Supporting Information

Palladium-Catalyzed Cyanothiolation of Internal Alkynes Using Organic Disulfides and *tert*-Butyl Isocyanide

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Contents

1. X-ray crystallography

Crystals of (*E*)-**4ca** or (*Z*)-**4da** suitable for X-ray structure analysis were obtained by slow diffusion of hexane into an ethyl acetate solution of **4ca** or by slow evaporation of a hexane solution of **4da**. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-Kα radiation at –150 °C. All calculations were performed using the *CrystalStructure*[S1] crystallographic software package except for refinements, which was performed using SHELXL Version2017/1.[S2] The structure was solved by direct methods (SHELXT Version 2014/5[S3]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Details of the X-ray diffraction study are summarized in Table S1.

References

(S1) *CrystalStructure 4.2.5: Crystal Structure Analysis Package;* Rigaku Corporation: Tokyo, Japan, (2000–2017).

(S2) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.

(S3) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Adv.* **2014**, *70*, C1437.

Table S1. X-ray crystallographic data for (*E*)-4ca and (*Z*)-4da.

	(*E*)-**4ca**	(*Z*)-**4da**
CCDC	1824372	1824371
empirical formula	$C_{13}H_{11}NO_4S$	$C_{21}H_{15}NS$
formula weight	277.29	313.42
dimension of crystals	0.200×0.050×0.040	0.180×0.120×0.080
crystal system	monoclinic	monoclinic
space group	C2/c (#15)	$P2_1/c$ (#14)
a [Å]	23.4985(5)	8.07707(17)
b [Å]	7.79477(15)	15.3472(3)
c [Å]	16.7618(3)	13.2213(3)
α [°]	90.0000	90.0000
β [°]	123.364(9)	93.8705(7)
γ [°]	90.0000	90.0000
V [Å^3]	2564.2(3)	1635.18(6)
Z	8	4
ρ_{calcd} [g cm^{-3}]	1.436	1.273
F(000)	1152	656
μ [cm^{-1}]	2.612	1.962
trans. factors range	0.747–0.990	0.912–0.984
index ranges	$-30 \le h \le 30$	$-10 \le h \le 10$
	$-9 \le k \le 10$	$-19 \le k \le 19$
	$-21 \le l \le 21$	$-17 \le l \le 17$
no. rflns measured	20569	16142
no. unique rflns	2926	3749
R_{int}	0.0278	0.0157
no. rflns ($I > 2\sigma(I)$)	2684	3515
no. params refined	174	208
*R*1 ($I > 2\sigma(I)$)[a]	0.0341	0.0314
R (All cata)	0.0377	0.0331
wR2 (All cata)[b]	0.0891	0.0833
GOF[c]	1.074	1.073
max diff peak/hole [e Å^{-3}]	0.42/–0.31	0.38/–0.24

[a] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2 F_o^2 + (aP)^2 + bP]$ (*a* and *b* are constants suggested by the refinement program; $P = [\max(F_o^2,0) + 2F_c^2] / 3$). [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{1/2}$.

2. X-ray crystal structure (ORTEP) of (*E*)-4ca

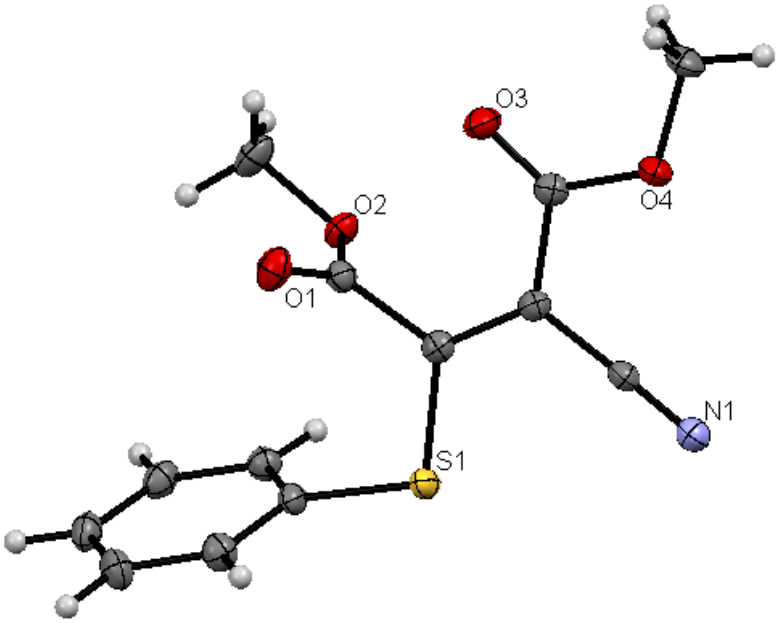


Figure S1. An ORTEP drawing of (*E*)-4ca with ellipsoids at 50% probability

3. X-ray crystal structure (ORTEP) of (*Z*)-4da

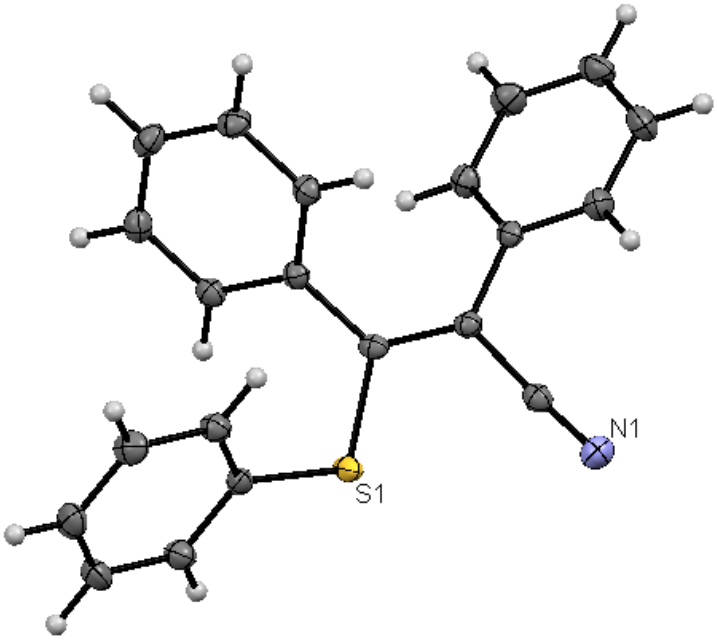
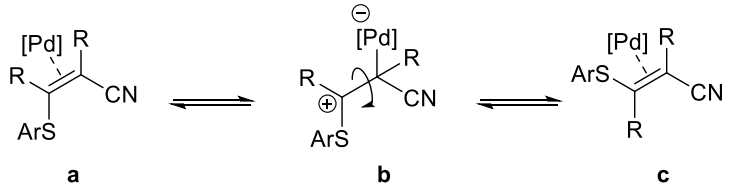


Figure S2. An ORTEP drawing of (*Z*)-4da with ellipsoids at 50% probability

4. The isomerization of alkenyl cyanide derivatives

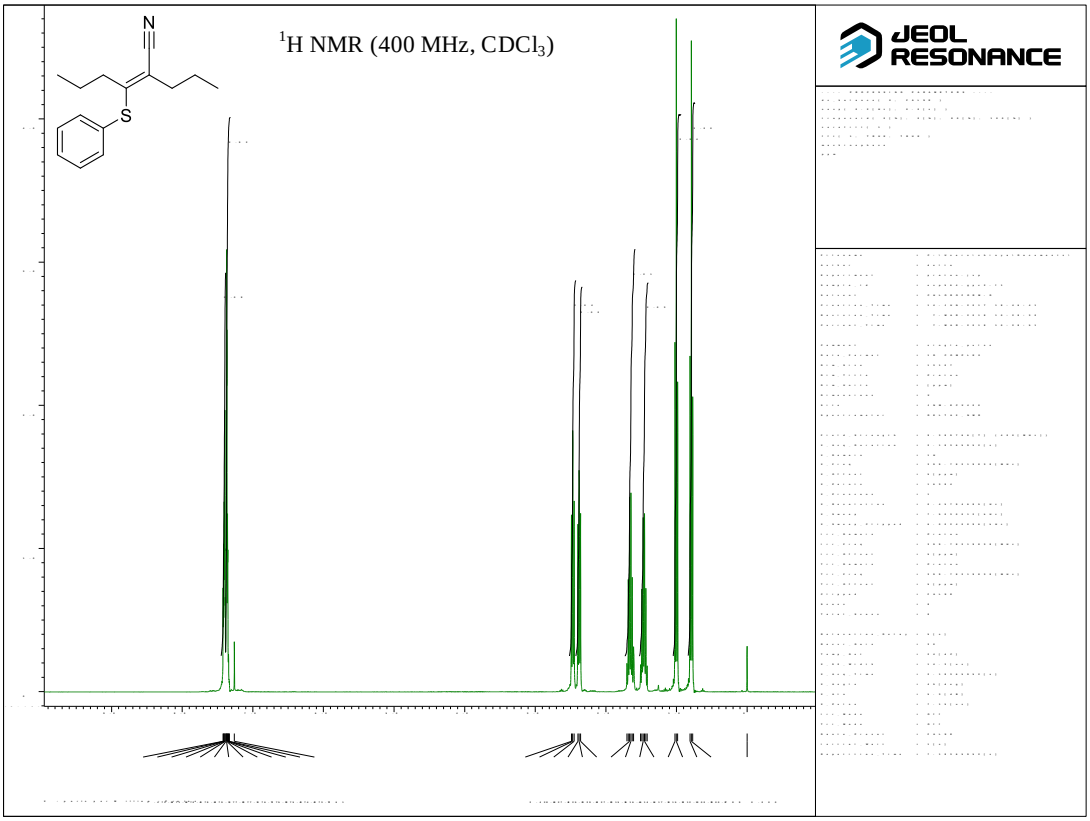
To gain further insight into the isomerization pathway of **4ad** in Eq. 1, we examined a similar reaction of **4ad** (*E*/*Z* = 3/97) using 40 mol % of PPh_3 which is known to be easily dissociated from the $Pd(PPh_3)_4$ catalyst in solution. As a result, the expected isomerization did not occur. From the present results, we assume that the slight isomerization in Eq. 1 proceeds via the formation of σ-alkylpalladium complex **b** from the palladium catalyst and electron-deficient alkene **4ad** (Scheme S1).

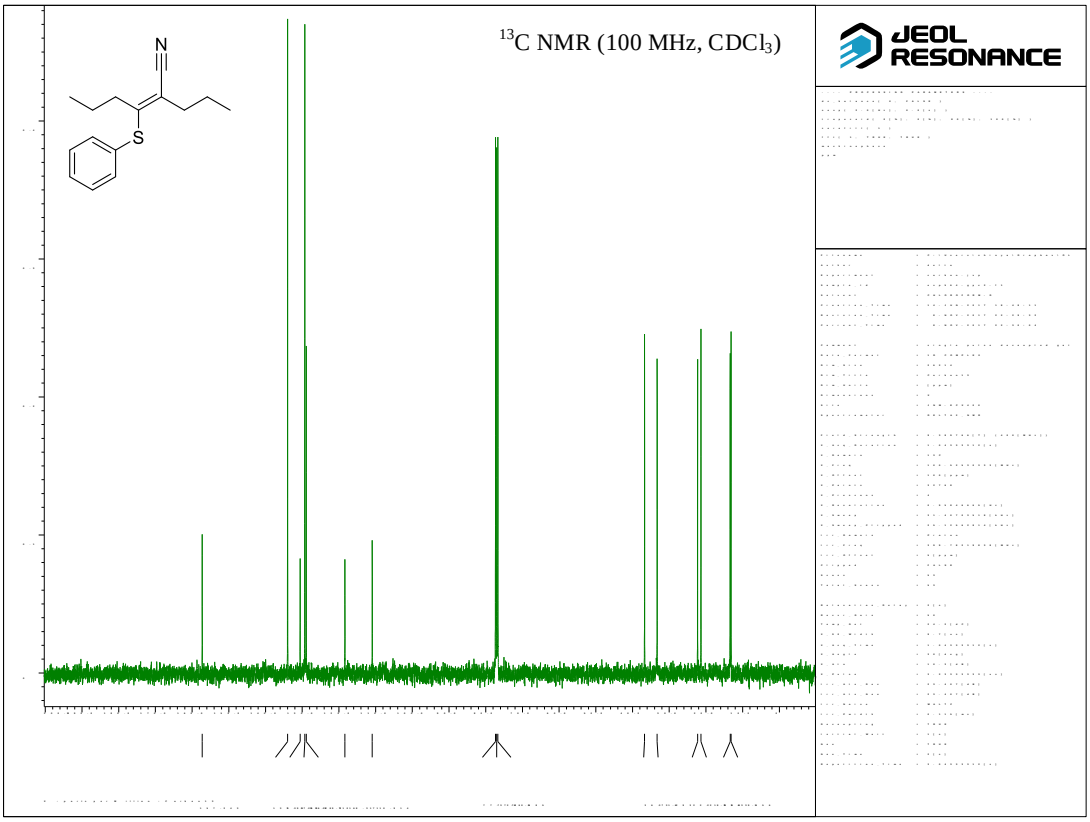
Scheme S1. Possible pathway for the isomerization of alkenyl cyanide derivatives



