Supporting Information

Synthesis of Unsymmetrically Tetrasubstituted Pyrroles and Studies of AIEE in Pyrrolo[1,2-*a*]pyrimidine Derivatives

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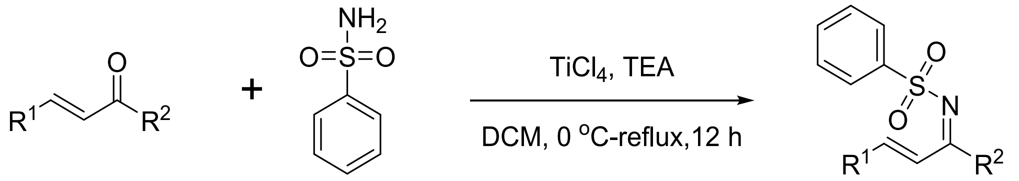
Contents

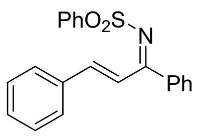
Materials and methods

All reactions were carried out under an atmosphere of nitrogen in glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Inert PureSolv MD5. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. Melting points were measured on a Melt-Temp apparatus and were uncorrected. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD and JEOL ECZ600R. Data for ^{1}H NMR and ^{13}C NMR spectra are reported relative to TMS as an internal standard (0 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. GC-MS data were recorded on Thermo ISQ QD. IR data were obtained from Bruker VERTEX 70.The UV-visible absorption spectra of samples were dissolved in THF(0.001mg/mL) and recorded on Shimadzu UV2450 UV-Vis spectrophotometer. Photoluminescence (PL) spectra of sample solutions were measured on the Edinburgh Instruments FLS5 fluorescence spectrofluorometer. The absolute fluorescence quantum yield of samples was dissolved in THF (0.1mg/mL) and measured on the Edinburgh Instruments FLS1000 three monochromator spectrophotometer. X-ray diffraction (XRD) measurement was performed on Rigaku XRD MiniFlex 600. HRMS data were recorded on Bruker Impact II UHR-TOF, Waters Micromass GCT Premier, or Thermo Fisher Scientific LTQ FT Ultra.

General procedure A: Synthesis of α,β-unsaturated sulfonimines



General procedure A :According to the reported synthetic methods for α,β-unsaturated sulfonimines from chalcone,[1] to a solution of benzenesulfonamide (785 mg, 5 mmol) and chalcone (5 mmol) in DCM (20 mL) at 0 °C, were successively added Et_3N (2.09 mL, 15 mmol) and $TiCl_4$ (0.6 mL, 5 mmol) under a nitrogen atmosphere. The reaction mixture was heated at reflux overnight. The solution was cooled to room temperature, quenched with water (10 mL), and extracted with DCM. The combined organic phase was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate and hexane) to afford the corresponding α,β-unsaturated sulfonimine.[2]



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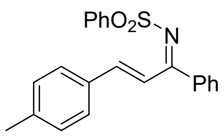

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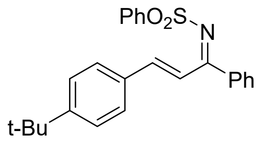

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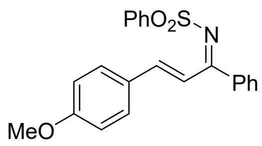

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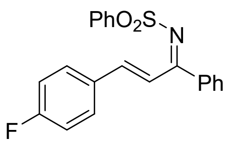

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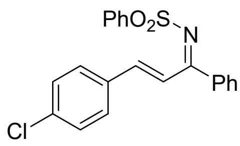

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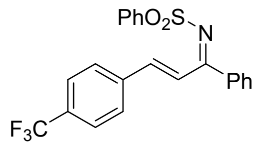

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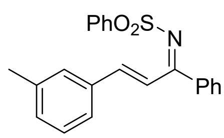

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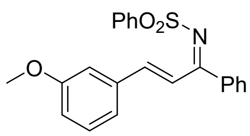

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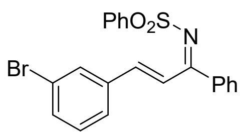

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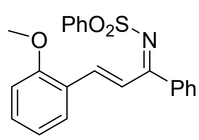

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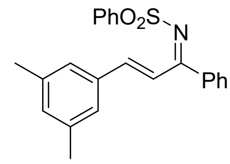

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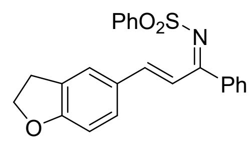

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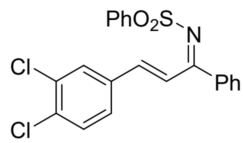

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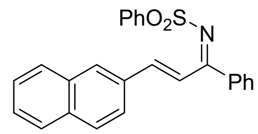

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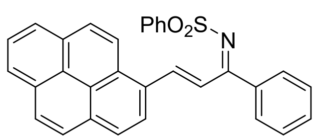

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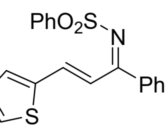

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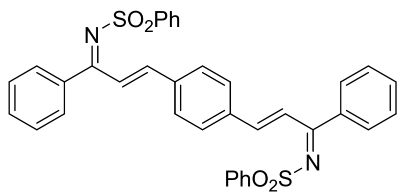

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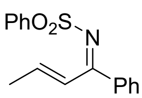

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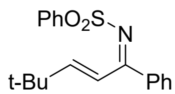

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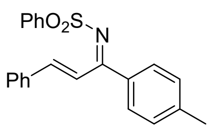

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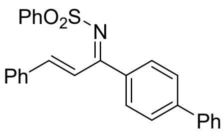

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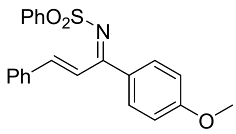

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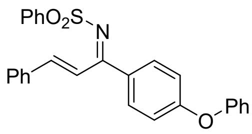

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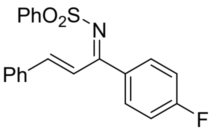

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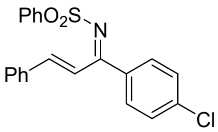

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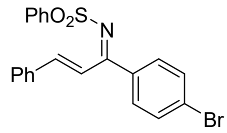

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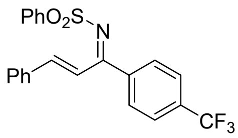

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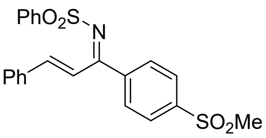

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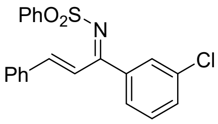

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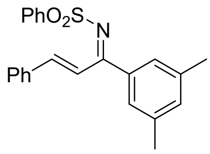

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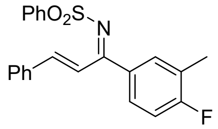

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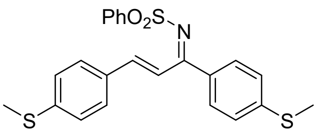

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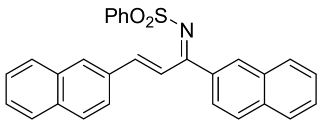

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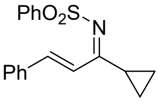

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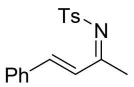

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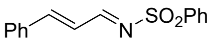
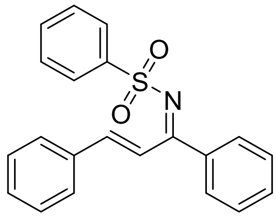


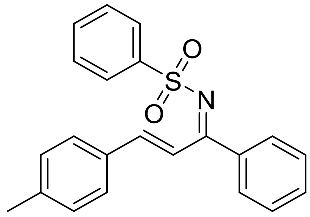
37s,15%

Characterization data for α,β-unsaturated sulfonimines



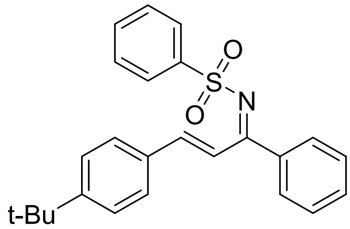
N-((1*E*,2*E*)-1,3-diphenylallylidene)benzenesulfonamide (**1s**)

Following the general procedure A, compound **1s** was obtained as a yellow solid (1.42 g, 82% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 – 7.82 (m, 3H), 7.77 – 7.37 (m, 13H), 7.09 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.0, 149.3, 141.7, 137.3, 134.6, 132.8, 132.2, 131.3, 130.4, 129.2, 129.0, 128.9, 128.5, 127.3, 122.6. The data matches with the reported value[2].



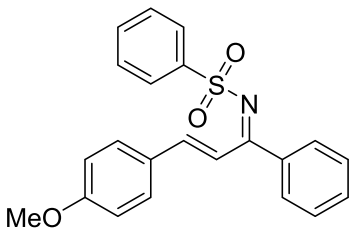
N-((1*E*,2*E*)-1-phenyl-3-(*p*-tolyl)allylidene)benzenesulfonamide (**2s**)

Following the general procedure A, compound **2s** was obtained as a yellow solid (1.39 g, 77% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.57 – 7.78 (m, 3H), 7.74 – 7.40 (m, 10H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 15.9 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.6, 142.0, 141.7, 132.6, 131.8, 130.2, 129.8, 128.9, 128.8, 128.4, 127.1, 21.6. The data matches with the reported value[2].



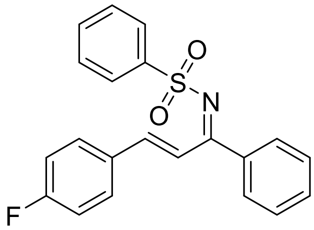
N-((1*E*,2*E*)-3-(4-(*tert*-butyl)phenyl)-1-phenylallylidene)benzenesulfonamide (**3s**)

Following the general procedure A, compound **3s** was obtained as a white solid (1.57 g, 78% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 – 7.89 (m, 3H), 7.77 – 7.60 (m, 2H), 7.59 – 7.47 (m, 6H), 7.47 – 7.40 (m, 4H), 7.07 (d, *J* = 15.6 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.1, 149.4, 141.7, 132.6, 131.8, 130.1, 128.8, 128.8, 128.4, 127.1, 126.1, 121.6, 35.0, 31.1. IR (thin film) ν 2963, 1615, 1537, 1306, 737 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{25}H_{25}NO_2SNa]^+$ ($[M+Na]^+$): 426.1498, found: 426.1501.



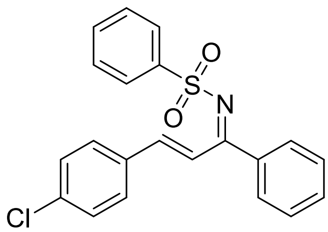
N-((1*E*,2*E*)-3-(4-methoxyphenyl)-1-phenylallylidene)benzenesulfonamide (**4s**)

Following the general procedure A, compound **4s** was obtained as a yellow solid (1.56 g, 83% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 – 7.76 (m, 3H), 7.75 – 7.58 (m, 2H), 7.58 – 7.46 (m, 6H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 15.8 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.3, 162.4, 149.7, 141.9, 132.6, 131.7, 130.9, 130.2, 128.9, 128.4, 127.4, 127.2, 122.6, 114.7, 55.6. The data matches with the reported value[2].



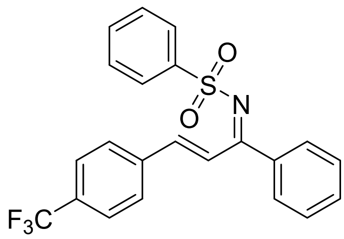
N-((1*E*,2*E*)-3-(4-fluorophenyl)-1-phenylallylidene)benzenesulfonamide (**5s**)

Following the general procedure A, compound **5s** was obtained as a white solid (1.17 g, 64% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 – 7.80 (m, 3H), 7.79 – 7.61 (m, 2H), 7.61 – 7.47 (m, 6H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.7, 164.5 (d, *J* = 253.1 Hz), 147.7, 141.5, 136.9, 132.8, 130.8, 130.8 (d, *J* = 8.6 Hz), 130.8, 130.1, 128.9, 128.5, 127.1, 122.4, 116.3 (d, *J* = 22.0 Hz). The data matches with the reported value[2].



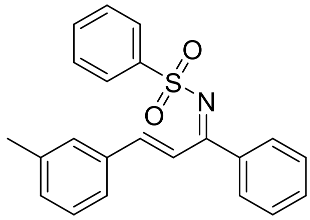
N-((1*E*,2*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)allylidene)benzenesulfonamide (**6s**)

Following the general procedure A, compound **6s** was obtained as a light-yellow solid (1.52 g, 73% yield). ^{1}H NMR (600 MHz,) δ 8.25 – 7.84 (m, 3H), 7.77 – 7.60 (m, 2H), 7.59 – 7.49 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 147.3, 141.5, 137.2, 136.9, 133.0, 132.8, 132.2, 130.2, 129.9, 129.4, 128.9, 128.5, 127.2, 123.0. The data matches with the reported value[2].



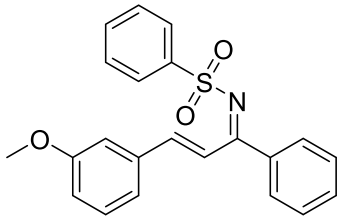
N-((1*E*,2*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)allylidene)benzenesulfonamide (**7s**)

Following the general procedure A, compound **7s** was obtained as a white solid (1.56 g, 75% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 – 7.95 (m, 3H), 7.82 – 7.59 (m, 6H), 7.58 – 7.48 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.2, 146.2, 141.4, 137.9, 136.9, 133.0. 132.5, 132.3, 130.3, 129.0, 128.9, 128.7, 127.3, 126.1, 126.1, 124.9, 124.7, 122.9. IR (thin film) ν 3067, 1618, 1544, 1324, 737 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{16}F_3NO_2SNa]^+$ ($[M+Na]^+$): 438.0746, found: 438.0746.



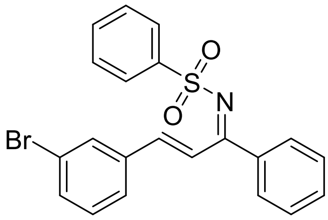
N-((1*E*,2*E*)-1-phenyl-3-(*m*-tolyl)allylidene)benzenesulfonamide (**8s**)

Following the general procedure A, compound **8s** was obtained as a yellow solid (1.26 g, 70% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 – 7.87 (m, 3H), 7.75 – 7.48 (m, 6H), 7.46 – 7.34 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 15.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 149.6, 141.7, 138.8, 137.2, 134.5, 132.7, 132.2, 132.0, 130.2, 129.3, 129.0, 128.9, 128.4, 127.2, 126.2, 122.4, 21.3. IR (thin film) ν 3061, 1616, 1538, 1307, 732 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{19}NO_2SNa]^+$ ($[M+Na]^+$): 384.1029, found: 384.1031.



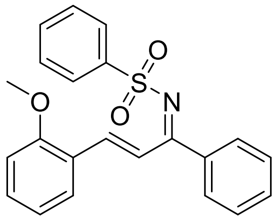
N-((1*E*,2*E*)-3-(3-methoxyphenyl)-1-phenylallylidene)benzenesulfonamide (**9s**)

Following the general procedure A, compound **9s** was obtained as a light-yellow solid (1.45 g, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 7.92 (m, 3H), 7.78 – 7.48 (m, 6H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.22 – 7.12 (m, 1H), 7.12 – 7.00 (m, 2H), 7.00 – 6.95 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 160.0, 149.1, 141.6, 137.2, 135.9, 132.7, 132.0, 130.3, 130.1, 128.9, 128.5, 127.2, 122.7, 121.5, 117.3, 113.4, 55.4. The data matches with the reported value[2].



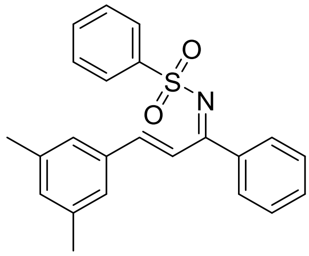
N-((1*E*,2*E*)-3-(3-bromophenyl)-1-phenylallylidene)benzenesulfonamide (**10s**)

Following the general procedure A, compound **10s** was obtained as a yellow solid (1.70 g, 80% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 7.84 (m, 3H), 7.71 – 7.60 (m, 3H), 7.60 – 7.48 (m, 6H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.22 (m, 1H), 6.98 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 146.8, 141.4, 136.9, 136.6, 133.8, 132.8, 131.5, 130.6, 130.2, 128.9, 128.5, 127.2, 127.0, 123.8, 123.2. The data matches with the reported value[2].



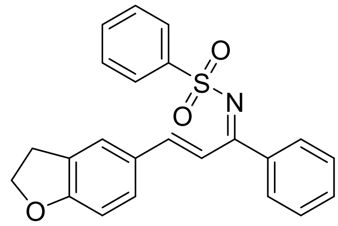
N-((1*E*,2*E*)-3-(2-methoxyphenyl)-1-phenylallylidene)benzenesulfonamide (**11s**)

Following the general procedure A, compound **11s** was obtained as a yellow solid (1.37 g, 73% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 – 7.91 (m, 3H), 7.77 – 7.59 (m, 3H), 7.59 – 7.34 (m, 8H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.8, 158.7, 145.1, 141.9, 137.4, 132.7, 132.7, 132.0, 130.5, 129.4, 128.9, 128.4, 127.2, 123.7, 122.9, 121.1, 111.3, 55.7. IR (thin film) ν 3067, 1607, 1527, 1305, 735 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{19}NO_3SNa]^+$ ($[M+Na]^+$): 400.0978, found: 400.0980.



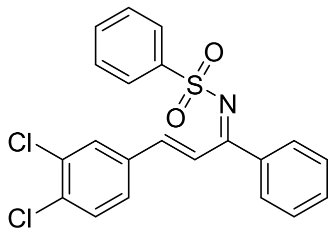
N-((1*E*,2*E*)-3-(3,5-dimethylphenyl)-1-phenylallylidene)benzenesulfonamide (**12s**)

Following the general procedure A, compound **12s** was obtained as a yellow solid (1.44 g, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.92 (m, 3H), 7.70 – 7.58 (m, 2H), 7.58 – 7.46 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.19 (s, 2H), 7.04 (d, *J* = 16.0 Hz, 2H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 150.0, 141.7, 138.6, 137.2, 134.4, 133.1, 132.6, 131.9, 130.1, 128.8, 128.3, 127.1, 126.7, 122.0, 21.1. IR (thin film) ν 2919, 1618, 1528, 1305, 1152 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{23}H_{21}NO_2SNa]^+$ ($[M+Na]^+$): 398.1185, found: 398.1185.



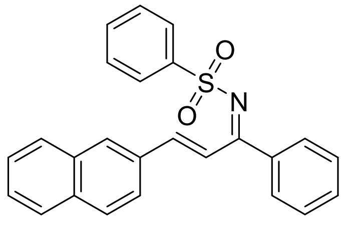
N-((1*E*,2*E*)-3-(2,3-dihydrobenzofuran-5-yl)-1-phenylallylidene)benzenesulfonamide (**13s**)

Following the general procedure A, compound **13s** was obtained as a yellow solid (1.59 g, 82% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 – 7.71 (m, 3H), 7.72 – 7.57 (m, 2H), 7.57 – 7.46 (m, 5H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.22 (m, 1H), 7.06 (d, *J* = 15.7 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 4.63 (t, *J* = 8.7 Hz, 2H), 3.22 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.3, 163.4, 150.3, 141.9, 137.4, 132.5, 131.6, 131.4, 130.0, 128.8, 128.6, 128.3, 127.4, 127.0, 125.0, 119.6, 109.8, 72.1, 29.1. The data matches with the reported value[2].



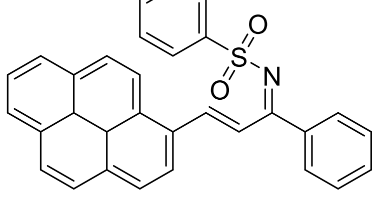
N-((1*E*,2*E*)-3-(3,4-dichlorophenyl)-1-phenylallylidene)benzenesulfonamide (**14s**)

Following the general procedure A, compound **14s** was obtained as a white solid (1.45 g, 70% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 7.87 (m, 3H), 7.75 – 7.59 (m, 3H), 7.58 – 7.49 (m, 4H), 7.48 – 7.36 (m, 4H), 6.95 (d, J = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.1, 145.5, 141.3, 136.7, 135.0, 134.5, 133.4, 132.9, 132.4, 131.1, 130.3, 130.2, 129.0, 128.6, 127.4, 127.2, 124.2. IR (thin film) ν 3067, 1624, 1556, 1306, 1154 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{15}Cl_2NO_2SNa]^+$ ($[M+Na]^+$): 438.0093, found: 438.0091.



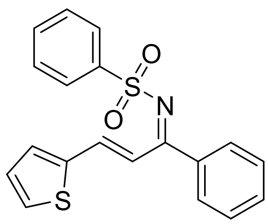
N-((1*E*,2*E*)-3-(naphthalen-2-yl)-1-phenylallylidene)benzenesulfonamide (**15s**)

Following the general procedure A, compound **15s** was obtained as a yellow solid (1.83 g, 92% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.34 – 7.99 (m, 3H), 7.94 – 7.78 (m, 5H), 7.76 – 7.62 (m, 2H), 7.60 – 7.50 (m, 6H), 7.47 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 15.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 141.6, 134.7, 133.2, 132.7, 132.1, 132.0, 131.2, 130.2, 129.0, 128.9, 128.8, 128.5, 127.9, 127.8, 127.2, 126.9, 123.9, 122.7. The data matches with the reported value[2].



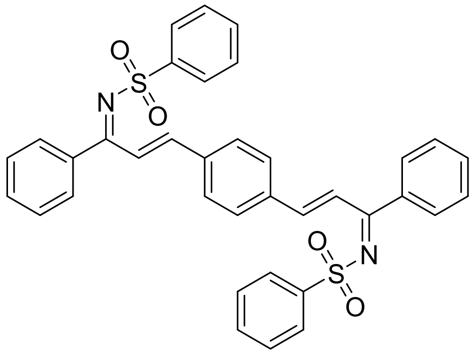
N-((1*E*,2*E*)-1-phenyl-3-(pyren-1-yl)allylidene)benzenesulfonamide (**16s**)

Following the general procedure A, compound **16s** was obtained as a red solid (1.67 g, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, J = 7.9 Hz, 1H), 8.44 – 8.16 (m, 5H), 8.15 – 7.98 (m, 7H), 7.82 (d, J = 6.6 Hz, 2H), 7.67 – 7.47 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.8, 141.7, 137.5, 133.4, 132.7, 132.1, 131.3, 130.5, 130.2, 129.1, 129.0, 128.9, 128.6, 128.2, 127.4, 127.2, 126.4, 126.4, 126.1, 125.4, 124.9, 124.8, 124.5, 122.1, 121.9. IR (thin film) ν 1634, 1528, 1306, 1152, 818 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{31}H_{21}NO_2SNa]^+$ ($[M+Na]^+$): 494.1185, found: 494.1189.



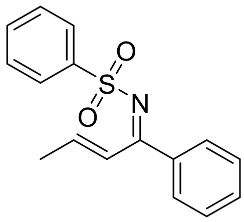
N-((1*E*,2*E*)-1-phenyl-3-(thiophen-2-yl)allylidene)benzenesulfonamide (**17s**)

Following the general procedure A, compound **17s** was obtained as a yellow solid (989 mg, 56% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 6.1 Hz, 2H), 7.95 – 7.58 (m, 3H), 7.58 – 7.35 (m, 7H), 7.26 (s, 1H), 7.19 (d, *J* = 15.6 Hz, 1H), 7.13 – 7.03 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 141.8, 141.6, 140.0, 132.7, 132.4, 131.8, 131.0, 129.9, 128.9, 128.6, 128.4, 127.2, 121.5. The data matches with the reported value[2].



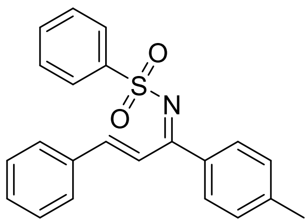
N,N'-((1*E*,1'*E*,2*E*,2'*E*)-1,4-phenylenebis(1-phenylprop-2-en-3-yl-1-ylidene))dibenzenesulfonamide (**18s**)

Following the general procedure A, compound **18s** was obtained as a yellow solid (862 mg, 28% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.52 – 7.87 (m, 6H), 7.83 – 7.31 (m, 20H), 7.17 – 6.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 147.3, 141.4, 136.9, 132.8, 132.3, 130.2, 129.3, 128.9, 128.5, 127.2, 123.8. IR (thin film) ν 1616, 1535, 1306, 1153, 725 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{36}H_{28}N_2O_4S_2Na]^+$ ($[M+Na]^+$): 639.1383, found: 639.1387.



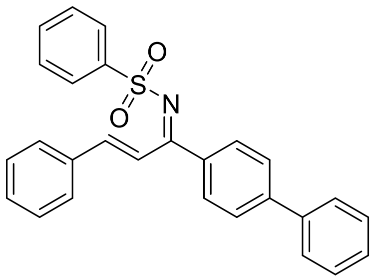
N-((1*E*,2*E*)-1-phenylbut-2-en-1-ylidene)benzenesulfonamide **(19s)**

Following the general procedure A, compound **19s** was obtained as a yellow oil (285 mg, 10% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.92 (m, 2H), 7.63 – 7.44 (m, 7H), 7.37 (t, *J* = 7.6 Hz, 2H), 6.52 – 6.34 (m, 1H), 2.03 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 150.6, 141.7, 137.4, 132.8, 132.1, 130.3, 128.9, 128.4, 127.2, 125.1, 19.7. IR (thin film) ν 3064, 1592, 1568 1448, 1310 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{16}H_{15}NO_2SNa]^+$ ($[M+Na]^+$): 308.0716, found: 308.0716.



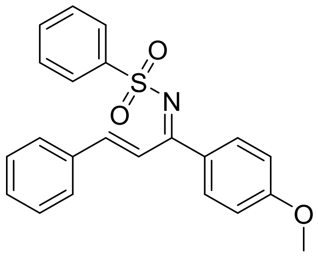
N-((1*E*,2*E*)-3-phenyl-1-(p-tolyl)allylidene)benzenesulfonamide (**21s**)

Following the general procedure A, compound **21s** was obtained as a yellow solid (1.46 g, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 7.93 (m, 3H), 7.67 – 7.42 (m, 7H), 7.42 – 7.34 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 16.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 148.6, 143.1, 141.8, 134.6, 134.3, 132.7, 131.1, 130.4, 129.2, 129.1, 128.9, 128.8, 127.1, 122.9, 21.7. IR (thin film) ν 3062, 2921, 1661, 1576, 1316 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{19}NO_2SNa]^+$ ($[M+Na]^+$): 384.1029, found: 384.1030.



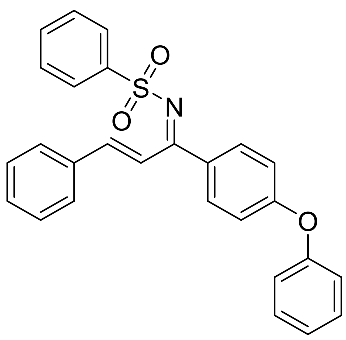
N-((1*E*,2*E*)-1-([1,1'-biphenyl]-4-yl)-3-phenylallylidene)benzenesulfonamide (**22s**)

Following the general procedure A, compound **22s** was obtained as a yellow solid (1.69 g, 80% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 – 7.89 (m, 3H), 7.75 – 7.70 (m, 2H), 7.70 – 7.37 (m, 15H), 7.16 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 148.9, 145.1, 141.7, 139.8, 135.9, 134.6, 132.8, 131.3, 130.9, 129.2, 129.1, 128.9, 128.9, 128.3, 127.3, 127.2, 127.1, 122.6. IR (thin film) ν 3060, 1611, 1526, 1317, 1152 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{27}H_{21}NO_2SNa]^+$ ($[M+Na]^+$): 446.1185, found: 446.1185.



N-((1*E*,2*E*)-1-(4-methoxyphenyl)-3-phenylallylidene)benzenesulfonamide (**23s**)

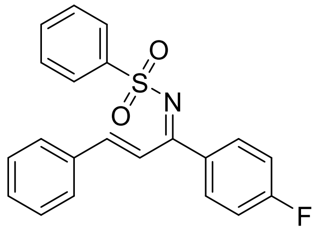
Following the general procedure A, compound **23s** was obtained as a yellow solid (1.32 g, 70% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.88 (m, 3H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.61 – 7.48 (m, 5H), 7.44 – 7.39 (m, 3H), 7.07 (d, *J* = 16.1 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.1, 163.4, 147.7, 141.9, 134.7, 132.6, 130.9, 129.1, 128.8, 128.6, 127.1, 113.9, 55.6. IR (thin film) ν 3061, 1603, 1578, 11521, 1306 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{19}NO_3SNa]^+$ ($[M+Na]^+$): 400.0978, found: 400.0978.



N-((1*E*,2*E*)-1-(4-phenoxyphenyl)-3-phenylallylidene)benzenesulfonamide (**24s**)

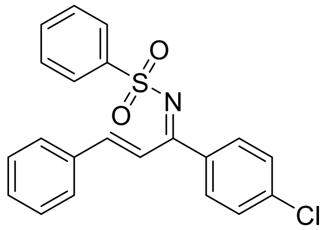
Following the general procedure A, compound **24s** was obtained as a light-yellow solid (1.47 g, 67% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.86 (m, 3H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.63 – 7.46 (m, 5H), 7.46 – 7.31 (m, 5H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.04 (m, 3H), 6.99 (d, *J* = 8.7 Hz, 2H). ^{13}C

NMR (101 MHz, Chloroform-*d*) δ 176.9, 161.7, 155.4, 148.1, 141.7, 134.5, 132.6, 132.4, 131.0, 130.1, 129.0, 128.8, 128.7, 127.1, 124.7, 120.2, 117.3. IR (thin film) ν 3062, 1614, 1585, 1529, 1317 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{27}H_{21}NO_3SNa]^+$ ($[M+Na]^+$): 462.1134, found: 462.1135.



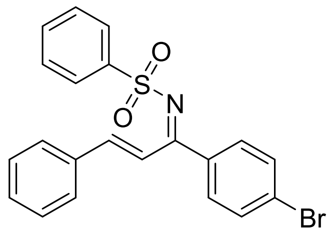
N-((1*E*,2*E*)-1-(4-fluorophenyl)-3-phenylallylidene)benzenesulfonamide (**25s**)

Following the general procedure A, compound **25s** was obtained as a white solid (1.30 g, 71% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.1 Hz, 3H), 7.79 – 7.62 (m, 2H), 7.62 – 7.47 (m, 5H), 7.47 – 7.34 (m, 3H), 7.18 – 6.99 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.5, 166.1, 164.5, 148.8, 141.4, 134.3, 132.8, 132.7, 131.3, 129.1, 129.0, 128.9, 128.8, 127.1, 122.4, 115.7, 115.6. IR (thin film) ν 3065, 1614, 1575, 1537, 1316 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{16}FNO_2SNa]^+$ ($[M+Na]^+$): 388.0778, found: 388.0782.



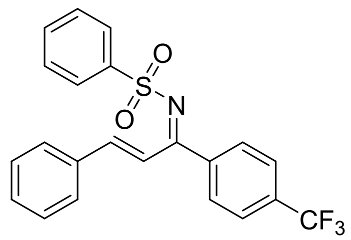
N-((1*E*,2*E*)-1-(4-chlorophenyl)-3-phenylallylidene)benzenesulfonamide (**26s**)

Following the general procedure A, compound **26s** was obtained as a white solid (1.28 g, 67% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.94 (m, 3H), 7.72 – 7.47 (m, 7H), 7.46 – 7.35 (m, 5H), 7.05 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 149.1, 141.4, 138.6, 135.5, 134.3, 131.6, 131.4, 129.2, 129.0, 128.9, 128.8, 127.2, 126.4, 122.2. The data matches with the reported value[2].



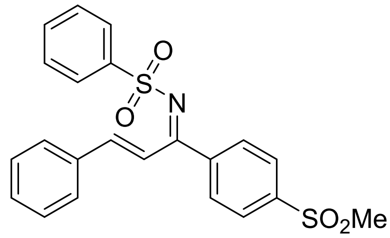
N-((1*E*,2*E*)-1-(4-bromophenyl)-3-phenylallylidene)benzenesulfonamide (**27s**)

Following the general procedure A, compound **27s** was obtained as a white solid (1.55 g, 73% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 7.97 (m, 3H), 7.75 – 7.47 (m, 9H), 7.42 – 7.37 (m, 3H), 7.06 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.7, 149.2, 141.4, 136.0, 134.3, 132.9, 131.8, 131.4, 129.2, 128.9, 128.9, 127.2, 122.2. IR (thin film) ν 3061, 1606, 1585, 1535, 1307 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{16}BrNO_2SNa]^+$ ($[M+Na]^+$): 447.9977, found: 447.9977.



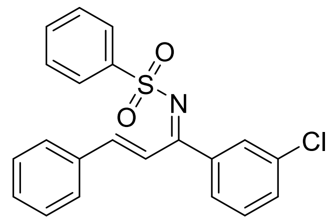
N-((1*E*,2*E*)-3-phenyl-1-(4-(trifluoromethyl)phenyl)allylidene)benzenesulfonamide (**28s**)

Following the general procedure A, compound **28s** was obtained as a yellow solid (1.20 g, 58% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 7.89 (m, 3H), 7.90 – 7.64 (m, 4H), 7.64 – 7.49 (m, 5H), 7.48 – 7.36 (m, 3H), 7.05 (d, *J* = 14.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.5, 150.0, 141.2, 140.7, 134.3, 133.1, 131.7, 130.5, 129.3, 129.1, 127.3, 125.5, 123.8 (q, *J* = 272.7 Hz), 122.8, 122.1, 121.0. IR (thin film) ν 3067, 1618, 1581, 1514, 1324 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{16}F_3NO_2SNa]^+$ ($[M+Na]^+$): 438.0746, found: 438.0747.



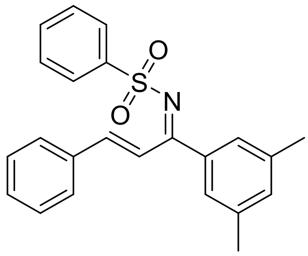
N-((1*E*,2*E*)-1-(4-(methylsulfonyl)phenyl)-3-phenylallylidene)benzenesulfonamide (**29s**)

Following the general procedure A, compound **29s** was obtained as a light-yellow solid (1.45 g, 68% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 – 7.91 (m, 5H), 7.87 – 7.71 (m, 2H), 7.63 – 7.49 (m, 5H), 7.47 – 7.39 (m, 3H), 7.05 (d, *J* = 14.6 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 150.3, 143.1, 142.2, 141.0, 134.0, 133.1, 131.8, 130.9, 129.2, 129.1, 127.5, 127.2, 121.8, 44.4. IR (thin film) ν 3026, 1659, 1601, 1574, 1541 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{19}NO_4S_2Na]^+$ ($[M+Na]^+$): 448.0648, found: 448.0646.



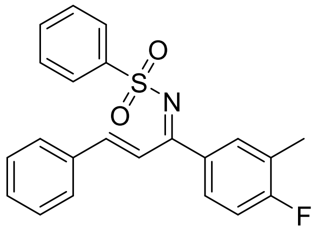
N-((1*E*,2*E*)-1-(3-chlorophenyl)-3-phenylallylidene)benzenesulfonamide (**30s**)

Following the general procedure A, compound **30s** was obtained as a light-yellow solid (991 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 7.86 (m, 3H), 7.85 – 7.47 (m, 8H), 7.46 – 7.35 (m, 4H), 7.07 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 149.5, 141.3, 138.8, 134.6, 134.3, 132.9, 131.9, 131.5, 129.7, 129.2, 129.0, 128.9, 128.3, 127.2, 122.2. IR (thin film) ν 3065, 1613, 1576 1540, 1316 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{21}H_{16}ClNO_2SNa]^+$ ($[M+Na]^+$): 404.0482, found: 404.0481.



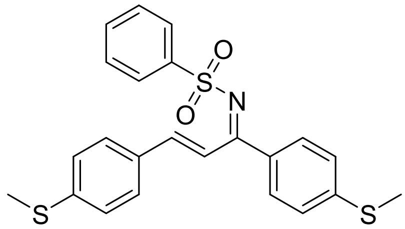
N-((1*E*,2*E*)-1-(3,5-dimethylphenyl)-3-phenylallylidene)benzenesulfonamide (**31s**)

Following the general procedure A, compound **31s** was obtained as a white solid (1.20 g, 64% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 – 7.81 (m, 3H), 7.65 – 7.48 (m, 5H), 7.45 – 7.39 (m, 3H), 7.32 – 7.12 (m, 3H), 7.07 (d, J = 16.0 Hz, 1H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 149.0, 141.7, 138.1, 137.2, 134.6, 133.8, 132.7, 131.1, 129.1, 128.9, 128.8, 127.9, 127.2, 122.7, 21.3. IR (thin film) ν 2919, 1618, 1528, 1445, 1306 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{21}NO_2SNa]^+$ ($[M+Na]^+$): 398.1185, found: 398.1187.



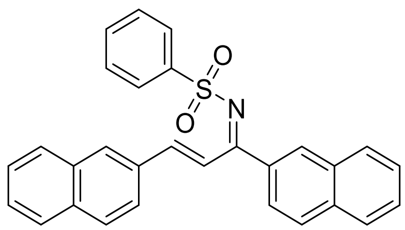
N-((1*E*,2*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylallylidene)benzenesulfonamide (**32s**)

Following the general procedure A, compound **32s** was obtained as a yellow solid (1.01 g, 53% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.93 (m, 3H), 7.66 – 7.45 (m, 7H), 7.44 – 7.37 (m, 3H), 7.12 – 7.00 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.0, 163.9 (d, J = 253.5 Hz), 148.8, 141.5, 134.5, 133.6, 132.8, 131.3, 130.0, 129.1, 128.9, 128.8, 127.2, 125.5 (d, J = 17.9 Hz), 122.7, 115.2 (d, J = 23.0 Hz), 14.6. IR (thin film) ν 3063, 1614, 1538, 1448, 1318 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{18}FNO_2SNa]^+$ ($[M+Na]^+$): 402.0934, found: 402.0935.



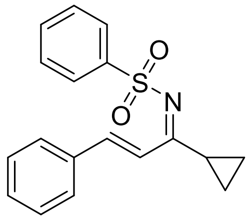
N-((1*E*,2*E*)-1,3-bis(4-(methylthio)phenyl)allylidene)benzenesulfonamide (**33s**)

Following the general procedure A, compound **33s** was obtained as a yellow solid (78% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 7.76 (m, 3H), 7.63 – 7.41 (m, 7H), 7.27 – 7.19 (m, 4H), 7.03 (d, J = 16.0 Hz, 1H), 2.49 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.2, 148.1, 145.0, 143.6, 141.8, 133.2, 132.6, 130.9, 130.7, 129.1, 128.9, 127.1, 125.8, 125.1, 121.8, 15.0, 14.9. IR (thin film) ν 3061, 2920, 1654, 1589, 1316 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{21}NO_2S_3Na]^+$ ($[M+Na]^+$): 462.0627, found: 462.0627.



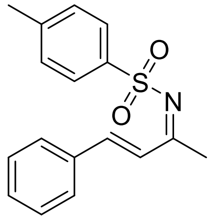
N-((1*E*,2*E*)-1,3-di(naphthalen-2-yl)allylidene)benzenesulfonamide (**34s**)

Following the general procedure A, compound **34s** was obtained as a yellow solid (85% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 – 8.16 (m, 2H), 8.14 – 8.05 (m, 2H), 7.93 – 7.75 (m, 9H), 7.54 (dp, *J* = 23.9, 7.4 Hz, 7H), 7.29 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 149.3, 144.9, 141.6, 134.9, 134.6, 133.2, 132.7, 132.4, 132.1, 131.1, 129.2, 129.0, 128.9, 128.7, 128.3, 128.2, 127.9, 127.8, 127.2, 126.9, 126.9, 123.8, 122.9. IR (thin film) ν 2991, 1628, 1539, 1304, 1152cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{29}H_{21}NO_2SNa]^+$ ($[M+Na]^+$): 471.1185, found: 471.1185.



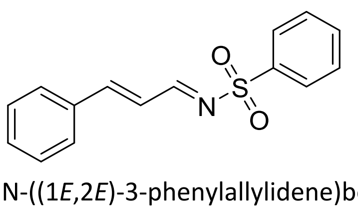
N-((1*Z*,2*E*)-1-cyclopropyl-3-phenylallylidene)benzenesulfonamide(**35s**)

Following the general procedure A, compound **35s** was obtained as a white solid (666 mg, 43% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.4 Hz, 3H), 7.74 – 7.47 (m, 6H), 7.47 – 7.36 (m, 3H), 2.58 – 2.15 (m, 1H), 1.24 – 1.03 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.2, 144.5, 142.0, 134.6, 132.4, 131.0, 129.0, 128.7, 126.7, 123.4, 29.7, 16.4, 13.2. IR (thin film) ν 3056, 1617, 1578, 1530, 1286 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO_2SNa]^+$ ($[M+Na]^+$): 334.0782, found: 334.0782.



4-methyl-N-((2*Z*,3*E*)-4-phenylbut-3-en-2-ylidene)benzenesulfonamide (**36s**)

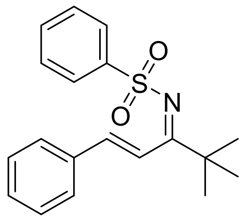
Following the general procedure A, compound **36s** was obtained as a yellow oil (234 mg, 16% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.43 – 7.37 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 16.3 Hz, 1H), 2.77 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.3, 144.1, 143.6, 138.5, 134.4, 130.8, 129.5, 129.0, 128.3, 127.1, 122.6, 21.6, 20.0. IR (thin film) ν 1638, 1478, 1318, 1205, 1146 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{17}H_{17}NO_2SNa]^+$ ($[M+Na]^+$):322.0872, found: 322.0872.



N-((1*E*,2*E*)-3-phenylallylidene)benzenesulfonamide (**37s**)

Following the general procedure A, compound **37s** was obtained as a white solid (196 mg, 15% yield).

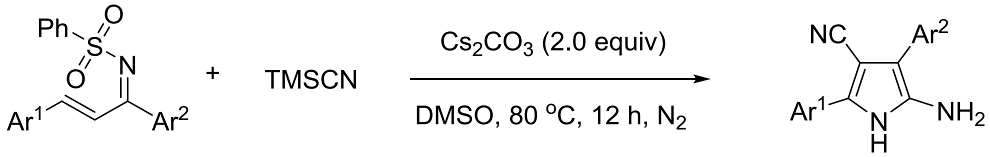
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 9.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.52 (m, 6H), 7.51 – 7.41 (m, 3H), 7.00 (dd, *J* = 15.8, 9.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 154.3, 138.5, 134.2, 133.6, 131.9, 129.3 (d, *J* = 3.8 Hz), 128.8, 128.0, 124.8. IR (thin film) ν 3054, 1617, 1579, 1448, 1318 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{15}H_{13}NO_2SNa]^+$ ($[M+Na]^+$): 294.0559, found: 294.0559.



N-((1*E*,2*E*)-4,4-dimethyl-1-phenylpent-1-en-3-ylidene)benzenesulfonamide (**38s**)

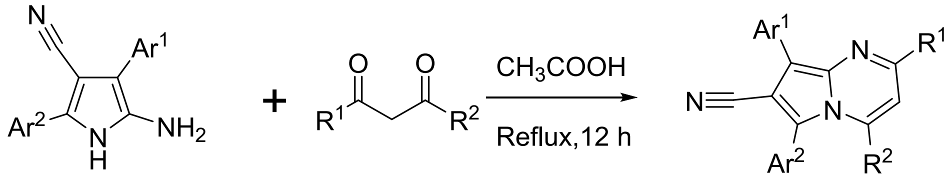
Following the general procedure A, compound **38s** was obtained as a white solid (916 mg, 56% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.35 (m, 9H), 7.09 (d, *J* = 16.5 Hz, 1H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.1, 142.1, 135.1, 132.3, 130.0, 128.9, 128.7, 127.9, 126.9, 121.3, 42.8, 28.4. IR (thin film) ν 2974, 1630, 1577, 1447, 1305 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{19}H_{21}NO_2SNa]^+$ ($[M+Na]^+$): 350.1185, found: 350.1189.

General procedure B for the synthesis of pyrroles



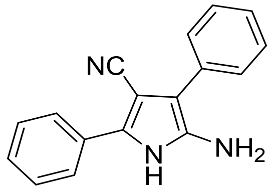
General procedure B: To a 25 mL of Schlenk tube with a stir bar was added the α,β-unsaturated sulfonimine (0.5 mmol), Cs_2CO_3 (1 mmol, 326 mg) and DMSO (4 mL) under a nitrogen atmosphere. Upon dissolution the imine, TMSCN (138 uL, 2.2 equiv) was added, and the mixture was stirred for 10 s - 1 min until the solution turned red. Then, the mixture was heated to 80 °C in an oil bath for 12 h. After cooling to rt, the solution was pooled into 20 mL of ice water until no solid precipitate. The desired pyrrole can be obtained through filtration without further purification.

General procedure C for the synthesis of pyrrolo[1,2-*a*]pyrimidine

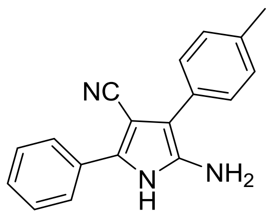


General procedure C: A mixture of NH-pyrrole (1 mmol) and 1,3-diketone (1.5-10 mmol) was refluxed in acetic acid (5 mL) overnight. After the reaction solution was cooled to room temperature, 10 mL of DCM was added. The organic layer was washed with water (3×20 mL) and saturated sodium carbonate solution (10 mL), dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography on silica gel (petroleum ether:DCM:EtOAc 20:5:1) to give the pure product.[3]

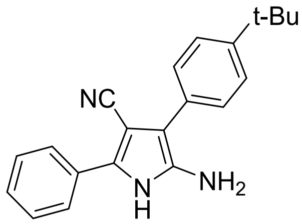
Characterization data for pyrroles



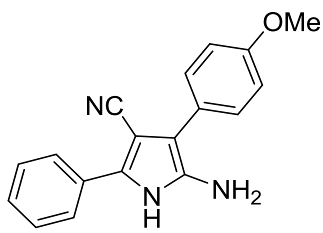
Following the general procedure B, compound **1** was obtained as a gray solid (104 mg, 80% yield). Mp > 300 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.40 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.84 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 138.0, 134.0, 131.8, 130.8, 129.6, 129.2, 127.7, 125.8, 125.1, 119.2, 105.2, 87.4. IR (thin film) ν 3373, 3267, 2211, 1600, 740 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{17}H_{13}N_3Na]^+$ ($[M+Na]^+$): 282.1002, found: 282.1003.



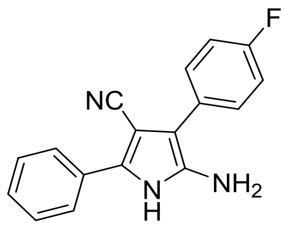
Following the general procedure B, compound **2** was obtained as a gray solid (121 mg, 89% yield). Mp 176.1-177.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.78 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.6, 134.9, 131.4, 131.0, 130.8, 129.7, 129.5, 127.6, 125.0, 119.1, 105.3, 87.4, 21.2. IR (thin film) ν 3373, 3247, 2212, 1609, 1520 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}N_3Na]^+$ ($[M+Na]^+$): 296.1158, found: 296.1559.



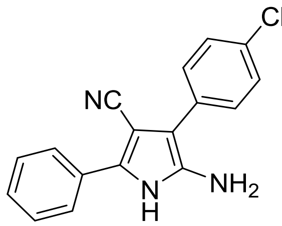
Following the general procedure B, compound **3** was obtained as a gray solid (106 mg, 67% yield). Mp 250.6-251.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.38 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.39 (m, 6H), 7.30 (t, *J* = 7.4 Hz, 1H), 4.82 (s, 2H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.1, 137.7, 131.4, 131.0, 130.8, 129.5, 127.6, 127.3, 125.9, 125.0, 119.2, 105.1, 87.4, 34.7, 31.6. IR (thin film) ν 3369, 3266, 2211, 1616, 1520 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{21}N_3Na]^+$ ($[M+Na]^+$): 338.1628, found: 338.1628.



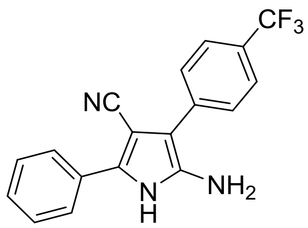
Following the general procedure B, compound **4** was obtained as a gray green solid (131 mg, 91% yield). Mp > 300 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.38 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.38 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 4.73 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 157.7, 137.2, 131.2, 130.8, 129.5, 129.0, 127.5, 126.2, 124.9, 119.2, 114.6, 105.4, 87.4, 55.6. IR (thin film) ν 3370, 3246, 2213, 1611, 1517 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{18}H_{15}N_3ONa]^+$ ($[M+Na]^+$): 312.1107, found: 312.1107.



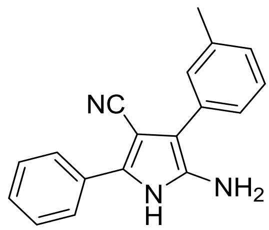
Following the general procedure B, compound **5** was obtained as a gray solid (133 mg, 96% yield). Mp 279.2-280.0 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.42 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.53 – 7.44 (m, 4H), 7.34 – 7.22 (m, 3H), 4.86 (s, 2H). ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -117.10. ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 160.7 (d, *J* = 242.4 Hz), 137.8, 131.7, 130.7, 130.3 (d, *J* = 3.1 Hz), 129.6 (d, *J* = 8.0 Hz), 129.5, 127.7, 125.1, 119.0, 115.9 (d, *J* = 21.2 Hz), 104.3, 87.3. IR (thin film) ν 3365, 3259, 2212, 1620, 1517 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{17}H_{12}FN_3Na]^+$ ($[M+Na]^+$): 300.0907, found: 300.0907.



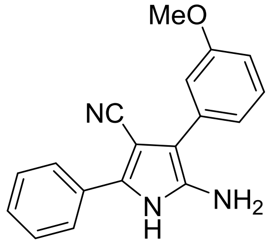
Following the general procedure B, compound **6** was obtained as a brown solid (143 mg, 72% yield). Mp 261.3-261.7 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.46 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.59 – 7.39 (m, 6H), 7.32 (t, *J* = 7.3 Hz, 1H), 4.97 (s, 2H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 138.3, 132.9, 132.0, 130.6, 130.1, 129.5, 129.2, 129.0, 127.8, 125.1, 118.9, 103.8, 87.1. IR (thin film) ν 3369, 3260, 2211, 1614, 1506 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{17}H_{12}ClN_3Na]^+$ ($[M+Na]^+$): 316.0612, found: 316.0612.



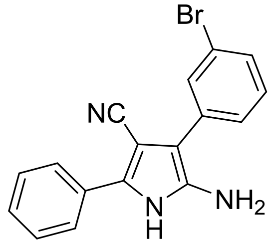
Following the general procedure B, compound **7** was obtained as a gray solid (136 mg, 83% yield). Mp 263.8-264.6 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.53 (s, 1H), 7.79 – 7.67 (m, 6H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.16 (s, 2H). ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -60.62. ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 139.2, 138.4, 132.6, 130.4, 129.5, 128.0, 127.7, 125.9, 125.9, 125.3, 118.9, 103.1, 87.0. IR (thin film) ν 3359, 3232, 2215, 1611, 1523 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{18}H_{12}F_3N_3Na]^+$ ($[M+Na]^+$): 350.0876, found: 350.0876.



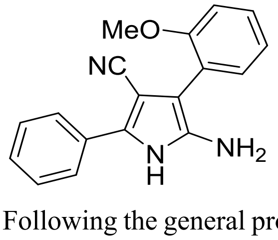
Following the general procedure B, compound **8** was obtained as a gray green solid (109 mg, 80% yield). Mp 191.3-193.5 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.40 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.24 (m, 4H), 7.03 (d, *J* = 5.4 Hz, 1H), 4.85 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.1, 137.9, 133.8, 131.6, 130.8, 129.5, 129.0, 128.3, 127.6, 126.5, 125.0, 124.8, 119.1, 105.2, 87.3, 21.7. IR (thin film) ν 3348, 2206, 1610, 1536, 693 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{18}H_{15}N_3Na]^+$ ($[M+Na]^+$): 296.1158, found: 296.1159.



Following the general procedure B, compound **9** was obtained as a brown solid (123 mg, 85% yield). Mp 198.3-199.4 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.41 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.08 – 7.00 (m, 2H), 6.74 (d, *J* = 7.3 Hz, 1H), 4.87 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.9, 138.1, 135.3, 131.8, 130.7, 130.1, 129.5, 127.7, 125.1, 119.9, 119.2, 113.0, 111.5, 104.9, 87.3, 55.3. IR (thin film) ν 3364, 2835, 2210, 1608, 692 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{18}H_{15}N_3ONa]^+$ ($[M+Na]^+$): 312.1107, found: 312.1107.

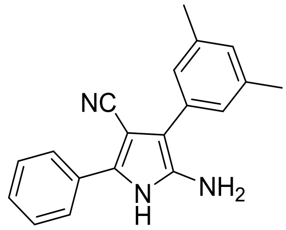


Following the general procedure B, compound **10** was obtained as a brown solid (130 mg, 77% yield). Mp 213.3-214.2 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.46 (s, 1H), 7.78 – 7.63 (m, 3H), 7.55 – 7.44 (m, 3H), 7.42 – 7.27 (m, 3H), 5.03 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.6, 136.5, 132.3, 131.1, 130.5, 129.8, 129.5, 128.3, 127.9, 126.4, 125.2, 122.5, 118.9, 103.3, 87.1. IR (thin film) ν 3371, 3276, 2209, 1619, 738 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{17}H_{12}N_3BrNa]^+$ ($[M+Na]^+$): 360.0107, found: 360.0108.

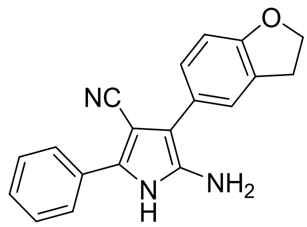


Following the general procedure B, compound **11** was obtained as a gray solid (134 mg, 93% yield).

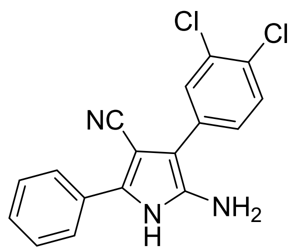
Mp 91.2-92.0 °C. [1]H NMR (400 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.08 (d, J = 8.1 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 4.48 (s, 2H), 3.82 (s, 3H). [13]C NMR (101 MHz, DMSO-d_6) δ 156.6, 138.2, 131.1, 131.0, 130.9, 129.4, 128.2, 127.4, 124.9, 122.2, 120.9, 118.9, 111.9, 102.7, 89.1, 55.7. IR (thin film) ν 3337, 3283, 2209, 1620, 756 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{18}H_{15}N_3ONa]^+$ ($[M+Na]^+$): 312.1107, found: 312.1107.



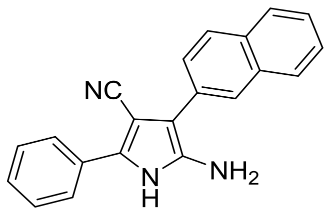
Following the general procedure B, compound **12** was obtained as a brown solid (129 mg, 90% yield). Mp 185.1-185.7 °C. [1]H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.09 (s, 2H), 6.85 (s, 1H), 4.82 (s, 2H), 2.30 (s, 6H). [13]C NMR (101 MHz, DMSO-d_6) δ 137.9, 137.8, 133.7, 131.5, 130.8, 129.5, 127.6, 127.4, 125.5, 125.0, 119.2, 105.3, 87.4, 21.6. IR (thin film) ν 3336, 3259, 2212, 1618, 1600 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{19}H_{17}N_3Na]^+$ ($[M+Na]^+$): 310.1315, found: 310.1316.



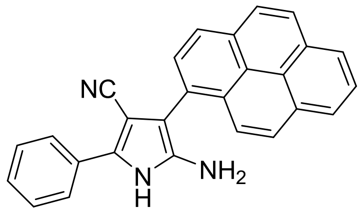
Following the general procedure B, compound **13** was obtained as a gray solid (126 mg, 84% yield). Mp 118.5-119.1 °C. [1]H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 1H), 7.79 – 7.66 (m, 2H), 7.60 – 7.41 (m, 2H), 7.37 – 7.24 (m, 2H), 7.17 (d, J = 6.7 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 4.69 (s, 2H), 4.54 (t, J = 8.8 Hz, 2H), 3.21 (t, J = 8.8 Hz, 2H). [13]C NMR (101 MHz, DMSO-d_6) δ 158.3, 137.1, 131.0, 130.9, 129.5, 128.1, 127.6, 127.4, 126.0, 124.9, 124.8, 119.2, 109.5, 106.0, 87.6, 71.4, 29.7. IR (thin film) ν 3353, 3293, 2209, 1612, 1537 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{19}H_{15}N_3ONa]^+$ ($[M+Na]^+$): 324.1107, found: 324.1109.



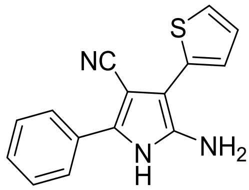
Following the general procedure B, compound **14** was obtained as a gray solid (119 mg, 73% yield). Mp 225.4-226.6 °C. [1]H NMR (400 MHz, DMSO-d_6) δ 11.54 (s, 1H), 7.77 – 7.62 (m, 4H), 7.54 – 7.43 (m, 3H), 7.33 (t, J = 7.0 Hz, 1H), 5.13 (s, 2H). [13]C NMR (101 MHz, DMSO-d_6) δ 139.0, 134.8, 132.5, 131.7, 131.1, 130.4, 129.5, 128.9, 128.0, 127.7, 127.5, 125.2, 118.8, 102.3, 86.9. IR (thin film) ν 3424, 3340, 2210, 1616, 1502 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{17}H_{11}Cl_2N_3Na]^+$ ($[M+Na]^+$): 350.0222, found: 350.0221.



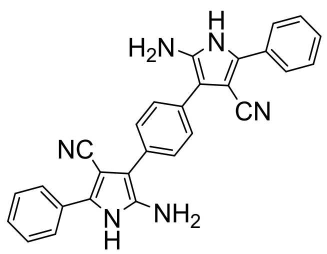
Following the general procedure B, compound **15** was obtained as a gray solid (139 mg, 90% yield). Mp 211.7-212.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 7.95 (d, J = 7.7 Hz, 2H), 7.89 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 8.9 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.33 (t, J = 7.3 Hz, 1H), 5.02 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.4, 133.9, 131.9, 131.6, 131.6, 130.7, 129.5, 128.4, 128.1, 127.9, 127.7, 126.6, 125.8, 125.4, 125.1, 119.2, 105.0, 87.4. IR (thin film) ν 3373, 3253, 2212, 1608, 1533 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{21}H_{15}N_3Na]^+$ ($[M+Na]^+$): 332.1158, found: 332.1157.



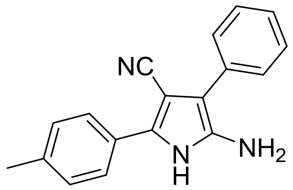
Following the general procedure B, compound **16** was obtained as a yellow solid (190 mg, 99% yield). Mp 144.3-145.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 8.35 (d, J = 7.9 Hz, 1H), 8.33 – 8.28 (m, 2H), 8.24 – 8.18 (m, 3H), 8.14 – 8.07 (m, 2H), 8.05 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 4.73 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.3, 129.2, 128.9, 128.6, 128.4, 127.8, 127.1, 126.9, 126.6, 126.5, 125.3, 125.2, 125.1, 125.0, 124.2, 123.7, 123.0, 122.9, 122.8, 122.5, 122.4, 122.1, 116.4, 101.7, 87.4. IR (thin film) ν 3447, 2211, 1617, 1508, 692 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{27}H_{17}N_3Na]^+$ ($[M+Na]^+$): 406.1315, found: 406.1308.



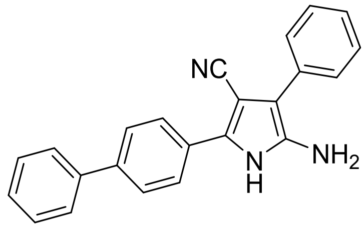
Following the general procedure B, compound **17** was obtained as a gray solid (93 mg, 70% yield). Mp 175.4-175.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.5 (s, 1H), 7.7 (d, J = 7.0 Hz, 2H), 7.5 – 7.4 (m, 3H), 7.4 – 7.3 (m, 1H), 7.2 (s, 1H), 7.1 (s, 1H), 5.0 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.1, 135.7, 131.9, 130.4, 129.5, 127.9, 125.2, 123.2, 122.9, 118.8, 99.6, 86.9. IR (thin film) ν 3356, 3258, 2211, 1616, 1523 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{15}H_{11}N_3SNa]^+$ ($[M+Na]^+$): 288.0566, found: 288.0566.



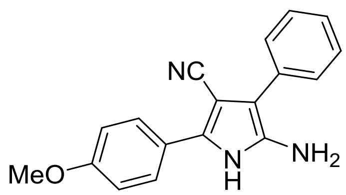
Following the general procedure B, compound **18** was obtained as a brown solid (176 mg, 80% yield). Mp >300 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.46 (s, 2H), 7.80 – 7.67 (m, 4H), 7.60 – 7.52 (m, 4H), 7.50 – 7.43 (m, 4H), 7.34 – 7.29 (m, 2H), 4.88 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.9, 131.6, 131.0, 130.7, 129.5, 127.7, 127.6, 125.0, 119.2, 105.2, 87.2. IR (thin film) ν 3359, 3247, 2212, 1595, 1522 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{28}H_{20}N_6Na]^+$ ($[M+Na]^+$): 463.1642, found: 463.1642.



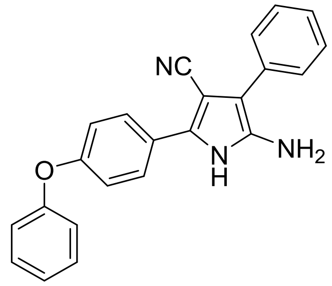
Following the general procedure B, compound **21** was obtained as a gray solid (120 mg, 88% yield). Mp 210.3-211.4 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.82 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.5, 137.2, 134.1, 132.1, 130.0, 129.1, 128.0, 127.6, 125.7, 125.0, 119.2, 104.8, 86.7, 21.3. IR (thin film) ν 3461, 3376, 2213, 1617, 1508 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{18}H_{15}N_3Na]^+$ ($[M+Na]^+$): 296.1158, found: 296.1158.



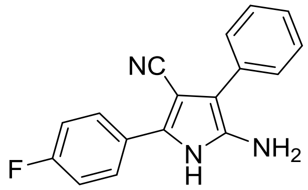
Following the general procedure B, compound **22** was obtained as a green solid (159 mg, 95% yield). Mp 236.3-238.0 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.54 (s, 1H), 7.87 – 7.79 (m, 4H), 7.74 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 4.94 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.8, 139.0, 138.2, 133.9, 131.2, 129.7, 129.5, 129.1, 128.0, 127.6, 126.9, 125.8, 125.4, 119.2, 105.3, 87.5. IR (thin film) ν 3375, 3254, 2212, 1600, 694 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{17}N_3Na]^+$ ($[M+Na]^+$): 358.1315, found: 358.1314.



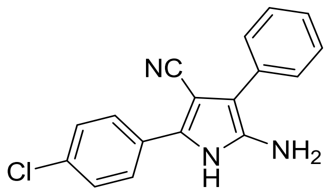
Following the general procedure B, compound **23** was obtained as a gray solid (138 mg, 82% yield). Mp 248.3-249.5 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.27 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 4.77 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.1, 137.1, 134.2, 132.4, 129.1, 127.5, 126.7, 125.6, 123.4, 119.4, 114.9, 104.6, 86.1, 55.7. IR (thin film) ν 3375, 3253, 2212, 1616, 1508 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{18}H_{14}N_3O]^-$ ($[M-H]^-$): 288.1131, found: 288.1129.



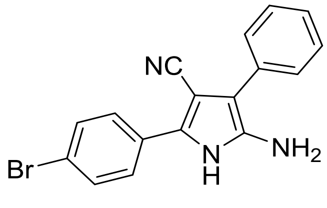
Following the general procedure B, compound **24** was obtained as a green solid (167 mg, 95% yield). Mp 227.2-228.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.44 – 7.40 (m, 3H), 7.24 – 7.16 (m, 3H), 7.13 – 7.06 (m, 4H), 4.84 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.3, 156.8, 138.1, 134.5, 132.0, 131.1, 129.5, 128.0, 127.4, 126.6, 126.2, 124.7, 120.0, 119.8, 119.6, 105.4, 87.3. IR (thin film) ν 3374, 3258, 2210, 1588, 1508 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{23}H_{17}N_3NaO]^+$ ($[M+Na]^+$): 374.1264, found: 374.1265.



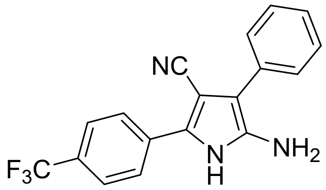
Following the general procedure B, compound **25** was obtained as a gray solid (126 mg, 91% yield). Mp 233.6-243.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.43 (s, 1H), 7.74 (dd, J = 8.2, 5.5 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 8.7 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.86 (s, 2H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.25. ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.7 (d, J = 245.0 Hz), 137.8, 133.9, 131.0, 129.1, 127.6, 127.4 (d, J = 3.3 Hz), 127.2 (d, J = 8.2 Hz), 125.8, 119.0, 116.5 (d, J = 21.8 Hz), 105.1, 87.3. IR (thin film) ν 3376, 3262, 2212, 1615, 1509 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{17}H_{12}FN_3Na]^+$ ($[M+Na]^+$): 300.0907, found: 300.0907.



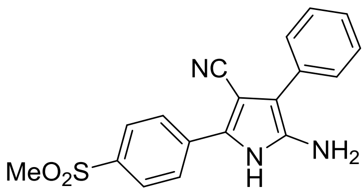
Following the general procedure B, compound **26** was obtained as a gray solid (145 mg, 99% yield). Mp 233.6-234.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.92 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.3, 133.8, 131.8, 130.2, 129.5, 129.5, 129.1, 127.7, 126.5, 125.9, 118.9, 105.4, 87.9. IR (thin film) ν 3376, 3259, 2212, 1614, 1507 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{17}H_{12}ClN_3Na]^+$ ($[M+Na]^+$): 316.0612, found: 316.0610.



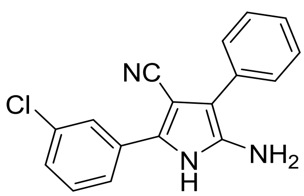
Following the general procedure B, compound **27** was obtained as a gray solid (147 mg, 87% yield). Mp 244.8-245.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 7.71 – 7.63 (m, 4H), 7.49 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 4.94 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.4, 133.8, 132.4, 130.2, 129.9, 129.1, 127.7, 126.8, 125.9, 120.3, 118.9, 105.4, 87.9. IR (thin film) ν 3375, 3244, 2214, 1616, 1508 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}BrN_3Na]^+$ ($[M+Na]^+$): 360.0107, found: 360.0107.



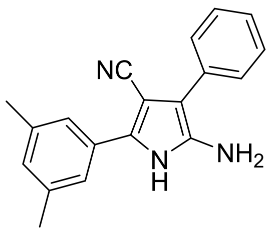
Following the general procedure B, compound **28** was obtained as a gray solid (123 mg, 75% yield). Mp 227.3-228.1 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.43 (s, 1H), 7.74 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 8.7 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.86 (s, 2H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.09. ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.2, 134.4, 133.5, 129.2, 129.1, 127.8, 126.5 (q, *J* = 3.9 Hz), 126.1, 125.0, 124.7 (q, *J* = 271.7 Hz), 118.7, 106.1, 89.2. IR (thin film) ν 3376, 3260, 2211, 1614, 1510 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{18}H_{12}F_3N_3Na]^+$ ($[M+Na]^+$): 350.0876, found: 350.0875.



Following the general procedure B, compound **29** was obtained as a green solid (142 mg, 84% yield). Mp 253.3-254.2 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 8.00 – 7.82 (m, 4H), 7.52 – 7.35 (m, 4H), 7.26 – 7.13 (m, 1H), 5.06 (s, 2H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.6, 138.5, 135.2, 133.4, 129.2, 128.8, 128.3, 127.8, 126.2, 124.8, 118.6, 106.4, 89.8, 44.0. IR (thin film) ν 3422, 2211, 1617, 1590, 1509 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}N_3O_2SNa]^+$ ($[M+Na]^+$): 360.0777, found: 360.0776.

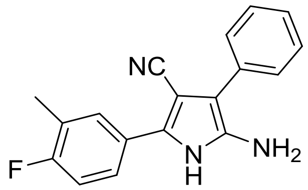


Following the general procedure B, compound **30** was obtained as a gray solid (102 mg, 69% yield). Mp 219.9-221.0 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 7.81 – 7.67 (m, 2H), 7.54 – 7.46 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.00 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.7, 134.2, 133.7, 132.6, 131.4, 129.4, 129.1, 127.7, 127.0, 125.9, 124.2, 123.3, 118.8, 105.5, 88.3. IR (thin film) ν 3368, 3259, 2211, 1615, 1510 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}ClN_3Na]^+$ ($[M+Na]^+$): 316.0612, found: 316.0612.

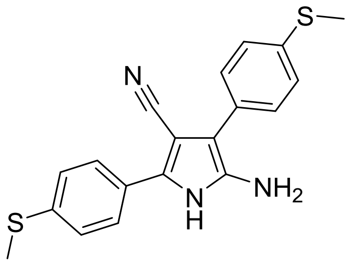


Following the general procedure B, compound **31** was obtained as a gray solid (98 mg, 68% yield).

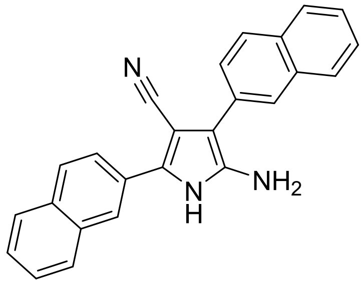
Mp 209.6-210.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.31 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (s, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.96 (s, 1H), 4.82 (s, 2H), 2.32 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.4, 137.7, 134.1, 131.9, 130.7, 129.2, 129.1, 127.6, 125.7, 122.8, 119.2, 104.9, 87.0, 21.5. IR (thin film) ν 3360, 3257, 2213, 1618, 1509 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{19}H_{17}N_3Na]^+$ ($[M+Na]^+$): 310.1315, found: 310.1314.



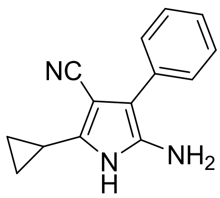
Following the general procedure B, compound **32** was obtained as a gray solid (143 mg, 98% yield). Mp 197.5-198.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.45 (s, 1H), 7.62 – 7.55 (m, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 9.1 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.87 (s, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.62. ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.3 (d, *J* = 244.5 Hz), 137.7, 134.0, 131.1, 129.1, 128.4 (d, *J* = 5.0 Hz), 127.6, 127.1 (d, *J* = 3.4 Hz), 125.7, 125.3 (d, *J* = 17.7 Hz), 124.7 (d, *J* = 8.1 Hz), 119.1, 116.1 (d, *J* = 22.7 Hz), 104.9, 87.1, 14.8. IR (thin film) ν 3375, 3260, 2211, 1618, 1508 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{18}H_{14}FN_3Na]^+$ ($[M+Na]^+$): 314.1064, found: 314.1064.



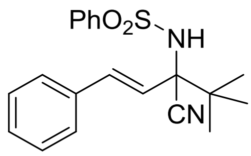
Following the general procedure B, compound **33** was obtained as a green solid (87% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.26 (m, 4H), 4.85 (s, 2H), 2.50 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.2, 137.1, 134.4, 130.8, 130.1, 127.5, 126.6, 126.5, 126.2, 124.8, 118.5, 104.0, 86.3, 15.0, 14.5. IR (thin film) ν 3370, 3243, 2211, 1610, 1507 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{19}H_{17}N_3S_2Na]^+$ ($[M+Na]^+$): 374.0756, found: 374.0756.



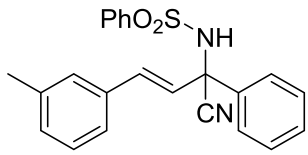
Following the general procedure B, compound **34** was obtained as a green solid (90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.66 (s, 1H), 8.21 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 8.01 – 7.86 (m, 7H), 7.73 (d, *J* = 9.5 Hz, 1H), 7.59 – 7.45 (m, 4H), 5.12 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.4, 134.4, 134.1, 132.9, 132.2, 132.1, 132.1, 129.6, 128.9, 128.7, 128.7, 128.6, 128.4, 127.9, 127.1, 126.3, 126.0, 124.0, 123.6, 119.8, 105.7, 88.5. IR (thin film) ν 3375, 2212, 1613, 1599, 1524 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{25}H_{17}N_3Na]^+$ ($[M+Na]^+$): 382.1315, found: 382.1315.



Following the general procedure B, compound **35** was obtained as a white solid (48 mg, 43% yield). Mp 130.5-131.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 4.51 (s, 2H), 1.98 – 1.88 (m, 1H), 0.99 – 0.91 (m, 2H), 0.84 – 0.77 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.3, 134.8, 134.6, 129.0, 127.1, 125.1, 118.7, 102.5, 87.1, 8.5, 7.5. IR (thin film) ν 3398, 2923, 2207, 1600, 1506 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{14}H_{13}N_3Na]^+$ ($[M+Na]^+$):246.1002, found: 246.1002.

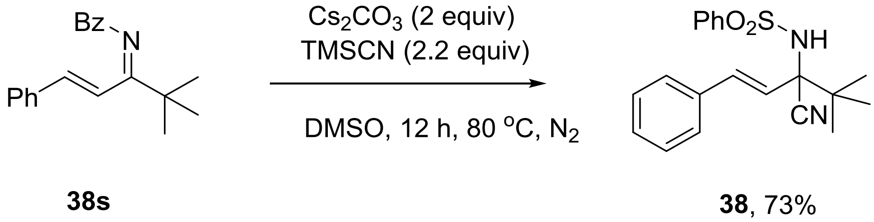


Following the general procedure B, compound **38** was obtained as a white solid (129 mg, 73% yield). Mp 134.8-135.1 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.26 – 7.22 (m, 2H), 6.75 (d, *J* = 16.1 Hz, 1H), 5.91 (d, *J* = 16.1 Hz, 1H), 5.38 (s, 1H), 1.12 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.9, 135.8, 134.9, 133.3, 129.1, 129.0, 128.8, 128.2, 127.1, 121.1, 117.1, 66.6, 40.3, 25.0. IR (thin film) ν 3307, 2969, 2245, 1645, 1157 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{20}H_{22}N_2NaSO_2]^+$ ($[M+Na]^+$): 377.1294, found: 377.1293.

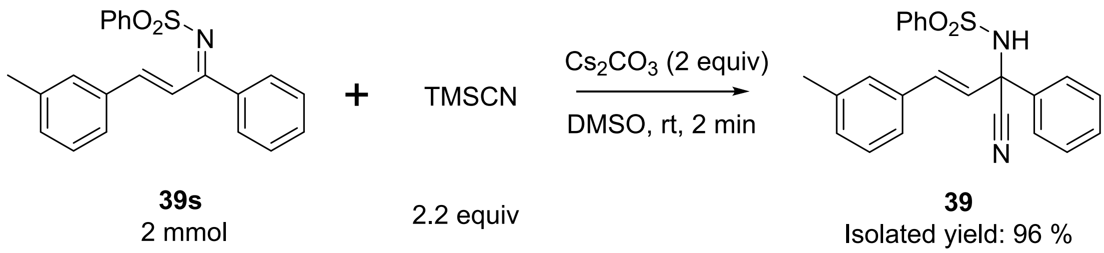


Compound **39** was obtained as a white solid (745 mg, 96% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.61 – 7.53 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.14 – 7.04 (m, 3H), 6.90 – 6.83 (m, 1H), 6.09 (d, *J* = 15.8 Hz, 1H), 5.37 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.0, 138.4, 136.5, 134.4, 133.3, 133.2, 129.9, 129.6, 129.3, 129.0, 128.6, 128.0, 127.7, 125.9, 125.0, 124.5, 117.1, 62.3, 21.3. IR (thin film) ν 3467, 3311, 2247, 1646, 1605 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{20}N_2O_2SNa]^+$ ($[M+Na]^+$): 411.1135, found: 411.1135.

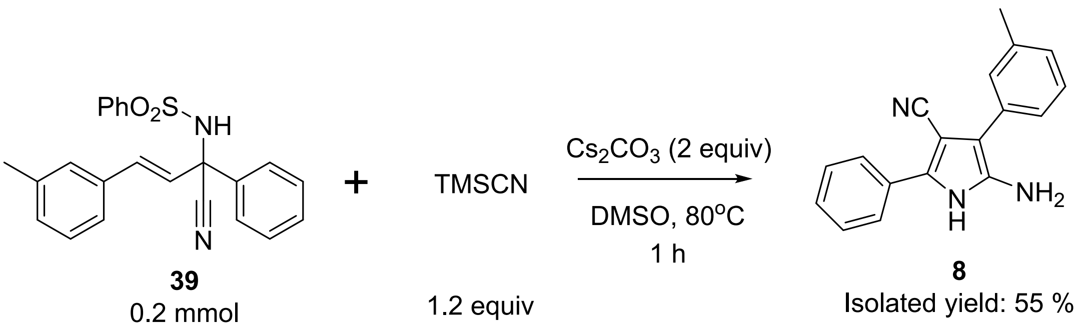
Mechanism experiments



To a 25 mL of Schlenk tube with a stir bar was added the α,β-unsaturated sulfonimine (0.5 mmol), Cs_2CO_3 (1 mmol, 326 mg) and DMSO (4 mL) under a nitrogen atmosphere. Upon dissolution the imine, TMSCN (138 uL, 2.2 equiv) was added, and the mixture was stirred for 10 s - 1 min until the solution turned red. Then, the mixture was heated to 80 °C in an oil bath for 12 h. Then, the mixture was pooled into 20 mL of water then extracted with EA/PE=1:1 (30mL*3). The organic phase was washed three times with a large amount of water, dried over anhydrous magnesium sulfate, evaporated to remove the solvent, and separated with a silica gel column (PE/EA=10:1-PE/EA=3:1). **38s** Not afford the desired pyrrole product but afforded 1,2-cyano addition product **38** in 73% yield.

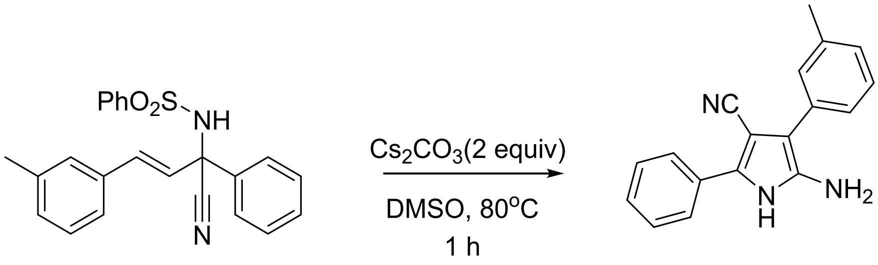


To a 50 mL of Schlenk tube with a stir bar was added the α,β-unsaturated sulfonimine (2 mmol), Cs_2CO_3 (4 mmol, 1.3 g) and DMSO (16 mL) under a nitrogen atmosphere. Upon dissolution the imine, TMSCN (552 uL, 4.4 equiv) was added, and the mixture was stirred for 1-5 min until complete disappearance of raw materials detected by TLC. Then, the mixture was pooled into 20 mL of water then extracted with EA/PE=1:1 (30mL*3). The organic phase was washed three times with a large amount of water, dried over anhydrous magnesium sulfate, evaporated to remove the solvent, and separated with a silica gel column(PE/EA=10:1-PE/EA=3:1).



To a 25 mL of Schlenk tube with a stir bar was added the 1,2-addtion product **39** (0.2 mmol), Cs_2CO_3 (0.4 mmol, 131 mg) and DMSO (1.5 mL) under a nitrogen atmosphere. Upon dissolution compound **39**, TMSCN (30 uL, 1.2 equiv) was added. Then, the mixture was heated to 80 °C in an oil bath for

1 h. After cooling to rt, the solution was pooled into 5 mL of ice water until no solid precipitate. The desired pyrrole can be obtained through filtration without further purification.



39
0.2 mmol

8
^{1}H NMR yield: 19 %

To a 25 mL of Schlenk tube with a stir bar was added the 1,2-addtion product **39** (0.2 mmol), Cs_2CO_3 (0.4 mmol, 131 mg) and DMSO (1.5 mL) under a nitrogen atmosphere. Upon dissolution the compound **39**, TMSCN (30 uL, 1.2 equiv) was added. Then, the mixture was heated to 80 ^{o}C in an oil bath for 1 h. After cooling to rt, Then, the mixture was pooled into 20 mL of water then extracted with EA/PE=1:1 (30mL*3). The organic phase was washed three times with a large amount of water, dried over anhydrous magnesium sulfate, evaporated to remove the solvent, and added CH_2Br_2 (0.2 mmol, 14 uL) as an internal standard.

Theoretical Study

Density functional theory (DFT) calculations have also been conducted on the basis of the experimental results to investigate the reaction mechanisms of cyclization and double cyanation. Since the reaction can be carried out starting from **39** without additional TMSCN but much less yields, the calculation of reversible CN elimination from **1SP** was initially considered. Deprotonation of **1SP** should be a readily process in the base reaction condition, and the intermediate **1A** can then eliminate the cyanide ion via **TS1** with a barrier of 13.3 kcal/mol to afford **1s**. The isolated CN^- ion therefore can add onto the carbon C4 of **1s** to deliver the intermediate **1B** through the transition state **TS2**, however, with a bit higher barrier of 23.0 kcal/mol indicating that there may be a competition between 1,2- and 1,4-addition of **1s** to reverse to the **1SP** or forward to the pyrrole without external TMSCN at high temperature. Transition state of cyanide addition onto C3 (**TS6**) has also been located but with too high barrier to be achieved.

Next, reaction pathways of rearrangement, desulfurization and second cyanide addition from **1B** were calculated. The rearranged intermediate **int1** with a relative free enthalpy -3.6 kcal/mol was found to be the more favorable conformation than **1B**. In addition, transition states of desulfurization (**TS7**) and second cyanide addition (**TS8**) have been located with barriers of 52.2 and 53.4 kcal/mol, respectively, which result in the less stable intermediates **int7** and **int8**. Transition state of desulfurization from **int1** was then found to be the most possible pathway with only 14.5 kcal/mol of barrier leading to the much stable intermediate **int2** with -11.4 kcal/mol of free enthalpy. Addition of second CN^- onto **int1** has also been considered, and as expected, **TS9** with very high barrier of 46.1 kcal/mol was located due to the deconjugation as **TS8**.

Cyclization and second cyanide addition from **int2** were therefore calculated. Transition state of cyclization, **TS4**, with a barrier of 16.6 kcal/mol was located to be the much lower state of reaction pathway. It is noteworthy that transition state of cyclization cannot be located starting from the intermediates **1B** and **int1**. Although the transition state of second cyanide addition, **TS12**, can be found from **int2**, the barrier is larger almost 10 kcal/mol than that of **TS4**. The annulated intermediate **int3** then should perform the proton transfer to afford intermediate **int4** with a free enthalpy of -17.5 kcal/mol. The second cyanide then can add onto **int4** via the transition state **TS5** to deliver the intermediate **int5** which will rearrange to the aromatic conformer **int6** with a much stable free energy of -20.2 kcal/mol.

On the other hand, we have also considered the protonation pathway from **1B** despite in the base reaction condition. Although the protonation intermediate **int10** is a stable species, second cyanide addition onto **int10** should overcome a much higher transition state, **TS10**. Besides, intermediate **int11** is less stable, and the relative free enthalpy of desulfurization, **TS11**, is even slightly higher than that of **TS10**. Since the standard reaction is in a base condition, the protonation pathway therefore may not be the favorable pathway.

DFT computational studies were carried out at B3LYP[4]-D3[5](SMD[6])/Def2-TZVP[7]//B3LYP-D3/Def2-SVP level of theory, in which the D3 dispersion correction is the original D3 damping function. The integration grid option was required at ultrafine for all of calculations. All of structures were optimized in gas-phase with thermal calculations and frequency analyses at 353 K. Transition state structures were searched by simply performing a crude relaxed potential energy surface (RPES) scan connecting reactants and products, and then optimized by the rational function optimization (RFO) method of TS.[8] Imaginary frequencies for all of transition states were verified to be the only one in theirs vibrations and were confirmed the correctness by viewing the normal mode vector or the intrinsic reaction coordinate (IRC)[9] path calculations. The reported Gibbs free energies were the single point electronic energy in dimethyl sulfoxide (DMSO) with the gas-phase free energy correction. All calculations were performed by the Gaussian 09 package.[10]

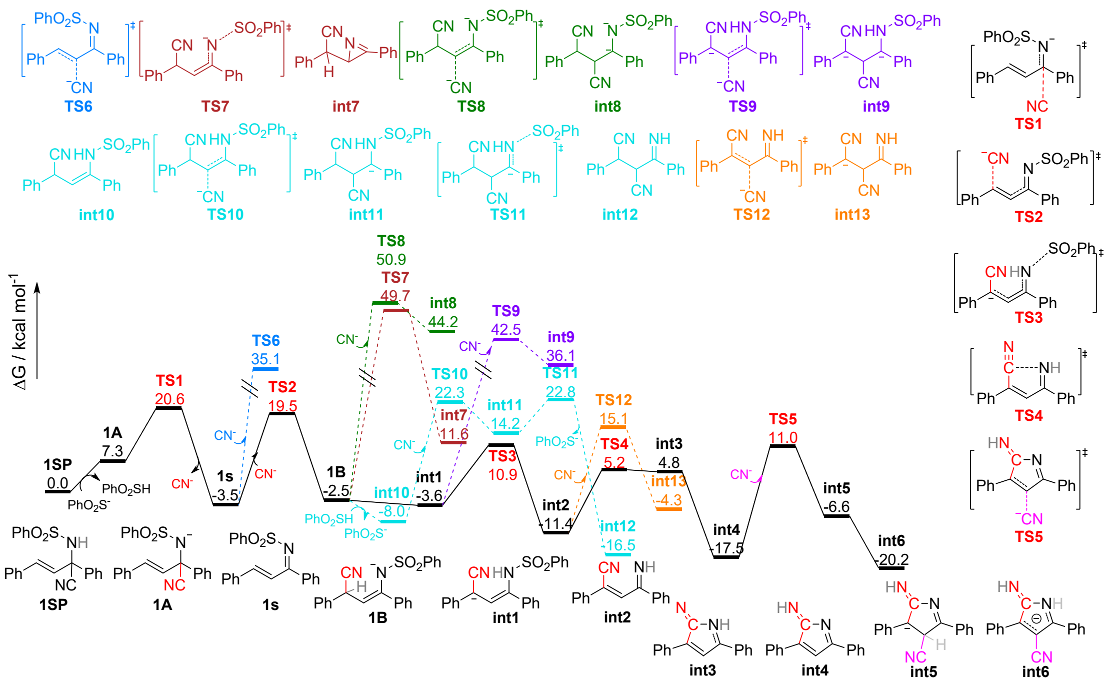
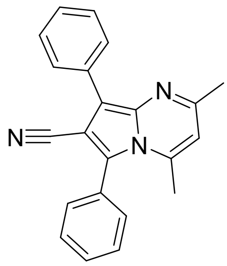
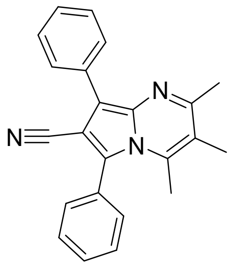


Figure S1. Gibbs free energy profile of the reaction pathways including various plausible second CN addition and the cyclization pathway.

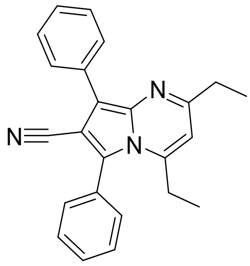
Characterization data for pyrrolo[1,2-*a*]pyrimidine



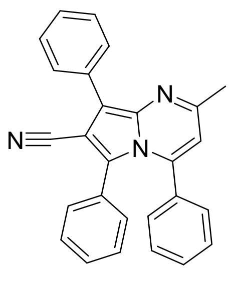
Following the general procedure C, compound **40** was obtained as a green solid (288 mg, 89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.41 (m, 7H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 2.51 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 142.7, 137.7, 132.1, 131.6, 131.1, 129.7, 129.0, 128.9, 128.7, 128.0, 127.0, 116.6, 113.3, 111.7, 100.4, 24.7, 22.0. IR (thin film) ν 2219, 1627, 1518, 736, 693 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{17}N_3Na]^+$ ($[M+Na]^+$): 346.1315, found: 346.1317.



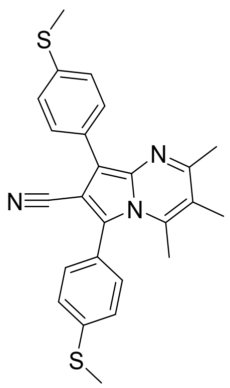
Following the general procedure C, compound **41** was obtained as a green solid (260 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.51-7.43 (m, 7H), 7.31 (t, *J* = 7.4 Hz, 1H), 2.54 (s, 3H), 2.20 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.6, 139.0, 136.5, 132.2, 131.8, 130.8, 129.2, 128.7, 128.5, 128.1, 126.7, 116.9, 116.8, 113.0, 99.9, 24.4, 18.3, 14.4. IR (thin film) ν 2218, 1633, 1545, 1511, 697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{19}N_3Na]^+$ ($[M+Na]^+$): 360.1471, found: 360.1471.



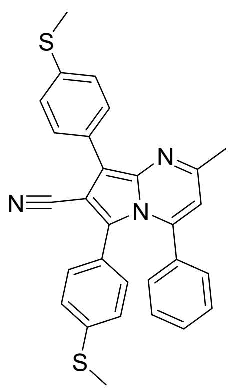
Following the general procedure C, compound **42** was obtained as a green solid (249 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.54 – 7.42 (m, 7H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.41 (s, 1H), 2.80 (q, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.5 Hz, 3H), 1.03 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6, 148.3, 137.8, 132.2, 131.4, 131.1, 129.5, 128.8, 128.7, 128.5, 128.0, 126.7, 116.6, 113.3, 107.8, 100.5, 31.2, 26.5, 12.3, 11.2. IR (thin film) ν 2974, 2217, 1623, 1548, 1515 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{24}H_{21}N_3Na]^+$ ($[M+Na]^+$): 374.1628, found: 374.1628.



