Supplementary Information (SI) for ChemComm.
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Supporting Information

External photocatalyst-free photocycloaddition between triplet vinylnitrenes with 1,3-biradical character and activated olefins under 420 nm LEDs

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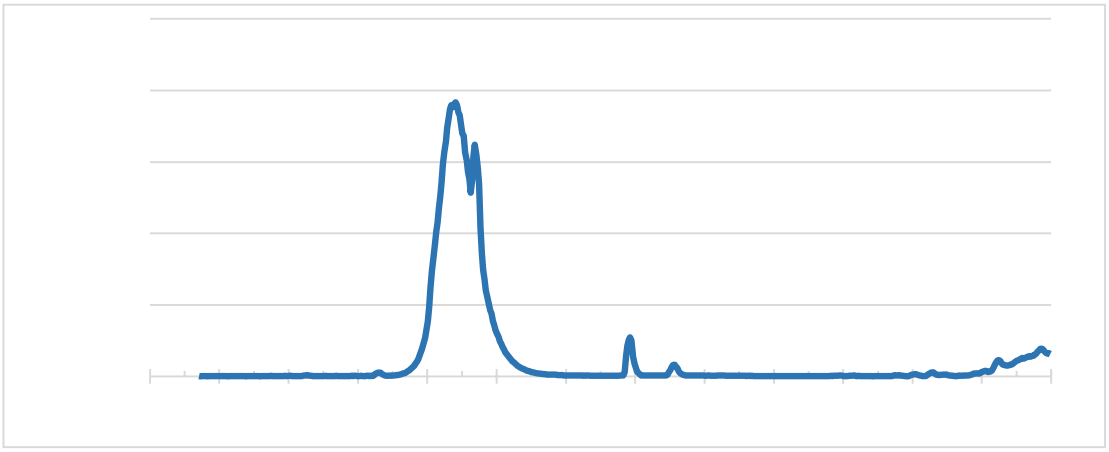
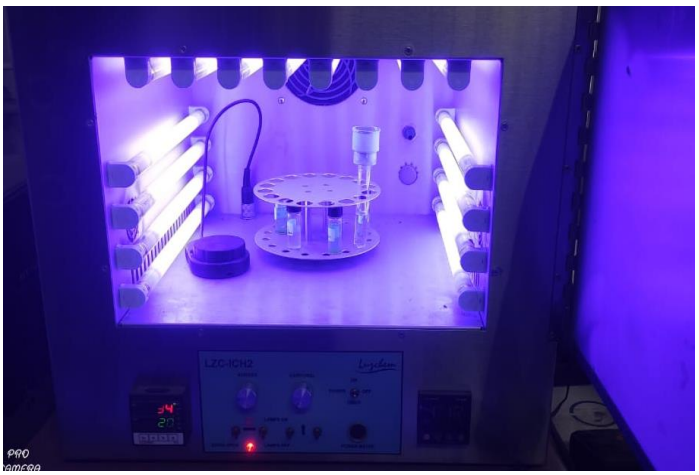
Experimental Section:

General Information: All reactions were achieved in oven-dried glassware. Reagents were bought at the very best commercial quality and used as obtained, unless otherwise certain. Reactions were monitored by using thin layer chromatography (TLC)accomplished on silica gel plates (Merck silica gel 60, f_{254}); the spots have been visualized with UV light (254 and 365 nm) and a solution of 5% H_2SO_4-MeOH or vanillin charring solution as developing. Flash column chromatography turned into performed using 230−400 mesh silica gel. Yields confer with isolated yields after chromatographic purification.^{1}H NMR (600 400 and 300 MHz) and ^{13}C NMR (150 and 101 MHz) spectra were recorded in $CDCl_3$ solvent and are reported relative to the residual solvent signal. Chemical shift (ppm), multiplicity, coupling constant (*J* in Hz), and integration data are presented for ^{1}H-NMR spectra. Chemical shift is used to describe ^{13}C-NMR data, and multiplicity and coupling constant are used to describe compounds containing fluorine ($J_{C\text{-}F}$ in Hz). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS, *m/z*) were recorded using ESI (Q-TOF and Orbitrap, positive ion) mode. Infrared (IR) spectra were recorded on Fourier transform infrared spectroscopy; only intense peaks were reported in terms of frequency of absorption (cm^{-1}). Single-crystal X-ray data were recorded in a diffractometer with MoKα radiation. Melting points were determined in open-end capillary tubes and are uncorrected.

Lamp Type	Luzchem LZC-420	Internal surface	Unpolished scattering aluminum
Filter	None	Chamber Temp.	25˚C
Filter effect	N/A	Measurement date	March 7, 2016
Photo reactor model	LZC- ICH2	Monitored range	235 to 850 nm
Number of lamps	8 over head lamps, Side lamps not used.	Harmonic peak interference	None observed
Measurement distance	~18 cm lamp to target	Resolved peaks	419 (broad), 434, 546, 578, 812, 842nm

Figure 1: Emission spectrum of the utilized Luzchem LZC-420





ESI-01: The safety issues for handling azido compounds[1]
Sodium azide (NaN_3)

Sodium azide is toxic (LD_{50} oral = 27 mg/kg for rats) and can be absorbed through the skin. Appropriate gloves are necessary when using it. It is decomposed explosively upon heating to above 275 °C. Sodium azide is relatively safe especially in aqueous solution, unless acidified to form HN_3, which is volatile and highly toxic. 2.2.

Organic azide

Organic azides are potentially explosive substances that decompose with the slight input of energy from external sources (heat, light, pressure, etc). When the designed organic azides are used for the project, we consider the following equation. It is noted that this equation takes into account all nitrogen atoms in the organic azide, not just those in the azido group.

$\frac{Nc+No}{Nn} \geq 3$ (N: number of the atom, c= carbon, o= oxygen, n=nitrogen)

All organic azides are enough stable to be stored under -20°C for at least 6 months.

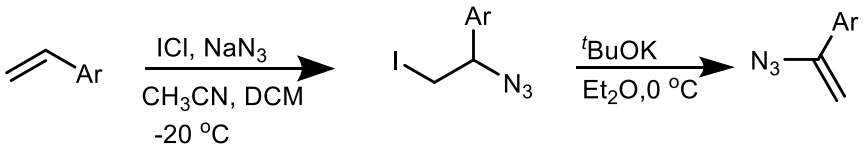
SI-02: General scheme for the synthesis of starting materials:

ESI-02-01: Synthetic procedures for vinyl azide:

1. Sodium azide (1.0 eq, 10 mmol) was dissolved in distilled CH_3CN (20 mL) and cooled at -20 °C, then solution of iodine mono chloride (1.5 eq, 15 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The mixture was stirred at the same temperature. After 90 min, a solution of alkene (1.0 eq, 10 mmol) in CH_2Cl_2 (8 mL) was added slowly, and the mixture was stirred for 1.0 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$, and the organic materials were extracted two times with Et_2O. The combined extracts were

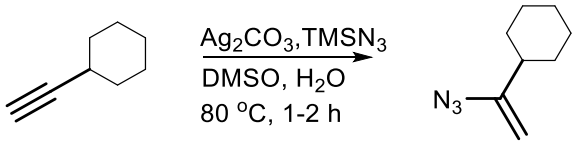
[1] (a) See http://www.ehs.ucsb.edu/units/labsfty/labrsc/factsheets/Azides_FS26.pdf. Date accessed: 01-Aug-2017. (b) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

washed with brine and dried over $MgSO_4$. After the evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification.



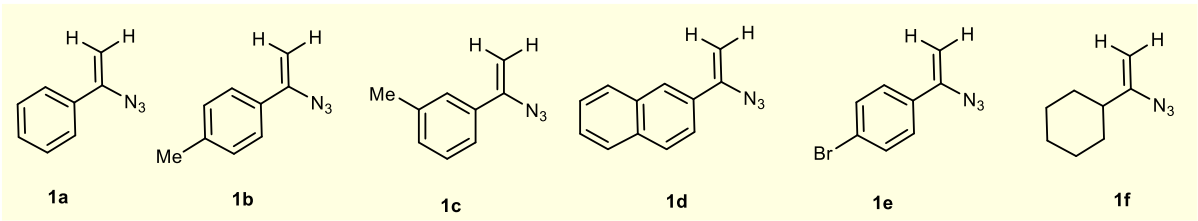
To a solution of the obtained compounds above in Et_2O (25 mL) was added ^tBuOK (1.5 eq,15.0 mmol) at 0 °C, and the mixture was stirred for 1.5 h at the same temperature. The reaction mixture was filtered through a celite pad, and the solvent was removed in vacuo. The resulting crude materials were purified by flash column chromatography (silica gel/*n*-hexane) to give vinyl azides. [2]

2. To a solution of alkyne (0.5 mmol, 1.0 eq), TMS-N_3 (0.132 mL, 1.0 mmol) and H_2O (18 µL, 1.0 mmol) in DMSO (2 mL), Ag_2CO_3 (13.8 mg, 0.05 mmol) was added. The mixture was then heated at 80 °C with an oil bath for 1.0-2.0 h until the substrate was consumed as indicated by TLC. The reaction mixture was cooled to room temperature and taken up by dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product with flash column chromatography (silica gel) and concentration in vacuo.[3]



1a-e was synthesized by **process 1** and **1f** was synthesized by **process 2**

Used vinyl azide:



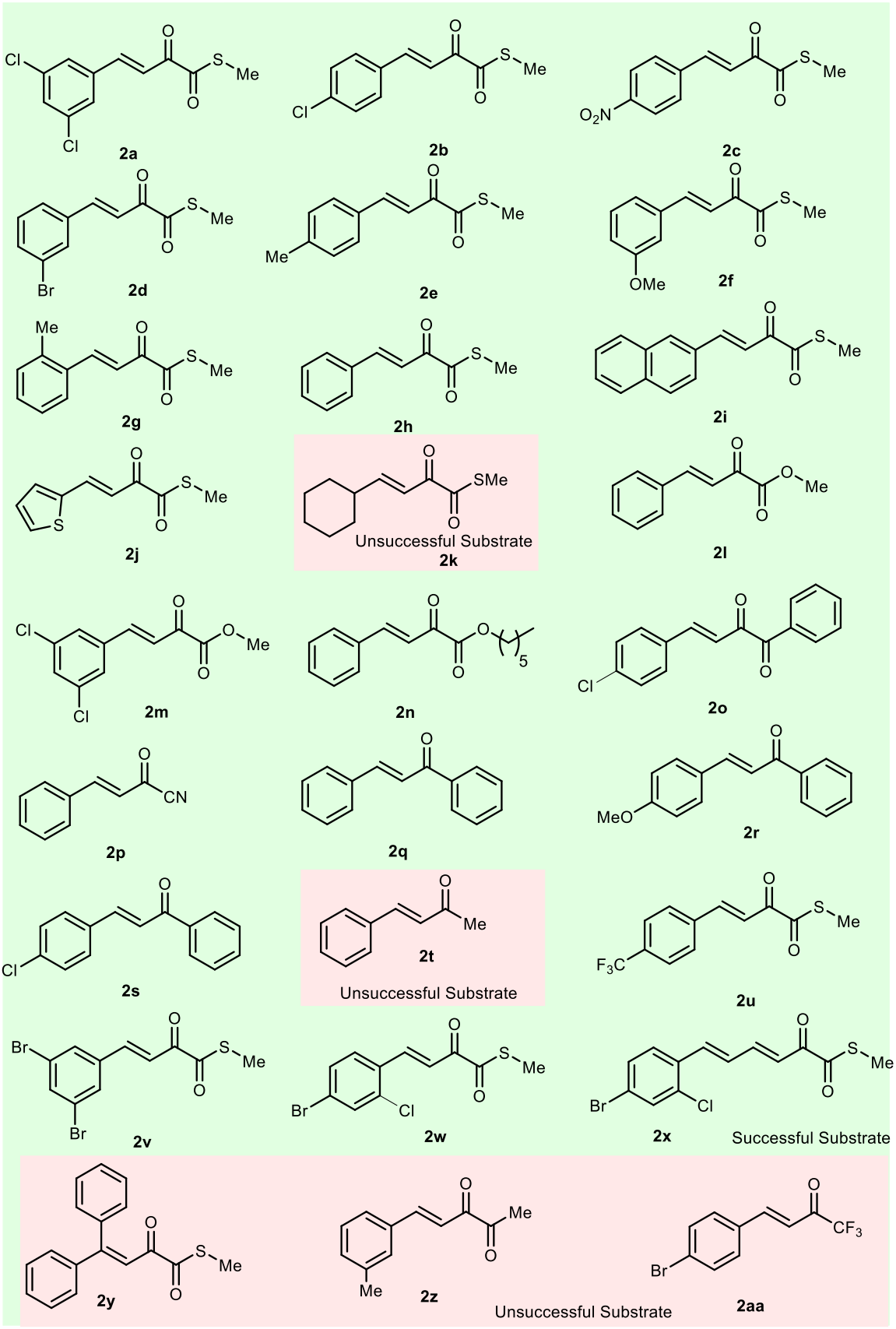
ESI-02-02: Synthetic procedures for α-Ketomethylthioesters (2a-k, 2u-y):

PPh_3•HBr (2 equiv/mmol) was taken in 25 mL two necked round bottom flask under argon atmosphere with condenser. Dry DMSO (2 mL) was added dropwise into it. Corresponding benzylidene acetone (1equiv) was introduced separately into the reaction mixtures at room temperature, and the mixtures were stirred at the same temperature or heated with stirring After completion of the reaction (TLC), saturated NH_4Cl solution was added, and the product

[2] Zhang, F.-L.; Feng, Yi.; Wang, Chiba, S. Amide Synthesis by Nucleophilic Attack of Vinyl Azides. *Angew. Chem., Int. Ed.* **2014**, *53*, 4390.

[3] Liu, Z. - H.; Liao, P.-Q.; Bi, X.-H. General Silver-Catalyzed Hydroazidation of Terminal Alkynes by Combining TMS-N_3 and H_2O: Synthesis of Vinyl Azides. *Org. Lett.* **2014**, *16*, 3668.

Used conjugated polarised alkenes:

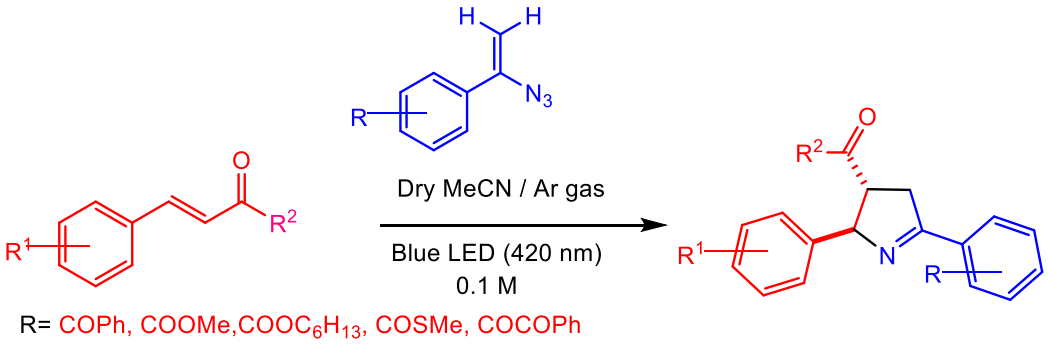


was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified over silica gel column chromatography [230-400; eluent: ethyl acetate/*n*-hexane] to obtain **2a-k, 2u-y.** [4]

As reported in previous literature, **2l-n**[5], **2o**[6], **2p**[7],**2z**[8] and **2aa**[9] were synthesized.

ESI-03: General procedure for the synthesis of 3a-3ad:

Under an argon atmosphere, conjugated enone (50 mg, 1 equiv) was added to a solution of vinyl azide (1.2 equiv) in acetonitrile (0.1 M). It was then irradiated with a 420 nm LED at room temperature (25 ˚C). After the completion reaction (TLC), the crude residue was purified by silica gel column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **3a-3ad**.



ESI-04: General procedure for the synthesis of 4a-4ae:

Under an argon atmosphere, conjugated enone (1 equiv) was added to a solution of vinyl azide (1.2 equiv) in acetonitrile (0.1 M). It was then irradiated with a 420 nm LED at room temperature (25 ˚C). After completion of the reaction (TLC), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DDQ (1.2 eq) was added to the same reaction mixture and stirred at room temperature, maintaining time as mentioned. After completion of the reaction (TLC), the crude residue was purified by silica gel column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **4a-4ae**.

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[4] Mal, K.; Sharma, A.; Maulik, P. R. ; Das, I. PPh_3·HBr-DMSO Mediated Expedient Synthesis of γ-Substituted β, γ-Unsaturated α-Ketomethylthioesters and α-Bromo Enals: Application to the Synthesis of 2-Methylsulfanyl-3(*2 H*)-furanones. *Chem. Eur. J.* **2014**, *20*, 662–667.

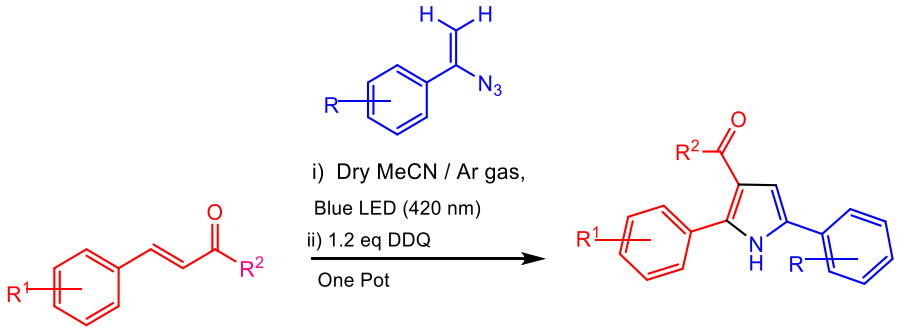
[5] Modrocká, V.; Veverková, E.; Mečiarová, M.; Šebesta, R. Bifunctional Amine-Squaramides as Organocatalysts in Michael/Hemiketalization Reactions of β, γ-Unsaturated α-Ketoesters and α, β-Unsaturated Ketones with 4-Hydroxycoumarins**.** *J. Org. Chem.* **2018**, *83*, 13111– 13120.

[6] Liu, J.; Das, D. K.; Zhang, G.; Yang, S.; Zhang, H.; Fang, X. N-Heterocyclic Carbene-Catalyzed Umpolung of β, γ-Unsaturated 1,2-Diketones. *Org. Lett.* **2018**, *20*, 64– 67.

[7] Goudedranche, S.; Bugaut, X.; Constantieux, T.; Bonne, D.; Rodriguez, J. α, β-Unsaturated Acyl Cyanides as New Bis-Electrophiles for Enantioselective Organocatalyzed Formal [3+3] Spiroannulation. *Chem. Eur. J.* **2014**, *20*, 410-415.

[8] Bleger, D.; Hecht, S. Visible-Light-Activated Molecular Switches. *Angew. Chem., Int. Ed.* **2015**, *54*, 11338–11349.

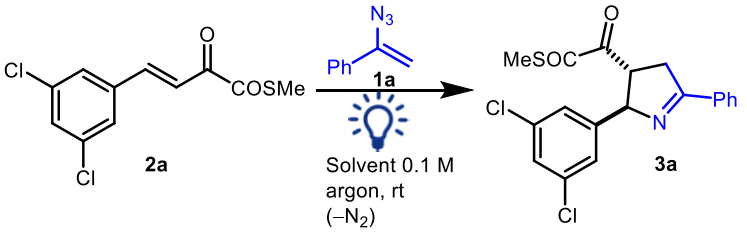
[9] Crotti, S.; Belletti, G.; Di Iorio, N.; Marotta, E.; Mazzanti, A.; Righi, P.; Bencivenni, G. Asymmetric Vinylogous Aldol Addition of Alkylidene Oxindoles on Trifluoromethyl-α, β-Unsaturated Ketones. *RSC Adv.* **2018**, *8*, 33451-33458.

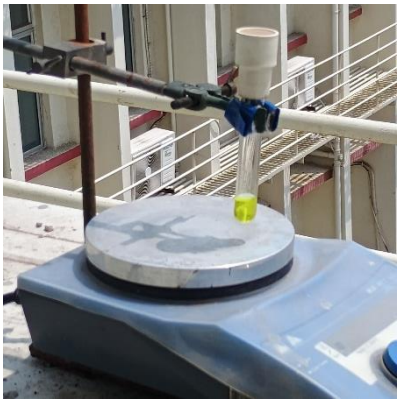


ESI-05: Optimization of the reaction conditions:

ESI-05-01: Screening of solvents and light:

Sun light Reaction





Entries	hv (nm)	Solvent	Time (h)	Yield **3a** (%)[b]
1	420 nm LED	DMSO	12	43
2	420 nm LED	EtOAc	10	58
3	420 nm LED	THF	10	82
4	420 nm LED	MeCN	10	94
5	420 nm LED	DCM	8	42
6	420 nm LED	$CHCl_3$	12	55
7	420 nm LED	DCE	12	64
8	420 nm LED	MeOH	5	5[c]
9	dark (without light)	MeCN	10	0[d]
10	390 nm LED	MeCN	10	42
11	456 nm LED	MeCN	12	54
12	Sunlight	MeCN	2	63

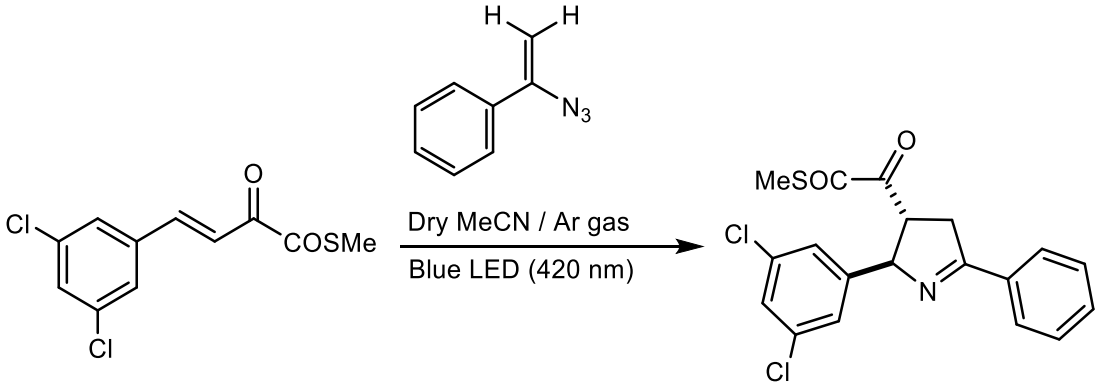
[a]Reaction Conditions: **1a** (0.13 mmol) and **2a** (0.11 mmol) in solvent 0.1 M concentration was irradiated under a LED at room temperature (25 °C) under argon atmosphere. [b]Isolated yield. [c]Decomposition. [d]Unreacted **2a** isolated.

ESI-05-02: Screening of Concentration:

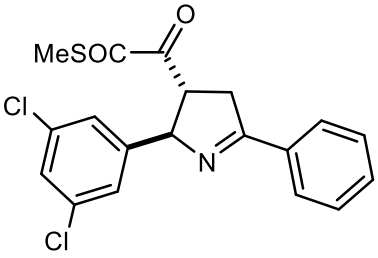
Entries	Volume	Concentration	Yeild (%)[b]
1	1 ml	0.1 M	94
2	2 ml	54 mM	93
3	3 ml	36 mM	85
4	4 ml	27 mM	81
5	5 ml	21 mM	76

[a]Reaction Conditions: **1a** (0.13 mmol) and **2a** (0.11 mmol) in mentioned solvent was irradiated under a LED at room temperature (25 °C) under argon atmosphere. [b]Isolated yeild.

ESI-06: Analytical and spectral data of **3a**



***S*-methyl 2-(2-(3,5-dichlorophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3a:** Prepared according to the general procedure discussed above: reaction time, 10 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid (67 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.90 (m, 2 H), 7.51 – 7.43 (m, 3 H), 7.27 (t, *J* = 2.0 Hz, 1 H), 7.17 (d, *J* = 2.0 Hz, 2 H), 5.55 (dt, *J* = 6.0, 2.0 Hz, 1 H), 3.90 (ddd, *J* = 10.0, 6.4, 5.6 Hz, 1 H), 3.50 (ddd, *J* = 17.2, 10.0, 2.0 Hz, 1 H), 3.34 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.40 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.5, 191.6, 172.5, 145.7, 135.3, 133.0, 131.6, 128.8 (2 CH), 128.2 (3 CH), 127.9, 125.4 (2 CH), 76.3, 52.1, 38.5, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{16}Cl_2NO_2S$ [*M* + H]$^+$: 392.0279; found: 392.0277.



^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3a**

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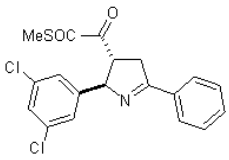

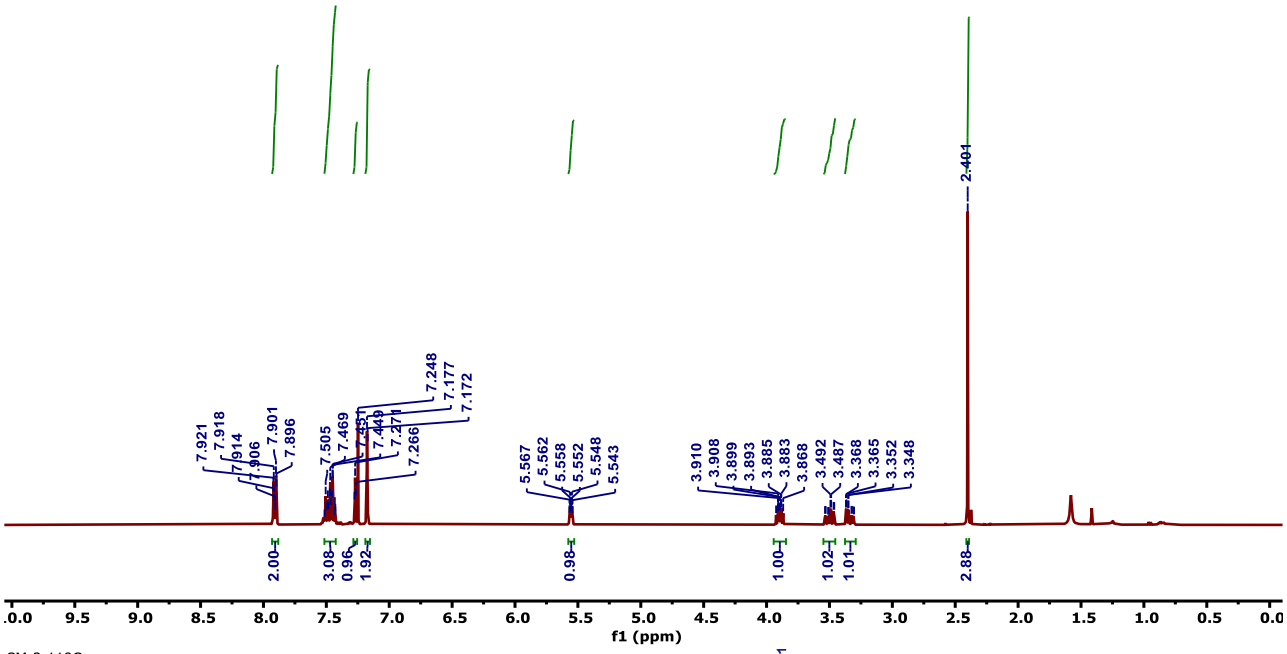

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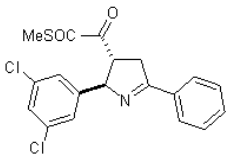
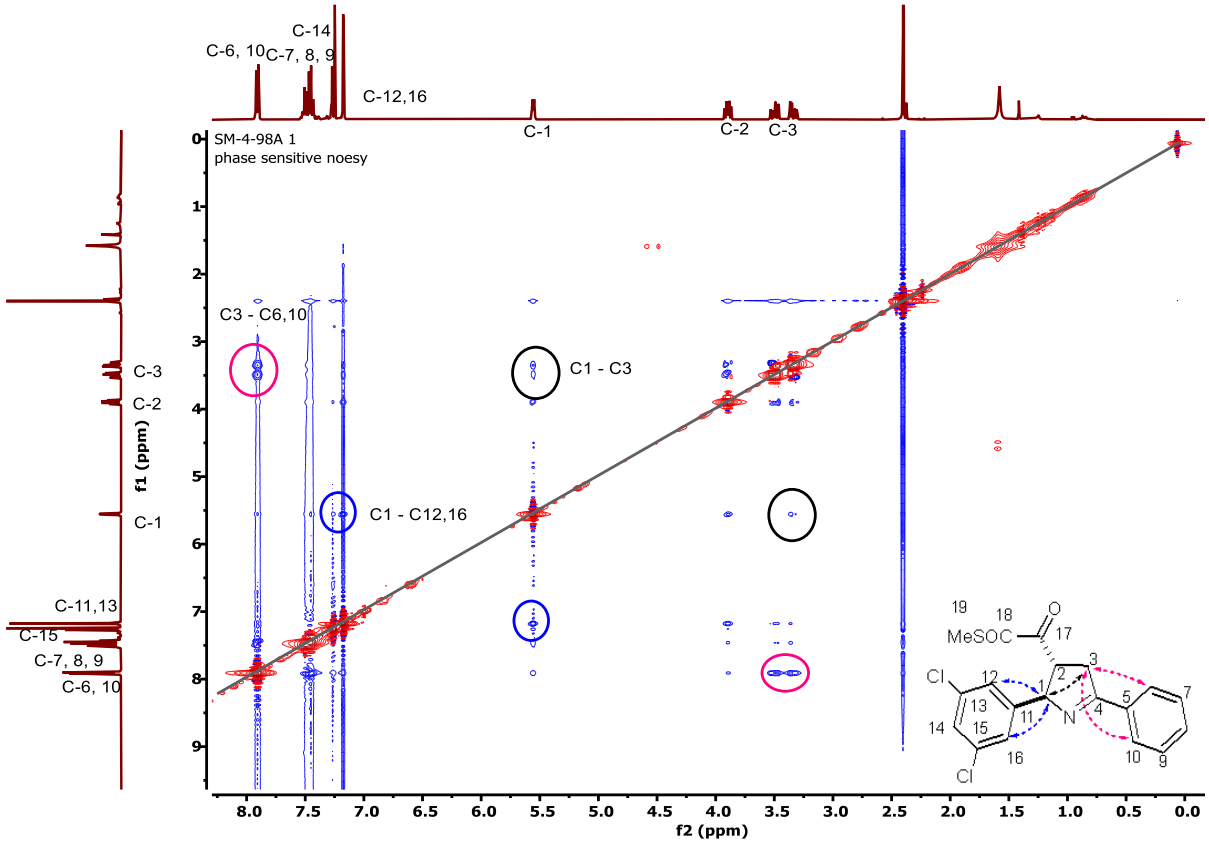
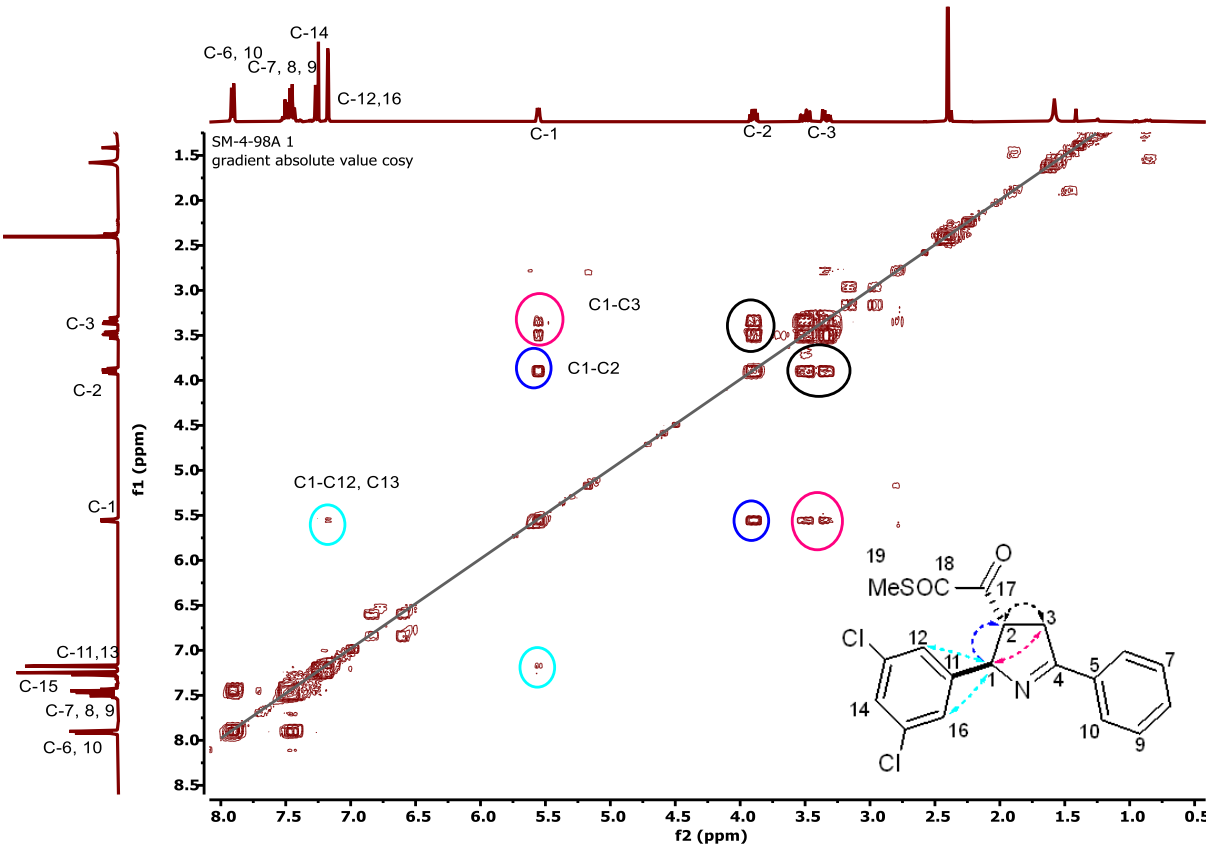
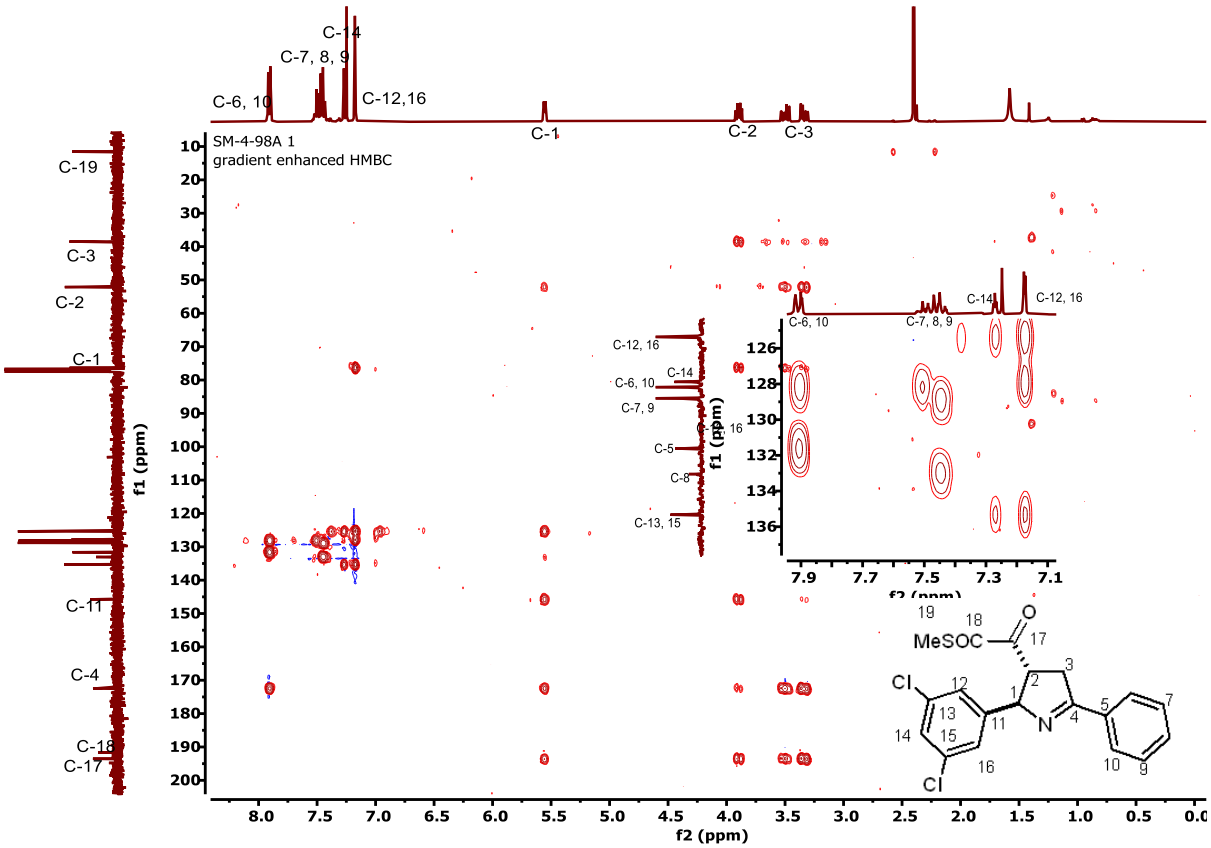


NOESY, COSY, HSQC, and HMBC (400 MHz, $CDCl_3$) NMR spectra of **3a:**



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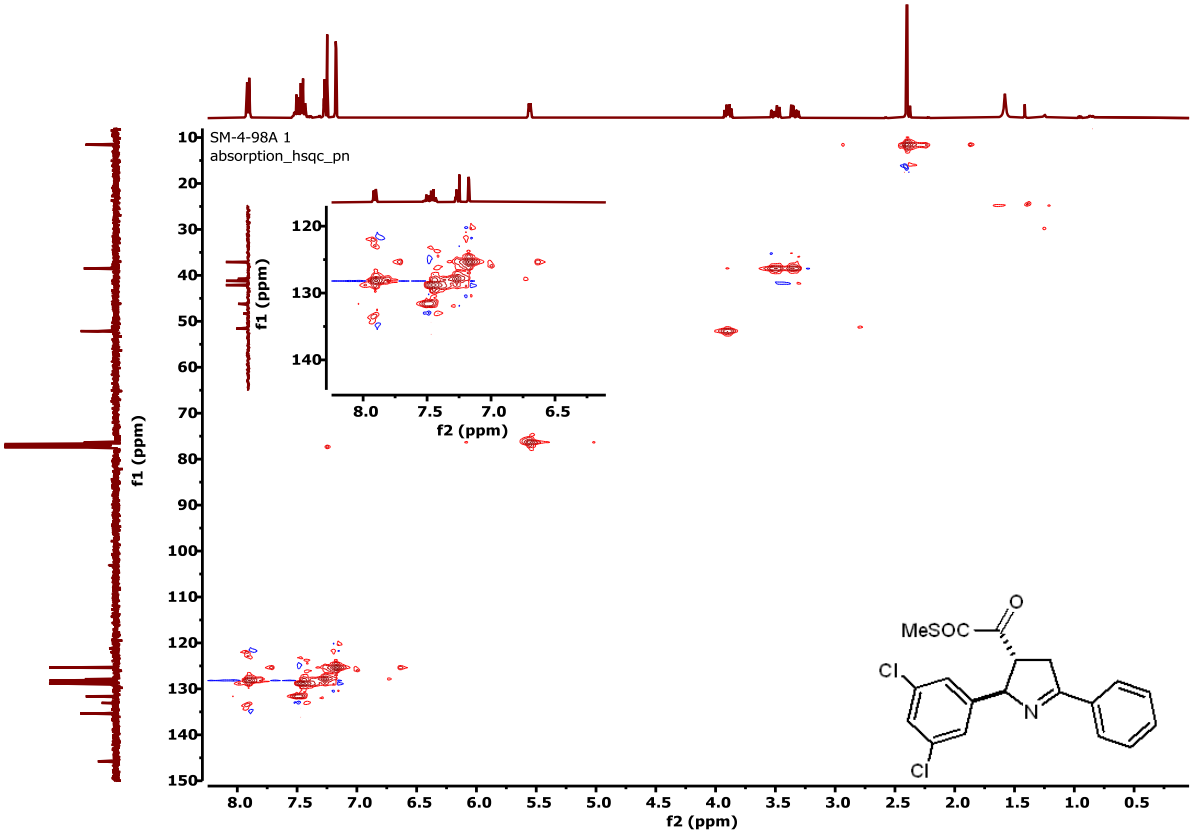
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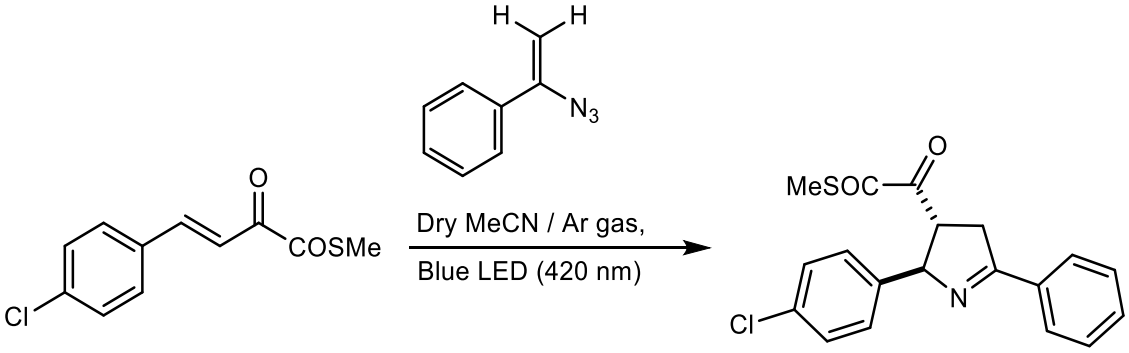
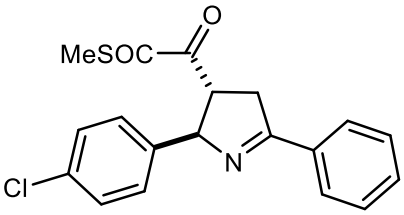
ESI-07: Analytical and spectral data of **3b**



***S*-methyl 2-(2-(4-chlorophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate**



3b: Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow liquid (55 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.91 (m, 2 H), 7.50 – 7.43 (m, 3 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H).5.58 (d, *J* = 5.6 Hz, 1 H), 3.95 – 3.90 (m, 1 H), 3.46 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.37 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.39 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.9, 191.7, 171.9, 140.8, 133.5, 133.3, 131.4, 128.9 (2 CH), 128.8 (2 CH), 128.1 (4 CH), 77.0, 52.23, 38.3, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{17}ClNO_2S$ [*M* + H]$^+$: 358.0668; found: 358.0668.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3b**

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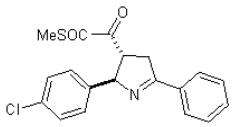

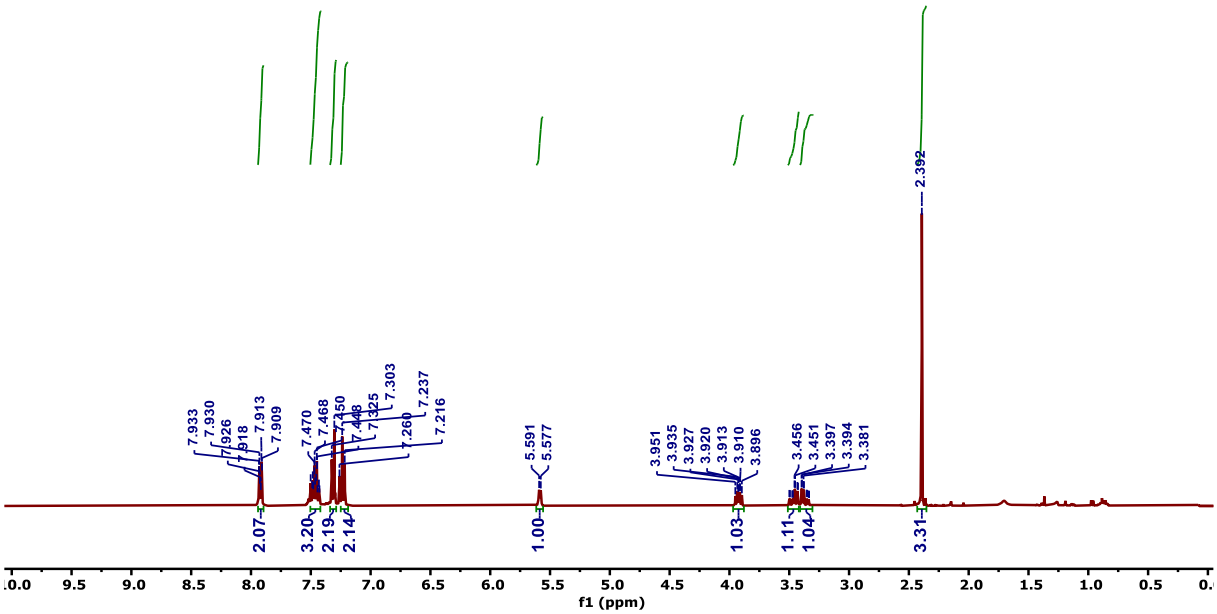

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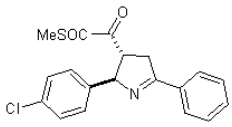
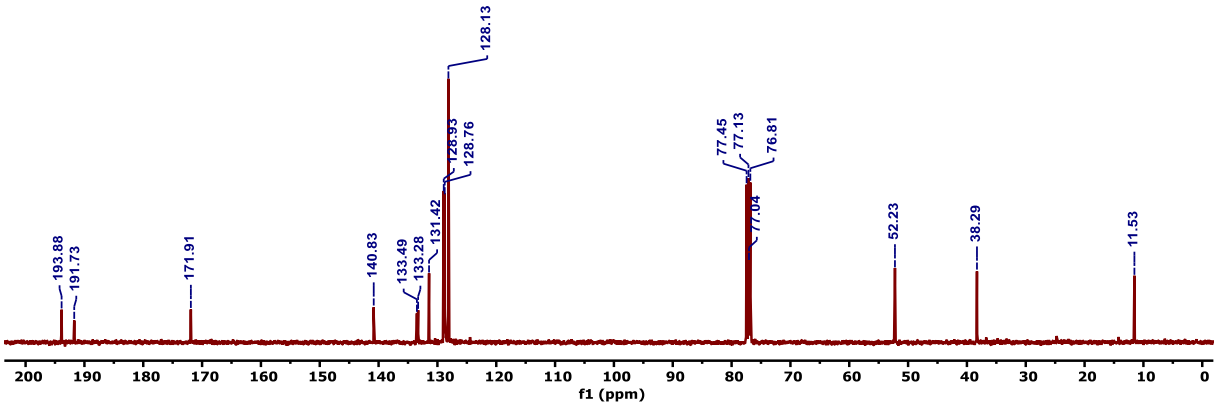
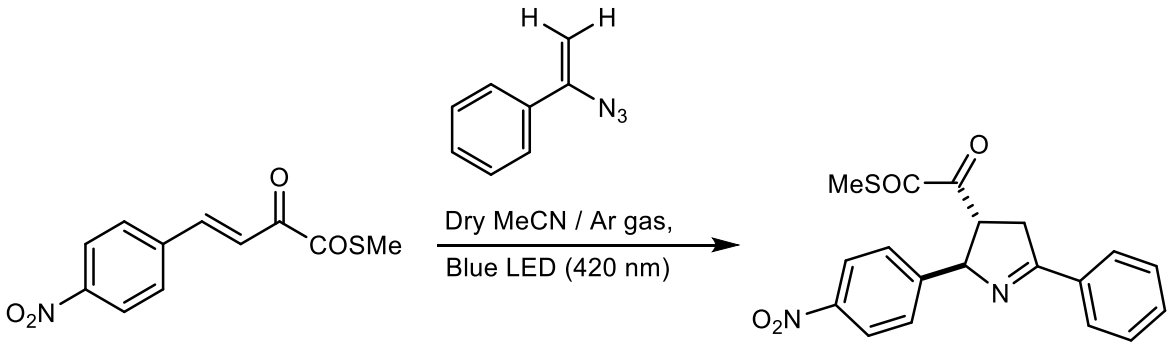
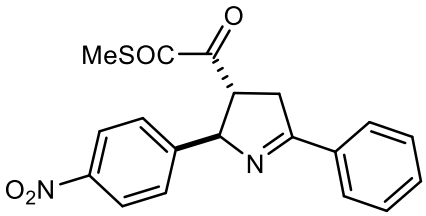




ESI-08: Analytical and spectral data of **3c**

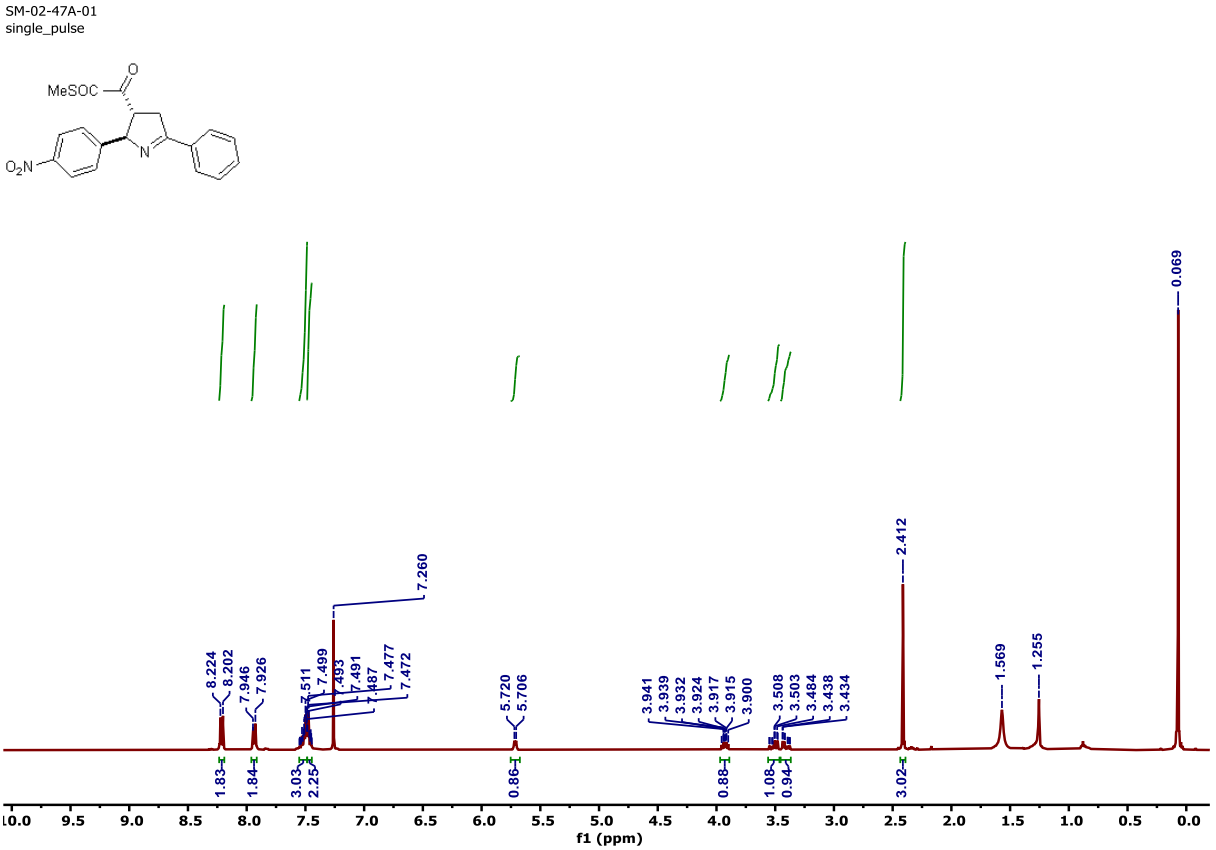


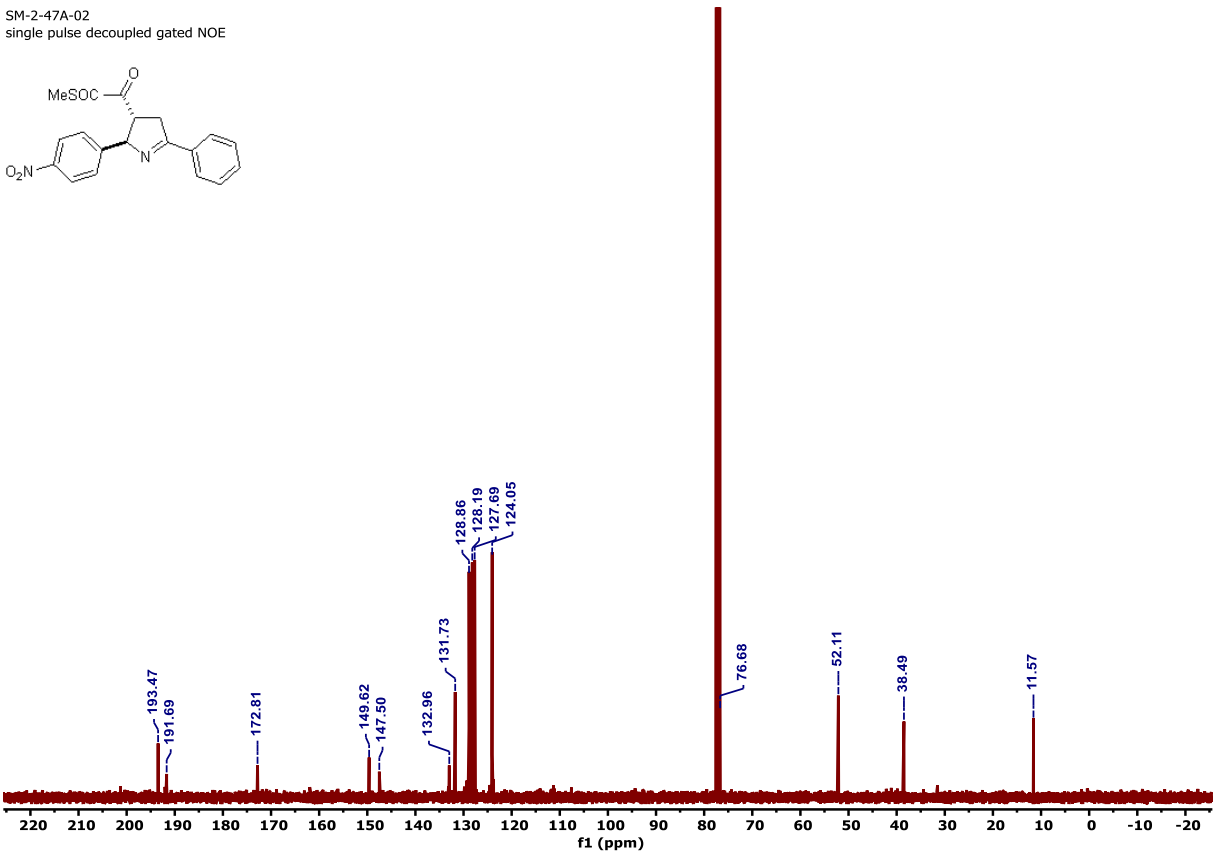
***S*-methyl 2-(2-(4-nitrophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate**



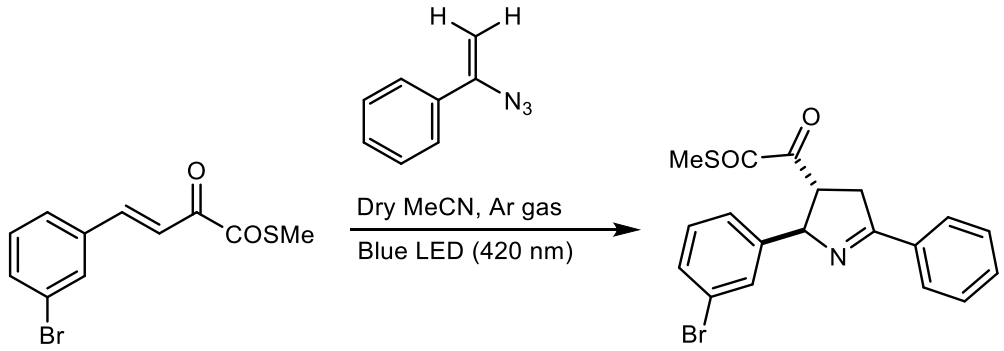
3c: Prepared according to the general procedure discussed above: reaction time, 8 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (15%); yellow gum (47 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.8 Hz, 2 H), 7.94 (d, *J* = 8.2 Hz, 2 H), 7.55 – 7.49 (m, 3 H), 7.48 – 7.45 (m, 2 H), 5.71 (d, *J* = 5.6 Hz, 1 H), 3.93 (ddd, *J* = 9.6, 6.8, 6.0 Hz, 1 H), 3.51 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.41 (ddd, *J* = 17.2, 6.8, 1.6 Hz, 1 H), 2.41 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.5, 191.7, 172.8, 149.6, 147.5, 133.0, 131.7, 128.9 (2 CH), 128.2 (2 CH), 127.7 (2 CH), 124.1 (2 CH), 76.7, 52.1, 38.5, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{17}N_2O_4S$ [*M* + H]$^+$: 369.0909; found: 369.0908.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3c**

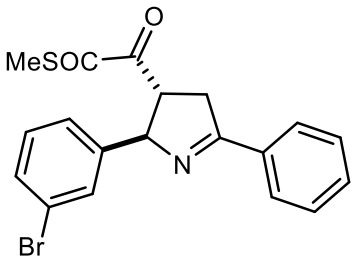




ESI-09: Analytical and spectral data of **3d**

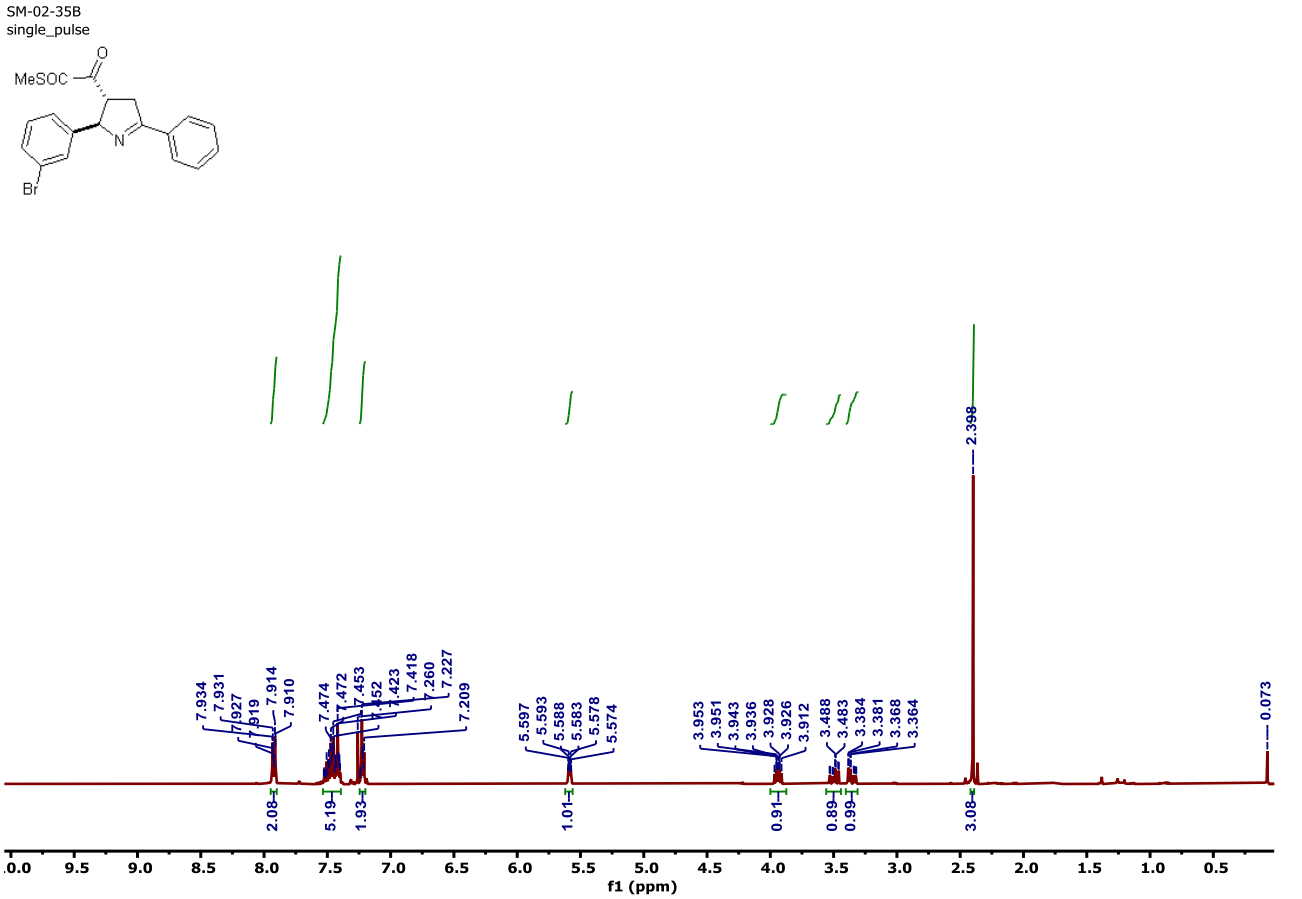


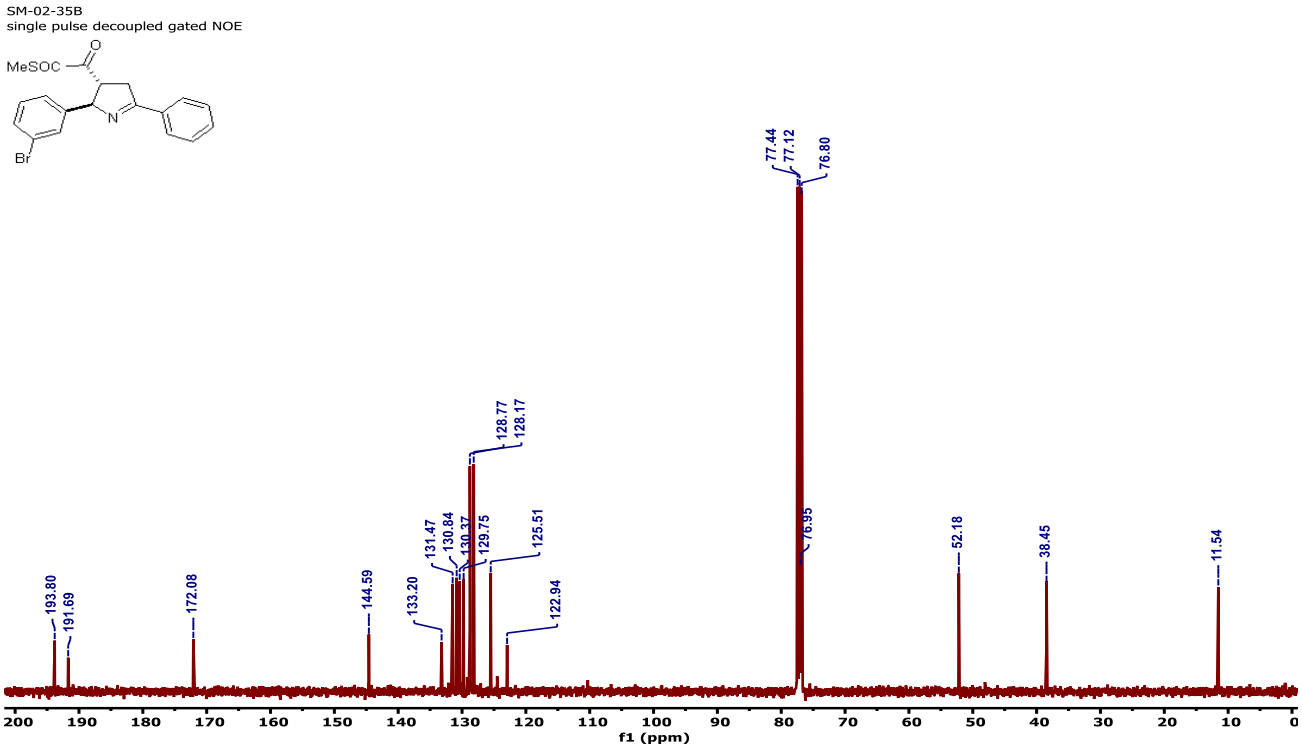
***S*-methyl 2-(2-(3-bromophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate**



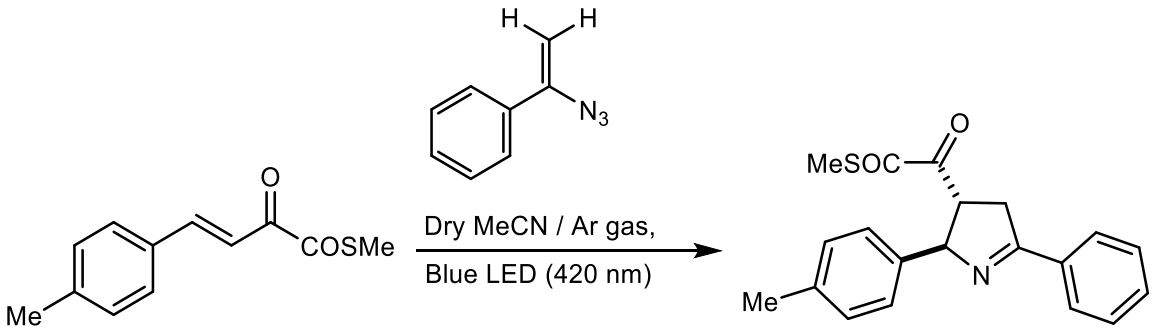
3d: Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow liquid (54 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.91 (m, 2 H), 7.50 – 7.40 (m, 5 H), 7.23 – 7.21 (m, 2 H), 5.59 (dt, *J* = 5.6, 1.6 Hz, 1H), 3.94 (ddd, *J* = 9.6, 6.4, 5.6 Hz, 1 H), 3.50 (ddd, *J* = 17.6, 10.0, 2.4 Hz, 1H), 3.35 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.40 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.8, 191.7, 172.1, 144.6, 133.2, 131.5, 130.8, 130.4, 129.75, 128.8 (2 CH), 128.2 (2 CH), 125.5, 122.9, 76.9, 52.2, 38.4, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{17}BrNO_2S$ [*M* + H]$^+$: 402.0163; found: 402.0161.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3d**

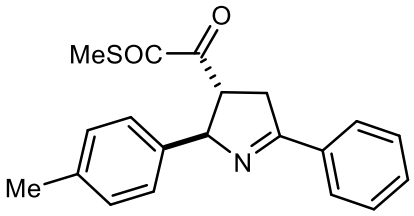




ESI-10: Analytical and spectral data of **3e**



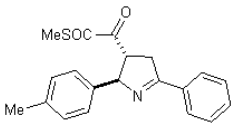
***S*-methyl 2-oxo-2-(5-phenyl-2-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)ethanethioate 3e:**

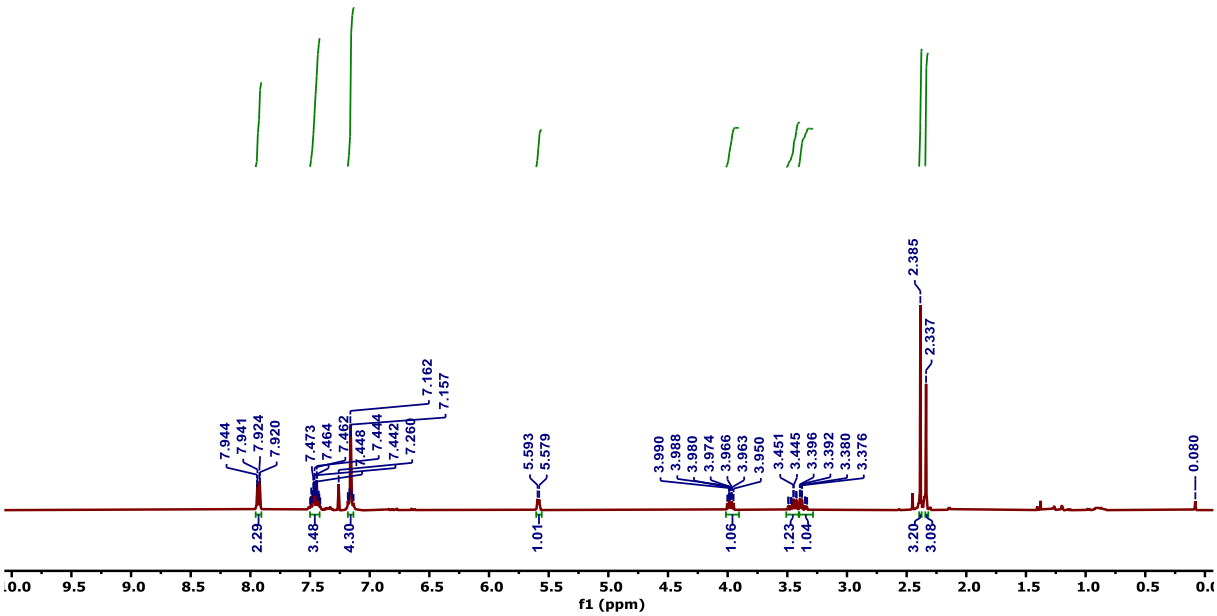


Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow liquid (53 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.90 (m, 2 H), 7.49 – 7.40 (m, 3 H), 7.18 – 7.13 (m, 4 H), 5.59 (d, *J* = 5.6 Hz, 1 H), 3.98 (ddd, *J* = 9.2, 6.0, 5.2 Hz, 1 H), 3.46 (ddd, *J* = 17.2, 9.6, 2.4 Hz, 1 H), 3.36 (ddd, *J* = 17.2, 6.4, 1.6 Hz, 1 H), 2.39 (s, 3 H), 2.34 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.2, 191.8, 171.3, 139.3, 137.4, 133.5, 131.2, 129.5 (2 CH), 128.7 (2 CH), 128.1 (2 CH), 126.6 (2 CH), 77.7, 52.2, 38.2, 21.2, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{20}NO_2S$ [*M* + H]$^+$: 338.1214; found: 338.1217.

