

- Electronic Supporting Information -

**Metal-Free Site-Selective Functionalization with Cyclic
Diaryl λ^3 -Chloranes: Suppression of Benzyne Formation
for Ligand-Coupling reactions**

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General information:

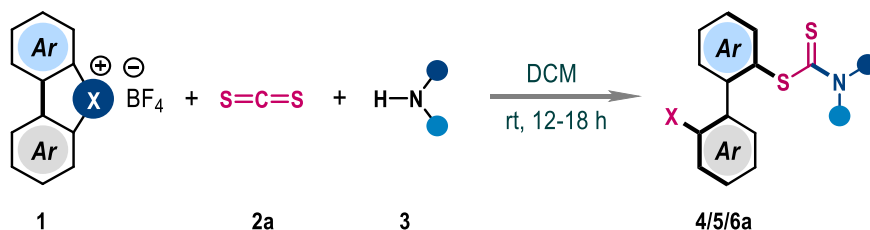
All non-aqueous reactions were carried out under an atmosphere of nitrogen in flame-dried glassware and were stirred using a magnetic stir plate. All reactions were carried out using commercial grade solvent unless otherwise noted. CH₃CN, DCE, and CH₂Cl₂ were dried over calcium hydride. Dry THF was prepared by distilling over sodium ketyl.

All reactions were monitored by thin layer chromatography (TLC) on WhatmanPartisil® K6F TLC plates (silica gel 60 Å, 0.25 mm thickness) and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 10 g phosphomolybdic acid/ 100 mL ethanol; KMnO₄: 0.75 g potassium permanganate, 5 g K₂CO₃, / 100mL water. Products were isolated by column chromatography (Merck silica gel 100-200µm). Yields refer to chromatographically and spectroscopically homogenous materials unless noted otherwise. ¹³C and ¹H NMR spectra were recorded on a Bruker400 or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak CDCl₃ δ = 7.2600 ppm for ¹H, δ = 77.16 for ¹³C, DMSO-d₆ δ = 2.500 ppm for ¹H, δ = 39.500 ppm for ¹³C; or calibrated to tetramethylsilane (δ = 0.00 ppm). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ¹H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad; app, apparent.

Mass spectra were recorded by electrospray ionization (ESI) method on a Q-TOF Micro with lock spray source. The crystal data were collected and integrated using a BrukerAxs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

The λ³-chloranes **1** were synthesized following literature procedures (*J. Am. Chem. Soc.* **2023**, *145*, 345).

General procedure for the synthesis of unsymmetrical biaryls (4/5/6a):

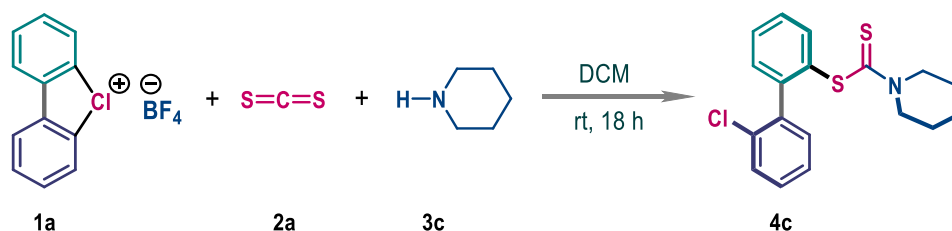


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with corresponding λ^3 -chlorane/bromane/iodane **1** (0.2 mmol, 1.0 equiv), CS_2 (**2a**, 0.5 mmol, 2.5 equiv), and amine **3** (0.24 mmol, 1.2 equiv) under N_2 atmosphere. Then, dry DCM (1.5 mL) was added via syringe. The reaction mixture was allowed to stir at rt. After completion of the reaction (12–18 h, TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **4/5**.

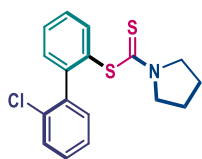
Compound **6a** was prepared similarly using λ^3 -iodane (**1a''**), CS_2 (**2a**) and pyrrolidine (**3a**) at 50 °C.

To minimize potential contamination from metal impurities, we prepared the chloranes using distilled biaryl precursors (Kugelrohr distillation). Additionally, we conducted two rounds of crystallization on the synthesized λ^3 -chloranes before employing them in the reaction.

Gram scale synthesis of compound **4c**:

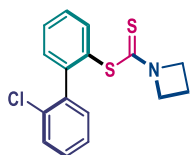


A 100 mL oven dried round bottom flask equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (3.64 mmol, 1.0 equiv), CS_2 (**2a**, 2.5 equiv), and piperidine **3c** (1.2 equiv) under N_2 atmosphere. Then, dry DCM (20 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 18 h. After completion, volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **4c** (1.05 g, 80%).



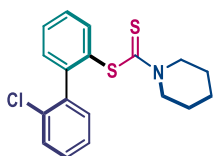
4a

Compound, **4a**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 88% (58 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.56 (d, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.41 – 7.37 (m, 2H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 7.21 – 7.13 (m, 2H), 3.78 – 3.64 (m, 2H), 3.57 – 3.51 (m, 1H), 3.37 – 3.31 (m, 1H), 1.93 – 1.76 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 192.4, 144.7, 139.5, 138.5, 133.2, 131.3, 130.8, 130.7, 130.2, 128.8, 128.7, 128.6, 126.1, 55.0, 51.1, 26.1, 24.3. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₇H₁₆ClNS₂H⁺ 334.0485; Found 334.0477.



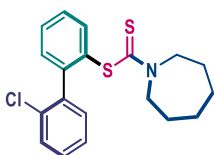
4b

Compound, **4b**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 85% (54 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.56 – 7.54 (m, 1H), 7.47 – 7.43 (m, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.31 (m, 2H), 7.28 – 7.16 (m, 3H), 4.15 – 4.01 (m, 3H), 3.88 – 3.81 (m, 1H), 2.25 – 2.12 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 193.7, 144.9, 139.5, 138.4, 133.3, 131.5, 130.8, 130.3, 130.0, 129.0, 128.9, 128.8, 126.3, 54.8, 54.0, 15.0. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₆H₁₄ClNS₂H⁺ 320.0329; Found 320.0324.



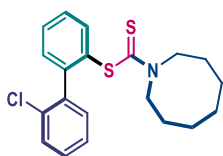
4c

Compound, **4c**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 87% (61 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.55 (d, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.37 – 7.32 (m, 2H), 7.25 (d, $J = 7.4$ Hz, 1H), 7.21 – 7.13 (m, 2H), 4.20 – 4.19 (m, 1H), 3.91 – 3.62 (m, 3H), 1.62 – 1.42 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.4, 144.8, 139.6, 138.7, 133.2, 131.4, 131.3, 130.7, 130.3, 128.79, 128.76, 128.7, 126.0, 53.1, 52.3, 25.8, 25.5, 24.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₈H₁₈ClNS₂H⁺ 348.0642; Found 348.0640.



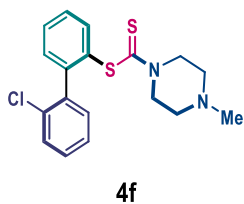
4d

Compound, **4d**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 80% (58 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.55 (d, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.44 – 7.40 (m, 1H), 7.37 – 7.32 (m, 2H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.21 – 7.12 (m, 2H), 4.25 – 4.19 (m, 1H), 3.83 – 3.67 (m, 2H), 3.54 – 3.48 (m, 1H), 1.78 – 1.17 (m, 8H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.1, 145.1, 139.7, 138.9, 133.3, 131.5, 131.2, 130.7, 130.4, 128.82, 128.78, 128.75, 126.1, 55.8, 53.4, 27.1, 26.4 (2×C), 26.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₂₀ClNS₂H⁺ 362.0798; Found 362.0799.

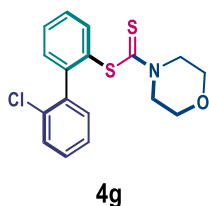


4e

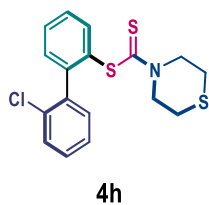
Compound, **4e**: pale yellow solid; eluent (2% ethyl acetate in hexane). **Yield**: 82% (62 mg). **MP**: 112 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.55 (d, $J = 1.5$ Hz, 1H), 7.50 – 7.46 (m, 1H), 7.44 – 7.39 (m, 1H), 7.36 – 7.32 (m, 2H), 7.27 (d, $J = 5.9$ Hz, 1H), 7.20 – 7.11 (m, 2H), 4.21 – 4.14 (m, 1H), 3.82 – 3.76 (m, 1H), 3.67 – 3.61 (m, 1H), 3.49 – 3.43 (m, 1H), 1.85 – 1.78 (m, 1H), 1.72 – 1.51 (m, 3H), 1.37 – 1.22 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.2, 145.2, 139.7, 139.0, 133.3, 131.6, 131.2, 130.8, 130.5, 128.9, 128.79, 128.76, 126.2, 56.6, 54.3, 26.8, 26.3, 25.3 (2×C), 25.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₂₂ClNS₂H⁺ 376.0955; Found 376.0952.



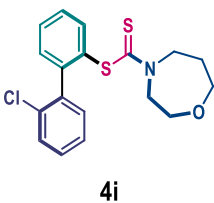
Compound, **4f**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 81% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.54 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.49 – 7.45 (m, 1H), 7.42 – 7.38 (m, 1H), 7.34 – 7.31 (m, 2H), 7.25 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.22 – 7.13 (m, 2H), 4.20 – 4.02 (m, 2H), 3.76 (bs, 2H), 2.35 – 2.22 (m, 4H), 2.18 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.9, 144.9, 139.6, 138.7, 133.4, 131.5, 131.1, 130.8, 130.5, 129.0, 128.90, 128.85, 126.2, 54.4 ((2×C), 51.4, 50.8, 45.6. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₈H₁₉ClN₂S₂H⁺ 363.0751; Found 363.0752.



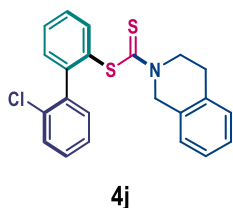
Compound, **4g**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 76% (53 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.48 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.26 (t, $J = 7.4$ Hz, 2H), 7.19 (d, $J = 7.5$ Hz, 1H), 7.20 – 7.07 (m, 2H), 3.98 – 3.36 (m, 8H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 197.3, 144.9, 139.5, 138.5, 133.3, 131.4, 130.8, 130.7, 130.5, 129.0, 128.88, 128.86, 126.1, 66.2, 51.5. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₇H₁₆ClNOS₂H⁺ 350.0435; Found 350.0436.



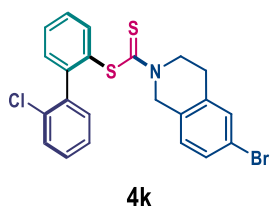
Compound, **4h**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 80% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.52 (d, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 7.1$ Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.13 (m, 3H), 4.60 – 3.90 (m, 4H), 2.67 – 2.07 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.8, 145.0, 139.5, 138.6, 133.3, 131.4, 130.84, 130.79, 130.6, 129.0, 128.9 (2×C), 126.0, 54.5, 54.1, 27.0 (2×C). **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₇H₁₆ClNS₃H⁺ 366.0206; Found 366.0208.



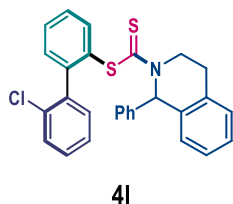
Compound, **4i**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 84% (61 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.58 – 7.54 (m, 1H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 1H), 7.38 – 7.34 (m, 2H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.26 – 7.16 (m, 2H), 4.49 – 4.30 (m, 1H), 4.01 – 3.83 (m, 2H), 3.75 – 3.24 (m, 4H), 3.23 – 3.02 (m, 1H), 2.03 – 1.67 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 197.5, 196.9, 145.12, 145.09, 139.7, 139.6, 138.79, 138.75, 133.4, 131.6, 131.5, 130.88, 130.85, 130.7, 129.04, 128.97, 128.90, 128.88, 128.8, 126.1, 70.1, 69.8, 69.5, 69.3, 58.6, 56.4, 53.7, 51.3, 27.8, 27.0. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₈H₁₈ClNOS₂H⁺ 364.0591; Found 364.0598.



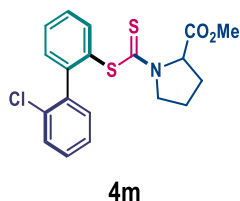
Compound, **4j**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 82% (65 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.60 (d, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.37 – 7.29 (m, 3H), 7.24 – 7.01 (m, 6H), 5.25 – 4.76 (m, 2H), 4.26 – 3.90 (m, 2H), 2.97 – 2.73 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.5, 144.9, 139.5, 138.6, 135.3, 133.8, 133.2, 132.0, 131.3, 130.8, 130.4, 130.2, 129.6, 129.5, 129.0, 128.9, 128.8, 127.9, 127.4, 127.2, 126.8, 126.6, 126.1, 53.9, 52.2, 50.0, 48.7, 31.6, 29.1. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₂H₁₈ClNS₂H⁺ 396.0642; Found 396.0652.



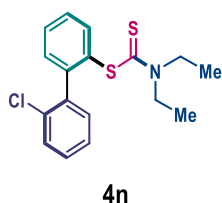
Compound, **4k**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 80% (76 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.64 (d, $J = 7.5$ Hz, 1H), 7.59 – 7.48 (m, 2H), 7.42 – 7.31 (m, 5H), 7.26 – 6.94 (m, 3H), 5.14 – 4.81 (m, 2H), 4.35 – 3.94 (m, 2H), 2.99 – 2.75 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.8, 144.9, 139.4, 138.6, 138.5, 133.2, 131.3, 130.9, 130.5, 129.9, 129.8, 128.93, 128.85, 128.8, 128.3, 126.6, 126.1, 120.8, 53.3, 51.8, 49.4, 48.2, 31.6, 28.8. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₂H₁₇Br⁸¹ClNS₂H⁺ 475.9747; Found 475.9742.



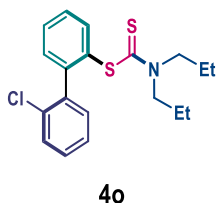
Compound, **4l**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 68% (1.5:1 dr) (64 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.96 – 7.88 (m, 1.51H), 7.73 – 7.69 (m, 1.20H), 7.63 – 7.47 (m, 7.88H), 7.45 – 7.11 (m, 28.33H), 7.04 – 6.96 (m, 2.12H), 6.91 – 6.78 (m, 2H), 6.75 – 6.68 (m, 1.46H), 5.00 – 4.83 (m, 1H), 4.22 – 4.06 (m, 1.46H), 3.61 – 3.41 (m, 2.44H), 3.12 – 2.90 (m, 2.13H), 2.74 – 2.53 (m, 3.04H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 197.34, 197.29, 196.2, 195.9, 145.2, 144.9, 140.5, 139.9, 139.6, 138.9, 138.8, 138.7, 135.3, 134.6, 133.20, 133.15, 131.5, 131.4, 131.3, 130.9, 130.8, 130.7, 130.5, 129.0, 128.92, 128.87, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 127.6, 127.53, 127.47, 126.6, 126.4, 126.0, 65.6, 64.5, 64.3, 64.2, 47.0, 45.8, 45.2, 28.5, 28.2, 27.7. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₈H₂₂ClNS₂H⁺ 472.0955; Found 472.0955.



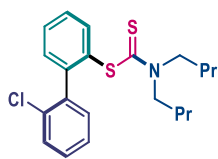
Compound, **4m**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 76% (3:1 dr) (60 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.58 – 7.52 (m, 4.77H), 7.49 – 7.26 (m, 18.52H), 7.24 – 7.11 (m, 8.46H), 4.88 – 4.78 (m, 3.05H), 4.64 – 4.40 (m, 1H), 3.97 – 3.56 (m, 18.46H), 3.48 – 3.39 (m, 2.61H), 2.39 – 1.75 (m, 15.49H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.13, 195.10, 194.4, 171.1, 170.9, 170.8, 170.5, 144.8, 144.7, 139.6, 139.3, 138.7, 138.6, 138.5, 138.4, 133.4, 133.1, 133.0, 132.9, 131.6, 131.4, 131.0, 130.74, 130.69, 130.6, 130.4, 130.3, 128.99, 128.95, 128.9, 128.82, 128.76, 128.7, 126.4, 126.20, 126.18, 126.1, 66.4, 66.2, 63.3, 62.8, 55.4, 55.2, 52.9, 52.6, 52.4, 52.3, 51.5, 51.4, 31.8, 31.5, 29.32, 29.27, 24.8, 22.6, 22.5. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₈ClNO₂S₂H⁺ 392.0540; Found 392.0546.



Compound, **4n**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 72% (48 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.65 – 7.45 (m, 3H), 7.43 – 7.37 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.28 (m, 1H), 7.24 – 7.19 (m, 1H), 4.01 – 3.86 (m, 2H), 3.73 – 3.49 (m, 2H), 1.35 – 1.05 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.6, 145.0, 139.7, 138.9, 133.3, 131.4, 131.3, 130.8, 130.4, 128.9, 128.84, 128.80, 126.1, 49.8, 47.4, 12.6, 11.7. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₇H₁₈ClNS₂H⁺ 336.0642; Found 336.0647.

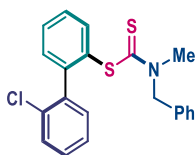


Compound, **4o**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 74% (54 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.63 (d, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.51 – 7.47 (m, 1H), 7.43 – 7.33 (m, 3H), 7.30 – 7.18 (m, 2H), 3.96 – 3.38 (m, 4H), 1.80 – 1.41 (m, 4H), 0.97 – 0.79 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.2, 145.0, 139.7, 138.9, 133.3, 131.40, 131.35, 130.8, 130.4, 128.82, 128.78 (2×C), 126.1, 56.9, 54.8, 20.9, 19.7, 11.3, 11.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₂₂ClNS₂H⁺ 364.0955; Found 364.0957.



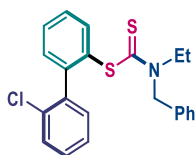
4p

Compound, **4p**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 83% (65 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.70 – 7.62 (m, 1H), 7.57 – 7.47 (m, 2H), 7.42 – 7.28 (m, 3H), 7.22 – 7.13 (m, 2H), 3.96 – 3.37 (m, 4H), 1.73 – 1.16 (m, 8H), 0.97 – 0.86 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.9, 145.1, 139.7, 138.9, 133.3, 131.4, 131.3, 130.7, 130.4, 128.81 (2×C), 128.79, 126.1, 55.1, 53.0, 29.5, 28.5, 20.1, 20.0, 14.0, 13.8. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₁H₂₆ClNS₂H⁺ 392.1268; Found 392.1266.



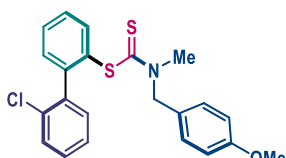
4q

Compound, **4q**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 70% (56 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.57 – 7.14 (m, 11H), 6.99 – 6.83 (m, 2H), 5.44 – 4.52 (m, 2H), 3.20 – 3.02 (m, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 198.9, 197.5, 145.2, 145.1, 139.6, 138.8, 138.6, 135.6, 134.7, 133.4, 131.5, 131.4, 130.9, 130.6, 128.9, 128.8, 128.0, 127.7, 127.6, 127.3, 126.2, 126.1, 59.6, 58.2, 43.2, 39.4. **HRMS (ESI/TOF-Q) m/z**: [M+Na]⁺ Calculated for C₂₁H₁₈ClNS₂Na⁺ 406.0461; Found 406.0465.



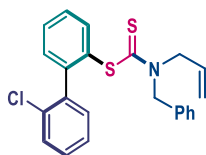
4r

Compound, **4r**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 75% (60 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.54 – 7.09 (m, 11H), 6.96 – 6.82 (m, 2H), 5.28 – 4.44 (m, 2H), 3.83 – 3.60 (m, 1H), 3.45 – 3.36 (m, 1H), 0.99 – 0.90 (m, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 198.1, 196.9, 145.1, 139.7, 138.8, 135.9, 133.3, 131.5, 131.2, 130.8, 130.6, 128.91, 128.87, 128.8, 128.6, 127.6, 127.3, 126.1, 57.0, 55.4, 49.4, 46.8, 12.2, 11.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₂H₂₀ClNS₂H⁺ 398.0798; Found 398.0791.



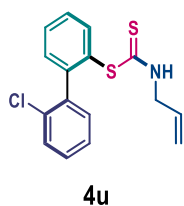
4s

Compound, **4s**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 78% (65 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.70 – 6.78 (m, 12H), 5.42 – 4.55 (m, 2H), 3.81 (s, 3H), 3.28 – 3.10 (m, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 198.6, 197.2, 159.4, 159.3, 145.2, 145.1, 139.8, 139.7, 138.9, 138.7, 133.9, 133.4, 131.7, 131.5, 131.4, 130.9, 130.6, 130.08, 130.06, 129.7, 129.58, 129.55, 129.1, 129.0, 128.9, 128.8, 127.5, 127.2, 126.8, 126.7, 126.6, 126.3, 126.1, 114.3, 114.2, 59.1, 57.7, 55.4, 43.0, 39.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₂H₂₀ClNOS₂H⁺ 414.0748; Found 414.0754.

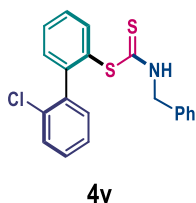


4t

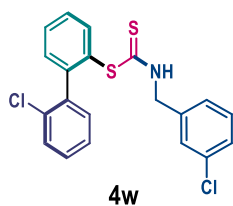
Compound, **4t**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 70% (57 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.68 – 7.28 (m, 11H), 7.20 – 6.98 (m, 2H), 5.79 – 5.57 (m, 1H), 5.37 – 4.90 (m, 3H), 4.95 – 4.31 (m, 2H), 4.17 – 4.03 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 199.1, 198.3, 145.2, 139.7, 138.8, 135.7, 134.8, 133.4, 131.7, 131.5, 131.4, 131.2, 130.9, 130.7, 130.2, 130.1, 129.7, 129.6, 129.0, 128.94, 128.91, 128.7, 127.8, 127.7, 127.4, 126.7, 126.2, 126.1, 118.6, 118.4, 56.7, 56.2, 54.9, 53.8. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₃H₂₀ClNS₂H⁺ 410.0798; Found 410.0797.



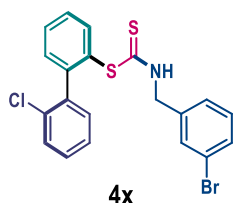
Compound, **4u**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 76% (49 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.73 (d, $J = 7.5$ Hz, 1H), 7.62 – 7.58 (m, 1H), 7.55 – 7.51 (m, 1H), 7.47 – 7.43 (m, 2H), 7.35 – 7.28 (m, 2H), 7.20 (d, $J = 7.1$ Hz, 1H), 6.67 (s, 1H), 5.78 – 5.69 (m, 1H), 5.12 (d, $J = 10.3$ Hz, 1H), 5.05 (d, $J = 17.2$ Hz, 1H), 4.32 – 4.25 (m, 1H), 4.13 – 4.06 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 194.7, 144.8, 138.3, 137.1, 132.9, 132.4, 131.7, 131.4 (2 \times C), 129.9, 129.8, 129.7, 128.4, 126.8, 118.1, 48.6. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₆H₁₄ClNS₂H⁺ 320.0329; Found 320.0332.



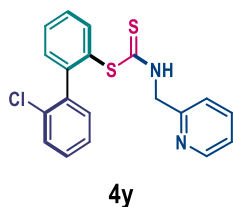
Compound, **4v**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 79% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.65 (d, $J = 7.5$ Hz, 1H), 7.50 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.18 (m, 5H), 7.07 – 7.01 (m, 3H), 6.79 (s, 1H), 4.86 (dd, $J = 15.0, 6.1$ Hz, 1H), 4.57 (dd, $J = 14.9, 5.0$ Hz, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 194.9, 144.7, 138.3, 137.1, 136.0, 132.9, 132.3, 131.4, 131.3, 129.8, 129.69, 129.66, 128.9, 128.1, 127.8, 126.7, 125.6, 50.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₆ClNS₂H⁺ 370.0485; Found 370.0485.



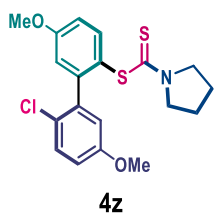
Compound, **4w**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 71% (57 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.73 (d, $J = 7.6$ Hz, 1H), 7.60 – 7.55 (m, 1H), 7.54 – 7.49 (m, 1H), 7.43 – 7.41 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.20 (m, 2H), 7.15 – 7.13 (m, 1H), 7.09 (s, 1H), 7.01 (d, $J = 7.0$ Hz, 1H), 6.88 (s, 1H), 4.90 – 4.85 (m, 1H), 4.70 – 4.62 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.4, 144.7, 138.2, 138.1, 137.1, 134.7, 132.8, 132.4, 131.5, 131.3, 130.1, 130.0, 129.8, 129.7, 128.22, 128.19, 127.8, 126.8, 125.9, 49.3. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₅Cl₂NS₂H⁺ 404.0096; Found 404.0095.



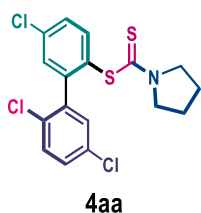
Compound, **4x**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 73% (65 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.59 – 7.57 (m, 1H), 7.47 – 7.35 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.14 (m, 2H), 7.14 – 7.10 (m, 2H), 7.04 – 6.98 (m, 2H), 6.91 (d, $J = 7.7$ Hz, 1H), 6.75 – 6.72 (m, 1H), 4.74 – 4.69 (m, 1H), 4.54 – 4.46 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.4, 144.7, 138.4, 138.1, 137.1, 132.8, 132.4, 131.5, 131.3, 131.1, 130.6, 130.4, 130.0, 129.8, 129.7, 128.2, 126.8, 126.4, 122.8, 49.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₅BrClNS₂H⁺ 447.9591; Found 447.9591.



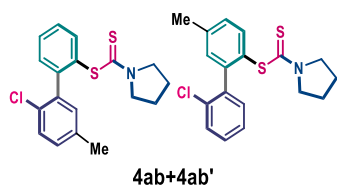
Compound, **4y**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 89% (66 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 8.36 (s, 1H), 8.24 (d, $J = 4.8$ Hz, 1H), 7.73 (d, $J = 7.5$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.7$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.24 – 7.22 (m, 1H), 7.18 – 7.11 (m, 4H), 4.83 – 4.77 (m, 1H), 4.72 – 4.67 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 194.7, 154.0, 148.7, 145.0, 138.8, 137.3, 137.0, 133.3, 131.9, 131.2, 130.9, 129.8, 129.6, 129.5, 128.6, 126.6, 122.7, 122.1, 50.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₅ClN₂S₂H⁺ 371.0438; Found 371.0446.



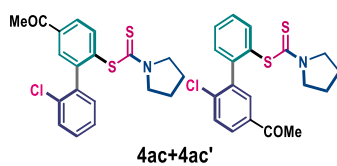
Compound, **4z**: pale yellow sticky liquid; eluent (4% ethyl acetate in hexane). **Yield**: 69% (45 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.51 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.09 (d, *J* = 3.0 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.88 (d, *J* = 2.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.86 (s, 3H), 3.82 – 3.76 (m, 2H), 3.73 (s, 3H), 3.68 – 3.61 (m, 1H), 3.50 – 3.44 (m, 1H), 2.07 – 1.97 (m, 2H), 1.97 – 1.89 (m, 2H). **¹³C NMR (126 MHz, Chloroform-*d*)** δ : 194.2, 161.1, 157.6, 146.5, 140.4, 140.1, 129.6, 124.4, 121.6, 116.3, 116.2, 115.5, 114.8, 55.9, 55.5, 55.3, 51.2, 26.3, 24.5. **HRMS (ESI/TOF-Q) *m/z***: [M+H]⁺ Calculated for C₁₉H₂₀ClNO₂S₂H⁺ 394.0697; Found 394.0696.



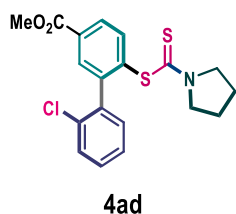
Compound, **4aa**: pale yellow sticky liquid; eluent (4% ethyl acetate in hexane). **Yield**: 78% (50 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.56 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 3.82 (t, *J* = 7.2 Hz, 2H), 3.65 – 3.59 (m, 1H), 3.48 – 3.42 (m, 1H), 2.04 – 1.90 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 191.5, 145.0, 140.0, 139.9, 136.7, 132.2, 131.8, 131.2, 130.7, 130.1, 129.6, 129.5, 129.4, 55.3, 51.4, 26.3, 24.5. **HRMS (ESI/TOF-Q) *m/z***: [M+H]⁺ Calculated for C₁₇H₁₄Cl₃NS₂H⁺ 401.9706; Found 401.9702.



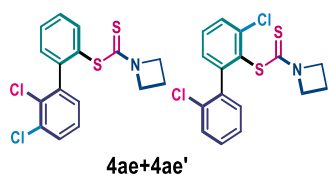
Compound, **4ab+4ab'**: pale yellow sticky liquid; eluent (3% ethyl acetate in hexane). **Yield**: 74% (2:1 rr) (52 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.63 – 7.61 (m, 2H), 7.53 – 7.38 (m, 7H), 7.31 – 7.23 (m, 9H), 7.16 – 7.12 (m, 1H), 7.08 – 7.05 (m, 2H), 3.86 – 3.79 (m, 3H), 3.78 – 3.71 (m, 3H), 3.64 – 3.58 (m, 3H), 3.47 – 3.39 (m, 3H), 2.42 (s, 3H), 2.28 (s, 6H), 2.02 – 1.85 (m, 12H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 193.2, 192.7, 144.9, 144.7, 140.6, 139.8, 139.3, 138.5, 138.4, 135.9, 133.3, 132.1, 131.6, 131.5, 131.0, 130.7, 130.3, 130.2, 129.7, 129.6, 128.8, 128.6, 128.5, 127.5, 126.2, 55.1, 55.1, 51.3, 51.2, 26.2, 24.4, 24.4, 21.6, 20.9. **HRMS (ESI/TOF-Q) *m/z***: [M+H]⁺ Calculated for C₁₈H₁₈CINS₂H⁺ 348.0642; Found 348.0640.



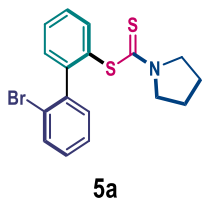
Compound, **4ac+4ac'**: pale yellow sticky liquid; eluent (3% ethyl acetate in hexane). **Yield**: 73% (6:1 rr) (54 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 8.12 (d, *J* = 2.2 Hz, 1H), 8.03 (dd, *J* = 8.1, 2.0 Hz, 6H), 7.93 – 7.90 (m, 7H), 7.75 (d, *J* = 8.1 Hz, 6H), 7.65 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.54 – 7.50 (m, 2H), 7.45 – 7.42 (m, 12H), 7.38 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.43 – 7.25 (m, 12H), 3.86 – 3.70 (m, 14H), 3.67 – 3.60 (m, 7H), 3.49 – 3.39 (m, 7H), 2.64 (s, 18H), 2.53 (s, 3H), 2.09 – 1.87 (m, 28H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 197.4, 191.2, 145.0, 138.9, 138.9, 138.8, 138.1, 136.6, 133.4, 132.4, 131.5, 130.8, 130.6, 129.5, 129.4, 129.4, 129.1, 128.3, 128.2, 126.5, 55.2, 55.2, 51.5, 51.3, 26.9, 26.3, 24.5, 24.5. **HRMS (ESI/TOF-Q) *m/z***: [M+H]⁺ Calculated for C₁₉H₁₈CINOS₂H⁺ 376.0591; Found 376.0587.



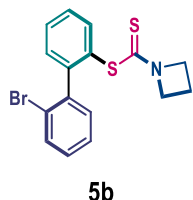
Compound, **4ad**: pale yellow sticky liquid; eluent (3% ethyl acetate in hexane). **Yield**: 71% (>20:1 rr) (55 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 8.12 (dd, *J* = 8.1, 1.9 Hz, 1H), 8.00 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.33 – 7.24 (m, 2H), 3.92 (s, 3H), 3.85 – 3.72 (m, 2H), 3.67 – 3.60 (m, 1H), 3.49 – 3.42 (m, 1H), 2.07 – 1.97 (m, 2H), 1.96 – 1.88 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 191.3, 166.5, 144.9, 138.9, 138.6, 136.4, 133.4, 131.9, 131.7, 131.5, 129.6, 129.3, 129.0, 126.4, 55.2, 52.5, 51.5, 26.3, 24.5. **HRMS (ESI/TOF-Q) *m/z***: [M+H]⁺ Calculated for C₁₉H₁₈CINO₂S₂H⁺ 392.0540; Found 392.0543.



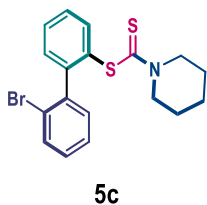
Compound, **4ae+4ae'**: pale yellow sticky liquid; eluent (3% ethyl acetate in hexane). **Yield:** 72% (1:1) (45 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.64 – 7.41 (m, 7H), 7.35 – 7.28 (m, 4H), 7.24 – 7.18 (m, 3H), 4.30 – 4.11 (m, 6H), 4.02 – 3.93 (m, 2H), 2.37 – 2.21 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 193.6, 191.4, 147.6, 144.8, 141.7, 141.6, 139.6, 138.6, 133.2, 132.7, 131.9, 131.3, 131.2, 130.6, 130.5, 130.1, 129.9, 129.81, 129.78, 129.7, 129.32, 129.28, 129.2, 129.0, 126.9, 126.4, 54.9 (2×C), 54.1, 54.0, 15.1, 15.0. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₆H₁₃Cl₂NS₂H⁺ 353.9939; Found 353.9947.



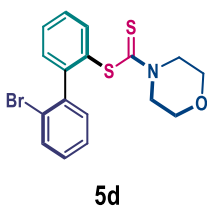
Compound, **5a**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield:** 69% (52 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.61 – 7.52 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.0, 1H), 7.24 – 7.16 (m, 2H), 7.14 – 7.07 (m, 1H), 3.79 – 3.65 (m, 2H), 3.58 – 3.52 (m, 1H), 3.39 – 3.32 (m, 1H), 1.95 – 1.80 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 192.6, 146.5, 141.7, 138.6, 132.0, 131.3, 130.74, 130.70, 130.3, 129.1, 128.8, 126.8, 123.8, 55.1, 51.3, 26.3, 24.4. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₇H₁₆Br⁸¹NS₂H⁺ 379.9980; Found 379.9976.



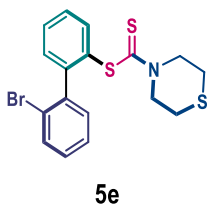
Compound, **5b**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield:** 67% (49 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.68 – 7.61 (m, 2H), 7.58 – 7.52 (m, 1H), 7.50 – 7.46 (m, 1H), 7.41 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.24 – 7.20 (m, 1H), 4.24 – 4.07 (m, 3H), 3.97 – 3.90 (m, 1H), 2.43 – 2.18 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 193.7, 146.6, 141.5, 138.4, 132.1, 131.4, 130.7, 130.4, 129.9, 129.2, 128.9, 126.9, 123.8, 54.8, 54.0, 15.1. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₆H₁₄BrNS₂H⁺ 363.9824; Found 363.9829.



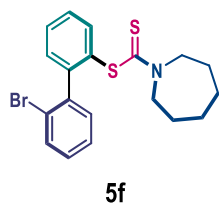
Compound, **5c**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield:** 71% (56 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.55 (t, *J* = 8.3 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.45 – 7.30 (m, 2H), 7.28 – 7.20 (m, 2H), 7.16 – 7.09 (m, 1H), 4.21 – 3.64 (m, 4H), 1.65 – 1.44 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 195.5, 146.6, 141.7, 138.7, 132.0, 131.4, 131.2, 130.7, 130.3, 129.0, 128.8, 126.7, 123.8, 53.2, 52.4, 25.8, 25.6, 24.3. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₈H₁₈BrNS₂H⁺ 392.0137; Found 392.0140.



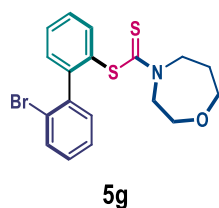
Compound, **5d**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield:** 65% (51 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.65 – 7.53 (m, 2H), 7.51 – 7.47 (m, 1H), 7.45 – 7.39 (m, 1H), 7.34 – 7.30 (m, 1H), 7.26 – 7.19 (m, 2H), 7.16 – 7.09 (m, 1H), 3.81 – 3.31 (m, 8H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 197.4, 146.6, 141.5, 138.6, 132.0, 131.3, 130.8, 130.60, 130.57, 129.2, 128.9, 126.7, 123.8, 66.3, 51.5. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₇H₁₆BrNOS₂H⁺ 393.9929; Found 393.9932.



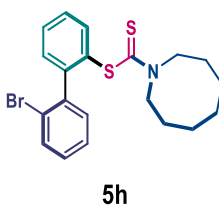
Compound, **5e**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield:** 68% (56 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.55 – 7.48 (m, 3H), 7.45 – 7.40 (m, 1H), 7.34 – 7.31 (m, 1H), 7.26 – 7.20 (m, 2H), 7.18 – 7.13 (m, 1H), 4.63 – 3.91 (m, 4H), 2.68 – 2.09 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.8, 146.6, 141.6, 138.7, 132.3, 131.3, 130.8, 130.73, 130.69, 129.2, 128.9, 126.6, 123.9, 54.7, 54.4, 27.1 (2×C). **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₇H₁₆BrNS₃H⁺ 409.9701; Found 409.9705.



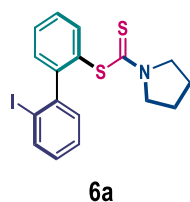
Compound, **5f**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 72% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.54 (t, $J = 8.0$ Hz, 2H), 7.48 (dd, $J = 7.5$, 1.4 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 (dd, $J = 7.5$, 1.7 Hz, 1H), 7.25 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 4.26 – 4.20 (m, 1H), 3.83 – 3.77 (m, 1H), 3.74 – 3.67 (m, 1H), 3.54 – 3.48 (m, 1H), 1.81 – 1.50 (m, 3H), 1.49 – 1.16 (m, 5H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.1, 146.7, 141.8, 138.9, 131.9, 131.4, 131.1, 130.7, 130.4, 129.0, 128.8, 126.7, 123.8, 55.8, 53.4, 27.2, 26.4 (2 \times C), 26.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₂₀BrNS₂H⁺ 406.0293; Found 406.0295.



Compound, **5g**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 67% (55 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.63 – 7.48 (m, 4H), 7.43 – 7.40 (m, 1H), 7.34 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 4.55 – 4.36 (m, 1H), 4.07 – 3.87 (m, 2H), 3.81 – 3.06 (m, 5H), 2.07 – 1.74 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 197.4, 196.8, 146.74, 146.72, 141.7, 141.6, 138.79, 138.76, 132.0, 131.9, 131.5, 131.4, 130.8, 130.71, 130.68, 129.2, 129.1, 128.9, 126.7, 123.9, 70.1, 69.8, 69.6, 69.3, 58.6, 56.4, 53.7, 51.3, 27.8, 27.0. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₈BrNOS₂H⁺ 408.0086; Found 408.0088.

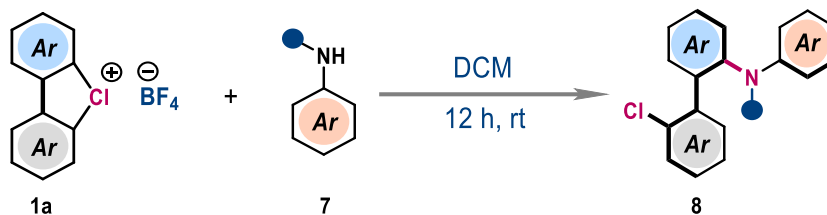


Compound, **5h**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 68% (57 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.62 – 7.58 (m, 2H), 7.55 (dd, $J = 7.4$, 1.4 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.44 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.33 (dd, $J = 7.6$, 1.5 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.19 – 7.15 (m, 1H), 4.29 – 4.23 (m, 1H), 3.90 – 3.84 (m, 1H), 3.74 – 3.68 (m, 1H), 3.56 – 3.50 (m, 1H), 1.95 – 1.52 (m, 5H), 1.45 – 1.21 (m, 5H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.1, 146.8, 141.7, 139.0, 131.9, 131.4, 131.0, 130.7, 130.4, 129.0, 128.8, 126.7, 123.8, 56.6, 54.3, 26.8, 26.3, 25.34, 25.31, 25.2. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₂₂Br⁸¹NS₂H⁺ 422.0450; Found 422.0451.



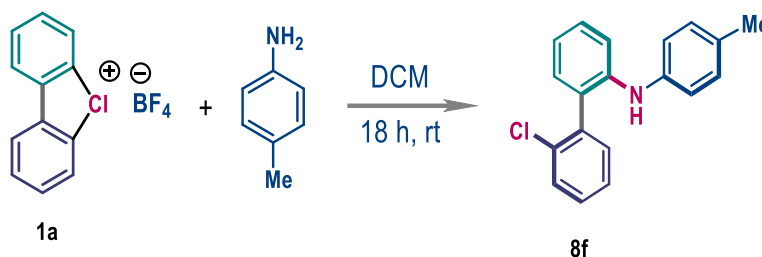
Compound, **6a**: pale yellow sticky liquid; eluent (2% ethyl acetate in hexane). **Yield**: 18% (15 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.76 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.44 – 7.30 (m, 2H), 7.32 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.14 (d, $J = 6.9$ Hz, 1H), 6.92 – 6.88 (m, 1H), 3.74 – 3.60 (m, 2H), 3.53 – 3.47 (m, 1H), 3.33 – 3.27 (m, 1H), 1.94 – 1.74 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 192.5, 149.6, 145.8, 138.7, 138.3, 130.7, 130.6, 130.40, 130.35, 129.1, 128.9, 127.6, 100.4, 55.1, 51.3, 26.3, 24.5. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₇H₁₆INS₂H⁺ 425.9842; Found 425.9844.

General procedure for the synthesis of compounds 8a-8p:

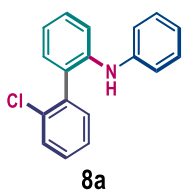


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv) and corresponding aniline **7** (0.2 mmol, 1.0 equiv) under N_2 atmosphere. Then, dry DCM (2 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 12 h. After completion of the reaction (TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **8**.

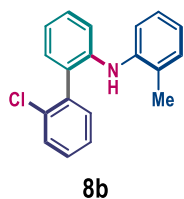
Gram scale synthesis of compound 8f:



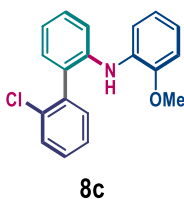
A 100 mL oven dried round bottom flask equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (3.64 mmol, 1.0 equiv) and 4-methylaniline (1.0 equiv) under N_2 atmosphere. Then, dry DCM (20 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 18 h. After completion of the reaction (TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **8f** (0.77 g, 72%).



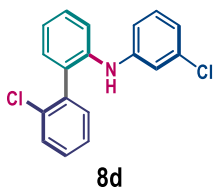
Compound, **8a**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 69% (39 mg); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ : 7.43 – 7.41 (m, 1H), 7.30 – 7.22 (m, 4H), 7.20 – 7.09 (m, 4H), 6.96 – 6.90 (m, 3H), 6.84 (t, $J = 7.4$ Hz, 1H), 5.24 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ : 143.2, 141.2, 137.9, 134.3, 132.2, 131.0, 130.1, 129.4, 129.3, 129.04, 128.99, 127.4, 121.5, 120.7, 119.0, 117.0. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{14}\text{ClNH}^+$ 280.0888; Found 280.0886.



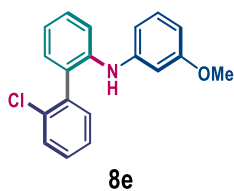
Compound, **8b**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 76% (45 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.54 – 7.50 (m, 1H), 7.40 – 7.29 (m, 3H), 7.27 – 7.23 (m, 2H), 7.19 – 7.17 (m, 1H), 7.15 – 7.07 (m, 3H), 6.98 – 6.90 (m, 2H), 5.11 (s, 1H), 2.08 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 141.9, 141.1, 138.0, 134.4, 132.1, 131.0, 130.7, 130.0, 129.5, 129.4, 129.0, 128.3, 127.4, 126.8, 122.5, 120.1, 119.9, 116.2, 17.8. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₆ClNH⁺ 294.1044; Found 294.1039.



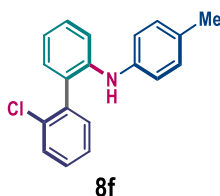
Compound, **8c**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 72% (45 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.53 – 7.47 (m, 2H), 7.37 – 7.27 (m, 5H), 7.23 – 7.21 (m, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.89 – 6.80 (m, 3H), 5.81 (s, 1H), 3.73 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 149.0, 140.8, 138.0, 134.3, 133.2, 132.1, 131.0, 130.1, 129.9, 129.1, 128.9, 127.1, 120.9 (2×C), 120.3, 118.0, 115.7, 111.0, 55.8. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₆ClNOH⁺ 310.0993; Found 310.0995.



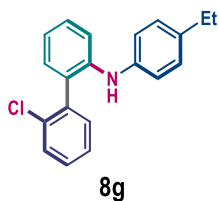
Compound, **8d**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 62% (39 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.51 – 7.48 (m, 1H), 7.40 – 7.28 (m, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.13 – 7.06 (m, 1H), 6.98 (s, 1H), 6.85 – 6.83 (m, 2H), 5.35 (s, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 145.0, 140.0, 137.7, 135.0, 134.1, 132.0, 131.2, 130.33, 130.30, 130.1, 129.4, 129.1, 127.4, 122.0, 120.9, 118.6, 117.6, 116.0. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₈H₁₃Cl₂NH⁺ 314.0498; Found 314.0508.



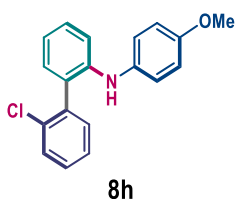
Compound, **8e**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 63% (39 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.51 – 7.49 (m, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.29 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.59 (s, 2H), 6.48 (d, *J* = 8.5 Hz, 1H), 5.32 (s, 1H), 3.76 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 160.8, 144.7, 140.9, 137.8, 134.3, 132.1, 131.0, 130.09, 130.07, 129.4, 129.3, 129.0, 127.4, 121.0, 117.8, 111.3, 106.7, 104.4, 55.4. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₆ClNOH⁺ 310.0993; Found 310.0995.



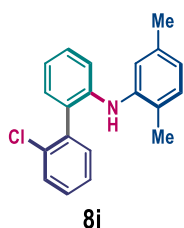
Compound, **8f**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 78% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.50 – 7.47 (m, 1H), 7.37 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.96 – 6.91 (m, 3H), 5.21 (s, 1H), 2.28 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 142.0, 140.4, 137.9, 134.3, 132.2, 131.5, 130.9, 130.1, 129.9, 129.3, 129.0, 128.1, 127.4, 120.1, 119.9, 116.0, 20.8. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₆ClNH⁺ 294.1044; Found 294.1039.



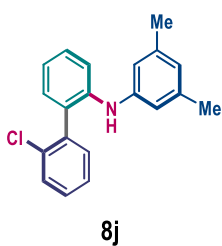
Compound, **8g**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 80% (49 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.53 – 7.51 (m, 1H), 7.37 – 7.28 (m, 5H), 7.17 (d, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 8.1$ Hz, 2H), 7.02 – 6.95 (m, 3H), 5.26 (s, 1H), 2.61 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 141.92, 140.57, 138.02, 137.91, 134.35, 132.22, 130.89, 130.08, 129.28, 128.98, 128.71, 128.17, 127.39, 120.06, 119.91, 116.02, 28.31, 15.86. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₈ClNH⁺ 308.1201; Found 308.1204.



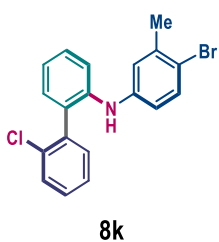
Compound, **8h**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 76% (47 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.53 – 7.51 (m, 1H), 7.41 – 7.31 (m, 3H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.15 – 7.05 (m, 4H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 2H), 5.14 (s, 1H), 3.79 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 155.81, 143.19, 137.94, 135.76, 134.35, 132.29, 130.75, 130.12, 129.30, 129.05, 127.47, 127.07, 123.59, 119.11, 114.75, 114.56, 55.69. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₆ClNOH⁺ 310.0993; Found 310.0995.



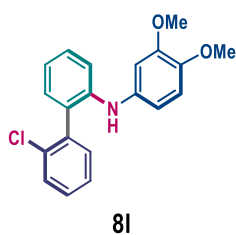
Compound, **8i**: white solid; eluent (1% ethyl acetate in hexane). **Yield**: 79% (49 mg); **MP**: 118 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.54 – 7.50 (m, 1H), 7.40 – 7.31 (m, 3H), 7.30 – 7.28 (m, 1H), 7.19 – 7.17 (m, 1H), 7.08 – 7.02 (m, 3H), 6.96 (t, $J = 7.4$ Hz, 1H), 6.75 (d, $J = 7.5$ Hz, 1H), 5.08 (s, 1H), 2.27 (s, 3H), 2.04 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 142.0, 140.7, 138.0, 136.5, 134.4, 132.1, 130.8, 130.7, 130.0, 129.3, 129.0, 128.1, 127.4, 126.5, 123.4, 120.9, 119.7, 116.1, 21.2, 17.4. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₈ClNH⁺ 308.1201; Found 308.1204.



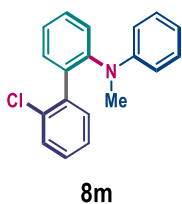
Compound, **8j**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 80% (49 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.52 – 7.50 (m, 1H), 7.39 – 7.28 (m, 5H), 7.18 (dd, $J = 7.6, 1.6$ Hz, 1H), 6.99 (t, $J = 7.3$ Hz, 1H), 6.68 (s, 2H), 6.59 (s, 1H), 5.25 (s, 1H), 2.25 (s, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 143.0, 141.3, 139.1, 137.9, 134.3, 132.2, 131.0, 130.1, 129.3, 129.0, 128.8, 127.4, 123.4, 120.3, 117.0, 116.8, 21.5. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₈ClNH⁺ 308.1201; Found 308.1204.



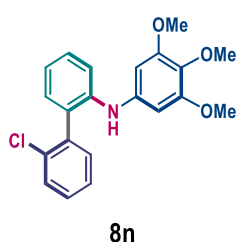
Compound, **8k**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 75% (56 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.51 – 7.48 (m, 1H), 7.34 – 7.29 (m, 6H), 7.20 – 7.18 (m, 1H), 7.05 – 7.01 (m, 1H), 6.88 (d, $J = 2.8$ Hz, 1H), 6.73 (dd, $J = 8.6, 2.7$ Hz, 1H), 5.24 (s, 1H), 2.31 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 142.7, 140.7, 138.7, 137.7, 134.2, 132.9, 132.1, 131.1, 130.1, 129.5, 129.4, 129.1, 127.4, 121.2, 120.8, 117.7, 117.6, 115.9, 23.1. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₅BrClNH⁺ 372.0149; Found 372.0153.



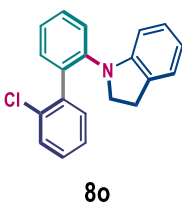
Compound, **8l**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 81% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.53 – 7.51 (m, 1H), 7.40 – 7.33 (m, 3H), 7.28 – 7.23 (m, 1H), 7.16 – 7.13 (m, 2H), 6.94 – 6.90 (m, 1H), 6.79 (d, $J = 8.3$ Hz, 1H), 6.68 – 6.65 (m, 2H), 5.16 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 149.7, 145.2, 142.9, 137.9, 136.3, 134.3, 132.3, 130.8, 130.1, 129.3, 129.1, 127.5, 127.3, 119.4, 115.0, 113.7, 112.2, 106.7, 56.4, 56.0. **HRMS (ESI/TOF-Q) m/z**: [M+Na]⁺ Calculated for C₂₀H₁₈ClNO₂Na⁺ 362.0918; Found 362.0929.



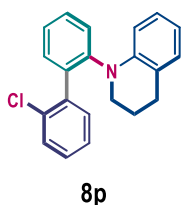
Compound, **8m**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 79% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.43 – 7.39 (m, 3H), 7.34 – 7.28 (m, 2H), 7.20 – 7.10 (m, 5H), 6.72 – 6.68 (m, 1H), 6.65 (d, $J = 8.1$ Hz, 2H), 2.92 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 149.4, 147.0, 138.7, 137.6, 133.2, 132.5, 131.5, 129.7, 129.5, 128.8, 128.7, 128.3, 126.5, 125.4, 117.6, 114.3, 39.4. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₉H₁₆ClNH⁺ 294.1044; Found 294.1039.



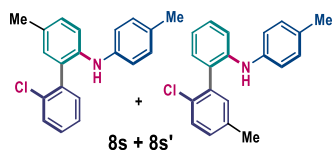
Compound, **8n**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 62% (49 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.53 – 7.50 (m, 1H), 7.37 – 7.27 (m, 5H), 7.18 – 7.16 (m, 1H), 7.00 – 6.95 (m, 1H), 6.29 (s, 2H), 5.20 (s, 1H), 3.80 (s, 3H), 3.79 (s, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 153.9, 141.7, 139.2, 137.8, 134.3, 133.4, 132.2, 131.1, 130.1, 129.4, 129.1, 128.5, 127.5, 120.3, 116.6, 97.7, 61.2, 56.2. **HRMS (ESI/TOF-Q) m/z**: [M+Na]⁺ Calculated for C₂₁H₂₀ClNO₃Na⁺ 392.1024; Found 392.1031.



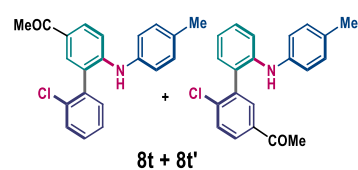
Compound, **8o**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 76% (47 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.56 – 7.54 (m, 1H), 7.45 – 7.32 (m, 4H), 7.27 – 7.23 (m, 3H), 7.07 (d, $J = 7.1$ Hz, 1H), 7.00 (t, $J = 8.2$ Hz, 1H), 6.69 – 6.65 (m, 2H), 3.40 – 3.32 (m, 2H), 2.94 – 2.87 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 149.7, 144.1, 139.4, 135.7, 133.6, 132.0, 131.8, 130.5, 129.7, 129.2, 128.6, 127.0, 126.7, 124.8, 124.5, 123.4, 118.3, 109.0, 54.1, 28.9. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₀H₁₆ClNH⁺ 306.1044; Found 306.1040.



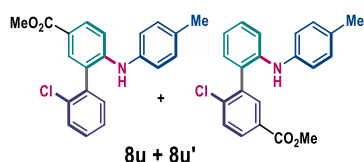
Compound, **8p**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 74% (47 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.44 – 7.36 (m, 4H), 7.32 – 7.28 (m, 1H), 7.25 – 7.14 (m, 3H), 6.94 – 6.89 (m, 2H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.55 (d, $J = 8.2$ Hz, 1H), 3.15 (d, $J = 50.3$ Hz, 2H), 2.72 – 2.66 (m, 2H), 1.77 – 1.60 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 146.4, 145.3, 138.7, 137.8, 132.5, 131.6, 129.7, 129.4, 129.3, 128.7, 128.5, 126.7, 126.51, 126.47, 125.4, 122.8, 117.2, 114.8, 50.6, 27.9, 21.9. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₁H₁₈ClNH⁺ 320.1201; Found 320.1205.



Compound, **8s+8s'**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 72% (2.4:1 rr) (44 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.43 – 7.38 (m, 1H), 7.30 – 7.28 (m, 2.52H), 7.26 – 7.19 (m, 3.96H), 7.18 – 7.12 (m, 2.92H), 7.09 – 6.93 (m, 16.96H), 6.91 – 6.80 (m, 10.22H), 5.17 (s, 2.41H), 5.05 (s, 1H), 2.27 (s, 7.19H), 2.25 (s, 3H), 2.21 (s, 7.21H), 2.19 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 142.0, 141.2, 140.4, 139.2, 138.1, 137.6, 137.3, 132.8, 132.2, 131.5, 131.4, 131.2, 130.8, 130.1, 130.0, 129.90, 129.85, 129.7, 129.6, 129.2, 128.9, 128.2, 127.3, 120.3, 119.8, 119.0, 117.3, 115.7, 21.0, 20.8, 20.8, 20.7. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₂₀H₁₈ClNH⁺ 308.1201; Found 308.1194.

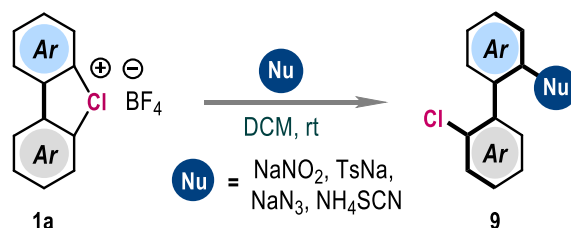


Compound, **8t+8t'**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 70% (2.3:1 rr) (47 mg); **¹H NMR (500 MHz, Chloroform-*d*)** δ : 7.94 – 7.90 (m, 2.02H), 7.87 – 7.84 (m, 2.07H), 7.76 (t, *J* = 1.9 Hz, 2.03H), 7.60 – 7.53 (m, 3.00H), 7.41 – 7.36 (m, 6.54H), 7.31 – 7.26 (m, 2.42H), 7.16 – 7.12 (m, 7.80H), 7.06 – 7.04 (m, 6.38H), 7.00 – 6.93 (m, 3.82H), 5.59 (s, 2.34H), 5.12 (s, 1.00H), 2.57 (s, 3.02H), 2.53 (s, 6.90H), 2.33 (s, 6.92H), 2.28 (s, 3.09H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 196.9, 196.4, 147.2, 142.0, 140.3, 139.7, 138.5, 137.9, 136.7, 136.3, 134.4, 134.2, 132.4, 132.3, 131.9, 131.7, 130.8, 130.4, 130.3, 130.3, 130.2, 130.0, 129.9, 129.5, 128.9, 128.2, 127.8, 125.8, 123.0, 120.3, 120.1, 116.6, 112.4, 26.7, 26.3, 21.0, 20.8. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₂₁H₁₈ClNOH⁺ 336.1150; Found 336.1151.

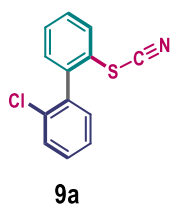


Compound, **8u+8u'**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 75% (2:1) (51 mg); **for major isomer;** **¹H NMR (500 MHz, Chloroform-*d*)** δ : 7.91 – 7.89 (m, 1H), 7.82 – 7.81 (m, 1H), 7.53 – 7.52 (m, 1H), 7.40 – 7.36 (m, 3H), 7.14 – 7.12 (m, 3H), 7.05 – 7.03 (m, 2H), 5.53 (s, 1H), 3.86 (s, 3H), 2.32 (s, 3H). **¹³C NMR (126 MHz, Chloroform-*d*)** δ : 167.1, 146.9, 138.1, 136.7, 134.4, 133.9, 132.7, 132.4, 131.2, 130.3, 130.2, 129.8, 127.7, 125.9, 122.7, 120.2, 112.6, 51.9, 21.0. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₂₁H₁₉ClNO₂H⁺ 352.1099; Found 352.1101. **for minor isomer;** **¹H NMR (400 MHz, Chloroform-*d*)** δ : 8.05 (d, *J* = 2.1 Hz, 1H), 7.98 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.13 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.06 – 7.04 (m, 2H), 6.98 – 6.93 (m, 3H), 5.11 (s, 1H), 3.91 (s, 3H), 2.28 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 166.3, 142.0, 140.1, 139.5, 138.4, 133.4, 131.7, 130.8, 130.3, 130.2, 129.9, 129.5, 129.4, 127.3, 120.2, 120.1, 116.18, 52.5, 20.9. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₂₁H₁₉ClNO₂H⁺ 352.1099; Found 352.1101.

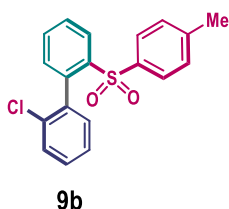
General procedure for the synthesis of compounds 9a-9d:



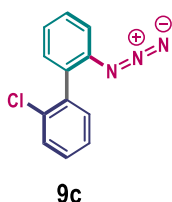
A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv) and corresponding nucleophile (0.2 mmol, 1.0 equiv) under N_2 atmosphere. Then, dry DCM (1.5 mL) was added via syringe. The reaction mixture was allowed to stir at rt. After completion of the reaction (8–18 h, TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **9**.



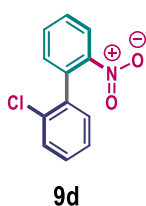
Compound, **9a**: yellow liquid; eluent (1% ethyl acetate in hexane). **Yield**: 91% (45 mg); ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.71 (d, $J = 7.2$ Hz, 1H), 7.42 – 7.36 (m, 3H), 7.33 – 7.26 (m, 2H), 7.22 (d, $J = 6.9$ Hz, 1H), 7.19 – 7.16 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ : 140.3, 137.3, 133.6, 131.3 (2 \times C), 130.43, 130.36, 130.0, 129.9, 129.5, 127.2, 125.1, 110.8. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{13}\text{H}_8\text{ClN}_2\text{S}^+$ 246.0139; Found 246.0140.



Compound, **9b**: yellow liquid; eluent (3% ethyl acetate in hexane). **Yield**: 85% (58 mg); ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.45 – 8.40 (m, 1H), 7.63 – 7.58 (m, 2H), 7.31 – 7.25 (m, 3H), 7.22 – 7.16 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ : 143.9, 140.0, 138.8, 137.5, 136.5, 134.0, 133.1, 132.91, 132.87, 129.6, 129.3, 128.91, 128.86, 128.5, 128.2, 125.7, 21.7. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{19}\text{H}_{15}\text{ClO}_2\text{S}^+$ 343.0554; Found 343.0559.

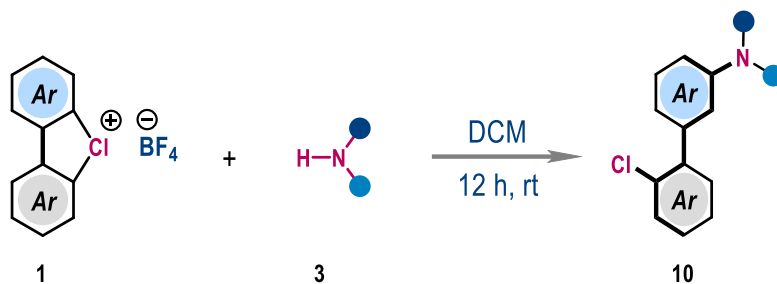


Compound, **9c**: colourless liquid; eluent (1% ethyl acetate in hexane). **Yield**: 90% (41 mg); ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.43 – 7.36 (m, 2H), 7.28 – 7.23 (m, 2H), 7.20 – 7.12 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ : 138.3, 137.3, 133.8, 131.6, 131.5, 131.4, 129.6, 129.5, 129.3, 126.6, 124.7, 118.6. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{12}\text{H}_8\text{ClN}_3\text{H}^+$ 230.0480; Found 230.0482.

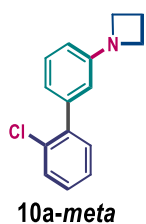


Compound, **9d**: yellow liquid; eluent (2% ethyl acetate in hexane). **Yield**: 88% (41 mg); ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.98 (d, $J = 8.1$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.35 – 7.33 (m, 1H), 7.24 – 7.21 (m, 2H), 7.16 – 7.14 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ : 148.8, 137.3, 134.5, 133.1, 132.9, 132.5, 130.0, 129.6 (2 \times C), 129.1, 127.1, 124.6. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{12}\text{H}_8\text{ClNO}_2\text{H}^+$ 234.0316; Found 234.0322.

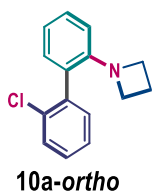
General procedure for the synthesis of compounds 10a-10p:



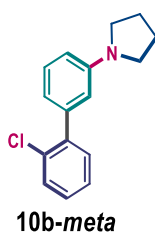
A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1** (0.2 mmol, 1.0 equiv) and corresponding secondary amine **3** (0.3 mmol, 1.5 equiv) under N_2 atmosphere. Then, dry DCM (1.5 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 12 h. After completion of the reaction (TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel chromatography to provide pure product **10**.



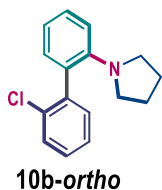
Compound, **10a-meta**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 60% (29 mg); **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ : 7.45 (dd, $J = 7.2, 1.9$ Hz, 1H), 7.35 (dd, $J = 7.3, 2.2$ Hz, 1H), 7.31 – 7.25 (m, 3H), 6.79 (d, $J = 7.5$ Hz, 1H), 6.50 – 6.46 (m, 2H), 3.91 (t, $J = 7.2$ Hz, 4H), 2.37 (p, $J = 7.2$ Hz, 2H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*)** δ : 152.0, 141.3, 140.2, 132.7, 131.5, 130.0, 128.7, 128.4, 126.8, 118.7, 112.6, 110.7, 52.6, 17.2. **HRMS (ESI/TOF-Q) m/z:** $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{15}\text{H}_{14}\text{ClNH}^+$ 244.0888; Found 244.0886.



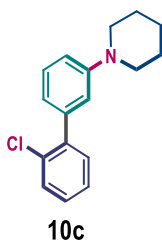
Compound, **10a-ortho**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 20% (9 mg); **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ : 7.46 – 7.41 (m, 1H), 7.36 – 7.33 (m, 1H), 7.29 – 7.23 (m, 3H), 7.04 (dd, $J = 7.5, 1.6$ Hz, 1H), 6.82 (td, $J = 7.4, 1.2$ Hz, 1H), 6.55 (dd, $J = 8.2, 1.2$ Hz, 1H), 3.51 (q, $J = 7.2$ Hz, 2H), 3.41 (q, $J = 7.2$ Hz, 2H), 2.08 (p, $J = 7.2$ Hz, 2H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*)** δ : 145.0, 140.0, 134.3, 132.6, 131.5, 129.4, 128.6, 128.5, 126.3, 125.0, 117.7, 112.8, 53.6, 17.1. **HRMS (ESI/TOF-Q) m/z:** $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{15}\text{H}_{14}\text{ClNH}^+$ 244.0888; Found 244.0886.



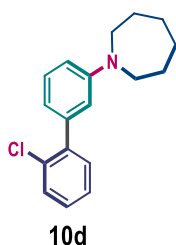
Compound, **10b-meta**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 74% (38 mg); **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ : 7.46 (d, $J = 7.7$ Hz, 1H), 7.39 – 7.37 (m, 1H), 7.30 – 7.26 (m, 3H), 6.71 (d, $J = 7.6$ Hz, 1H), 6.61 – 6.59 (m, 2H), 3.34 – 3.30 (m, 4H), 2.03 – 1.99 (m, 4H). **$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*)** δ : 147.7, 141.7, 140.4, 132.7, 131.5, 129.9, 128.9, 128.3, 126.7, 116.7, 112.8, 111.0, 47.8, 25.6. **HRMS (ESI/TOF-Q) m/z:** $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{16}\text{ClNH}^+$ 258.1044; Found 258.1045.



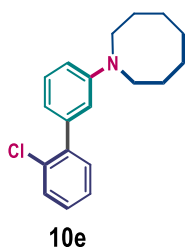
Compound, **10b-ortho**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 9% (5 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.42 – 7.38 (m, 1H), 7.34 – 7.31 (m, 1H), 7.24 – 7.18 (m, 3H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.82 – 6.76 (m, 2H), 2.94 – 2.83 (m, 4H), 1.79 – 1.70 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 147.8, 142.2, 134.0, 132.5, 132.3, 129.3, 128.6, 128.0, 126.3 (2 \times C), 117.0, 114.2, 50.3, 25.8. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₆H₁₆ClNH⁺ 258.1044; Found 258.1045.



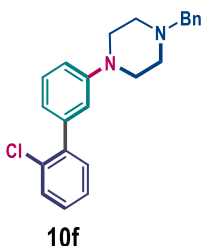
Compound, **10c**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 85% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (d, $J = 7.5$ Hz, 1H), 7.36 (d, $J = 7.4$ Hz, 1H), 7.33 – 7.26 (m, 3H), 7.00 (s, 1H), 6.96 (d, $J = 8.5$ Hz, 1H), 6.89 (d, $J = 7.6$ Hz, 1H), 3.22 – 3.19 (m, 4H), 1.74 – 1.70 (m, 4H), 1.60 – 1.57 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 152.0, 141.3, 140.3, 132.6, 131.5, 130.0, 128.8, 128.4, 126.8, 120.4, 117.9, 115.7, 50.7, 26.0, 24.4. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₇H₁₈ClNH⁺ 272.1201; Found 272.1209.



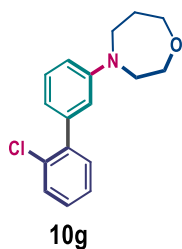
Compound, **10d**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 90% (52 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.48 – 7.46 (m, 1H), 7.39 (d, $J = 7.4$ Hz, 1H), 7.33 – 7.26 (m, 3H), 6.75 – 6.68 (m, 3H), 3.50 – 3.47 (m, 4H), 1.81 – 1.80 (m, 4H), 1.58 (brs, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 148.6, 141.8, 140.5, 132.7, 131.5, 130.0, 129.0, 128.3, 126.8, 116.4, 112.6, 110.6, 49.3, 28.0, 27.3. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₈H₂₀ClNH⁺ 286.1357; Found 286.1363.



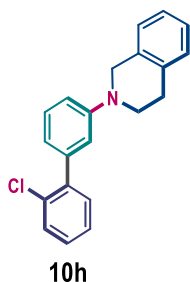
Compound, **10e**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield:** 88% (53 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.44 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 7.3$ Hz, 1H), 7.30 – 7.23 (m, 3H), 6.70 – 6.67 (m, 3H), 3.47 – 3.44 (m, 4H), 1.76 – 1.74 (m, 4H), 1.58 – 1.55 (m, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 148.0, 141.8, 140.4, 132.7, 131.5, 130.0, 128.9, 128.3, 126.8, 116.3, 112.6, 110.5, 50.9, 27.4, 27.3, 27.1. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₁₉H₂₂ClNH⁺ 300.1514; Found 300.1514.



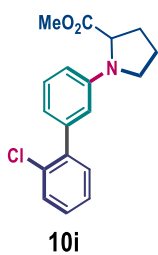
Compound, **10f**: colourless sticky liquid; eluent (3% ethyl acetate in hexane). **Yield:** 82% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.37 – 7.35 (m, 1H), 7.28 – 7.14 (m, 9H), 6.89 (s, 1H), 6.85 – 6.81 (m, 2H), 3.49 (s, 2H), 3.17 – 3.15 (m, 4H), 2.55 – 2.52 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 151.1, 141.1, 140.4, 138.0, 132.6, 131.4, 130.0, 129.4, 128.9, 128.5, 128.4, 127.3, 126.8, 120.8, 117.5, 115.3, 63.2, 53.2, 49.2. **HRMS (ESI/TOF-Q) m/z:** [M+H]⁺ Calculated for C₂₃H₂₃ClN₂H⁺ 363.1623; Found 363.1625.



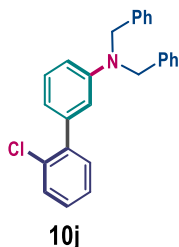
Compound, **10g**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 82% (47 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 7.3$ Hz, 1H), 7.32 – 7.26 (m, 3H), 6.76 – 6.73 (m, 3H), 3.86 – 3.84 (m, 2H), 3.73 – 3.70 (m, 2H), 3.67 – 3.63 (m, 4H), 2.08 – 2.04 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 148.0, 141.4, 140.7, 132.6, 131.4, 130.0, 129.3, 128.5, 126.8, 117.5, 113.3, 111.2, 70.22, 70.16, 52.3, 47.7, 29.3. **HRMS (ESI/TOF-Q) *m/z***: $[M+H]^+$ Calculated for $C_{17}H_{18}ClNOH^+$ 288.1150; Found 288.1155.



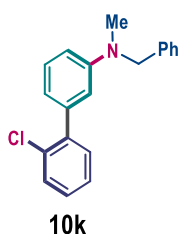
Compound, **10h**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 79% (51 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.48 – 7.36 (m, 4H), 7.26 – 7.19 (m, 3H), 7.13 – 7.09 (m, 3H), 7.05 – 7.01 (m, 2H), 4.22 – 4.13 (m, 2H), 3.12 – 2.96 (m, 2H), 2.47 – 2.44 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 150.8, 140.0, 135.2, 135.0, 133.4, 133.3, 132.1, 132.0, 129.9, 129.0, 128.9, 128.3, 126.6, 126.5, 126.1, 125.7, 122.1, 118.8, 52.7, 50.5, 29.2. **HRMS (ESI/TOF-Q) *m/z***: $[M+H]^+$ Calculated for $C_{21}H_{18}ClNH^+$ 320.1201; Found 320.1203.



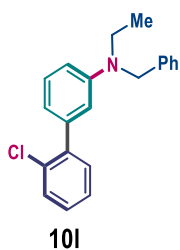
Compound, **10i**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 72% (45 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.45 (dd, $J = 7.4, 1.9$ Hz, 1H), 7.35 (dd, $J = 7.1, 2.2$ Hz, 1H), 7.31 – 7.24 (m, 3H), 6.77 (d, $J = 7.5$ Hz, 1H), 6.61 (s, 1H), 6.57 (dd, $J = 8.2, 2.6$ Hz, 1H), 4.29 (dd, $J = 8.5, 2.1$ Hz, 1H), 3.73 (s, 3H), 3.64 – 3.59 (m, 1H), 3.43 – 3.37 (m, 1H), 2.35 – 2.23 (m, 1H), 2.21 – 2.12 (m, 2H), 2.10 – 2.00 (m, 1H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 175.0, 146.5, 141.4, 140.5, 132.7, 131.5, 130.0, 129.1, 128.4, 126.8, 118.1, 113.3, 111.4, 61.0, 52.3, 48.5, 31.1, 24.0. **HRMS (ESI/TOF-Q) *m/z***: $[M+H]^+$ Calculated for $C_{18}H_{18}ClNO_2H^+$ 316.1099; Found 316.1099.



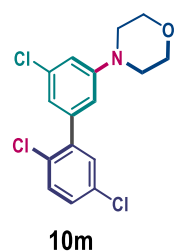
Compound, **10j**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 81% (62 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.40 – 7.29 (m, 8H), 7.25 – 7.07 (m, 7H), 6.81 (s, 1H), 6.75 (d, $J = 6.9$ Hz, 2H), 4.65 (s, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 149.1, 141.2, 140.4, 138.6, 132.6, 131.5, 130.0, 129.0, 128.8, 128.4, 127.0, 126.9, 126.8, 118.1, 114.0, 111.9, 54.3. **HRMS (ESI/TOF-Q) *m/z***: $[M+H]^+$ Calculated for $C_{26}H_{22}ClNH^+$ 384.1514; Found 384.1517.



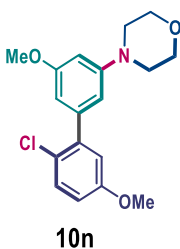
Compound, **10k**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 68% (42 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.43 (dd, $J = 7.2, 2.0$ Hz, 1H), 7.34 – 7.28 (m, 4H), 7.27 – 7.21 (m, 5H), 6.82 (s, 1H), 6.78 – 6.75 (m, 2H), 4.55 (s, 2H), 3.03 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 149.6, 141.5, 140.4, 139.1, 132.7, 131.5, 130.0, 129.0, 128.7, 128.4, 127.03, 126.96, 126.8, 117.9, 113.8, 111.8, 56.9, 38.7. **HRMS (ESI/TOF-Q) *m/z***: $[M+H]^+$ Calculated for $C_{20}H_{18}ClNH^+$ 308.1201; Found 308.1209.



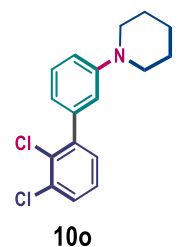
Compound, **10l**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 71% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.40 (d, $J = 7.7$ Hz, 1H), 7.30 – 7.21 (m, 9H), 6.78 (s, 1H), 6.73 (d, $J = 7.8$ Hz, 2H), 4.53 (s, 2H), 3.49 – 3.47 (m, 2H), 1.23 – 1.20 (m, 3H). **¹³C NMR (126 MHz, Chloroform-*d*)** δ : 141.3, 140.4, 132.6, 131.5, 130.0, 129.0, 128.7 (2 \times C), 128.4, 127.0, 126.8, 122.3, 120.2, 117.6, 113.8, 111.8, 54.4, 45.5, 12.3. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₂₁H₂₀ClNH⁺ 322.1357; Found 322.1369.



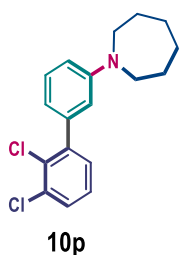
Compound, **10m**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 90% (62 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.42 (d, $J = 8.6$ Hz, 1H), 7.30 – 7.26 (m, 2H), 7.23 (d, $J = 2.6$ Hz, 1H), 7.21 – 7.17 (m, 2H), 3.67 (t, $J = 5.0$ Hz, 4H), 3.54 (brs, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 146.2, 139.7, 134.9, 132.2, 132.0, 131.6, 131.4, 130.18, 130.16, 129.3, 128.7, 118.5, 66.41, 66.39. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₆H₁₄Cl₃NOH⁺ 342.0214; Found 342.0218.



Compound, **10n**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 84% (56 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.45 (d, $J = 8.9$ Hz, 1H), 7.23 (d, $J = 7.1$ Hz, 1H), 6.90 (dd, $J = 8.9, 2.9$ Hz, 1H), 6.82 (d, $J = 3.1$ Hz, 1H), 6.79 – 6.76 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.69 (t, $J = 5.0$ Hz, 4H), 3.50 (brs, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 158.1, 157.8, 141.4, 140.2, 136.3, 129.6, 125.4, 118.2, 116.9, 115.2, 114.8, 114.4, 66.5, 55.7 (2 \times C), 48.1. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₈H₂₀ClNO₃H⁺ 334.1204; Found 334.1205.

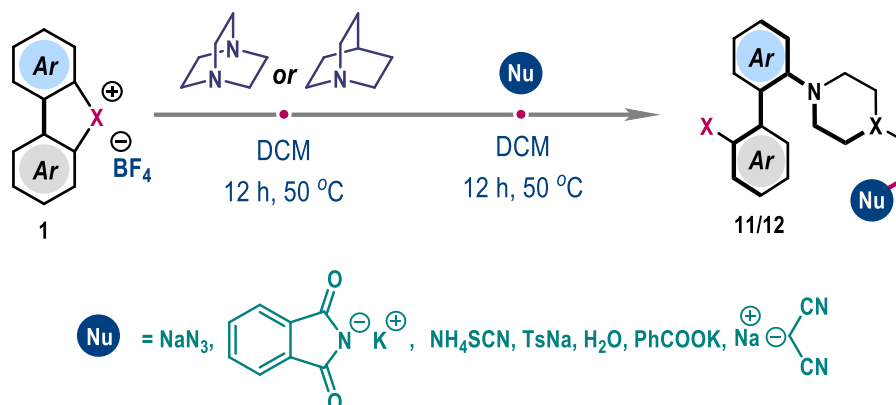


Compound, **10o**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 76% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.44 (dd, $J = 7.2, 2.4$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.26 – 7.20 (m, 2H), 6.98 – 6.94 (m, 2H), 6.84 – 6.82 (m, 1H), 3.20 (t, $J = 5.4$ Hz, 4H), 1.75 – 1.69 (m, 4H), 1.62 – 1.57 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 152.0, 143.7, 140.2, 133.6, 131.3, 129.6, 129.3, 128.9, 127.1, 120.0, 117.6, 115.9, 50.6, 26.0, 24.5. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₇H₁₇Cl₂NH⁺ 306.0811; Found 306.0810.



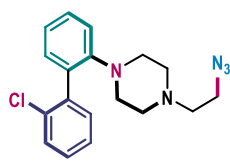
Compound, **10p**: colourless sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 79% (50 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.44 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.28 – 7.20 (m, 3H), 6.73 (dd, $J = 8.3, 2.7$ Hz, 1H), 6.69 (s, 1H), 6.63 (d, $J = 7.6$ Hz, 1H), 3.48 (t, $J = 6.0$ Hz, 4H), 1.81 – 1.79 (m, 4H), 1.59 – 1.56 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 148.7, 144.2, 140.4, 133.5, 131.3, 129.6, 129.2, 129.1, 127.1, 116.2, 112.4, 110.9, 49.3, 27.9, 27.3. **HRMS (ESI/TOF-Q) m/z**: [M+H]⁺ Calculated for C₁₈H₁₉Cl₂NH⁺ 320.0967; Found 320.0976.

General procedure for the synthesis of compounds 11/12:



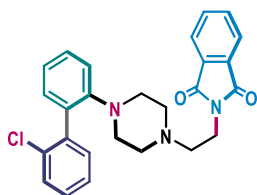
A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv) and tertiary amine DABCO or quinuclidine (0.2 mmol, 1.0 equiv) under N_2 atmosphere. Then, dry DCM (1.5 mL) was added via syringe. The reaction mixture was allowed to stir at 50 °C for 12 h. Then, the corresponding nucleophile (1.2 equiv; for water, 6 equiv) was added in the reaction mixture and allowed to stir further for 12 h at 50 °C. After completion of the reaction, volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **11/12**.