Following the general procedure C, compound **43** was obtained as a yellow solid (380 mg, 85% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.10 – 6.94 (m, 9H), 6.53 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.1, 144.5, 138.3, 132.6, 131.9, 129.8, 129.5, 129.4, 129.2, 128.9, 128.6, 127.9, 127.9, 127.8, 127.6, 127.1, 116.7, 114.3, 113.1, 100.1, 24.7. IR (thin film) ν 2222, 1634, 1508, 1492, 695 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{27}H_{19}N_3Na]^+$ ($[M+Na]^+$): 408.1471, found: 408.1469.

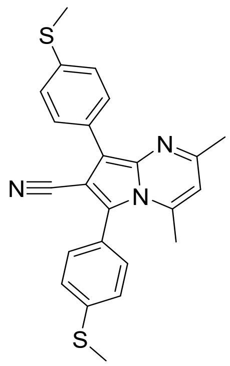


Following the general procedure C, compound **44** was obtained as a green solid (335 mg, 78% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 4H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.55 (s, 3H), 2.54 (s, 3H), 2.52 (s, 3H), 2.20 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.7, 140.5, 139.1, 136.7, 136.6, 131.1, 129.3, 129.0, 128.0, 127.1, 125.4, 117.1, 116.9, 112.6, 99.7, 24.5, 18.5, 16.2, 15.4, 14.5. IR (thin film) ν 2921, 2222, 1638, 1508, 1431 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{25}H_{23}N_3S_2Na]^+$ ($[M+Na]^+$): 452.1226, found: 452.1225.

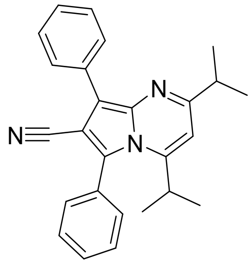


Following the general procedure C, compound **45** was obtained as an orange solid (353 mg, 74% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.20 (t, *J* = 6.8 Hz, 1H), 7.10 – 6.98 (m, 4H), 6.91–6.84 (m, 4H), 6.52 (s, 1H), 2.59 (s, 3H), 2.54 (s, 3H), 2.41 (s, 3H).

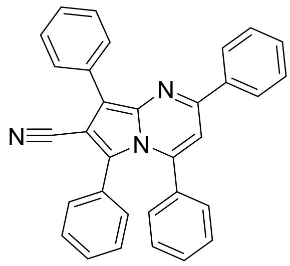
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 144.5, 138.9, 138.2, 137.1, 132.6, 129.6, 129.3, 129.1, 128.8, 128.7, 128.1, 127.8, 127.0, 126.3, 125.5, 116.7, 113.7, 113.1, 99.6, 24.7, 16.0, 15.7. IR (thin film) ν 29117, 2220, 1618, 1505, 1493 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{29}H_{23}N_3S_2Na]^+$ ($[M+Na]^+$): 500.1226, found: 500.1225.



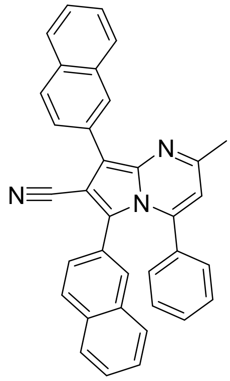
Following the general procedure C, compound **46** was obtained as a green solid (296 mg, 71% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.33 (s, 1H), 2.55 (s, 3H), 2.52 (s, 3H), 2.50 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1, 142.7, 141.0, 137.6, 136.8, 131.6, 129.0, 128.4, 127.1, 127.0, 125.1, 116.5, 112.7, 111.7, 100.2, 24.5, 22.0, 16.1, 15.2. IR (thin film) ν 2919, 2220, 1629, 1516, 1497 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{24}H_{21}N_3S_2Na]^+$ ($[M+Na]^+$): 438.1069, found: 438.1070.



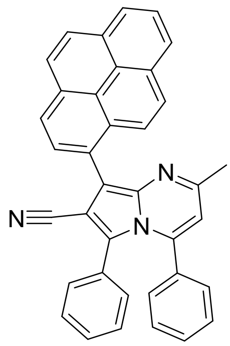
Following the general procedure C, compound **47** was obtained as a green solid (148 mg, 39% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.41 (m, 7H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.50 (s, 1H), 3.12 – 2.93 (m, 2H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 153.8, 138.1, 132.3, 131.6, 130.6, 129.5, 128.6, 128.5, 128.4, 128.3, 126.6, 113.3, 104.9, 100.9, 36.2, 28.1, 21.5, 21.1. IR (thin film) ν 2968, 2929, 2224, 1621, 1515 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{25}N_3Na]^+$ ($[M+Na]^+$): 402.1941, found: 402.1940.



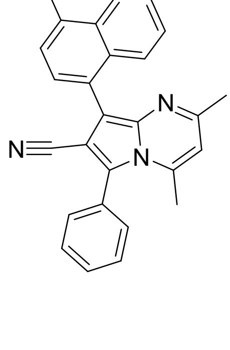
Following the general procedure C, compound **48** was obtained as a red solid (240 mg, 54% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.27 – 8.11 (m, 4H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.21 – 6.99 (m, 11H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.7, 145.1, 138.5, 136.9, 133.0, 132.0, 130.2, 129.7, 129.6, 129.5, 129.0, 128.9, 128.6, 128.1, 127.9, 127.6, 127.1, 126.9, 116.6, 116.0, 109.4, 100.7. IR (thin film) ν 3059, 2224, 1613, 1547, 1493 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{19}N_3Na]^+$ ($[M+Na]^+$): 470.1628, found: 470.1628.



Following the general procedure C, compound **49** was obtained as an orange solid (388 mg, 80% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 8.30 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.98 (t, *J* = 7.9 Hz, 2H), 7.91 – 7.86 (m, 1H), 7.72 – 7.62 (m, 2H), 7.60 (s, 1H), 7.54 – 7.40 (m, 5H), 7.14 – 7.02 (m, 3H), 6.97 – 6.68 (m, 3H), 6.58 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 144.7, 138.7, 133.7, 132.6, 132.4, 132.3, 129.5, 129.4, 129.3, 129.2, 128.4, 128.1, 128.1, 128.0, 127.7, 127.6, 127.5, 127.2, 127.1, 126.6, 126.4, 126.2, 126.0, 125.8, 116.8, 114.4, 113.2, 100.5, 24.8. IR (thin film) ν 2222, 1631, 1511, 1488, 697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{35}H_{23}N_3Na]^+$ ($[M+Na]^+$): 508.1784, found: 508.1783.



Following the general procedure C, compound **50** was obtained as a orange solid (290 mg, 57% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 – 8.26 (m, 2H), 8.24 – 8.16 (m, 3H), 8.16 – 8.10 (m, 2H), 8.10 – 8.06 (m, 1H), 8.01 (t, *J* = 7.6 Hz, 1H), 7.22 – 6.98 (m, 10H), 6.60 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.4, 144.6, 139.1, 132.7, 131.4, 131.2, 131.2, 129.9, 129.5, 129.0, 128.1, 127.9, 127.9, 127.7, 127.6, 127.5, 127.2, 126.8, 126.1, 125.8, 125.3, 125.0, 125.0, 124.9, 124.9, 116.2, 114.5, 113.2, 103.0, 24.7. IR (thin film) ν 2921, 2225, 1633, 1512, 1489 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{37}H_{23}N_3Na]^+$ ($[M+Na]^+$): 532.1784, found: 532.1784.



Following the general procedure C, compound **51** was obtained as a yellow solid (371 mg, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.27 (m, 1H), 8.25 – 8.21 (m, 1H), 8.20 – 8.09 (m, 5H), 8.06 – 8.03 (m, 1H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 6.2 Hz, 1H), 7.58 – 7.46 (m, 4H), 6.36 (s, 1H), 2.38 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5, 142.8, 138.4, 131.5, 131.5, 131.4, 131.1, 131.0, 129.8, 129.6, 129.4, 128.7, 128.0, 128.0, 127.5, 127.1, 126.9, 126.1, 125.8, 125.3, 125.0, 124.9, 124.9, 116.0, 113.3, 111.7, 103.2, 24.5, 21.9. IR (thin film) ν 3049, 2927, 1627, 1601, 1585 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{32}H_{21}N_3Na]^+$ ($[M+Na]^+$): 470.1628, found: 470.1628.

Supplementary figure of pyrrolo[1,2-*a*]pyrimidine

UV spectrum and PL spectra of pyrrolo[1,2-*a*]pyrimidine

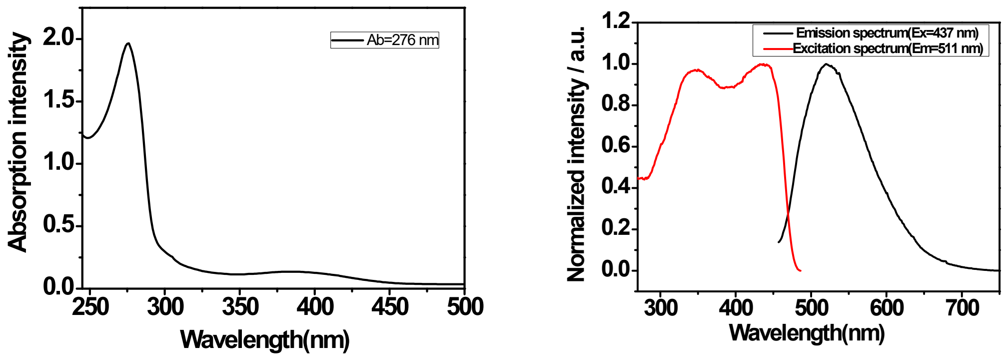


Figure S2. UV spectrum of **40** in THF solution (0.001 mg/mL) a0nd PL spectra of **40** in THF solution (0.1 mg/mL).

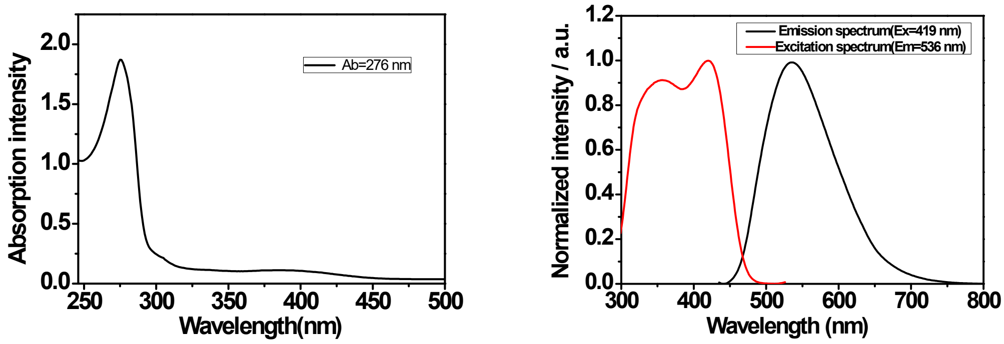


Figure S3. UV spectrum of **41** in THF solution (0.001 mg/mL) and PL spectra of **41** in THF solution (0.1 mg/mL).

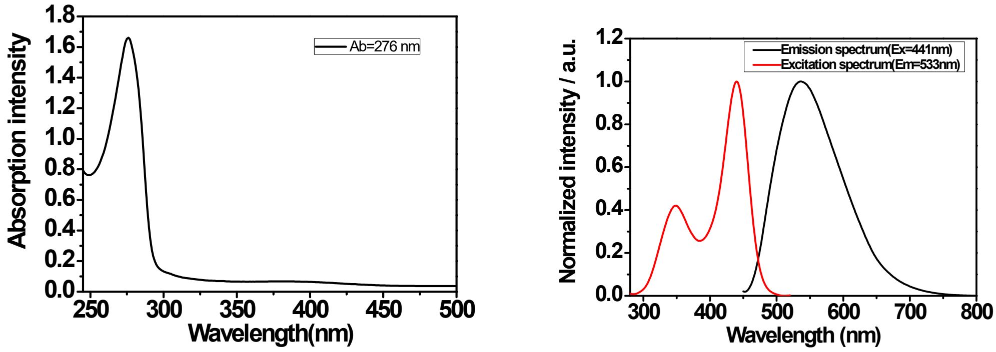


Figure S4. UV spectrum of **42** in THF solution (0.001 mg/mL) and PL spectra of **42** in THF solution (0.1 mg/mL).

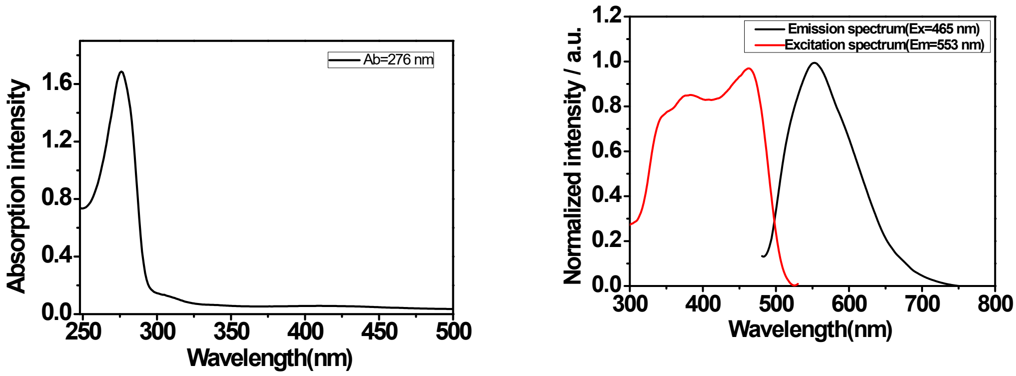


Figure S5. UV spectrum of **43** in THF solution (0.001 mg/mL) and PL spectra of **43** in THF solution (0.1 mg/mL).

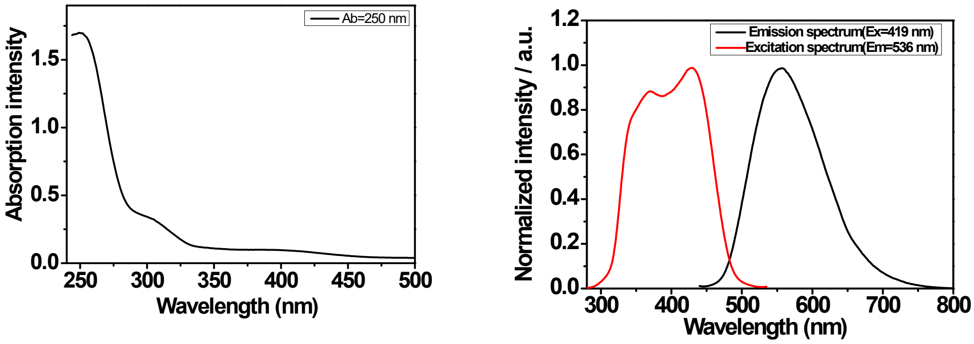


Figure S6. UV spectrum of **44** in THF solution (0.001 mg/mL) and PL spectra of **44** in THF solution (0.1 mg/mL).

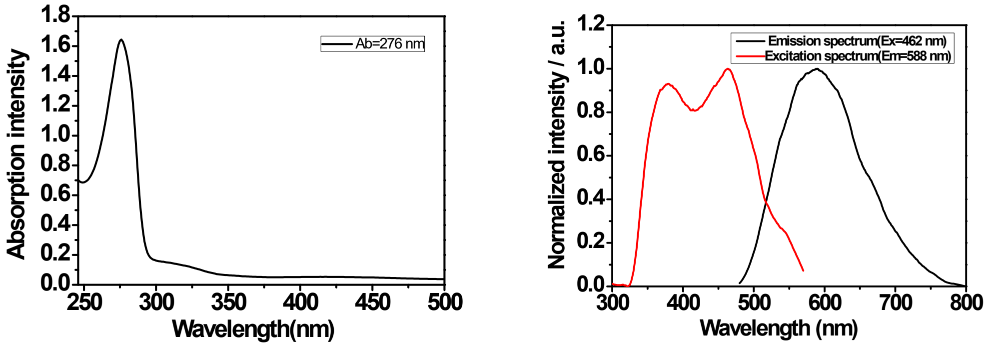


Figure S7. UV spectrum of **45** in THF solution (0.001 mg/mL) and PL spectra of **45** in THF solution (0.1 mg/mL).

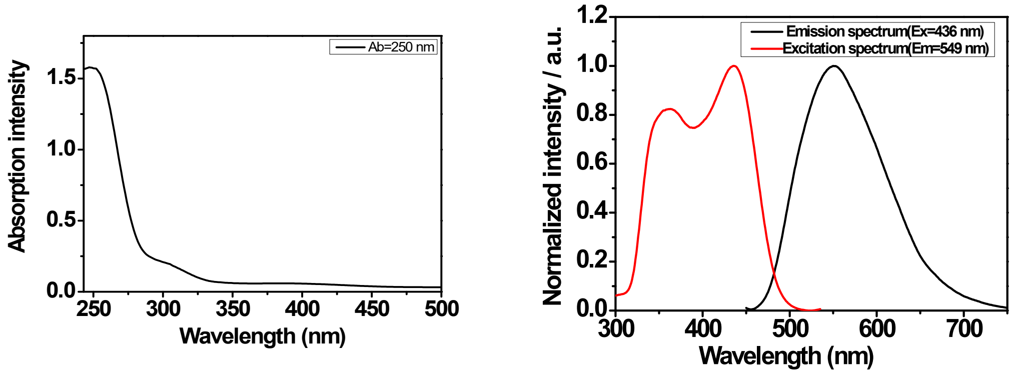


Figure S8. UV spectrum of **46** in THF solution (0.001 mg/mL) and PL spectra of **46** in THF solution (0.1 mg/mL).

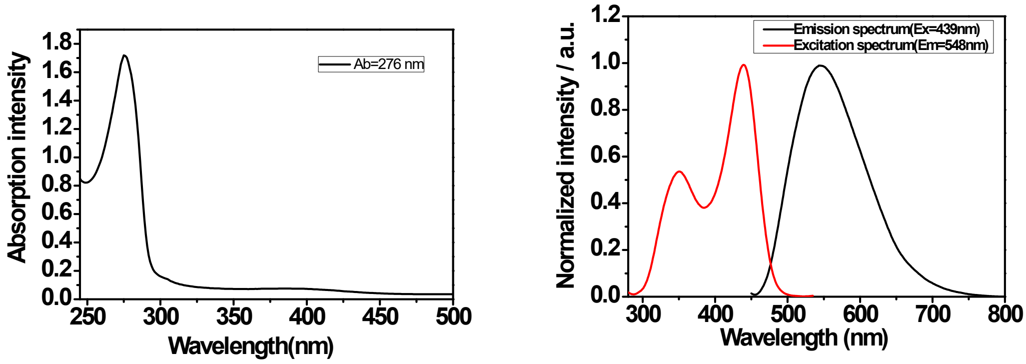


Figure S9. UV spectrum of **47** in THF solution (0.001 mg/mL) and PL spectra of **47** in THF solution (0.1 mg/mL).

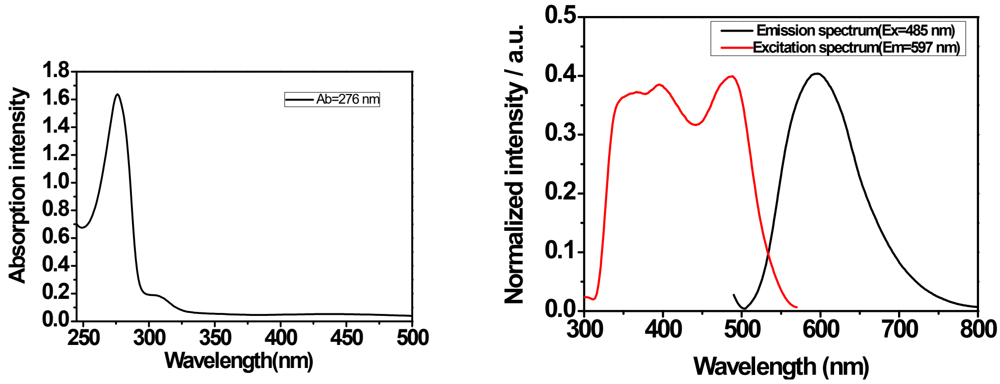


Figure S10. UV spectrum of **48** in THF solution (0.001 mg/mL) and PL spectra of **48** in THF solution (0.1 mg/mL).

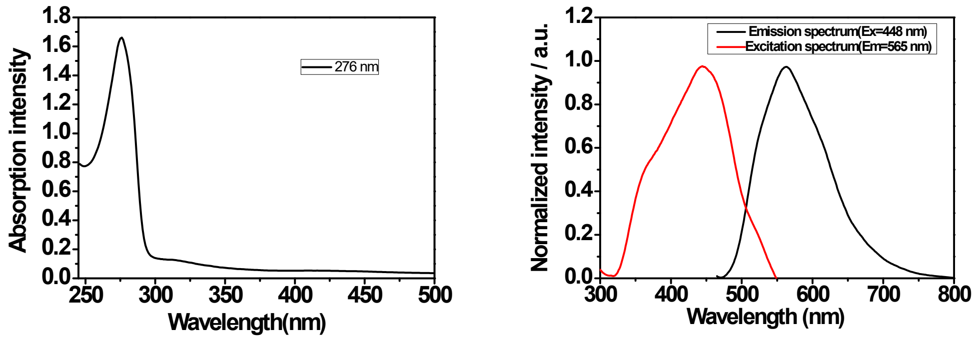


Figure S11. UV spectrum of **49** in THF solution (0.001 mg/mL) and PL spectra of **49** in THF solution (0.1 mg/mL).

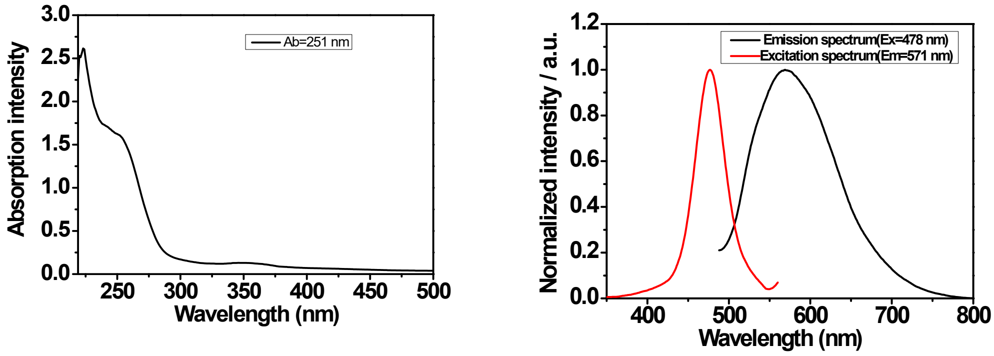


Figure S12. UV spectrum of **50** in THF solution (0.001 mg/mL) and PL spectra of **50** in THF solution (0.1 mg/mL).

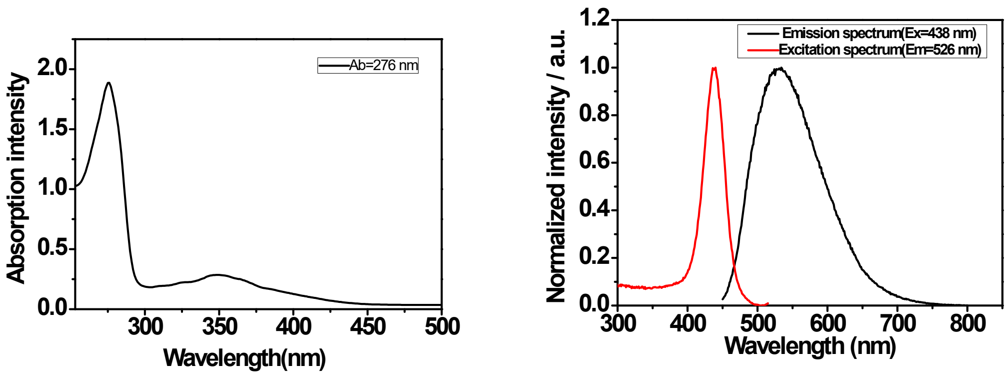


Figure S13. UV spectrum of **51** in THF solution (0.001 mg/mL) and PL spectra of **51** in THF solution (0.1 mg/mL).

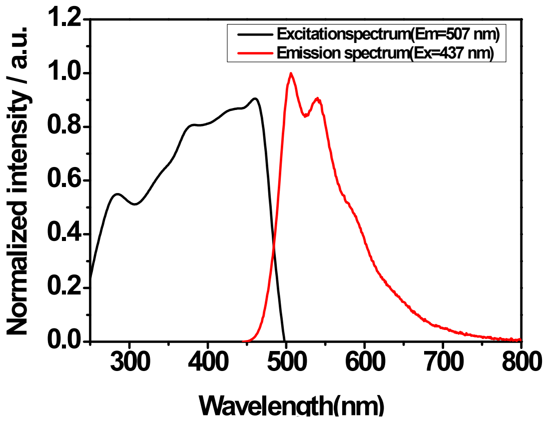


Figure S14. Excitation and emission spectra of **40** powder.

Emission spectra of pyrrolo[1,2-*a*]pyrimidine in THF and water mixtures

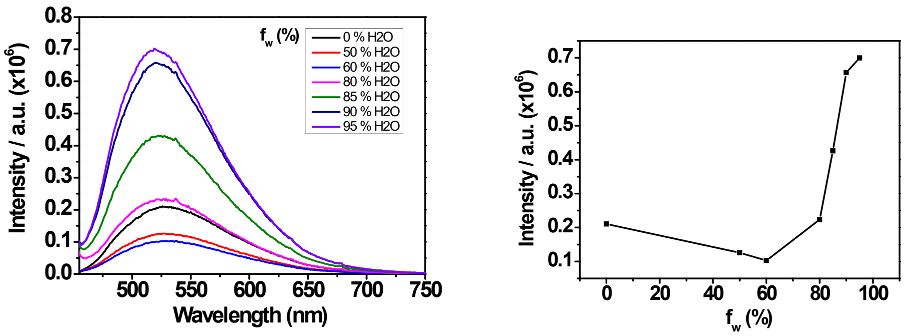


Figure S15. Emission spectra of **40** in THF and water mixtures (0.1 mg/mL) at different f_w, λ_{ex} =437 nm. The emission intensity at 518 nm with different f_w.

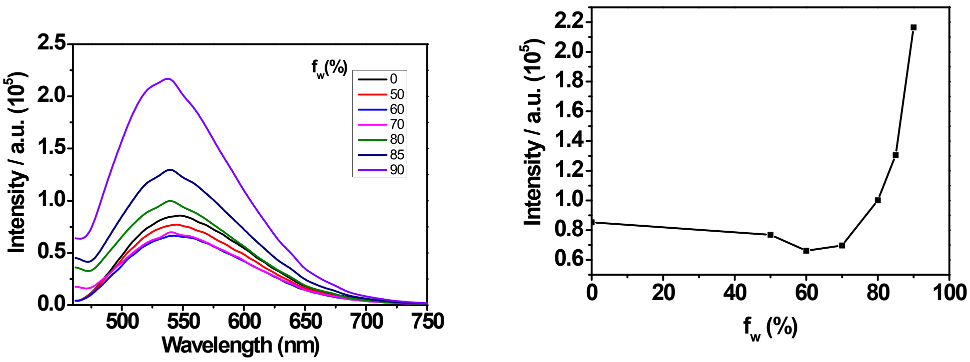


Figure S16. Emission spectra of **47** in THF and water mixtures (0.1 mg/mL) at different f_w, λ_{ex} =439 nm. The emission intensity at 538 nm with different f_w.

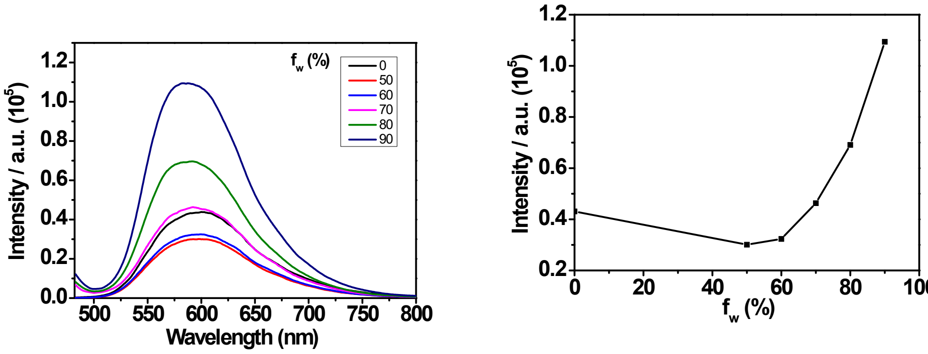


Figure S17. Emission spectra of **48** in THF and water mixtures (0.1 mg/mL) at different f_w, λ_{ex} =485 nm. The emission intensity at 588 nm with different f_w.

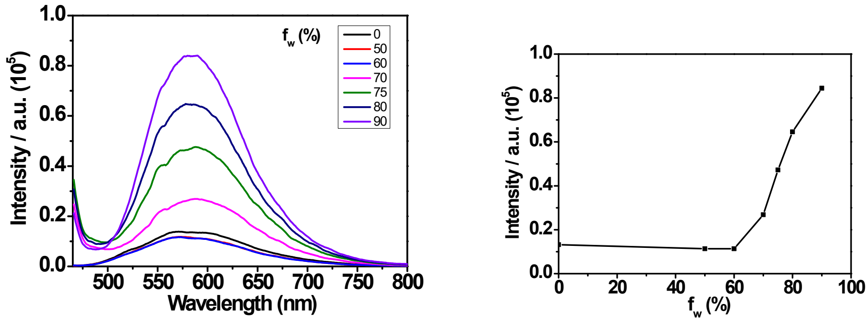


Figure S18. Emission spectra of **49** in THF and water mixtures (0.1 mg/mL) at different f_w, λ_{ex} =448 nm.

The emission intensity at 585 nm with different f_w.

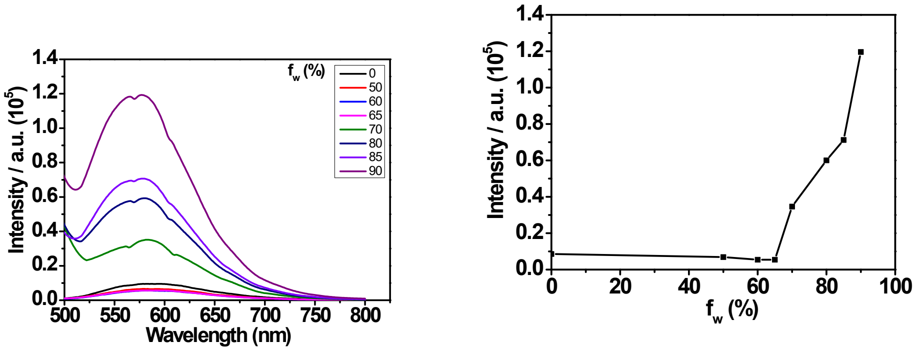


Figure S19. Emission spectra of **50** in THF and water mixtures (0.1 mg/mL) at different f_w, λ_{ex} =478 nm.

The emission intensity at 578 nm with different f_w.

Time-dependent emission enhancement after different scan times

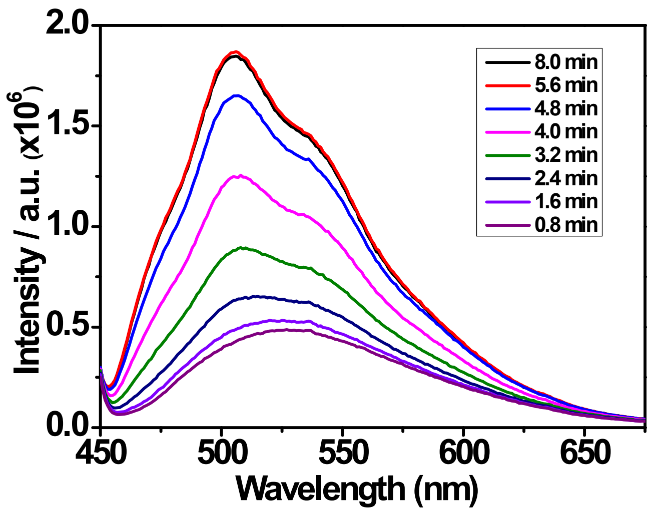


Figure S20. PL spectra of **41** in 10% THF and 90% water mixtures (0.2 mg/mL) after different scan times ranging from 0 to 8 min under ambient conditions, λ_{ex} =419 nm.

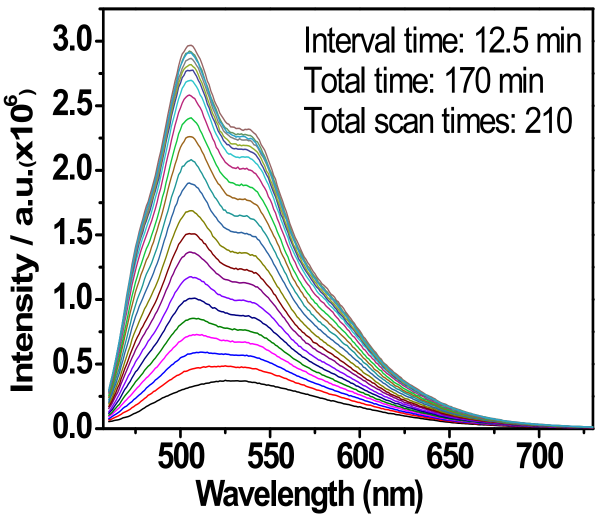


Figure S21. PL spectra of **42** in 10% THF and 90% water mixtures (0.2 mg/mL) after different scan times ranging from 0 to 170 min under ambient conditions, λ_{ex} =441 nm.

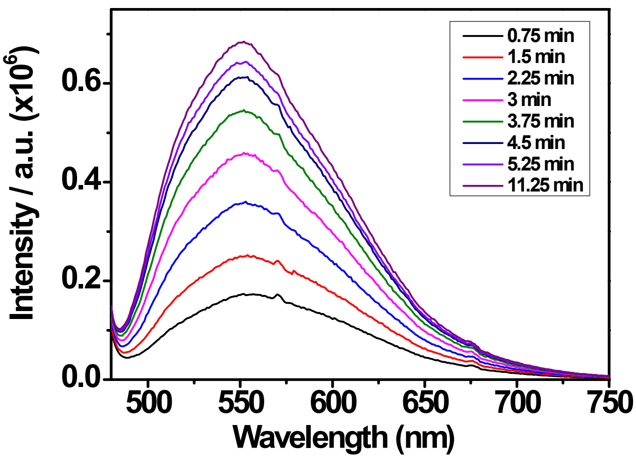


Figure S22. PL spectra of **43** in 10% THF and 90% water mixtures (0.2 mg/mL) after different scan times ranging from 0 to 11.3 min under ambient conditions, λ_{ex} =465 nm.

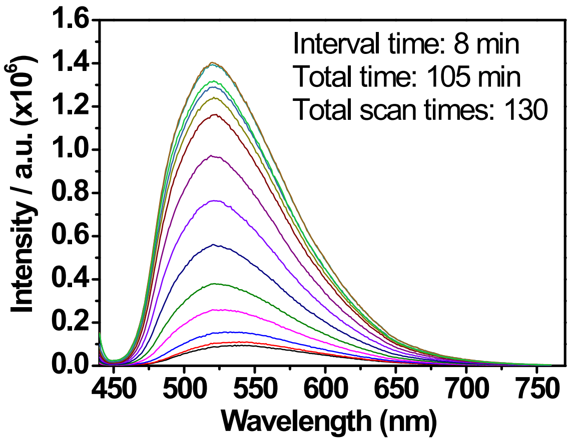


Figure S23. PL spectra of **44** in 10% THF and 90% water mixtures (0.2 mg/mL) after different scan times ranging from 0 to 105 min under ambient conditions, λ_{ex} =428 nm.

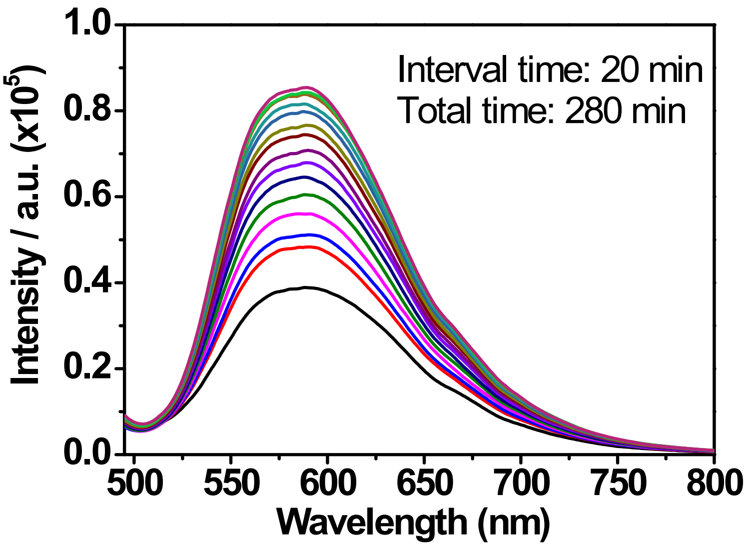


Figure S24. PL spectra of **45** in 10% THF and 90% water mixtures (0.2 mg/mL) after different scan times ranging from 0 to 280 min under ambient conditions, λ_{ex} =462 nm.

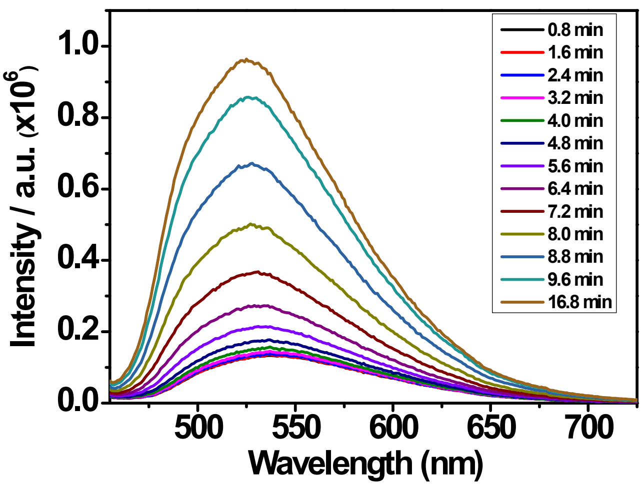


Figure S25. PL spectra of **46** in 10% THF and 90% water mixtures (0.2 mg/mL) after different scan times ranging from 0 to 16.8 min under ambient conditions, λ_{ex} =436 nm.

Crystal packing of pyrrolo[1,2-*a*]pyrimidine

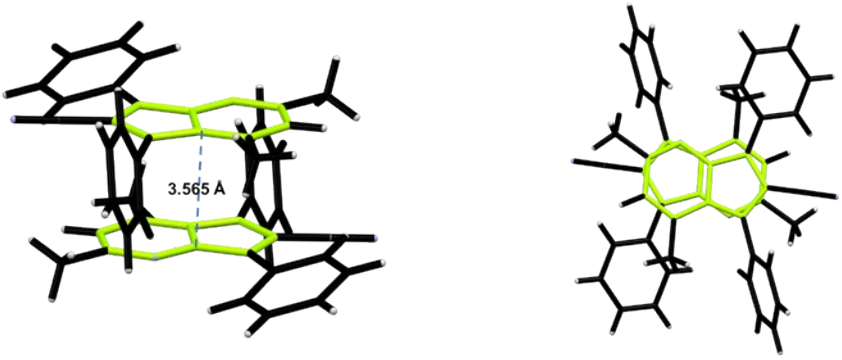


Figure S26. Single-crystal structure and molecular packing of **40**.

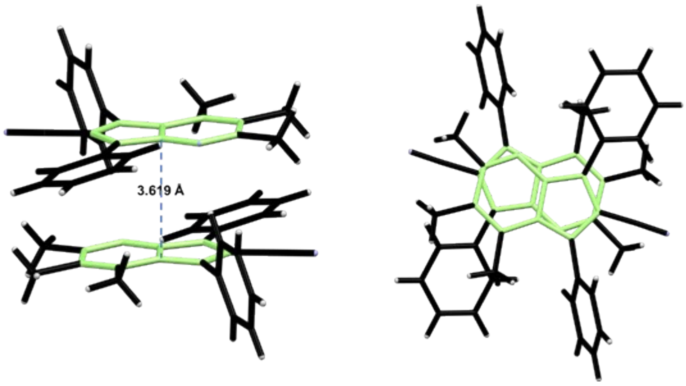


Figure S27. Single-crystal structure and molecular packing of **41**.

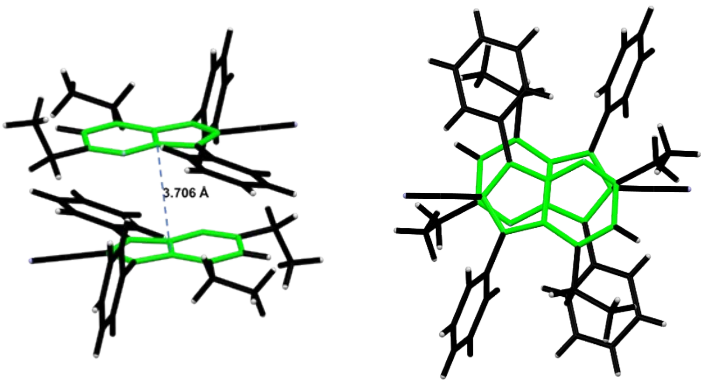


Figure S28. Single-crystal structure and molecular packing of **42**.

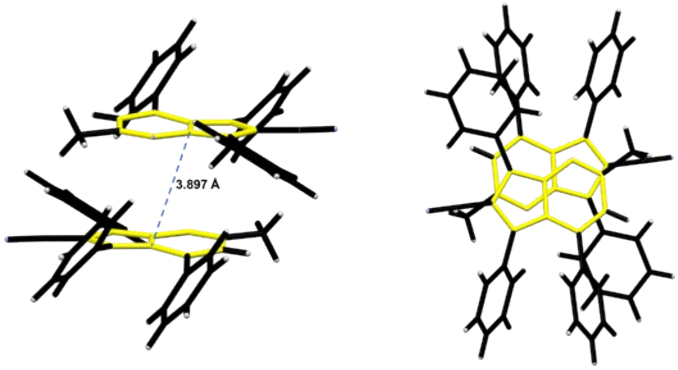


Figure S29. Single-crystal structure and molecular packing of **43**.

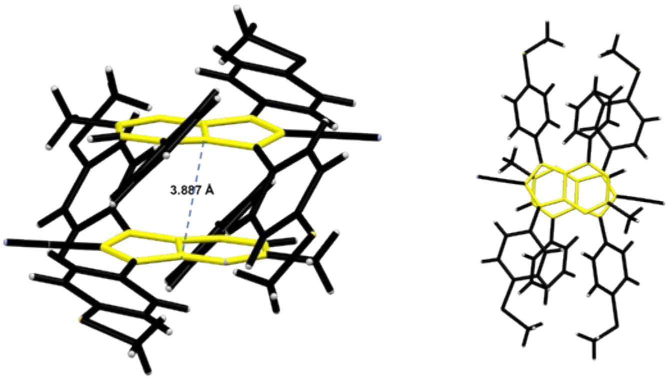


Figure S30. Single-crystal structure and molecular packing of **45**.

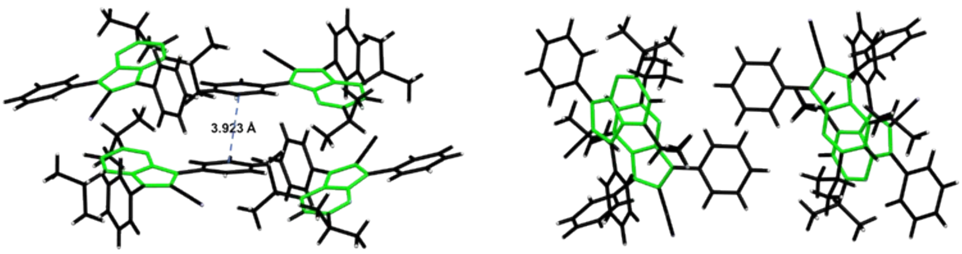


Figure S31. Single-crystal structure and molecular packing of **47**.

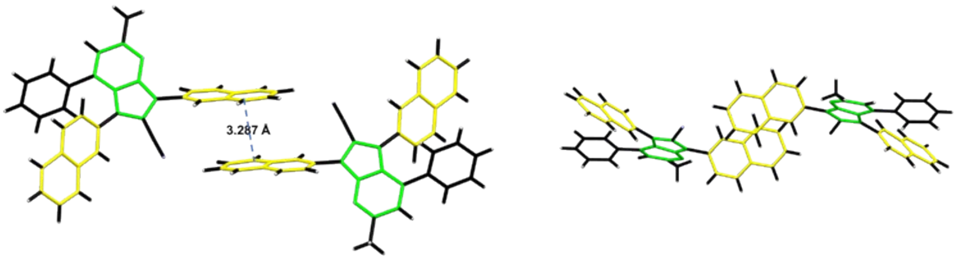


Figure S32. Single-crystal structure and molecular packing of **49**.

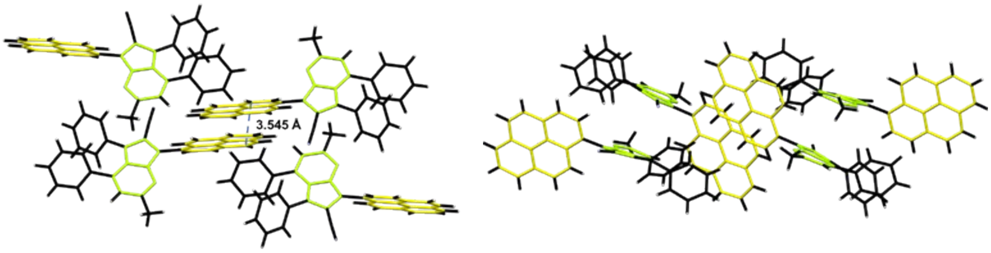
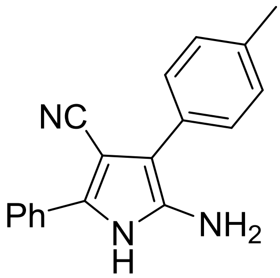
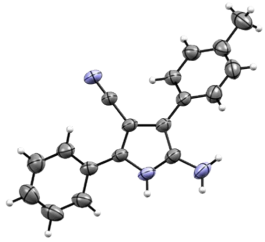


Figure S33. Single-crystal structure and molecular packing of **50**.

Single crystal data

X-ray diffractions for single crystals of **2, 40, 41, 42, 43, 45, 47, 49** and **50** were carried out on Rikagu Synergy Custom (Liquid MetalJet D2 Plus) diffractometer using Ga Kα radiation (λ = 1.3405 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT and refined with the SHELXL using least-squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. Crystal data and structure refinements of **2, 40, 41, 42, 43, 45, 47, 49** and **50** are listed in **Table S1, Table S2, Table S3, Table S4, Table S5, Table S6, Table S7, Table S8** and **Table S9**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

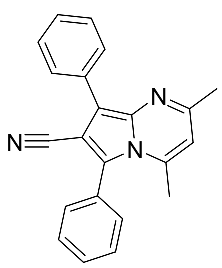




CCDC 2133476

Table S1. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	$C_{18}H_{15}N_3$	
Formula weight	273.33	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	a = 13.5606(15)	α = 90
	b = 14.1429(16)	β = 93.620(9)
	c = 7.6056(7)	γ = 90
Volume (Å)	1455.7(3)	
Z	4	
Calculated density (g cm^{-3})	1.247	
Absorption coefficient (mm^{-1})	0.375	
F_{000}	576	
Crystal size (mm^3)	0.23 × 0.20 × 0.06	
θ range for data collection (°)	3.931 to 61.207	
Miller index ranges	$-17 \le h \le 17$, $-12 \le k \le 18$, $-9 \le l \le 9$	
Reflections collected	10673	
Independent reflections	3239 [R_{int} = 0.0262]	
Completeness to θ_{max} (%)	0.956	
Max. and min. transmission	0.65015 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3239 / 0 / 200	
Goodness-of-fit on F^2	1.128	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0458, $wR2$ = 0.1241	
R indices (all data)	$R1$ = 0.0671, $wR2$ = 0.1545	
Extinction coefficient	0.014(2)	
Largest diff. peak and hole (e Å^{-3})	0.169 and -0.191	



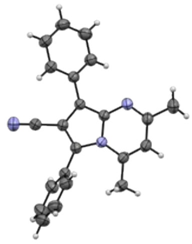


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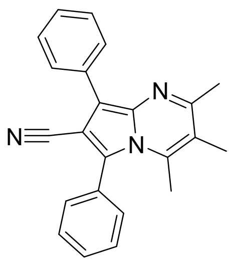
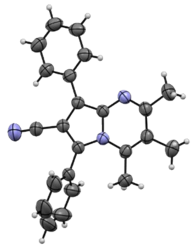
Table S2. Crystal data and structure refinement for **40**.

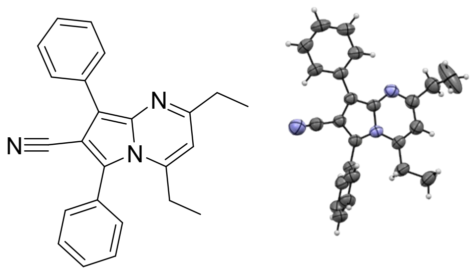
Identification code	**40**	
Empirical formula	$C_{22}H_{17}N_3$	
Formula weight	323.38	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions (Å, °)	a = 7.5636(2)	α = 104.037(2)
	b = 10.6070(3)	β = 99.019(2)
	c = 11.4880(3)	γ = 104.020(3)
Volume (Å)	844.44(4)	
Z	2	
Calculated density (g cm^{-3})	1.272	
Absorption coefficient (mm^{-1})	0.378	
F_{000}	340	
Crystal size (mm^3)	0.18 × 0.16 × 0.05	
θ range for data collection (°)	5.653 to 60.617	
Miller index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-10 \leq l \leq 14$	
Reflections collected	10297	
Independent reflections	3772 [R_{int} = 0.0226]	
Completeness to θ_{max} (%)	0.970	
Max. and min. transmission	0.74060 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3772 / 0 / 229	
Goodness-of-fit on F^2	1.048	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0415, $wR2$ = 0.1057	
R indices (all data)	$R1$ = 0.0503, $wR2$ = 0.1110	
Extinction coefficient	0.032(3)	
Largest diff. peak and hole (e Å^{-3})	0.211 and -0.143	

CCDC 2144280

Table S3. Crystal data and structure refinement for **41**.

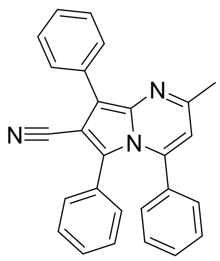
Identification code	**41**	
Empirical formula	$C_{23}H_{19}N_3$	
Formula weight	337.41	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions (Å, °)	a = 7.4368(5)	α = 107.748(4)
	b = 11.5205(6)	β = 101.471(5)
	c = 11.7843(5)	γ = 103.216(6)
Volume (Å)	895.98(9)	
Z	2	
Calculated density (g cm^{-3})	1.251	
Absorption coefficient (mm^{-1})	0.369	
F_{000}	356	
Crystal size (mm^3)	0.20 × 0.18 × 0.06	
θ range for data collection (°)	3.577 to 61.476	
Miller index ranges	$-9 \le h \le 7$, $-14 \le k \le 14$, $-15 \le l \le 15$	
Reflections collected	11963	
Independent reflections	4000 [R_{int} = 0.0321]	
Completeness to θ_{max} (%)	0.947	
Max. and min. transmission	0.86643 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4000 / 0 / 239	
Goodness-of-fit on F^2	1.115	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0484, $wR2$ = 0.1389	
R indices (all data)	$R1$ = 0.0675, $wR2$ = 0.1573	
Extinction coefficient	0.0076(17)	
Largest diff. peak and hole (e Å^{-3})	0.186 and -0.217	

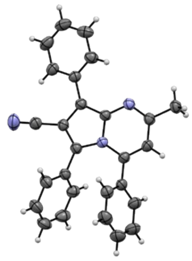


CCDC 2144282

Table S4. Crystal data and structure refinement for **42**.

Identification code	**42**	
Empirical formula	$C_{24}H_{21}N_3$	
Formula weight	351.44	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	a = 10.9544(12)	α = 90
	b = 15.4590(15)	β = 113.683(12)
	c = 12.2647(13)	γ = 90
Volume (Å)	1902.0(4)	
Z	4	
Calculated density (g cm^{-3})	1.227	
Absorption coefficient (mm^{-1})	0.360	
F_{000}	744	
Crystal size (mm^3)	0.18 × 0.15 × 0.14	
θ range for data collection (°)	4.230 to 60.800	
Miller index ranges	$-14 \le h \le 13$, $-19 \le k \le 19$, $-15 \le l \le 15$	
Reflections collected	14592	
Independent reflections	4270 [R_{int} = 0.0534]	
Completeness to θ_{max} (%)	0.971	
Max. and min. transmission	0.84312 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4270 / 0 / 247	
Goodness-of-fit on F^2	1.377	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0802, $wR2$ = 0.2643	
R indices (all data)	$R1$ = 0.1215, $wR2$ = 0.3583	
Extinction coefficient	0.015(5)	
Largest diff. peak and hole (e Å^{-3})	0.344 and -0.479	

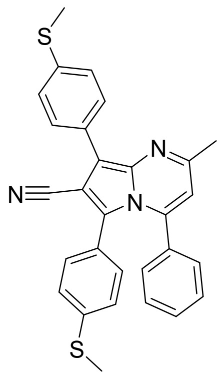


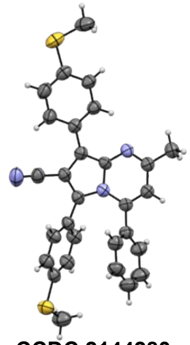


CCDC 2144281

Table S5. Crystal data and structure refinement for **43**.

Identification code	**43**	
Empirical formula	$C_{27}H_{19}N_3$	
Formula weight	385.45	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions (Å, °)	a = 7.4603(7)	α = 90
	b = 14.0260(12)	β = 98.736(9)
	c = 19.2722(15)	γ = 90
Volume (Å)	1993.2(3)	
Z	4	
Calculated density (g cm^{-3})	1.284	
Absorption coefficient (mm^{-1})	0.378	
F_{000}	808	
Crystal size (mm^3)	0.20 × 0.08 × 0.06	
θ range for data collection (°)	4.880 to 61.269	
Miller index ranges	$-7 \le h \le 9$, $-17 \le k \le 18$, $-25 \le l \le 25$	
Reflections collected	15293	
Independent reflections	4475 [R_{int} = 0.0811]	
Completeness to θ_{max} (%)	0.956	
Max. and min. transmission	0.64115 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4475 / 0 / 273	
Goodness-of-fit on F^2	1.059	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0911, $wR2$ = 0.2560	
R indices (all data)	$R1$ = 0.1169, $wR2$ = 0.2871	
Extinction coefficient	0.0103(16)	
Largest diff. peak and hole (e Å^{-3})	0.365 and -0.398	

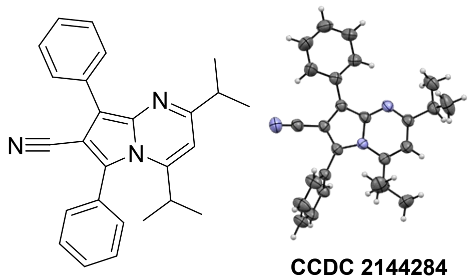




CCDC 2144283

Table S6. Crystal data and structure refinement for **45**.

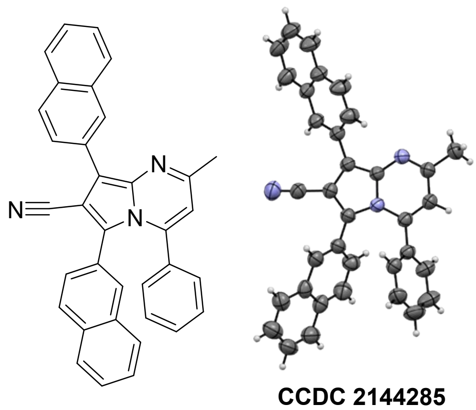
Identification code	**45**	
Empirical formula	$C_{29}H_{23}N_3S_2$	
Formula weight	477.62	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions (Å, °)	a = 17.7692(18)	α = 90
	b = 7.5870(6)	β = 91.248(8)
	c = 17.8377(14)	γ = 90
Volume (Å)	2404.2(4)	
Z	4	
Calculated density (g cm^{-3})	1.319	
Absorption coefficient (mm^{-1})	1.429	
F_{000}	2010	
Crystal size (mm^3)	0.20 × 0.06 × 0.05	
θ range for data collection (°)	3.019 to 61.341	
Miller index ranges	$-22 \le h \le 23$, $-9 \le k \le 5$, $-23 \le l \le 22$	
Reflections collected	18194	
Independent reflections	5419 [R_{int} = 0.0380]	
Completeness to θ_{max} (%)	0.959	
Max. and min. transmission	0.63518 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5419 / 0 / 311	
Goodness-of-fit on F^2	1.155	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0787, $wR2$ = 0.2282	
R indices (all data)	$R1$ = 0.1065, $wR2$ = 0.2975	
Extinction coefficient	0.0075(13)	
Largest diff. peak and hole (e Å^{-3})	0.542 and -0.733	



CCDC 2144284

Table S7. Crystal data and structure refinement for **47**.

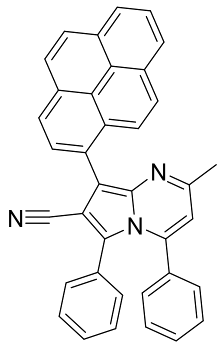
Identification code	**47**	
Empirical formula	$C_{26}H_{25}N_3$	
Formula weight	379.49	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	orthorhombic	
Space group	*Pbcn*	
Unit cell dimensions (Å, °)	a = 19.753(2)	α = 90
	b = 10.6344(12)	β = 90
	c = 20.535(3)	γ = 90
Volume (Å)	4313.7(9)	
Z	8	
Calculated density (g cm^{-3})	1.169	
Absorption coefficient (mm^{-1})	0.339	
F_{000}	1616	
Crystal size (mm^3)	0.23 × 0.03 × 0.02	
θ range for data collection (°)	3.743 to 61.322	
Miller index ranges	$-23 \le h \le 25$, $-10 \le k \le 13$, $-23 \le l \le 26$	
Reflections collected	18140	
Independent reflections	4878 [R_{int} = 0.0429]	
Completeness to θ_{max} (%)	0.963	
Max. and min. transmission	0.56368 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4878 / 0 / 267	
Goodness-of-fit on F^2	1.135	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0596, $wR2$ = 0.1549	
R indices (all data)	$R1$ = 0.0911, $wR2$ = 0.2038	
Extinction coefficient	0.0017(3)	
Largest diff. peak and hole (e Å^{-3})	0.249 and -0.245	

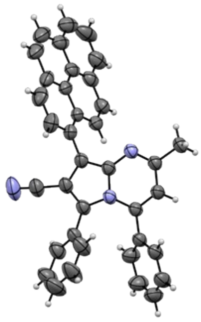


CCDC 2144285

Table S8. Crystal data and structure refinement for **49**.

Identification code	**49**	
Empirical formula	$C_{35}H_{23}N_3$	
Formula weight	485.56	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	a = 9.7978(12)	α = 90
	b = 27.007(2)	β = 116.236(16)
	c = 10.7502(14)	γ = 90
Volume (Å)	2551.5(6)	
Z	4	
Calculated density (g cm^{-3})	1.264	
Absorption coefficient (mm^{-1})	0.367	
F_{000}	1016	
Crystal size (mm^3)	0.22 × 0.05 × 0.04	
θ range for data collection (°)	2.845 to 61.289	
Miller index ranges	$-11 \le h \le 12$, $-33 \le k \le 34$, $-13 \le l \le 9$	
Reflections collected	22817	
Independent reflections	5767 [R_{int} = 0.0378]	
Completeness to θ_{max} (%)	0.964	
Max. and min. transmission	0.42123 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5767 / 0 / 345	
Goodness-of-fit on F^2	1.090	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0883, $wR2$ = 0.2547	
R indices (all data)	$R1$ = 0.1109, $wR2$ = 0.2749	
Extinction coefficient	0.0011(4)	
Largest diff. peak and hole (e Å^{-3})	0.841 and -0.328	



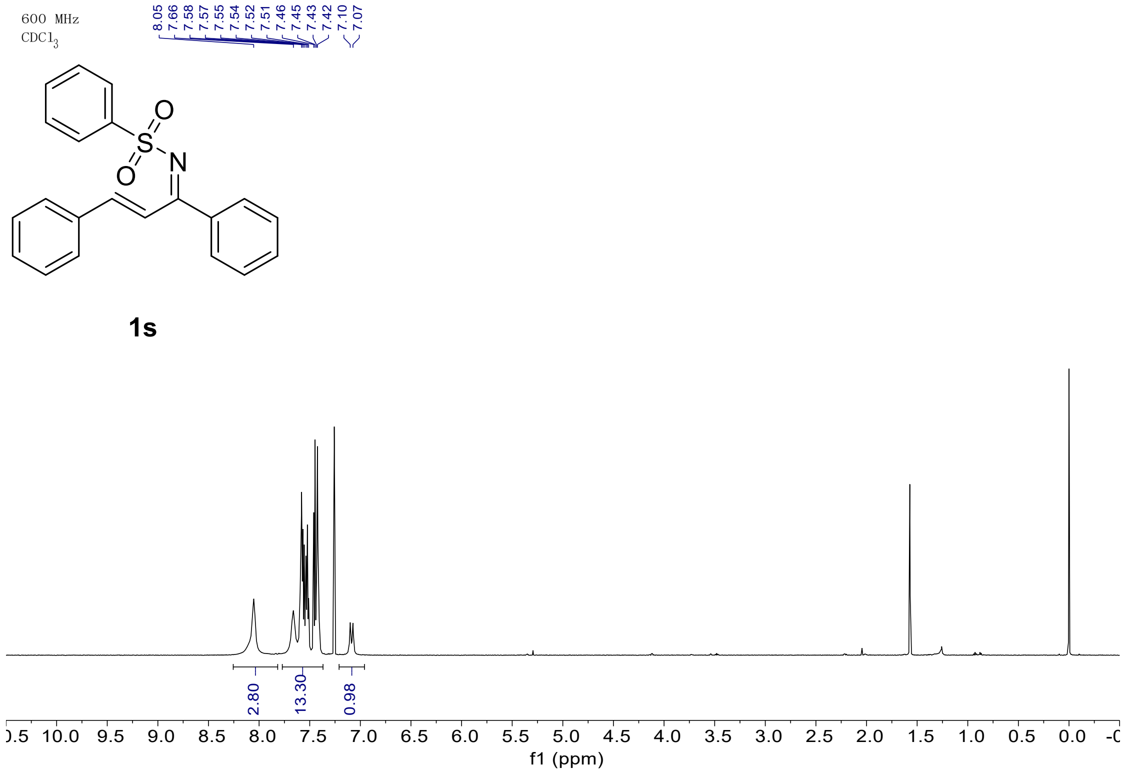


CCDC 2144296

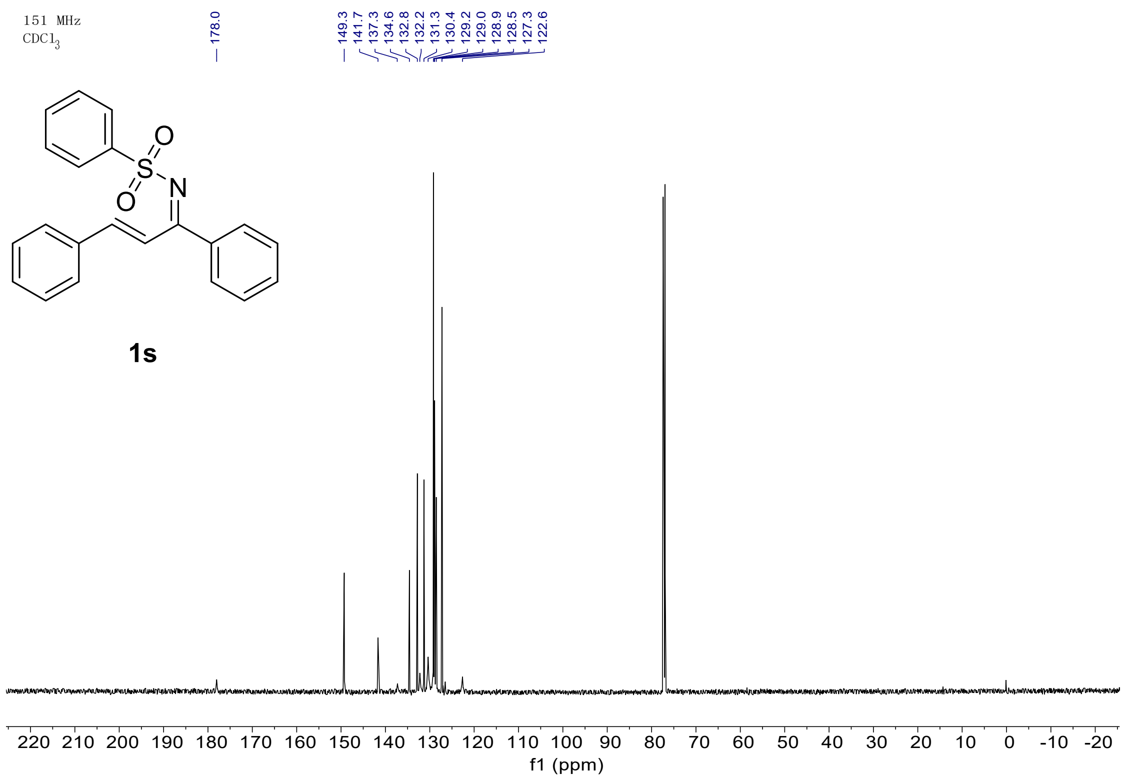
Table S9. Crystal data and structure refinement for **50**.

Identification code	**50**	
Empirical formula	$C_{38}H_{25}Cl_2N_3$	
Formula weight	594.51	
Temperature (K)	293(2)	
Wavelength (Å)	1.3405	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	a = 11.6662(4)	α = 90
	b = 23.9537(7)	β = 115.611(4)
	c = 12.5820(4)	γ = 90
Volume (Å)	3170.6(2)	
Z	4	
Calculated density (g cm^{-3})	1.245	
Absorption coefficient (mm^{-1})	1.367	
F_{000}	1232	
Crystal size (mm^3)	× ×	
θ range for data collection (°)	3.748 to 60.706	
Miller index ranges	$-15 \le h \le 15$, $-30 \le k \le 29$, $-11 \le l \le 16$	
Reflections collected	28166	
Independent reflections	7132 [R_{int} = 0.0266]	
Completeness to $θ_{max}$ (%)	0.975	
Max. and min. transmission	0.86075 and 1.00000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7132 / 0 / 408	
Goodness-of-fit on F^2	1.755	
Final R indices [$I > 2σ(I)$]	$R1$ = 0.1166, $wR2$ = 0.3977	
R indices (all data)	$R1$ = 0.1305, $wR2$ = 0.4111	
Largest diff. peak and hole (e Å^{-3})	1.047 and -0.477	

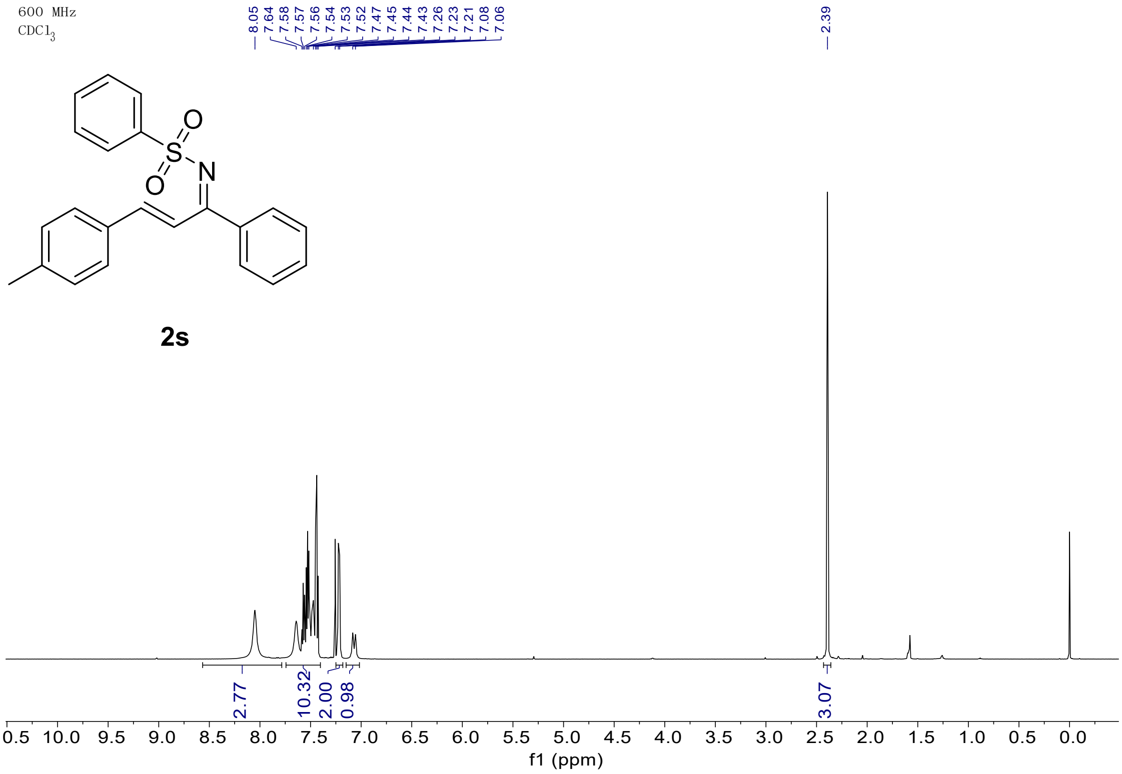
NMR Spectra

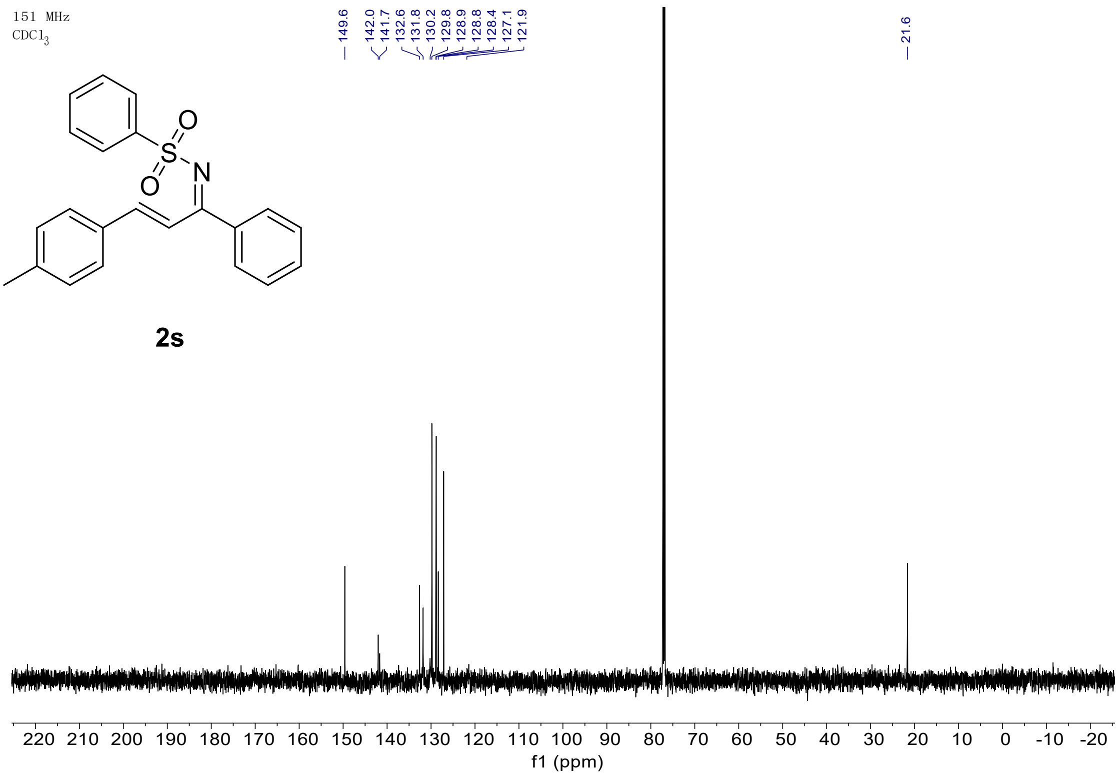


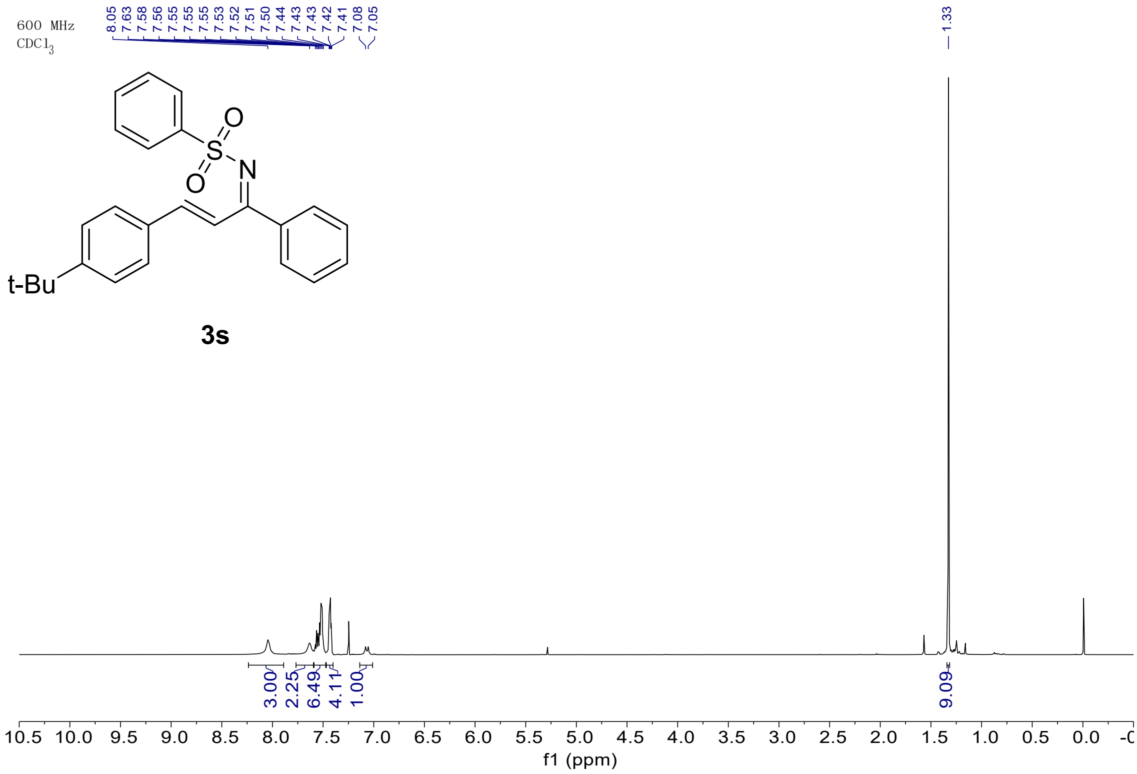
600 MHz
$CDCl_3$
8.05 7.66 7.58 7.57 7.55 7.54 7.52 7.51 7.46 7.45 7.43 7.42 7.10 7.07
O
S
N
O
1s
2.80
13.30
0.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

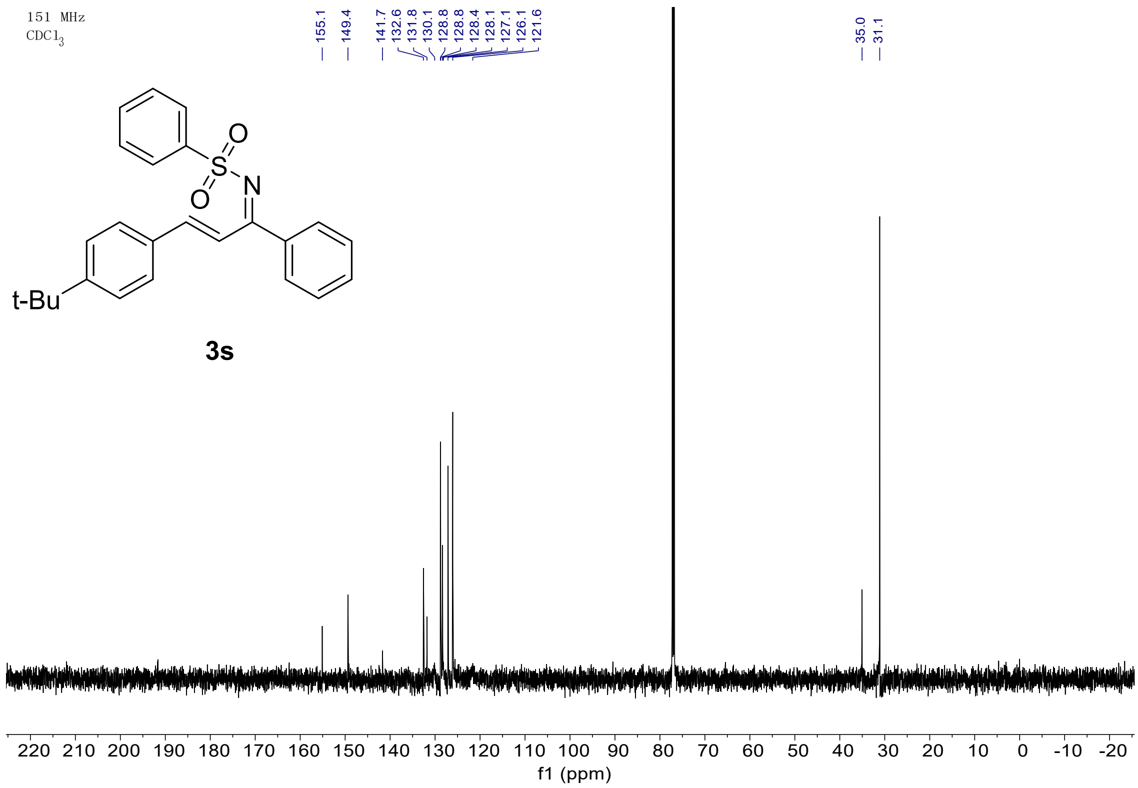


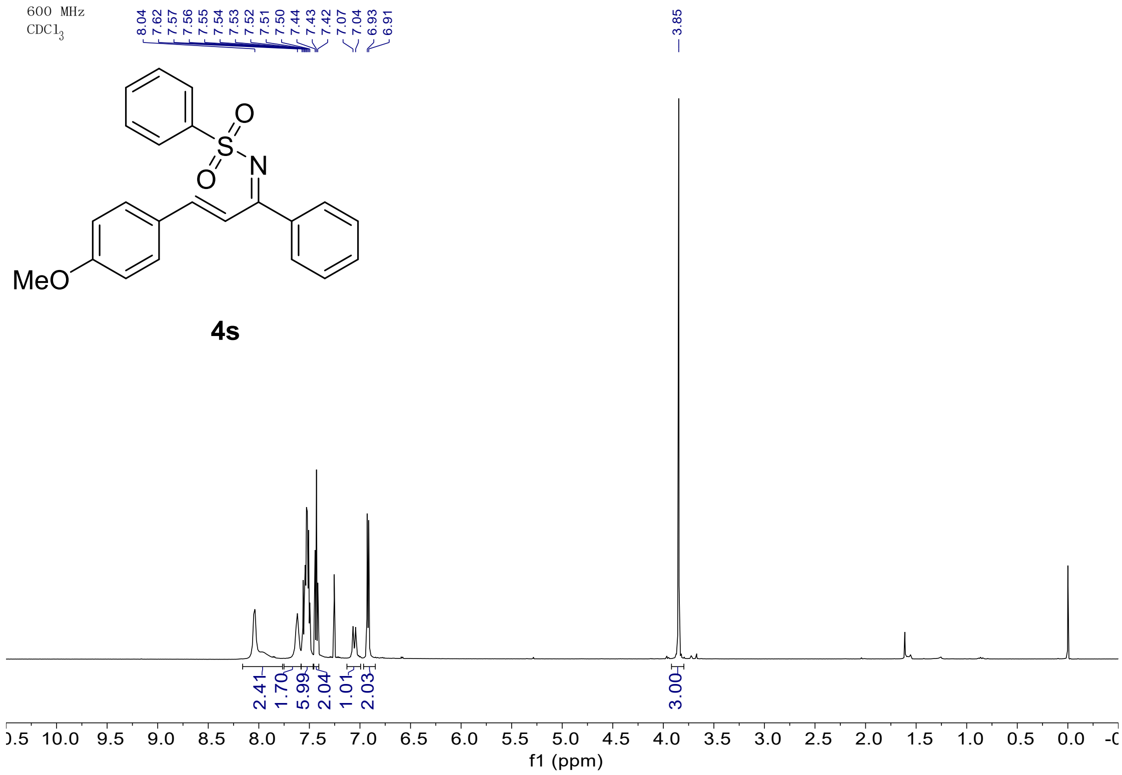
151 MHz
$CDCl_3$
178.0
149.3 141.7 137.3 134.6 132.8 132.2 131.3 130.4 129.2 129.0 128.9 128.5 127.3 122.6
O
S
N
O
1s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

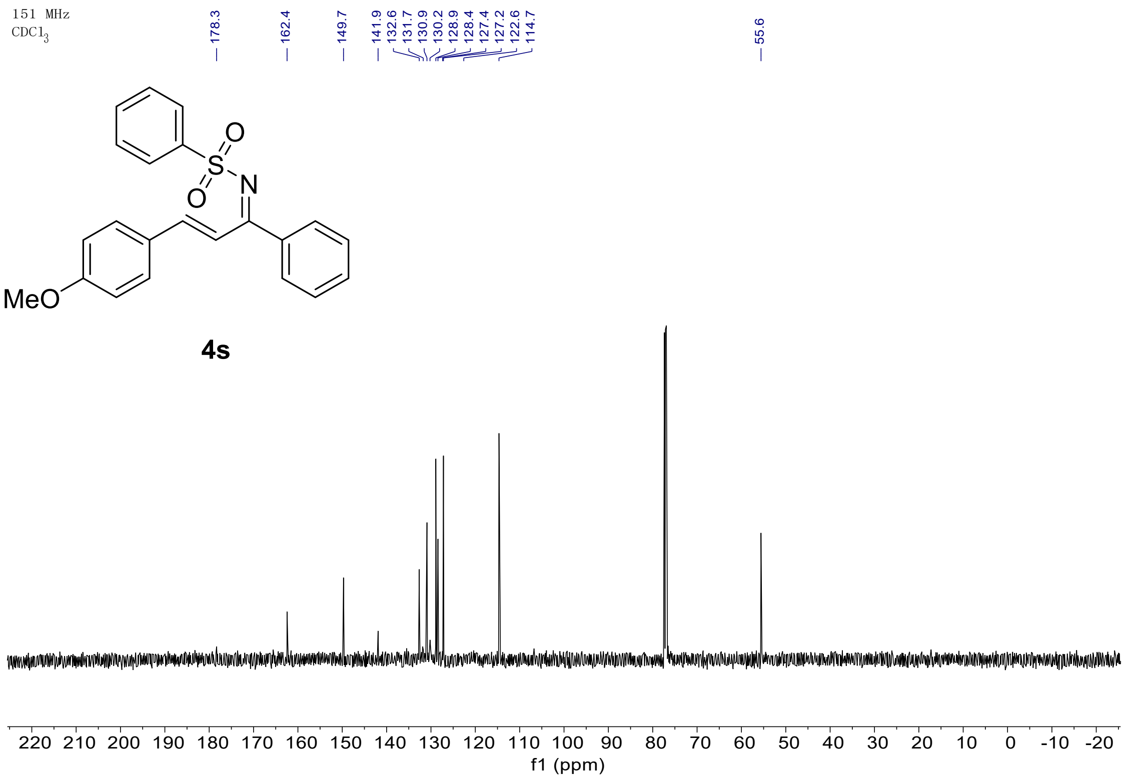

600 MHz
CDCl3
8.05
7.64
7.58
7.57
7.56
7.54
7.53
7.52
7.47
7.45
7.44
7.43
7.26
7.23
7.21
7.08
7.06
2.39
O
S
N
O
2s
2.77
10.32
2.00
0.98
3.07
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

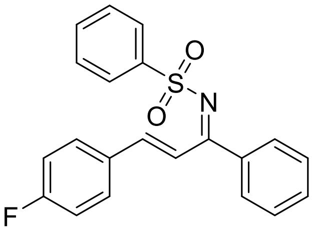

151 MHz
CDCl3
149.6
142.0
141.7
132.6
131.8
130.2
129.8
128.9
128.8
128.4
127.1
121.9
21.6
O
S
N
O
2s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


600 MHz
$CDCl_3$
8.05 7.63 7.58 7.56 7.55 7.55 7.55 7.53 7.52 7.51 7.50 7.44 7.43 7.43 7.42 7.41 7.08 7.05
1.33
O
S
N
O
t-Bu
3s
3.00 2.25 6.49 4.11 1.00
9.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

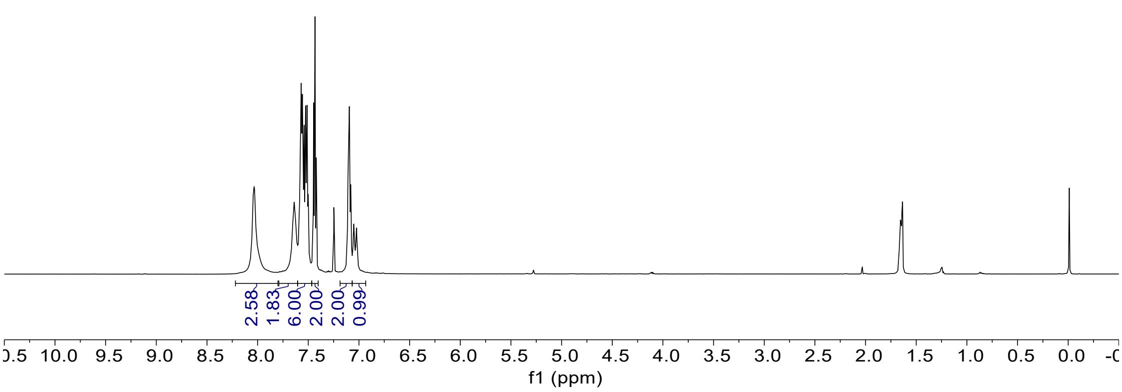

151 MHz
$CDCl_3$
155.1 149.4 141.7 132.6 131.8 130.1 128.8 128.8 128.4 128.1 127.1 126.1 121.6
35.0 31.1
O
S
N
O
t-Bu
3s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

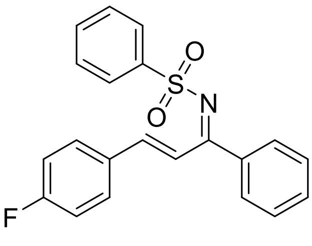

600 MHz
CDCl3
8.04 7.62 7.57 7.56 7.55 7.54 7.53 7.52 7.51 7.50 7.44 7.43 7.42 7.07 7.04 6.93 6.91
3.85
O
S
O
N
MeO
4s
2.41 1.70 5.99 2.04 1.01 2.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151 MHz
CDCl3
178.3
162.4
149.7
141.9 132.6 131.7 130.9 130.2 128.9 128.4 127.4 127.2 122.6 114.7
55.6
O
S
O
N
MeO
4s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