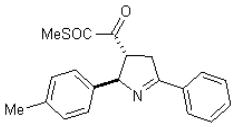
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3d**

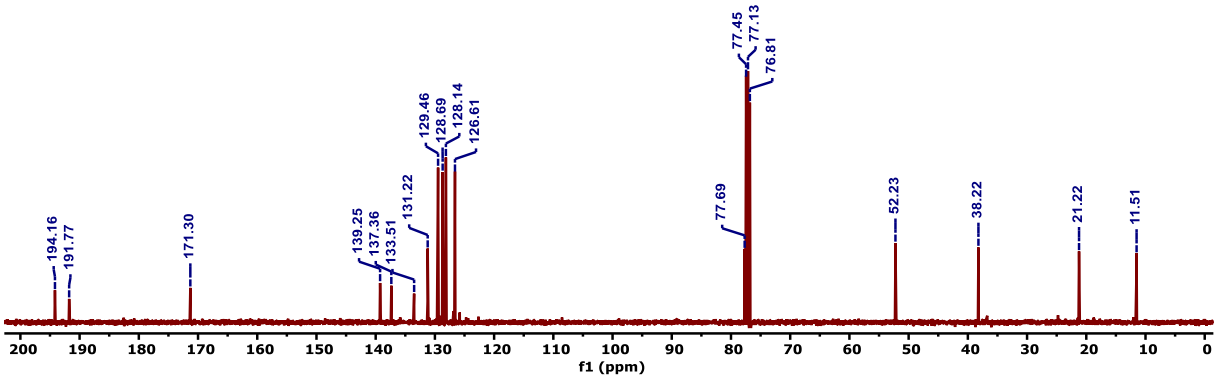
JAY-2-34B
single_pulse



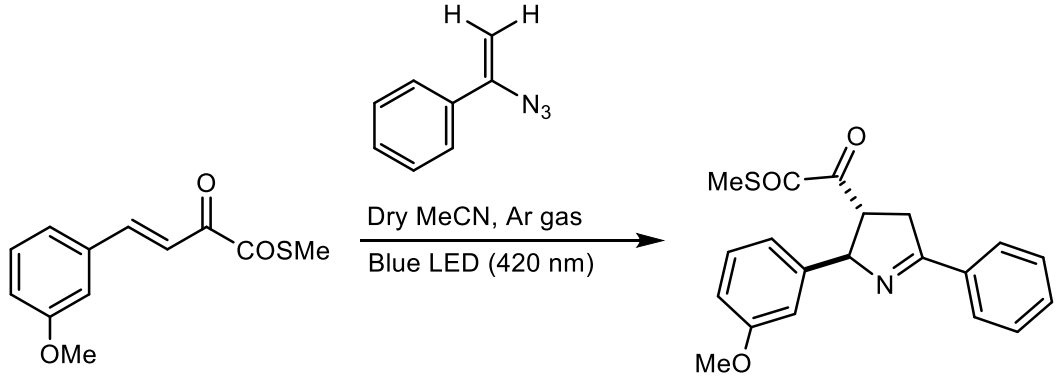


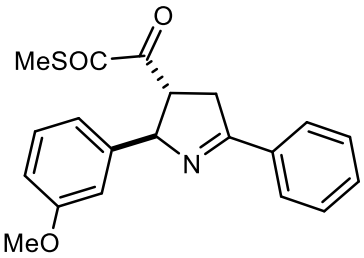
JAY-2-34B
single pulse decoupled gated NOE





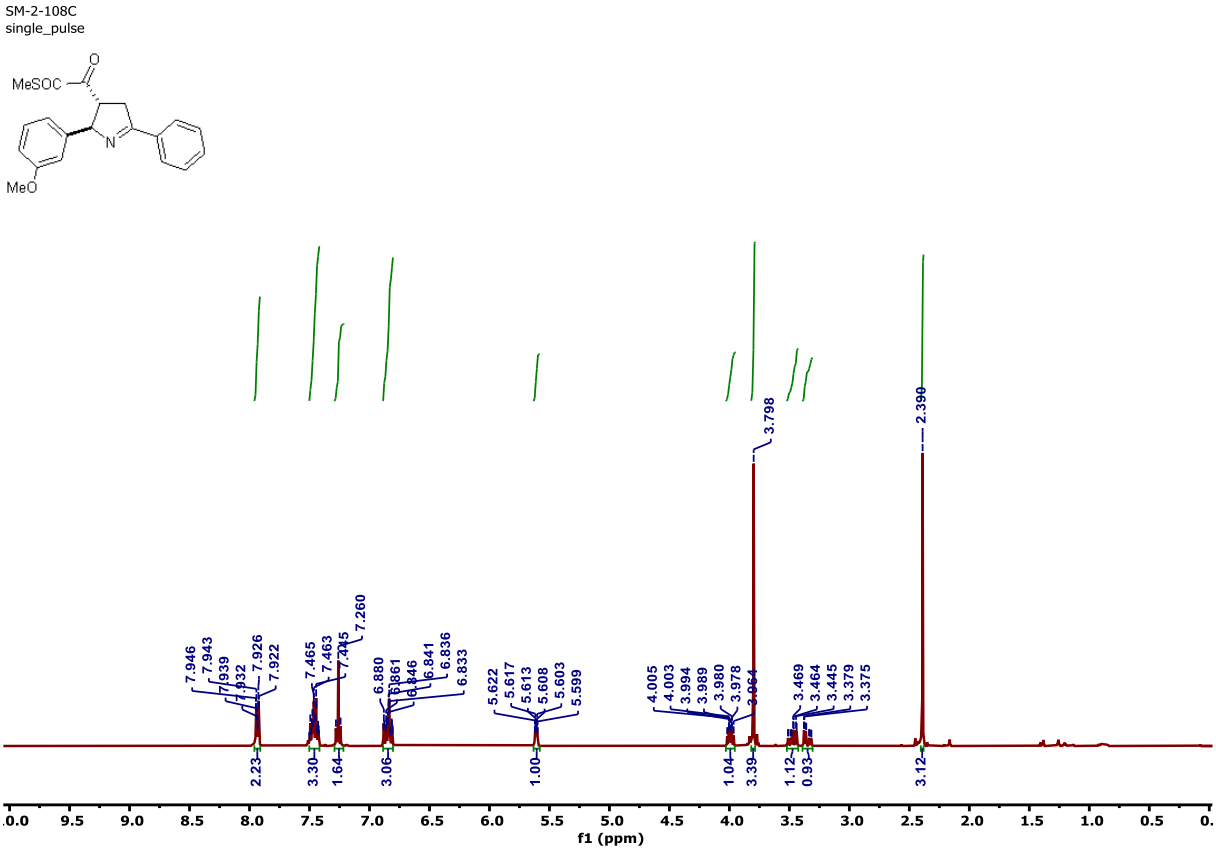
ESI-11: Analytical and spectral data of **3f**

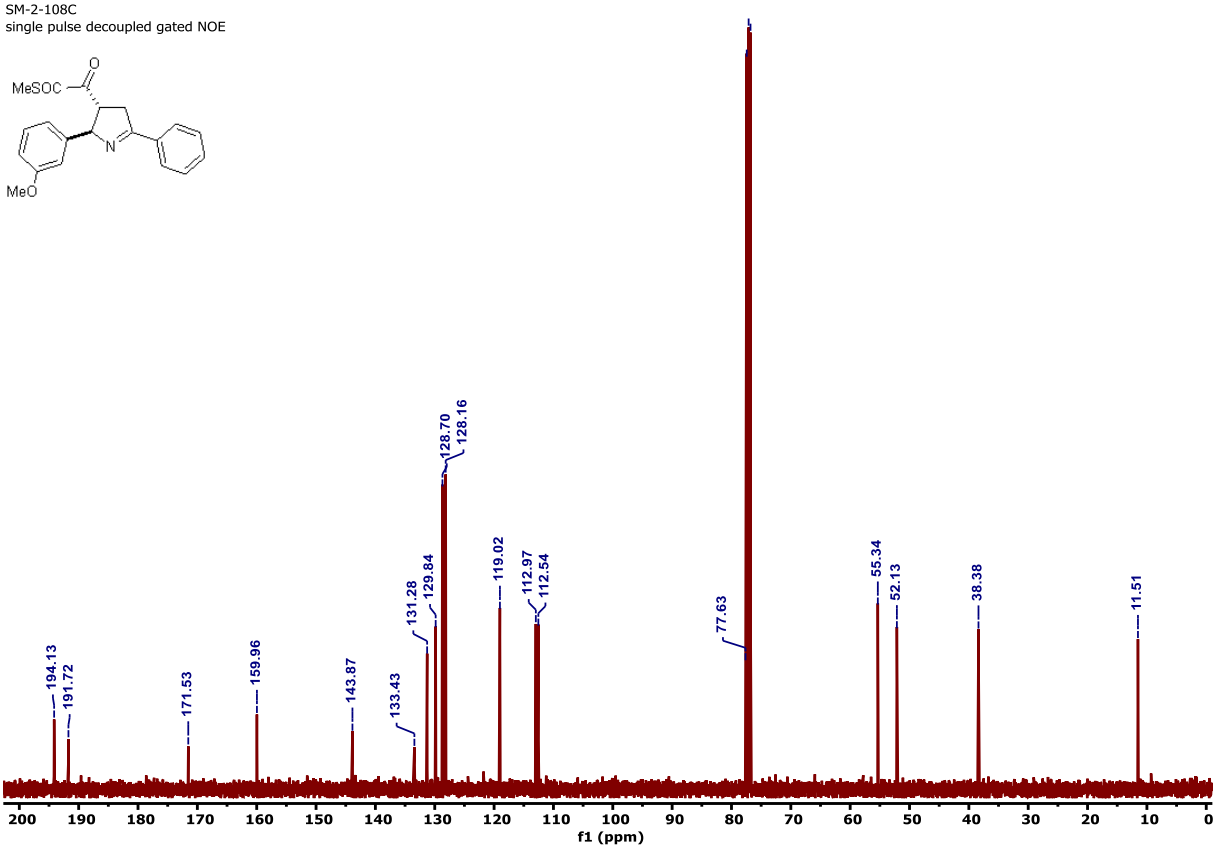




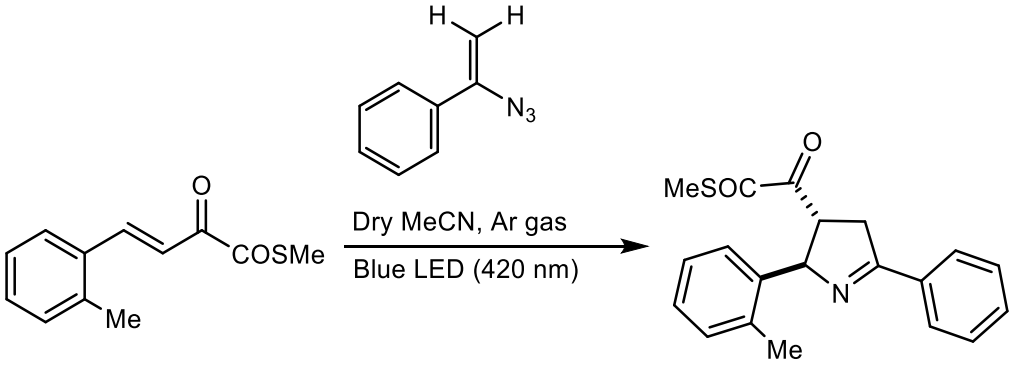
***S*-methyl 2-(2-(3-methoxyphenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3f:** Prepared according to the general procedure discussed above: reaction time, 16 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow liquid (60 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.92 (m, 2 H), 7.50 – 7.42 (m, 3 H), 7.26 (t, *J* = 8.0 Hz, 1 H), 6.88 – 6.81 (m, 3 H), 5.61 (dt, *J* = 5.6, 2.0 Hz, 1 H), 3.99 (ddd, *J* = 10.0, 6.4, 5.6 Hz, 1 H), 3.80 (s, 3 H), 3.48 (ddd, *J* = 17.2, 10.0, 2.0 Hz, 1 H), 3.35 (ddd, *J* = 17.2, 6.4, 1.6 Hz, 1 H), 2.39 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.1, 191.7, 171.5, 160.0, 143.9, 133.4, 131.3, 129.8, 128.7 (2 CH), 128.2 (2 CH), 119.0, 113.0, 112.5, 77.6, 55.3, 52.1, 38.4, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{20}NO_3S$ [*M* + H]$^+$: 354.1164; found: 354.1158.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3f**

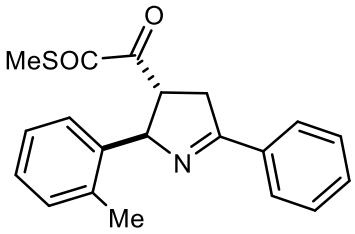




ESI-12: Analytical and spectral data of **3g**

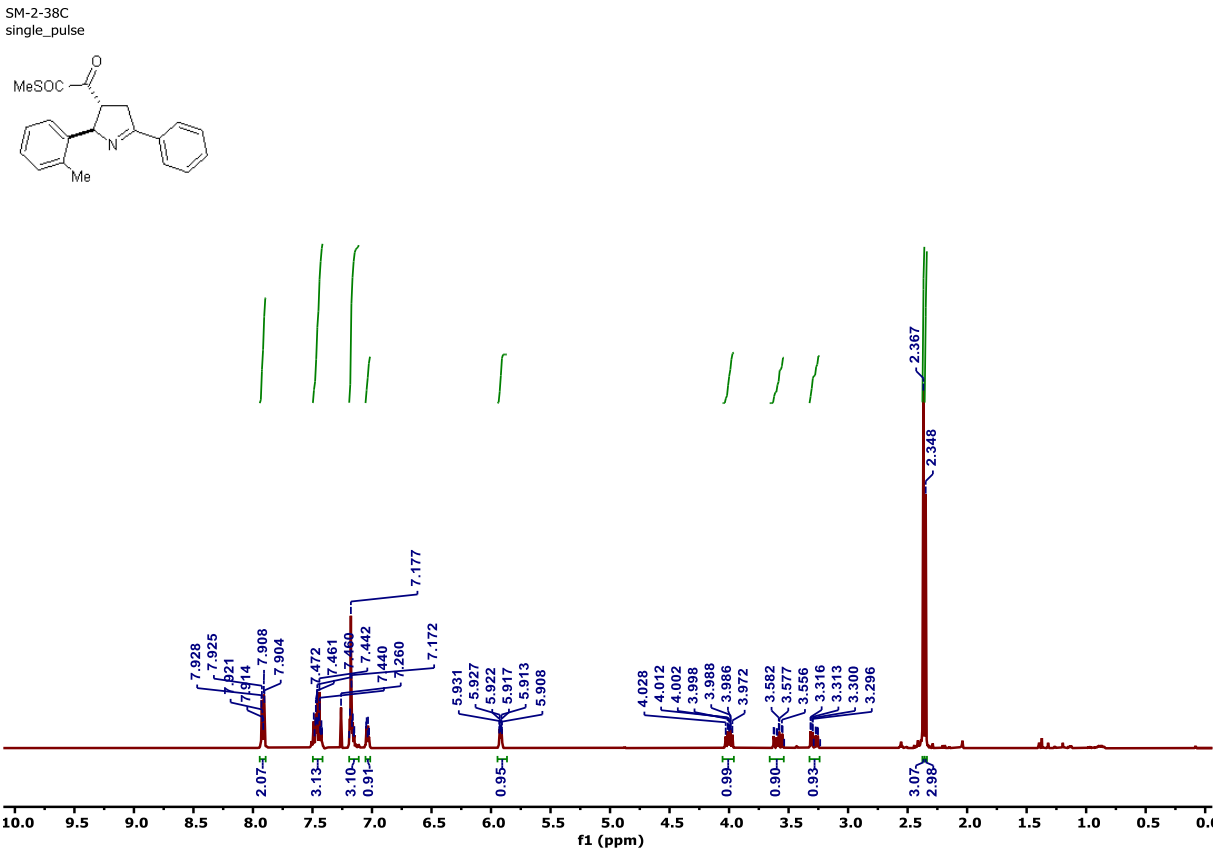


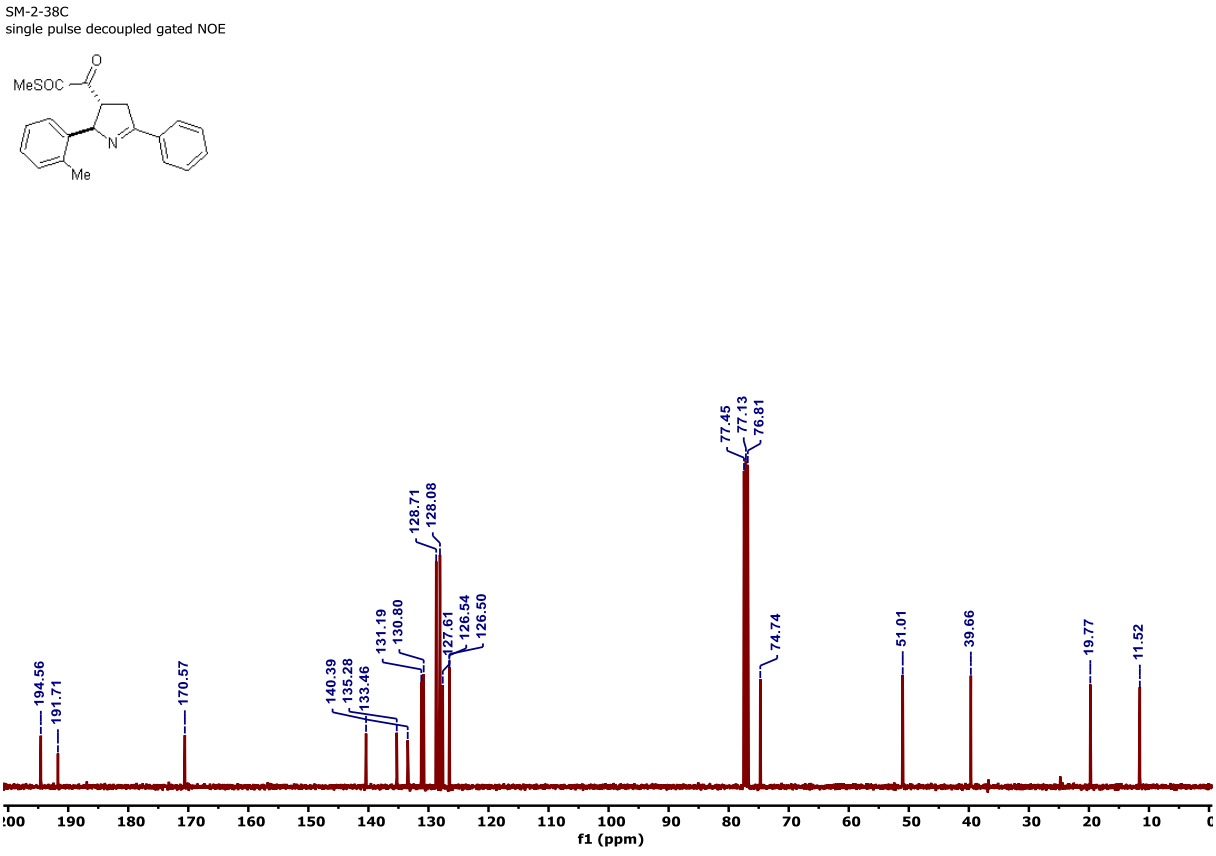
***S*-methyl 2-oxo-2-(5-phenyl-2-(*o*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)ethanethioate 3g:**



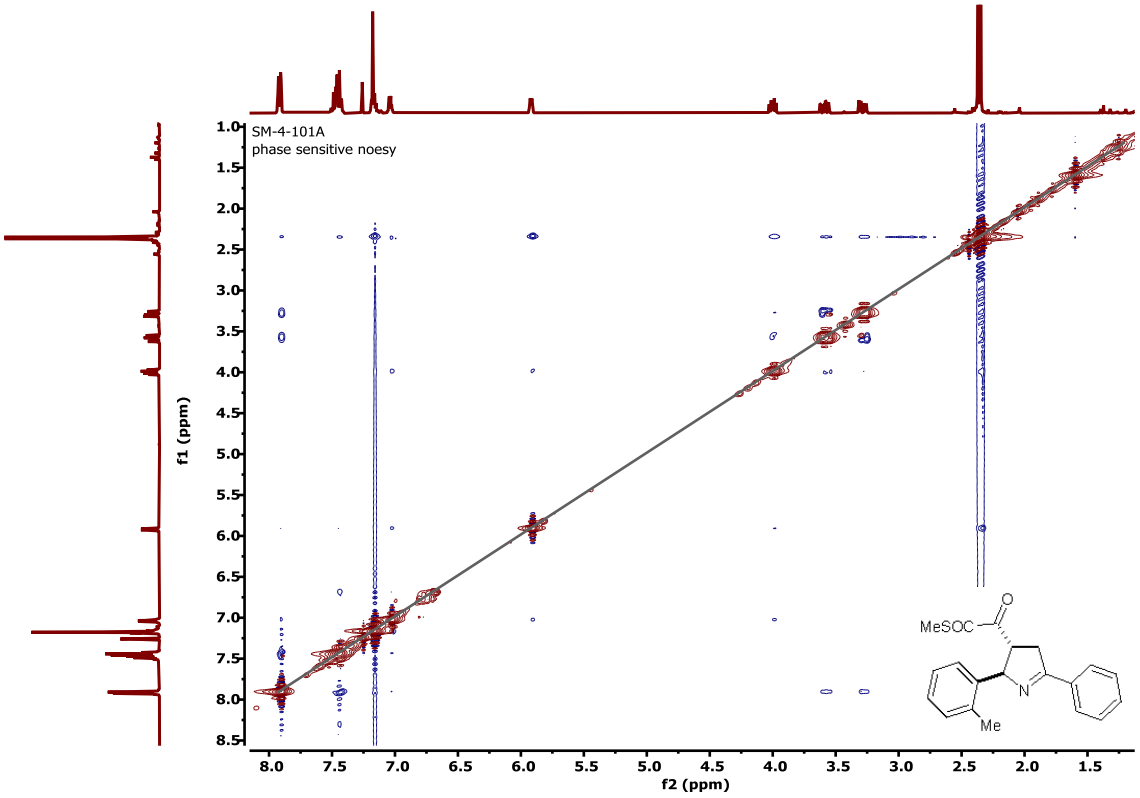
Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow liquid (56 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.90 (m, 2 H), 7.49 - 7.42 (m, 3 H), 7.20 – 7.14 (m, 3 H),7.05 – 7.03 (m, 1 H), 5.92 (dt, *J* = 5.6, 1.6 Hz, 1H), 4.03 – 3.97 (m, 1 H), 3.59 (ddd, *J* = 17.6, 10.8, 2.4 Hz, 1H), 3.28 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.37 (s, 3 H), 2.35 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.6, 191.7, 170.6, 140.4, 135.3, 133.5, 131.2, 130.8, 128.7 (2 CH), 128.1 (2 CH), 127.6, 126.5, 126.5, 74.7, 51.0, 39.7, 19.8, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{20}NO_2S$ [*M* + H]$^+$: 338.1214; found: 338.1211.

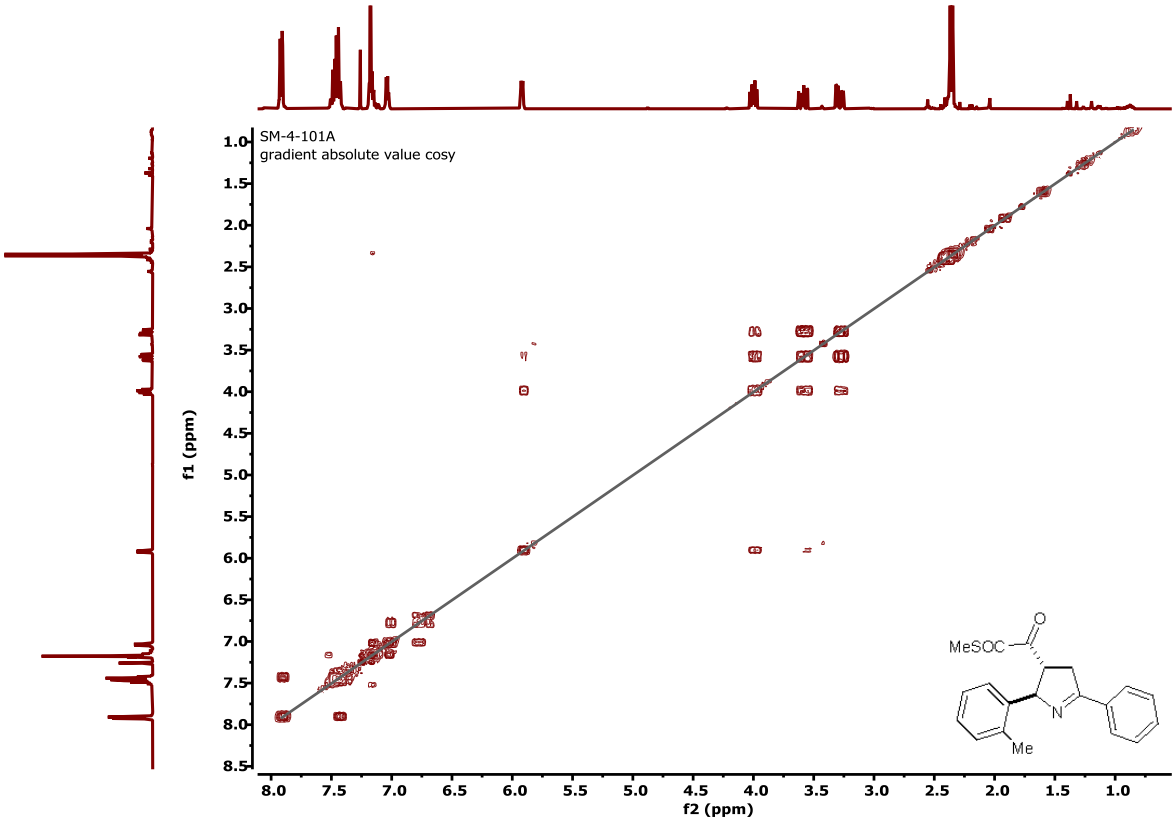
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3g**

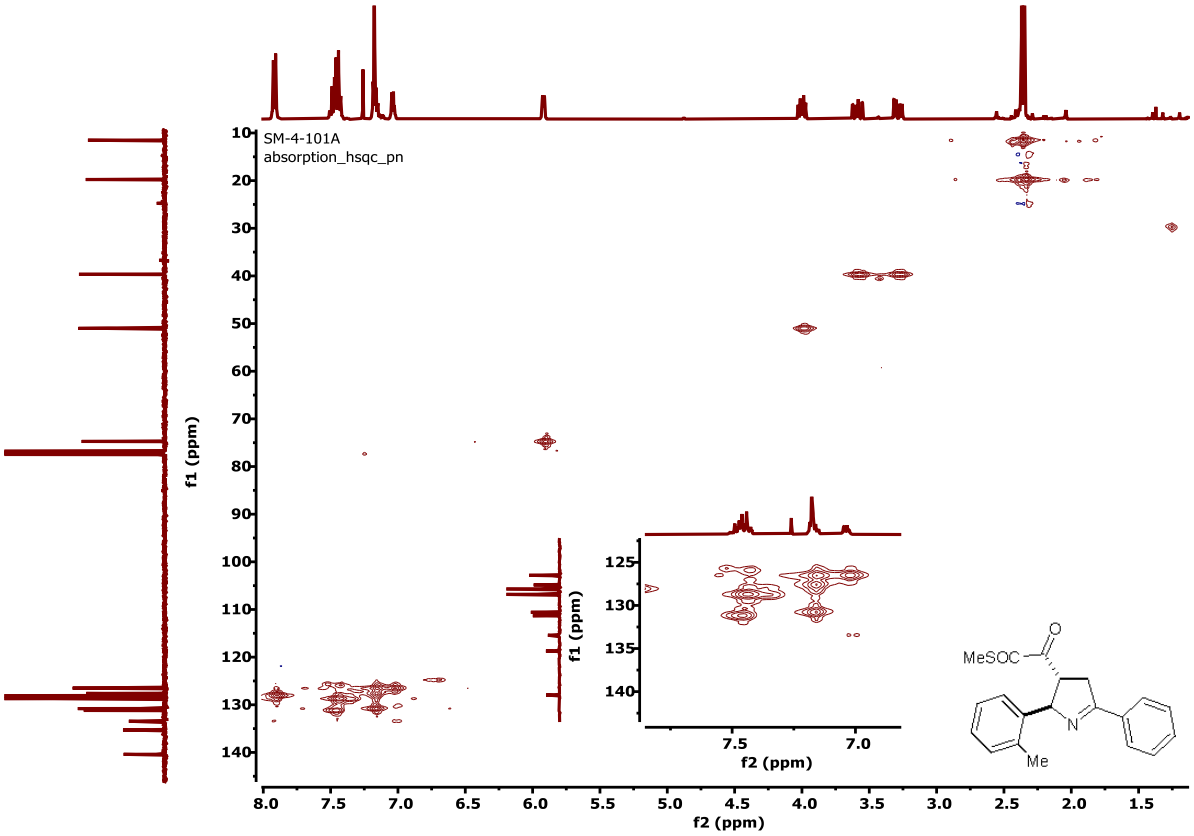




NOESY, COSY, HSQC, and HMBC (400 MHz, $CDCl_3$) NMR spectra of **3g**






SM-4-101A
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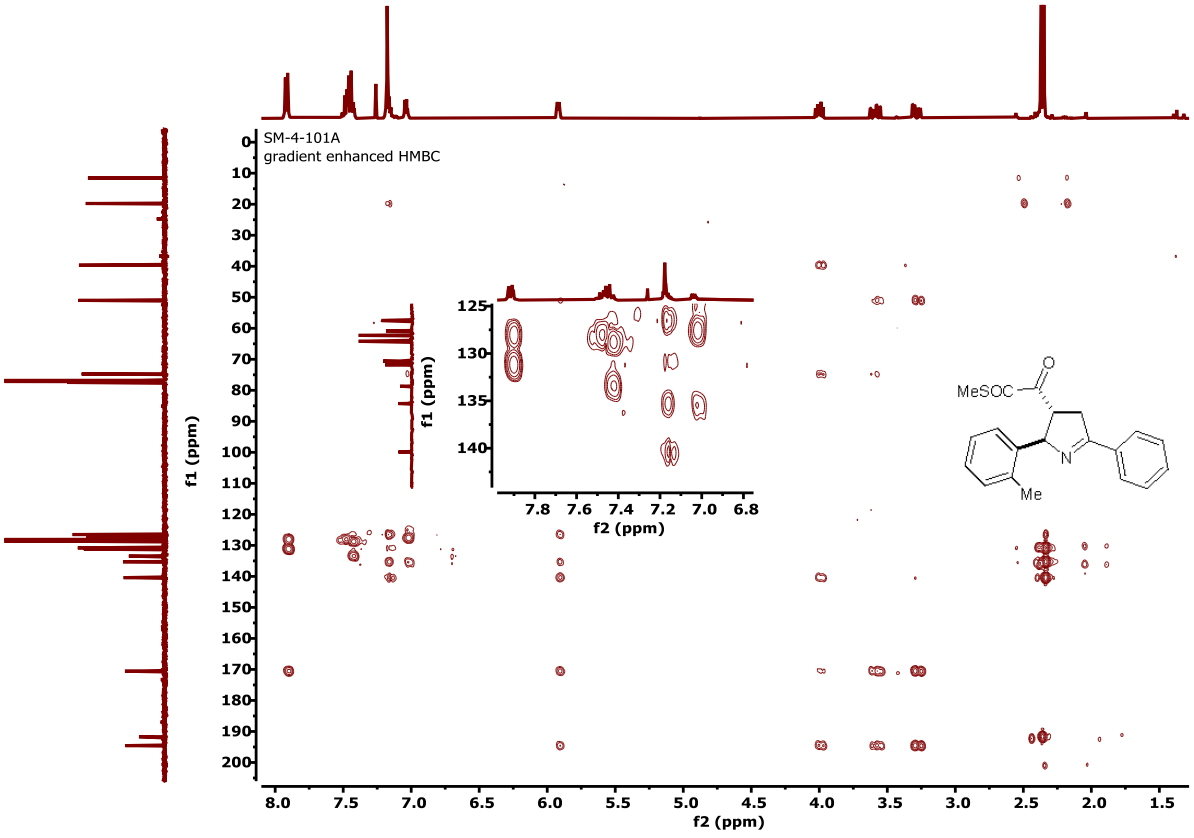
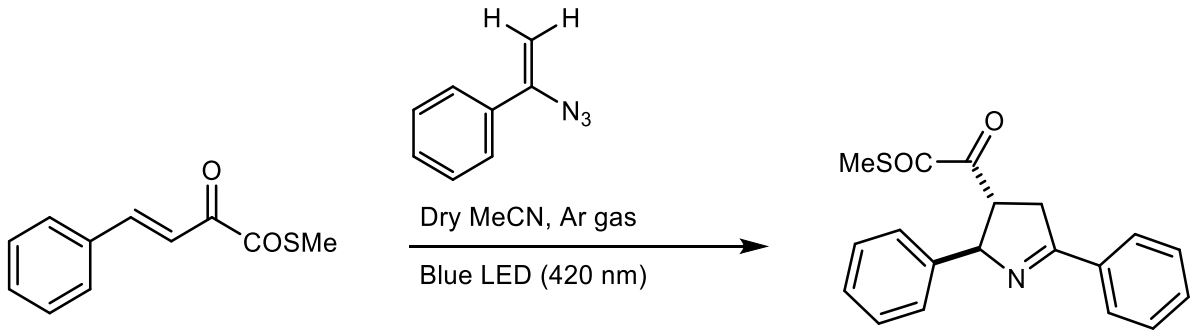
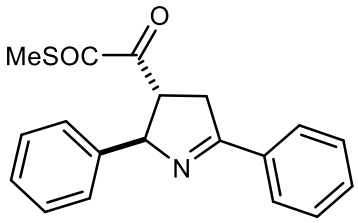
f1 (ppm)
f2 (ppm)
MeSOC
N
Me

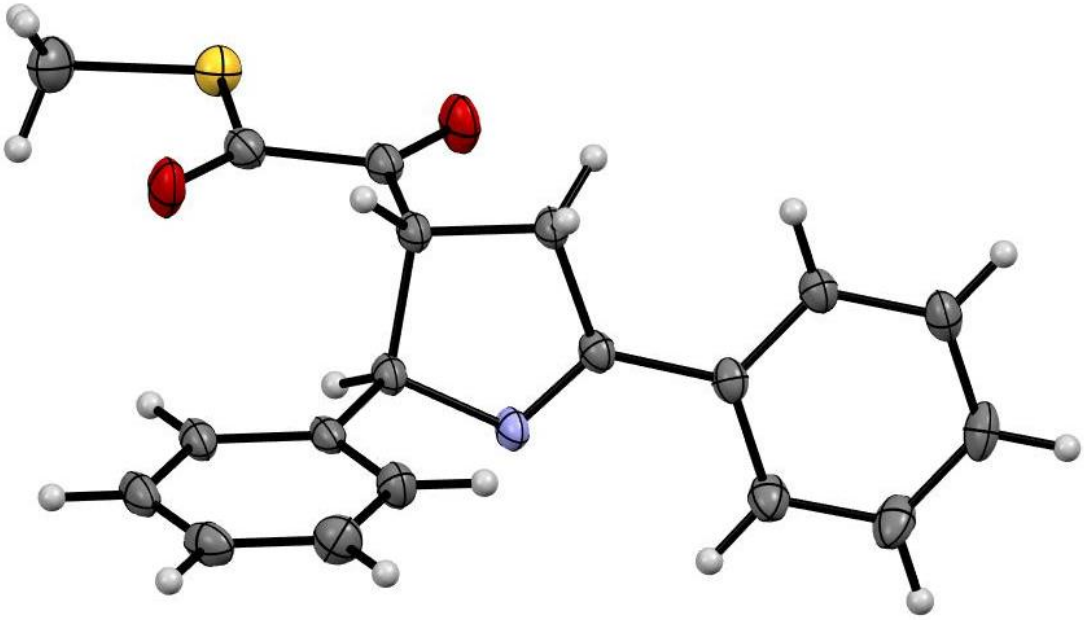

SM-4-101A
gradient enhanced HMBC
f1 (ppm)
f2 (ppm)
MeSOC
N
Me

ESI-13: Analytical and spectral data of **3h:**





***S*-methyl 2-(2,5-diphenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3h:** Prepared according to the general procedure discussed above: reaction time, 14 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow solid (56 mg, 71%); mp 40–45 °C; solvent of crystallization, *n*-hexane/EtOAc = 2 mL:1 mL. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.93 (m, 2 H), 7.51 – 7.42 (m, 3 H), 7.35 – 7.27 (m, 5 H), 5.63 (d, *J* = 5.2 Hz, 1 H), 3.99 (ddd, *J* = 9.6, 6.4, 5.2 Hz, 1 H), 3.48 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.37 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.39 (s, 3 H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 194.1, 191.8, 171.5, 142.2, 133.5, 131.3, 128.8 (2 CH), 128.7 (2 CH), 128.1 (2 CH), 127.7, 126.7 (2 CH), 77.8, 52.2, 38.3, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{18}NO_2S$ $[M + H]^+$: 324.1058; found: 324.1071.



X-ray determined molecular structure of **3h**; **CCDC 2347214**.

Datablock: 3h

Bond precision: C-C = 0.0026 A Wavelength=1.54178

Cell: a=8.7535(9) b=9.7512(10) c=11.0588(12)
alpha=108.448(4) beta=99.312(4) gamma=107.231(3)

Temperature: 100 K

	Calculated	Reported
Volume	820.53(15)	820.53(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H17 N O2 S	C19 H17 N O2 S
Sum formula	C19 H17 N O2 S	C19 H17 N O2 S
Mr	323.40	323.39
Dx,g cm-3	1.309	1.309
Z	2	2
Mu (mm-1)	1.821	1.821
F000	340.0	340.0
F000'	341.57	
h,k,lmax	10,12,13	10,12,13
Nref	3225	3125
Tmin,Tmax	0.729,0.721	0.570,0.754
Tmin'	0.662	

Correction method= # Reported T Limits: Tmin=0.570 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 0.969 Theta(max)= 72.101

R(reflections)= 0.0439(3036) wR2(reflections)= 0.1155(3125)

S = 1.053 Npar= 210

The following ALERTS were generated.

Alert level C

PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C17 - C18 . 1.55 Ang.
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4 Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.118 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 49 Report

1 0 0, 2 0 0, -2 1 0, -1 1 0, 1 1 0, -1 -2 1,
1 -2 1, -1 -1 1, 1 -1 1, 2 -1 1, -1 0 1, 1 0 1,
2 0 1, -1 1 1, 0 1 1, 1 1 1, 3 1 1, -2 5 1,
-7 10 1, 0 -4 2, -1 -3 2, -1 -2 2, -1 -1 2, 1 -1 2,
2 -1 2, 4 -1 2, -1 0 2, 0 0 2, -1 1 2, -4 2 2,
-3 -2 3, -1 -2 3, 2 -1 3, 4 -1 3, 3 0 3, -3 2 3,
-3 3 3, -2 -4 4, -2 1 4, -2 2 4, -1 3 4, 3 5 5,

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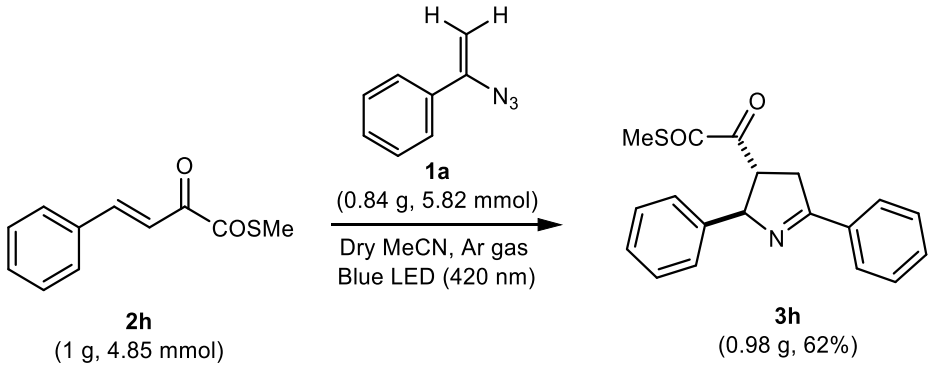
2 1 10,

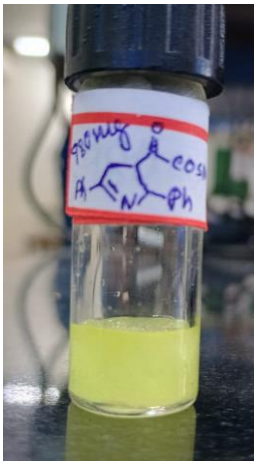
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 18 Note
2 0 0, 1 -2 1, 2 0 1, 1 1 1, 0 -4 2, -1 -3 2,
-1 -2 2, -1 -1 2, 1 -1 2, 2 -1 2, 4 -1 2, -4 2 2,
-3 -2 3, -1 -2 3, 4 -1 3, 3 0 3, -2 -4 4, -2 1 4,

Alert level G

PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 2 Note
0 1 0, 0 0 1,
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 49 Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ..... 3.01 Note
Predicted wR2: Based on SigI**2 3.84 or SHELX Weight 11.35
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 13 Info

ESI-13-01: Gram Scale Reaction:

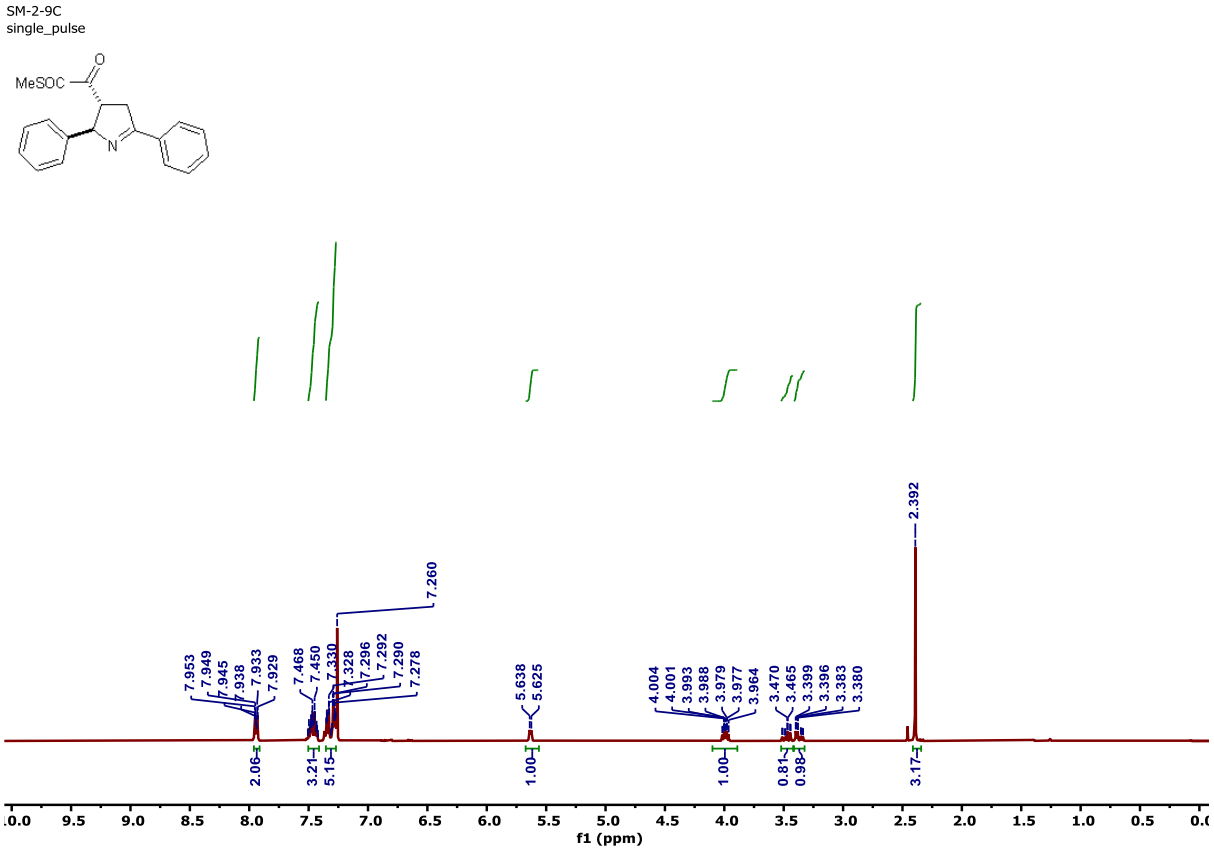


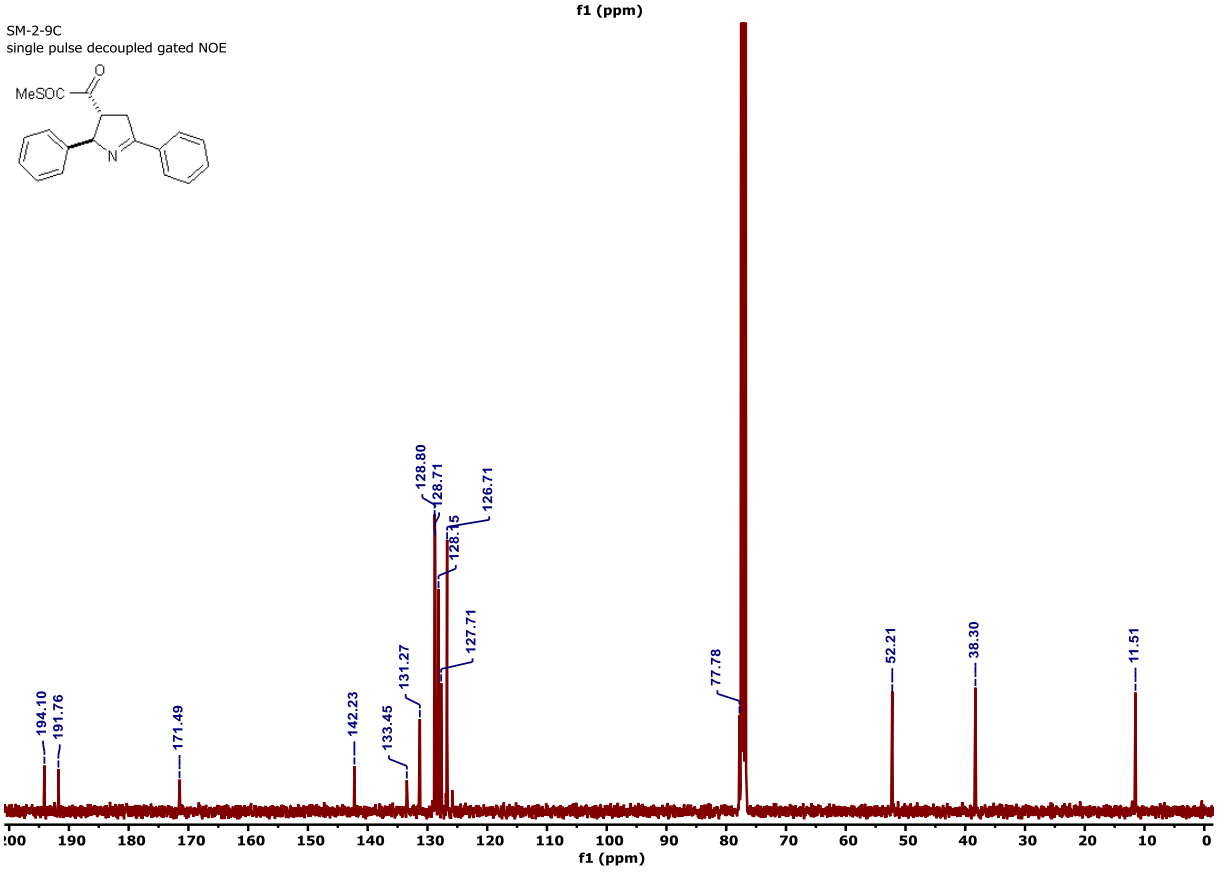


1	**1a**	0.84 g	5.82 mmol
2	**2h**	1 g	4.85 mmol
3	**3h**	0.98 g	3.030 mmol

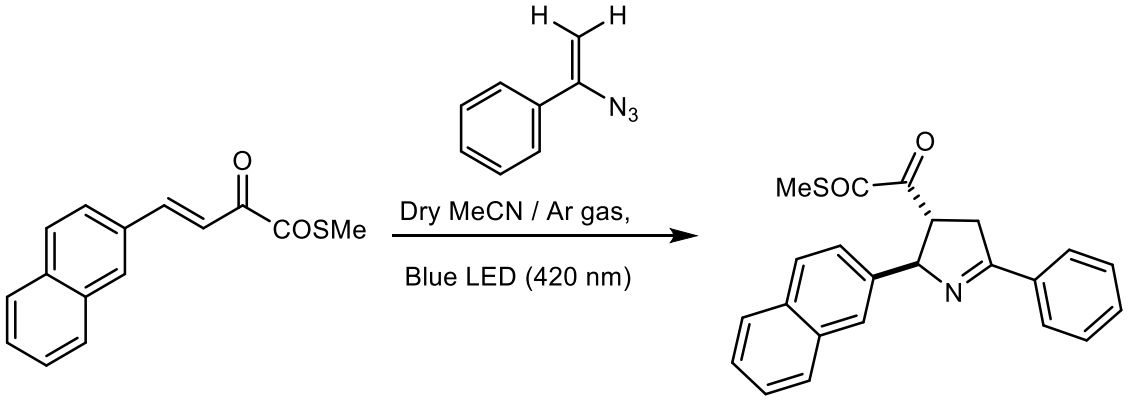
Following the standard reaction conditions, the reaction mixture was irradiated and purified by column chromatography after completion.
MeCN taken: 40 mL
Reaction time: 20 h
Product Yield: 62%

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3h:**

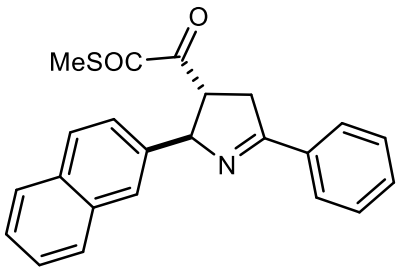




ESI-14: Analytical and spectral data of **3i**



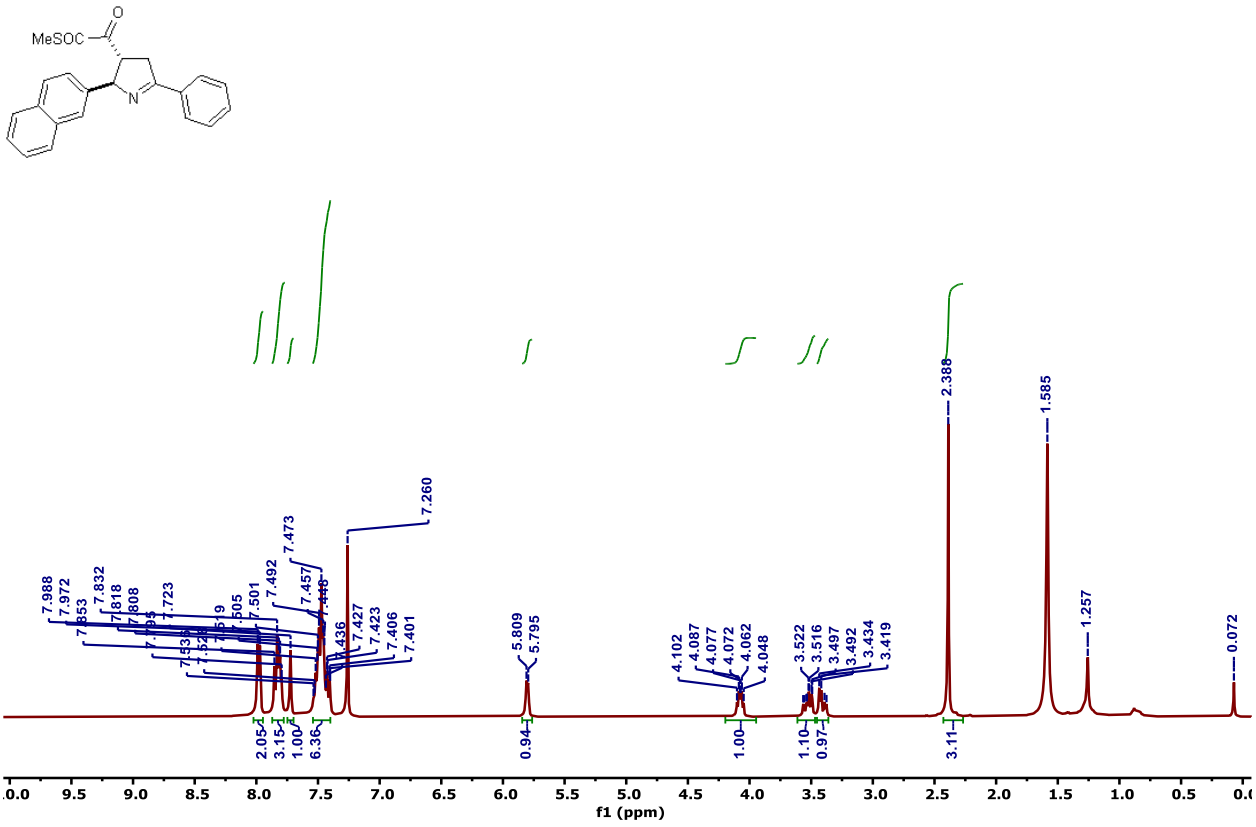
***S*-methyl 2-(2-(naphthalen-2-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate**



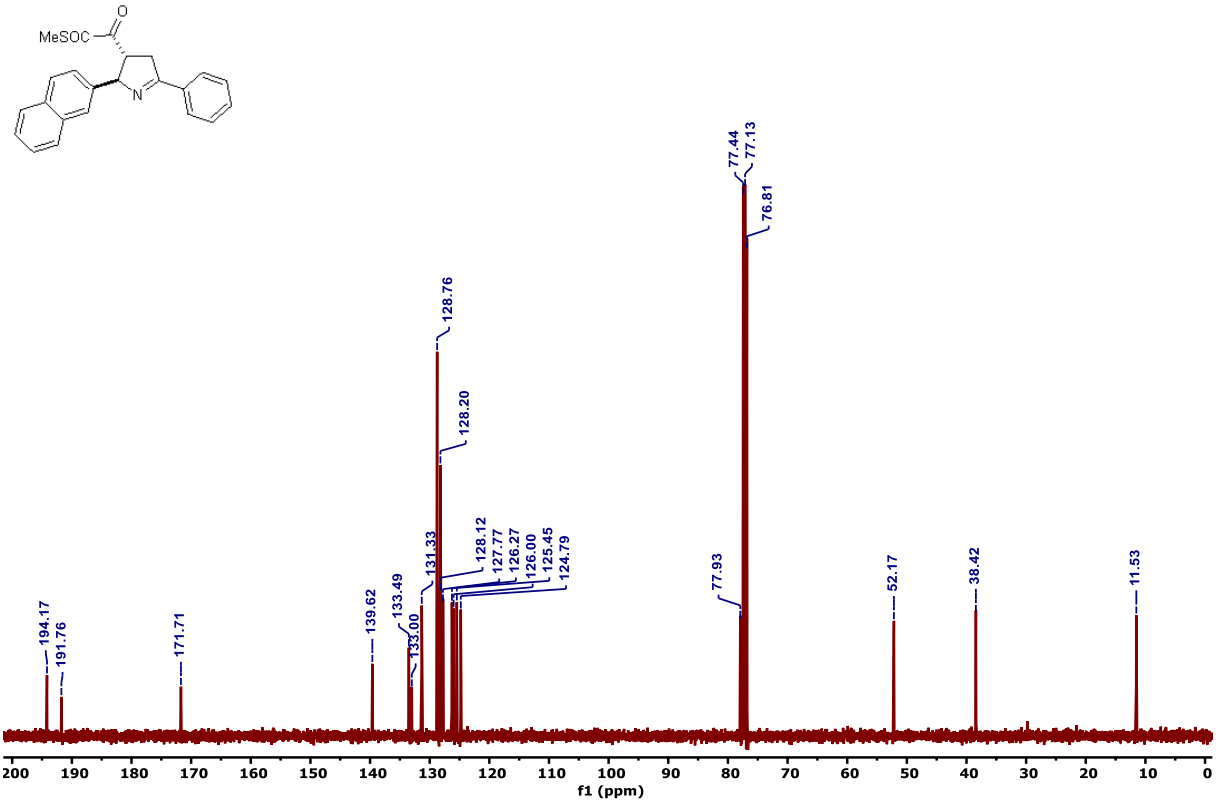
3i: Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); light yellow gum (55 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 6.4 Hz, 2 H), 7.83 – 7.808 (m, 3 H), 7.72 (s, 1 H), 7.52 – 7.40 (m, 6 H), 5.80 (d, *J* = 5.6 Hz, 1 H), 4.07 (dt, *J* = 9.7, 6.0 Hz, 1 H), 3.56 – 3.37 (m, 2 H), 2.39 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.2, 191.8, 171.7, 139.6, 133.5, 133.0, 131.3, 128.8 (4 CH), 128.2 (2 CH), 128.1, 127.8, 126.3, 126.0, 125.4, 124.8, 77.9, 52.2, 38.4, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{23}H_{20}NO_2S$ [*M* + H]$^+$: 374.1214; found: 374.1223.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3i**

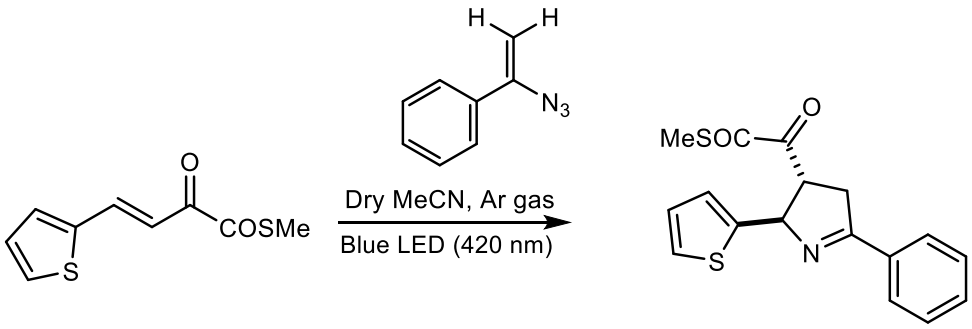
JAY-399B-02
single_pulse



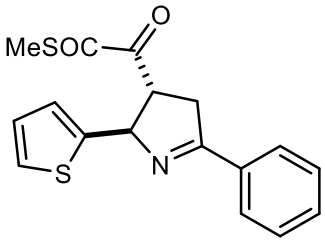
JAY-399B
single pulse decoupled gated NOE



ESI-15: Analytical and spectral data of **3j**

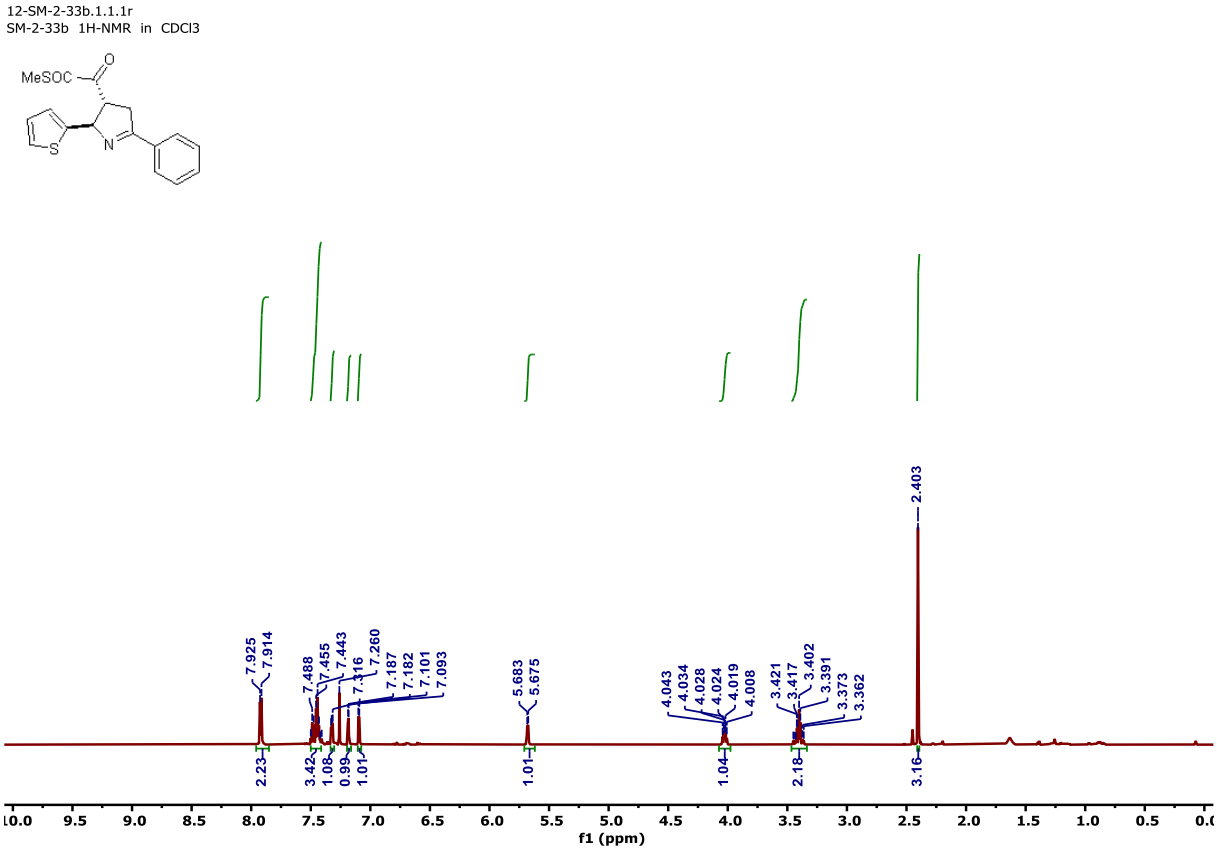


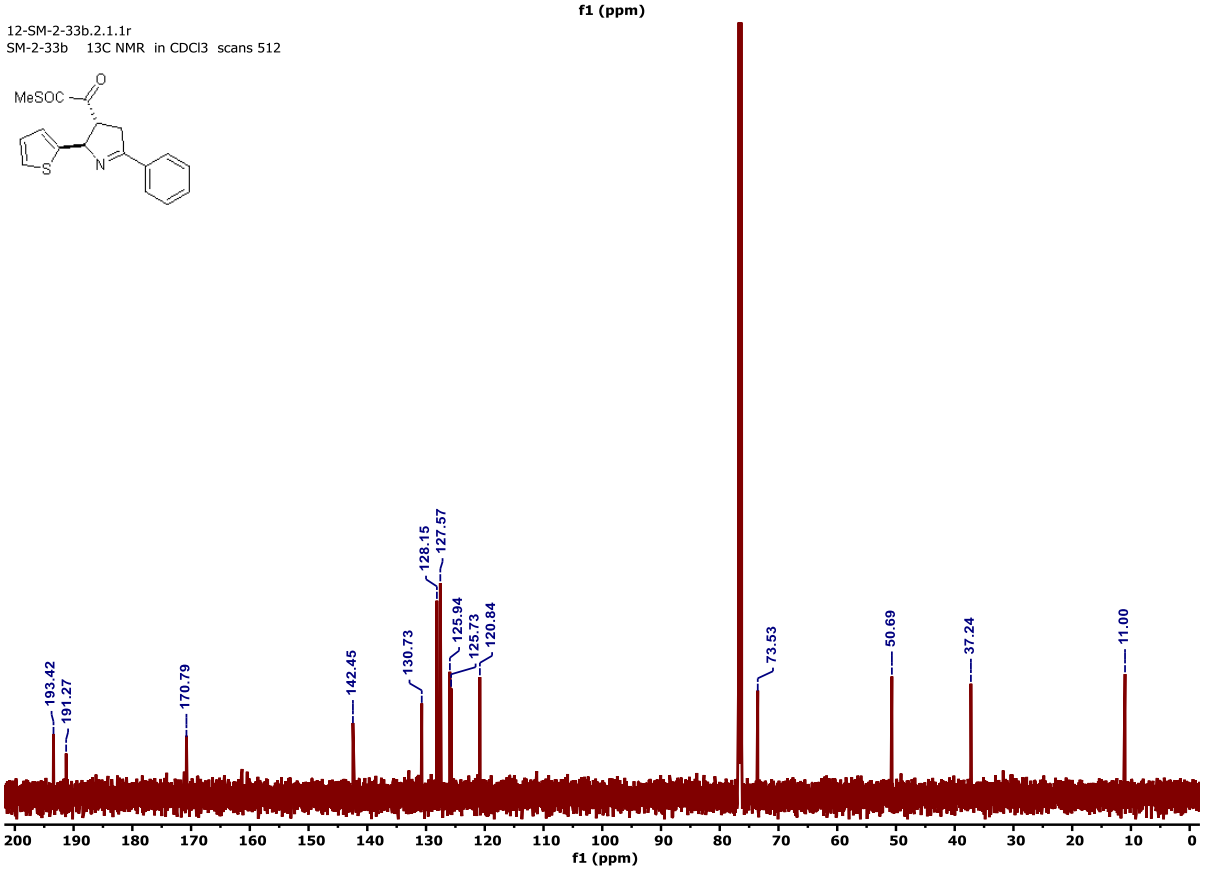
***S*-methyl 2-oxo-2-(5-phenyl-2-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrol-3-yl)ethanethioate**



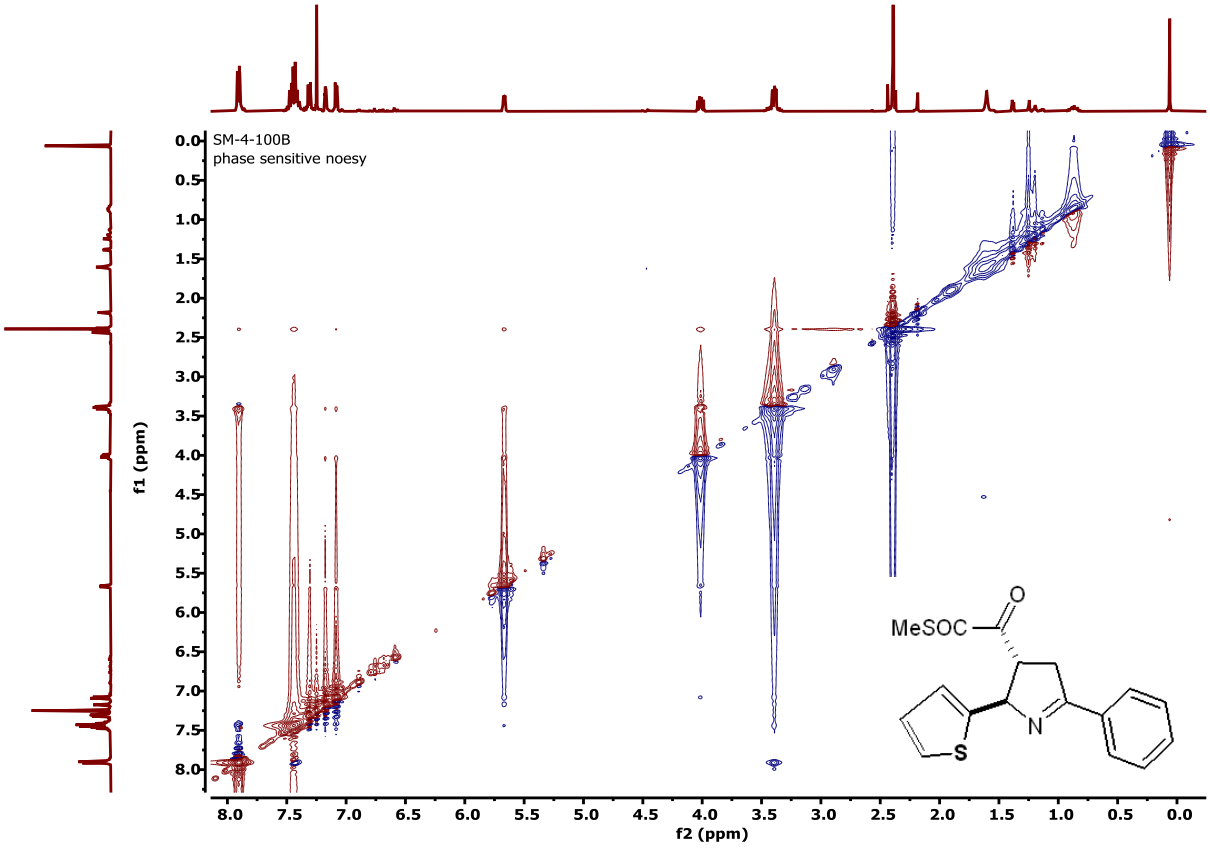
3j: Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid (54 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 6.6 Hz, 2 H), 7.50 – 7.41 (m, 3 H), 7.32 (dd, *J* = 4.8, 3.0 Hz, 1 H), 7.18 (d, *J* = 3.0 Hz, 1 H), 7.10 (d, *J* = 4.8 Hz, 1 H), 5.68 (d, *J* = 4.8 Hz, 1 H), 4.04 – 4.01 (m, 1 H), 3.45 – 3.36 (m, 2 H), 2.40 (s, 3 H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 193.4, 191.3, 170.8, 142.4, 130.7, 128.2 (2 CH), 127.6 (2 CH), 125.9, 125.7, 120.8, 73.5, 50.7, 37.2, 11.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{16}NO_2S_2$ [*M* + H]$^+$: 330.0622; found: 330.0617.

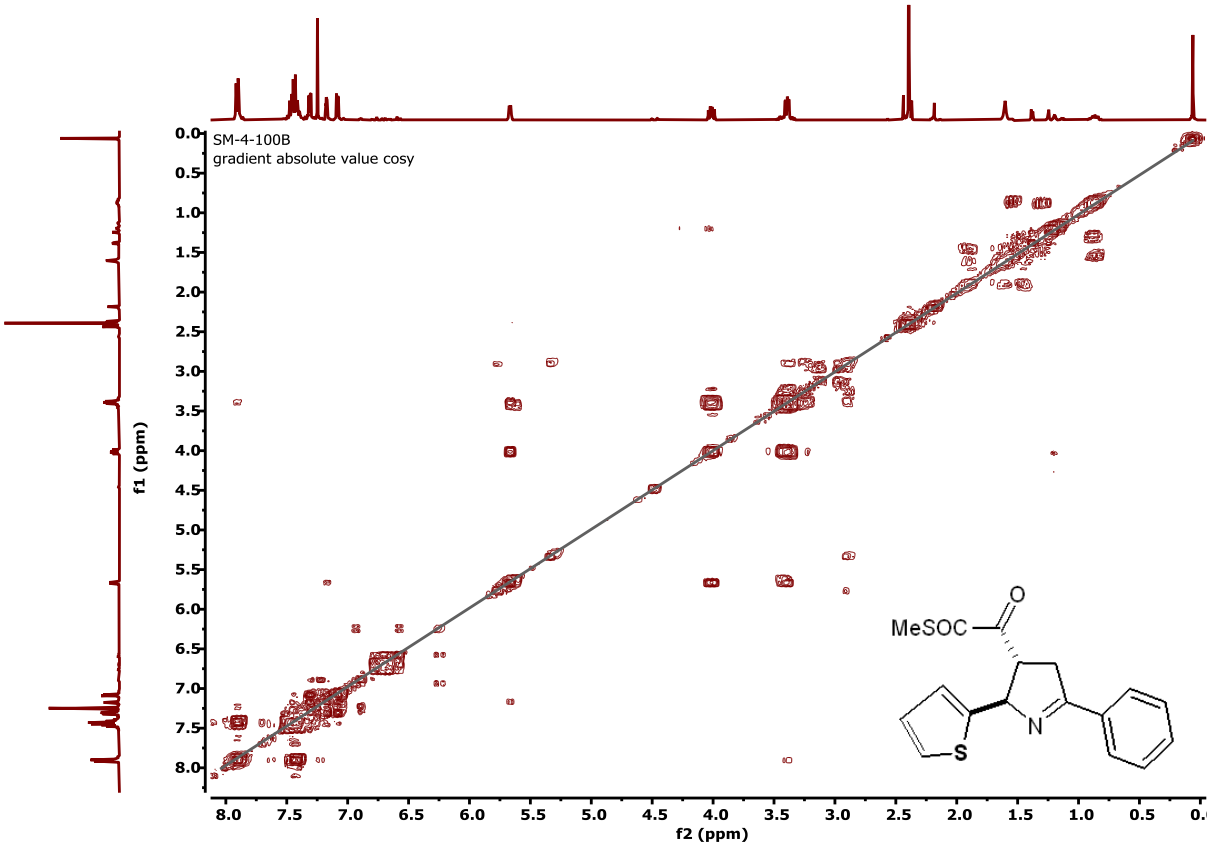
^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **3j**

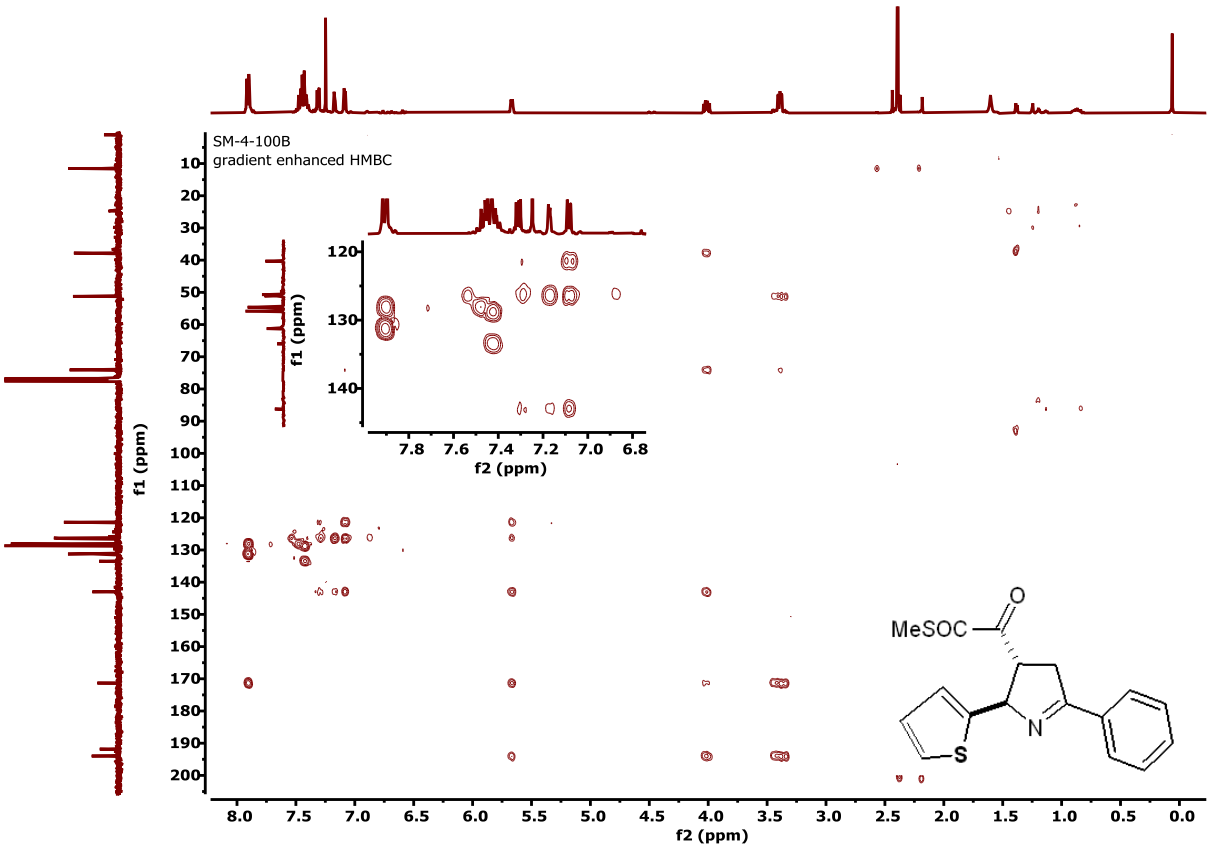


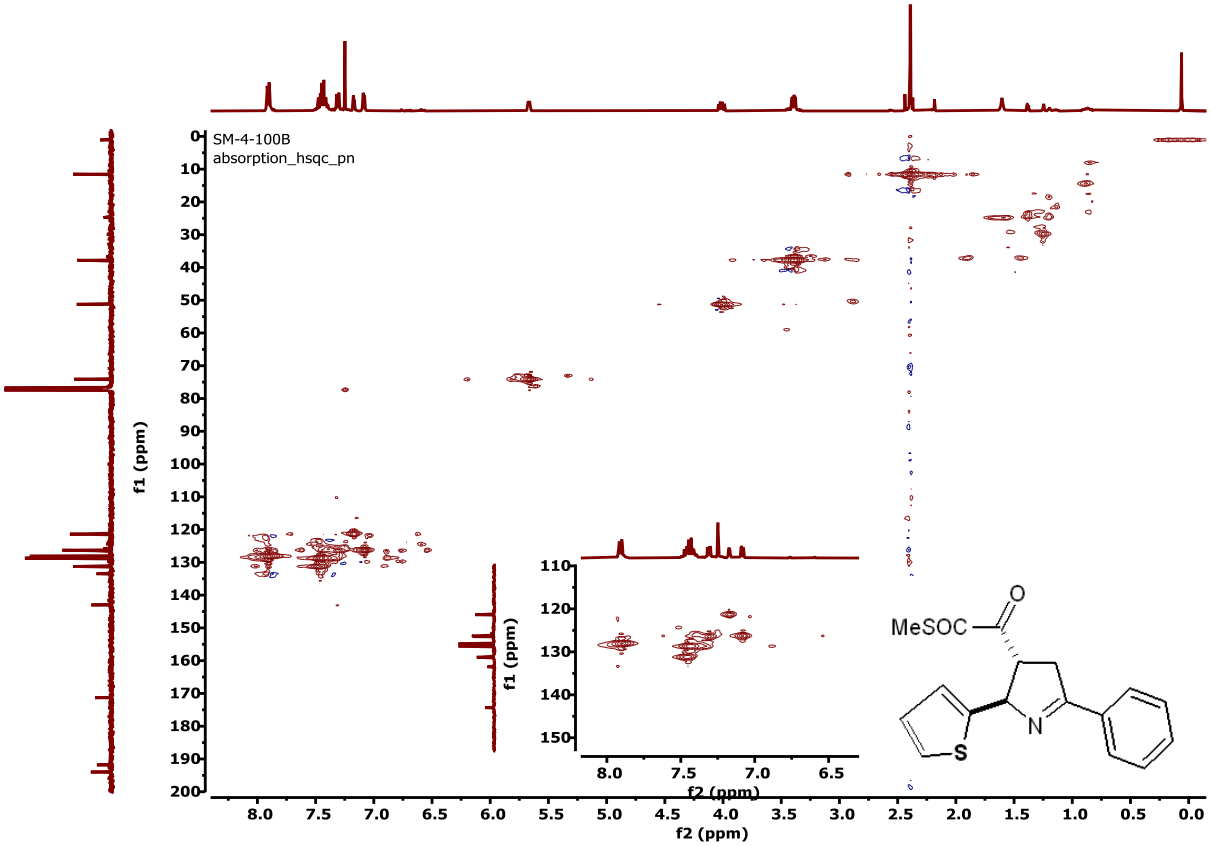


NOESY, COSY, HSQC, and HMBC (400 MHz, $CDCl_3$) NMR spectra of **3j:**

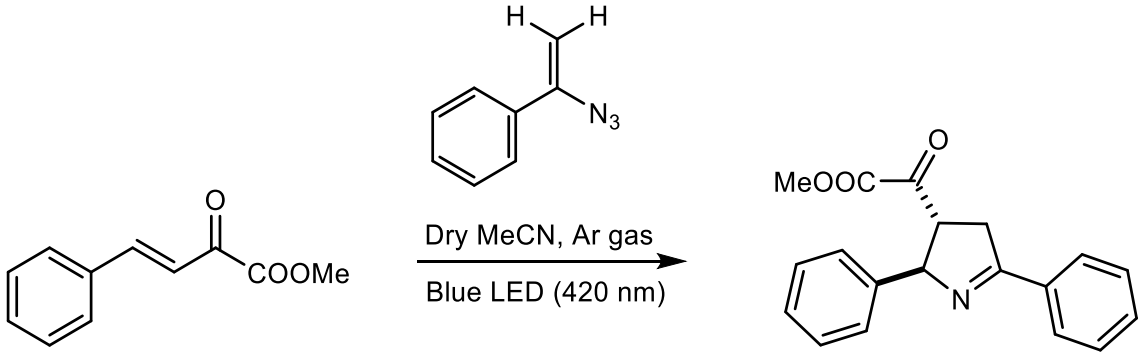




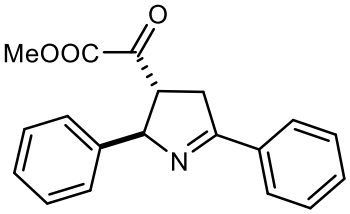

SM-4-100B
gradient enhanced HMBC
f1 (ppm)
f2 (ppm)
MeSOC
O
N
S


SM-4-100B
absorption_hsqc_pn
f1 (ppm)
f2 (ppm)
MeSOC
O
N
S

ESI-16: Analytical and spectral data of **3l**

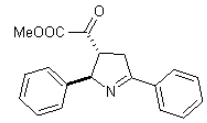


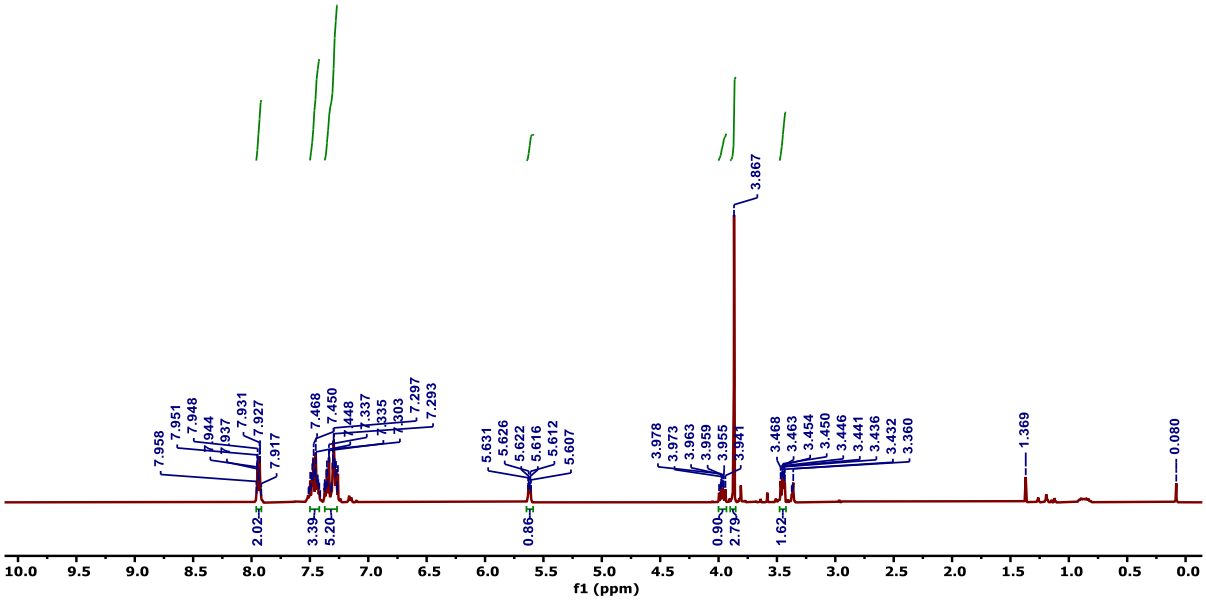
Methyl 2-(2,5-diphenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoacetate 3l: Prepared according to the general procedure discussed above: reaction time, 14 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); yellow liquid (62 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.92 (m, 2 H), 7.51 – 7.41 (m, 3 H), 7.38 – 7.27 (m, 5 H), 5.62 (dt, *J* = 6.0, 2.0 Hz, 1 H), 3.97 (ddd, *J* = 9.2, 7.2, 6.0 Hz, 1 H), 3.87 (s, 3 H), 3.47 – 3.43 (m, 2 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.1, 171.5, 161.5, 142.3, 133.5, 131.3, 128.8 (2 CH), 128.7 (2 CH), 128.1 (2 CH), 127.8, 126.7 (2 CH), 77.9, 54.8, 53.3, 38.1. ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{18}NO_3$ [*M* + H]$^+$: 308.1286; found: 308.1275.



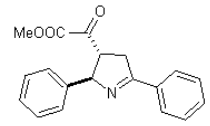
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3l**

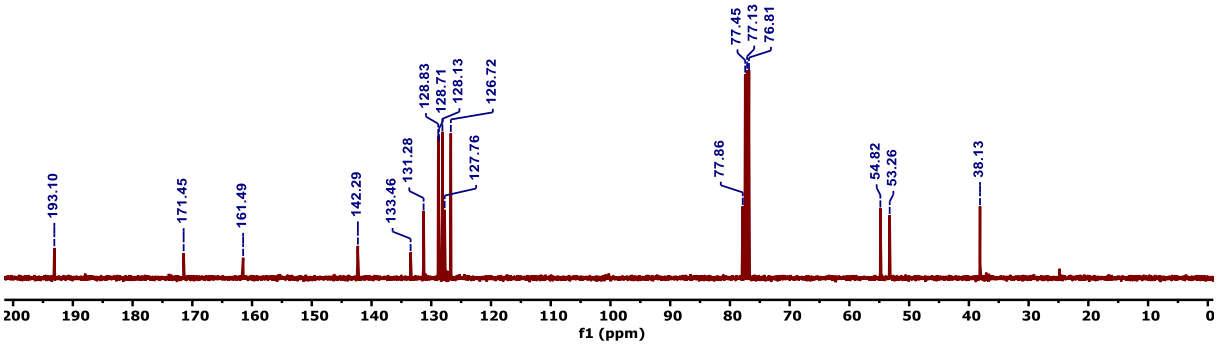
SM-2-61B
single_pulse



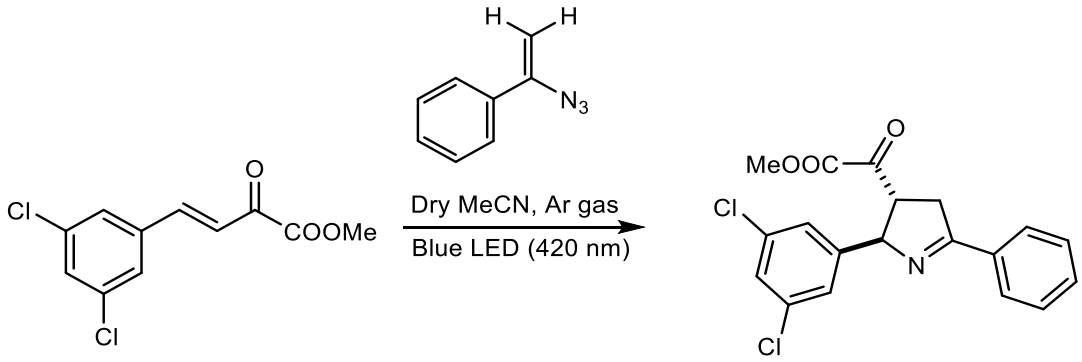


SM-2-61B
single pulse decoupled gated NOE

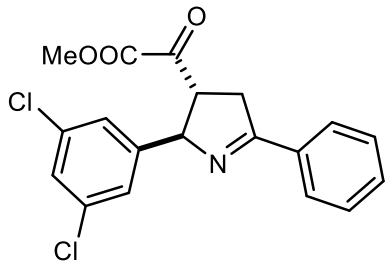




ESI-17: Analytical and spectral data of **3m**



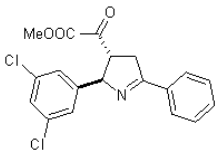
Methyl 2-(2-(3,5-dichlorophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoacetate 3m:

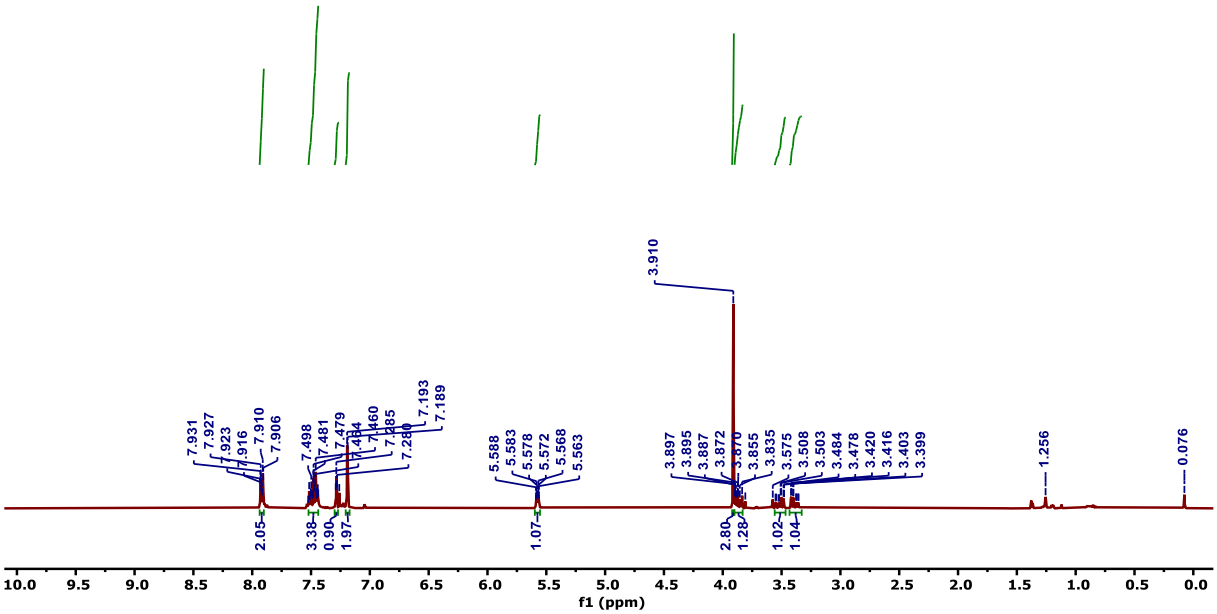


Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); light yellow liquid (61 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.91 (m, 2 H), 7.52 – 7.44 (m, 3 H), 7.28 (t, *J* = 2.0 Hz, 1 H), 7.19 (d, *J* = 1.6 Hz, 2 H), 5.58 (dt, *J* = 6.4, 2.0 Hz, 1 H), 3.91 (s, 3 H), 3.90 – 3.81 (m, 1 H), 3.51 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.39 (ddd, *J* = 17.2, 6.8, 1.6 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 192.4, 172.4, 161.2, 145.8, 135.4, 133.0, 131.6, 128.8 (2 CH), 128.7, 128.2 (2 CH), 127.9, 125.4 (2 CH), 76.3, 54.6, 53.5, 38.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{16}Cl_2NO_3$ [*M* + H]$^+$: 376.0507; found: 376.0491.

