

Organocatalytic Photoinduced Carboamination of Dienes

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SUPPORTING INFORMATION

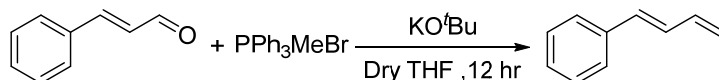
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A. General Information:

Infrared (FT-IR) spectra were recorded on PerkinElmer spectrum Two NTM Spectrometer, ν_{max} in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), weak (w). ¹H-NMR spectra were recorded on a BRUKER-AV400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 7.26 ppm, DMSO-d_6 : δ 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ¹³C-NMR spectra were recorded on a BRUKER-AV400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16, DMSO-d_6 : δ 39.50 ppm). Mass spectra were measured with a Q-TOF microspectrometer. Melting points were measured using ANALAB μ -Thermocal 10 melting point apparatus in open glass capillary and values are uncorrected. Unless otherwise noted all reactions have been carried out with dried and distilled solvents under atmosphere of nitrogen. Oven (100 °C) dried glassware with standard vacuum line techniques were used. All work up and purification were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F₂₅₄ pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 mesh). The photochemical reactions were performed with SynLED Parallel Photoreactor of Sigma-Aldrich (Blue LED 465-470 nm) (Catalog Number Z742680).

B. Starting Preparation and Characterization:¹

Synthesis of (*E*)-Buta-1, 3-dien-1-ylbenzene (1a)

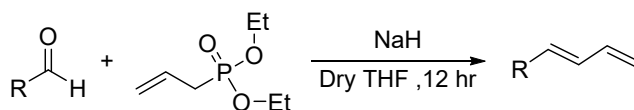


A mixture of methyltriphenylphosphonium bromide (6.4 g, 18 mmol) in THF (90 mL) was cooled to 0 °C and potassium *tert*-butoxide (2.01 g, 18 mmol) was added in portions. The mixture was warmed to 25 °C and stirred for 1 h. To the resultant mixture of *trans*-cinnamaldehyde (1.98 g, 15 mmol) in THF (8 mL) was added and the mixture was stirred for additional 12 h. The reaction was quenched by adding saturated aq. NH_4Cl solution (50 mL) and the mixture was extracted with Et_2O (3×100 mL). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4 , and the solvents were removed

1 (a) M.-Y. Hu, Q. He, S.-J. Fan, Z.-C. Wang, L.-Y. Liu, Y.-J. Mu, Q. Peng and S.-F. Zhu, *Nat. Commun.* 2018, **9**, 221. (b) M. H. Al-Huniti, M. A. Perez, M. K. Garr and M. P. Croatt, *Org. Lett.* 2018, **20**, 7375-7379. (c) B. Gérardin, I. Traboulsi, S. Pal, G. Lebunetelle, Y. Ramondenc, C. Hoarau and C. Schneider, *Org. Lett.* 2022, **24**, 8164-8169. (d) R. A. Fernandes, P. Kumar, A. Bhowmik and D. A. Gorge, *Org. Lett.* 2022, **24**, 3435-3439. (e) X. Zhu, W. Jian, M. Huang, D. Li, Y. Li, X. Zhang and H. Bao, *Nat. Commun.* 2021, **12**, 6670. (f) D. Forster, W. Guo, Q. Wang and J. Zhu, *ACS Catal.* 2021, **11**, 10871-10877.

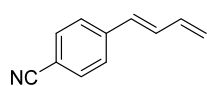
under reduced pressure. Purification by column chromatography over 230-400 silica gel mesh with hexane as eluent furnished **1a** as colorless oil (1.63 g, 12.52 mmol, 83% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.28-7.24 (m, 1H), 6.82 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.62-6.50 (m, 2H), 5.37 (d, *J* = 16.9 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 137.3, 137.2, 133.0, 129.7, 128.7, 127.8, 126.6, 117.7. The spectroscopic data are in agreement with literature.^{1a}

Procedure for synthesis of 1-arylbutadienes (**1**):



A solution of diethyl allyl phosphonate (1.5 equiv) in THF (12 ml/ mmol) was cooled to 0 °C and NaH (1.5 equiv) was added in portions. The resultant mixture was stirred for 15 min and a solution of corresponding aldehyde (5.0 mmol) in THF (2 ml/mmol) was added. The reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched by adding saturated aq. NH₄Cl solution (50 mL) and the mixture was extracted with Et₂O. The combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, and the solvents were removed under reduced pressure. Purification by column chromatography over 230-400 silica gel mesh with petroleum ether/EtOAc (99:1 to 95:5) as eluent furnished **1**

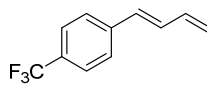
(E)-4-(buta-1, 3-dien-1-yl) benzonitrile (1b): white solid (700 mg, 4.5 mmol, 75% yield).



¹H-NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H) 6.87 (dd, *J* = 15.6 Hz, 10.6 Hz, 1H), 6.57-6.47 (m, 2H), 5.46-5.42 (m, 1H), 5.32-5.30 (m, 1H). The spectroscopic data are in agreement with

literature.^{1c}

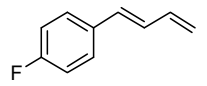
(E)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl) benzene (1c): colorless oil (210 mg, 1.03



mmol, 53% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H) 6.85 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.60-6.47 (m, 2H), 5.40 (d, *J* = 16.8 Hz, 1H), 5.26 (d, *J* = 10.1 Hz, 1H), 3.12 (s, 1H). ¹⁹F-NMR (376 MHz, CDCl₃): δ -62.5. The spectroscopic data are in agreement with

literature.^{1c}

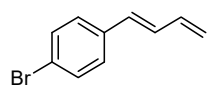
(E)-1-(buta-1, 3-dien-1-yl)-4-fluorobenzene (1d): colorless oil (750 mg, 5.06 mmol, 51% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.39-7.35 (m, 2H), 7.03-6.99 (m,



2H), 6.70 (dd, *J* = 15.4 Hz, 10.5 Hz, 1H), 6.55-6.45 (m, 2H), 5.33 (d, *J* = 16.2 Hz, 1H), 5.18 (d, *J* = 9.4 Hz, 1H). ¹⁹F-NMR (376 MHz, CDCl₃): δ -

114.19. ¹³C-NMR (100 MHz, CDCl₃): δ 162.5 (d, *J* = 247.3 Hz), 137.1, 131.7, 129.5 (d, *J* = 2.4 Hz), 128.1 (d, *J* = 7.8 Hz), 117.8, 115.6 (d, *J* = 21.6 Hz). The spectroscopic data are in agreement with literature.^{1a}

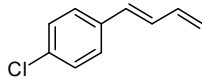
(E)-1-bromo-4-(buta-1, 3-dien-1-yl) benzene (1d): *E/Z* (66:34) colorless oil (517 mg, 3.14 mmol, 63% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.48-7.43 (m, 2H),



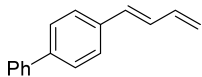
7.27 (d, *J* = 8.4 Hz, 1H) 7.18 (d, *J* = 8.6 Hz, 1H), 6.86-6.74 (m, 1H), 6.54-

6.25 (m, 2H), 5.42-5.34 (m, 1H), 5.28-5.20 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 137.0, 136.4, 132.8, 131.6, 130.3, 129.2, 128.2, 120.5, 118.4. The spectroscopic data are in agreement with literature.^{1d}

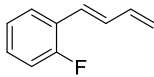
(E)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (1e): colorless oil (517 mg, 3.14 mmol, 63% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.34-7.28 (m, 4H), 6.78-6.73 (m, 1H), 6.54-6.46 (m, 2H), 5.38-5.34 (m, 1H), 5.21 (d, $J = 9.3$ Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 137.0, 135.8, 133.3, 131.6, 130.3, 128.9, 127.7, 118.3. The spectroscopic data are in agreement with literature.^{1a}



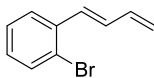
(E)-4-(buta-1,3-dien-1-yl)-1,1'-biphenyl (1f): white solid (355 mg, 1.7 mmol, 34% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.69-7.57 (m, 4H), 7.50-7.43 (m, 4H), 6.85 (dd, $J = 15.6$ Hz, 10.4 Hz, 1H), 6.64-6.51 (m, 2H), 5.39-5.35 (m, 1H), 5.22-5.20 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 140.8, 140.5, 137.3, 136.3, 132.5, 129.8, 127.5, 127.4, 127.1, 127.0, 117.8. The spectroscopic data are in agreement with literature.^{1c}



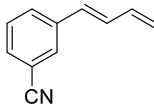
(E)-1-(buta-1,3-dien-1-yl)-2-fluorobenzene (1h): colorless oil (310 mg, 2.09 mmol, 42% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.51-7.47 (m, 1H), 7.23-7.17 (m, 1H), 7.11-7.01 (m, 2H), 6.87 (dd, $J = 15.8$ Hz, 10.3 Hz, 1H), 6.73 (d, $J = 15.8$ Hz, 1H), 6.58-6.49 (m, 1H), 5.36 (d, $J = 16.8$ Hz, 1H), 5.2 (d, $J = 10.2$ Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 161.7, 159.2, 137.5, 137.1, 132.0 (d, $J = 5.2$ Hz), 128.9 (d, $J = 8.9$ Hz), 127.2 (d, $J = 3.6$ Hz), 125.2 (d, $J = 3.4$ Hz), 124.2 (d, $J = 3.6$ Hz), 118.6, 116.0, 115.8. The spectroscopic data are in agreement with literature.^{1d}



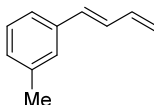
(E)-1-bromo-2-(buta-1,3-dien-1-yl) benzene (1i): ($E/Z = 79:21$) colorless oil (768 mg, 3.67 mmol, 37% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.60-7.54 (m, 2H), 7.31-7.25 (m, 1H), 7.15-7.06 (m, 1H), 6.93 (d, $J = 15.6$ Hz, 1H), 6.77-6.50 (m, 2H), 5.44-5.37 (m, 1H), 5.27-5.23 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 137.1, 133.2, 132.3, 131.4, 128.9, 127.6, 126.7, 124.1, 120.4, 118.9. The spectroscopic data are in agreement with literature.^{1d}



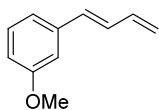
(E)-3-(buta-1,3-dien-1-yl) benzonitrile (1j): white viscous (824 mg, 5.31 mmol, 53% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.66-7.65 (m, 1H), 7.61-7.59 (m, 1H), 7.50-7.48 (m, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 6.85-6.79 (m, 1H), 6.55-6.45 (m, 2H), 5.44-5.40 (m, 1H), 5.29-5.26 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 138.5, 136.5, 132.2, 130.8, 130.5, 130.3, 129.9, 129.5, 119.9, 118.8, 113.0. The spectroscopic data are in agreement with literature.¹



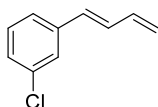
(E)-1-(buta-1,3-dien-1-yl)-3-methylbenzene (1k): colorless oil (768 mg, 4.98 mmol, 50% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.24-7.22 (m, 3H), 7.07-7.05 (m, 1H), 6.79 (dd, $J = 15.5$ Hz, 10.6 Hz, 1H), 6.57-6.47 (m, 2H), 5.36-5.31 (m, 1H), 5.19-5.16 (m, 1H), 2.36 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 138.2, 137.4, 137.2, 133.1, 129.6, 128.6, 128.5, 127.3, 123.8, 117.5, 21.5s. The spectroscopic data are in agreement with literature.^{1c}



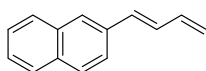
(E)-1-(buta-1, 3-dien-1-yl)-3-methoxybenzene (1l): colorless oil (870 mg, 5.43 mmol, 54% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.24 (t, *J* = 8.0 Hz, 1H), 7.02(d, *J* = 7.6 Hz, 1H) 6.96 (t, *J* = 2.1 Hz, 1H), 6.83-6.77 (m, 2H), 6.58-6.47(m, 2H), 5.36 (d, *J* = 16.8 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H) 3.83 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 160.0, 138.7, 137.2, 132.9, 130.1, 129.7, 119.3, 117.9, 113.5, 111.8, 55.3. The spectroscopic data are in agreement with literature.^{1c}



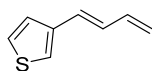
(E)-1-(buta-1, 3-dien-1-yl)-3-chlorobenzene (1m): colorless oil (670 mg, 4.06 mmol, 41% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.38 (s, 1H), 7.30-7.17 (m, 3H), 6.80-6.74 (m, 1H), 6.53-6.43 (m, 2H), 5.38-5.34 (m, 1H), 5.23-5.20 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 139.2, 136.9, 134.7, 131.4, 131.1, 129.9, 127.6, 126.4, 124.8, 118.9. The spectroscopic data are in agreement with literature.^{1c}



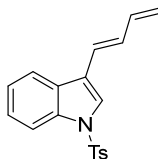
(E)-2-(buta-1, 3-dien-1-yl) naphthalene (1n): white solid (520 mg, 2.88 mmol, 29% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.83-7.77 (m, 4H), 7.65 (dd, *J* = 8.6 Hz, 1.6 Hz, 1H), 7.50-7.44 (m, 2H), 6.95 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.59 (dt, *J* = 16.9 Hz, 10.2 Hz 1H), 5.42 (d, *J* = 16.9 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 137.4, 134.8, 133.8, 133.2, 133.1, 130.1, 128.4, 128.1, 127.81, 126.7, 126.0, 123.6, 117.9. The spectroscopic data are in agreement with literature.^{1c}



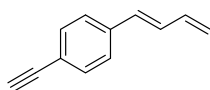
(E)-3-(buta-1, 3-dien-1-yl) thiophene (1o): colorless oil (745 mg, 5.46 mmol, 55% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.30-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.17 (dd, *J* = 2.8 Hz, 1.2 Hz, 1H), 6.68-6.43 (m, 3H), 5.53 (dd, *J* = 16.3 Hz, 1.3 Hz, 1H), 5.16 (dd, *J* = 10.0 Hz, 1.5 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 140.0, 137.3, 129.8, 127.0, 126.2, 125.0, 122.4, 117.3. The spectroscopic data are in agreement with literature.^{1c}



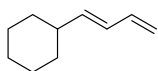
(E)-3-(buta-1,3-dien-1-yl)-1-tosyl-1H-indole (1p): E/Z (60:40) colorless oil (768 mg, 4.98 mmol, 50% yield). ¹H-NMR (400 MHz, CDCl₃): δ 8.0-7.98 (m, 1H), 7.79-7.73 (m, 2H), 7.61 (d, *J* = 6.6 Hz, 1H), 7.52-7.50 (m, 1H), 7.35-7.19 (m, 4H), 6.89-6.79 (m, 1H), 6.64-6.34 (m, 2H), 5.45-5.31 (m, 1H), 5.30-5.16 (m, 1H), 2.33 (s, 1.8H), 2.32 (s, 1.2H). ¹³C-NMR (100 MHz, CDCl₃): δ 145.2, 137.5, 135.3, 134.8, 133.6, 132.2, 130.9, 130.7, 130.1, 126.9, 125.1, 124.3, 123.9, 123.7, 123.5, 123.3, 120.5, 120.1, 119.9, 119.2, 117.6, 113.9, 113.7, 21.7. The spectroscopic data are in agreement with literature.^{1f}



(E)-1-(buta-1, 3-dien-1-yl)-4-ethynylbenzene (1q): colorless oil (768 mg, 4.98 mmol, 50% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H) 6.79 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.55-6.46 (m, 2H), 5.37 (d, *J* = 16.5 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 3.12 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 137.8, 137.1, 132.5, 132.1, 130.9, 126.5, 121.2, 118.7, 83.9, 78.0. The spectroscopic data are in agreement with literature.^{1c}

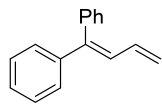


(E)-buta-1, 3-dien-1-ylcyclohexane (1r): colorless oil (560 mg, 4.10 mmol, 41% yield). ¹H-NMR (400 MHz, CDCl₃): δ 6.35-6.25 (m, 2H), 6.01 (dd, *J* = 15.2 Hz, 10.3

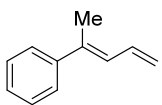


1H) 5.65 (dd, $J = 15.4$ Hz, 7.0 Hz, 1H), 5.10 (d, $J = 17.0$ Hz, 1H), 4.95 (d, $J = 10.1$ Hz, 1H), 2.01-1.97 (m, 1H), 1.74-1.63 (m, 6H), 1.20-1.04 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 141.4, 137.8, 128.5, 114.8, 40.8, 32.9, 26.3, 26.1. The spectroscopic data are in agreement with literature.^{1b}

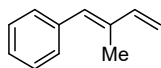
Buta-1, 3-diene-1, 1-diylbenzene (1s): colorless oil (970 mg, 4.70 mmol, 47% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.40-7.20 (m, 10H), 6.70 (d, $J = 11.0$ Hz, 1H), 6.44 (dt, $J = 16.9, 10.5$ Hz, 1H), 5.39 (dd, $J = 16.8, 1.1$ Hz, 1H), 5.13 (dd, $J = 10.1, 1.9$ Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 143.2, 142.1, 139.7, 135.0, 130.4, 128.5, 128.2, 128.1, 127.6, 127.5, 127.4, 118.6. The spectroscopic data are in agreement with literature.^{1a}



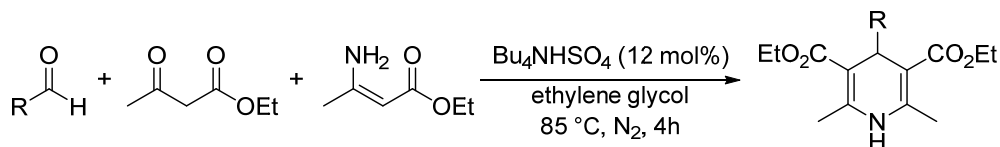
(E)-penta-2, 4-dien-2-ylbenzene (1t): colorless oil (530 mg, 3.67 mmol, 37% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.45 (d, $J = 7.8$ Hz, 2H), 7.35-7.29 (m, 2H), 7.27-7.21 (m, 1H), 6.82-6.70 (m, 1H), 6.46 (d, $J = 11.0$ Hz, 1H), 5.32 (d, $J = 16.7$ Hz, 1H), 5.19 (d, $J = 10.0$ Hz, 1H), 2.17 (s, 3H). The spectroscopic data are in agreement with literature.^{1a}



(E)-(2-methylbuta-1,3-dien-1-yl)benzene (1u): yellow oil (840 mg, 5.82 mmol, 58% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.40-7.33 (m, 4H), 7.27-7.24 (m, 1H), 6.63-6.57 (m, 2H), 5.34 (d, $J = 17.4$ Hz, 1H), 5.17 (d, $J = 10.7$ Hz, 1H), 2.04 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 142.0, 137.9, 136.1, 131.8, 129.4, 128.3, 126.7, 113.1, 13.3. The spectroscopic data are in agreement with literature.^{1b}



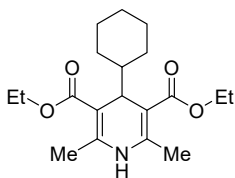
Synthesis of 1, 4-Dihydropyridines: The 1, 4-Dihydropyridines used in this study were prepared by following literature procedure.^{2a}



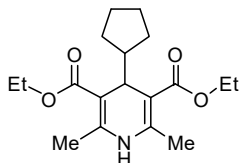
To the mixture of (Z)-3-aminobut-2-enoate (1 equiv.), ethyl acetoacetate (1 equiv.) and aldehyde (1 equiv.) in ethylene glycol (2.5 M), Bu_4NHSO_4 (12 mol%) was added in one portion. The mixture was heated at 85 °C for 4 hours under Ar. The reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to 25 °C, diluted with ethyl acetate and water, the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine. The combined organic phase was dried over Na_2SO_4 , filtered and concentrated under vacuum to give the crude product. Purification by column chromatography over 230-400 silica gel mesh with petroleum ether/EtOAc mixture as eluent furnished **2**

[2] (a) X. Chen, F. Ye, X. Luo, X. Liu, J. Zhao, S. Wang, Q. Zhou, G. Chen and P. Wang, *J. Am. Chem. Soc.* 2019, **141**, 18230-18237. (b) G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang and Z. Tang, *Angew. Chem. Int. Ed.* 2013, **52**, 8432-8436. (c) C. Verrier, N. Alandini, C. Pezzetta, M. Moliterno, L. Buzzetti, H. B. Hepburn, A. Vega-Peñaloza, M. Silvi and P. Melchiorre, *ACS Catal.* 2018, **8**, 1062-1066.

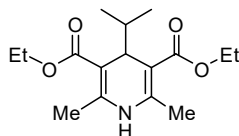
Diethyl 4-cyclohexyl-2, 6-dimethyl-1, 4-dihydropyridine-3,5-dicarboxylate (2a): white solid (4.7g, 14.01 mmol, 53% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.68 (br, s 1H), 4.25-4.09 (m, 4H), 3.90 (d, $J = 5.6$ Hz, 1H), 2.28 (s, 6H), 1.64-1.63 (m, 2H), 1.54-1.52 (m, 3H) 1.28 (t, $J = 7.1$ Hz, 6H), 1.24-1.17 (m, 1H), 1.08-1.04 (m, 3H), 0.95-0.89 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 168.9, 144.6, 102.0, 59.7, 45.9, 38.5, 29.0, 26.8, 26.7, 19.5, 14.5. The spectroscopic data are in agreement with literature.^{2a}



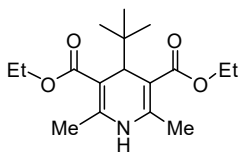
Diethyl 4-cyclopentyl-2, 6-dimethyl-1, 4-dihydropyridine-3, 5-dicarboxylate (2b): white solid (1.7g, 5.29 mmol, 53% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.66 (br s, 1H), 4.25-4.10 (m, 4H), 3.99 (d, $J = 7.2$ Hz, 1H), 2.29 (s, 6H), 1.76-1.69 (m, 1H), 1.57-1.36 (m, 6H) 1.29 (t, $J = 7.1$ Hz, 6H), 1.19 – 1.11 (m, 2H), 1.08 – 1.04 (m, 3H), 0.95 – 0.86 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 168.8, 144.7, 102.9, 59.7, 48.3, 35.9, 28.5, 24.2, 19.5, 14.5. The spectroscopic data are in agreement with literature.^{2b}



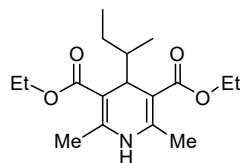
Diethyl 4-isopropyl-2, 6-dimethyl-1, 4-dihydropyridine-3, 5-dicarboxylate (2c): white solid (1.7g, 5.75 mmol, 50% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.69 (br s, 1H), 4.24-4.08 (m, 4H), 3.90 (d, $J = 5.4$ Hz, 1H), 2.28 (s, 6H), 1.62-1.53 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 6H), 0.73 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 168.7, 144.6, 102.0, 59.7, 39.0, 35.7, 19.5, 18.6, 14.5. The spectroscopic data are in agreement with literature.^{2a}



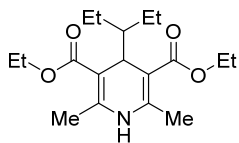
Diethyl 4-(tert-butyl)-2, 6-dimethyl-1, 4-dihydropyridine-3, 5-dicarboxylate (2d): white solid (320 mg, 1.03 mmol, 12% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.67 (br s, 1H), 4.26-4.09 (m, 4H), 4.00 (s, 1H), 2.31 (s, 6H), 1.29 (t, $J = 7.1$ Hz, 6H), 0.70 (s, 9H). The spectroscopic data are in agreement with literature.^{2a}



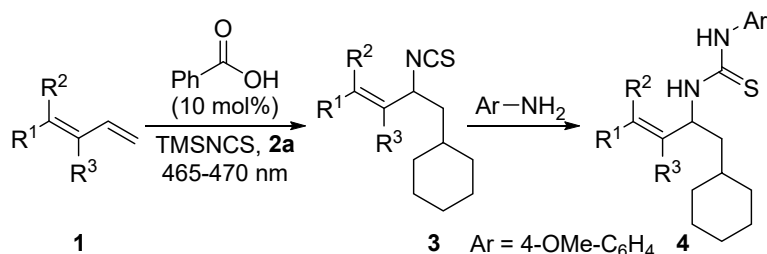
Diethyl 4-(sec-butyl)-2, 6-dimethyl-1, 4-dihydropyridine-3,5-dicarboxylate (2e): white solid (710 mg, 2.29 mmol, 38% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.55 (br s, 1H), 4.24-4.11 (m, 4H), 4.01 (d, $J = 4.3$ Hz, 1H), 2.28 (d, $J = 2.4$ Hz, 6H), 1.29 (t, $J = 7.2$ Hz, 6H), 1.03-0.91(m, 2H), 0.85 (t, $J = 7.2$ Hz, 3H), 0.72 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 169.0, 168.7, 144.7, 144.6, 102.5, 101.6, 59.7, 43.2, 37.7, 25.4, 19.5, 19.4, 14.8, 14.5, 14.4, 12.3. The spectroscopic data are in agreement with literature.^{2b}



Diethyl 2, 6-dimethyl-4-(pentan-3-yl)-1, 4-dihydropyridine-3,5-dicarboxylate (2f): white solid (740 mg, 2.28 mmol, 46% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.75 (br s, 1H), 4.19-4.09 (m, 5H), 2.26 (s, 6H), 1.29 (t, $J = 7.1$ Hz, 6H), 1.21-1.01 (m, 5H), 0.84 (t, $J = 7.2$ Hz, 6H). The spectroscopic data are in agreement with literature.^{2c}

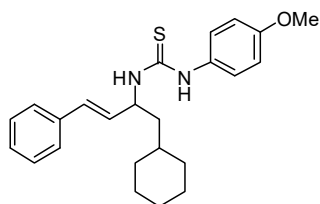


C. General procedure for organocatalytic carboisothiocyanation of 1,3-dienes:



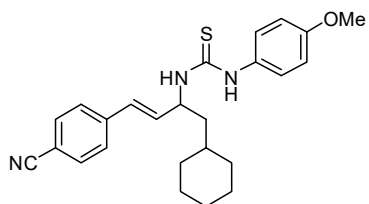
In an oven dried 5 mL reaction vial **1** (0.17 mmol, 1.7 equiv.), **2** (0.10 mmol, 1.0 equiv.), TMSNCS (0.17 mmol, 1.7 equiv.) and benzoic acid (0.01 mmol, 0.1 equiv.) were taken. The reaction vial was degassed in *vacuo* (three times) and acetone (1 mL) was added. The mixture was irradiated under SynLED Parallel Photoreactor (465-470 nm blue LED) at 25 °C for 24 h. The reaction mixture was concentrated under reduced pressure and filtered through a short silica plug with hexane as eluent and concentrated carefully under reduced pressure with 0-5 °C water bath temperature. To the resultant liquid 4-methoxy aniline (0.30 mmol, 3 equiv.) and acetone (2 mL) was added. The mixture was stirred at 40 °C for 12 h. 1N HCl (4 mL) was added to the reaction mixture and it was extracted with DCM (2 × 5 mL). The reaction mixture was concentrated under reduced pressure and purified by column chromatography over 230-400 silica gel mesh using *n*-Hexane /EtOAc as eluent to obtain **4**.

(E)-1-(1-cyclohexyl-4-phenylbut-3-en-2-yl)-3-(4-methoxyphenyl) thiourea (4a): yellowish

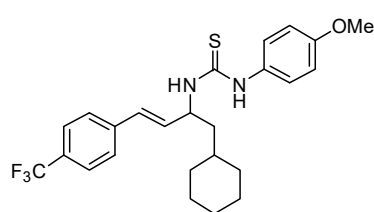


viscous (27 mg, 0.068 mmol, 68% yield). **FT-IR (thin film):** 3437 (br), 2072 (br), 1636 (s), 684 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.73 (br s, 1H), 7.35-7.27 (m, 4H), 7.23-7.22 (m, 1H), 7.18-7.14 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 16.1 Hz, 1H), 6.05 (dd, *J* = 16.0 Hz, 6.3 Hz, 1H), 5.71 (br s, 1H), 5.26 (br s, 1H), 3.82 (s, 3H), 1.83-1.63 (m, 6H), 1.52-1.45 (m, 2H), 1.23-1.12 (m, 3H), 1.01-0.92 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.7, 159.2, 136.8, 130.9, 129.5, 128.7, 128.0, 127.8, 126.6, 115.5, 55.7, 54.8, 42.9, 34.5, 33.5, 33.4, 26.6, 26.4, 26.3. **HRMS (ESI+):** Calcd. For C₂₄H₃₁N₂OS ([M + H]⁺): 395.2157, Found: 395.2156.

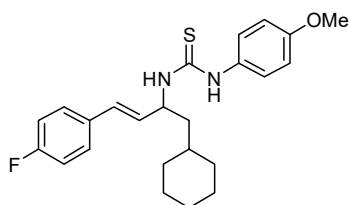
(E)-1-(4-(4-cyanophenyl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea(4b):



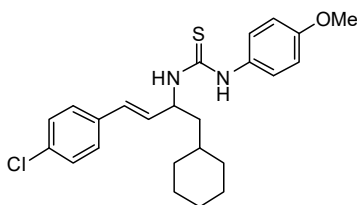
yellowish solid (28 mg, 0.067 mmol, 67% yield). m.p. 110-113 °C. **FT-IR (thin film):** 3434 (br), 2920 (m), 1622 (m), 1383 (m), 1068 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.64 (br s, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 15.6 Hz, 6.2 Hz, 1H), 5.67-5.66 (br, 1H), 5.29 (br s, 1H), 3.83 (s, 3H), 1.82-1.64 (m, 6H), 1.48 (t, *J* = 6.9 Hz, 2H), 1.22-1.11 (m, 3H), 1.01-0.91 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.9, 159.3, 141.4, 133.8, 132.5, 129.2, 128.3, 128.1, 127.1, 119.0, 115.6, 110.9, 55.7, 54.6, 42.6, 34.5, 33.6, 33.3, 26.5, 26.3, 26.2. **HRMS (ESI+):** Calcd. For C₂₅H₃₀N₃OS ([M + H]⁺): 420.2110, Found: 420.2112.

(E)-1-(1-cyclohexyl-4-(4-(trifluoromethyl) phenyl) but-3-en-2-yl)-3-(4-methoxyphenyl) thiourea (4c):

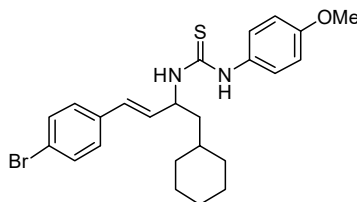
yellow solid (29 mg, 0.0626 mmol, 63% yield). m.p. 137-139 °C. **FT-IR (thin film):** 3898 (m), 3438 (br), 1637(s), 1458 (m), 1069 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.54 (d, *J* = 8.1 Hz, 3H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 16.2 Hz, 6.2 Hz, 1H), 5.67-5.66 (br s, 1H), 5.29 (br s, 1H), 3.83 (s, 3H), 1.84-1.64 (m, 6H), 1.49 (t, *J* = 7.1 Hz, 2H), 1.21-1.13 (m, 3H), 1.02-0.92 (m, 2H). **¹⁹F-NMR (376 MHz, CDCl₃):** δ -62.51. **¹³C-NMR (100 MHz, CDCl₃):** δ 180.9, 159.3, 140.3, 132.4, 129.5, 128.1, 126.7, 125.6, 115.6, 55.7, 54.6, 42.7, 34.5, 33.6, 33.4, 26.5, 26.4, 26.3. **HRMS (ESI+):** Calcd. For C₂₅H₃₀F₃N₂OS ([M + H]⁺): 463.2031, Found: 463.2030.

(E)-1-(1-cyclohexyl-4-(4-fluorophenyl)but-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4d):

yellowish solid (21 mg, 0.0509 mmol, 51% yield). m.p. 109-111 °C. **FT-IR (thin film):** 3885 (m), 3402 (br), 2923 (m), 1650(m), 1385 (br), 1154 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.59 (br s, 1H), 7.32-7.27 (m, 2H), 7.17-7.14 (m, 2H), 7.01-6.94 (m, 4H), 6.49 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.9 Hz, 6.30 Hz, 1H), 5.67 (br s, 1H), 5.25 (br s, 1H), 3.83 (s, 3H), 1.83-1.62 (m, 6H), 1.50-1.46 (m, 2H), 1.22-1.12 (m, 3H), 1.01-0.91 (m, 2H). **¹⁹F-NMR (376 MHz, CDCl₃):** δ -114.42. **¹³C-NMR (100 MHz, CDCl₃):** δ 180.8, 163.7, 161.2, 159.2, 132.9, 129.5 (d, *J* = 46.4 Hz), 128.1, 128.0, 115.7, 115.5, 55.7, 54.7, 42.9, 34.5, 33.5, 33.4, 26.5, 26.4, 26.3. **HRMS (ESI+):** Calcd. For C₂₄H₃₀FN₂OS ([M + H]⁺): 413.2063, Found: 413.2063.

(E)-1-(4-(4-chlorophenyl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4e):

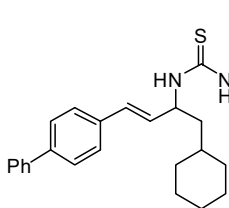
brown solid (23 mg, 0.0536 mmol, 54% yield). m.p. 148-150 °C. **FT-IR (thin film):** 3913 (m), 3400 (br), 2922 (m), 1632 (s), 1458 (m), 1069 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.67 (br s, 1H), 7.26 (s, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.47 (dd, *J* = 15.9 Hz, 1.1 Hz, 1H), 6.02 (dd, *J* = 16.0 Hz, 6.28 Hz, 1H), 5.67 (br s, 1H), 5.25 (br s, 1H), 3.82 (s, 3H), 1.83-1.62 (m, 6H), 1.49-1.46 (m, 2H), 1.25-1.12 (m, 3H), 1.00-0.93 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.8, 159.2, 135.3, 133.4, 130.3, 129.6, 128.8, 128.0, 127.8, 115.5, 55.7, 54.6, 42.8, 34.5, 33.5, 33.4, 26.5, 26.4, 26.3. **HRMS (ESI+):** Calcd. For C₂₄H₃₀ClN₂OS ([M + H]⁺): 429.1767, Found: 429.1770.

(E)-1-(4-(4-bromophenyl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4f):

brown solid (22 mg, 0.0464 mmol, 46% yield). m.p. 153-155 °C. **FT-IR (thin film):** 3913 (m), 3400 (br), 1632(s), 1402 (s), 1067 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.74 (br s, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.23-7.13 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 16.2 Hz, 1H), 6.04 (dd, *J* = 15.9 Hz, 6.2 Hz, 1H), 5.68 (br s, 1H), 5.24 (br s, 1H), 3.82 (s, 3H),

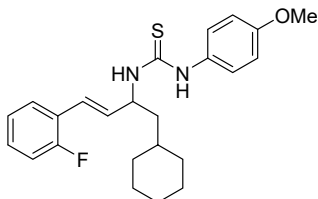
1.82-1.60 (m, 6H), 1.49-1.44 (m, 2H), 1.22-1.12 (m, 3H), 1.01-0.90 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 180.5, 159.3, 135.7, 131.8, 131.7, 130.3, 129.7, 128.8, 128.3, 128.1, 128.0, 127.9, 121.5, 115.5, 55.7, 54.7, 42.8, 34.4, 33.5, 33.4, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $\text{C}_{24}\text{H}_{30}\text{BrN}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 473.1262, Found: 473.1263.

(E)-1-(4-([1,1'-biphenyl]-4-yl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea



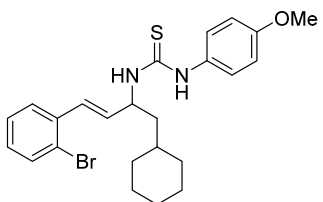
(4g): yellow solid (21 mg, 0.0446 mmol, 45% yield). m.p. 139-141 °C. **FT-IR (thin film)**: 3912 (m), 3372 (br), 2922 (s), 1628 (m), 1511 (s), 1383 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.99 (br s, 1H), 7.60-7.53 (m, 4H), 7.45-7.41 (m, 4H), 7.36-7.32 (m, 1H), 7.19-7.16 (m, 2H), 6.94 (d, $J = 8.9$ Hz, 2H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.11 (dd, $J = 15.9$ Hz, 6.2 Hz, 1H), 5.74 (br s, 1H), 5.26 (br s, 1H), 3.82 (s, 3H), 1.83-1.63 (m, 6H), 1.56-1.48 (m, 2H), 1.24-1.14 (m, 3H), 1.04-0.93 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 180.0, 159.3, 140.7, 140.6, 135.7, 130.7, 129.4, 128.9, 128.0, 127.5, 127.4, 127.0, 115.5, 55.7, 54.8, 42.9, 34.5, 33.5, 33.4, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $\text{C}_{30}\text{H}_{35}\text{N}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 471.2470, Found: 471.2470.

(E)-1-(1-cyclohexyl-4-(2-fluorophenyl)but-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4h):

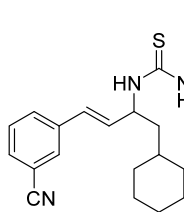


brown viscous (22 mg, 0.0533 mmol, 53% yield). **FT-IR (thin film)**: 3913 (m), 3399 (br), 2923 (s), 1631 (m), 1402 (s), 1153 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.79 (br s, 1H), 7.42-7.38 (m, 1H), 7.21-7.13 (m, 3H), 7.09-6.98 (m, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 6.62 (d, $J = 16.1$ Hz, 1H), 6.17 (dd, $J = 16.1$ Hz, 5.8 Hz, 1H), 5.71 (br s, 1H), 5.26 (br, 1H), 3.82 (s, 3H), 1.88-1.63 (m, 6H), 1.49 (t, $J = 6.7$ Hz, 2H), 1.22-1.10 (m, 3H), 1.01-0.91 (m, 2H). $^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -117.61. $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 180.5, 161.6, 159.2 (d, $J = 16.2$ Hz), 132.2 (d, $J = 4.8$ Hz), 129.0 (d, $J = 8.5$ Hz), 128.1, 127.6 (d, $J = 3.9$ Hz), 124.6, 124.5, 124.2 (d, $J = 3.4$ Hz), 123.0, 115.6 (d, $J = 22.1$ Hz), 115.5, 115.4, 55.7, 54.9, 42.8, 34.4, 33.5, 33.4, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $\text{C}_{24}\text{H}_{30}\text{FN}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 413.2063, Found: 413.2058.