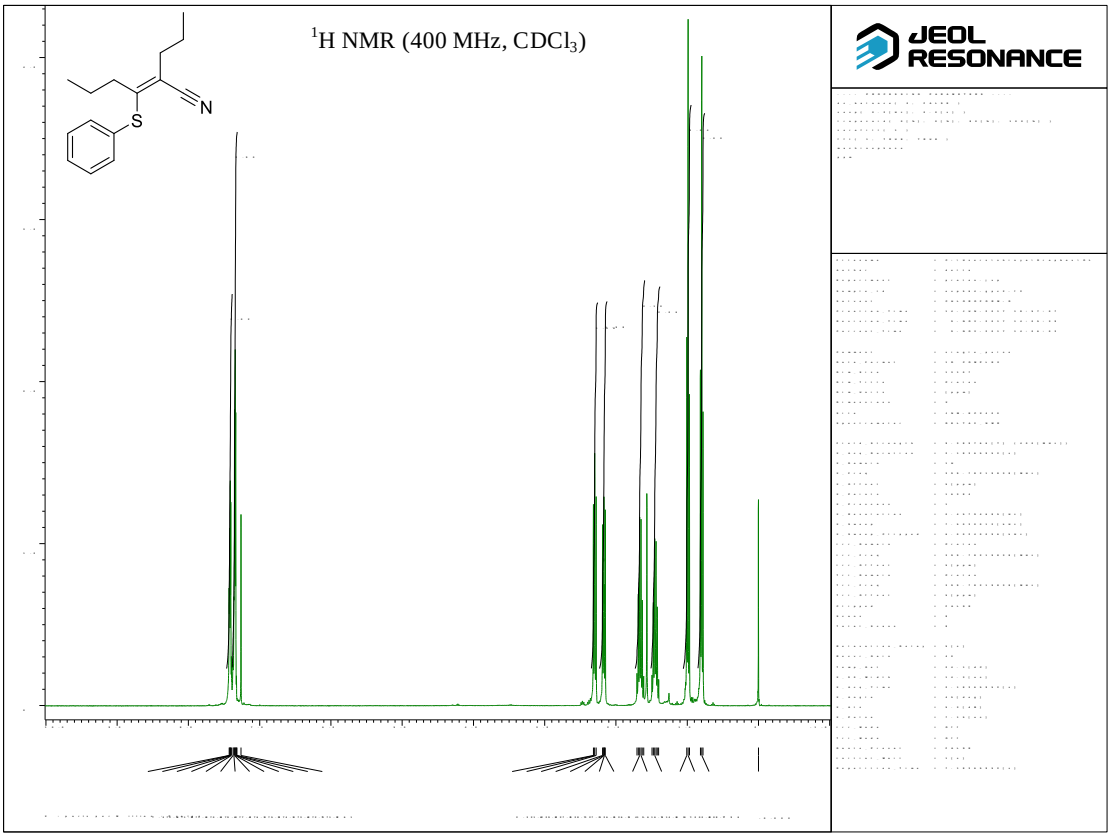
5. ^{1}H and ^{13}C NMR spectra

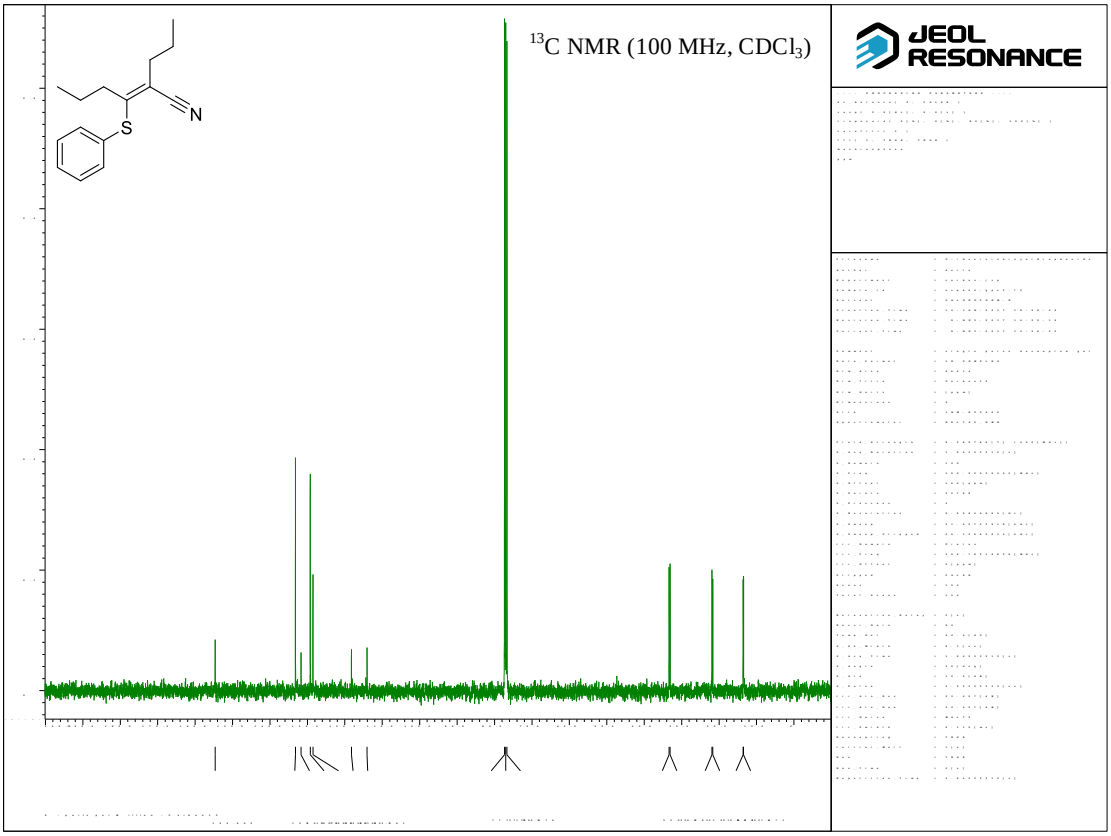
(E)-3-(Phenylthio)-2-propylhex-2-enenitrile ((E)-4aa)



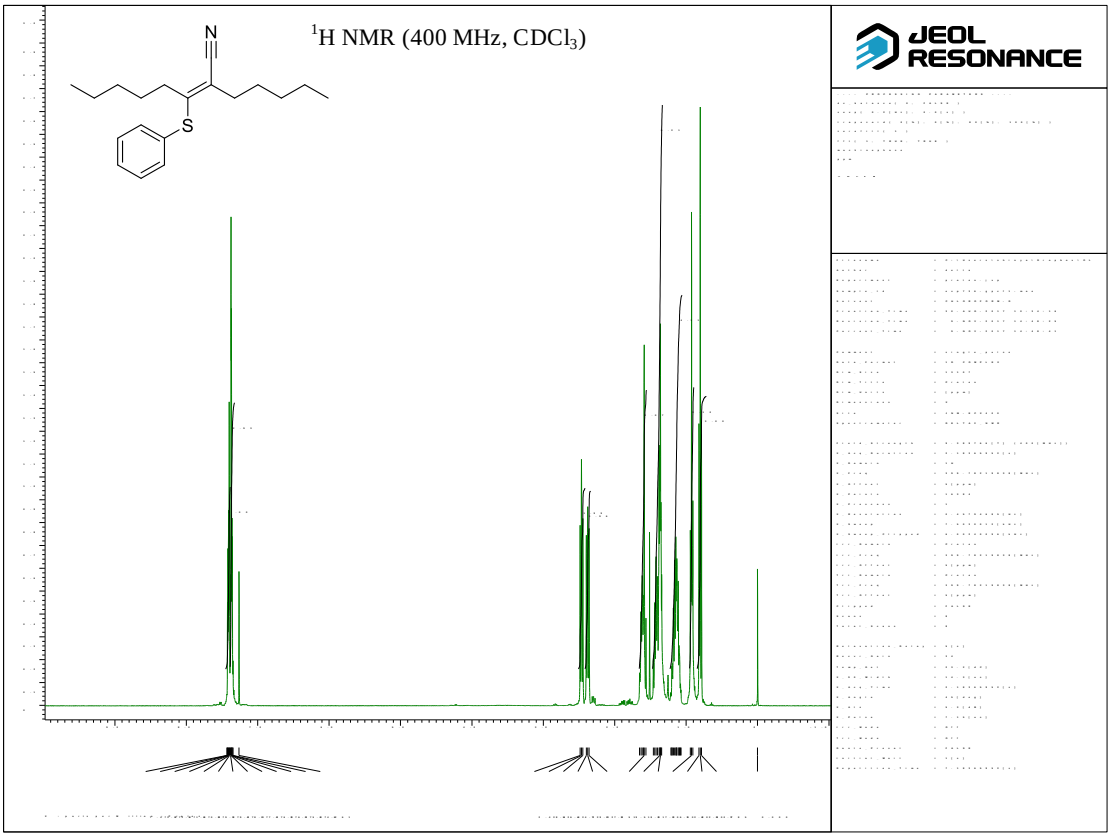


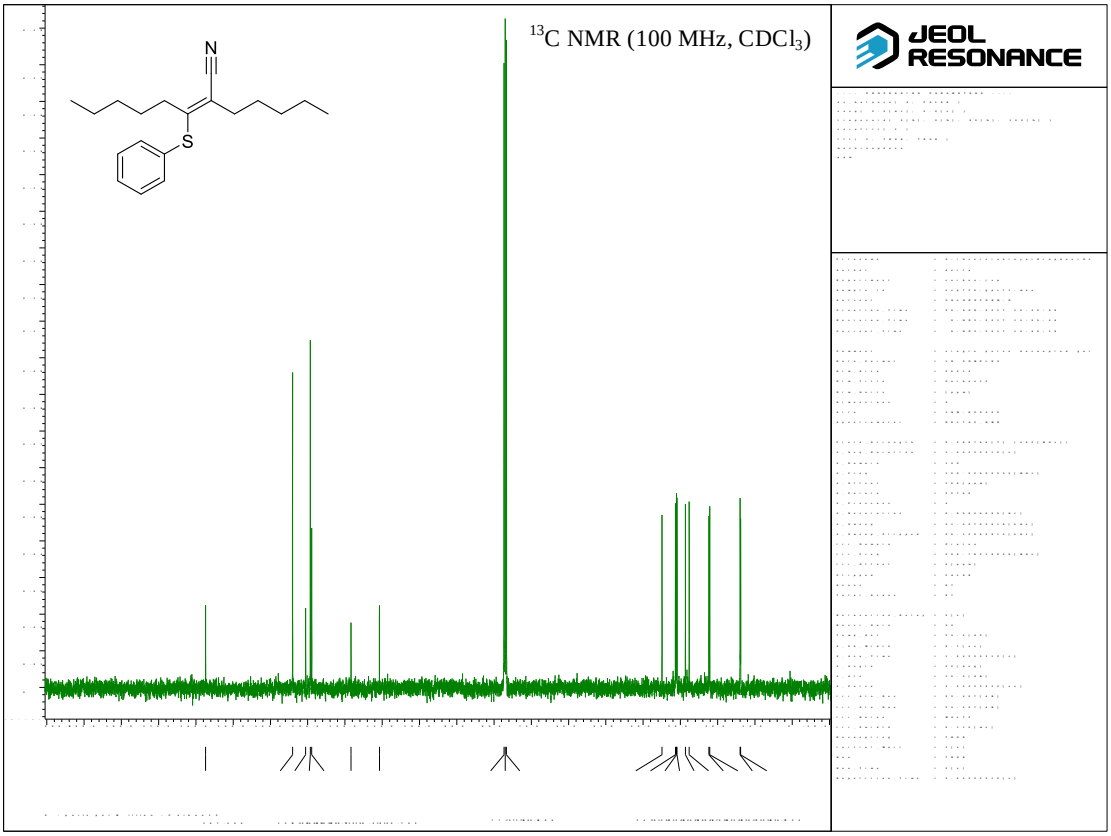
(Z)-3-(Phenylthio)-2-propylhex-2-enenitrile ((Z)-4aa)