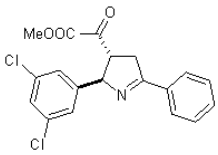
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3m**

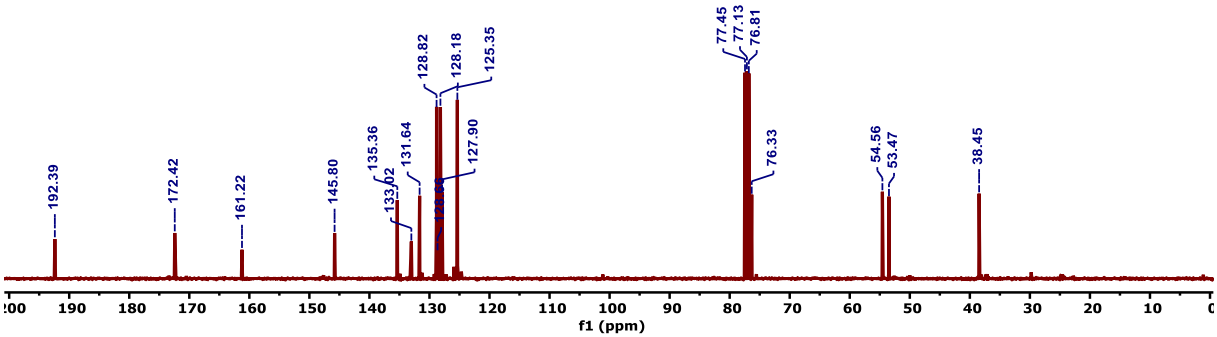
SM-2-54B
single_pulse



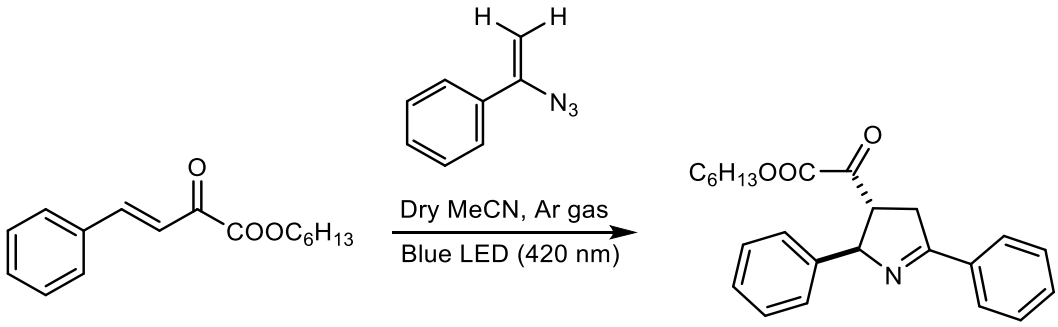


SM-2-54B
single pulse decoupled gated NOE

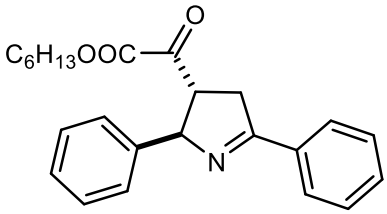




ESI-18: Analytical and spectral data of **3n**

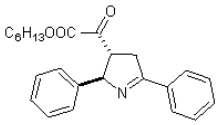


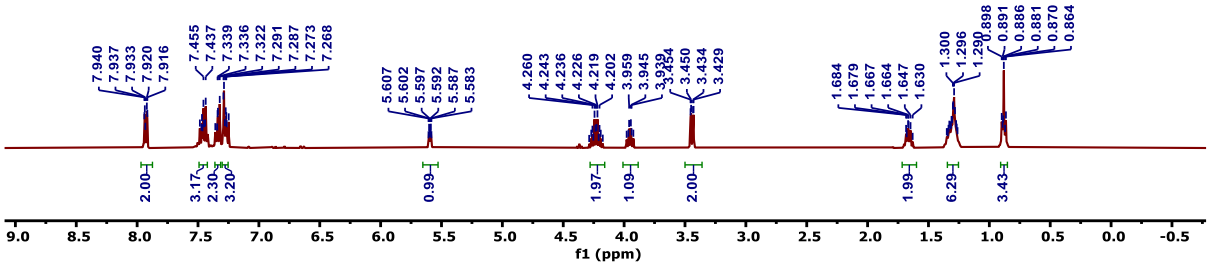
Hexyl 2-(2,5-diphenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoacetate 3n: Prepared according to the general procedure discussed above: reaction time, 14 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); yellow liquid (52 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.92 (m, 2 H), 7.49 – 7.41 (m, 3 H), 7.36 – 7.32 (m, 2 H), 7.30 – 7.25 (m, 3 H), 5.59 (dt, *J* = 6.0, 2.0 Hz, 1 H), 4.29 – 4.12 (m, 2 H), 3.95 (td, *J* = 8.0, 5.6 Hz, 1 H), 3.44 (dd, *J* = 8.0, 1.6 Hz, 2 H), 1.81 – 1.57 (m, 2 H), 1.37 – 1.19 (m, 6 H), 1.01 – 0.76 (m, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.5, 171.6, 161.3, 142.3, 133.4, 131.3, 128.8 (2 CH), 128.7 (2 CH), 128.1 (2 CH), 127.8, 126.8 (2 CH), 77.9, 67.0, 54.8, 38.1, 31.4, 28.3, 25.5, 22.6, 14.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{28}NO_3$ [*M* + H]$^+$: 378.2069; found: 378.2071.



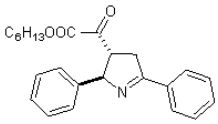
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3n**

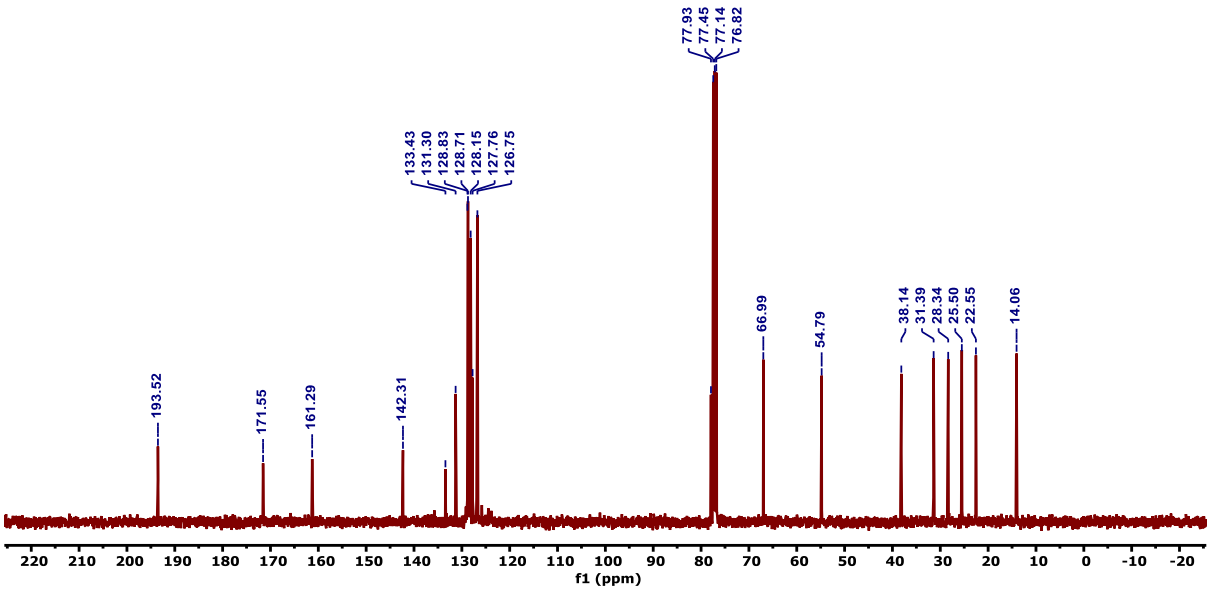
SM-3-139B
single_pulse



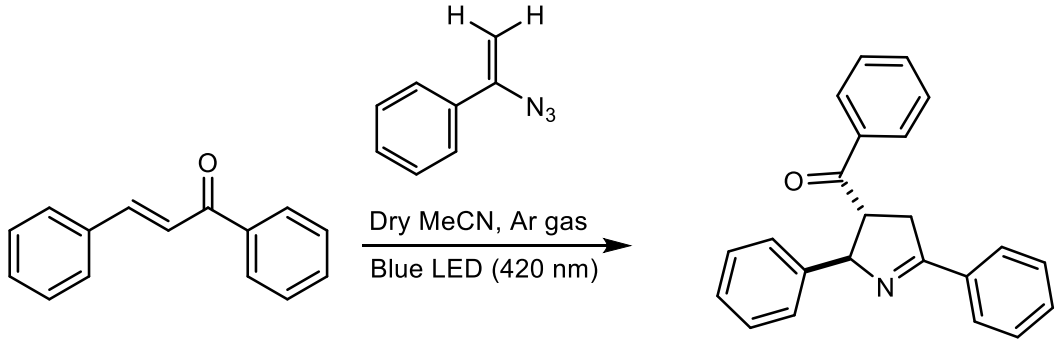


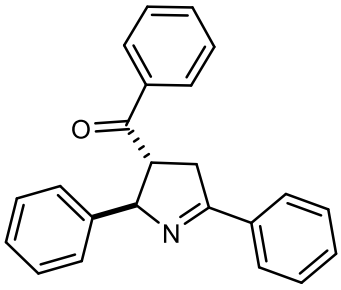
SM-3-139B
single pulse decoupled gated NOE





ESI-19: Analytical and spectral data of **3q**

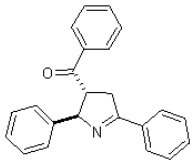


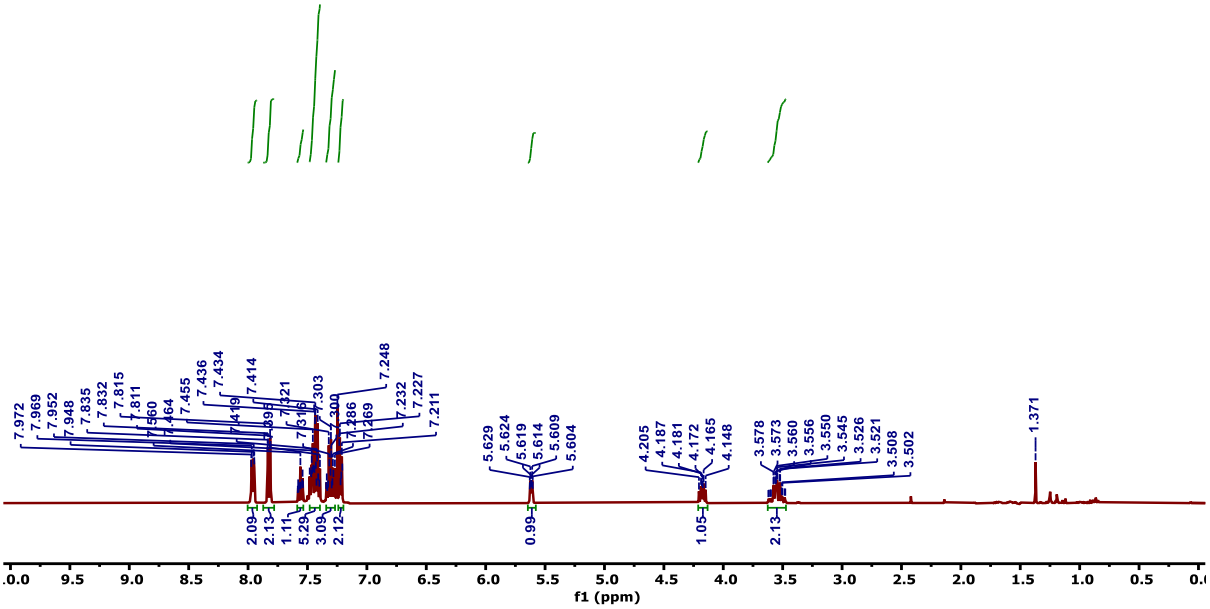


(2,5-Diphenyl-3,4-dihydro-2*H*-pyrrol-3-yl) (phenyl)methanone 3q: Prepared according to the general procedure discussed above: reaction time, 16 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); Colourless liquid (41 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dt, *J* = 6.8, 1.6 Hz, 2 H), 7.82 (dt, *J* = 6.8, 1.6 Hz, 2 H), 7.60 – 7.51 (m, 1 H), 7.51 – 7.37 (m, 5 H), 7.37 – 7.25 (m, 3 H), 7.24 – 7.20 (m, 2 H), 5.62 (dt, *J* = 6.0, 2.0 Hz, 1 H), 4.18 (ddd, *J* = 13.2, 6.8, 2.4 Hz, 1 H), 3.66 – 3.45 (m, 2 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 199.6, 142.9, 136.3, 133.6 (2 CH), 131.2, 128.9 (2 CH), 128.8 (2 CH), 128.8 (2 CH), 128.7 (2 CH), 128.2 (2 CH), 127.7 (2 CH), 127.0 (2 CH), 79.6, 53.7, 40.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{23}H_{20}NO$ [*M* + H]$^+$: 326.1545; found: 326.1543.

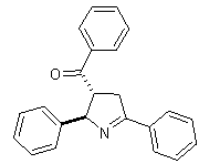
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3q**

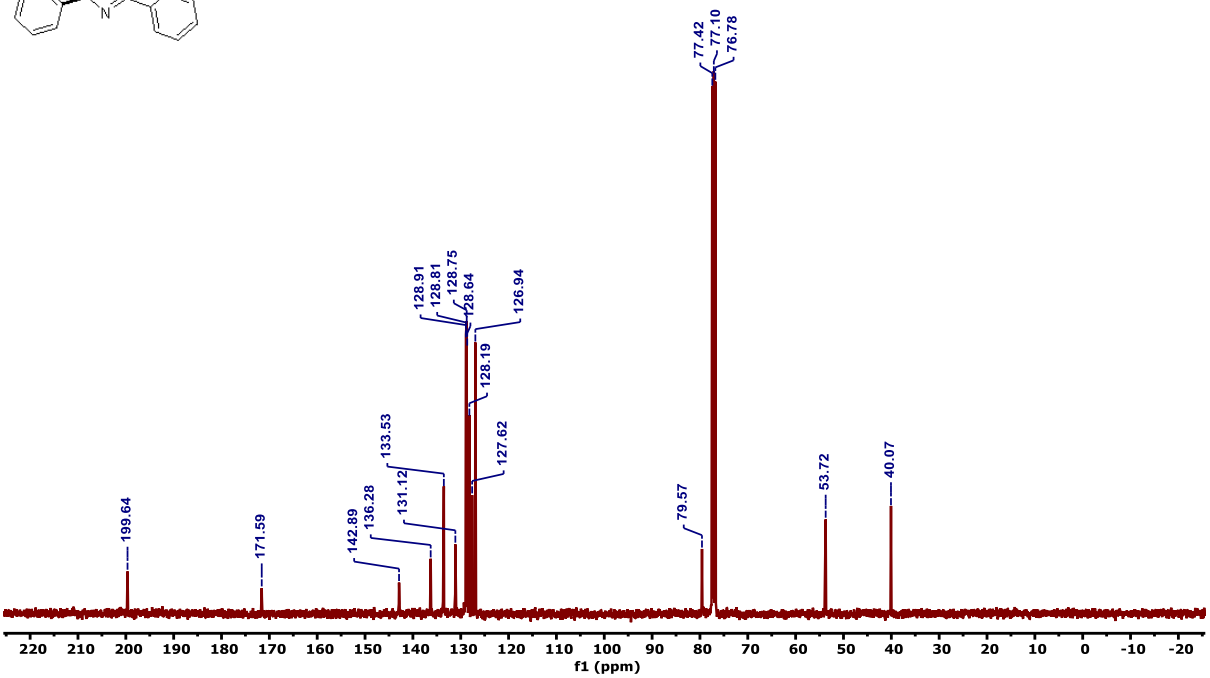
SM-2-117A
single_pulse



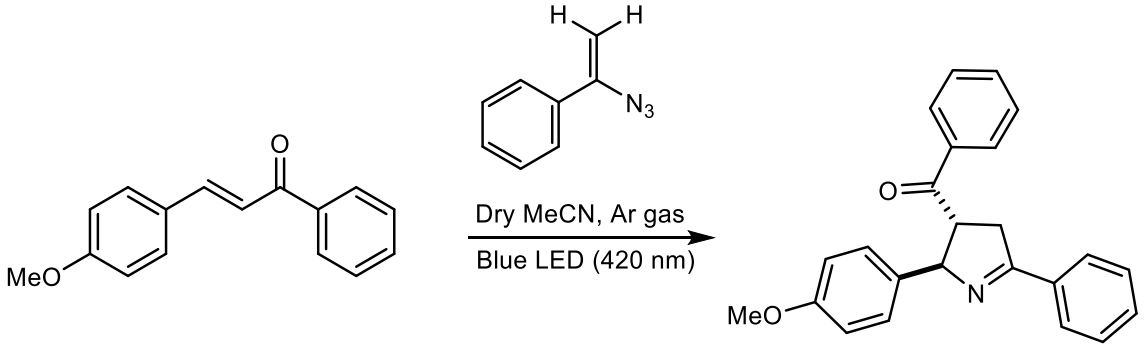


SM-3-137A
single pulse decoupled gated NOE

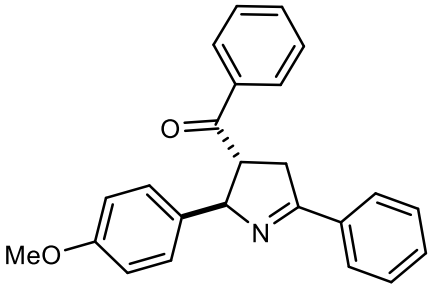




ESI-20: Analytical and spectral data of **3r**

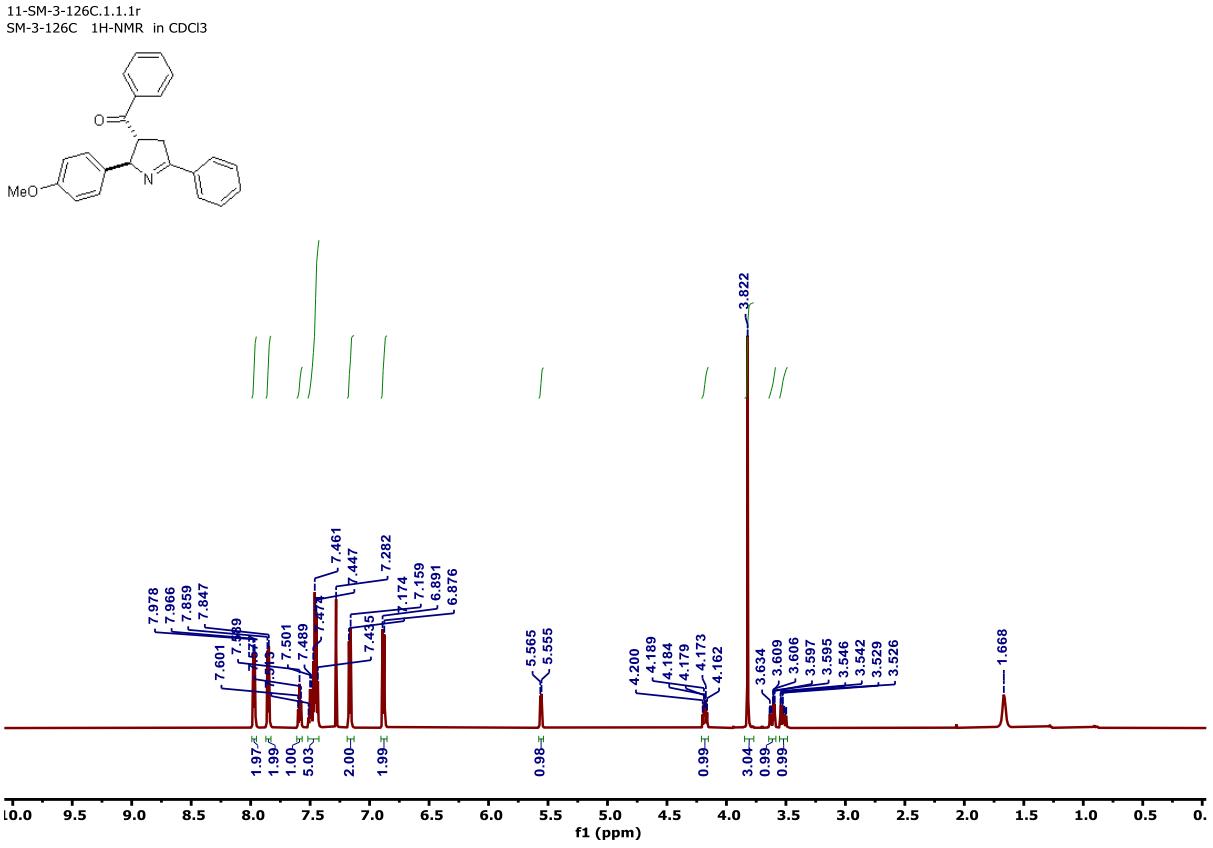


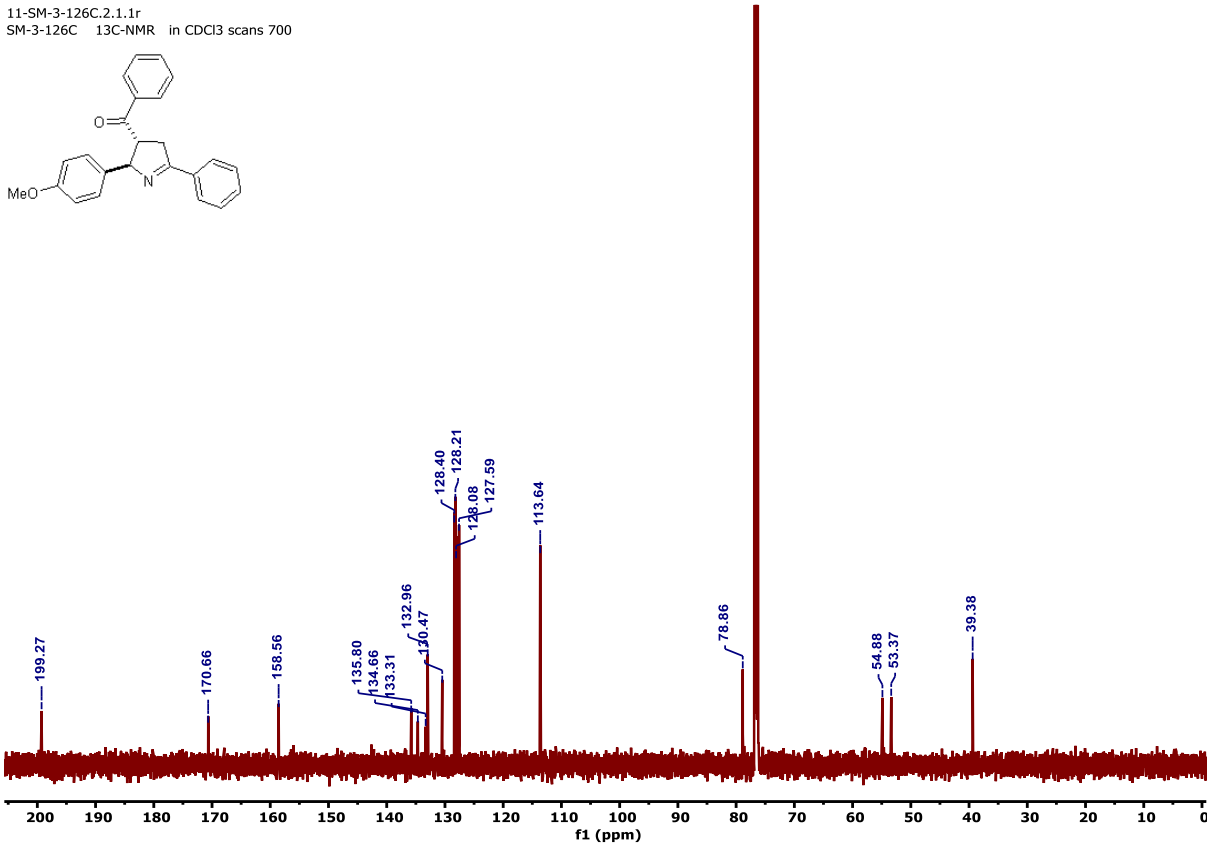
(2-(4-Methoxyphenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl) (phenyl) methanone 3r:



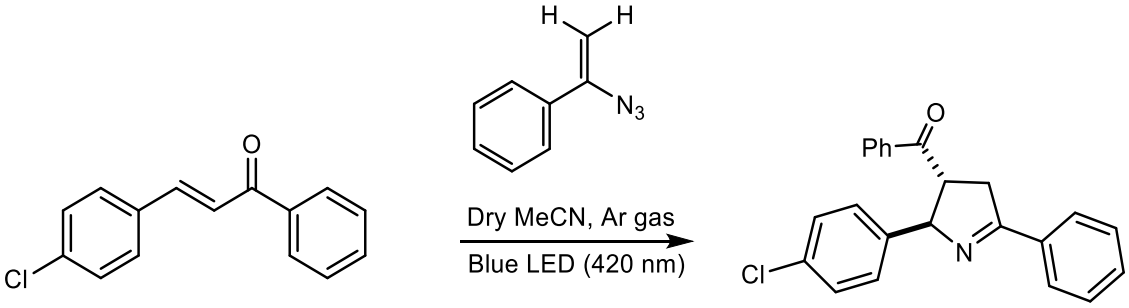
Prepared according to the general procedure discussed above: reaction time, 18 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (15%); Colourless liquid (43 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.2 Hz, 2 H), 7.85 (d, *J* = 7.2 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.51 – 7.43 (m, 5 H), 7.17 (d, *J* = 9.0 Hz, 2 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 5.56 (d, *J* = 6.0 Hz, 1 H), 4.18 (dt, *J* = 9.6, 6.6 Hz, 1 H), 3.82 (s, 3 H), 3.62 (ddd, *J* = 16.8, 6.6, 1.8 Hz, 1 H), 3.52 (ddd, *J* = 17.4, 10.2, 2.4 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 199.3, 170.7, 158.6, 135.8, 134.7, 133.3, 133.0, 130.5, 128.4 (2 CH), 128.2 (2 CH), 128.1 (2 CH), 127.6 (2 CH), 127.6 (2 CH), 113.6 (2 CH), 78.9, 54.9, 53.4, 39.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{22}NO_2$ [*M* + H]$^+$: 356.1650; found: 356.1664.

^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **3r:**

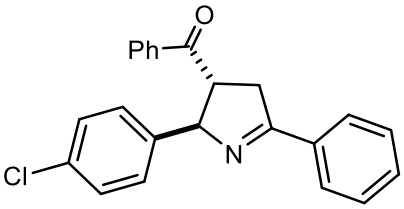




ESI-21: Analytical and spectral data of **3s**



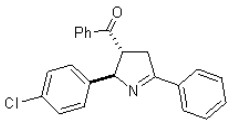
(2-(4-Chlorophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl) (phenyl)methanone 3s:

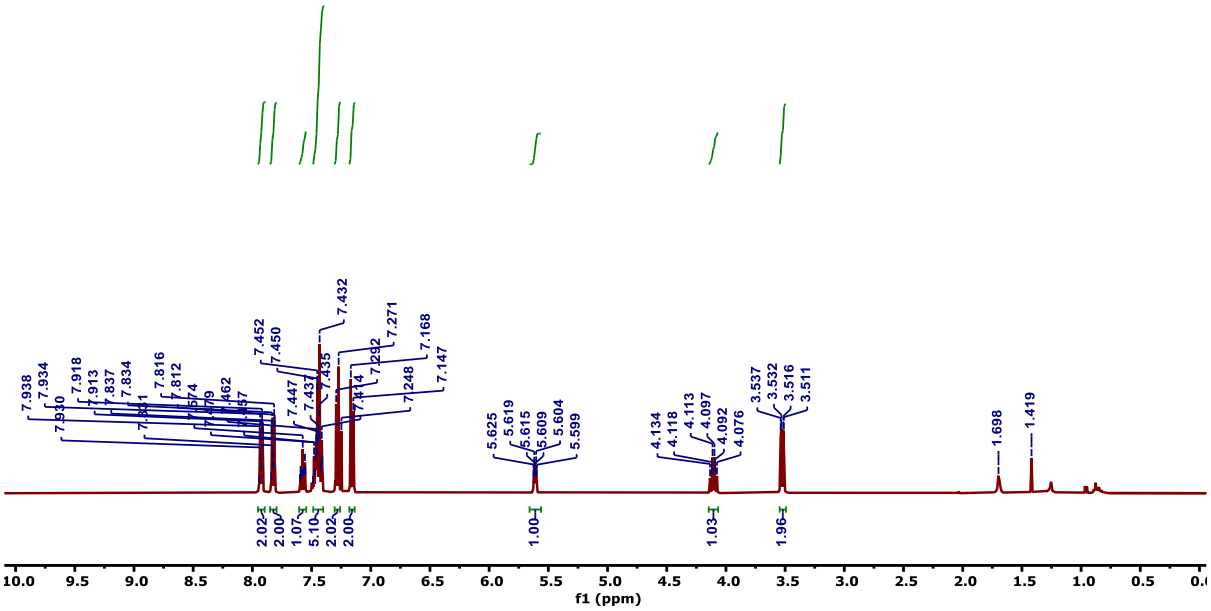


Prepared according to the general procedure discussed above: R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); Colourless liquid (47 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.91 (m, 2 H), 7.84 – 7.81 (m, 2 H), 7.60 – 7.55 (m, 1 H), 7.49 – 7.40 (m, 5 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 5.61 (dt, *J* = 6.4, 2.4 Hz, 1 H), 4.11 (td, *J* = 8.4, 6.4 Hz, 1 H), 3.52 (dd, *J* = 8.4, 2.0 Hz, 2 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 199.5, 171.7, 141.7, 136.3, 133.7, 133.7, 133.3, 131.2, 128.9 (2 CH), 128.9 (4 CH), 128.7 (2 CH), 128.3 (2 CH), 128.1 (2 CH), 78.7, 53.9, 40.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{23}H_{19}ClNO$ [*M* + H]$^+$: 360.1155; found: 360.1150.

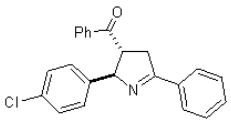
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3s**:

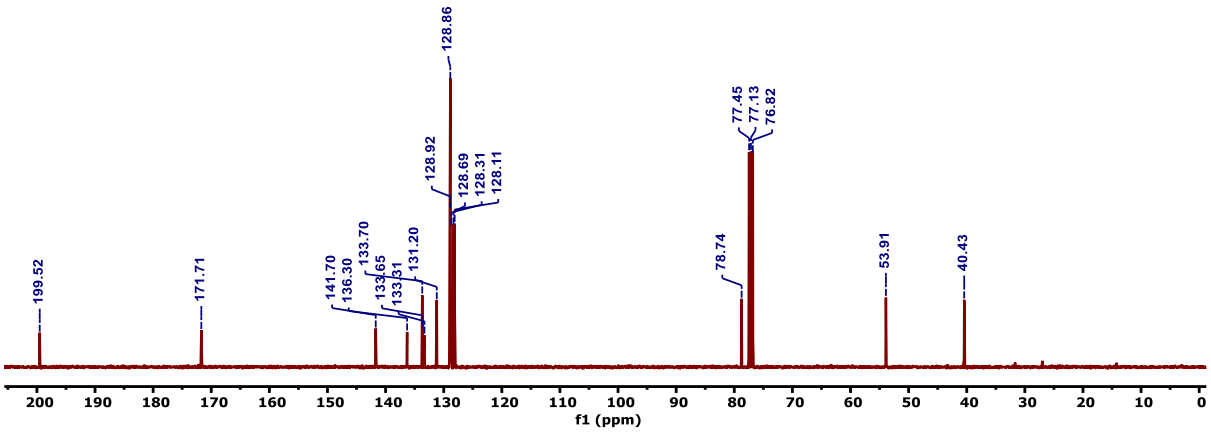
JAY-3-131B
single_pulse



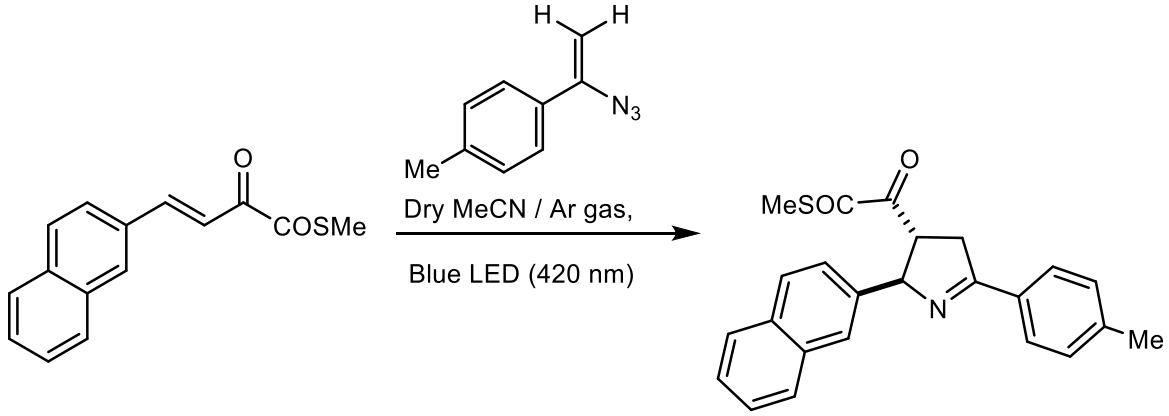


JAY-3-131B
single pulse decoupled gated NOE



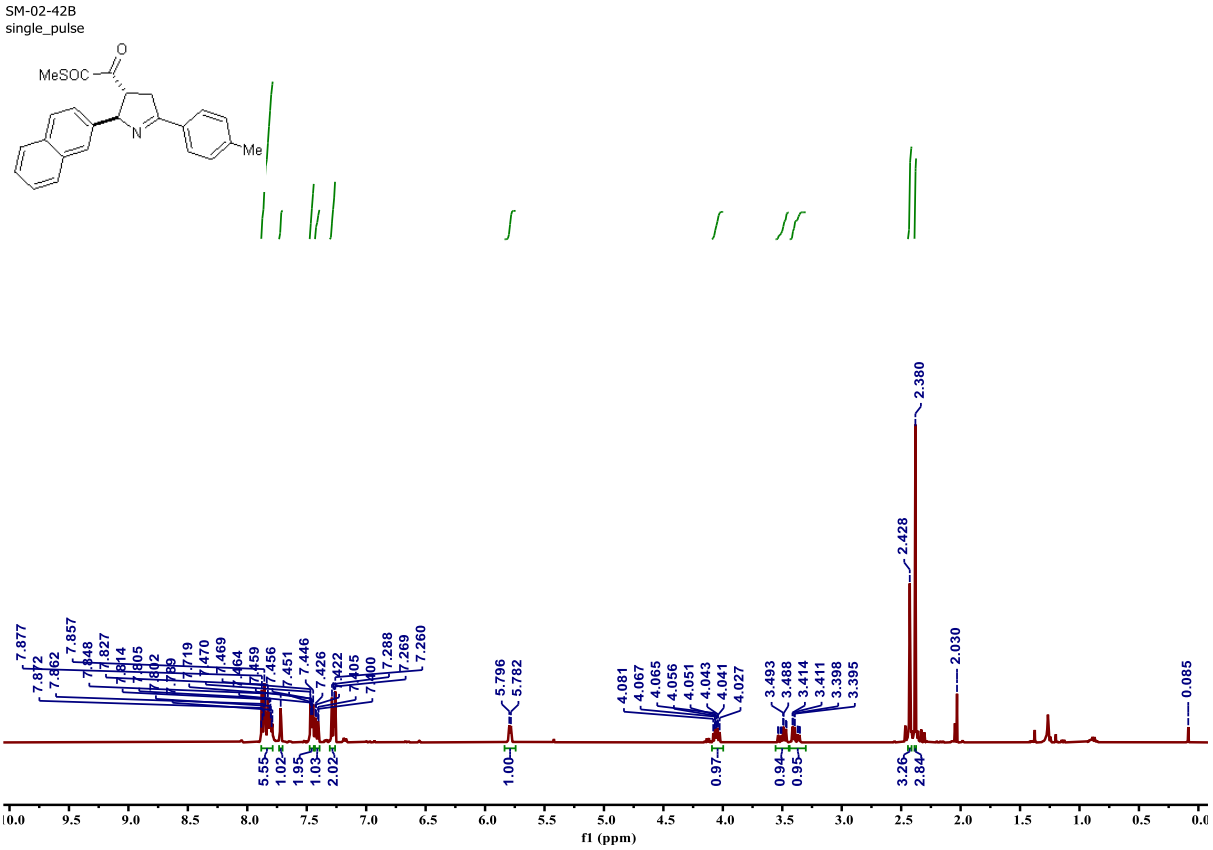


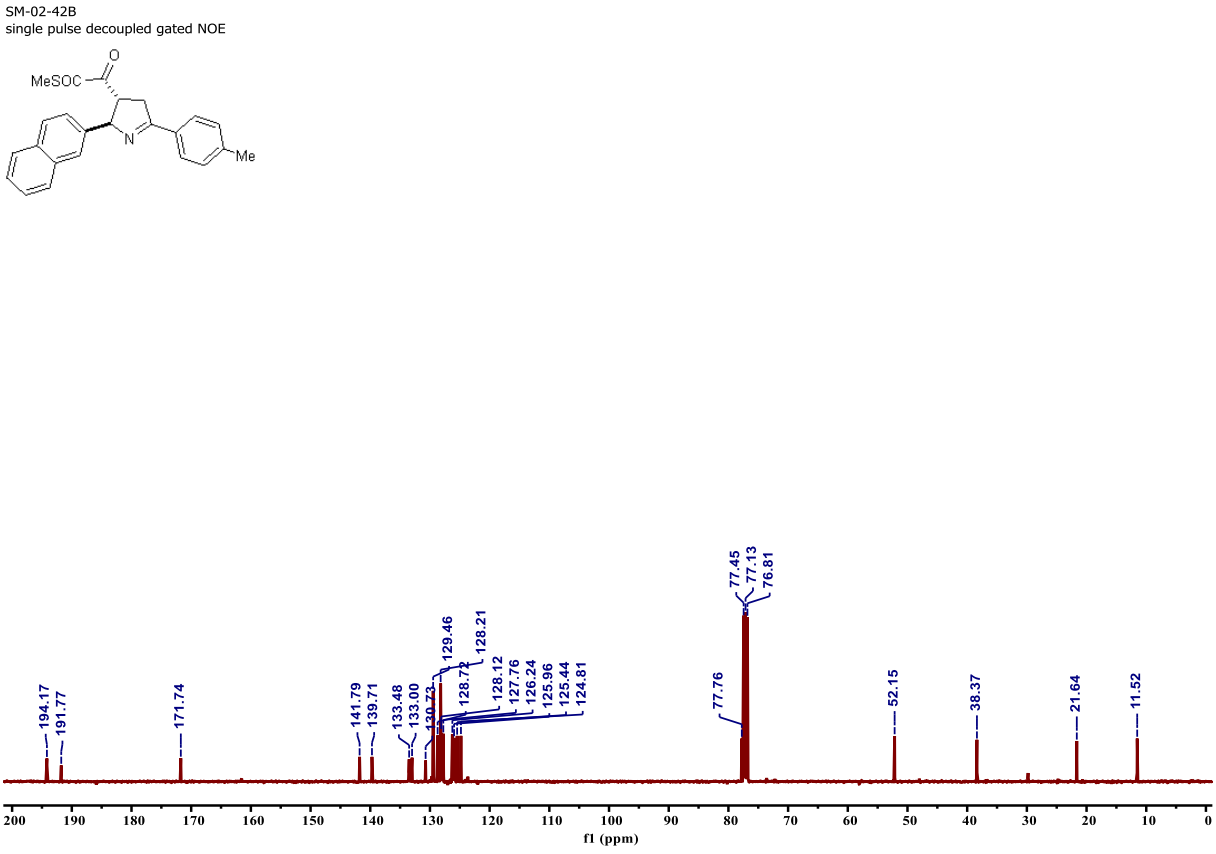
ESI-22: Analytical and spectral data of **3u:**



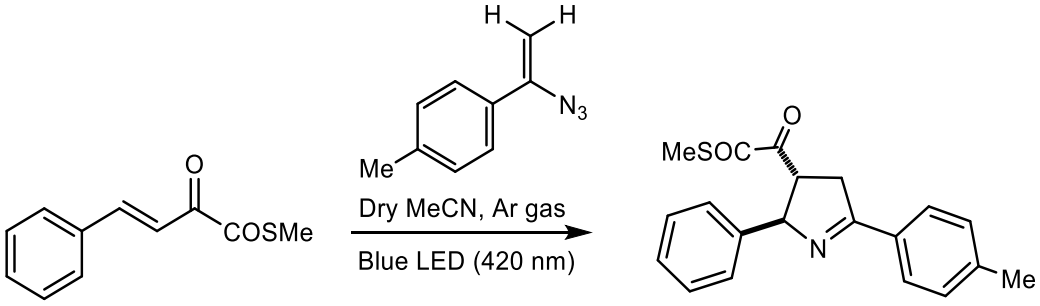
***S*-methyl 2-(2-(naphthalen-2-yl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3u:** Prepared according to the general procedure discussed above: reaction time, 14 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); yellow liquid (54 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 – 7.80 (m, 5 H), 7.72 (s, 1 H), 7.47 – 7.40 (m, 3 H), 7.28 (d, *J* = 7.6 Hz, 2 H), 5.79 (d, *J* = 5.6 Hz, 1 H), 4.05 (ddd, *J* = 10.0, 6.4, 5.6 Hz, 1 H), 3.50 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.38 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.43 (s, 3 H), 2.38 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.2, 191.78, 171.7, 141.8, 139.7, 133.5, 133.0, 130.7, 129.5 (2 CH), 128.7, 128.2 (2 CH), 128.1, 127.8, 126.2, 126.0, 125.4, 124.8, 77.8, 52.2, 38.4, 21.6, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{22}NO_2S$ $[M + H]^+$: 388.1371; found: 388.1365.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3u**

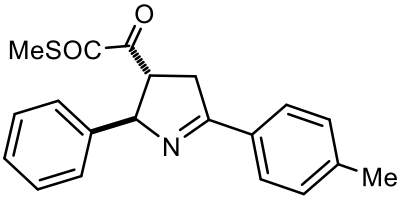




ESI-23: Analytical and spectral data of **3v**

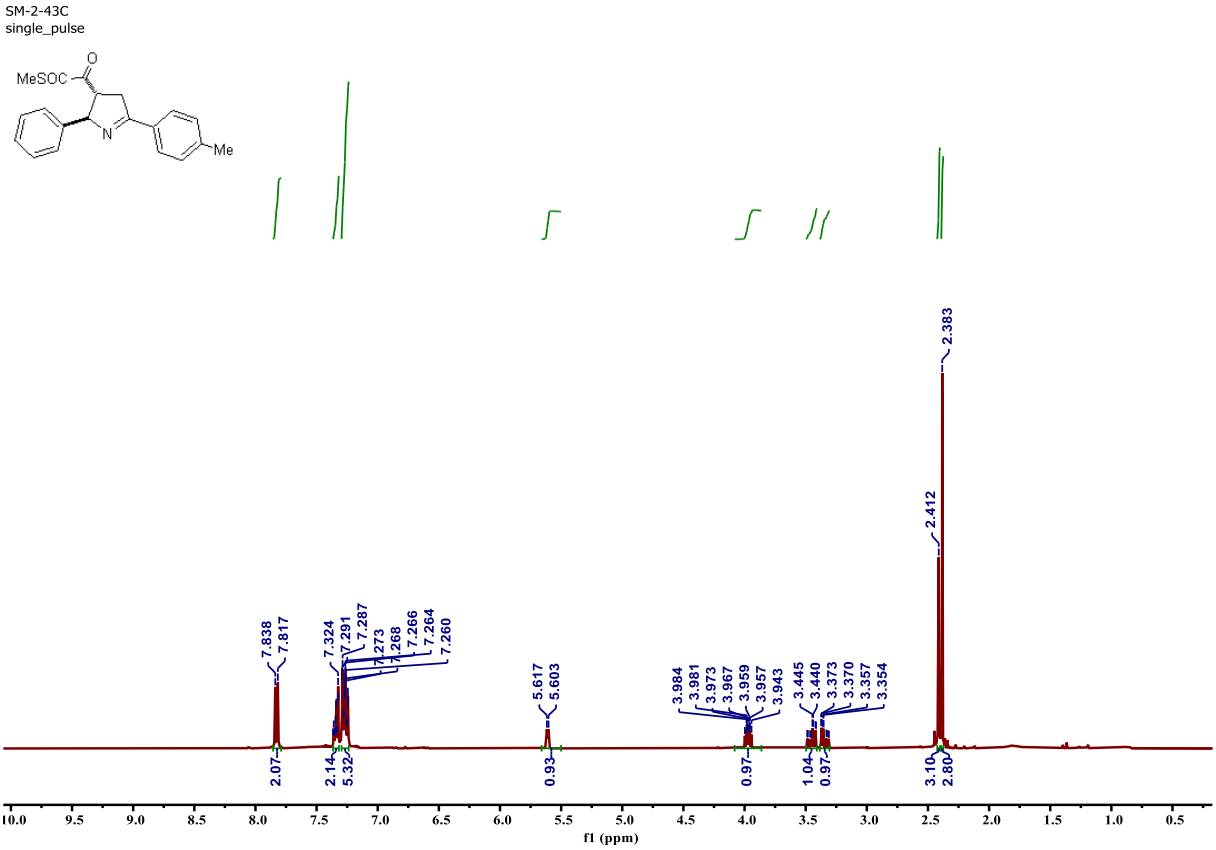


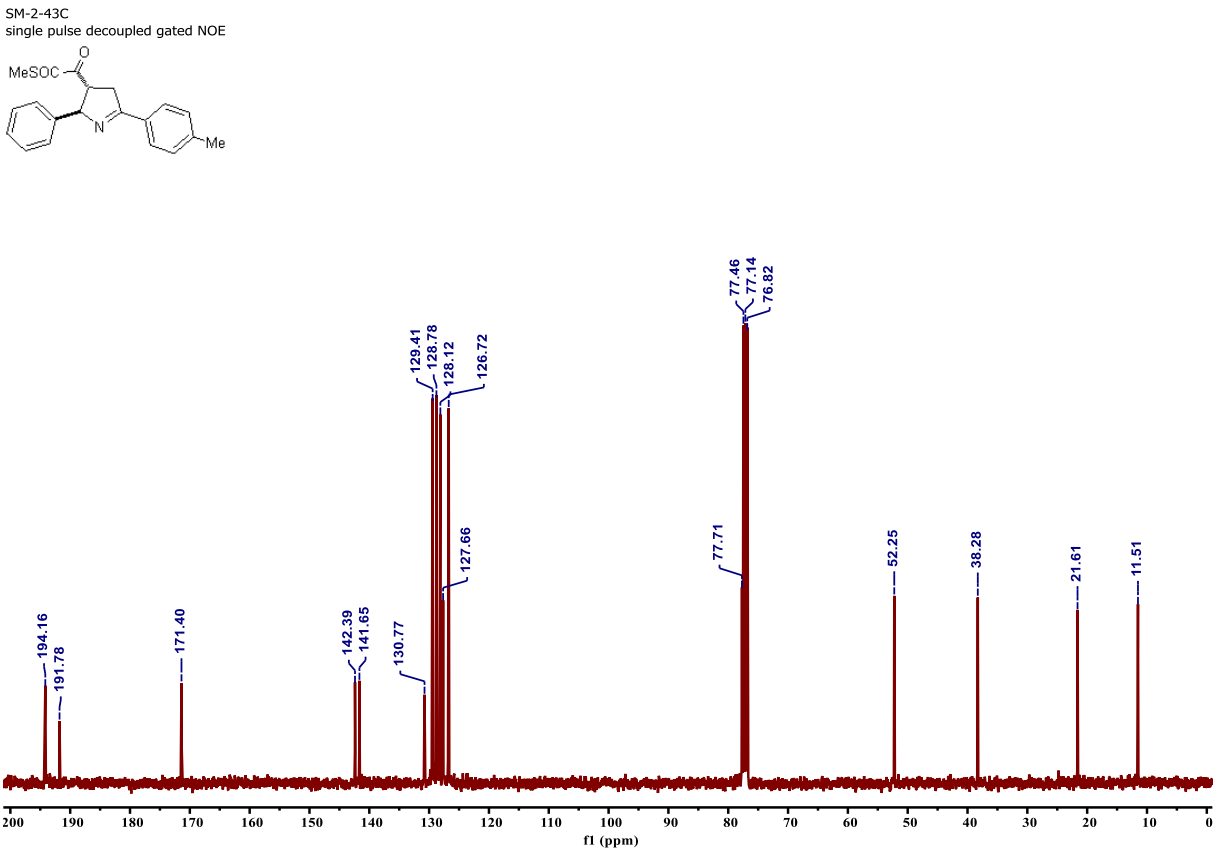
***S*-methyl 2-oxo-2-(2-phenyl-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)ethanethioate 3v:**



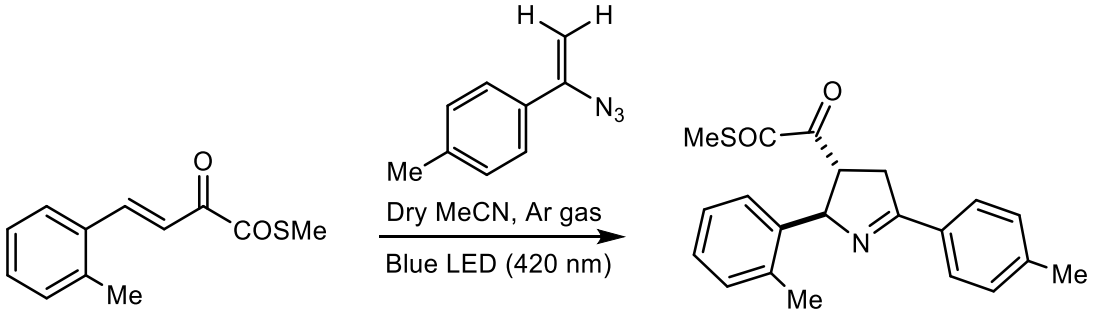
Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (15%); light yellow liquid (56 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 – 7.82 (m, 2 H), 7.37 – 7.24 (m, 7 H), 5.61 (d, *J* = 5.6 Hz, 1 H), 3.97 (ddd, *J* = 9.6, 6.4, 5.2 Hz, 1 H), 3.45 (ddd, *J* = 17.2, 10.0, 2.4 Hz, 1 H), 3.34 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.41 (s, 3 H), 2.38 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.2, 191.8, 171.4, 142.4, 141.7, 130.8, 129.4 (2 CH), 128.8 (2 CH), 128.1 (2 CH), 127.7, 126.7 (2 CH), 77.7, 52.3, 38.3, 21.6, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{20}NO_2S$ [*M* + H]$^+$: 338.1214; found: 338.1211.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3v**

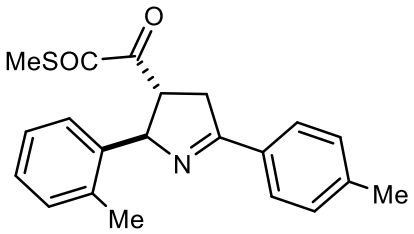




ESI-24: Analytical and spectral data of **3w**

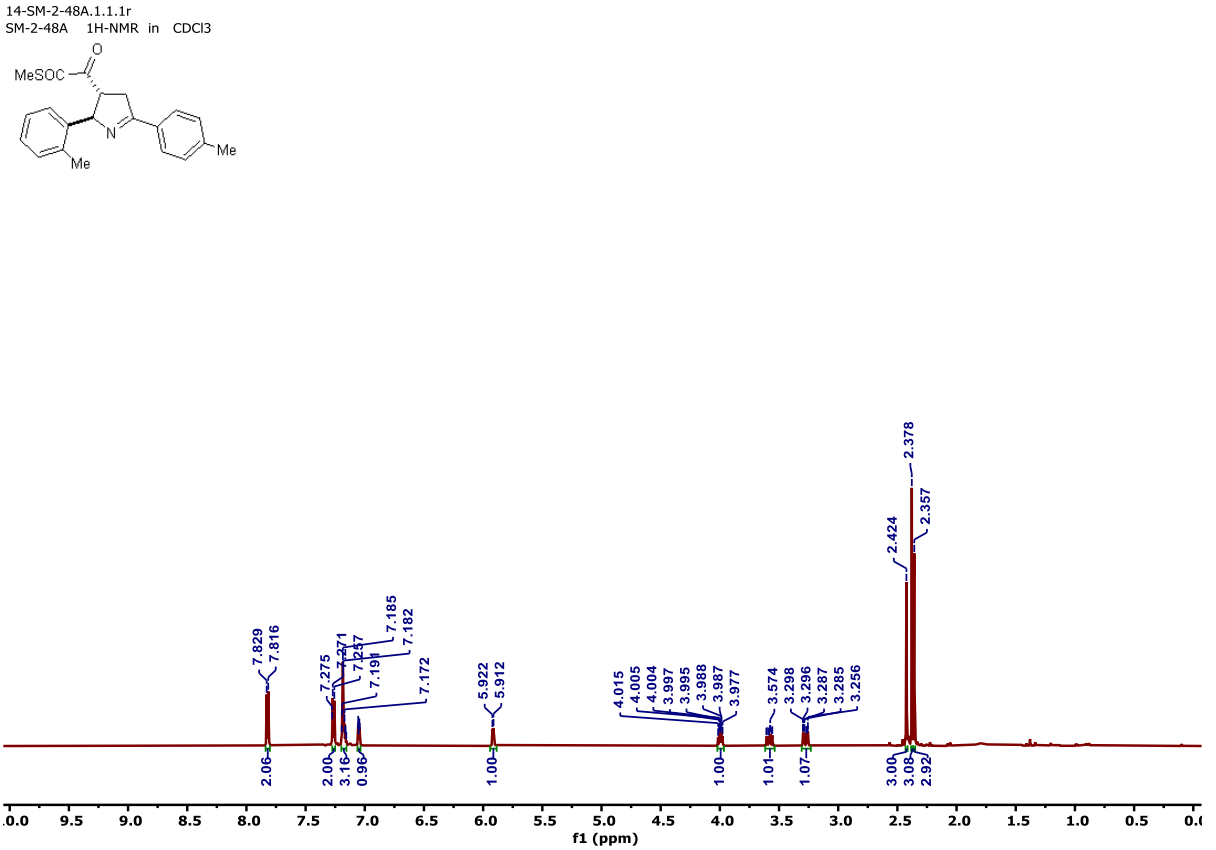


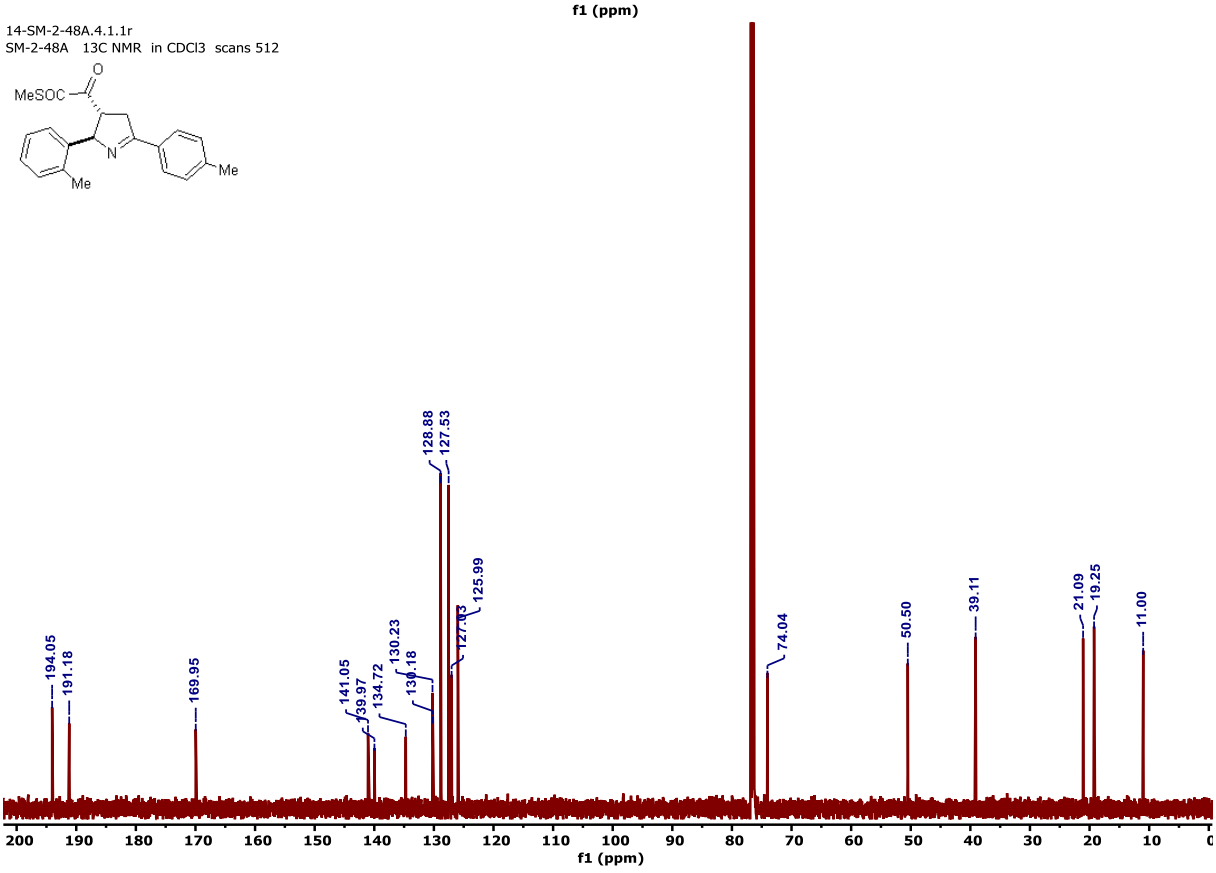
***S*-methyl 2-oxo-2-(2-(*o*-tolyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl) ethanethioate 3w:**



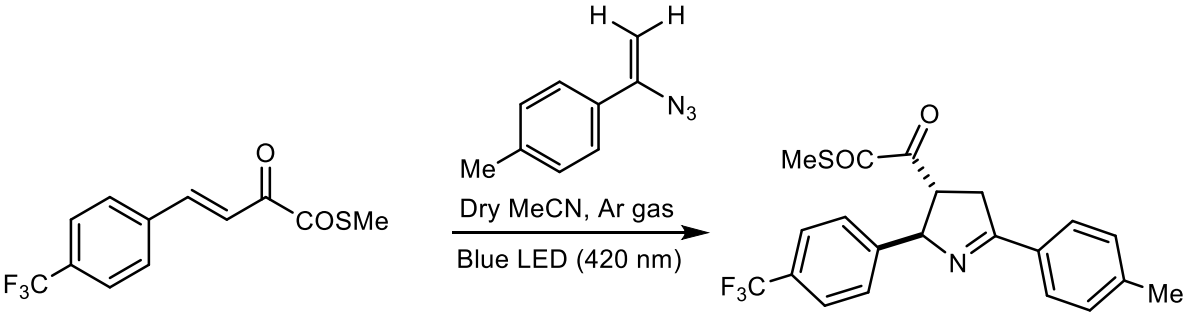
Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid (55 mg, 69%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.80 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.21 – 7.16 (m, 3 H), 7.06 – 7.04 (m, 1 H), 5.92 (d, *J* = 6.0 Hz, 1 H), 4.01 – 3.98 (m, 1 H), 3.58 (ddd, *J* = 17.4, 10.8, 2.4 Hz, 1 H), 3.28 (ddd, *J* = 17.4, 6.6, 1.2 Hz, 1 H), 2.42 (s, 3 H), 2.38 (s, 3 H), 2.36 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 194.0, 191.2, 170.0, 141.1, 140.0, 134.7, 130.2, 130.2, 128.9 (2 CH), 127.5 (2 CH), 127.0, 126.0 (2 CH), 74.0, 50.5, 39.1, 21.1, 19.2, 11.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{21}H_{22}NO_2S$ [*M* + H]$^+$: 352.1371; found: 352.1362.

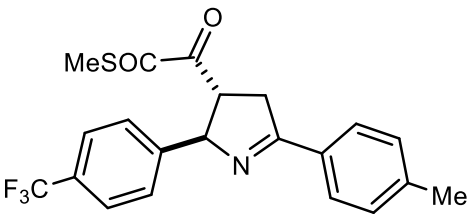
^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **3w**





ESI-25: Analytical and spectral data of **3x**

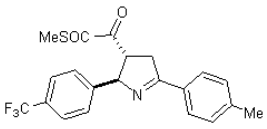


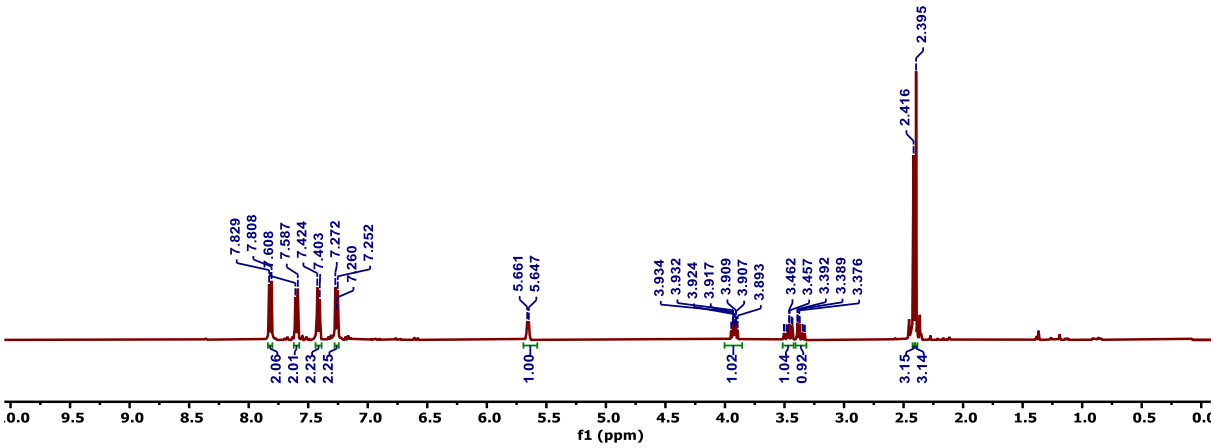
***S*-methyl 2-oxo-2-(5-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyrrol-3-yl) ethanethioate 3x:** 

Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid; (53 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 5.65 (d, *J* = 5.6 Hz, 1 H), 3.92 (ddd, *J* = 9.6, 6.4, 5.6 Hz, 1 H), 3.47 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.36 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.42 (s, 3 H), 2.39 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.8, 191.7, 172.2, 146.4, 142.0, 130.5, 130.0, 129.7, 129.5 (2 CH), 128.1 (2 CH), 127.1 (2 CH), 126.9, 125.7 (q, *J* = 4.1 Hz, 1 C), 76.9, 52.1, 38.4, 21.6, 11.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.4 ppm. HRMS (ESI-QTOF): *m/z* calcd for $C_{21}H_{19}F_3NO_2S$ [*M* + H]$^+$: 406.1088; found: 406.1080.

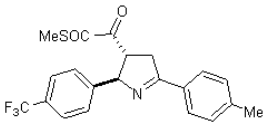
^{1}H (400 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$), and ^{19}F (376 MHz, $CDCl_3$) NMR spectra of **3x**

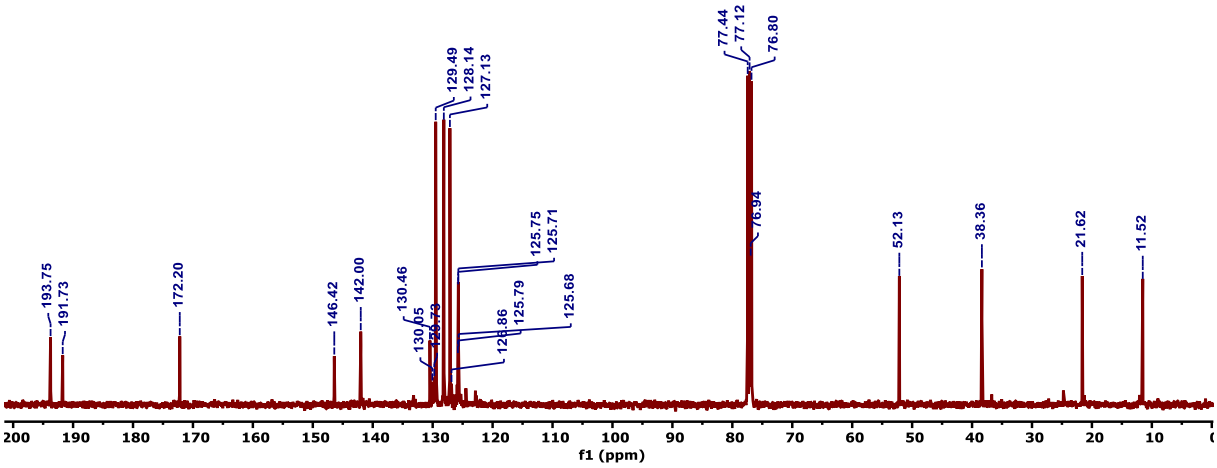
SM-2-50A-02
single_pulse



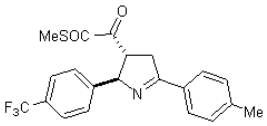


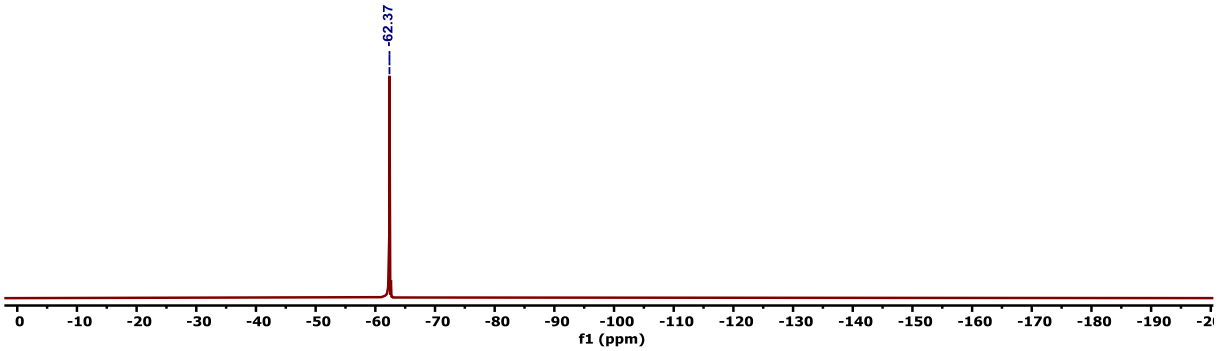
SM-2-50A-02
single pulse decoupled gated NOE



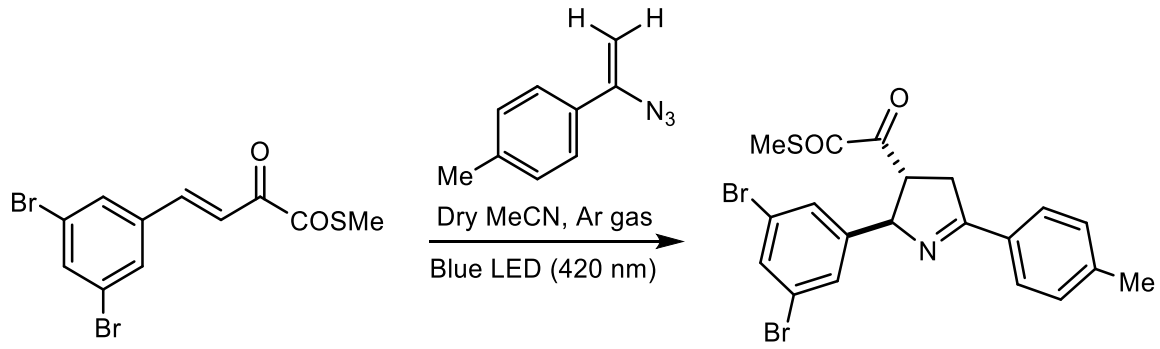


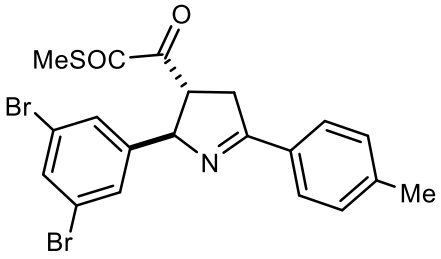
SM-02-50A-02
single pulse decoupled gated NOE





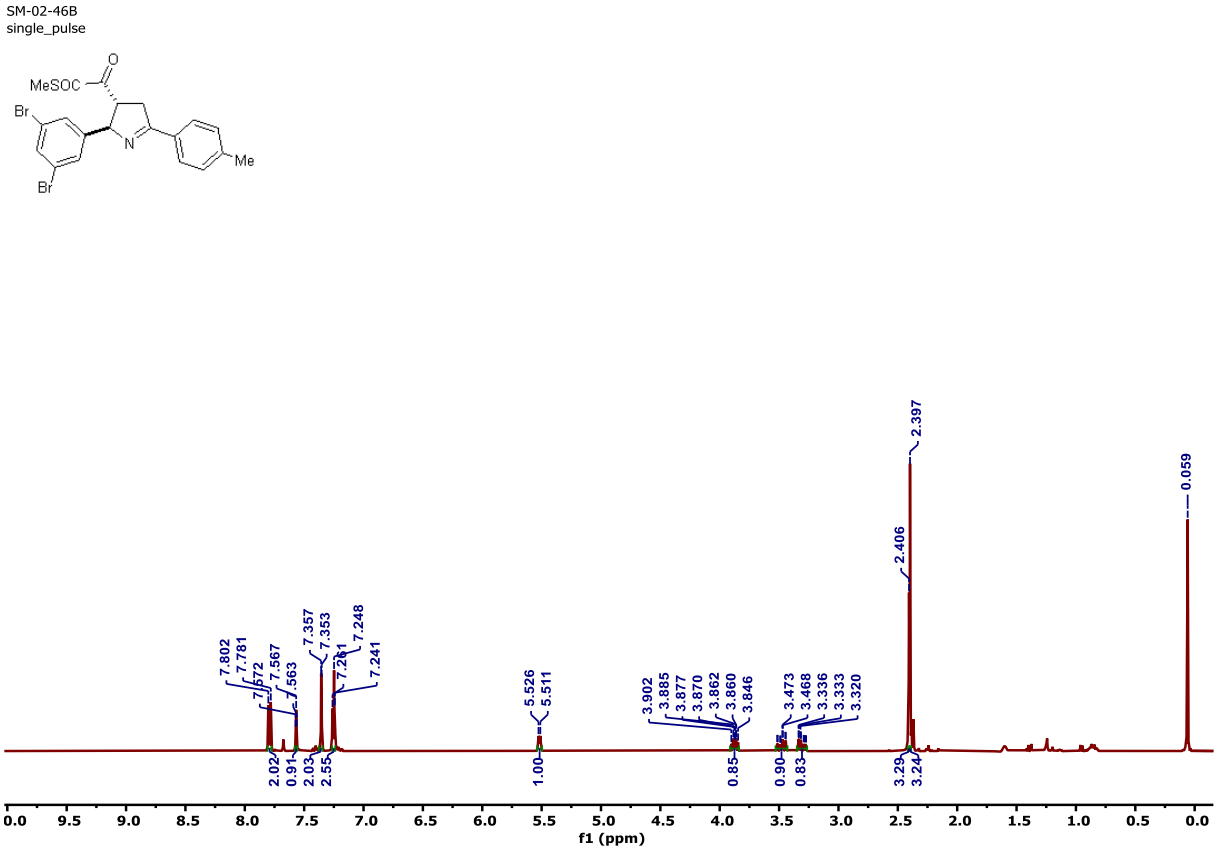
ESI-26: Analytical and spectral data of **3y**

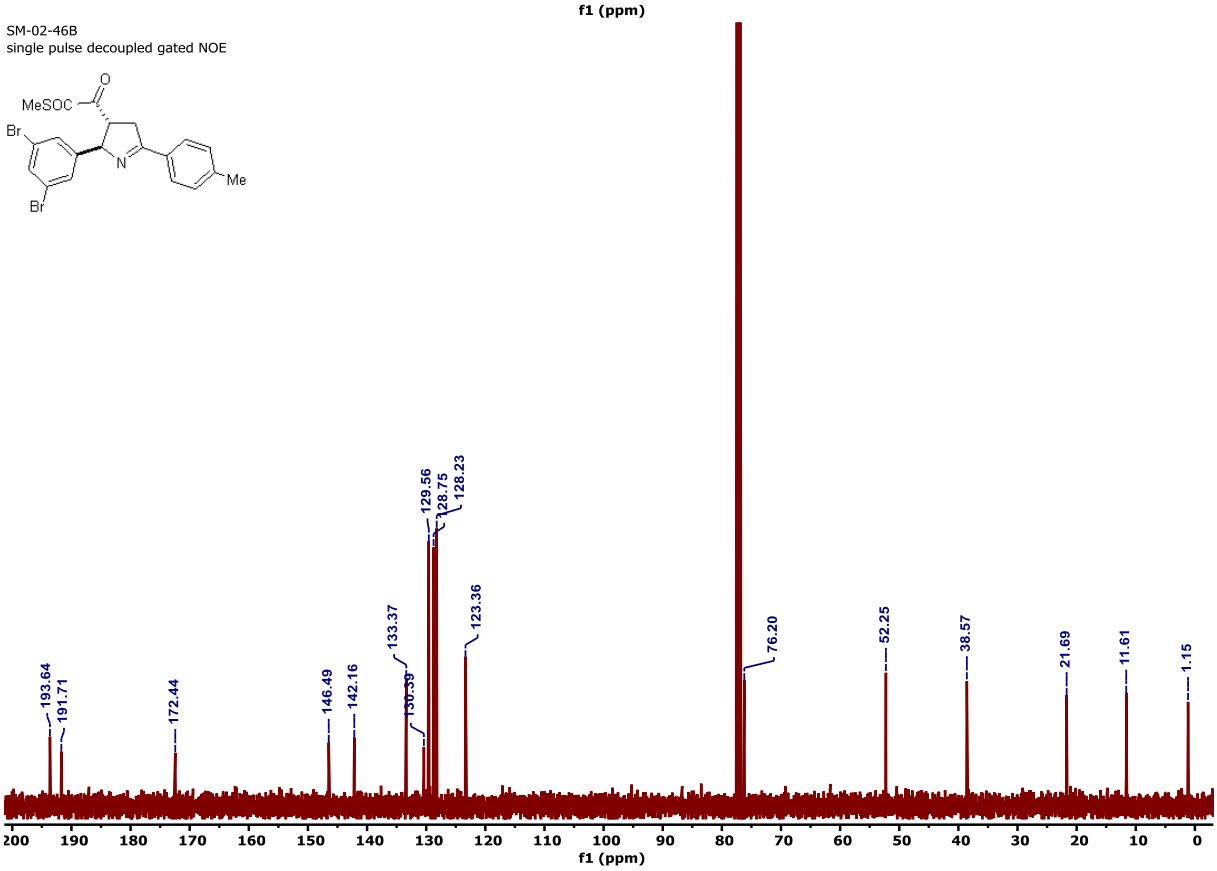




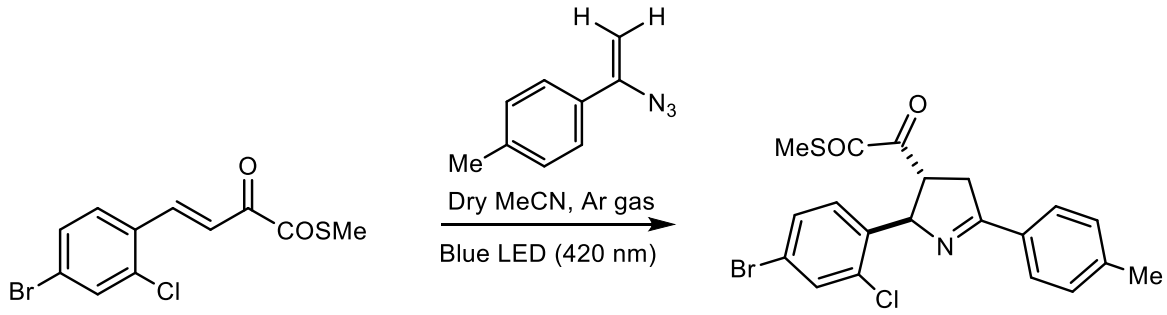
***S*-methyl 2-(2-(3,5-dibromophenyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3y:** Prepared according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid; (58 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.78 (m, 2 H), 7.57 (t, *J* = 2.0 Hz, 1 H), 7.35 (d, *J* = 1.6 Hz, 2 H), 7.26 (s, 1 H), 7.24 (d, *J* = 2.8 Hz, 1 H), 5.52 (d, *J* = 6.0 Hz, 1 H), 3.91 – 3.84 (m, 1 H), 3.48 (ddd, *J* = 17.2, 10.0, 2.1 Hz, 1 H), 3.30 (ddd, *J* = 17.2, 6.4, 1.2 Hz, 1 H), 2.41 (s, 3 H), 2.40 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.6, 191.7, 172.4, 146.4, 142.1, 133.3, 130.3, 129.5 (2 CH), 128.7 (2 CH), 128.8 (3 CH), 123.3, 76.2, 52.3, 38.5, 21.6, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{18}Br_2NO_2S$ [*M* + H]$^+$: 493.9425; found: 493.9427.