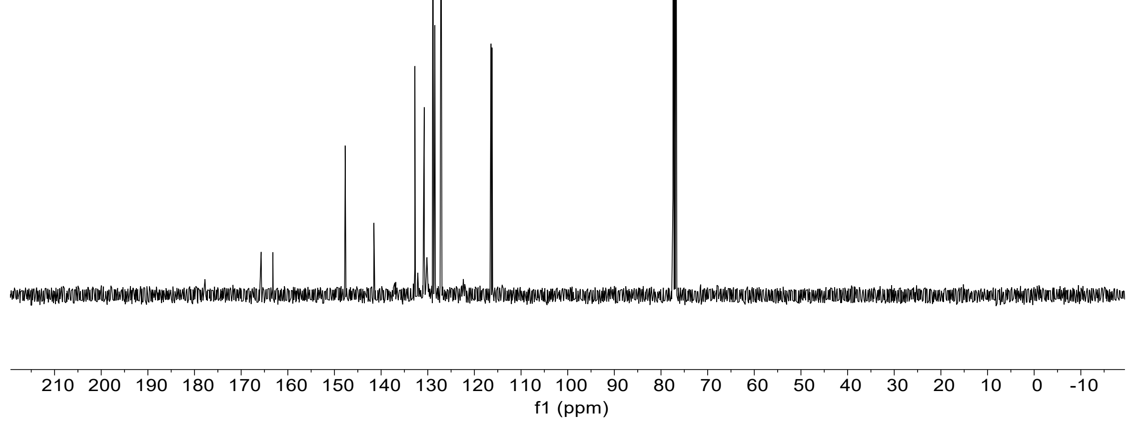


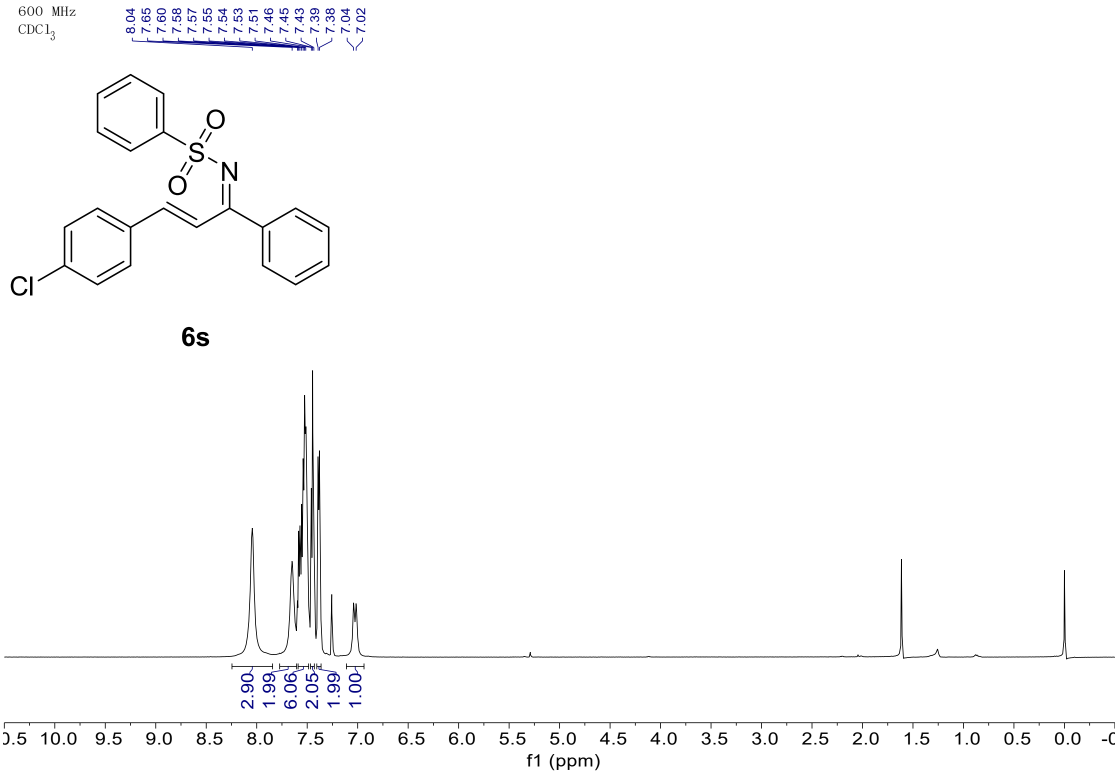
5s

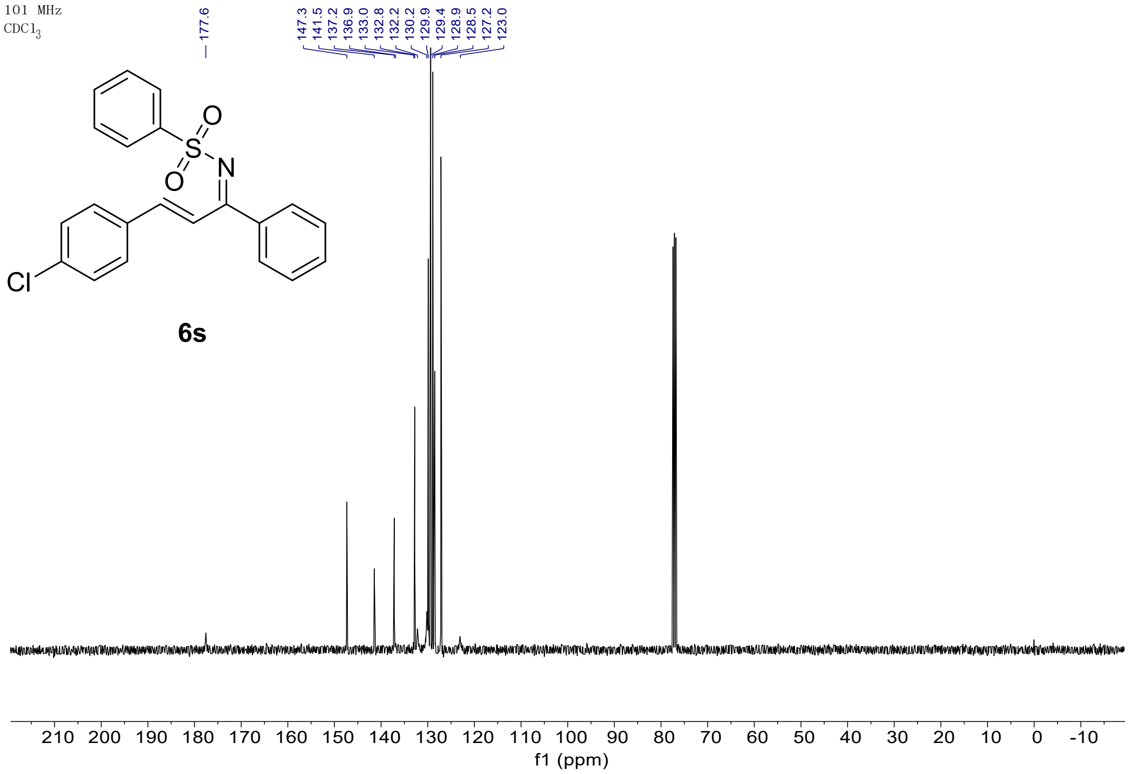

600 MHz
$CDCl_3$
8.04 7.64 7.57 7.56 7.54 7.53 7.51 7.45 7.43 7.42 7.11 7.09 7.08 7.05 7.02
2.58 1.83 6.00 2.00 2.00 0.99
f1 (ppm)

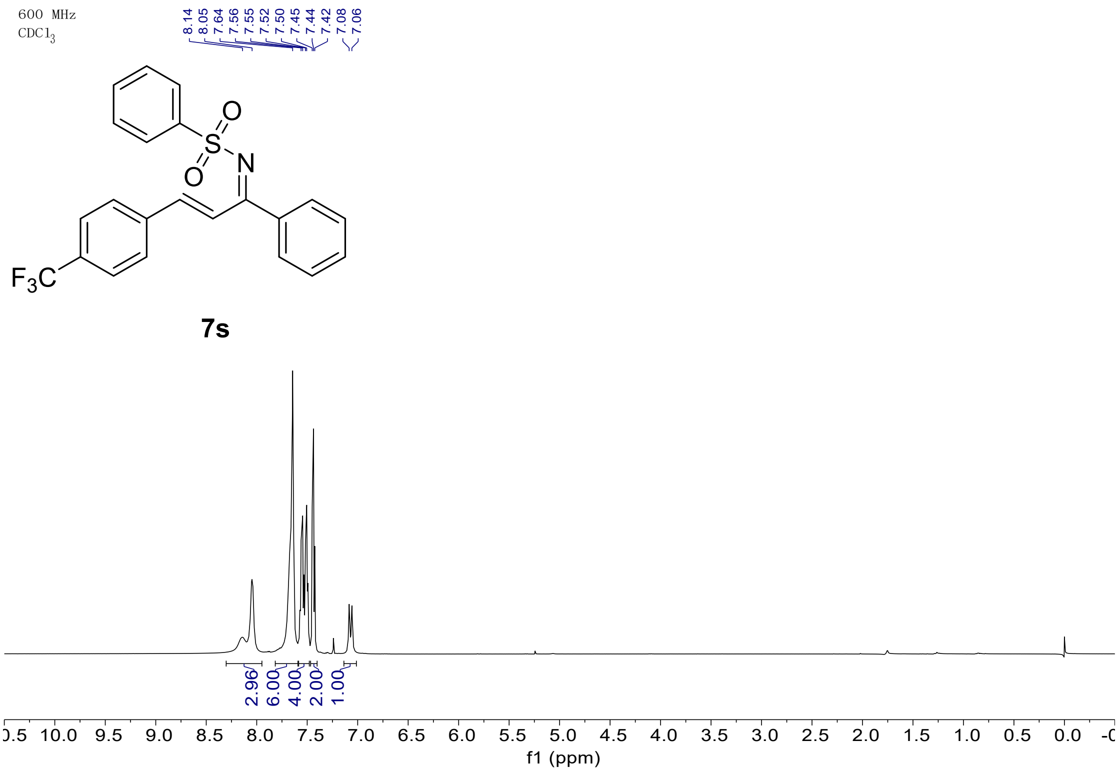


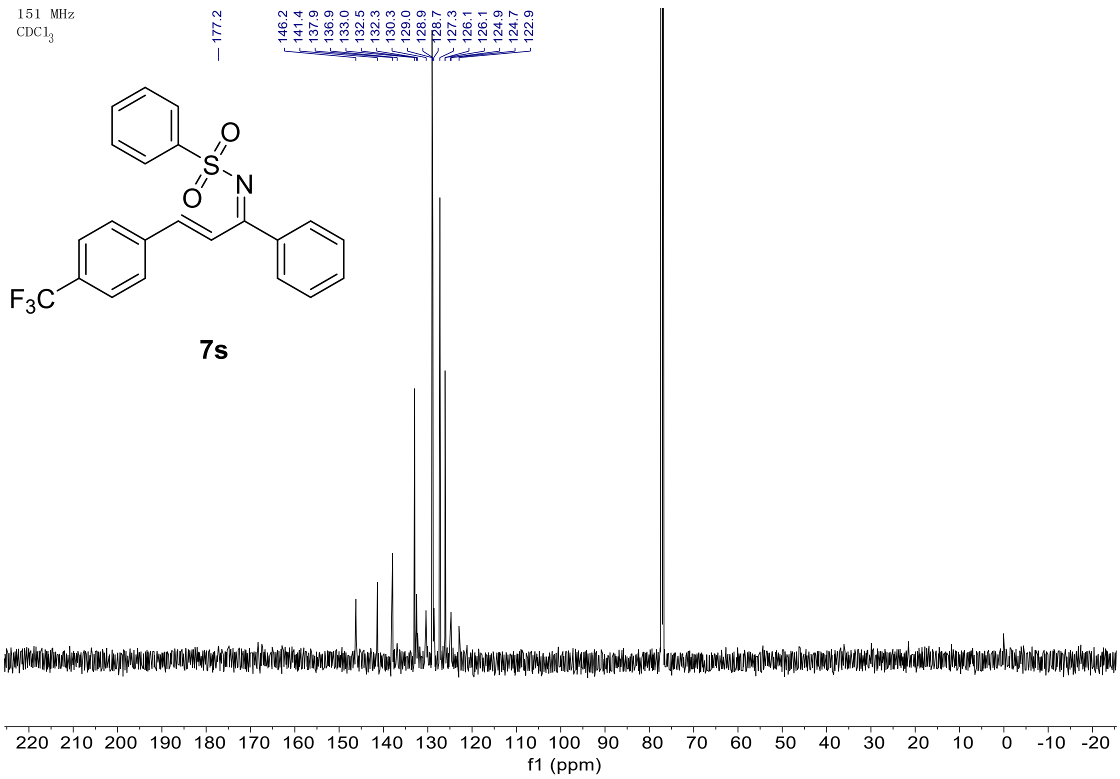
5s

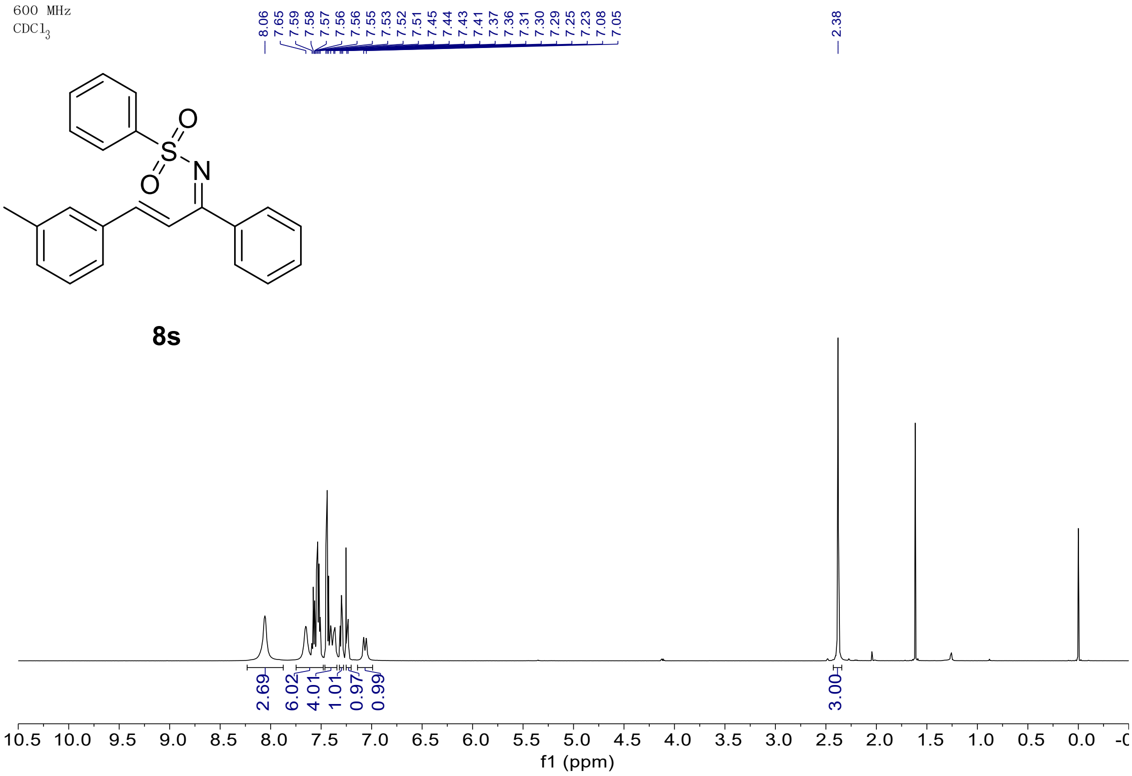

101 MHz
$CDCl_3$
177.7 165.7 163.2 147.7 141.5 136.9 132.8 132.0 130.8 130.8 130.8 130.8 130.1 128.9 128.5 127.1 122.4 116.4 116.2
f1 (ppm)

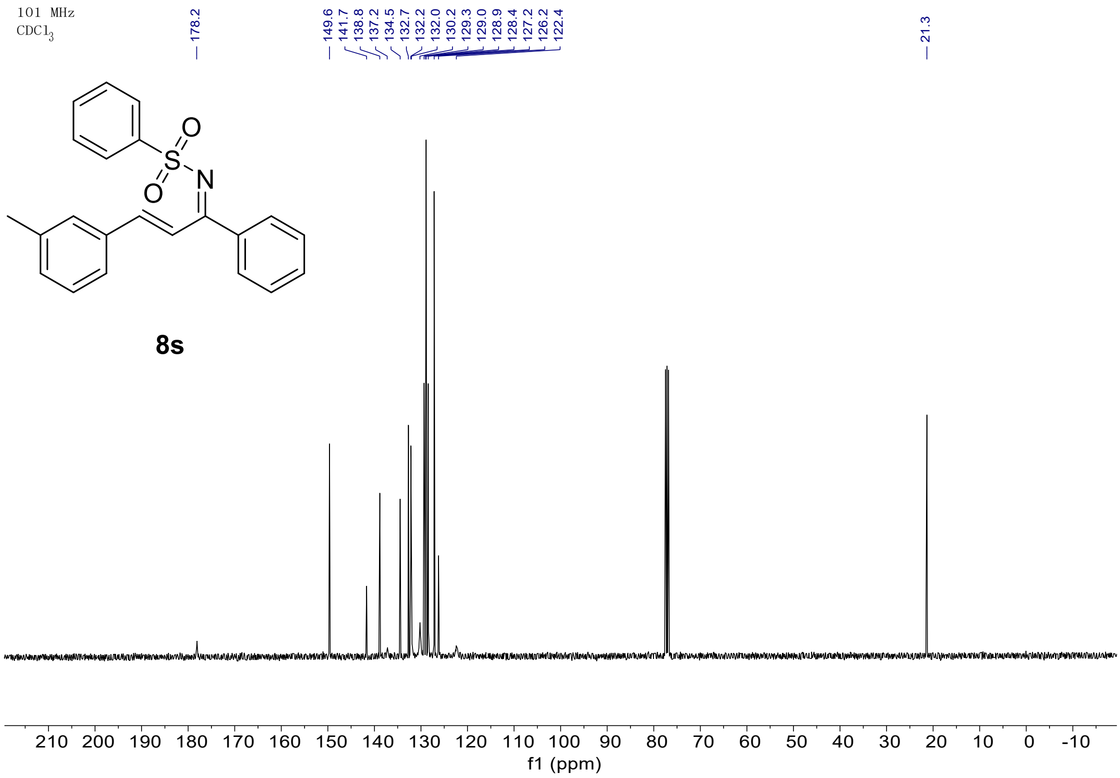

600 MHz
CDCl3
8.04
7.65
7.60
7.58
7.57
7.55
7.54
7.53
7.51
7.46
7.45
7.43
7.39
7.38
7.04
7.02
6s
2.90
1.99
6.06
2.05
1.99
1.00
f1 (ppm)

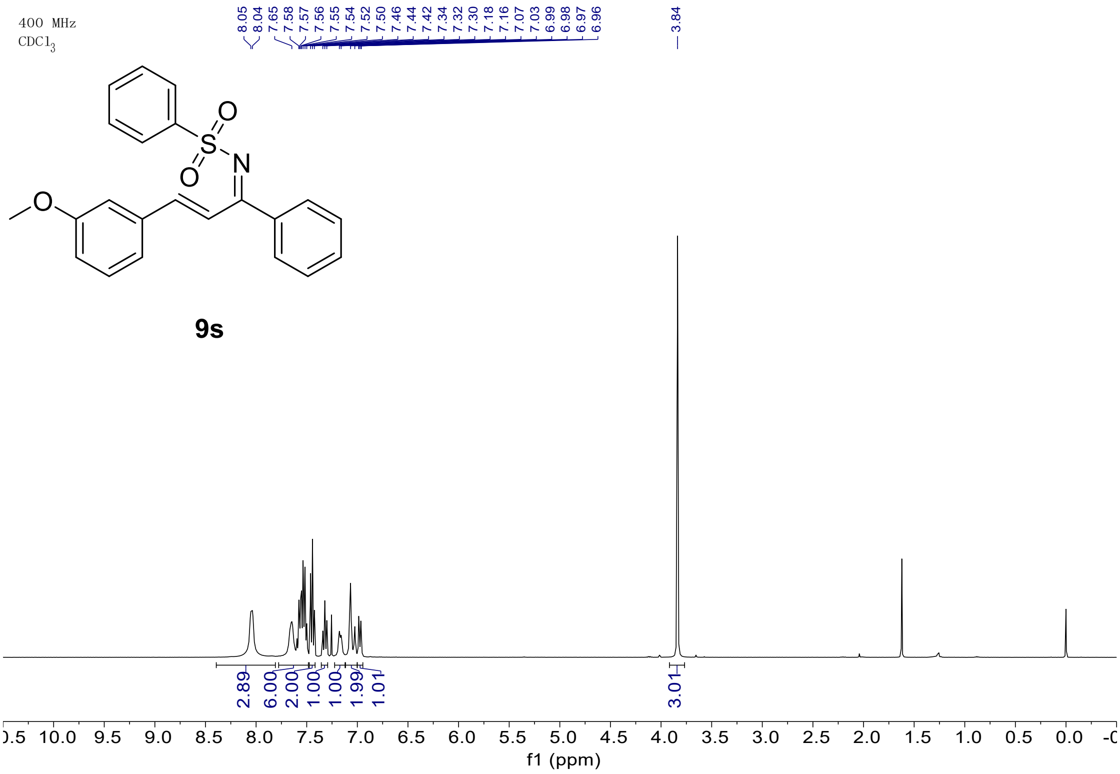

101 MHz
CDCl3
177.6
147.3
141.5
137.2
136.9
133.0
132.8
132.2
130.2
129.9
129.4
128.9
128.5
127.2
123.0
6s
f1 (ppm)

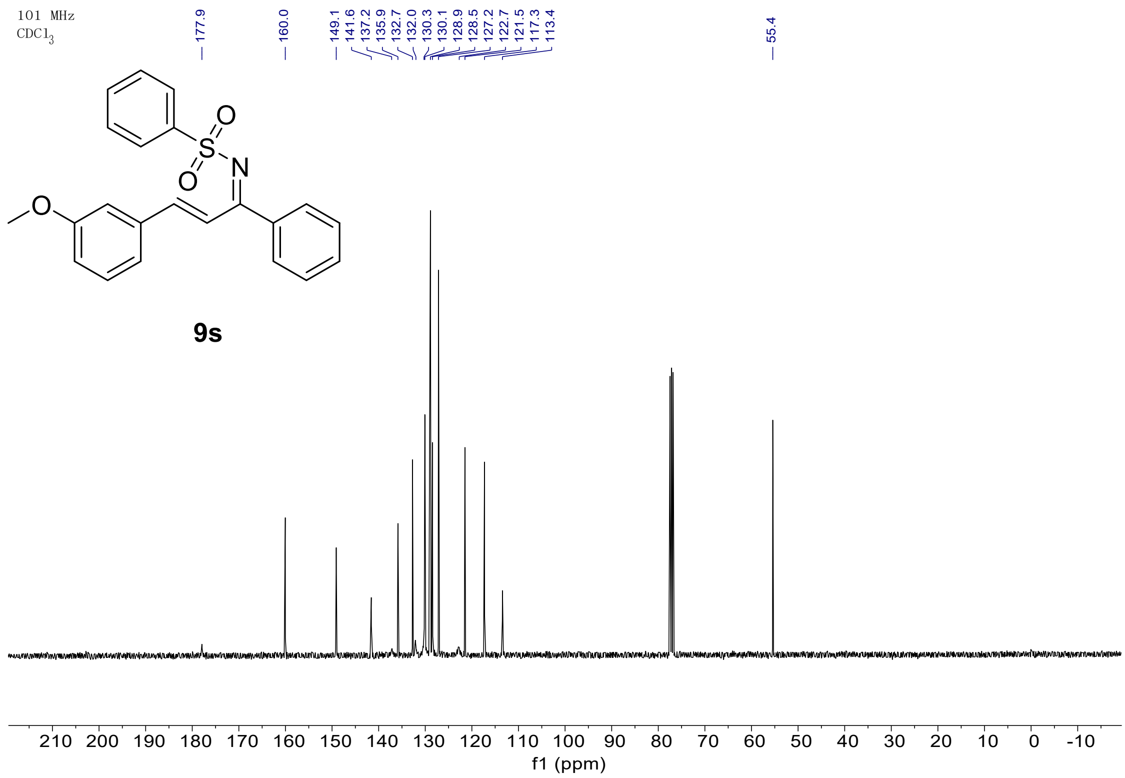

600 MHz
CDCl3
8.14
8.05
7.64
7.56
7.55
7.52
7.50
7.45
7.44
7.42
7.08
7.06
7s
2.96
6.00
4.00
2.00
1.00
f1 (ppm)

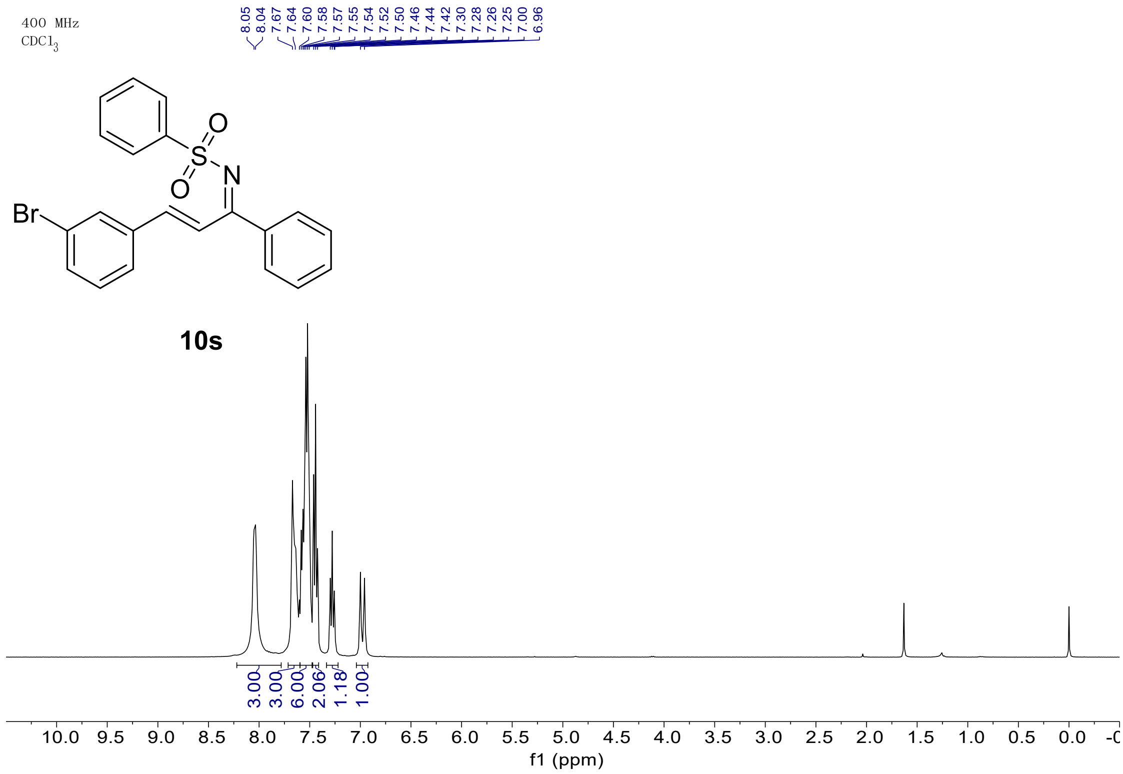

151 MHz
CDCl3
177.2
146.2
141.4
137.9
136.9
133.0
132.5
132.3
130.3
129.0
128.9
128.7
127.3
126.1
124.9
124.7
122.9
7s
f1 (ppm)

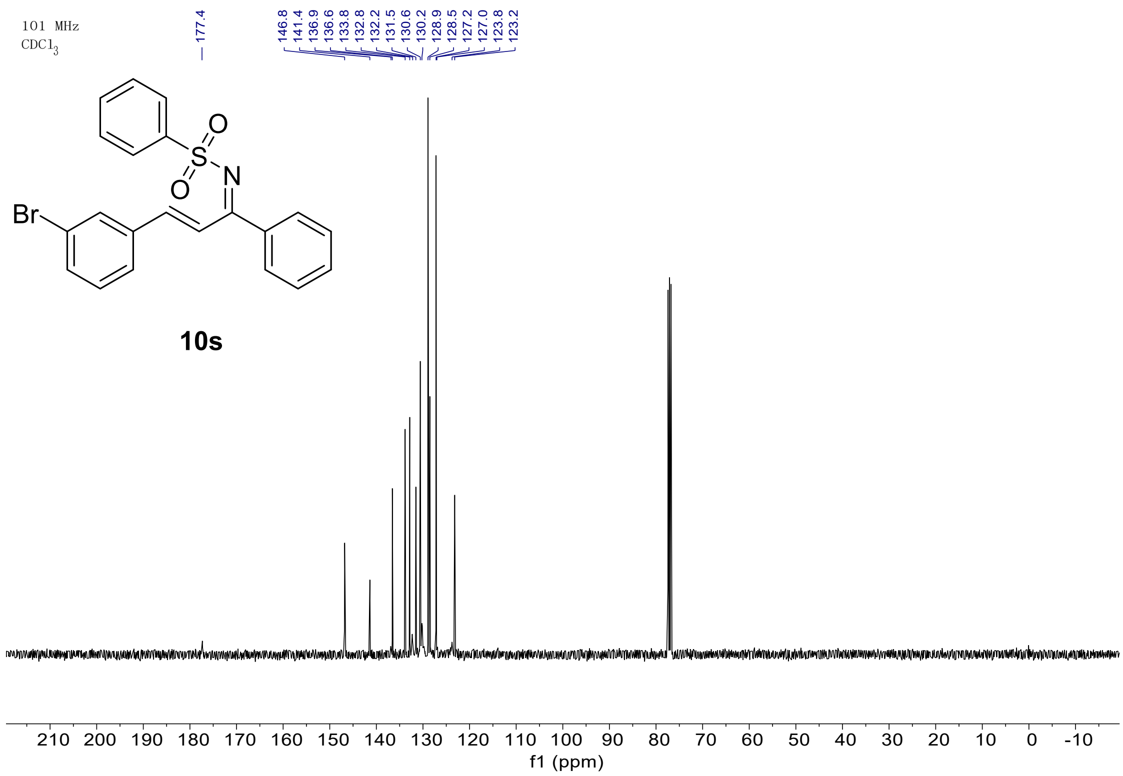

600 MHz
CDCl3
8.06 7.65 7.59 7.58 7.57 7.56 7.56 7.55 7.53 7.52 7.51 7.45 7.44 7.43 7.41 7.37 7.36 7.31 7.30 7.29 7.25 7.23 7.08 7.05
2.38
O
S
O
N
8s
2.69
6.02
4.01
1.01
0.97
0.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

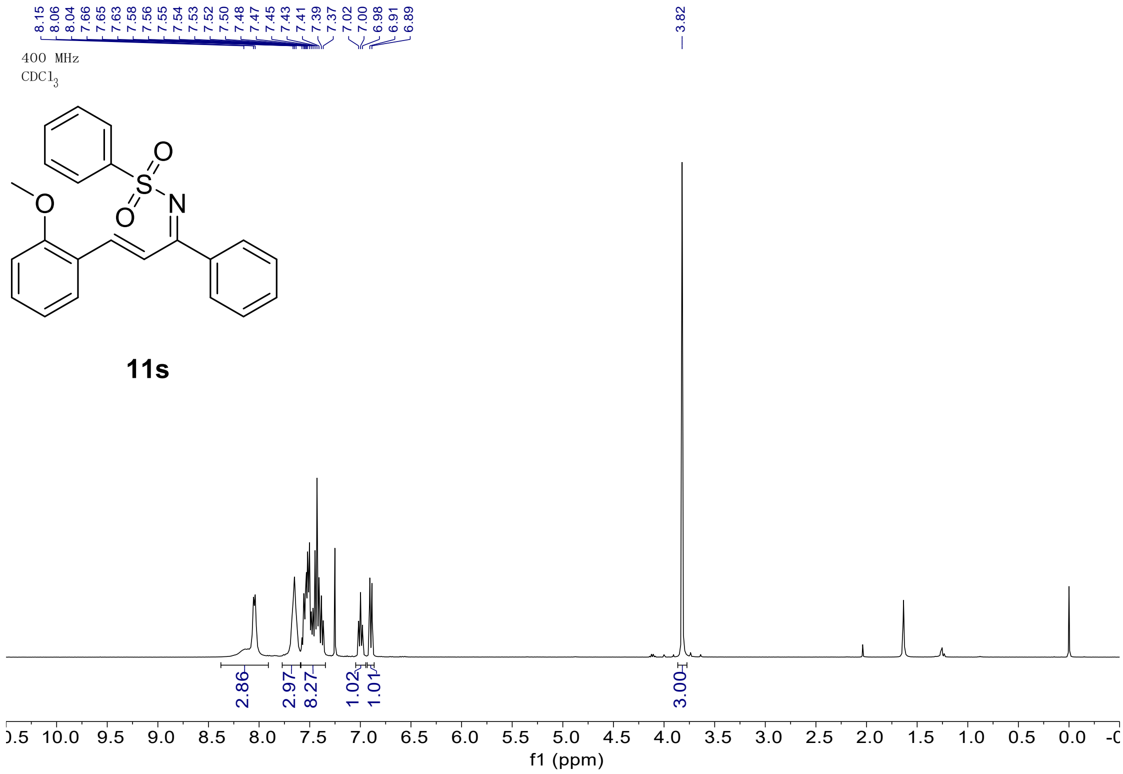

101 MHz
CDCl3
178.2
149.6 141.7 138.8 137.2 134.5 132.7 132.2 132.0 130.2 129.3 129.0 128.9 128.4 127.2 126.2 122.4
21.3
O
S
O
N
8s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
CDCl3
8.05
8.04
7.65
7.58
7.57
7.56
7.55
7.54
7.52
7.50
7.46
7.44
7.42
7.34
7.32
7.30
7.18
7.16
7.07
7.03
6.99
6.98
6.97
6.96
3.84
9s
2.89
6.00
2.00
1.00
1.00
1.99
1.01
3.01
f1 (ppm)

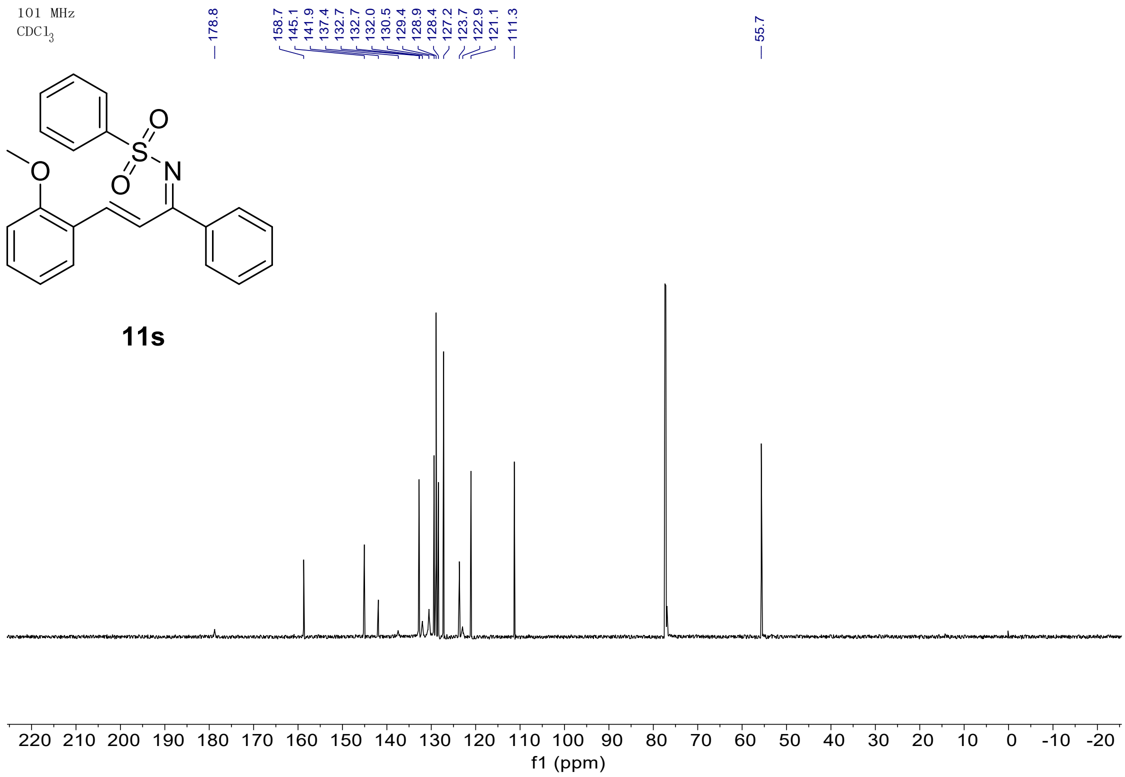

101 MHz
CDCl3
177.9
160.0
149.1
141.6
137.2
135.9
132.7
132.0
130.3
130.1
128.9
128.5
127.2
122.7
121.5
117.3
113.4
55.4
9s
f1 (ppm)


400 MHz
CDCl3
8.05
8.04
7.67
7.64
7.60
7.58
7.57
7.55
7.54
7.52
7.50
7.46
7.44
7.42
7.30
7.28
7.26
7.25
7.00
6.96
O
S
O
N
Br
10s
3.00
3.00
6.00
2.06
1.18
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

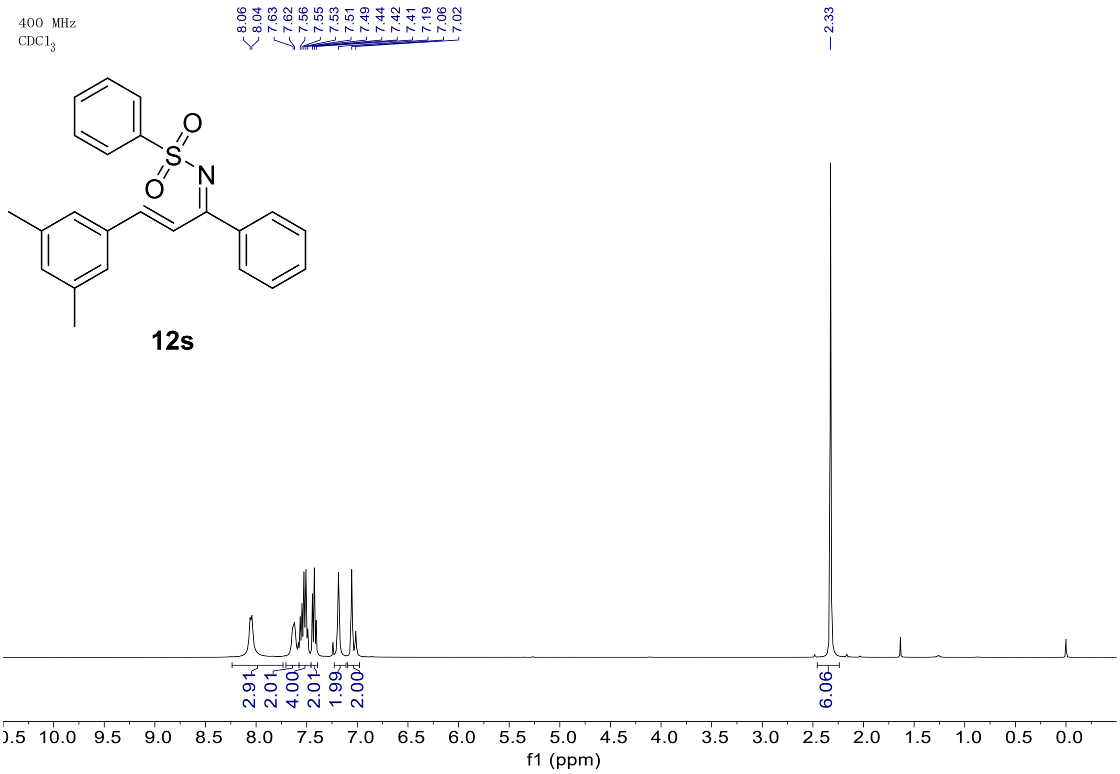

101 MHz
CDCl3
177.4
146.8
141.4
136.9
136.6
133.8
132.8
132.2
131.5
130.6
130.2
128.9
128.5
127.2
127.0
123.8
123.2
O
S
O
N
Br
10s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

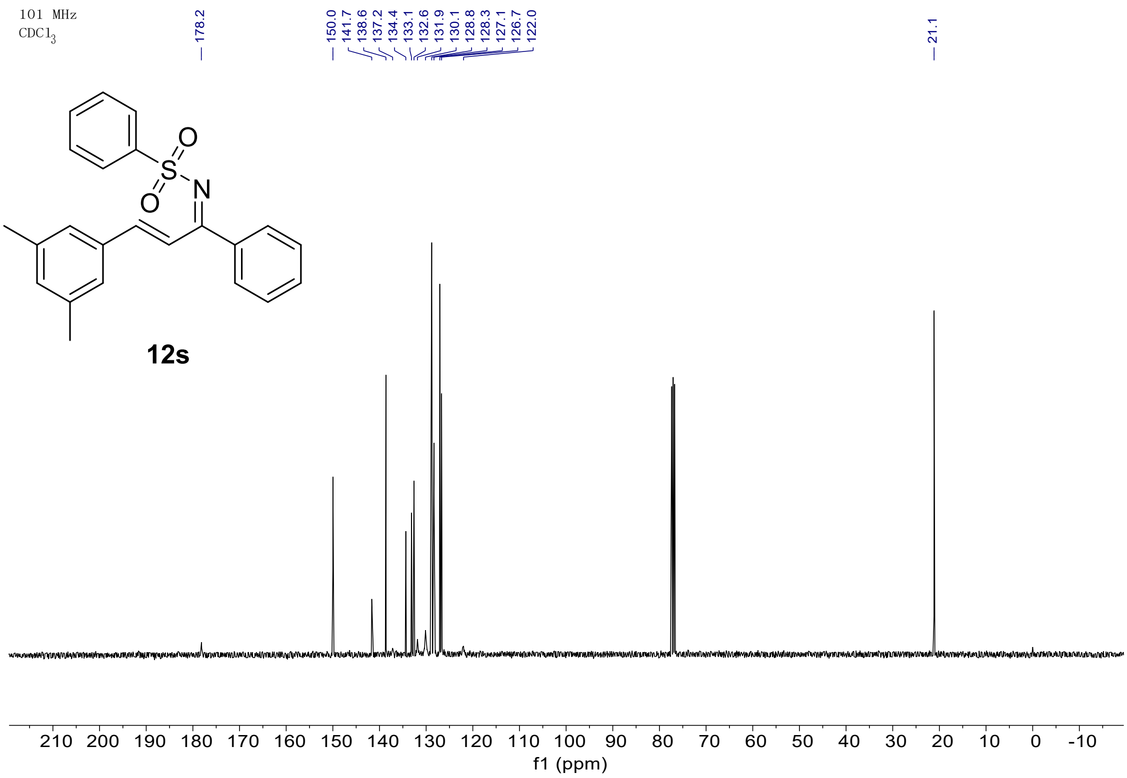


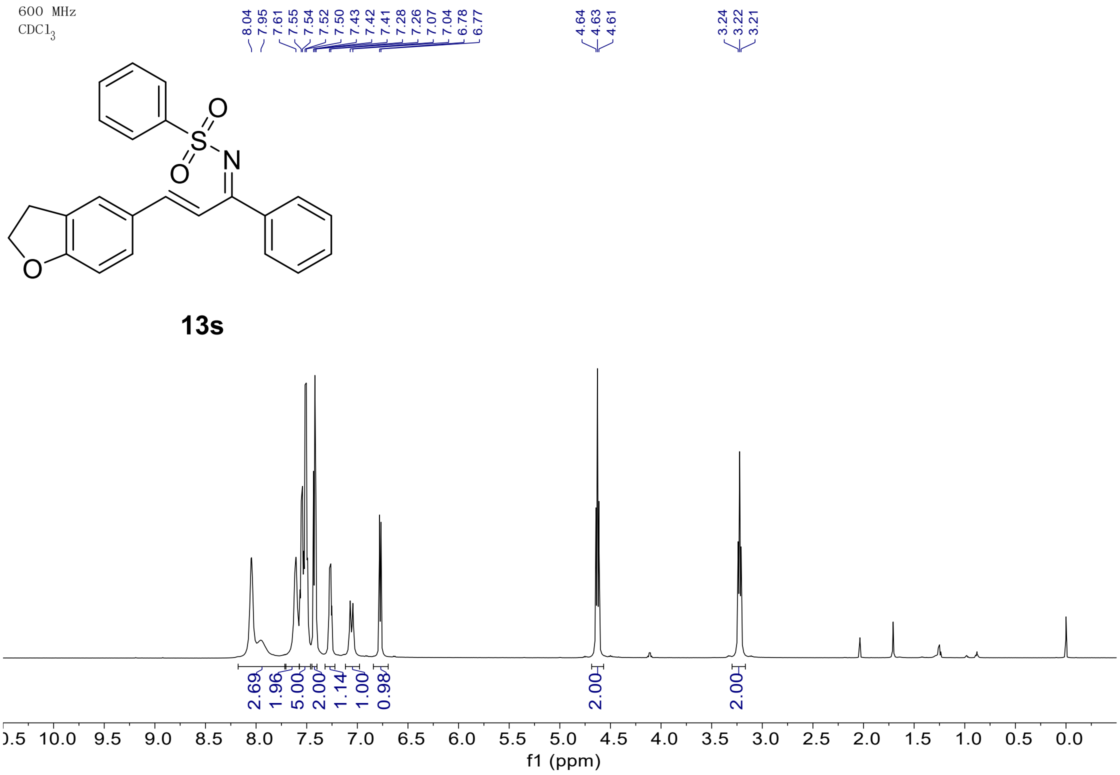
400 MHz
CDCl3
8.15 8.06 8.04 7.66 7.65 7.63 7.58 7.56 7.55 7.54 7.53 7.52 7.50 7.48 7.47 7.45 7.43 7.41 7.39 7.37 7.02 7.00 6.98 6.91 6.89
3.82
11s
2.86 2.97 8.27 1.02 1.01 3.00
f1 (ppm)

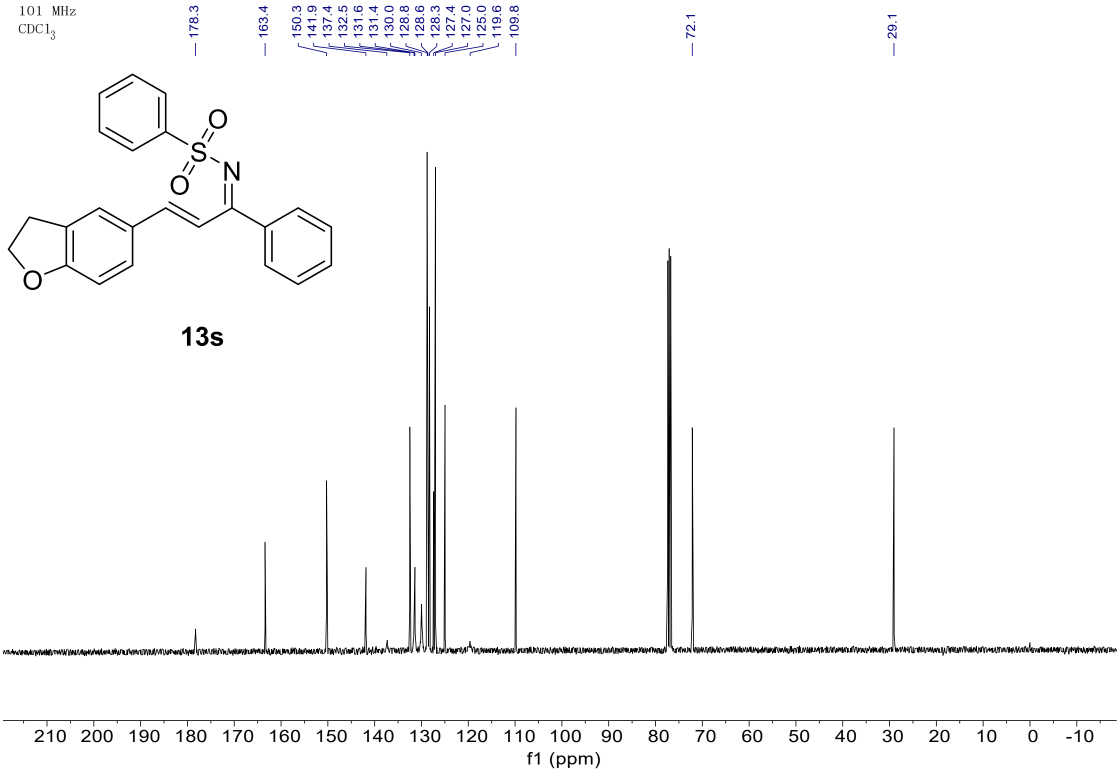


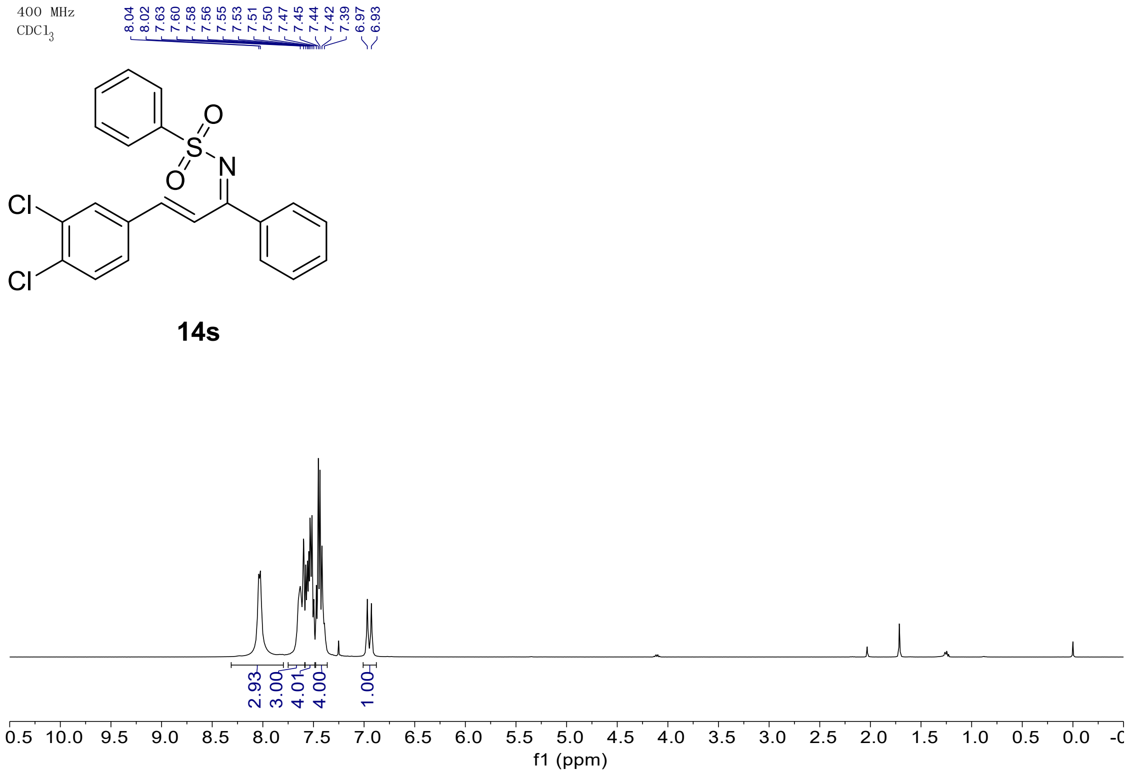
101 MHz
CDCl3
178.8
158.7 145.1 141.9 137.4 132.7 132.7 132.0 130.5 129.4 128.9 128.4 127.2 123.7 122.9 121.1 111.3
55.7
11s
f1 (ppm)

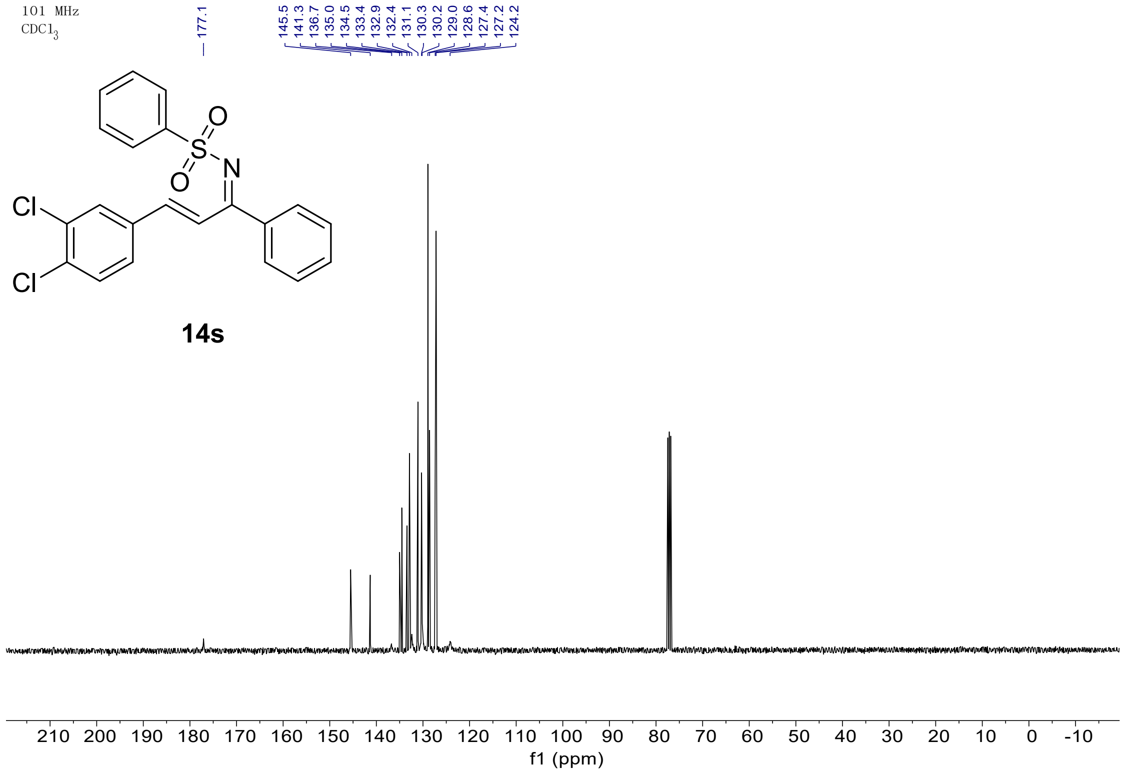

400 MHz
CDCl3
8.06
8.04
7.63
7.62
7.56
7.55
7.53
7.51
7.49
7.44
7.42
7.41
7.19
7.06
7.02
2.33
12s
2.91
2.01
4.00
2.01
1.99
2.00
6.06
f1 (ppm)

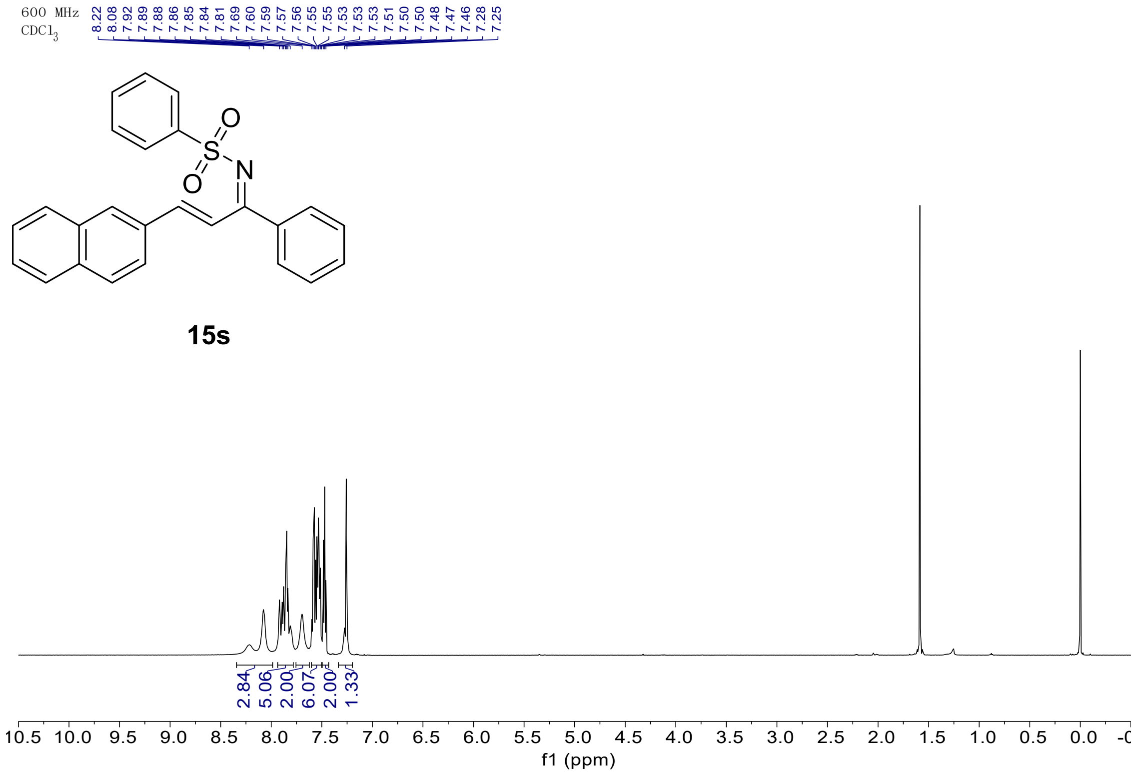

101 MHz
CDCl3
178.2
150.0
141.7
138.6
137.2
134.4
133.1
132.6
131.9
130.1
128.8
128.3
127.1
126.7
122.0
21.1
12s
f1 (ppm)

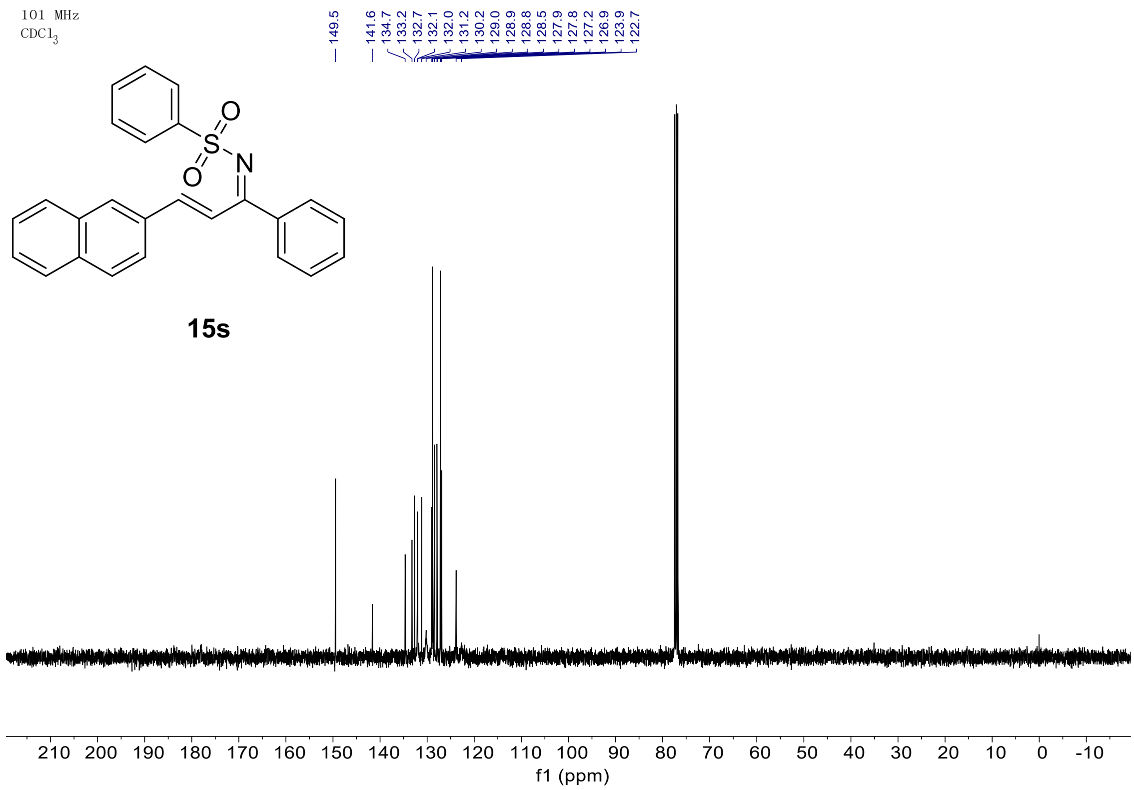

600 MHz
CDCl3
8.04 7.95 7.61 7.55 7.54 7.52 7.50 7.43 7.42 7.41 7.28 7.26 7.07 7.04 6.78 6.77
4.64 4.63 4.61
3.24 3.22 3.21
13s
2.69 1.96 5.00 2.00 1.14 1.00 0.98
2.00
2.00
f1 (ppm)

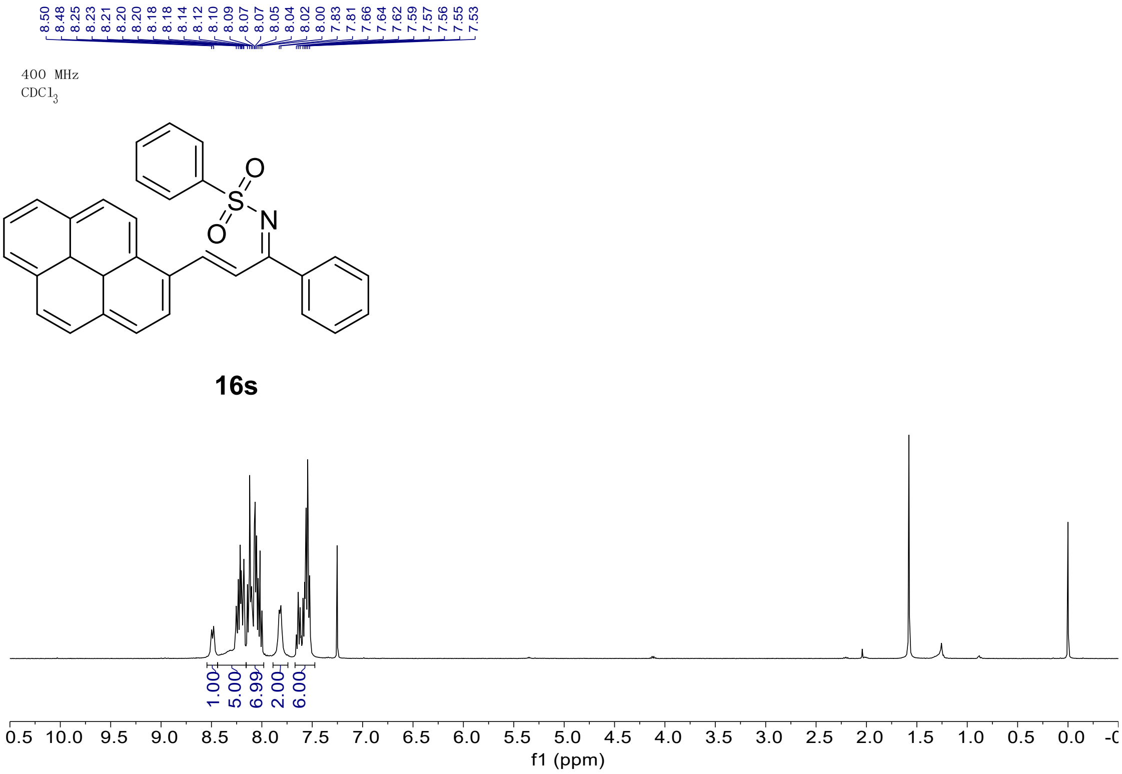

101 MHz
CDCl3
178.3
163.4
150.3 141.9 137.4 132.5 131.6 131.4 130.0 128.8 128.6 128.3 127.4 127.0 125.0 119.6 109.8
72.1
29.1
13s
f1 (ppm)

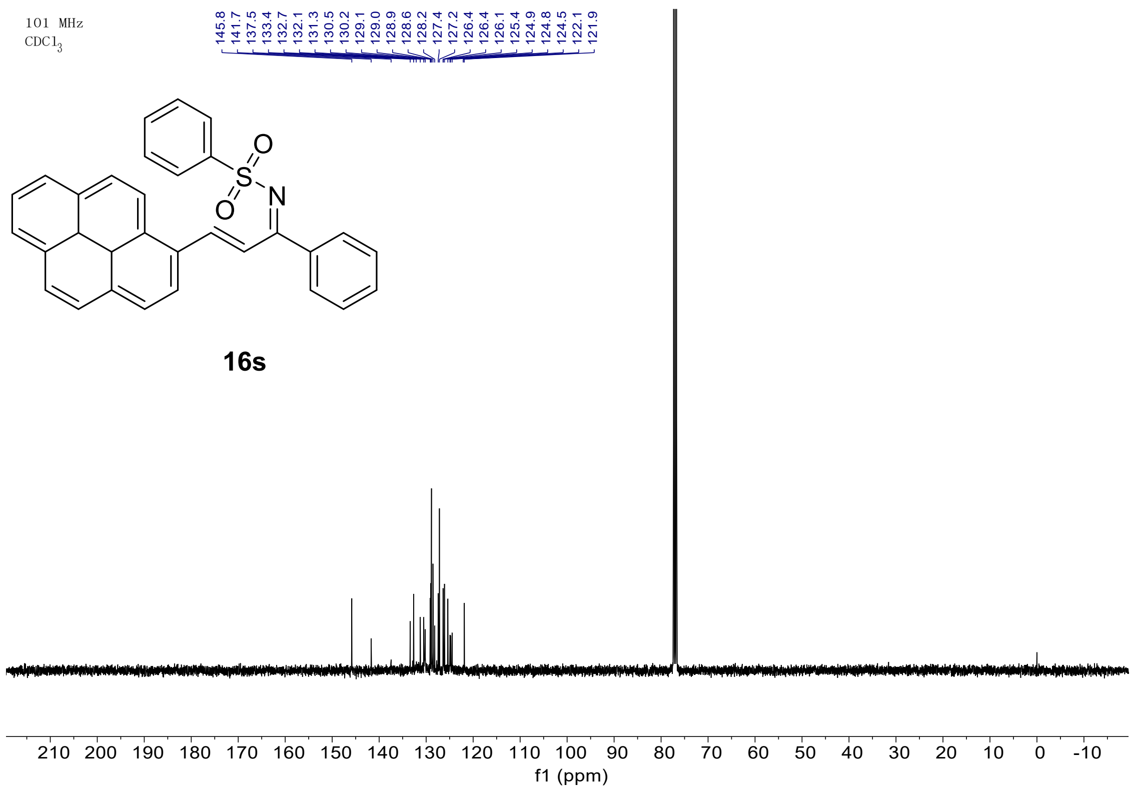

400 MHz
CDCl3
8.04
8.02
7.63
7.60
7.58
7.56
7.55
7.53
7.51
7.50
7.47
7.45
7.44
7.42
7.39
6.97
6.93
Cl
Cl
O
S
O
N
14s
2.93
3.00
4.01
4.00
1.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

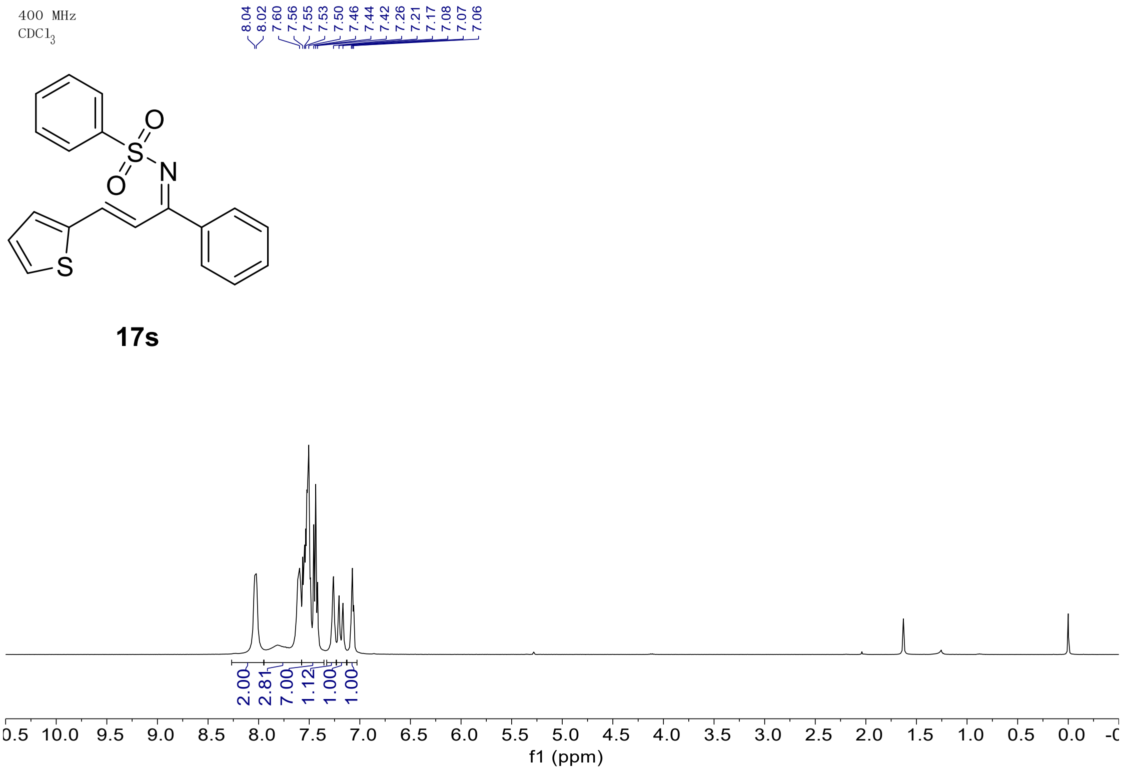

101 MHz
CDCl3
177.1
145.5
141.3
136.7
135.0
134.5
133.4
132.9
132.4
131.1
130.3
130.2
129.0
128.6
127.4
127.2
124.2
Cl
Cl
O
S
O
N
14s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

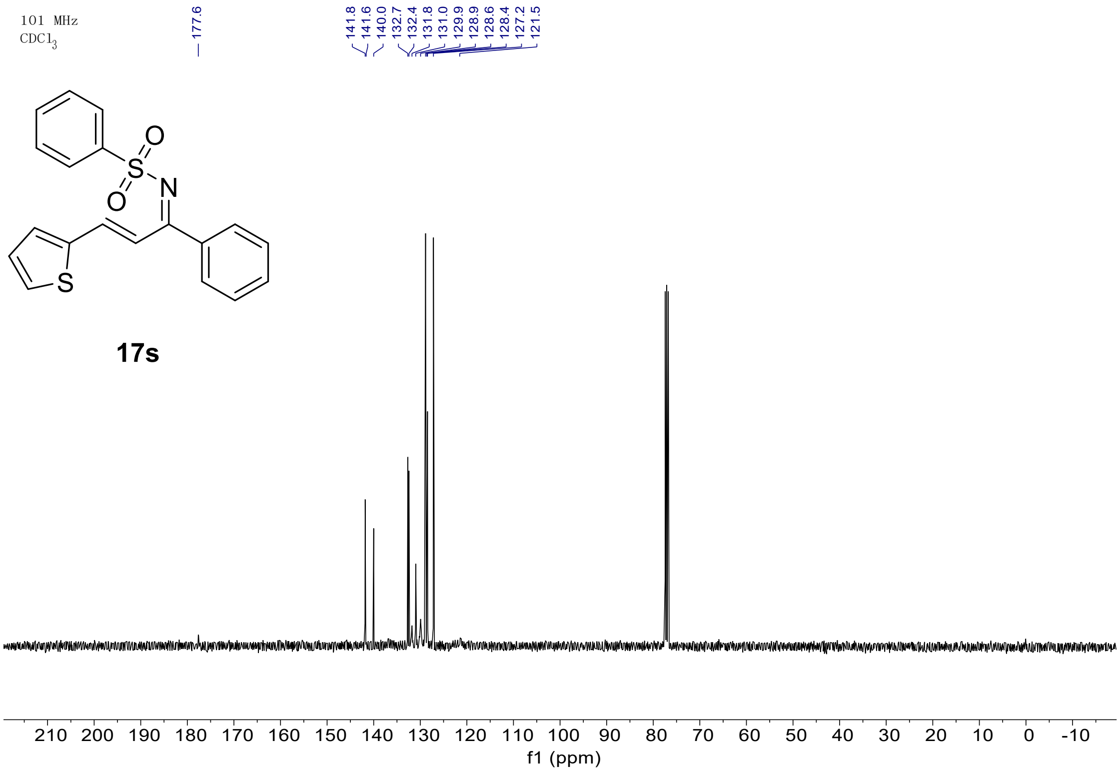

600 MHz
CDCl3
8.22 8.08 7.92 7.89 7.88 7.86 7.85 7.84 7.81 7.69 7.60 7.59 7.57 7.56 7.55 7.55 7.53 7.53 7.53 7.51 7.50 7.50 7.48 7.47 7.46 7.28 7.25
O
S
N
O
15s
2.84 5.06 2.00 6.07 2.00 1.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

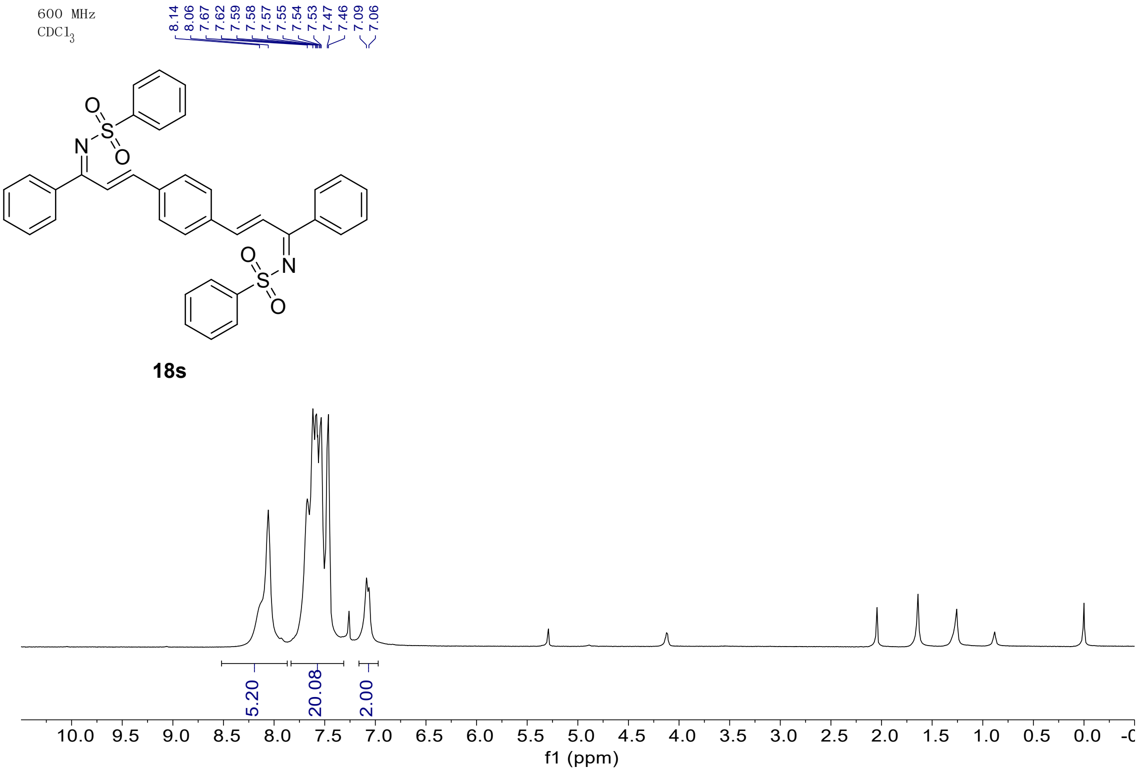

101 MHz
CDCl3
149.5
141.6 134.7 133.2 132.7 132.1 132.0 131.2 130.2 129.0 128.9 128.8 128.5 127.9 127.8 127.2 126.9 123.9 122.7
O
S
N
O
15s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

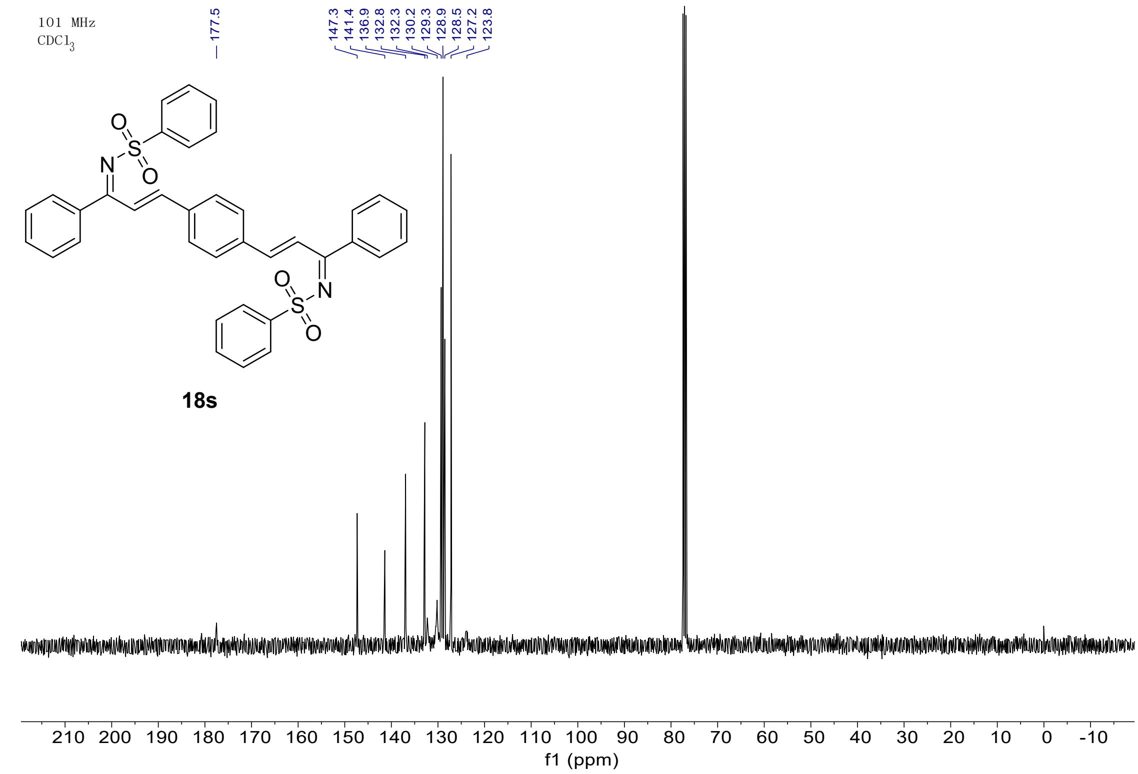

8.50 8.48 8.25 8.23 8.21 8.20 8.20 8.18 8.18 8.14 8.12 8.10 8.09 8.07 8.07 8.05 8.04 8.02 8.00 7.83 7.81 7.66 7.64 7.62 7.59 7.57 7.56 7.55 7.53
400 MHz
CDCl3
O
S
O
N
16s
1.00
5.00
6.99
2.00
6.00
f1 (ppm)

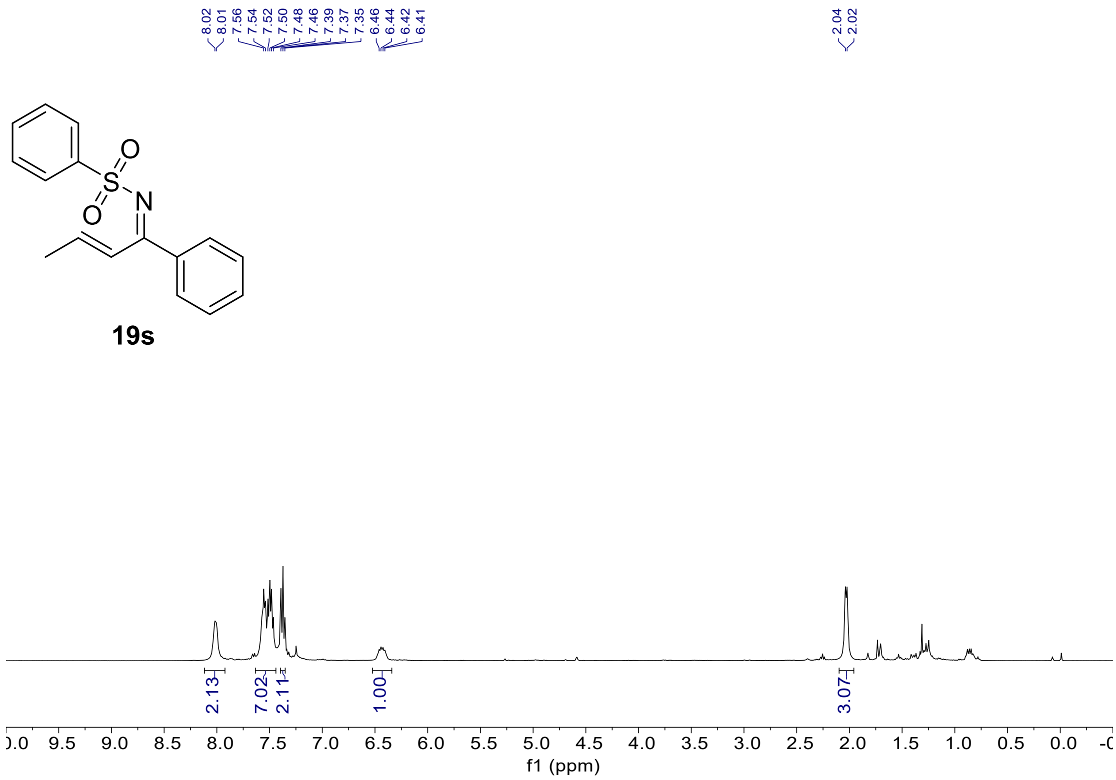

101 MHz
CDCl3
145.8 141.7 137.5 133.4 132.7 132.1 131.3 130.5 130.2 129.1 129.0 128.9 128.6 128.2 127.4 127.2 126.4 126.4 126.1 125.4 124.9 124.8 124.5 122.1 121.9
O
S
O
N
16s
f1 (ppm)

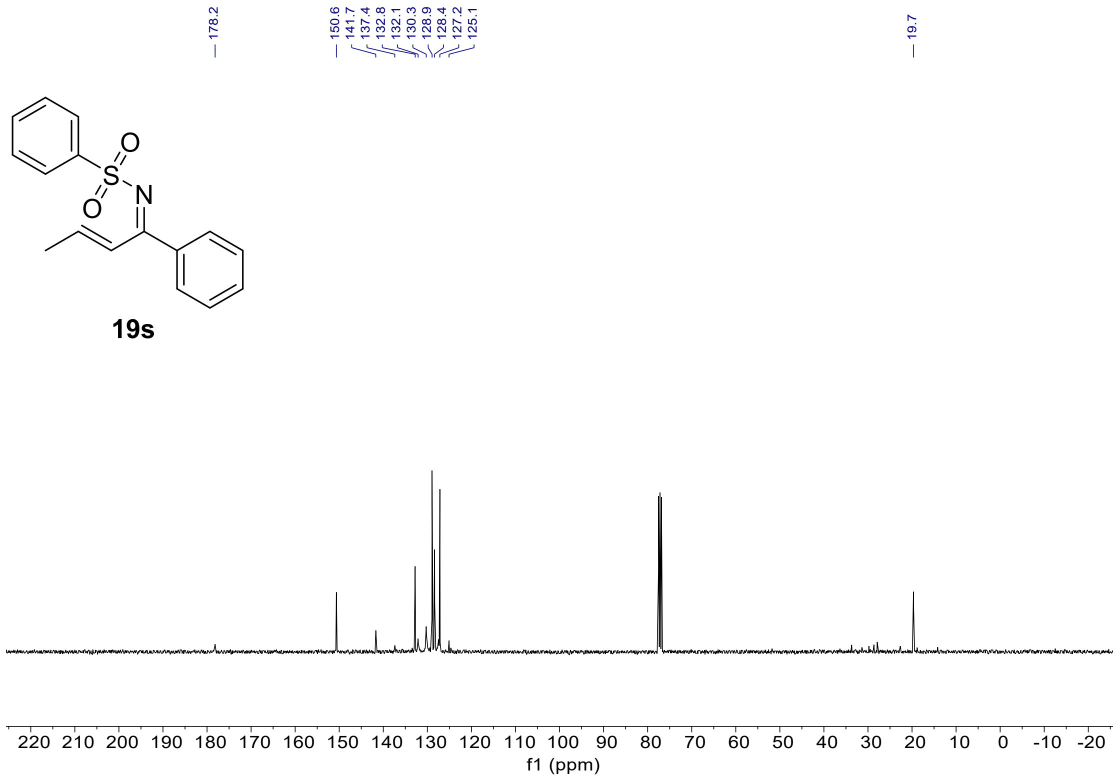

400 MHz
CDCl3
8.04
8.02
7.60
7.56
7.55
7.53
7.50
7.46
7.44
7.42
7.26
7.21
7.17
7.08
7.07
7.06
O
S
N
O
S
17s
2.00
2.81
7.00
1.12
1.00
1.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

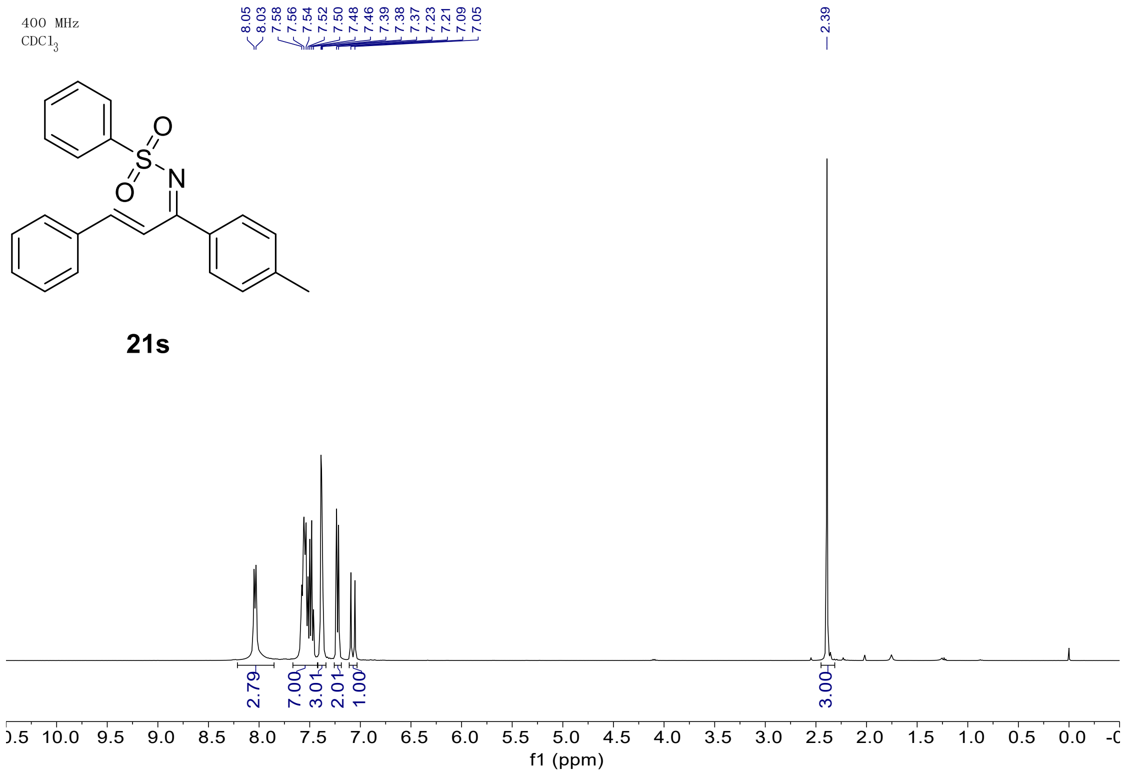

101 MHz
CDCl3
177.6
141.8
141.6
140.0
132.7
132.4
131.8
131.0
129.9
128.9
128.6
128.4
127.2
121.5
O
S
N
O
S
17s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

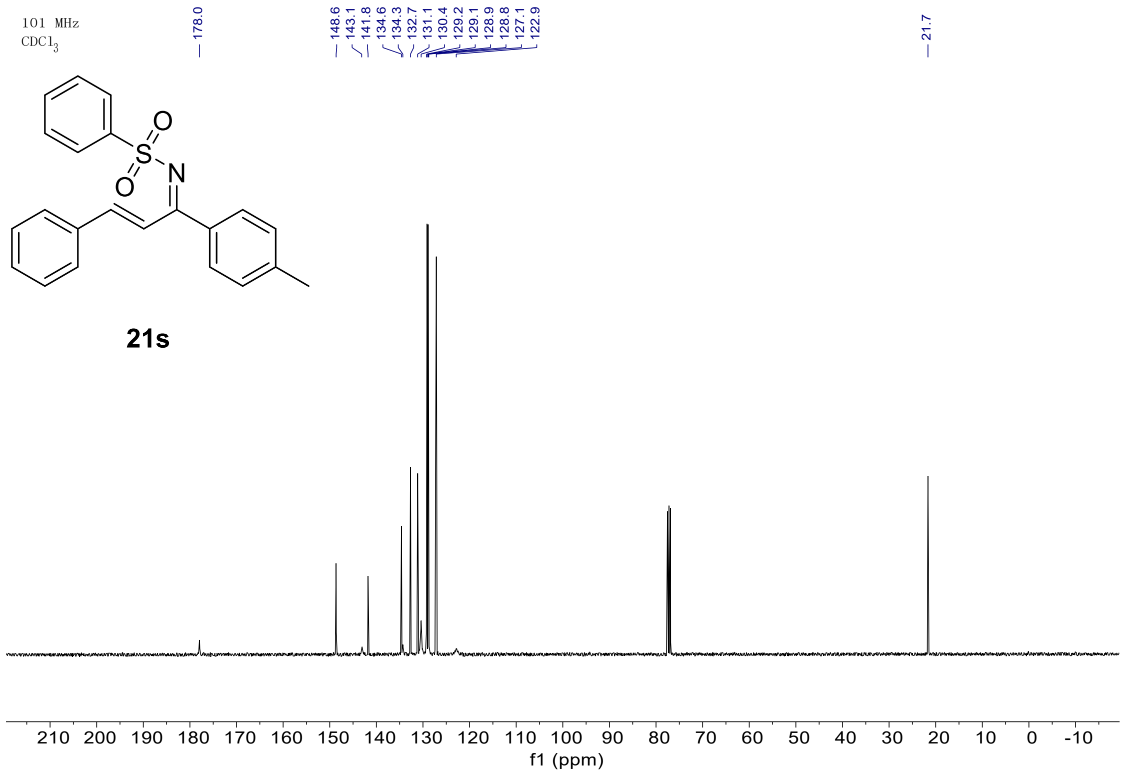

600 MHz
CDCl3
8.14
8.06
7.67
7.62
7.59
7.58
7.57
7.55
7.54
7.53
7.47
7.46
7.09
7.06
O
S
N
O
O
S
O
N
18s
5.20
20.08
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

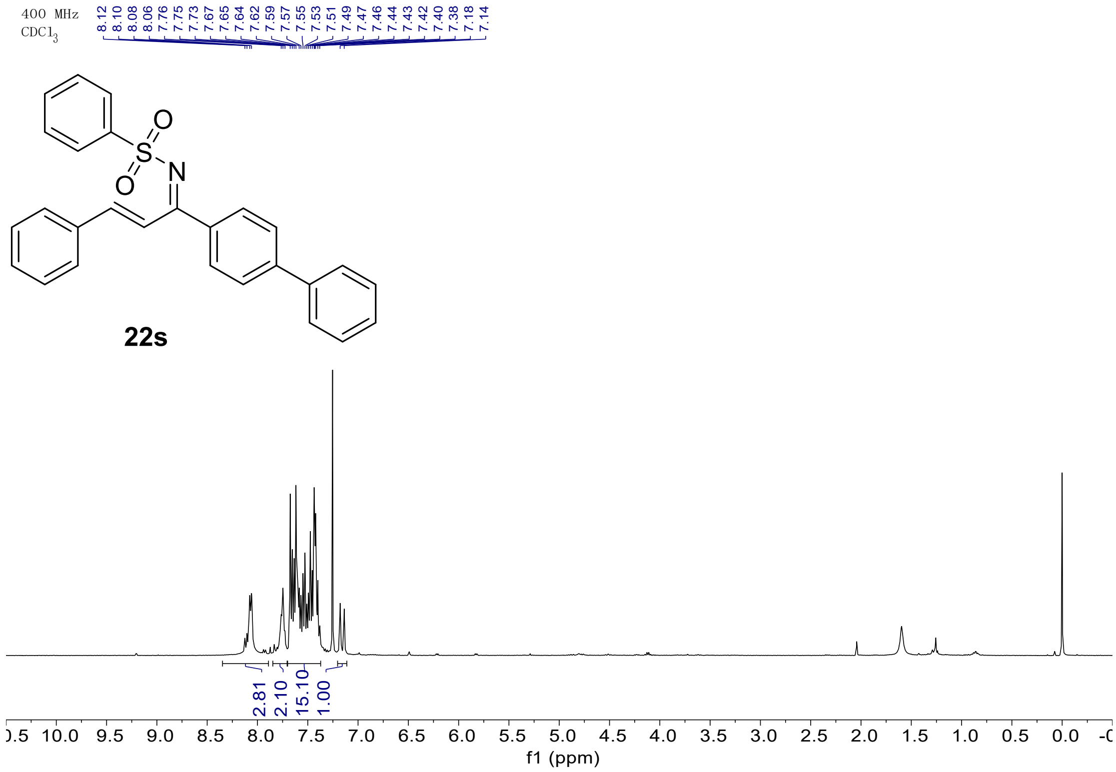

101 MHz
CDCl3
177.5
147.3
141.4
136.9
132.8
132.3
130.2
129.3
128.9
128.5
127.2
123.8
O
S
N
O
O
S
O
N
18s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

