Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Hydrogen Bonding-directed Sequential 1,6/1,4-Addition of Heteroatom Nucleophiles onto Electron-deficient 1,3-Diynes

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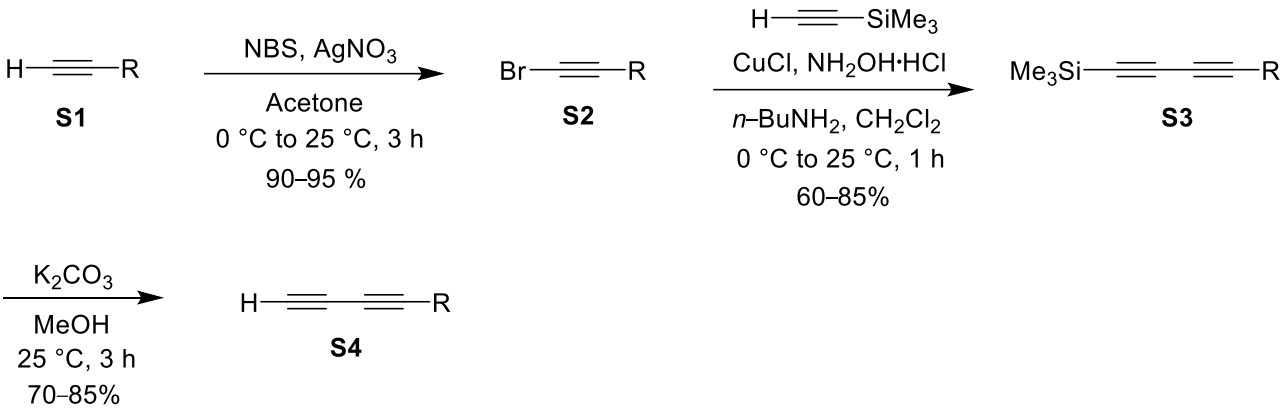
General Information

All reactions were carried out in oven or flame-dried glassware unless otherwise noted. Reagents which were commercially available, were purchased from Sigma - Aldrich, Alfa Aesar, Acros, and Oakwood Products unless otherwise noted. Known compounds were prepared according to literature procedure. Anhydrous acetonitrile from Sigma-Aldrich was distilled over calcium hydride (CaH_2) under nitrogen atmosphere. Acetic acid was purchased from Fischer Scientific. Column chromatography was performed using silica gel 60 Å (32−63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040−0.063 mm). Yield was calculated on basis of chromatographically and spectroscopically pure isolated compound. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer at 298 K, unless otherwise stated. ^{1}H NMR chemical shifts (δ) were reported in parts per million (ppm) downfield of TMS and were referenced relative to the residual proteated solvent peak ($CDCl_3$ (7.26 ppm)). ^{13}C chemical shifts (δ) were reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$, δ 77.2 ppm). Multiplicities in ^{1}H NMR were abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), sept (septet) or m (multiplet). ^{1}H NMR signals that fall within a *ca*. 0.3 ppm range are generally reported as a multiplet, with a range of chemical shift values corresponding to the peak or center of the peak. Coupling constants, *J*, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima (Waters Corporation, Milford, MA, USA) at the University of Illinois at Urbana-Champaign.

Experimental Details

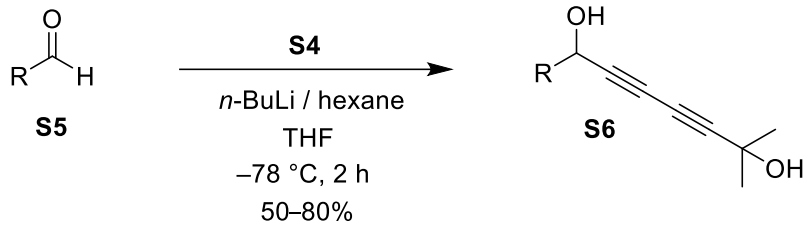
Procedure for synthesis of diynone substrates



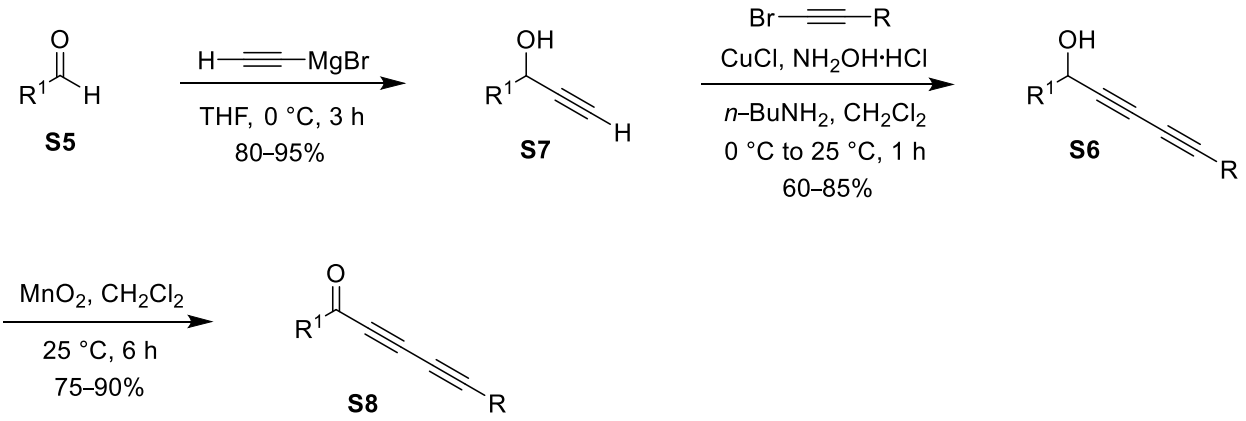
To a stirred solution of alkyne **S1** (5.05 g, 60.0 mmol) in acetone at 25 °C, *N*-bromosuccinimide (12.81 g, 72.0 mmol) and $AgNO_3$ (1.02 g, 6.0 mmol) were sequentially added under N_2 atmosphere in the dark. After addition, the mixture was stirred for 3 h. Upon complete consumption of the alkyne, the reaction mixture was concentrated under reduced pressure and filtered through silica gel. Purification by flash column chromatography (SiO_2, EtOAc–hexane, 1:5 to 1:3) provided the bromide **S2** (8.81–9.30 g, 90–95% yield) as clear oil.

To a mixture of 30% aqueous *n*-$BuNH_2$ (20 mL, 2 mL per 1.0 mmol of terminal alkyne), CuCl (0.29 g, 3.0 mmol) and a pinch of $NH_2OH{\cdot}HCl$ in a two-necked round-bottomed flask, a solution of terminal alkyne (0.98 g, 10.0 mmol) in CH_2Cl_2 was added slowly at 0 °C under N_2 atmosphere. Then, **S2** (1.96 g, 12.0 mmol) diluted in CH_2Cl_2 was added dropwise into the reaction mixture over 30 min. After 5 min, the ice bath was removed and stirring was continued for additional 25 min at room temperature (TLC monitoring). A pinch of $NH_2OH{\cdot}HCl$ was added several times into the reaction mixture when the solution becomes blue. The reaction was quenched by a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine sequentially and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:50 to 1:20) to provide the pure diyne **S3** (1.30–1.84 g, 60–85% yield) as white solid.

To a stirred solution of **S3** (1.37 g, 4.0 mmol) in MeOH at 25 °C, K_2CO_3 (0.55 g, 4.0 mmol) was added and the stirring was continued for additional 3 h. Then, the reaction was quenched by a saturated solution of NH_4Cl and extracted with Et_2O. The combined organic extracts were washed with water and brine sequentially and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and ice. The crude material was purified by flash column chromatography (SiO_2, Et_2O–pentane, 1:10 to 1:5) to provide the pure diyne **S4** (0.58–0.70 g, 70–85% yield) as clear oil.



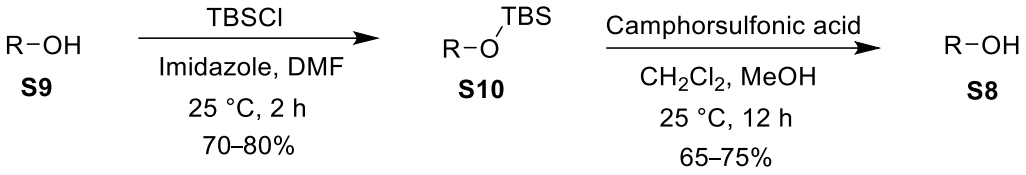
To a stirred solution of **S5** (0.27g, 2.0 mmol) in THF at –78 °C, *n*-BuLi (2.5 M, 1.76 mL, 4.4 mmol) in hexane was added slowly under N_2 atmosphere and the stirring was continued for additional 40 min. The dry ice bath was removed and the diyne **S4** (0.24 g, 2.2 mmol) in THF was added. The stirring was continued for additional 1 h at room temperature. The reaction was quenched by aqueous NH_4Cl and extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:40 to 1:10) to provide pure product **S6** (0.27–0.44 g, 50–80% yield) as yellow oil.



To a stirred solution of **S5** (1.06 g, 10.0 mmol) in THF at 0 °C, ethynyl magnesium-bromide (0.5 M, 24 mL, 12.0 mmol) in hexane was added slowly under N_2 atmosphere and the mixture was stirred for 30 min and additional 2 h at room temperature. The reaction was quenched by a saturated solution of NH_4Cl and extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:50 to 1:20) to provide the pure product **S7** (1.05–1.19 g, 80–90% yield) as yellow oil.

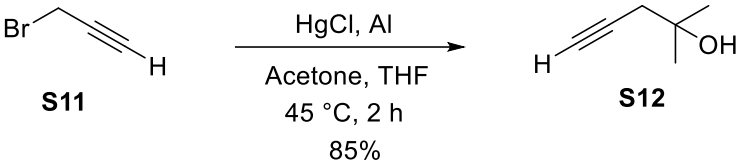
To a mixture of 30% aqueous *n*-$BuNH_2$ (20 mL, 2 mL per 1.0 mmol of terminal alkyne), CuCl (0.29 g, 3.0 mmol) and a pinch of $NH_2OH{\cdot}HCl$ in a two-necked round-bottomed flask, a solution of terminal alkyne, **S7** (1.32 g, 10.0 mmol) in CH_2Cl_2 was added slowly at 0 °C under N_2 atmosphere. Then, **S2** (1.96 g, 12.0 mmol) diluted in CH_2Cl_2 was added dropwise into the reaction mixture over 30 min. After 5 min, the mixture was stirred for additional 25 min at room temperature (TLC monitoring). A pinch of $NH_2OH{\cdot}HCl$ was added several times into the reaction mixture when the solution becomes blue. The reaction was quenched by a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:50 to 1:20) to provide the pure product **S6** (1.28–1.82 g, 60–85% yield) as pale-yellow oil.

To a stirred solution of **S6** (0.21 g, 1.0 mmol) in CH_2Cl_2 at 25 °C**,** MnO_2 (1.30 g, 15.0 mmol) was added and the mixture was stirred for 6 h. After the completion of the reaction, the reaction mixture was filtered through a celite column. Purification by flash column chromatography (SiO_2, EtOAc–hexane, 1:40 to 1:10) provided the pure product **S8** (0.16–0.19 g, 75–90% yield) as pale-yellow solid.

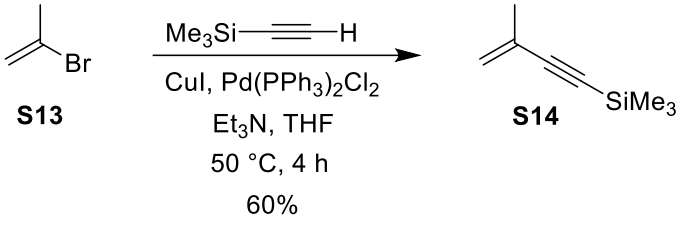


To a stirred solution of **S9** (2.02 g, 15.0 mmol) in DMF (2 mL, 1 mL per 7.5 mmol of the alcohol) at 25 °C**,** TBSCl (2.49 g, 16.5 mmol) and imidazole (1.23 g, 18.00 mmol) were added, and the stirring was continued for 2 h. Upon completion of the reaction, the reaction mixture was filtered through silica gel with hexane. The filtration provided the product **S10** (2.64–3.01 g, 70–80% yield) as clear oil and was used for the next step without any further purification.

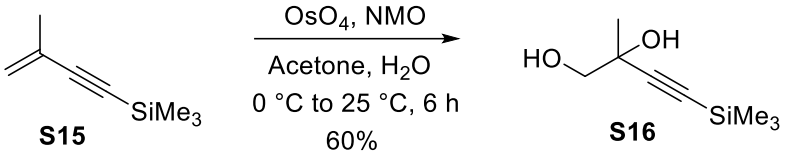
For the deprotection of the alcohol, to a stirred solution of **S10** (0.32 g, 1.0 mmol) in CH_2Cl_2:MeOH (5:1) at 25 °C, (1S)-(+)-Camphorsulfonic acid (23.2 mg, 0.1 mmol) was added and the stirring was continued for 12 h. The reaction was quenched by a saturated solution of NH_4Cl and extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:50 to 1:20) to provide the pure alcohol **S8** (0.13–0.15 g, 65–75% yield) as yellow oil.



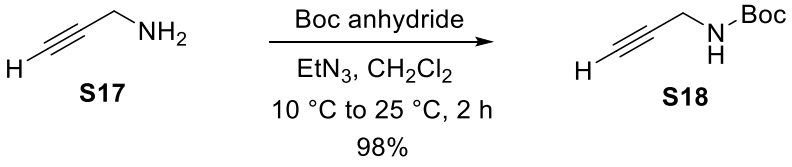
To a mixture of Al (0.27 g, 10.0 mmol) and $HgCl_2$ (27.2 mg, 0.1 mmol) in THF at 45 °C, bromide **S11** (1.19 g, 10.0 mmol) in THF was added and the mixture was stirred for 30 min. Then the reaction mixture was cooled down to 0 °C and acetone (0.9 mL, 12 mmol) in THF was added. The reaction mixture was again heated up to 45 °C and the stirring was continued for another 30 min. The reaction was quenched by pouring the reaction mixture to a solution of ice water and saturated solution of NH_4Cl and extracted with Et_2O. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and ice. The crude material was purified by flash column chromatography (SiO_2, Et_2O–pentane, 1:10 to 1:5) to provide the pure terminal alkyne **S12** (0.19 g, 85% yield) as clear oil.



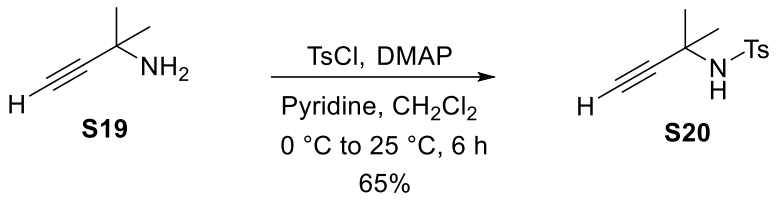
To a stirred solution of bromide **S13** (1.00 g, 8.27 mmol) in THF at 25 °C, $Pd(PPh_3)_2Cl_2$ (0.17 g, 0.25 mmol) and terminal alkyne (1.06 g, 10.7 mmol) were added sequentially under N_2 atmosphere. Then CuI (81.3 mg, 0.58 mmol) and Et_3N (1.7 mL, 12.4 mmol) were added and the reaction mixture was stirred at 50 °C for 4 h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure and filtered through silica gel. Purification by flash column chromatography (SiO, EtOAc–hexane, 1:20) provided the enyne **S14** (0.69 g, 60% yield) as white solid.



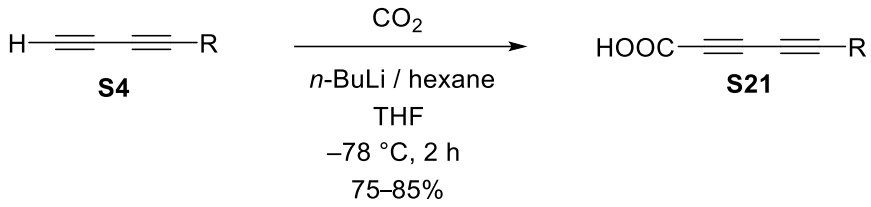
To a stirred solution of enyne **S15** (1.00 g, 7.2 mmol) in acetone at 0 °C, NMO (1.02 g, 8.7 mmol) and OsO_4 in water (0.09 g, 0.36 mmol) were added and the mixture was stirred at 25 °C for 6 h. The reaction was quenched by aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:15 to 1:10) to provide the pure diol **S16** (0.75 g, 60% yield) as white soild.



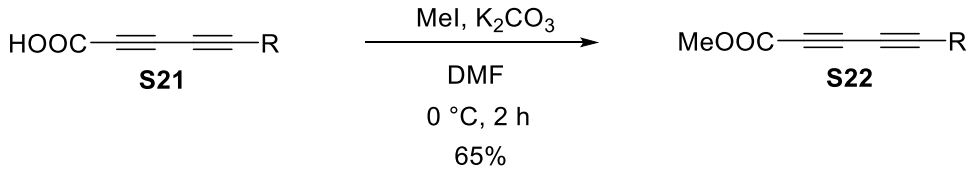
To a stirred solution of amine **S17** (1.00 g, 18 mmol) in CH_2Cl_2 at 10 °C, NEt_3 (2.5 mL, 18 mmol) and Boc anhydride in CH_2Cl_2 (7.86 g, 36 mmol) were added and the mixture was stirred at 25 °C for 2 h. The reaction was quenched by water and extracted with CH_2Cl_2. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:50 to 1:20) to provide the pure product **S18** (2.76 g, 98% yield) as pale-yellow soild.



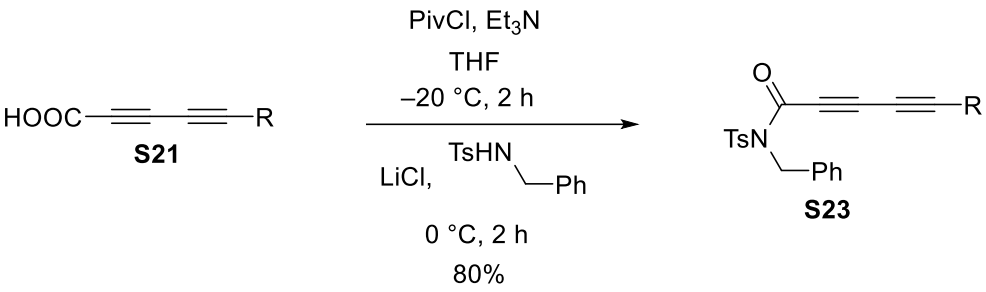
To a stirred solution of amine **S19** (0.54 g, 6.5 mmol) in CH_2Cl_2 at 0 °C, pyridine (0.74 mL, 9.1 mmol) tosyl chloride (1.24 g, 7.8 mmol) and DMAP (6.11 mg, 0.08 mmol) were added and the mixture was stirred at 25 °C for 6 h. The reaction was quenched by water and extracted with CH_2Cl_2. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:50 to 1:20) to provide the pure product **S20** (1.00 g, 65% yield) as pale-yellow oil.



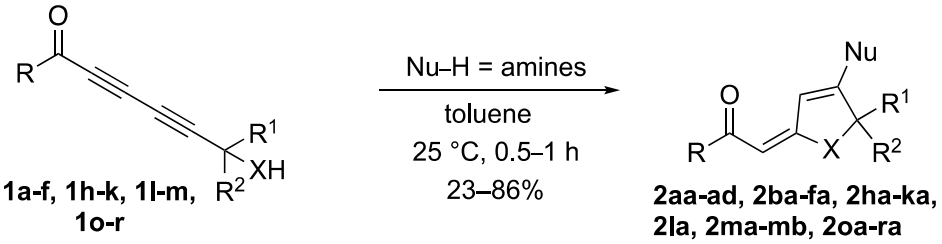
To a stirred solution of **S4** (1.00g, 9.2 mmol) in THF at –78 °C, *n*-BuLi (2.5 M, 7.40 mL, 1.8 mmol) in hexane was added slowly under N_2 atmosphere and the stirring was continued for additional 30 min. Then CO_2 was bubbled into the reaction mixture at –78 °C and the dry ice bath was removed. The stirring was continued for additional 1 h at room temperature. The reaction was quenched by aqueous HCl (1M) and extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:20 to 1:5) to provide pure product **S21** (1.06–1.20 g, 75–85% yield) as pale-yellow soild.



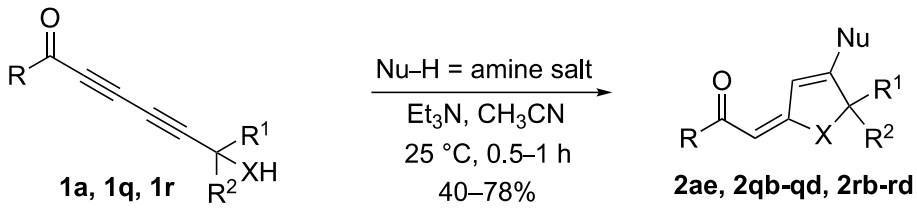
To a stirred solution of **S21** (0.20 g, 1.3 mmol) in DMF at 0 °C under N_2 atmosphere, K_2CO_3 (0.20 g, 1.5 mmol) and MeI (0.40 g, 2.8 mmol) were added and the mixture was stirred at 0 °C for 30 minutes. Then the ice bath was removed and stirring was continued for additional 1 h at room temperature. The reaction was quenched by aqueous NH_4Cl and extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:10 to 1:4) to provide the pure product **S22** (0.14 g, 65% yield) as pale-yellow oil.



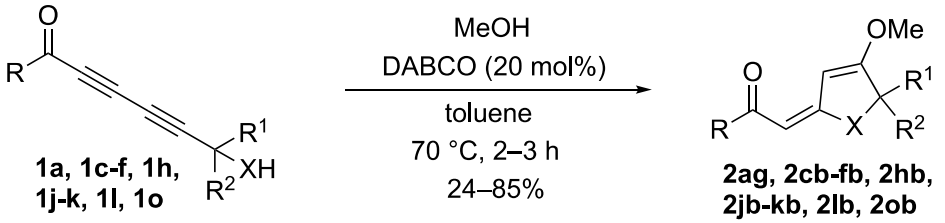
To a stirred solution of **S21** (0.10 g, 0.7 mmol) in THF at –20 °C under N_2 atmosphere, PivCl (0.11 g, 0.9 mmol) and Et_3N (0.23 mL, 1.6 mmol) were added and the mixture was stirred at –20 °C for 2 hours. Then LiCl (0.04g, 1.0 mmol) and the amine (0.17g, 0.7 mmol) were added and the dry ice bath was removed and stirring was continued for additional 1 h at room temperature. The reaction was quenched by aqueous NH_4Cl and extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:20 to 1:10) to provide the pure product **S23** (0.21 g, 80% yield) as pale-yellow oil.



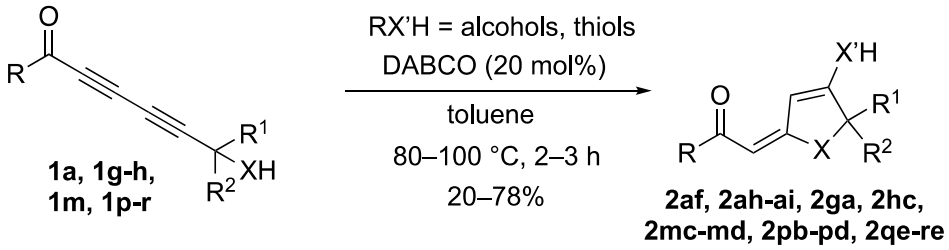
To a stirred solution of **1a-f, 1h-k, 1l-m, 1o-r** (45 mg, 0.2 mmol) in toluene at 25 °C, Nu–H (0.04 mL, 0.4 mmol) was added. Then the reaction mixture was stirred for 0.5–1 h. Upon completion of the reaction, the crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:10 to 1:1) to provide pure products **2aa-ad, 2ba-fa, 2ha-ka, 2la, 2ma-mb, 2oa-ra** (15–54 mg, 23–86% yield) as an oil.



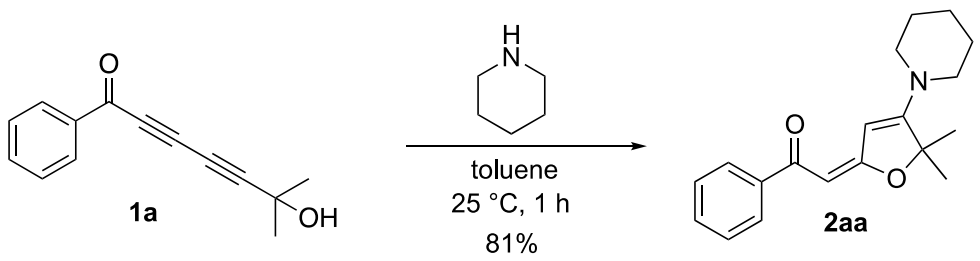
To a stirred solution of **1a, 1q, 1r** (45 mg, 0.2 mmol) in CH_3CN at 25 °C, Et_3N (0.09 mL, 0.6 mmol) and Nu–H (0.04 mL, 0.4 mmol) were added. Then the reaction mixture was stirred for 0.5–1 h. Upon completion of the reaction, the crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:10 to 1:1) to provide pure products **2ae, 2qb-qd, 2rb-rd** (25–49 mg, 40–78% yield) as an oil.



To a stirred solution of **1a, 1c-f, 1h, 1j-k, 1l, 1o** (45 mg, 0.2 mmol) in toluene at 70 °C, DABCO (5 mg, 0.04 mmol) and MeOH (0.04 mL, 1.0 mmol) were added. Then the reaction mixture was stirred for 2–3 h. Upon completion of the reaction, the crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:10 to 1:5) to provide pure products **2ag, 2cb-fb, 2hb, 2jb-kb, 2lb, 2ob** (13–44 mg, 24–85% yield) as an oil.



To a stirred solution of **1a, 1g-h, 1m, 1p-r** (45 mg, 0.2 mmol) in toluene at 80–100 °C, DABCO (5 mg, 0.04 mmol) and RX'H (46 mg, 0.4 mmol) were added. Then the reaction mixture was stirred for 2–3 h. Upon completion of the reaction, the crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:10 to 1:5) to provide pure products **2af, 2ah-ai, 2ga, 2hc, 2mc-md, 2pb-pd, 2qe-re** (14–53 mg, 20–78% yield) as an oil.

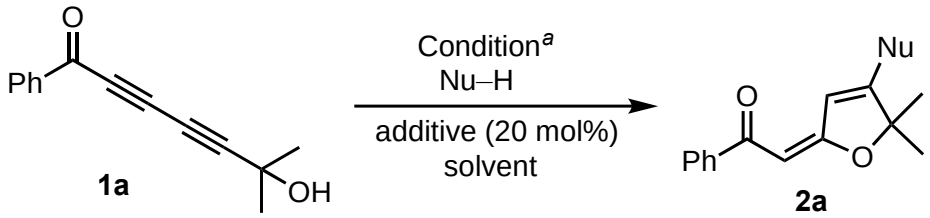


To a stirred solution of **1a** (0.28 g, 1.3 mmol) in toluene at 25 °C, piperidine (0.28 mL, 2.6 mmol) was added. Then the reaction mixture was stirred for 0.5 h. Upon completion of the reaction, the crude material was purified by flash column chromatography (SiO_2, EtOAc–hexane, 1:10 to 1:2) to provide pure product **2aa** (0.32 g, 81% yield) as a pale-yellow oil.

References:

1. H. Hofmeister, K. Annen, H. Laurent, H. Wiechert, *Angew. Chem., Int. Ed*. **1984**, *23*, 727.
2. (a) W. Chodkiewicz, *Ann. Chim*. **1957**, *2*, 819. (b) P. Cadiot, W. Chodkiewicz, In *Chemistry of Acetylenes* (Ed.: H. G. Viehe), Marcel Dekker, New York, **1969**, pp. 597.
3. For **2al'**: (a) Fan, M.-J.; Li. G.-Q.; Liang, Y.-M. DABCO-catalyzed reaction of various nucleophiles with activated alkynes leading to the formation of alkenoic acid esters, 1,4-dioxane, morpholine, and piperazinone derivatives. *Tetrahedron* **2006**, *62*, 6782–6791. (b) Nguyen, Van T. H.; Anders, J. T.; Ma, Q.; Herbs-Irmer, R.; Langer, P. Synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones and their ring-transformation into 5,6-dihydrobenzo[h]chromones, 5,6,7,8-tetrahydrochromones and pyran-4-ones. *Tetrahedron* **2007**, *63*, 12975.

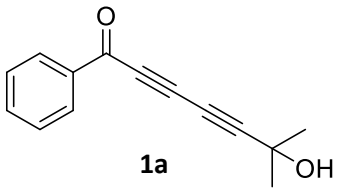
Table S1. Optimizing Reaction Conditions with Screening Solvents, Temperature and Base Additives



entry	Nu–H	additive	solvent	temp (°C)	time (h)	yield (%)[b]
1	none	DABCO	toluene	90	6.0	0
2	piperidine[c]	none	toluene	rt	0.5	78
3	piperidine	none	CH_3CN	rt	0.5	52
4	piperidine	none	CH_2Cl_2	rt	0.5	57
5	MeOH[d]	none	toluene	rt	6.0	0
6	MeOH	DABCO	toluene	rt	6.0	0
7	MeOH	DABCO	toluene	55	6.0	0
8	MeOH	DABCO	toluene	70	2.5	72
9	MeOH	Et_3N	toluene	70	4.0	66
10	MeOH	pyridine	toluene	70	5.0	61

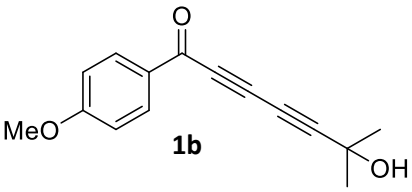
[a]Condition: undistilled solvents and reagents. [b]Isolated yield. [c]Lower amount of piperidine (0.5 and 1 equiv) led to incomplete conversion and reaction was completed with 2 equiv amines. [d]With 5 equiv of MeOH.

Characterization Data of Substrates



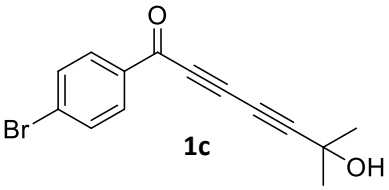
1a

130 mg (88% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.95 (d, 2H, *J* = 7.6 Hz), 7.48 (t, 1H, *J* = 7.5 Hz), 7.39–7.30 (m, 2H), 4.39 (s, 1H), 1.54 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.1, 136.2, 134.8, 129.6, 128.7, 92.8, 77.6, 74.6, 65.5, 65.3, 30.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}O_2$ 213.0916; found 213.0915.



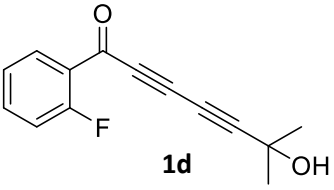
1b

200 mg (86% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.03 (d, 2H, *J* = 8.6 Hz), 8.03 (d, 2H, *J* = 8.6 Hz), 3.84 (s, 3H), 3.27 (s, 1H), 1.58 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.5, 164.9, 132.1, 129.9, 114.0, 91.5, 76.2, 75.0, 65.6, 65.7, 55.7, 30.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}O_3$ 243.1021; found 243.1021.



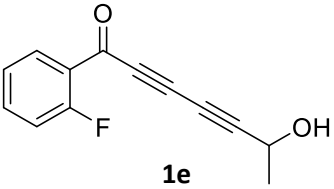
1c

800 mg (89% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.88 (d, 2H, *J* = 8.5 Hz), 7.56 (d, 2H, *J* = 8.5 Hz), 3.46 (s, 1H), 1.57 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.9, 135.1, 132.1, 130.9, 130.3, 92.9, 77.8, 74.4, 65.6, 65.4, 30.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}BrO_2$ 291.0021; found 291.0018.



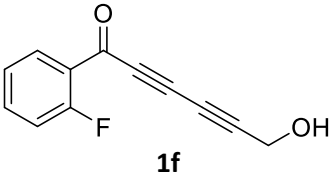
1d

180 mg (85% yield), off white solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.01–7.94 (m, 1H), 7.60–7.52 (m, 1H), 7.25–7.20 (m, 1H), 7.15–7.09 (m, 1H), 3.00 (s, 1H), 1.57 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 173.3, 162.1 (d, *J* = 263.1 Hz), 136.2 (d, *J* = 9.2 Hz), 132.0, 125.0 (d, *J* = 7.4 Hz), 124.4 (d, *J* = 4.2 Hz), 117.2 (d, *J* = 21.3 Hz), 92.9, 77.1, 75.7, 65.7, 65.6, 30.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}FO_2$ 231.0821; found 231.0820.



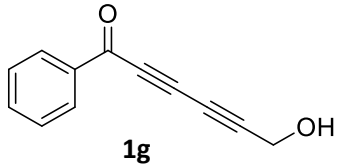
1e

220 mg (84% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.02–7.96 (m, 1H), 7.61–7.54 (m, 1H), 7.27–7.22 (m, 1H), 7.17–7.11 (m, 1H), 4.68 (q, *J* = 6.9 Hz, 1H), 2.65 (s, 1H), 1.53 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 173.5, 161.1, 136.2 (d, *J* = 9.2 Hz), 132.0, 124.9, 124.4 (d, *J* = 4.0 Hz), 117.2 (d, *J* = 21.7 Hz), 90.1, 76.8, 75.6, 67.3, 58.7, 23.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{10}FO_2$ 217.0665; found 217.0659.



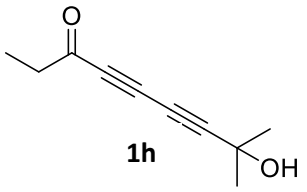
1f

180 mg (84% yield), pale-yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.01–7.90 (m, 1H), 7.62–7.48 (m, 1H), 7.28–7.20 (m, 1H), 7.17–7.07 (m, 1H), 4.45 (s, 2H), 3.11 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 173.5, 163.2, 161.1, 136.4 (d, *J* = 9.7 Hz), 132.1, 124.4 (d, *J* = 4.2 Hz), 117.2 (d, *J* = 21.7 Hz), 87.2, 77.1, 75.3, 68.6, 51.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_8FO_2$ 203.0508; found 203.0511.



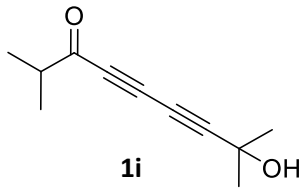
1g

40 mg (85% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.10 (d, 2H, *J* = 7.7 Hz), 7.63 (t, 1H, *J* = 7.5 Hz), 7.49 (t, 2H, *J* = 7.7 Hz), 4.47 (s, 2H), 2.43 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.1, 136.3, 134.8, 129.7, 128.8, 86.0, 76.9, 74.5, 68.8, 51.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_9O_2$ 185.0603, found 185.0602.



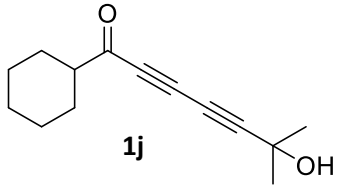
1h

400 mg (80% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 3.68 (s, 1H), 2.52 (q, 2H, *J* = 7.3 Hz), 1.47 (s, 6H), 1.06 (t, 3H, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 187.9, 92.2, 75.2, 75.1, 65.4, 65.1, 38.8, 30.6, 7.8; **HRMS** (EI) m/z: $[M]^+$ calcd for $C_{10}H_{13}O_2$ 165.09156, found 165.09078.



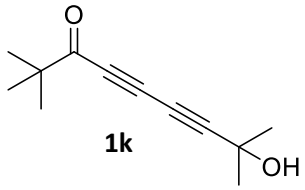
1i

420 mg (78% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 3.81 (s, 1H), 2.57 (hept, 1H, *J* = 6.9 Hz), 1.46 (s, 6H), 1.09 (d, 6H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 191.4, 92.1, 76.0, 74.5, 65.4, 65.1, 43.1, 30.6, 17.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{15}O_2$ 179.1072, found 179.1071.



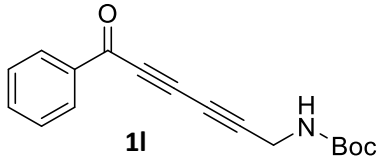
1j

200 mg (78% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 2.95 (s, 1H), 2.38 (tt, 1H, *J* = 11.1, 3.6 Hz), 1.97–1.89 (m, 2H), 1.75 (dt, 2H, *J* = 13.1, 3.9 Hz), 1.66–1.58 (m, 1H), 1.53 (s, 6H), 1.43–1.33 (m, 2H), 1.32–1.21 (m, 2H), 1.23–1.14 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 190.6, 91.8, 75.5, 75.1, 65.6, 65.4, 52.3, 30.7, 28.0, 25.6, 25.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}O_2$ 219.1385, found 219.1380.



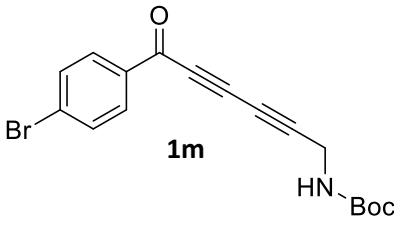
1k

200 mg (83% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 2.21 (s, 1H), 1.56 (s, 6H), 1.20 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 193.1, 91.2, 75.9, 74.3, 65.7, 65.6, 45.1, 30.8, 25.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}O_2$ 193.1229, found 193.1219.



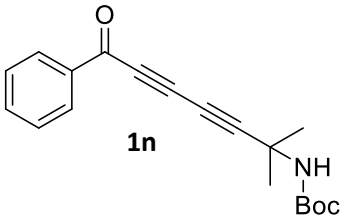
1l

220 mg (80% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.03 (d, 2H, *J* = 7.8 Hz), 7.56 (t, 1H, *J* = 7.4 Hz), 7.42 (t, 2H, *J* = 7.8 Hz), 5.31 (s, 1H), 4.08 (s, 2H), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 176.8, 155.3, 136.4, 134.6, 129.6, 128.7, 84.9, 80.5, 77.0, 73.3, 66.2, 31.2, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}NO_3$ 284.1106, found 284.1102.



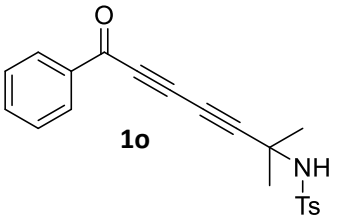
1m

500 mg (85% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.86 (d, 2H, *J* = 8.5 Hz), 7.55 (d, 2H, *J* = 8.5 Hz), 5.31 (s, 1H), 4.08 (d, 2H, *J* = 6.0 Hz), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.6, 155.3, 135.1, 132.1, 130.9, 130.2, 85.7, 80.4, 77.6, 72.8, 65.9, 31.2, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}BrNO_3$ 362.0211, found 362.0207.



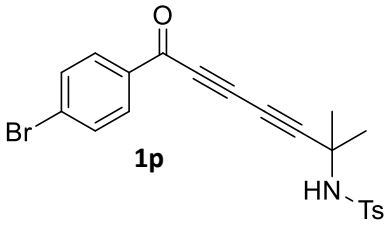
1n

80 mg (88% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.11 (d, 2H, *J* = 7.7 Hz), 7.61 (t, 1H, *J* = 7.4 Hz), 7.48 (t, 2H, *J* = 7.7 Hz), 4.79 (s, 1H), 1.62 (s, 6H), 1.47 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.0, 153.9, 136.5, 134.5, 129.7, 128.7, 91.3, 80.3, 77.4, 74.1, 64.3, 47.6, 29.1, 28.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{22}NO_3$ 312.1419, found 312.1421.



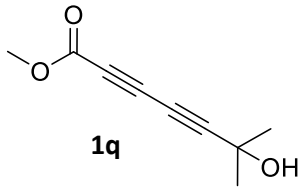
1o

250 mg (86% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.04 (d, 2H, *J* = 8.2 Hz), 7.84 (d, 2H, *J* = 8.3 Hz), 7.65–7.58 (m, 1H), 7.48 (t, 2H, *J* = 7.8 Hz), 7.31 (d, 2H, *J* = 8.3 Hz), 5.88 (s, 1H), 2.32 (s, 3H), 1.60 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 176.6, 144.0, 137.9, 136.4, 134.7, 129.6, 129.6, 128.8, 127.7, 88.6, 76.3, 74.8, 66.5, 50.2, 30.2, 21.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_3S$ 366.1164, found 366.1157.



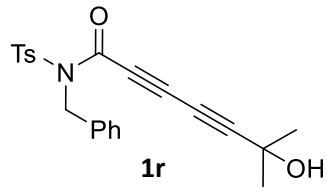
1p

250 mg (87% yield), white solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.89 (d, 2H, *J* = 8.6 Hz), 7.83 (d, 2H, *J* = 8.3 Hz), 7.62 (d, 2H, *J* = 8.6 Hz), 7.31 (d, 2H, *J* = 8.3 Hz), 5.86 (s, 1H), 2.34 (s, 3H), 1.59 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.5, 144.0, 137.9, 135.2, 132.1, 130.9, 130.2, 129.7, 127.7, 89.1, 76.9, 74.4, 66.4, 50.2, 30.1, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{19}NO_3SBr$ 444.0269, found 444.0262.



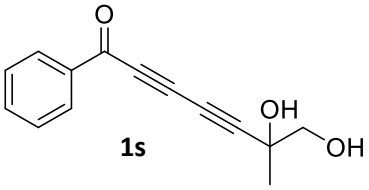
1q

80 mg (76% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexan es, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 3.78 (s, 3H), 3.72 (s, 1H), 1.55 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 153.1, 100.2, 89.2, 70.6, 68.8, 65.5, 53.1, 30.7; **HRMS** (EI) m/z: $[M]^+$ calcd for for $C_9H_{11}O_3$ 167.07083, found 167.07094.



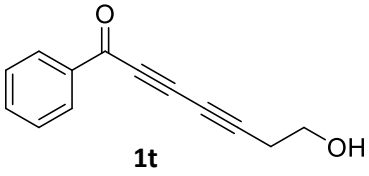
1r

130 mg (77% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.55 (d, 2H, *J* = 8.4 Hz), 7.38–7.29 (m, 5H), 7.19 (d, 2H, *J* = 8.4 Hz), 5.17 (s, 2H), 2.38 (s, 3H), 1.53 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 151.7, 145.4, 135.8, 135.3, 129.4, 128.8, 128.7, 128.3, 128.1, 92.5, 78.2, 69.1, 65.6, 65.0, 50.2, 30.7, 21.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}NO_4S$ 396.1270, found 396.1264.



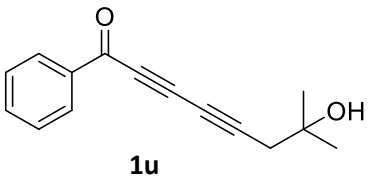
1s

30 mg (80% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.11 (d, 2H, *J* = 7.8 Hz), 7.64 (t, 1H, *J* = 7.4 Hz), 7.50 (t, 2H, *J* = 7.8 Hz), 3.78 (d, 1H, *J* = 10.6 Hz), 3.58 (d, 1H, *J* = 10.6 Hz), 2.93 (s, 1H), 2.21 (s, 1H), 1.54 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 176.8, 136.3, 134.7, 129.7, 128.8, 89.0, 76.2, 74.9, 70.2, 69.3, 67.5, 24.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}O_3$ 229.0786, found 229.0786.



1t

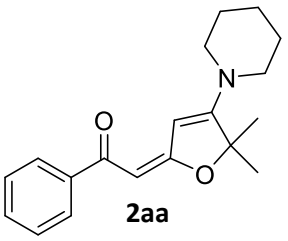
100 mg (82% yield), pale-yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.10 (d, 2H, *J* = 8.4 Hz), 7.61 (t, 1H, *J* = 7.7 Hz), 7.48 (t, 2H, *J* = 7.7 Hz), 3.84 (t, 2H, *J* = 6.4 Hz), 2.69 (t, 2H, *J* = 6.4 Hz), 2.16 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.1, 136.5, 134.5, 129.6, 128.7, 87.3, 77.9, 71.8, 65.5, 60.3, 24.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}O_2$ 199.0759, found 199.0758.



1u

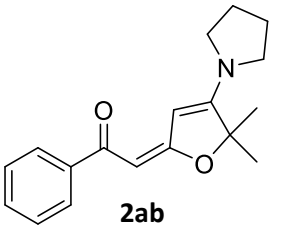
30 mg (81% yield), pale-yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.07 (d, 2H, *J* = 8.3 Hz), 7.57 (t, 1H, *J* = 7.8 Hz), 7.44 (t, 2H, *J* = 7.8 Hz), 2.59 (s, 2H), 2.51 (s, 1H), 1.35 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.2, 136.4, 134.5, 129.6, 128.7, 87.7, 78.2, 71.8, 70.6, 66.2, 35.2, 29.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}O_2$ 227.1072, found 227.1070.

Characterization Data of Products



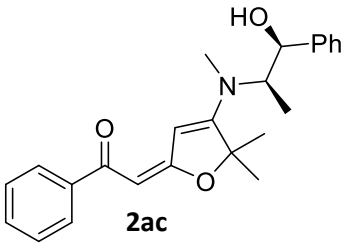
2aa

22 mg (78% yield), red oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.90 (d, 2H, *J* = 8.1 Hz), 7.50–7.24 (m, 3H), 6.53 (s, 1H), 5.96 (s, 1H), 3.40 (t, 4H, *J* = 5.4 Hz), 1.69–1.62 (m, 6H), 1.61 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.1, 177.3, 171.0, 141.5, 130.4, 128.0, 127.2, 90.2, 87.2, 85.8, 49.7, 25.9, 25.6, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}NO_2$ 298.1807, found 298.1802.



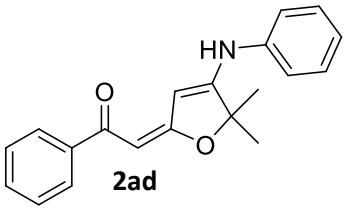
2ab

34 mg (86% yield), orange oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.91 (d, 2H, *J* = 6.0 Hz), 7.43–7.32 (m, 3H), 6.32 (s, 1H), 5.97 (s, 1H), 3.45 (t, 4H, *J* = 6.8 Hz), 2.01–1.96 (m, 4H), 1.61 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.0, 177.5, 169.3, 141.5, 130.3, 128.0, 127.2, 90.6, 87.1, 85.7, 49.1, 25.4, 24.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}NO_2$ 284.1651, found 284.1650.



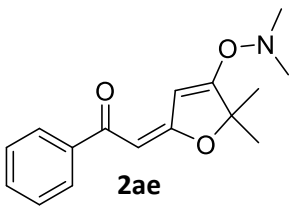
2ac

12 mg (72% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.86 (d, 2H, *J* = 6.7 Hz), 7.41–7.29 (m, 7H), 7.29–7.26 (m, 1H), 6.49 (s, 1H), 5.90 (s, 1H), 4.89 (d, 1H, *J* = 6.1 Hz), 3.85 (p, 1H, *J* = 6.6 Hz), 3.00 (s, 3H), 1.73 (s, 1H), 1.43 (s, 3H), 1.38–1.34 (m, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.3, 177.1, 172.0, 141.7, 141.4, 130.4, 128.6, 128.1, 128.0, 127.2, 126.1, 90.8, 87.3, 86.0, 75.7, 61.1, 34.0, 25.4, 25.3, 13.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{28}O_3N$ 378.2069, found 378.2066.



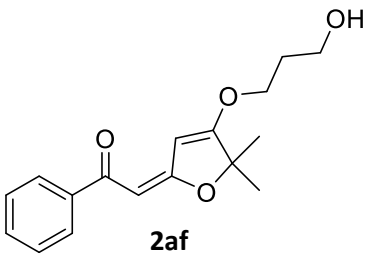
2ad

14 mg (40% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.92 (d, 2H, *J* = 8.3 Hz), 7.44 (t, 1H, *J* = 7.2 Hz), 7.40 (t, 2H, *J* = 7.2 Hz), 7.34 (t, 2H, *J* = 8.0 Hz), 7.23 (d, 2H, *J* = 7.5 Hz), 7.14–7.07 (m, 2H), 6.49 (s, 1H), 6.19 (s, 1H), 1.61 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.9, 177.8, 164.0, 140.9, 139.6, 130.9, 129.6, 128.2, 127.3, 124.4, 120.1, 91.8, 89.7, 86.6, 25.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$ 306.1494, found 306.1489.



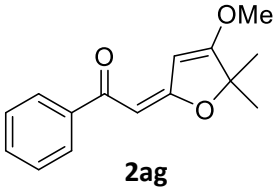
2ae

17 mg (78% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.91 (d, 2H, *J* = 6.8 Hz), 7.47–7.36 (m, 3H), 6.54 (s, 1H), 6.14 (s, 1H), 3.70 (s, 3H), 3.16 (s, 3H), 1.61 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.1, 175.8, 170.6, 140.8, 130.9, 128.2, 127.4, 93.6, 90.0, 88.0, 60.8, 39.0, 25.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}O_3N$ 274.1443, found 274.1443.



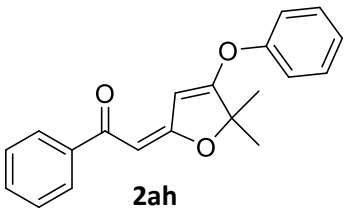
2af

38 mg (78% yield), orange oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.90 (d, 2H, *J* = 7.6 Hz), 7.46 (t, 1H, *J* = 7.2 Hz), 7.41 (t, 2H, *J* = 7.6 Hz), 6.72 (s, 1H), 6.23 (s, 1H), 4.25 (t, 2H, *J* = 6.3 Hz), 3.79 (t, 2H, *J* = 6.3 Hz), 2.08–2.00 (m, 2H), 1.46 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.6, 179.7, 176.3, 140.5, 131.3, 128.3, 127.4, 92.5, 91.7, 85.6, 69.7, 58.9, 31.5, 24.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}O_4$ 289.1440, found 289.1438.



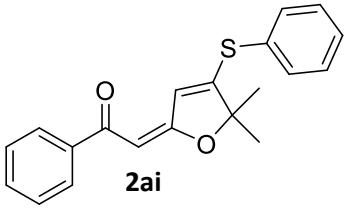
2ag

12 mg (72% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.92 (d, 2H, *J* = 7.0 Hz), 7.47 (t, 1H, *J* = 7.2 Hz), 7.42 (t, 2H, *J* = 7.2 Hz), 6.74 (s, 1H), 6.25 (s, 1H), 3.93 (s, 3H), 1.47 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.5, 180.6, 176.0, 140.5, 131.3, 128.2, 127.5, 92.3, 91.7, 85.5, 59.5, 24.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}O_3$ 245.1178, found 245.1178.



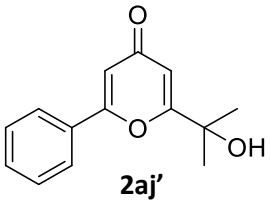
2ah

10 mg (20% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.87 (d, 2H, *J* = 7.1 Hz), 7.49–7.36 (m, 5H), 7.29 (t, 1H, *J* = 7.5 Hz), 7.20–7.17 (m, 2H), 6.50 (s, 1H), 6.28 (s, 1H), 1.65 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.3, 178.7, 175.3, 154.7, 140.2, 131.4, 130.3, 128.3, 127.5, 126.5, 120.1, 95.3, 92.5, 85.6, 24.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}O_3$ 307.1334, found 307.1335.



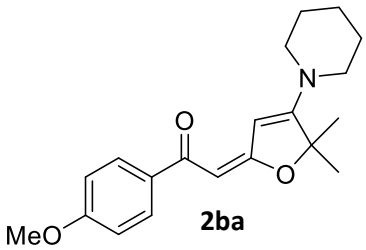
2ai

40 mg (76% yield), orange oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.87–7.83 (m, 2H), 7.63–7.58 (m, 2H), 7.50–7.46 (m, 3H), 7.45–7.43 (m, 1H), 7.41–7.36 (m, 2H), 6.84 (s, 1H), 6.22 (s, 1H), 1.61 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.3, 173.5, 168.1, 140.2, 134.6, 131.5, 130.3, 130.2, 128.3, 128.2, 127.5, 114.4, 91.7, 91.1, 26.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}O_2S$ 323.1106, found 323.1106.



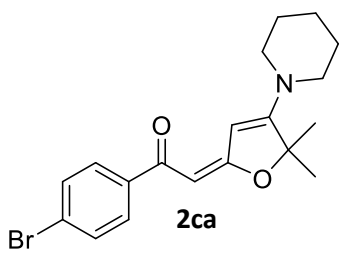
2aj'

48–13 mg, (84–42% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.72 (d, 2H, *J* = 6.3 Hz), 7.51–7.44 (m, 3H), 6.68 (d, 1H, *J* = 2.2 Hz), 6.63 (d, 1H, *J* = 2.2 Hz), 4.01 (s, 1H), 1.63 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 181.1, 174.0, 163.6, 131.5, 131.2, 129.1, 125.8, 110.7, 110.2, 71.1, 28.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}O_3$ 231.1021, found 231.1024.



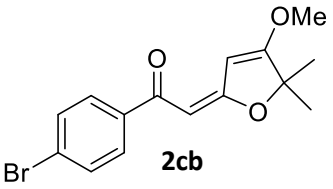
2ba

20 mg (68% yield), red oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.91 (d, 2H, *J* = 8.9 Hz), 6.89 (d, 2H, *J* = 8.9 Hz), 6.52 (s, 1H), 5.95 (s, 1H), 3.84 (s, 3H), 3.40 (s, 4H), 1.72–1.63 (m, 6H), 1.62 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 187.0, 176.8, 170.6, 161.6, 134.1, 129.1, 113.2, 90.3, 86.9, 85.8, 55.3, 49.6, 25.9, 25.7, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{26}NO_3$ 328.1913, found 328.1914.



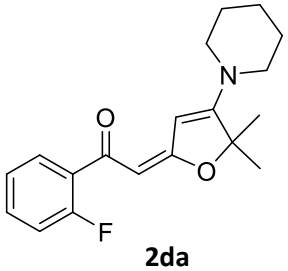
2ca

30 mg (73% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.77 (d, 2H, *J* = 8.4 Hz), 7.50 (d, 2H, *J* = 8.4 Hz), 6.51 (s, 1H), 5.89 (s, 1H), 3.54–3.27 (m, 4H), 1.83–1.61 (m, 6H), 1.61 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 186.6, 177.7, 171.3, 140.4, 131.2, 128.8, 124.9, 90.1, 86.8, 85.9, 49.7, 25.9, 25.6, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{23}BrNO_2$ 376.0912, found 376.0909.



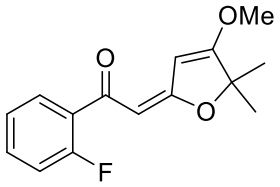
2cb

43 mg (85% yield), off-white solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.78 (d, 2H, *J* = 8.5 Hz), 7.54 (d, 2H, *J* = 8.5 Hz), 6.71 (s, 1H), 6.17 (s, 1H), 3.93 (s, 3H), 1.46 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.2, 181.0, 176.5, 139.3, 131.5, 129.1, 126.0, 92.3, 91.3, 85.7, 59.5, 24.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}BrO_3$ 323.0283, found 323.0284.



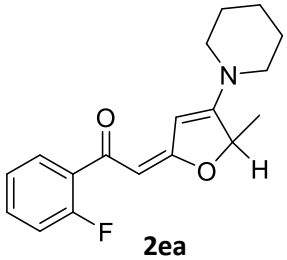
2da

38 mg (76% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.93–7.62 (m, 1H), 7.35–7.27 (m, 1H), 7.18–7.09 (m, 1H), 7.05–6.99 (m, 1H), 6.50 (s, 1H), 5.84 (s, 1H), 3.44–3.35 (m, 4H), 1.73–1.61 (m, 6H), 1.60 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 184.9, 177.4, 171.5, 160.5 (d, *J* = 250.6 Hz), 131.2 (d, *J* = 8.8 Hz), 130.5, 130.4 (d, *J* = 3.2 Hz), 123.8 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 24.0 Hz), 91.4 (d, *J* = 7.9 Hz), 90.4, 85.9, 49.7, 25.9, 25.5, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{23}FNO_2$ 316.1713, found 316.1711.



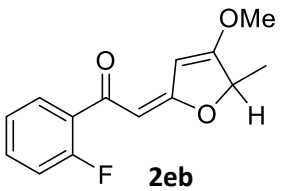
2db

38 mg (77% yield), pale-yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.81–7.74 (m, 1H), 7.42–7.34 (m, 1H), 7.21–7.13 (m, 1H), 7.10–7.03 (m, 1H), 6.70 (s, 1H), 6.13 (s, 1H), 3.93 (s, 3H), 1.45 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 186.9, 181.1, 176.2, 160.7 (d, *J* = 252.0 Hz), 132.2 (d, *J* = 8.3 Hz), 130.4 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 13.4 Hz), 124.1 (d, *J* = 3.2 Hz), 116.3 (d, *J* = 24.0 Hz), 95.9 (d, *J* = 7.4 Hz), 92.6, 85.7, 59.5, 24.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}FO_3$ 263.1083, found 263.1085.



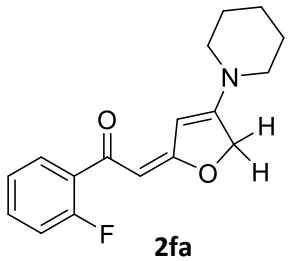
2ea

28 mg (81% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.84–7.74 (m, 1H), 7.36–7.29 (m, 1H), 7.18–7.10 (m, 1H), 7.07–6.98 (m, 1H), 6.54 (s, 1H), 5.91 (s, 1H), 5.10 (q, 1H, *J* = 6.4 Hz) 3.30 (t, 4H, *J* = 4.4 Hz), 1.71–1.58 (m, 6H), 1.51 (d, 3H, *J* = 6.4 Hz) ; **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 185.0, 179.6, 169.9, 161.5, 159.5, 131.3 (d, *J* = 8.3 Hz), 130.4 (d, *J* = 3.7 Hz), 123.9 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 23.6 Hz), 92.0 (d, *J* = 7.4 Hz), 90.7, 78.2, 49.8, 25.5, 23.8, 19.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{21}O_2NF$ 302.1556, found 302.1556.



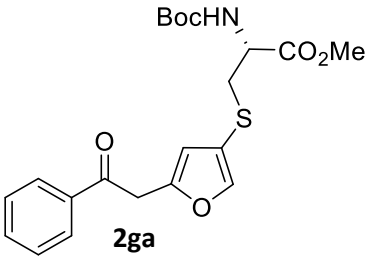
2eb

6 mg (24% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.82–7.74 (m, 1H), 7.44–7.36 (m, 1H), 7.22–7.15 (m, 1H), 7.11–7.04 (m, 1H), 6.79 (s, 1H), 6.17 (s, 1H), 4.97 (q, 1H, *J* = 7.0 Hz), 3.94 (s, 3H), 1.46 (d, 3H, *J* = 7.0 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 186.9, 178.5, 177.5, 160.7 (d, *J* = 252.0 Hz), 132.3 (d, *J* = 8.8 Hz), 131.1, 130.4, 124.1, 116.3 (d, *J* = 24.0 Hz), 102.1 (d, *J* = 22.2 Hz), 95.9, 94.2, 59.4 (d, *J* = 7.9 Hz), 17.9; **HRMS** (EI) m/z: $[M]^+$ calcd for for $C_{14}H_{14}O_3F$ 248.08488, found 248.08507.



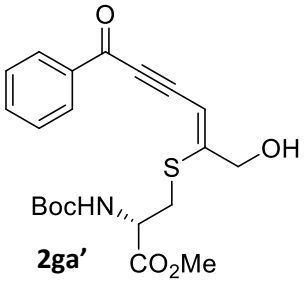
2fa

25 mg (77% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.83–7.76 (m, 1H), 7.36–7.30 (m, 1H), 7.20–7.12 (m, 1H), 7.07–7.00 (m, 1H), 6.54 (s, 1H), 5.93 (s, 1H), 4.89 (s, 2H), 3.27 (s, 4H), 1.71–1.60 (m, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 184.7, 181.6, 165.4, 161.5, 159.5, 131.4 (d, *J* = 8.3 Hz), 130.4 (d, *J* = 3.7 Hz), 123.9 (d, *J* = 3.7 Hz), 116.1 (d, *J* = 24.0 Hz), 91.9 (d, *J* = 7.4 Hz), 90.4, 71.3, 49.5, 25.4, 23.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{19}O_2NF$ 288.1400, found 288.1402.



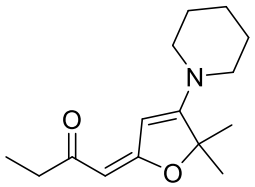
2ga

25 mg (50% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.99 (d, 2H, *J* = 7.8 Hz), 7.59 (t, 1H, *J* = 7.5 Hz), 7.48 (t, 2H, *J* = 7.8 Hz), 7.39 (s, 1H), 6.31 (s, 1H), 5.35 (d, 1H, *J* = 8.6 Hz), 4.53–4.46 (m, 1H), 4.27 (s, 2H), 3.58 (s, 3H), 3.15–3.04 (m, 2H), 1.44 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 194.3, 171.1, 155.1, 149.6, 144.5, 136.1, 133.6, 128.8, 128.6, 115.8, 112.7, 80.2, 52.9, 52.3, 38.3, 38.0, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{26}O_6NS$ 420.1300, found 420.1302.



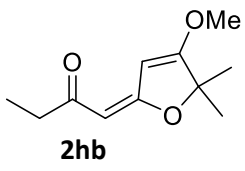
2ga'

25 mg (12% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.24 (d, 2H, *J* = 7.7 Hz), 7.62 (t, 1H, *J* = 7.4 Hz), 7.52 (t, 2H, *J* = 7.7 Hz), 6.17 (s, 1H), 5.45 (d, 1H, *J* = 6.9 Hz), 4.72–4.53 (m, 1H), 4.39 (d, 2H, *J* = 6.2 Hz), 3.74 (s, 3H), 3.53 (dd, 1H, *J* = 14.3, 5.2 Hz), 3.36 (dd, 1H, *J* = 14.3, 5.2 Hz), 2.52 (s, 1H), 1.44 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.8, 170.9, 156.2, 155.3, 136.9, 134.1, 129.8, 128.7, 106.7, 94.7, 89.0, 80.7, 64.9, 53.6, 52.9, 33.8, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{26}O_6NS$ 420.1300, found 420.1295.



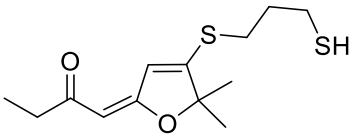
2ha

13 mg (23% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.31 (s, 1H), 5.25 (s, 1H), 3.34 (t, 4H, *J* = 5.5 Hz), 2.32 (q, 2H, *J* = 7.5 Hz), 1.68 –1.60 (m, 6H), 1.56 (s, 6H), 1.09 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 199.0, 175.3, 169.9, 89.8, 89.2, 85.5, 49.5, 36.2, 25.8, 25.7, 24.0, 9.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{24}O_2N$ 250.1807, found 250.1806.



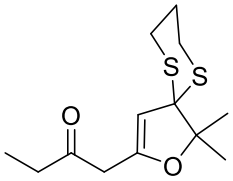
2hb

12 mg (48% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.54 (s, 1H), 5.51 (s, 1H), 3.88 (s, 3H), 2.38 (q, 2H, *J* = 7.4 Hz), 1.41 (s, 6H), 1.09 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 200.3, 179.5, 173.6, 94.0, 91.9, 85.1, 59.3, 36.7, 24.4, 9.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{17}O_3$ 197.1178, found 197.1180.



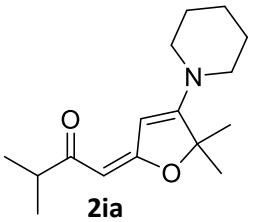
2hc

5 mg (10% yield), orange oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.11 (s, 1H), 5.51 (s, 1H), 3.08–3.02 (m, 2H), 2.66 (q, 2H, *J* = 7.2 Hz), 2.39–2.37 (m, 2H), 2.09–2.00 (m, 2H), 1.44 (s, 6H), 1.09 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 200.1, 171.5, 152.5, 112.7, 93.5, 91.1, 36.7, 31.8, 30.9, 25.3, 23.4, 9.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{21}O_2S_2$ 273.0983, found 273.0980.



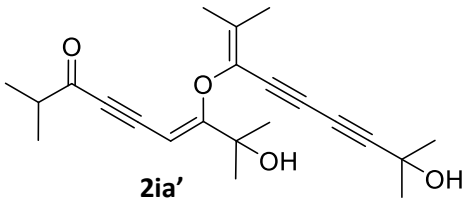
2hc'

10 mg (20% yield), orange oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 5.77 (s, 1H), 3.94 (s, 2H), 3.13–3.07 (m, 2H), 2.83 (q, 2H, *J* = 7.6 Hz), 2.45–2.40 (m, 2H), 2.18–2.09 (m, 1H), 1.93–1.81 (m, 1H), 1.49 (s, 6H), 1.07 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 201.0, 171.2, 99.1, 90.4, 59.1, 47.0, 36.9, 28.1, 26.4, 23.5, 8.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{21}O_2S_2$ 273.0983, found 273.0980.



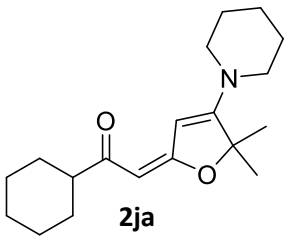
2ia

15 mg (32% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.34 (s, 1H), 5.27 (s, 1H), 3.34 (t, 4H, *J* = 5.5 Hz), 2.49 (h, 1H, *J* = 6.8 Hz), 1.71–1.58 (m, 6H), 1.57 (s, 6H), 1.09 (d, 6H, *J* = 6.8 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 202.5, 175.8, 169.9, 90.0, 88.3, 85.5, 49.5, 40.7, 25.8, 25.7, 24.0, 19.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{26}O_2N$ 264.1858, found 264.1852.



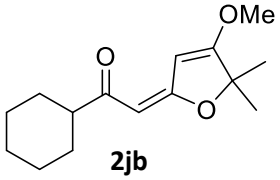
2ia'

20 mg (18% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 5.49 (s, 1H), 2.61 (hept, 1H, *J* = 6.8 Hz), 2.17 (s, 1H), 2.03 (s, 1H), 1.93 (s, 3H), 1.81 (s, 3H), 1.54 (s, 6H), 1.43 (s, 6H), 1.16 (d, 6H, *J* = 6.8 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 192.0, 172.1, 135.2, 129.7, 92.3, 88.4, 87.5, 81.8, 77.6, 72.6, 71.8, 66.7, 65.7, 42.8, 31.0, 28.0, 20.3, 18.1, 17.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{29}O_4$ 357.2060, found 357.2060.



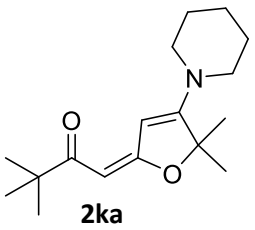
2ja

19 mg (34% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.33 (s, 1H), 5.26 (s, 1H), 3.34 (t, 4H, *J* = 5.4 Hz), 2.19 (tt, 1H, *J* = 11.6, 3.4 Hz), 1.85–1.79 (m, 2H), 1.78–1.71 (m, 2H), 1.69–1.57 (m, 6H), 1.56 (s, 6H), 1.44–1.33 (m, 2H), 1.31–1.14 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 201.7, 175.7, 169.8, 90.0, 88.6, 85.5, 51.3, 49.5, 29.8, 26.2, 25.8, 25.7, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{30}NO_2$ 304.2277, found 304.2275.



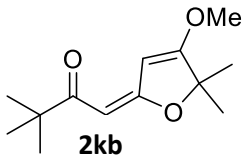
2jb

19 mg (64% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.55 (s, 1H), 5.53 (s, 1H), 3.86 (s, 3H), 2.25 (tt, 1H, *J* = 11.5, 3.4 Hz), 1.87–1.79 (m, 2H), 1.80–1.73 (m, 2H), 1.41 (s, 6H), 1.40–1.33 (m, 2H), 1.32–1.15 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 203.0, 179.5, 174.2, 93.4, 92.0, 85.0, 59.2, 51.5, 29.4, 26.1, 26.0, 24.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{23}O_3$ 251.1647, found 251.1653.



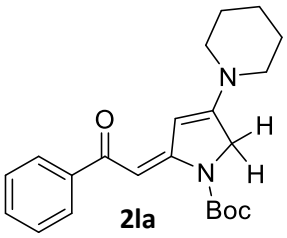
2ka

18 mg (76% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.36 (s, 1H), 5.47 (s, 1H), 3.34 (t, 4H, *J* = 5.4 Hz), 1.70–1.58 (m, 6H), 1.57 (s, 6H), 1.14 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 204.1, 176.2, 169.8, 90.0, 85.8, 85.4, 49.5, 42.3, 27.8, 25.8, 25.7, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{28}NO_2$ 278.2120, found 278.2120.



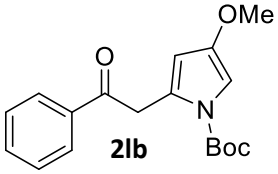
2kb

14 mg (70% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.58 (s, 1H), 5.74 (s, 1H), 3.86 (s, 3H), 1.42 (s, 6H), 1.15 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 205.2, 179.4, 174.7, 92.0, 90.6, 85.0, 59.2, 42.8, 27.3, 24.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{21}O_3$ 225.1491, found 225.1494.



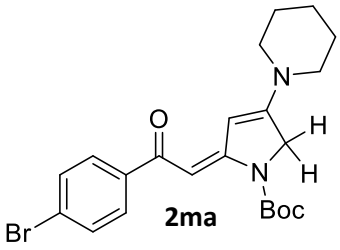
2la

20 mg (81% yield), orange oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.96 (d, 2H, *J* = 8.0 Hz), 7.43–7.36 (m, 3H), 7.26 (s, 1H), 6.97 (s, 1H), 4.38 (s, 2H), 3.29 (t, 4H, *J* = 4.9 Hz), 1.69–1.61 (m, 6H), 1.59 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.9, 161.9, 158.6, 158.6, 142.0, 130.5, 128.0, 127.5, 93.7, 92.0, 82.4, 52.3, 48.7, 29.7, 28.4, 25.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{29}N_2O_3$ 369.2178, found 369.2175.



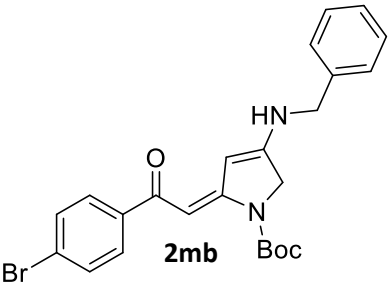
2lb

12 mg (45% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.99 (d, 2H, *J* = 7.7 Hz), 7.57 (t, 1H, *J* = 7.4 Hz), 7.47 (t, 2H, *J* = 7.7 Hz), 6.72 (s, 1H), 5.87 (s, 1H), 4.49 (s, 2H), 3.72 (s, 3H), 1.45 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 196.1, 149.1, 148.9, 136.9, 133.0, 129.6, 128.6, 128.2, 107.0, 100.9, 83.3, 57.4, 39.4, 28.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}O_4N$ 316.1368, found 316.1366.



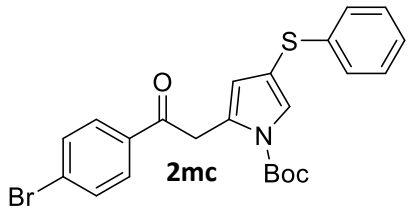
2ma

30 mg (86% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.82 (d, 2H, *J* = 8.5 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.21 (s, 1H), 6.94 (s, 1H), 4.37 (s, 2H), 3.29 (t, 4H, *J* = 4.9 Hz), 1.69–1.60 (m, 6H), 1.57 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 187.3, 162.5, 162.5, 159.0, 140.8, 131.2, 129.1, 125.0, 93.6, 91.3, 82.5, 52.3, 48.8, 28.4, 25.4, 23.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{28}N_2O_3Br$ 447.1283, found 447.1279.



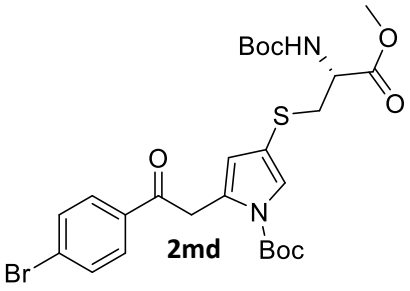
2mb

11 mg (44% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.83 (d, 2H, *J* = 8.5 Hz), 7.53 (d, 2H, *J* = 8.5 Hz), 7.39–7.35 (m, 2H), 7.34–7.30 (m, 3H), 7.00 (s, 1H), 4.73 (s, 1H), 4.39 (s, 2H), 4.38 (s, 2H), 1.56 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.1, 161.8, 159.0, 156.8, 140.4, 136.8, 131.3, 129.2, 129.0, 128.2, 127.8, 125.4, 94.1, 92.8, 82.5, 53.0, 49.1, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{26}O_3N_2Br$ 469.1127, found 469.1123.



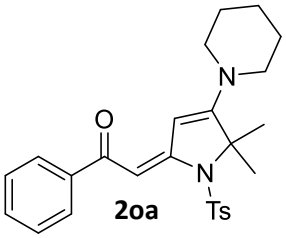
2mc

20 mg (63% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.86 (d, 2H, *J* = 8.6 Hz), 7.62 (d, 2H, *J* = 8.6 Hz), 7.47 (s, 1H), 7.27–7.21 (m, 4H), 7.14–7.10 (m, 1H), 6.13 (s, 1H), 4.50 (s, 2H), 1.48 (t, 9H, *J* = 1.7 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 195.0, 148.6, 138.3, 135.5, 132.0, 129.7, 129.1, 128.9, 128.2, 127.0, 126.6, 125.4, 118.9, 112.7, 84.5, 39.0, 27.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}NO_3SBr$ 472.0582, found 472.0595.



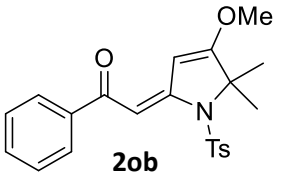
2md

45 mg (72% yield), yellow solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:10). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.84 (d, 2H, *J* = 7.1 Hz), 7.62 (d, 2H, *J* = 7.1 Hz), 7.30 (s, 1H), 6.11 (s, 1H), 5.35 (s, 1H), 4.57–4.35 (m, 3H), 3.66 (s, 3H), 3.13 (s, 2H), 1.47 (s, 9H), 1.44 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 194.9, 171.3, 155.1, 148.5, 135.5, 132.0, 129.7, 128.6, 128.2, 125.0, 118.0, 114.2, 84.4, 80.1, 53.1, 52.3, 38.9, 38.4, 28.3, 27.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{34}N_2O_7SBr$ 597.1090, found 597.1118.



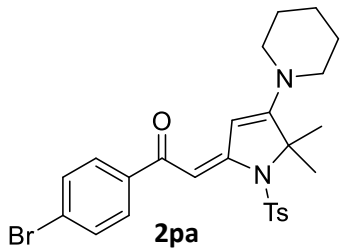
2oa

30 mg (70% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.86 (d, 2H, *J* = 8.4 Hz), 7.76 (d, 2H, *J* = 6.9 Hz), 7.42–7.33 (m, 3H), 7.27 (d, 2H, *J* = 8.4 Hz), 6.91 (s, 1H), 6.48 (s, 1H), 3.44 (t, 4H, *J* = 5.3 Hz), 2.39 (s, 3H), 1.96 (s, 6H), 1.72–1.62 (m, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.1, 166.6, 159.0, 144.1, 141.7, 138.3, 130.6, 129.7, 128.1, 127.4, 127.3, 92.3, 90.9, 71.9, 49.8, 25.8, 25.5, 24.09, 21.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{31}N_2O_3S$ 451.2055, found 451.2059.



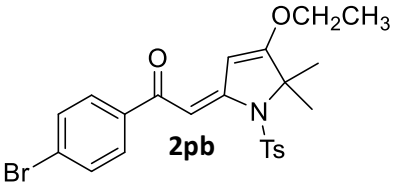
2ob

30 mg (80% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.86 (d, 2H, *J* = 8.4 Hz), 7.82 (d, 2H, *J* = 7.4 Hz), 7.48 (t, 1H, *J* = 7.3 Hz), 7.42 (t, 2H, *J* = 7.4 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 6.95 (s, 1H), 6.78 (s, 1H), 3.89 (s, 3H), 2.40 (s, 3H), 1.74 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.2, 175.7, 157.4, 144.5, 140.6, 137.4, 131.5, 129.8, 128.3, 127.6, 127.4, 95.1, 92.9, 70.6, 58.6, 24.9, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{24}NO_4S$ 398.1426, found 398.1424.