Compound **11h** was prepared similarly using λ^3 -bromane (**1a**), DABCO, and NaN_3 .



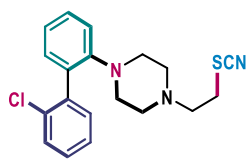
11a

Compound, **11a**: yellow sticky liquid; eluent (4% ethyl acetate in hexane). **Yield**: 84% (57 mg); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ : 7.48 – 7.45 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.11 – 7.08 (m, 2H), 3.30 (t, $J = 6.1$ Hz, 2H), 2.86 (t, $J = 4.9$ Hz, 4H), 2.52 (t, $J = 6.1$ Hz, 2H), 2.33 – 2.31 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ : 150.9, 139.9, 134.0, 133.6, 132.0, 131.5, 129.8, 129.1, 128.2, 126.5, 122.7, 119.2, 57.2, 53.5, 51.2, 48.3. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{20}\text{ClN}_5\text{H}^+$ 342.1480; Found 342.1482.



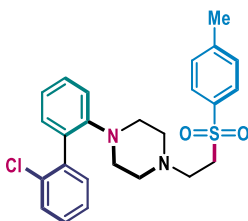
11b

Compound, **11b**: yellow sticky liquid; eluent (5% ethyl acetate in hexane). **Yield**: 66% (59 mg); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ : 7.87 – 7.78 (m, 2H), 7.77 – 7.67 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.35 (m, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.16 (m, 1H), 7.08 – 7.03 (m, 2H), 3.77 (t, $J = 6.6$ Hz, 2H), 2.78 (t, $J = 4.9$ Hz, 4H), 2.56 (t, $J = 6.7$ Hz, 2H), 2.34 (brs, 4H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ : 168.5, 151.0, 139.9, 134.0, 133.9, 133.5, 132.3, 132.0, 131.5, 129.8, 129.0, 128.3, 126.5, 123.3, 122.5, 119.1, 55.8, 53.3, 51.2, 35.3. **HRMS (ESI/TOF-Q) m/z**: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{26}\text{H}_{24}\text{ClN}_3\text{O}_2\text{H}^+$ 446.1630; Found 446.1638.



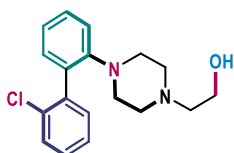
11c

Compound, **11c**: yellow sticky liquid; eluent (3% ethyl acetate in hexane). **Yield**: 78% (56 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (dd, $J = 7.2, 2.1$ Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.19 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.12 – 7.08 (m, 2H), 3.13 (t, $J = 6.7$ Hz, 2H), 2.84 (t, $J = 4.9$ Hz, 4H), 2.66 (t, $J = 6.7$ Hz, 2H), 2.33 – 2.27 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 150.8, 139.8, 134.0, 133.6, 132.0, 131.5, 129.8, 129.1, 128.3, 126.5, 122.8, 119.2, 113.2, 56.3, 53.0, 51.1, 32.6. **HRMS (ESI/TOF-Q) m/z** : $[M+H]^+$ Calculated for $C_{19}H_{20}ClN_3SH^+$ 358.1139; Found 358.1152.



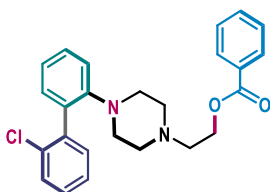
11d

Compound, **11d**: yellow sticky liquid; eluent (4% ethyl acetate in hexane). **Yield**: 65% (59 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.77 – 7.73 (m, 2H), 7.45 – 7.42 (m, 1H), 7.35 – 7.30 (m, 4H), 7.29 – 7.22 (m, 2H), 7.17 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.10 – 7.06 (m, 1H), 7.02 (d, $J = 7.7$ Hz, 1H), 3.23 – 3.20 (m, 2H), 2.72 – 2.66 (m, 6H), 2.44 (s, 3H), 2.20 – 2.16 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 150.7, 144.8, 139.8, 136.8, 134.0, 133.5, 132.0, 131.6, 130.0, 129.8, 129.1, 128.3, 128.2, 126.5, 122.8, 119.1, 53.7, 53.1, 51.4, 51.0, 21.8. **HRMS (ESI/TOF-Q) m/z** : $[M+H]^+$ Calculated for $C_{25}H_{27}ClN_2O_2SH^+$ 455.1555; Found 455.1556.



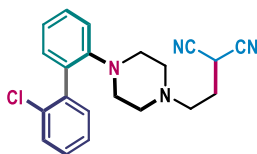
11e

Compound, **11e**: yellow sticky liquid; eluent (5% ethyl acetate in hexane). **Yield**: 83% (53 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (d, $J = 7.4$ Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.19 (d, $J = 7.5$ Hz, 1H), 7.11 – 7.08 (m, 2H), 3.52 (t, $J = 7.2$ Hz, 2H), 2.87 – 2.84 (m, 4H), 2.67 – 2.63 (m, 2H), 2.33 – 2.31 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 150.9, 139.9, 134.0, 133.6, 132.1, 131.5, 129.8, 129.1, 128.3, 126.5, 122.7, 119.2, 60.0, 53.5, 51.2, 41.0. **HRMS (ESI/TOF-Q) m/z** : $[M+H]^+$ Calculated for $C_{18}H_{21}ClN_2OH^+$ 317.1415; Found 317.1410.



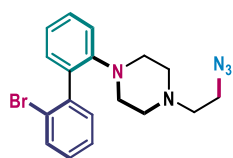
11f

Compound, **11f**: yellow sticky liquid; eluent (5% ethyl acetate in hexane). **Yield**: 58% (76 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.91 (d, $J = 7.7$ Hz, 2H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.35 – 7.31 (m, 3H), 7.28 – 7.22 (m, 2H), 7.19 – 7.08 (m, 3H), 7.01 – 6.97 (m, 2H), 4.32 (t, $J = 5.9$ Hz, 2H), 2.77 (t, $J = 4.9$ Hz, 4H), 2.64 (t, $J = 6.0$ Hz, 2H), 2.37 – 2.29 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 166.6, 150.9, 139.9, 133.9, 133.5, 133.1, 132.0, 131.5, 130.3, 129.8, 129.7, 129.1, 128.5, 128.3, 126.5, 122.7, 119.2, 62.5, 56.7, 53.6, 51.2. **HRMS (ESI/TOF-Q) m/z** : $[M+H]^+$ Calculated for $C_{25}H_{25}ClN_2O_2H^+$ 421.1677; Found 421.1672.



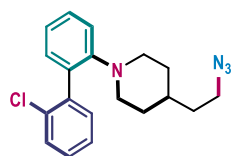
11g

Compound, **11g**: yellow sticky liquid; eluent (3% ethyl acetate in hexane). **Yield**: 60% (44 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (d, $J = 7.4$ Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 7.19 (d, $J = 7.4$ Hz, 1H), 7.12 – 7.07 (m, 2H), 4.10 (t, $J = 7.2$ Hz, 1H), 2.83 (t, $J = 4.9$ Hz, 4H), 2.52 (t, $J = 6.1$ Hz, 2H), 2.31 – 2.25 (m, 4H), 2.12 (q, $J = 6.5$ Hz, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 150.7, 139.9, 134.0, 133.6, 132.0, 129.8, 129.2, 128.3, 126.6, 122.9, 119.2, 113.0, 53.3 (2 \times C), 51.2, 28.5, 19.9. **HRMS (ESI/TOF-Q) m/z** : $[M+H]^+$ Calculated for $C_{21}H_{21}ClN_4H^+$ 365.1528; Found 365.1529.



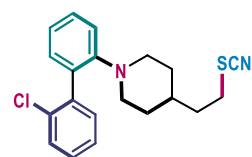
11h

Compound, **11h**: yellow sticky liquid; eluent (4% ethyl acetate in hexane). **Yield**: 39% (30 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.65 (d, $J = 8.0$ Hz, 1H), 7.38 – 7.31 (m, 3H), 7.19 – 7.15 (m, 2H), 7.11 – 7.07 (m, 2H), 3.29 (t, $J = 6.1$ Hz, 2H), 2.86 (t, $J = 4.8$ Hz, 4H), 2.51 (t, $J = 6.1$ Hz, 2H), 2.35 – 2.30 (m, 4H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 150.7, 141.9, 135.7, 133.0, 132.1, 131.5, 129.1, 128.4, 127.1, 124.1, 122.7, 119.2, 57.2, 53.5, 51.2, 48.4. **HRMS (ESI/TOF-Q) m/z**: $[M+H]^+$ Calculated for $C_{18}H_{20}BrN_5H^+$ 386.0975; Found 386.0980.



12a

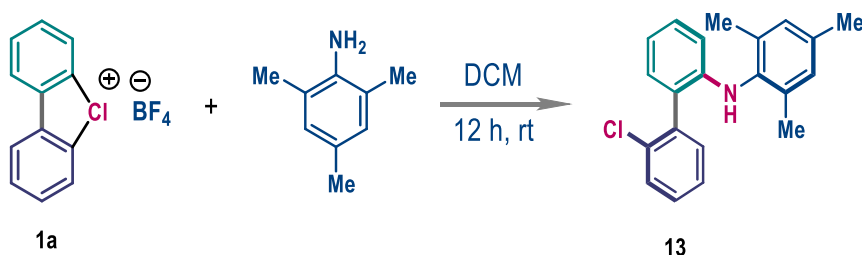
Compound, **12a**: yellow sticky liquid; eluent (4% ethyl acetate in hexane). **Yield**: 67% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.39 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 7.18 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.08 – 7.05 (m, 2H), 3.24 (t, $J = 7.1$ Hz, 2H), 3.04 – 3.00 (m, 2H), 2.60 – 2.52 (m, 2H), 1.51 – 1.44 (m, 4H), 1.40 – 1.30 (m, 1H), 1.02 – 0.87 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 151.9, 140.1, 134.0, 133.6, 132.1, 131.5, 129.7, 129.0, 128.1, 126.4, 122.3, 119.3, 52.1, 51.9, 49.1, 35.4, 33.2, 32.5, 32.3. **HRMS (ESI/TOF-Q) m/z**: $[M+H]^+$ Calculated for $C_{19}H_{21}ClN_4H^+$ 341.1528; Found 341.1525.



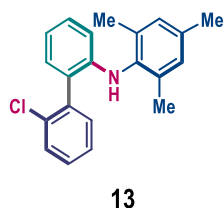
12b

Compound, **12b**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 65% (46 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.46 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.38 – 7.35 (m, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.17 (m, 1H), 7.09 – 7.06 (m, 2H), 3.05 – 3.02 (m, 2H), 2.90 (t, $J = 7.6$ Hz, 2H), 2.61 – 2.52 (m, 2H), 1.69 (q, $J = 7.2$ Hz, 2H), 1.53 – 1.49 (m, 2H), 1.46 – 1.34 (m, 1H), 1.05 – 0.88 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 151.7, 140.0, 134.1, 133.6, 132.0, 131.5, 129.7, 129.0, 128.2, 126.5, 122.4, 119.3, 112.3, 52.1, 51.8, 36.6, 34.5, 32.3, 32.1, 31.7. **HRMS (ESI/TOF-Q) m/z**: $[M+H]^+$ Calculated for $C_{20}H_{21}ClN_2SH^+$ 357.1187; Found 357.1188.

Synthesis of compound 13:

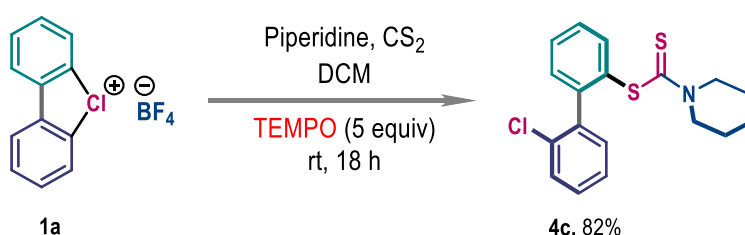


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv) and 2,4,6-trimethylaniline (0.2 mmol, 1.0 equiv) under N_2 atmosphere. Then, dry DCM (2 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 12 h. After completion, volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **13**.

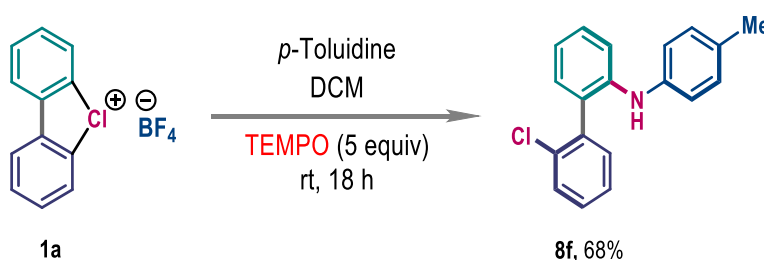


Compound, **13**: yellow sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 65% (42 mg); **¹H NMR (400 MHz, Chloroform-*d*)** δ : 7.56 – 7.54 (m, 1H), 7.45 – 7.33 (m, 3H), 7.15 – 7.08 (m, 2H), 6.90 (s, 2H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.22 (d, $J = 8.1$ Hz, 1H), 4.74 (s, 1H), 2.28 (s, 3H), 2.12 (s, 6H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ : 143.8, 138.2, 136.3, 135.6, 135.3, 134.7, 132.1, 130.17, 130.16, 129.32, 129.26, 129.2, 127.4, 125.2, 117.3, 111.5, 21.1, 18.3. **HRMS (ESI/TOF-Q) m/z : [M+H]⁺** Calculated for C₂₁H₂₀ClNH⁺ 322.1357; Found 322.1348.

Ligand coupling reaction in the presence of radical quencher:

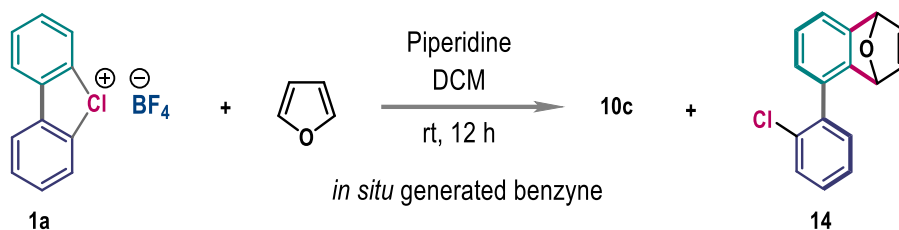


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv), CS₂ (**2a**, 2.5 equiv), piperidine (**3c**, 1.2 equiv), and TEMPO (5.0 equiv) under N₂ atmosphere. Then, dry DCM (2 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 18 h. After completion, volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **4c** (57 mg, 82% yield).

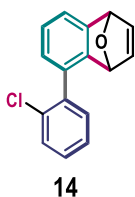


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv), *p*-toluidine (1.0 equiv), and TEMPO (5.0 equiv) under N₂ atmosphere. Then, dry DCM (2 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 18 h. After completion, volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography to provide pure product **8f** (40 mg, 68% yield).

Aryne trapping experiment:

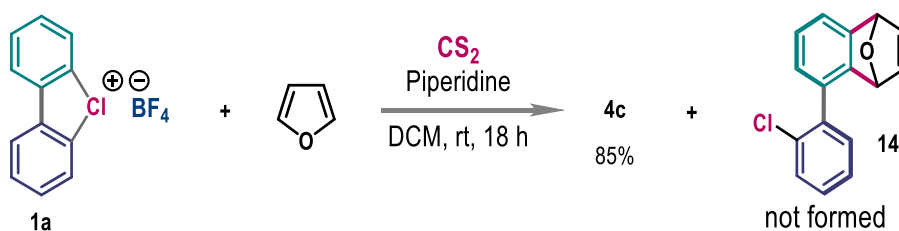


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv) and furan (10.0 equiv) under N_2 atmosphere. Then, dry DCM (1.5 mL) was added via syringe. After that, piperidine (0.3 mmol, 1.5 equiv) was added slowly. The reaction mixture was allowed to stir at rt for 12 h. After completion of the reaction (TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel chromatography to provide pure product **14**.



Compound, **14**: sticky liquid; eluent (1% ethyl acetate in hexane). **Yield**: 56% (29 mg); **1H NMR (400 MHz, Chloroform-*d*)** δ : 7.52 – 7.48 (m, 1H), 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 2H), 7.16 – 7.13 (m, 1H), 7.10 – 7.04 (m, 2H), 6.95 (d, $J = 7.8$ Hz, 1H), 5.77 – 5.77 (m, 1H), 5.53 (s, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ : 149.0, 148.5, 143.0, 138.6, 132.9, 132.5, 131.6, 129.9, 129.2, 127.0, 126.4, 125.2, 119.7, 82.7, 81.8. **HRMS (ESI/TOF-Q) m/z**: $[M+H]^+$ Calculated for $C_{16}H_{11}ClOH^+$ 255.0571; Found 255.0567.

Investigation of aryne formation during three-component ligand coupling reaction:

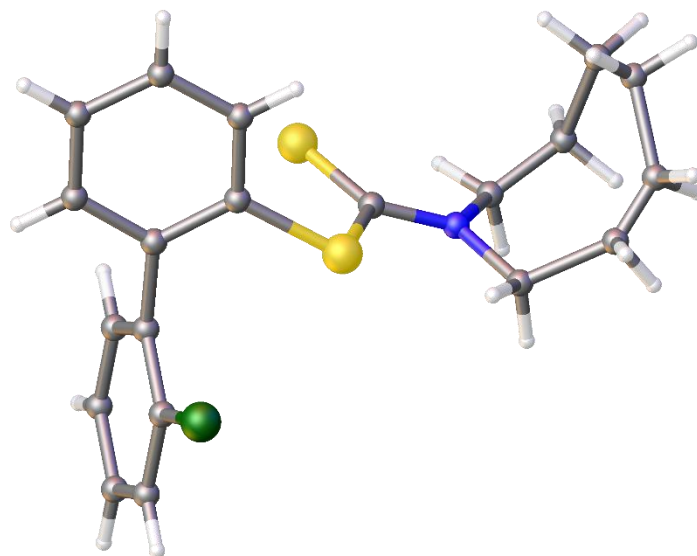


A 16x100 mm oven dried reaction tube equipped with a magnetic stir was charged with λ^3 -chlorane **1a** (0.2 mmol, 1.0 equiv), CS_2 (**2a**, 2.5 equiv), piperidine (**3c**, 1.2 equiv), and furan (10.0 equiv) under N_2 atmosphere. Then, dry DCM (2 mL) was added via syringe. The reaction mixture was allowed to stir at rt for 18 h. After completion of the reaction (TLC monitored), volatiles were removed under reduced pressure and the crude product was purified by silica gel chromatography to provide pure product **4c**. We did not observe the formation of compound **14**.

Crystallographic experimental section

Crystallization: Crystals of compound **4e** were obtained through slow evaporation technique at room temperature from a solution in hexane/DCM solvent combinations.

Crystal structure of compound **4e** (CCDC number: 2340860, Ellipsoid Probability 50%):

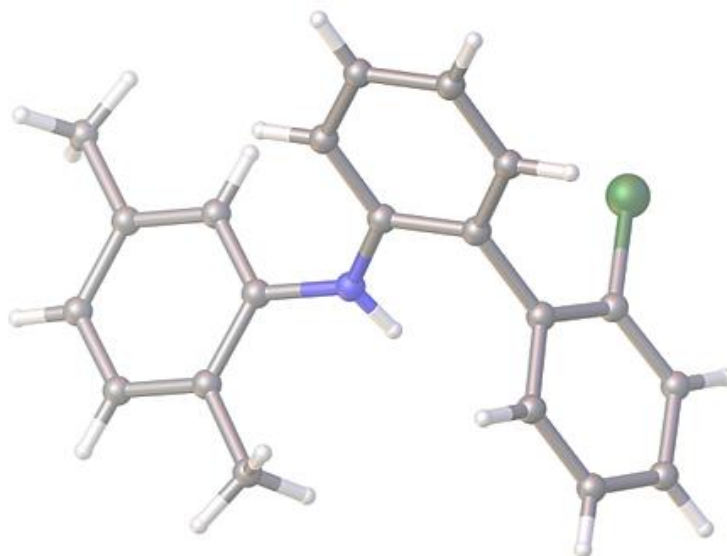


Identification code	4e
Empirical formula	C ₂₀ H ₂₂ Cl N S ₂
Formula weight	375.95
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2 ₁ /c
Unit cell dimensions	a = 9.7904(14) Å alpha = 90 deg. b = 13.791(2) Å beta = 99.606(5) deg. c = 14.347(2) Å gamma = 90 deg.
Volume	1909.9(5) Å ³

Z, Calculated density	4, 1.307 Mg/m ³
Absorption coefficient	0.420 mm ⁻¹
F(000)	792
Crystal size	0.241 x 0.147 x 0.092 mm
Theta range for data collection	3.118 to 26.344 deg.
Limiting indices	-12<=h<=12, -17<=k<=17, -17<=l<=17
Reflections collected / unique	55860 / 3879 [R(int) = 0.0831]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.5420
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3879 / 0 / 263
Goodness-of-fit on F ²	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0620, wR2 = 0.1506
R indices (all data)	R1 = 0.0810, wR2 = 0.1619
Extinction coefficient	n/a
Largest diff. peak and hole	0.393 and -0.348 e.A ⁻³

Crystallization: Crystals of compound **8i** obtained through slow evaporation technique at room temperature from a solution in hexane/acetonitrile solvent combinations.

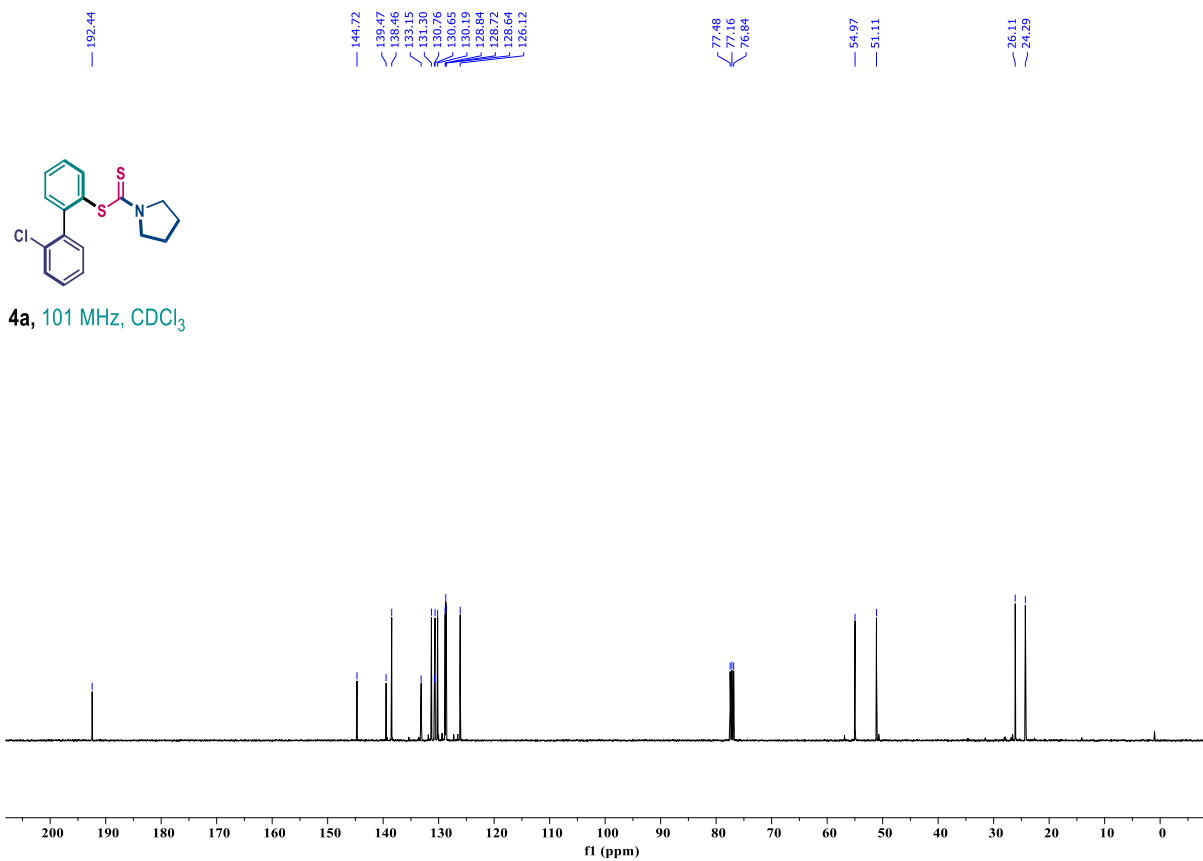
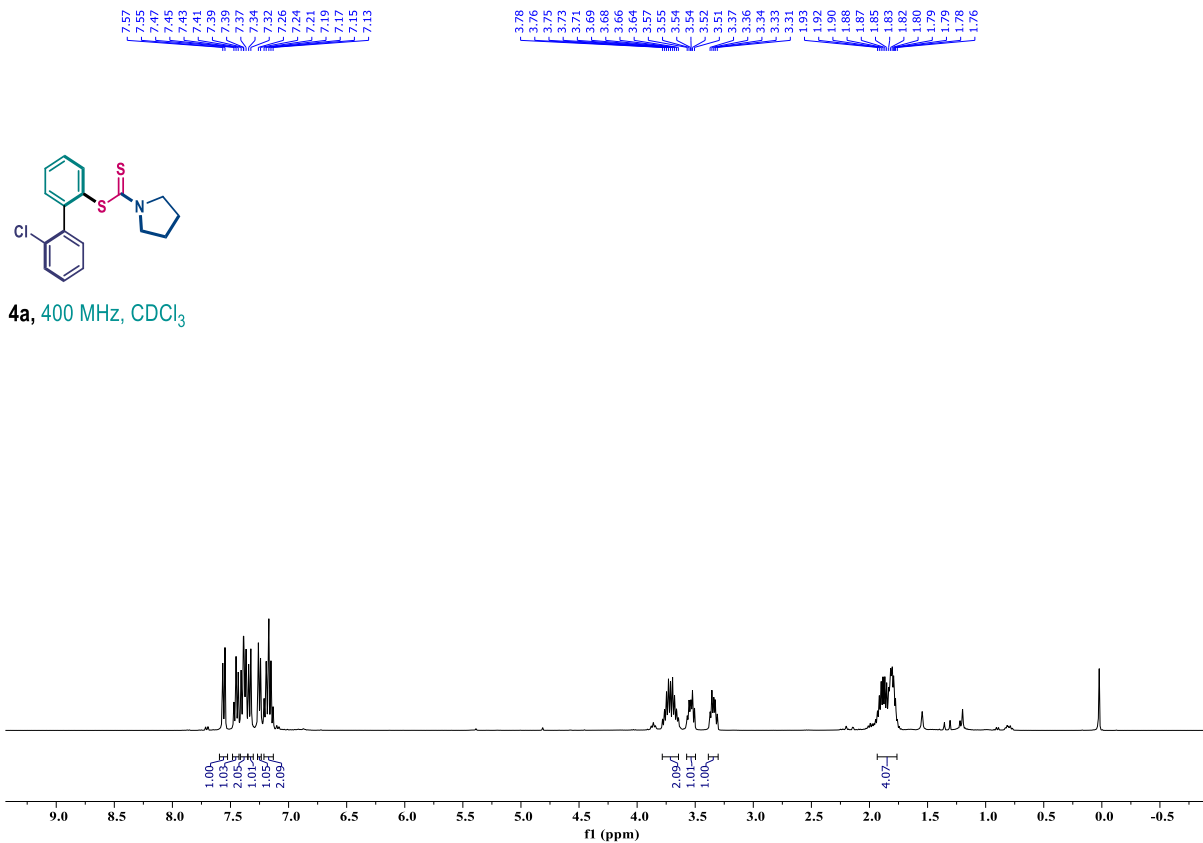
Crystal structure of compound **8i** (CCDC number: 2354443, Ellipsoid Probability 50%):

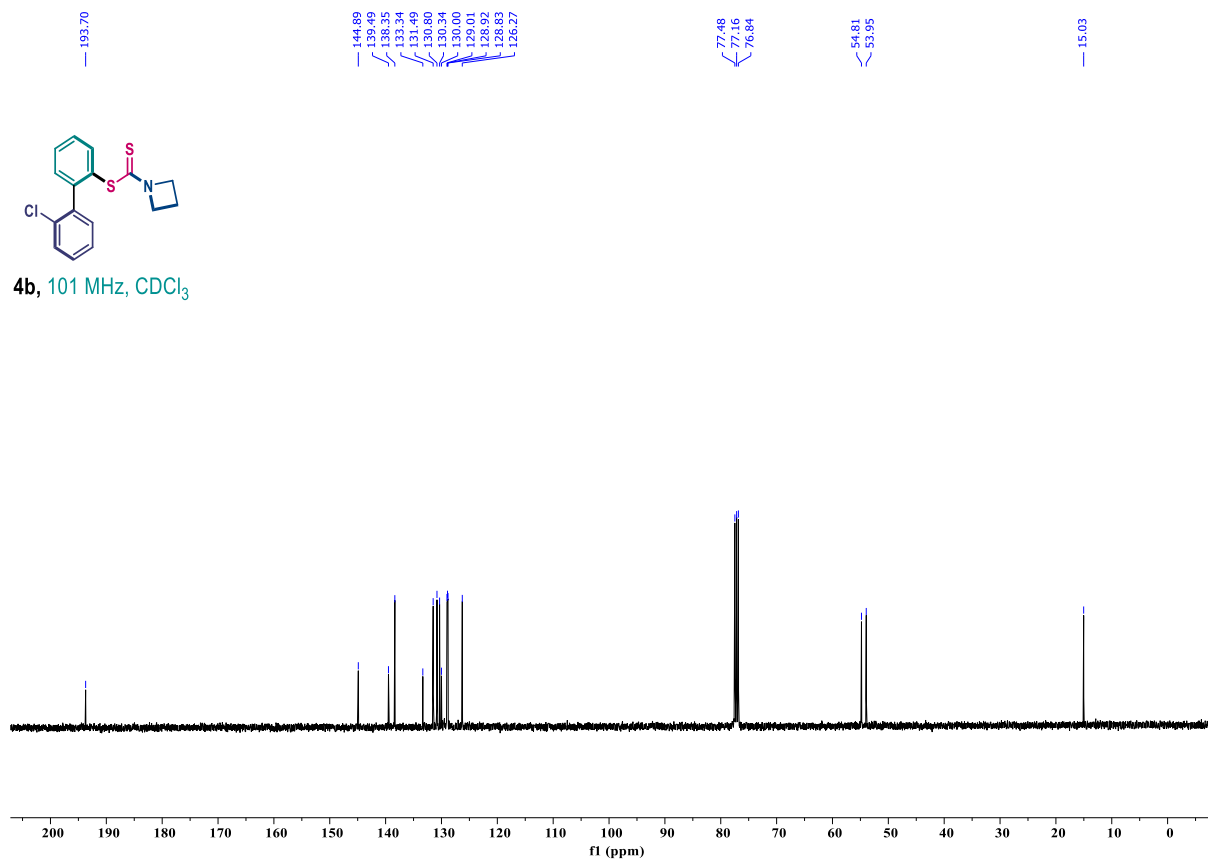
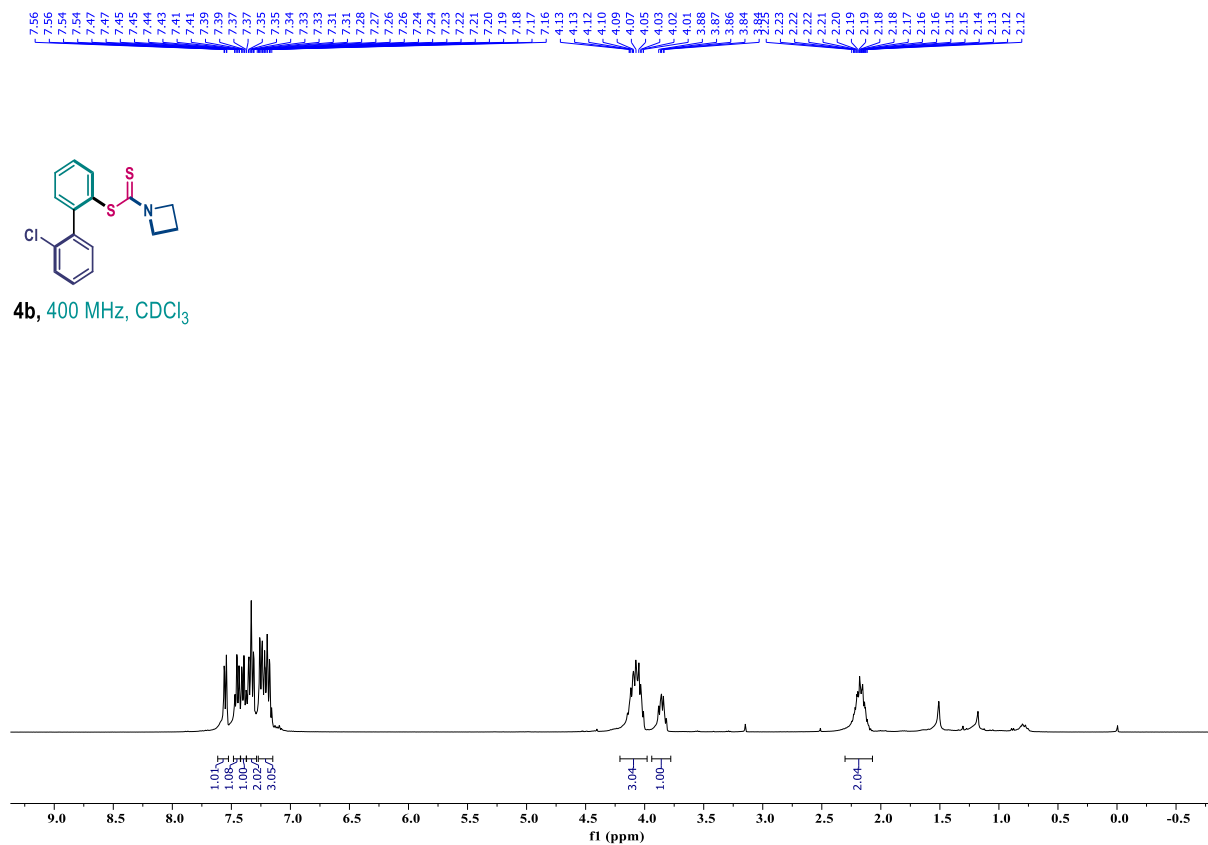


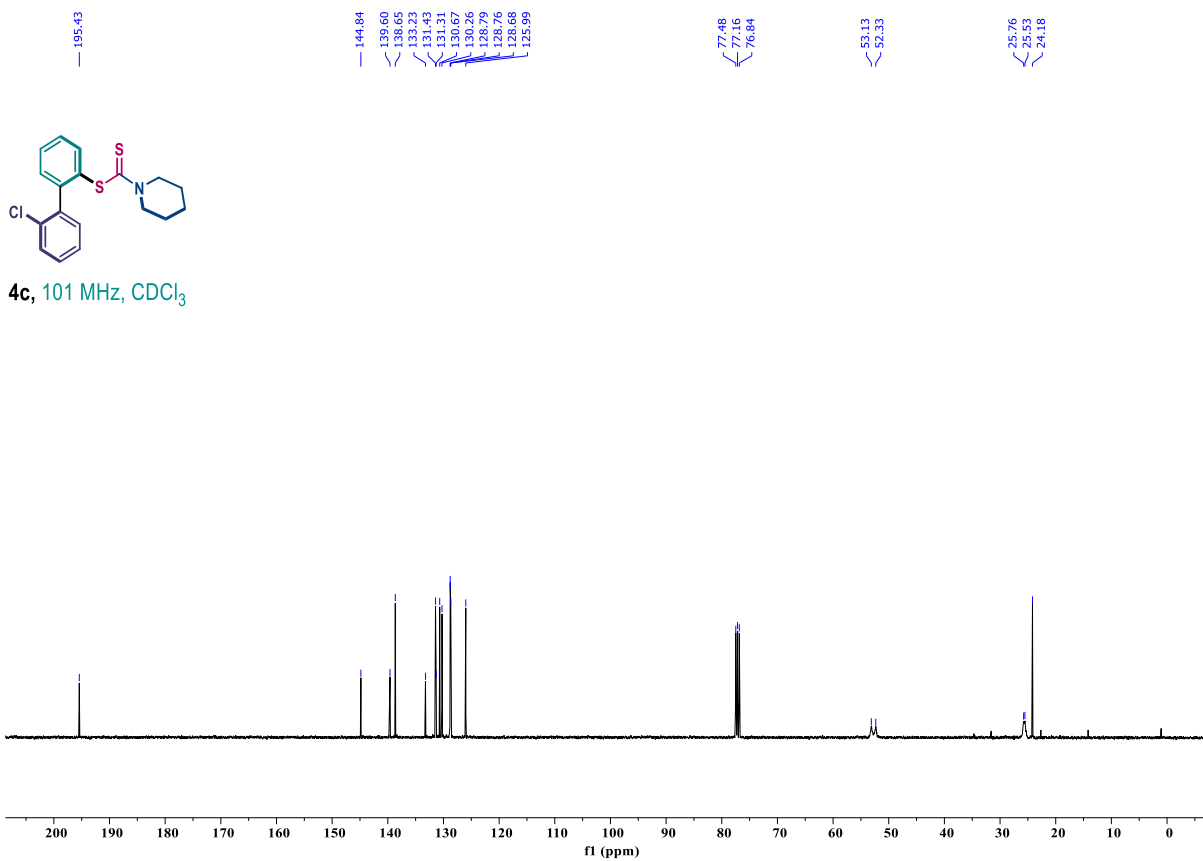
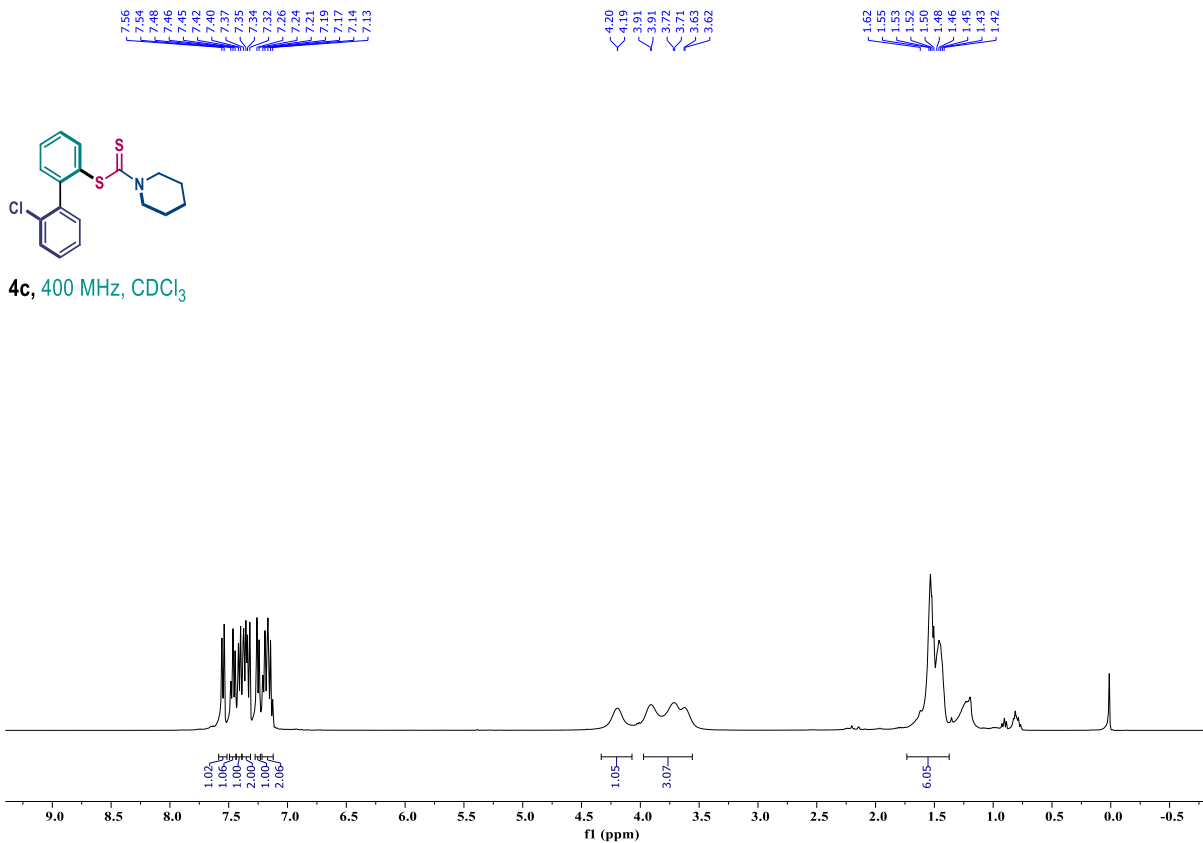
Identification code	8i
Empirical formula	C ₂₀ H ₁₈ Cl N
Formula weight	307.80
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 17.9856(9) Å alpha = 90 deg. b = 7.6368(3) Å beta = 92.914(2) deg. c = 23.5135(13) Å gamma = 90 deg.
Volume	3225.5(3) Å ³
Z, Calculated density	8, 1.268 Mg/m ³
Absorption coefficient	0.233 mm ⁻¹

F(000)	1296
Crystal size	0.320 x 0.260 x 0.120 mm
Theta range for data collection	1.734 to 24.999 deg.
Limiting indices	$-20 \leq h \leq 21, -9 \leq k \leq 7, -27 \leq l \leq 27$
Reflections collected / unique	9434 / 2841 [R(int) = 0.0230]
Completeness to theta = 24.999	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2841 / 0 / 202
Goodness-of-fit on F ²	1.049
Final R indices [I > 2σ(I)]	R1 = 0.0449, wR2 = 0.1142
R indices (all data)	R1 = 0.0579, wR2 = 0.1235
Extinction coefficient	0.0024(3)
Largest diff. peak and hole	0.435 and -0.333 e.Å ⁻³

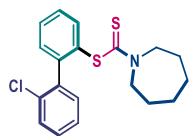
NMR spectra of synthesized compounds



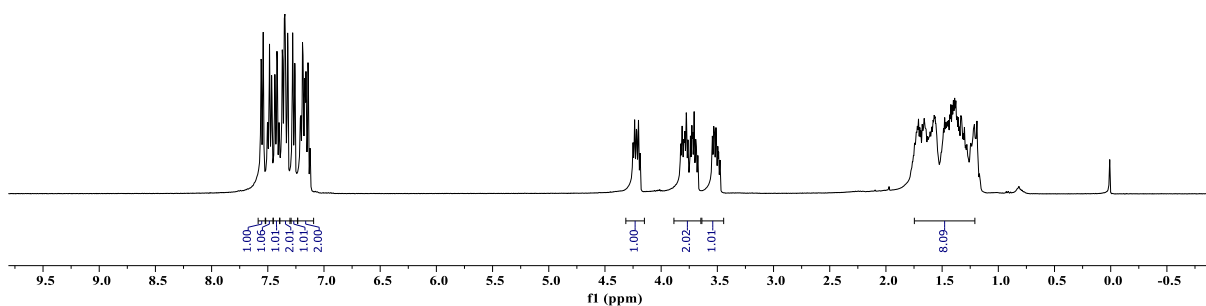




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4d, 400 MHz, CDCl₃



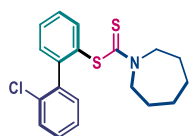
196.13

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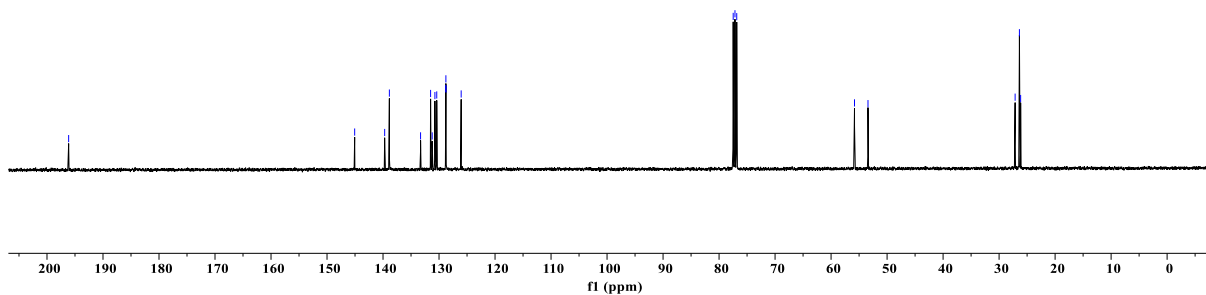
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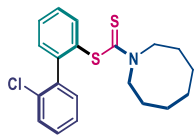
27.14
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26.15



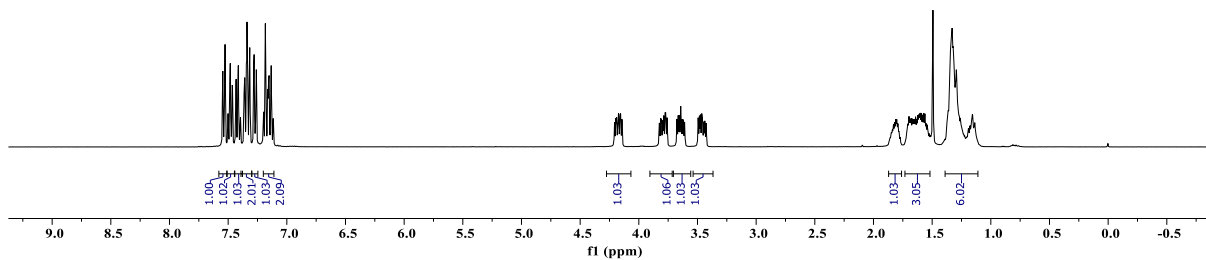
4d, 101 MHz, CDCl₃



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1.26



4e, 400 MHz, CDCl₃



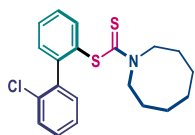
196.15

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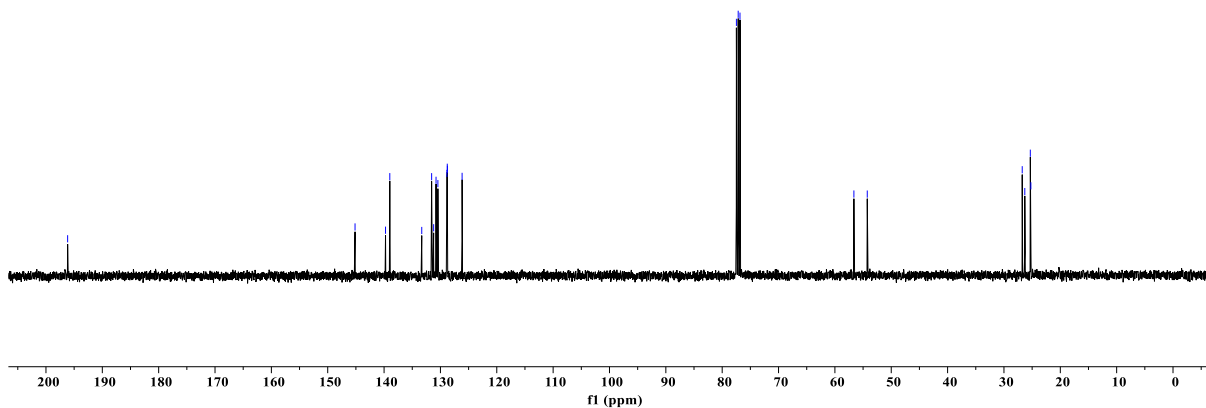
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25.22



4e, 101 MHz, CDCl₃

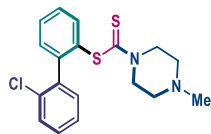


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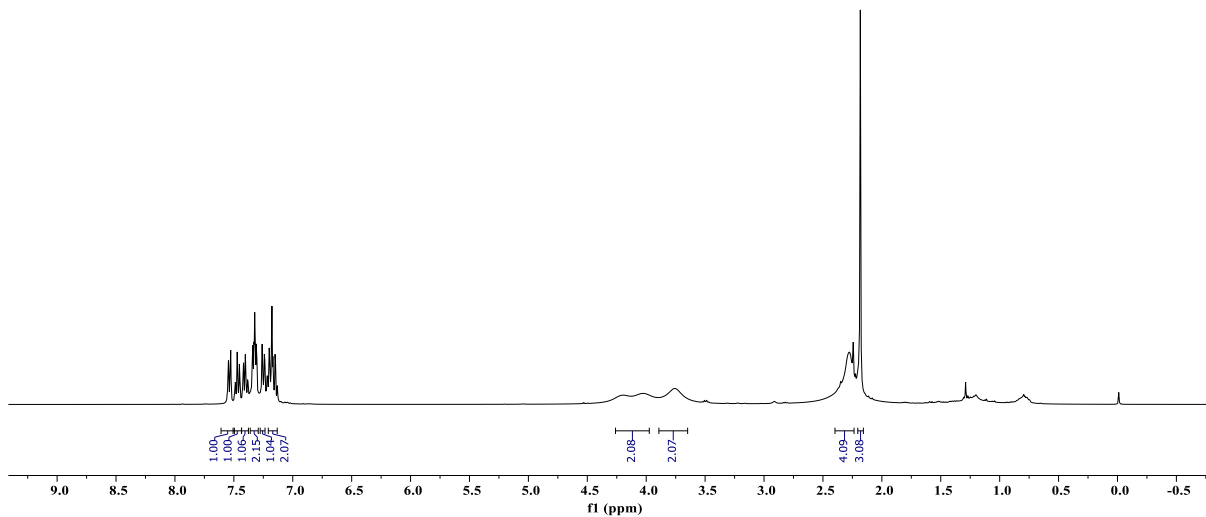
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2.18



4f, 400 MHz, CDCl₃

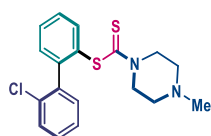


196.94

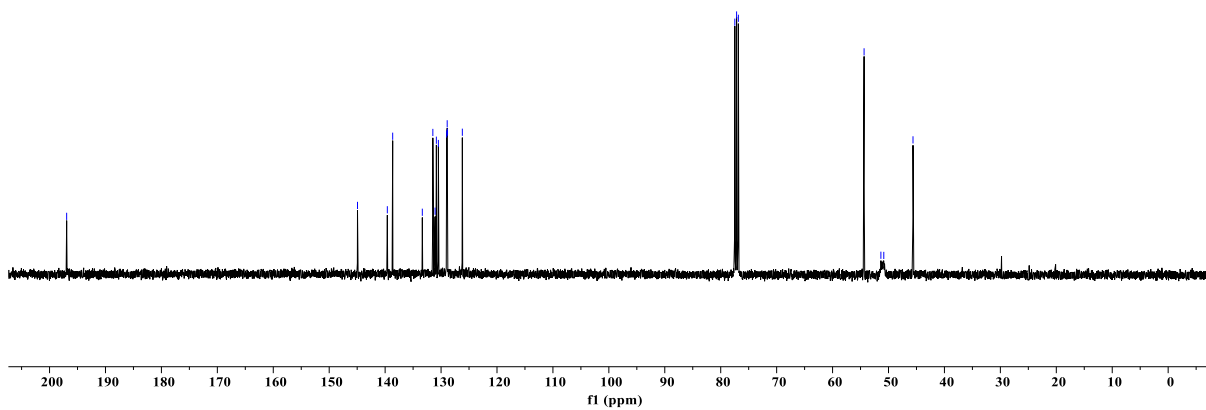
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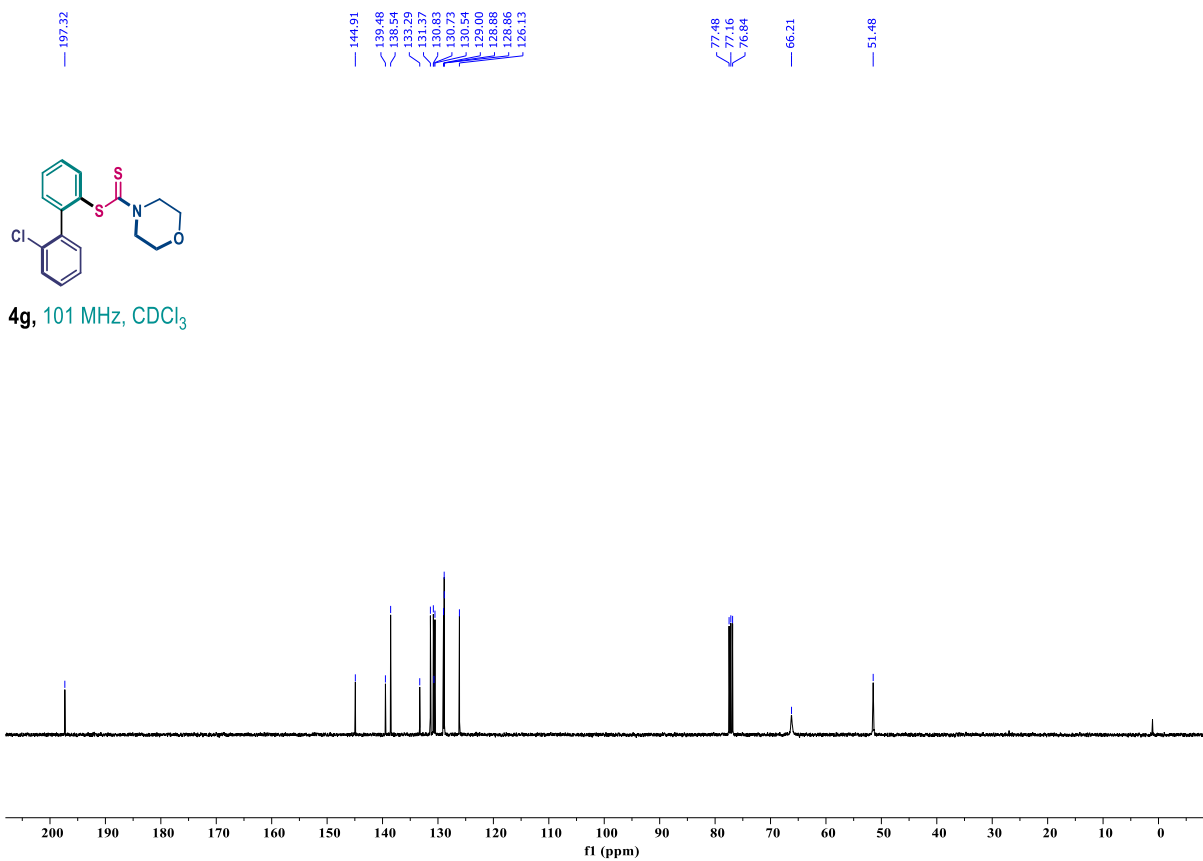
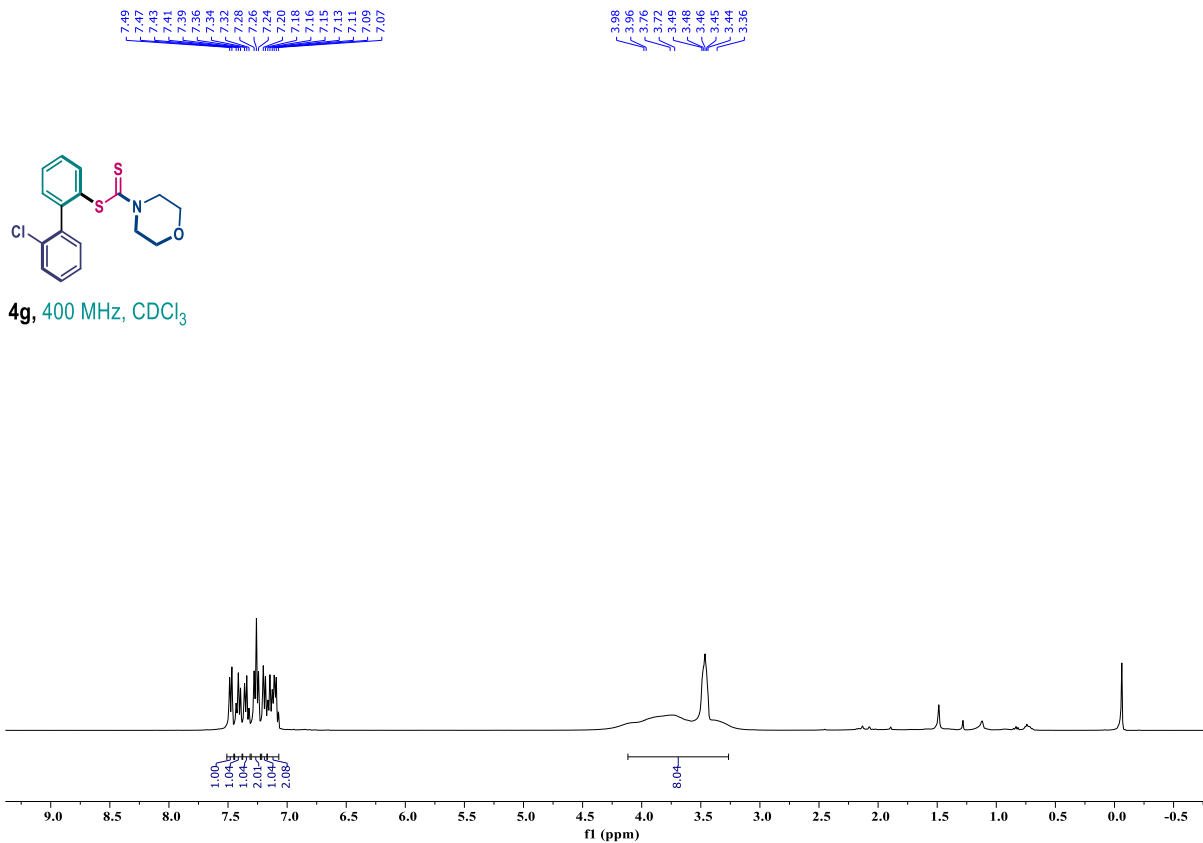
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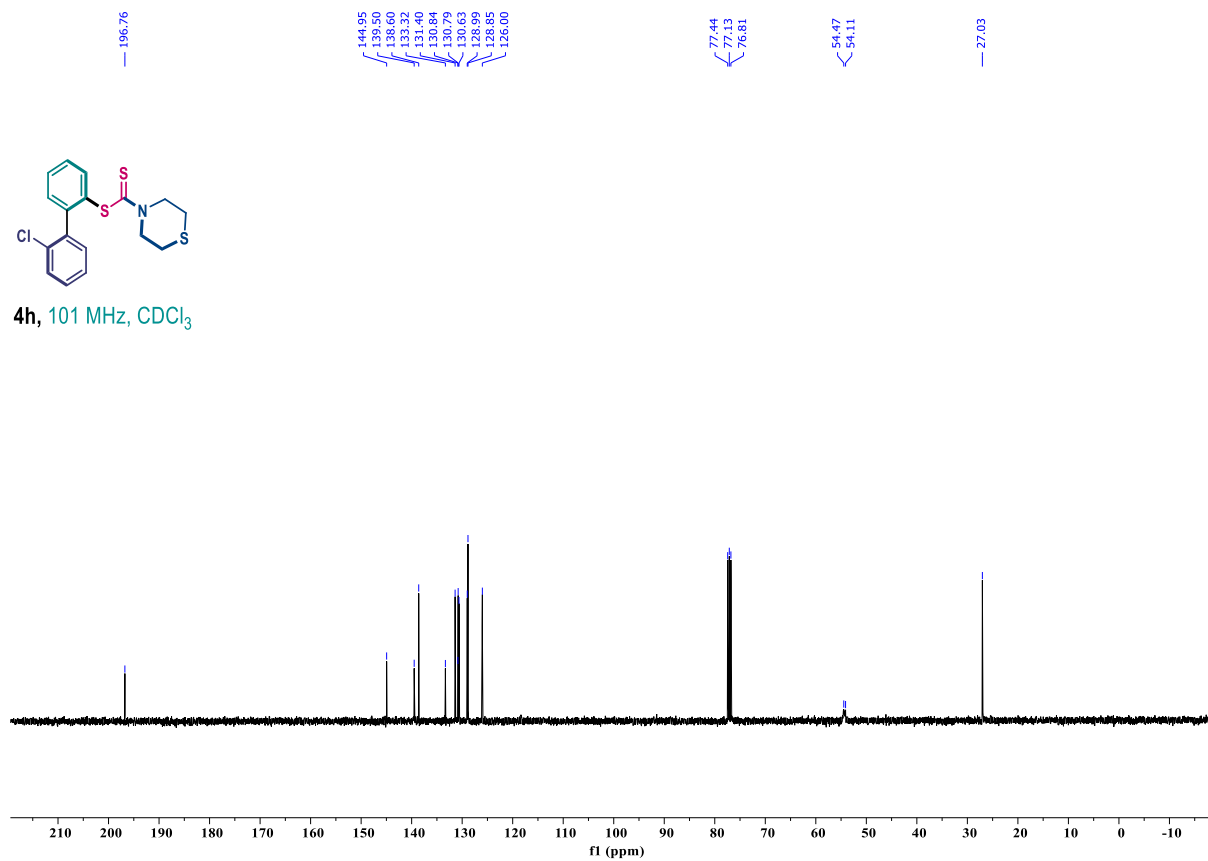
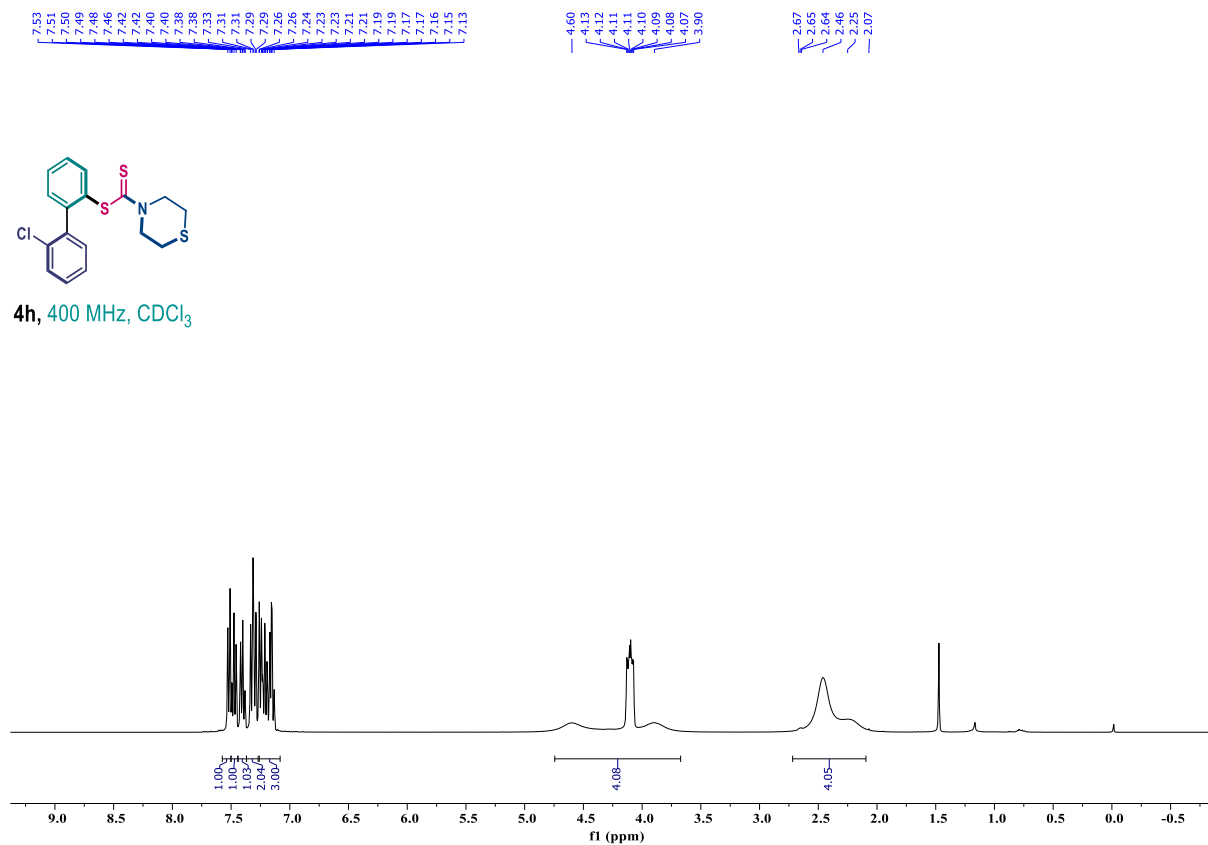
54.37
51.36
50.84
45.62



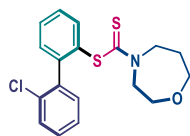
4f, 101 MHz, CDCl₃



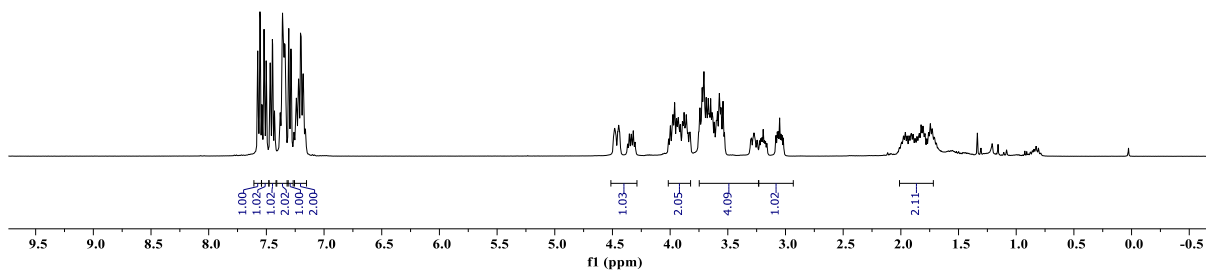




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1.80
1.74
1.73



4i, 400 MHz, CDCl₃
(1.33:1.0 ratio of rotamer)



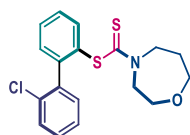
197.45
196.85

145.12
145.09
139.66
139.63
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138.75
137.56
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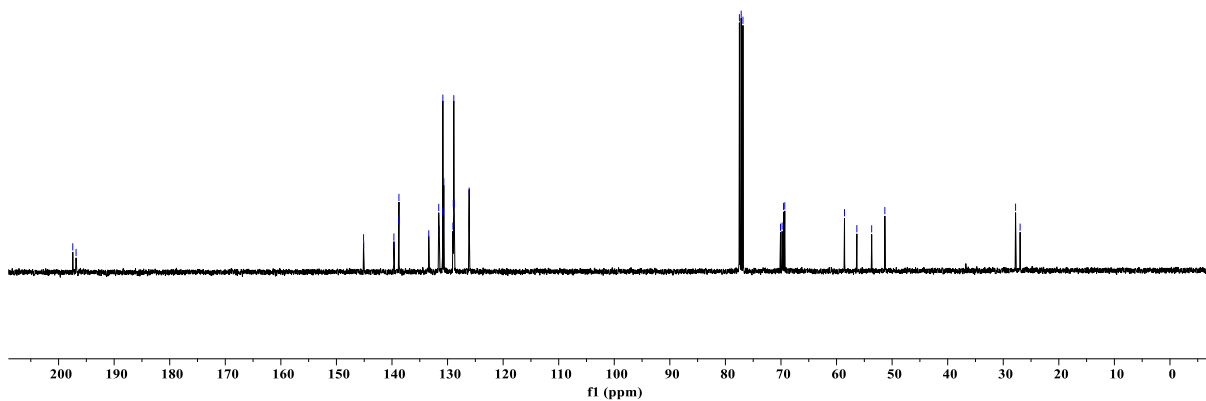
77.48
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77.08
70.08
69.80
69.53
69.32

58.57
56.35
53.68
51.31

27.78
26.97



4i, 101 MHz, CDCl₃
(1.33:1.0 ratio of rotamer)



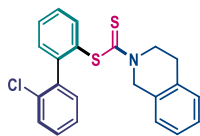
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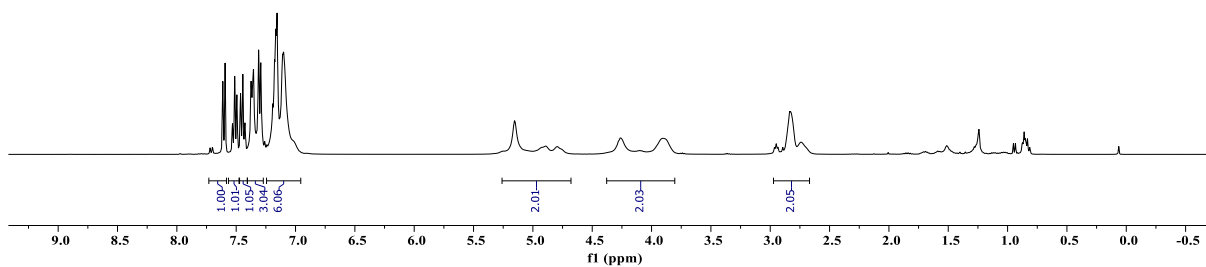
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4j, 400 MHz, CDCl₃
(1.5:1.0 ratio of rotamer)



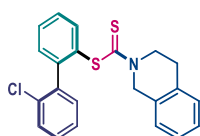
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127.86
127.43
127.18
126.82
126.64
126.14

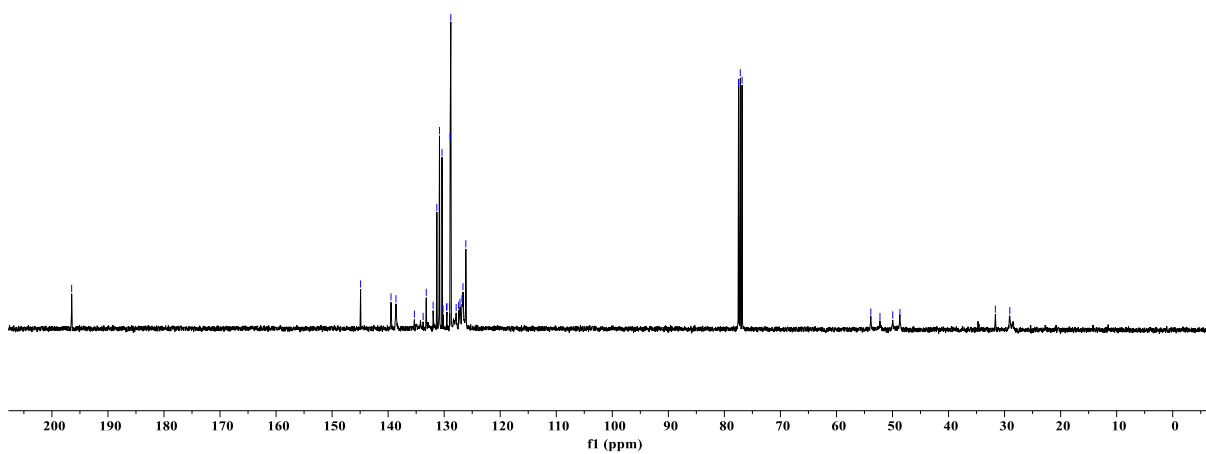
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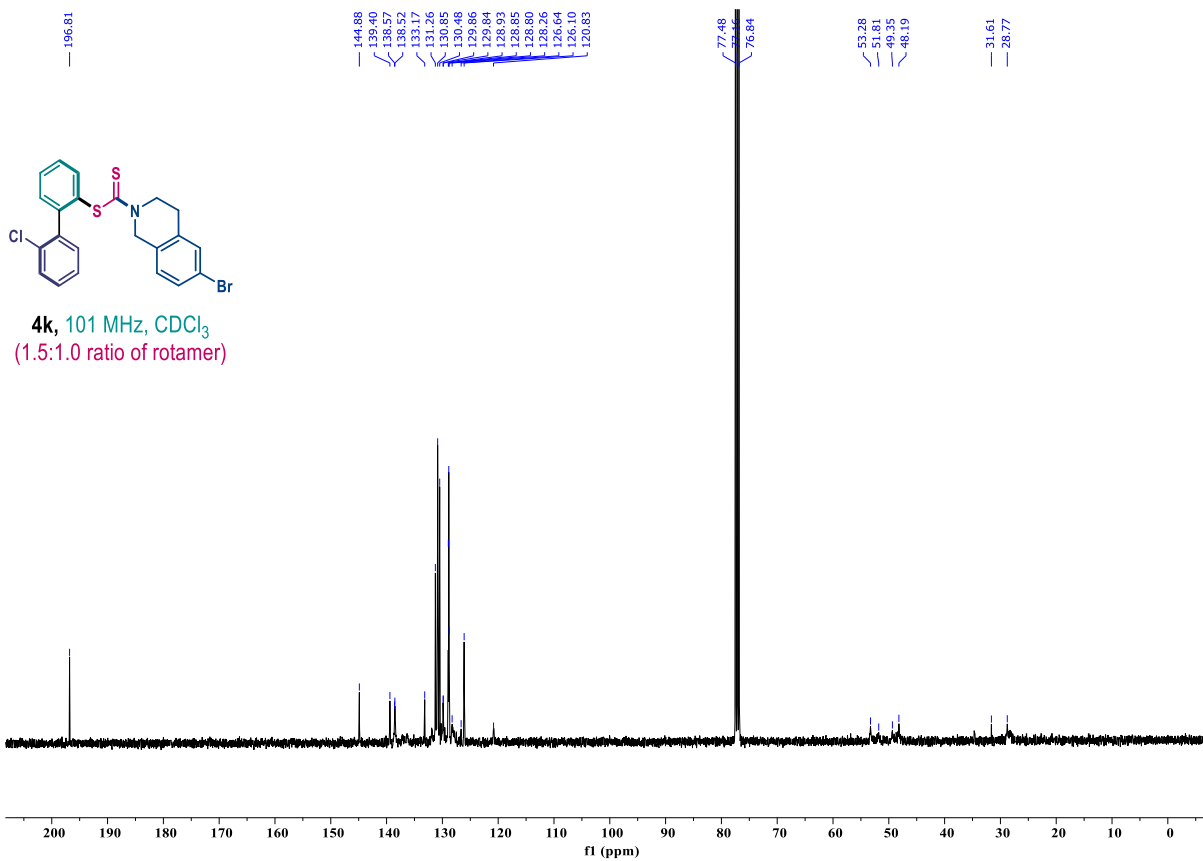
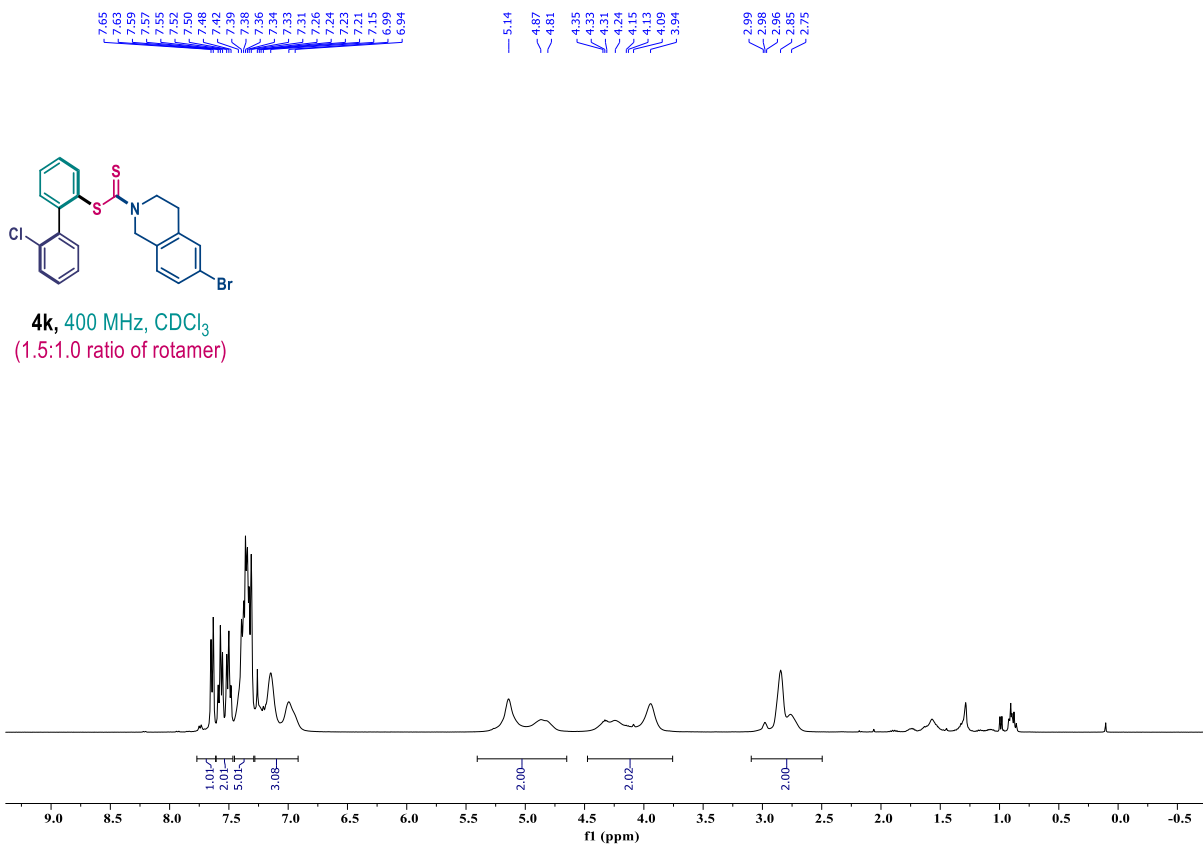
53.87
52.24
49.96
48.68

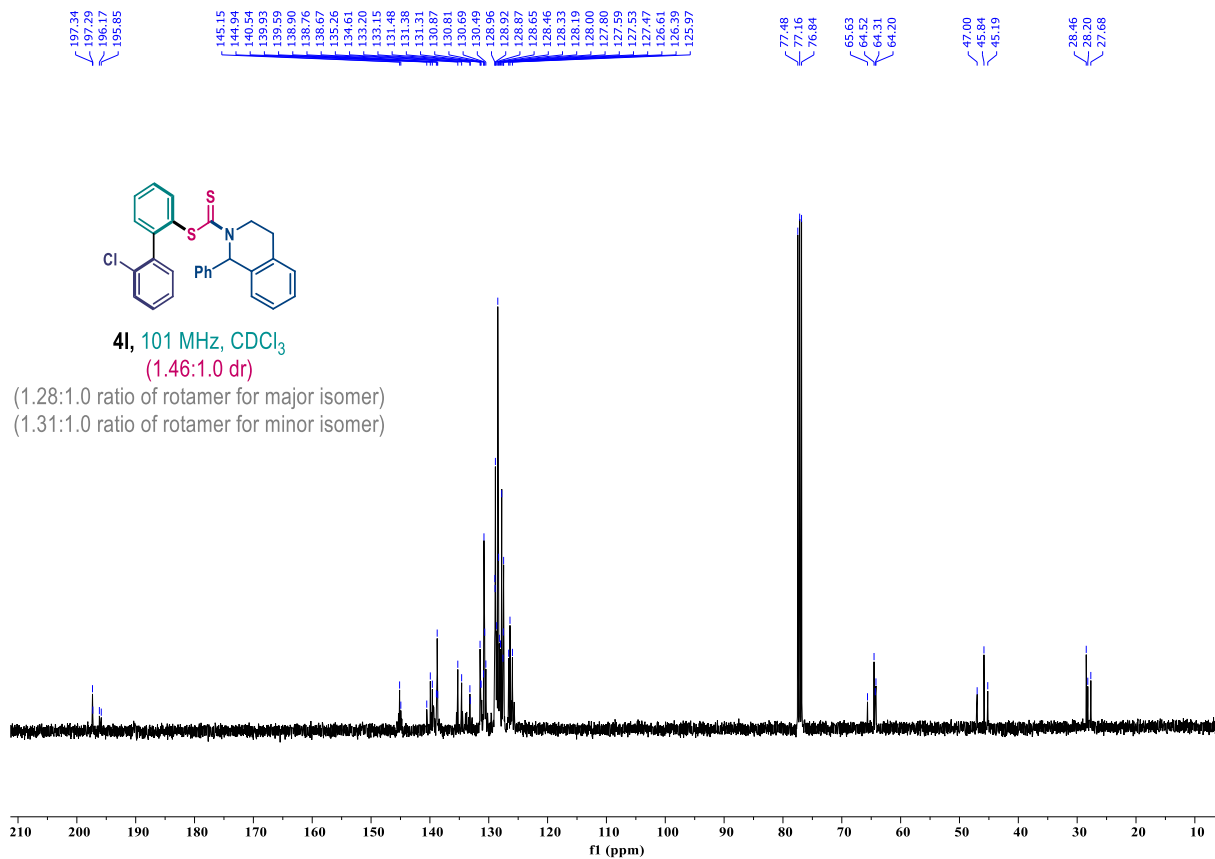
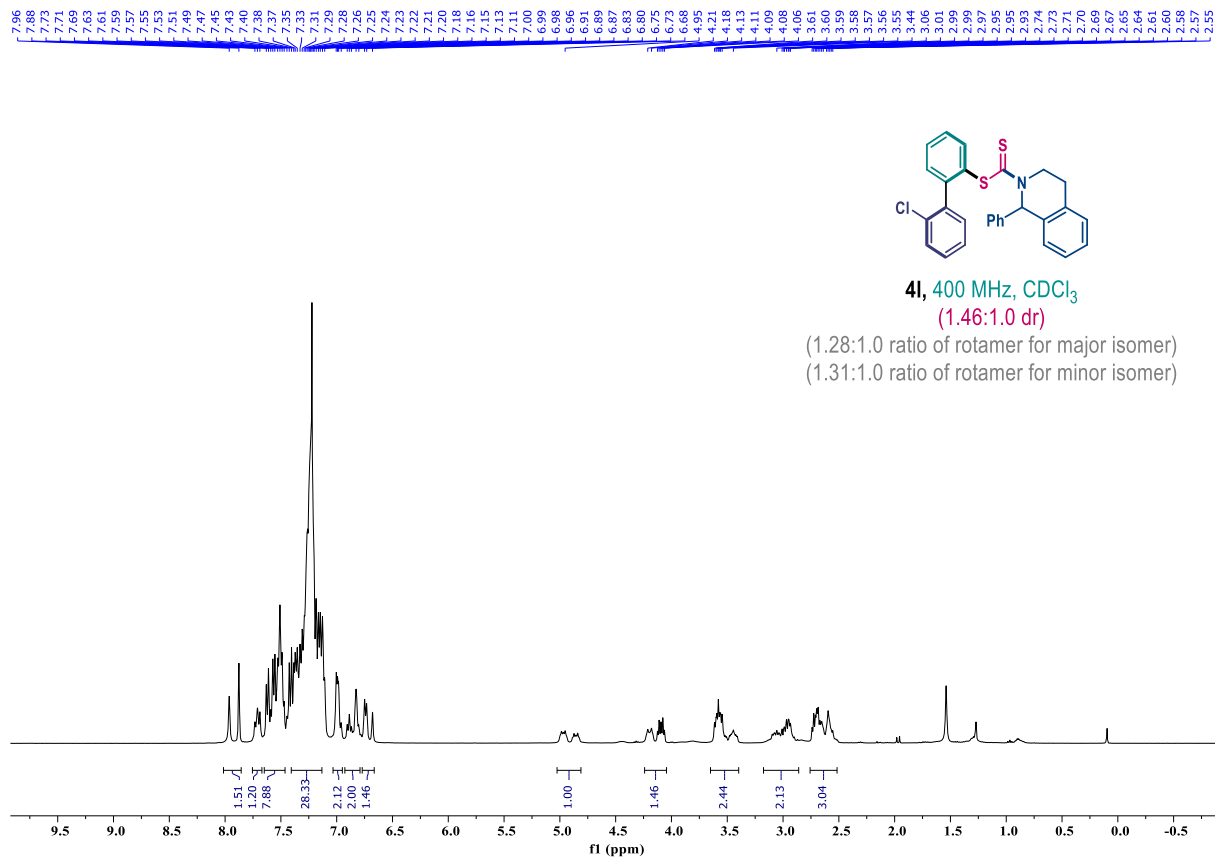
31.64
29.07