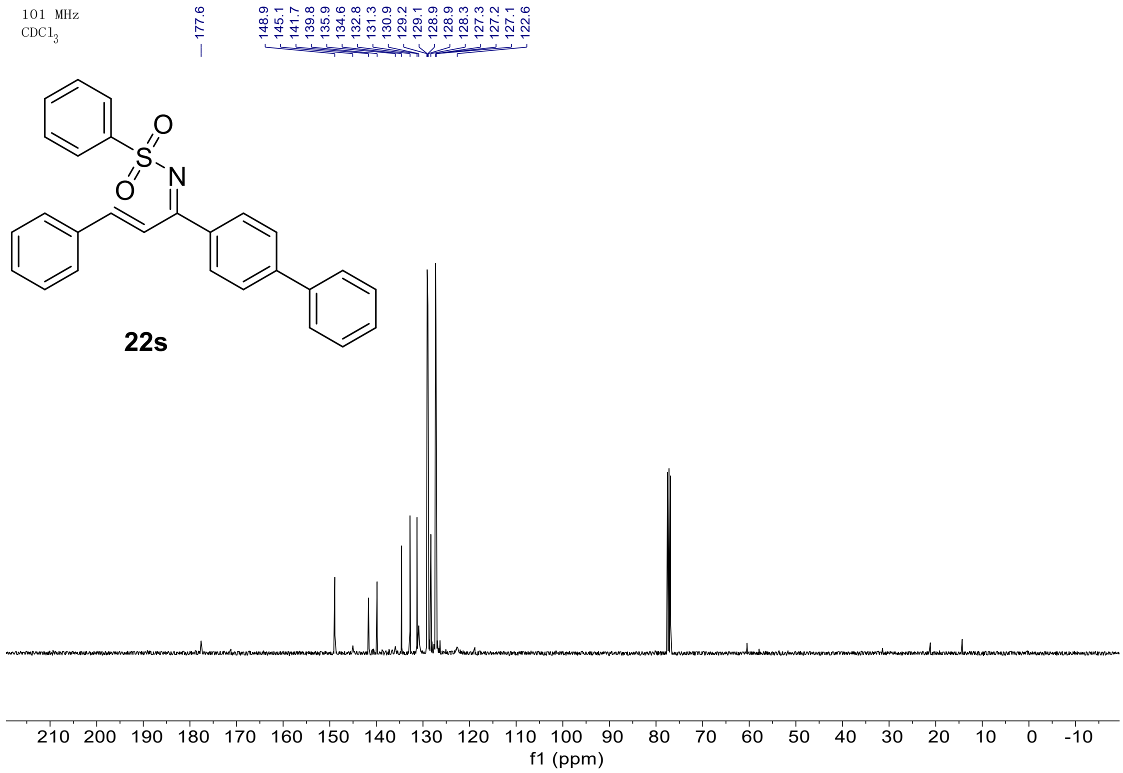

8.02
8.01
7.56
7.54
7.52
7.50
7.48
7.46
7.39
7.37
7.35
6.46
6.44
6.42
6.41
2.04
2.02
19s
2.13
7.02
2.11
1.00
3.07
f1 (ppm)

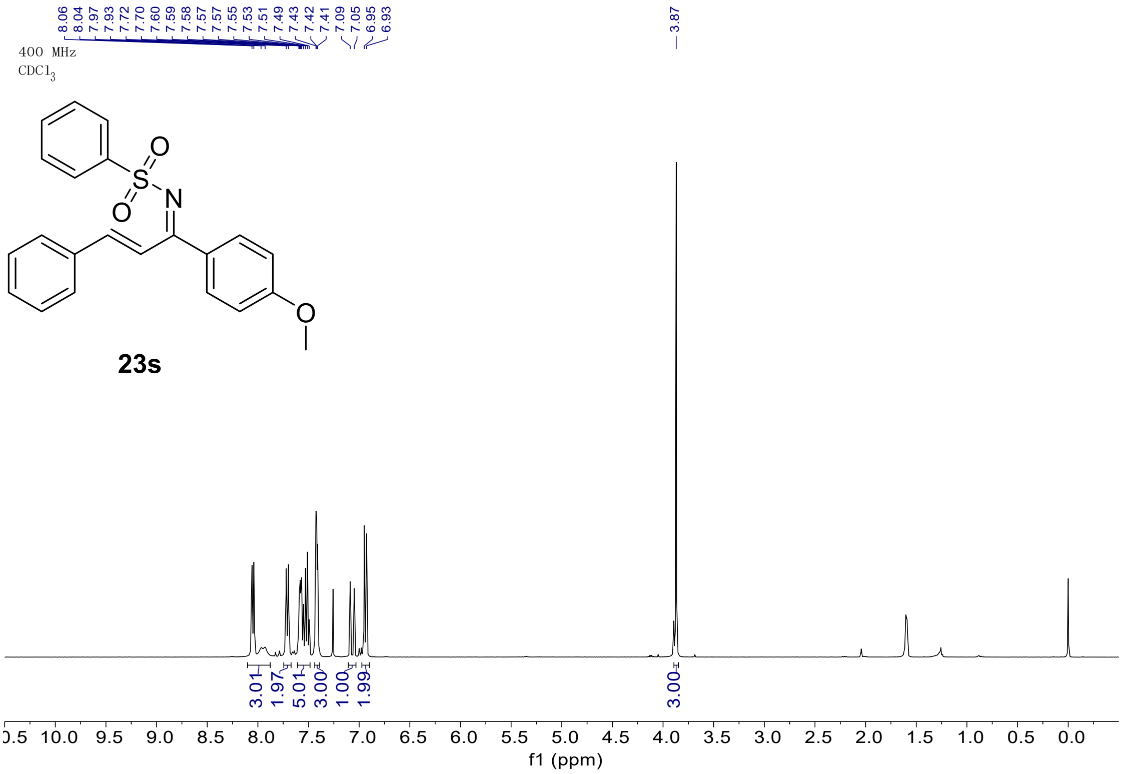

178.2
150.6
141.7
137.4
132.8
132.1
130.3
128.9
128.4
127.2
125.1
19.7
19s
f1 (ppm)

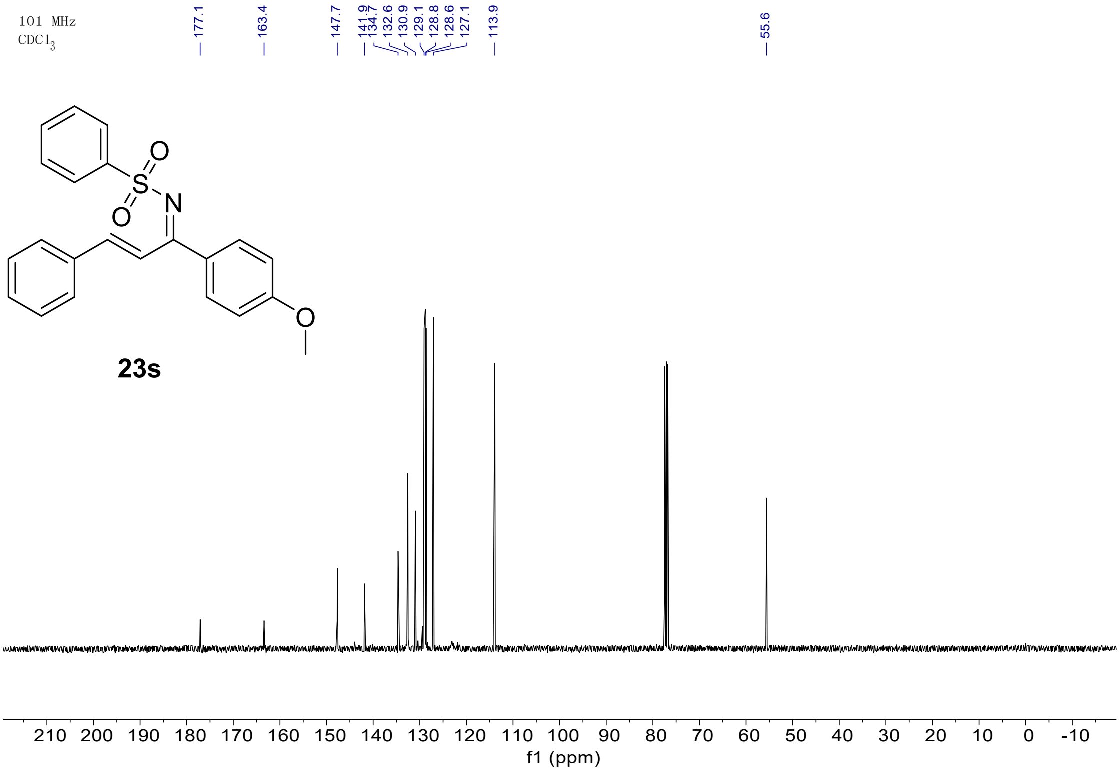

400 MHz
CDCl3
8.05
8.03
7.58
7.56
7.54
7.52
7.50
7.48
7.46
7.39
7.38
7.37
7.23
7.21
7.09
7.05
2.39
21s
2.79
7.00
3.01
2.01
1.00
3.00
f1 (ppm)


101 MHz
CDCl3
178.0
148.6
143.1
141.8
134.6
134.3
132.7
131.1
130.4
129.2
129.1
128.9
128.8
127.1
122.9
21.7
21s
f1 (ppm)

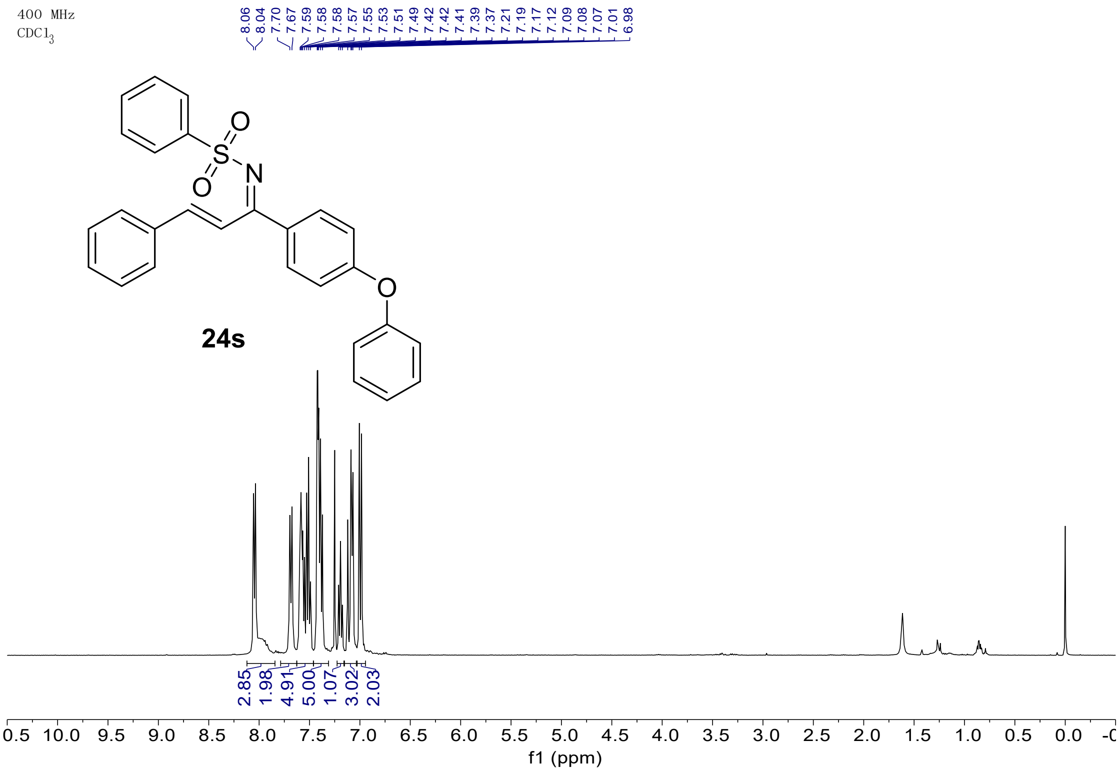

400 MHz
CDCl3
8.12 8.10 8.08 8.06 7.76 7.75 7.73 7.67 7.65 7.64 7.62 7.59 7.57 7.55 7.53 7.51 7.49 7.47 7.46 7.44 7.43 7.42 7.40 7.38 7.18 7.14
O
S
N
O
22s
2.81
2.10
15.10
1.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


101 MHz
CDCl3
177.6
148.9 145.1 141.7 139.8 135.9 134.6 132.8 131.3 130.9 129.2 129.1 128.9 128.9 128.3 127.3 127.2 127.1 122.6
O
S
N
O
22s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
$CDCl_3$
8.06 8.04 7.97 7.93 7.72 7.70 7.60 7.59 7.58 7.57 7.57 7.55 7.53 7.51 7.49 7.43 7.42 7.41 7.09 7.05 6.95 6.93
3.87
23s
3.01 1.97 5.01 3.00 1.00 1.99
3.00
f1 (ppm)

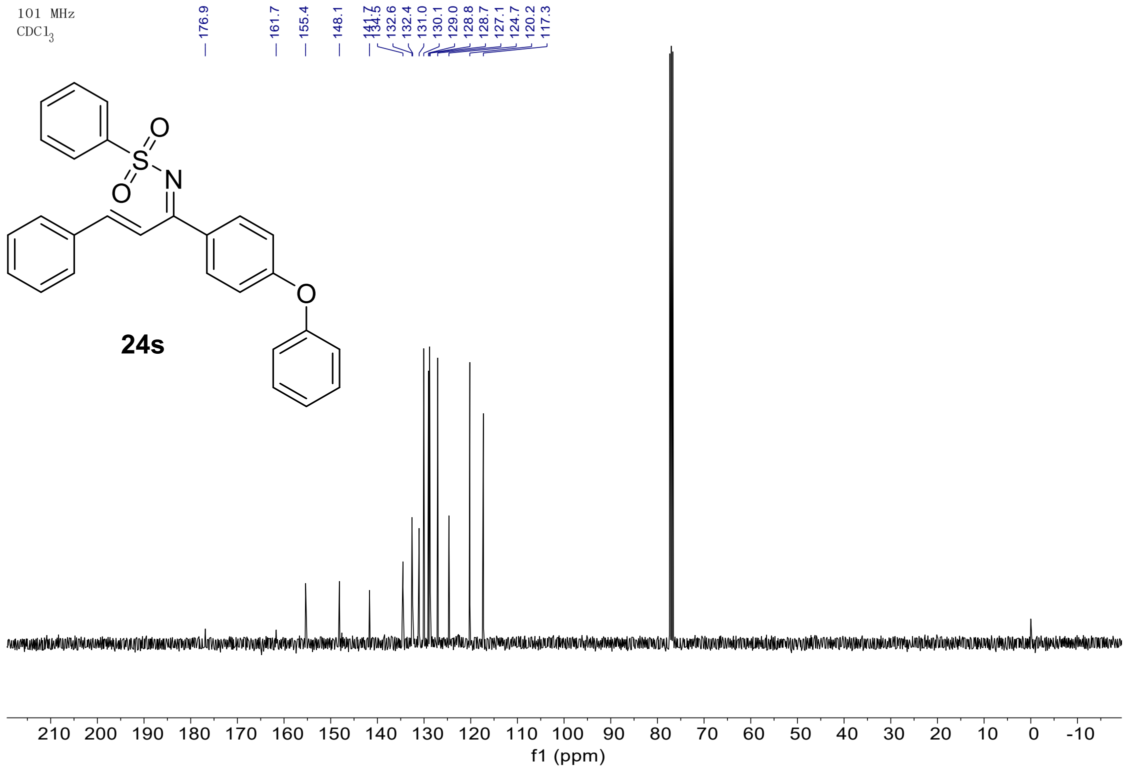

101 MHz
$CDCl_3$
177.1
163.4
147.7
141.9 134.7 132.6 130.9 129.1 128.8 128.6 127.1
113.9
55.6
23s
f1 (ppm)

400 MHz
CDCl3

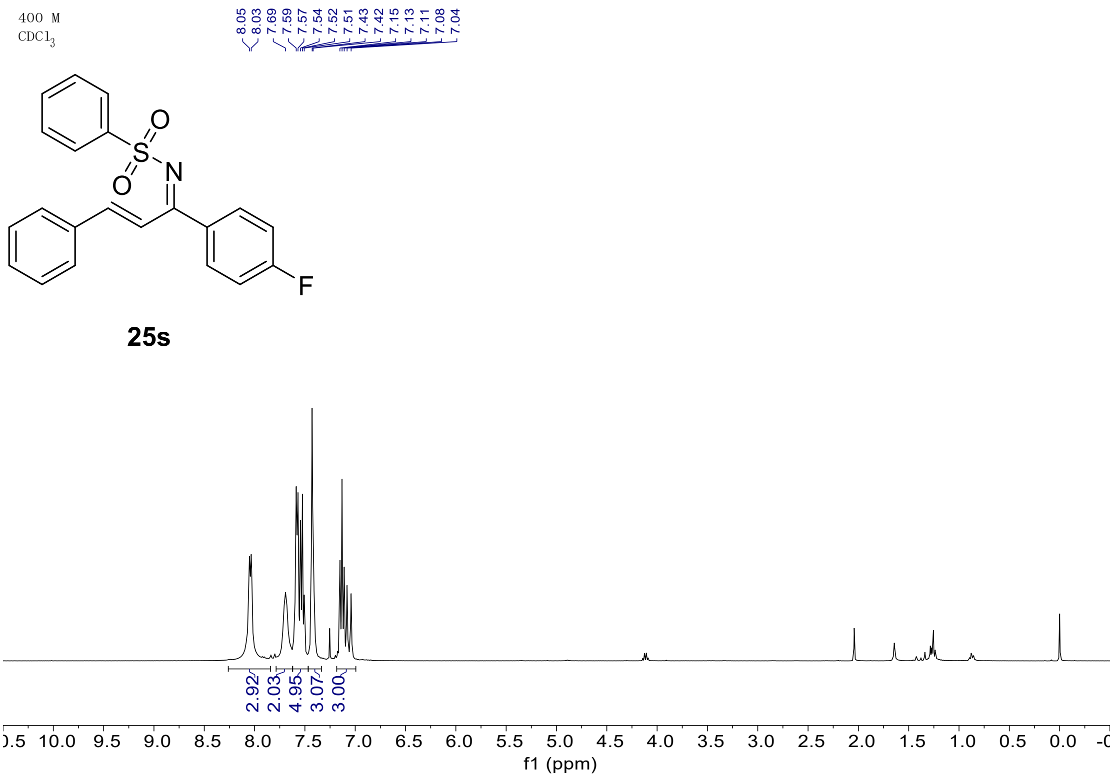


24s

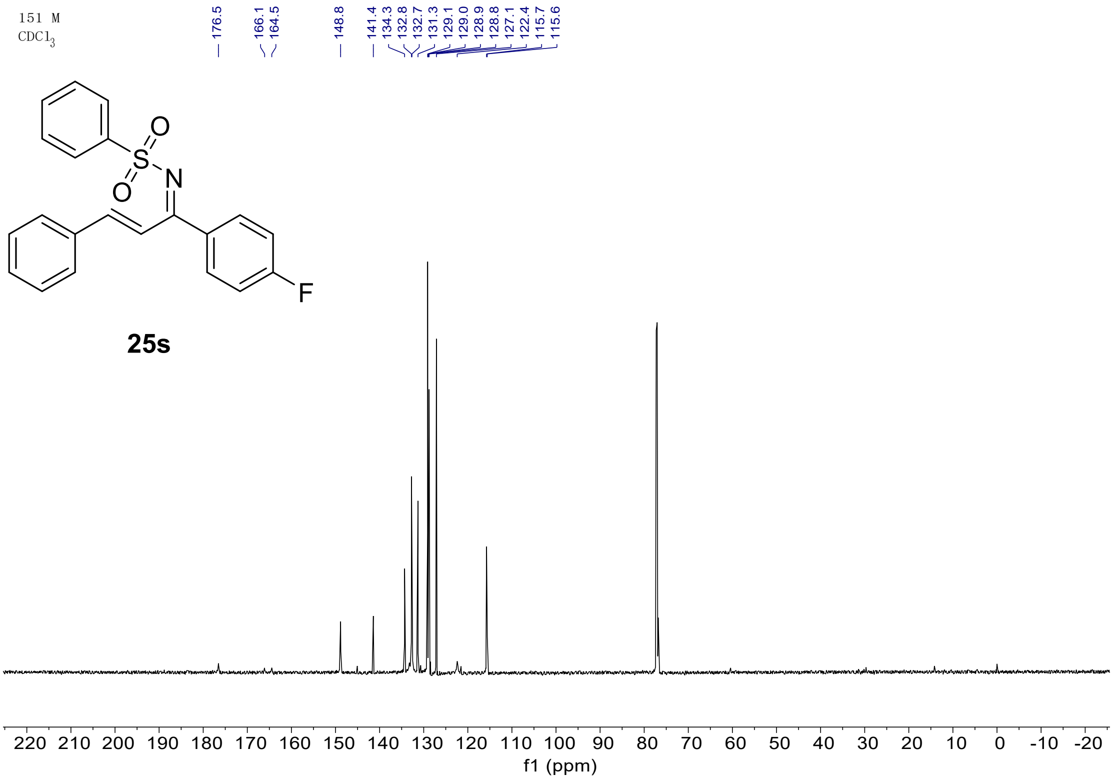
101 MHz
CDCl3



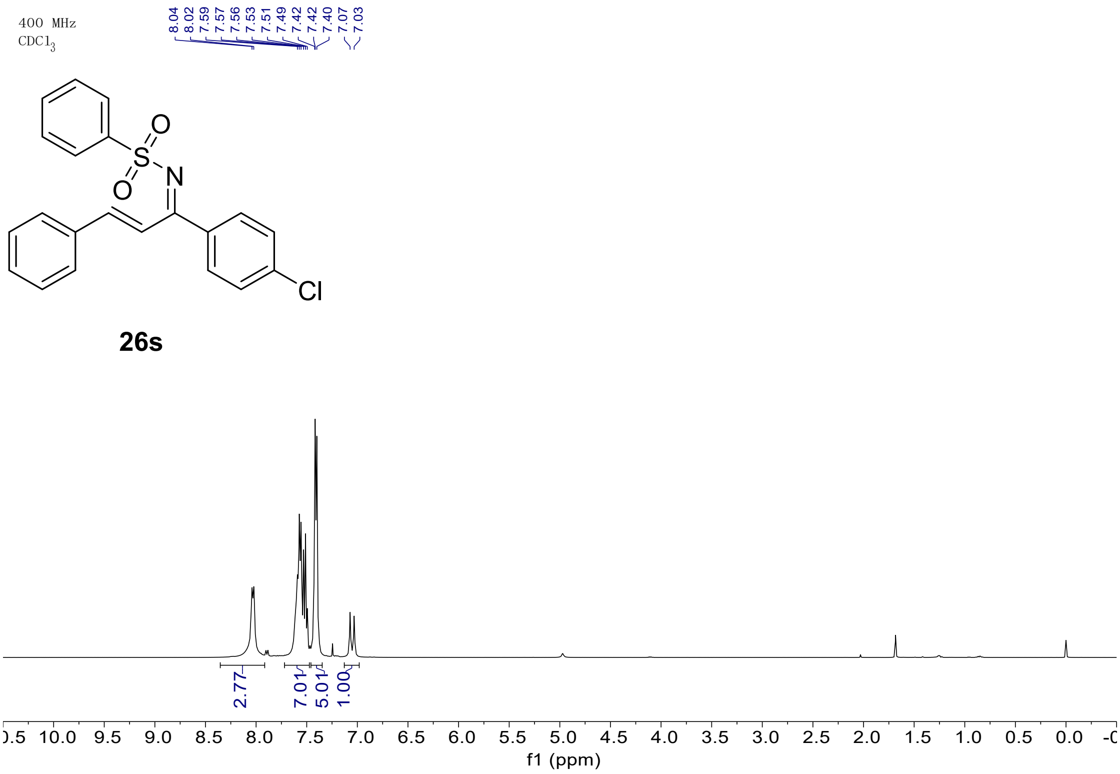
24s


400 M
$CDCl_3$
8.05
8.03
7.69
7.59
7.57
7.54
7.52
7.51
7.43
7.42
7.15
7.13
7.11
7.08
7.04
O
S
O
N
F
2.92
2.03
4.95
3.07
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

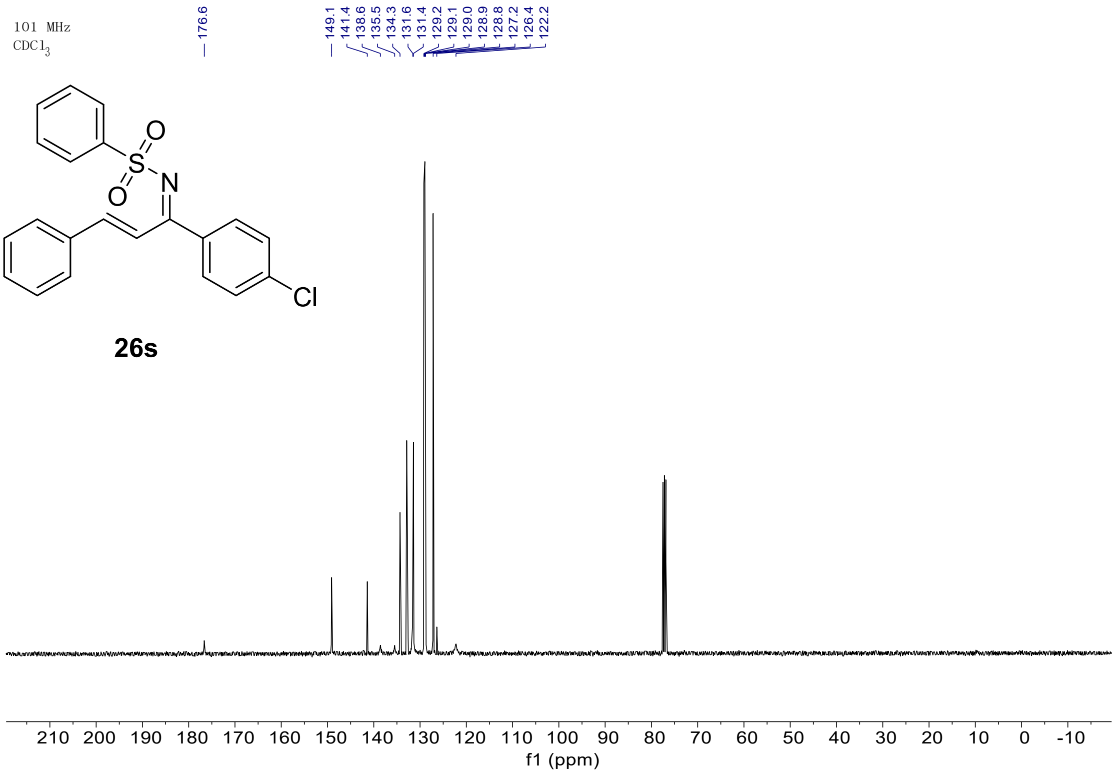
25s


151 M
$CDCl_3$
176.5
166.1
164.5
148.8
141.4
134.3
132.8
132.7
131.3
129.1
129.0
128.9
128.8
127.1
122.4
115.7
115.6
O
S
O
N
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

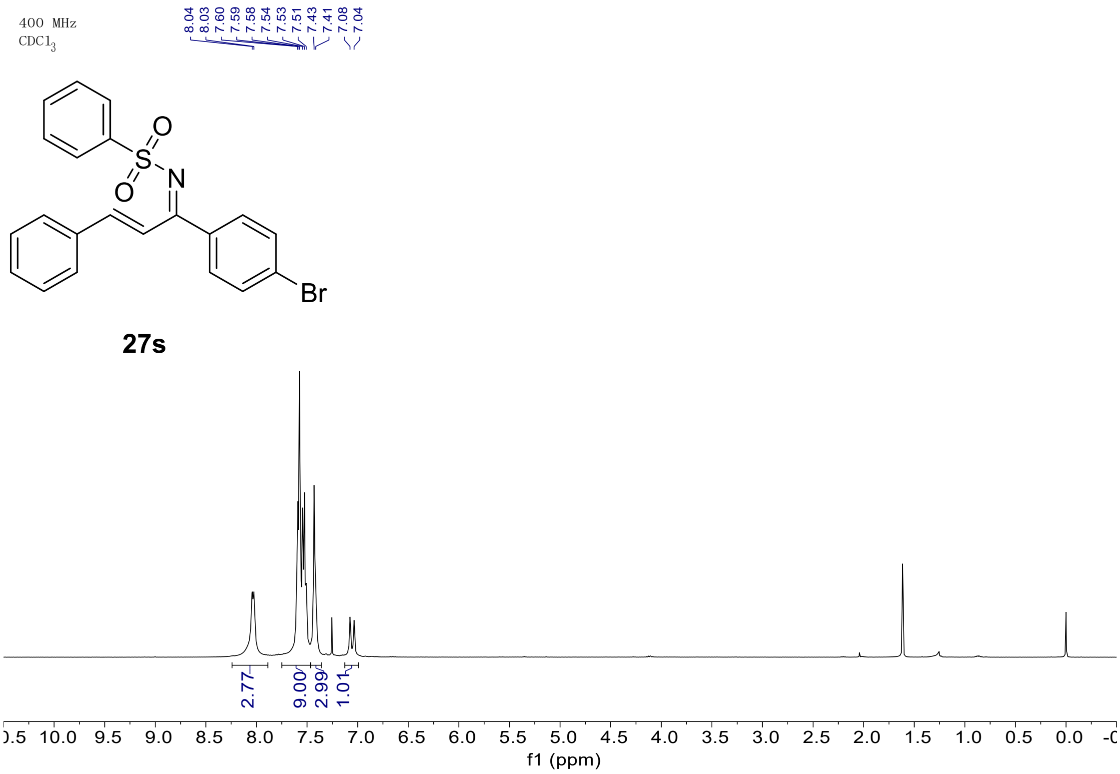
25s

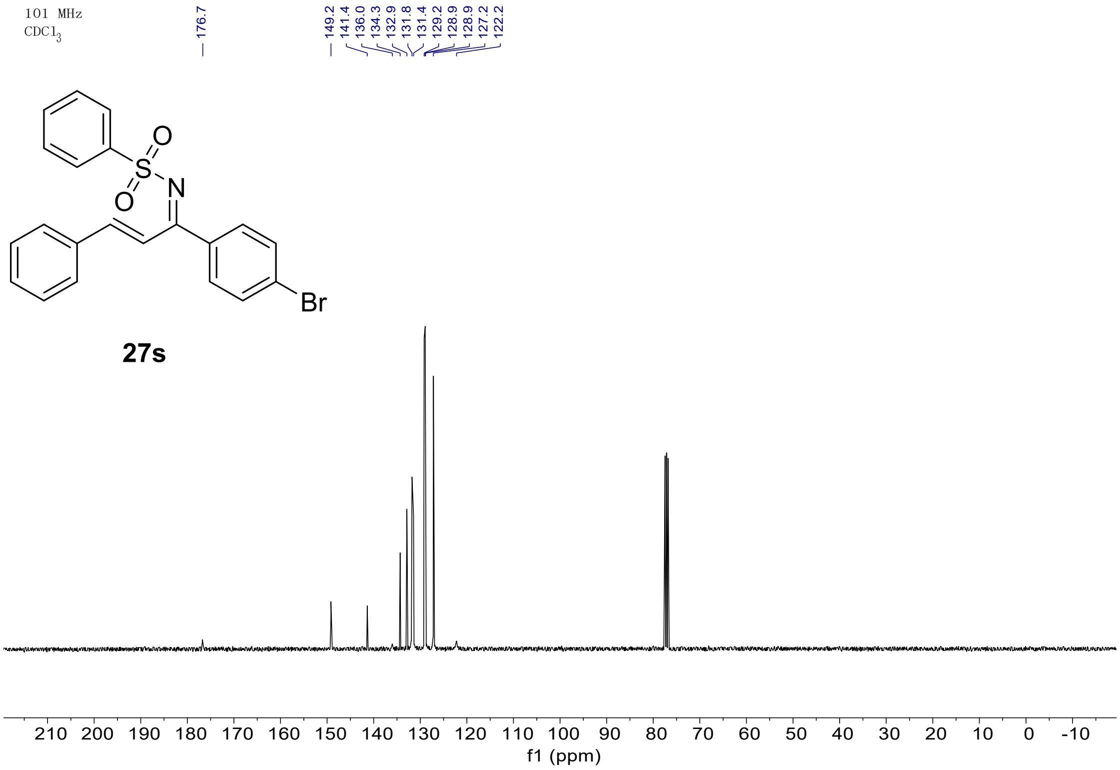

400 MHz
CDCl3
8.04
8.02
7.59
7.57
7.56
7.53
7.51
7.49
7.42
7.42
7.40
7.07
7.03
O
S
O
N
Cl
2.77
7.01
5.01
1.00
f1 (ppm)

26s


101 MHz
CDCl3
176.6
149.1
141.4
138.6
135.5
134.3
131.6
131.4
129.2
129.1
129.0
128.9
128.8
127.2
126.4
122.2
O
S
O
N
Cl
f1 (ppm)

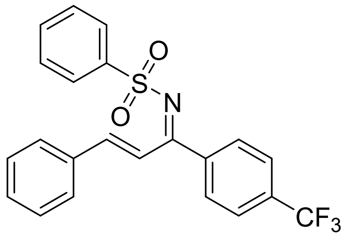
26s


400 MHz
$CDCl_3$
8.04
8.03
7.60
7.59
7.58
7.54
7.53
7.51
7.43
7.41
7.08
7.04
O
S
N
O
Br
27s
2.77
9.00
2.99
1.01
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

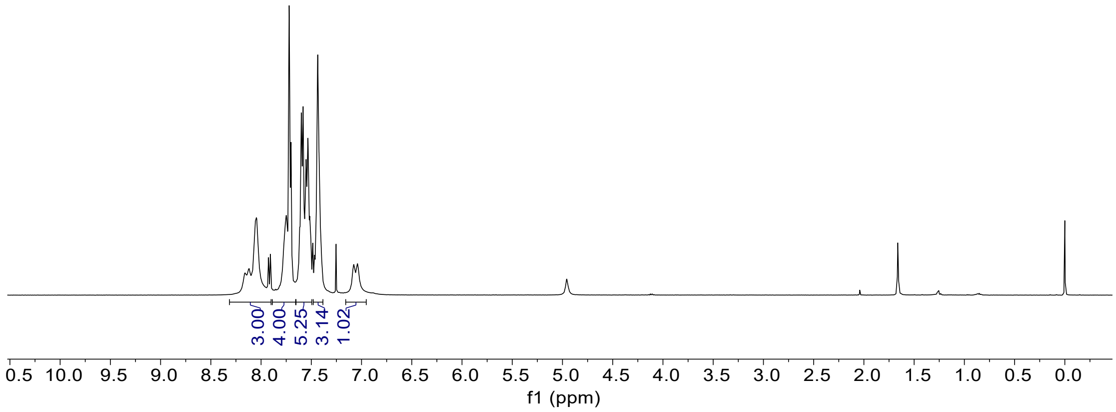

101 MHz
$CDCl_3$
176.7
149.2
141.4
136.0
134.3
132.9
131.8
131.4
129.2
128.9
128.9
127.2
122.2
O
S
N
O
Br
27s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

400 M
CDCl$_3$

8.16, 8.12, 8.05, 7.93, 7.90, 7.75, 7.72, 7.70, 7.62, 7.60, 7.58, 7.55, 7.53, 7.52, 7.51, 7.49, 7.47, 7.44, 7.42, 7.08, 7.04

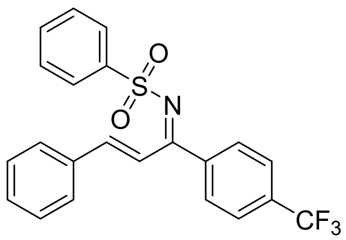


28s

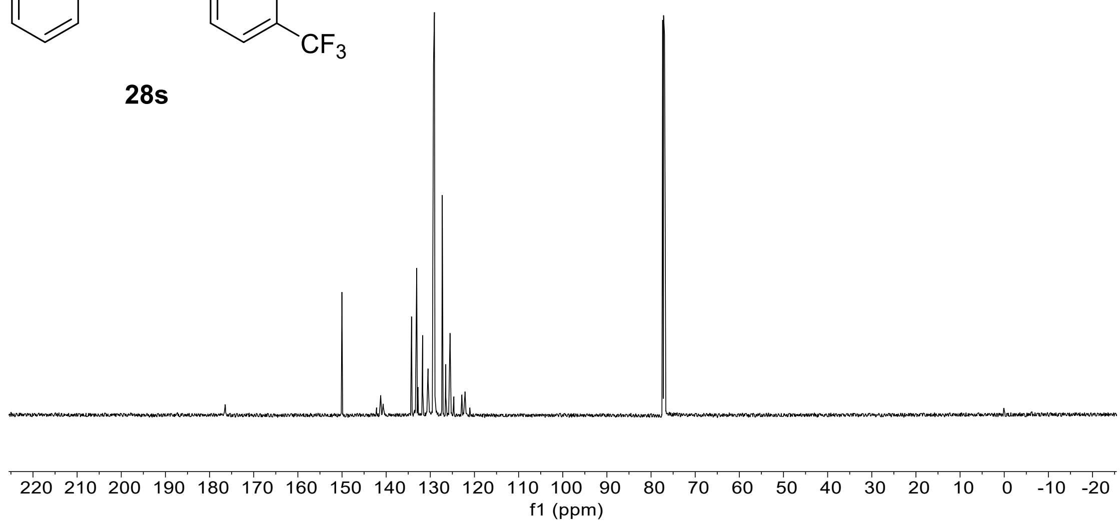


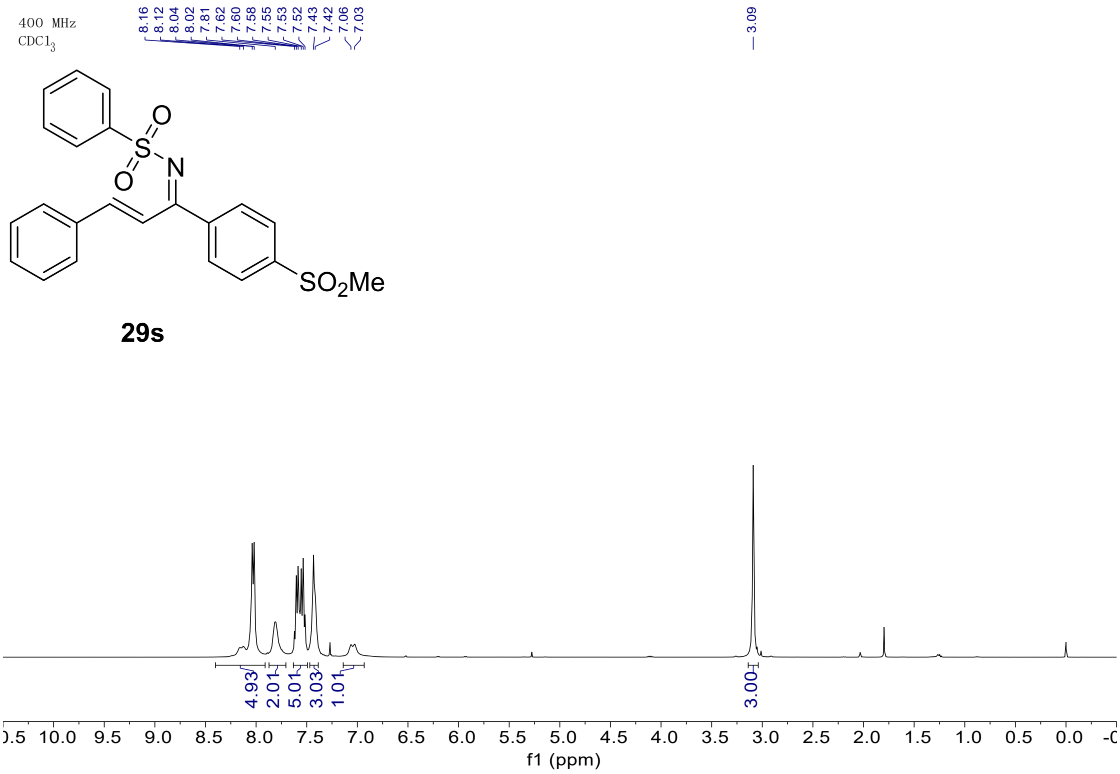
151 M
CDCl$_3$

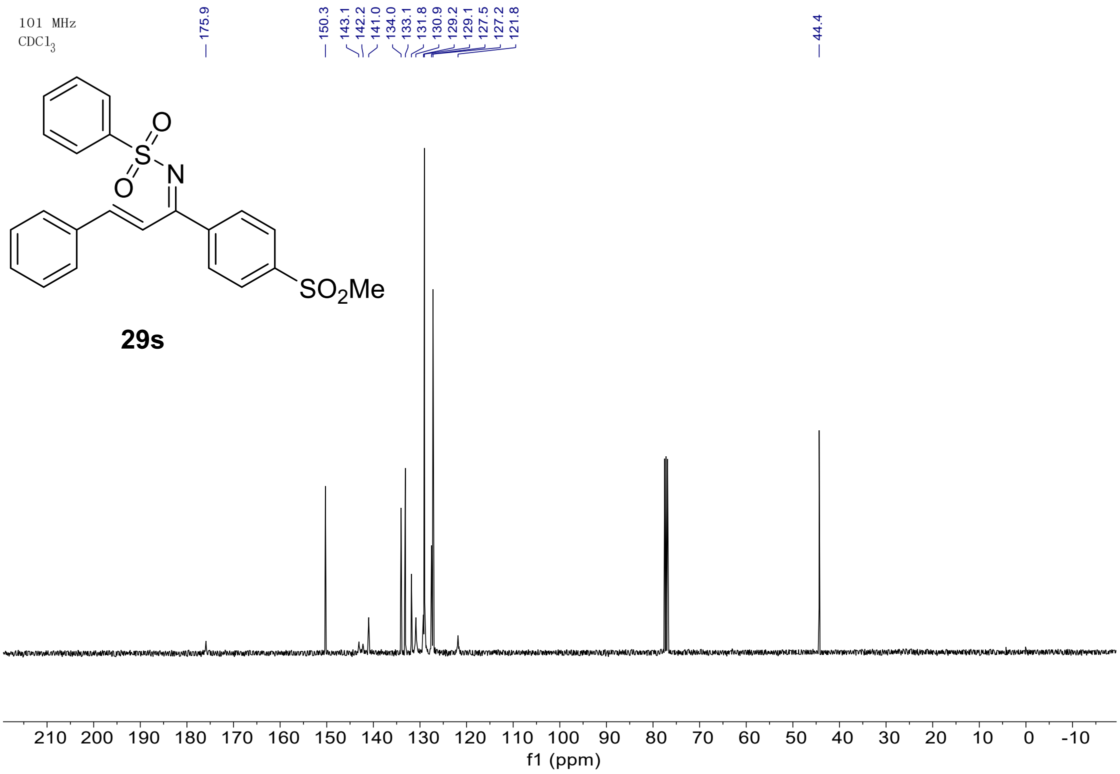
176.4, 150.0, 142.2, 141.2, 140.6, 134.3, 133.1, 132.8, 131.7, 130.5, 129.3, 129.2, 129.1, 127.3, 126.5, 125.5, 124.7, 122.8, 122.1, 121.0



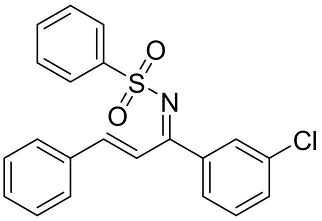
28s



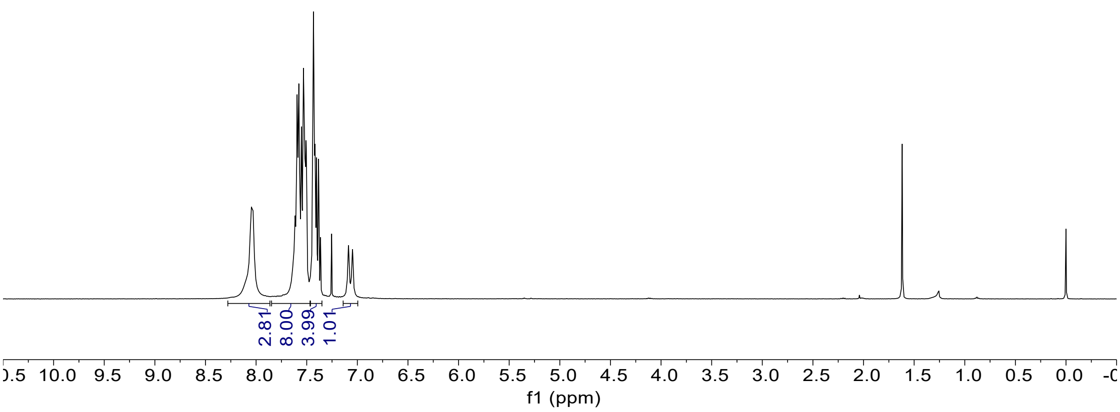

400 MHz
CDCl3
8.16 8.12 8.04 8.02 7.81 7.62 7.60 7.58 7.55 7.53 7.52 7.43 7.42 7.06 7.03
3.09
SO2Me
29s
4.93 2.01 5.01 3.03 1.01
3.00
f1 (ppm)


101 MHz
CDCl3
175.9
150.3 143.1 142.2 141.0 134.0 133.1 131.8 130.9 129.2 129.1 127.5 127.2 121.8
44.4
SO2Me
29s
f1 (ppm)

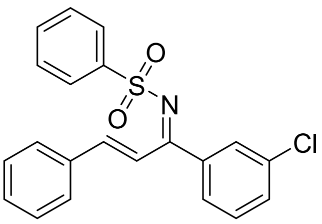
400 MHz
$CDCl_3$



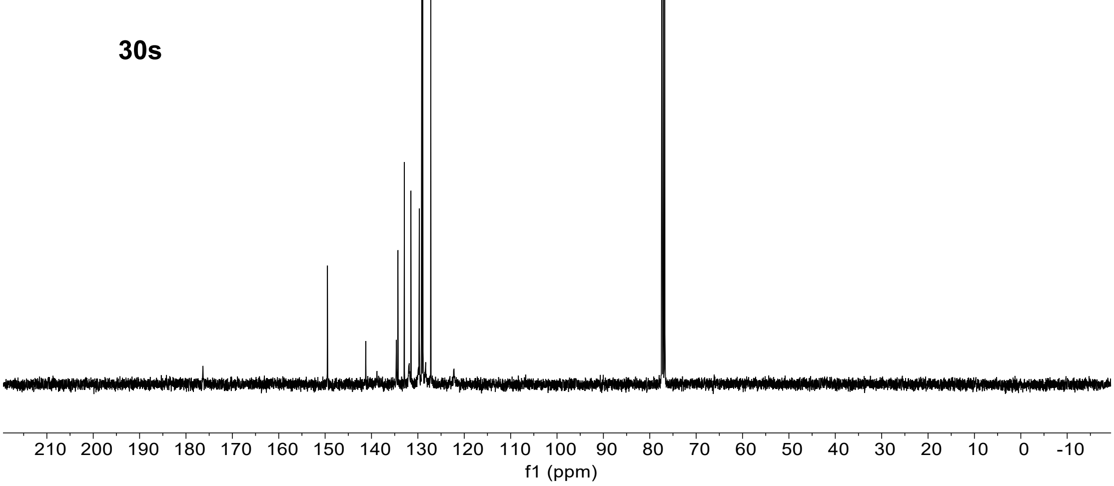
30s

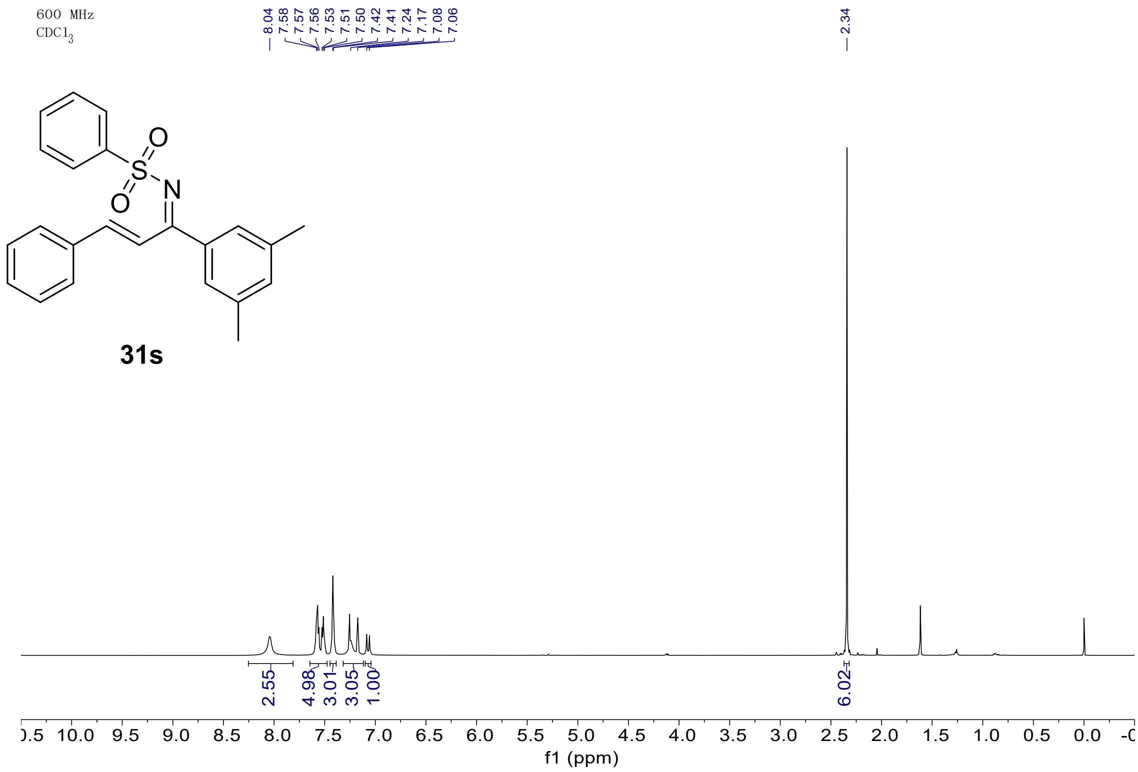


101 MHz
$CDCl_3$

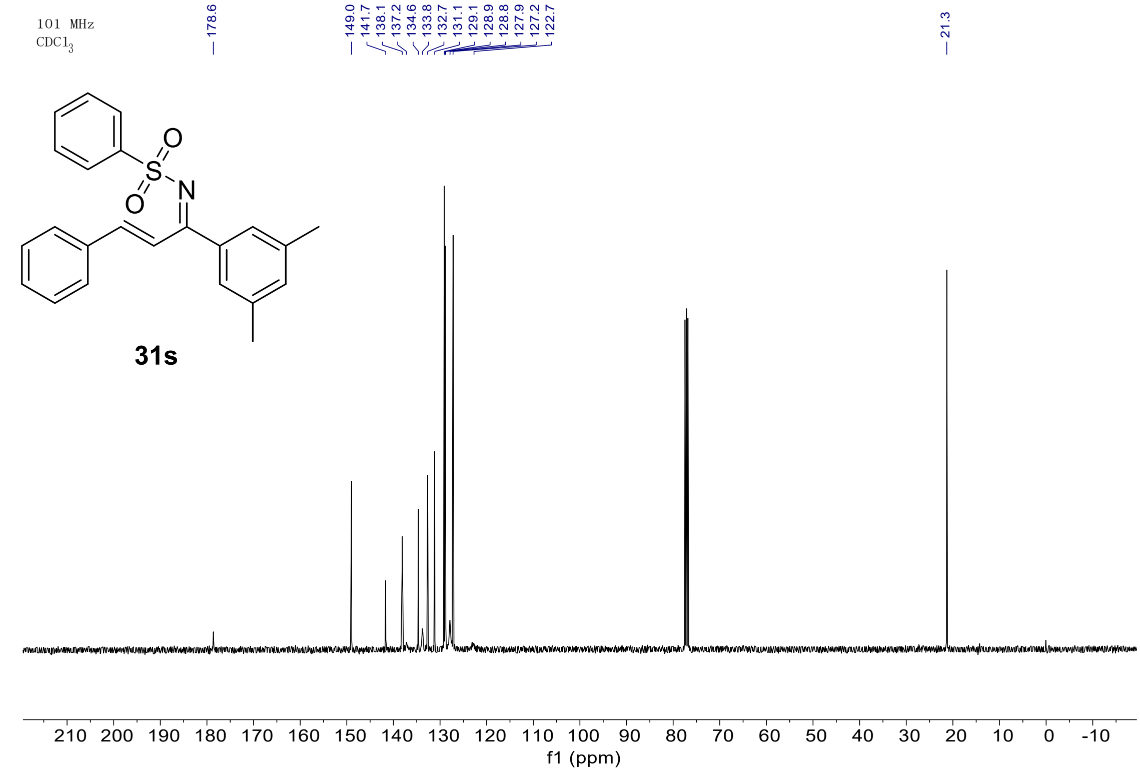


30s

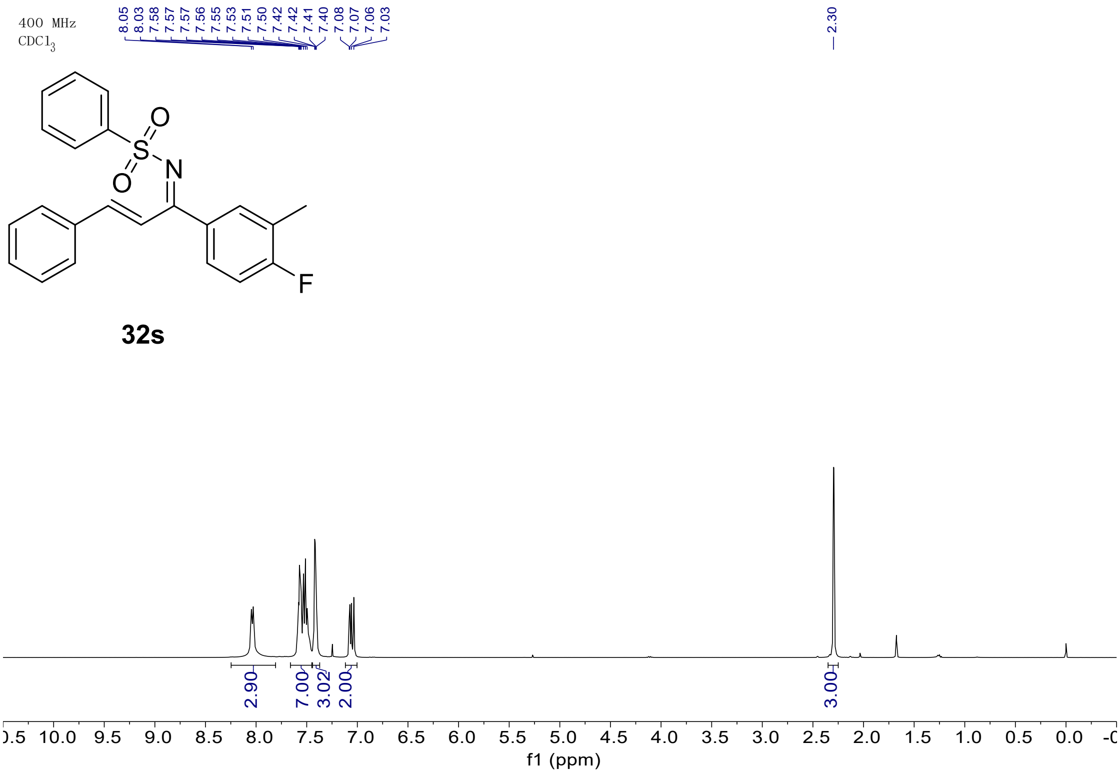


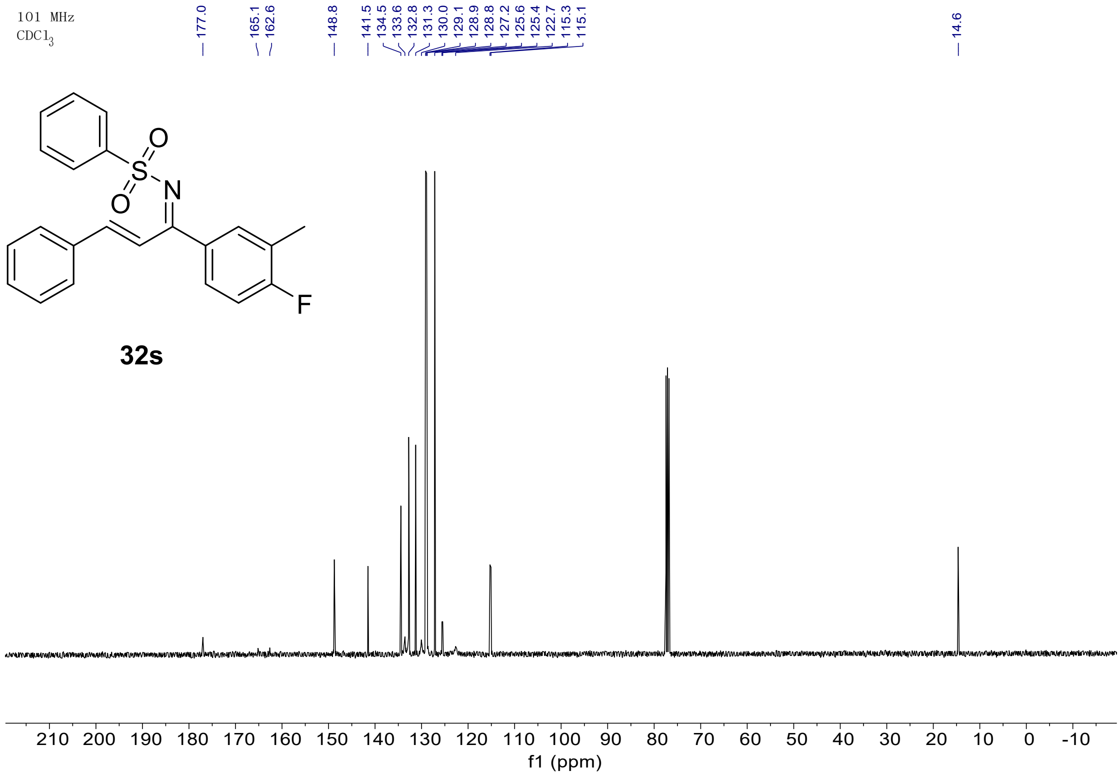


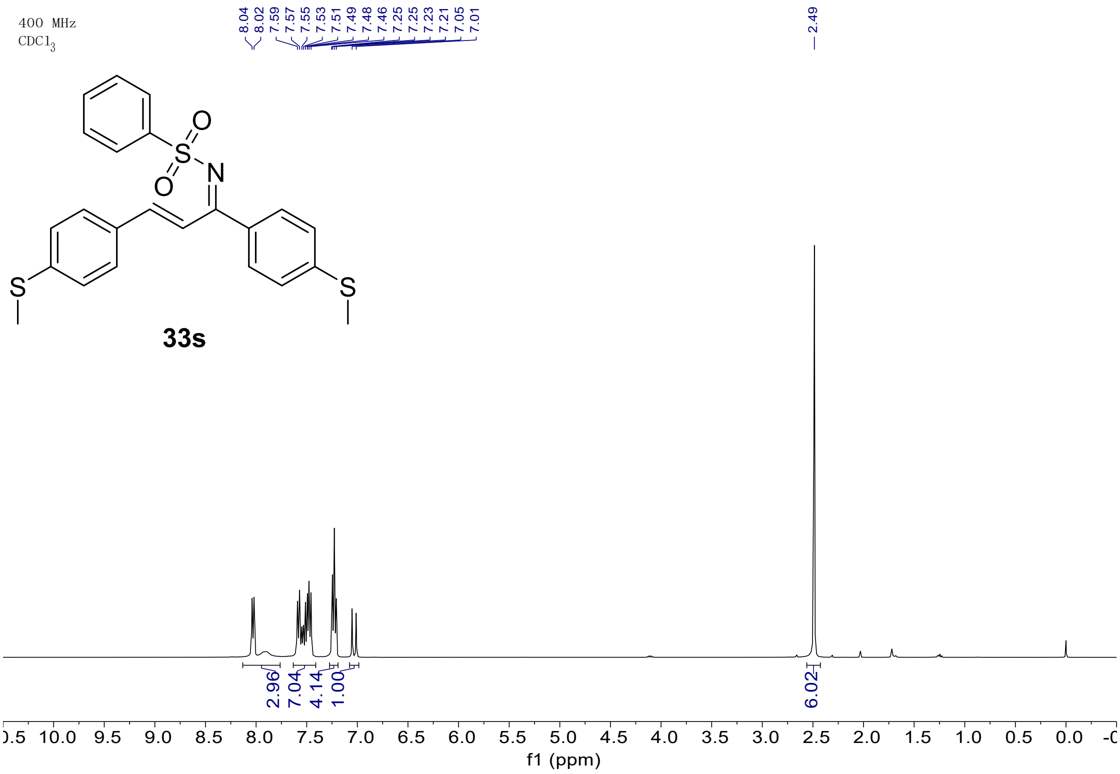
600 MHz
CDCl3
8.04
7.58
7.57
7.56
7.53
7.51
7.50
7.42
7.41
7.24
7.17
7.08
7.06
2.34
31s
2.55
4.98
3.01
3.05
1.00
6.02
f1 (ppm)



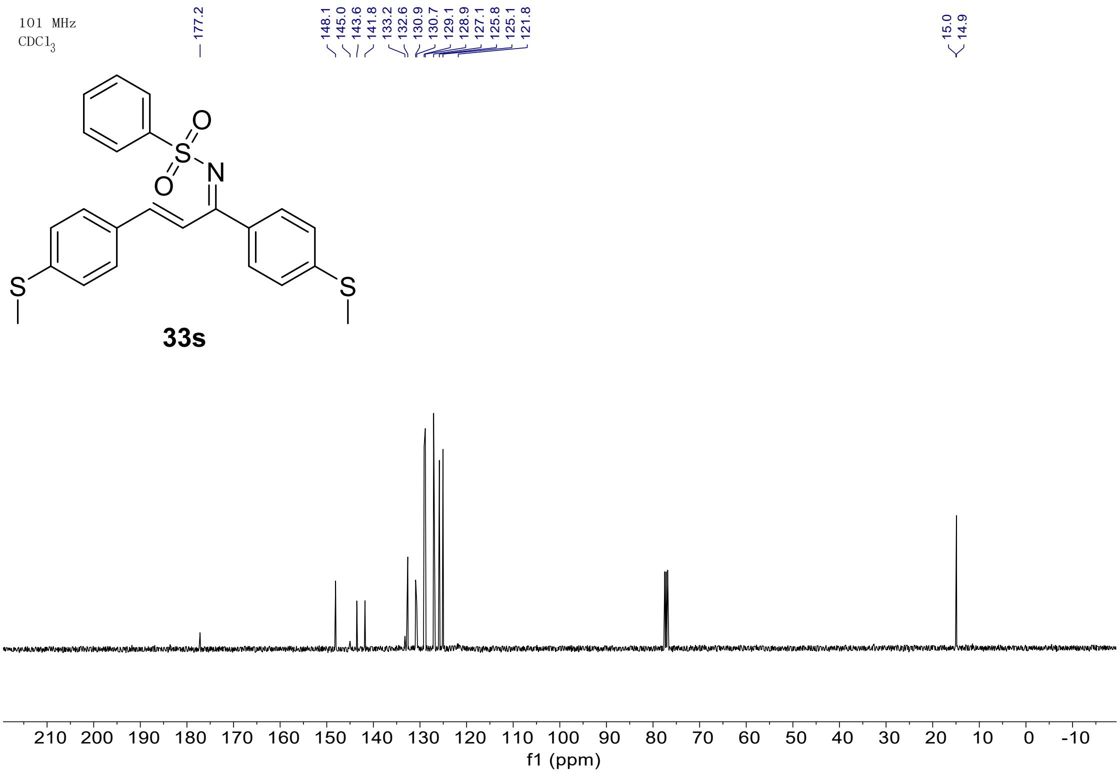
101 MHz
CDCl3
178.6
149.0
141.7
138.1
137.2
134.6
133.8
132.7
131.1
129.1
128.9
128.8
127.9
127.2
122.7
21.3
31s
f1 (ppm)


400 MHz
CDCl3
8.05
8.03
7.58
7.57
7.57
7.56
7.55
7.53
7.51
7.50
7.42
7.42
7.41
7.40
7.08
7.07
7.06
7.03
2.30
O
S
N
O
F
32s
2.90
7.00
3.02
2.00
3.00
f1 (ppm)

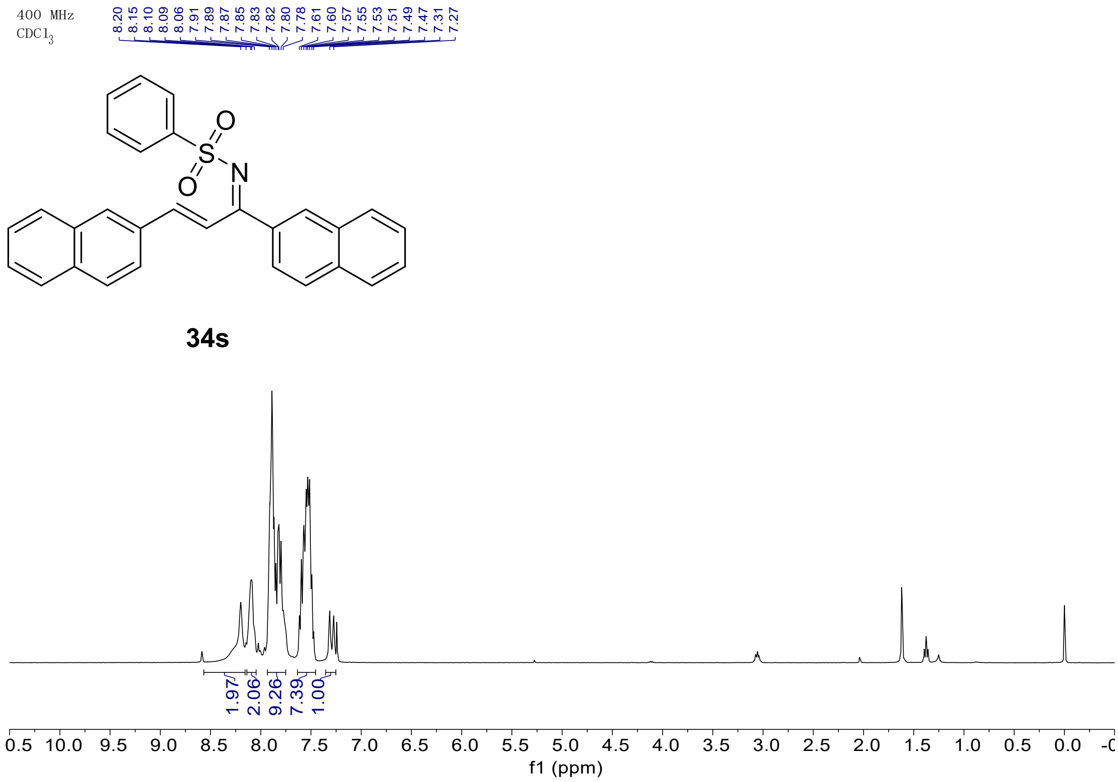

101 MHz
CDCl3
177.0
165.1
162.6
148.8
141.5
134.5
133.6
132.8
131.3
130.0
129.1
128.9
128.8
127.2
125.6
125.4
122.7
115.3
115.1
14.6
O
S
N
O
F
32s
f1 (ppm)

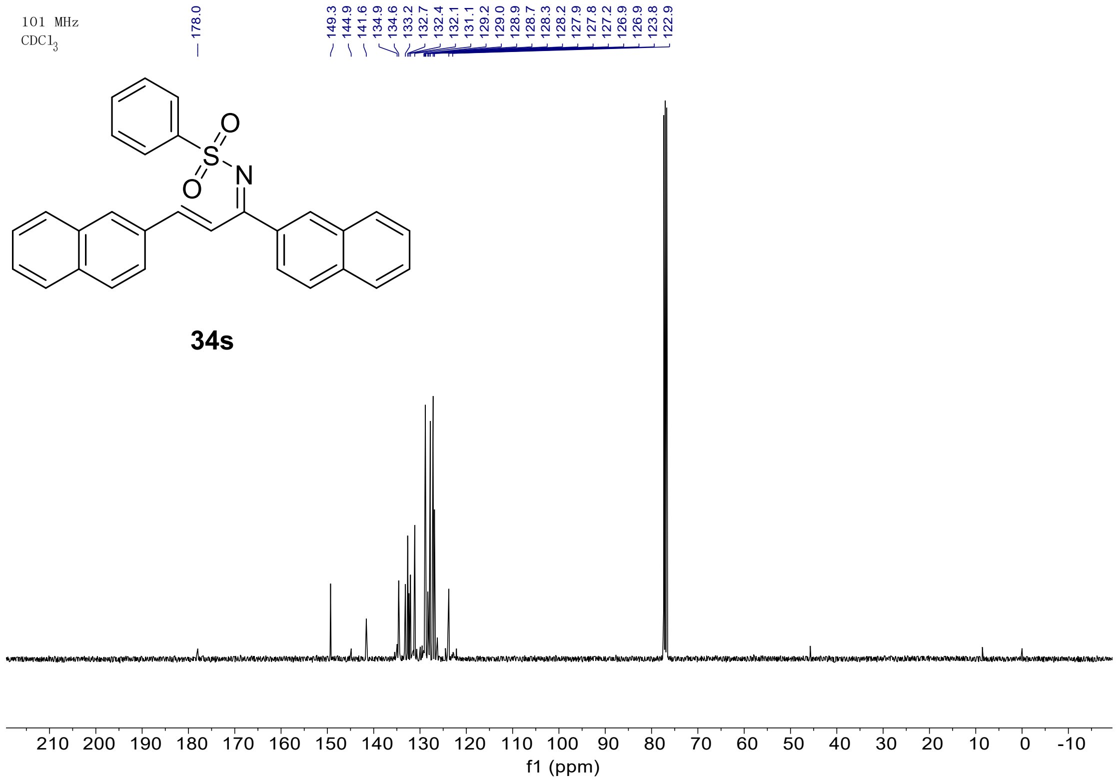

400 MHz
CDCl3
8.04
8.02
7.59
7.57
7.55
7.53
7.51
7.49
7.48
7.46
7.25
7.25
7.23
7.21
7.05
7.01
2.49
2.96
7.04
4.14
1.00
6.02
f1 (ppm)

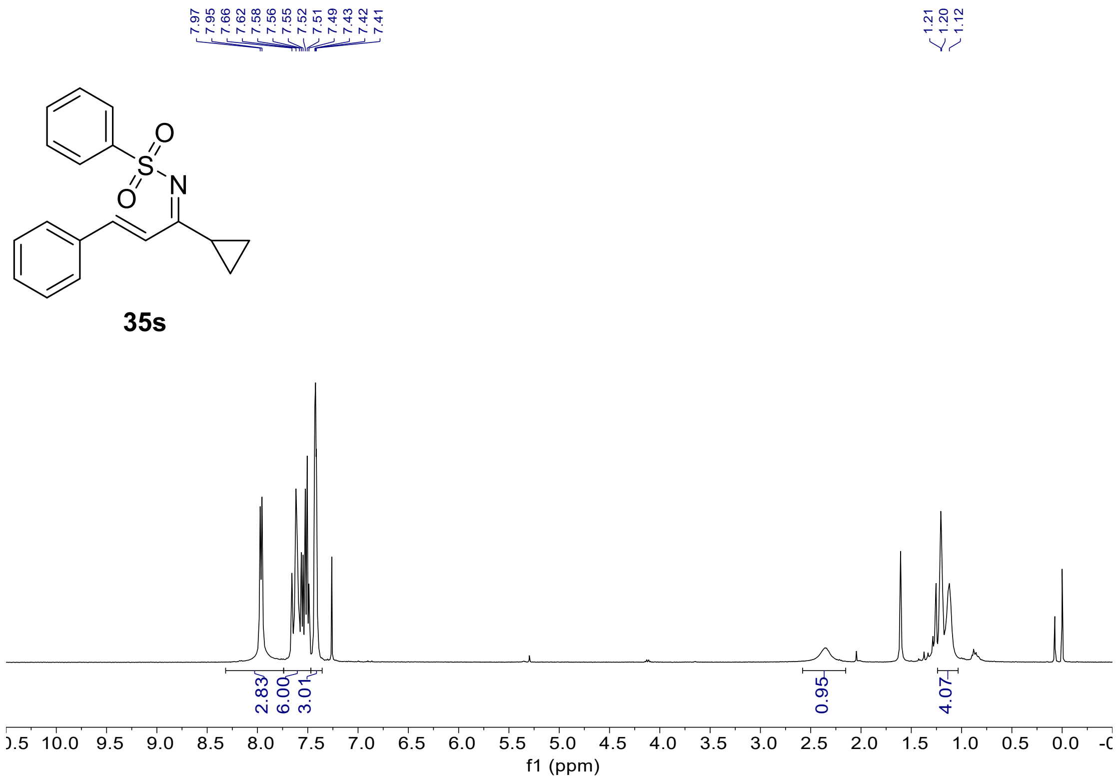
33s

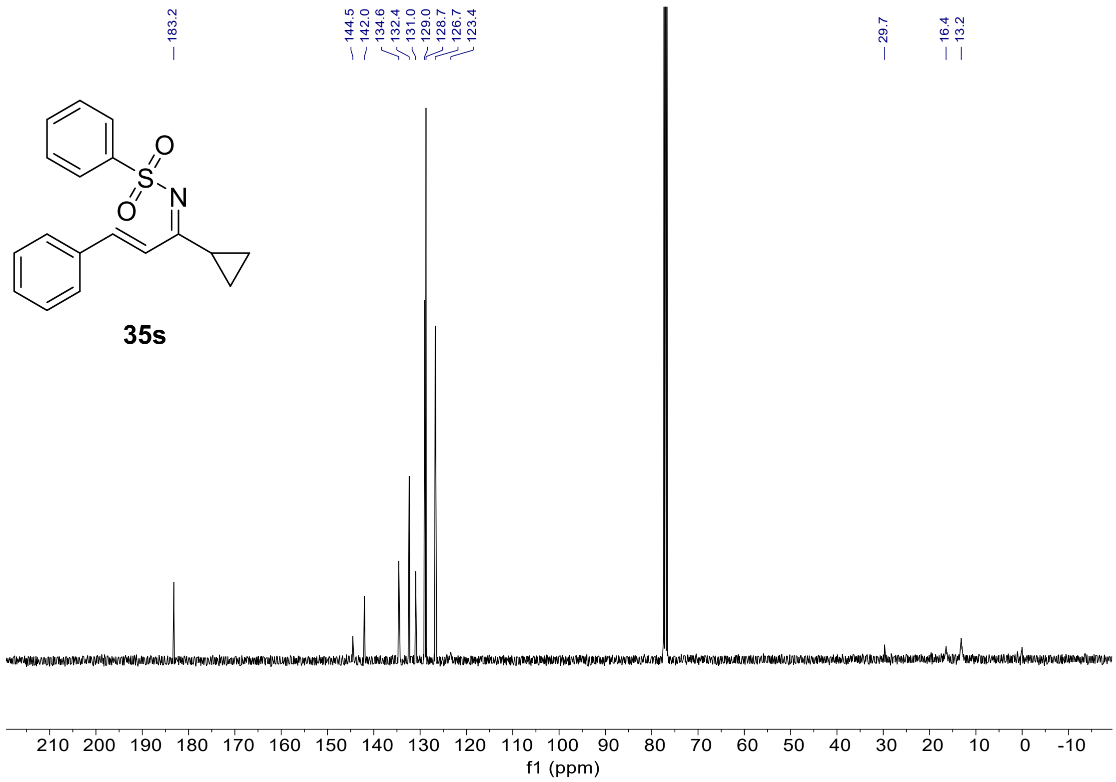

101 MHz
CDCl3
177.2
148.1
145.0
143.6
141.8
133.2
132.6
130.9
130.7
129.1
128.9
127.1
125.8
125.1
121.8
15.0
14.9
f1 (ppm)

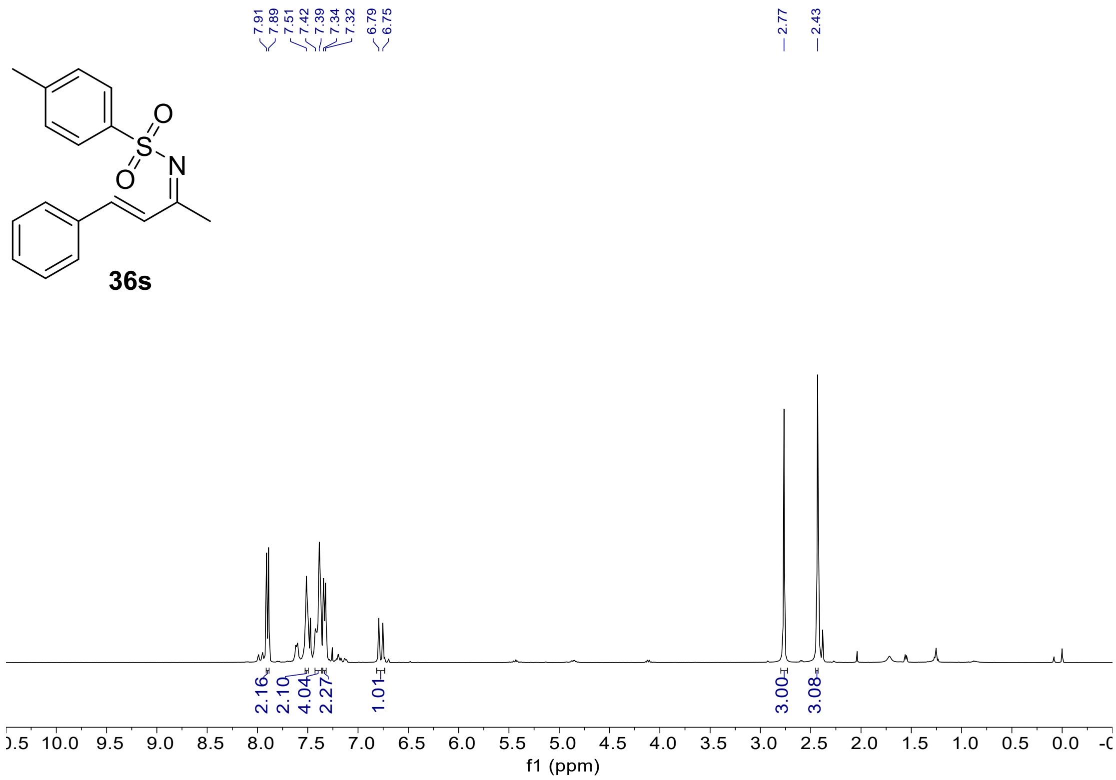
33s

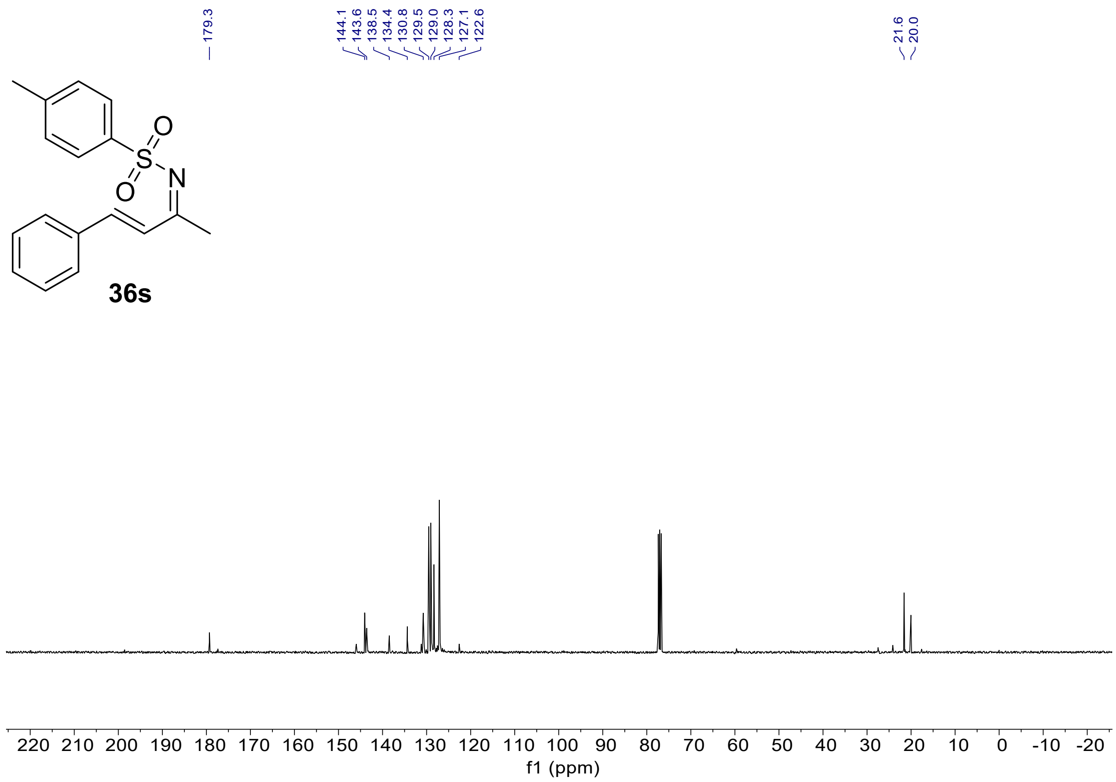

400 MHz
CDCl3
8.20 8.15 8.10 8.09 8.06 7.91 7.89 7.87 7.85 7.83 7.82 7.80 7.78 7.61 7.60 7.57 7.55 7.53 7.51 7.49 7.47 7.31 7.27
O
S
N
O
34s
1.97 2.06 9.26 7.39 1.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

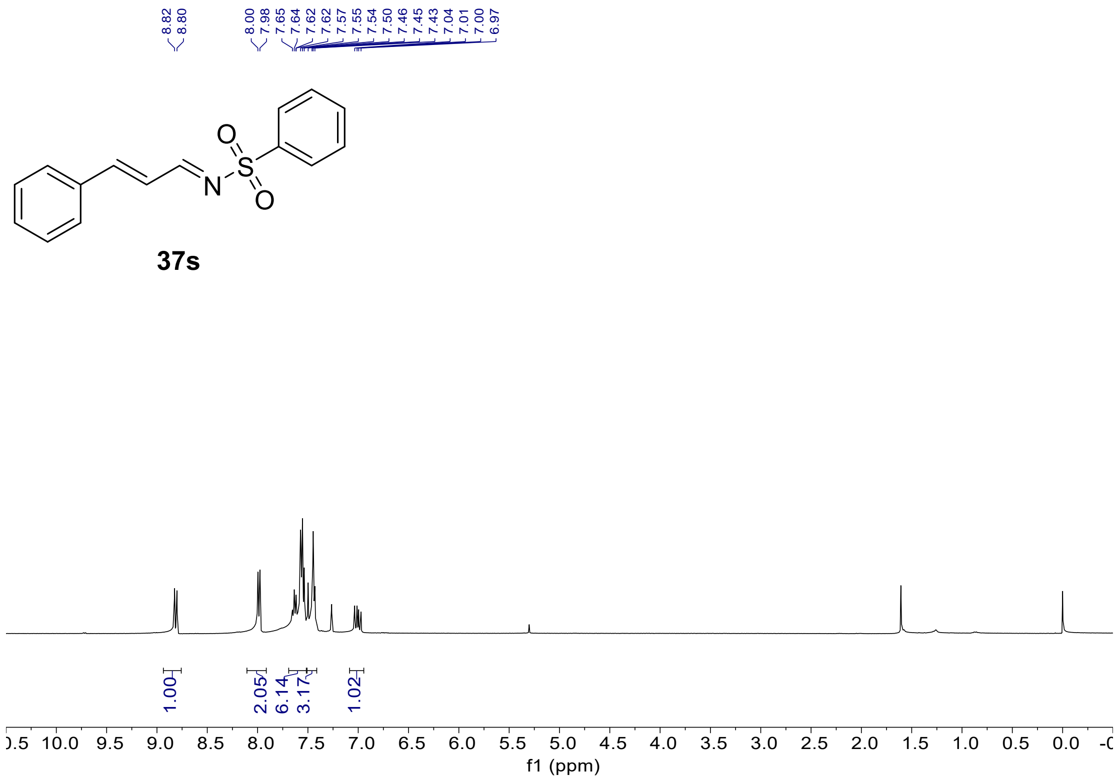

101 MHz
CDCl3
178.0
149.3 144.9 141.6 134.9 134.6 133.2 132.7 132.4 132.1 131.1 129.2 129.0 128.9 128.7 128.3 128.2 127.9 127.8 127.2 126.9 126.9 123.8 122.9
O
S
N
O
34s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

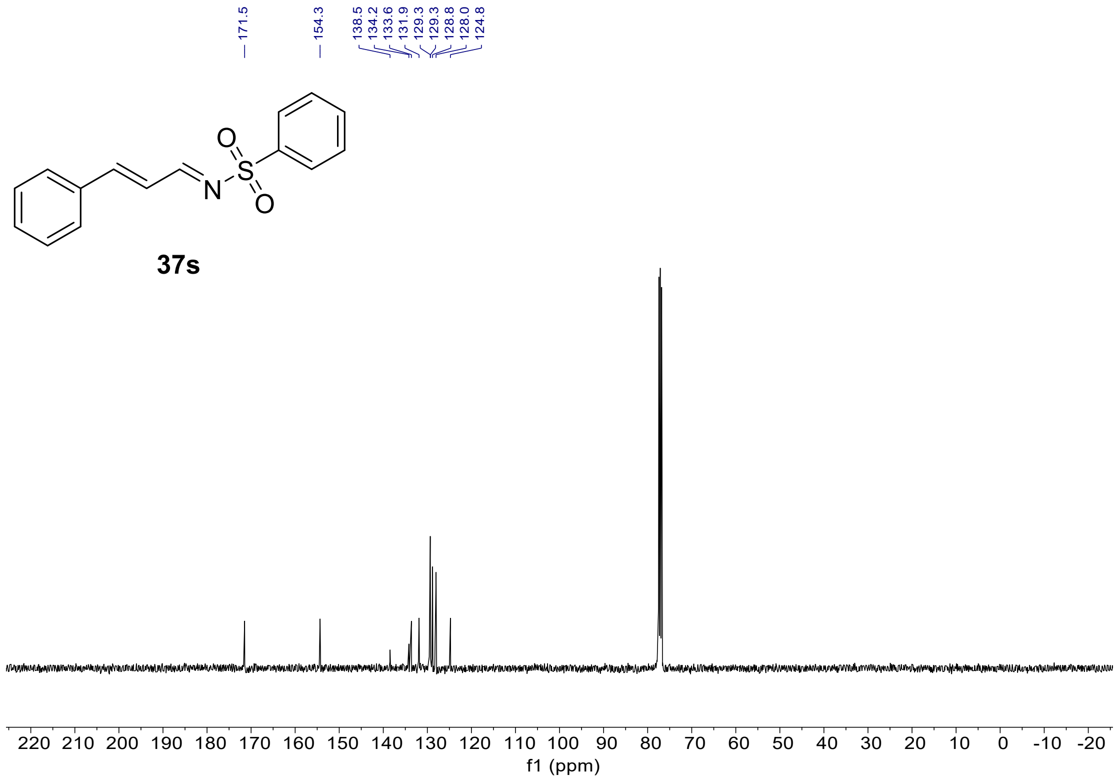

7.97 7.95 7.66 7.62 7.58 7.56 7.55 7.52 7.51 7.49 7.43 7.42 7.41
1.21 1.20 1.12
35s
2.83 6.00 3.01 0.95 4.07
f1 (ppm)