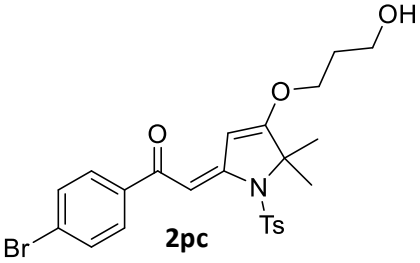
2pa

28 mg (71% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.83 (d, 2H, *J* = 8.3 Hz), 7.62 (d, 2H, *J* = 8.6 Hz), 7.49 (d, 2H, *J* = 8.6 Hz), 7.28 (d, 2H, *J* = 8.3 Hz), 6.89 (s, 1H), 6.39 (s, 1H), 3.44 (t, 4H, *J* = 5.3 Hz), 2.39 (s, 3H), 1.96 (s, 6H), 1.75–1.61 (m, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 186.6, 167.1, 159.5, 144.3, 140.6, 138.2, 131.2, 129.7, 129.0, 127.2, 125.2, 92.2, 90.3, 72.0, 49.9, 25.9, 25.5, 24.1, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{30}N_2O_3SBr$ 529.1161, found 529.1154.



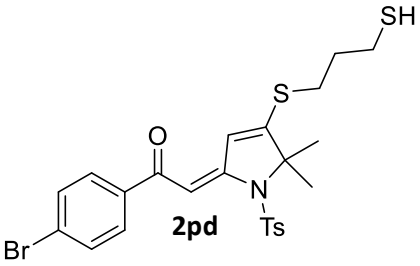
2pb

25 mg (61% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.84 (d, 2H, *J* = 8.4 Hz), 7.67 (d, 2H, *J* = 8.5 Hz), 7.54 (d, 2H, *J* = 8.5 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 6.89 (s, 1H), 6.68 (s, 1H), 4.12 (q, 2H, *J* = 7.1 Hz), 2.41 (s, 3H), 1.74 (s, 6H), 1.41 (t, 3H, *J* = 7.1 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 187.8, 175.3, 158.4, 144.6, 139.5, 137.3, 131.5, 129.8, 129.2, 127.4, 126.3, 94.3, 92.9, 70.8, 67.6, 24.9, 21.6, 14.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{25}NO_4SBr$ 490.0688, found 490.0682.



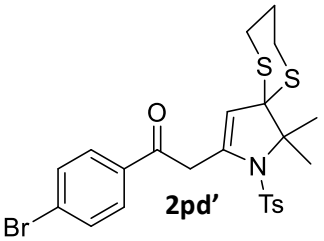
2pc

25 mg (70% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.84 (d, 2H, *J* = 8.3 Hz), 7.66 (d, 2H, *J* = 8.5 Hz), 7.54 (d, 2H, *J* = 8.5 Hz), 7.30 (d, 2H, *J* = 8.3 Hz), 6.93 (s, 1H), 6.68 (s, 1H), 4.21 (t, 2H, *J* = 6.2 Hz), 3.82–3.74 (m, 2H), 2.41 (s, 3H), 2.04 (t, 2H, *J* = 6.2 Hz), 1.74 (s, 6H), 1.62 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 187.9, 175.1, 158.1, 144.7, 139.5, 137.3, 131.5, 129.8, 129.2, 127.4, 126.3, 94.5, 93.2, 70.8, 68.7, 59.1, 31.4, 24.9, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{27}NO_5SBr$ 520.0793, found 520.0789.



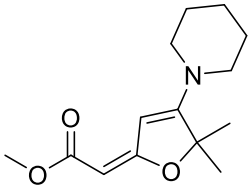
2pd

9 mg (23% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.83 (d, 2H, *J* = 8.3 Hz), 7.66 (d, 2H, *J* = 8.5 Hz), 7.55 (d, 2H, *J* = 8.5 Hz), 7.48 (s, 1H), 7.31 (d, 2H, *J* = 8.3 Hz), 6.63 (s, 1H), 3.13 (t, 2H, *J* = 7.1 Hz), 2.72–2.63 (m, 2H), 2.41 (s, 3H), 2.05 (t, 2H, *J* = 7.1 Hz), 1.81 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 178.2, 159.3, 144.3, 137.4, 134.1, 131.6, 131.4, 129.9, 129.3, 127.4, 126.6, 113.4, 94.6, 71.6, 31.7, 30.2, 23.4, 22.7, 21.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{27}NO_3S_3Br$ 552.0336, found 552.0334.



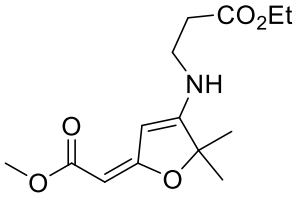
2pd'

17 mg (47% yield), orange solid, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.88 (d, 2H, *J* = 8.3 Hz), 7.61 (d, 2H, *J* = 8.5 Hz), 7.53 (d, 2H, *J* = 8.5 Hz), 7.35 (d, 2H, *J* = 8.3 Hz), 6.93 (s, 1H), 4.09 (s, 2H), 3.08 (t, 2H, *J* = 13.8 Hz), 2.83–2.75 (m, 2H), 2.44 (s, 3H), 2.19–2.09 (m, 2H), 1.78 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.7, 156.7, 144.7, 138.7, 137.4, 131.6, 129.9, 129.4, 127.1, 126.9, 100.4, 65.6, 61.0, 44.1, 27.5, 27.2, 25.2, 24.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{27}NO_3S_3Br$ 552.0336, found 552.0334.



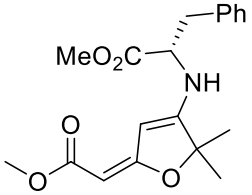
2qa

15 mg (71% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.00 (s, 1H), 4.74 (s, 1H), 3.64 (s, 3H), 3.30 (t, 4H, *J* = 5.4 Hz), 1.68–1.59 (m, 6H), 1.56 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.6, 170.2, 167.6, 88.9, 86.2, 78.3, 50.1, 49.3, 25.9, 25.7, 24.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}NO_3$ 252.1600, found 252.1601.



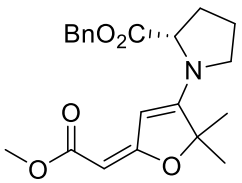
2qb

9 mg (75% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.00 (s, 1H), 4.85 (s, 1H), 4.68 (s, 1H), 4.16 (q, 2H, *J* = 7.2 Hz), 3.65 (s, 3H), 3.44 (q, 2H, *J* = 6.1 Hz), 2.62 (q, 2H, *J* = 6.1 Hz), 1.40 (s, 6H), 1.27 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 176.1, 172.4, 170.1, 165.7, 86.7, 85.9, 80.0, 61.0, 50.3, 40.6, 32.7, 25.4, 14.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}NO_5$ 284.1498, found 284.1500.



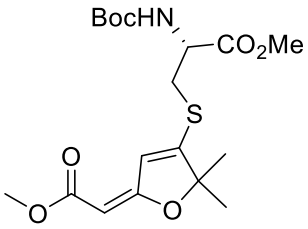
2qc

9 mg (62% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.31–7.23 (m, 3H), 7.04 (d, 2H, *J* = 6.0 Hz), 6.06 (s, 1H), 4.89 (s, 1H), 4.53 (d, 1H, *J* = 7.5 Hz), 4.35 (dt, 1H, *J* = 7.5, 5.3 Hz), 3.78 (s, 3H), 3.66 (s, 3H), 3.28 (dd, 1H, *J* = 14.0, 5.1 Hz), 3.12 (dd, 1H, *J* = 14.0, 5.1 Hz), 1.40 (d, 6H, *J* = 8.2 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.7, 171.5, 170.0, 163.7, 135.0, 129.3, 128.6, 127.4, 87.6, 86.2, 80.7, 57.7, 52.6, 50.3, 36.7, 25.6, 25.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}NO_5$ 346.1654, found 346.1649.



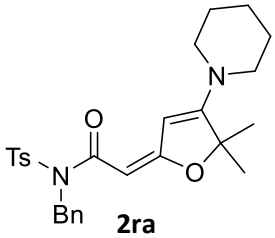
2qd

6 mg (40% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.39–7.30 (m, 5H), 5.87 (s, 1H), 5.20 (d, 1H, *J* = 12.1 Hz), 5.13 (d, 1H, *J* = 12.1 Hz), 4.79 (s, 1H), 4.32 (dd, 1H, *J* = 8.7, 2.2 Hz), 3.64 (s, 3H), 3.51–3.45 (m, 1H), 2.31–2.20 (m, 1H), 2.14–1.99 (m, 4H), 1.51 (s, 3H), 1.46 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 175.0, 172.0, 169.8, 164.5, 135.2, 128.7, 128.6, 128.5, 91.0, 86.3, 79.6, 67.3, 62.1, 50.2, 48.8, 30.3, 25.4, 24.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{26}NO_5$ 372.1811, found 372.1808.



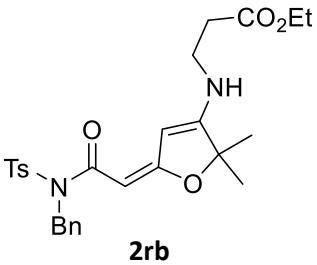
2qe

14 mg (58% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 6.95 (s, 1H), 5.34–5.28 (m, 1H), 5.04 (s, 1H), 4.69 (s, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 3.49 (dd, 1H, *J* = 13.2, 6.1 Hz), 3.33 (dd, 1H, *J* = 13.2, 6.1 Hz), 1.45 (s, 9H), 1.44 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 172.1, 170.5, 168.9, 161.6, 154.9, 112.7, 91.8, 84.8, 80.6, 53.0, 52.1, 50.7, 35.4, 28.3, 26.5, 26.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{28}NO_7S$ 402.1586, found 402.1580.



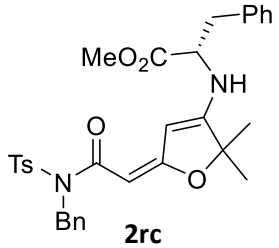
2ra

25 mg (76% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.71 (d, 2H, *J* = 8.4 Hz), 7.39 (d, 2H, *J* = 7.8 Hz), 7.30 (t, 2H, *J* = 7.6 Hz), 7.25–7.18 (m, 3H), 6.04 (s, 1H), 5.34 (s, 1H), 5.08 (s, 2H), 3.30 (t, 4H, *J* = 5.5 Hz), 2.38 (s, 3H), 1.68–1.61 (m, 2H), 1.58 (t, 4H, *J* = 5.5 Hz), 1.51 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.7, 169.8, 167.2, 143.3, 138.3, 138.2, 129.2, 128.4, 127.7, 127.3, 126.9, 89.6, 86.1, 80.4, 49.5, 49.1, 25.8, 25.6, 23.9, 21.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{33}N_2O_4S$ 481.2161, found 481.2164.



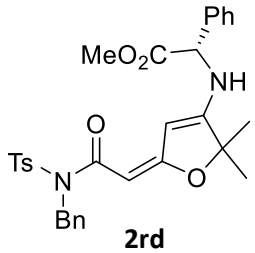
2rb

20 mg (77% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.71 (d, 2H, *J* = 8.3 Hz), 7.39 (d, 2H, *J* = 7.8 Hz), 7.30 (t, 2H, *J* = 7.6 Hz), 7.26–7.19 (m, 3H), 6.04 (s, 1H), 5.45 (s, 1H), 5.09 (s, 2H), 4.86 (t, 1H, *J* = 6.2 Hz), 4.14 (q, 2H, *J* = 7.2 Hz), 3.40 (q, 2H, *J* = 6.1 Hz), 2.57 (t, 2H, *J* = 5.9 Hz), 2.38 (s, 3H), 1.34 (s, 6H), 1.25 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 178.3, 172.3, 168.2, 167.3, 143.4, 138.1, 129.3, 128.4, 127.7, 127.3, 127.0, 87.6, 85.8, 81.9, 61.0, 49.2, 40.6, 32.8, 25.3, 21.6, 14.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{33}N_2O_6S$ 513.2059, found 513.2064.



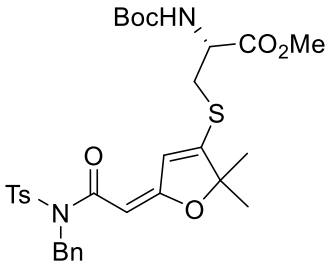
2rc

8 mg (55% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.73 (d, 2H, *J* = 8.3 Hz), 7.40 (d, 2H, *J* = 7.2 Hz), 7.32 (t, 2H, *J* = 7.6 Hz), 7.27–7.17 (m, 6H), 6.99 (d, 2H, *J* = 7.6 Hz), 6.10 (s, 1H), 5.50 (s, 1H), 5.10 (s, 2H), 4.63 (d, 1H, *J* = 7.6 Hz), 4.33 (dt, 1H, *J* = 7.6, 5.2 Hz), 3.77 (s, 3H), 3.23 (dd, 1H, *J* = 14.0, 5.4 Hz), 3.08 (dd, 1H, *J* = 14.0, 5.4 Hz), 2.39 (s, 3H), 1.34 (d, 6H, *J* = 5.3 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.9, 171.3, 167.2, 166.1, 143.5, 138.1, 138.0, 134.8, 129.3, 128.6, 128.5, 127.8, 127.5, 127.3, 127.1, 88.5, 86.1, 82.6, 57.5, 52.7, 49.2, 36.7, 25.5, 25.2, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{35}N_2O_6S$ 575.2216, found 575.2214.



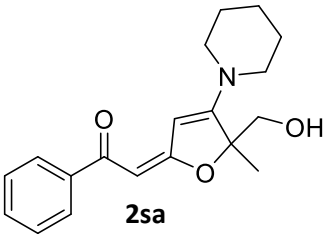
2rd

6 mg (50% yield), pale-yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.67 (d, 2H, *J* = 8.3 Hz), 7.36–7.25 (m, 9H), 7.25–7.20 (m, 1H), 7.19 (d, 2H, *J* = 8.3 Hz), 5.89 (s, 1H), 5.47 (s, 1H), 5.35 (d, 1H, *J* = 7.1 Hz), 5.01 (d, 1H, *J* = 7.1 Hz), 4.62 (s, 2H), 3.74 (s, 3H), 2.37 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.7, 171.0, 166.9, 165.7, 143.5, 138.1, 137.9, 135.2, 129.3, 129.2, 129.0, 128.4, 128.1, 127.7, 127.3, 127.0, 89.6, 86.1, 83.0, 60.7, 53.3, 49.0, 25.4, 25.2, 21.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{33}N_2O_6S$ 561.2059, found 561.2054.



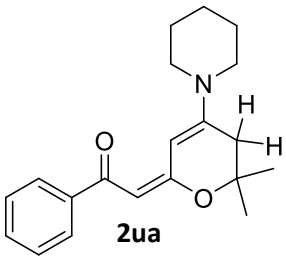
2re

15 mg (41% yield), clear oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.70 (d, 2H, *J* = 8.4 Hz), 7.37 (d, 2H, *J* = 7.8 Hz), 7.31 (t, 2H, *J* = 7.5 Hz), 7.28–7.22 (m, 3H), 6.92 (s, 1H), 5.71 (s, 1H), 5.31–5.25 (m, 1H), 5.09 (s, 2H), 4.64 (s, 1H), 3.66 (s, 3H), 3.46 (dd, 1H, *J* = 13.6, 5.1 Hz), 3.29 (dd, 1H, *J* = 13.6, 5.1 Hz), 2.40 (s, 3H), 1.43 (s, 9H), 1.38 (d, 6H, *J* = 2.5 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 174.0, 170.4, 166.6, 164.6, 154.9, 143.9, 137.6, 129.4, 128.5, 127.8, 127.4, 127.3, 113.3, 92.0, 86.0, 80.6, 52.9, 52.0, 49.2, 35.5, 28.3, 26.4, 26.2, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{39}N_2O_8S_2$ 631.2148, found 631.2141.



2sa

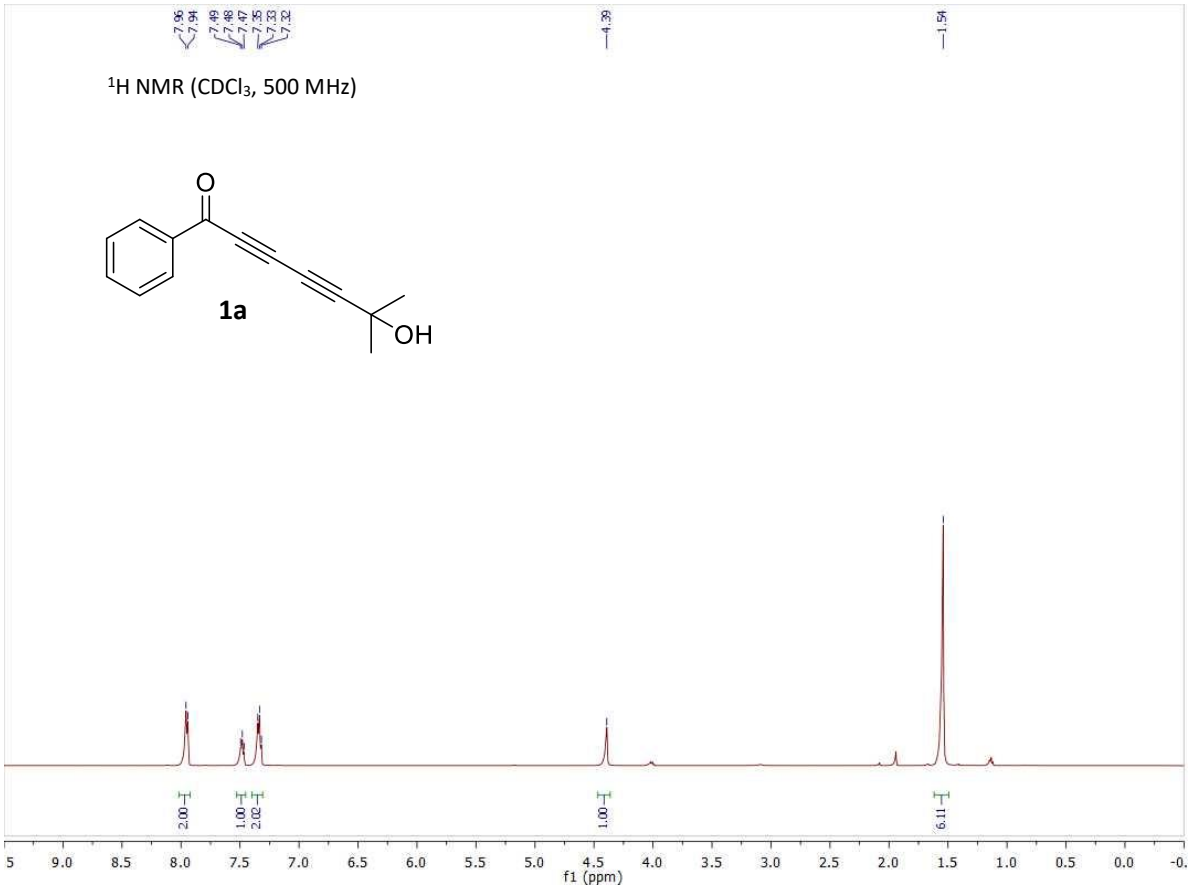
8 mg (65% yield), red oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.91 (d, 2H, *J* = 7.9 Hz), 7.44–7.35 (m, 3H), 6.62 (s, 1H), 6.03 (s, 1H), 3.93–3.82 (m, 2H), 3.41 (t, 4H, *J* = 5.3 Hz), 2.08 (s, 1H), 1.69–1.62 (m, 6H), 1.59 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.2, 177.1, 167.2, 141.3, 130.6, 128.1, 127.2, 92.5, 89.0, 87.5, 67.2, 49.9, 25.8, 24.0, 20.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}NO_3$ 314.1572, found 314.1567.



2ua

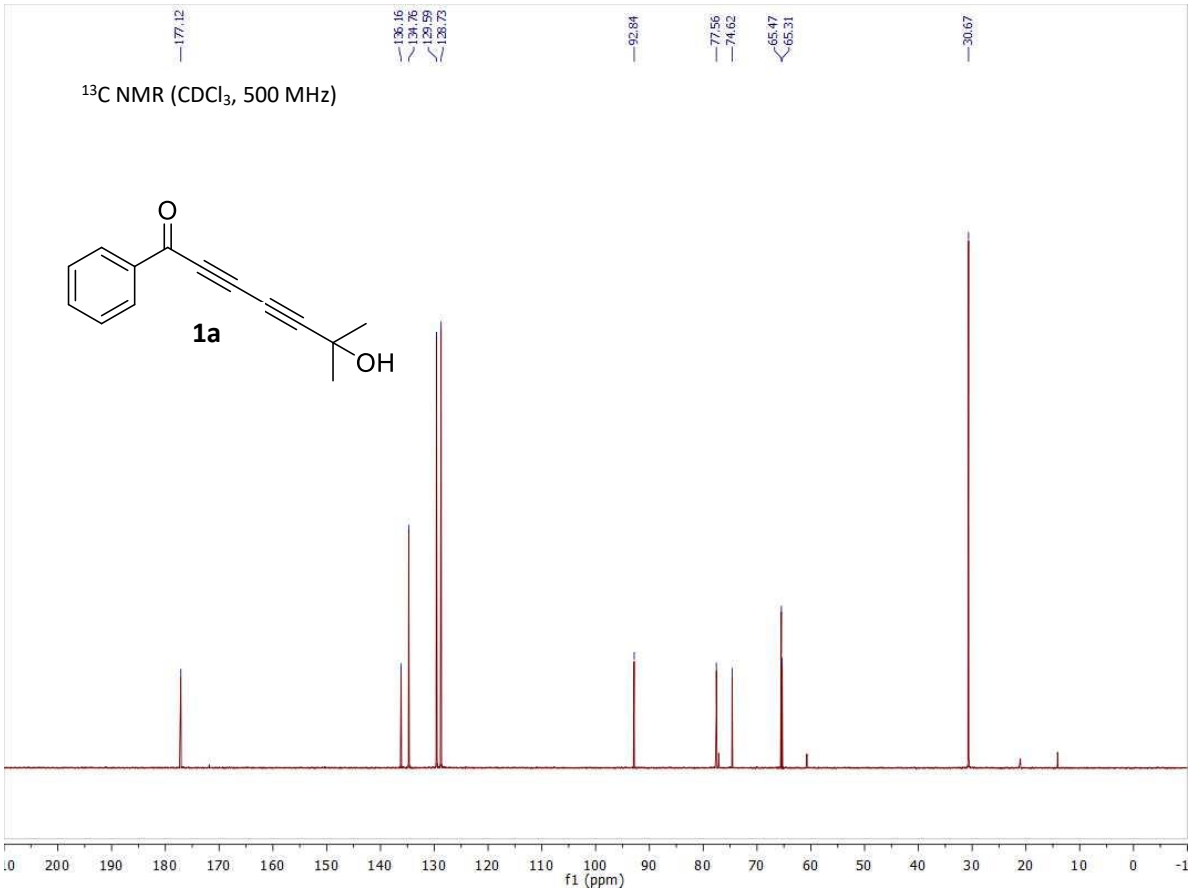
9 mg (20% yield), yellow oil, purified by flash column chromatography (SiO_2, EtOAc–hexanes, 1:5). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.91 (d, 2H, *J* = 8.2 Hz), 7.42–7.34 (m, 3H), 7.31 (s, 1H), 5.96 (s, 1H), 3.40 (t, 4H, *J* = 5.3 Hz), 2.44 (s, 2H), 1.72–1.60 (m, 6H), 1.42 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 188.4, 169.7, 154.3, 142.2, 130.2, 127.9, 127.2, 93.9, 89.0, 75.0, 47.5, 37.6, 27.2, 25.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{26}NO_2$ 312.1964, found 312.1960.

^{1}H and ^{13}C NMR Spectra of Substrates



^{1}H NMR ($CDCl_3$, 500 MHz)

1a

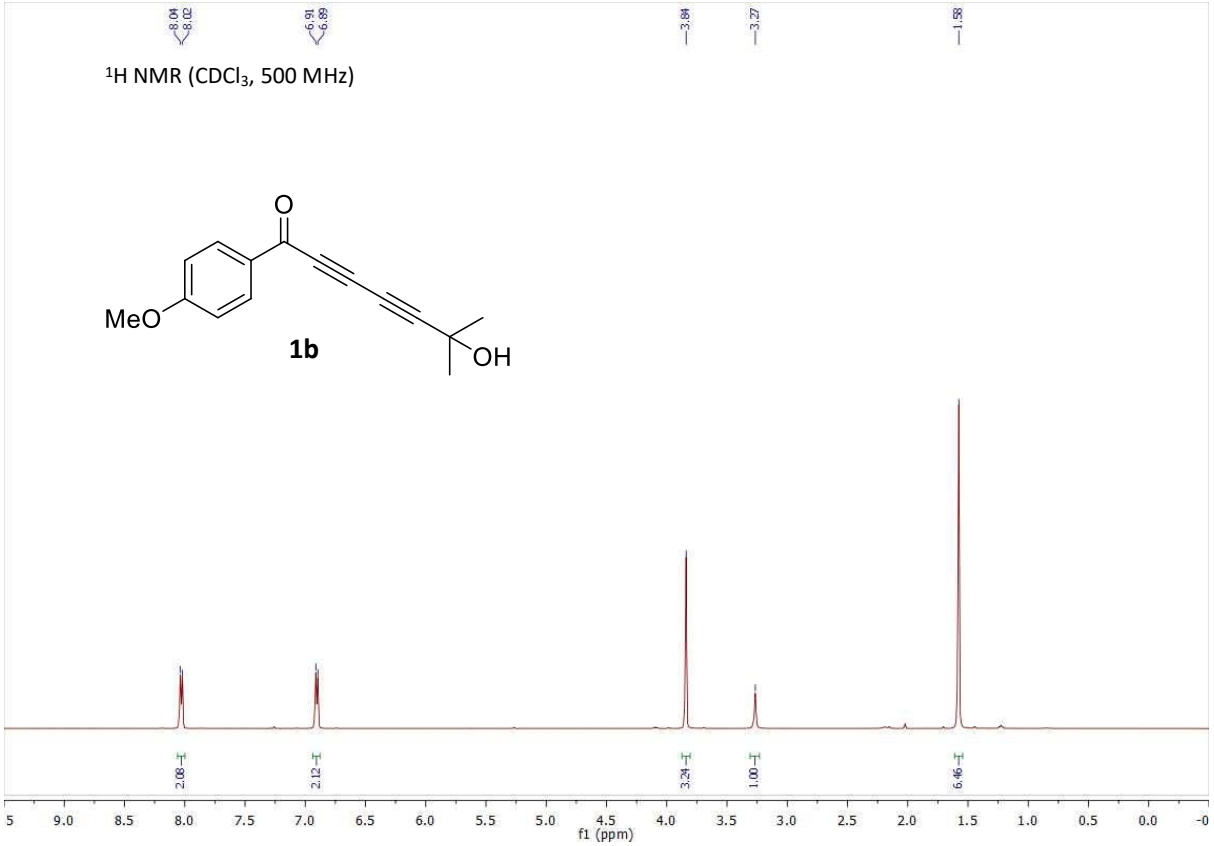


^{13}C NMR ($CDCl_3$, 500 MHz)

1a

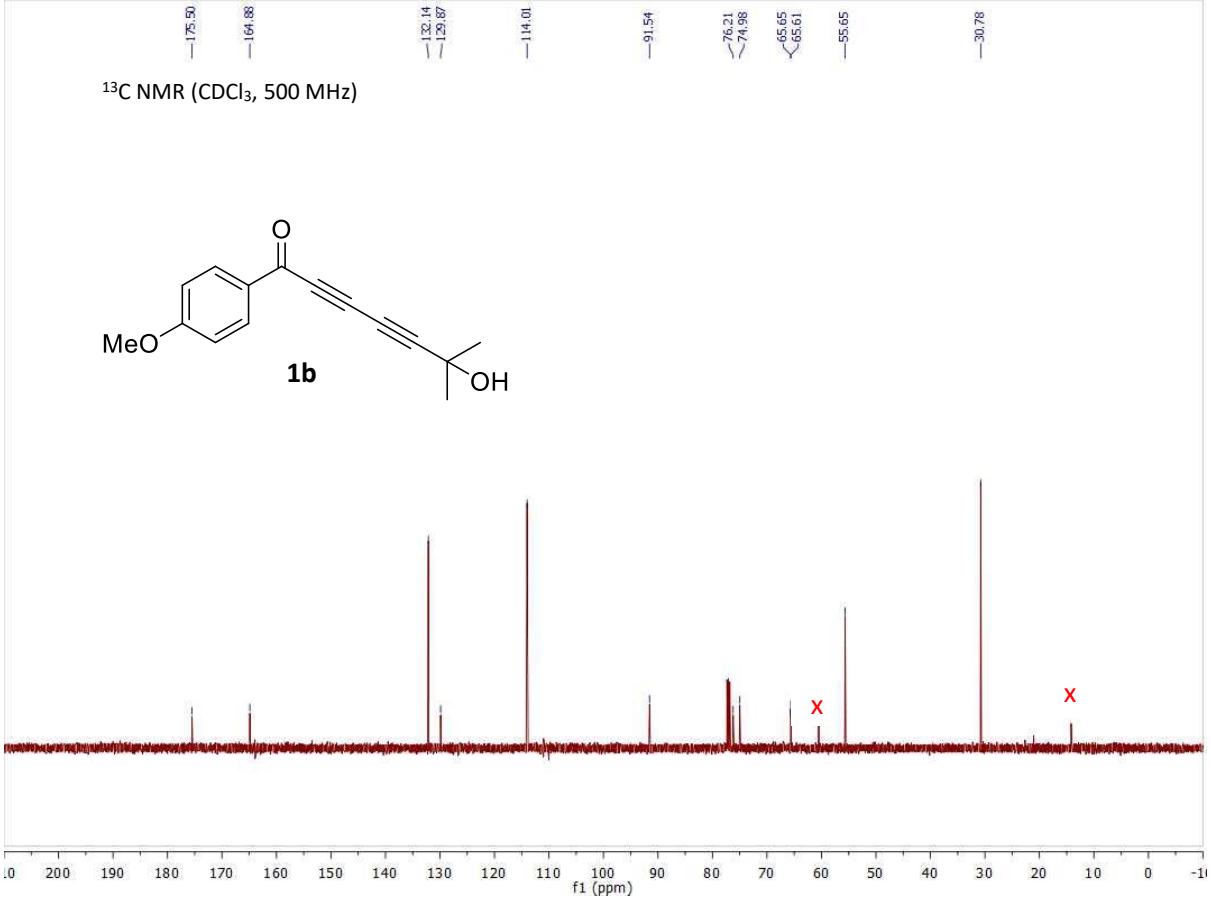
^{1}H NMR ($CDCl_3$, 500 MHz)

1b



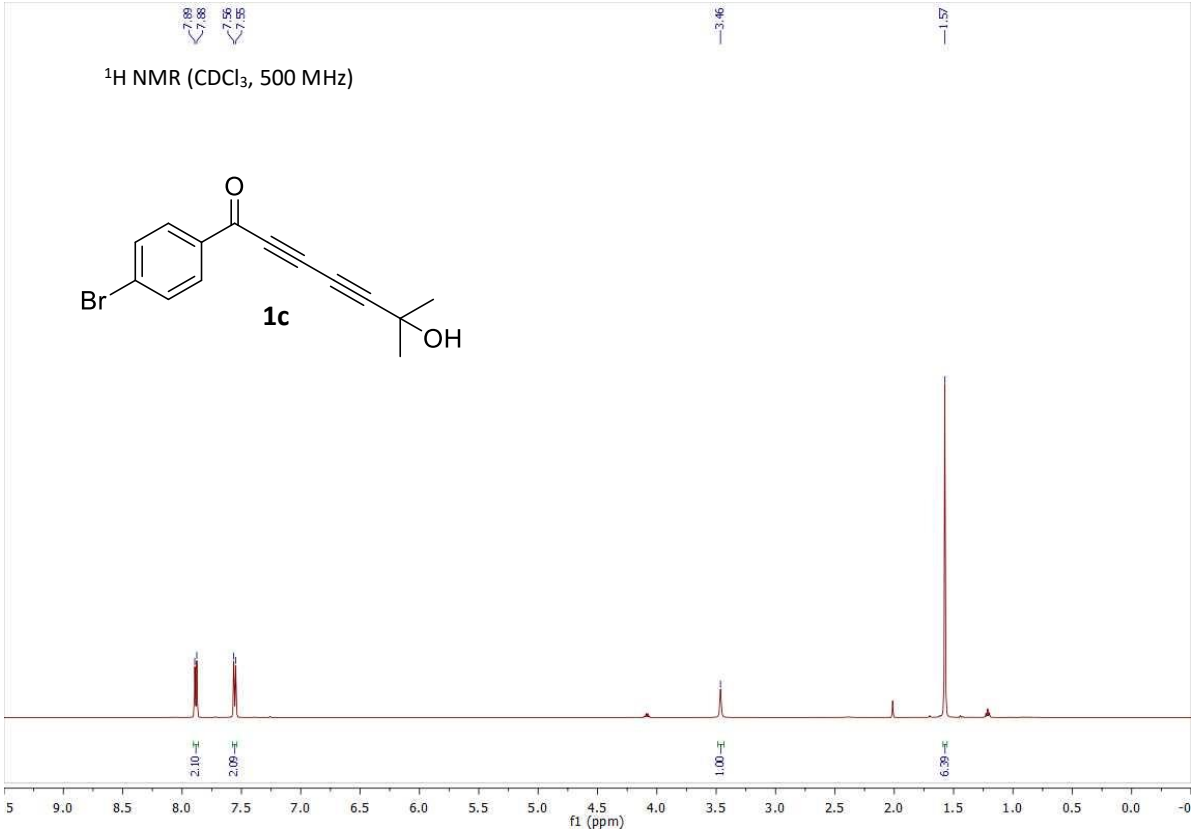
^{13}C NMR ($CDCl_3$, 500 MHz)

1b



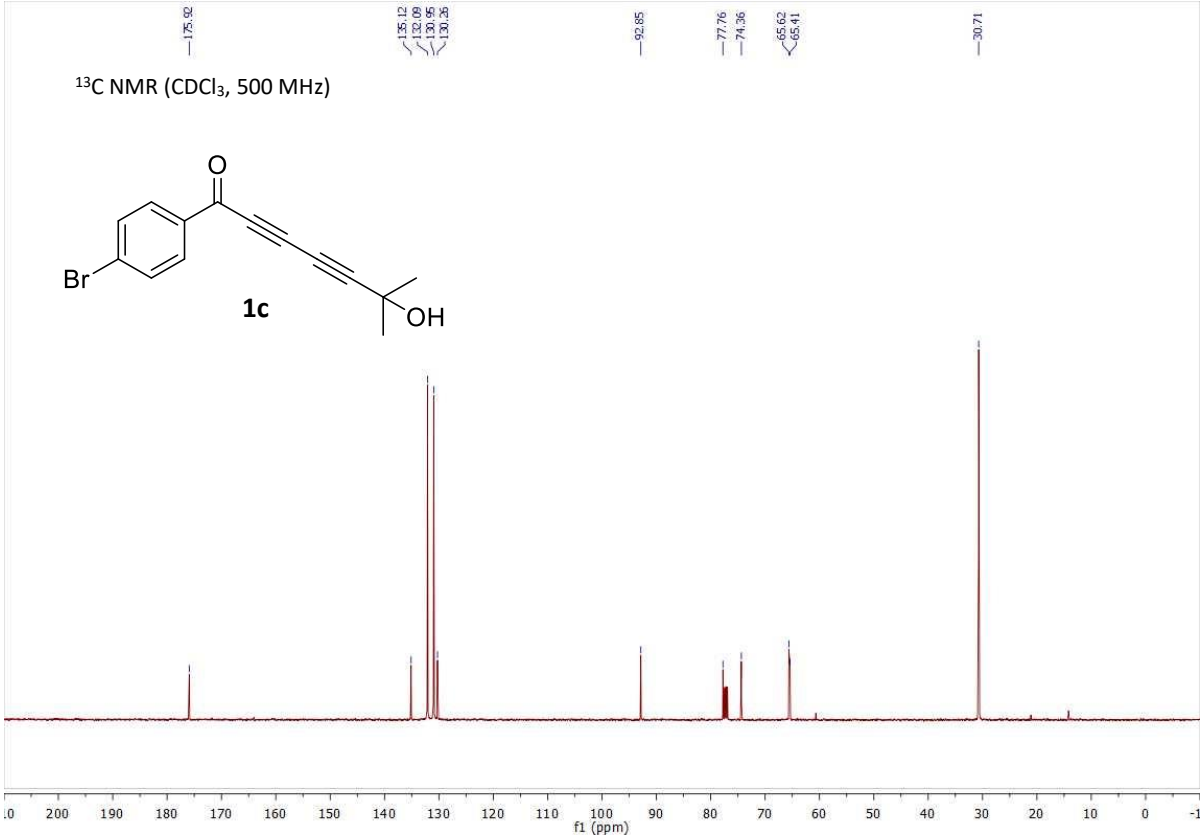
^{1}H NMR ($CDCl_3$, 500 MHz)

1c



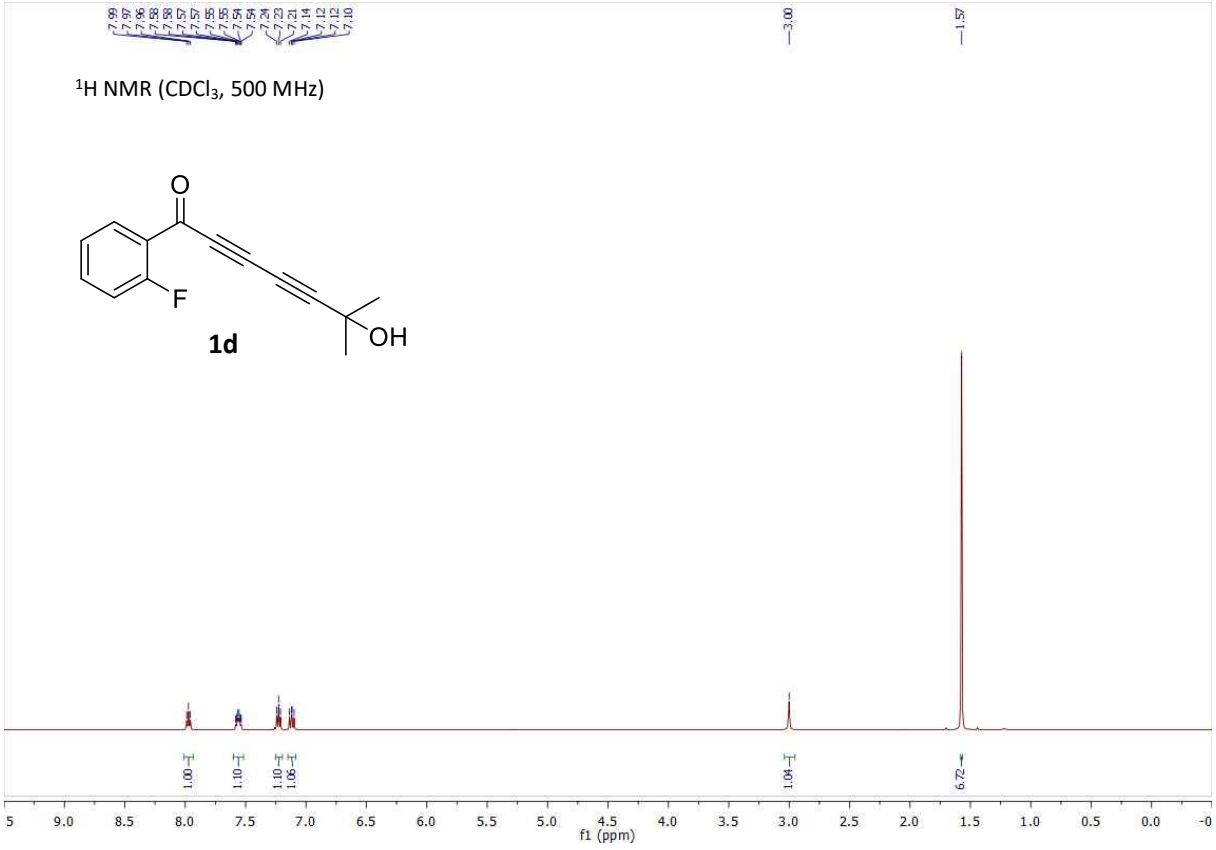
^{13}C NMR ($CDCl_3$, 500 MHz)

1c



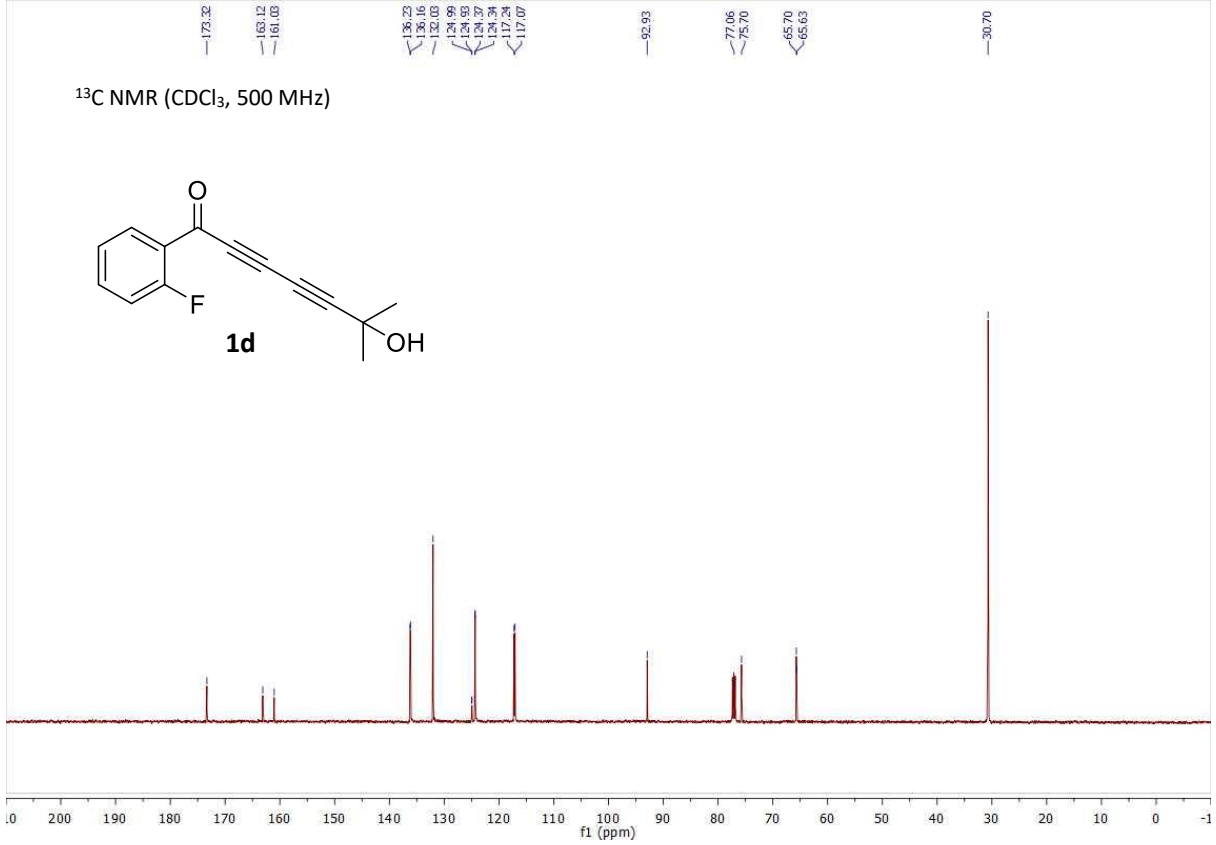
^{1}H NMR ($CDCl_3$, 500 MHz)

1d



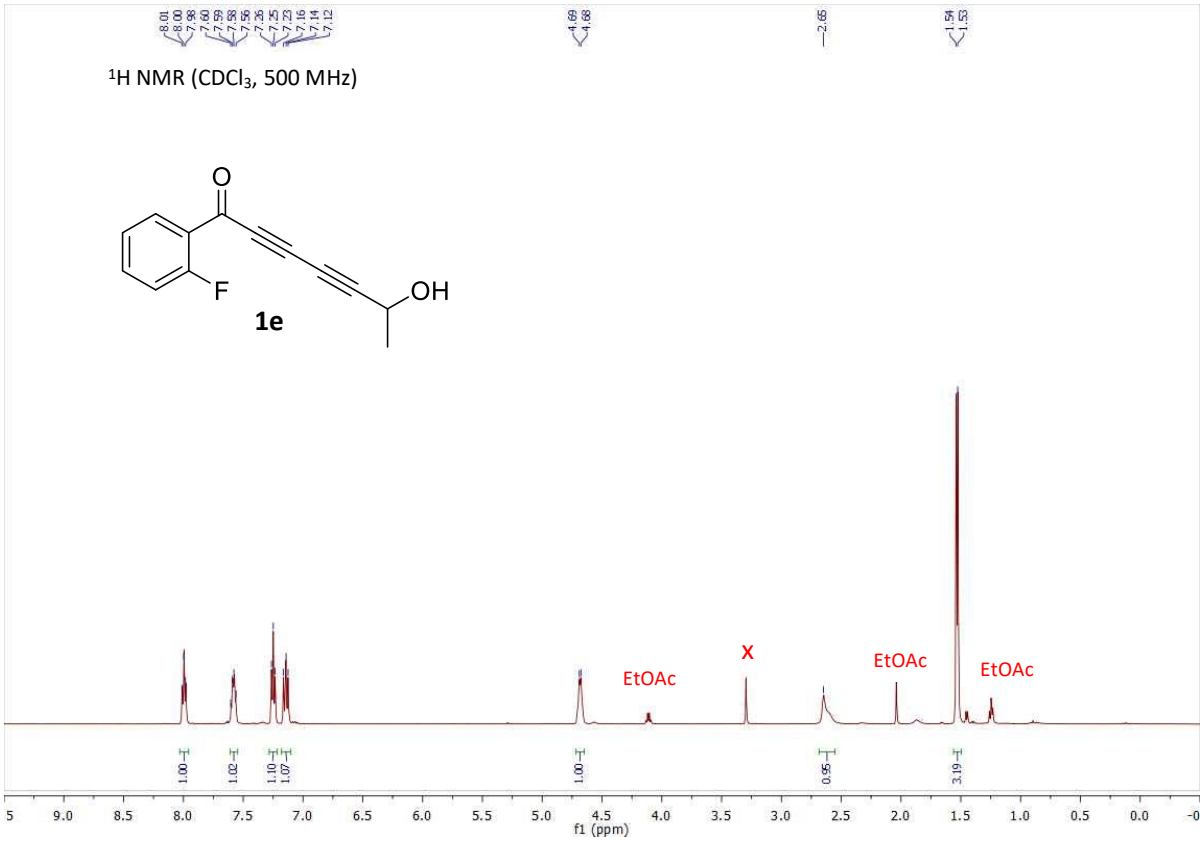
^{13}C NMR ($CDCl_3$, 500 MHz)

1d



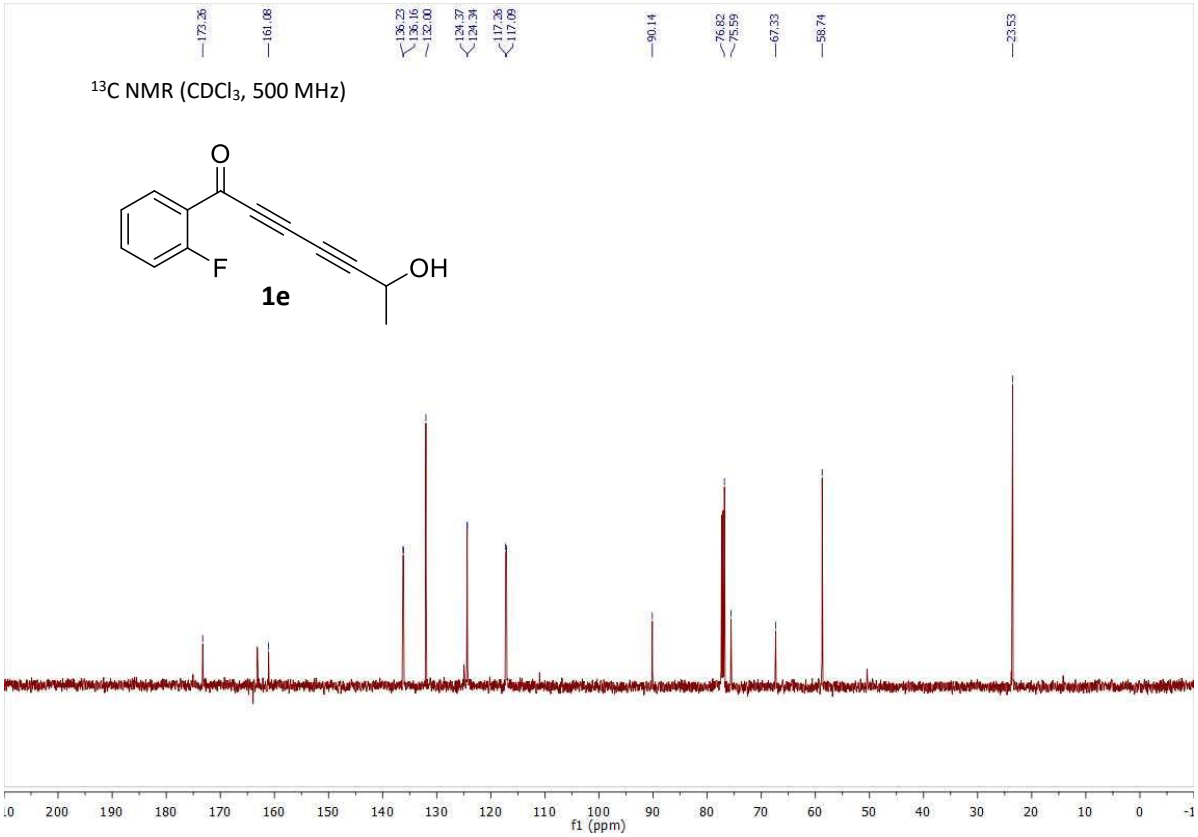
^{1}H NMR ($CDCl_3$, 500 MHz)

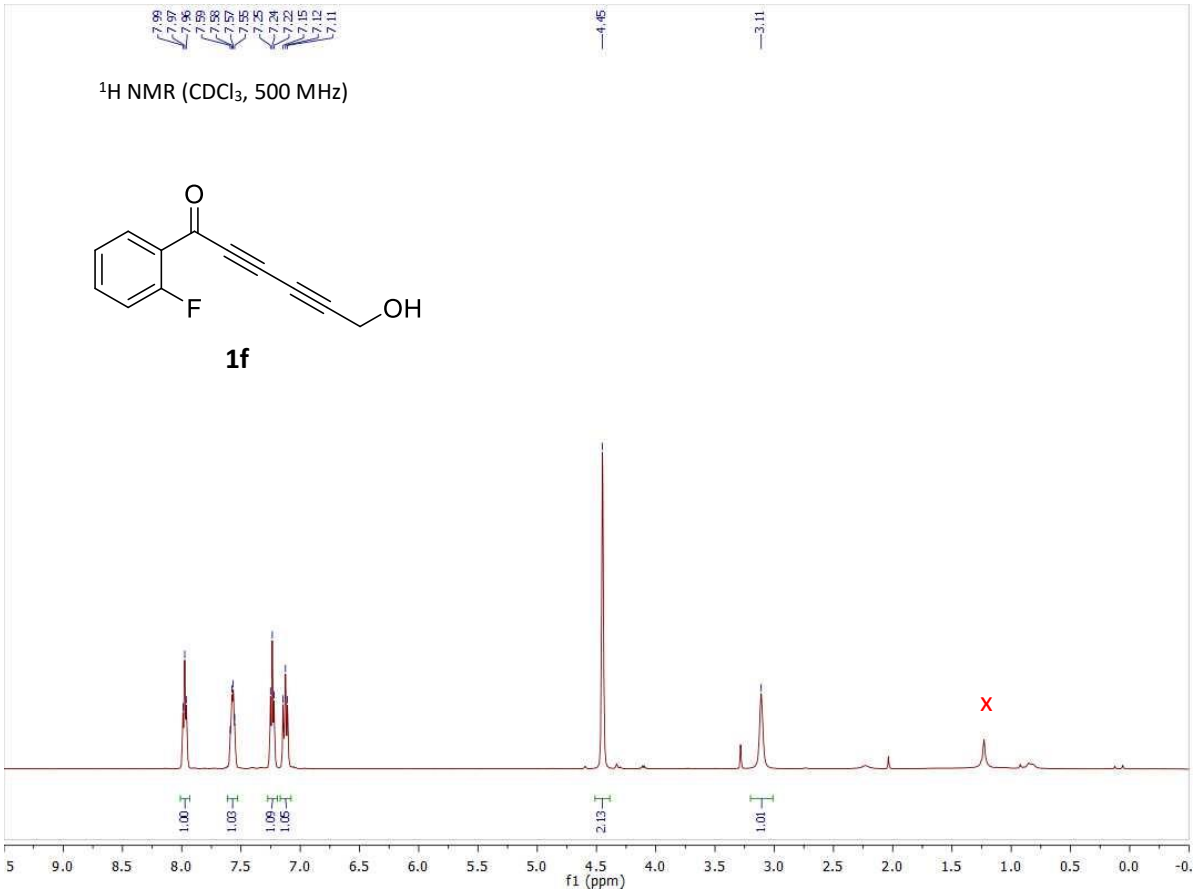
1e



^{13}C NMR ($CDCl_3$, 500 MHz)

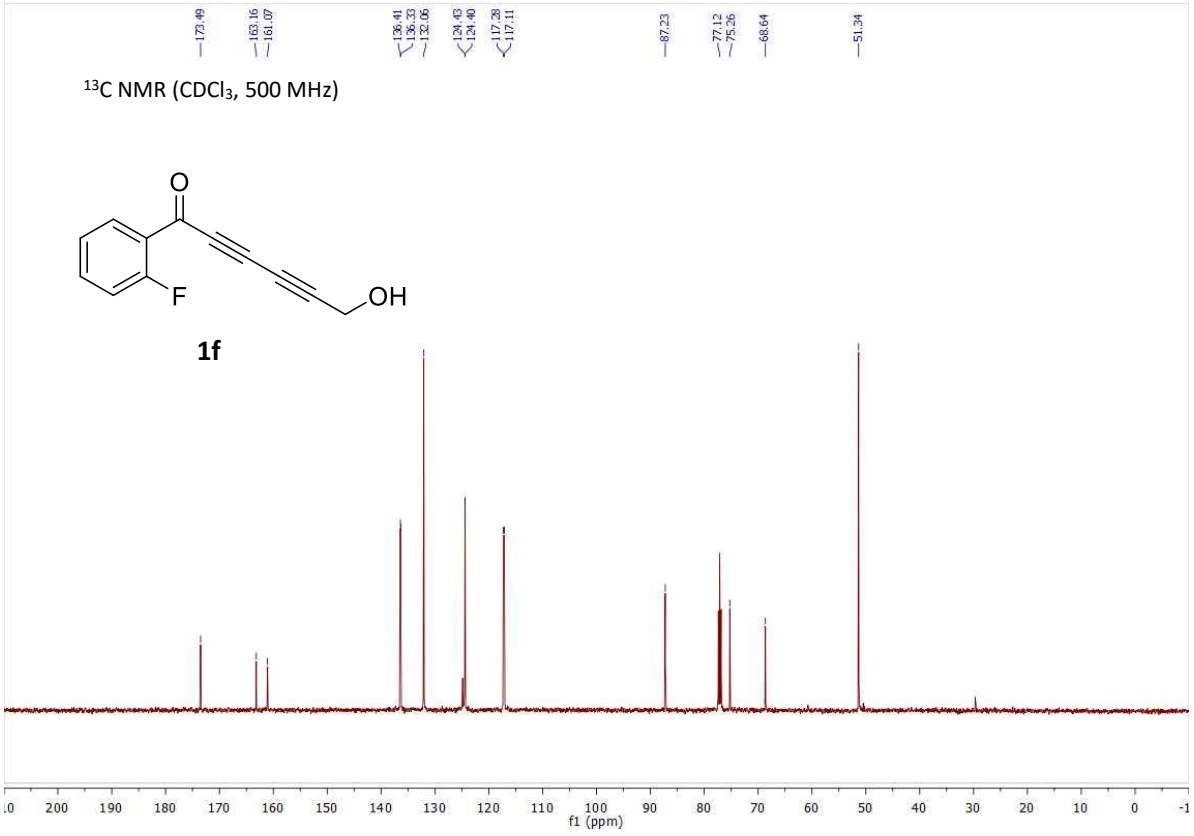
1e





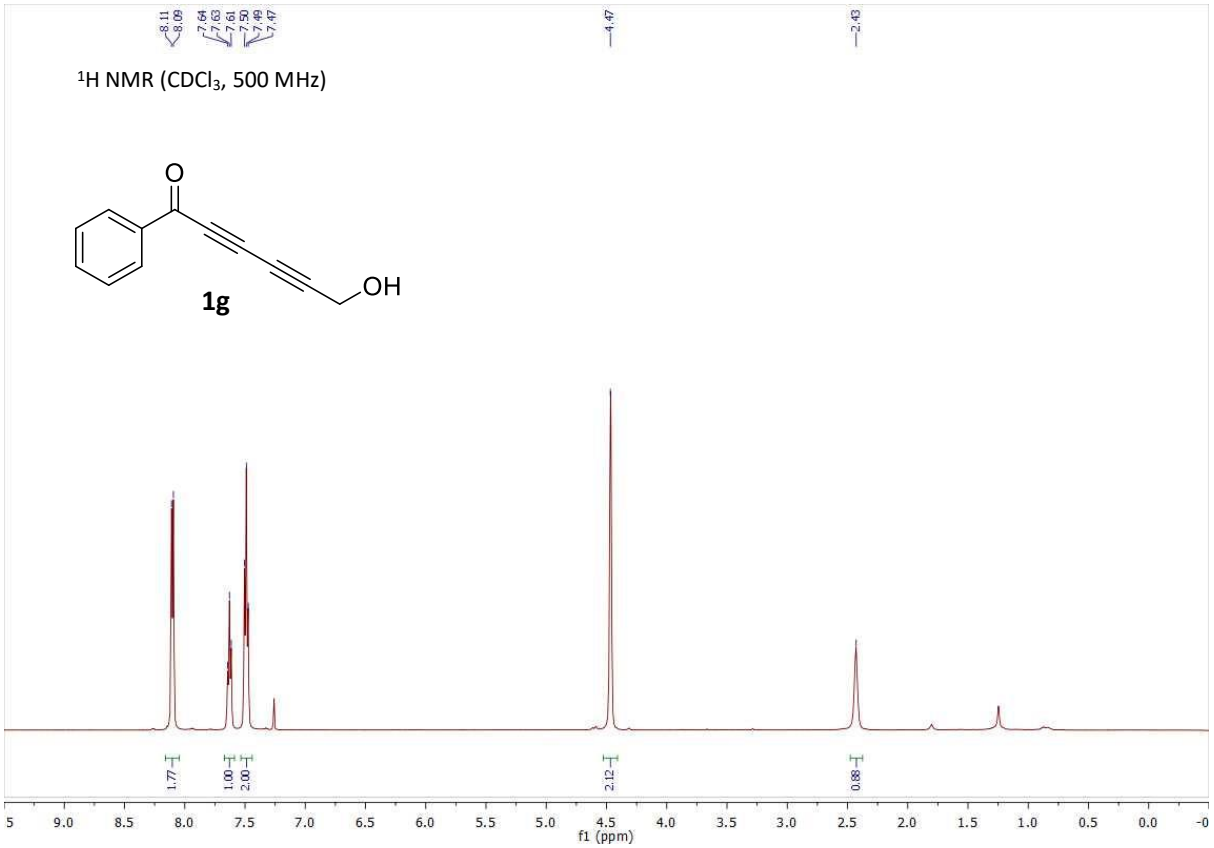
^{1}H NMR ($CDCl_3$, 500 MHz)

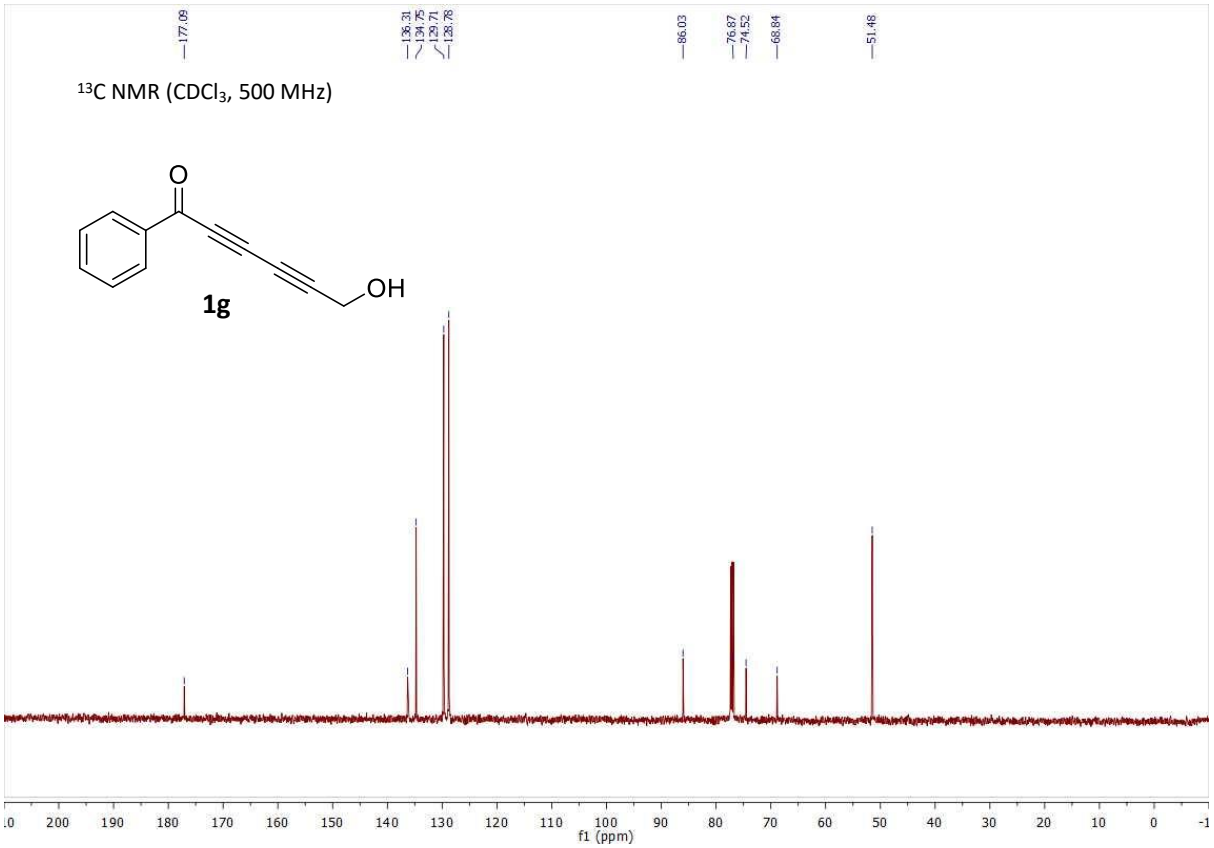
1f



^{13}C NMR ($CDCl_3$, 500 MHz)

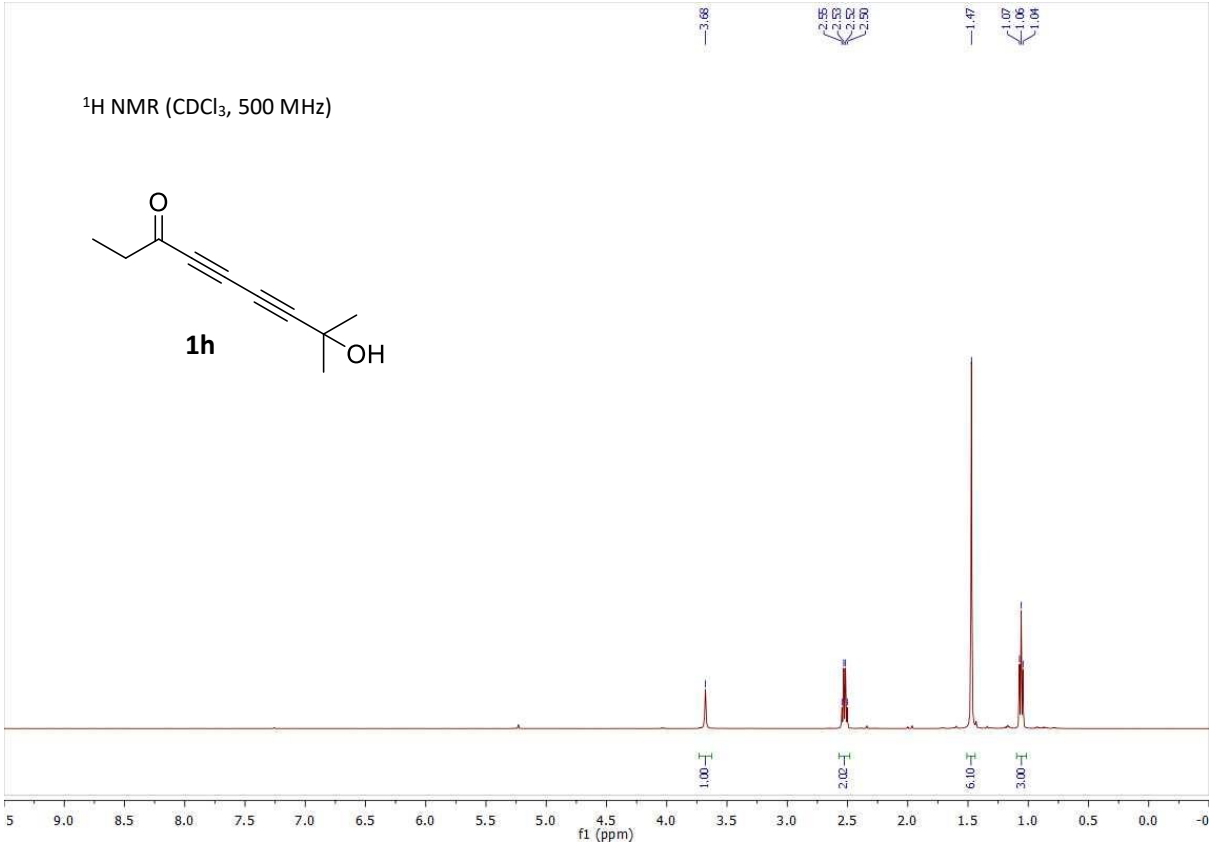
1f


8.11
8.09
7.64
7.63
7.61
7.50
7.49
7.47
4.47
2.43
1H NMR (CDCl3, 500 MHz)
O
OH
1g
1.77
1.00
2.00
2.12
0.88
f1 (ppm)


177.09
136.31
134.75
129.71
128.78
86.03
76.87
74.52
68.84
51.48
13C NMR (CDCl3, 500 MHz)
O
OH
1g
f1 (ppm)

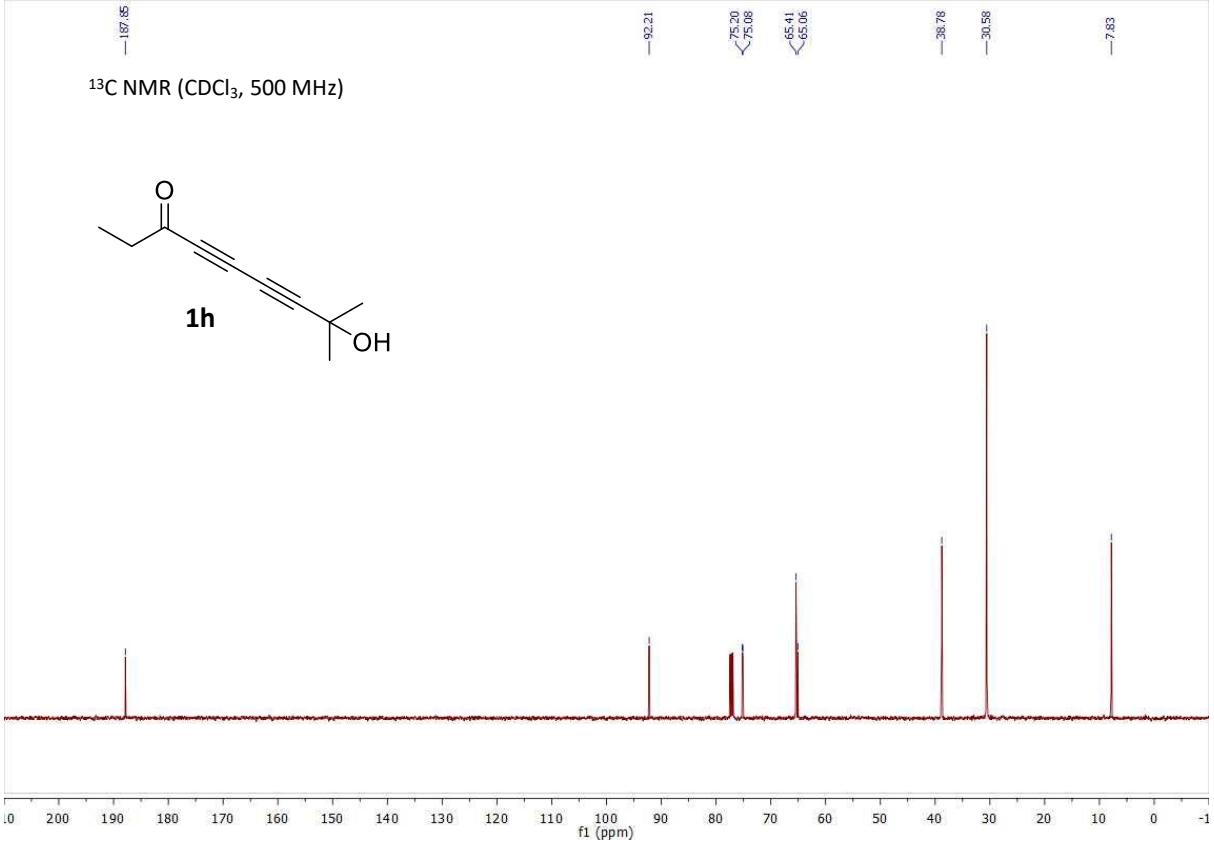
^{1}H NMR ($CDCl_3$, 500 MHz)

1h



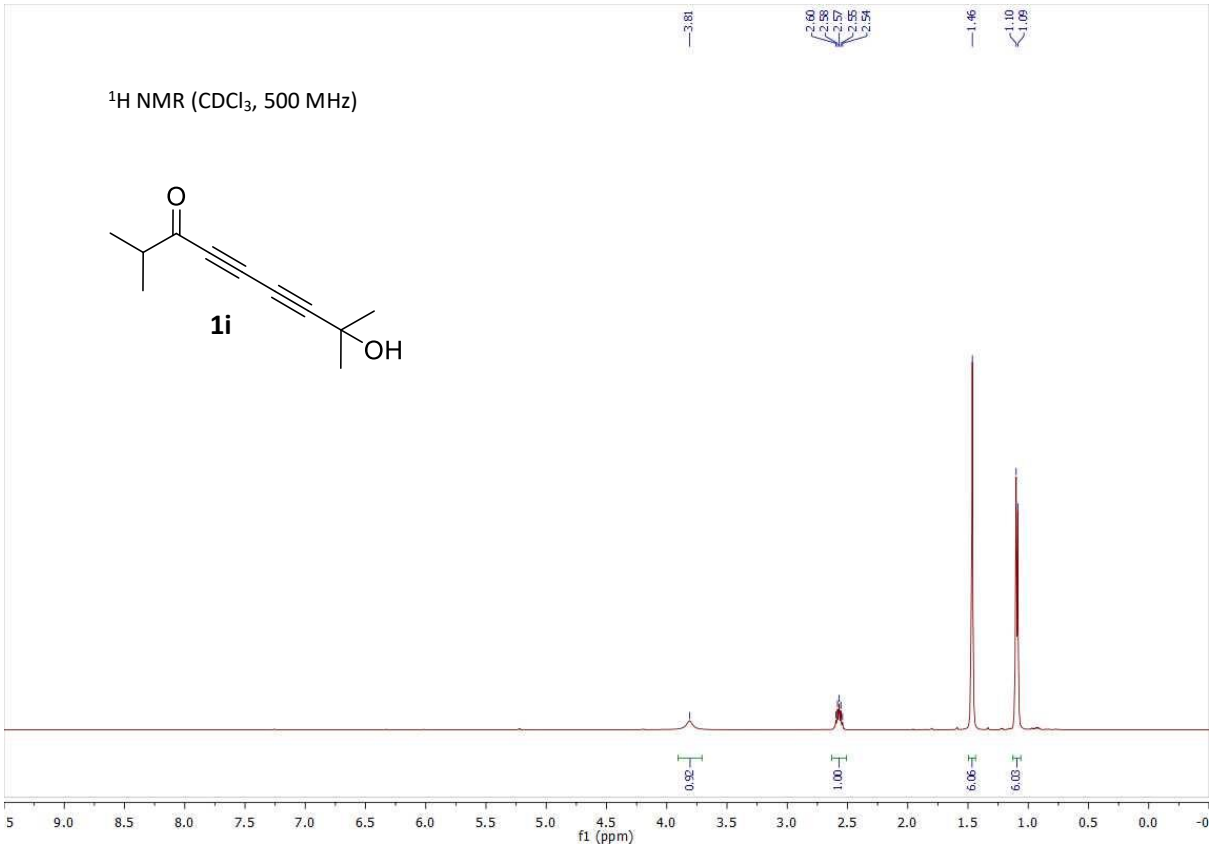
^{13}C NMR ($CDCl_3$, 500 MHz)

1h



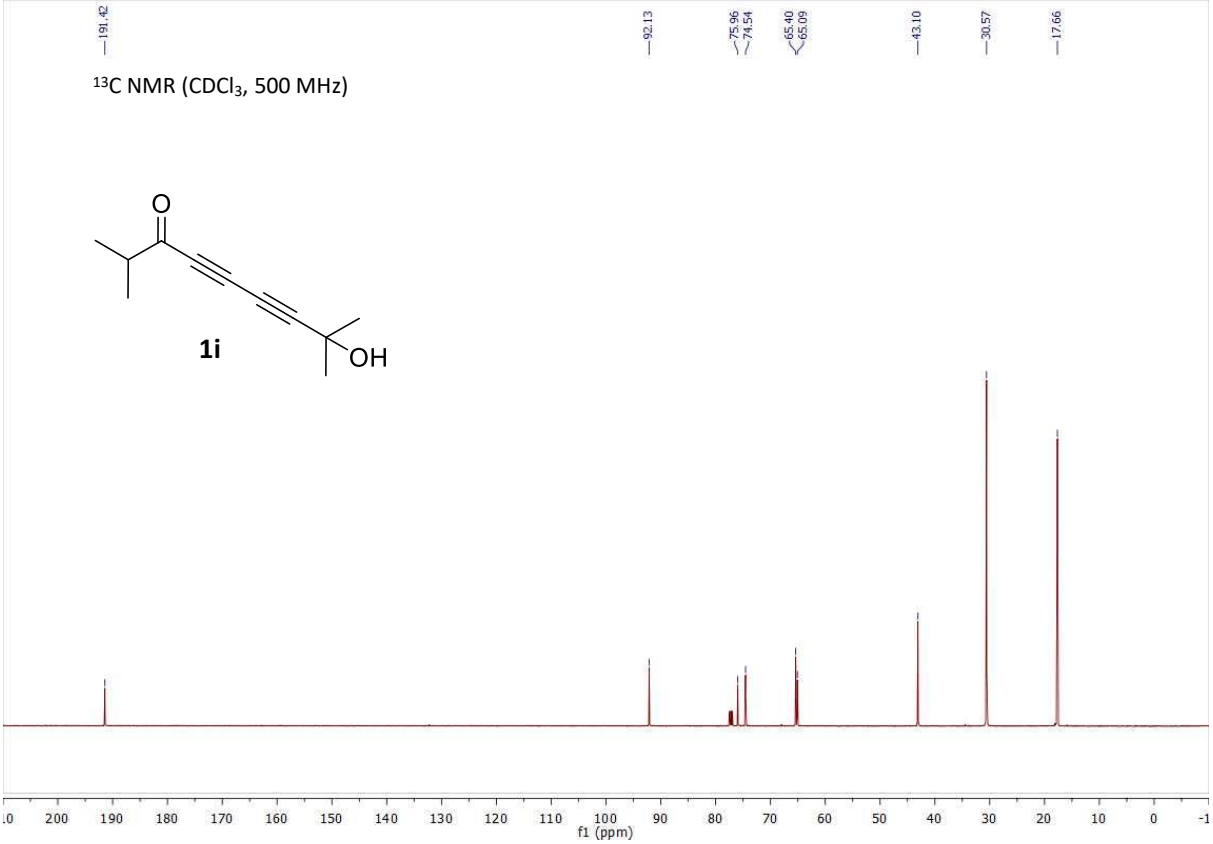
^{1}H NMR ($CDCl_3$, 500 MHz)