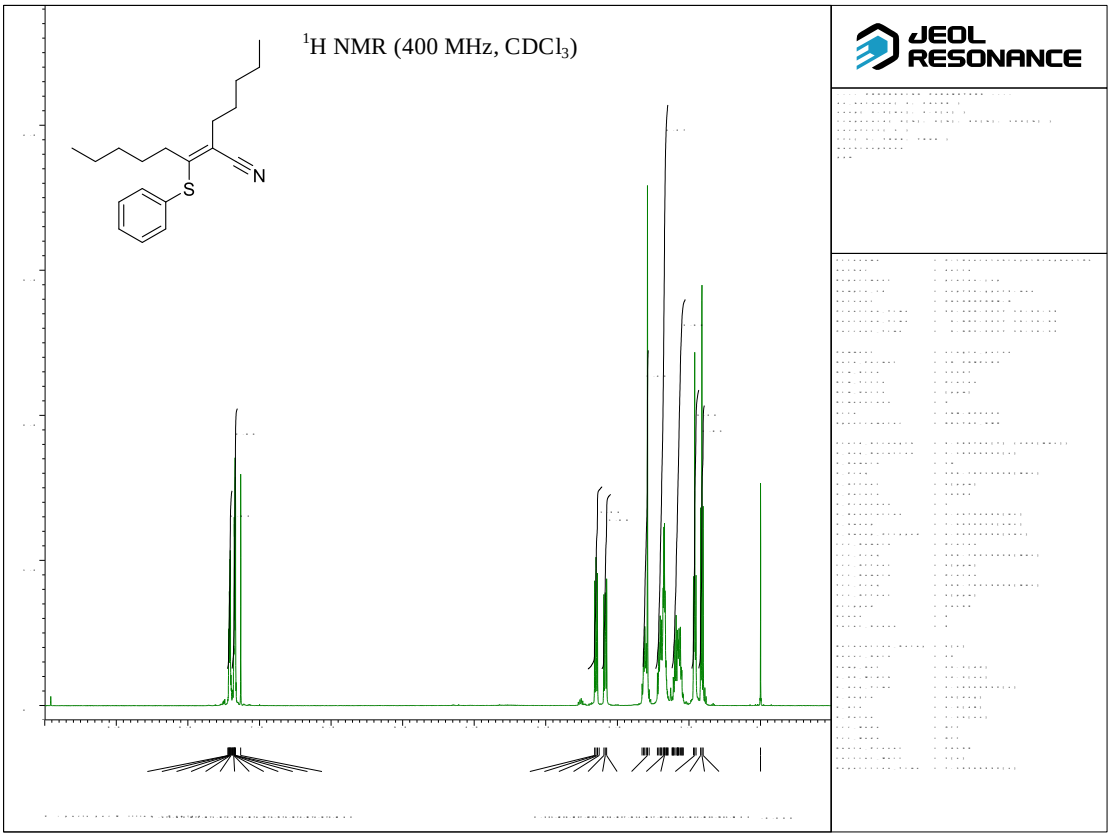


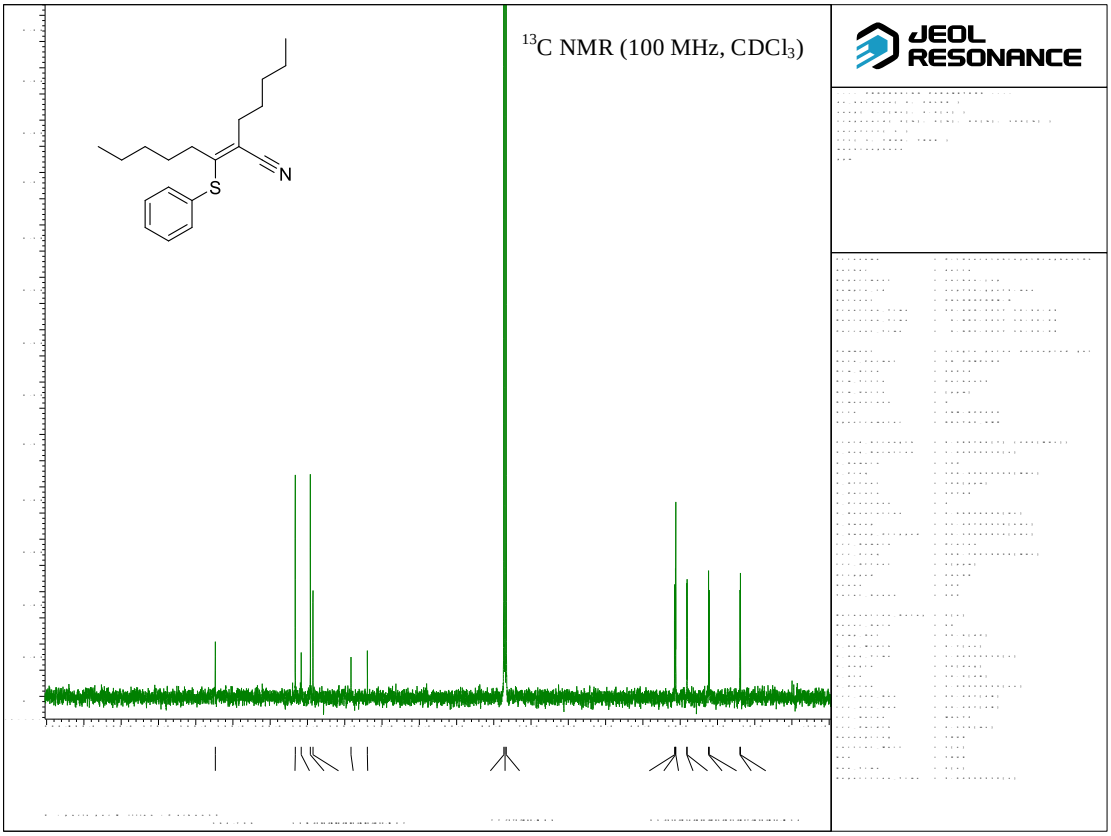
(E)-2-Pentyl-3-(phenylthio)oct-2-enenitrile ((E)-4ba)



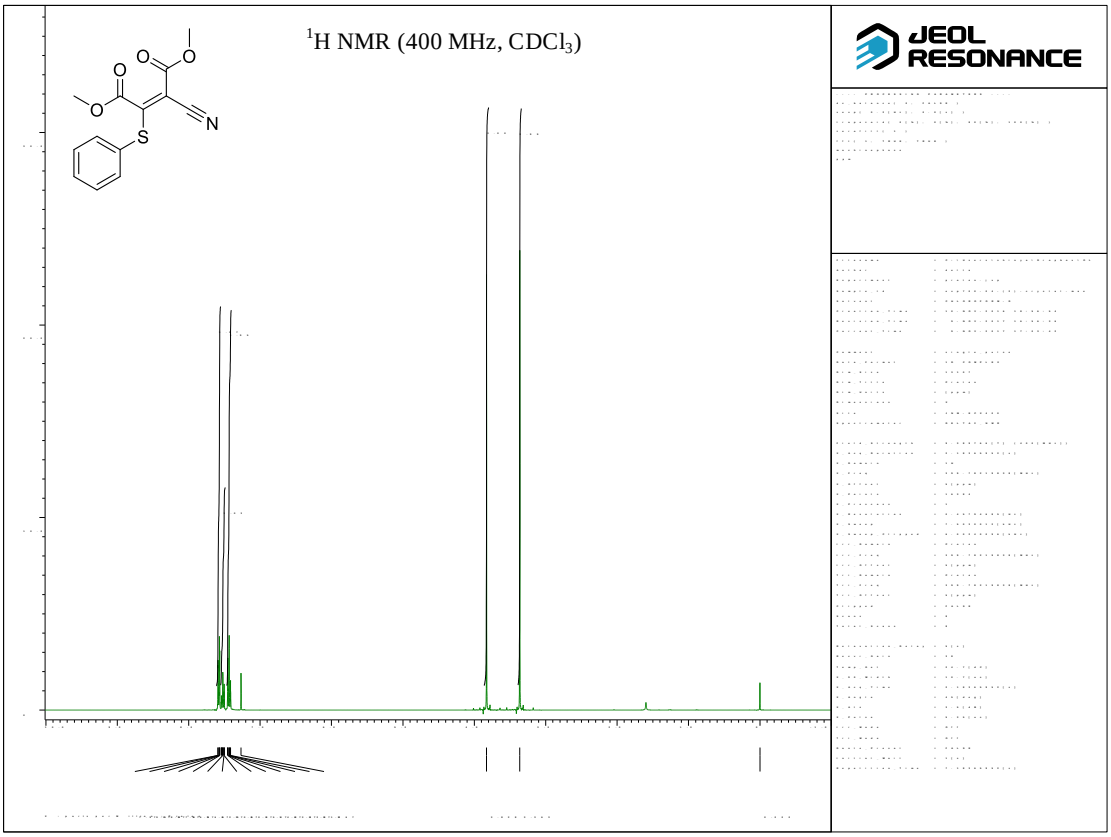


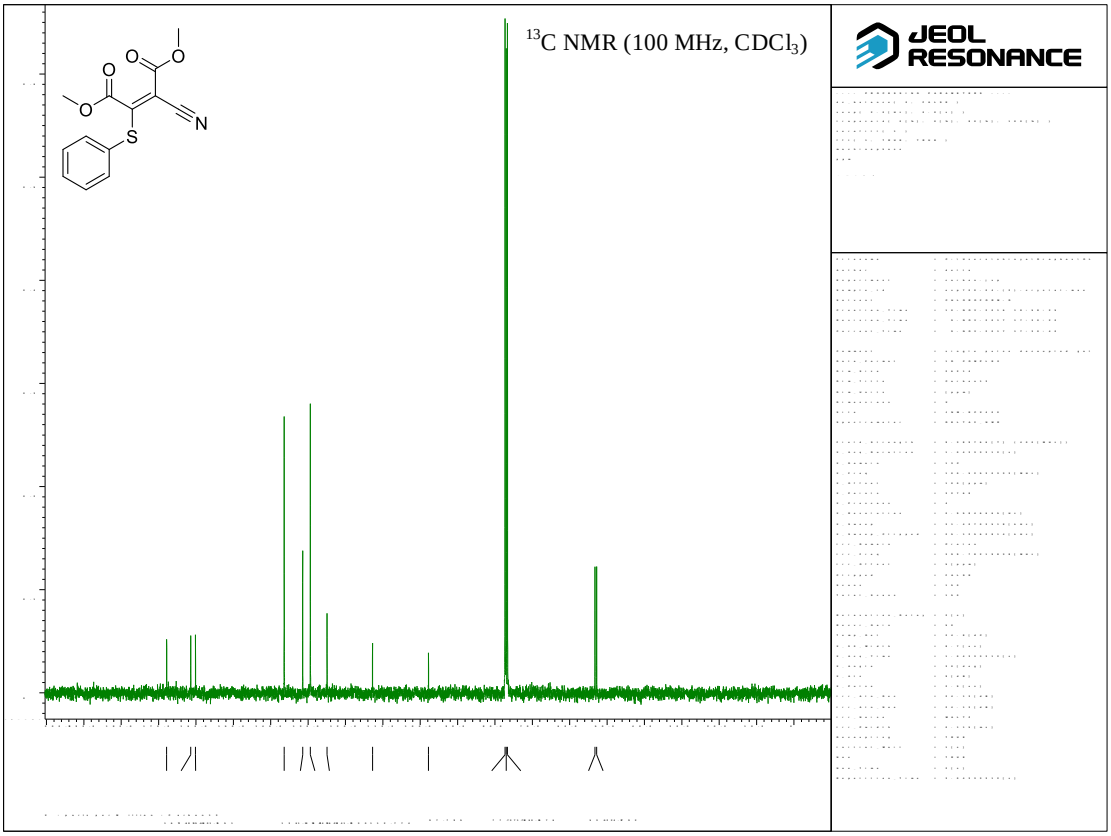
(Z)-2-Pentyl-3-(phenylthio)oct-2-enenitrile ((Z)-4ba)



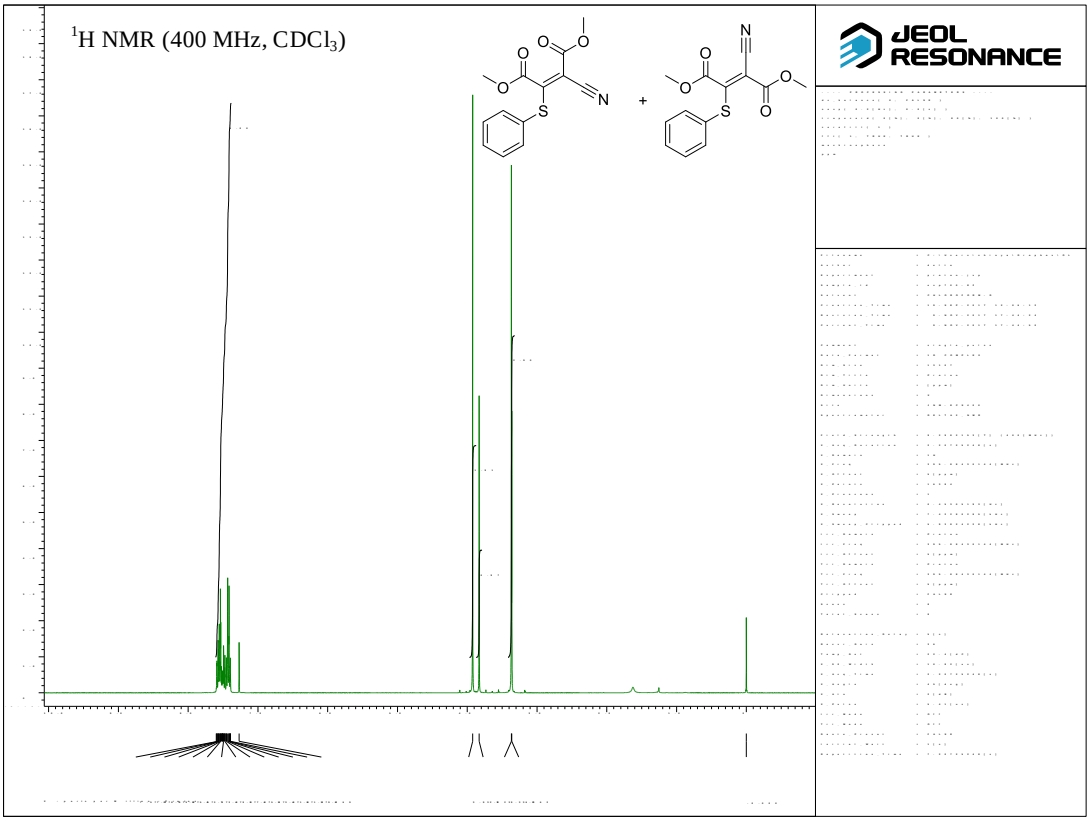


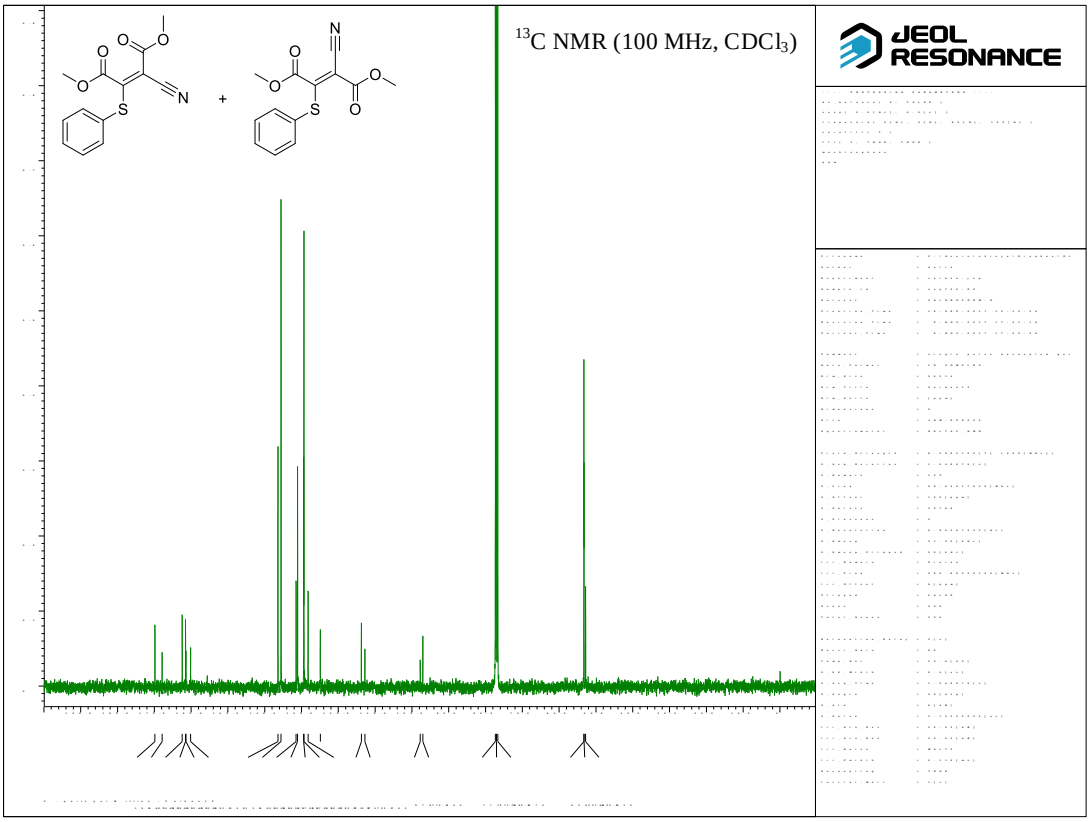
Dimethyl (E)-2-Cyano-3-(phenylthio)but-2-enedioate ((E)-4ca)