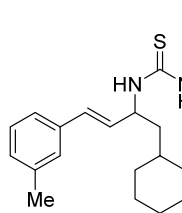
(E)-1-(4-(2-bromophenyl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl) thiourea (4i):



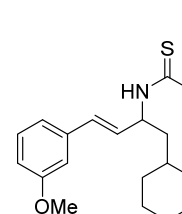
brown viscous (23 mg, 0.0485 mmol, 48% yield). **FT-IR (thin film)**: 3913 (m), 3392 (br), 2923 (s), 1632 (m), 1402 (s), 1154 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.86 (br s, 1H), 7.53-7.51 (m, 1H), 7.45 (dd, $J = 7.7$ Hz, 1.4 Hz, 1H), 7.24-7.18 (m, 3H), 7.10-7.06 (m, 1H), 6.94 (d, $J = 8.6$ Hz, 2H), 6.78 (d, $J = 15.6$ Hz, 1H), 6.05 (dd, $J = 15.9$ Hz, 5.5 Hz, 1H), 5.74 (br s, 1H), 5.29 (br s, 1H), 3.82 (s, 3H), 1.89-1.63 (m, 6H), 1.50 (t, $J = 6.3$ Hz, 2H), 1.22-1.13 (m, 3H), 1.01-0.91 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 180.5, 159.2, 136.7, 133.6, 132.9, 132.7, 129.5, 128.9, 128.2, 127.9, 127.6, 127.2, 123.8, 115.5, 55.6, 54.5, 42.7, 34.5, 33.5, 33.4, 33.1, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $\text{C}_{24}\text{H}_{30}\text{BrN}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 473.1262, Found: 473.1259.

(E)-1-(4-(3-cyanophenyl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4j):

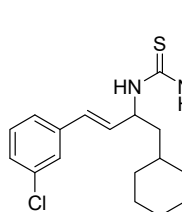
brown solid (25 mg, 0.0595 mmol, 59% yield). m.p. 141-143 °C. **FT-IR (thin film):** 3913 (m), 3399 (br), 2922 (s), 1630 (m), 1402 (s), 1383 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.71 (br s, 1H), 7.61 (s, 1H), 7.56-7.49 (s, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.19-7.15 (m, 2H), 6.99-6.95 (m, 2H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9 Hz, 6.2 Hz, 1H), 5.68 (br s, 1H), 5.27 (br s, 1H), 3.84 (s, 3H), 1.83-1.64 (m, 6H), 1.48 (t, *J* = 7.1 Hz, 2H), 1.23-1.13 (m, 3H), 1.02-0.89 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.4, 159.4, 138.1, 132.5, 131.0, 130.9, 129.9, 129.5, 128.8, 128.1, 118.8, 115.6, 112.9, 55.7, 54.6, 42.7, 34.5, 33.5, 33.4, 26.5, 26.4, 26.3. **HRMS (ESI⁺):** Calcd. For C₂₅H₃₀N₃OS ([M + H]⁺): 420.2110, Found: 420.2110.

(E)-1-(1-cyclohexyl-4-(m-tolyl) but-3-en-2-yl)-3-(4-methoxyphenyl) thiourea (4k):

yellow solid (21 mg, 0.0513 mmol, 51% yield). m.p. 67-69 °C. **FT-IR (thin film):** 3911 (m), 3371 (br), 2921 (s), 1510 (s), 1382 (s), 966 (s). **¹H-NMR (400 MHz, CDCl₃):** δ 7.90 (br s, 1H), 7.20-7.12 (m, 5H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 15.9 Hz, 6.4 Hz, 1H), 5.74 (br s, 1H), 5.25 (br s, 1H), 3.81 (s, 3H), 2.32 (s, 3H), 1.82-1.63 (m, 6H), 1.52-1.45 (m, 2H), 1.22-1.13 (m, 3H), 1.02-0.92 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.5, 159.0, 138.1, 136.7, 130.9, 129.3, 128.5, 127.9, 127.2, 123.7, 115.3, 55.6, 54.6, 42.8, 34.4, 33.5, 33.4, 26.5, 26.3, 26.2, 21.4. **HRMS (ESI⁺):** Calcd. For C₂₅H₃₃N₂OS ([M + H]⁺): 409.2313, Found: 409.2306.

(E)-1-(1-cyclohexyl-4-(3-methoxyphenyl)but-3-en-2-yl)-3-(4-methoxyphenyl)thiourea

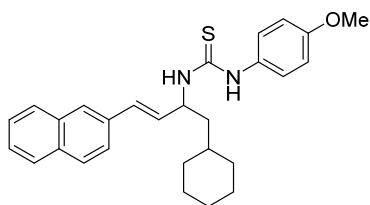
(4l): brown viscous (25 mg, 0.0588 mmol, 59% yield). **FT-IR (thin film):** 3781 (m), 3402 (br), 2922 (s), 1634 (s), 1154 (m), 1068 (br). **¹H-NMR (400 MHz, CDCl₃):** δ 7.64 (br s, 1H), 7.23-7.15 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 3H), 6.88-6.87 (m, 1H), 6.78 (dd, *J* = 8.0 Hz, 2.2 Hz, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 6.05 (dd, *J* = 16.0 Hz, 6.3 Hz, 1H), 5.70 (br s, 1H), 5.26 (br s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 1.83-1.65 (m, 6H), 1.51-1.46 (m, 2H), 1.24-1.12 (m, 3H), 1.01-0.92 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.7, 159.9, 159.2, 138.3, 130.8, 129.8, 129.6, 128.0, 119.2, 115.5, 113.4, 111.9, 55.7, 55.4, 54.7, 42.9, 34.5, 33.5, 33.4, 26.6, 26.4, 26.3. **HRMS (ESI⁺):** Calcd. For C₂₅H₃₃N₂O₂S ([M + H]⁺): 425.2263, Found: 425.2259.

(E)-1-(4-(3-chlorophenyl)-1-cyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea(4m):

white solid (23 mg, 0.0536 mmol, 54% yield). m.p. 89-91 °C. **FT-IR (thin film):** 3782 (m), 3401 (br), 1639 (s), 1153 (m). **¹H-NMR (400 MHz, CDCl₃):** δ 7.52 (br s, 1H), 7.33 (s, 1H), 7.23-7.15 (m, 5H), 6.97-6.93 (m, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 15.9 Hz, 6.2 Hz, 1H), 5.67-5.65 (br, 1H), 5.26-5.25 (br, 1H), 3.83 (s, 3H), 1.82-1.63 (m, 6H), 1.49-1.46 (m, 2H), 1.22-1.10 (m, 3H), 1.01-0.91 (m, 2H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.9, 159.3, 138.7, 134.6, 131.3, 129.9, 129.6, 128.1, 128.0, 127.7, 126.4, 124.9, 115.5, 55.7, 54.7, 42.8, 34.5, 33.5,

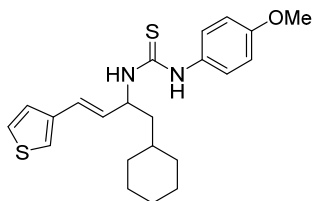
33.4, 26.6, 26.4, 26.3. **HRMS (ESI+)**: Calcd. For $C_{24}H_{30}ClN_2OS$ ($[M + H]^+$): 429.1767, Found: 429.1761.

(E)-1-(1-cyclohexyl-4-(naphthalen-2-yl)but-3-en-2-yl)-3-(4-methoxyphenyl)thiourea



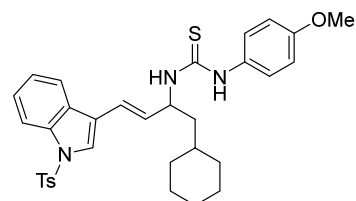
(4n): yellow solid (25 mg, 0.0562 mmol, 56% yield). **m.p.** 129-131 °C. **FT-IR (thin film)**: 3782 (m), 2921 (br), 1510 (s), 1299 (s). **1H -NMR (400 MHz, $CDCl_3$)**: δ 7.79-7.75 (m, 3H), 7.70 (s, 1H), 7.62 (s, 1H), 7.54 (dd, $J = 8.52$ Hz, 1.6 Hz, 1H), 7.47-7.40 (m, 2H), 7.19-7.16 (m, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 16.1$ Hz, 1H), 6.19 (dd, $J = 16.1$ Hz, 6.2 Hz, 1H), 5.74 (br s, 1H), 5.29 (br s, 1H), 3.81 (s, 3H), 1.86-1.61 (m, 6H), 1.57-1.51 (m, 2H), 1.24-1.13 (m, 3H), 1.04-0.94 (m, 2H). **^{13}C -NMR (100 MHz, $CDCl_3$)**: δ 180.7, 159.1, 134.2, 133.6, 133.1, 130.9, 129.9, 128.2, 128.0, 127.9, 127.7, 126.5, 126.4, 126.0, 123.7, 115.4, 55.6, 54.7, 42.9, 34.5, 33.5, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $C_{28}H_{33}N_2OS$ ($[M + H]^+$): 445.2314, Found: 445.2319.

(E)-1-(1-cyclohexyl-4-(thiophen-3-yl)but-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (**4o**):



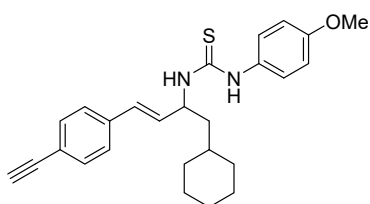
yellow solid (19 mg, 0.0474 mmol, 47% yield). **m.p.** 112-114 °C. **FT-IR (thin film)**: 3697 (m), 3399 (br), 2923 (s), 1630 (s), 1244 (m). **1H -NMR (400 MHz, $CDCl_3$)**: δ 7.71 (br s, 1H), 7.25-7.23 (m, 1H), 7.16-7.12 (m, 4H), 6.95-6.92 (m, 2H), 6.54 (d, $J = 15.9$ Hz, 1H), 5.90 (dd, $J = 15.9$ Hz, 6.3 Hz, 1H), 5.68 (br s, 1H), 5.22 (br s, 1H), 3.82 (s, 3H), 1.82-1.63 (m, 6H), 1.49-1.43 (m, 2H), 1.20-1.12 (m, 3H), 1.00-0.89 (m, 2H). **^{13}C -NMR (100 MHz, $CDCl_3$)**: δ 180.6, 159.1, 139.4, 129.3, 127.9, 126.1, 125.2, 125.1, 122.4, 115.4, 55.6, 54.6, 42.8, 34.4, 33.5, 33.4, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $C_{22}H_{29}N_2OS_2$ ($[M + H]^+$): 401.1721, Found: 401.1716.

(E)-1-(1-cyclohexyl-4-(1-tosyl-1H-indol-3-yl)but-3-en-2-yl)-3-(4-methoxyphenyl)



thiourea (4p): brown solid (21 mg, 0.0357 mmol, 36% yield). **m.p.** 149-151 °C. **FT-IR (thin film)**: 3785 (m), 3432 (br), 1634 (s), 1402 (s). **1H -NMR (400 MHz, $DMSO-d_6$)**: δ 9.28 (br s, 1H), 7.98-7.94 (m, 2H), 7.86-7.81 (m, 3H), 7.56-7.55 (br, 1H), 7.40-7.28 (m, 6H), 6.89 (d, $J = 8.9$ Hz, 2H), 6.63 (d, $J = 16.2$ Hz, 1H), 6.38 (dd, $J = 16.3$ Hz, 6.4 Hz, 1H), 5.25 (br s, 1H), 3.73 (s, 3H), 2.27 (s, 3H), 1.87-1.48 (m, 8H), 1.15-1.05 (m, 3H), 1.02-0.89 (m, 2H). **^{13}C -NMR (100 MHz, $DMSO-d_6$)**: δ 180.1, 156.4, 145.5, 134.8, 133.9, 132.6, 130.2, 128.4, 126.6, 125.6, 125.0, 124.5, 123.7, 120.6, 119.8, 119.7, 113.8, 113.4, 79.1, 55.2, 53.5, 42.1, 33.7, 32.9, 32.6, 26.1, 25.8, 25.7, 20.9. **HRMS (ESI+)**: Calcd. For $C_{33}H_{37}N_3O_3S_2$ ($[M + H]^+$): 588.2354, Found: 588.2353.

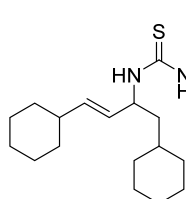
(E)-1-(1-cyclohexyl-4-(4-ethynylphenyl)but-3-en-2-yl)-3-(4-methoxyphenyl)thiourea



(4q): yellow solid (21 mg, 0.0501 mmol, 50% yield). **m.p.** 90-92 °C. **FT-IR (thin film)**: 3783 (m), 3400 (br), 1631 (m), 1402 (s). **1H -NMR (400 MHz, $CDCl_3$)**: δ 8.22-8.20 (br, 1H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.21-7.14

(m, 2H), 6.94 (d, $J = 8.8$ Hz, 1H), 6.49 (d, $J = 16.2$ Hz, 1H), 6.05 (dd, $J = 15.9$ Hz, 6.2 Hz, 1H), 5.70 (br s, 1H), 5.20 (br s, 1H), 3.82 (s, 3H), 3.10 (s, 1H), 1.81-1.60 (m, 6H), 1.50-1.45 (m, 2H), 1.23-1.13 (m, 3H), 1.00-0.91 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 180.0, 159.3, 137.2, 132.4, 130.7, 130.2, 128.0, 126.5, 121.3, 115.5, 83.7, 77.9, 55.6, 54.7, 42.8, 34.4, 33.5, 33.4, 26.5, 26.3, 26.2. **HRMS (ESI+)**: Calcd. For $\text{C}_{26}\text{H}_{31}\text{N}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 419.2157, Found: 419.2156.

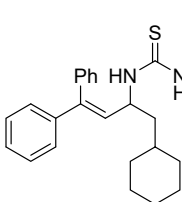
(E)-1-(1,4-dicyclohexylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4r): yellow solid (21 mg, 0.052 mmol, 52% yield). m.p. 93-95 °C. **FT-IR (thin film)**:



3781 (m), 3394 (br), 2922 (s), 1511 (s), 1298 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.63 (br s, 1H), 7.16-7.12 (m, 2H), 6.93-6.90 (m, 2H), 5.74 (br s, 1H), 5.52 (br s, 1H), 5.21 (dd, $J = 15.1$ Hz, 6.1 Hz, 1H), 4.96-4.83 (br, 1H), 3.81 (s, 3H), 1.90-1.60 (m, 13H), 1.21-0.82 (m, 11H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 180.4,

158.8, 138.0, 131.9, 128.4, 127.7 (d, $J = 15.1$ Hz), 127.0, 115.2, 61.5, 55.5, 54.6, 42.9, 42.3, 40.3 (d, $J = 9.4$ Hz), 37.8, 34.3, 33.1, 33.0 (d, $J = 5.0$ Hz), 32.8, 29.1 (d, $J = 11.1$ Hz), 26.5 (t, $J = 7.5$ Hz), 26.3, 26.2, 26.1, 26.0, 25.9. **HRMS (ESI+)**: Calcd. For $\text{C}_{24}\text{H}_{37}\text{N}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 401.2627, Found: 401.2627.

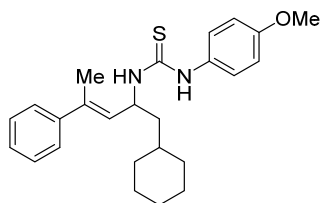
1-(1-cyclohexyl-4,4-diphenylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4s): yellow



solid (18 mg, 0.038 mmol, 38% yield). m.p. 160-162 °C. **FT-IR (thin film)**: 3633 (m), 3400 (br), 2853 (s), 1631 (br), 1402 (br). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 9.18 (br s, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.41-7.22 (m, 10H), 7.18-7.16 (m, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 6.04 (d, $J = 9.1$ Hz, 1H), 5.15-5.11 (br, 1H), 3.73 (s, 3H), 1.61-1.50 (m, 5H), 1.35-1.19 (m, 4H), 1.03 (br, 2H), 0.76-

0.65 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 179.6, 156.3, 141.8, 140.9, 138.9, 131.9, 130.7, 129.4, 128.2, 128.1, 127.2, 127.1, 126.8, 125.4, 113.8, 55.1, 51.4, 42.9, 33.6, 32.7, 32.5, 26.0, 25.6. **HRMS (ESI+)**: Calcd. For $\text{C}_{30}\text{H}_{35}\text{N}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 471.2470, Found: 471.2467.

(E)-1-(1-cyclohexyl-4-phenylpent-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4t): yellow

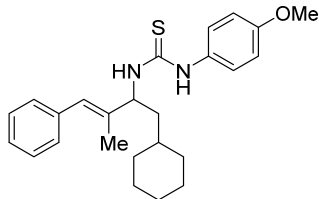


solid (16 mg, 0.0391 mmol, 39% yield). m.p. 85-87 °C. **FT-IR (thin film)**: 3784 (m), 3433 (br), 1634 (br), 1402 (s). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 9.18 (br s, 1H), 7.50 (d, $J = 8.1$ Hz, 1H), 7.40 (d, $J = 7.7$ Hz, 2H), 7.35-7.22 (m, 5H), 6.89 (d, $J = 8.7$ Hz, 2H), 5.71 (d, $J = 8.9$ Hz, 1H), 5.43-5.37 (br, 1H), 3.73 (s, 3H), 2.11 (s, 3H), 1.87-1.57 (m, 6H), 1.39-1.32 (m, 2H), 1.21-

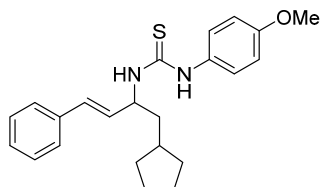
1.15 (m, 3H), 1.0-0.91 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6): δ 179.6, 156.3, 142.4, 135.0, 131.9, 129.4, 128.2, 127.0, 125.5, 125.4, 113.8, 55.2, 50.4, 42.9, 33.8, 33.0, 32.9, 26.1, 25.8, 25.7, 16.2. **HRMS (ESI+)**: Calcd. For $\text{C}_{25}\text{H}_{33}\text{N}_2\text{OS}$ ($[\text{M} + \text{H}]^+$): 409.2314, Found: 409.2317.

(E)-1-(1-cyclohexyl-3-methyl-4-phenylbut-3-en-2-yl)-3-(4-methoxyphenyl)thiourea (4u): yellow viscous (13 mg, 0.0318 mmol, 32% yield). **FT-IR (thin film)**: 3889 (m), 3633 (m),

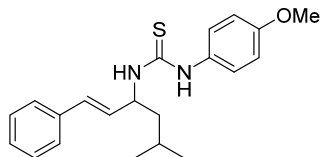
3399 (br), 1629 (s), 1402 (s), 1154 (m). ¹H-NMR (400 MHz, CDCl₃): δ 7.84 (br s, 1H), 7.34-7.29 (m, 2H), 7.24-7.15 (m, 5H), 6.94-6.90 (m, 2H), 6.45 (br s, 1H), 6.16-5.82 (br, 1H), 5.40 (br, 0.4H), 5.06 (br, 0.5H), 3.82 (d, *J* = 3.8 Hz, 3H), 1.96-1.66 (m, 8H), 1.53-1.38 (m, 3H), 1.23-1.13 (m, 3H), 0.99-0.92 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 180.7, 159.0, 137.2, 133.6, 129.0, 128.7, 128.2, 127.8, 127.2, 126.6, 115.3, 60.1, 55.6, 41.5, 38.4, 35.7, 34.6, 33.4 (d, *J* = 17.0 Hz), 26.6, 26.5 (d, *J* = 8.2 Hz), 26.3 (d, *J* = 6.8 Hz), 14.5. HRMS (ESI⁺): Calcd. For C₂₅H₃₃N₂OS ([M + H]⁺): 409.2314, Found: 409.2303.



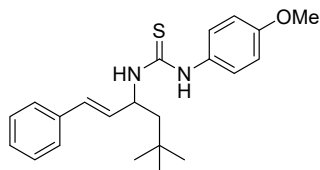
(E)-1-(1-cyclohexyl-4-phenylbut-3-en-2-yl)-3-(4-methoxyphenyl) thiourea (4v): white solid (24 mg, 0.0630 mmol, 63% yield). m.p. 127-129 °C. FT-IR (thin film): 3439 (br), 2067 (br), 1636 (s), 694 (m). ¹H-NMR (400 MHz, CDCl₃): δ 7.81 (br s, 1H), 7.35-7.27 (m, 4H), 7.24-7.16 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J* = 15.9 Hz, 6.4 Hz, 1H), 5.76 (br s, 1H), 5.20 (br s, 1H), 3.82 (s, 3H), 1.85-1.78 (m, 3H), 1.69-1.48 (m, 6H), 1.20-1.10 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 180.2, 159.0, 136.6, 130.9, 129.1, 128.6, 127.9, 127.7, 126.5, 115.3, 56.5, 55.5, 41.4, 36.8, 33.2, 32.7, 25.1, 25.0. HRMS (ESI⁺): Calcd. For C₂₃H₂₉N₂OS ([M + H]⁺): 381.2001, Found: 381.1994.



(E)-1-(4-methoxyphenyl)-3-(5-methyl-1-phenylhex-1-en-3-yl) thiourea (4w): yellow solid (23 mg, 0.0648 mmol, 65% yield). m.p. 115-117 °C. FT-IR (thin film): 3437 (br), 2069 (br), 1636 (s), 679 (br). ¹H-NMR (400 MHz, CDCl₃): δ 7.58 (br s, 1H), 7.35-7.27 (m, 4H), 7.24-7.20 (m, 1H), 7.18-7.14 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.53 (d, *J* = 16.2 Hz, 1H), 6.05 (dd, *J* = 15.9 Hz, 6.3 Hz, 1H), 5.69 (br s, 1H), 5.26 (br s, 1H), 3.82 (s, 3H), 1.70-1.61 (m, 1H), 1.56-1.43 (m, 2H), 0.97 (dd, *J* = 6.6 Hz, 2.4 Hz, 6H). ¹³C-NMR (100 MHz, CDCl₃): δ 180.7, 159.2, 136.7, 130.9, 129.3, 128.7, 128.0, 127.8, 126.6, 115.5, 55.7, 55.4, 44.3, 25.1, 22.9, 22.7. HRMS (ESI⁺): Calcd. For C₂₁H₂₇N₂OS ([M + H]⁺): 355.1844, Found: 355.1838.

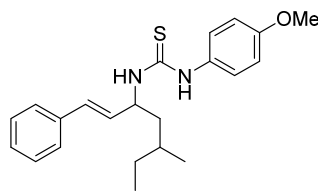


(E)-1-(4-methoxyphenyl)-3-(5-methyl-1-phenylhex-1-en-3-yl) thiourea (4x): white solid (23 mg, 0.0624 mmol, 62% yield). m.p. 147-149 °C. FT-IR (thin film): 3432 (br), 2923 (m), 1633 (s), 1381 (m). ¹H-NMR (400 MHz, CDCl₃): δ 7.82 (br s, 1H), 7.34-7.27 (m, 4H), 7.23-7.14 (m, 3H), 6.94-6.92 (m, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0 Hz, 6.1 Hz, 1H), 5.66 (br s, 1H), 5.37 (br s, 1H), 3.82 (s, 3H), 1.58 (dd, *J* = 14.4 Hz, 4.3 Hz, 1H), 1.43 (dd, *J* = 14.5 Hz, 8.4 Hz, 1H), 0.98 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃): δ 180.2, 159.2, 136.8, 130.8, 129.9, 128.6, 128.3, 127.7, 126.5, 115.4, 55.6, 54.5, 49.2, 30.8, 30.2. HRMS (ESI⁺): Calcd. For C₂₂H₂₉N₂OS ([M + H]⁺): 369.2001, Found: 369.2012.

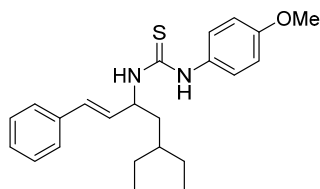


(E)-1-(4-methoxyphenyl)-3-(5-methyl-1-phenylhept-1-en-3-yl)thiourea (4y): Brown viscous (23 mg, 0.0624 mmol, 62% yield, dr = 1.5:1). FT-IR (thin film): 3434 (br), 2921

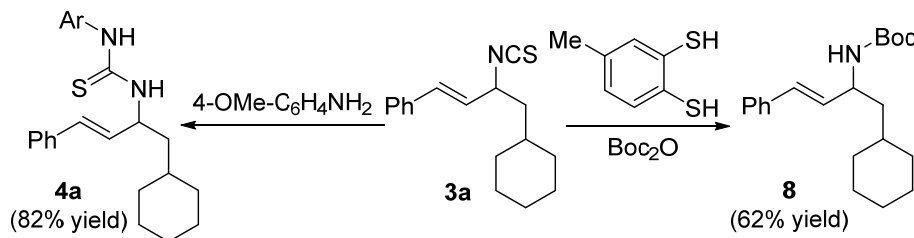
(m), 1633 (s), 1069 (br). **¹H-NMR (400 MHz, CDCl₃):** δ 7.95 (br s, 1H), 7.35-7.27 (m, 4H), 7.25-7.15 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.53 (t, *J* = 15.1 Hz, 1H), 6.06 (dd, *J* = 15.9 Hz, 6.1 Hz, 0.6H), 6.04 (dd, *J* = 15.9 Hz, 6.1 Hz, 0.4H), 5.73-5.68 (br, 1H), 5.24 (br s, 1H), 3.82 (s, 3H), 1.63-1.55 (m, 2H), 1.49-1.38 (m, 2H), 0.96 (dd, *J* = 14.0 Hz, 6.1 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 4H). **¹³C-NMR (125 MHz, CDCl₃):** δ 180.2, 179.8, 159.2, 136.7, 131.5, 130.8, 129.5, 128.9, 128.7, 128.3, 128.1, 127.9, 127.8, 127.7, 126.6, 126.5, 115.5, 55.6, 55.5, 55.1, 42.2, 42.1, 32.0, 31.4, 31.3, 29.8, 29.7, 29.6, 19.7, 19.2, 11.4, 11.3. **HRMS (ESI⁺):** Calcd. For C₂₂H₂₉N₂OS ([M + H]⁺): 369.2001, Found: 369.2006.



(E)-1-(5-ethyl-1-phenylhept-1-en-3-yl)-3-(4-methoxyphenyl)thiourea (4z): brown solid (21 mg, 0.0548 mmol, 55% yield). m.p. 76-78 °C. **FT-IR (thin film):** 3436 (br), 2922 (m), 1636 (s), 771 (br). **¹H-NMR (400 MHz, CDCl₃):** δ 7.81 (br s, 1H), 7.34-7.27 (m, 4H), 7.24-7.15 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 16.1 Hz, 1H), 6.05 (dd, *J* = 15.9 Hz, 6.2 Hz, 1H), 5.70 (br s, 1H), 5.24 (br s, 1H), 3.82 (s, 3H), 1.57-1.49 (m, 2H), 1.41-1.30 (m, 5H), 0.87-0.83 (m, 6H). **¹³C-NMR (100 MHz, CDCl₃):** δ 180.7, 159.1, 136.7, 130.9, 129.5, 129.1, 128.6, 128.3, 128.0, 127.7, 126.5, 125.4, 115.4, 55.6, 55.1, 38.8, 37.0, 25.7, 25.4, 10.8, 10.7. **HRMS (ESI⁺):** Calcd. For C₂₃H₃₁N₂OS ([M + H]⁺): 383.2157, Found: 383.2162.



D. Synthetic Application:



General procedure for the synthesis of thiourea (4a)

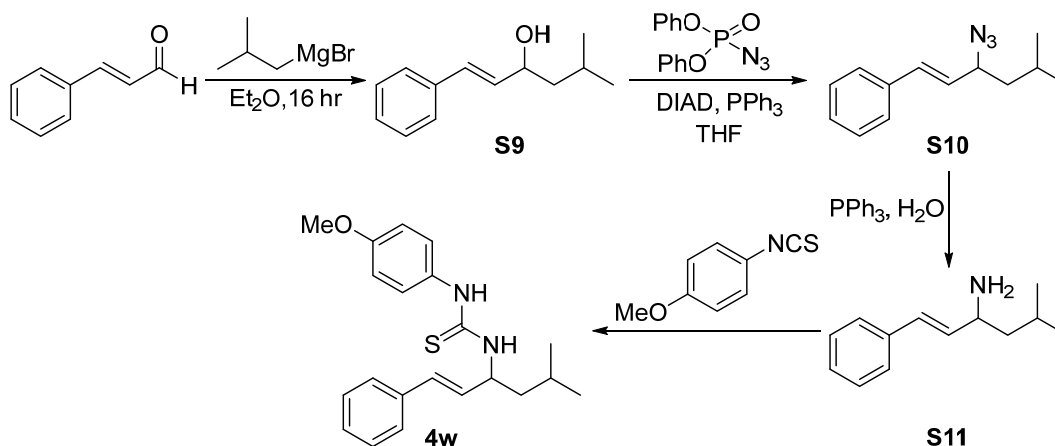
In an oven flask solution of **3a** (60 mg, 0.22 mmol, 1 equiv.) and 4-methoxyphenylamine (43 mg, 0.34 mmol, 1.5 equiv.) in CH₂Cl₂ (3.0 mL) was taken. The mixture was stirred at 40 °C for 12 h. 1N HCl (4 mL) was added to the reaction mixture and it was extracted with DCM (2 × 5 mL). The reaction mixture was concentrated under reduced pressure and purified by column chromatography over 230-400 silica gel mesh using *n*-Hexane /EtOAc (19:1) as eluent to obtain **4a** (71 mg, 0.18 mmol, 82% yield).

General procedure for the synthesis of BOC protected amine (8): The reaction was carried out by following the reported literature procedure.³ To a solution of **3a** (40 mg, 0.14 mmol, 1 equiv.) in MeOH (0.6 mL), 3,4-dimercaptotoluene (0.056 mL, 0.42 mmol, 1.2

3. W. Guo, Q. Wang and J. Zhu, *Angew. Chem. Int. Ed.* 2021, **60**, 4085-4089.

equiv.) was added in one portion. The mixture was stirred at room temperature for 3 h. After completion of the reaction the solvent was removed under vacuum and Boc_2O (61.0 mg, 0.28 mmol, 2 equiv.) and THF (1 mL) were added. The mixture was stirred at 25 °C for 24 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography over neutral alumina with *n*-Hexane /EtOAc (99:1) as an eluent to afford **8** as white solid (29 mg, 62% yield). m.p. 101-103 °C. **FT-IR (thin film)**: 3433 (br), 1635 (s), 1401 (m), 1166 (m). **¹H NMR (400MHz, CDCl₃)**: δ 7.35 (d, J = 3.6 Hz, 2H), 7.30 (t, J = 3.7 Hz, 2H), 7.21 (t, J = 3.6 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.06 (dd, J = 15.9 Hz, 6.0 Hz, 1H), 4.45-4.41 (br, 1H), 4.35-4.29 (br, 1H), 1.82-1.61 (m, 5H), 1.45 (s, 9H), 1.43-1.41 (m, 2H), 1.23-1.11(m, 3H), 1.00-0.89 (m, 3H). **¹³C-NMR (125 MHZ, CDCl₃)**: δ 155.4, 137.2, 131.4, 129.7, 128.6, 127.5, 126.5, 50.2, 43.7, 34.3, 33.6, 33.3, 28.6, 26.4, 26.3. **HRMS (ESI+)**: Calcd. For $\text{C}_{21}\text{H}_{32}\text{NO}_2$ ($[\text{M} + \text{H}]^+$): 330.2433, Found: 330.2434.

E. Synthesis of 4w through alternate route: The intermediate S-10 utilized in this synthesis was prepared by following the reported literature procedure.⁴



(E)-5-methyl-1-phenylhex-1-en-3-ol (S9): The solution of cinnamaldehyde (3.0 mmol) in diethyl ether (10 mL) was cooled to 0 °C and isobutylmagnesium bromide (1.0 M in Et₂O) (2.0 equiv.) was added dropwise. The mixture was gradually warm to 25 °C and stirred for 16 h. The reaction was cooled to 0 °C and saturated aq. ammonium chloride solution (10 mL) was added to the mixture. The organic phase was separated, and the aqueous layer was extracted with diethyl ether (2 × 15 mL). The combined organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography over 230-400 mesh with ethyl acetate/hexane (1:10) as eluent to obtain **S9** as colorless oil (400 mg, 2.1 mmol, 70 % yield). **¹H-NMR (400 MHz, CDCl₃)**: δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.57 (d, J = 16.0 Hz, 1H), 6.21 (dd, J = 15.8 Hz, 6.8 Hz, 1H), 4.35 (q, J = 6.7 Hz, 1H), 1.81-1.73 (m, 1H), 1.60-1.54 (m, 2H), 1.46-1.39 (m, 1H), 0.96 (d, J = 1.7 Hz, 3H), 0.94 (d, J = 1.7 Hz, 3H). **¹³C-**

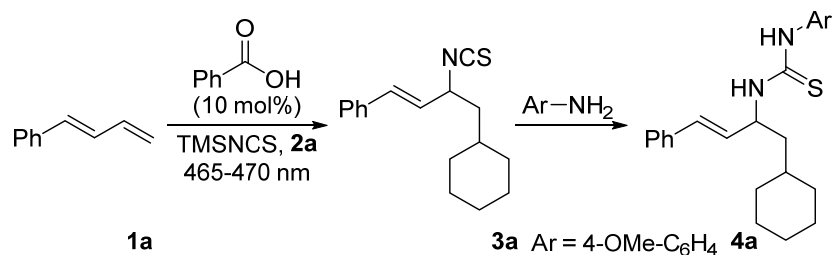
4. J. Hou, C. Feng, Z. Li, Q. Fang, H. Wang, G. Gu, Y. Shi, P. Liu, F. Xu, Z. Yin, J. Shen and P. Wang, *Eur. J. Med. Chem.* 2011, **46**, 3190-3200.

NMR (100 MHz, CDCl₃): δ 136.9, 133.0, 130.1, 128.7, 127.7, 126.5, 71.4, 46.6, 24.7, 23.1, 22.6. The spectroscopic data are in agreement with literature.⁴

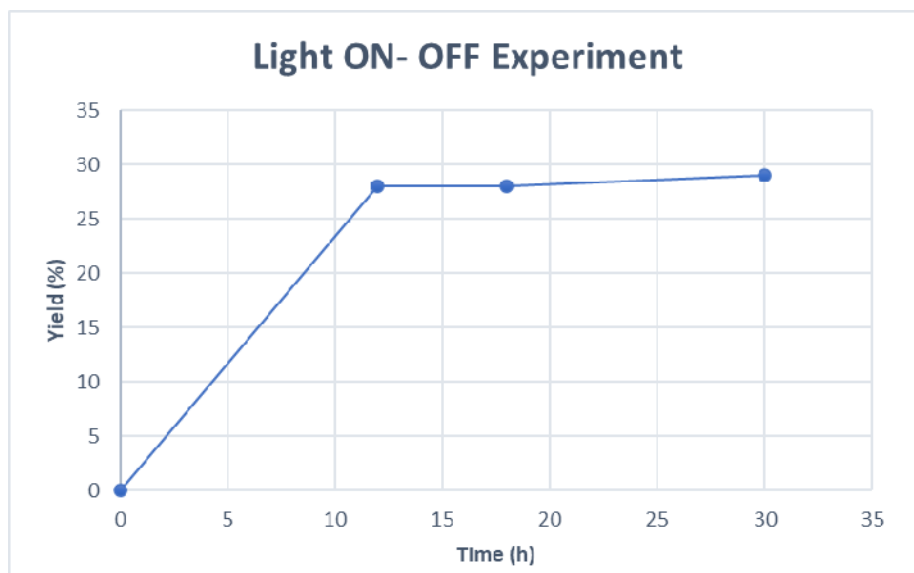
(E)-(3-azido-5-methylhex-1-en-1-yl)benzene (S10): In a 100 mL 2-necked round-bottom flask, alcohol (**9**) (1.0 equiv.) and triphenylphosphine (1.2 equiv.) were taken. To this mixture dry THF (0.2M) was added and the solution was cooled to 0 °C. Diisopropyl azodicarboxylate (DIAD) (1.2 equiv.) was added at once and stirred for 15 min at 0 °C. To the mixture diphenyl phosphoryl azide (1.2 equiv.) was added dropwise over 10 min at 0 °C. The resulting solution was allowed to warm to 25 °C and stirred for 16 h and subsequently the reaction was quenched with 1N HCl (4ml/mmol). Aqueous layer was extracted with Et₂O. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by silica gel column chromatography over 230-400 mesh with hexane as eluent furnished **S10** as colorless oil (387 mg, 1.8 mmol, 86 % yield). **¹H-NMR (400 MHz, CDCl₃):** δ 7.42-7.39 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.27 (m, 1H), 6.61 (d, J = 15.7 Hz, 1H), 6.09 (dd, J = 15.8 Hz, 8.2 Hz, 1H), 4.05 (q, J = 7.3 Hz, 1H), 1.80-1.70 (m, 1H), 1.60-1.53 (m, 1H), 1.46-1.39 (m, 1H), 0.94 (dd, J = 6.6 Hz, 5.0 Hz, 6H). **¹³C-NMR (100 MHz, CDCl₃):** δ 136.2, 133.2, 130.1, 128.8, 128.2, 127.6, 126.8, 63.3, 43.8, 25.0, 22.7, 22.5. The spectroscopic data are in agreement with literature.⁴

(E)-5-methyl-1-phenylhex-1-en-3-amine (S11): In a 50 mL round-bottom flask, **S10** (387 mg, 1.8 mmol, 1.0 equiv.) and triphenylphosphine (705 mg, 2.69 mmol, 1.5 equiv.) were taken. To this mixture THF (10 ml) and H₂O (2 ml) was added. The resulting solution was stirred for 16 h at 25 °C. The reaction mixture was quenched with saturated aq. NH₄Cl solution (10 ml). The aqueous phase was extracted with Et₂O (20 mL \times 3). The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product (284 mg) was used directly for next step without any characterization.

