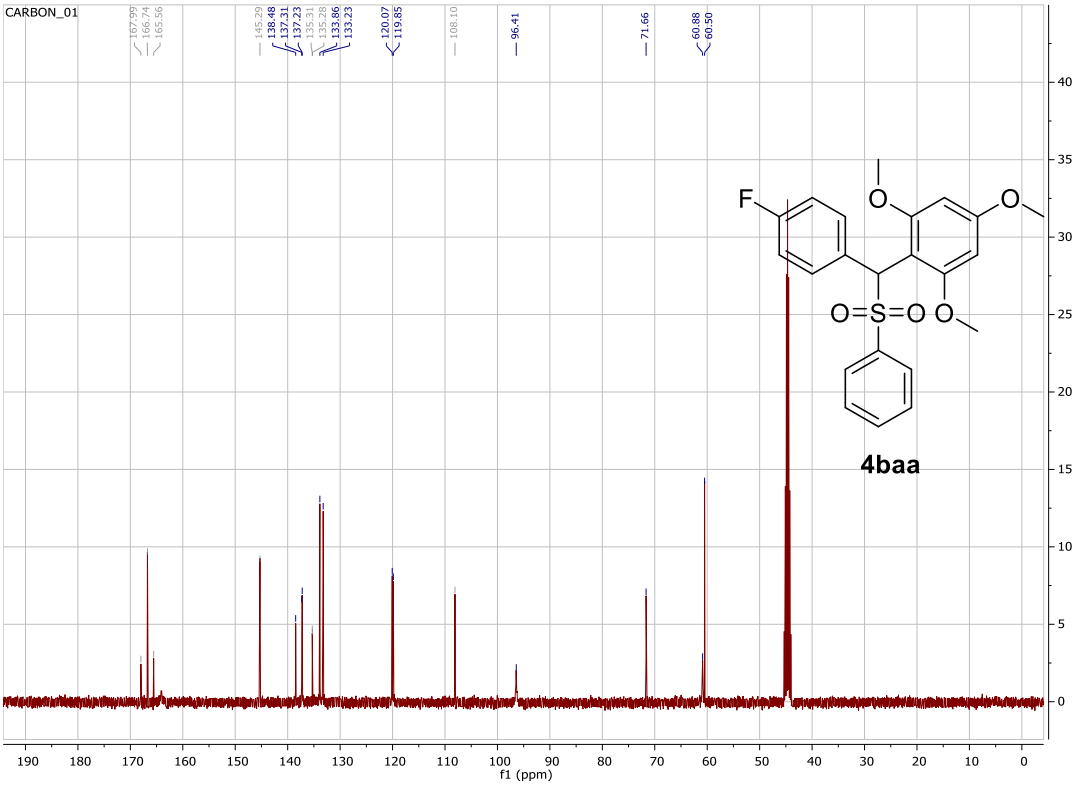
1. ^{1}HNMR & ^{13}CNMR spectra of 4aaa



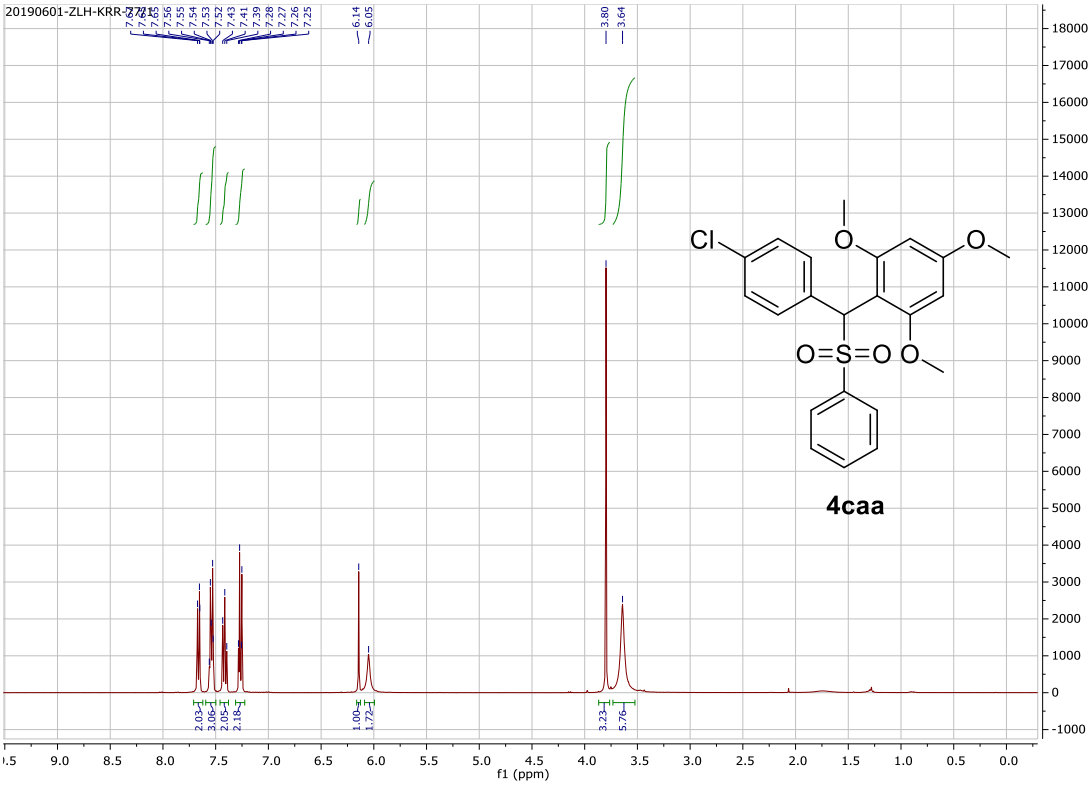


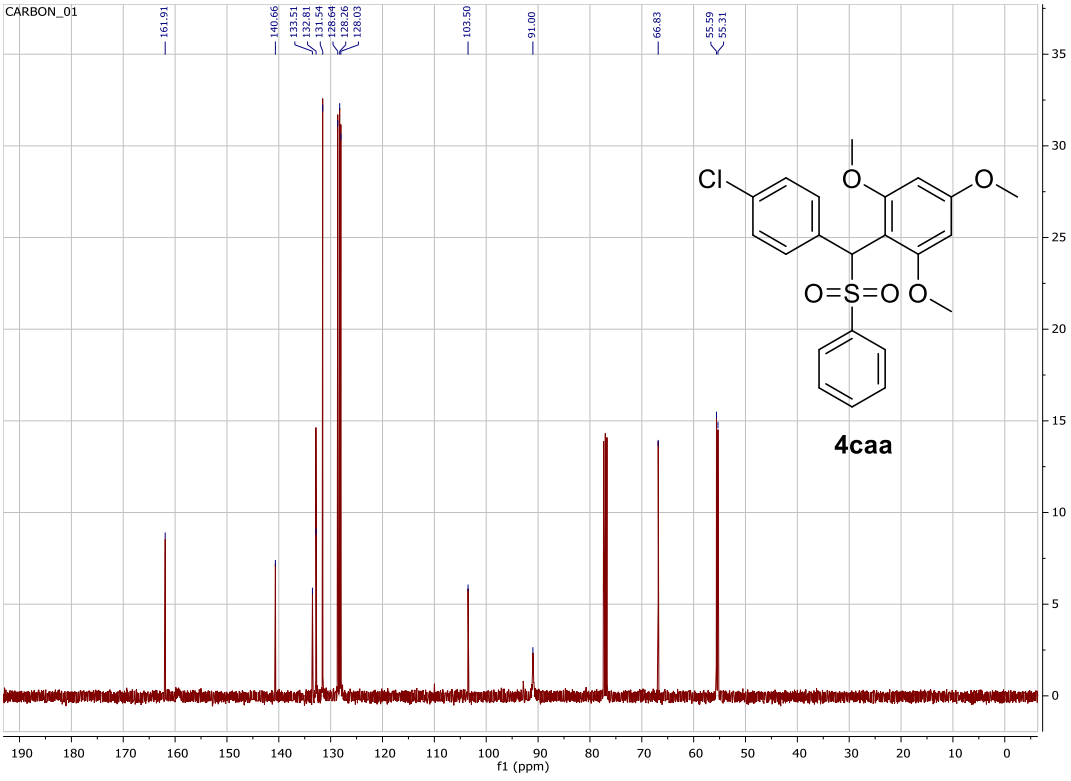
2. ^{1}HNMR & ^{13}CNMR spectra of **4baa**



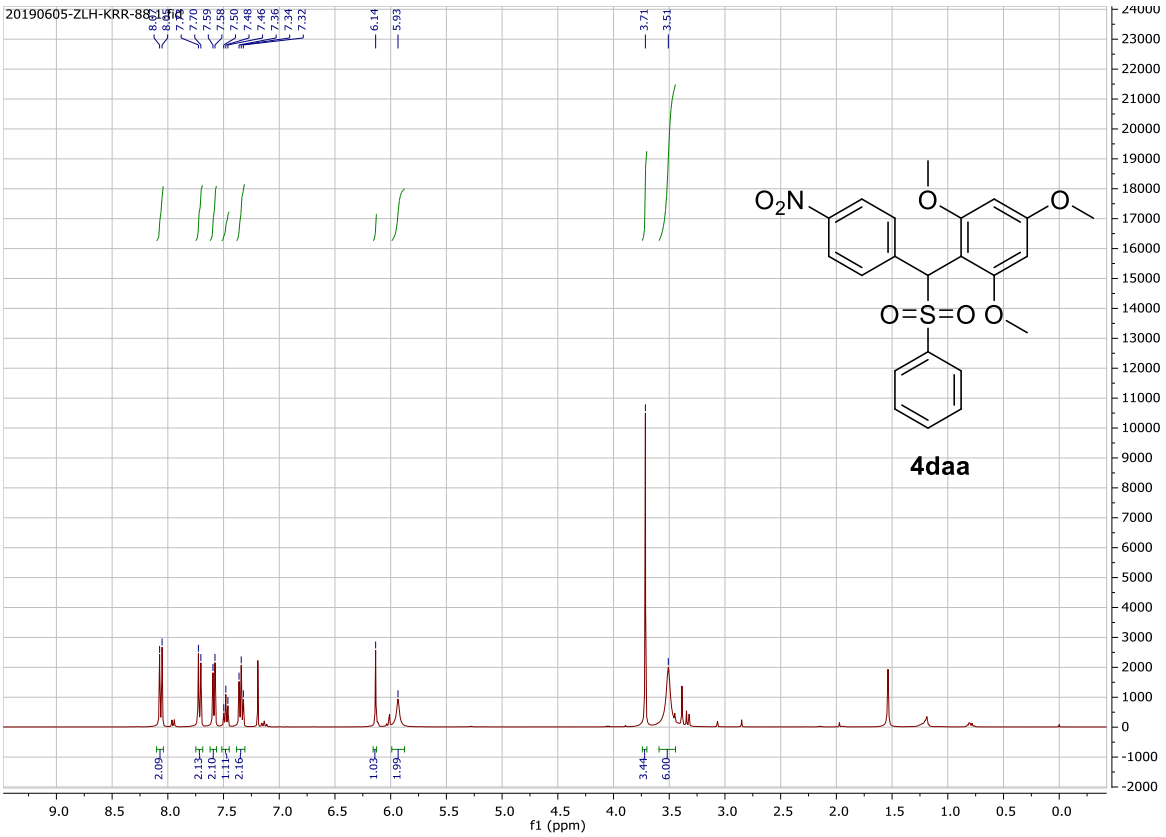


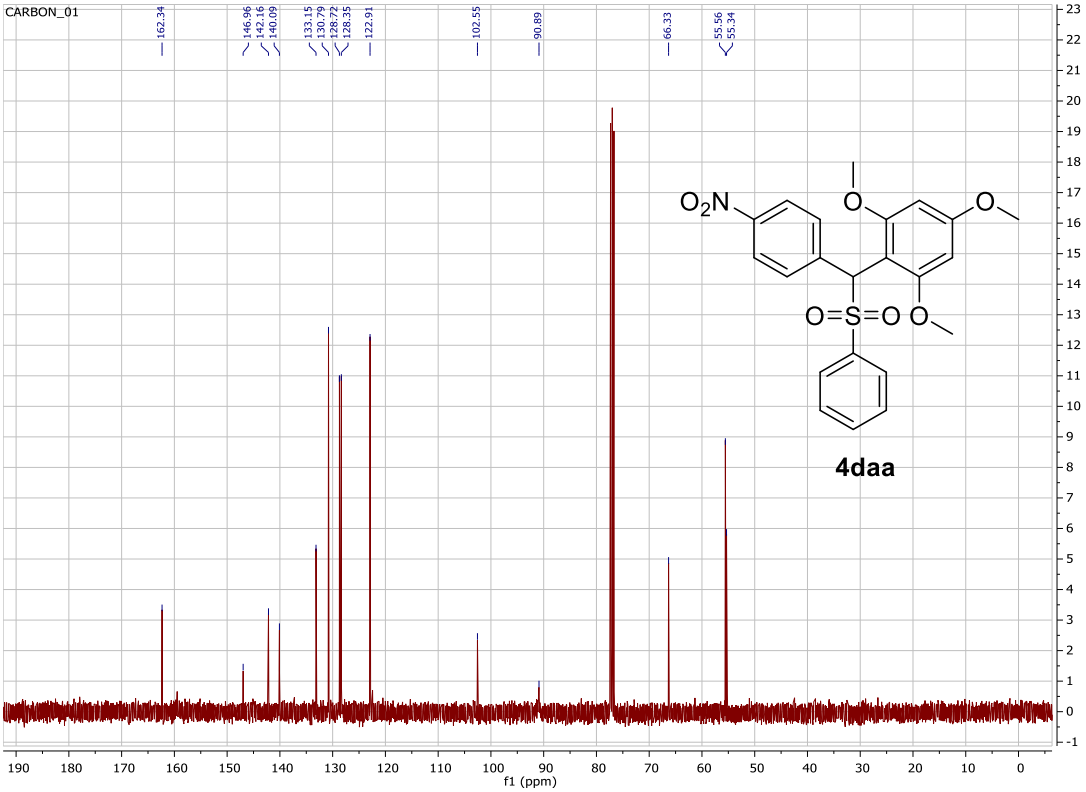
3. . ^{1}HNMR & ^{13}CNMR spectra of **4caa**



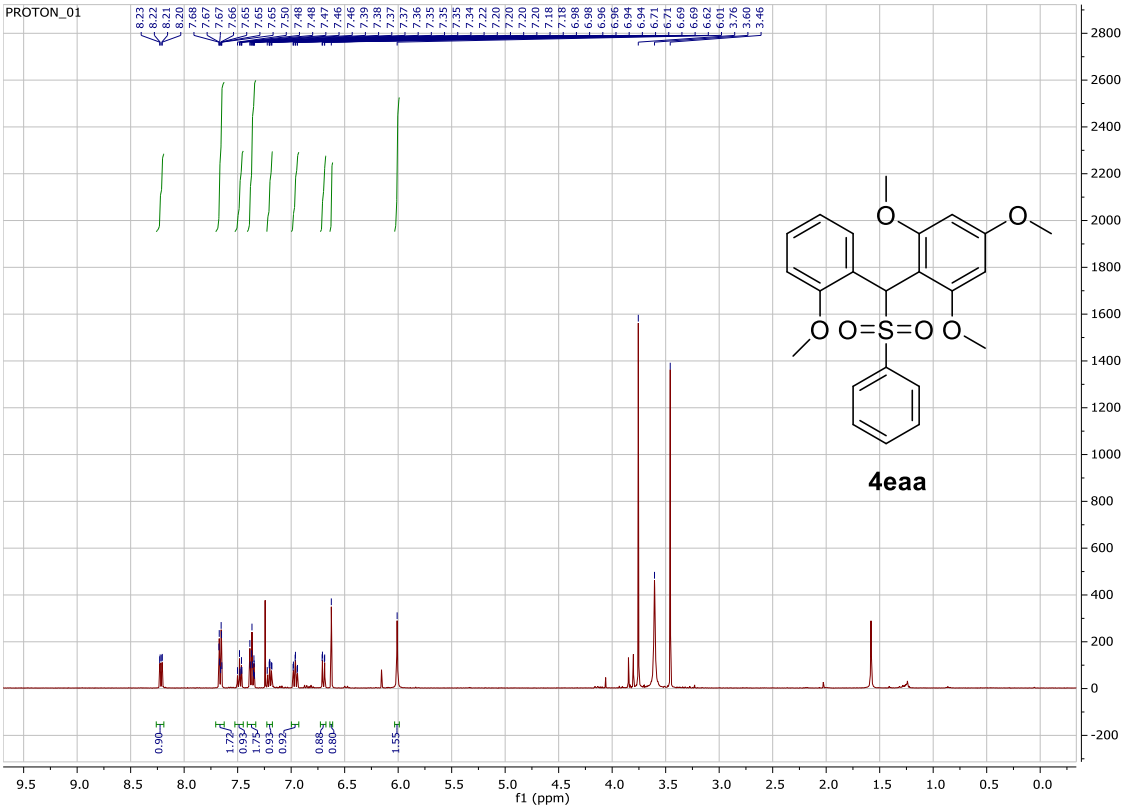


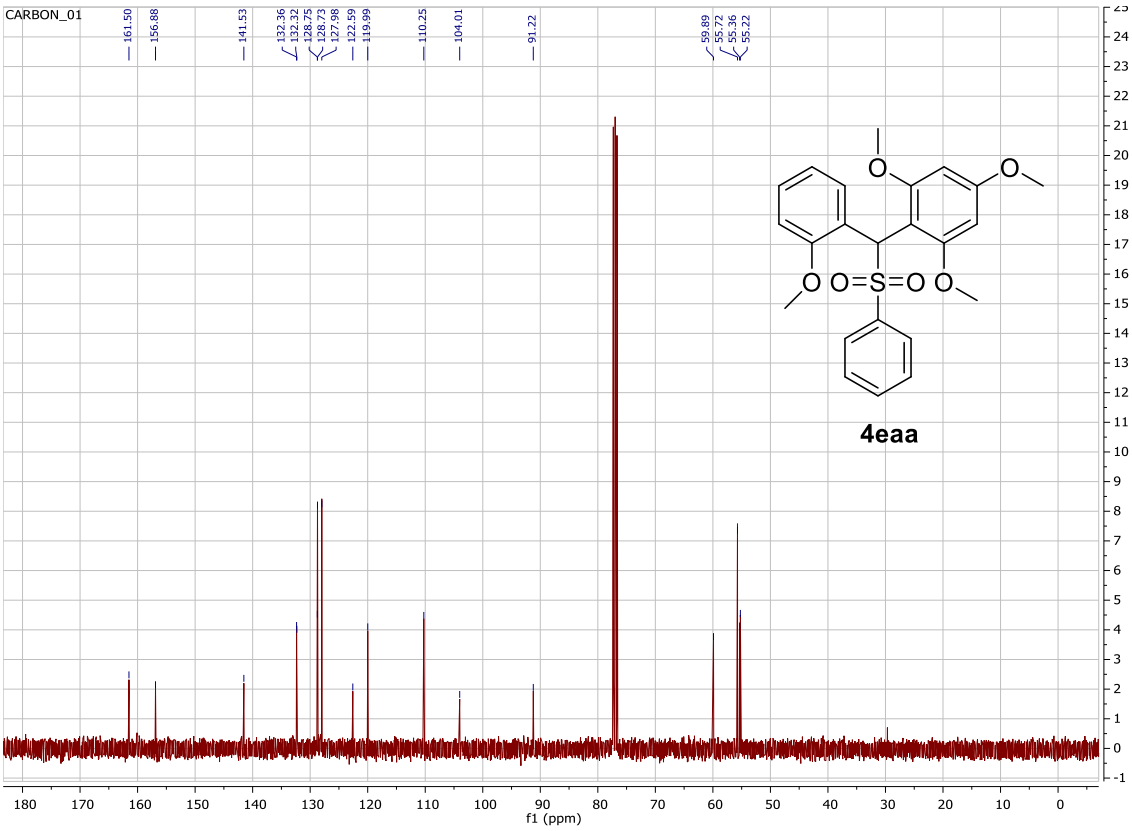
4. ^{1}HNMR & ^{13}CNMR spectra of **4daa**