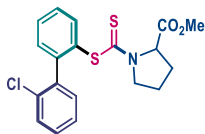
4j, 101 MHz, CDCl₃
(1.5:1.0 ratio of rotamer)







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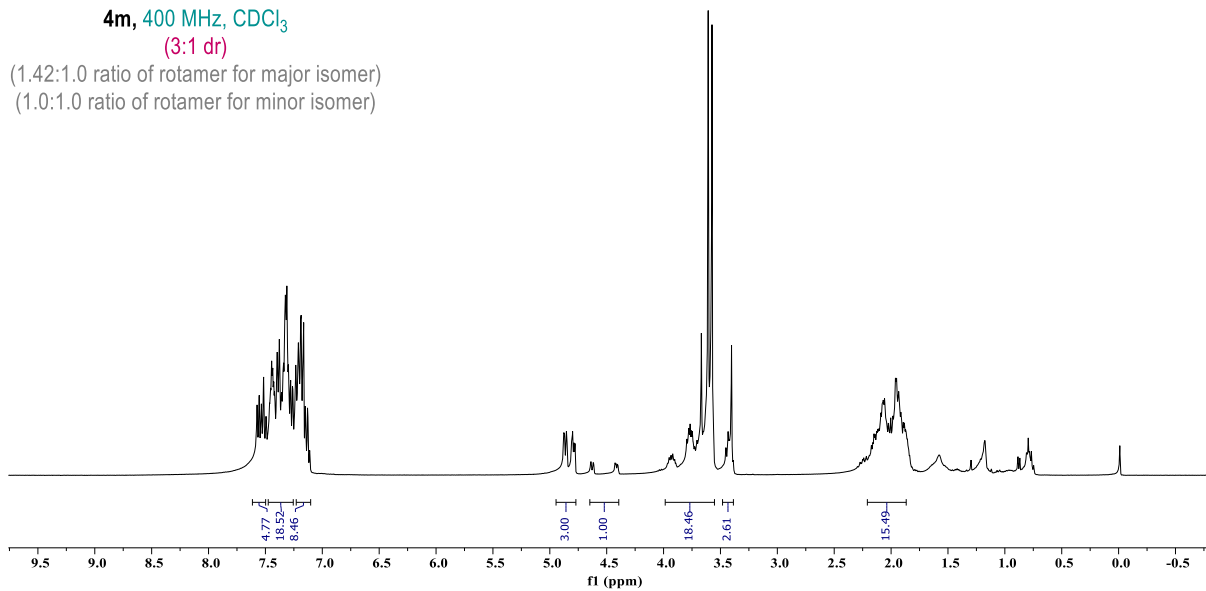


4m, 400 MHz, CDCl₃

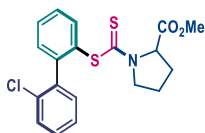
(3:1 dr)

(1.42:1.0 ratio of rotamer for major isomer)

(1.0:1.0 ratio of rotamer for minor isomer)



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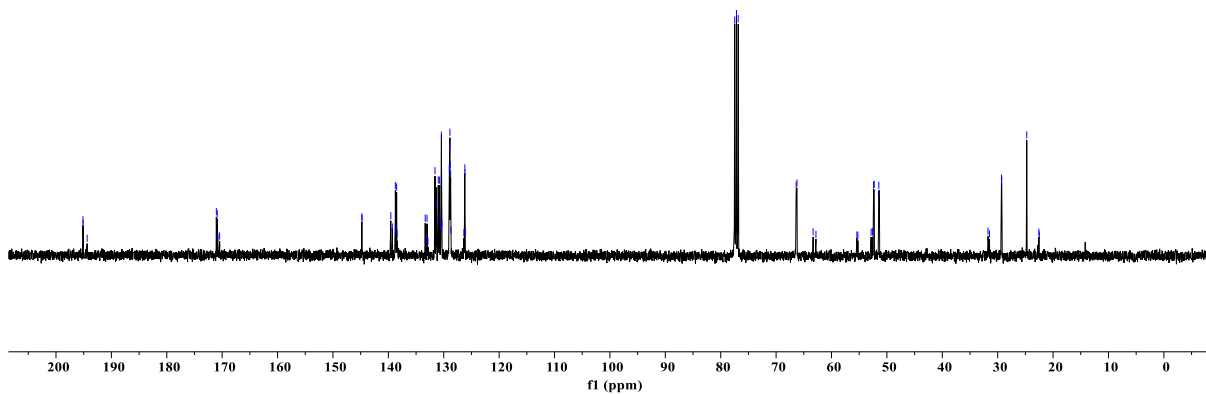


4m, 101 MHz, CDCl₃

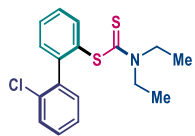
(3:1 dr)

(1.42:1.0 ratio of rotamer for major isomer)

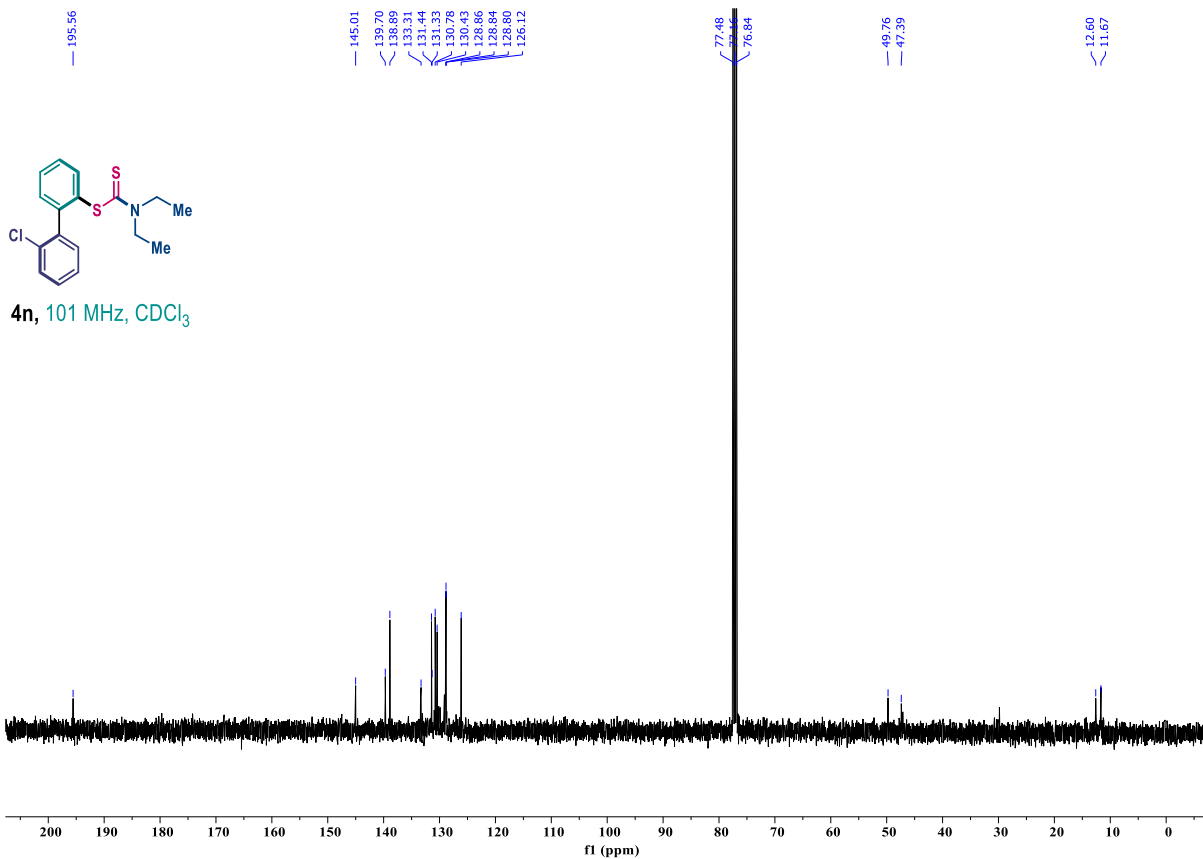
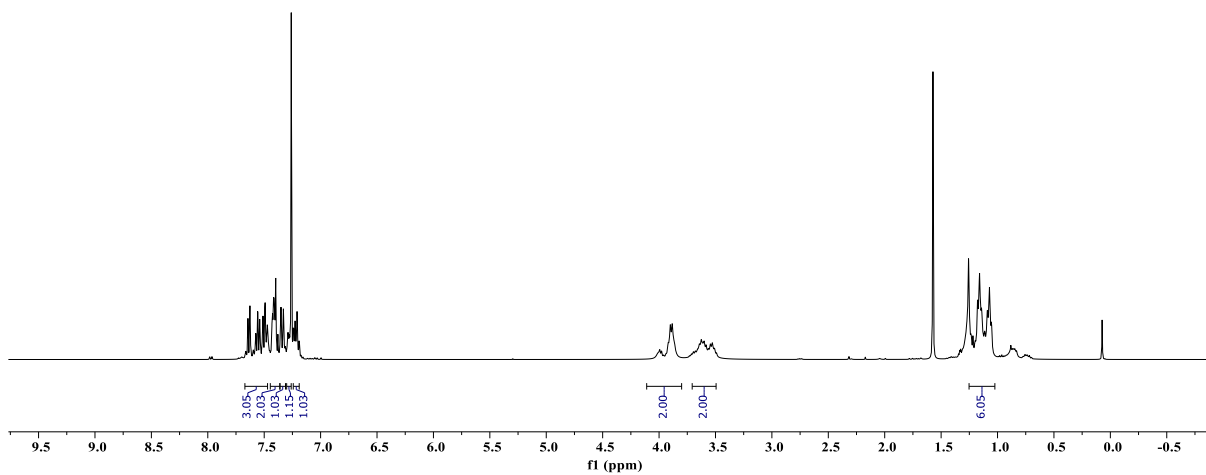
(1.0:1.0 ratio of rotamer for minor isomer)

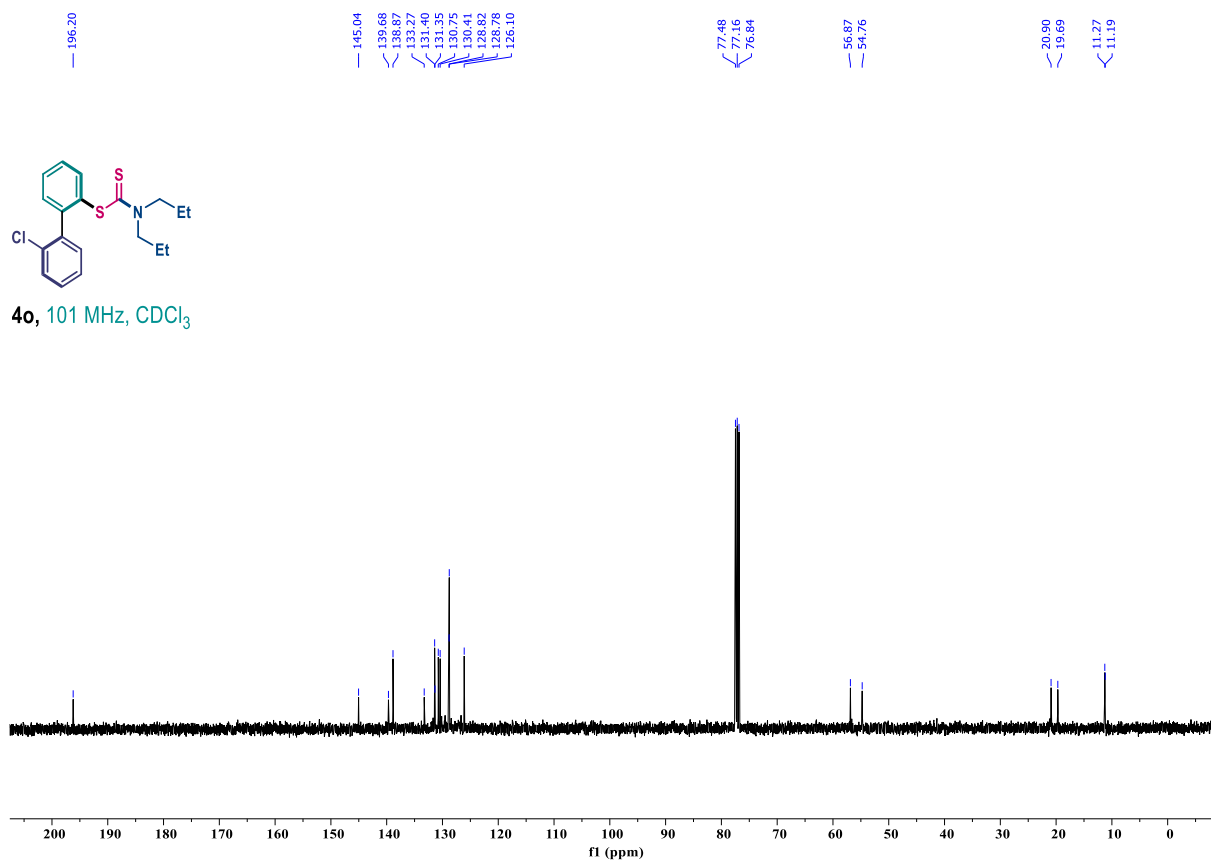
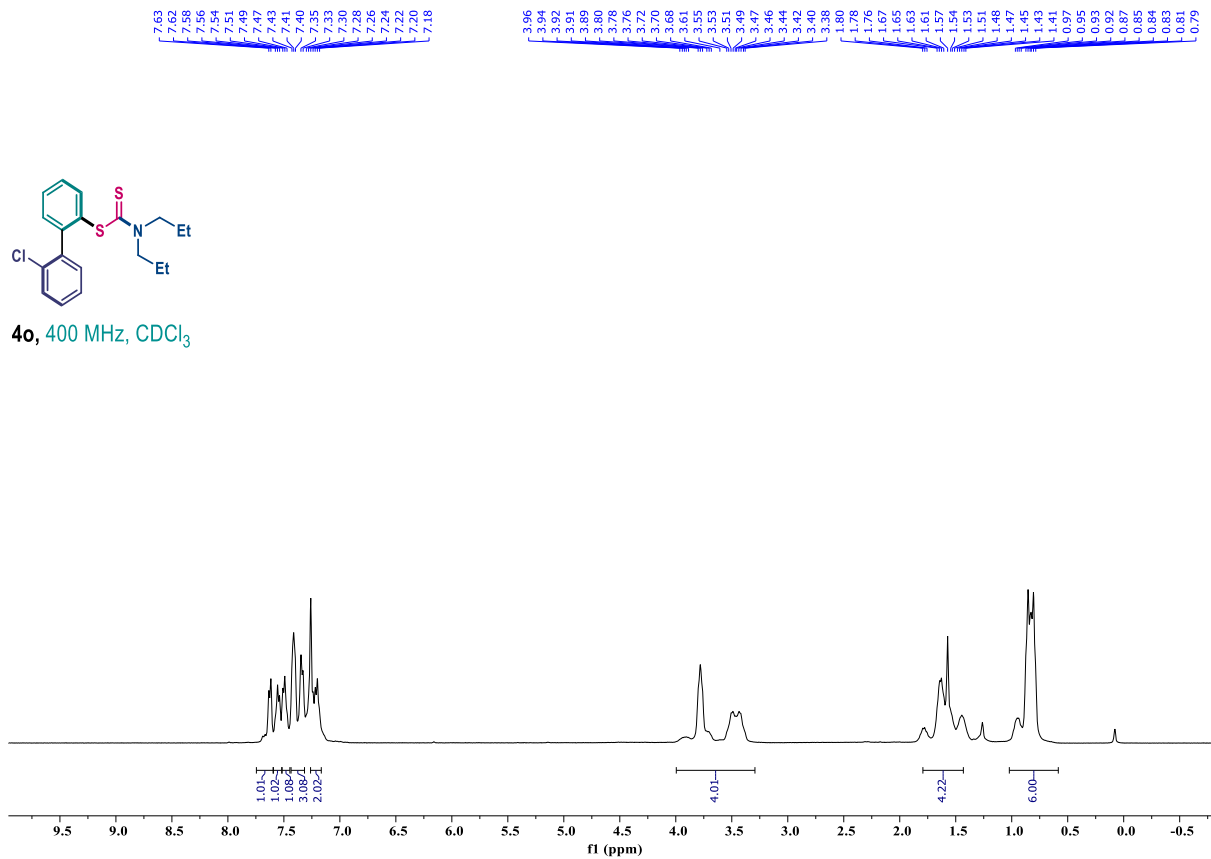


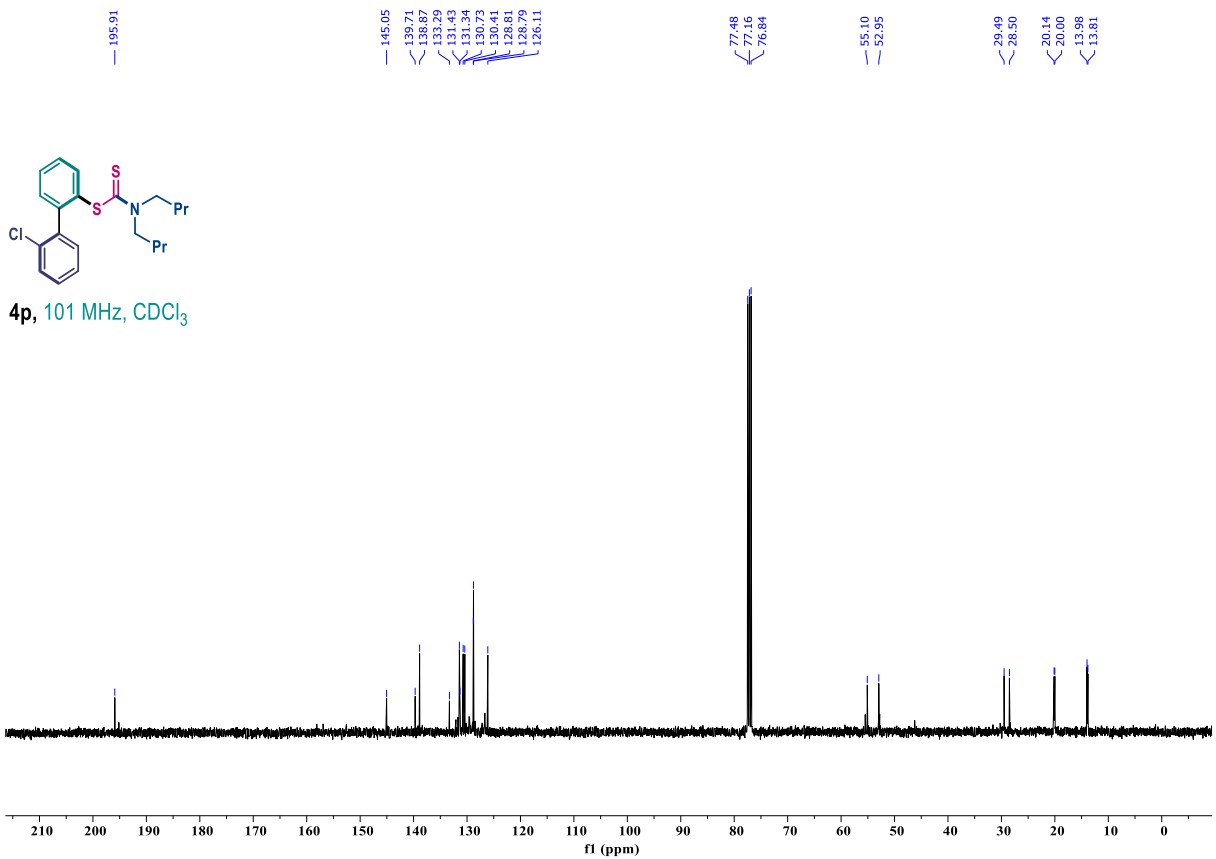
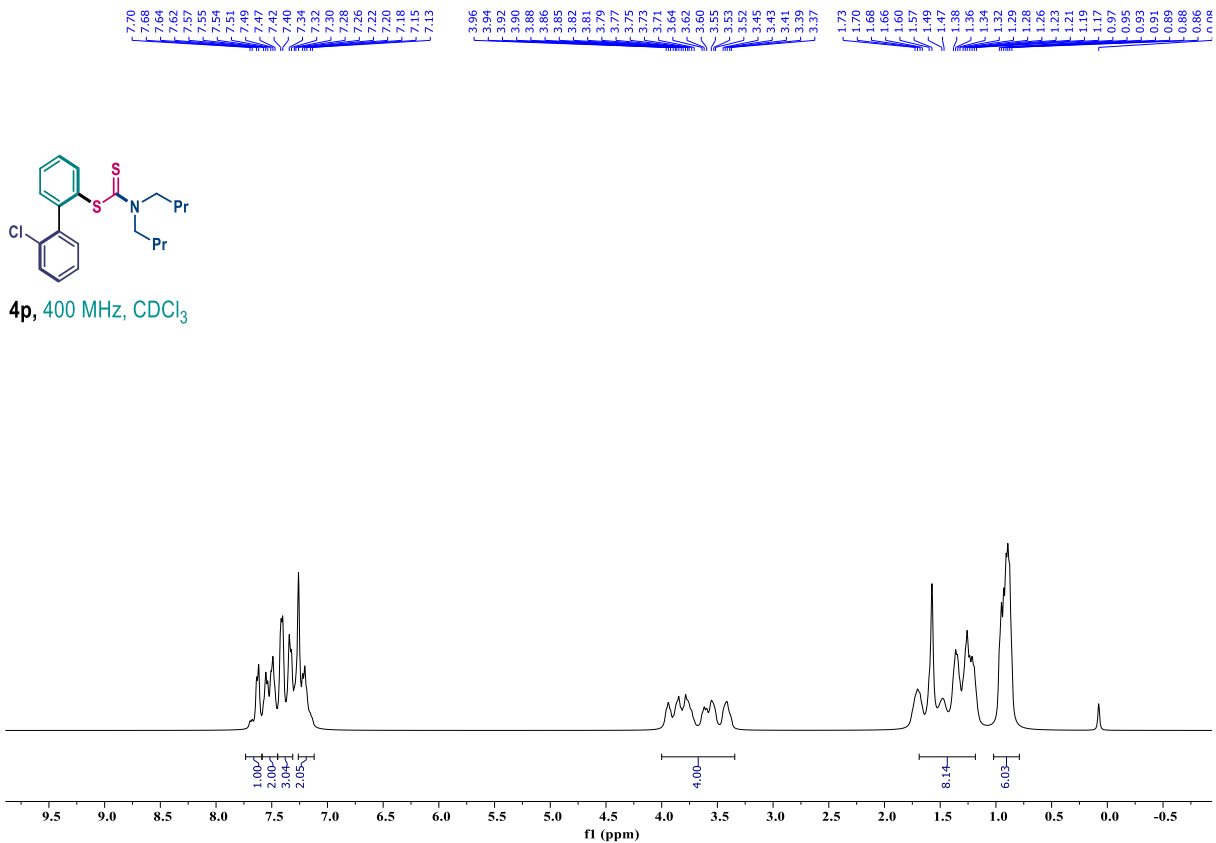
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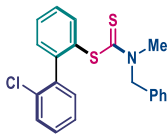
4n, 400 MHz, CDCl₃



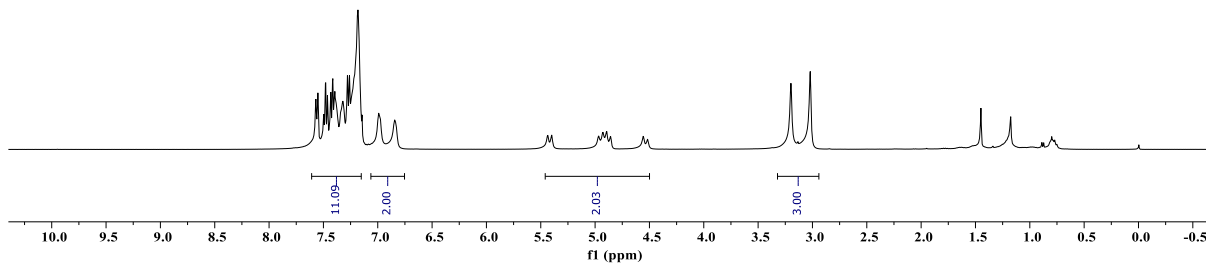




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4q, 400 MHz, CDCl₃
(1.1:1.0 ratio of rotamer)



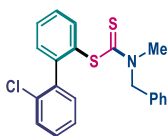
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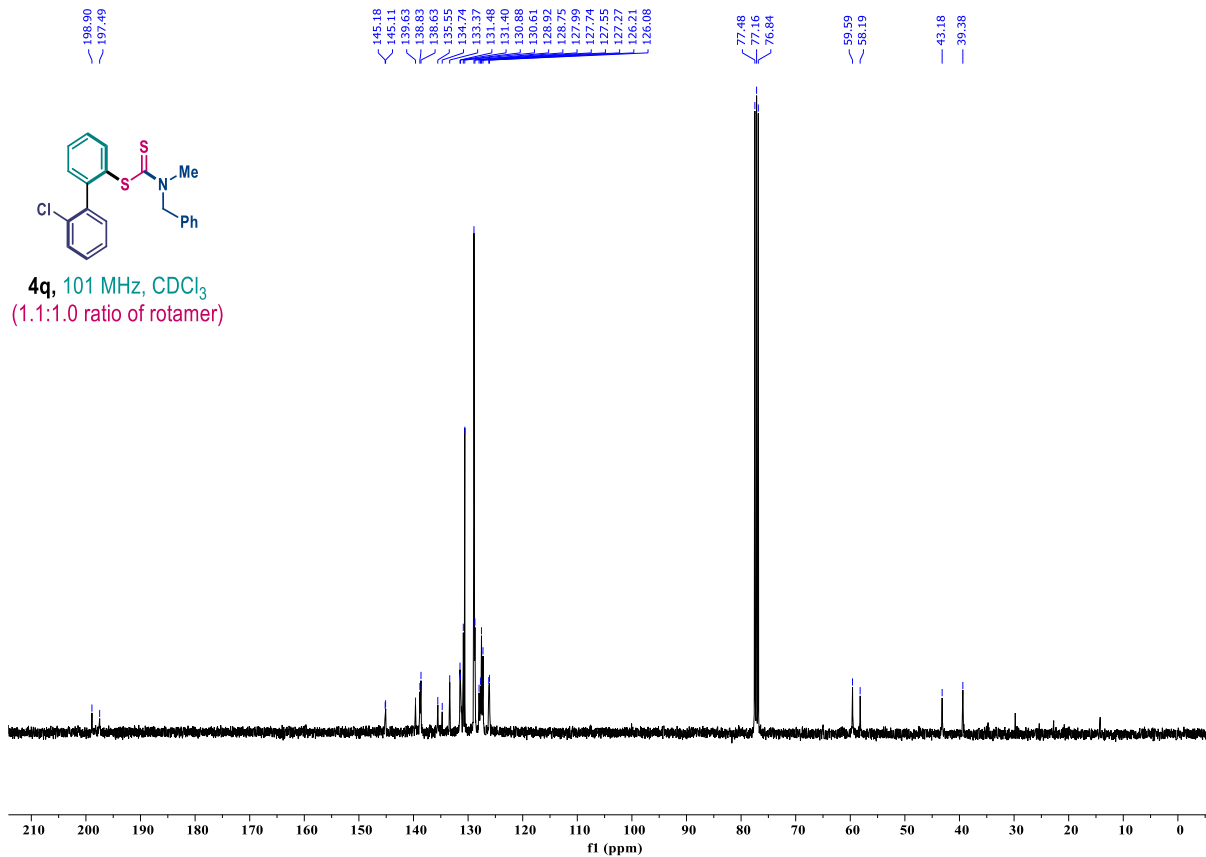
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77.16
76.84

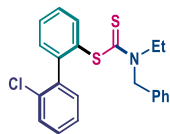
59.59
58.19

43.18
39.38

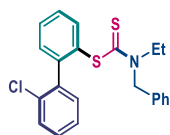
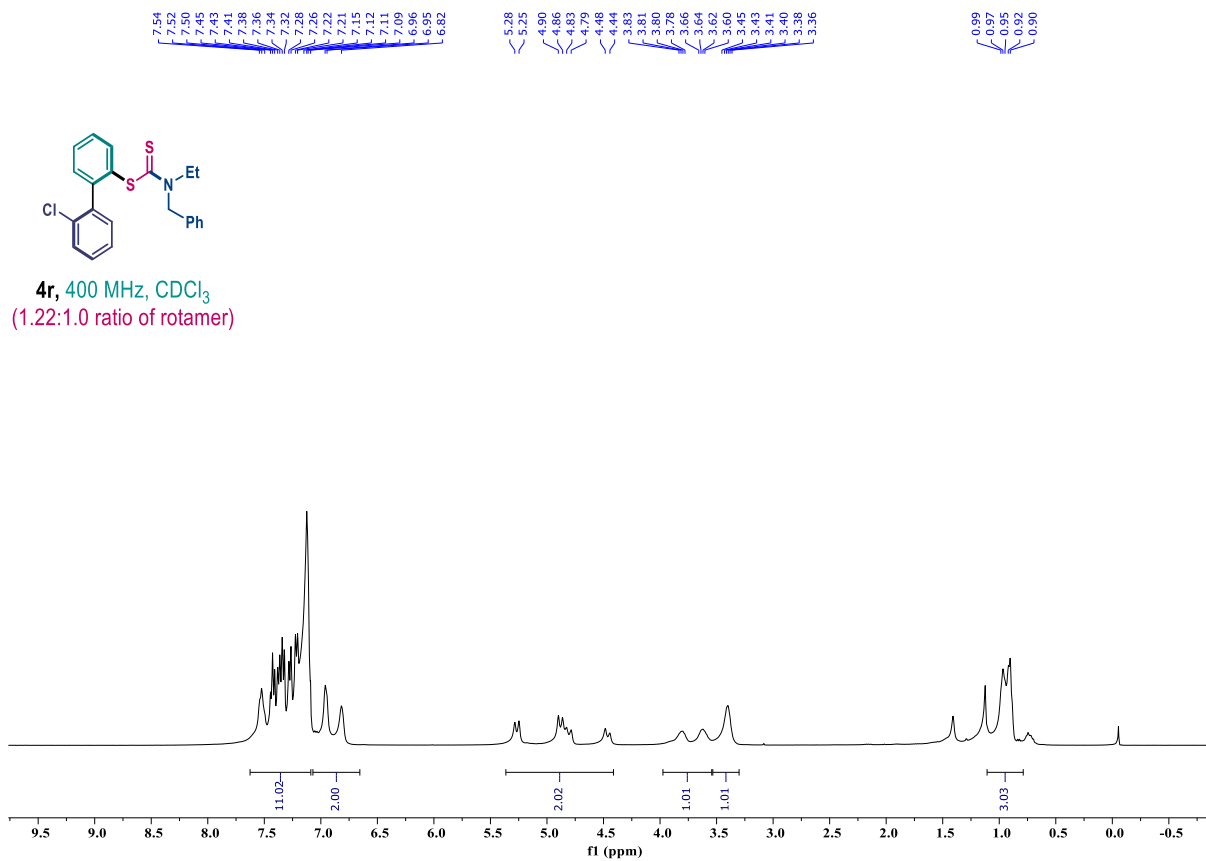


4q, 101 MHz, CDCl₃
(1.1:1.0 ratio of rotamer)

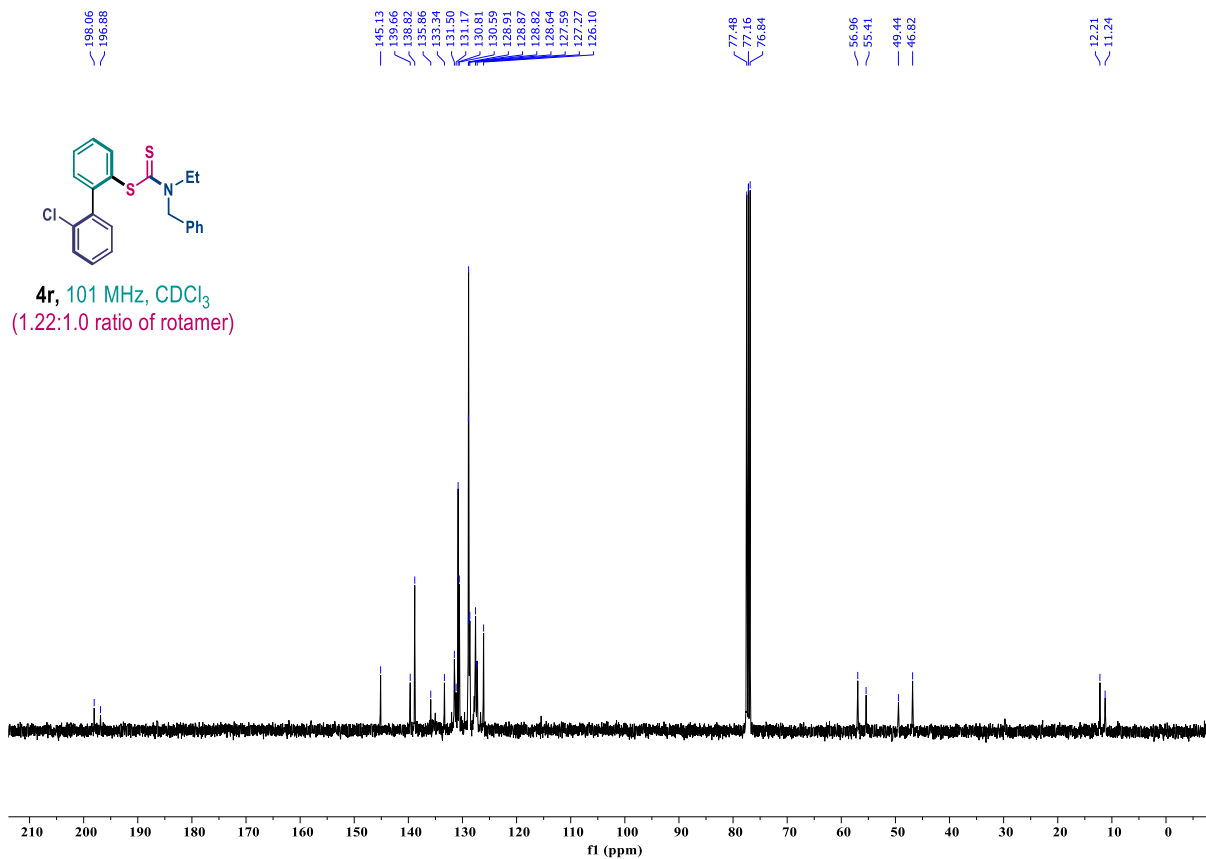


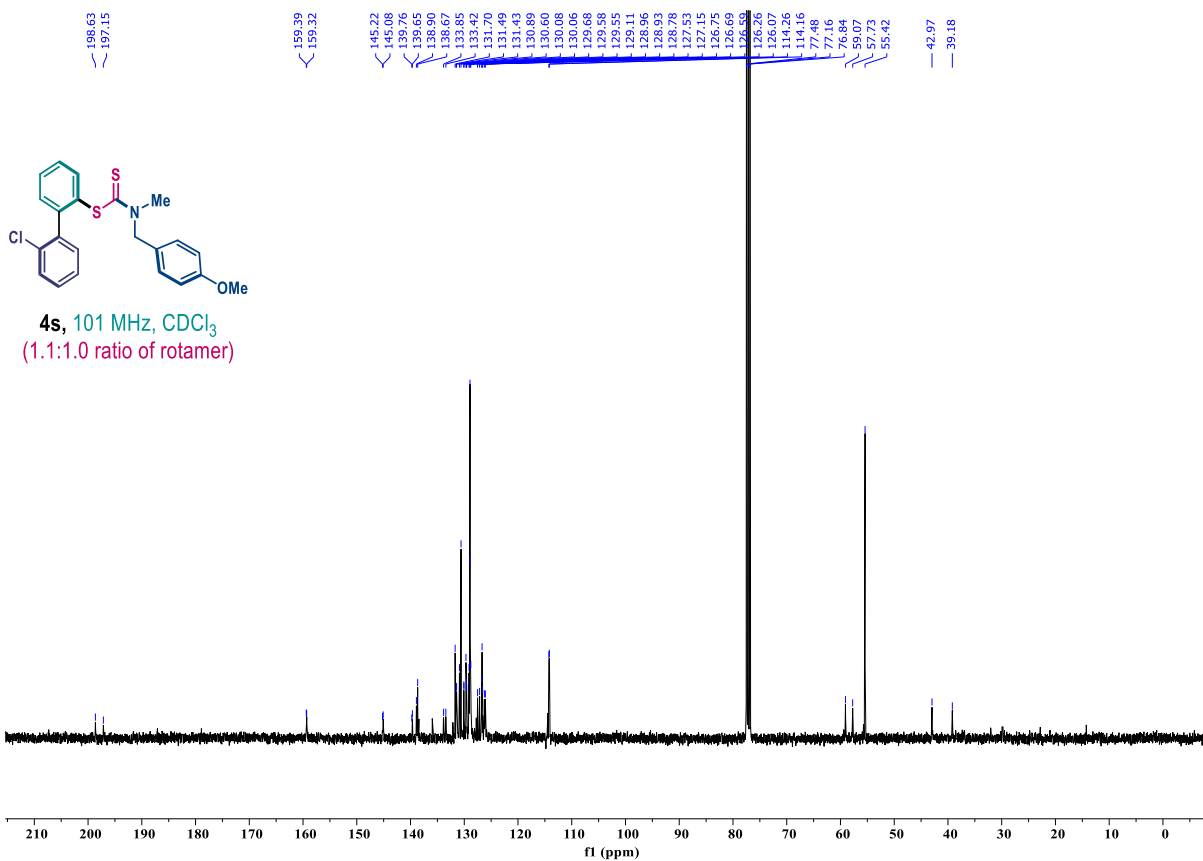
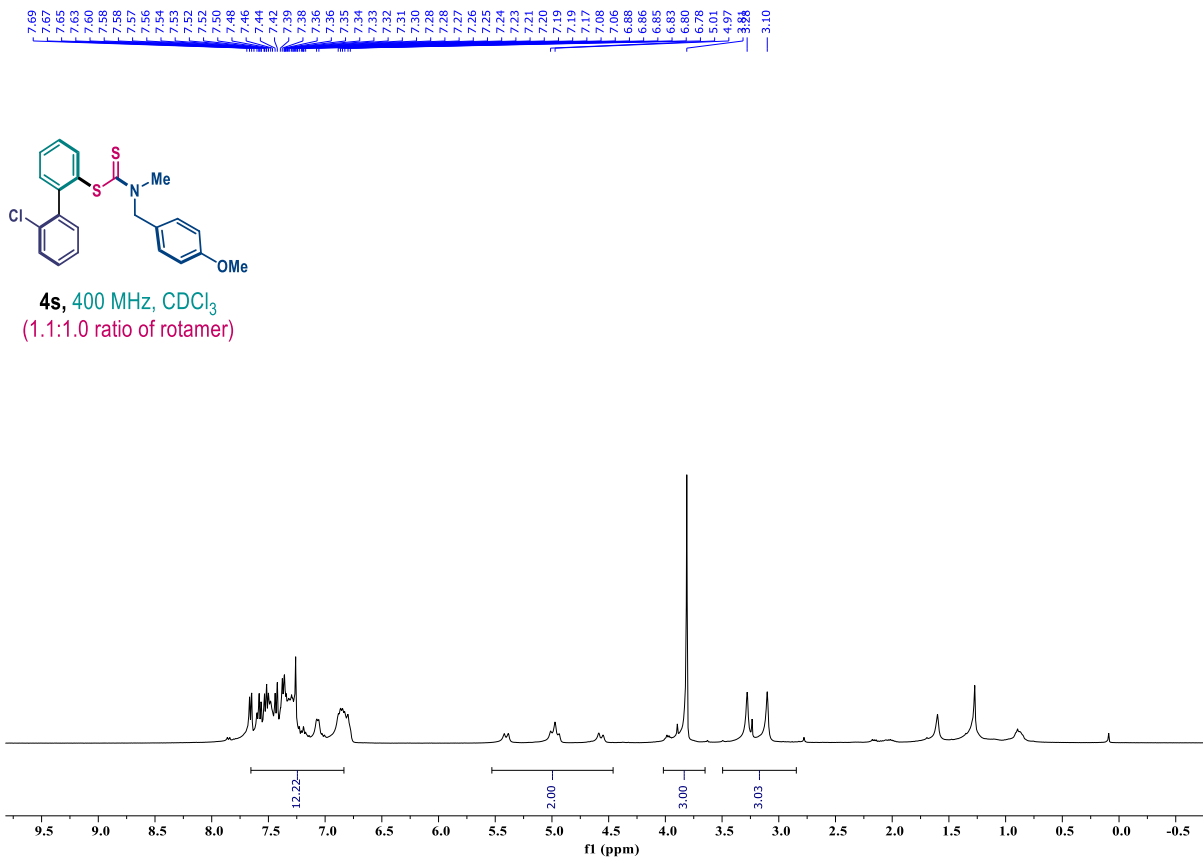


4r, 400 MHz, CDCl₃
(1.22:1.0 ratio of rotamer)

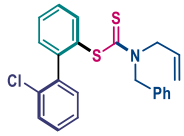


4r, 101 MHz, CDCl₃
(1.22:1.0 ratio of rotamer)

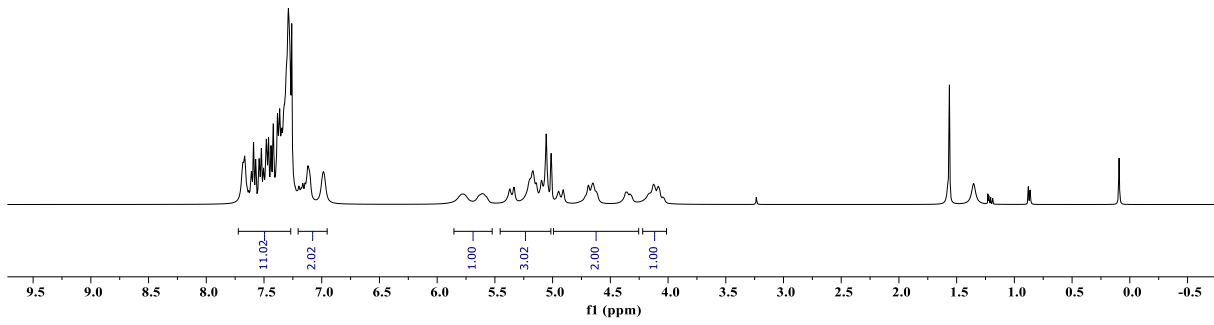




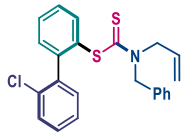
7.69
7.67
7.61
7.59
7.57
7.54
7.52
7.50
7.48
7.46
7.44
7.43
7.36
7.35
7.33
7.31
7.29
7.28
7.26
7.24
7.15
7.12
7.10
6.99
6.98
5.78
5.75
5.64
5.61
5.59
5.58
5.57
5.37
5.33
5.20
5.17
5.14
5.10
5.06
5.01
4.95
4.91
4.80
4.72
4.69
4.65
4.62
4.61
4.37
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4.31
4.17
4.13
4.12
4.09
4.07
4.05
4.03



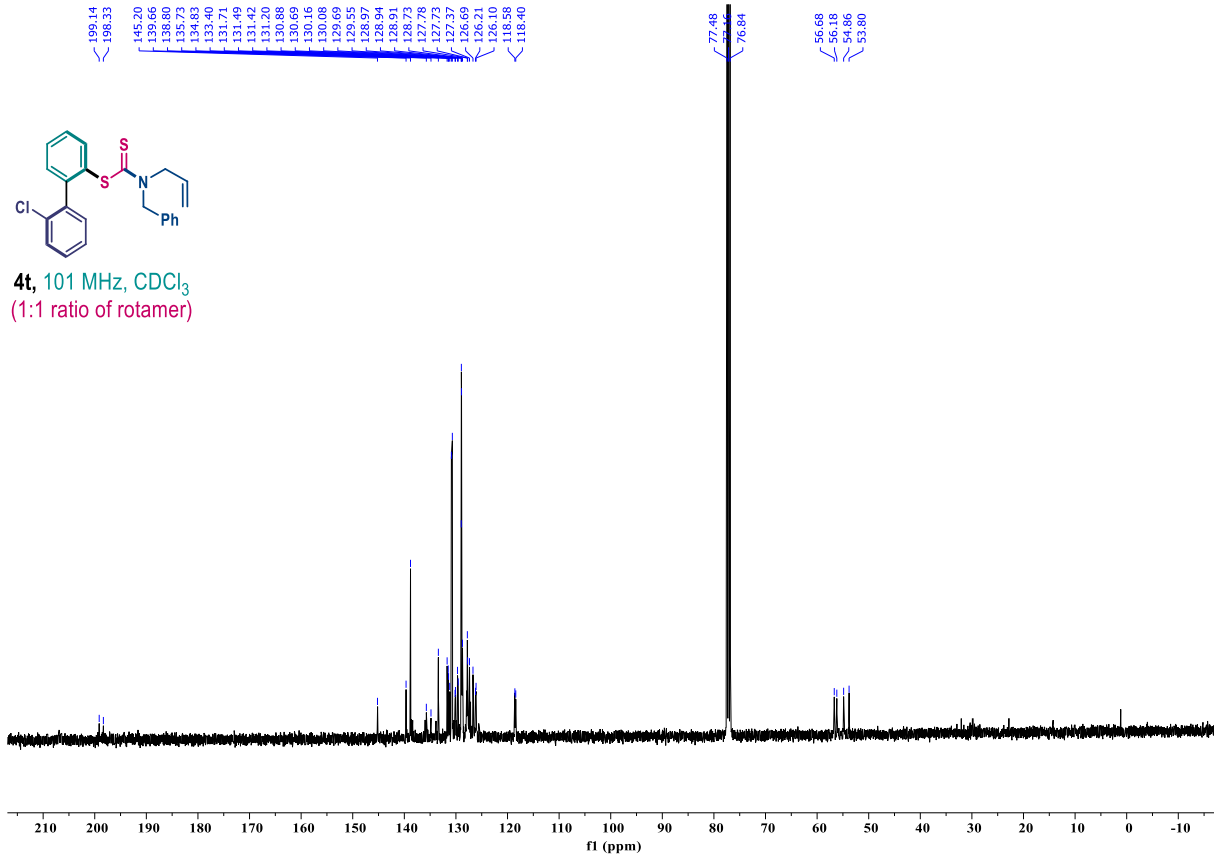
4t, 400 MHz, CDCl₃
(1:1 ratio of rotamer)

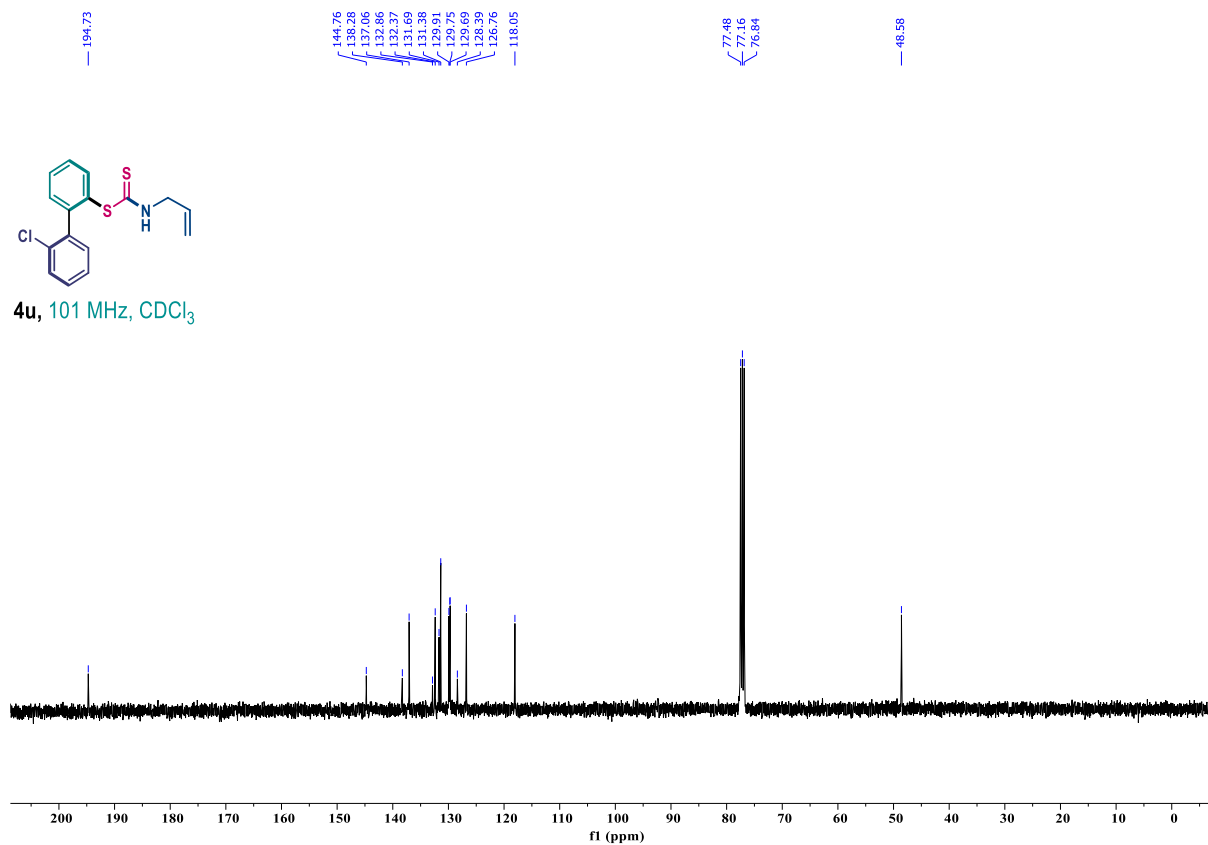
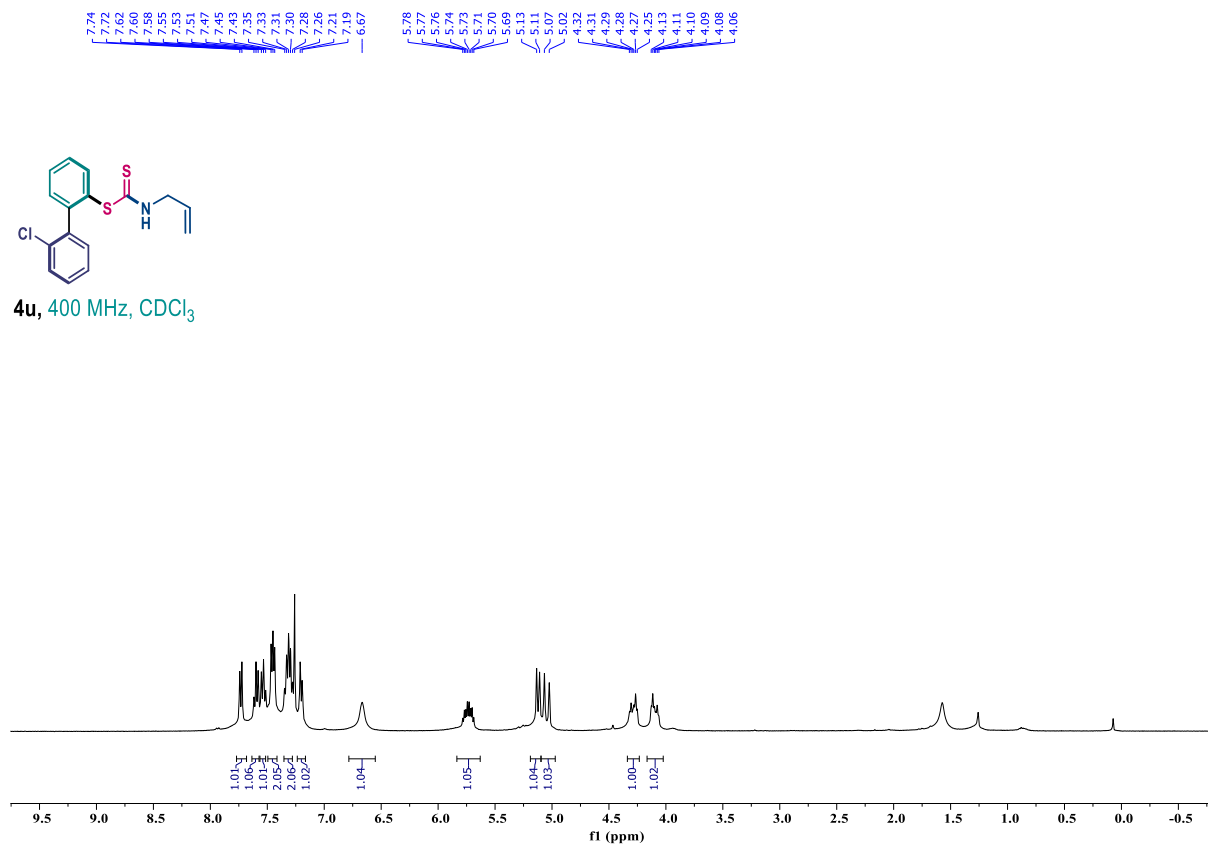


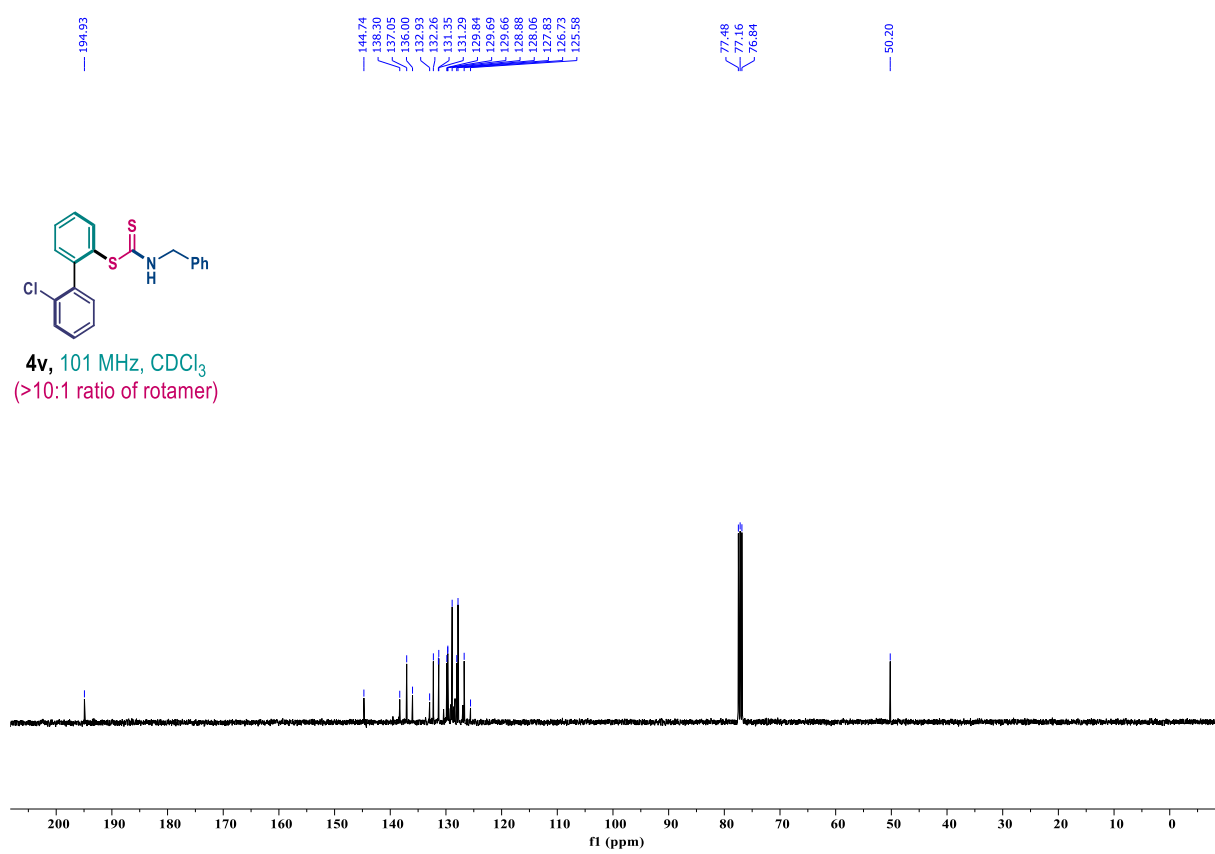
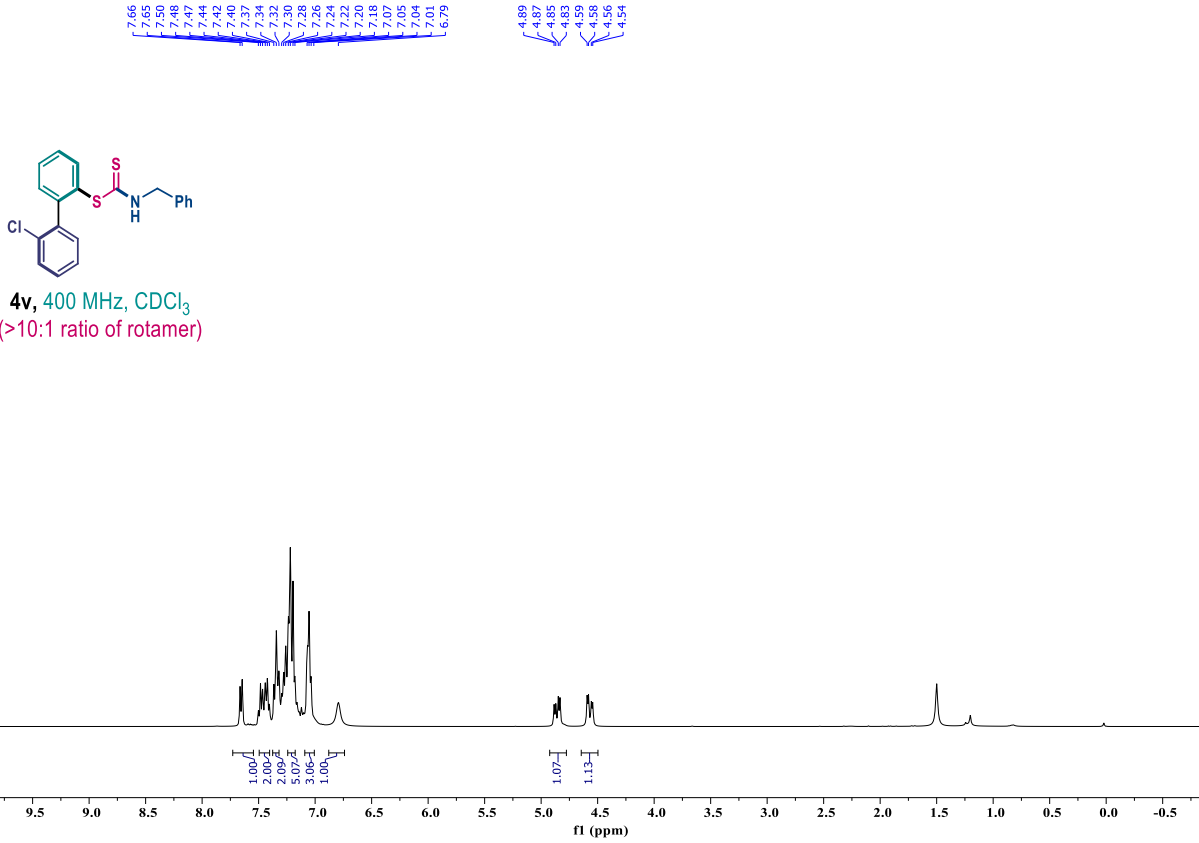
199.14
196.33
145.20
139.66
138.60
138.43
133.40
131.71
131.49
131.42
131.20
130.88
130.69
130.16
130.08
129.69
129.55
128.97
128.94
128.91
128.73
127.78
127.73
127.72
126.69
126.21
126.10
118.58
118.40



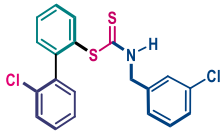
4t, 101 MHz, CDCl₃
(1:1 ratio of rotamer)



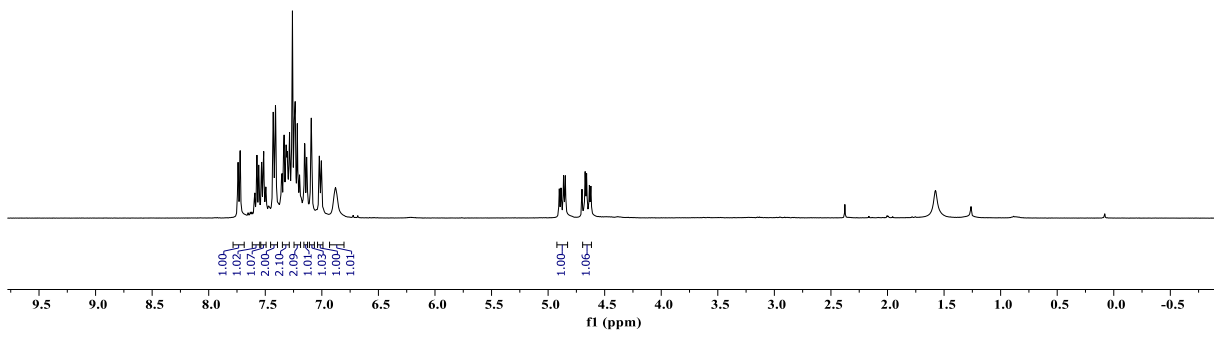




7.74
7.72
7.60
7.59
7.57
7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.43
7.43
7.42
7.41
7.41
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.22
7.20
7.20
7.15
7.14
7.13
7.09
7.02
7.00
6.88
4.90
4.88
4.85
4.70
4.69
4.67
4.64
4.62



4w, 400 MHz, CDCl₃

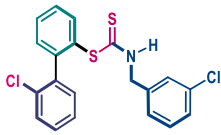


195.42

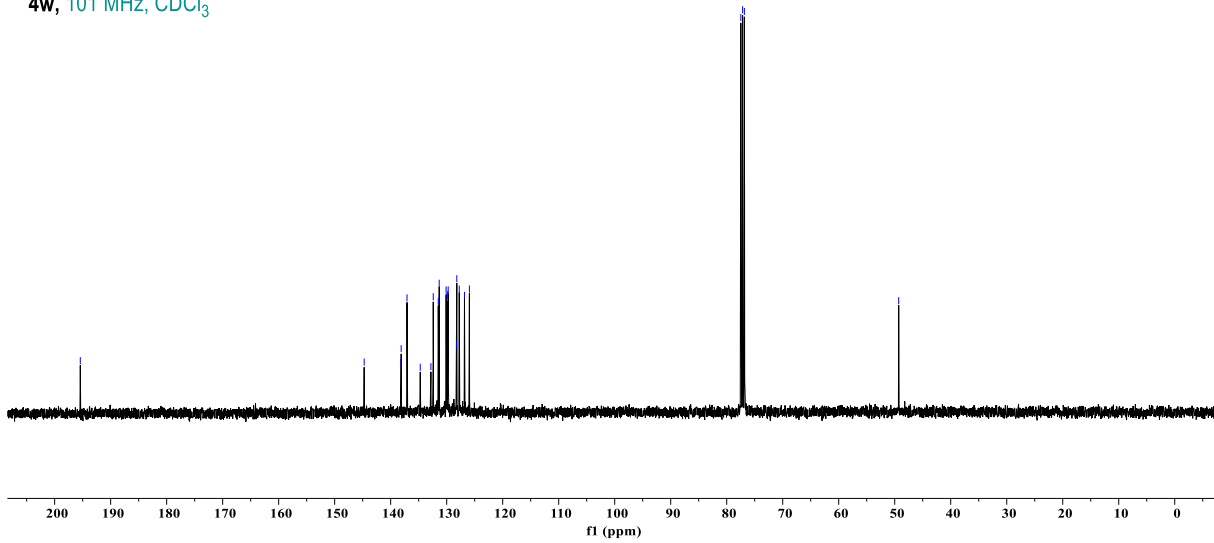
144.73
138.17
138.13
137.08
136.72
132.82
132.40
131.50
131.33
130.10
129.95
129.80
129.73
128.22
127.66
127.75
126.82
125.94

77.48
77.16
76.84

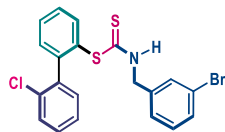
49.29



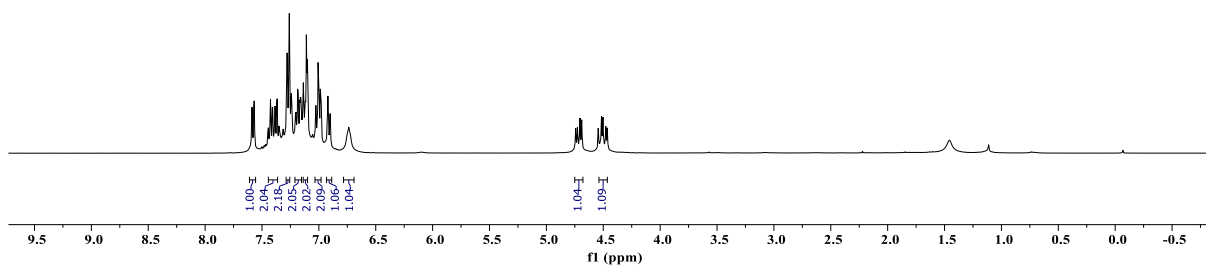
4w, 101 MHz, CDCl₃



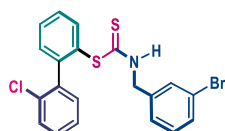
7.59
7.57
7.57
7.46
7.44
7.44
7.43
7.42
7.41
7.41
7.38
7.37
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7.35
7.35
7.28
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7.26
7.26
7.24
7.24
7.21
7.21
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.12
7.11
7.10
7.10
7.04
7.03
7.03
7.01
7.00
7.00
6.99
6.98
6.98
6.98
6.92
6.90
6.75
6.74
6.74
6.72
6.72
4.74
4.73
4.70
4.69
4.69
4.54
4.53
4.52
4.50
4.48
4.46



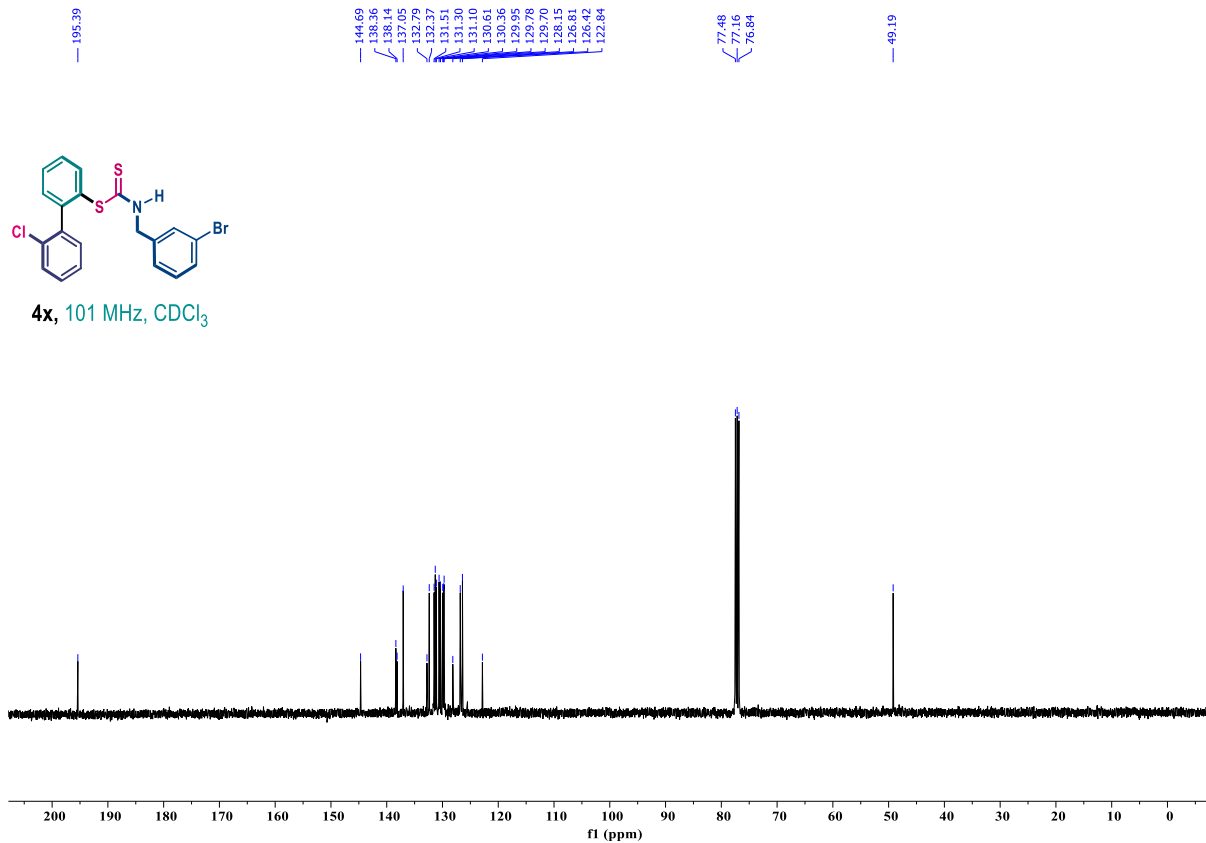
4x, 400 MHz, CDCl₃

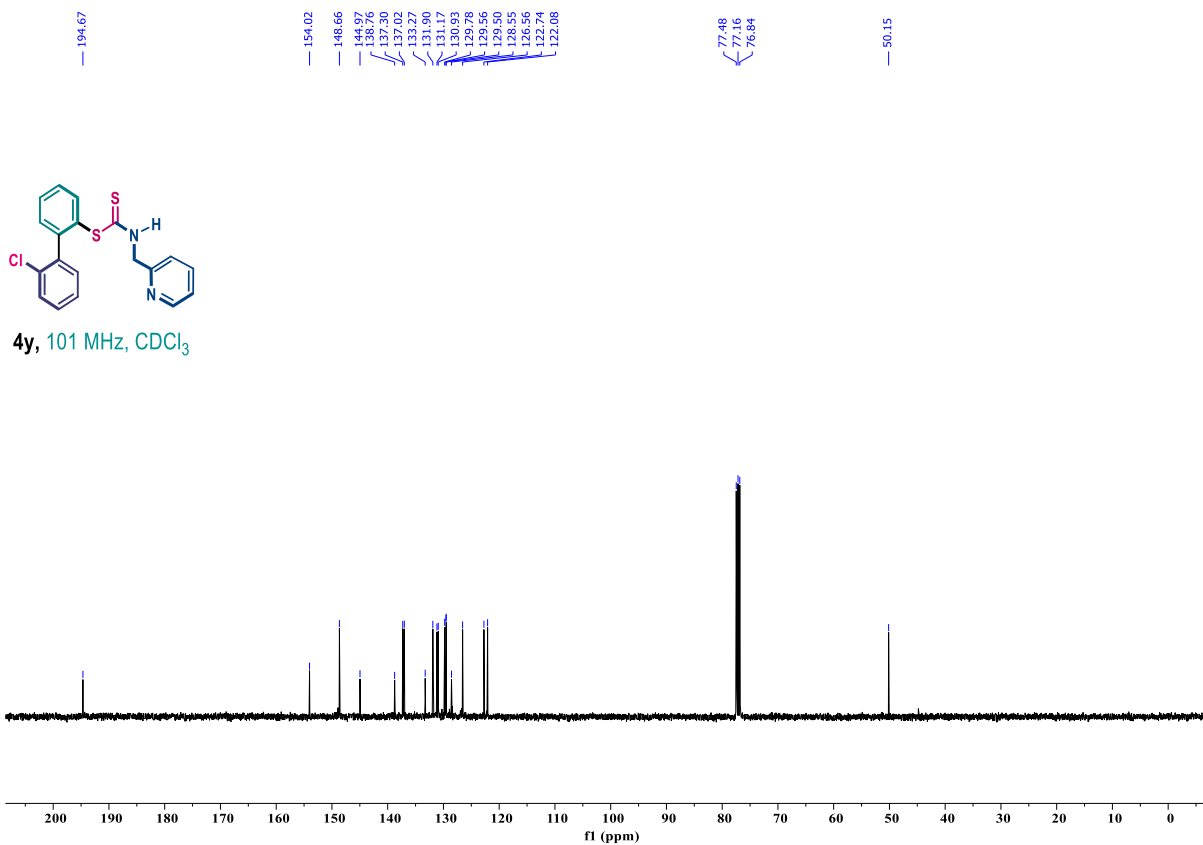
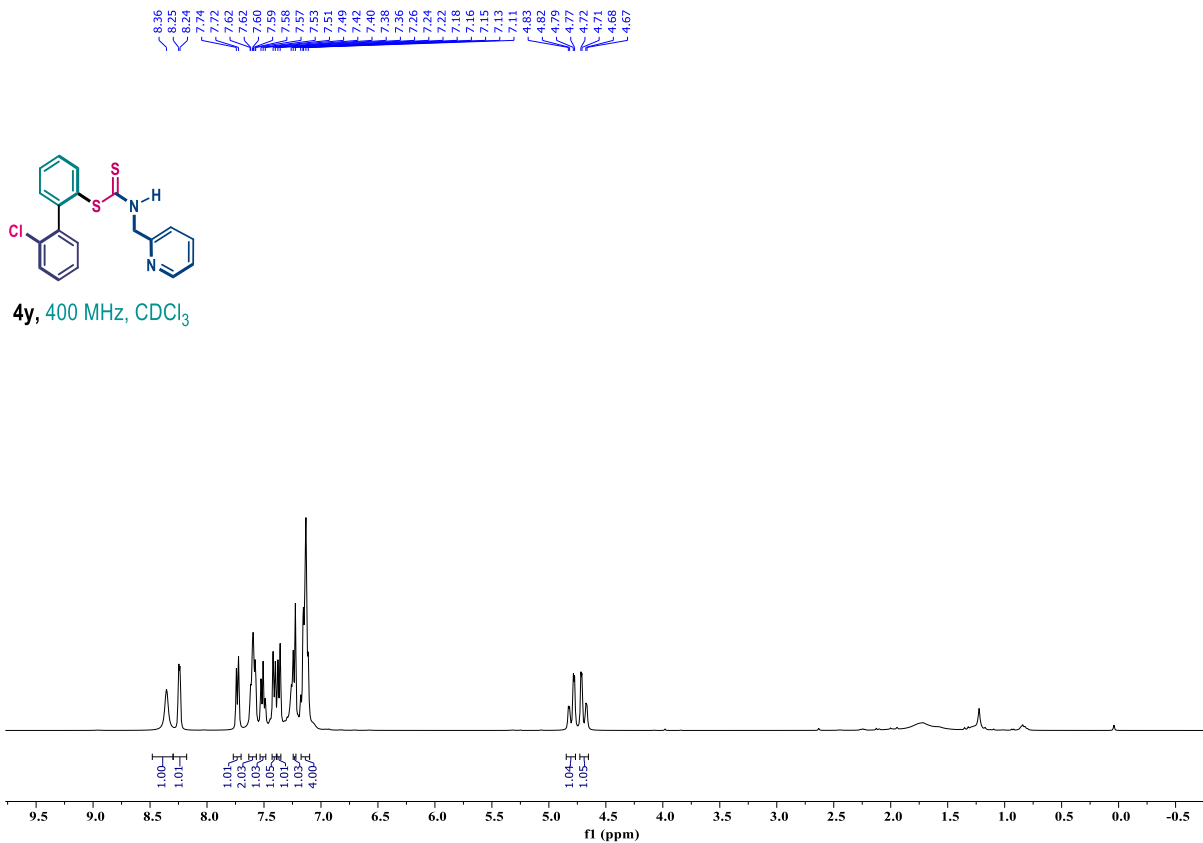


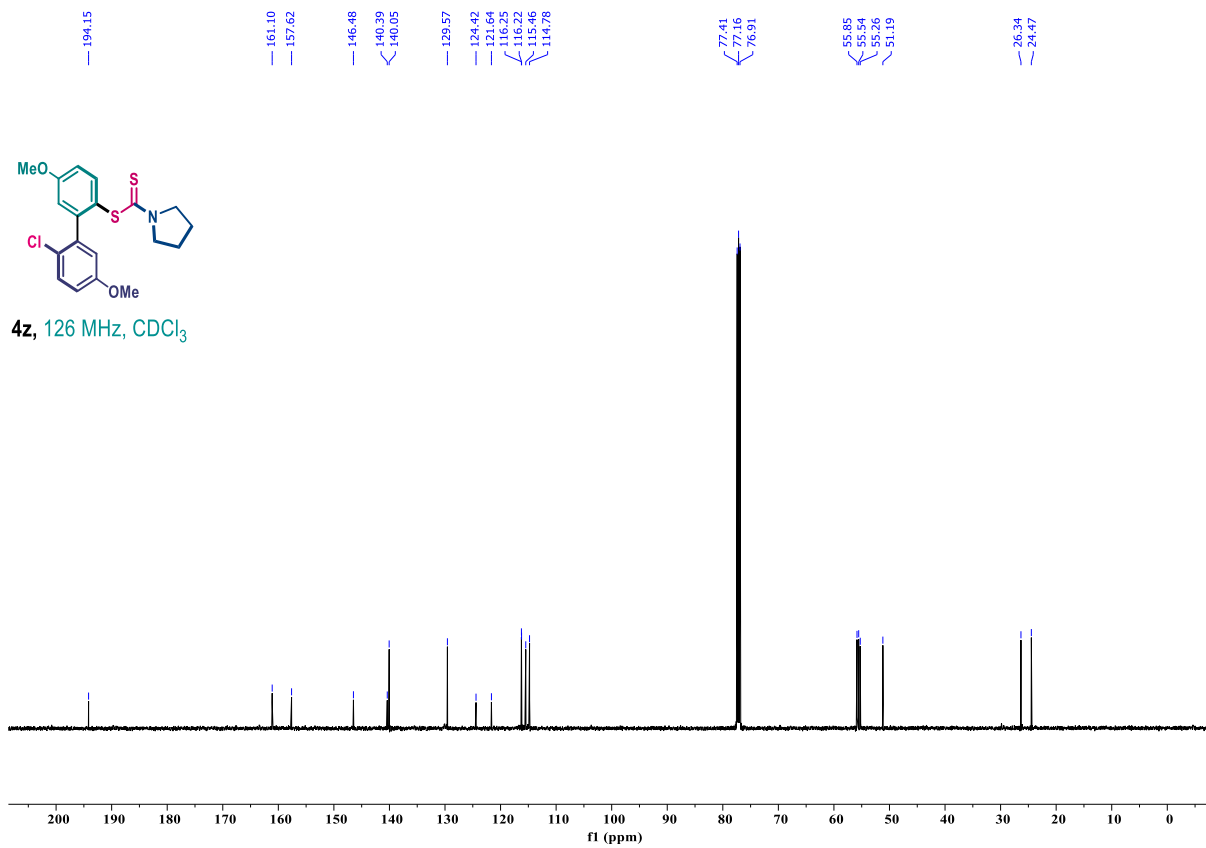
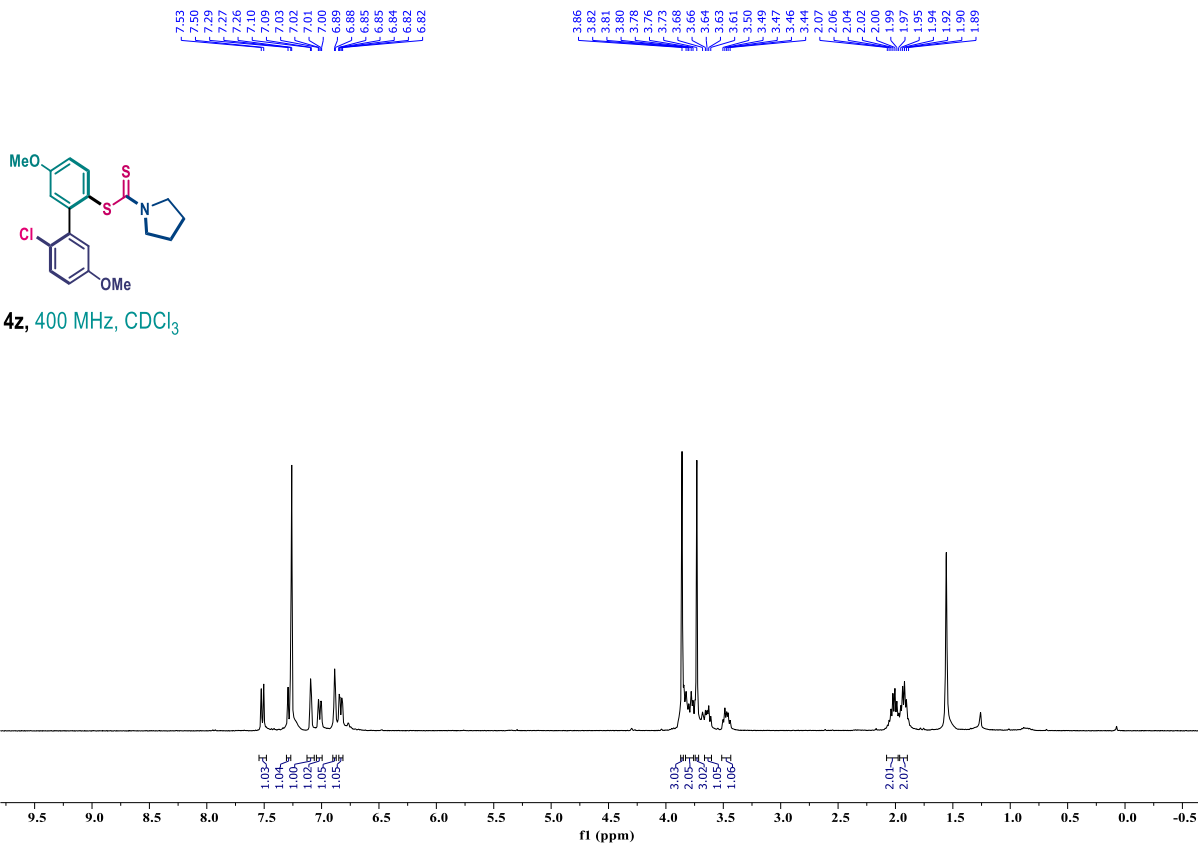
195.39