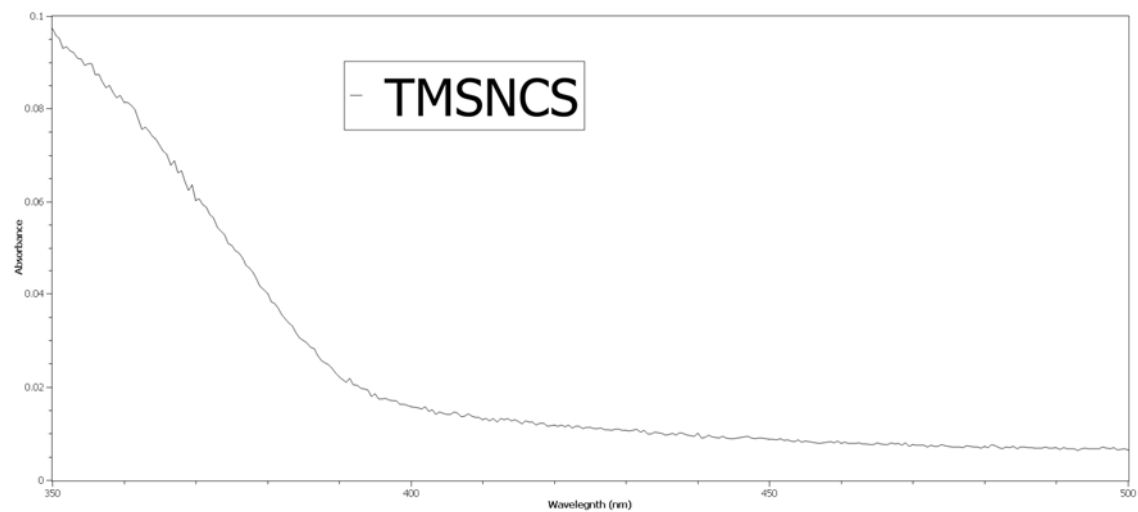
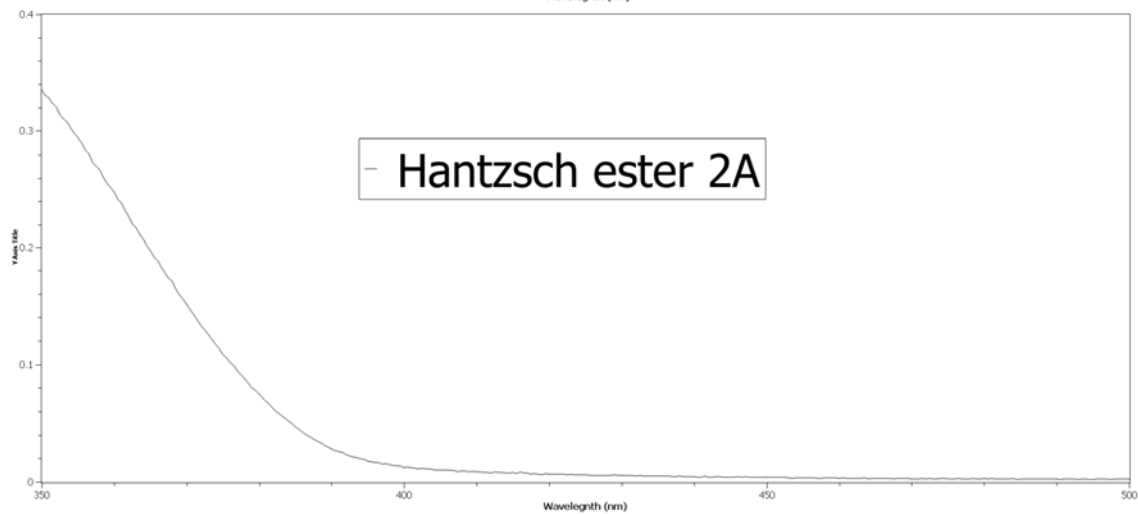
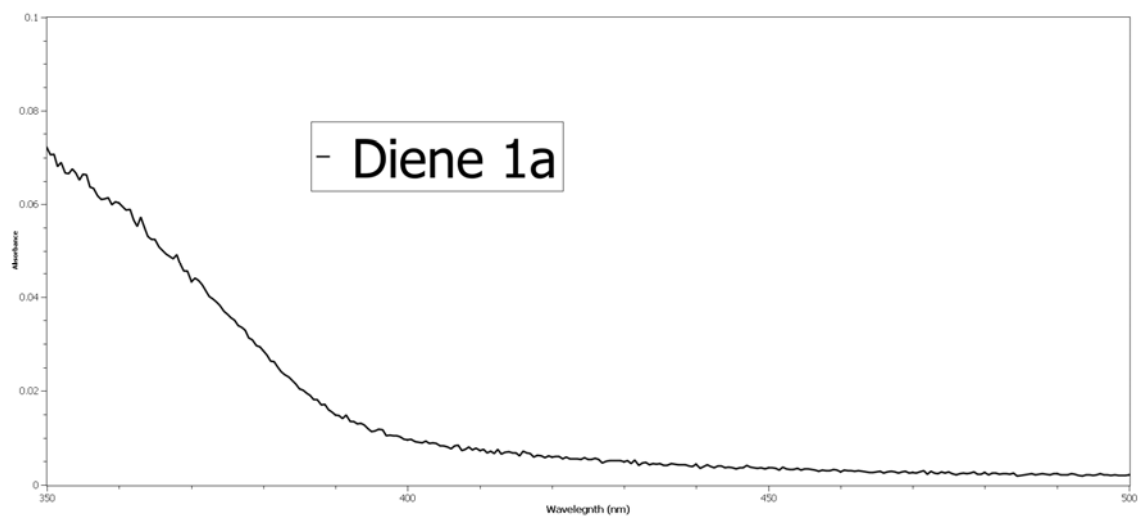
(E)-1-(4-methoxyphenyl)-3-(5-methyl-1-phenylhex-1-en-3-yl) thiourea (4w): In a 50 mL round-bottom flask, crude amine (284 mg) and 4-Methoxyphenyl isothiocyanate (371.7 mg, 2.25 mmol, 1.5 equiv.) were taken. To this mixture DCM (15 ml) was added. The resulting solution was stirred at 25 °C for 16 hr. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography over silica gel (230-400 mesh) using hexane/ethyl acetate (92:8) as eluent furnished **4w**.

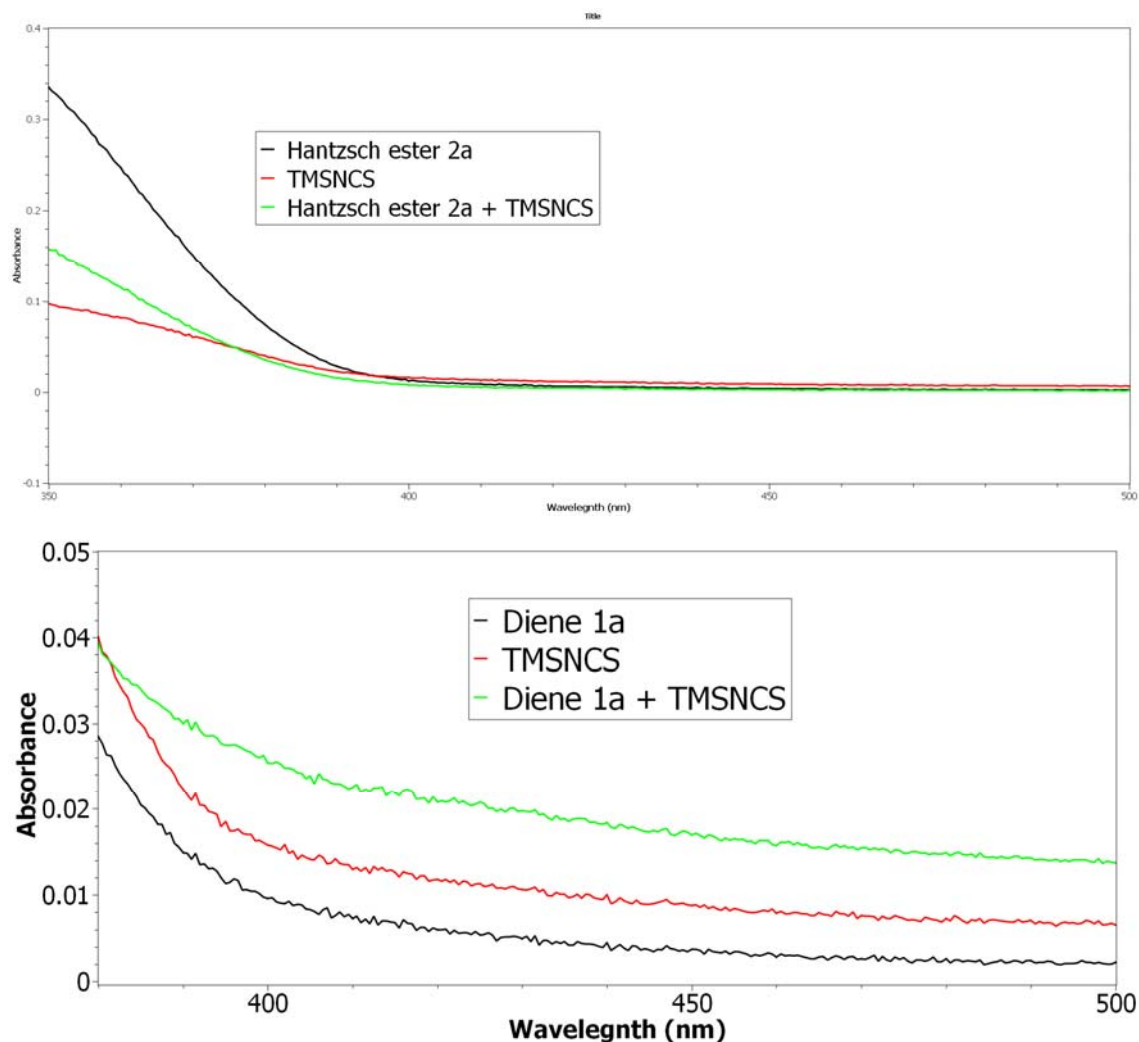
F. Light ON-OFF Experiment:

The reaction was irradiated for a fixed time interval. During the first and the third phase, the reaction was irradiated under SynLED Parallel Photoreactor (Blue LED 465-470 nm) light and in the second phase the reaction was stirred under dark. The reaction occurred only in the presence of light in first phase for 12 h in the second phase the reaction was stirred in dark for 6 h and no further conversion was observed. Notably in the third phase the irradiation was again started for 12 h however the reaction did not proceed further. Thus could be attributed to the background hydroamination reaction between **1a** and TMSNCS. These experiments clearly establish that continuous light irradiation is essential for the reaction.



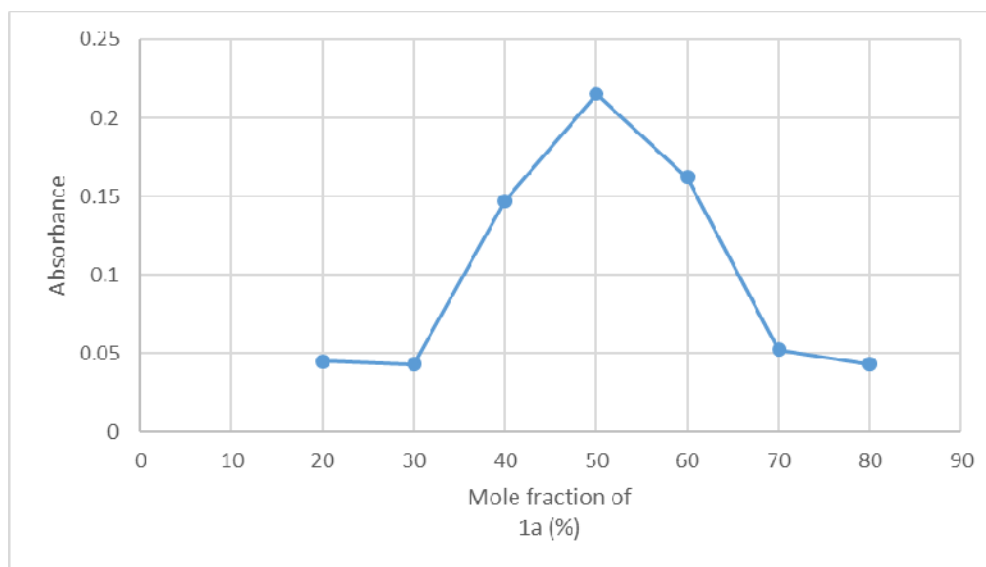
G. UV-Visible studies: UV-Visible absorption spectra were recorded in acetone with JascoV-750 spectrophotometer. With the help of these studies, the formation of EDA complex between **1a** and TMSNCS was established.



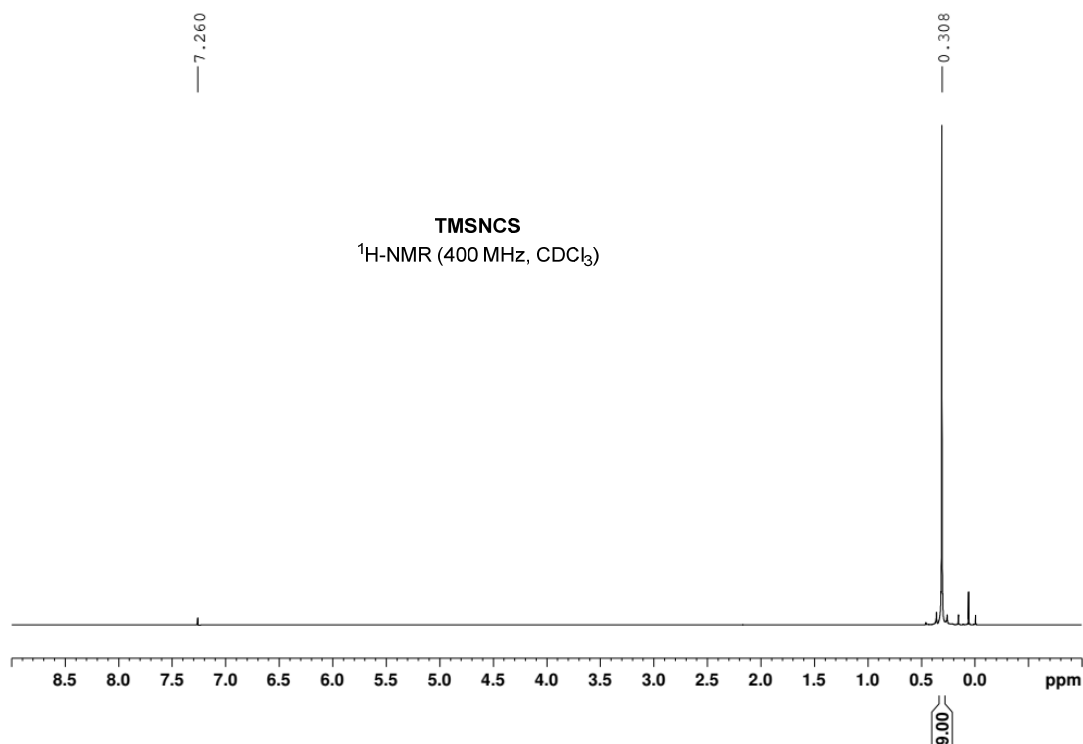


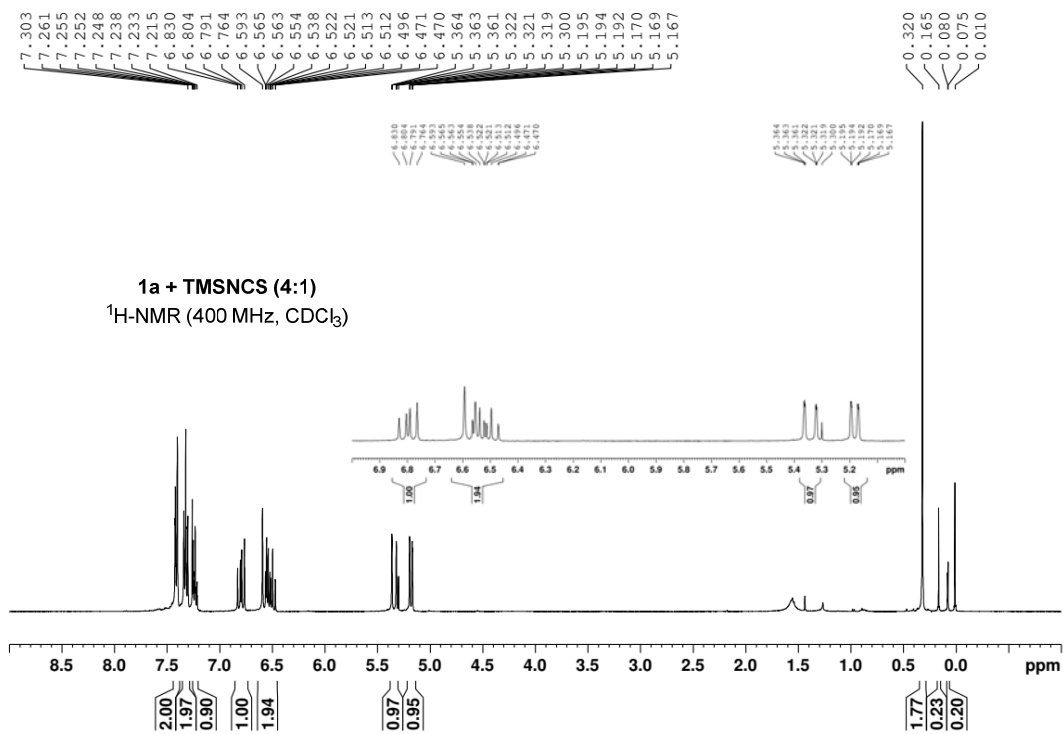
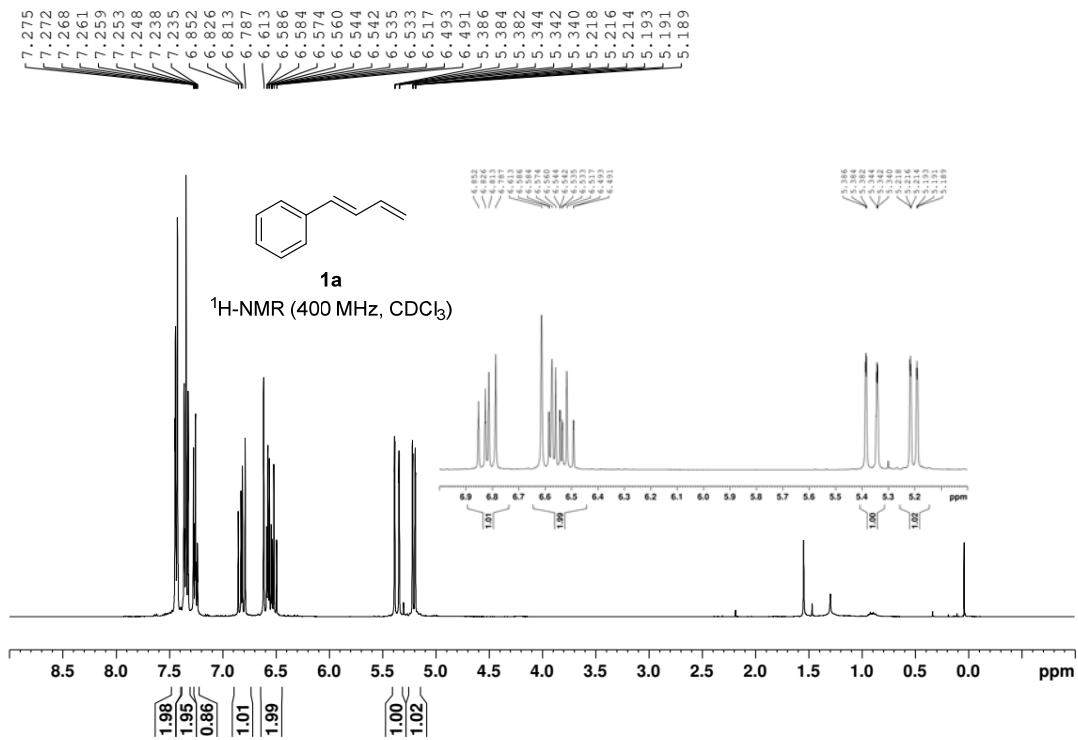
H. Job's plot: The Job's plot was constructed to evaluate the stoichiometry of the EDA complex between **1a** (Diene) and TMSNCS in acetone (0.1 M). We recorded the absorption at 455 nm with a constant overall concentration but with different donor/acceptor ratio.⁵ All the absorption spectra recorded by using JASCOV-750 UV-visible spectrophotometer with 10 mm quartz cuvette. The value of absorbance was plotted against the mole fraction of **1a**. The maximum absorbance was obtained at approximately 1:1 ratio of **1a**:TMSNCS and thus demonstrating the stoichiometry of EDA complex.⁵

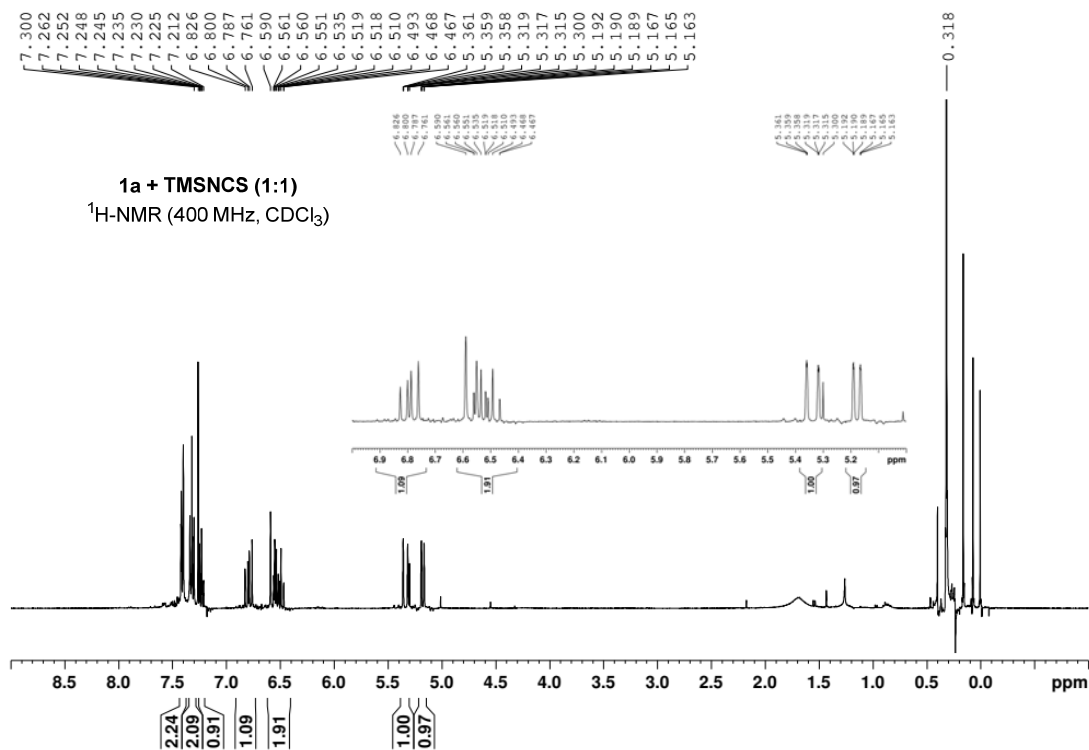
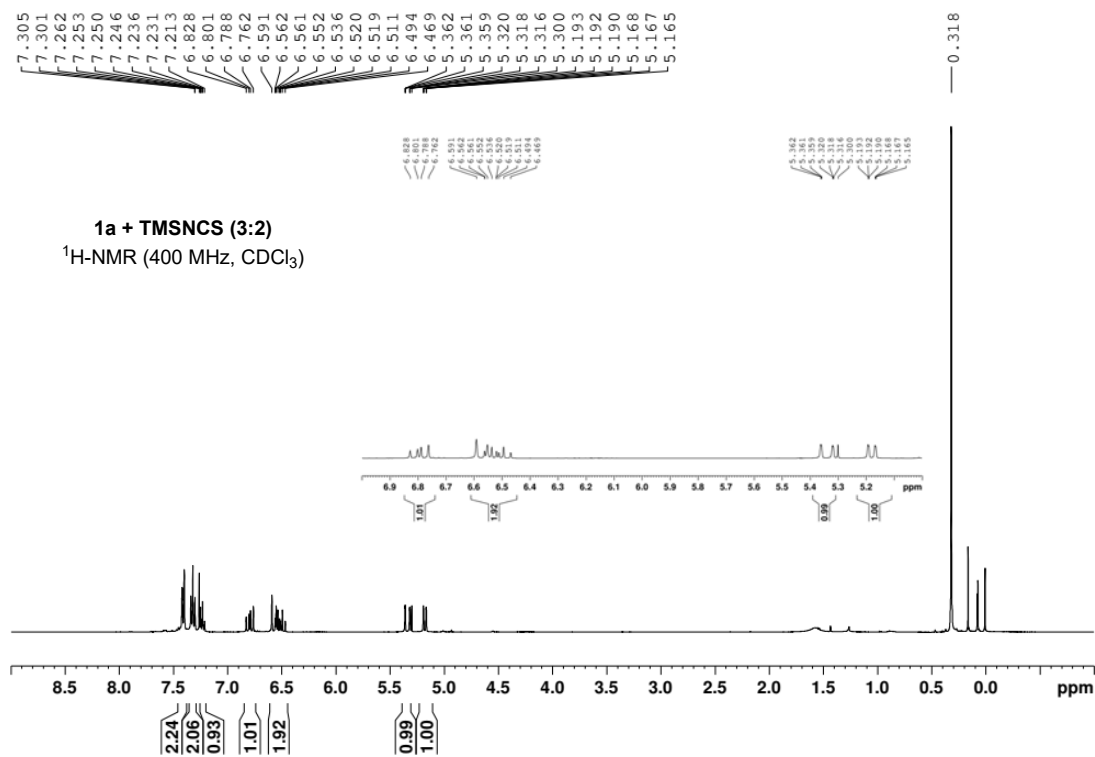
5. S. R. Kandukuri, A. Bahamonde, I. Chatterjee, I. D. Jurberg, E. C. Escudero-Adán and P. Melchiorre, *Angew. Chem. Int. Ed.* 2015, **54**, 1485-1489.

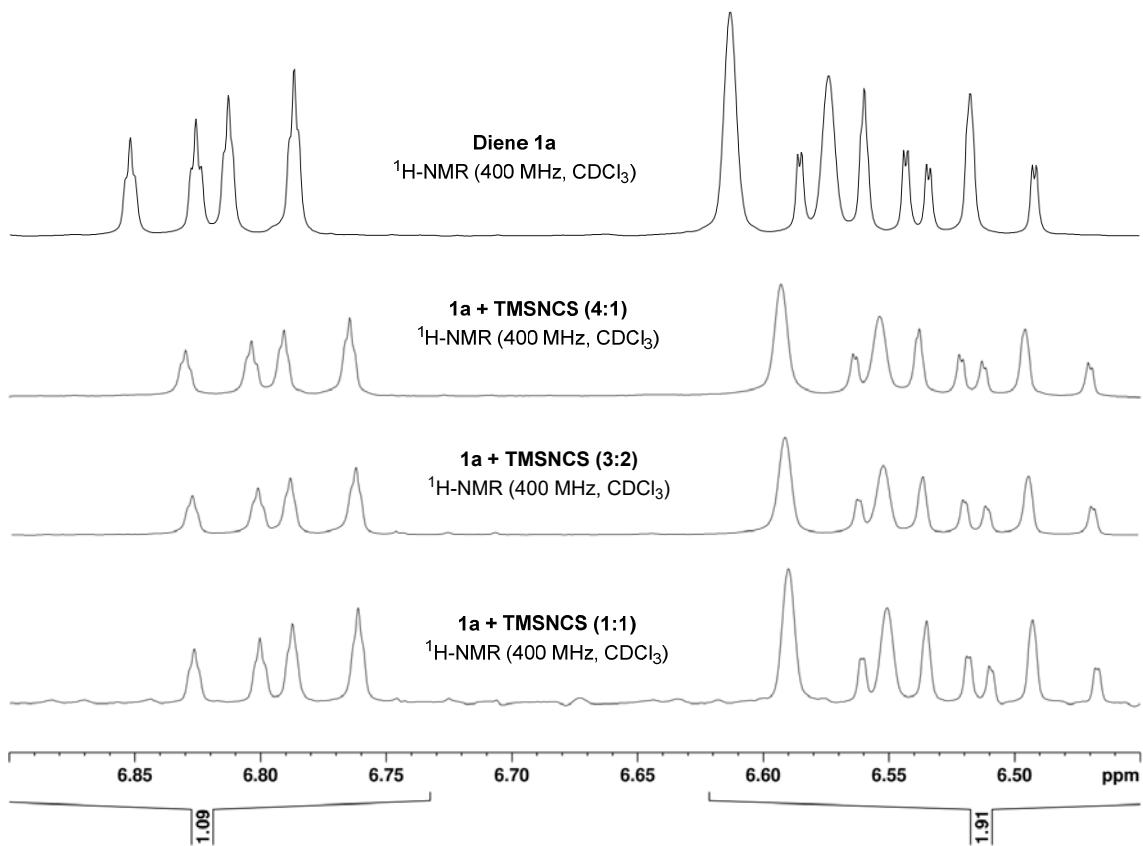
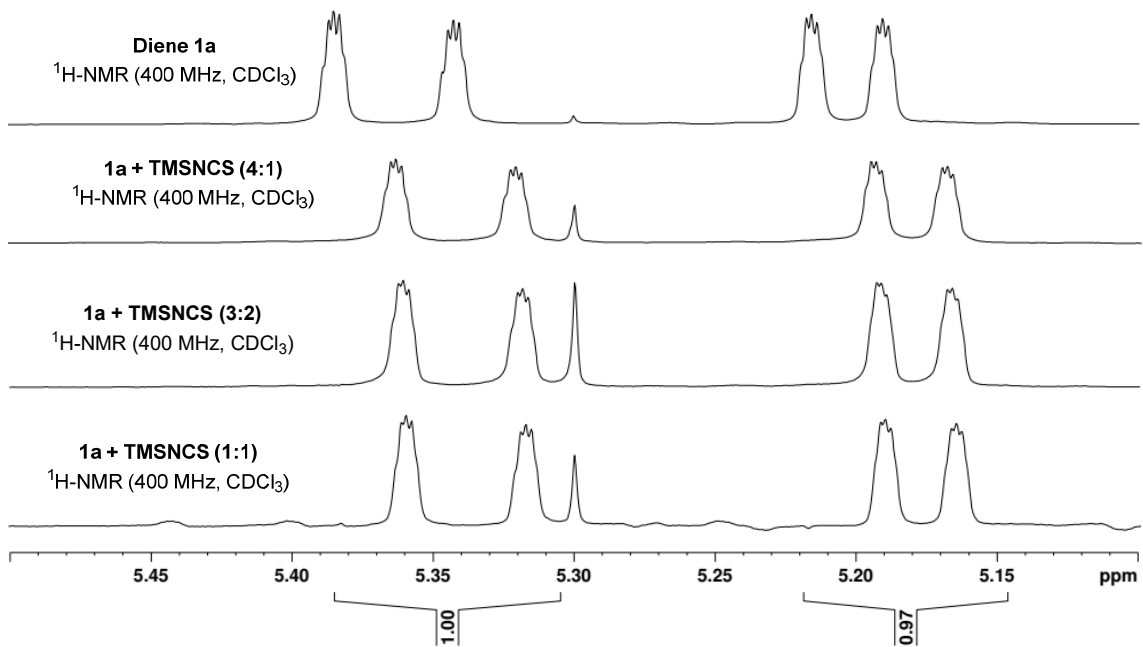


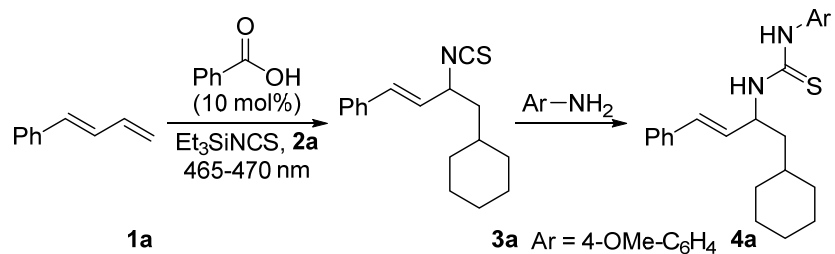
I. Interaction between diene 1a and TMSNCS by $^1\text{H-NMR}$: The $^1\text{H-NMR}$ (400 MHz, CDCl_3) spectra of diene and TMSNCS mixture was recorded. A clear shift was noticed in the olefinic peak of the dienes and thus establishing the interaction between these two reagents.



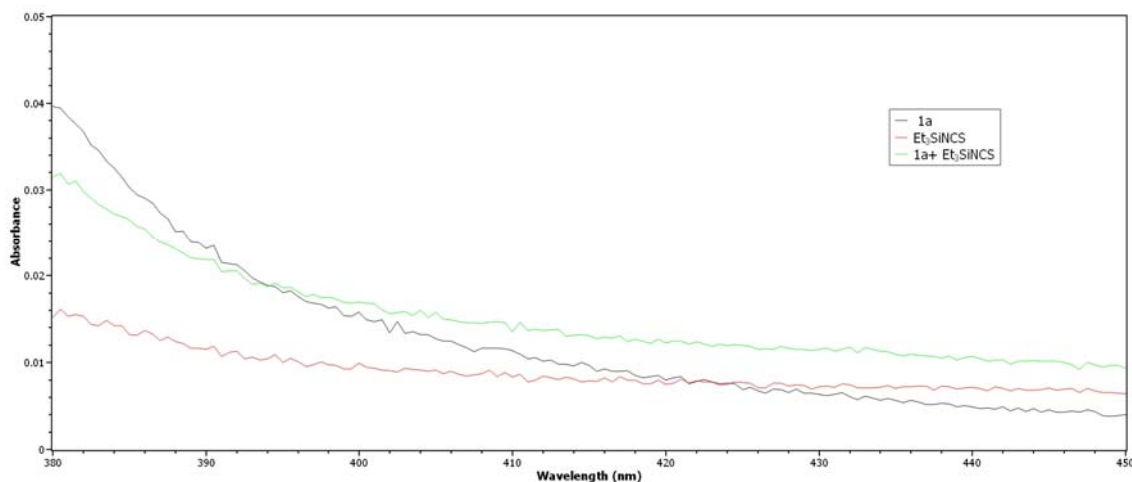
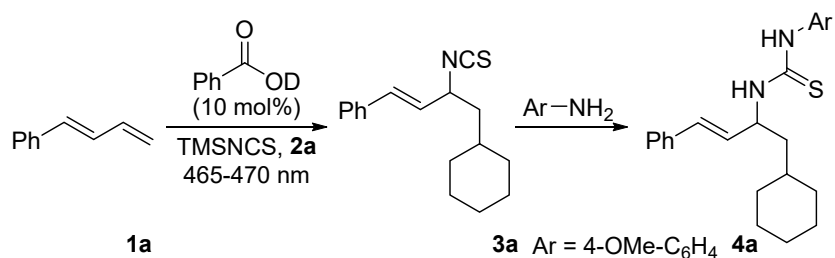




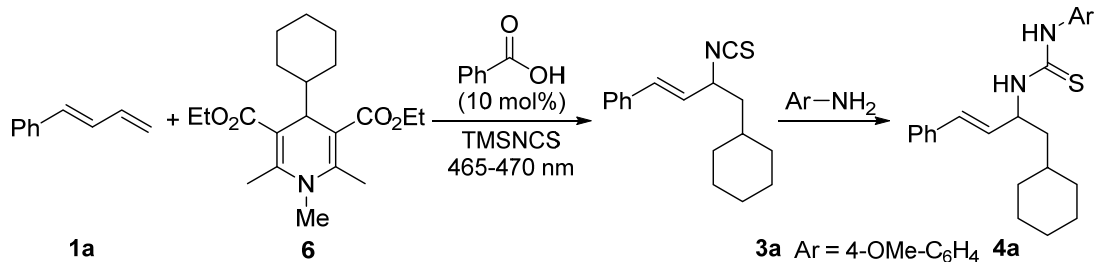


J. Reaction with Et₃SiNCS:

To probe the significance of TMSNCS in this carboamination protocol the same reaction was attempted with Et₃SiNCS under the optimized reaction conditions. However, this change greatly affected the reaction yield and **4a** was obtained in 10% yield. It is also notable that upon recording the UV-Visible absorption spectra a clear shift was observed with the mixture of diene and Et₃SiNCS.

**K. Deuteration studies:**

The effect of deuterated benzoic acid on the optimized reaction outcome was also probed. By using the general carboamination protocol the reaction mixture was irradiated for 12 h and **4a** was obtained in 28% yield. The reaction outcome was same as the reaction with benzoic acid (28% yield after 12 h) and thus ruling out the effect of deuterated benzoic acid.

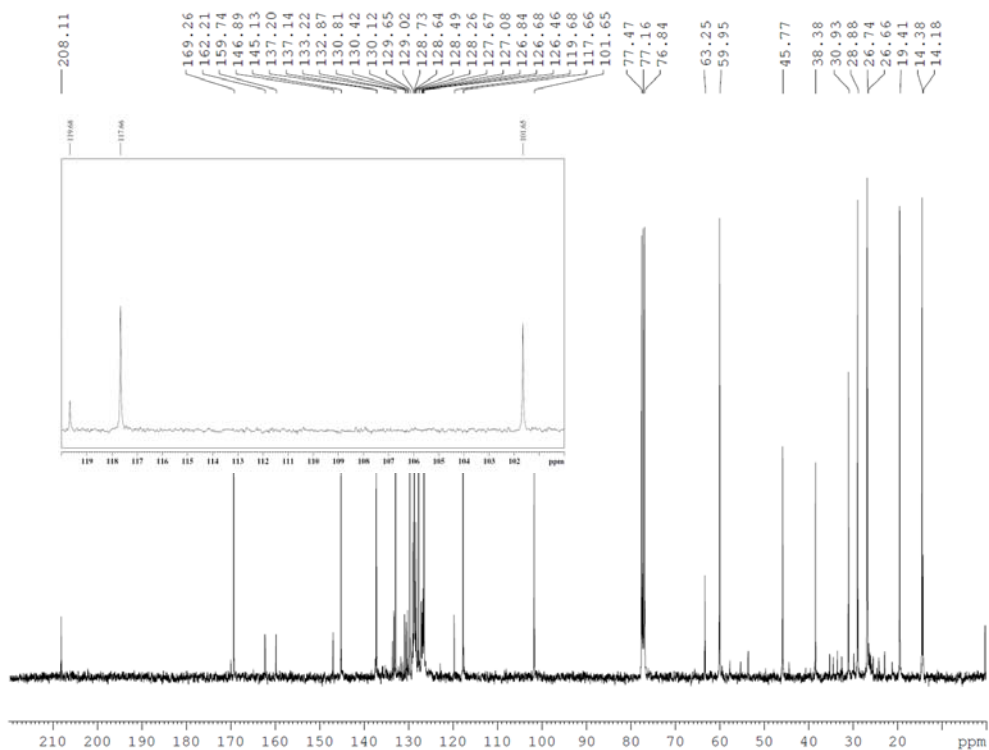
L. Reaction with *N*-methyl radical precursor:

The reaction was also carried out with *N*-methyl radical precursor (**6**) under the optimized reaction conditions. However, in this case the product **4a** was not observed and thus establishing that the N-H bond of radical source **2** play an important role in the reaction.