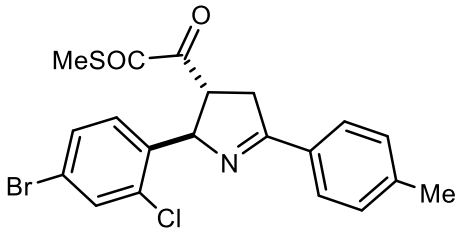
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3y**





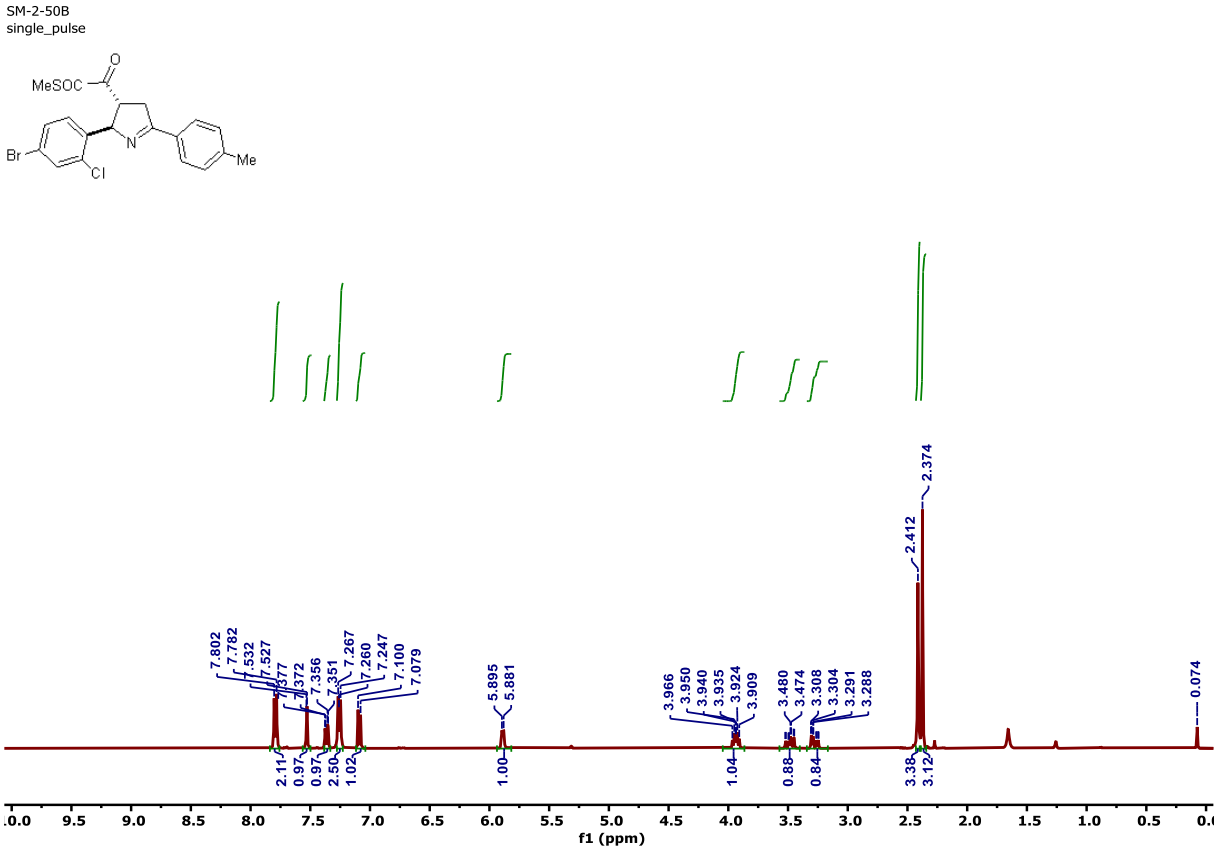
ESI-27: Analytical and spectral data of **3z**

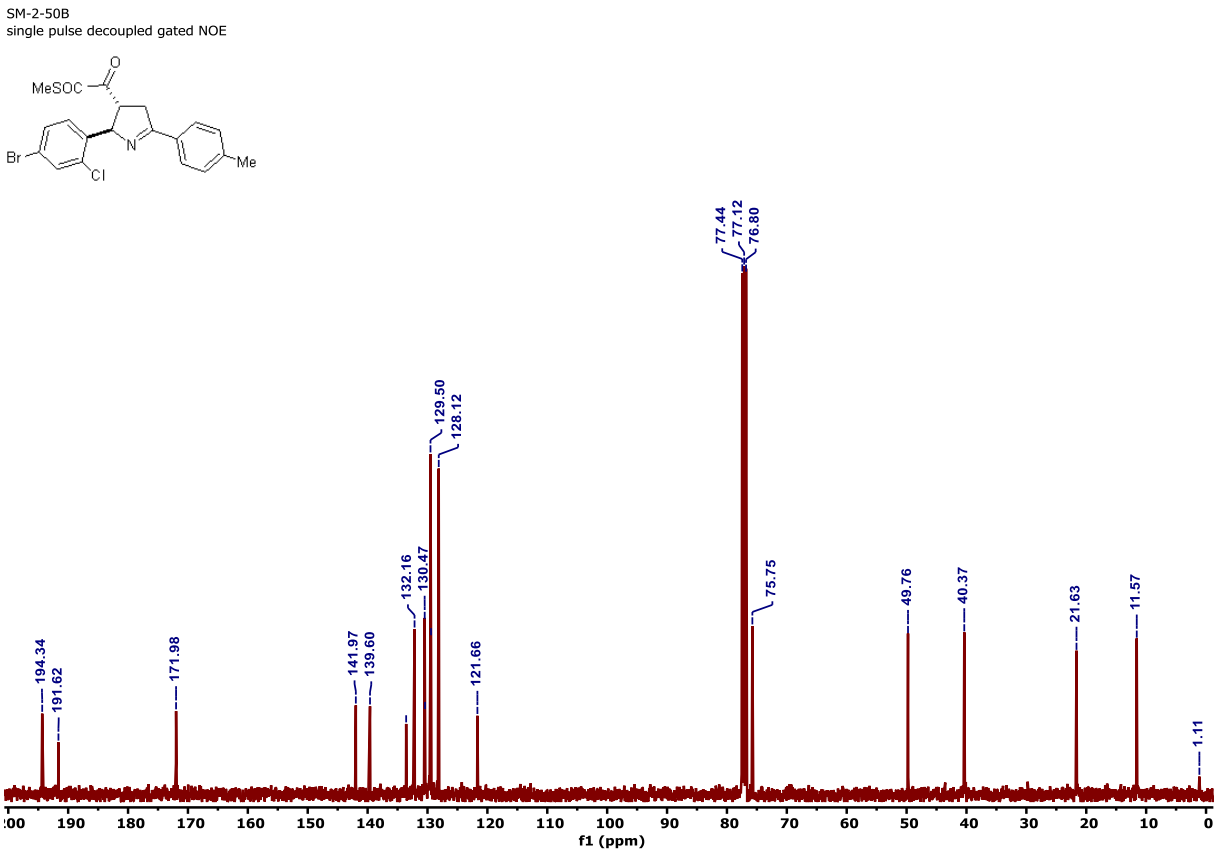


***S*-methyl 2-(2-(4-bromo-2-chlorophenyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3z:** 

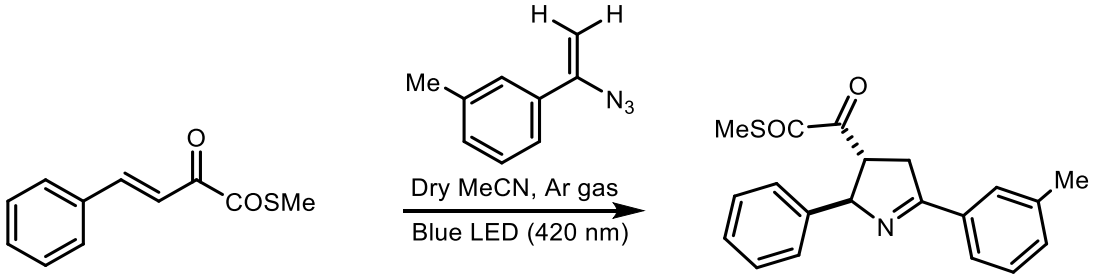
Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid (57 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 2.0 Hz, 1 H), 7.36 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.27 – 7.23 (m, 2 H), 7.09 (d, *J* = 8.4 Hz, 1 H), 5.89 (d, *J* = 5.6 Hz, 1 H), 3.94 (dt, *J* = 10.4, 6.4 Hz, 1 H), 3.49 (ddd, *J* = 17.6, 10.8, 2.4 Hz, 1 H), 3.28 (ddd, *J* = 17.6, 6.8, 1.6 Hz, 1 H), 2.41 (s, 3 H), 2.37 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.3, 191.6, 172.0, 142.0, 139.6, 133.6, 132.2, 130.5, 130.4, 129.5 (2 CH), 129.4, 128.1 (2 CH), 121.7, 75.8, 49.8, 40.4, 21.6, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{18}BrClNO_2S$ $[M + H]^+$: 449.9930; found: 449.9945

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3z**

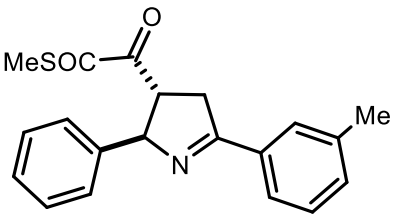




ESI-28: Analytical and spectral data of **3aa**

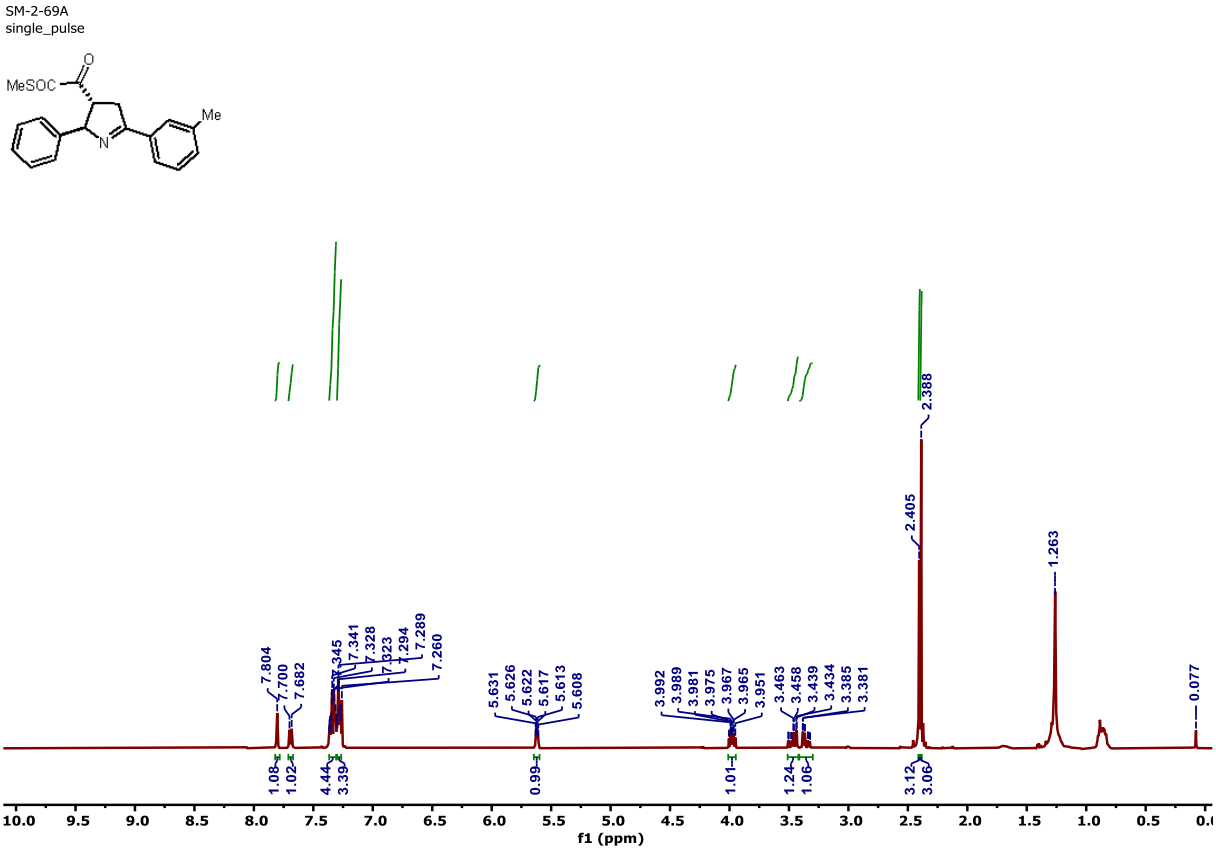


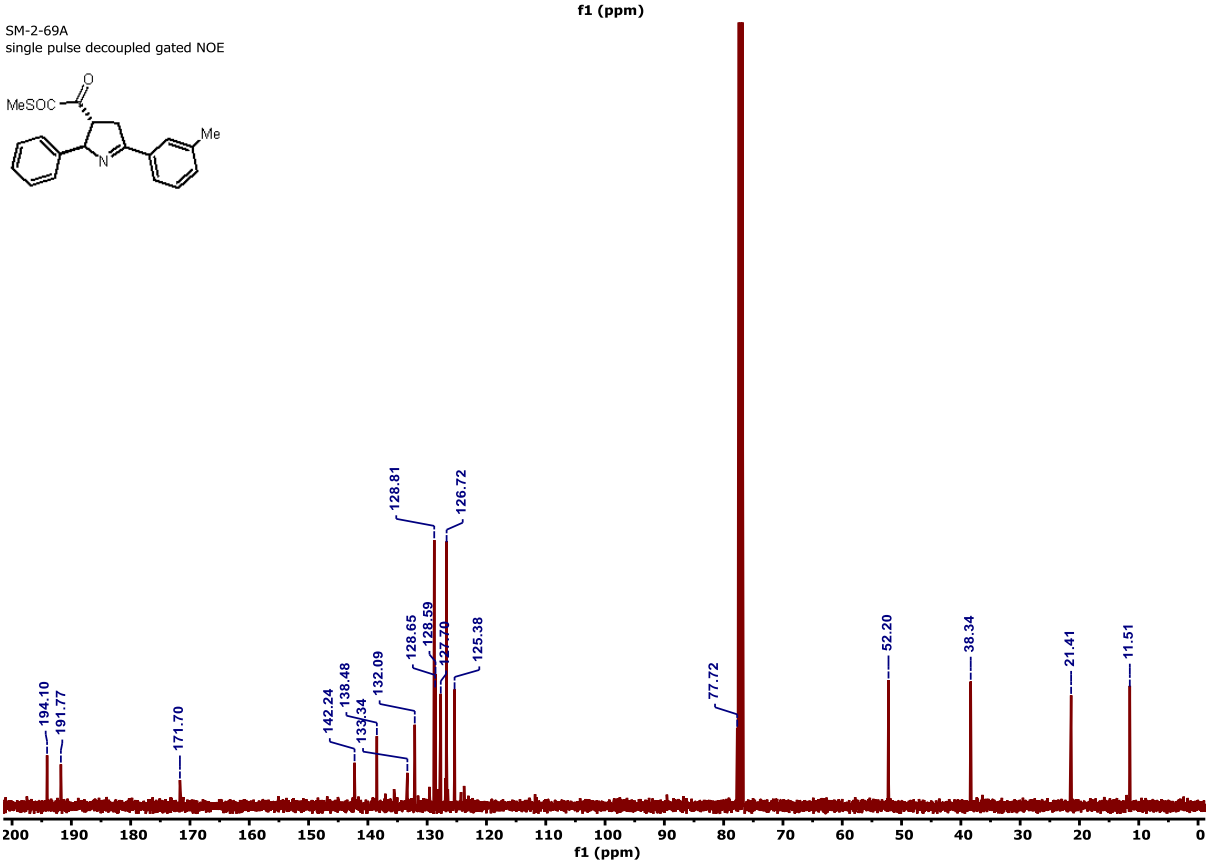
***S*-methyl 2-oxo-2-(2-phenyl-5-(*m*-tolyl)-3,4-dihydro-2*H*-pyrrol-3-yl)ethanethioate 3aa:**



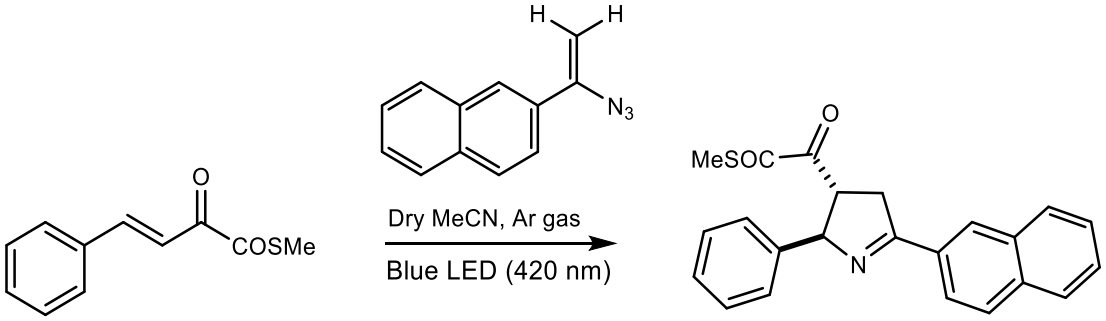
Prepared according to the general procedure discussed above: reaction time, 15 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid (56.2 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 1 H), 7.37 – 7.31 (m, 4 H), 7.30 – 7.27 (m, 3 H), 5.62 (dt, *J* = 5.6, 2.0 Hz, 1 H), 3.98 (ddd, *J* = 9.6, 6.4, 5.2 Hz, 1 H), 3.47 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.35 (ddd, *J* = 17.2, 6.4, 1.6 Hz, 1 H), 2.41 (s, 3 H), 2.39 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.1, 191.8, 171.7, 142.3, 138.5, 133.3, 132.1, 128.8 (2 CH), 128.7, 128.6, 127.7, 126.7 (2 CH), 125.4, 77.7, 52.2, 38.3, 21.4, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{20}NO_2S$ [*M* + H]$^+$: 338.1214; found: 338.1203.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3aa:**

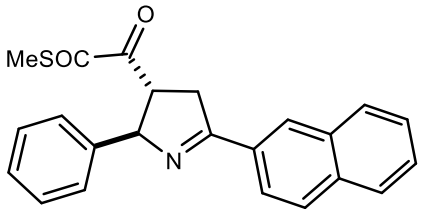




ESI-29: Analytical and spectral data of **3ab**



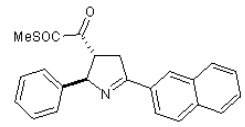
***S*-methyl 2-(5-(naphthalen-2-yl)-2-phenyl-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate**

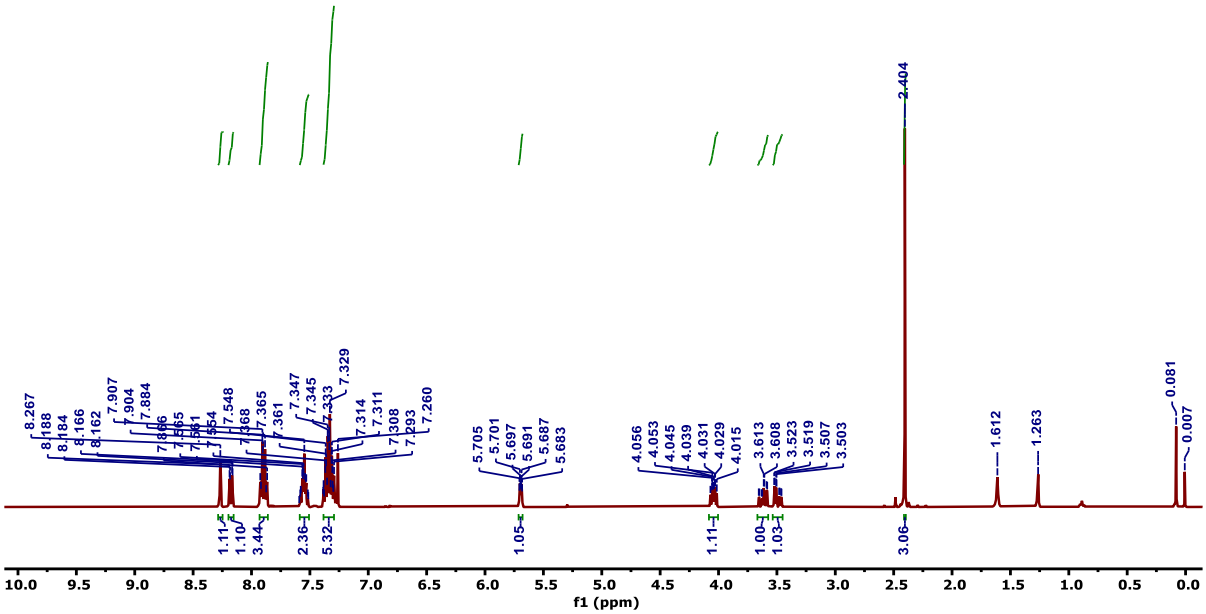


3ab: Prepared according to the general procedure discussed above: reaction time, 14 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); light yellow liquid (66 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 8.18 (dd, *J* = 8.8, 1.6 Hz, 1 H), 7.93 – 7.87 (m, 3 H), 7.59 – 7.51 (m, 2 H), 7.39 – 7.29 (m, 5 H), 5.69 (dt, *J* = 5.6, 1.6 Hz, 1 H), 4.04 (ddd, *J* = 9.6, 6.4, 5.2 Hz, 1 H), 3.62 (ddd, *J* = 17.2, 9.6, 2.0 Hz, 1 H), 3.49 (ddd, *J* = 17.2, 6.4, 1.6 Hz, 1 H), 2.40 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.1, 191.8, 171.4, 142.3, 134.8, 133.0, 131.0, 128.9 (2 CH), 128.8 (2 CH), 128.5, 127.9, 127.7, 127.6, 126.8 (2 CH), 126.7, 124.7, 77.9, 52.4, 38.4, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{23}H_{20}NO_2S$ [*M* + H]$^+$: 374.1214; found: 374.1201.

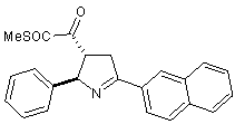
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3ab**

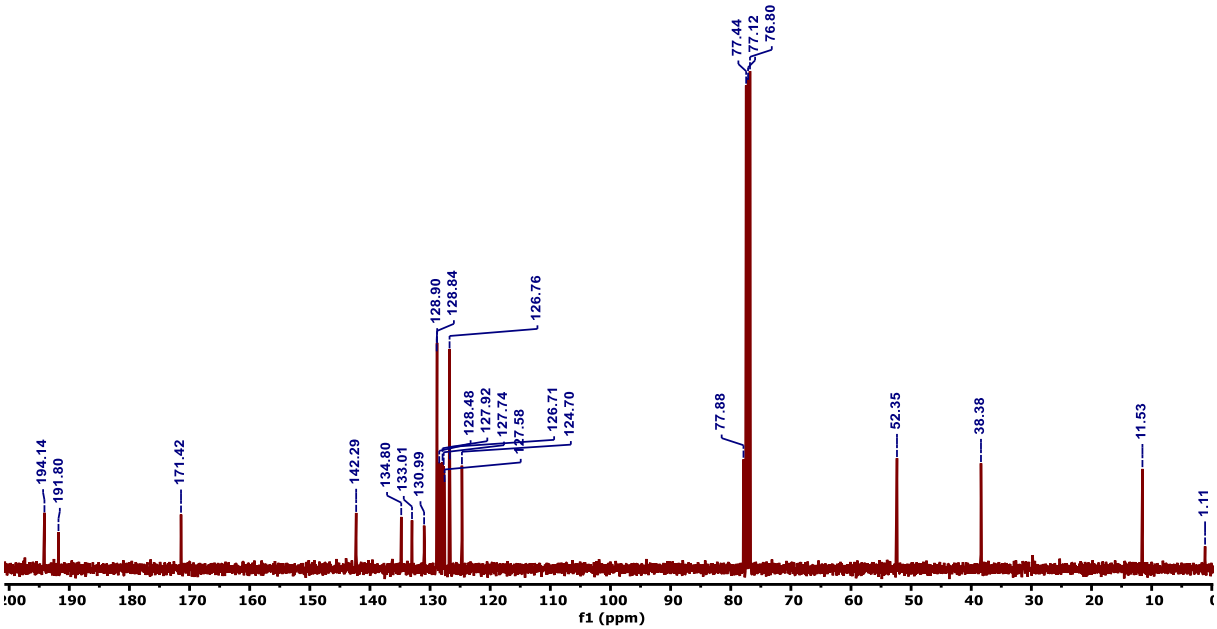
SM-2-97B
single_pulse



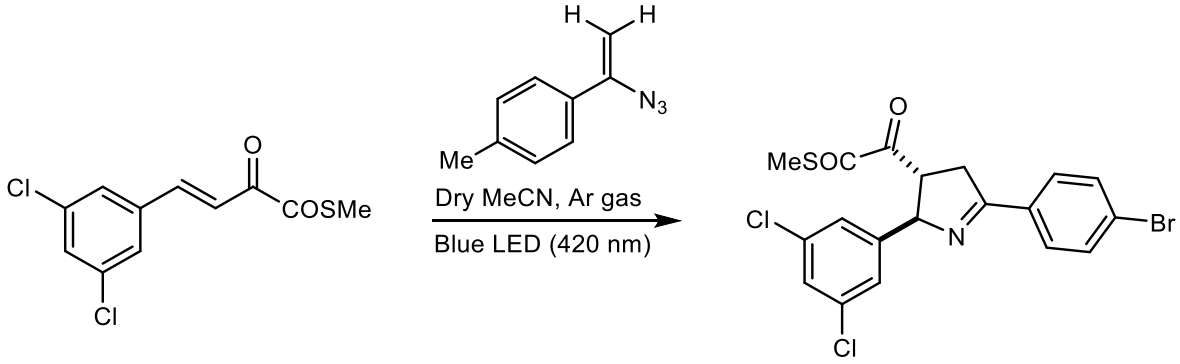


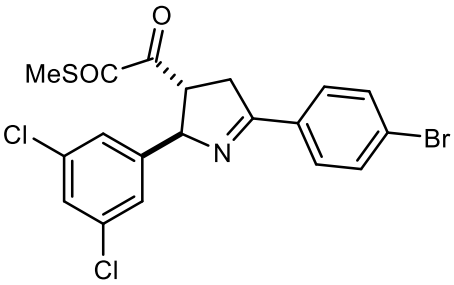
SM-2-97B
single pulse decoupled gated NOE





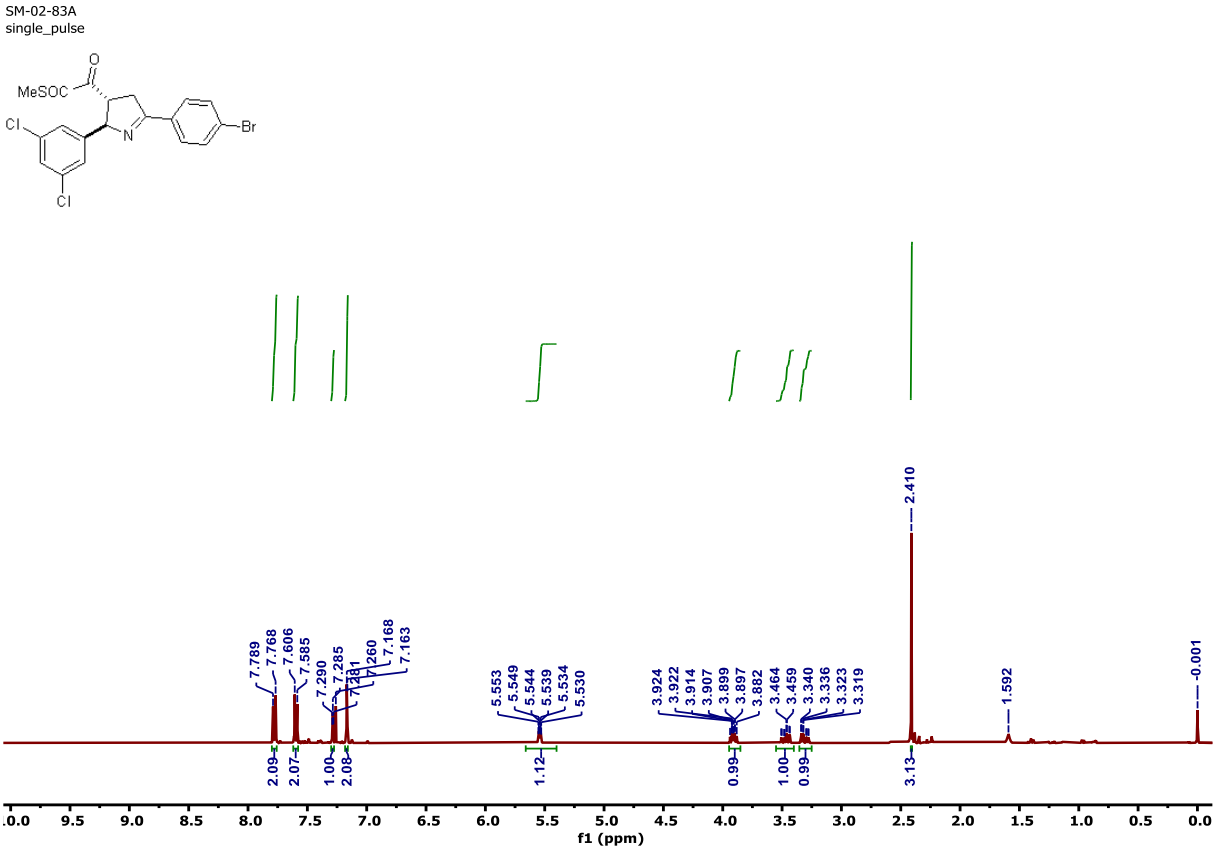
ESI-30: Analytical and spectral data of **3ac**

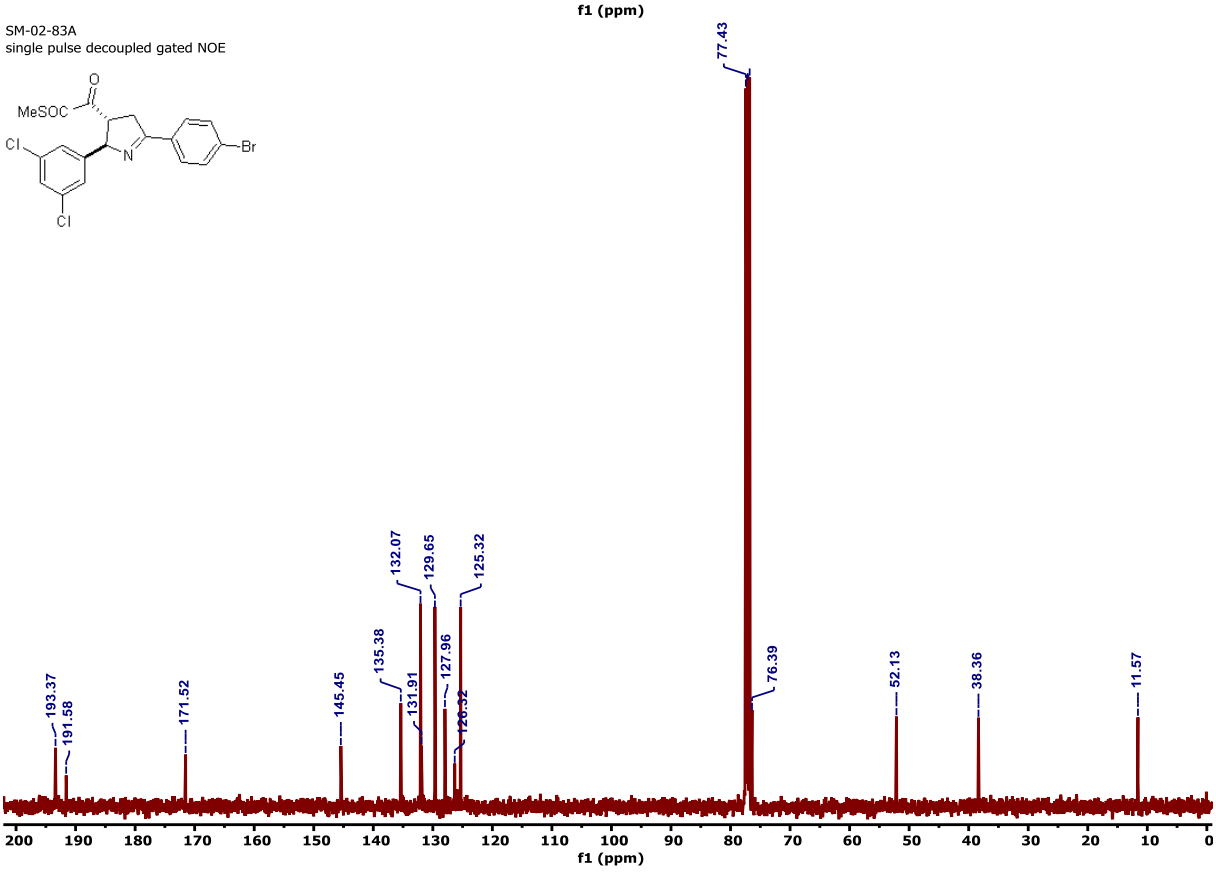




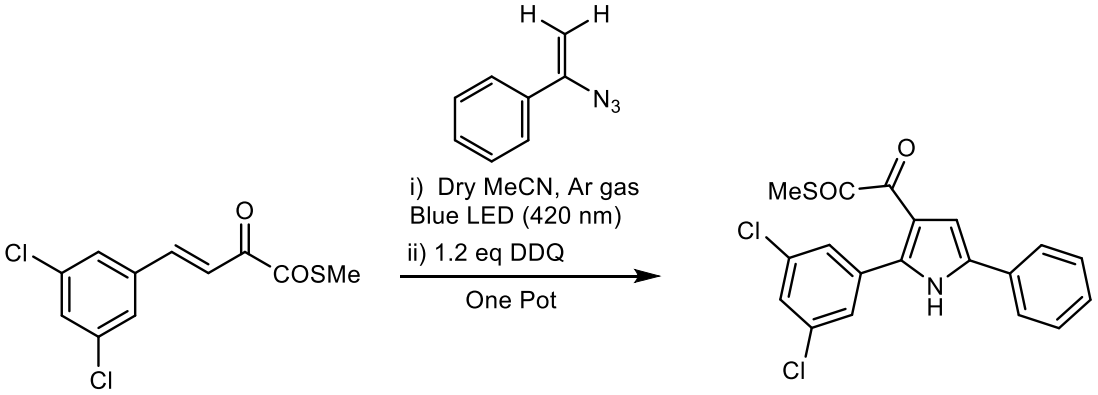
***S*-methyl 2-(5-(4-bromophenyl)-2-(3,5-dichlorophenyl)-3,4-dihydro-2*H*-pyrrol-3-yl)-2-oxoethanethioate 3ac:** Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); light yellow liquid (72 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 – 7.76 (m, 2 H), 7.61 – 7.59 (m, 2 H), 7.29 (t, *J* = 2.0 Hz, 1 H), 7.17 (d, *J* = 2.0 Hz, 2 H), 5.54 (dt, *J* = 5.6, 1.6 Hz, 1 H), 3.91 (ddd, *J* = 9.6, 6.4, 5.6 Hz, 1 H), 3.47 (ddd, *J* = 17.6, 10.0, 2.4 Hz, 1 H), 3.31 (ddd, *J* = 17.2, 6.8, 1.6 Hz, 1 H), 2.41 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.4, 191.6, 171.5, 145.5, 135.4, 132.1 (2 CH), 131.9, 129.7 (3 CH), 128.0, 126.32 (2 CH), 125.3, 76.4, 52.1, 38.4, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{15}BrCl_2NO_2S$ [*M* + H]$^+$: 469.9384; found: 469.9379.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **3ac:**

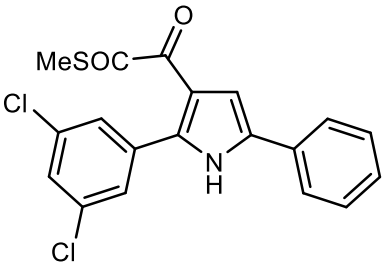




ESI-31: Analytical and spectral data of **4a**

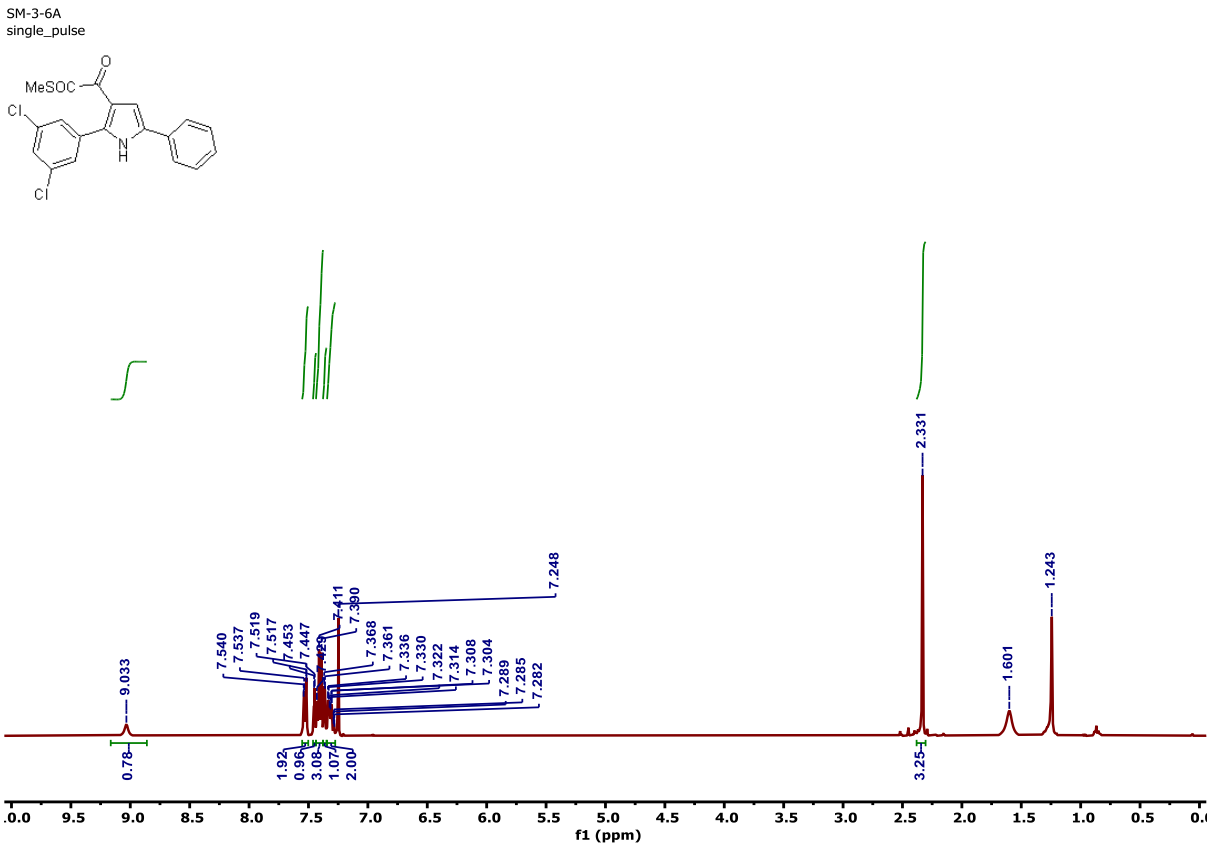


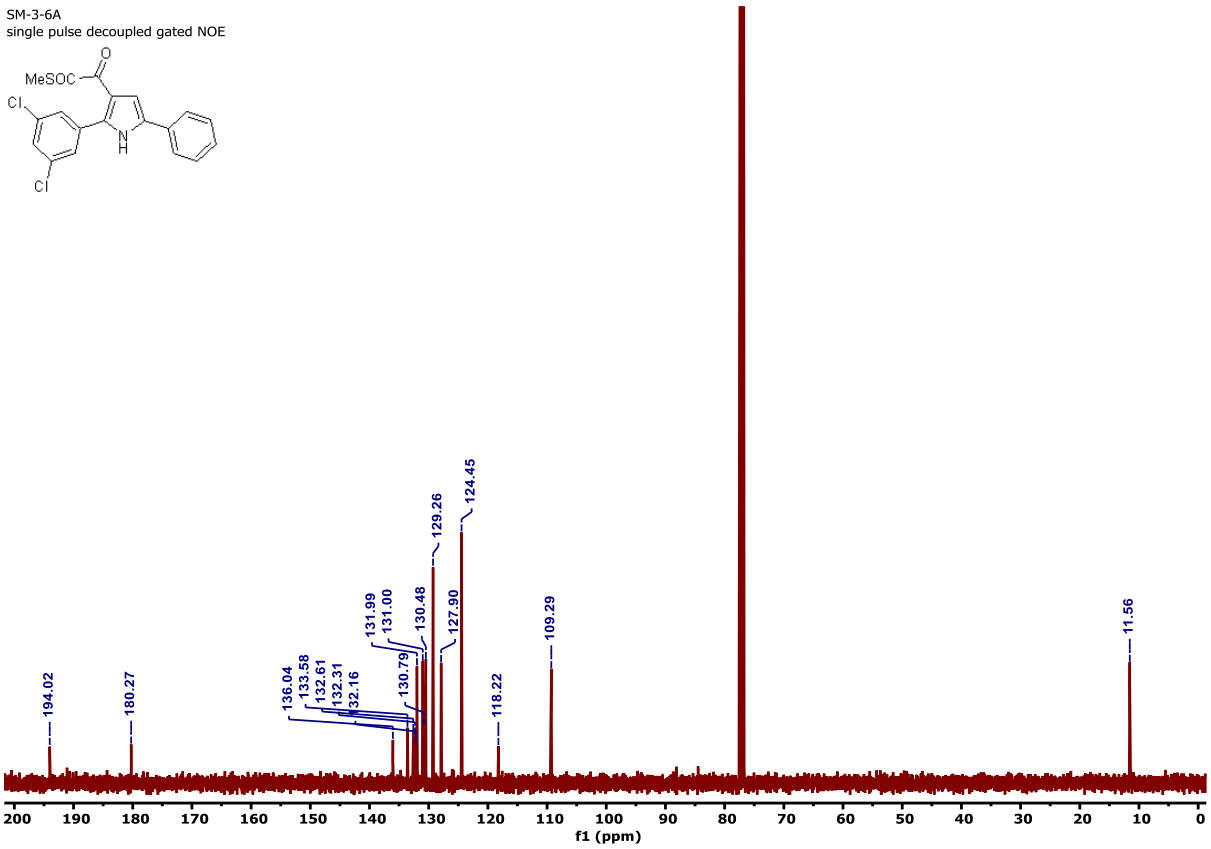
***S*-methyl 2-(2-(3,5-dichlorophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4a:**



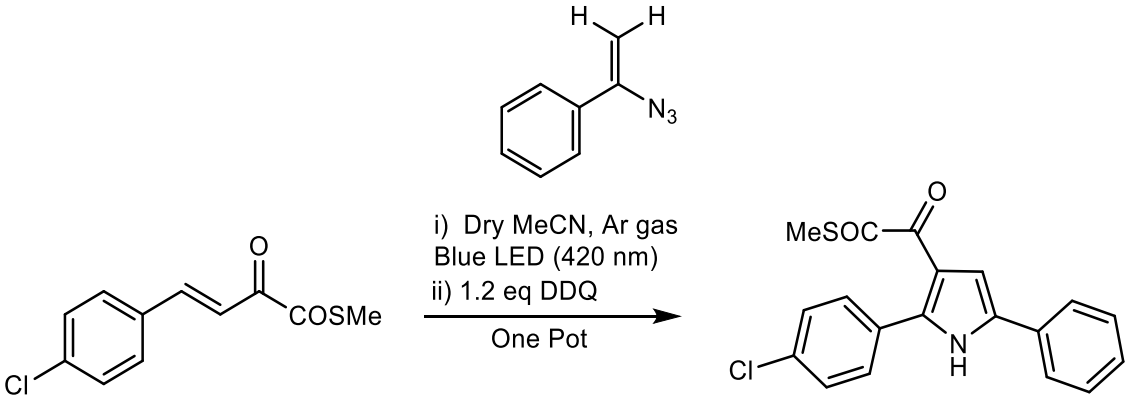
Prepared according to the general procedure discussed above: reaction time, 30 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); red solid (61 mg, 86%); mp 130–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 7.53 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.45 (d, *J* = 2.4 Hz, 1 H), 7.41 (t, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 2.8 Hz, 1 H), 7.37 – 7.26 (m, 2 H), 2.33 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.0, 180.3, 136.0, 133.6, 132.6, 132.3, 132.2, 132.0, 131.0, 130.8, 130.5, 129.3 (2 CH), 127.9, 124.5 (2 CH), 118.2, 109.3, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{14}Cl_2NO_2S$ [*M* + H]$^+$: 390.0122; found: 390.0109.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4a**

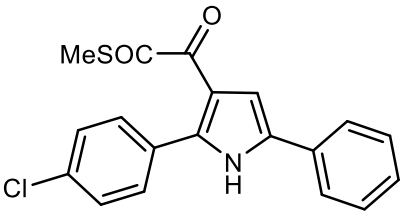




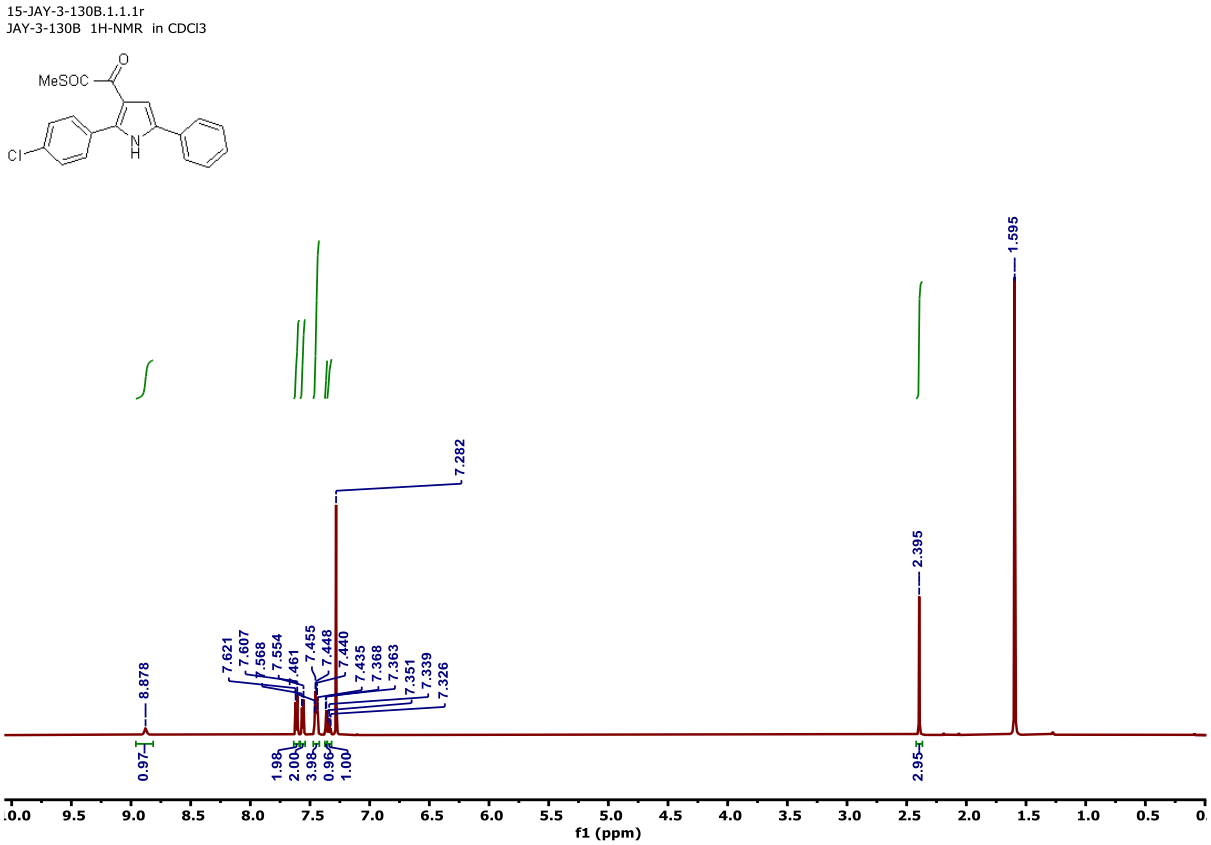
ESI-32: Analytical and spectral data of **4b**

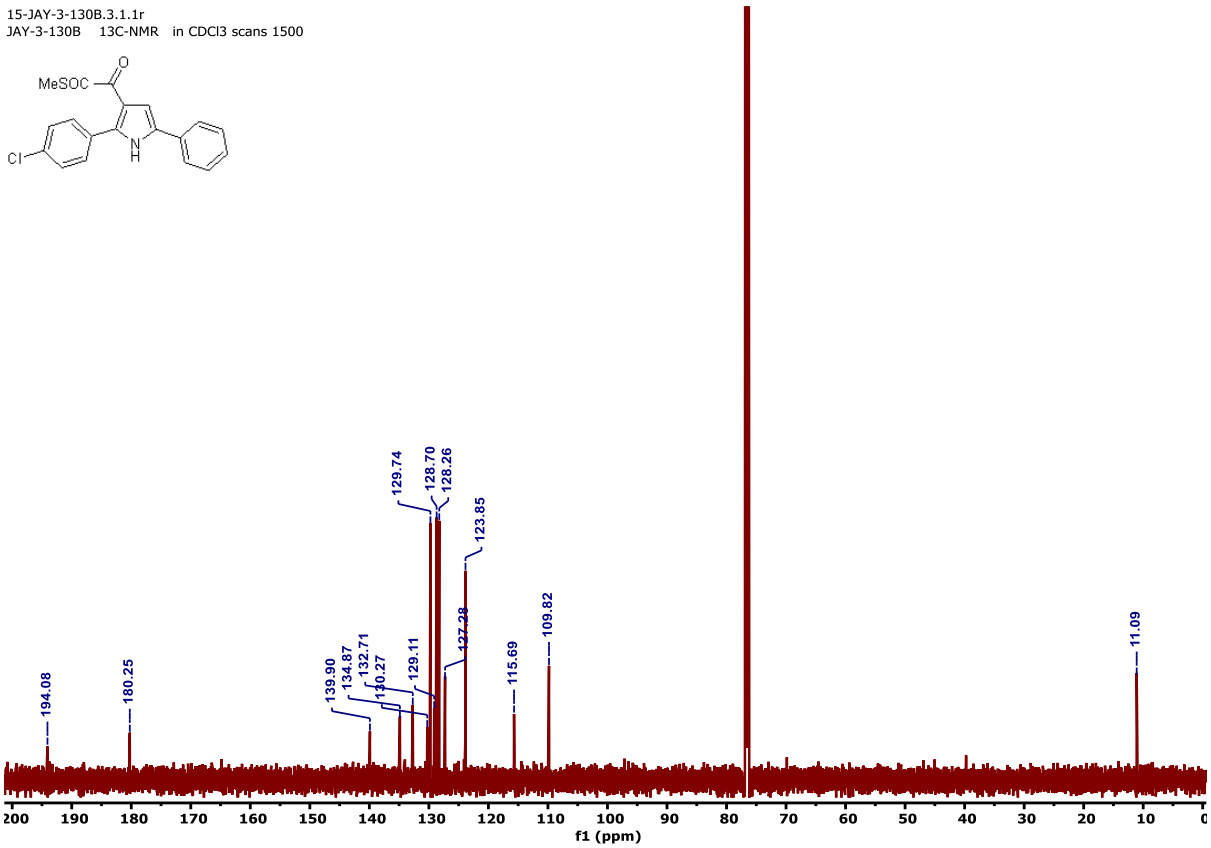


***S*-methyl 2-(2-(4-chlorophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4b:** Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10 %); red solid (56 mg, 76%), mp 140–145 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.88 (s, 1 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.45 (dt, *J* = 7.8, 3.6 Hz, 4 H), 7.37 (d, *J* = 3.0 Hz, 1 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 2.40 (s, 3 H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 194.1, 180.2, 139.9, 134.9, 132.7, 130.3, 129.7 (2 CH), 129.1, 128.7 (2 CH), 128.3 (2 CH), 127.3, 123.8 (2 CH), 115.7, 109.8, 11.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{14}ClNO_2SNa$ $[M + Na]^+$: 378.0332; found: 378.0343.

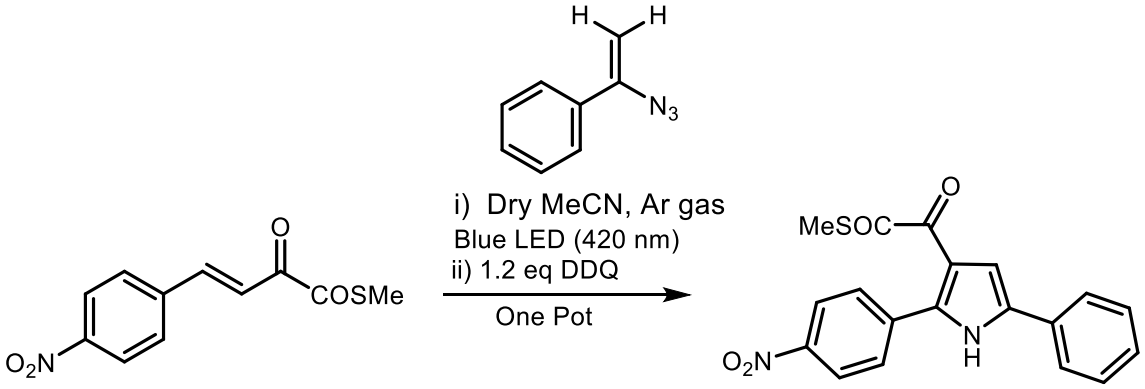


^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **4b**

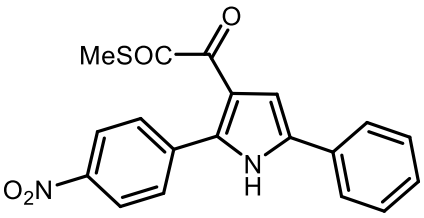




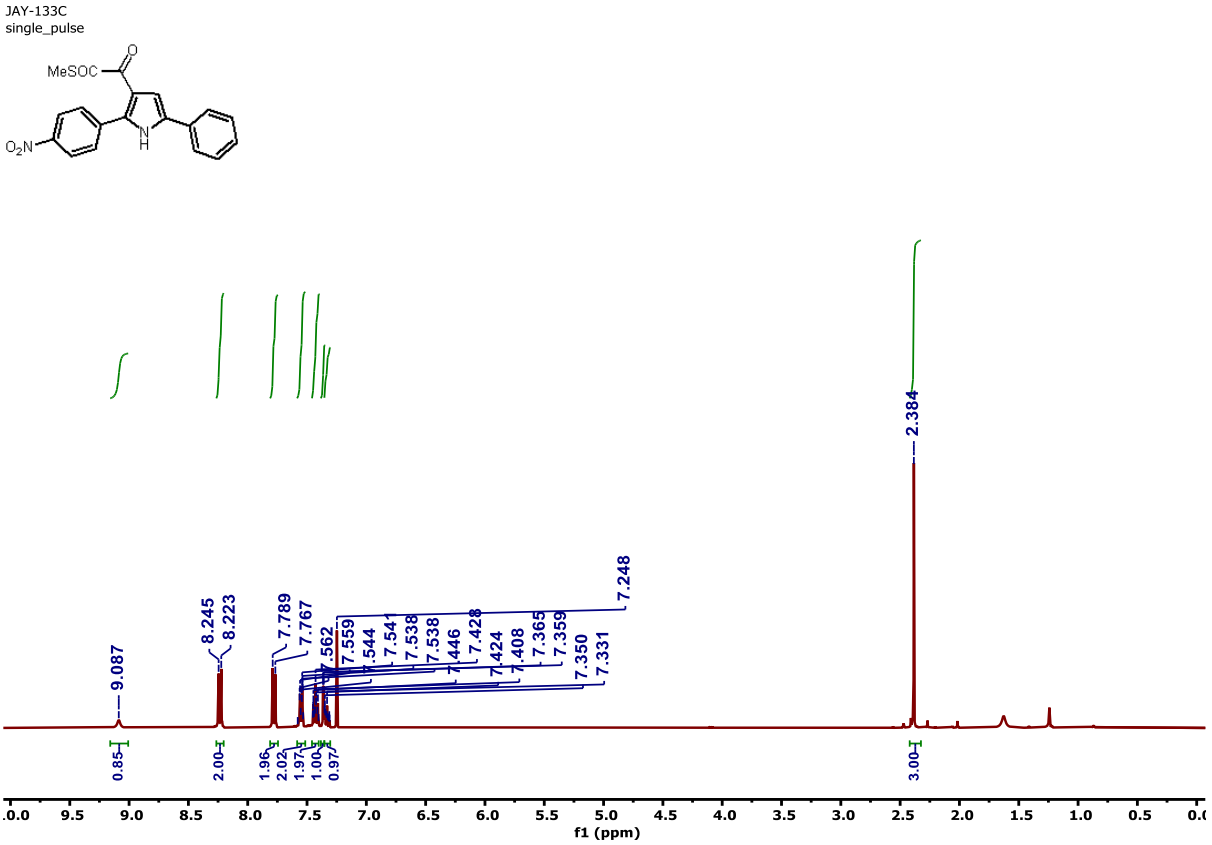
ESI-33: Analytical and spectral data of **4c**

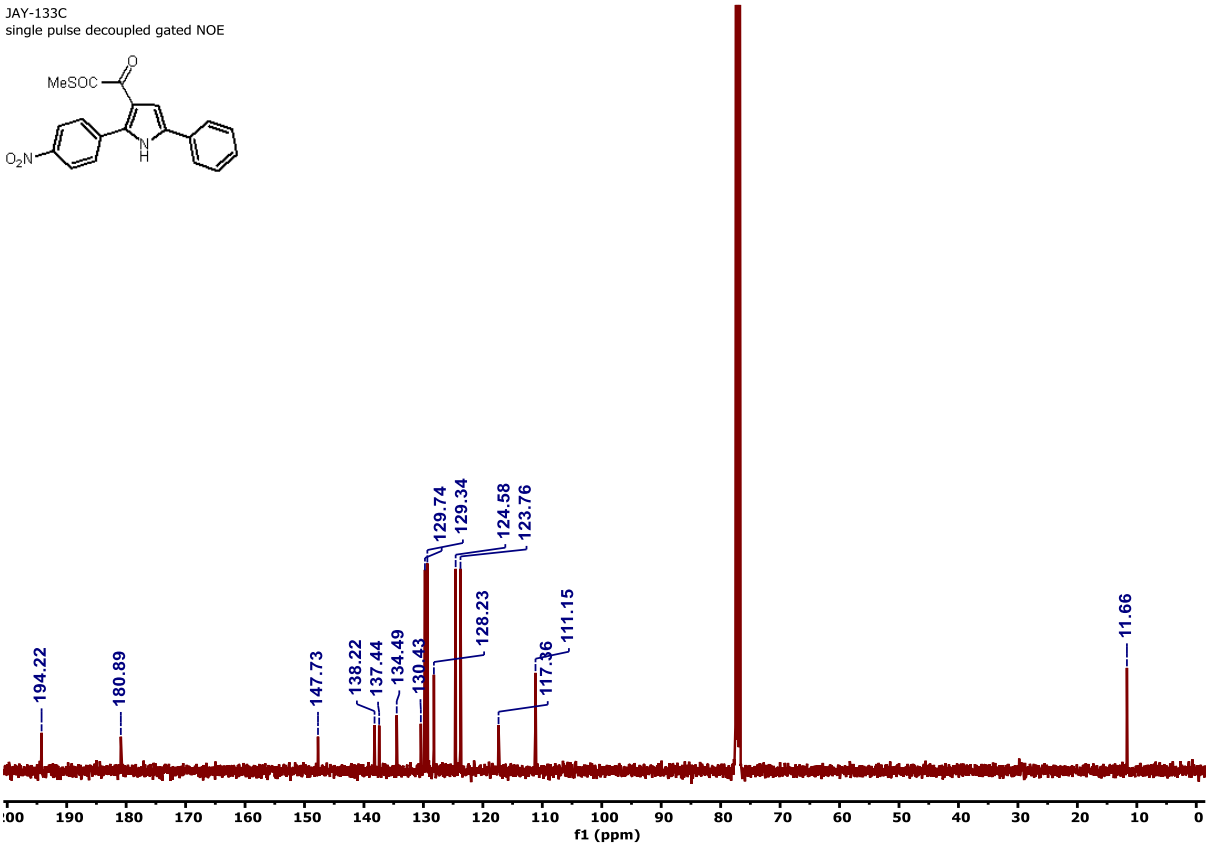


***S*-methyl 2-(2-(4-nitrophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4c:** Prepared according to the general procedure discussed above: reaction time, 14 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (15%); red solid (48 mg, 67%), mp 163-168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.09 (s, 1 H), 8.23 (d, *J* = 8.8 Hz, 2 H), 7.78 (d, *J* = 8.8 Hz, 2 H), 7.58 – 7.53 (m, 2 H), 7.45 – 7.40 (m, 2 H), 7.36 (d, *J* = 2.4 Hz, 1 H), 7.35 – 7.31 (m, 1 H), 2.38 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.2, 180.9, 147.7, 138.2, 137.4, 134.5, 130.4, 129.7 (2 CH), 129.3 (2 CH), 128.2, 124.6 (2 CH), 123.8 (2 CH), 117.4, 111.1, 11.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{14}N_2O_4SK$ [*M* + K]$^+$: 405.0311; found: 405.0317.

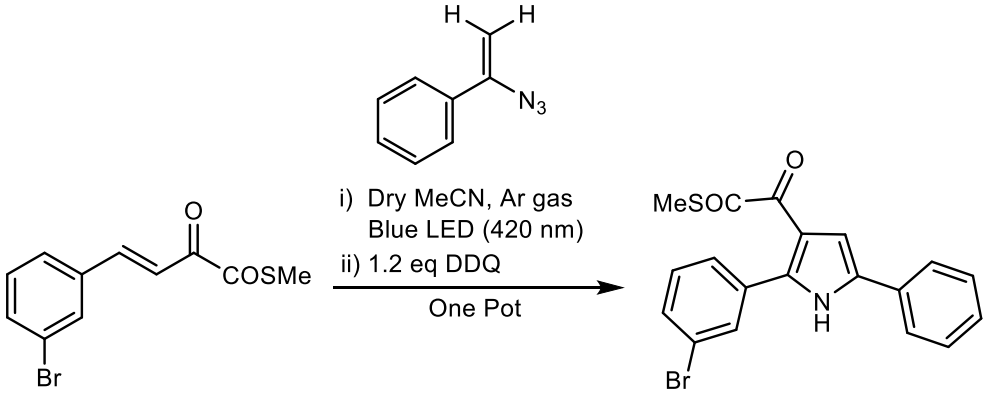


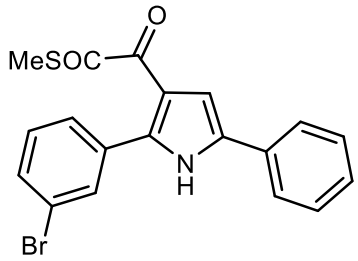
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4c**





ESI-34: Analytical and spectral data of **4d**

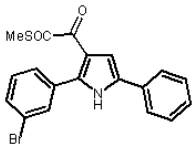


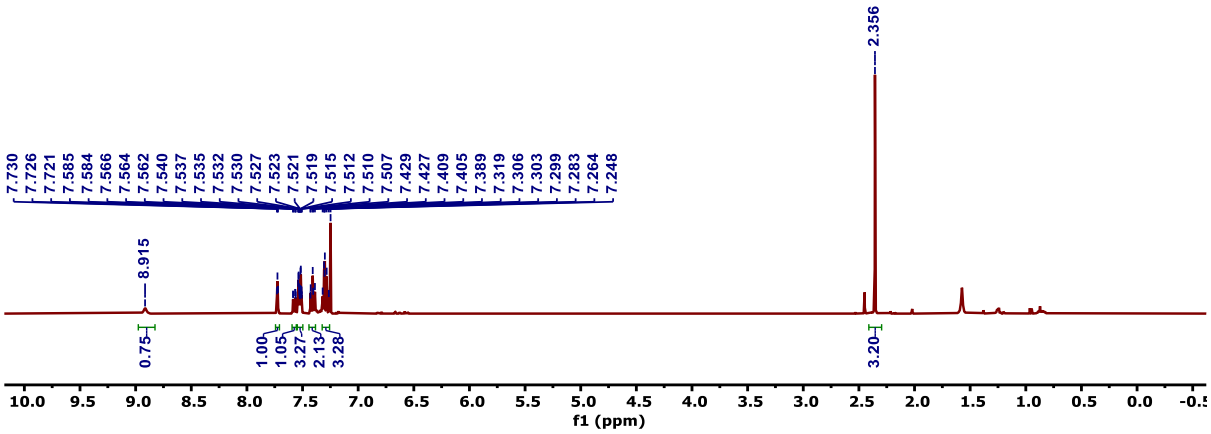


***S*-methyl 2-(1-(2-(3-bromophenyl)-5-phenyl-1*H*-pyrrol-3-yl)ethan-1-one)-2 oxoethanethioate 4d:** Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10 %); red solid (53 mg, 76%), mp 72-75 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 7.73 (t, J = 1.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.50 (m, 3H), 7.43 – 7.39 (m, 2 H), 7.34 – 7.26 (m, 3 H), 2.36 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.5, 181.0, 139.7, 133.5, 133.2, 132.2, 131.6, 130.8, 130.0, 129.3 (2 CH), 127.87 (2 CH), 124.4 (2 CH), 122.5, 116.6, 110.3, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{15}BrNO_2S$ [M + H]$^+$: 400.0007; found: 399.9988.

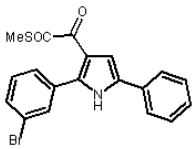
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4d**

SM-3-157B
single_pulse

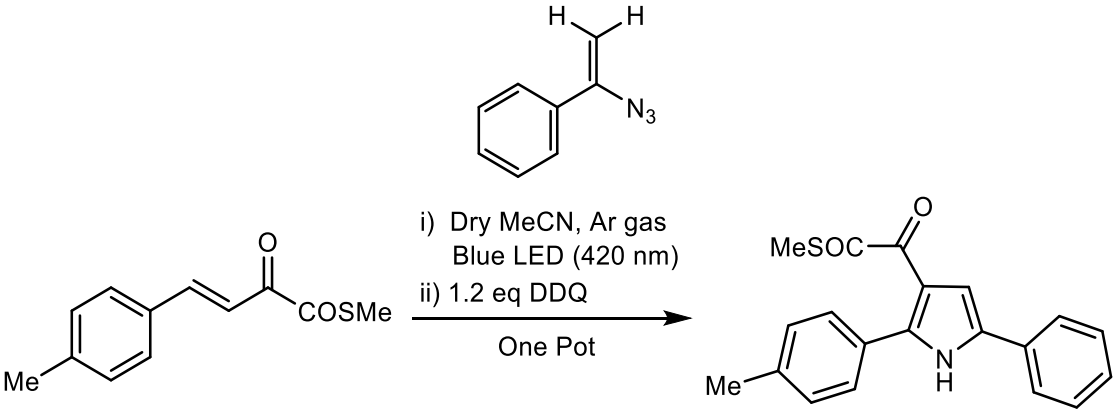


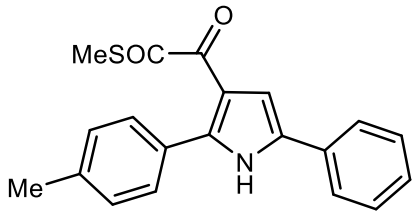


SM-3-157B
single pulse decoupled gated NOE



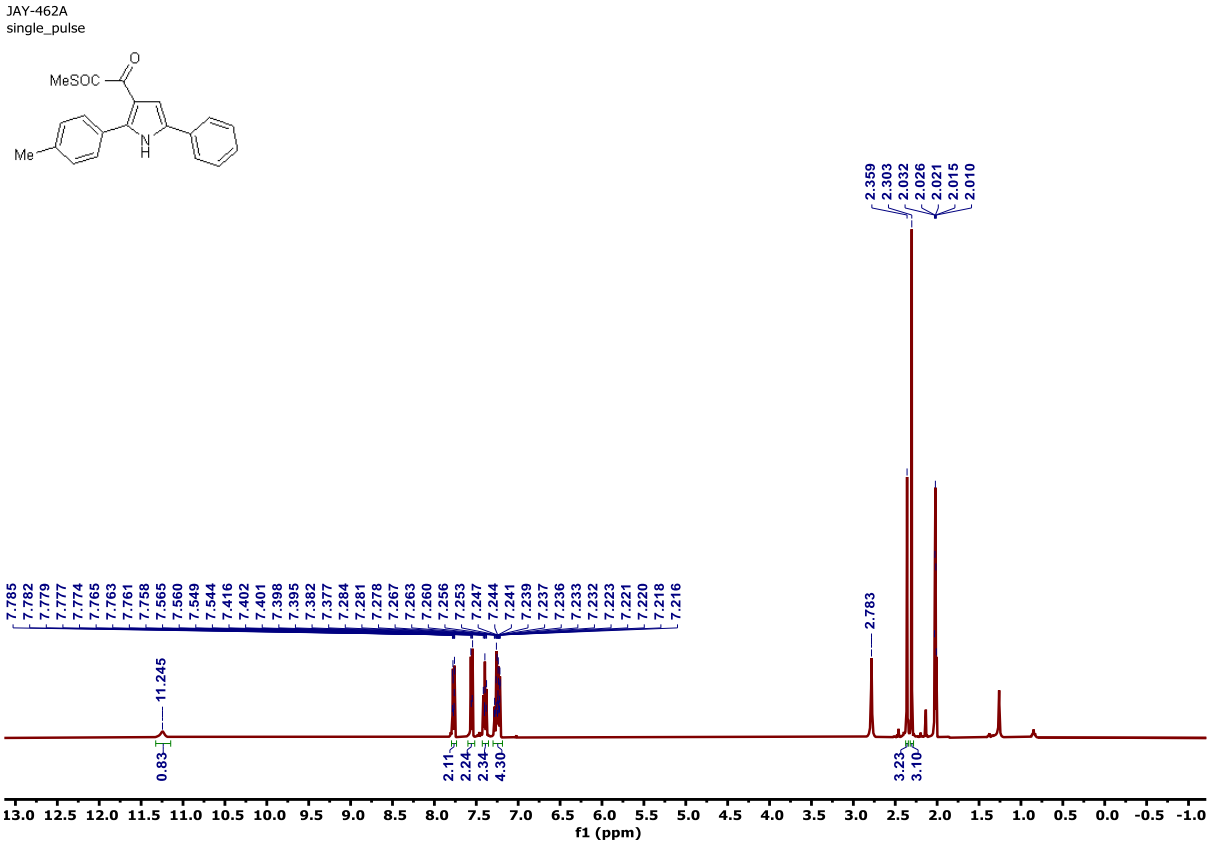
ESI-35: Analytical and spectral data of **4e**

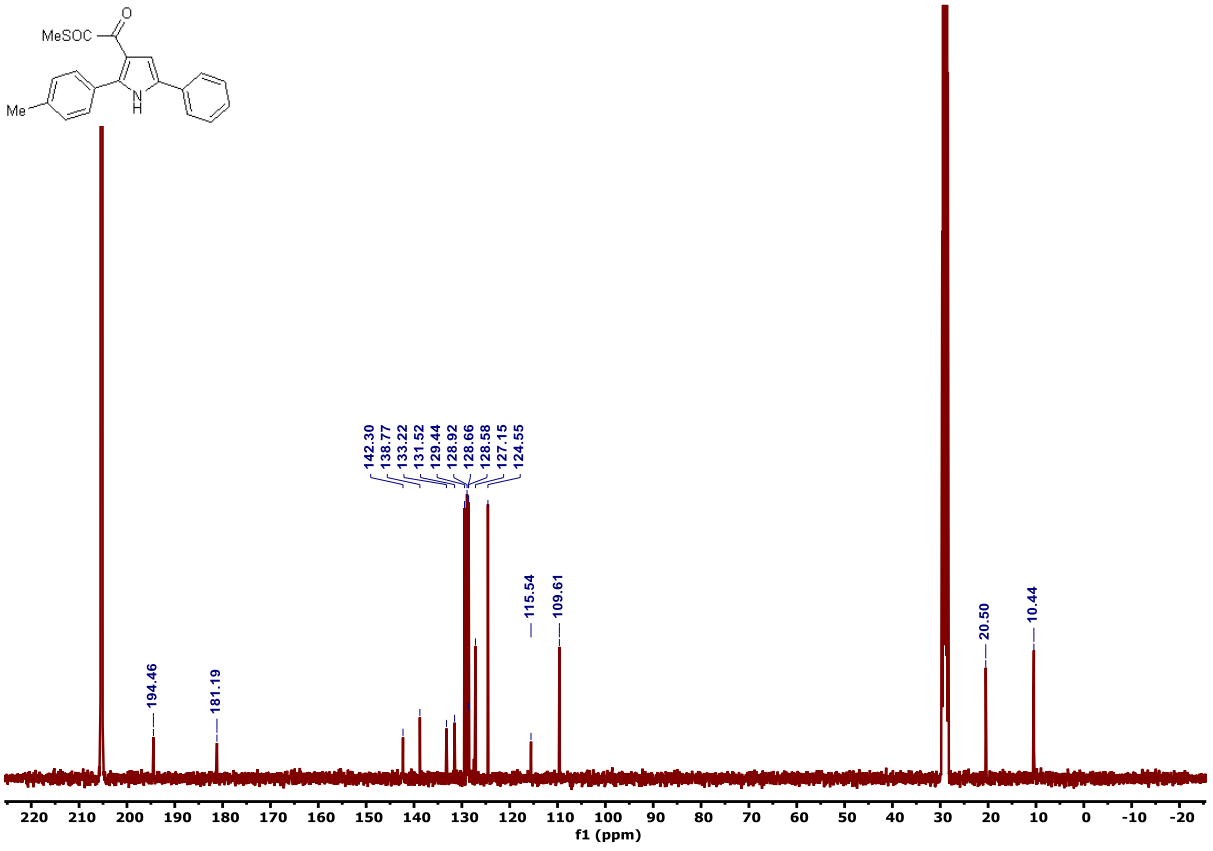




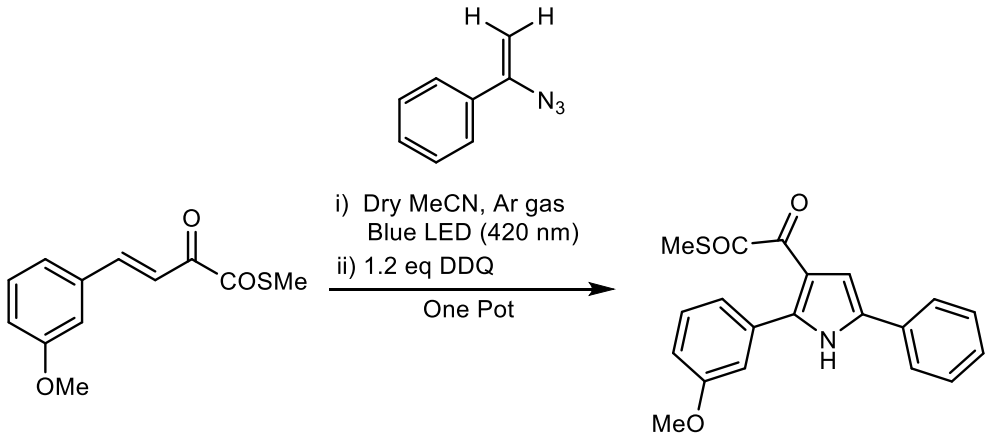
***S*-methyl 2-oxo-2-(5-phenyl-2-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanethioate 4e:** Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); red solid (55 mg, 72%), mp 122–127 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.27 (s, 1 H), 7.85 – 7.74 (m, 2 H), 7.65 – 7.55 (m, 2 H), 7.50 – 7.37 (m, 2 H), 7.33 – 7.20 (m, 4 H), 2.39 (s, 3 H), 2.33 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.5, 181.2, 142.3, 138.8, 133.2, 131.5, 129.4 (2 CH), 128.9 (2 CH), 128.7, 128.6 (2 CH), 127.2, 124.6 (2 CH), 115.5, 109.6, 20.5, 10.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{17}NO_2SNa$ [*M* + Na]$^+$: 358.0878; found: 358.0883.