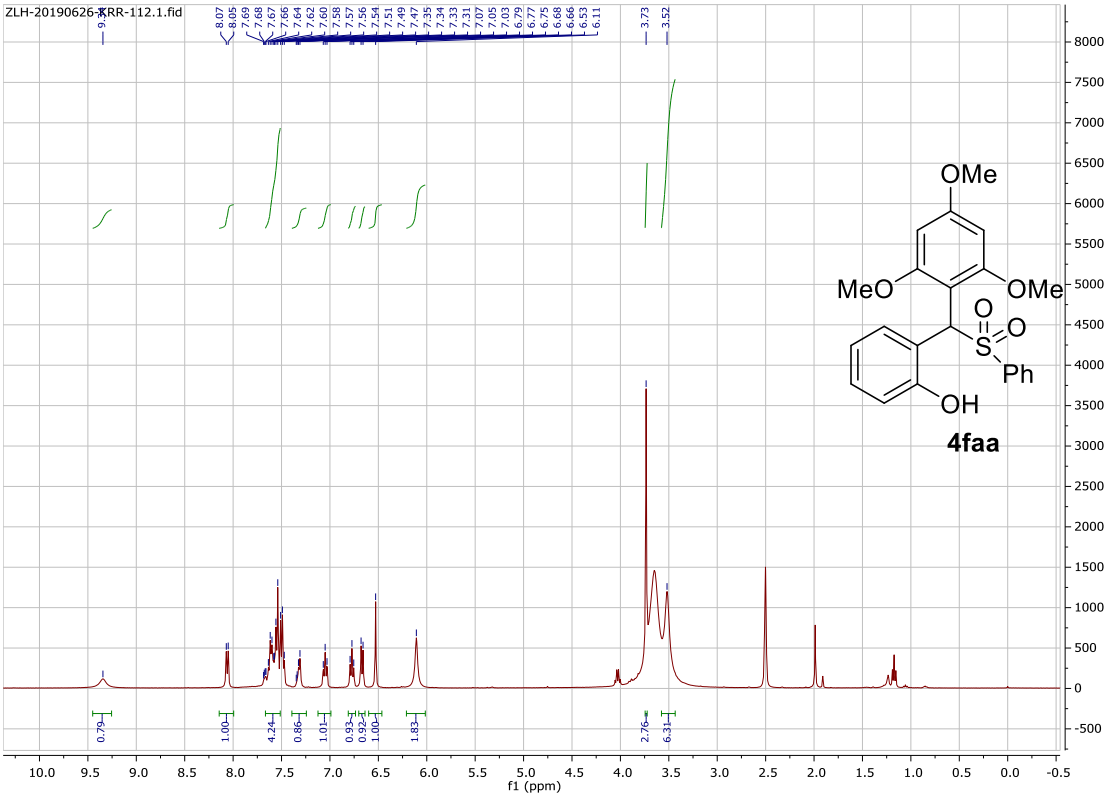


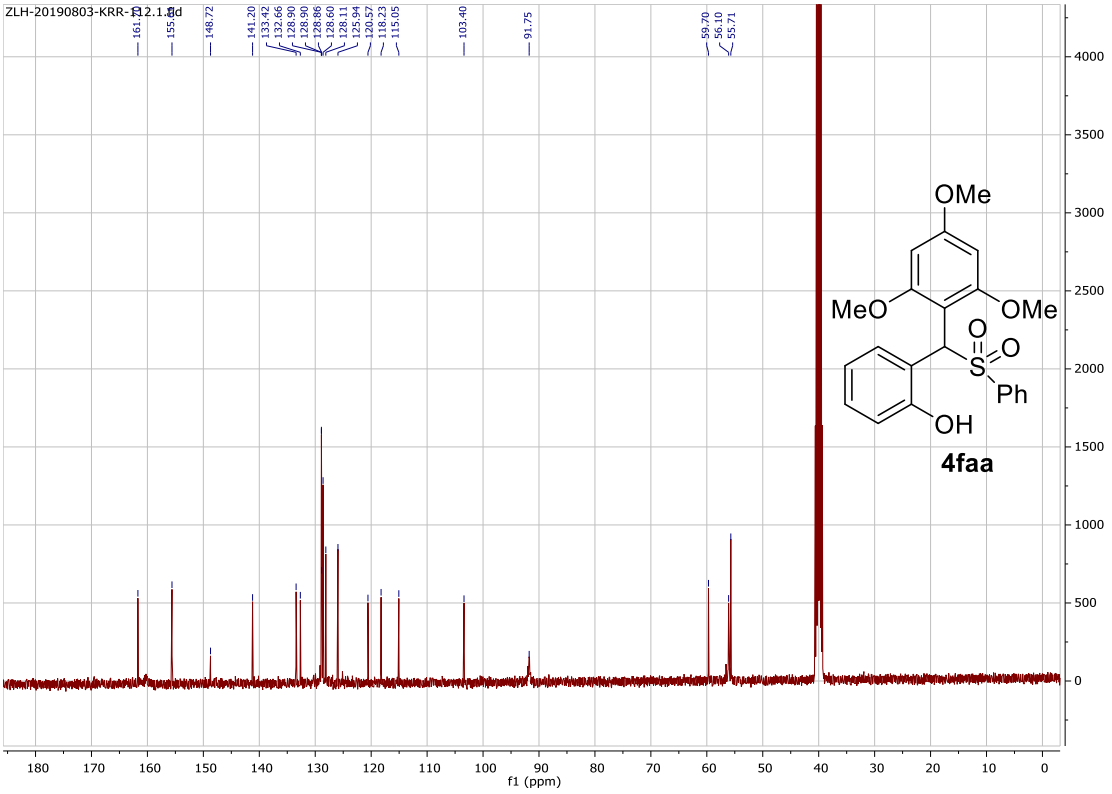
5. . ^{1}HNMR & ^{13}CNMR spectra of **4eaa**



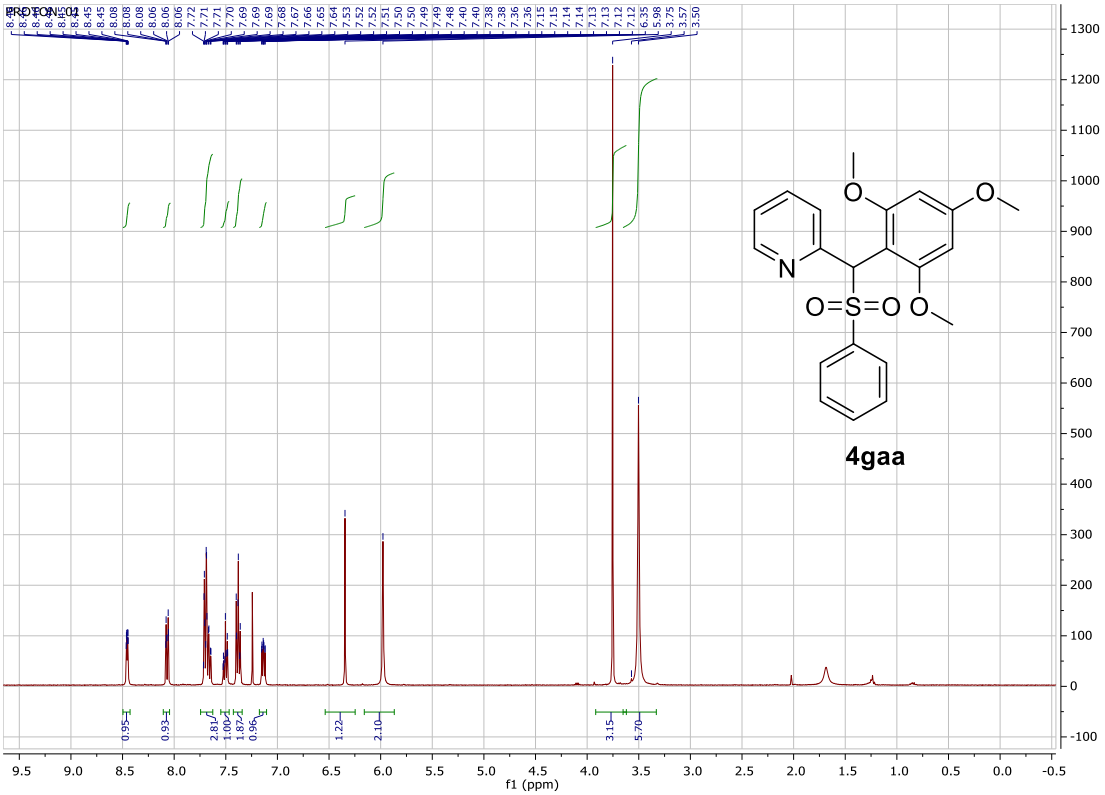


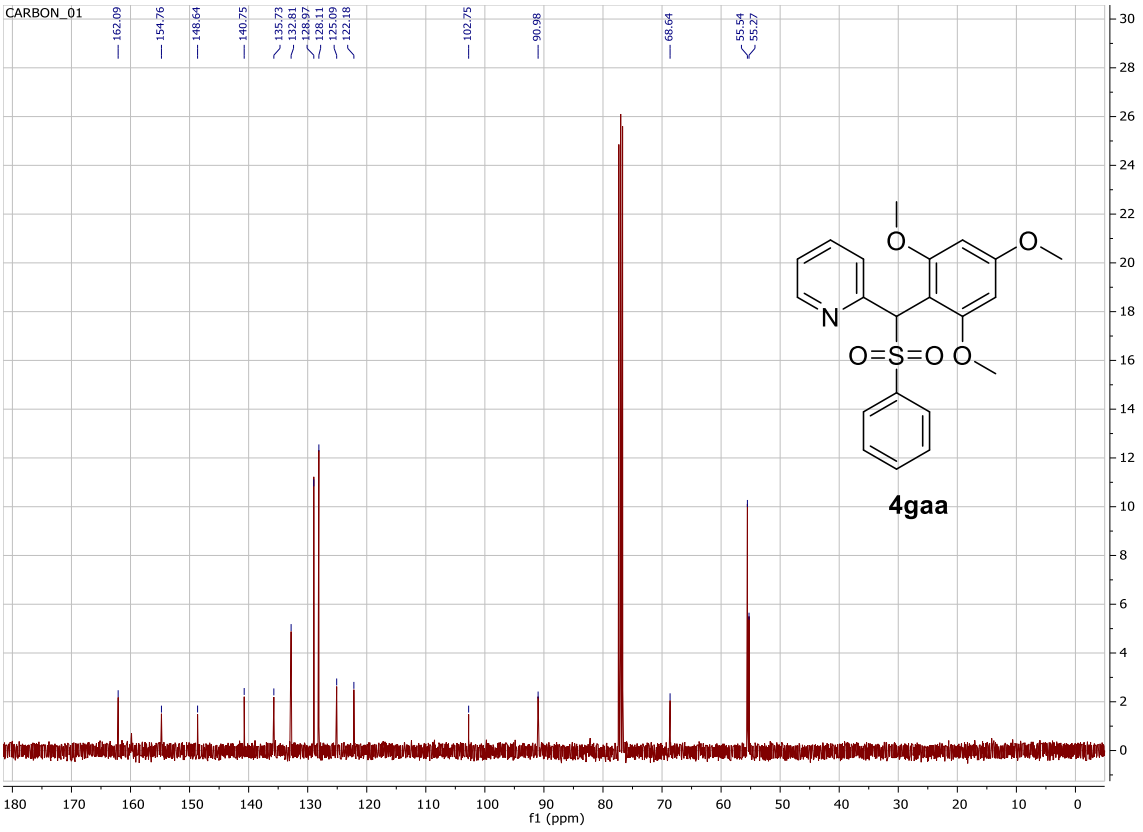
6. ^{1}HNMR & ^{13}CNMR spectra of **4faa**



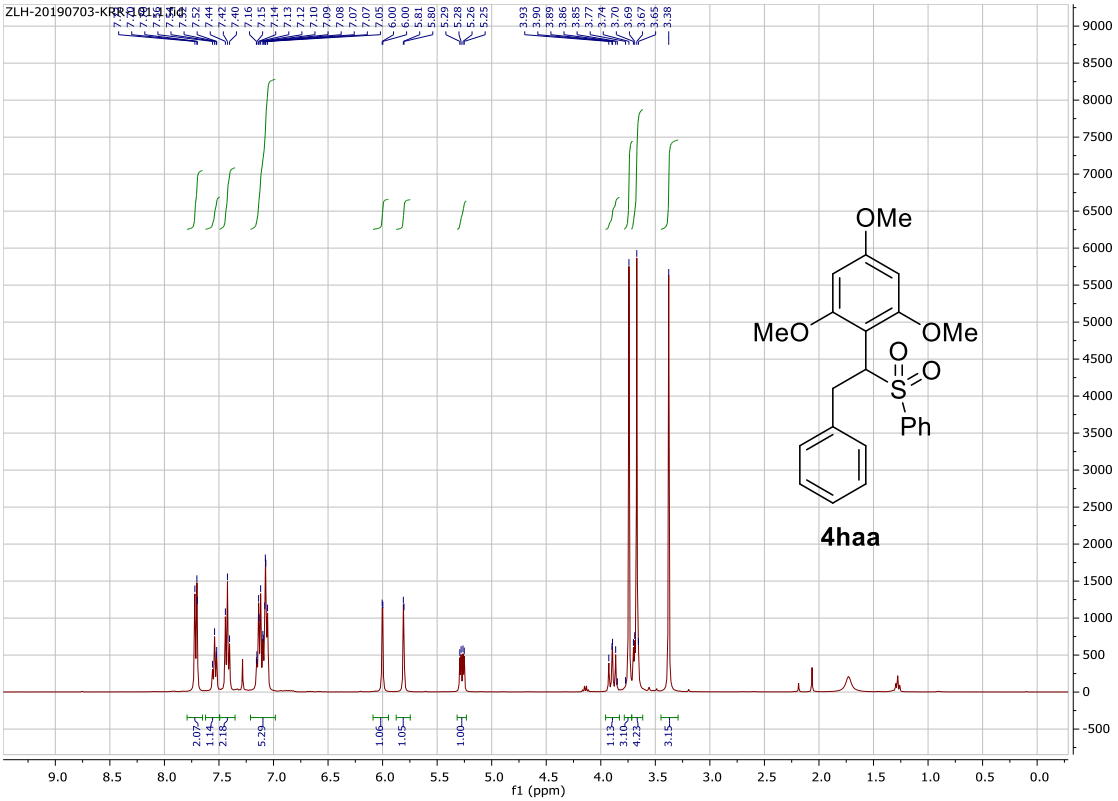


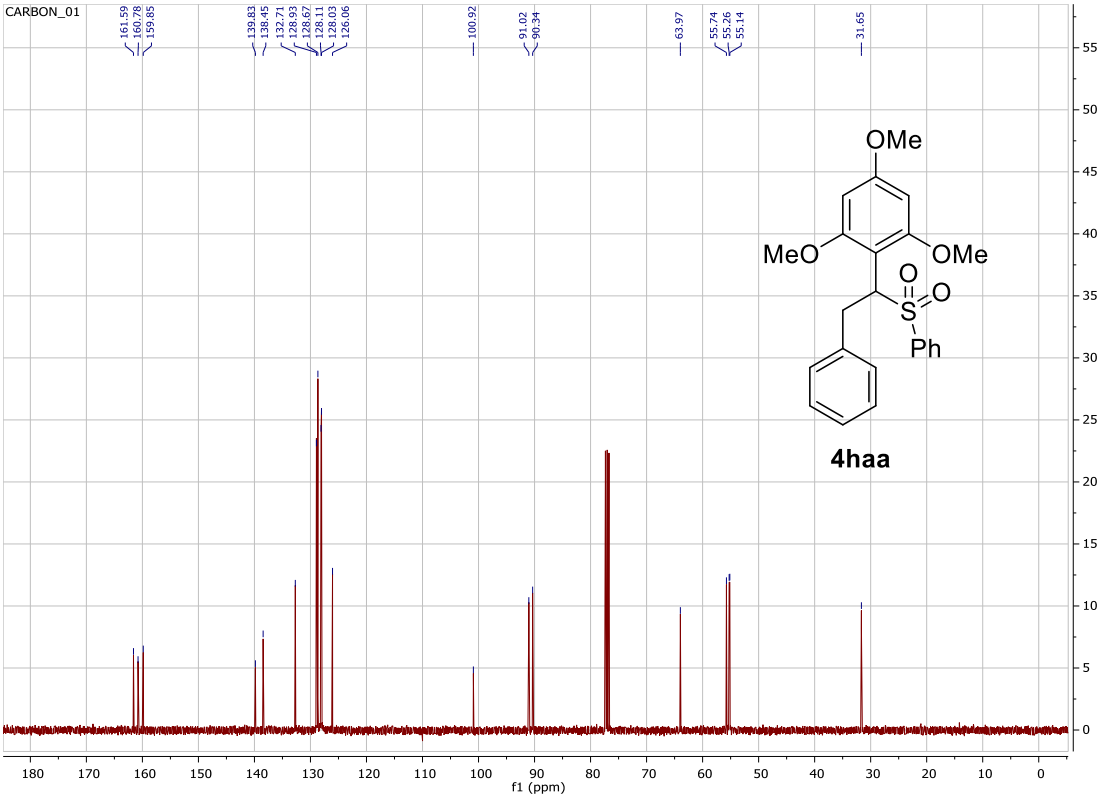
7. ^{1}HNMR & ^{13}CNMR spectra of **4gaa**