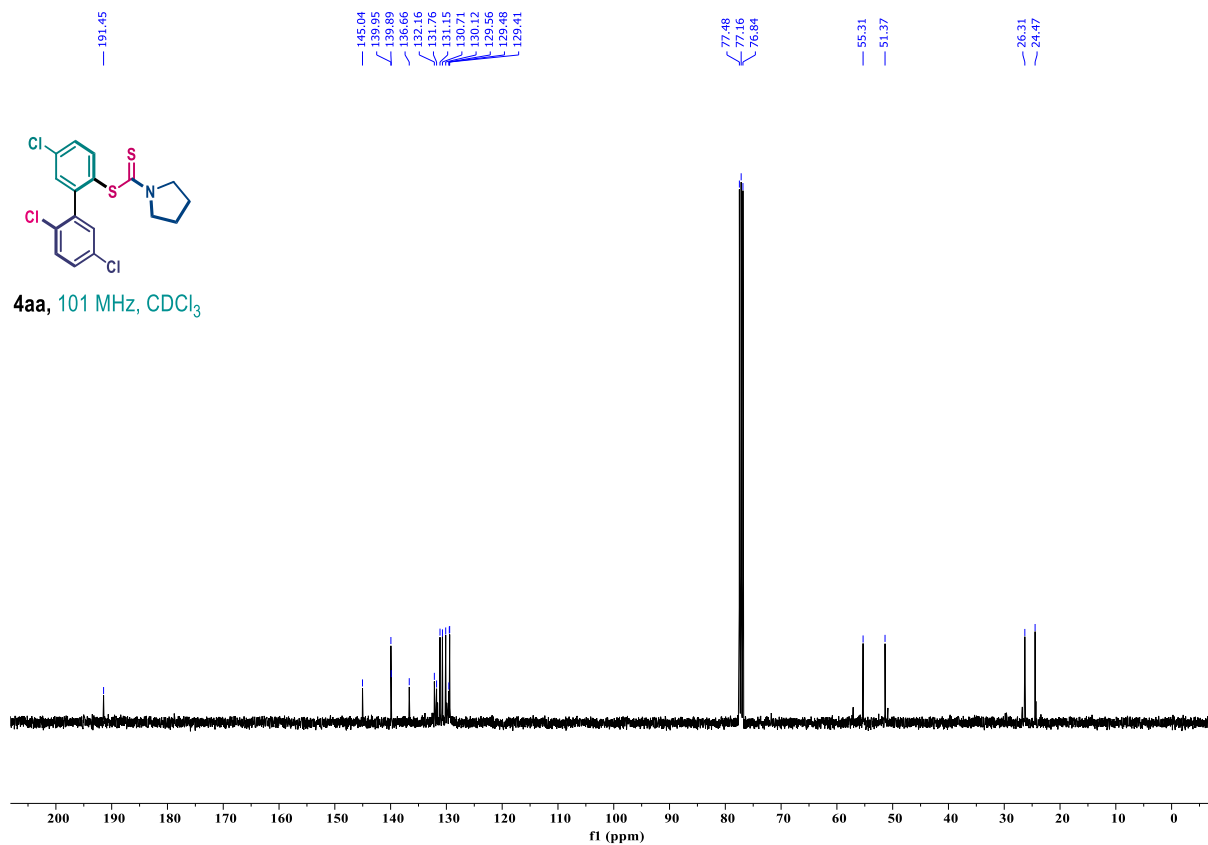
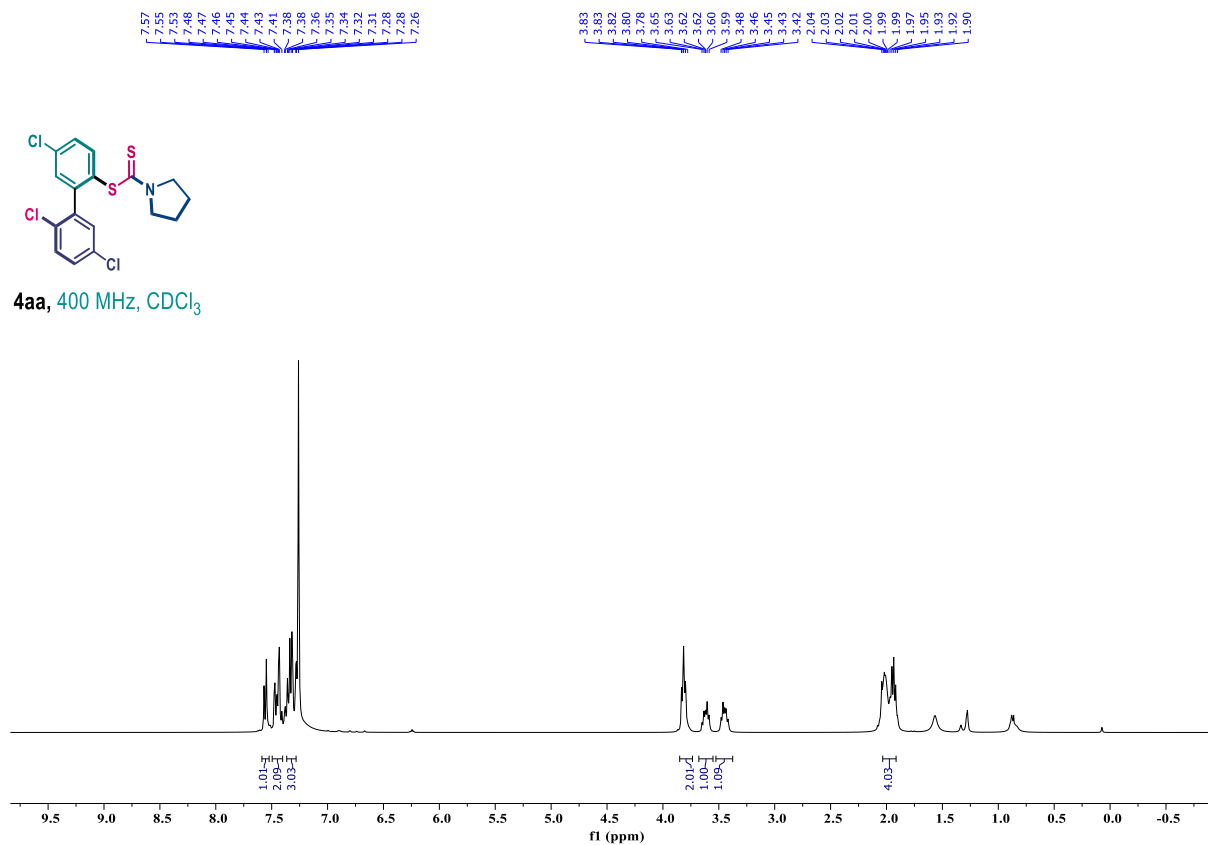


4x, 101 MHz, CDCl₃

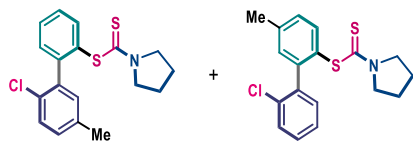




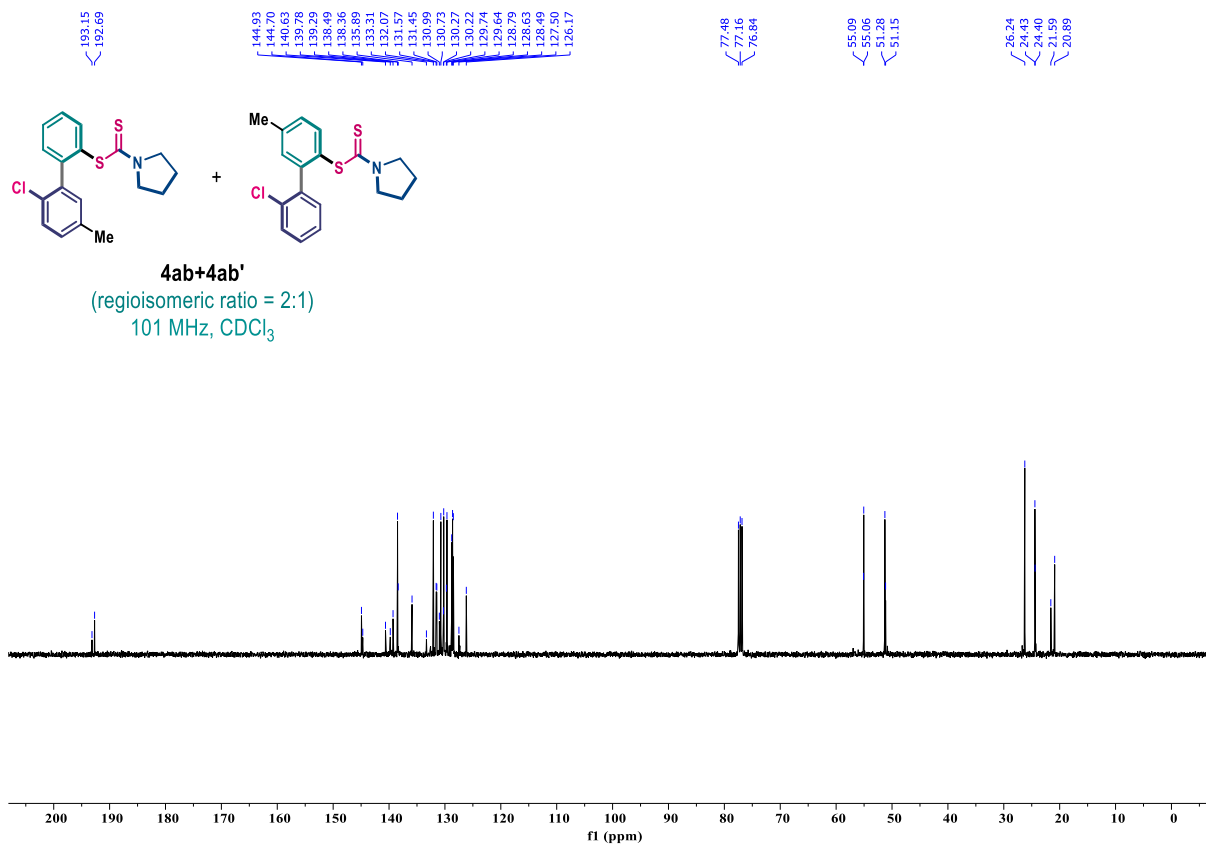
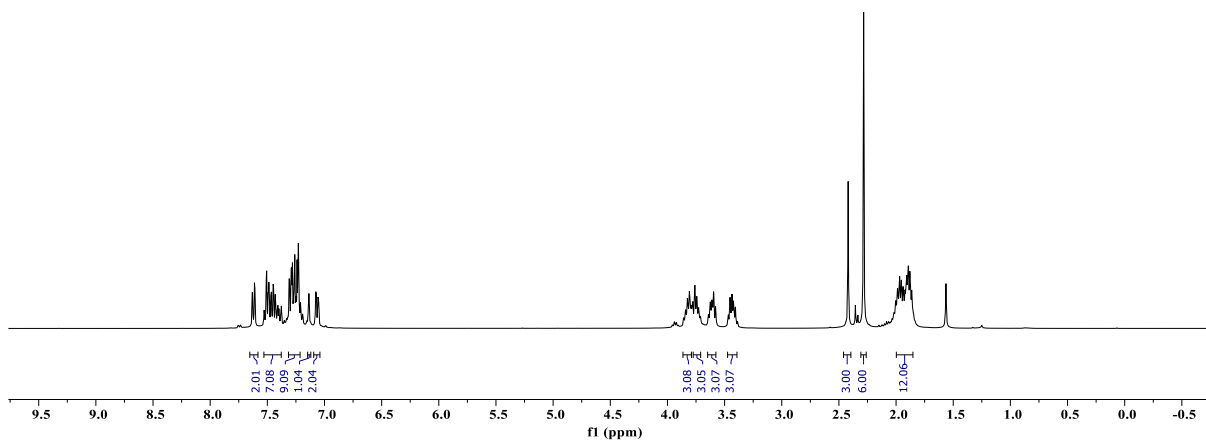




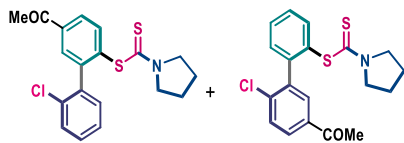
7.63
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7.61
7.52
7.52
7.51
7.49
7.49
7.48
7.47
7.46
7.45
7.45
7.43
7.43
7.41
7.41
7.40
7.40
7.38
7.38
7.31
7.31
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.14
7.13
7.13
7.08
7.07
7.06
7.05
3.84
3.83
3.83
3.82
3.81
3.80
3.80
3.79
3.78
3.78
3.74
3.74
3.72
3.63
3.61
3.61
3.60
3.58
3.45
3.44
3.42
3.42
3.41
3.41
2.42
2.28
2.28
2.02
2.02
2.00
1.99
1.97
1.97
1.95
1.94
1.94
1.91
1.91
1.90
1.89
1.89
1.87
1.86
1.85



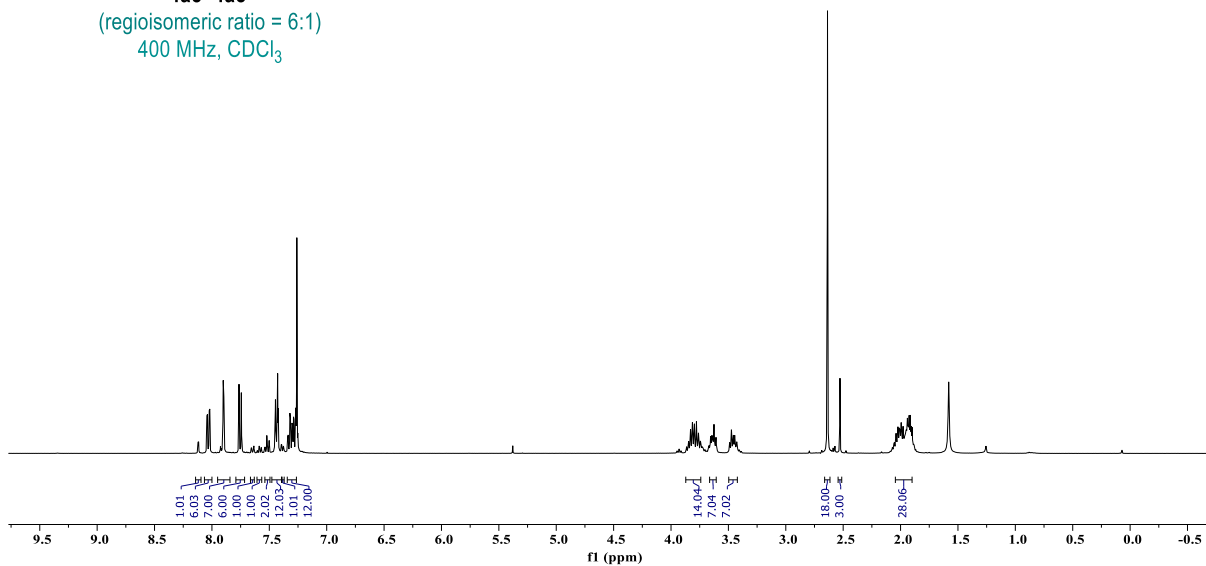
4ab+4ab'
(regioisomeric ratio = 2:1)
400 MHz, CDCl₃



8.12, 8.04, 8.04, 8.02, 7.90, 7.90, 7.76, 7.74, 7.52, 7.50, 7.45, 7.45, 7.00, 7.00, 7.00, 7.00, 7.43, 7.43, 7.42, 7.42, 7.40, 7.40, 7.34, 7.33, 7.32, 7.32, 7.30, 7.30, 7.29, 7.29, 7.27, 7.27, 7.26, 7.25, 7.25, 7.25, 3.85, 3.85, 3.81, 3.81, 3.80, 3.80, 3.78, 3.78, 3.76, 3.74, 3.74, 3.65, 3.65, 3.64, 3.64, 3.63, 3.61, 3.61, 3.49, 3.49, 3.49, 3.47, 3.46, 3.46, 3.44, 3.44, 3.43, 2.64, 2.53, 2.06, 2.06, 2.05, 2.04, 2.04, 2.03, 2.03, 2.02, 2.01, 2.00, 2.00, 1.99, 1.99, 1.98, 1.97, 1.97, 1.96, 1.96, 1.95, 1.95, 1.94, 1.94, 1.93, 1.92, 1.92, 1.91, 1.91, 1.89, 1.89, 1.88



4ac+4ac'
(regioisomeric ratio = 6:1)
400 MHz, CDCl₃



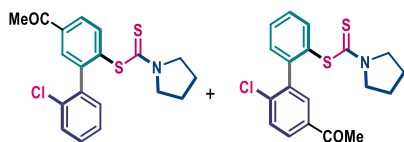
197.38
191.22

145.04
138.91
138.85
138.81
138.14
136.55
133.44
132.42
131.87
131.80
130.64
129.48
129.39
129.35
129.07
128.25
128.21
126.46

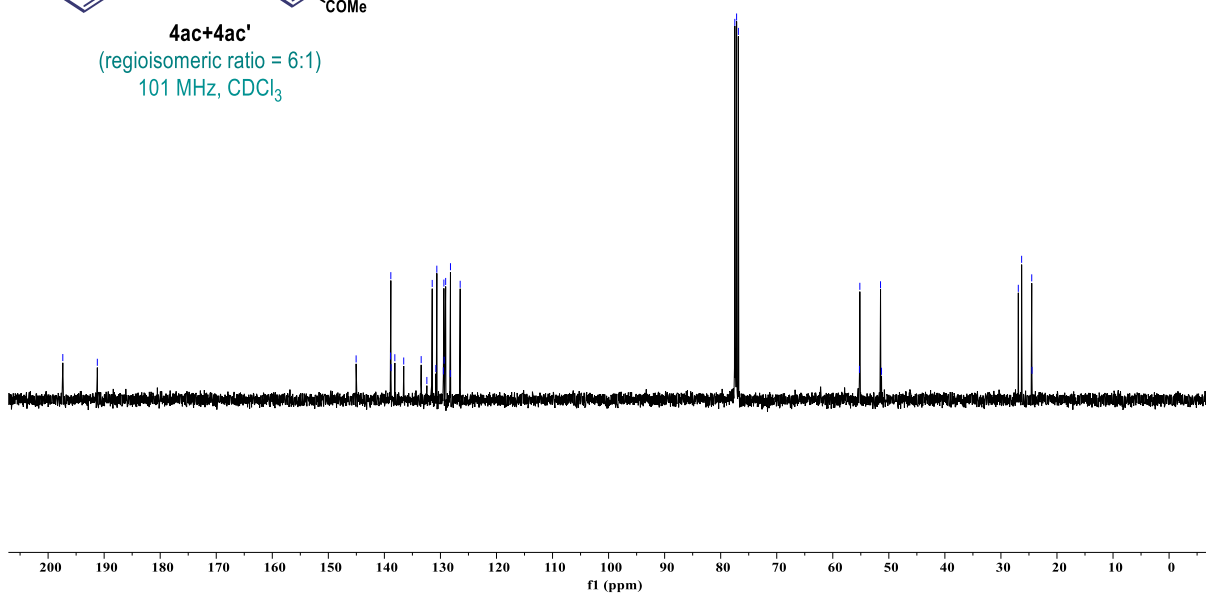
77.48
77.16
76.84

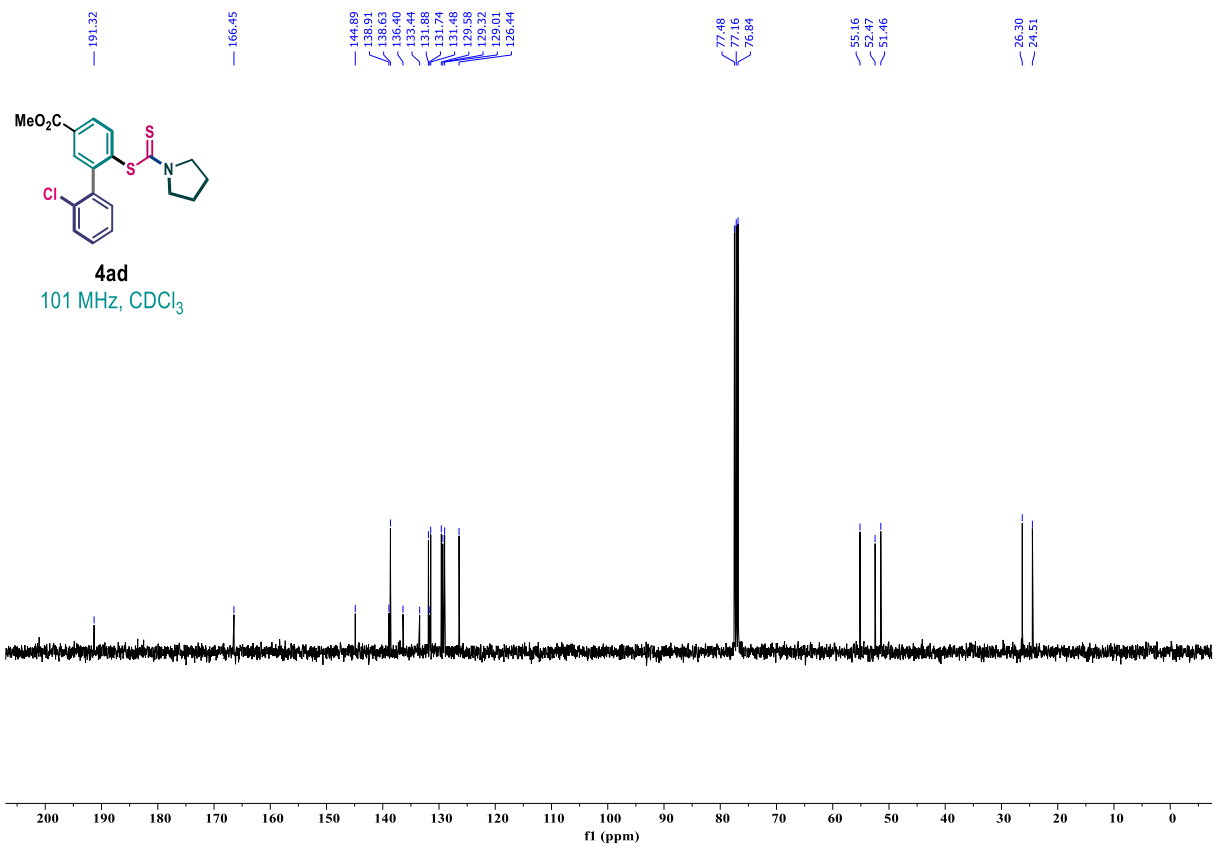
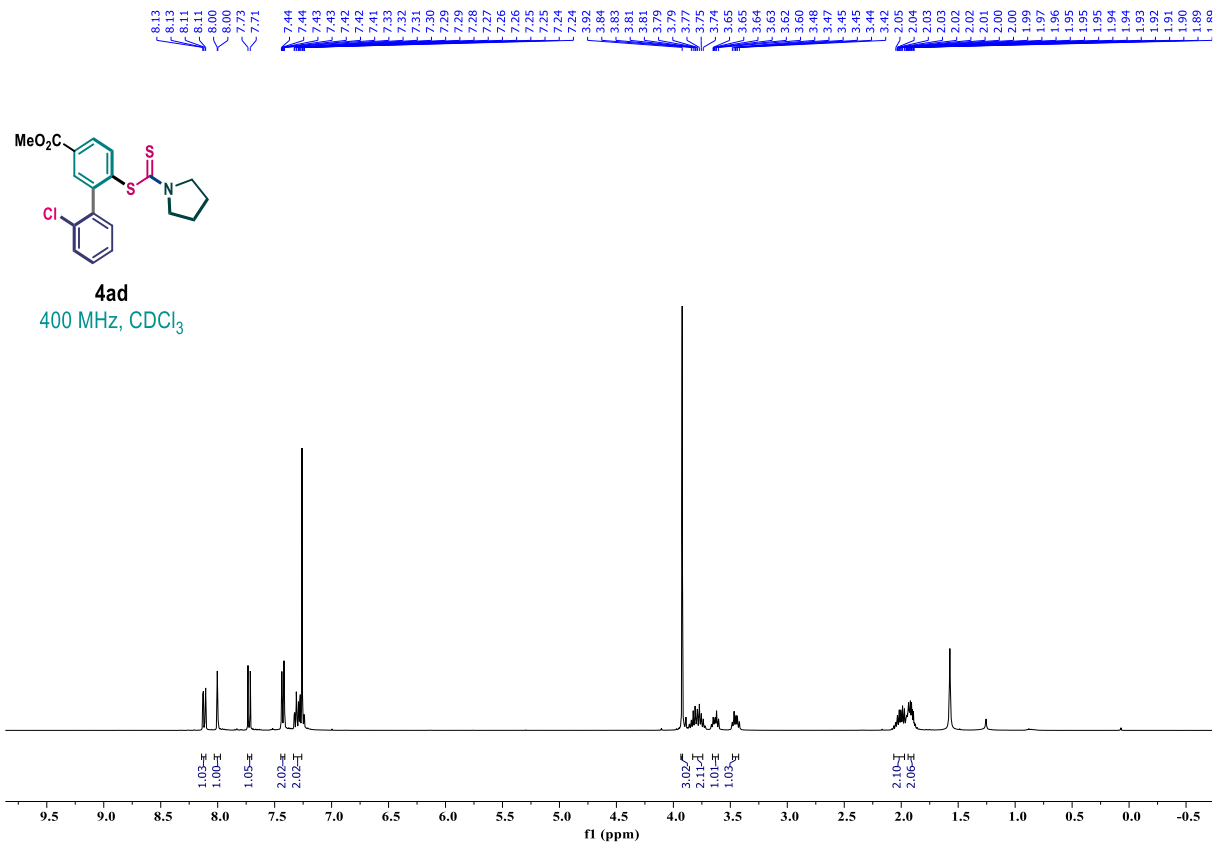
55.24
55.17
51.48
51.30

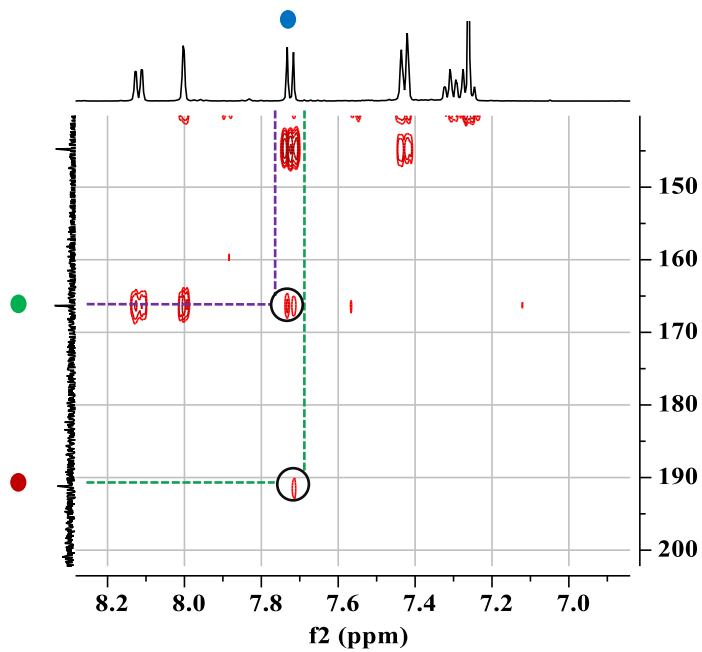
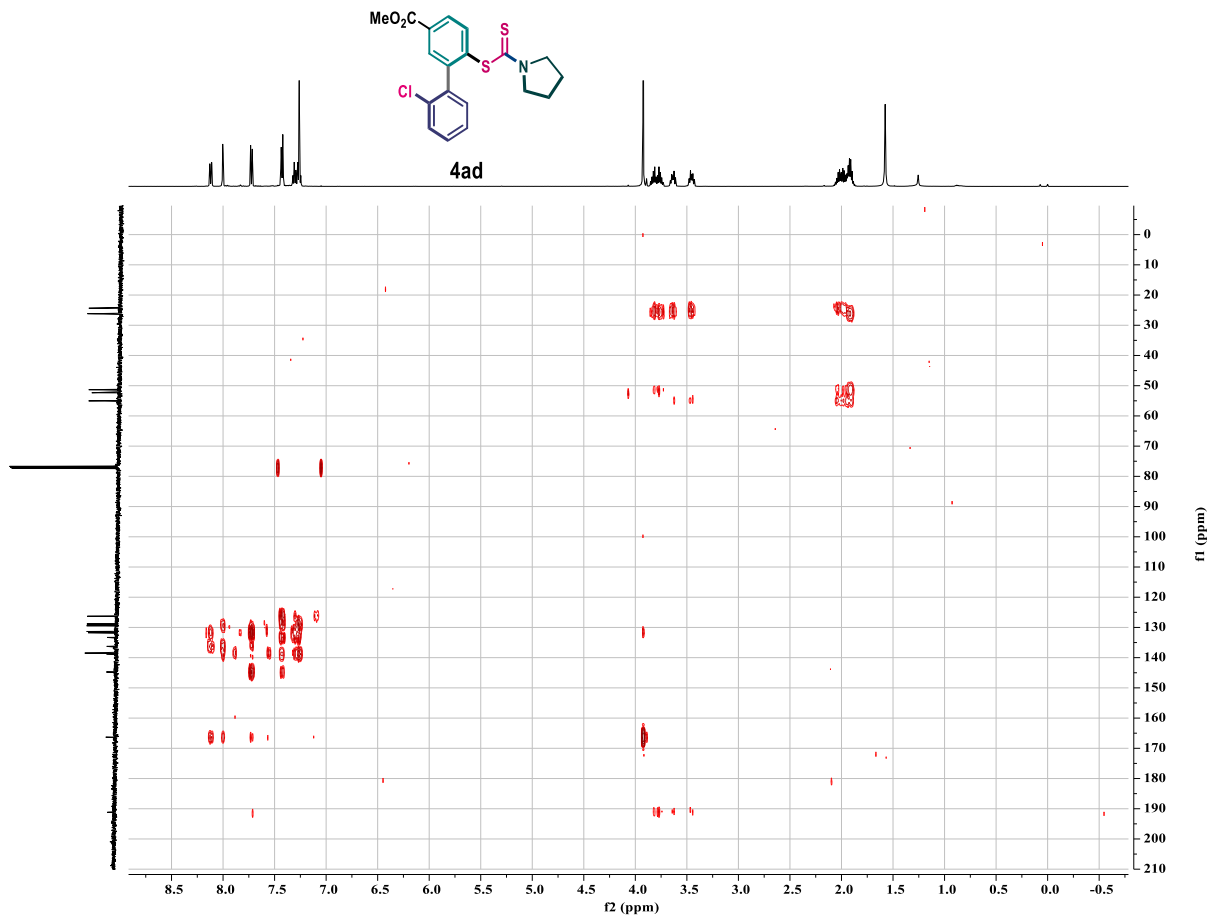
26.90
26.31
24.50
24.46

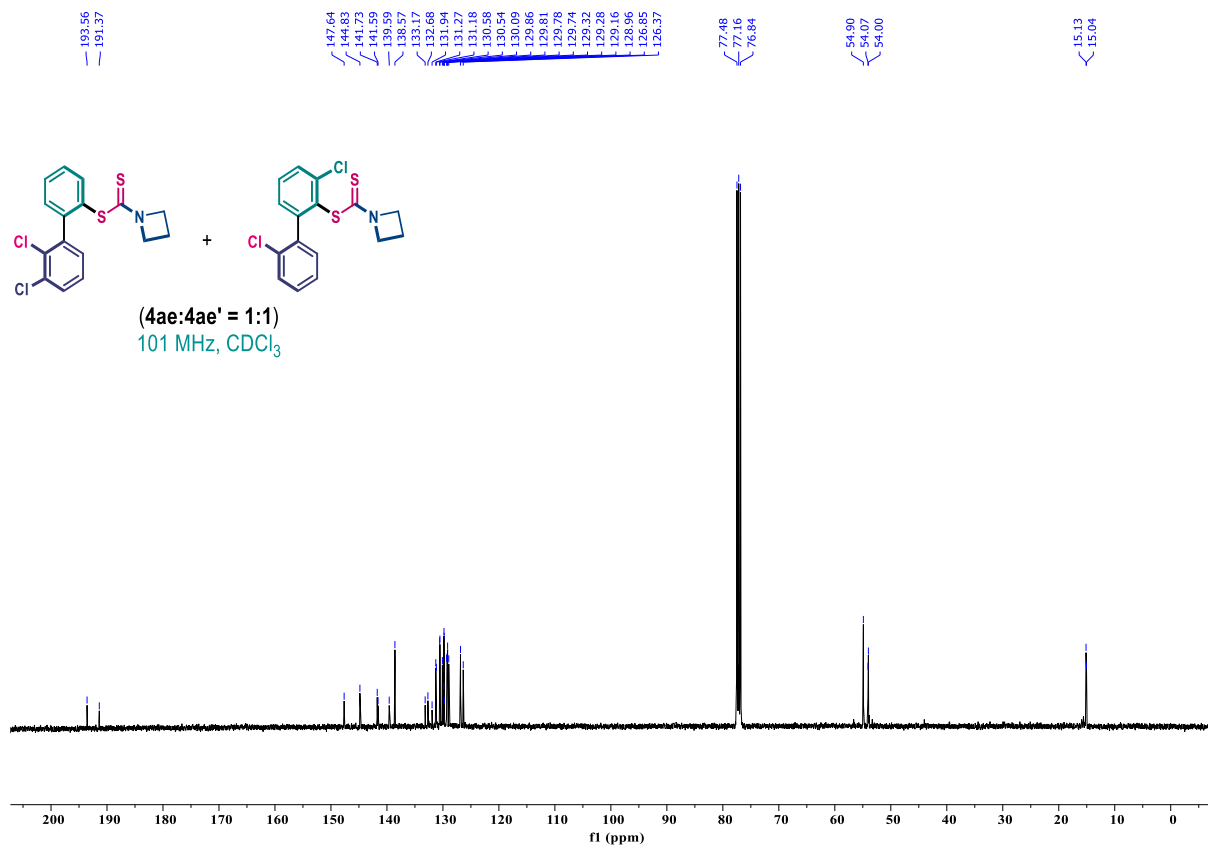
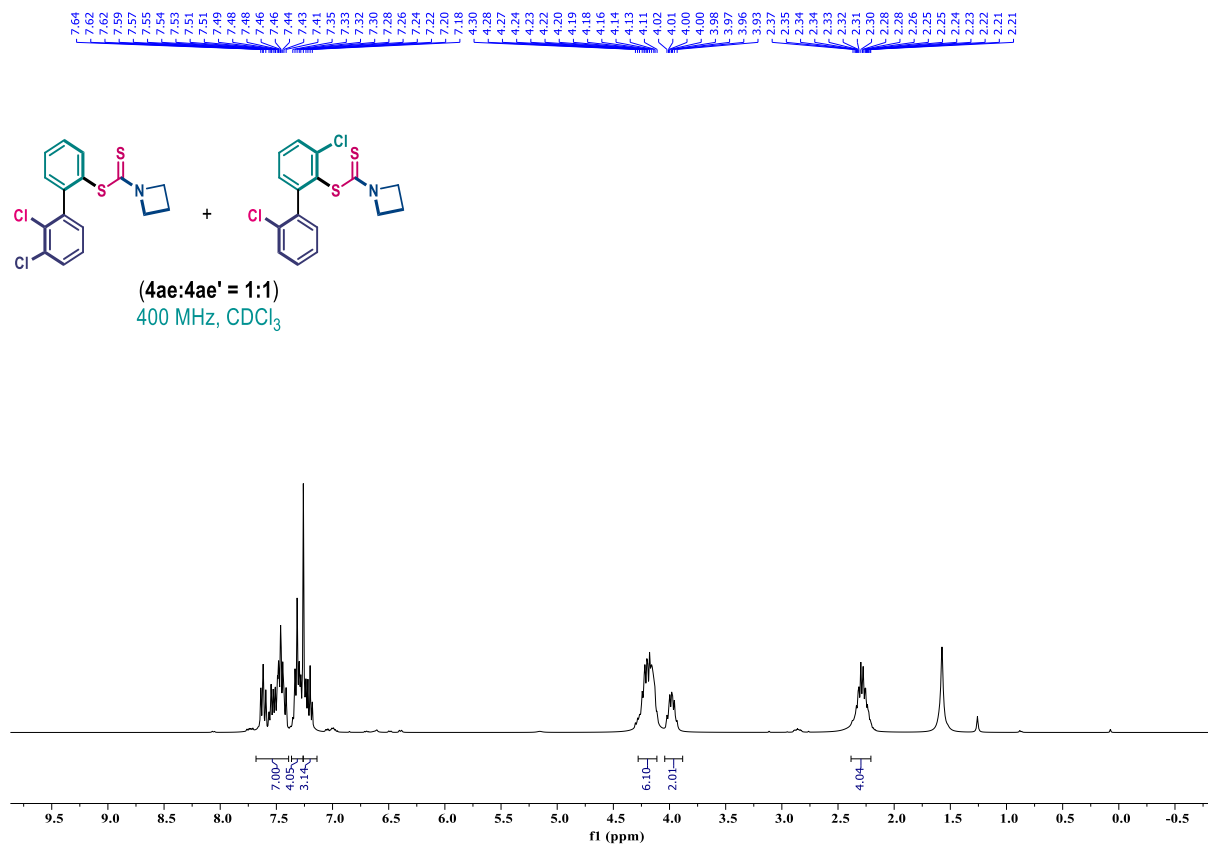


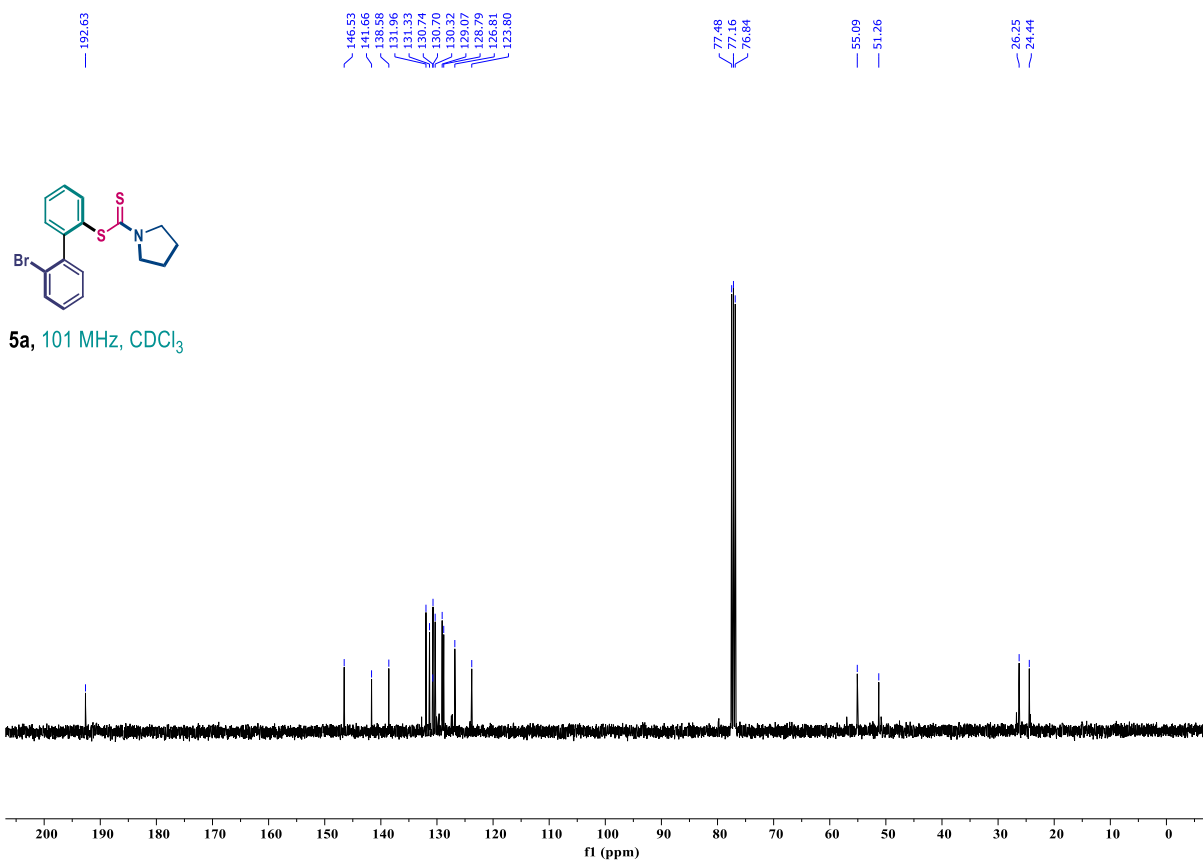
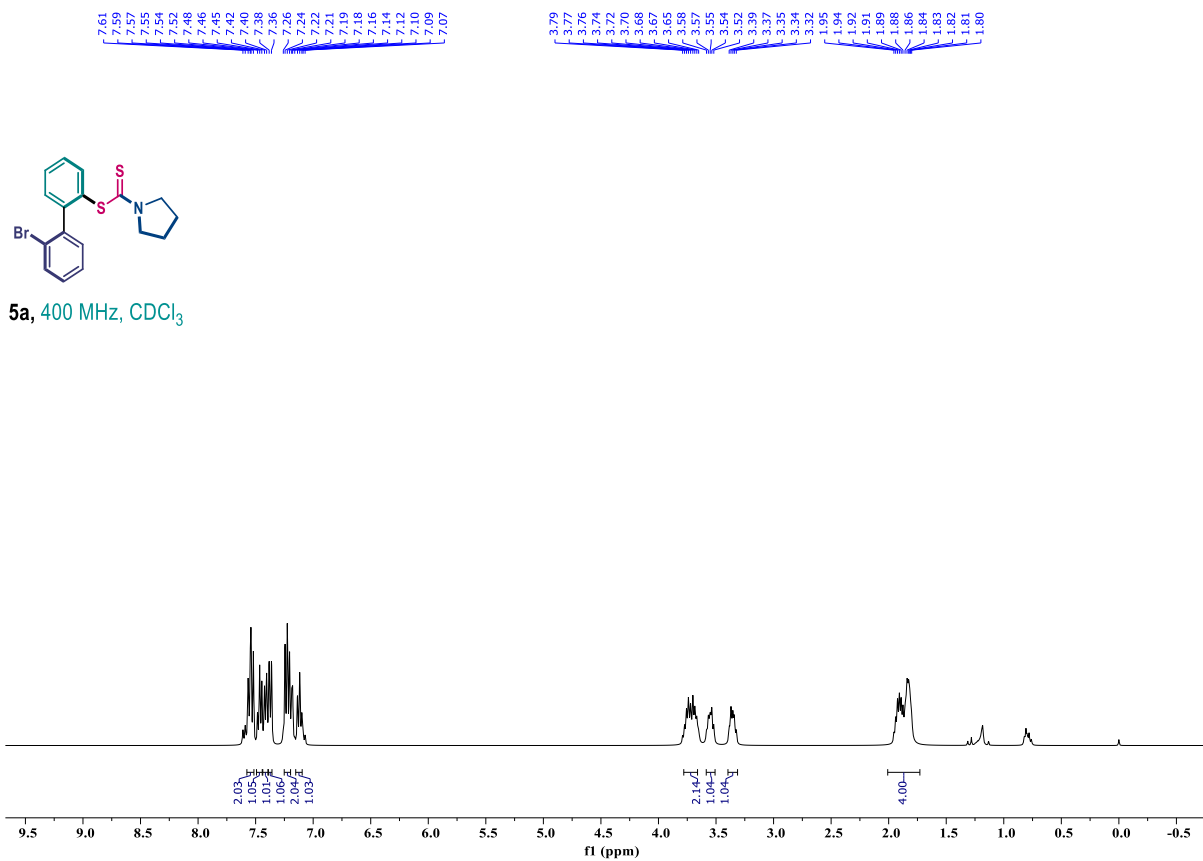
4ac+4ac'
(regioisomeric ratio = 6:1)
101 MHz, CDCl₃



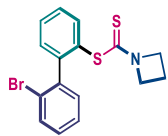




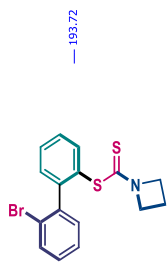
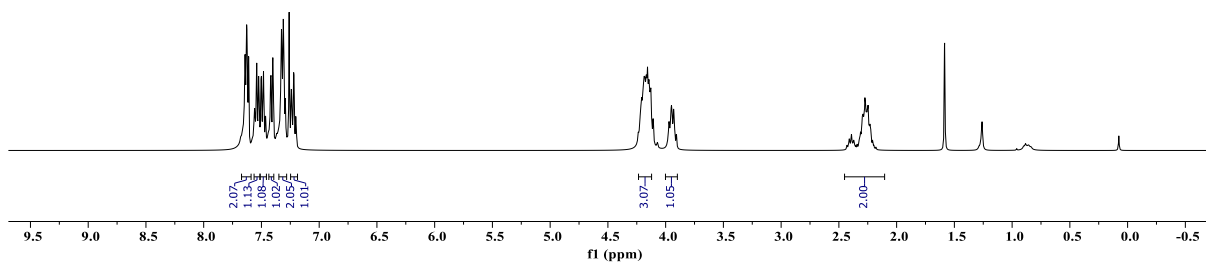




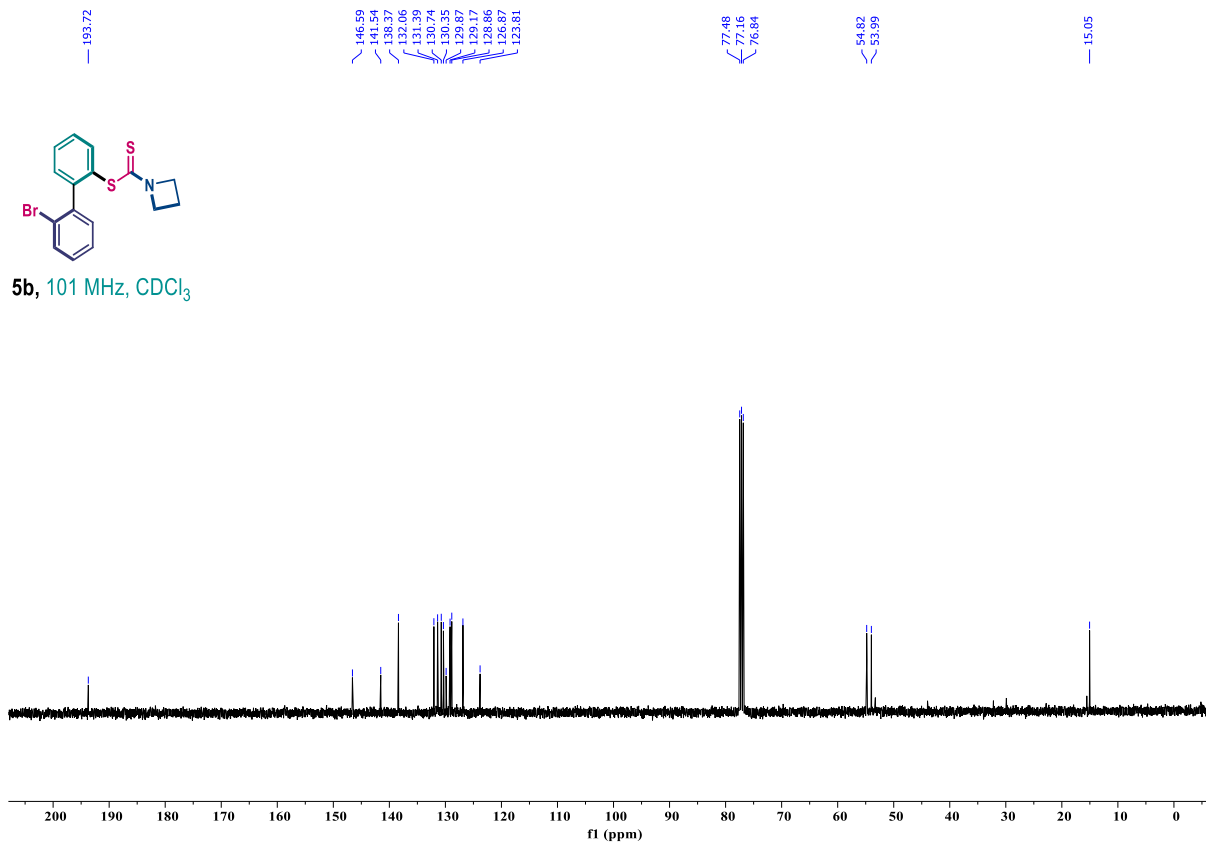
7.68
7.67
7.66
7.64
7.64
7.63
7.63
7.61
7.58
7.56
7.54
7.54
7.52
7.52
7.50
7.50
7.49
7.48
7.47
7.46
7.44
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7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.28
7.24
7.24
7.22
7.22
7.20
7.20
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.16
4.16
4.14
4.13
4.13
4.11
4.07
3.97
3.95
3.95
3.93
3.92
3.91
3.90
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2.29
2.28
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2.22
2.22
2.21
2.20



5b, 400 MHz, CDCl₃

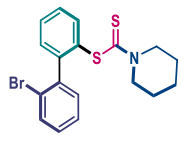


5b, 101 MHz, CDCl₃

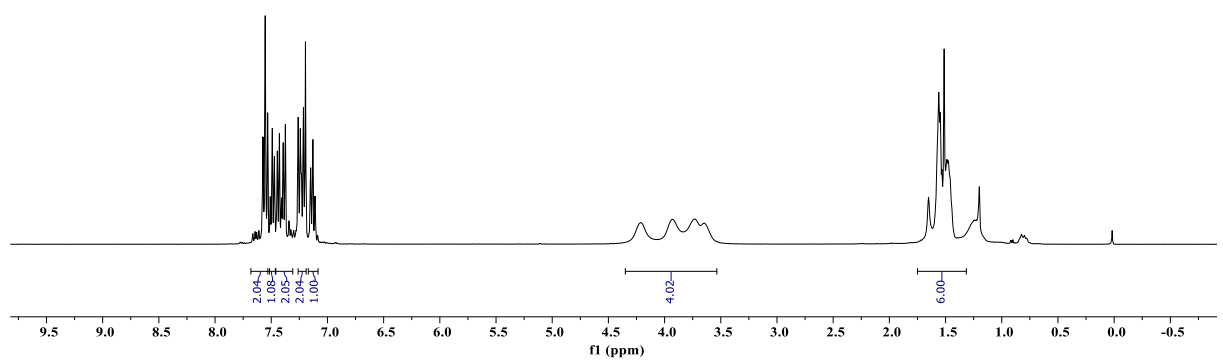


7.57
7.55
7.53
7.51
7.49
7.48
7.47
7.45
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.28
7.26
7.24
7.24
7.23
7.21
7.20
7.16
7.15
7.15
7.13
7.13
7.11
7.11
7.09
3.83
3.73
3.64

1.65
1.65
1.57
1.56
1.55
1.53
1.51
1.49
1.46
1.44



5c, 400 MHz, CDCl₃



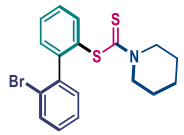
195.54

146.57
141.72
138.73
131.96
131.38
131.23
130.67
130.34
129.00
128.76
128.68
128.82

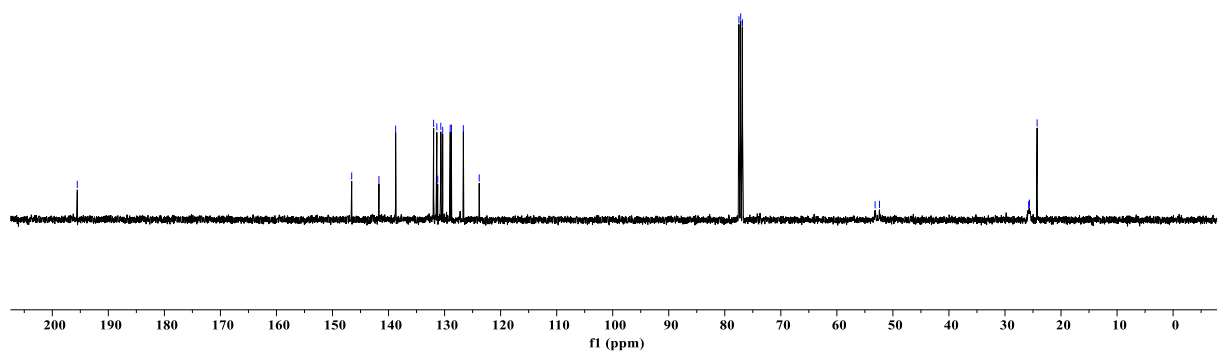
77.48
77.16
76.84

53.18
52.40

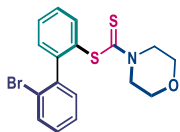
25.77
25.63
24.27



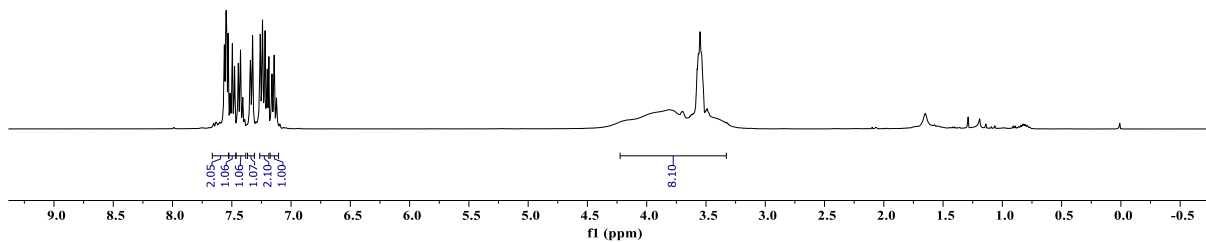
5c, 101 MHz, CDCl₃



7.65
7.63
7.62
7.61
7.60
7.59
7.56
7.55
7.55
7.54
7.53
7.51
7.51
7.50
7.49
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.34
7.34
7.33
7.32
7.30
7.26
7.24
7.24
7.22
7.20
7.19
7.16
7.14
7.14
7.12
7.11
7.11
3.81
3.71
3.70
3.68
3.63
3.62
3.61
3.59
3.58
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3.54
3.52
3.49
3.48
3.38
3.32
3.31



5d, 400 MHz, CDCl₃



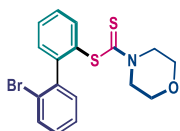
197.35

146.58
141.54
138.57
133.03
131.26
130.77
130.60
130.57
129.17
128.90
126.74
125.80

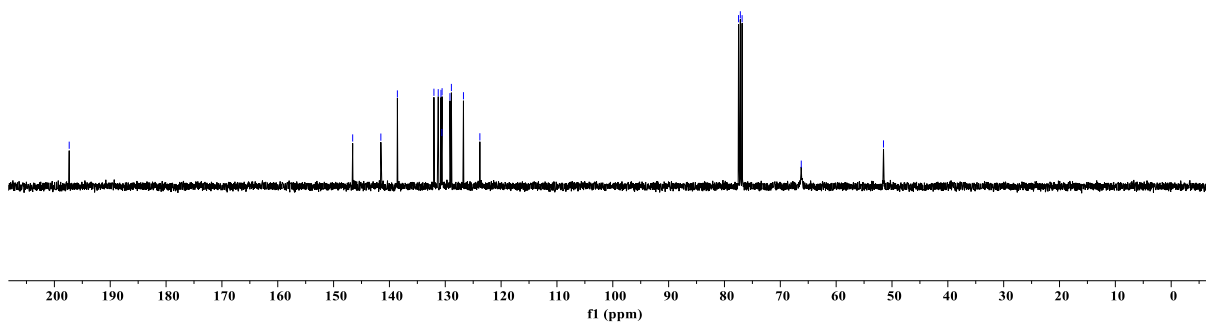
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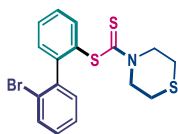
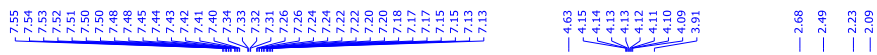
66.25

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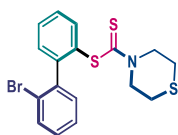
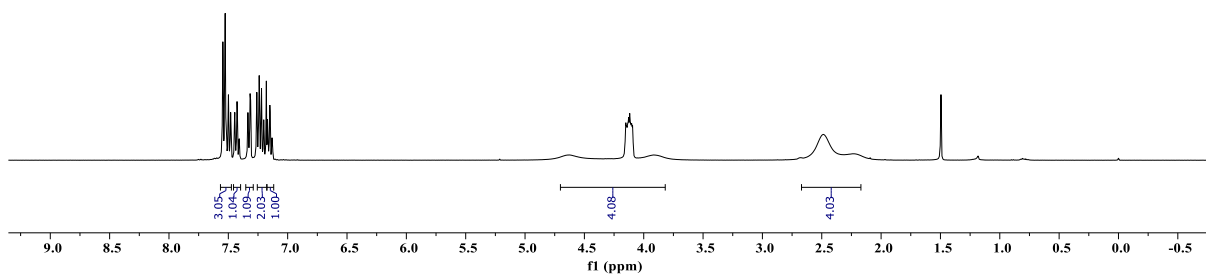


5d, 101 MHz, CDCl₃

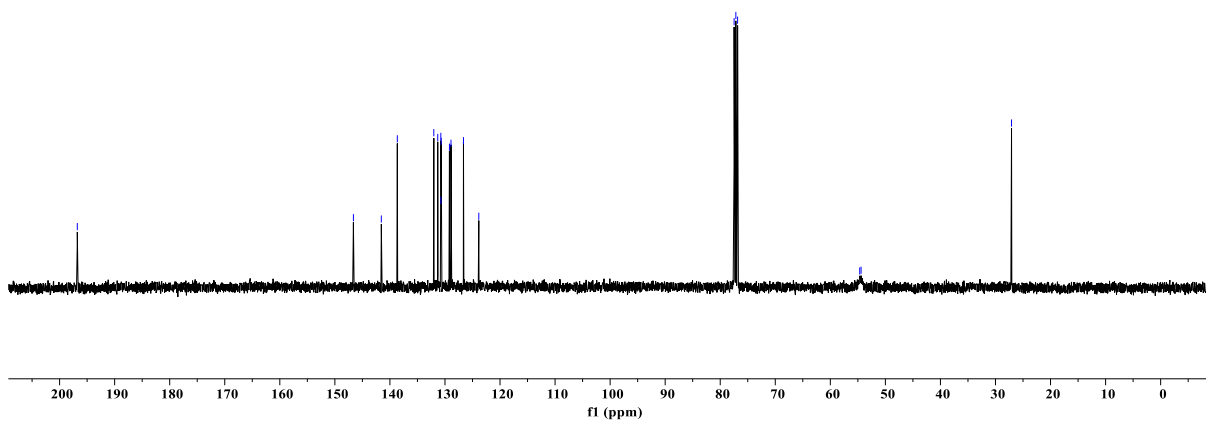




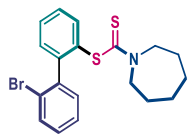
5e, 400 MHz, CDCl₃



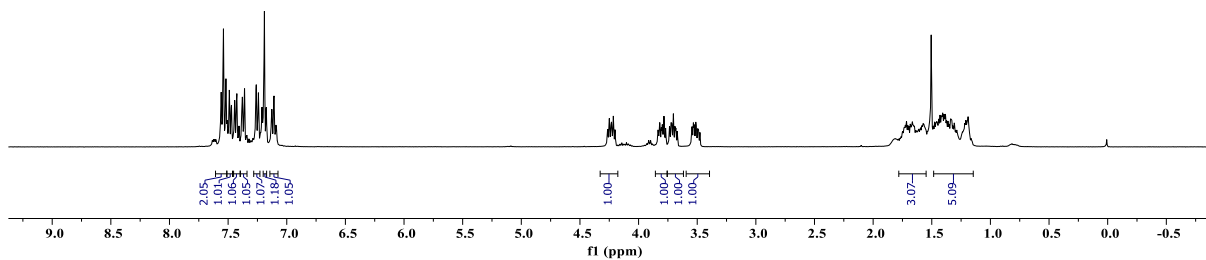
5e, 101 MHz, CDCl₃



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5f, 400 MHz, CDCl₃



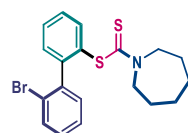
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146.73
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128.96
126.66
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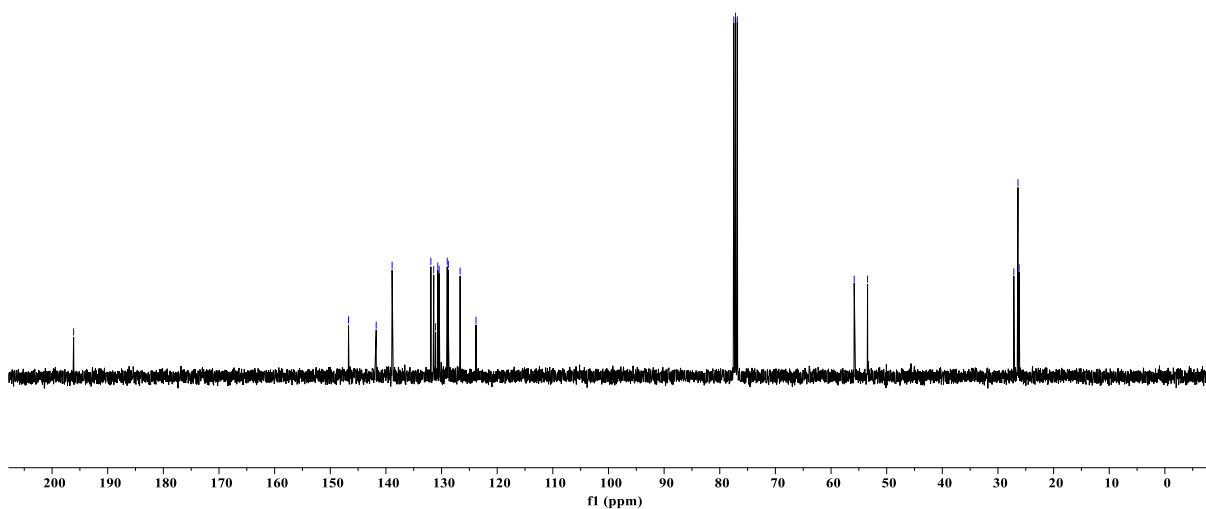
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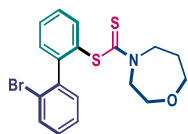
27.15
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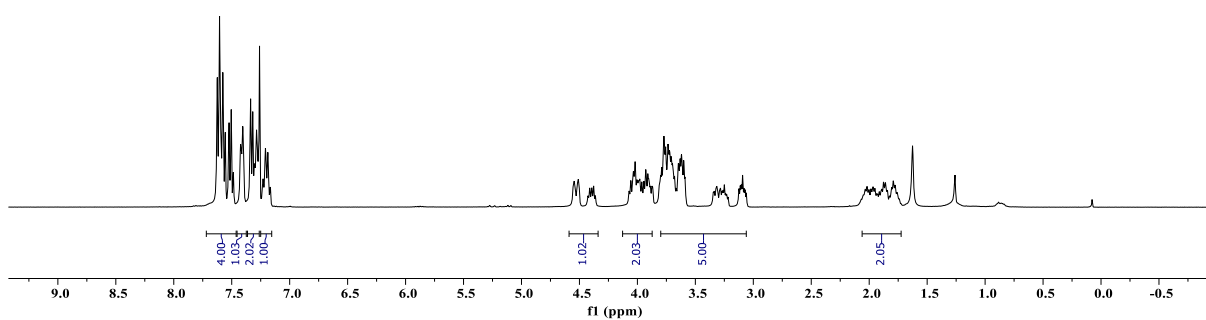
5f, 101 MHz, CDCl₃



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5g, 400 MHz, CDCl₃
(1.1:1.0 ratio of rotamer)



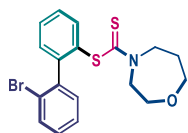
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128.70
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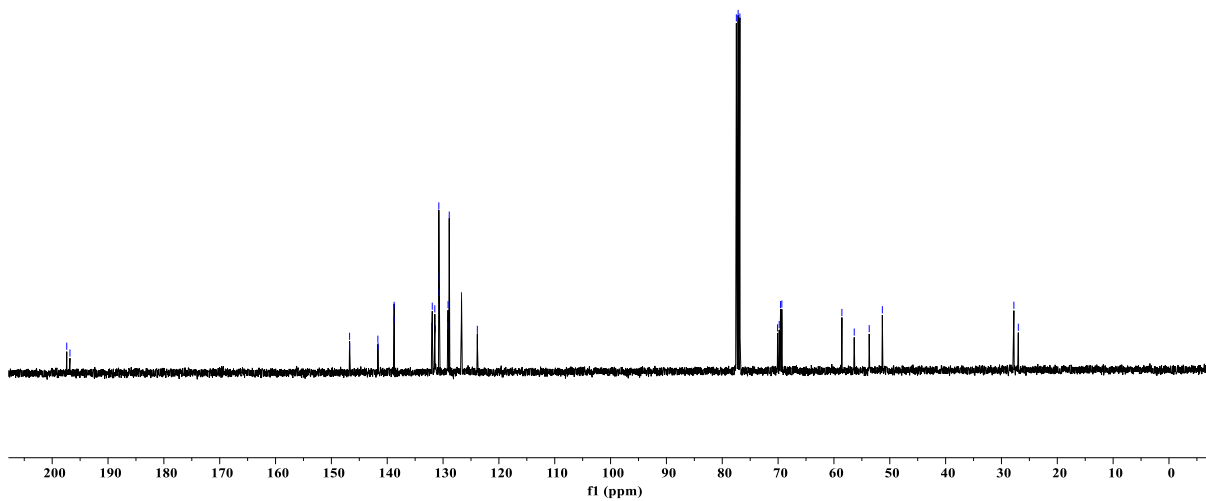
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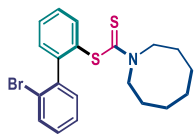
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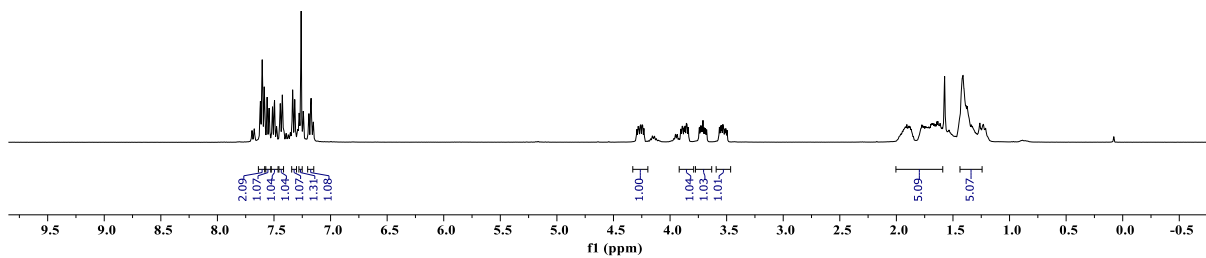
5g, 101 MHz, CDCl₃
(1.1:1.0 ratio of rotamer)



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5h, 400 MHz, CDCl₃



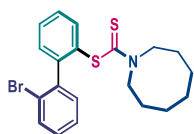
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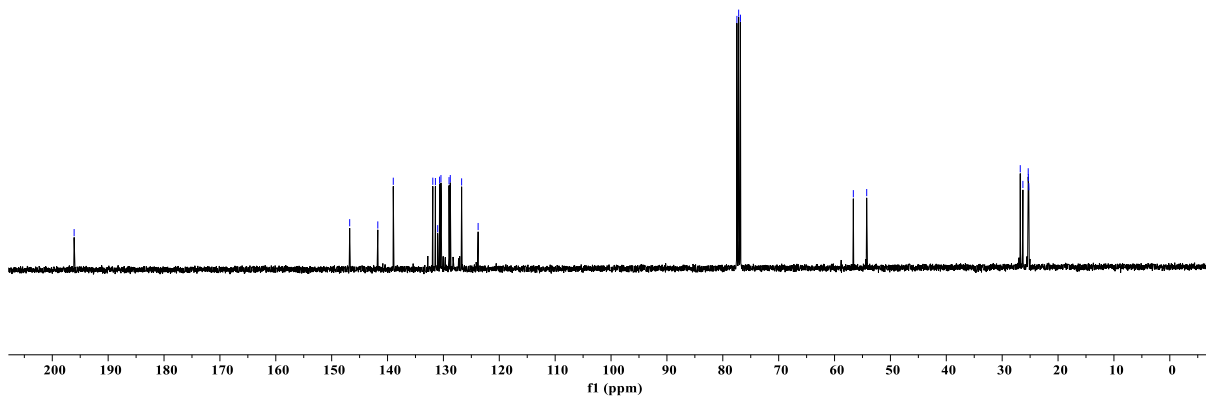
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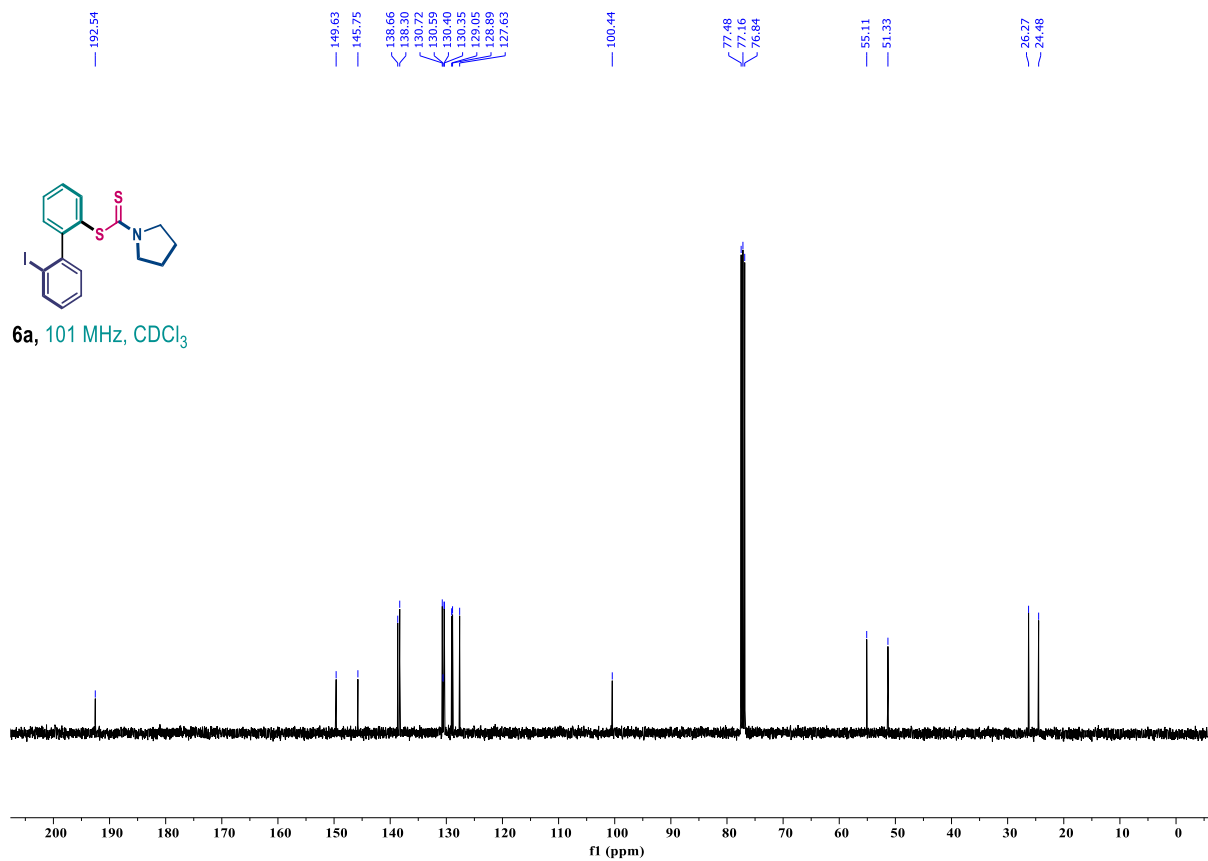
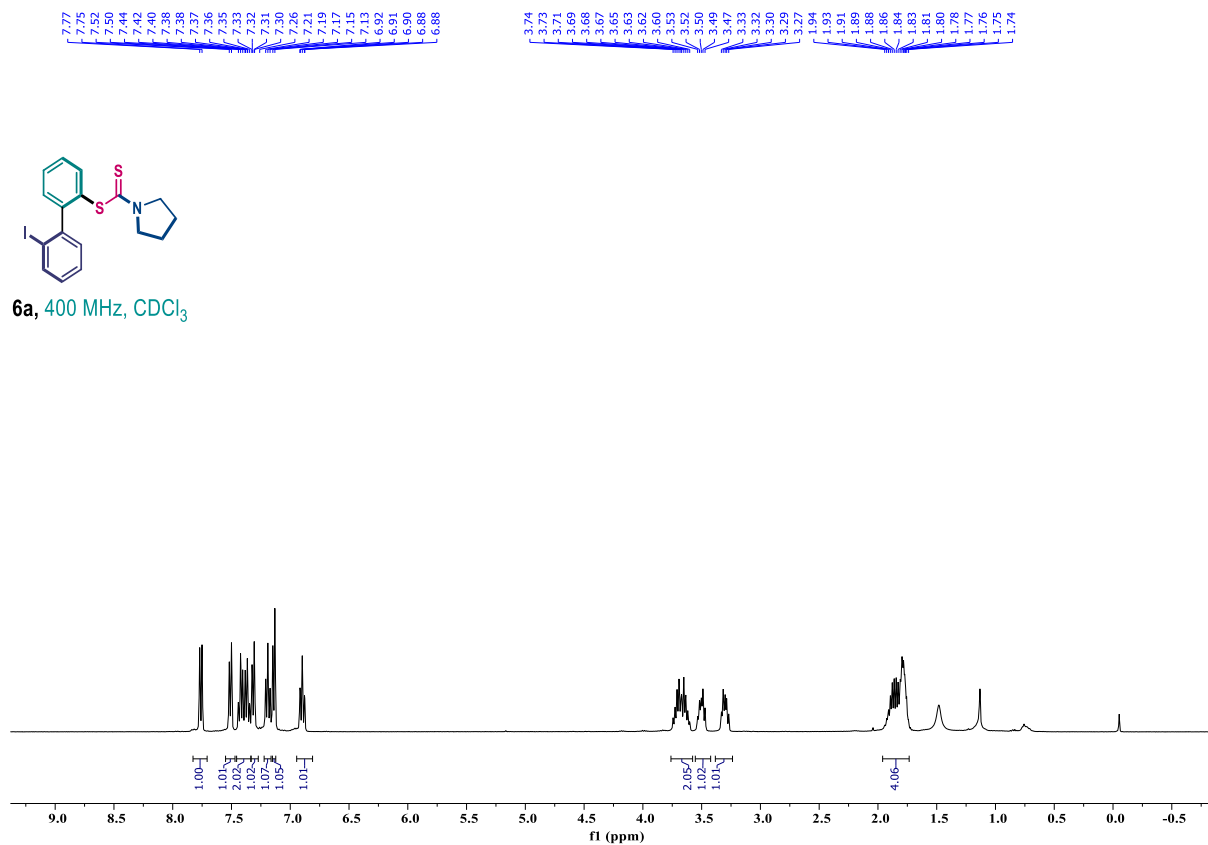
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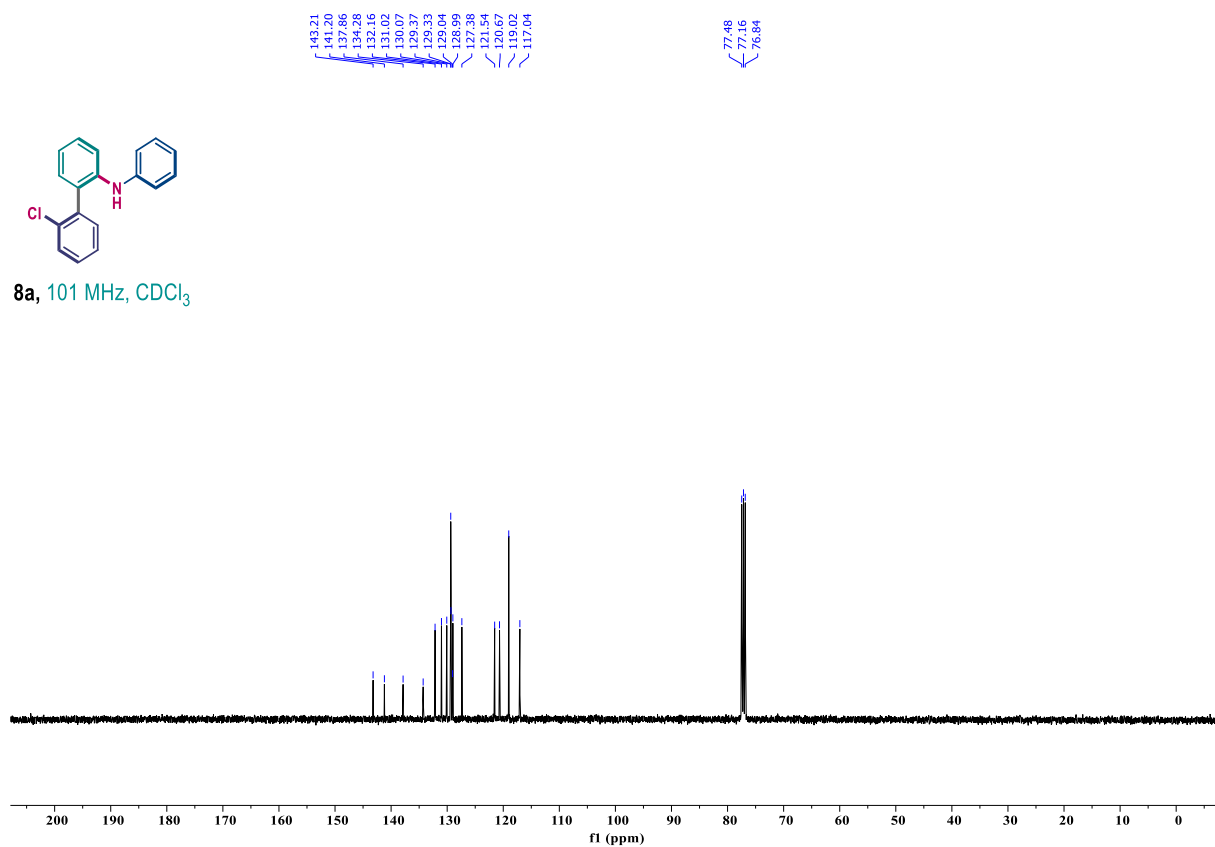
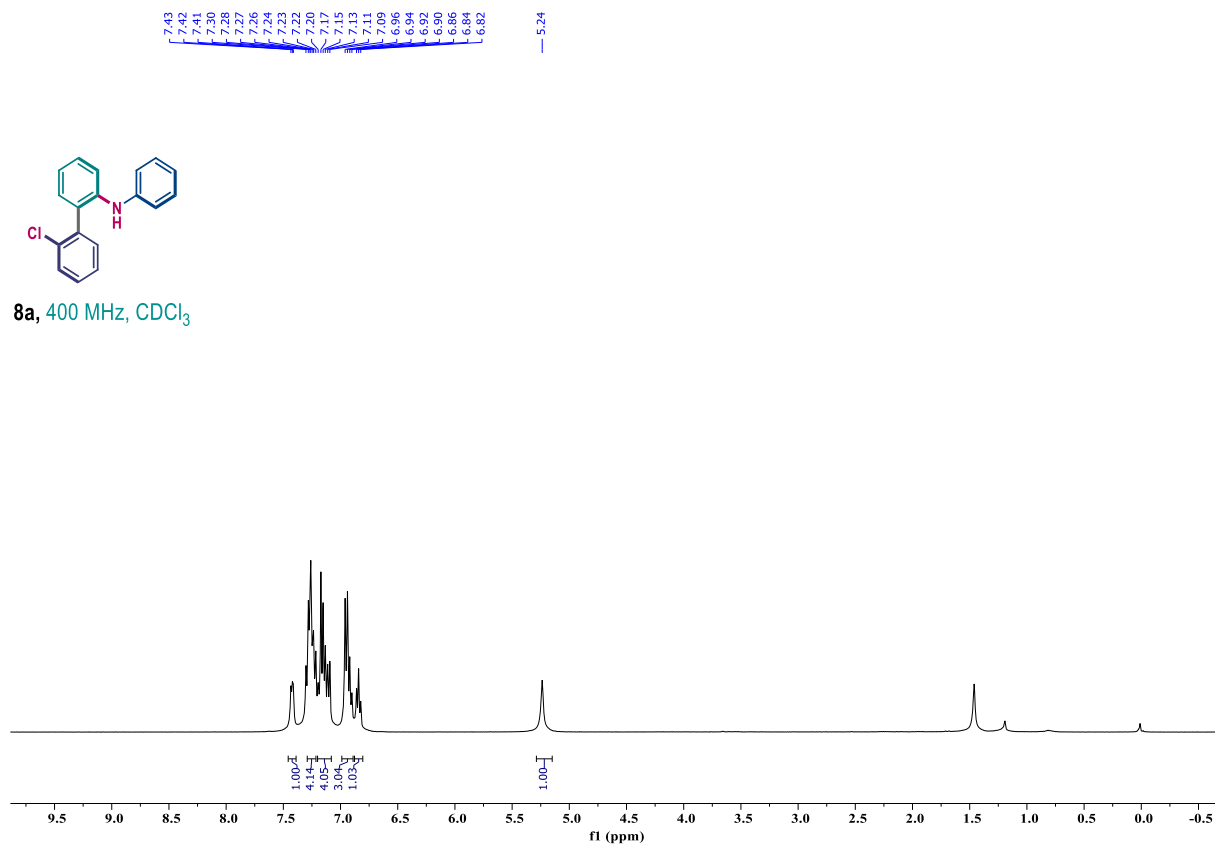
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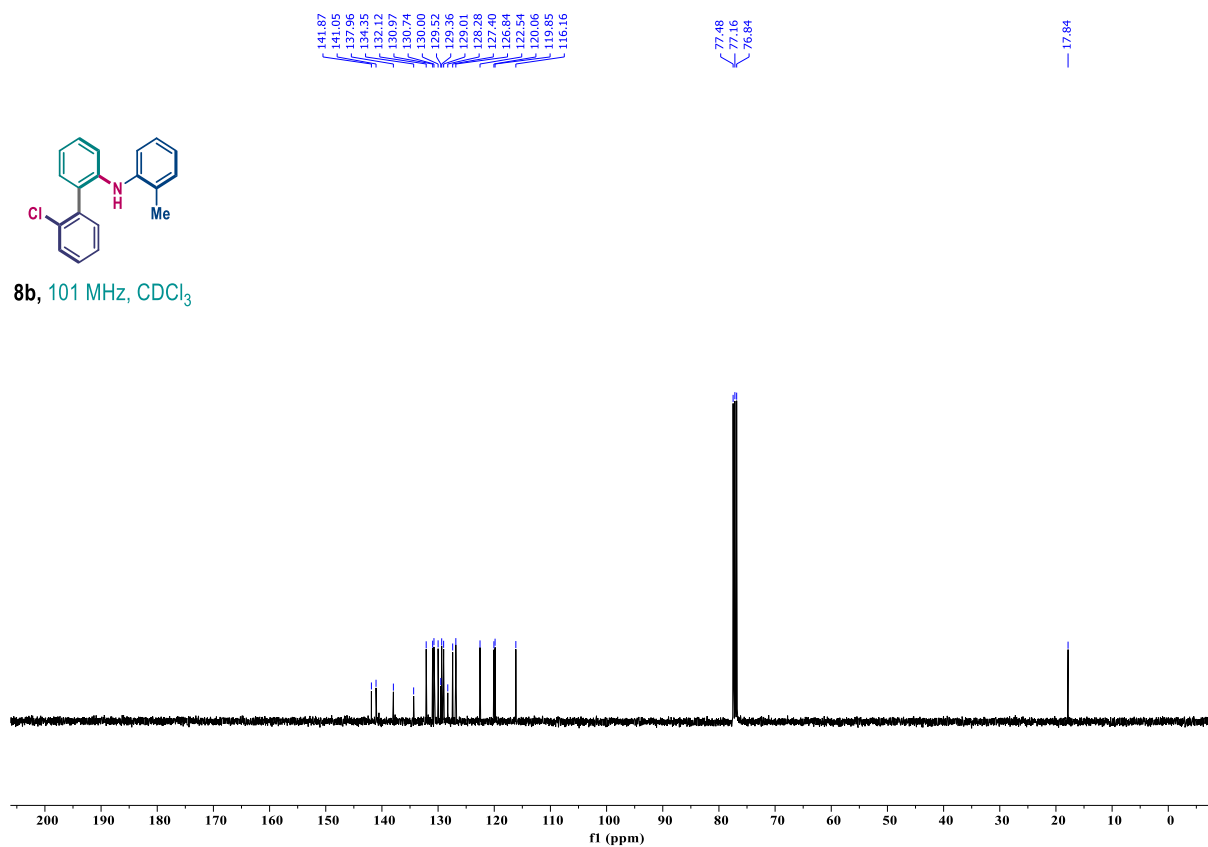
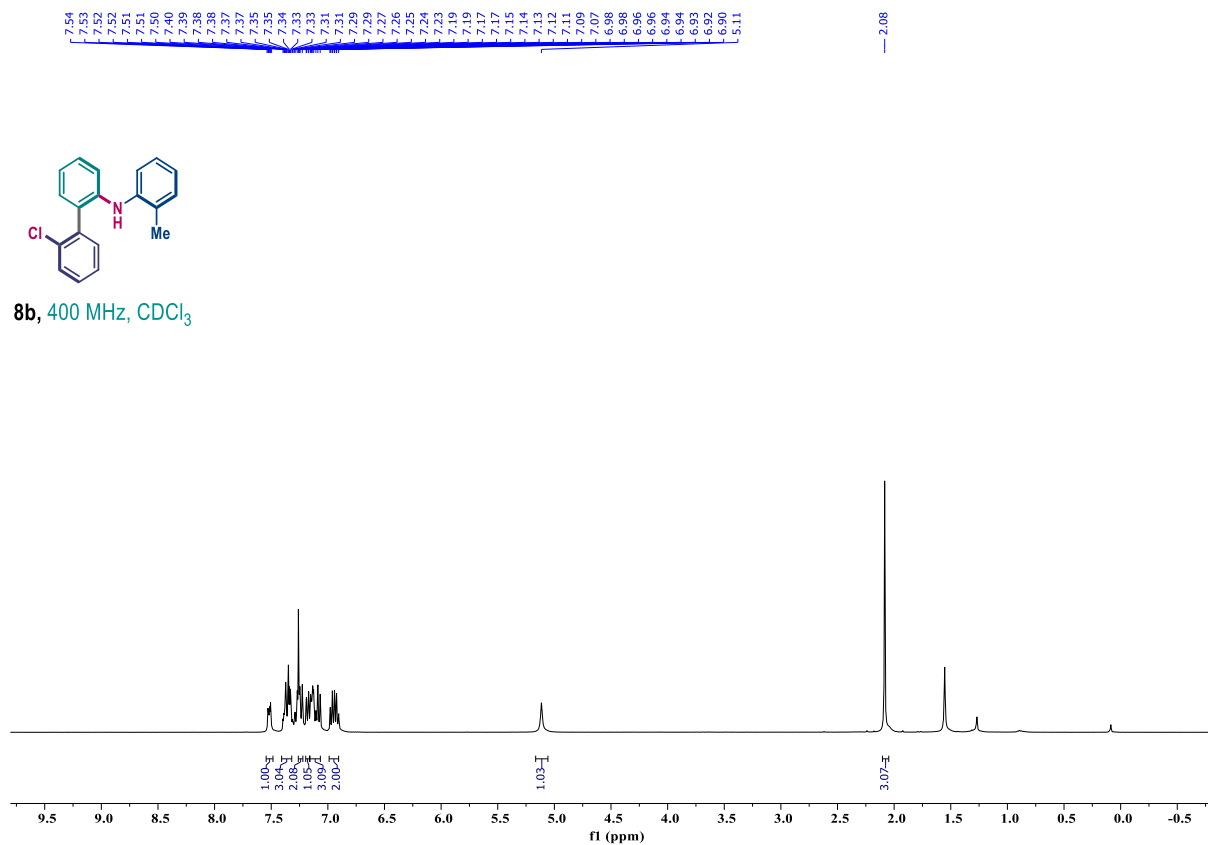