1i



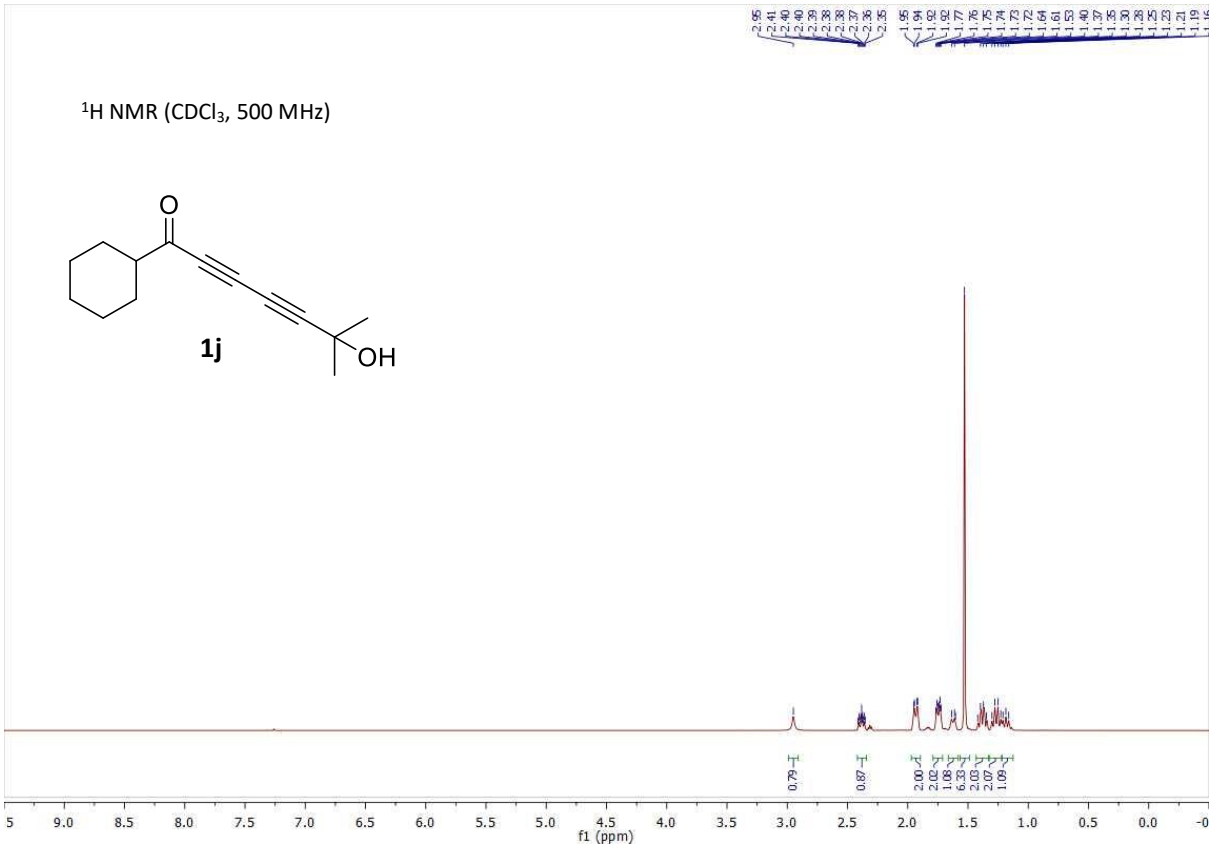
^{13}C NMR ($CDCl_3$, 500 MHz)

1i



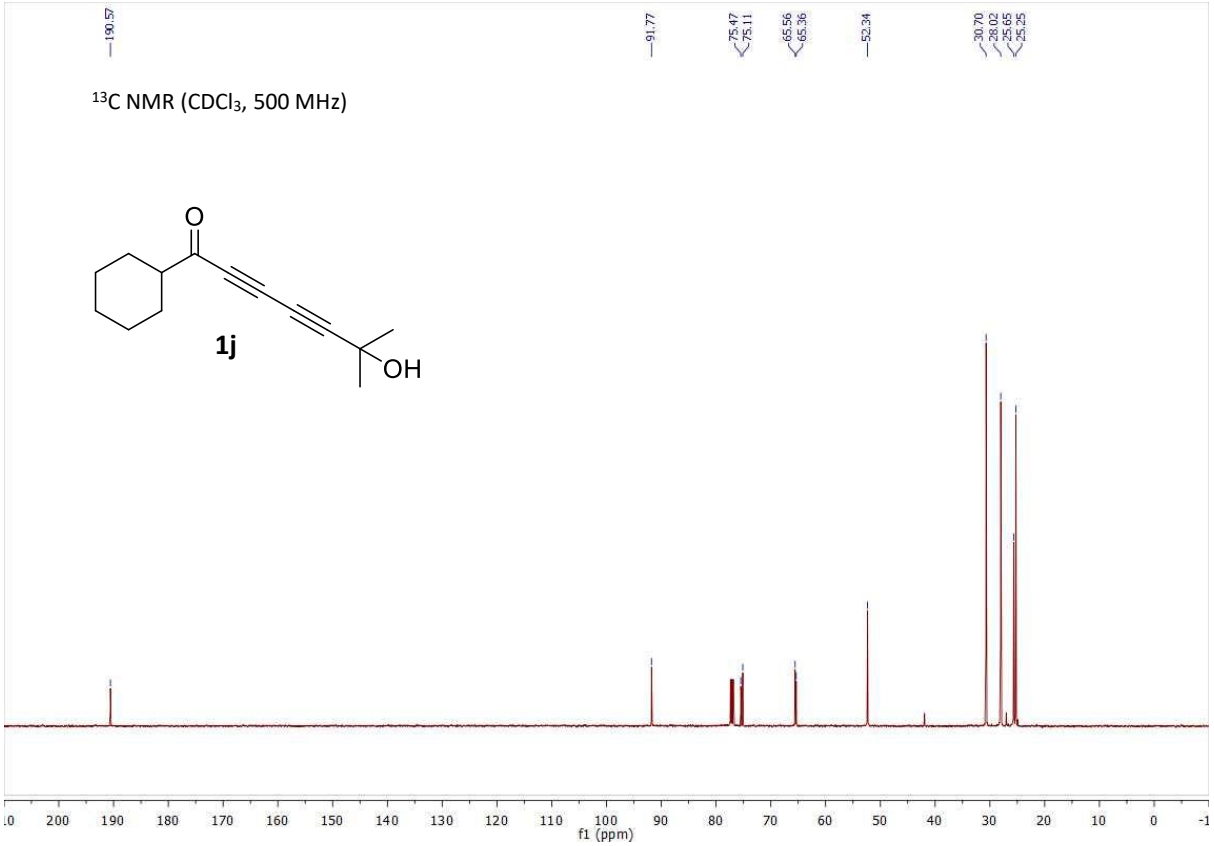
^{1}H NMR ($CDCl_3$, 500 MHz)

1j



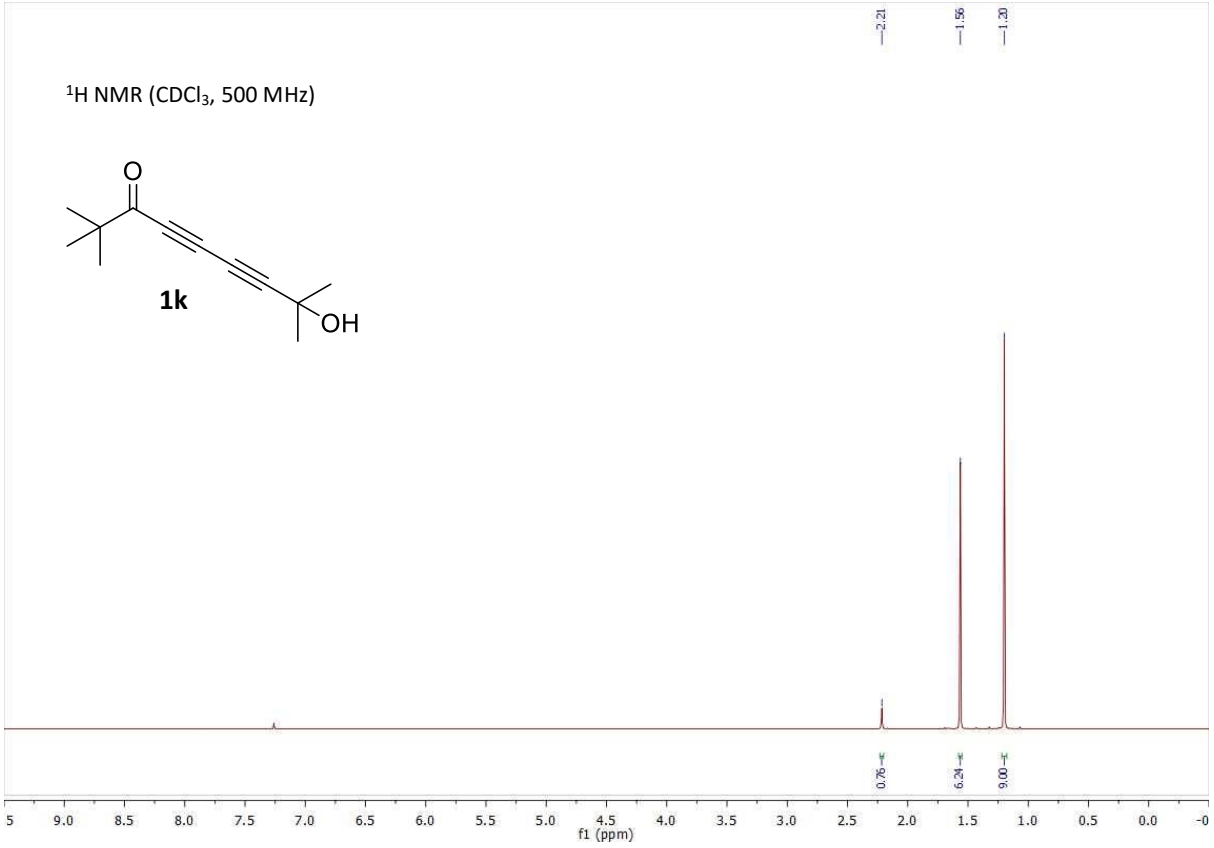
^{13}C NMR ($CDCl_3$, 500 MHz)

1j



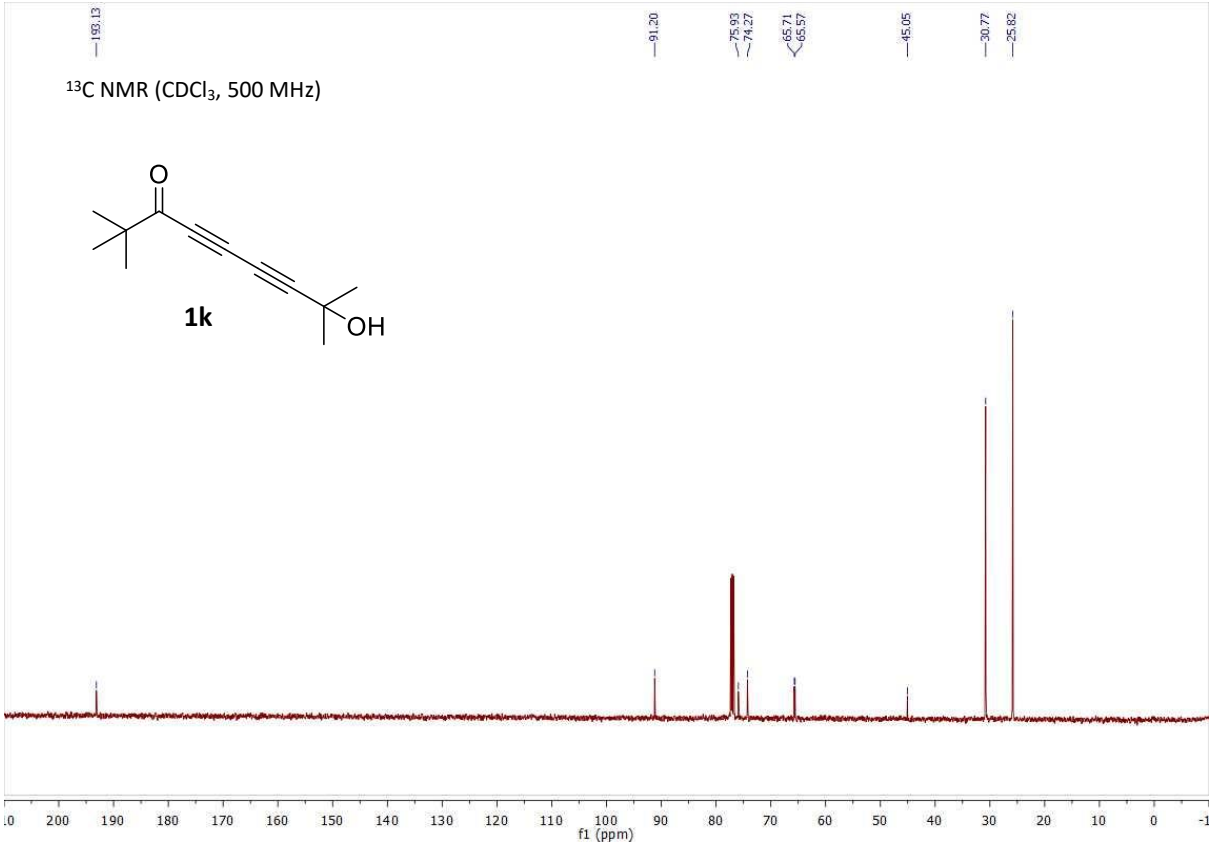
^{1}H NMR ($CDCl_3$, 500 MHz)

1k

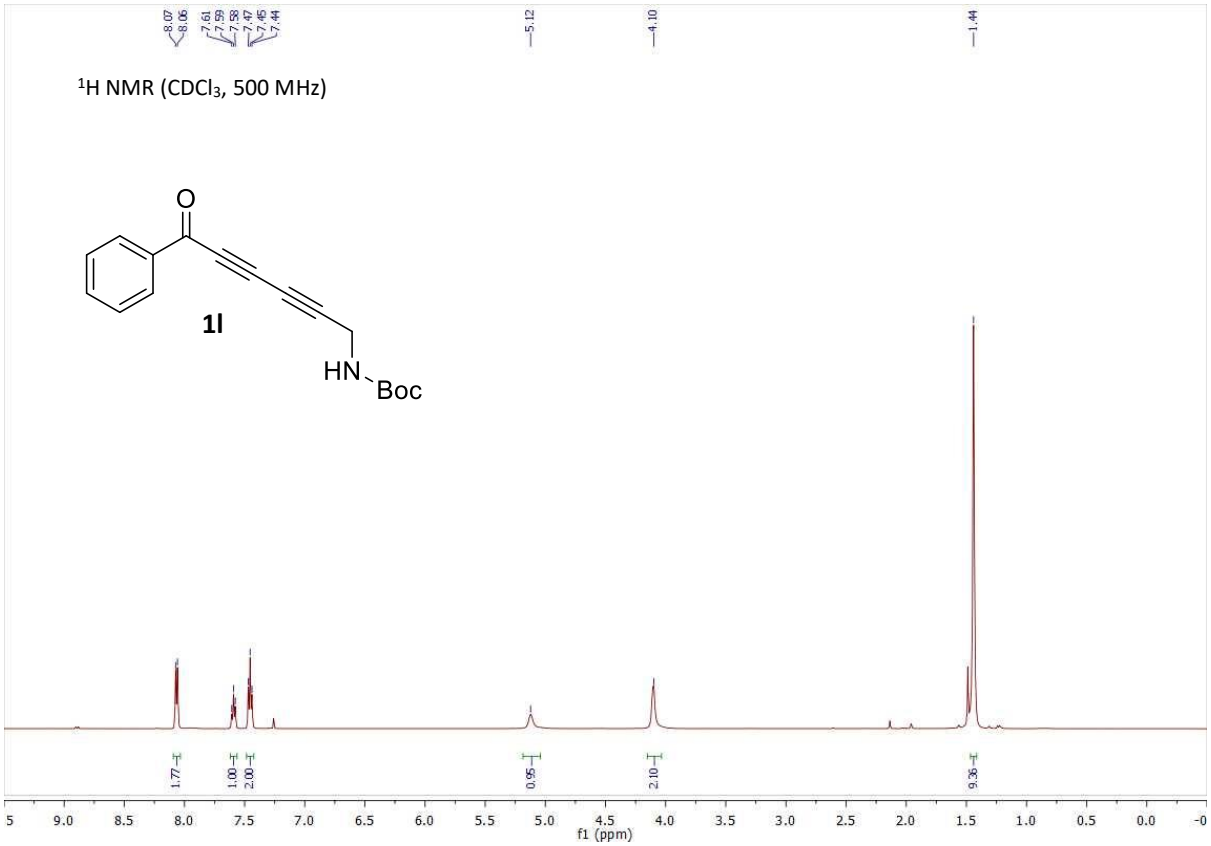


^{13}C NMR ($CDCl_3$, 500 MHz)

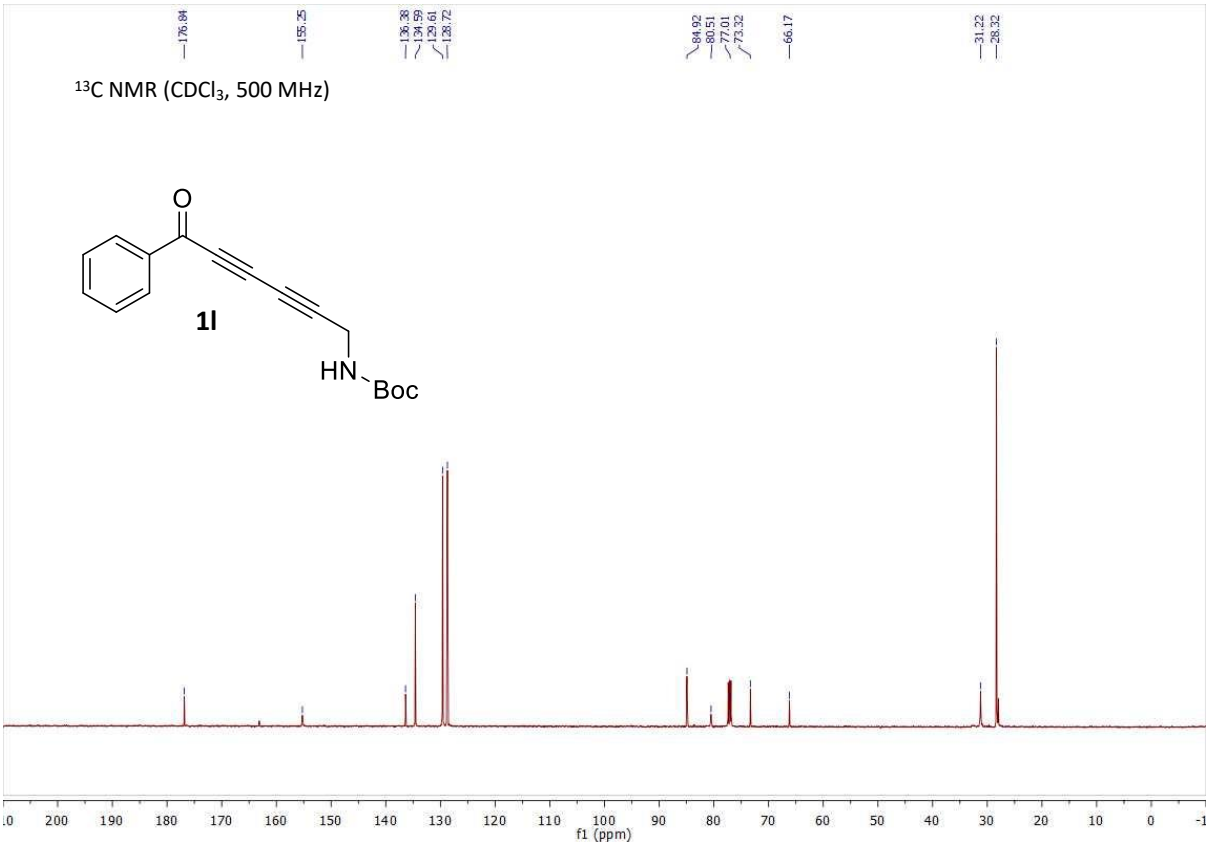
1k



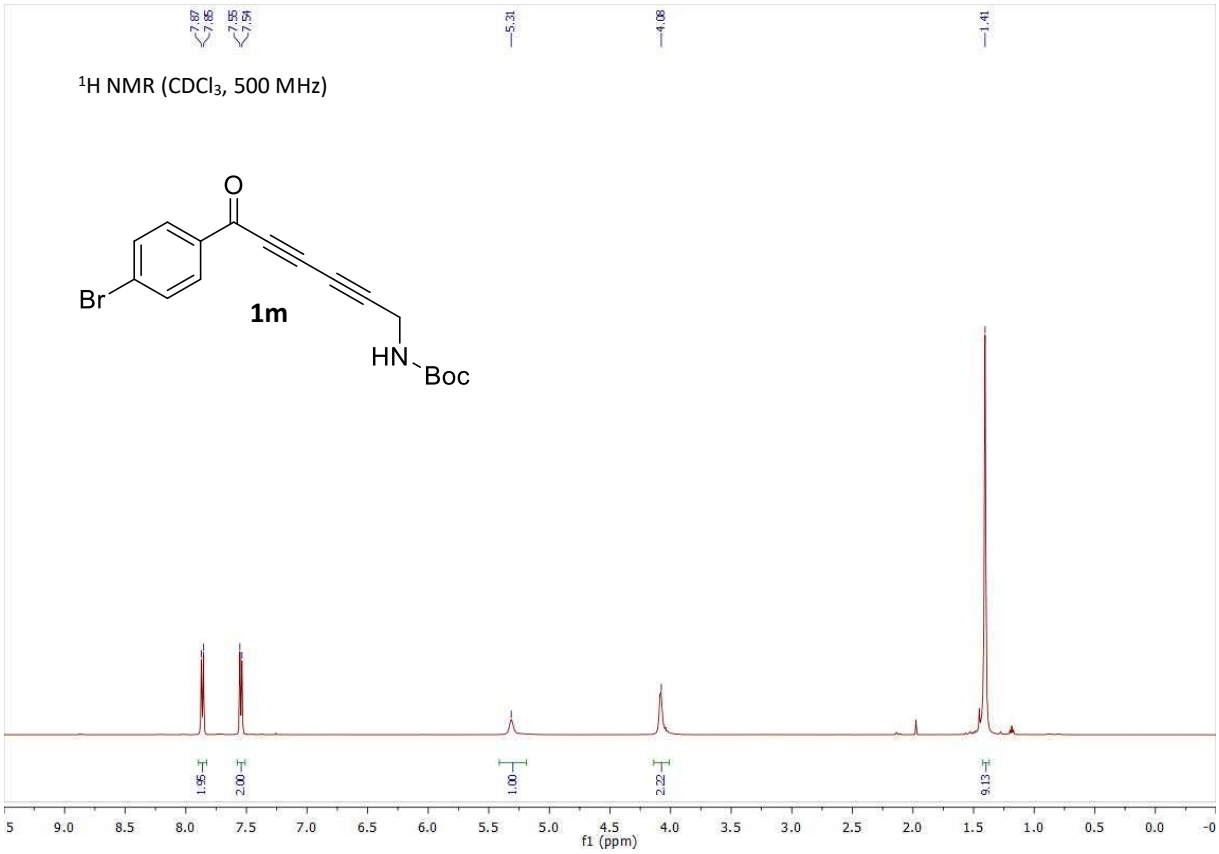
^{1}H NMR ($CDCl_3$, 500 MHz)



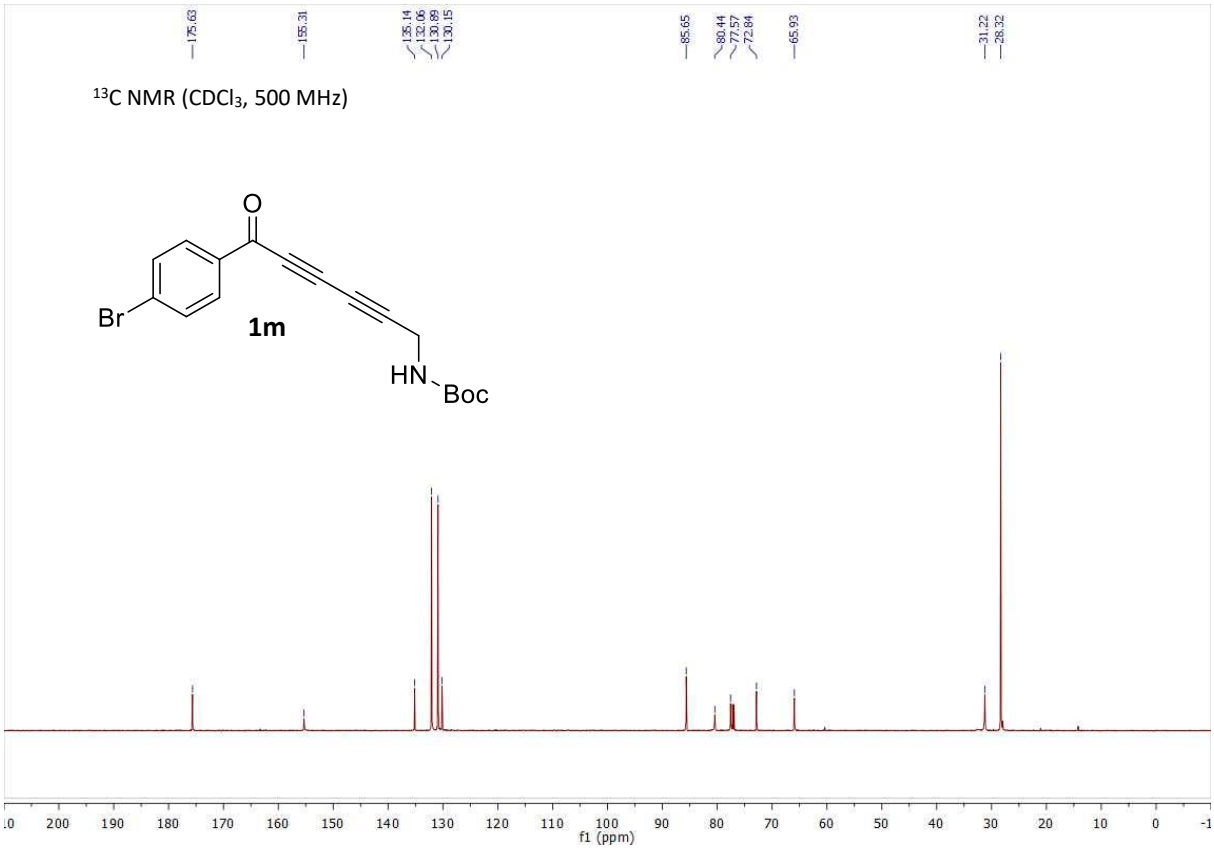
^{13}C NMR ($CDCl_3$, 500 MHz)

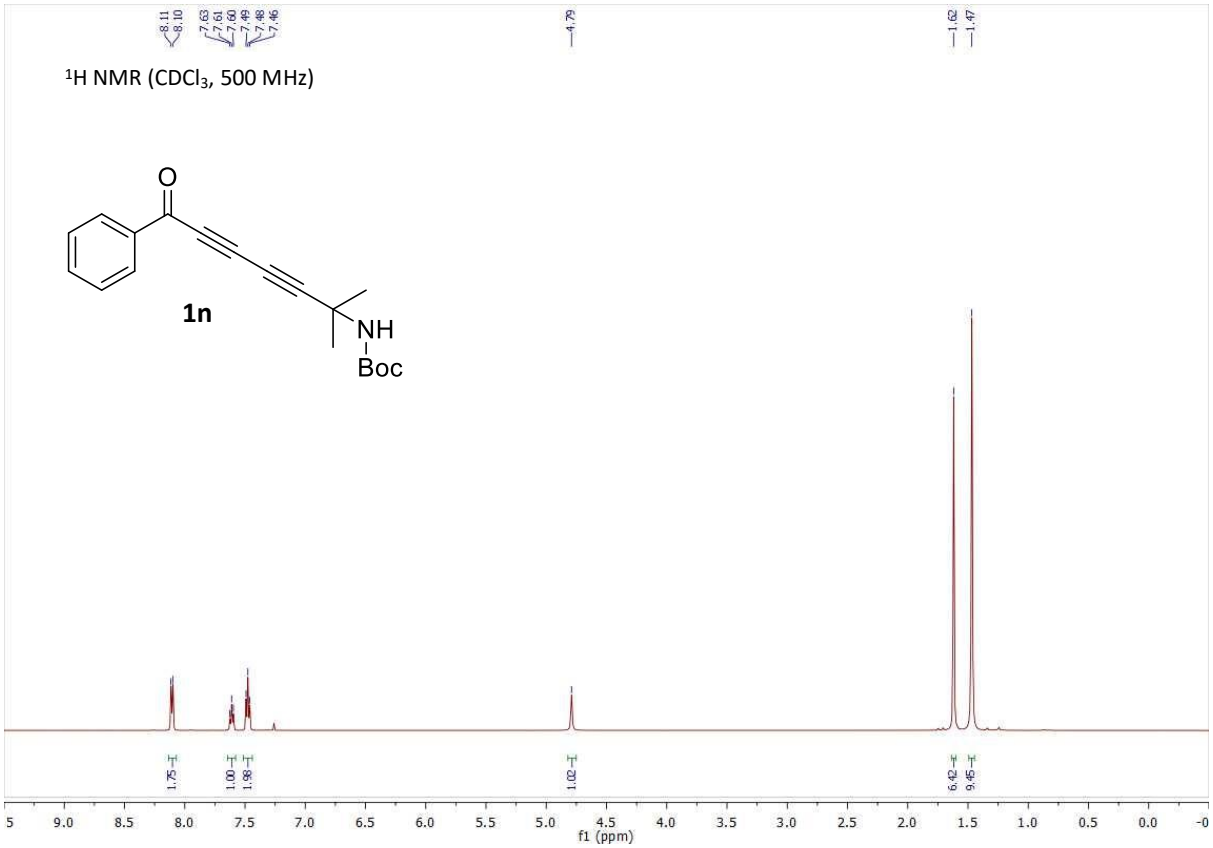


^{1}H NMR ($CDCl_3$, 500 MHz)



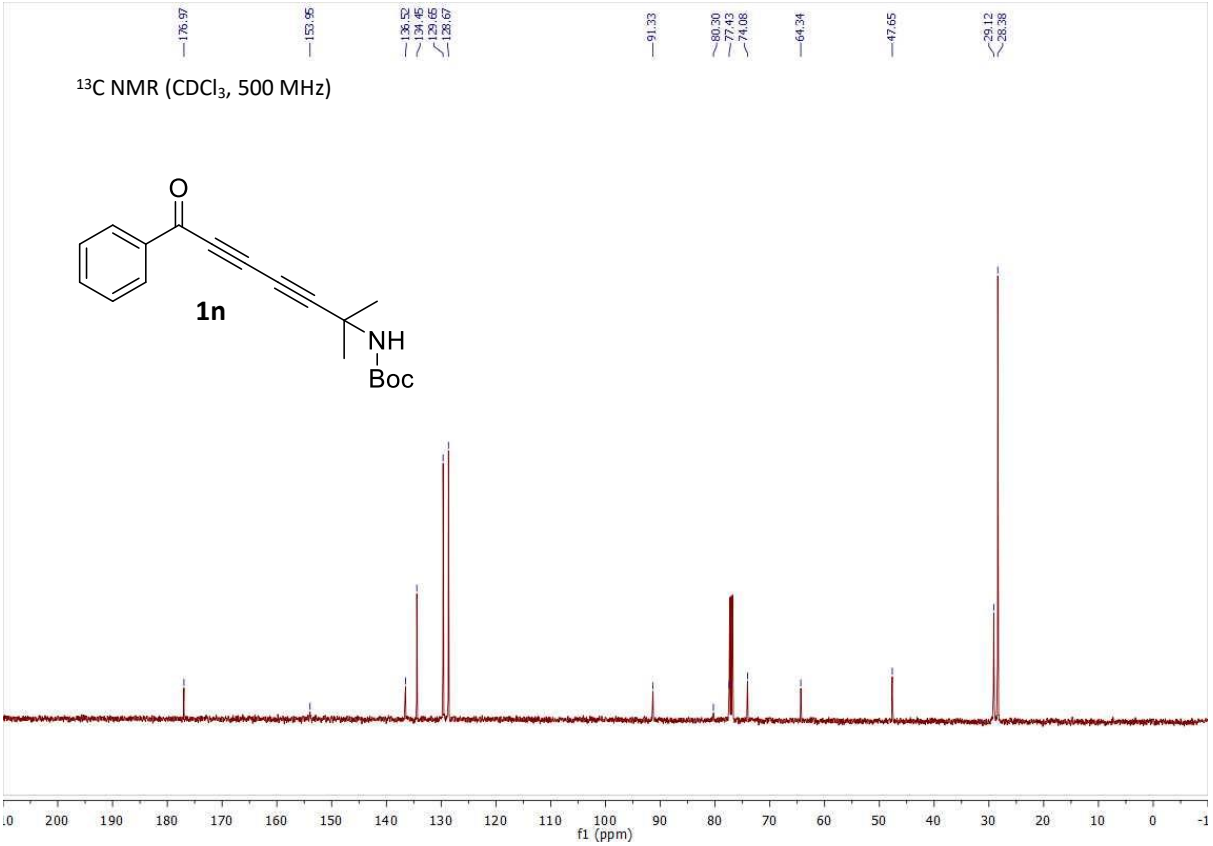
^{13}C NMR ($CDCl_3$, 500 MHz)





^{1}H NMR ($CDCl_3$, 500 MHz)

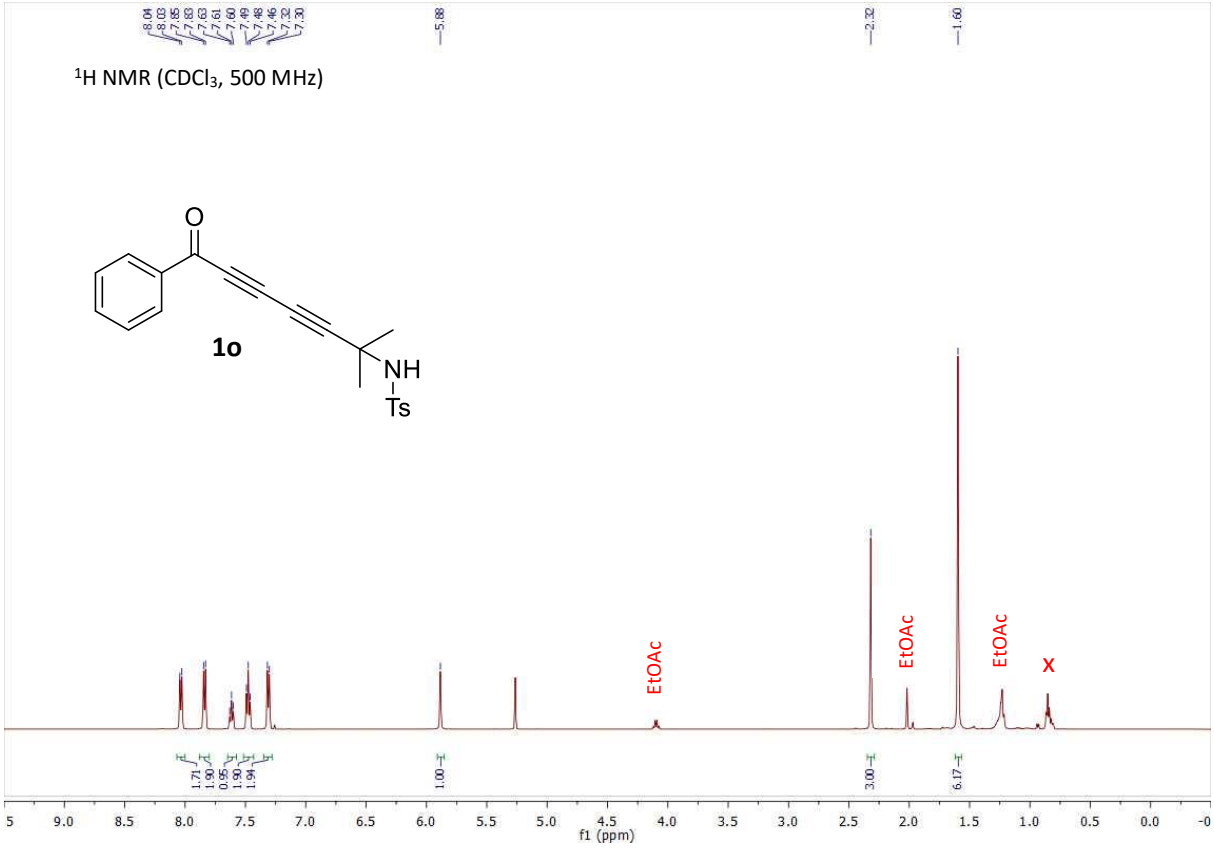
1n



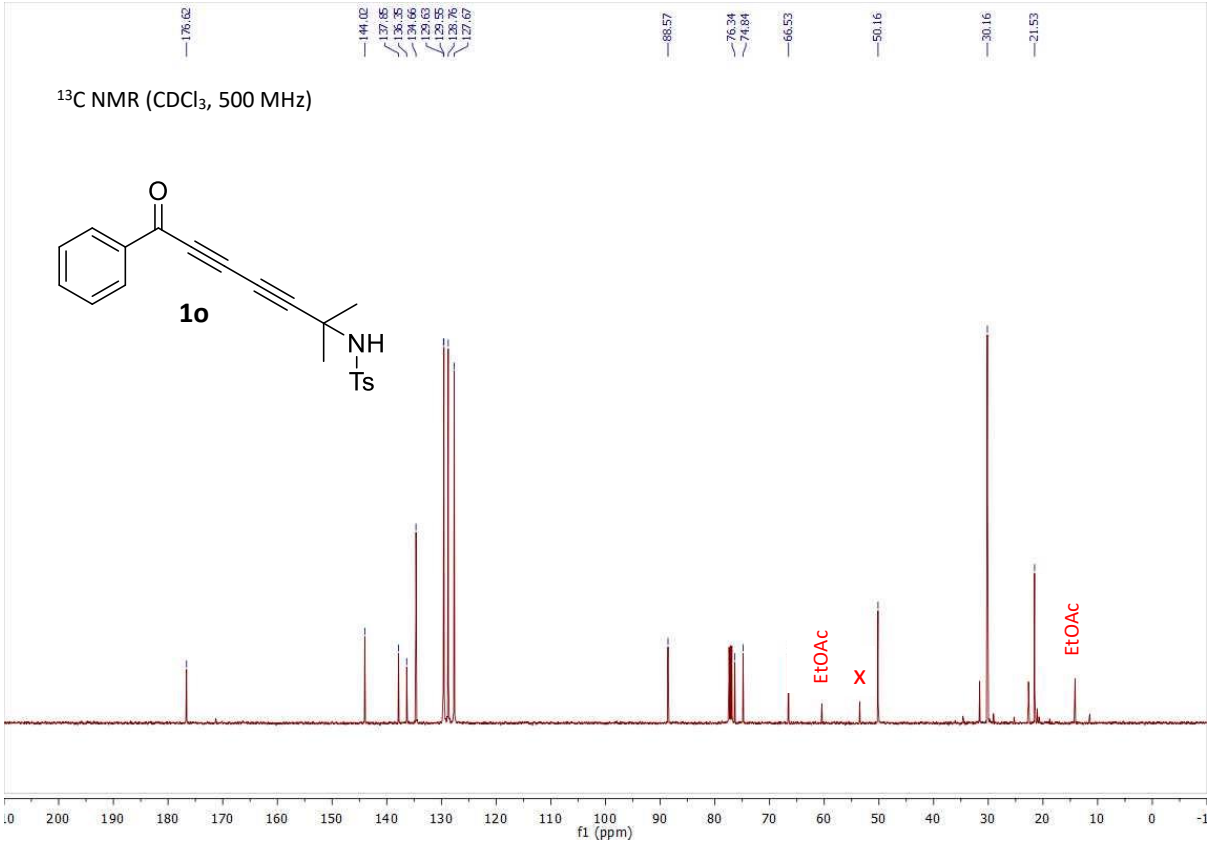
^{13}C NMR ($CDCl_3$, 500 MHz)

1n

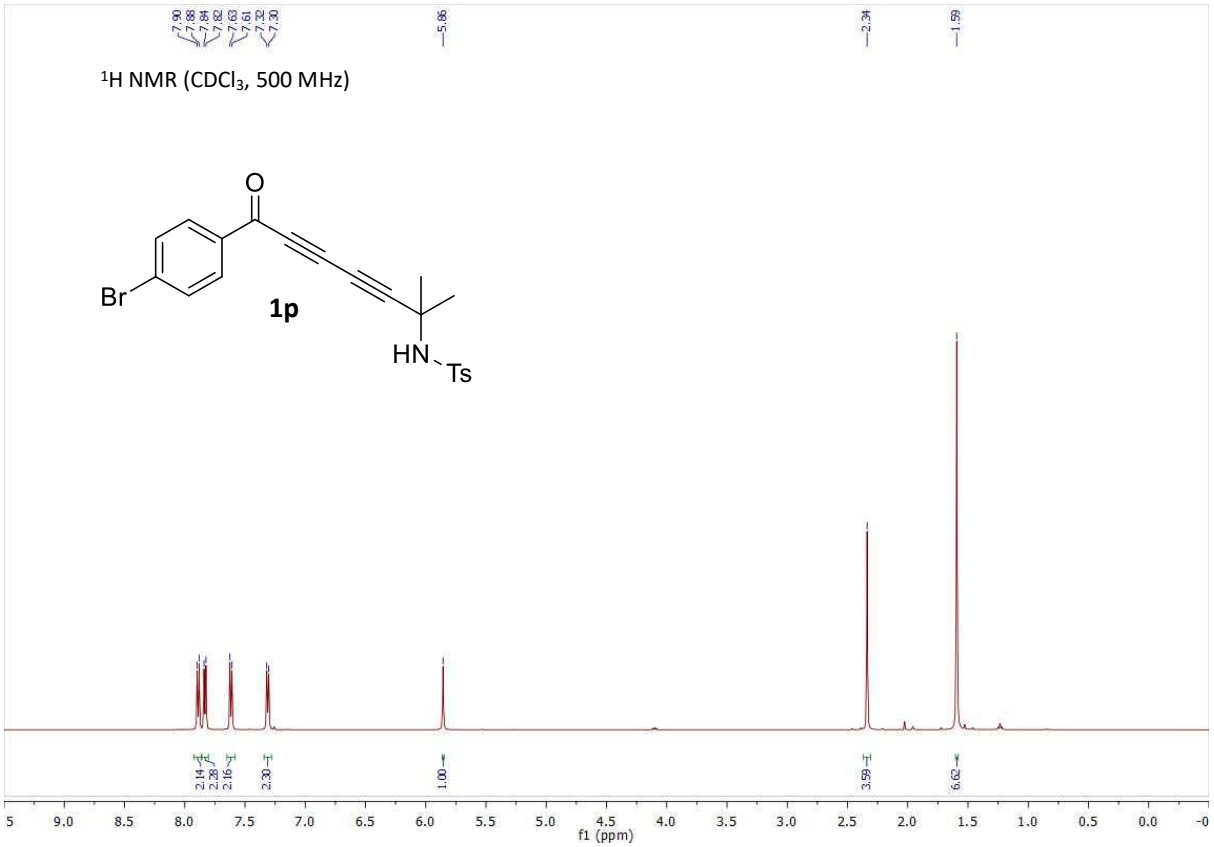
^{1}H NMR ($CDCl_3$, 500 MHz)



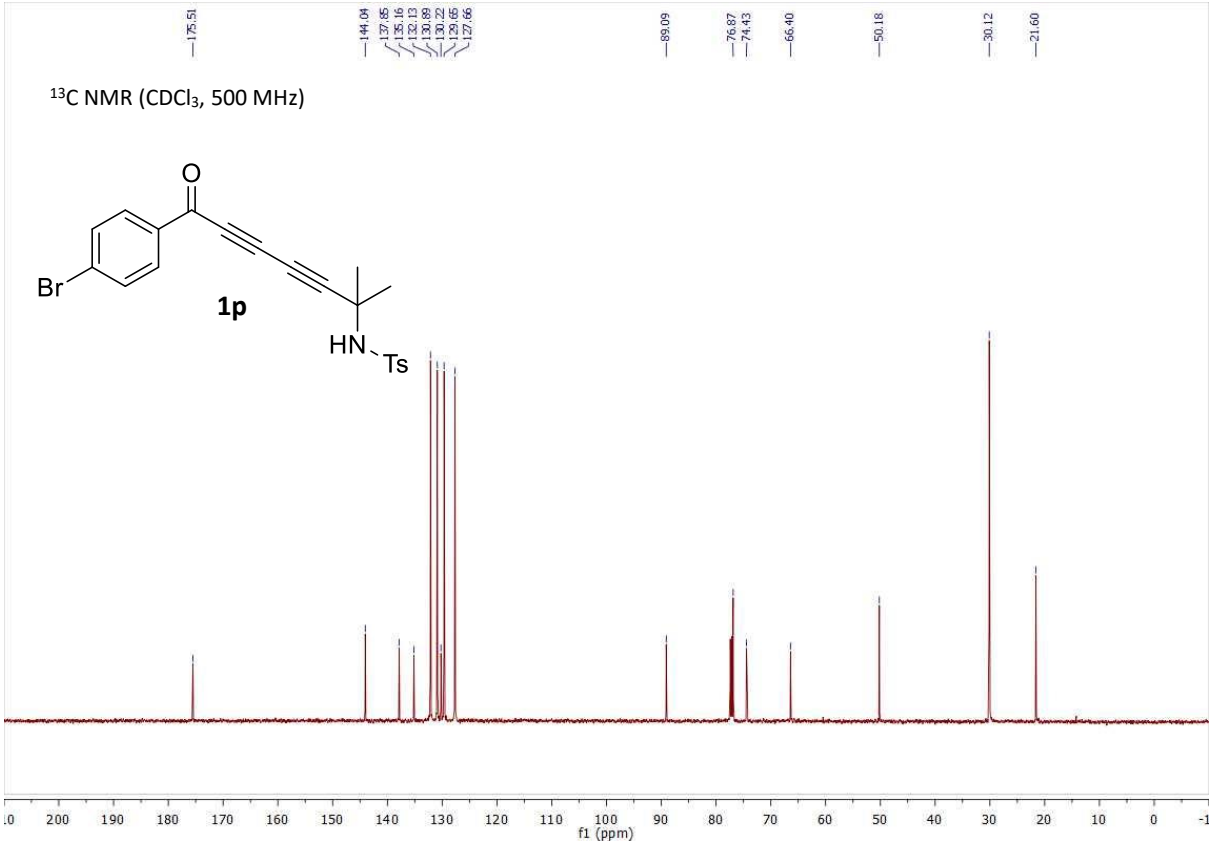
^{13}C NMR ($CDCl_3$, 500 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)

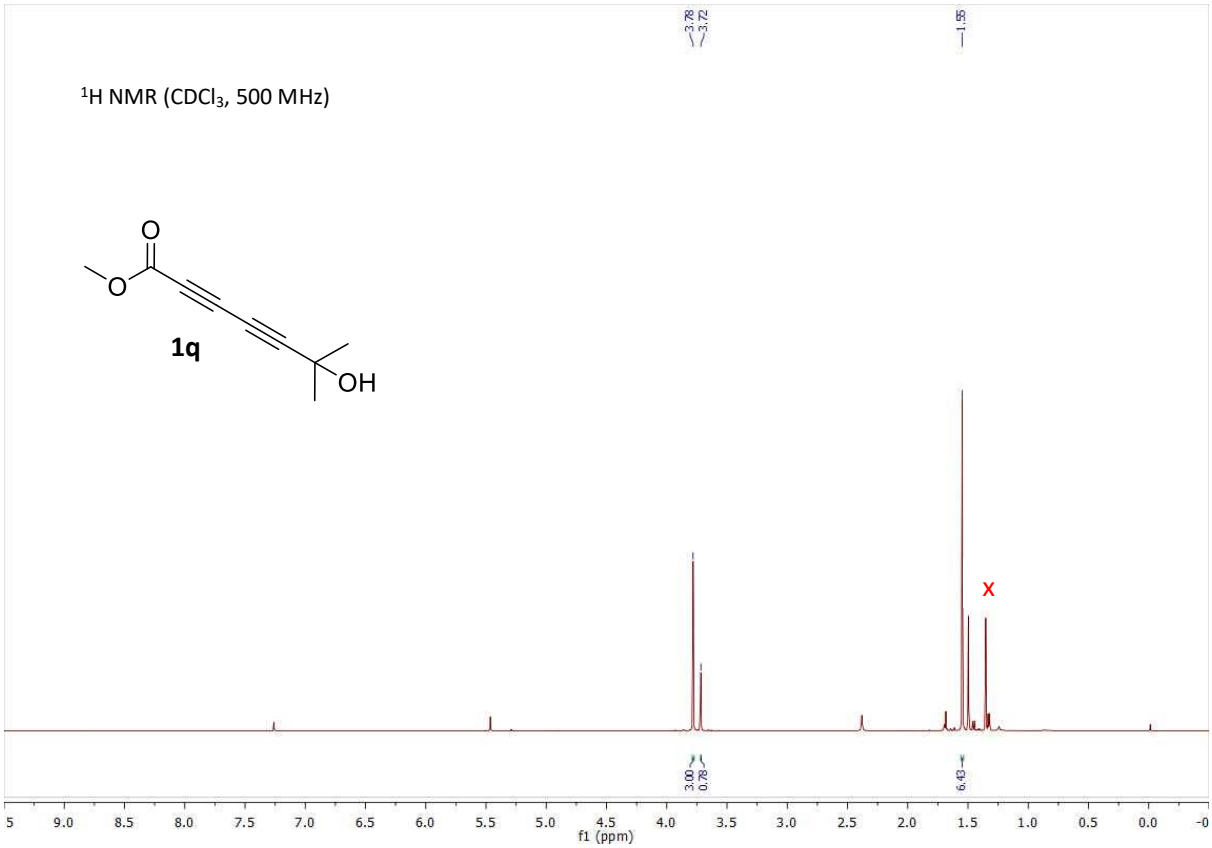


^{13}C NMR ($CDCl_3$, 500 MHz)



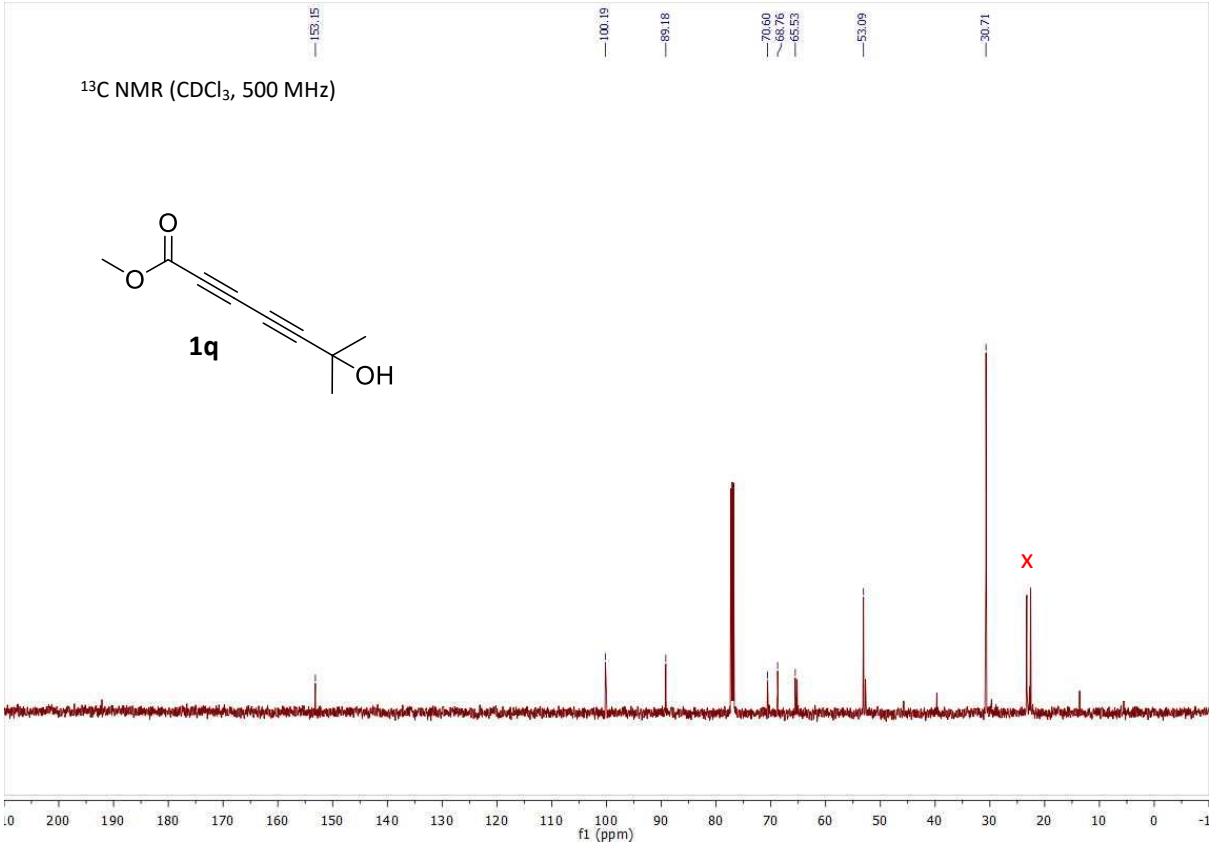
^{1}H NMR ($CDCl_3$, 500 MHz)

1q

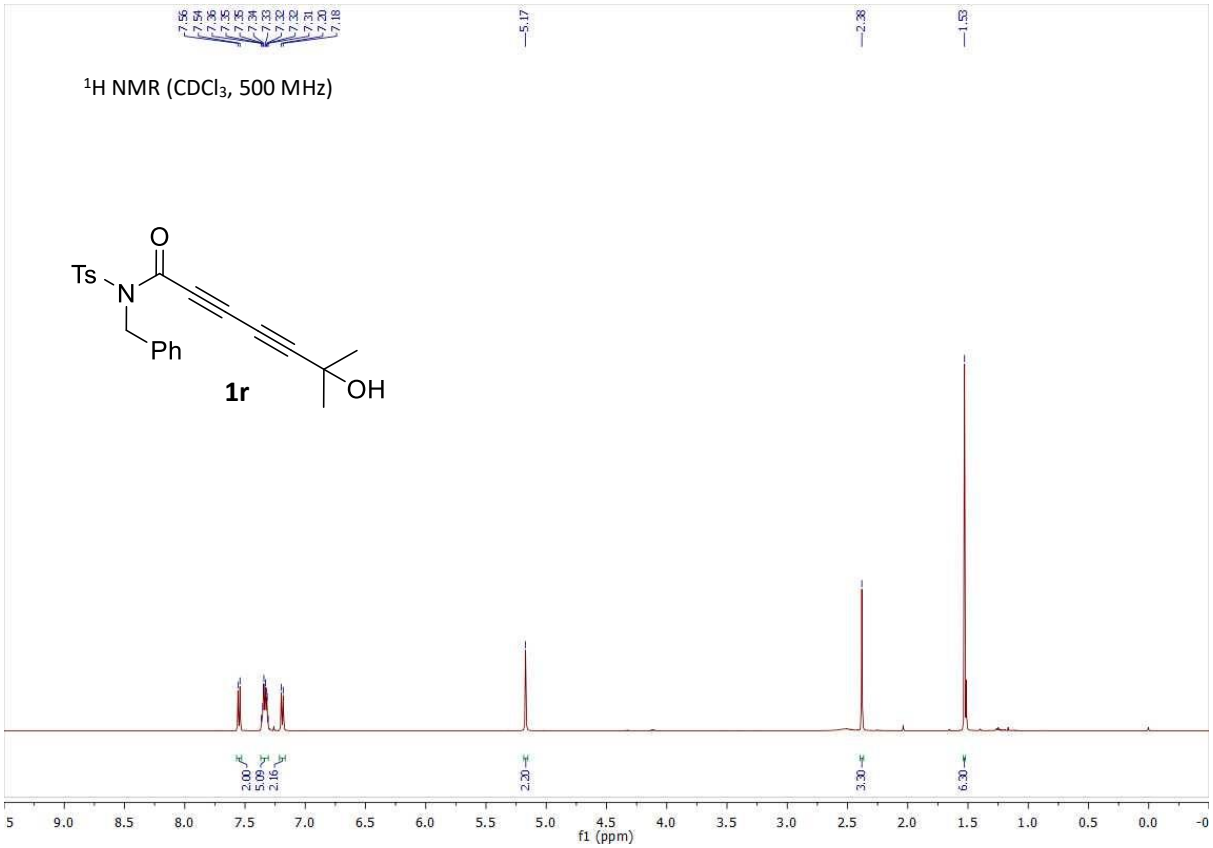


^{13}C NMR ($CDCl_3$, 500 MHz)

1q

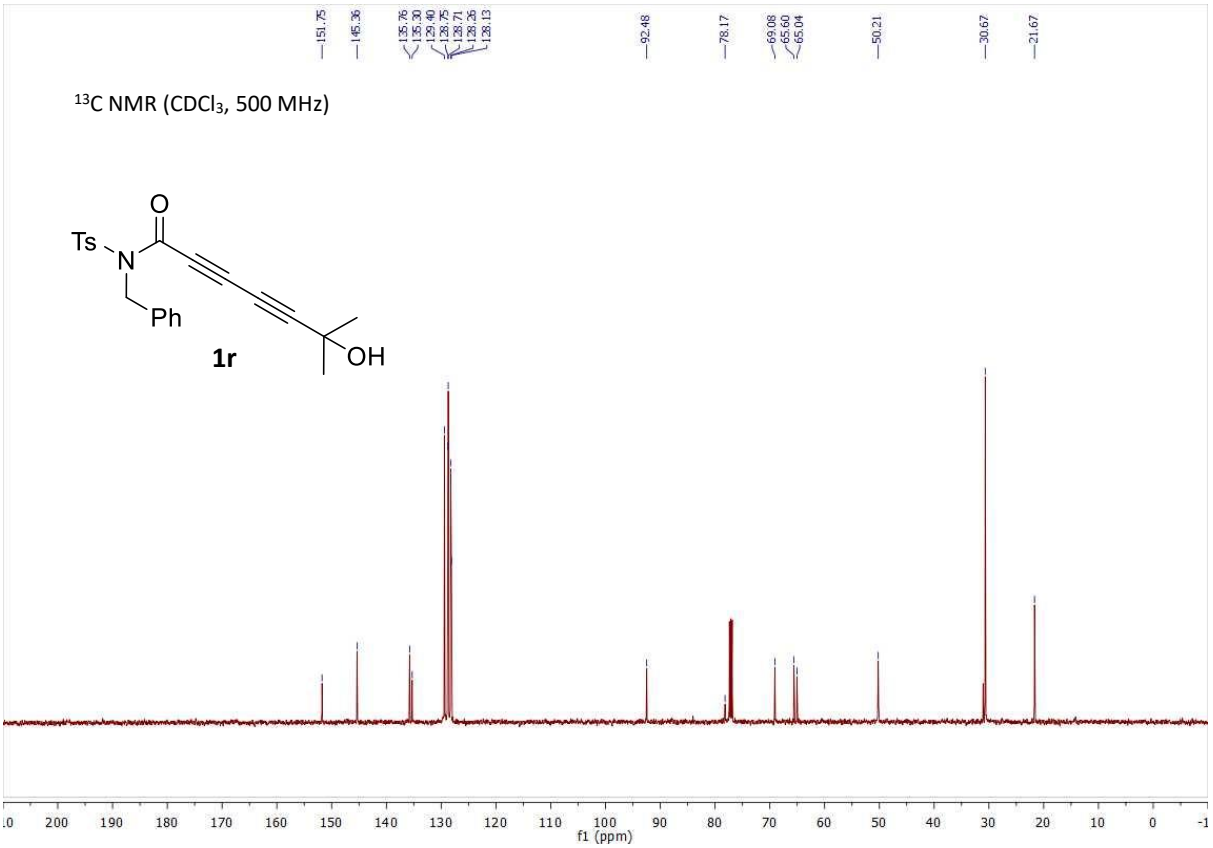


^{1}H NMR ($CDCl_3$, 500 MHz)



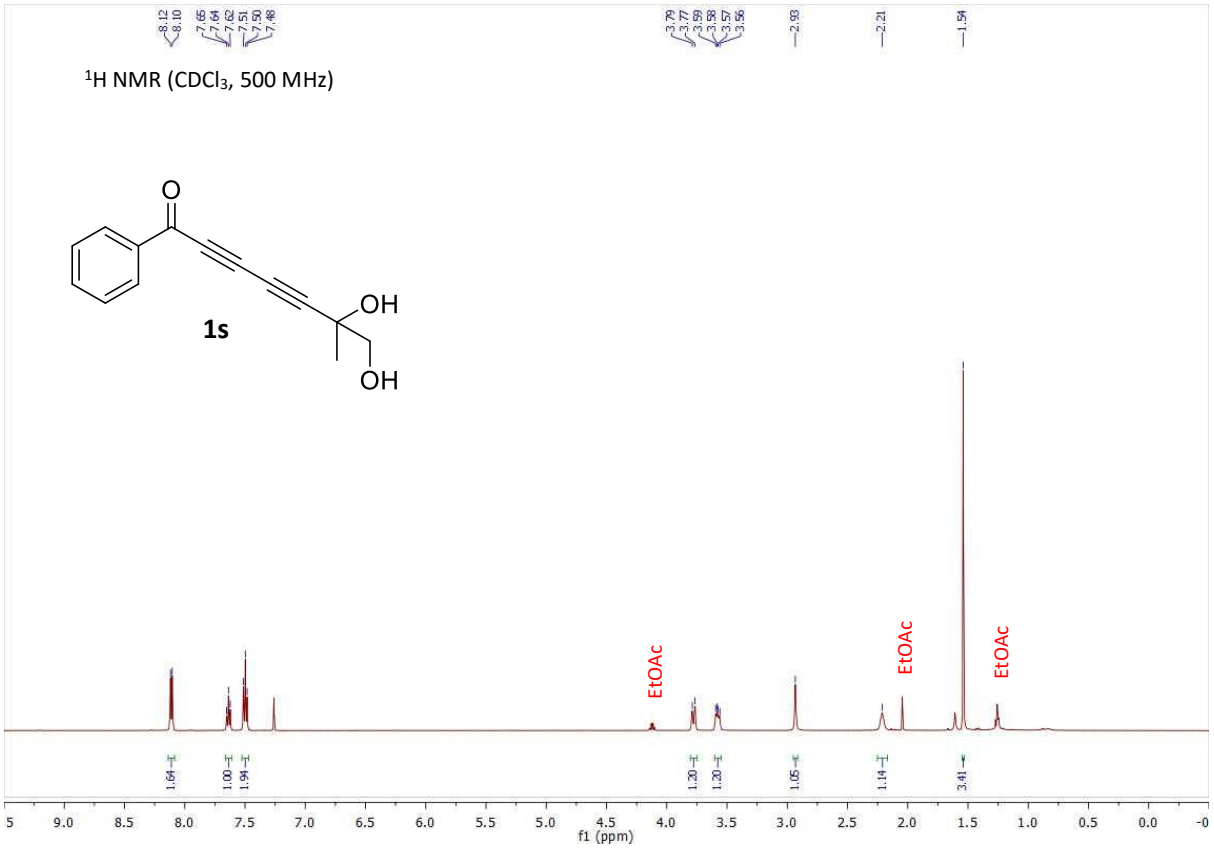
1r

^{13}C NMR ($CDCl_3$, 500 MHz)

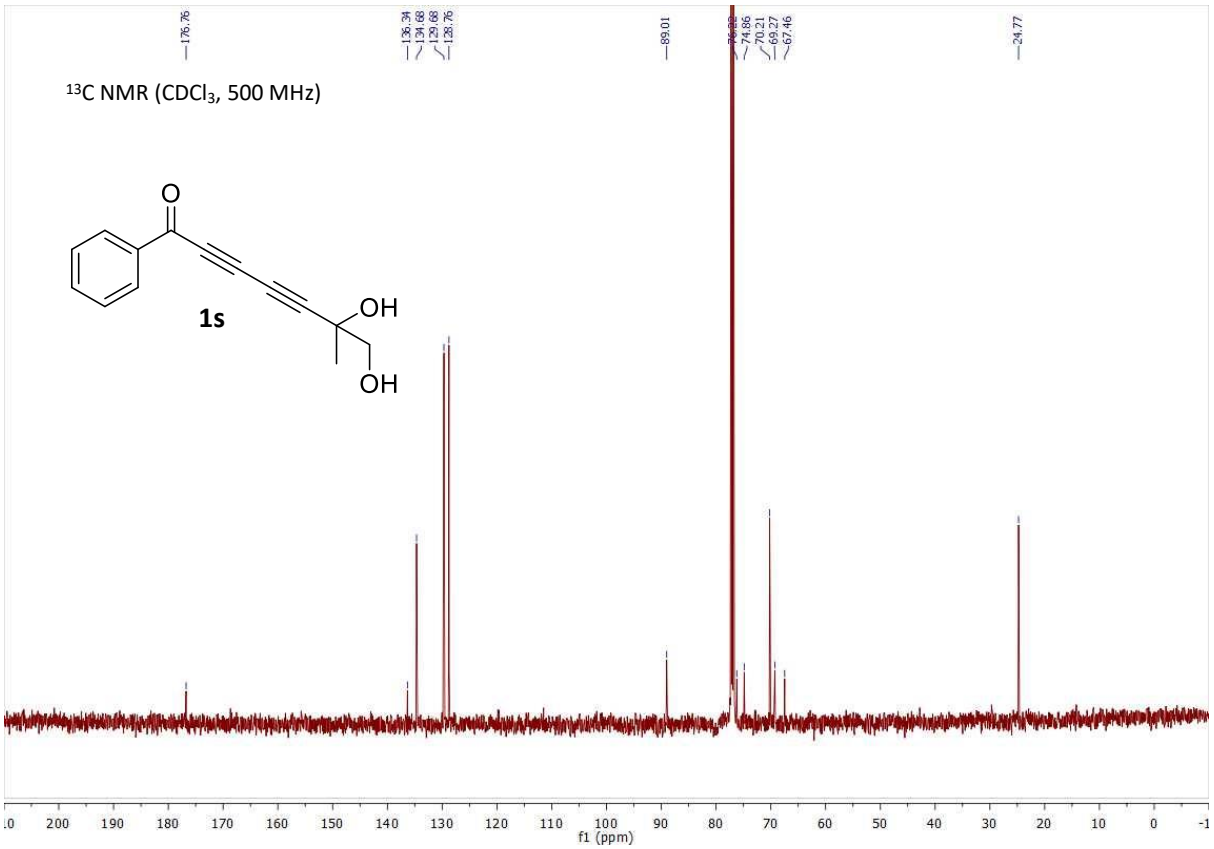


1r

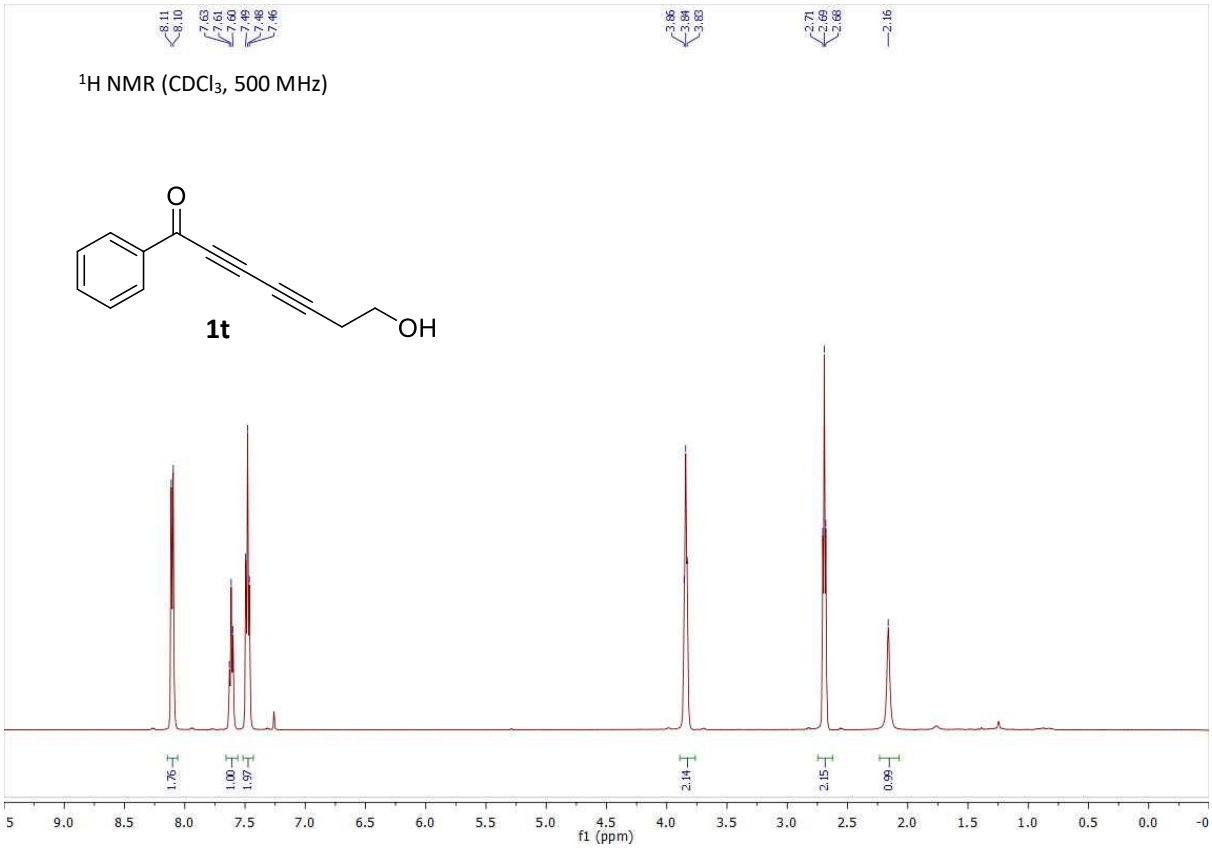
^{1}H NMR ($CDCl_3$, 500 MHz)



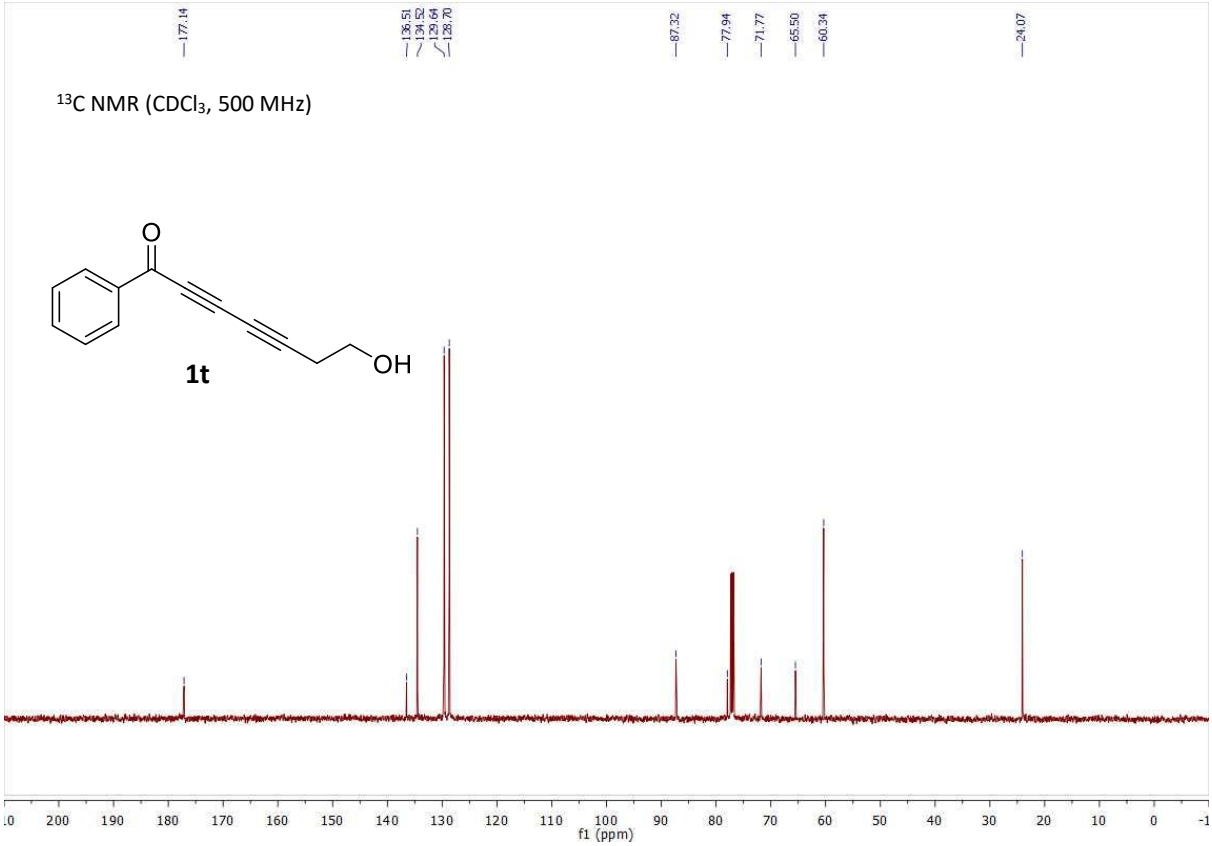
^{13}C NMR ($CDCl_3$, 500 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)

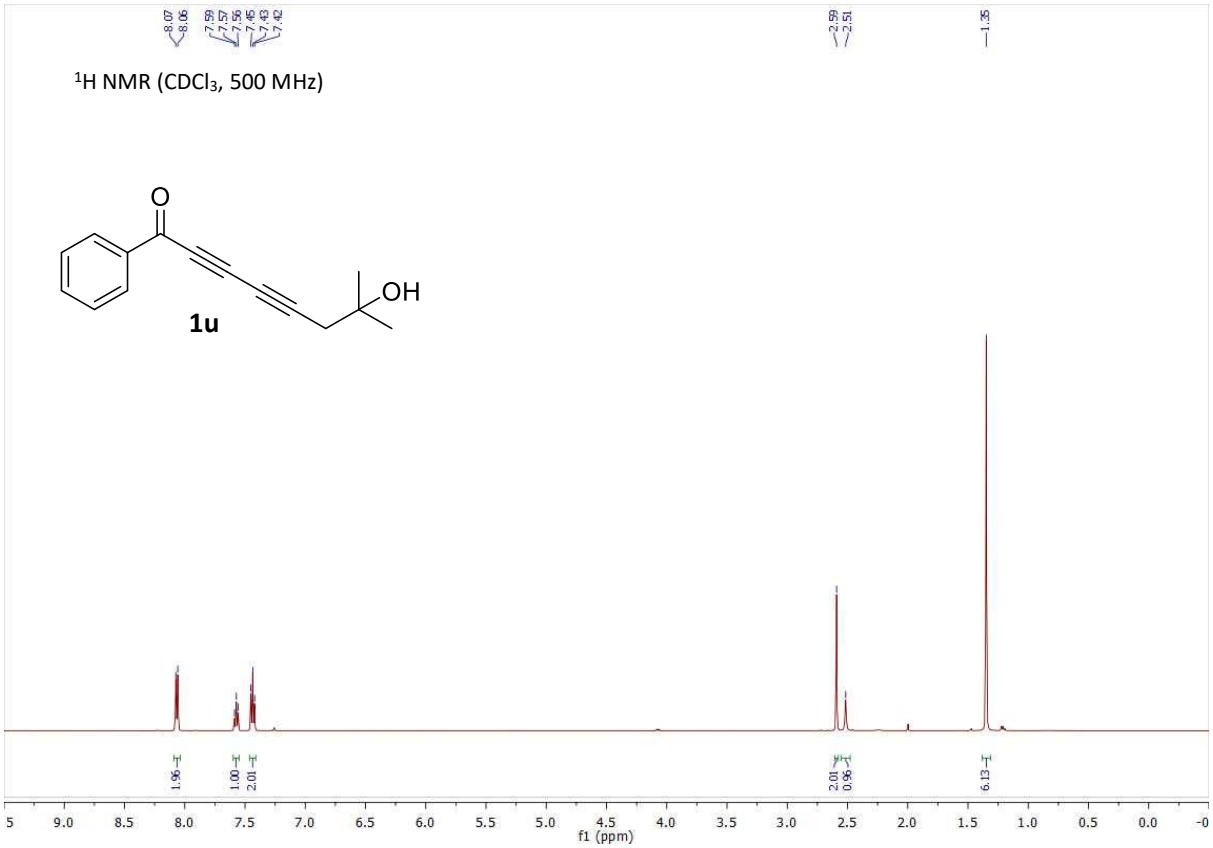


^{13}C NMR ($CDCl_3$, 500 MHz)