^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4e**

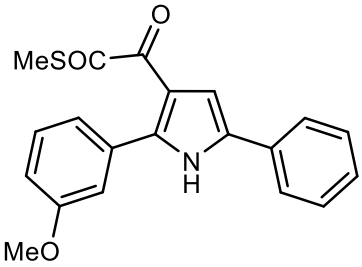




ESI-36: Analytical and spectral data of **4f**

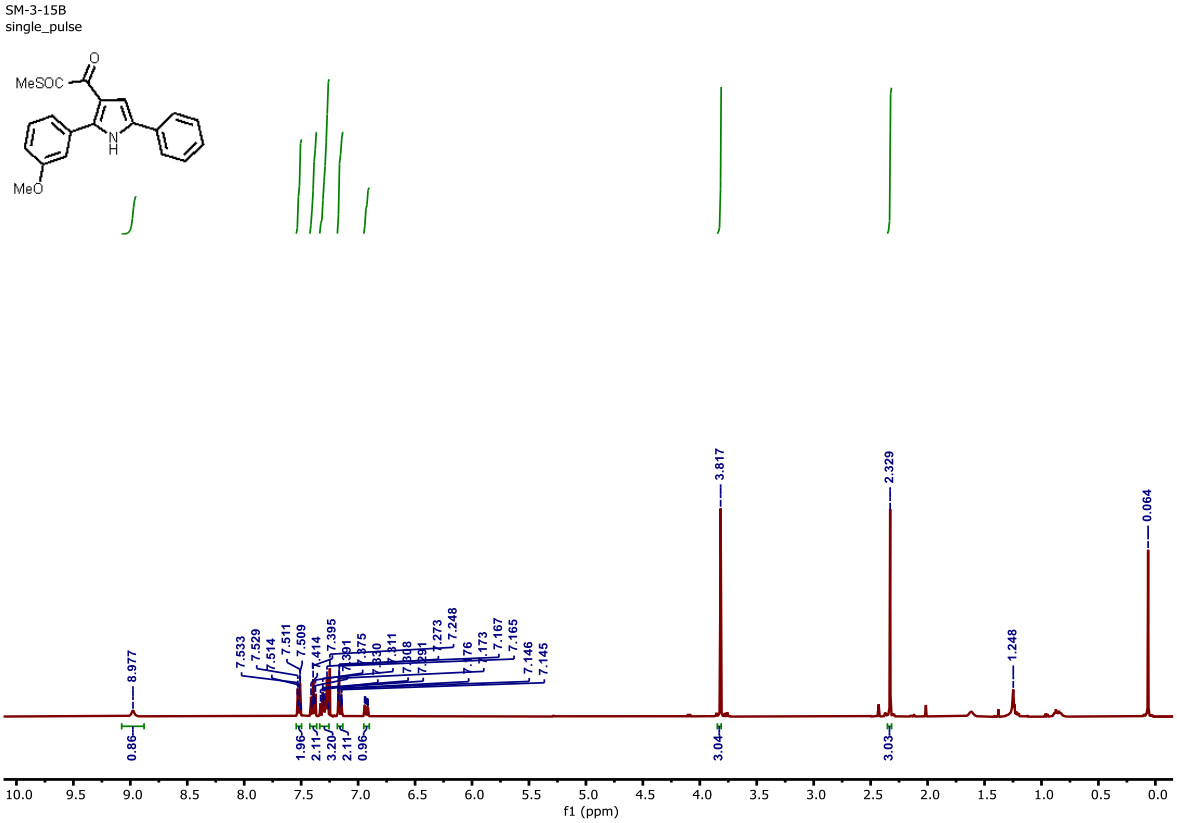


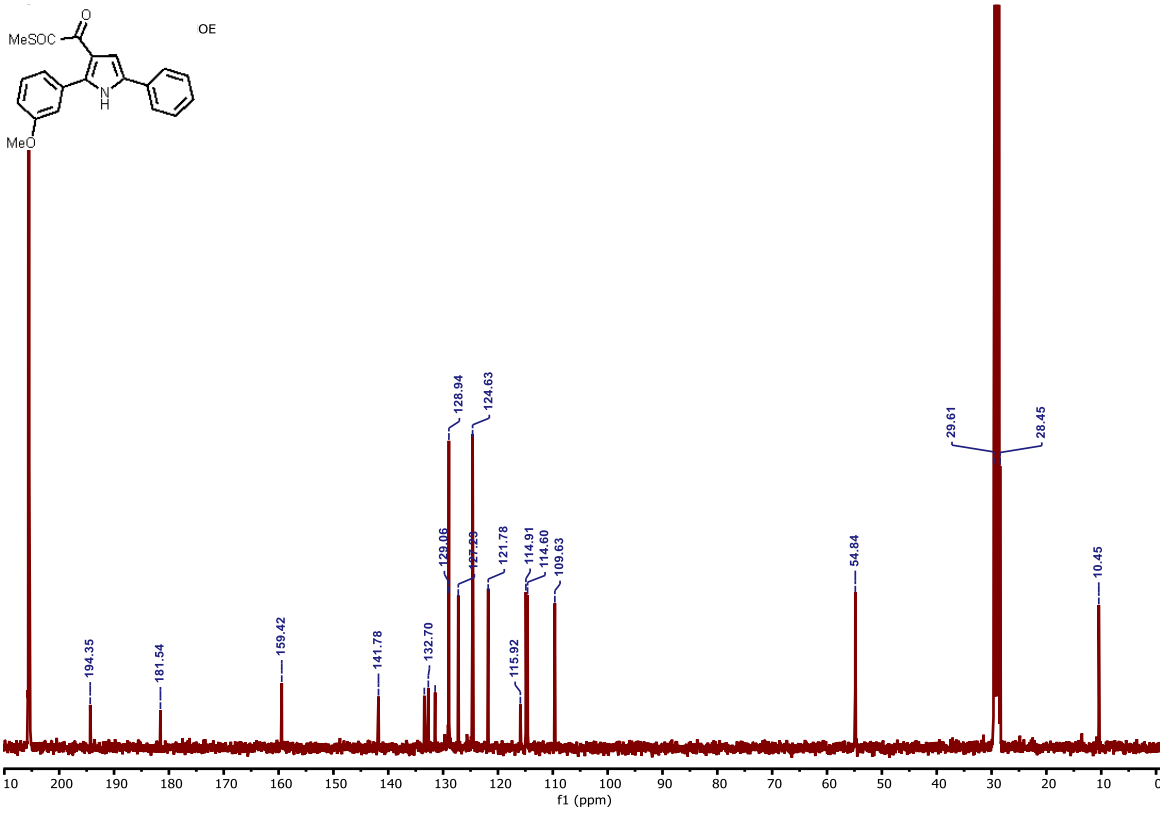
***S*-methyl 2-(2-(3-methoxyphenyl)-5-phenyl-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4f:**



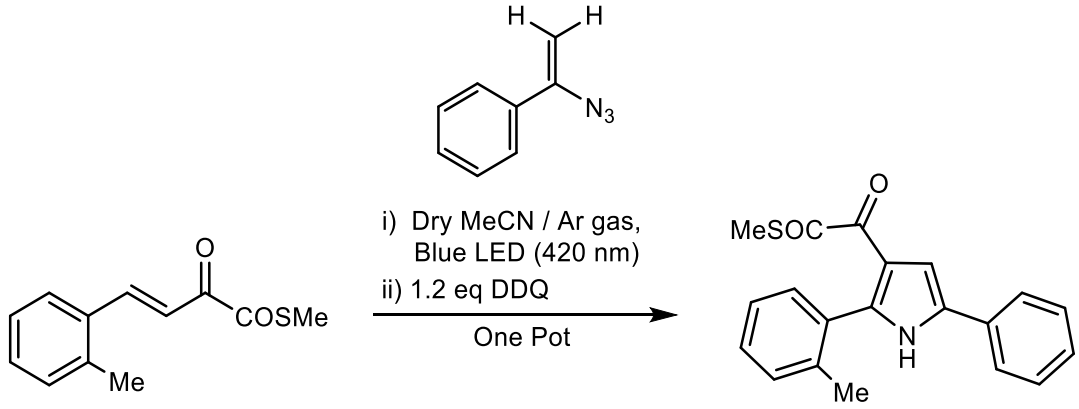
Prepared according to the general procedure discussed above: reaction time, 42 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); red solid (60 mg, 81%); mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (s, 1 H), 7.53 – 7.50 (m, 2 H), 7.41 – 7.37 (m, 2 H), 7.33 – 7.26 (m, 3 H), 7.18 – 7.14 (m, 2 H), 6.93 (ddd, J = 8.4, 2.4, 1.2 Hz, 1 H), 3.82 (s, 3 H), 2.33 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.3, 181.5, 159.4, 141.8, 133.4, 132.7, 131.5, 129.1, 128.9 (2 CH), 127.2, 124.6 (2 CH), 121.8, 115.9, 114.9, 114.6, 109.6, 54.8, 10.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{17}NO_3SNa$ $[M + Na]^+$: 374.0827; found: 374.0817.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, Acetone-d_6) NMR spectra of **4f**



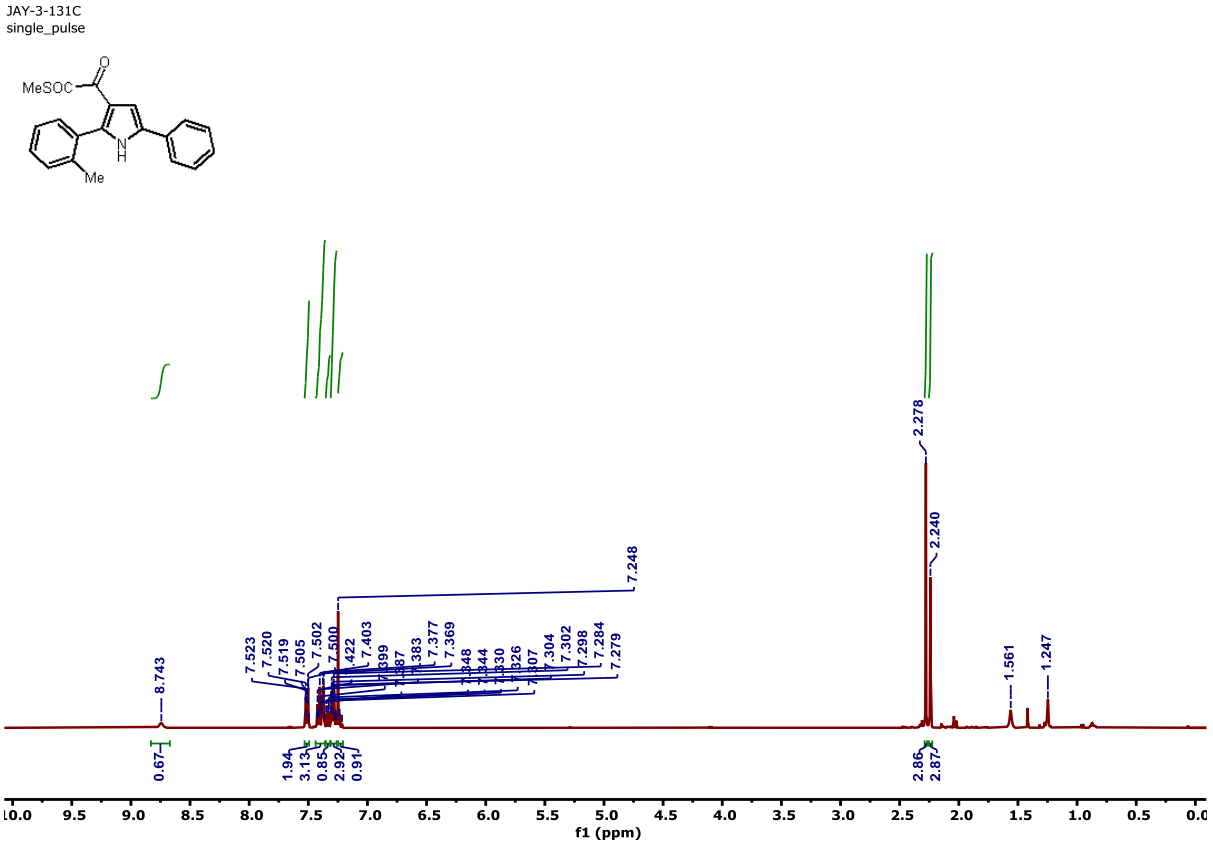


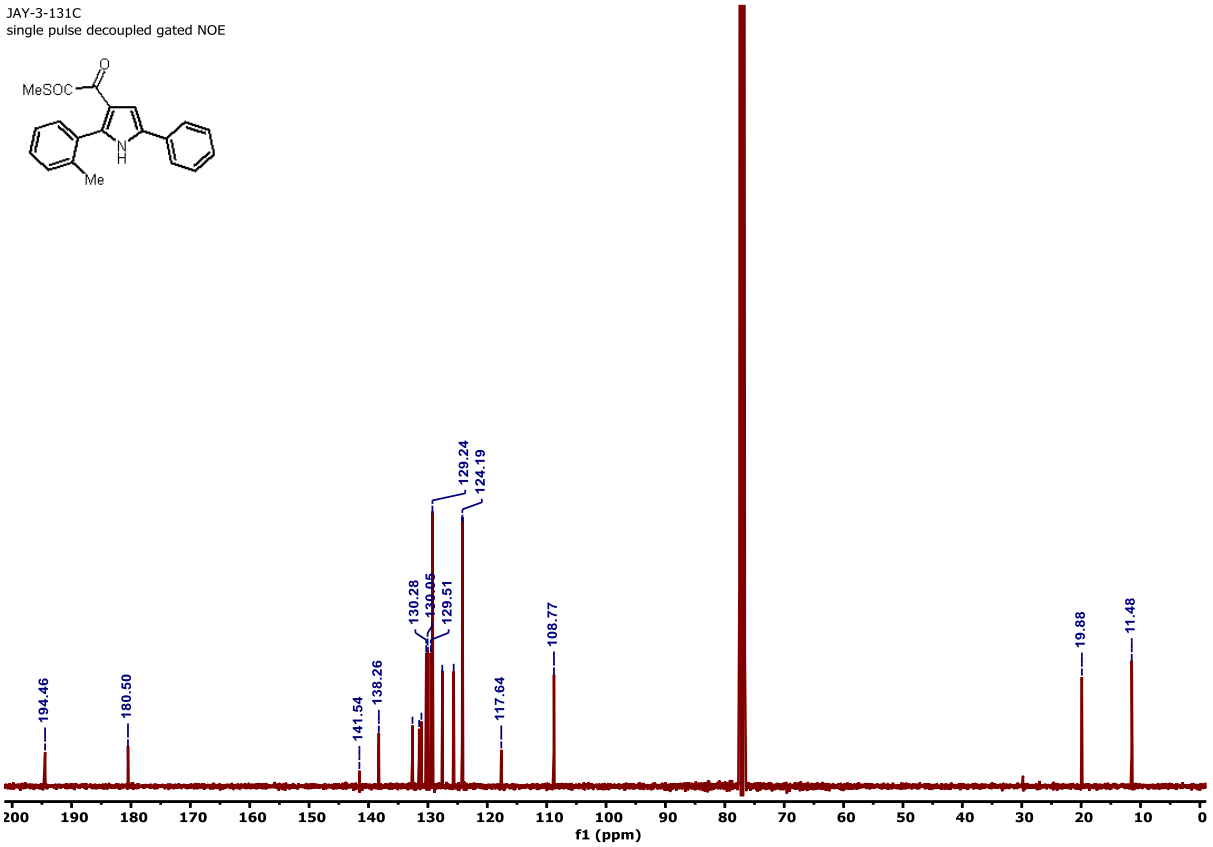
ESI-37: Analytical and spectral data of **4g**



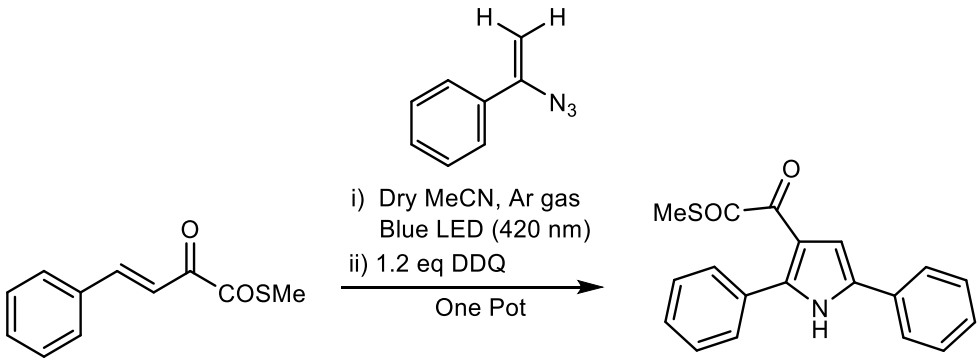
***S*-methyl 2-oxo-2-(5-phenyl-2-(*o*-tolyl)-1*H*-pyrrol-3-yl)ethanethioate 4g:** Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); red solid (56 mg, 74%); mp 122-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 7.52 – 7.49 (m, 2 H), 7.43 – 7.36 (m, 3 H), 7.34 (dd, *J* = 7.2, 1.6 Hz, 1 H), 7.31 – 7.26 (m, 3 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 2.28 (s, 3 H), 2.24 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.5, 180.5, 141.5, 138.3, 132.6, 131.5, 131.1, 130.3, 130.1, 129.5, 129.2 (2 CH), 127.6, 125.7, 124.2 (2 CH), 117.6, 108.8, 19.9, 11.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{18}NO_2S$ [*M* + H]$^+$: 336.1058; found: 336.1055.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4g**

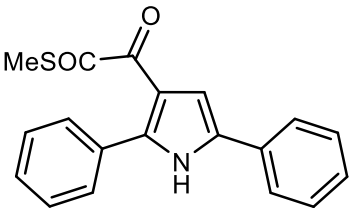




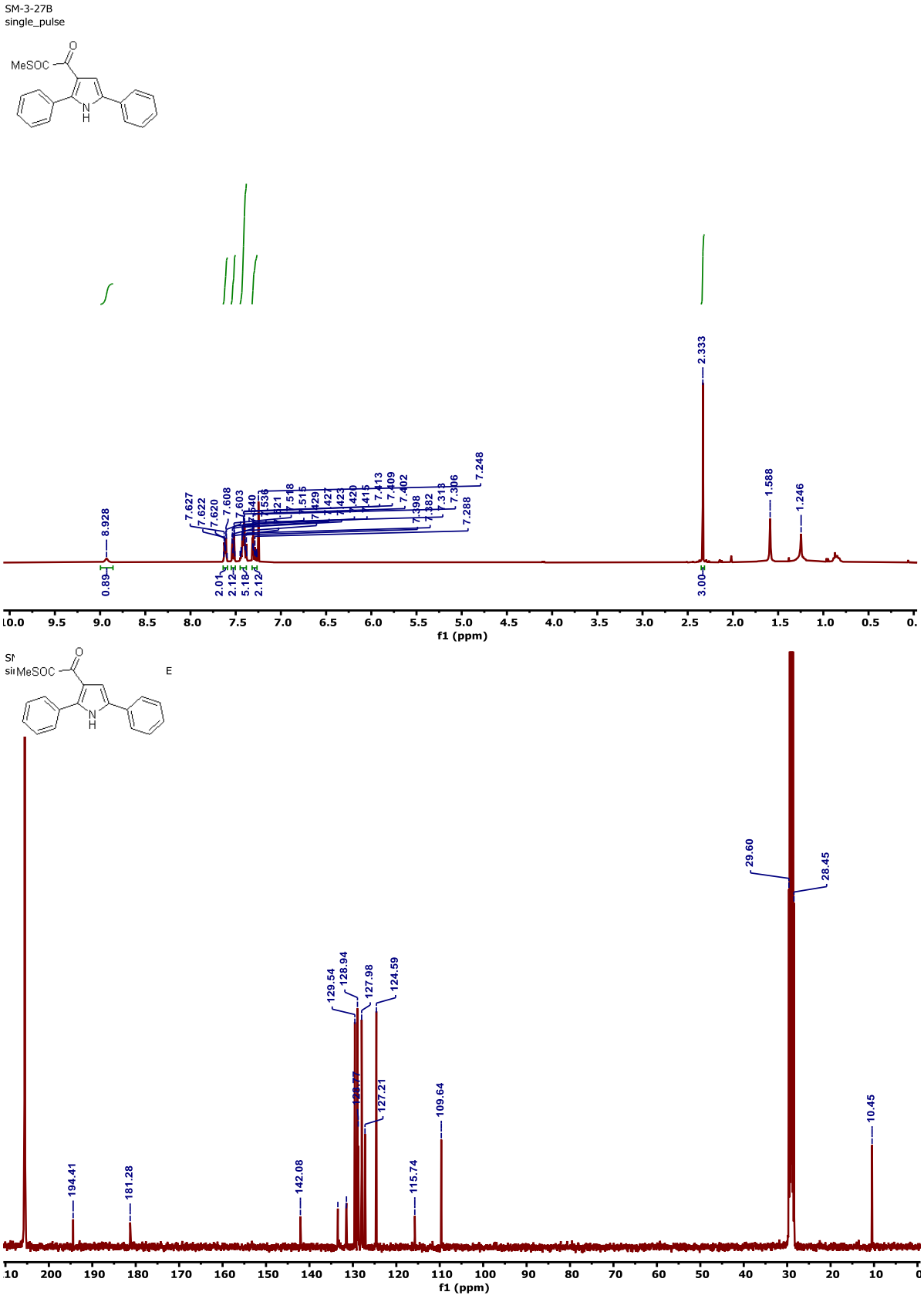
ESI-38: Analytical and spectral data of **4h**



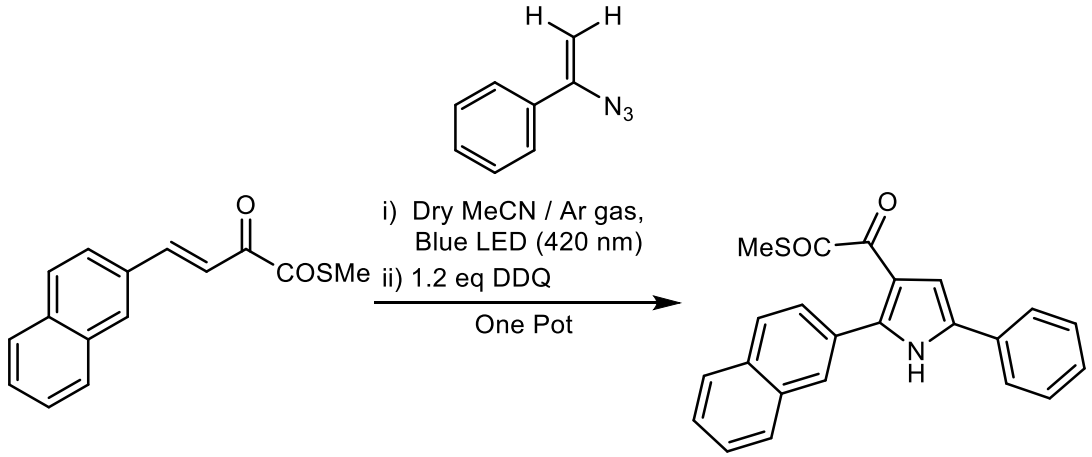
***S*-methyl 2-(2,5-diphenyl-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4h:** Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); red solid (57 mg, 73%); mp 80-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 7.63 – 7.60 (m, 2 H), 7.54 – 7.51 (m, 2 H), 7.45 – 7.38 (m, 5 H), 7.31 – 7.27 (m, 2 H), 2.33 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.4, 181.3, 142.1, 133.5, 131.5, 131.5, 129.5 (2 CH), 128.9 (2 CH), 128.8, 128.0 (2 CH), 127.2, 124.6 (2 CH), 115.7, 109.6, 10.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{16}NO_2S$ $[M + H]^+$: 322.0901; found: 322.0901.

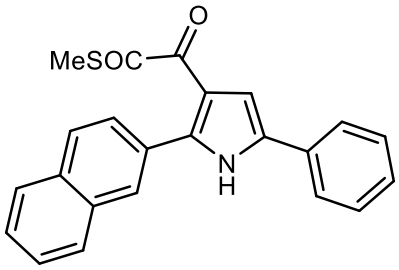


^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, Acetone-d_6) NMR spectra of **4h**

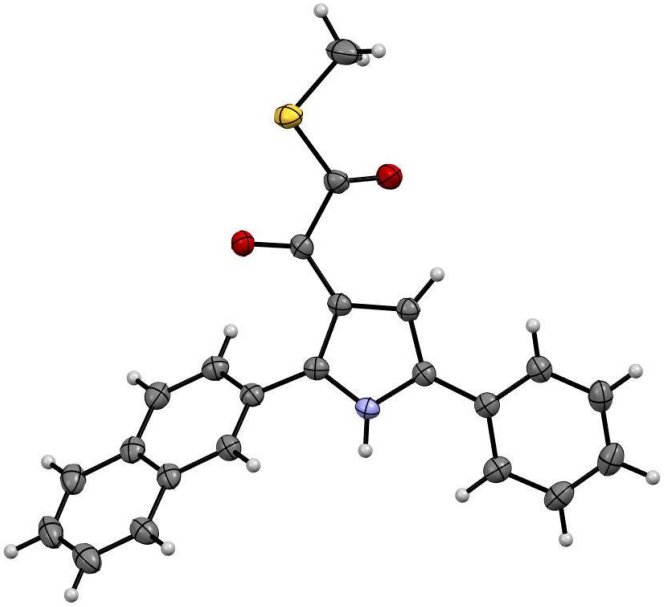


ESI-39: Analytical and spectral data of **4i**





***S*-methyl 2-(2-(naphthalen-2-yl)-5-phenyl-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4i**: Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); red solid (64 mg, 73%); mp 175–180 °C; solvent of crystallization, MeCN/DCM (2 mL:1 mL, v/v) at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1 H), 8.05 (d, *J* = 2.0 Hz, 1 H), 7.87 – 7.82 (m, 3 H), 7.69 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.57 – 7.53 (m, 2 H), 7.52 – 7.48 (m, 2 H), 7.44 – 7.39 (m, 2 H), 7.32 (d, *J* = 2.8 Hz, 1 H), 7.32 – 7.28 (m, 1 H), 2.30 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.7, 181.0, 141.9, 133.5, 133.2, 133.0, 131.0, 129.2 (2 CH), 128.8, 128.4, 128.2, 128.1, 127.9, 127.7, 127.0, 126.7, 126.5, 124.4 (2 CH), 116.4, 110.3, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{23}H_{17}NO_2SNa$ [*M* + Na]$^+$: 394.0878; found: 394.0874.



X-ray determined molecular structure of **4i**; **CCDC 2347215**.

Datablock: 4i

Bond precision: C-C = 0.0041 A Wavelength=1.54178

Cell: a=7.4754(5) b=9.5803(7) c=25.2169(18)
alpha=90 beta=90 gamma=90

Temperature: 130 K

	Calculated	Reported
Volume	1806.0(2)	1805.9(2)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C23 H17 N O2 S	C23 H17 N O2 S
Sum formula	C23 H17 N O2 S	C23 H17 N O2 S
Mr	371.44	371.43
Dx,g cm-3	1.366	1.366
Z	4	4
Mu (mm-1)	1.734	1.734
F000	776.0	776.0
F000'	779.42	
h,k,lmax	9,11,31	9,11,31
Nref	3695[2141]	3606
Tmin,Tmax	0.768,0.969	0.435,0.754
Tmin'	0.673	

Correction method= # Reported T Limits: Tmin=0.435 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.68/0.98 Theta(max)= 74.468

R(reflections)= 0.0404(3548) wR2(reflections)= 0.1056(3606)

S = 1.090 Npar= 245

The following ALERTS were generated.

Alert level C

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00408 Ang.
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C21 - C22 . 1.54 Ang.
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4 Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 19 Report
2 0 0, 2 1 0, 0 2 0, 1 2 0, 2 2 0, 2 0 1,
1 1 1, 2 1 1, 2 1 2, 1 2 2, 1 1 3, 2 1 3,
0 0 4, 1 0 4, 0 1 4, 1 1 4, 2 1 4, 0 0 8,
0 1 10,
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 15 Note
2 1 0, 1 2 0, 2 2 0, 2 0 1, 0 1 1, 2 1 1,
2 1 2, 1 2 2, 1 1 3, 2 1 3, 0 0 4, 1 0 4,
0 1 4, 2 1 4, 0 1 10,

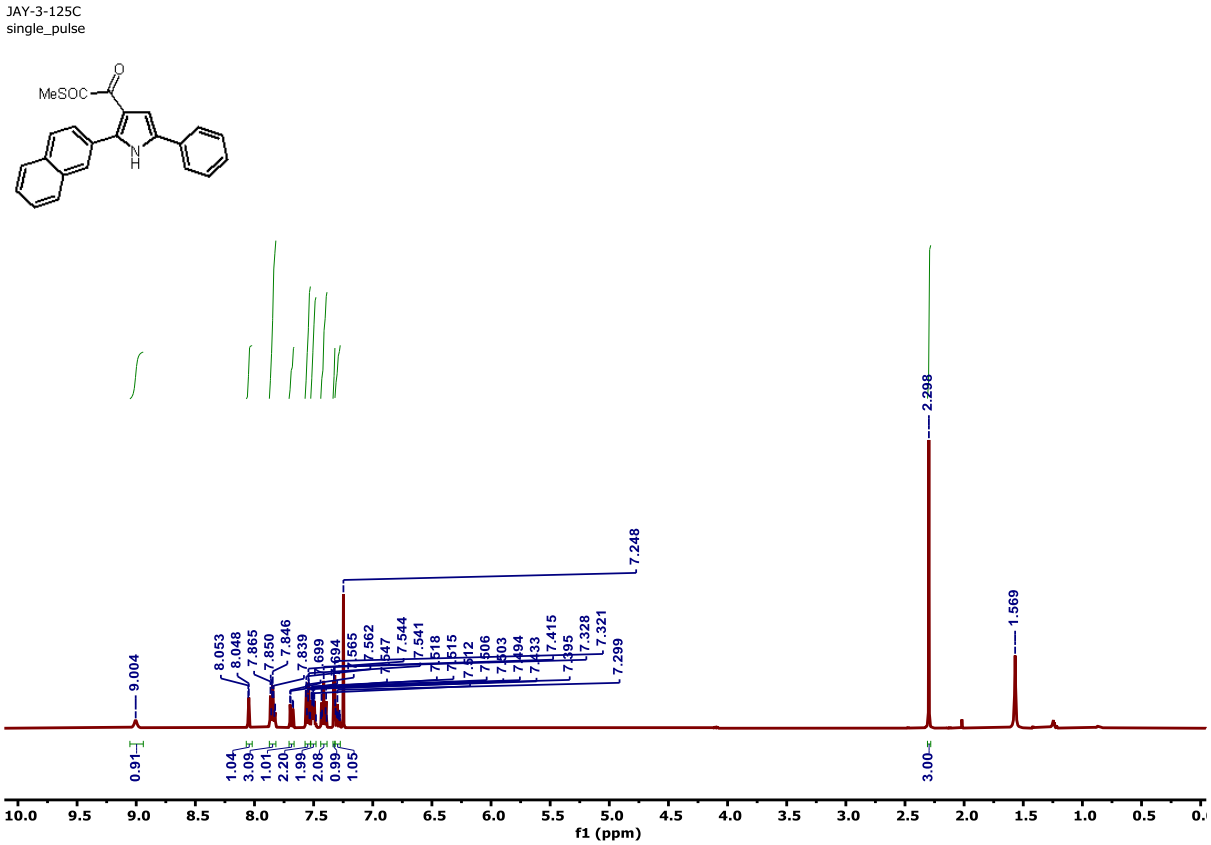
PLAT987_ALERT_1_C The Flack x is >> 0 - Do a BASF/TWIN Refinement Please Check

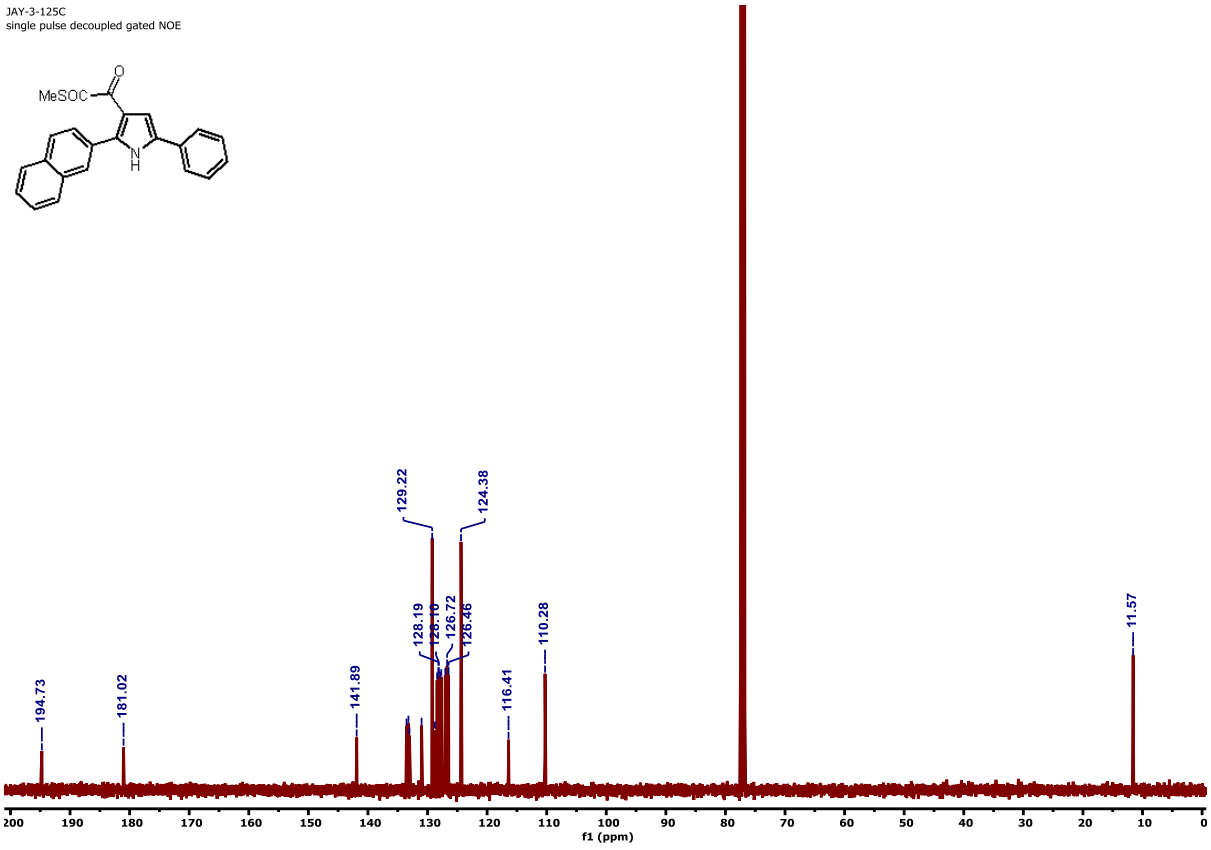
---

Alert level G

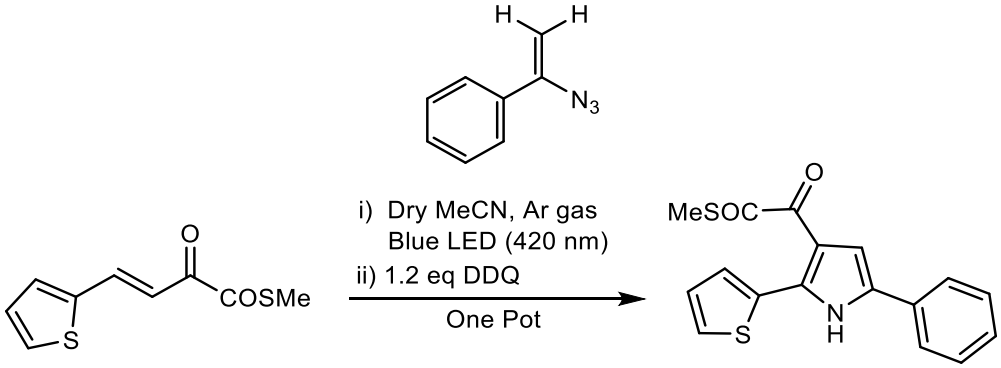
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
H1
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero . 0.052 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 2 Note
0 1 1, 0 0 2,
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 13 Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ..... 3.16 Note
Predicted wR2: Based on SigI**2 3.35 or SHELX Weight 10.04
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info

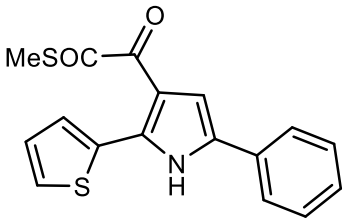
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4i**





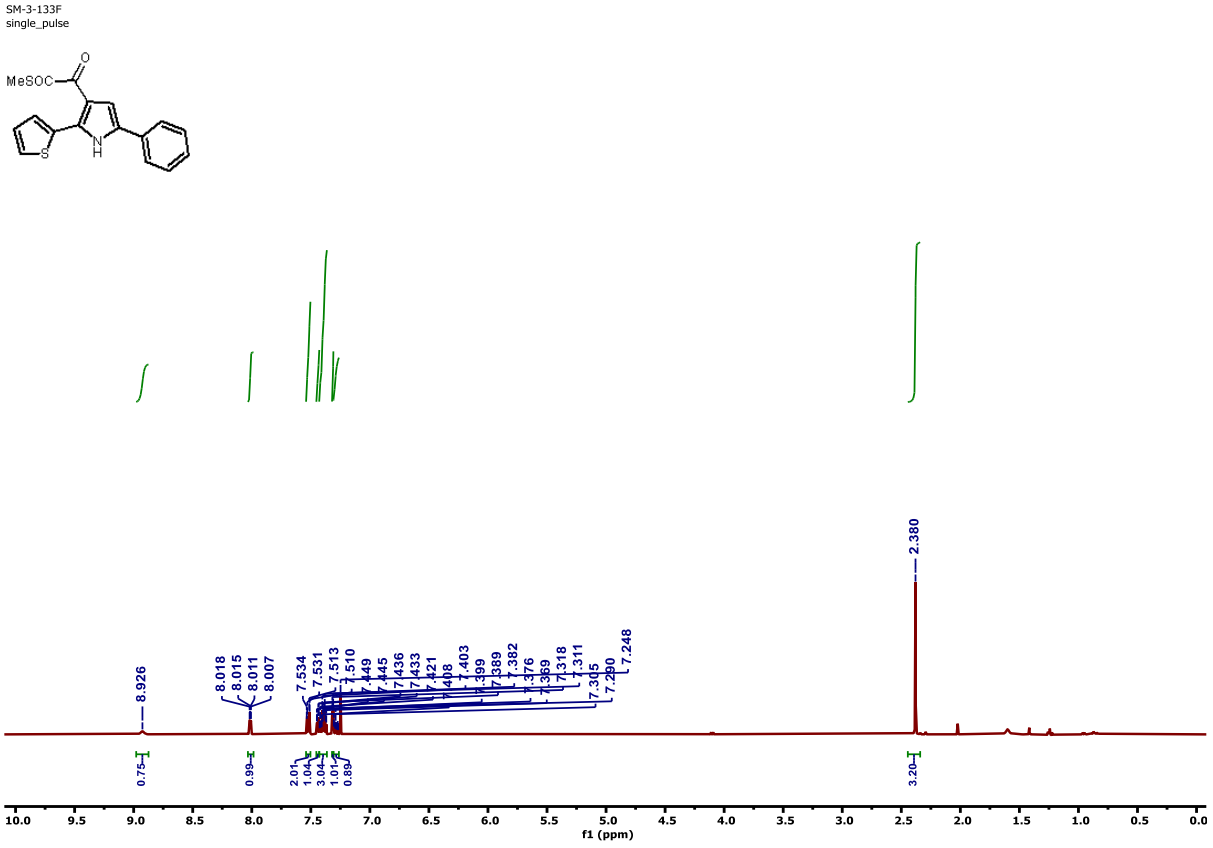
ESI-40: Analytical and spectral data of **4j**

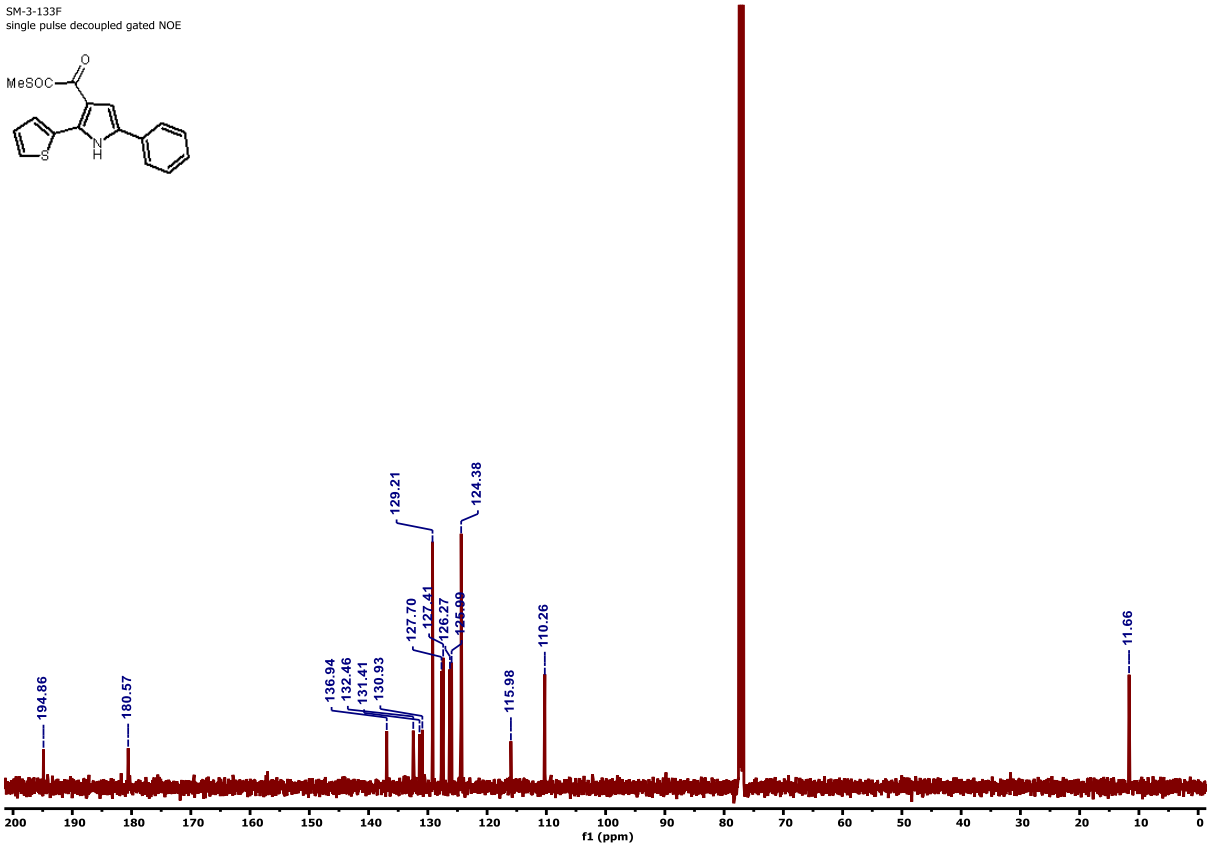




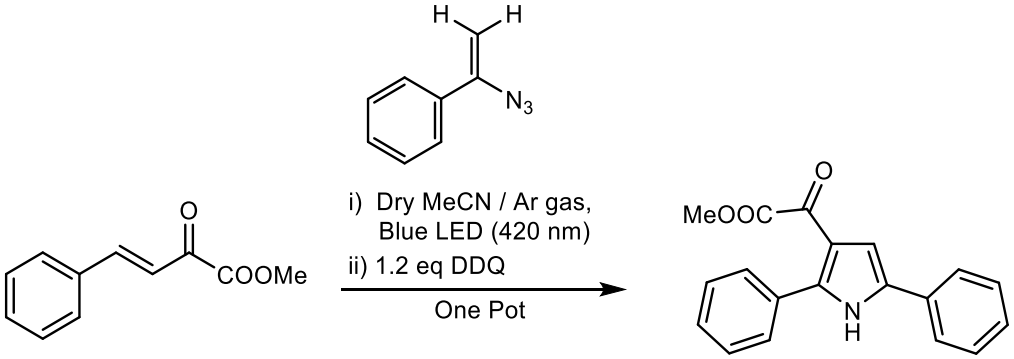
***S*-methyl 2-oxo-2-(5-phenyl-2-(thiophen-2-yl)-1*H*-pyrrol-3-yl)ethanethioate 4j:** Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); red gummy liquid (52 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 8.01 (dd, *J* = 2.8, 1.2 Hz, 1 H), 7.52 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.44 (dd, *J* = 5.2, 1.6 Hz, 1 H), 7.43 – 7.37 (m, 3 H), 7.31 (d, *J* = 2.8 Hz, 1 H), 7.31 – 7.27 (m, 1 H), 2.38 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.9, 180.6, 136.9, 132.5, 131.4, 130.9, 129.2 (2 CH), 127.7, 127.4, 126.3, 126.0, 124.4 (2 CH), 116.0, 110.3, 11.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{14}NO_2S_2$ [*M* + H]$^+$: 328.0466; found: 328.0453.

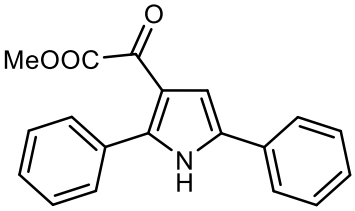
^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **4j**





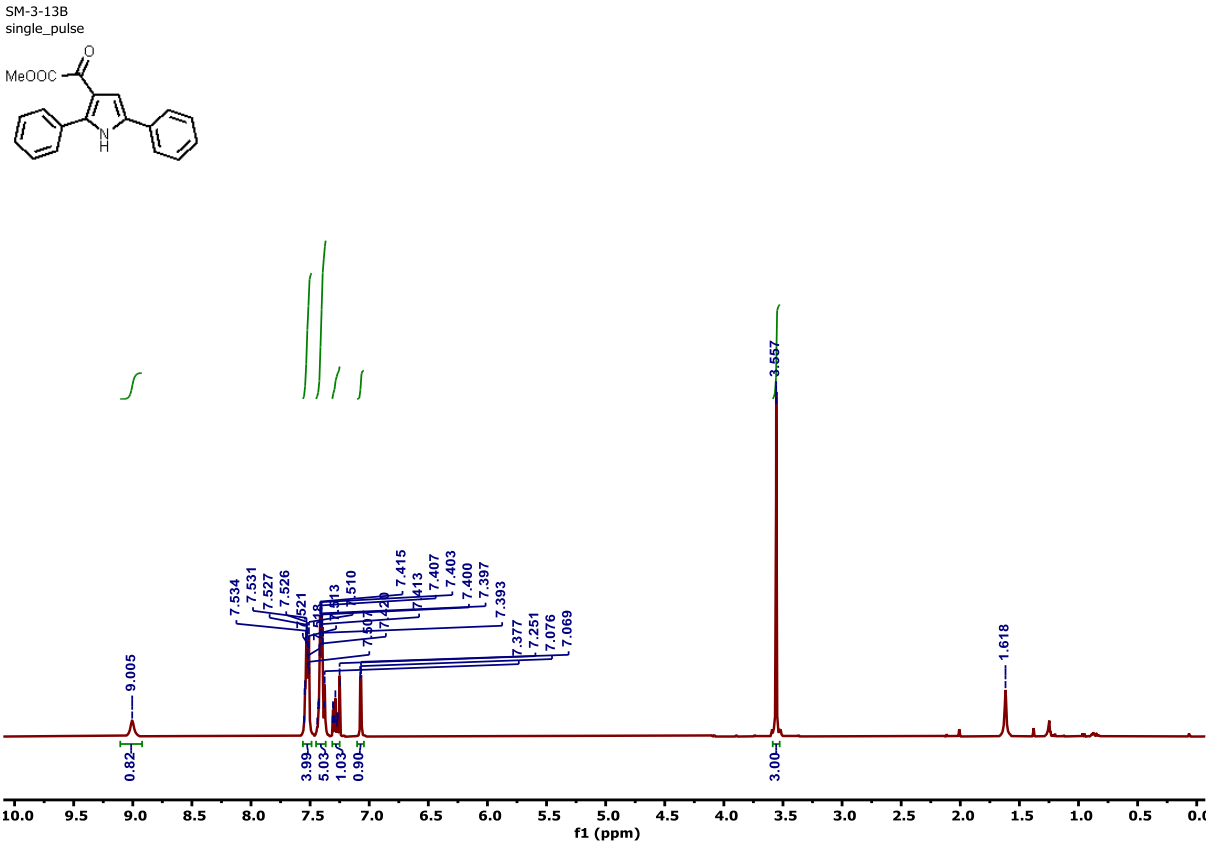
ESI-41: Analytical and spectral data of **4l**

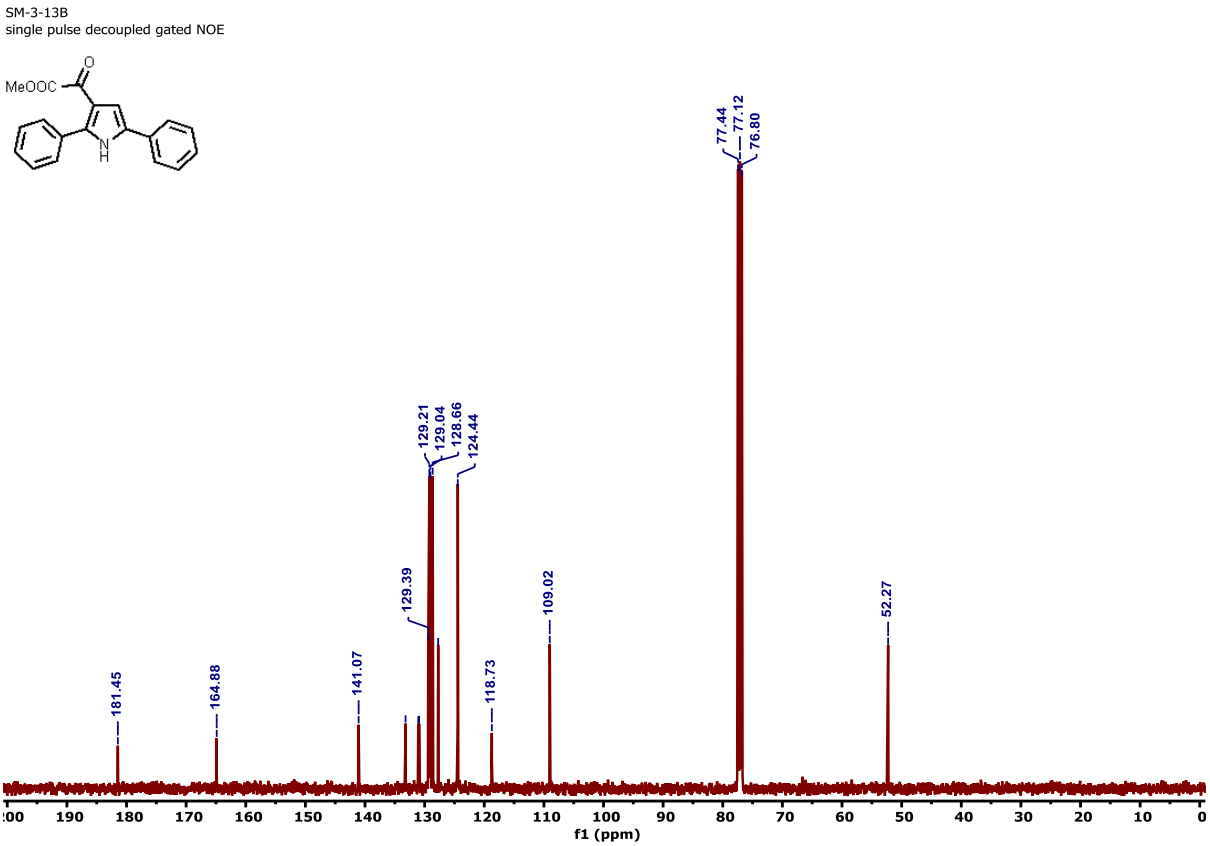




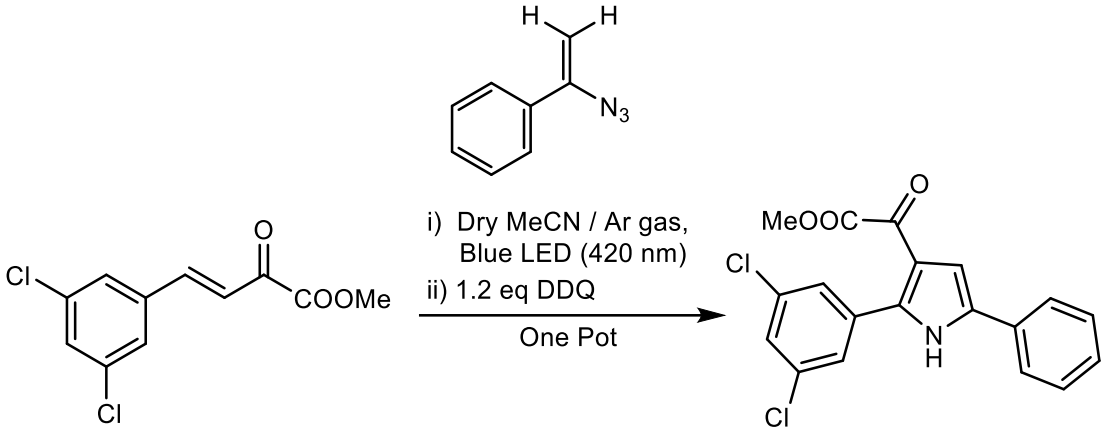
Methyl 2-(2,5-diphenyl-1*H*-pyrrol-3-yl)-2-oxoacetate 4l: Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); yellow solid (58 mg, 72%); mp 112-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (s, 1 H), 7.55 – 7.51 (m, 4 H), 7.44 – 7.38 (m, 5 H), 7.31 – 7.25 (m, 1 H), 7.07 (d, *J* = 2.8 Hz, 1 H), 3.56 (s, 3 H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 181.5, 164.9, 141.1, 133.2, 131.1, 130.9, 129.4, 129.2 (2 CH), 129.0 (2 CH), 128.7 (2 CH), 127.7, 124.4 (2 CH), 118.7, 109.0, 52.3 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{15}NO_3Na$ [*M* + Na]$^+$: 328.0950; found: 328.0943.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4l:**



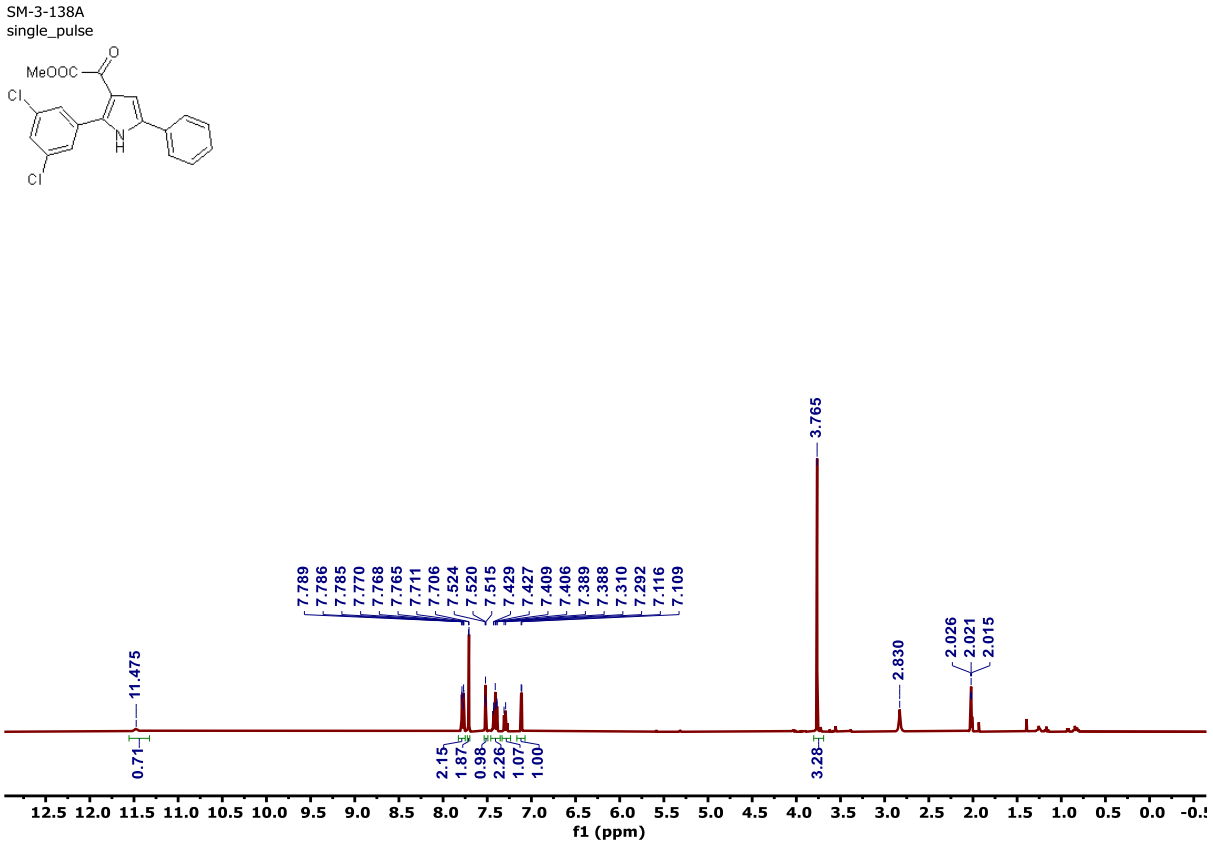


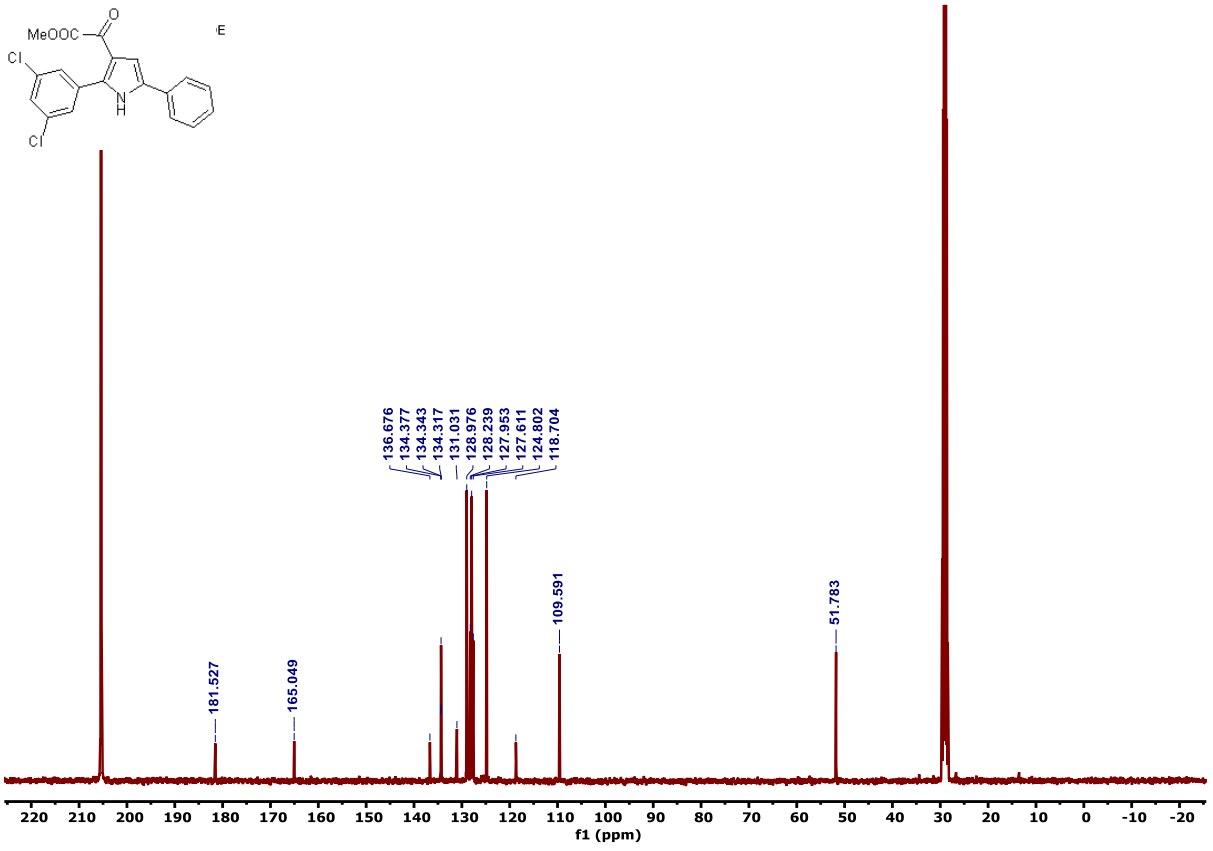
ESI-42: Analytical and spectral data of **4m**



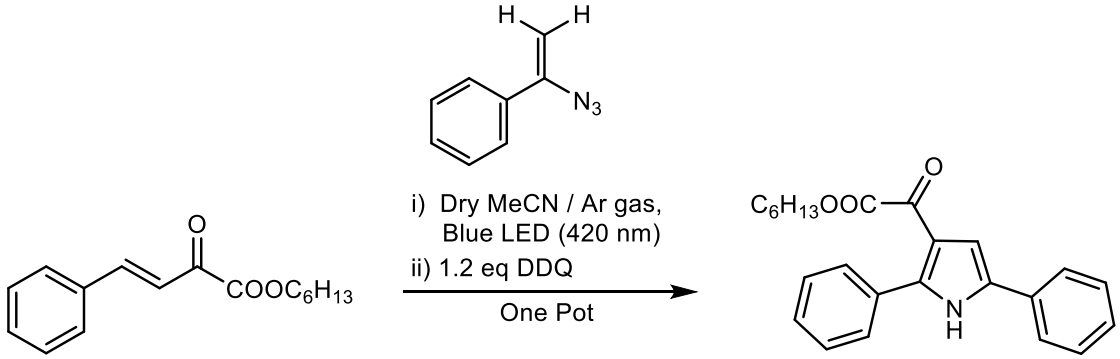
Methyl 2-(2-(3,5-dichlorophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-2-oxoacetate 4m: Prepared according to the general procedure discussed above: reaction time, 34 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); yellow solid; (53 mg, 74%); mp 133-138 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.47 (s, 1 H), 7.79 – 7.77 (m, 2 H), 7.71 (d, *J* = 1.9 Hz, 2 H), 7.52 (t, *J* = 1.9 Hz, 1 H), 7.43 – 7.39 (m, 2 H), 7.29 (ddt, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 7.11 (d, *J* = 2.8 Hz, 1 H), 3.76 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 181.5, 165.1, 136.7, 134.4, 134.3, 134.3, 134.3, 131.0, 129.0 (2 CH), 128.2, 128.0 (2 CH), 127.6, 124.8 (2 CH), 118.7, 109.6, 51.8 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{14}Cl_2NO_3$ [*M* + H]$^+$: 374.0350; found: 374.0366.

^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4m**

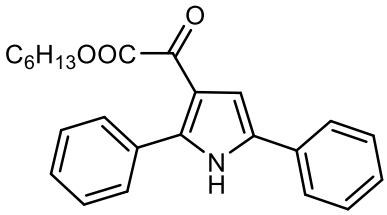




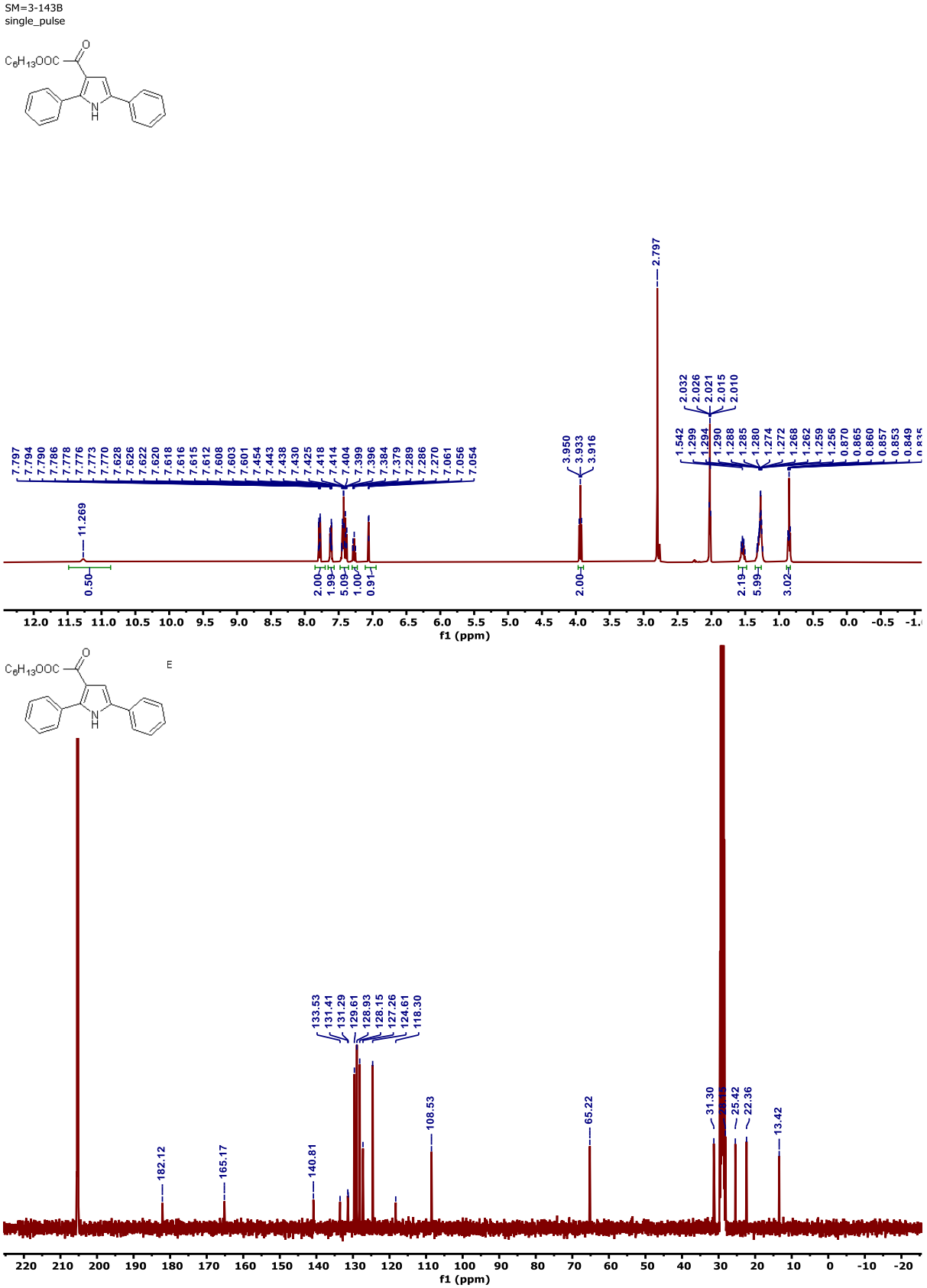
ESI-43: Analytical and spectral data of **4n**



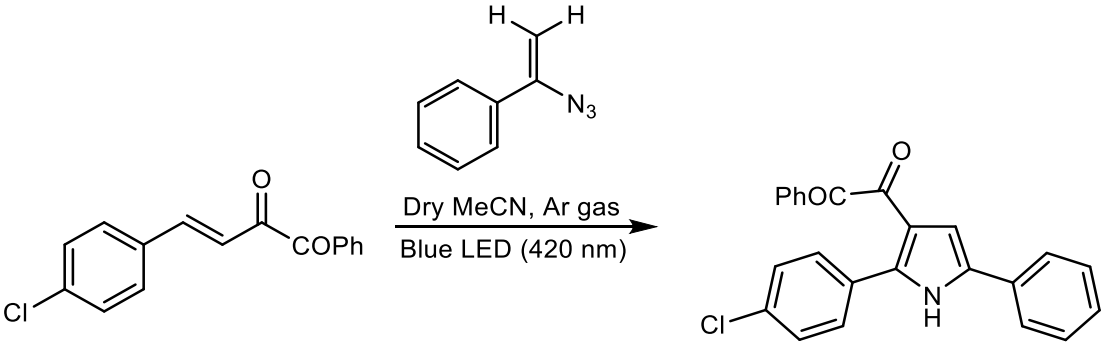
Hexyl 2-(2,5-diphenyl-1*H*-pyrrol-3-yl)-2-oxoacetate 4n: Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); light yellow solid (50 mg, 70%), mp 54-56 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.27 (s, 1 H), 7.82 – 7.77 (m, 2 H), 7.63 – 7.60 (m, 2H), 7.44 – 7.38 (m, 5 H), 7.29 – 7.25 (m, 1 H), 7.06 – 7.05 (m, 1 H), 3.93 (t, *J* = 6.8 Hz, 2 H), 1.56 – 1.05 (m, 2 H), 1.29 – 1.26 (m, 6 H), 0.87 – 0.83 (m, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 182.1, 165.2, 140.8, 133.5, 131.4, 131.3, 129.6 (3 CH), 128.9 (2 CH), 128.2 (2 CH), 127.3, 124.6 (2 CH), 118.3, 108.5, 65.2, 31.3, 28.2, 25.4, 22.4, 13.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{26}NO_3$ [*M* + H]$^+$: 376.1912; found: 376.1904.



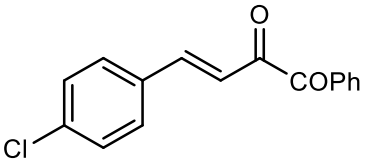
^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4n**



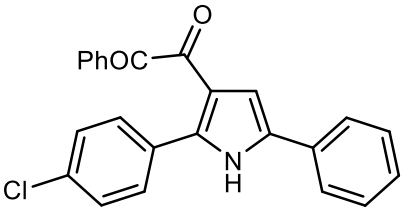
ESI-44: Analytical and spectral data of **2o** and **4o**



(*E*)-4-(4-chlorophenyl)-1-phenylbut-3-ene-1,2-dione; 2o: Prepared according to the literature[6]: R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Yellow solid (486 mg, 58%) mp 78–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 – 7.99 (m, 2 H), 7.71 – 7.60 (m, 2 H), 7.57 – 7.45 (m, 4 H), 7.42 – 7.34 (m, 2 H), 7.11 (d, J = 16.4 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ δ = 193.0, 192.3, 147.2, 137.7, 134.8, 132.8, 132.6, 130.3 (2 CH), 130.1 (2 CH), 129.5 (2 CH), 129.0 (2 CH), 122.8 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{16}H_{12}ClO_2$ [*M* + H]$^+$: 271.0526; found: 271.0518.

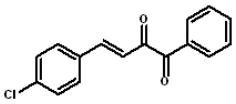


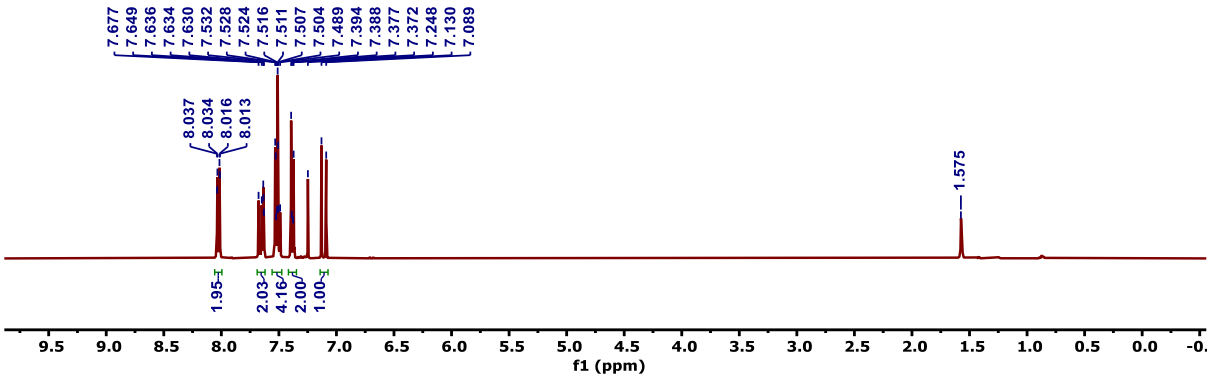
1-(2-(4-chlorophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-2-phenylethane-1,2-dione 4o: Prepared according to the general procedure discussed above: reaction time, 12 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); red solid (51 mg, 72%); mp 194–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (s, 1 H), 7.90 (dd, J = 8.0, 1.2 Hz, 2 H), 7.62 – 7.54 (m, 3 H), 7.49 – 7.42 (m, 4 H), 7.40 – 7.33 (m, 3 H), 7.32 – 7.25 (m, 2 H), 6.88 (d, J = 2.8 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.4, 189.9, 138.6, 135.5, 134.5, 133.4, 133.2, 130.7, 130.5 (2 CH), 130.0 (2 CH), 129.3, 129.2 (2 CH), 128.9 (2 CH), 128.8 (2 CH), 127.9, 124.4 (2 CH), 119.1, 109.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{17}ClNO_2$ [*M* + H]$^+$: 386.0948; found: 386.0944.



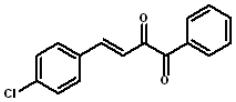
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **2o**

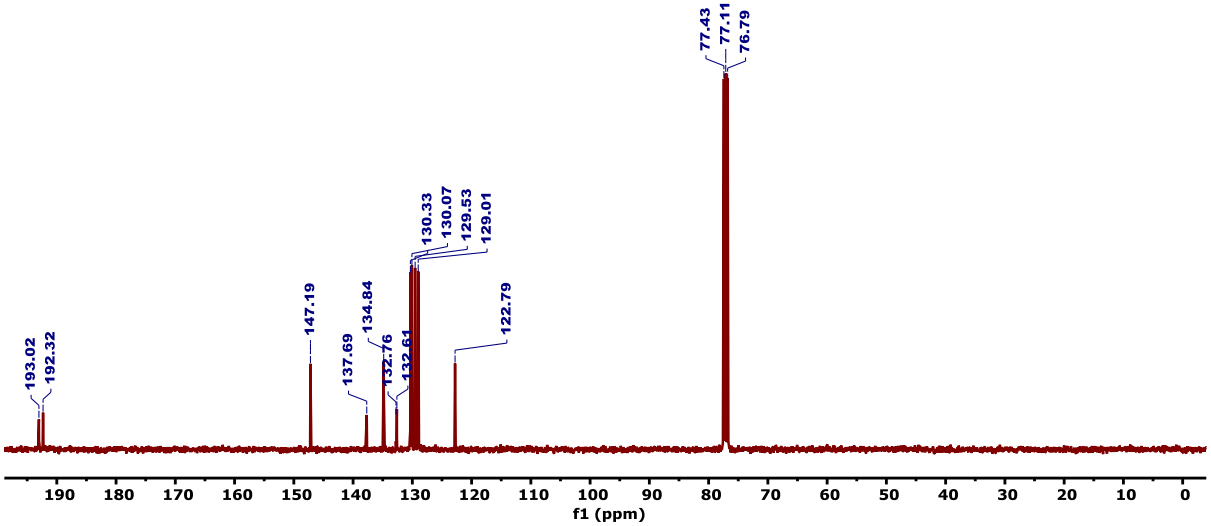
SM-3-123C
single_pulse





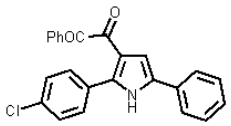
SM-3-123C
single pulse decoupled gated NOE

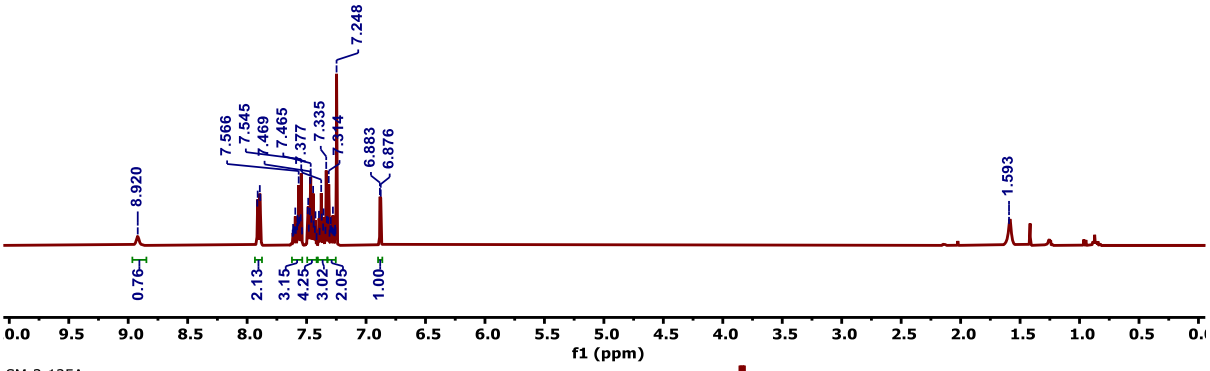




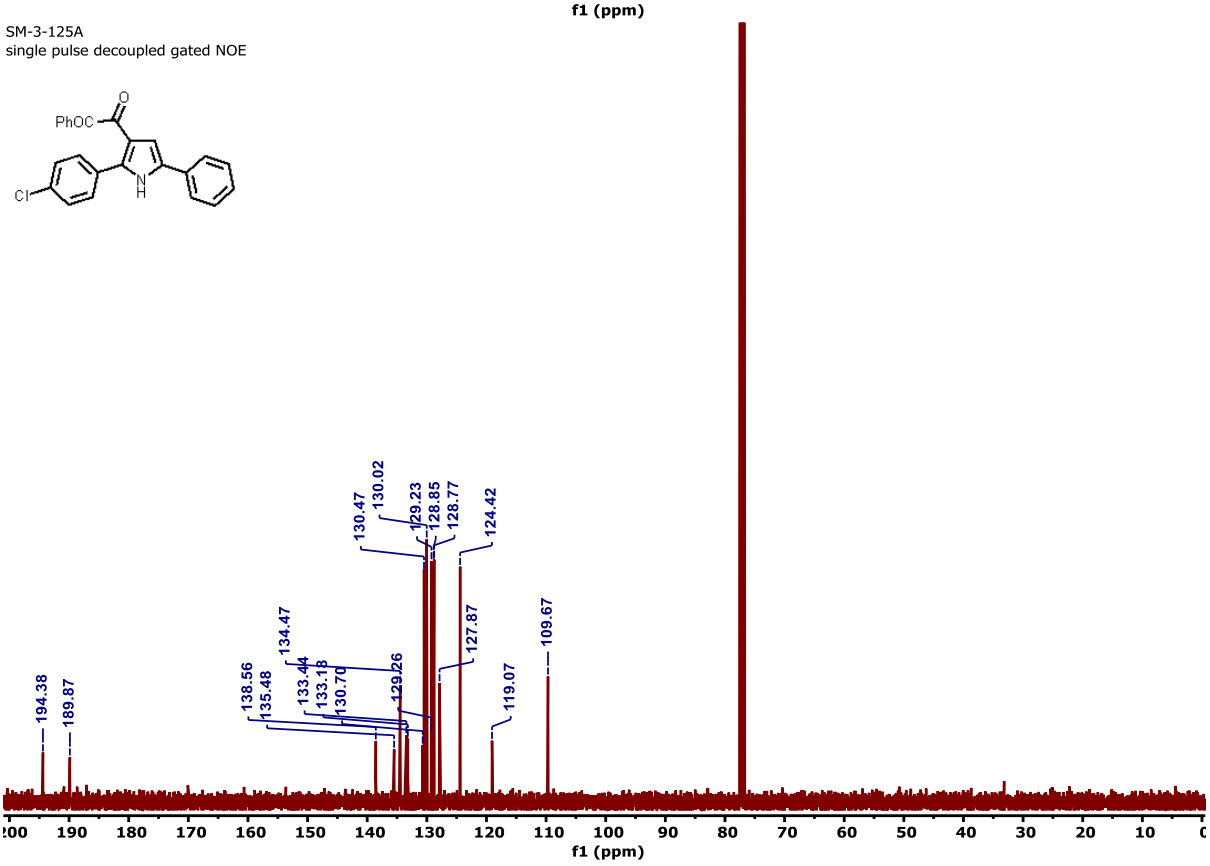
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4ab**

SM-3-125A
single_pulse

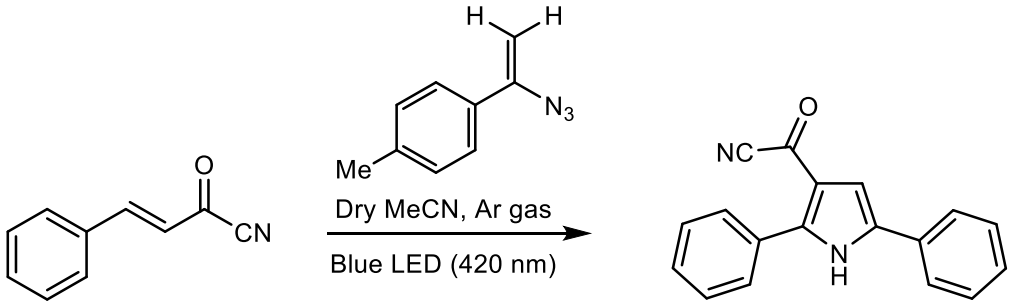




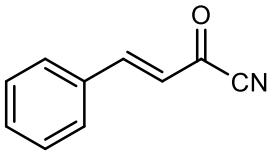
SM-3-125A
single pulse decoupled gated NOE



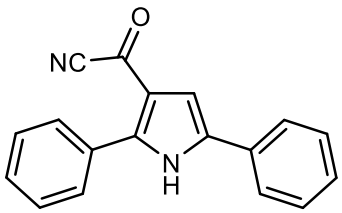
ESI-45: Analytical and spectral data of **2p** and **4p**:



Cinnamoyl cyanide 2p: Prepared according to the literature procedure[7] discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (15%); white solid (0.65 g, 80%); mp 110-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 16.4 Hz, 1 H), 7.66 – 7.59 (m, 2 H), 7.56 – 7.43 (m, 3 H), 6.85 (d, *J* = 16.4 Hz, 1 H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 167.6, 155.1, 133.2, 132.9, 129.6 (4 CH), 125.4, 112.5 ppm; HRMS (EI): *m/z* calcd for $C_{10}H_7NO$ $[M]^+$: 157.0528; found: 157.0520.

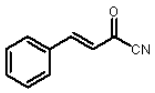


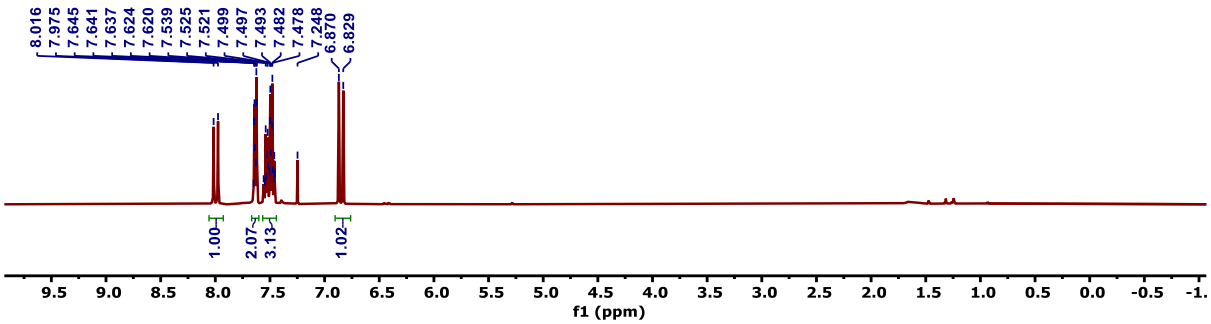
2,5-diphenyl-1*H*-pyrrole-3-carbonyl cyanide 4p: Prepared according to the general procedure discussed above: reaction time, 16 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); yellow solid (44 mg, 52%); mp 145-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1 H), 7.71 – 7.61 (m, 2 H), 7.60 – 7.50 (m, 2 H), 7.53 – 7.40 (m, 5 H), 7.40 – 7.30 (m, 1 H), 7.16 (d, *J* = 3.2 Hz, 1 H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 178.7, 161.3, 133.9, 130.3, 130.2, 129.6, 129.4 (2 CH), 129.0, 128.9 (2 CH), 128.4 (2 CH), 124.5 (2 CH), 120.3, 114.3, 110.1 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{18}H_{13}N_2O$ $[M + H]^+$: 273.1028; found: 273.1017.