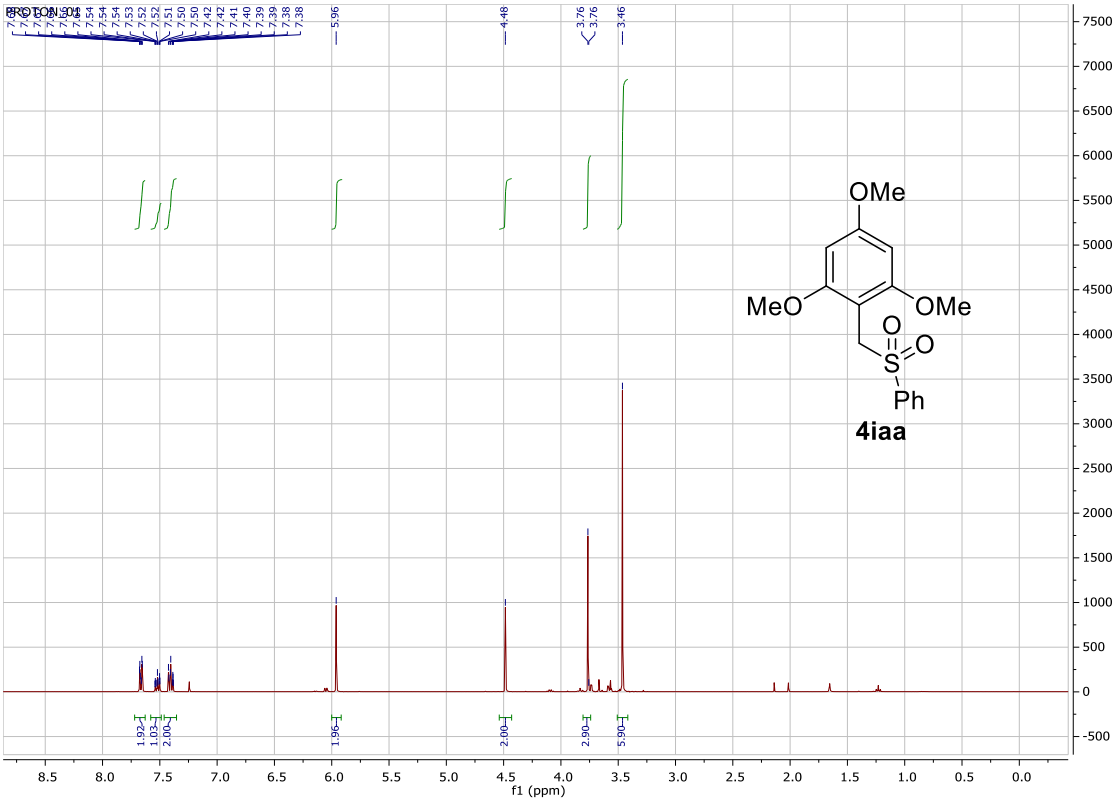


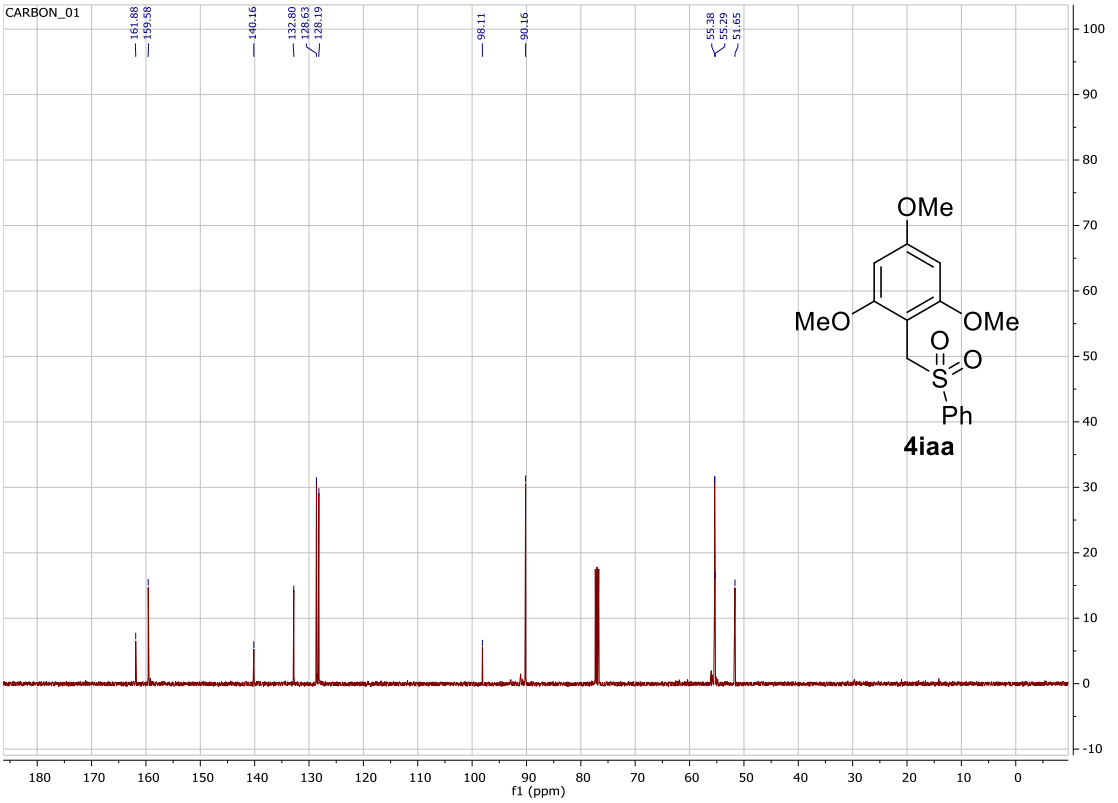
8. ^{1}HNMR & ^{13}CNMR spectra of **4haa**



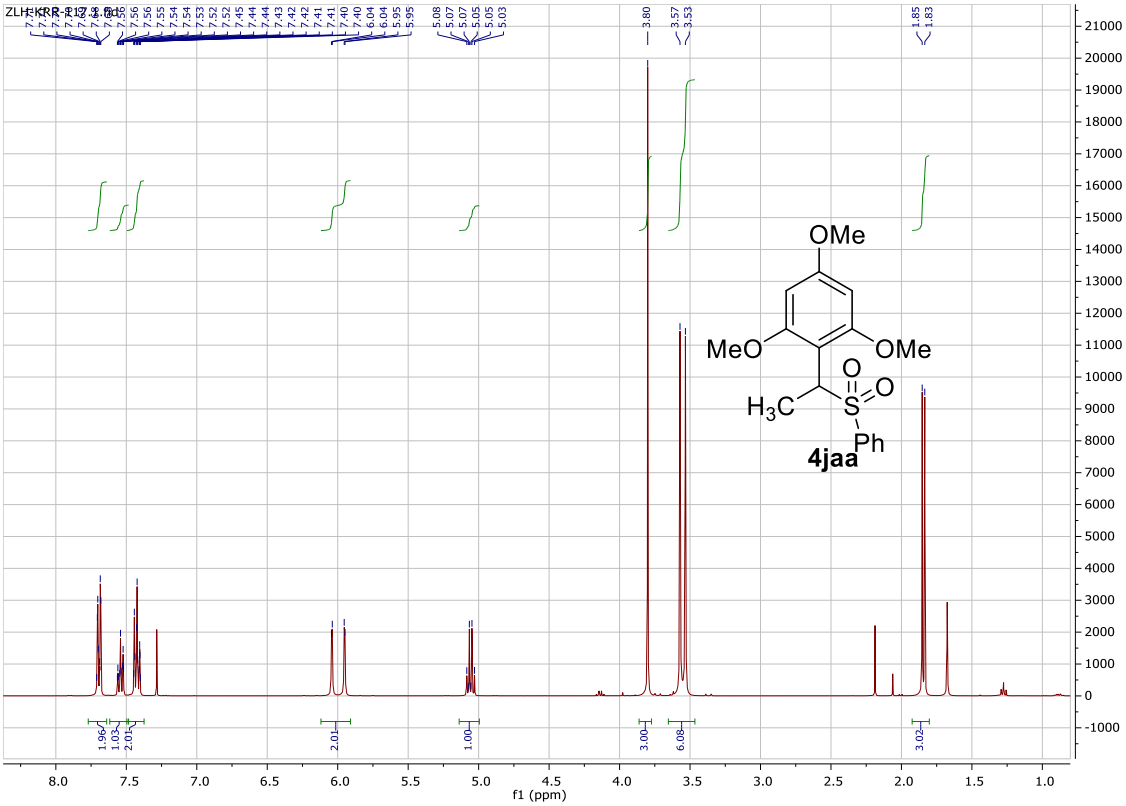


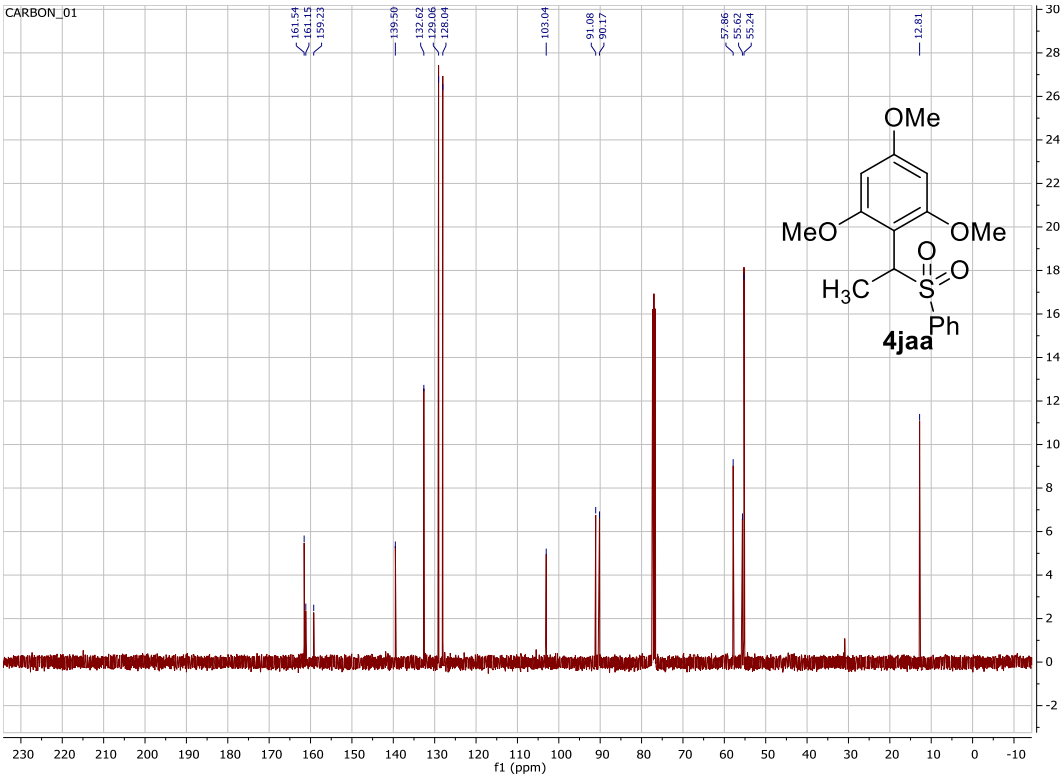
9. ^{1}HNMR & ^{13}CNMR spectra of **4iaa**



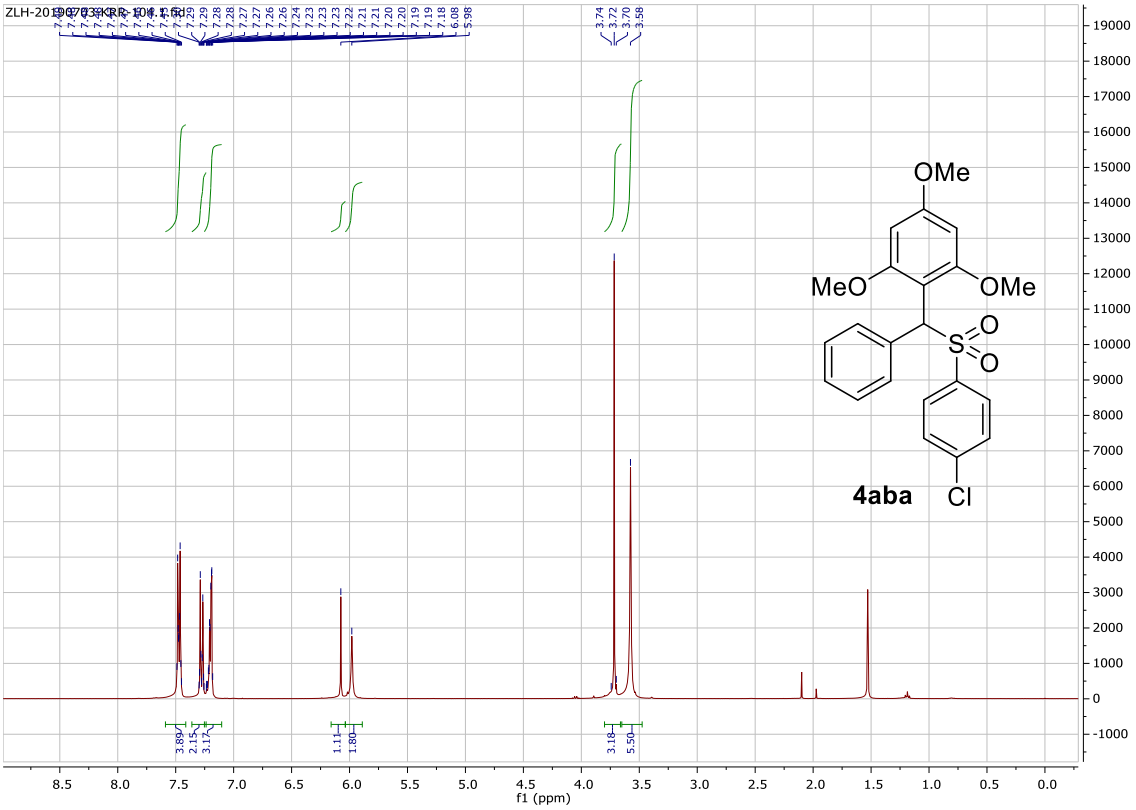


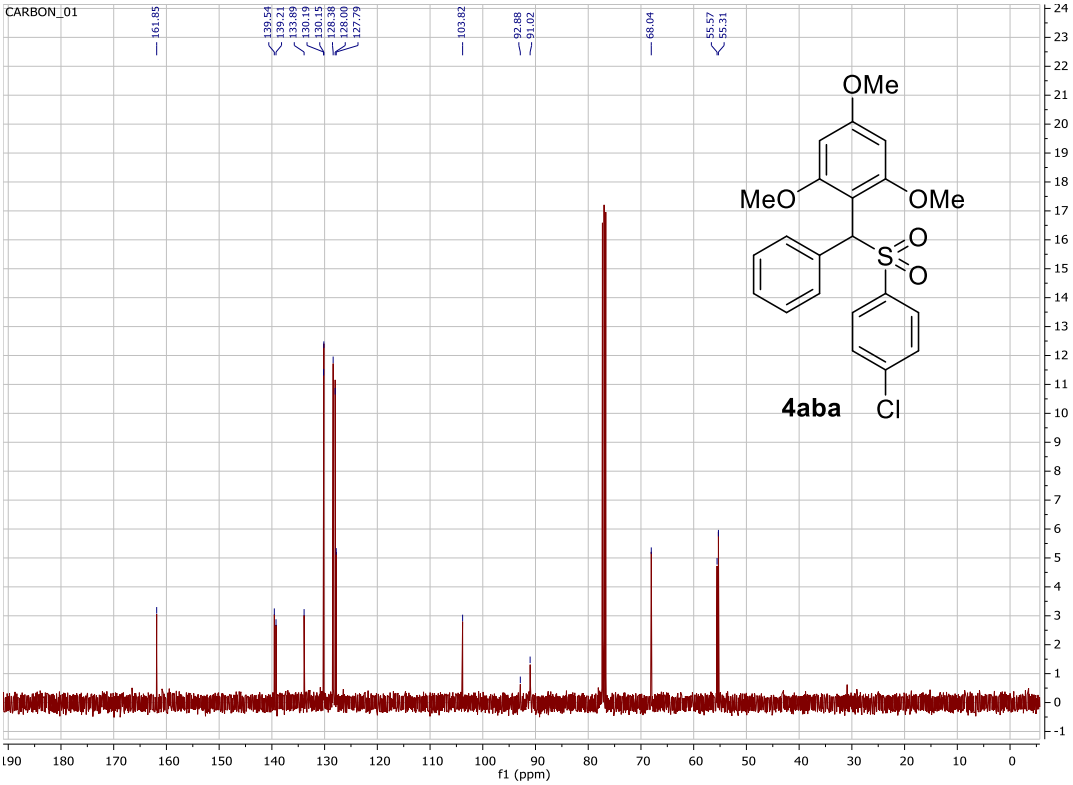
10. ^{1}HNMR & ^{13}CNMR spectra of **4jaa**



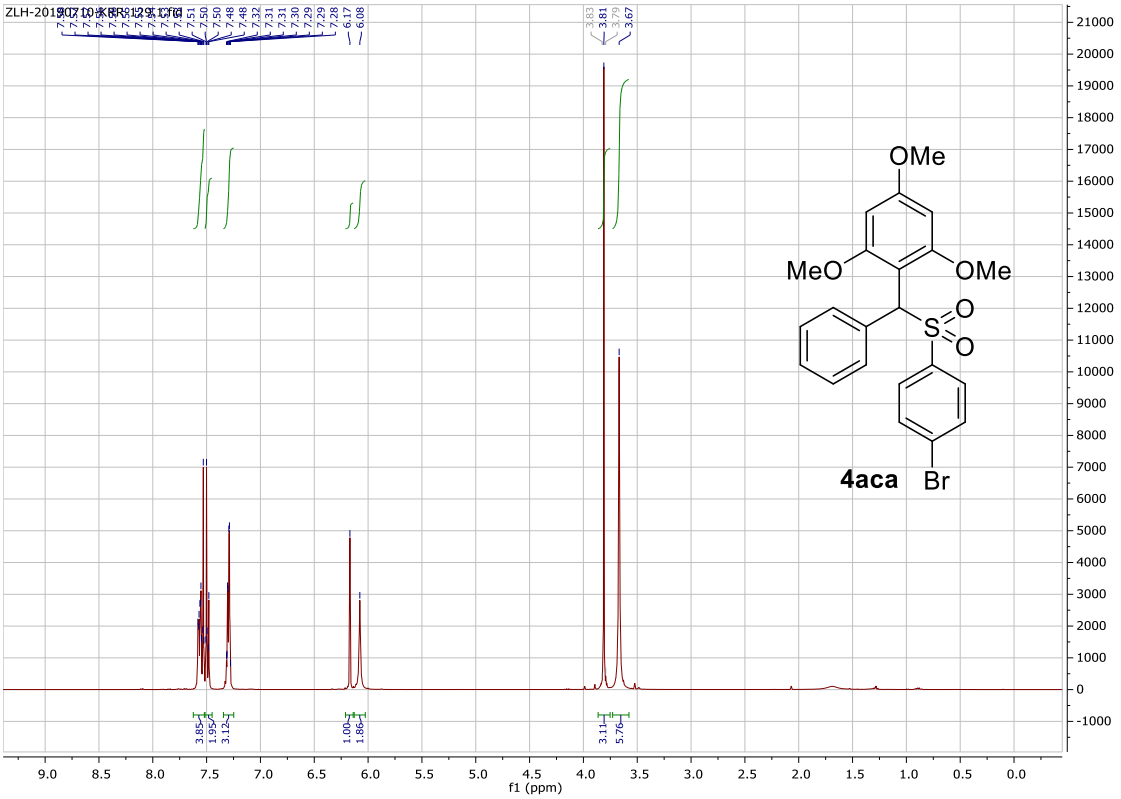


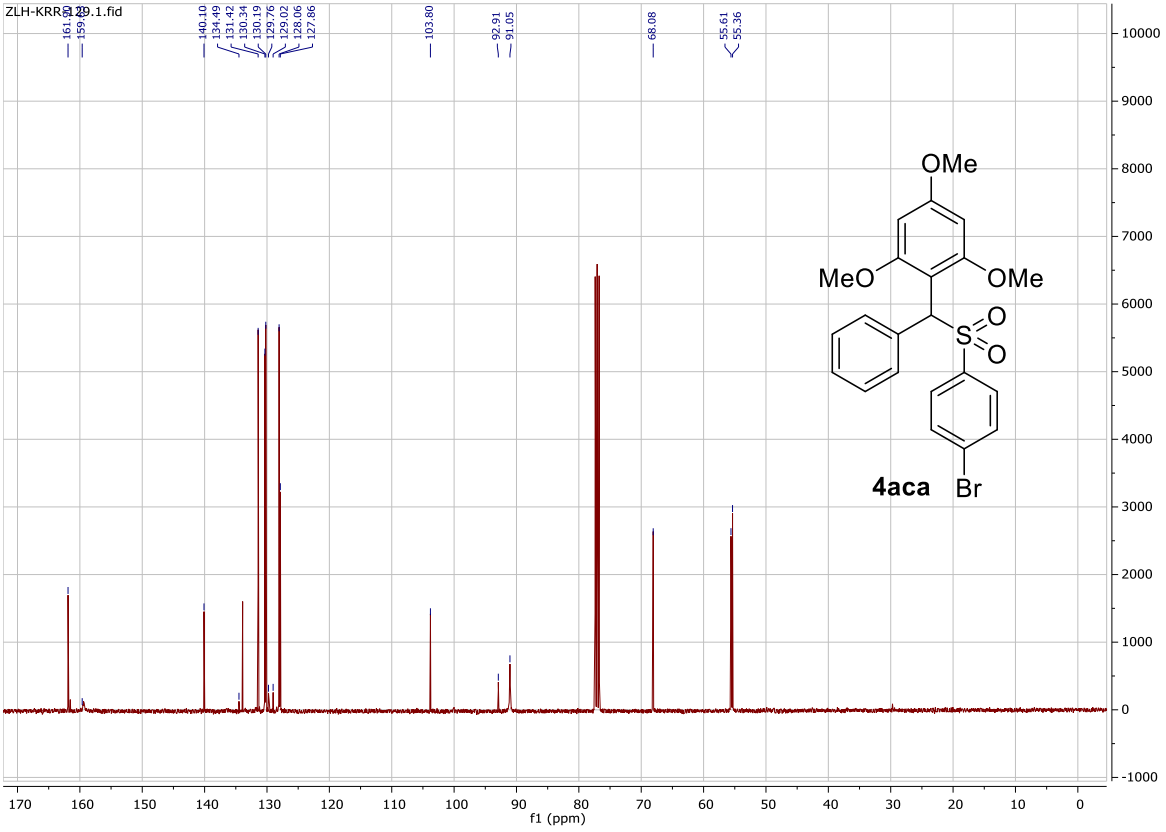
11. ^{1}HNMR & ^{13}CNMR spectra of **4aba**