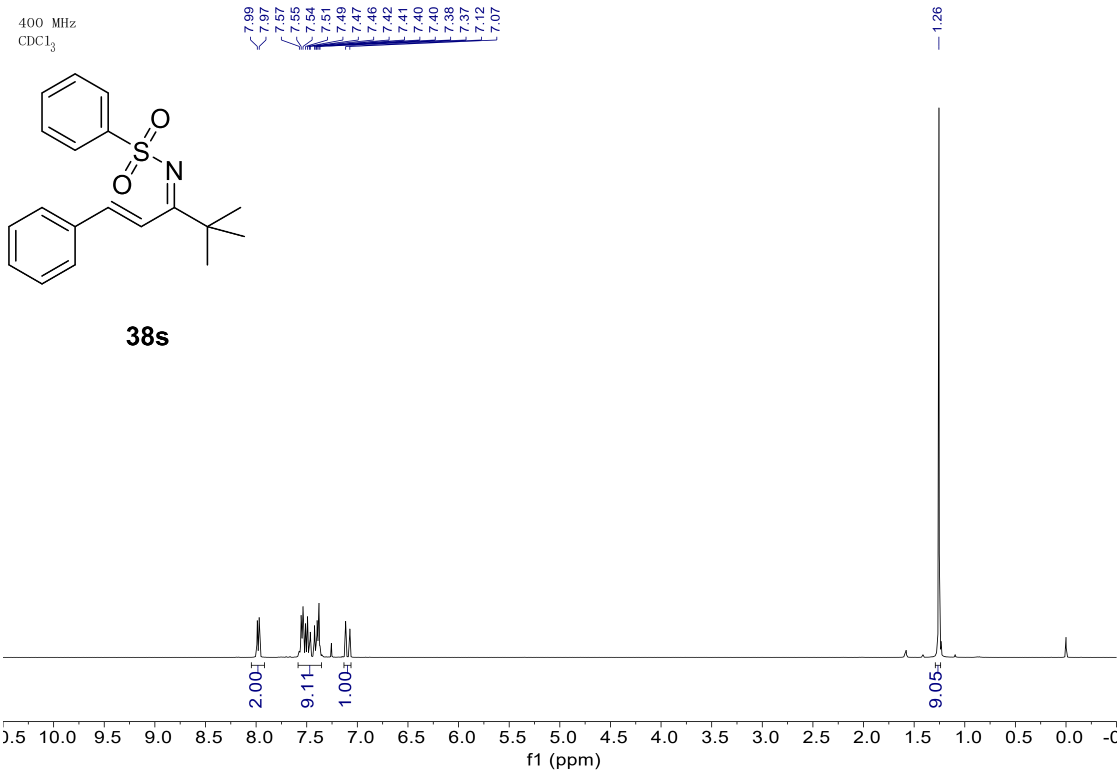

183.2
144.5 142.0 134.6 132.4 131.0 129.0 128.7 126.7 123.4
29.7
16.4 13.2
35s
f1 (ppm)


36s
7.91
7.89
7.51
7.42
7.39
7.34
7.32
6.79
6.75
2.77
2.43
2.16
2.10
4.04
2.27
1.01
3.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

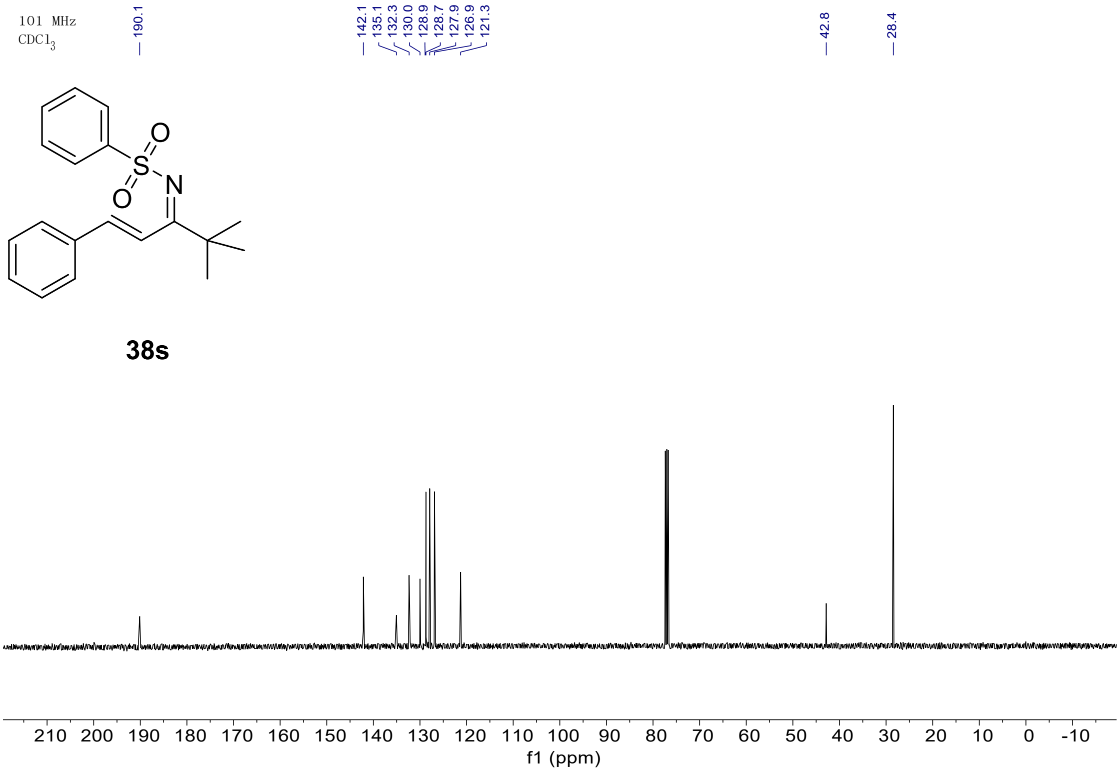

36s
179.3
144.1
143.6
138.5
134.4
130.8
129.5
129.0
128.3
127.1
122.6
21.6
20.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.82
8.80
8.00
7.98
7.65
7.64
7.62
7.62
7.57
7.55
7.54
7.50
7.46
7.45
7.43
7.04
7.01
7.00
6.97
37s
1.00
2.05
6.14
3.17
1.02
f1 (ppm)

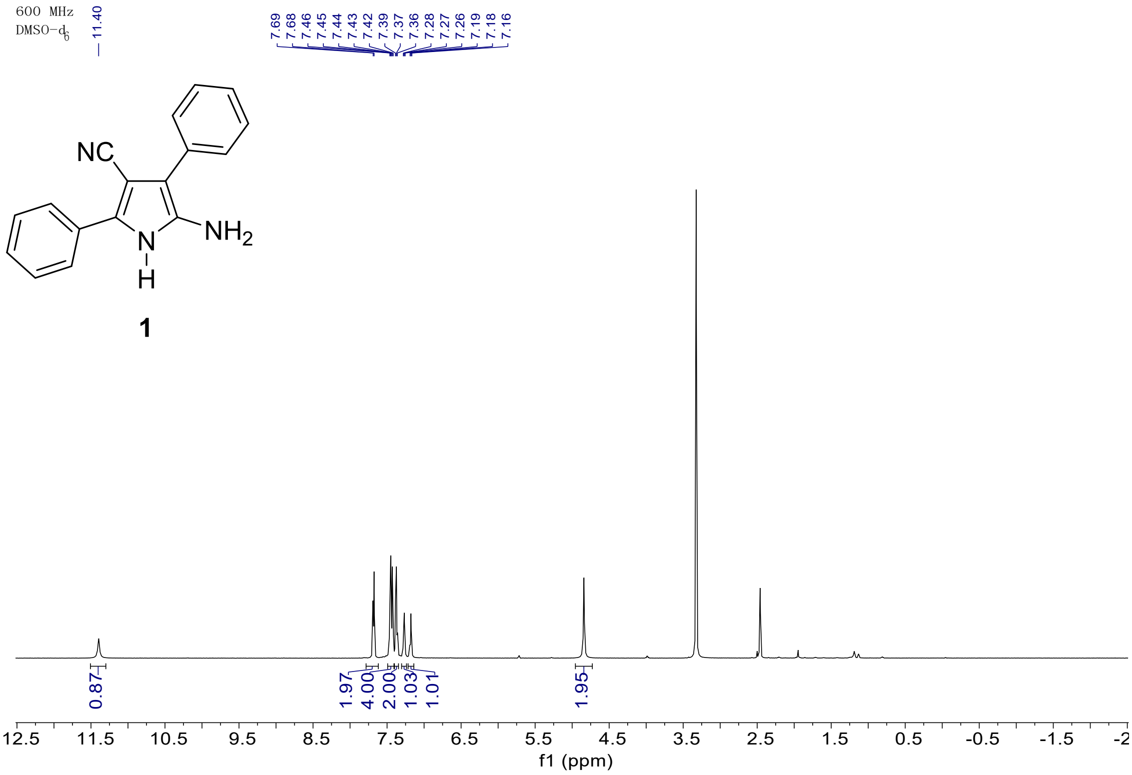

171.5
154.3
138.5
134.2
133.6
131.9
129.3
129.3
128.8
128.0
124.8
37s
f1 (ppm)

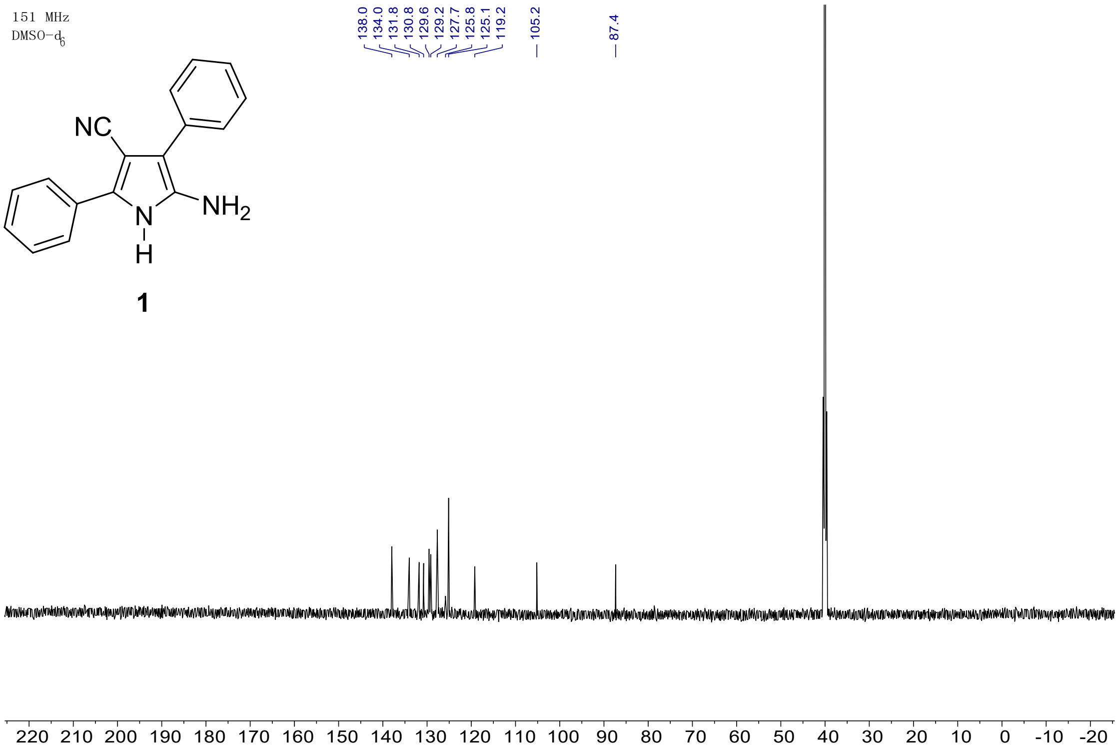

400 MHz
$CDCl_3$
7.99
7.97
7.57
7.55
7.54
7.51
7.49
7.47
7.46
7.42
7.41
7.40
7.40
7.38
7.37
7.12
7.07
1.26
2.00
9.11
1.00
9.05
f1 (ppm)

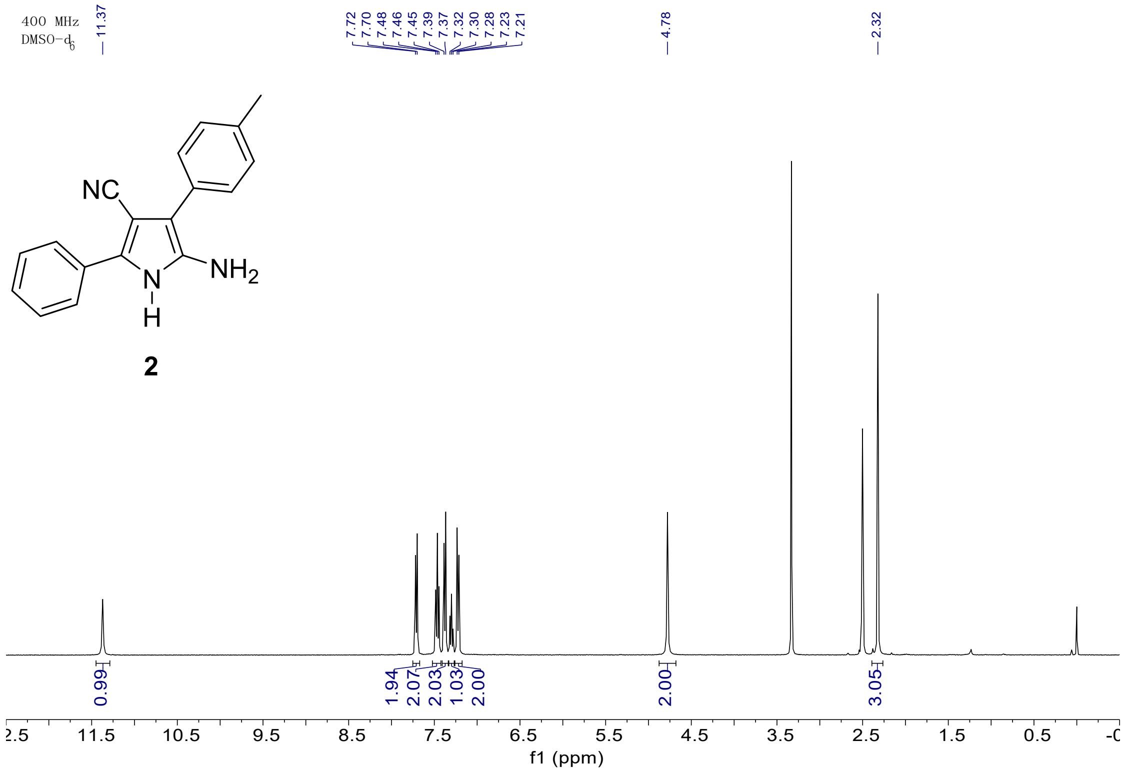
38s

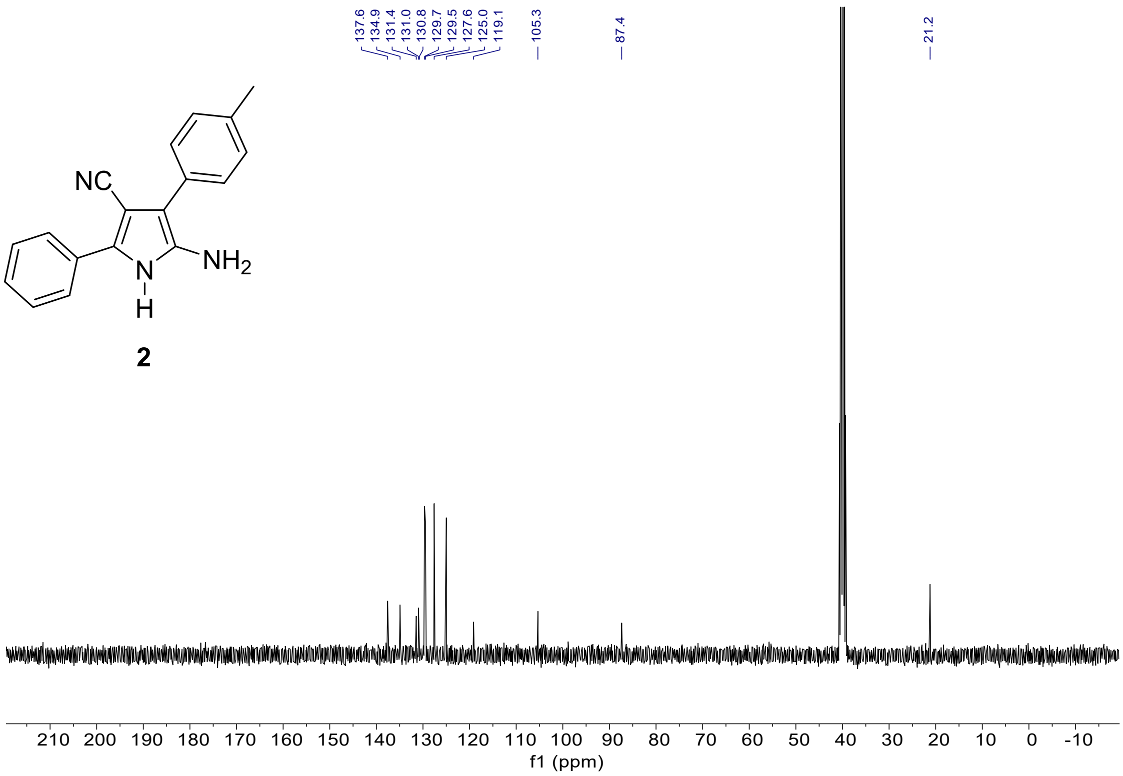

101 MHz
$CDCl_3$
190.1
142.1
135.1
132.3
130.0
128.9
128.7
127.9
126.9
121.3
42.8
28.4
f1 (ppm)

38s


600 MHz
DMSO-d6
11.40
7.69 7.68 7.46 7.45 7.44 7.43 7.42 7.39 7.37 7.36 7.28 7.27 7.26 7.19 7.18 7.16
NC
NH2
N
H
1
0.87
1.97 4.00 2.00 1.03 1.01
1.95
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5 -2
f1 (ppm)


151 MHz
DMSO-d6
138.0 134.0 131.8 130.8 129.6 129.2 127.7 125.8 125.1 119.2
105.2
87.4
NC
NH2
N
H
1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


400 MHz
DMSO-d6
11.37
7.72
7.70
7.48
7.46
7.45
7.39
7.37
7.32
7.30
7.28
7.23
7.21
4.78
2.32
NC
NH2
N
H
2
0.99
1.94
2.07
2.03
1.03
2.00
2.00
3.05
f1 (ppm)


137.6
134.9
131.4
131.0
130.8
129.7
129.5
127.6
125.0
119.1
105.3
87.4
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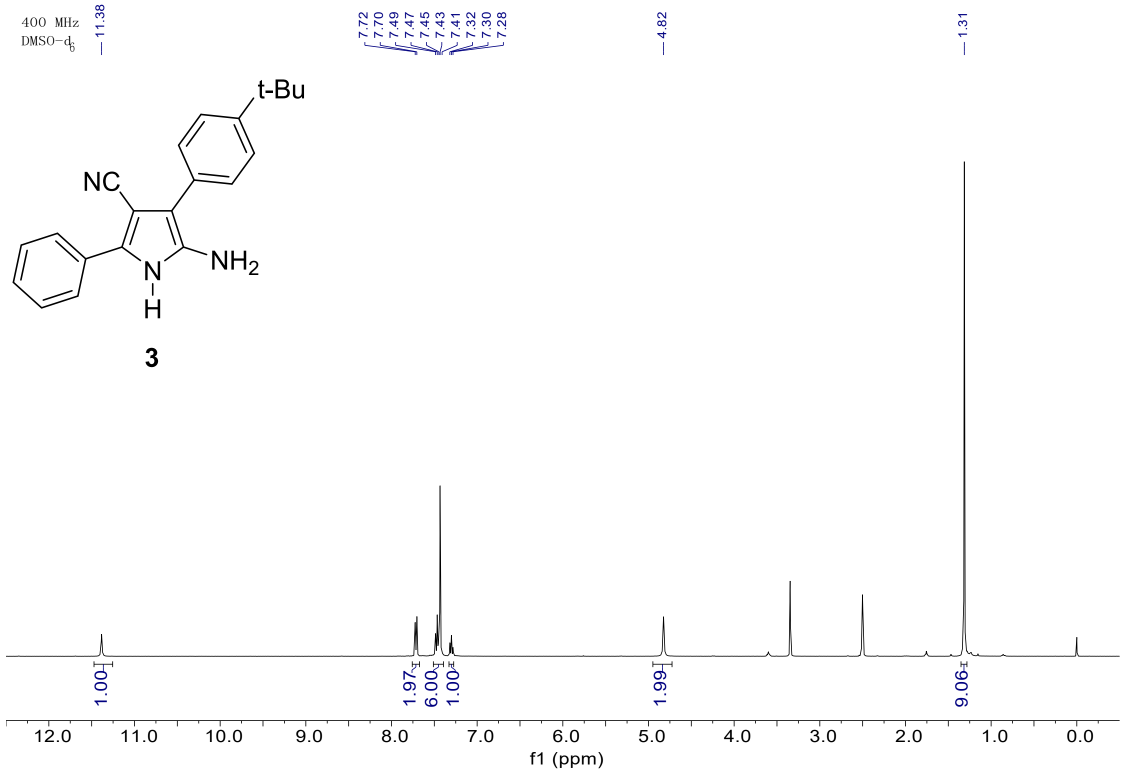
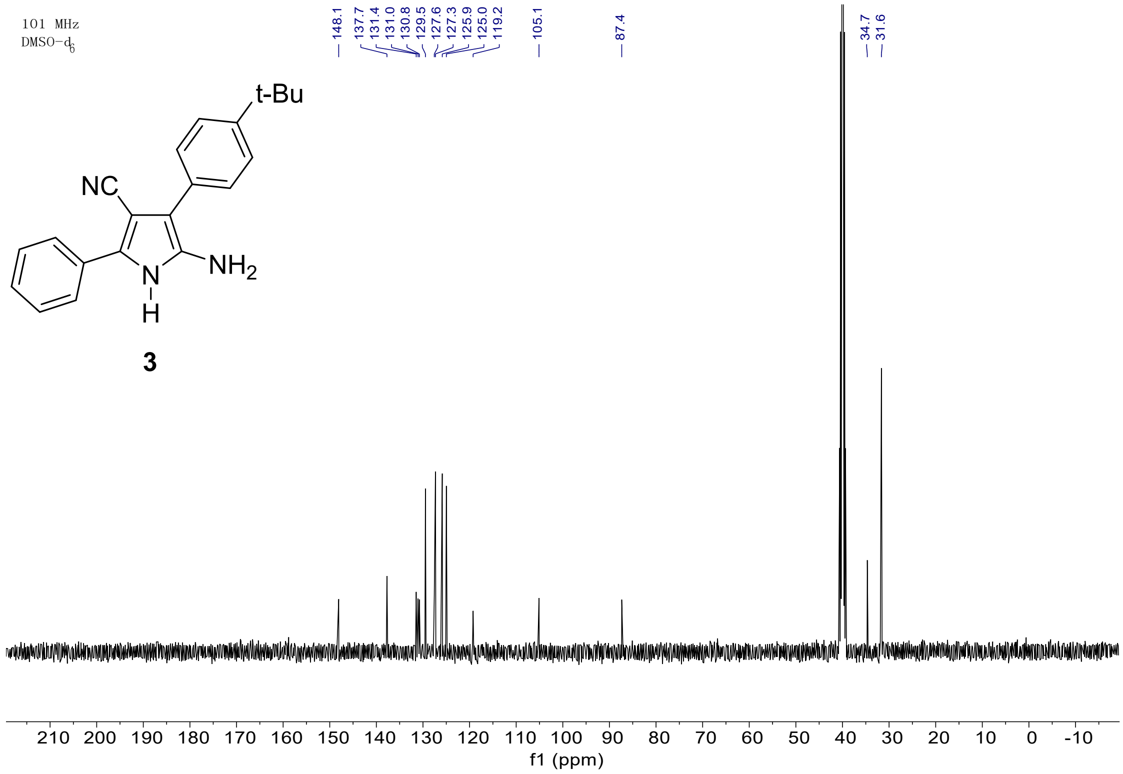
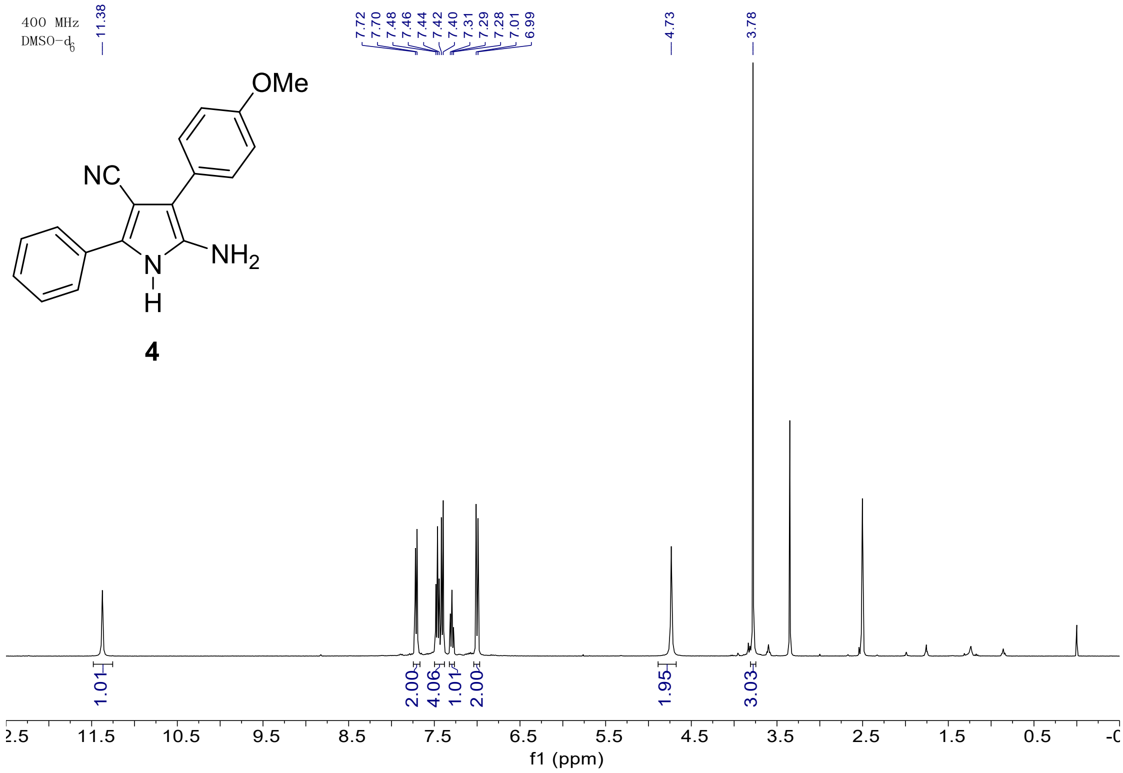
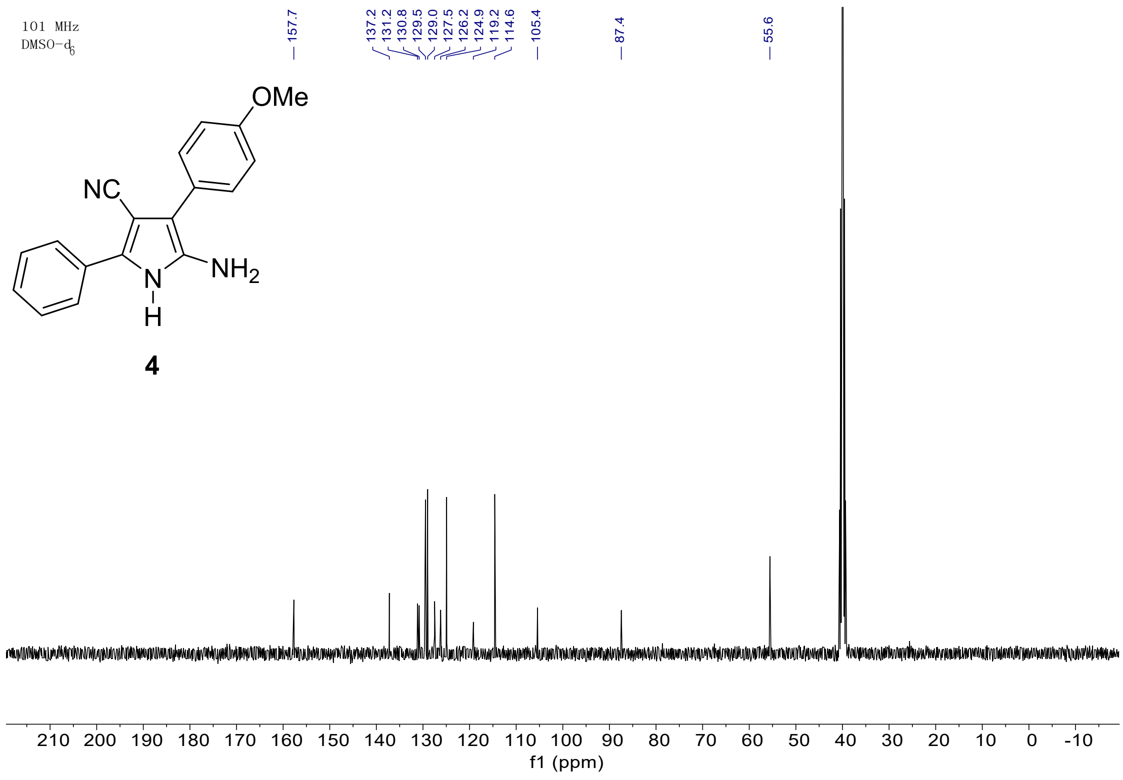
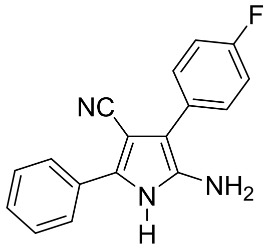
N
H
2
f1 (ppm)


400 MHz
DMSO-d6
11.38
7.72 7.70 7.49 7.47 7.45 7.43 7.41 7.32 7.30 7.28
4.82
1.31
t-Bu
NC
NH2
N
H
3
1.00
1.97
6.00
1.00
1.99
9.06
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


101 MHz
DMSO-d6
148.1 137.7 131.4 131.0 130.8 129.5 127.6 127.3 125.9 125.0 119.2
105.1
87.4
34.7
31.6
t-Bu
NC
NH2
N
H
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

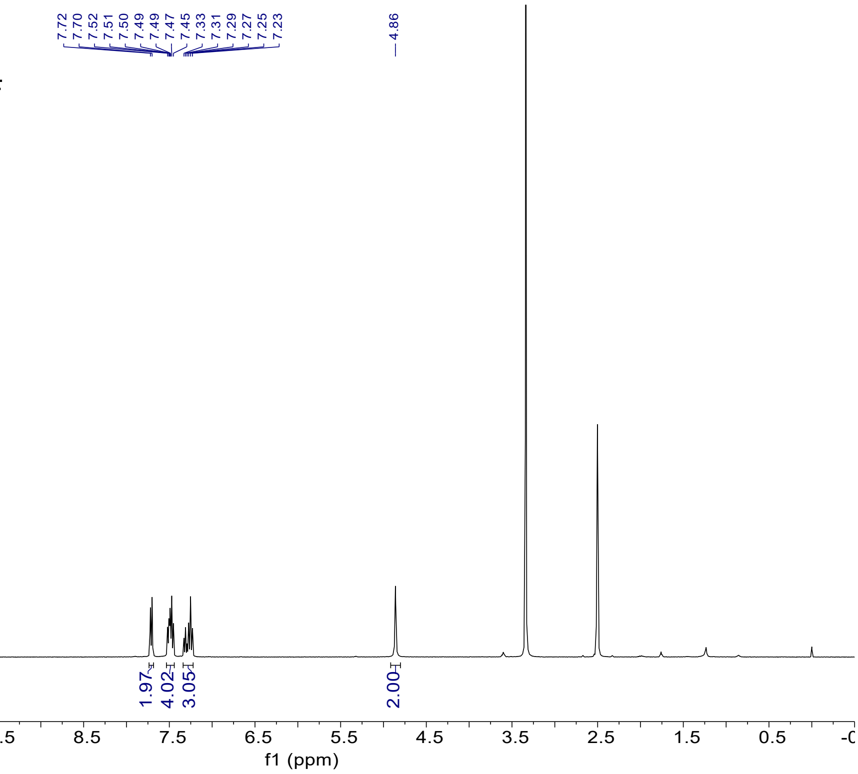

400 MHz
DMSO-d6
11.38
7.72
7.70
7.48
7.46
7.44
7.42
7.40
7.31
7.29
7.28
7.01
6.99
4.73
3.78
OMe
NC
NH2
N
H
4
1.01
2.00
4.06
1.01
2.00
1.95
3.03
f1 (ppm)


101 MHz
DMSO-d6
157.7
137.2
131.2
130.8
129.5
129.0
127.5
126.2
124.9
119.2
114.6
105.4
87.4
55.6
OMe
NC
NH2
N
H
4
f1 (ppm)

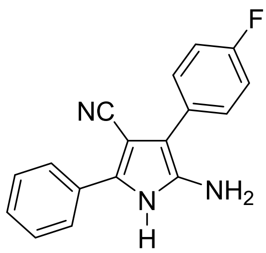


F
NC
NH2
N
H

5

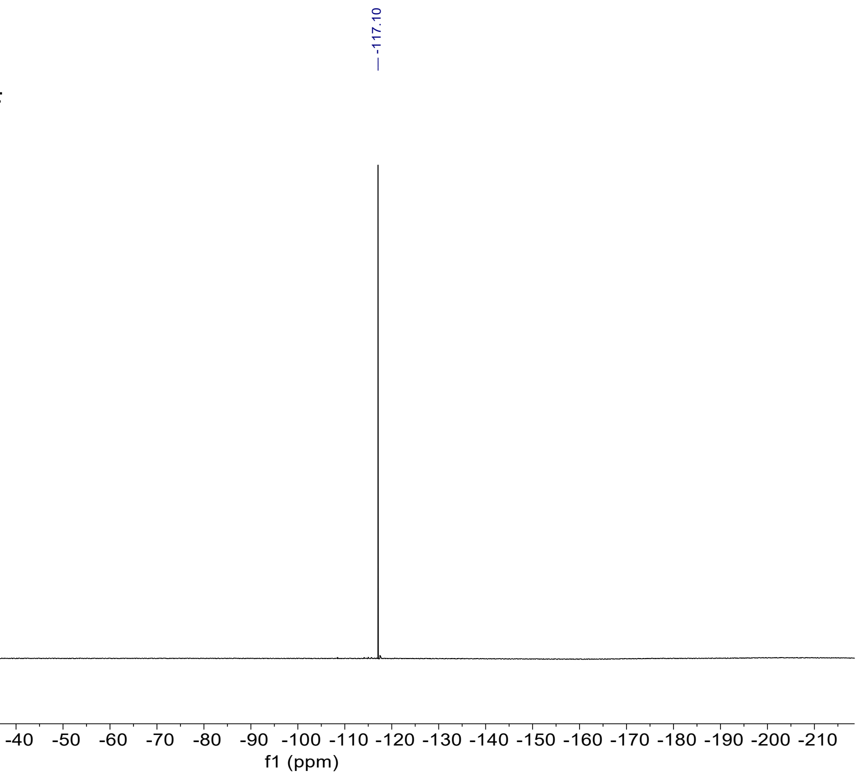


400 MHz
DMSO-d6
11.42
7.72
7.70
7.52
7.51
7.50
7.49
7.47
7.45
7.33
7.31
7.29
7.27
7.25
7.23
4.86
1.01
1.97
4.02
3.05
2.00
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

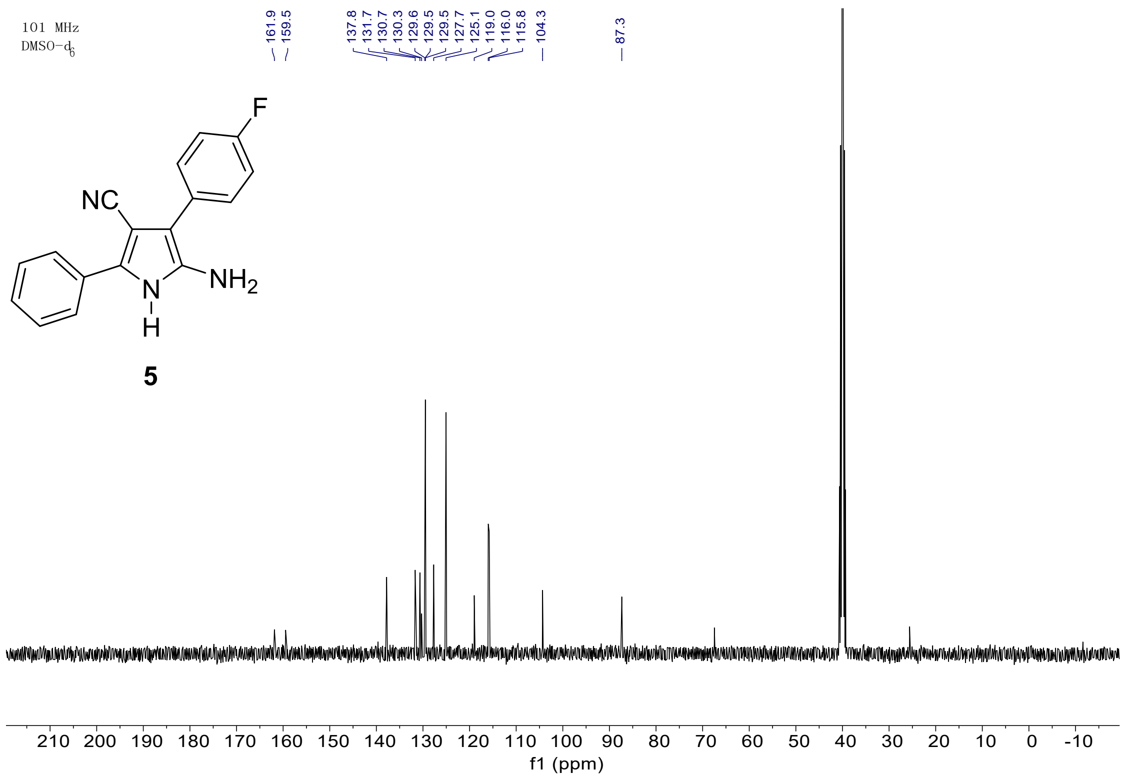


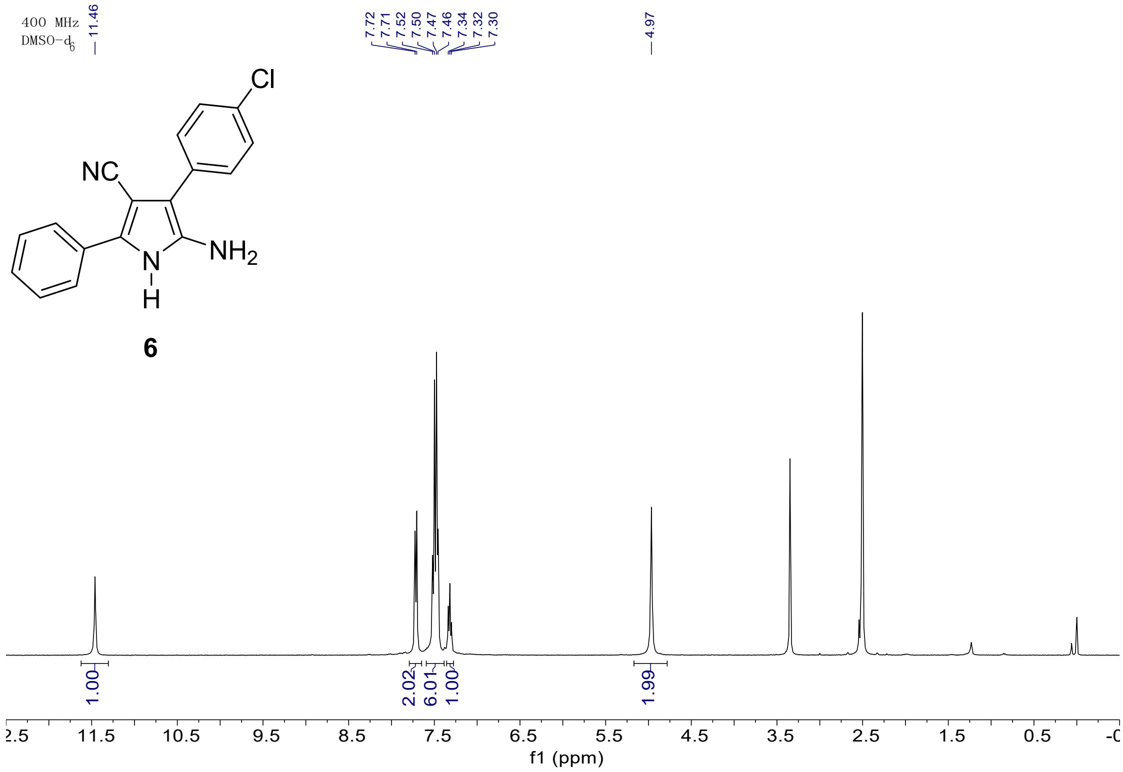
F
NC
NH2
N
H

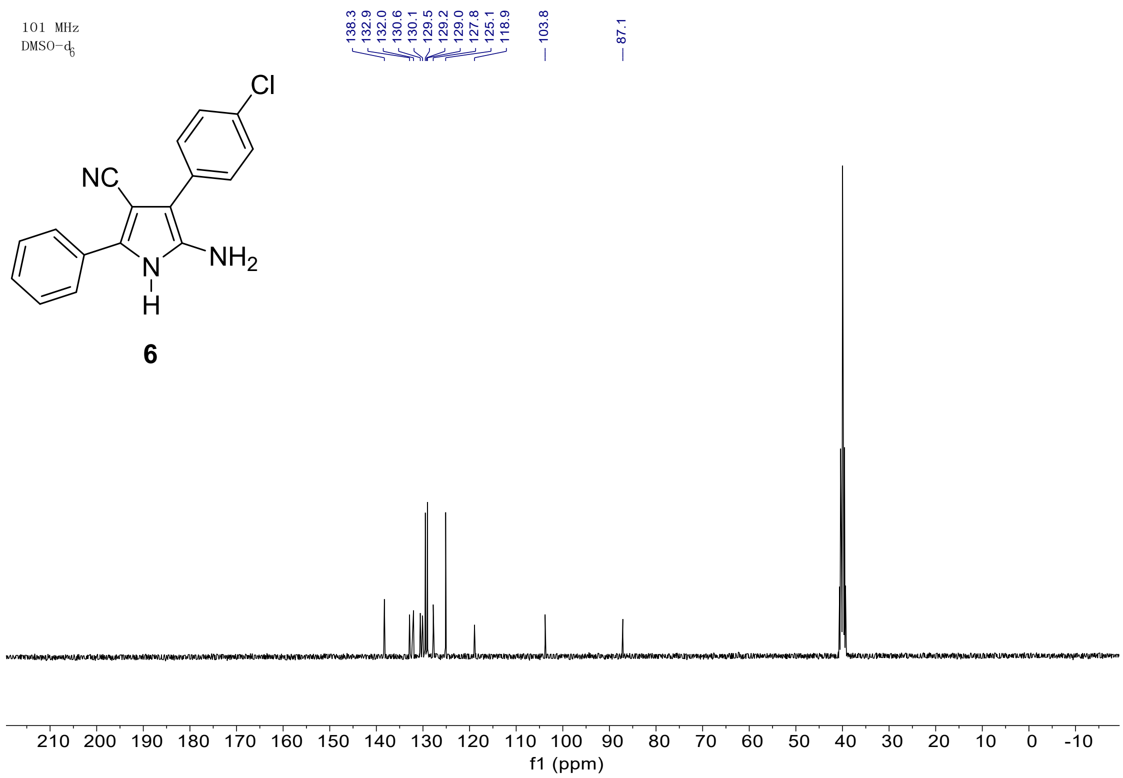
5

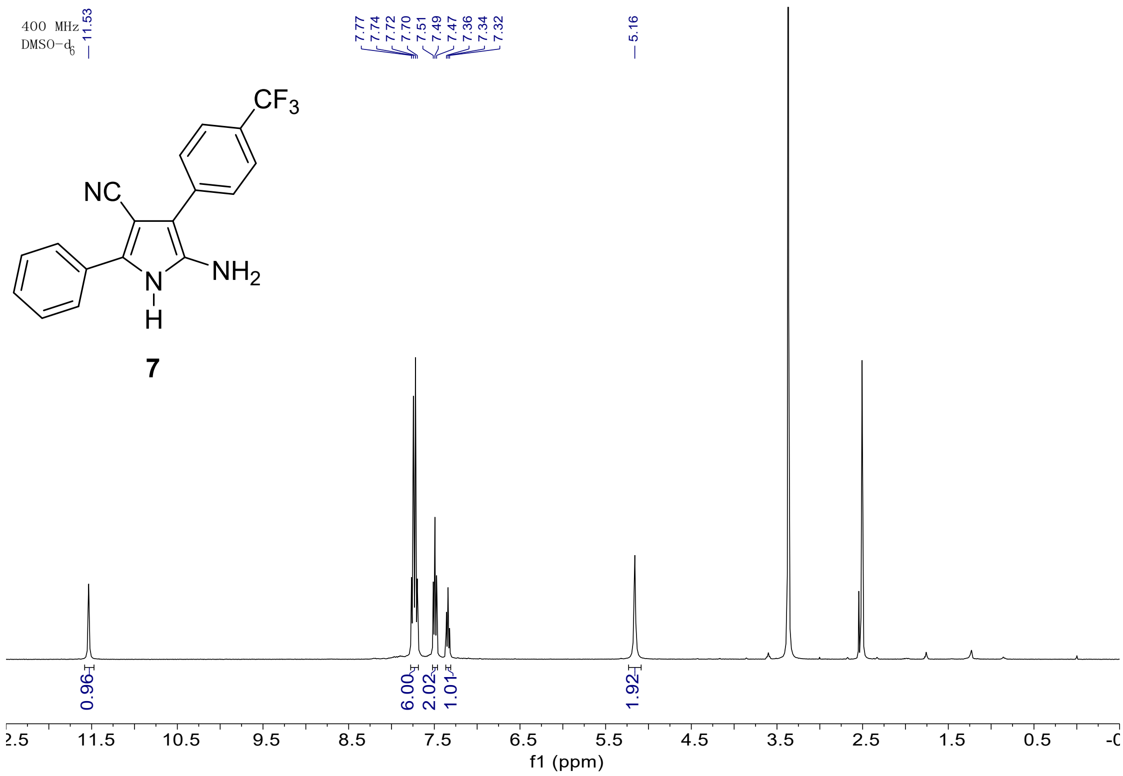


376 MHz
DMSO-d6
-117.10
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


101 MHz
DMSO-d6
161.9
159.5
137.8
131.7
130.7
130.3
129.6
129.5
129.5
127.7
125.1
119.0
116.0
115.8
104.3
87.3
F
NC
NH_2
N
H
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
DMSO-d6
11.46
7.72
7.71
7.52
7.50
7.47
7.46
7.34
7.32
7.30
4.97
Cl
NC
NH_2
N
H
6
1.00
2.02
6.01
1.00
1.99
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


101 MHz
DMSO-d6
138.3
132.9
132.0
130.6
130.1
129.5
129.2
129.0
127.8
125.1
118.9
103.8
87.1
NC
Cl
NH2
N
H
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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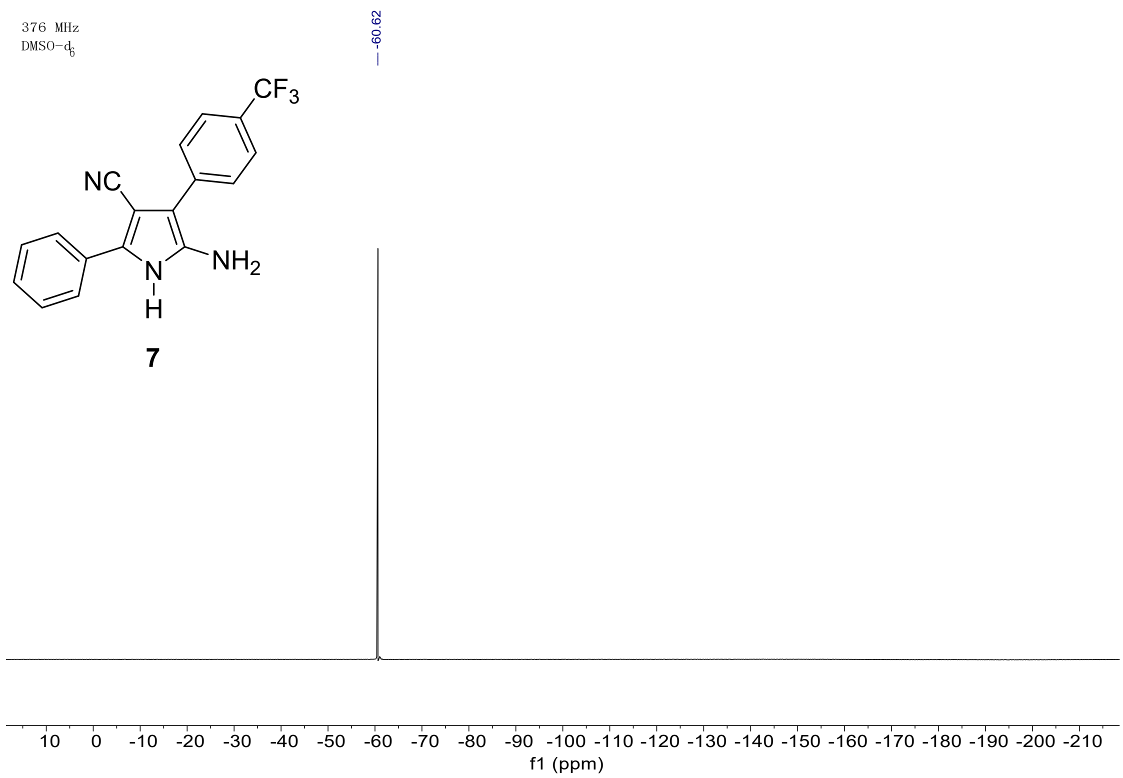
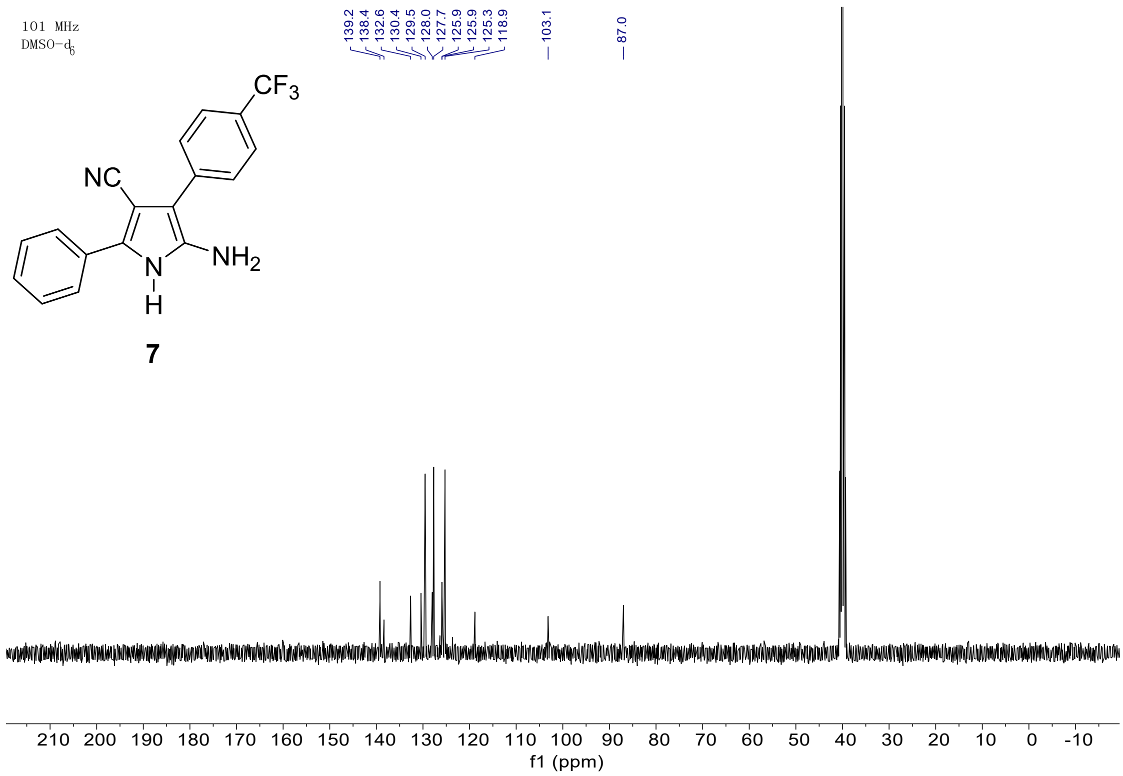
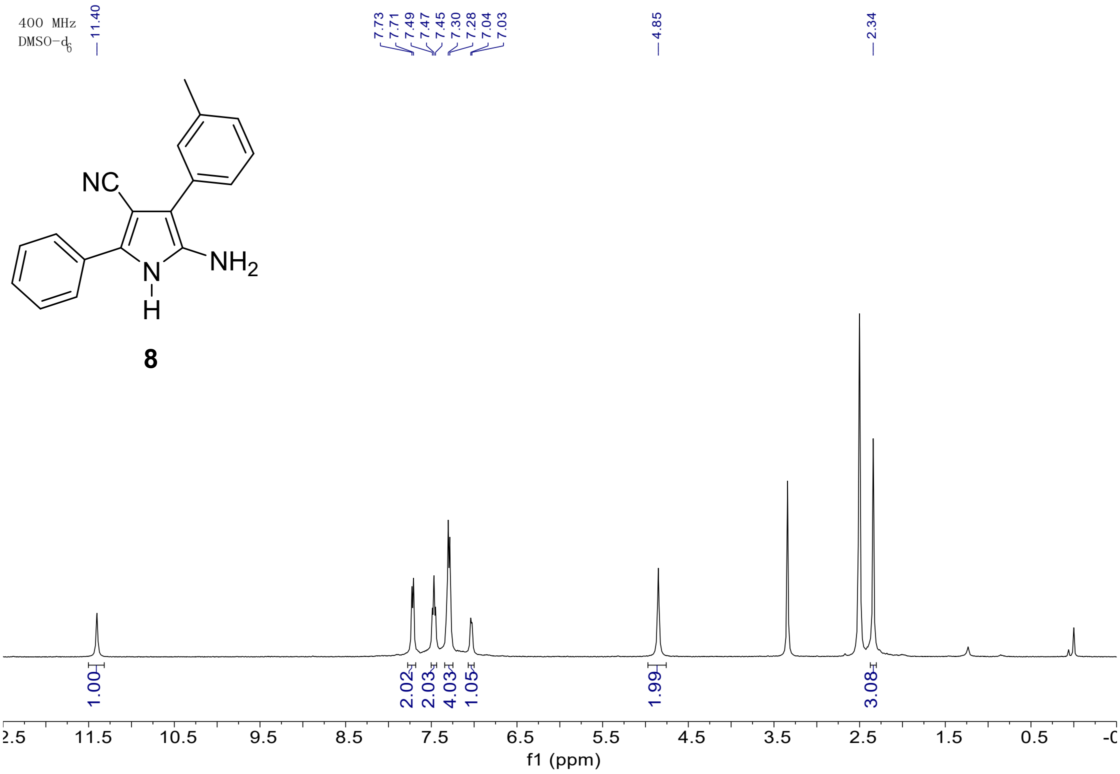
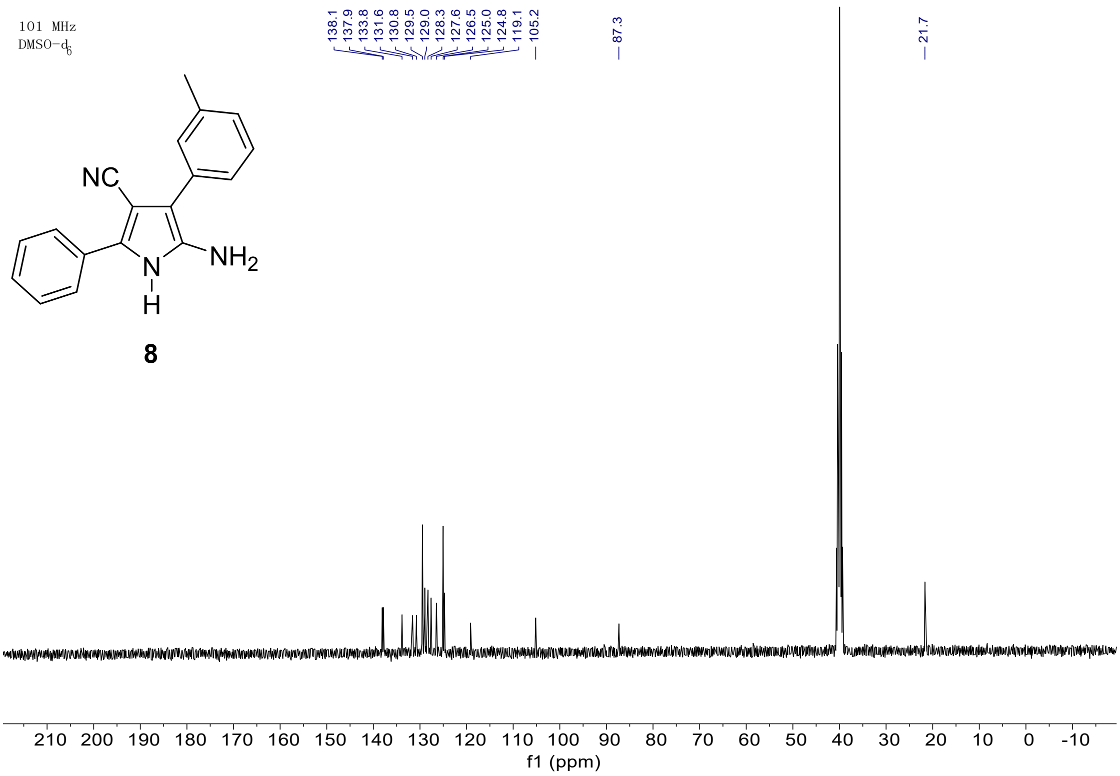
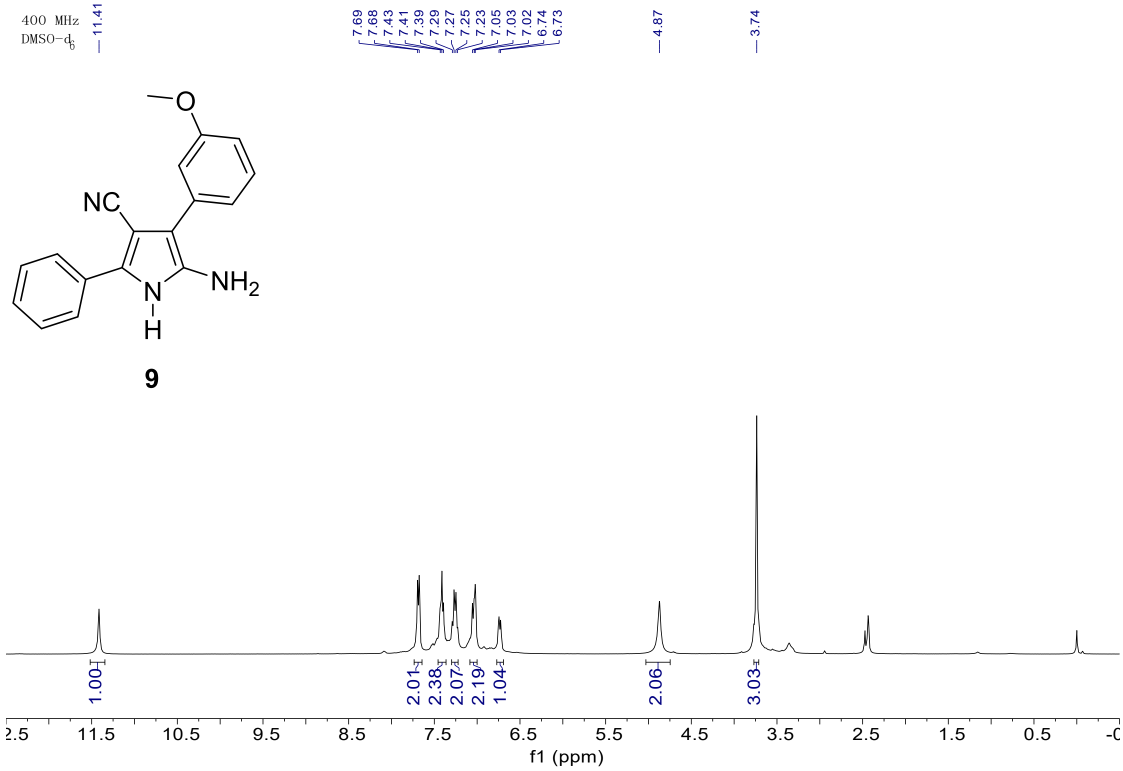
DMSO-d6
11.53
7.77
7.74
7.72
7.70
7.51
7.49
7.47
7.36
7.34
7.32
5.16
CF3
NC
NH2
N
H
7
0.96
6.00
2.02
1.01
1.92
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


376 MHz
DMSO-d6
-60.62
CF3
NC
NH2
N
H
7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


101 MHz
DMSO-d6
139.2
138.4
132.6
130.4
129.5
128.0
127.7
125.9
125.9
125.3
118.9
103.1
87.0
CF3
NC
NH2
N
H
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
DMSO-d6
11.40
7.73
7.71
7.49
7.47
7.45
7.30
7.28
7.04
7.03
4.85
2.34
NC
NH2
N
H
8
1.00
2.02
2.03
4.03
1.05
1.99
3.08
f1 (ppm)


101 MHz
DMSO-d6
138.1
137.9
133.8
131.6
130.8
129.5
129.0
128.3
127.6
126.5
125.0
124.8
119.1
105.2
87.3
21.7
NC
NH2
N
H
8
f1 (ppm)


400 MHz
DMSO-d6
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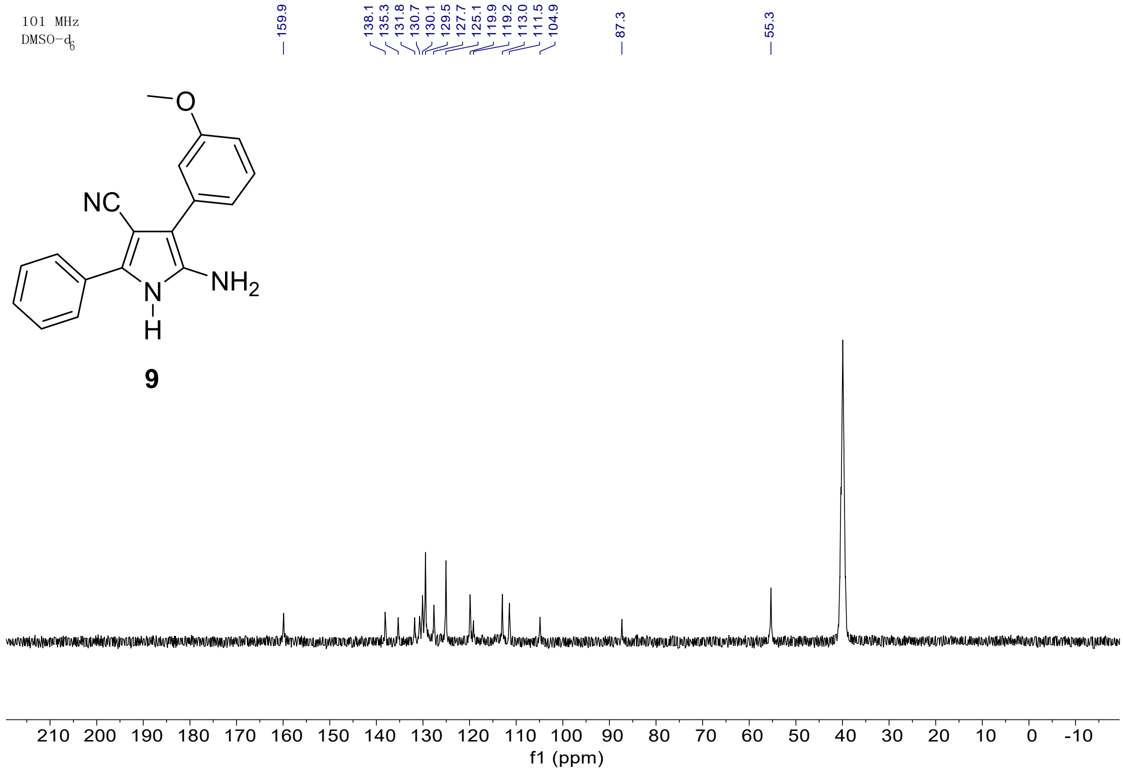
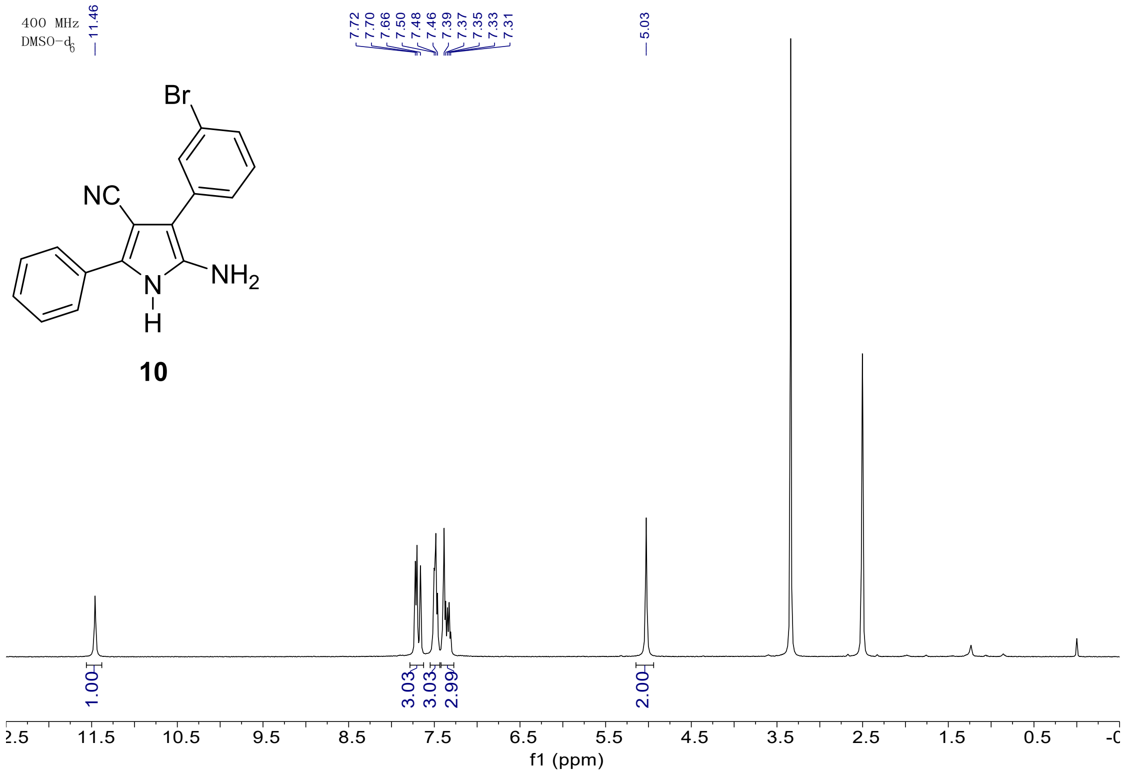
4.87
3.74
O
NC
NH2
N
H
9
1.00
2.01 2.38 2.07 2.19 1.04
2.06
3.03
f1 (ppm)


101 MHz
DMSO-d6
159.9
138.1 135.3 131.8 130.7 130.1 129.5 127.7 125.1 119.9 119.2 113.0 111.5 104.9
87.3
55.3
O
NC
NH2
N
H
9
f1 (ppm)


400 MHz
DMSO-d6
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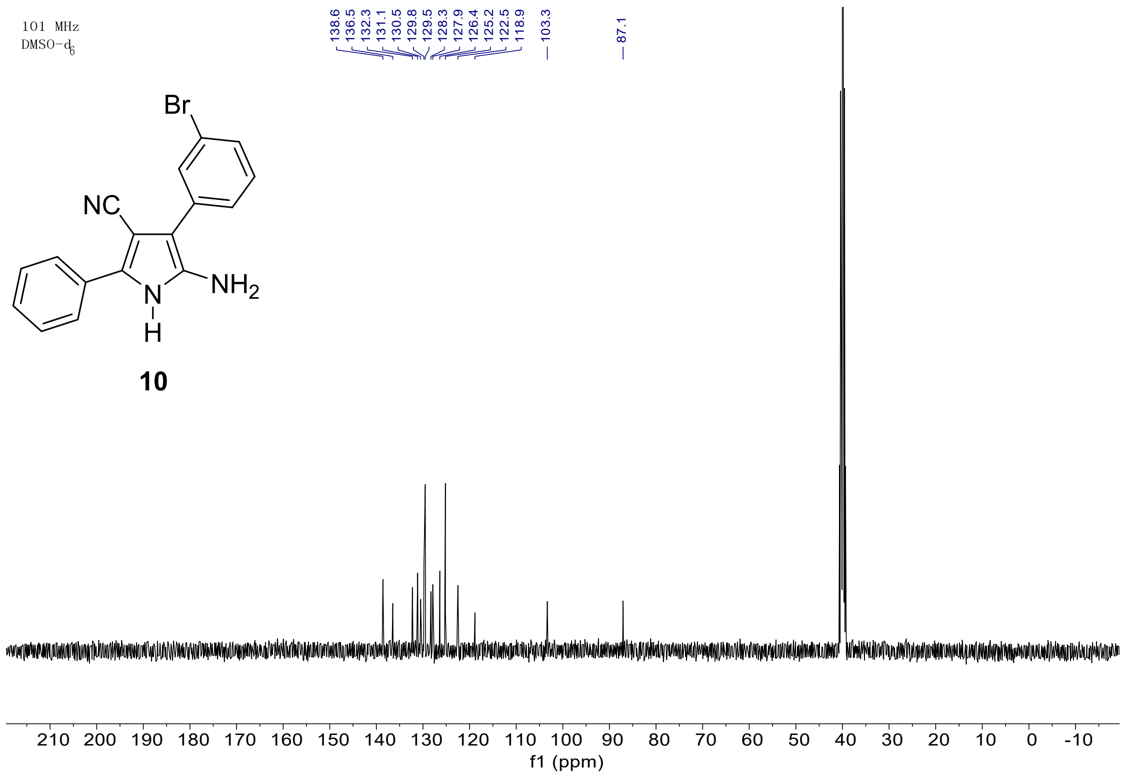
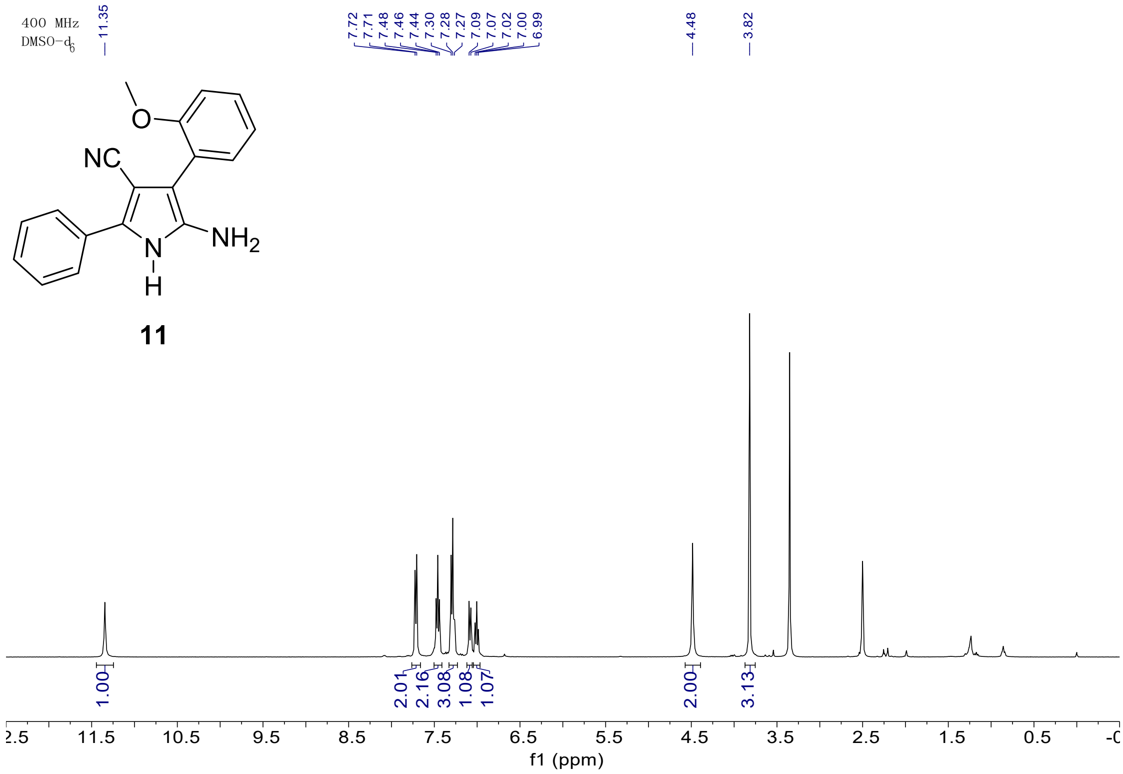
7.70
7.66
7.50
7.48
7.46
7.39
7.37
7.35
7.33
7.31
5.03
Br
NC
NH2
N
H
10
1.00
3.03
3.03
2.99
2.00
f1 (ppm)


101 MHz
DMSO-d6
138.6
136.5
132.3
131.1
130.5
129.8
129.5
128.3
127.9
126.4
125.2
122.5
118.9
103.3
87.1
Br
NC
NH2
N
H
10
f1 (ppm)


400 MHz
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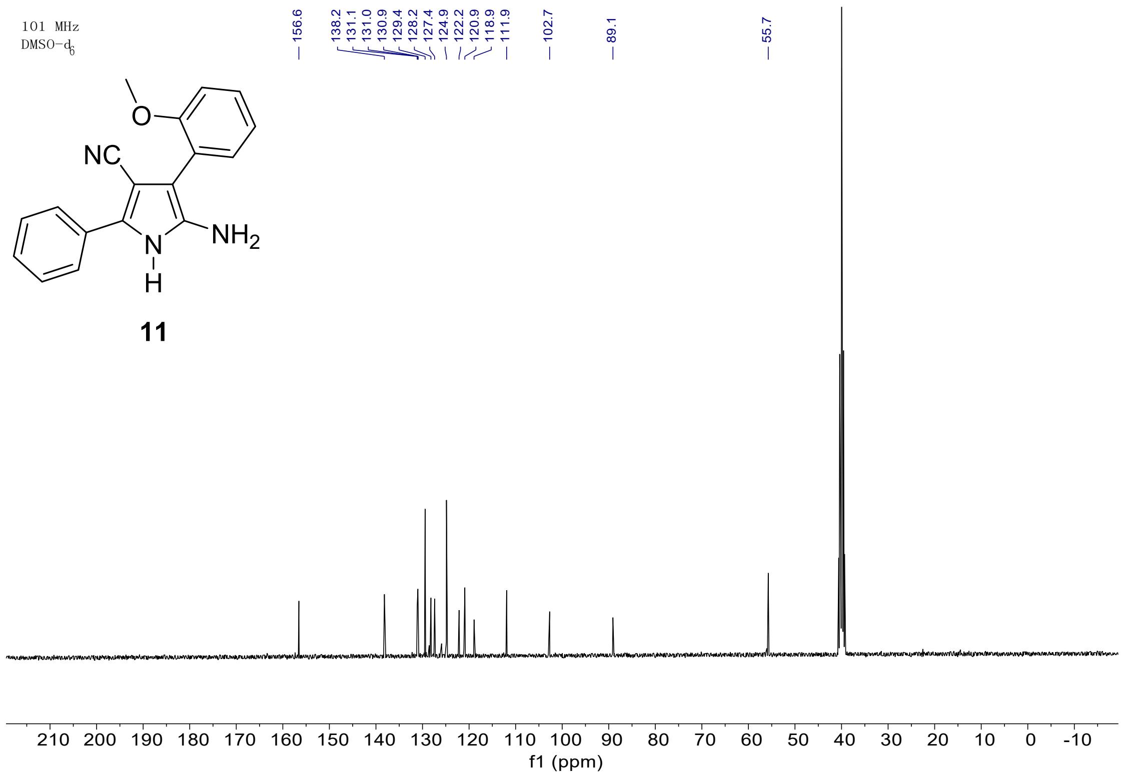
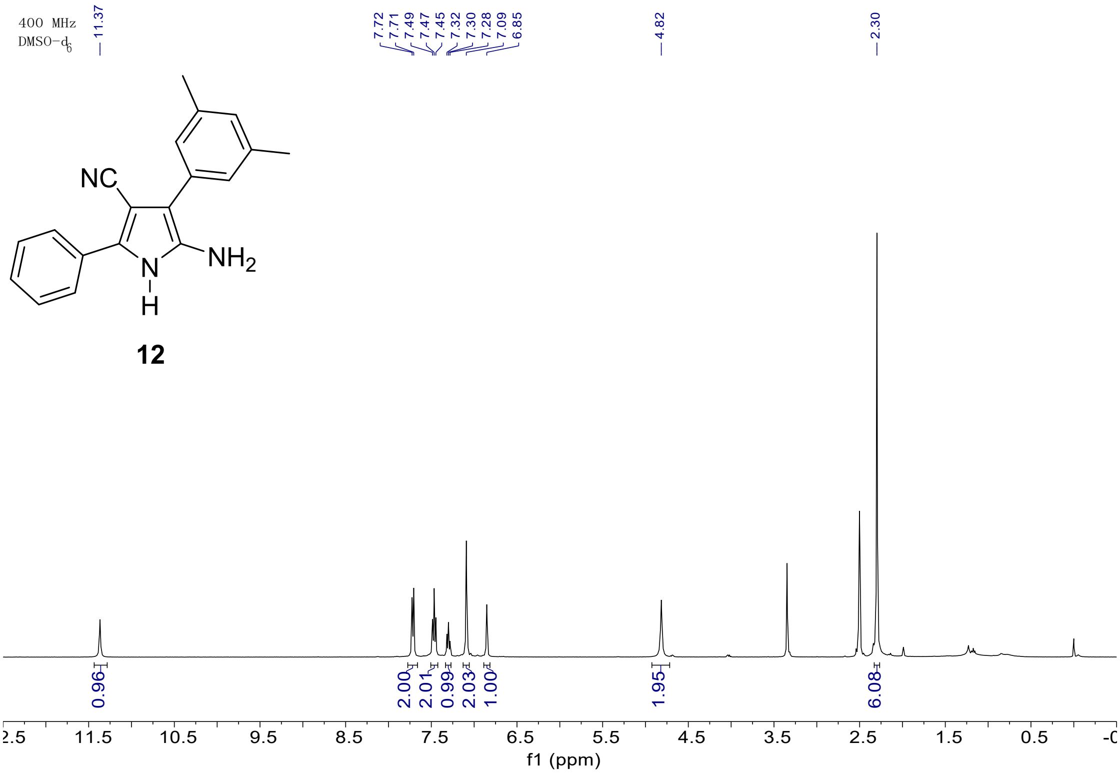
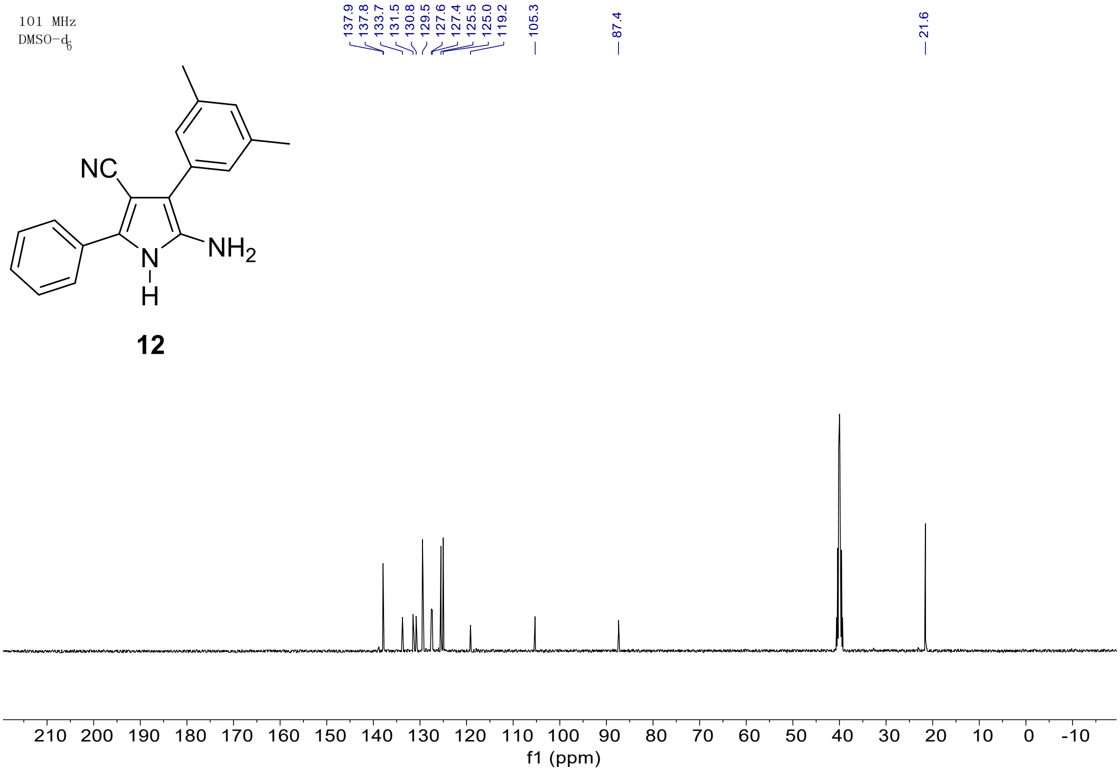
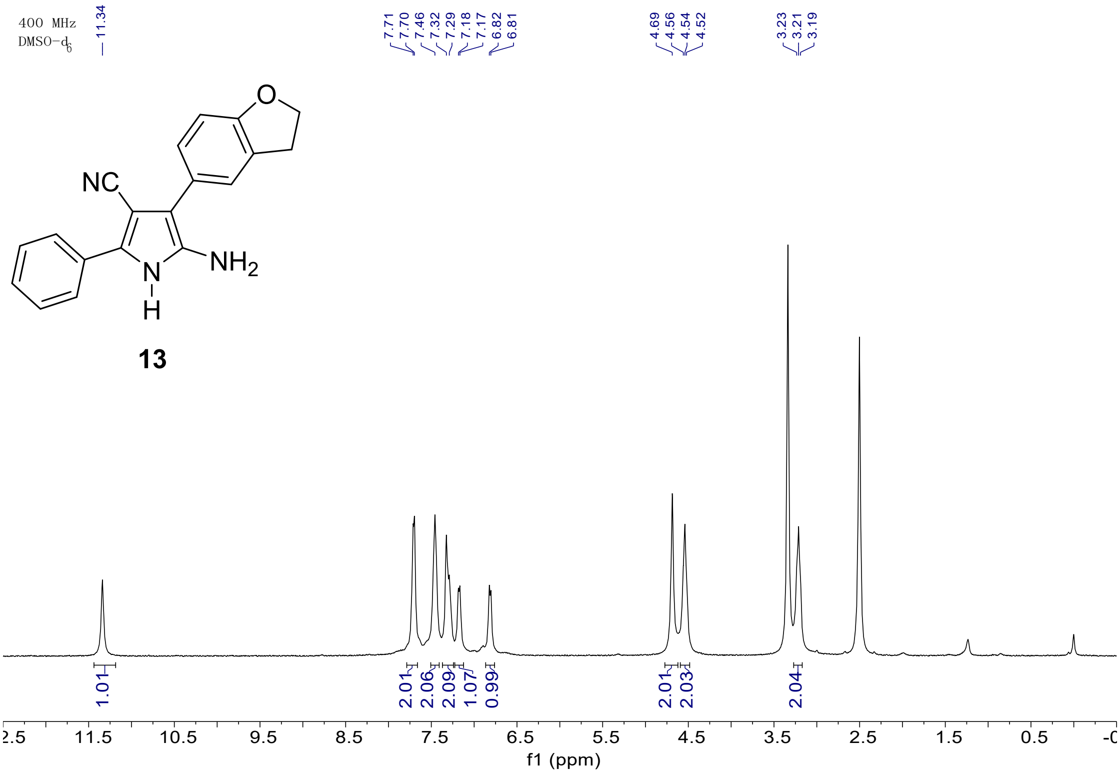
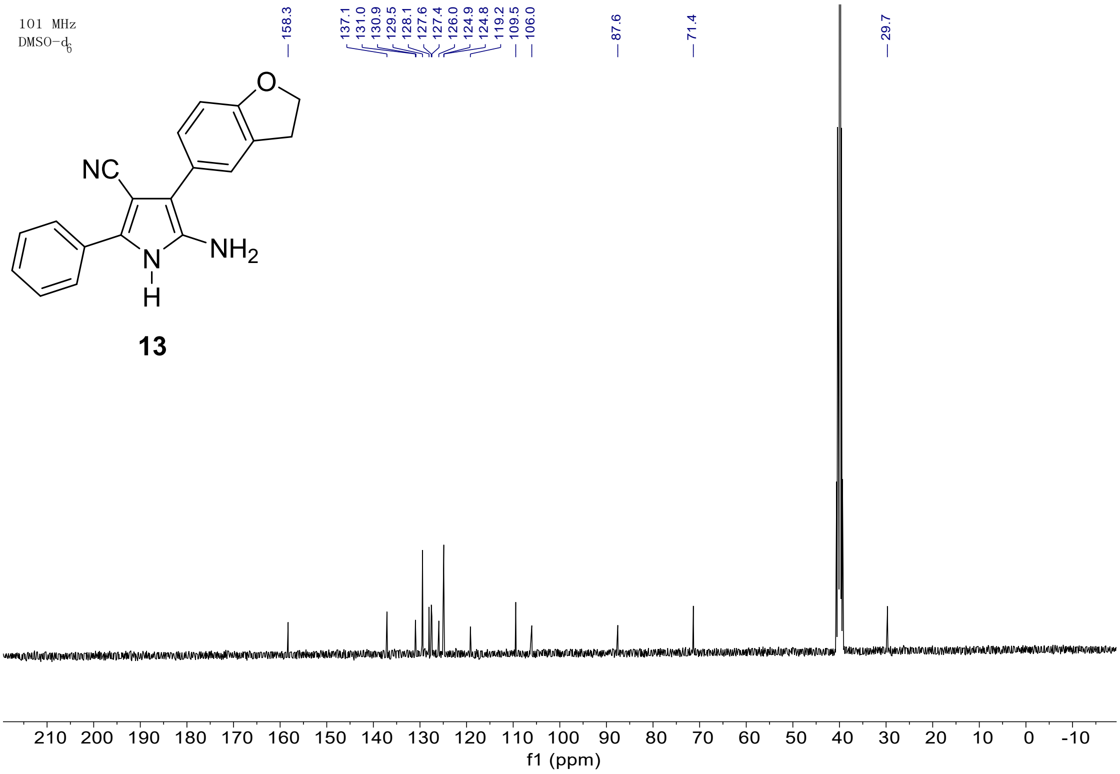
4.48
3.82
NC
O
NH2
N
H
11
1.00
2.01 2.16 3.08 1.08 1.07
2.00
3.13
f1 (ppm)

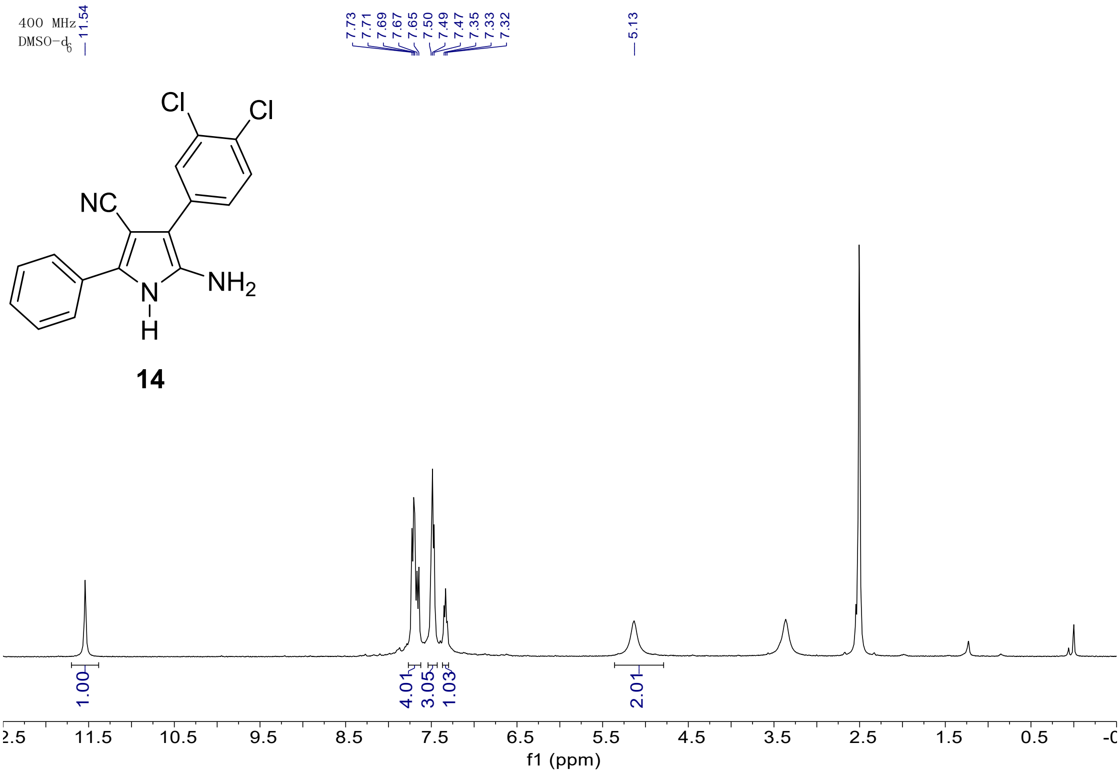

101 MHz
DMSO-d6
156.6
138.2 131.1 131.0 130.9 129.4 128.2 127.4 124.9 122.2 120.9 118.9 111.9
102.7
89.1
55.7
NC
O
NH2
N
H
11
f1 (ppm)


400 MHz
DMSO-d6
11.37
7.72
7.71
7.49
7.47
7.45
7.32
7.30
7.28
7.09
6.85
4.82
2.30
NC
NH2
N
H
12
0.96
2.00
2.01
0.99
2.03
1.00
1.95
6.08
f1 (ppm)