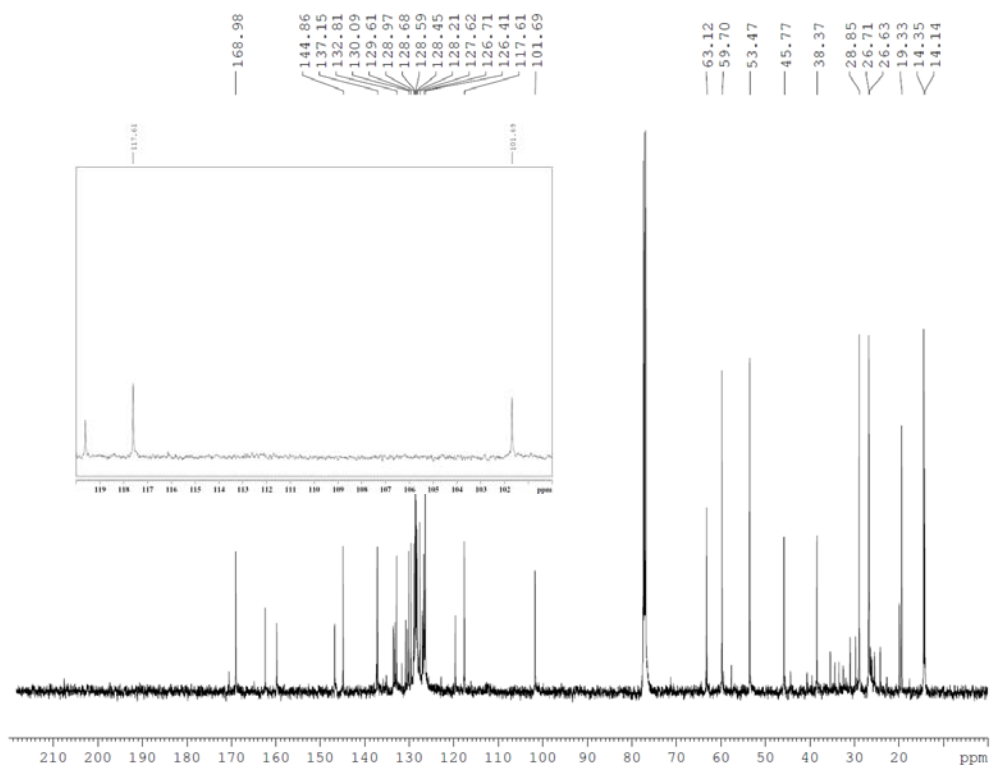
M. Exploration of possible intermediates:

The possibility of thiocyanation adduct as plausible intermediate and its subsequent rearrangement to **3a** as potential pathway was also considered. For the analysis of this part, the reaction was monitored through crude ¹³C-NMR at different intervals (15 h and 20 h). However, in both cases, the thiocyanation peak was not observed.

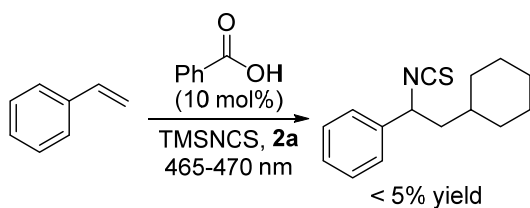
¹³C-NMR of crude reaction mixture at 15 h:



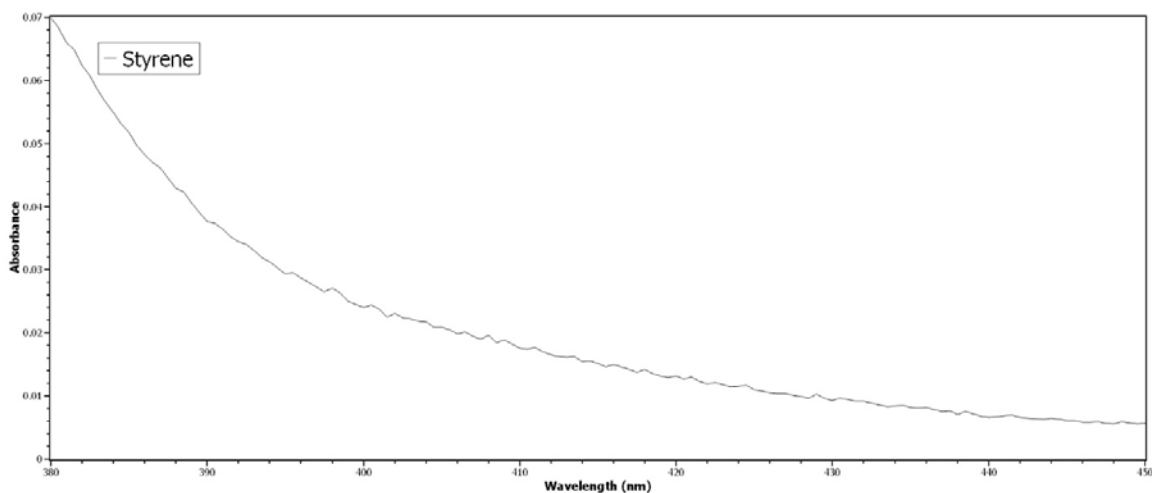
^{13}C -NMR of crude reaction mixture at 20 h:

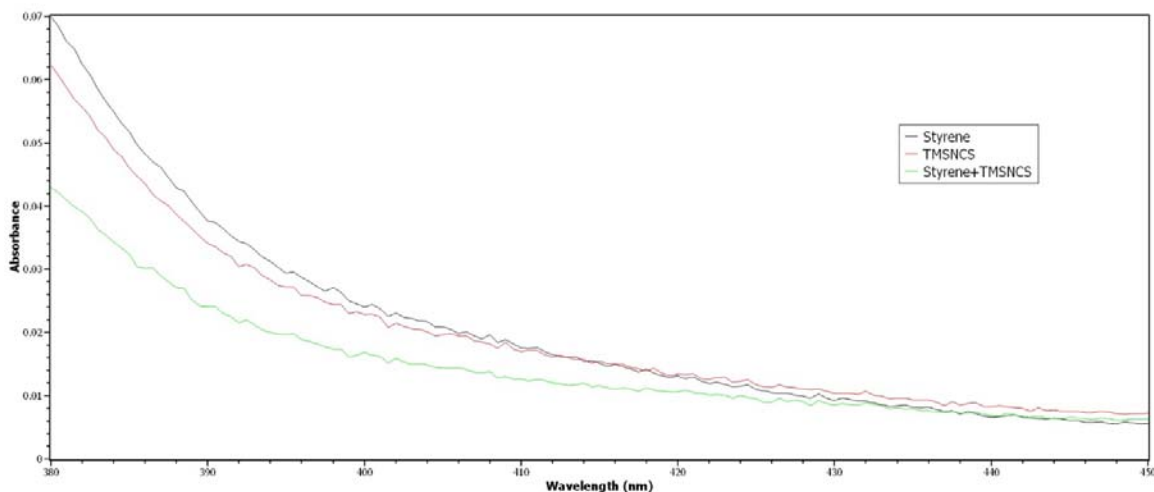


N. Organocatalytic carboamination with alkene:

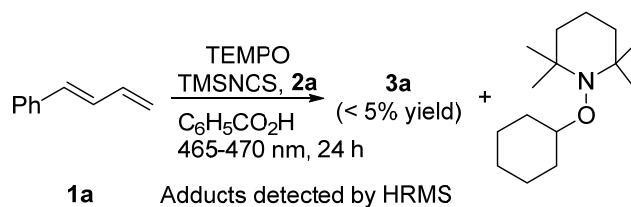


The carboamination protocol was also applied to the alkene. However, in this case, the desired product was not formed. This result can be attributed to the absence of EDA complexation between alkene and TMSNCS.

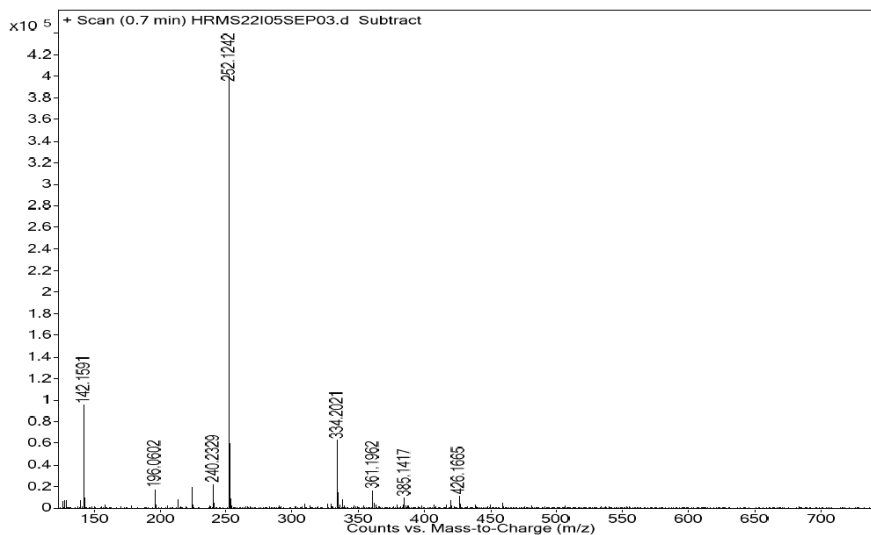




O. Control Experiments with TEMPO: In order to probe the radical intermediates in the reaction the optimized reaction was carried out with 1.0 equiv. of TEMPO. After irradiating the reaction mixture for 24 h. Under this condition formation of **3a** was completely inhibited however the TEMPO adducts were also characterized through HRMS analysis. didn't formed in the presence of radical scavenger TEMPO and formation of TEMPO adduct were characterized by HRMS analysis



For a Cyclohexyl TEMPO adduct (ESI+): Cal. for $C_{15}H_{29}NO$ $\{M+[H]\}^+$: 240.2327, Found: 240.2329.



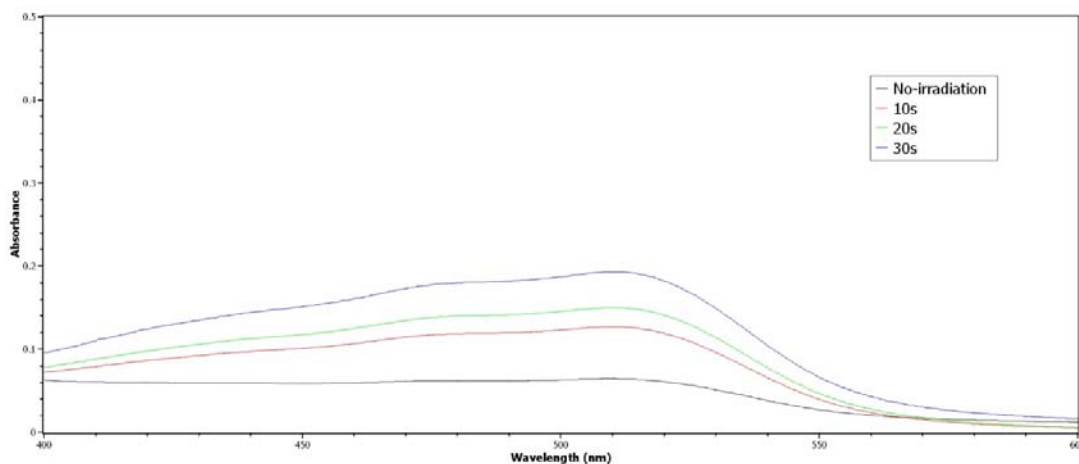
P. Quantum yield measurement:

Quantum yield calculated through standard ferrioxalate actinometry.⁶ It measures the decomposition of ferric ion to ferrous ion formed complex with 1,10-phenanthroline which was monitored by UV-Visible absorbance at 510nm.

The solution prepared and stored in the dark to avoid the effect of light on measurement. Potassium ferrioxalate solution (0.15M in 0.05M H₂SO₄) and buffer solution of phenanthroline (50 mg 1,10-phenanthroline and 11.25 g of sodium acetate was dissolved in 50 ml of 0.5M H₂SO₄) were prepared.

The measurements were done as follows-

In a dark room 04 mL of 0.15M ferrioxalate solution added to a vial, irradiated it for 10 s under SynLED Parallel Photoreactor (Blue LED 465-470 nm). After irradiation, quickly transferred to a volumetric flask covered with aluminum foil containing 0.50 mL of the buffer solution. Deionized water added to the flask to make the total volume of 10mL. Shaked it properly and then stored it in the dark for 01h. After 01h, 1.0mL of it added to quartz cuvette and measured the absorbance at 510nm by JASCOV-750 UV/Visible spectrophotometer. In the same way a sample with irradiation time (20s, 30s) and non-irradiated one were prepared and recorded the absorbance at the same wavelength.

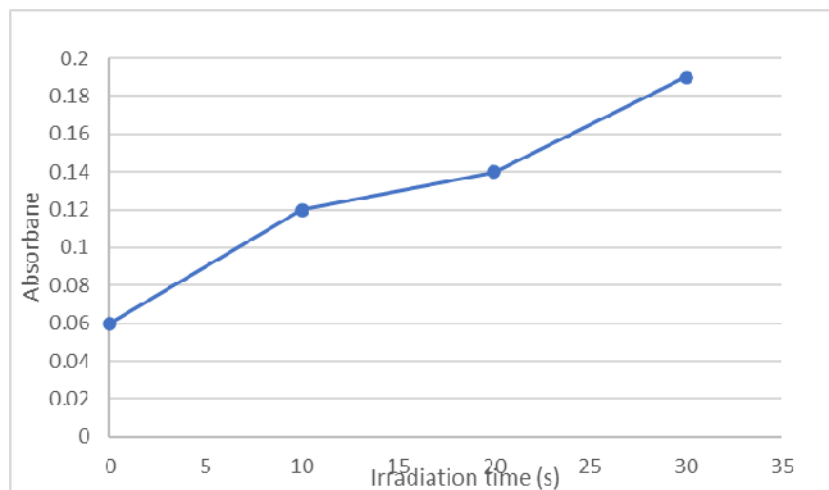


The mole of Fe²⁺ formed in each sample determined according to the formula-

$$\text{moles of Fe}^{2+} = \frac{V_1 \times V_3 \times \Delta A (510\text{nm})}{V_2 \times l \times \epsilon (510\text{nm})}$$

6 (a) X. Li, C. Golz and M. Alcarazo, *Angew. Chem. Int. Ed.* 2021, **60**, 6943-6948. (b) C. B. Tripathi, T. Ohtani, M. T. Corbett and T. Ooi, *Chem. Sci.* 2017, **8**, 5622-5627.

Where V_1 is the irradiated volume (4 mL), V_2 is the volume used for determination of Fe^{2+} (0.5 mL), V_3 is the final volume after mixing with phenanthroline buffer solution (10 mL), L is optical path length of the irradiated cell (1cm), ΔA is difference in optical absorbance between irradiated and non-irradiated solutions at 510nm and ϵ is the molar absorptivity at 510 nm ($11,100 \text{ Lmol}^{-1}\text{cm}^{-1}$).



After which photon flux were calculated using formula-

$$\text{photon flux} = \frac{\text{moles of Fe}^{2+}}{\phi \times t \times f}$$

Where ϕ is the quantum yield of ferrioxalate actinometer (approximated as 1.01, which was reported for a 0.15M solution at $\lambda = 436 \text{ nm}$), t is the irradiation time, and f is the fraction of light absorbed at 440nm (0.960636836).

The fraction of light absorbed was determined by using-

$$f = 1 - 10^{-A}$$

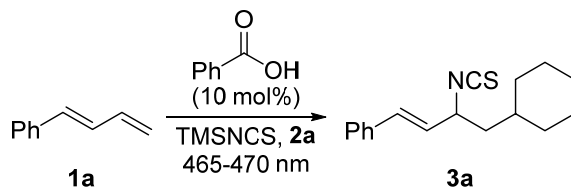
Where A is the absorbance (1.40491) of the 0.15 M solution of potassium ferrioxalate in blue LED.

Irradiation time (s)	Absorbance	ΔA	mole Fe^{2+}	Radiant flux (Einstein/s)
–	0.064488			
10s	0.126732	0.0622435	4.486×10^{-7}	8.197×10^{-8}
20s	0.149936	0.0854475	6.158×10^{-7}	5.694×10^{-8}

30s	0.193061	0.1285725	9.266×10^{-7}	5.712×10^{-8}
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The average photon flux 6.567×10^{-8} Einstein/s.

Determination of quantum yield-



In an oven dried vial, which is cooled under atmospheric air, **2a** (0.1 mmol, 1.0 equiv.), **Benzoic acid** (0.01 mmol, 0.01 equiv.), **TMSNCS** (0.17 mmol, 1.7 equiv.) and **1a** (0.17 mmol, 1.7 equiv.) were taken. The reaction vial was evacuated and back filled with nitrogen three times following which acetone was added under nitrogen. The reaction mixture was irradiated under Blue LED for different time period and the yield of **3a** was determined.

The quantum yield is calculated using the formula-

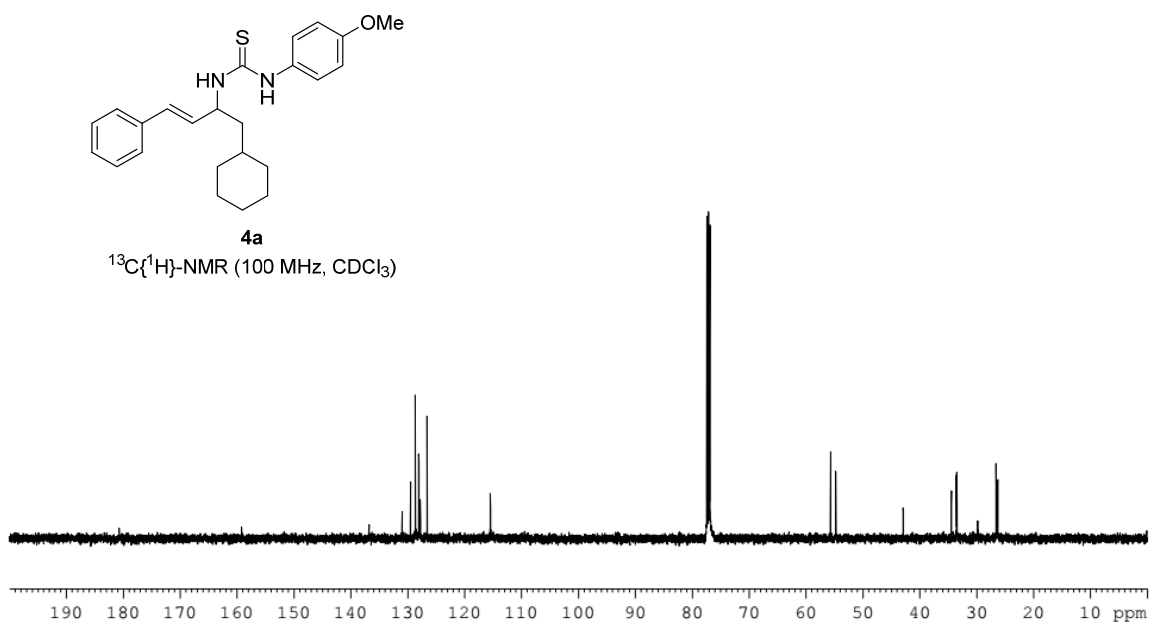
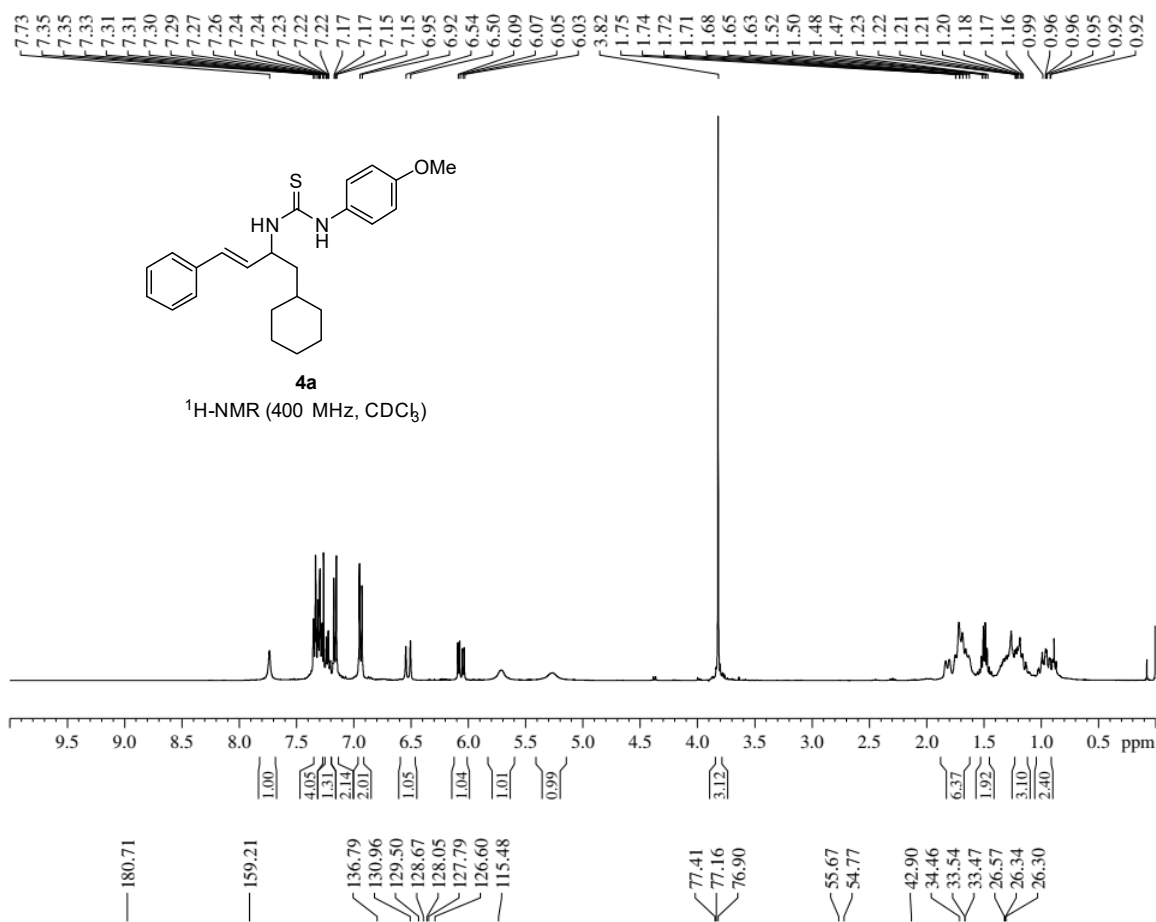
$$\phi = \frac{\text{moles of product}}{\text{photon flux} \times t \times f}$$

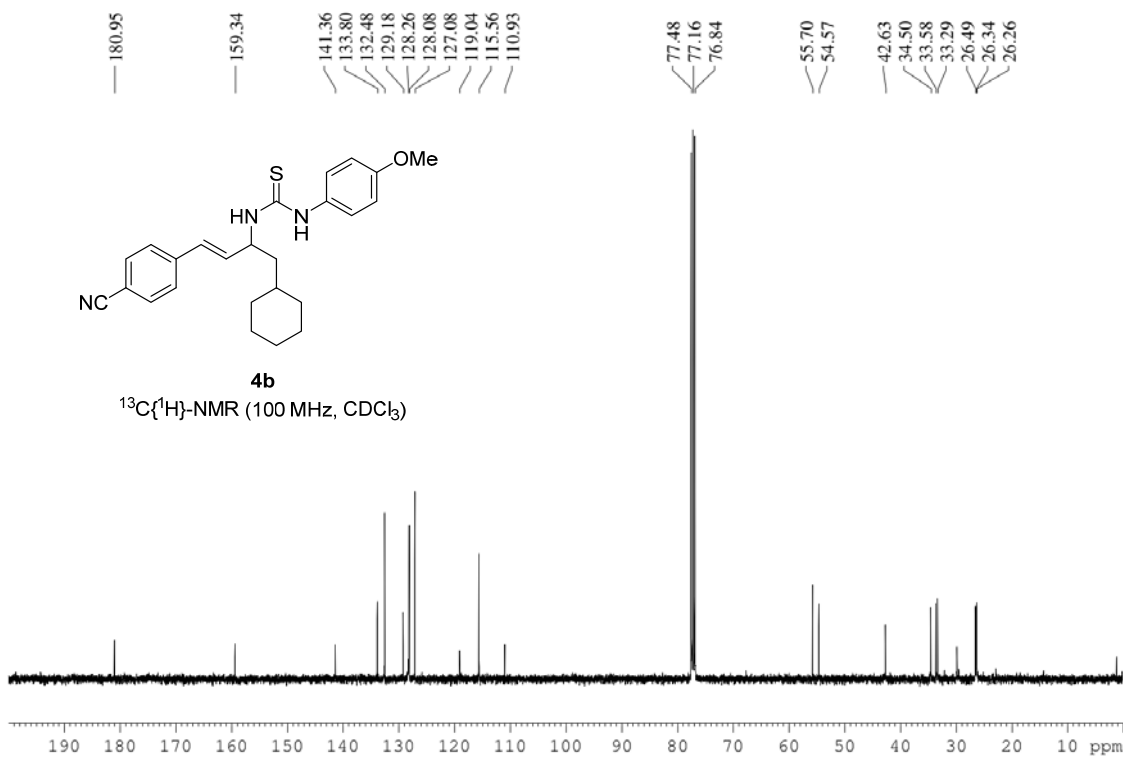
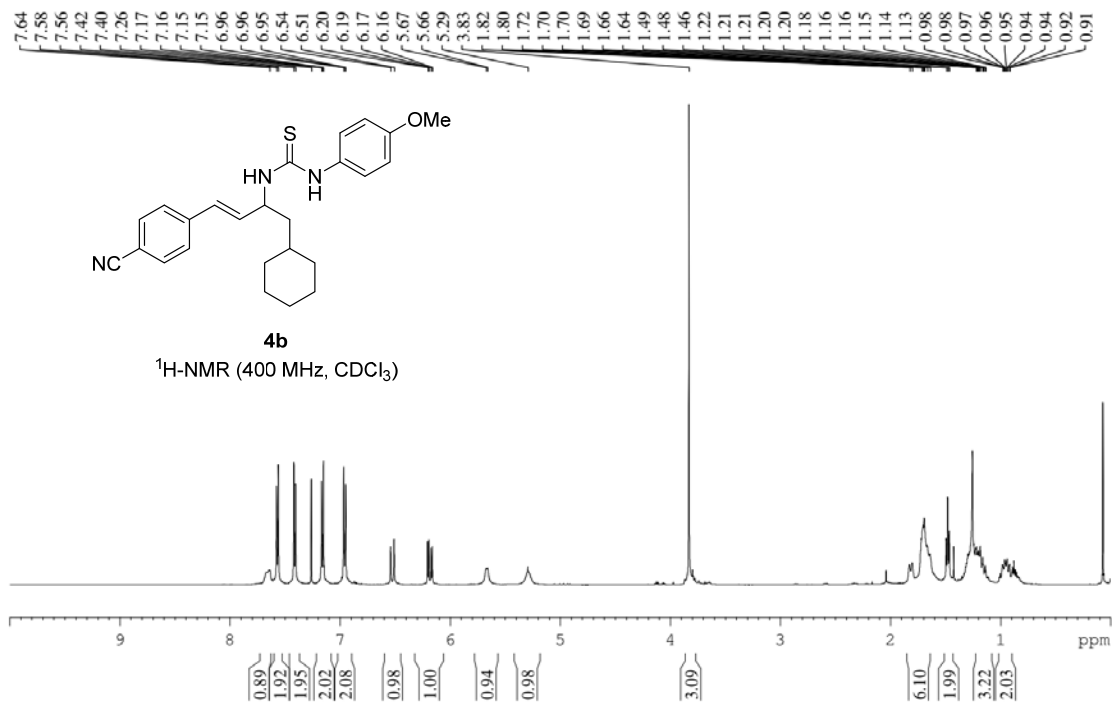
All the incident light is assumed to be absorbed ($f > 0.999$) under the reaction condition.

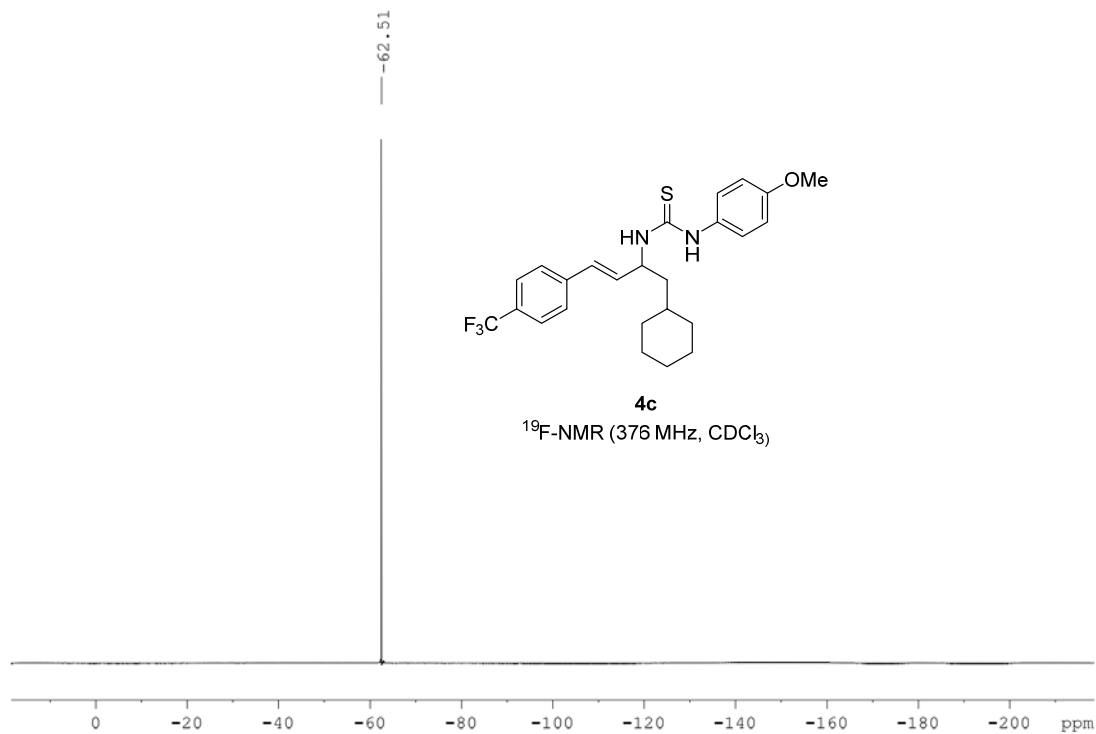
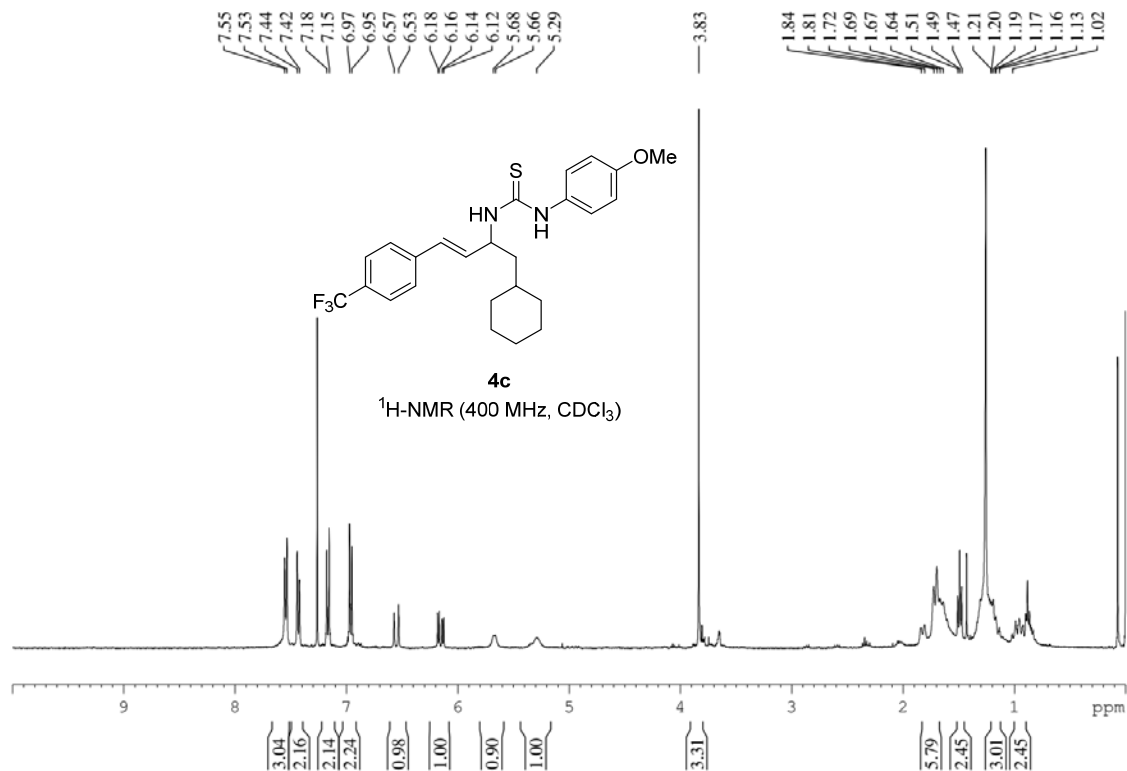
reaction time (s)	yield	moles of product	quantum yield (ϕ)
57,600	66	6.6×10^{-5}	0.0174
86,400	77	7.7×10^{-5}	0.0203

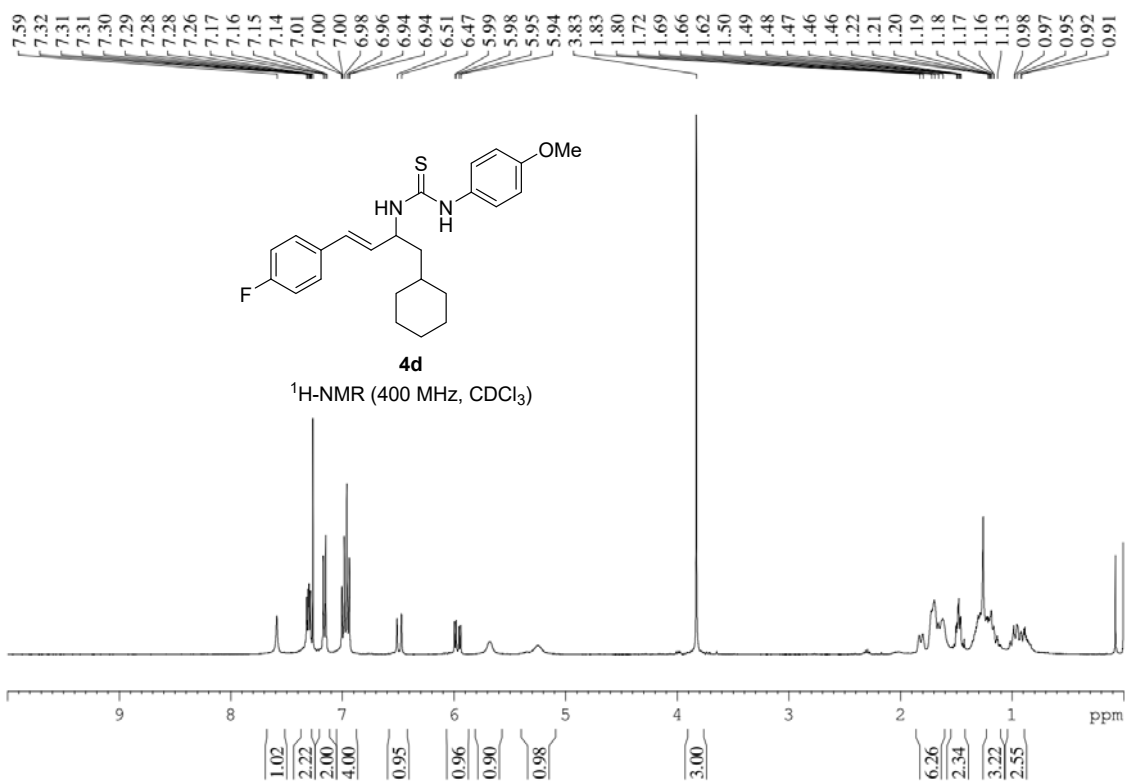
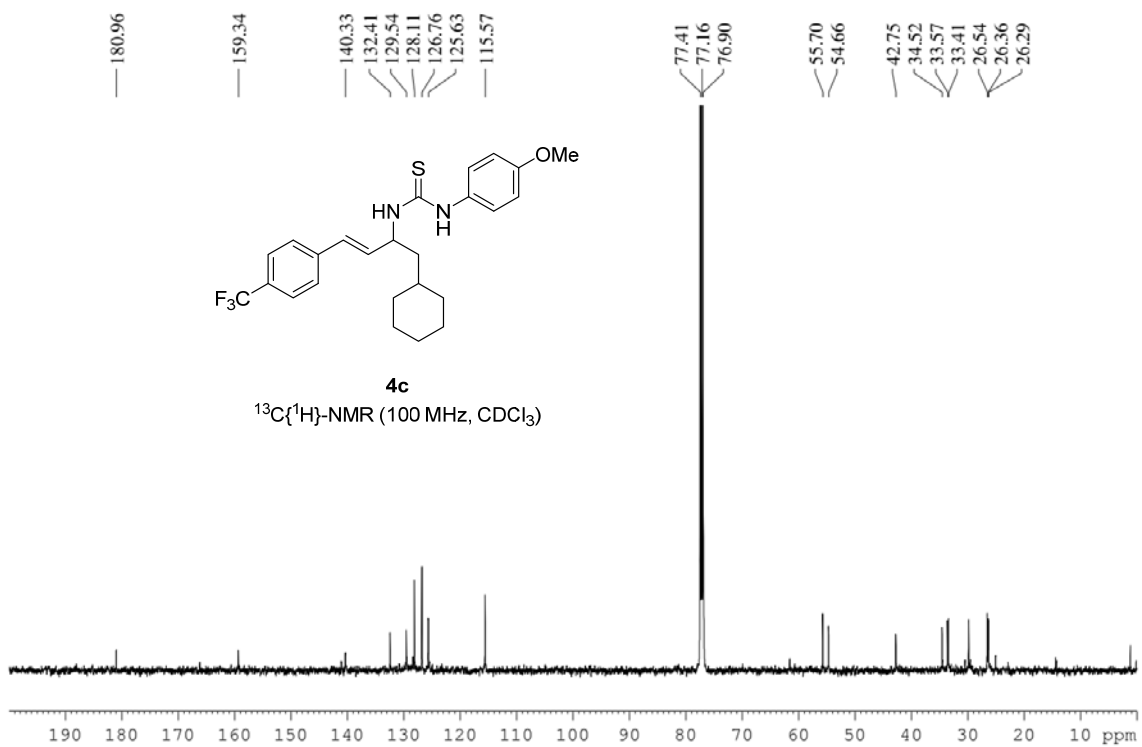
The average quantum yield is 0.0188.