5h, 101 MHz, CDCl₃



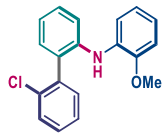




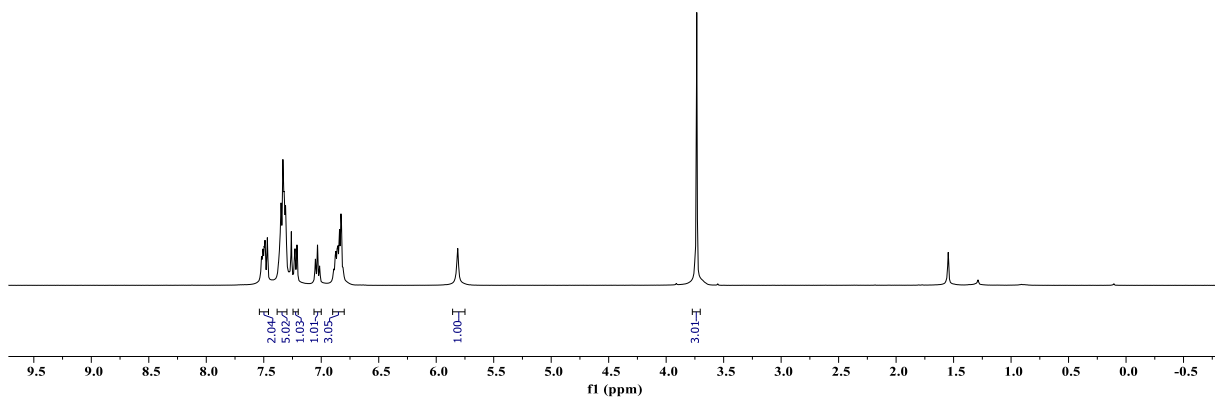


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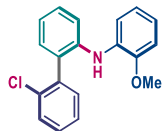
8c, 400 MHz, CDCl₃



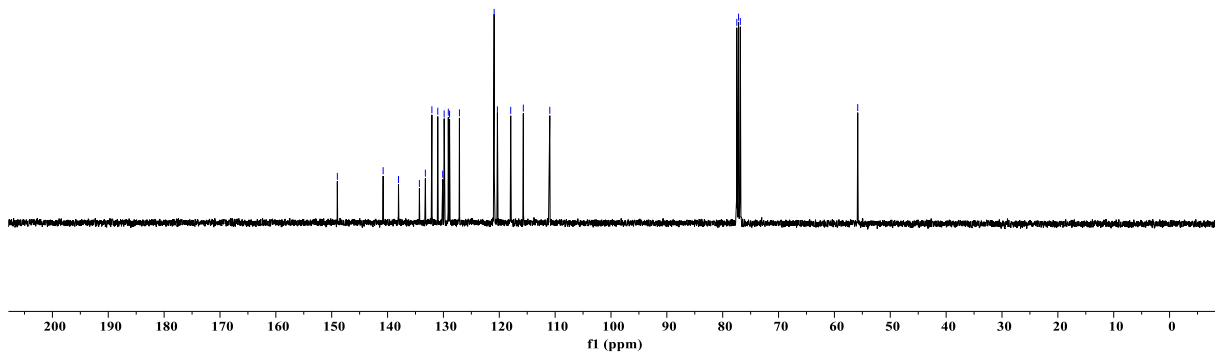
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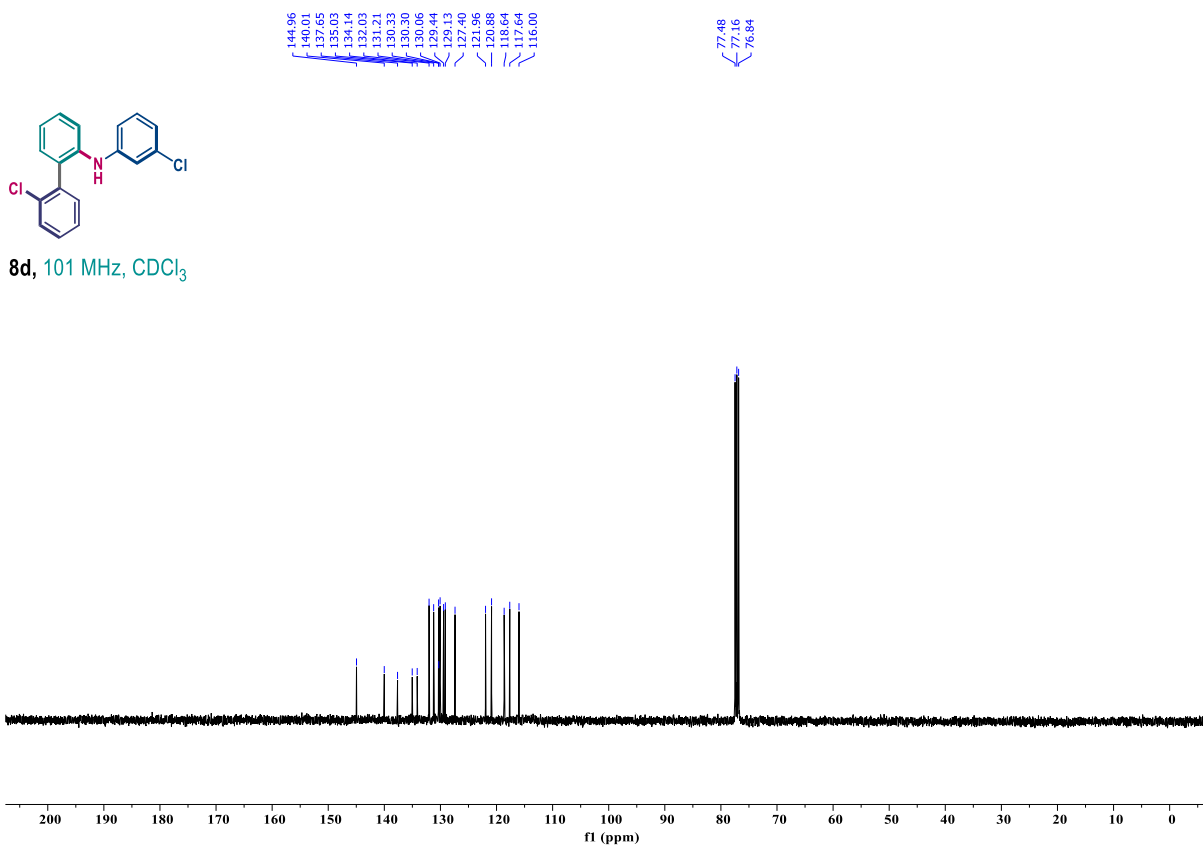
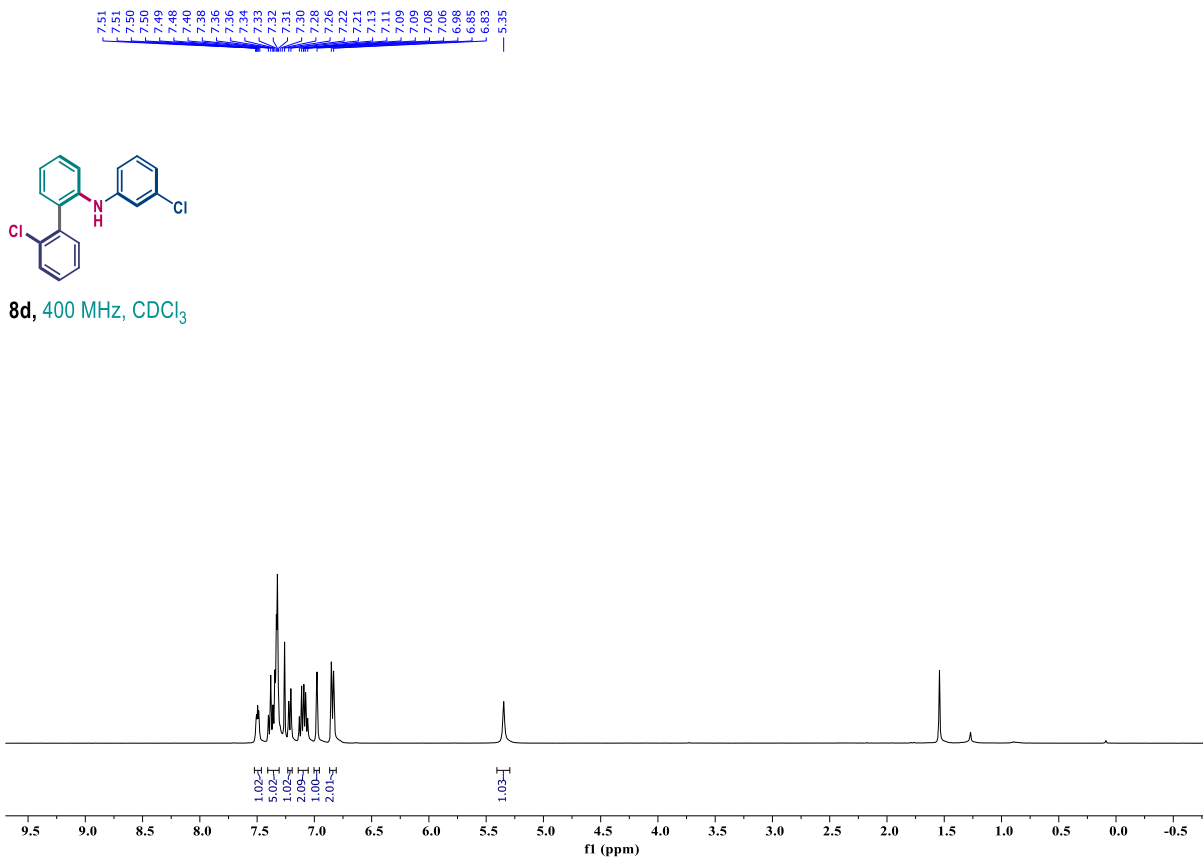
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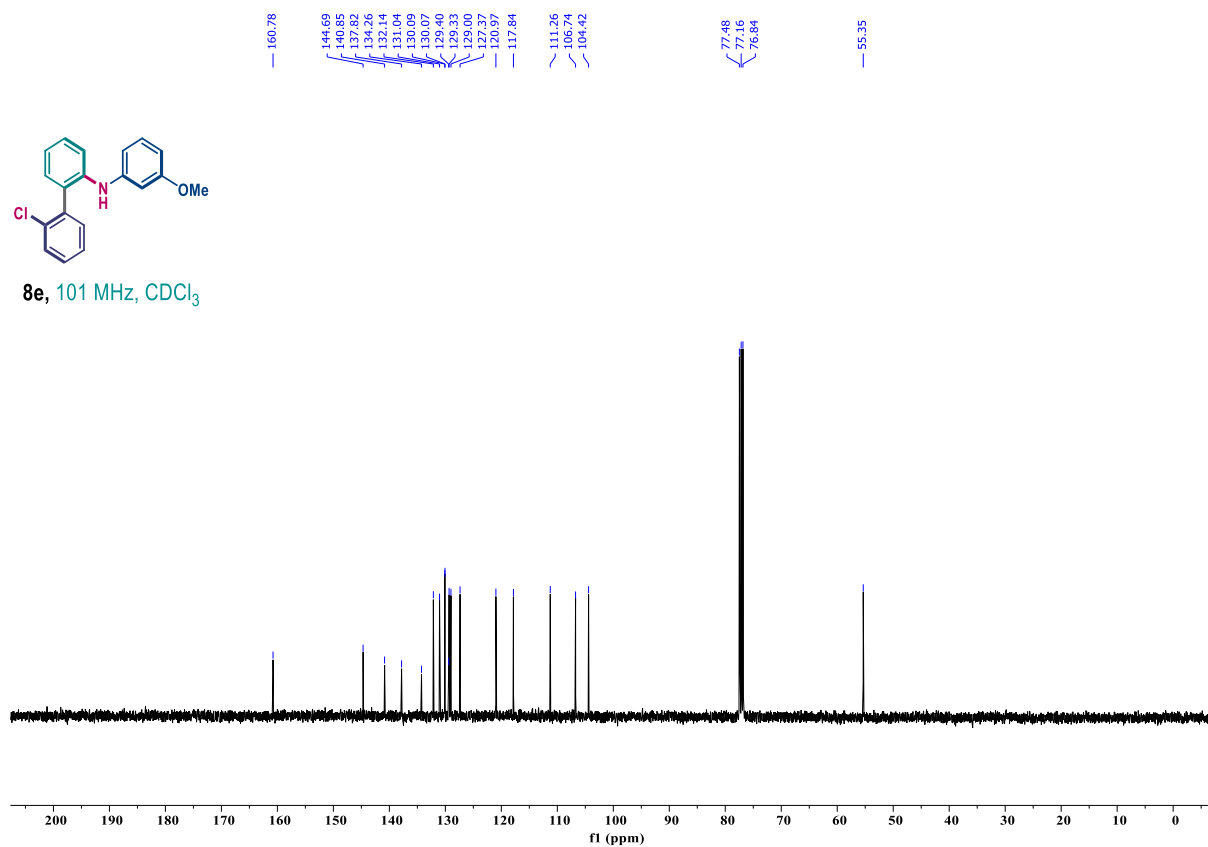
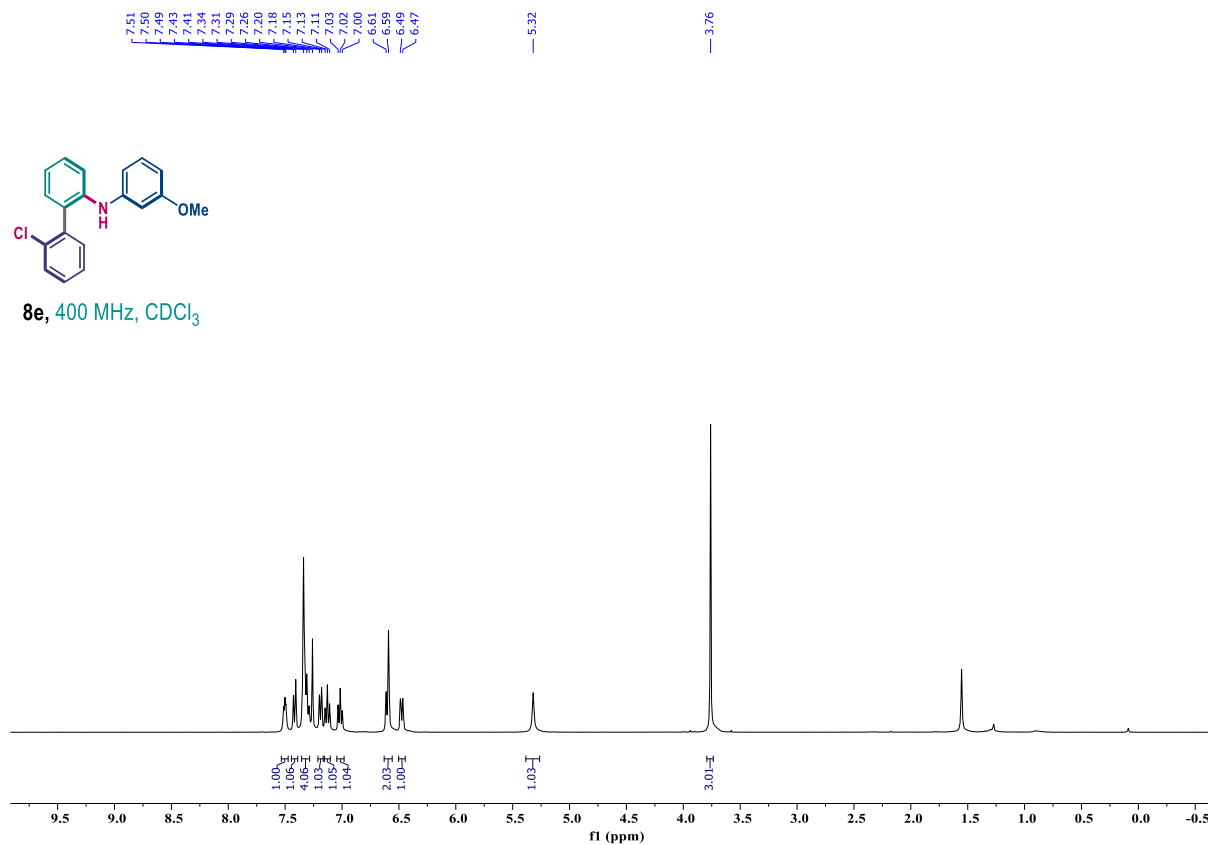
55.83

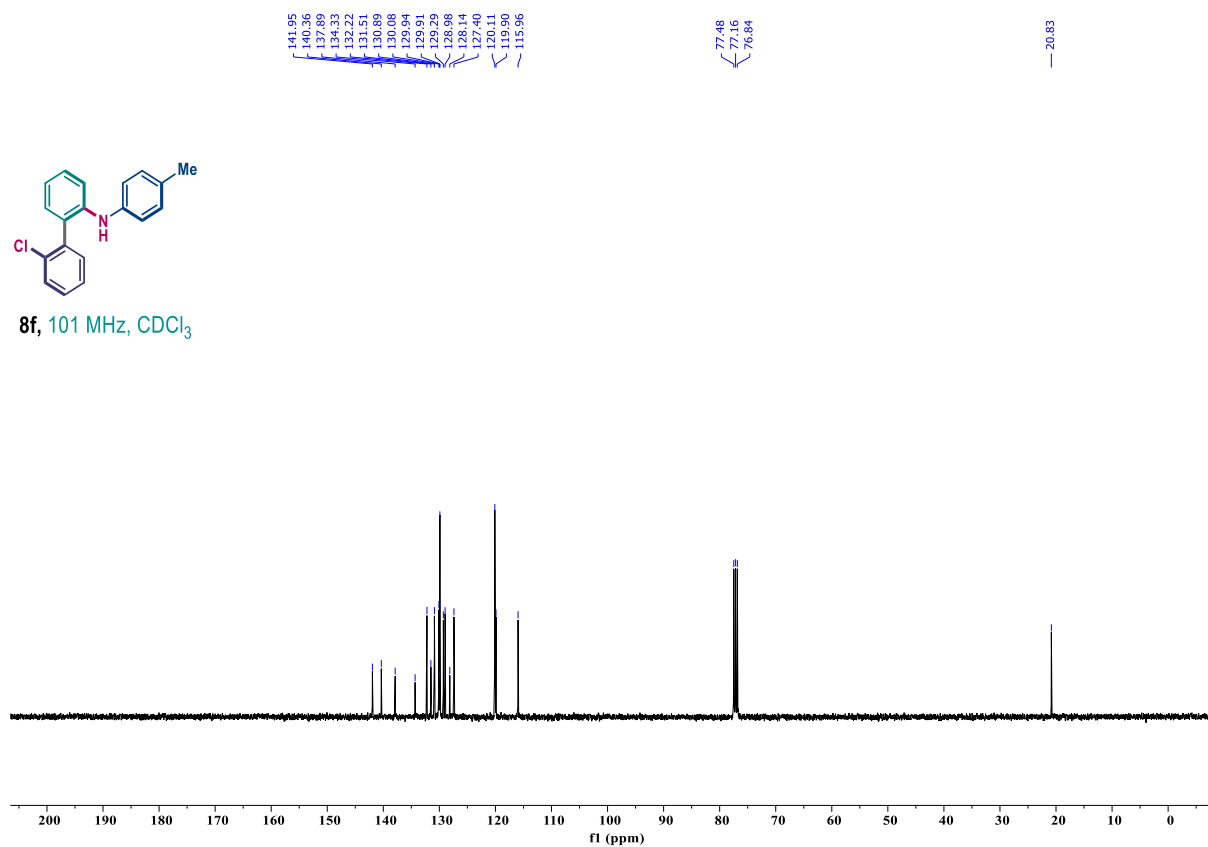
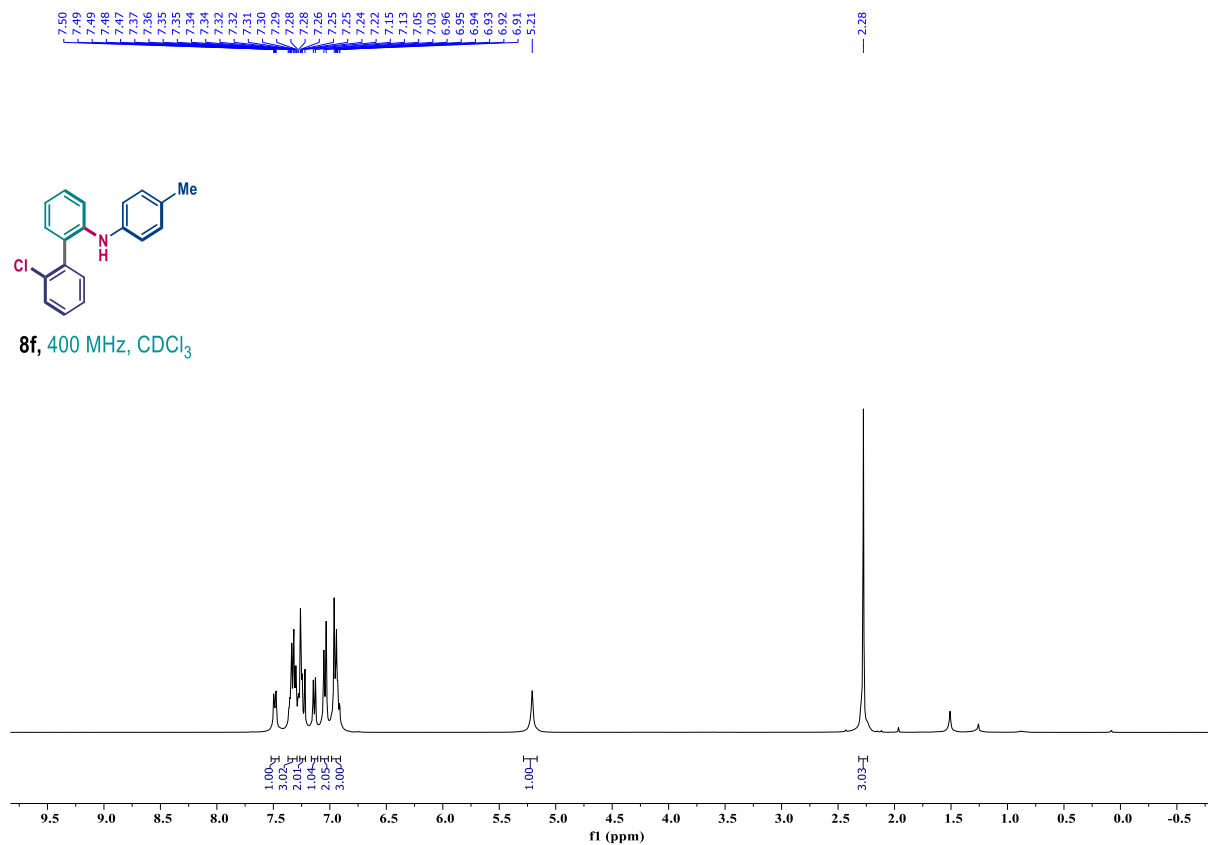


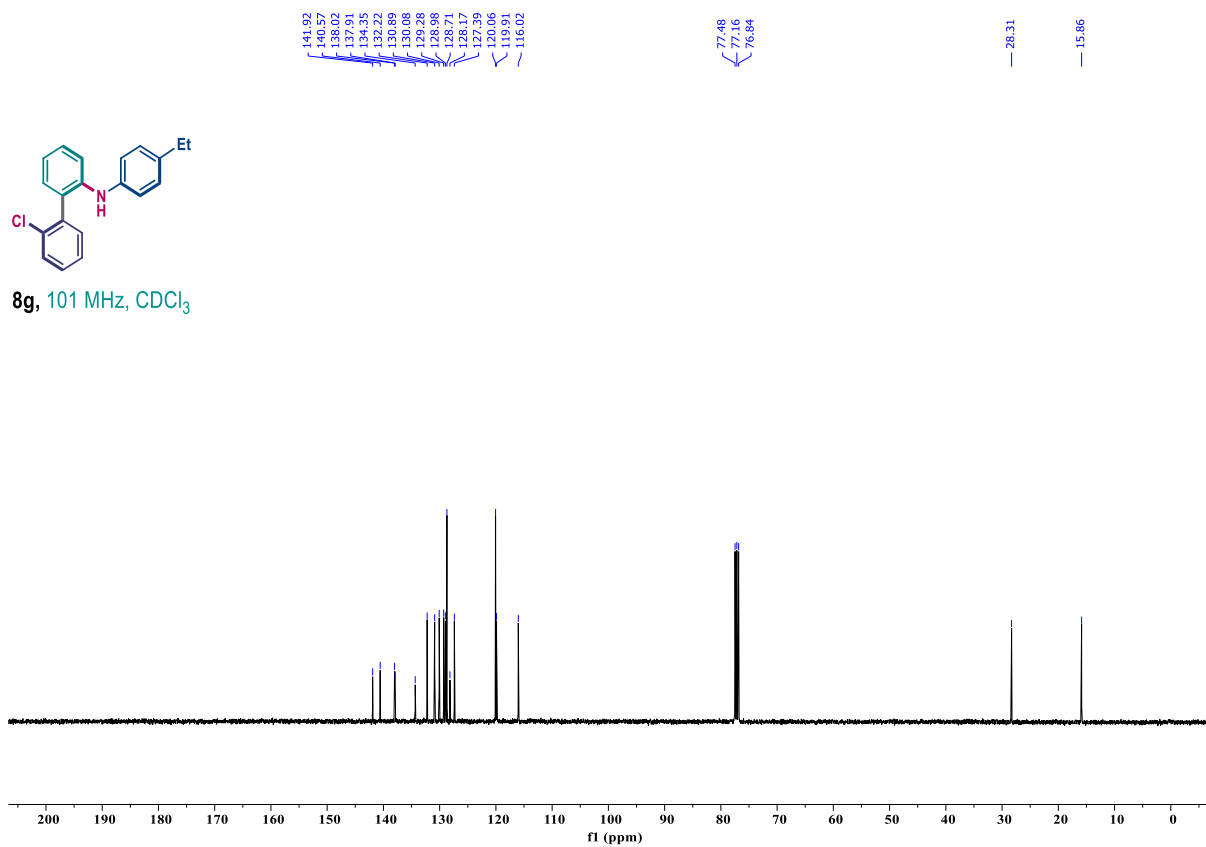
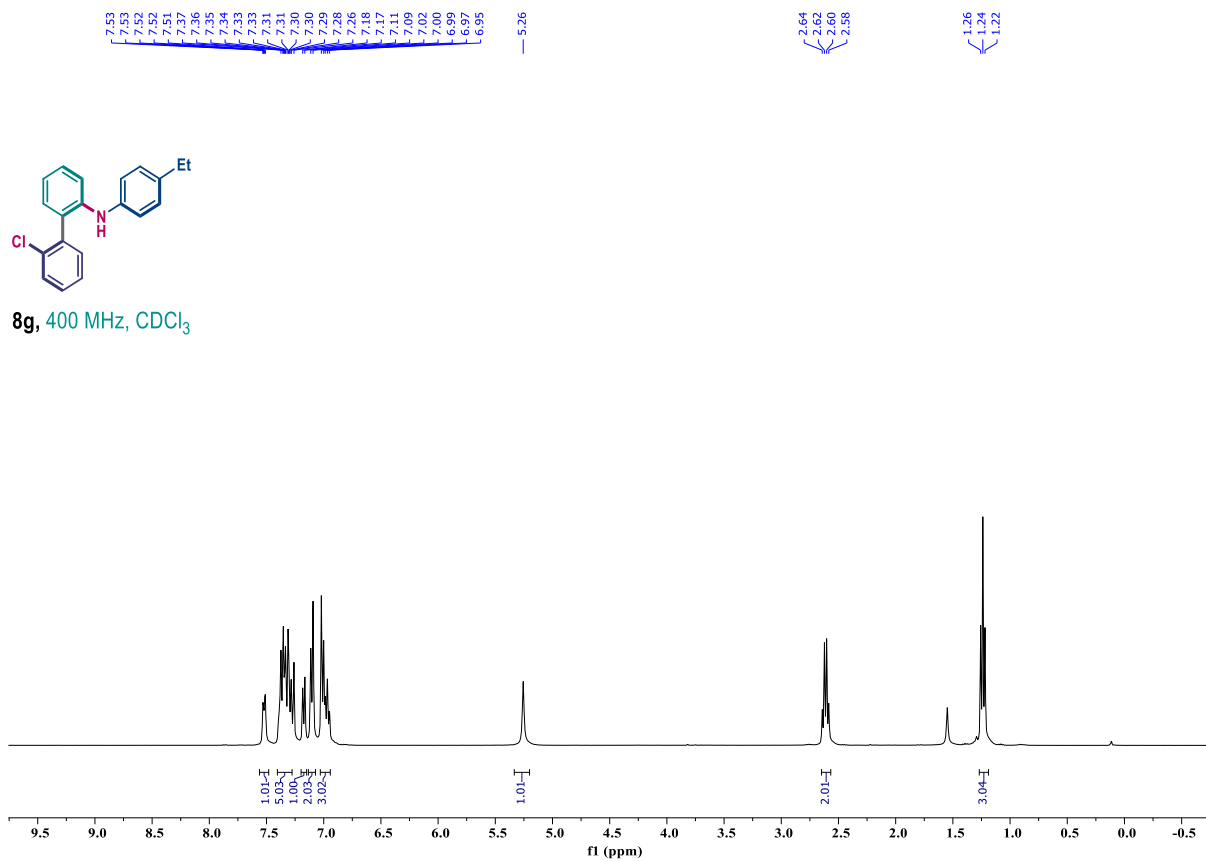
8c, 101 MHz, CDCl₃

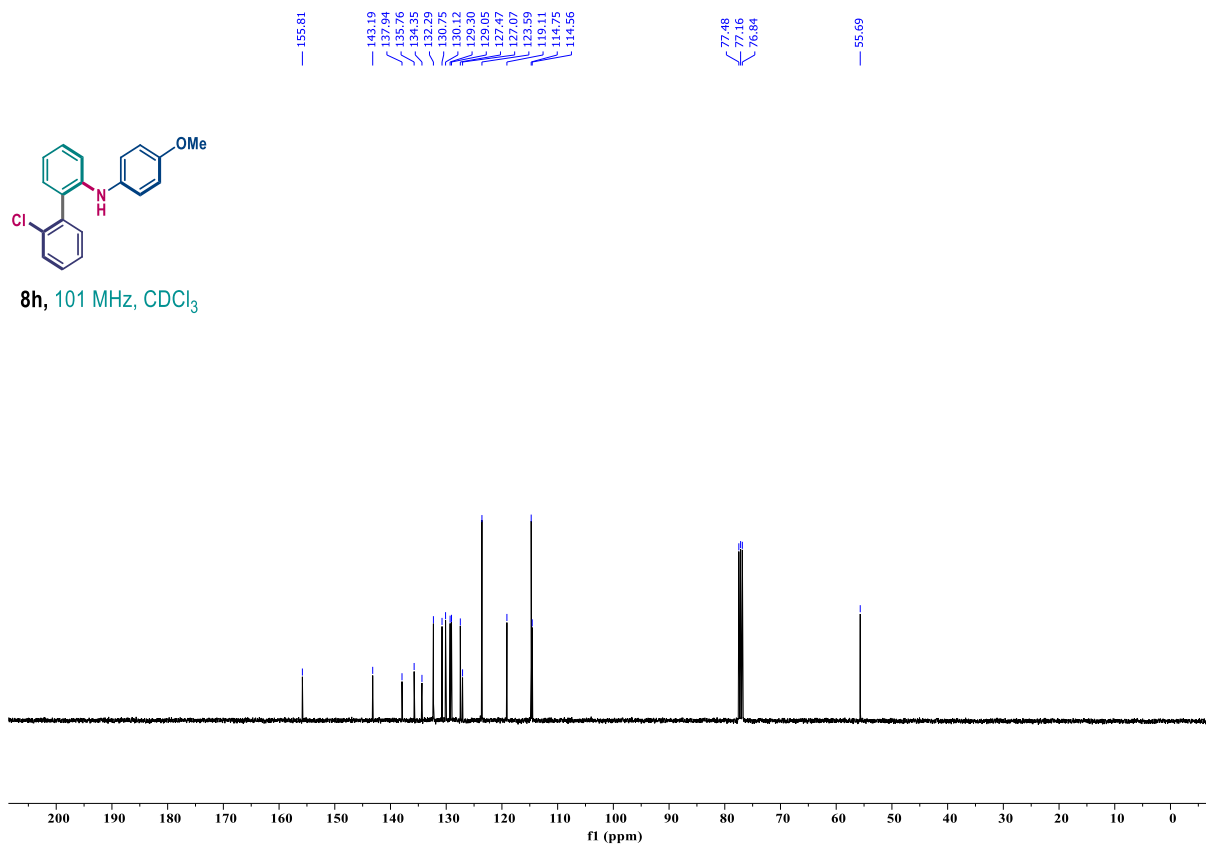
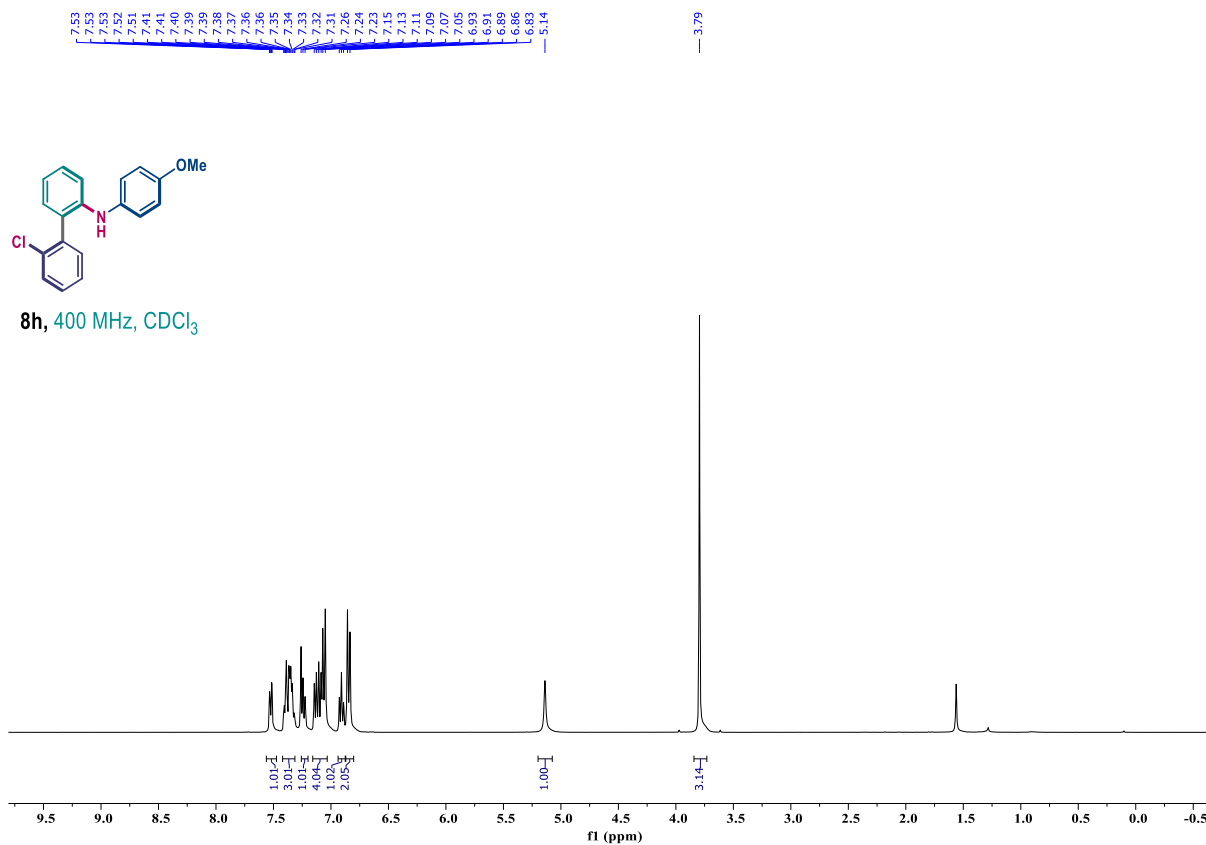


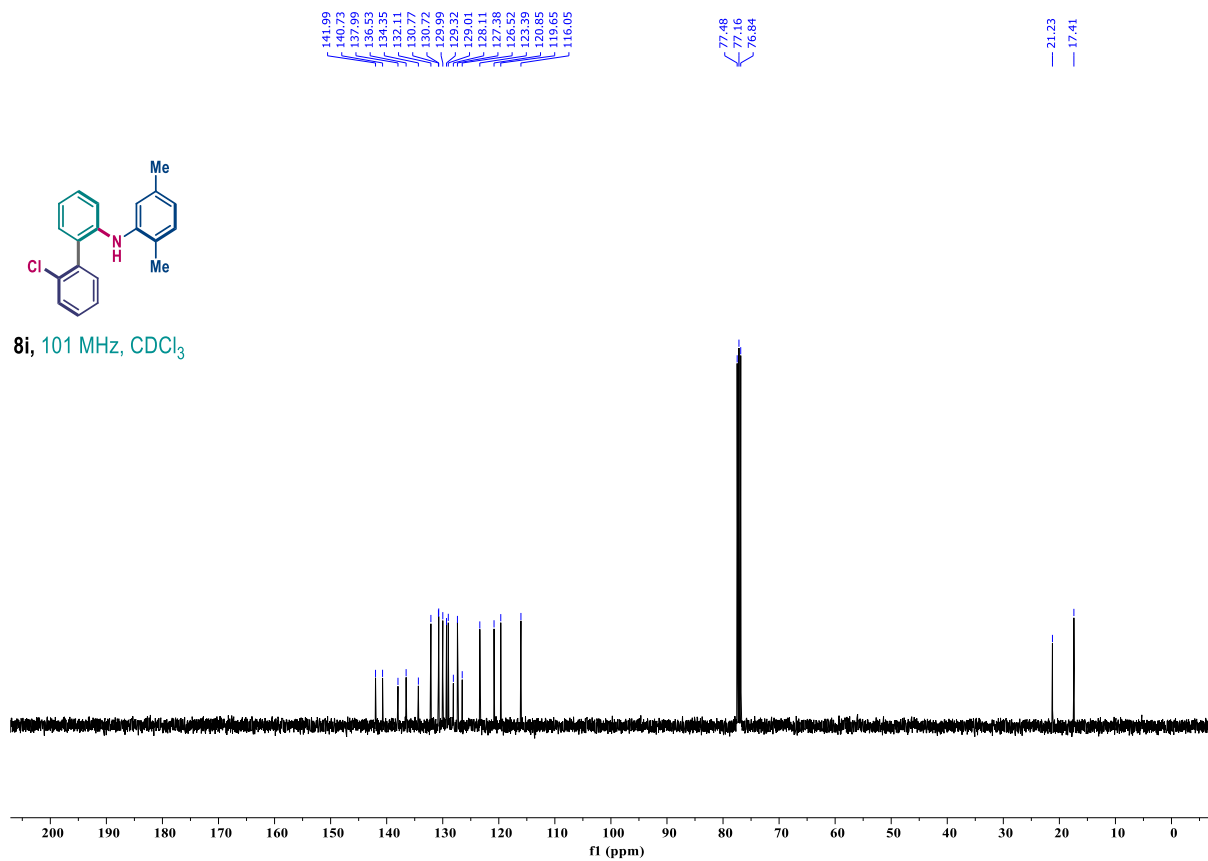
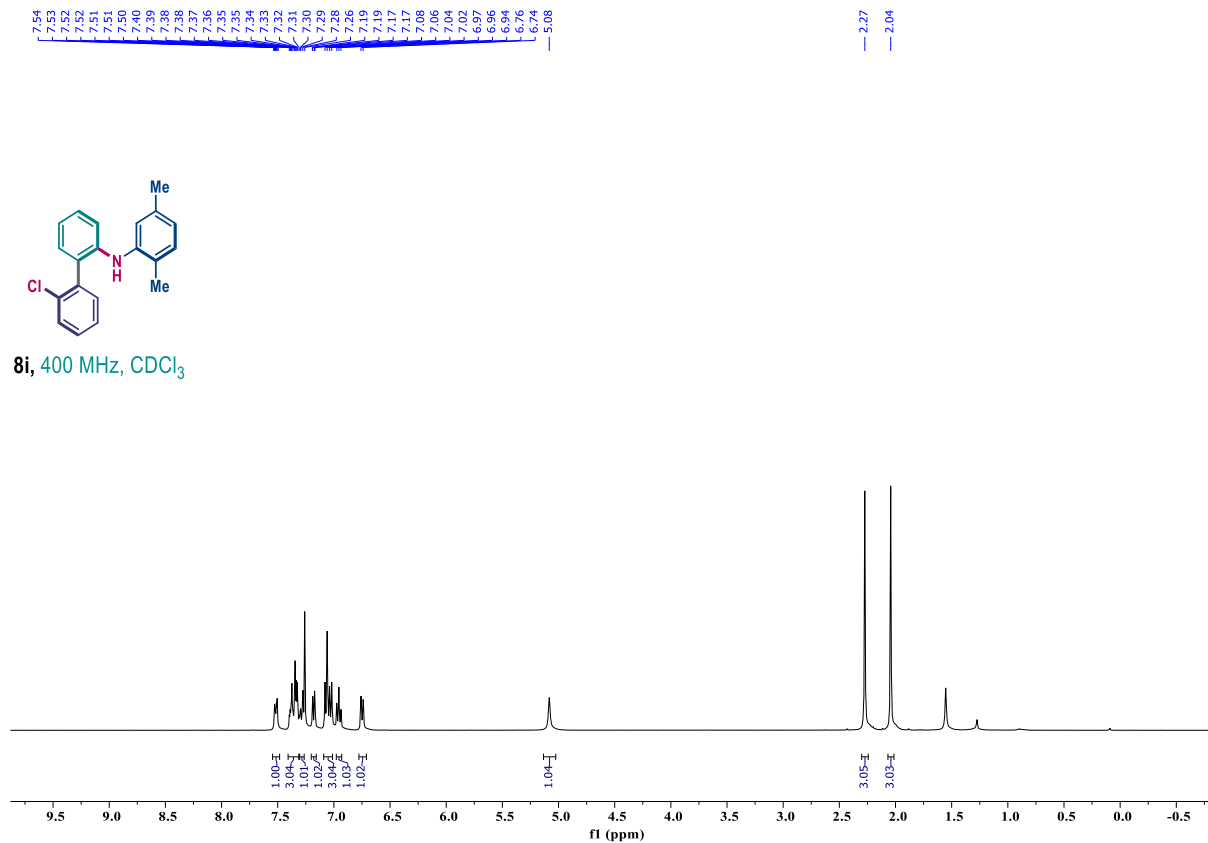


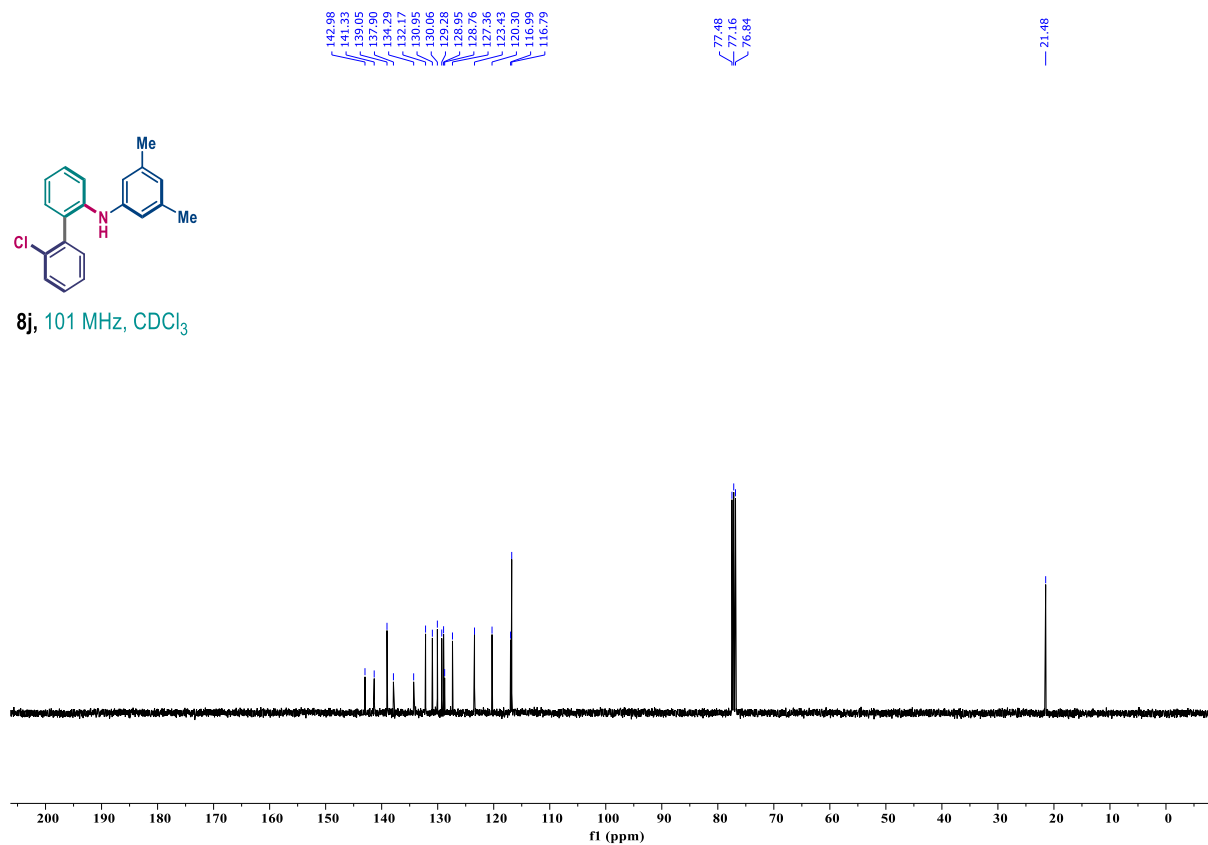
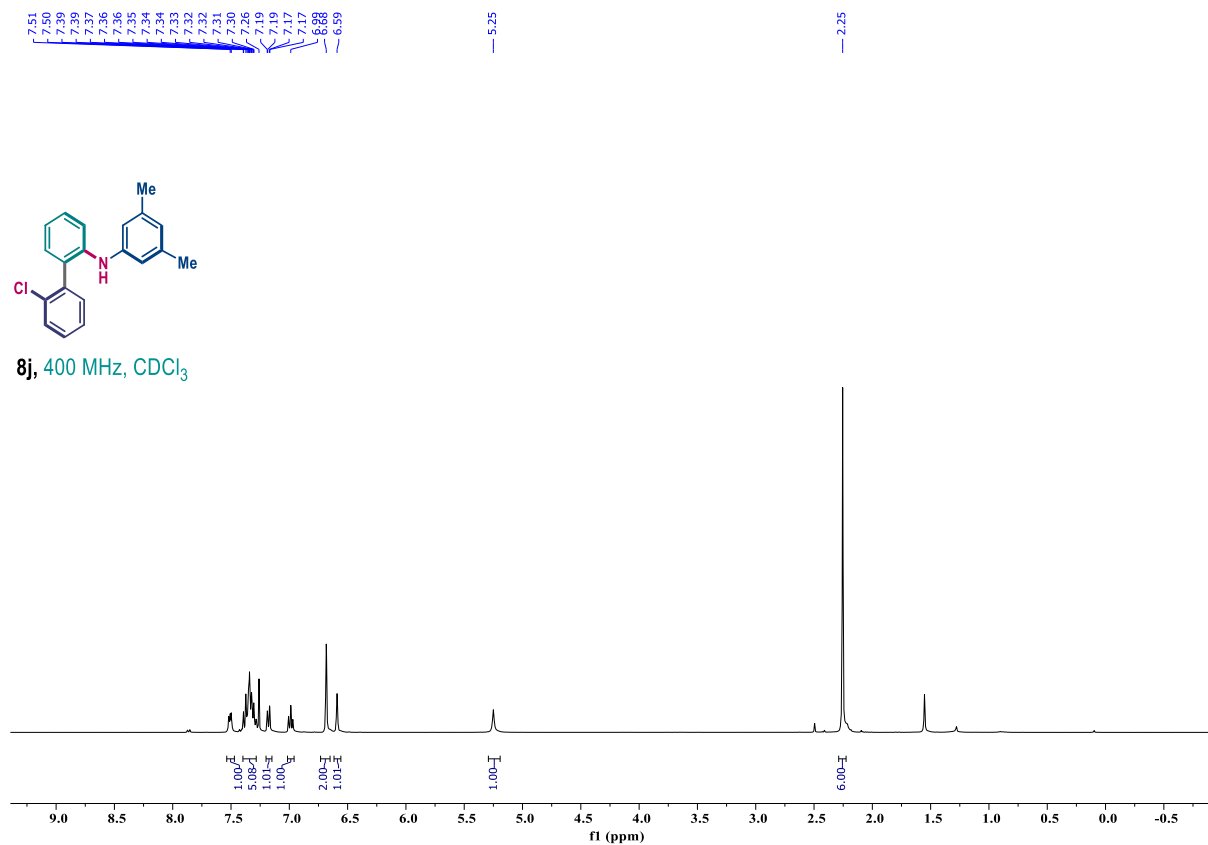


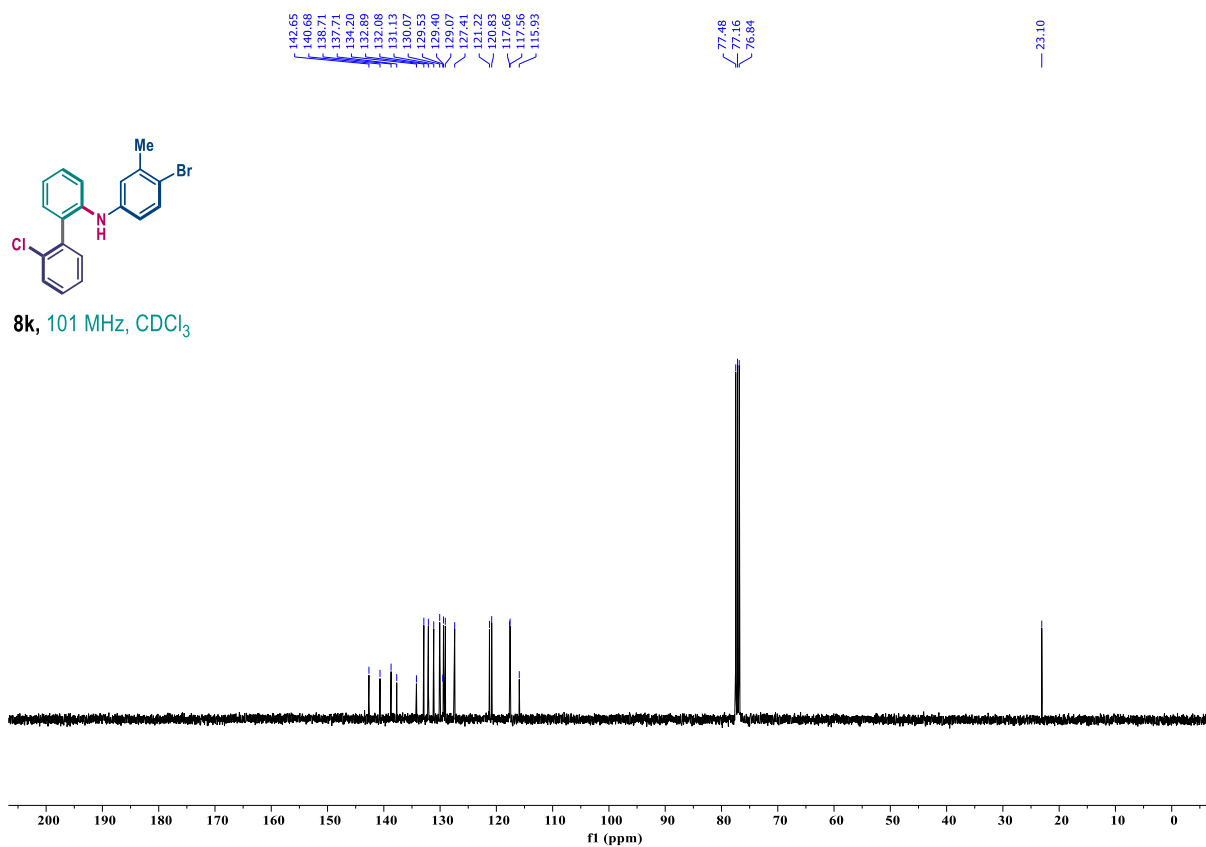
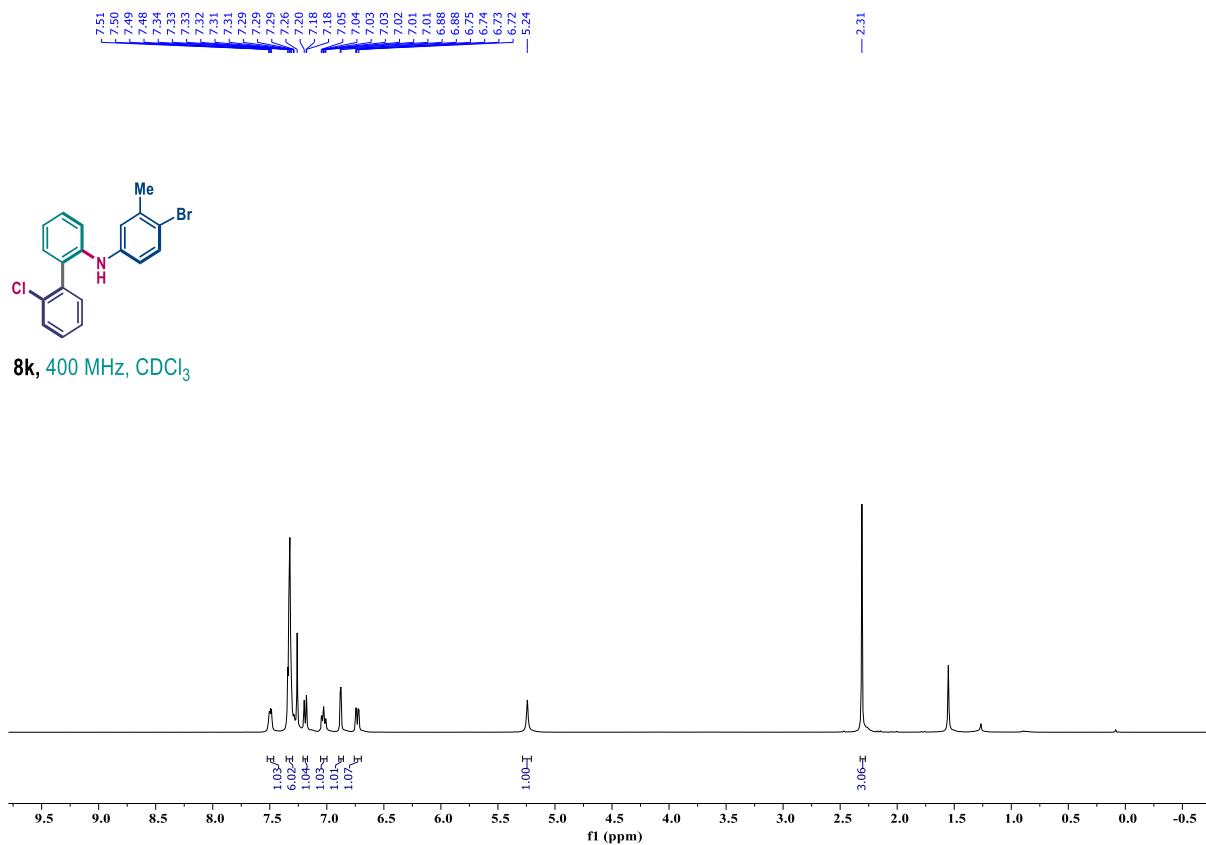


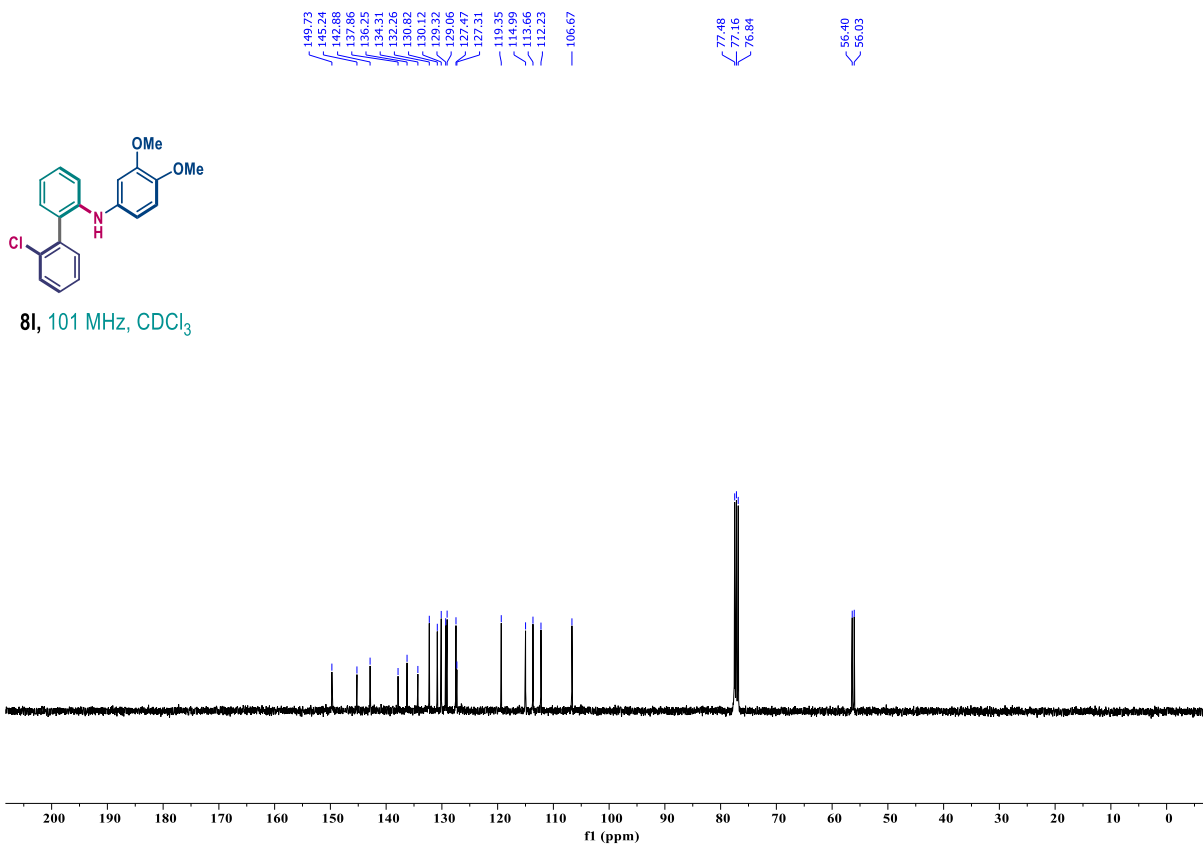
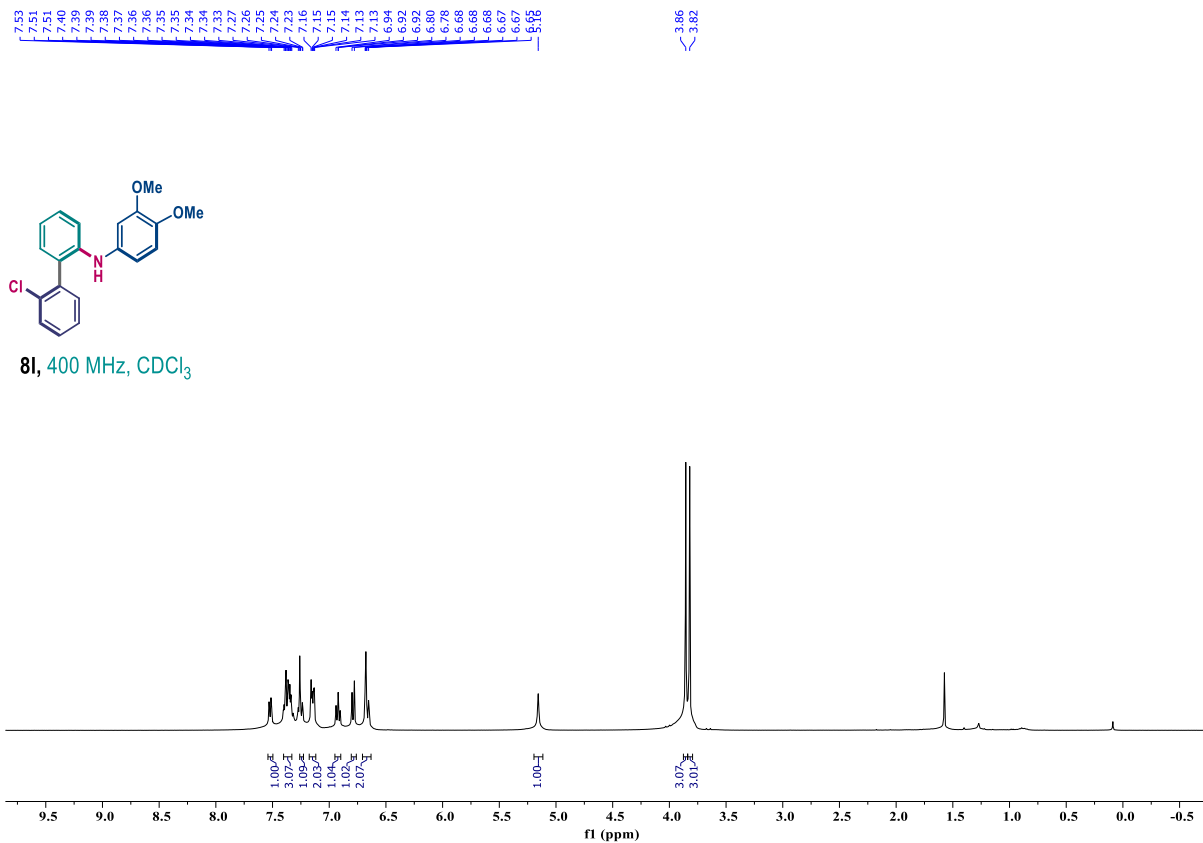


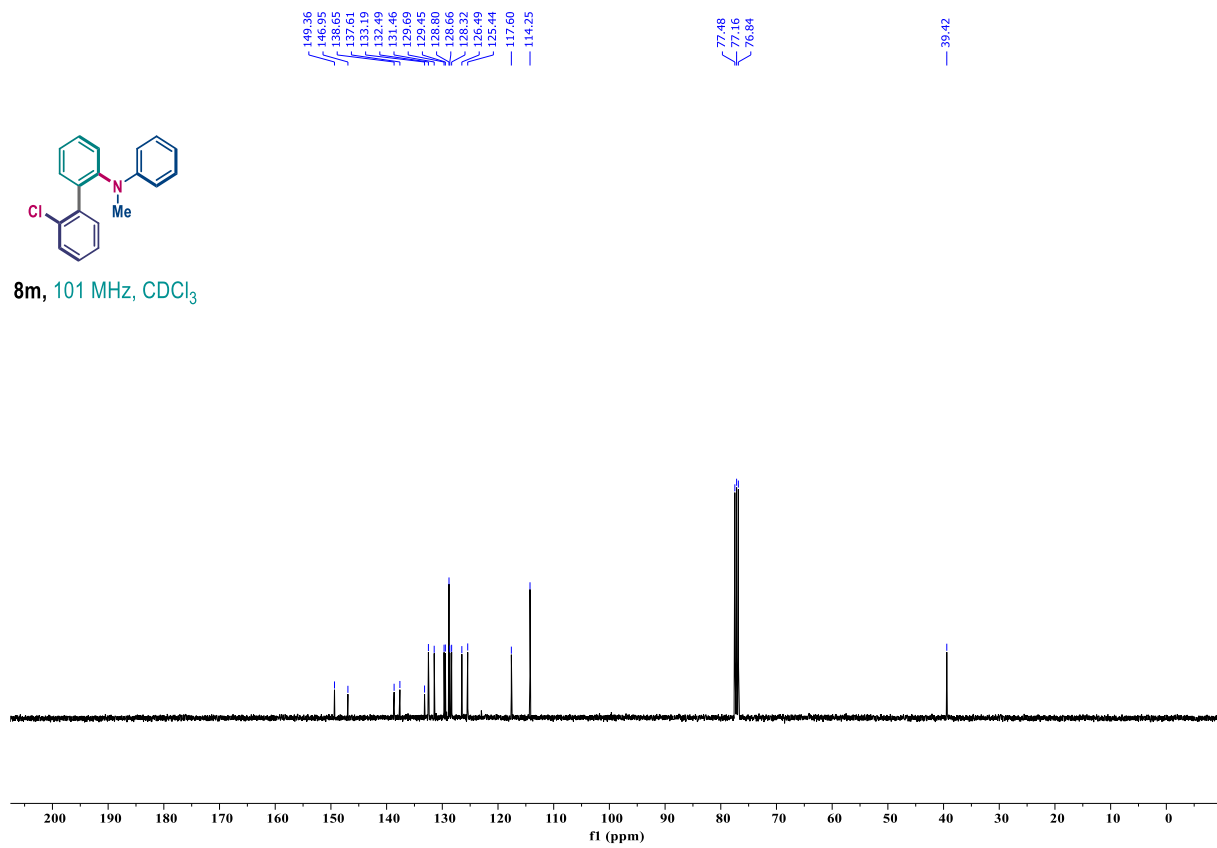
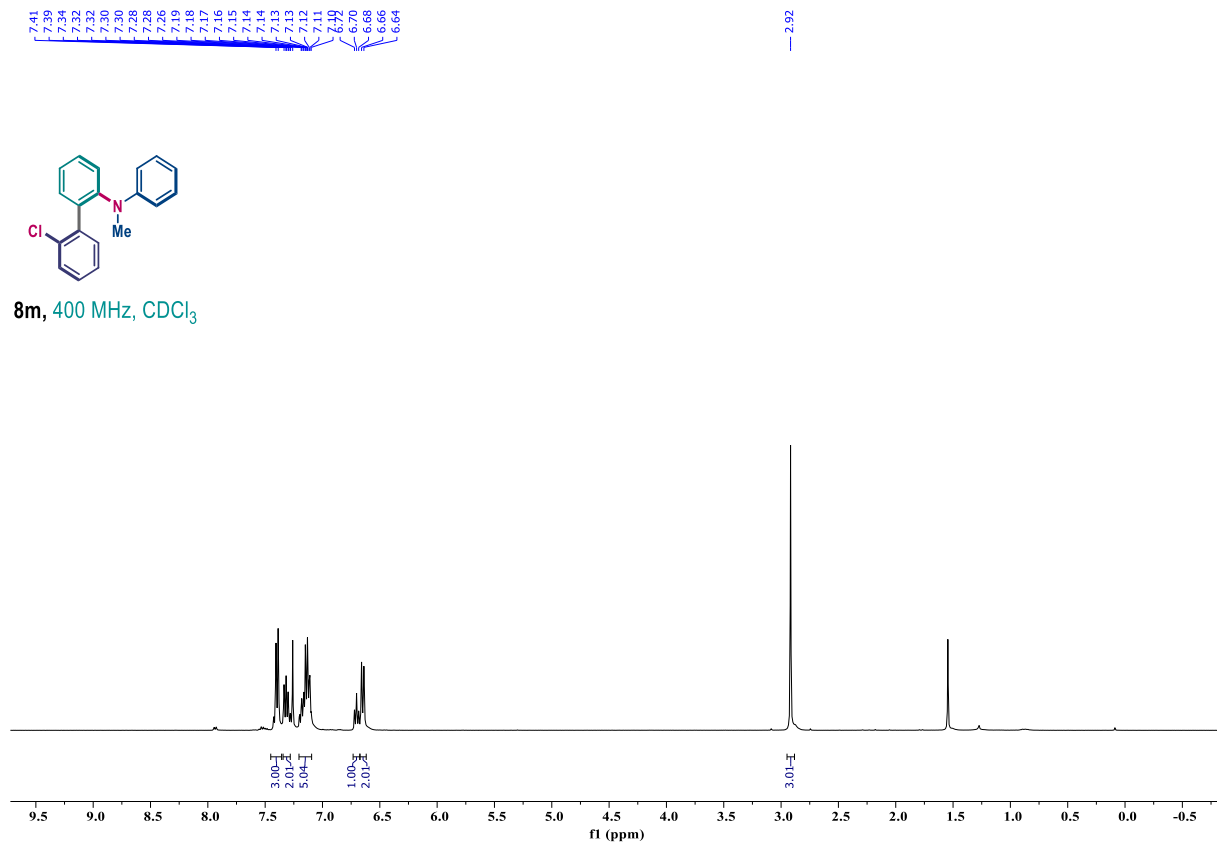