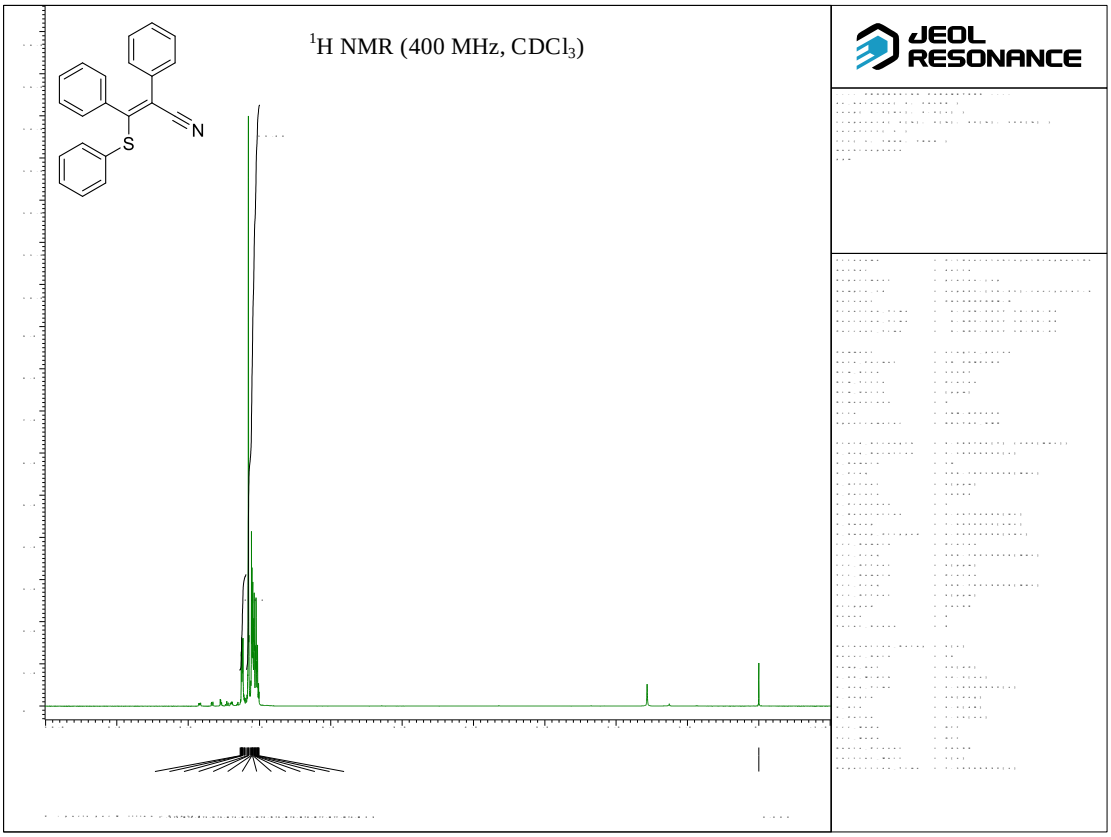


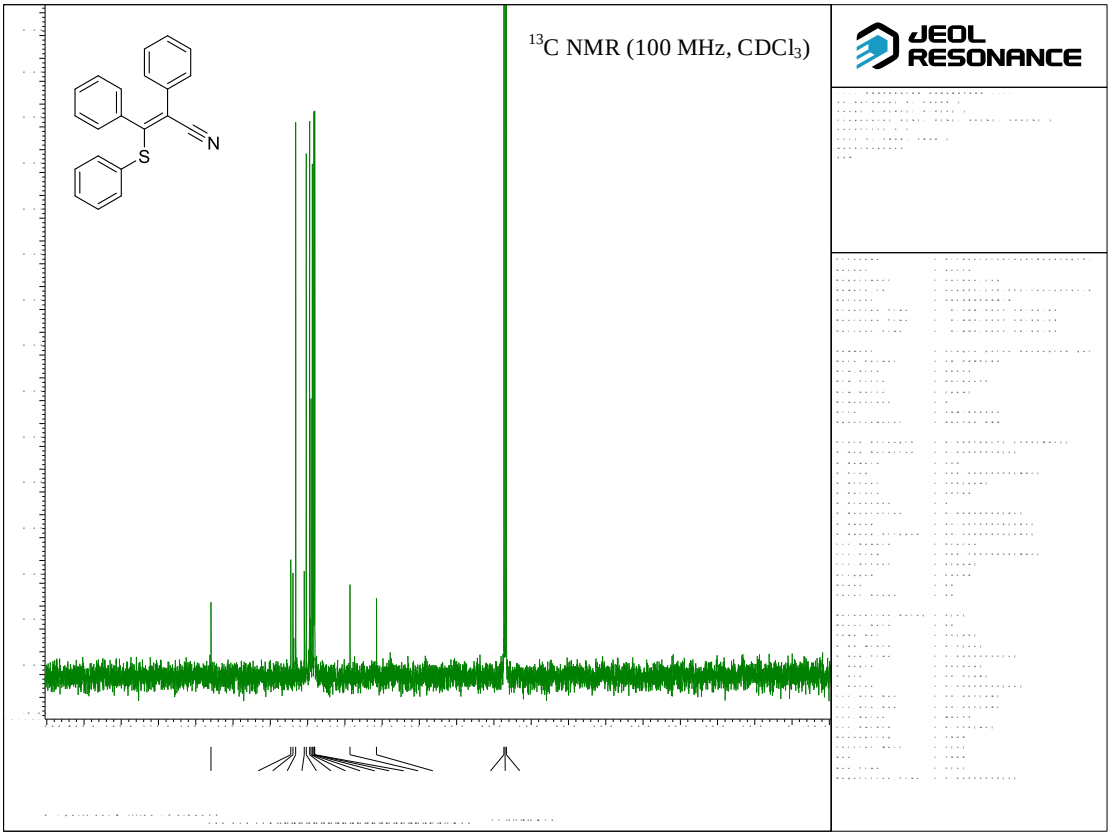
Dimethyl (E)-2-Cyano-3-(phenylthio)but-2-enedioate ((E)-4ca) and Dimethyl (Z)-2-Cyano-3-(phenylthio)but-2-enedioate ((Z)-4ca)





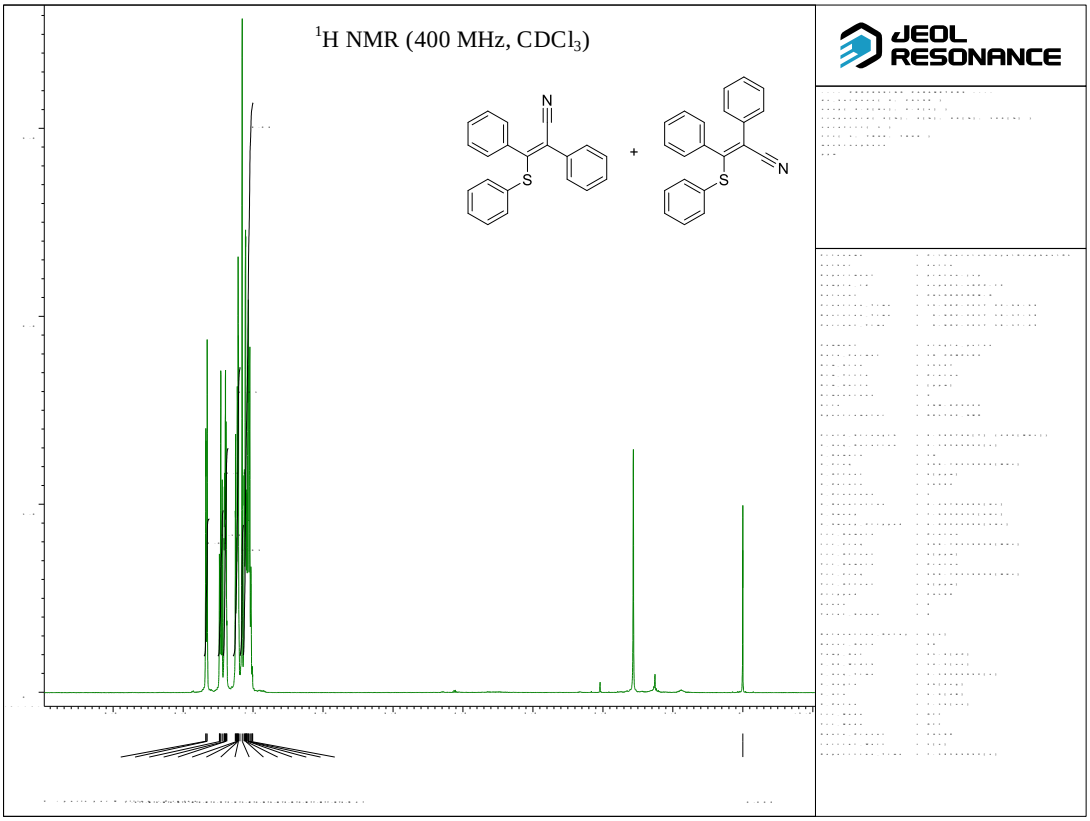
(Z)-2,3-Diphenyl-3-(phenylthio)acrylonitrile ((Z)-4da)

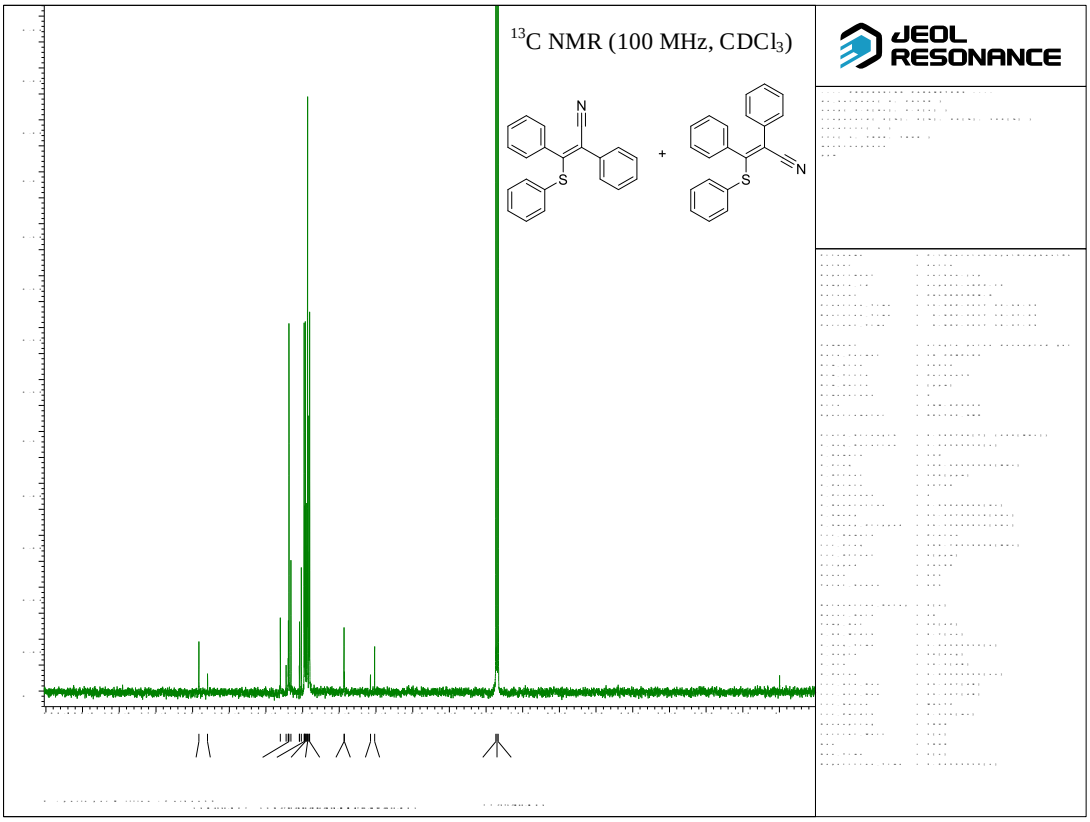




(E)-2,3-Diphenyl-3-(phenylthio)acrylonitrile ((E)-4da) and

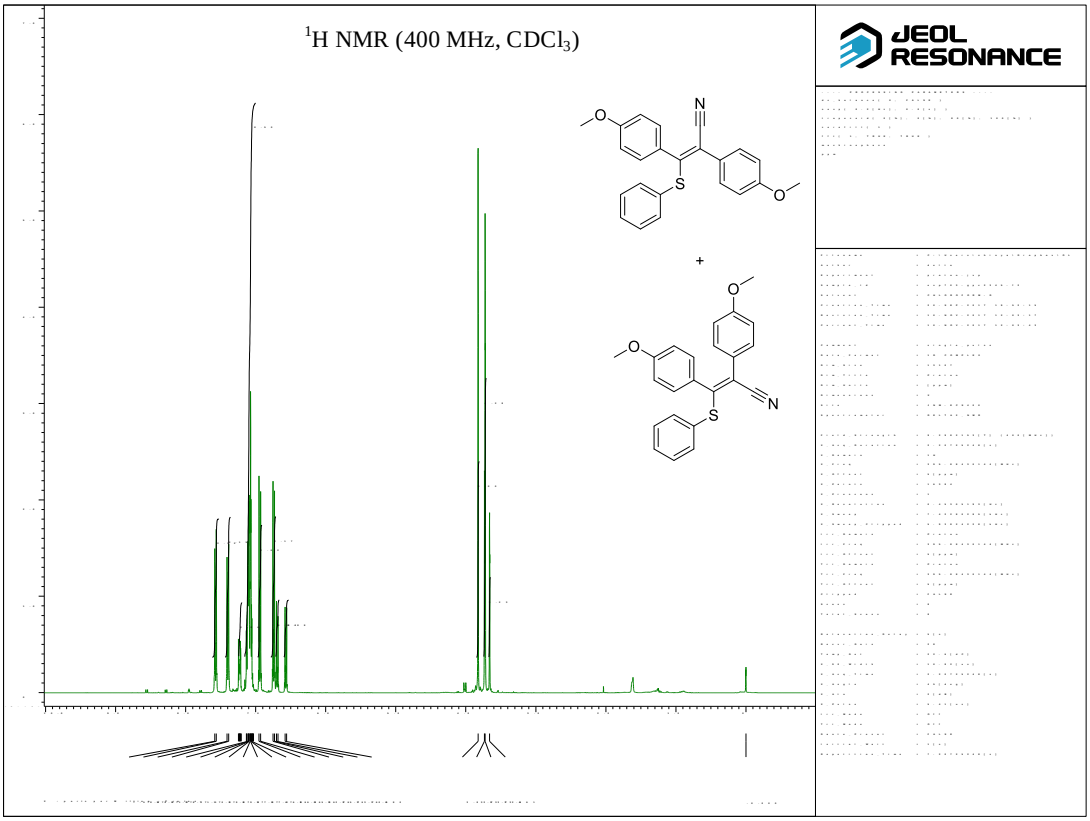
(Z)-2,3-Diphenyl-3-(phenylthio)acrylonitrile ((Z)-4da)