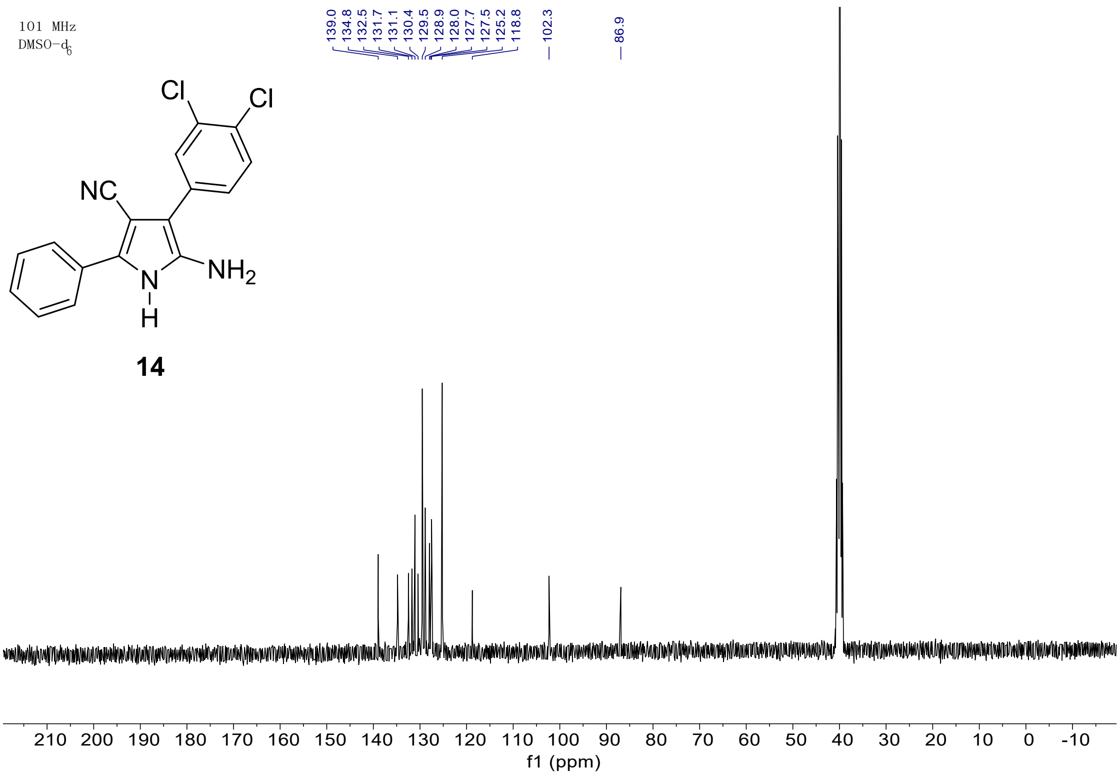

101 MHz
DMSO-d6
137.9
137.8
133.7
131.5
130.8
129.5
127.6
127.4
125.5
125.0
119.2
105.3
87.4
21.6
NC
NH2
N
H
12
f1 (ppm)


400 MHz
DMSO-d6
11.34
7.71 7.70 7.46 7.32 7.29 7.18 7.17 6.82 6.81
4.69 4.56 4.54 4.52
3.23 3.21 3.19
NC
O
NH2
N
H
13
1.01
2.01 2.06 2.09 1.07 0.99
2.01 2.03
2.04
f1 (ppm)

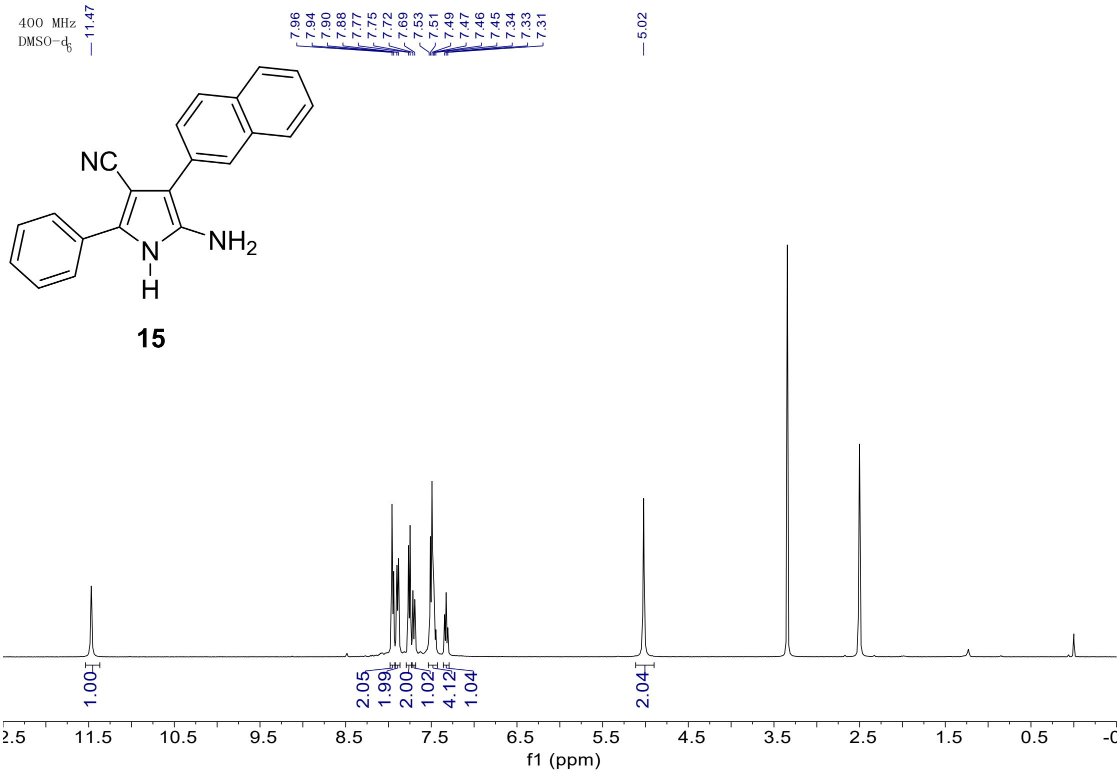

101 MHz
DMSO-d6
158.3
137.1 131.0 130.9 129.5 128.1 127.6 127.4 126.0 124.9 124.8 119.2 109.5 106.0
87.6
71.4
29.7
NC
O
NH2
N
H
13
f1 (ppm)

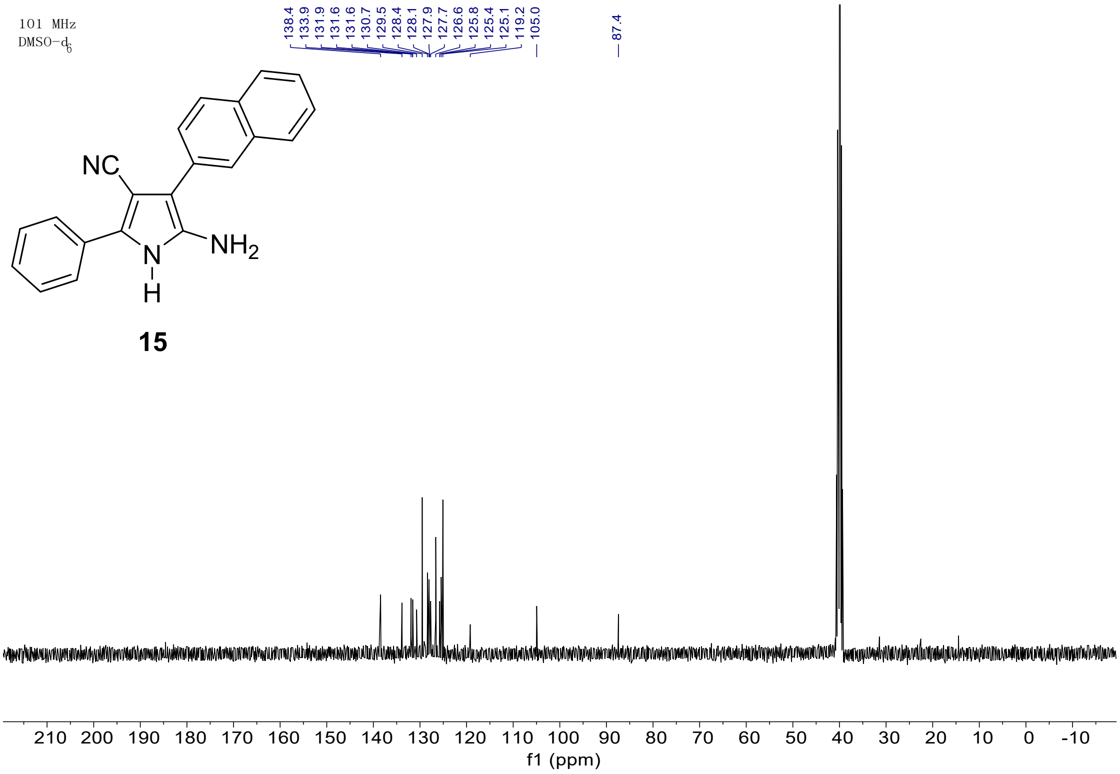

400 MHz
DMSO-d6
11.54
7.73 7.71 7.69 7.67 7.65 7.50 7.49 7.47 7.35 7.33 7.32
5.13
Cl
Cl
NC
NH2
N
H
1.00
4.01 3.05 1.03
2.01
f1 (ppm)

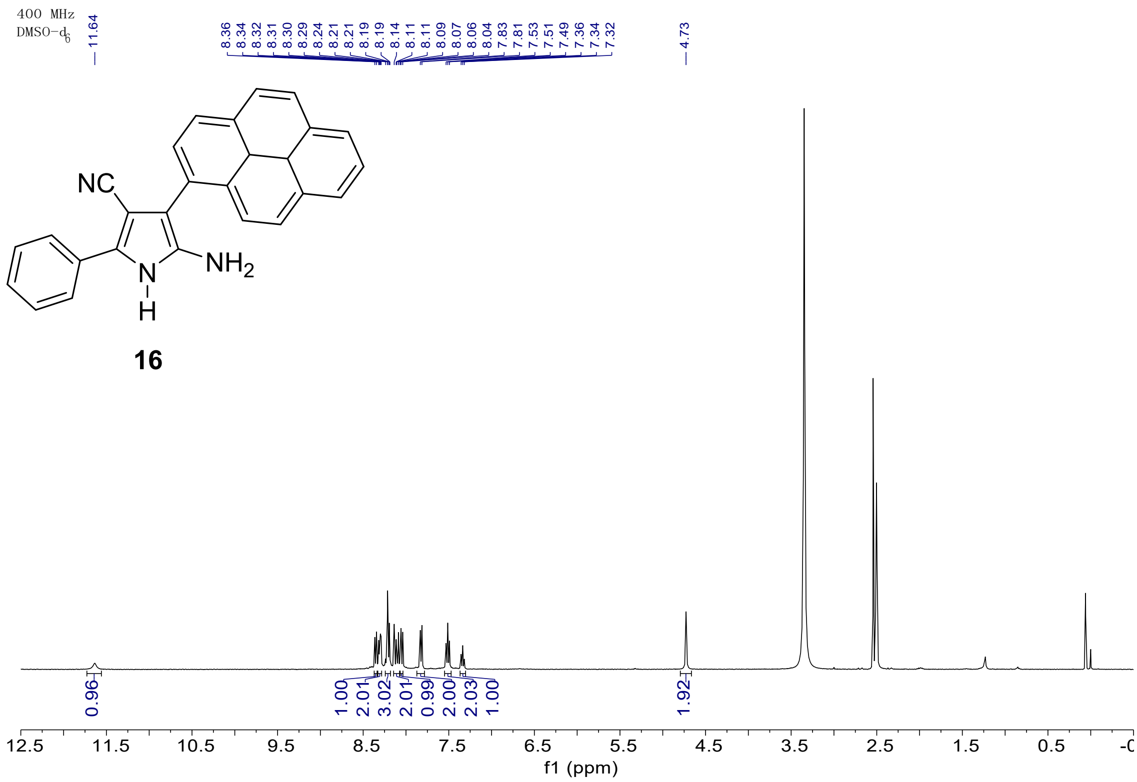
14

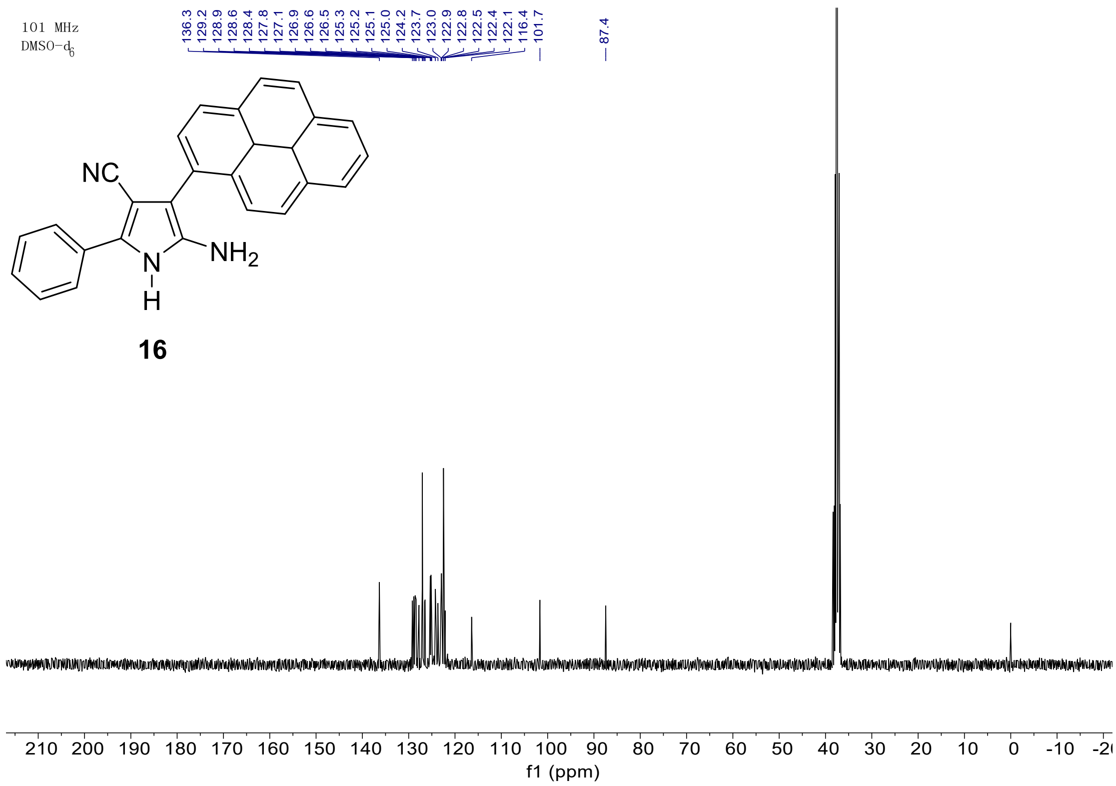

101 MHz
DMSO-d6
139.0 134.8 132.5 131.7 131.1 130.4 129.5 128.9 128.0 127.7 127.5 125.2 118.8
102.3
86.9
Cl
Cl
NC
NH2
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

14


400 MHz
DMSO-d6
11.47
7.96 7.94 7.90 7.88 7.77 7.75 7.72 7.69 7.53 7.51 7.49 7.47 7.46 7.45 7.34 7.33 7.31
5.02
NC
NH2
N
H
15
1.00
2.05 1.99 2.00 1.02 4.12 1.04
2.04
f1 (ppm)


101 MHz
DMSO-d6
138.4 133.9 131.9 131.6 130.7 129.5 128.4 128.1 127.9 127.7 126.6 125.8 125.4 125.1 119.2 105.0
87.4
NC
NH2
N
H
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
DMSO-d_6
11.64
8.36 8.34 8.32 8.31 8.30 8.29 8.24 8.21 8.21 8.19 8.19 8.14 8.11 8.11 8.09 8.07 8.06 8.04 7.83 7.81 7.53 7.51 7.49 7.36 7.34 7.32
4.73
NC
NH2
N
H
16
0.96
1.00 2.01 3.02 2.01 0.99 2.00 2.03 1.00
1.92
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


101 MHz
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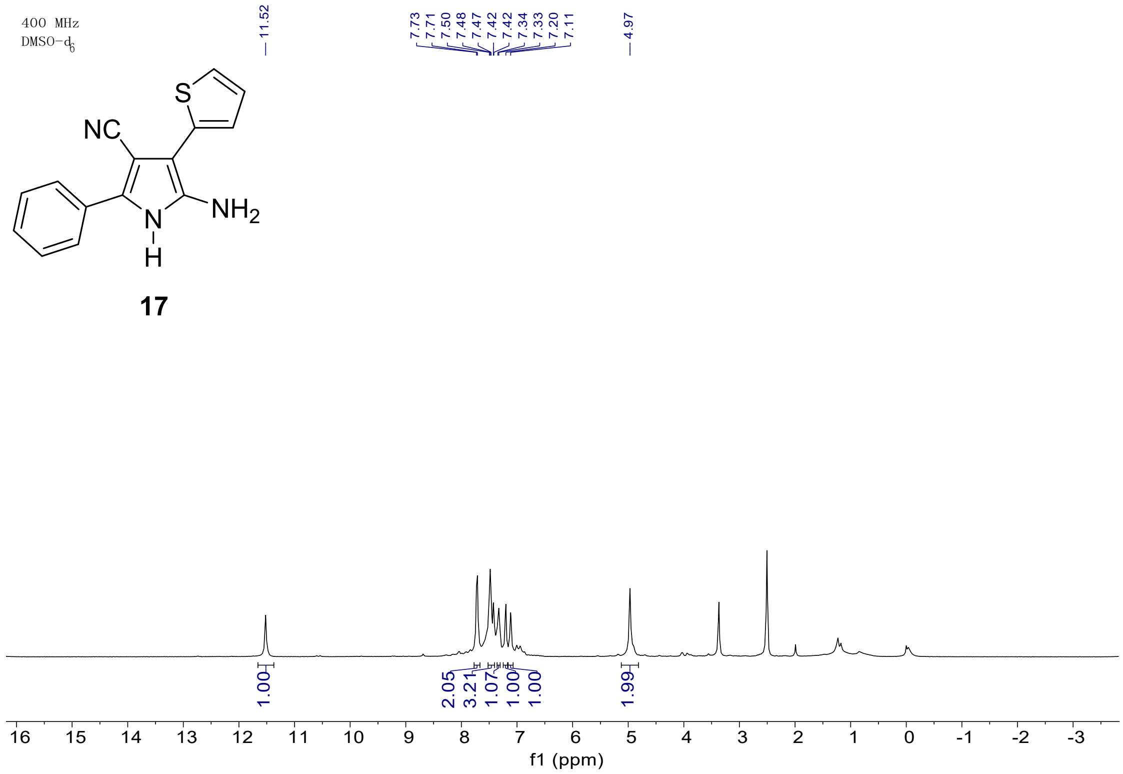
136.3 129.2 128.9 128.6 128.4 127.8 127.1 126.9 126.6 126.5 125.3 125.2 125.1 125.0 124.2 123.7 123.0 122.9 122.8 122.5 122.4 122.1 116.4 101.7
87.4
NC
NH2
N
H
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
DMSO-d6
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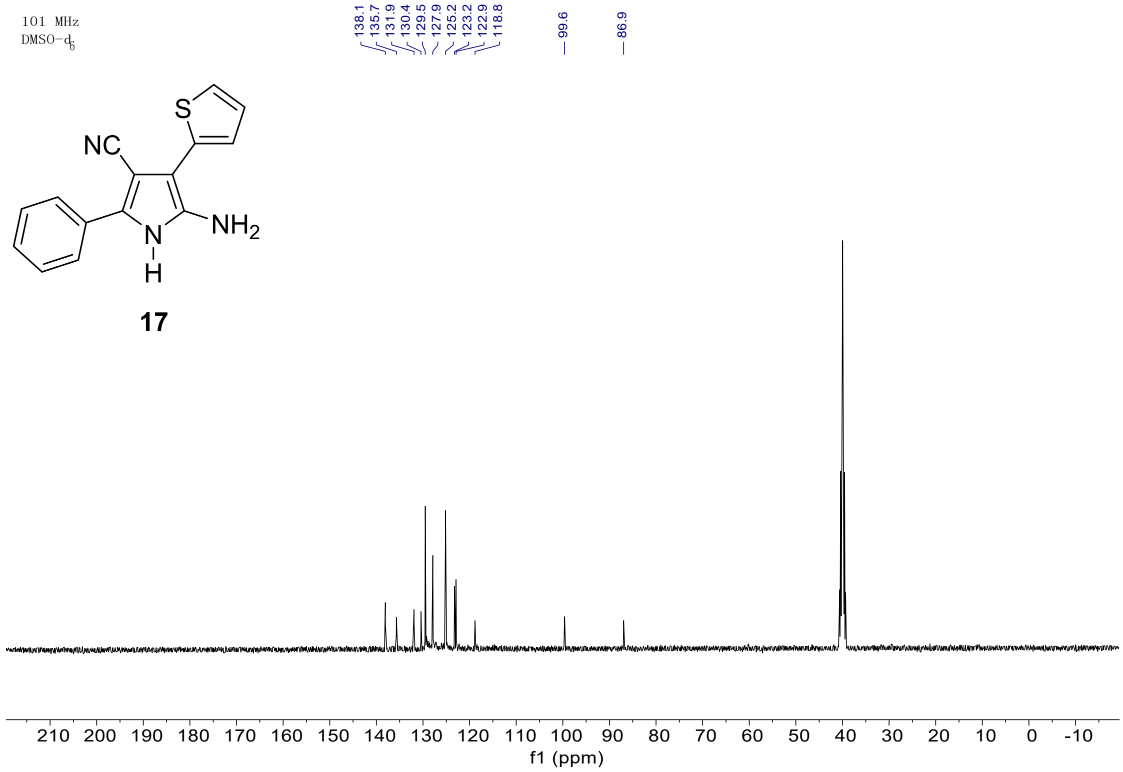
S
NH2
N
H
17
1.00
2.05 3.21 1.07 1.00 1.00
1.99
f1 (ppm)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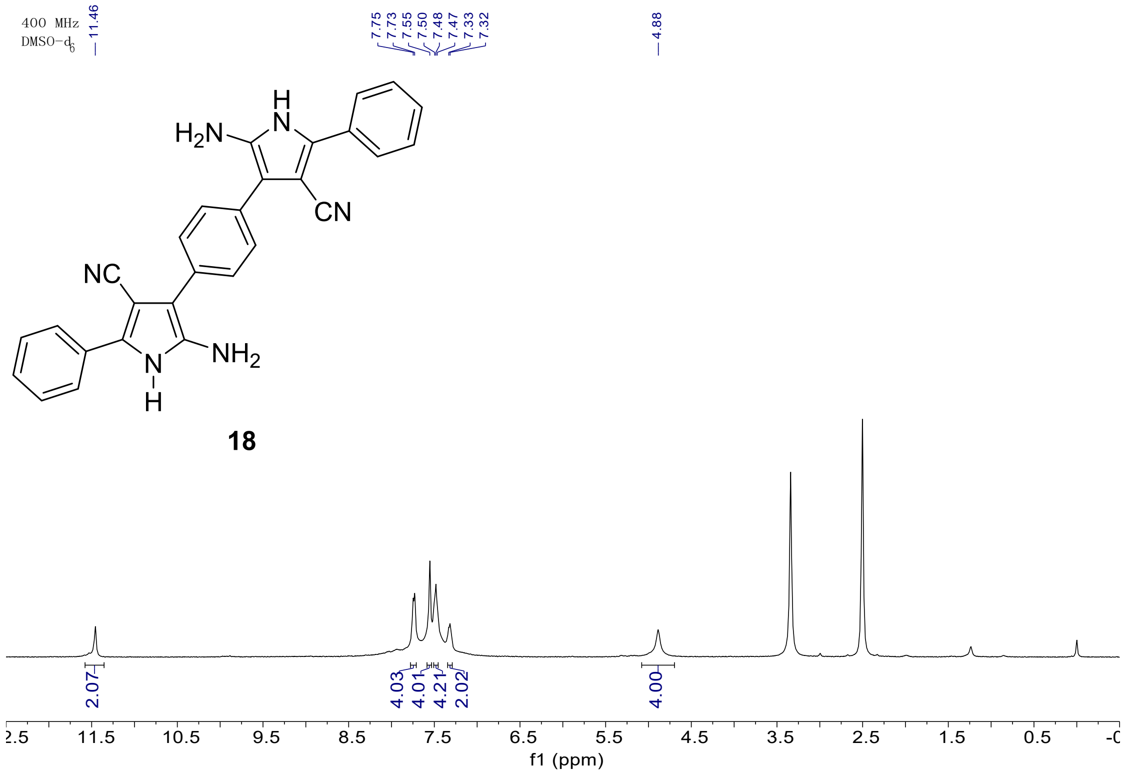
DMSO-d6
138.1 135.7 131.9 130.4 129.5 127.9 125.2 123.2 122.9 118.8
99.6
86.9
NC
S
NH2
N
H
17
f1 (ppm)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DMSO-d6
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7.73
7.55
7.50
7.48
7.47
7.33
7.32
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H2N
NC
CN
NH2
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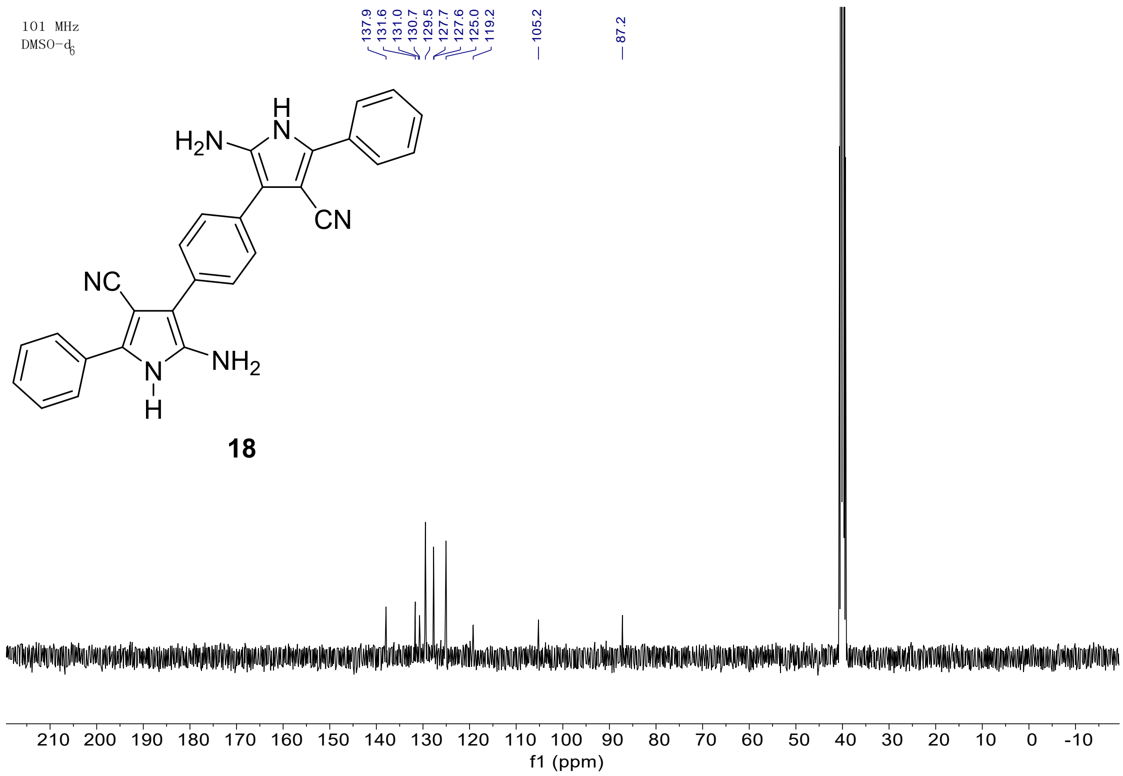
2.07
4.03
4.01
4.21
2.02
4.00
f1 (ppm)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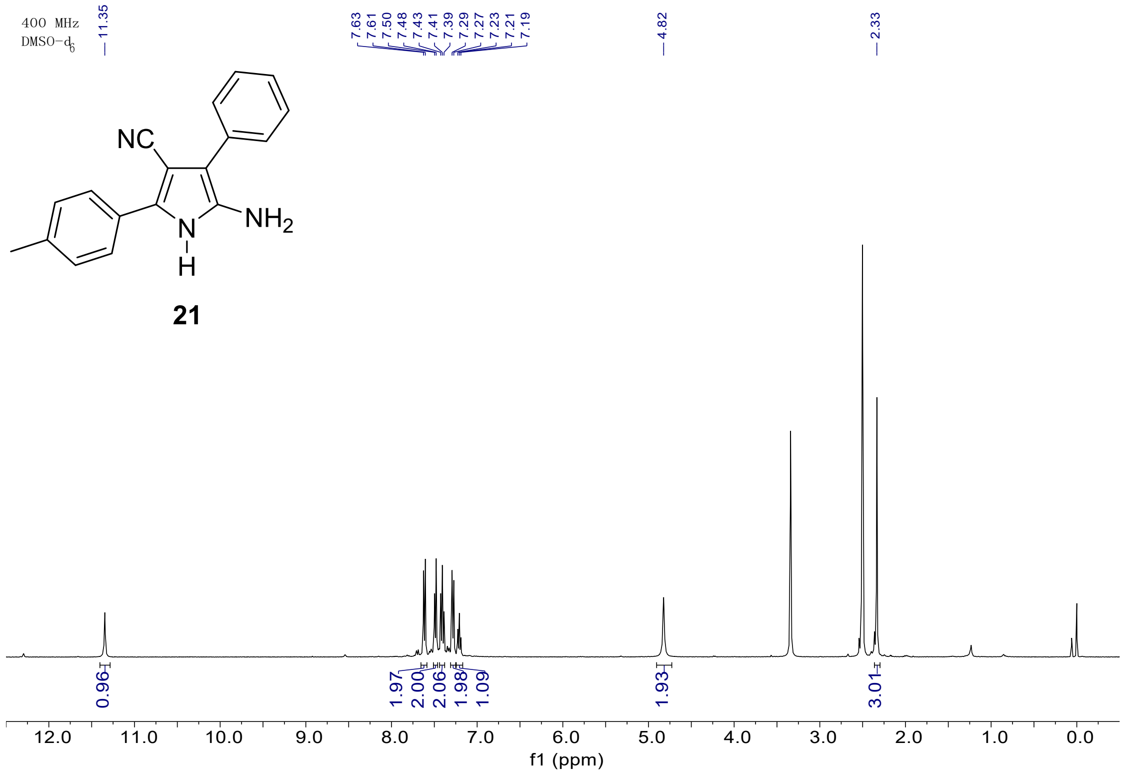
137.9
131.6
131.0
130.7
129.5
127.7
127.6
125.0
119.2
105.2
87.2
H2N
NC
CN
NH2
18
f1 (ppm)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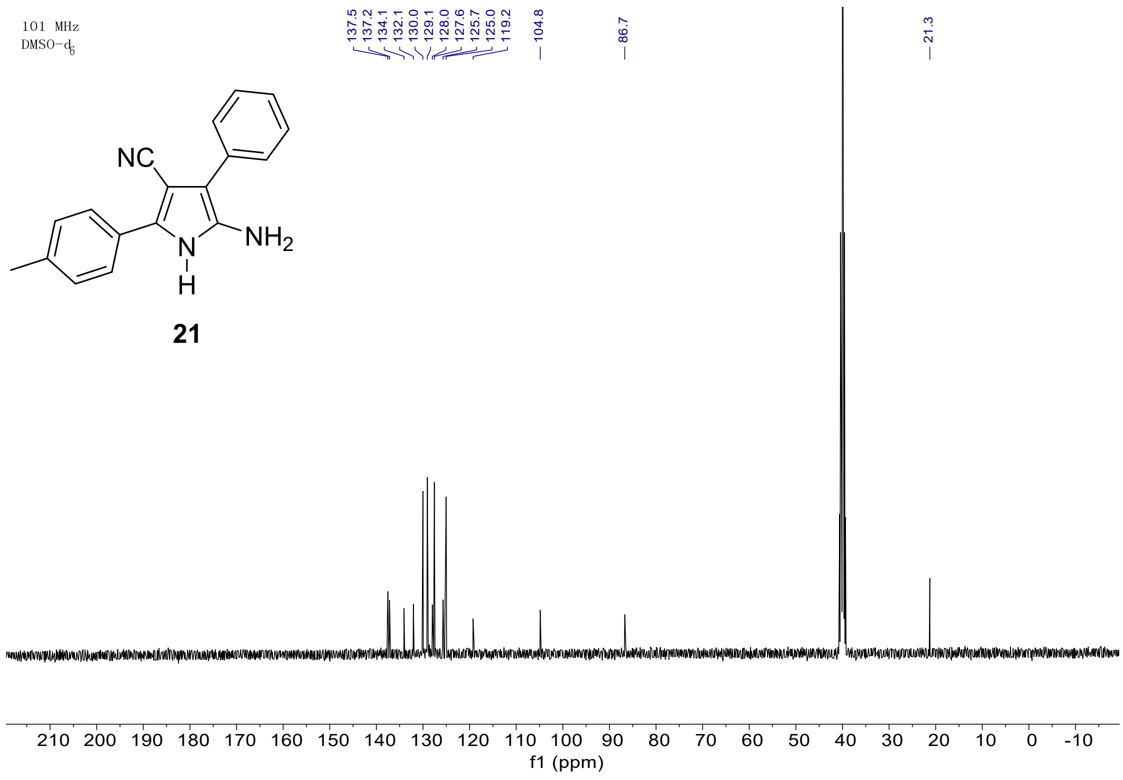
7.63
7.61
7.50
7.48
7.43
7.41
7.39
7.29
7.27
7.23
7.21
7.19
4.82
2.33
NC
NH2
N
H
21
0.96
1.97
2.00
2.06
1.98
1.09
1.93
3.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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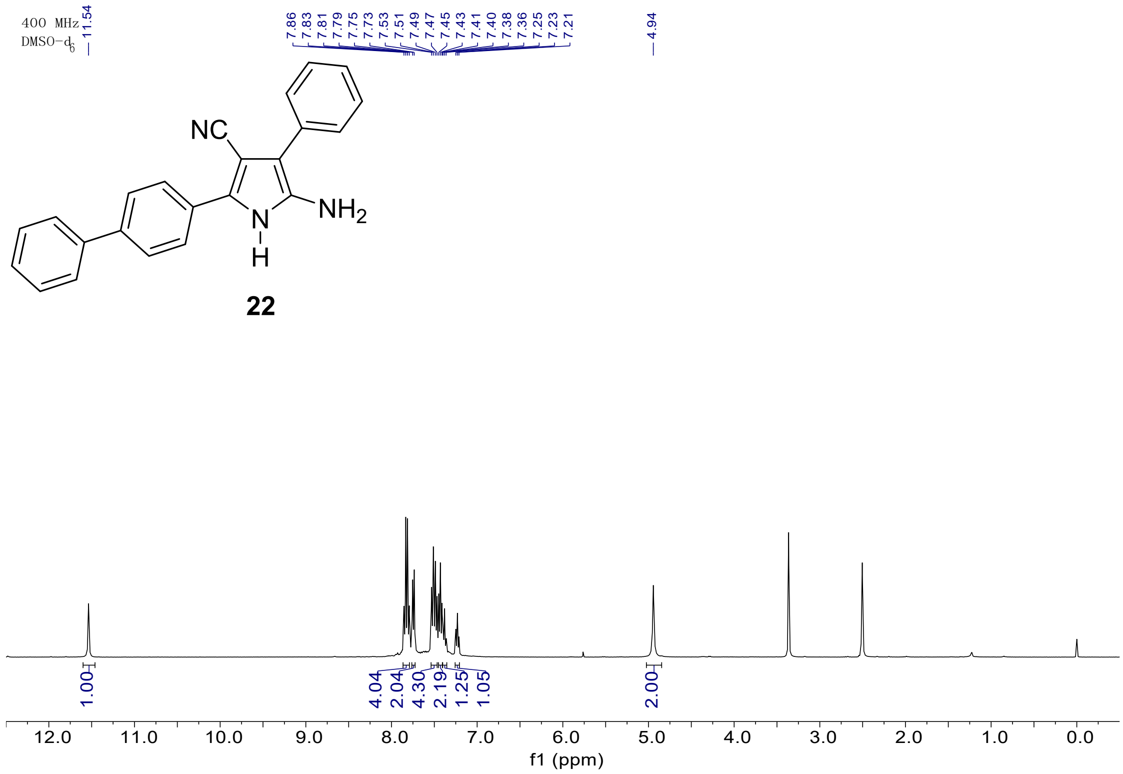
137.2
134.1
132.1
130.0
129.1
128.0
127.6
125.7
125.0
119.2
104.8
86.7
21.3
NC
NH2
N
H
21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


400 MHz
DMSO-d6
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4.94
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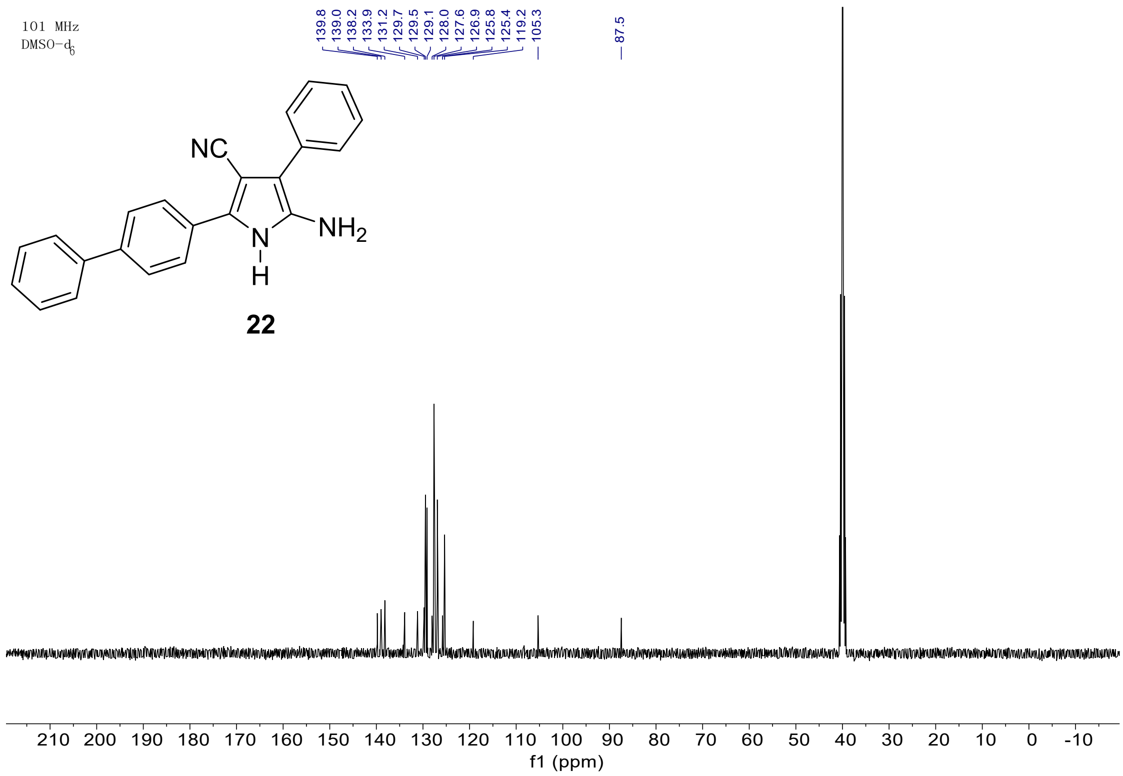
NH2
N
H
22
1.00
4.04 2.04 4.30 2.19 1.25 1.05
2.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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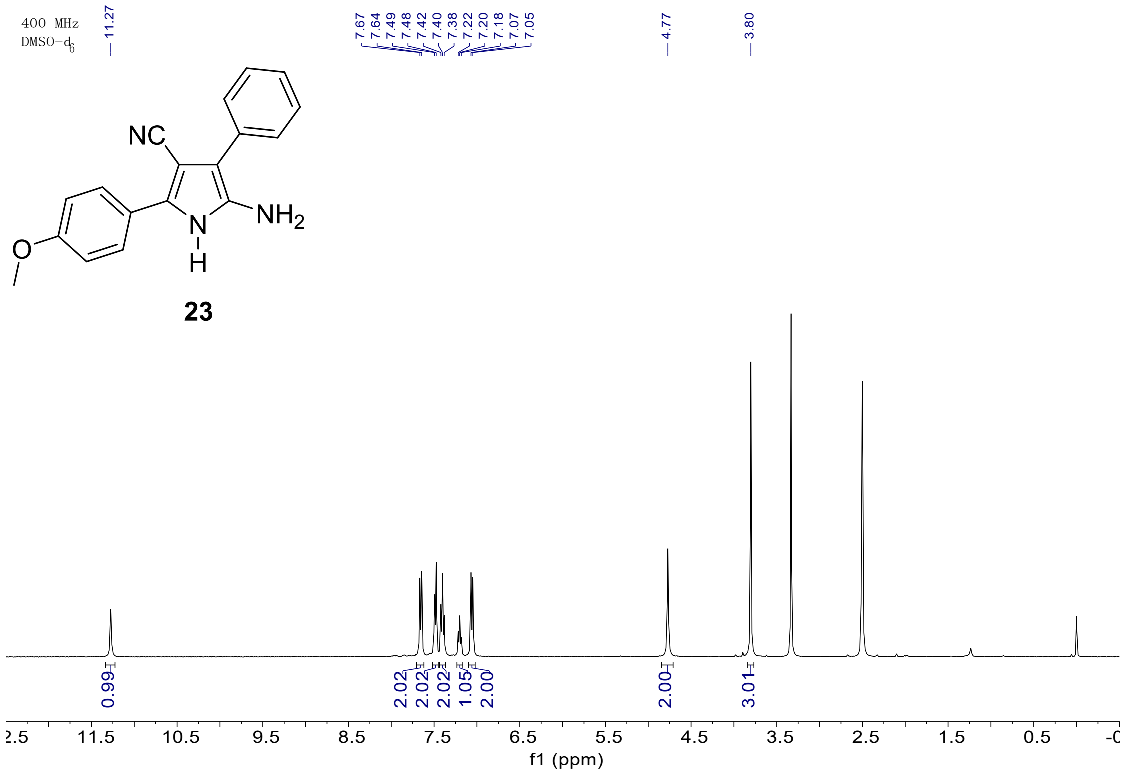
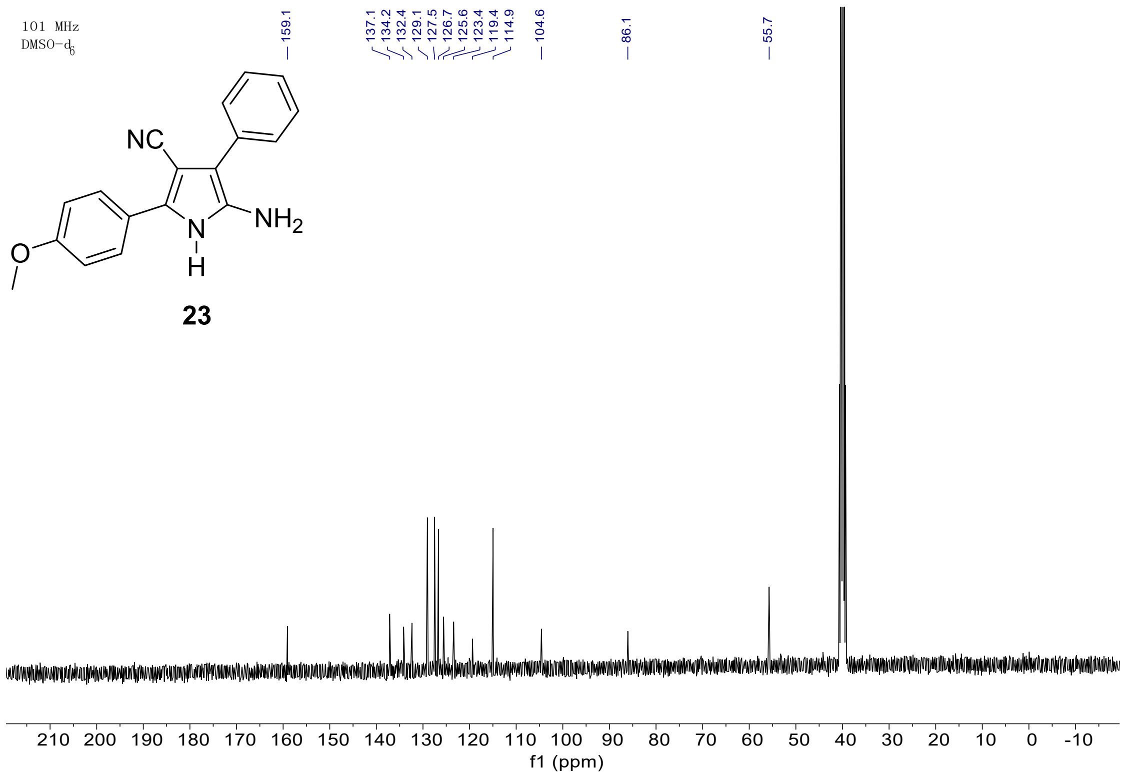
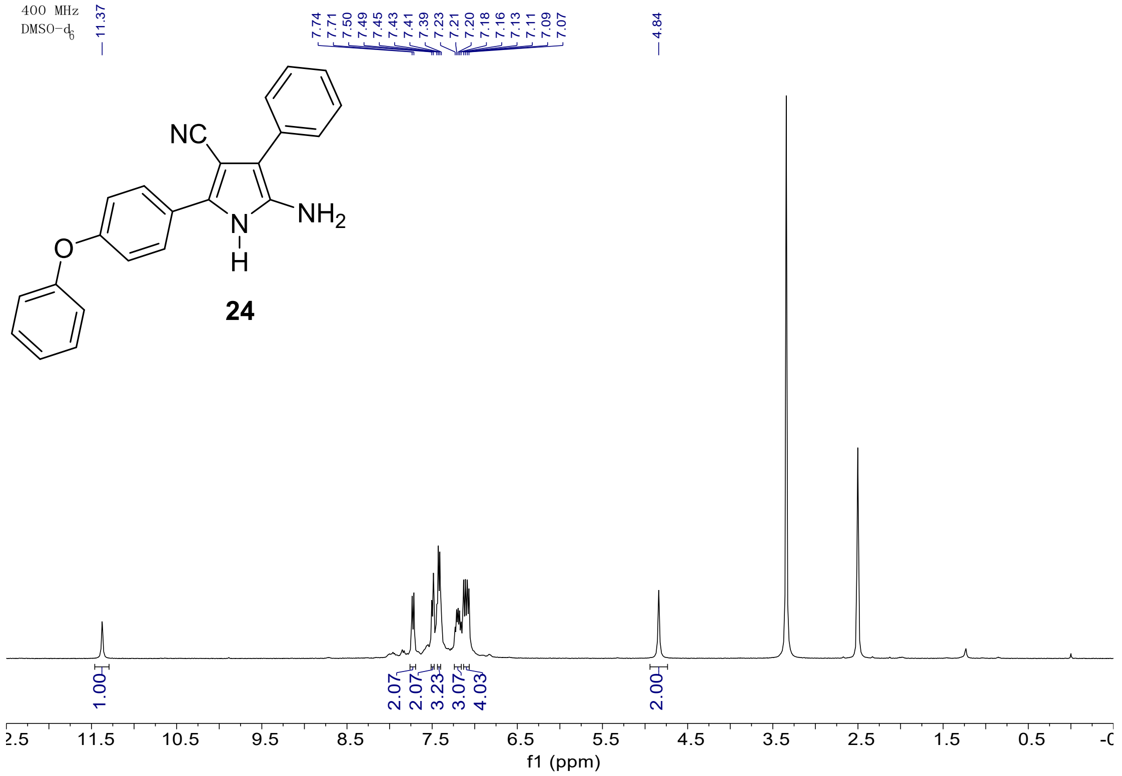
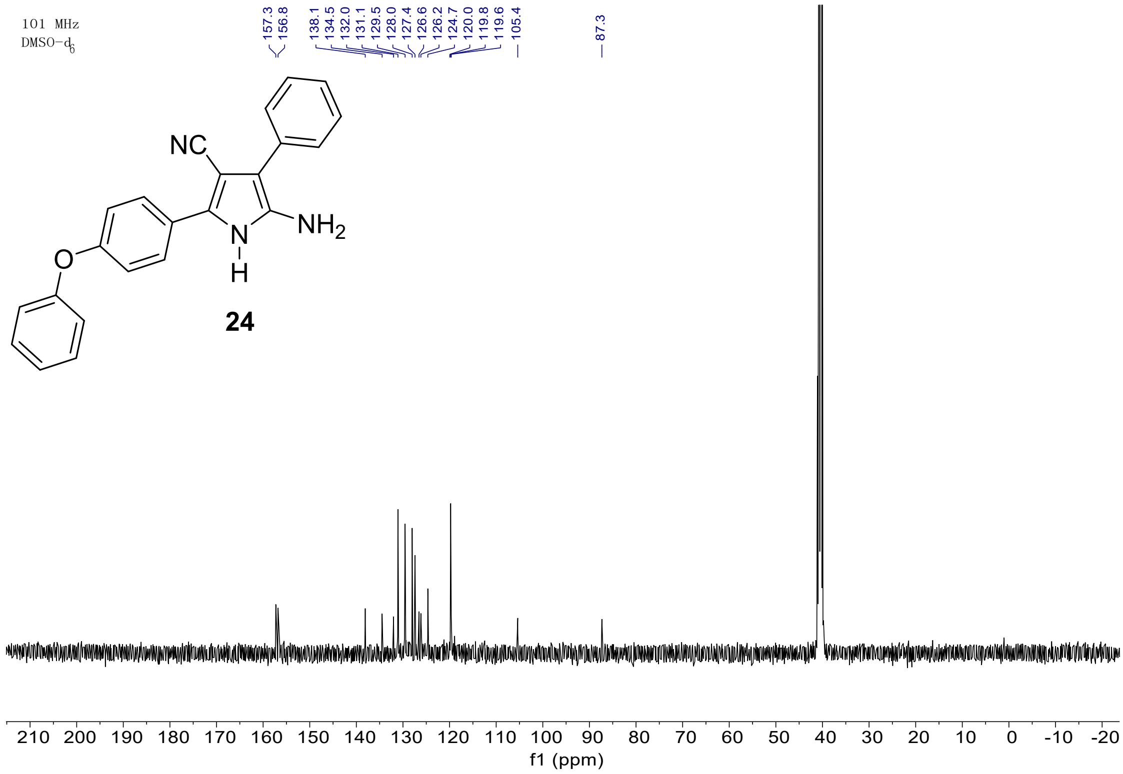
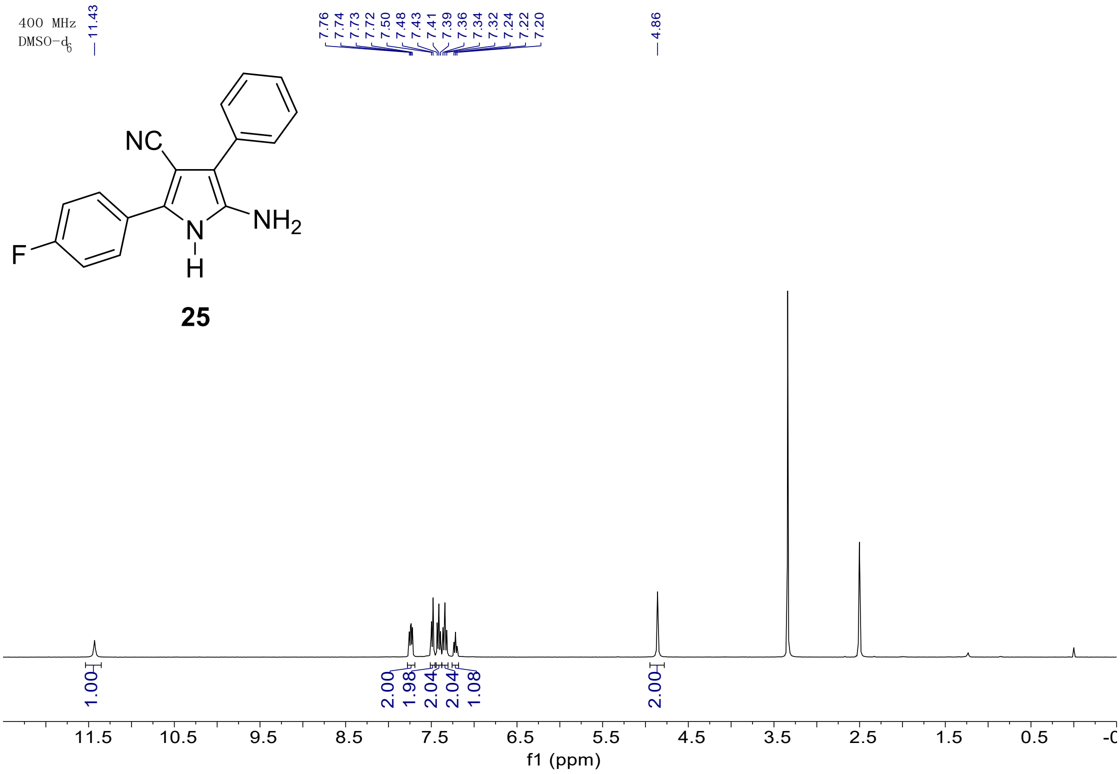
DMSO-d6
139.8 139.0 138.2 133.9 131.2 129.7 129.5 129.1 128.0 127.6 126.9 125.8 125.4 119.2 105.3
87.5
NC
NH2
N
H
22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
DMSO-d6
11.27
7.67
7.64
7.49
7.48
7.42
7.40
7.38
7.22
7.20
7.18
7.07
7.05
4.77
3.80
NC
NH2
N
H
23
0.99
2.02
2.02
2.02
1.05
2.00
2.00
3.01
2.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


101 MHz
DMSO-d6
159.1
137.1
134.2
132.4
129.1
127.5
126.7
125.6
123.4
119.4
114.9
104.6
86.1
55.7
NC
NH2
N
H
23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


400 MHz
DMSO-d6
11.37
7.74 7.71 7.50 7.49 7.45 7.43 7.41 7.39 7.23 7.21 7.20 7.18 7.16 7.13 7.11 7.09 7.07
4.84
NC
NH2
N
H
24
1.00
2.07
2.07
3.23
3.07
4.03
2.00
f1 (ppm)


101 MHz
DMSO-d6
157.3 156.8
138.1 134.5 132.0 131.1 129.5 128.0 127.4 126.6 126.2 124.7 120.0 119.8 119.6
105.4
87.3
NC
NH2
N
H
24
f1 (ppm)


400 MHz
DMSO-d6
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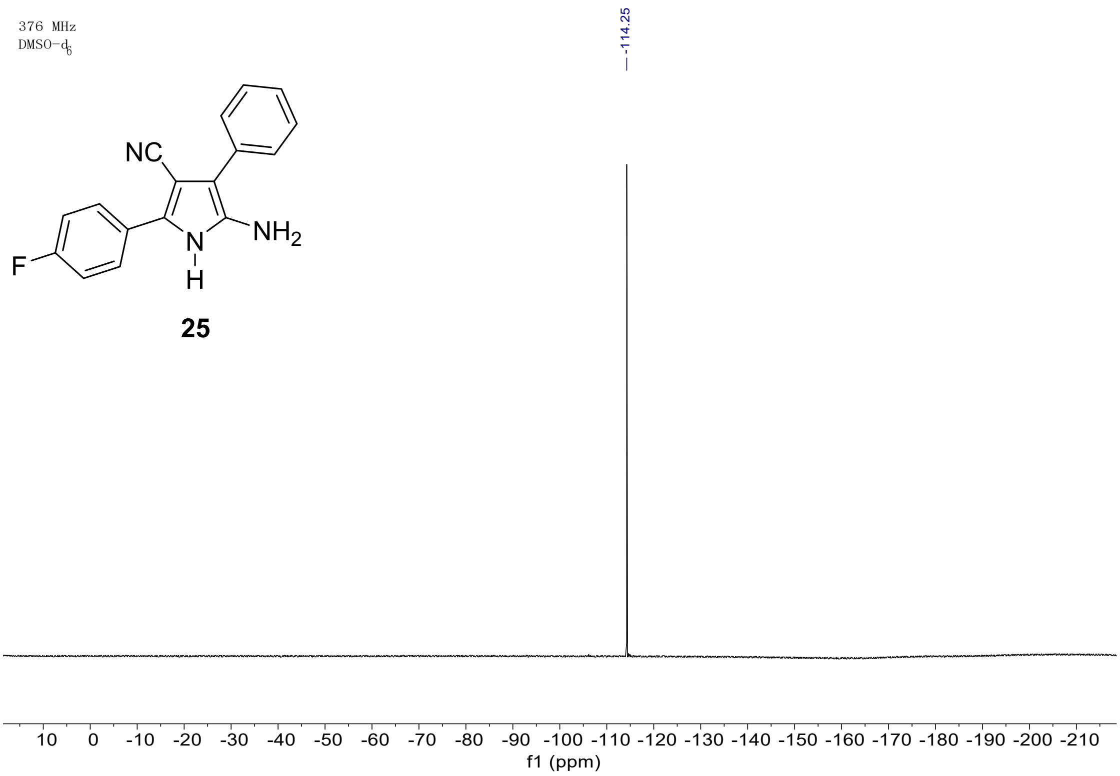
7.76
7.74
7.73
7.72
7.50
7.48
7.43
7.41
7.39
7.36
7.34
7.32
7.24
7.22
7.20
4.86
NC
NH2
F
N
H
25
1.00
2.00
1.98
2.04
2.04
1.08
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


376 MHz
DMSO-d6
-114.25
NC
NH2
F
N
H
25
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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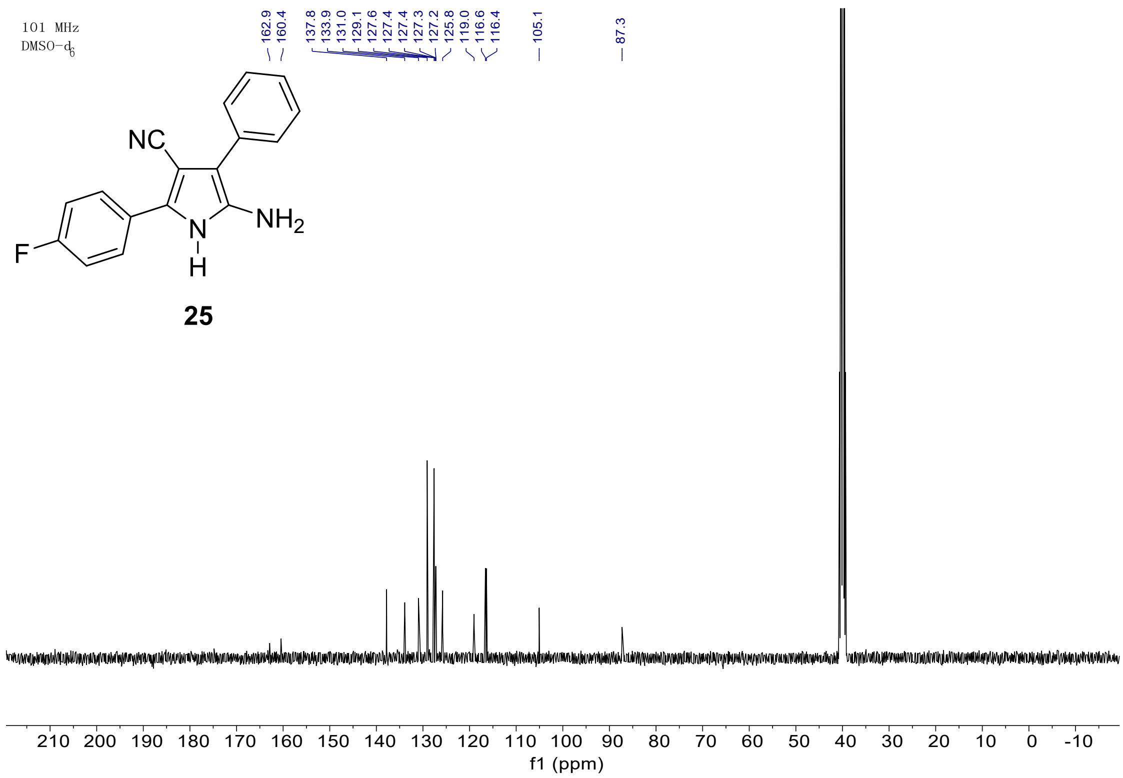
-200
-210
f1 (ppm)


101 MHz
DMSO-d6
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160.4
137.8
133.9
131.0
129.1
127.6
127.4
127.4
127.3
127.2
125.8
119.0
116.6
116.4
105.1
87.3
NC
NH2
F
N
H
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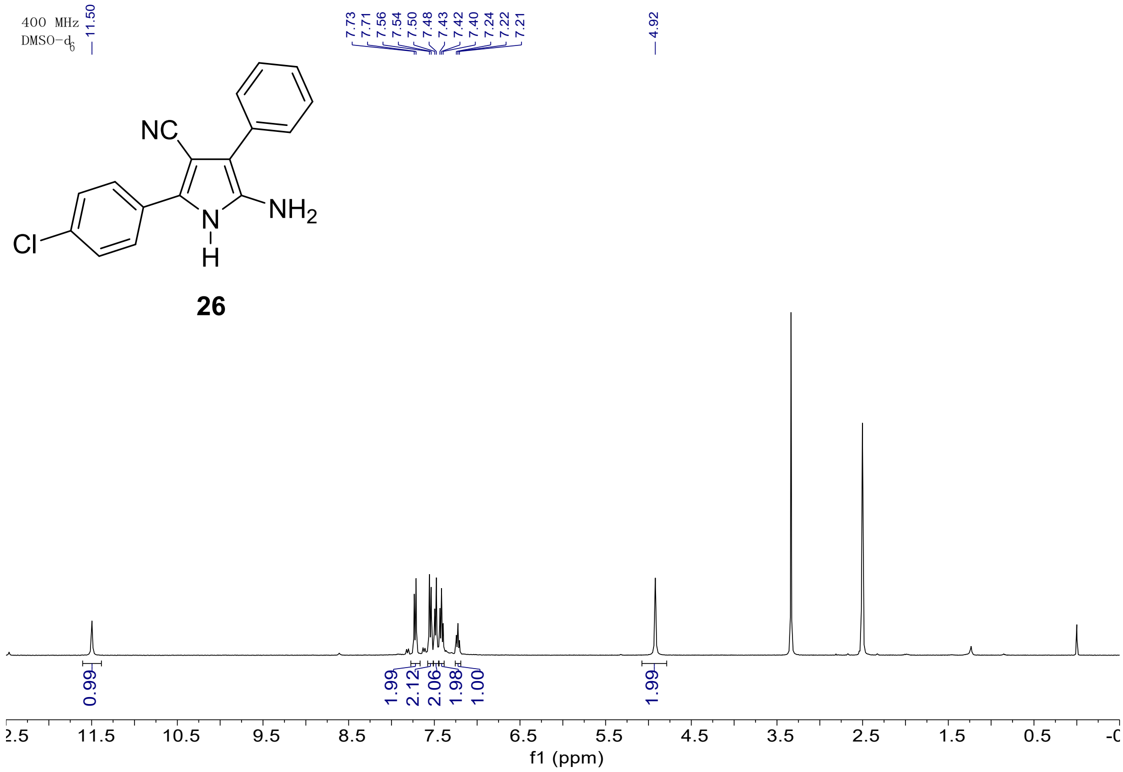
f1 (ppm)


400 MHz
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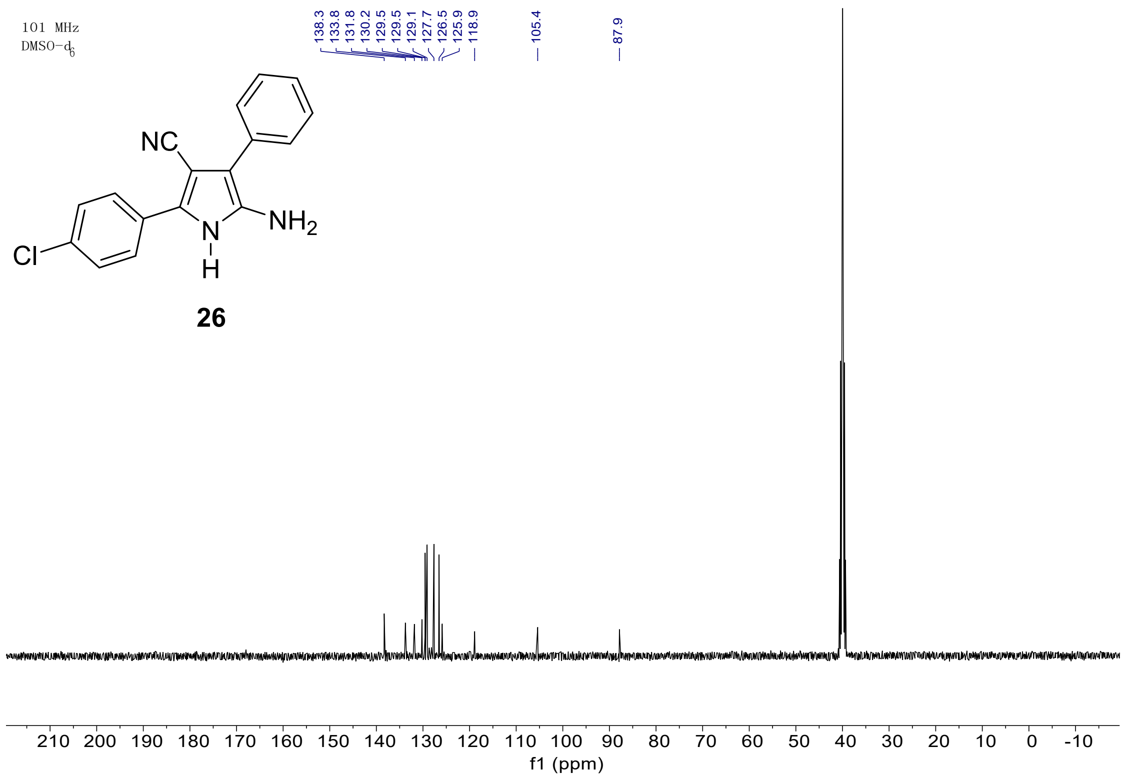
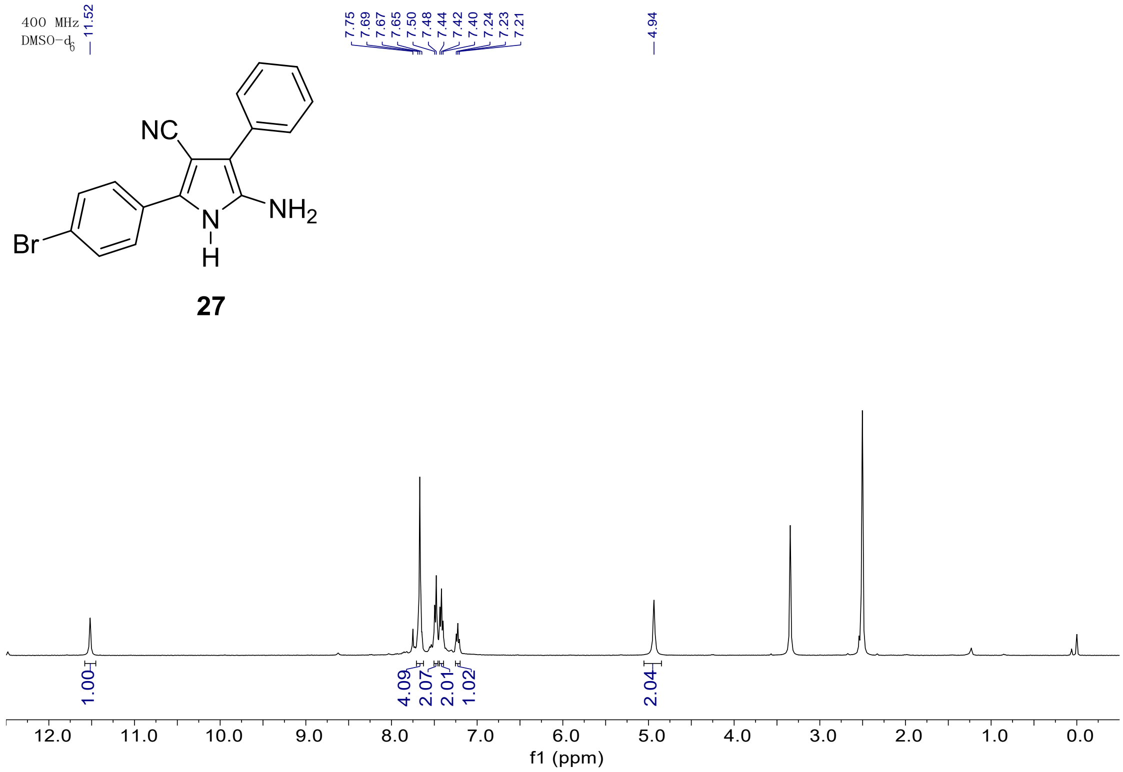
7.71
7.56
7.54
7.50
7.48
7.43
7.42
7.40
7.24
7.22
7.21
4.92
NC
NH2
Cl
N
H
26
0.99
1.99
2.12
2.06
1.98
1.00
1.99
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


101 MHz
DMSO-d6
138.3
133.8
131.8
130.2
129.5
129.5
129.1
127.7
126.5
125.9
118.9
105.4
87.9
NC
NH2
Cl
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

26


400 MHz
DMSO-d6
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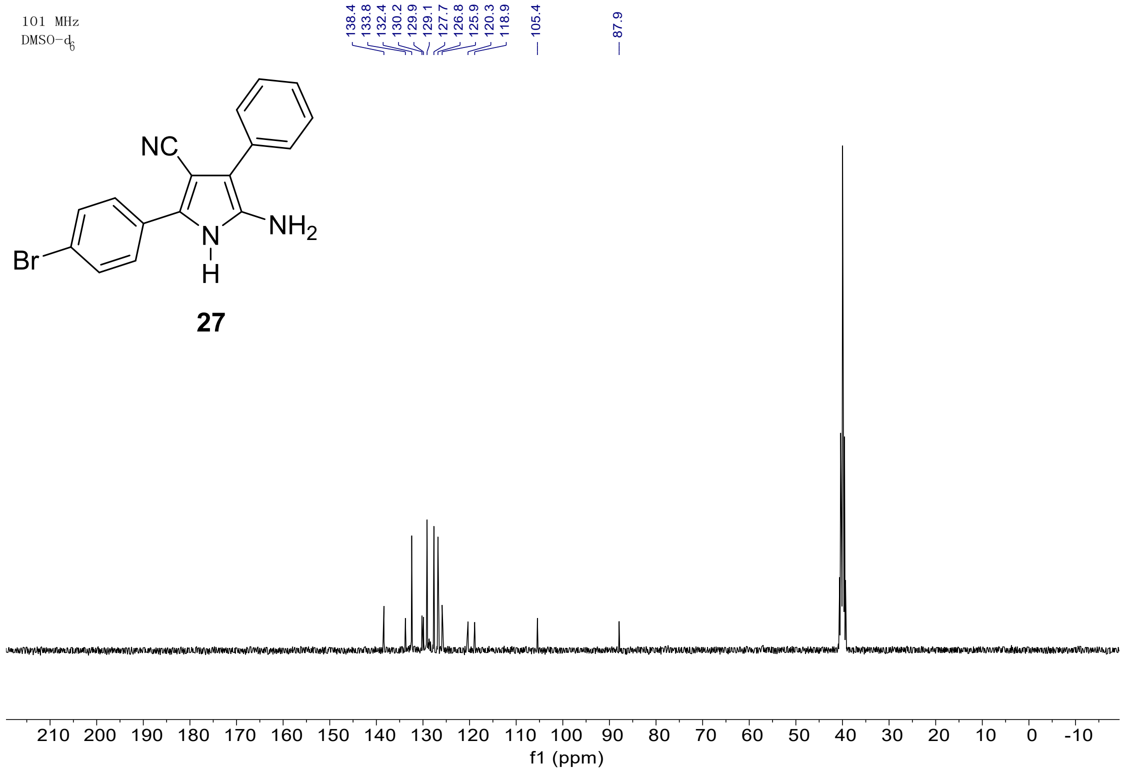
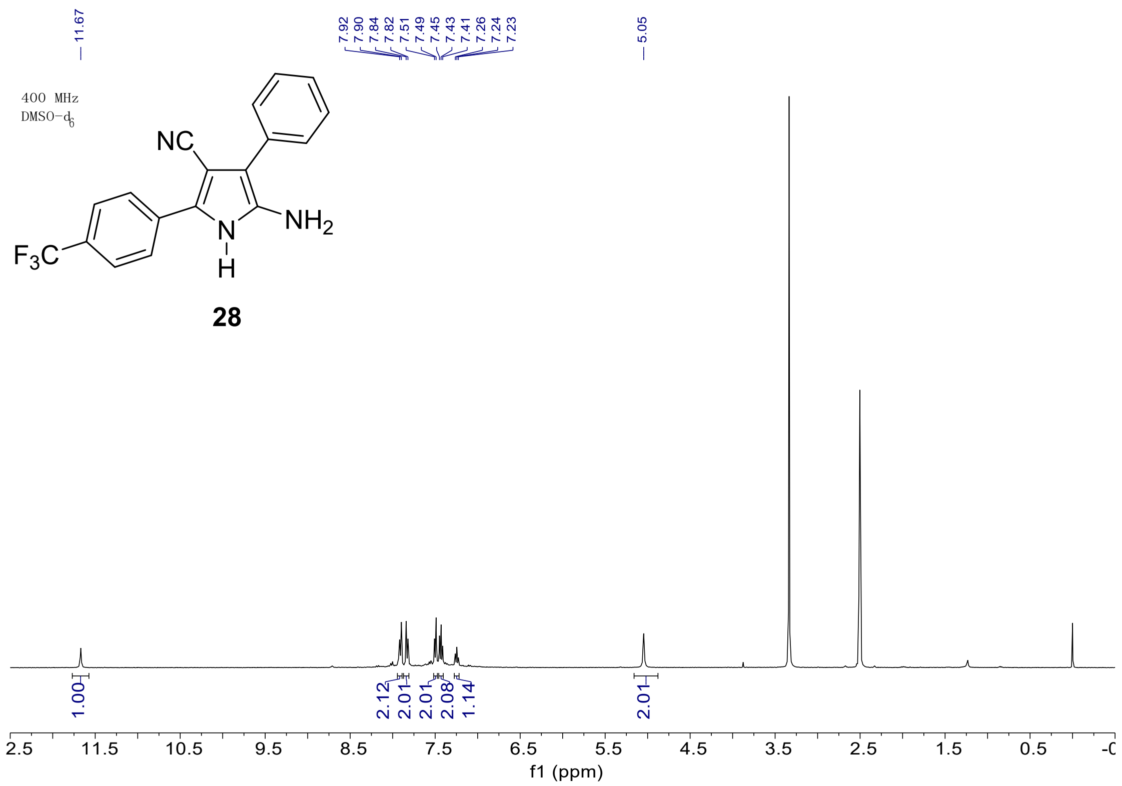
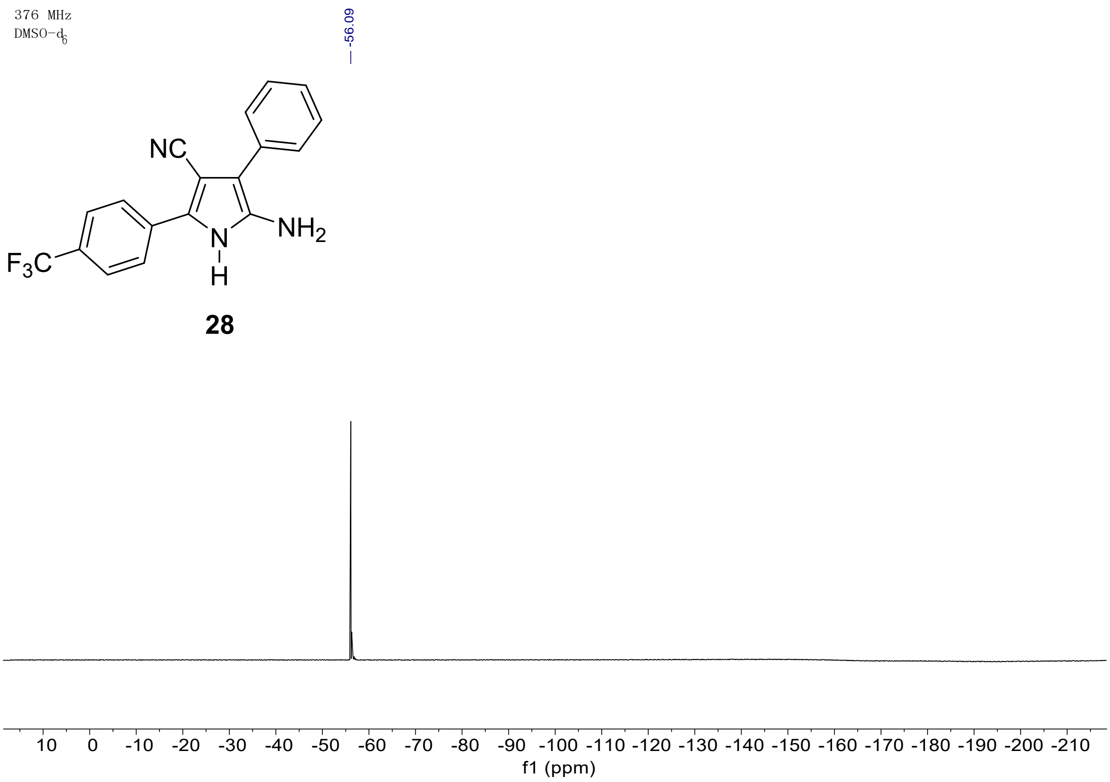
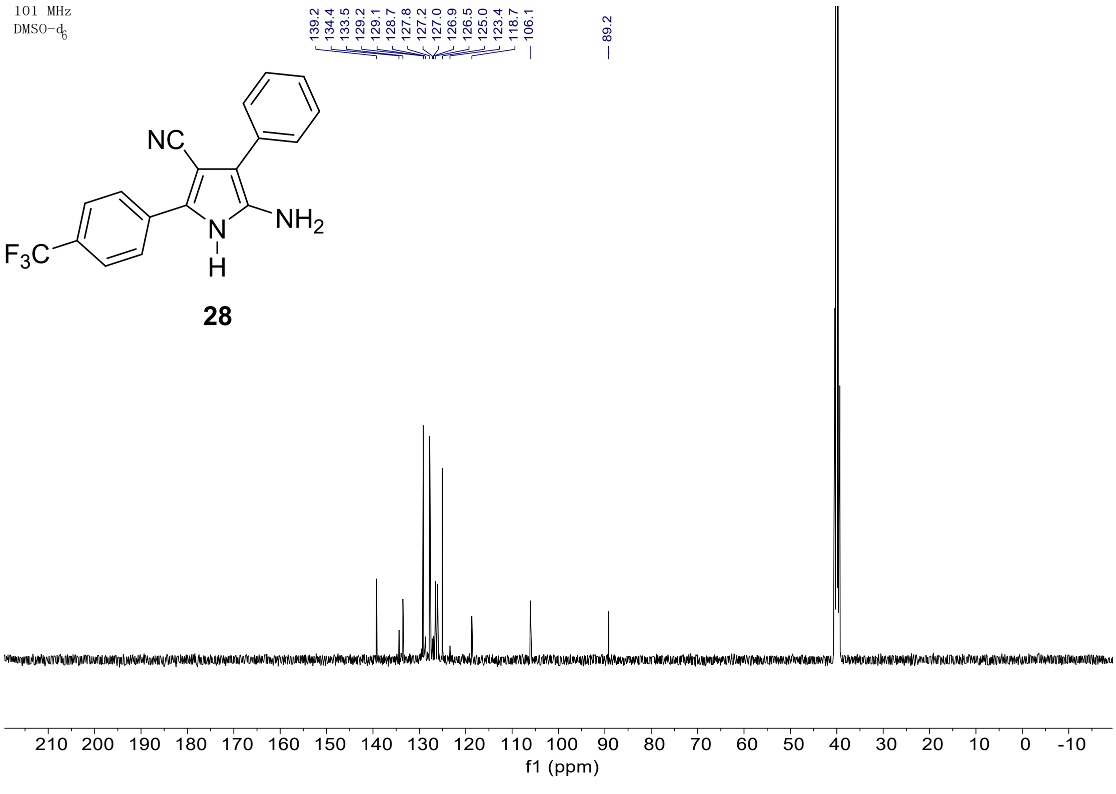
7.75
7.69
7.67
7.65
7.50
7.48
7.44
7.42
7.40
7.24
7.23
7.21
4.94
NC
NH2
Br
N
H
1.00
4.09
2.07
2.01
1.02
2.04
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

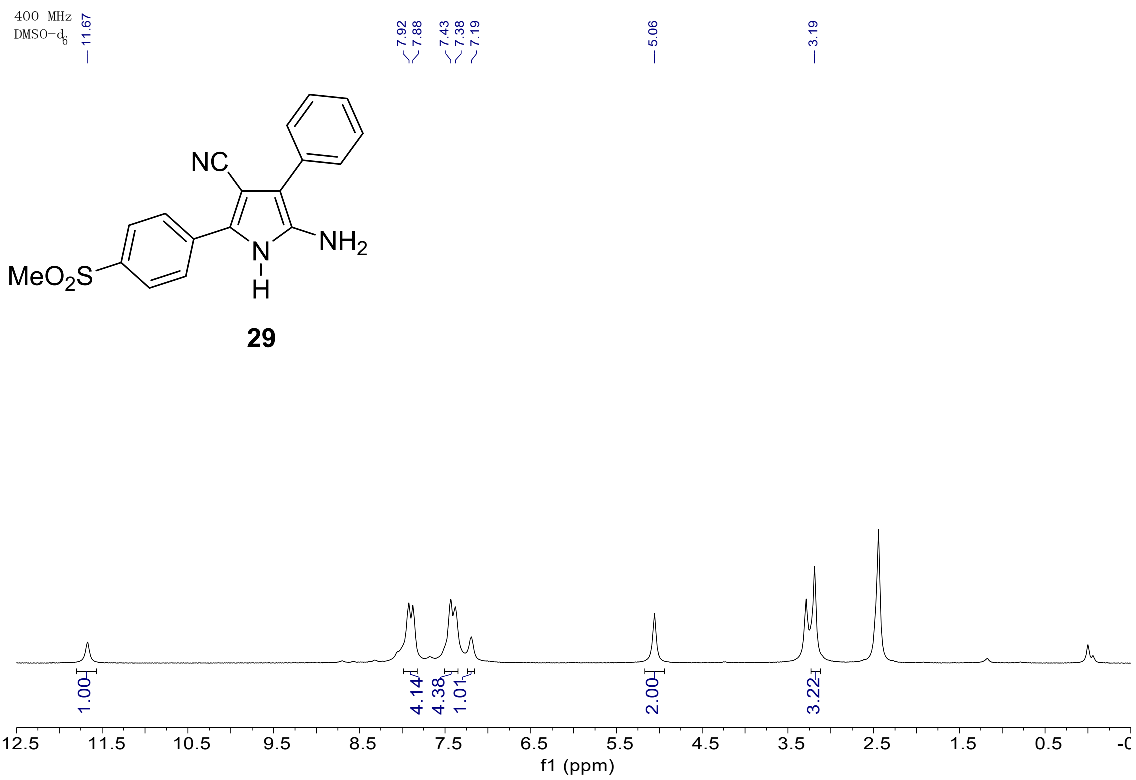
27

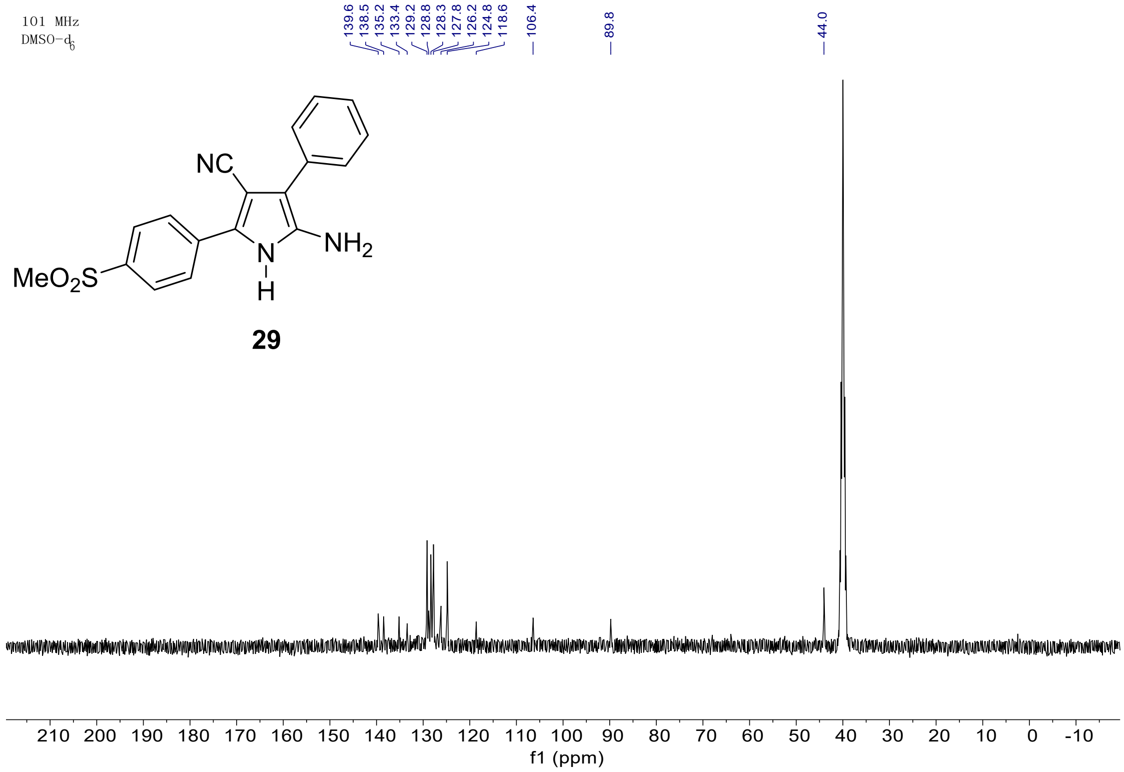

101 MHz
DMSO-d6
138.4 133.8 132.4 130.2 129.9 129.1 127.7 126.8 125.9 120.3 118.9
105.4
87.9
NC
NH2
Br
N
H
27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

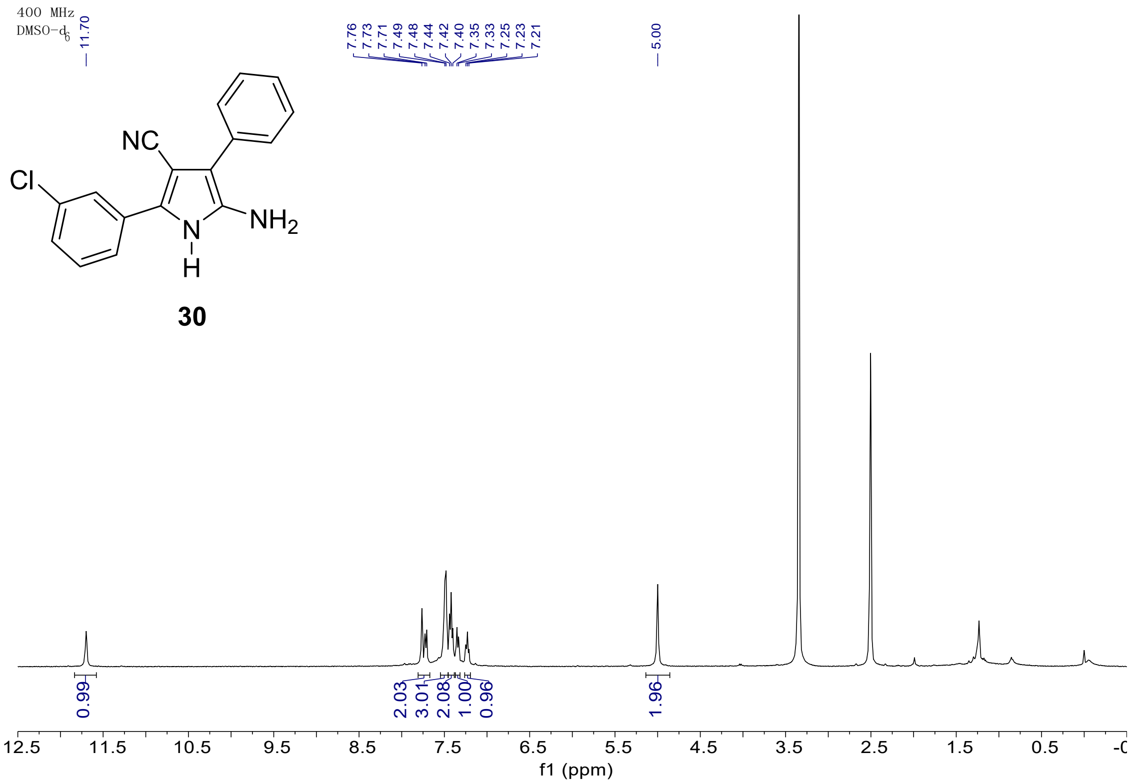

11.67
7.92 7.90 7.84 7.82 7.51 7.49 7.45 7.43 7.41 7.26 7.24 7.23
5.05
400 MHz
DMSO-d6
NC
NH2
F3C
N
H
28
1.00
2.12 2.01 2.01 2.08 1.14
2.01
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