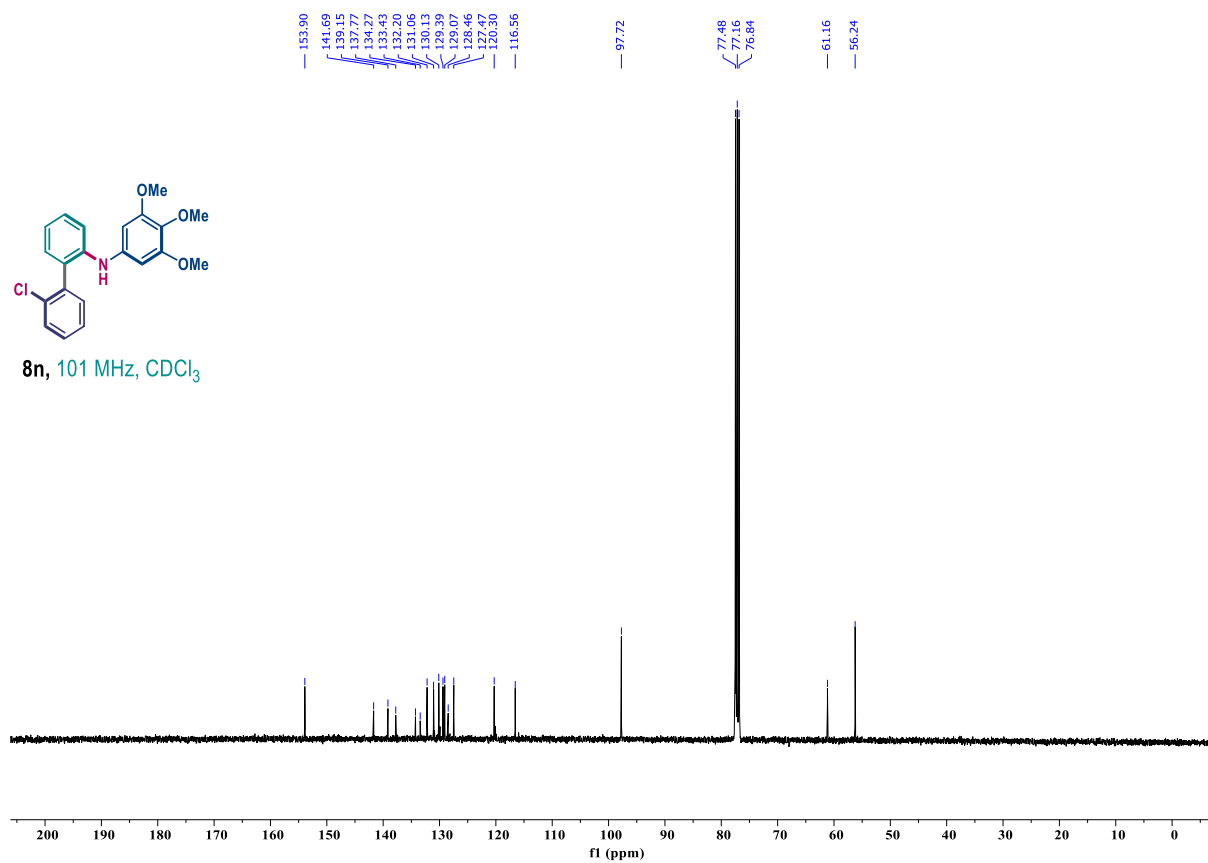
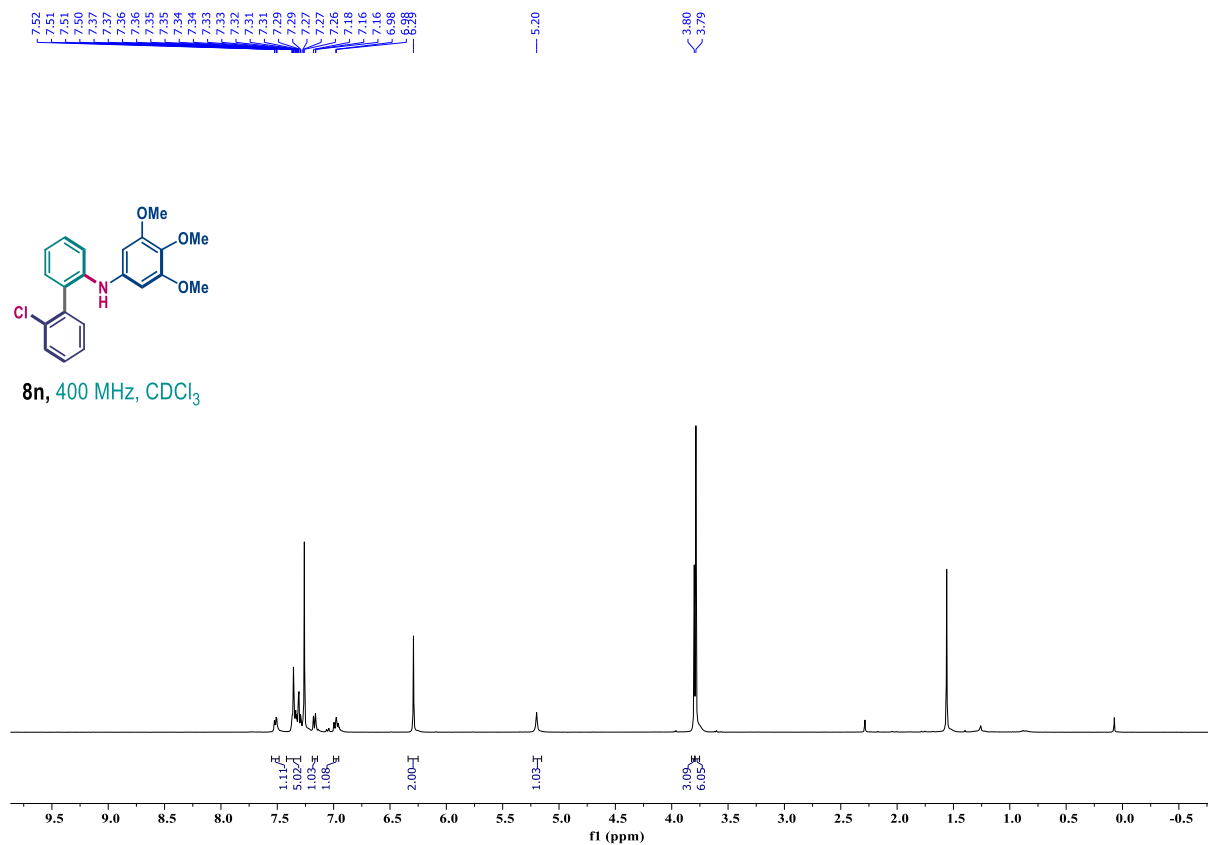






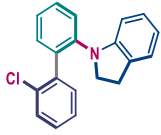




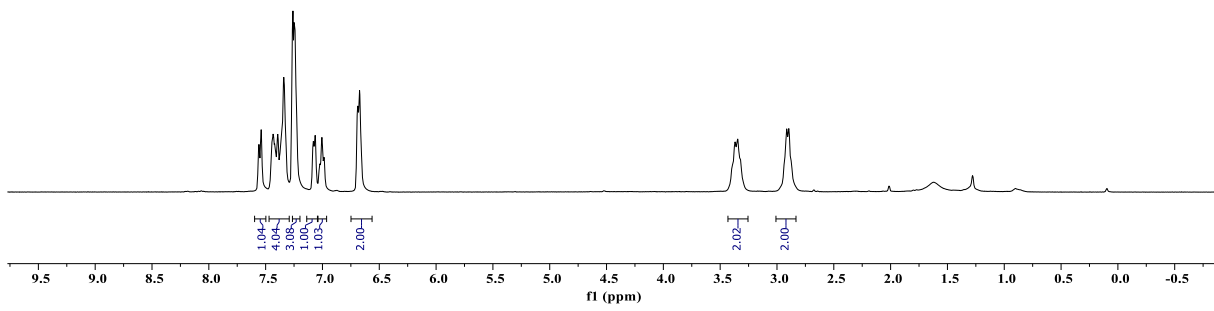


7.56
7.54
7.54
7.45
7.44
7.43
7.42
7.41
7.38
7.36
7.34
7.34
7.32
7.27
7.26
7.25
7.24
7.23
7.23
7.06
7.03
7.00
6.98
6.67
6.65

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3.35
3.32
3.24
2.92
2.89
2.87



8o, 400 MHz, CDCl₃



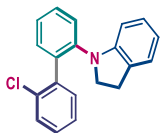
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144.10
139.35
138.69
133.62
132.03
131.76
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129.16
128.59
127.03
126.68
124.75
124.52
123.16
118.27

105.00

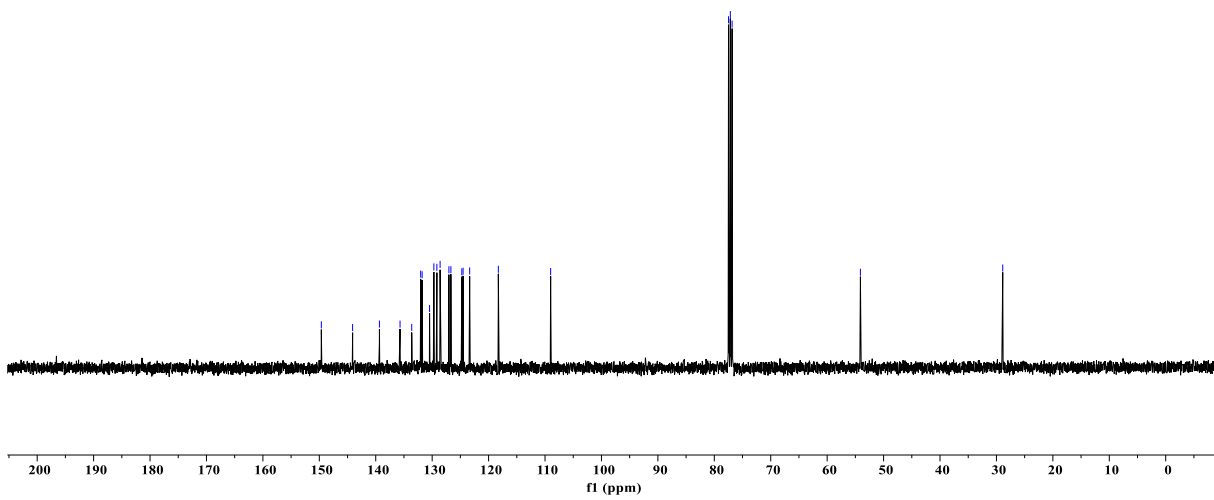
77.48
77.16
76.84

54.11

28.88

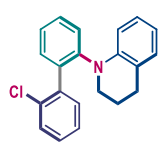


8o, 101 MHz, CDCl₃

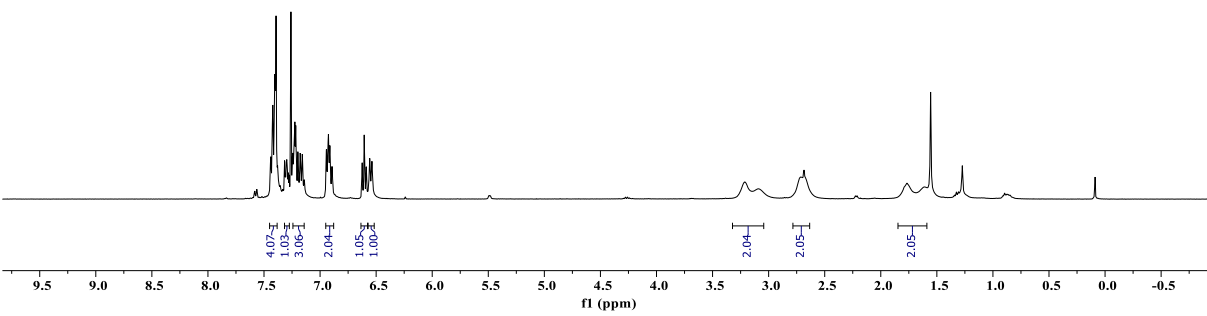


7.44
7.43
7.42
7.41
7.40
7.39
7.30
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.20
7.18
7.16
6.94
6.93
6.81
6.82
6.81
6.59
6.56
6.54

3.21
3.09
2.72
2.68
2.66
1.77
1.60

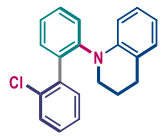


8p, 400 MHz, CDCl₃

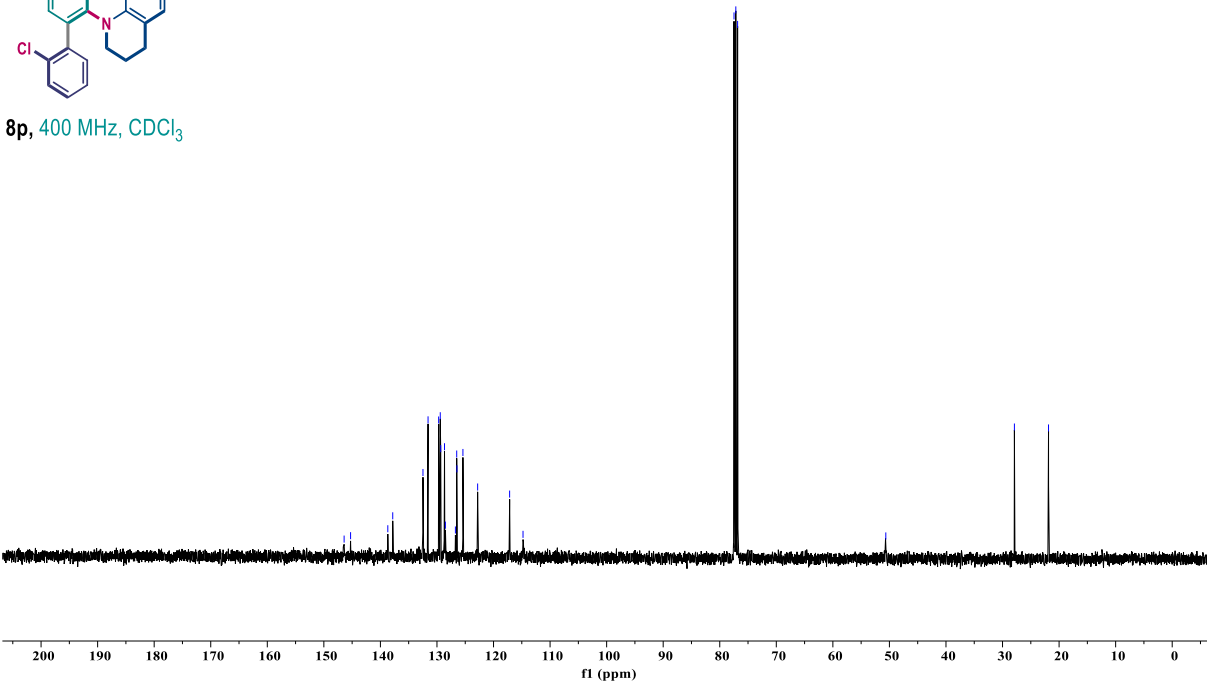


146.42
145.27
138.69
137.82
132.47
131.57
129.70
129.42
128.33
128.67
128.51
128.44
126.54
126.47
125.41
122.81
117.15
114.78

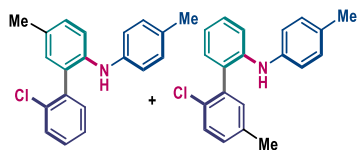
77.48
77.16
76.84
50.64
27.90
21.87



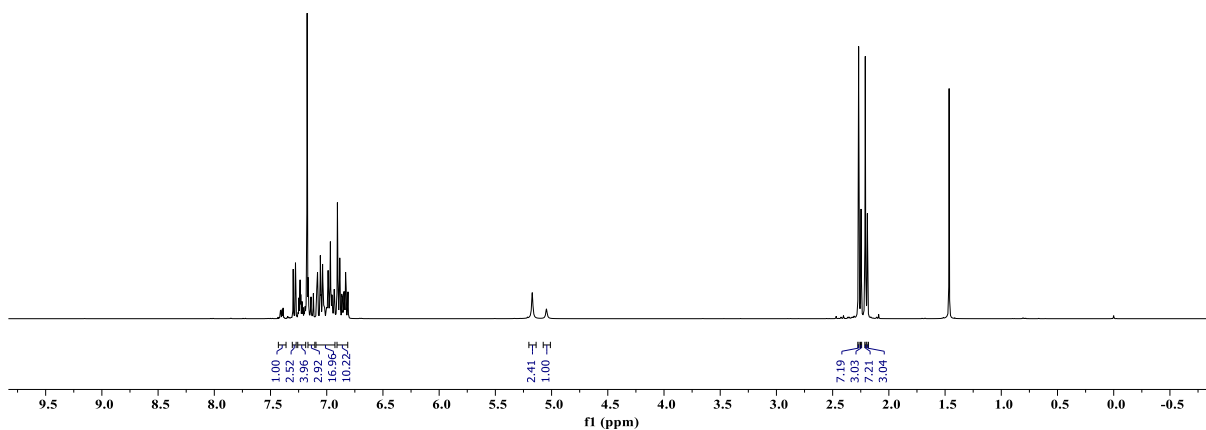
8p, 400 MHz, CDCl₃



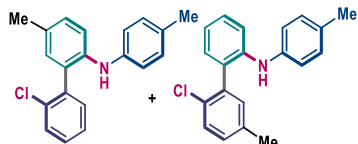
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7.40
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7.39
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7.24
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7.19
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7.18
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7.17
7.16
7.16
7.14
7.14
7.12
7.12
7.09
7.09
7.08
7.08
7.06
7.06
7.05
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7.05
7.04
7.04
7.04
7.04
7.03
7.03
7.02
7.02
7.01
7.01
7.00
7.00
6.99
6.99
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6.96
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6.90
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6.84
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6.81
5.17
5.05
2.27
2.25
2.21
2.19



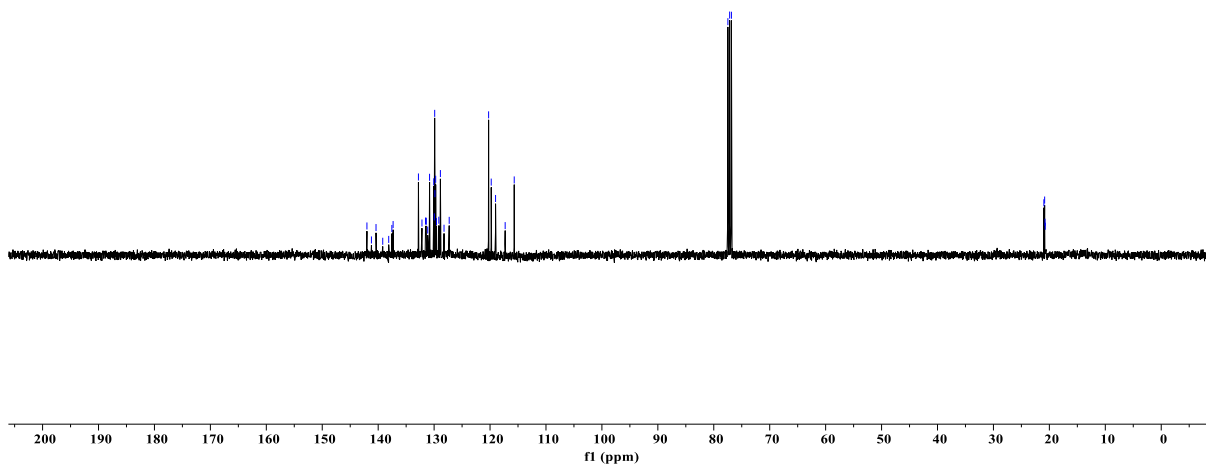
8s + 8s'
(regioisomeric ratio = 2.4:1)
400 MHz, CDCl₃

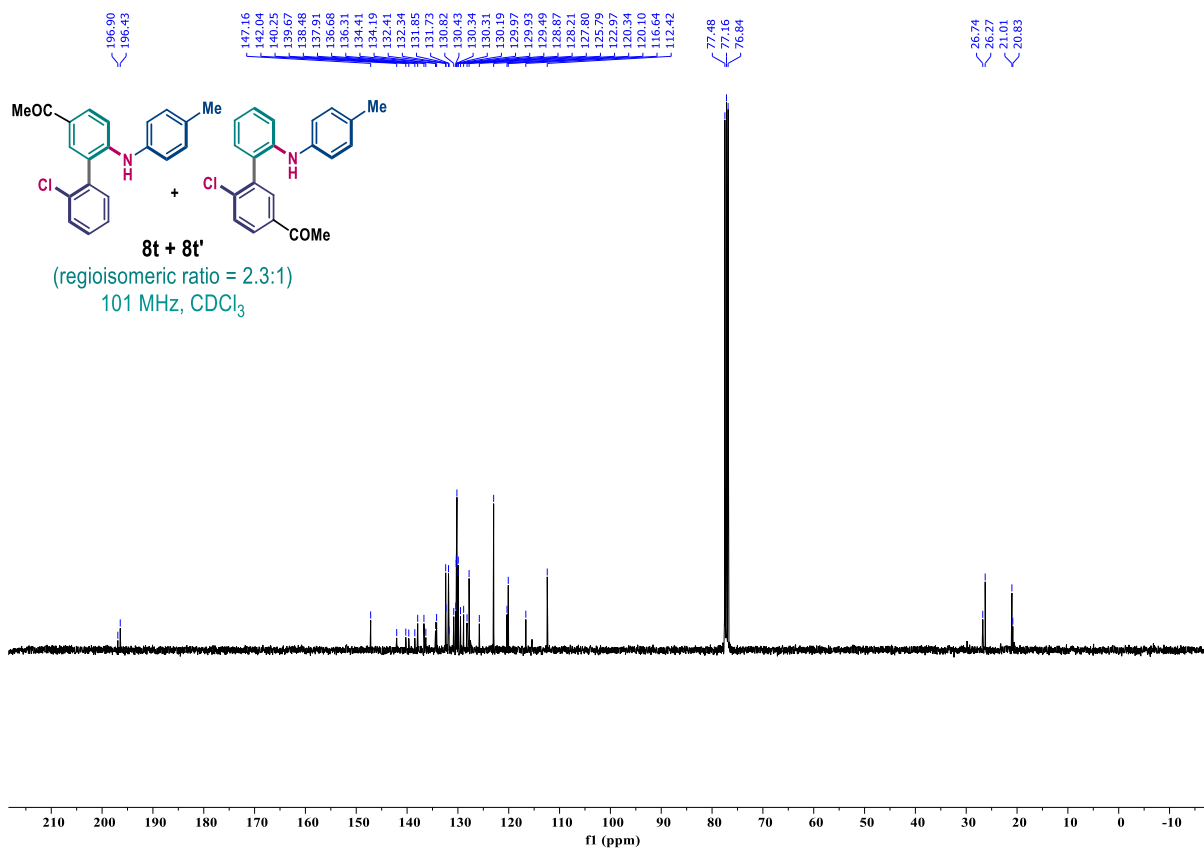
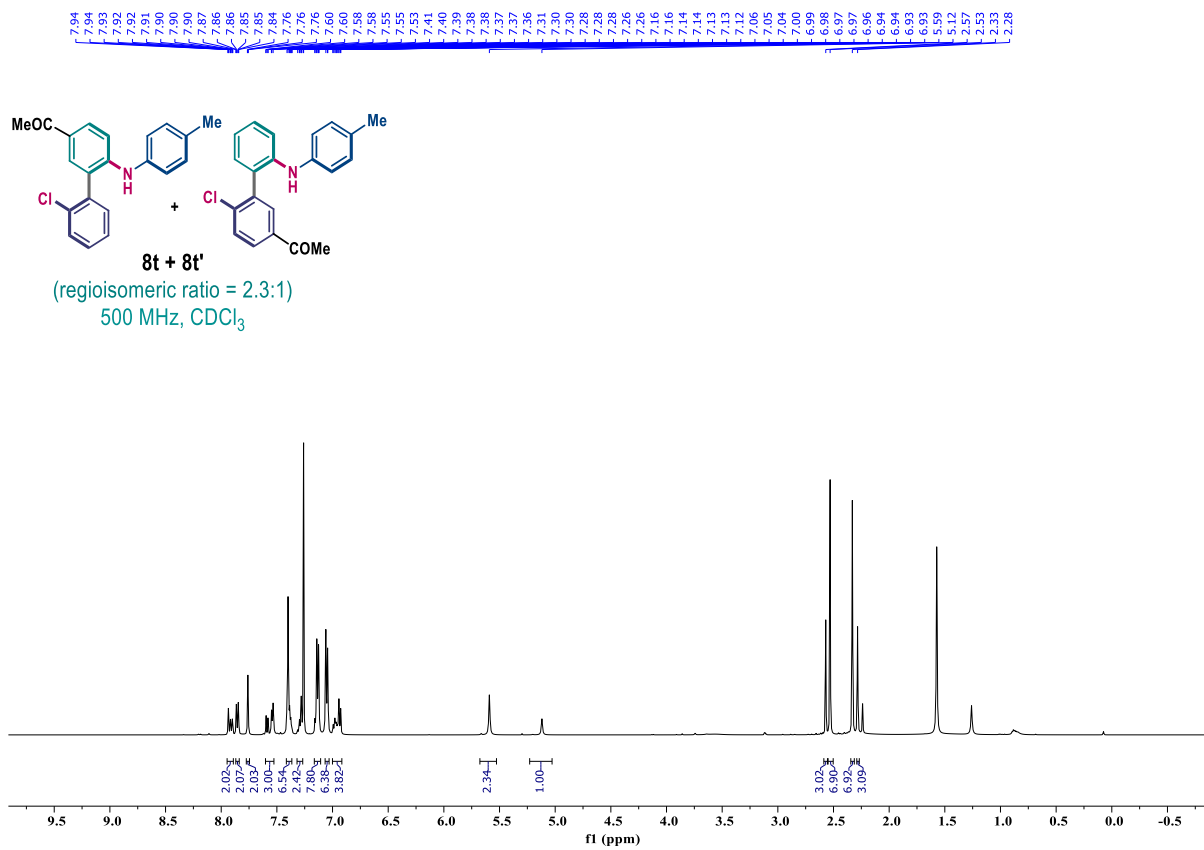


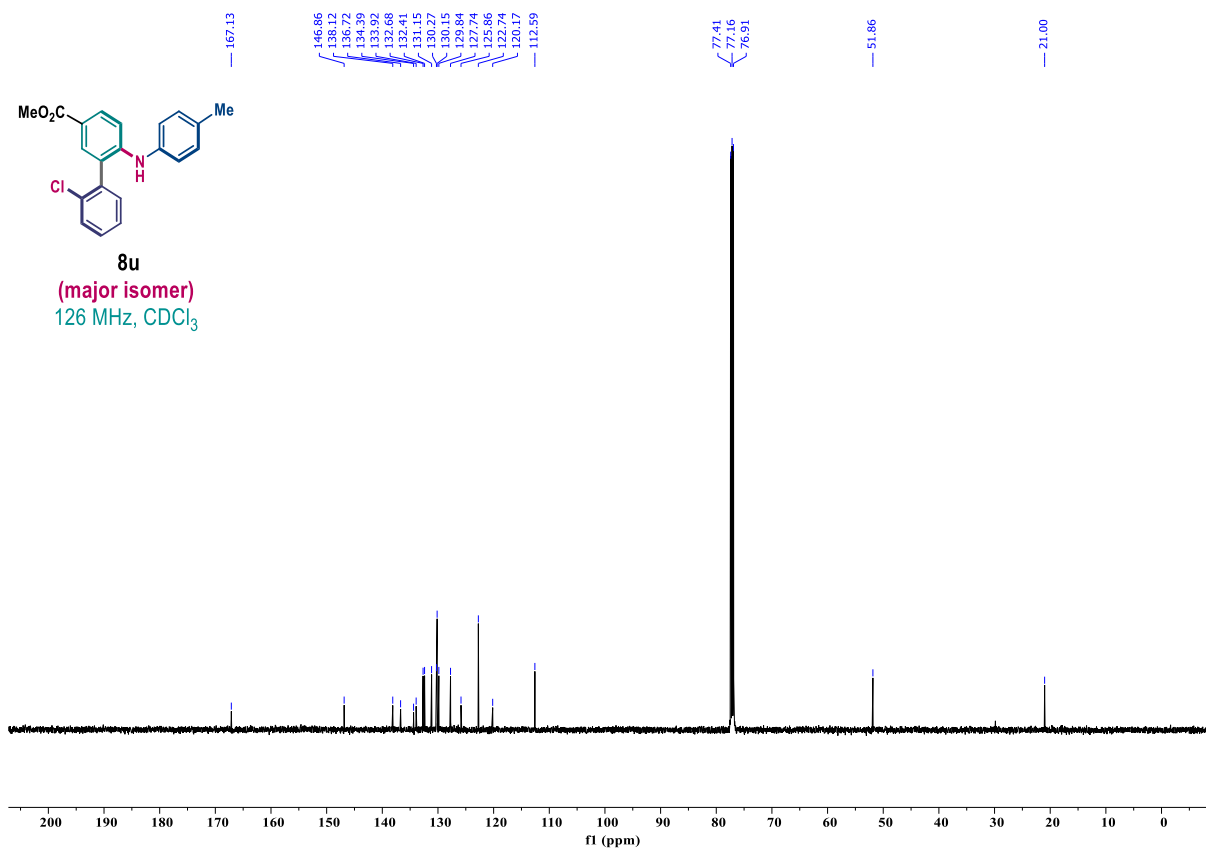
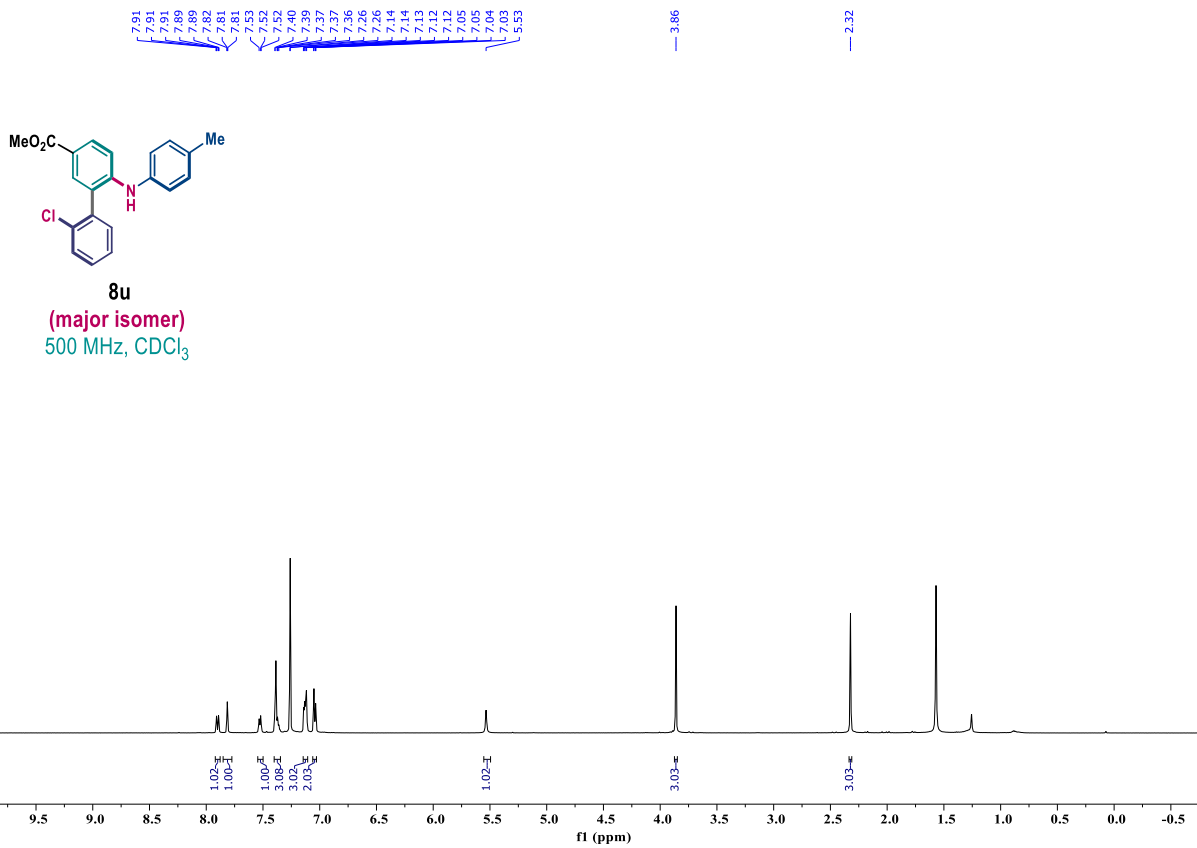
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144.21
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139.19
138.12
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137.33
132.80
132.17
131.78
131.59
131.15
130.81
130.07
129.97
129.90
129.85
129.72
129.71
129.16
128.88
128.23
127.30
120.26
119.79
119.02
117.80
115.68
77.48
77.16
76.84
20.98
20.84
20.78
20.74

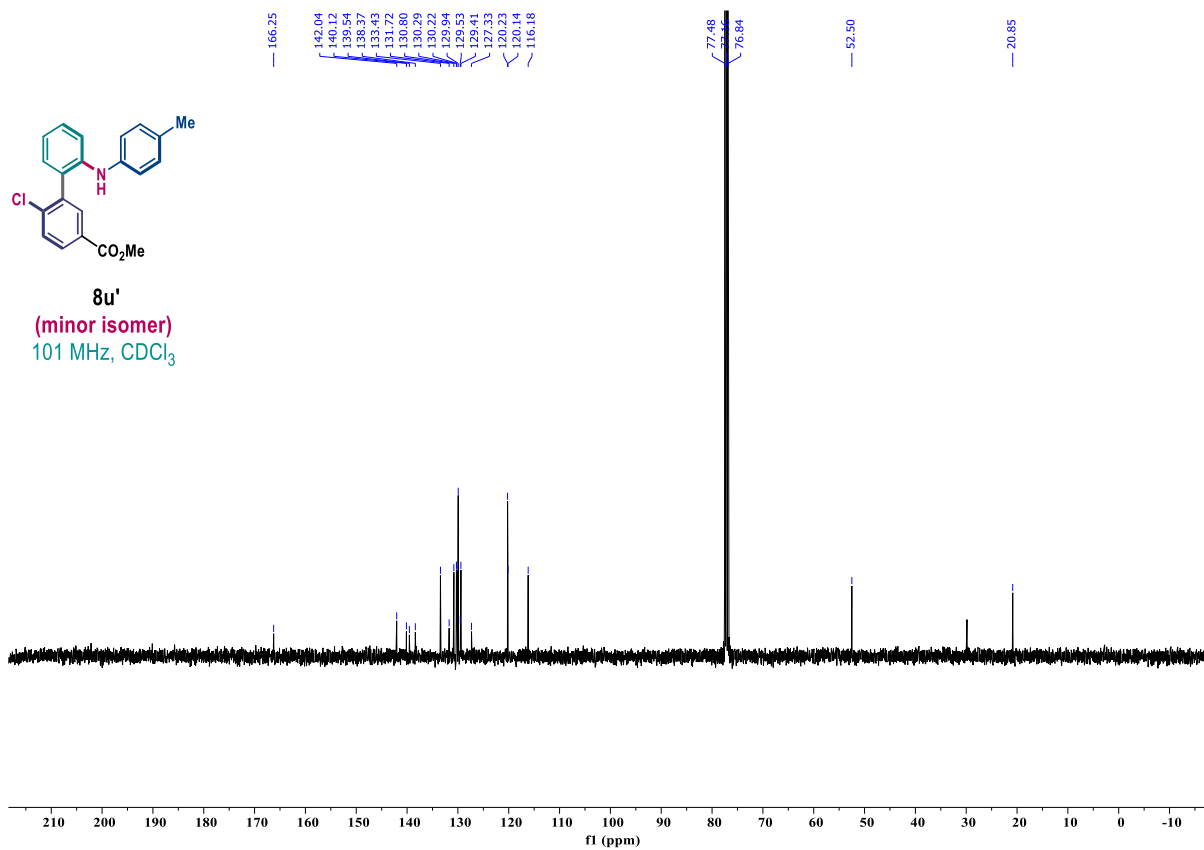
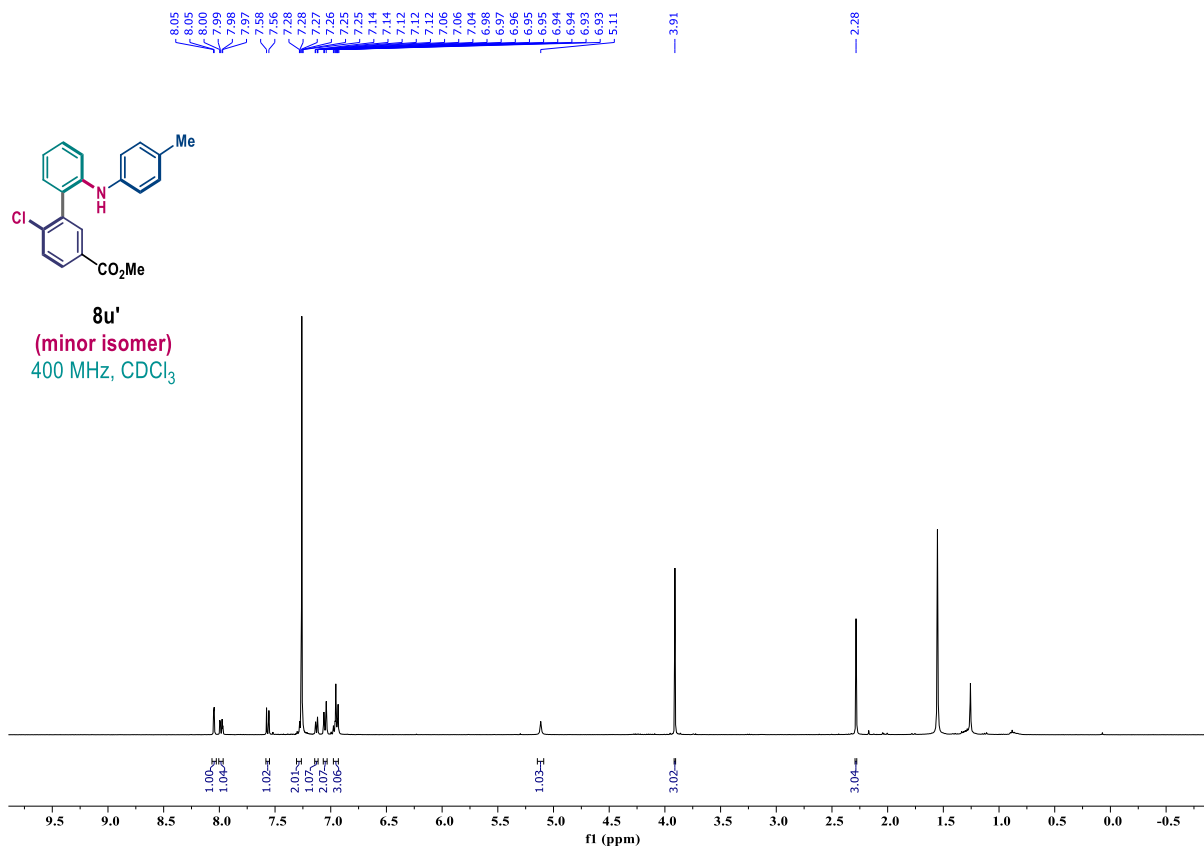


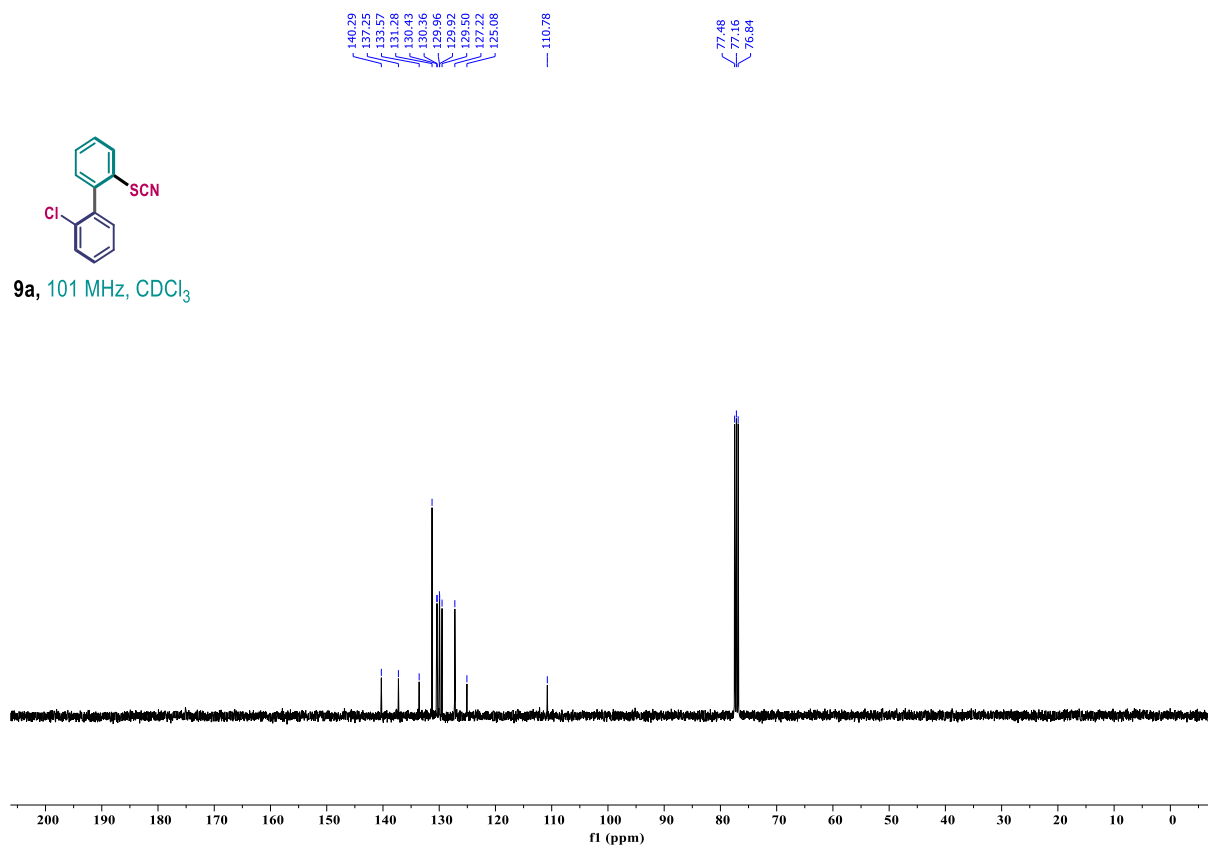
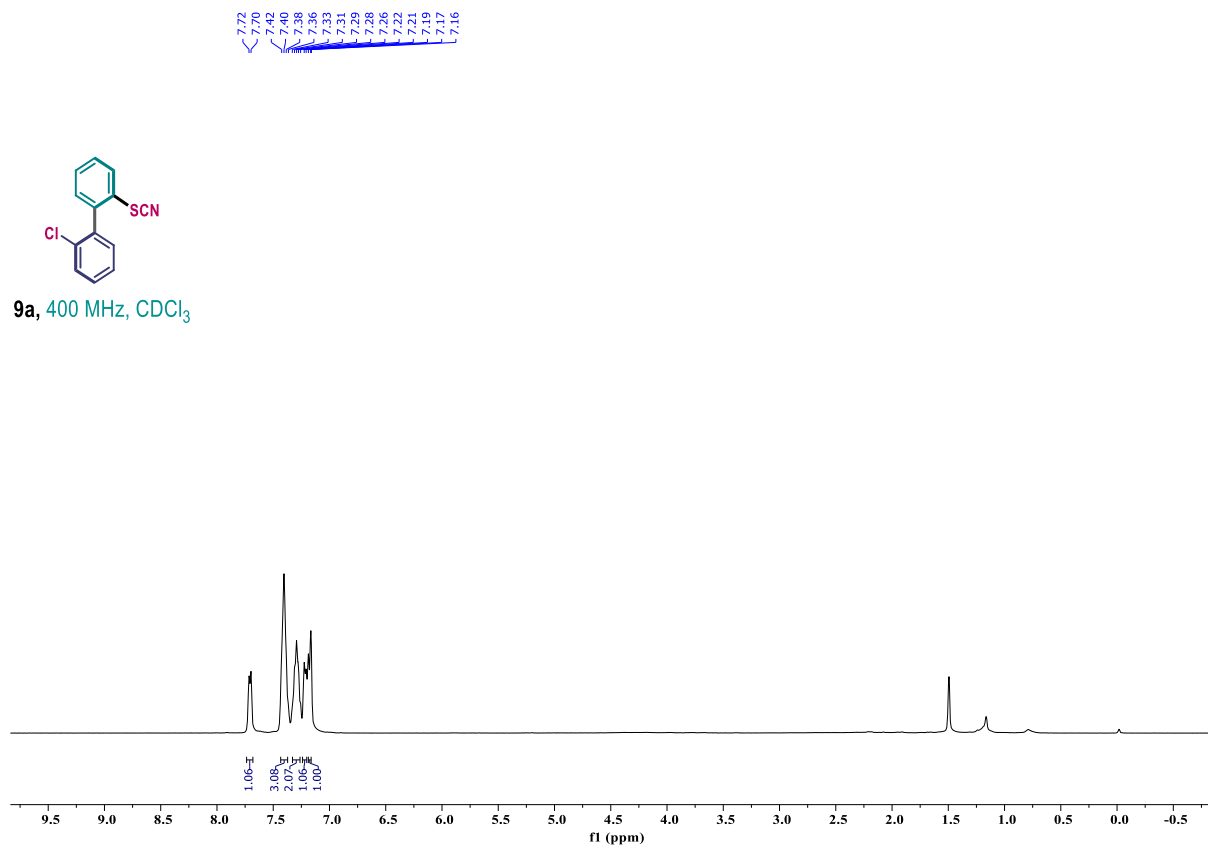
8s + 8s'
(regioisomeric ratio = 2.4:1)
101 MHz, CDCl₃

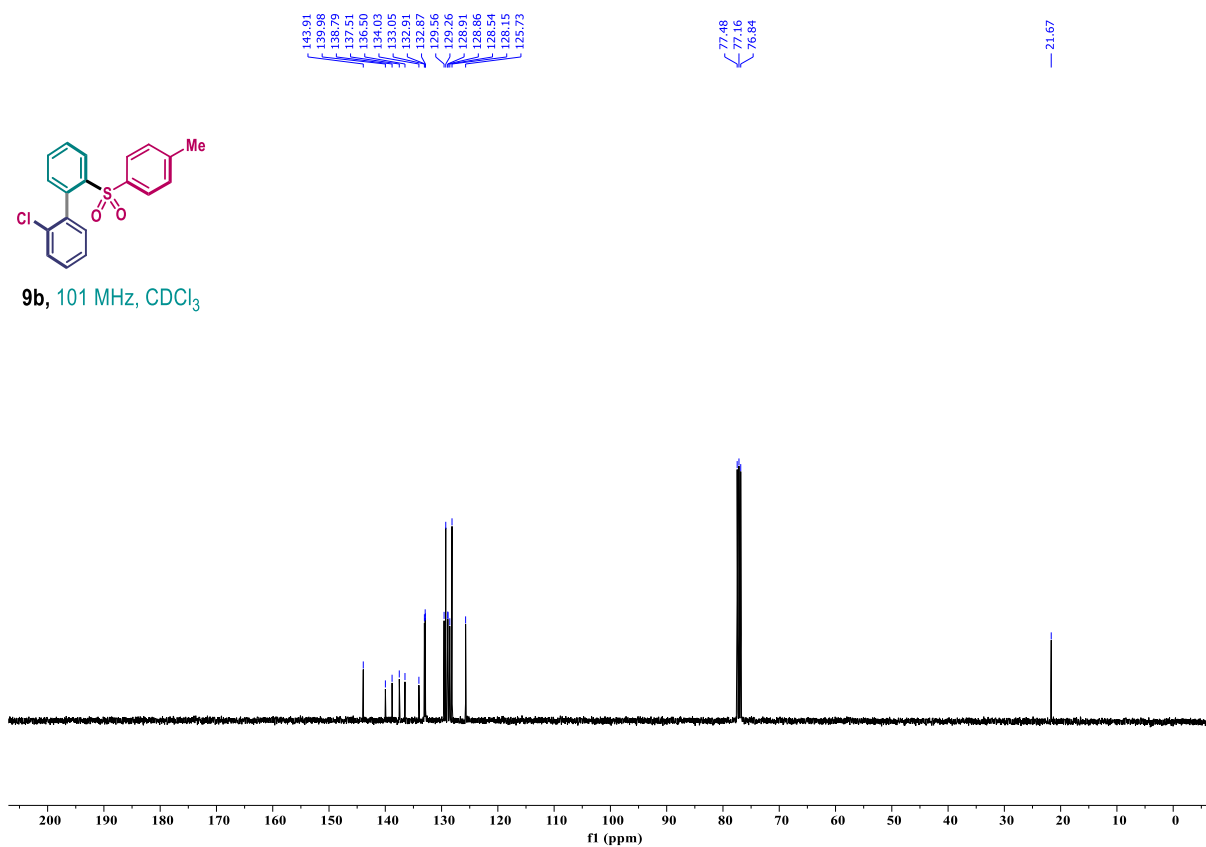
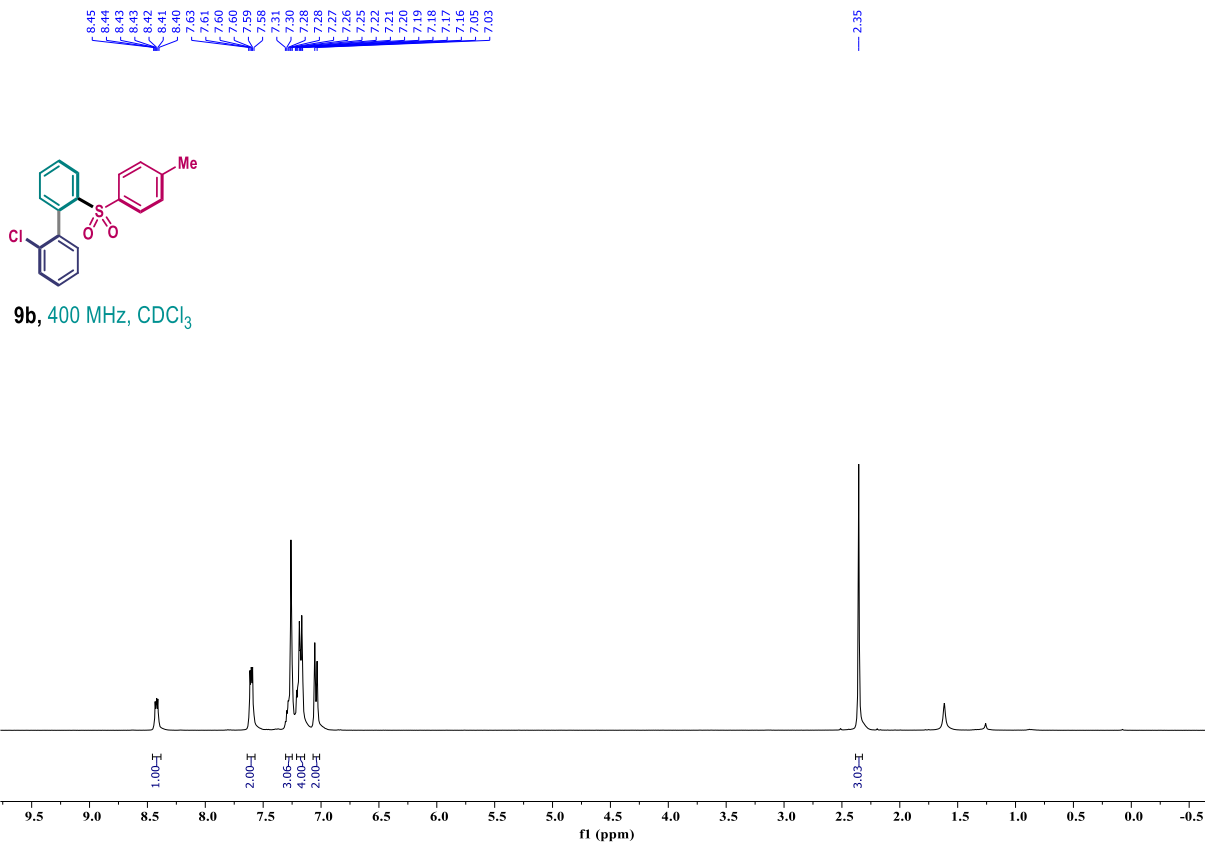


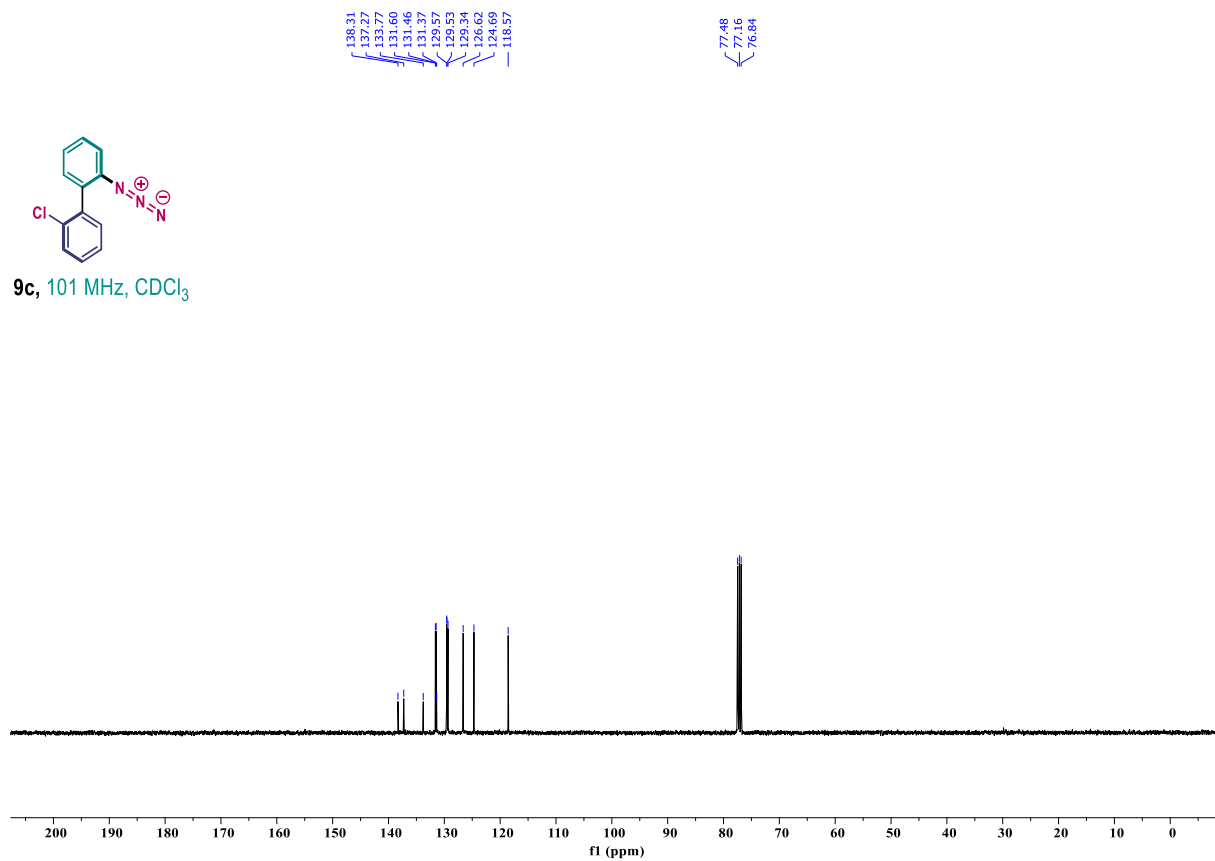
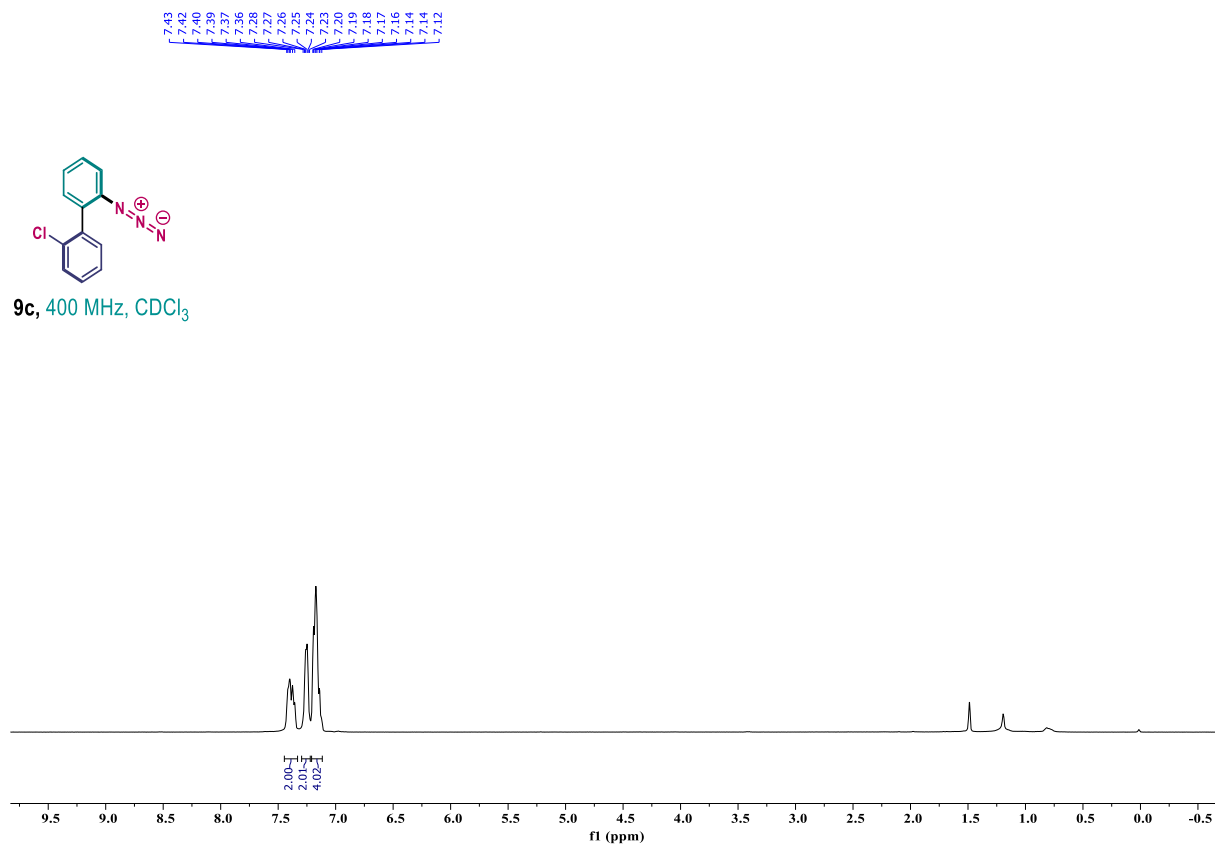


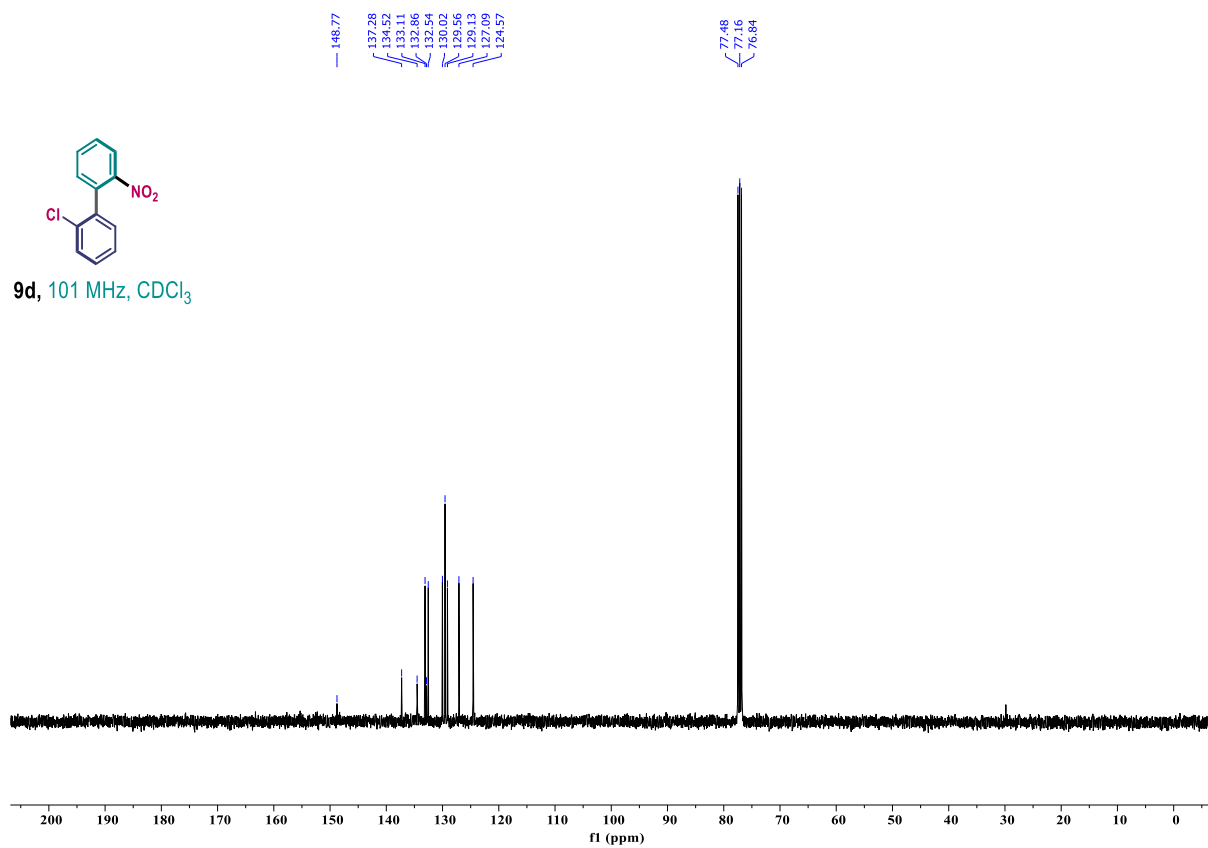
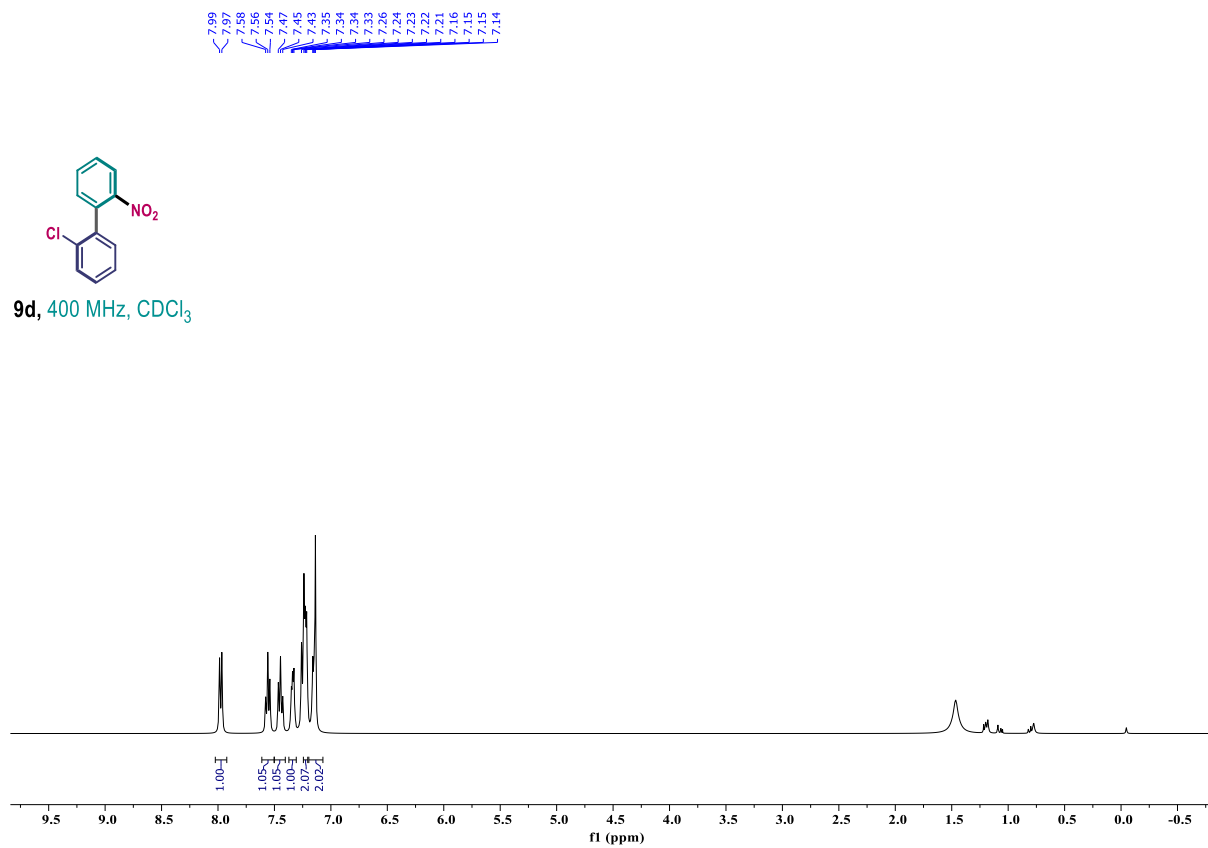


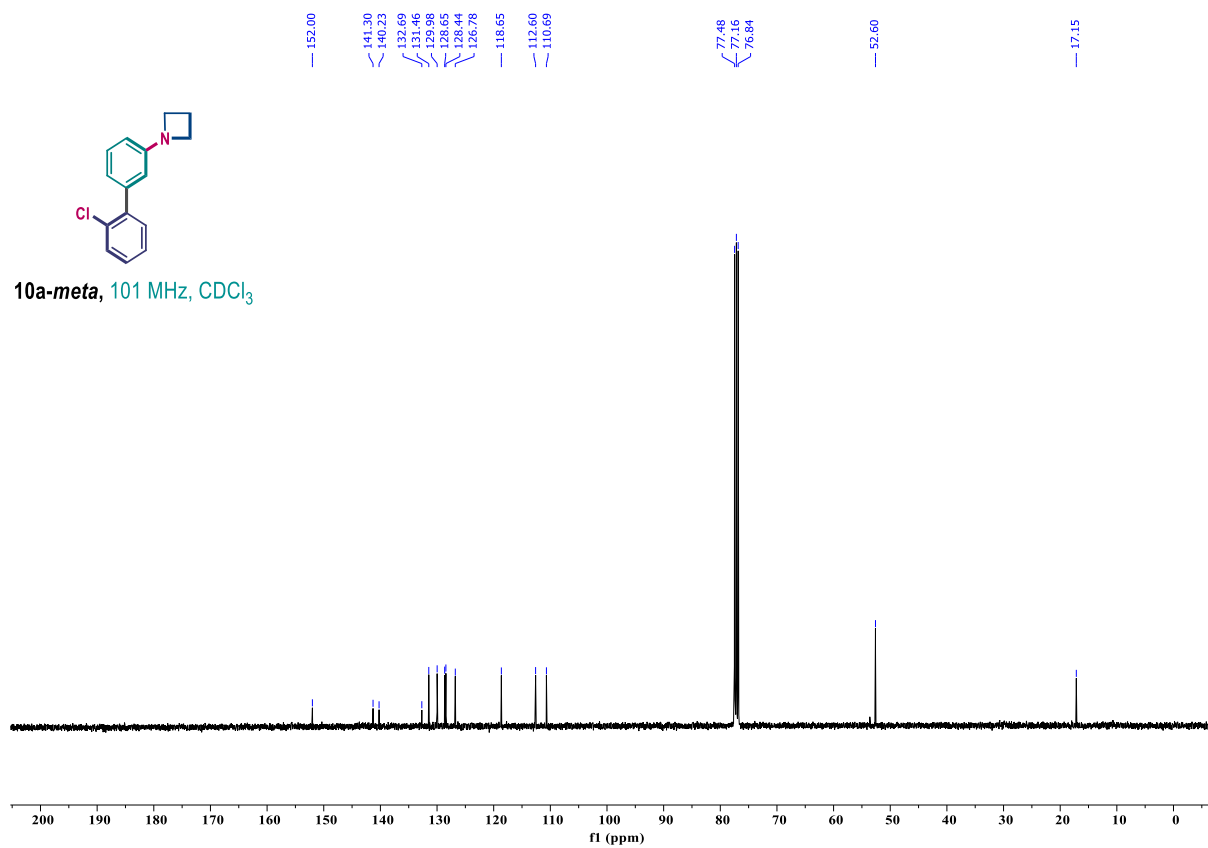
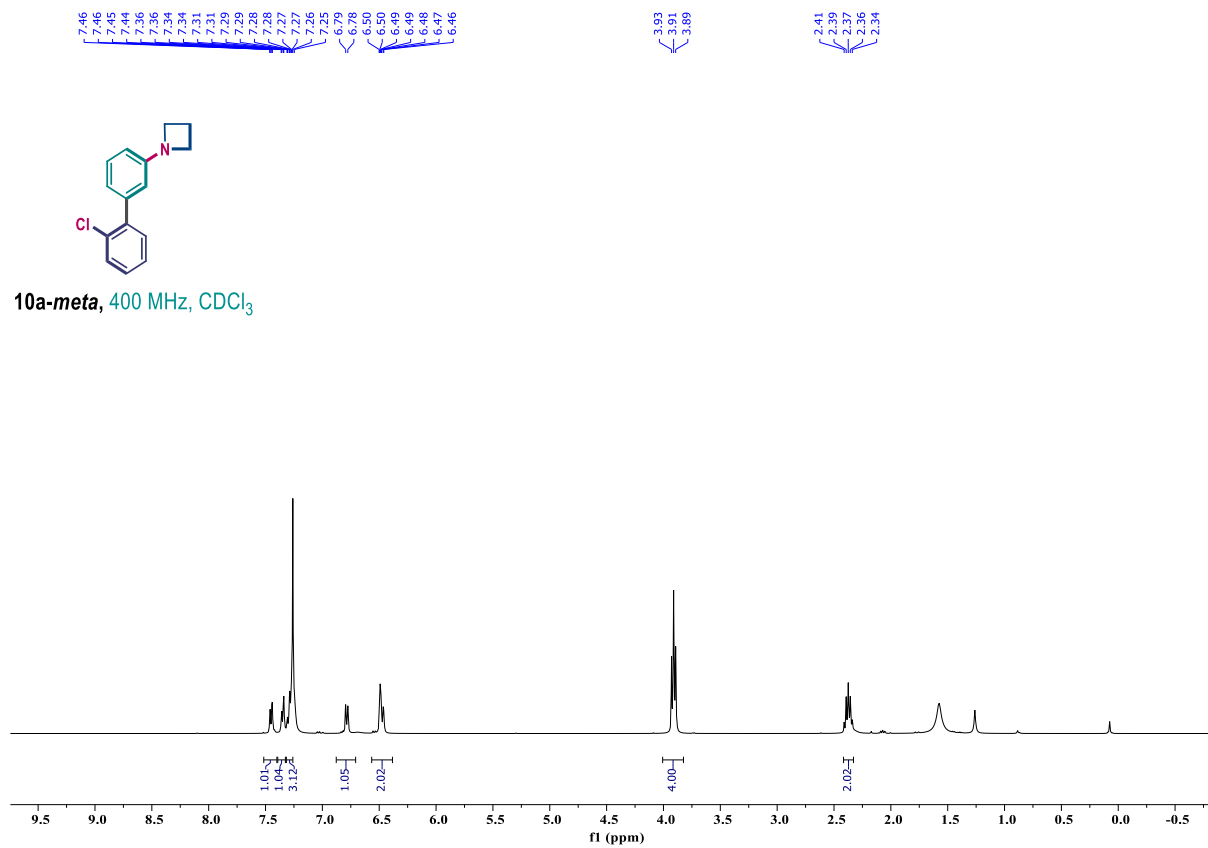




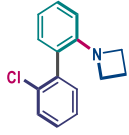




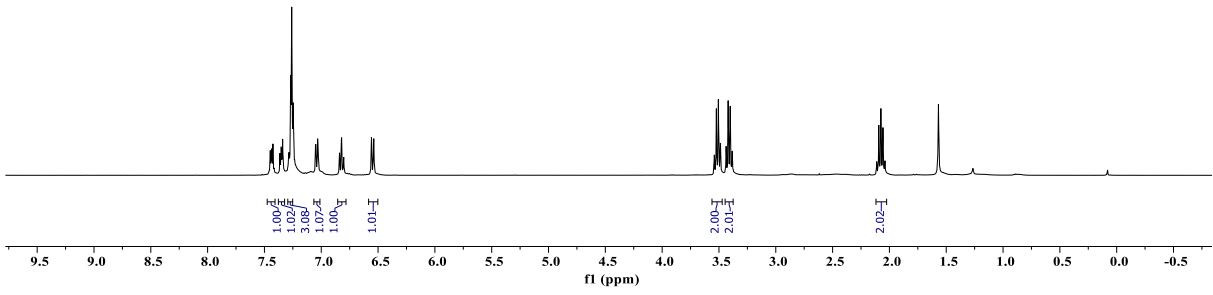




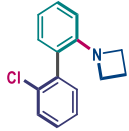
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7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.36
7.35
7.35
7.34
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7.33
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.23
7.23
7.05
7.05
7.03
7.03
6.84
6.84
6.82
6.82
6.80
6.80
6.56
6.56
6.54
6.54
3.54
3.52
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3.44
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3.38
2.11
2.09
2.08
2.06
2.04



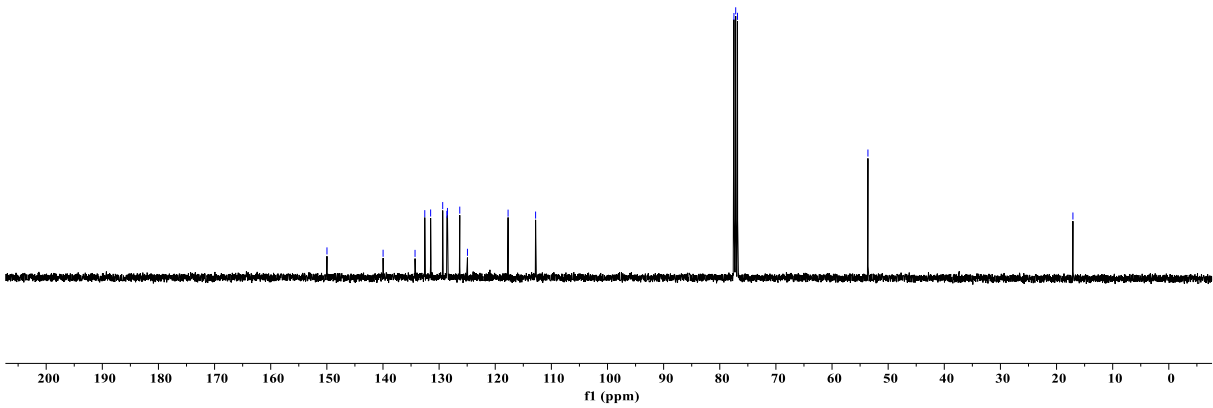
10a-ortho, 400 MHz, CDCl₃

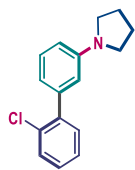


149.98
139.98
134.29
132.55
131.51
129.36
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128.51
128.32
126.82
117.71
112.81
77.48
77.06
76.84
53.60
17.09

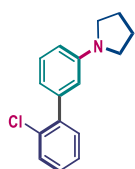
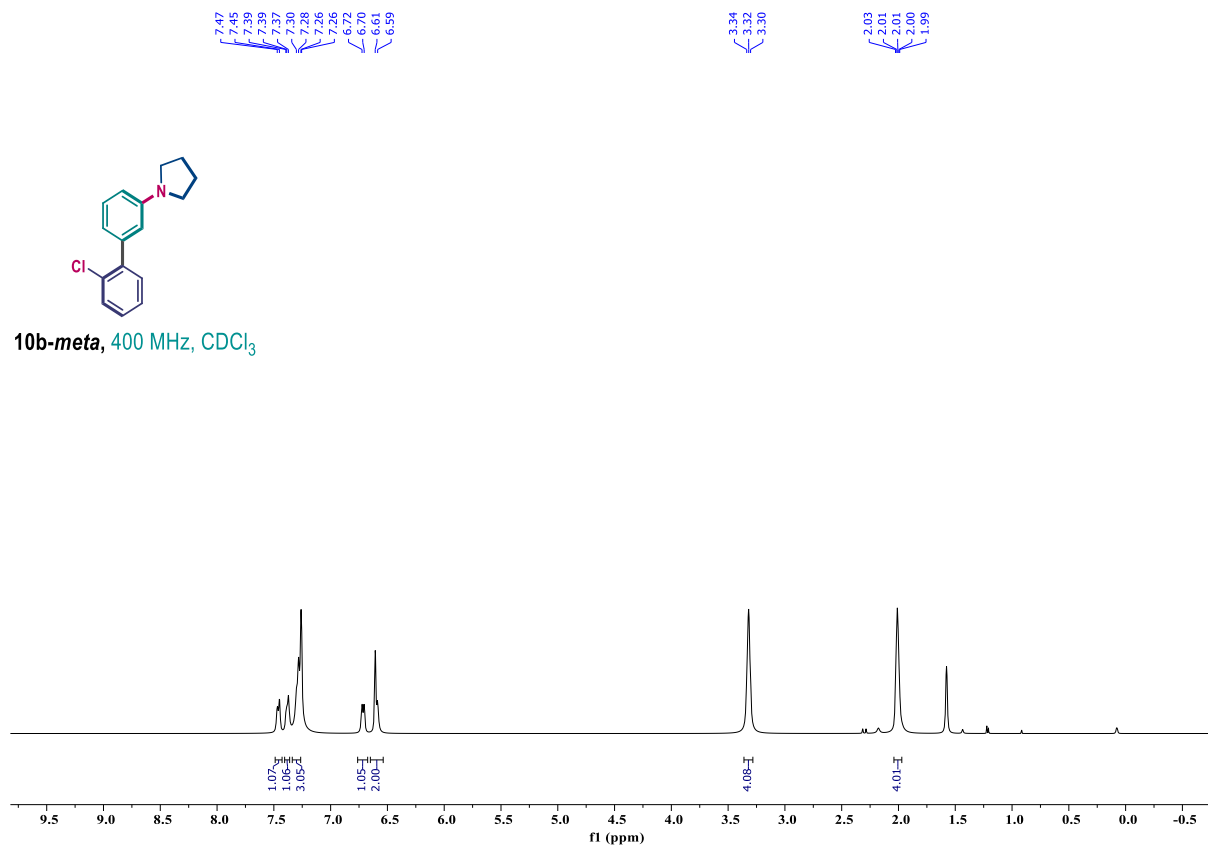


10a-ortho, 101 MHz, CDCl₃

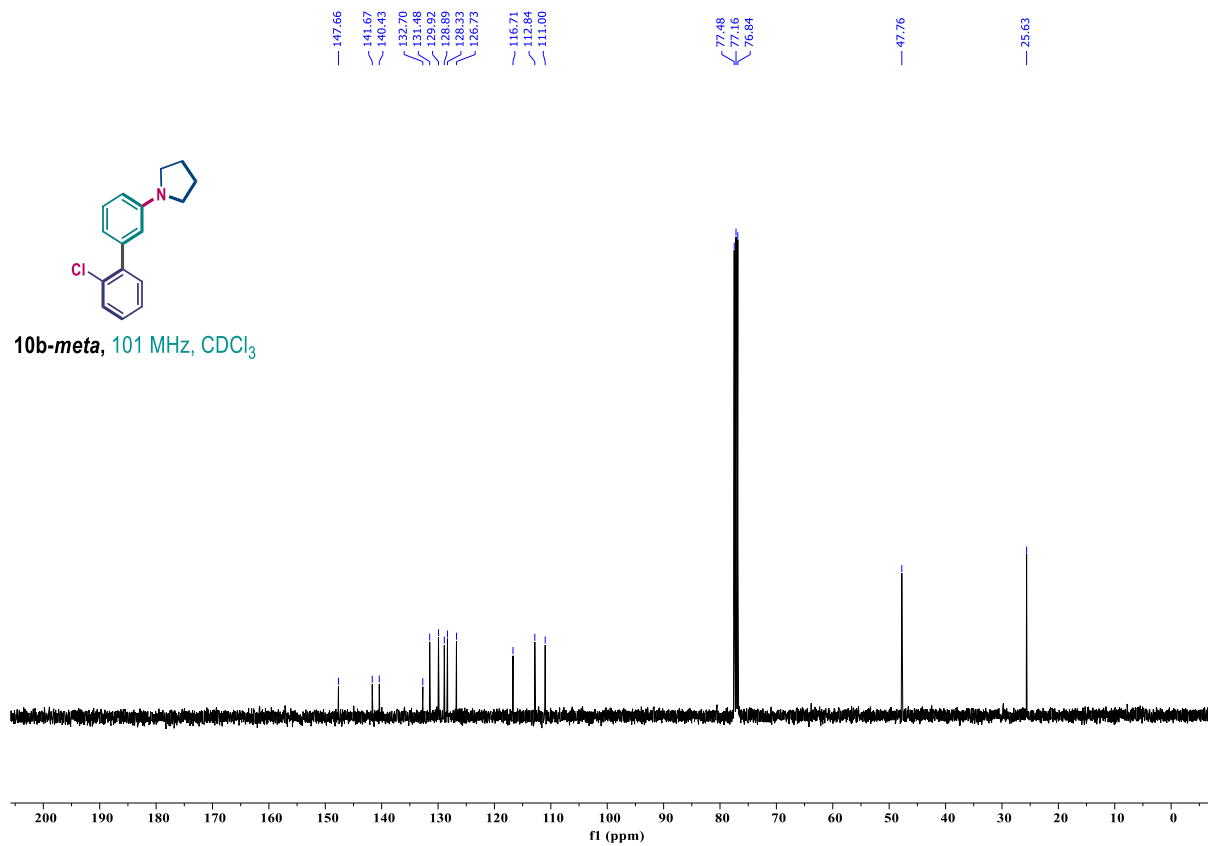


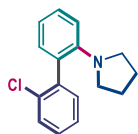


10b-meta, 400 MHz, CDCl₃

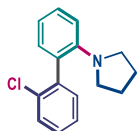
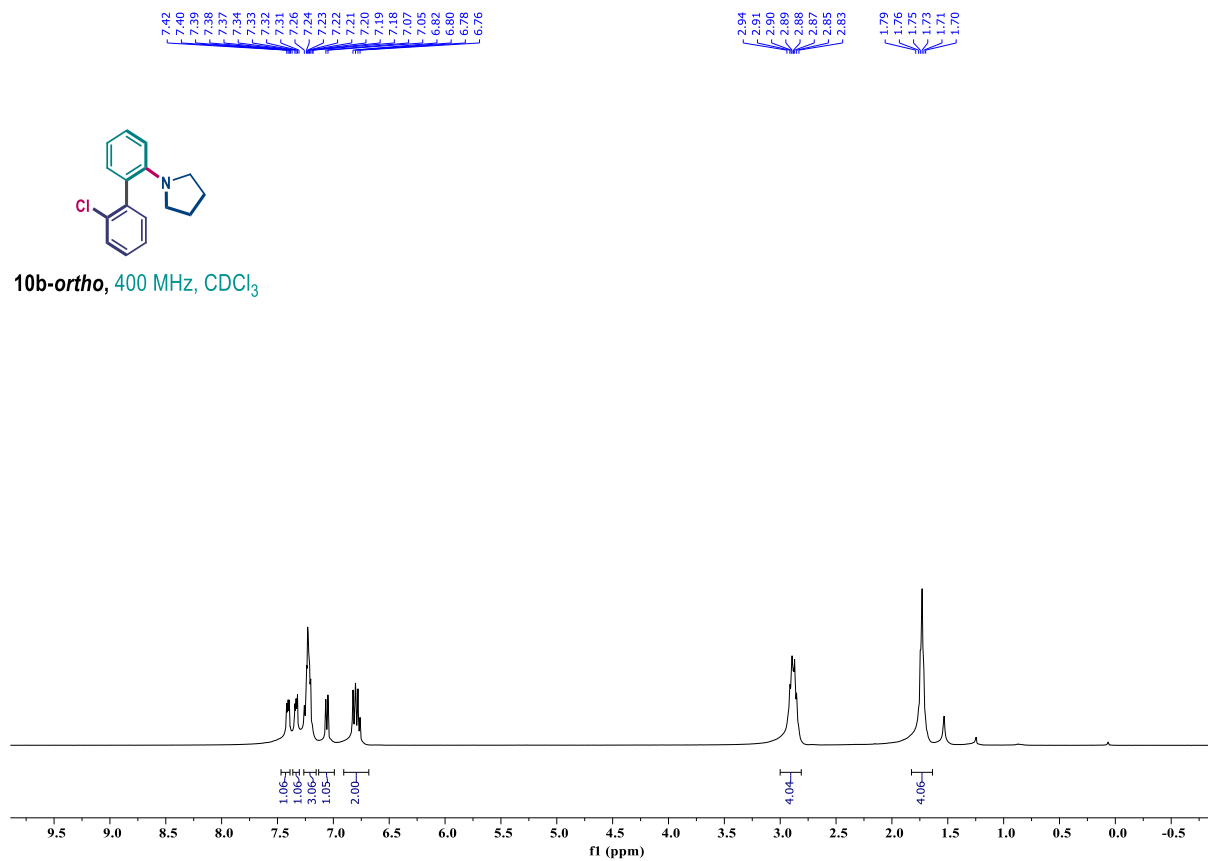