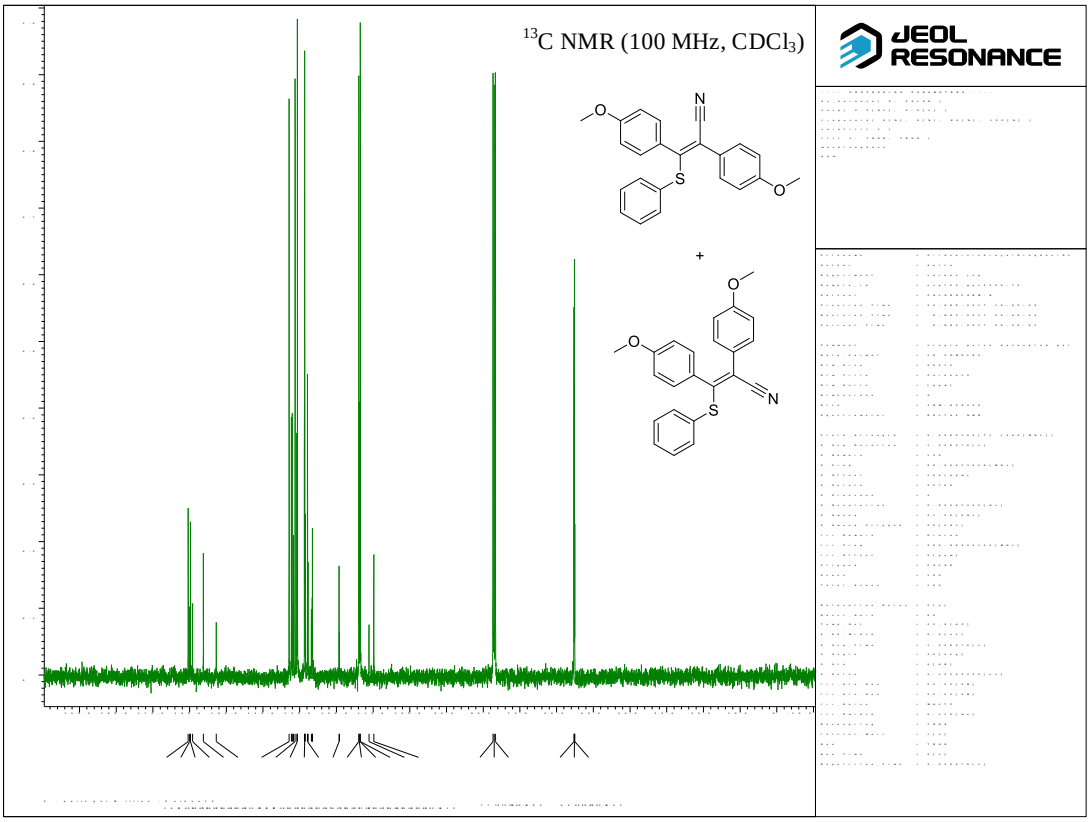




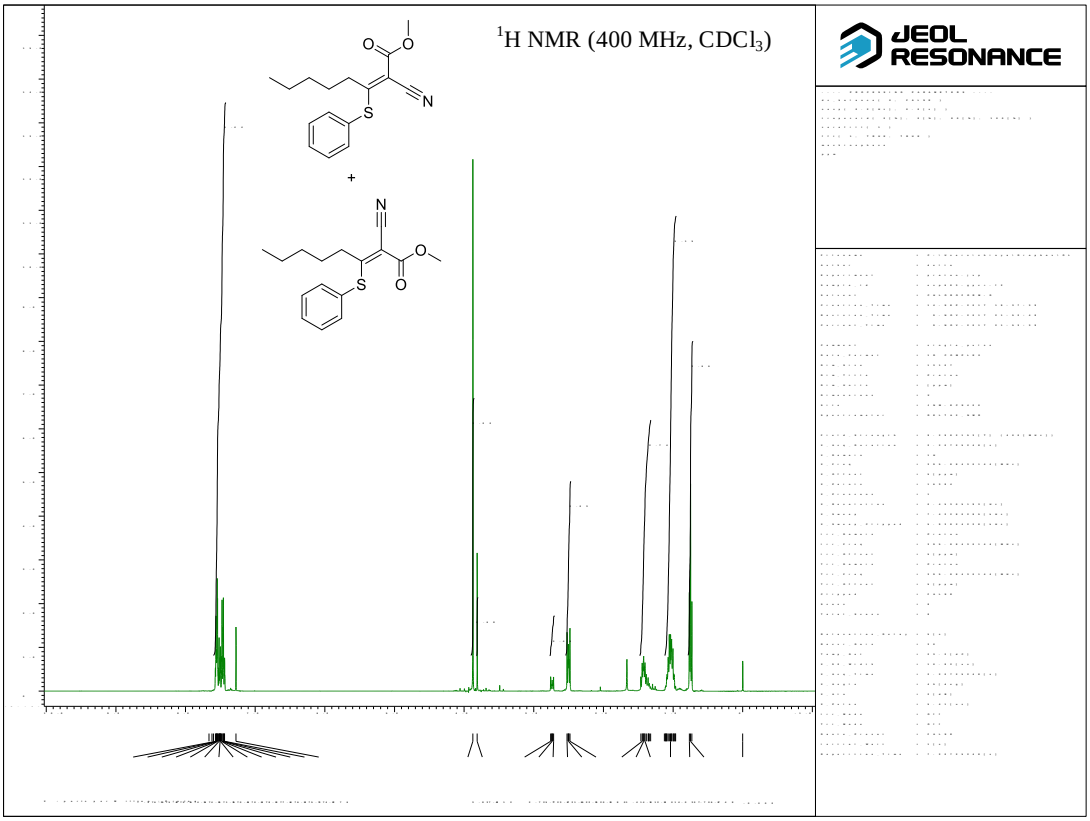
(E)-2,3-Bis(4-methoxyphenyl)-3-(phenylthio)acrylonitrile ((E)-4ea) and

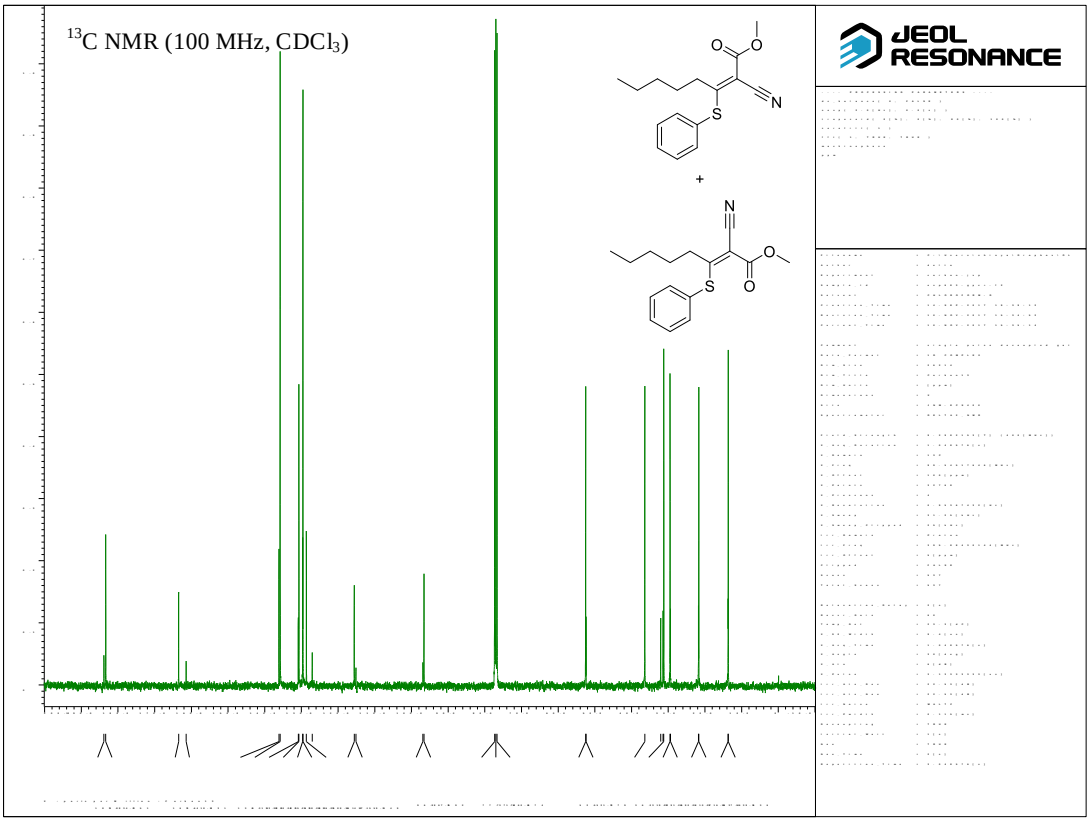
(Z)-2,3-Bis(4-methoxyphenyl)-3-(phenylthio)acrylonitrile ((Z)-4ea)



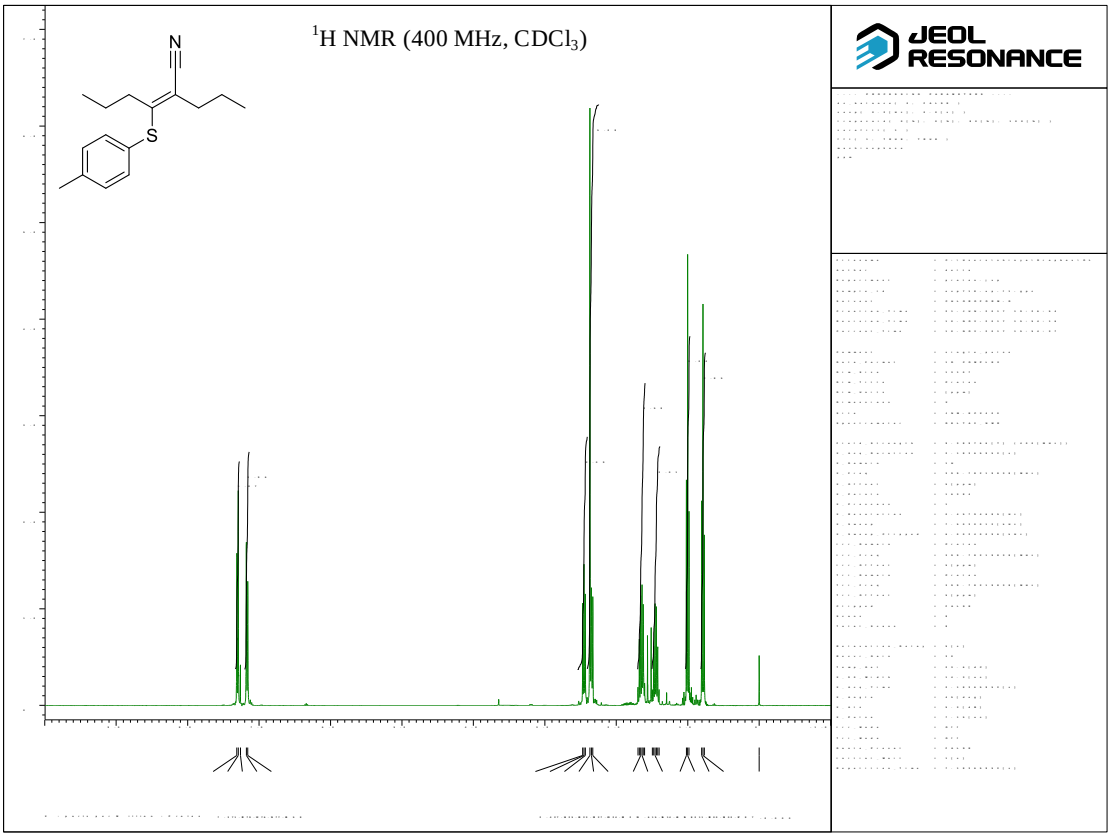


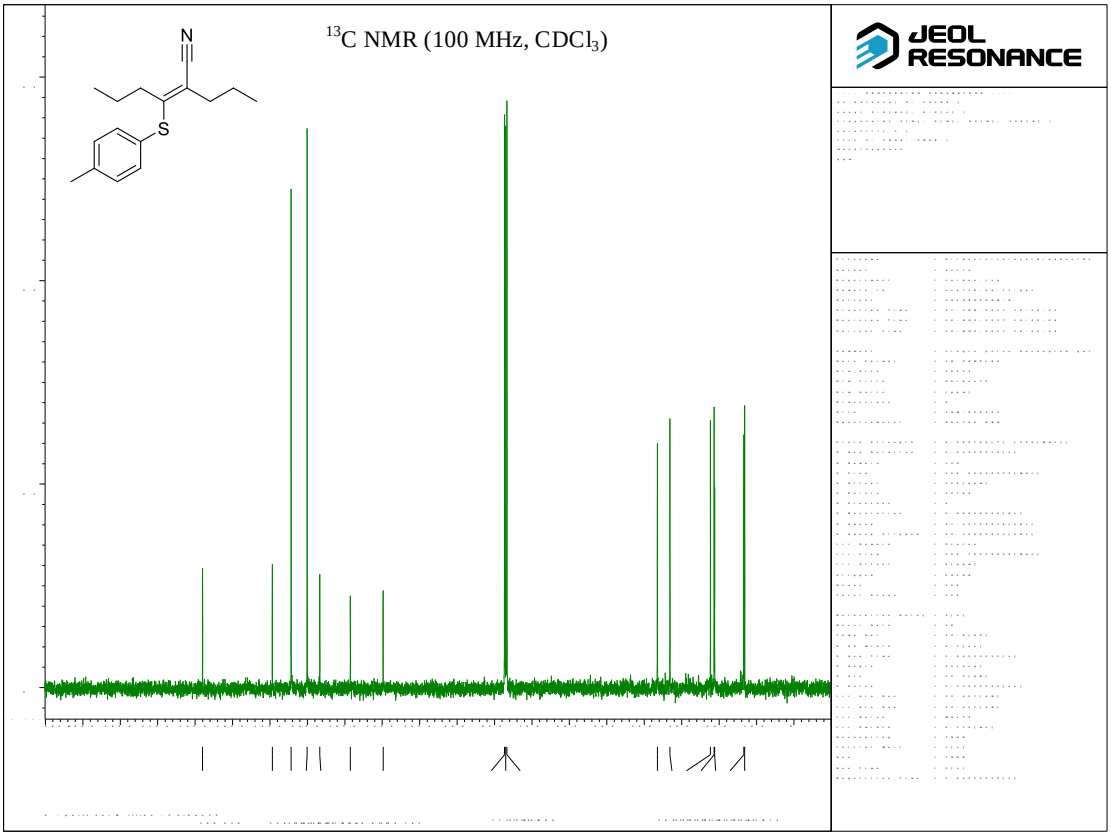
Methyl (E)-2-Cyano-3-(phenylthio)oct-2-enoate ((E)-4fa) and Methyl (Z)-2-Cyano-3-(phenylthio)oct-2-enoate ((Z)-4fa)