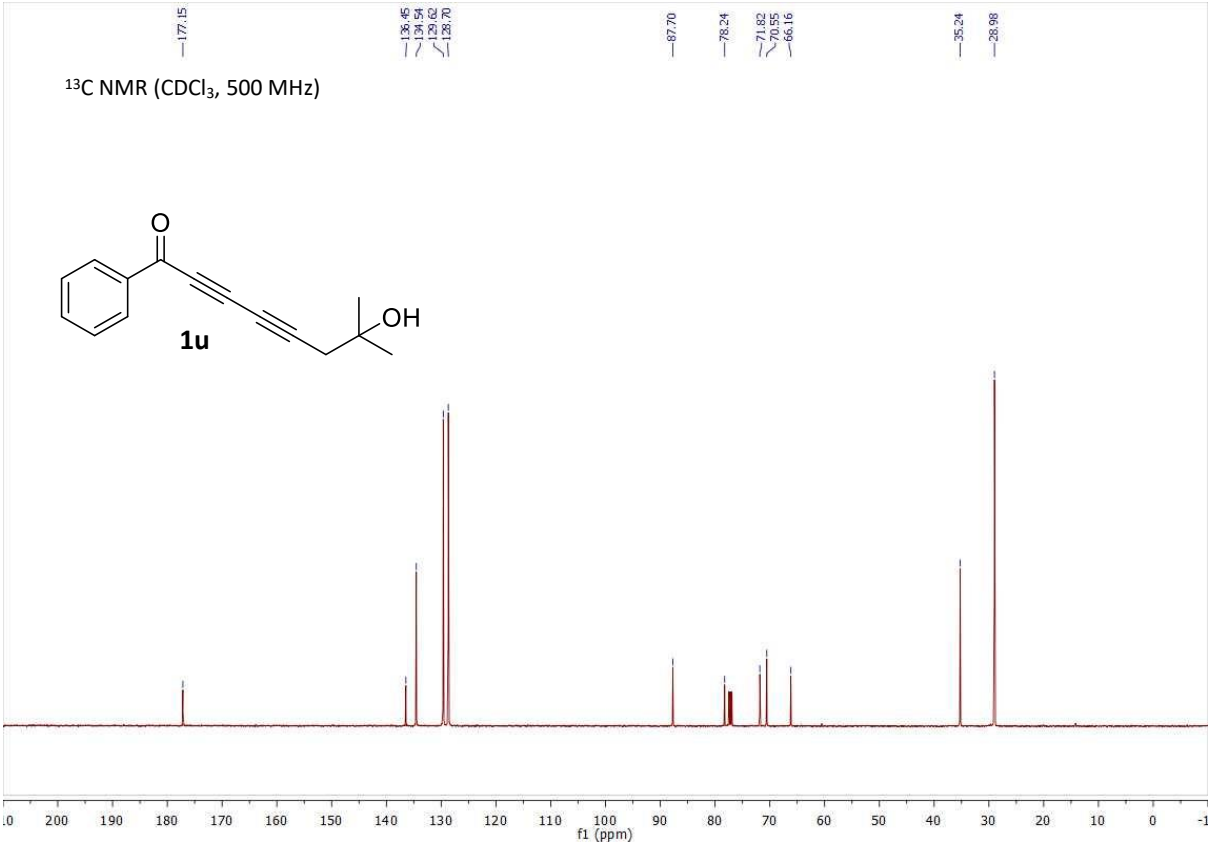
^{1}H NMR ($CDCl_3$, 500 MHz)

1u

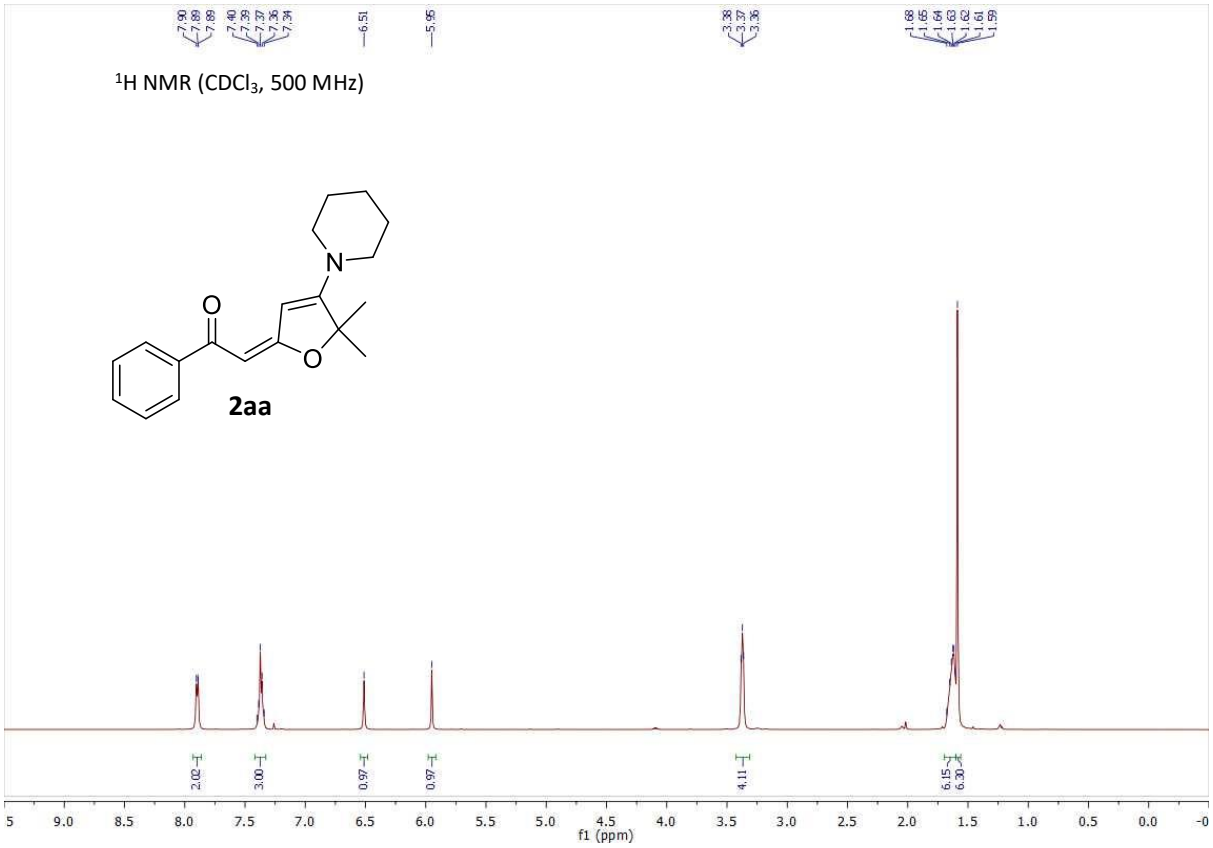


^{13}C NMR ($CDCl_3$, 500 MHz)

1u

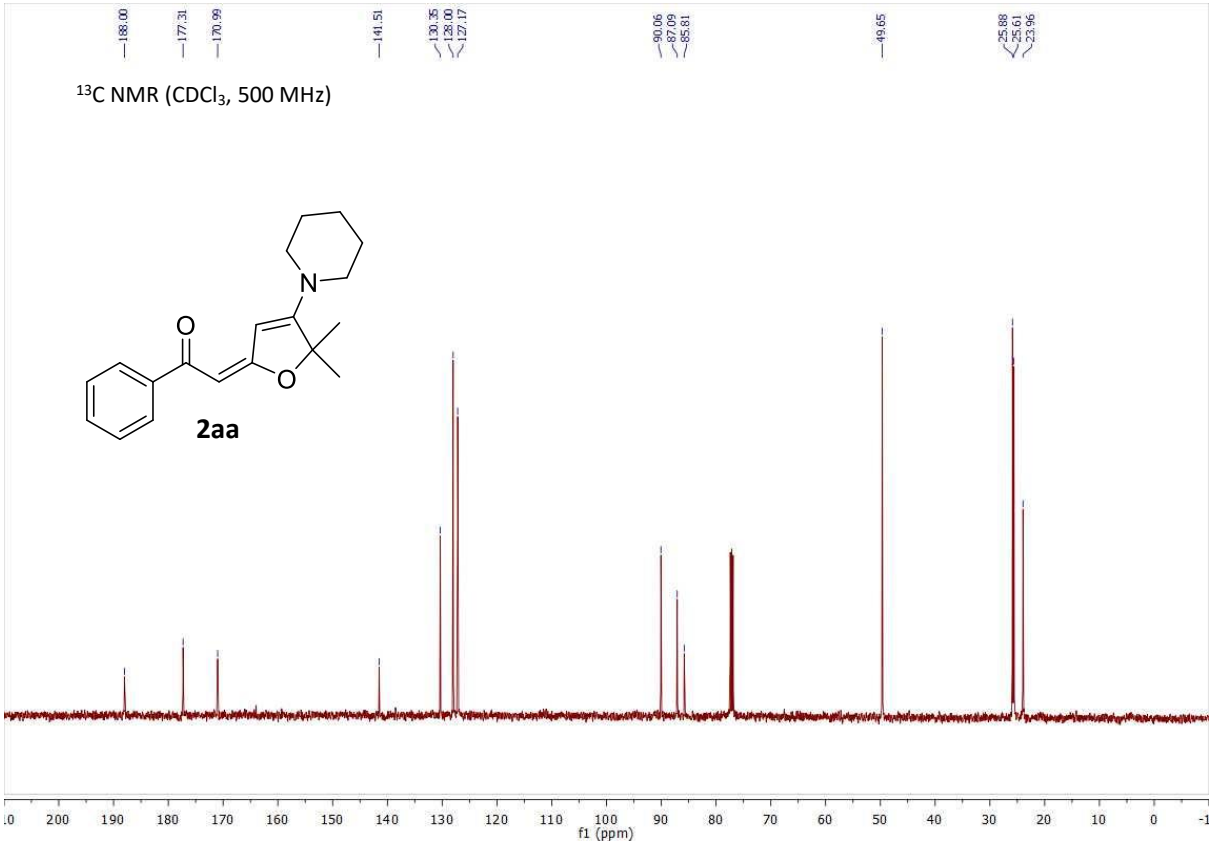


^{1}H and ^{13}C NMR Spectra of Products



^{1}H NMR ($CDCl_3$, 500 MHz)

2aa

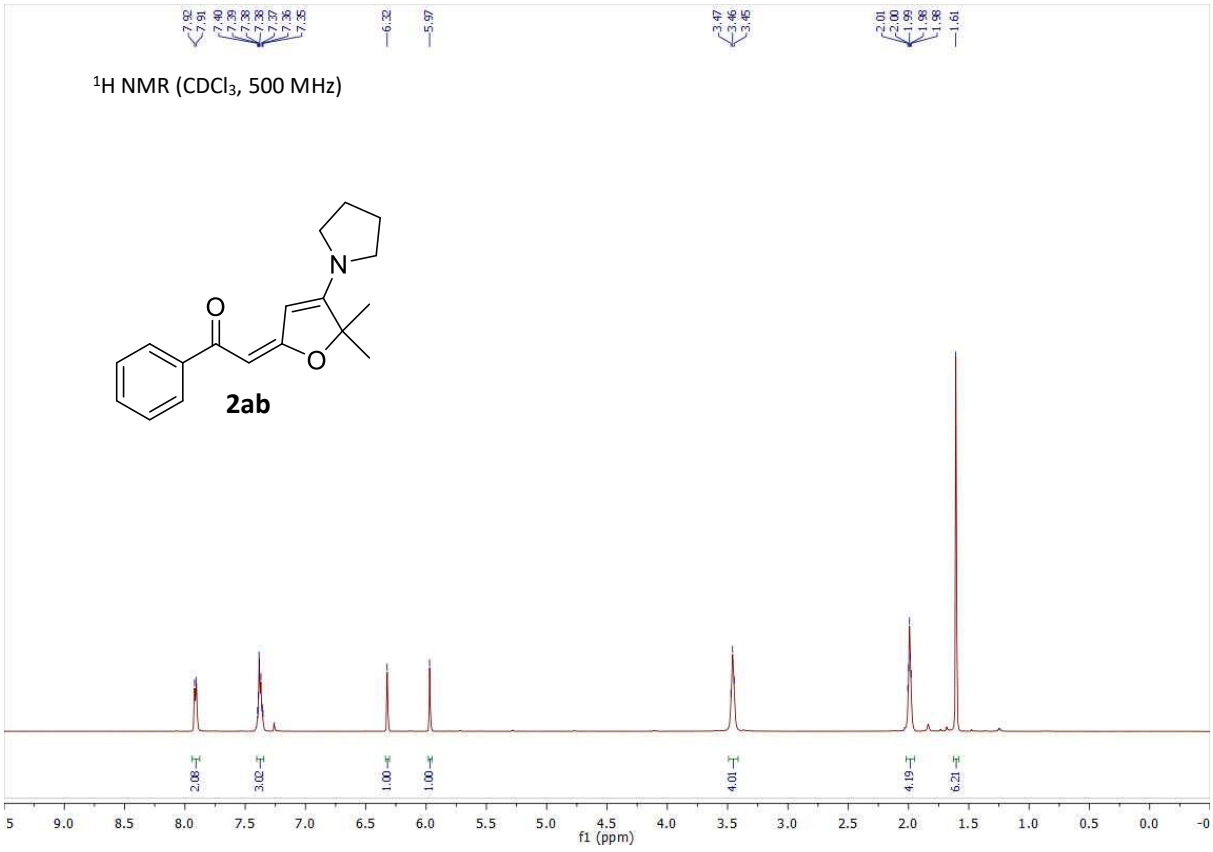


^{13}C NMR ($CDCl_3$, 500 MHz)

2aa

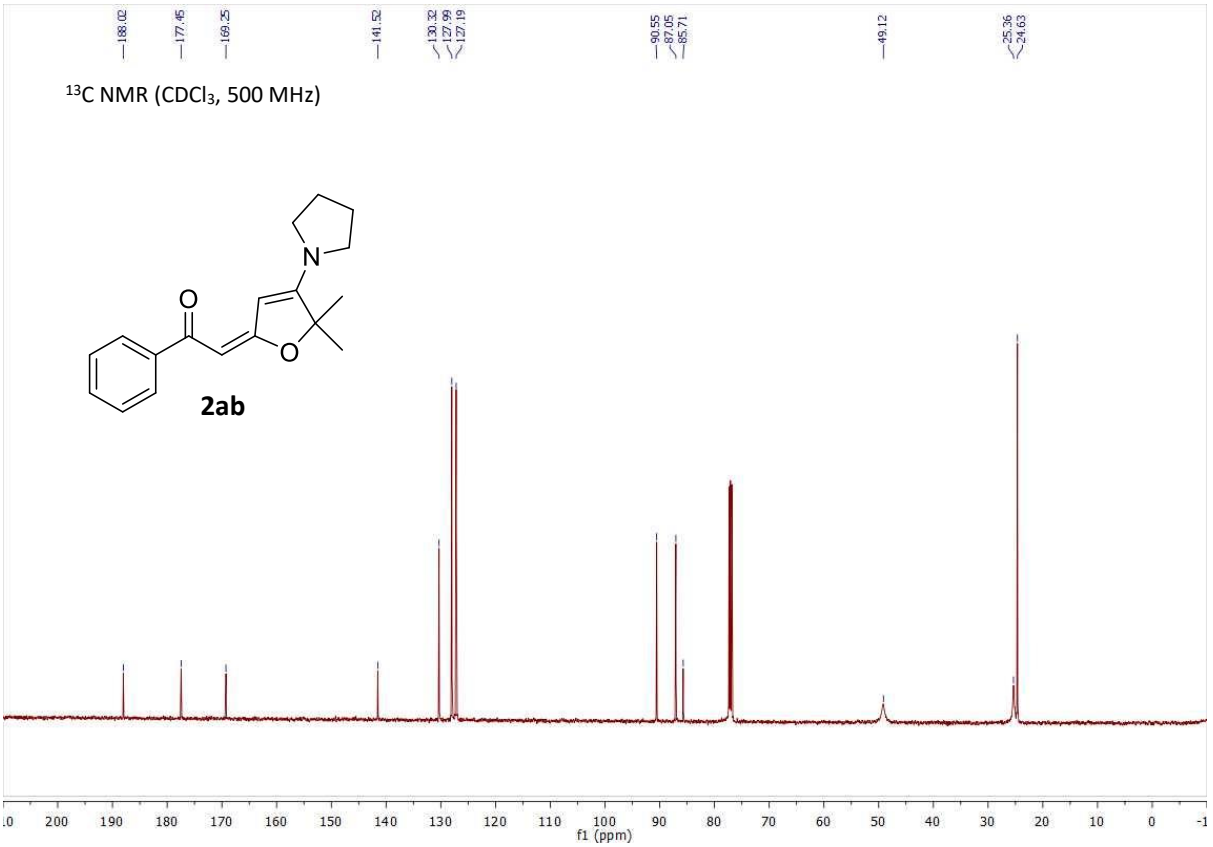
^{1}H NMR ($CDCl_3$, 500 MHz)

2ab

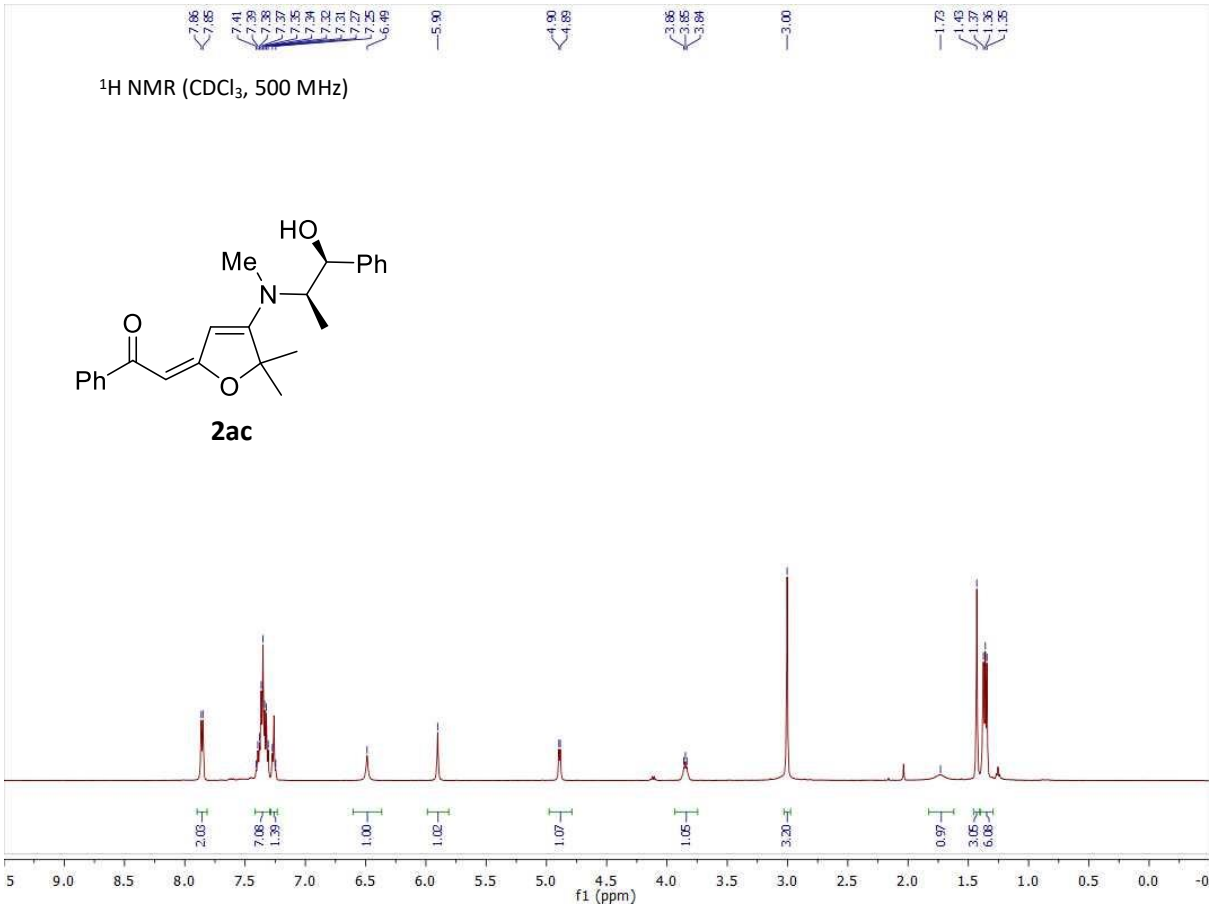


^{13}C NMR ($CDCl_3$, 500 MHz)

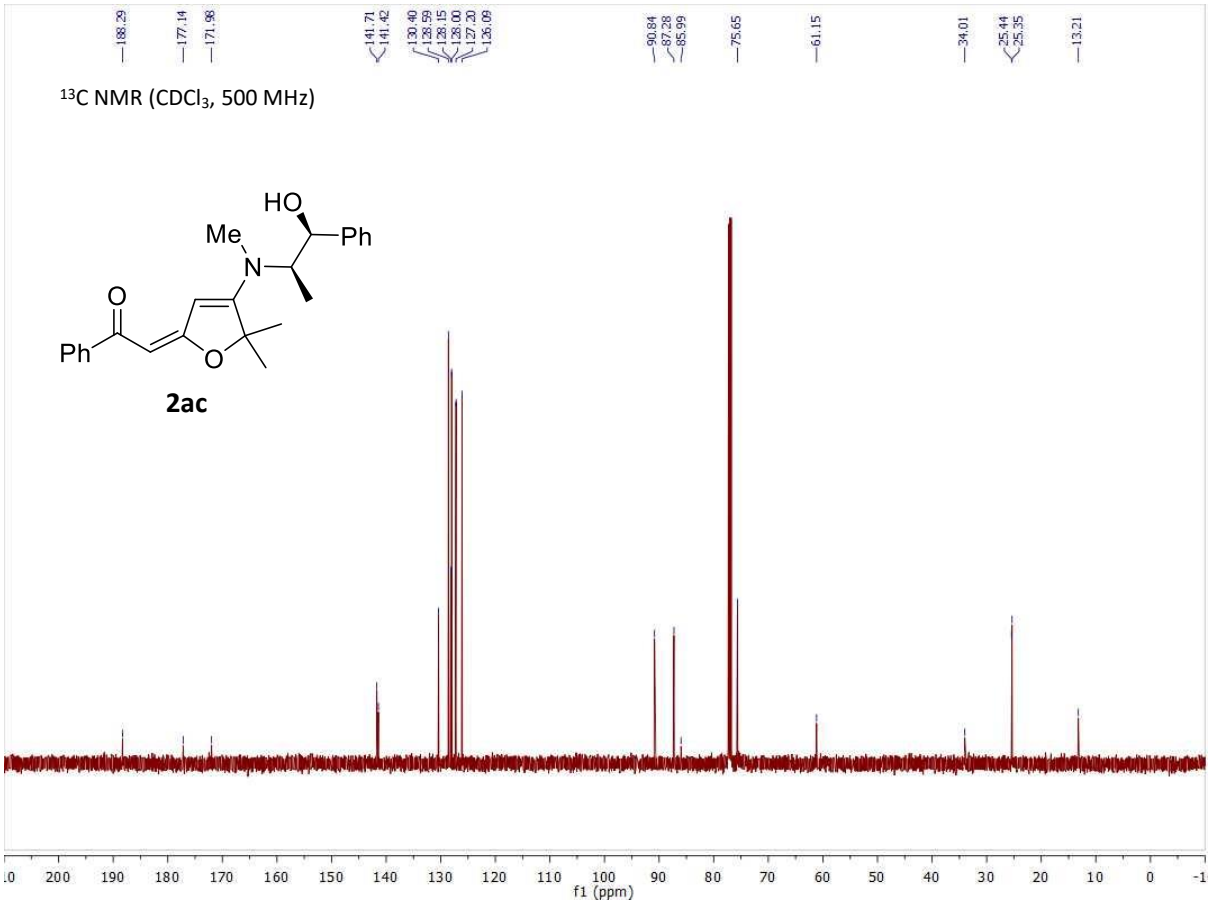
2ab



^{1}H NMR ($CDCl_3$, 500 MHz)

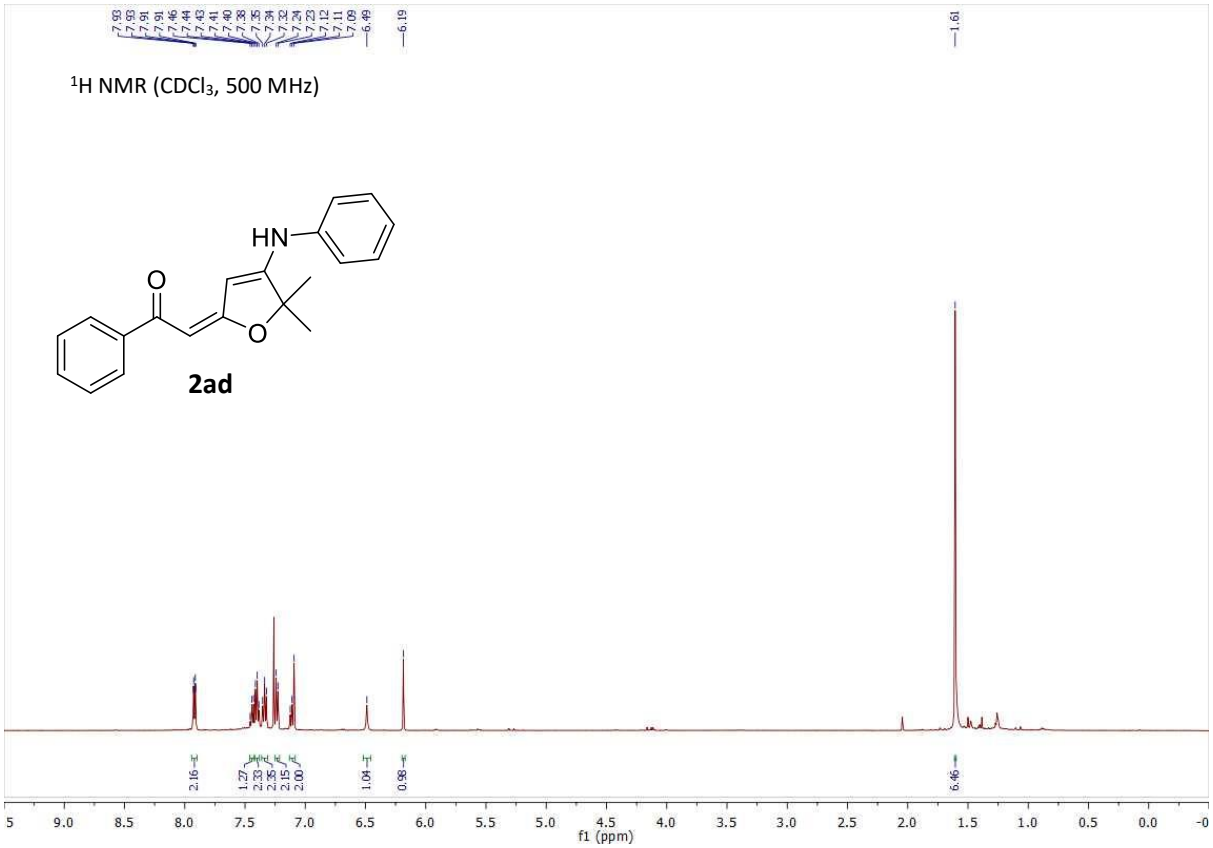


^{13}C NMR ($CDCl_3$, 500 MHz)



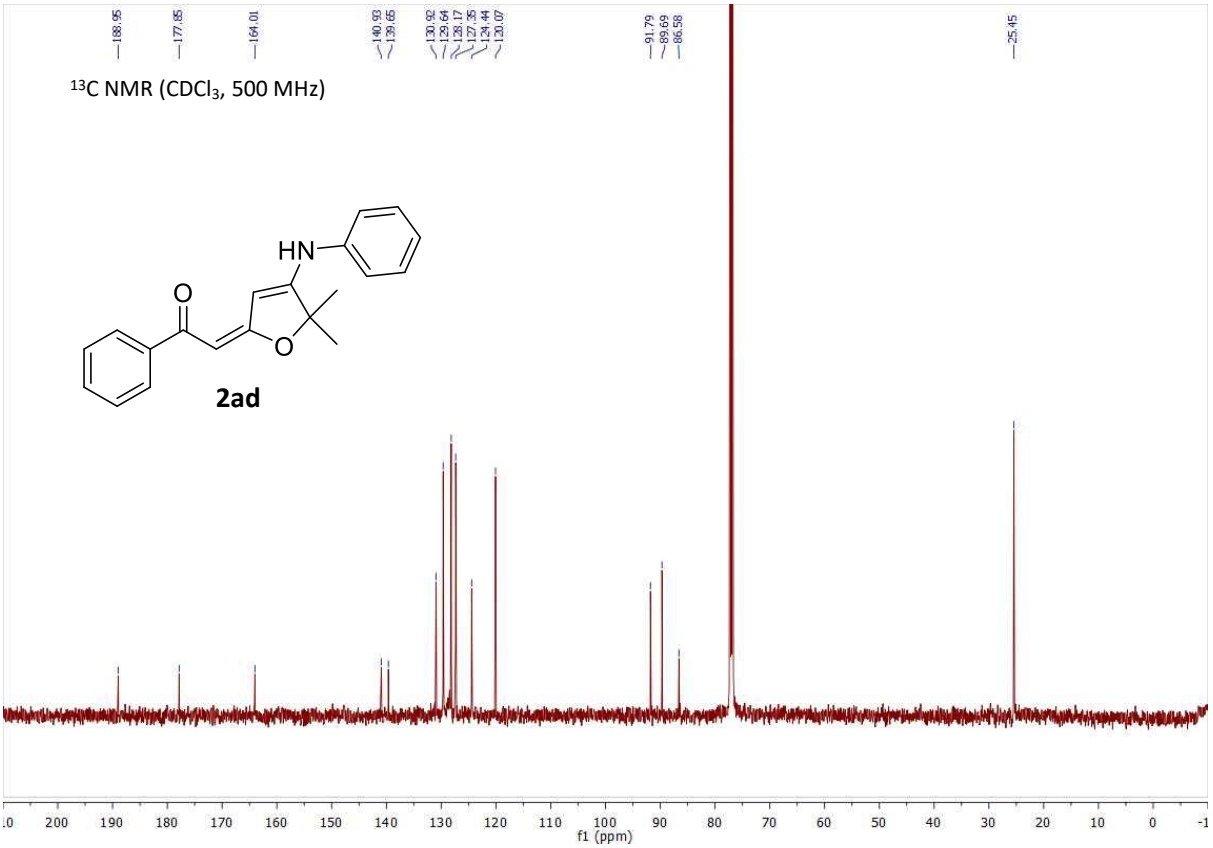
^{1}H NMR ($CDCl_3$, 500 MHz)

2ad



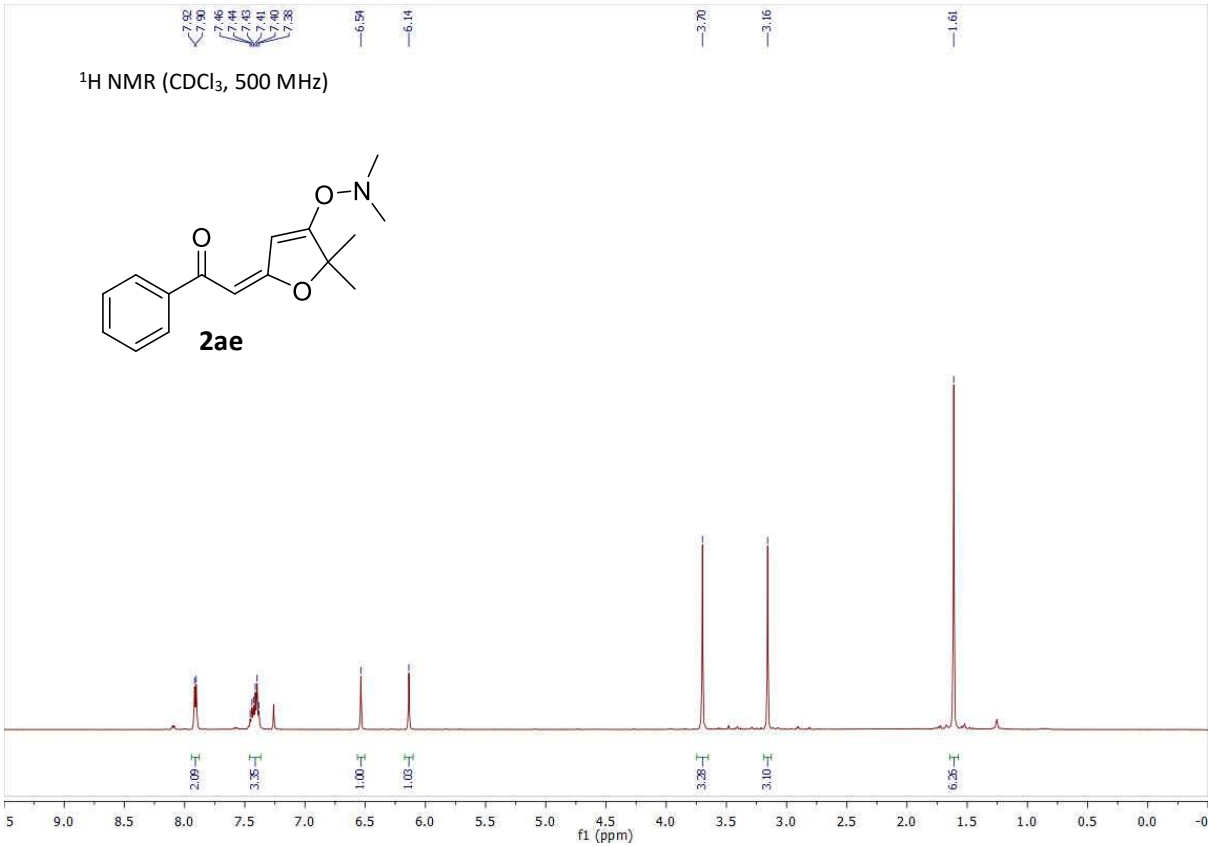
^{13}C NMR ($CDCl_3$, 500 MHz)

2ad



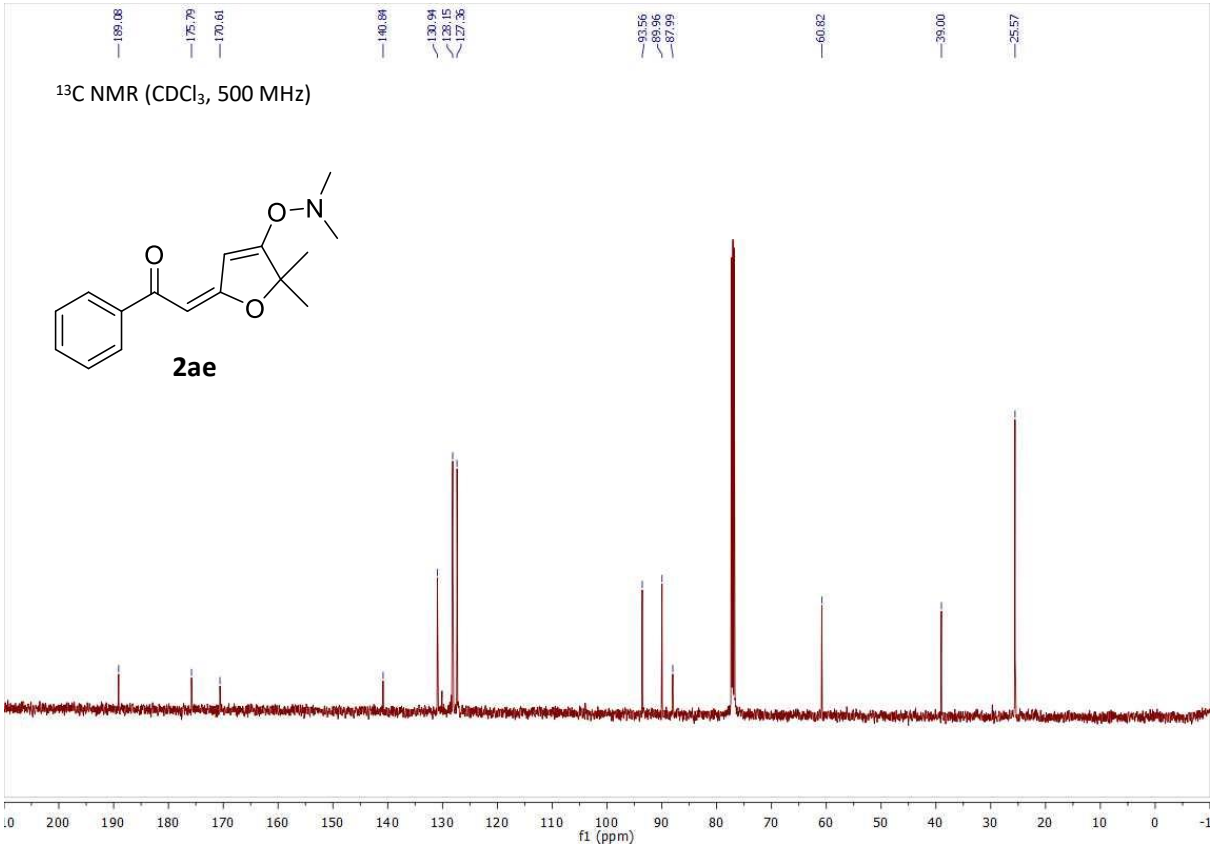
^{1}H NMR ($CDCl_3$, 500 MHz)

2ae

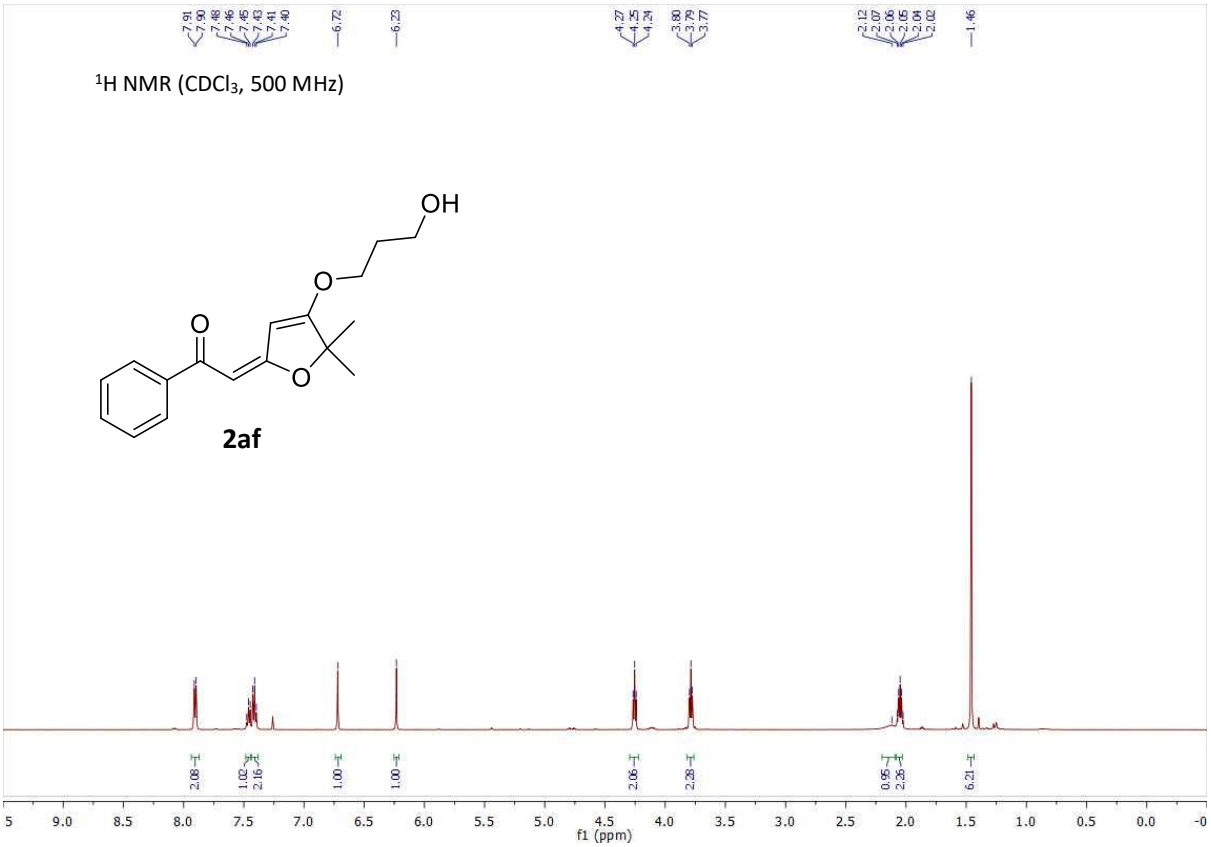


^{13}C NMR ($CDCl_3$, 500 MHz)

2ae

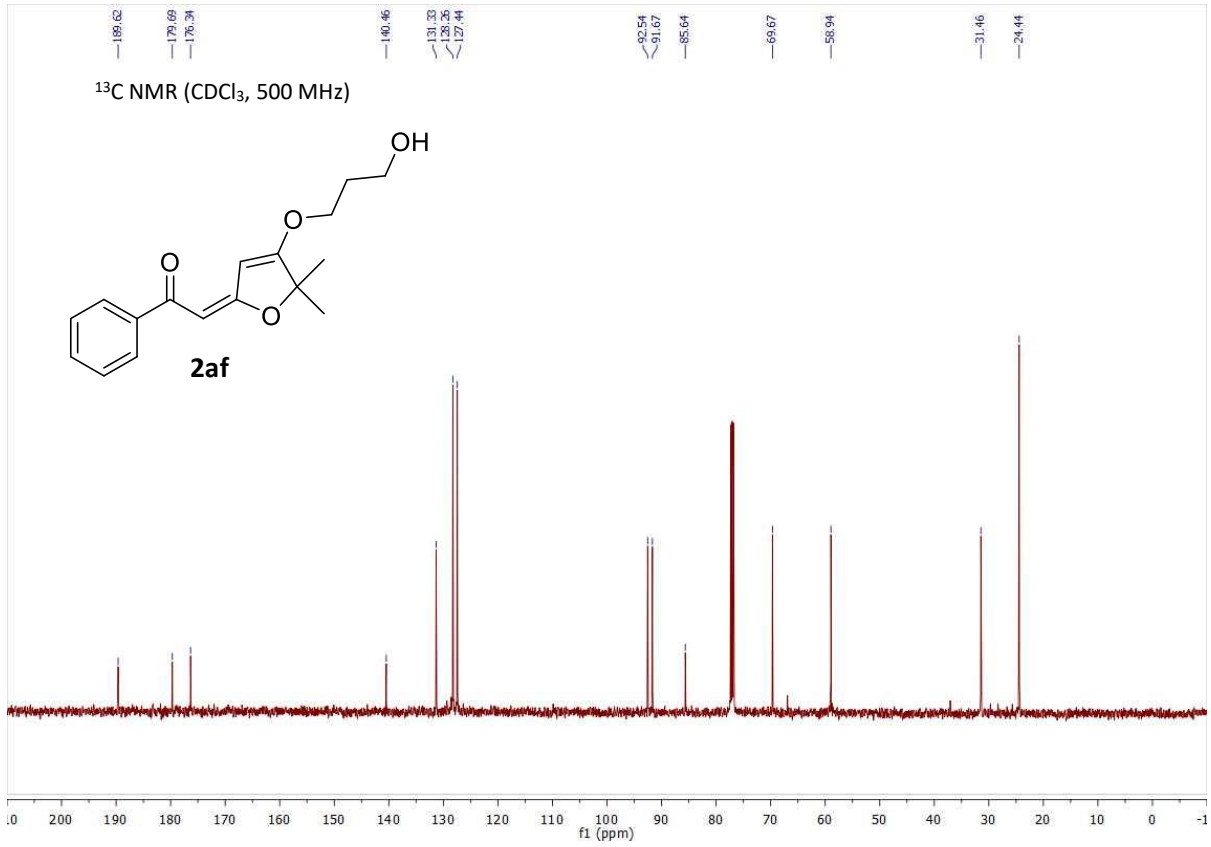


^{1}H NMR ($CDCl_3$, 500 MHz)

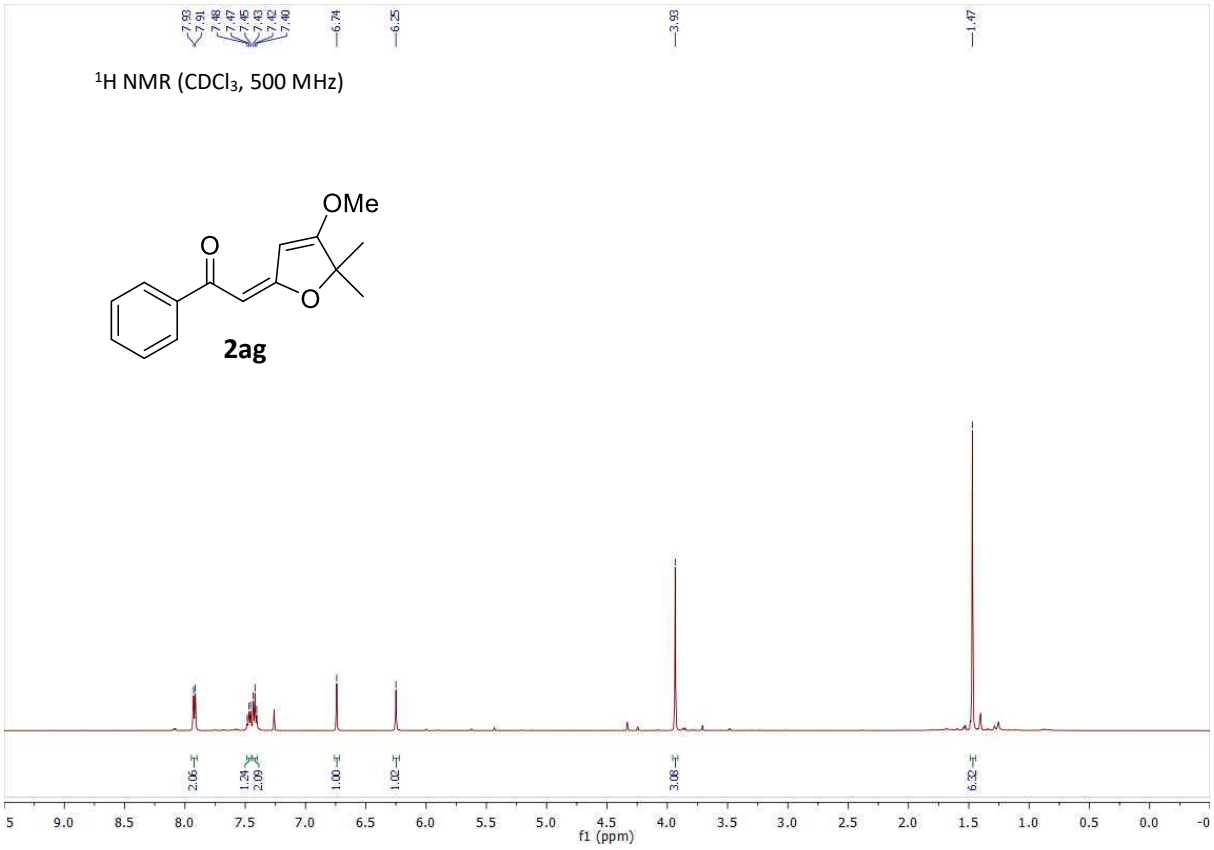


2af

^{13}C NMR ($CDCl_3$, 500 MHz)

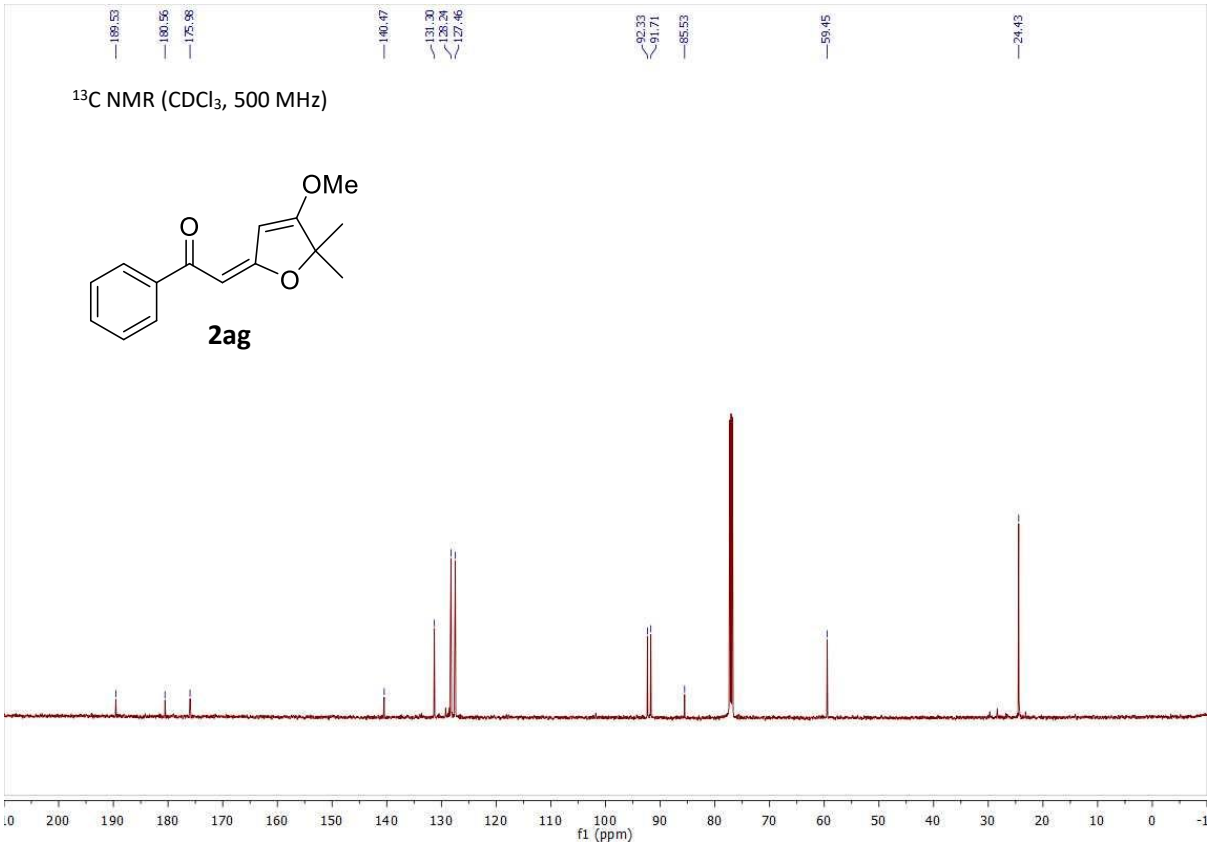


2af



^{1}H NMR ($CDCl_3$, 500 MHz)

2ag

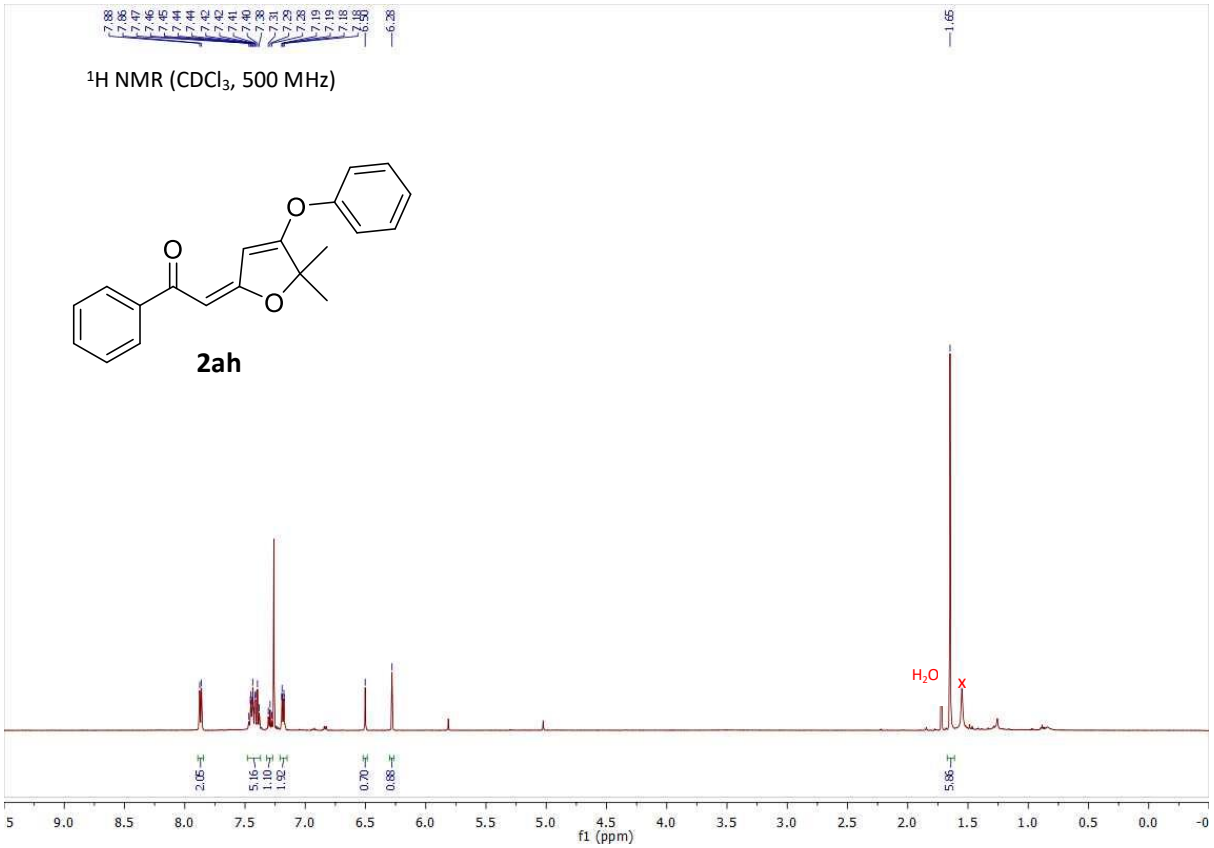


^{13}C NMR ($CDCl_3$, 500 MHz)

2ag

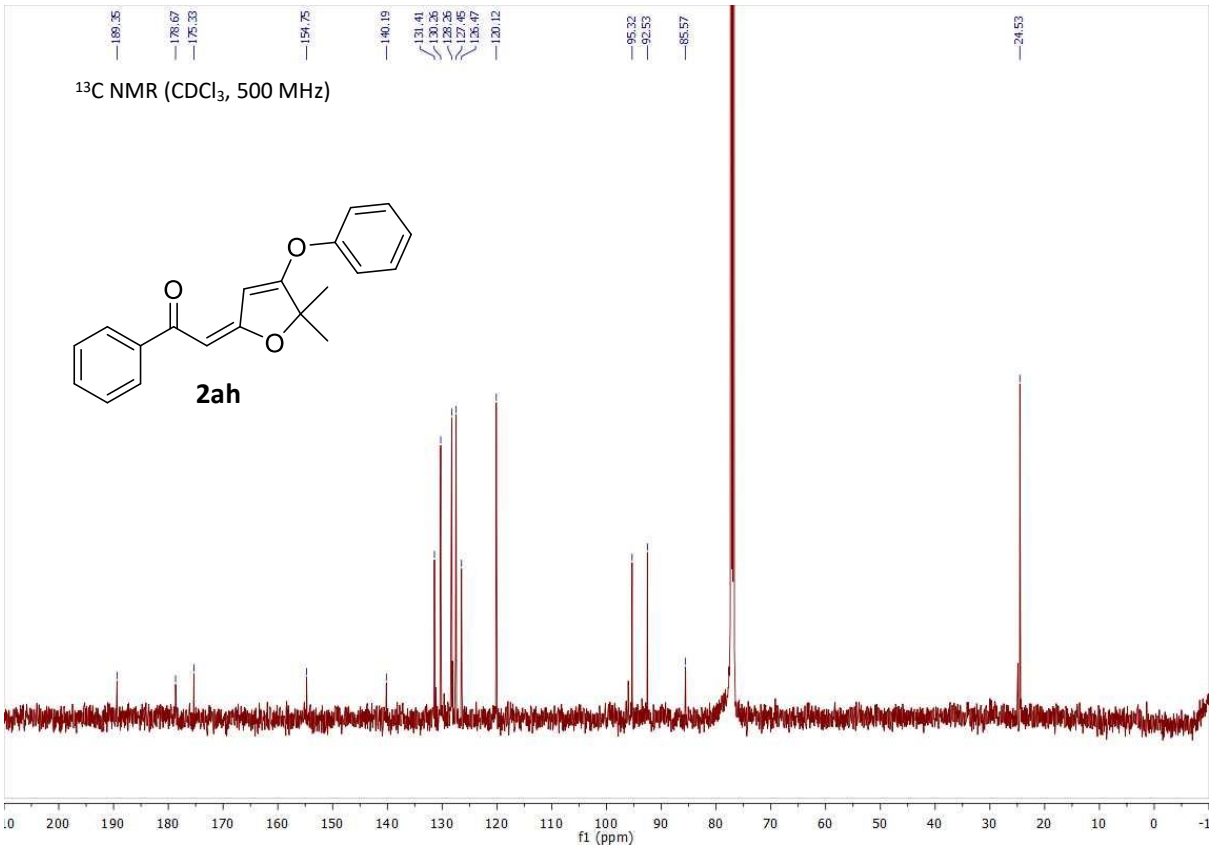
^{1}H NMR ($CDCl_3$, 500 MHz)

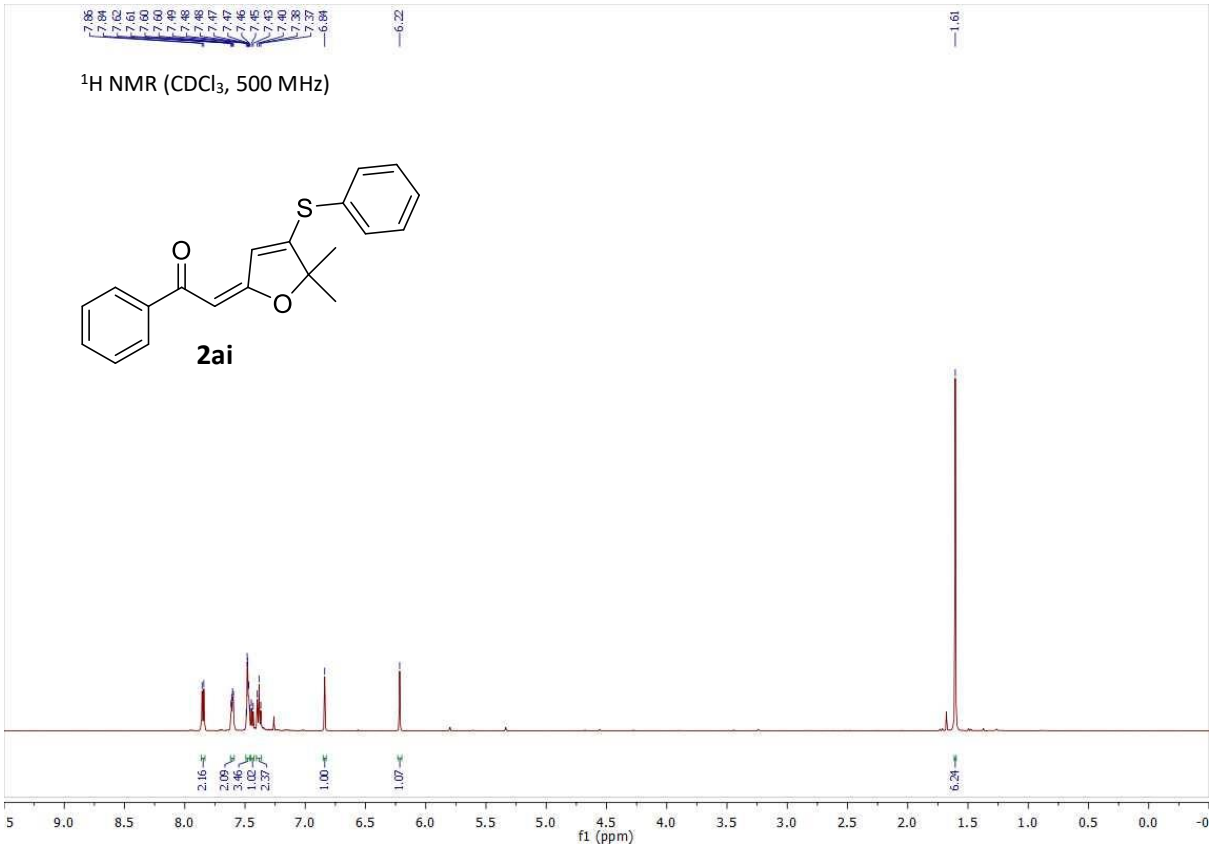
2ah



^{13}C NMR ($CDCl_3$, 500 MHz)

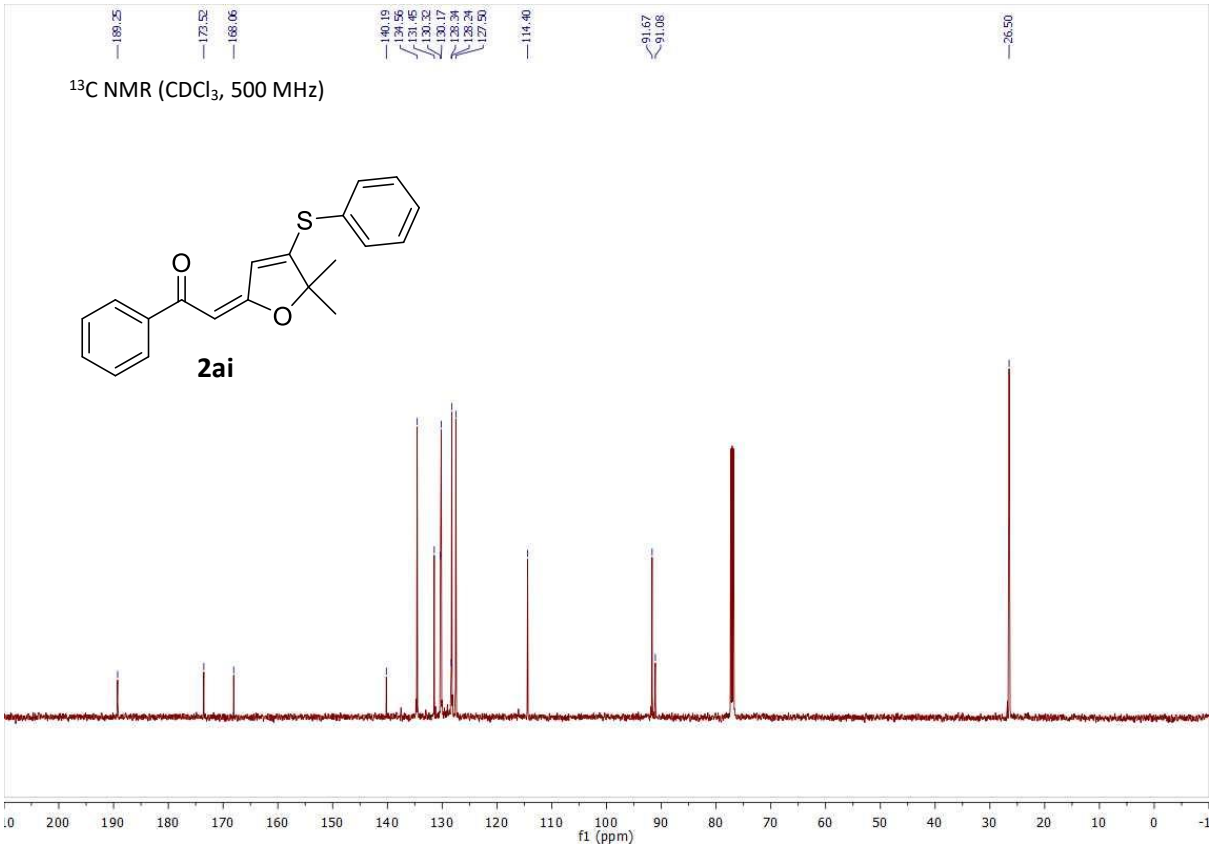
2ah





^{1}H NMR ($CDCl_3$, 500 MHz)

2ai

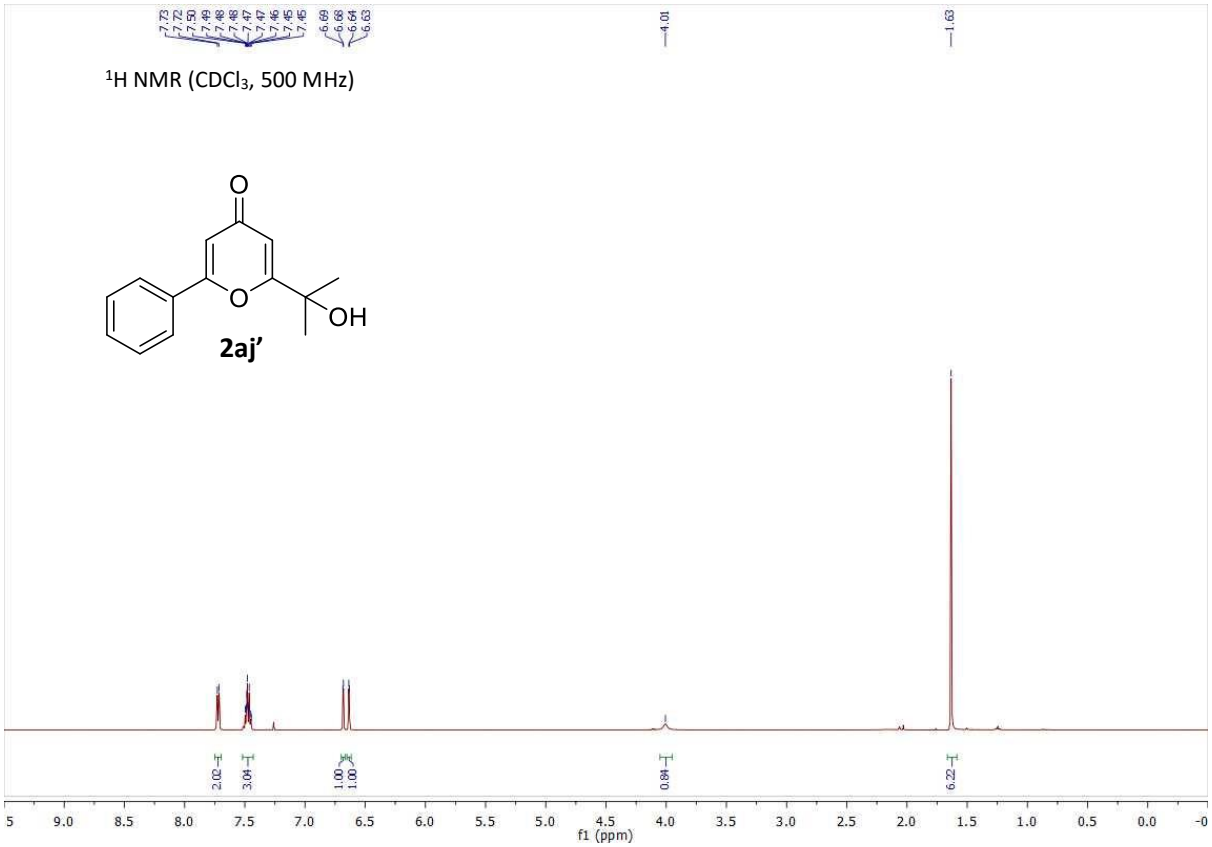


^{13}C NMR ($CDCl_3$, 500 MHz)

2ai

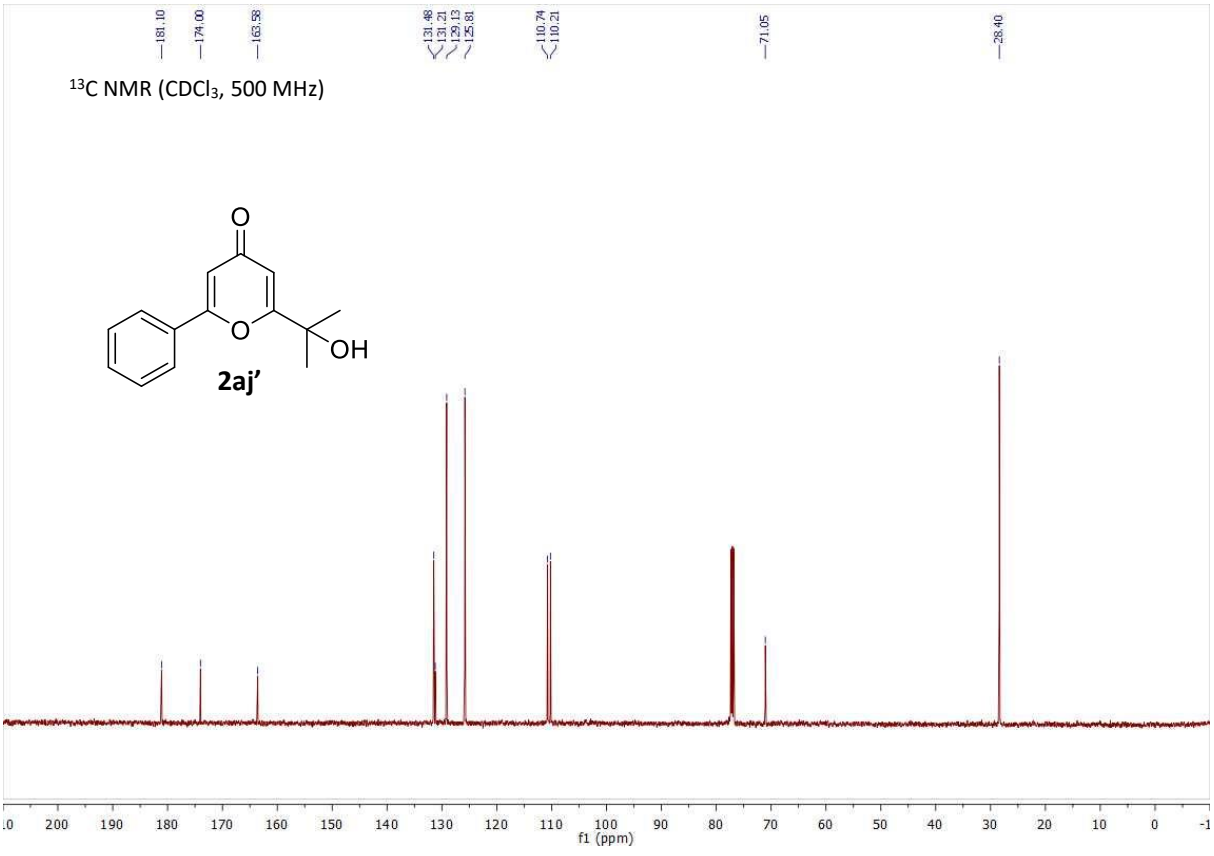
^{1}H NMR ($CDCl_3$, 500 MHz)

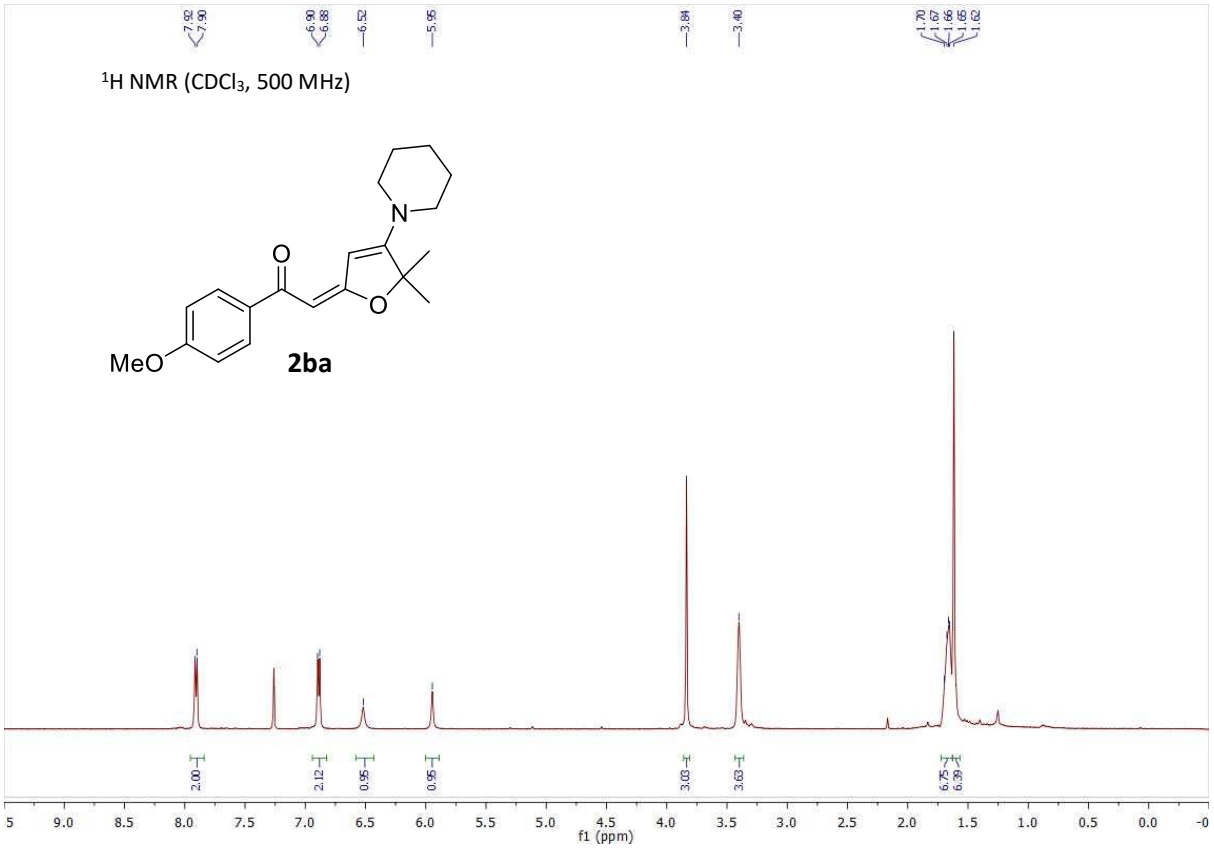
2aj'



^{13}C NMR ($CDCl_3$, 500 MHz)

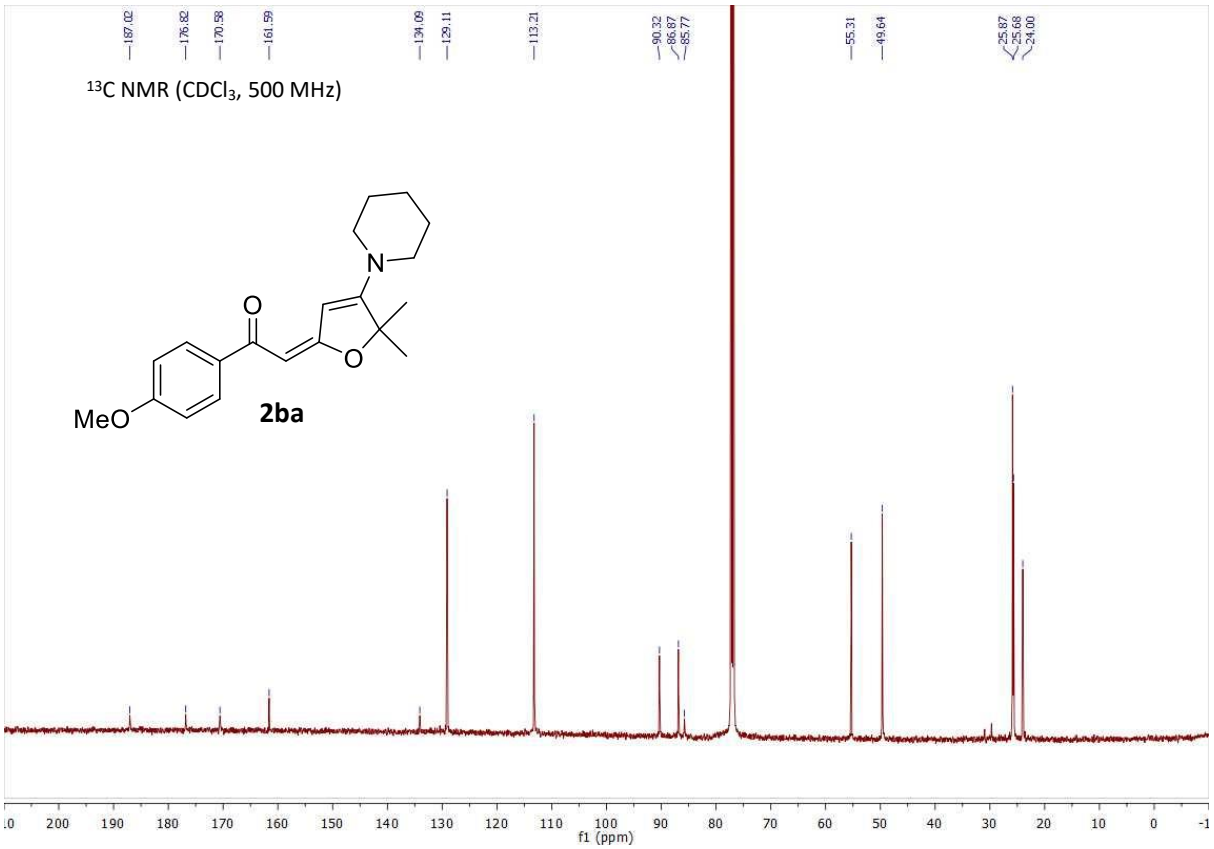
2aj'





^{1}H NMR ($CDCl_3$, 500 MHz)

