

Supporting Information

Direct C–H Sulfonation of Hydrazones Involving the Insertion of SO₂

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Table of Contents

- I. General remarks
- II. General procedure for the three-component sulfonylation of hydrazones
- III. General procedure for the sulfonylation of hydrazones with sulfonyl chlorides
- IV. Gram scale procedure for the synthesis of **3a**
- V. Procedure for radical capture experiment with 1,1-diphenylethylene
- VI. References
- VII. Copies of NMR spectra

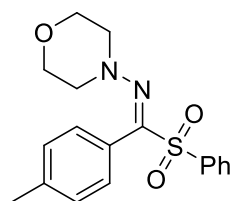
I. General remarks

NMR spectra were obtained on Bruker AV-400 MHz and AV-600 MHz spectrometers. The ^1H NMR chemical shifts were measured relative to CDCl_3 as the internal reference (CDCl_3 : $\delta = 7.26$ ppm). The ^{13}C NMR chemical shifts were given using CDCl_3 and $\text{DMSO-}d_6$ as the internal standard (CDCl_3 : $\delta = 77.16$ ppm; $\text{DMSO-}d_6$: $\delta = 39.52$ ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Aldehyde-derived hydrazones were prepared via condensation of hydrazines with aldehydes.¹ Aryldiazonium tetrafluoroborates were prepared according to the literature procedures.² Ultra dry solvents were purchased from J&K Scientific.

II. General procedure for the three-component sulfonylation of hydrazones

Hydrazone **1** (0.2 mmol, 1.0 equiv), aryldiazonium tetrafluoroborate **2** (0.4 mmol, 2.0 equiv), DABSO (0.4 mmol, 2.0 equiv), FeCl_3 (0.1 mmol, 50 mol%), quinoline (0.1 mmol, 50 mol%) were added to a 10-mL Schlenk tube. The tube was evacuated and backfilled with N_2 three times before MeCN (2 mL) was added. The reaction mixture was stirred at 25 °C for 24 h. The solvent was evaporated under reduced pressure. The residue was purified directly by flash chromatograph (petroleum ether/EtOAc) to give the corresponding product.



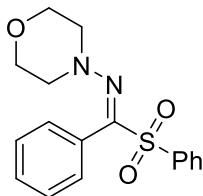
(*E*)-*N*-Morpholino-1-(phenylsulfonyl)-1-(*p*-tolyl)methanimine (**3a**)¹

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 87% yield. M.p.: 90-91 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 7.6$ Hz, 2H), 7.56–7.52 (m, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.15–7.11 (m, 4H), 3.58–3.55 (m, 4H), 3.04–3.02 (m, 4H), 2.34 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3): δ 142.76, 140.44, 139.49, 133.02, 129.90, 129.41, 128.86, 128.64, 127.53, 66.10, 54.10, 21.59 ppm.

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 345.1273, found 345.1268.



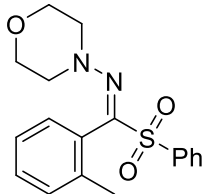
(E)-N-Morpholino-1-phenyl-1-(phenylsulfonyl)methanimine (3b)³

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 90% yield. M.p.: 130-131 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, J = 8 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 3.58–3.56 (m, 4H), 3.05–3.03 (m, 4H) ppm.

^{13}C NMR (151 MHz, CDCl_3): δ 142.35, 139.43, 133.12, 130.78, 130.20, 130.15, 128.91, 128.71, 66.13, 54.19 ppm.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 331.1116, found 331.1114.



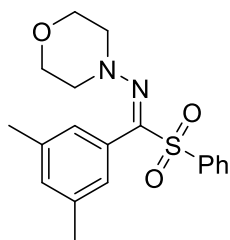
(E)-N-Morpholino-1-(phenylsulfonyl)-1-(o-tolyl)methanimine (3c)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as colorless oil. 71% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.75–7.73 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8 Hz, 2H), 7.33–7.27 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 3.59–3.56 (m, 4H), 3.04–3.00 (m, 4H), 1.94 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ 141.79, 139.55, 138.91, 133.13, 130.58, 130.50, 130.32, 130.03, 129.04, 128.71, 125.93, 66.41, 53.80, 19.77 ppm.

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 345.1273, found 345.1270



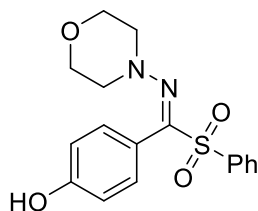
(E)-1-(3,5-Dimethylphenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3d)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 80% yield. M.p.: 142-143 °C. The *E*-configuration of the product **3d** was determined by a strong NOE signal of between *N*-methylene hydrogen (3.02 ppm, t, 4H) and an aromatic hydrogen (6.84 ppm, s, 2H).

¹H NMR (600 MHz, CDCl₃): δ 7.78–7.76 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.00 (s, 1H), 6.84 (s, 2H), 3.56 (t, *J* = 4.8 Hz, 4H), 3.02 (t, *J* = 4.8 Hz, 4H), 2.25 (s, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 143.05, 139.45, 138.28, 133.01, 131.90, 130.37, 129.01, 128.55, 127.63, 66.11, 54.10, 21.32 ppm.

HRMS (ESI): calcd for C₁₉H₂₃N₂O₃S [M+H]⁺ 359.1429, found 359.1424.



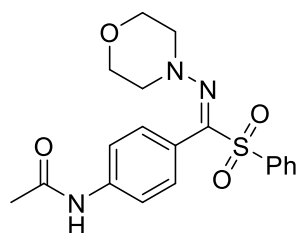
(E)-4-((Morpholinoimino)(phenylsulfonyl)methyl)phenol (3e)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 1/1, v/v) as a white solid. 77% yield. M.p.: 119-120°C.

¹H NMR (400 MHz, CDCl₃): δ 7.78–7.76 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.15–7.12 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.59–3.57 (m, 4H), 3.05–3.03 (m, 4H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ 158.01, 142.47, 139.11, 133.27, 131.62, 128.89, 128.79, 121.44, 116.05, 66.14, 54.05 ppm.

HRMS (ESI): calcd for C₁₇H₁₉N₂O₄S [M+H]⁺ 347.1066, found 347.1059.



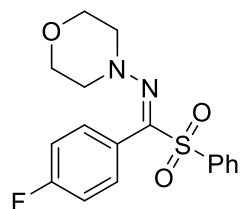
(E)-N-(4-((Morpholinoimino)(phenylsulfonyl)methyl)phenyl)acetamide (3f)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 1/2, v/v) as a green solid. 77% yield. M.p.: 227-229 °C.

¹H NMR (600 MHz, CDCl₃): δ 8.09 (s, 1H), 7.78–7.77 (m, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51–7.48 (m, 4H), 7.12 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 3.57–3.55 (m, 4H), 3.03–3.02 (m, 4H), 2.15 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 169.14, 141.75, 140.17, 139.19, 133.33, 130.84, 128.84, 125.19, 119.52, 66.11, 54.12, 24.73, 14.32 ppm.

HRMS (ESI): calcd for C₁₉H₂₂N₃O₄S [M+H]⁺ 388.1331, found 388.1340.



(E)-1-(4-Fluorophenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3g)

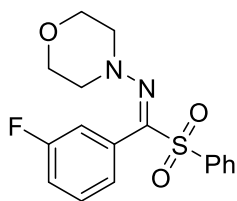
The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as yellow oil. 82% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.75–7.73 (m, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.27–7.24 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 2H), 3.60–3.58 (m, 4H), 3.06–3.03 (m, 4H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 163.61 (d, *J* = 252.0 Hz), 141.27, 139.20, 133.23, 132.22 (d, *J* = 8.5 Hz), 128.81 (d, *J* = 9.8 Hz), 126.61 (d, *J* = 3.8 Hz), 116.05 (d, *J* = 21.9 Hz), 66.05, 54.16 ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ -108.92 ppm.

HRMS (ESI): calcd for C₁₇H₁₈FN₂O₃S [M+H]⁺ 349.1022, found 349.1020.



(E)-1-(3-Fluorophenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3h)

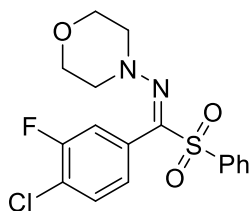
The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as colorless oil. 77% yield.

^1H NMR (600 MHz, CDCl_3): δ 7.80–7.78 (m, 2H), 7.62–7.59 (m, 1H), 7.50–7.47 (m, 2H), 7.37–7.33 (m, 1H), 7.15–7.13 (m, 1H), 7.07–7.06 (m, 1H), 7.03–7.01 (m, 1H), 3.63–3.61 (m, 4H), 3.10–3.08 (m, 4H) ppm.

^{13}C NMR (151 MHz, CDCl_3): δ 162.37 (d, $J = 249.9$ Hz), 140.33, 139.26, 133.30, 132.73 (d, $J = 7.8$ Hz), 130.37 (d, $J = 8.3$ Hz), 128.84 (d, $J = 4.9$ Hz), 126.11 (d, $J = 3.2$ Hz), 117.42 (dd, $J = 20.8$ Hz), 117.38, 117.23, 66.07, 54.19 ppm.

^{19}F NMR (565 MHz, CDCl_3): δ -110.97 ppm.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{18}\text{FN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 349.1022, found 349.1020.



(E)-1-(4-Chloro-3-fluorophenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3i)

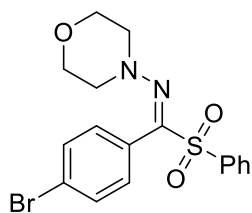
The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as yellow oil. 71% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.77–7.75 (m, 2H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 8.0$ Hz, 2H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.10 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.00 (dd, $J = 8.4, 1.2$ Hz, 1H), 3.62–3.60 (m, 4H), 3.08–3.06 (m, 4H) ppm.

^{13}C NMR (151 MHz, CDCl_3): δ 157.83 (d, $J = 252.8$ Hz), 139.22, 139.12, 133.44, 131.05, 130.97 (d, $J = 6.8$ Hz), 128.88 (d, $J = 14.8$ Hz), 126.83 (d, $J = 3.9$ Hz), 123.57 (d, $J = 17.2$ Hz), 118.56, 118.41, 66.06, 54.24 ppm.

^{19}F NMR (377 MHz, CDCl_3): δ -112.83 ppm.

HRMS (ESI): calcd for C₁₇H₁₇ClFN₂O₃S [M+H]⁺ 383.0632, found 383.0626.



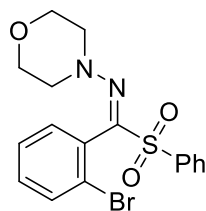
(E)-1-(4-Bromophenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3j)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as colorless oil. 57% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.81–7.78 (m, 3H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47–7.43 (m, 2H), 7.41–7.37 (m, 2H), 7.12–7.08 (m, 1H), 3.66–3.62 (m, 4H), 3.22–3.07 (m, 4H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 140.79, 139.21, 133.27, 132.02, 131.68, 129.66, 128.83, 124.87, 66.06, 54.20 ppm.

HRMS (ESI): calcd for C₁₇H₁₇BrNaN₂O₃S [M+Na]⁺ 431.0041 found 431.0018.



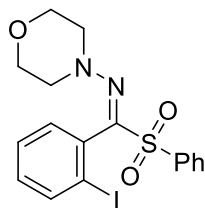
(E)-1-(2-Bromophenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3k)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as yellow oil. 50% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.79–7.77 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.48–7.42 (m, 3H), 7.38–7.35 (m, 1H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.64–3.62 (m, 4H), 3.22–3.07 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 139.87, 137.16, 133.13, 132.88, 132.78, 132.70, 131.67, 129.10, 128.70, 127.42, 125.28, 66.54, 53.47 ppm.

HRMS (ESI): calcd for C₁₇H₁₇BrNaN₂O₃S [M+Na]⁺ 431.0041 found 431.0025.



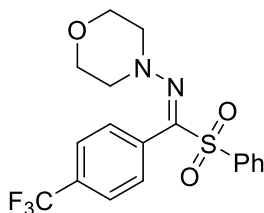
(E)-1-(2-Iodophenyl)-N-morpholino-1-(phenylsulfonyl)methanimine (3l)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 51% yield. M.p.: 132-133 °C.

¹H NMR (600 MHz, CDCl₃): δ 7.75–7.73 (m, 2H), 7.58–7.55 (m, 1H), 7.49–7.47 (m, 2H), 7.46–7.44 (m, 2H), 7.13–7.12 (m, 2H), 3.59–3.57 (m, 4H), 3.06–3.04 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 140.89, 139.26, 133.28, 132.04, 131.69, 129.69, 128.86, 128.83, 124.89, 66.08, 54.22 ppm.

HRMS (ESI): calcd for C₁₇H₁₈IN₂O₃S [M+H]⁺ 457.0083, found 457.0051.



(E)-N-Morpholino-1-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)methanimine (3m)

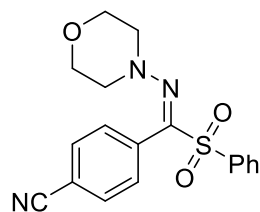
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as white solid. 65% yield. M.p.: 117-118 °C.

¹H NMR (600 MHz, CDCl₃): δ 7.76–7.74 (m, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 3.61–3.58 (m, 4H), 3.07–3.04 (m, 4H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 139.98, 139.14, 134.75, 133.40, 132.07 (q, *J* = 32.9 Hz), 130.69, 128.89, 128.83, 125.62 (q, *J* = 3.8 Hz), 123.65 (q, *J* = 272.7 Hz), 66.03, 54.26 ppm.

¹⁹F NMR (377 MHz, CDCl₃): δ -62.95 ppm.

HRMS (ESI): calcd for C₁₈H₁₈F₃N₂O₃S [M+H]⁺ 399.0990, found 399.0986.



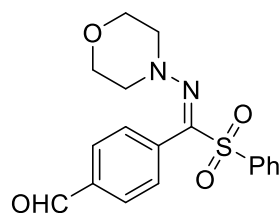
(E)-4-((Morpholinoimino)(phenylsulfonyl)methyl)benzonitrile (3n)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 1/2, v/v) as a white solid. 75% yield. M.p.: 128-130°C.

¹H NMR (400 MHz, CDCl₃): δ 7.76–7.73 (m, 2H), 7.67–7.64 (m, 2H), 7.62–7.58 (m, 1H), 7.49–7.45 (m, 2H), 7.41–7.39 (m, 2H), 3.61–3.59 (m, 4H), 3.06–3.04 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 139.29, 139.09, 135.87, 133.53, 132.31, 131.04, 129.00, 128.83, 117.97, 114.08, 66.02, 54.36 ppm.

HRMS (ESI): calcd for C₁₈H₁₈N₃O₃S [M+H]⁺ 356.1069, found 356.1062.



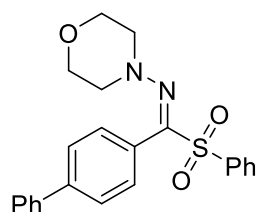
(E)-4-((Morpholinoimino)(phenylsulfonyl)methyl)benzaldehyde (3o)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as a white solid. 65% yield. M.p.: 121-123°C.

¹H NMR (400 MHz, CDCl₃): δ 10.03 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.76–7.74 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 4H), 3.60–3.58 (m, 1H), 3.07–3.05 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 191.46, 140.19, 139.25, 137.13, 137.09, 133.42, 131.00, 129.68, 128.92, 128.85, 66.06, 54.34 ppm.

HRMS (ESI): calcd for C₁₈H₁₉N₂O₄S [M+H]⁺ 359.1066, found 359.1060.



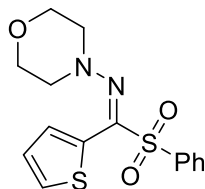
(E)-1-([1,1'-Biphenyl]-4-yl)-N-morpholino-1-(phenylsulfonyl)methanimine (3p)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 73% yield. M.p.: 161-163 °C.

¹H NMR (600 MHz, CDCl₃): δ 7.80 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.61–7.56 (m, 5H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.40–7.37 (m, 1H), 7.35–7.33 (m, 2H), 3.61–3.59 (m, 4H), 3.10–3.09 (m, 4H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 142.83, 142.19, 139.77, 139.44, 133.13, 130.51, 129.41, 129.04, 128.90, 128.72, 128.15, 127.23, 127.16, 66.10, 54.19 ppm.

HRMS (ESI): calcd for C₂₃H₂₃N₂O₃S [M+H]⁺ 407.1429, found 407.1436.



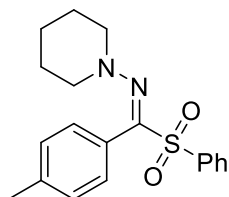
(E)-N-Morpholino-1-(phenylsulfonyl)-1-(thiophen-2-yl)methanimine (3q)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a yellow solid. 82% yield. M.p.: 138-139 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.99–7.97 (m, 2H), 7.59–7.55 (m, 3H), 7.52–7.48 (m, 2H), 6.93 (d, *J* = 3.9 Hz, 1H), 3.85 (m, 4H), 3.19–3.13 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 150.89, 142.27, 140.64, 133.63, 133.33, 129.41, 127.76, 127.46, 124.98, 66.30, 51.39 ppm.

HRMS (ESI): calcd for C₁₅H₁₇N₂O₃S₂ [M+H]⁺ 337.0681, found 337.0677.



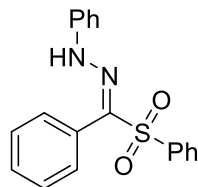
(E)-1-(Phenylsulfonyl)-N-(piperidin-1-yl)-1-(p-tolyl)methanimine (3r)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 10/1, v/v) as yellow oil. 73% yield.

¹H NMR (600 MHz, CDCl₃): δ 7.75 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.13–7.09 (m, 4H), 3.07–3.05 (m, 4H), 2.35 (s, 3H), 1.46–1.44 (m, 6H) ppm.

^{13}C NMR (151 MHz, CDCl_3): δ 140.4, 139.9, 138.6, 132.7, 130.1, 129.3, 128.7, 128.6, 128.4, 54.8, 25.1, 23.8, 21.6 ppm.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 343.1480, found 343.1471.



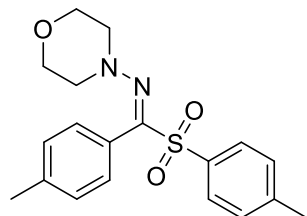
(E)-1-Phenyl-2-(phenyl(phenylsulfonyl)methylene)hydrazine (3s)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as yellow oil. 84% yield.

^1H NMR (600 MHz, CDCl_3): δ 7.93 (d, $J = 7.8$ Hz, 2H), 7.89 (s, 1H), 7.66 (t, $J = 7.8$ Hz, 1H), 7.57–7.54 (m, 5H), 7.37–7.36 (m, 2H), 7.24 (t, $J = 7.8$ Hz, 2H), 6.97 (t, $J = 7.8$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 2H) ppm.

^{13}C NMR (151 MHz, CDCl_3): δ 142.6, 142.3, 139.2, 133.5, 131.1, 123.0, 129.9, 129.4, 129.1, 129.0, 126.2, 122.6, 113.9 ppm.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 337.1011, found 337.1013.



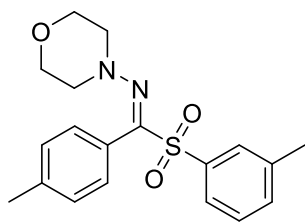
(E)-N-Morpholino-1-(p-tolyl)-1-tosylmethanimine (4a)¹

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 85% yield. M.p.: 124–126 °C.

^1H NMR (600 MHz, CDCl_3): δ 7.62 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.15–7.12 (m, 4H), 3.59–3.55 (m, 4H), 3.05–3.02 (m, 4H), 2.40 (s, 3H), 2.35 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ 143.89, 143.23, 140.38, 136.52, 129.89, 129.41, 129.34, 128.91, 127.68, 66.16, 54.13, 21.76, 21.64 ppm.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 359.1429, found 359.1424.



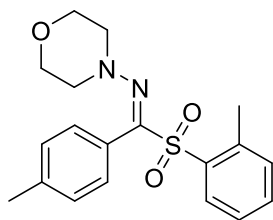
(E)-N-Morpholino-1-(p-tolyl)-1-(m-tolylsulfonyl)methanimine (4b)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as yellow oil. 80% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.56–7.51 (m, 2H), 7.35–7.28 (m, 2H), 7.13 (s, 4H), 3.58–3.56 (m, 4H), 3.05–3.03 (m, 4H), 2.35 (d, $J = 2.8$ Hz, 6H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ 142.99, 140.40, 139.30, 138.77, 133.82, 129.94, 129.38, 129.15, 128.50, 127.66, 126.09, 66.13, 54.13, 21.59, 21.34 ppm.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 359.1429, found 359.1424.



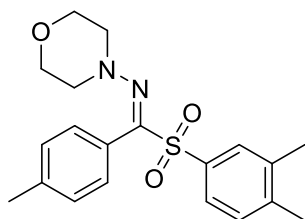
(E)-N-Morpholino-1-(p-tolyl)-1-(o-tolylsulfonyl)methanimine (4c)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 75% yield. M.p.: 101–103 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.81 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.42 (td, $J = 7.5, 1.3$ Hz, 1H), 7.26–7.18 (m, 4H), 7.13 (d, $J = 8.0$ Hz, 2H), 3.59–3.56 (m, 4H), 3.02–2.99 (m, 4H), 2.64 (s, 3H), 2.34 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ 143.27, 140.54, 139.00, 137.26, 133.20, 132.03, 130.81, 129.71, 129.46, 127.18, 126.03, 66.15, 54.16, 21.63, 20.87 ppm.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 359.1429, found 359.1424.



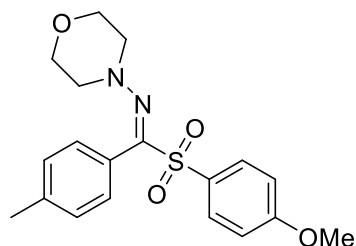
(E)-1-((3,4-Dimethylphenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4d)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 73% yield. M.p.: 111-113 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.51 (s, 1H), 7.44 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 4H), 3.59–3.57 (m, 4H), 3.05–3.03 (m, 4H), 2.36 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 143.48, 142.62, 140.36, 137.38, 136.67, 129.95, 129.86, 129.62, 129.39, 127.83, 126.56, 66.20, 54.17, 21.64, 20.15, 19.83 ppm.

HRMS (ESI): calcd for C₂₀H₂₅N₂O₃S [M+H]⁺ 373.1586, found 373.1583.



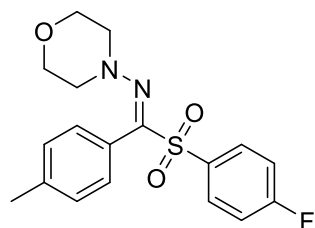
(E)-1-((4-Methoxyphenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4e)¹

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a yellow semisolid. 73% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.68–7.64 (m, 2H), 7.14 (s, 4H), 6.91–6.88 (m, 2H), 3.85 (s, 3H), 3.58–3.56 (m, 4H), 3.03–3.01 (m, 4H), 2.35 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 163.37, 143.73, 140.37, 131.08, 130.94, 129.88, 129.42, 127.75, 113.92, 66.17, 55.70, 54.16, 21.63 ppm.

HRMS (ESI): calcd for C₁₉H₂₃N₂O₄S [M+H]⁺ 375.1379, found 375.1371.



(E)-1-((4-Fluorophenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4f)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as colorless oil. 79% yield.

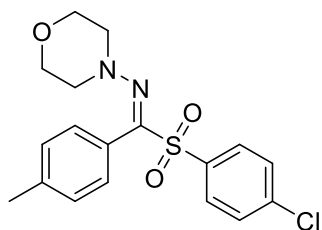
¹H NMR (600 MHz, CDCl₃): δ 7.76–7.74 (m, 2H), 7.16–7.09 (m, 6H), 3.58–3.56 (m, 4H), 3.04–3.02 (m, 4H), 2.35 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 165.55 (d, *J* = 255.8 Hz), 142.55, 140.63, 135.50,

131.65 (d, $J = 9.5$ Hz), 129.93, 129.51, 127.36, 115.94 (d, $J = 22.6$ Hz), 66.11, 54.12, 21.62 ppm.

^{19}F NMR (377 MHz, CDCl_3): δ -104.86 ppm.

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{FN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 363.1179, found 363.1175.



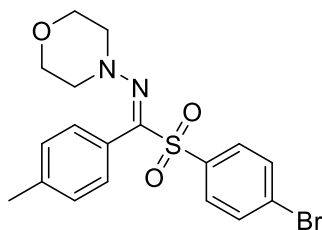
(E)-1-((4-Chlorophenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4g)¹

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 81% yield. M.p.: 130-132 °C

^1H NMR (400 MHz, CDCl_3): δ 7.70–7.67 (m, 2H), 7.42–7.40 (m, 2H), 7.18–7.13 (m, 4H), 3.59–3.57 (m, 4H), 3.06–3.02 (m, 4H), 2.37 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ 142.19, 140.70, 139.70, 138.15, 130.35, 129.98, 129.56, 129.01, 127.33, 66.13, 54.14, 21.65 ppm.

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{ClN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 379.0883, found 379.0876.



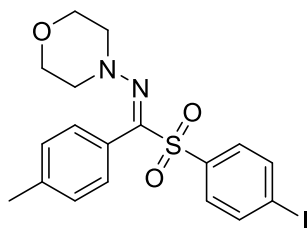
(E)-1-((4-Bromophenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4h)¹

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 75% yield. M.p.: 143-145 °C

^1H NMR (400 MHz, CDCl_3): δ 7.63–7.56 (m, 4H), 7.18–7.13 (m, 4H), 3.59–3.57 (m, 4H), 3.06–3.03 (m, 4H), 2.36 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ 142.09, 140.70, 138.73, 131.99, 130.43, 129.98, 129.56, 128.28, 127.32, 66.13, 54.14, 21.64 ppm.

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{BrN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 423.0378, found 423.0374.



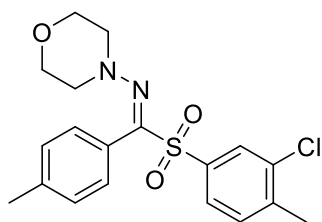
(E)-1-((4-Iodophenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4i)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 79% yield. M.p.: 142-144 °C

¹H NMR (400 MHz, CDCl₃): δ 7.81–7.79 (m, 2H), 7.47–7.45 (m, 2H), 7.18–7.12 (m, 4H), 3.59–3.57 (m, 4H), 3.06–3.04 (m, 4H), 2.37 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 142.07, 140.70, 139.46, 137.97, 130.29, 130.00, 129.56, 127.35, 100.87, 66.15, 54.15, 21.66 ppm.

HRMS (ESI): calcd for C₁₈H₂₀IN₂O₃S [M+H]⁺ 471.0239, found 471.0236.