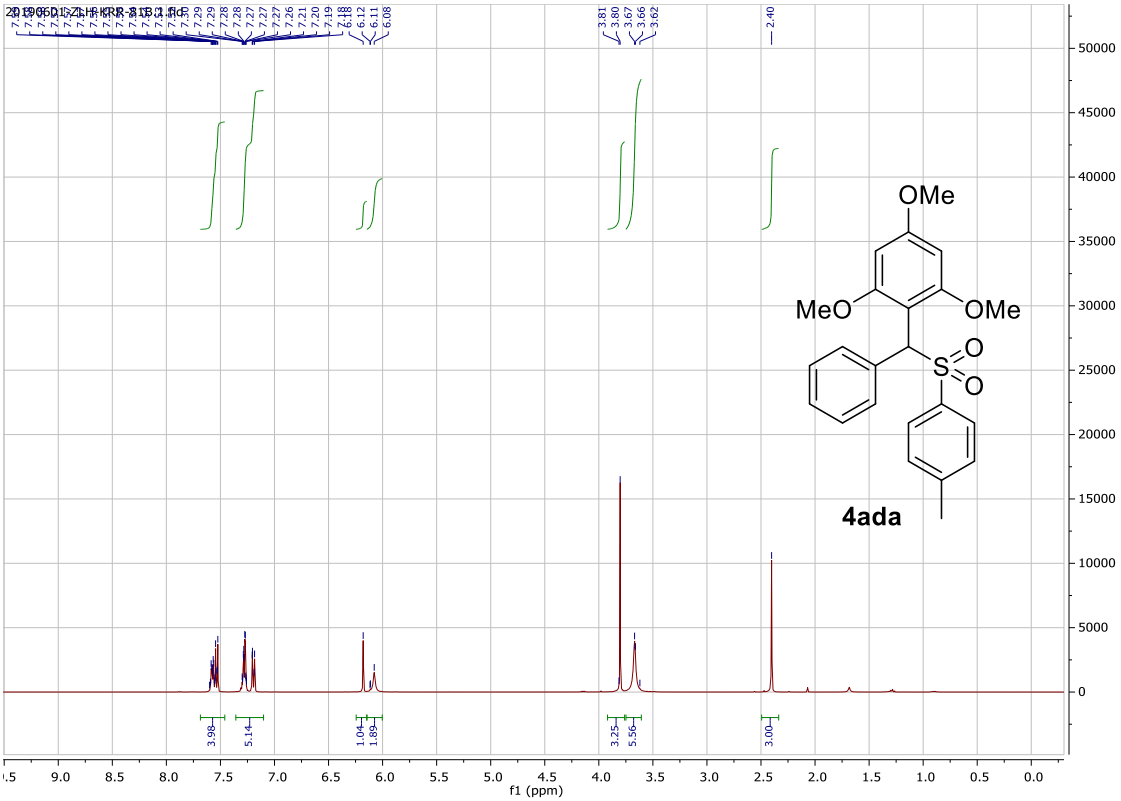


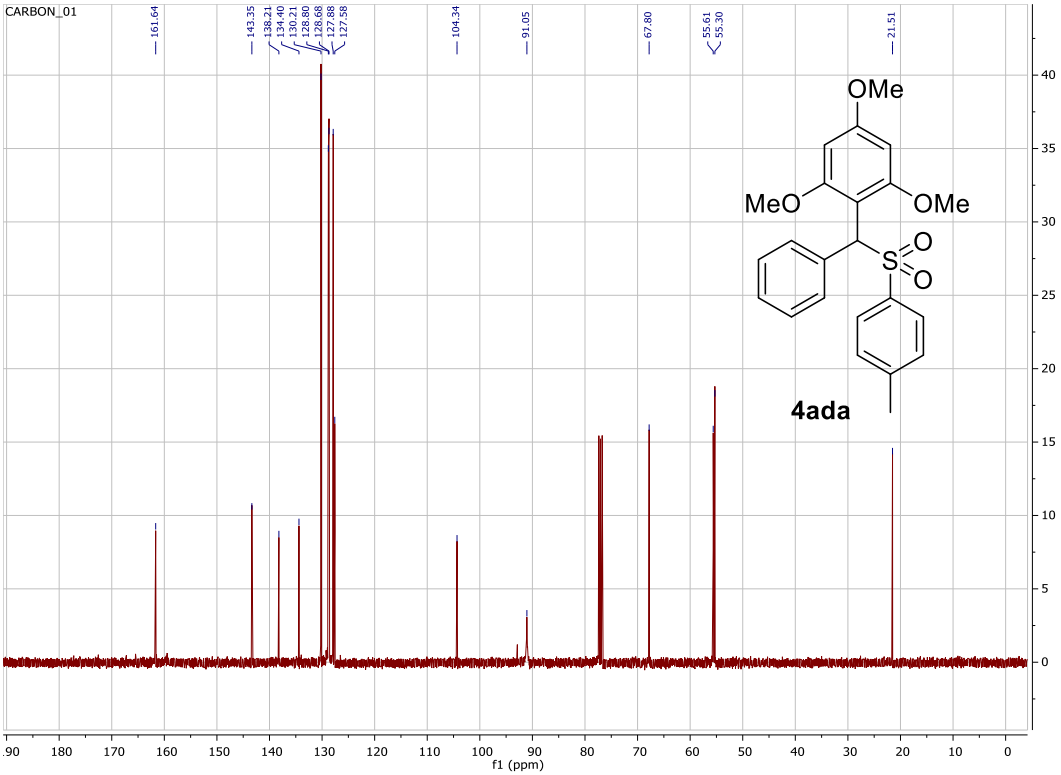
12. ^{1}HNMR & ^{13}CNMR spectra of **4aca**



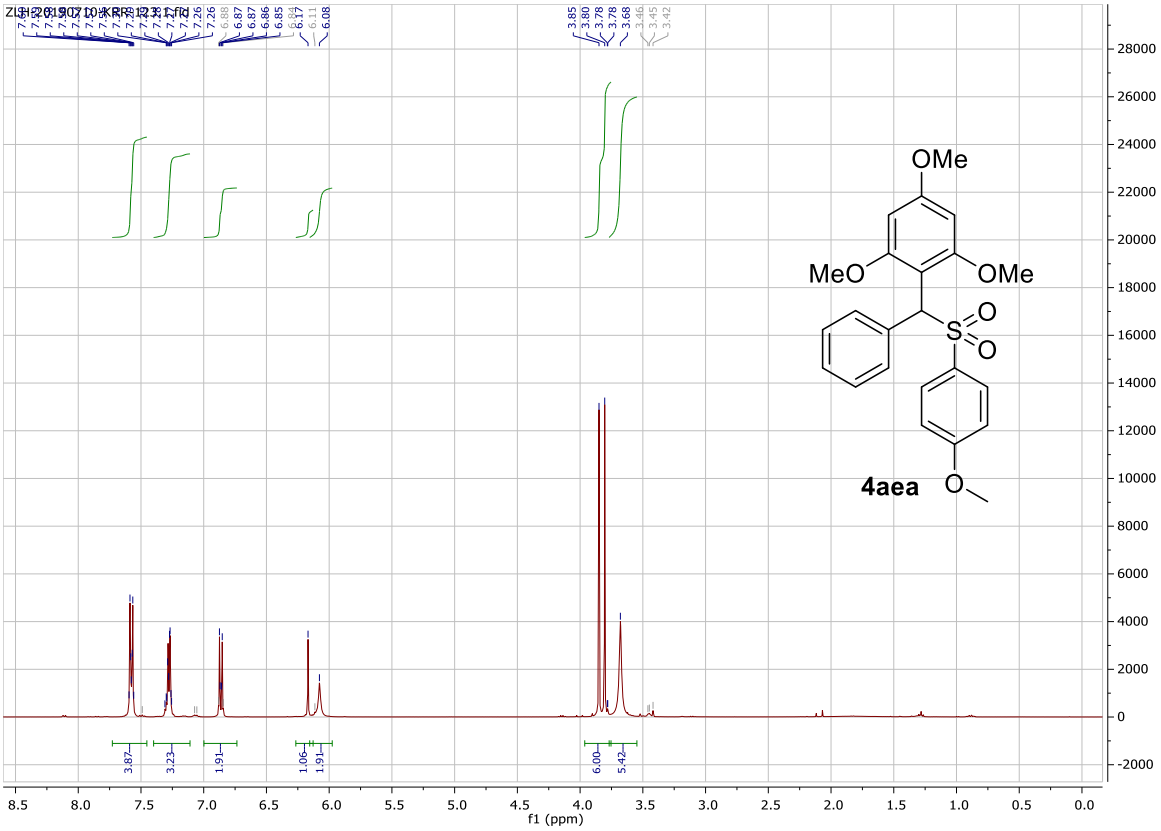


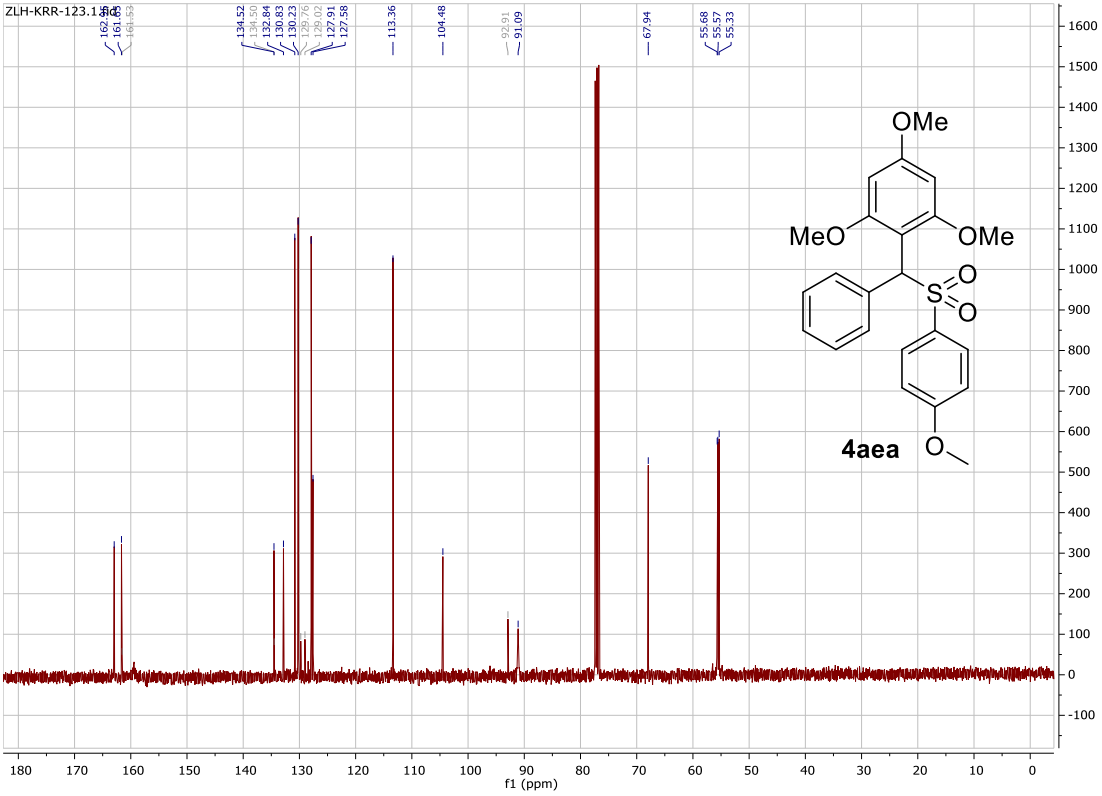
13. ^{1}HNMR & ^{13}CNMR spectra of **4ada**



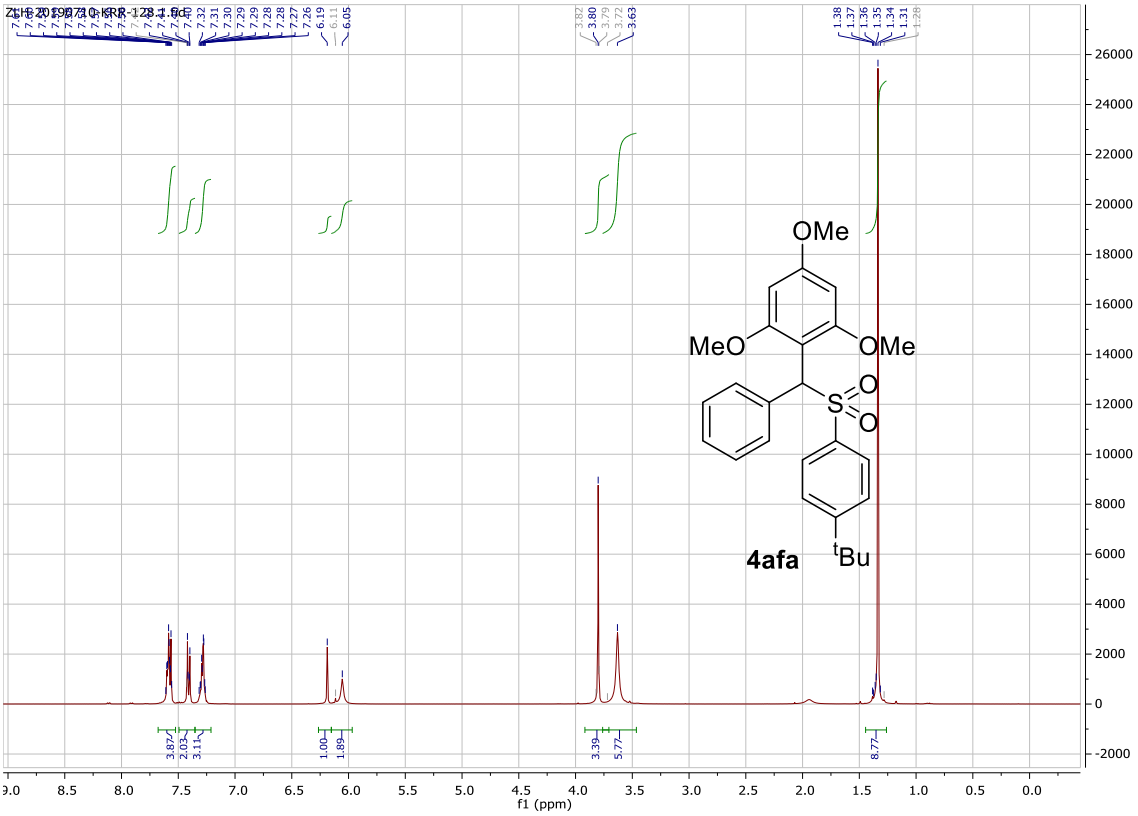


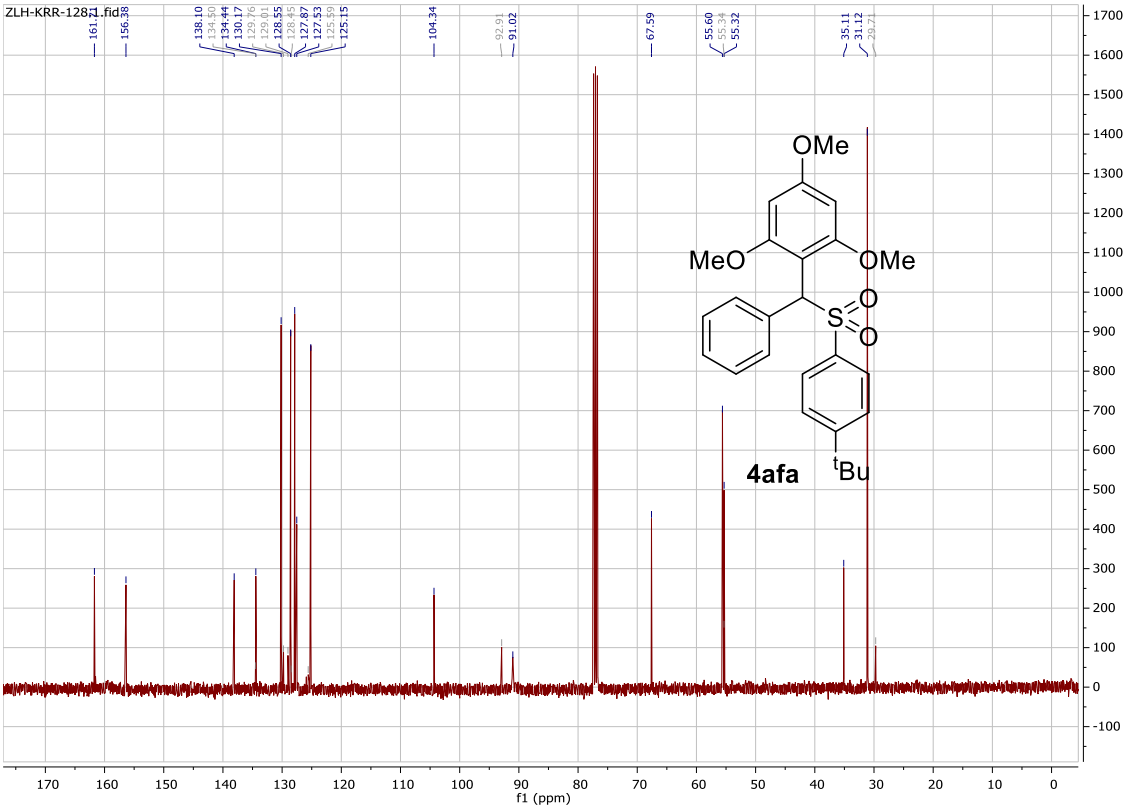
14. ^{1}HNMR & ^{13}CNMR spectra of **4aea**