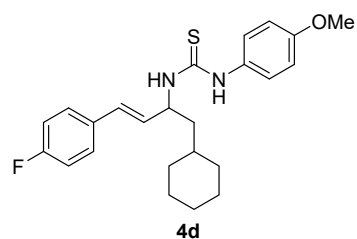
Q. Spectra of compounds:



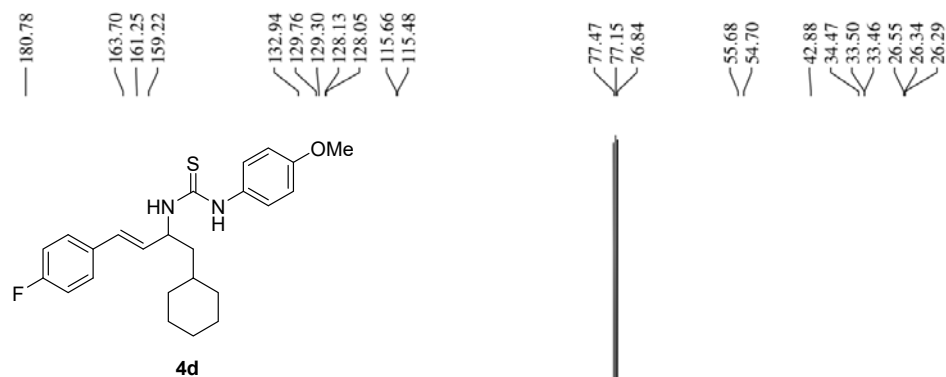
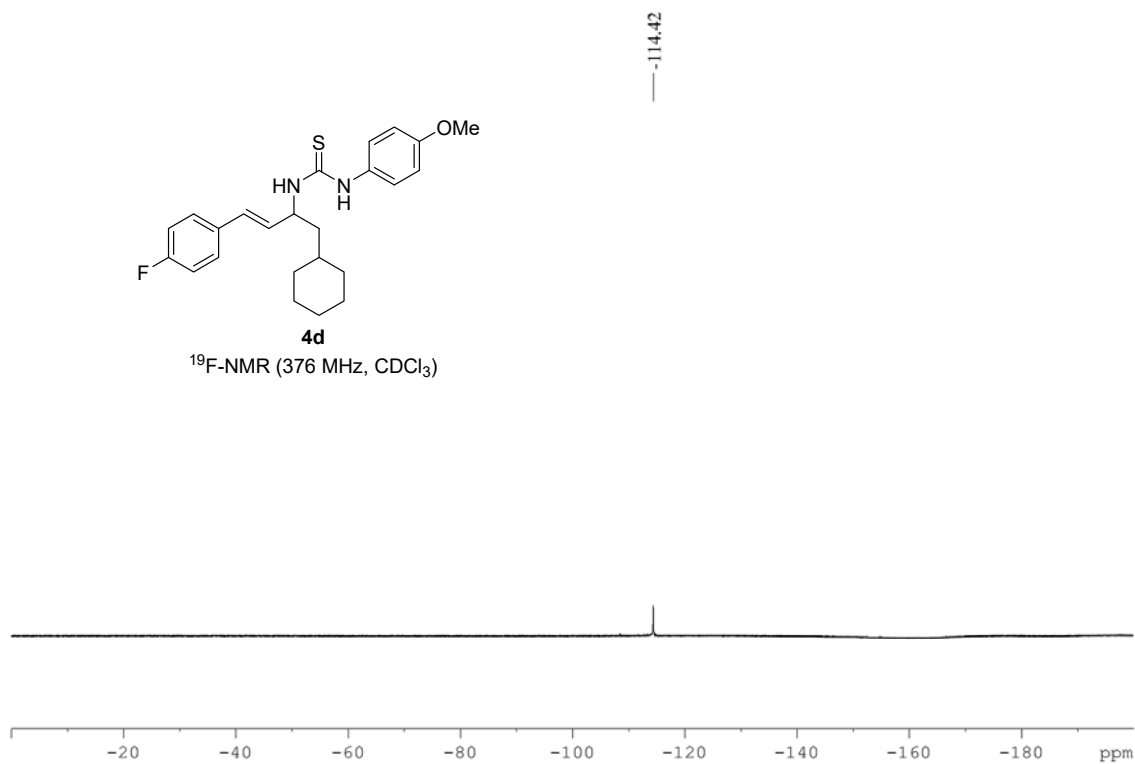




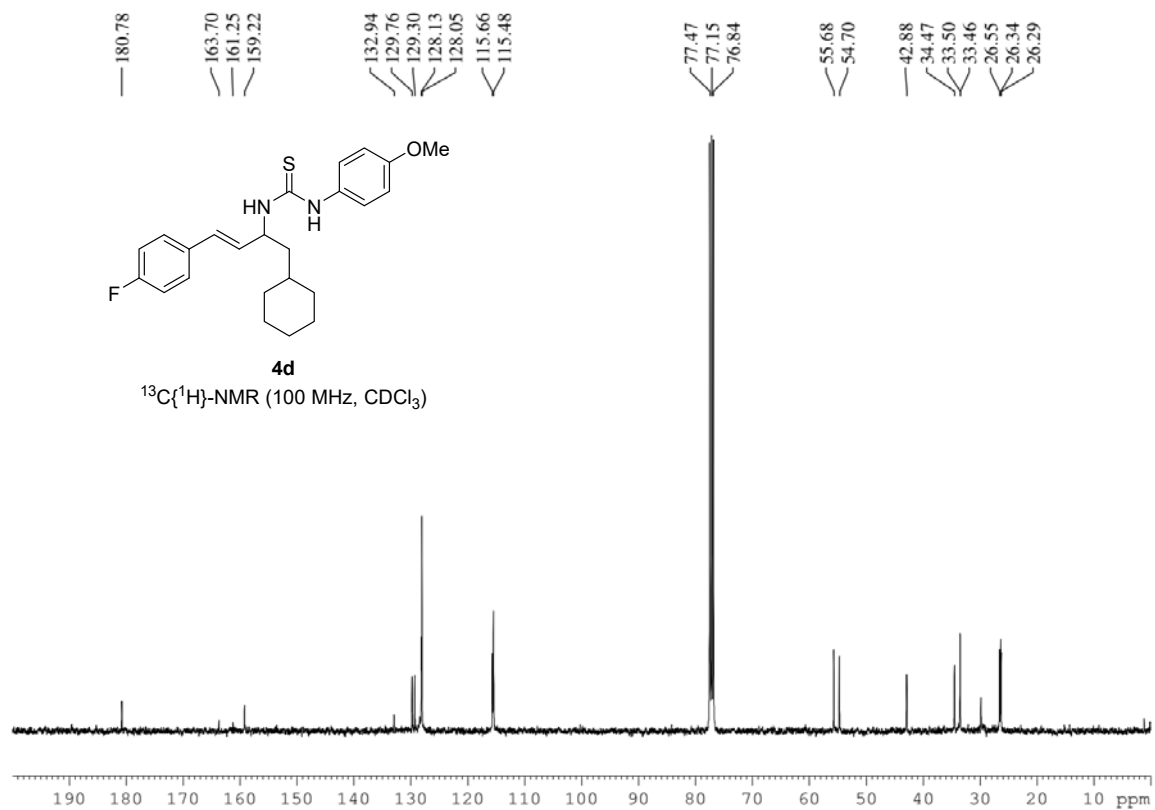


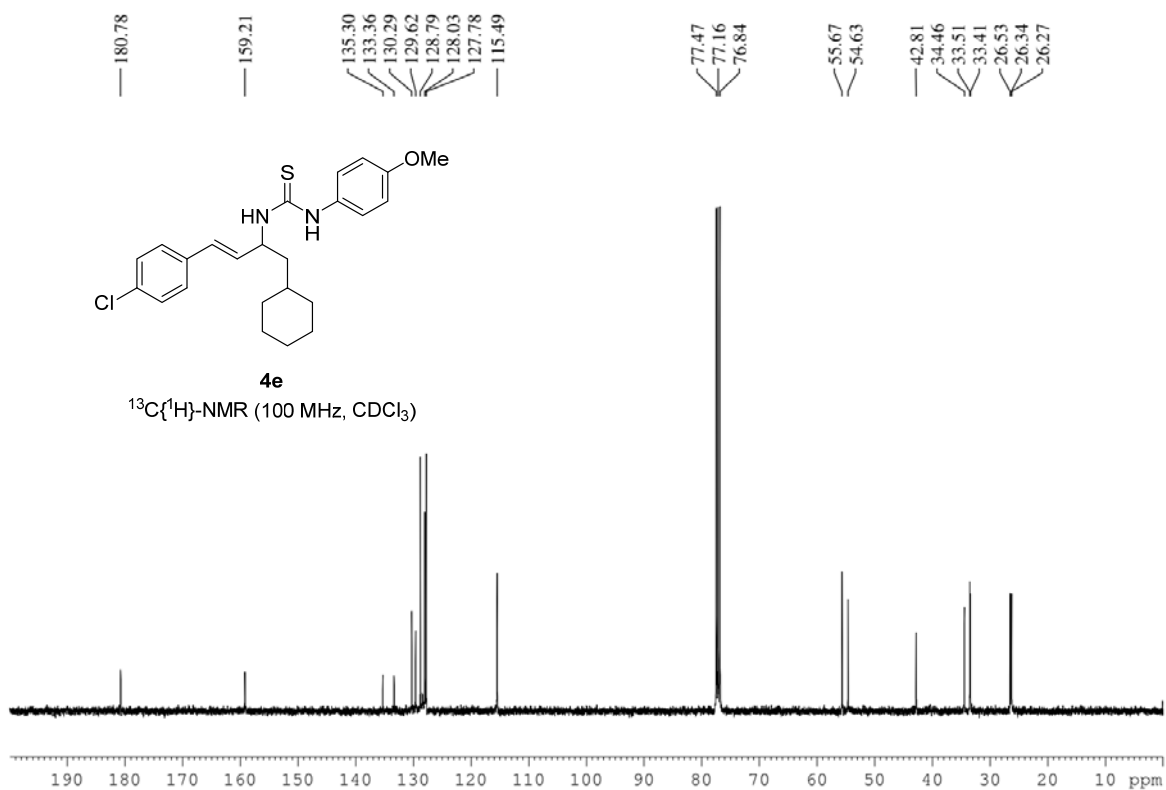
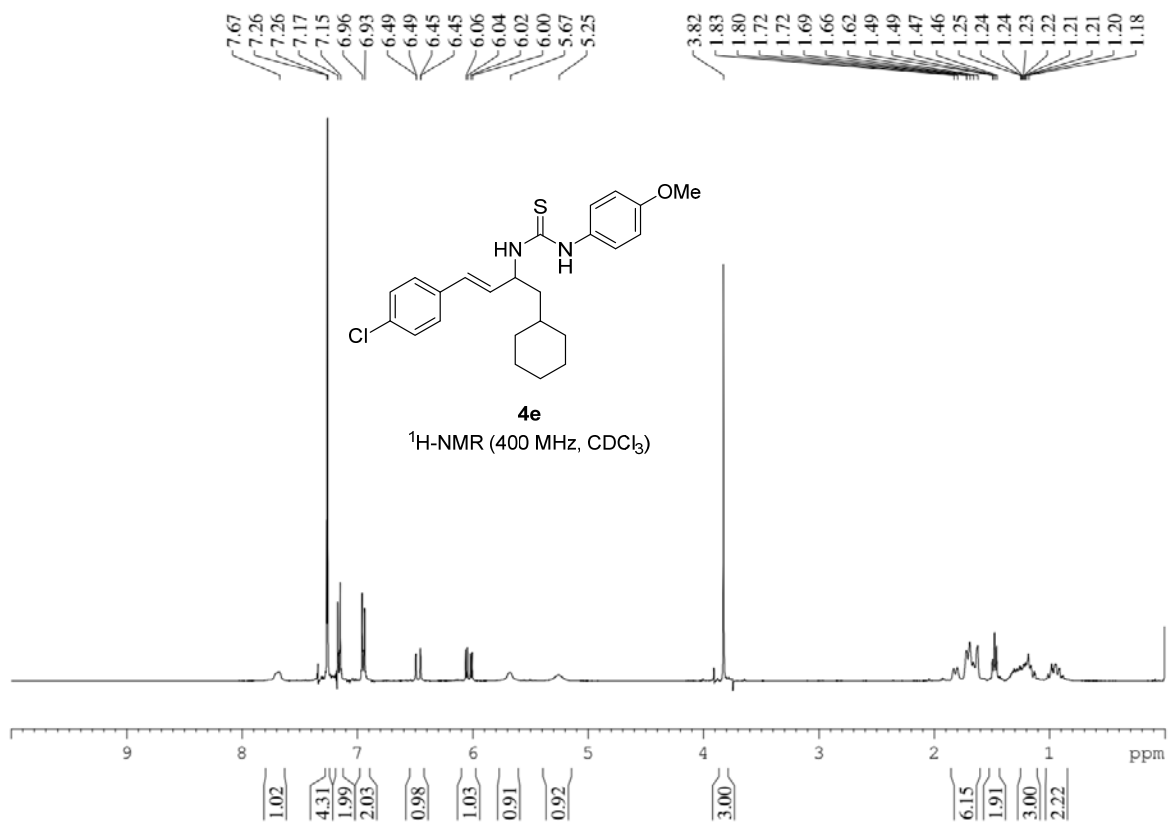


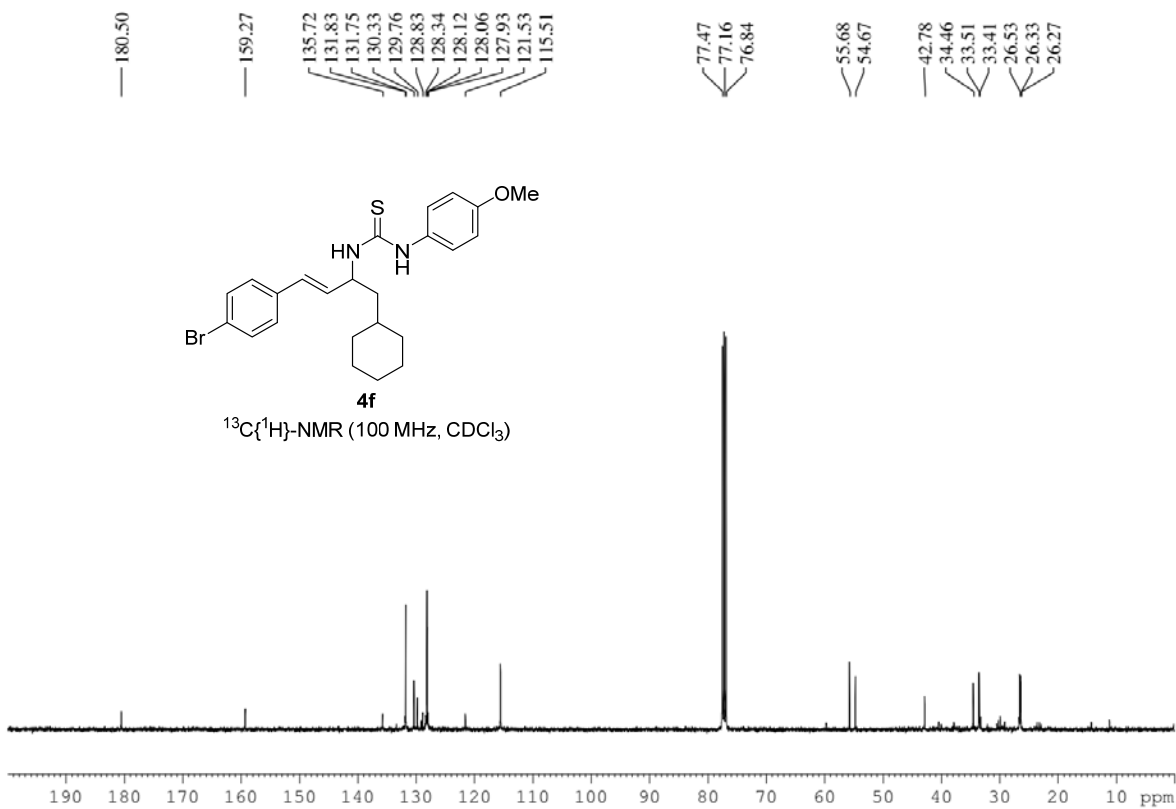
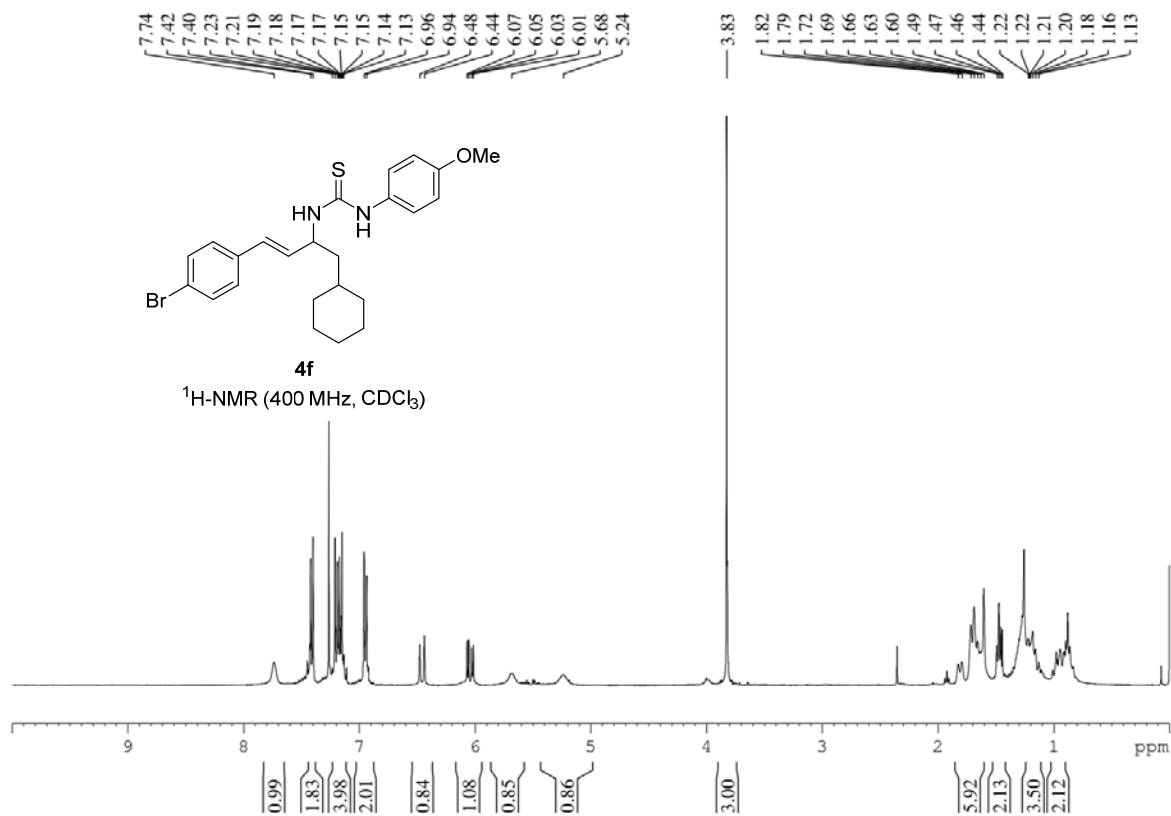
^{19}F -NMR (376 MHz, CDCl_3)

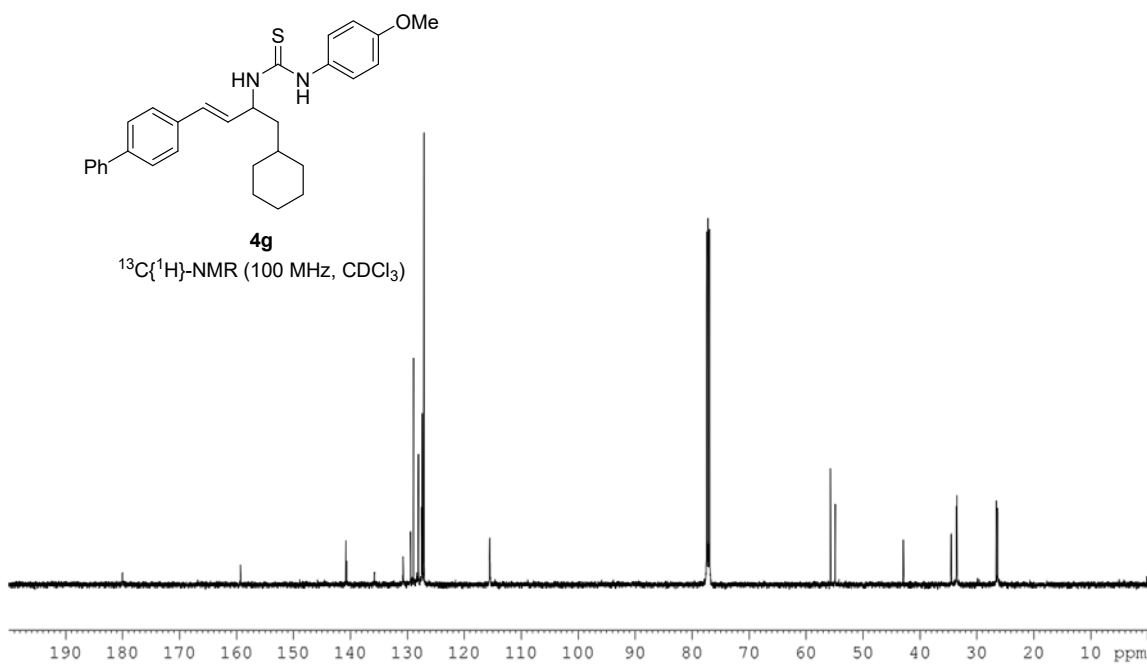
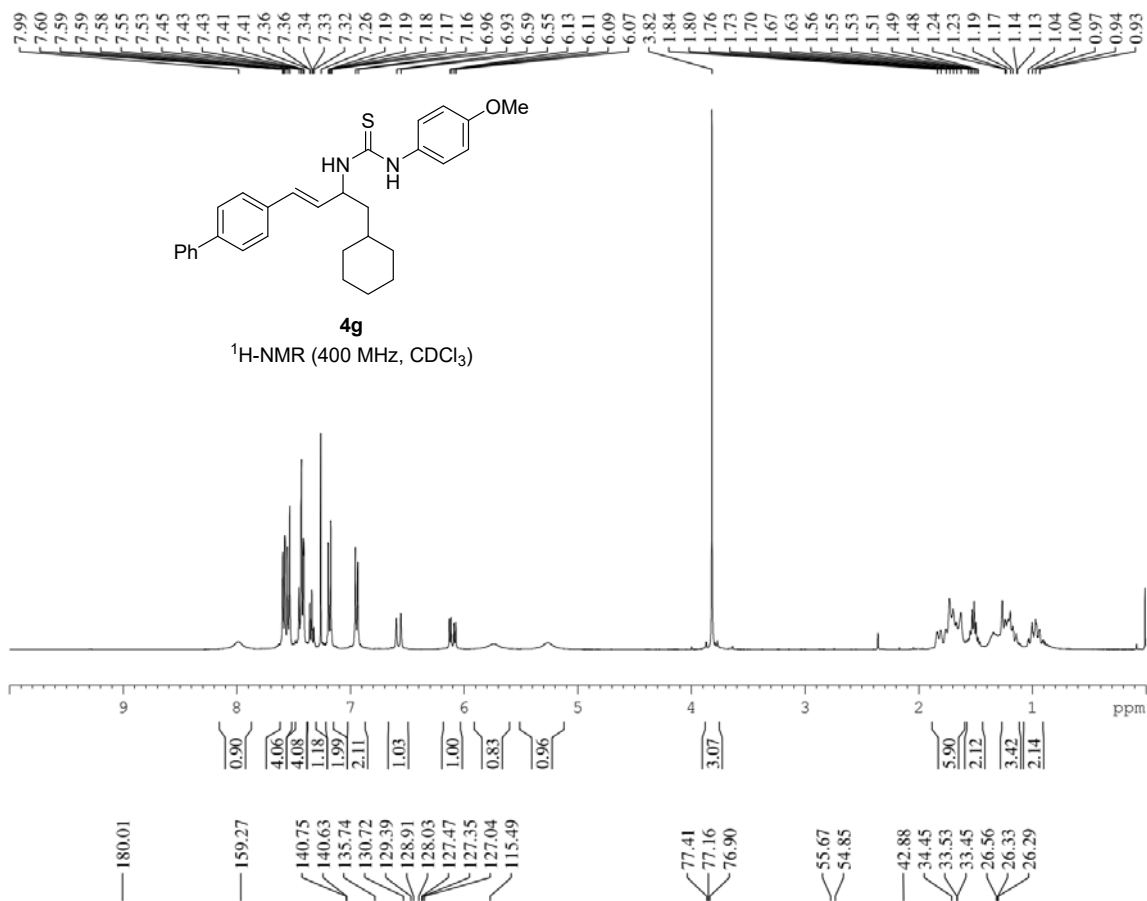


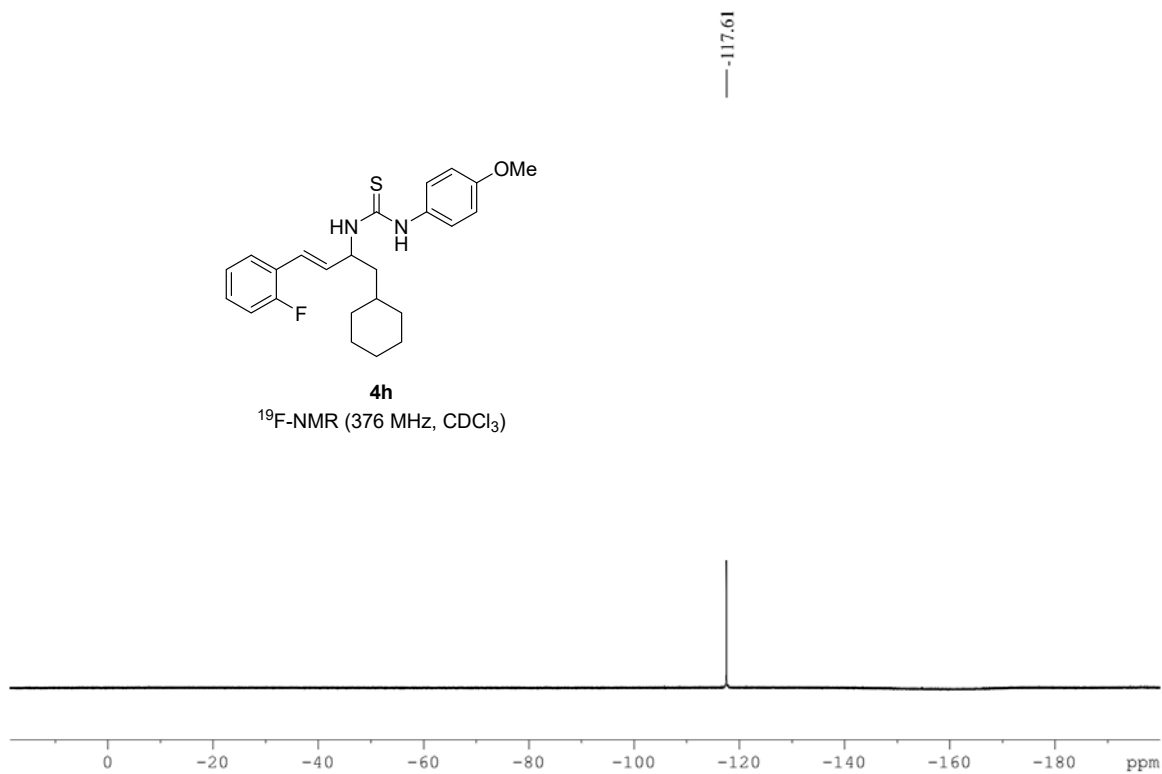
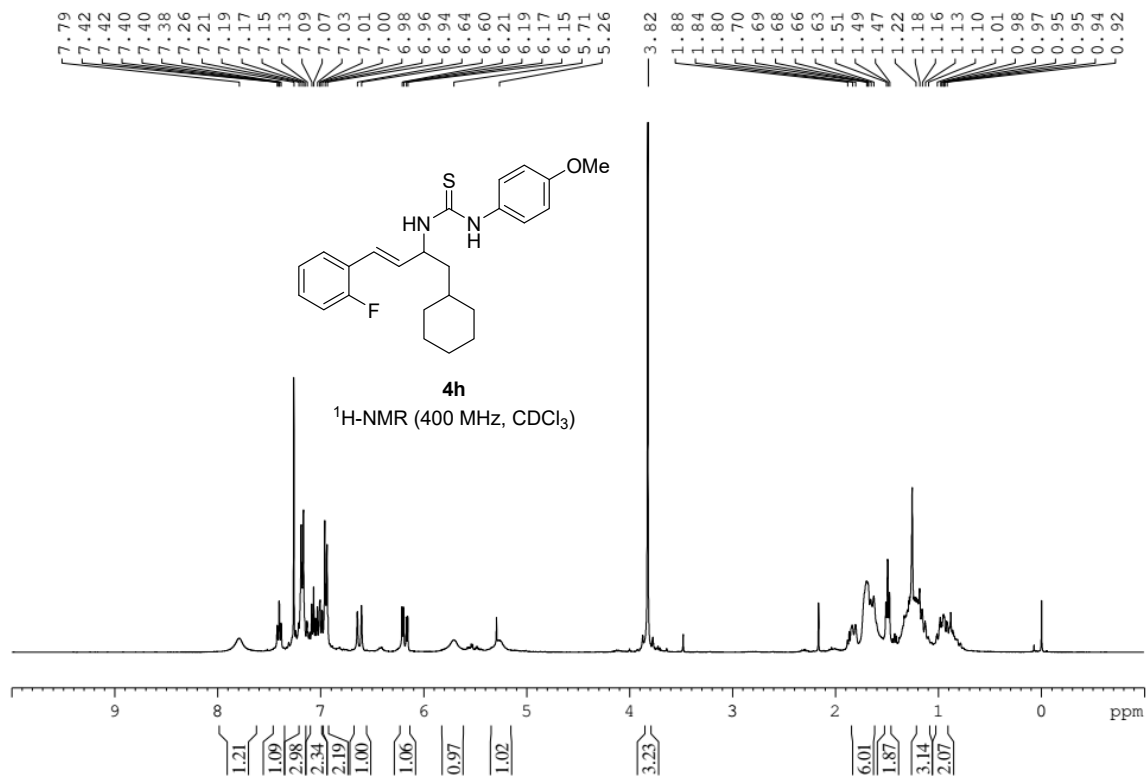
$^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3)

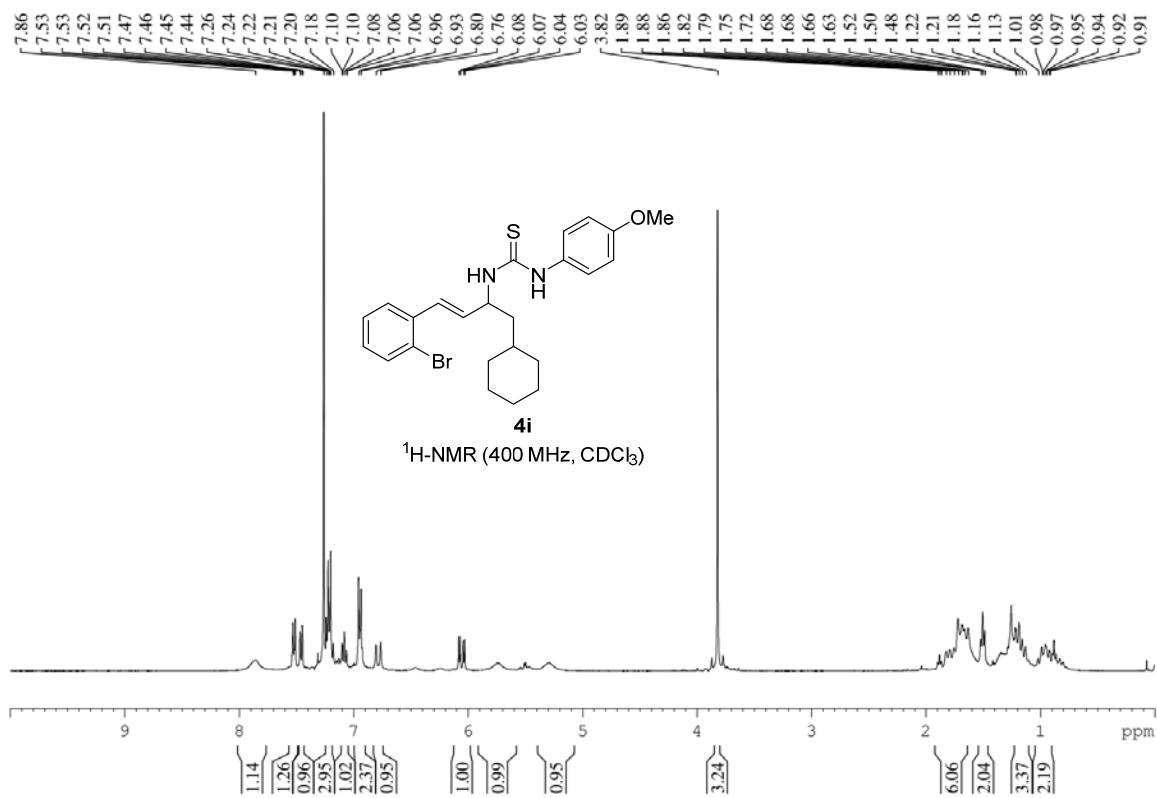
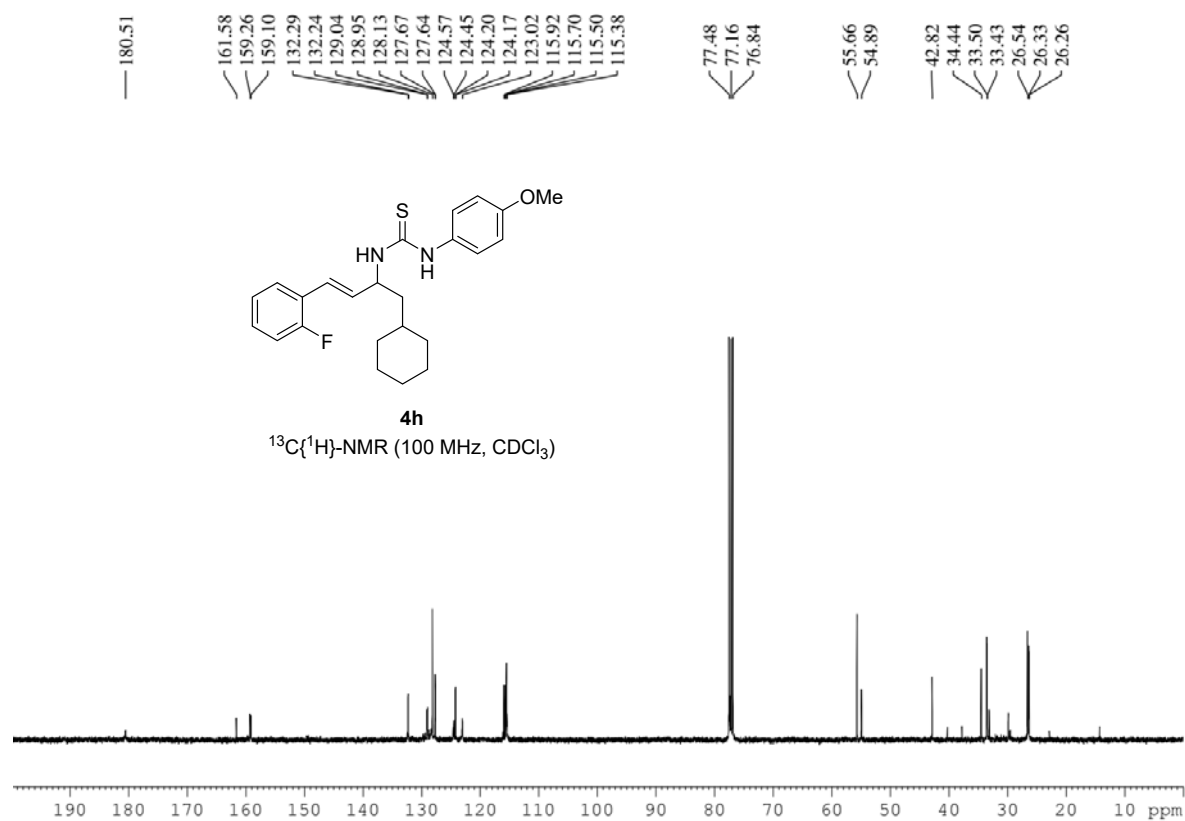