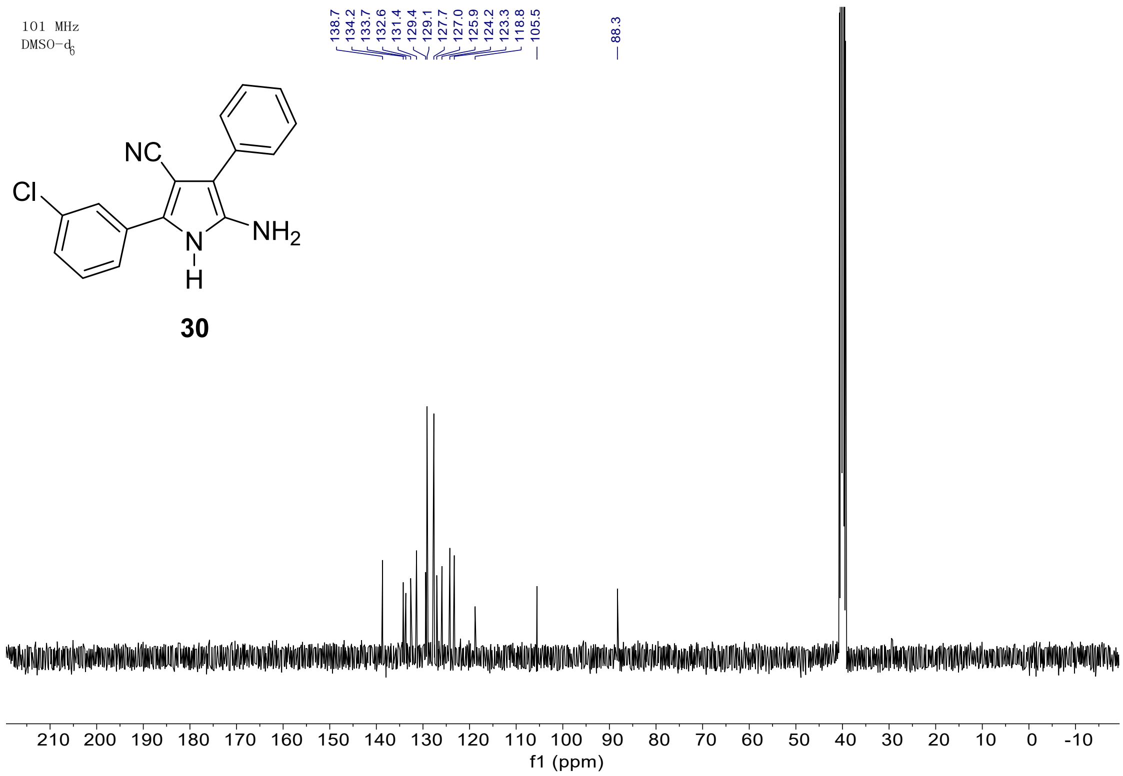

376 MHz
DMSO-d6
-56.09
NC
NH2
F3C
N
H
28
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

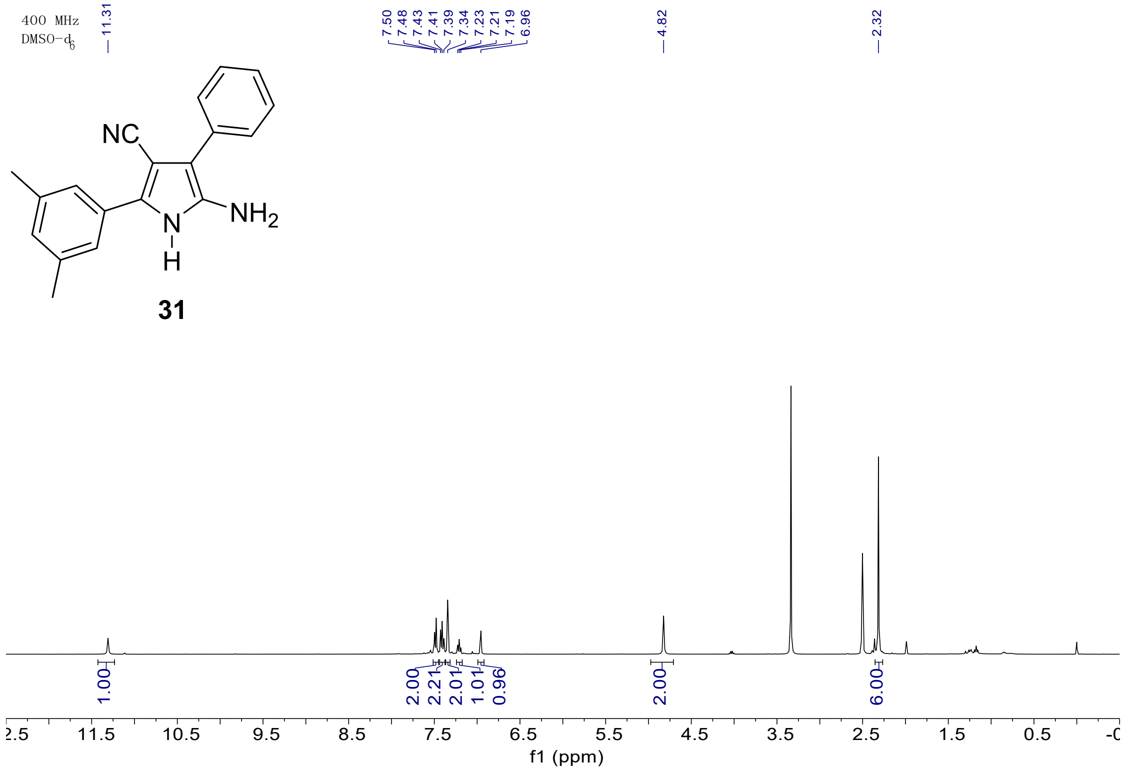

101 MHz
DMSO-d6
139.2
134.4
133.5
129.2
129.1
128.7
127.8
127.2
127.0
126.9
126.5
125.0
123.4
118.7
106.1
89.2
NC
NH2
F3C
N
H
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

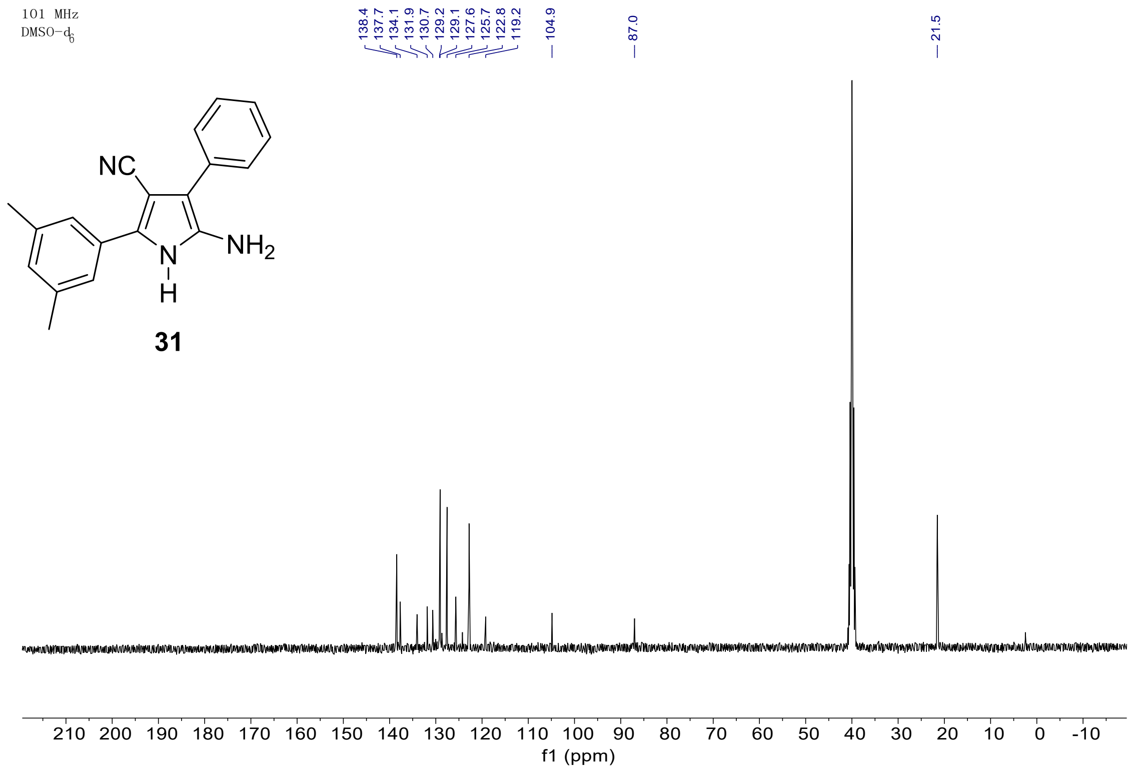

400 MHz
DMSO-d_6
11.67
7.92
7.88
7.43
7.38
7.19
5.06
3.19
NC
NH_2
MeO_2S
N
H
29
1.00
4.14
4.38
1.01
2.00
3.22
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

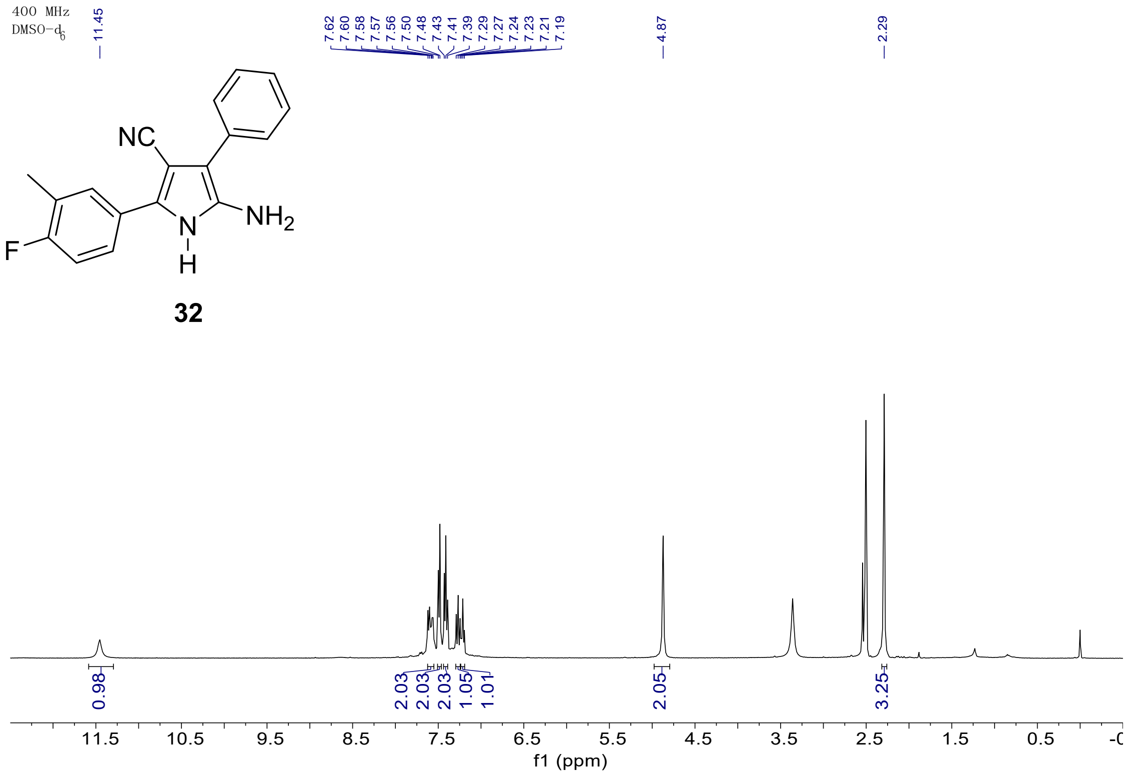

101 MHz
DMSO-d_6
139.6
138.5
135.2
133.4
129.2
128.8
128.3
127.8
126.2
124.8
118.6
106.4
89.8
44.0
NC
NH_2
MeO_2S
N
H
29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

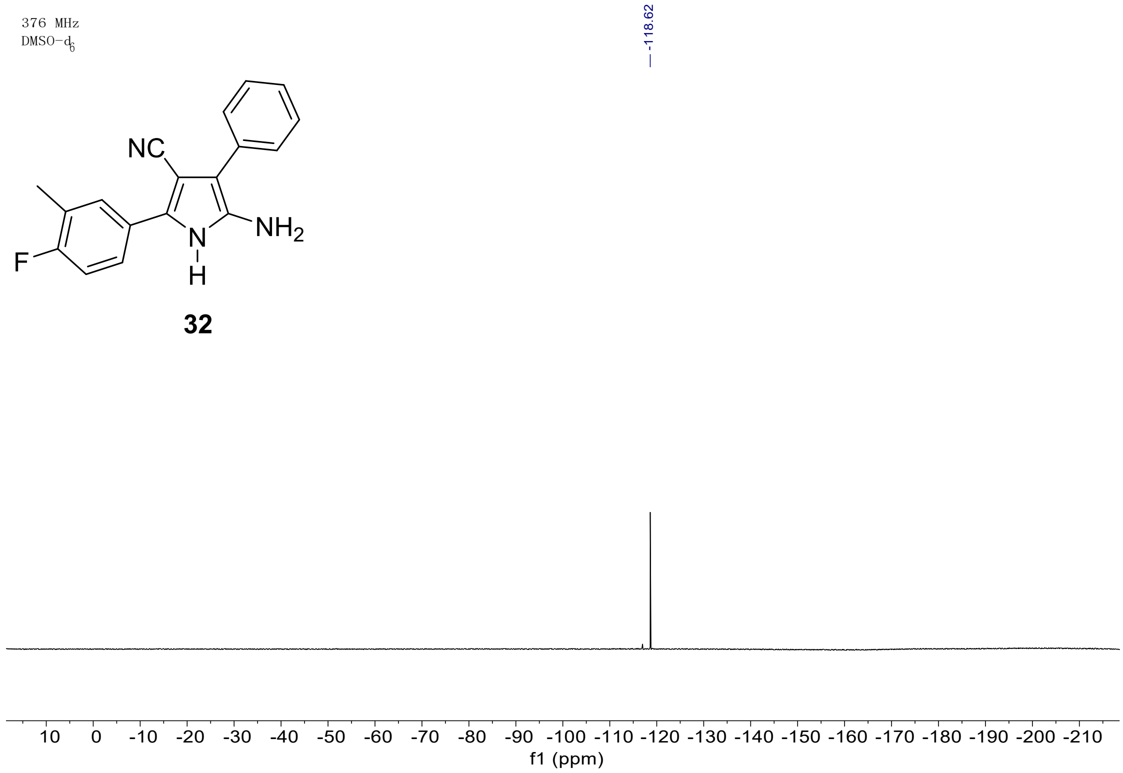

400 MHz
DMSO-d6
11.70
7.76 7.73 7.71 7.49 7.48 7.44 7.42 7.40 7.35 7.33 7.25 7.23 7.21
5.00
NC
Cl
NH2
N
H
30
0.99
2.03 3.01 2.08 1.00 0.96
1.96
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

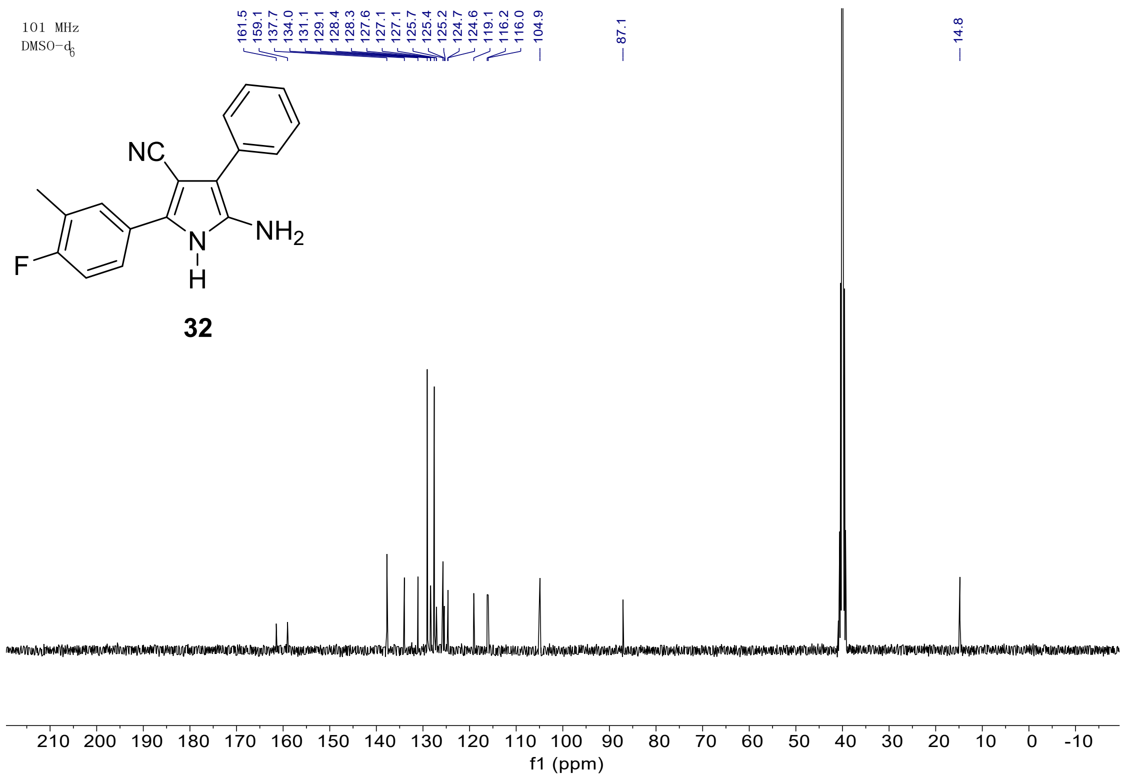

101 MHz
DMSO-d6
138.7 134.2 133.7 132.6 131.4 129.4 129.1 127.7 127.0 125.9 124.2 123.3 118.8 105.5
88.3
NC
Cl
NH2
N
H
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

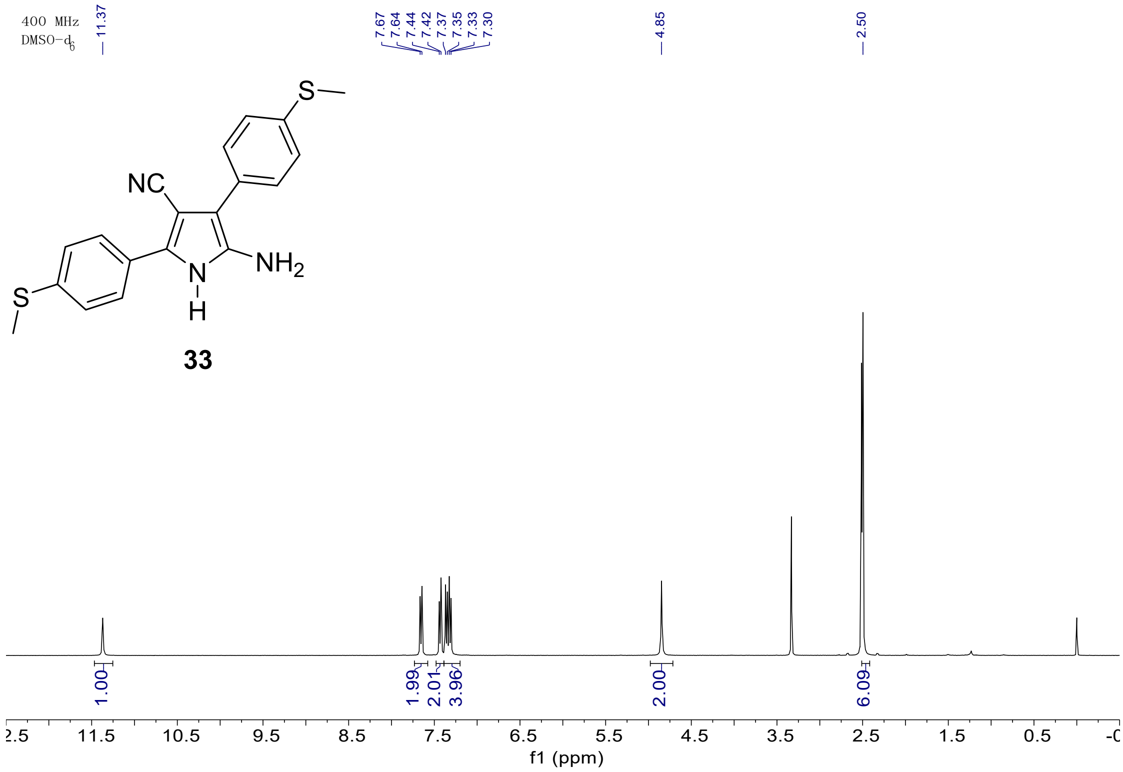

400 MHz
DMSO-d6
11.31
7.50 7.48 7.43 7.41 7.39 7.34 7.23 7.21 7.19 6.96
4.82
2.32
NC
NH2
N
H
31
1.00
2.00 2.21 2.01 1.01 0.96
2.00
6.00
2.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

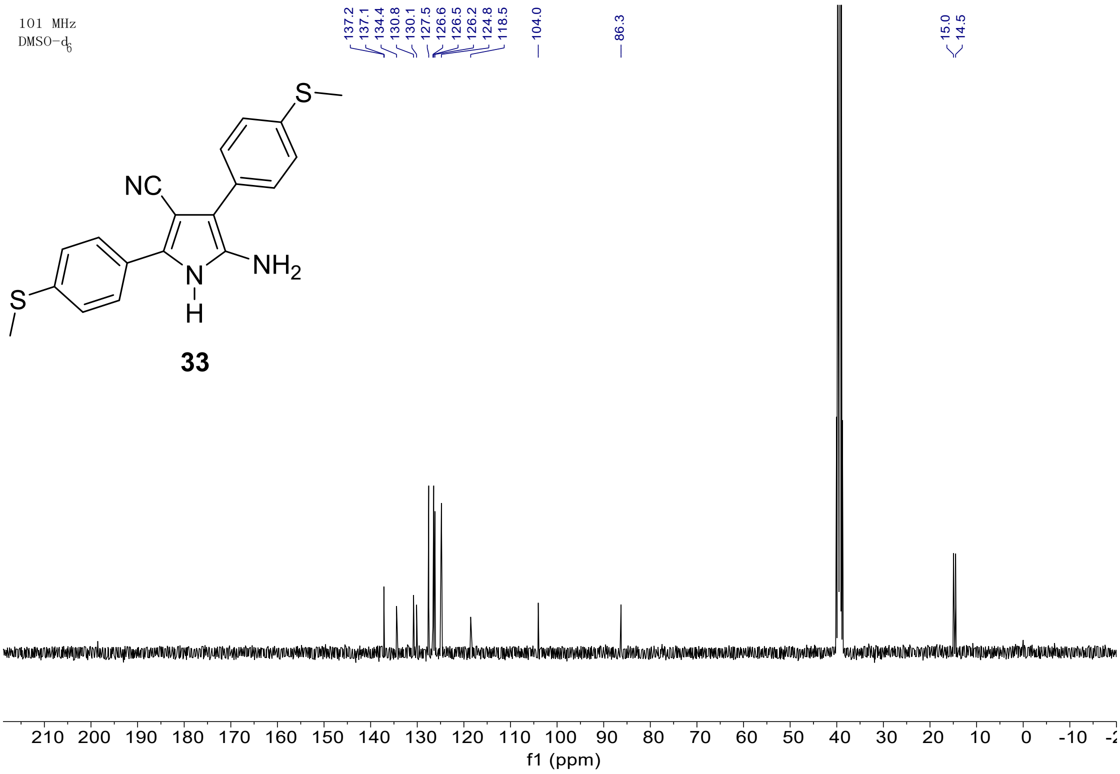

101 MHz
DMSO-d6
138.4 137.7 134.1 131.9 130.7 129.2 129.1 127.6 125.7 122.8 119.2
104.9
87.0
21.5
NC
NH2
N
H
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
DMSO-d_6
11.45
7.62 7.60 7.58 7.57 7.56 7.50 7.48 7.43 7.41 7.39 7.29 7.27 7.24 7.23 7.21 7.19
4.87
2.29
NC
NH_2
N
H
F
32
0.98
2.03 2.03 2.03 1.05 1.01
2.05
3.25
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

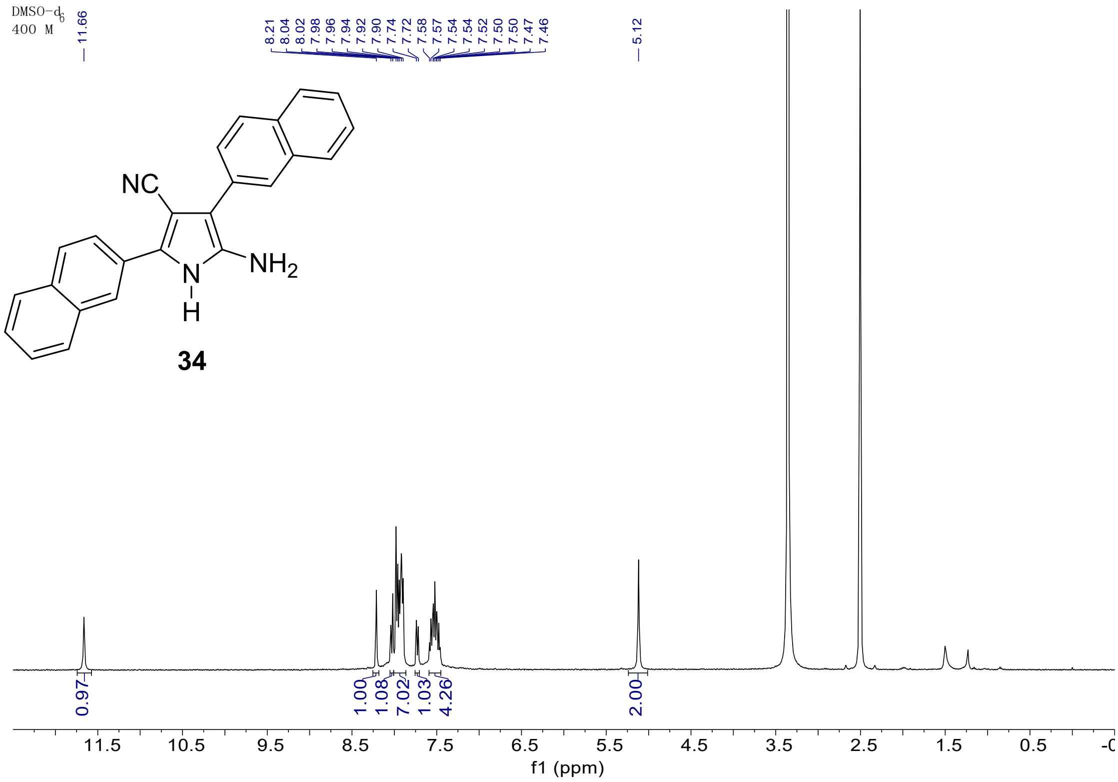

376 MHz
DMSO-d_6
-118.62
NC
NH_2
N
H
F
32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


101 MHz
DMSO-d6
161.5
159.1
137.7
134.0
131.1
129.1
128.4
128.3
127.6
127.1
127.1
125.7
125.4
125.2
124.7
124.6
119.1
116.2
116.0
104.9
87.1
14.8
NC
NH2
F
N
H
32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

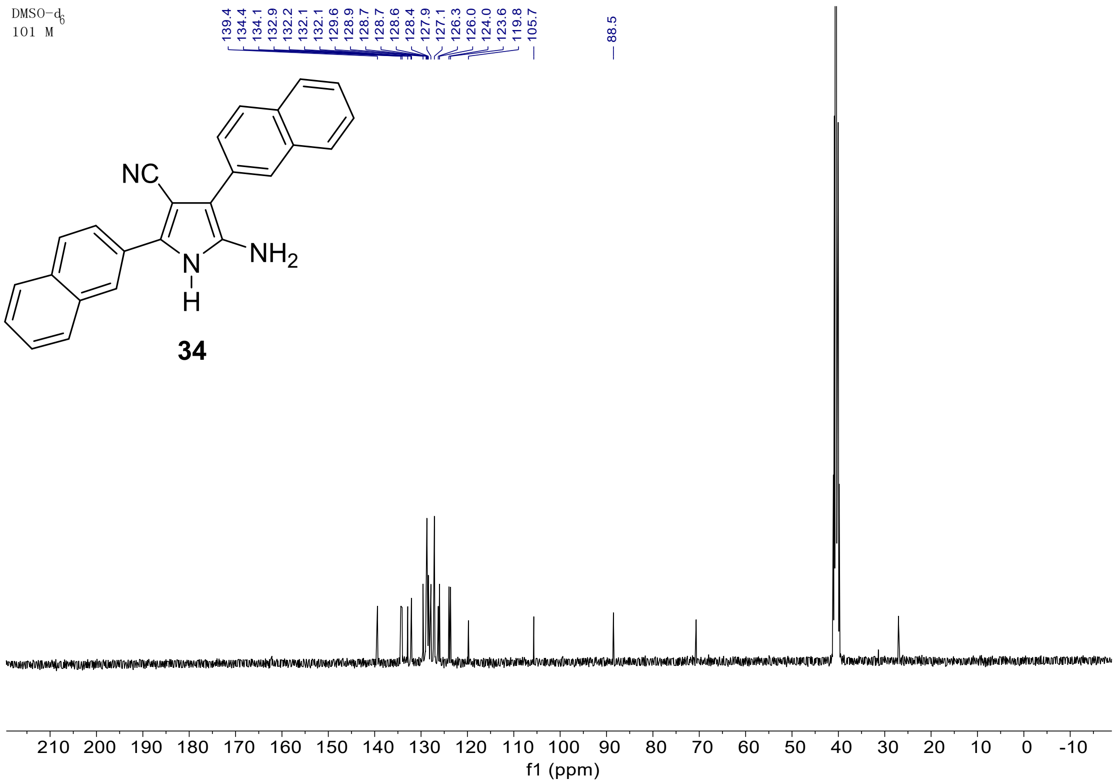

400 MHz
DMSO-d6
11.37
7.67
7.64
7.44
7.42
7.37
7.35
7.33
7.30
4.85
2.50
S
NC
NH2
S
N
H
33
1.00
1.99
2.01
3.96
2.00
6.09
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)



101 MHz
DMSO-d6
137.2 137.1 134.4 130.8 130.1 127.5 126.6 126.5 126.2 124.8 118.5
104.0
86.3
15.0 14.5
NC
S
NH2
N
H
33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

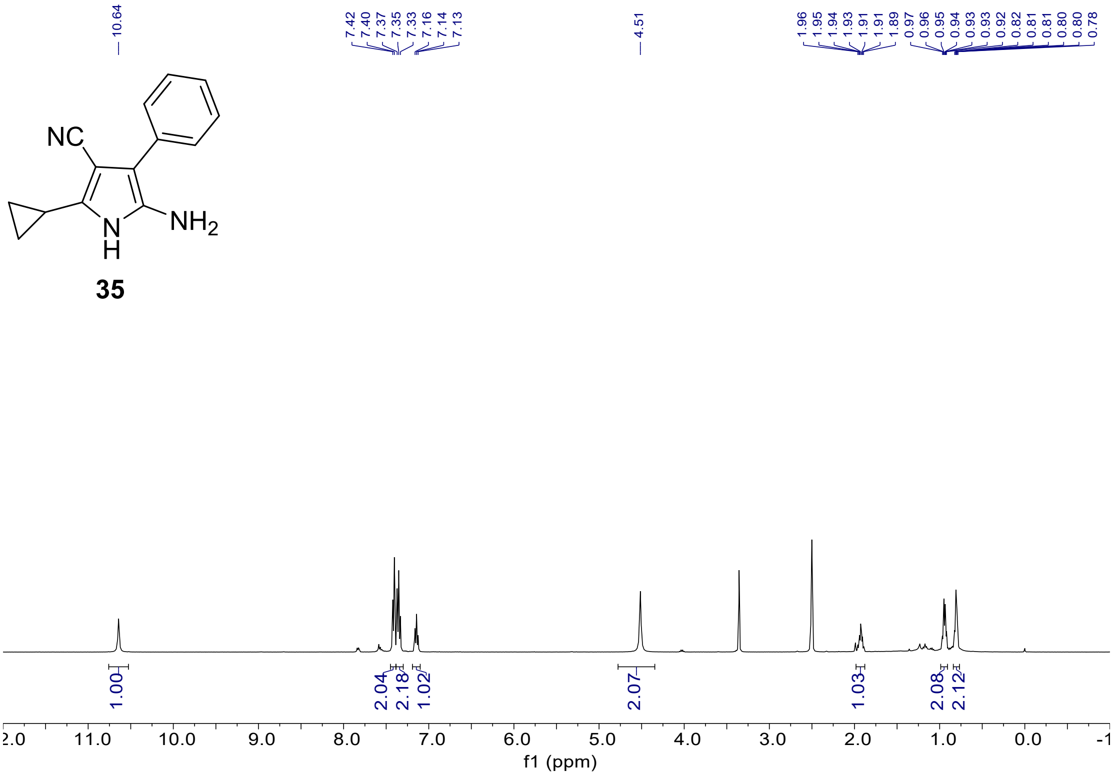


DMSO-d6
400 M
11.66
8.21 8.04 8.02 7.98 7.96 7.94 7.92 7.90 7.74 7.72 7.58 7.57 7.54 7.54 7.52 7.50 7.47 7.46
5.12
NC
NH2
N
H
34
0.97
1.00 1.08 7.02 1.03 4.26
2.00
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)



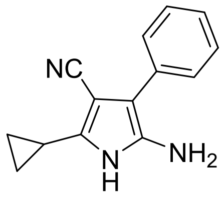
DMSO-d6
101 M
139.4
134.4
134.1
132.9
132.2
132.1
132.1
129.6
128.9
128.7
128.7
128.6
128.4
127.9
127.1
126.3
126.0
124.0
123.6
119.8
105.7
88.5
NC
NH2
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

34

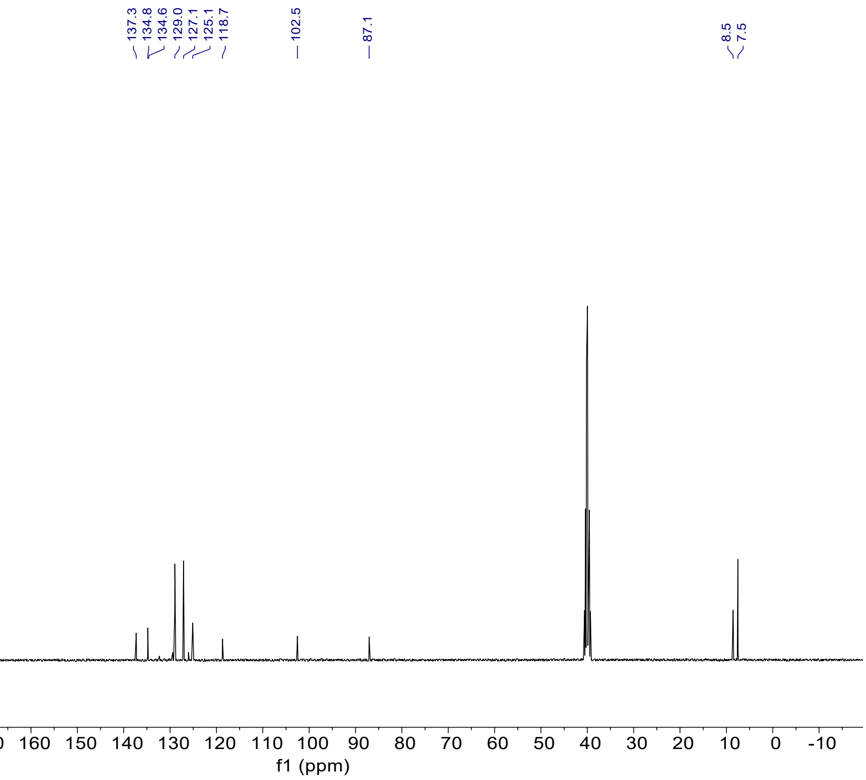


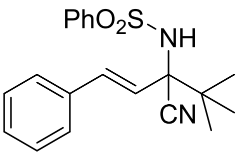
10.64
7.42
7.40
7.37
7.35
7.33
7.16
7.14
7.13
4.51
1.96
1.95
1.94
1.93
1.91
1.91
1.89
0.97
0.96
0.95
0.94
0.93
0.93
0.92
0.82
0.81
0.81
0.80
0.80
0.78
NC
NH2
N
H
1.00
2.04
2.18
1.02
2.07
1.03
2.08
2.12
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
f1 (ppm)

35

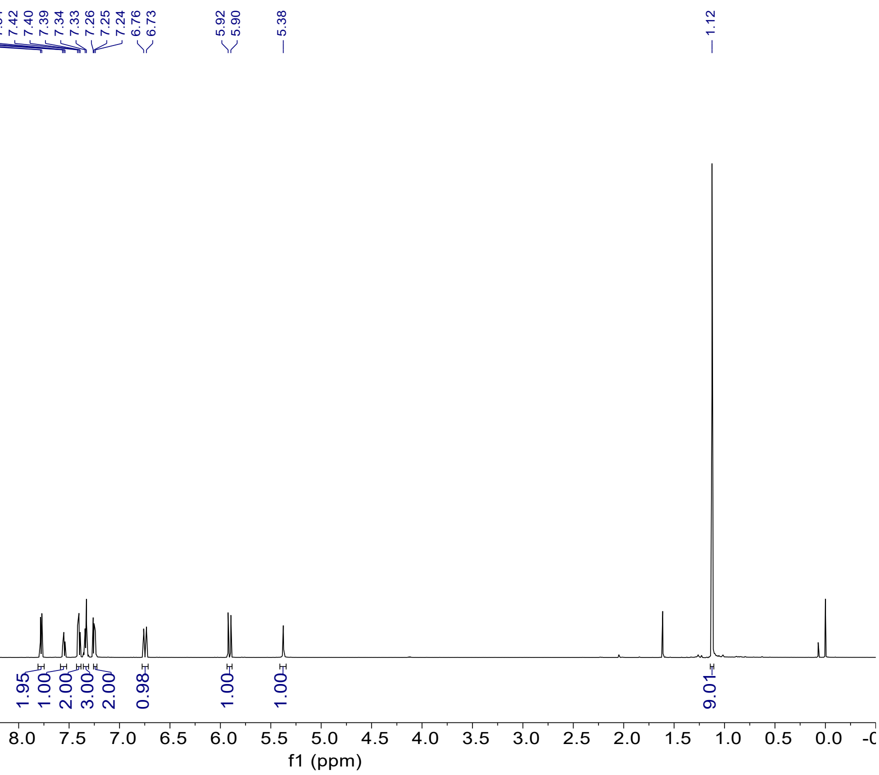


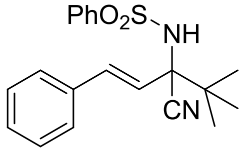
35


137.3
134.8
134.6
129.0
127.1
125.1
118.7
102.5
87.1
8.5
7.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

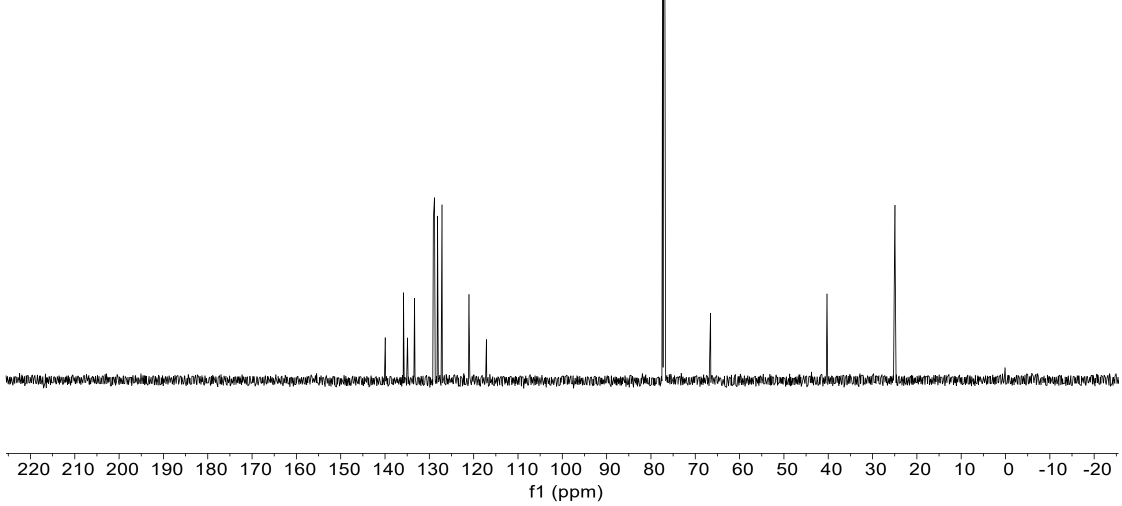


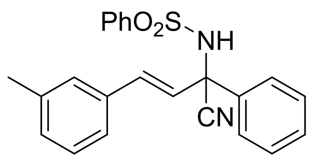
38


600 MHz
CDCl3
7.78
7.77
7.57
7.55
7.54
7.42
7.40
7.39
7.34
7.33
7.26
7.25
7.24
6.76
6.73
5.92
5.90
5.38
1.12
1.95
1.00
2.00
3.00
2.00
0.98
1.00
1.00
9.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

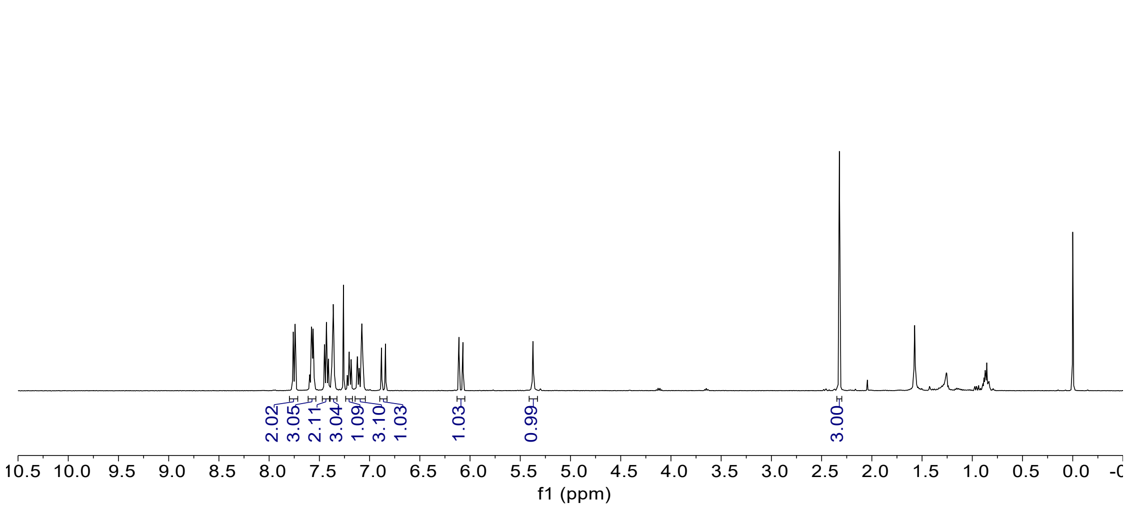


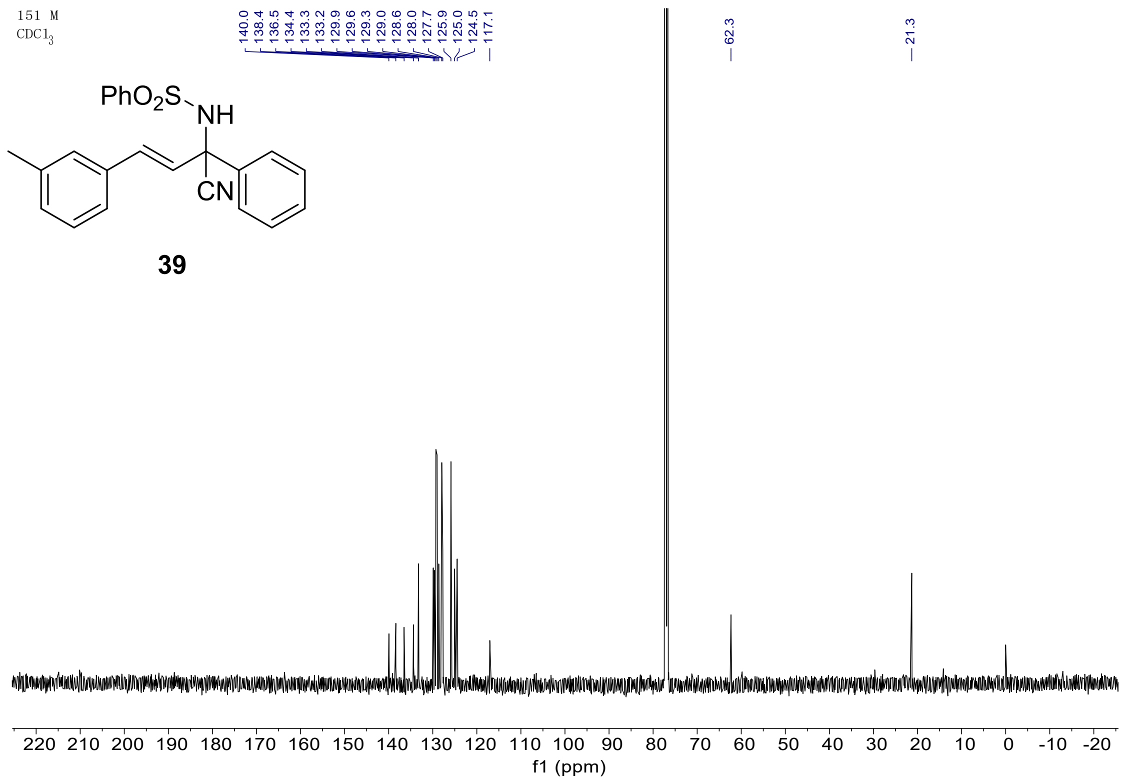
38

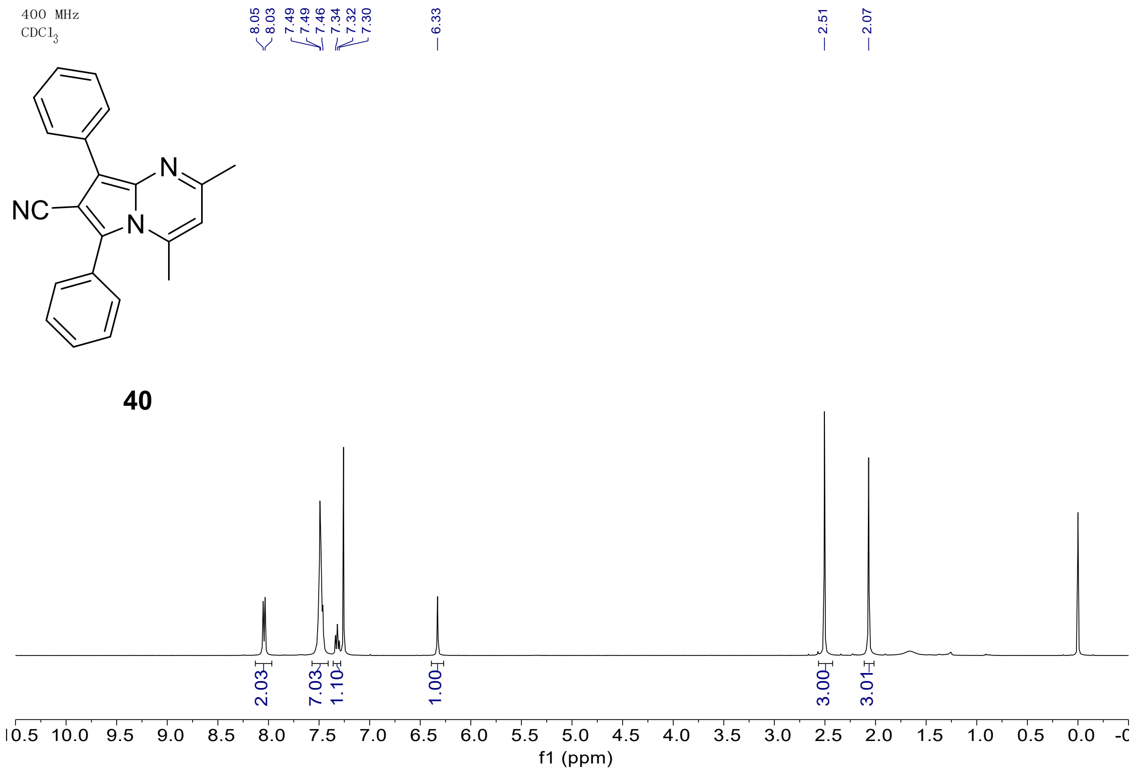

151 MHz
CDCl3
139.9
135.8
134.9
133.3
129.1
129.0
128.8
128.2
127.1
121.1
117.1
66.6
40.3
25.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



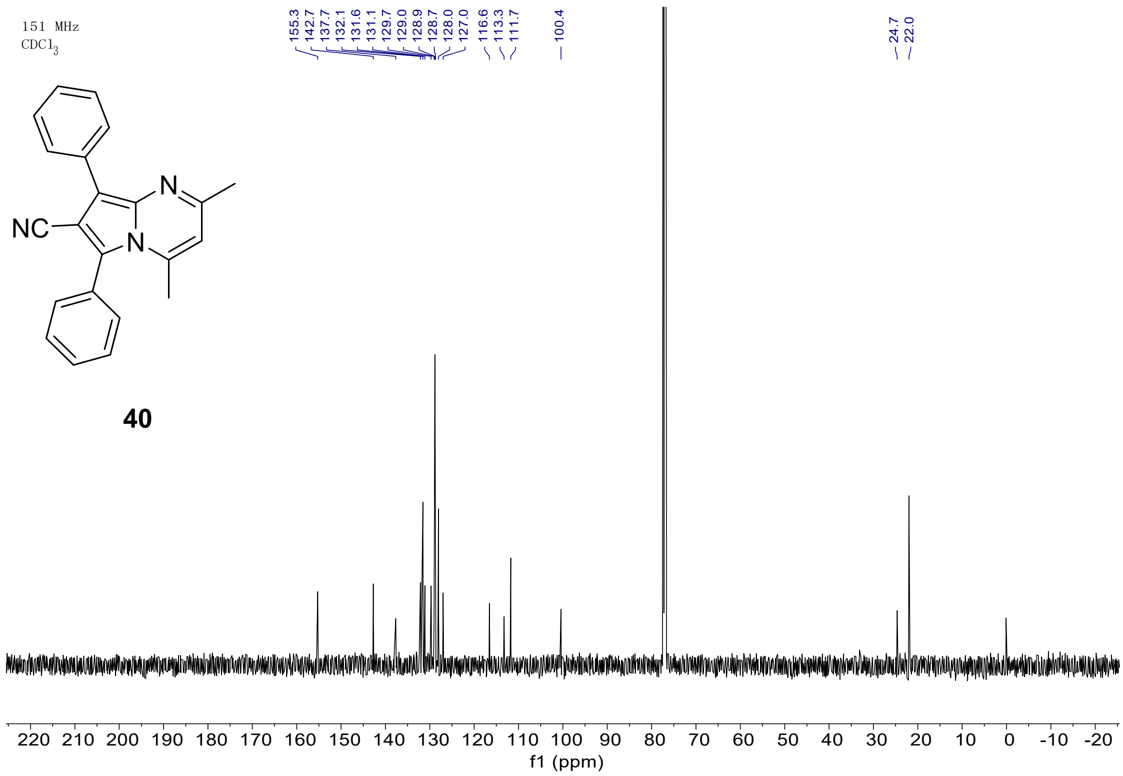
39


400 M
CDCl3
7.76
7.74
7.60
7.58
7.57
7.56
7.56
7.45
7.43
7.41
7.37
7.36
7.36
7.22
7.20
7.18
7.12
7.10
7.08
6.88
6.84
6.11
6.07
5.37
2.32
2.02
3.05
2.11
3.04
1.09
3.10
1.03
1.03
0.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

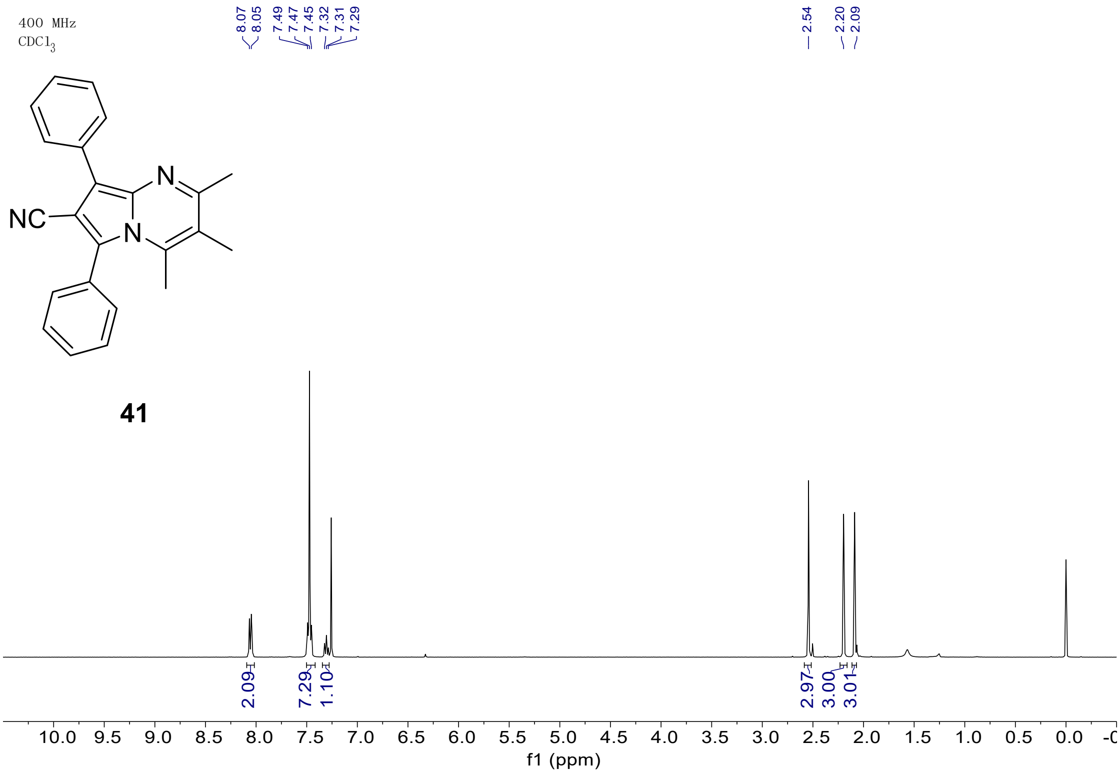

151 M
CDCl3
140.0
138.4
136.5
134.4
133.3
133.2
129.9
129.6
129.3
129.0
128.6
128.0
127.7
125.9
125.0
124.5
117.1
62.3
21.3
PhO2S
NH
CN
39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

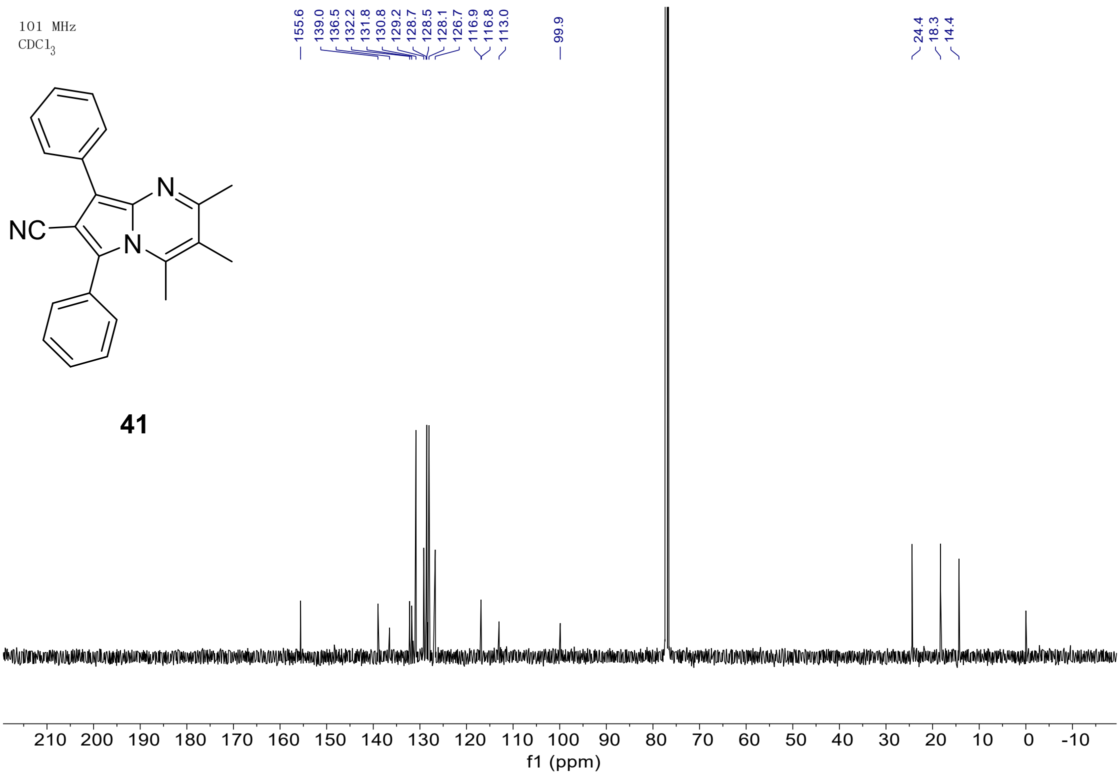


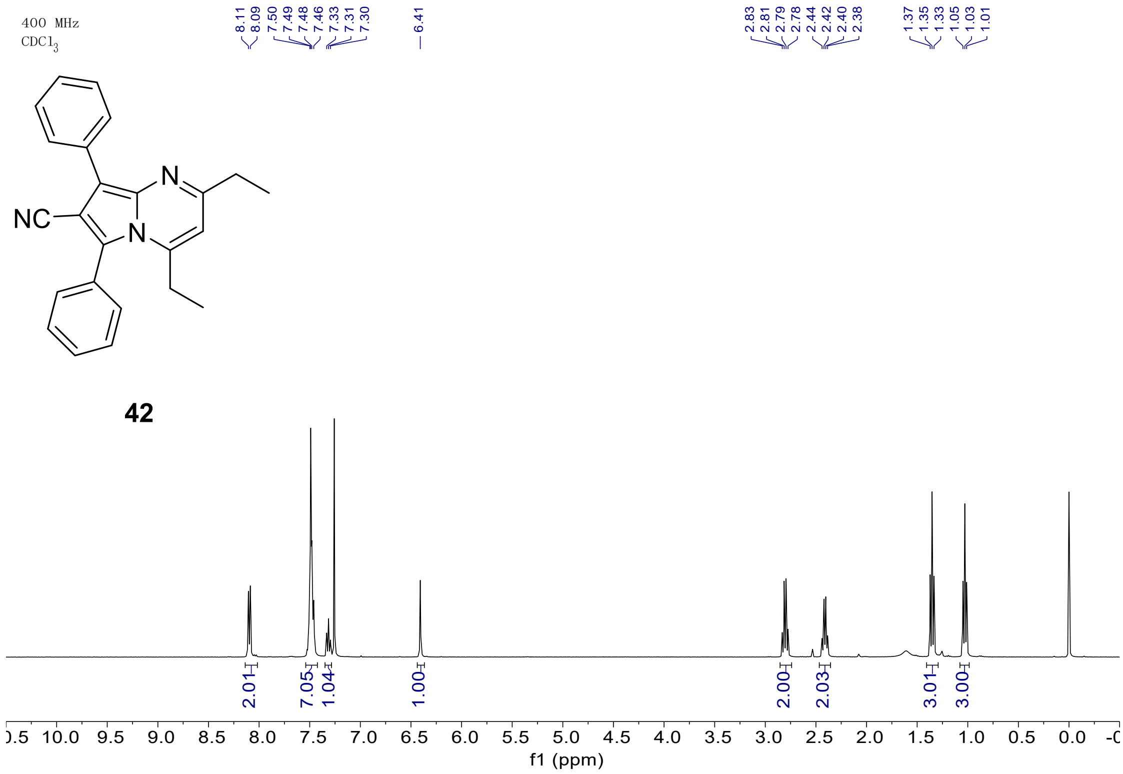
400 MHz
CDCl3
8.05
8.03
7.49
7.49
7.46
7.34
7.32
7.30
6.33
2.51
2.07
NC
N
N
40
2.03
7.03
1.10
1.00
3.00
3.01
f1 (ppm)

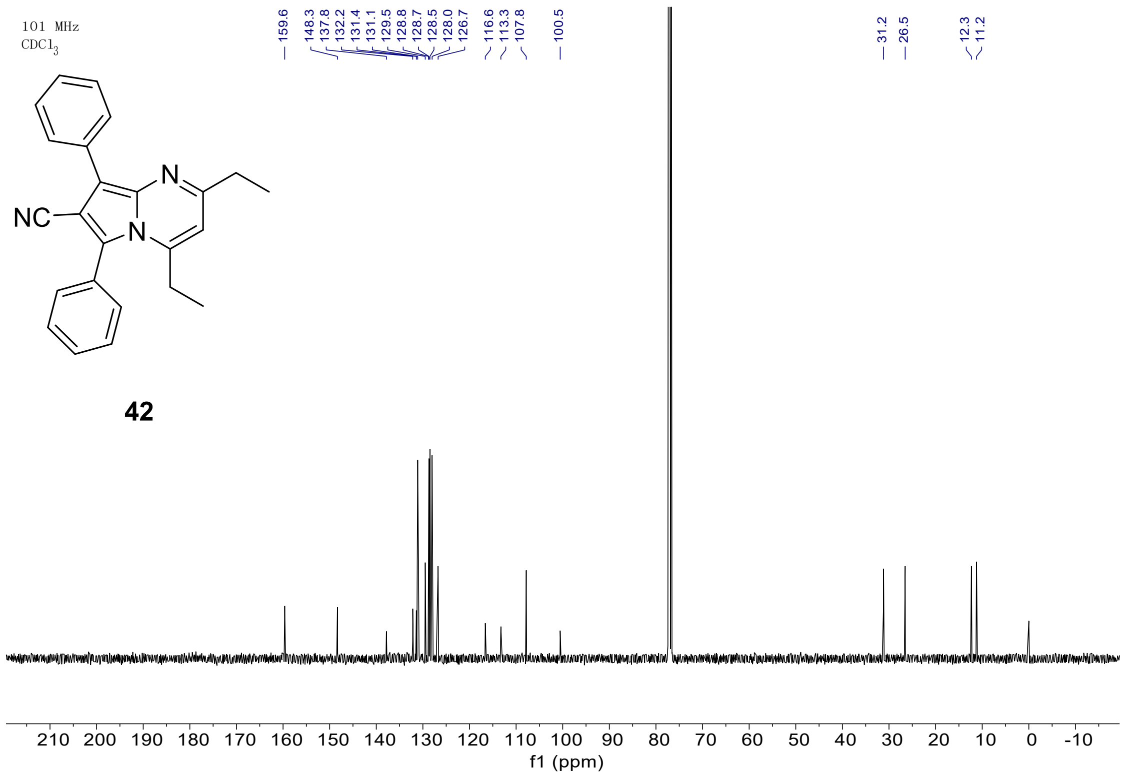


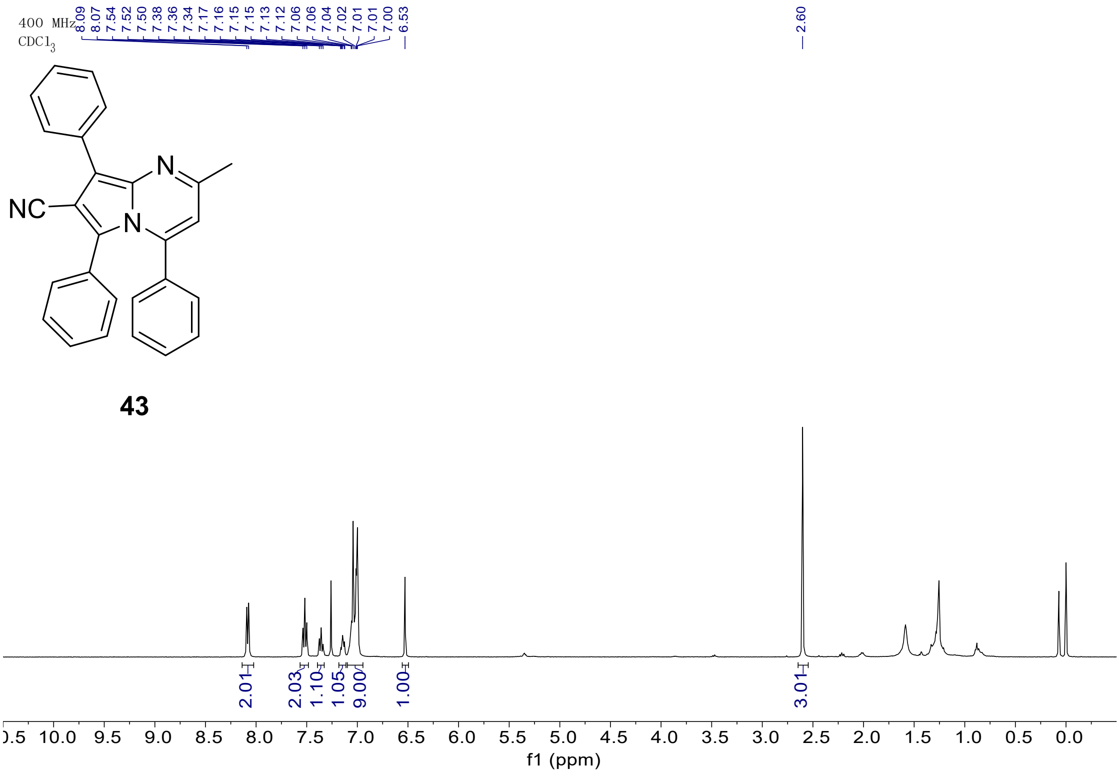
151 MHz
CDCl3
155.3
142.7
137.7
132.1
131.6
131.1
129.7
129.0
128.9
128.7
128.0
127.0
116.6
113.3
111.7
100.4
24.7
22.0
NC
N
N
40
f1 (ppm)


400 MHz
$CDCl_3$
8.07
8.05
7.49
7.47
7.45
7.32
7.31
7.29
2.54
2.20
2.09
NC
N
N
41
2.09
7.29
1.10
2.97
3.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

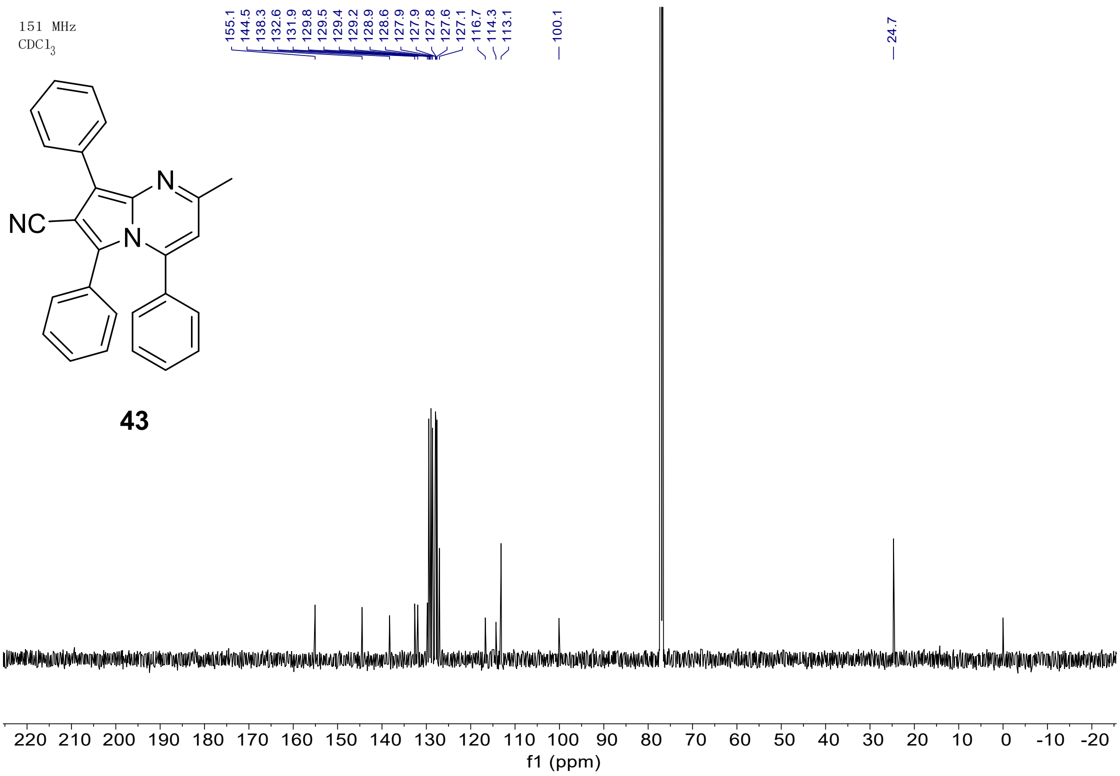

101 MHz
$CDCl_3$
155.6
139.0
136.5
132.2
131.8
130.8
129.2
128.7
128.5
128.1
126.7
116.9
116.8
113.0
99.9
24.4
18.3
14.4
NC
N
N
41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


400 MHz
CDCl3
NC
N
N
42
8.11
8.09
7.50
7.49
7.48
7.46
7.33
7.31
7.30
6.41
2.83
2.81
2.79
2.78
2.44
2.42
2.40
2.38
1.37
1.35
1.33
1.05
1.03
1.01
2.01
7.05
1.04
1.00
2.00
2.03
3.01
3.00
f1 (ppm)

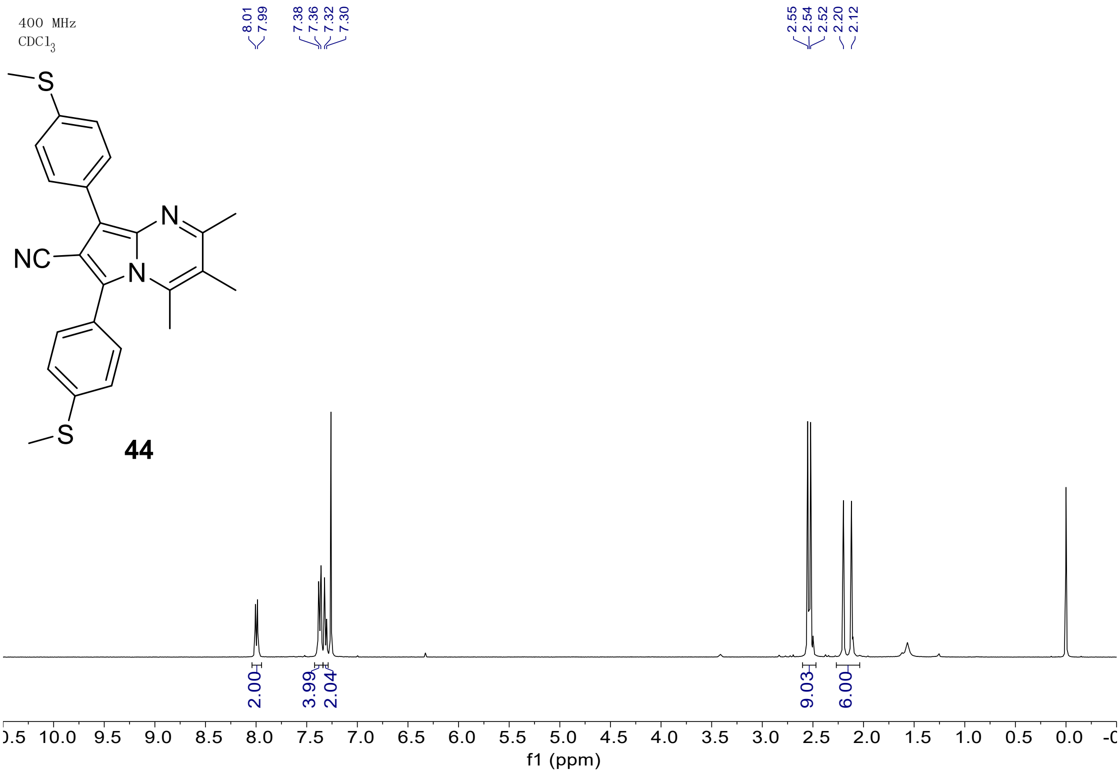

101 MHz
CDCl3
NC
N
N
42
159.6
148.3
137.8
132.2
131.4
131.1
129.5
128.8
128.7
128.5
128.0
126.7
116.6
113.3
107.8
100.5
31.2
26.5
12.3
11.2
f1 (ppm)

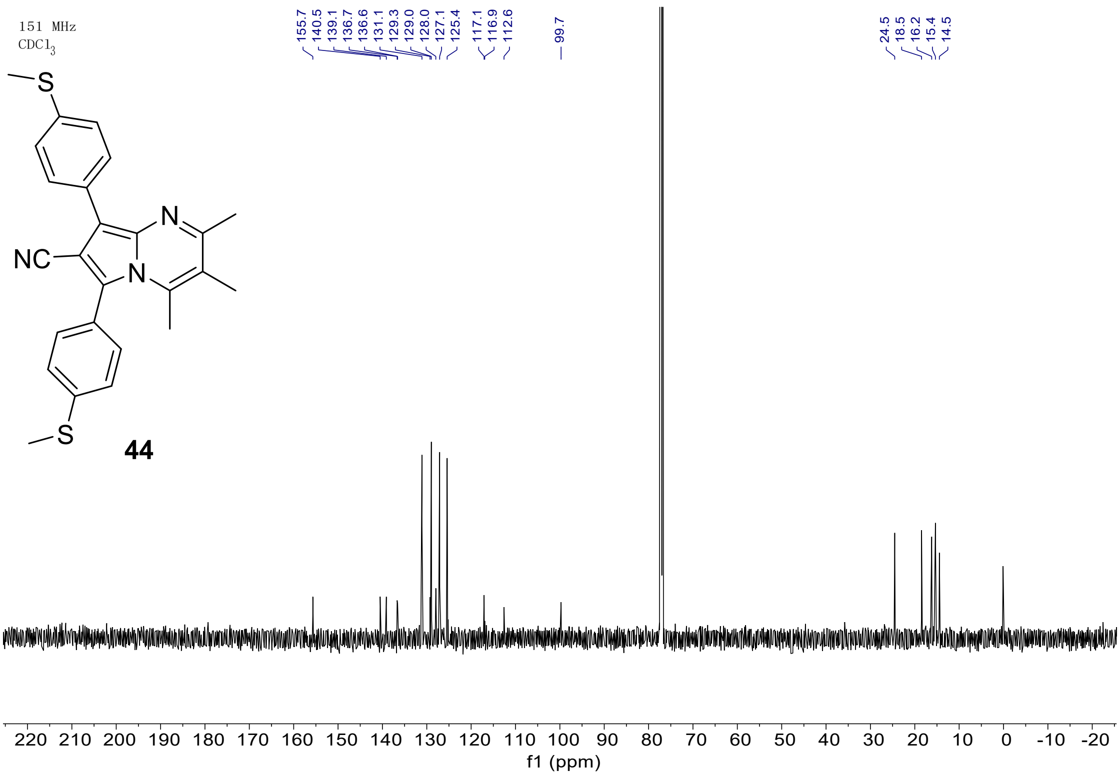

400 MHz
CDCl3
8.09
8.07
7.54
7.52
7.50
7.38
7.36
7.34
7.17
7.16
7.15
7.15
7.13
7.12
7.06
7.06
7.04
7.02
7.01
7.01
7.00
6.53
2.60
NC
N
N
2.01
2.03
1.10
1.05
9.00
1.00
3.01
f1 (ppm)

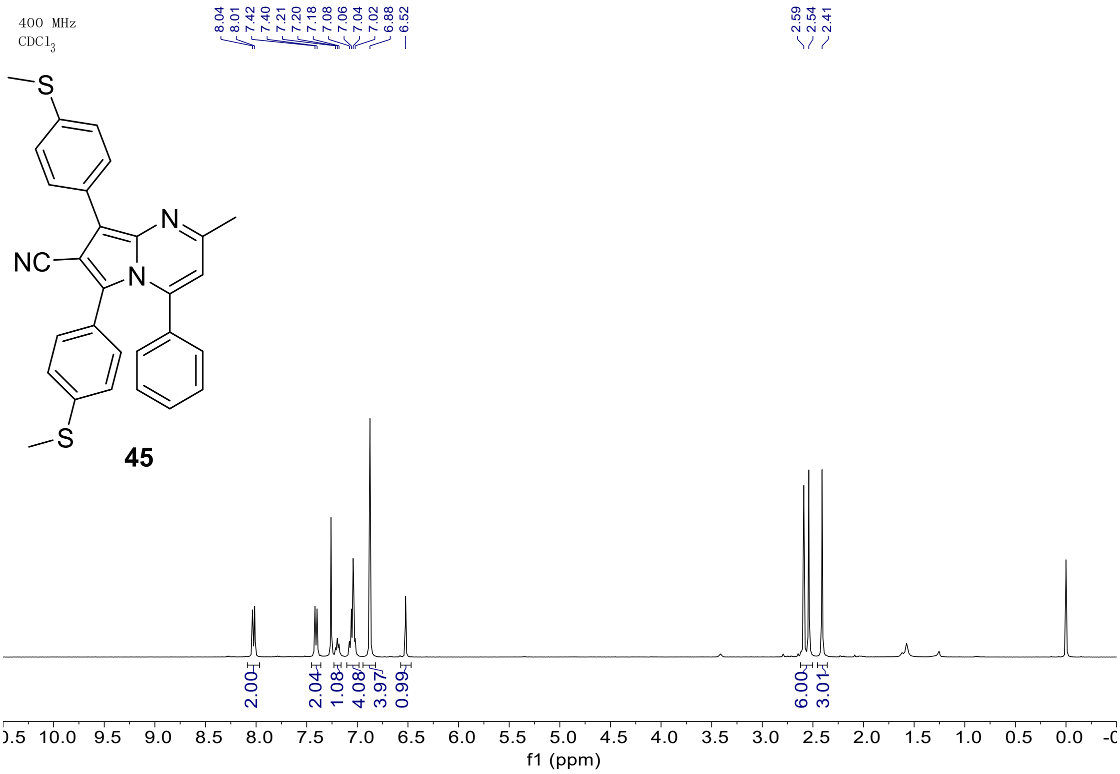
43

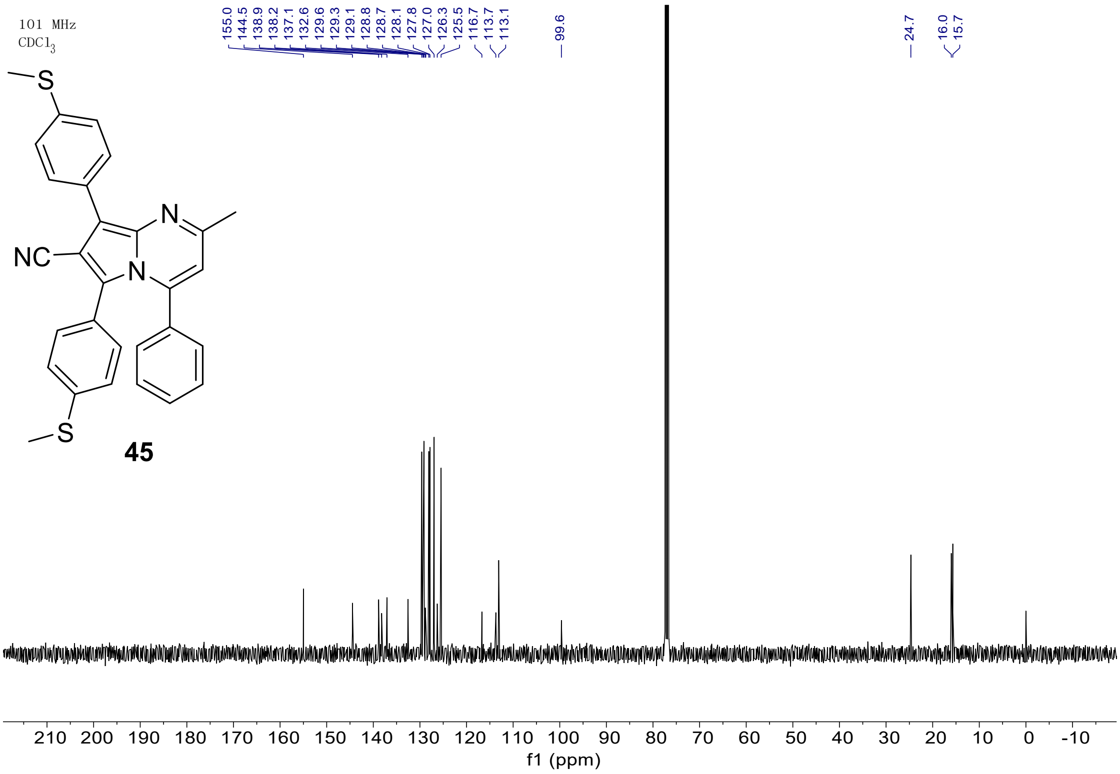

151 MHz
CDCl3
155.1
144.5
138.3
132.6
131.9
129.8
129.5
129.4
129.2
128.9
128.6
127.9
127.9
127.8
127.6
127.1
116.7
114.3
113.1
100.1
24.7
NC
N
N
f1 (ppm)

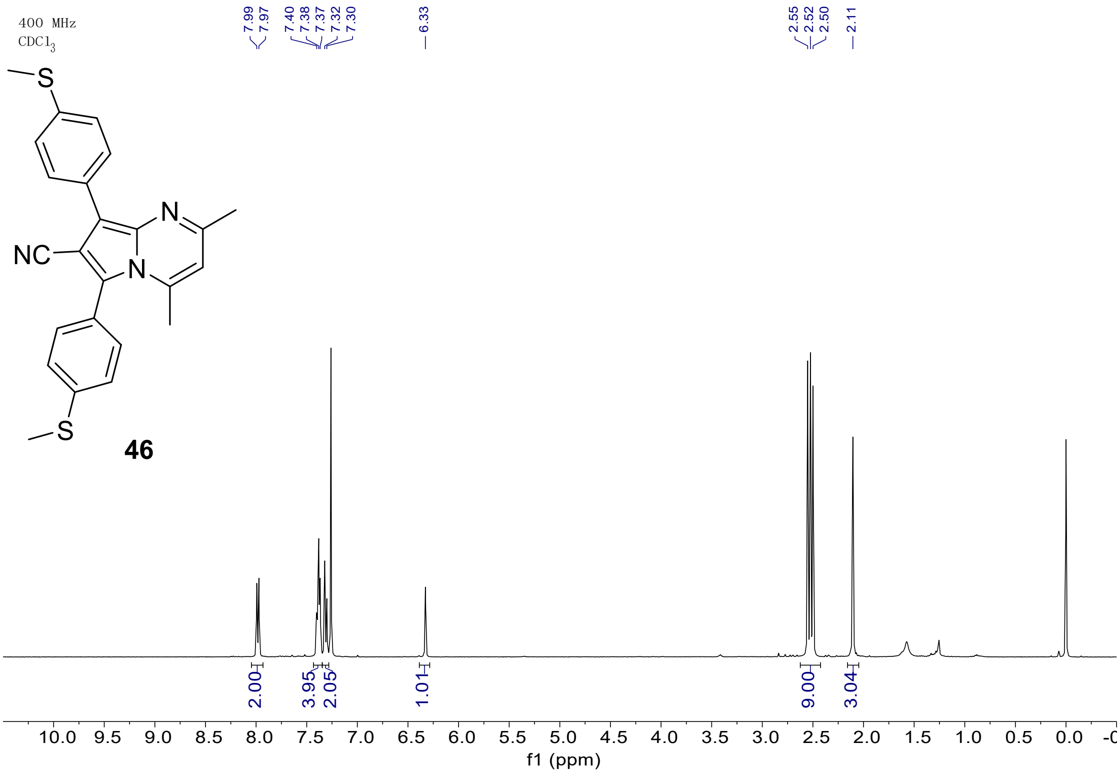
43

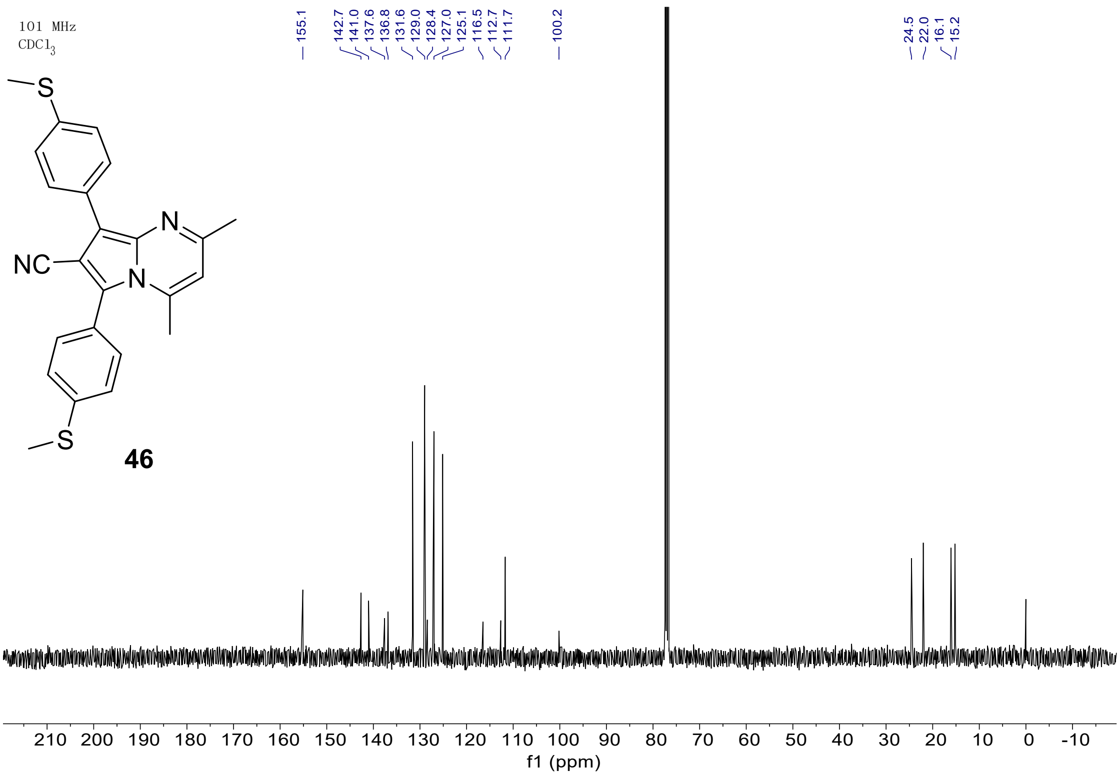

400 MHz
CDCl3
8.01
7.99
7.38
7.36
7.32
7.30
2.55
2.54
2.52
2.20
2.12
NC
N
N
S
S
44
2.00
3.99
2.04
9.03
6.00
f1 (ppm)

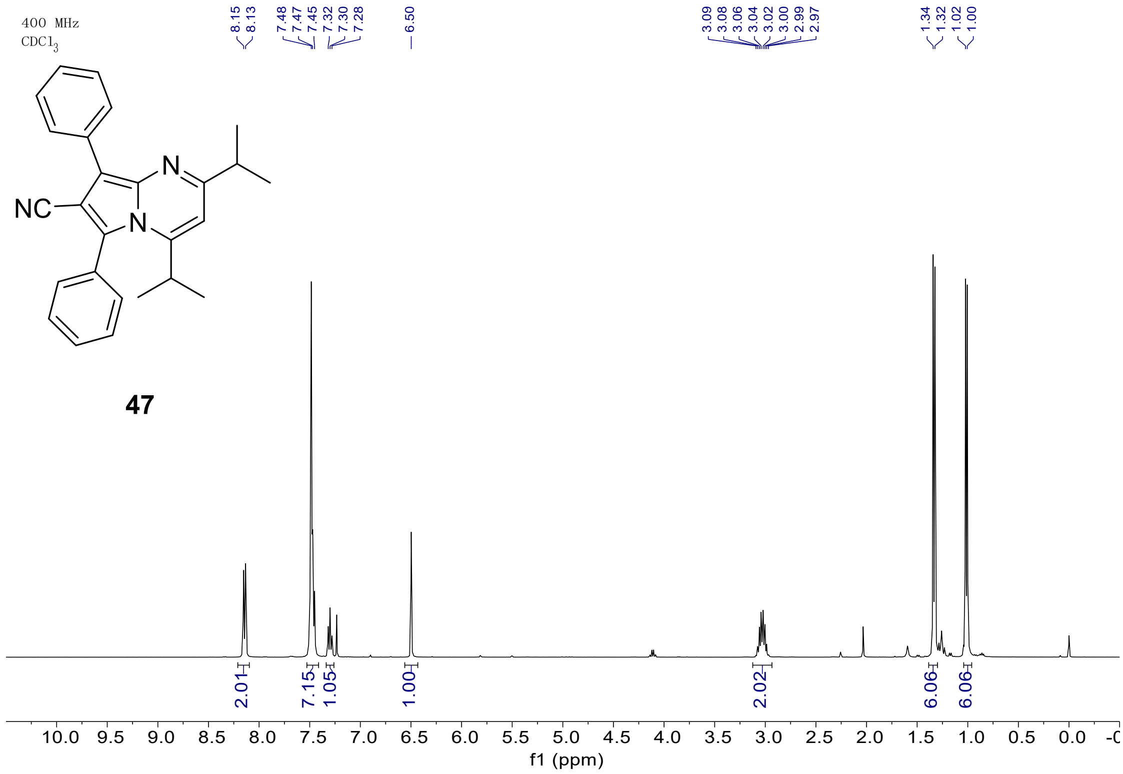

151 MHz
CDCl3
155.7
140.5
139.1
136.7
136.6
131.1
129.3
129.0
128.0
127.1
125.4
117.1
116.9
112.6
99.7
24.5
18.5
16.2
15.4
14.5
NC
N
N
S
S
44
f1 (ppm)


400 MHz
CDCl3
8.04 8.01 7.42 7.40 7.21 7.20 7.18 7.08 7.06 7.04 7.02 6.88 6.52
2.59 2.54 2.41
NC
N
S
45
2.00 2.04 1.08 4.08 3.97 0.99
6.00 3.01
f1 (ppm)