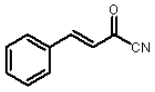
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **2p**

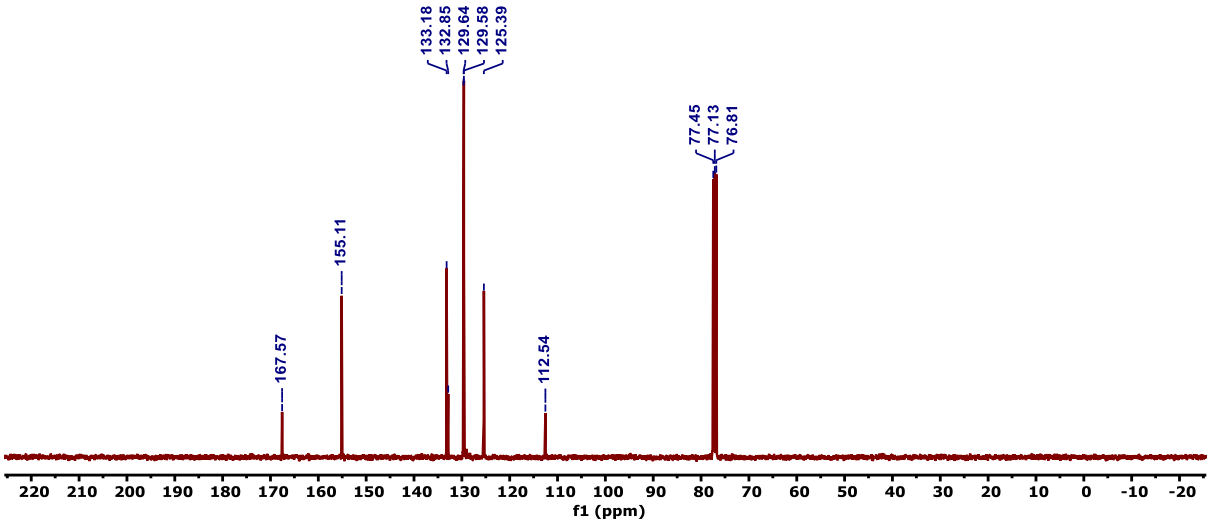
SM-3-146B
single_pulse





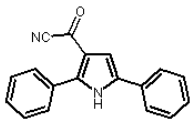
SM-3-146B
single pulse decoupled gated NOE

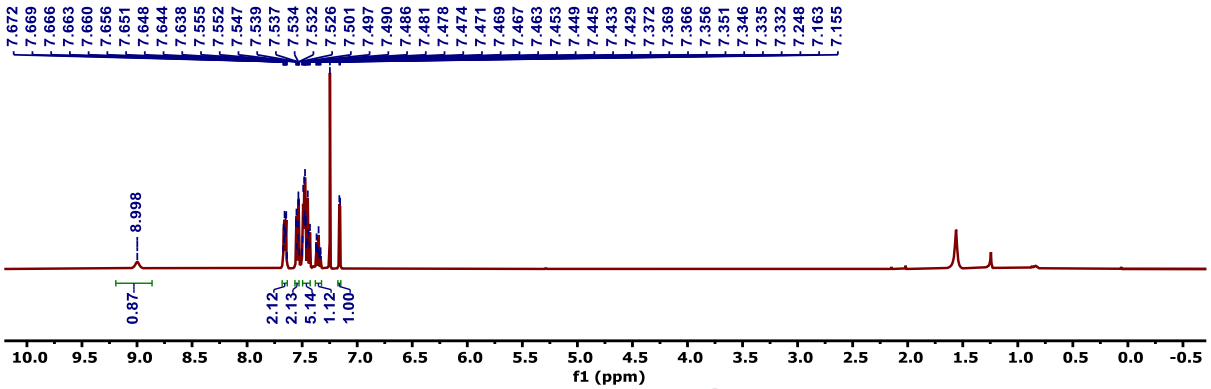




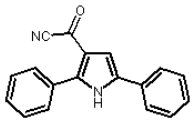
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4p**

SM-3-151C
single_pulse

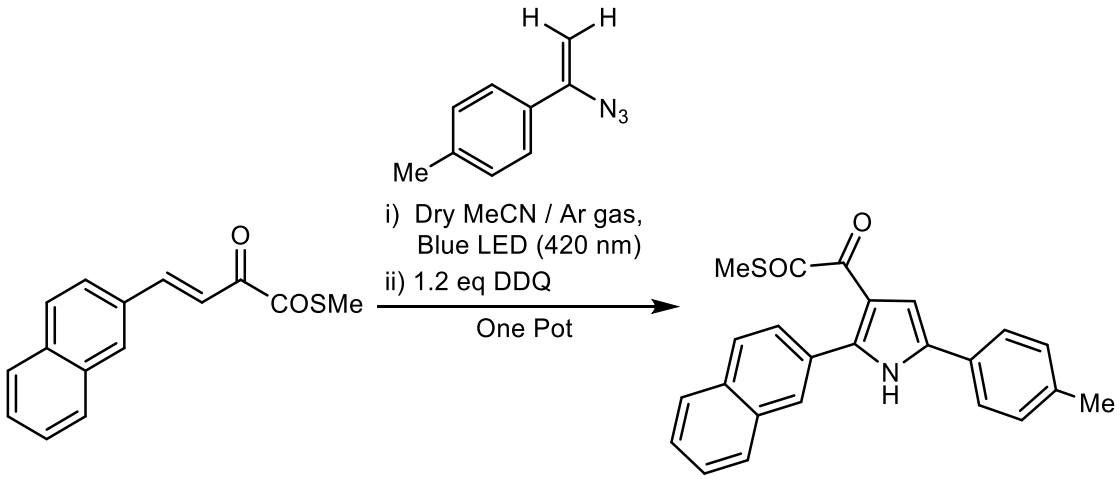




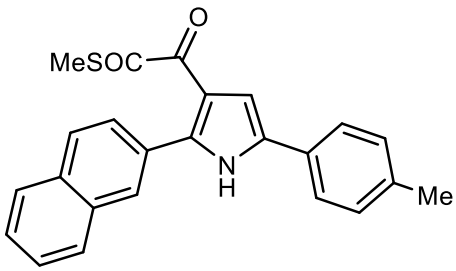
SM-3-151C
single pulse decoupled gated NOE



ESI-46: Analytical and spectral data of **4u**

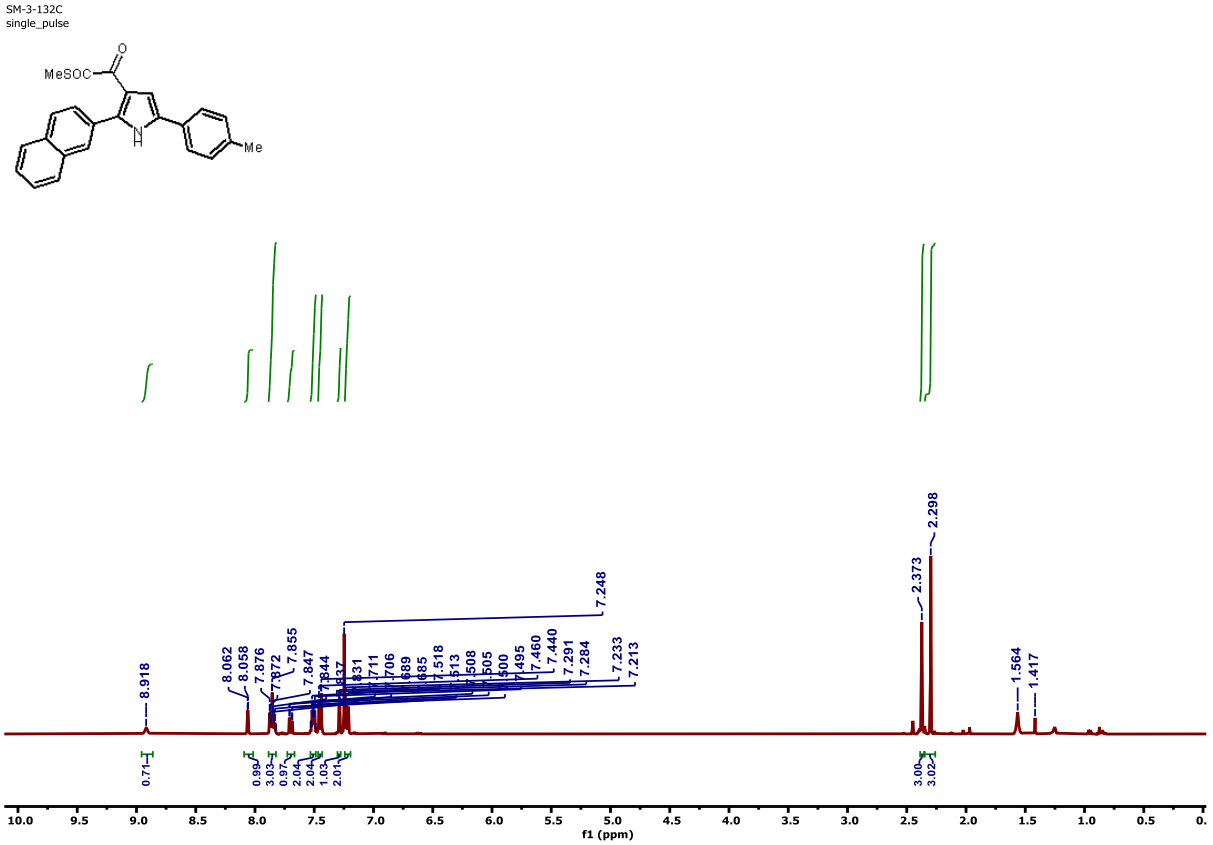


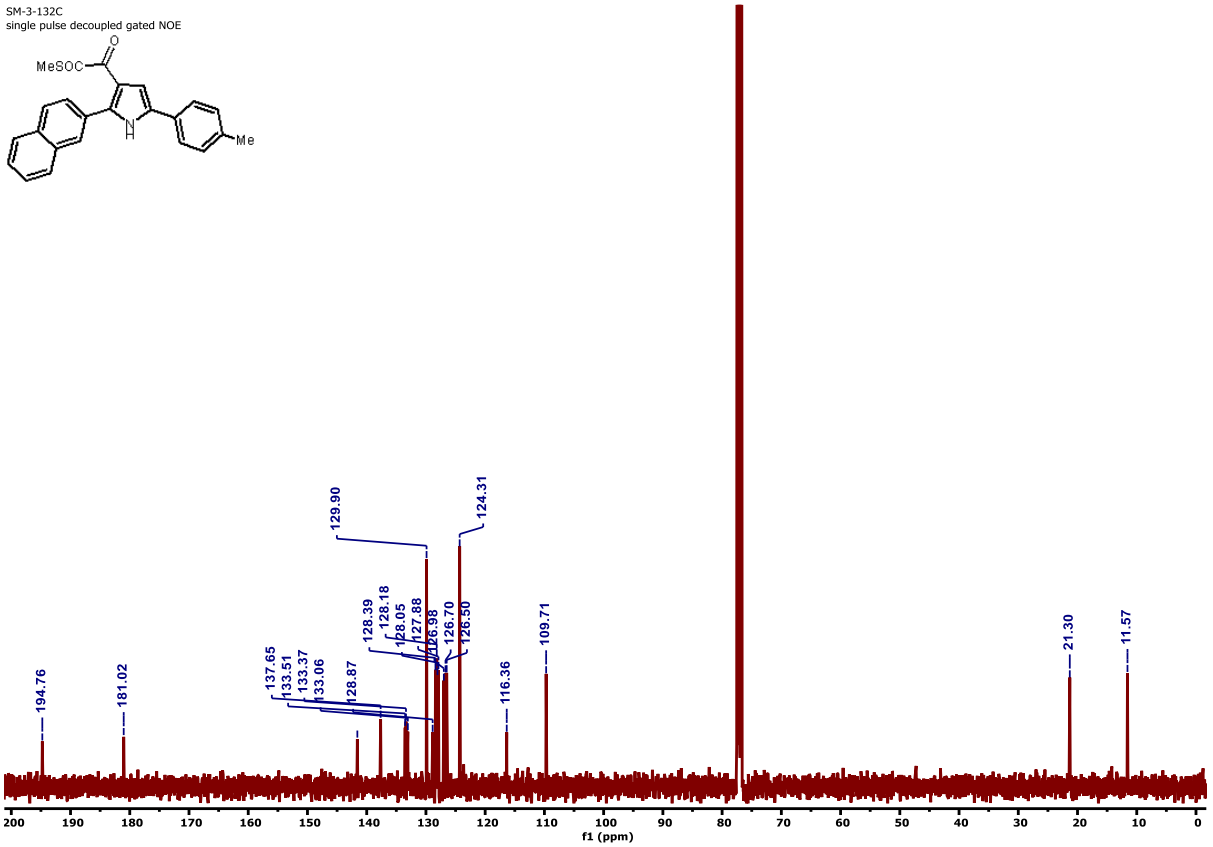
***S*-methyl 2-(2-(naphthalen-2-yl)-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4u:**



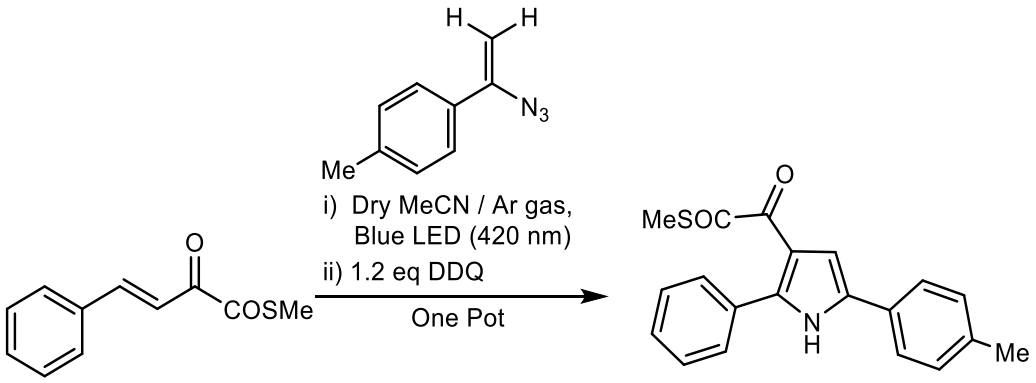
Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); red solid (54 mg, 72%), mp 85-88 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (s, 1 H), 8.06 (d, *J* = 1.6 Hz, 1 H), 7.88 – 7.82 (m, 3 H), 7.70 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.53 – 7.49 (m, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 2.8 Hz, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 2.37 (s, 3 H), 2.30 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.8, 181.0, 141.6, 137.6, 133.5, 133.4, 133.1, 129.9 (2 CH), 128.9, 128.4, 128.2, 128.2, 128.1, 127.9, 127.0, 126.7, 126.5, 124.3 (2 CH), 116.4, 109.7, 21.3, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{20}NO_2S$ [*M* + H]$^+$: 386.1214; found: 386.1217.

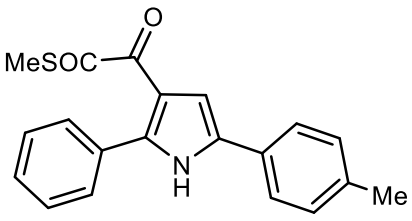
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4u**





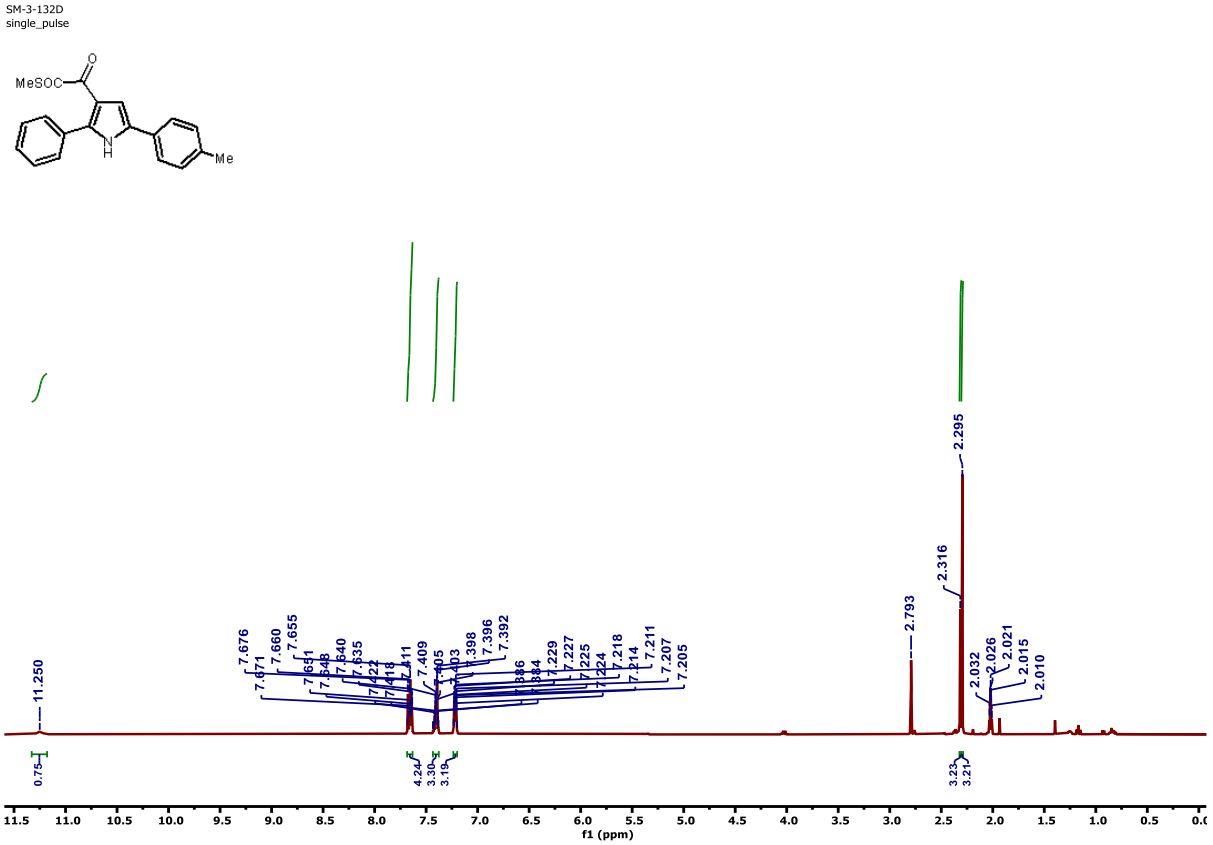
ESI-47: Analytical and spectral data of **4v**

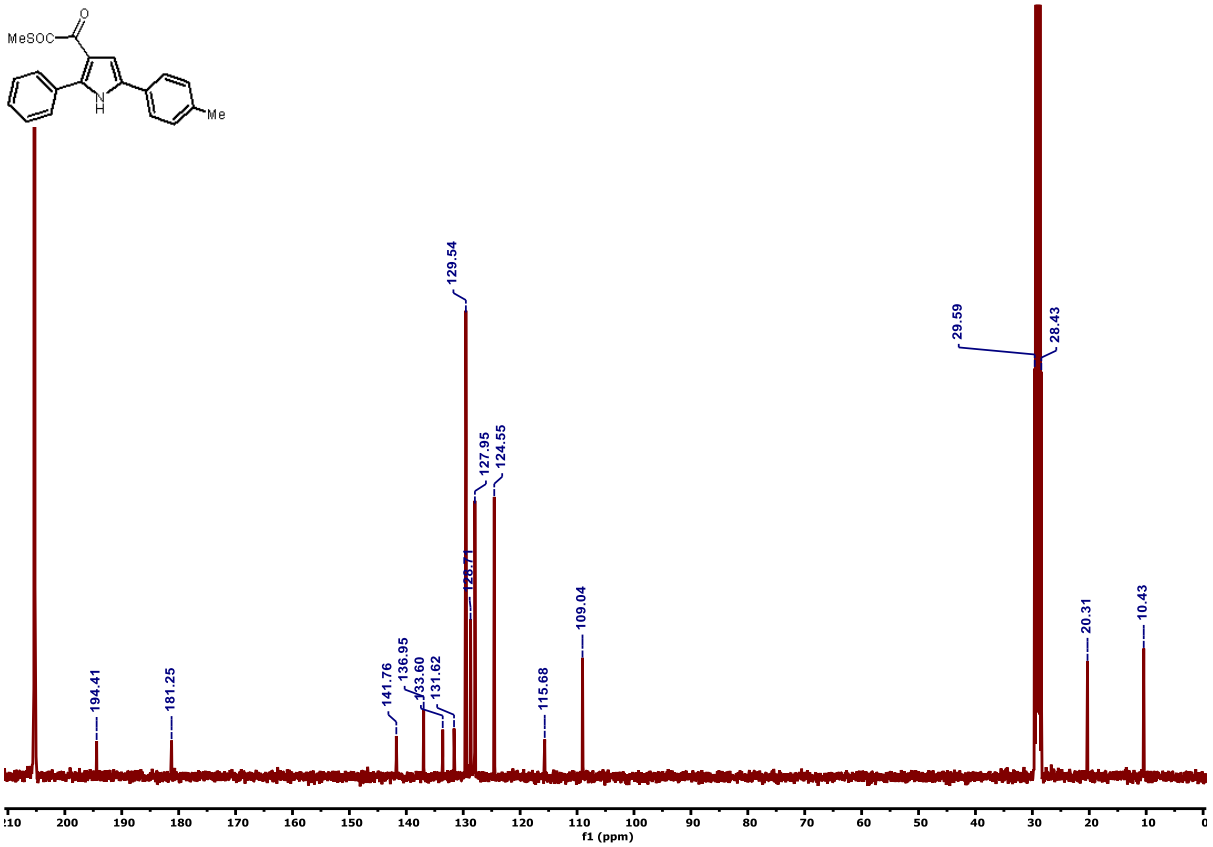




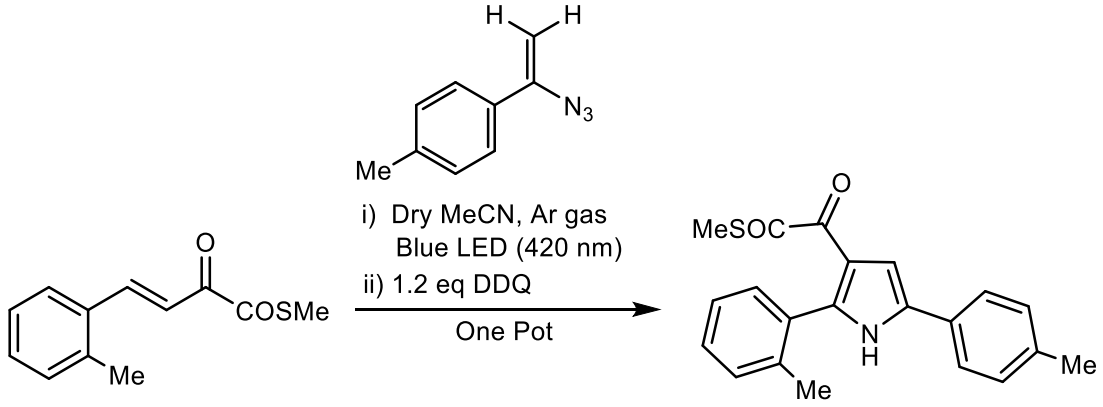
***S*-methyl 2-oxo-2-(2-phenyl-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanethioate 4v:** Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); red solid (57 mg, 70%); mp 112-117℃; ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.25 (s, 1 H), 7.68 – 7.63 (m, 4 H), 7.43 – 7.38 (m, 3 H), 7.23 – 7.20 (m, 3 H), 2.32 (s, 3 H), 2.30 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.4, 181.2, 141.8, 137.0, 133.6, 131.6, 129.5 (3 CH), 128.7 (2 CH), 128.0 (2 CH), 124.5 (2 CH), 115.7, 109.0 (2 CH), 20.3, 10.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{18}NO_2S$ [*M* + H]$^+$: 336.1058; found: 336.1047.

^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4v**

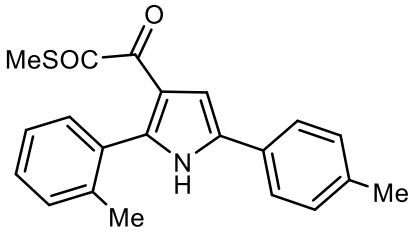




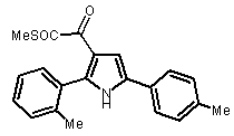
ESI-48: Analytical and spectral data of **4w**

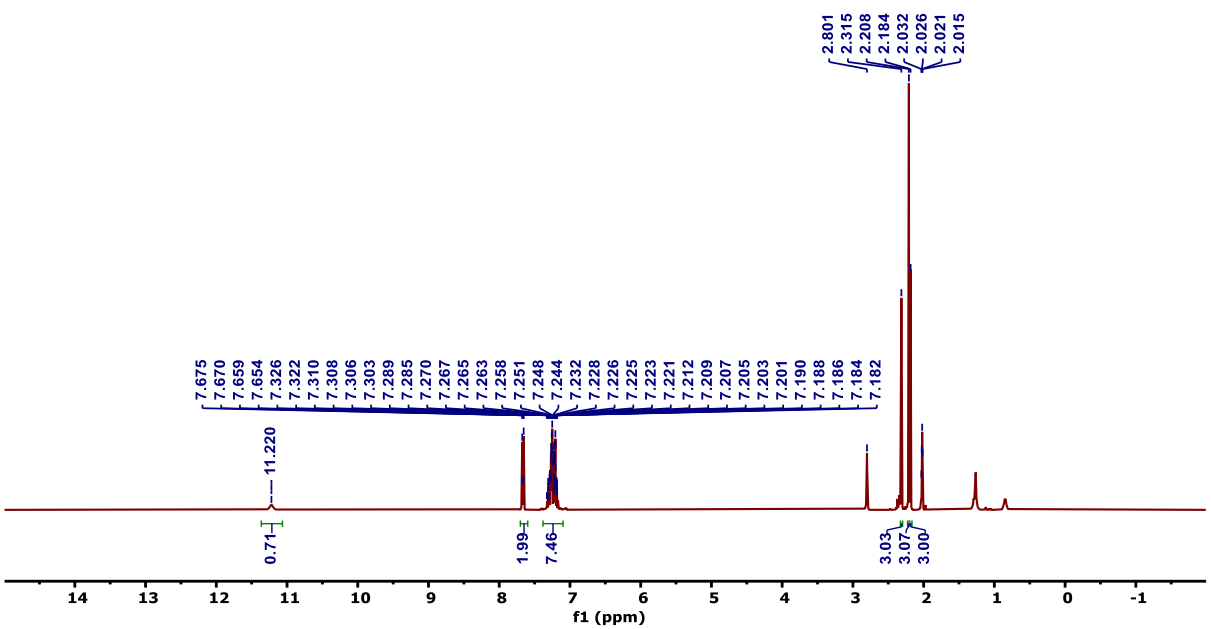


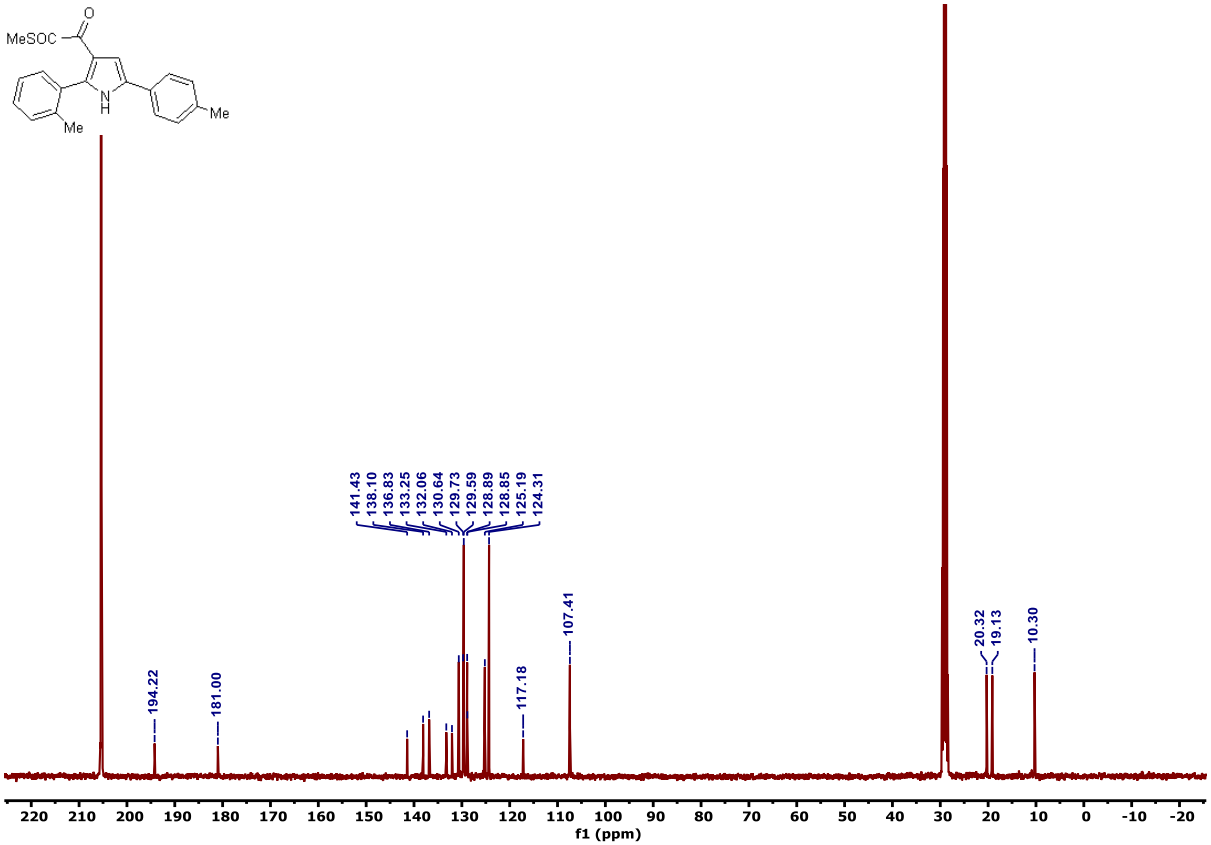
***S*-methyl 2-oxo-2-(2-(*o*-tolyl)-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanethioate 4w:** Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); red solid (56 mg, 71%), mp 62–66 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.22 (s, 1 H), 7.66 (d, J = 8.4 Hz, 2 H), 7.33 – 7.18 (m, 7 H), 2.31 (s, 3 H), 2.21 (s, 3 H), 2.18 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.2, 181.0, 141.4, 138.1, 136.8, 133.3, 132.1, 130.6, 129.7, 129.6 (2 CH), 128.9, 128.9, 125.2, 124.3 (2 CH), 117.2, 107.4, 20.3, 19.1, 10.3 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{21}H_{20}NO_2S$ [M + H]$^+$: 350.1214; found: 350.1213.



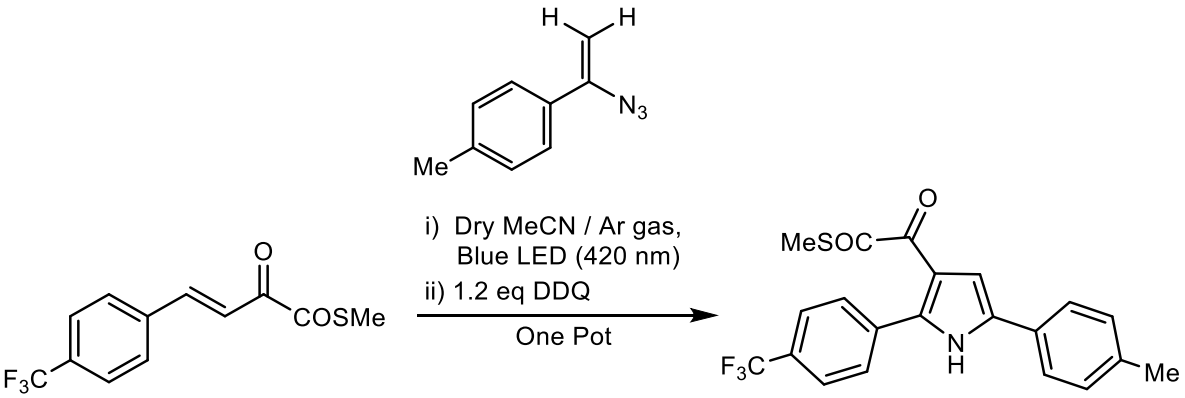
^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4w**



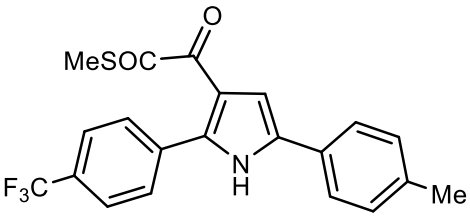




ESI-49: Analytical and spectral data of **4x**



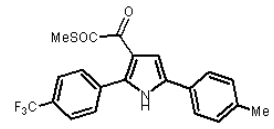
***S*-methyl 2-oxo-2-(5-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-yl)ethanethioate**

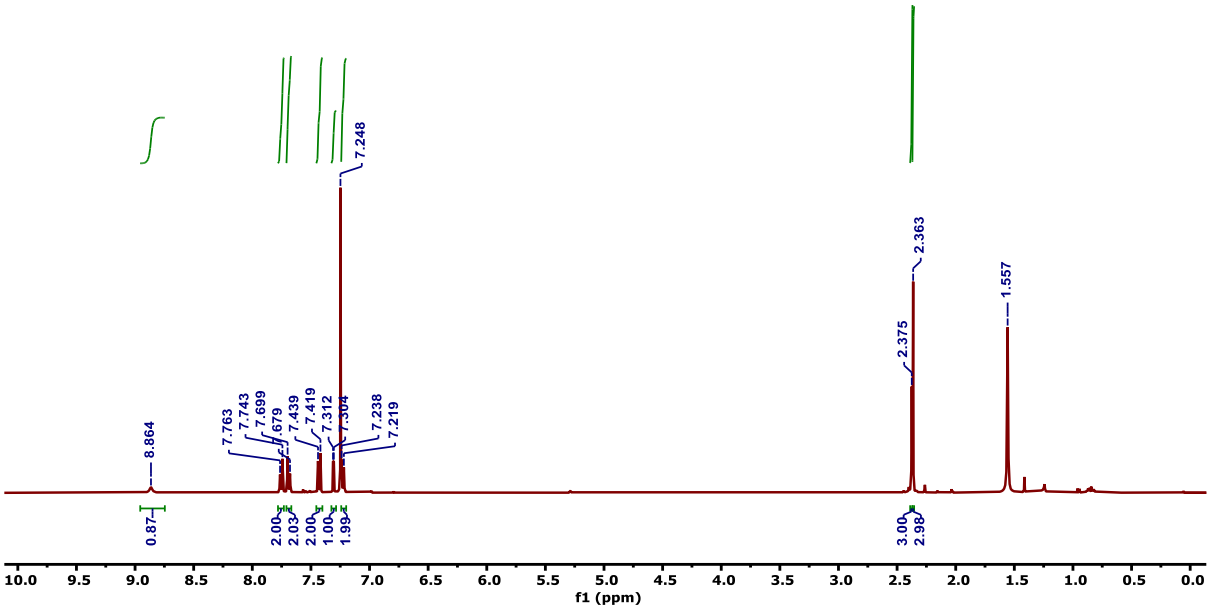


4x: Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); red solid (53 mg, 72%); mp 83-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (s, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 3.2 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 2.37 (s, 3 H), 2.36 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.5, 180.8, 139.3, 138.0, 133.9, 131.2, 130.0 (2 CH), 129.3 (2 CH), 127.9, 125.5 (q, *J* = 4.0 Hz, 1 C), 124.4 (2 CH), 116.7, 110.1 (2 CH), 21.3, 11.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{21}H_{16}F_3NO_2SNa$ [*M* + Na]$^+$: 426.0752; found: 426.0751.

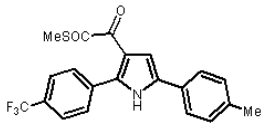
^{1}H (400 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$), and ^{19}F (376 MHz, $CDCl_3$) NMR spectra of **4x**

SM-3-129D
single_pulse

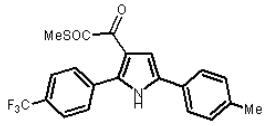


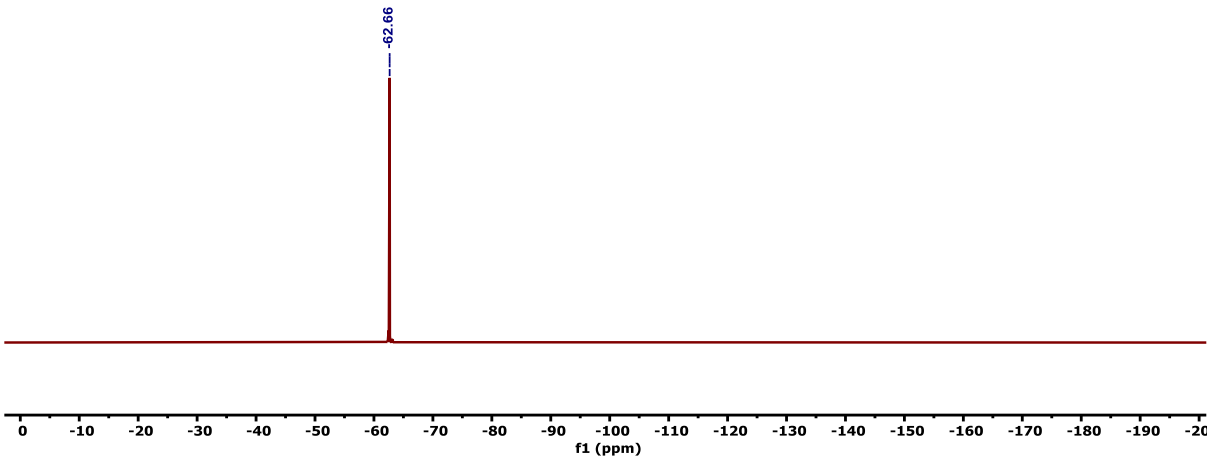


SM-3-129D
single pulse decoupled gated NOE

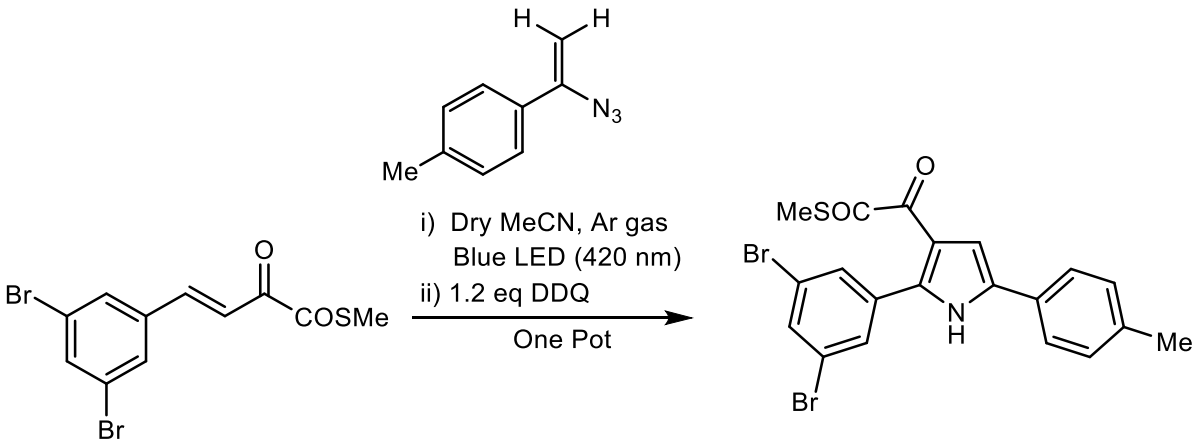


SM-3-129D
single pulse decoupled gated NOE

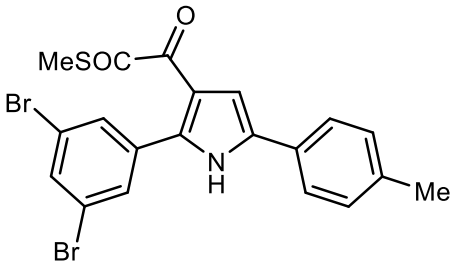




ESI-50: Analytical and Spectral data of **4y**

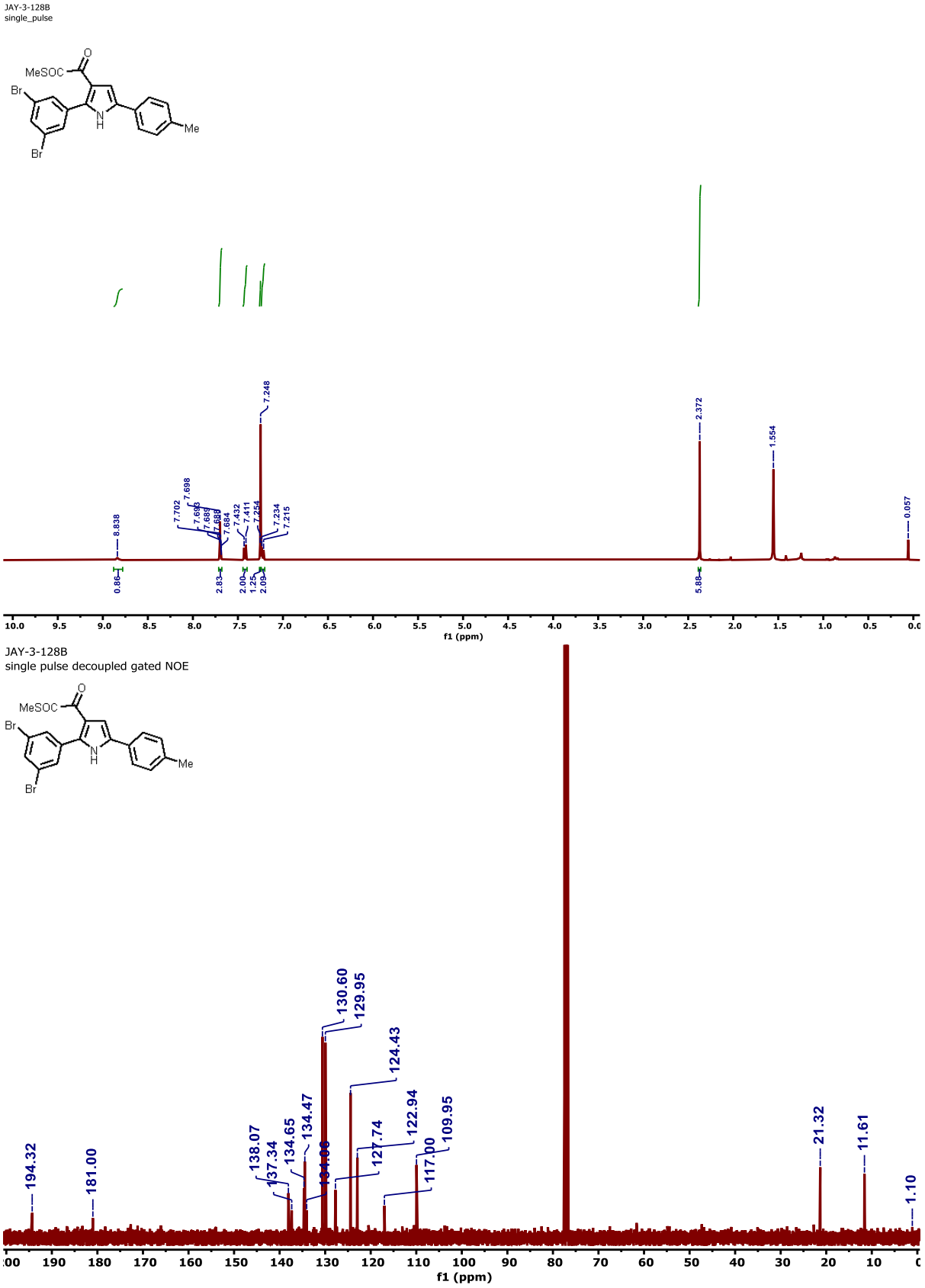


***S*-methyl 2-(2-(3,5-dibromophenyl)-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4y:**

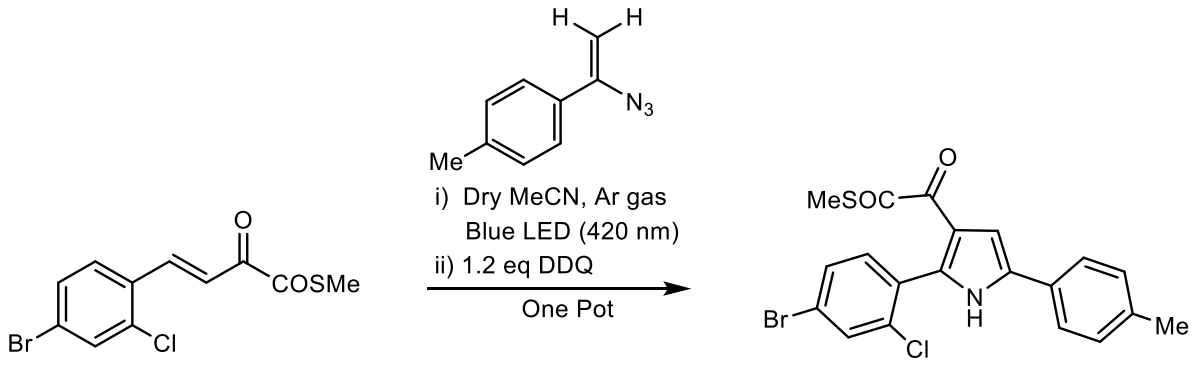


Prepared according to the general procedure discussed above: reaction time, 34 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); red solid (55.5 mg, 82%); mp 145-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 1 H), 7.70 – 7.68 (m, 3 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 2.4 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 2 H), 2.37 (s, 6 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.3, 181.0, 138.1, 137.3, 134.6, 134.5, 134.1, 130.6 (2 CH), 130.0 (2 CH), 127.7, 124.4 (2 CH), 122.9, 117.0, 110.0 (2 CH), 21.3, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{15}Br_2NO_2SNa$ [*M* + Na]$^+$: 513.9088; found: 513.9075.

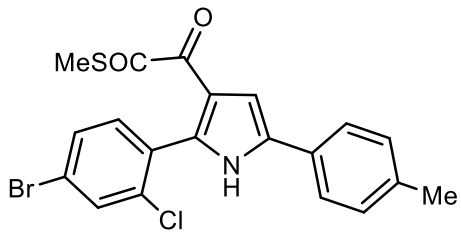
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4y**



ESI-51: Analytical and spectral data of **4z**

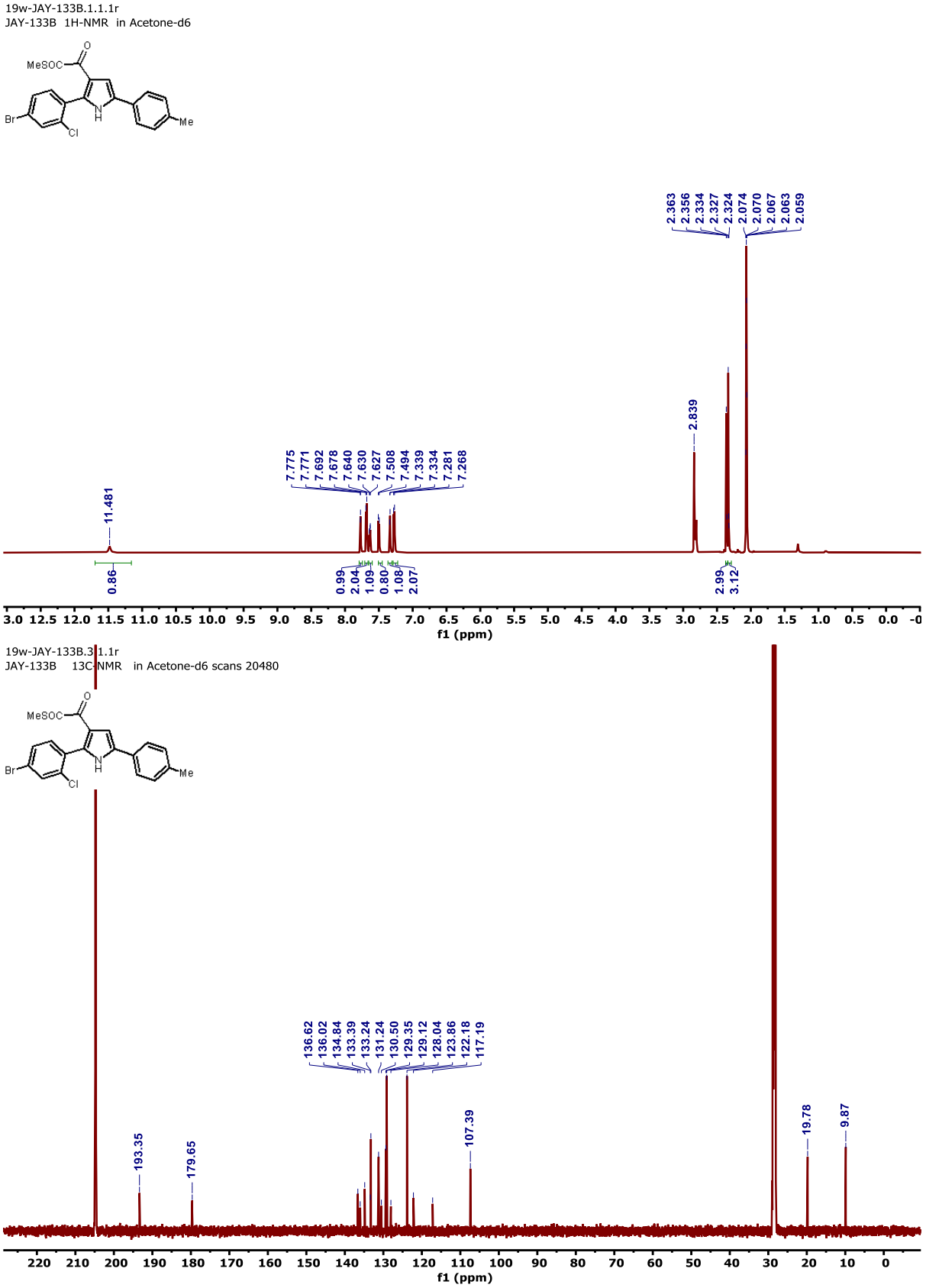


***S*-methyl 2-(2-(4-bromo-2-chlorophenyl)-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)-2-oxoethanethioate**

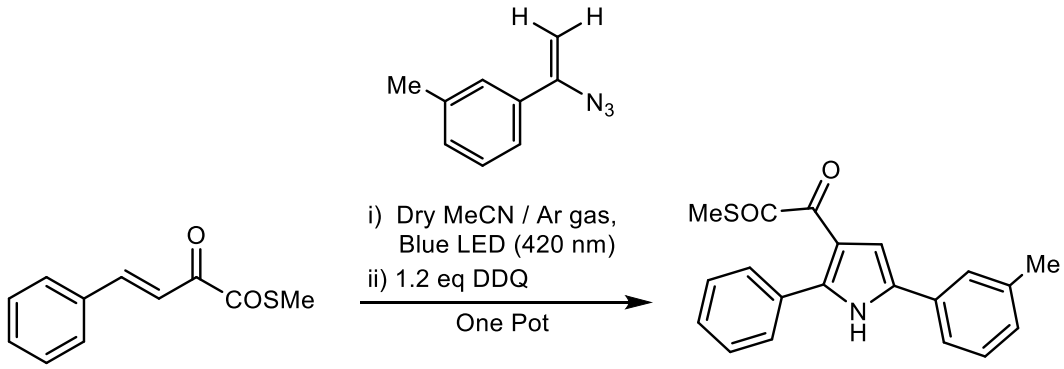


4z: Prepared according to the general procedure discussed above: reaction time, 35 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); red solid (54.7 mg, 78%); mp 168–173 °C. ^{1}H NMR (600 MHz, Acetone-d_6): δ = 11.48 (s, 1H), 7.77 (d, J = 2.4 Hz, 1 H), 7.69 (d, J = 8.4 Hz, 2 H), 7.64 – 7.63 (m, 1 H), 7.50 (d, J = 8.4 Hz, 1 H), 7.34 (d, J = 3.0 Hz, 1 H), 7.27 (d, J = 7.8 Hz, 2 H), 2.36 (s, 3 H), 2.33 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (151 MHz, Acetone-d_6): δ = 193.4, 179.7, 136.6, 136.0, 134.8, 133.4, 133.2, 131.2, 130.5, 129.4, 129.1 (2 CH), 128.0, 123.9 (2 CH), 122.2, 117.2, 107.4, 19.8, 9.9 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{15}BrClNO_2S$ [M + H]$^+$: 447.9773; found: 447.9776.

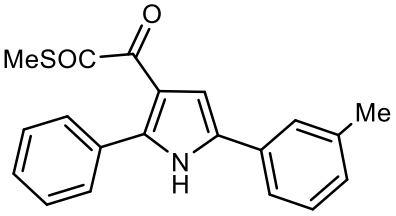
^{1}H (600 MHz, Acetone-d_6) and $^{13}C\{^{1}H\}$ (151 MHz, Acetone-d_6) NMR spectra of **4z**



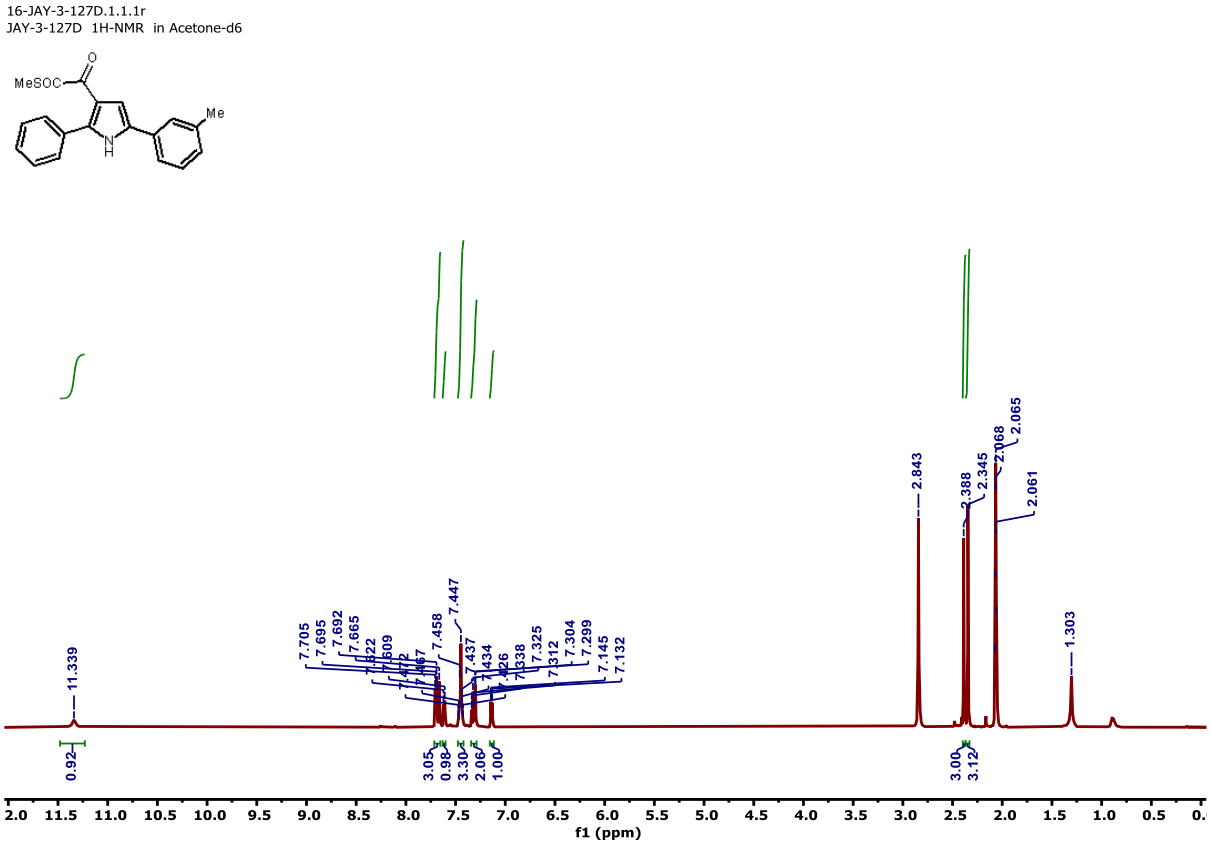
ESI-52: Analytical and spectral data of **4aa**

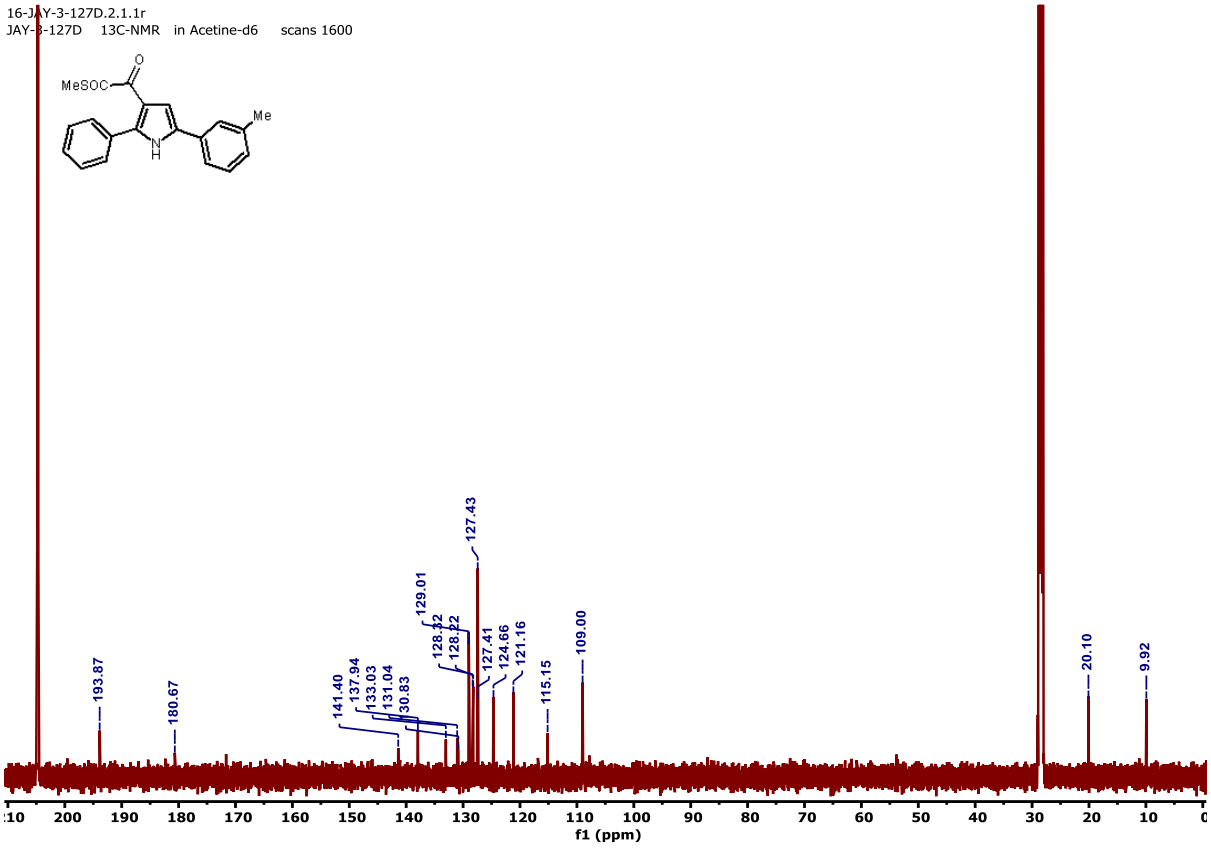


***S*-methyl 2-oxo-2-(2-phenyl-5-(*m*-tolyl)-1*H*-pyrrol-3-yl)ethanethioate 4aa:** Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (5%); red gum (58 mg, 71%). ^{1}H NMR (600 MHz, Acetone-d_6): δ = 11.34 (s, 1 H), 7.71 – 7.66 (m, 3 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.47 – 7.43 (m, 3 H), 7.34 – 7.30 (m, 2 H), 7.14 (d, *J* = 7.8 Hz, 1 H), 2.39 (s, 3 H), 2.34 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (151 MHz, Acetone-d_6): δ = 193.9, 180.7, 141.4, 137.9, 133.0, 131.0, 130.8, 129.0 (2 CH), 128.3, 128.2, 127.4 (2 CH), 127.4, 124.7, 121.2, 115.1, 109.0, 20.1, 9.9 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{20}H_{18}NO_2S$ [*M* + H]$^+$: 336.1058; found: 336.1067.

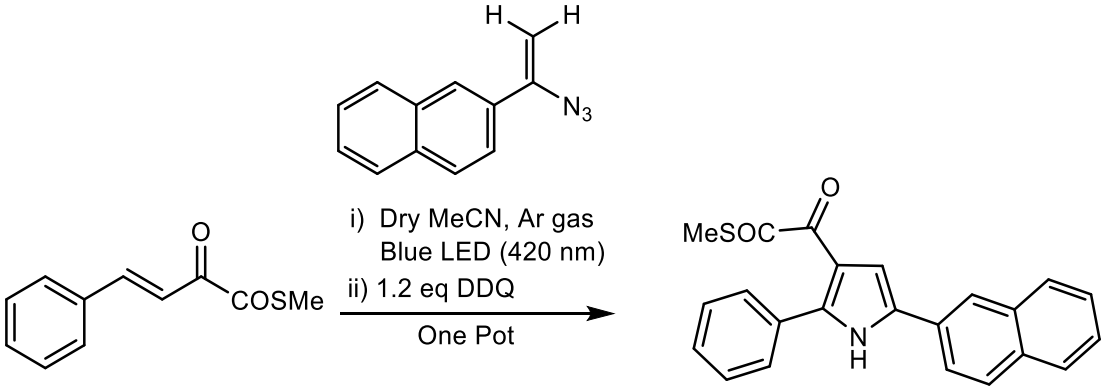


^{1}H (600 MHz, Acetone-d_6) and ^{13}C{^{1}H} (151 MHz, Acetone-d_6) NMR spectra of **4aa:**

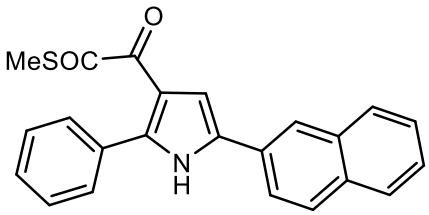




ESI-53: Analytical and spectral data of **4ab**

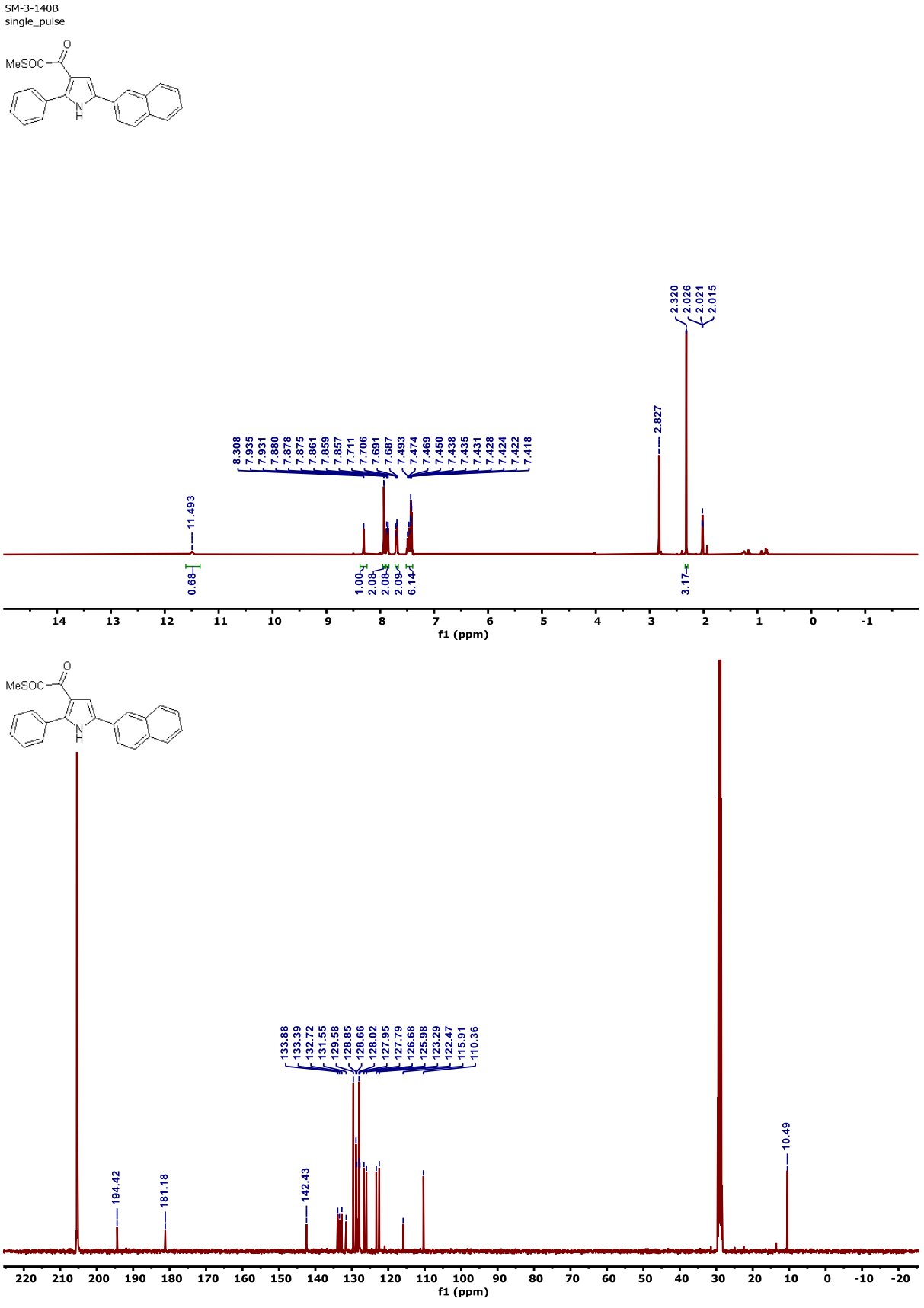


***S*-methyl 2-(5-(naphthalen-2-yl)-2-phenyl-1-*H*-pyrrol-3-yl)-2-oxoethanethioate 4ab:**

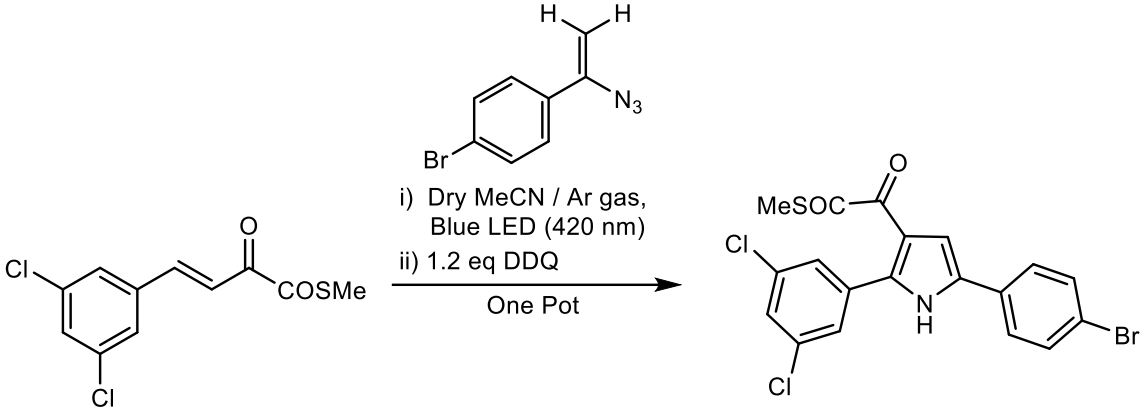


Prepared according to the general procedure discussed above: reaction time, 38 h; R_f = 0.3; eluent, EtOAc/*n*-hexane (10%); red solid (68.4 mg, 76%), mp 165–168 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.49 (s, 1H), 8.31 (s, 1H), 7.93 (d, J = 1.6 Hz, 2H), 7.80 – 7.86 (m, 2H), 7.71 – 7.69 (m, 2H), 7.50 – 7.42 (m, 6H), 2.32 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.4, 181.2, 142.4, 133.9, 133.4, 132.7, 131.6, 129.6 (2 CH), 128.9 (2 CH), 128.7, 128.0 (3 CH), 127.8, 126.7, 126.0, 123.3, 122.5, 115.9, 110.4, 10.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{23}H_{18}NO_2S$ [M + H] $^+$: 372.1058; found: 372.1053.

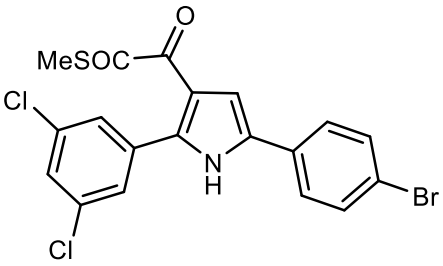
^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4ab**



ESI-54: Analytical and spectral data of **4ac**

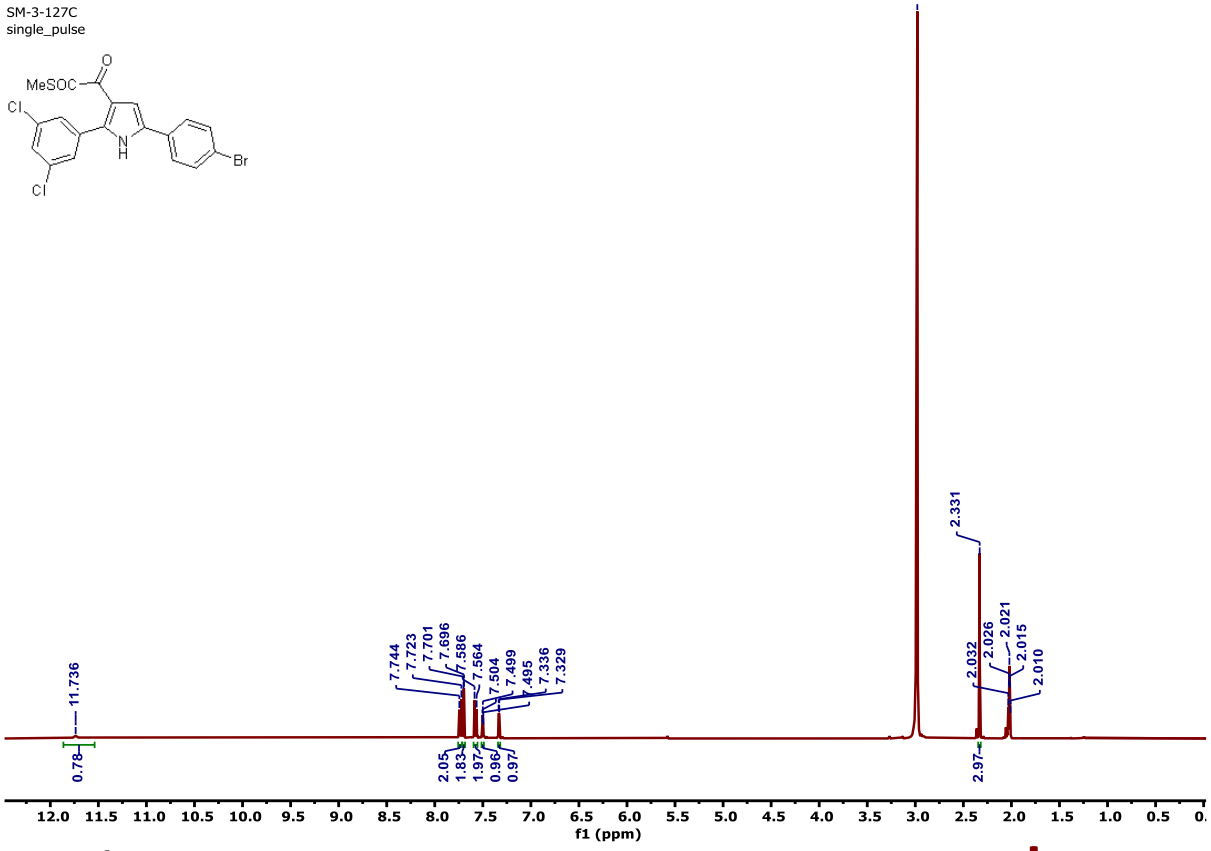


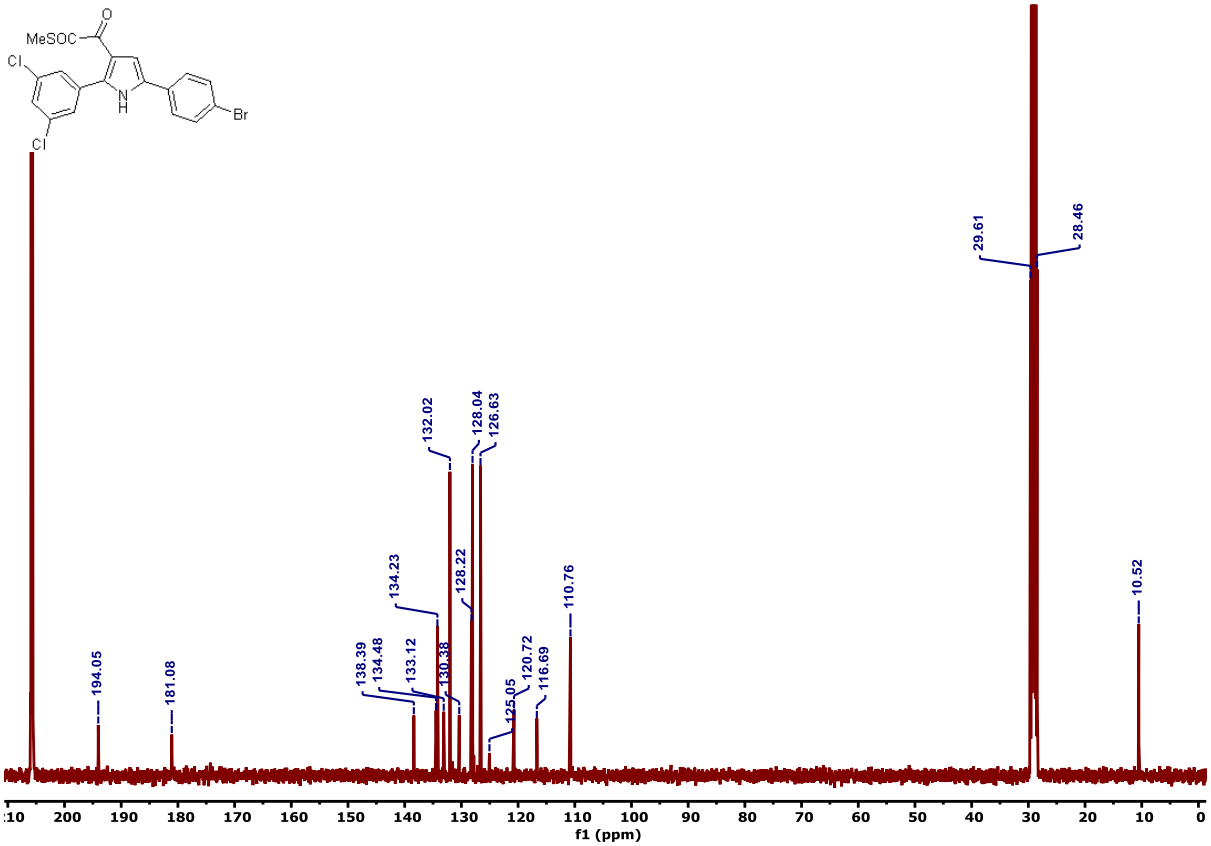
***S*-methyl 2-(5-(4-bromophenyl)-2-(3,5-dichlorophenyl)-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4ac:** Prepared according to the general procedure discussed above:



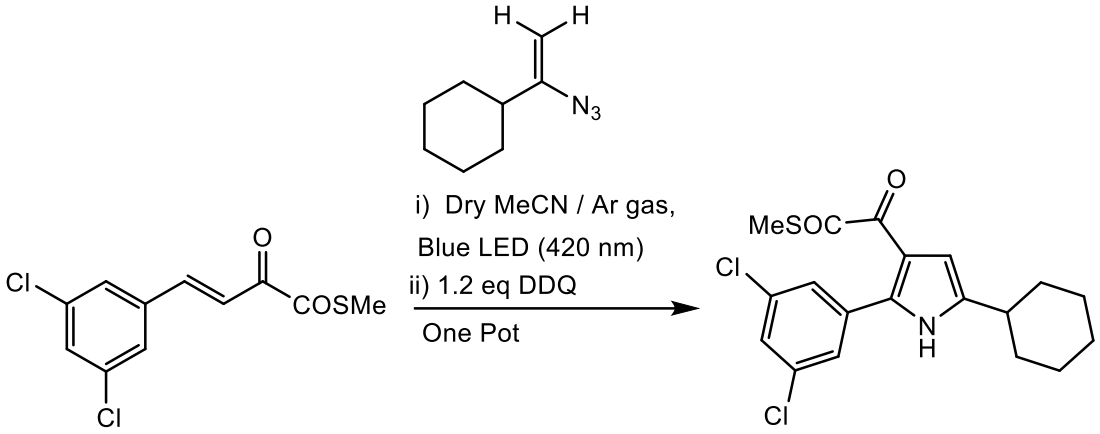
reaction time, 32 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); yellow solid (66 mg, 78%); mp 140-145 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 11.74 (s, 1 H), 7.73 (d, J = 8.4 Hz, 2 H), 7.70 (d, J = 2.0 Hz, 2 H), 7.58 (d, J = 8.8 Hz, 2 H), 7.50 (t, J = 2.0 Hz, 1 H), 7.33 (d, J = 2.8 Hz, 1 H), 2.33 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.0, 181.2, 138.4, 134.5, 134.2, 133.1, 132.0 (2 CH), 130.4, 128.2, 128.0 (2 CH), 126.6 (2 CH), 125.1, 120.7, 116.7, 110.8, 10.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{12}BrCl_2NO_2SNa$ [M + Na]$^+$: 489.9047; found: 480.9052.

^{1}H (400 MHz, Acetone-d_6) and ^{13}C{^{1}H} (101 MHz, Acetone-d_6) NMR spectra of **4ac**

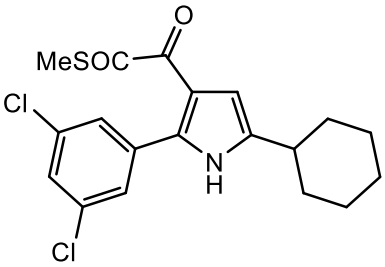




ESI-55: Analytical and spectral data of **4ad**



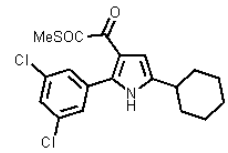
***S*-methyl 2-(5-cyclohexyl-2-(3,5-dichlorophenyl)-1*H*-pyrrol-3-yl)-2-oxoethanethioate 4ad:**

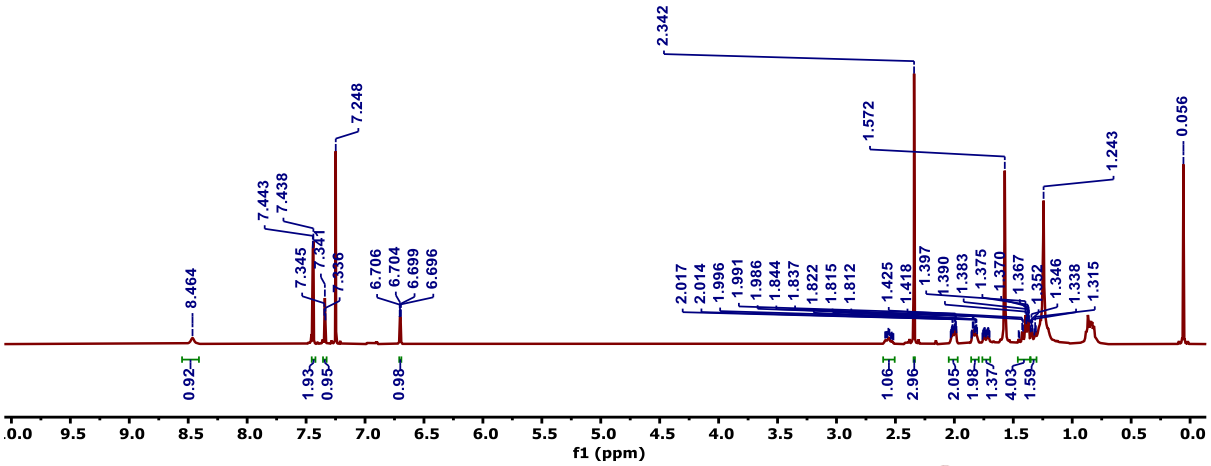


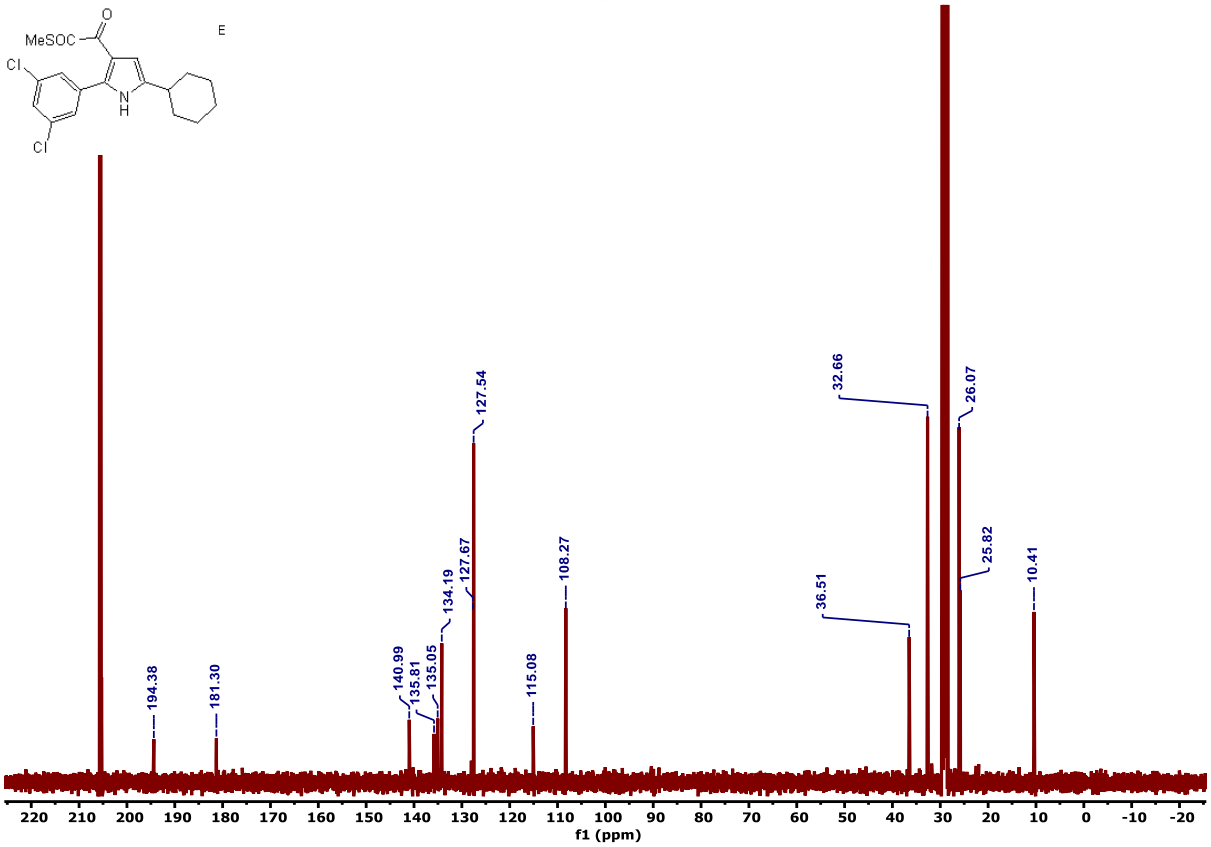
Prepared according to the general procedure discussed above: reaction time, 36 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); red solid (39.6 mg, 55%); mp 96-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 7.44 (d, *J* = 2.0 Hz, 2 H), 7.34 (t, *J* = 1.6 Hz, 1 H), 6.70 (dd, *J* = 2.8, 0.8 Hz, 1 H), 2.59 - 2.52 (m, 1 H), 2.34 (s, 3 H), 2.03 – 1.98 (m, 2 H), 1.85 – 1.81 (m, 2 H), 1.76 – 1.70 (m, 1 H), 1.46 – 1.37 (m, 4 H), 1.35 – 1.31 (m, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ = 194.4, 181.3, 141.0, 135.8, 135.1, 134.2, 127.7, 127.5 (3 CH), 115.1, 108.3, 36.5, 32.7 (2 CH_2), 26.1 (2 CH_2), 25.8, 10.4 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{19}H_{29}Cl_2NO_2SNa$ [*M* + Na]$^+$: 418.0412; found: 418.0401.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, Acetone-d_6) NMR spectra of **4ad**

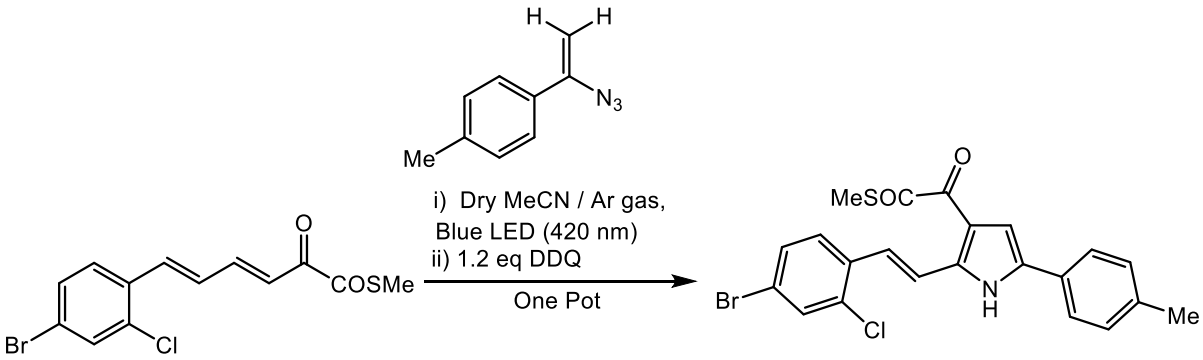
SM-3-17B
single_pulse



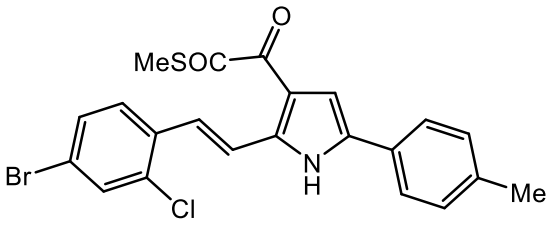




ESI-56: Analytical and spectral data of **4ae**

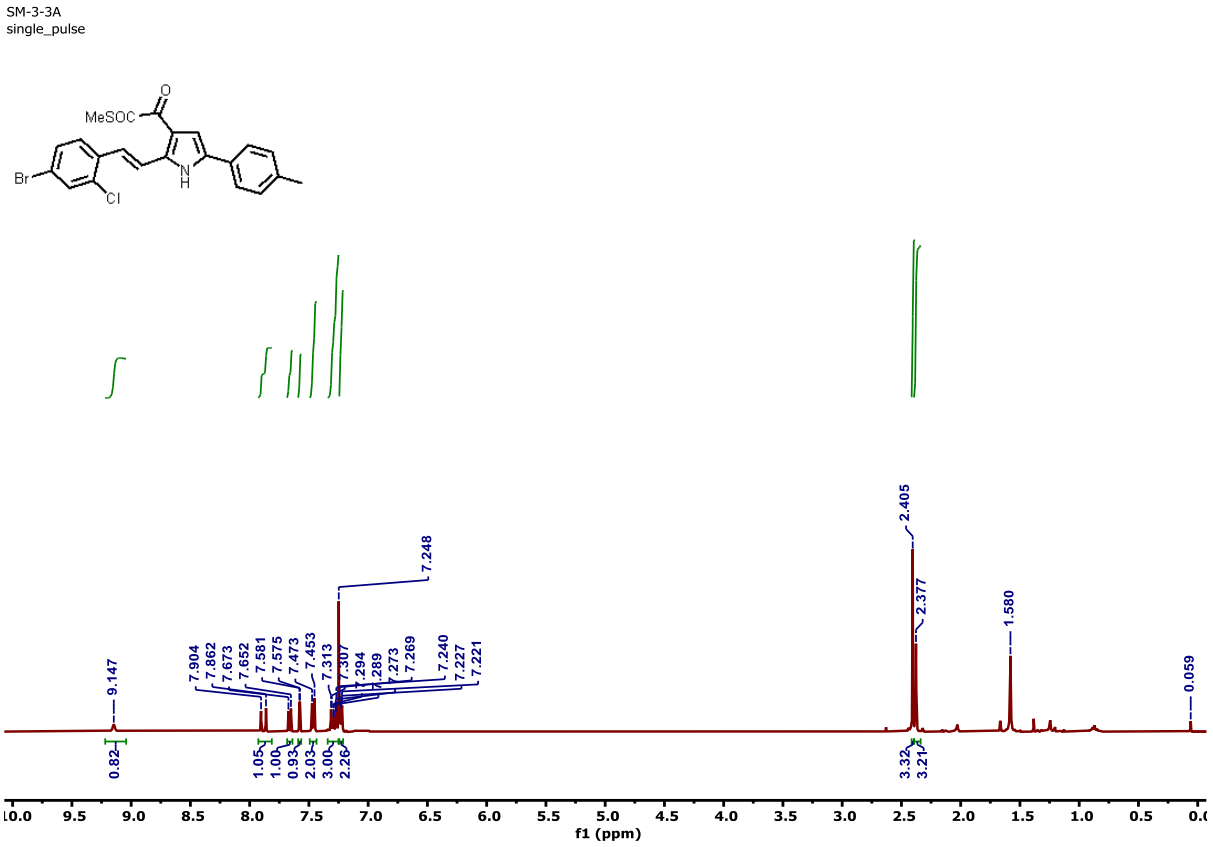


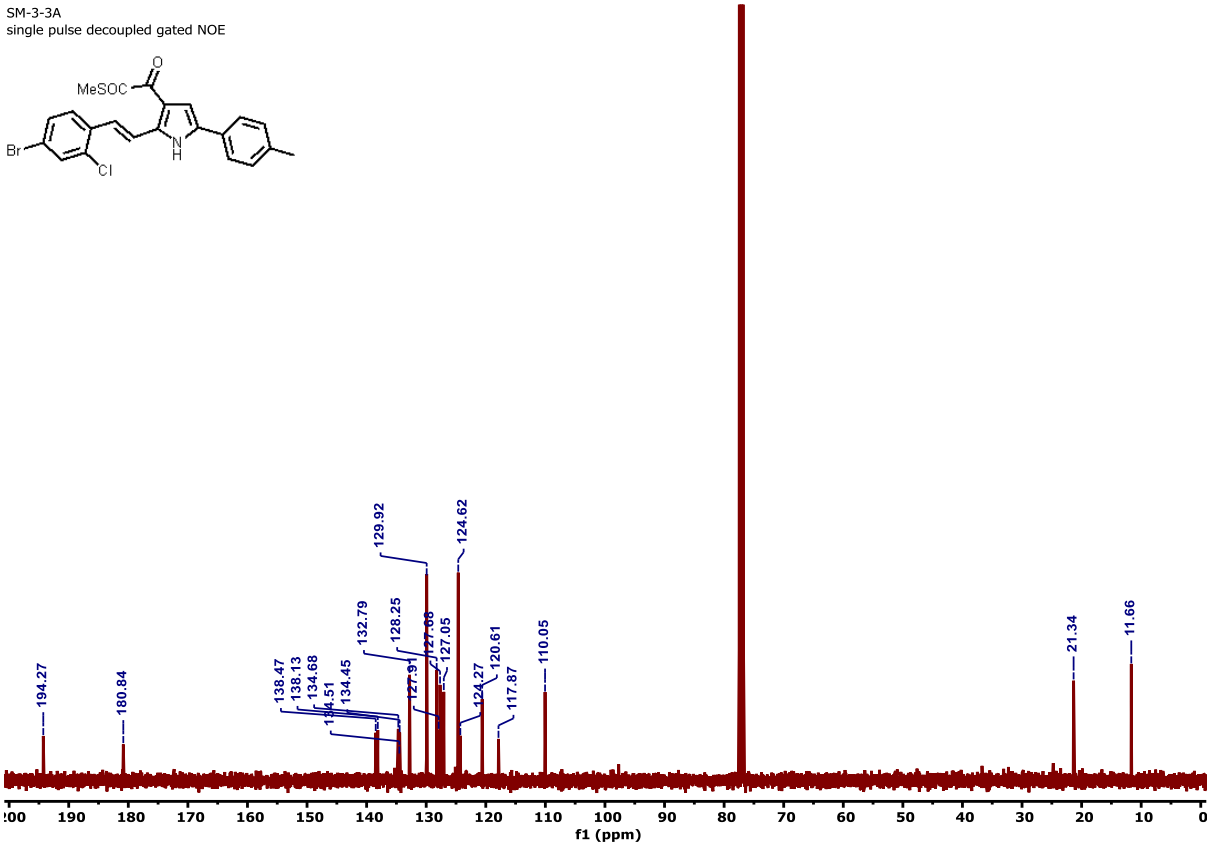
***S*-methyl (*E*)-2-(2-(4-bromo-2-chlorostyryl)-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)-2-oxoethanethioate**



4ae: Prepared according to the general procedure discussed above: reaction time, 28 h; R_f = 0.2; eluent, EtOAc/*n*-hexane (10%); red solid (27.2 mg, 40%); mp 212-215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.15 (s, 1 H), 7.88 (d, *J* = 16.8 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.58 (d, *J* = 2.4 Hz, 1 H), 7.46 (d, 2 H), 7.32 – 7.26 (m, 3 H), 7.24 – 7.21 (m, 2 H), 2.40 (s, 3 H), 2.38 (s, 3 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.3, 180.8, 138.5, 138.1, 134.7, 134.5, 134.5, 132.8, 129.9 (2 CH), 128.2, 127.9, 127.7, 127.0, 124.6 (2 CH), 124.3, 120.6, 117.9, 110.1, 21.3, 11.7 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{22}H_{18}BrClNO_2S$ [*M* + H]$^+$: 473.9930; found: 473.9926.