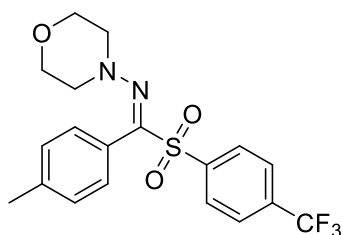
(E)-1-((3-Chloro-4-methylphenyl)sulfonyl)-N-morpholino-1-(p-tolyl)methanimine (4j)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 72% yield. M.p.: 120-122 °C

¹H NMR (600 MHz, CDCl₃): δ 7.74 (s, 1H), 7.50 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.15 (q, *J* = 8.2 Hz, 4H), 3.59–3.58 (m, 4H), 3.06–3.05 (m, 4H), 2.42 (s, 3H), 2.37 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 142.21, 141.88, 140.65, 138.53, 134.88, 131.06, 129.98, 129.52, 129.32, 127.38, 127.03, 66.15, 54.13, 21.65, 20.53 ppm.

HRMS (ESI): calcd for C₁₉H₂₂ClN₂O₃S [M+H]⁺ 393.1040, found 393.1036.



(E)-N-Morpholino-1-(p-tolyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)methanimine (4k)¹

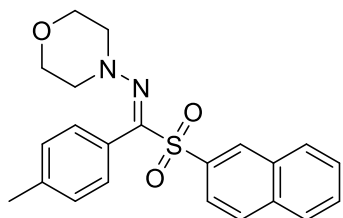
The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a red solid. 53% yield. M.p.: 141-142 °C

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.19–7.13 (m, 4H), 3.60–3.57 (m, 4H), 3.07–3.05 (m, 4H), 2.37 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 143.42, 141.37, 140.86, 134.63 (q, *J* = 33.1 Hz), 130.03, 129.62, 129.40, 127.14, 125.80 (q, *J* = 3.6 Hz), 123.43 (q, *J* = 274.0 Hz), 66.11, 54.12, 21.64 ppm.

¹⁹F NMR (377 MHz, CDCl₃): δ -63.03 ppm.

HRMS (ESI): calcd for C₁₉H₂₀F₃N₂O₃S [M+H]⁺ 413.1147, found 413.1143.



(E)-N-Morpholino-1-(naphthalen-2-ylsulfonyl)-1-(p-tolyl)methanimine (4l)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid. 70% yield. M.p.: 130-132 °C

¹H NMR (400 MHz, CDCl₃): δ 8.33 (s, 1H), 7.92–7.88 (m, 3H), 7.75 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.66–7.63 (m, 1H), 7.60–7.56 (m, 1H), 7.17–7.12 (m, 4H), 3.58–3.55 (m, 4H), 3.05–3.03 (m, 4H), 2.35 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 142.85, 140.53, 136.68, 135.13, 132.18, 130.32, 129.99, 129.53, 139.49, 128.99, 128.74, 128.00, 127.64, 127.39, 124.11, 66.16, 54.16, 21.65 ppm.

HRMS (ESI): calcd for C₂₂H₂₃N₂O₃S [M+H]⁺ 395.1429, found 395.1423.

III. General procedure for the sulfonylation of hydrazones with sulfonyl

chlorides

Hydrazone **1a** (0.2 mmol, 1.0 equiv), arylsulfonyl chloride **5** (0.4 mmol, 2.0 equiv), [Ir{dFCF₃ppy}₂(bpy)]PF₆ (2 mol%), Na₂CO₃ (0.4 mmol, 2.0 equiv) were added to a 10-mL Schlenk tube. The tube was evacuated and backfilled with N₂ three times before MeCN (2 mL) was added. The reaction mixture was stirred at 25 °C for 24 h under 25 W blue LED. The solvent was evaporated under reduced pressure. The residue was purified directly by flash chromatograph (petroleum ether/EtOAc) to give the corresponding product.

IV. Gram scale procedure for the synthesis of **3a**

To a screw-cap reaction tube (50 mL) were added (*E*)-*N*-morpholino-1-(*p*-tolyl)methanimine **1a** (1.0 g, 4.9 mmol, 1.0 equiv), **2a** (1.9 g, 9.8 mmol, 2.0 equiv), DABSO (2.4 g, 9.8 mmol, 2.0 equiv), FeCl₃ (0.4 g, 2.45 mmol, 50 mol%), quinoline (0.3 g, 2.45 mmol, 50 mol%). The tube was evacuated and backfilled with N₂ three times before MeCN (30 mL) was added. The reaction mixture was stirred at 25 °C for 24 h. When the reaction was complete (monitor by TLC), the mixture was filtered through a Celite pad, and the Celite pad was washed with dichloromethane. The combined filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **3a** with a yield of 70% (1.18 g).

V. Procedure for radical capture experiment with 1,1-diphenylethylene

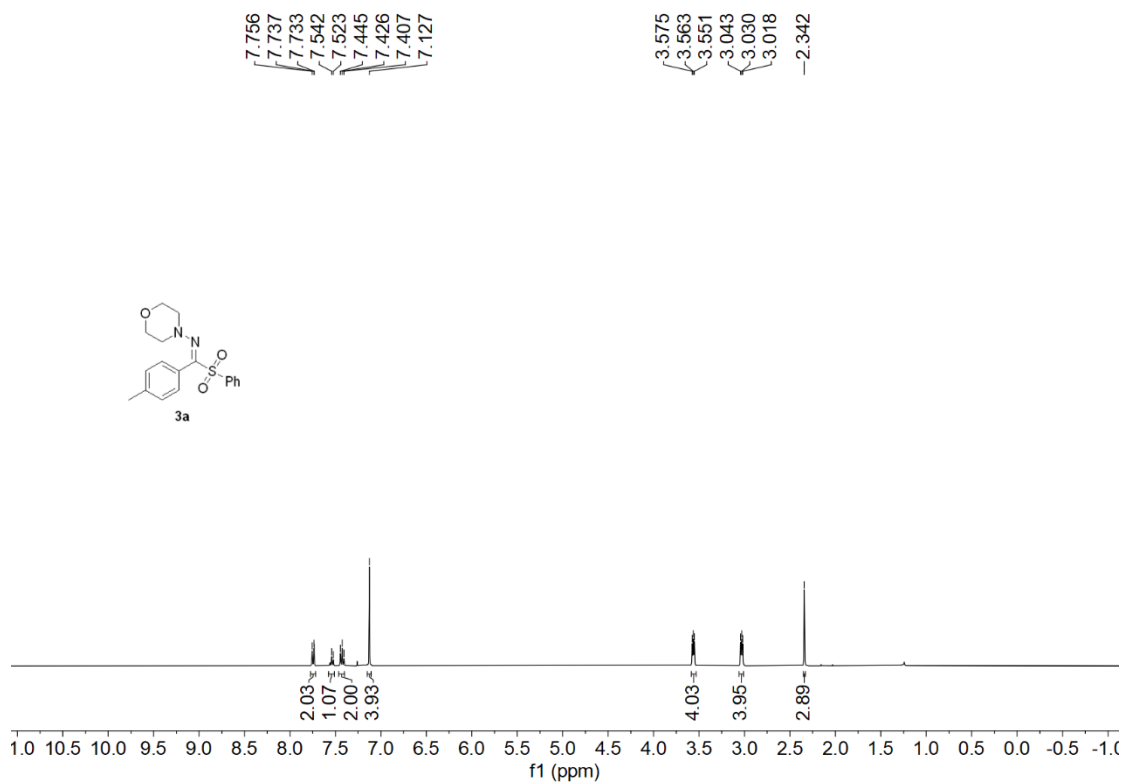
1a (0.2 mmol, 1.0 equiv), aryldiazonium tetrafluoroborate **2** (0.4 mmol, 2.0 equiv), DABSO (0.4 mmol, 2.0 equiv), FeCl₃ (0.1 mmol, 50 mol%), quinoline (0.1 mmol, 50 mol%), and 1,1-diphenylethylene (0.4 mmol, 2.0 equiv) were added to a 10-mL Schlenk tube. The tube was evacuated and backfilled with N₂ three times before MeCN (2 mL) was added. The reaction mixture was stirred at 25 °C for 24 h. The solvent was evaporated under reduced pressure. The residue was purified directly by flash chromatograph (petroleum ether/EtOAc = 3/1, v/v) to give (2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene **6** as colorless oil in 48% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.59–7.56 (m, 2H), 7.51–7.46 (m, 1H), 7.40–7.34 (m, 4H), 7.33–7.26 (m, 4H), 7.23–7.20 (m, 2H), 7.09–7.06 (m, 2H), 7.03 (s, 1H) ppm. ¹³C

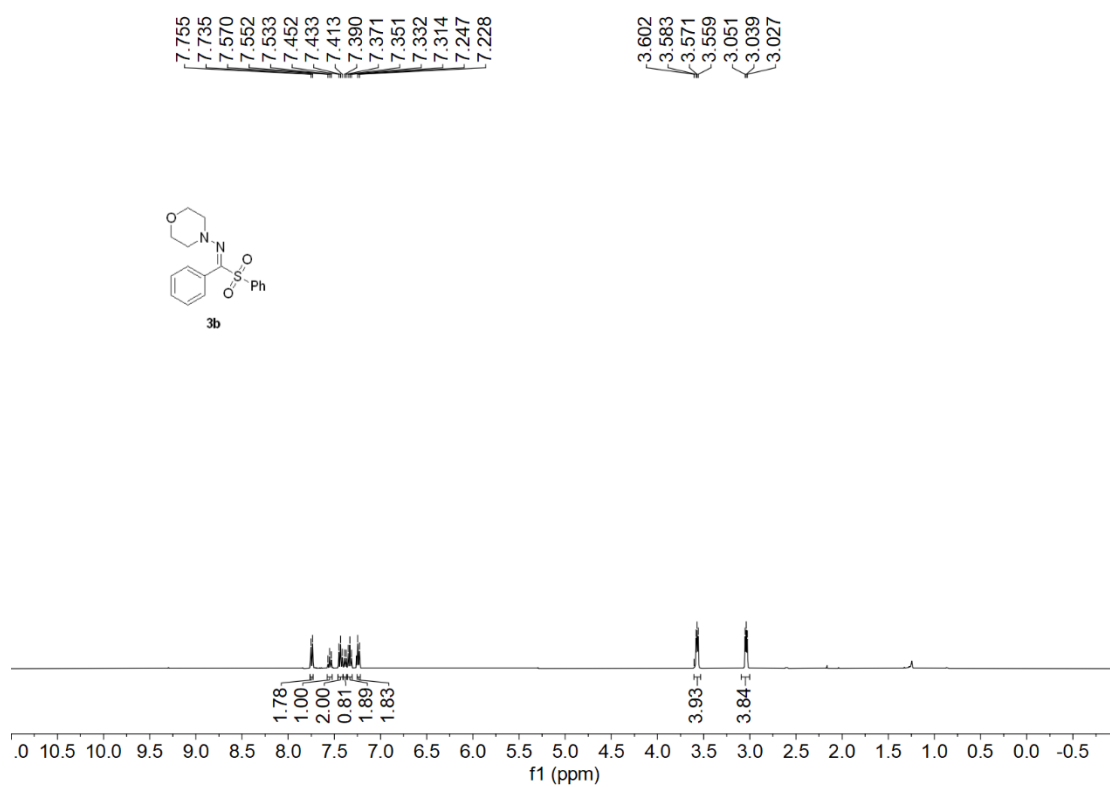
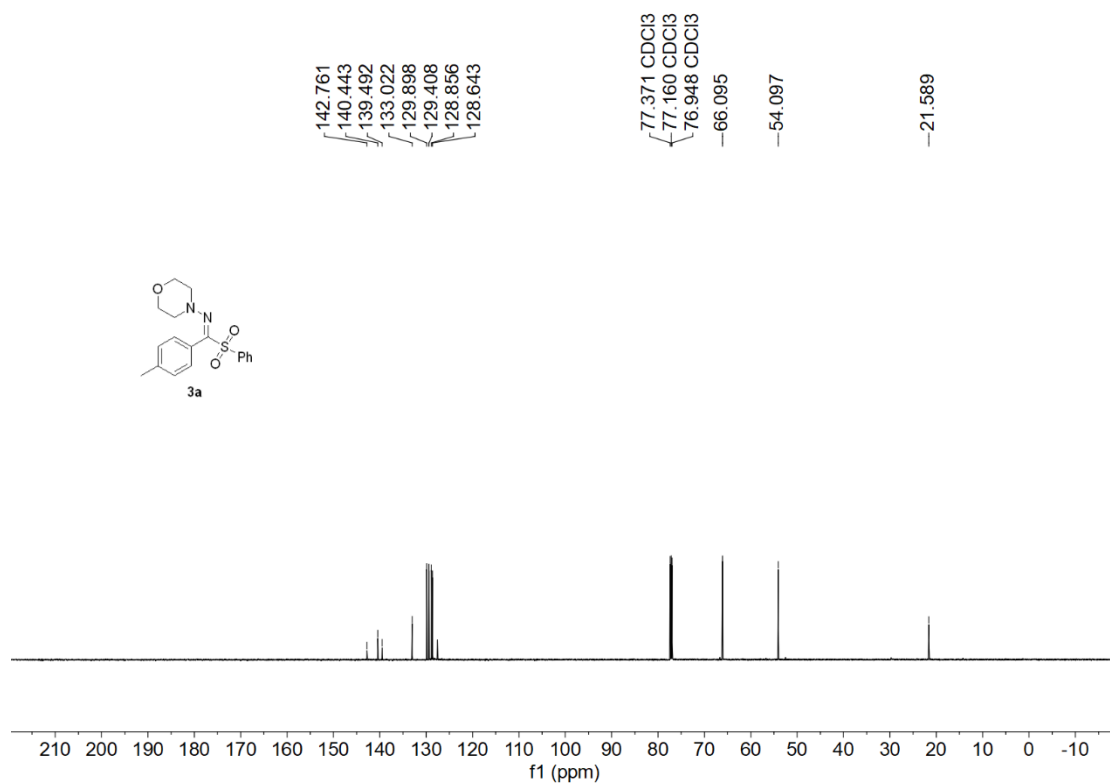
NMR (101 MHz, CDCl₃): δ 155.4, 141.6, 139.2, 135.6, 133.0, 130.5, 129.9, 129.0, 128.9, 128.8, 128.7, 128.4, 128.0, 127.8 ppm. HRMS (ESI): calcd for C₂₀H₁₇O₂S [M+H]⁺ 321.0949, found 321.0940.

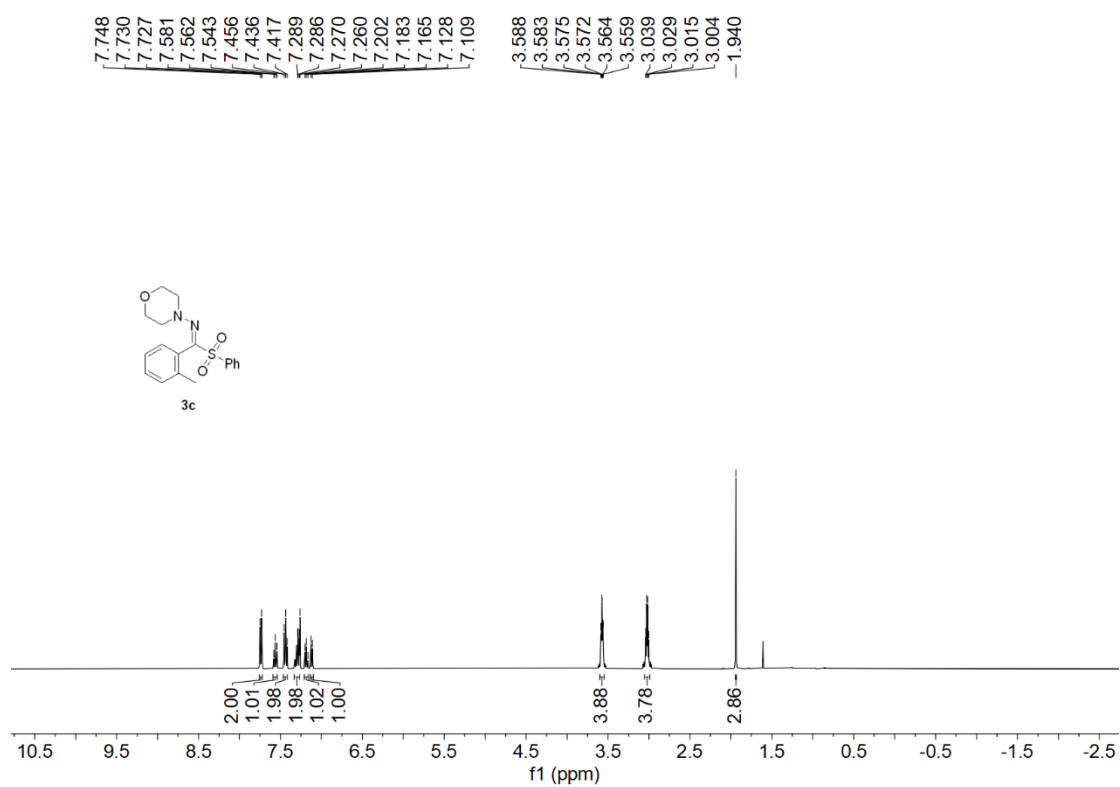
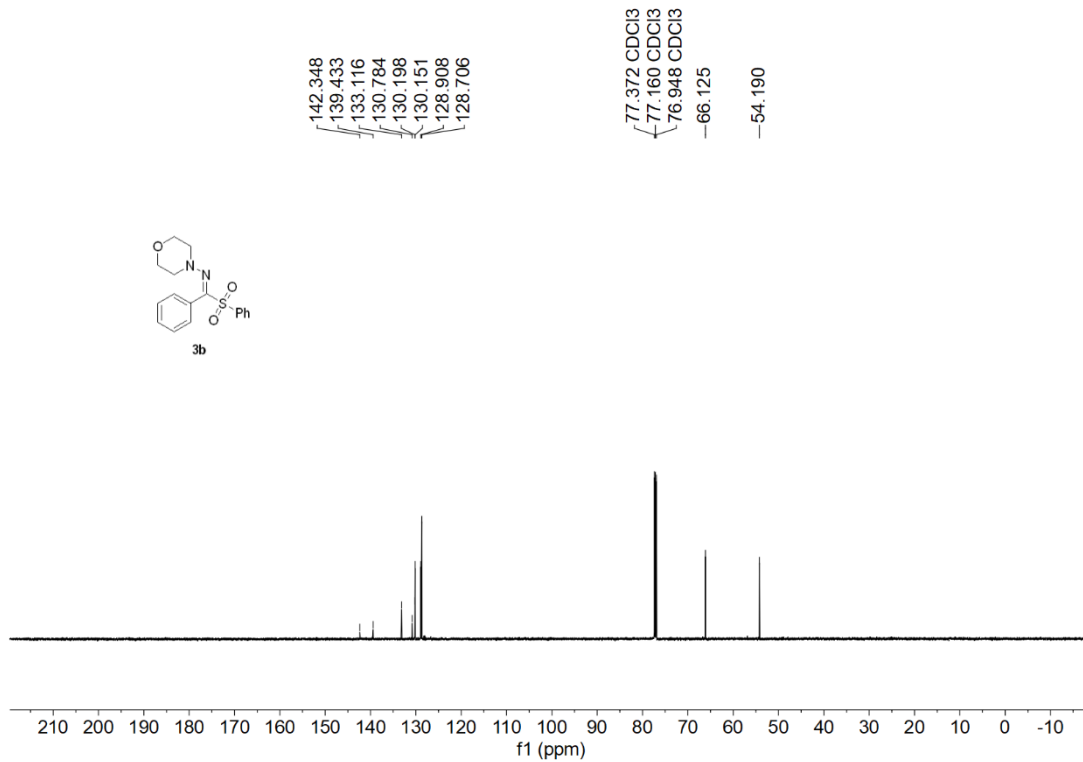
VI. References

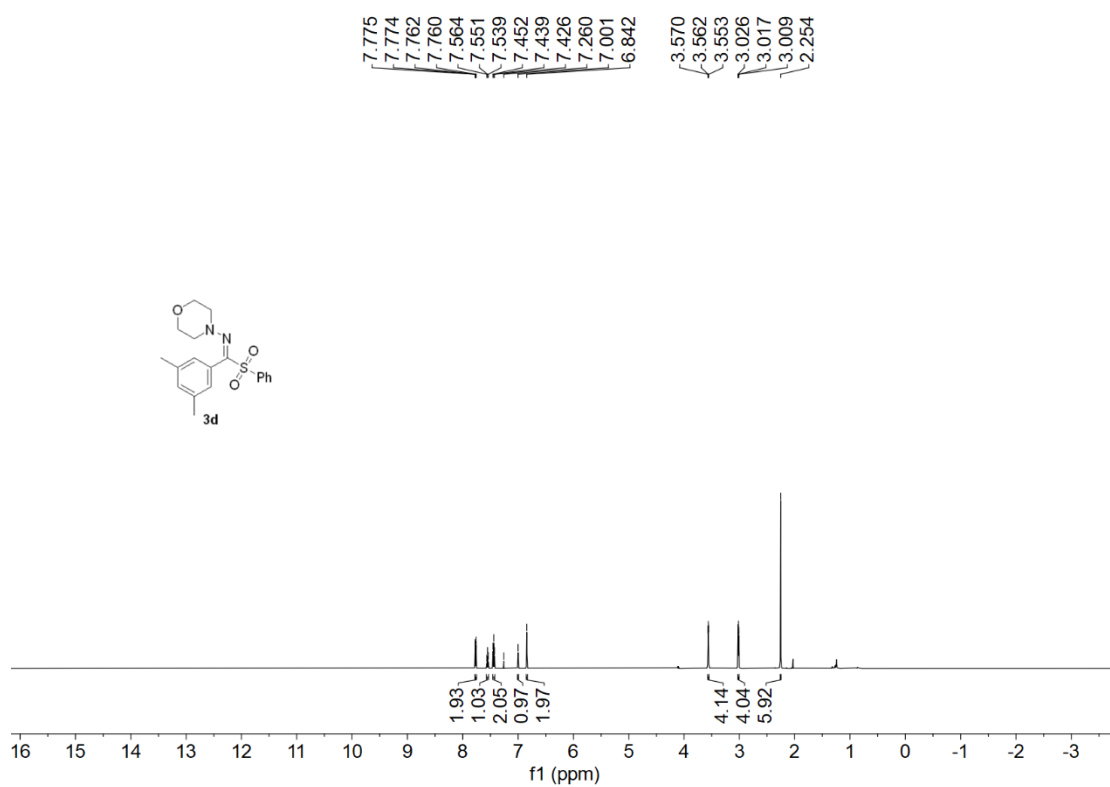
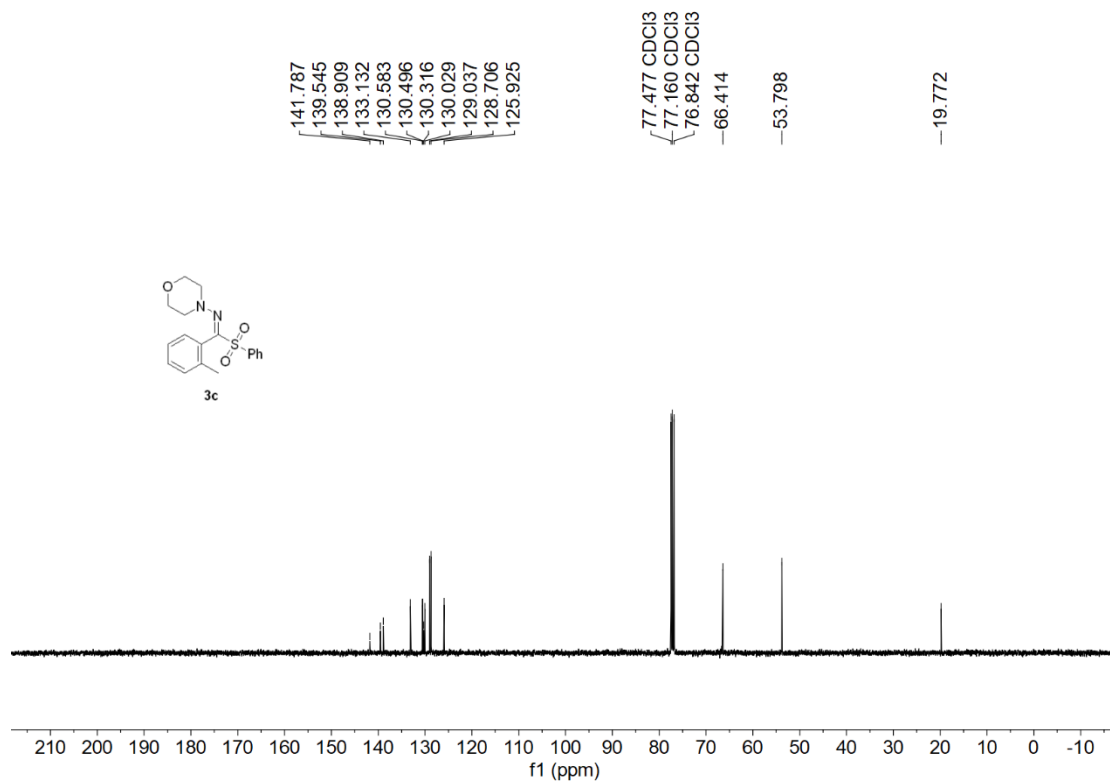
- (1) S. Biswajit, G. Payel and H. Alakananda, Electrochemical C–H Sulfonylation of Hydrazones, *Org. Lett.*, 2023, **25**, 3440-3444.
- (2) (a) R. Mao, Z. Yuan, R. Zhang, Y. Ding, X. Fan and J. Wu, A copper(ii)-catalyzed three-component reaction of aryldiazonium tetrafluoroborates, sulfur dioxide, with alkenes, *Org. Chem. Front.*, 2016, **3**, 1498-1502; (b) H. Wang, S. Sun and J. Cheng, Copper-Catalyzed Arylsulfonylation and Cyclizative Carbonation of *N*-(Arylsulfonyl)acrylamides Involving Desulfonative Arrangement toward Sulfonated Oxindoles, *Org. Lett.*, 2017, **19**, 5844-5847.
- (3) Q.-L. Yang, P.-P. Lei, E.-J. Hao, B.-N. Zhang, H.-H. Zhou, W.-W. Li and H.-M. Guo, Oxidative C–H Sulfonylation of Hydrazones Enabled by Electrochemistry, *SynOpen*, 2023, **7**, 535-547.