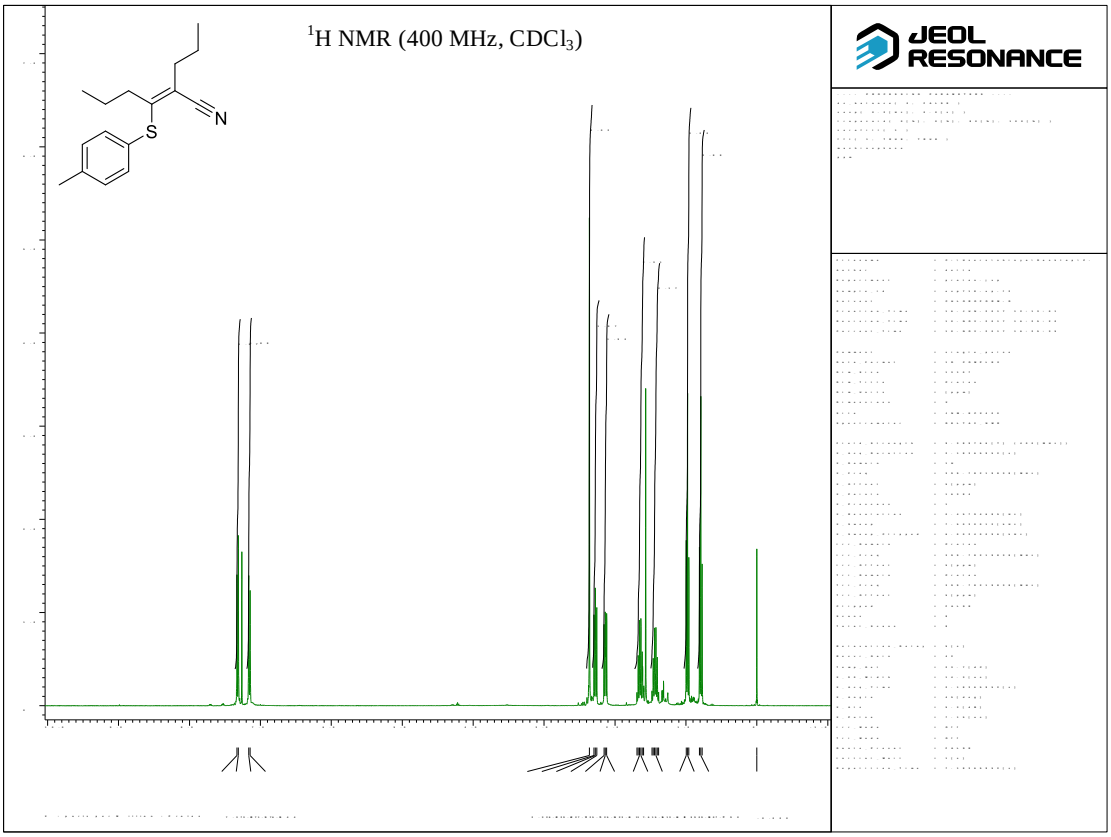


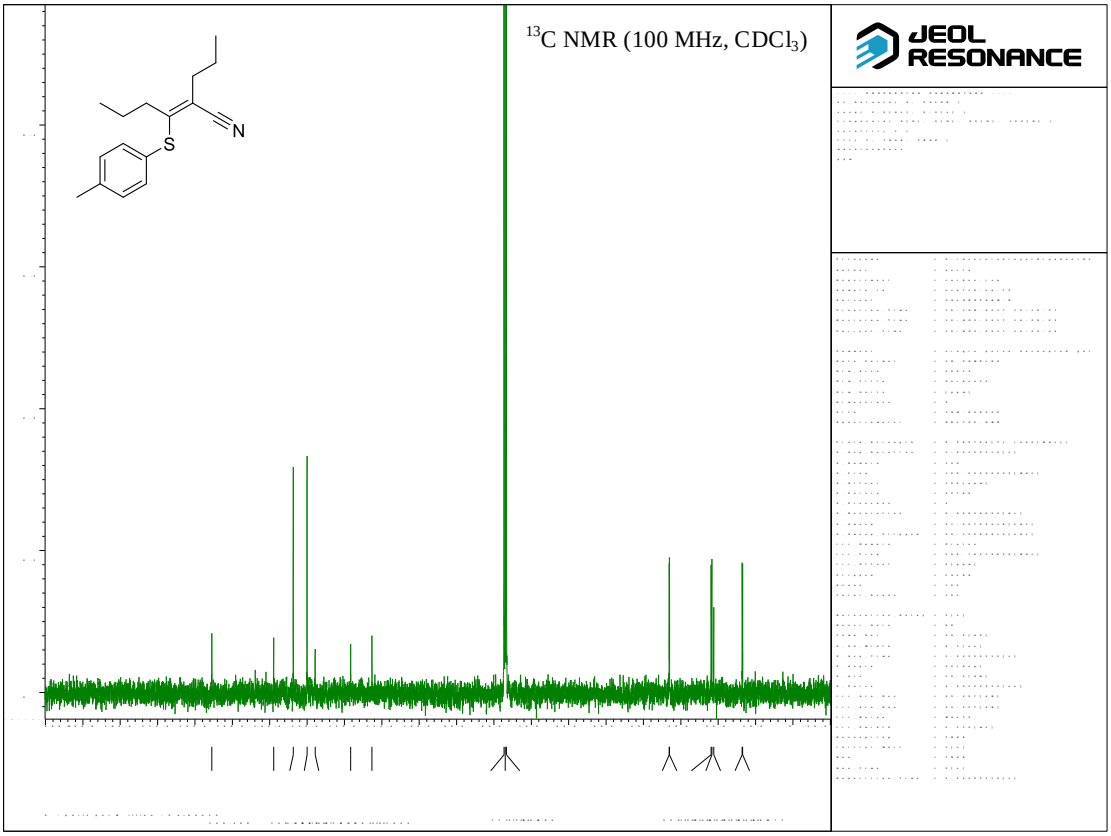
(E)-2-Propyl-3-(p-tolylthio)hex-2-enenitrile ((E)-4ab)





(Z)-2-Propyl-3-(p-tolylthio)hex-2-enenitrile ((Z)-4ab)





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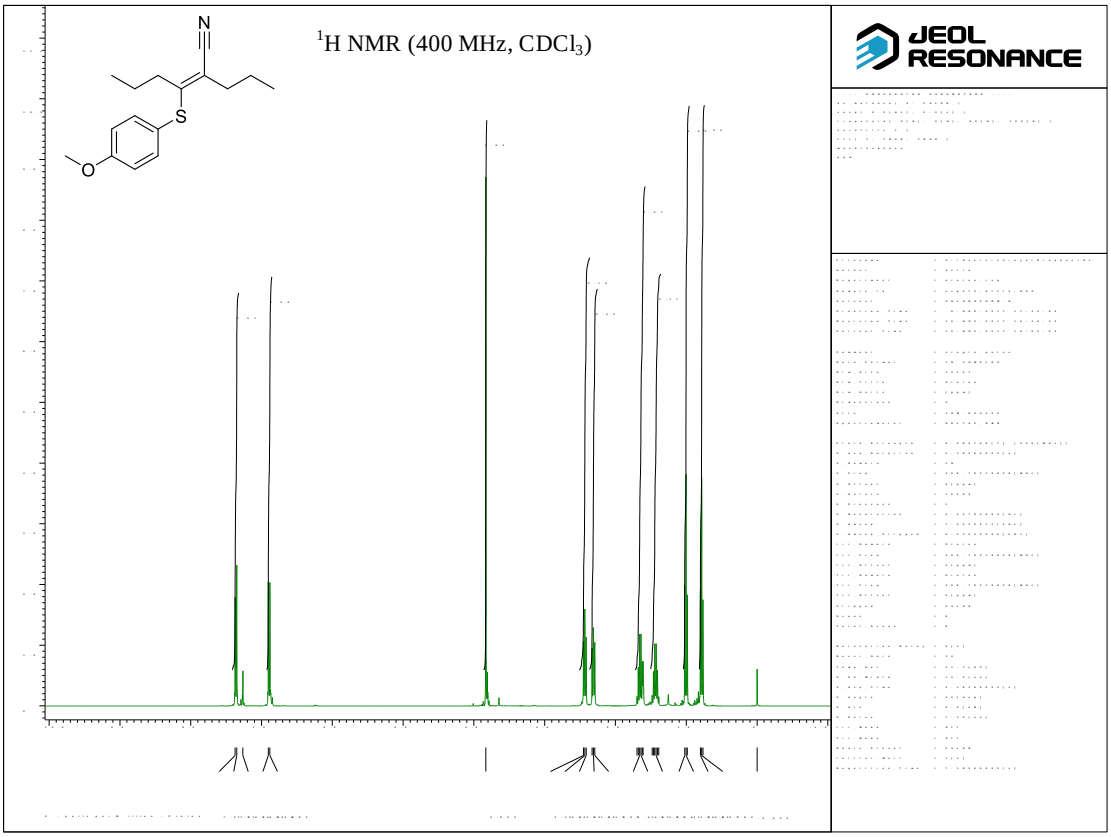

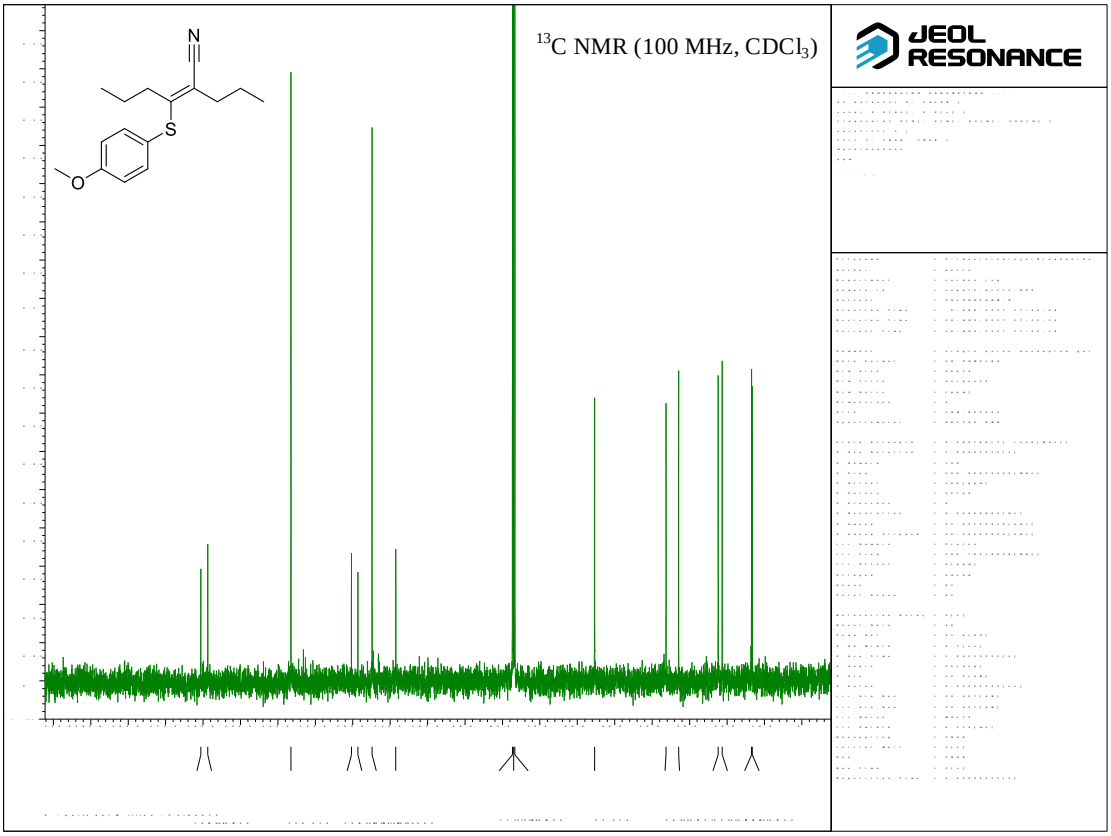

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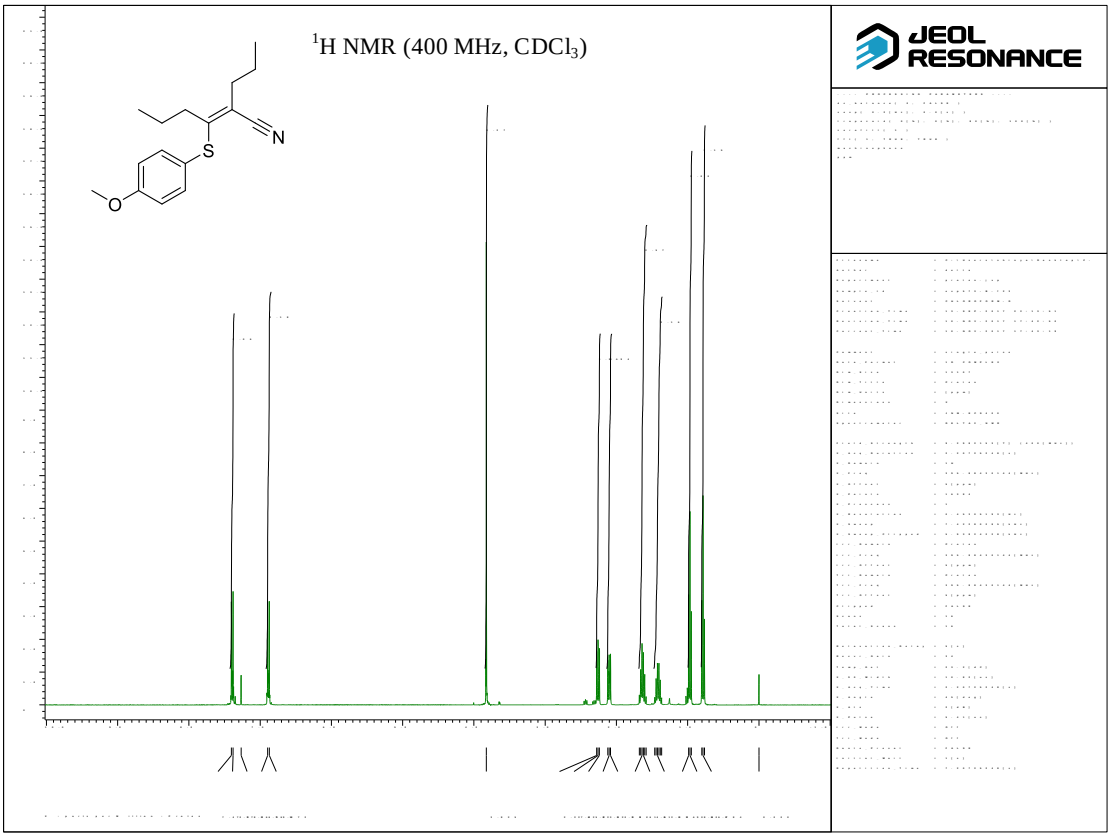