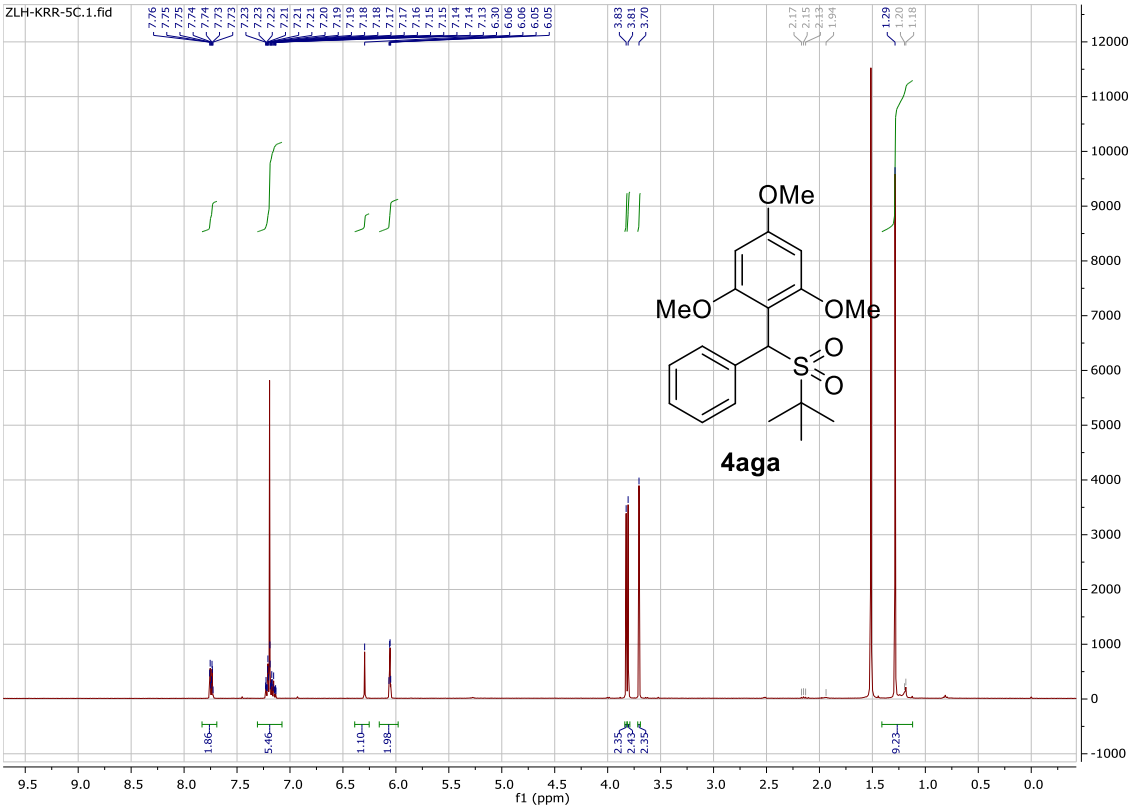


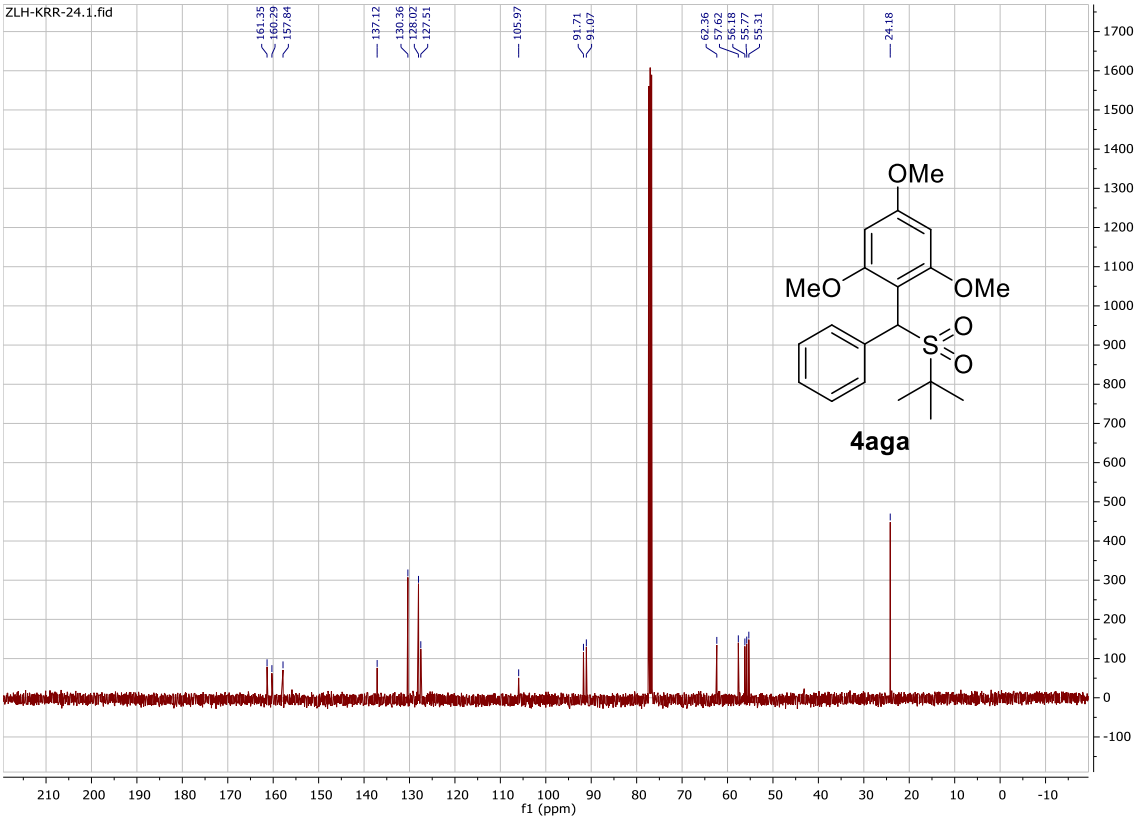
15. ^{1}HNMR & ^{13}CNMR spectra of **4afa**



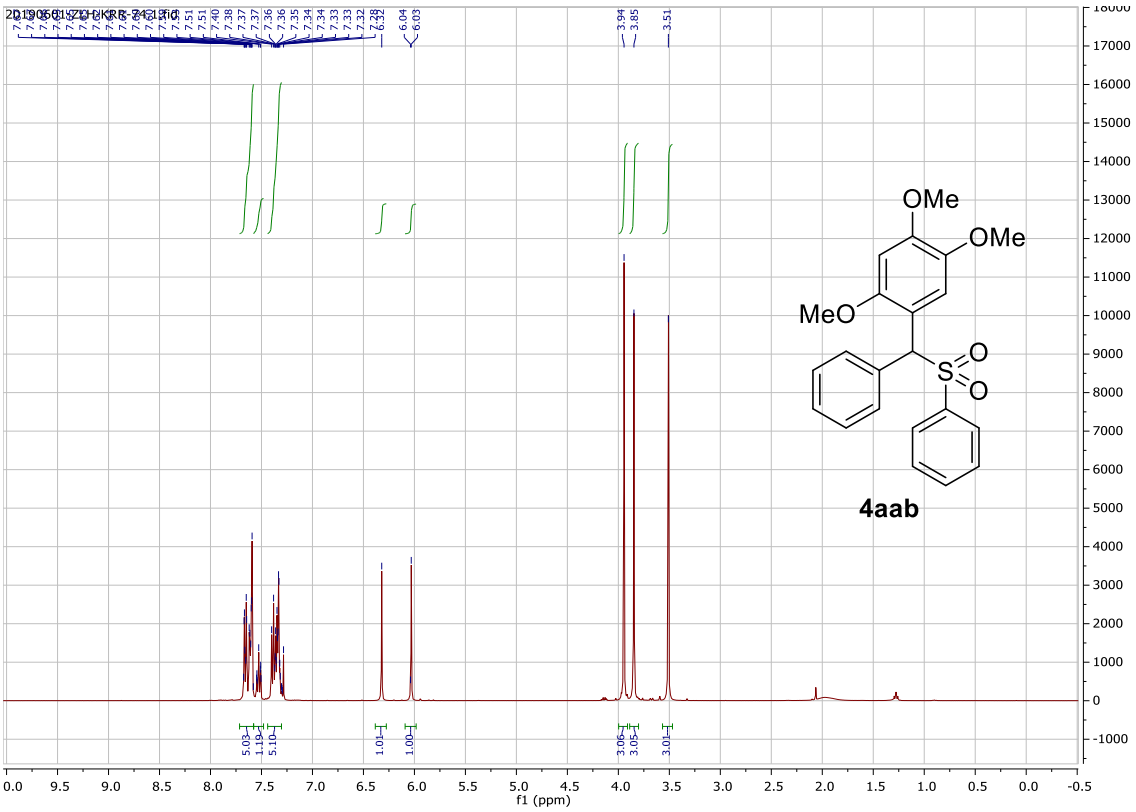


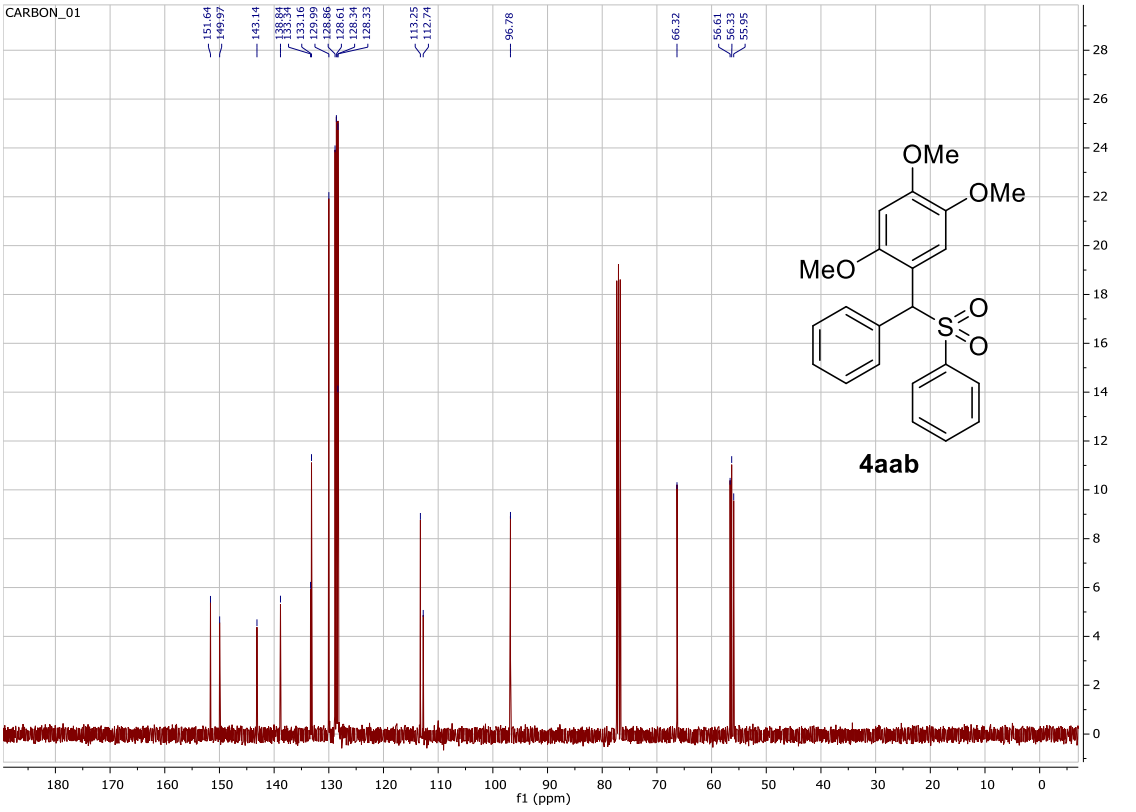
16. ^{1}HNMR & ^{13}CNMR spectra of **4aga**



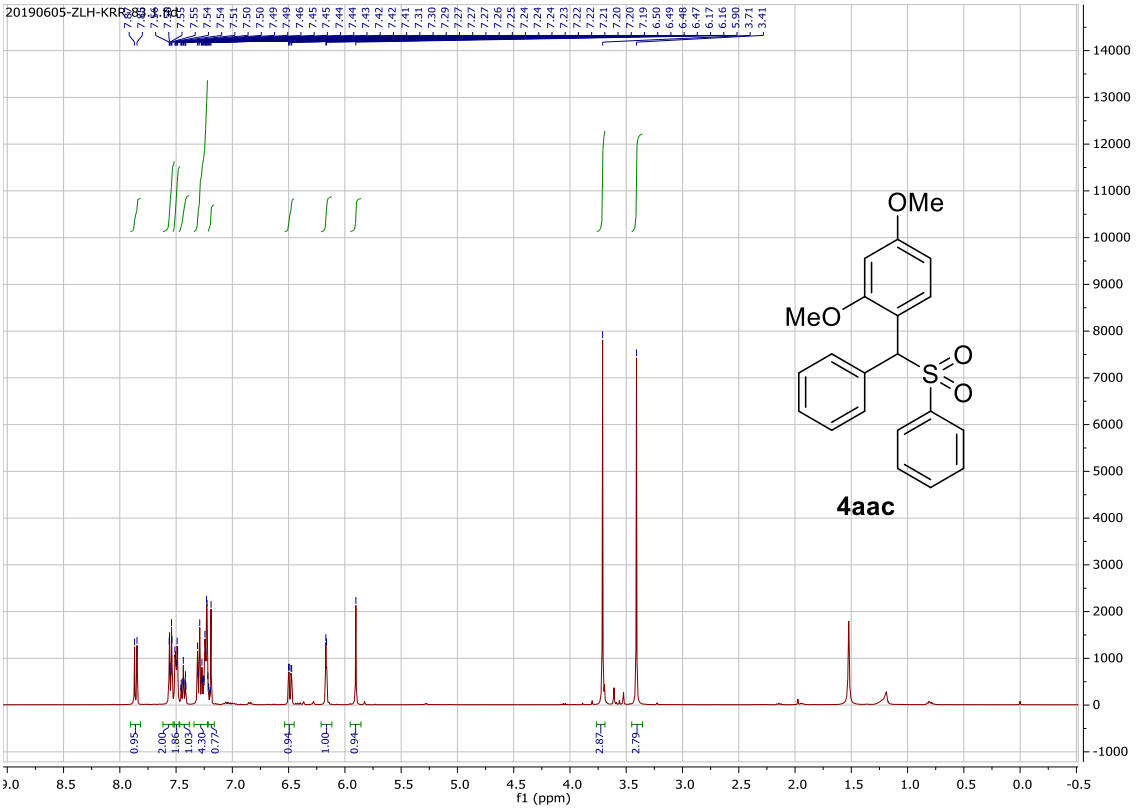


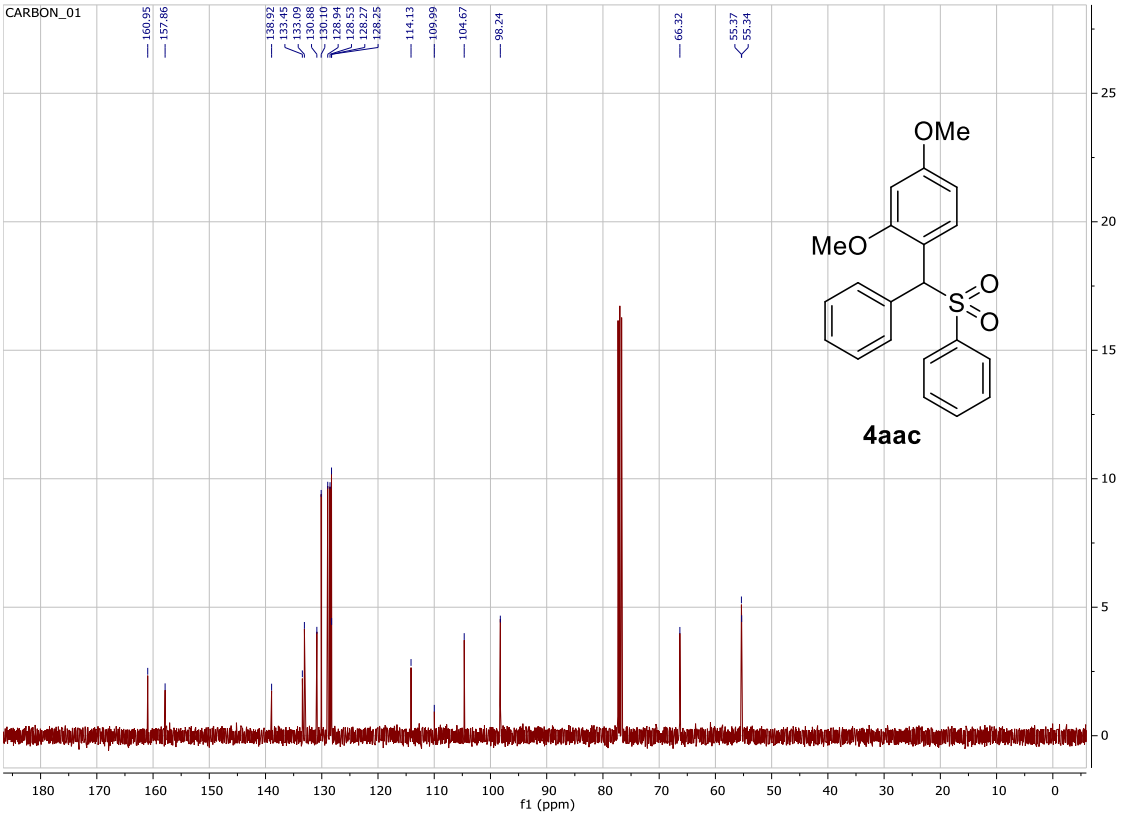
17. ^{1}HNMR & ^{13}CNMR spectra of **4aab**