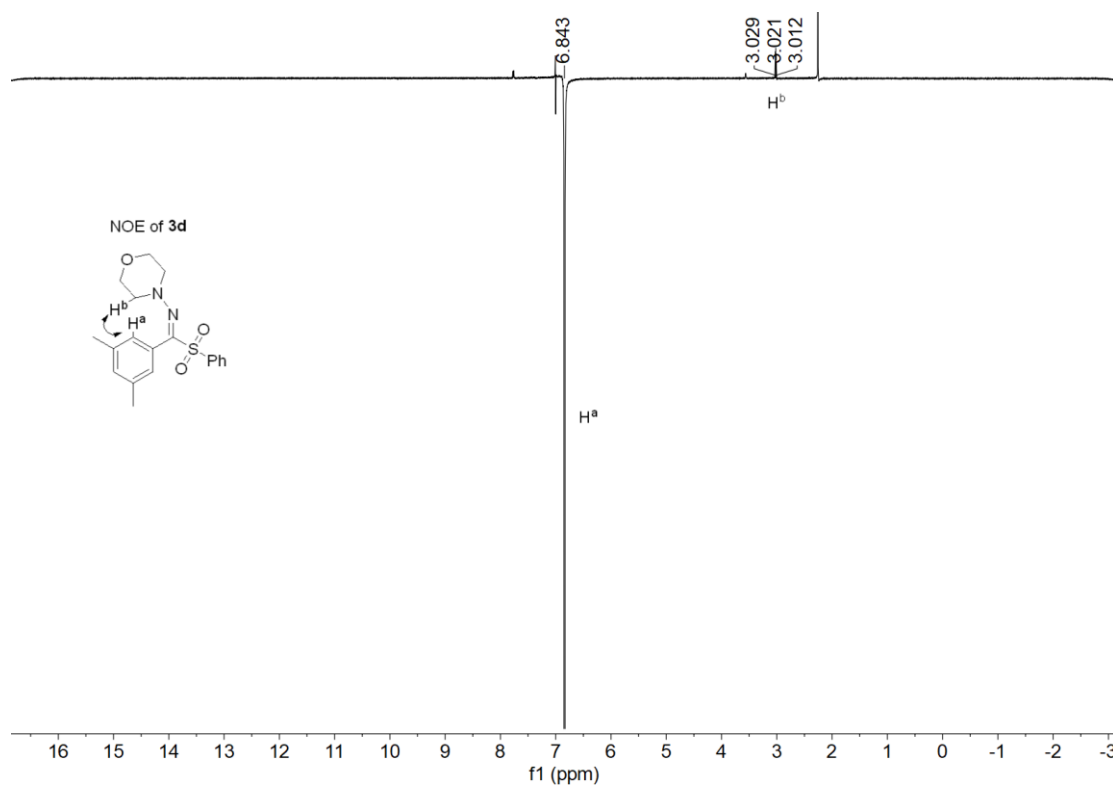
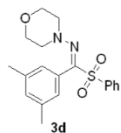
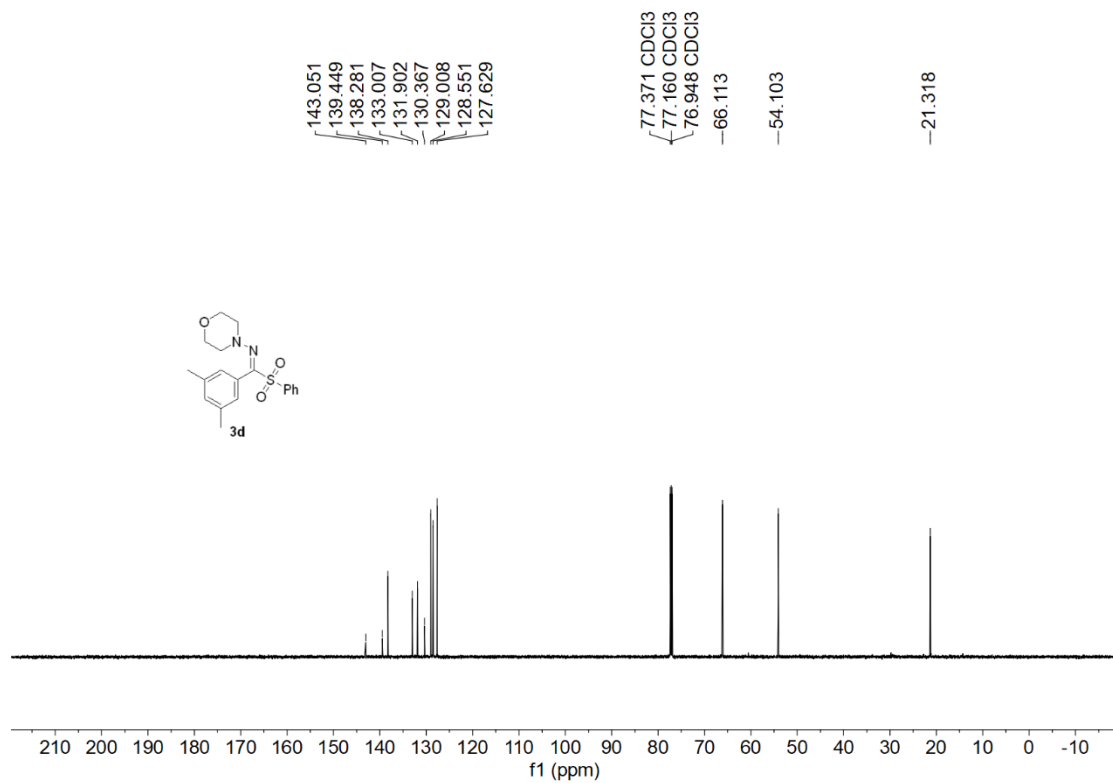
VII. Copies of NMR spectra



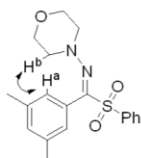


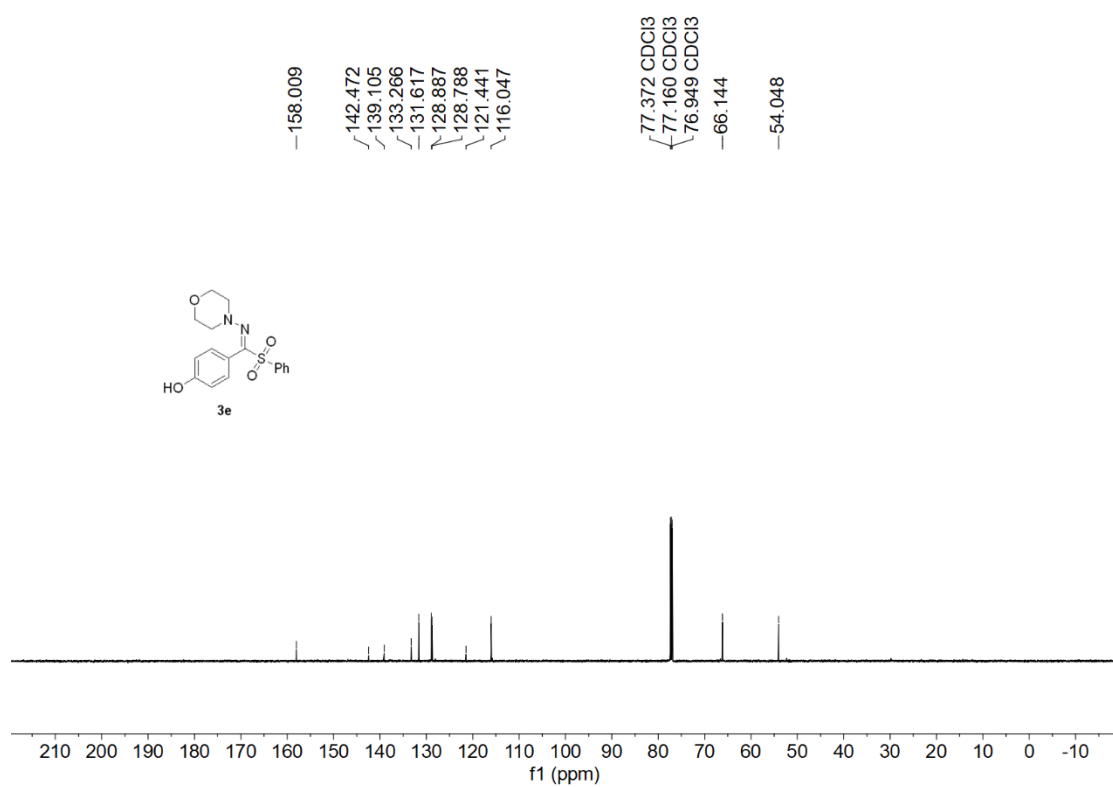
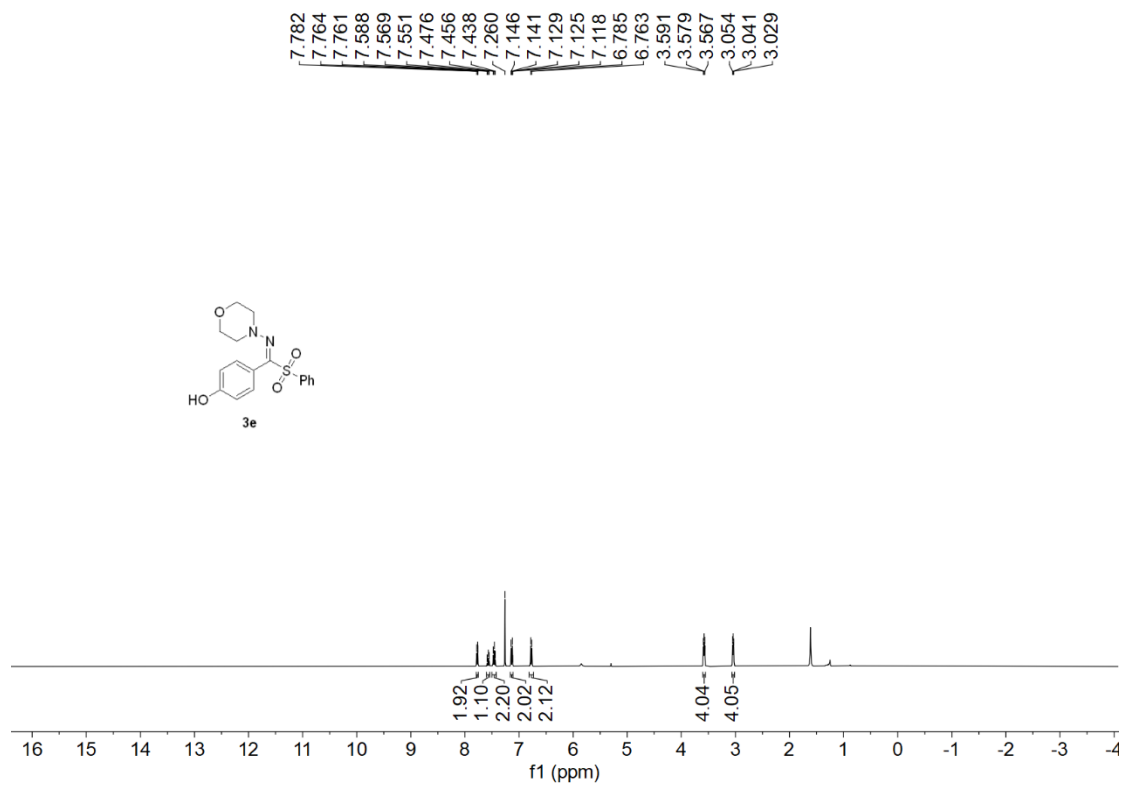


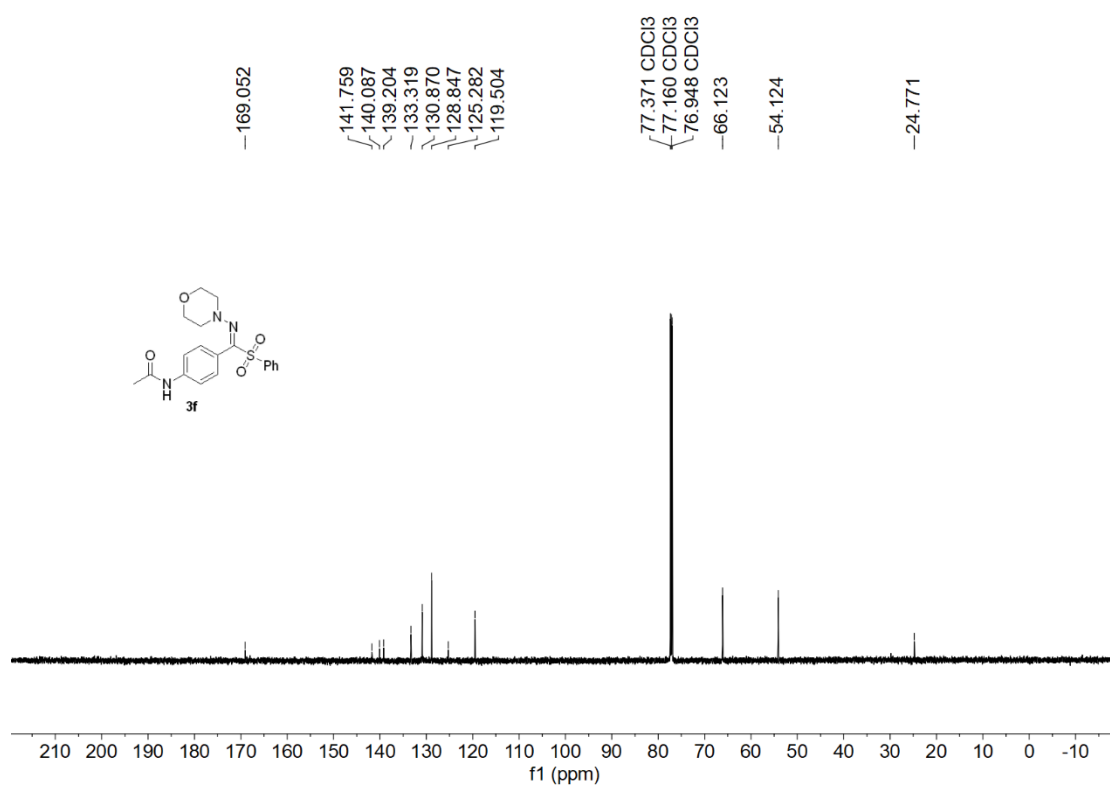
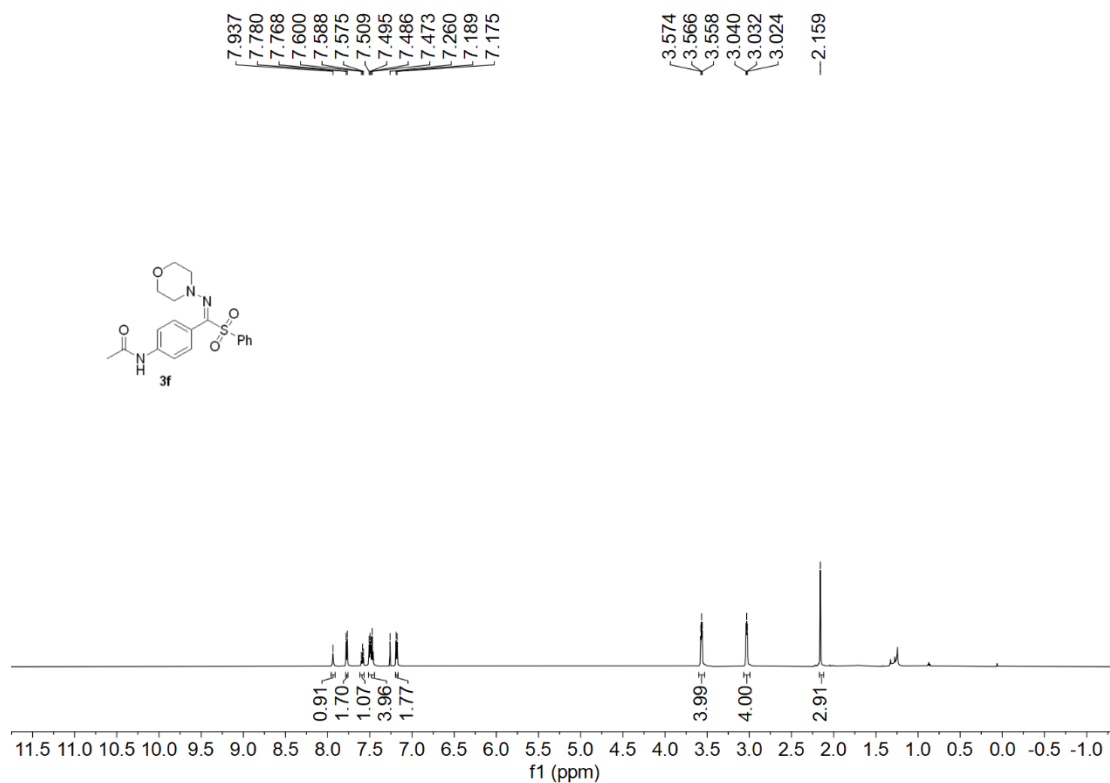


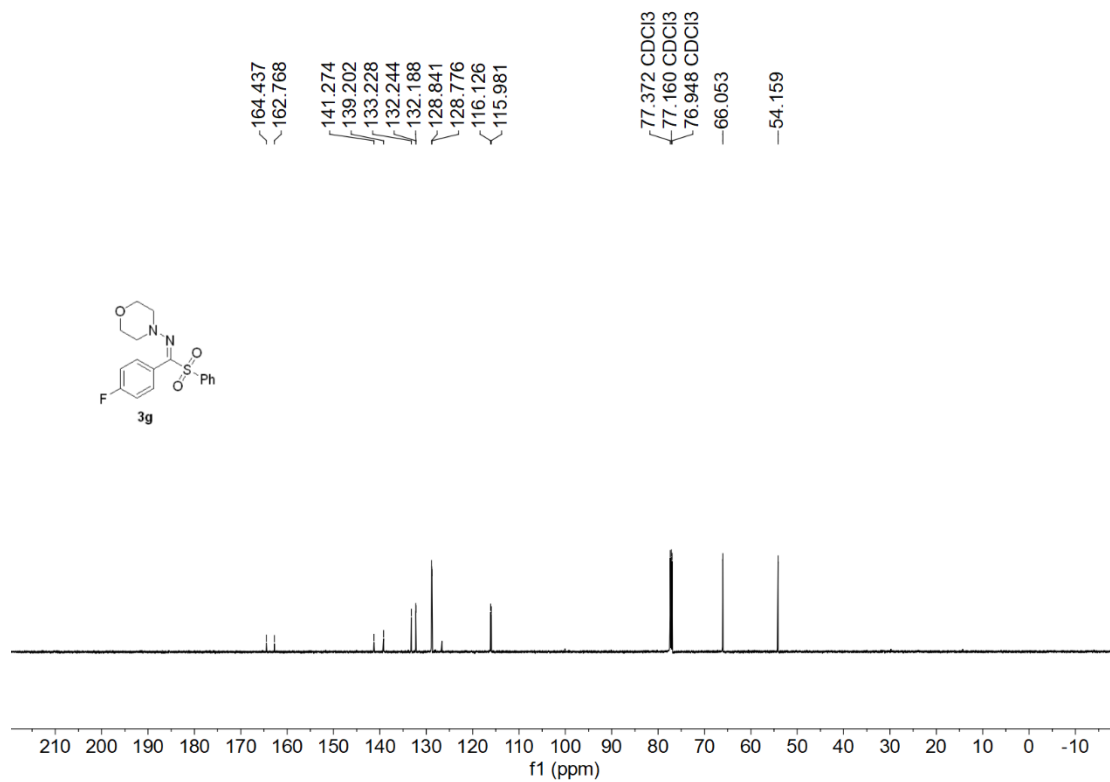
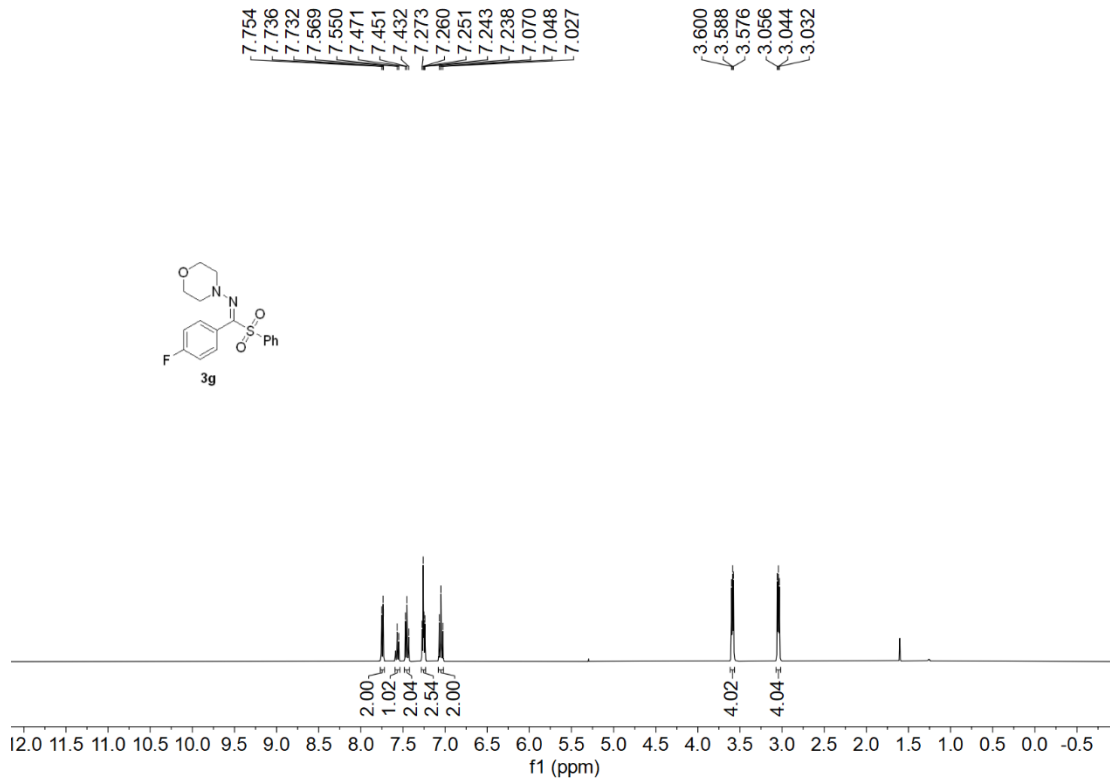


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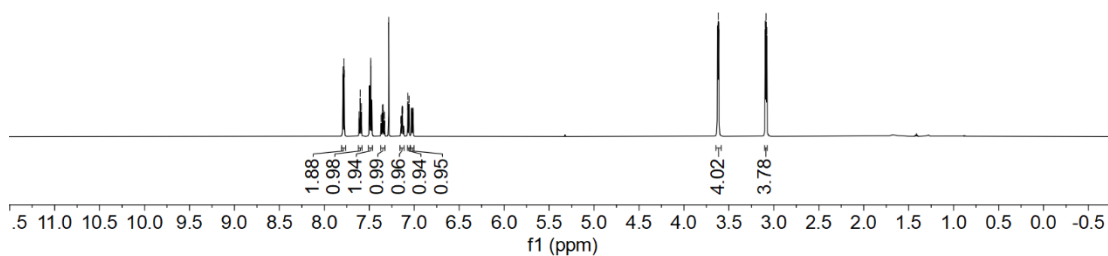
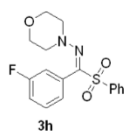
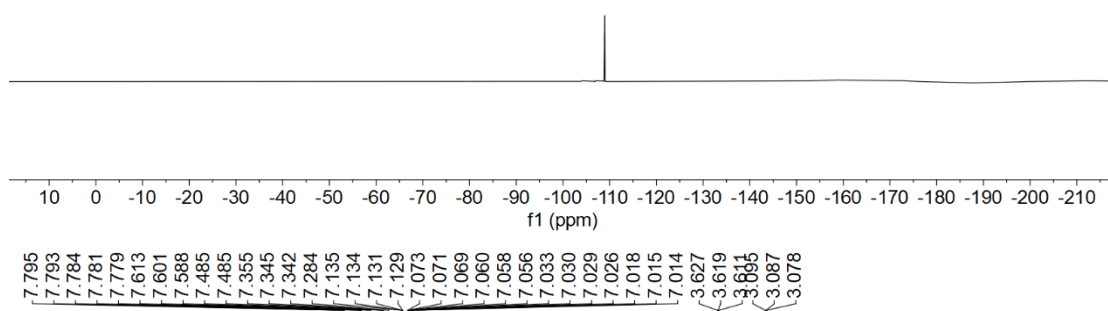
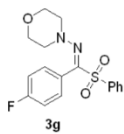


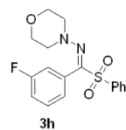
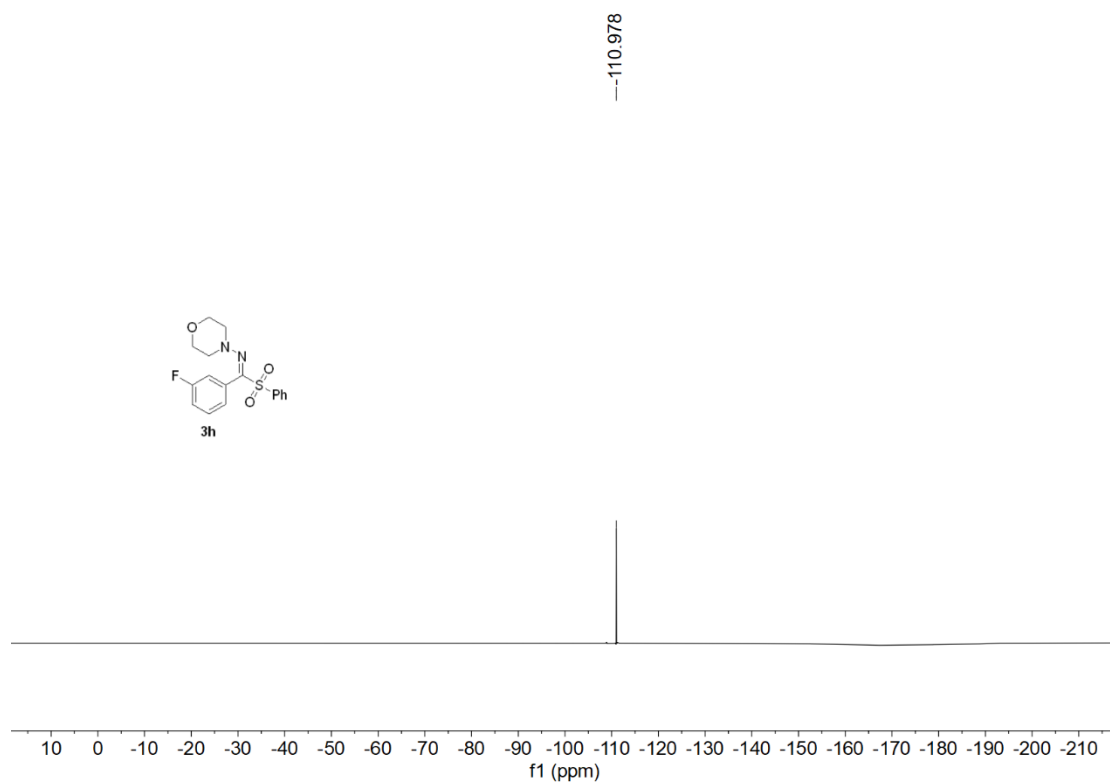
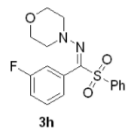
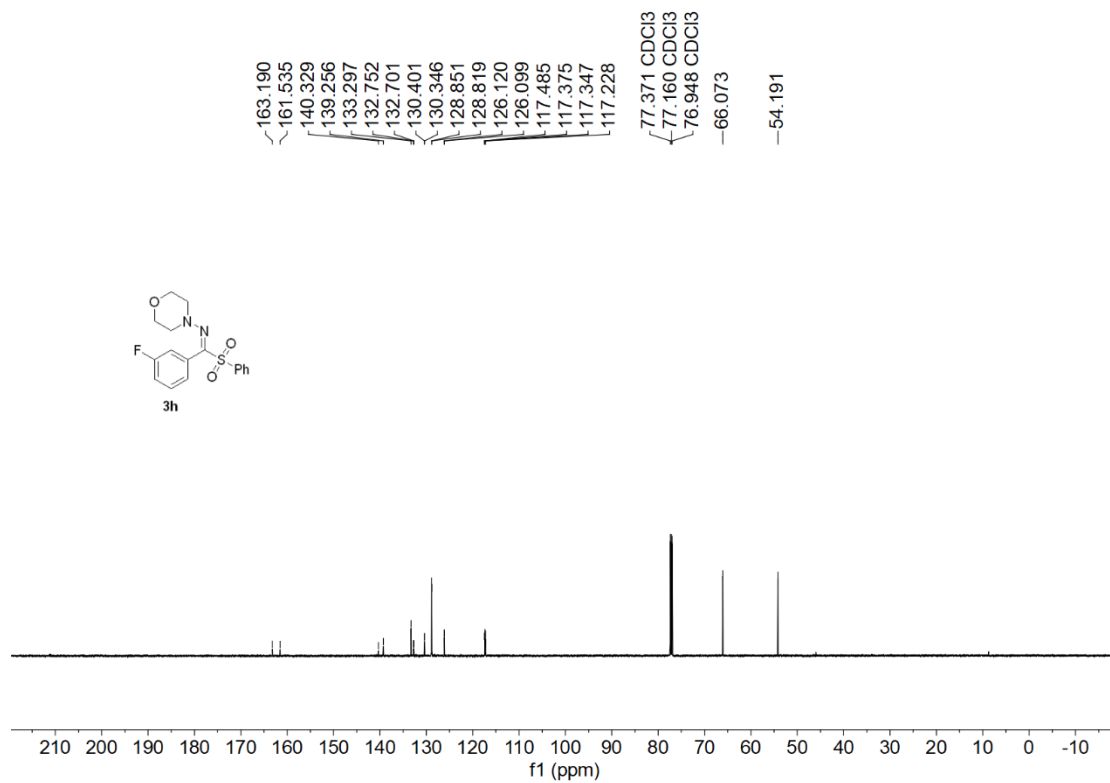