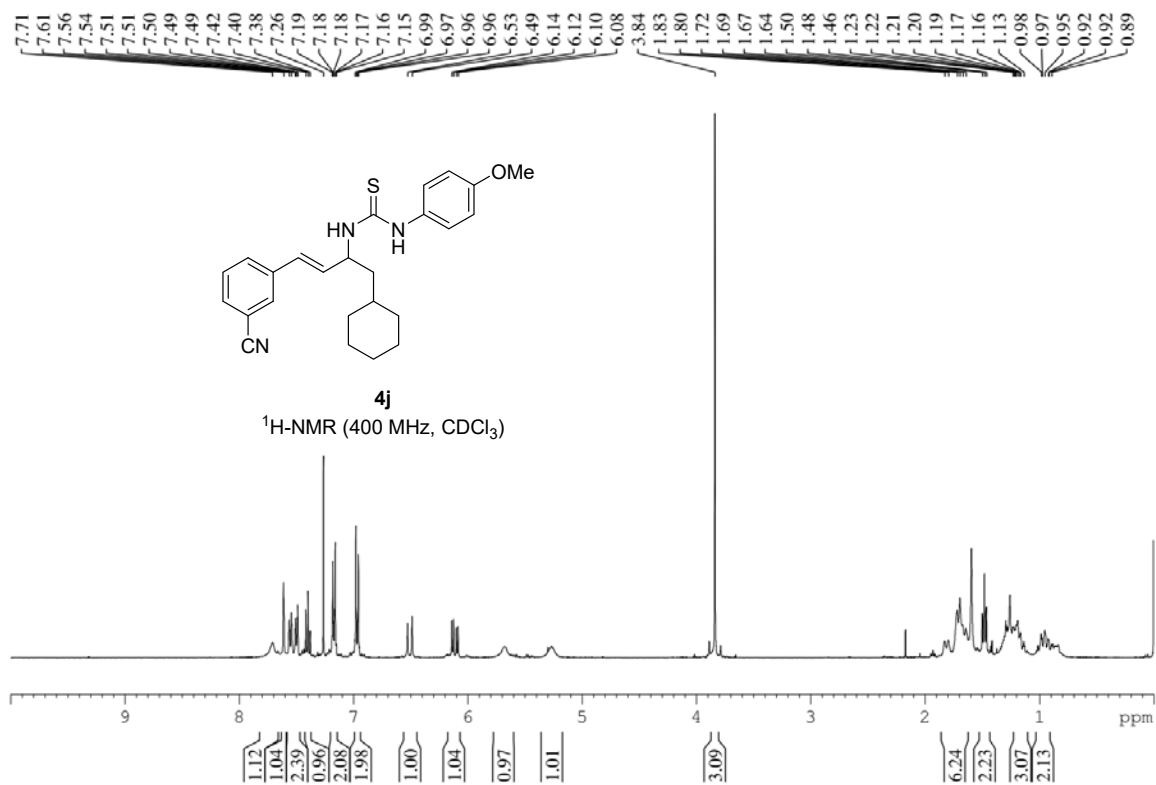
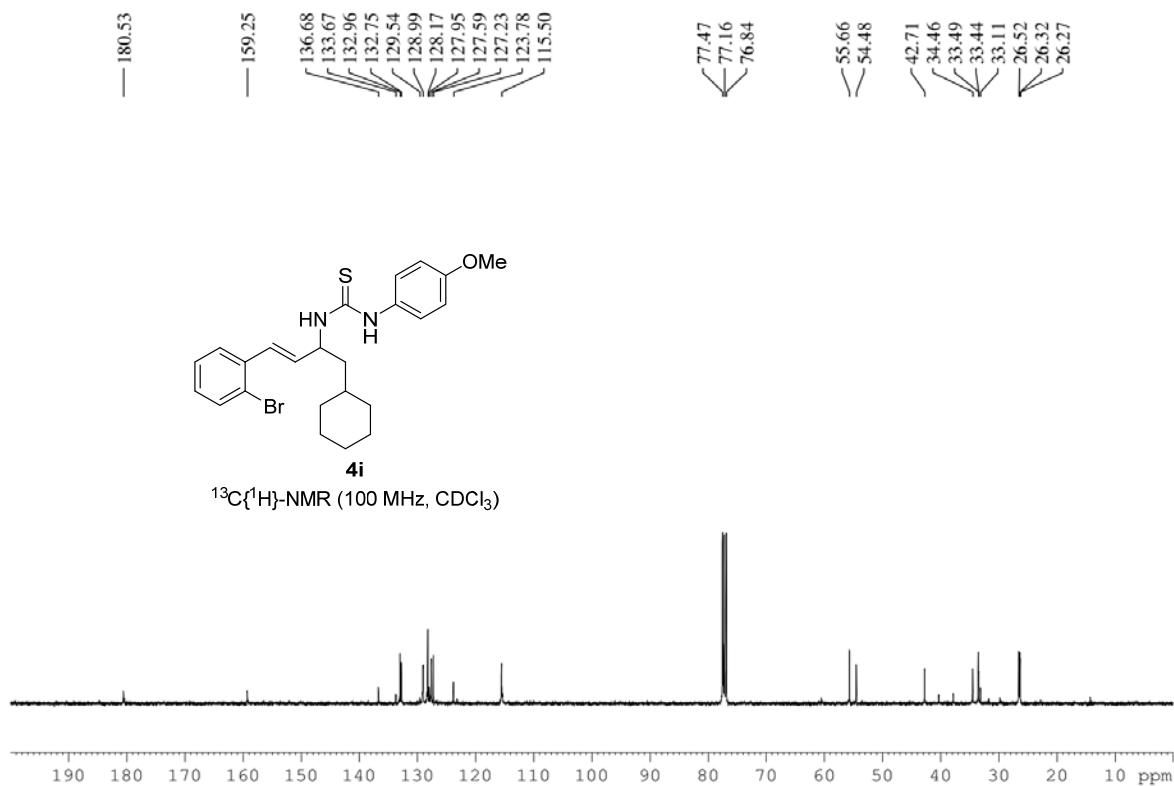


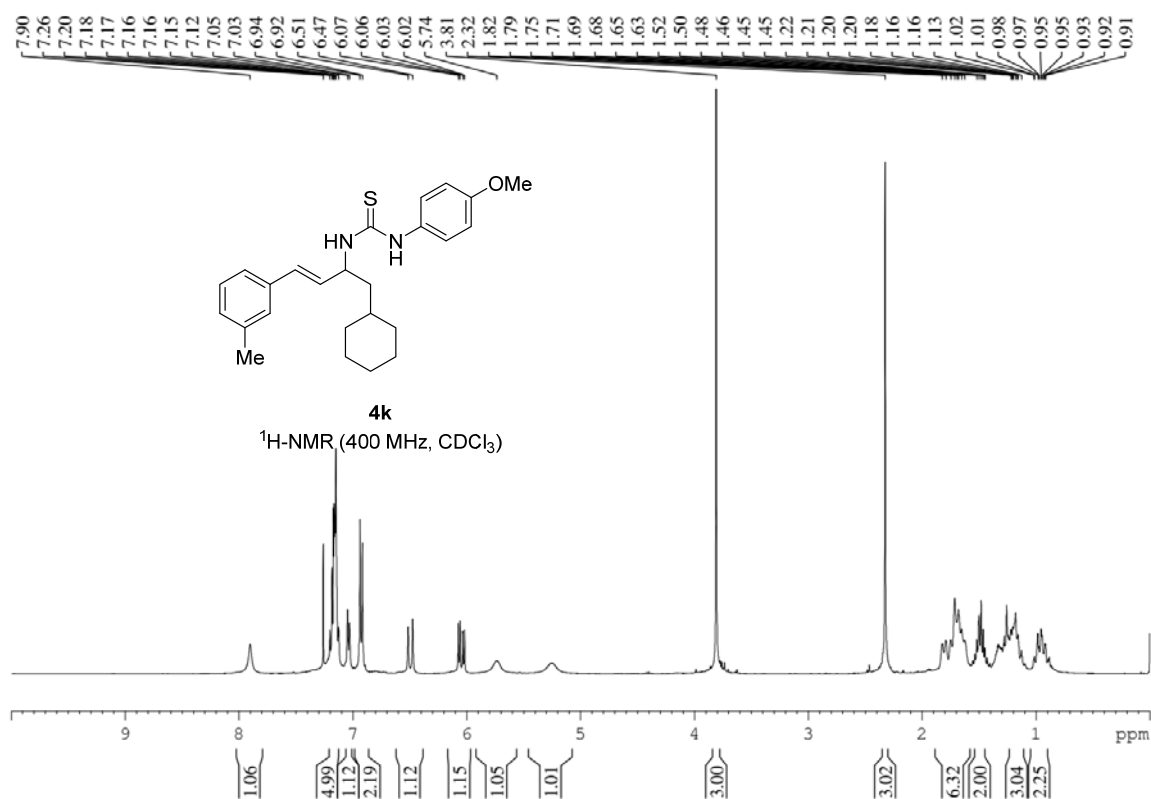
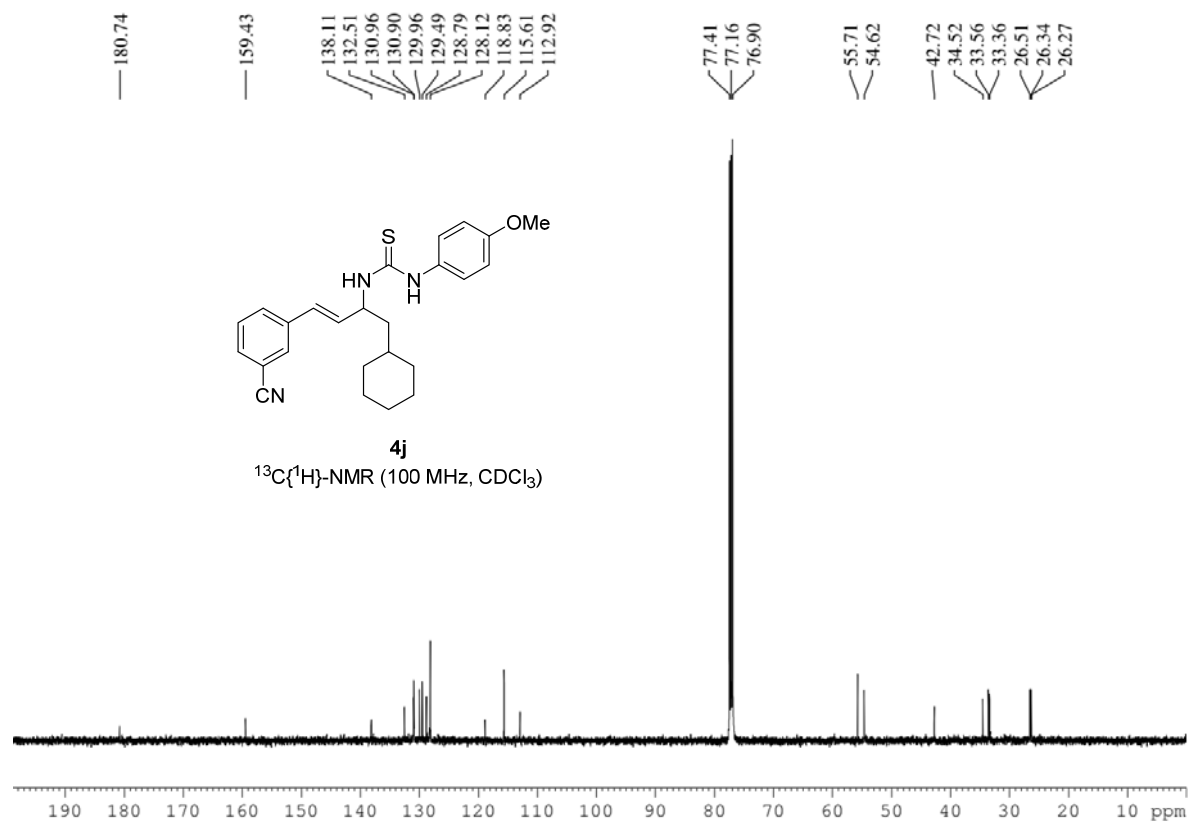


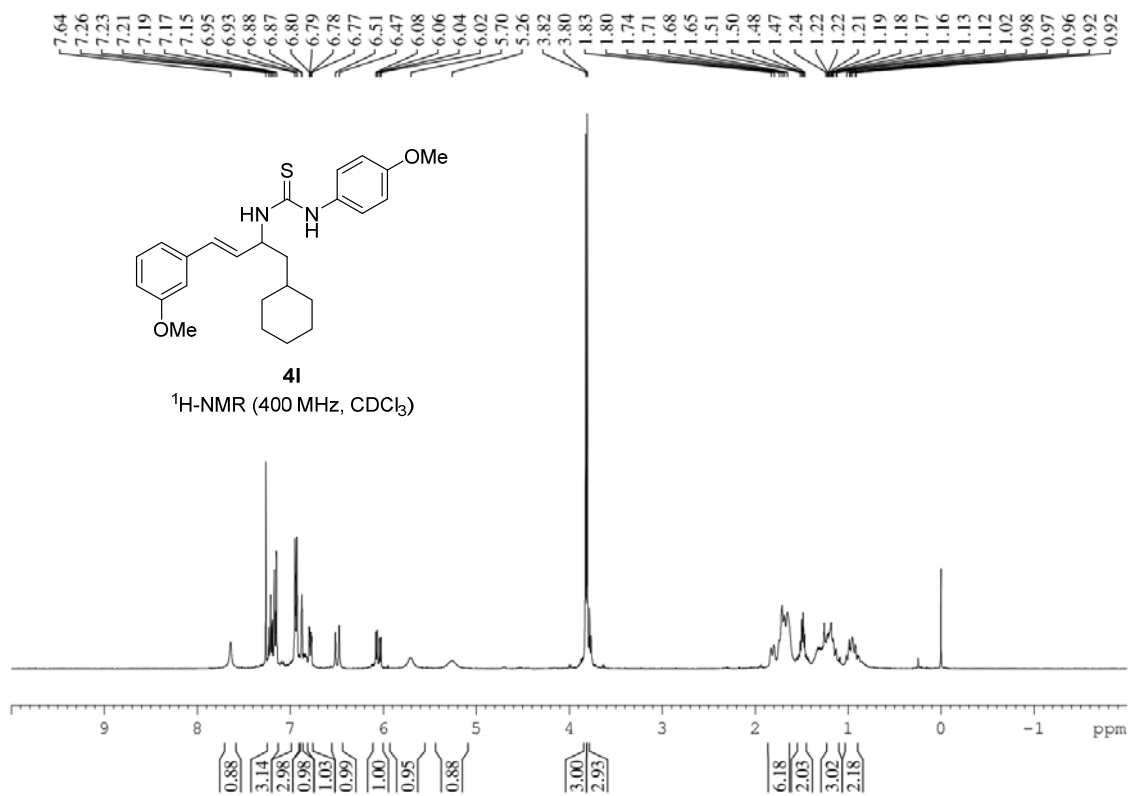
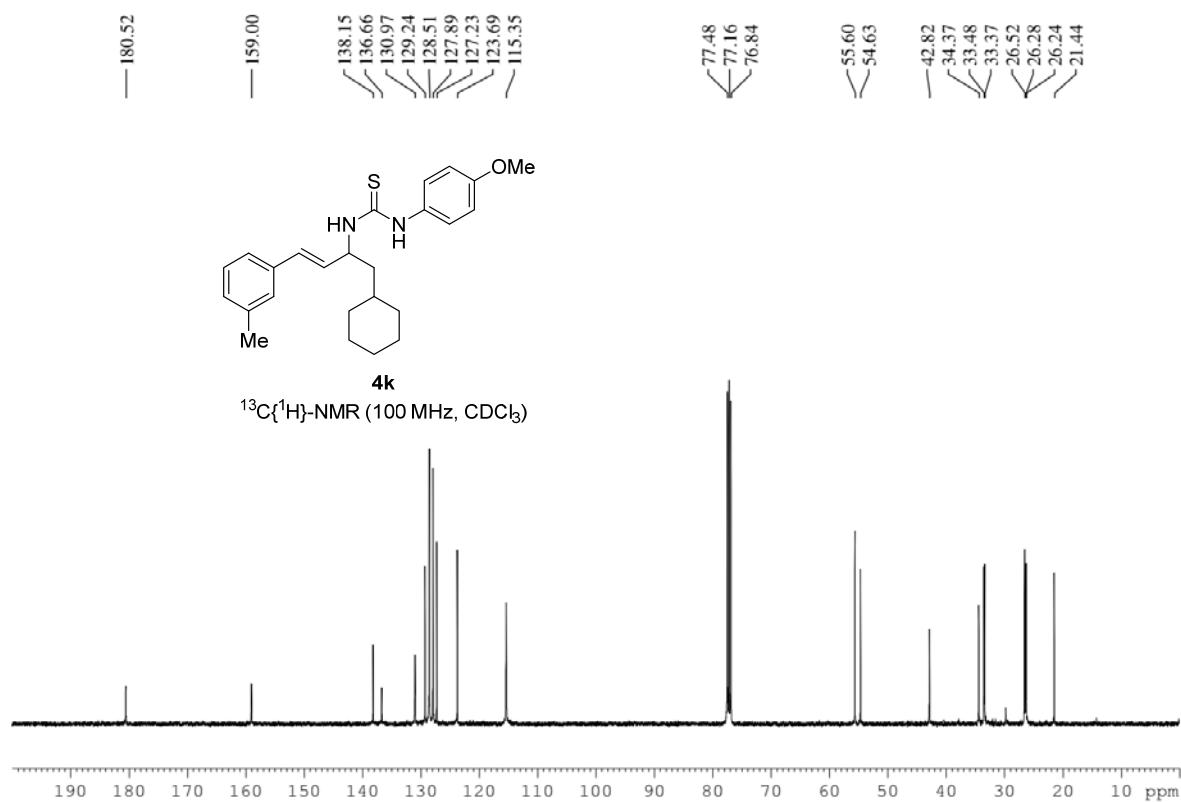


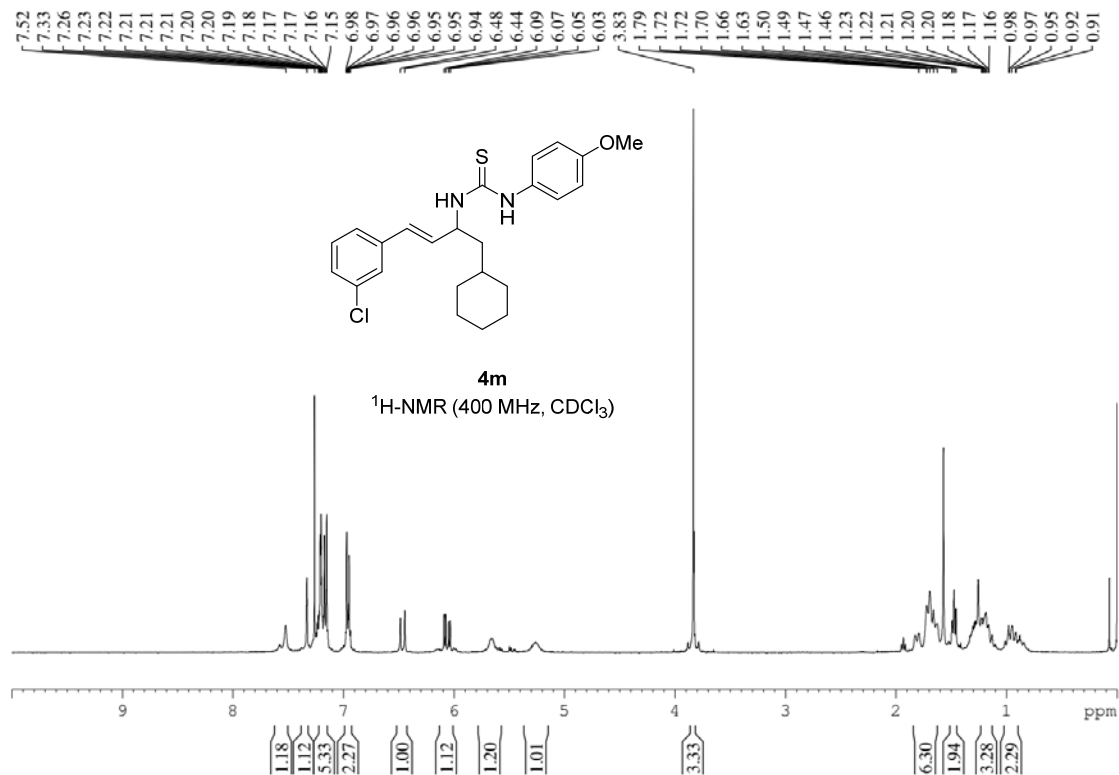
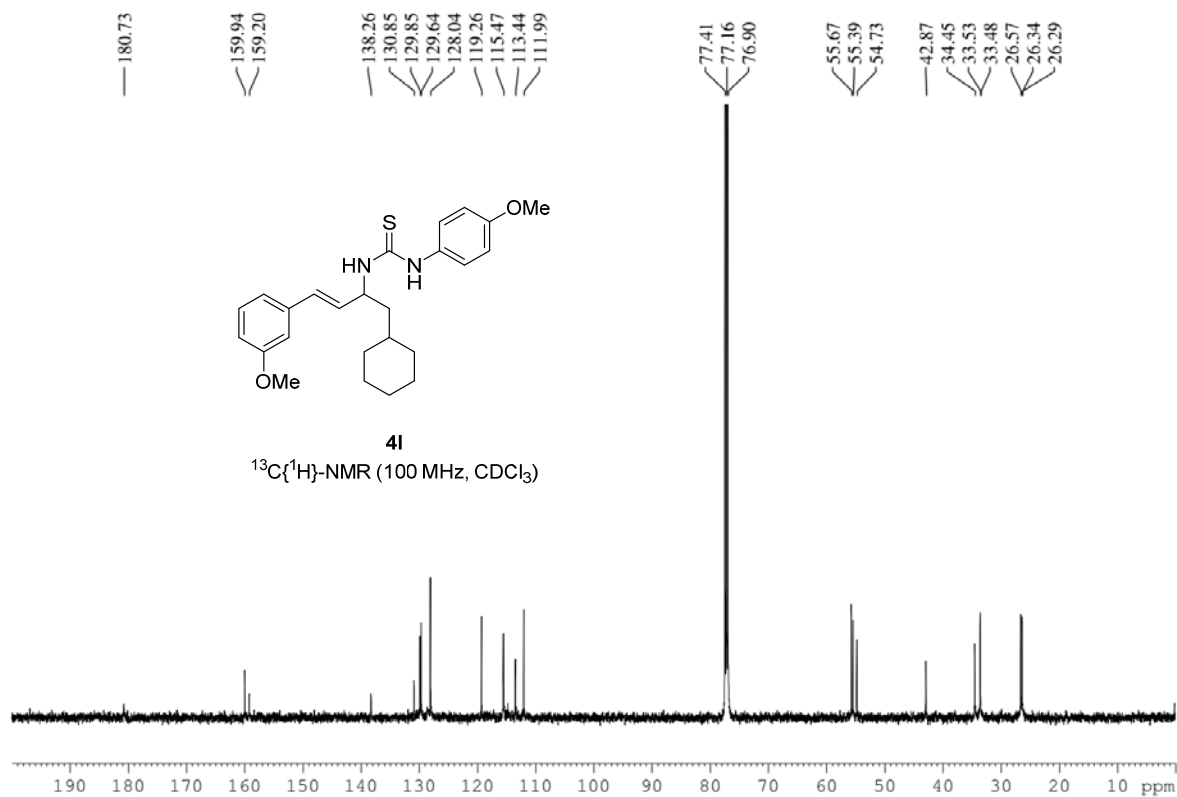


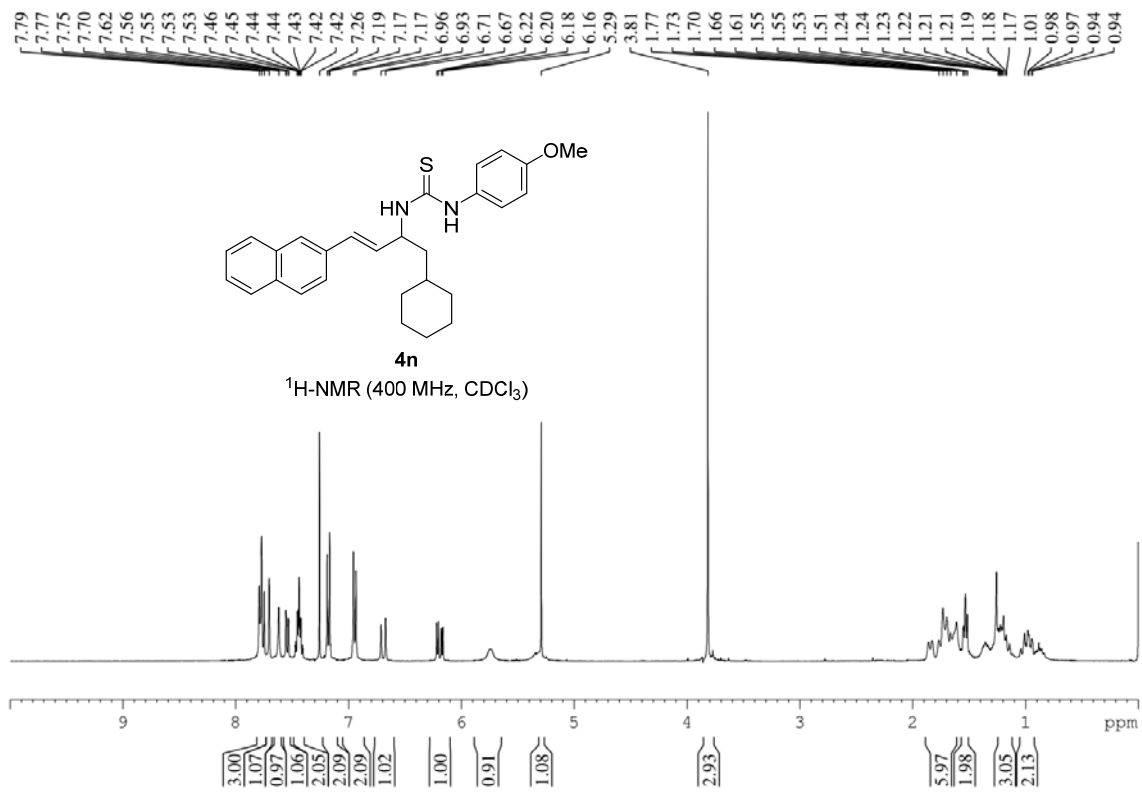
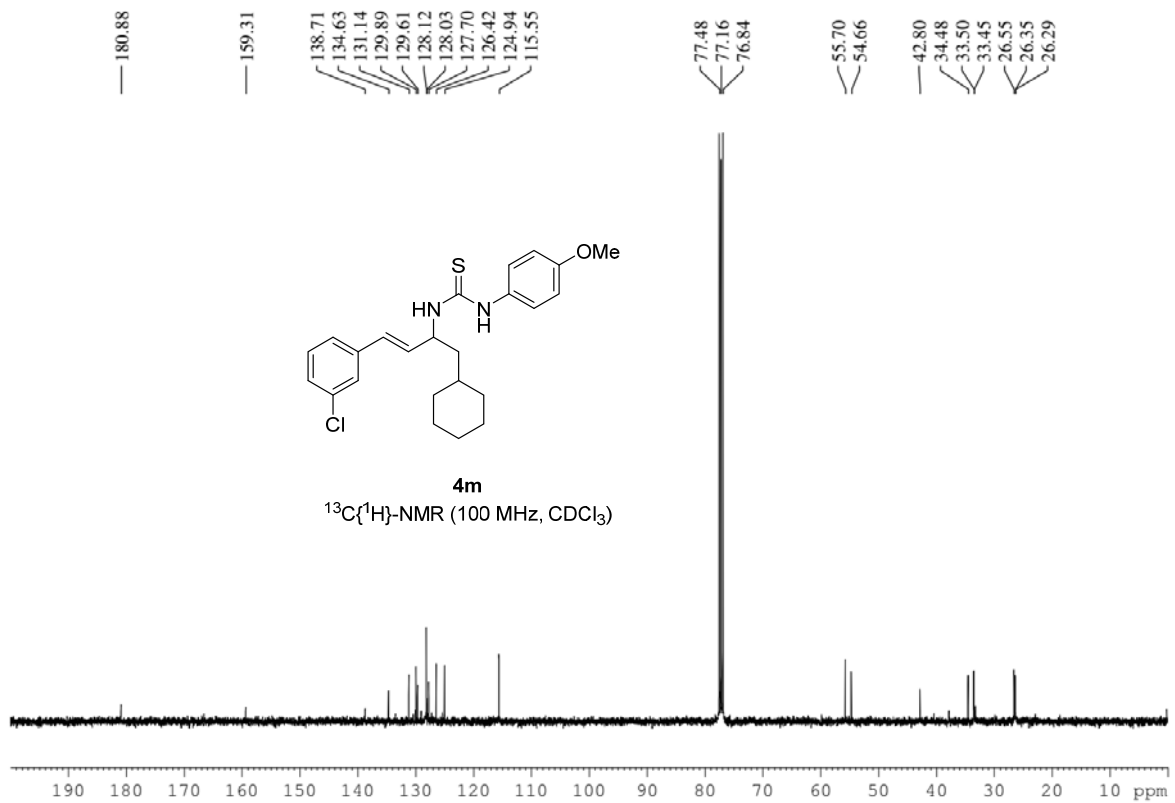


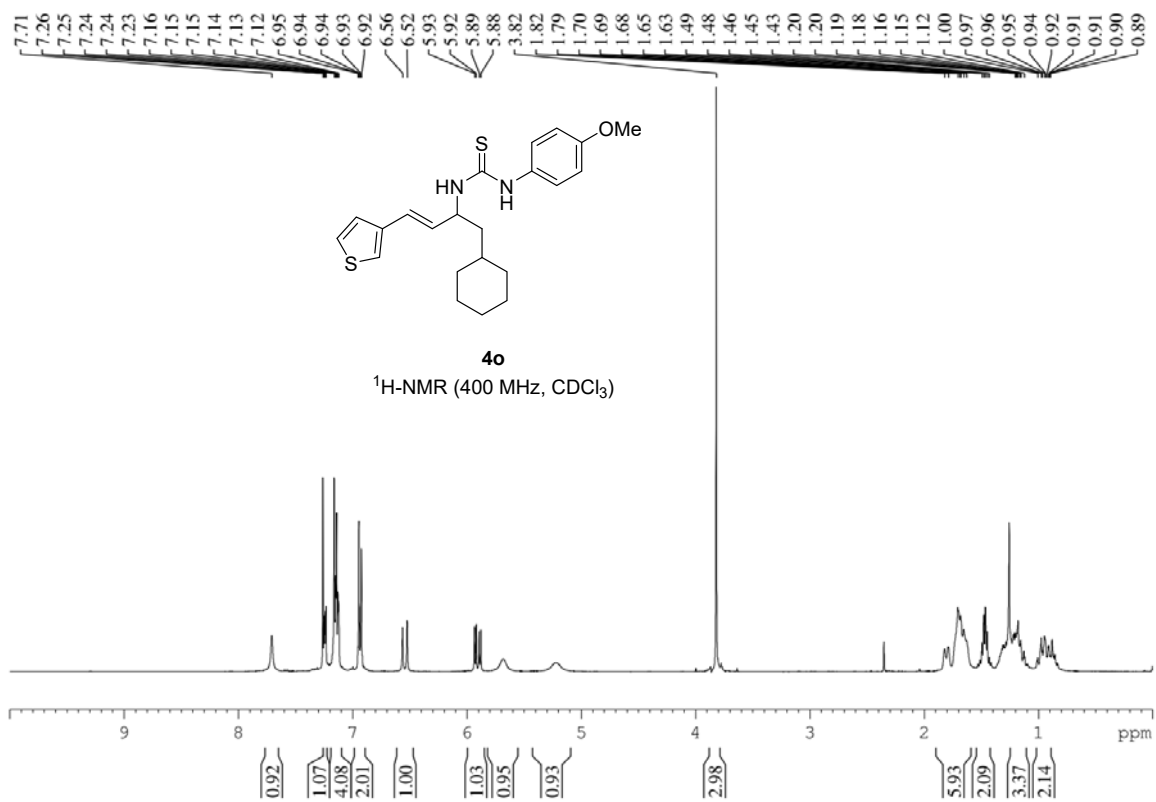
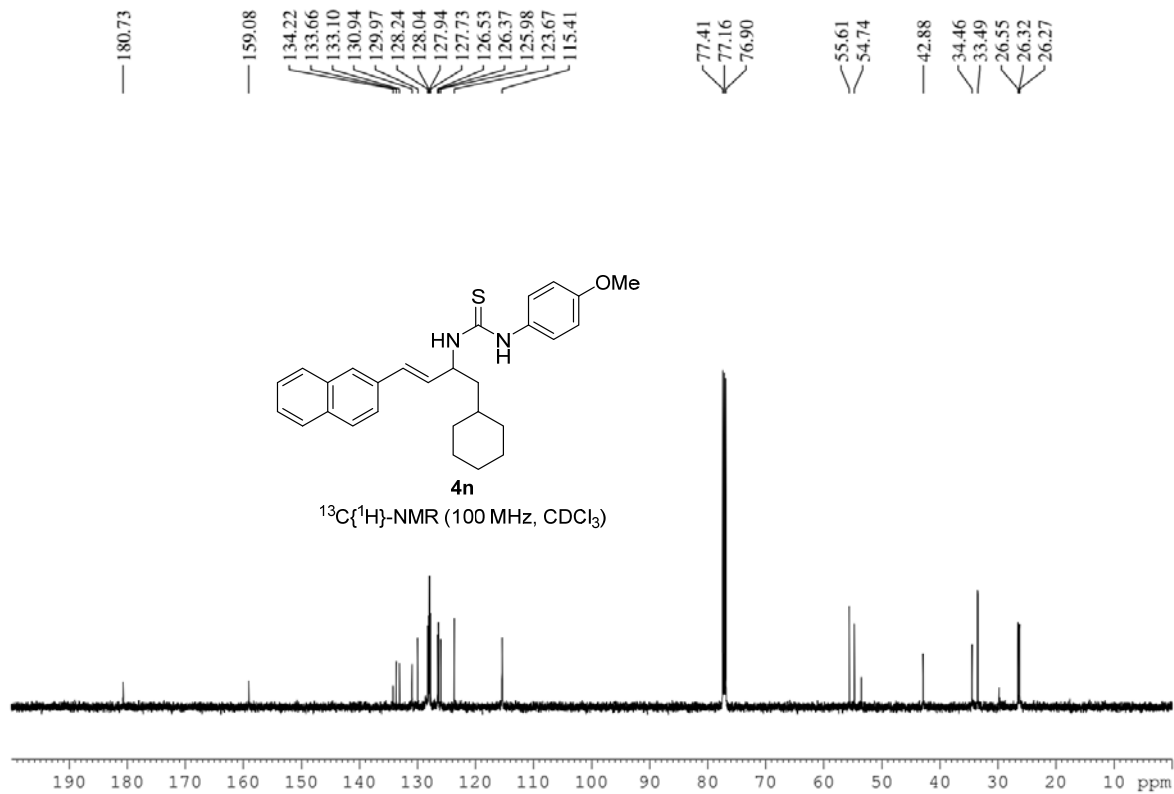