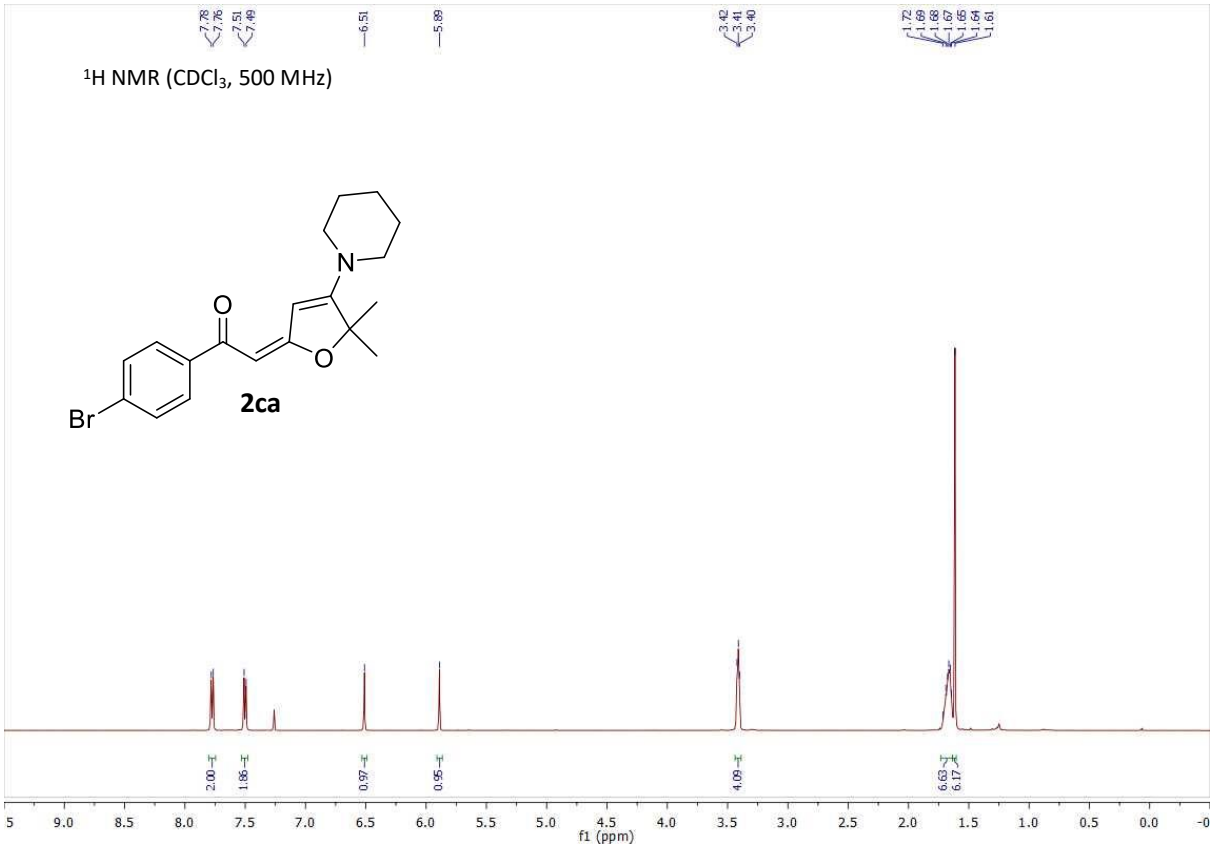
2ba



^{13}C NMR ($CDCl_3$, 500 MHz)

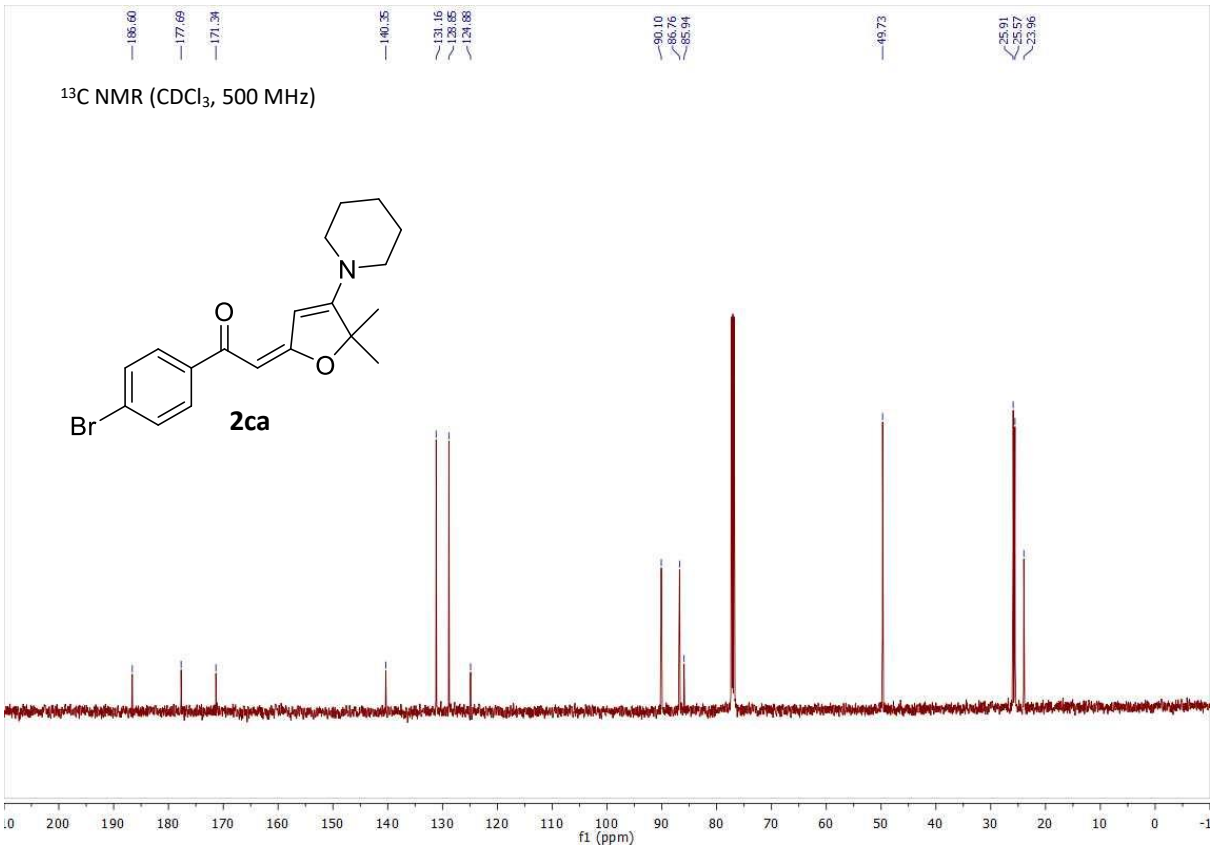
2ba

^{1}H NMR ($CDCl_3$, 500 MHz)

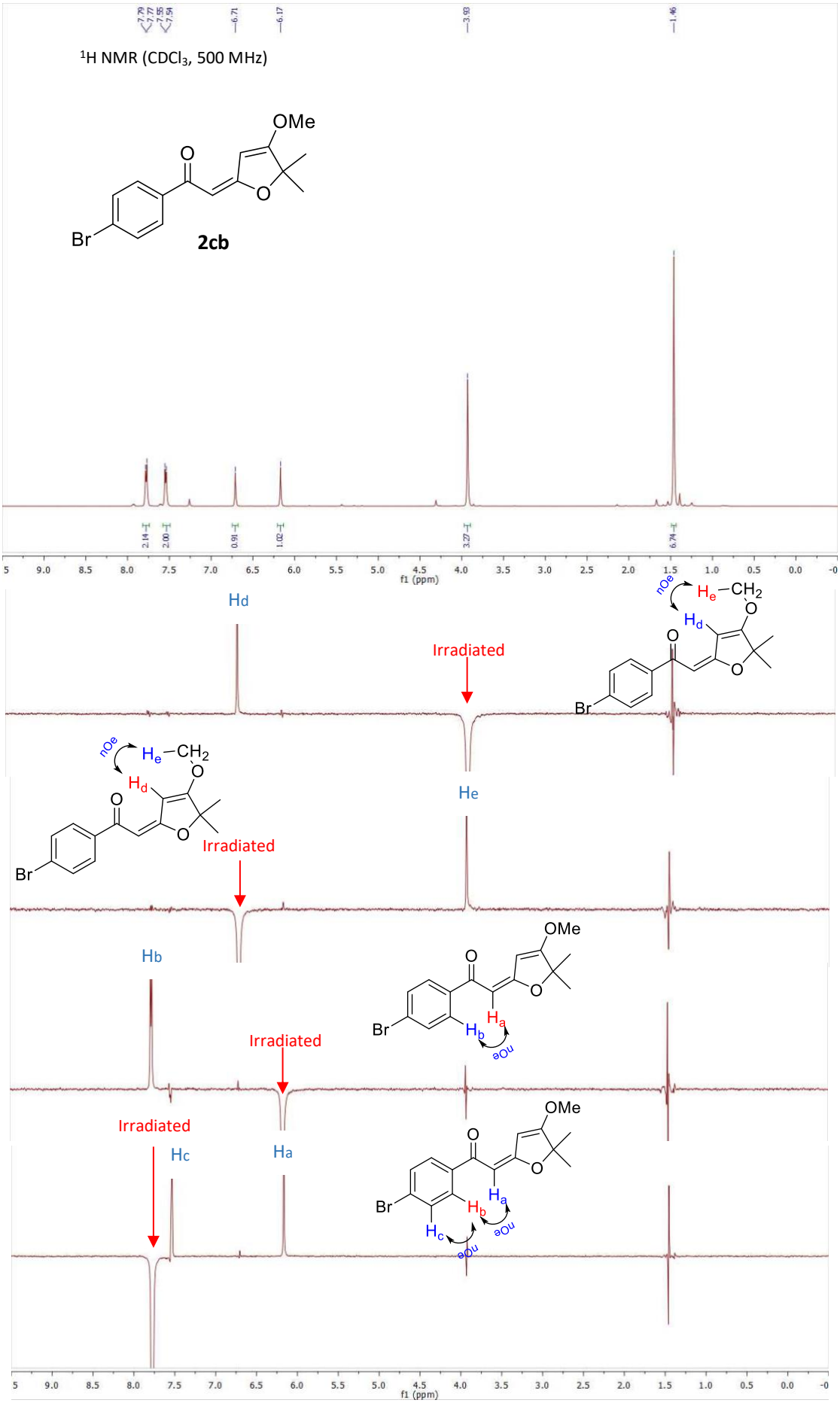


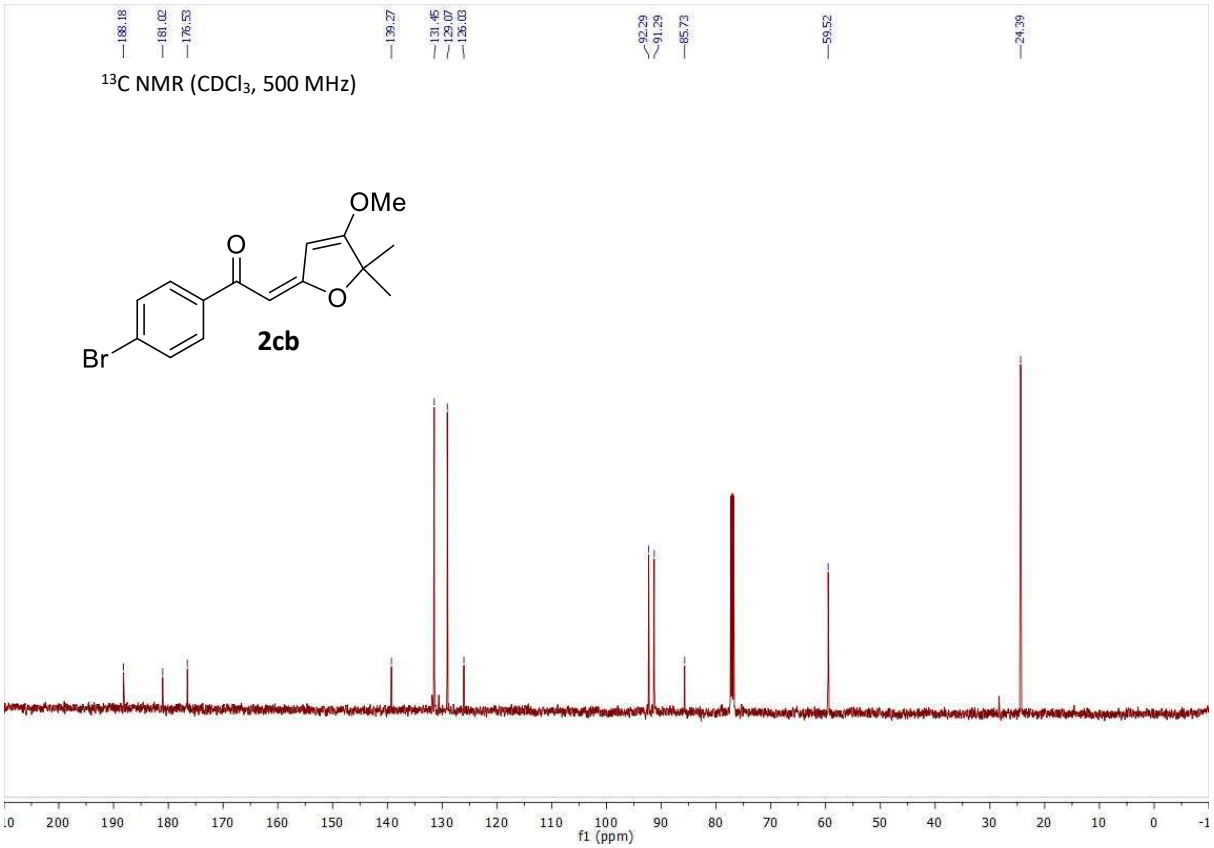
2ca

^{13}C NMR ($CDCl_3$, 500 MHz)

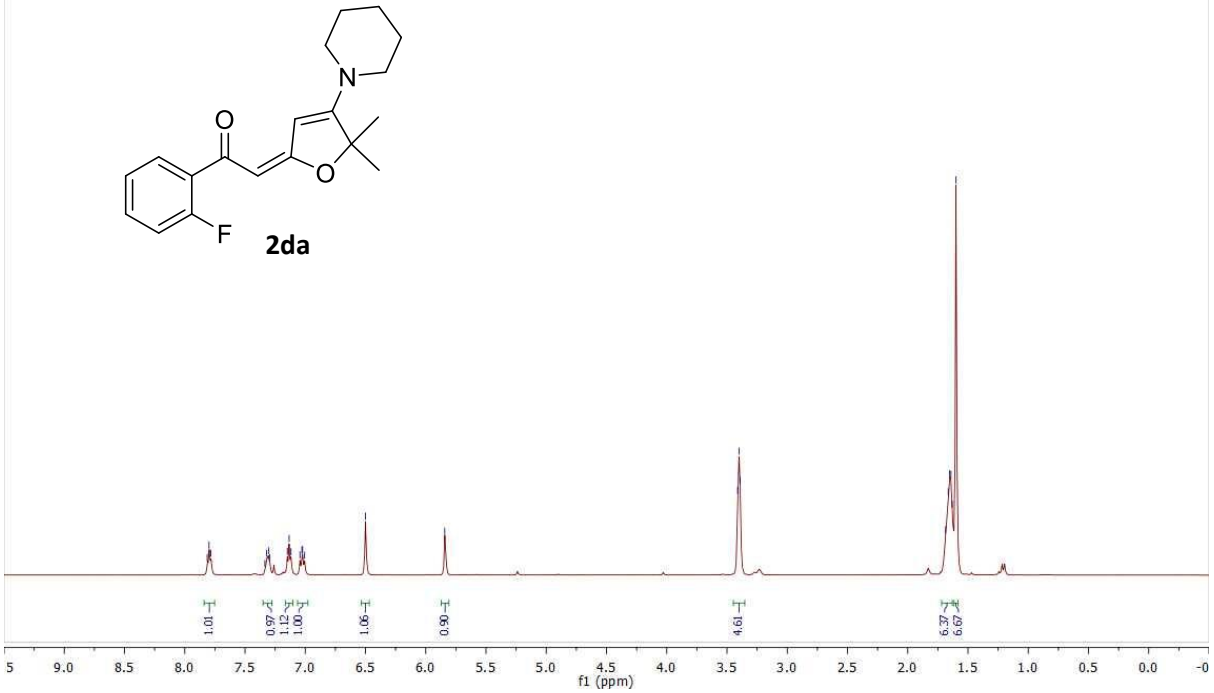


2ca


7.79
7.77
7.55
7.54
6.71
6.17
3.93
1.46
^{1}H NMR ($CDCl_3$, 500 MHz)
OMe
O
O
Br
2cb
2.14
2.00
0.91
1.02
3.27
6.74
f1 (ppm)
Hd
Irradiated
nOe
He
CH2
Hd
O
Br
He
Irradiated
Hb
OMe
Ha
Hb
aOu
Irradiated
Irradiated
Hc
Ha
Hc
Hb
Ha
aOu
aOu
f1 (ppm)

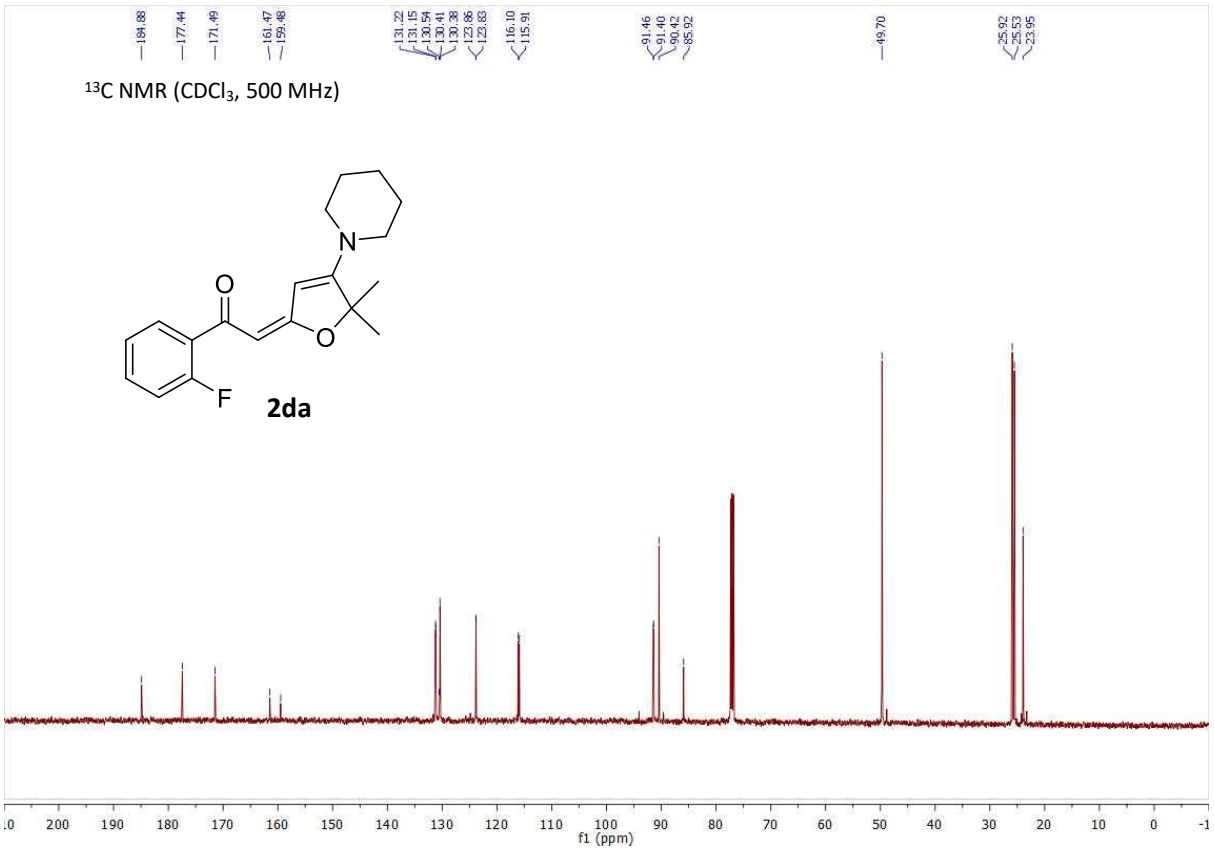

188.18
181.02
176.53
139.27
131.45
129.07
126.03
92.29
91.29
85.73
59.52
24.39
13C NMR (CDCl3, 500 MHz)
OMe
O
O
Br
2cb
f1 (ppm)

^{1}H NMR ($CDCl_3$, 500 MHz)



2da

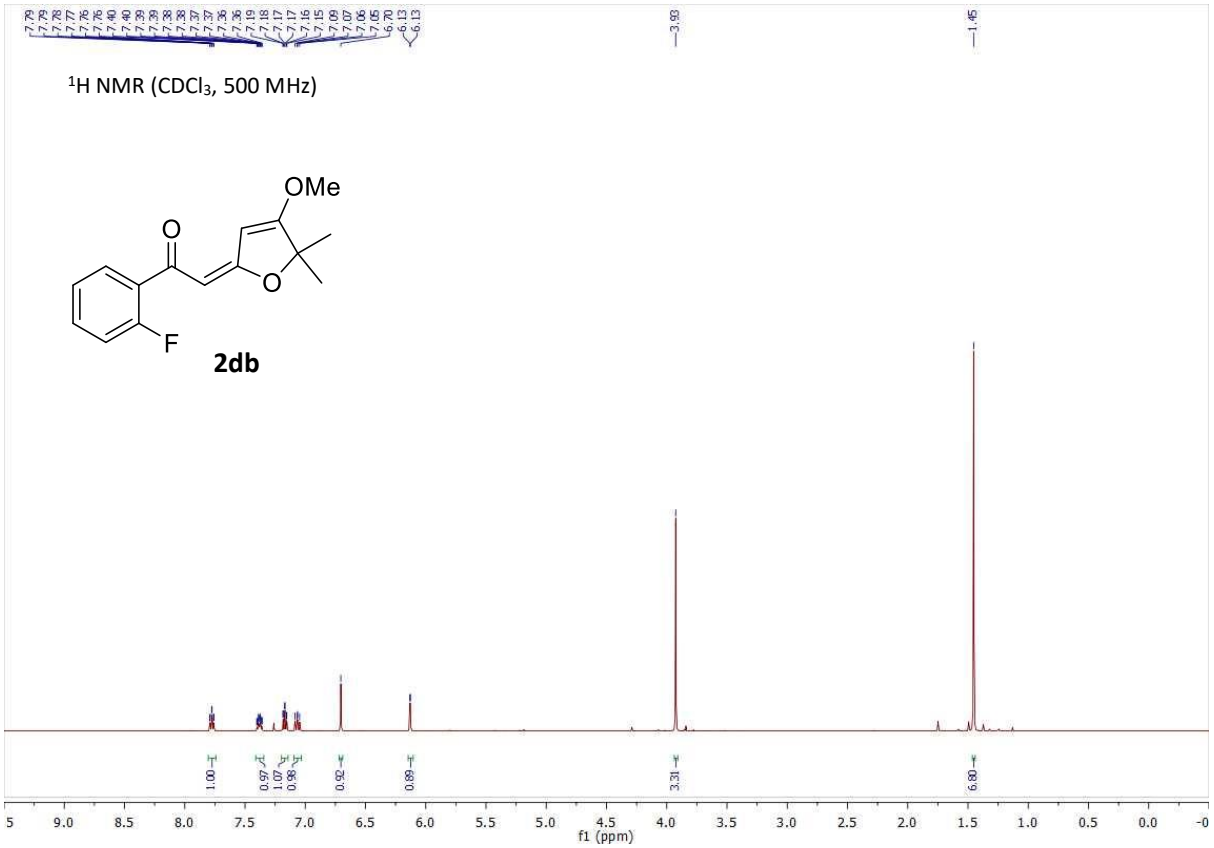
^{13}C NMR ($CDCl_3$, 500 MHz)



2da

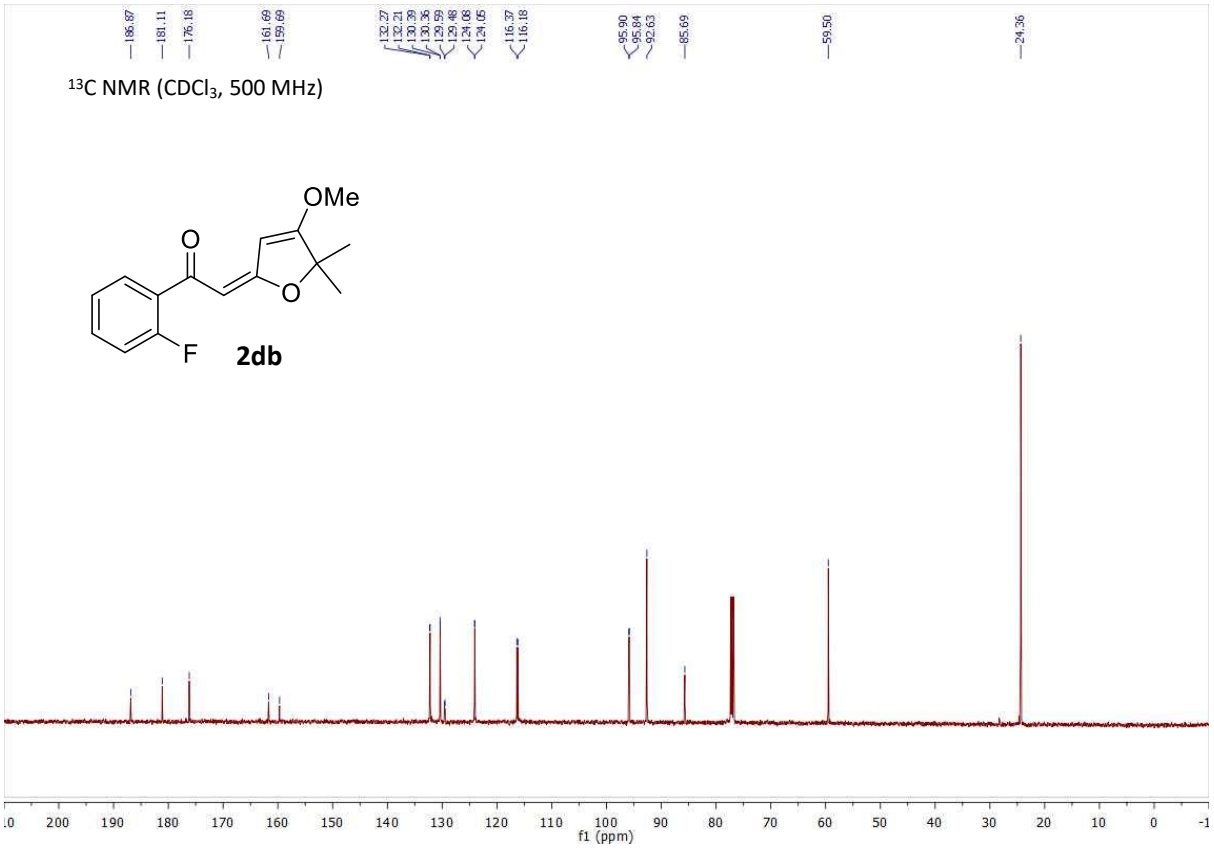
^{1}H NMR ($CDCl_3$, 500 MHz)

2db



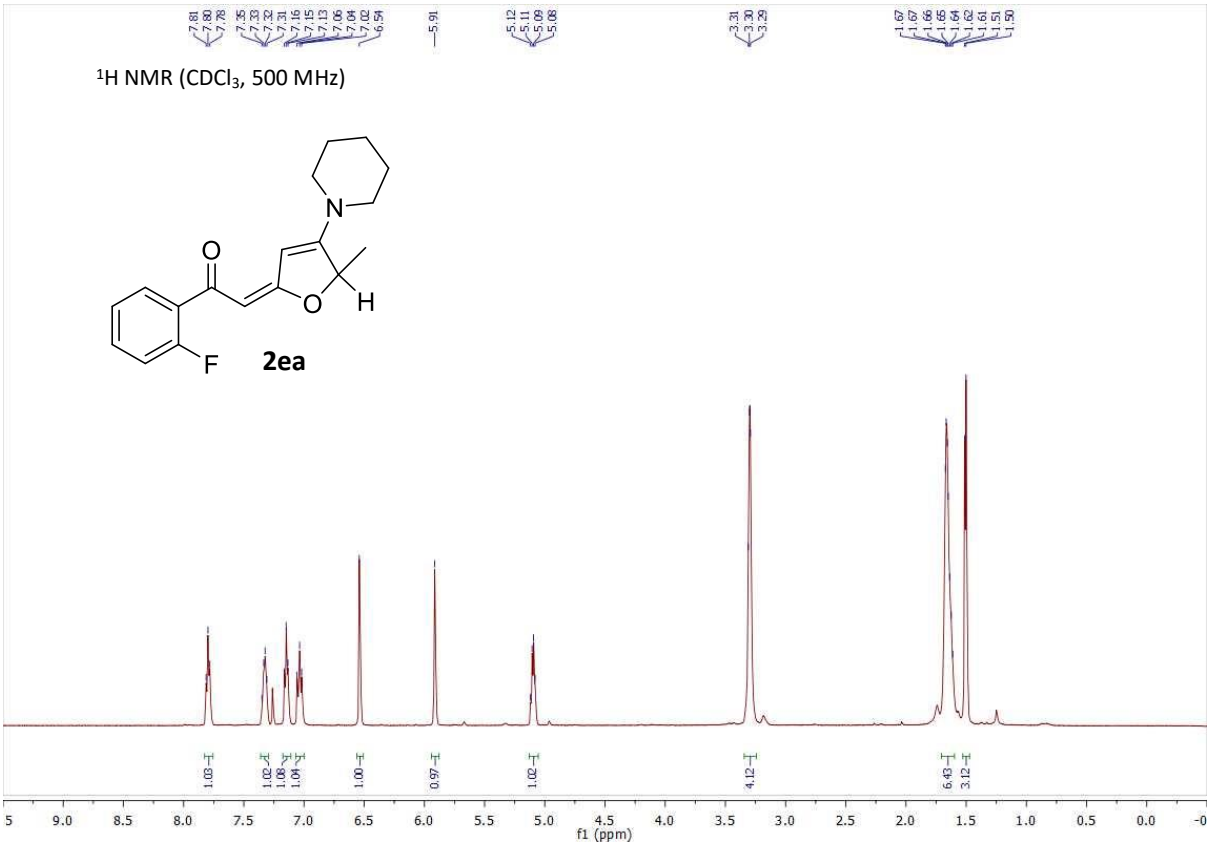
^{13}C NMR ($CDCl_3$, 500 MHz)

2db



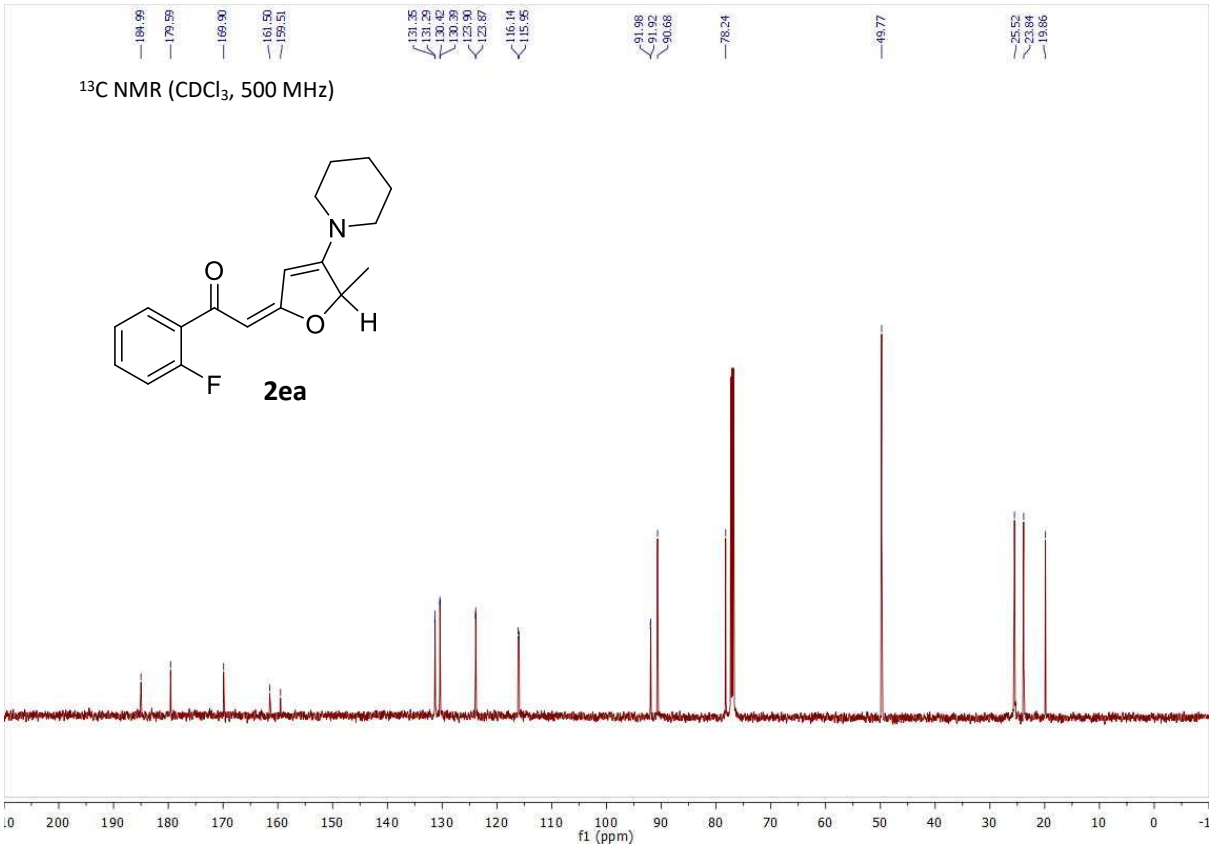
^{1}H NMR ($CDCl_3$, 500 MHz)

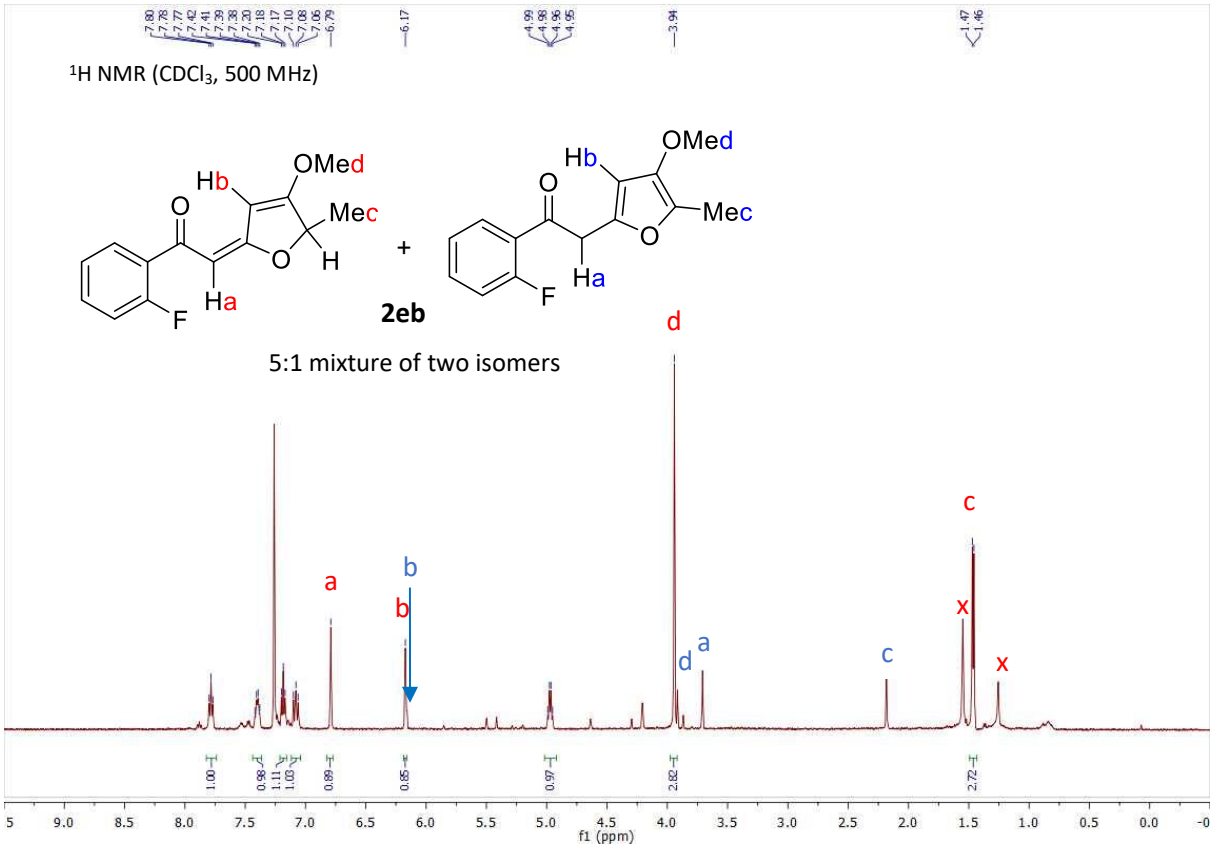
2ea

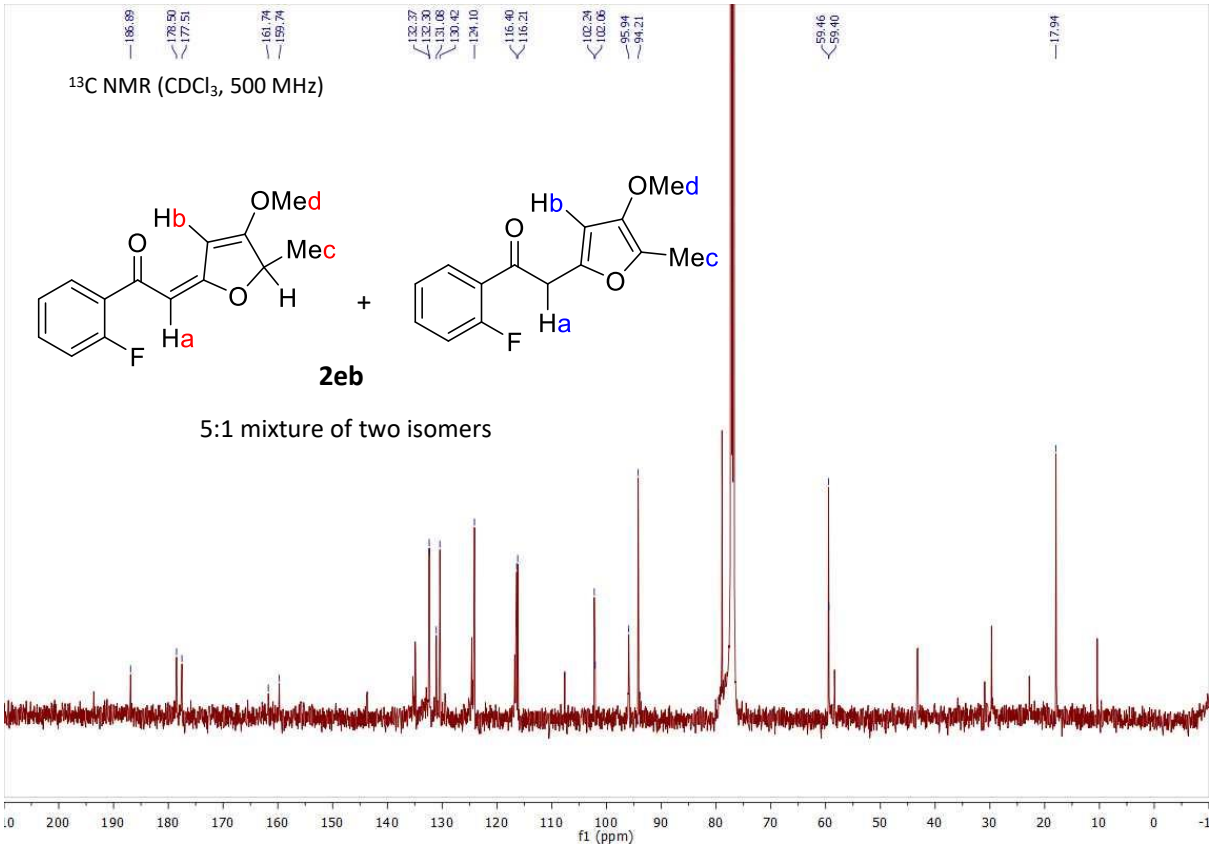


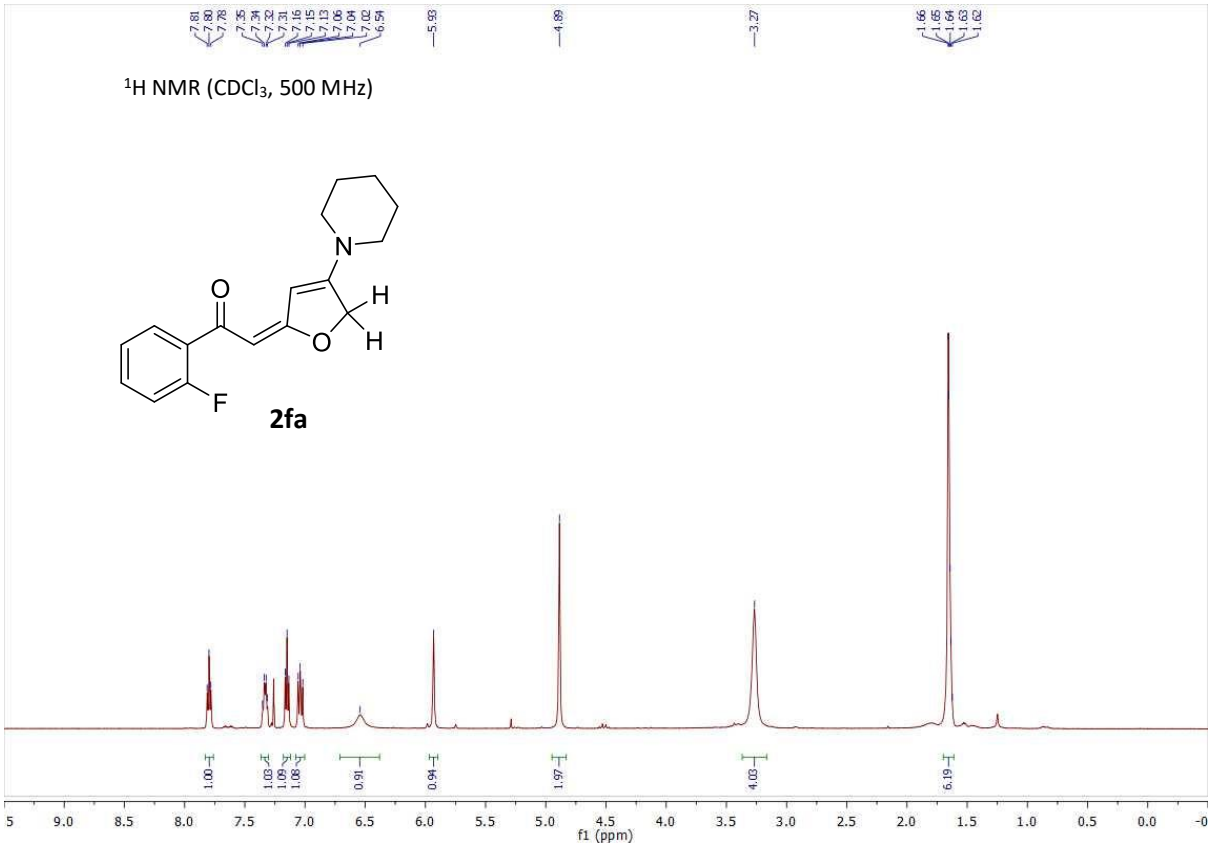
^{13}C NMR ($CDCl_3$, 500 MHz)

2ea



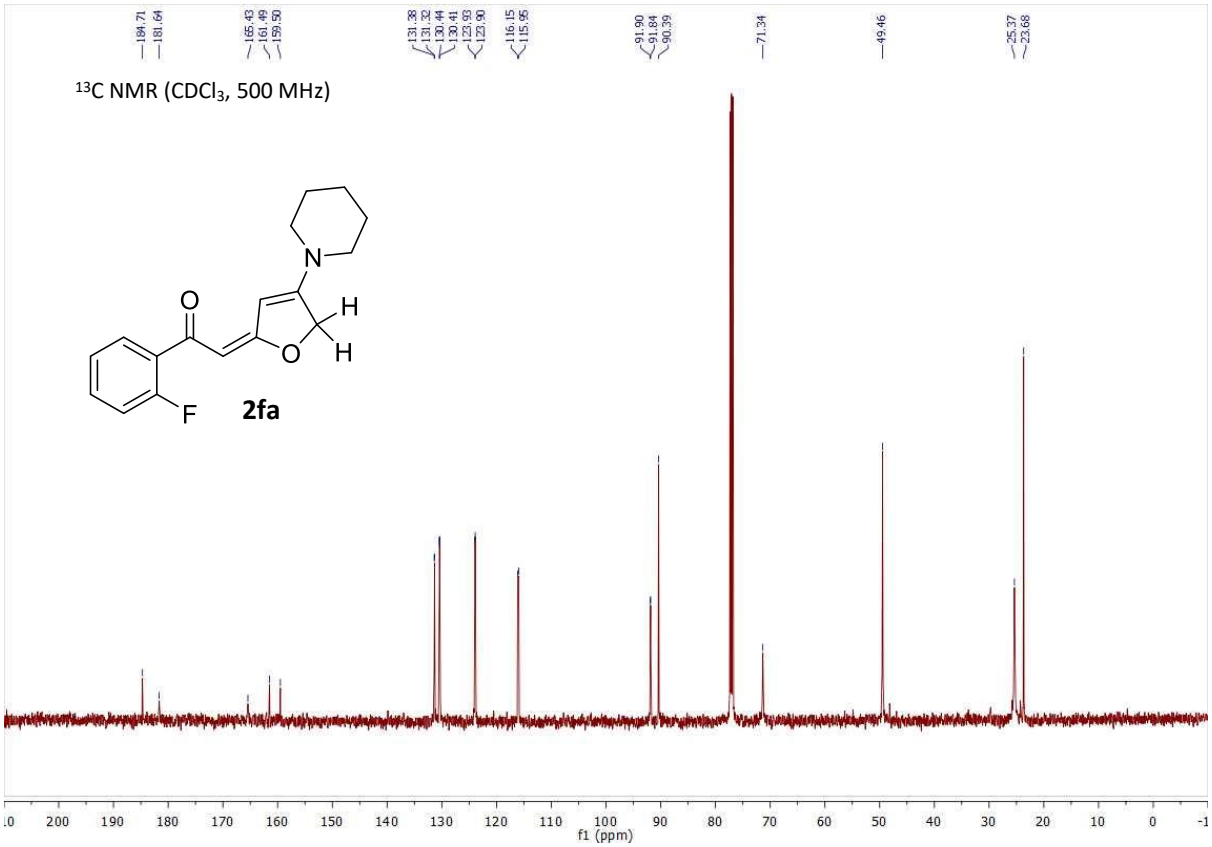

1H NMR (CDCl3, 500 MHz)
OMed
Hb
Mec
O
H
Ha
F
+
2eb
5:1 mixture of two isomers
d
a
b
b
a
c
x
c
x
f1 (ppm)


13C NMR (CDCl3, 500 MHz)
OMed
Hb
Mec
O
H
Ha
F
+
2eb
5:1 mixture of two isomers
f1 (ppm)



^{1}H NMR ($CDCl_3$, 500 MHz)

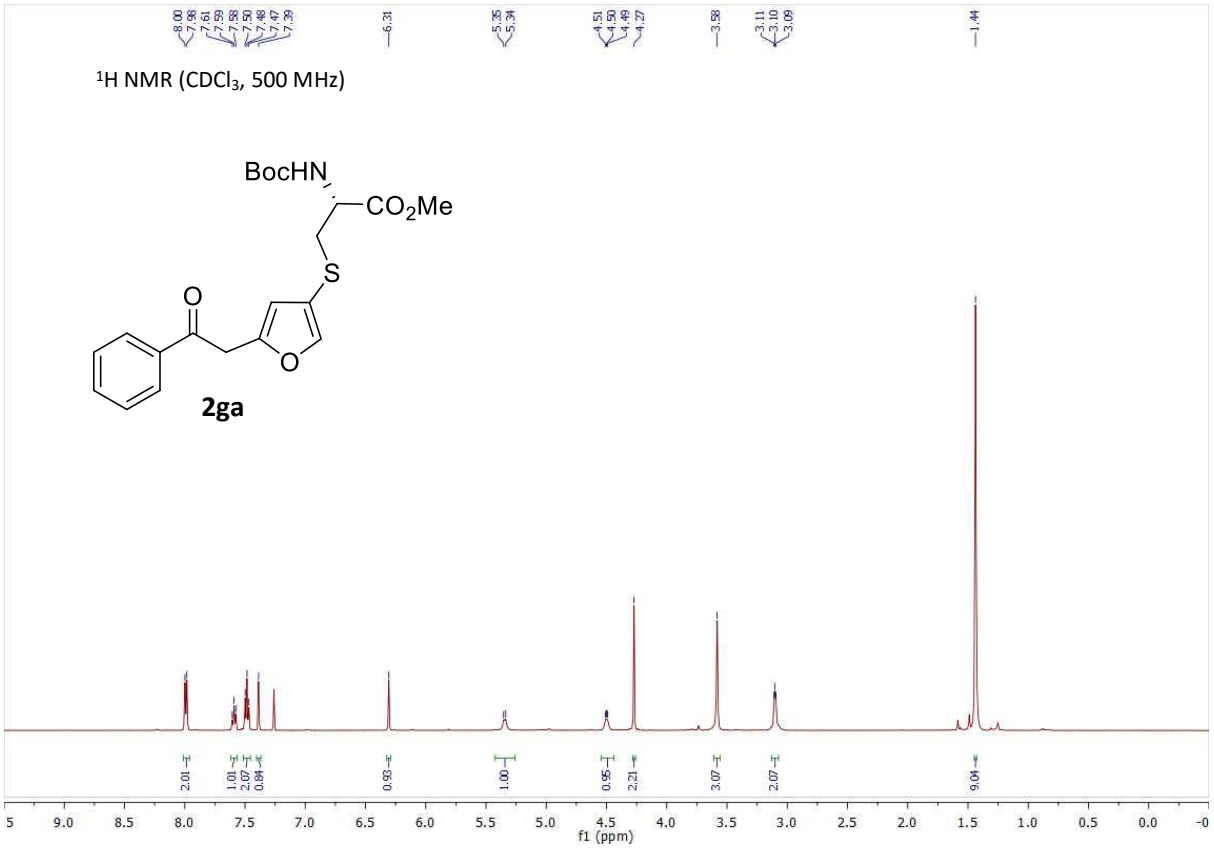
2fa



^{13}C NMR ($CDCl_3$, 500 MHz)

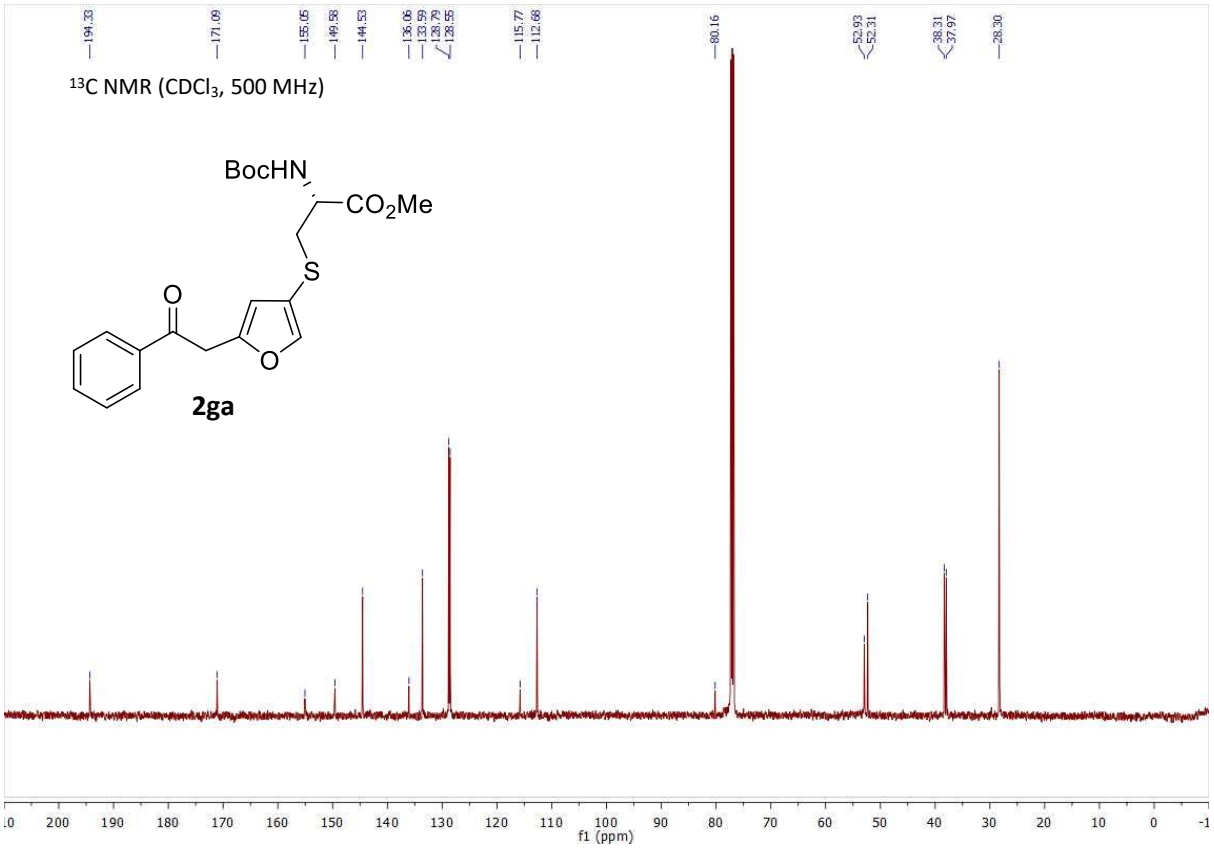
2fa

^{1}H NMR ($CDCl_3$, 500 MHz)



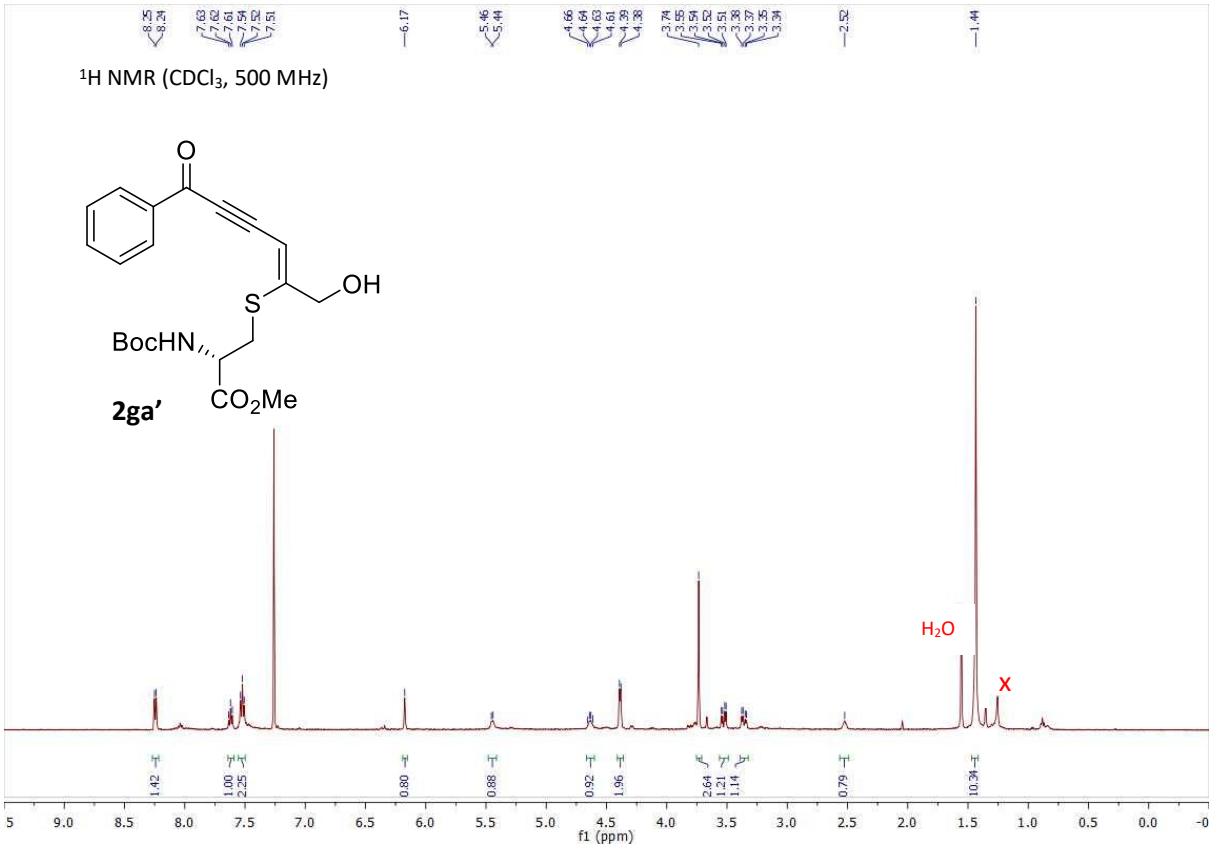
2ga

^{13}C NMR ($CDCl_3$, 500 MHz)

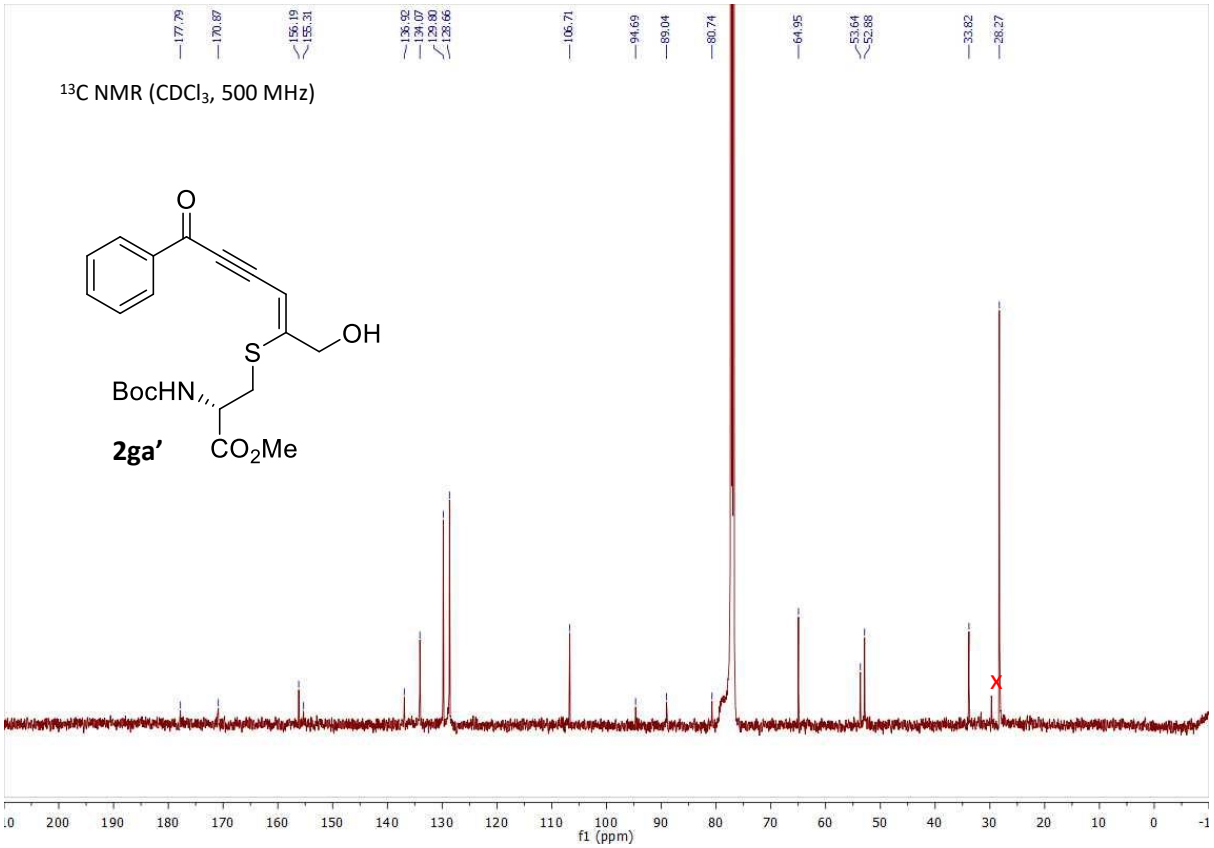


2ga

^{1}H NMR ($CDCl_3$, 500 MHz)

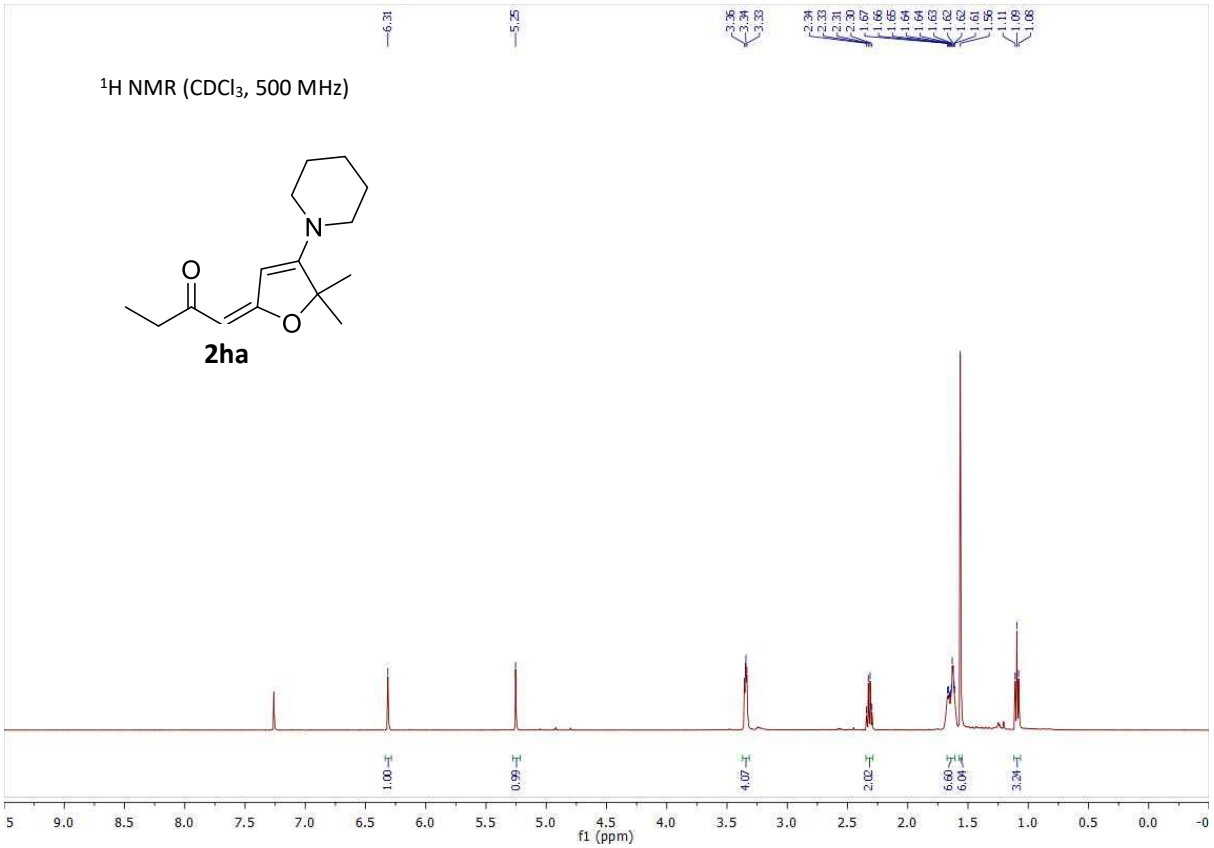


^{13}C NMR ($CDCl_3$, 500 MHz)



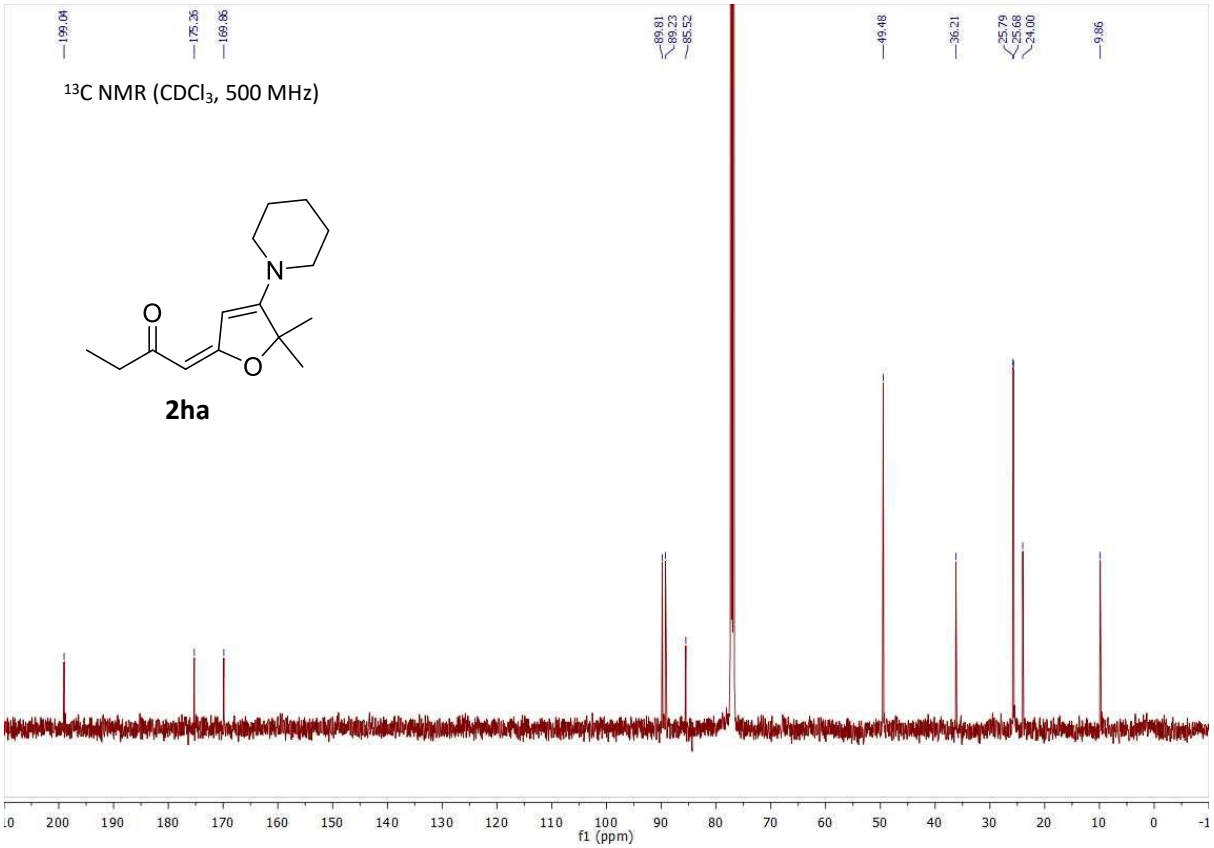
^{1}H NMR ($CDCl_3$, 500 MHz)

2ha



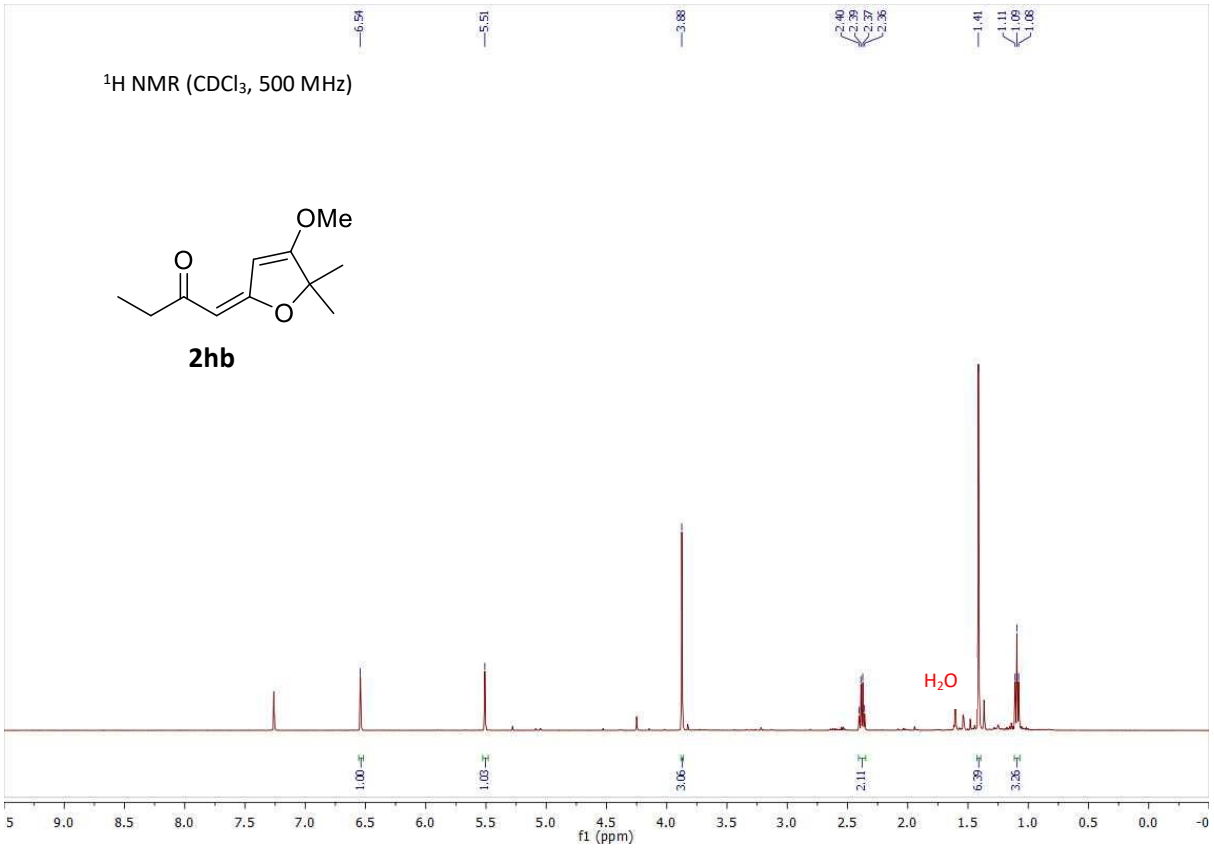
^{13}C NMR ($CDCl_3$, 500 MHz)

2ha



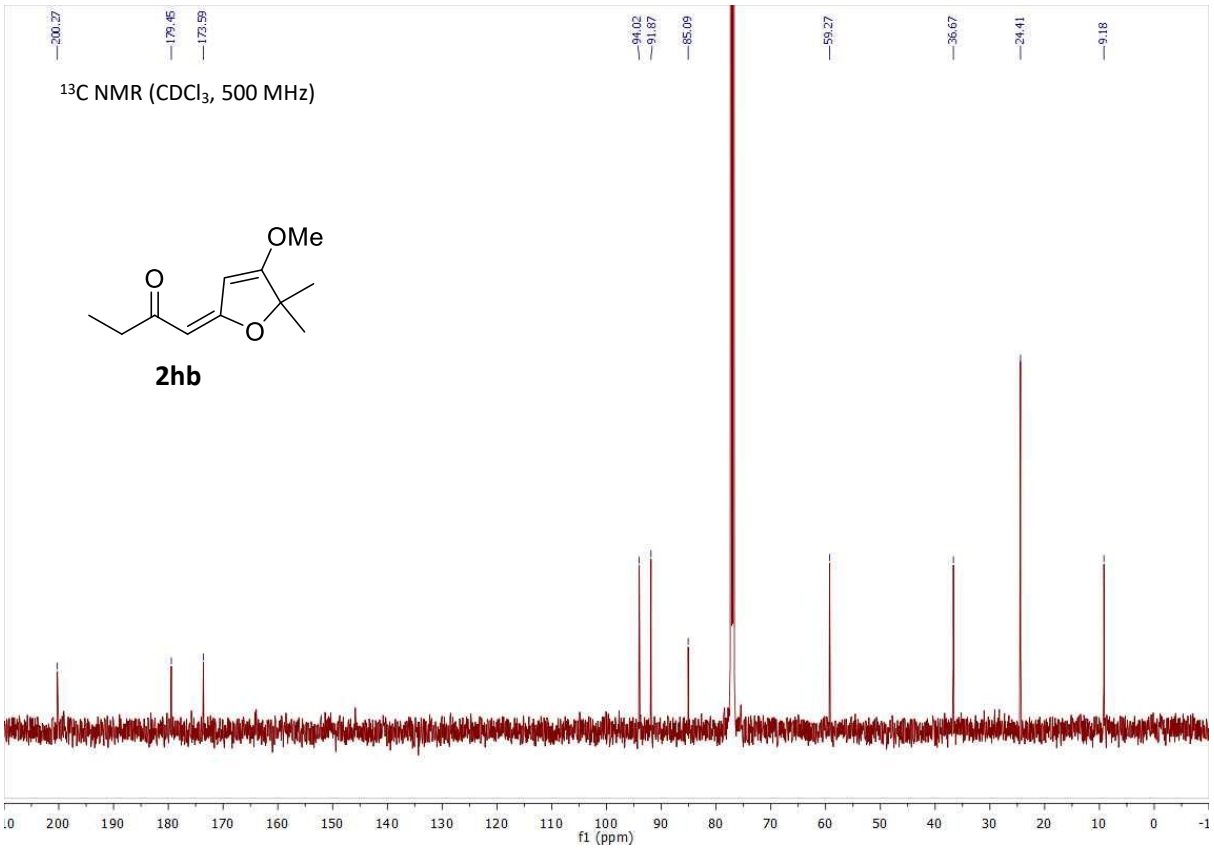
^{1}H NMR ($CDCl_3$, 500 MHz)

2hb



^{13}C NMR ($CDCl_3$, 500 MHz)

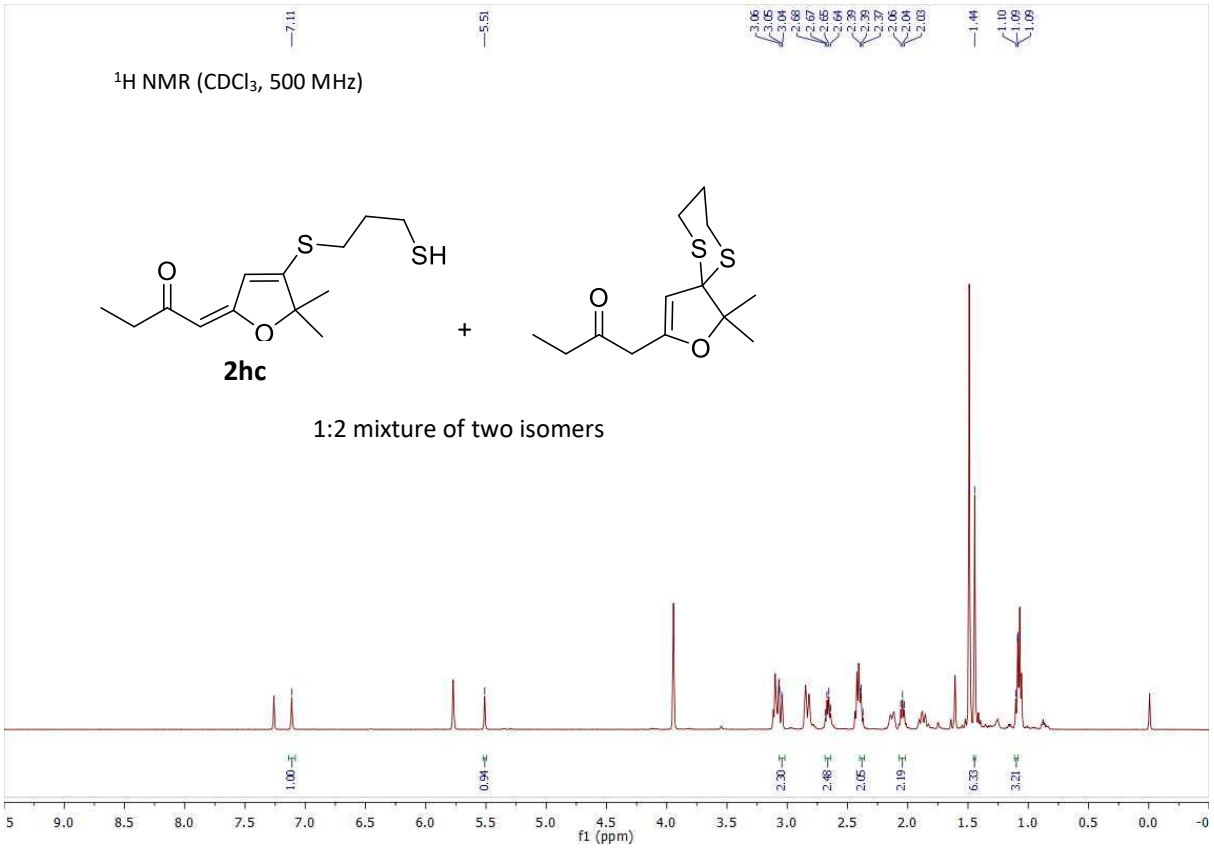
2hb



^{1}H NMR ($CDCl_3$, 500 MHz)