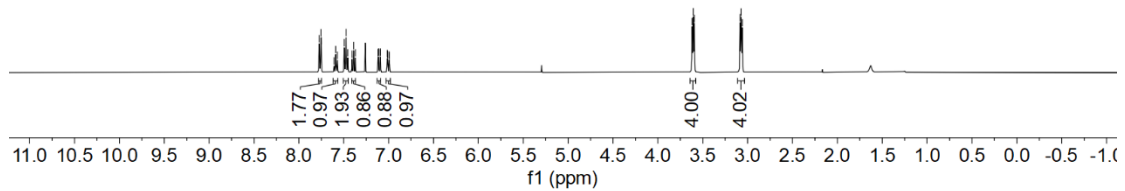
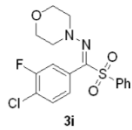
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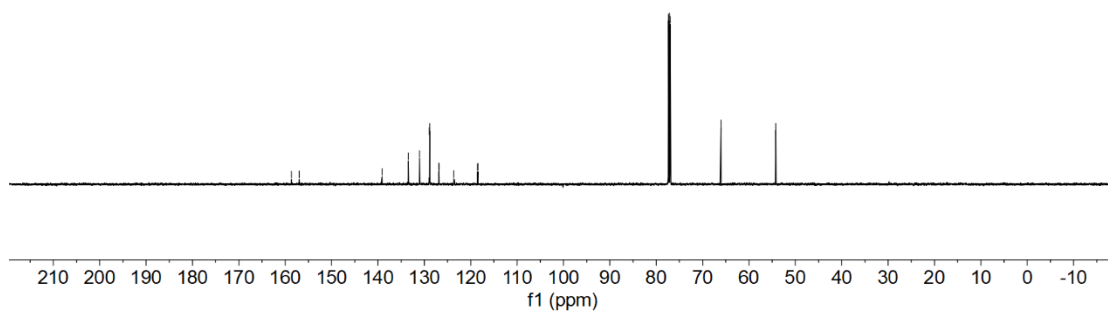
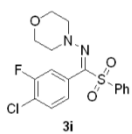
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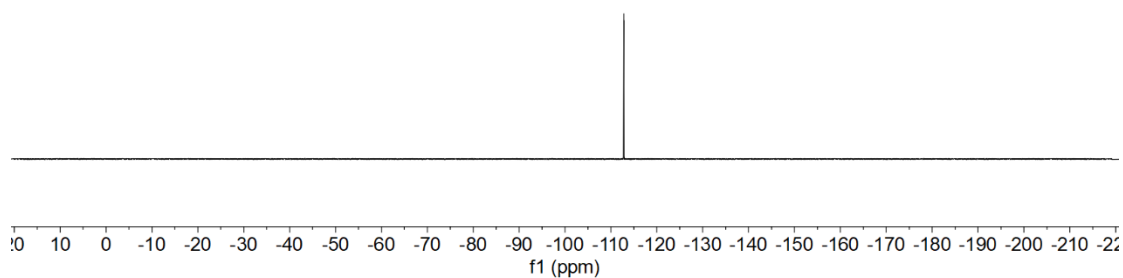
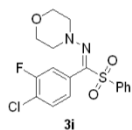


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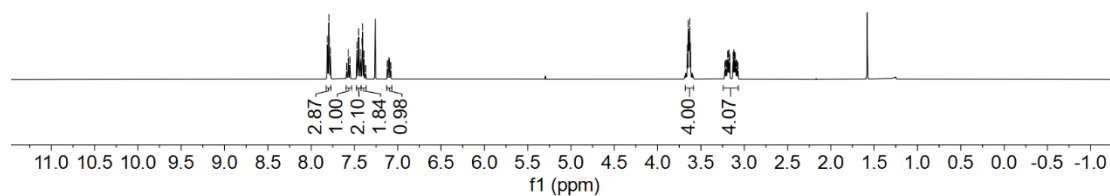
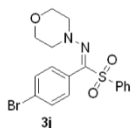
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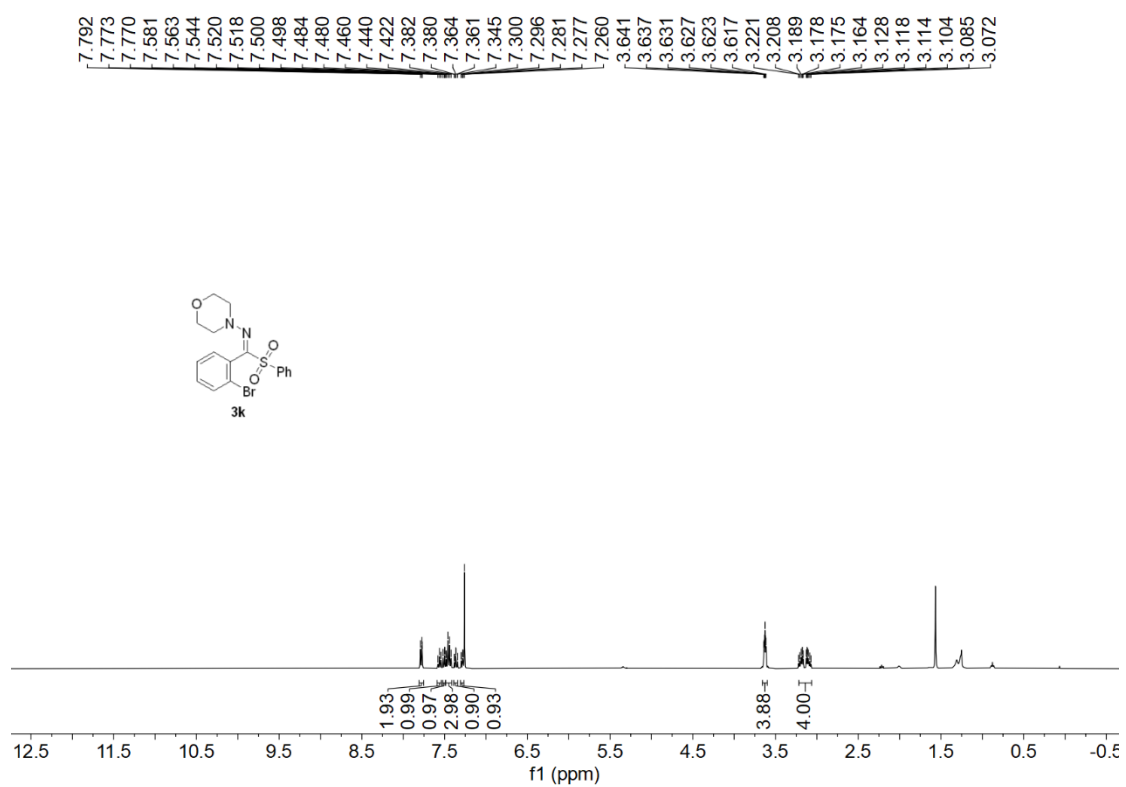
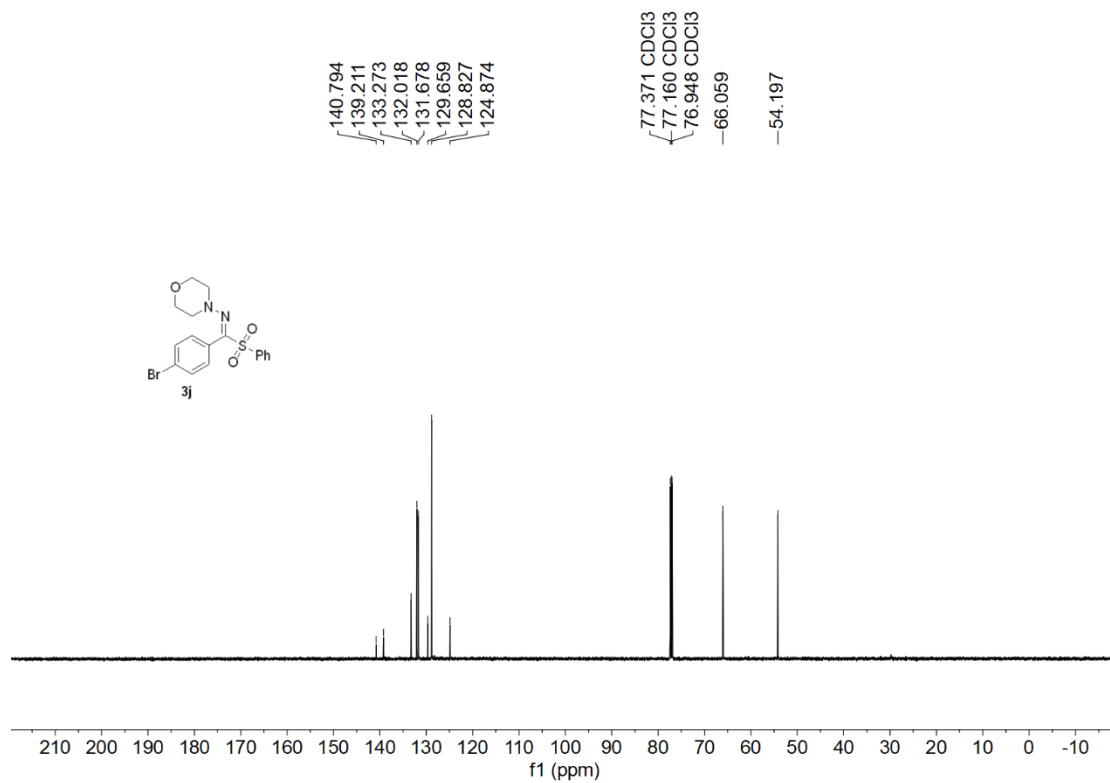
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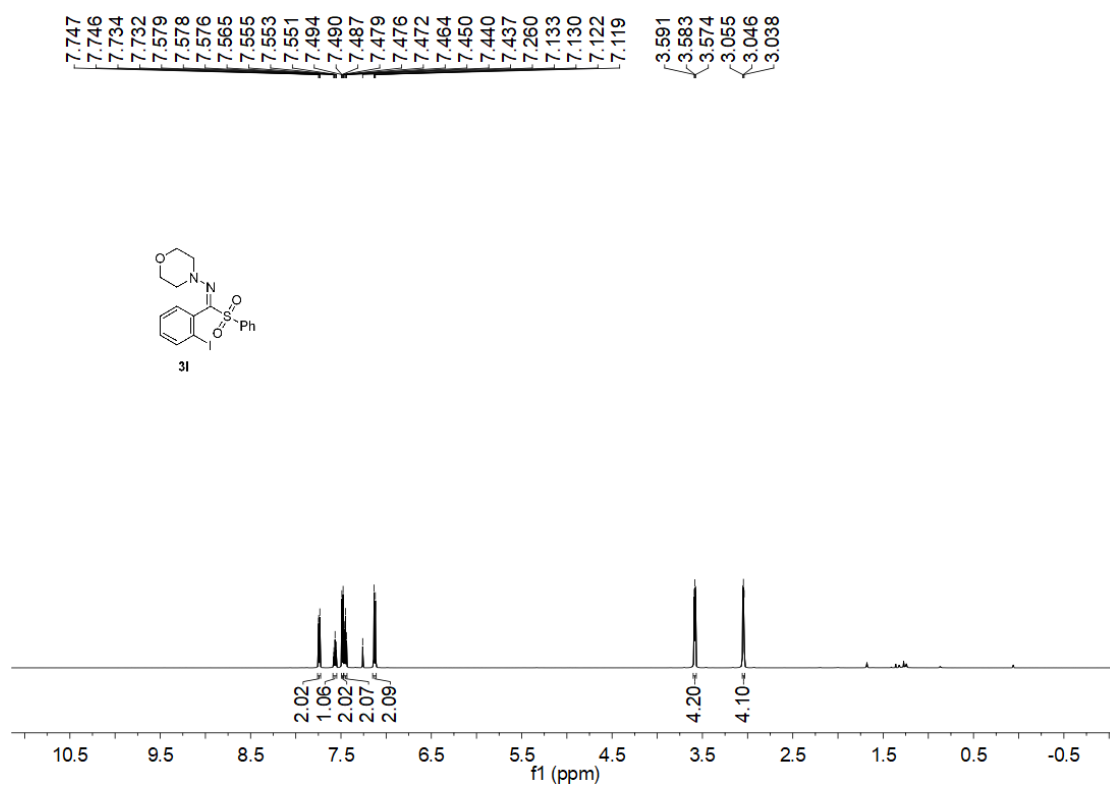
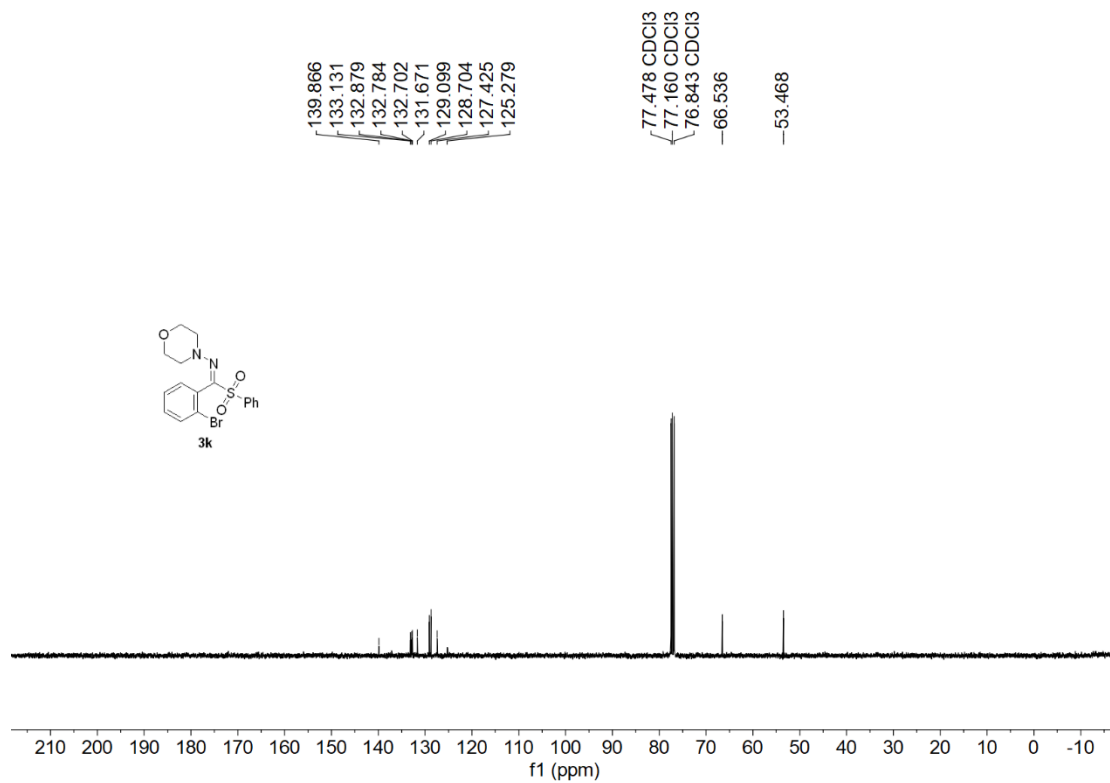


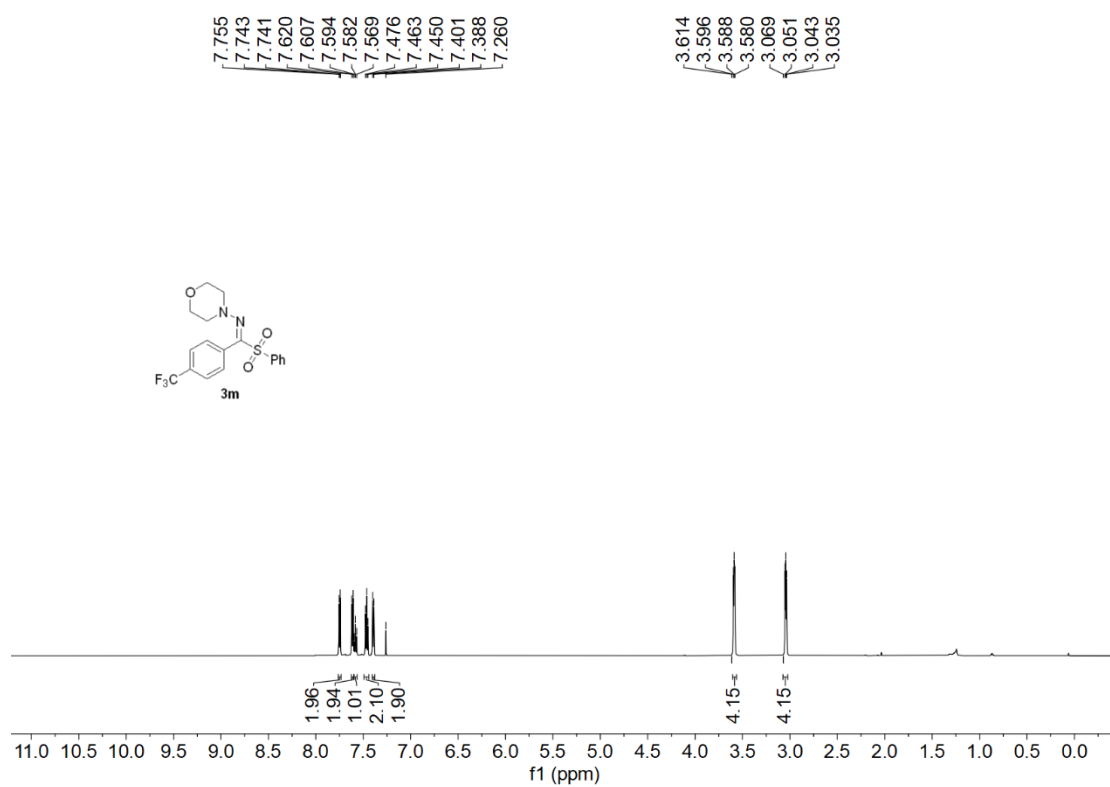
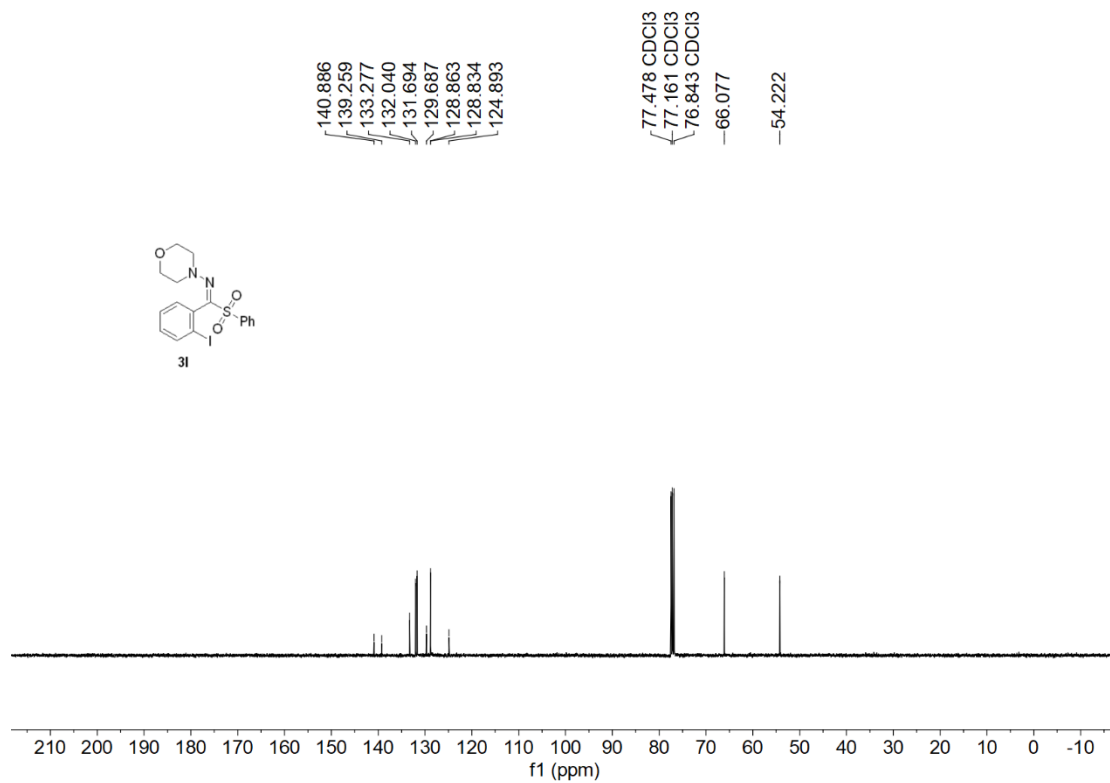
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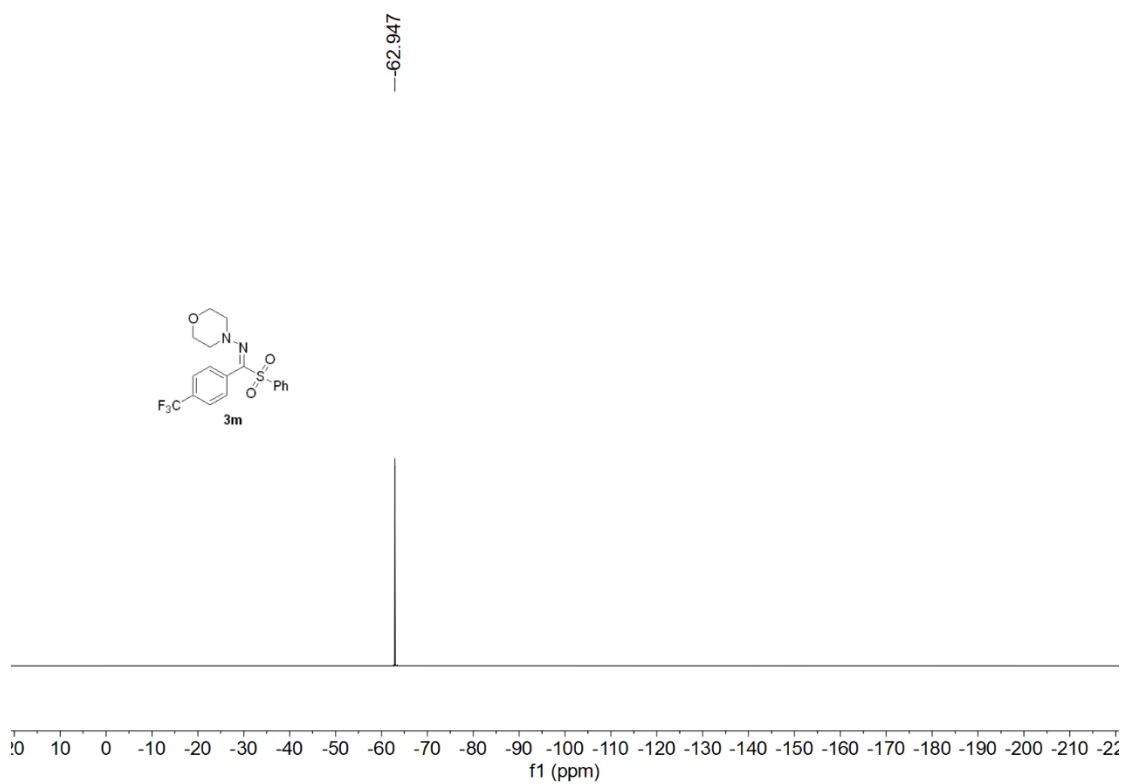
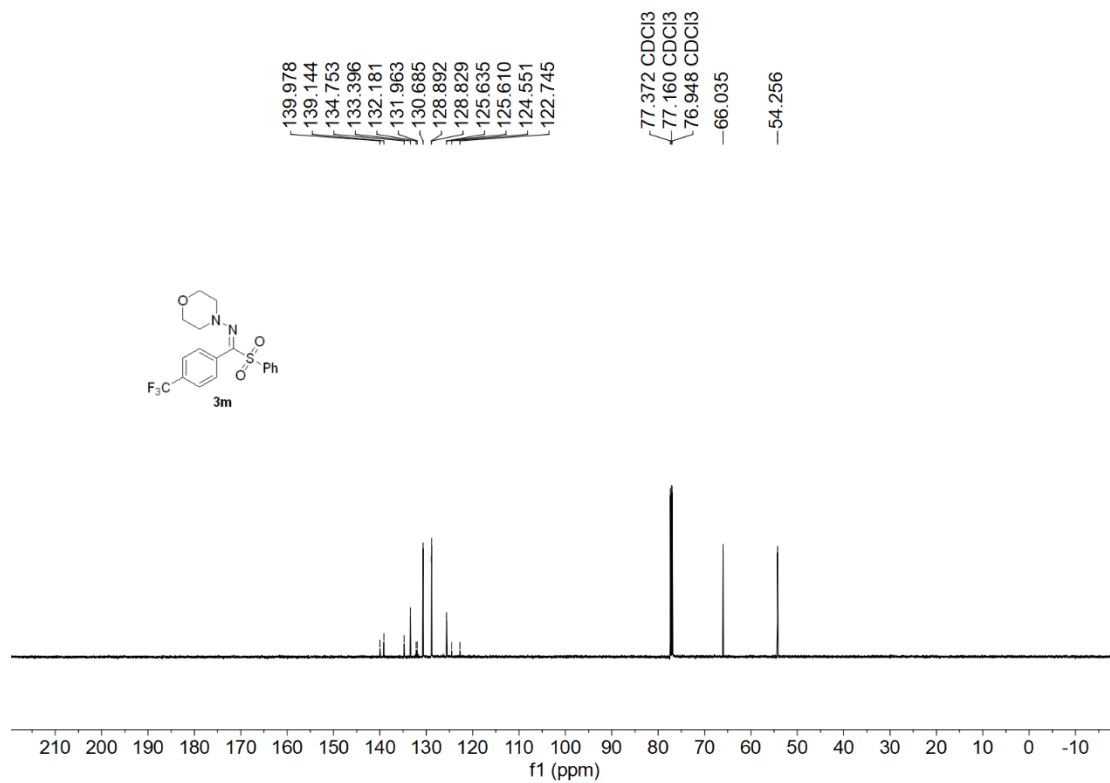