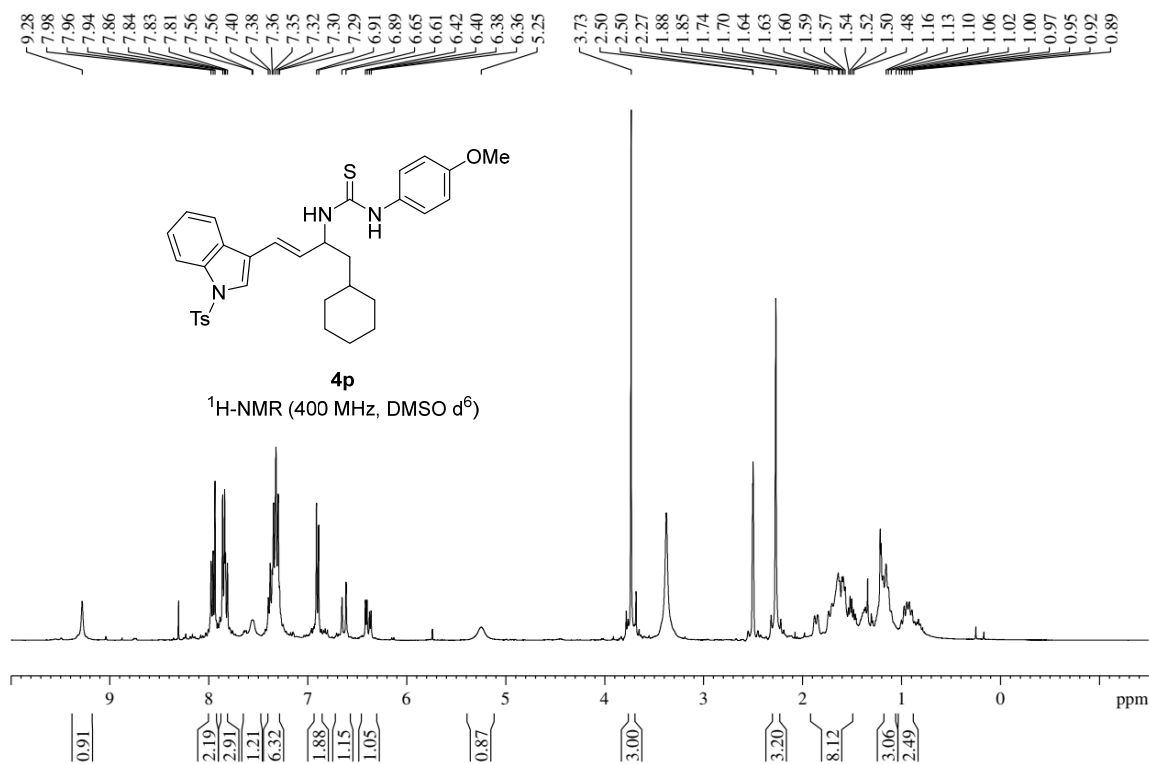
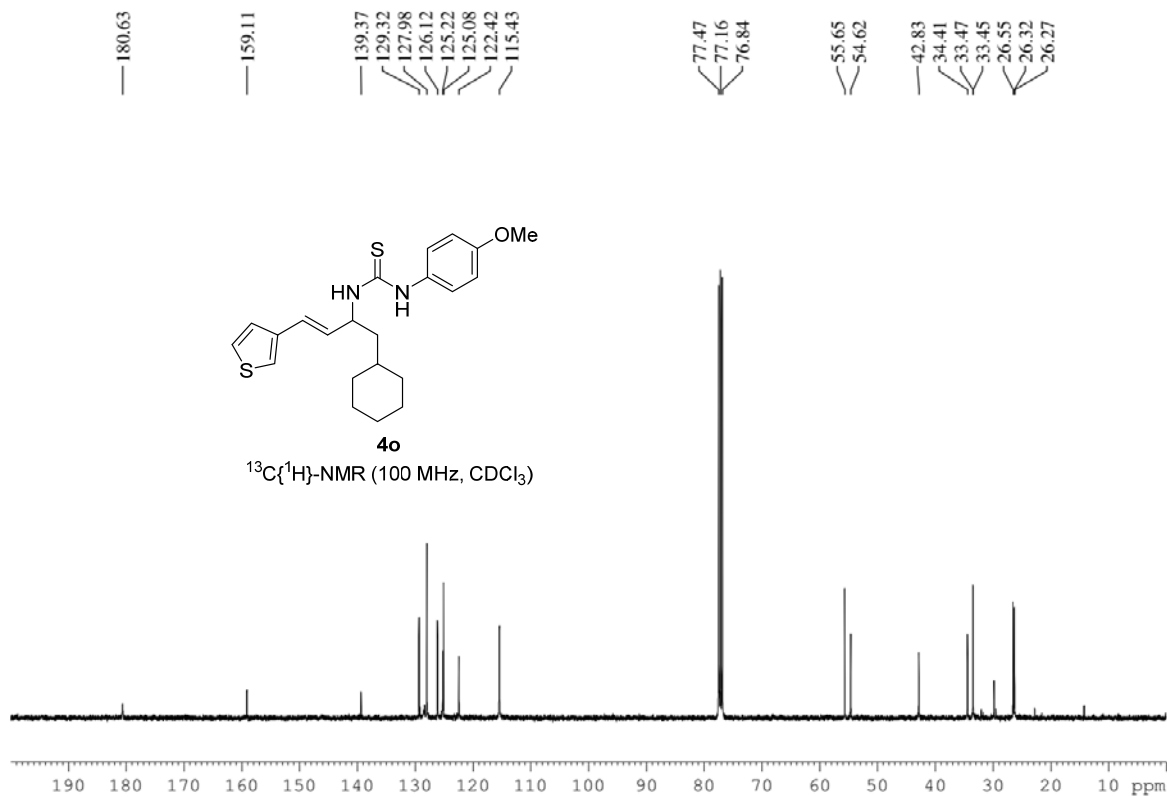


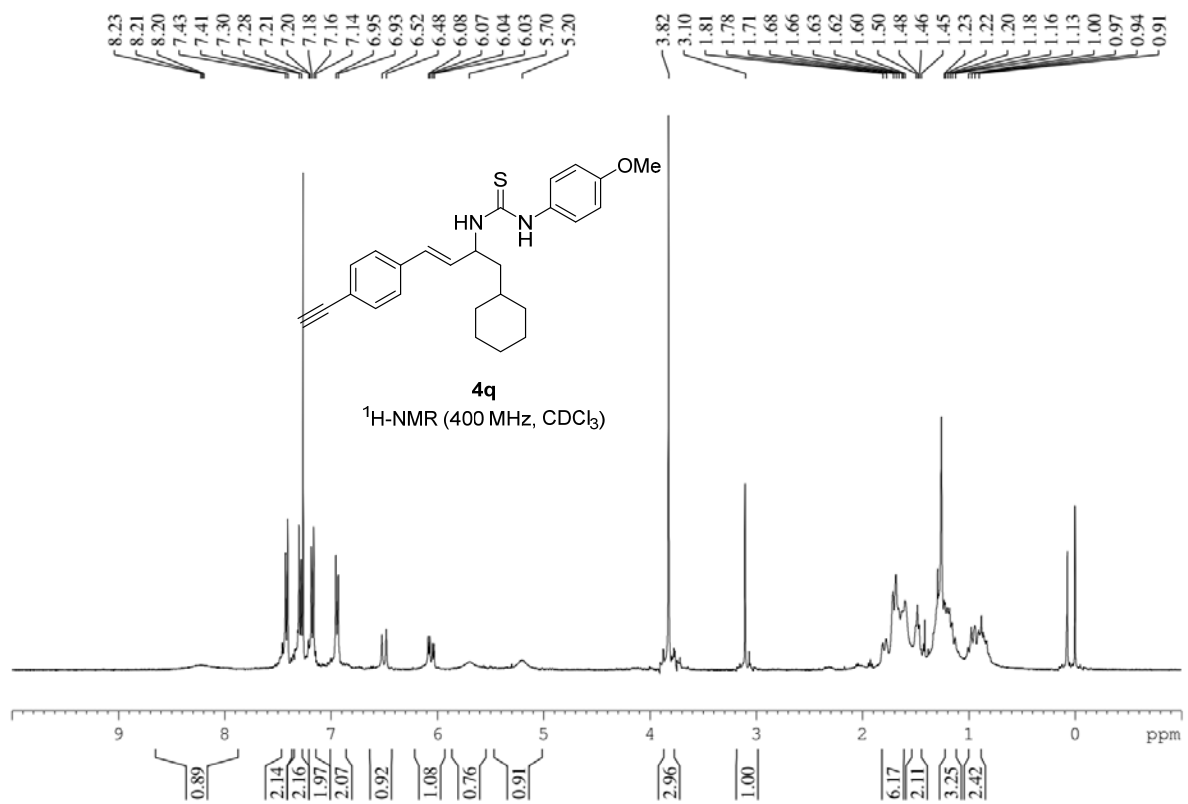
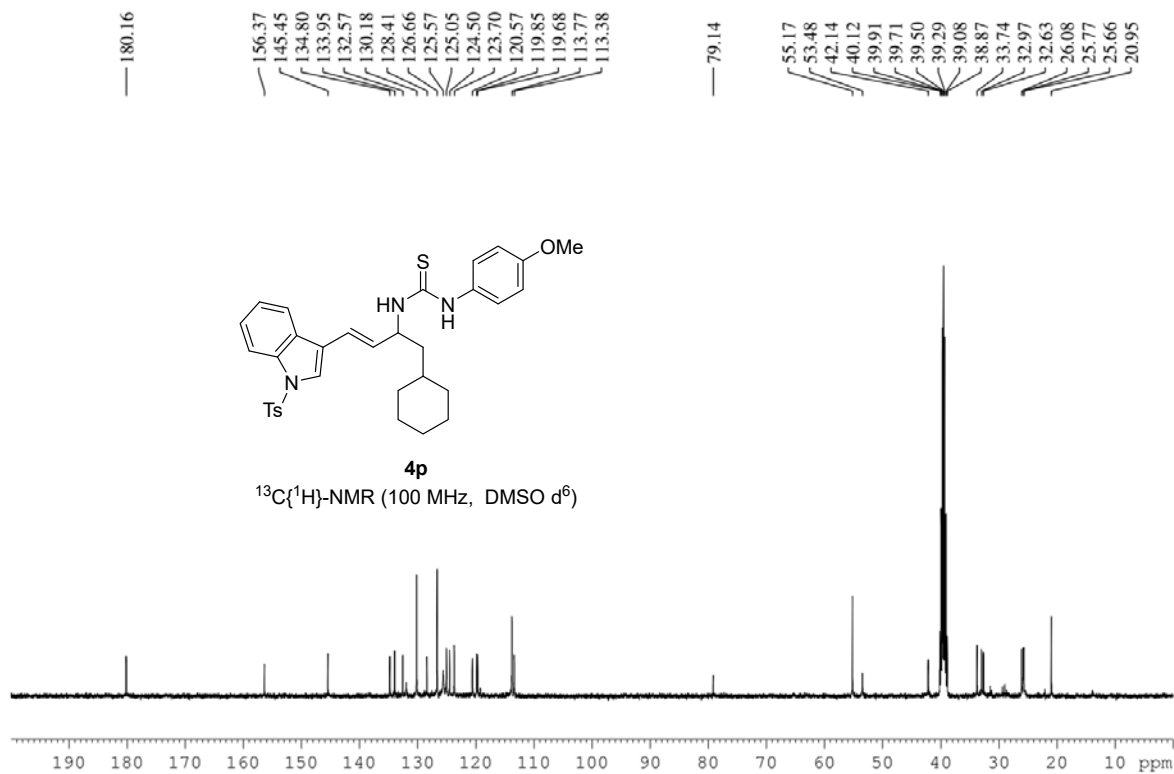


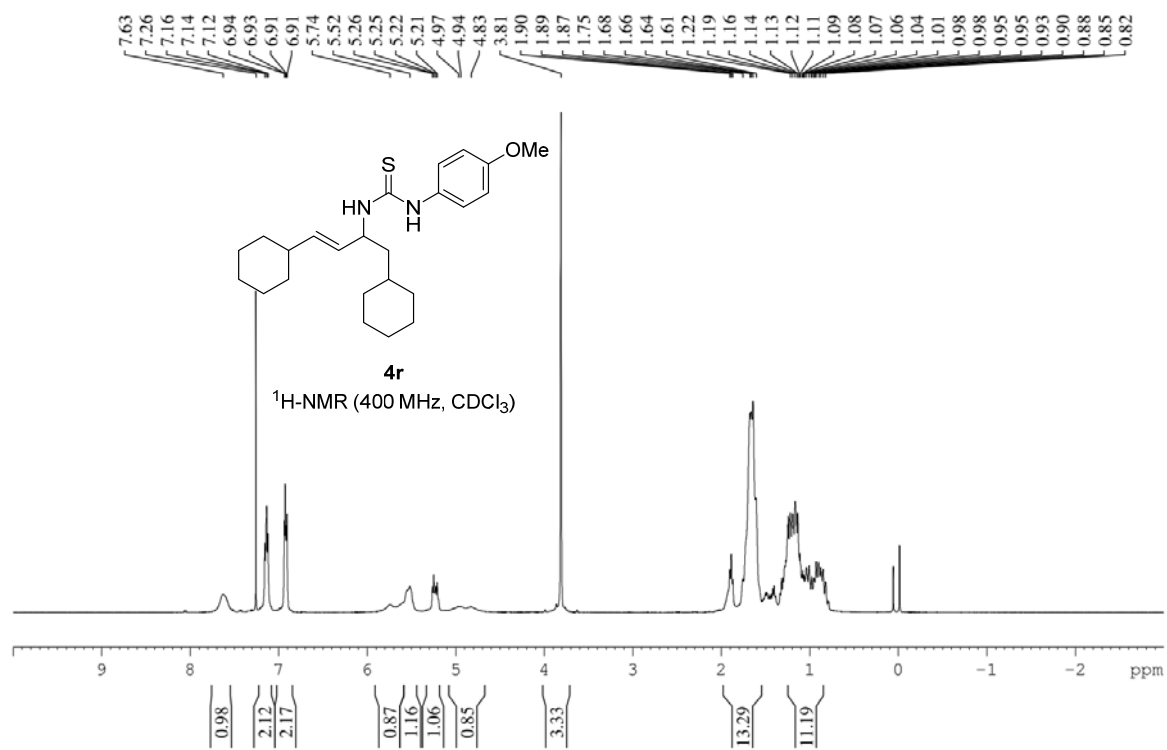
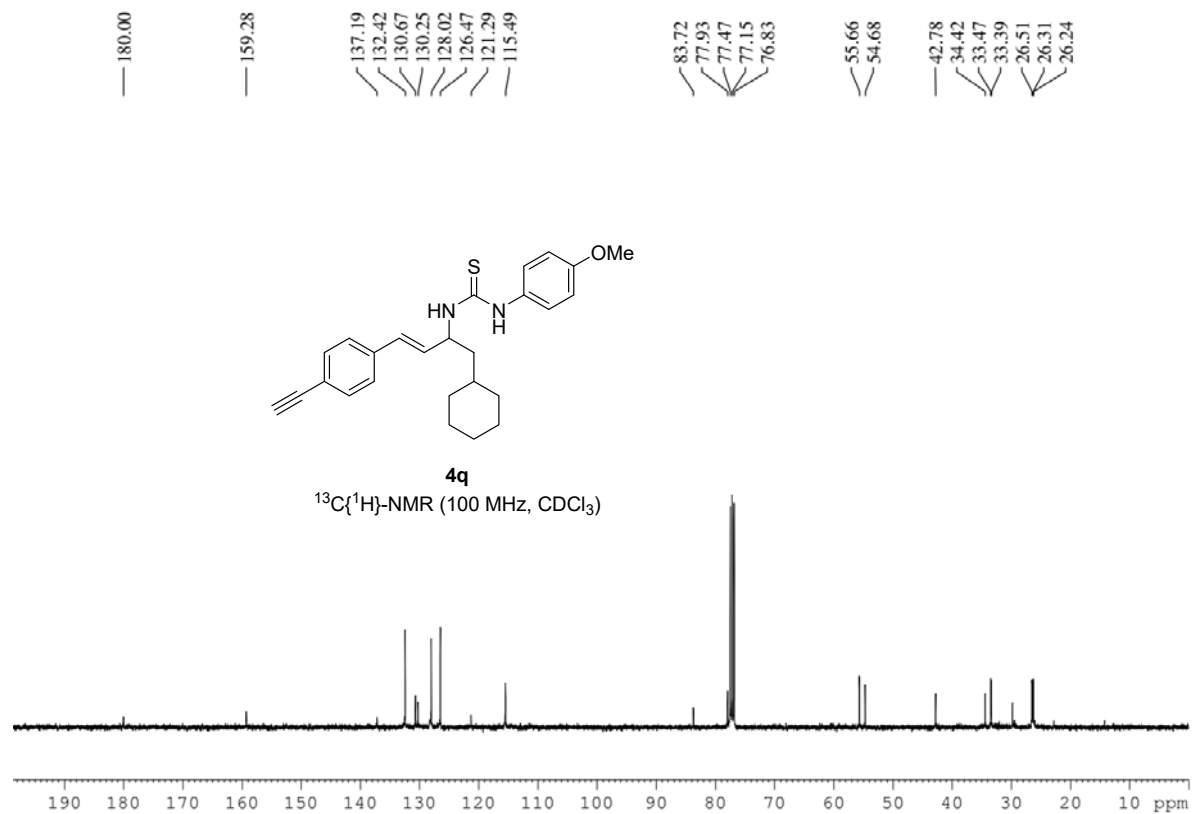


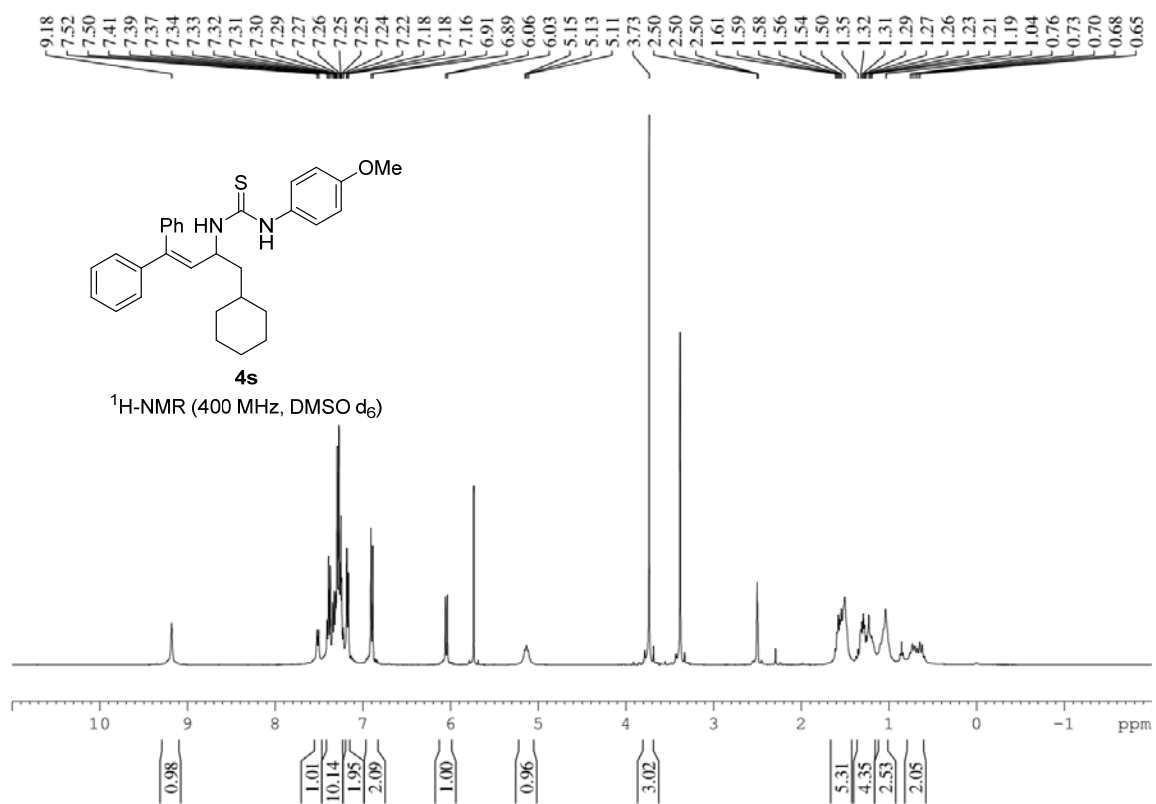
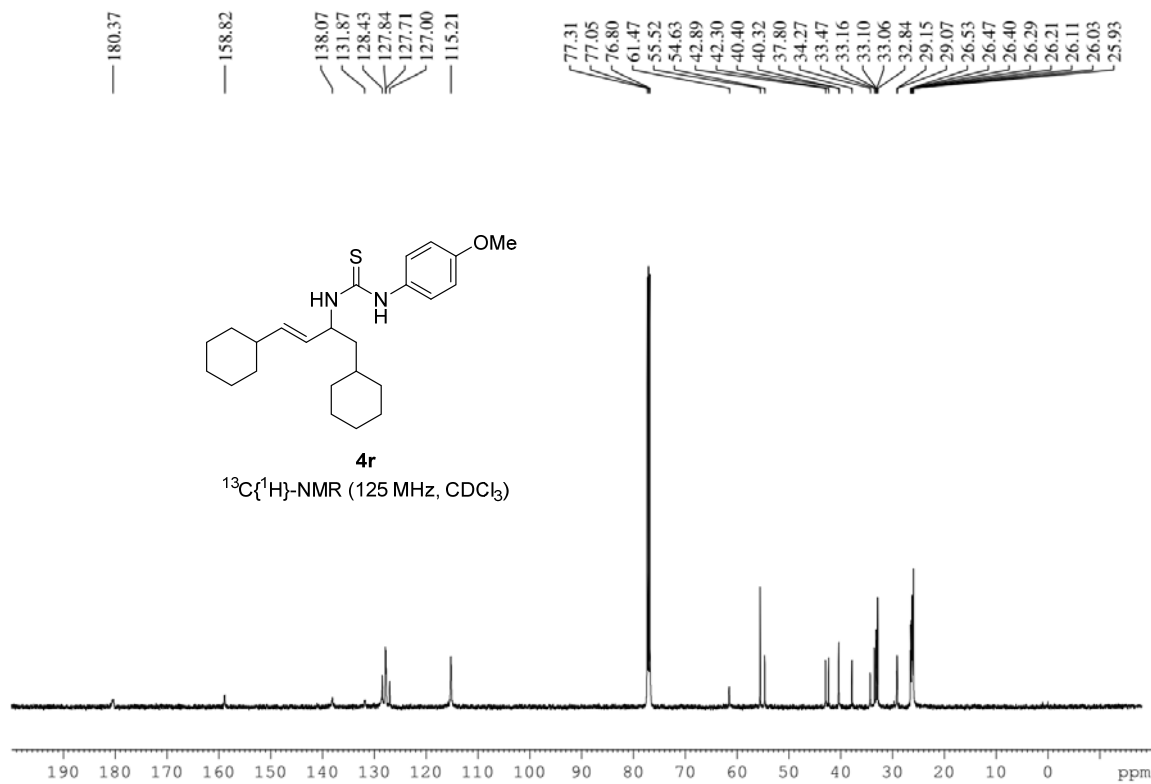


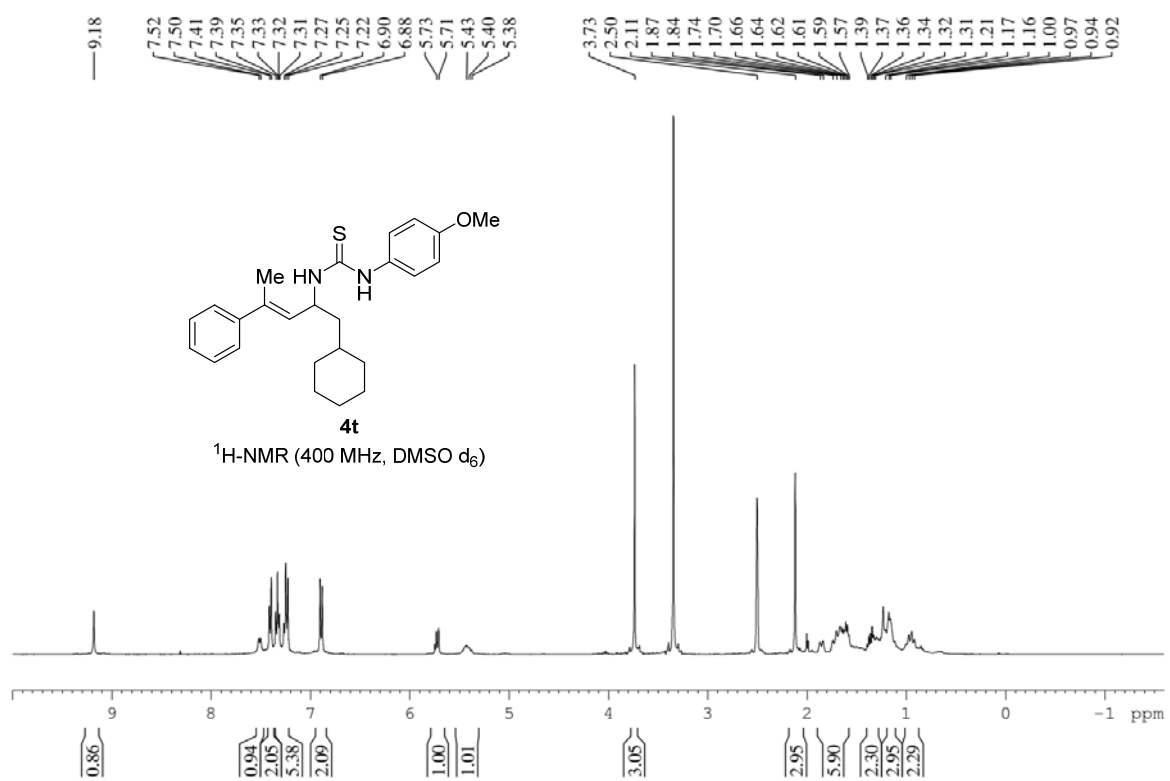
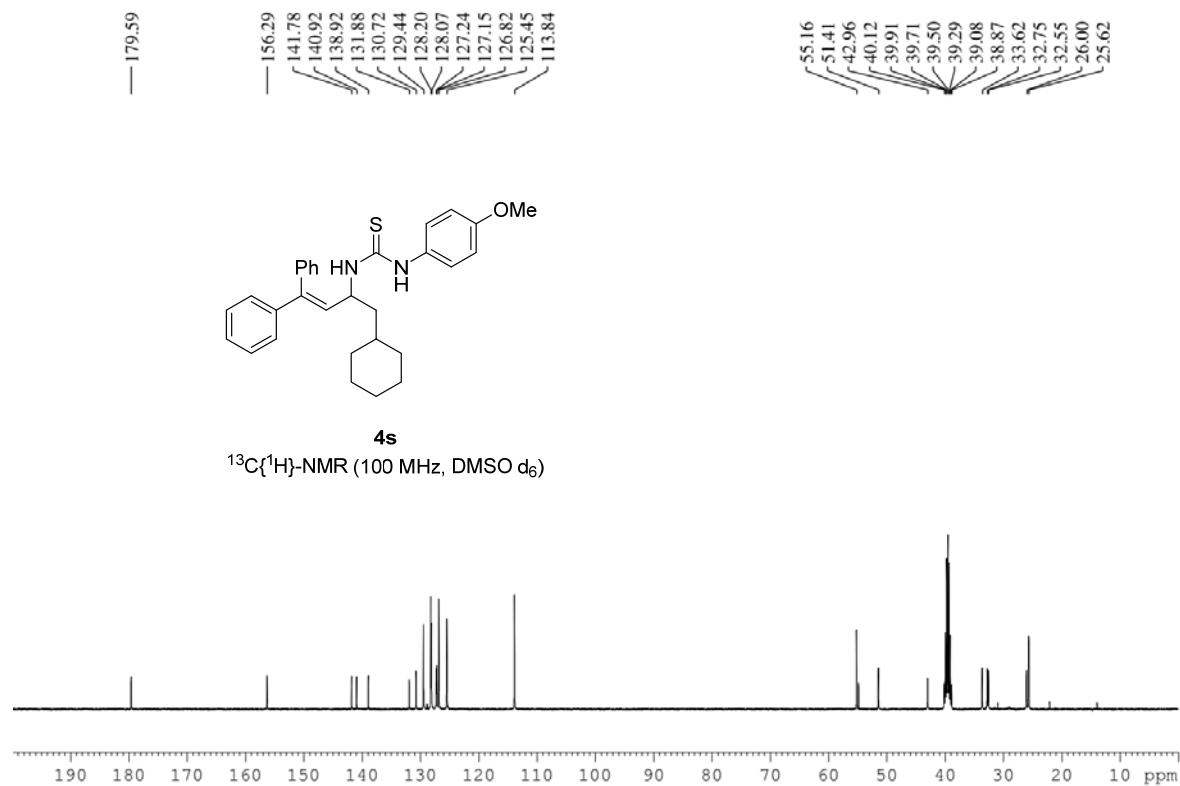


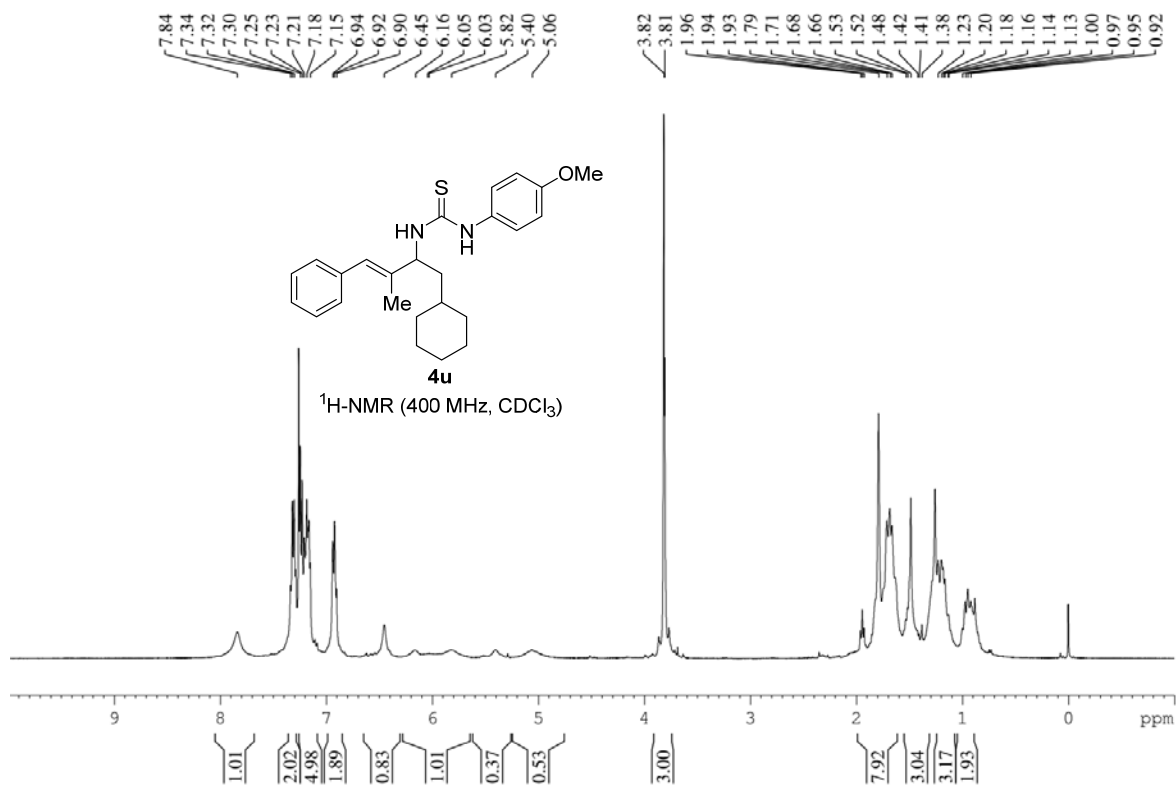
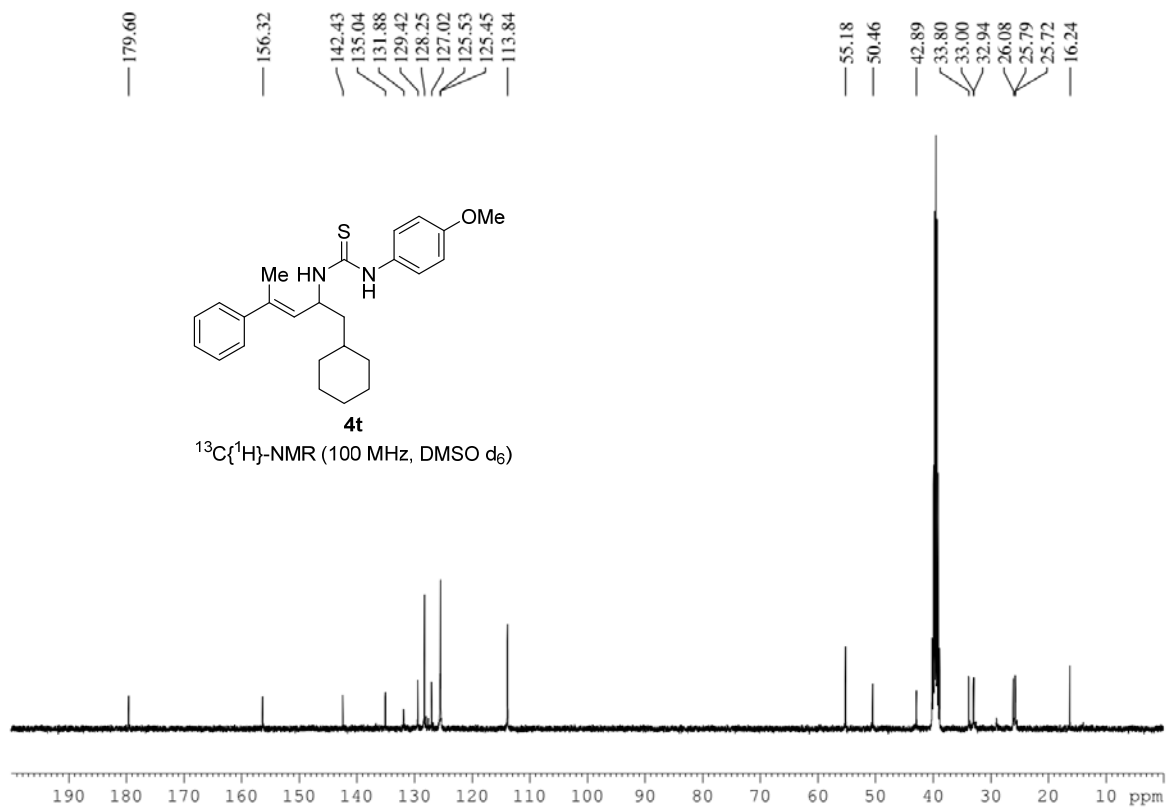


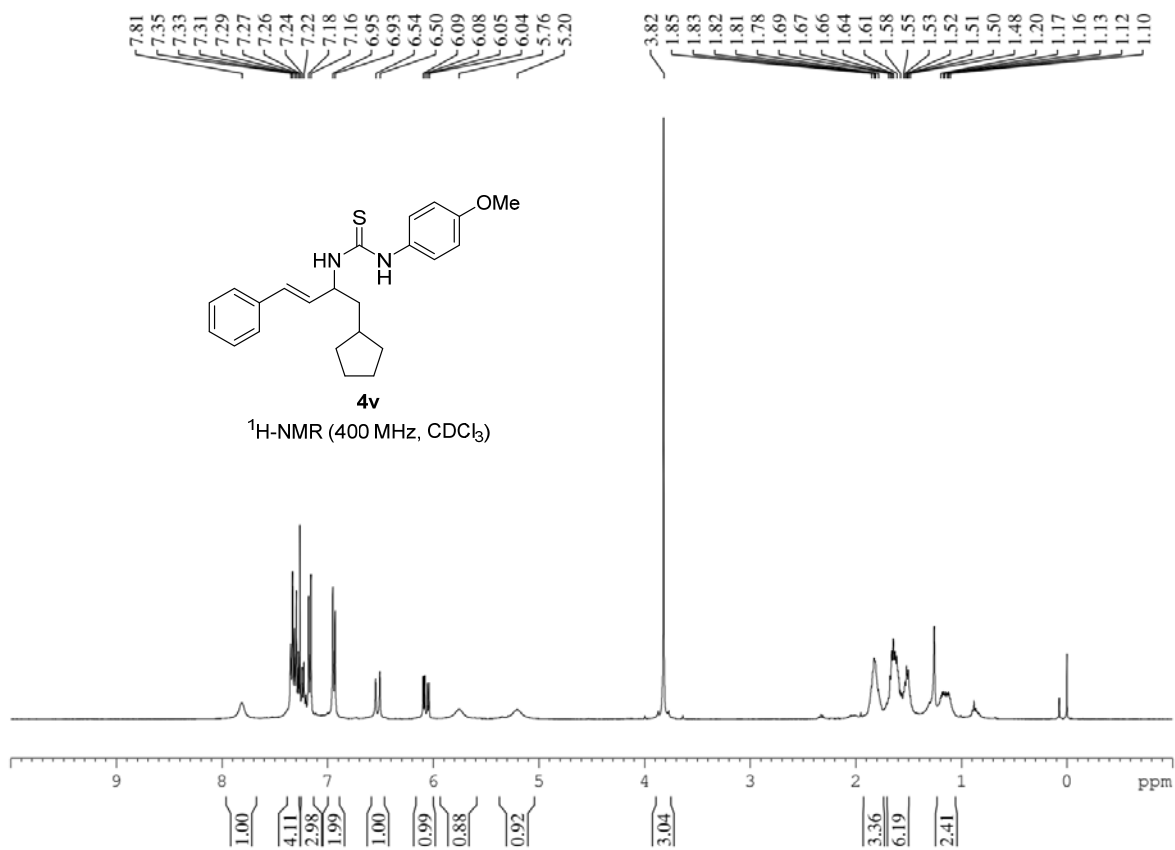
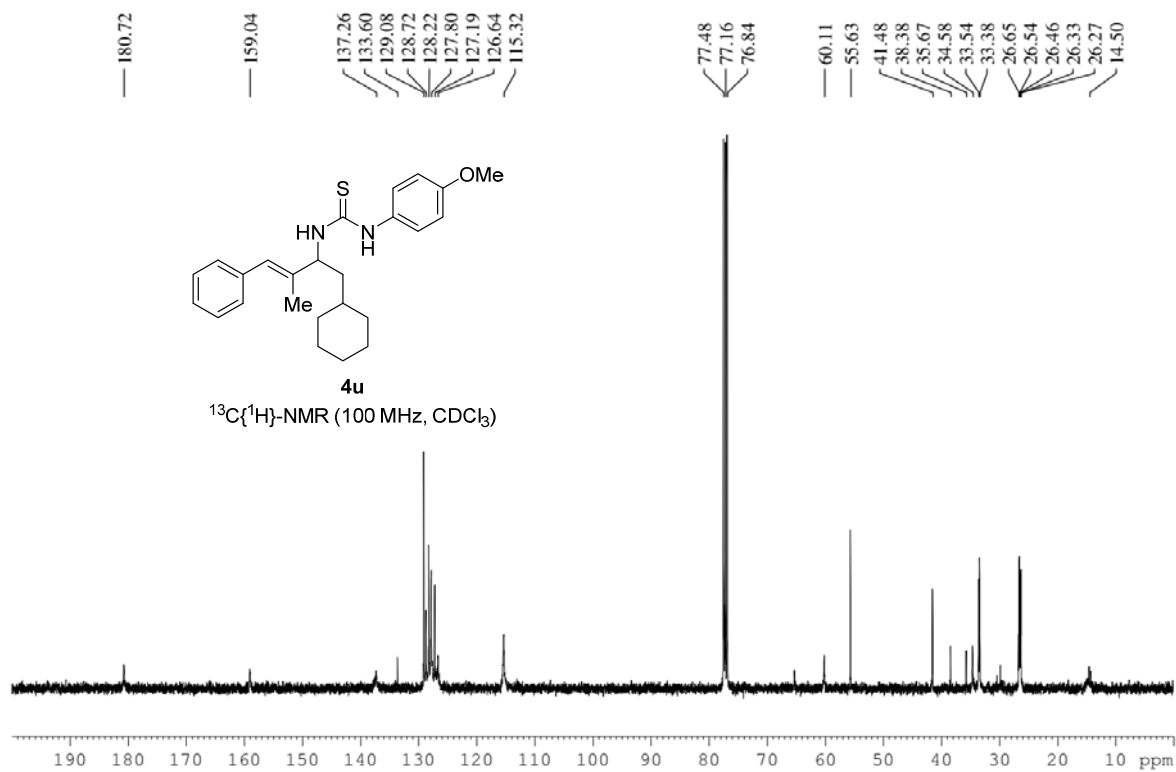