2hc +

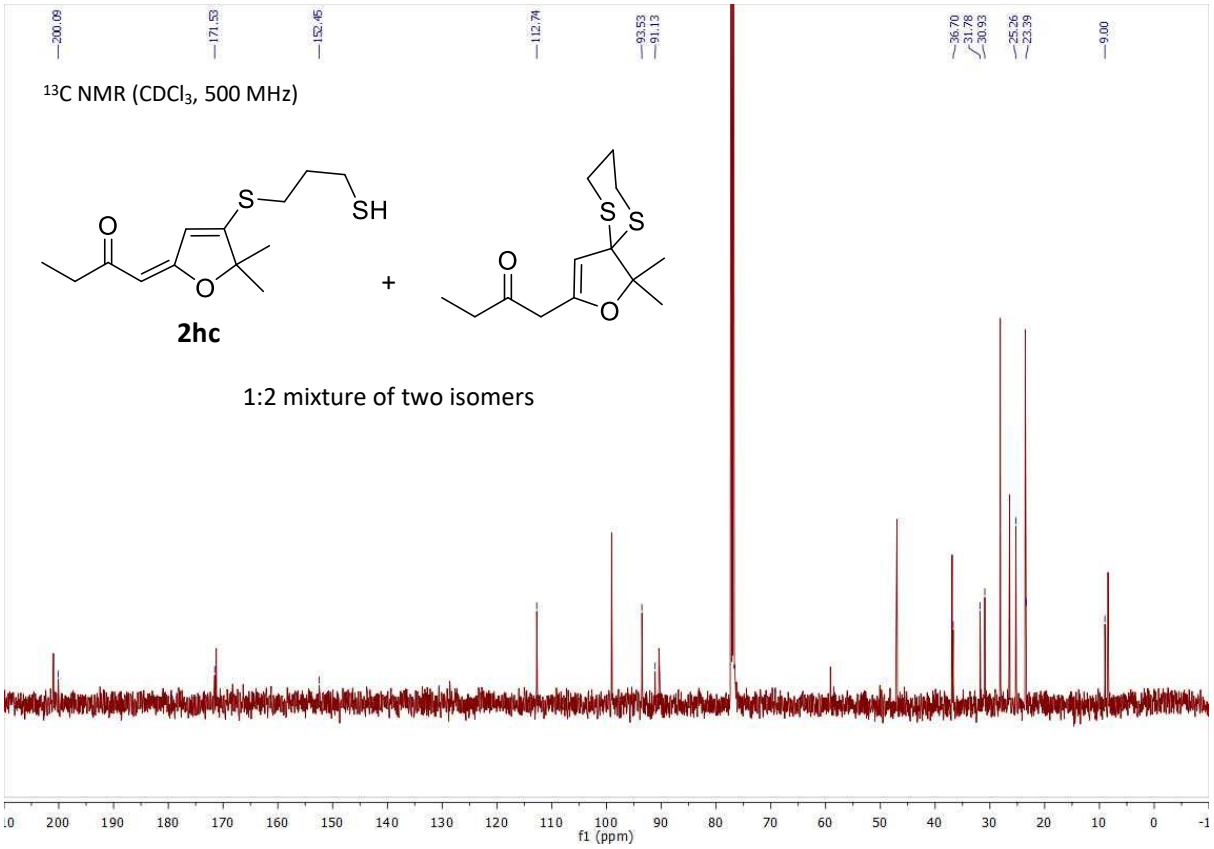
1:2 mixture of two isomers



^{13}C NMR ($CDCl_3$, 500 MHz)

2hc +

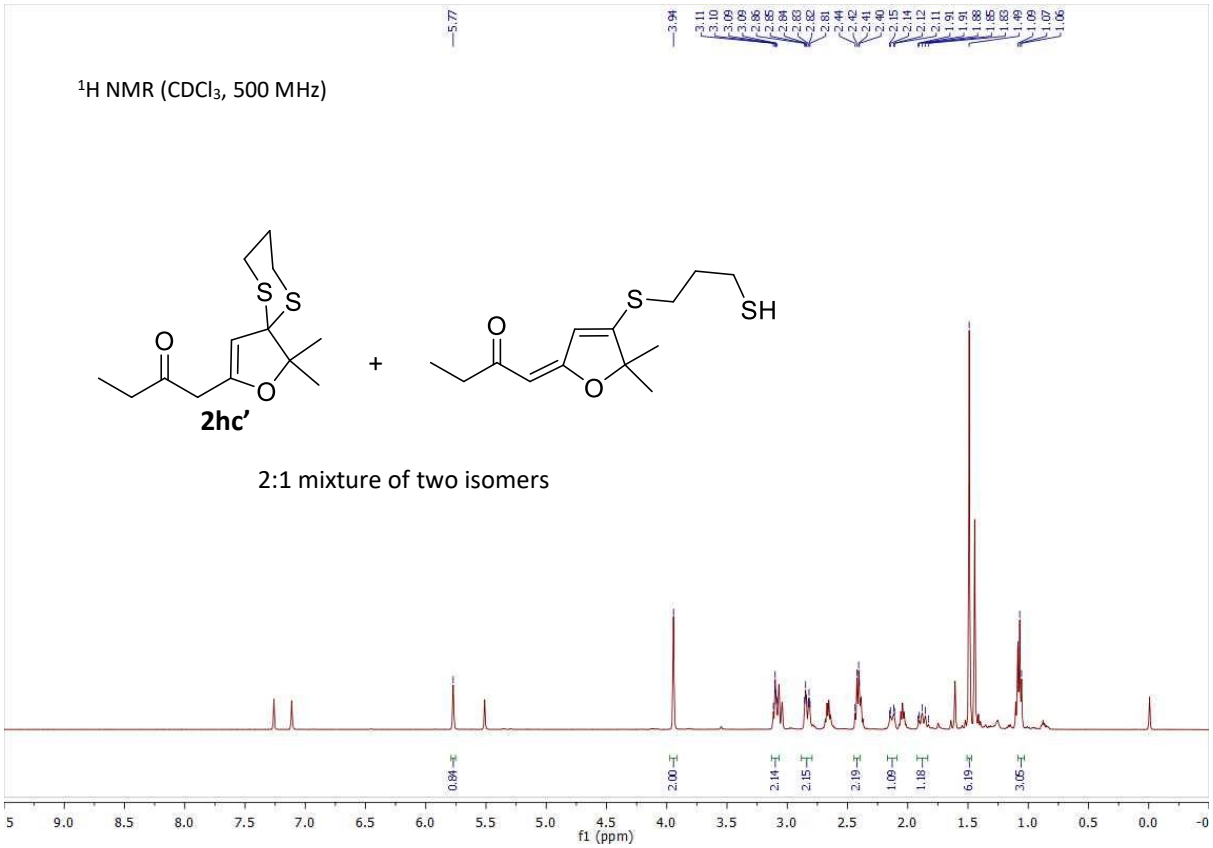
1:2 mixture of two isomers



^{1}H NMR ($CDCl_3$, 500 MHz)

2hc'

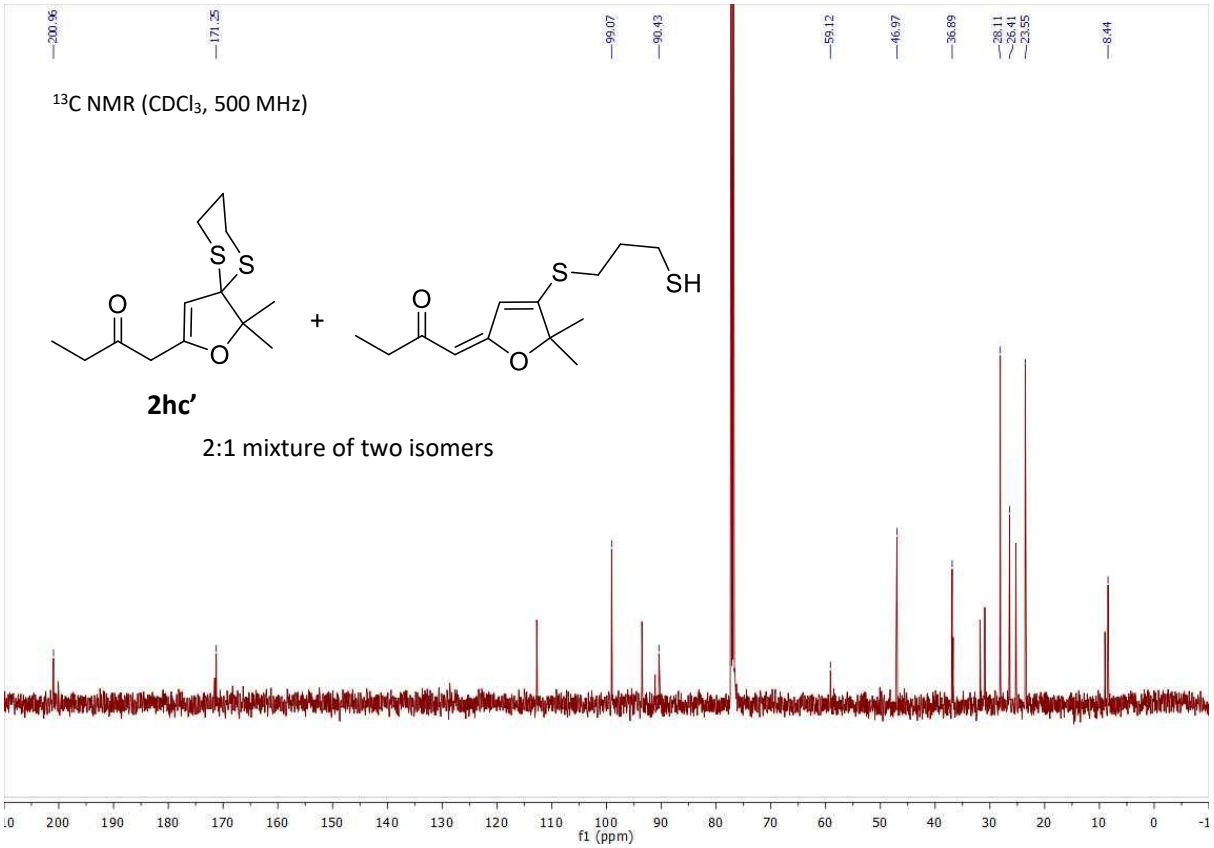
2:1 mixture of two isomers



^{13}C NMR ($CDCl_3$, 500 MHz)

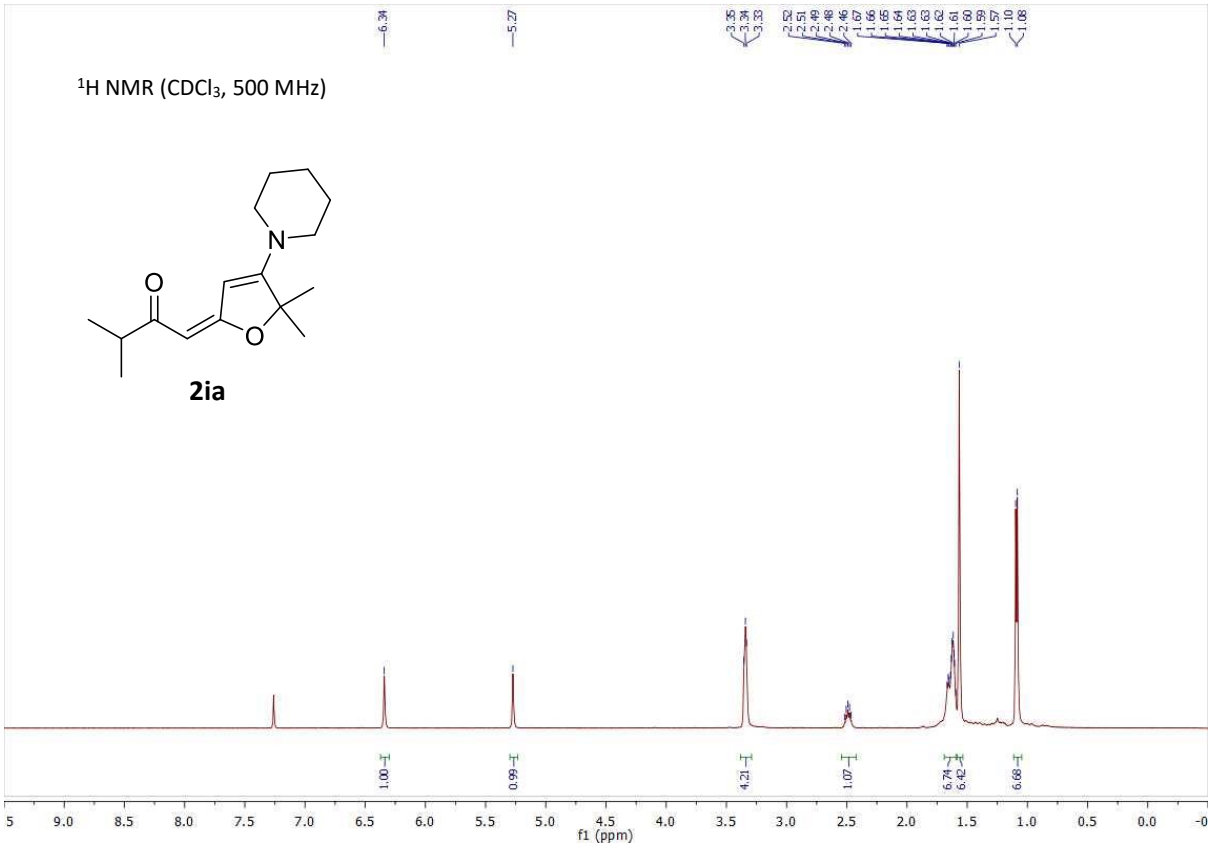
2hc'

2:1 mixture of two isomers



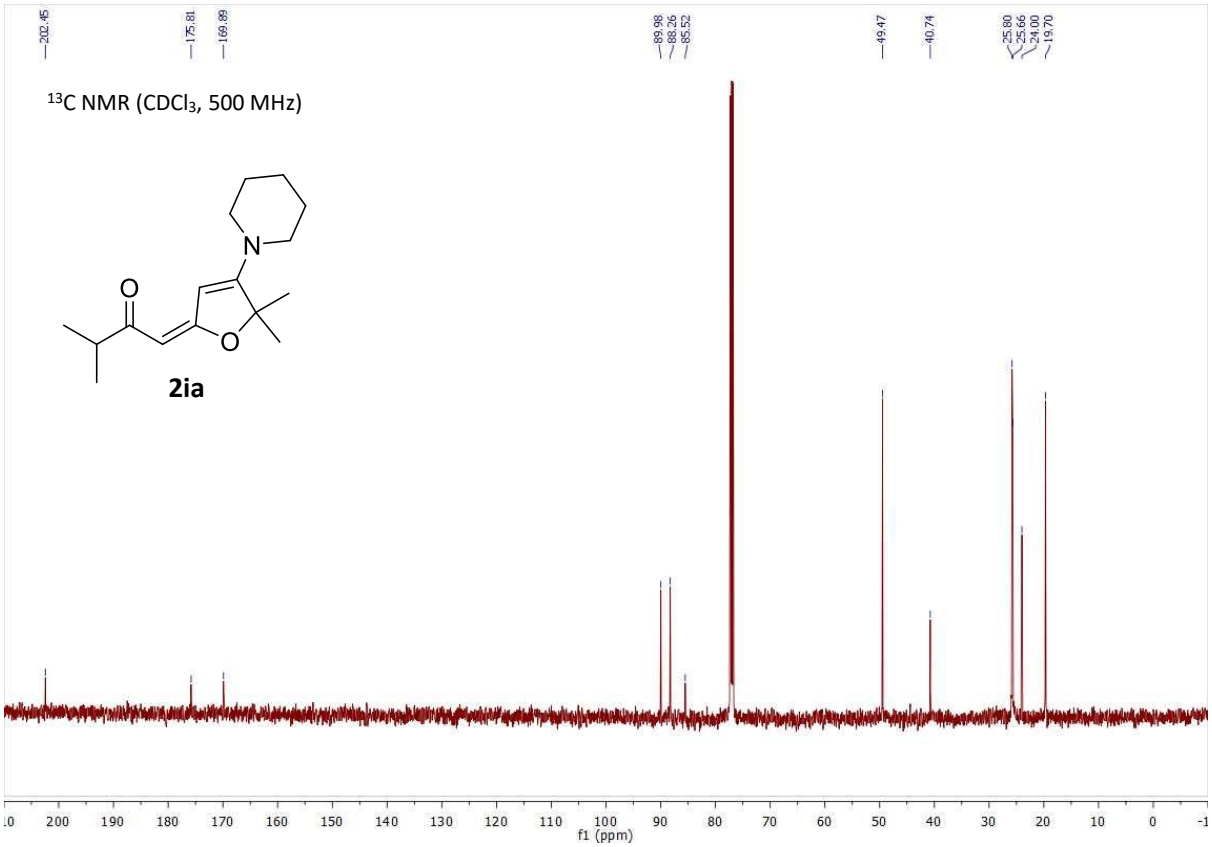
^{1}H NMR ($CDCl_3$, 500 MHz)

2ia



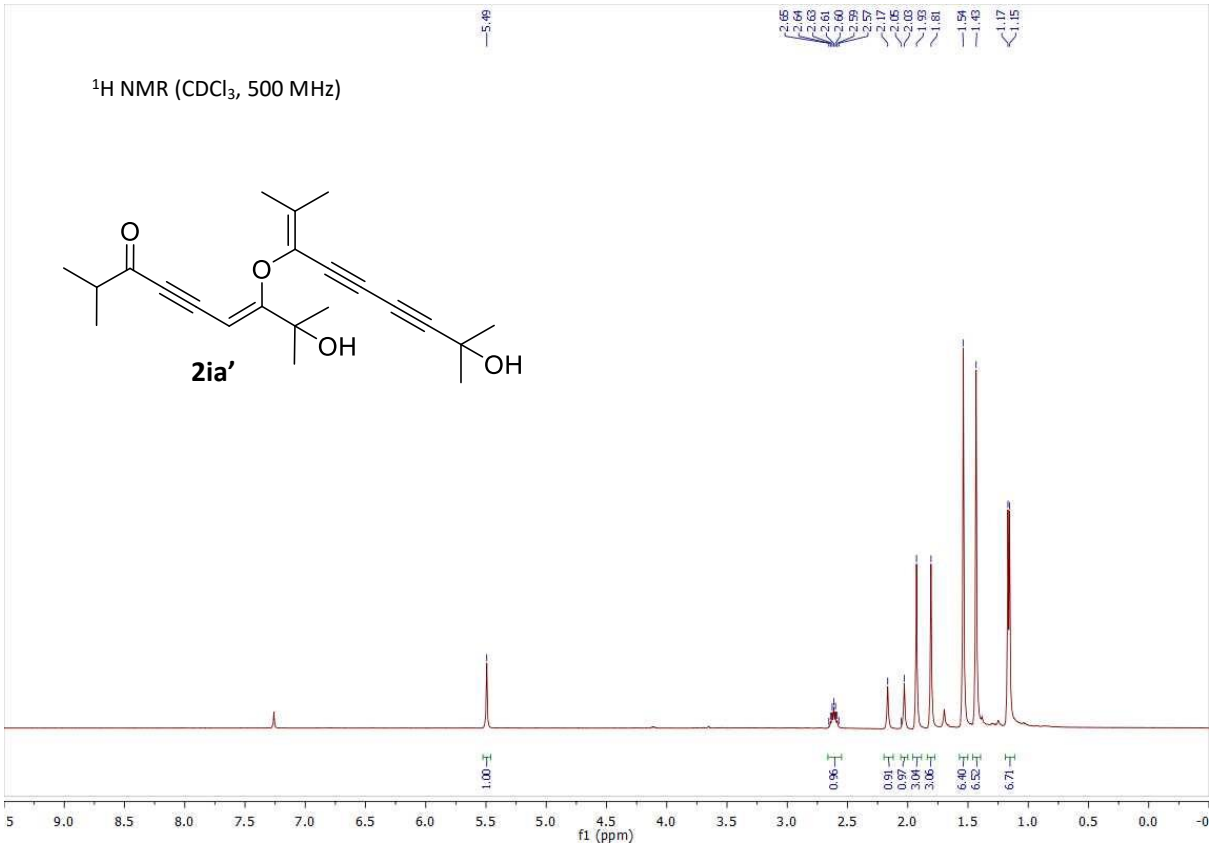
^{13}C NMR ($CDCl_3$, 500 MHz)

2ia



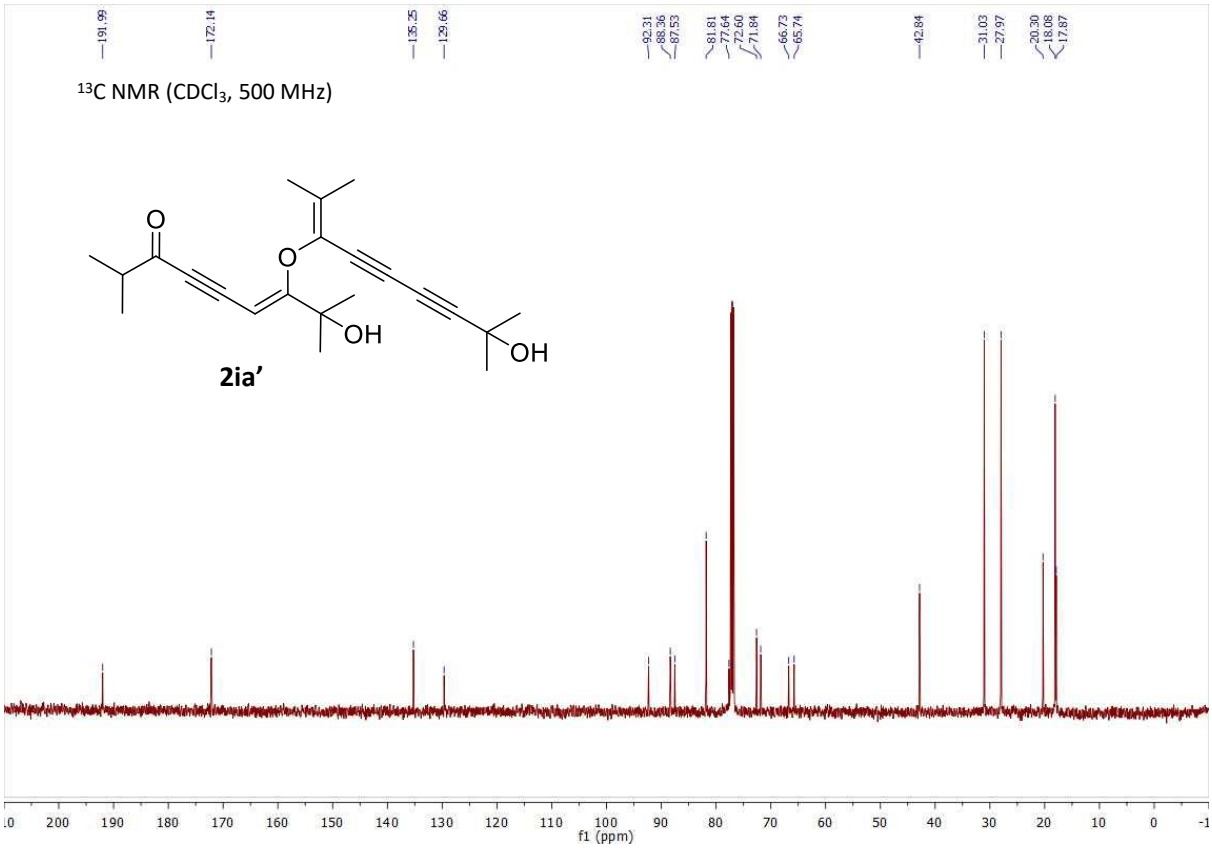
^{1}H NMR ($CDCl_3$, 500 MHz)

2ia'



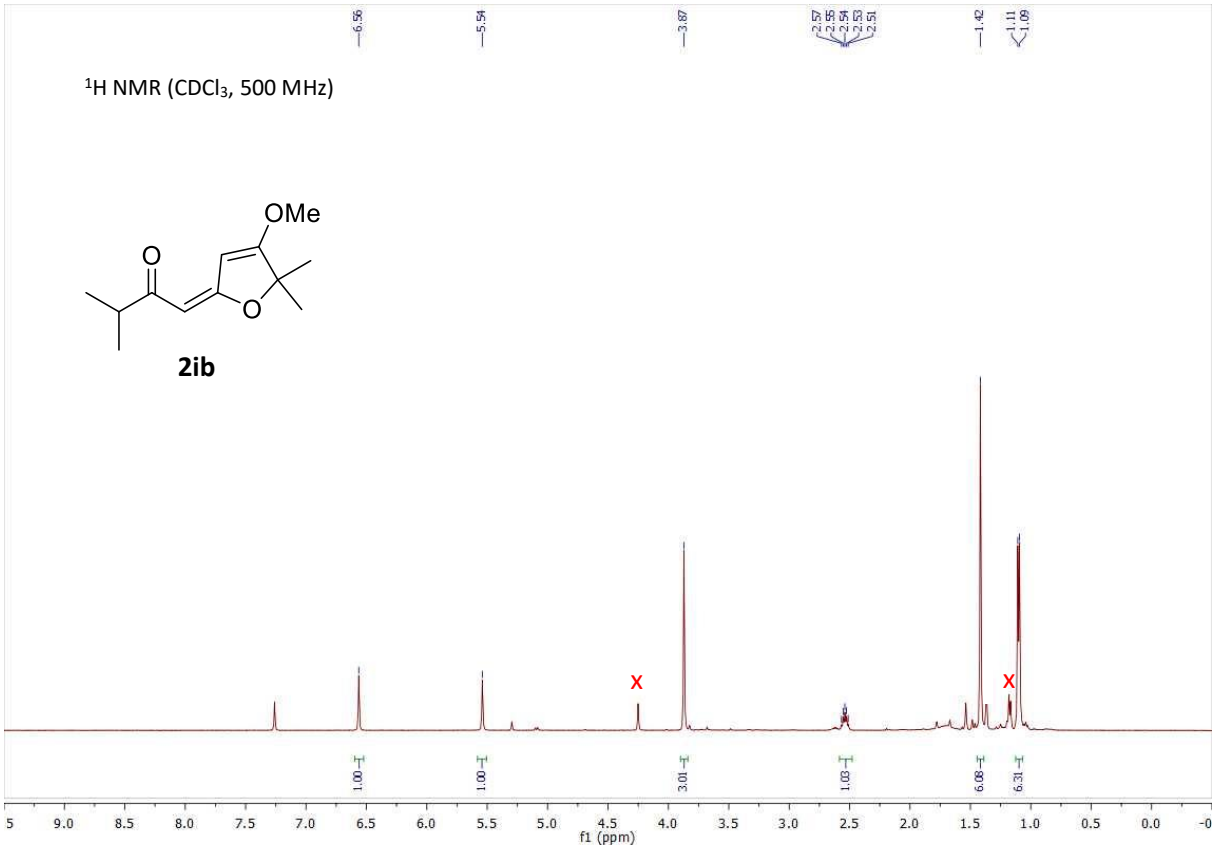
^{13}C NMR ($CDCl_3$, 500 MHz)

2ia'



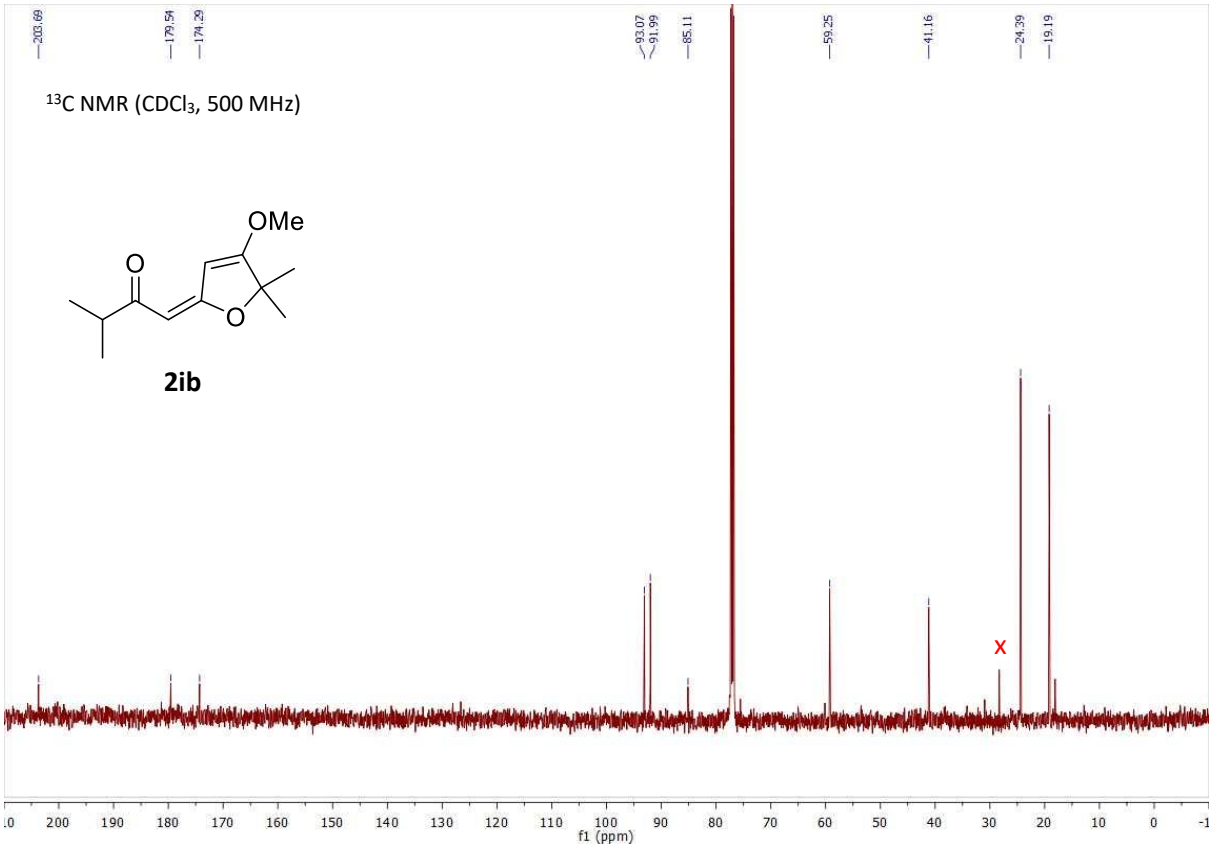
^{1}H NMR ($CDCl_3$, 500 MHz)

2ib



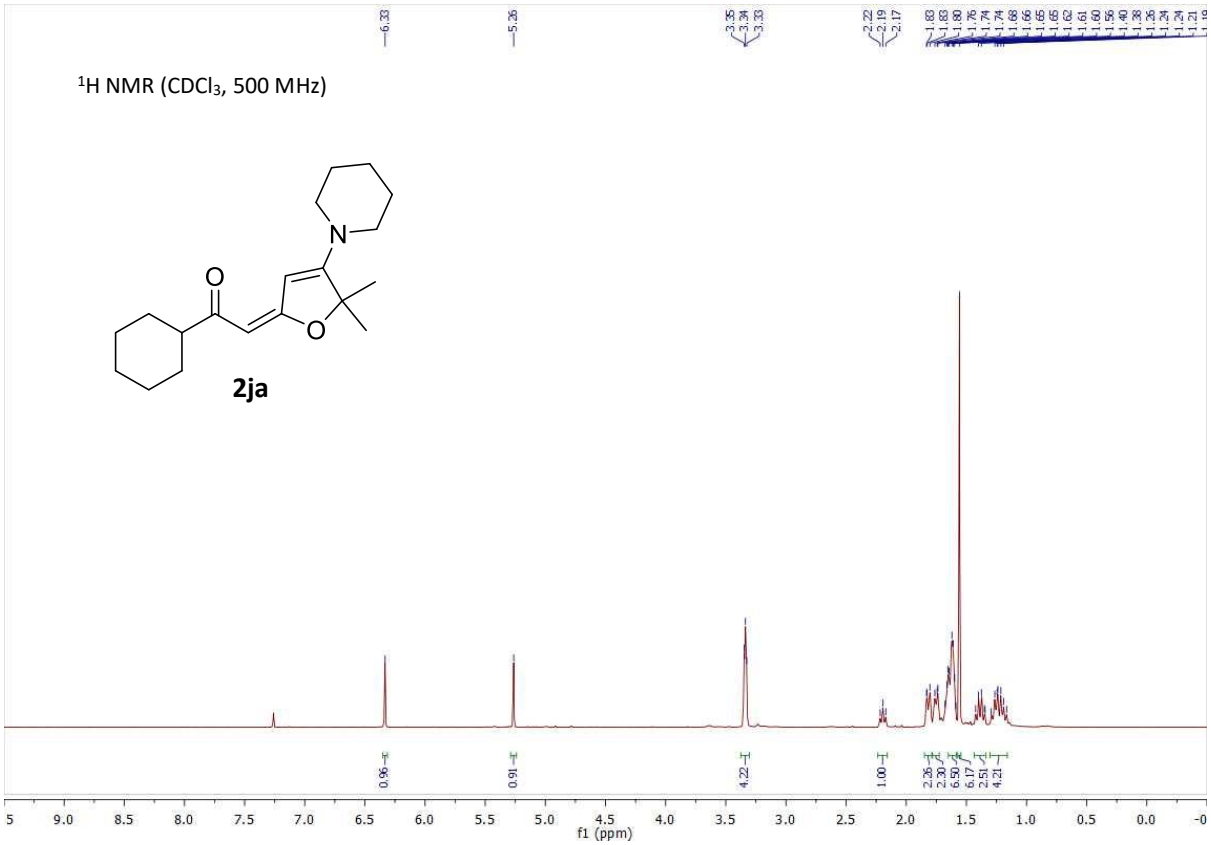
^{13}C NMR ($CDCl_3$, 500 MHz)

2ib



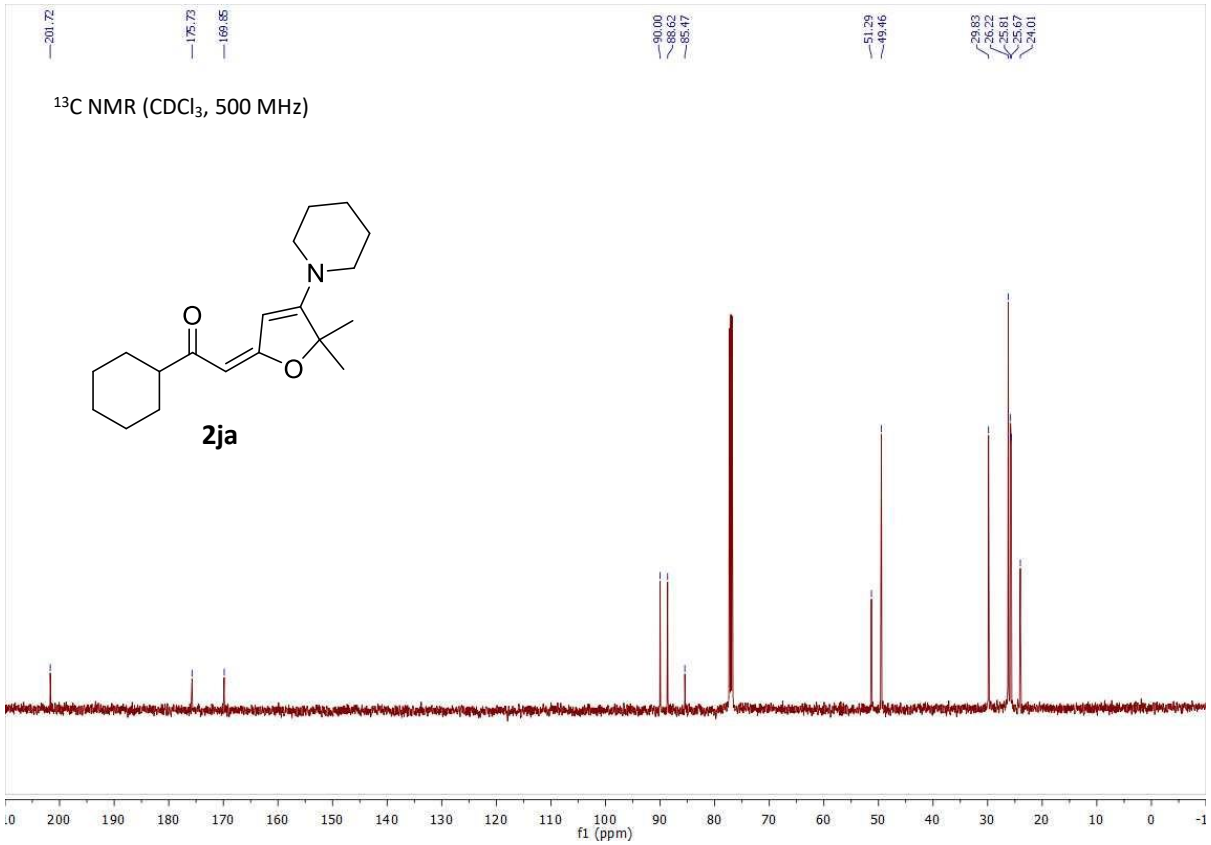
^{1}H NMR ($CDCl_3$, 500 MHz)

2ja



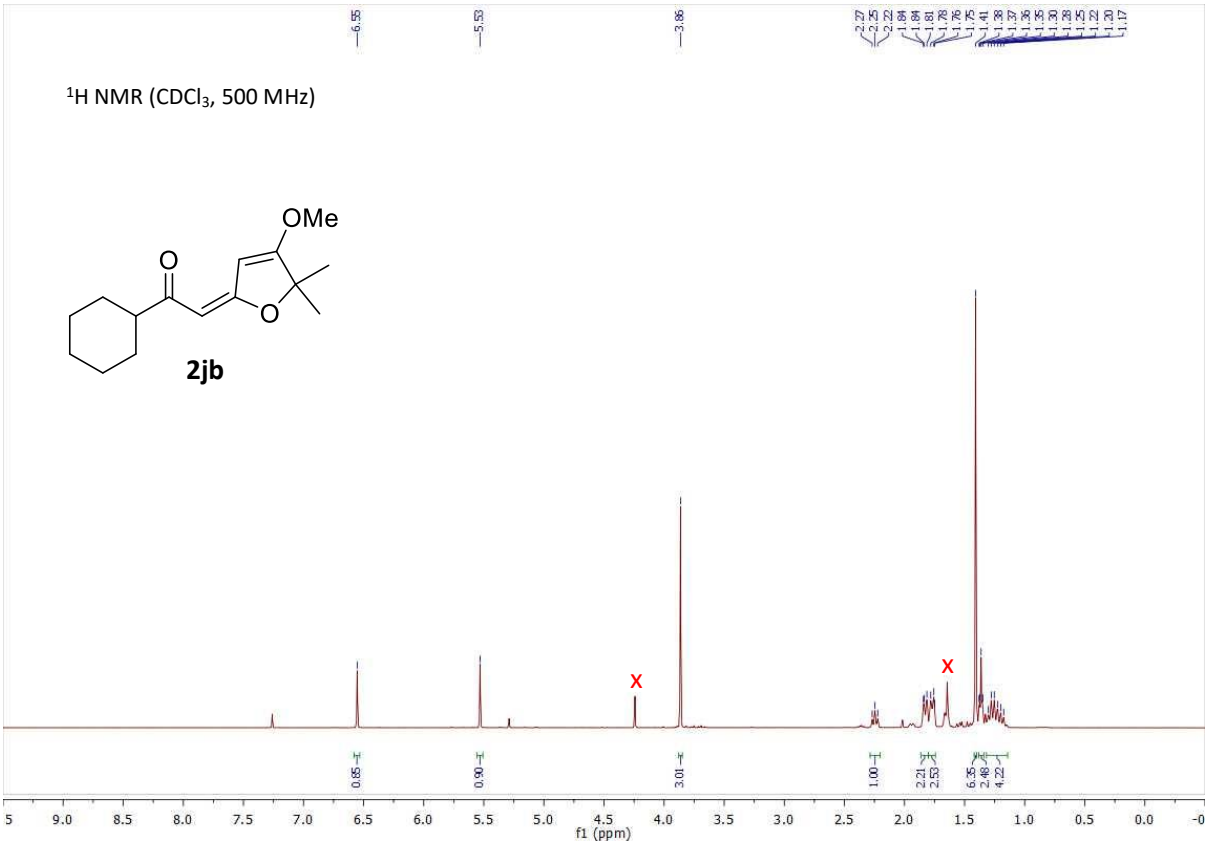
^{13}C NMR ($CDCl_3$, 500 MHz)

2ja



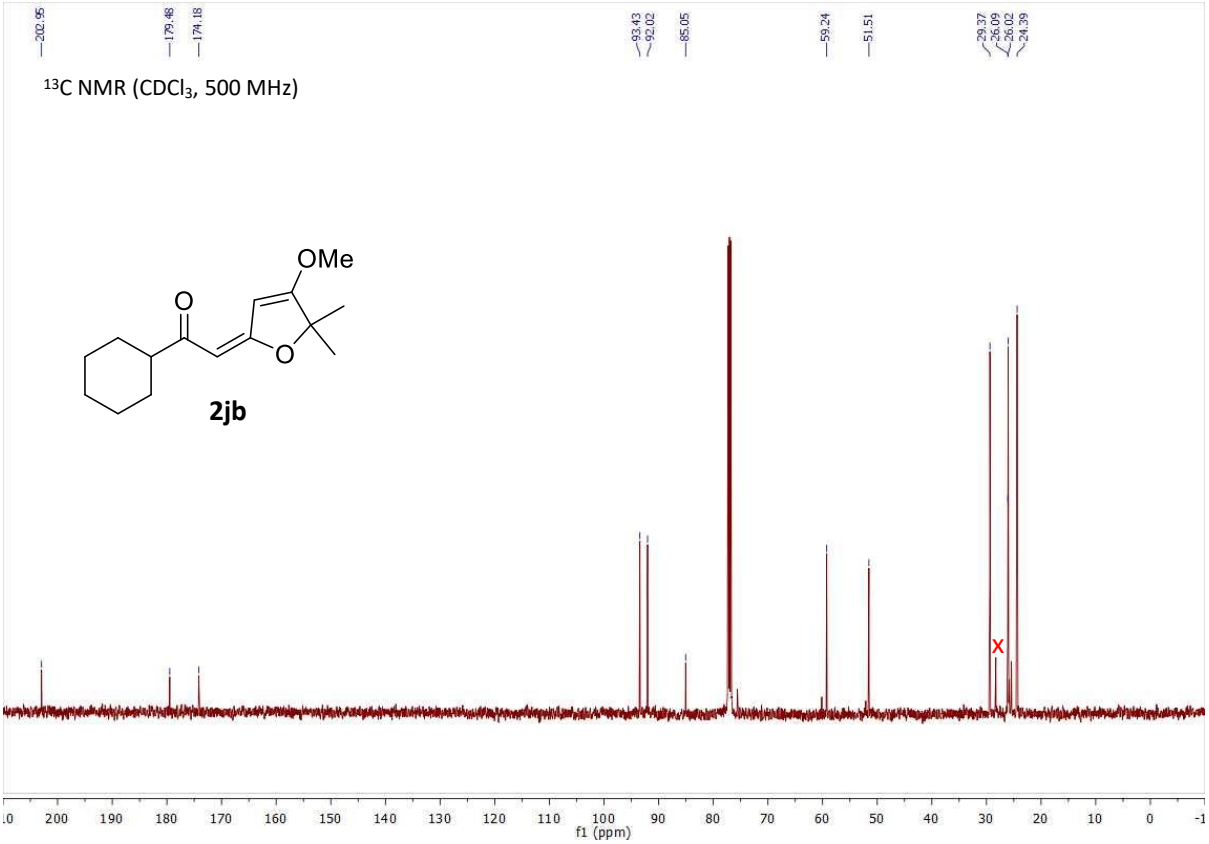
^{1}H NMR ($CDCl_3$, 500 MHz)

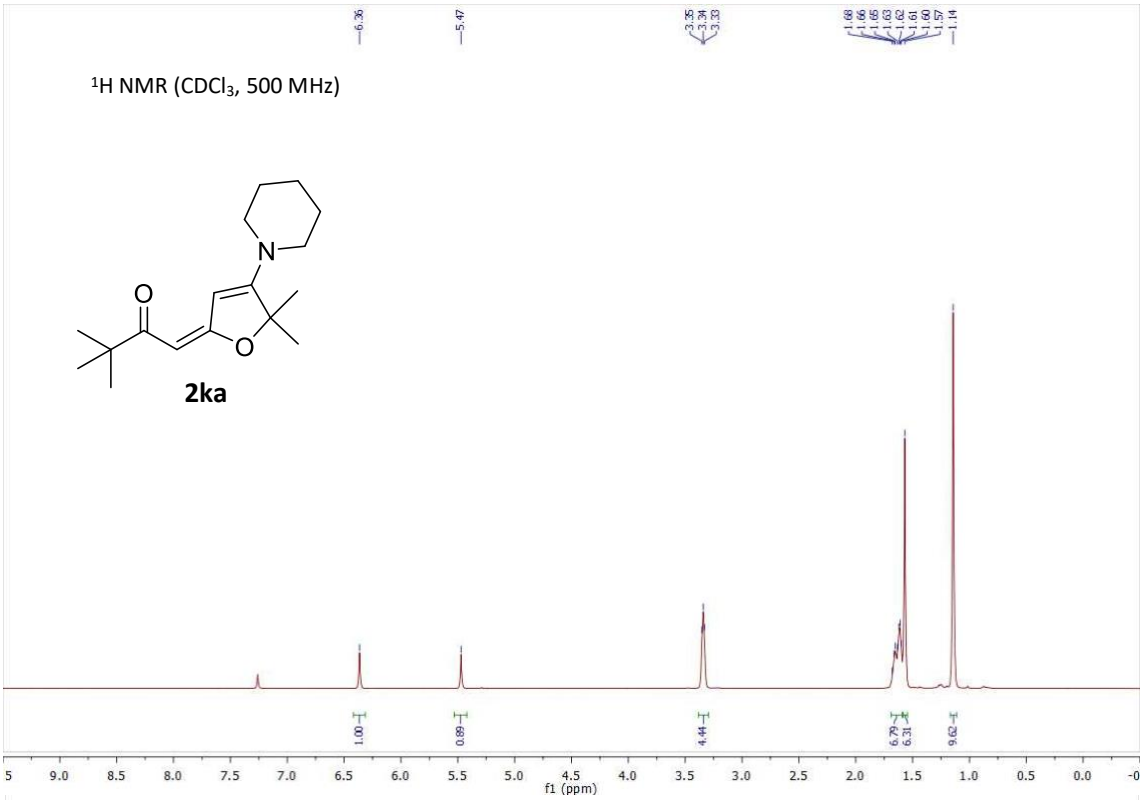
2jb

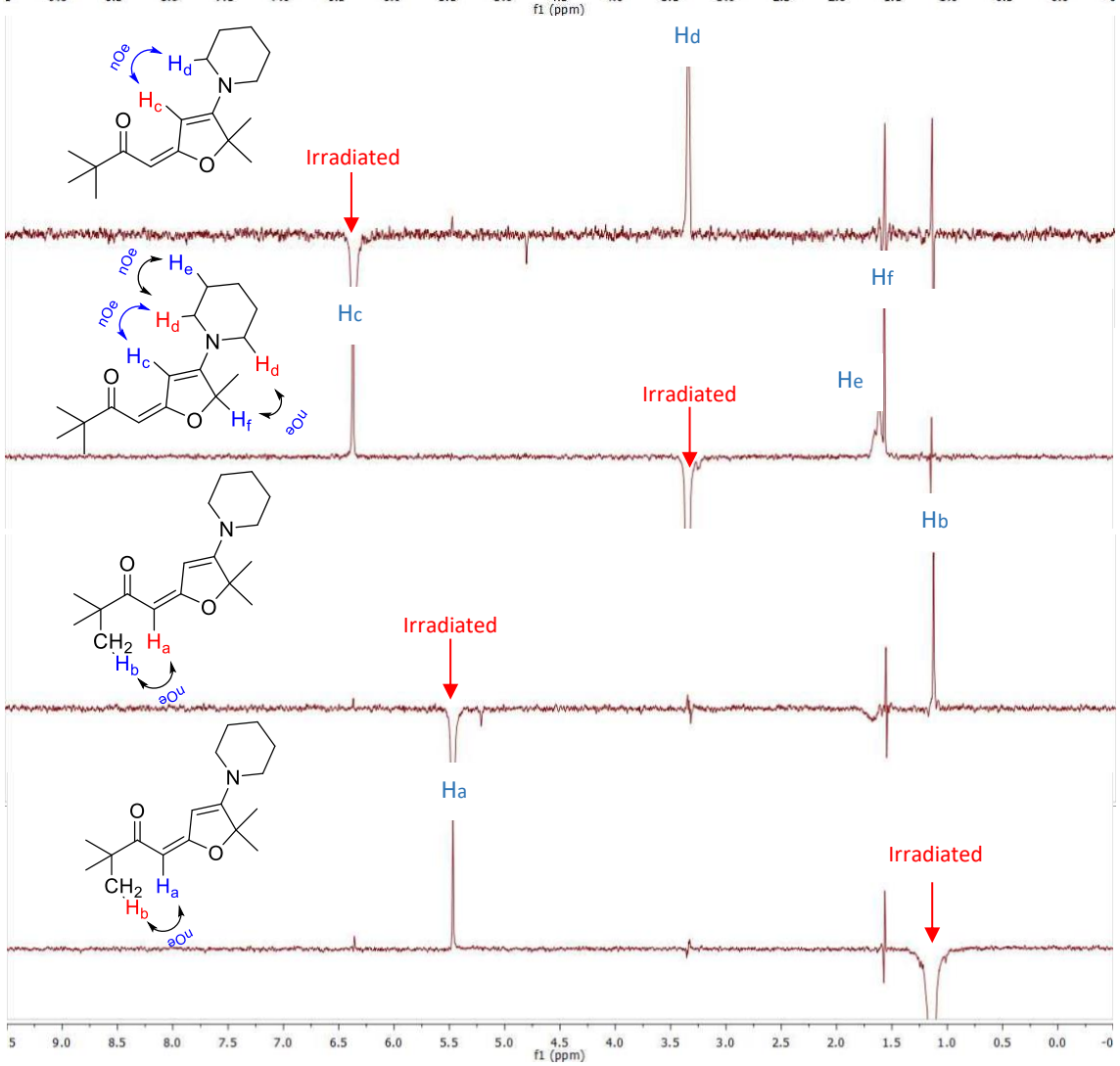


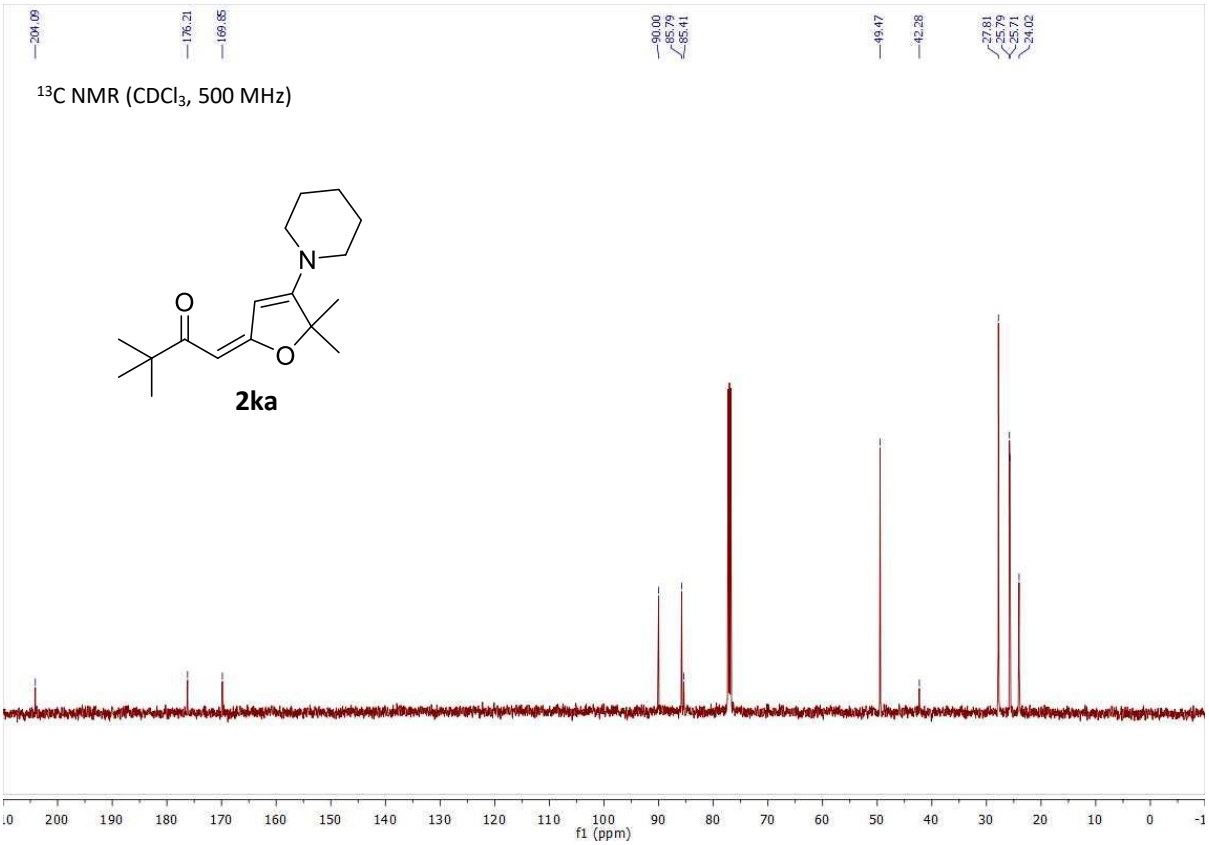
^{13}C NMR ($CDCl_3$, 500 MHz)

2jb



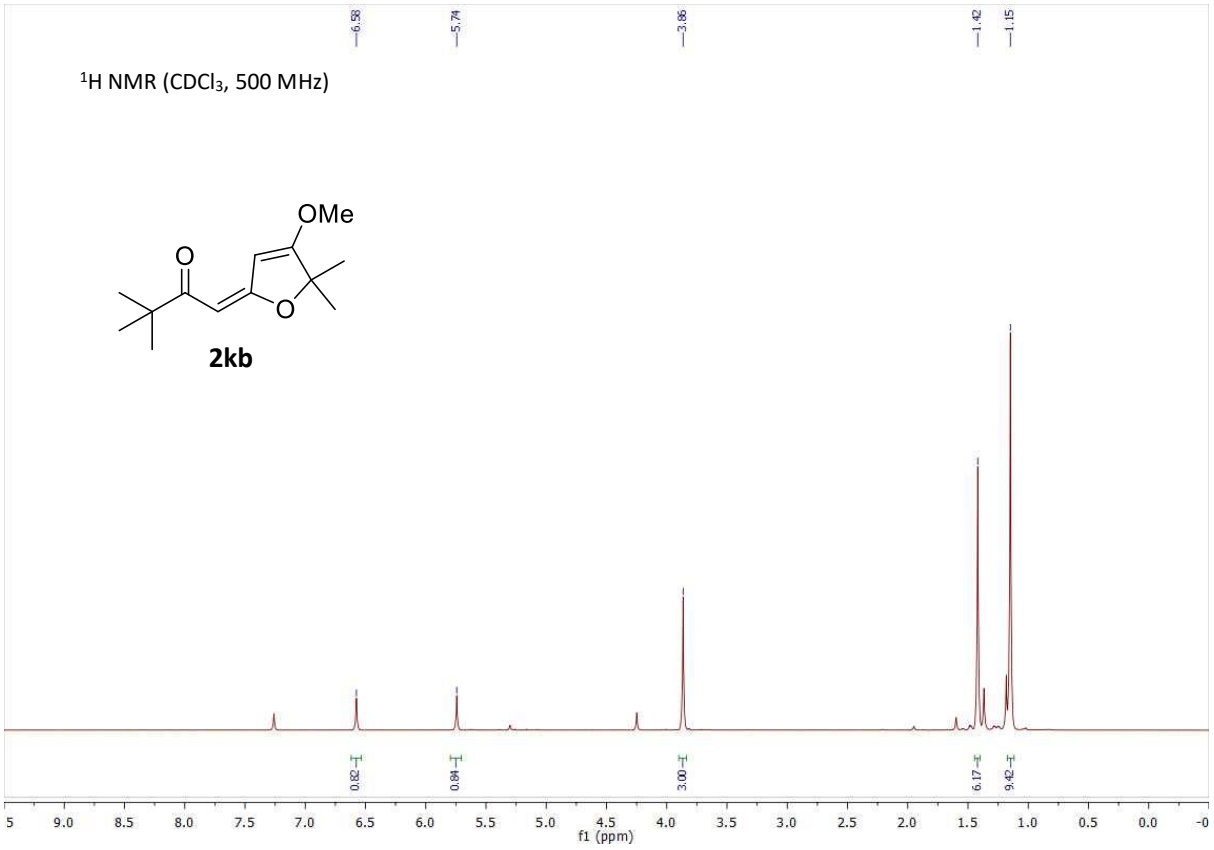

6.36
5.47
3.35
3.34
3.33
1.68
1.66
1.65
1.63
1.62
1.61
1.60
1.57
1.14
1H NMR (CDCl3, 500 MHz)
2ka
1.00
0.89
4.44
6.79
6.31
9.62
f1 (ppm)


nOe
Hd
Hc
Irradiated
Hd
Hf
Hc
He
Hd
Hf
Irradiated
He
Hb
CH2
Ha
Hb
Irradiated
Ha
Irradiated
f1 (ppm)


204.09
176.21
169.85
90.00
85.79
85.41
49.47
42.28
27.81
25.79
25.71
24.02
13C NMR (CDCl3, 500 MHz)
N
O
O
2ka
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

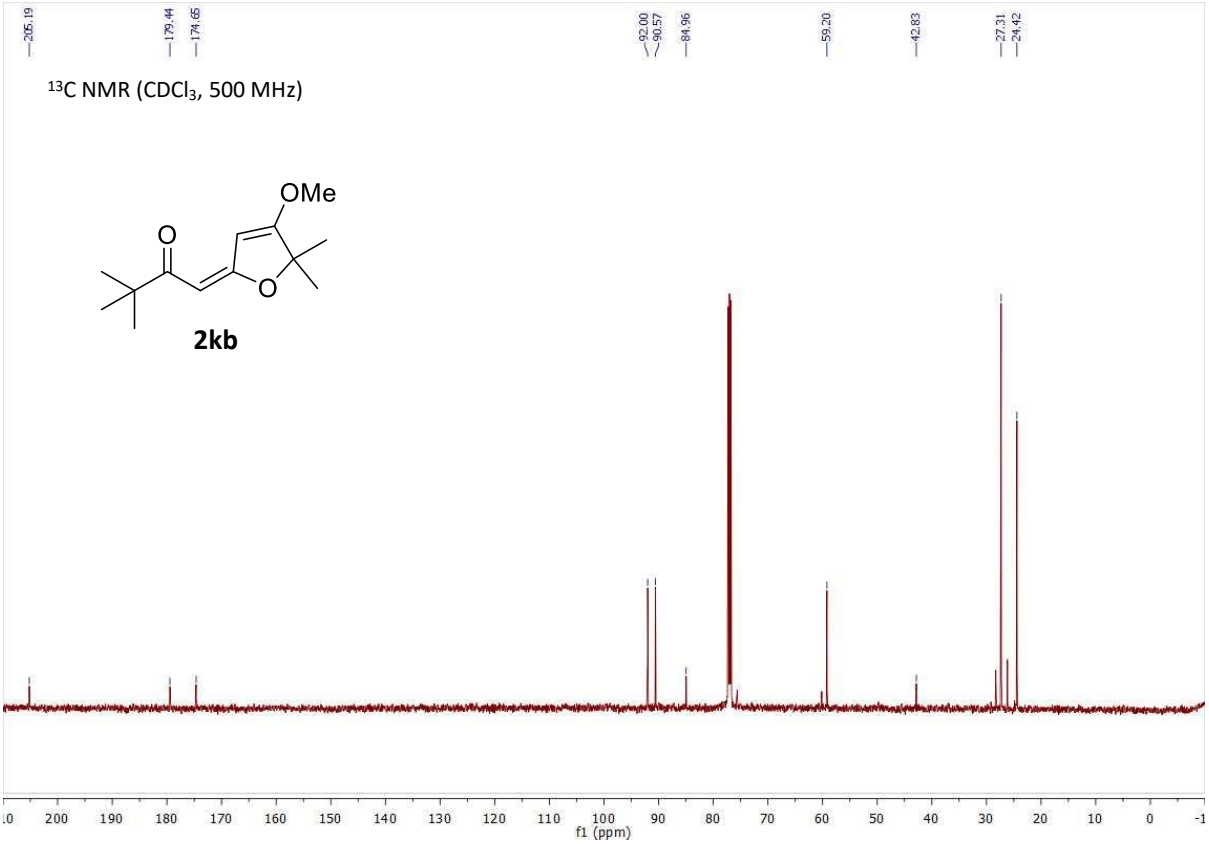
^{1}H NMR ($CDCl_3$, 500 MHz)

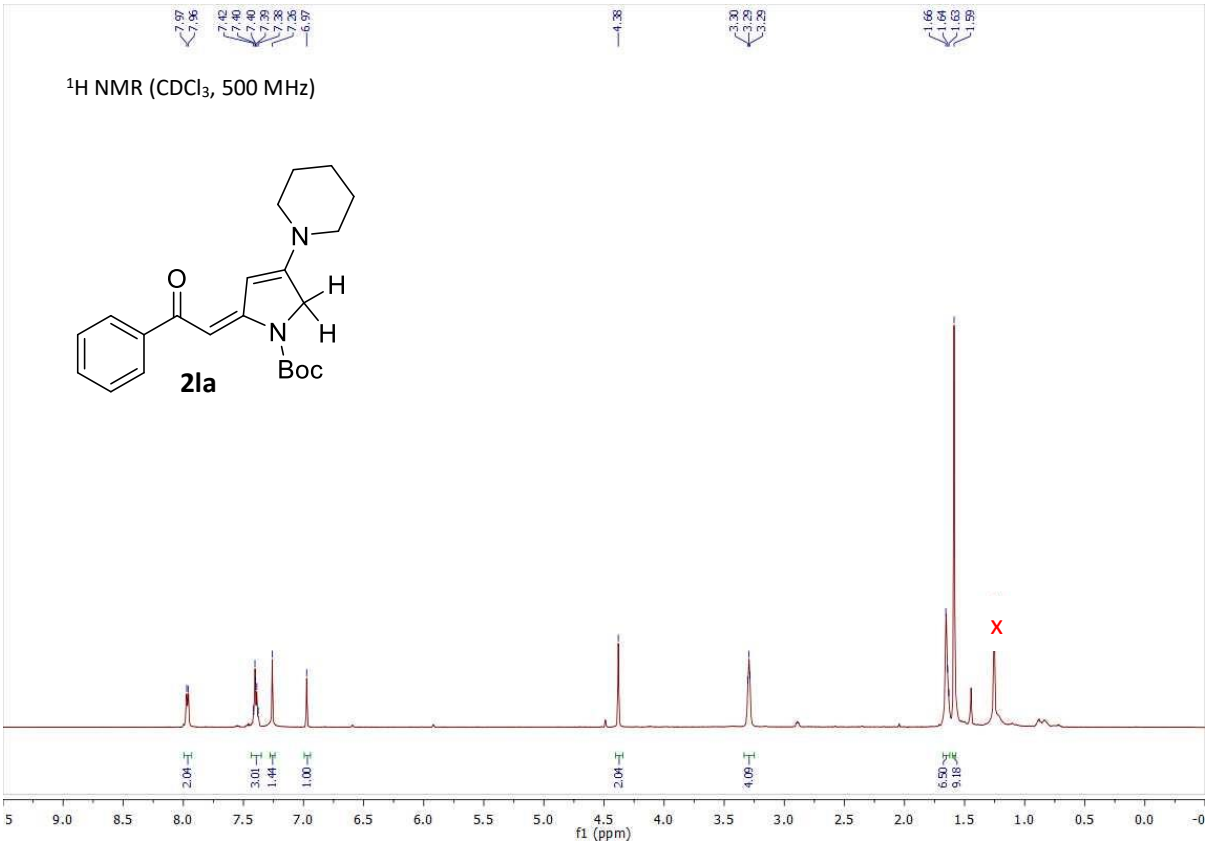
2kb

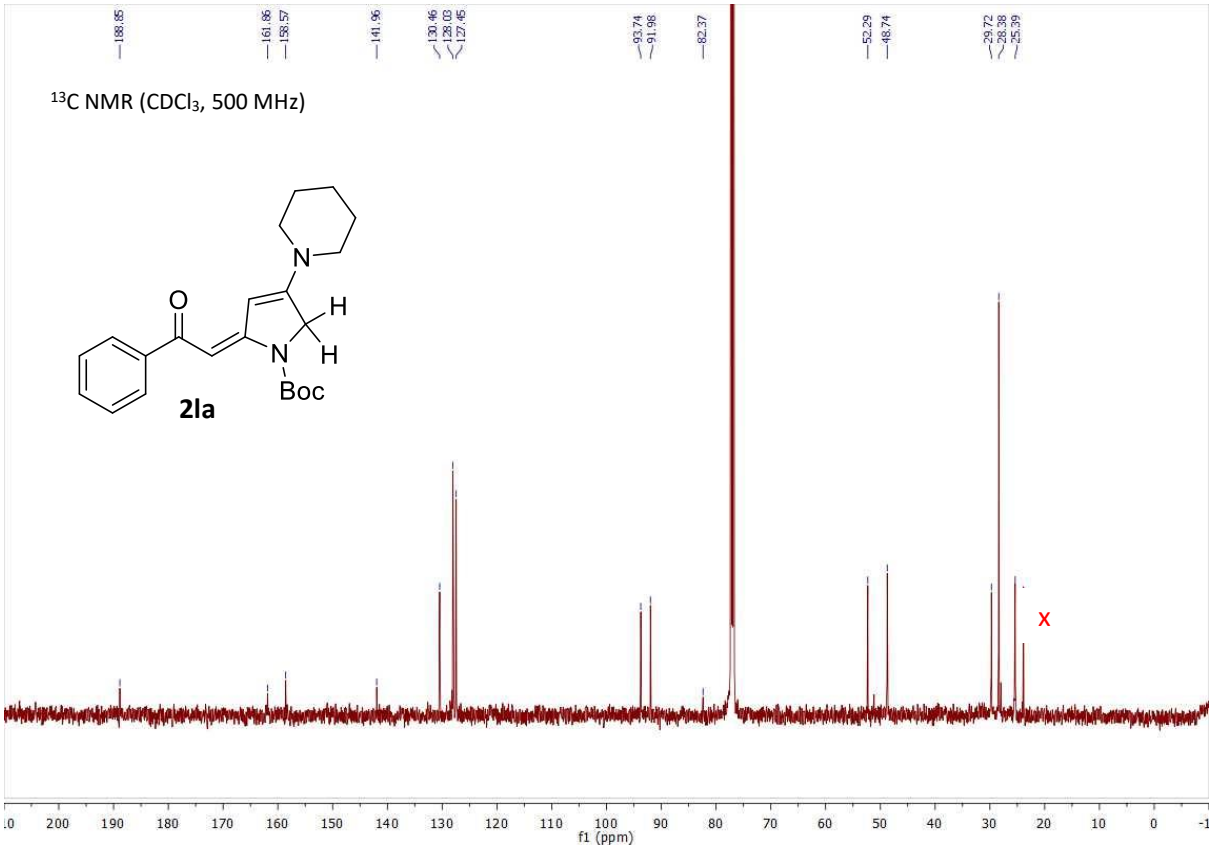


^{13}C NMR ($CDCl_3$, 500 MHz)

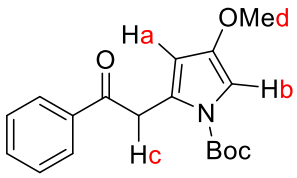
2kb



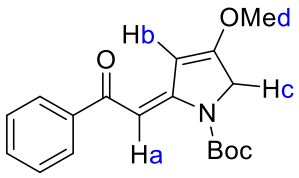

7.97
7.96
7.42
7.40
7.40
7.39
7.38
7.26
6.97
4.38
3.30
3.29
3.29
1.66
1.64
1.63
1.59
^{1}H NMR ($CDCl_3$, 500 MHz)
O
N
H
N
H
Boc
2la
X
2.04
3.01
1.44
1.00
2.04
4.09
6.50
9.18
f1 (ppm)


188.85
161.86
158.57
141.96
130.46
128.03
127.45
93.74
91.98
82.37
52.29
48.74
29.72
28.38
25.39
^{13}C NMR ($CDCl_3$, 500 MHz)
O
N
H
N
H
Boc
2la
X
f1 (ppm)

^{1}H NMR ($CDCl_3$, 500 MHz)

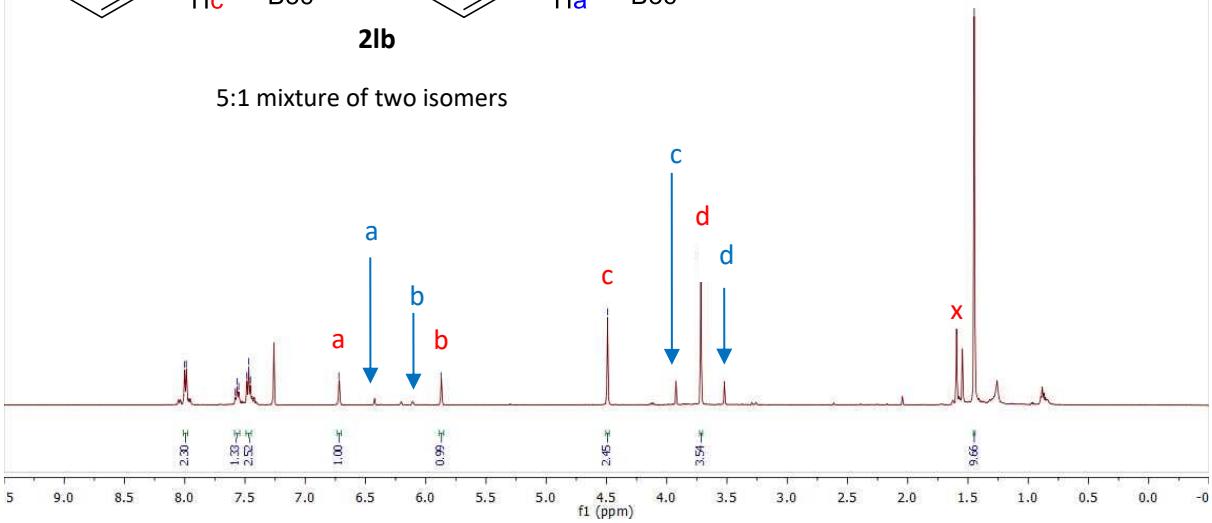


+



2lb

5:1 mixture of two isomers

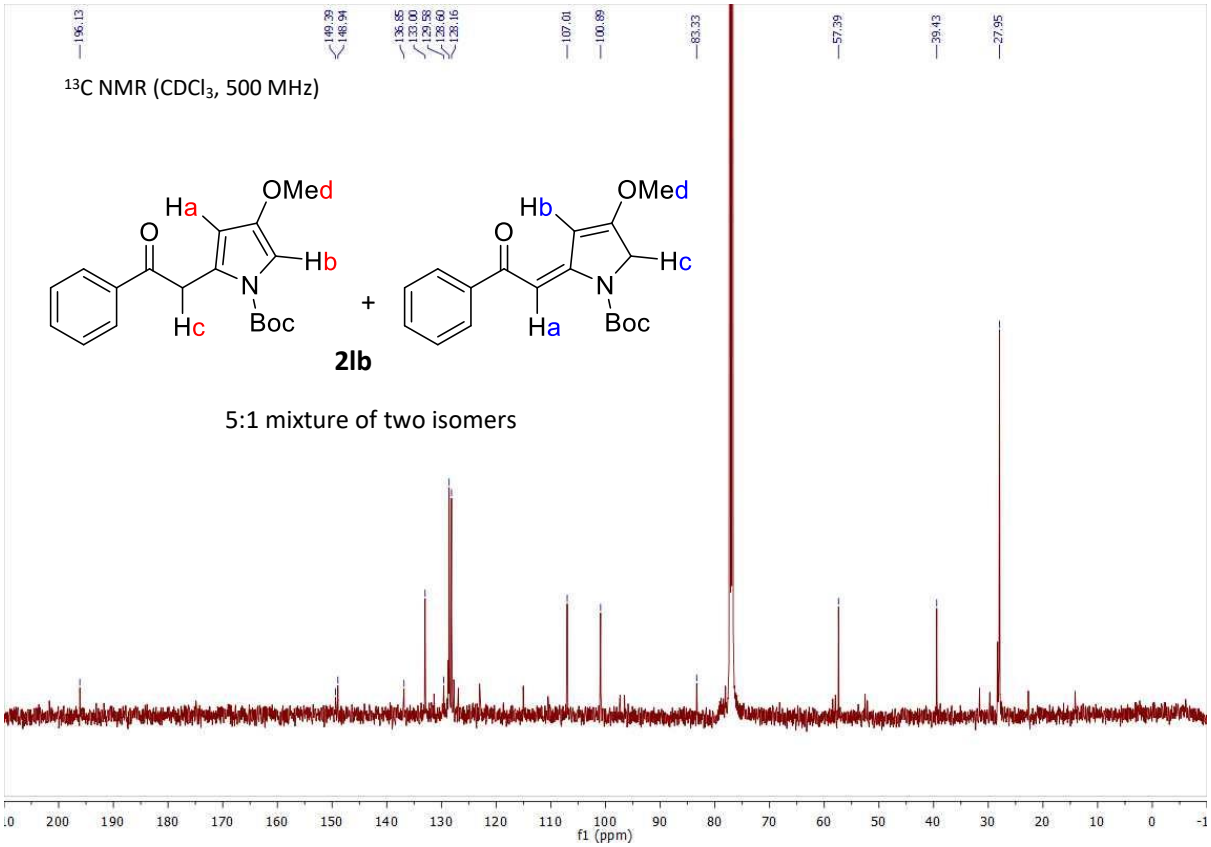


^{13}C NMR ($CDCl_3$, 500 MHz)