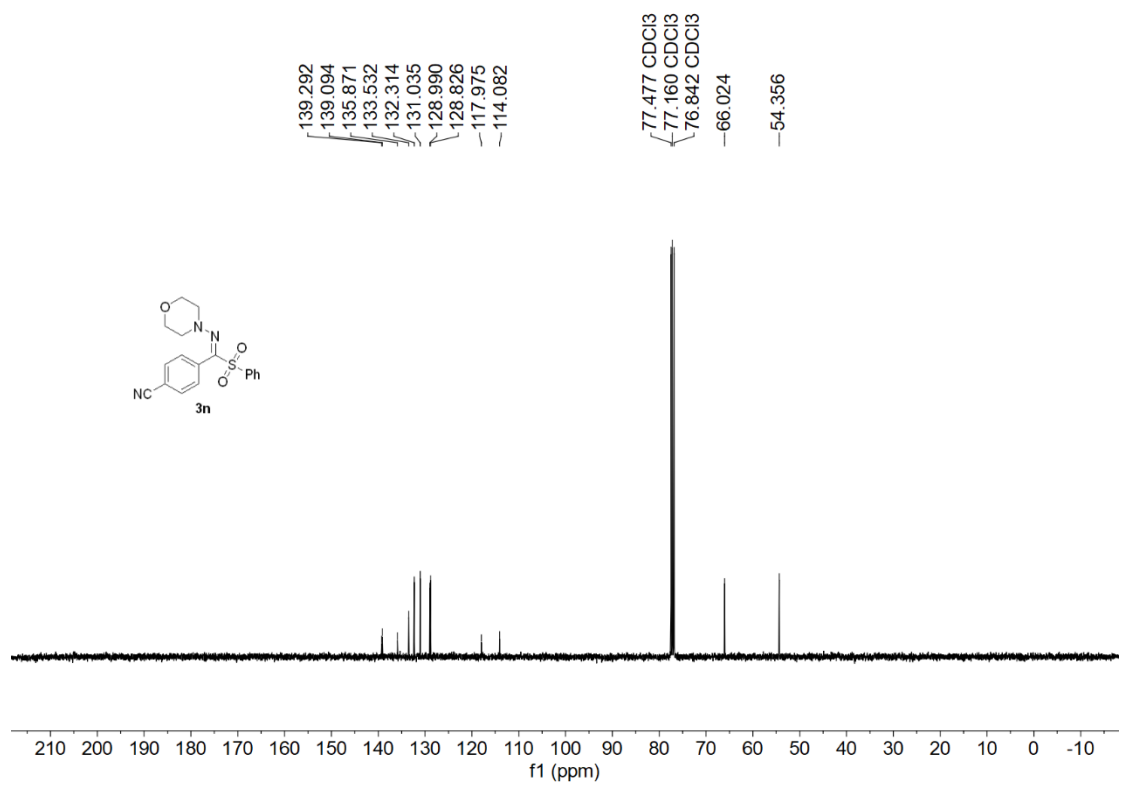
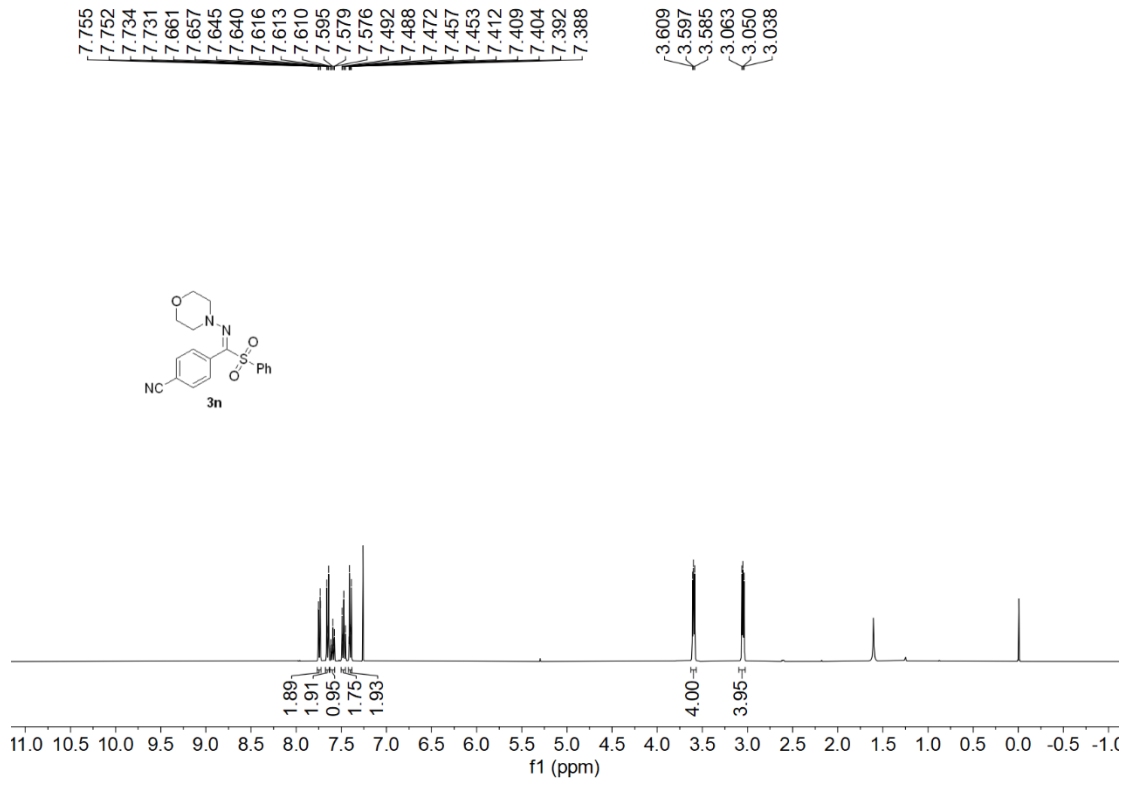
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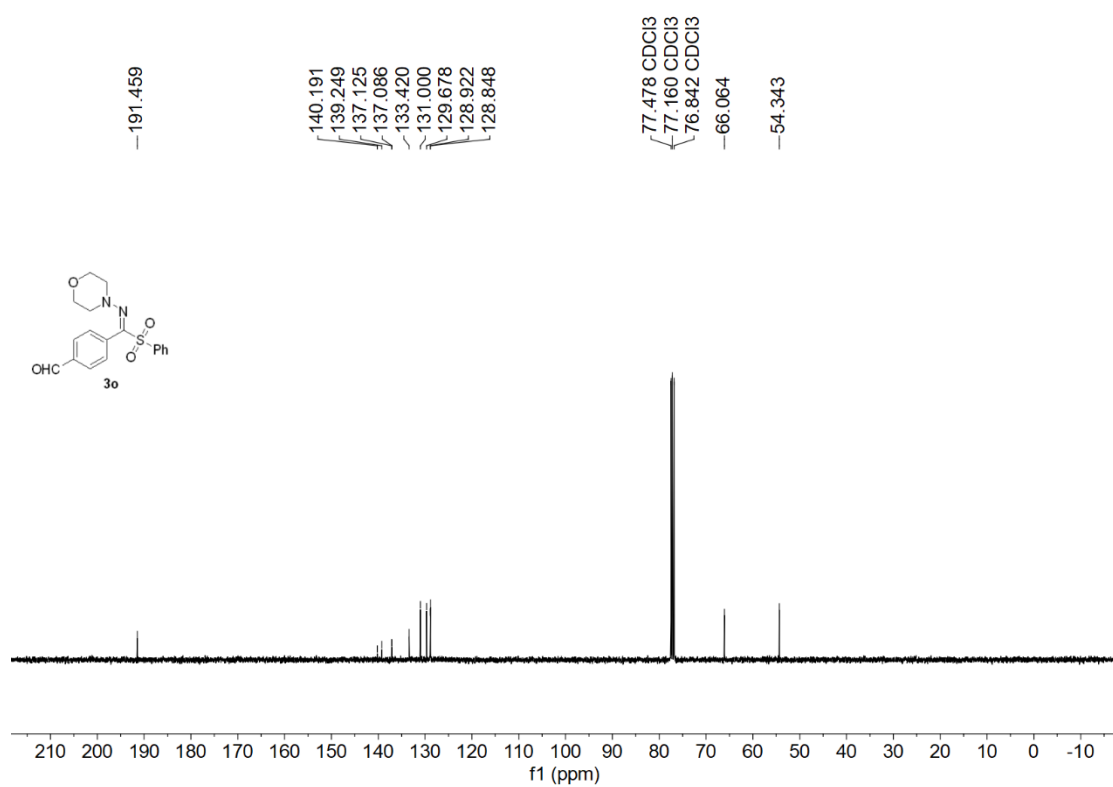
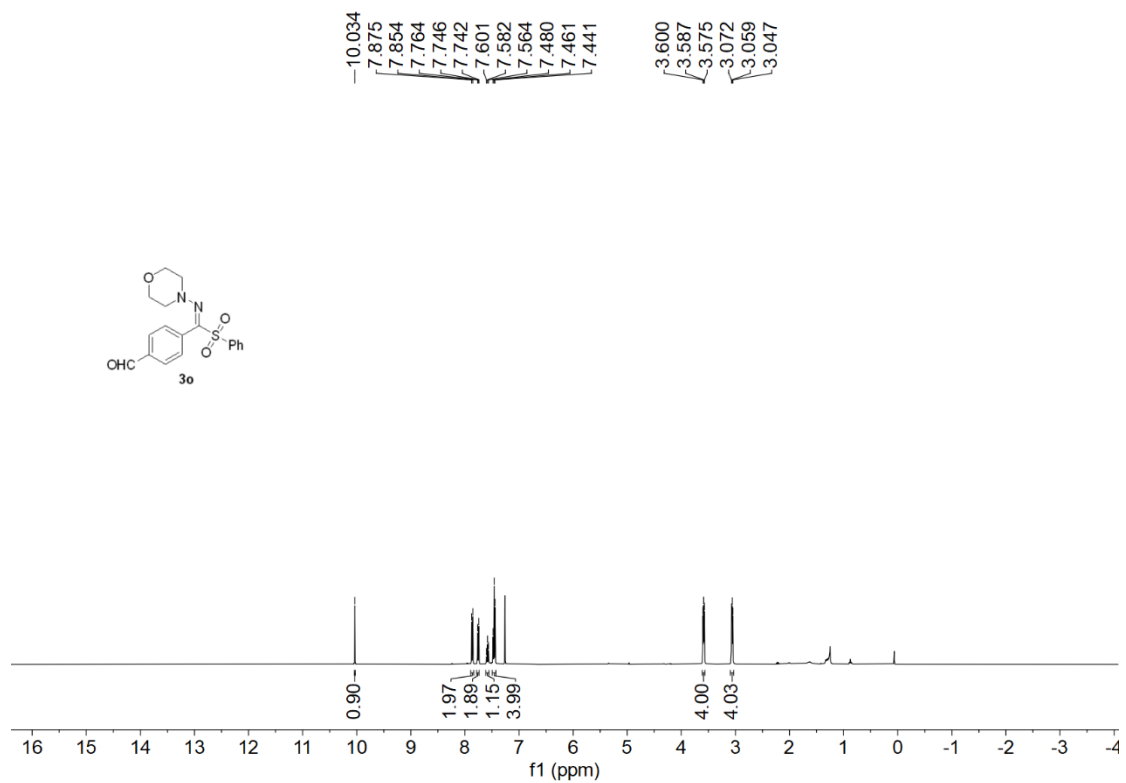


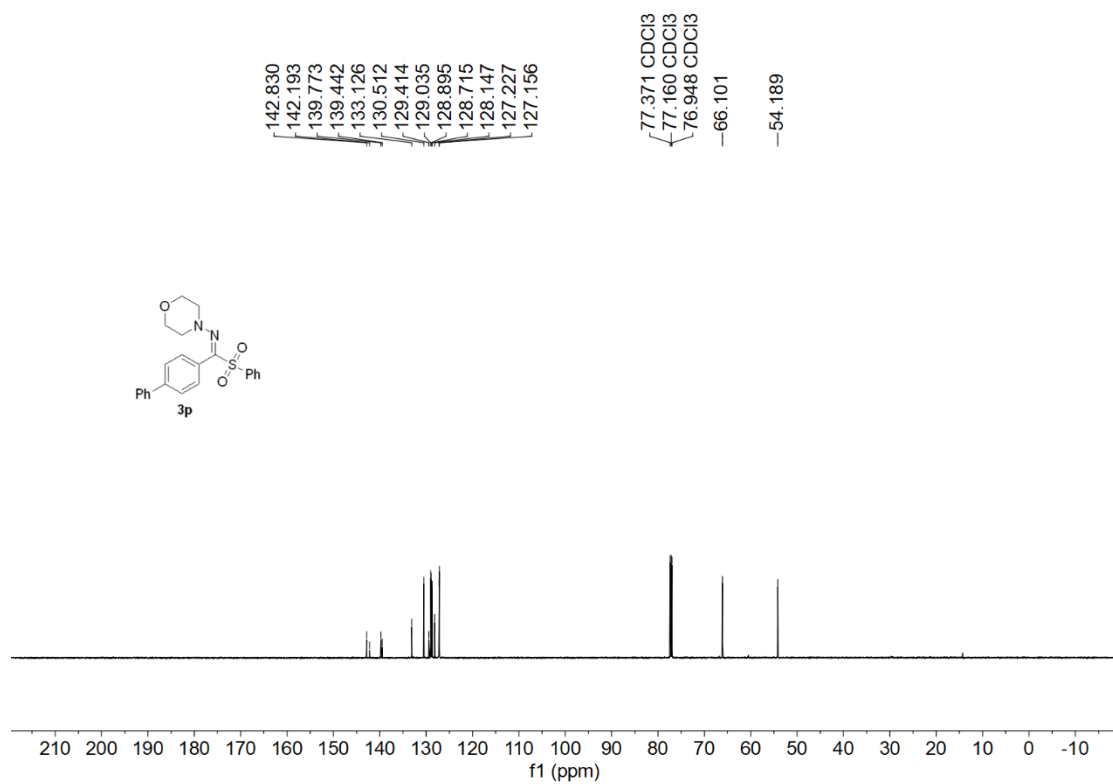
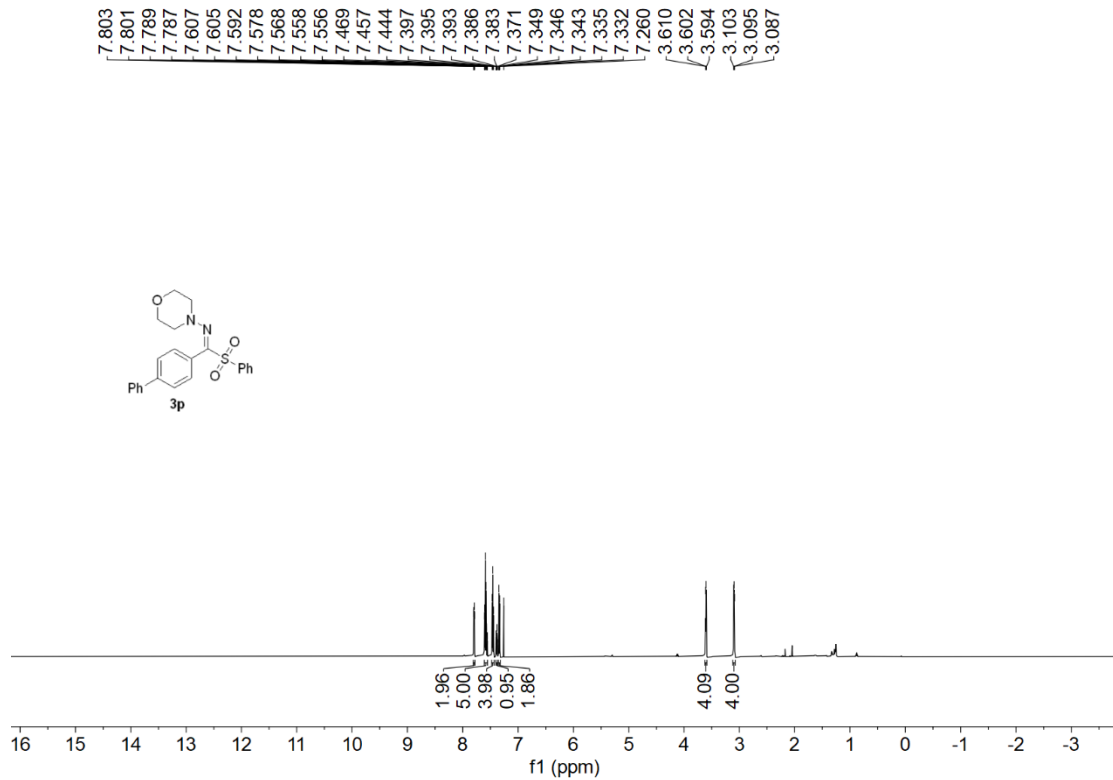


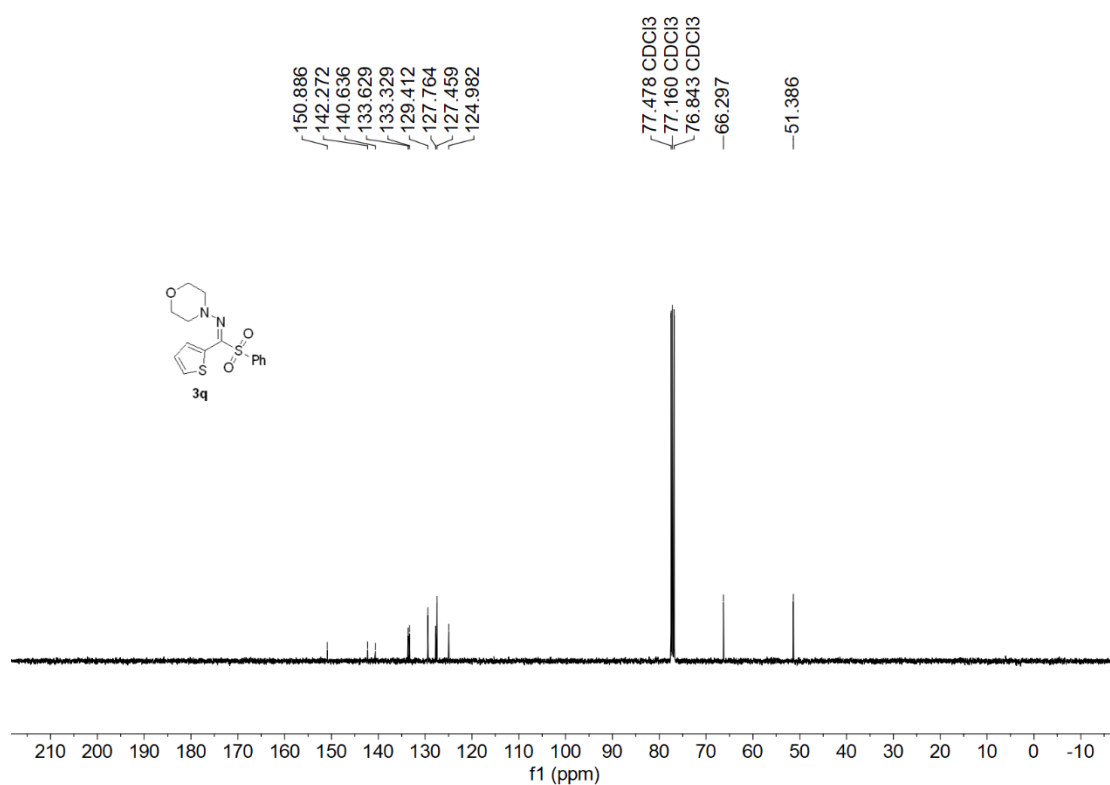
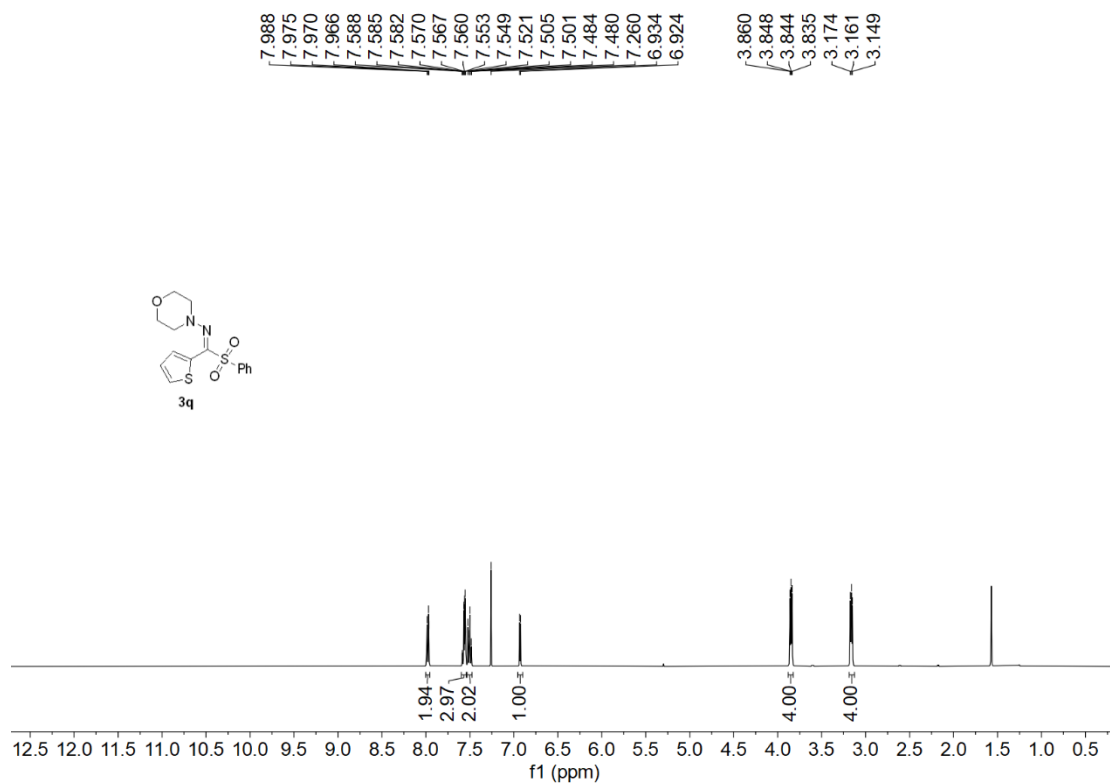


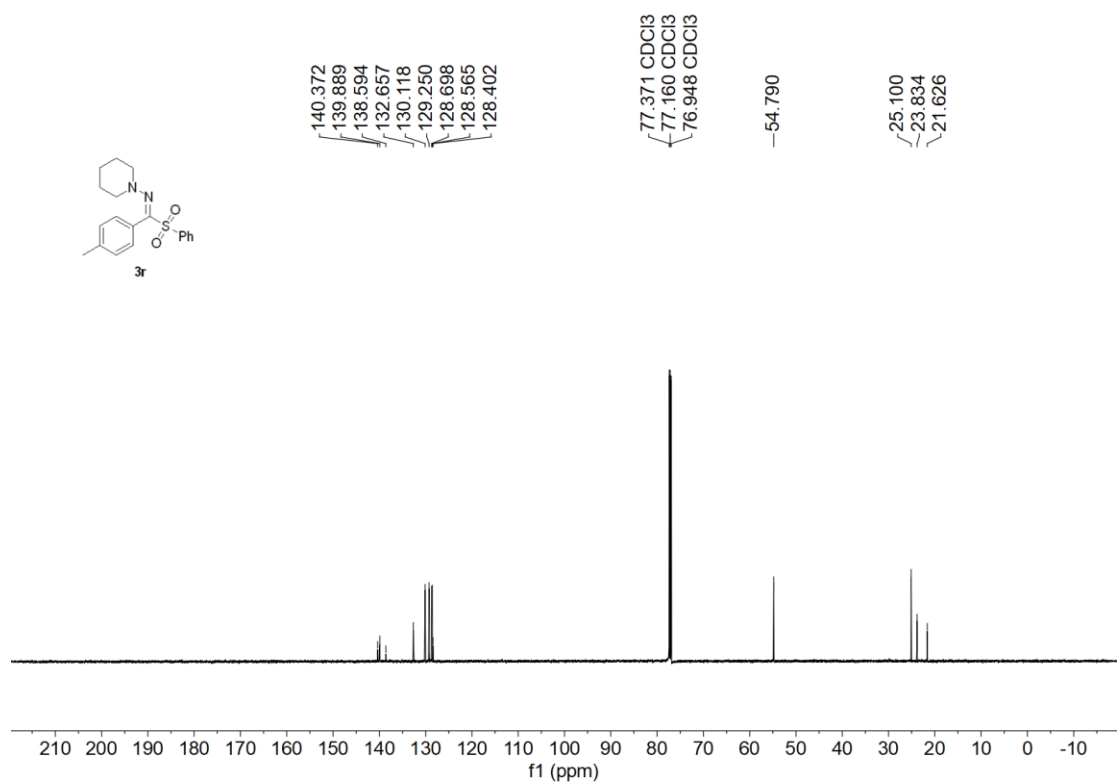
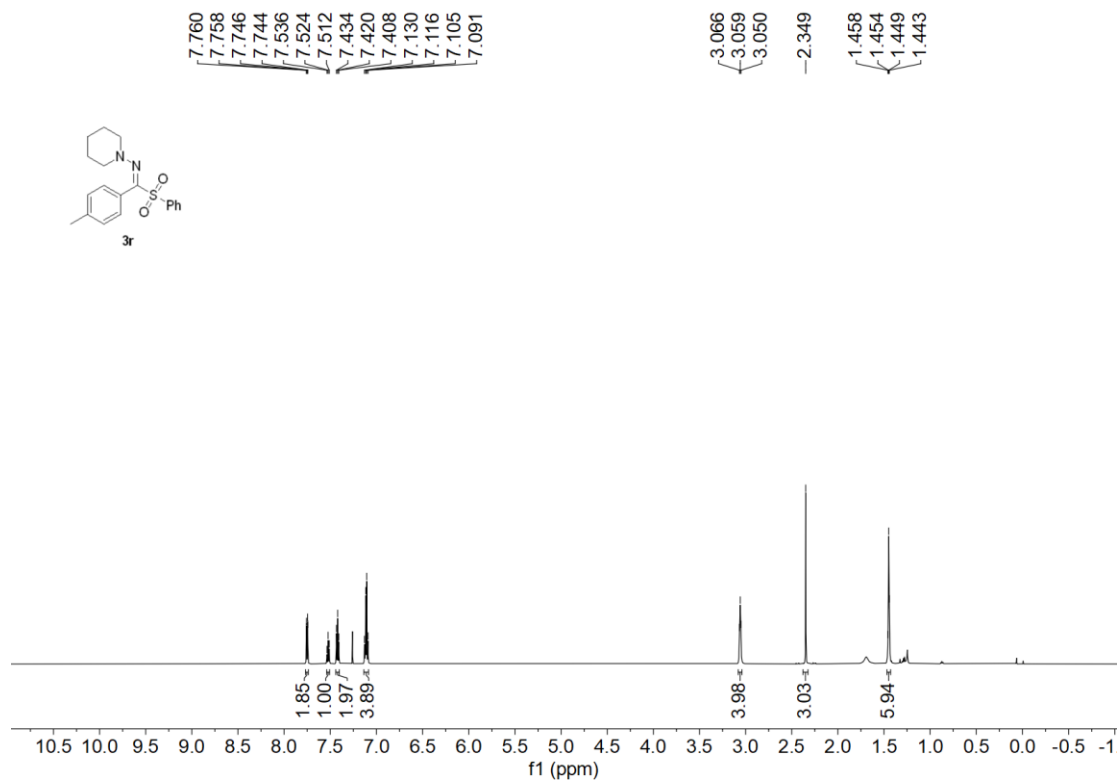