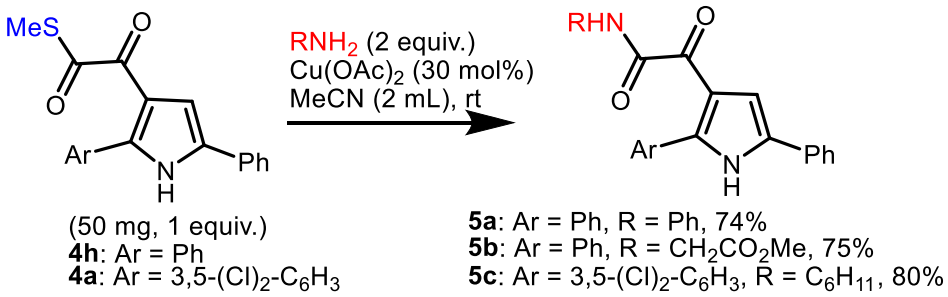
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **4ae**





ESI-57: General procedure for the synthesis of 5a-c[10]

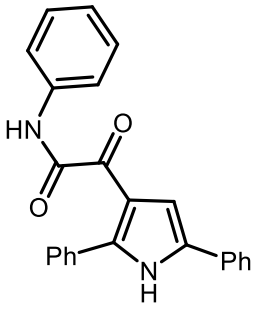
Aniline, glycine methyl ester, or cyclohexyl amine (2 equiv/mmol) was added into a solution of **4h** (50 mg, 0.16 mmol, 1 equiv) or **4a** (50 mg, 0.12 mmol, 1 equiv) in MeCN (2 mL) and 30 mol% of copper acetate [$Cu(OAc)_2$]. The mixture was stirred at room temperature for 8 h. After the reaction (TLC), a saturated ammonium chloride solution was added, and the product was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was passed through a short pad of silica gel column [230– 400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain the desired **5a-c**.



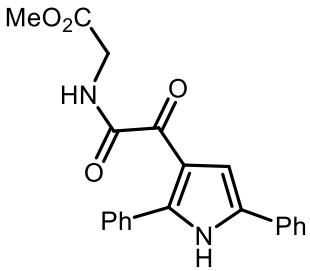
(50 mg, 1 equiv.)
4h: Ar = Ph
4a: Ar = 3,5-$(Cl)_2$-C_6H_3

5a: Ar = Ph, R = Ph, 74%
5b: Ar = Ph, R = CH_2CO_2Me, 75%
5c: Ar = 3,5-$(Cl)_2$-C_6H_3, R = C_6H_{11}, 80%

2-(2,5-Diphenyl-1*H*-pyrrol-3-yl)-2-oxo-*N*-phenylacetamide 5a: Prepared according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (25%); Yellow solid (42 mg, 74%); mp 140–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.10 (s, 1 H), 8.90 (s, 1 H), 7.82 (d, *J* = 2.8 Hz, 1 H), 7.70 – 7.60 (m, 4 H), 7.57 – 7.53 (m, 2 H), 7.49 – 7.34 (m, 7 H), 7 .31 – 7.26 (m, 1 H), 7.20 – 7.11 (m, 1 H).; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$δ = 181.8, 160.3, 142.3, 137.0, 132.6, 131.9, 131.2,129.3, 129.3 (2 CH), 129.2 (2 CH), 129.0 (2 CH), 128.5 (2 CH), 127.5, 125.0, 124.3 (2 CH), 119.8 (2 CH), 117.6, 111.5 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{18}N_2O_2Na$ [*M* + Na]$^+$: 389.1266; found: 389.1260.

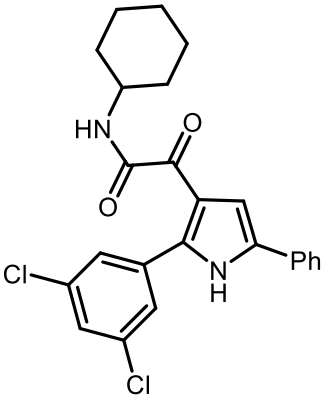


(Methyl (2-(2,5-diphenyl-1*H*-pyrrol-3-yl)-2-oxoacetyl)glycinate 5b: Prepared according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (20%); yellow solid (42.2 mg, 75%); mp 112-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$ δ = 8.93 (s, 1 H), 7.65 (d, *J* = 2.8 Hz, 1 H), 7.65 – 7.56 (m, 3 H), 7.56 – 7.48 (m, 2 H), 7.48 – 7.33 (m, 5H), 7.28 (d, *J* = 7.2 Hz, 1 H), 4.09 (d, *J* = 5.6 Hz, 2 H), 3.76 (s, 3 H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 181.4, 169.6, 163.1, 141.8, 132.5, 131.8, 131.2, 129.2, 129.1 (2 CH), 129.0 (2 CH), 128.5 (2 CH), 127.5,124.3 (2 CH), 117.7, 111.3, 52.6, 41.2 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{21}H_{18}N_2O_4Na$ [*M* + Na]$^+$: 385.1165; found: 385.1164.



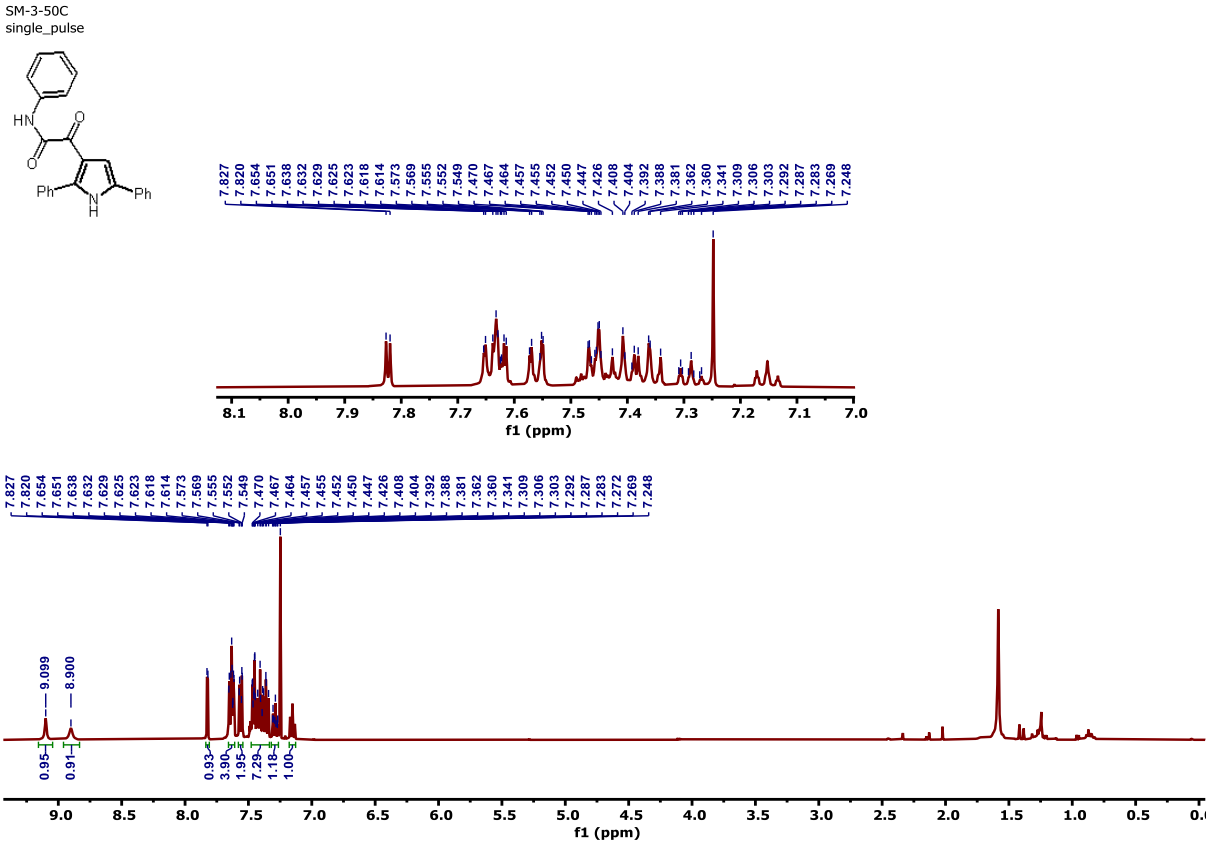
[10] Maity, R.; Ghosh,S.; Das, I. Integrating Regioselective *E*→*Z* Isomerization of Trienones with Cascade Sequences under Photosensitizer-Free Direct Irradiation at 390 nm. *Chem. Eur. J.* 2023, **29**, e202300421.

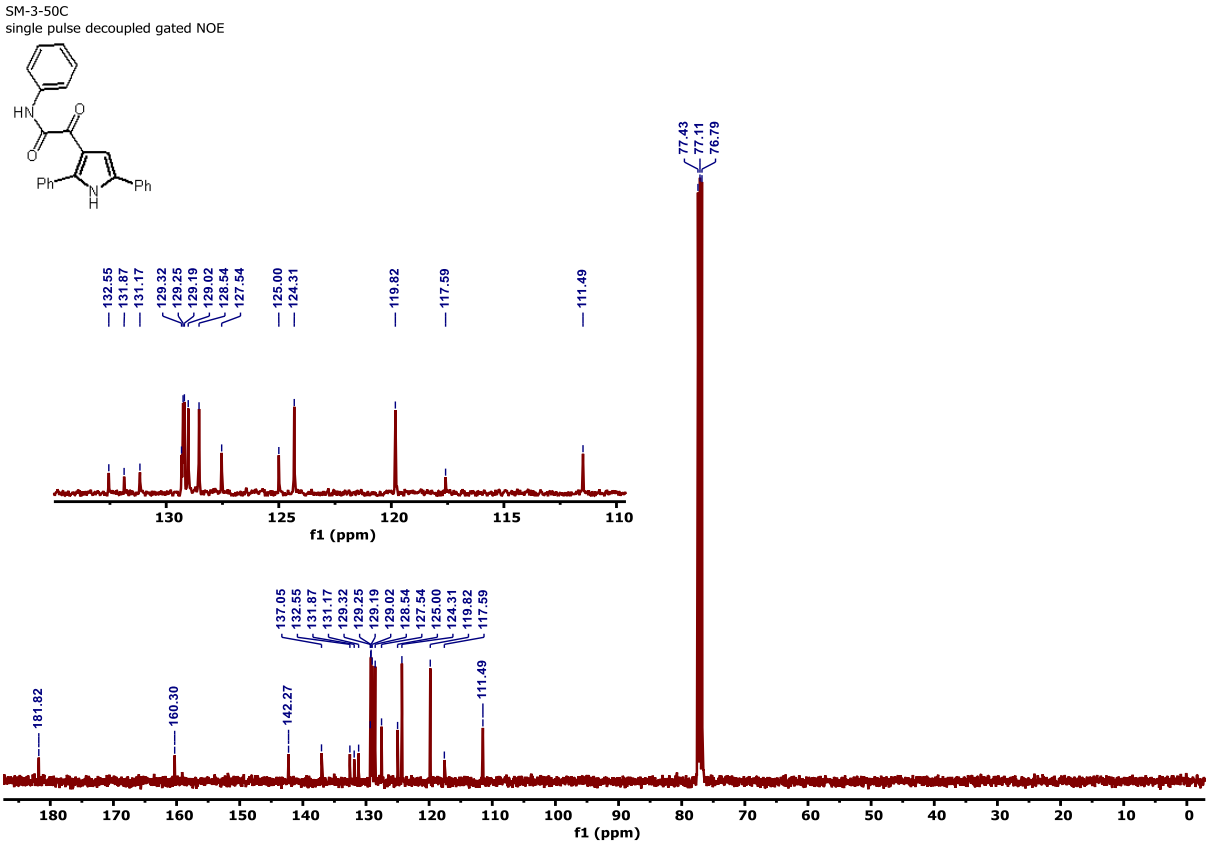
_N_-cyclohexyl-2-(5-(3,5-dichlorophenyl)-2-phenyl-1_H_-pyrrol-3-yl)-2-oxoacetamide; 5c:



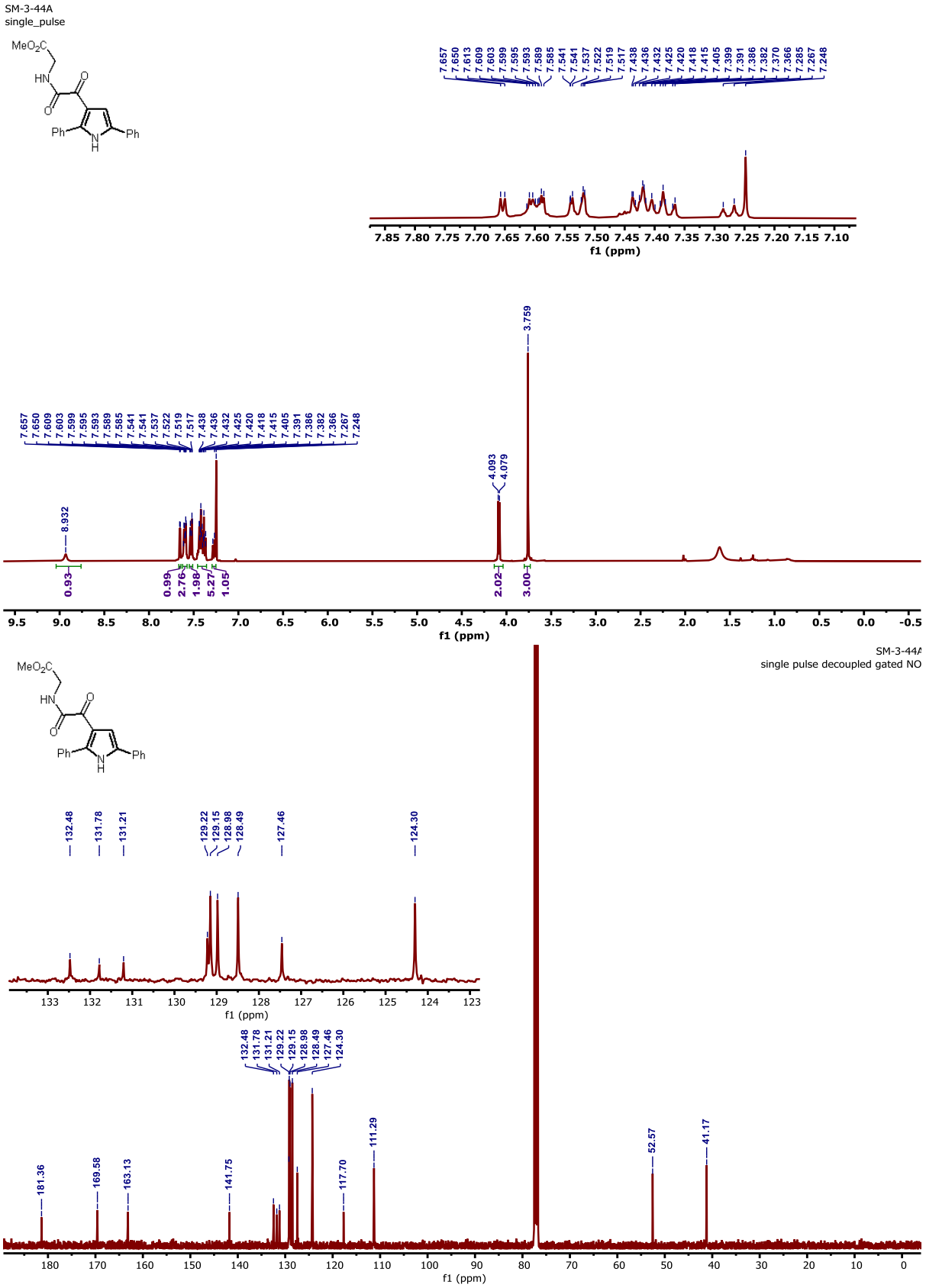
Prepared according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (10 %); Yellow solid (45.1 mg, 80%); mp 215–220 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.21 (s, 1 H), 8.44 (d, *J* = 8.0 Hz, 1 H), 7.75 – 7.72 (m, 2 H), 7.68 (d, *J* = 2..0 Hz, 2 H), 7.62 (t, *J* = 2.0 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.10 (d, *J* = 2.4 Hz, 1 H), 3.54 – 3.47 (m, 1 H), 1.71 – 1.51 (m, 4 H), 1.53 (d, *J* = 12.4 Hz, 1 H), 1.30 – 1.03 (m, 5 H) ppm; ^{13}C{^{1}H} NMR (101 MHz DMSO-d_6): δ = 186.4, 165.2, 136.5, 135.0, 134.0, 133.8 (2 CH), 131.5, 129.4 (2 CH), 128.5 (2 CH), 128.1, 127.7, 125.2 (2 CH), 119.2, 110.7, 48.2, 32.5 (2 CH_2), 25.6, 25.2 (2 CH_2) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{24}H_{23}Cl_2N_2O_2$ $[M + H]^+$: 441.1136; found: 441.1129.

^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **5a**

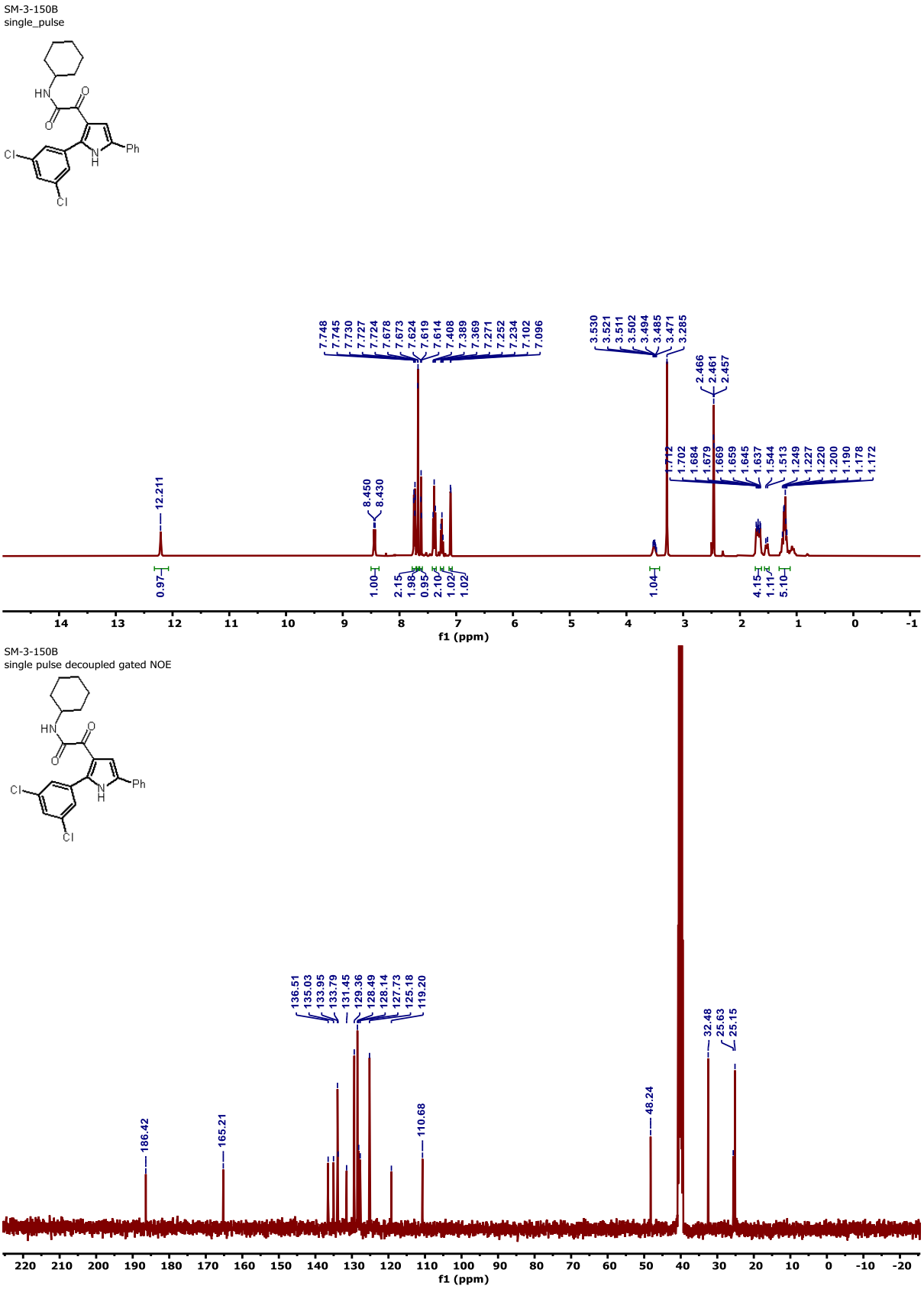




^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **5b**



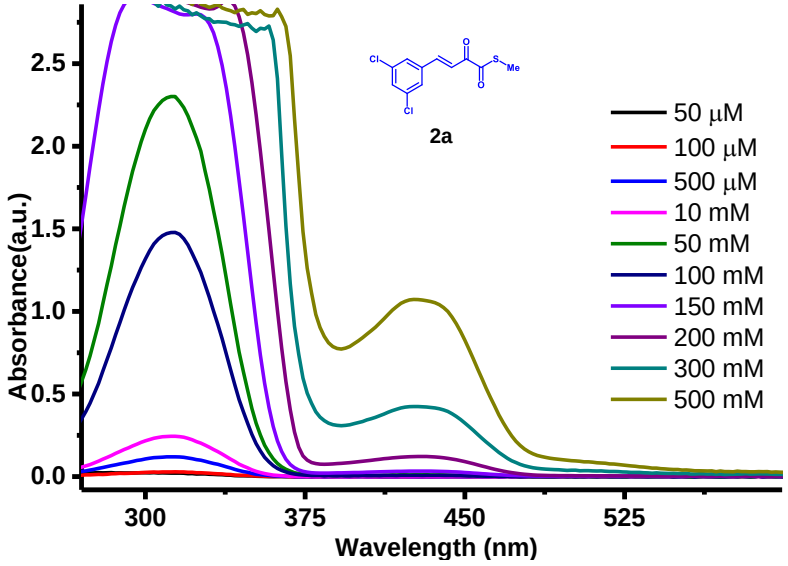
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **5c**

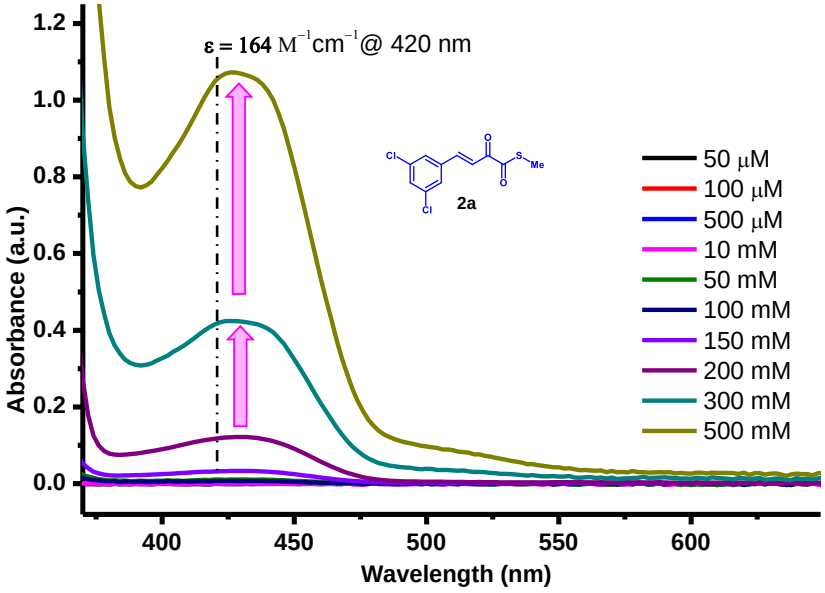


ESI-58: Mechanistic Studies:

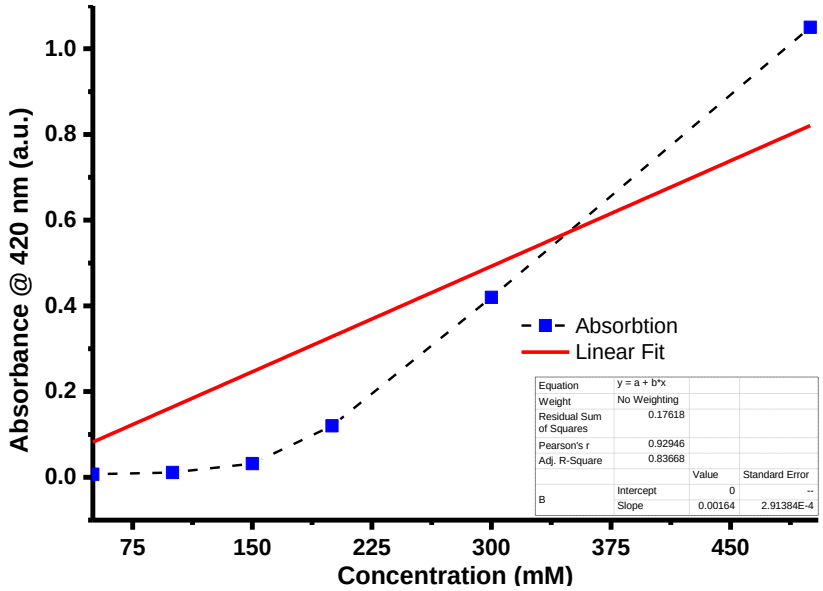
ESI-58-01: UV-vis Spectrum:

1. UV-vis absorption data for compound **2a** is reported for 10 different concentrations of acetonitrile solvent. Interestingly, it can be observed from the spectrum that increasing the concentration leads to an elongation of the absorption tail towards 550 nm.



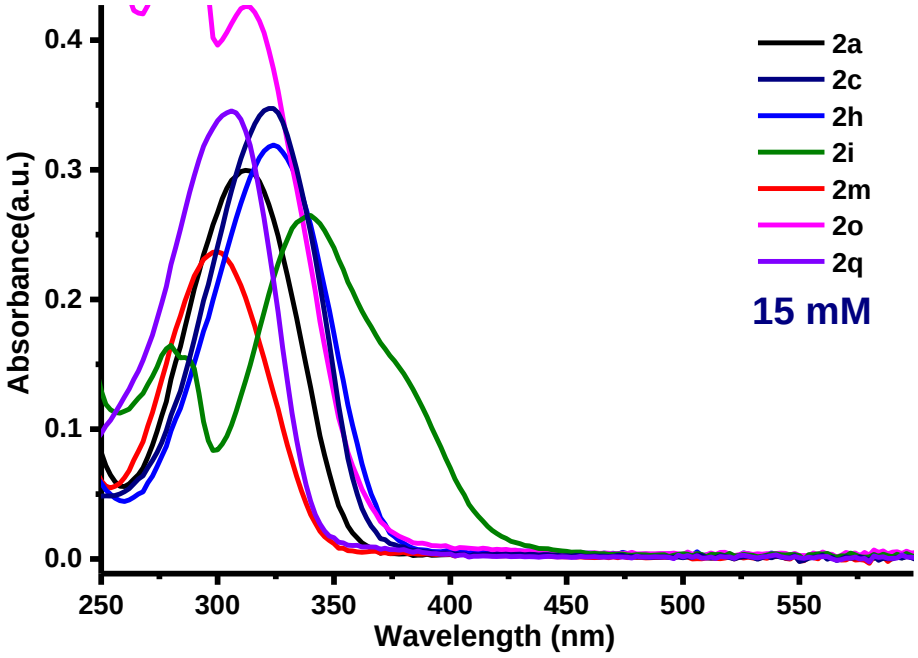


Entry	Concentration (mM)	Absorption
1	50	0.007
2	100	0.011
3	150	0.032
4	200	0.12
5	300	0.42
6	500	1.05



Molar Absorptivity (ε) at 420 nm = 164 $M^{-1}cm^{-1}$

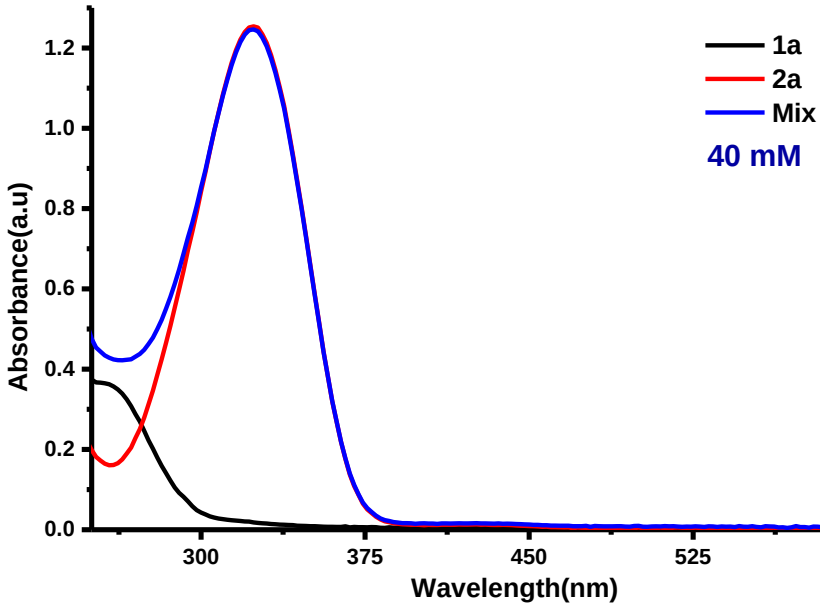
2. UV-vis absorption data for compounds **2a**, **2c**, **2h**, **2i**, **2m**, **2o**, and **2q** in acetonitrile solvent at 15 mM concentration are reported.



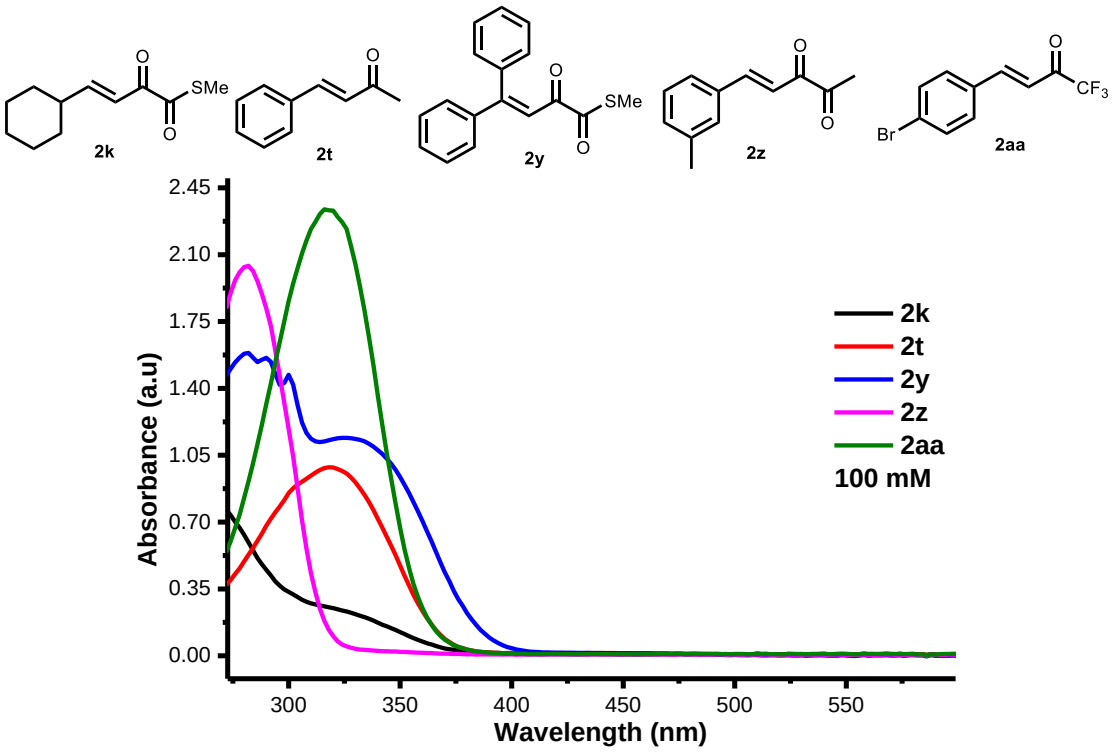
3. UV-vis absorption data for compounds olefin **2a**, vinyl azide **1a**, and their mixture in acetonitrile solvent at 40 mM concentration are reported.

Entry	Compound	λ_{max} (nm)
1	**2a**	318
2	**1a**	254
3	**1a**+**2a**	318

The **absence** of a new peak in the absorption spectra of the mixture **2a** + **1a** provides conclusive evidence that the formation of any donor-acceptor complex can be ruled out.[11]



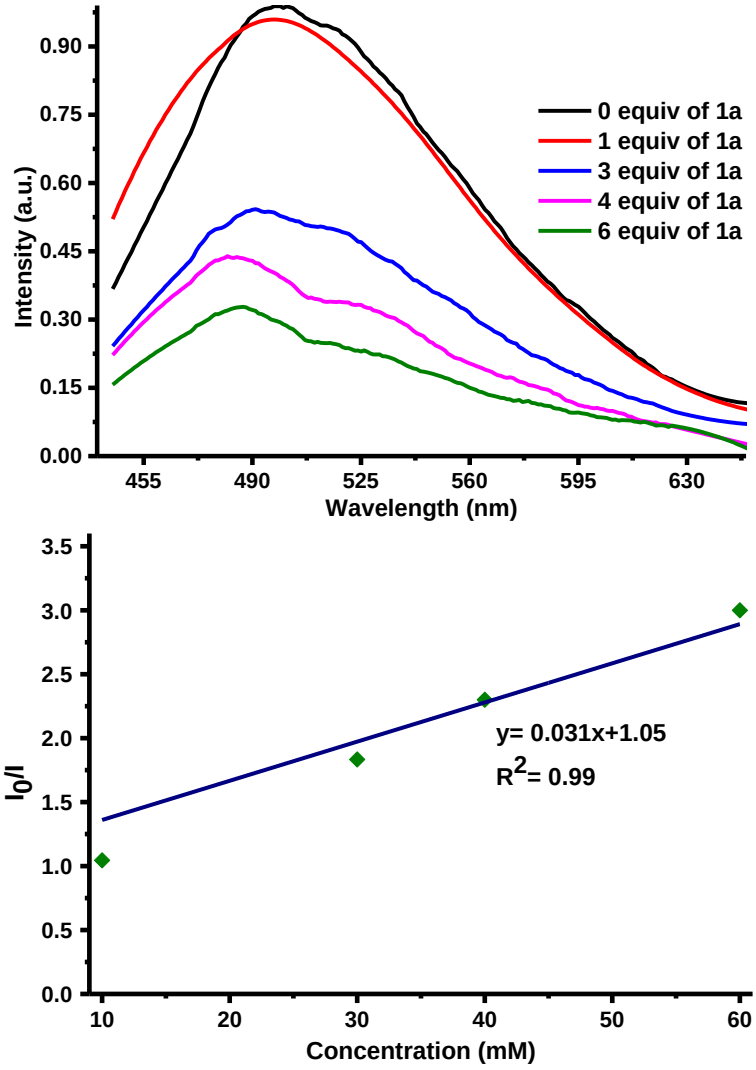
4. UV-vis absorption spectra for olefins **2k, 2t, 2y, 2z,** and **2aa** in MeCN solvent at 100 mM concentration are reported. None of them absorbed in the visible region or their tail show any such absorption, except **2y**. So, olefins **2k, 2t, 2z,** and **2aa** did not undergo photocycloaddition. Although **2y** absorbs in the visible region, but it did not undergo photocycloaddition due to the steric hindrance from the phenyl rings.



[11] Rai, P.; Maji, K.; Jana, S. K.; Maji, B. Intermolecular dearomative [4 + 2] cycloaddition of naphthalenes via visible-light energy-transfer-catalysis. *Chem. Sci.* **2022**, *13*, 12503– 12510.

ESI-58-02: Fluorescence quenching experiments[12]

An experiment on fluorescence quenching was conducted using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer, with an excitation wavelength of 425 nm and an emission wavelength of 500 nm. The experiment was performed in a solution of 10 mM of thioester **2a**. The maximum emission of vinyl azide **1a** (10 mM in CH_3CN) was observed at 500 nm. Upon the gradual addition of **1a** (1.0-6.0 equiv.), the fluorescence intensity gradually decreased, as demonstrated in the data below.



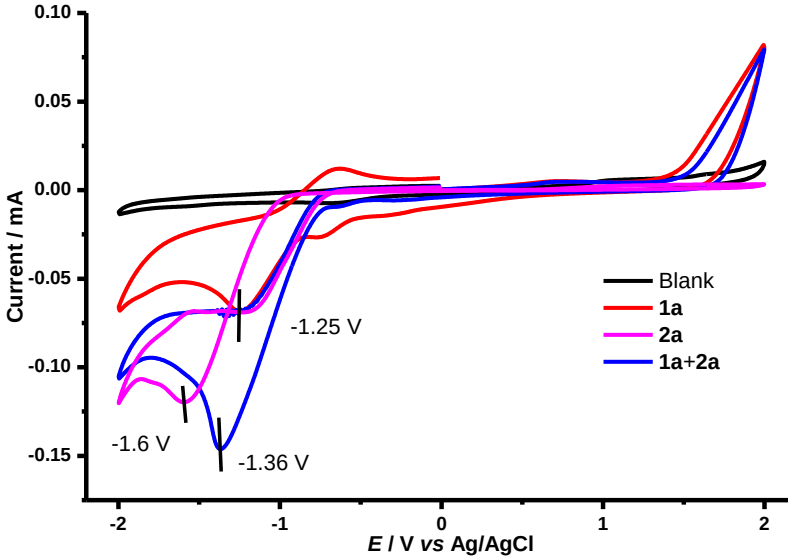
ESI-58-03: Cyclic Voltammetry Analysis:

All cyclic voltammetry studies were measured using the Admiral Squidstat Solo instrument at room temperature in acetonitrile solvent (5.0 mL). Before collecting CV data, the solution was degassed with argon gas. $^{n}Bu_4NPF_6$ (0.1 M) was used as the supporting electrolyte, and a glassy carbon electrode was used as the working electrode while the counter electrode

[12] Li, L.; Li, J.-Z.; Sun, Y.-B.; Luo, C.-M.; Qiu, H.; Tang, K.; Liu, H.; Wei, W.-T. Visible-Light-Catalyzed Tandem Radical Addition/ 1,5-Hydrogen Atom Transfer/Cyclization of 2-Alkynylarylethers with Sulfonyl Chlorides. *Org. Lett.* **2022**, *24*, 4704-4709.

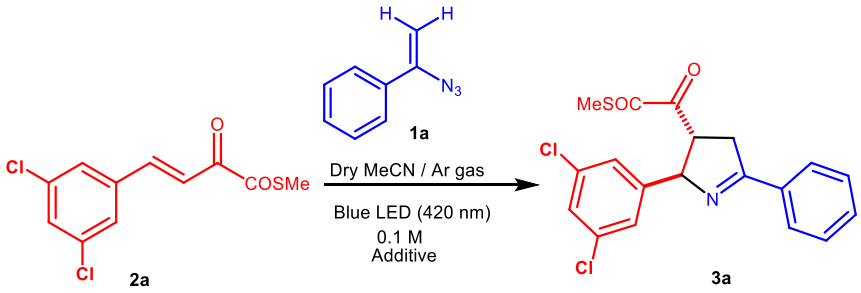
was a platinum plate. The reference was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution. The scan rate was 100 mV/s ranging from -2.0 V to +2.0 V.

Discussion: The CV of thioester **2a** (0.01 M) showed a reduction potential -1.6 V (vs Ag/AgCl) and Vinyl azide **1a** reduction potential -1.25 V (vs Ag/AgCl). So, in this reaction vinyl azide **1a** preferentially undergo reduction to form diradical to initiate the reaction. During the CV, the overall reduction potential of mixture value changes -1.36 V (vs. Ag/AgCl), so there might be some interaction between **2a** and **1a**.



5.0 mL of CH_3CN solvent: (i) containing 0.1 M of $^nBu_4NPF_6$ (**black line**); (ii) containing 0.1 M of $^nBu_4NPF_6$ with 0.01 M of **1a** (**red line**); (iii) containing 0.1 M of $^nBu_4NPF_6$ with 0.01 M of **2a** (**pink line**); (iv) containing 0.1 M of $^nBu_4NPF_6$ with 0.01 M of **1a** and 0.01 M of **2a** (**blue line**).

ESI-58-04: Effects of triplet and singlet quenchers on the reaction efficiency:



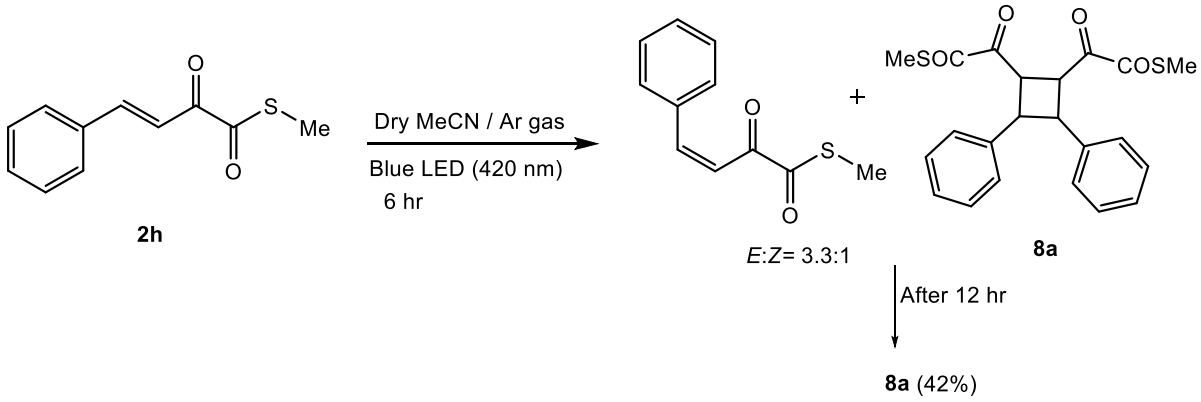
Additive	Reaction time (h)	Yield (%)
none	12	94
O_2 atmosphere	12	38
1,3-cyclohexadiene (1 equiv.)	12	47
Azulene (1 equiv.)	15	33

To understand whether a singlet or triplet diradical involved in the reaction, we performed control experiments in the presence of singlet and triplet quenchers. The reaction efficiency and product yield were significantly affected when **2a (0.1 mmol)** and **1a** (0.12 mmol) were exposed to irradiation in the presence of 0.1 M acetonitrile solvent medium either in an

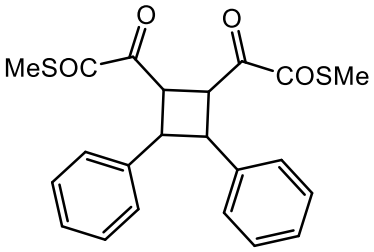
oxygen atmosphere, or using 1,3-cycloheaxadiene (1 equiv) as a triplet quencher. The expected product **3a** was obtained in very less yeild, with 38 % and 47% yields, respectively. While the addition of azulene (1 equiv), a singlet and triplet quencher, had a detrimental effect on the yield (33%) with an increased reaction time (15 h). With these observations, we proposed that the reaction might proceed through a triplet state mechanism[13].

ESI-58-05: Analytical and spectral data of **8a**

To verify that compound **2** forms its triplet excited state, we studied the potential *E*-*Z* isomerization of the olefin, since triplet intermediates are known to be capable of *trans-cis* isomerization[14]. When we exposed olefin **2h** (50 mg, 0.24 mmol), dissolved into acetonitrile (2 mL, 0.12 M), to 420 nm irradiation for 6 hr at room temperature, the *Z*-**2h** isomer was produced (*E*/*Z* ratio = 3.3:1) along with the very less [2+2] cycloaddition product, and after completion of the reaction(TLC), the [2+2] cycloaddition product **8a** can be isolated with 42% yield by purifying through column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane].



***S*,*S*'-dimethyl 2,2'-(3,4-diphenylcyclobutane-1,2-diyl)bis(2-oxoethanethioate) 8a:** Prepared

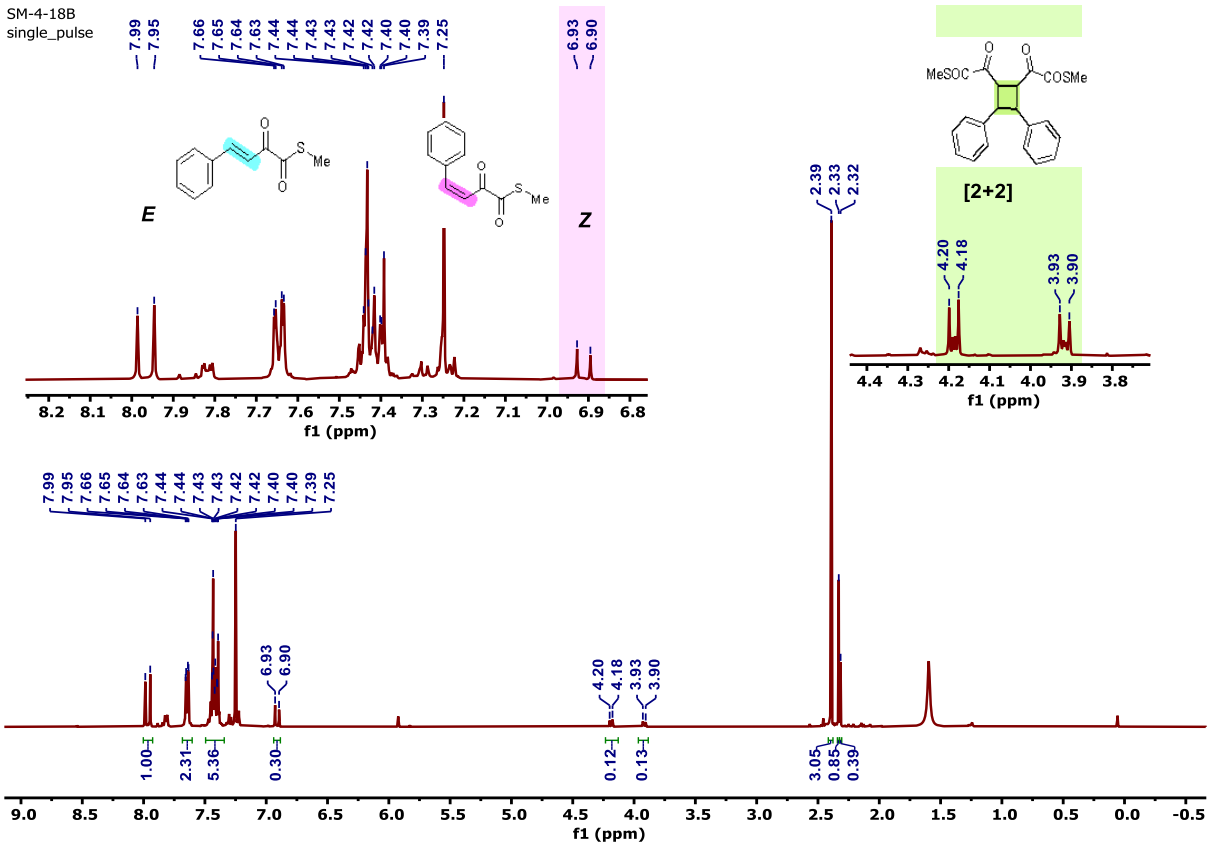


according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Light yellow liquid (21 mg, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.26 (m, 4 H), 7.26 (d, *J* = 1.3 Hz, 3 H), 7.24 (d, *J* = 1.6 Hz, 3 H), 4.23 – 4.15 (m, 2 H), 3.97 – 3.87 (m, 2 H), 2.32 (s, 6 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 192.4 (2 CO), 191.35 (2 CO), 140.3 (2 CH), 128.8 (4 CH), 127.5 (2 CH), 127.0 (4 CH), 46.6 (2 CH), 45.7 (2 CH), 11.4 (2 CH) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{22}H_{20}O_4S_2Na$ [*M* + Na]$^+$: 435.0701; found: 435.0693.

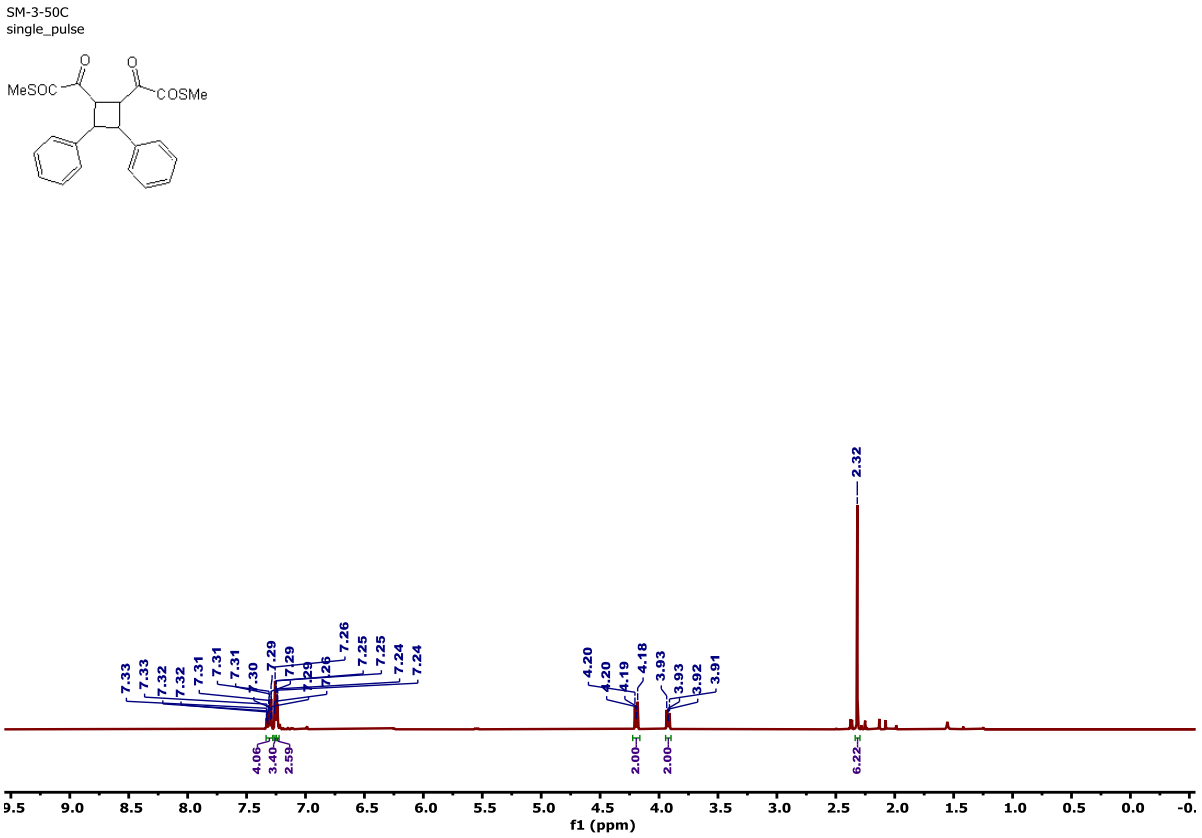
[13] Le, T. M. T.; Brégent,T.; Jubault,P.; Poisson, T. Photocatalytic *E* → *Z Contra*-Thermodynamic Isomerization of Vinyl Silanes with Lewis Base**.** *Chem.Eur. J.* **2022**, *28*, e202201514.

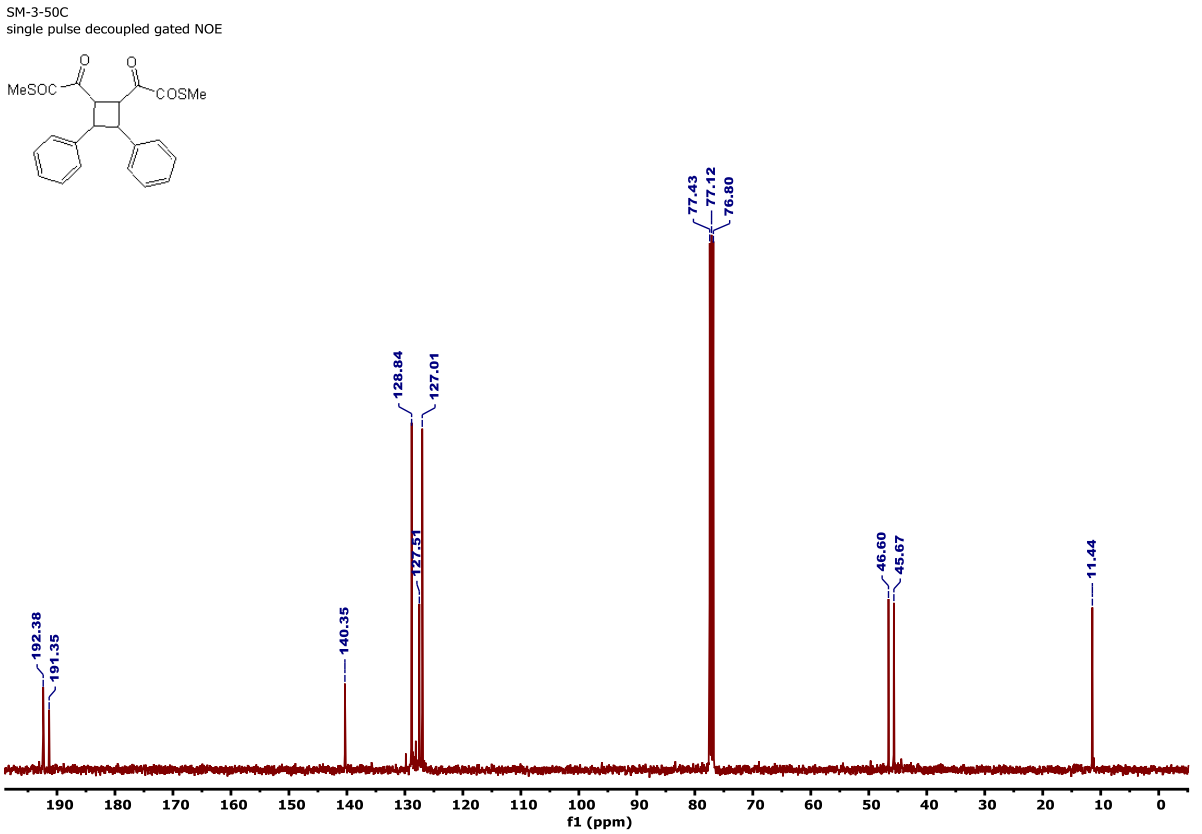
[14] Wang, J. S.; Wu, K.; Yin, C. Z.; Li, K.; Huang, Y. H.; Ruan, J.; Feng, X. M.; Hu, P.; Su, C. Y. Cage-confined photocatalysis for wide-scope unusually selective 2 + 2 cycloaddition through visible-light triplet sensitization. *Nat. Commun.* **2020**, *11*, 4675.

^{1}H (400 MHz, $CDCl_3$) spectra of crude reaction after 6 hr.



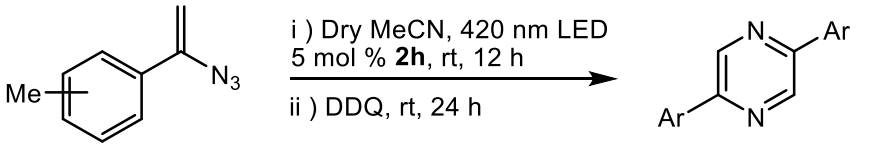
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **8a**





ESI-58-06: Analytical and spectral data of **6a** and **6b**:

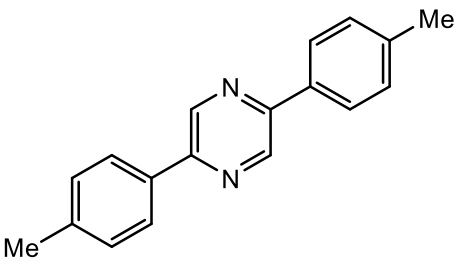
Under an argon atmosphere, vinyl azide **1** (50 mg) was dissolved into acetonitrile (2 mL, 0.16 M) and 5 mol % of our alkene compound **2a** was added to it. It was then irradiated with a 420 nm LED at room temperature (25–30 °C) for 12 hr. After the completion reaction (TLC), we immediately added DDQ (1.2 equiv) and stirred for another 24 hours. After the completion (TLC), the crude residue was purified by silica gel column chromatography [230–400 mesh; eluent: ethyl acetate/*n*-hexane] to obtain **6a** and **6b**. [15]



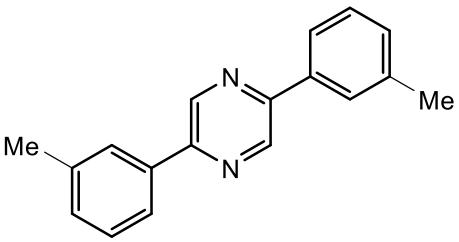
1b (4-Me)
or **1c** (3-Me)

6a: Ar = 4-Me-C_6H_4
6b: Ar = 3-Me-C_6H_4

2,5-di-*p*-tolylpyrazine 6a: Prepared according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); yellow solid (15 mg, 36%); mp 178–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (s, 2 H), 7.96 (d, J = 8.2 Hz, 4 H), 7.33 (d, J = 8.0 Hz, 4 H), 2.44 (s, 6 H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.4 (2 CH), 141.0 (2 CH), 139.9 (2 CH), 133.6 (2 CH), 129.8 (4 CH), 126.6 (4 CH), 21.39 (2 CH_3) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{18}H_{17}N_2$ [M + H]$^+$: 261.1392; found: 261.1384.



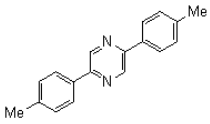
2,5-di-*m*-tolylpyrazine 6b: Prepared according to the general procedure discussed above: R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); yellow solid (6 mg, 20%); mp 50-56 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.08 (s, 2H), 7.91 (s, 2 H), 7.86 (d, J = 7.8 Hz, 2 H), 7.44 (t, J = 7.2 Hz, 2 H), 7.32 (d, J = 7.8 Hz, 2 H), 2.49 (s, 6 H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 150.3 (2 CH), 140.8 (2 CH), 138.4 (2 CH), 135.8 (2 CH), 130.1 (2 CH), 128.5 (2 CH), 127.0 (2 CH), 123.4 (2 CH), 21.1 (2 CH_3) ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{18}H_{17}N_2$ [M + H]$^+$: 261.1392; found: 261.1384.

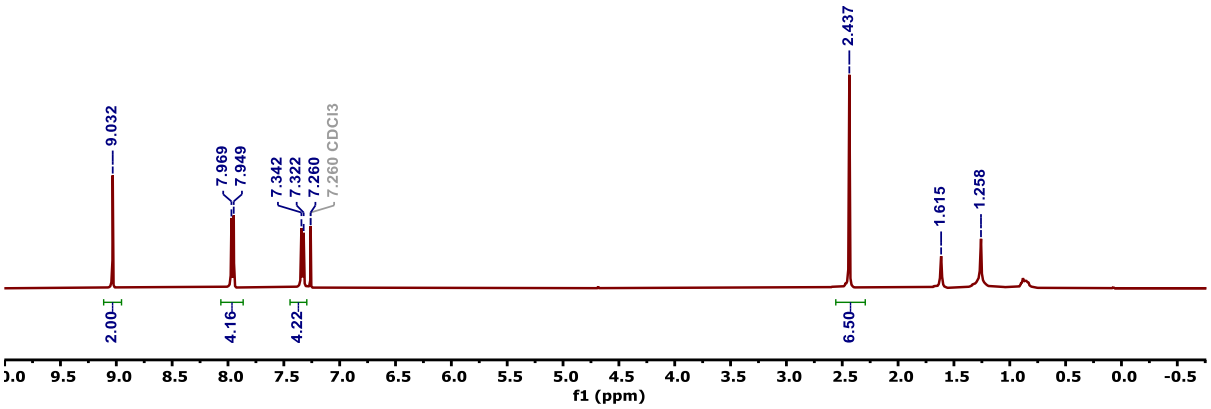


[15] Chen, Z.; Ye, D.; Xu, G.; Ye, M.; Liu, L. Highly efficient synthesis of 2,5-disubstituted pyrazines from (*Z*)-β-haloenol acetates. *Org. Biomol. Chem*. **2013**, *11*, 6699–6702.

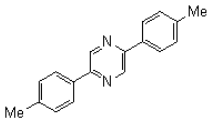
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **6a**

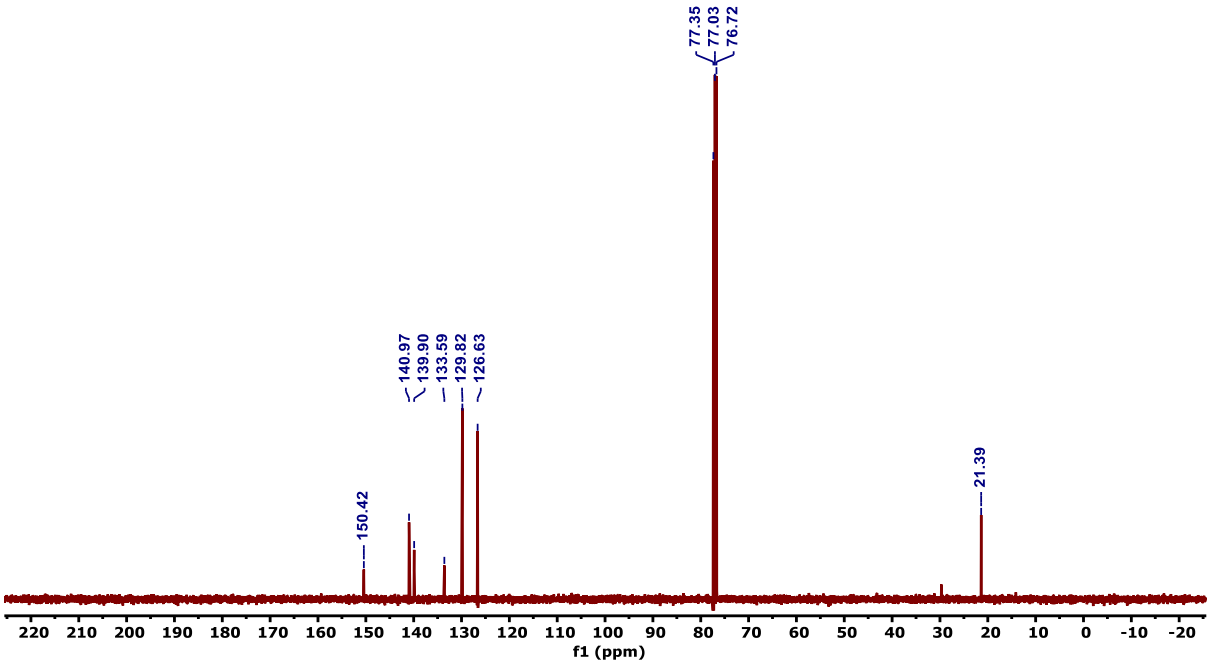
SM-3-148B
single_pulse



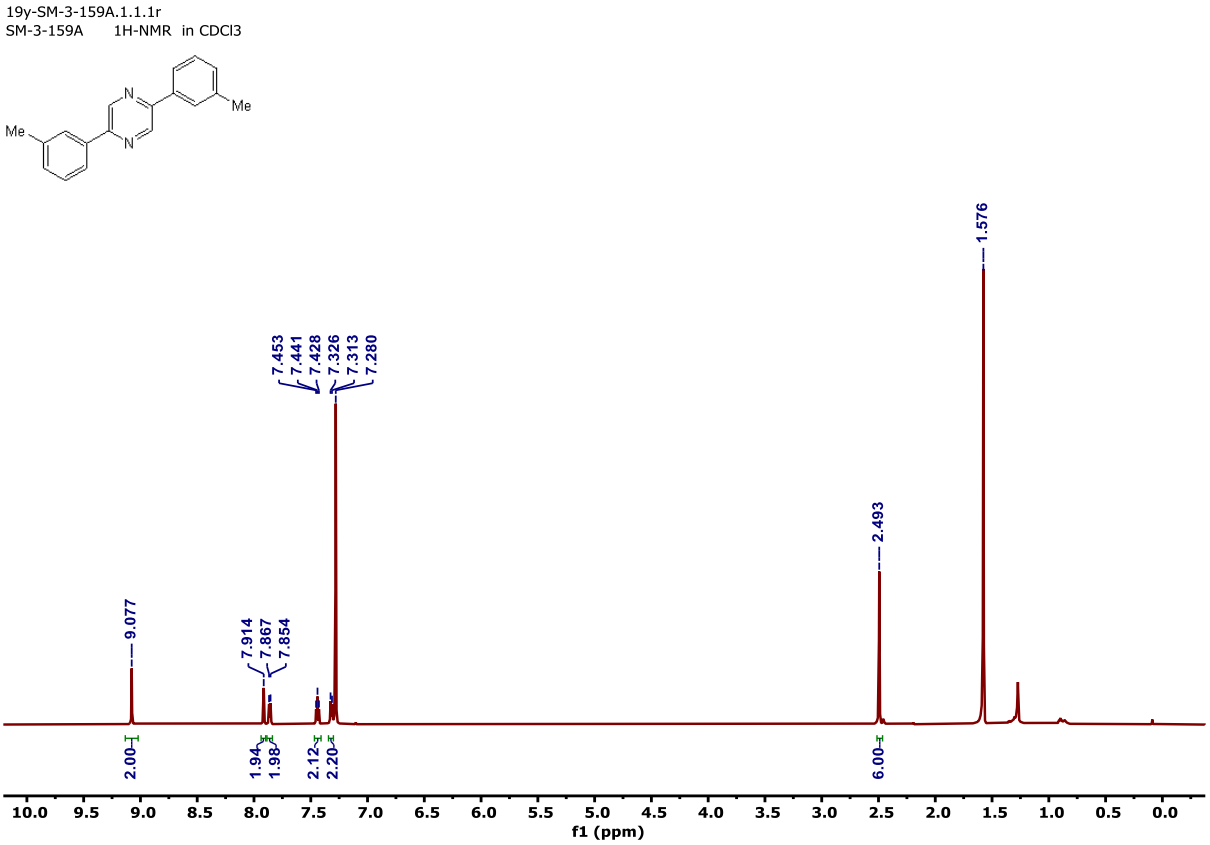


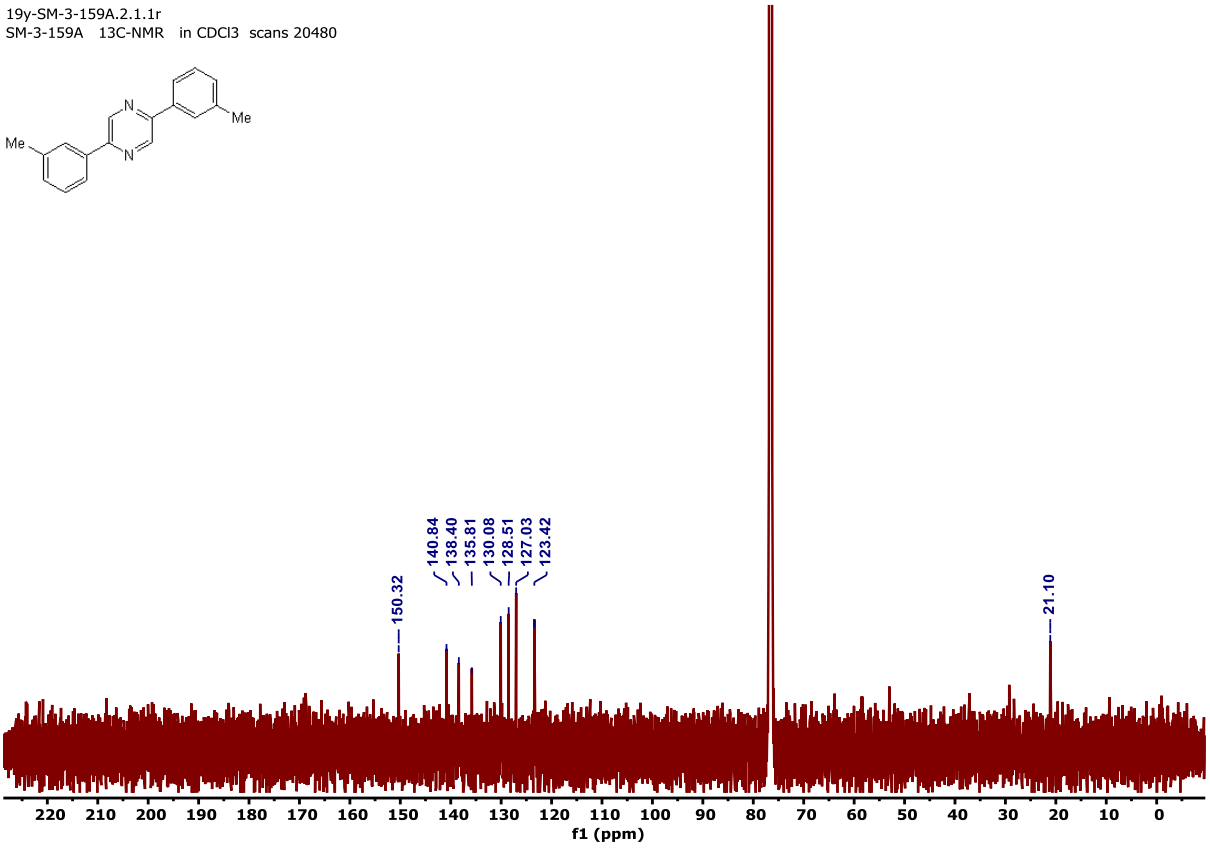
SM-3-148B
single pulse decoupled gated NOE



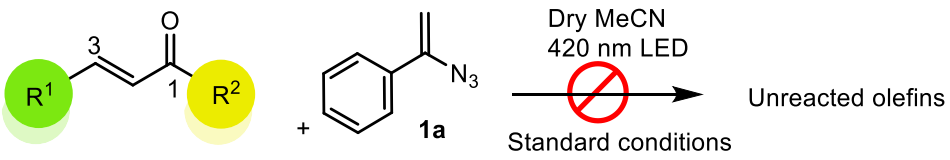


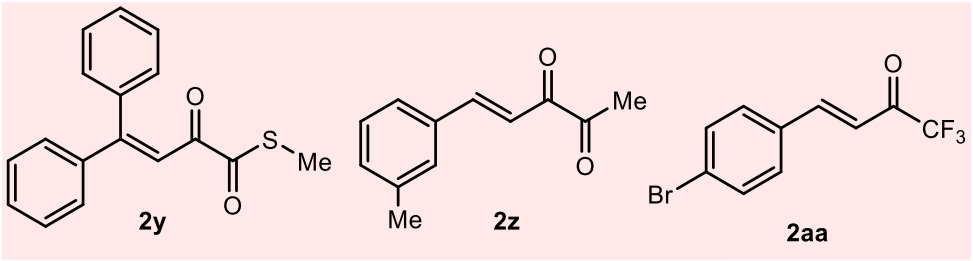
^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **6b**



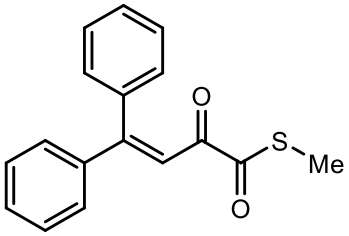


ESI-58-07: Analytical and spectral data of **2y**, **2z**, and **2aa:**

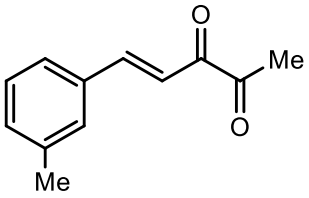




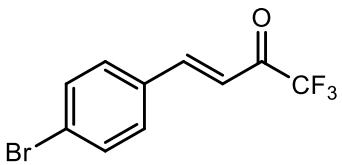
***S*-methyl 2-oxo-4,4-diphenylbut-3-enethioate 2y[4]:** R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Yellow Liquid (17 mg, 27%); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.50 – 7.35 (m, 8 H), 7.32 (s, 1 H), 7.27 – 7.21 (m, 1 H), 2.30 (s, 3 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 193.9, 182.8, 162.8, 140.7, 138.4, 130.8, 129.6 (2 CH), 129.2 (3 CH), 128.6 (2 CH), 128.3 (2 CH), 116.2, 11.6 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{17}H_{14}O_2SNa$ $[M + Na]^+$: 305.0612; found: 305.0611.



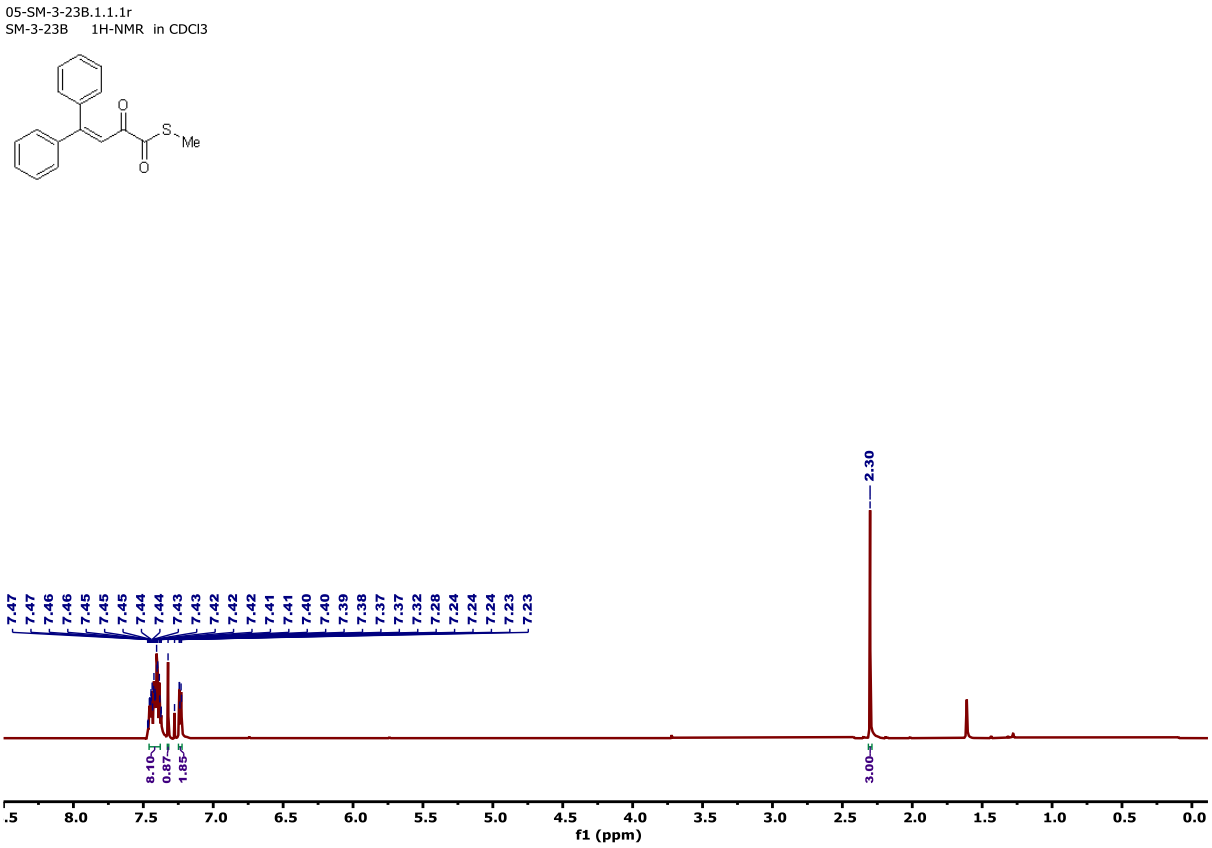
(*E*)-5-(*m*-tolyl)pent-4-ene-2,3-dione 2z: Prepared according to the literature[8], R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Yellow Liquid (17 mg, 27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 16.4 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.20 (m, 1H), 2.44 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.10, 186.92, 148.12, 138.86, 134.46, 132.40, 129.59, 129.02, 126.39, 117.82, 24.49, 21.36 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{13}N_2O_2$ $[M + H]^+$: 189.0916; found: 189.0915.