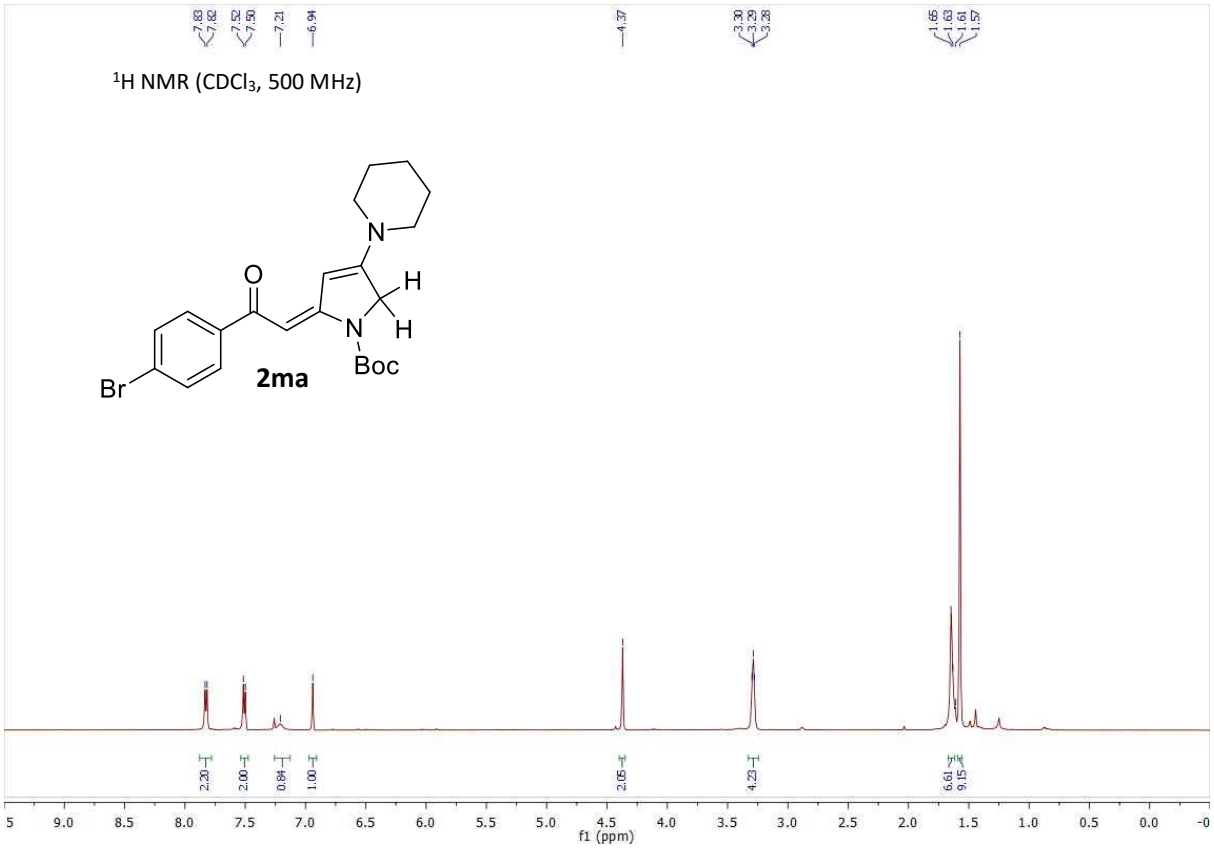
+

2lb

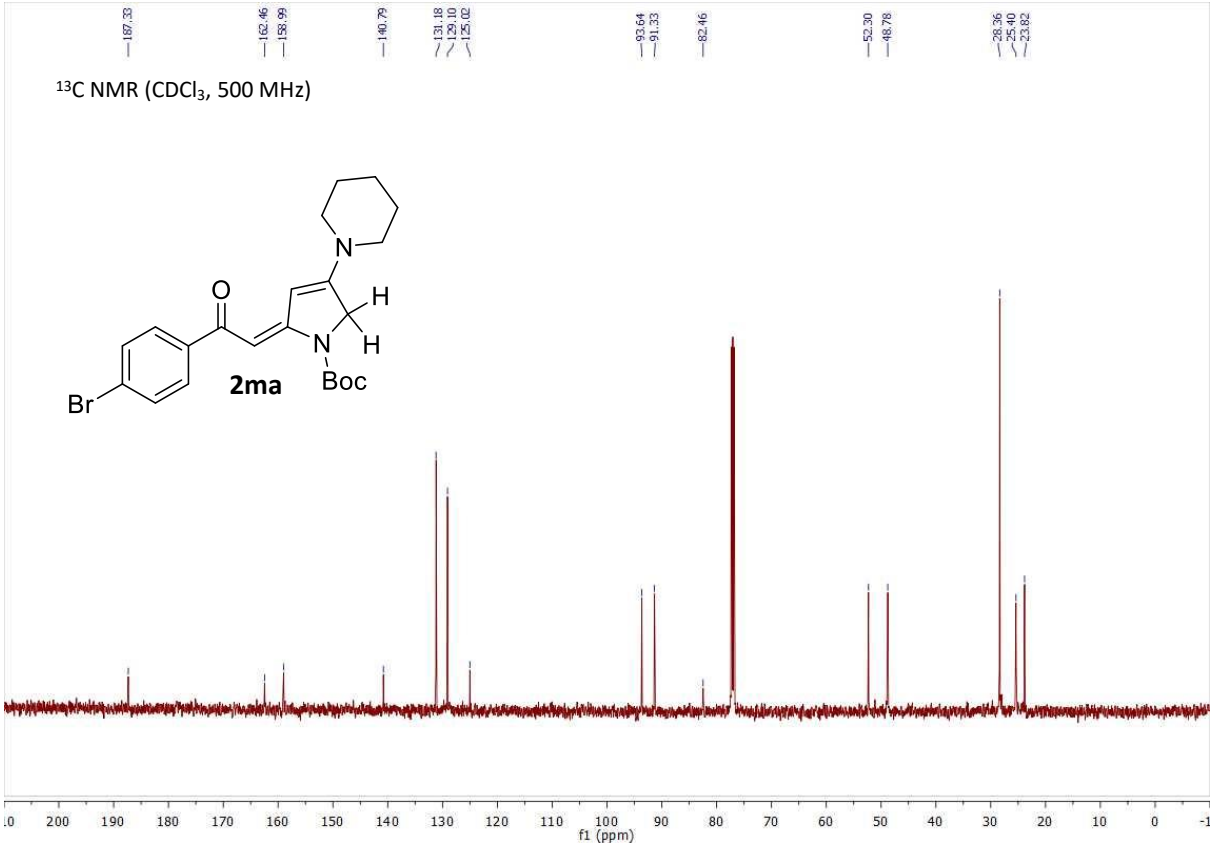
5:1 mixture of two isomers

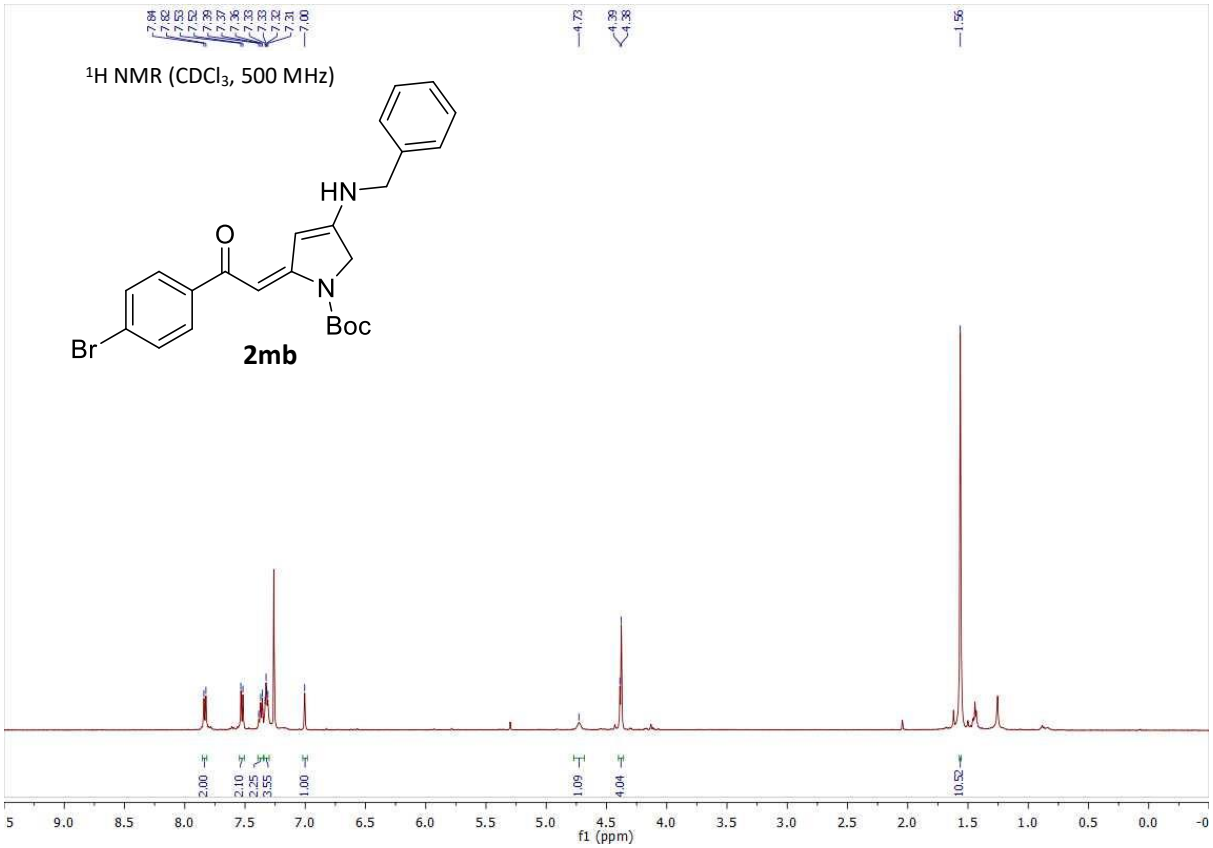


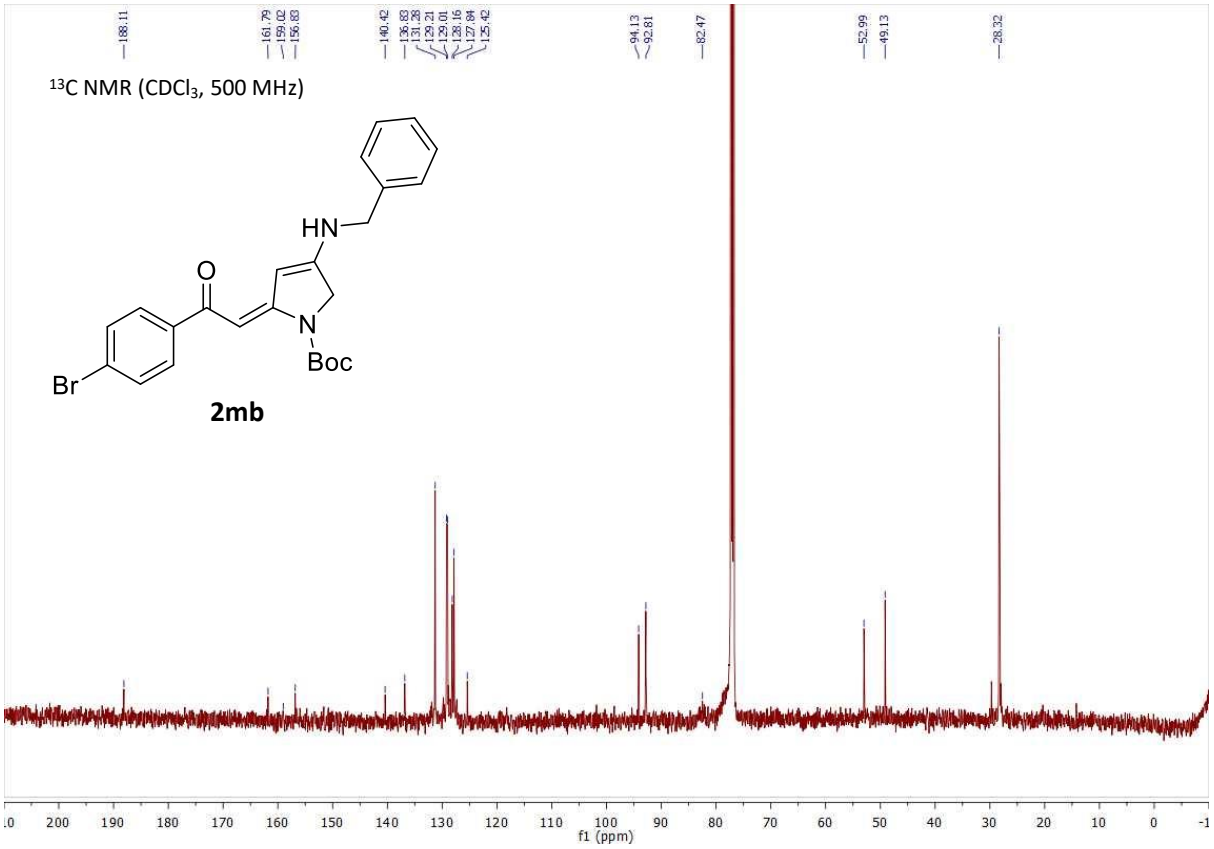
^{1}H NMR ($CDCl_3$, 500 MHz)

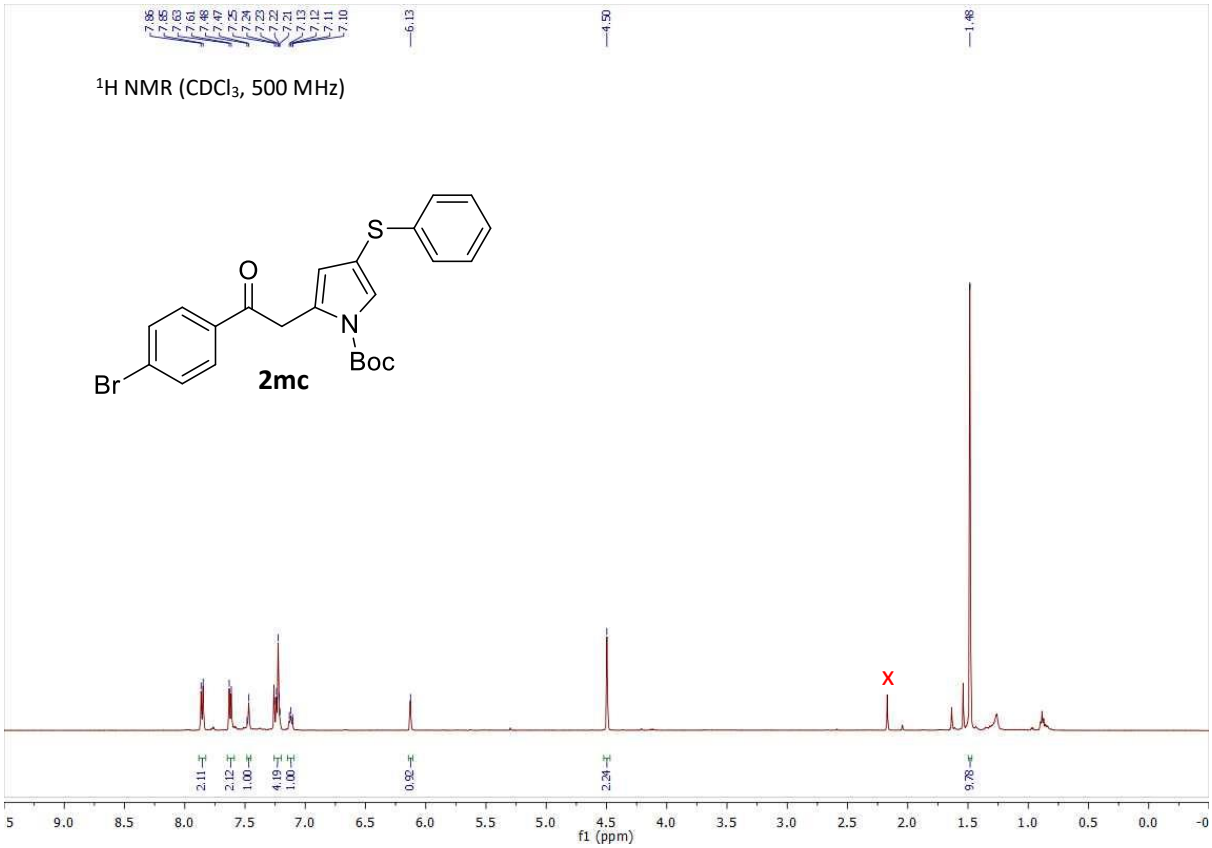


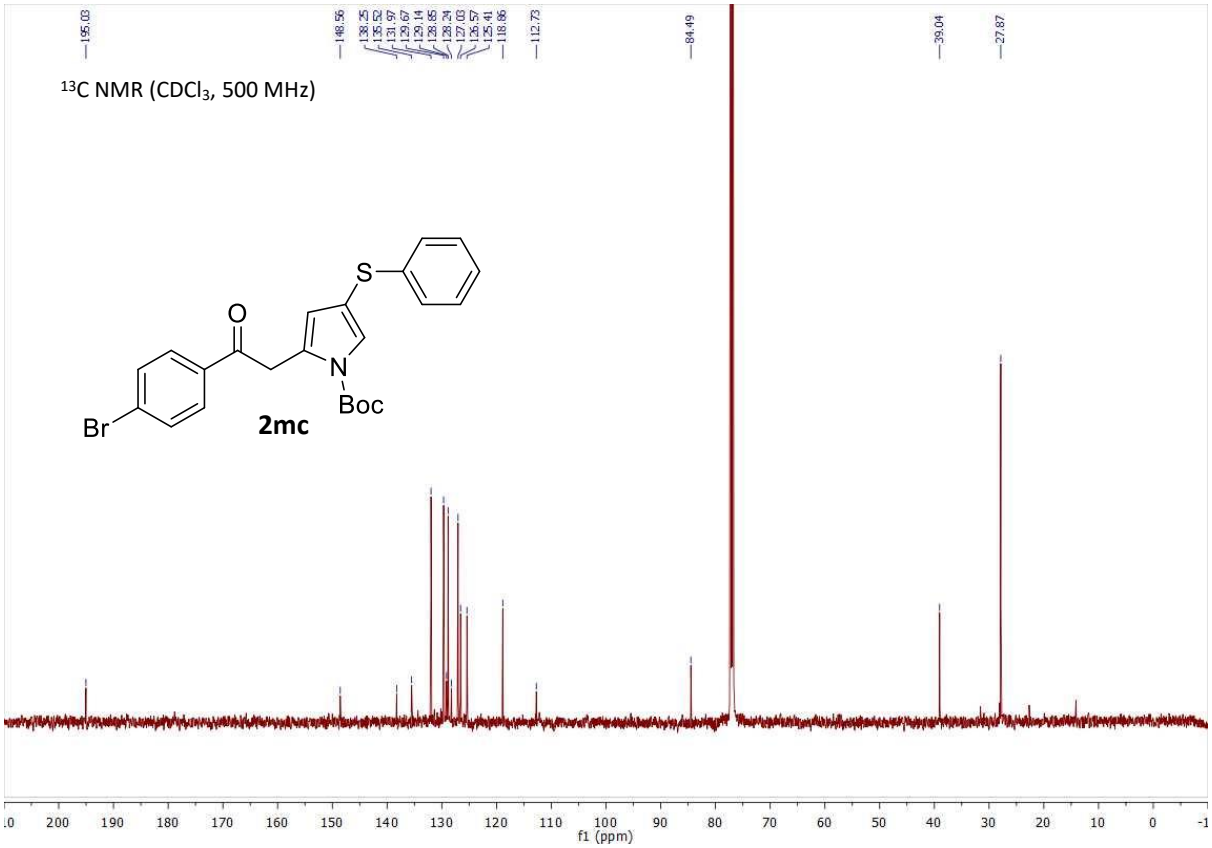
^{13}C NMR ($CDCl_3$, 500 MHz)

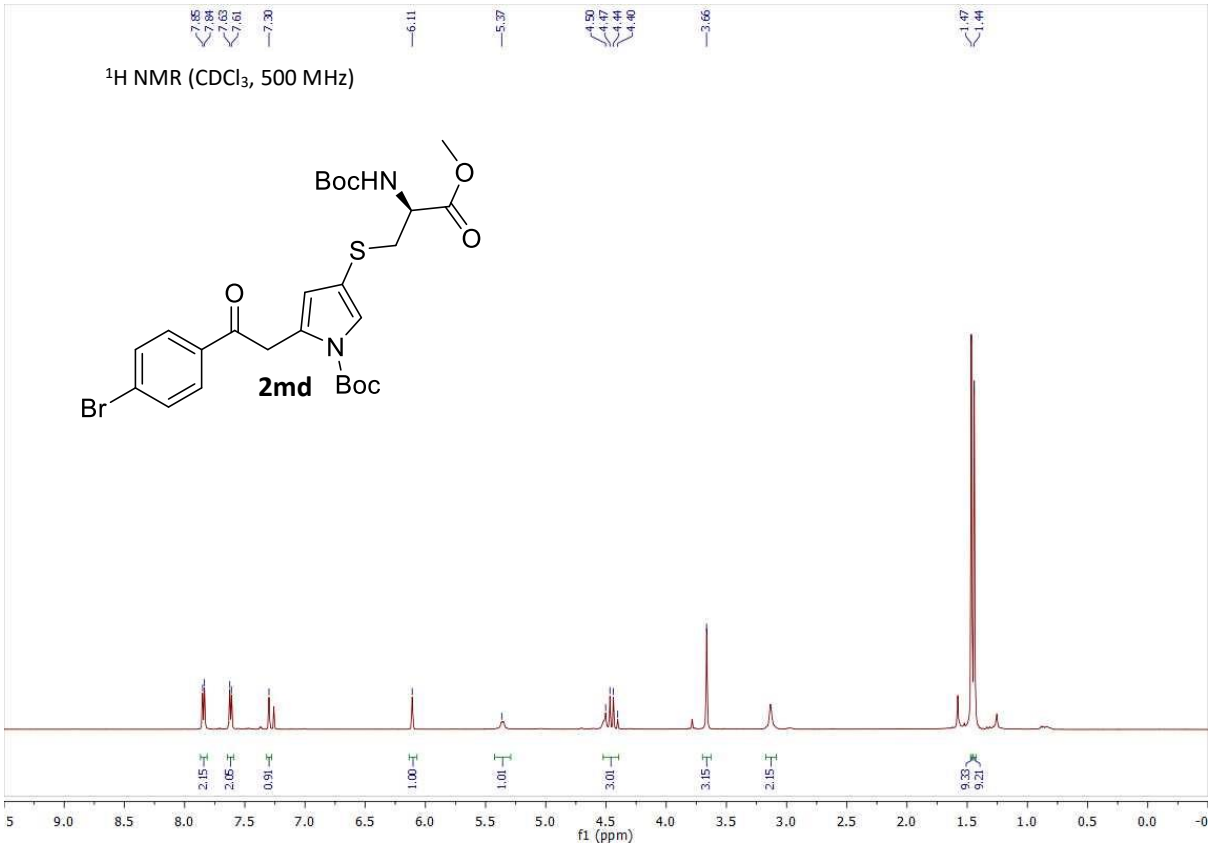


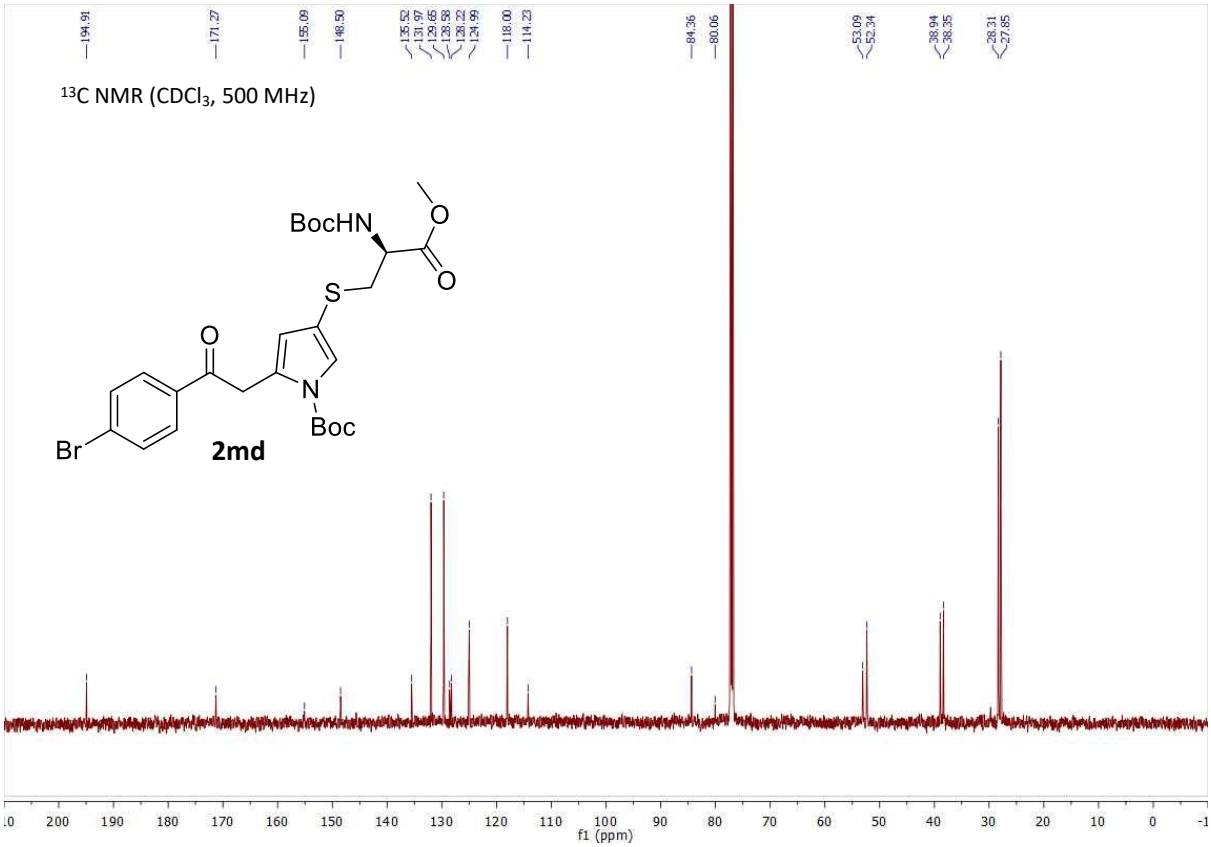

7.84
7.82
7.53
7.52
7.39
7.37
7.36
7.33
7.32
7.31
7.00
4.73
4.39
4.38
1.56
^{1}H NMR ($CDCl_3$, 500 MHz)
HN
O
N
Boc
Br
2mb
2.00
2.10
2.25
3.55
1.00
1.09
4.04
10.52
f1 (ppm)

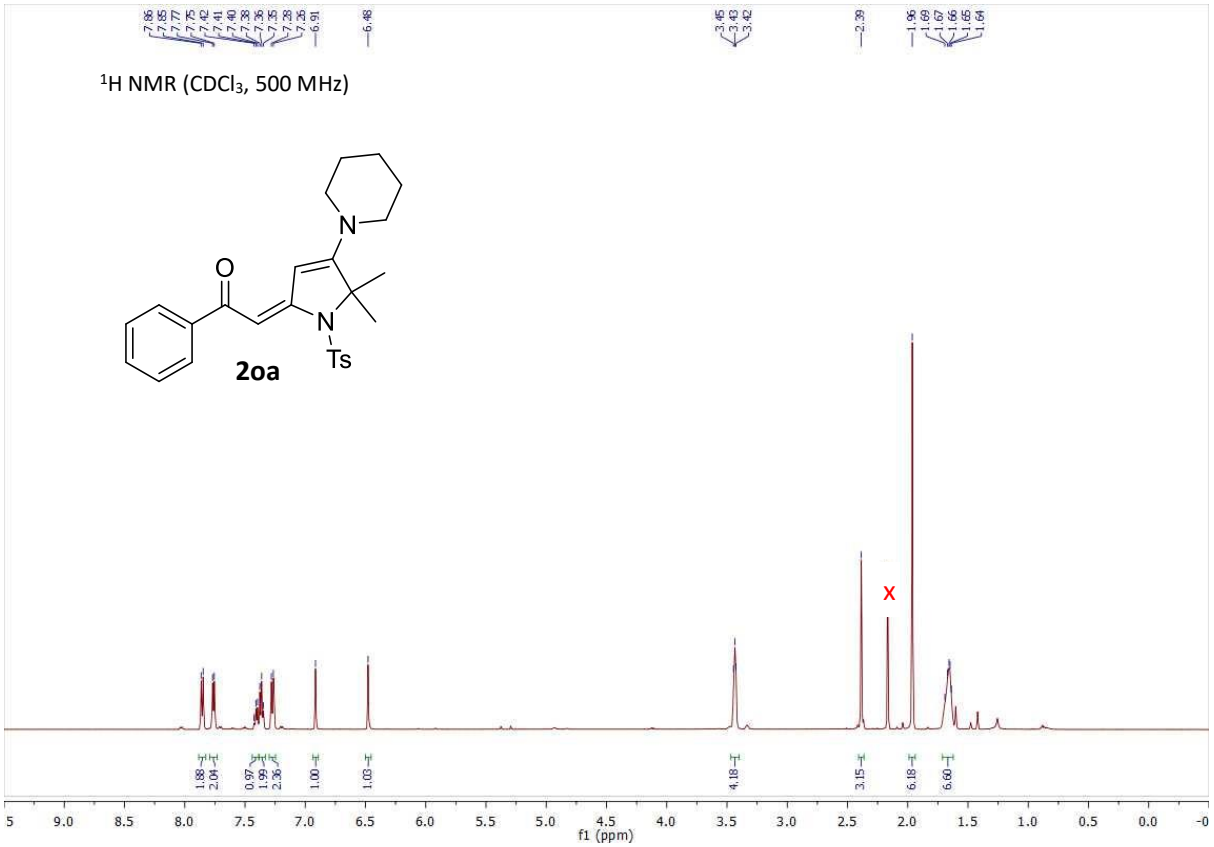

188.11
161.79
159.02
156.83
140.42
136.83
131.26
129.21
129.01
128.16
127.84
125.42
94.13
92.81
82.47
52.99
49.13
28.32
^{13}C NMR ($CDCl_3$, 500 MHz)
HN
O
N
Boc
Br
2mb
f1 (ppm)

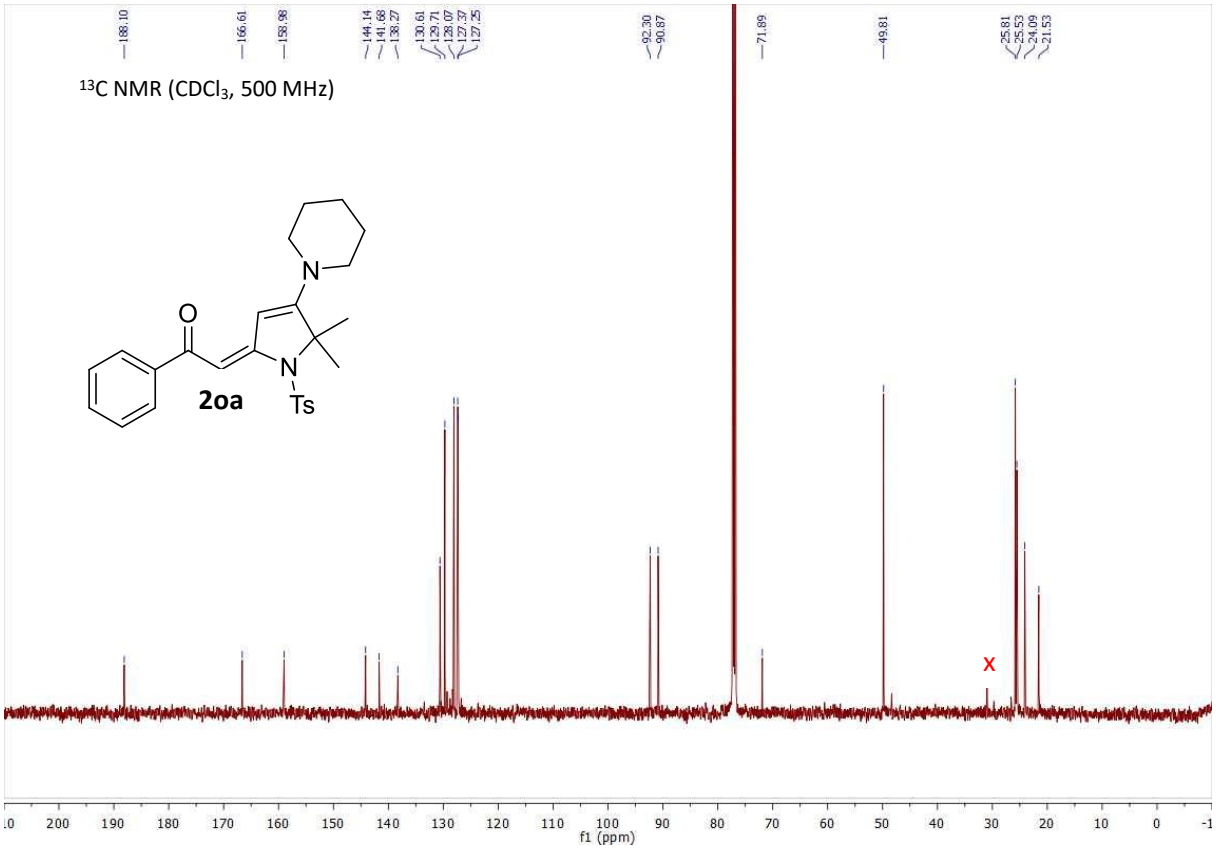

1H NMR (CDCl3, 500 MHz)
S
O
N
Boc
Br
2mc
X
f1 (ppm)


13C NMR (CDCl3, 500 MHz)
S
O
N
Boc
Br
2mc
f1 (ppm)

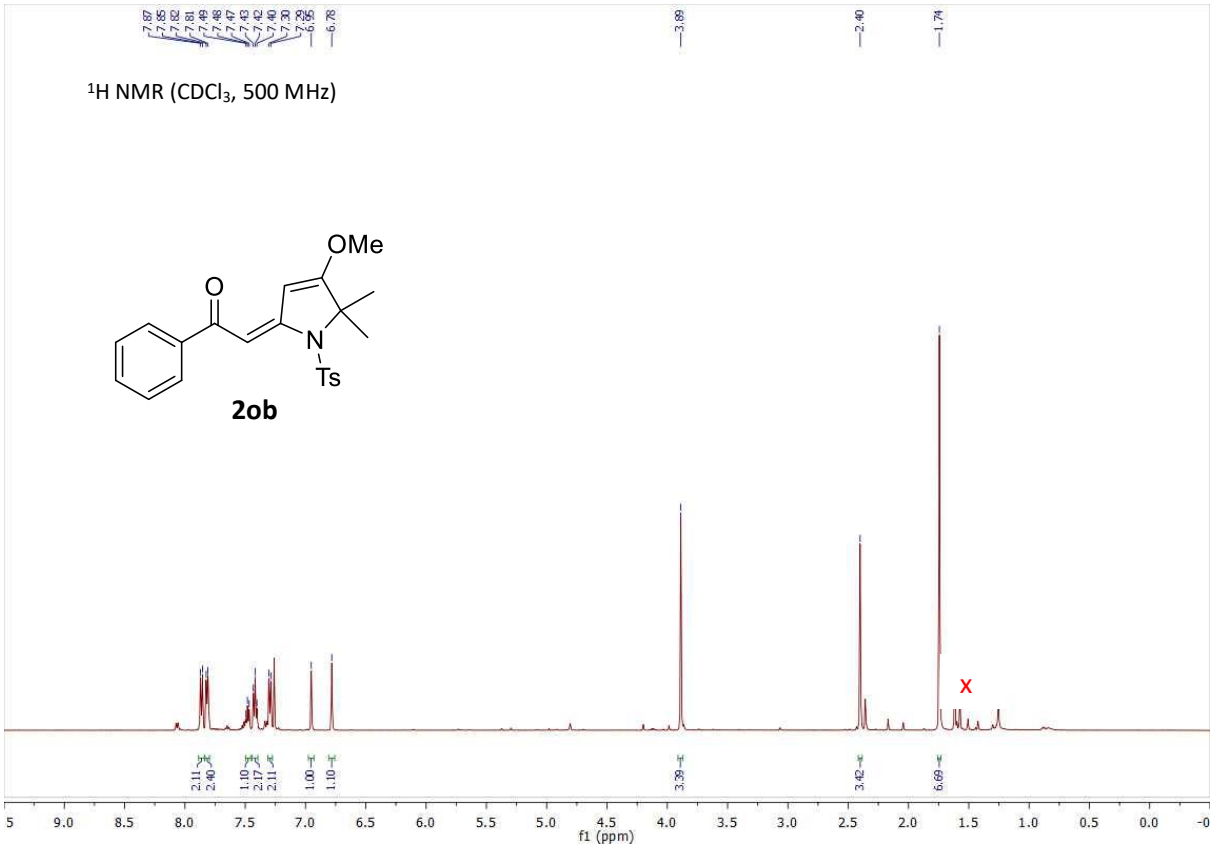

7.85
7.84
7.63
7.61
7.30
6.11
5.37
4.50
4.47
4.44
4.40
3.66
1.47
1.44
^{1}H NMR ($CDCl_3$, 500 MHz)
BocHN
O
O
S
O
N
Boc
Br
2md
2.15
2.05
0.91
1.00
1.01
3.01
3.15
2.15
9.33
9.21
f1 (ppm)


194.91
171.27
155.09
148.50
135.52
131.97
129.65
128.58
128.22
124.99
118.00
114.23
84.36
80.06
53.09
52.34
38.94
38.35
28.31
27.85
^{13}C NMR ($CDCl_3$, 500 MHz)
BocHN
O
O
S
O
N
Boc
Br
2md
f1 (ppm)

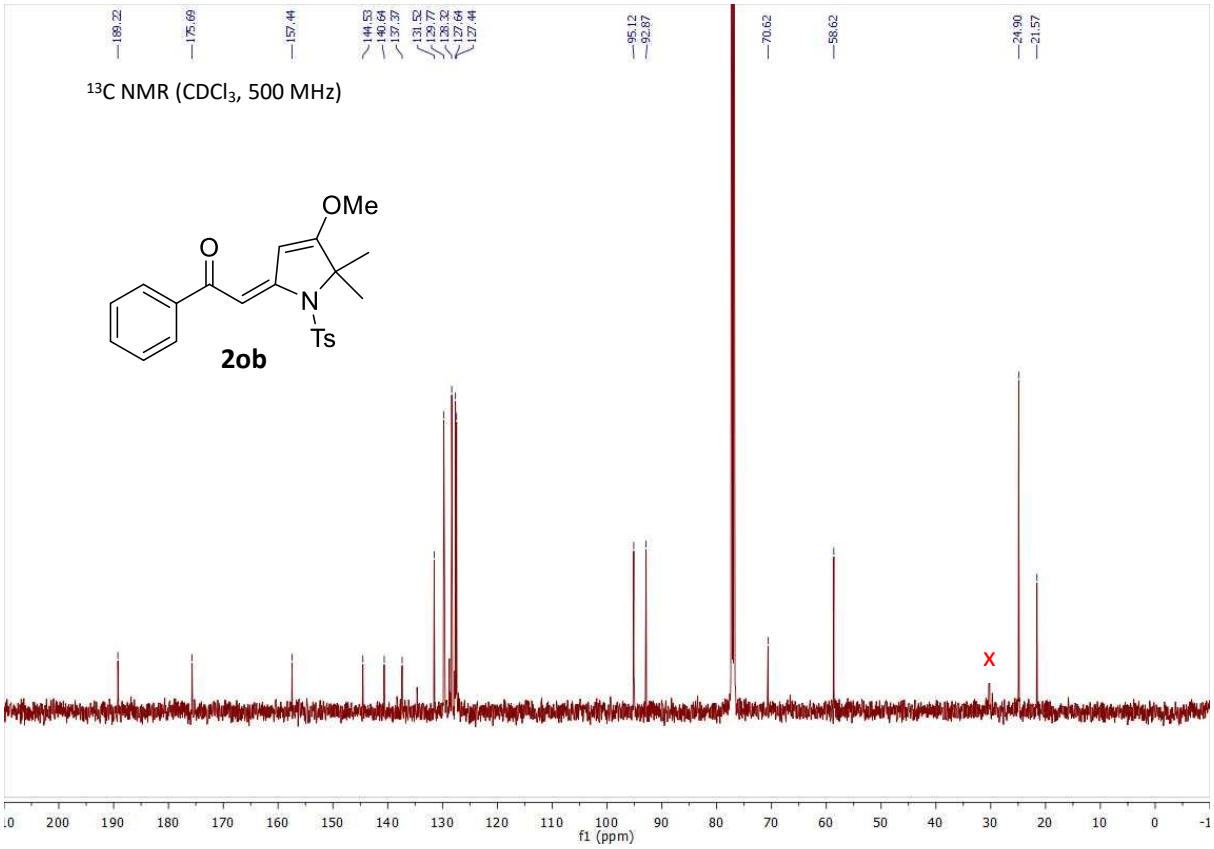

7.86
7.85
7.77
7.75
7.42
7.41
7.40
7.38
7.36
7.35
7.28
7.26
6.91
6.48
3.45
3.43
3.42
2.39
1.96
1.69
1.67
1.66
1.65
1.64
1H NMR (CDCl3, 500 MHz)
N
O
N
Ts
2oa
X
1.88
2.04
0.97
1.99
2.36
1.00
1.03
4.18
3.15
6.18
6.60
f1 (ppm)

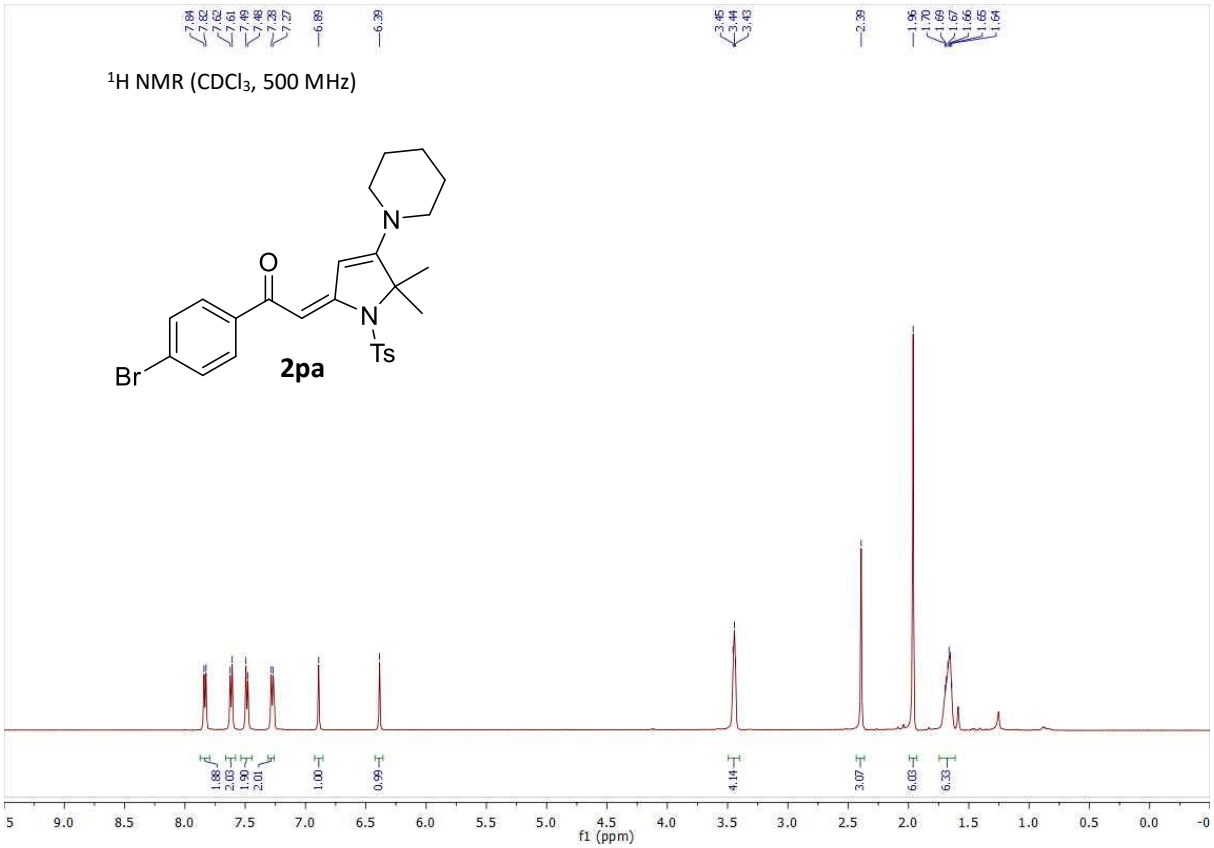

188.10
166.61
158.98
144.14
141.68
138.27
130.61
129.71
128.07
127.37
127.25
92.30
90.87
71.89
49.81
25.81
25.53
24.09
21.53
13C NMR (CDCl3, 500 MHz)
N
O
N
Ts
2oa
X
f1 (ppm)

^{1}H NMR ($CDCl_3$, 500 MHz)



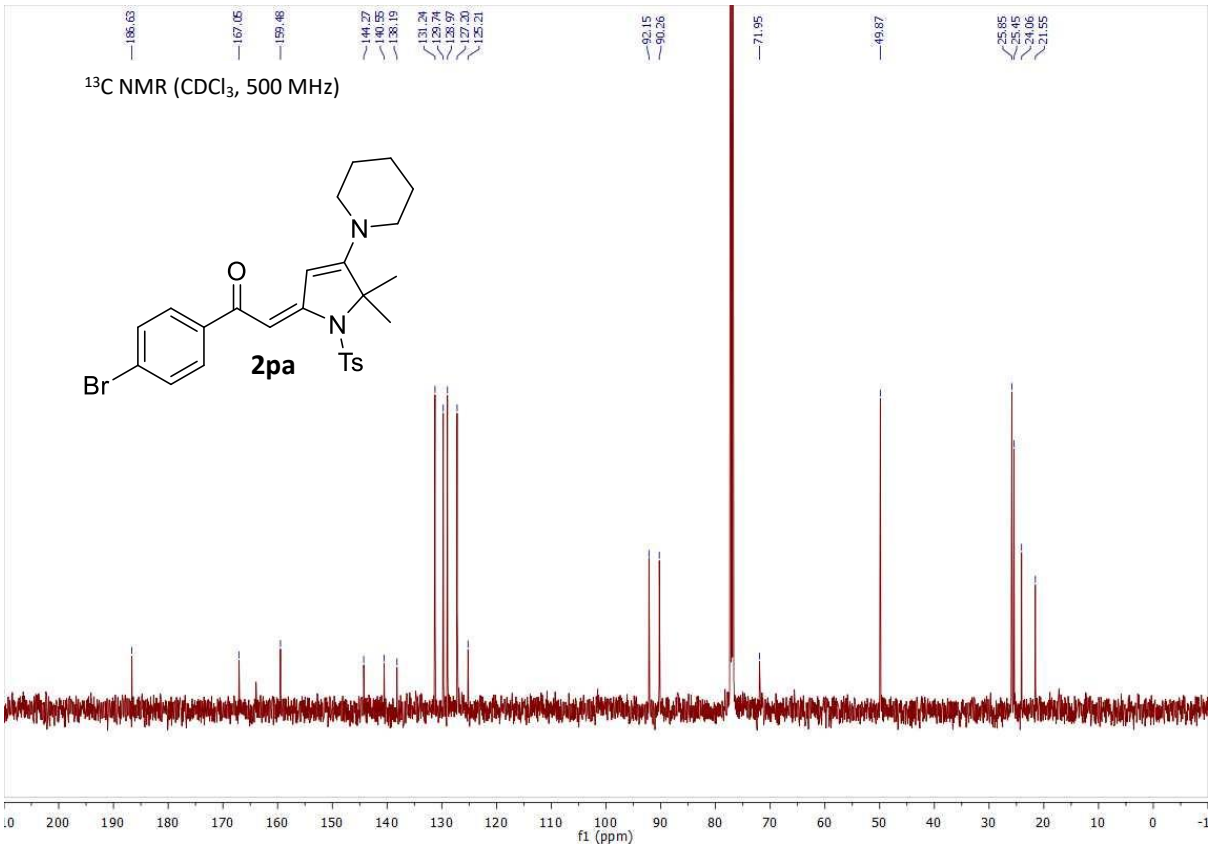
^{13}C NMR ($CDCl_3$, 500 MHz)





^{1}H NMR ($CDCl_3$, 500 MHz)

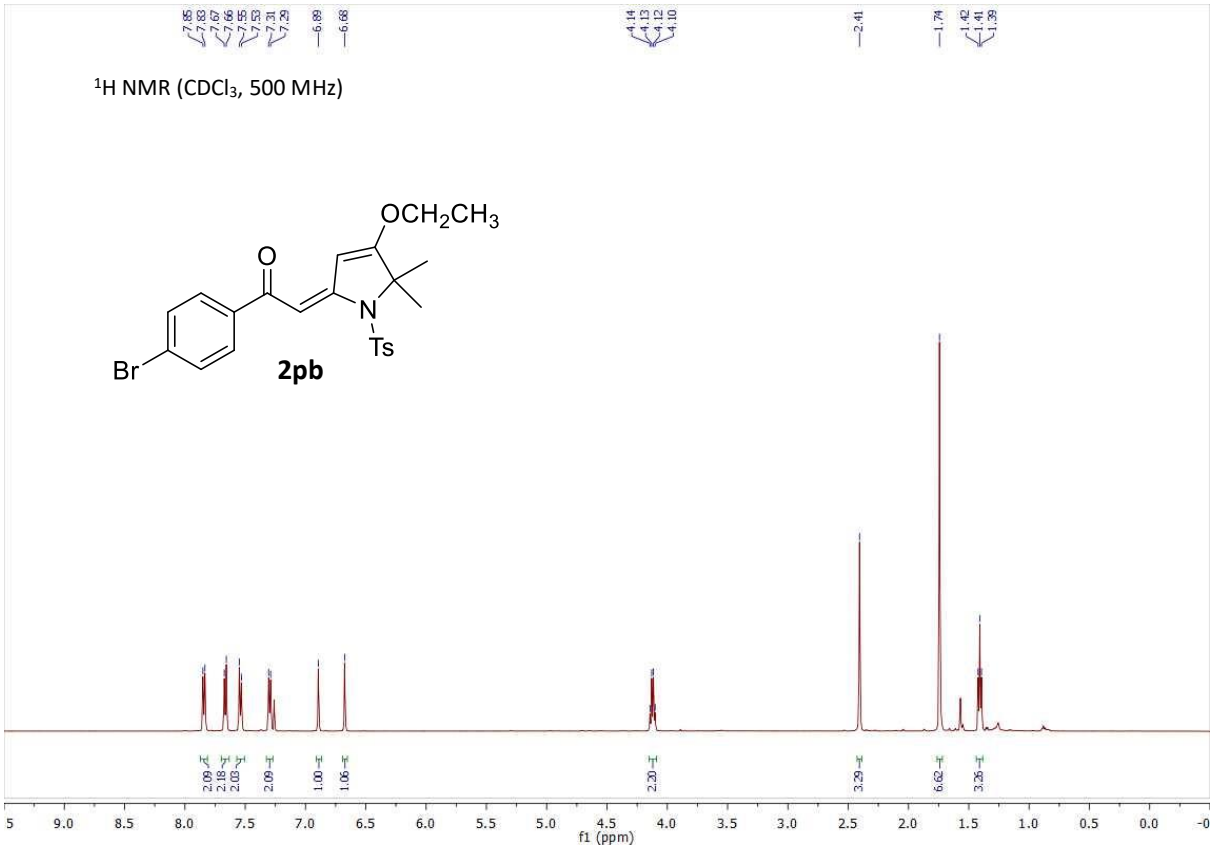
2pa



^{13}C NMR ($CDCl_3$, 500 MHz)

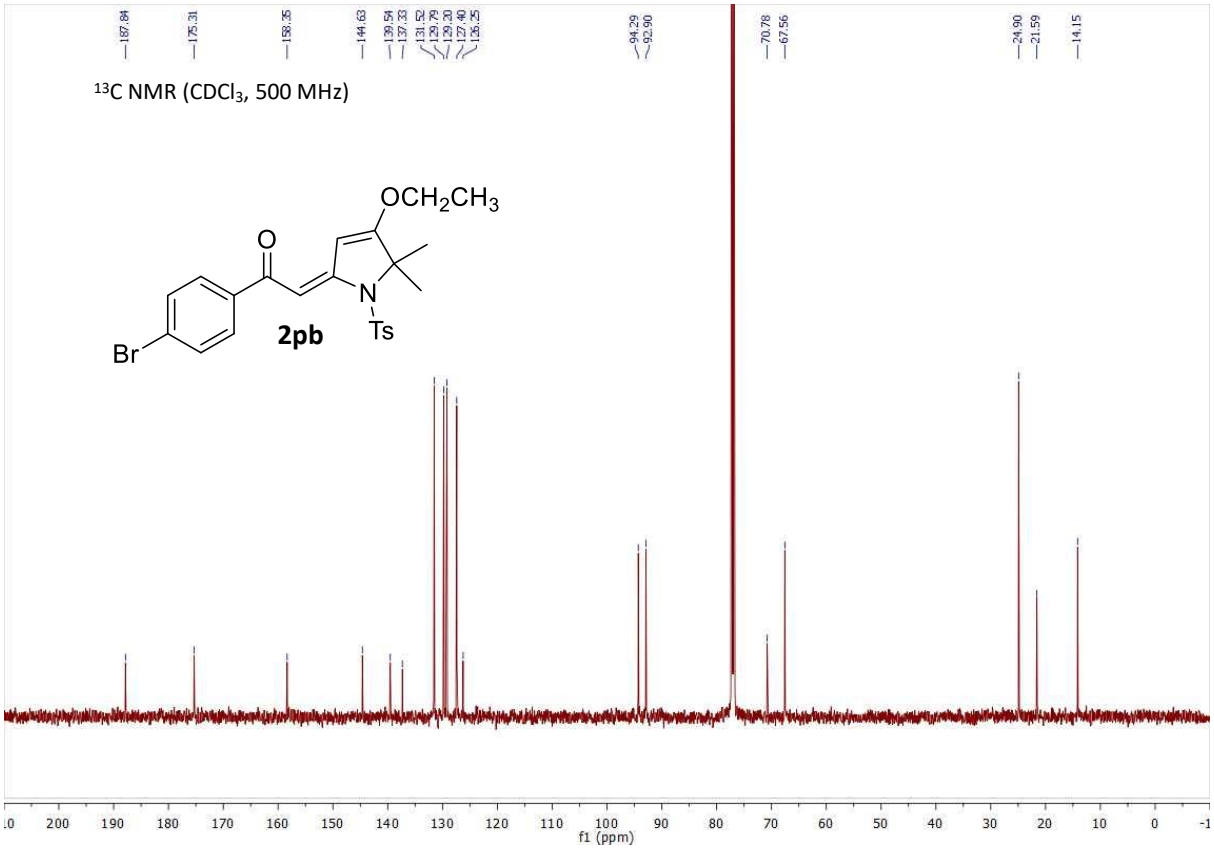
2pa

^{1}H NMR ($CDCl_3$, 500 MHz)

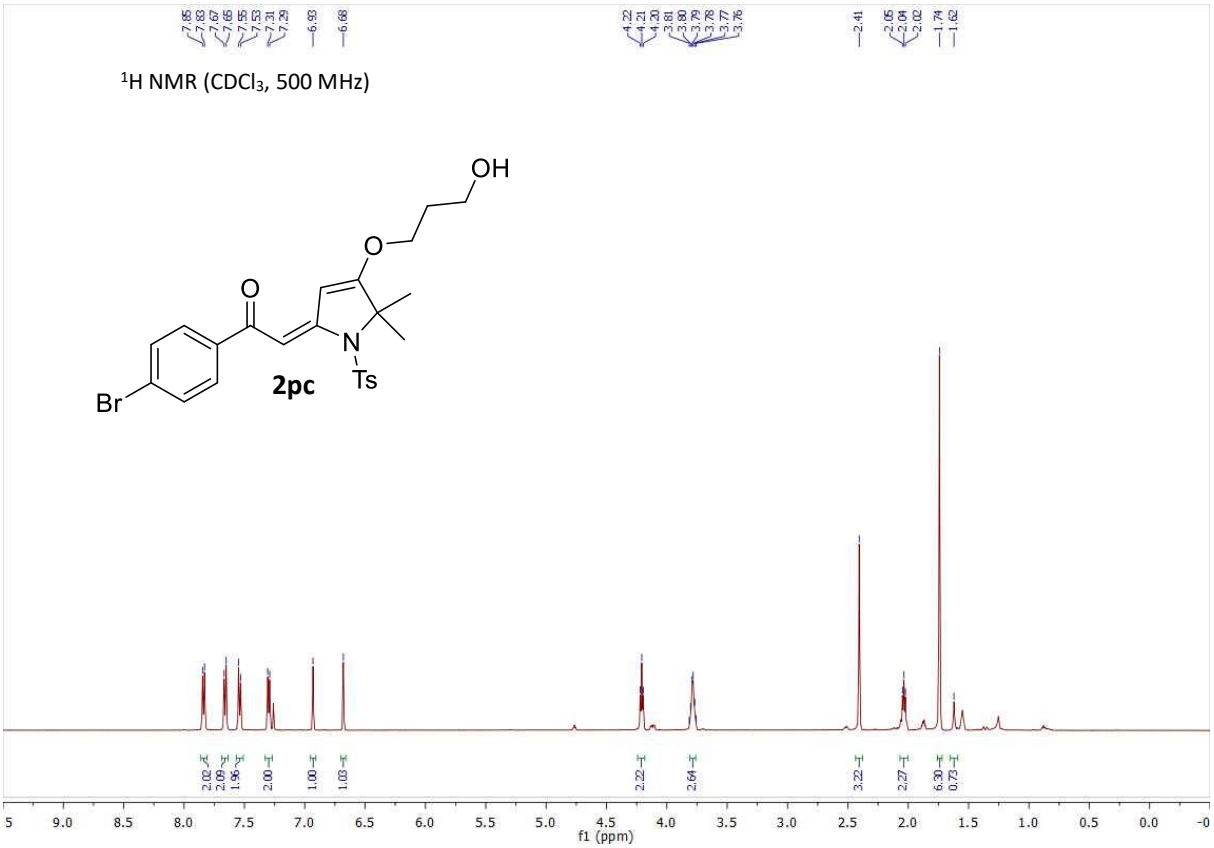


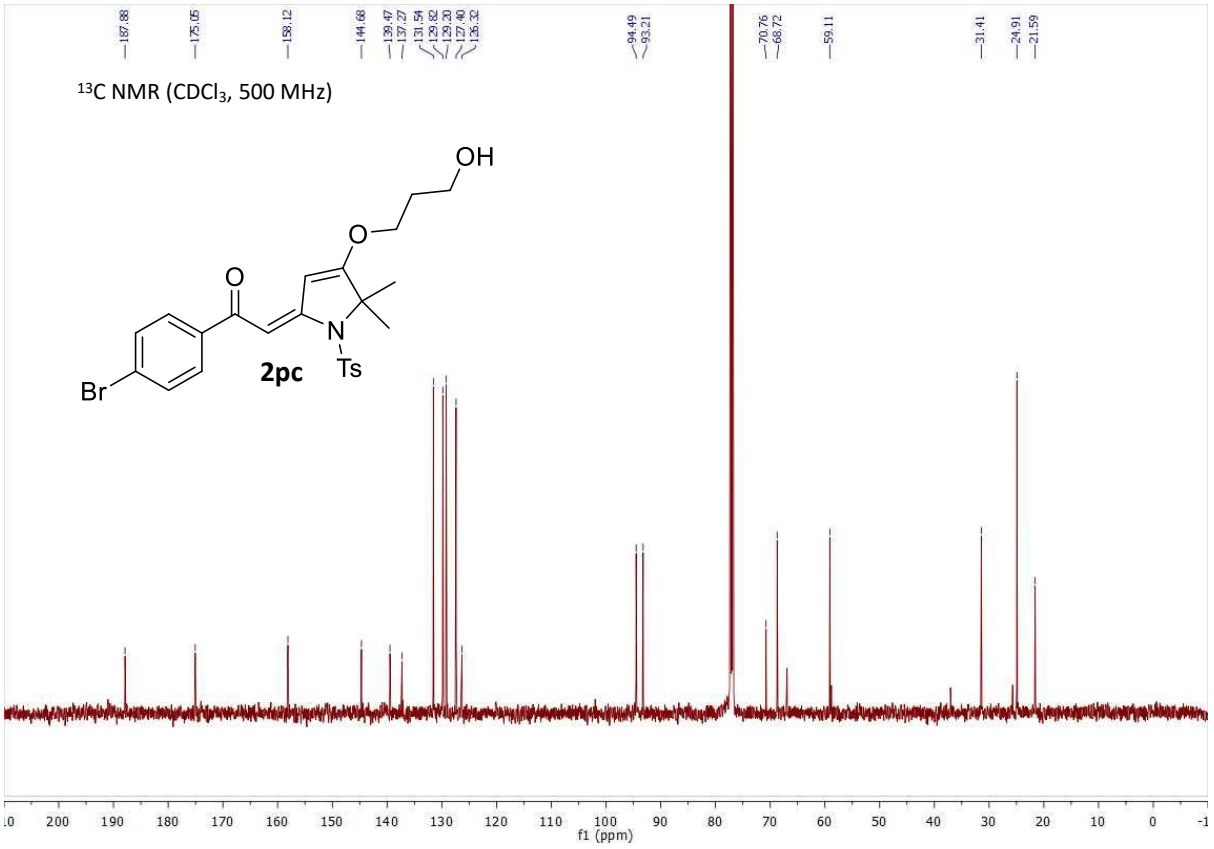
2pb

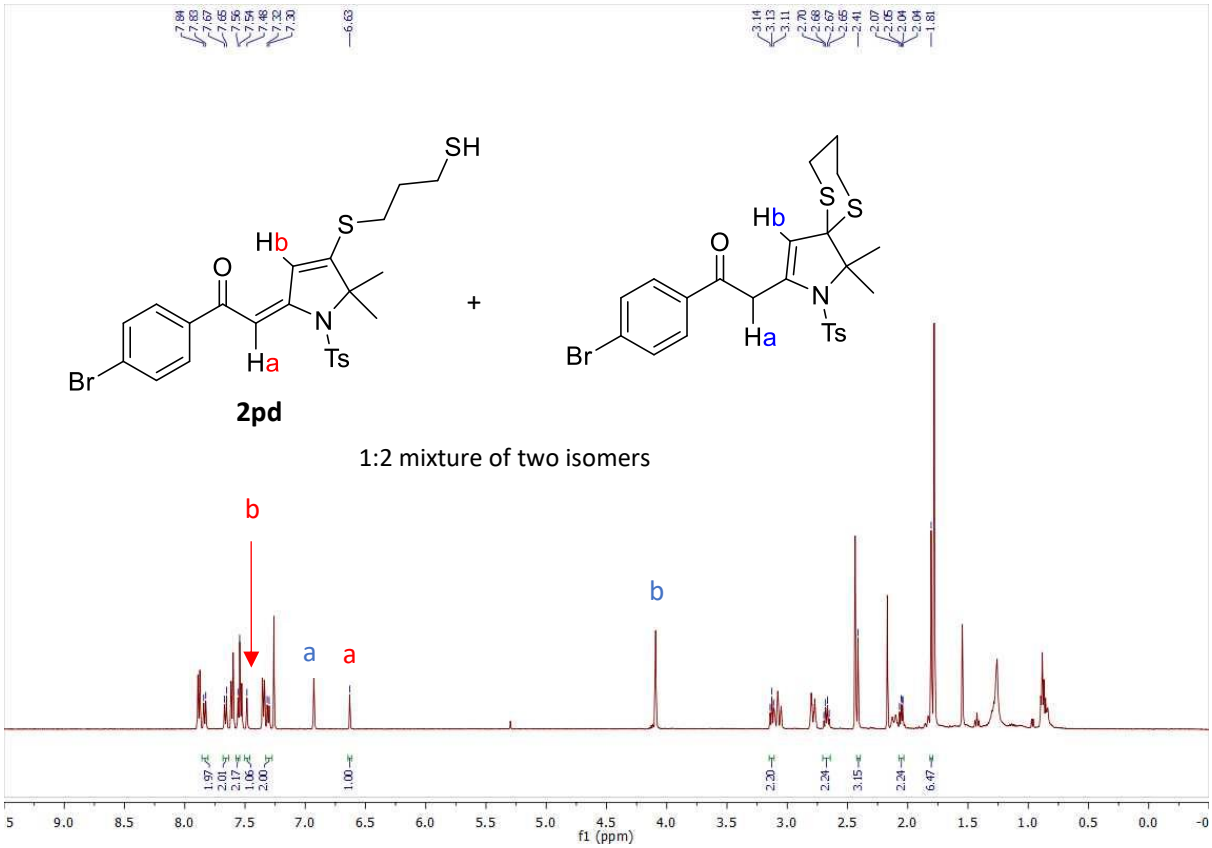
^{13}C NMR ($CDCl_3$, 500 MHz)

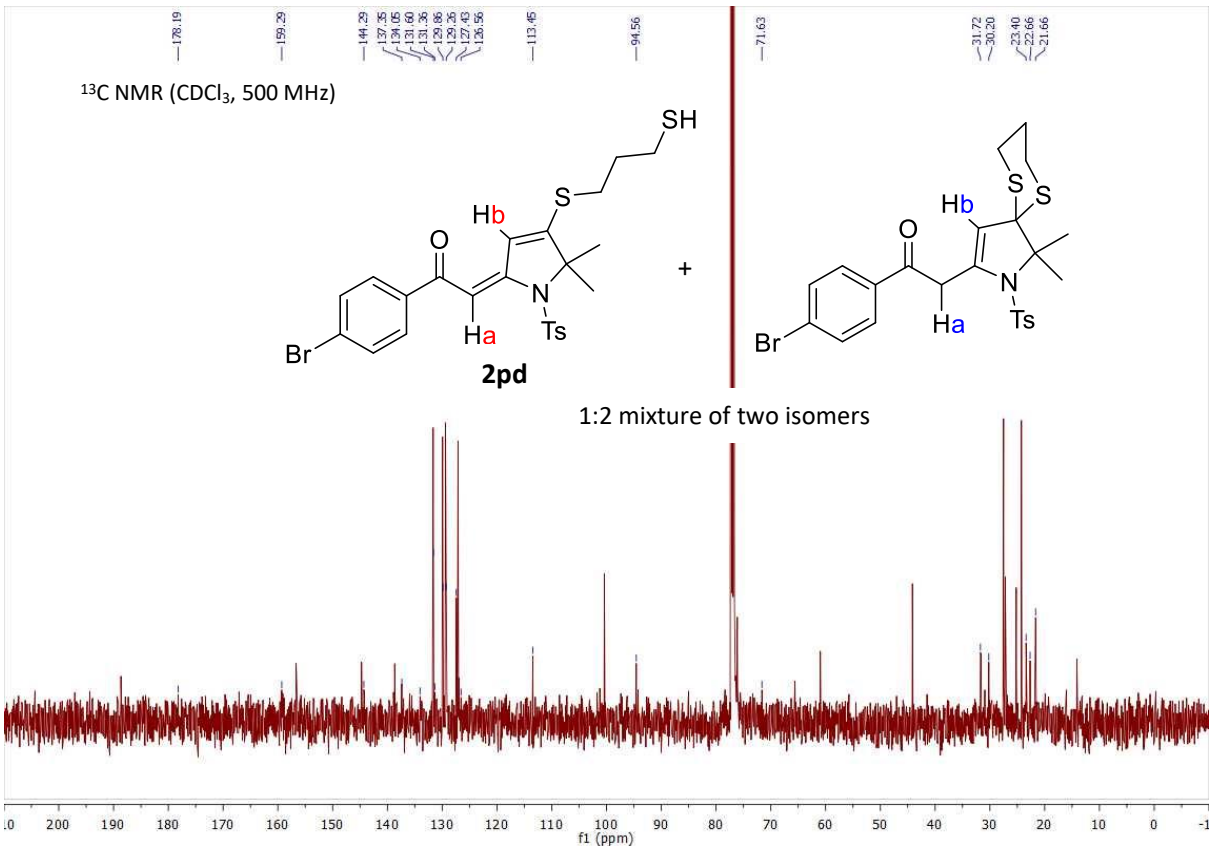


2pb

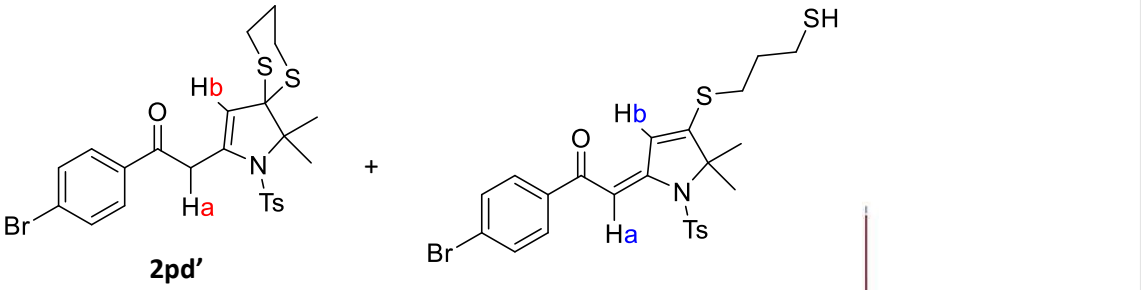

7.85
7.83
7.67
7.65
7.55
7.53
7.31
7.29
6.93
6.68
4.22
4.21
4.20
3.81
3.80
3.79
3.78
3.77
3.76
2.41
2.05
2.04
2.02
1.74
1.62
^{1}H NMR ($CDCl_3$, 500 MHz)
OH
O
O
N
Ts
Br
2pc
2.02
2.09
1.96
2.00
1.00
1.03
2.22
2.64
3.22
2.27
6.30
0.73
f1 (ppm)


187.88
175.05
158.12
144.68
139.47
137.27
131.54
129.82
129.20
127.40
126.32
94.49
93.21
70.76
68.72
59.11
31.41
24.91
21.59
^{13}C NMR ($CDCl_3$, 500 MHz)
OH
O
O
N
Ts
Br
2pc
f1 (ppm)


SH
S
Hb
O
N
Ts
Ha
Br
+
S
S
Hb
O
N
Ts
Ha
Br
2pd
1:2 mixture of two isomers
b
a
a
b
f1 (ppm)

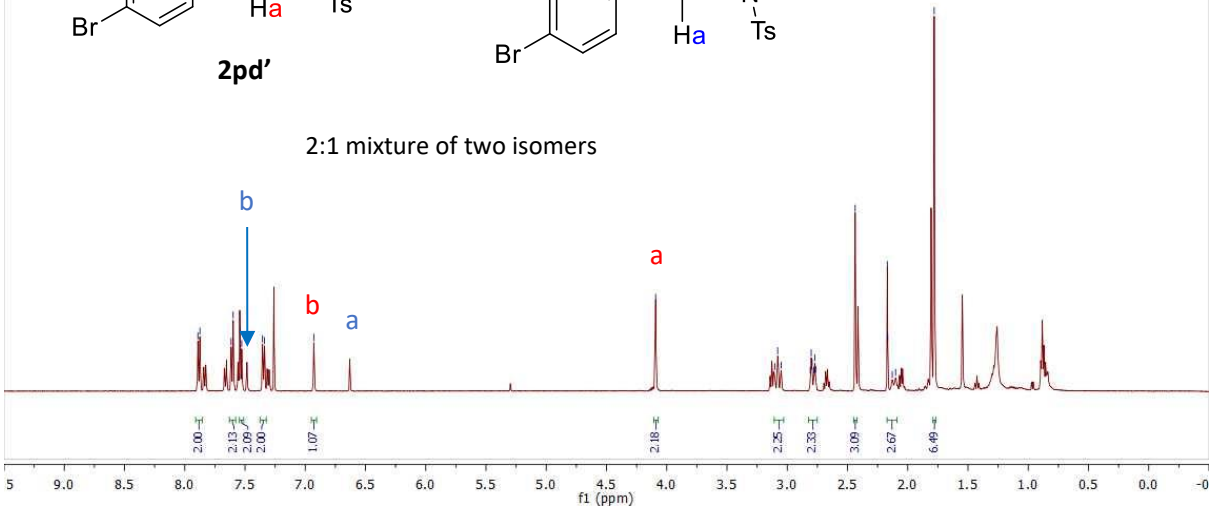

^{13}C NMR ($CDCl_3$, 500 MHz)
SH
S
Hb
O
N
Ts
Ha
Br
+
S
S
Hb
O
N
Ts
Ha
Br
2pd
1:2 mixture of two isomers
f1 (ppm)

^{1}H NMR ($CDCl_3$, 500 MHz)

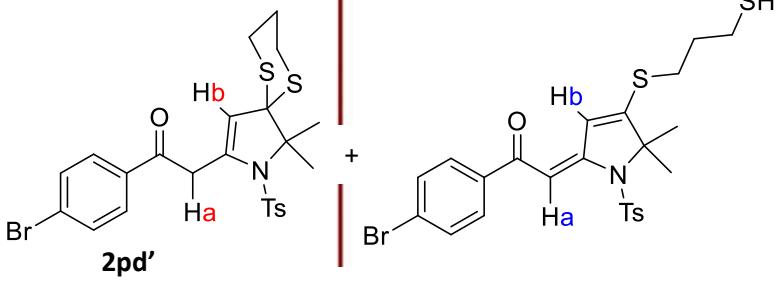


2pd'

2:1 mixture of two isomers

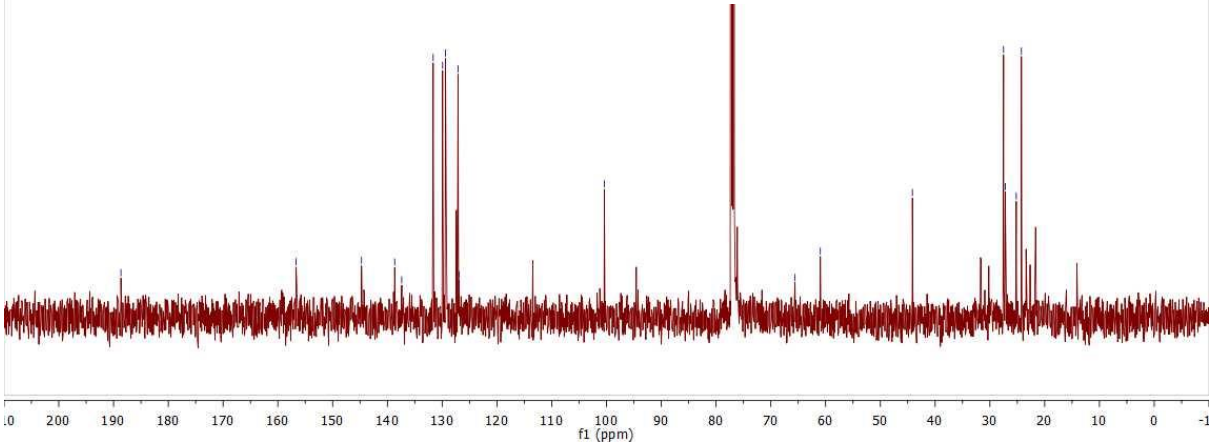


^{13}C NMR ($CDCl_3$, 500 MHz)



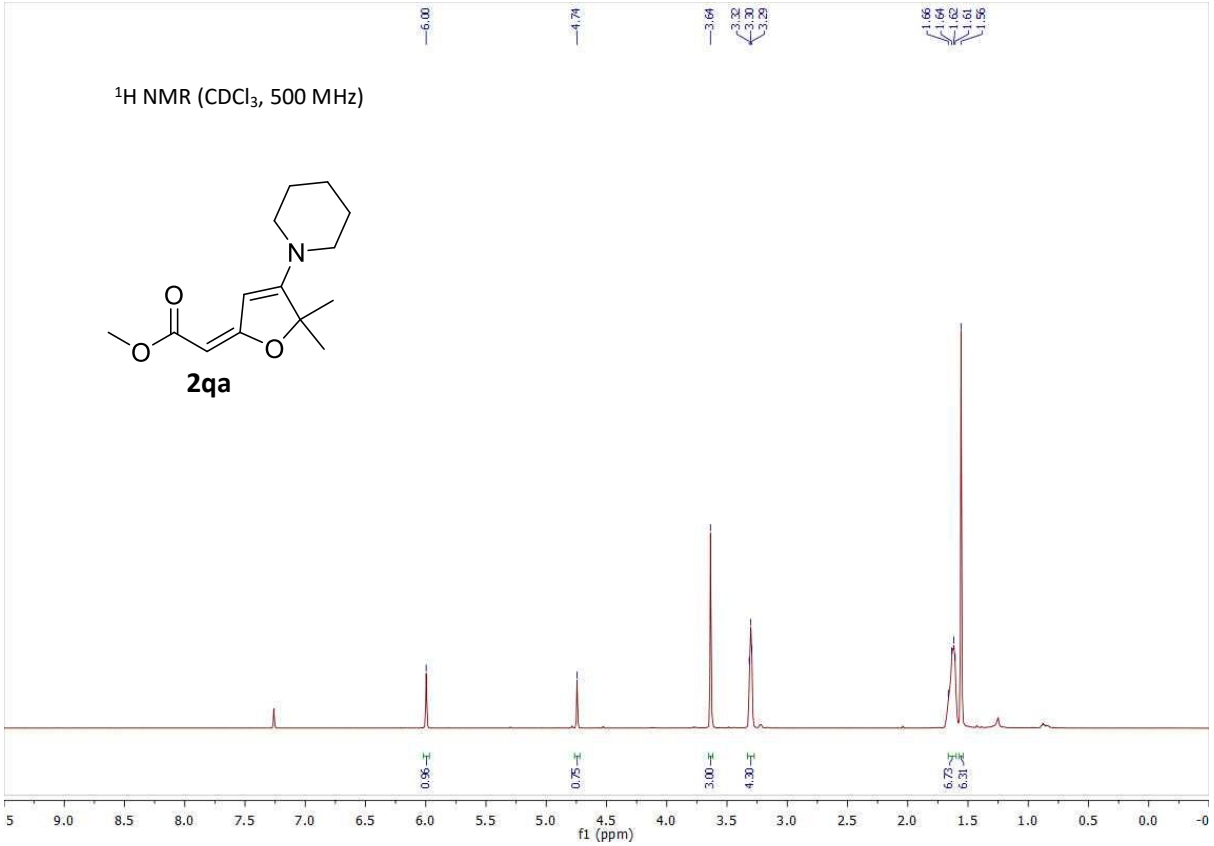
2pd'