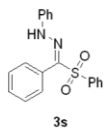
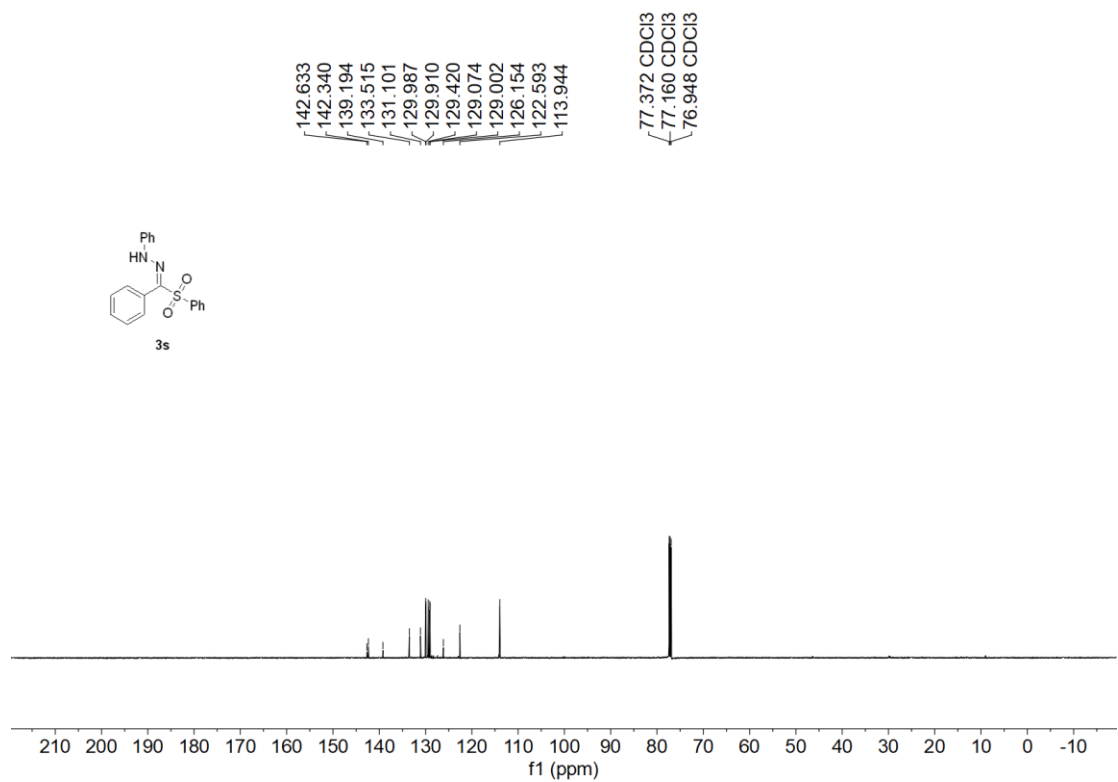
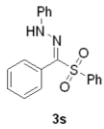
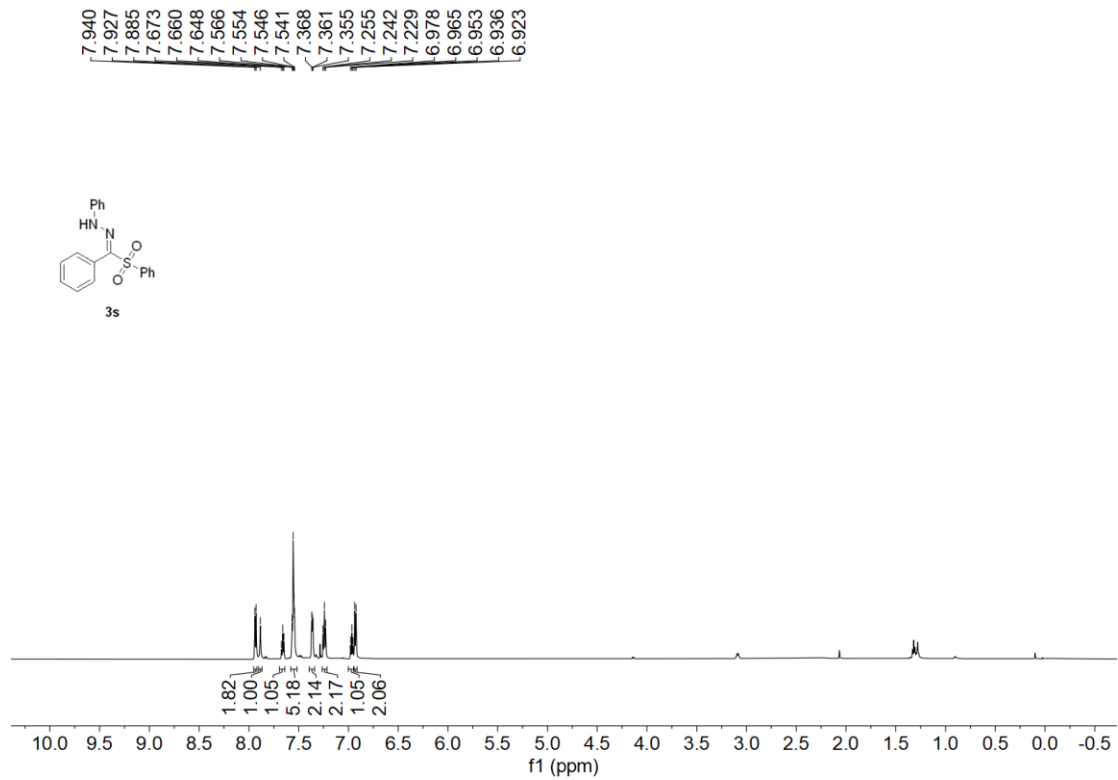


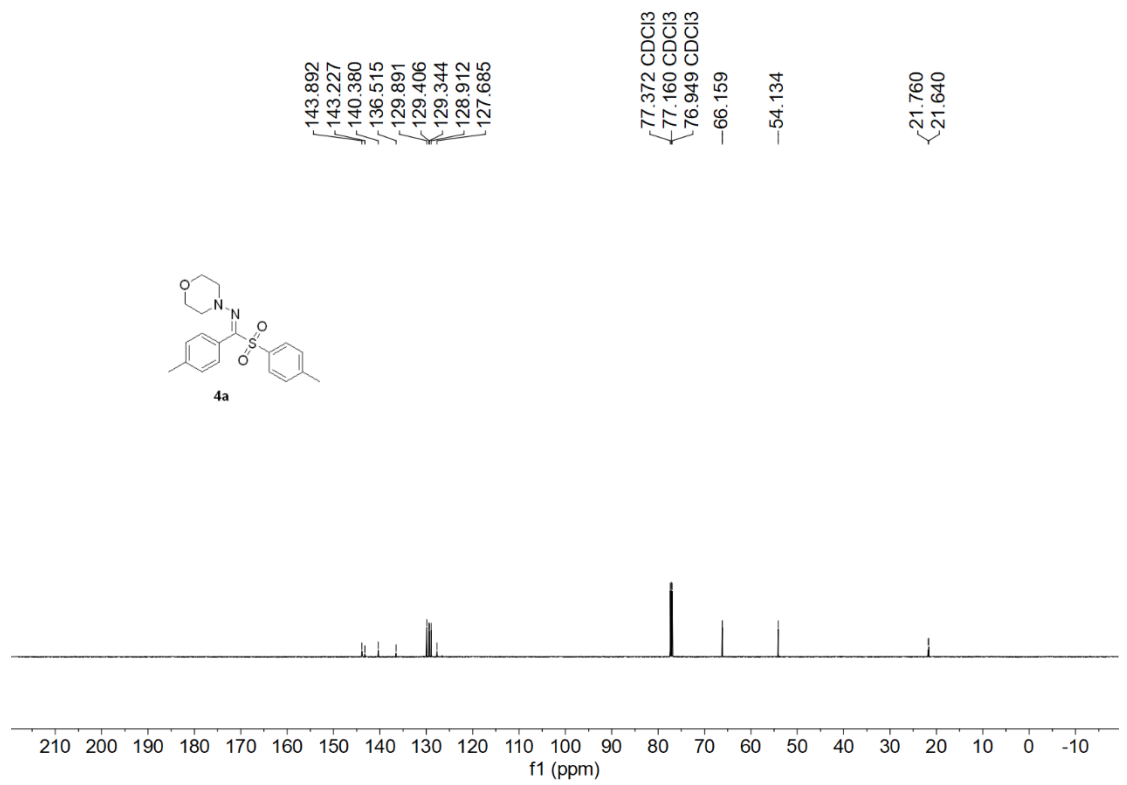
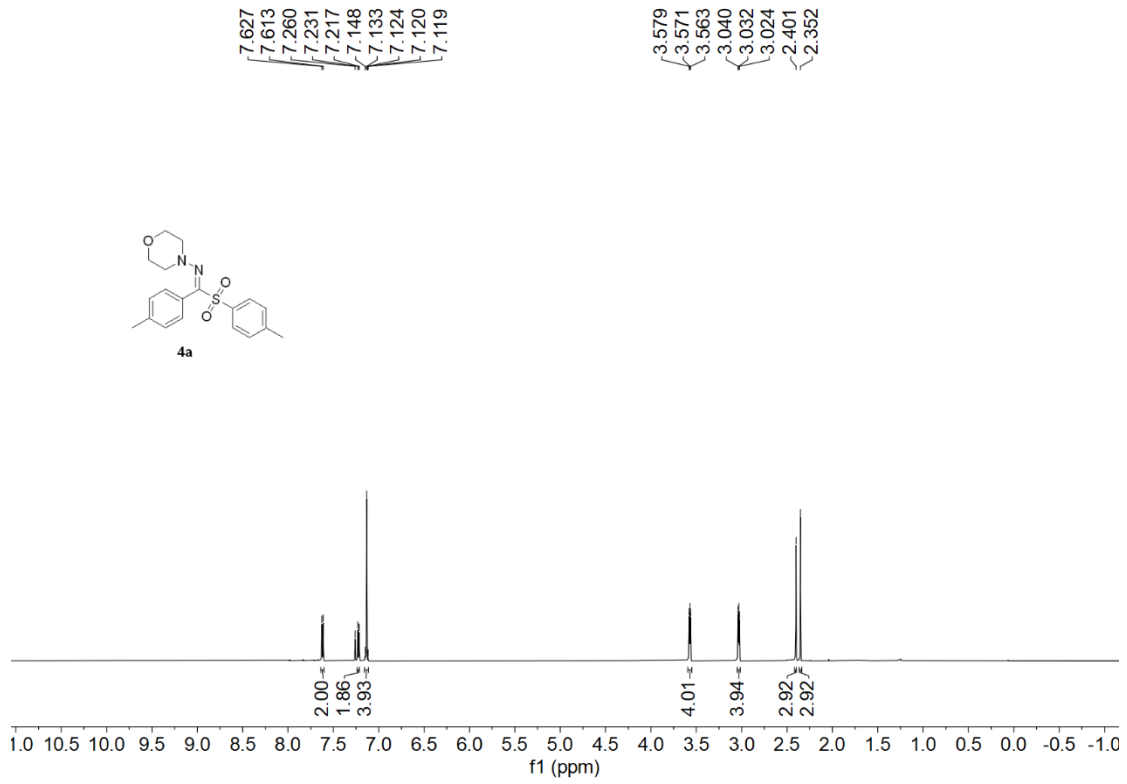


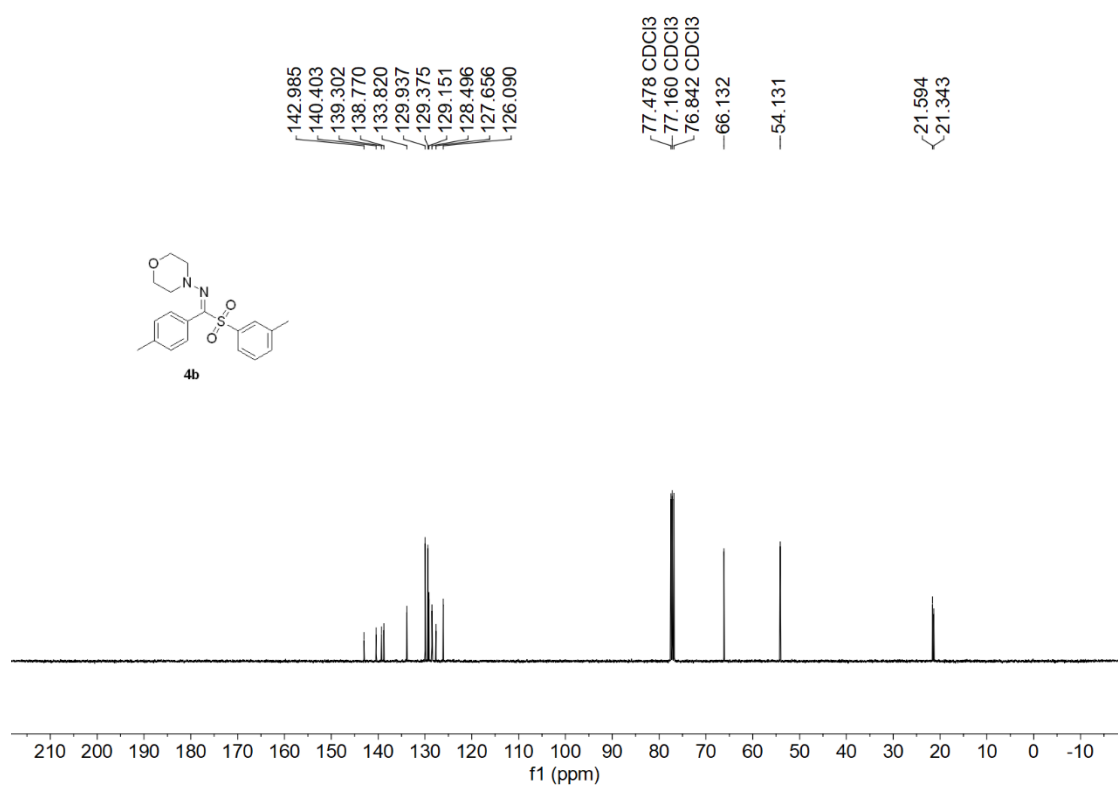
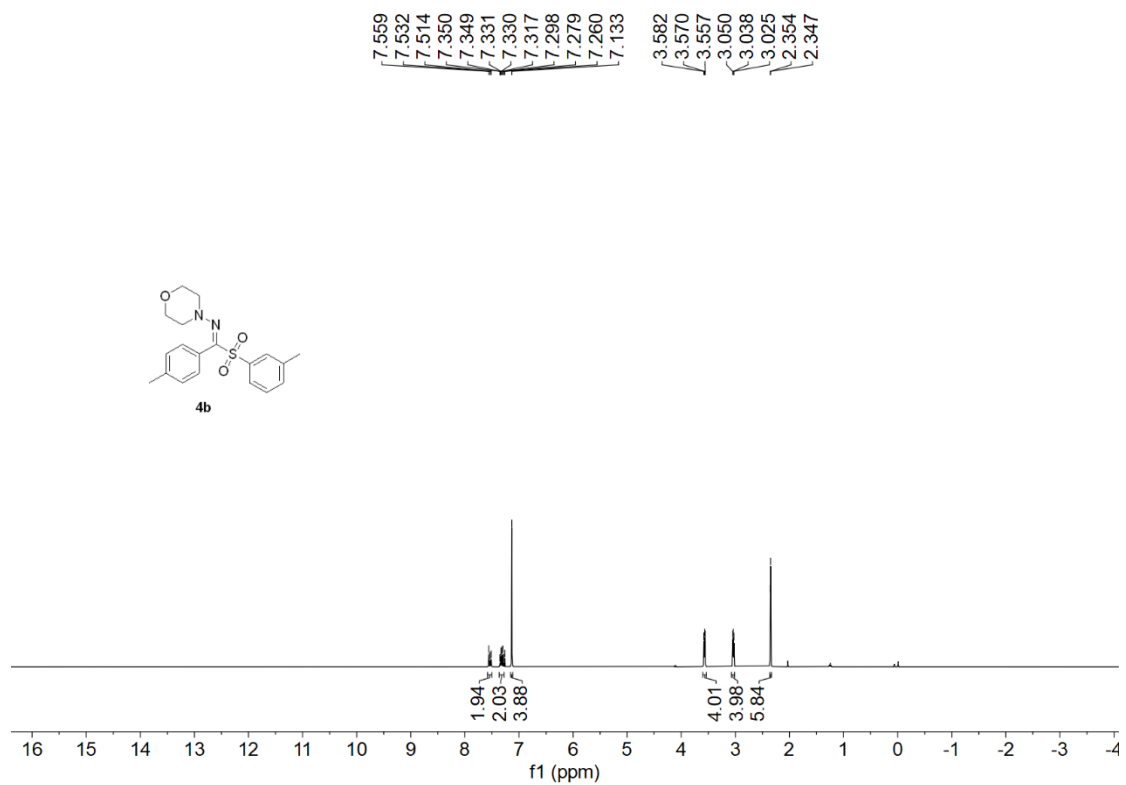


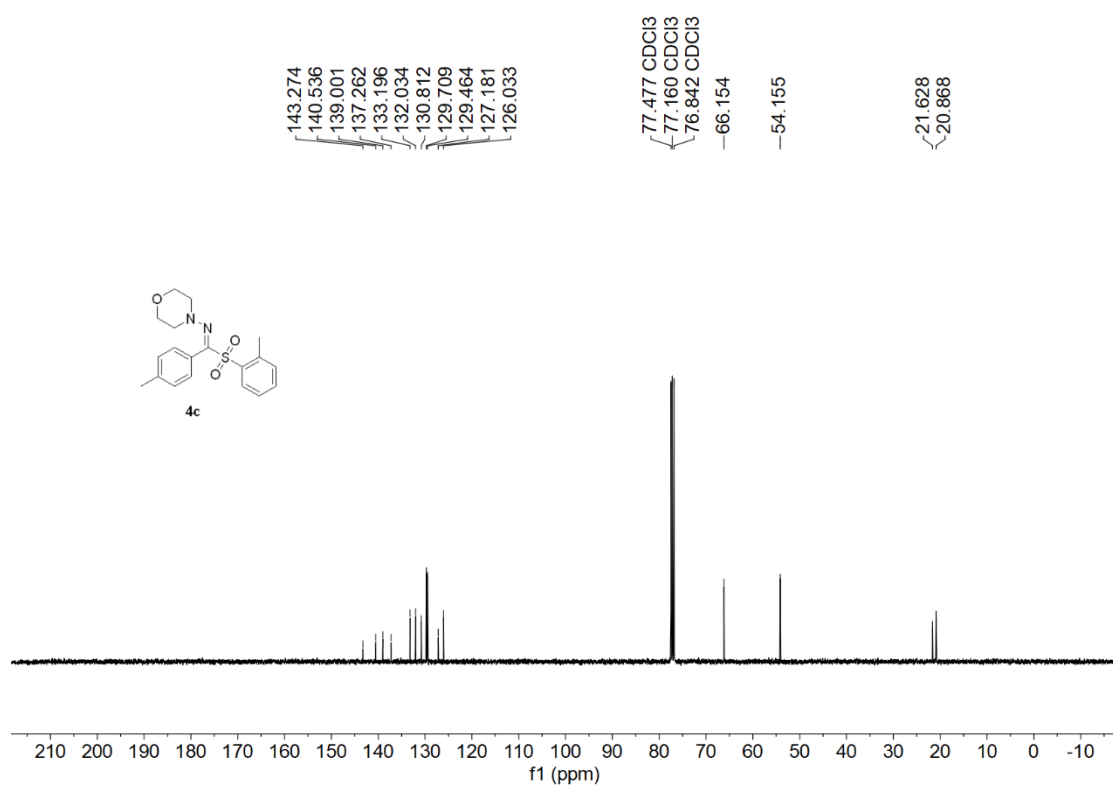
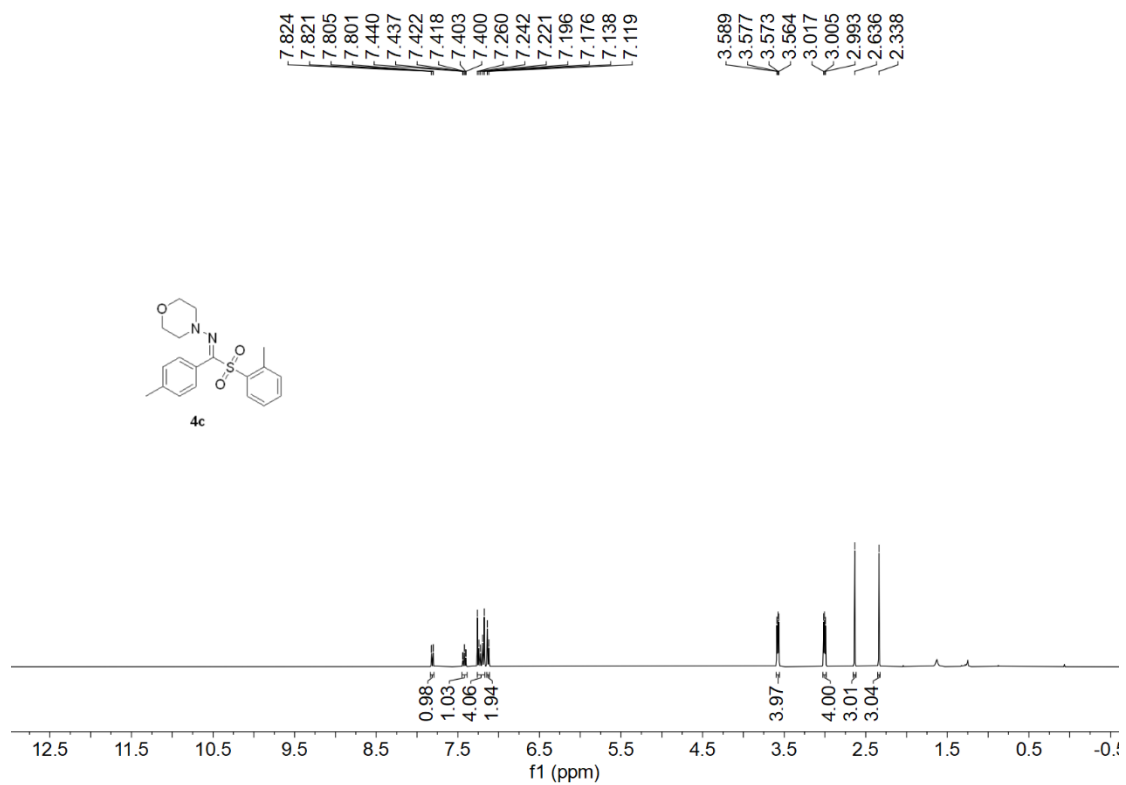