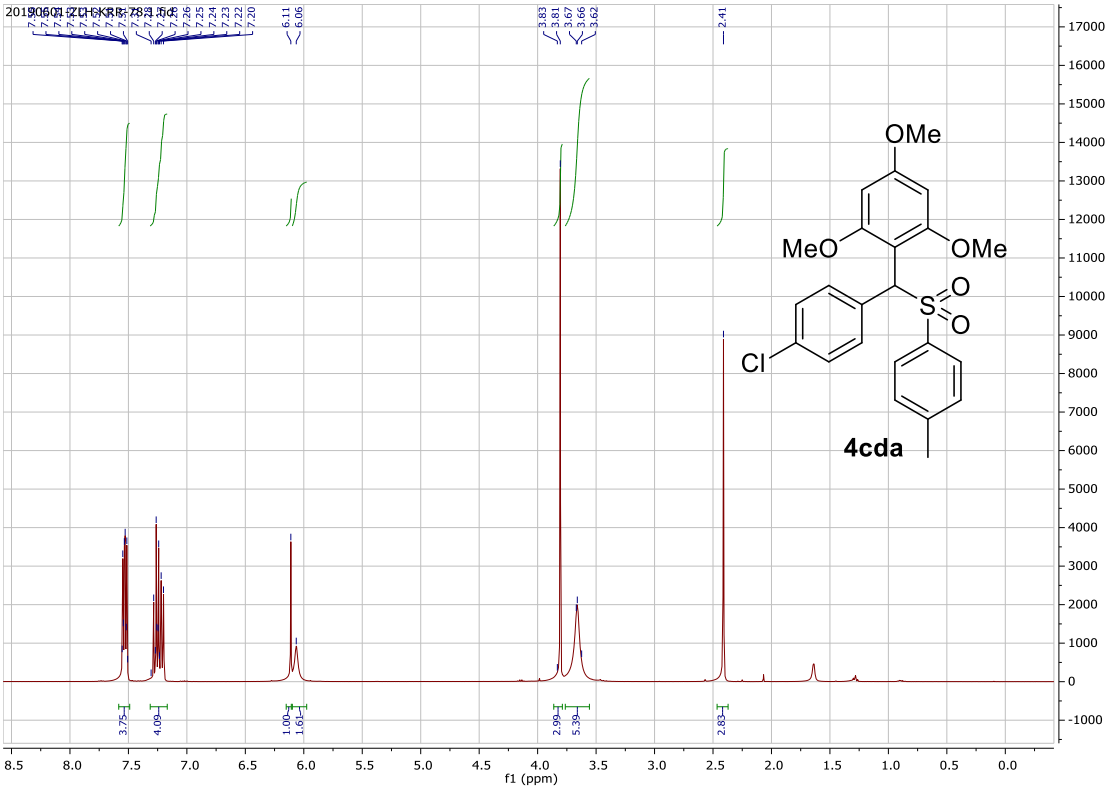


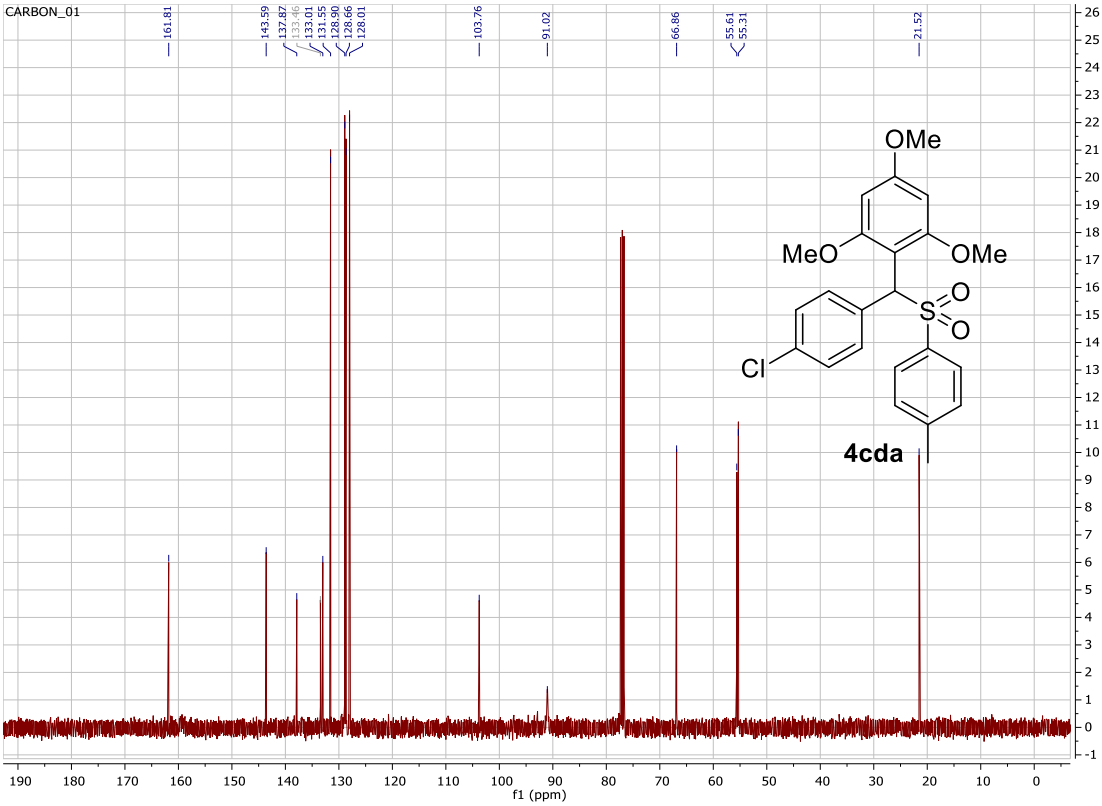
18. ^{1}HNMR & ^{13}CNMR spectra of **4aac**



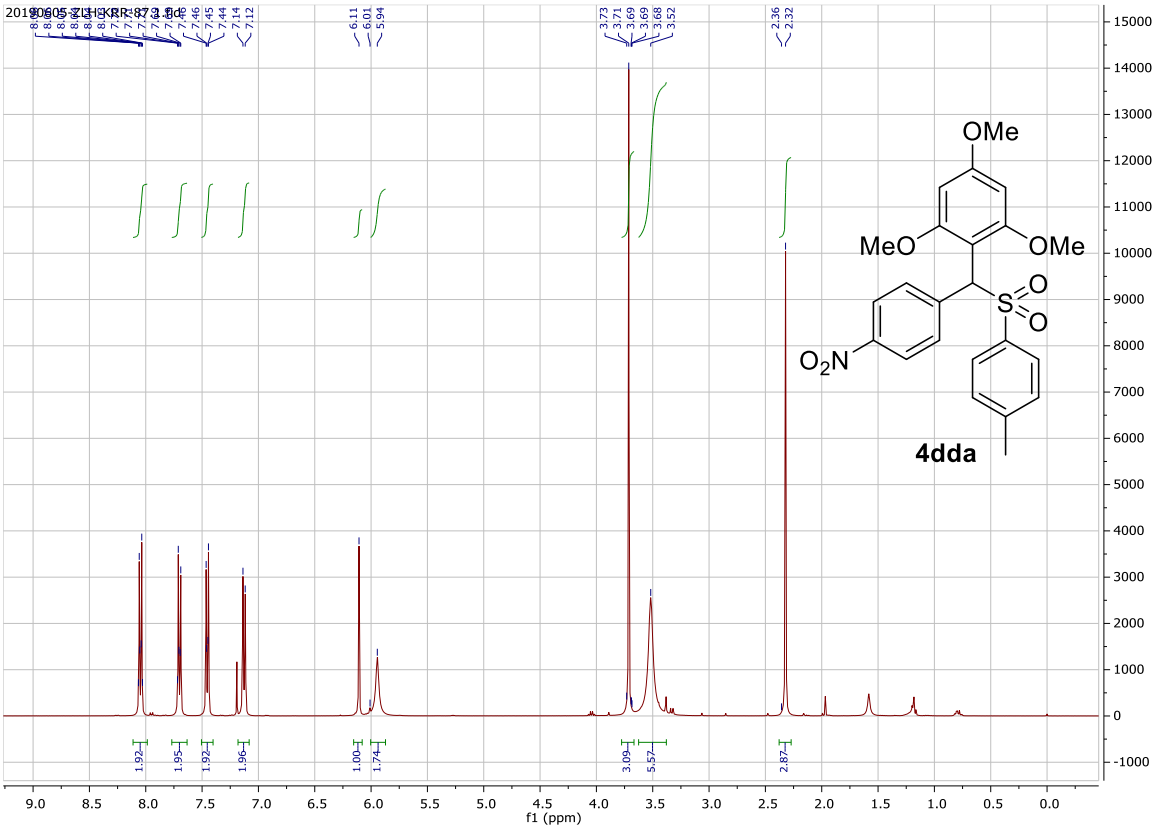


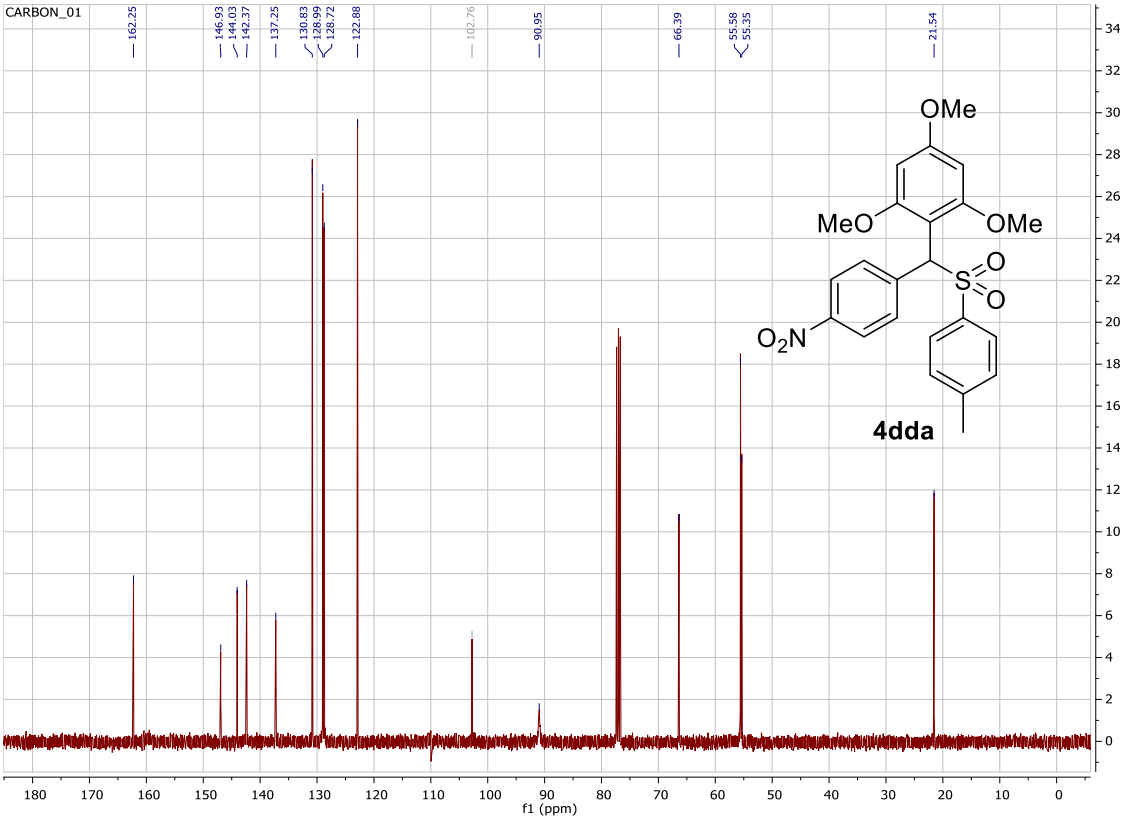
19. ^{1}HNMR & ^{13}CNMR spectra of **4cda**



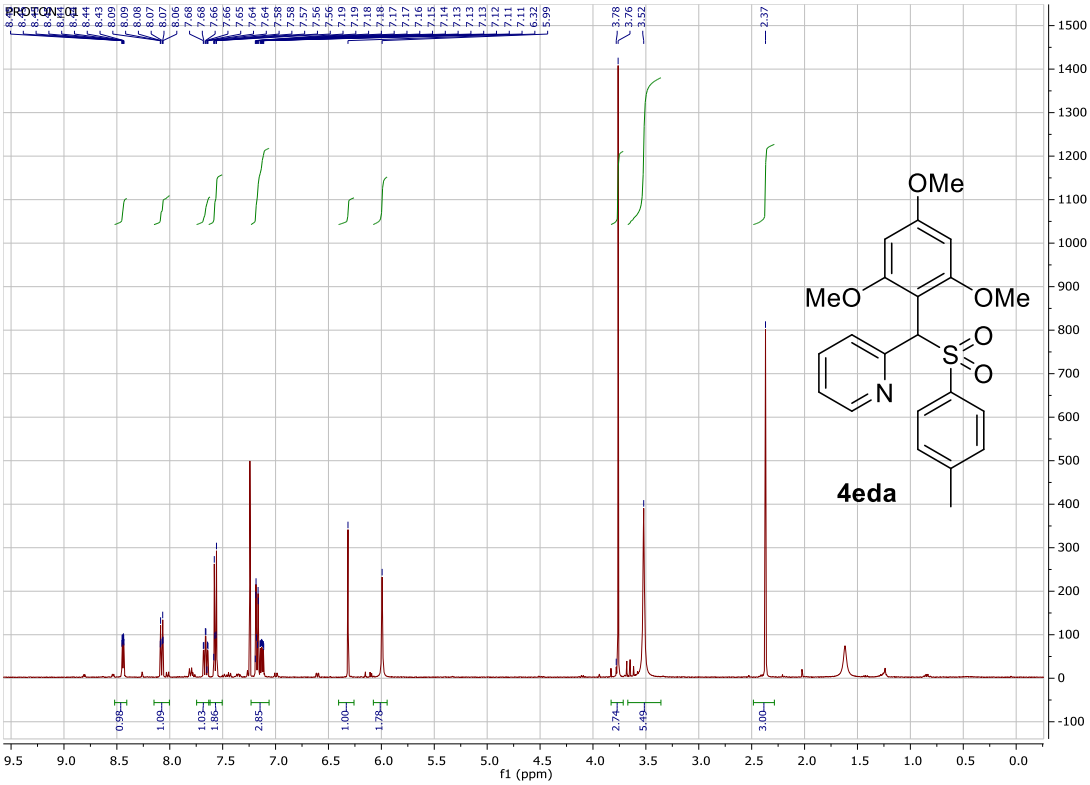


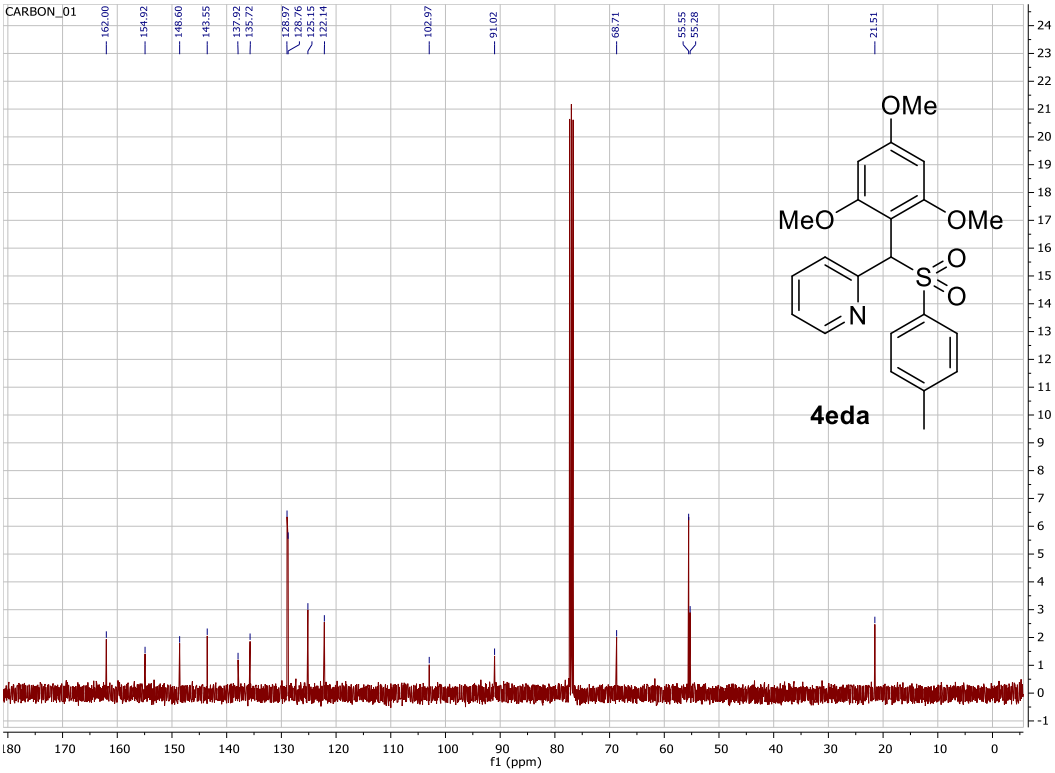
20. ^{1}HNMR & ^{13}CNMR spectra of **4dda**