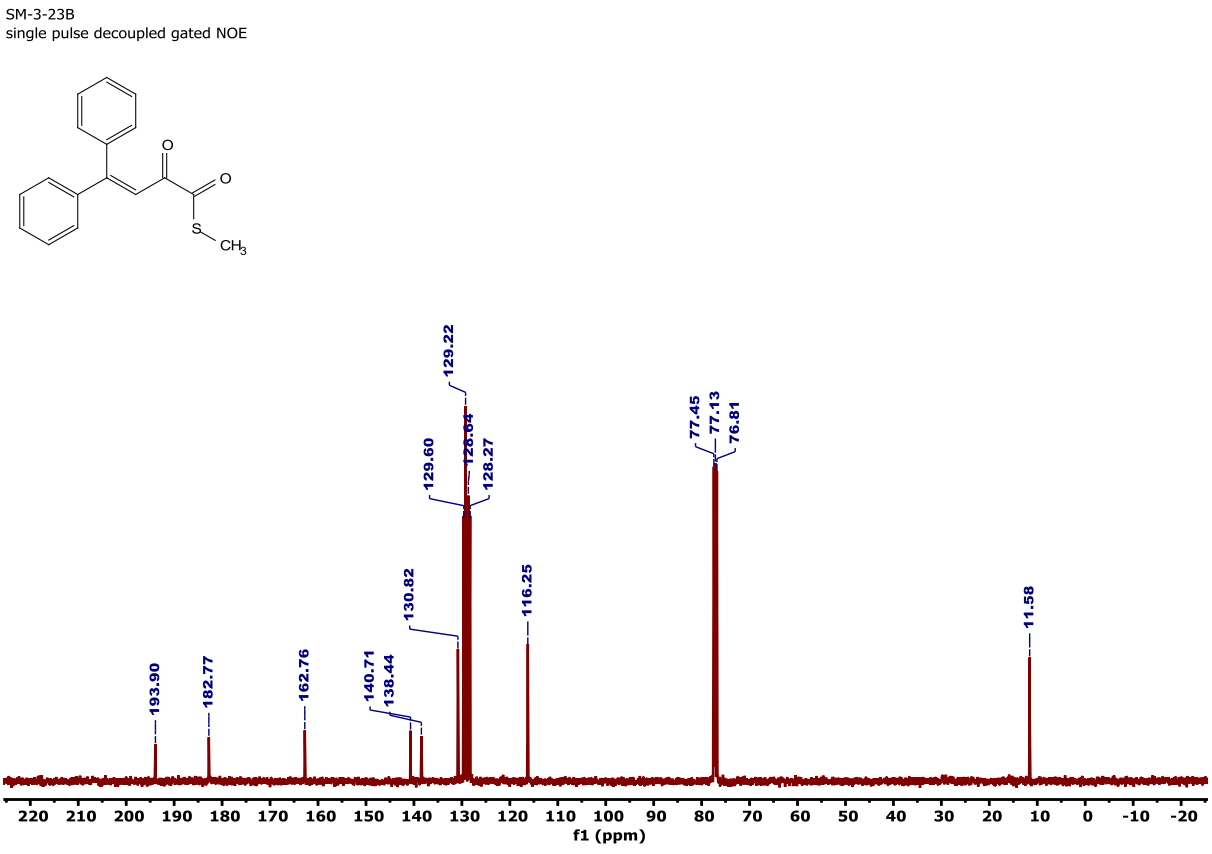


(*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-one 2aa: Prepared according to the literature procedure[9]: R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); Yellow solid (0.15 mg, 54%); mp 57–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.53 – 7.44 (m, 2H), 6.99 (dd, *J* = 16.0, 1.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 180.0 (q, $J_{C\text{-}F}$ = 35.6 Hz), 148.7, 132.7, 132.3, 130.6, 127.1, 116.1 (q, $J_{C\text{-}F}$ = 290.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -77.6 ppm. HRMS (EI): *m/z* calcd for $C_{10}H_6BrF_3O$ $[M]^+$: 277.9554; found: 277.9559.



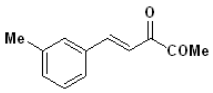
^{1}H (600 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$) NMR spectra of **2y:**

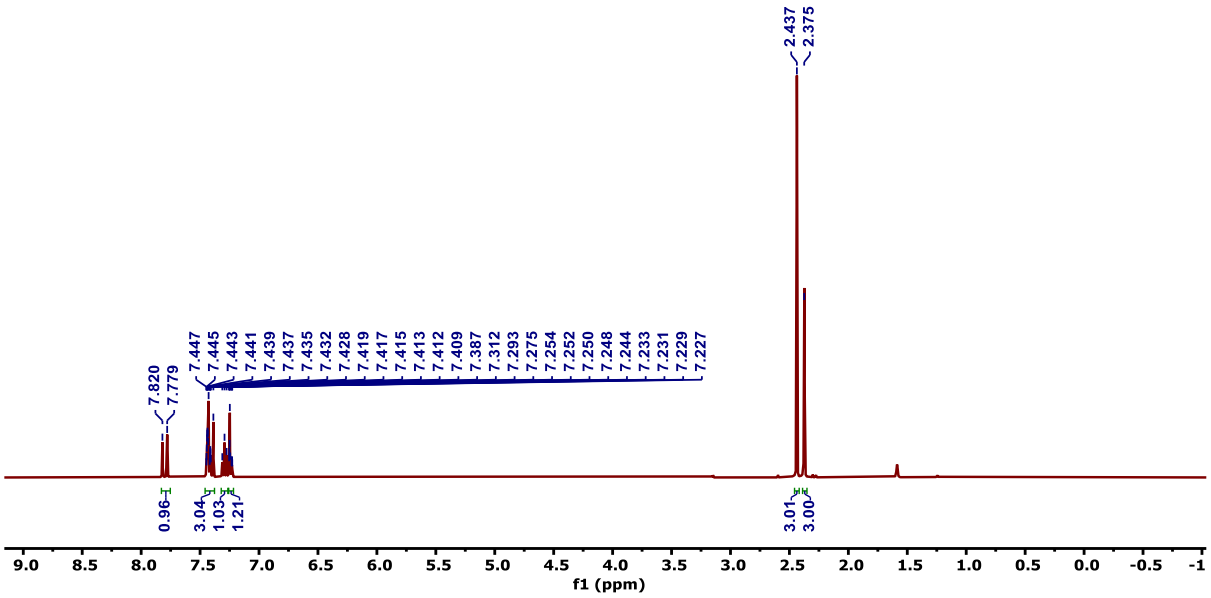




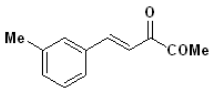
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **2z:**

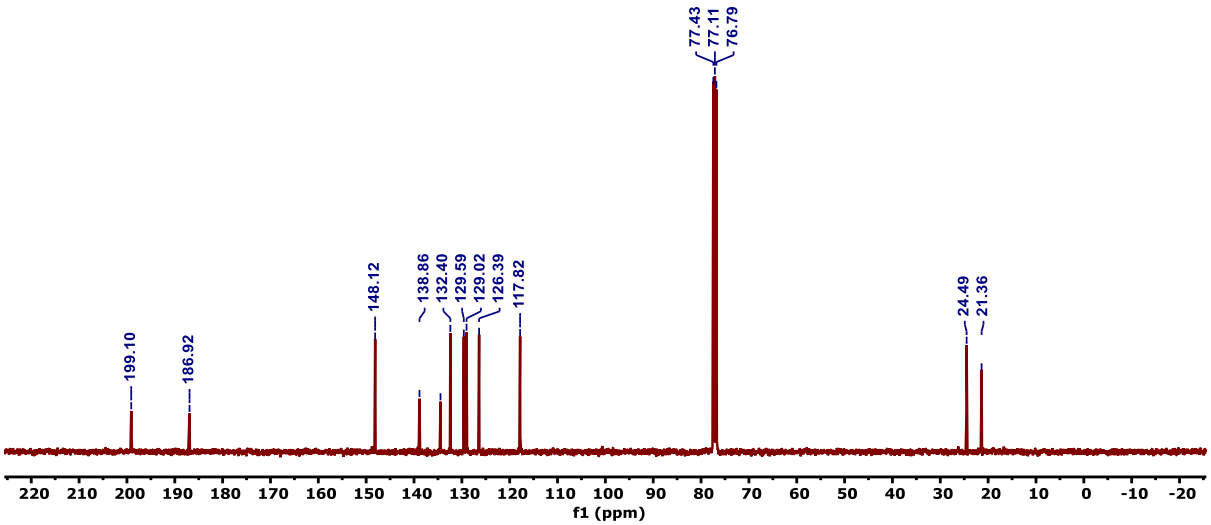
SM-03-138C
single_pulse





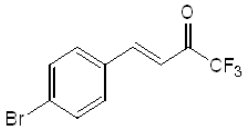
SM-03-138C
single pulse decoupled gated NOE

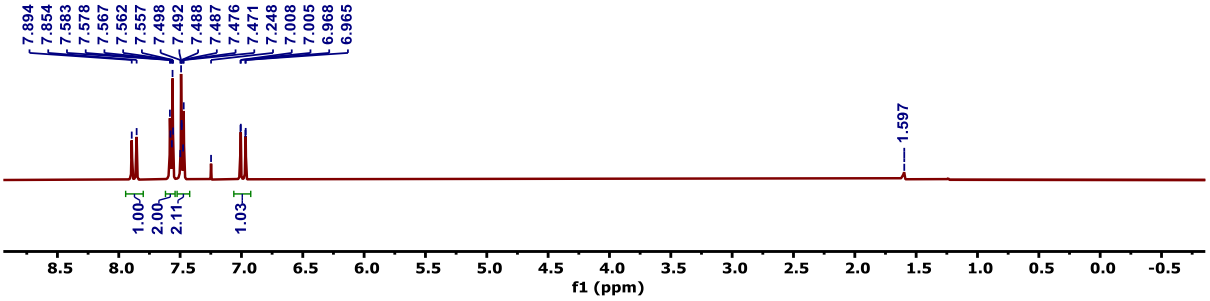




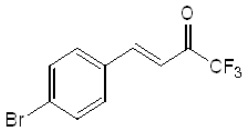
^{1}H (400 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$), and ^{19}F (376 MHz, $CDCl_3$) NMR spectra of **2aa:**

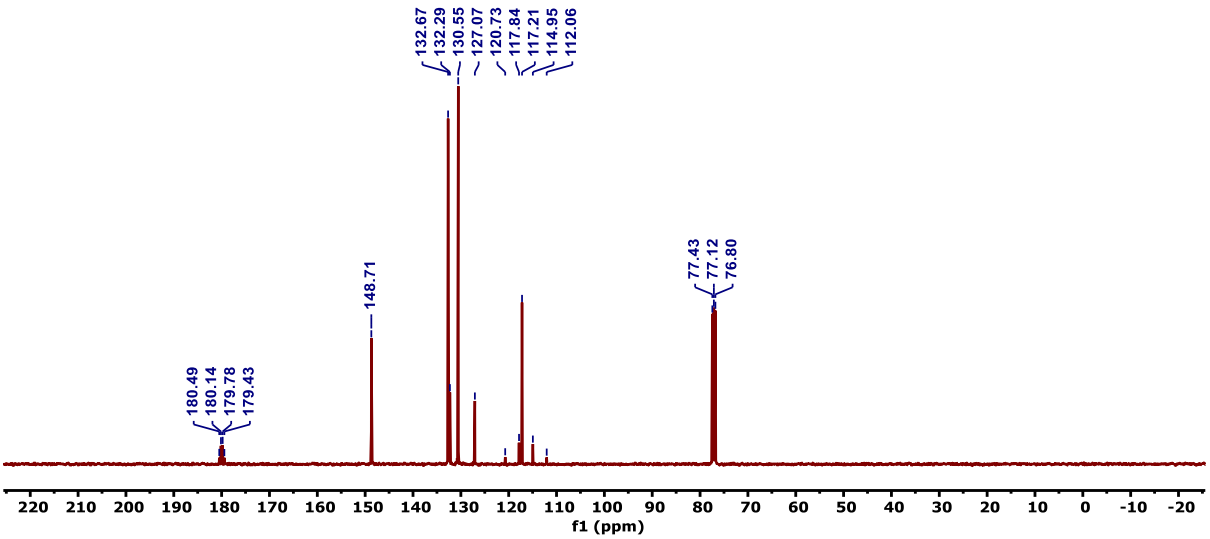
SM-3-149B
single_pulse



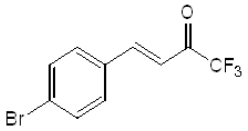


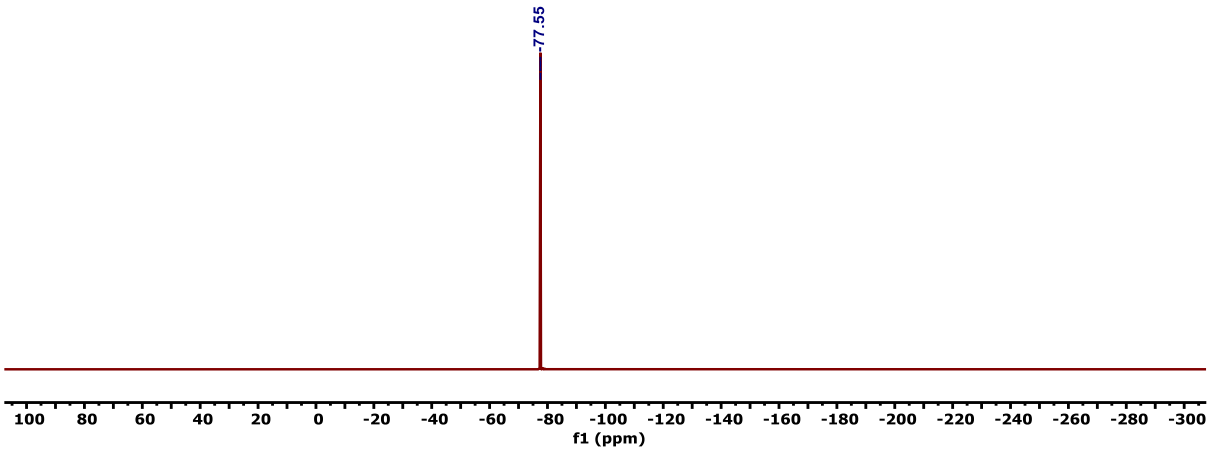
SM-3-149B
single pulse decoupled gated NOE



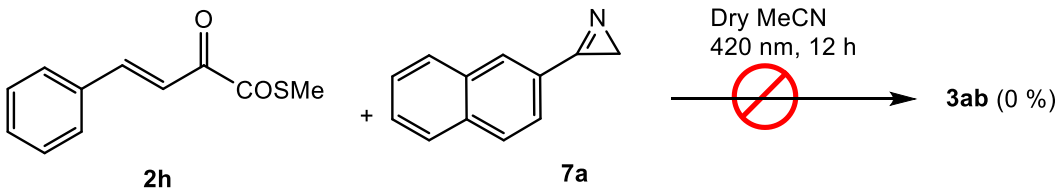


SM-3-149B
single pulse decoupled gated NOE

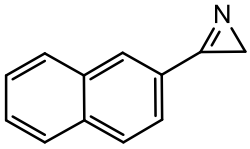




ESI-58-08: Analytical and spectral data of **7a**:

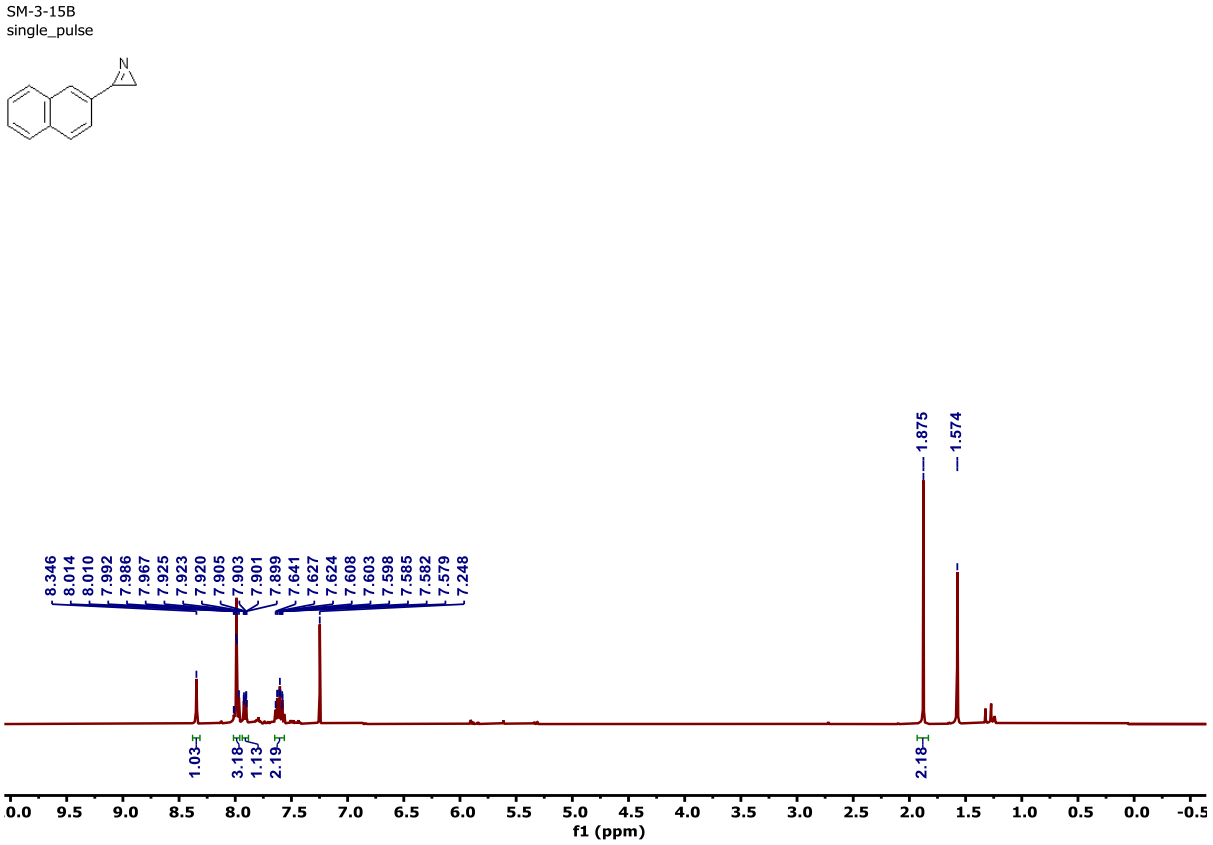


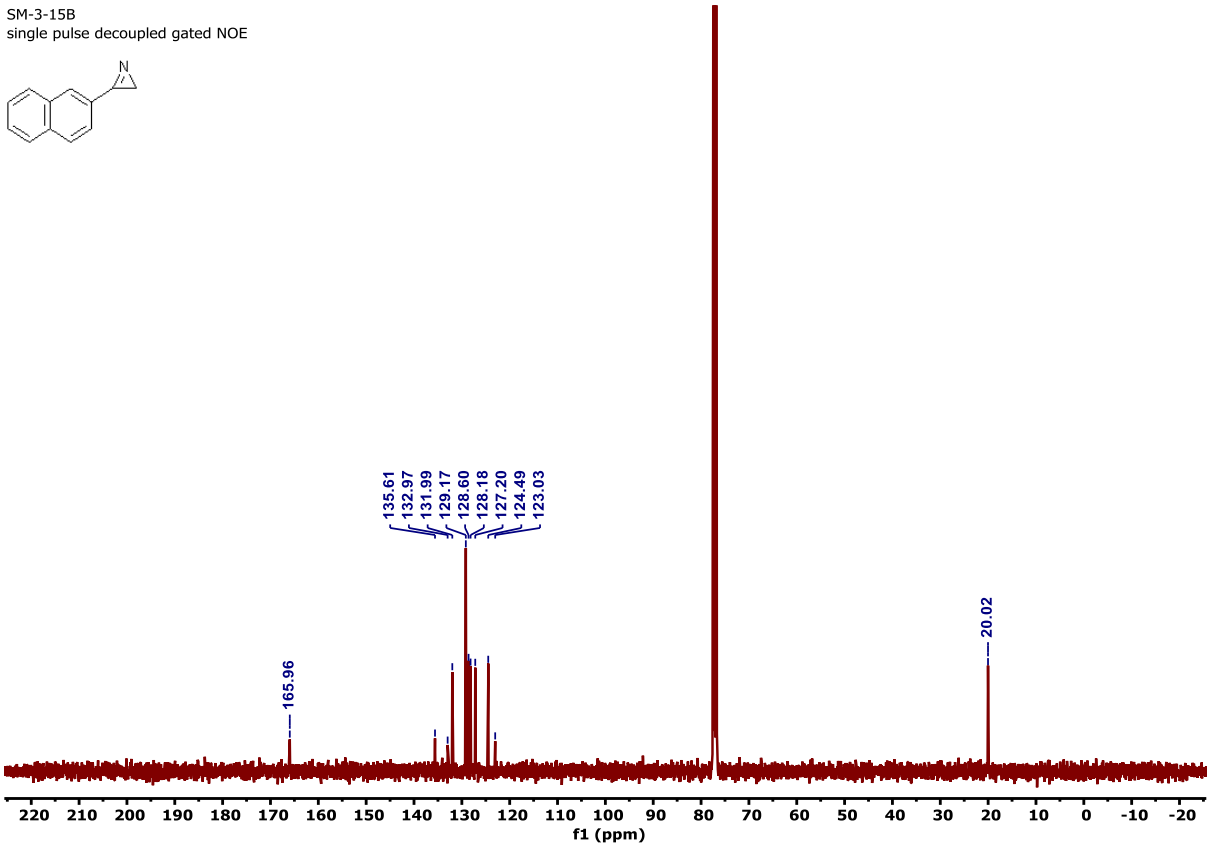
3-(Naphthalen-2-yl)-2*H*-azirine 7a: Prepared according to the general procedure discussed in literature[16]: batch size, 200 mg; R_f = 0.2; eluent, EtOAc/*n*-hexane (5%); colorless oil (52 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (s, 1 H), 8.02 – 7.97 (m, 3 H), 7.93 – 7.89 (m, 1 H), 7.68 – 7.54 (m, 2 H), 1.88 (s, 2 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.0, 135.6, 133.0, 132.0, 129.2 (2 CH), 128.6, 128.2, 127.2, 124.5, 123.0, 20.0 ppm; HRMS (ESI-QTOF): *m/z* calcd for $C_{12}H_{10}N$ $[M + H]^+$: 168.0813, Found: 168.0806.



[16] Jiang, Y.; Park, C. M.; Loh, T. P. Transition-metal-free synthesis of substituted pyridines via ring expansion of 2-allyl-2*H*-azirines. *Org. Lett.* **2014**, *16*, 3432– 3435

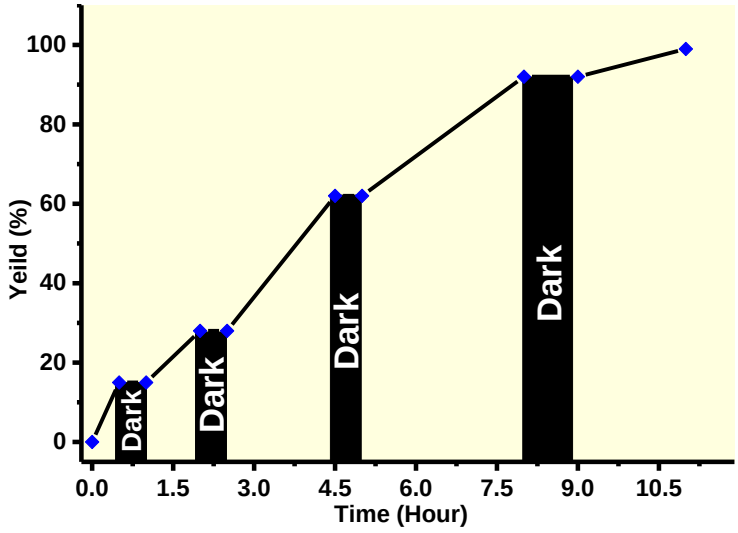
^{1}H (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR spectra of **7a:**





ESI-58-09: **Light On-Off Experiments**

On/off visible-light irradiation experiments proceeded to investigate the effect of photo-irradiation on the system, and the result further clearly indicates that visible-light irradiation is necessary for the reaction.



ESI-58-10: Determination of Quantum Yield[17]:

(A) Determination of photon flux of Luzchem light λ = 420 nm (Intensity = 4300 lx):

We light up all the lamps in the photoreactor with λ=420 nm and measure the intensity using a Luxmeter, which reads 4300 lx. Then we calculate the photon flux.

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. The following solutions were prepared and stored in the dark:

Potassium ferrioxalate solution: 0.737 g of potassium ferrioxalate trihydrate was dissolved in 10 mL H_2SO_4 (0.05 M) and stored in the dark.

Buffered solution: Buffer solution was prepared by dissolving 2.5 g of sodium acetate and 0.5 mL of H_2SO_4 (95-98%) in 50 mL of distilled water.

General Protocol to assess the photon flux of the 420 nm blue LEDs: To a 10 mL Schlenk flask containing a stirring bar, 1 mL of the actinometer solution was added. Then, the solution was irradiated for 60 s. Immediately, a 100 µL aliquot was added to a 10 mL volumetric flask containing 15 mg of 1, 10-phenanthroline in 3 mL of the buffer solution. The flask was filled with distilled water. The absorbance of this solution was then measured at 510 nm by UV/Vis spectrophotometry. In a similar manner, this procedure is repeated with the actinometer

[17] (*a*) S. K. Hota, G. Singh and S. Murarka *Chem. Commun.*, 2024,**60**, 6268-6271; (*b*) X. Huang, X. Li, X. Xie, K. Harms, R. Riedel and E. Meggers. *Nat Commun,* 2017, **8**, 2245; (*c*) X. Huang, T. R. Quinn, K. Harms , R. D. Webster , L. Zhang , O. Wiest and E. Meggers , *J. Am. Chem. Soc.*, 2015, **139** , 9120 —9123; (*d*) C. Wang, K. Harms and E. Meggers, *Angew. Chem. Int. Ed.* 2016, **55**, 13495-13498.

solution stored in the dark. Using then the Beer's Law, the number of moles of Fe^{2+} produced by light irradiation is obtained by:

$$\text{mol } Fe^{2+} = \frac{v_1 \times v_3 \times \Delta A(510\ nm)}{10^3 \times v_2 \times \text{l} \times \varepsilon}$$

Where:

v_1 = Irradiated volume (1 mL).

v_2 = The aliquot of the irradiated solution taken to estimate Fe^{+} ions (0.100 mL).

v_3 = Final volume of the solution after complexation with 1, 10-phenanthroline (10 mL).

ε (510 nm) = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 L mol^{-1} cm^{-1}).

l = Optical path length of the cuvette (1 cm).

ΔA (510 nm) = 0.576 (absorbance difference between the irradiated solution and the solution stored in the dark).

$$\text{mol } Fe^{2+} = \frac{1 \times 10 \times 0.576}{10^3 \times 0.1 \times 1 \times 11100}$$

$$= 5.19 \times 10^{-6} \text{ mol}$$

The photon flux (F) is obtained by using the following equation at 420 nm:

$$F_{4300\ \text{lx}}(420\ \text{nm}) = \frac{mol\ of\ Fe^{2+}}{\Phi.t.f_{4300\ \text{lx}}}$$

Where Φ (420 nm) is the quantum yield for the ferrioxalate actinometer (1.04 here), *t* is the irradiated time, and *f* is the fraction of light absorbed at λ = 420 nm. The measurement of the fraction of the light at 420 nm for the ferrioxalate solution was shown in UV below. The absorbance of the ferrioxalate solution at 420 nm is 0.734.

$$f_{4300\ \text{lx}} = 1 - 10^{-A\ (420\ \text{nm})}$$

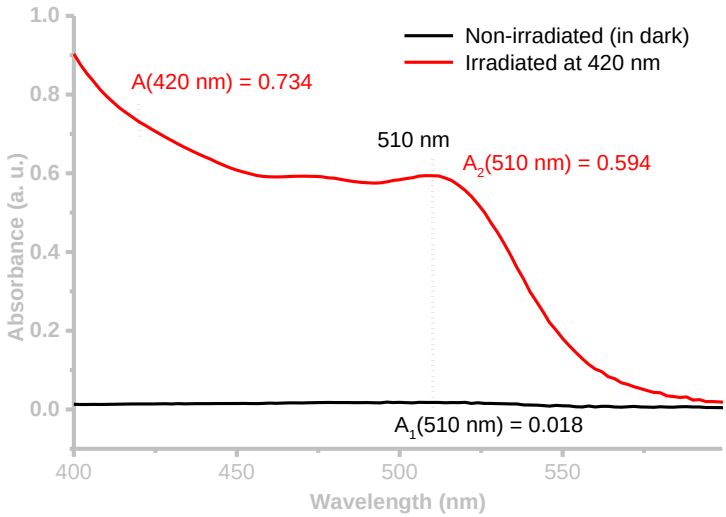
$$= 1 - 10^{-0.734}$$

$$= 0.815$$

The photon flux can be calculated as follows:

$$F_{4300\ \text{lx}}(420\ \text{nm}) = \frac{5.19 \times 10^{-6}}{1.04 \times 60 \times 0.815}$$

$$= 1.02 \times 10^{-7} \text{ einsteins } s^{-1}$$



(B) Determination of photon flux of Luzchem light at λ=420 nm (Intensity = 1400 lx):

We reduce the light intensity by using only four lamps, which produce an intensity of 1400 lx. Then, at this intensity, we calculate the photon flux following the previous step.

Where:

v_1 = Irradiated volume (1 mL).

v_2 = The aliquot of the irradiated solution taken to estimate Fe^{+} ions (0.100 mL).

v_3 = Final volume of the solution after complexation with 1, 10-phenanthroline (10 mL).

ε (510 nm) = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 L mol^{-1} cm^{-1}).

l = Optical path length of the cuvette (1 cm).

ΔA (510 nm) = 0.271 (absorbance difference between the irradiated solution and the solution stored in the dark).

$$\text{mol } Fe^{2+} = \frac{1 \times 10 \times 0.271}{10^3 \times 0.1 \times 1 \times 11100}$$

$$= 2.44 \times 10^{-6} \text{ mol}$$

$$f_{1400\,lx} = 1 - 10^{-A\ (420\ nm)}$$

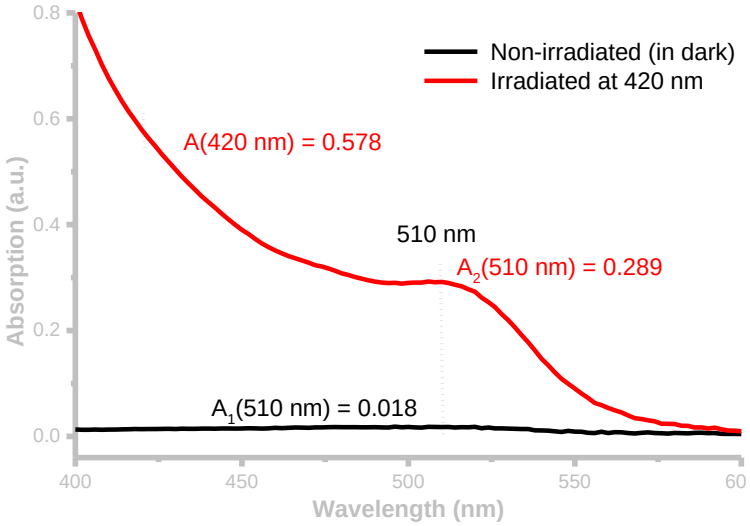
$$= 1 - 10^{-0.578}$$

$$= 0.735$$

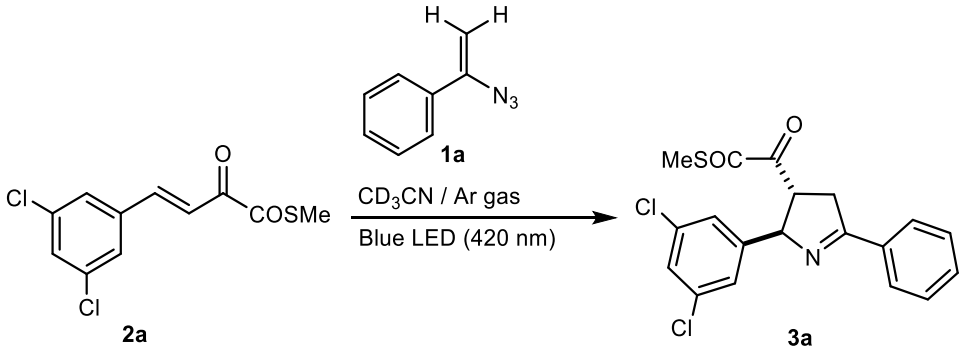
The photon flux ($F_{1400\,lx}$) is obtained by using the following equation at 420 nm:

$$F_{1400\,lx} = \frac{2.44 \times 10^{-6}}{1.04 \times 60 \times 0.735}$$

$$= 5.3 \times 10^{-8} \text{ einsteins } s^{-1}$$



(B) Quantum Yield Calculation:



S-methyl (*E*)-4-(3,5-dichlorophenyl)-2-oxobut-3-enethioate (**2a**) (30 mg, 1 eq), (1-azidovinyl) benzene (**1a**) (19 mg, 0.13 mmol, 1.2 equiv), were added in a predried 10 mL two different reaction tube. Then, CD_3CN (1.1 mL) was added to each tube under an argon atmosphere. Then, the first reaction tube was irradiated for 30 minutes using a Luzchem blue LED (420 nm) lamp when the light intensity was at 4300 lux, and the second tube was also irradiated for 30 minutes using the same lamp but at 1400 lux intensity. After 30 min, a 0.5 mL reaction aliquot from each reaction tube was taken out by a syringe and ^{1}H NMR was carried out. The NMR yield of product **3a** was determined.

The quantum yield for 4300 lx was calculated as follows:

$$\Phi = \frac{mol\ product}{\mathrm{F}_{4300\ \mathrm{lux}} \times t \times f_{4300\ \mathrm{lx}}}$$

$$\Phi_{\ 4300\ \mathrm{lx}} = \frac{1.63 \times 10^{-5}}{1.02 \times 10^{-7} \times 1800 \times 0.815}$$

$$\Phi_{\ 4300\ \mathrm{lx}} = 0.109$$

Where the mol of the product (**3a**) formation is 1.63 x 10^{-5} mol, flux [$F_{\ 4300\ lx}$] is the photon flux determined by ferrioxalate actinometry (1.02 × 10^{-7} Einstein/s), *t* is the time (1800 s),

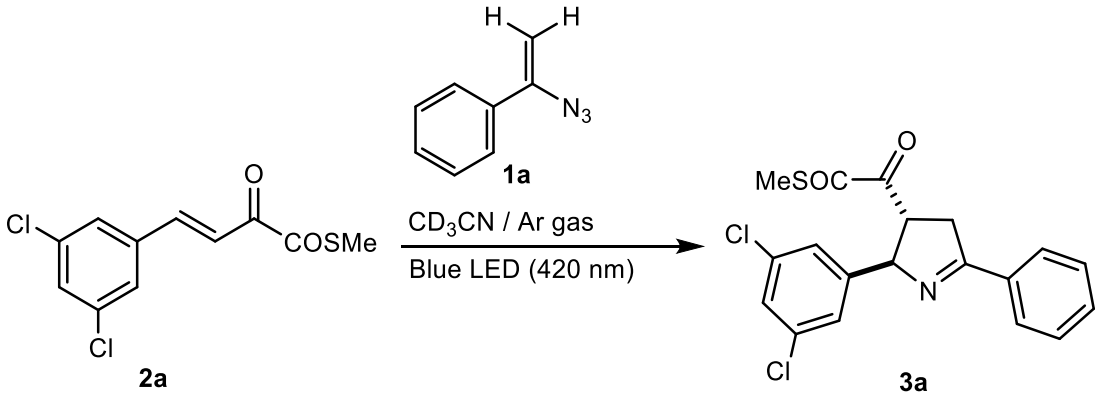
and $f_{4300\ lx}$ is the fraction of light absorbed by **1a** and **2a** at 420 nm under the reaction condition mentioned above (0.815).

$$\text{And}\quad \Phi_{1400\ lx} = \frac{6.2\times10^{-6}}{5.63\times10^{-8}\times 1800\times 0.735}$$

$$\Phi_{1400\ lx} = 0.0832$$

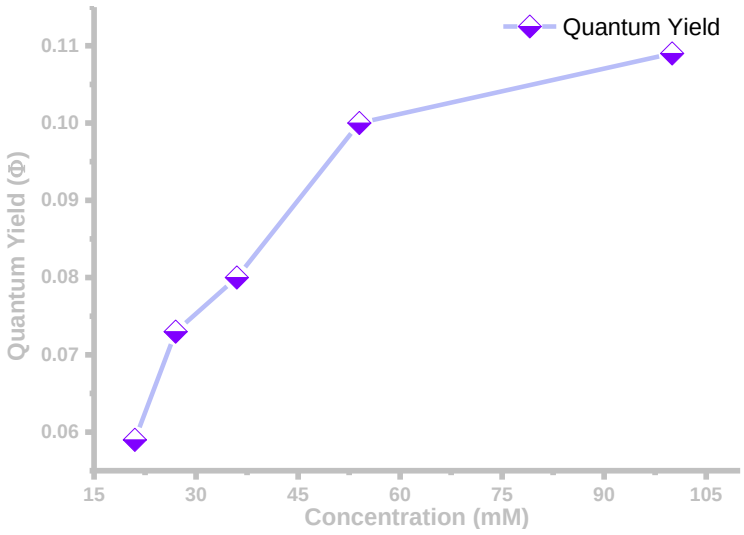
Where the mol of the product (**3a**) formation is 6.2 x 10^{-6} mol, flux [$F_{1400\ lux}$] is the photon flux determined by ferrioxalate actinometry (5.3 x 10^{-8} Einstein/s), *t* is the time (1800 s), and $f_{1400\ lx}$ is the fraction of light absorbed by **1a** and **2a** at 420 nm under the reaction condition mentioned above.
So, by decreasing the light intensity, the quantum yield(Φ) of the reaction lowers down.

(C) The relation between concentration and the quantum yield:

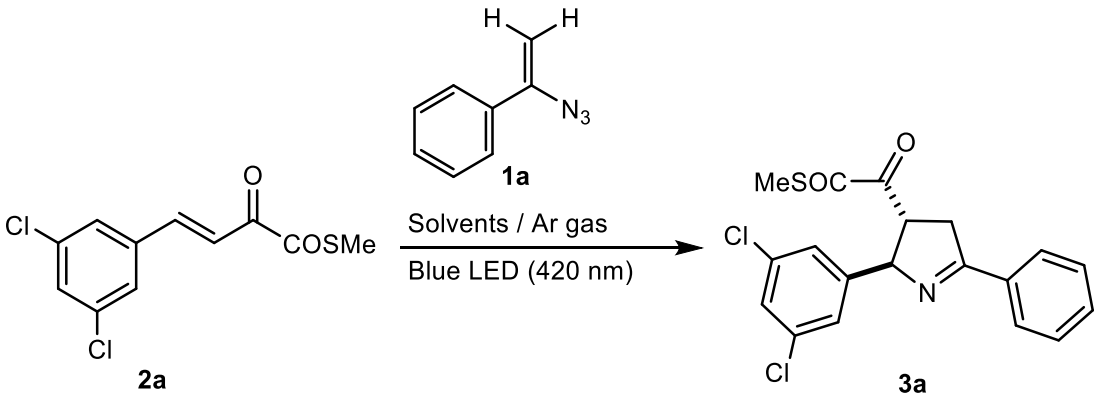


S-methyl (*E*)-4-(3,5-dichlorophenyl)-2-oxobut-3-enethioate (**2a**) (30 mg, 1 eq), (1-azidovinyl) benzene (**1a**) (19 mg, 0.13 mmol, 1.2 equiv), were added in five predried 10 mL reaction tubes. Then, CD_3CN was added in different volumes under an argon atmosphere in each tube to make different concentrations. Then, the mixture was irradiated for 30 minutes using a Luzchem blue LED (420 nm, 4300 lx) lamp. After 30 min, a 0.5 mL reaction aliquot was removed by a syringe, and ^{1}H NMR was carried out. The NMR yield of product **3a** was determined.
After the yield determination, we calculate the Quantum Yield (Φ)

Entry	Concentration (mM)	NMR Yield	Mol of **3a**	Quantum Yield(Φ)
1	100	15 %	1.63 x 10^{-5}	0.109
2	54	14 %	1.5 x 10^{-5}	0.100
3	36	11 %	1.21 x 10^{-5}	0.080
4	27	10 %	1.1 x 10^{-5}	0.073
5	21	8 %	8.8 x 10^{-6}	0.059

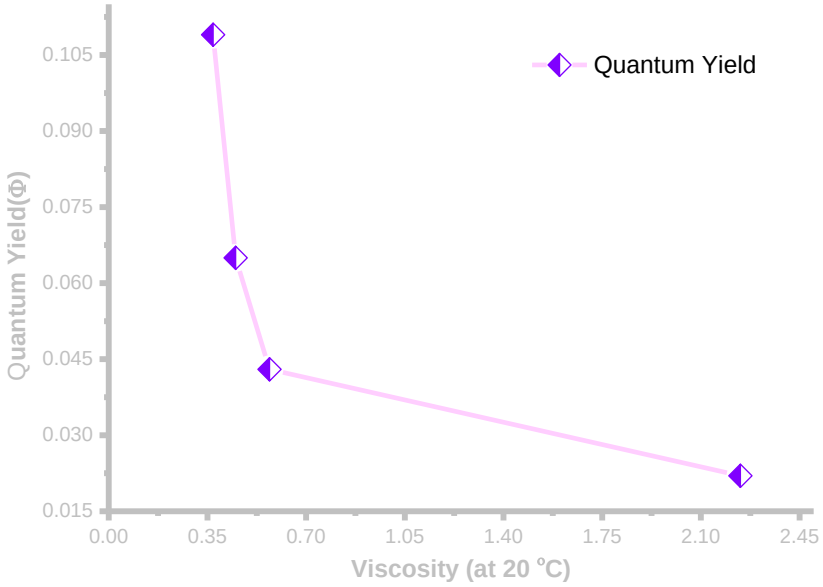


(D) The relation between viscosity and the quantum yield:

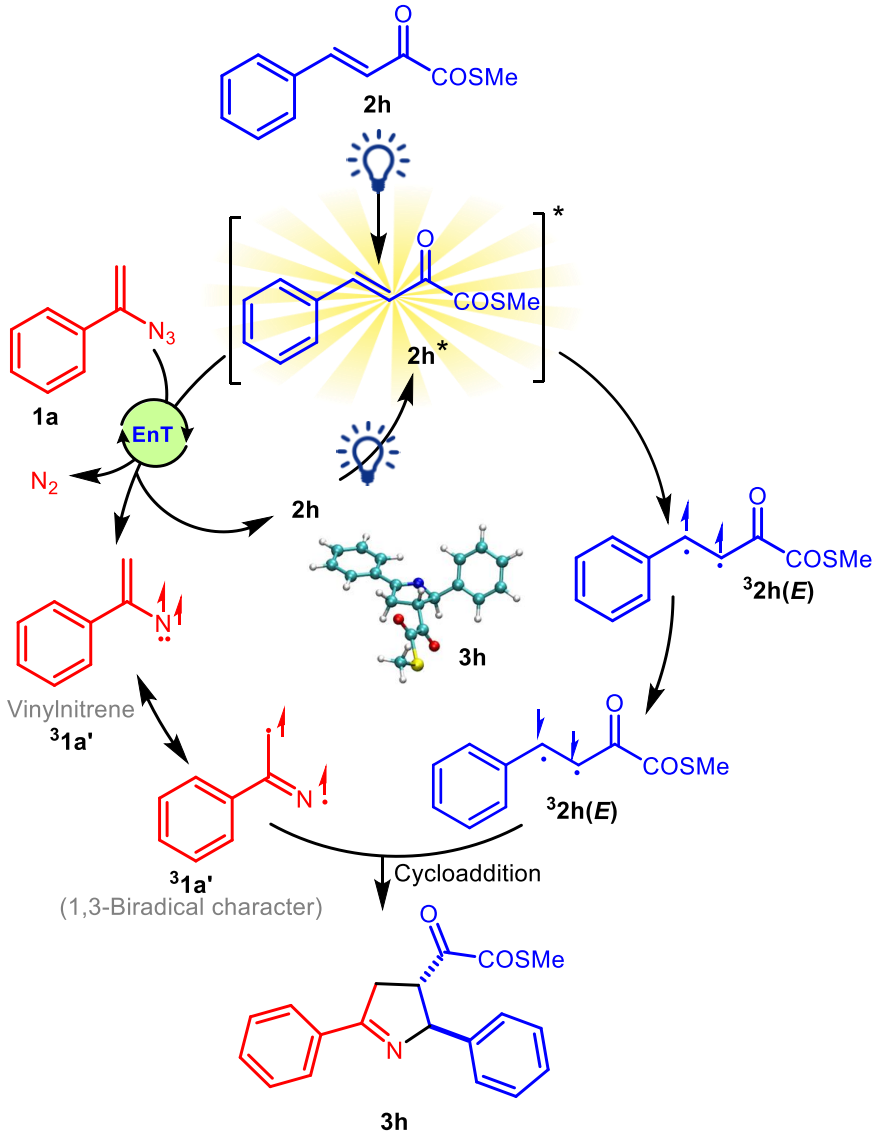


S-methyl (*E*)-4-(3,5-dichlorophenyl)-2-oxobut-3-enethioate (**2a**) (30 mg, 1 eq), (1-azidovinyl) benzene (**1a**) (19 mg, 0.13 mmol, 1.2 equiv), were added in four predried 10 mL reaction tube. Then, each tube added different deuterated solvents (in 0.1 M) under an argon atmosphere. Then, the mixture was irradiated for 30 minutes using a Luzchem blue LED (420 nm, 4300 lx) lamp. After 30 min, a 0.5 mL reaction aliquot was removed by a syringe, and ^{1}H NMR was carried out. The NMR yield of product **3a** was determined.
After the yield determination, we calculate the Quantum Yield (Φ)

Entry	Solvent	Viscosity (20 ˚C)	Yield	mol of **3a**	Quantum Yield(Φ)
1	DMSO-d_6	2.24	3 %	3.3×10^{-6}	0.022
2	$CDCl_3$	0.57	6 %	6.5×10^{-6}	0.043
3	$CDCl_2$	0.45	9 %	9.8×10^{-6}	0.065
4	CD_3CN	0.37	15 %	1.63×10^{-5}	0.109



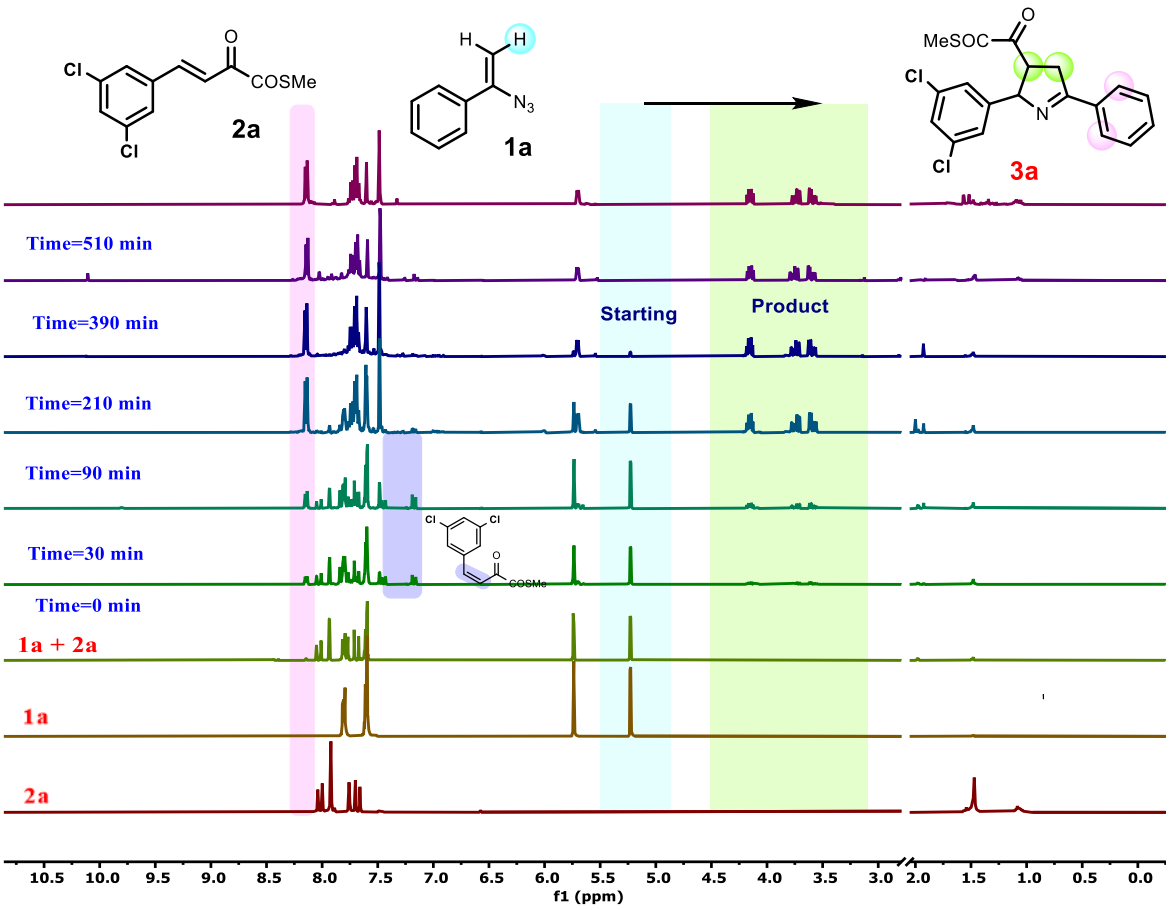
ESI-58-10: Plausible Mechanism

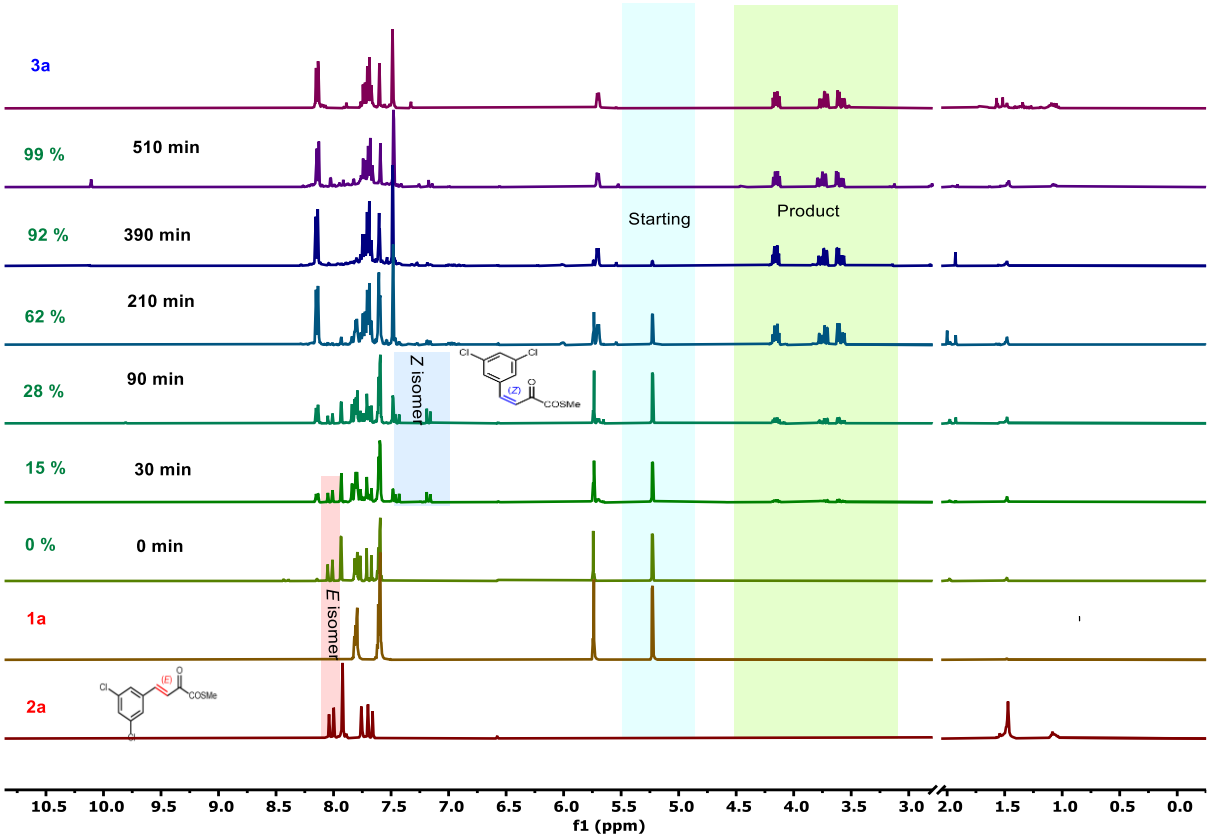


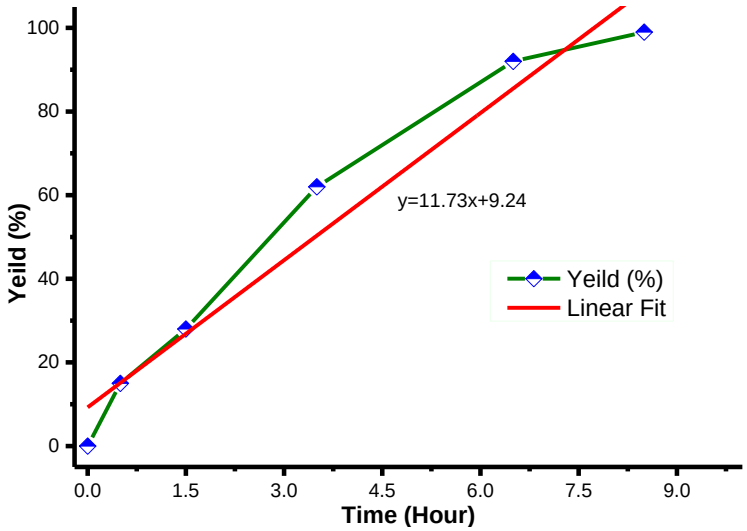
ESI-59: Kinetic Study:

Time-dependent reaction progress monitoring during the formation of 3a from the reactants (1a and 2a) by ^{1}H NMR analysis (400 MHz, CD_3CN)

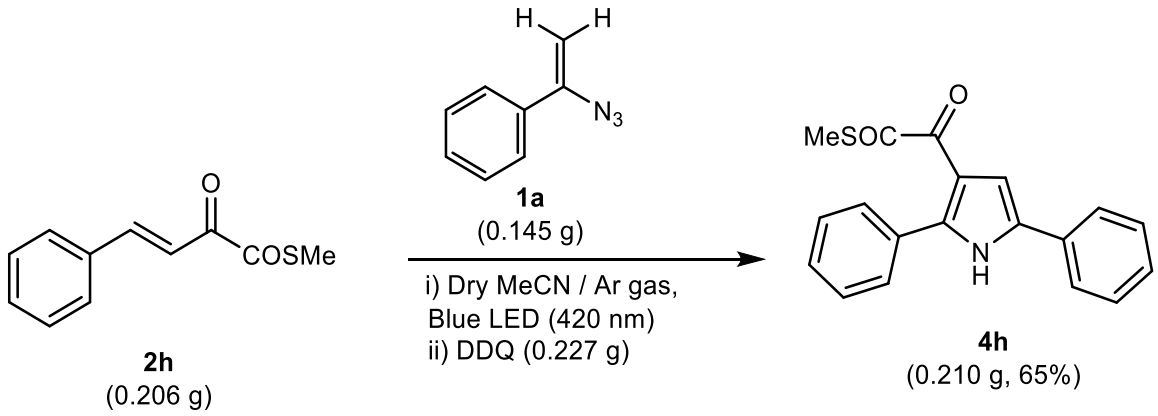
1a and **2a** were mixed in CD_3CN in a round bottom flask under argon. Eleven equal portions of the reaction mixture were divided into septum-sealed screw-cap vials. The aliquots were exposed to 420 nm irradiation at r.t. for 0, 30, 90, 210, 390, and 510 minutes. After exposure, those aliquots were directly transferred in an NMR tube (diluted in additional CD_3CN if required), and then the NMR data were recorded as shown below.




3a
99 %
510 min
92 %
390 min
62 %
210 min
28 %
90 min
15 %
30 min
0 %
0 min
1a
2a
Starting
Product
Z isomer
E isomer
f1 (ppm)


Yeild (%)
Time (Hour)
y=11.73x+9.24
Yeild (%)
Linear Fit

ESI-60: Green chemistry metrics and Eco-scale calculations[18]:



$$\text{Atom economy (\%)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

(AE)

$$\text{Reaction mass efficiency (\%)} = \frac{\text{Mass of desired product}}{\text{Mass of all reactants}} \times 100$$

(RME)

1	Reactant 1	**1a**	0.145 g	1 mmol	FW 145.165
2	Reactant 2	**2h**	0.206 g	1 mmol	FW 206.259
3	Reactant 3	**DDQ**	0.227 g	1 mmol	FW 227.000
4	Additive solvent	CH_3CN (10 mL)	7.86 g		
5	Recycled solvent	CH_3CN (7 mL)	5.5 g		
6	Product	**3h**	0.210 g		FW 321.394

Product Yield = 65%

***E*- factor** = $\frac{0.145+0.206+0.227+7.86-(5.5+0.21)}{0.21}$ = 12.99 Kg waste/ 1 Kg product

Atom economy = $\frac{321.394}{206.259+145.165+227.0} \times 100$ = 55%

Atom efficiency = (55% x 65%)/ 100 =35.75%

Carbon Efficiency = $\frac{19}{11+8+8} \times 100$ = 70%

Reaction mass efficiency = $\frac{0.210\ \text{g}}{0.145\ \text{g}+0.206\ \text{g}+0.227\ \text{g}} \times 100$ = 36.33%

.

[18] Dam, B.; Sahoo, A. K.; Patel, B. K. Visible-Light-Mediated Synthesis of β-keto Sulfones using g-C_3N_4 as a Recyclable Photocatalyst under Sustainable Conditions. *Green Chem.* **2022**, *24*, 7122– 7130.

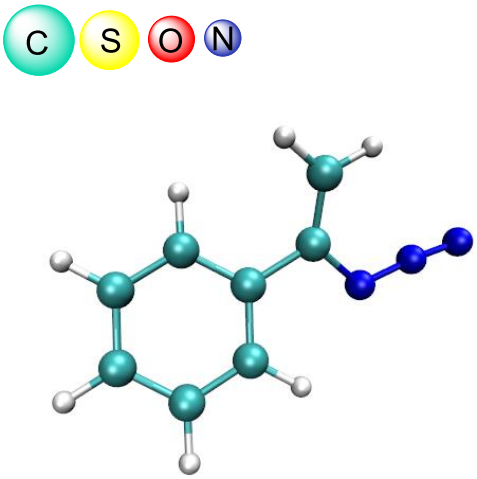
ESI-61: Computational Studies:

All the molecules (**1a**, **2h**, ^{3}**1a**, and ^{3}**2h(*E*),** ^{3}**2h(*Z*)**) were optimized at B3LYP/6-31G(d)[19] level of theory using Q-Chem quantum chemistry software.[20] These structures were further used for TDDFT calculations to obtain the singlet and triplet excited states. The basis set was kept as 6-31G(d). The transition state (TS) was found using UB3LYP/6-31G(d) level of theory using the Gaussian 16 program package.[21] The final product (**3h**) was also optimized at the same levels of theory**.**

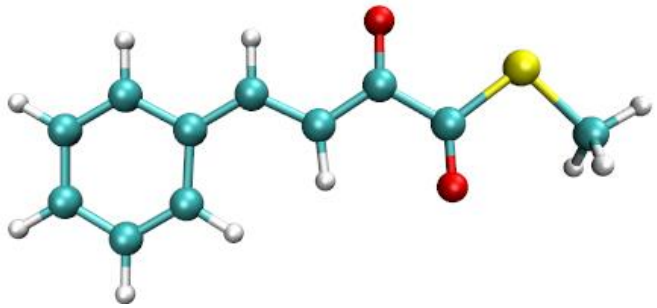
ESI-61-01: Excitation energies of the species: TD-DFT excitation energies (B3LYP/6-31G(d))

State	**2h**	**1a**
Excited singlet (Bright state)	3.60	4.82
T1	2.16	2.52

The experimental irradiation of 420 nm corresponds to ~ 3 eV, which agrees reasonably with the absorption energy of the bright state of **2h**.



1a

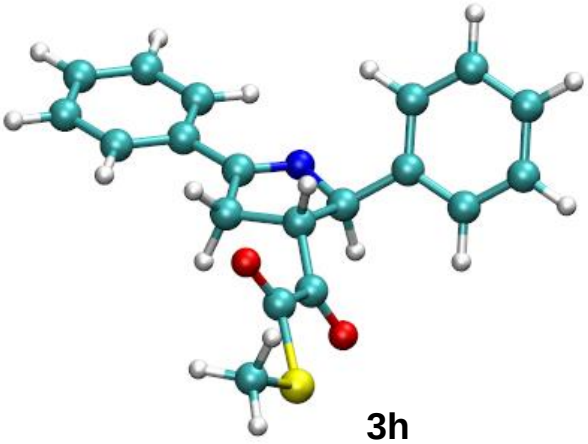


2h

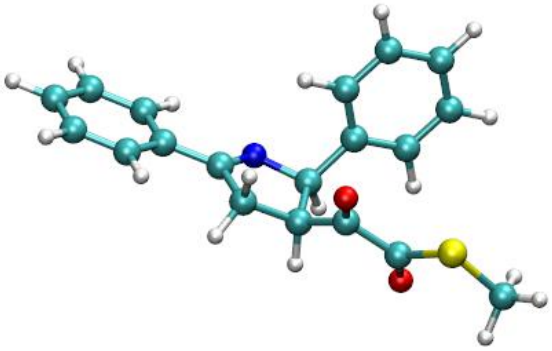
[19] (a) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648– 5652. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B.* **1988**, *37*, 785– 789.

[20] Shao Y, Gan Z, Epifanovsky E, Gilbert ATB, Wormit M, Kussmann J, Lange AW, Behn A, Deng J, Feng X et al (**2015**) Advances in molecular quantum chemistry contained in the q-chem 4 program package. Mol Phys 113, 184–215.

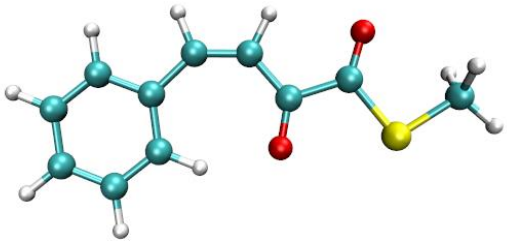
[21] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; ; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*; Gaussian Inc.: **2016**.



3h

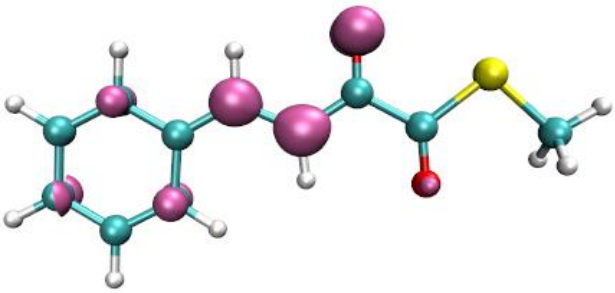


3h'

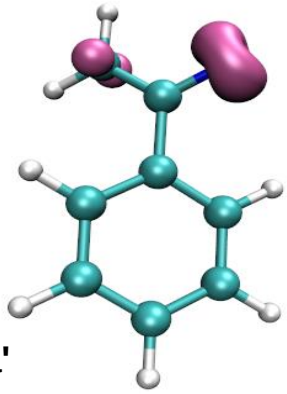


^{3}2h(*Z*)

Spin Density Diagram: The purple-colored blobs are the spin densities accumulated on the atoms. (calculated in B3LYP/6-31G(d) level of theory)

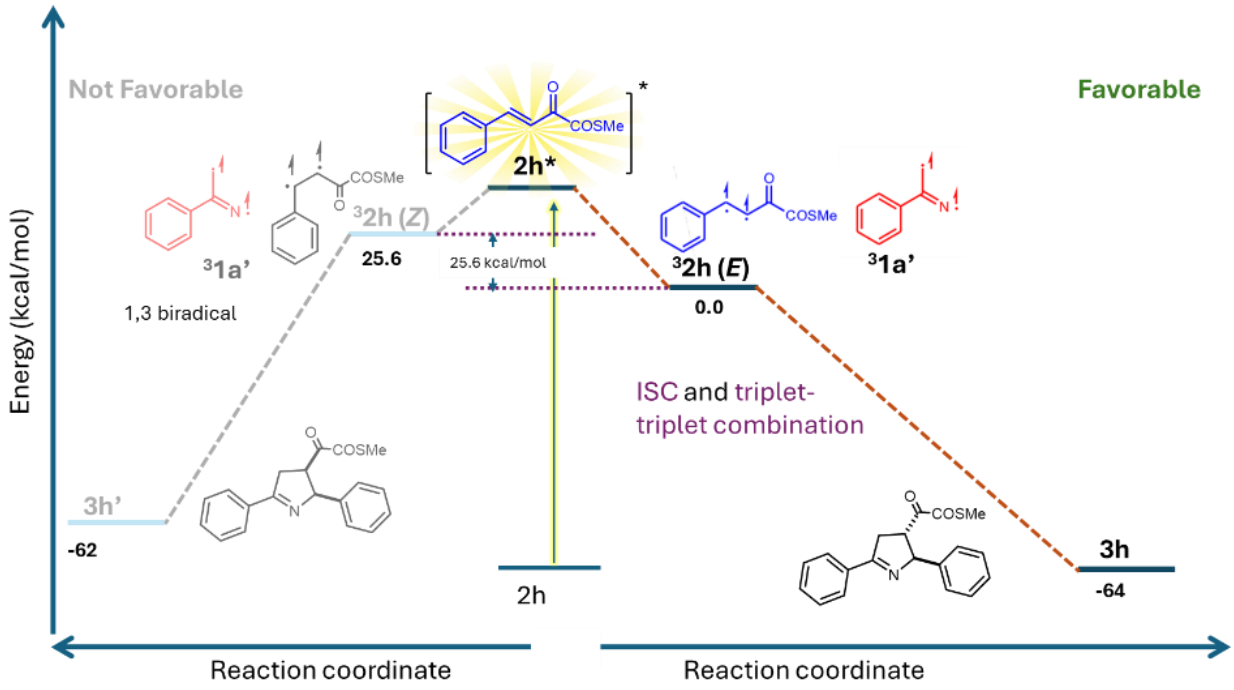


^{3}2h(*E*)



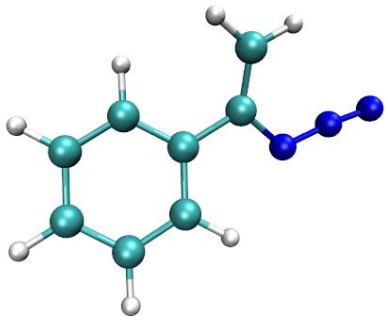
^{3}1a'

ESI-61-03: Reaction Profile Diagram: Relative energies of the reactants, TS, and the product are shown. (B3LYP/6-31G(d) level of theory)



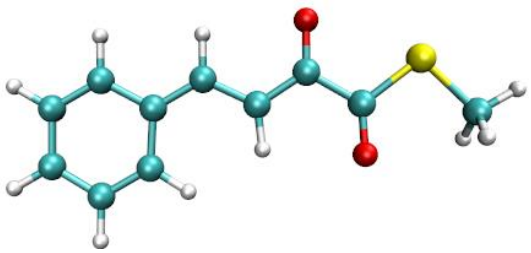
ESI-61-02: Cartesian Coordinates:

1a



C	1.6365447152	0.9873733227	0.2182285244
C	0.5160023402	0.1671364031	0.0202214831
C	0.7170663329	-1.2064282685	-0.1711541337
C	2.0033312675	-1.7394548559	-0.1899039184
C	3.1098507629	-0.9130041214	-0.0089691884
C	2.9201002651	0.4531867724	0.1991231014
H	1.5026096842	2.0447816346	0.4117362628
H	-0.1400533455	-1.8528030533	-0.3095673352
H	2.1401822305	-2.8035336061	-0.3453717126
H	4.1111022716	-1.3286254945	-0.0188952115
H	3.7729360487	1.1032032036	0.3607658767
C	-0.8512305317	0.7399699258	0.0059122898
N	-4.1396857574	0.3062300091	0.3273409376
N	-1.8434048209	-0.2366711061	0.3264144947
N	-3.0255234312	0.1058326207	0.3070749904
C	-1.1455275227	2.0157455916	-0.2884931973
H	-0.3688593443	2.7103792891	-0.5728572446
H	-2.1598902082	2.3946308453	-0.2692940561

2h



C	5.1946688687	-0.5917152019	0.0024614690
C	4.8736604806	0.7678720617	-0.0010064036
C	3.5373247215	1.1656645503	-0.0023603766
C	2.4961704905	0.2159956221	-0.0004133609
C	2.8382081663	-1.1528968381	0.0032050380
C	4.1718676656	-1.5492460588	0.0045923904
H	5.6611992748	1.5155285773	-0.0026018659
H	2.0581177656	-1.9075672880	0.0050020022
H	4.4193874032	-2.6066942847	0.0074268330
C	1.1180822395	0.6967949247	-0.0022003247
H	0.9950959981	1.7795067762	-0.0032607673
C	-0.0175007589	-0.0393732715	-0.0028620508
H	-0.0220282083	-1.1235078444	-0.0020568453
C	-1.3262273908	0.6212047248	-0.0048809841
C	-2.5509660252	-0.3243355750	-0.0039491763
O	-1.5164694750	1.8310644269	-0.0047047962
O	-2.4463254765	-1.5367499038	-0.0044021409
S	-4.0975329143	0.5566772451	-0.0015364403
C	-5.2148985076	-0.8873403762	-0.0001992081
H	-5.0498583609	-1.4990632710	0.8883891387
H	-6.2309746445	-0.4884089984	0.0051780408
H	-5.0577955326	-1.4948409521	-0.8931273129

H	6.2339195583	-0.9072000515	0.0035642891
H	3.2873256170	2.2233171158	-0.0050528665

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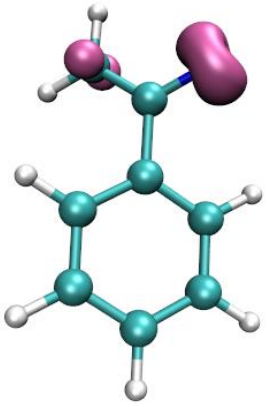
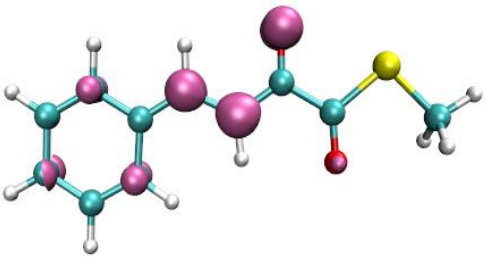


C	0.3996165504	-1.1995068088	0.0031629065
C	-0.2809790297	0.0235837688	0.0014432809
C	0.4667359240	1.2097277925	-0.0012813804
C	1.8569818233	1.1716540954	-0.0024048189
C	2.5259007990	-0.0517070607	-0.0008201119
C	1.7920123593	-1.2358998921	0.0019741045
H	-0.1454695202	-2.1349490882	0.0057896538
H	-0.0492124584	2.1622498487	-0.0026452944
H	2.4188207932	2.0988516751	-0.0045698203
H	3.6095835893	-0.0820816941	-0.0017202617
H	2.3022178115	-2.1925176292	0.0033676855
C	-1.7818409083	0.1010491785	0.0027276126
N	-2.3590763087	1.2750786673	0.0105313849
C	-2.6114383933	-1.0343699886	-0.0041563054
H	-2.2173615995	-2.0408022234	-0.0112697549
H	-3.6853769423	-0.9036782623	-0.0025597314

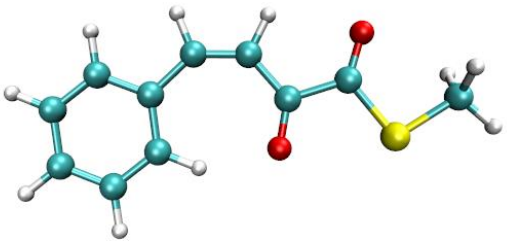
^{3}2h(*E*)



C	3.94203786	-0.84806526	0.01051189
C	3.73002858	0.53863753	-0.00207901
C	2.44460594	1.02688832	-0.00922760
C	1.28337213	0.15742479	-0.00446907
C	1.57822257	-1.25685937	0.00756574
C	2.85948712	-1.74469454	0.01507479
H	4.57134078	1.21803383	-0.00596328
H	0.75664862	-1.95974748	0.01219234
H	3.04442936	-2.81093492	0.02495576
C	-0.01236392	0.65852124	-0.00909844
H	-0.16974147	1.72846778	-0.01244068
C	-1.20759271	-0.15377119	-0.01059211
H	-1.16472552	-1.23539477	-0.01881118
C	-2.49801238	0.43186596	0.00042244
C	-3.67854743	-0.52496747	-0.00811687
O	-2.69023374	1.66935285	0.01982504
O	-3.56021620	-1.73235035	-0.03862749
S	-5.24788684	0.32470359	0.02907838
C	-6.33323247	-1.14184524	0.00118862
H	-6.15228947	-1.76790993	0.87378103

H	-7.35523693	-0.76376772	0.01923613
H	-6.16628557	-1.72169966	-0.90540487
H	4.94205046	-1.22863868	0.01673059
H	2.29547233	2.08640263	-0.01864018

^{3}2h(*Z*)



C	4.352265	-0.325749	0.002097
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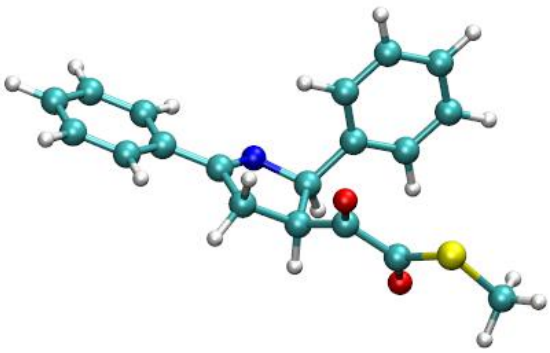
C	1.542510	-0.098374	0.004565
C	2.162095	-1.366769	0.025117
C	3.550343	-1.469756	0.023988
H	4.371643	1.833683	-0.034194
H	1.545822	-2.255885	0.041806
H	4.010567	-2.453898	0.040284
C	0.104744	0.150244	0.005206
H	-0.114825	1.218742	0.005065
C	-1.023371	-0.615614	0.005426
H	-1.964740	-0.074916	0.006838
C	-1.213270	-2.061560	-0.002166
C	-2.701476	-2.499273	-0.006054
O	-0.369909	-2.951603	-0.008538
O	-3.634714	-1.723865	0.000837
S	-2.874407	-4.278958	-0.021443
C	-4.700802	-4.334433	-0.020728
H	-5.098609	-3.834741	-0.906167
H	-4.981136	-5.389918	-0.029699
H	-5.097409	-3.850207	0.873800
H	5.435105	-0.418032	0.000881
H	1.911687	2.032476	-0.029816

3h'

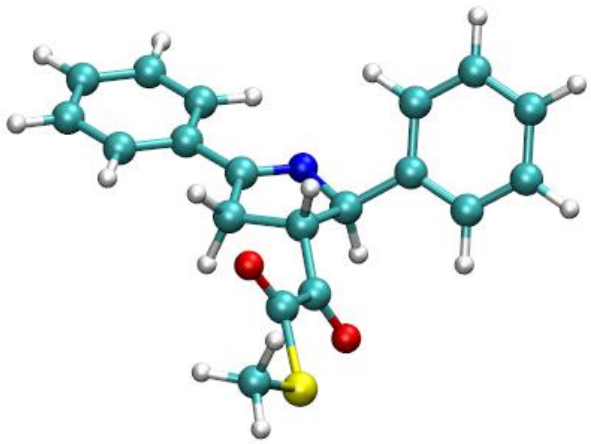


C	-6.303092	-0.308148	0.262662
C	-5.525406	-1.312416	0.838897
C	-4.146536	-1.337357	0.626626
C	-3.528023	-0.355758	-0.162612
C	-4.321422	0.653343	-0.736820
C	-5.695754	0.674837	-0.526215
H	-5.990104	-2.077916	1.454327
H	-6.298183	1.459210	-0.976615
C	-2.068106	-0.366919	-0.389818
N	-1.482229	0.557067	-1.060652
C	0.721630	1.455765	-0.422226

C	0.270919	2.002619	0.786148
C	1.904725	1.950863	-0.985996
C	0.992140	3.014044	1.419970
H	-0.656463	1.647321	1.225056
C	2.628432	2.962185	-0.352269
H	2.262170	1.535988	-1.925086
C	2.173736	3.496619	0.853869
H	0.627822	3.428584	2.356220
H	3.542640	3.336386	-0.805679
H	2.733461	4.286476	1.347645
H	-3.835578	1.409855	-1.344010
H	-7.377315	-0.289173	0.426210
H	-3.551967	-2.122963	1.083392
C	-0.039590	0.334084	-1.119076
C	-1.152569	-1.446006	0.167271
C	0.181575	-1.133157	-0.522707
H	0.348376	-1.793778	-1.378849
C	1.385416	-1.259978	0.380522
C	2.752508	-1.310962	-0.337500
S	4.122041	-1.462012	0.791990
C	5.458620	-1.480672	-0.453248
H	6.396499	-1.585217	0.096225
H	5.330251	-2.321012	-1.138140
H	5.460248	-0.548699	-1.021833
O	1.346979	-1.332046	1.591980
O	2.853576	-1.264892	-1.547333
H	-1.068351	-1.368341	1.258457
H	-1.510029	-2.456570	-0.057651
H	0.269806	0.330161	-2.168980

3h

C	-5.855530	-1.582759	0.146446
C	-4.813917	-2.462630	0.439893
C	-3.488823	-2.041964	0.320715
C	-3.189101	-0.735944	-0.095697
C	-4.247242	0.141788	-0.392120
C	-5.566972	-0.278659	-0.270019
H	-5.030400	-3.477403	0.762452
H	-6.375663	0.409512	-0.501169
C	-1.791589	-0.275838	-0.229281
N	-1.499283	0.905967	-0.633254
C	0.453138	2.406937	-0.235830
C	-0.249839	3.122326	0.740372



C	1.660406	2.927503	-0.720424
C	0.246655	4.332943	1.226118
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C	2.159596	4.135283	-0.231668
H	2.208816	2.382936	-1.485395
C	1.454022	4.841761	0.744304
H	-0.313076	4.880875	1.979946
H	3.096437	4.527618	-0.618947
H	1.839557	5.785185	1.121942
H	-4.007649	1.148476	-0.717967
H	-6.887756	-1.909484	0.240088
H	-2.687684	-2.737774	0.551900
C	-0.044067	1.063396	-0.737368
C	-0.595612	-1.178017	0.055014
C	0.565368	-0.148575	0.032483
H	0.788040	0.135746	1.066913
C	1.828700	-0.712413	-0.573990
C	2.601920	-1.717625	0.312584
S	4.088263	-2.325123	-0.463278
C	4.638861	-3.418496	0.893232
H	5.574007	-3.876545	0.564516
H	4.805395	-2.839901	1.803854
H	3.892020	-4.190640	1.087523
O	2.252393	-0.451223	-1.681815
O	2.212934	-2.043226	1.415601
H	-0.657614	-1.712831	1.006142
H	0.219973	0.975918	-1.800088
H	-0.503007	-1.934109	-0.737940