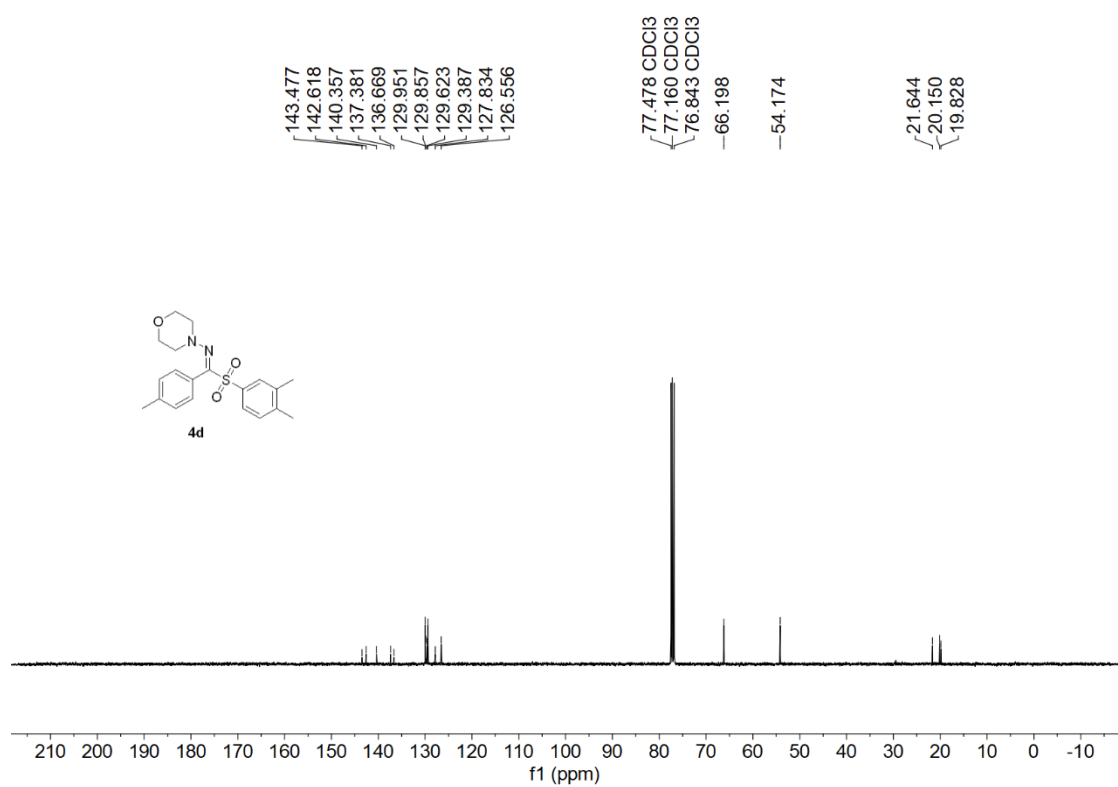
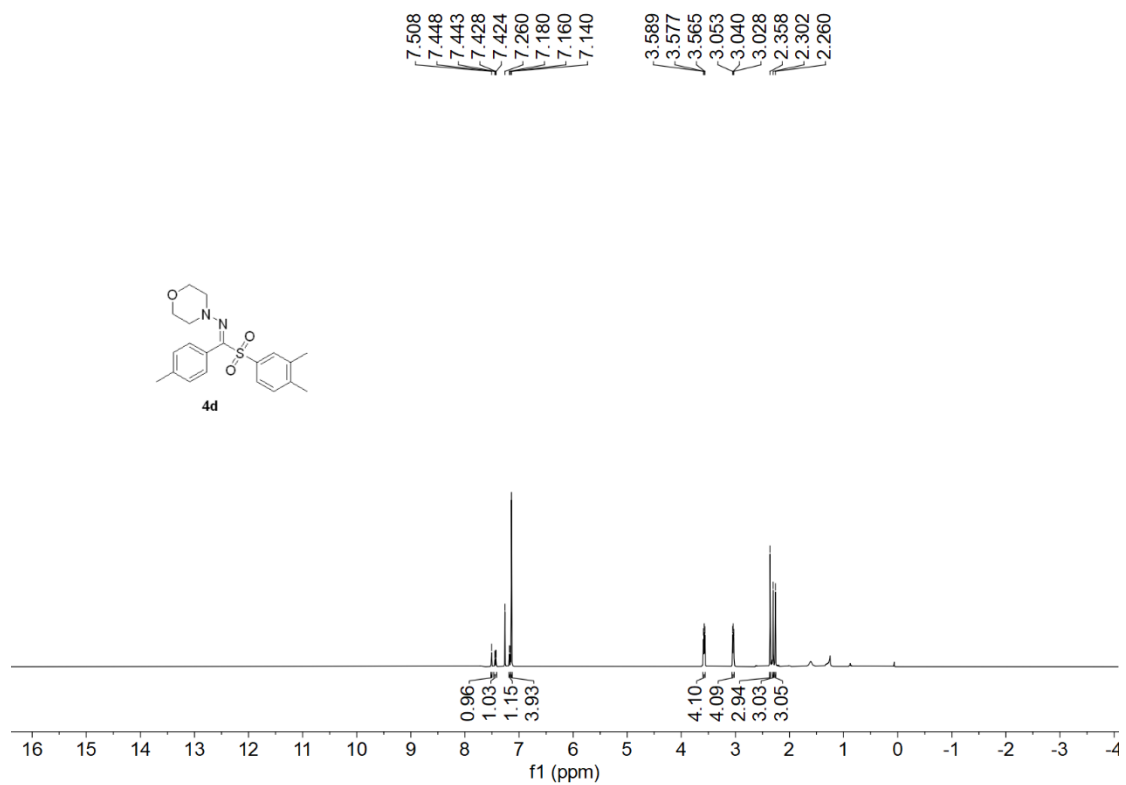


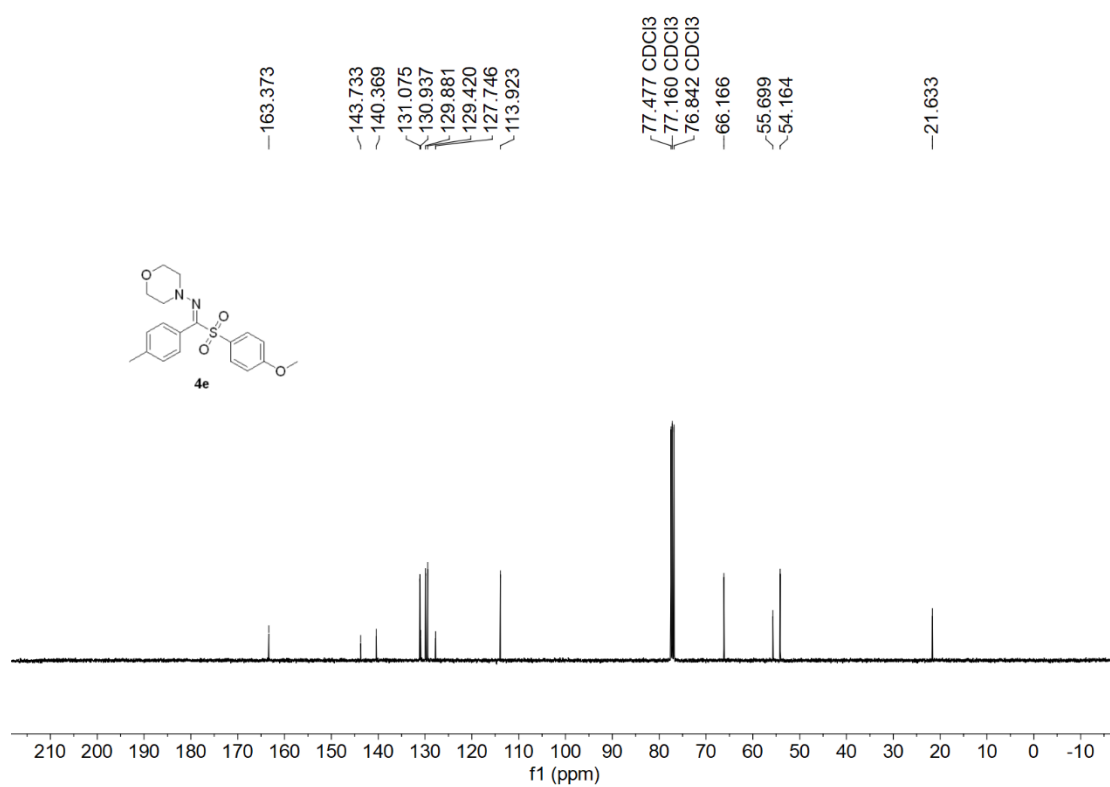
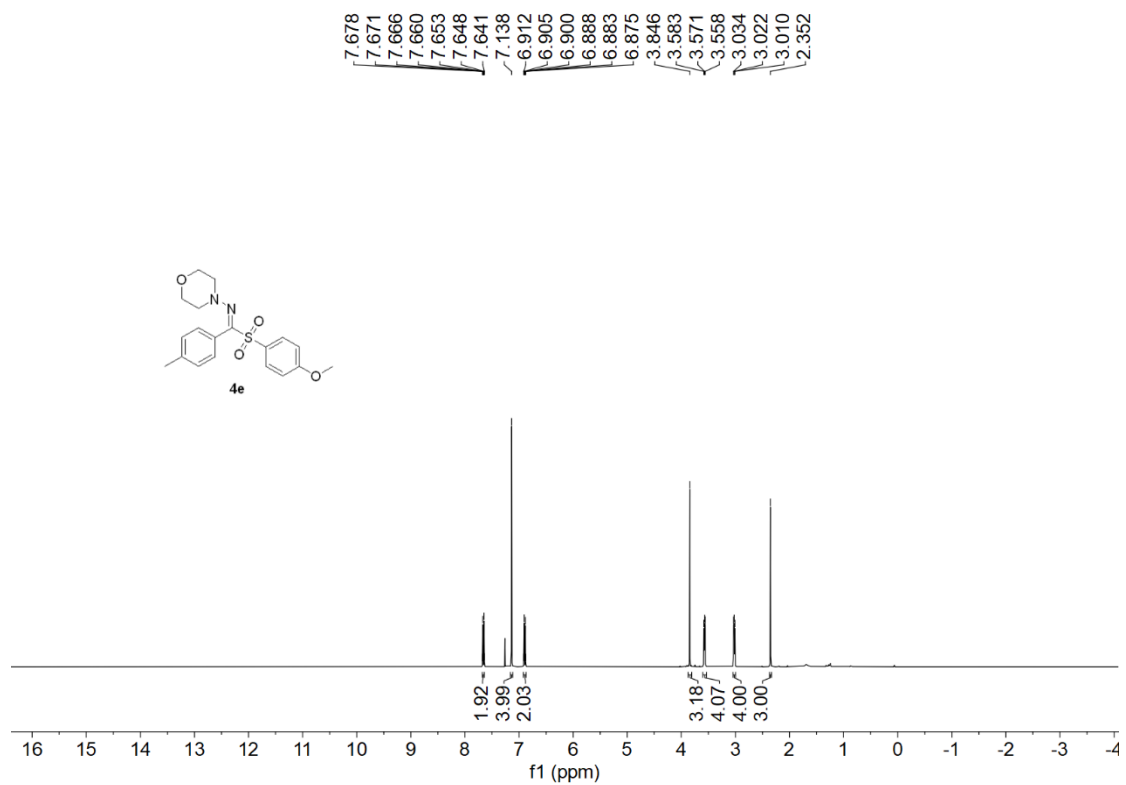


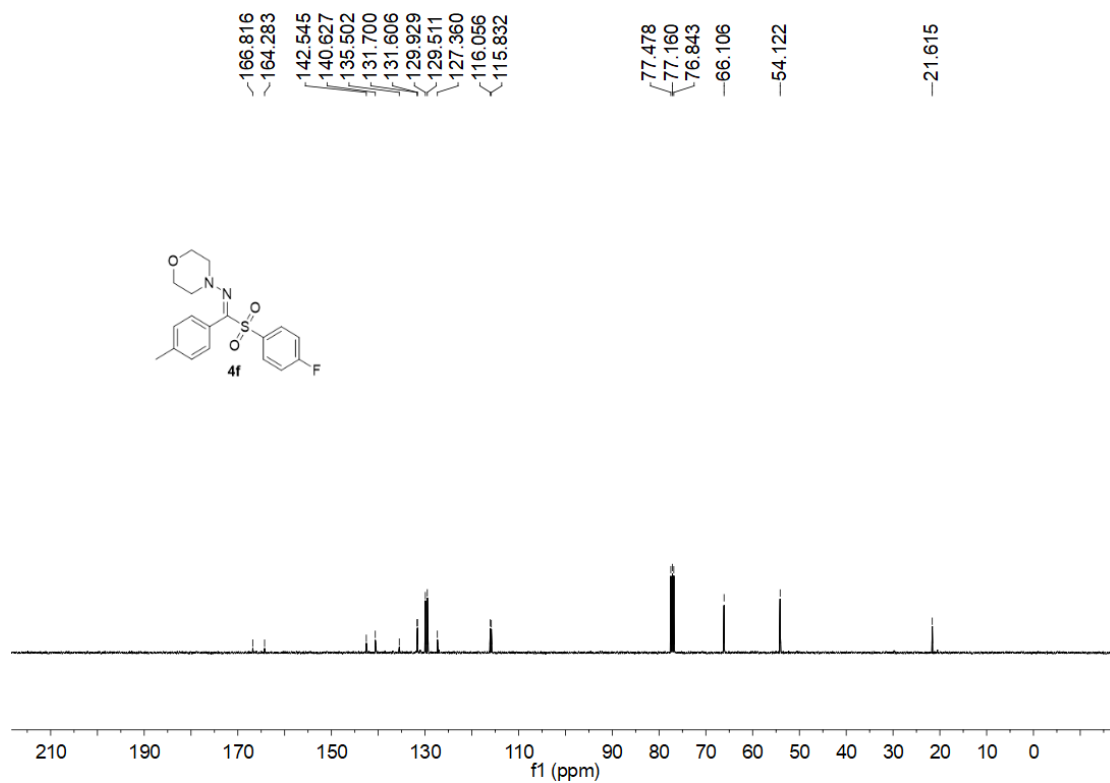
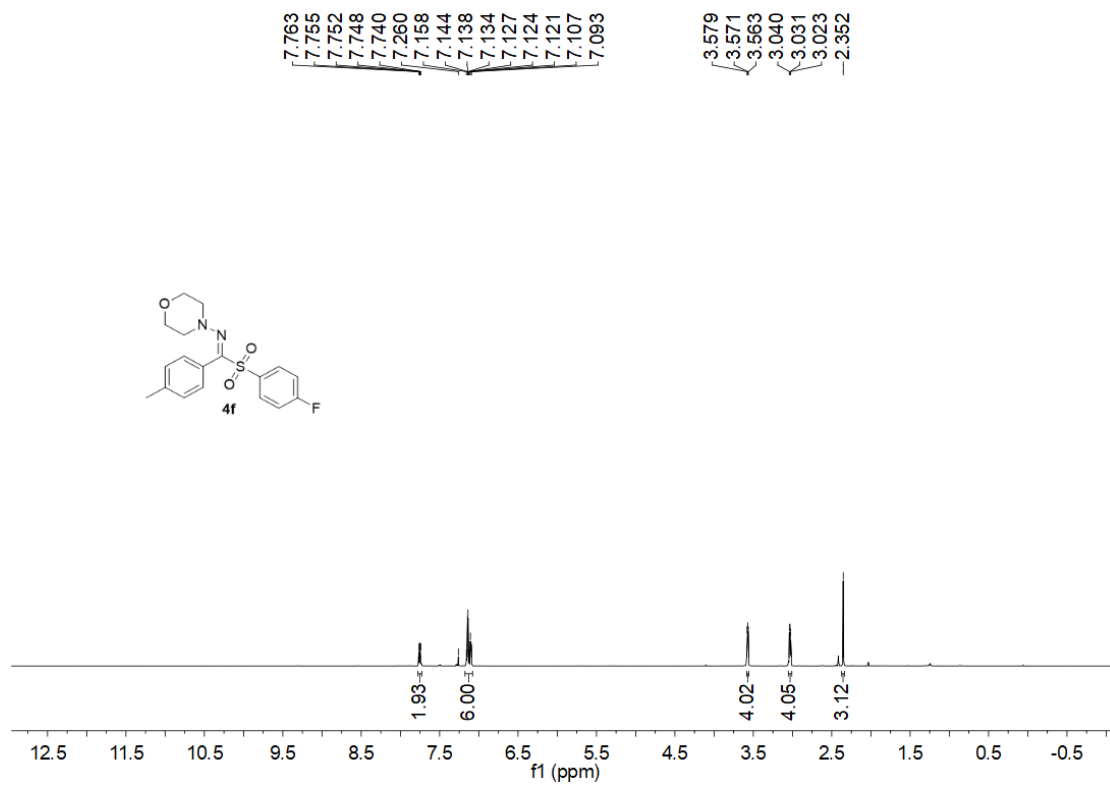


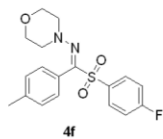
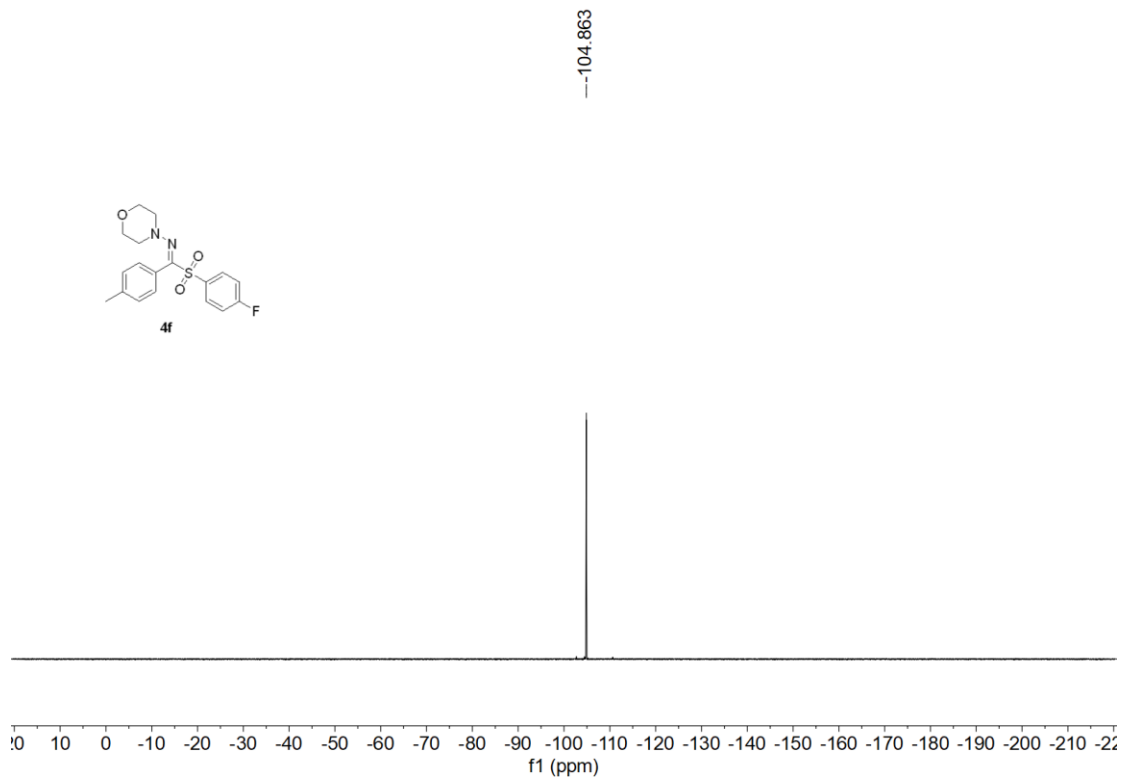






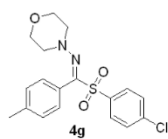
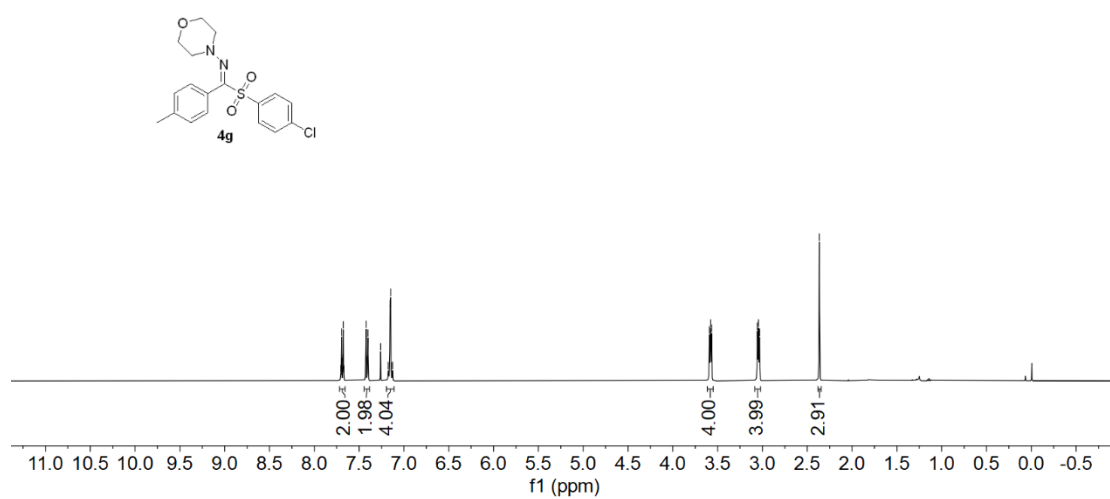