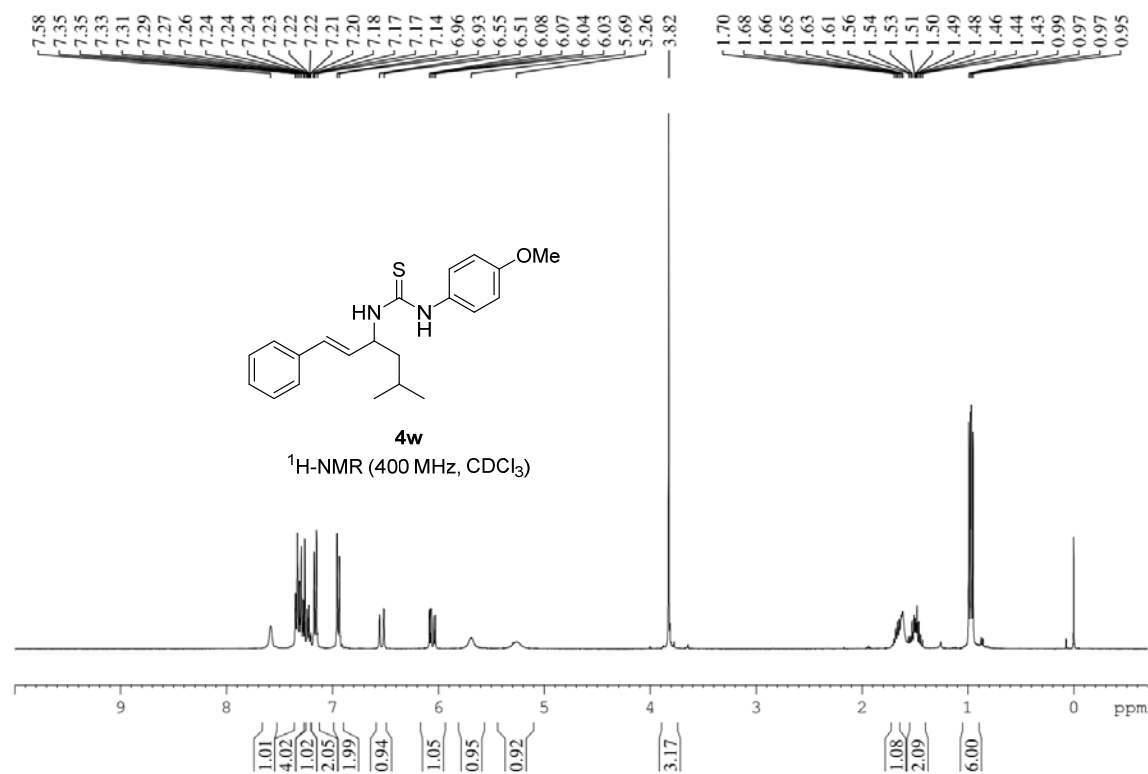
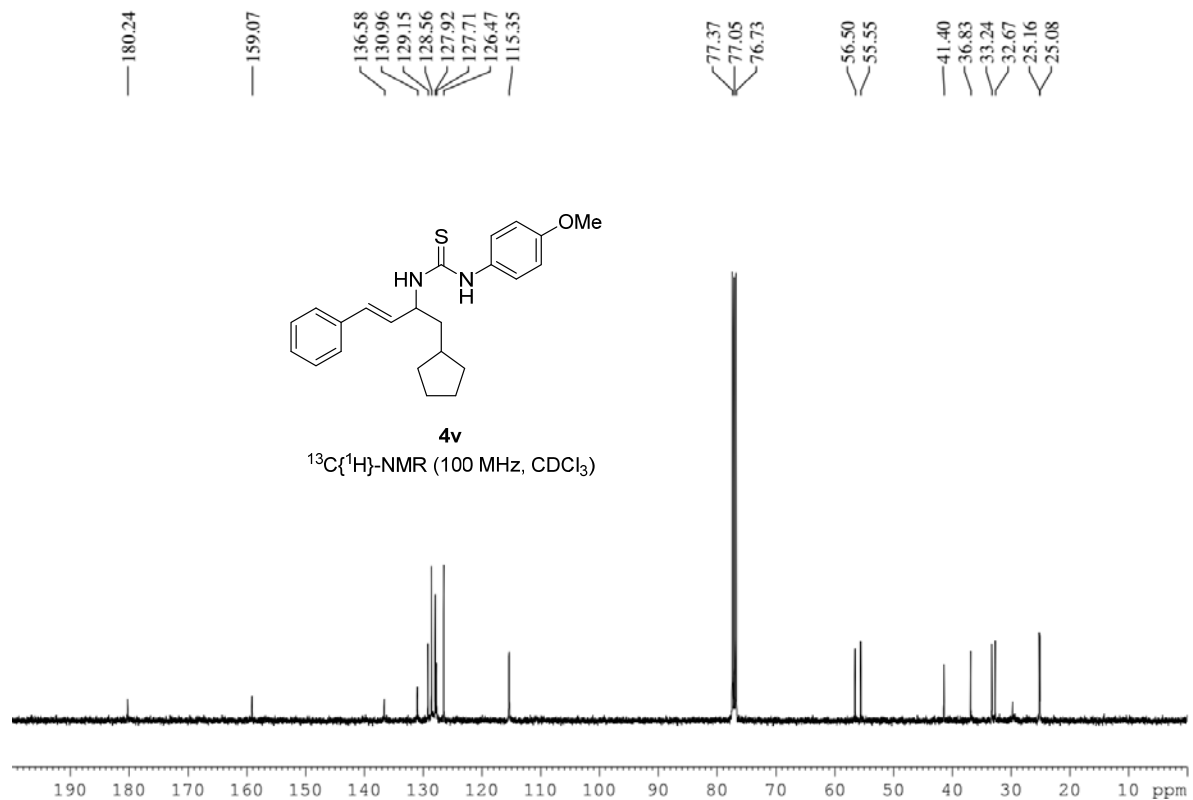


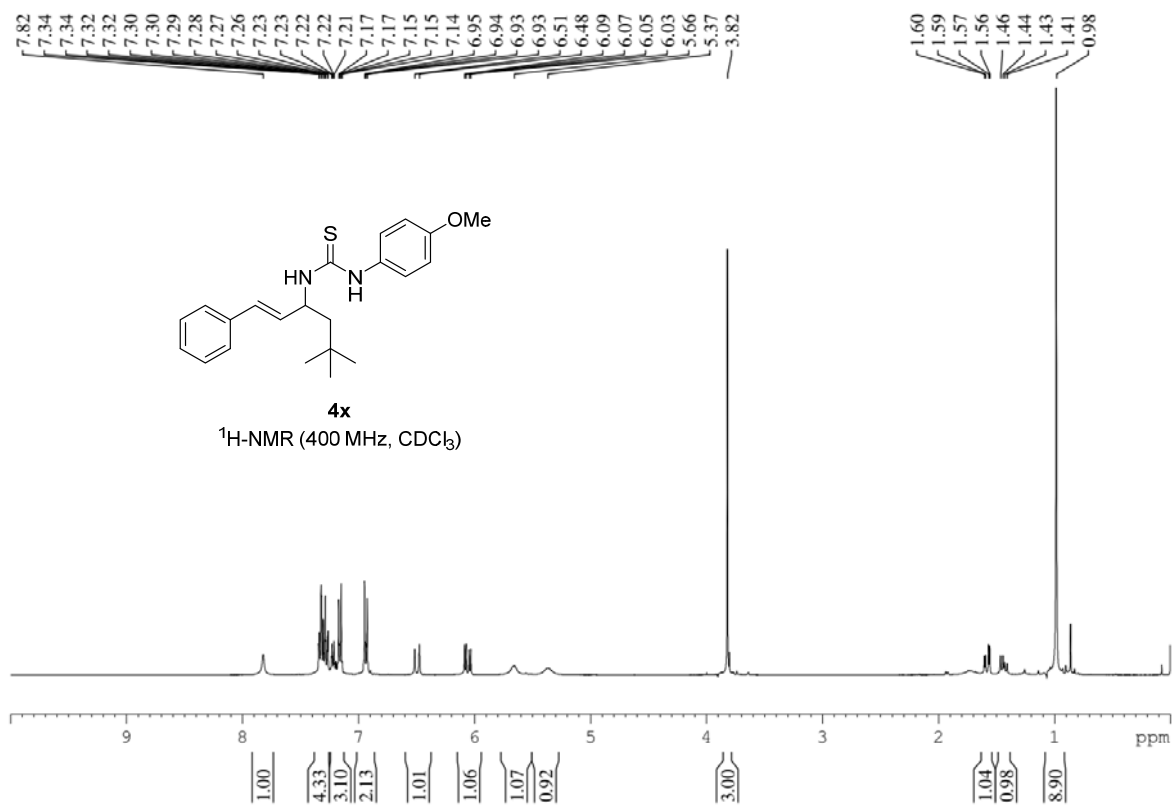
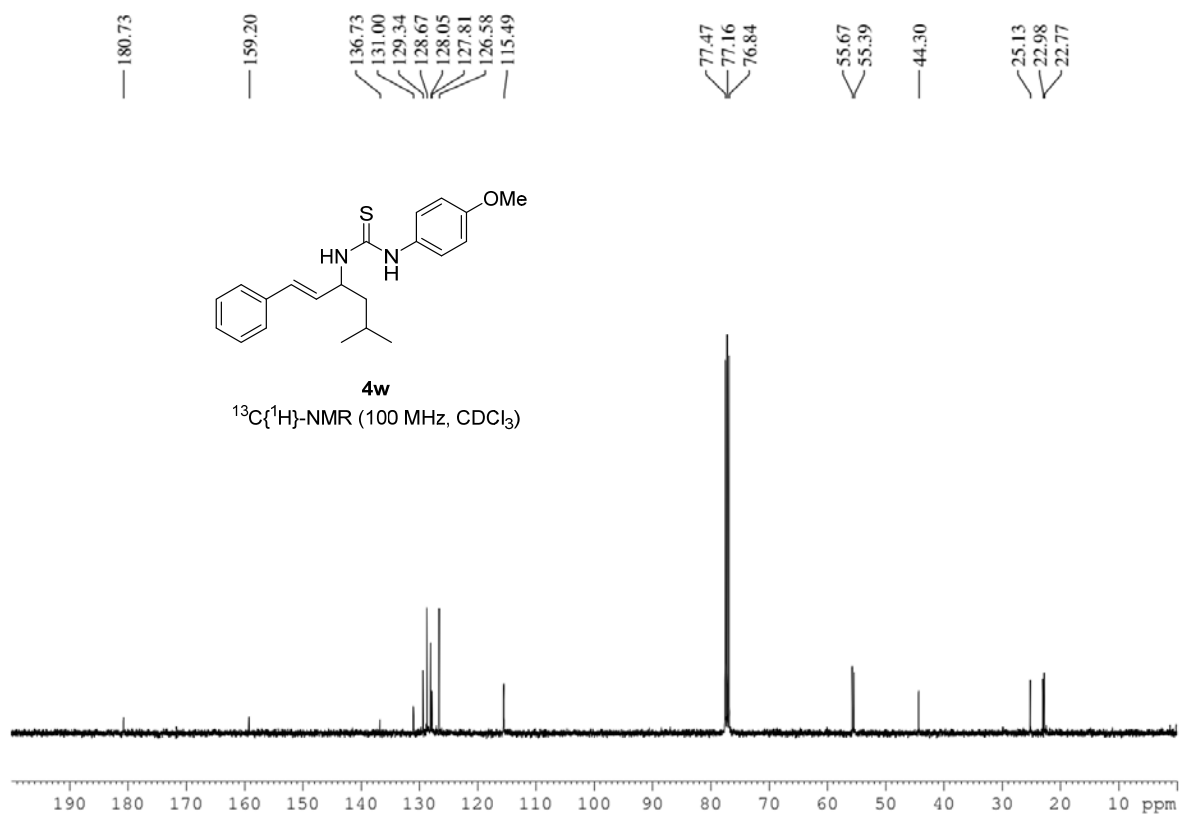


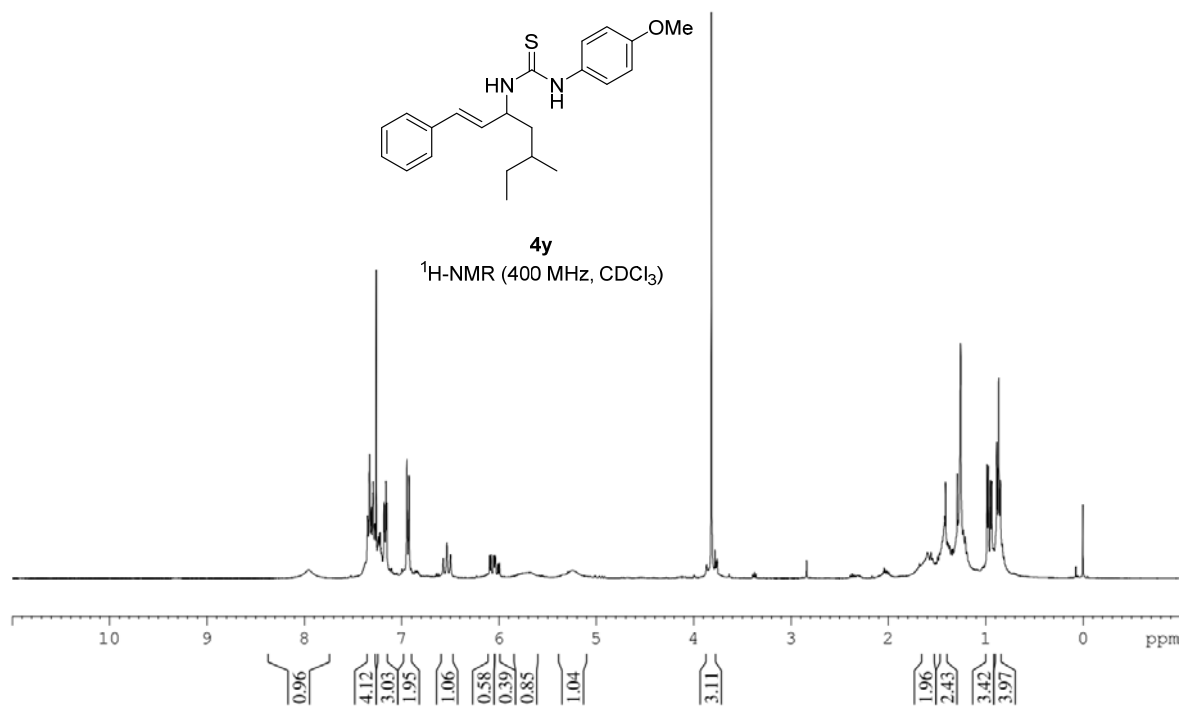
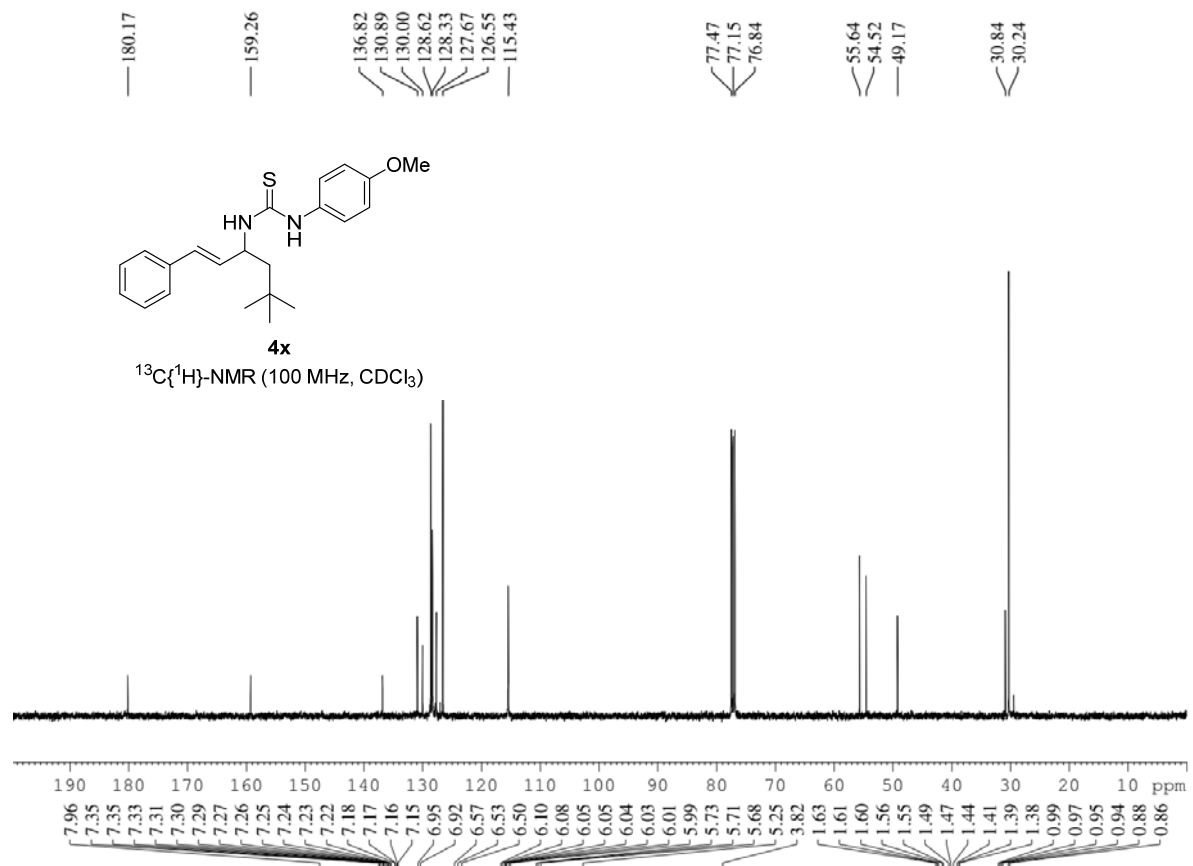


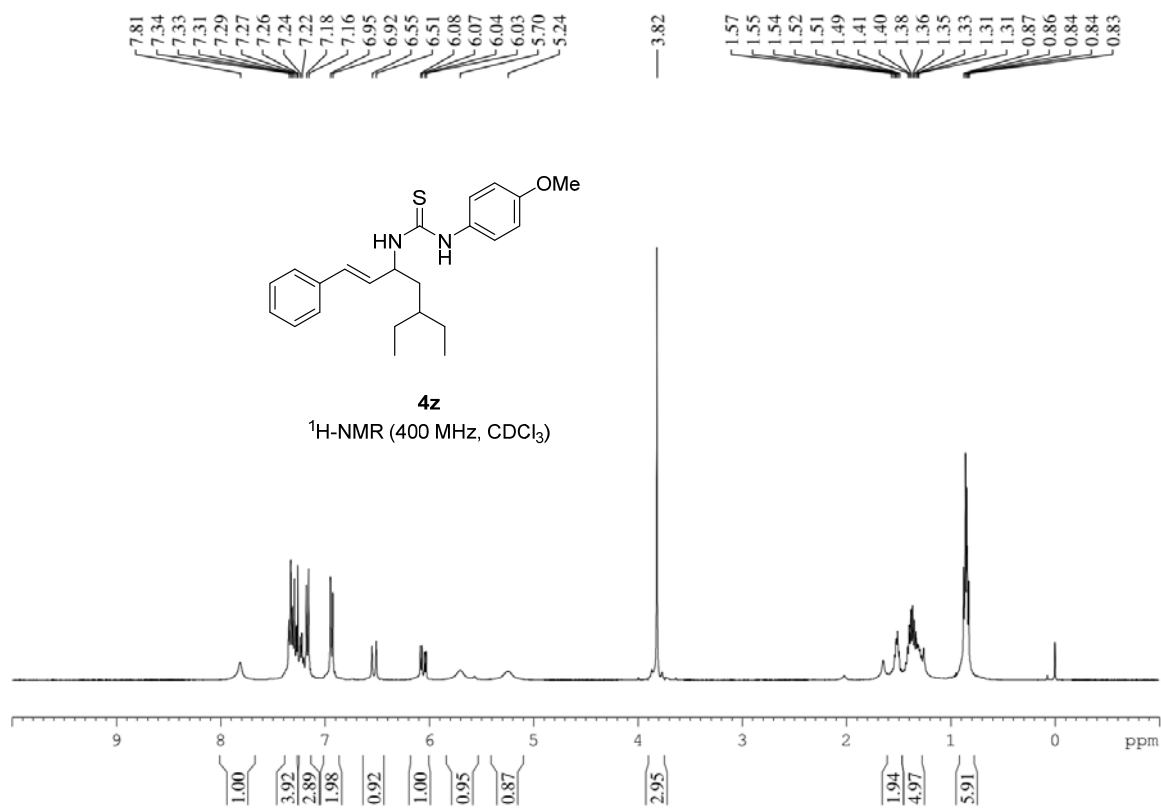
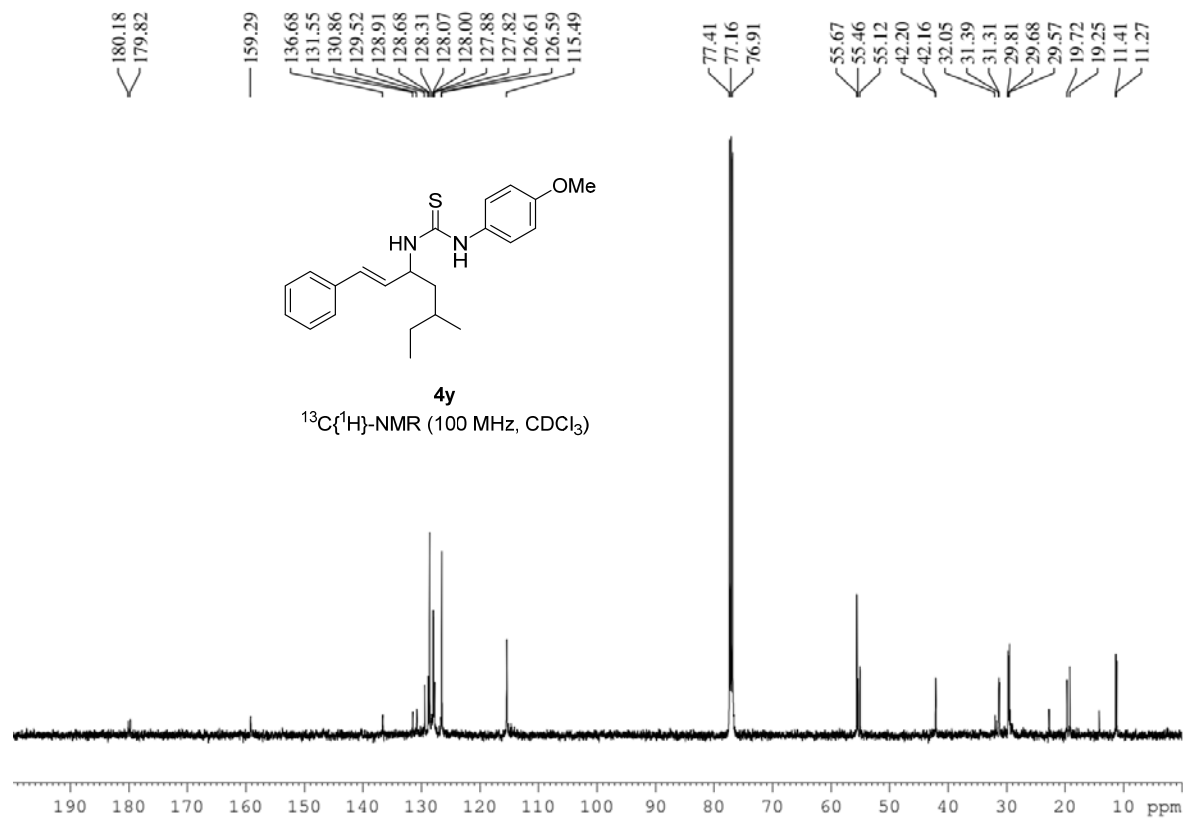


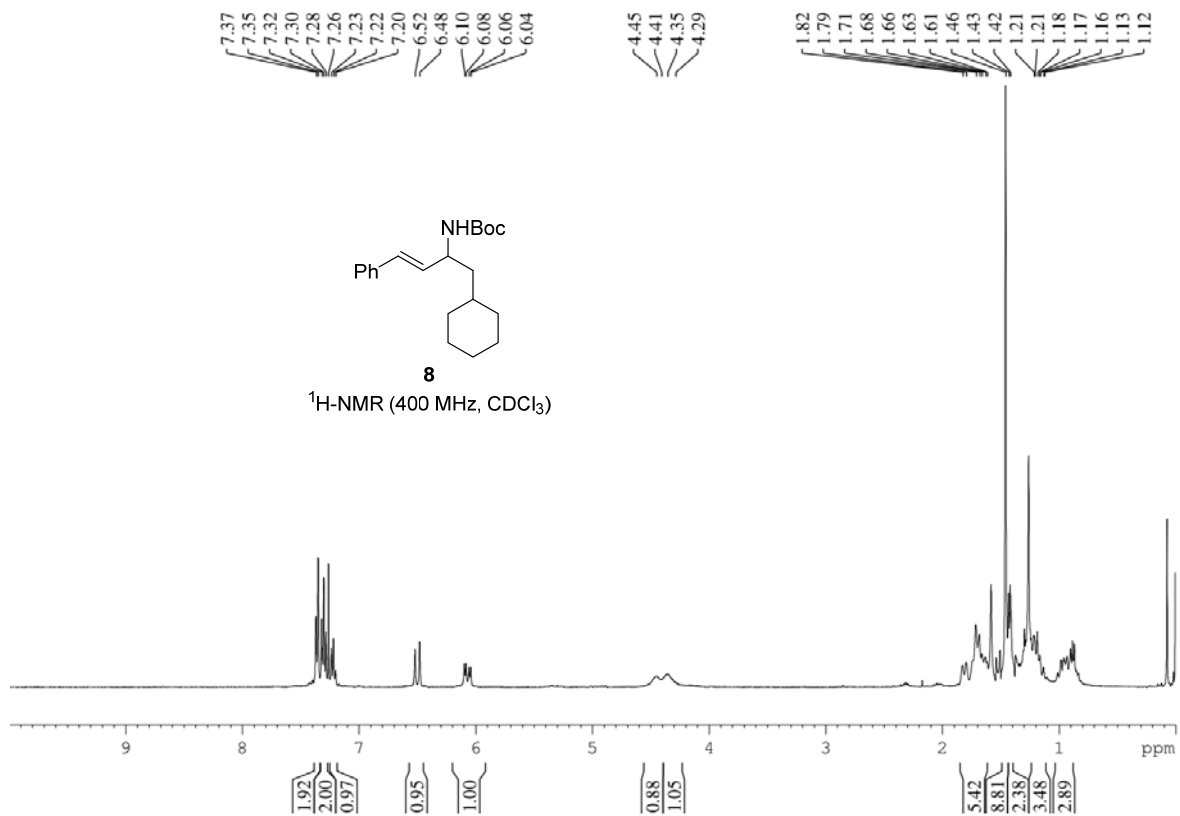
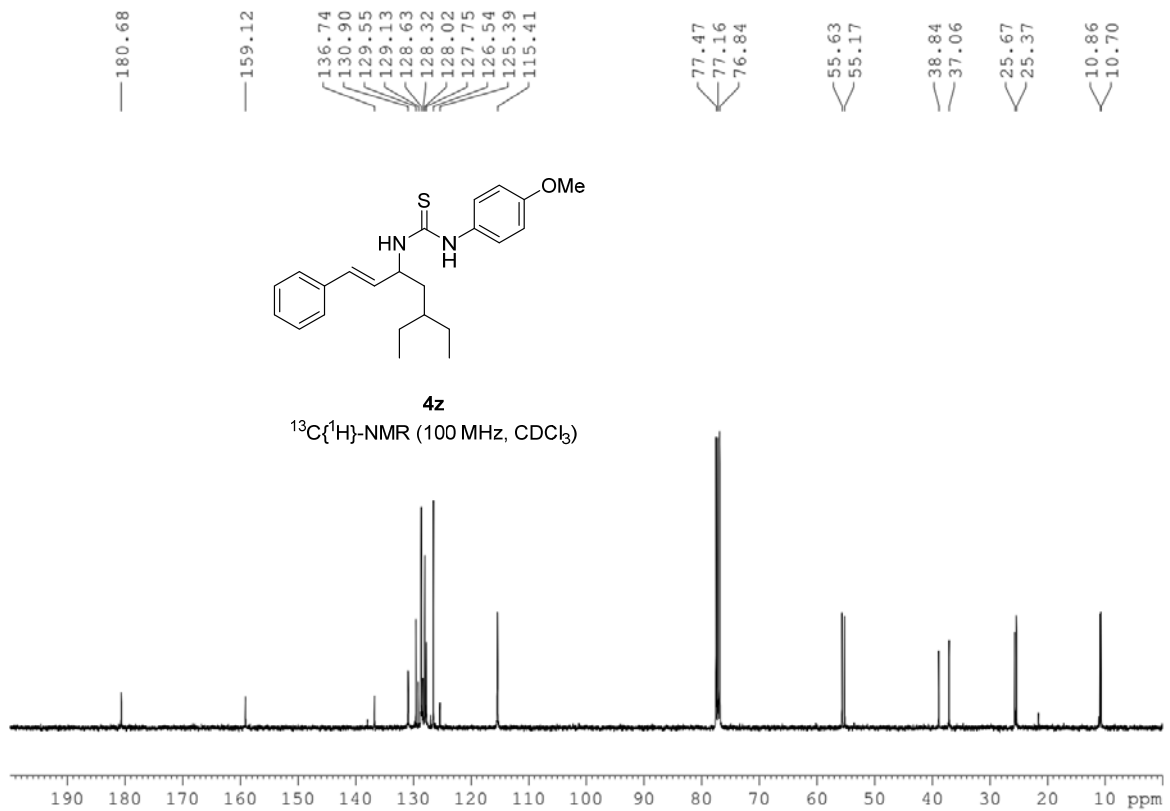


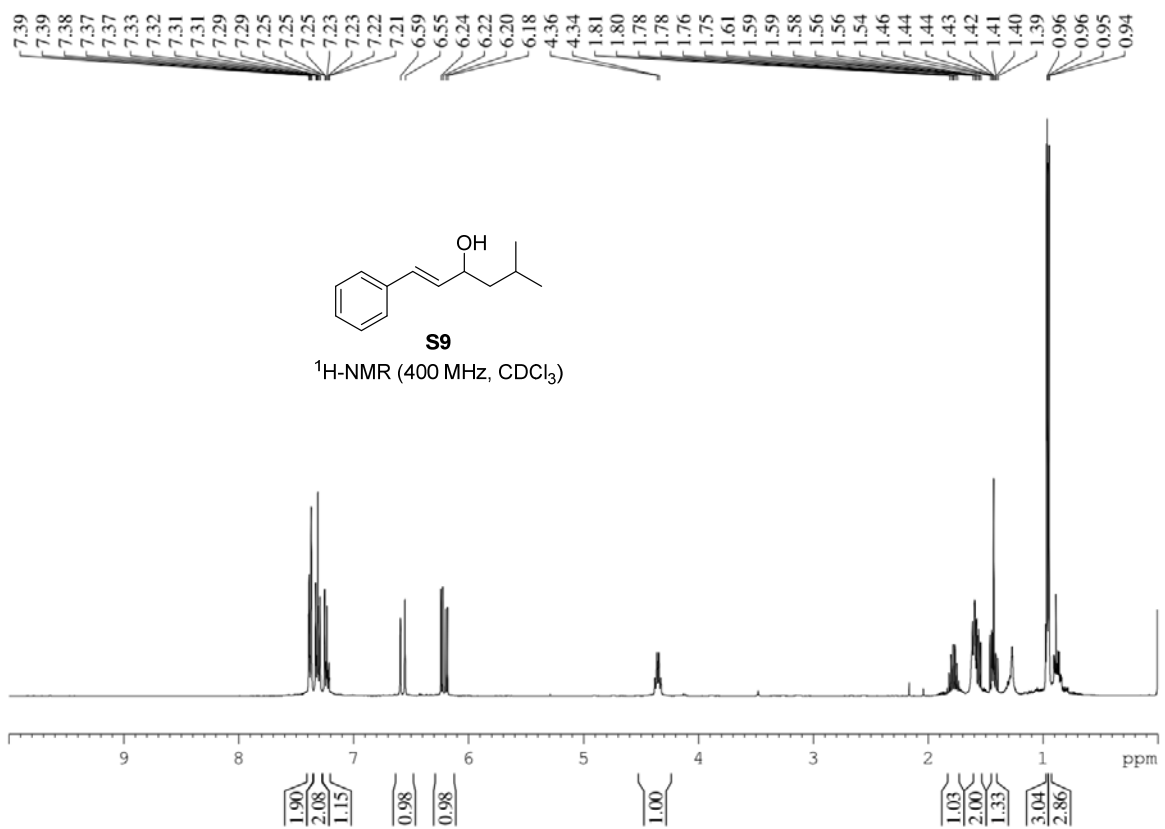
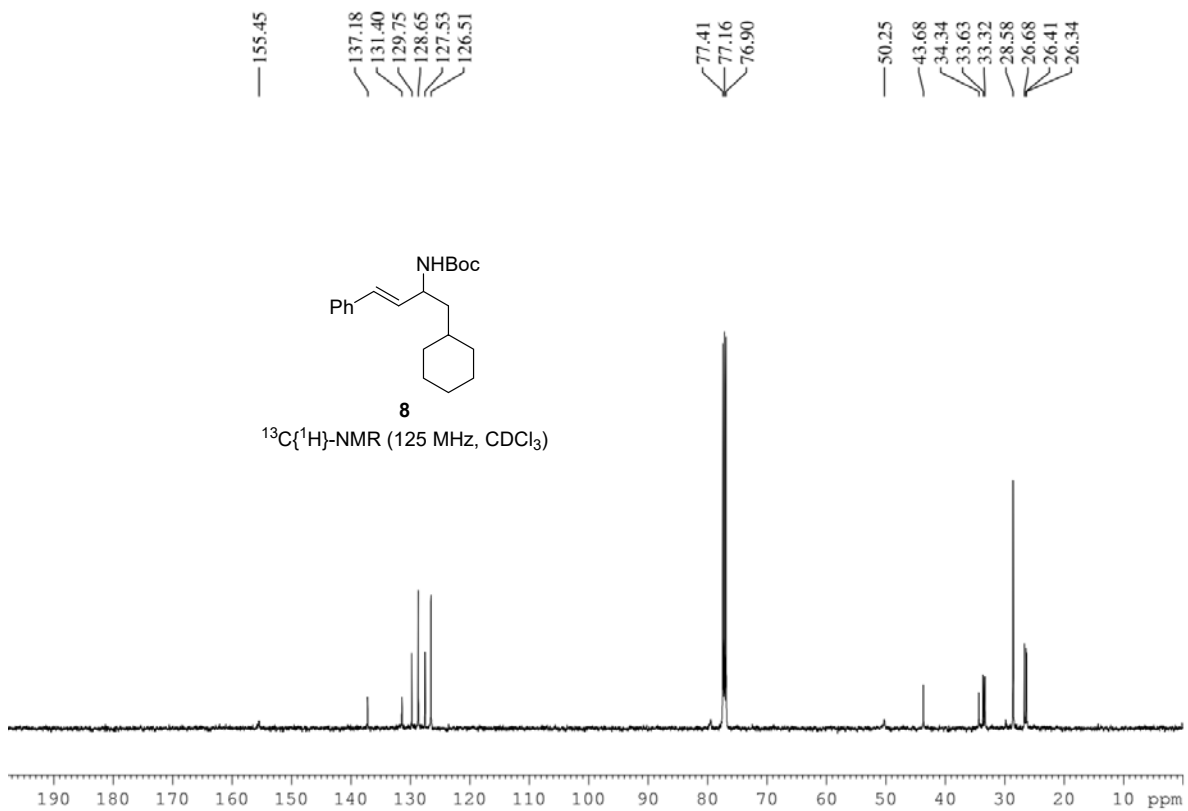










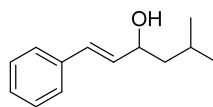


136.92
133.05
130.18
128.69
127.73
126.58

77.41
77.16
76.91
71.46

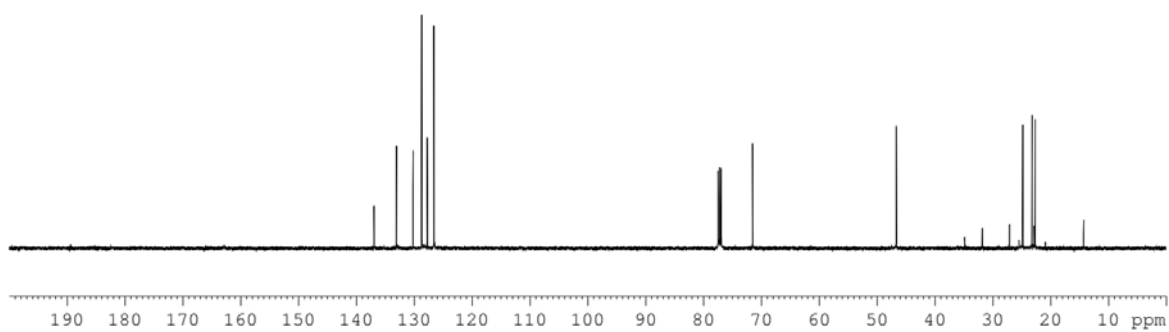
46.62

24.75
23.14
22.61



S9

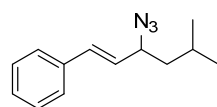
$^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3)



7.42
7.41
7.41
7.40
7.39
7.35
7.35
7.33
7.33
7.32
7.32
7.29
7.28
7.28
7.27
7.27
7.26
6.63
6.59
6.13
6.11
6.09
6.07

4.08
4.06
4.04
4.02

1.80
1.78
1.77
1.75
1.73
1.72
1.70
1.60
1.58
1.58
1.57
1.56
1.53
1.46
1.45
1.43
1.41
1.39



S10

^1H -NMR (400 MHz, CDCl_3)