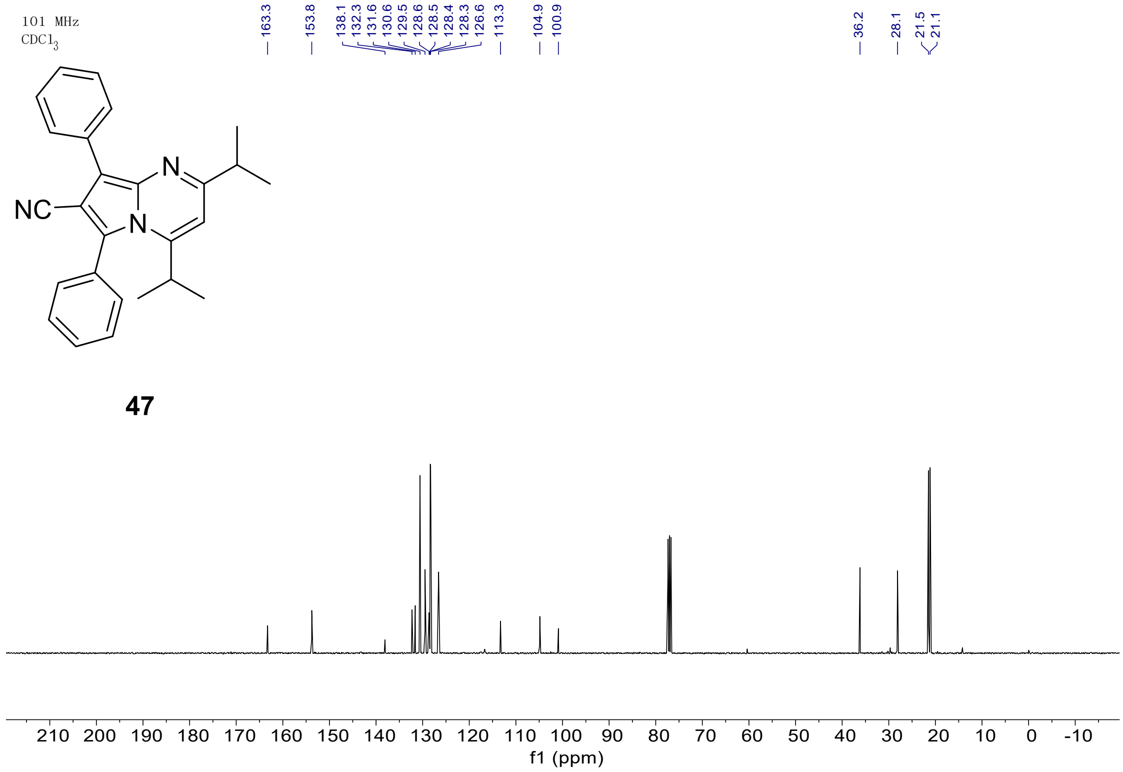

101 MHz
CDCl3
155.0 144.5 138.9 138.2 137.1 132.6 129.6 129.3 129.1 128.8 128.7 128.1 127.8 127.0 126.3 125.5 116.7 113.7 113.1
99.6
24.7 16.0 15.7
NC
N
S
45
f1 (ppm)


400 MHz
CDCl3
7.99
7.97
7.40
7.38
7.37
7.32
7.30
6.33
2.55
2.52
2.50
2.11
NC
N
S
46
2.00
3.95
2.05
1.01
9.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

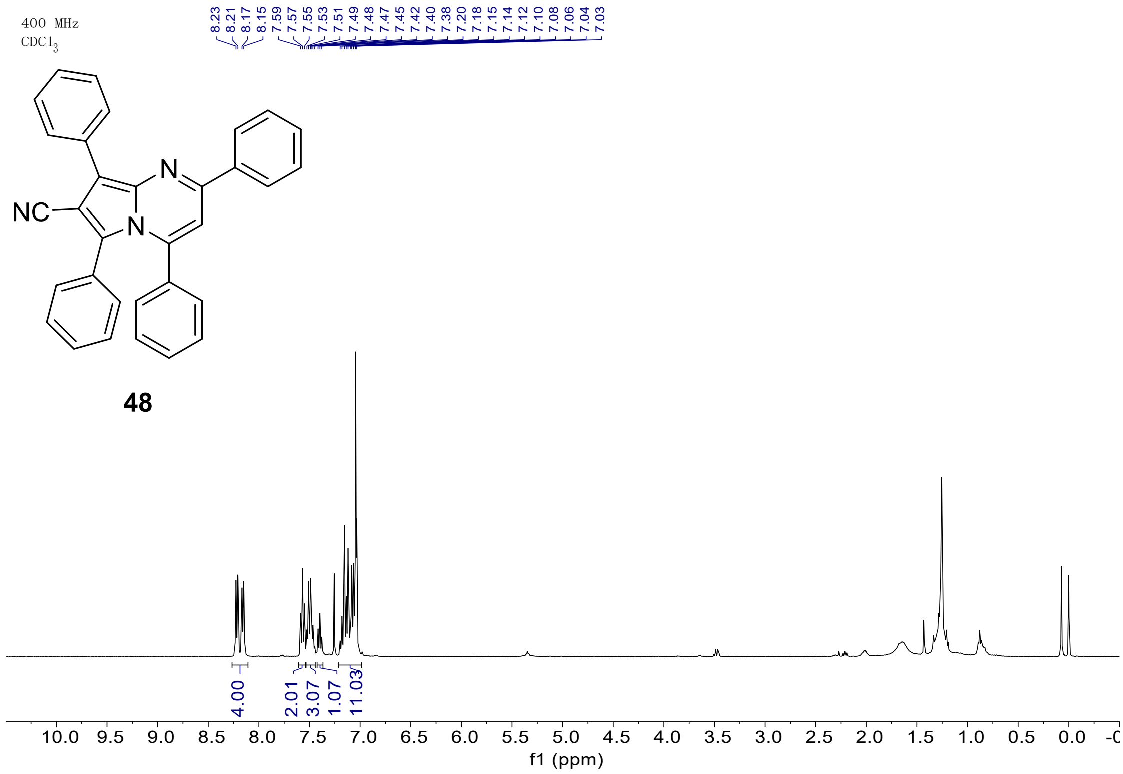

101 MHz
CDCl3
155.1
142.7
141.0
137.6
136.8
131.6
129.0
128.4
127.0
125.1
116.5
112.7
111.7
100.2
24.5
22.0
16.1
15.2
NC
N
S
46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

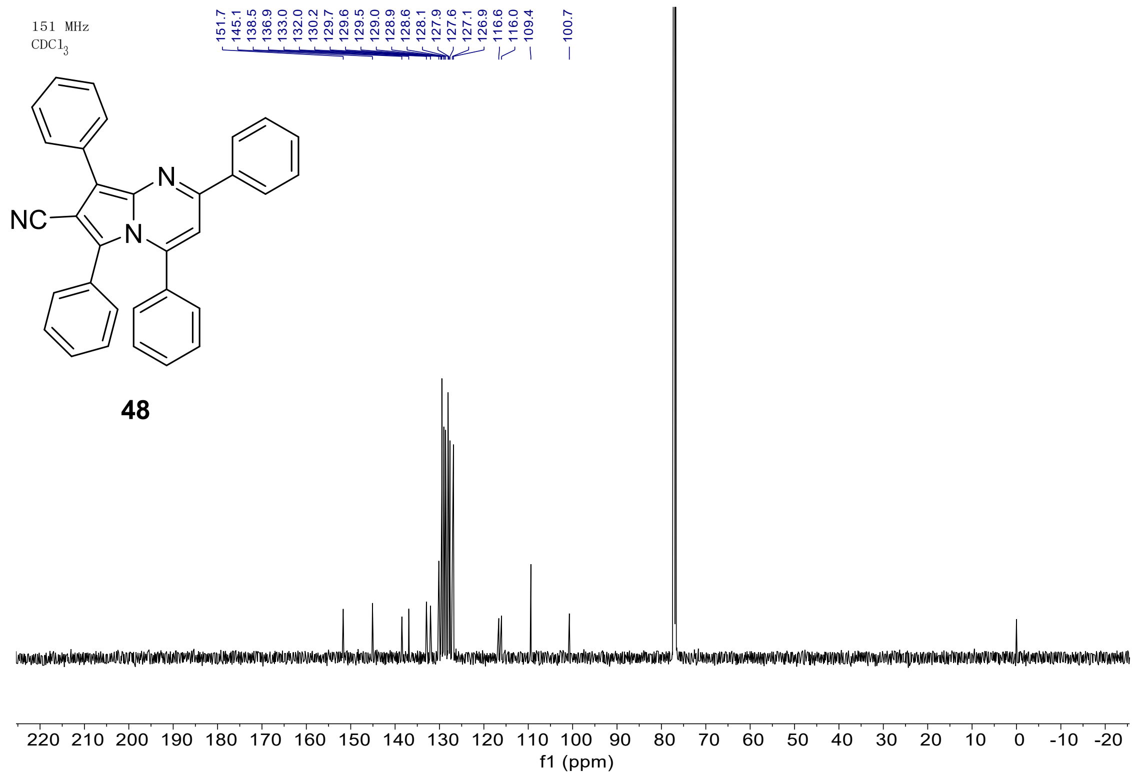

400 MHz
CDCl3
8.15
8.13
7.48
7.47
7.45
7.32
7.30
7.28
6.50
3.09
3.08
3.06
3.04
3.02
3.00
2.99
2.97
1.34
1.32
1.02
1.00
NC
N
N
2.01
7.15
1.05
1.00
2.02
6.06
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

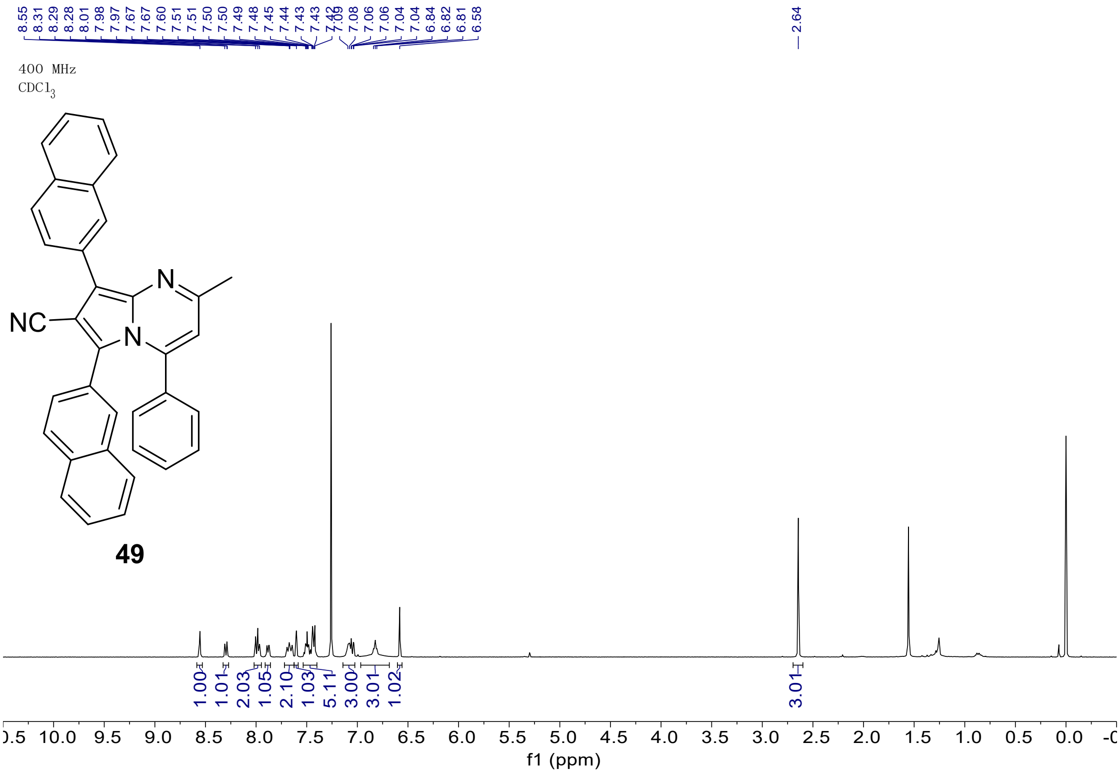
47

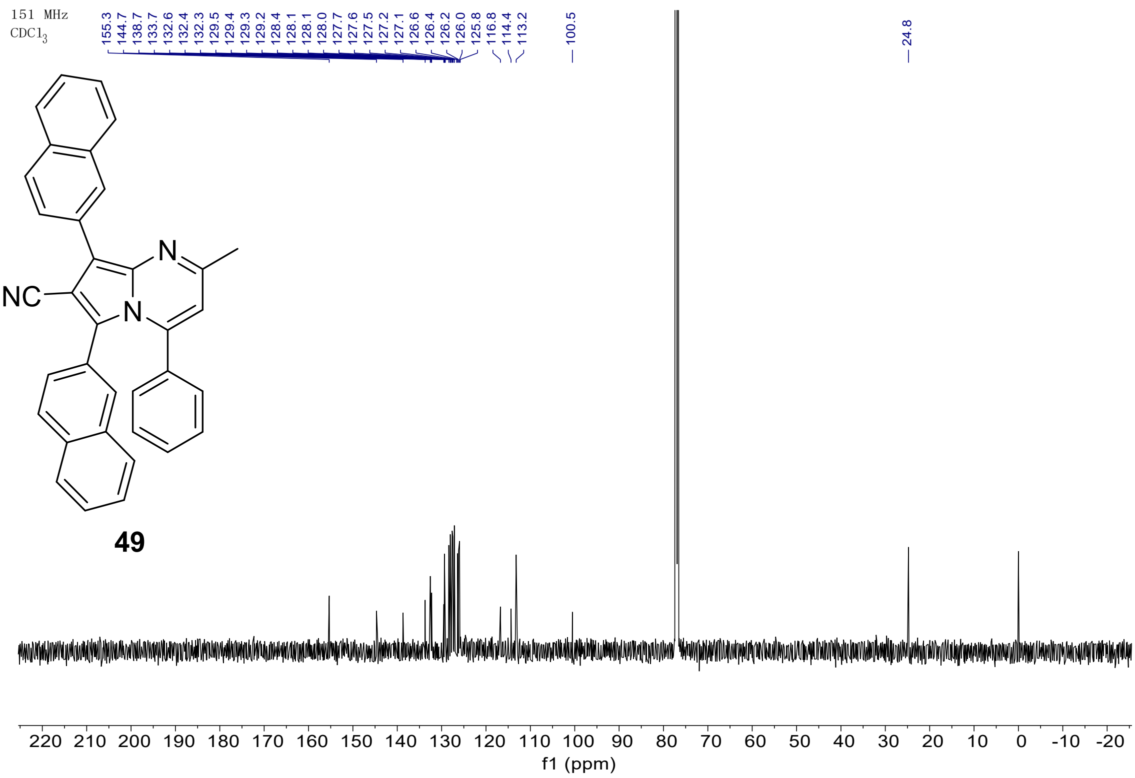

101 MHz
CDCl3
163.3
153.8
138.1
132.3
131.6
130.6
129.5
128.6
128.5
128.4
128.3
126.6
113.3
104.9
100.9
36.2
28.1
21.5
21.1
NC
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

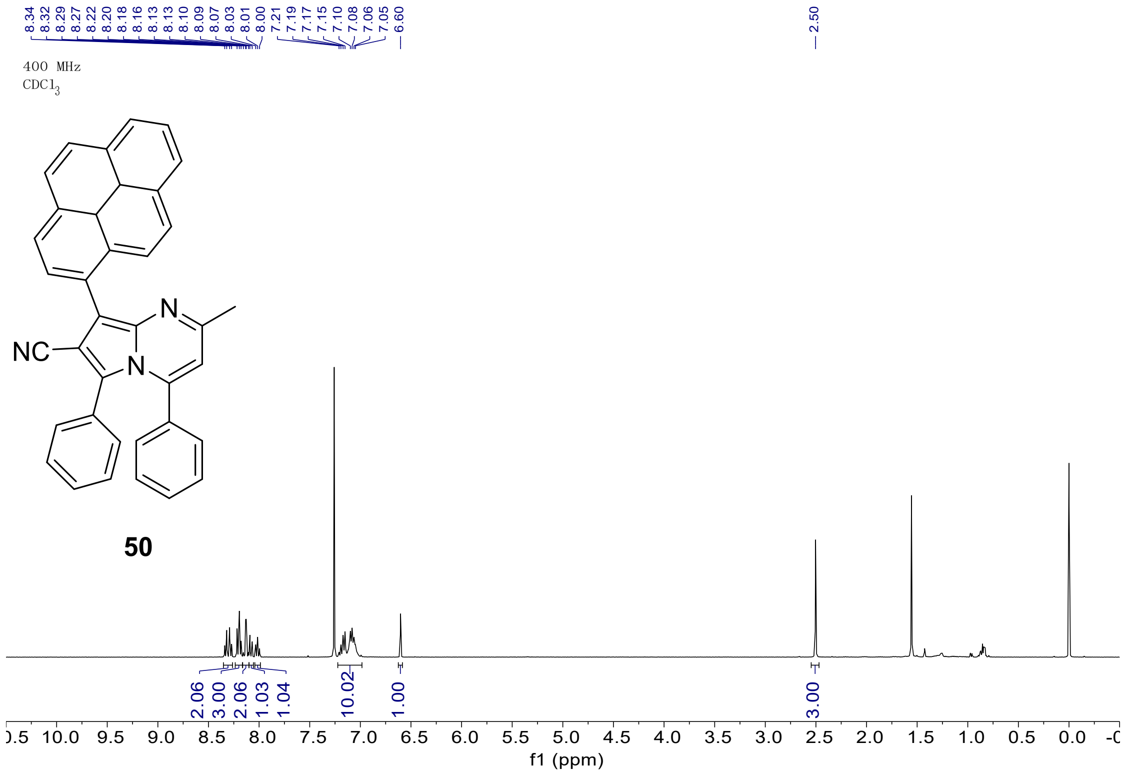
47

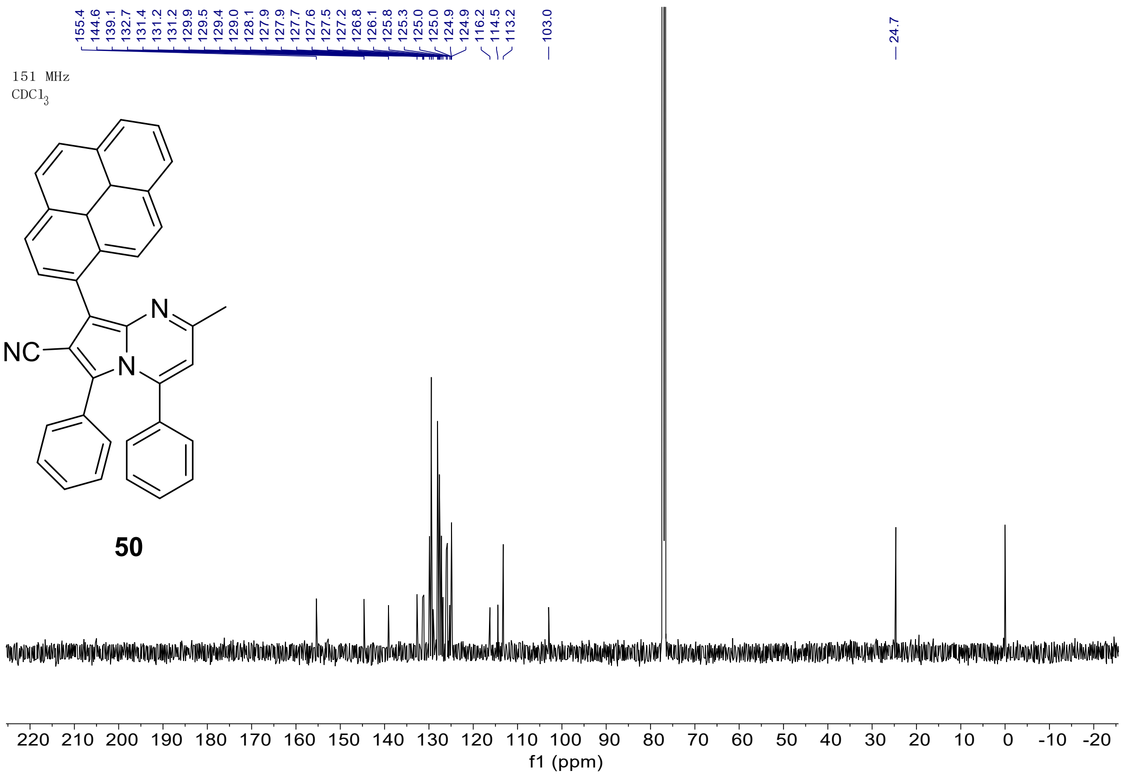

400 MHz
CDCl3
8.23
8.21
8.17
8.15
7.59
7.57
7.55
7.53
7.51
7.49
7.48
7.47
7.45
7.42
7.40
7.38
7.20
7.18
7.15
7.14
7.12
7.10
7.08
7.06
7.04
7.03
NC
N
N
48
4.00
2.01
3.07
1.07
11.03
f1 (ppm)

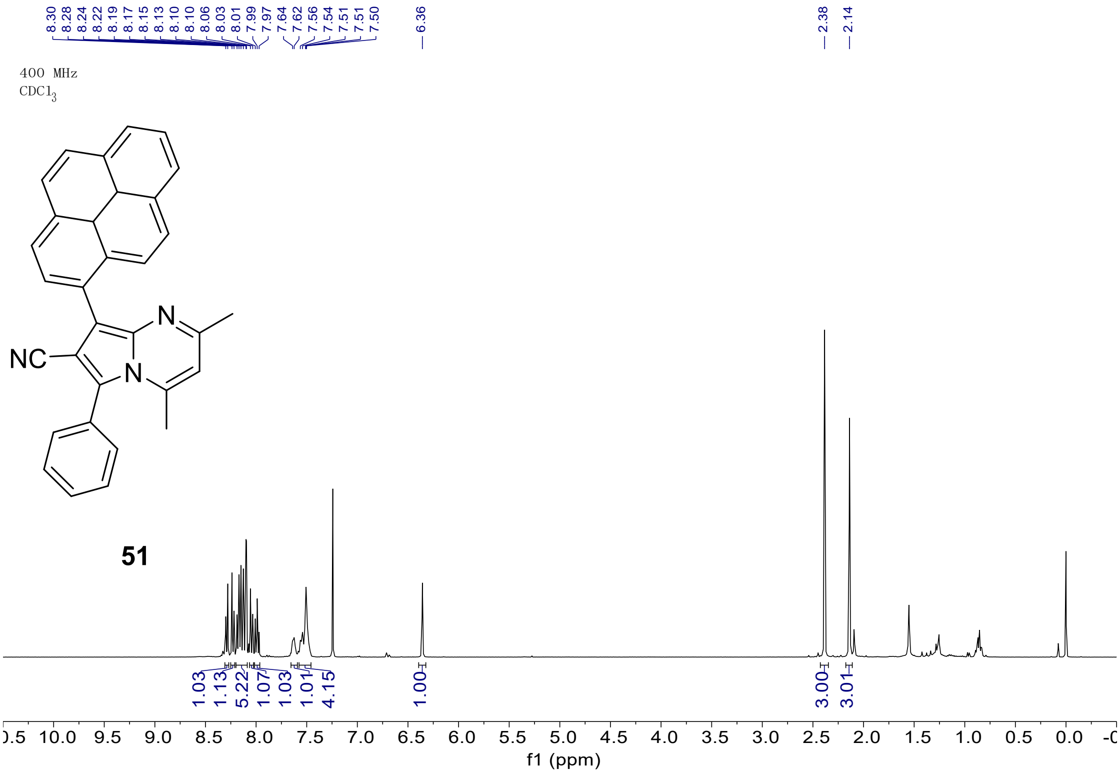

151 MHz
CDCl3
151.7
145.1
138.5
136.9
133.0
132.0
130.2
129.7
129.6
129.5
129.0
128.9
128.6
128.1
127.9
127.6
127.1
126.9
116.6
116.0
109.4
100.7
NC
N
N
48
f1 (ppm)


8.55 8.31 8.29 8.28 8.01 7.98 7.97 7.67 7.67 7.60 7.51 7.51 7.50 7.50 7.49 7.48 7.45 7.44 7.43 7.43 7.42 7.09 7.08 7.06 7.06 7.04 7.04 6.84 6.82 6.81 6.58
2.64
400 MHz
CDCl$_3$
NC
N
N
49
1.00 1.01 2.03 1.05 2.10 1.03 5.11 3.00 3.01 1.02
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

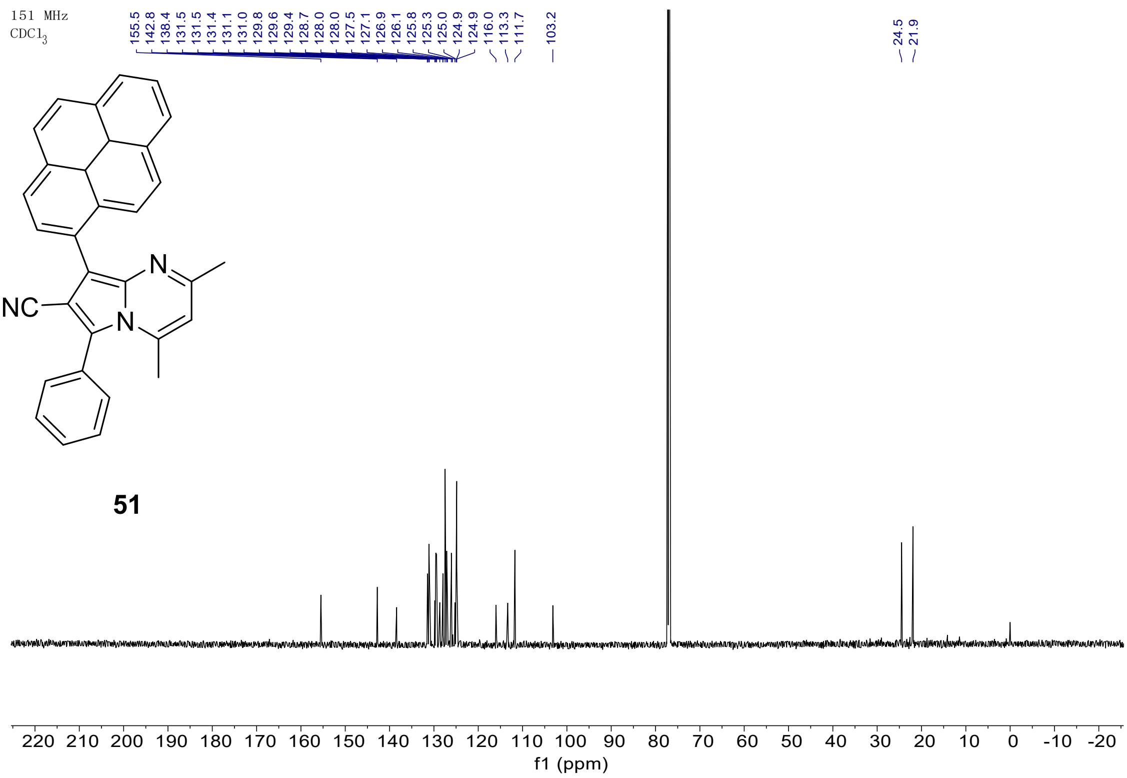

151 MHz
CDCl$_3$
155.3 144.7 138.7 133.7 132.6 132.4 132.3 129.5 129.4 129.3 129.2 128.4 128.1 128.1 128.0 127.7 127.6 127.5 127.2 127.1 126.6 126.4 126.2 126.0 125.8 116.8 114.4 113.2
100.5
24.8
NC
N
N
49
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)






400 MHz
CDCl3
8.30 8.28 8.24 8.22 8.19 8.17 8.15 8.13 8.10 8.10 8.06 8.03 8.01 7.99 7.97 7.64 7.62 7.56 7.54 7.51 7.50
6.36
2.38
2.14
NC
N
N
1.03 1.13 5.22 1.07 1.03 1.01 4.15
1.00
3.00
3.01
f1 (ppm)

51


151 MHz
CDCl3
155.5 142.8 138.4 131.5 131.4 131.1 131.0 129.8 129.6 129.4 128.7 128.0 128.0 127.5 127.1 126.9 126.1 125.8 125.3 125.0 124.9 124.9 116.0 113.3 111.7
103.2
24.5 21.9
NC
N
N
f1 (ppm)

51

Table S10. Electronic potential energies and correction to zero point energies, thermal energies, enthalpies, free energies (in Hartree) and imaginary frequencies (cm^{-1}) of optimized structures calculated at the B3LYP-D3/Def2-TZVP/(SMD-DMSO)//B3LYP-D3/Def2-SVP.

Entry	Structure	$E_{el,sol}$	$E_{el,gas}$	$cZPE_{gas}$	$cU_{353,gas}$	$cH_{353,gas}$	$cG_{353,gas}$	Imaginary Frequency
1	**1SP**	-1507.776911	-1506.336978	0.349340	0.381476	0.382594	0.275755	
2	$^{-}SO_2Ph$	-780.598768	-779.886120	0.097049	0.107498	0.108617	0.055690	
3	HSO_2Ph	-781.067749	-780.446585	0.109587	0.120608	0.121727	0.067874	
4	**1A**	-1507.296365	-1505.793686	0.335618	0.367261	0.368380	0.263638	
5	**TS1**	-1507.272975	-1505.762705	0.333687	0.365736	0.366854	0.261443	-142.2036
6	**1s**	-1414.292661	-1412.963548	0.328292	0.357209	0.358327	0.259726	
7	CN^{-}	-92.998758	-92.763823	0.004942	0.007740	0.008858	-0.018278	
8	**TS2**	-1507.273792	-1505.761701	0.333801	0.365968	0.367086	0.260568	-150.8187
9	**1B**	-1507.313429	-1505.815812	0.336645	0.368002	0.369121	0.265101	
10	**int1**	-1507.318409	-1505.830647	0.337182	0.368354	0.369473	0.268384	
11	**TS3**	-1507.291662	-1505.809139	0.334903	0.366358	0.367476	0.264648	-150.7898
12	**int2**	-726.699669	-725.890984	0.236214	0.256473	0.257591	0.180188	
13	**TS4**	-726.674824	-725.859719	0.235577	0.254592	0.255711	0.181836	-262.7868
14	**int3**	-726.676378	-725.860103	0.236602	0.255983	0.257101	0.182787	
15	**int4**	-726.713605	-725.912891	0.238500	0.257419	0.258537	0.184454	
16	**TS5**	-819.687054	-818.703896	0.243939	0.266082	0.267201	0.186195	-267.8221
17	**int5**	-819.718467	-818.739459	0.245517	0.267198	0.268316	0.189580	
18	**int6**	-819.740845	-818.767902	0.246601	0.268437	0.269555	0.190322	
19	**TS6**	-1507.249116	-1505.740724	0.333239	0.365385	0.366504	0.260750	-249.2426
20	**TS7**	-1507.225244	-1505.740898	0.332107	0.364322	0.365440	0.260091	-368.9274
21	**int7**	-726.662278	-725.856063	0.235634	0.255819	0.256938	0.179559	
22	**TS8**	-1600.249204	-1598.481388	0.341756	0.376026	0.377145	0.268894	-427.7573
23	**int8**	-1600.260897	-1598.501294	0.342479	0.376760	0.377878	0.269953	
24	**TS9**	-1600.261741	-1598.499069	0.341494	0.376125	0.377244	0.268037	-373.0715
25	**int9**	-1600.273395	-1598.519667	0.342741	0.377344	0.378462	0.269511	
26	**int10**	-1507.792024	-1506.355489	0.350625	0.382379	0.383497	0.278152	
27	**TS10**	-1600.762520	-1599.152000	0.355553	0.390633	0.391751	0.279803	-263.5716
28	**int11**	-1600.777390	-1599.177853	0.356708	0.391631	0.392749	0.281833	
29	**TS11**	-1600.764930	-1599.176030	0.356105	0.390381	0.391499	0.283004	-200.3615
30	**int12**	-820.199765	-819.278550	0.258126	0.281287	0.282406	0.198378	

31	**TS12**	-819.677132	-818.694317	0.242448	0.265769	0.266888	0.182888	-170.3237
32	**int13**	-819.709713	-818.730196	0.244027	0.267008	0.268126	0.184537	

Coordinate of optimized structures

Structure S1. **1SP**

E(RB3LYP)sol = -1507.77691124 E(RB3LYP)gas = -1506.33697826

6	6.244056	-2.192153	0.102681
6	5.547994	-2.253438	-1.107203
6	4.241099	-1.767834	-1.187297
6	3.601660	-1.207782	-0.064425
6	4.317093	-1.157255	1.149450
6	5.620931	-1.642402	1.230391
1	7.266452	-2.572097	0.170282
1	6.023539	-2.681178	-1.993393
1	3.703020	-1.818004	-2.138209
1	3.849438	-0.739528	2.043564
1	6.157147	-1.594300	2.181575
6	2.226675	-0.705893	-0.212679
1	1.785161	-0.864380	-1.201890
6	1.501003	-0.064063	0.716184
1	1.915819	0.168767	1.699815
6	0.094516	0.503890	0.507257
7	-0.535604	-0.167933	-0.627058
6	0.256603	2.020540	0.257793
6	0.580450	2.463818	-1.031040
6	0.168005	2.942449	1.304496
6	0.808428	3.818471	-1.267746
1	0.629345	1.744700	-1.850079
6	0.402209	4.300866	1.064925
1	-0.098998	2.609456	2.309814
6	0.722677	4.742721	-0.219810
1	1.047892	4.156469	-2.279011
1	0.323713	5.014616	1.888714
1	0.899044	5.804665	-0.408065
16	-2.107975	0.165313	-1.189323
8	-2.438588	1.510994	-0.727642
8	-2.079078	-0.207991	-2.601112
6	-3.172263	-1.010608	-0.349820
6	-3.809240	-0.632581	0.834922
6	-3.343410	-2.282236	-0.909195
6	-4.620373	-1.565354	1.485949
1	-3.666866	0.371661	1.233932
6	-4.154640	-3.204043	-0.245146
1	-2.862958	-2.527484	-1.858366
6	-4.788453	-2.846645	0.951197
1	-5.120434	-1.287473	2.416410
1	-4.301129	-4.200897	-0.667840
1	-5.423467	-3.571528	1.466575
7	-1.264751	0.024208	2.728559
6	-0.667616	0.253373	1.763045
1	-0.319711	-1.159460	-0.708698

Structure S2. $^{-}SO_2Ph$

E(RB3LYP)sol = -780.598768184 E(RB3LYP)gas = -779.886120382

16	1.798807	0.000100	-0.351794
8	2.169379	-1.290273	0.373218
8	2.169362	1.290119	0.373867
6	-0.094995	0.000037	-0.123514
6	-0.790514	-1.209278	-0.062769
6	-0.790606	1.209305	-0.063003
6	-2.186954	-1.212665	0.037346
1	-0.201786	-2.132927	-0.066436
6	-2.187058	1.212608	0.037093
1	-0.201946	2.132996	-0.066973
6	-2.889155	-0.000050	0.081475
1	-2.734884	-2.160680	0.092803
1	-2.735048	2.160597	0.092389
1	-3.981483	-0.000099	0.160478

Structure S3. HSO_2Ph

E(RB3LYP)sol = -781.067749243 E(RB3LYP)gas = -780.446585051

16	-1.697194	-0.021501	-0.418301
8	-2.173223	1.322113	0.009362
8	-1.945874	-1.169311	0.814770
6	0.102378	-0.025343	-0.158663
6	0.723418	1.196984	0.095644
6	2.114170	1.231743	0.238917
6	2.861231	0.055542	0.119471
6	2.222809	-1.164039	-0.139365
6	0.834492	-1.210293	-0.282155
1	0.108919	2.095586	0.188684
1	2.614993	2.180804	0.445924
1	3.948208	0.087033	0.229222
1	2.809010	-2.082419	-0.224899
1	0.322430	-2.157695	-0.465395
1	-2.846666	-1.509269	0.683130

Structure S4. 1A

E(RB3LYP)sol = -1507.29636505 E(RB3LYP)gas = -1505.79368563

6	5.944139	-2.525682	-0.058799
6	4.945816	-3.047630	-0.886527
6	3.675066	-2.468188	-0.906995
6	3.360260	-1.354110	-0.101847
6	4.383576	-0.839209	0.723497
6	5.652587	-1.416042	0.745329
1	6.940738	-2.975464	-0.040350
1	5.157368	-3.912463	-1.522169
1	2.898450	-2.881101	-1.556677
1	4.181143	0.029995	1.353081
1	6.425619	-0.994690	1.394790
6	2.003534	-0.793029	-0.164089
1	1.309181	-1.223341	-0.892970
6	1.508585	0.201179	0.585985
1	2.103383	0.703901	1.354803
6	0.079214	0.745202	0.425526
7	-0.579426	0.021334	-0.619980
6	0.254564	2.271761	0.164468
6	0.203478	2.744305	-1.152827
6	0.542741	3.170850	1.199178
6	0.442205	4.092173	-1.427681
1	-0.053471	2.039988	-1.945896
6	0.779578	4.521748	0.924413
1	0.562021	2.816237	2.233443
6	0.734000	4.987928	-0.392516
1	0.388646	4.448791	-2.460609
1	0.991704	5.213167	1.745603
1	0.913135	6.045100	-0.610186
16	-2.123720	0.305072	-0.908876
8	-2.671691	1.466042	-0.157908
8	-2.371225	0.241684	-2.366512
6	-3.002098	-1.147137	-0.250688
6	-3.578403	-1.099718	1.021828
6	-3.061735	-2.316149	-1.017821
6	-4.205418	-2.240193	1.534854
1	-3.521367	-0.172270	1.593136
6	-3.689469	-3.450825	-0.499377
1	-2.622785	-2.308661	-2.017640
6	-4.261481	-3.416331	0.779385
1	-4.652343	-2.208441	2.532967
1	-3.739083	-4.366807	-1.096392
1	-4.753021	-4.306103	1.184318
7	-1.014876	0.335732	2.816469
6	-0.551800	0.547385	1.773490

Structure S5. TS1

E(RB3LYP)sol = -1507.27297462 E(RB3LYP)gas = -1505.76270527

6	6.243188	-1.935581	-0.251178
6	5.319942	-2.544195	-1.106968
6	3.992495	-2.111907	-1.131000
6	3.545719	-1.056998	-0.307023
6	4.491157	-0.463003	0.558620
6	5.816639	-0.893570	0.582760
1	7.283072	-2.273015	-0.227072
1	5.635031	-3.363619	-1.759730
1	3.275789	-2.594033	-1.801879
1	4.174843	0.335919	1.232429
1	6.525387	-0.417166	1.266478
6	2.144422	-0.634763	-0.380923
1	1.467436	-1.270303	-0.960203
6	1.607055	0.458200	0.193316
1	2.215132	1.164438	0.760811
6	0.172721	0.831361	0.064346
7	-0.599215	-0.045110	-0.532280
6	-0.075374	2.325137	0.054996
6	-0.540521	2.899446	-1.140785
6	0.271313	3.171451	1.118525
6	-0.659112	4.285781	-1.265632
1	-0.823684	2.252804	-1.973630
6	0.155399	4.556443	0.990617
1	0.588625	2.713254	2.056562
6	-0.309501	5.121772	-0.202170
1	-1.033341	4.711418	-2.201049
1	0.415598	5.199312	1.836694
1	-0.408410	6.207256	-0.297214
16	-2.226060	0.165986	-0.749559
8	-2.832298	1.173567	0.136313
8	-2.498369	0.249824	-2.200691
6	-2.813707	-1.444553	-0.189942
6	-2.684749	-1.782720	1.162101
6	-3.419765	-2.301992	-1.108982
6	-3.173498	-3.020634	1.586635
1	-2.188624	-1.107896	1.866430
6	-3.912096	-3.534528	-0.666365
1	-3.493624	-1.989999	-2.152464
6	-3.788553	-3.893572	0.679786
1	-3.065755	-3.302605	2.637410
1	-4.390838	-4.215777	-1.375942
1	-4.170118	-4.859507	1.024096
7	-0.509367	-0.217916	3.241812

6	-0.047200	0.403057	2.360849

Frequencies -- -142.2036
Red. masses -- 10.2542
Frc consts -- 0.1222
IR Inten -- 95.3380

Structure S6. **1s**

E(RB3LYP)sol = -1414.29266090 E(RB3LYP)gas = -1412.96354785

6	-6.342143	-1.291591	0.001858
6	-5.380158	-2.305271	0.029936
6	-4.024050	-1.978776	0.073872
6	-3.597880	-0.634245	0.089907
6	-4.584337	0.376101	0.062925
6	-5.937442	0.050187	0.019008
1	-7.405179	-1.543002	-0.031872
1	-5.687393	-3.353941	0.018128
1	-3.273704	-2.773744	0.096178
1	-4.289017	1.427186	0.079781
1	-6.686100	0.846172	-0.000352
6	-2.163780	-0.355051	0.133180
1	-1.503645	-1.227805	0.182953
6	-1.560909	0.855854	0.118267
1	-2.148979	1.774282	0.066878
6	-0.097313	1.027150	0.180921
7	0.616166	-0.030909	0.411225
6	0.409005	2.419422	-0.003462
6	-0.113228	3.221097	-1.034628
6	1.377097	2.960552	0.861232
6	0.342830	4.527259	-1.215961
1	-0.860346	2.808573	-1.717037
6	1.811836	4.275116	0.691016
1	1.789848	2.350753	1.665881
6	1.302818	5.059089	-0.348865
1	-0.052995	5.132191	-2.035491
1	2.559595	4.686809	1.373059
1	1.653784	6.085382	-0.483984
16	2.305774	-0.066407	0.363416
8	2.845037	0.713081	-0.758536
8	2.801891	0.154444	1.730325
6	2.521999	-1.804982	-0.023362
6	2.725978	-2.182618	-1.351800
6	2.498026	-2.738962	1.015447
6	2.895603	-3.538298	-1.646749
1	2.759336	-1.417256	-2.129225
6	2.667943	-4.090290	0.707169
1	2.358640	-2.398764	2.043088
6	2.863678	-4.488933	-0.620813
1	3.058696	-3.852154	-2.680717
1	2.654165	-4.835139	1.506701
1	2.998882	-5.547728	-0.856105

Structure S7. CN⁻

E(RB3LYP)sol = -92.9987583882 E(RB3LYP)gas = -92.7638229989

7	0.000000	0.000000	0.544137
6	0.000000	0.000000	-0.634826

Structure S8. **TS2**

E(RB3LYP)sol = -1507.27379179 E(RB3LYP)gas = -1505.76170084

6	6.293527	-0.674351	-0.648563
6	5.429377	-1.776930	-0.675768
6	4.057653	-1.597366	-0.511622
6	3.506530	-0.314128	-0.323344
6	4.386370	0.782970	-0.302840
6	5.764037	0.605055	-0.459028
1	7.371378	-0.813520	-0.772342
1	5.831594	-2.784426	-0.815429
1	3.385839	-2.458384	-0.490192
1	3.991151	1.792132	-0.174168
1	6.427125	1.474931	-0.437792
6	2.040794	-0.169425	-0.211340
1	1.450427	-1.000824	-0.594415
6	1.381622	1.037786	-0.079219
1	1.926937	1.937643	0.207453
6	-0.039732	1.154940	-0.215488
7	-0.731616	0.107529	-0.611622
6	-0.636960	2.500815	0.064956
6	-0.228845	3.243154	1.185750
6	-1.589691	3.056970	-0.806882
6	-0.762648	4.510100	1.433201
1	0.490711	2.806476	1.881876
6	-2.108093	4.329770	-0.567612
1	-1.933632	2.477793	-1.665857
6	-1.698808	5.060968	0.552774
1	-0.449386	5.066830	2.320940
1	-2.846233	4.749444	-1.256637
1	-2.114565	6.054685	0.743194
16	-2.374863	-0.039985	-0.514106
8	-2.956755	0.659381	0.646880
8	-2.991586	0.192288	-1.839275

6	-2.474090	-1.807446	-0.178906
6	-1.680066	-2.359526	0.829065
6	-3.384112	-2.581541	-0.901264
6	-1.790786	-3.722688	1.107650
1	-0.943898	-1.763708	1.370952
6	-3.500199	-3.943364	-0.601526
1	-3.972838	-2.112596	-1.692090
6	-2.703676	-4.513430	0.398884
1	-1.131849	-4.144676	1.870563
1	-4.207131	-4.563205	-1.160953
1	-2.787947	-5.582111	0.618183
7	1.172876	-2.271872	2.441585
6	1.739136	-1.515612	1.744763

Frequencies -- -150.8187
Red. masses -- 9.3110
Frc consts -- 0.1248
IR Inten -- 178.9041

Structure S9. 1B

E(RB3LYP)sol = -1507.31342909 E(RB3LYP)gas = -1505.81581222

6	4.336327	2.948034	-1.314163
6	4.594703	2.622887	0.019080
6	3.731479	1.767925	0.716445
6	2.600187	1.233884	0.087704
6	2.340728	1.565262	-1.255150
6	3.205681	2.413786	-1.946933
1	5.011335	3.613854	-1.859992
1	5.474173	3.033138	0.524473
1	3.943662	1.510810	1.757387
1	1.447501	1.144969	-1.728897
1	2.995248	2.661419	-2.991481
6	1.594502	0.319675	0.795596
1	1.423888	-0.550474	0.139594
6	0.240260	0.977036	0.994817
1	0.146643	1.681074	1.824044
6	-0.787014	0.769499	0.119580
7	-0.563411	0.099682	-1.072422
6	-2.121933	1.395209	0.383412
6	-2.595959	1.626476	1.686753
6	-2.933909	1.783338	-0.697130
6	-3.828039	2.248694	1.904559
1	-2.000934	1.286806	2.537733
6	-4.162127	2.407913	-0.481988
1	-2.578835	1.574429	-1.707288
6	-4.616096	2.648017	0.820403
1	-4.181043	2.409511	2.927868
1	-4.776375	2.702802	-1.338059
1	-5.583921	3.129805	0.988817
16	-1.380280	-1.241260	-1.413242
8	-2.759138	-1.298505	-0.869706
8	-1.180163	-1.570921	-2.836380
6	-0.449576	-2.485818	-0.468448
6	-0.716000	-2.649197	0.895554
6	0.621372	-3.152356	-1.072271
6	0.115017	-3.468654	1.664756
1	-1.566802	-2.124248	1.334063
6	1.440601	-3.979461	-0.299190
1	0.793343	-3.000543	-2.140062
6	1.195040	-4.131942	1.071239
1	-0.072751	-3.580961	2.736022
1	2.281161	-4.502547	-0.765164
1	1.849442	-4.763010	1.678826
7	2.498200	-0.584224	3.093842
6	2.103028	-0.196786	2.074162

Structure S10. int1

E(RB3LYP)sol = -1507.31840878 E(RB3LYP)gas = -1505.83064681

6	-4.690755	2.453421	-0.406738
6	-4.686205	1.624533	0.724376
6	-3.499411	1.085644	1.213802
6	-2.248808	1.339368	0.589671
6	-2.278993	2.171229	-0.560761
6	-3.469039	2.720099	-1.036883
1	-5.623886	2.875355	-0.790022
1	-5.626658	1.395860	1.236576
1	-3.524723	0.442201	2.096707
1	-1.357389	2.357081	-1.115253
1	-3.443145	3.352181	-1.930793
6	-1.013880	0.738616	1.084803
1	1.033871	-1.179615	1.926364
6	0.269017	1.105552	0.592039
1	0.302697	2.084668	0.105010
6	1.476654	0.427253	0.635196
7	1.525255	-0.945784	1.061484
6	2.756306	1.045205	0.263307
6	2.893433	2.443244	0.064659
6	3.928090	0.266713	0.094935
6	4.107751	3.015731	-0.313125
1	2.039032	3.101255	0.234485
6	5.142366	0.845633	-0.269585
1	3.863349	-0.811015	0.228822
6	5.249683	2.225119	-0.485552

1	4.165425	4.099749	-0.455869
1	6.020199	0.203742	-0.395020
1	6.204014	2.675563	-0.772916
16	1.245808	-2.189841	-0.046113
8	2.193471	-2.020327	-1.155237
8	1.218393	-3.422996	0.749889
6	-0.395687	-1.940837	-0.736080
6	-0.543999	-1.118321	-1.856716
6	-1.497721	-2.501871	-0.085509
6	-1.830767	-0.833784	-2.318059
1	0.343898	-0.705131	-2.336869
6	-2.777927	-2.211753	-0.561002
1	-1.342728	-3.118185	0.800235
6	-2.945123	-1.373327	-1.667859
1	-1.966839	-0.168692	-3.174240
1	-3.651052	-2.620680	-0.046624
1	-3.950700	-1.118137	-2.011183
7	-1.193244	-1.051497	2.941443
6	-1.117869	-0.244329	2.095198

Structure S11. TS3

E(RB3LYP)sol = -1507.29166243 E(RB3LYP)gas = -1505.80913899

6	5.310164	-1.438468	-0.486500
6	5.297496	-0.632109	0.657861
6	4.092317	-0.208641	1.217224
6	2.847485	-0.577289	0.654870
6	2.881616	-1.370889	-0.516551
6	4.089037	-1.800197	-1.067084
1	6.255631	-1.767780	-0.926130
1	6.239853	-0.328917	1.124127
1	4.105055	0.418742	2.111440
1	1.950237	-1.619540	-1.026424
1	4.074432	-2.408626	-1.976586
6	1.574290	-0.133868	1.254541
1	-0.546842	1.358883	2.137797
6	0.359357	-0.750199	0.963860
1	0.450836	-1.669679	0.382368
6	-0.978263	-0.366111	1.277996
7	-1.343477	0.824222	1.785580
6	-2.089166	-1.280777	0.901707
6	-1.912735	-2.672070	0.740952
6	-3.387254	-0.760976	0.693748
6	-2.972783	-3.502051	0.368187
1	-0.936207	-3.121933	0.934607
6	-4.443562	-1.593695	0.323539
1	-3.545481	0.313318	0.795600
6	-4.248334	-2.970150	0.153412
1	-2.800756	-4.577242	0.256402
1	-5.433017	-1.157111	0.156510
1	-5.079048	-3.619133	-0.138781
16	-1.567373	2.362229	0.073512
8	-3.007864	2.421677	-0.328614
8	-0.822261	3.646403	0.250883
6	-0.719965	1.466516	-1.289957
6	-1.406677	0.475191	-1.990152
6	0.635206	1.710873	-1.520229
6	-0.722387	-0.280652	-2.949090
1	-2.463442	0.304263	-1.775257
6	1.308945	0.966174	-2.490743
1	1.142533	2.476155	-0.928399
6	0.630746	-0.032658	-3.202079
1	-1.248213	-1.070306	-3.493443
1	2.370142	1.148079	-2.678158
1	1.166054	-0.628237	-3.947345
7	1.797583	1.808737	2.956008
6	1.660878	0.948388	2.178857

Frequencies -- -150.7898

Red. masses -- 12.0207

Frc consts -- 0.1610

IR Inten -- 221.6585

Structure S12. int2

E(RB3LYP)sol = -726.699668746 E(RB3LYP)gas = -725.890983808

6	4.848948	-1.465761	-0.052371
6	4.671855	-0.368577	0.794759
6	3.472238	0.345514	0.780300
6	2.420718	-0.033077	-0.075554
6	2.617645	-1.130820	-0.935976
6	3.817623	-1.840713	-0.921026
1	5.790064	-2.021002	-0.044890
1	5.473055	-0.062317	1.471664
1	3.347309	1.203630	1.444374
1	1.836956	-1.418658	-1.643078
1	3.953603	-2.684973	-1.601395
6	1.133131	0.713510	-0.062410
1	-0.660098	2.526540	-1.176729
6	-0.052676	0.180783	-0.456057
1	-0.054307	-0.873308	-0.743366
6	-1.370804	0.867777	-0.526810
7	-1.543276	2.075598	-0.921659
6	-2.569629	0.053808	-0.153484
6	-2.459724	-1.123044	0.607289

6	-3.848722	0.488427	-0.547651
6	-3.599052	-1.851956	0.960954
1	-1.481658	-1.467856	0.951204
6	-4.983123	-0.242398	-0.200137
1	-3.926019	1.409228	-1.128074
6	-4.862611	-1.416468	0.554490
1	-3.497417	-2.760626	1.559592
1	-5.969935	0.103505	-0.518378
1	-5.753562	-1.988274	0.826565
7	1.307305	3.148662	0.838448
6	1.196482	2.067043	0.431182

Structure S13. TS4

E(RB3LYP)sol = -726.674824006 E(RB3LYP)gas = -725.859719085

6	5.116064	-1.132467	0.141266
6	4.883648	0.240336	0.015459
6	3.580594	0.736135	-0.044108
6	2.477277	-0.141066	0.021511
6	2.728000	-1.525334	0.148170
6	4.030552	-2.014967	0.207345
1	6.138409	-1.516904	0.187862
1	5.725874	0.935051	-0.037011
1	3.379647	1.805167	-0.143003
1	1.897451	-2.231813	0.201056
1	4.202415	-3.089859	0.305626
6	1.100866	0.371981	-0.041939
1	-1.479425	2.513752	-0.275229
6	-0.047355	-0.375153	0.017178
1	-0.114688	-1.452735	0.141281
6	-1.219379	0.473503	-0.055603
7	-0.857978	1.718998	-0.157017
6	-2.612229	-0.008599	-0.007810
6	-2.933867	-1.304172	-0.452499
6	-3.641514	0.819939	0.477461
6	-4.255108	-1.753192	-0.426023
1	-2.149505	-1.954295	-0.844915
6	-4.959364	0.365557	0.511971
1	-3.403122	1.817746	0.853705
6	-5.269978	-0.921140	0.057248
1	-4.494141	-2.756713	-0.786026
1	-5.747442	1.014988	0.900433
1	-6.303353	-1.275676	0.082295
7	1.386928	2.886916	-0.268097
6	0.795997	1.826954	-0.171339

Frequencies -- -262.7868

Red. masses -- 6.7421

Frc consts -- 0.2743

IR Inten -- 22.0422

Structure S14. int3

E(RB3LYP)sol = -726.676378113 E(RB3LYP)gas = -725.860103341

6	5.144345	-1.067533	0.136335
6	4.876251	0.299305	0.010683
6	3.561006	0.760746	-0.048332
6	2.482103	-0.147079	0.018464
6	2.767981	-1.524486	0.145296
6	4.083300	-1.979304	0.203485
1	6.176618	-1.424782	0.181917
1	5.700583	1.015203	-0.042384
1	3.323650	1.823280	-0.146609
1	1.955143	-2.251440	0.199787
1	4.284603	-3.049071	0.301938
6	1.097500	0.332052	-0.043307
1	-1.400927	2.481883	-0.273827
6	-0.043800	-0.437297	0.008884
1	-0.108457	-1.516277	0.126079
6	-1.203596	0.412327	-0.059294
7	-0.813354	1.662283	-0.159587
6	-2.605814	-0.026895	-0.009215
6	-2.958352	-1.324716	-0.424667
6	-3.617015	0.838491	0.450750
6	-4.289982	-1.740247	-0.392857
1	-2.188485	-2.002939	-0.797595
6	-4.945897	0.417958	0.488263
1	-3.357664	1.838683	0.806170
6	-5.286411	-0.871500	0.063954
1	-4.552056	-2.746328	-0.728818
1	-5.719318	1.096420	0.855945
1	-6.328426	-1.199441	0.091851
7	1.318887	2.855074	-0.252110
6	0.717714	1.777061	-0.163871

Structure S15. int4

E(RB3LYP)sol = -726.713605392 E(RB3LYP)gas = -725.912891489

6	5.177988	-1.007979	0.039550
6	4.863314	0.344469	0.196322
6	3.534129	0.771620	0.173258
6	2.484834	-0.154040	-0.005469
6	2.820484	-1.516508	-0.170479

6	4.147667	-1.938027	-0.146708
1	6.219791	-1.338267	0.057465
1	5.660673	1.078587	0.337983
1	3.288517	1.827190	0.284631
1	2.033084	-2.255399	-0.332572
1	4.382322	-2.997312	-0.279208
6	1.078455	0.265912	-0.012994
1	0.596202	3.551702	-0.136796
6	-0.034646	-0.512721	0.021323
1	-0.072999	-1.597944	0.079702
6	-1.209975	0.387658	-0.013856
7	-0.871992	1.645850	-0.063587
6	-2.612801	-0.050628	0.007097
6	-2.960837	-1.413431	0.057771
6	-3.640803	0.913891	-0.024701
6	-4.301798	-1.802722	0.076285
1	-2.184228	-2.179564	0.082625
6	-4.976904	0.522972	-0.006061
1	-3.358612	1.967281	-0.064060
6	-5.311990	-0.836982	0.044525
1	-4.558886	-2.864043	0.115635
1	-5.765480	1.279232	-0.030980
1	-6.361395	-1.142456	0.059091
7	1.235371	2.747214	-0.107136
6	0.539109	1.679775	-0.065605

Structure S16. TS5

E(RB3LYP)sol = -819.687054118 E(RB3LYP)gas = -818.703896246

6	5.188735	-0.704952	-0.592374
6	4.863893	0.651560	-0.459305
6	3.544833	1.056699	-0.255919
6	2.492604	0.109594	-0.187421
6	2.841558	-1.260931	-0.292078
6	4.164286	-1.654770	-0.497276
1	6.225356	-1.017309	-0.751495
1	5.654031	1.408306	-0.512463
1	3.297050	2.111540	-0.131277
1	2.069424	-2.021750	-0.159024
1	4.399728	-2.721789	-0.566777
6	1.104703	0.503971	-0.013903
1	0.529137	3.595031	0.949809
6	-0.008996	-0.320769	-0.174377
1	-0.044698	-1.169654	-0.855577
6	-1.197164	0.559456	0.074217
7	-0.858125	1.748464	0.449366
6	-2.609269	0.173362	-0.127610
6	-2.985137	-1.154259	-0.399651
6	-3.609531	1.163373	-0.078885
6	-4.325318	-1.478692	-0.624092
1	-2.227600	-1.939082	-0.391879
6	-4.946841	0.836673	-0.300462
1	-3.301733	2.188865	0.134297
6	-5.310869	-0.487212	-0.577272
1	-4.602195	-2.517216	-0.826042
1	-5.711917	1.617680	-0.259594
1	-6.359763	-0.745086	-0.751130
7	1.224846	2.876854	0.716761
6	0.581848	1.799760	0.428872
7	0.093411	-2.774583	1.755991
6	-0.313958	-1.750310	1.355256

Frequencies -- -267.8221
Red. masses -- 10.5702
Frc consts -- 0.4467
IR Inten -- 446.1321

Structure S17. int5

E(RB3LYP)sol = -819.718466522 E(RB3LYP)gas = -818.739458604

6	5.247696	-0.755995	-0.430503
6	4.909873	0.583256	-0.173147
6	3.587880	0.983387	-0.008782
6	2.511021	0.045997	-0.100007
6	2.878750	-1.309553	-0.359328
6	4.209148	-1.692683	-0.518731
1	6.291237	-1.060729	-0.553983
1	5.703549	1.335657	-0.097064
1	3.330268	2.025170	0.189146
1	2.103754	-2.077799	-0.426082
1	4.439772	-2.746309	-0.713262
6	1.149235	0.455030	0.039335
1	0.537444	3.650909	0.417835
6	-0.032850	-0.474901	-0.089404
1	-0.076801	-1.008912	-1.064031
6	-1.205895	0.512618	-0.007338
7	-0.815841	1.724792	0.148181
6	-2.626991	0.139463	-0.128594
6	-3.040622	-1.186472	-0.362214
6	-3.617521	1.140049	-0.027128
6	-4.396003	-1.500582	-0.489805
1	-2.299765	-1.984565	-0.433941
6	-4.967717	0.824005	-0.156340
1	-3.286484	2.164498	0.153244
6	-5.367141	-0.499532	-0.388986

1	-4.694121	-2.537882	-0.666776
1	-5.719497	1.614737	-0.074445
1	-6.427746	-0.747309	-0.488776
7	1.249076	2.916125	0.363855
6	0.627786	1.782243	0.205523
7	-0.193831	-2.333972	1.771847
6	-0.129554	-1.509012	0.957274

Structure S18. int6

E(RB3LYP)sol = -819.740845297 E(RB3LYP)gas = -818.767901997

6	-5.303556	-0.687592	0.052431
6	-4.909039	0.655177	-0.001767
6	-3.562456	1.014505	-0.028097
6	-2.530380	0.033297	0.000048
6	-2.954708	-1.322718	0.054108
6	-4.304988	-1.669023	0.079481
1	-6.362315	-0.963656	0.072534
1	-5.668316	1.444894	-0.025016
1	-3.260323	2.061777	-0.074176
1	-2.220303	-2.125638	0.077509
1	-4.579433	-2.728511	0.121452
6	-1.129599	0.429550	-0.027464
1	1.327572	2.509136	-0.267967
6	0.048236	-0.399467	-0.015103
6	1.207891	0.404595	-0.044570
7	0.741907	1.714916	-0.051140
6	2.620464	0.109007	-0.013096
6	3.156678	-1.177274	-0.304620
6	3.564855	1.129696	0.299534
6	4.527356	-1.412218	-0.285448
1	2.484371	-1.995794	-0.557605
6	4.936386	0.884452	0.306924
1	3.211374	2.125737	0.577376
6	5.440294	-0.388377	0.014248
1	4.894152	-2.416841	-0.518765
1	5.622712	1.699804	0.558371
1	6.516492	-0.580814	0.021575
7	-1.334167	2.926213	-0.155296
6	-0.655223	1.810392	-0.082826
1	-0.689066	3.722815	-0.171591
7	0.186585	-2.976379	0.156867
6	0.108255	-1.815025	0.085097

Structure S19. TS6

E(RB3LYP)sol = -1507.24911595 E(RB3LYP)gas = -1505.74072430

6	-5.884347	-2.342855	-0.553157
6	-4.934436	-2.571047	-1.559218
6	-3.644056	-2.060311	-1.446056
6	-3.239803	-1.289960	-0.322495
6	-4.214024	-1.087080	0.692825
6	-5.504044	-1.600616	0.573187
1	-6.897908	-2.743900	-0.641150
1	-5.206462	-3.157022	-2.443316
1	-2.914079	-2.249249	-2.239277
1	-3.937255	-0.541854	1.597835
1	-6.224704	-1.428863	1.379378
6	-1.897343	-0.770725	-0.237662
1	-1.158972	-1.157924	-0.944887
6	-1.441933	0.096891	0.755938
1	-2.186455	0.697318	1.280138
6	-0.216285	0.857810	0.380744
7	0.866543	0.162194	0.287198
6	-0.381592	2.319750	0.130096
6	-1.545100	2.778893	-0.518780
6	0.580758	3.258831	0.544935
6	-1.735116	4.139945	-0.757735
1	-2.285292	2.049287	-0.854151
6	0.378177	4.621094	0.312984
1	1.485619	2.919786	1.049574
6	-0.774399	5.067794	-0.339698
1	-2.636975	4.477677	-1.275867
1	1.132917	5.338792	0.646005
1	-0.923715	6.135468	-0.524826
16	2.380564	0.628711	-0.200137
8	2.410288	1.203987	-1.556230
8	3.066770	1.355801	0.886619
6	3.120035	-1.010992	-0.264074
6	4.039640	-1.272905	-1.281117
6	2.825513	-1.953912	0.729529
6	4.693855	-2.508668	-1.303478
1	4.219741	-0.514554	-2.045894
6	3.485797	-3.184592	0.689543
1	2.069217	-1.746284	1.494283
6	4.418598	-3.462058	-0.317956
1	5.413526	-2.728563	-2.097034
1	3.256467	-3.935434	1.450064
1	4.926068	-4.430852	-0.339920
7	-0.047183	-1.658312	2.965695
6	-0.758685	-0.866733	2.474625

Frequencies -- -249.2426

Red. masses -- 11.0438

Frc consts -- 0.4042
IR Inten -- 373.2481

Structure S20. TS7

E(RB3LYP)sol = -1507.22524392 E(RB3LYP)gas = -1505.74089811

6	-5.471237	0.217696	-1.052267
6	-5.369223	-1.032537	-0.437620
6	-4.140873	-1.461381	0.079172
6	-3.001628	-0.651512	-0.020130
6	-3.106478	0.605171	-0.643126
6	-4.335889	1.032071	-1.149246
1	-6.430590	0.558015	-1.453397
1	-6.248425	-1.678286	-0.352450
1	-4.071236	-2.433847	0.574275
1	-2.224197	1.240498	-0.758341
1	-4.401124	2.013166	-1.627758
6	-1.630875	-1.107800	0.497030
1	-1.119701	-0.225038	0.911832
6	-0.705052	-1.712057	-0.546216
1	-1.026939	-2.659032	-0.999313
6	0.460956	-1.018579	-1.013203
7	-0.174212	-0.034447	-1.537020
6	1.885397	-1.385545	-0.994554
6	2.300914	-2.507023	-0.256755
6	2.844249	-0.616436	-1.681522
6	3.649356	-2.864645	-0.210236
1	1.547408	-3.077116	0.294102
6	4.193821	-0.966538	-1.614444
1	2.533231	0.275203	-2.229496
6	4.601372	-2.091760	-0.886505
1	3.962721	-3.739124	0.367475
1	4.934945	-0.352312	-2.133621
1	5.660570	-2.361749	-0.840053
16	0.755777	2.078296	-1.023759
8	2.048240	2.624476	-1.582173
8	-0.443819	2.990268	-1.038231
6	1.094910	1.824158	0.778723
6	2.342583	1.346568	1.187116
6	0.052948	1.972556	1.698185
6	2.543990	0.999964	2.526550
1	3.140670	1.252757	0.447367
6	0.257390	1.624479	3.037772
1	-0.901697	2.369223	1.342192
6	1.500825	1.131483	3.451691
1	3.517457	0.619005	2.849760
1	-0.555936	1.734402	3.761417
1	1.656047	0.846950	4.496365
7	-1.846691	-2.848918	2.466690
6	-1.759902	-2.066641	1.613808

Frequencies -- -368.9274
Red. masses -- 5.2109
Frc consts -- 0.4179
IR Inten -- 366.5893

Structure S21. int7

E(RB3LYP)sol = -726.662278279 E(RB3LYP)gas = -725.856062557

6	-5.212827	-0.564150	0.109010
6	-4.792741	0.764805	0.195189
6	-3.440611	1.088886	0.035180
6	-2.497629	0.084307	-0.212424
6	-2.924123	-1.251645	-0.296002
6	-4.273170	-1.572106	-0.136744
1	-6.269013	-0.816101	0.233414
1	-5.518424	1.558917	0.388418
1	-3.121553	2.131586	0.103845
1	-2.189565	-2.040049	-0.476415
1	-4.592832	-2.615156	-0.204027
6	-1.008463	0.374982	-0.392201
1	-0.706194	0.046504	-1.402919
6	-0.137366	-0.393449	0.614036
1	-0.468204	-0.284758	1.656480
6	1.220001	-0.793740	0.308291
7	0.406673	-1.757493	0.206940
6	2.616127	-0.442797	0.157948
6	3.012430	0.899889	0.295031
6	3.570727	-1.436928	-0.131176
6	4.357028	1.242940	0.143632
1	2.260474	1.664592	0.505308
6	4.911033	-1.086016	-0.276901
1	3.245929	-2.474881	-0.235204
6	5.304072	0.252682	-0.139622
1	4.667156	2.285498	0.245220
1	5.655779	-1.854195	-0.498754
1	6.356461	0.524052	-0.256197
7	-0.340810	2.908525	-0.192632
6	-0.667998	1.801803	-0.299801

Structure S22. TS8

E(RB3LYP)sol = -1600.24920401 E(RB3LYP)gas = -1598.48138817

6	-4.939503	-1.035431	-1.488841

6	-4.752384	-1.702386	-0.274017
6	-3.624859	-1.432678	0.507144
6	-2.667731	-0.493361	0.092239
6	-2.856578	0.171413	-1.129626
6	-3.986549	-0.102027	-1.908757
1	-5.819149	-1.247550	-2.106668
1	-5.481912	-2.444170	0.067161
1	-3.477651	-1.963309	1.448956
1	-2.107602	0.875328	-1.497714
1	-4.109748	0.420366	-2.862688
6	-1.442510	-0.187333	0.960795
1	-1.102459	0.824419	0.695509
6	-0.200182	-1.103731	0.812716
1	0.266578	-1.316257	1.777935
6	0.722552	-0.790584	-0.226145
7	0.239474	-0.033040	-1.320604
6	2.033970	-1.408001	-0.213903
6	2.417866	-2.406404	0.737555
6	3.029572	-1.051149	-1.175063
6	3.706013	-2.937599	0.761917
1	1.679740	-2.810654	1.430212
6	4.311175	-1.593793	-1.136888
1	2.773124	-0.318484	-1.940319
6	4.681922	-2.536311	-0.162938
1	3.946651	-3.702976	1.510280
1	5.042033	-1.273132	-1.889848
1	5.692929	-2.957595	-0.137077
16	0.641769	1.447426	-1.671640
8	1.954616	1.662530	-2.354195
8	-0.498041	2.113234	-2.376875
6	0.832033	2.355834	-0.095599
6	1.855511	1.979354	0.789501
6	-0.128529	3.294466	0.297678
6	1.900955	2.544894	2.068761
1	2.612672	1.263666	0.463586
6	-0.065089	3.871138	1.570167
1	-0.919736	3.544347	-0.413571
6	0.946882	3.490260	2.462951
1	2.686313	2.237554	2.766942
1	-0.811845	4.613133	1.872601
1	0.984719	3.923136	3.467803
7	-2.156091	-0.023049	3.489966
6	-1.839434	-0.107934	2.376350
7	-0.625859	-4.026784	0.875280
6	-0.931473	-2.894075	0.812201

Frequencies -- -427.7573

Red. masses -- 10.6036

Frc consts -- 1.1431

IR Inten -- 764.3115

Structure S23. int8

E(RB3LYP)sol = -1600.26089718 E(RB3LYP)gas = -1598.50129417

6	-4.983353	-0.935695	-1.420212
6	-4.795854	-1.634149	-0.223541
6	-3.646341	-1.413129	0.540030
6	-2.667401	-0.495051	0.126287
6	-2.853422	0.197529	-1.082555
6	-4.008027	-0.024893	-1.840205
1	-5.881296	-1.105535	-2.024230
1	-5.542000	-2.359064	0.117409
1	-3.504632	-1.965796	1.471618
1	-2.090325	0.886619	-1.452847
1	-4.133601	0.521647	-2.779995
6	-1.412857	-0.268061	0.970315
1	-0.998482	0.717392	0.721043
6	-0.213046	-1.280533	0.745225
1	0.315493	-1.351629	1.714166
6	0.791215	-0.805081	-0.310371
7	0.231499	-0.016253	-1.319392
6	2.105190	-1.329230	-0.253054
6	2.559309	-2.281463	0.740549
6	3.122517	-0.931372	-1.201971
6	3.878014	-2.718206	0.804042
1	1.851878	-2.707308	1.456157
6	4.427774	-1.391536	-1.119688
1	2.841745	-0.231476	-1.989004
6	4.852339	-2.287073	-0.113595
1	4.152329	-3.437663	1.587941
1	5.150443	-1.040625	-1.868861
1	5.887632	-2.639440	-0.057431
16	0.605856	1.491090	-1.673422
8	1.872398	1.708739	-2.431183
8	-0.583743	2.134585	-2.318830
6	0.834466	2.324979	-0.083291
6	1.857696	1.851094	0.767730
6	-0.177974	3.150667	0.430197
6	1.843293	2.213440	2.120967
1	2.667435	1.244406	0.357905
6	-0.165840	3.528487	1.774168
1	-0.974612	3.464460	-0.249642
6	0.842944	3.047159	2.630839
1	2.623751	1.827779	2.785786
1	-0.947071	4.189838	2.164701
1	0.834818	3.312586	3.692913
7	-2.060740	-0.213275	3.520448

6	-1.767077	-0.232571	2.396669
7	-1.087549	-3.737353	0.325957
6	-0.730050	-2.645655	0.507820

Structure S24. TS9

E(RB3LYP)sol = -1600.26174116 E(RB3LYP)gas = -1598.49906858

6	4.455718	-2.143954	-1.177879
6	4.532802	-1.521123	0.080720
6	3.390451	-1.159122	0.781793
6	2.070977	-1.380404	0.266378
6	2.023358	-2.046421	-0.999188
6	3.175863	-2.408497	-1.690176
1	5.358156	-2.426768	-1.728986
1	5.514264	-1.310473	0.523581
1	3.489849	-0.667752	1.752508
1	1.055417	-2.246822	-1.461892
1	3.072340	-2.900914	-2.664977
6	0.900855	-0.917336	0.961731
1	-0.984619	0.968845	2.056154
6	-0.469114	-1.239932	0.527068
1	-0.475616	-1.942515	-0.305189
6	-1.518925	-0.254349	0.419216
7	-1.397511	0.987289	1.121600
6	-2.786177	-0.565657	-0.182467
6	-3.084613	-1.862947	-0.710110
6	-3.841876	0.394559	-0.289622
6	-4.306883	-2.149259	-1.317165
1	-2.356388	-2.667671	-0.604845
6	-5.056781	0.091571	-0.891089
1	-3.662318	1.399978	0.088239
6	-5.316348	-1.183455	-1.426738
1	-4.479767	-3.163042	-1.699513
1	-5.825056	0.872761	-0.951831
1	-6.274398	-1.414720	-1.904282
16	-0.828941	2.381289	0.359691
8	-1.741923	2.705615	-0.750944
8	-0.603081	3.371896	1.429105
6	0.755781	2.036971	-0.421812
6	0.771257	1.450415	-1.691533
6	1.937986	2.312182	0.270901
6	2.001458	1.129285	-2.271543
1	-0.174432	1.248597	-2.195510
6	3.158519	1.999463	-0.328805
1	1.878687	2.719940	1.280648
6	3.193164	1.409164	-1.597876
1	2.029613	0.632762	-3.245067
1	4.090316	2.181493	0.213342
1	4.149385	1.115000	-2.037455
7	1.277813	0.451527	3.118075
6	1.092543	-0.183919	2.146590
7	-1.376755	-3.412782	2.652170
6	-1.064543	-2.690843	1.785243

Frequencies -- -373.0715
Red. masses -- 12.0212
Frc consts -- 0.9858
IR Inten -- 405.6994

Structure S25. int9

E(RB3LYP)sol = -1600.27339475 E(RB3LYP)gas = -1598.51966685

6	4.000275	-2.410467	-1.376705
6	4.288288	-1.794914	-0.144375
6	3.280552	-1.334815	0.690720
6	1.889094	-1.458877	0.357472
6	1.626151	-2.096473	-0.899305
6	2.648209	-2.552588	-1.726581
1	4.798653	-2.769170	-2.033978
1	5.332694	-1.666185	0.166984
1	3.542244	-0.852477	1.635867
1	0.594307	-2.188018	-1.245512
1	2.381266	-3.016476	-2.684253
6	0.859231	-0.970858	1.220782
1	-0.985398	1.144659	2.002592
6	-0.616806	-1.308625	1.004489
1	-0.640144	-2.131942	0.274729
6	-1.554832	-0.211013	0.504940
7	-1.359040	1.083939	1.052923
6	-2.769310	-0.525205	-0.157662
6	-3.128270	-1.865442	-0.551620
6	-3.748527	0.475465	-0.503368
6	-4.306983	-2.152225	-1.235328
1	-2.471715	-2.699456	-0.293313
6	-4.921334	0.165020	-1.173299
1	-3.527785	1.512301	-0.252849
6	-5.234922	-1.153227	-1.566613
1	-4.513904	-3.196542	-1.504955
1	-5.619831	0.979158	-1.408625
1	-6.160964	-1.386580	-2.102160
16	-0.660171	2.385381	0.207261
8	-1.524024	2.693641	-0.947757
8	-0.408322	3.427409	1.223860
6	0.920727	1.920181	-0.511617
6	0.937474	1.286159	-1.758532

6	2.100800	2.171666	0.195864
6	2.166451	0.911110	-2.309464
1	-0.005265	1.102385	-2.274731
6	3.319081	1.807316	-0.375965
1	2.039985	2.612219	1.191886
6	3.355352	1.182613	-1.630268
1	2.193726	0.380537	-3.264698
1	4.247852	1.979740	0.175066
1	4.308919	0.854575	-2.051035
7	1.504298	0.515641	3.227434
6	1.205701	-0.177245	2.323521
7	-1.628991	-2.403362	3.206071
6	-1.167568	-1.935347	2.246080

Structure S26. int10

E(RB3LYP)sol = -1507.79202358 E(RB3LYP)gas = -1506.35548936

6	-2.182779	-4.754972	-1.146076
6	-2.475293	-4.506671	0.196880
6	-2.120979	-3.285968	0.783093
6	-1.469897	-2.305156	0.026583
6	-1.175236	-2.559972	-1.322084
6	-1.531431	-3.775990	-1.906050
1	-2.461997	-5.708043	-1.602162
1	-2.985115	-5.264962	0.796522
1	-2.360723	-3.095782	1.831920
1	-0.659535	-1.795765	-1.910079
1	-1.301173	-3.961431	-2.958297
6	-1.019088	-0.961926	0.612430
1	-1.318090	-0.168280	-0.088826
6	0.488626	-0.946863	0.757856
1	0.899116	-1.648610	1.486764
6	1.340640	-0.203491	0.023805
7	0.853377	0.784838	-0.883468
6	2.814639	-0.386630	0.086147
6	3.372804	-1.669957	0.237159
6	3.681258	0.717926	-0.019959
6	4.756196	-1.842366	0.302616
1	2.714413	-2.540822	0.277659
6	5.064628	0.541902	0.045436
1	3.272418	1.724166	-0.120617
6	5.607515	-0.736467	0.208408
1	5.172158	-2.846893	0.414302
1	5.721709	1.412243	-0.025151
1	6.691010	-0.871644	0.255110
16	0.516266	2.385290	-0.339069
8	1.056447	2.555783	1.010403
8	0.941031	3.226235	-1.461834
6	-1.267885	2.438784	-0.235273
6	-1.876556	2.419902	1.020167
6	-2.009348	2.492493	-1.421364
6	-3.273290	2.429461	1.087728
1	-1.264666	2.376685	1.921605
6	-3.401326	2.505141	-1.337642
1	-1.497009	2.530376	-2.384381
6	-4.031109	2.469167	-0.085416
1	-3.762403	2.387448	2.062905
1	-3.999308	2.545219	-2.251146
1	-5.122309	2.471691	-0.027401
7	-2.162823	-0.413537	2.913942
6	-1.665752	-0.655970	1.895941
1	1.429521	0.900252	-1.717799

Structure S27. TS10

E(RB3LYP)sol = -1600.76251971 E(RB3LYP)gas = -1599.15199981

6	1.733536	4.286279	-1.479175
6	0.832663	4.427421	-0.415965
6	0.603273	3.363111	0.456970
6	1.270304	2.141199	0.283711
6	2.174618	2.008863	-0.778951
6	2.403829	3.074033	-1.657843
1	1.907595	5.118491	-2.166695
1	0.301256	5.371820	-0.270244
1	-0.105383	3.474413	1.280961
1	2.693785	1.057752	-0.922718
1	3.105845	2.950177	-2.486874
6	1.010145	0.964818	1.227494
1	1.550309	0.087989	0.842407
6	-0.476371	0.600696	1.315560
1	-1.034355	1.202672	2.034334
6	-1.163296	0.273595	0.136194
7	-0.441337	0.012763	-1.059807
6	-2.617867	0.174015	0.092979
6	-3.398487	0.144355	1.276227
6	-3.315899	0.101782	-1.138056
6	-4.792219	0.095416	1.222962
1	-2.904017	0.111399	2.248656
6	-4.706647	0.052422	-1.182932
1	-2.740897	0.077027	-2.064879
6	-5.464475	0.058320	-0.003613
1	-5.360343	0.066634	2.158360
1	-5.209149	0.002416	-2.154433
1	-6.556746	0.014302	-0.041215

16	-0.079289	-1.474641	-1.727883
8	-1.178957	-2.401266	-1.460872
8	0.380780	-1.179341	-3.095307
6	1.350215	-2.062745	-0.805247
6	1.142655	-2.669012	0.434105
6	2.636785	-1.787834	-1.283380
6	2.249410	-2.969793	1.232737
1	0.132349	-2.855441	0.798303
6	3.736600	-2.115132	-0.486554
1	2.752229	-1.324171	-2.265023
6	3.541885	-2.694688	0.774981
1	2.078568	-3.386582	2.227362
1	4.748803	-1.907483	-0.844795
1	4.404435	-2.923351	1.406898
7	2.090383	1.611030	3.536574
6	1.592311	1.275201	2.545004
1	0.040591	0.756235	-1.561768
7	-0.538230	-1.992286	3.115141
6	-0.330727	-0.921613	2.688386

Frequencies -- -263.5716

Red. masses -- 10.1046

Frc consts -- 0.4136

IR Inten -- 321.0813

Structure S28. int11

E(RB3LYP)sol = -1600.77739038 E(RB3LYP)gas = -1599.17785287

6	0.111516	4.180219	-1.857962
6	-0.920751	3.856010	-0.970144
6	-0.721302	2.894918	0.025935
6	0.514673	2.244329	0.140537
6	1.540811	2.565578	-0.757508
6	1.345441	3.533433	-1.748688
1	-0.050362	4.928760	-2.638641
1	-1.893959	4.346064	-1.057906
1	-1.541222	2.638376	0.698383
1	2.496132	2.038365	-0.686260
1	2.155400	3.770771	-2.443936
6	0.762885	1.182785	1.208018
1	1.533315	0.497726	0.822602
6	-0.504891	0.322722	1.526861
1	-1.213765	0.971604	2.076819
6	-1.160287	-0.203766	0.271383
7	-0.349981	-0.334843	-0.862650
6	-2.561418	-0.450879	0.206484
6	-3.443251	-0.278575	1.321656
6	-3.190183	-0.858101	-1.014987
6	-4.821585	-0.447738	1.203536
1	-3.034835	-0.035426	2.305792
6	-4.565155	-1.026704	-1.113315
1	-2.563764	-1.050327	-1.888378
6	-5.412589	-0.815580	-0.012031
1	-5.448604	-0.301988	2.090569
1	-4.991230	-1.337798	-2.073880
1	-6.493799	-0.955295	-0.095600
16	0.347062	-1.778639	-1.417324
8	-0.303919	-2.944463	-0.813992
8	0.491822	-1.627199	-2.878616
6	2.004916	-1.685597	-0.713020
6	2.230516	-2.203040	0.565073
6	2.992820	-0.964583	-1.392663
6	3.463966	-1.971912	1.181954
1	1.436051	-2.748158	1.076204
6	4.225144	-0.749344	-0.771185
1	2.777666	-0.581725	-2.392154
6	4.458353	-1.245016	0.518779
1	3.635727	-2.349054	2.192989
1	5.005897	-0.187323	-1.291413
1	5.417629	-1.058973	1.009238
7	1.747564	2.319125	3.366666
6	1.315465	1.806180	2.420284
1	-0.433832	0.291327	-1.667837
7	0.165698	-1.624519	3.185969
6	-0.130367	-0.745963	2.486265

Structure S29. TS11

E(RB3LYP)sol = -1600.76493040 E(RB3LYP)gas = -1599.17602950

6	-5.187955	0.860315	1.028268
6	-4.851655	1.312029	-0.251248
6	-3.745041	0.772603	-0.914166
6	-2.959703	-0.212945	-0.304083
6	-3.298658	-0.662051	0.980503
6	-4.409451	-0.129347	1.639174
1	-6.053703	1.279425	1.549187
1	-5.452561	2.085469	-0.737692
1	-3.493517	1.118055	-1.920899
1	-2.660959	-1.404201	1.465784
1	-4.662488	-0.483767	2.642398
6	-1.758890	-0.816730	-1.029835
1	-1.326220	-1.595389	-0.382577
6	-0.629375	0.226991	-1.326218
1	-1.075214	1.021577	-1.957682
6	-0.052025	0.818438	-0.052048

7	-0.402307	0.187943	1.124155
6	0.807765	1.958290	-0.083066
6	1.096115	2.690556	-1.279830
6	1.421145	2.467192	1.109663
6	1.890892	3.831845	-1.270044
1	0.699551	2.345009	-2.236842
6	2.214662	3.611121	1.100222
1	1.279735	1.935664	2.054689
6	2.462110	4.319761	-0.084081
1	2.078808	4.351477	-2.216127
1	2.658042	3.952817	2.042056
1	3.091010	5.213893	-0.086719
16	0.577943	-1.216871	1.879219
8	1.054538	-0.803574	3.222720
8	-0.297848	-2.415186	1.783277
6	1.980226	-1.532448	0.779176
6	2.954731	-0.547107	0.607879
6	2.017679	-2.729553	0.059498
6	3.986320	-0.769951	-0.306003
1	2.897788	0.391377	1.162295
6	3.063247	-2.948483	-0.838663
1	1.223747	-3.463626	0.208259
6	4.040890	-1.966812	-1.027081
1	4.737415	0.007126	-0.468818
1	3.100535	-3.877873	-1.412765
1	4.840048	-2.127785	-1.755587
7	-2.604554	-1.973795	-3.236159
6	-2.214078	-1.471573	-2.266605
1	-0.435536	0.804629	1.938151
7	1.261641	-0.849330	-2.827984
6	0.415955	-0.396739	-2.175191

Frequencies -- -200.3615
Red. masses -- 9.1766
Frc consts -- 0.2171
IR Inten -- 241.0007

Structure S30. int12

E(RB3LYP)sol = -820.199765206 E(RB3LYP)gas = -819.278550472

6	-2.656933	-3.024980	0.446883
6	-2.501296	-2.120382	1.502099
6	-2.192742	-0.783924	1.238252
6	-2.032333	-0.338677	-0.082147
6	-2.192082	-1.248681	-1.135716
6	-2.504499	-2.585338	-0.871350
1	-2.902110	-4.070024	0.652237
1	-2.627657	-2.453995	2.534970
1	-2.092787	-0.077200	2.066992
1	-2.054383	-0.907784	-2.163532
1	-2.630281	-3.285742	-1.700897
6	-1.646188	1.111165	-0.367687
1	-1.768995	1.317831	-1.441010
6	-0.138374	1.360410	-0.028030
1	0.022125	1.081231	1.025146
6	0.779562	0.502874	-0.927902
7	0.410863	0.339184	-2.134738
6	2.008565	-0.065651	-0.303905
6	2.742236	0.648572	0.660792
6	2.453250	-1.343655	-0.688073
6	3.906082	0.104411	1.207926
1	2.425630	1.648592	0.965511
6	3.608703	-1.890901	-0.129356
1	1.870363	-1.924525	-1.407518
6	4.340725	-1.165871	0.816905
1	4.476637	0.677206	1.942858
1	3.934523	-2.890617	-0.426707
1	5.246844	-1.593169	1.253361
7	-3.170742	2.761415	0.994536
6	-2.501794	2.044717	0.377929
1	1.092805	-0.211932	-2.665808
7	0.576196	3.875485	-0.280188
6	0.242628	2.772167	-0.165435

Structure S31. TS12

E(RB3LYP)sol = -819.677132478 E(RB3LYP)gas = -818.694316548

6	4.702952	-1.458995	-0.900243
6	4.686307	-0.074240	-1.107994
6	3.562408	0.679708	-0.772863
6	2.406547	0.074796	-0.226129
6	2.448805	-1.320590	0.003849
6	3.578109	-2.068786	-0.334980
1	5.584953	-2.050425	-1.162424
1	5.559972	0.426017	-1.537577
1	3.568512	1.759849	-0.938860
1	1.615499	-1.814321	0.506166
1	3.581736	-3.144516	-0.134304
6	1.207722	0.873425	0.098373
1	-0.670840	2.671619	0.942069
6	-0.039019	0.268526	0.282413
1	-0.108866	-0.726938	-0.150626
6	-1.353404	0.990045	0.338650
7	-1.542978	2.209146	0.674692
6	-2.563257	0.210893	-0.109244

6	-2.663511	-1.186448	0.011843
6	-3.647023	0.914863	-0.664675
6	-3.812166	-1.856369	-0.421249
1	-1.862624	-1.748507	0.495136
6	-4.788440	0.244275	-1.105224
1	-3.566202	2.000990	-0.736882
6	-4.875709	-1.147973	-0.987370
1	-3.875914	-2.942048	-0.305207
1	-5.615834	0.810207	-1.543853
1	-5.770325	-1.676189	-1.330458
7	1.645415	3.406685	0.414508
6	1.413523	2.267840	0.292218
7	0.089981	-1.791551	2.702324
6	-0.228343	-0.800251	2.161984

Frequencies -- -170.3237

Red. masses -- 11.0237

Frc consts -- 0.1884

IR Inten -- 360.2726

Structure S32. int13

E(RB3LYP)sol = -819.709712887 E(RB3LYP)gas = -818.730196076

6	4.064012	-2.427823	0.388825
6	4.557705	-1.170708	-0.001014
6	3.718681	-0.071103	-0.129016
6	2.314963	-0.155454	0.128120
6	1.836582	-1.446232	0.506427
6	2.691798	-2.541299	0.636587
1	4.729215	-3.290098	0.487242
1	5.626900	-1.047231	-0.206740
1	4.134006	0.894474	-0.428826
1	0.769612	-1.604975	0.680554
1	2.269093	-3.509059	0.929009
6	1.451146	0.991529	0.002094
1	0.480291	0.370341	-1.910443
6	-0.003416	0.880329	0.406349
1	-0.077368	0.228011	1.298562
6	-0.920290	0.224943	-0.686328
7	-0.494675	0.027709	-1.867037
6	-2.301242	-0.225246	-0.317316
6	-2.844912	-0.057040	0.968353
6	-3.089564	-0.864812	-1.294700
6	-4.133594	-0.513517	1.266349
1	-2.277023	0.448515	1.749456
6	-4.372829	-1.318703	-0.998092
1	-2.656028	-0.992312	-2.288097
6	-4.902550	-1.146022	0.287564
1	-4.536988	-0.367142	2.272137
1	-4.966903	-1.812314	-1.772849
1	-5.910023	-1.501608	0.522178
7	2.406276	3.238188	-0.831950
6	1.957900	2.224608	-0.445331
7	-1.087379	3.148060	1.181147
6	-0.583446	2.164165	0.829914

References

1. (a) B.-C. Da, Q.-J. Liang, Y.-C. Luo, T. Ahmad, Y.-H. Xu and T.-P. Loh, *ACS Catalysis*, 2018, **8**, 6239; (b) Z. Shi, P. Yu, T. P. Loh and G. Zhong, *Angew Chem Int Ed Engl*, 2012, **51**, 7825.
2. Z. Shi, Q. Tong, W. W. Leong and G. Zhong, *Chemistry*, 2012, **18**, 9802.
3. E. E. Galenko, S. A. Linnik, O. V. Khoroshilova, M. S. Novikov and A. F. Khlebnikov, *J Org Chem*, 2019, **84**, 11275.
4. (a) A. D. Becke, *The Journal of Chemical Physics*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785.
5. (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich and L. Goerigk, *Journal of Computational Chemistry*, 2011, **32**, 1456.
6. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *The Journal of Physical Chemistry B*, 2009, **113**, 6378.
7. (a) F. Weigend and R. Ahlrichs, *Physical Chemistry Chemical Physics*, 2005, **7**, 3297; (b) F. Weigend, *Physical Chemistry Chemical Physics*, 2006, **8**, 1057.
8. E. Besalú and J. M. Bofill, *Theoretical Chemistry Accounts*, 1998, **100**, 265.
9. K. Fukui, *Accounts of Chemical Research*, 1981, **14**, 363.
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2013.