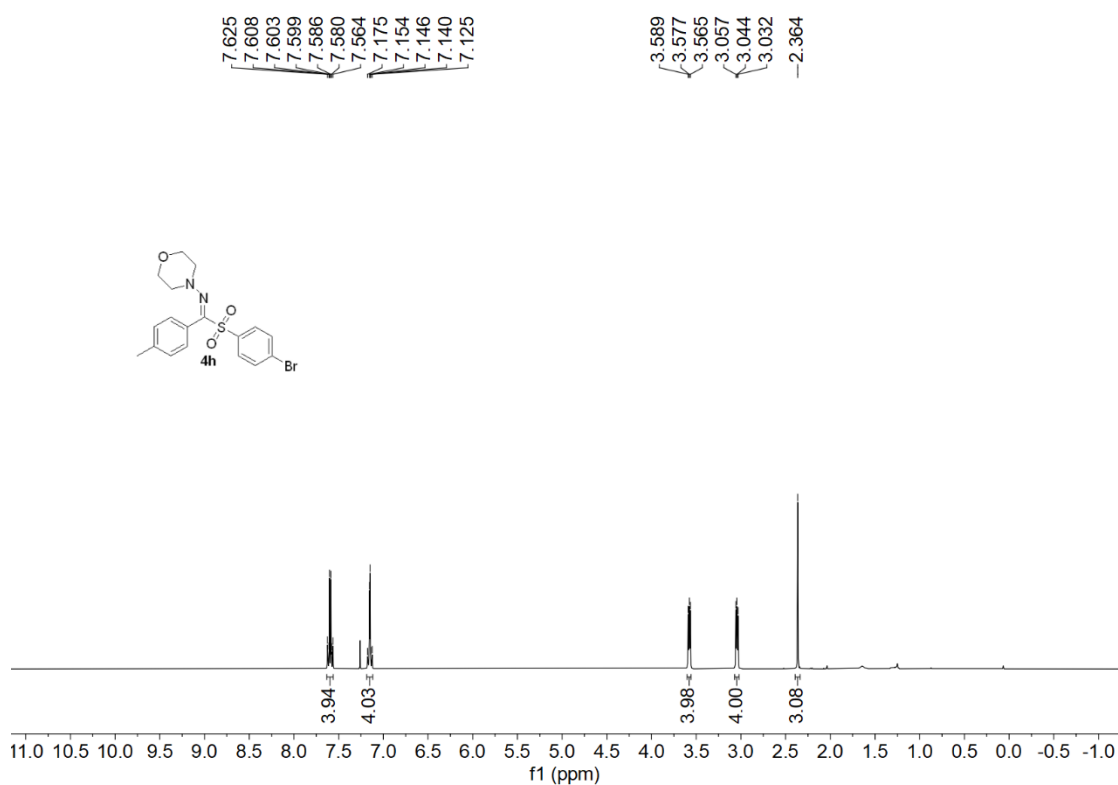
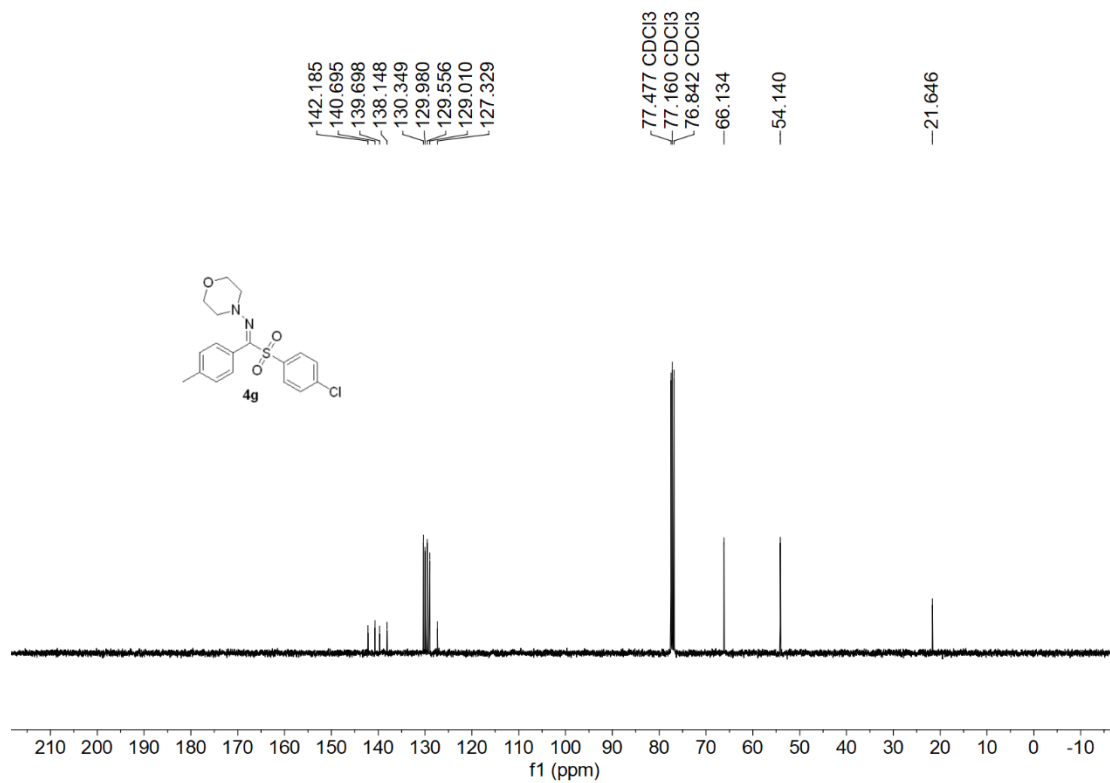
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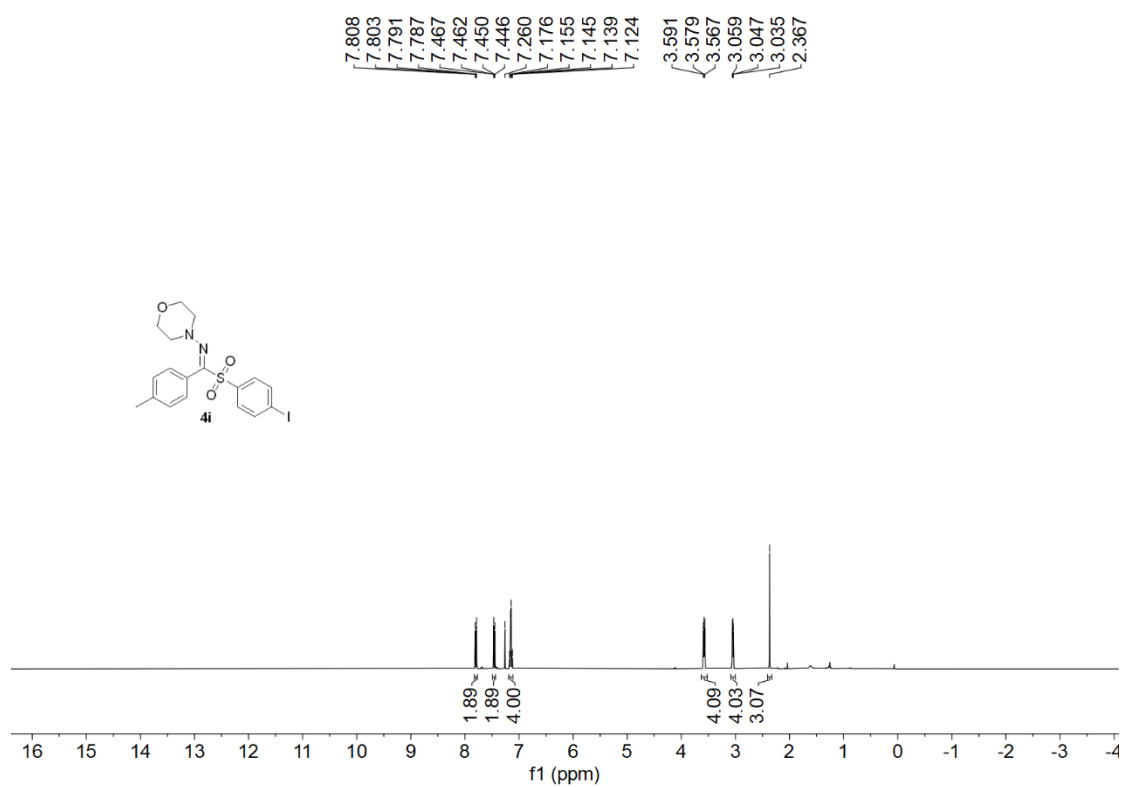
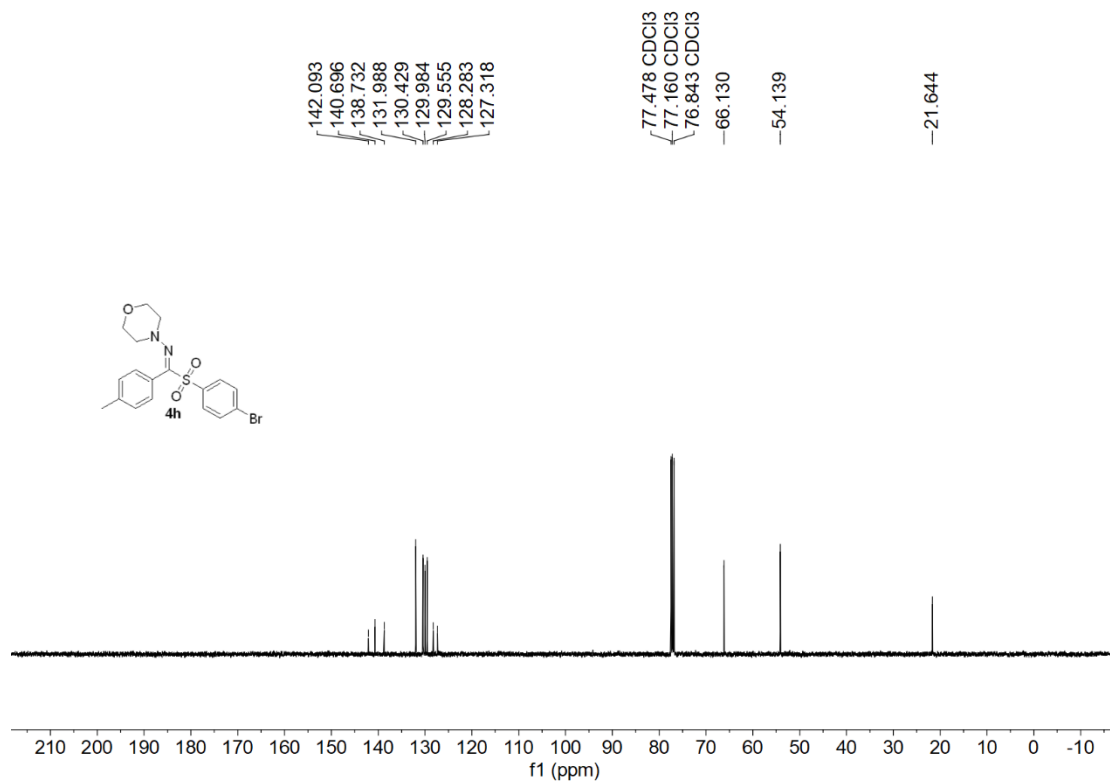
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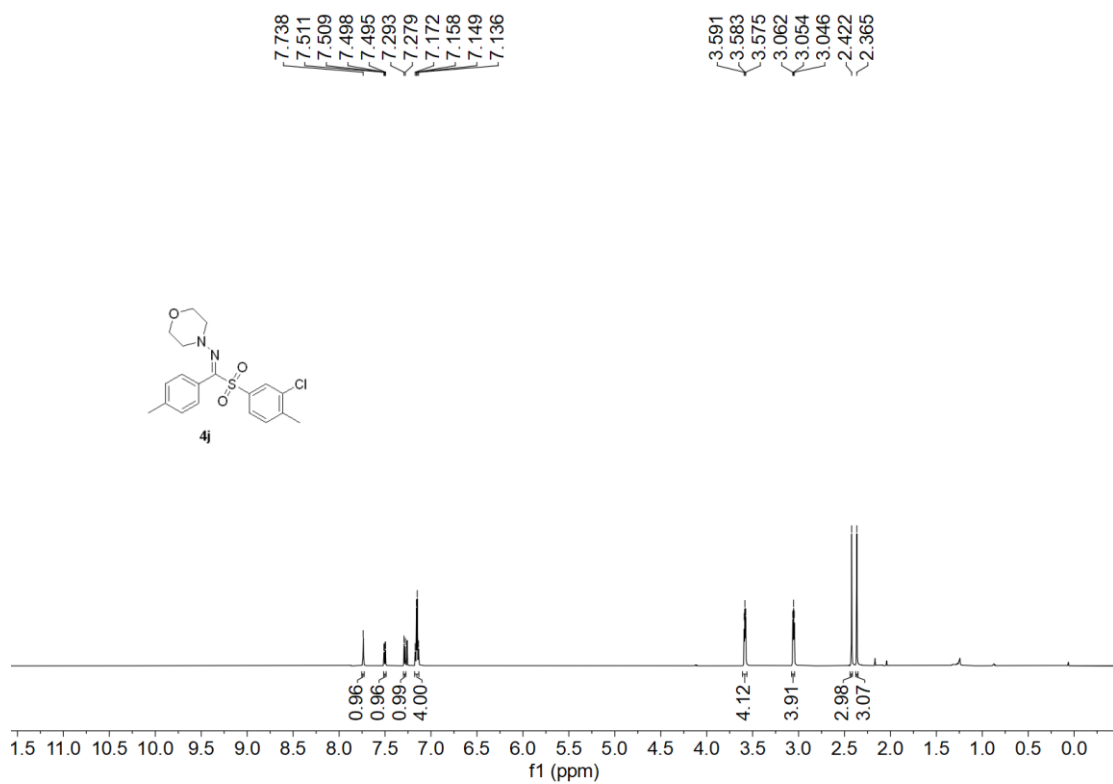
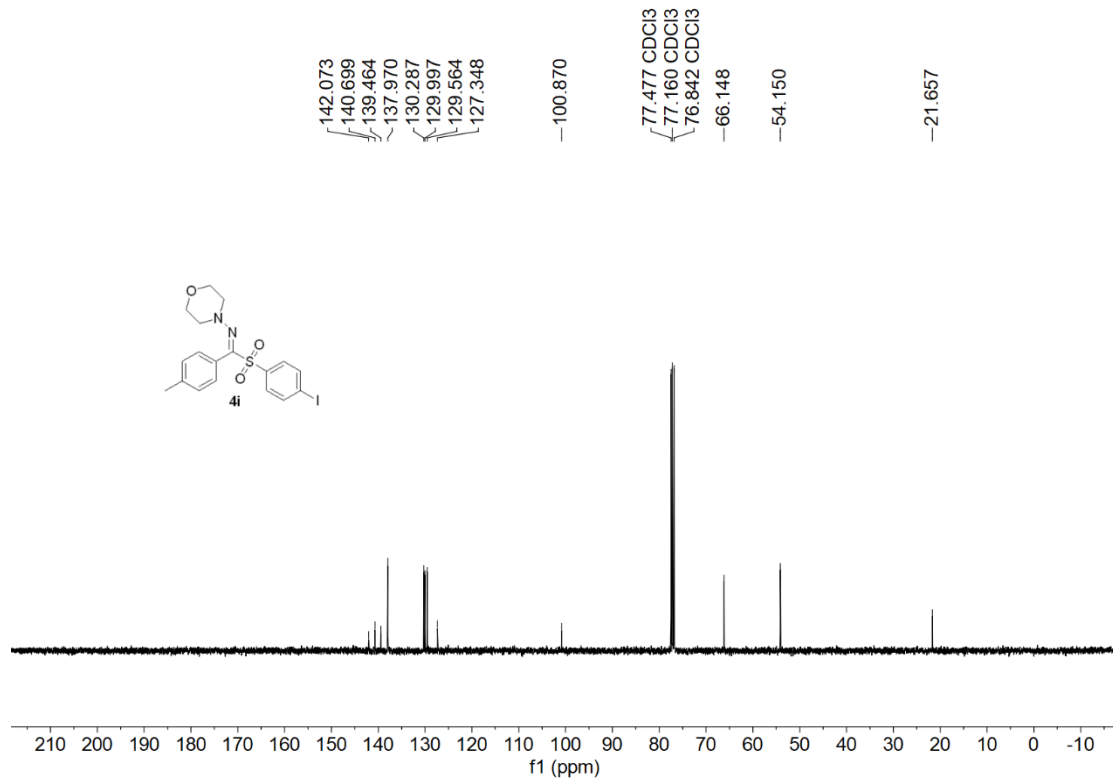


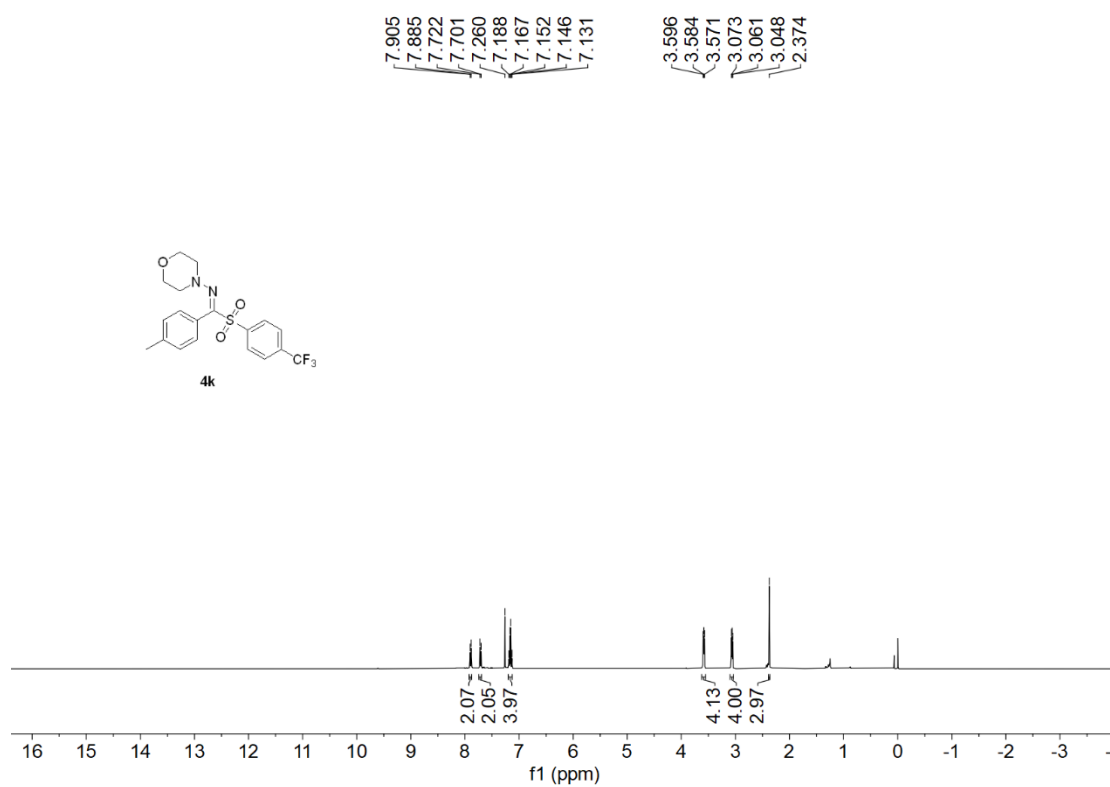
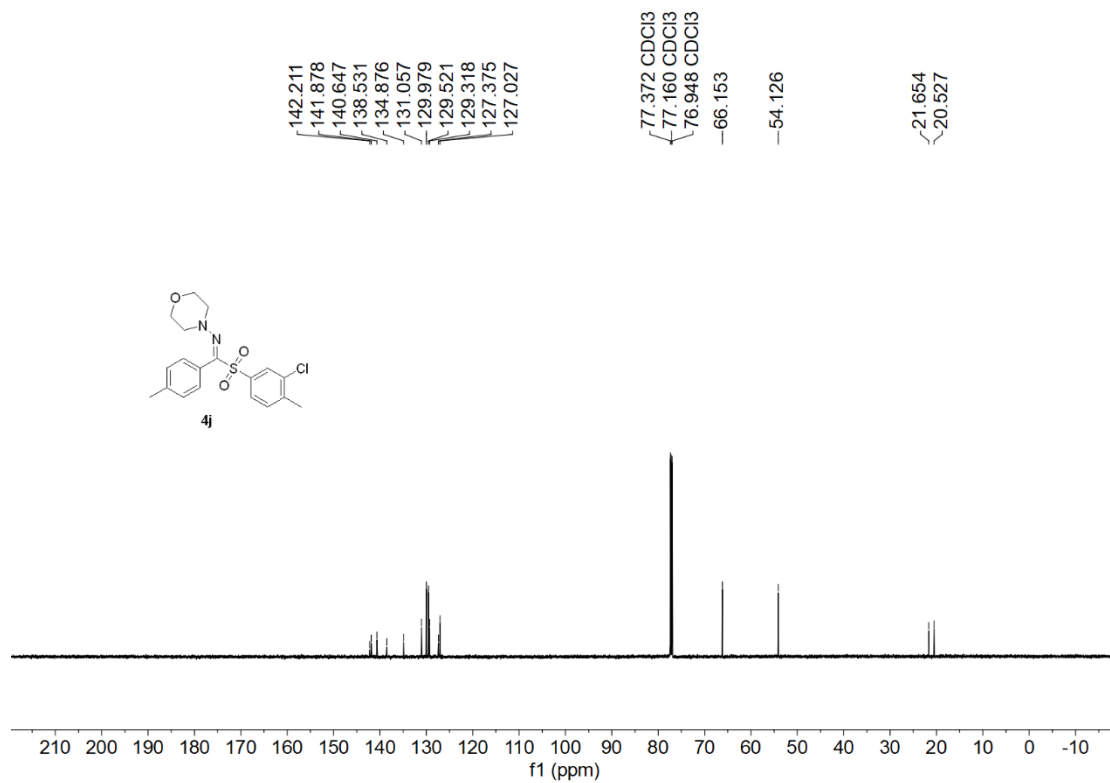
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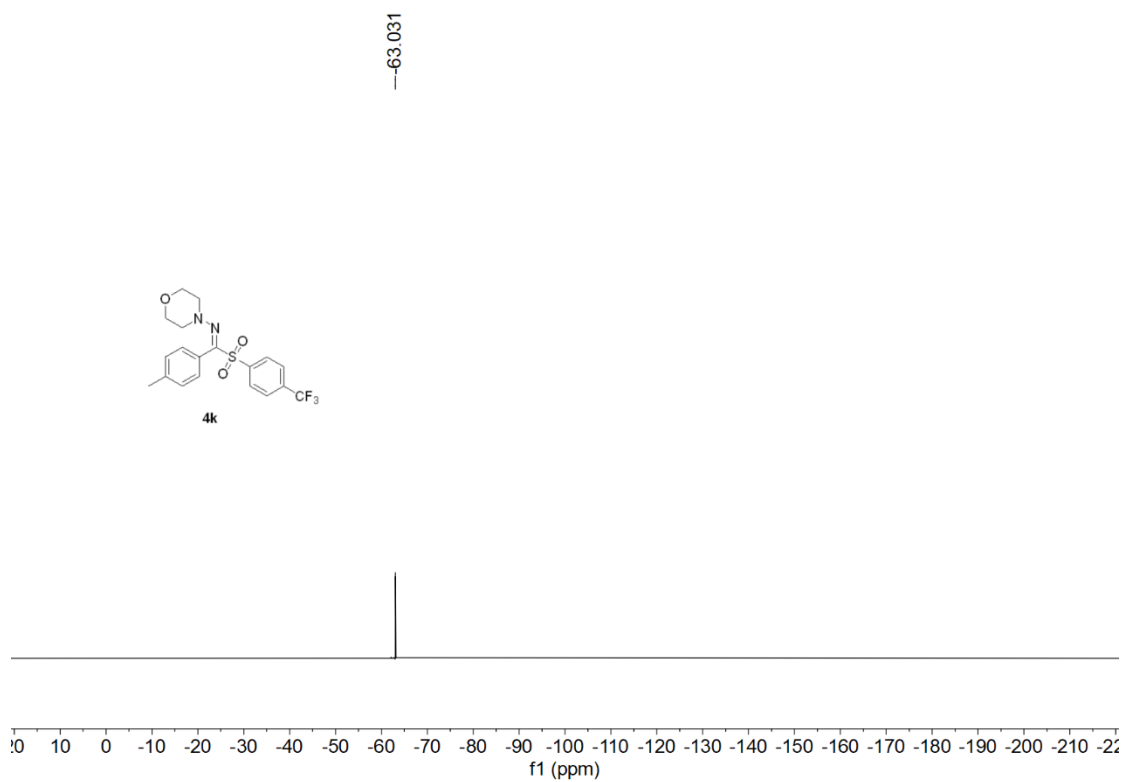
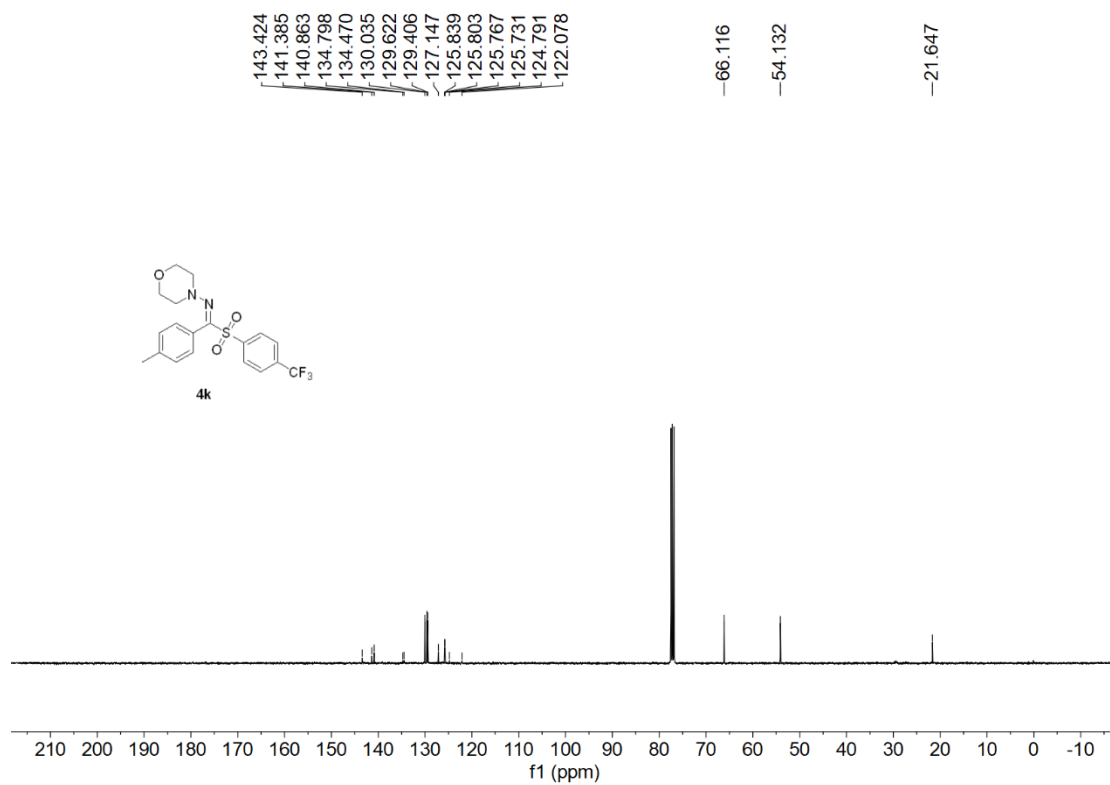
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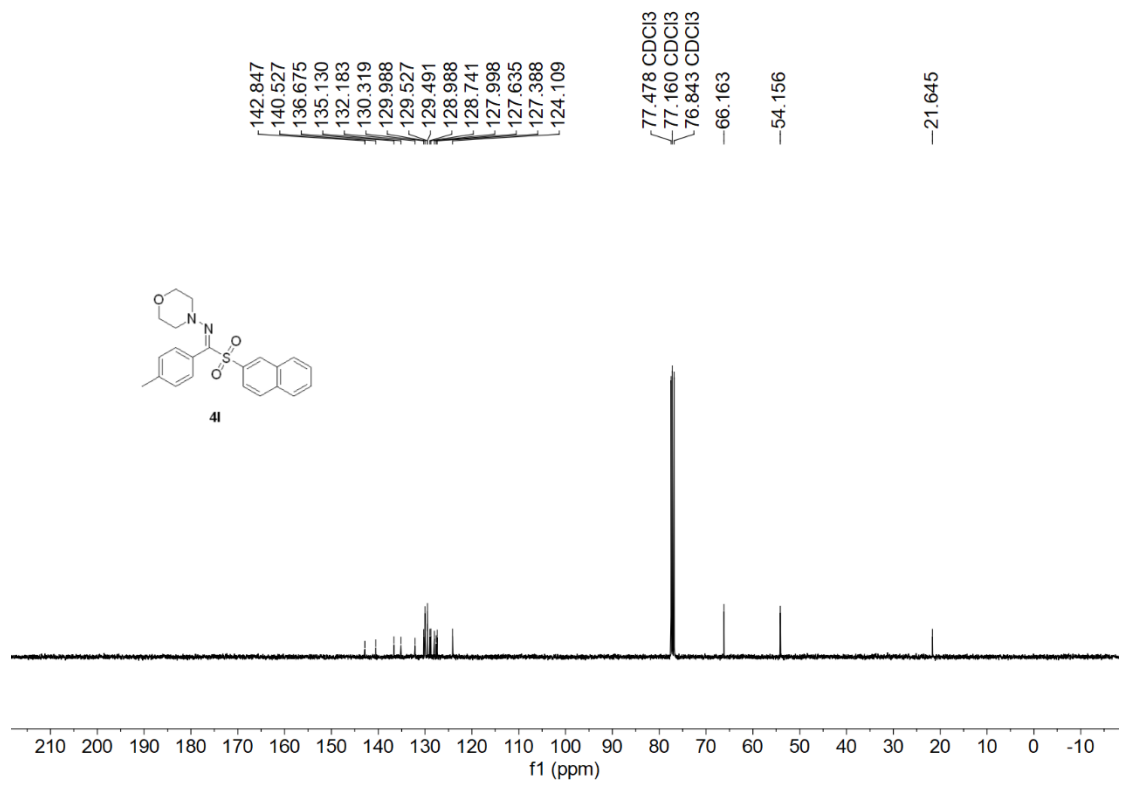
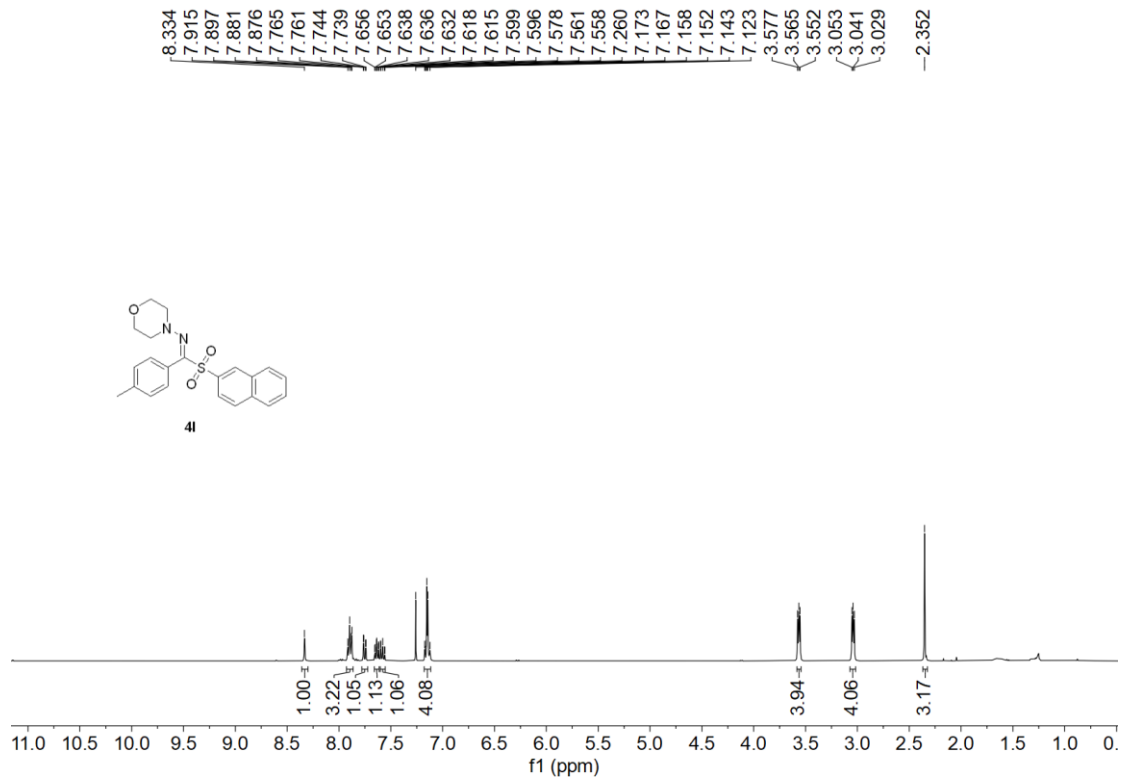




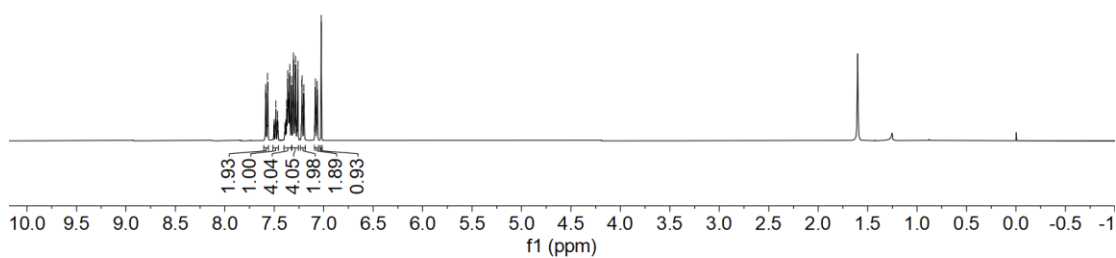
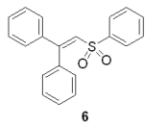








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