2:1 mixture of two isomers



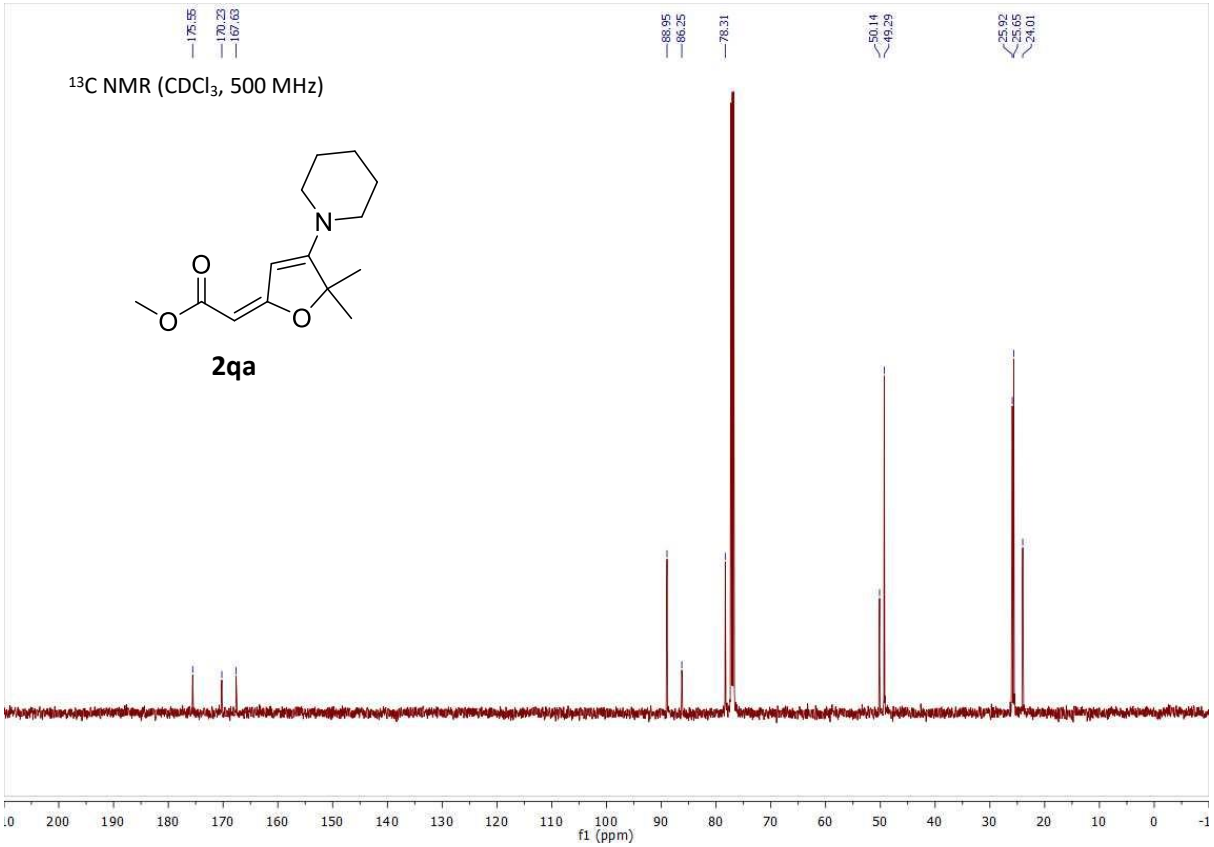
^{1}H NMR ($CDCl_3$, 500 MHz)

2qa



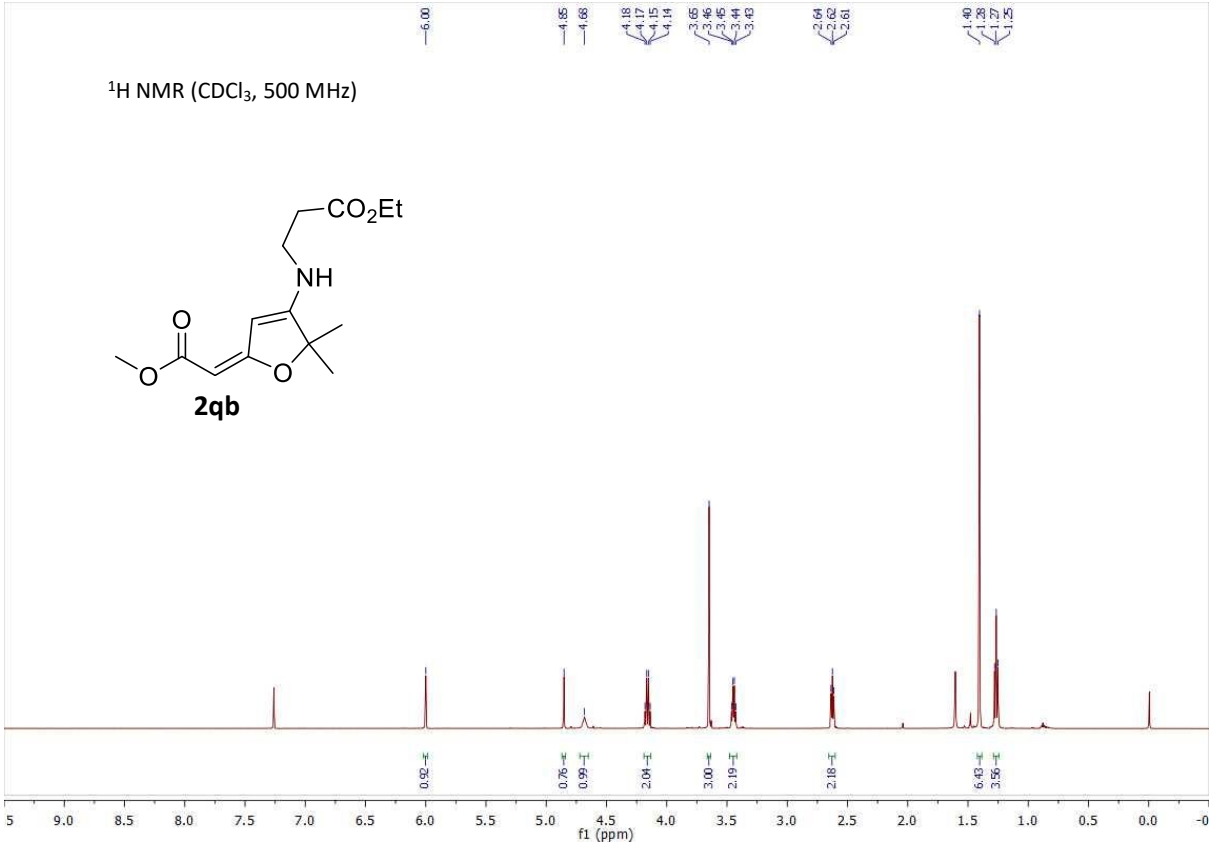
^{13}C NMR ($CDCl_3$, 500 MHz)

2qa



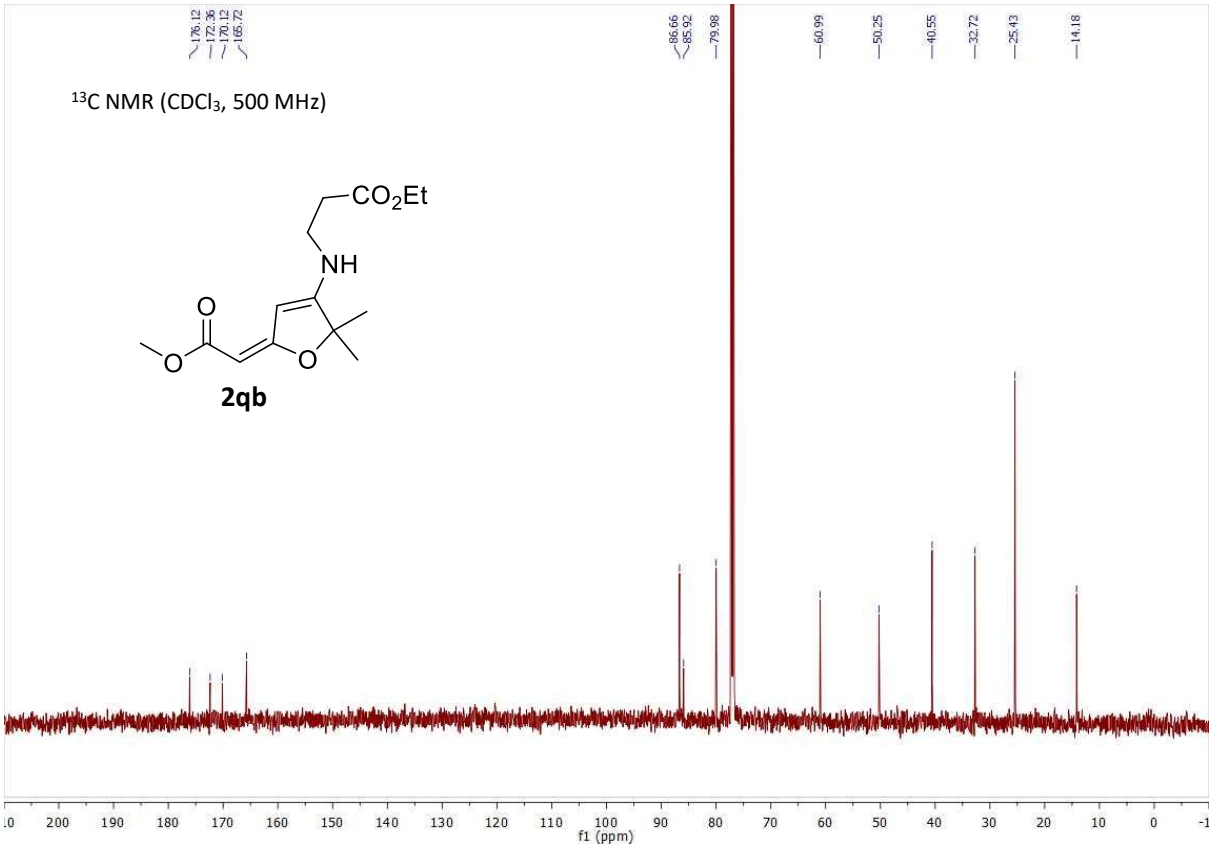
^{1}H NMR ($CDCl_3$, 500 MHz)

2qb



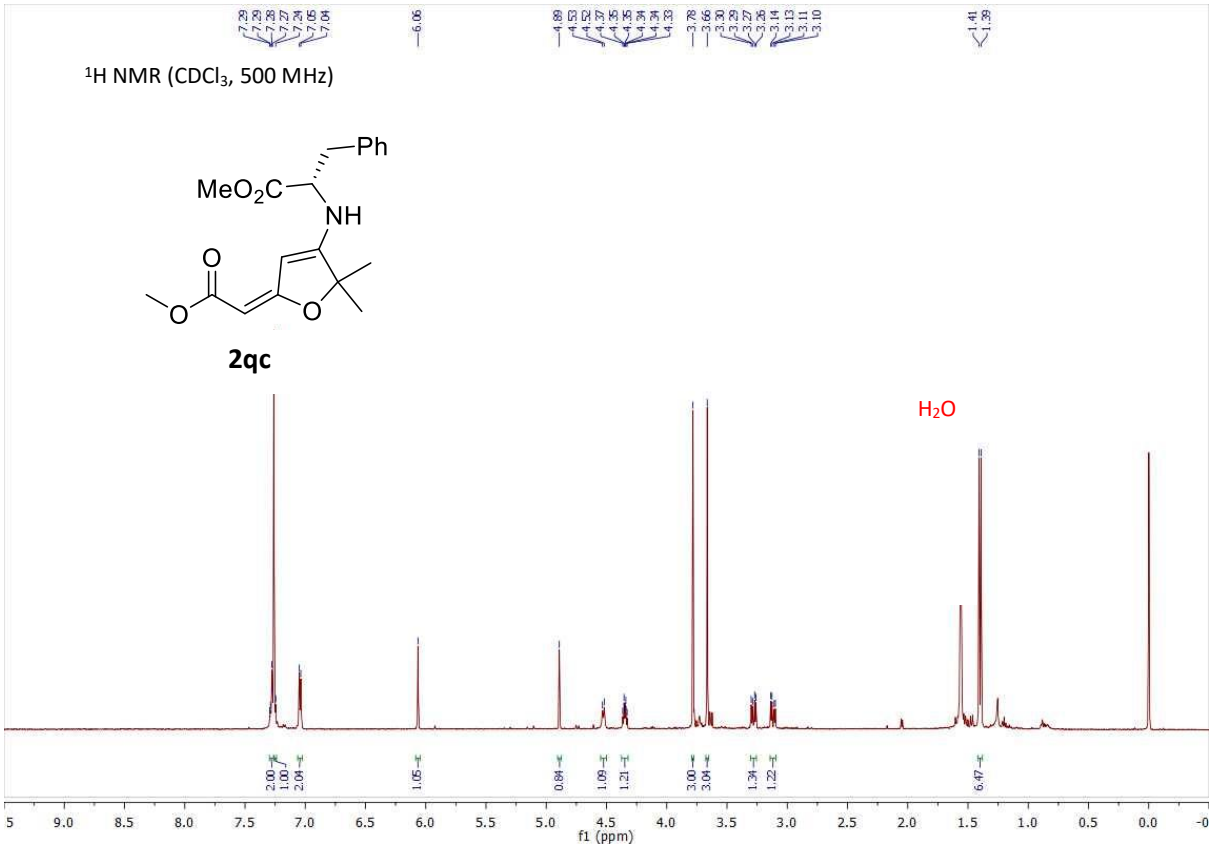
^{13}C NMR ($CDCl_3$, 500 MHz)

2qb



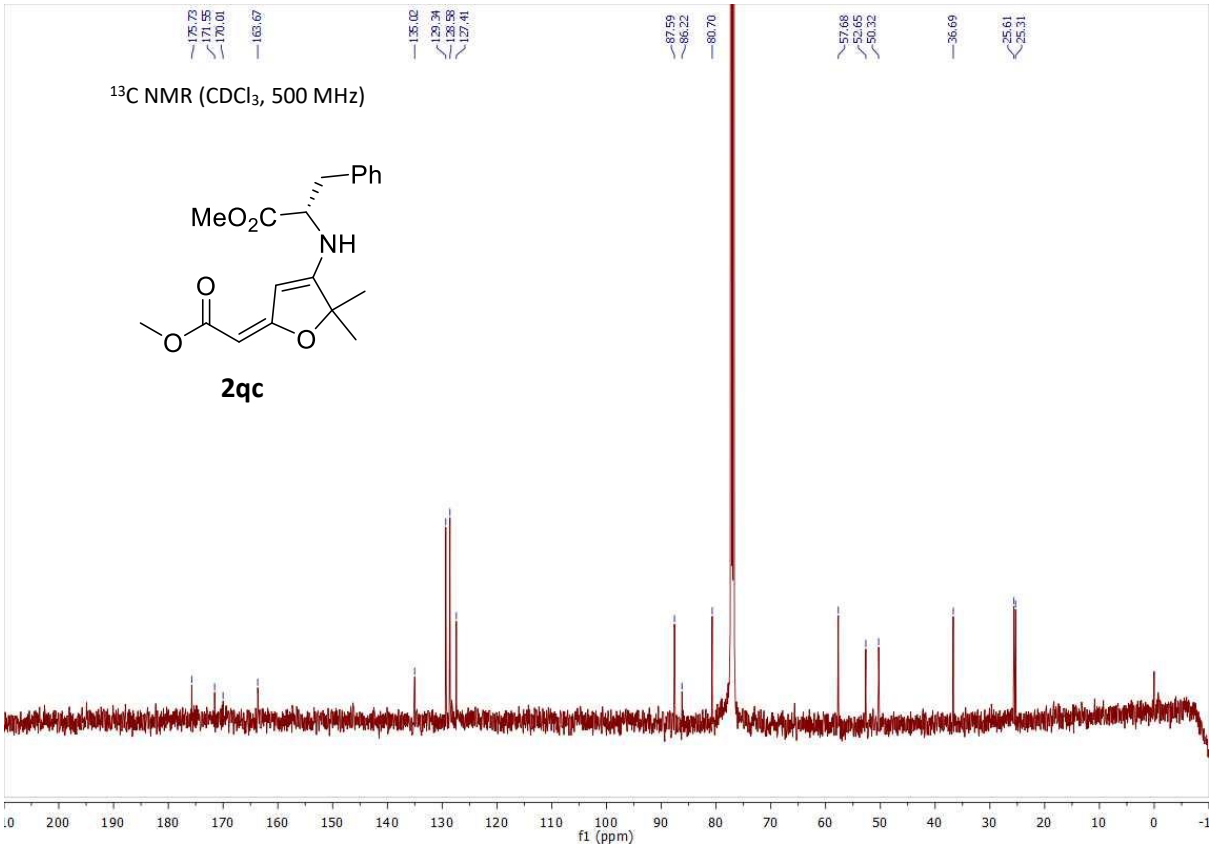
^{1}H NMR ($CDCl_3$, 500 MHz)

2qc

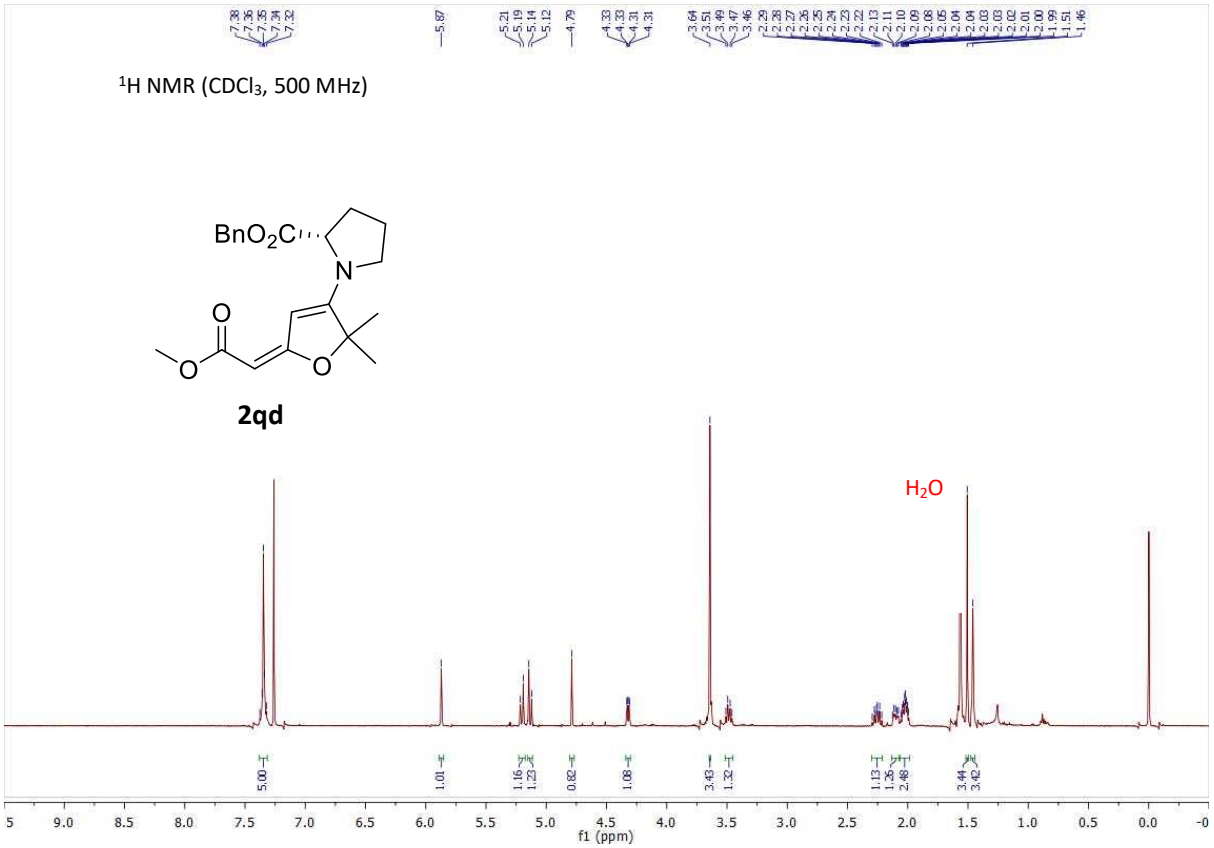


^{13}C NMR ($CDCl_3$, 500 MHz)

2qc

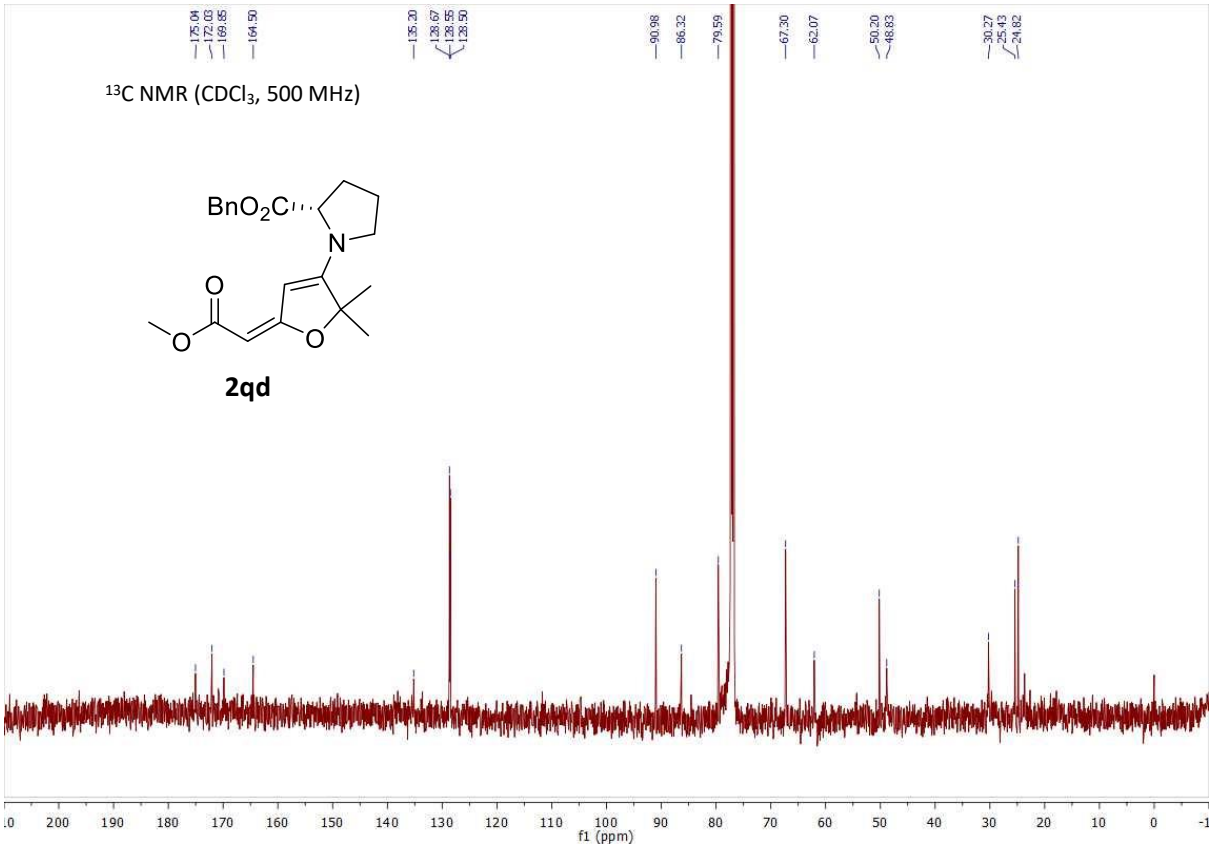


^{1}H NMR ($CDCl_3$, 500 MHz)



2qd

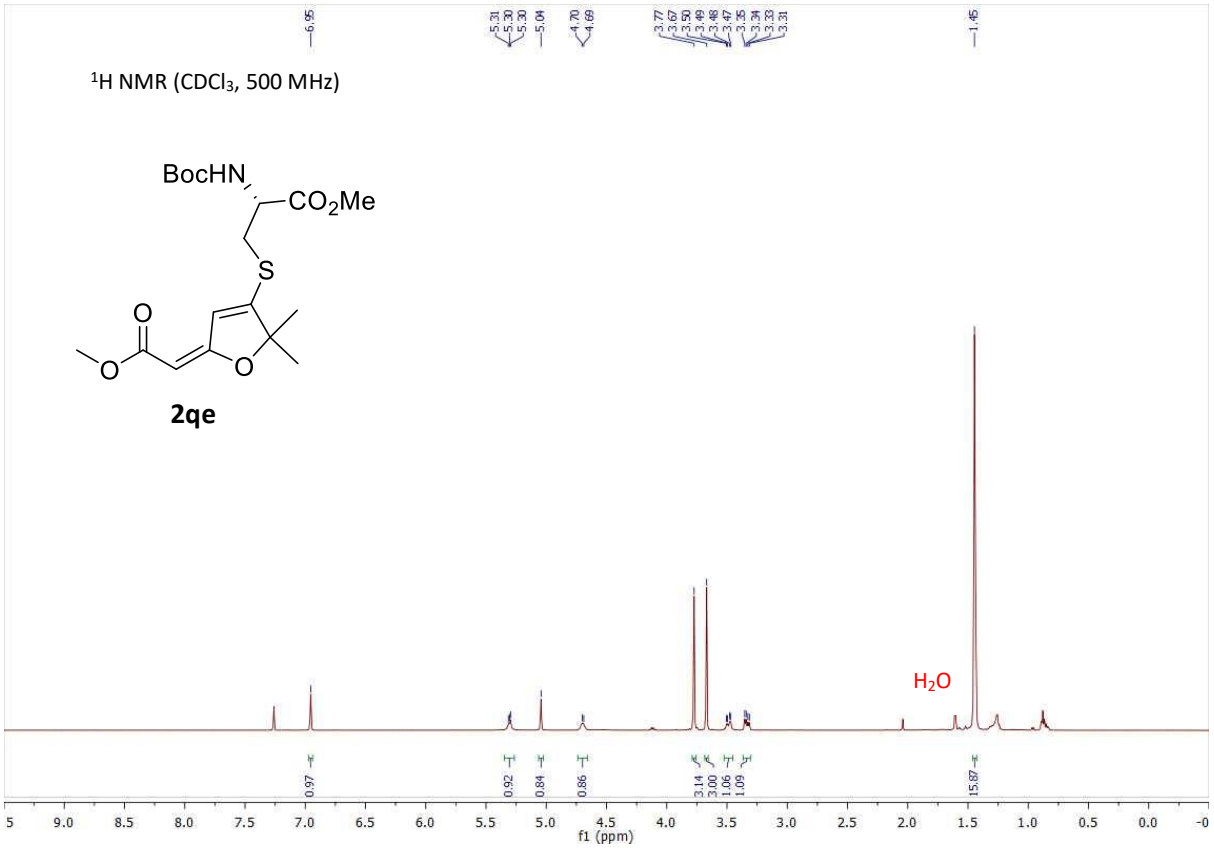
^{13}C NMR ($CDCl_3$, 500 MHz)



2qd

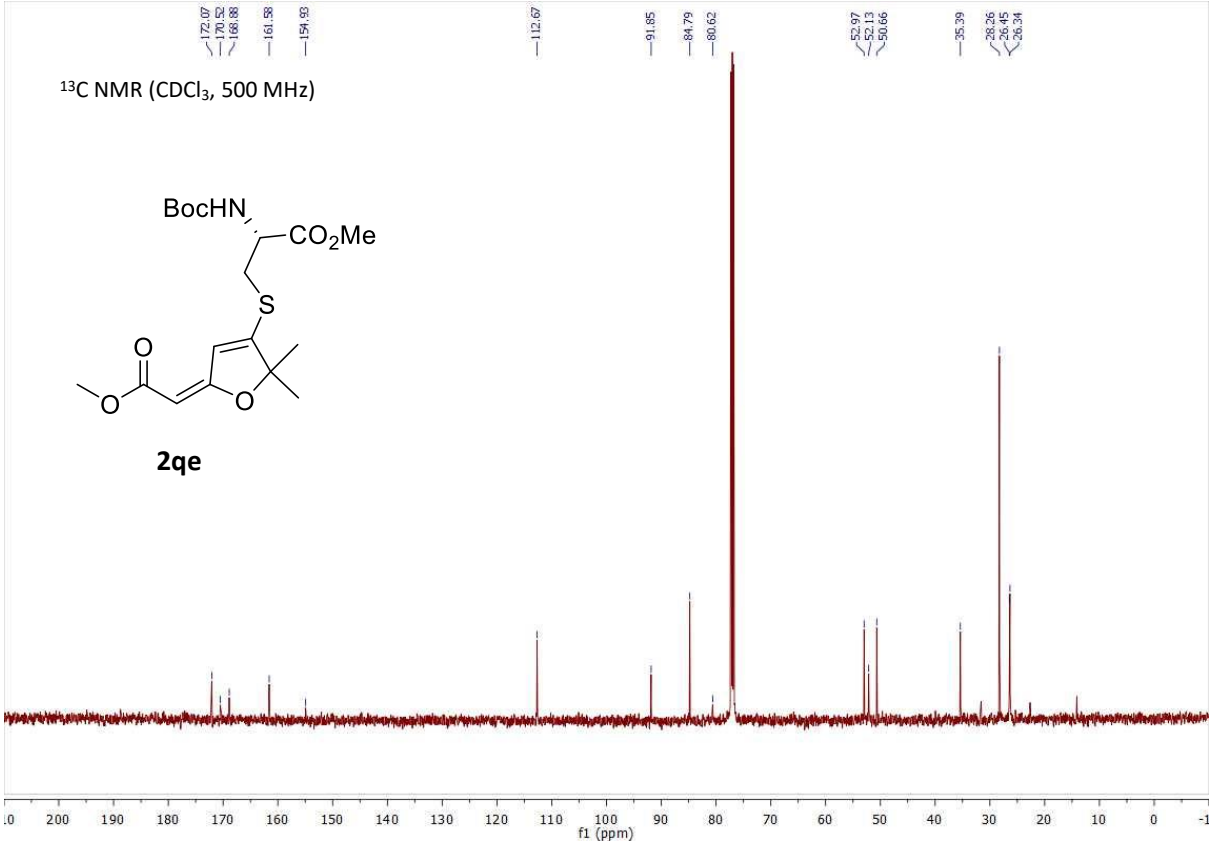
^{1}H NMR ($CDCl_3$, 500 MHz)

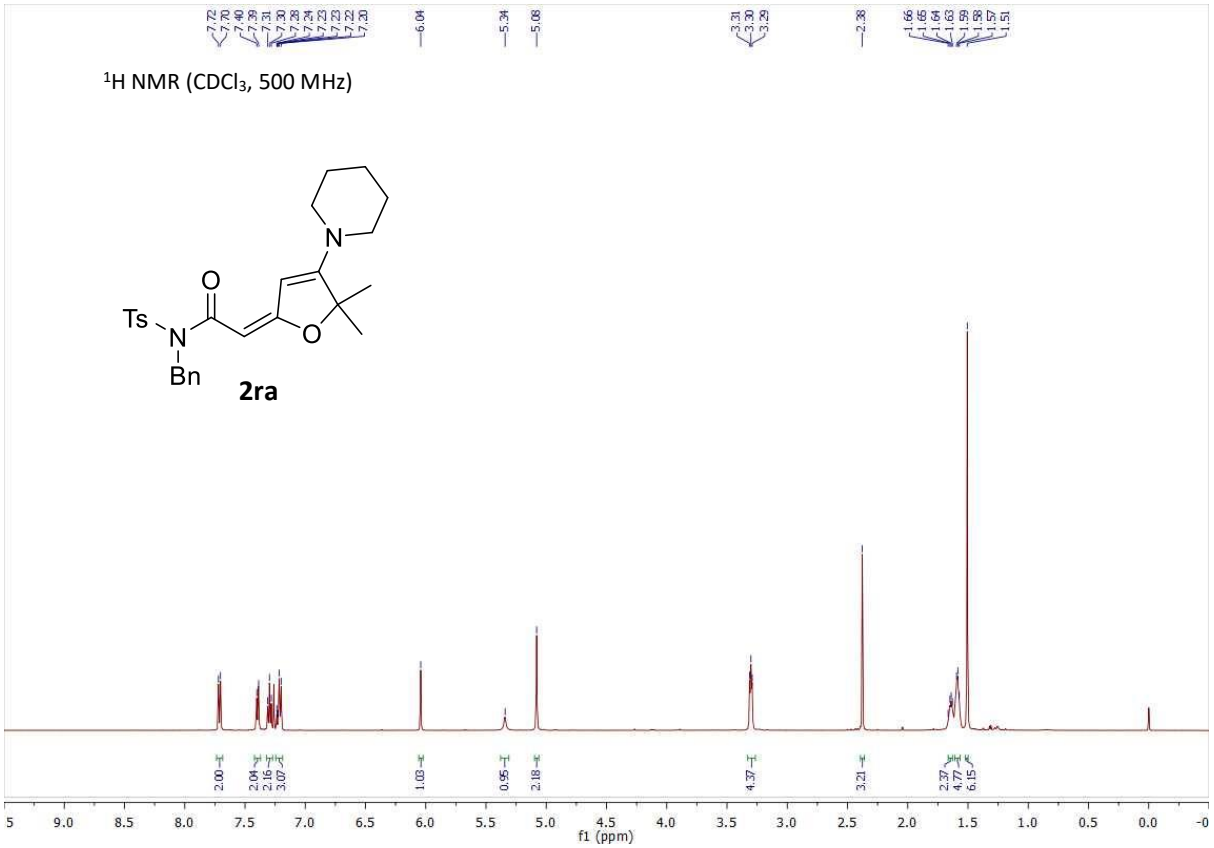
2qe



^{13}C NMR ($CDCl_3$, 500 MHz)

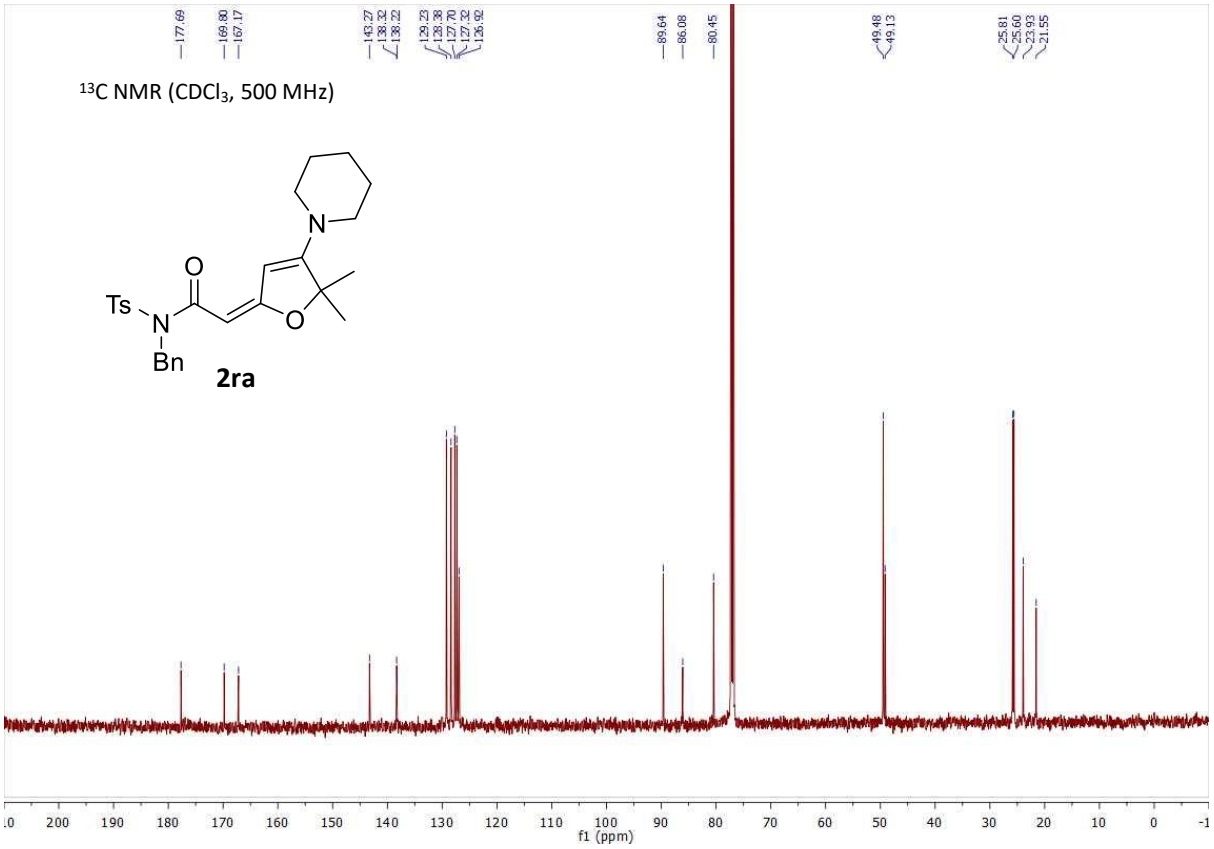
2qe





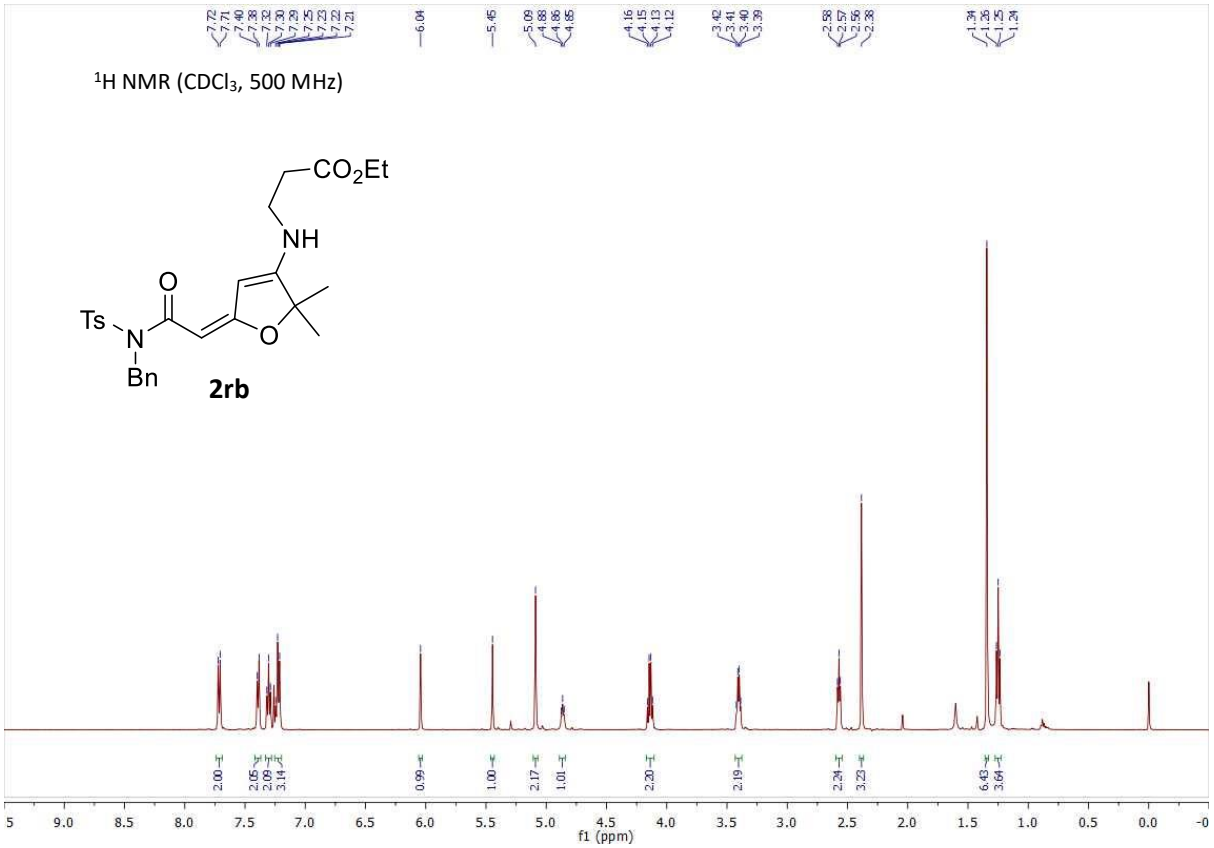
^{1}H NMR ($CDCl_3$, 500 MHz)

2ra



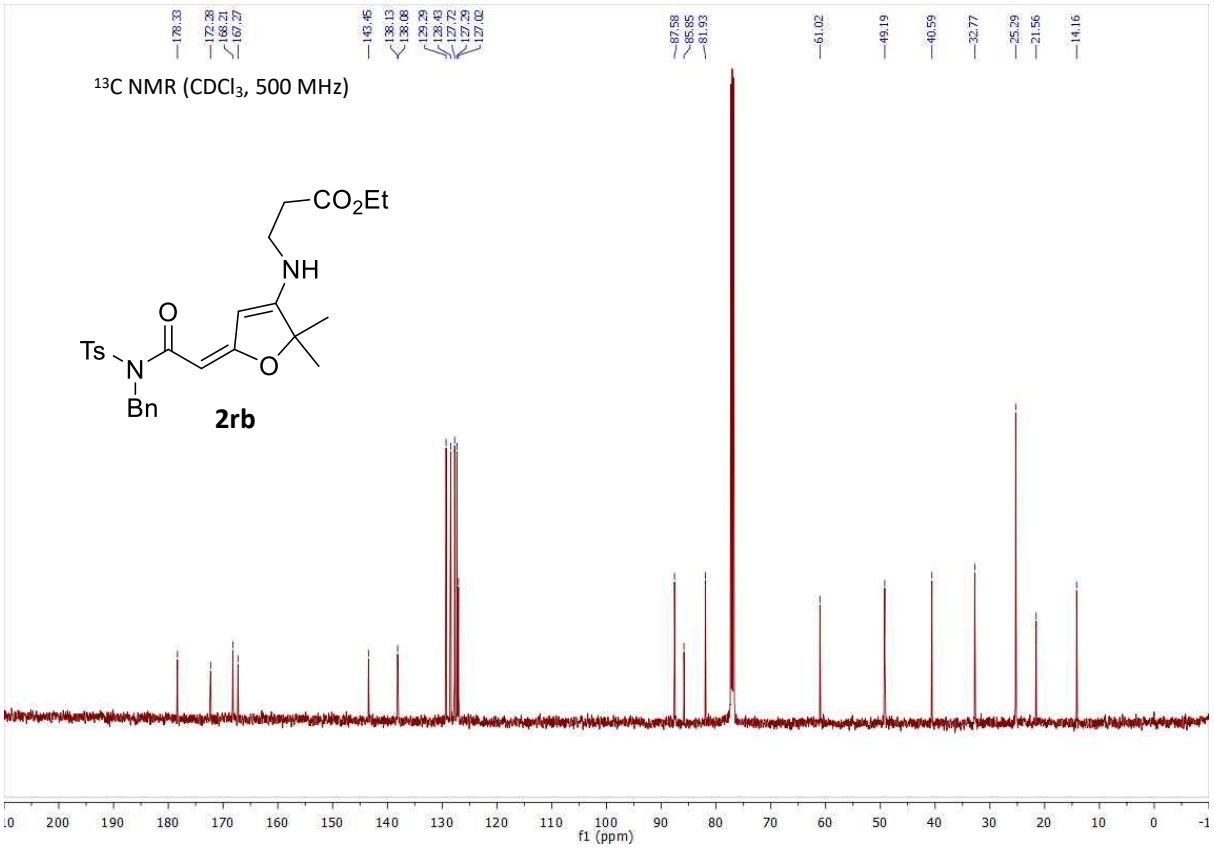
^{13}C NMR ($CDCl_3$, 500 MHz)

2ra



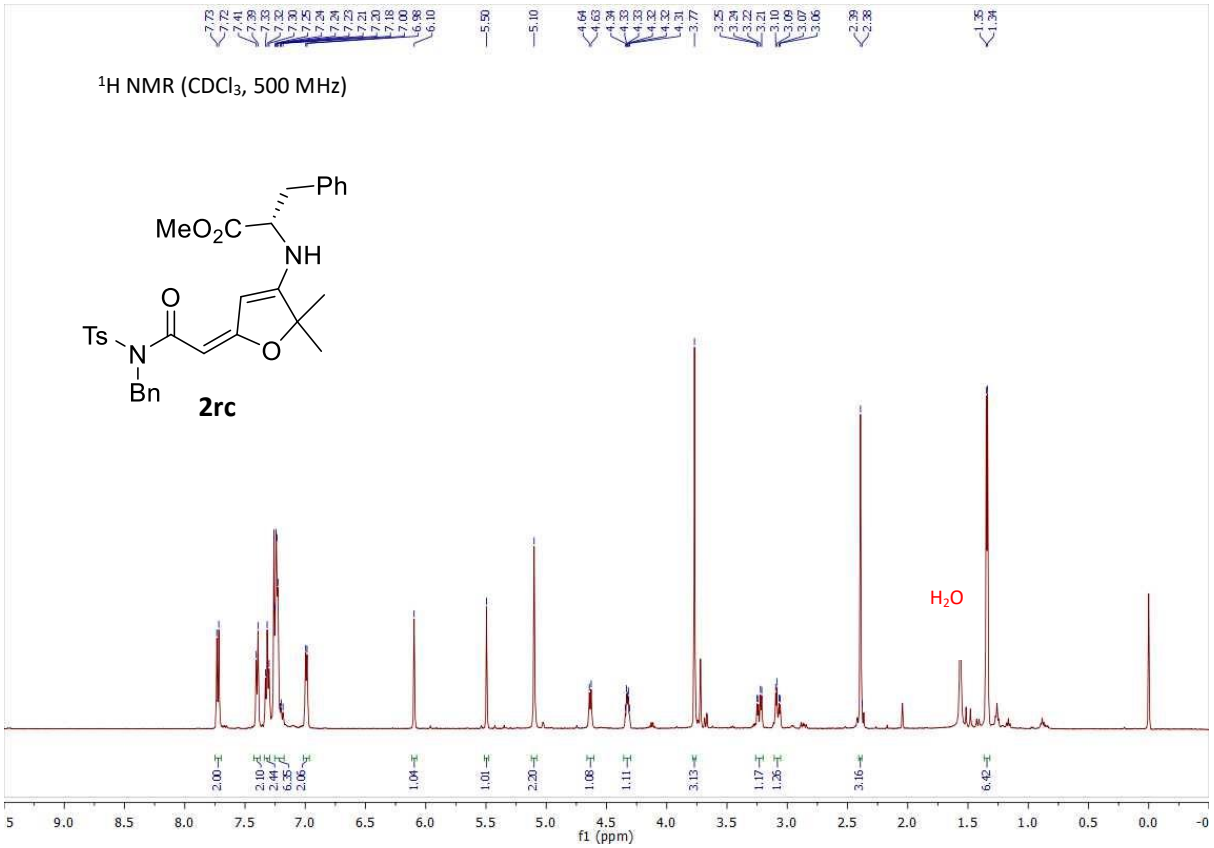
^{1}H NMR ($CDCl_3$, 500 MHz)

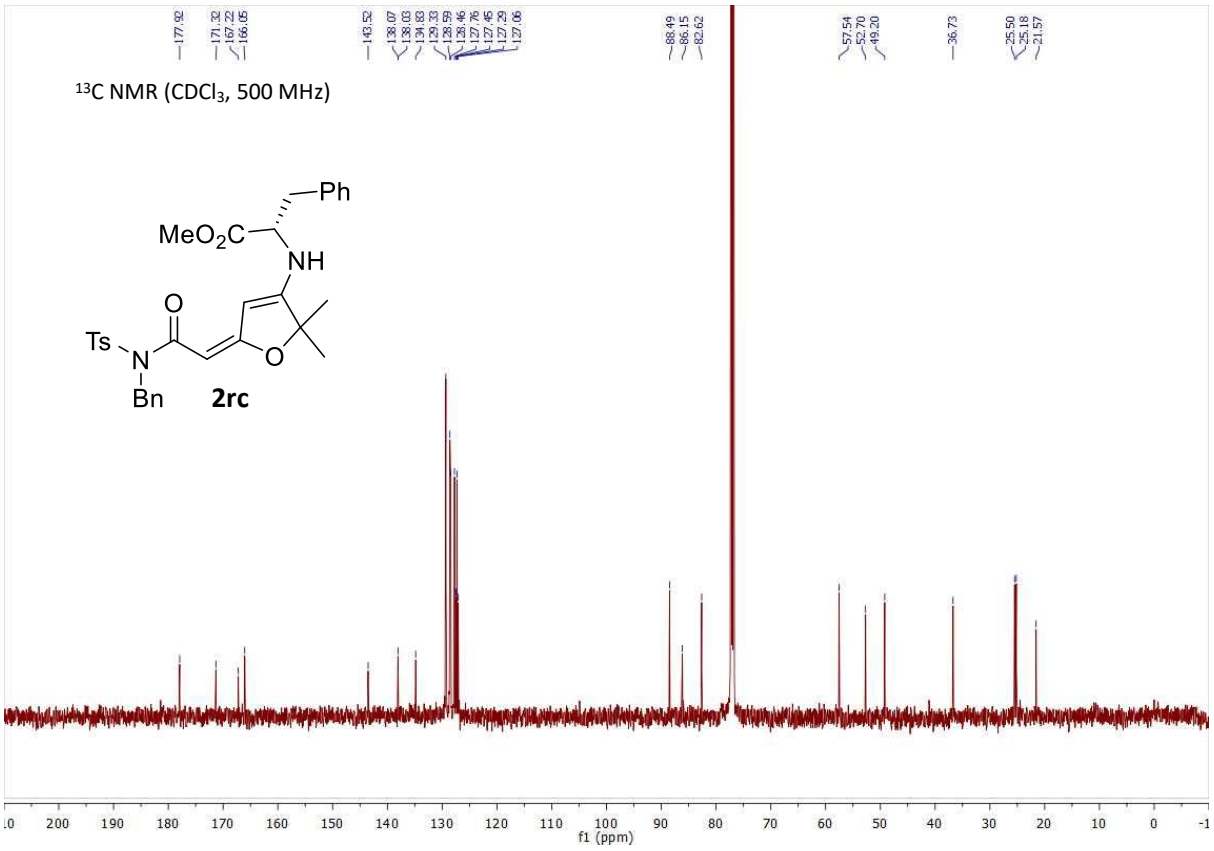
2rb



^{13}C NMR ($CDCl_3$, 500 MHz)

2rb

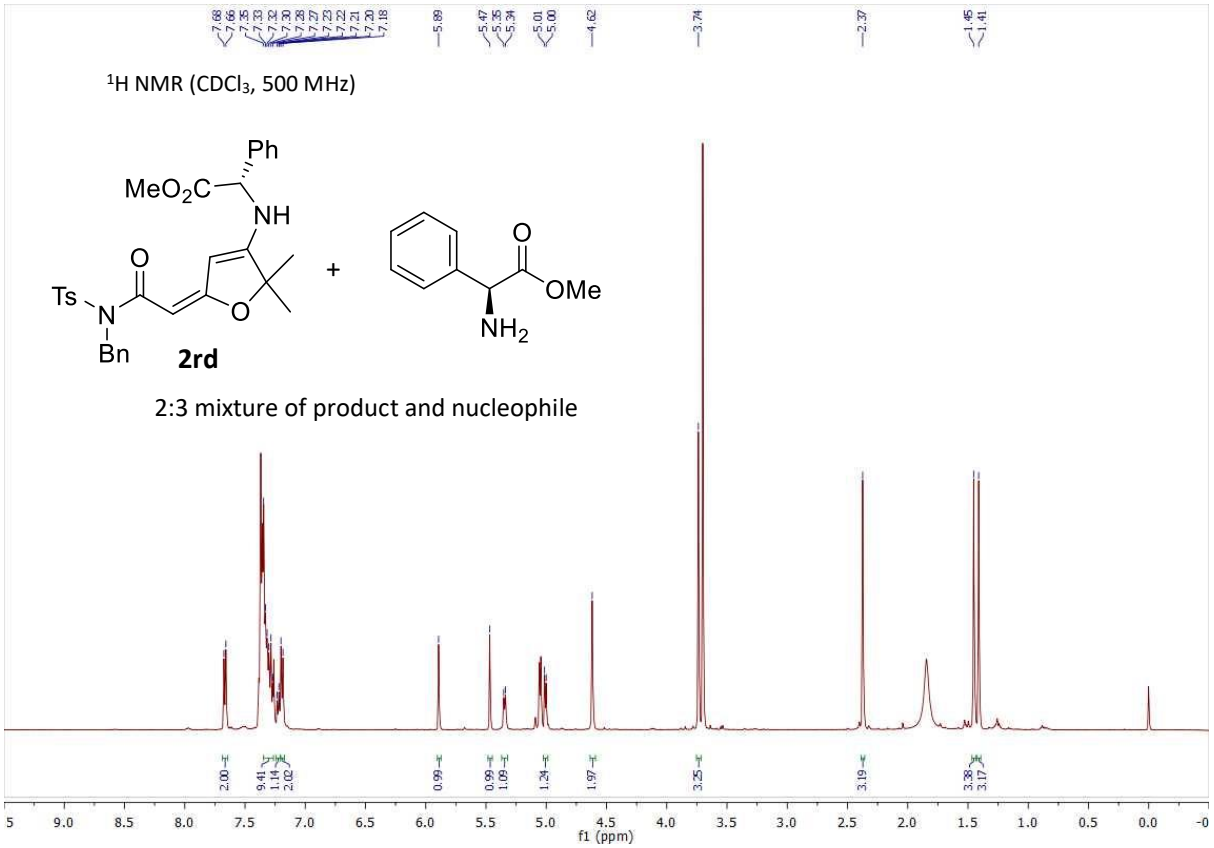

7.73
7.72
7.41
7.39
7.33
7.32
7.30
7.25
7.24
7.24
7.23
7.21
7.20
7.18
7.00
6.98
6.10
5.50
5.10
4.64
4.63
4.34
4.33
4.33
4.32
4.32
4.31
3.77
3.25
3.24
3.22
3.21
3.10
3.09
3.07
3.06
2.39
2.38
1.35
1.34
1H NMR (CDCl3, 500 MHz)
Ph
MeO2C
NH
O
Ts
N
Bn
O
2rc
H2O
2.00
2.10
2.44
6.35
2.06
1.04
1.01
2.20
1.08
1.11
3.13
1.17
1.26
3.16
6.42
f1 (ppm)


177.92
171.32
167.22
166.05
143.52
138.07
138.03
134.83
129.33
128.59
128.46
127.76
127.45
127.29
127.06
88.49
86.15
82.62
57.54
52.70
49.20
36.73
25.50
25.18
21.57
13C NMR (CDCl3, 500 MHz)
Ph
MeO2C
NH
O
Ts
N
Bn
O
2rc
f1 (ppm)

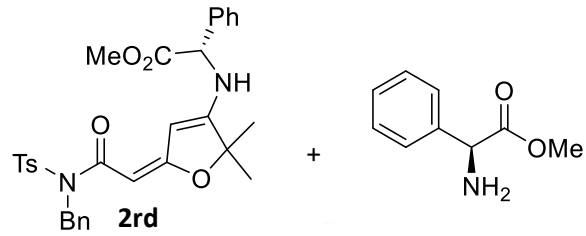
^{1}H NMR ($CDCl_3$, 500 MHz)

2rd

2:3 mixture of product and nucleophile

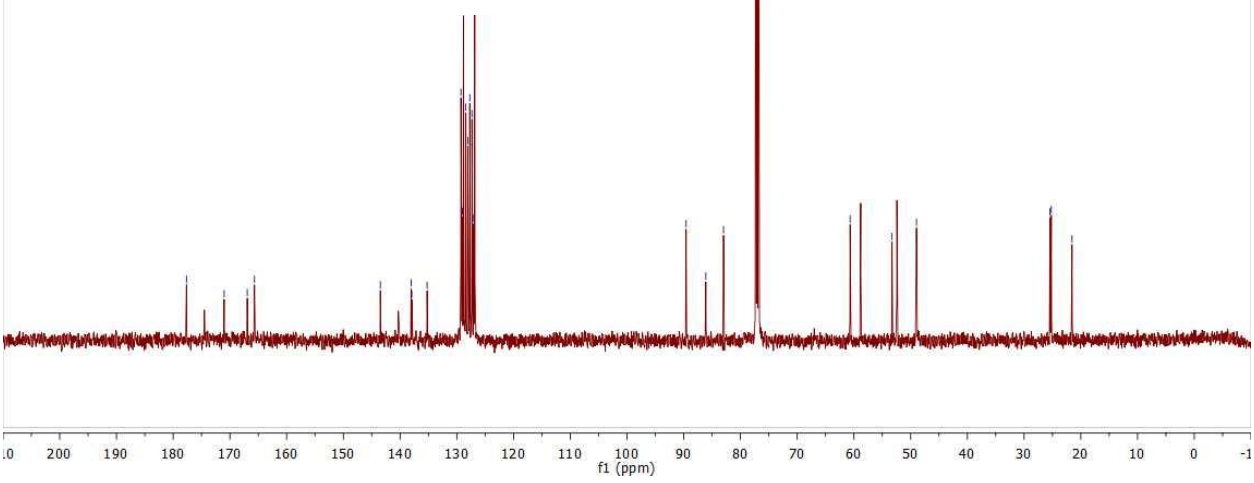


^{13}C NMR ($CDCl_3$, 500 MHz)



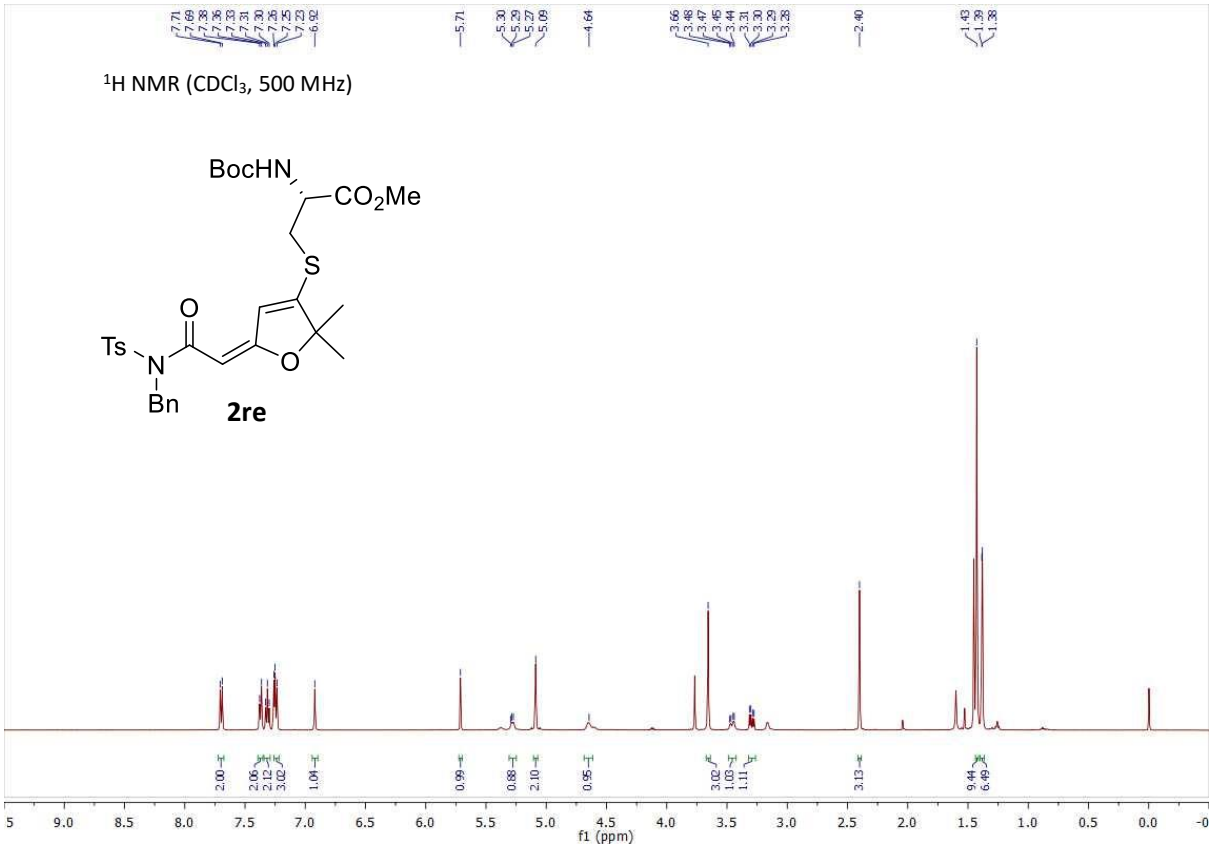
2rd

2:3 mixture of product and nucleophile



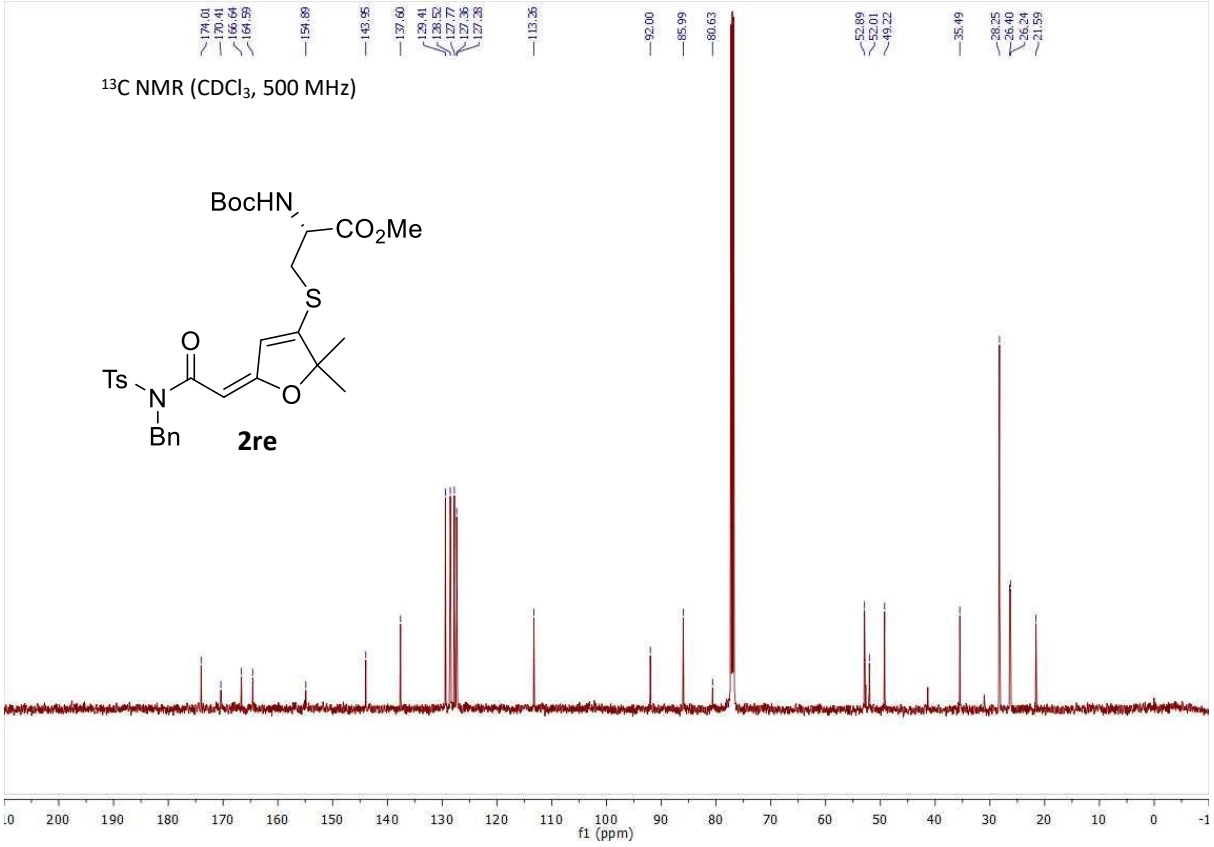
^{1}H NMR ($CDCl_3$, 500 MHz)

2re



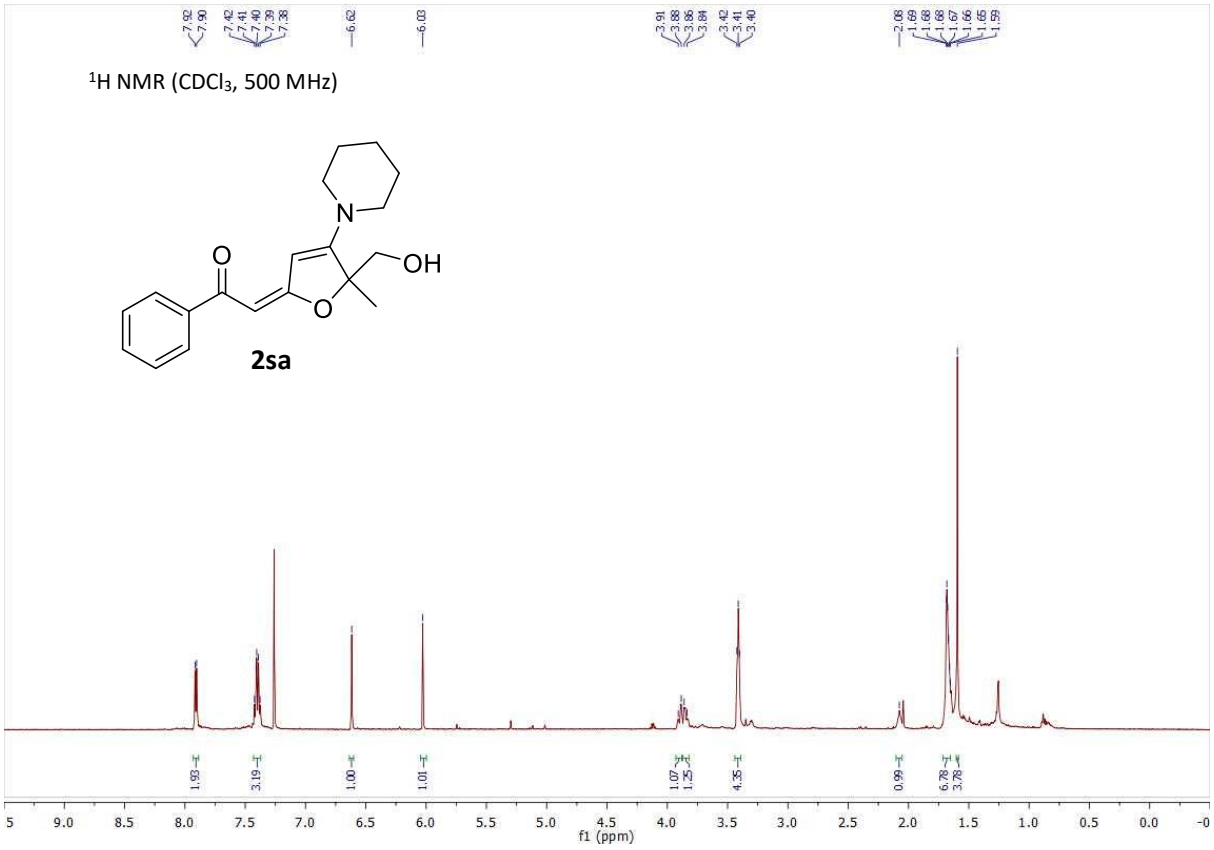
^{13}C NMR ($CDCl_3$, 500 MHz)

2re



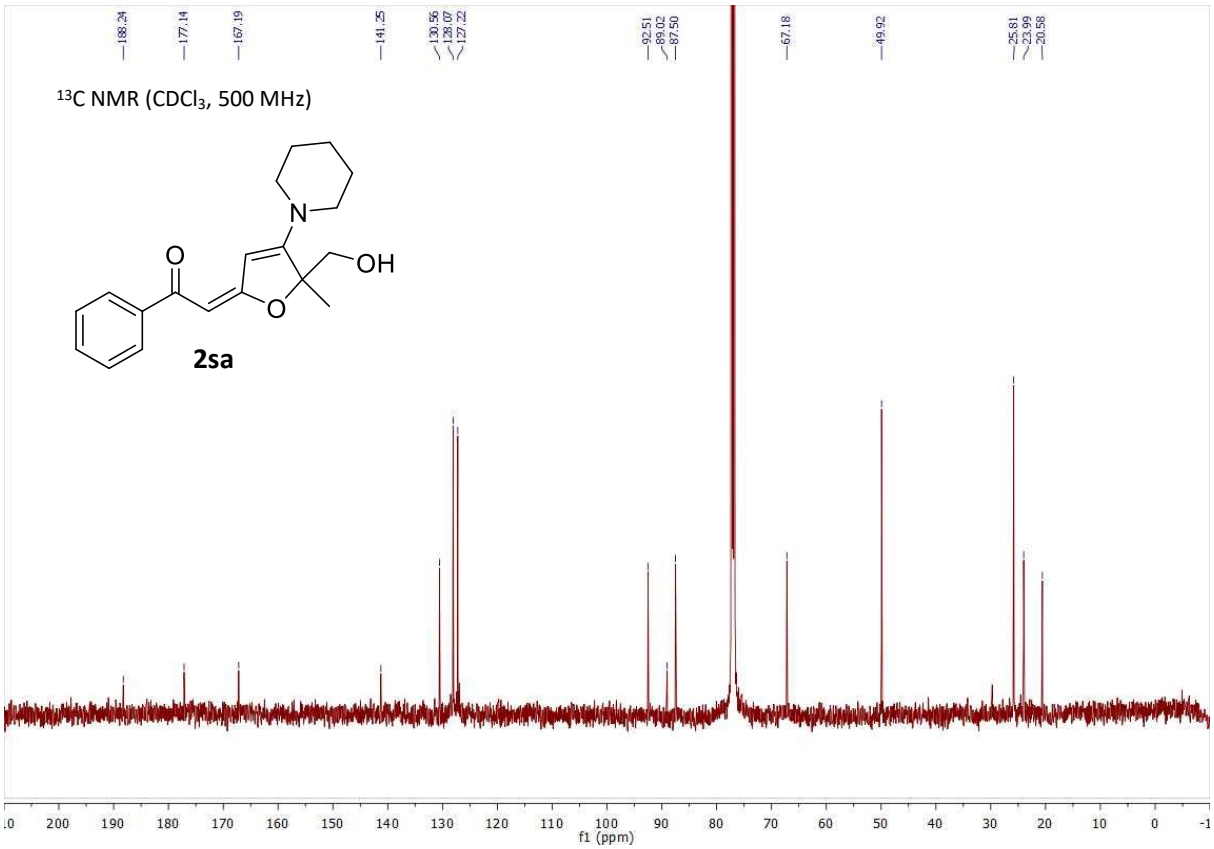
^{1}H NMR ($CDCl_3$, 500 MHz)

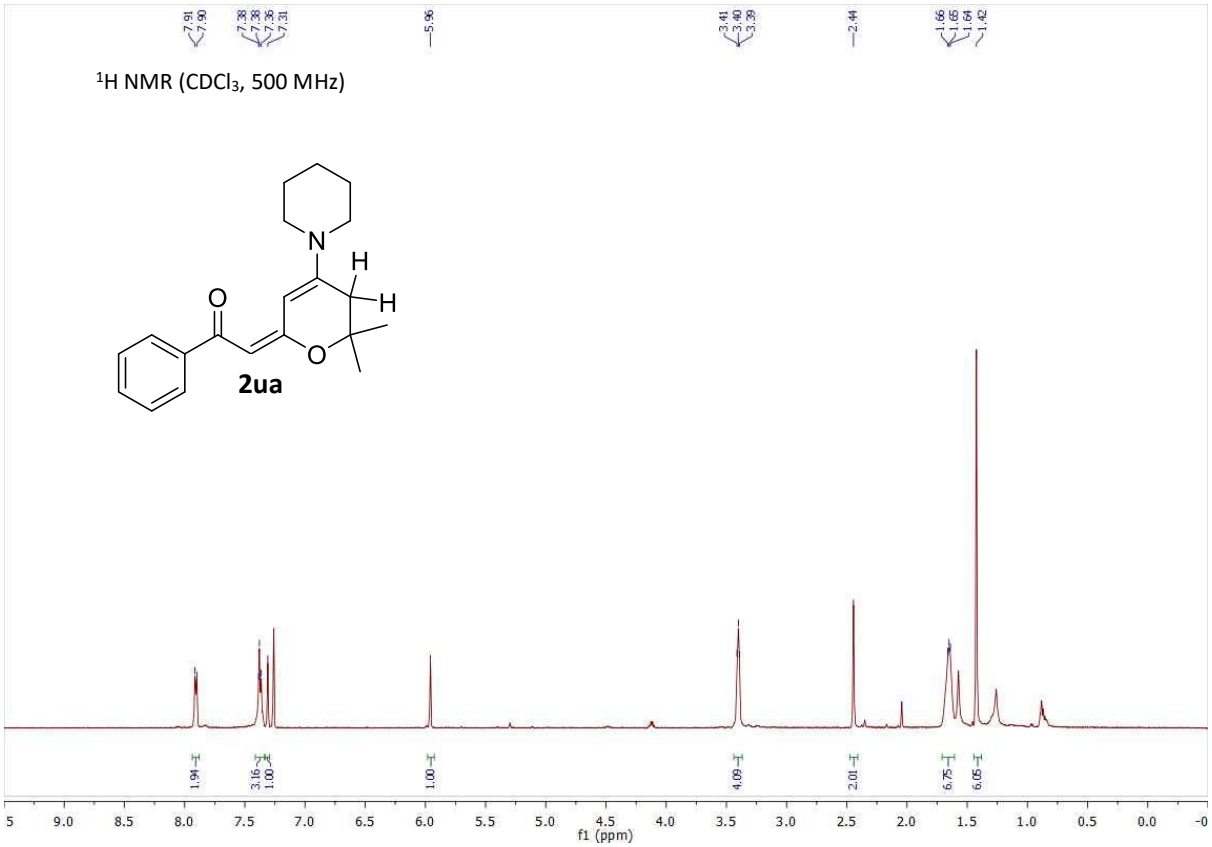
2sa

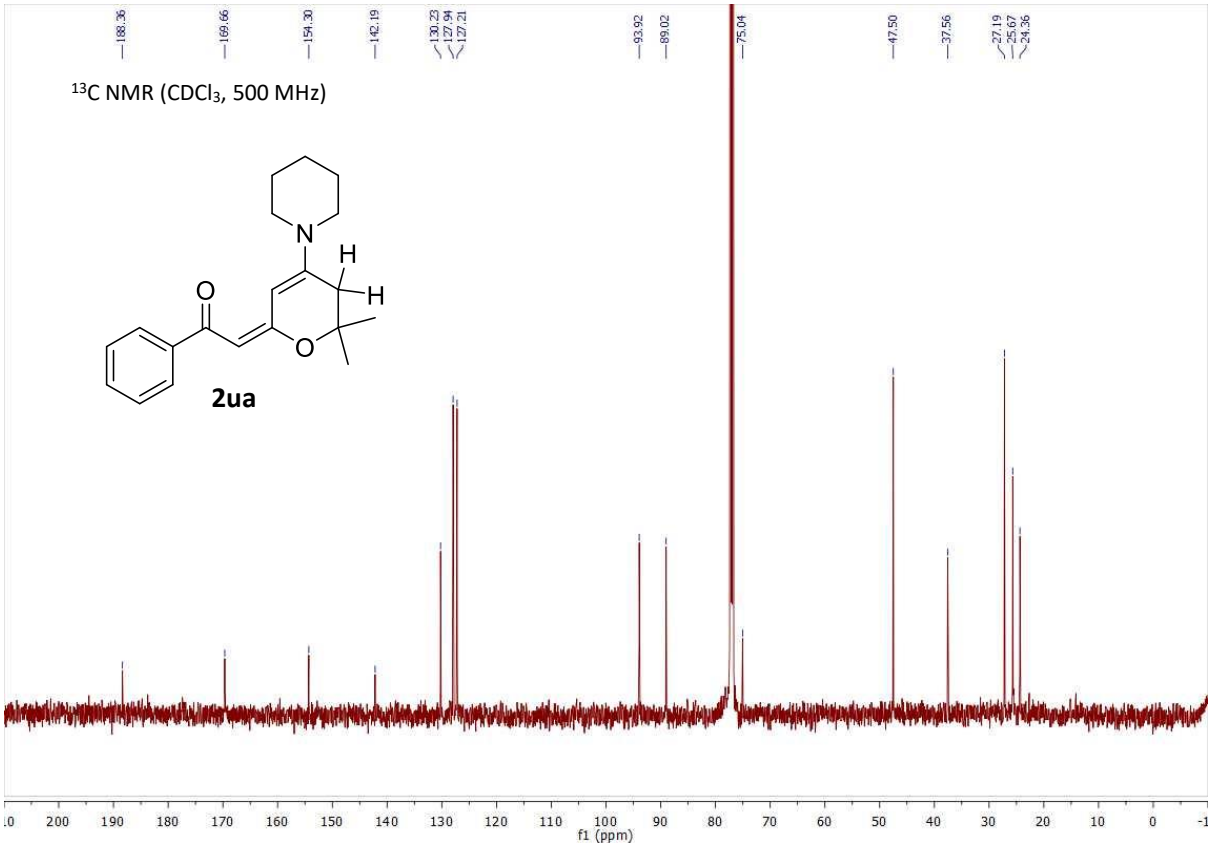


^{13}C NMR ($CDCl_3$, 500 MHz)

2sa




7.91
7.90
7.38
7.38
7.36
7.31
5.96
3.41
3.40
3.39
2.44
1.66
1.65
1.64
1.42
1H NMR (CDCl3, 500 MHz)
N
H
H
O
O
2ua
1.94
3.16
1.00
1.00
4.09
2.01
6.75
6.05
f1 (ppm)


188.36
169.66
154.30
142.19
130.23
127.94
127.21
93.92
89.02
75.04
47.50
37.56
27.19
25.67
24.36
13C NMR (CDCl3, 500 MHz)
N
H
H
O
O
2ua
f1 (ppm)