10b-meta, 101 MHz, CDCl₃

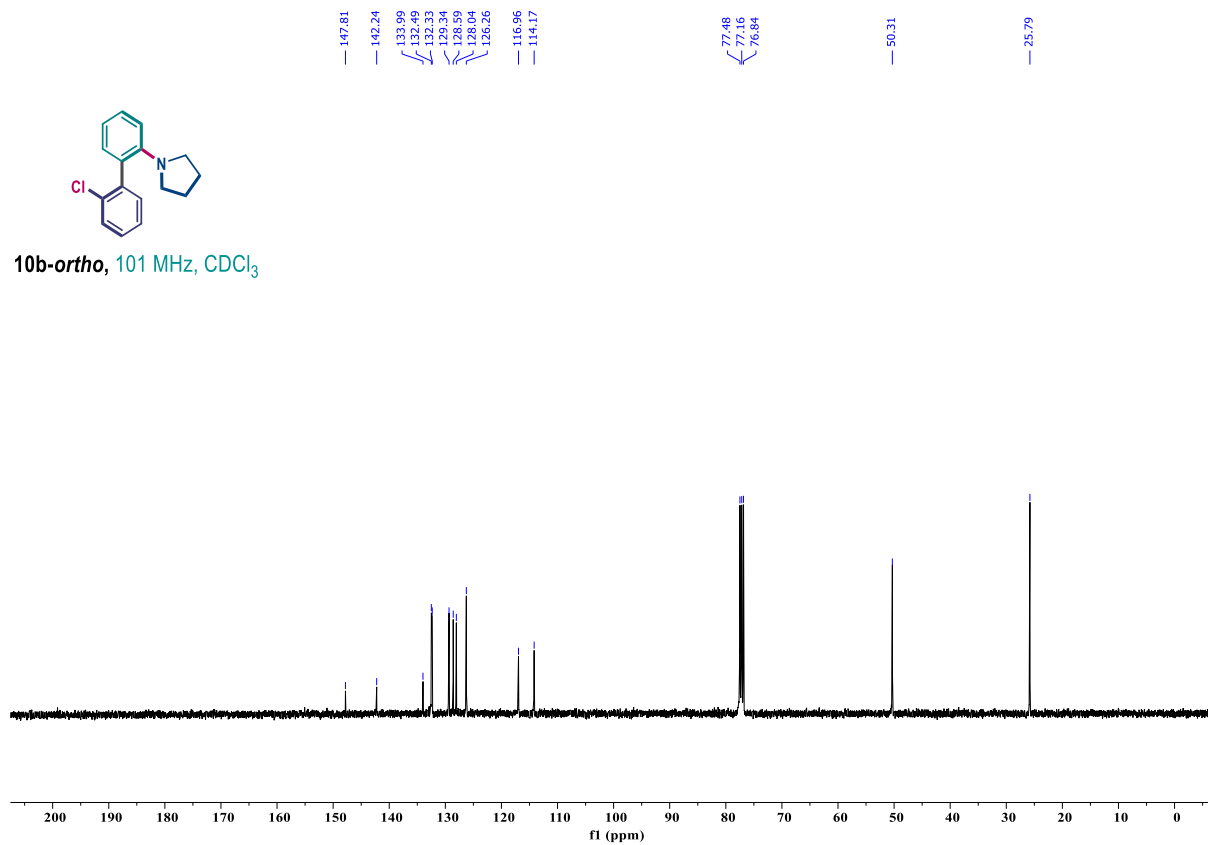


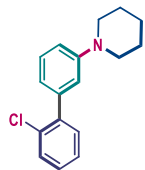


10b-ortho, 400 MHz, CDCl₃

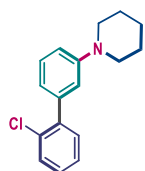
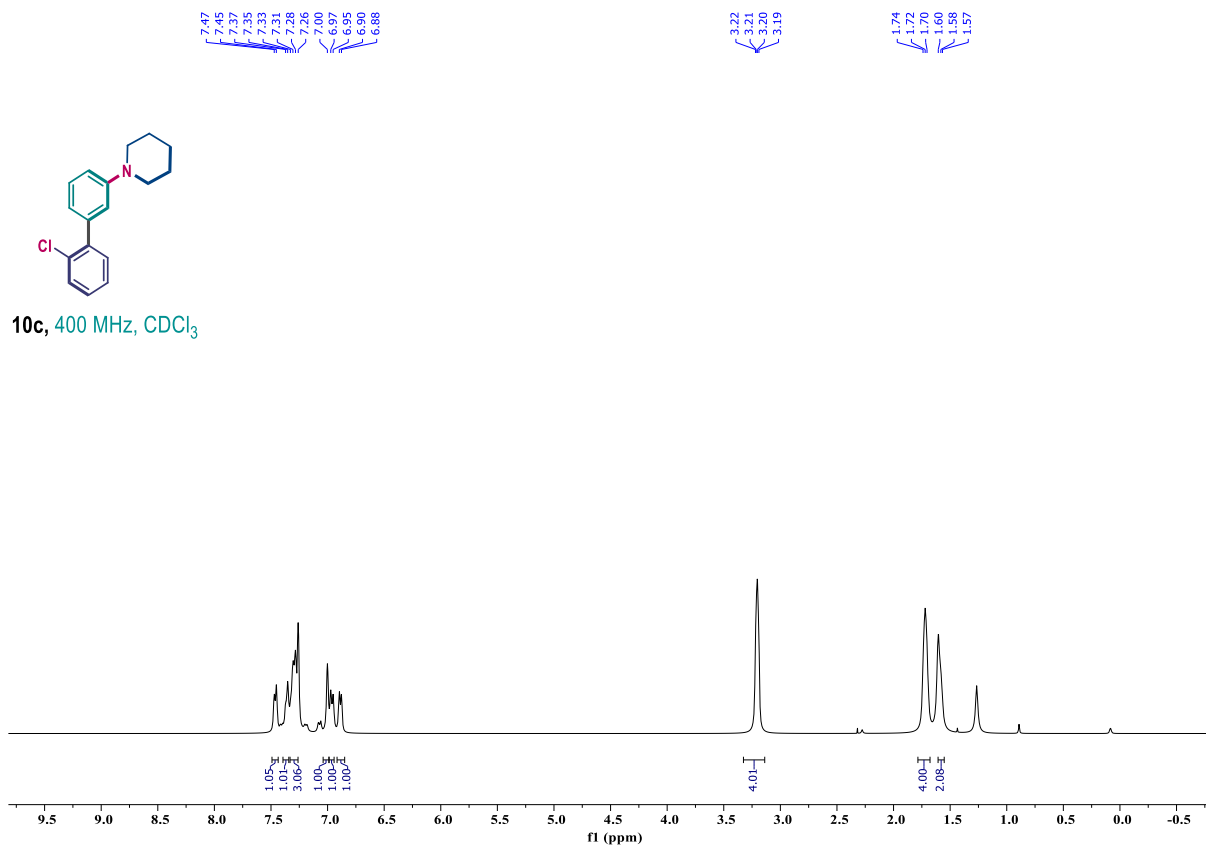


10b-ortho, 101 MHz, CDCl₃

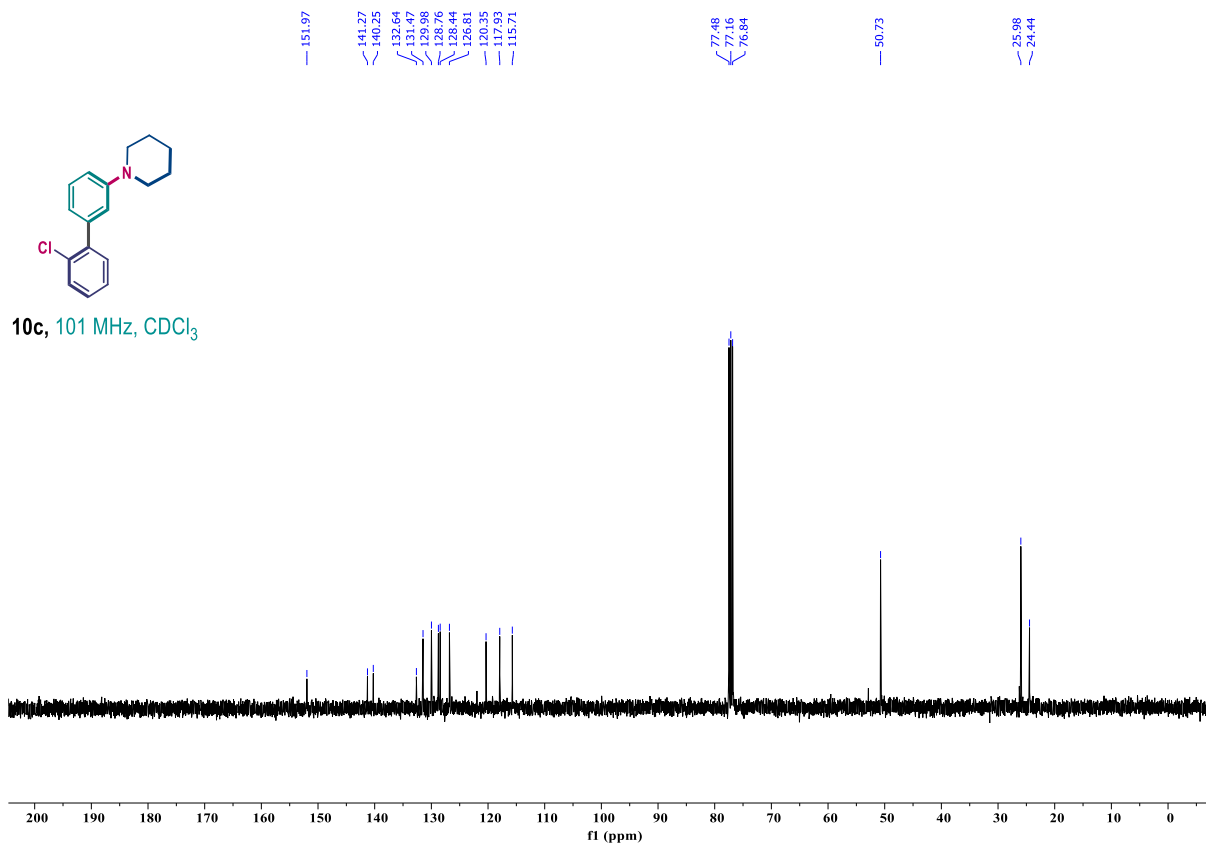


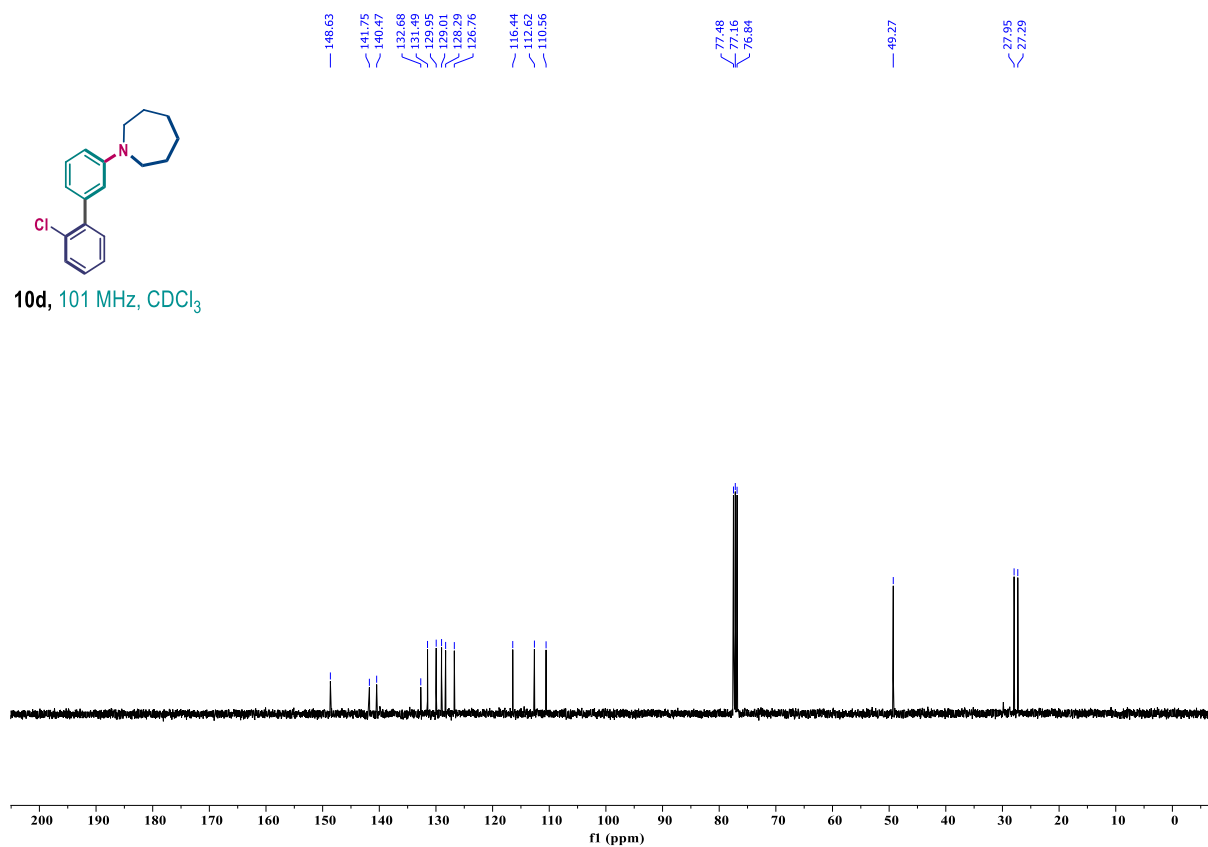
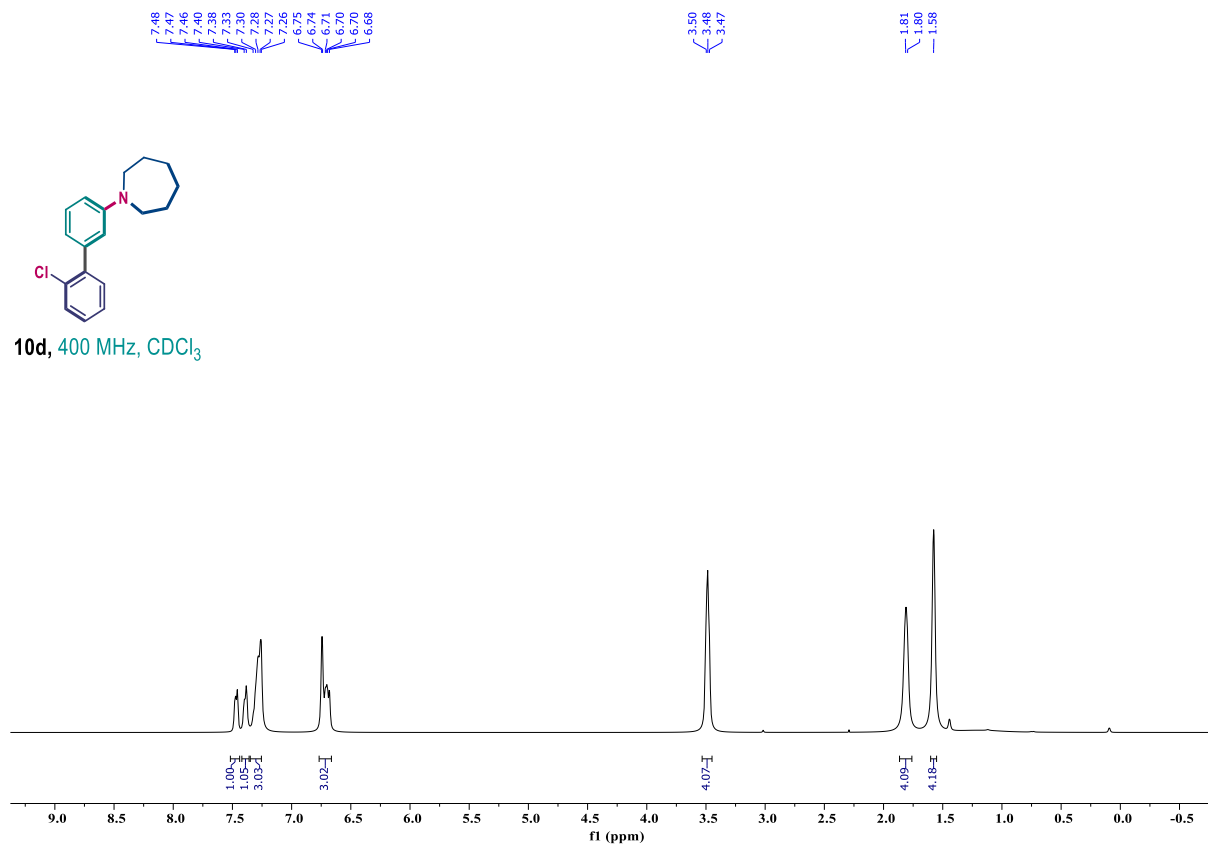


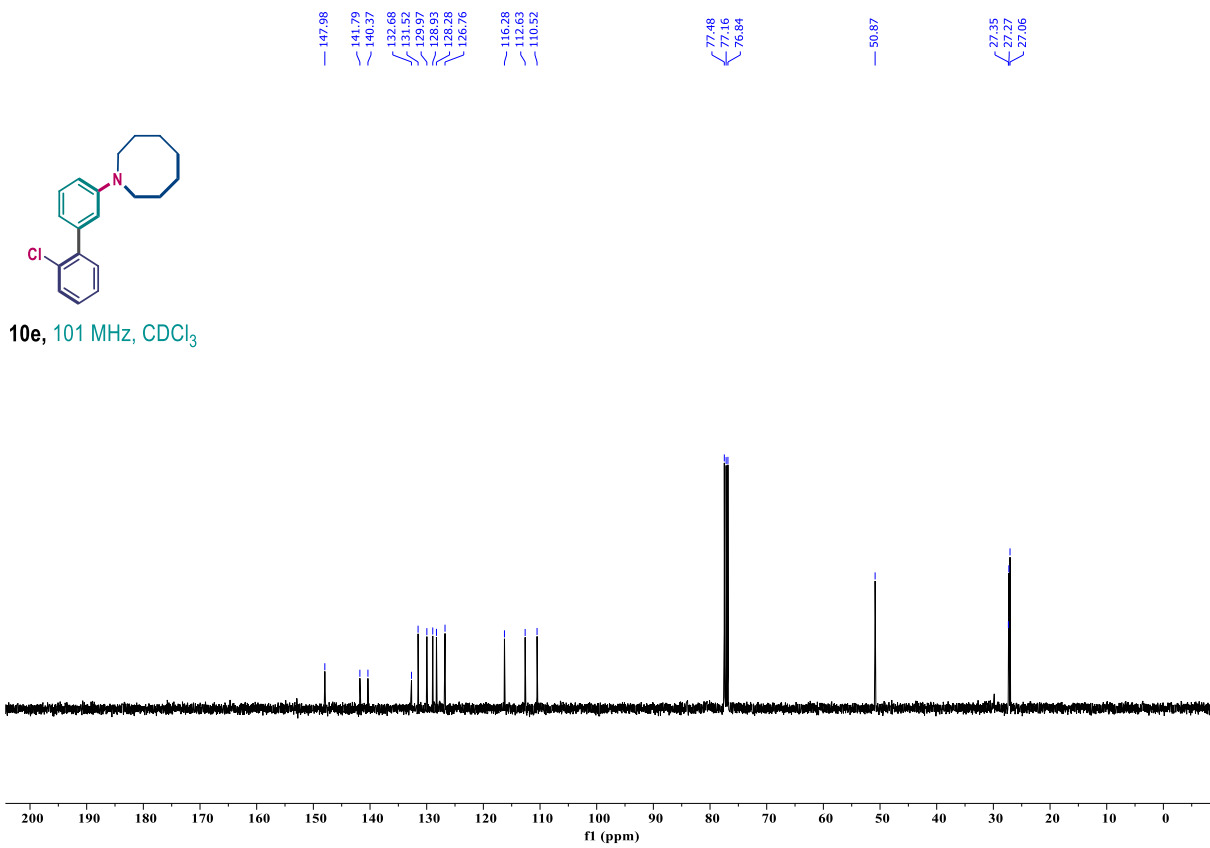
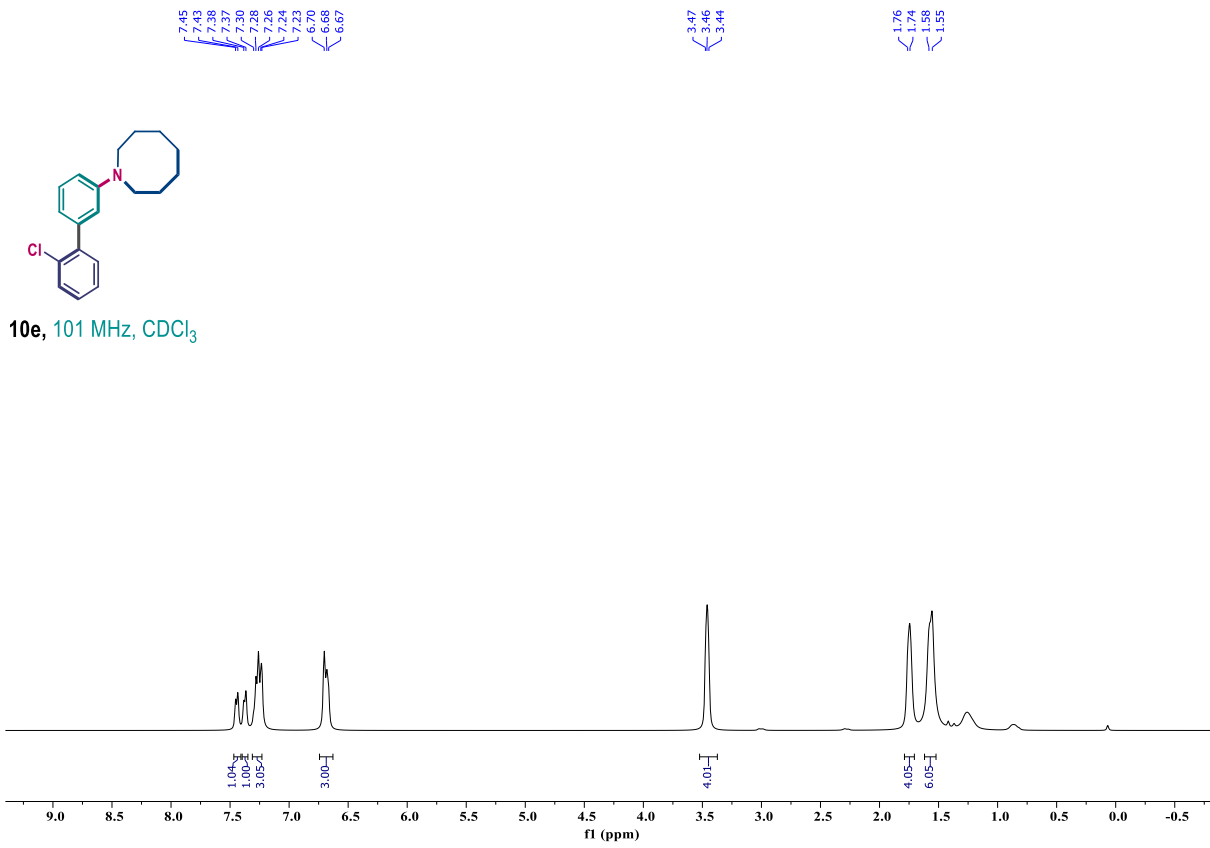
10c, 400 MHz, CDCl₃

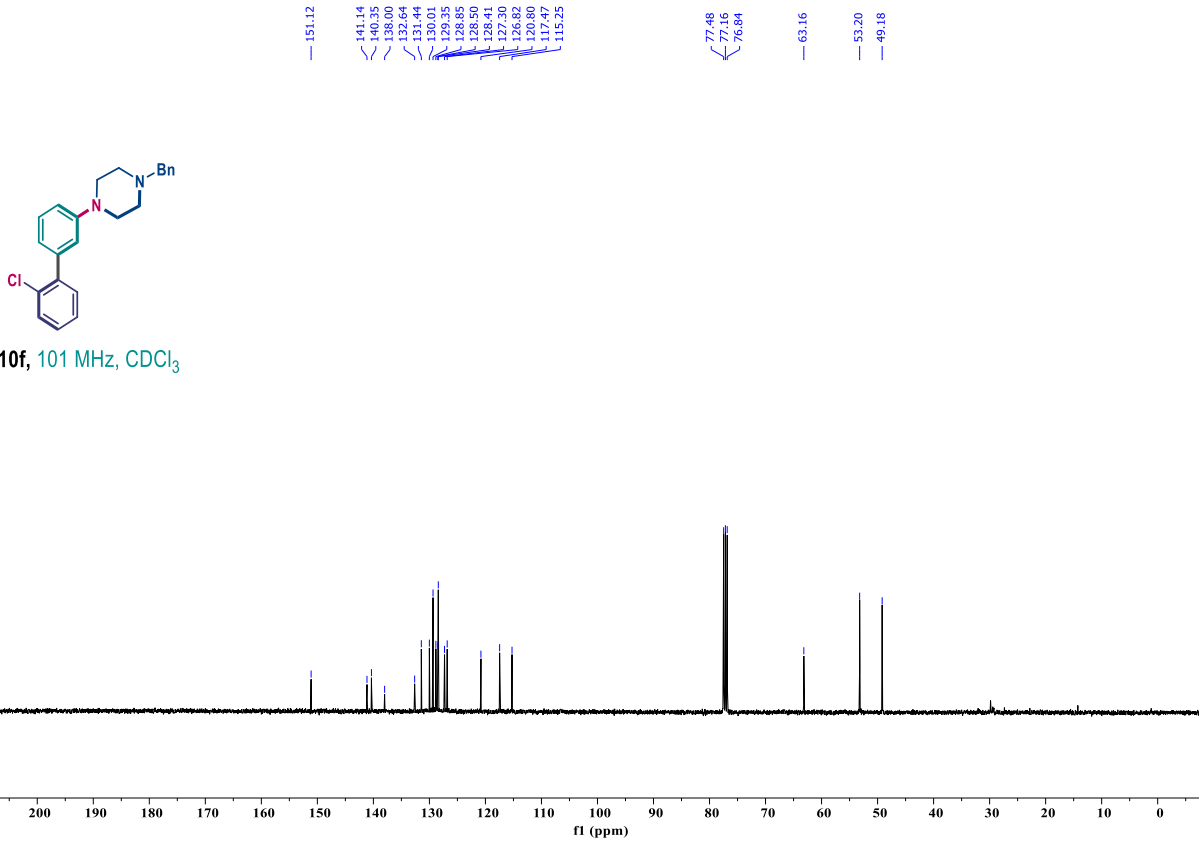
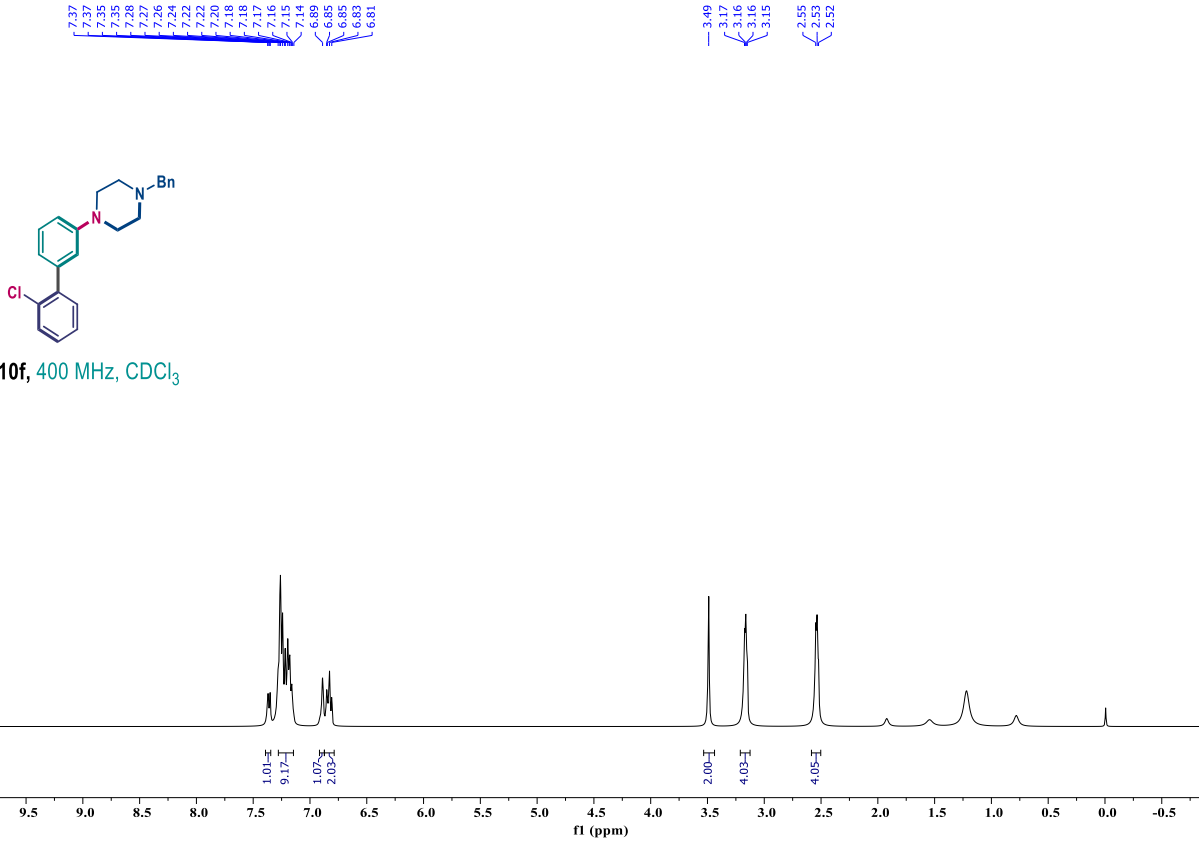


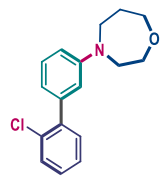
10c, 101 MHz, CDCl₃



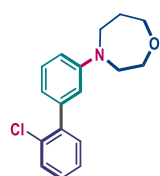
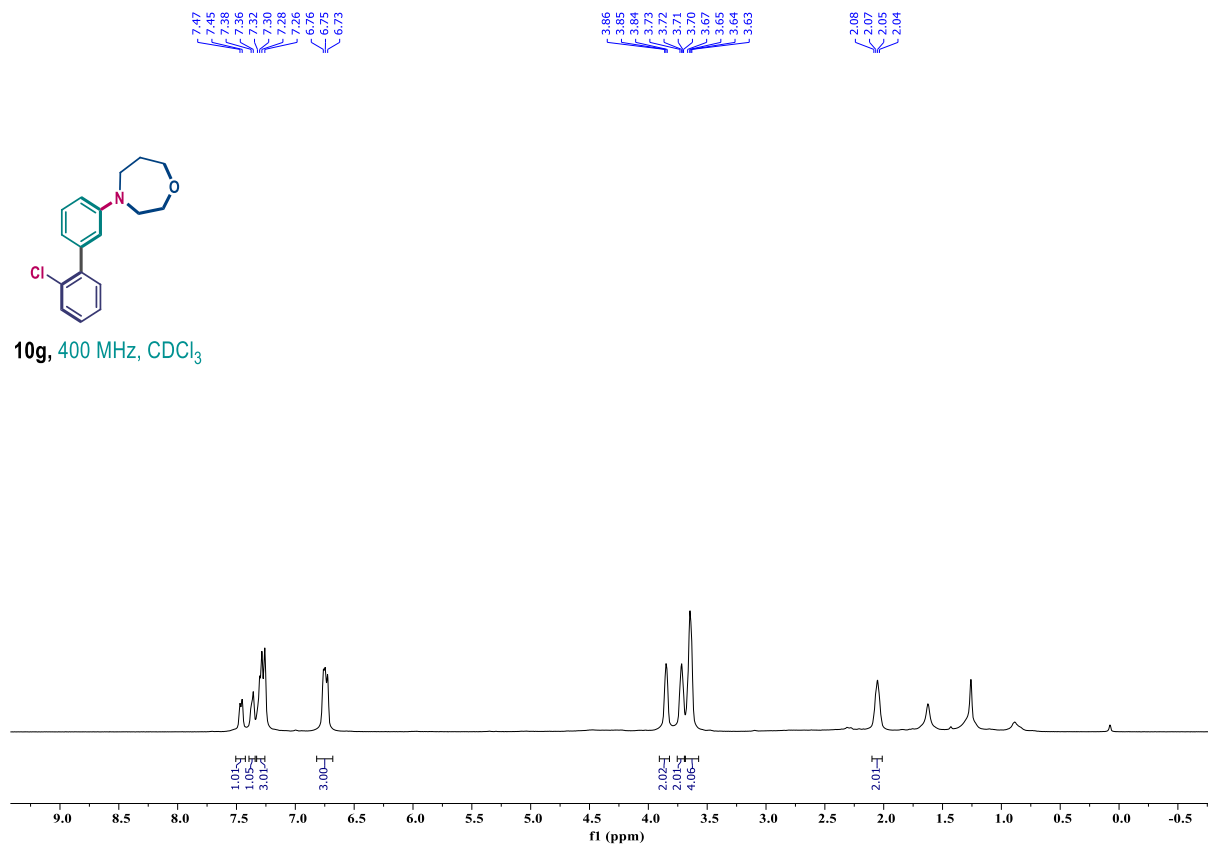




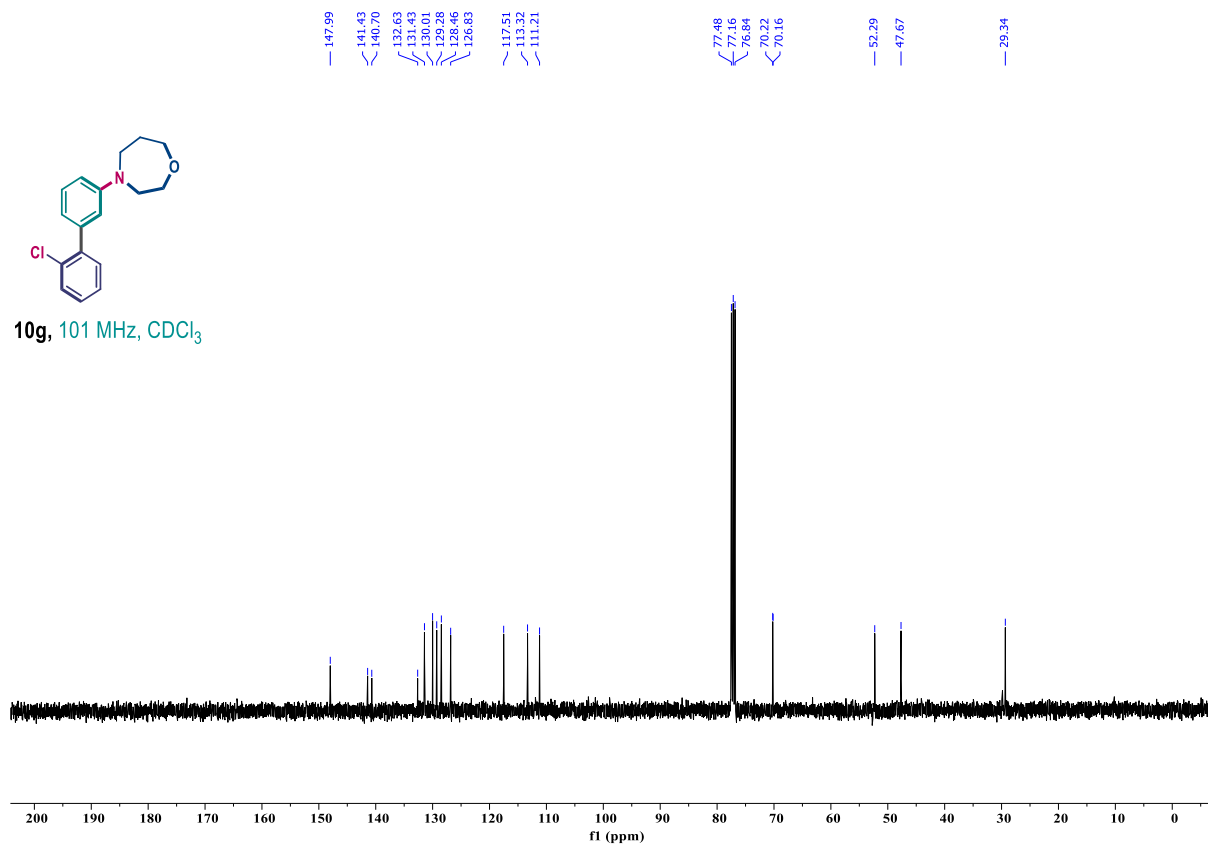


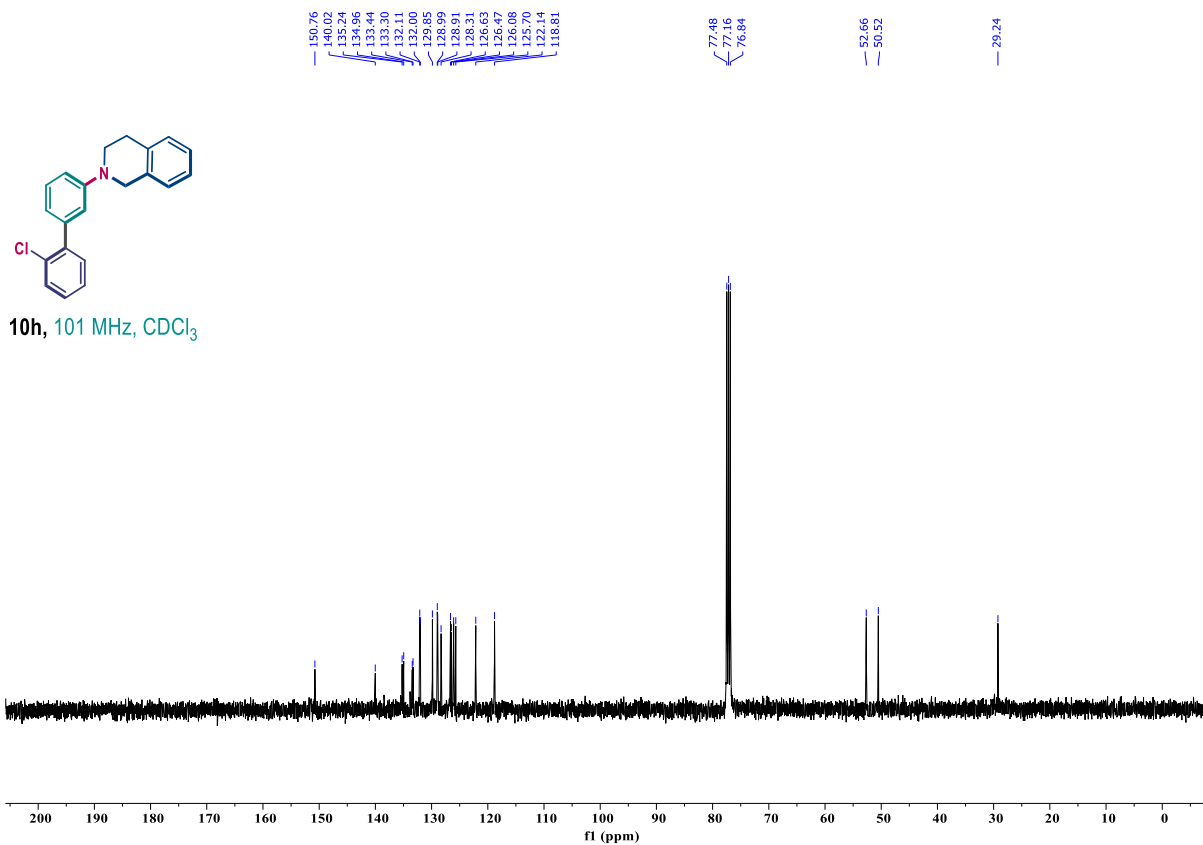
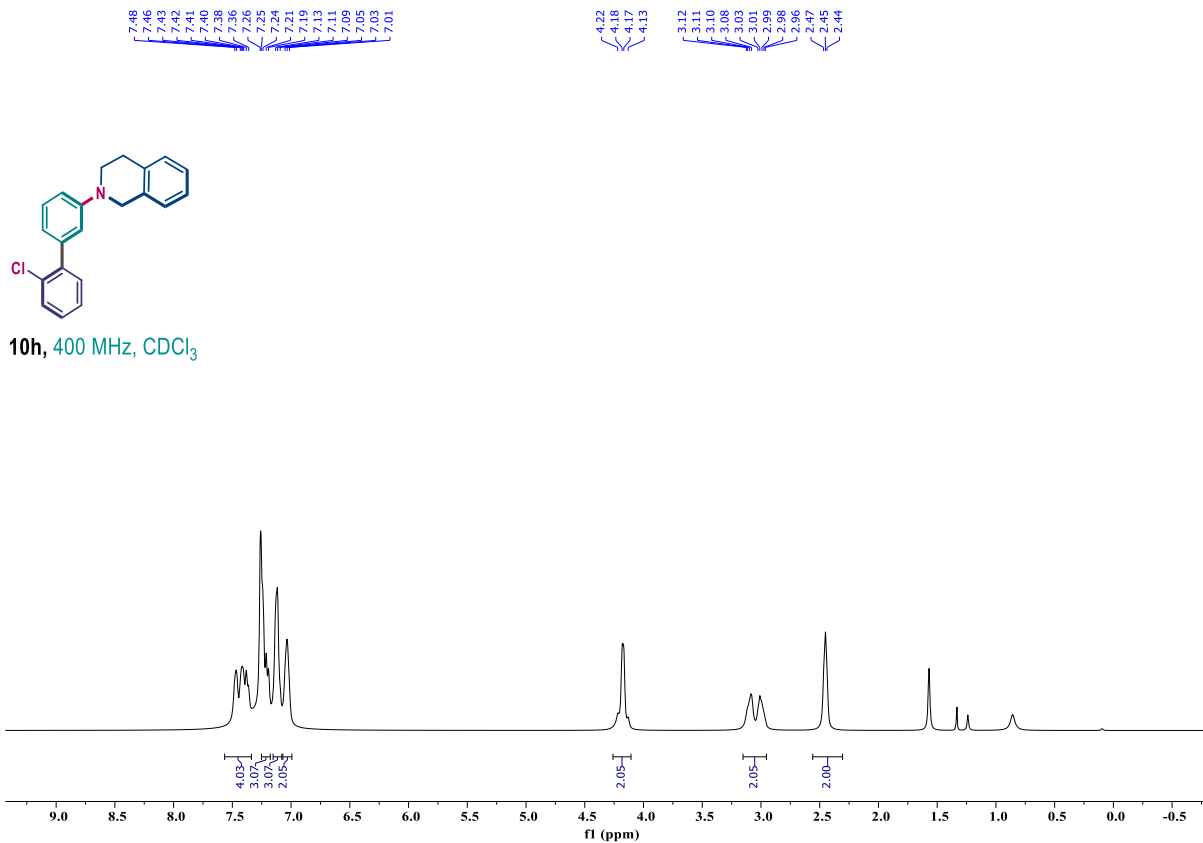


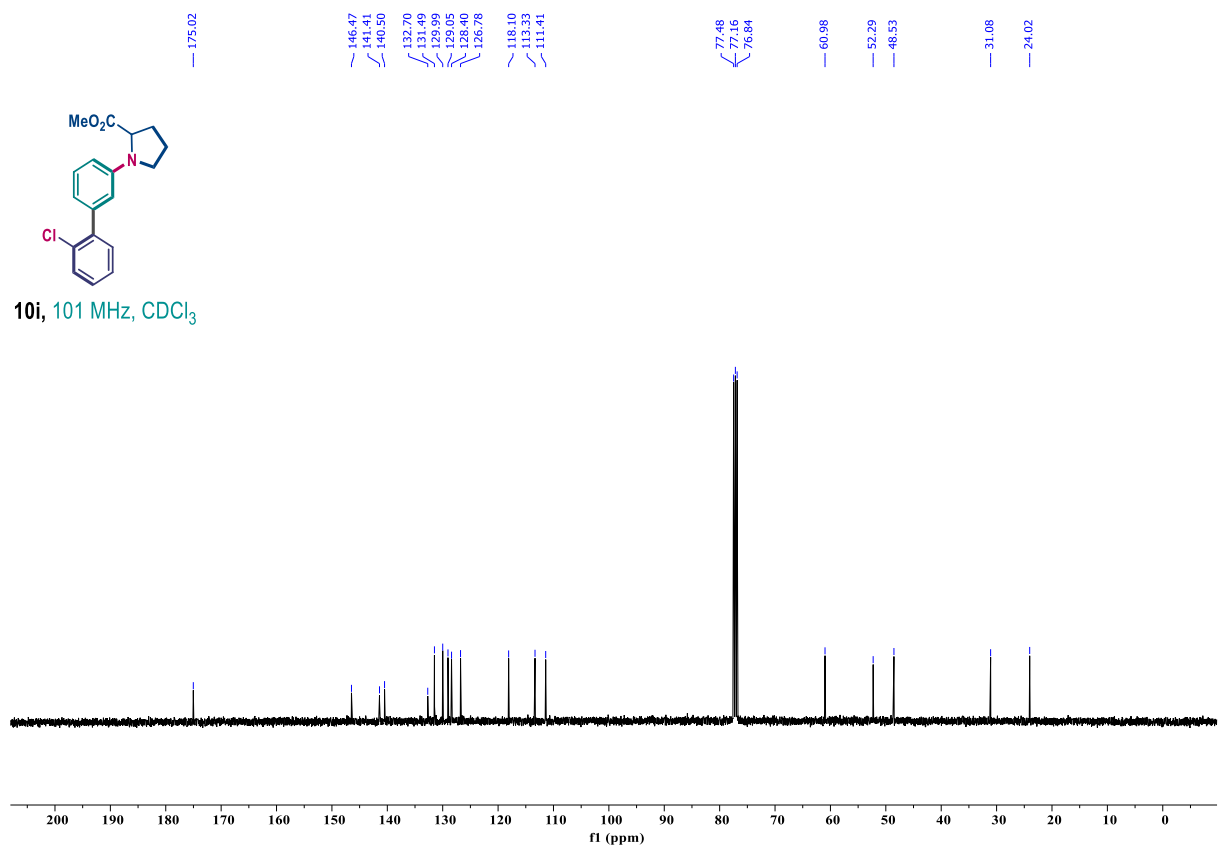
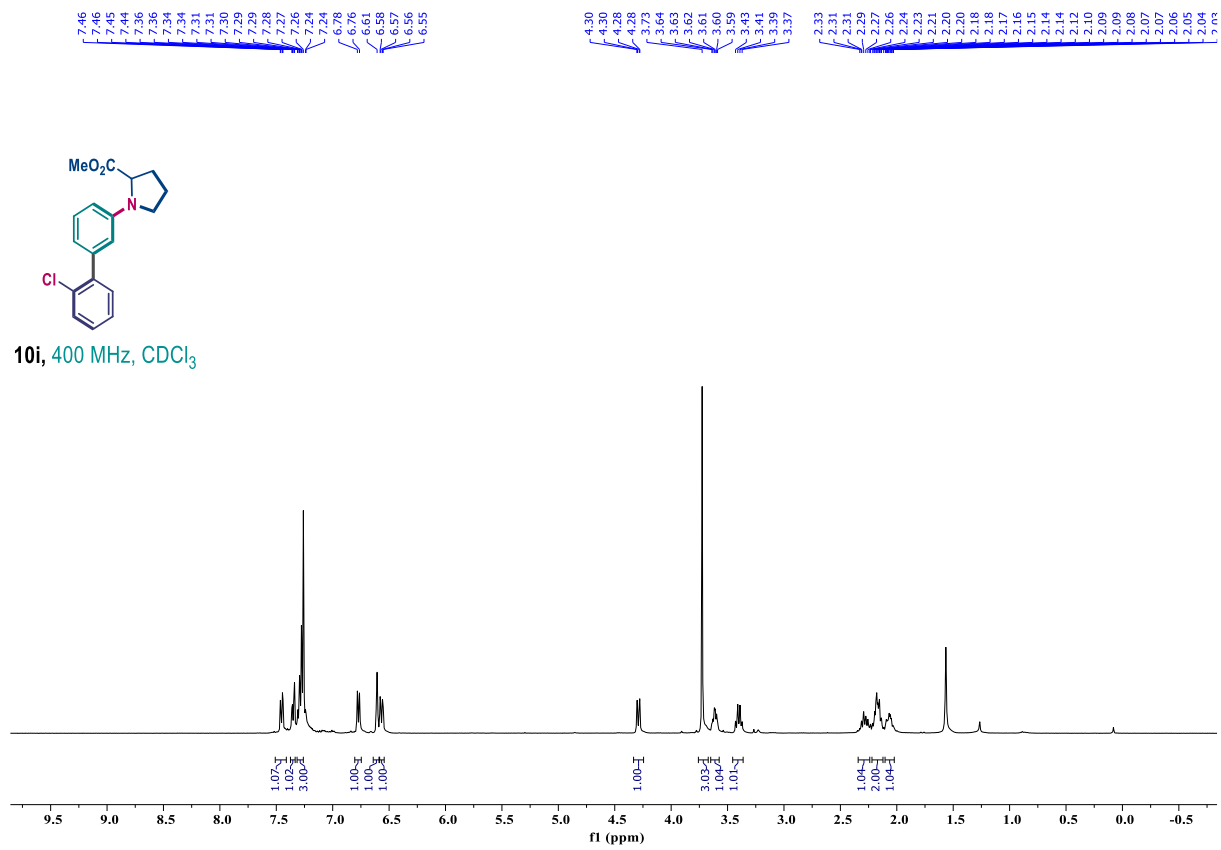
10g, 400 MHz, CDCl₃

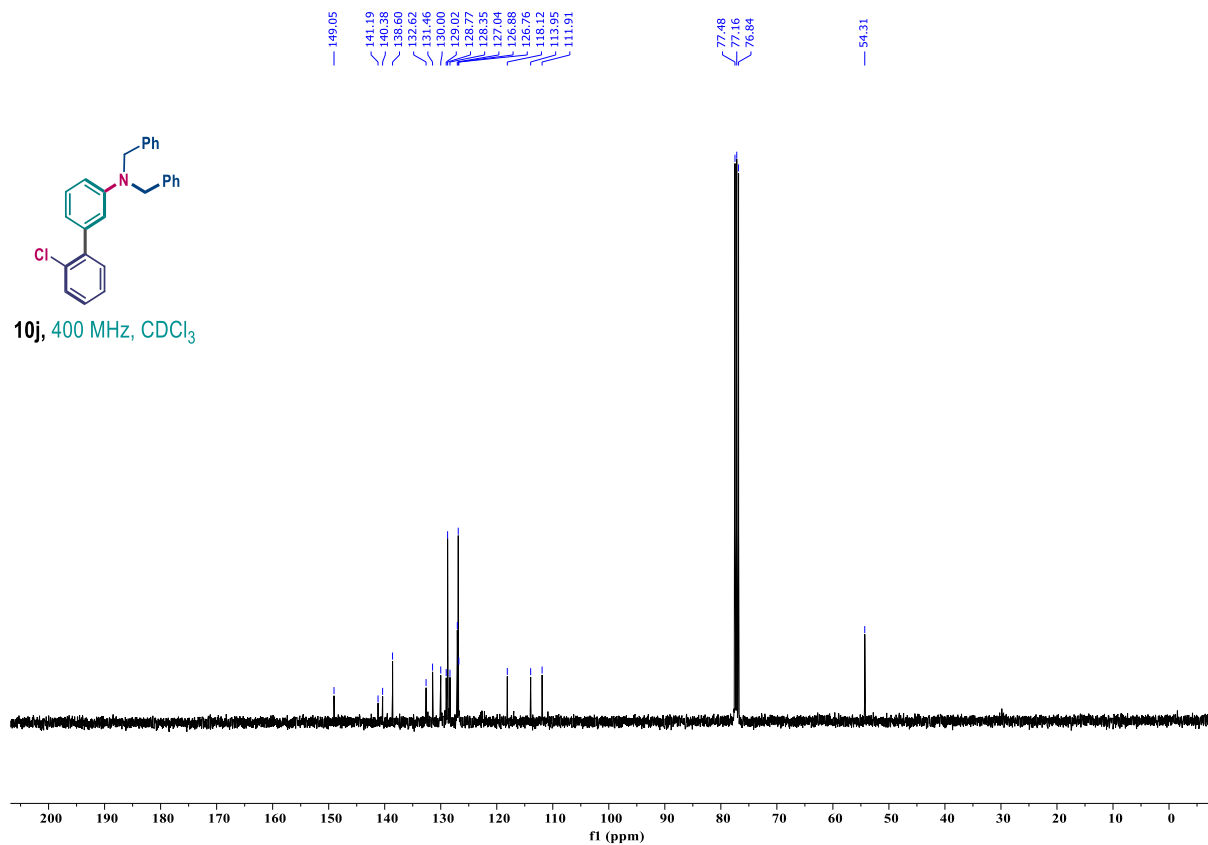
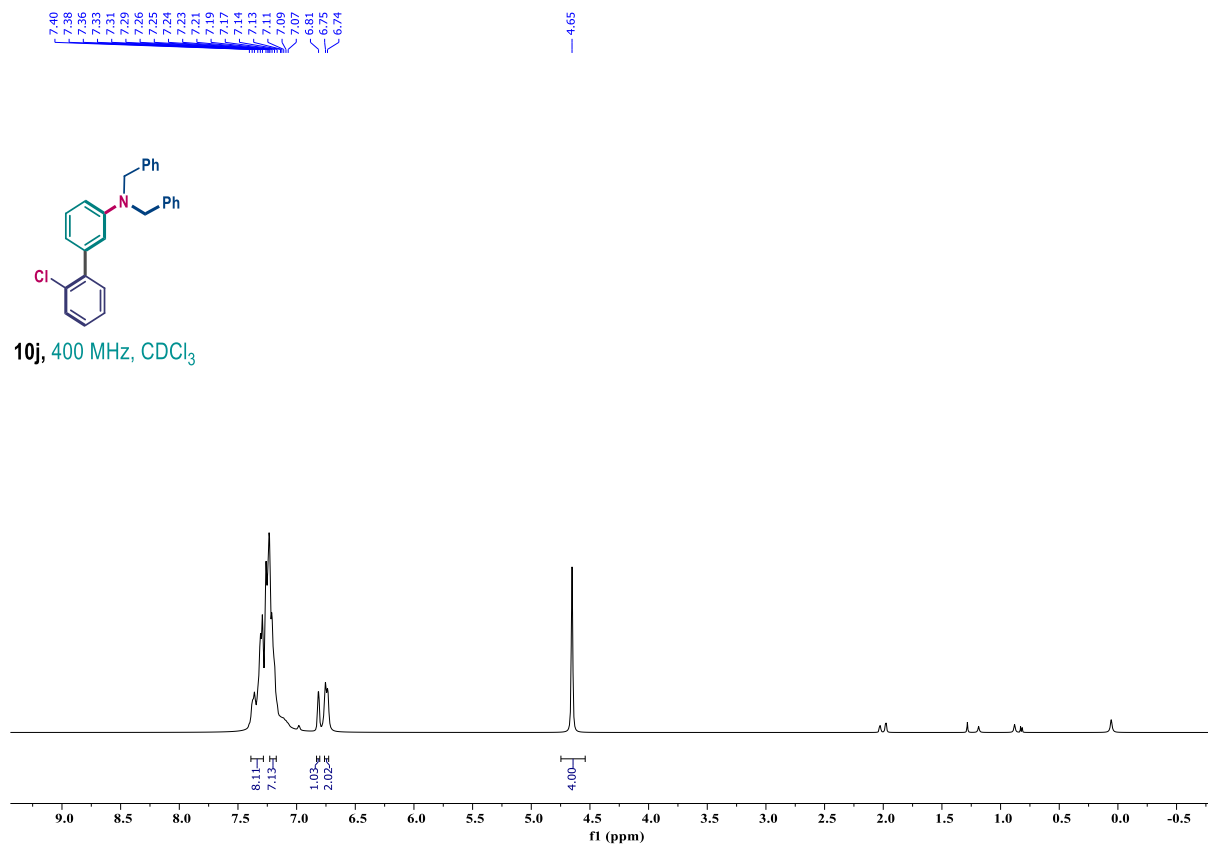


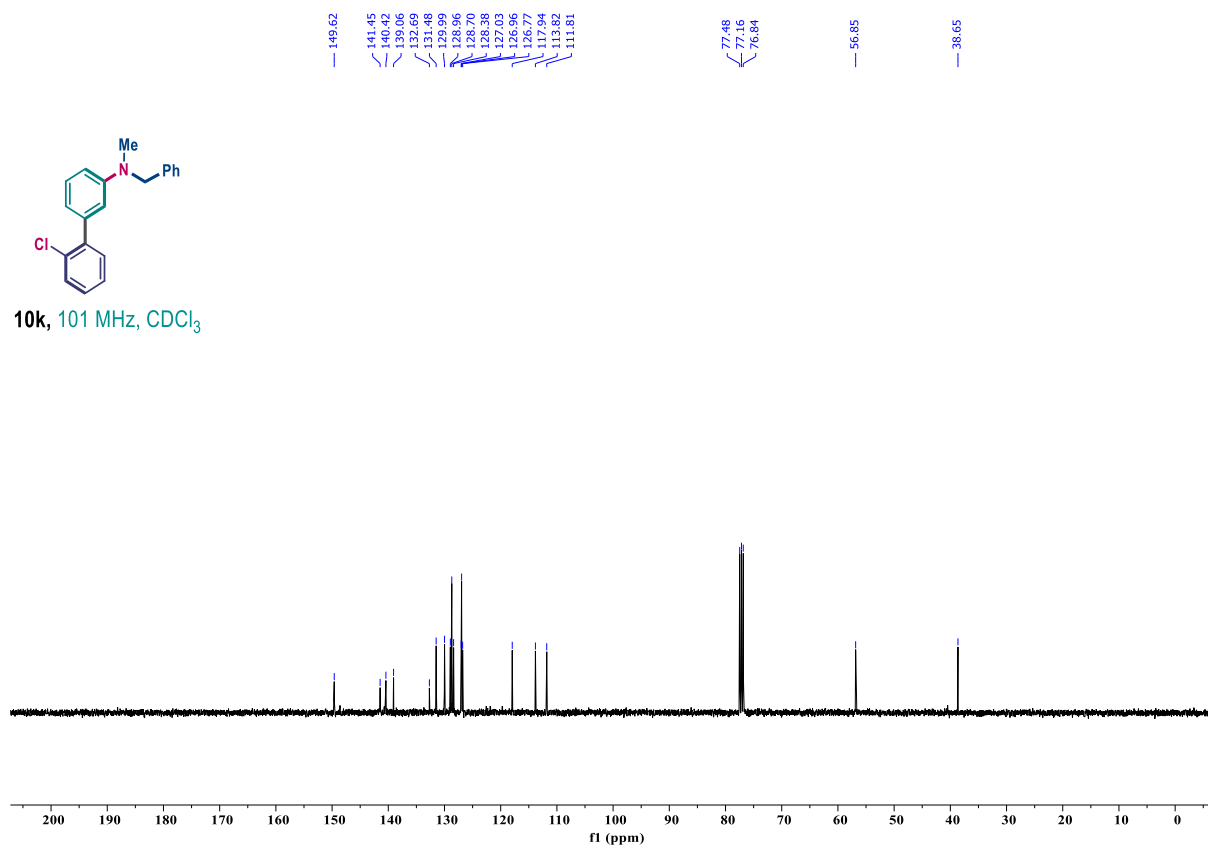
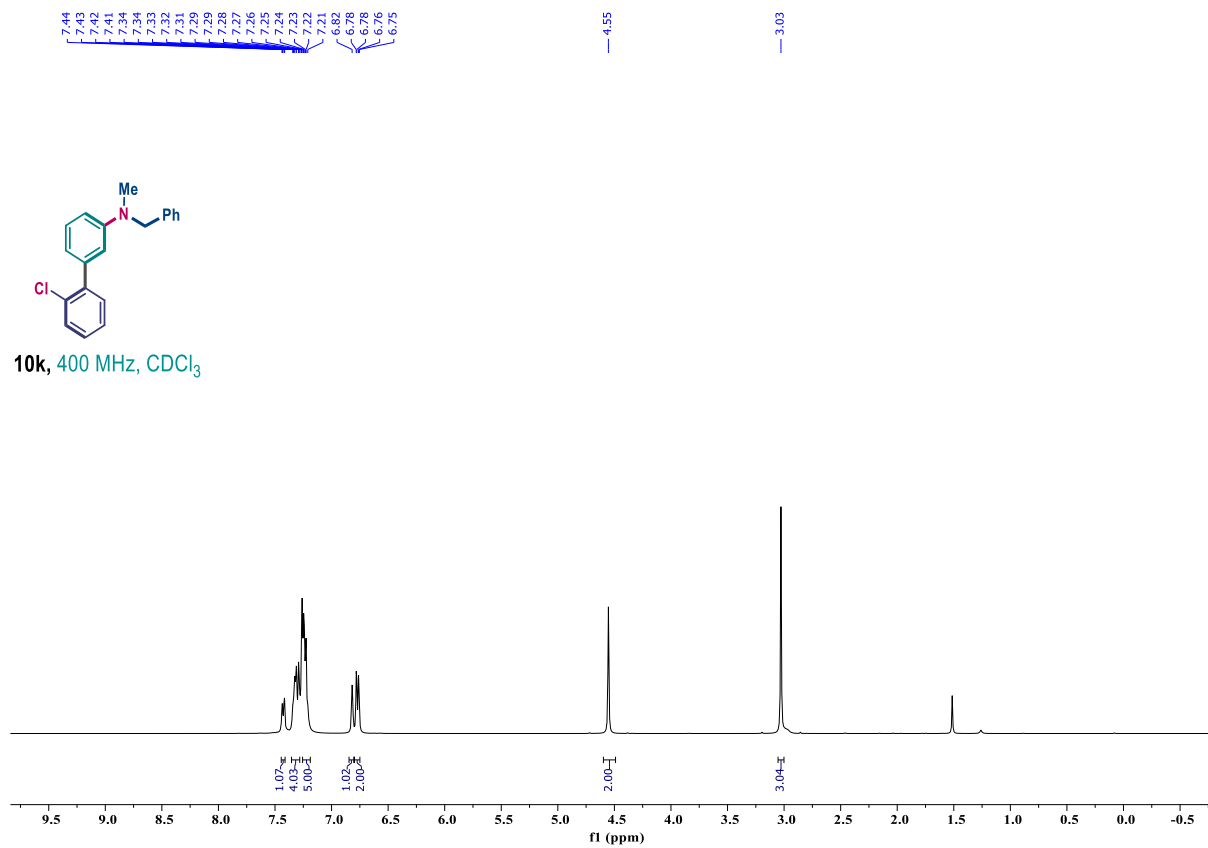
10g, 101 MHz, CDCl₃

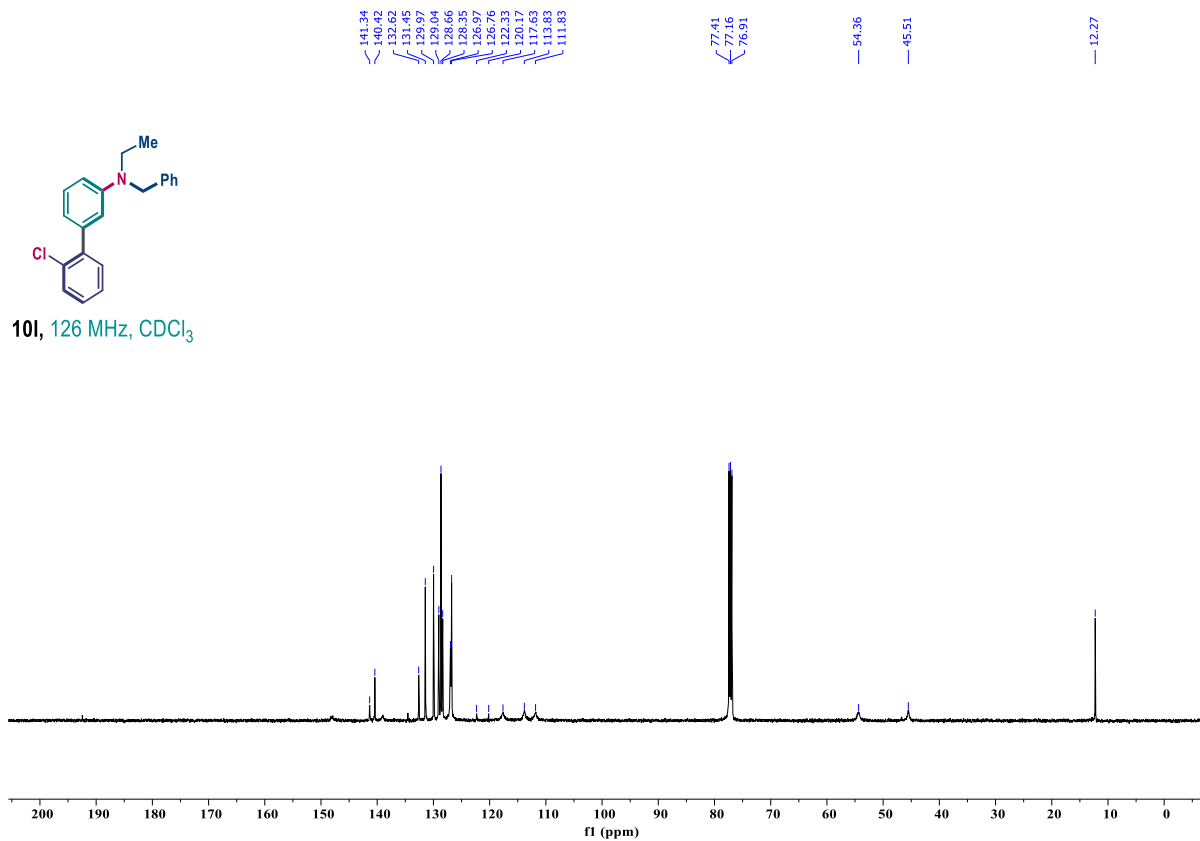
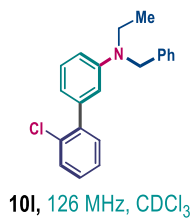
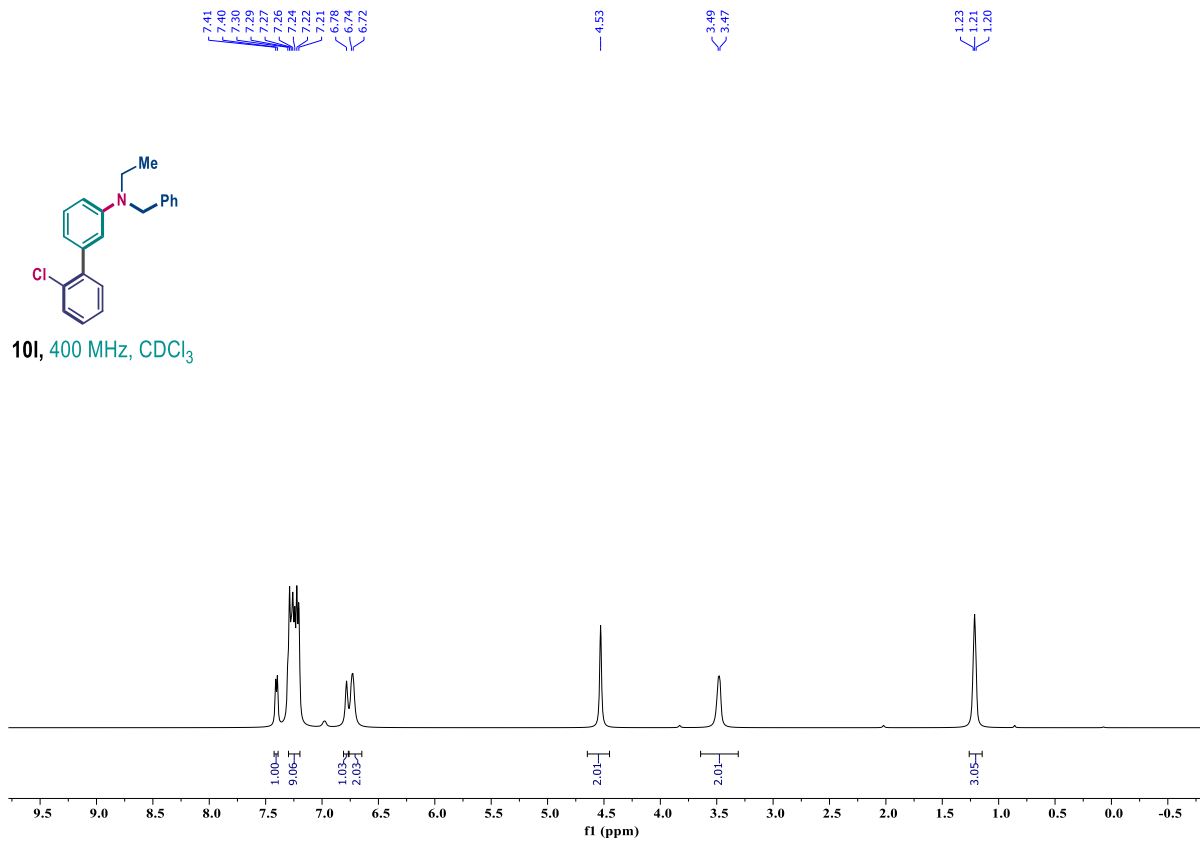
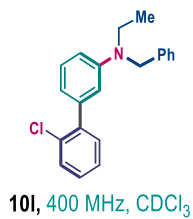


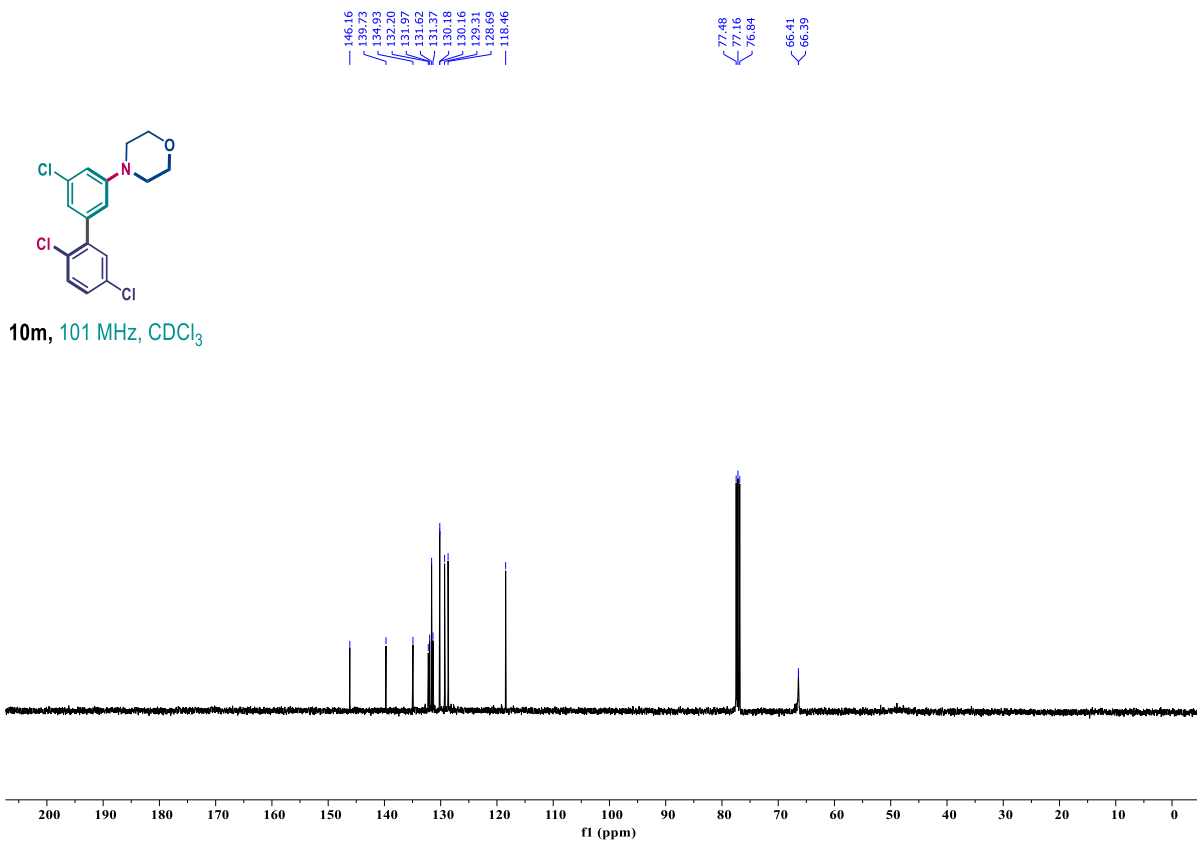
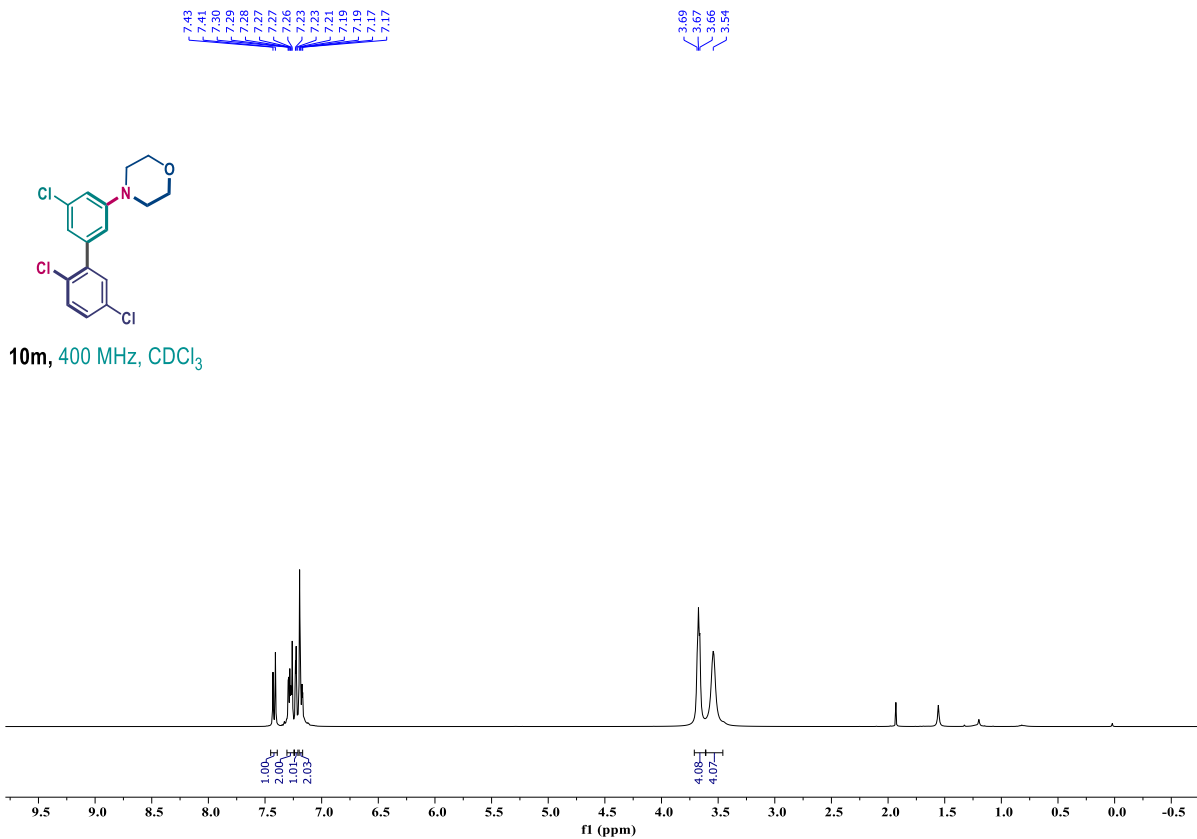


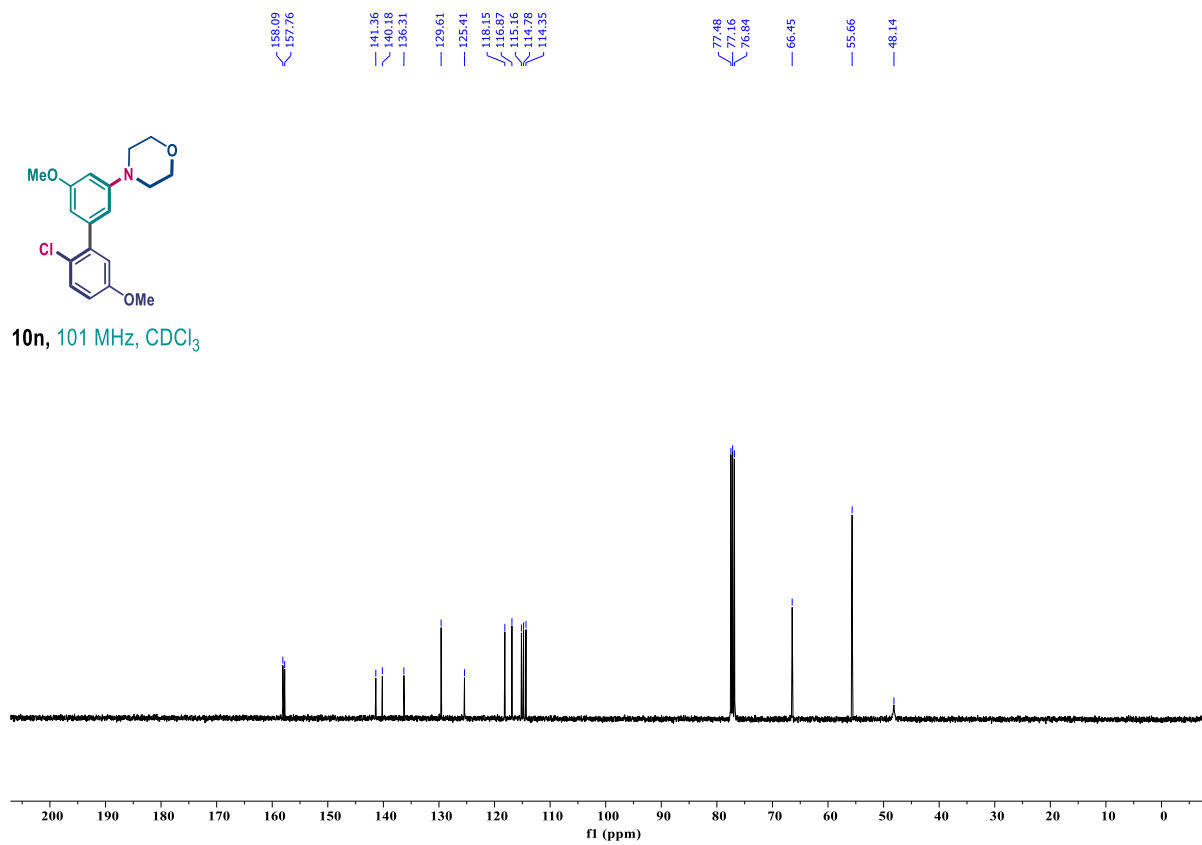
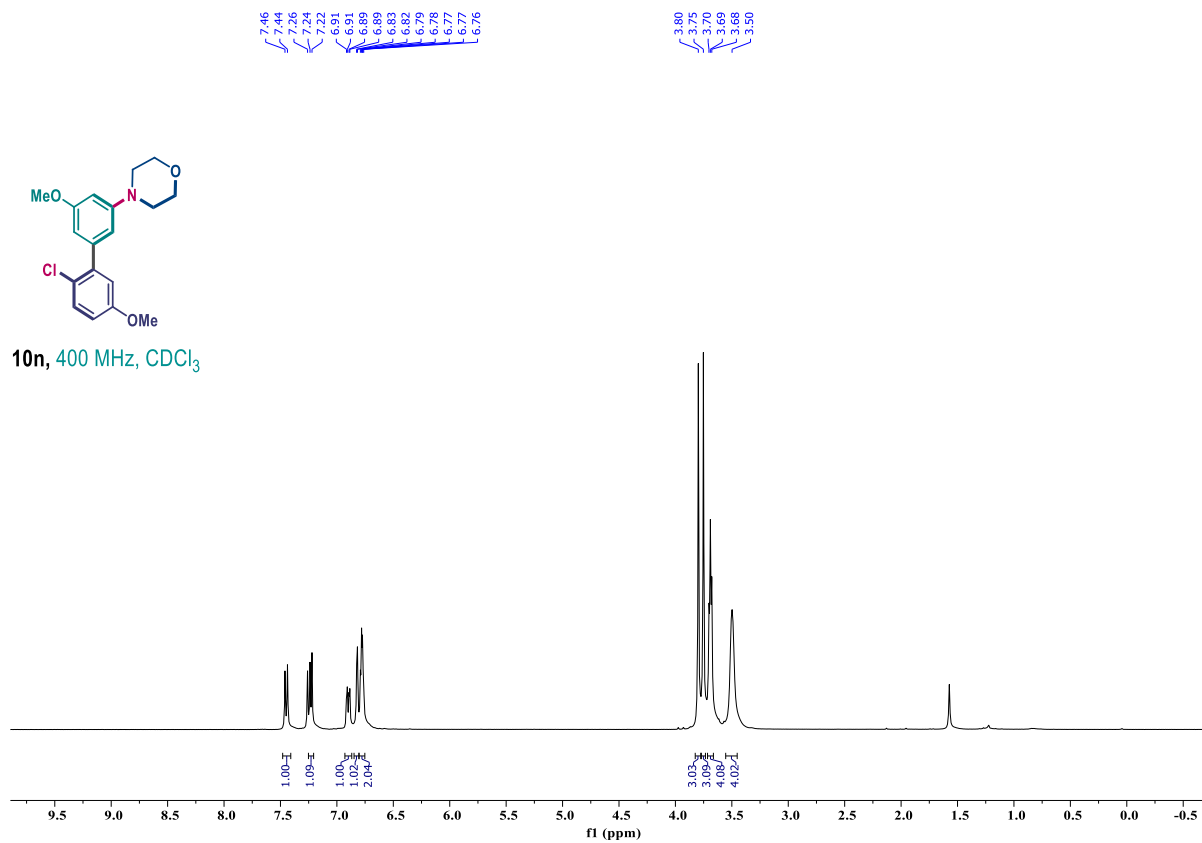