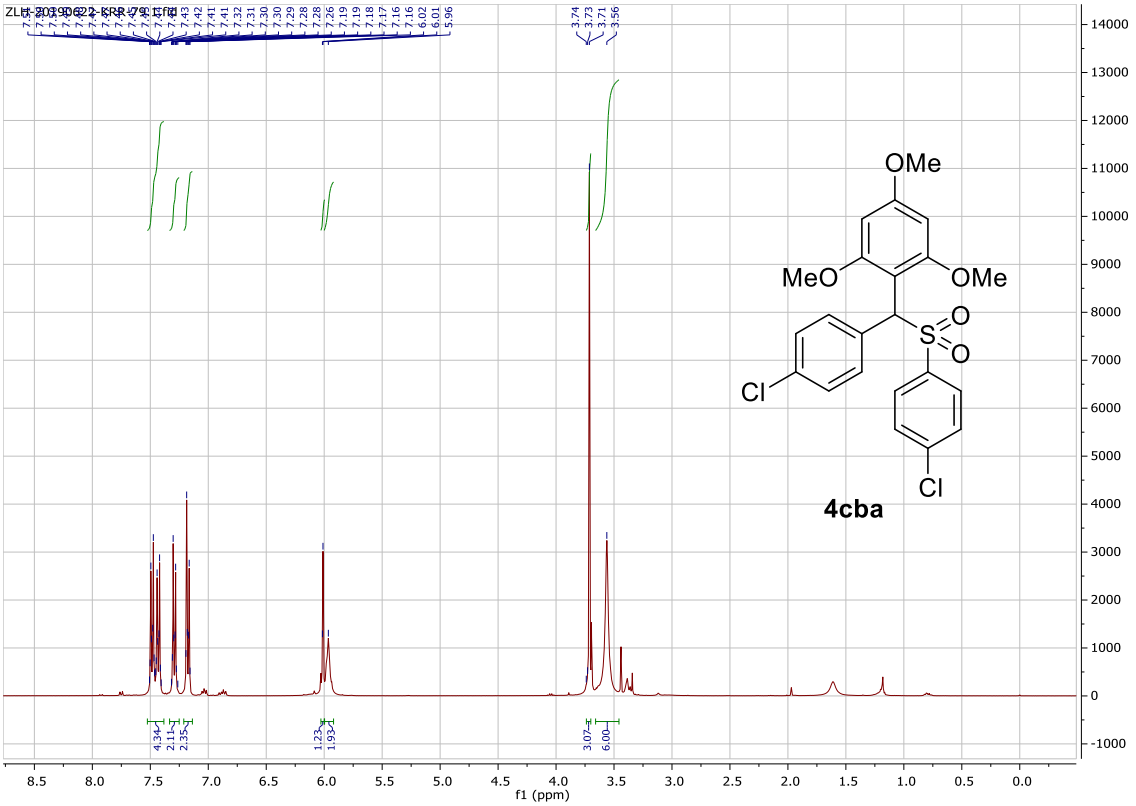


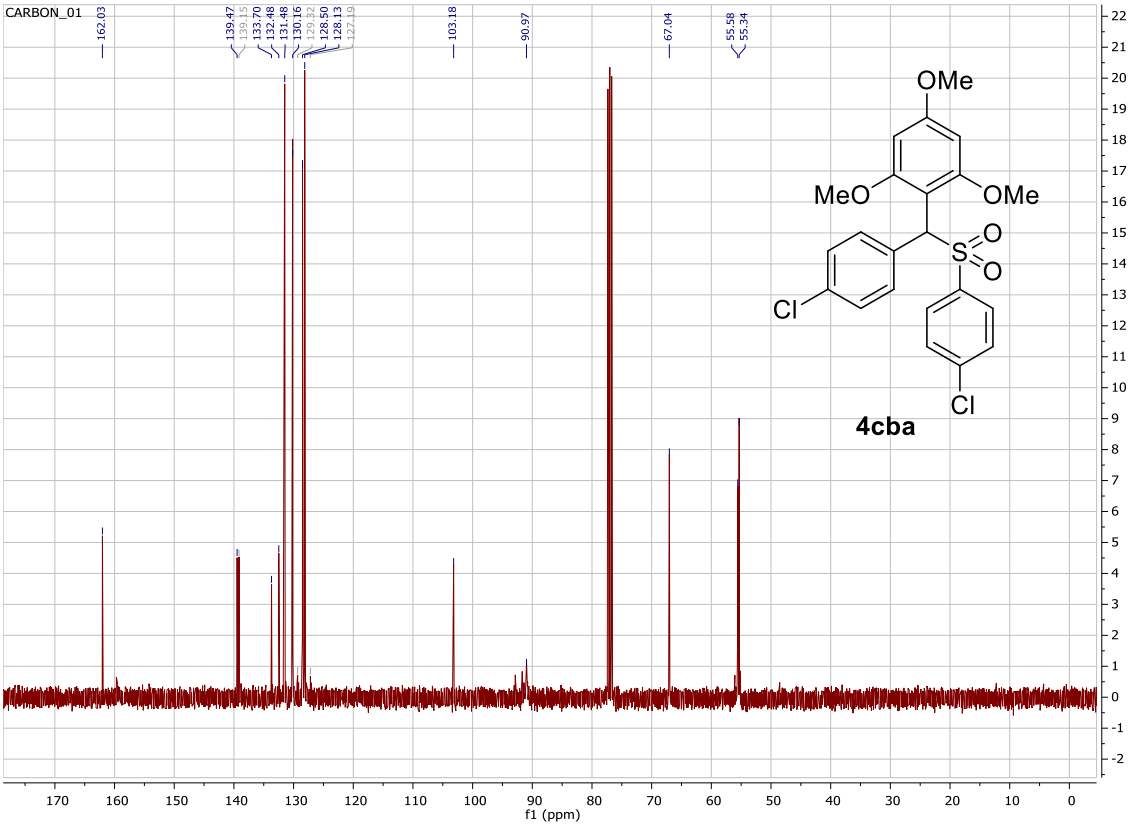
21. ^{1}HNMR & ^{13}CNMR spectra of **4eda**



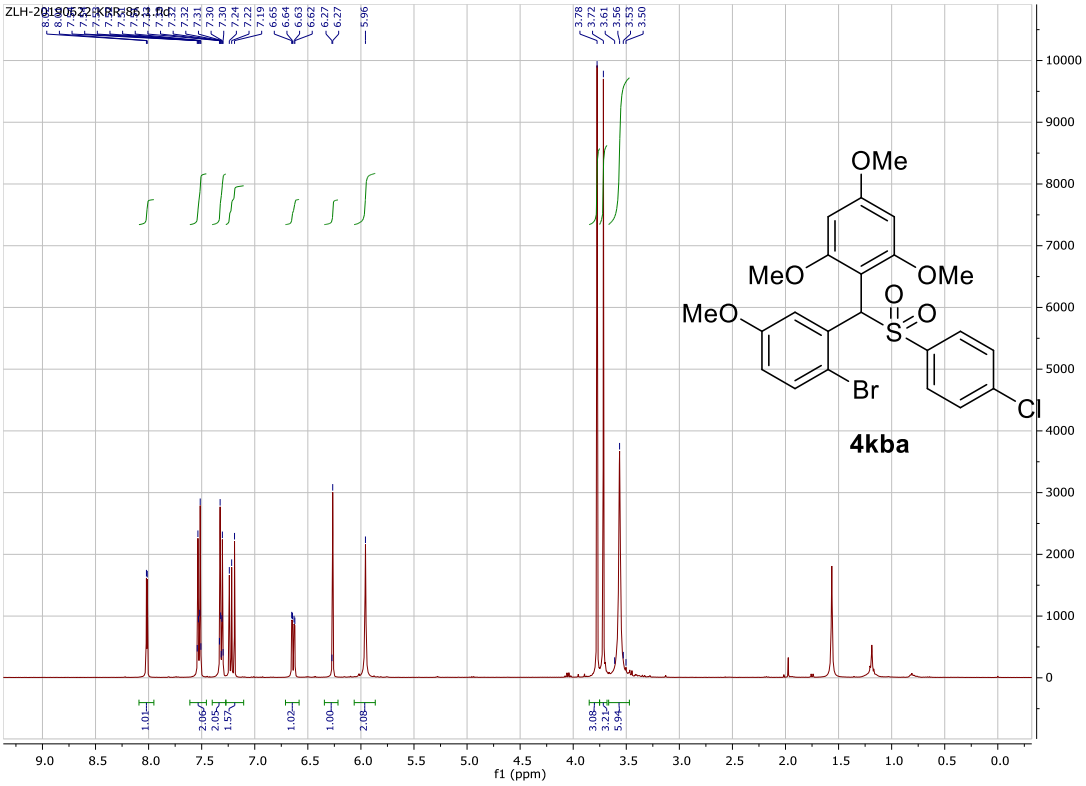


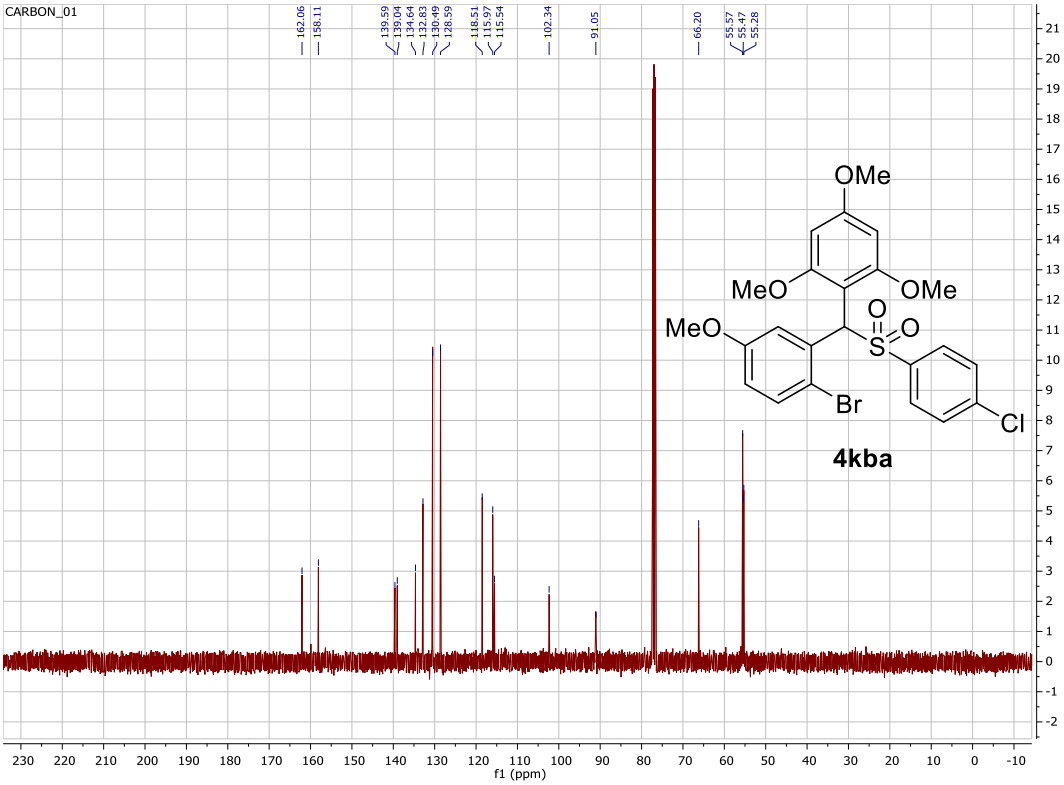
22. ^{1}HNMR & ^{13}CNMR spectra of **4cba**



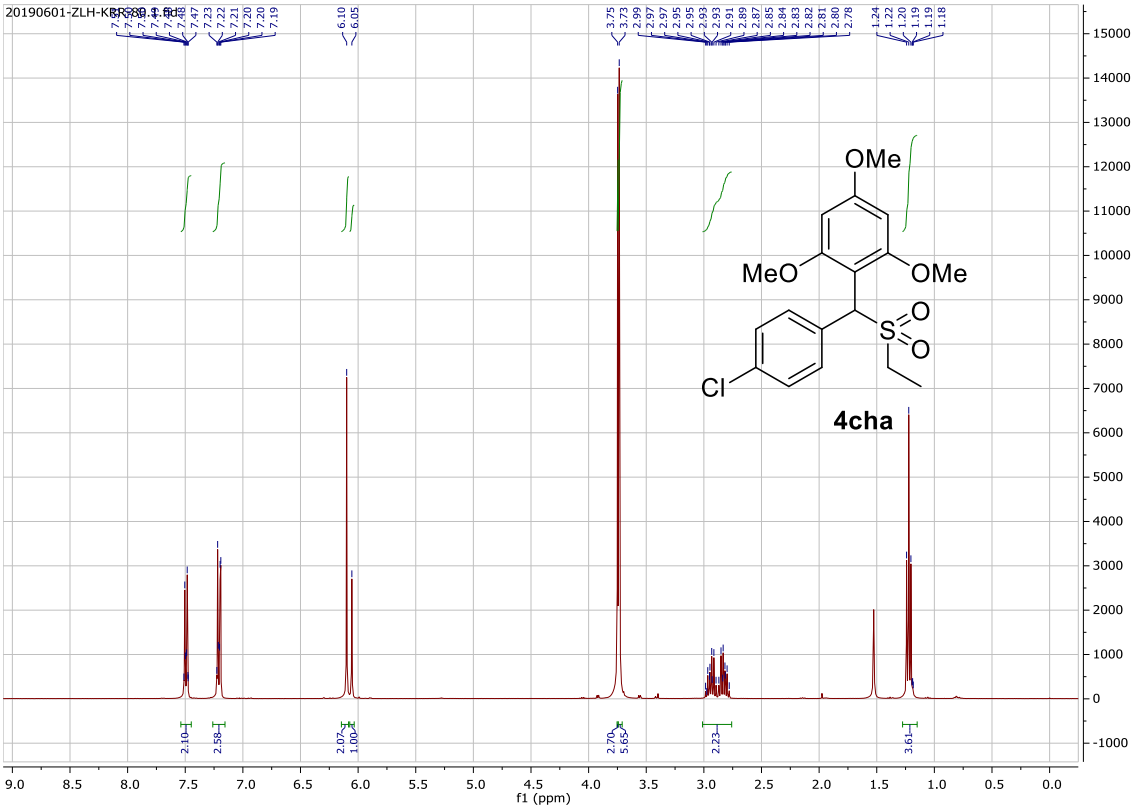


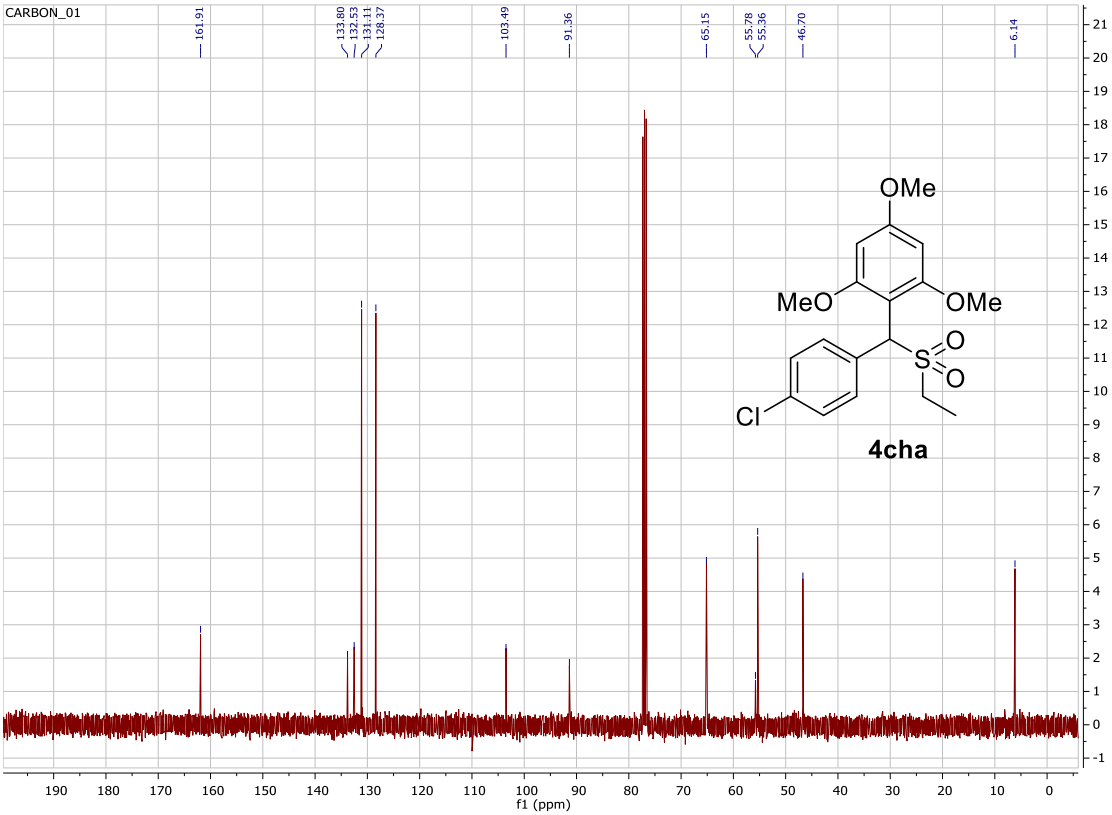
23. ^{1}HNMR & ^{13}CNMR spectra of **4kba**



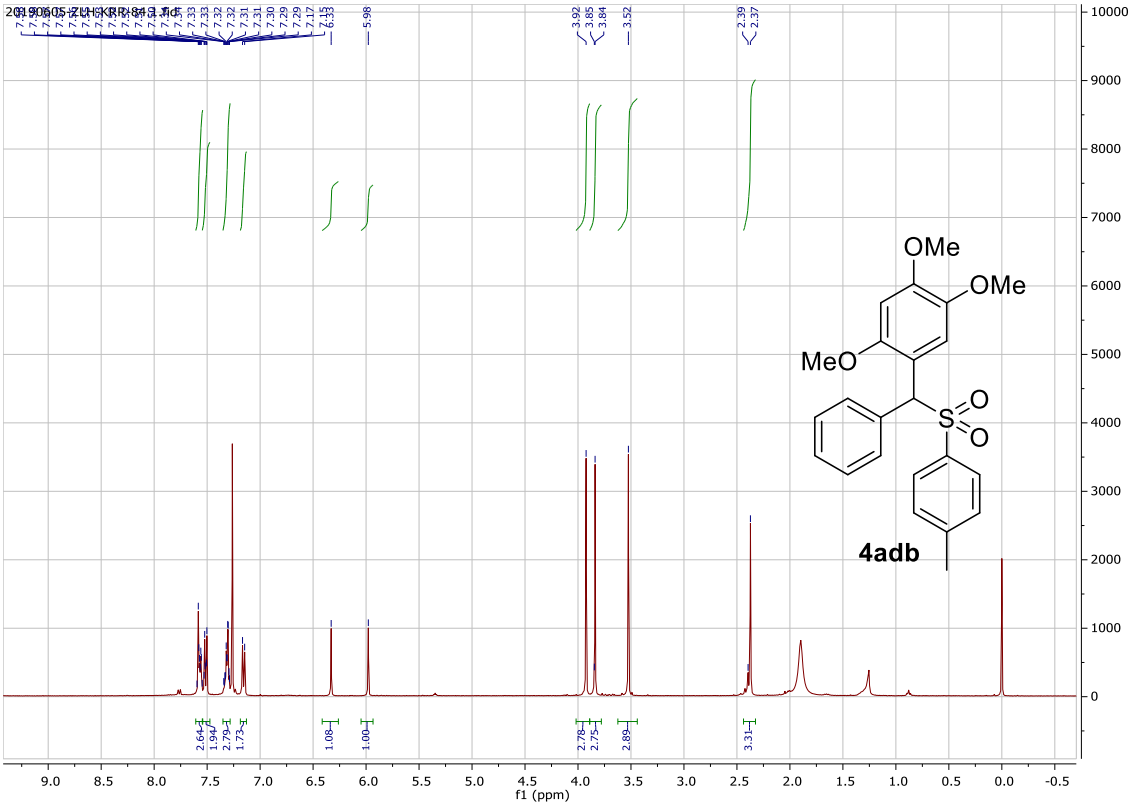


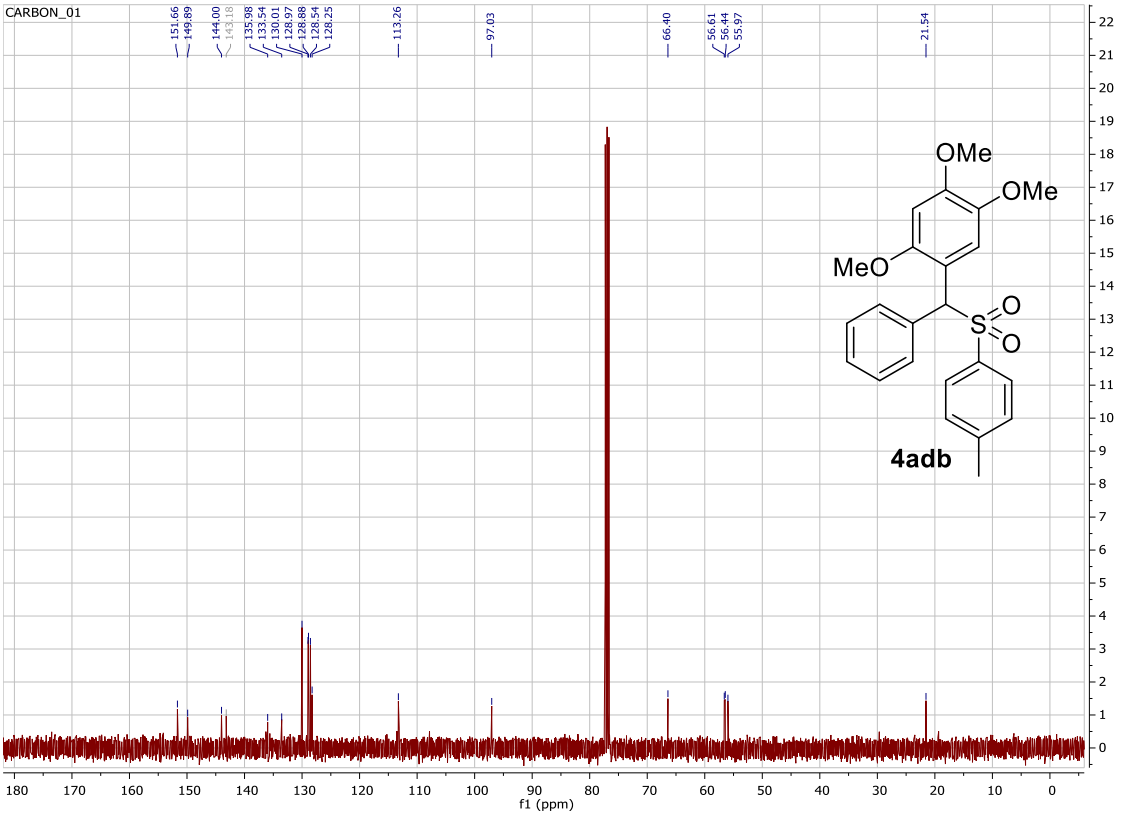
24. ^{1}HNMR & ^{13}CNMR spectra o**f 4cha**