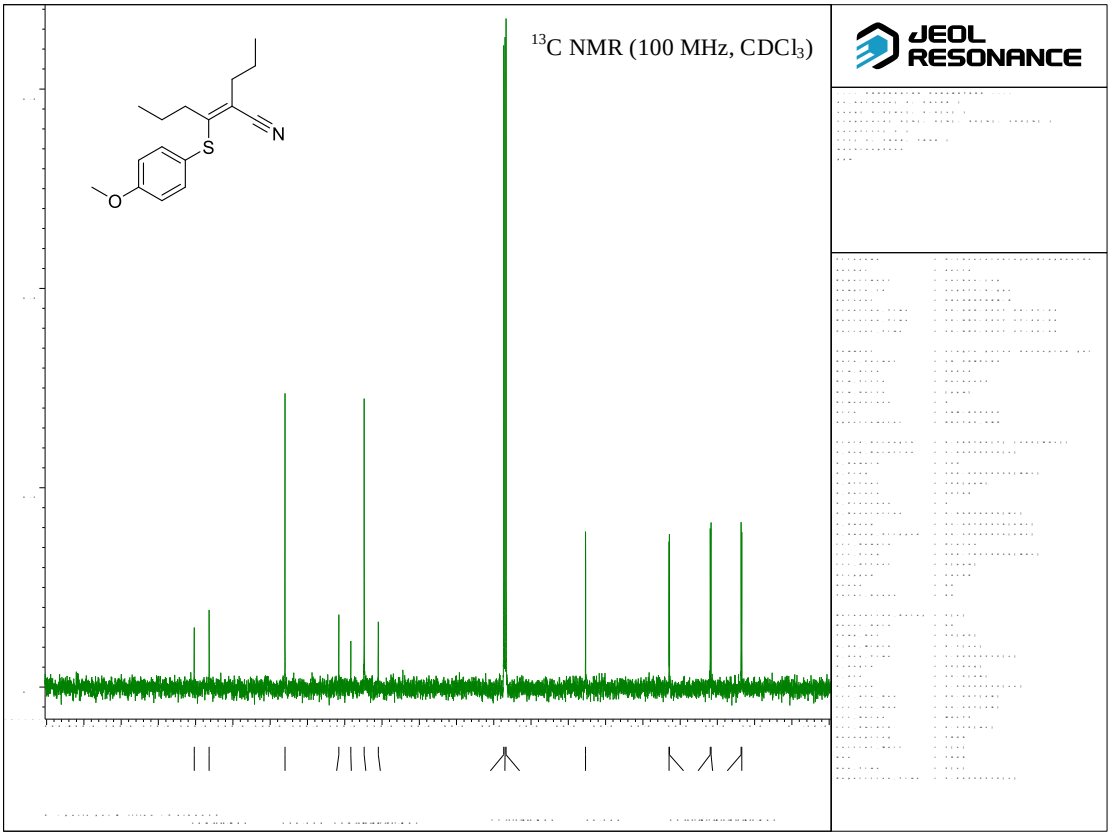

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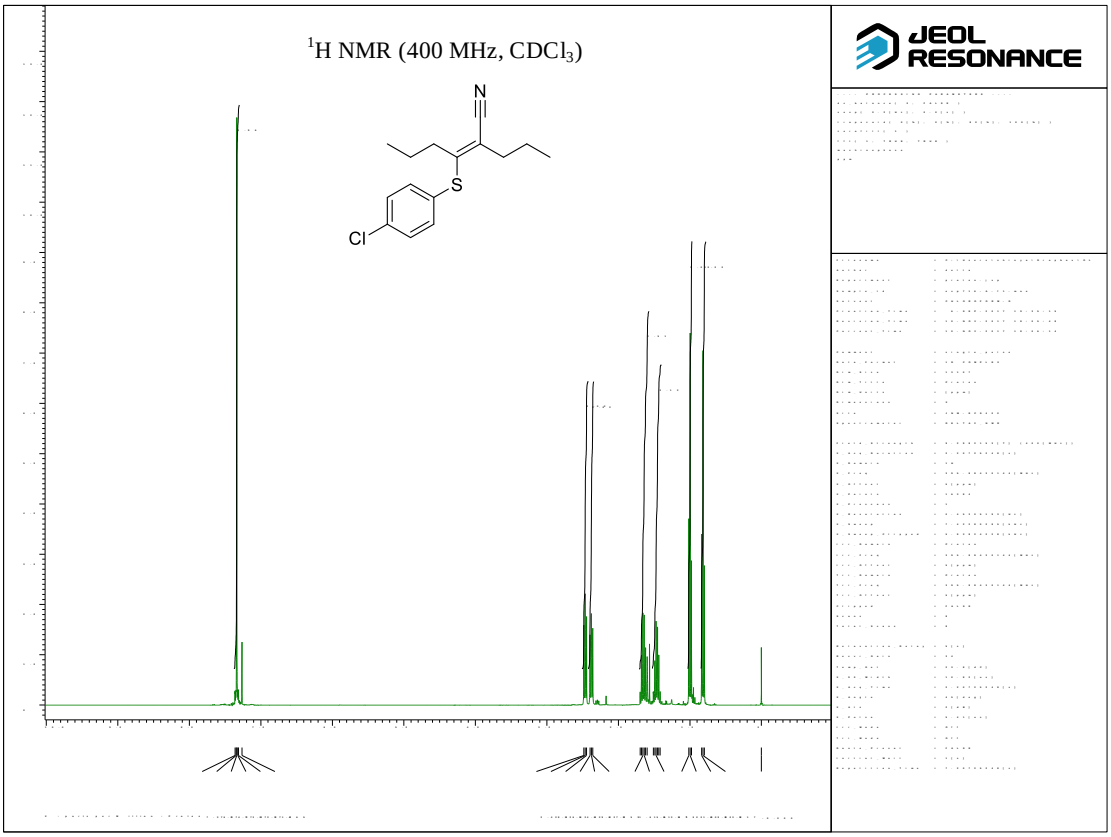

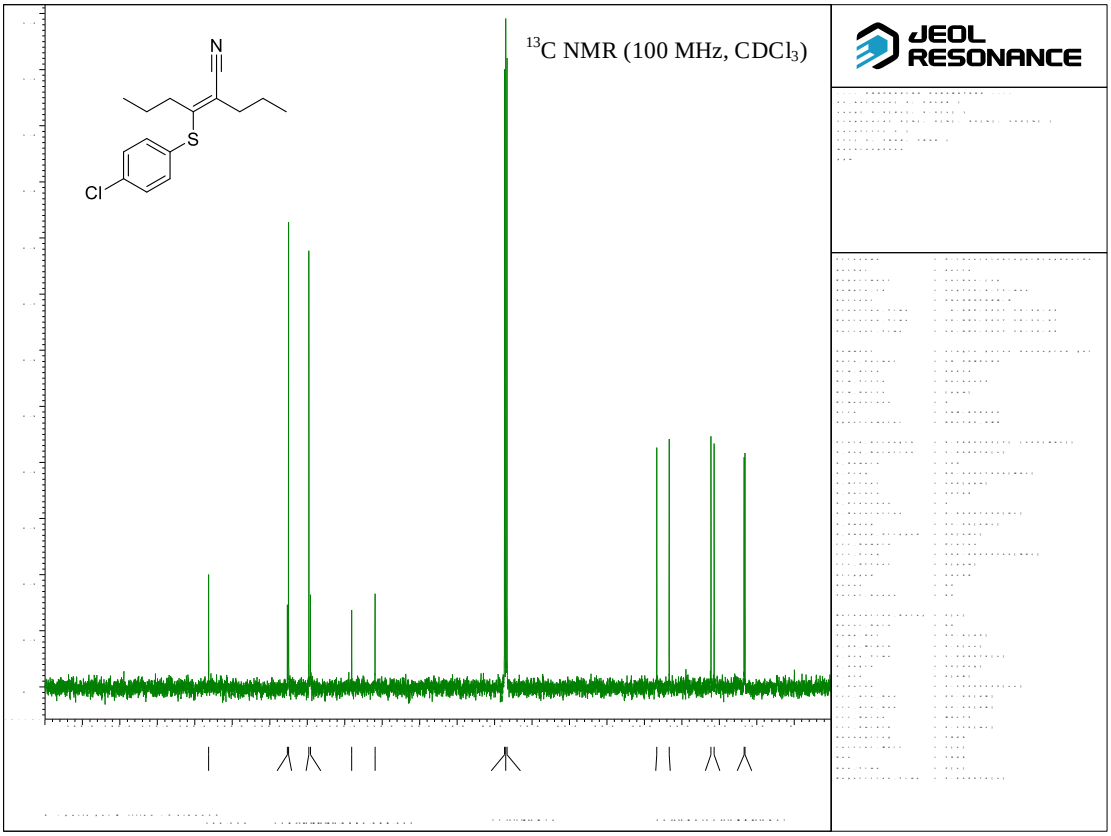

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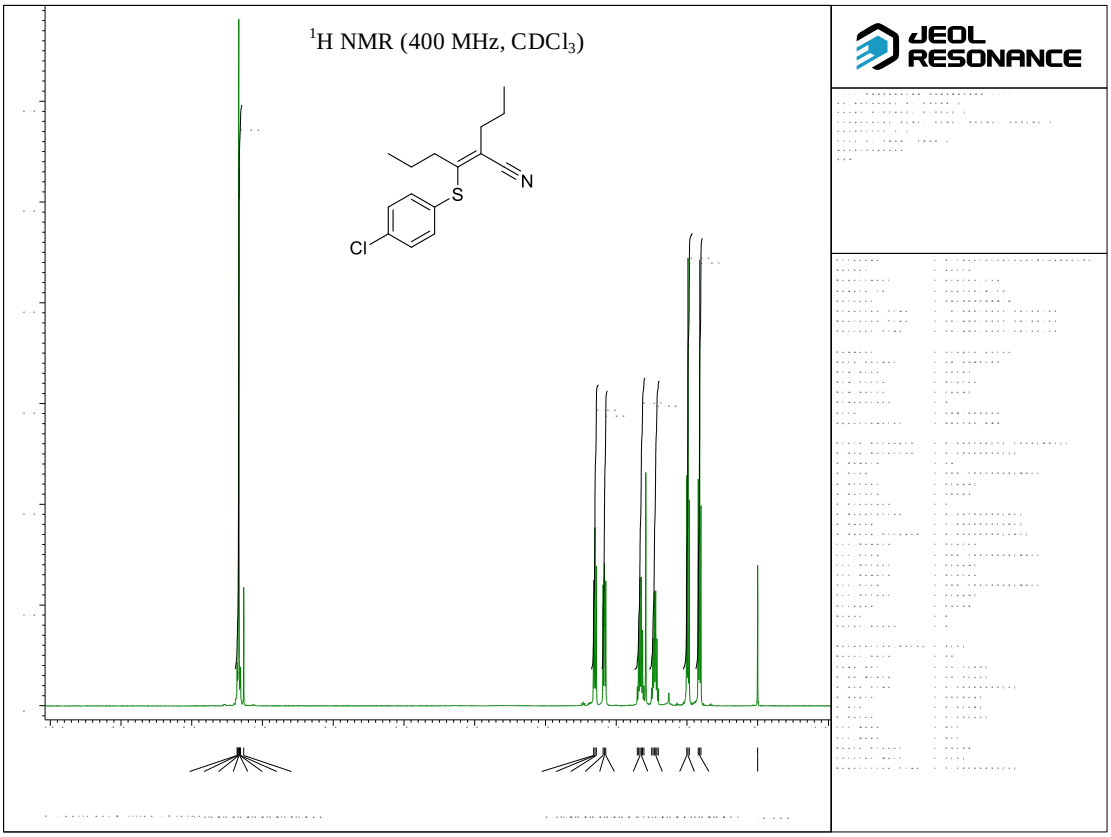