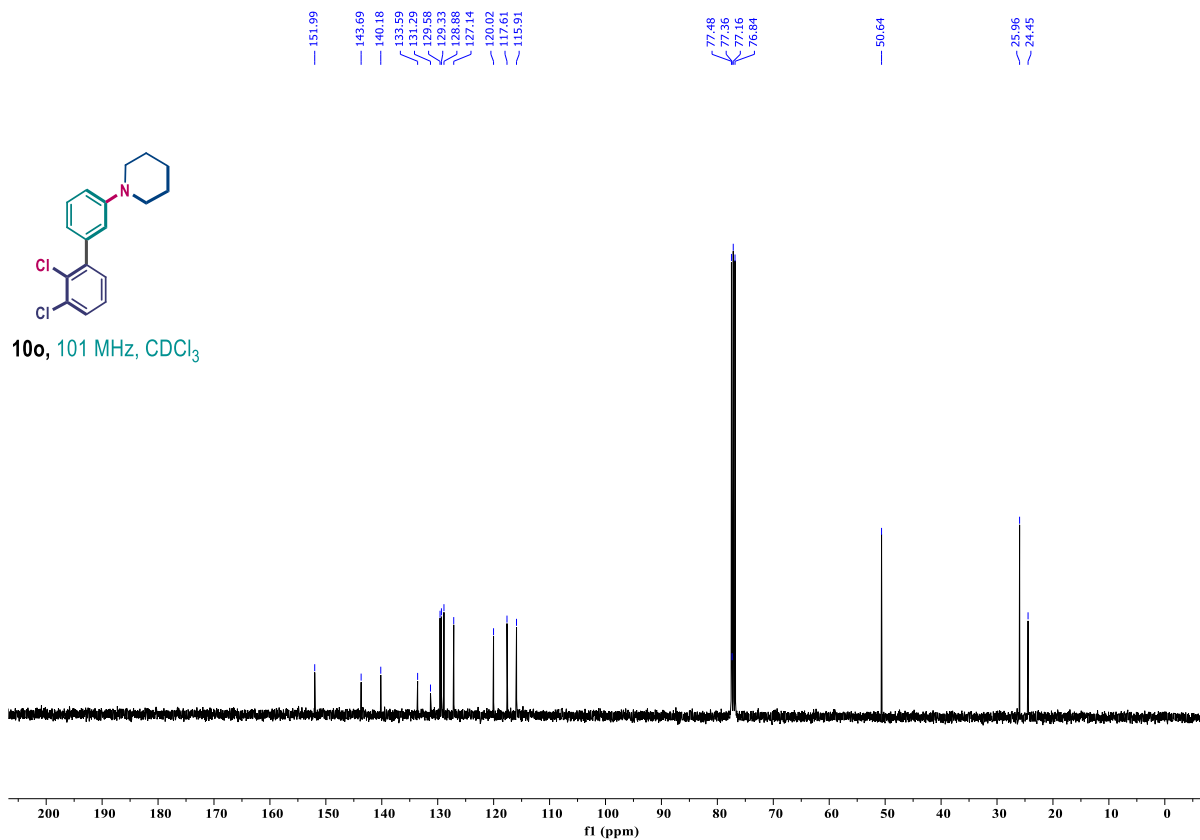
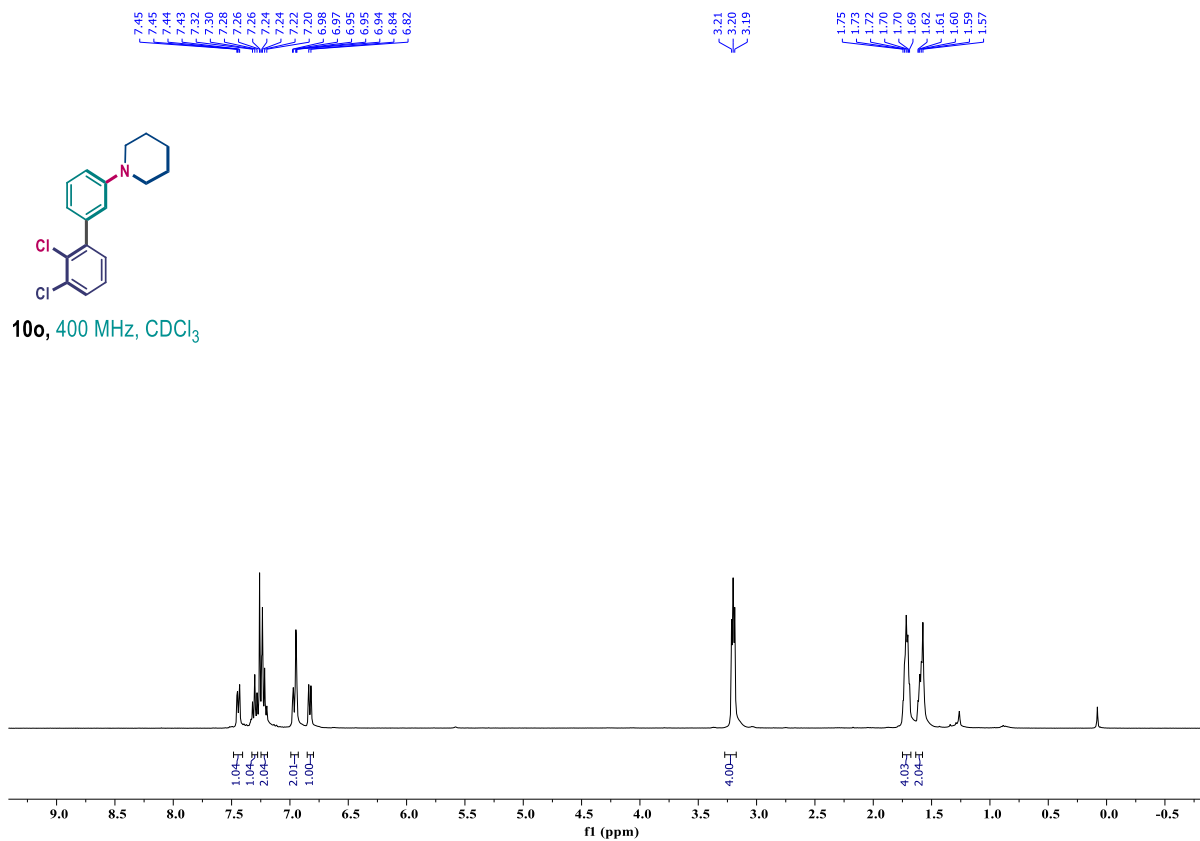


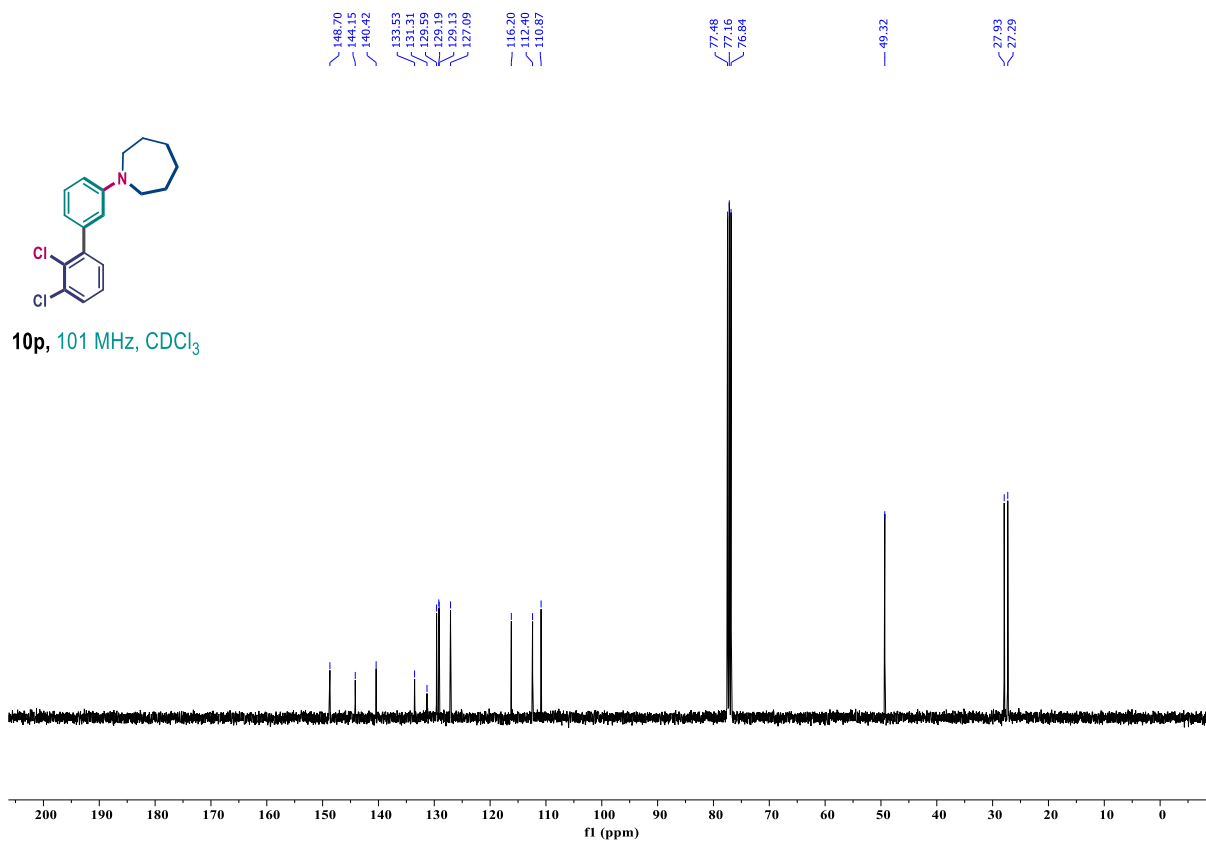
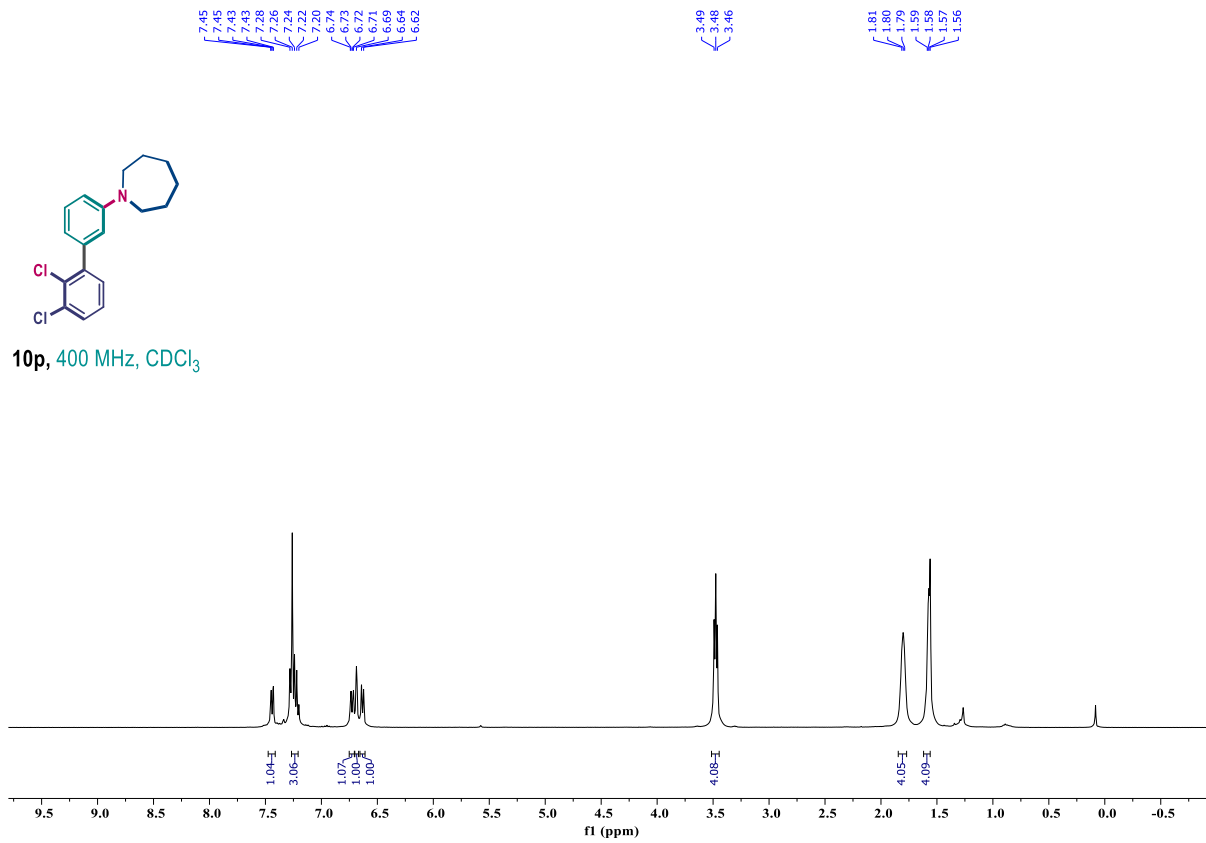


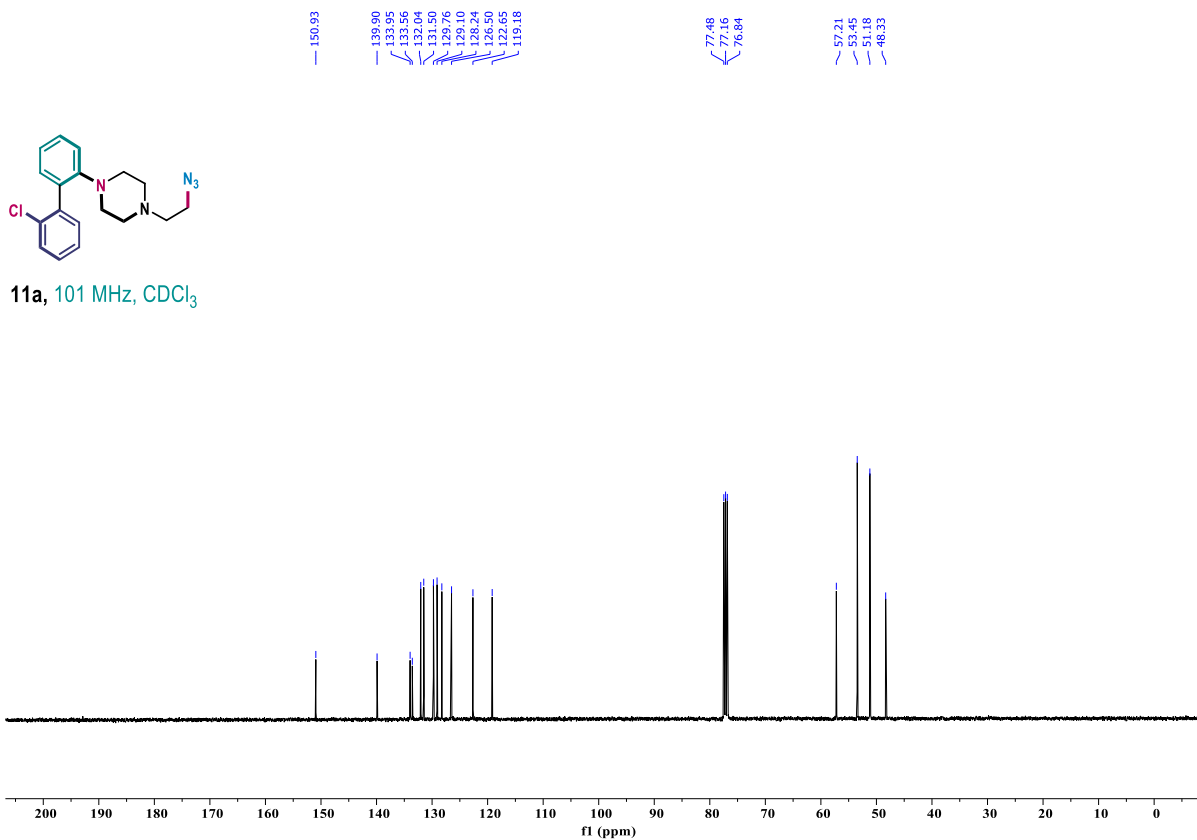
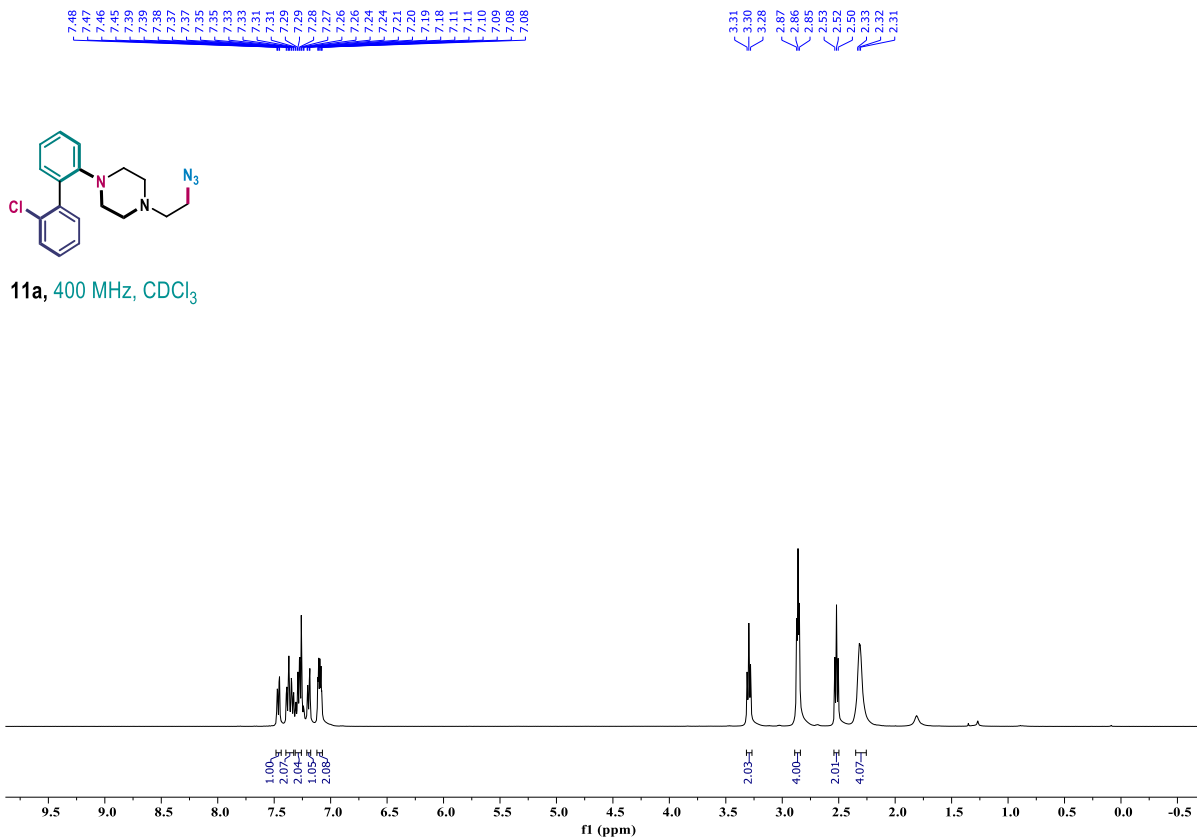


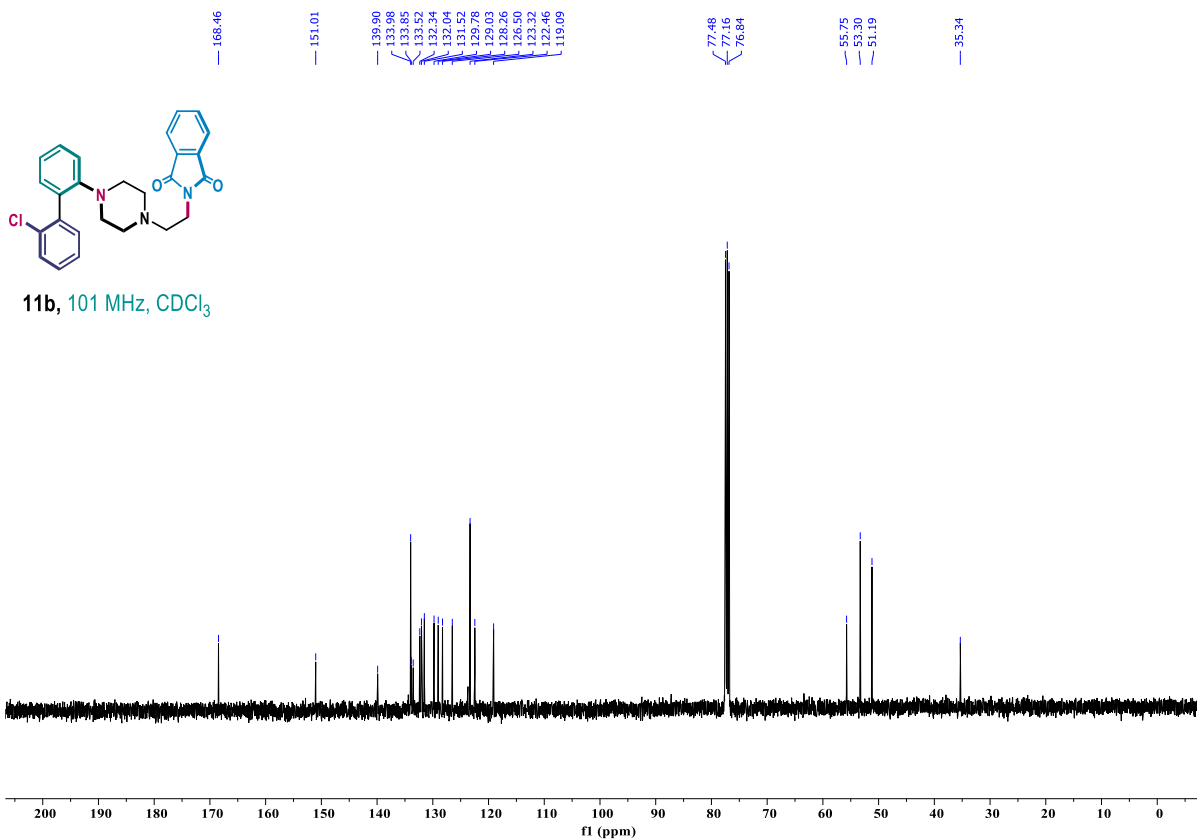
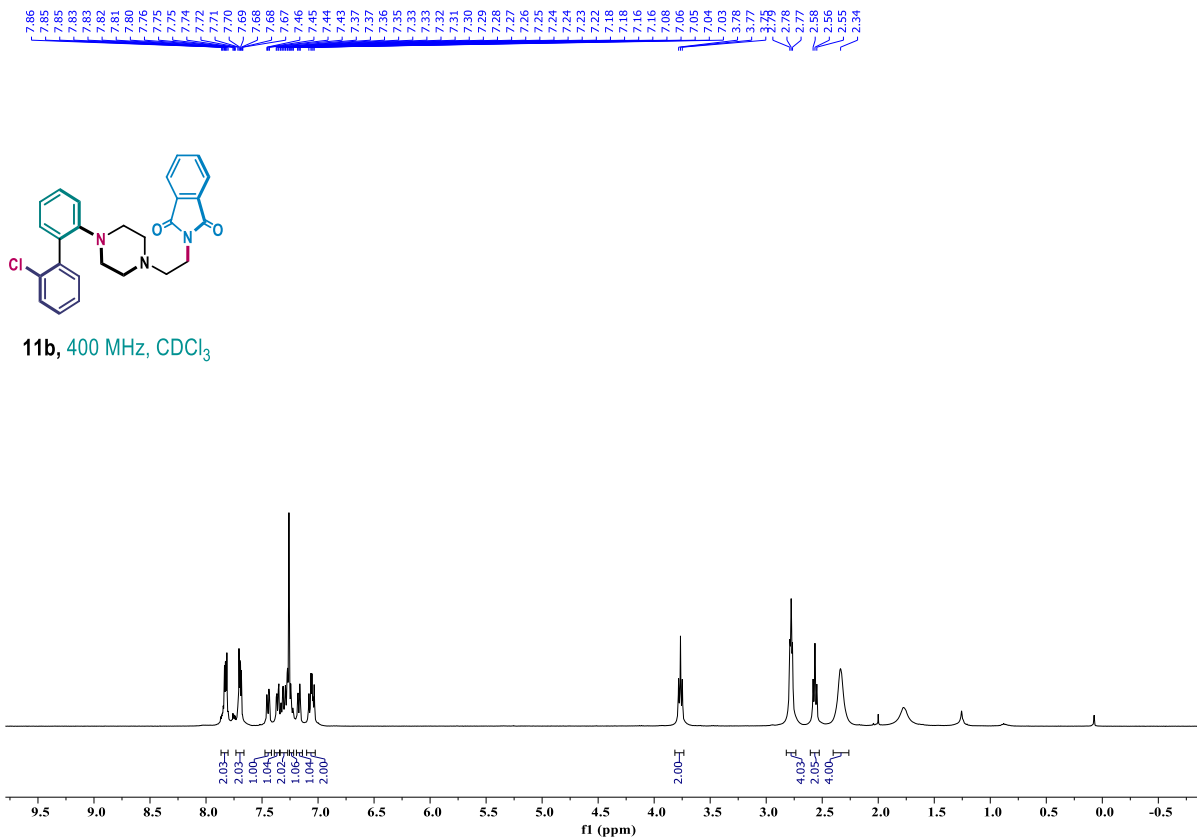


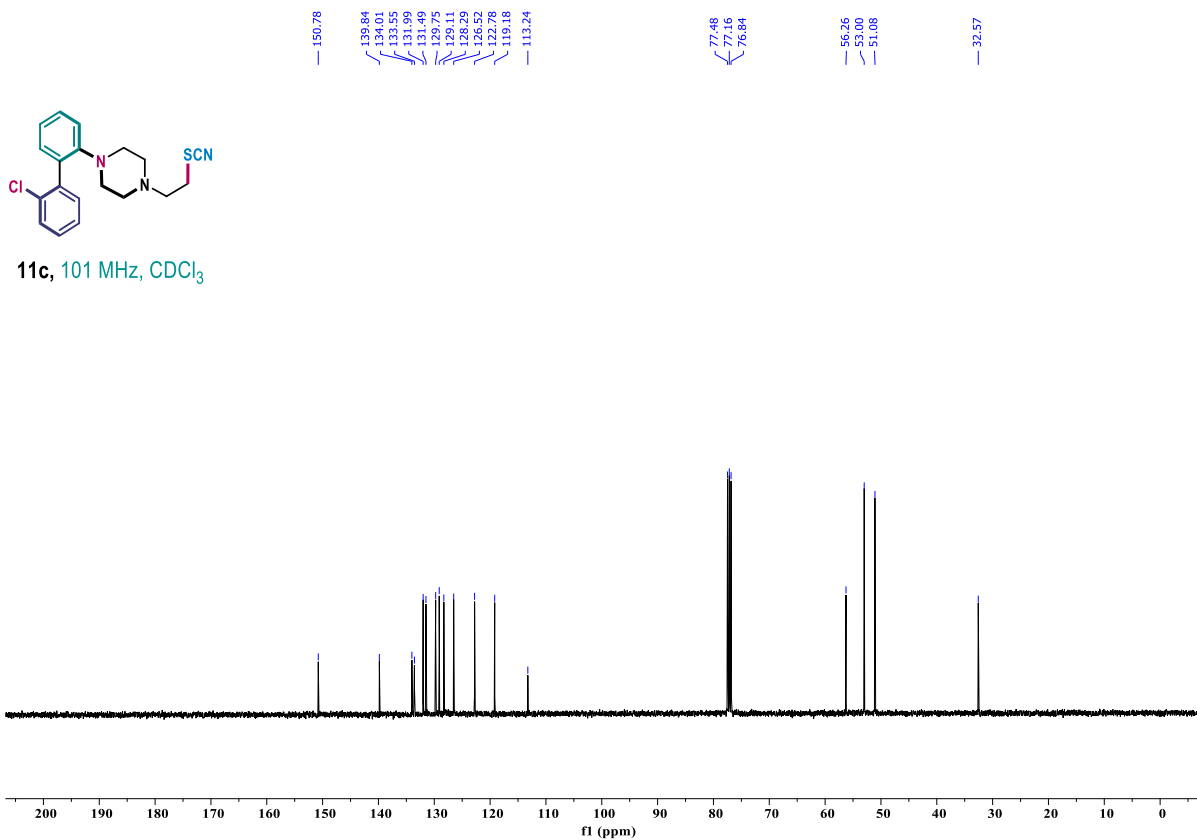
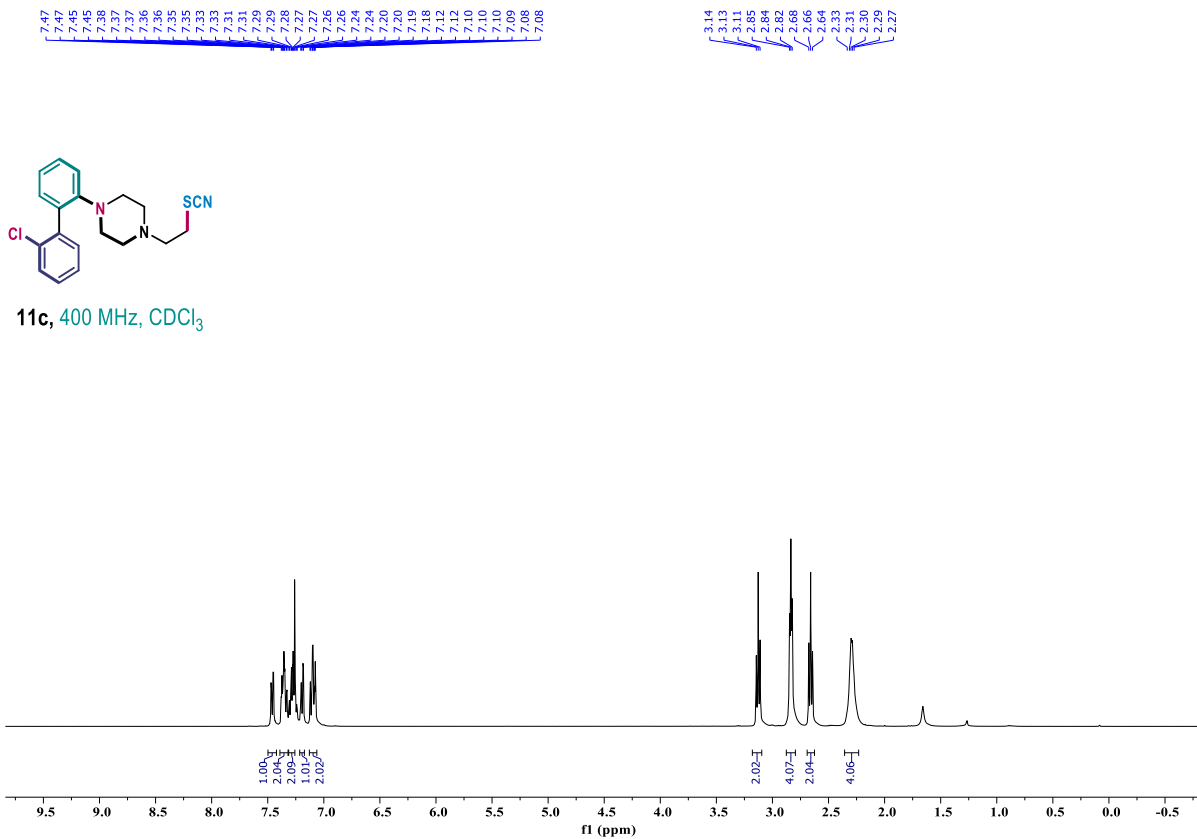


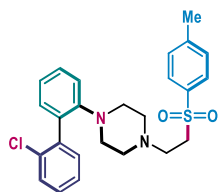




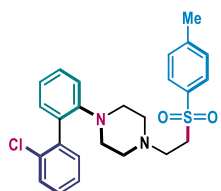
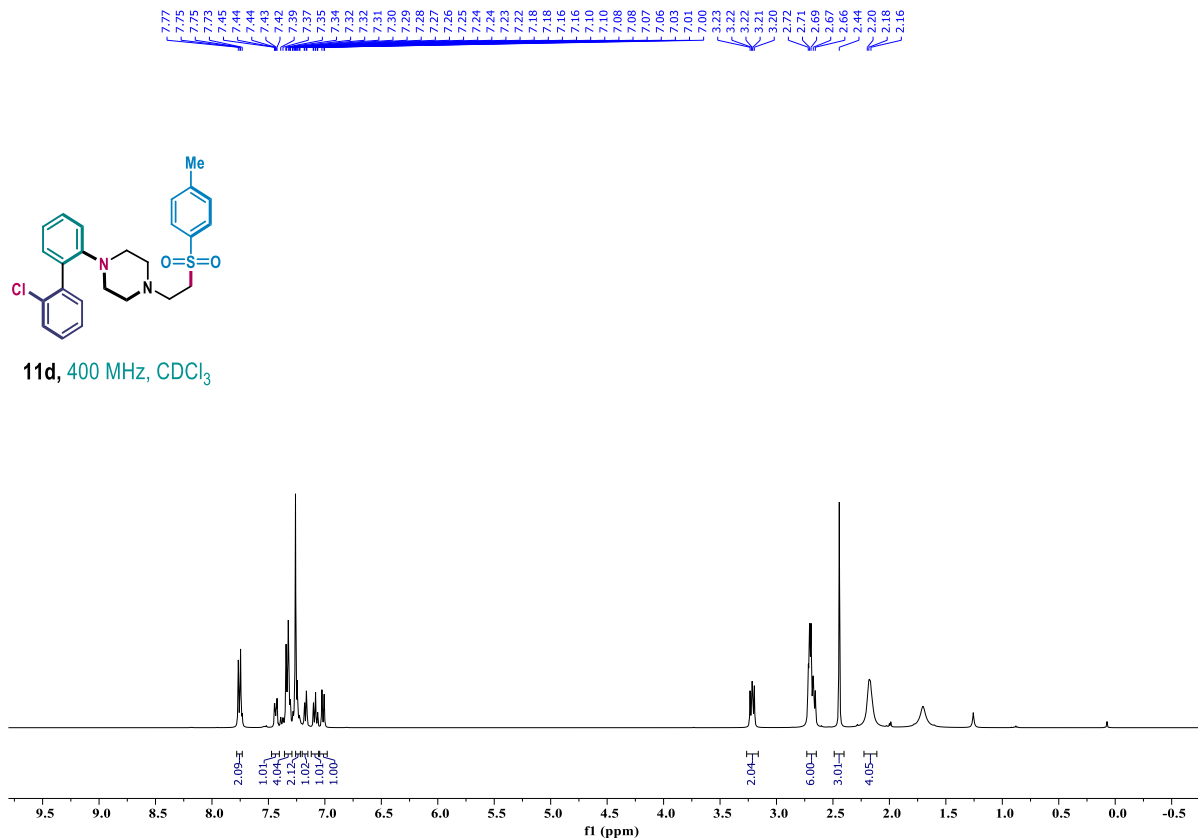




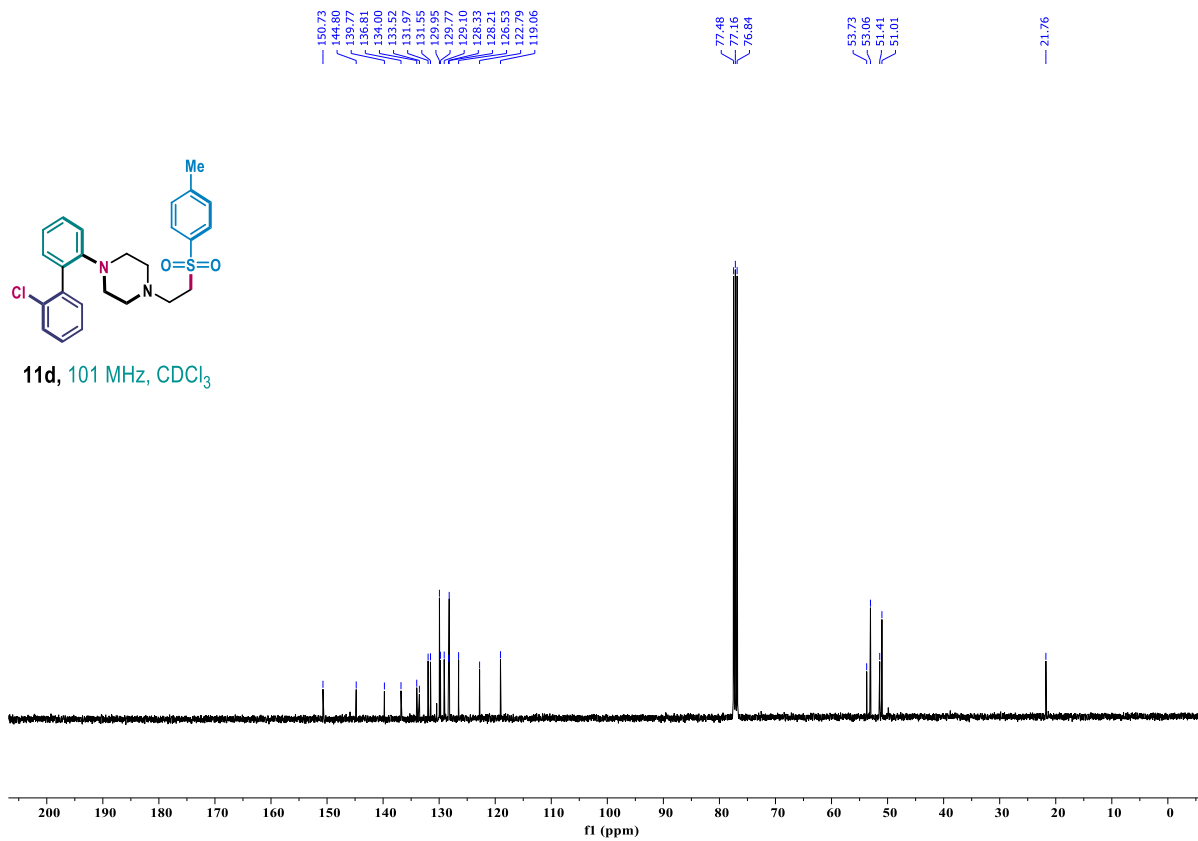


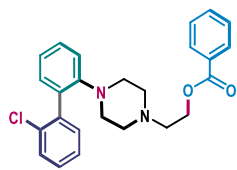


11d, 400 MHz, CDCl₃

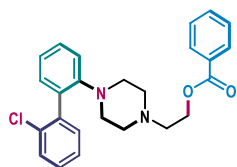
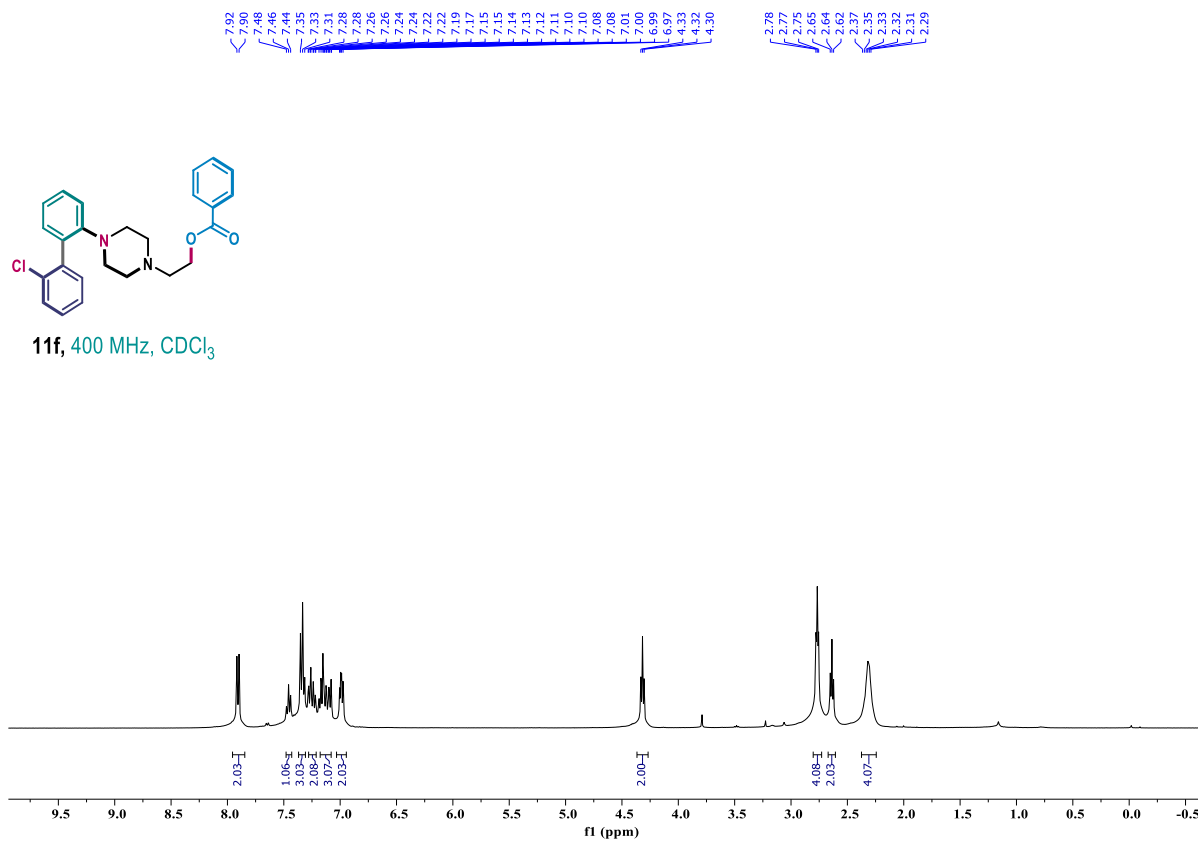


11d, 101 MHz, CDCl₃

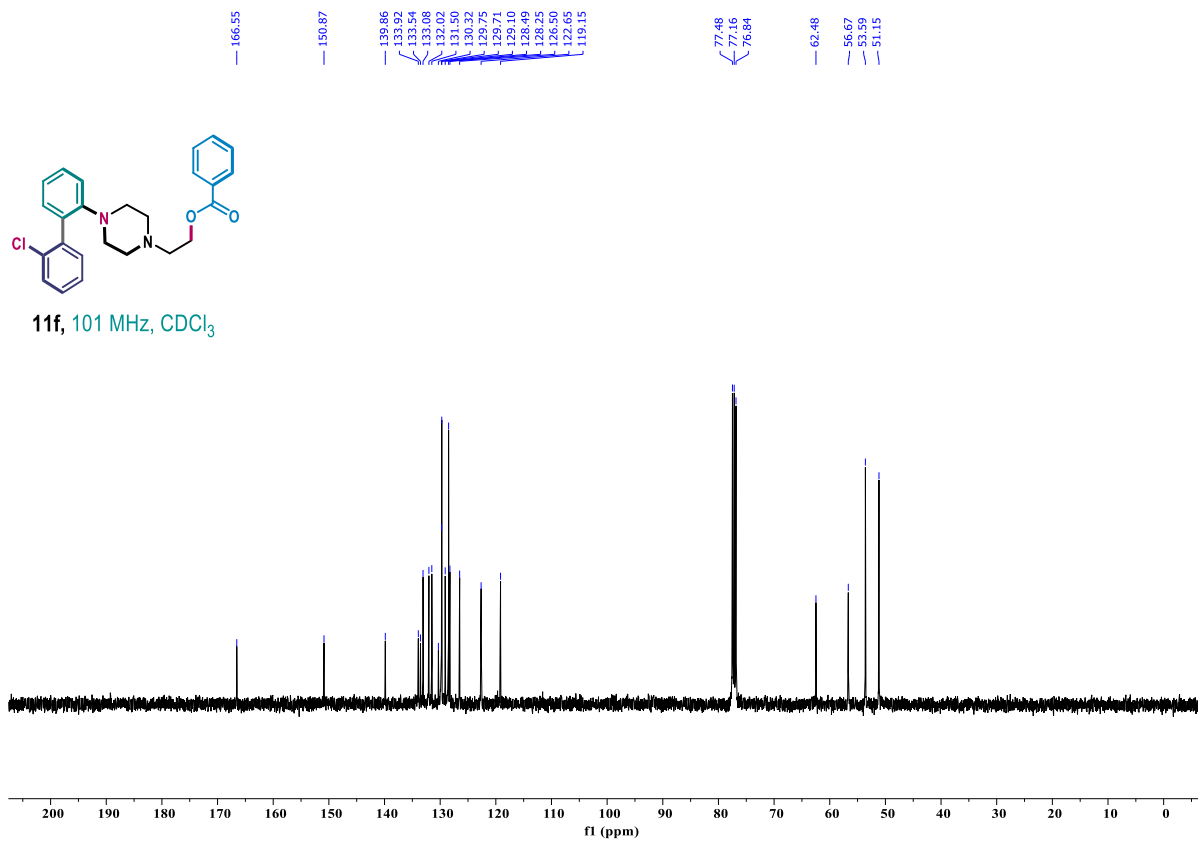


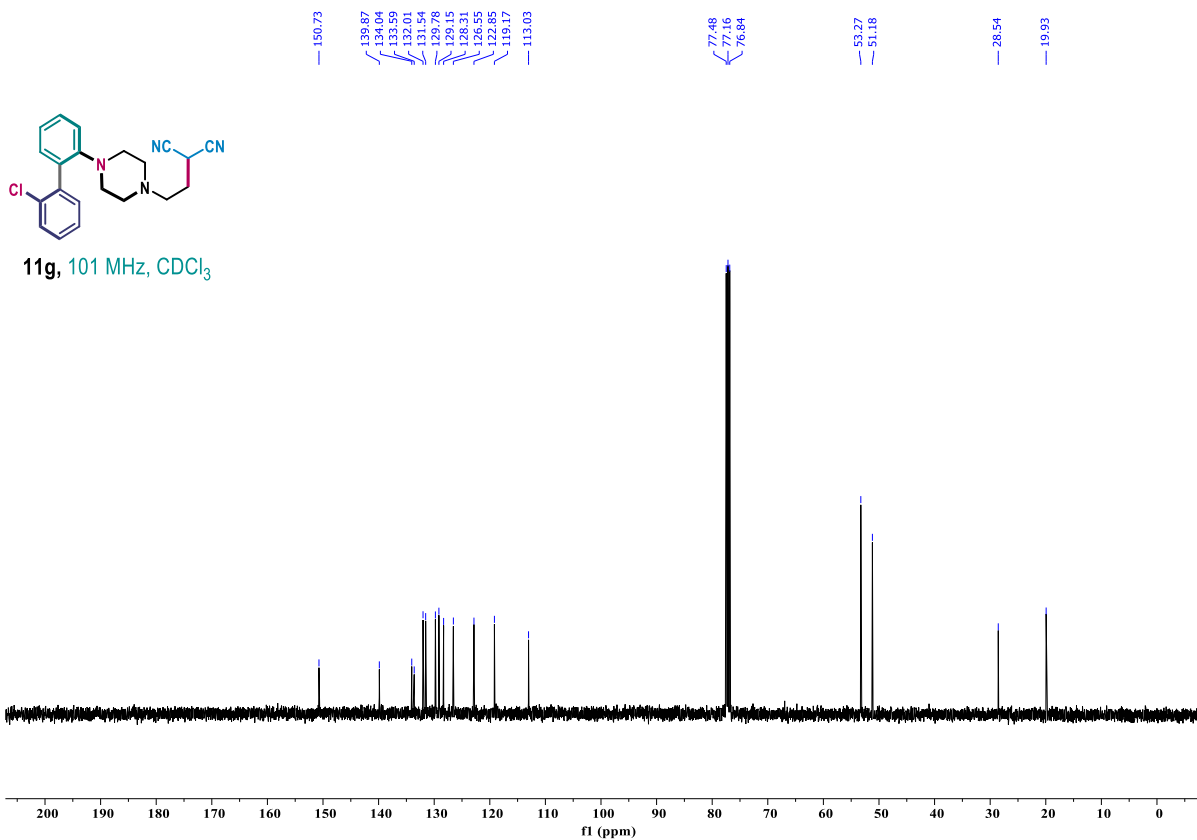
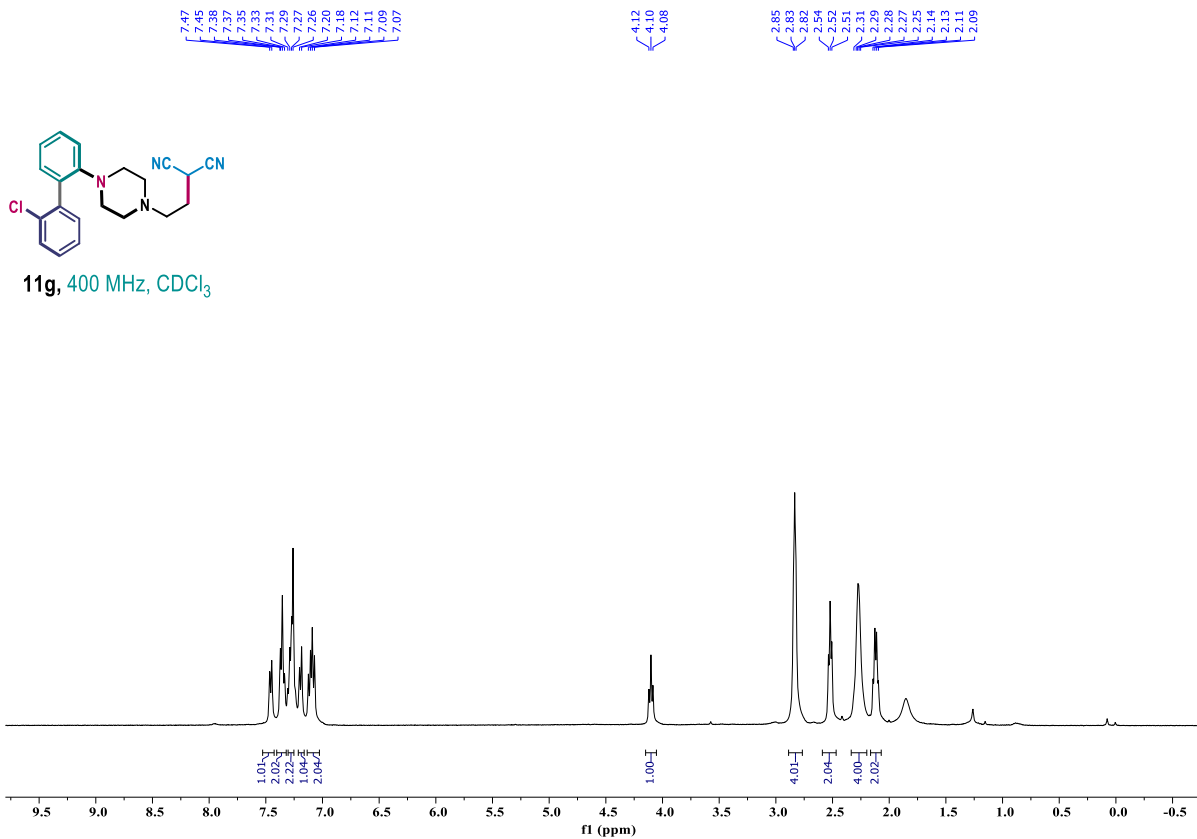


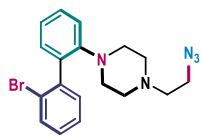
11f, 400 MHz, CDCl₃



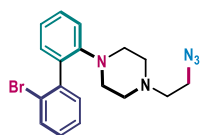
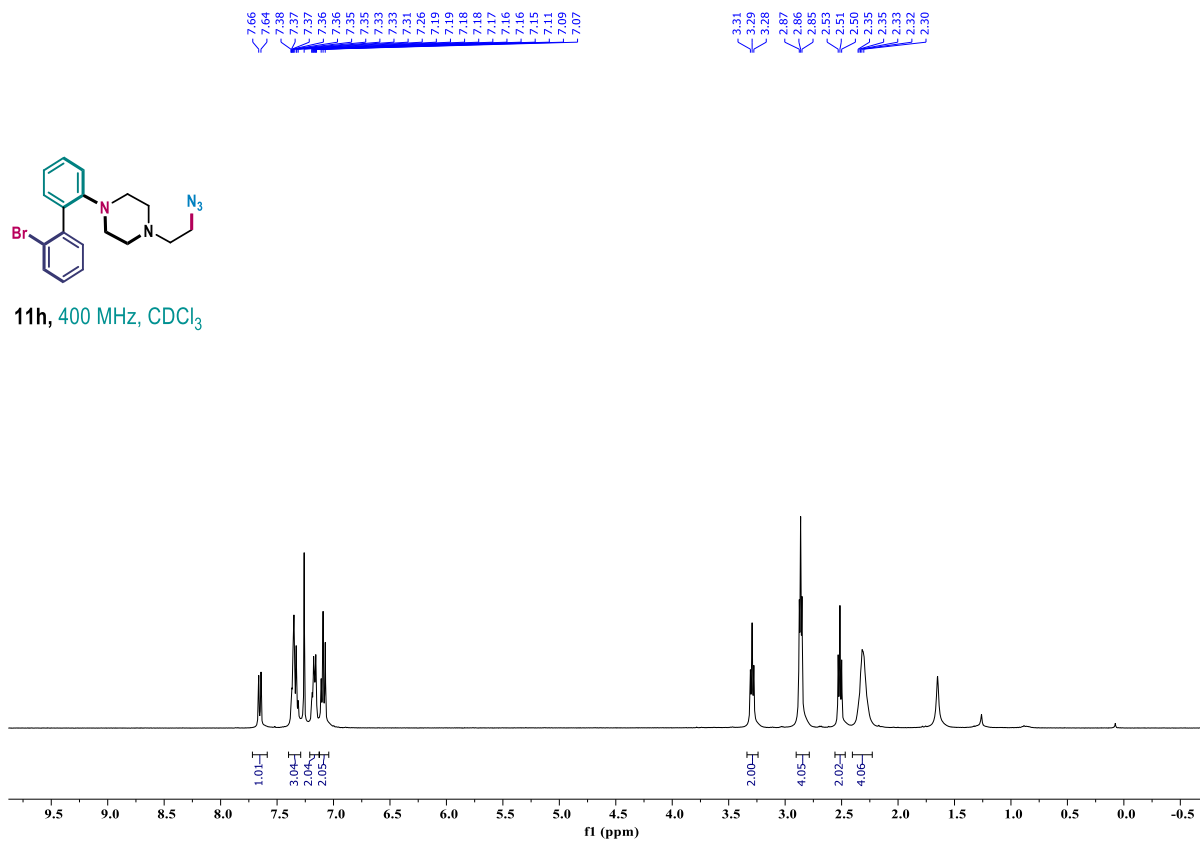
11f, 101 MHz, CDCl₃



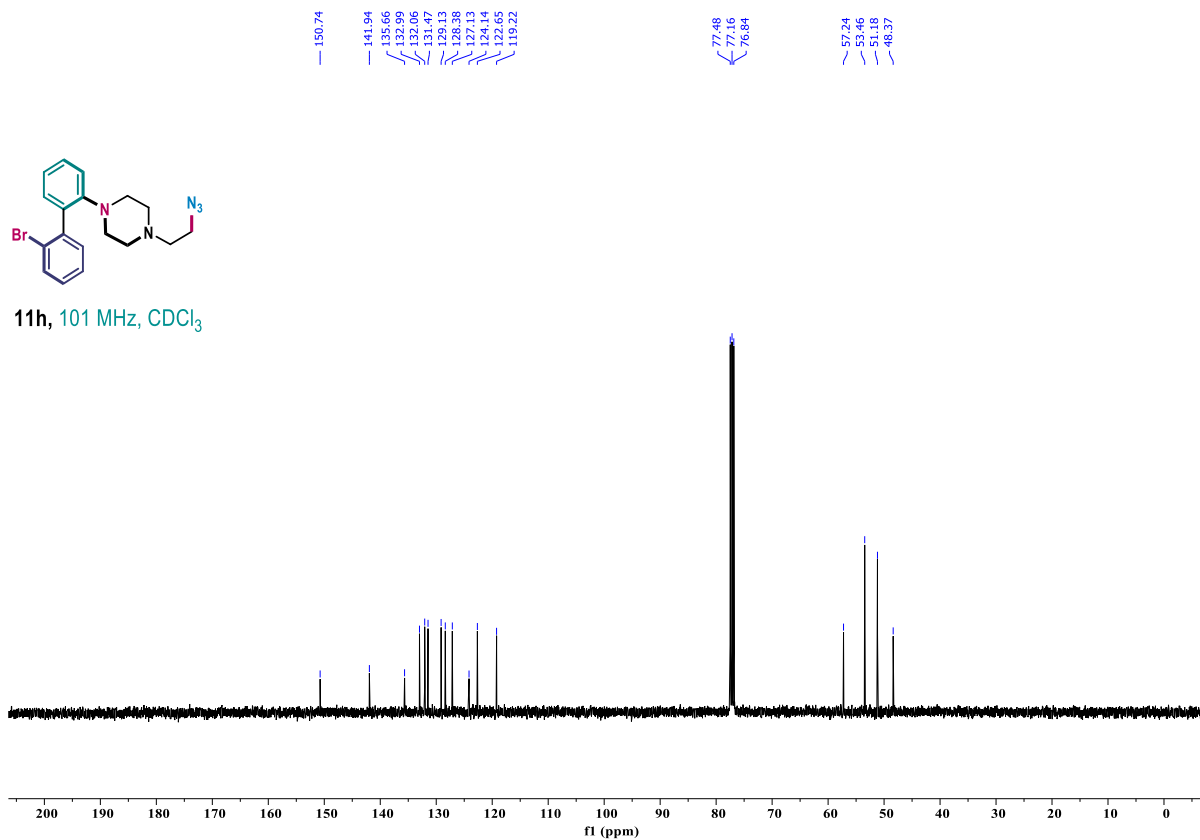


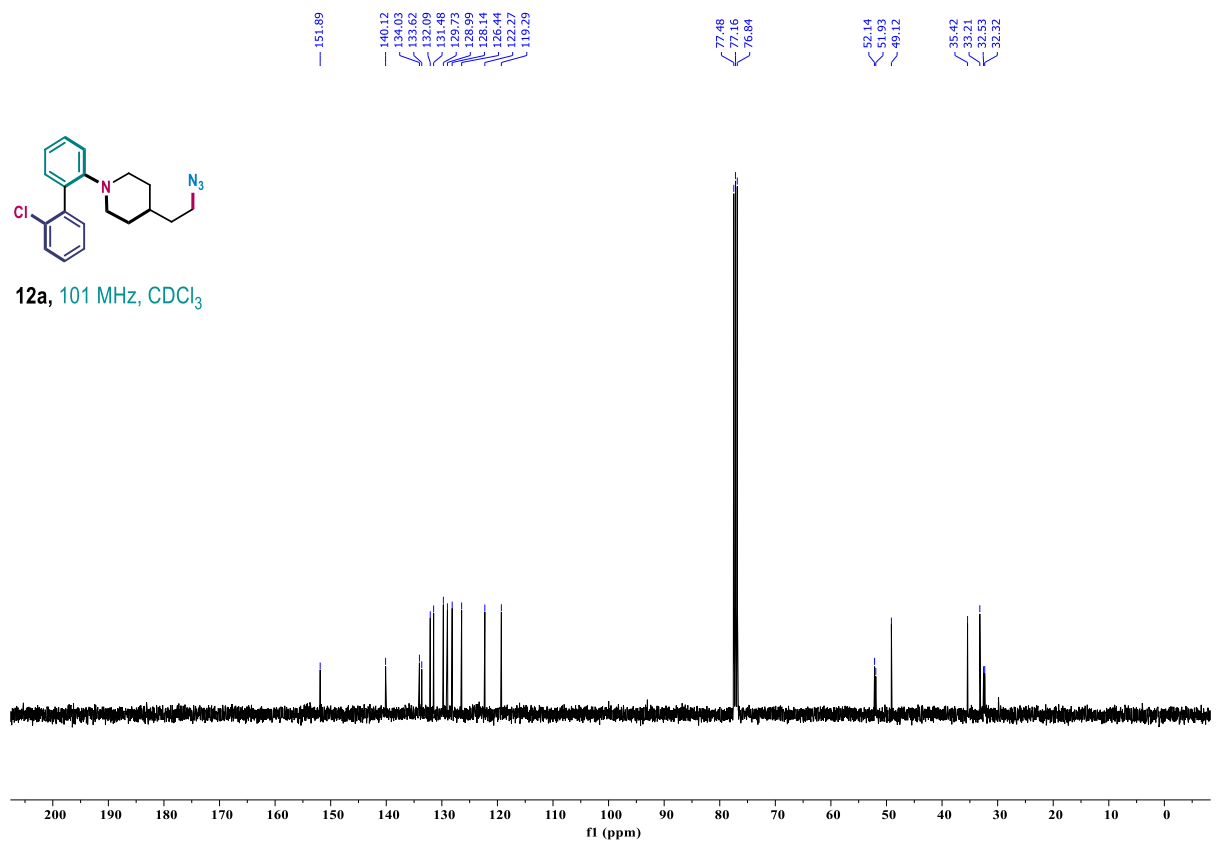
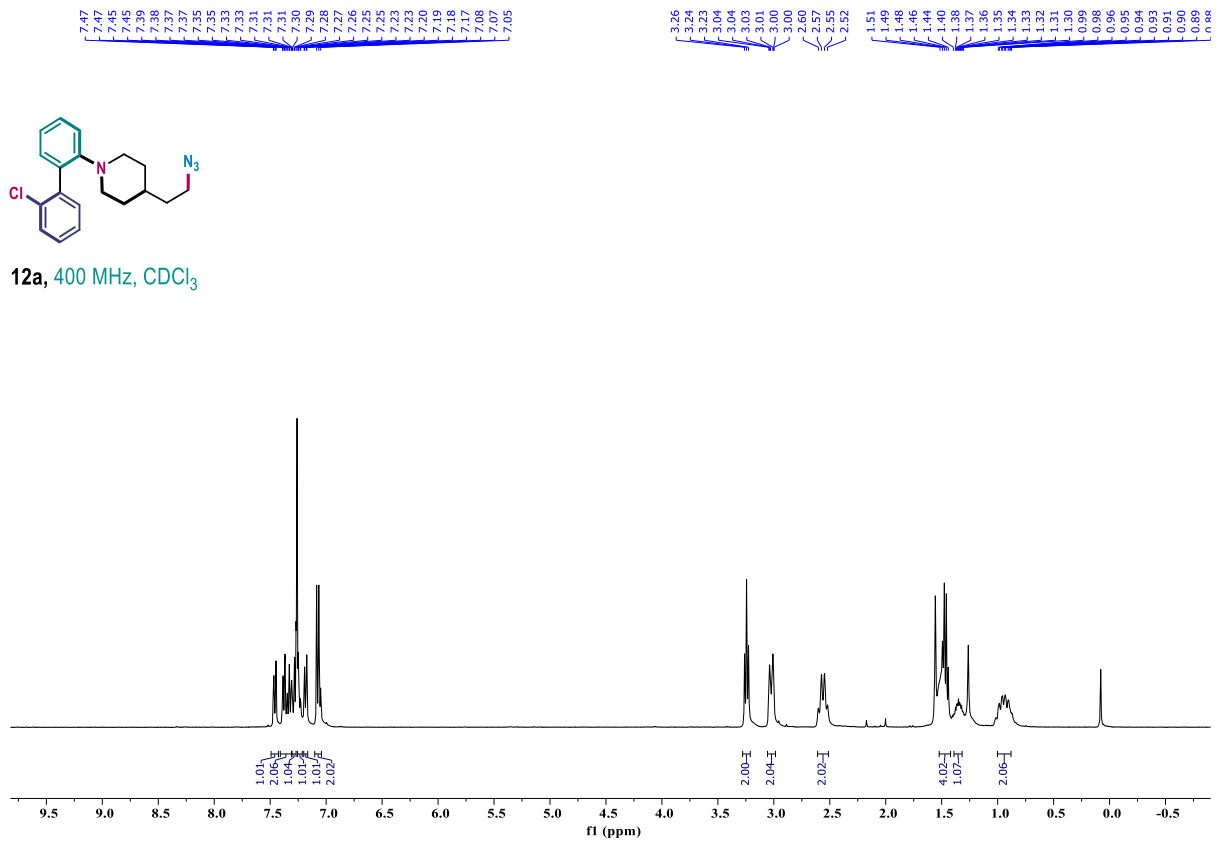


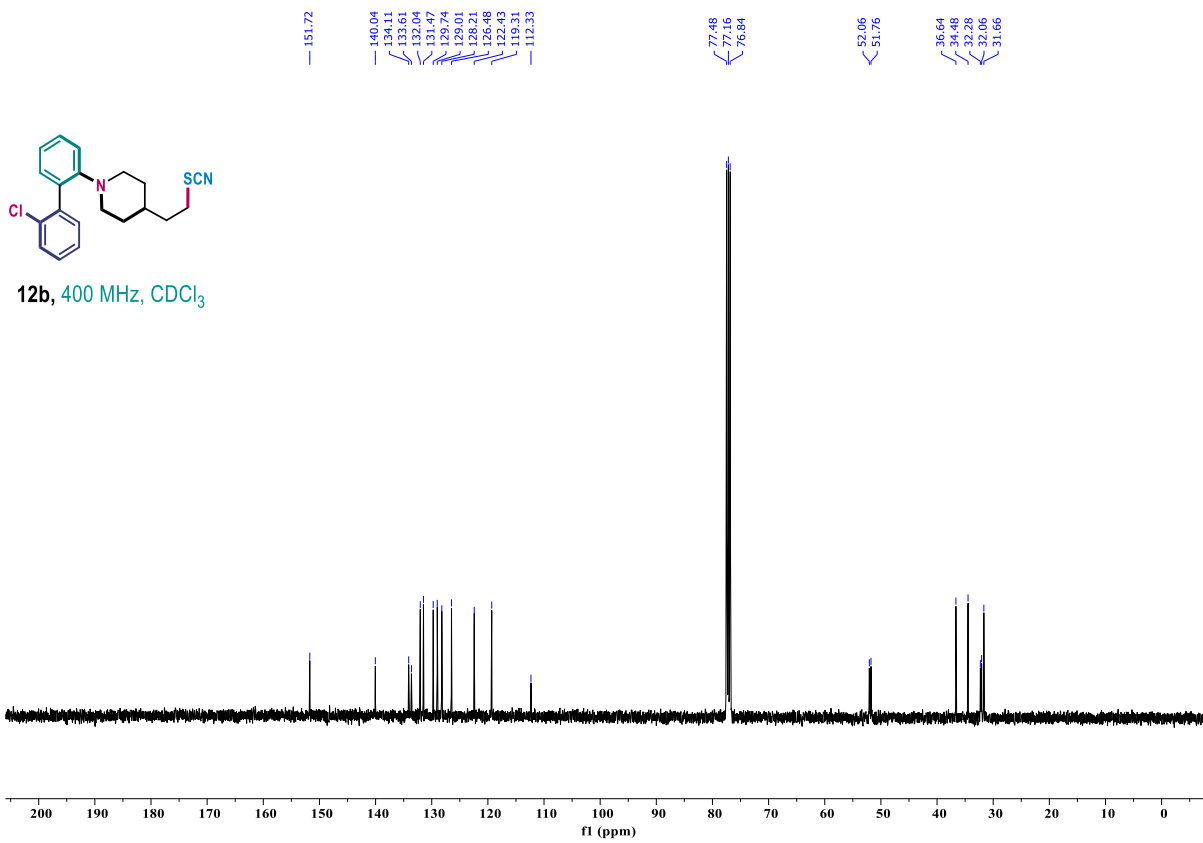
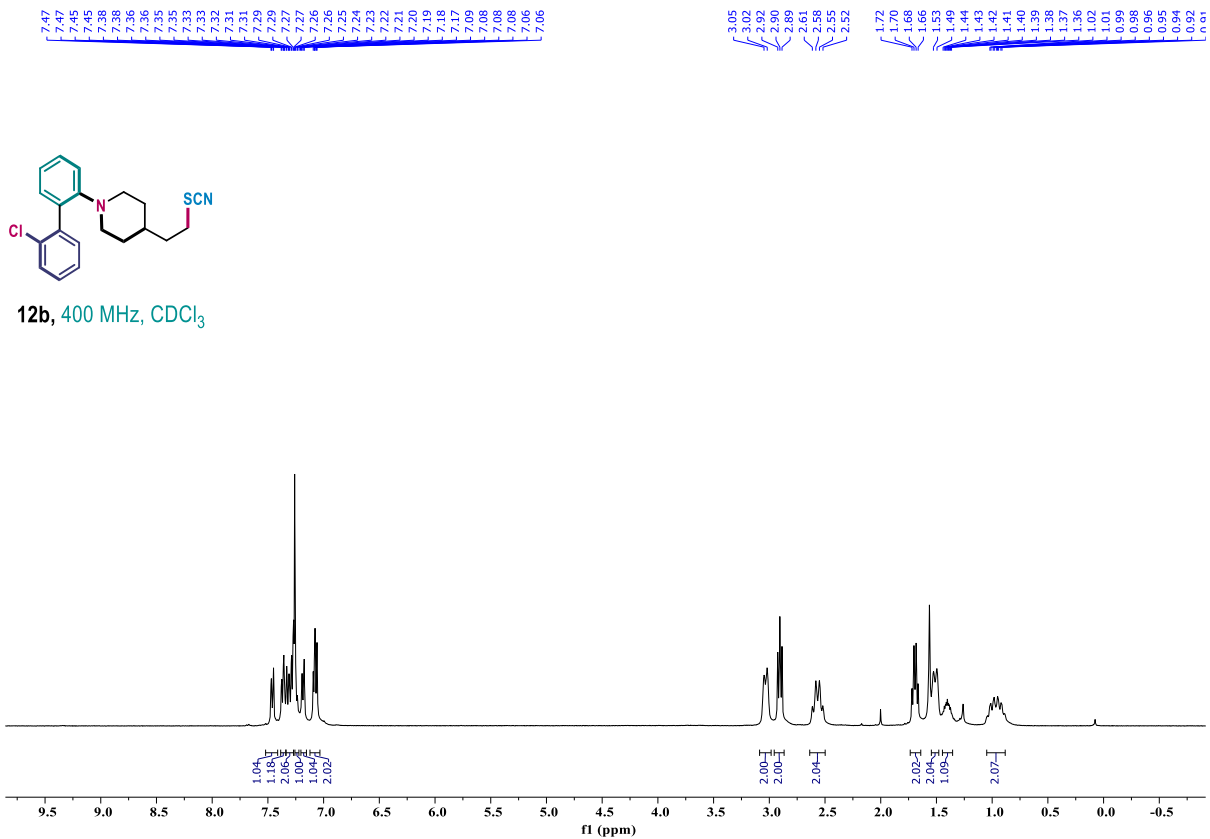
11h, 400 MHz, CDCl₃

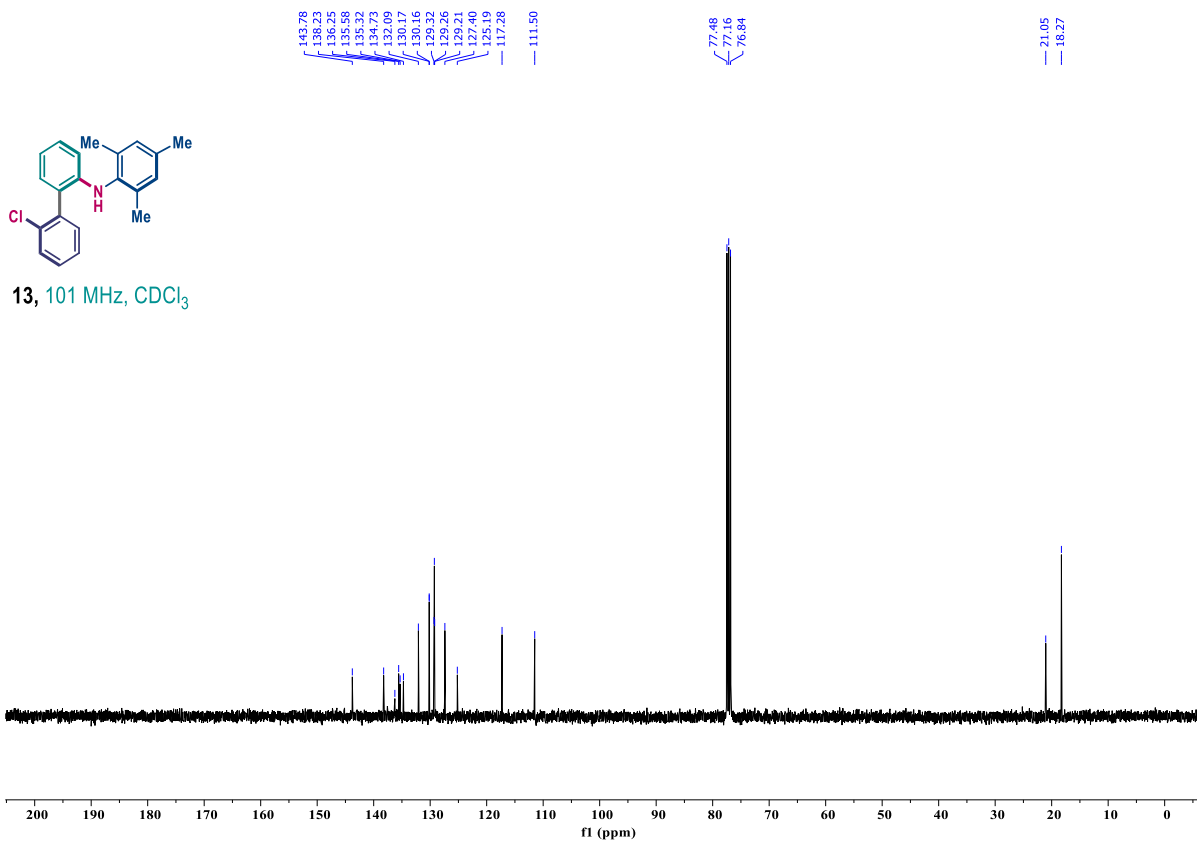
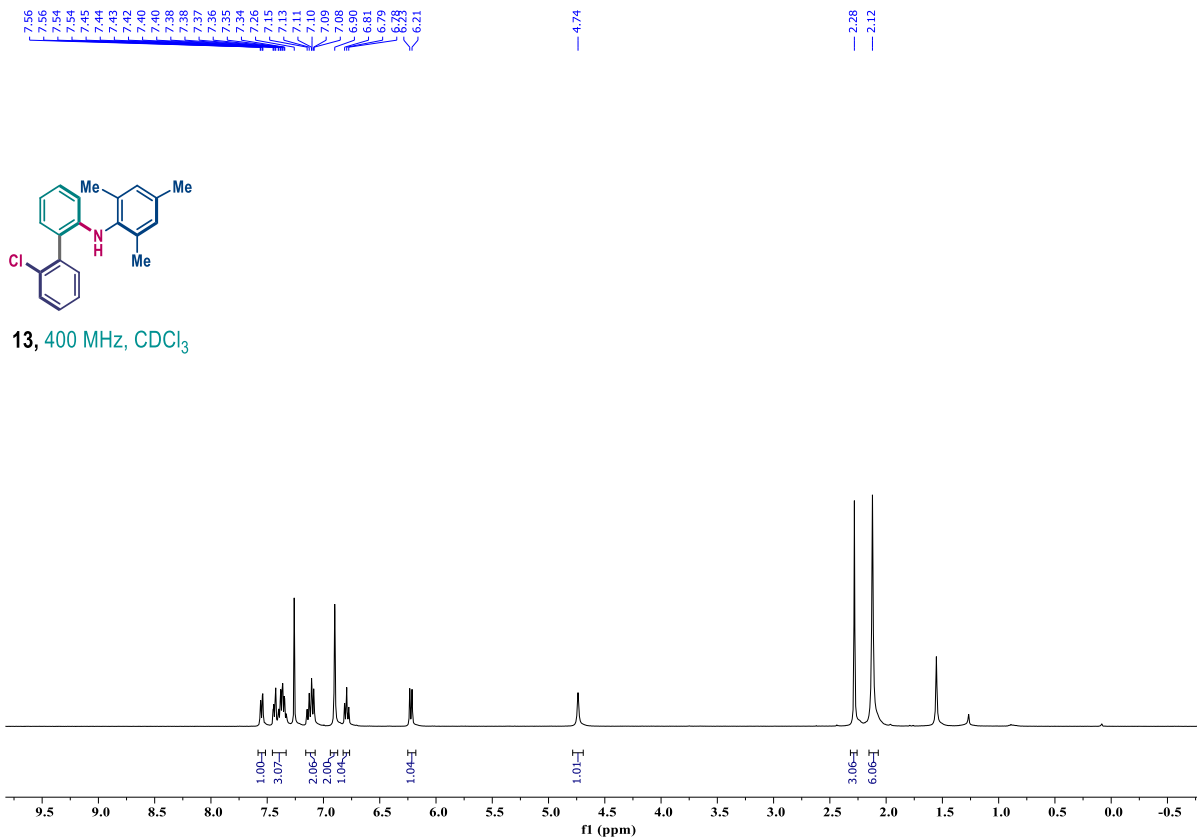


11h, 101 MHz, CDCl₃

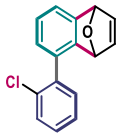




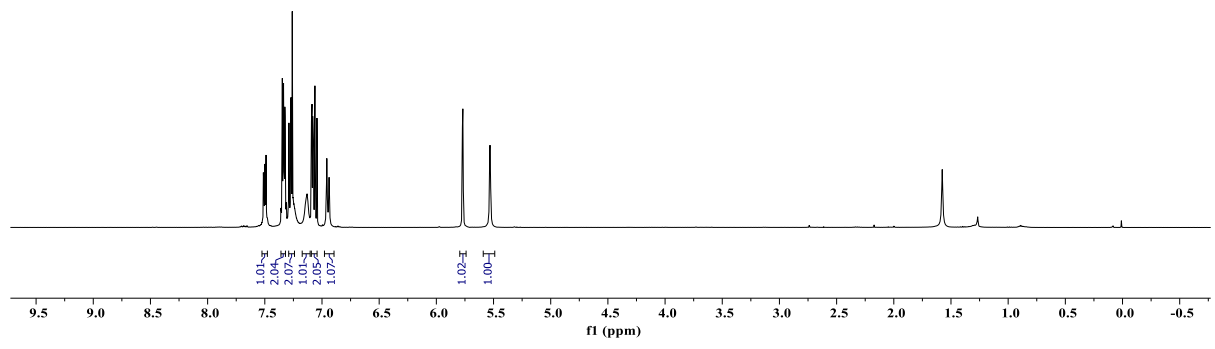




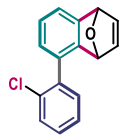
7.52
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5.77
5.77
5.53



14, 400 MHz, CDCl₃



149.01
148.48
142.95
138.60
132.88
132.66
131.95
129.92
129.15
126.99
126.44
125.18
119.70
82.71
81.82
77.48
77.16
76.84



14, 101 MHz, CDCl₃