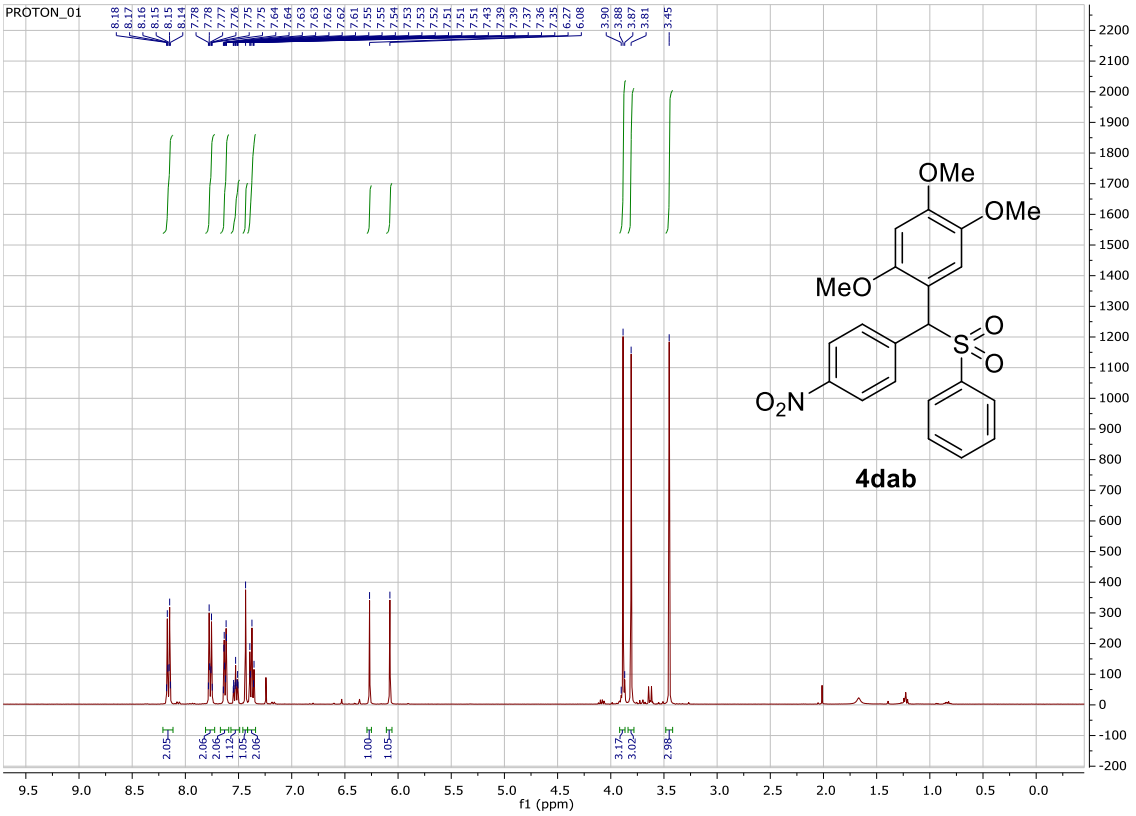


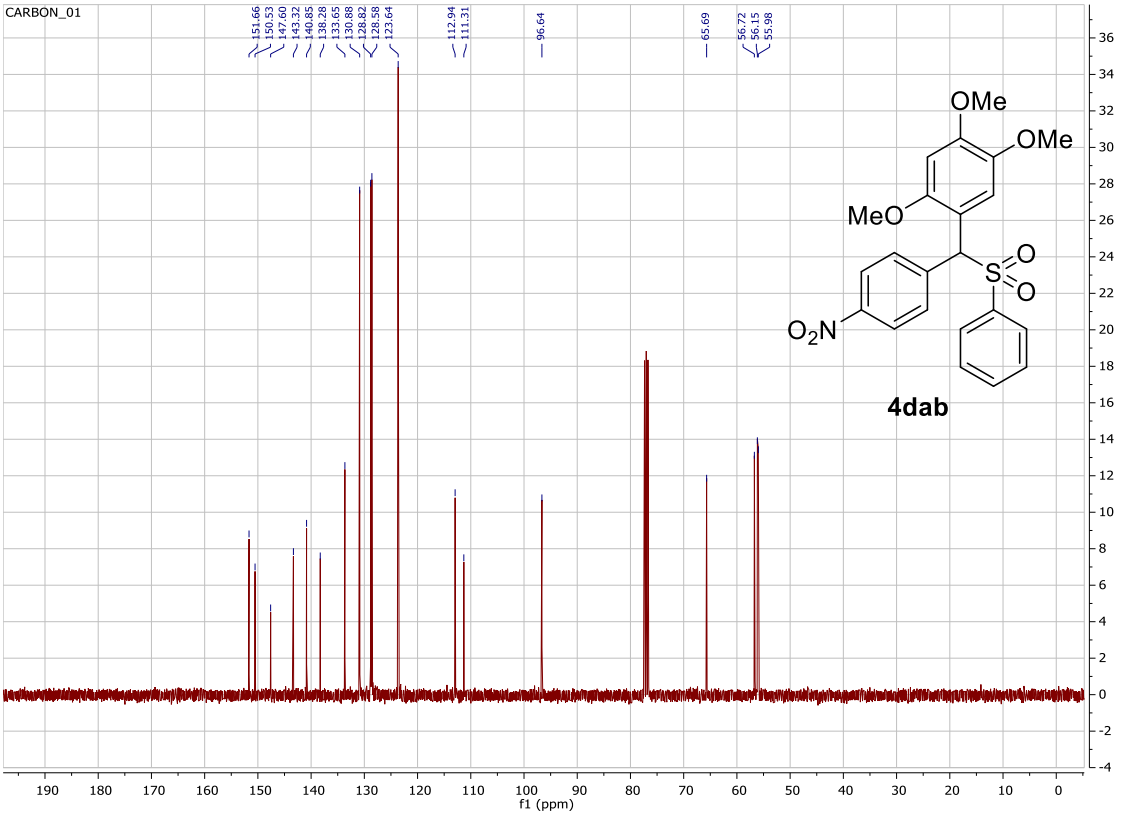
25. ^{1}HNMR & ^{13}CNMR spectra of **4adb**



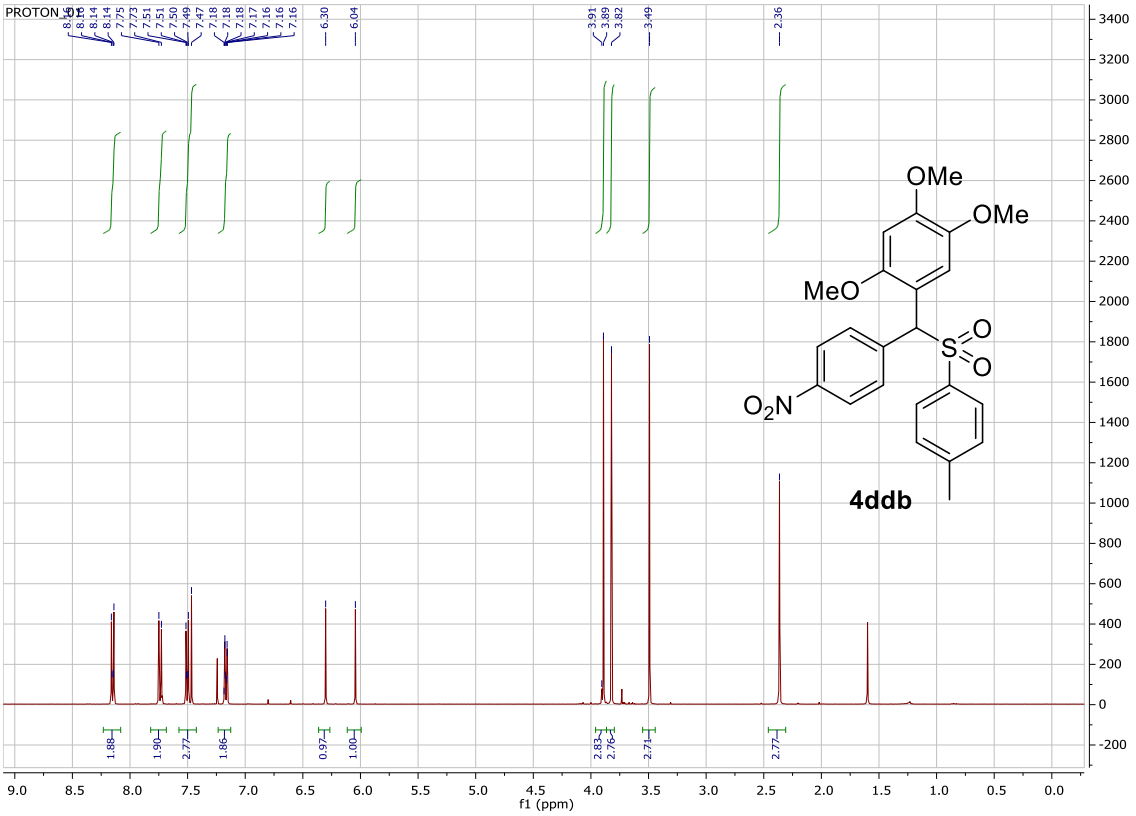


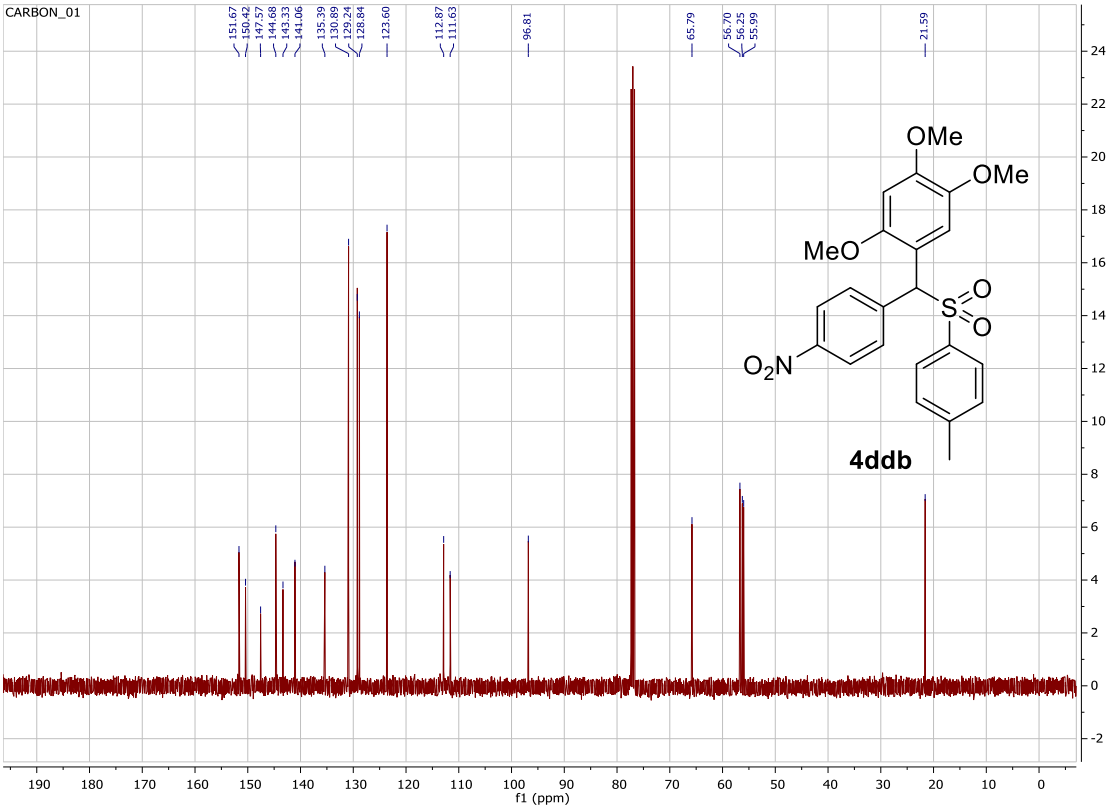
26. ^{1}HNMR & ^{13}CNMR spectra of **4dab**



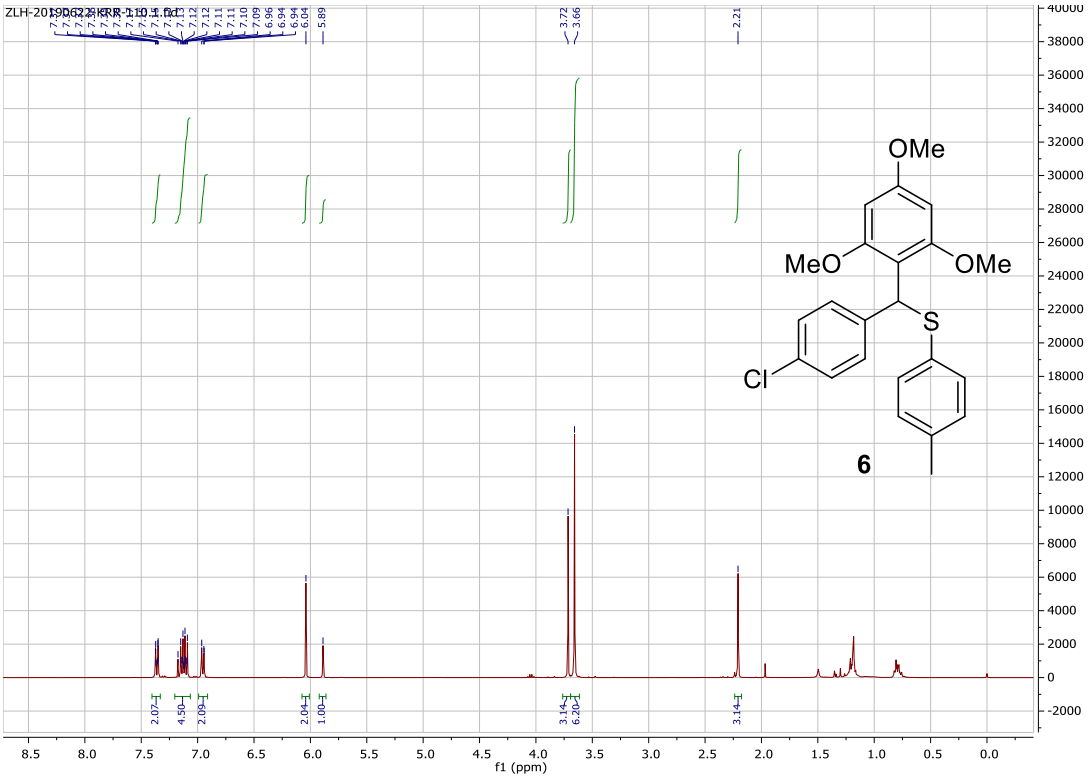


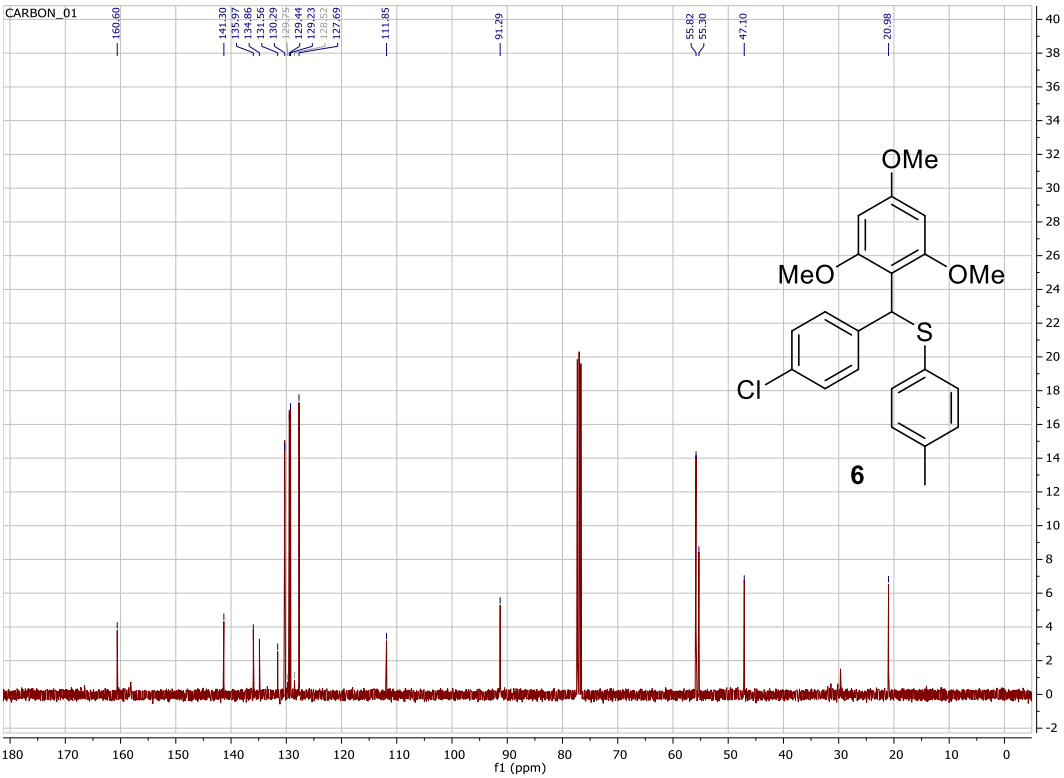
27. ^{1}HNMR & ^{13}CNMR spectra o**f 4ddb**





28. ^{1}HNMR & ^{13}CNMR spectra of **6**





6. References

1. E. Baciocchi, O. Lanzalunga and B. Pirozzi, *Tetrahedron* **1997** , 53, 12287-12298.
2. P. Thirupathi and S. S. Kim, *Eur. J. Org. Chem.* **2010**, 9, 1798-1808.