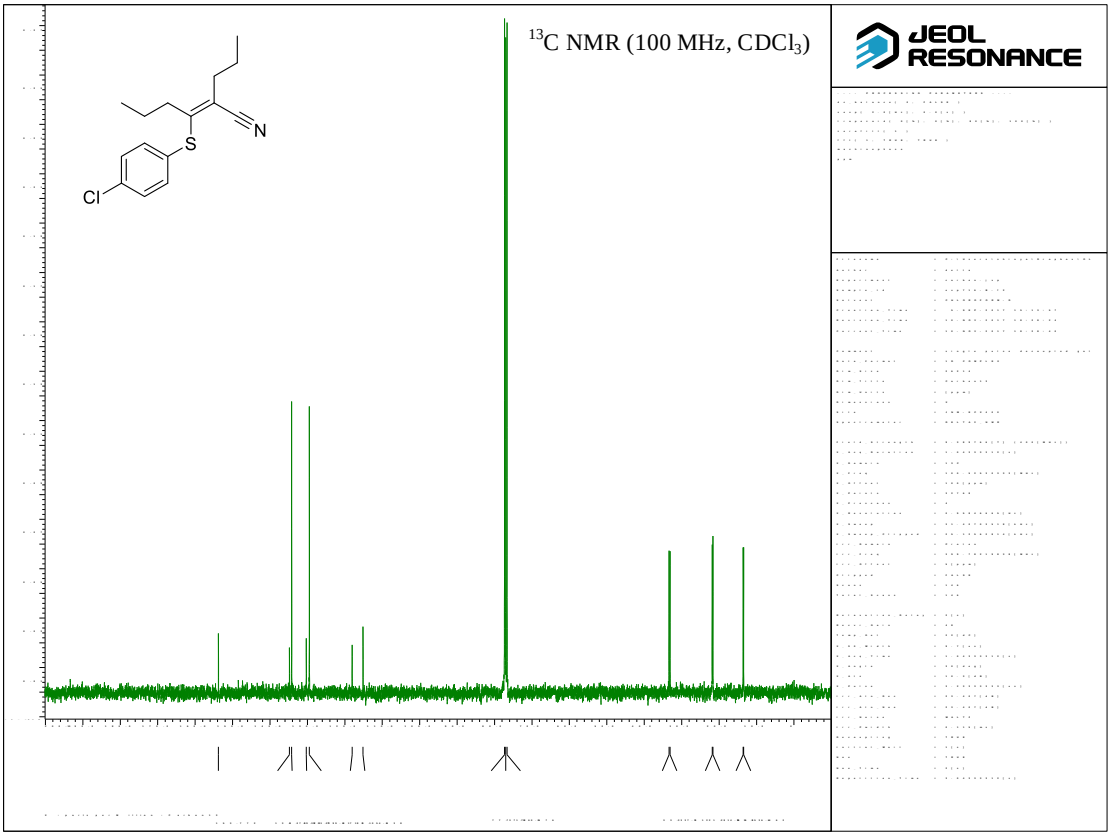

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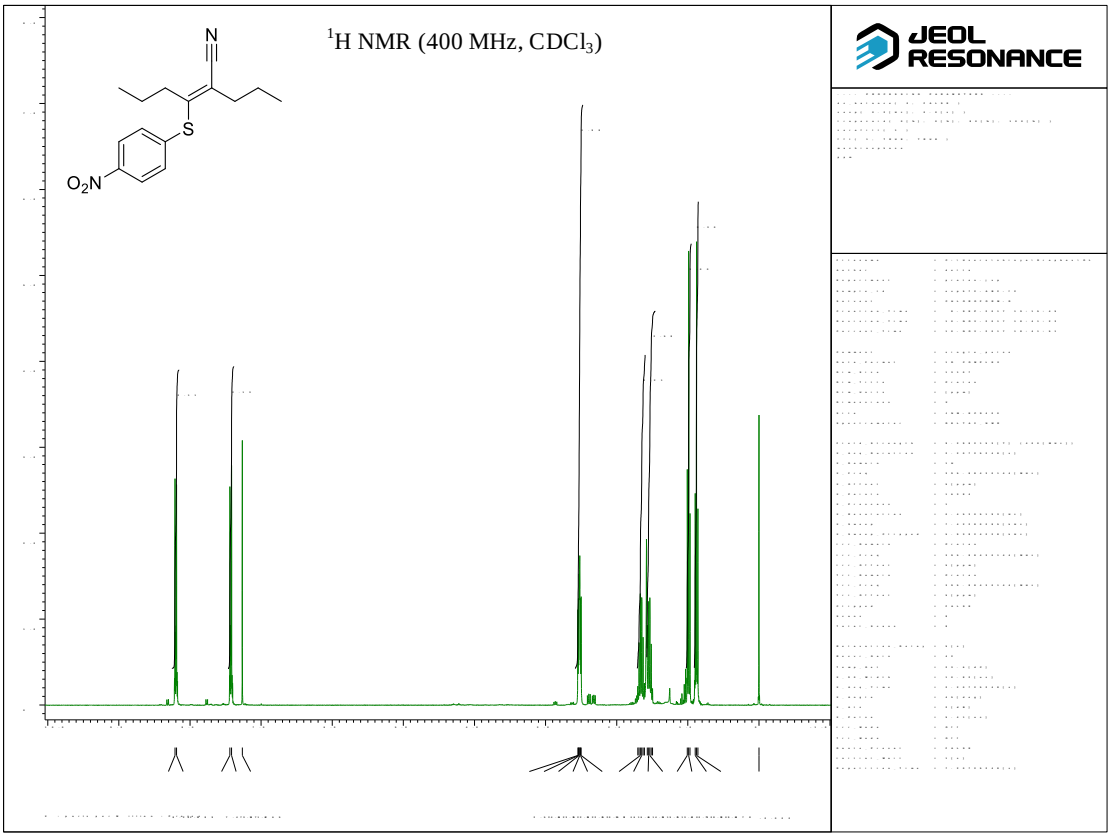
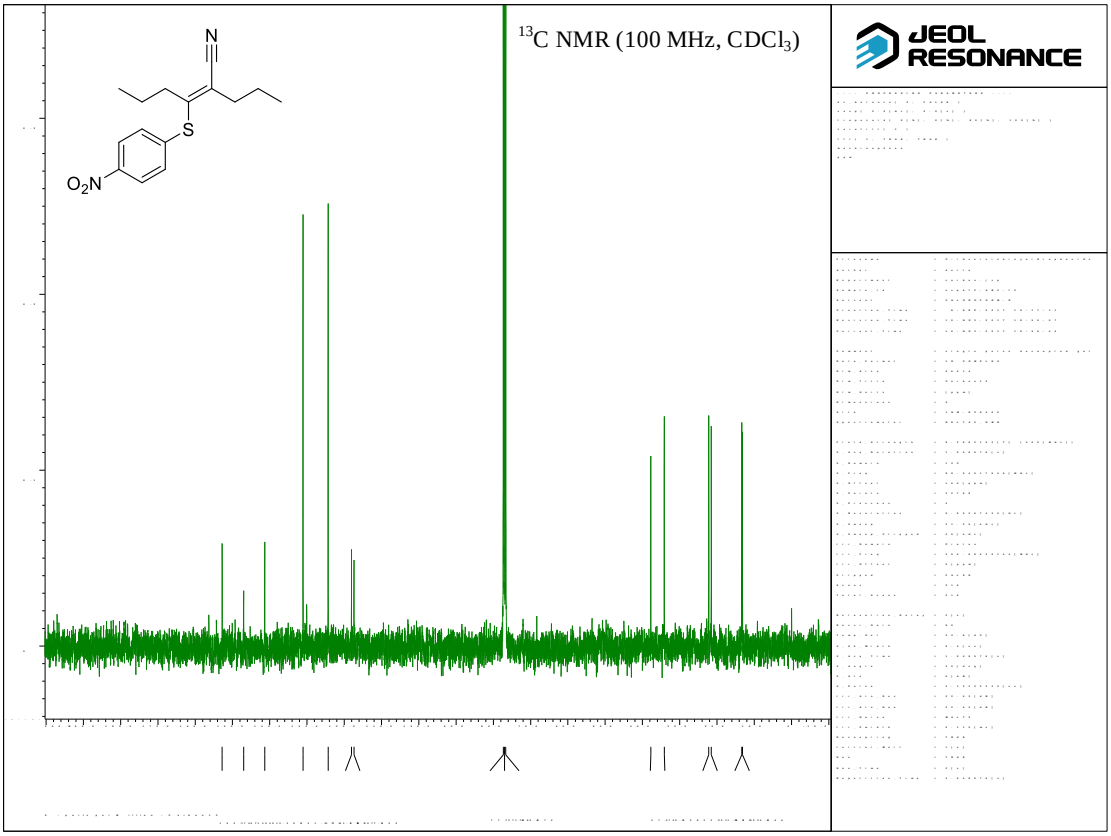
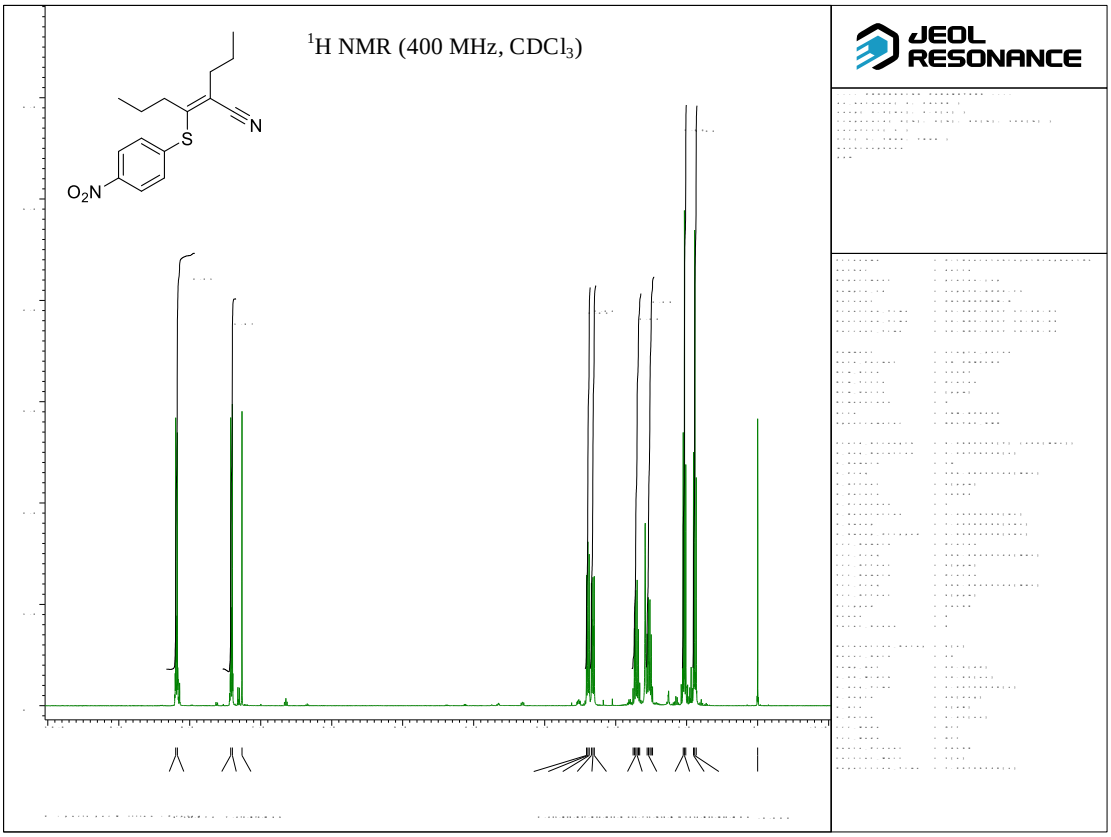
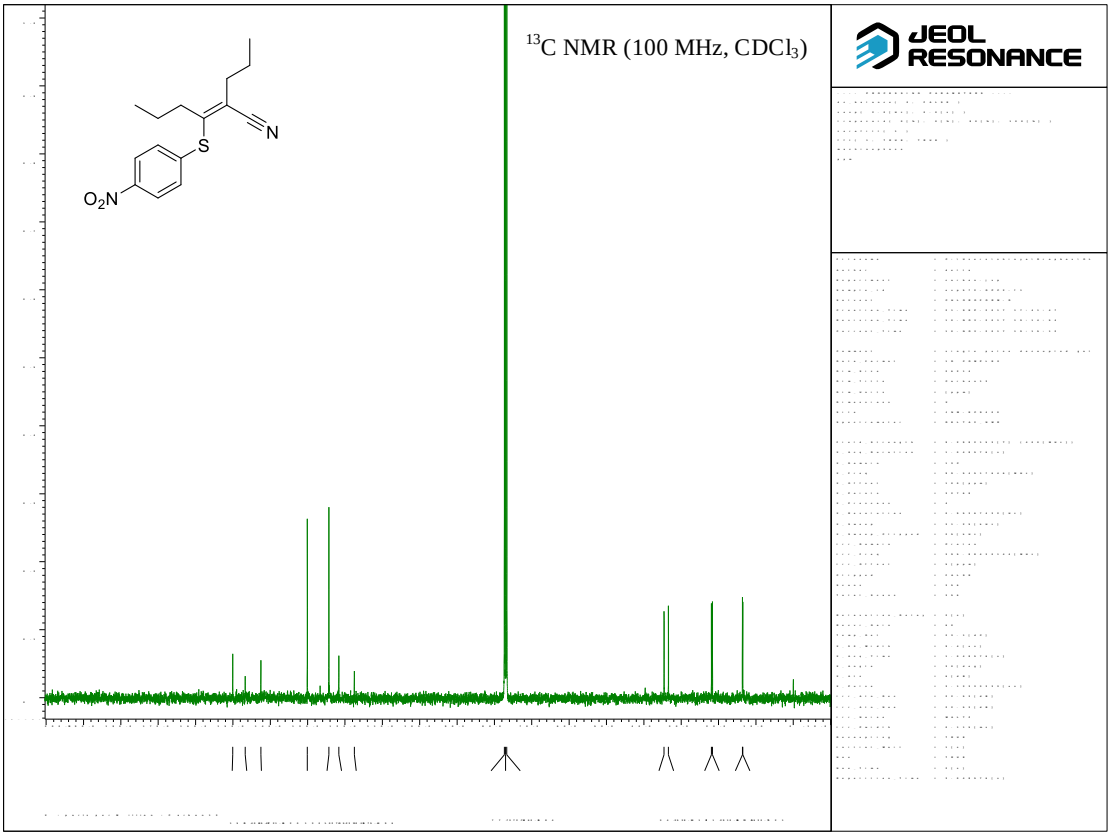




(Z)-3-((4-Nitrophenyl)thio)-2-propylhex-2-enenitrile ((Z)-4ae)





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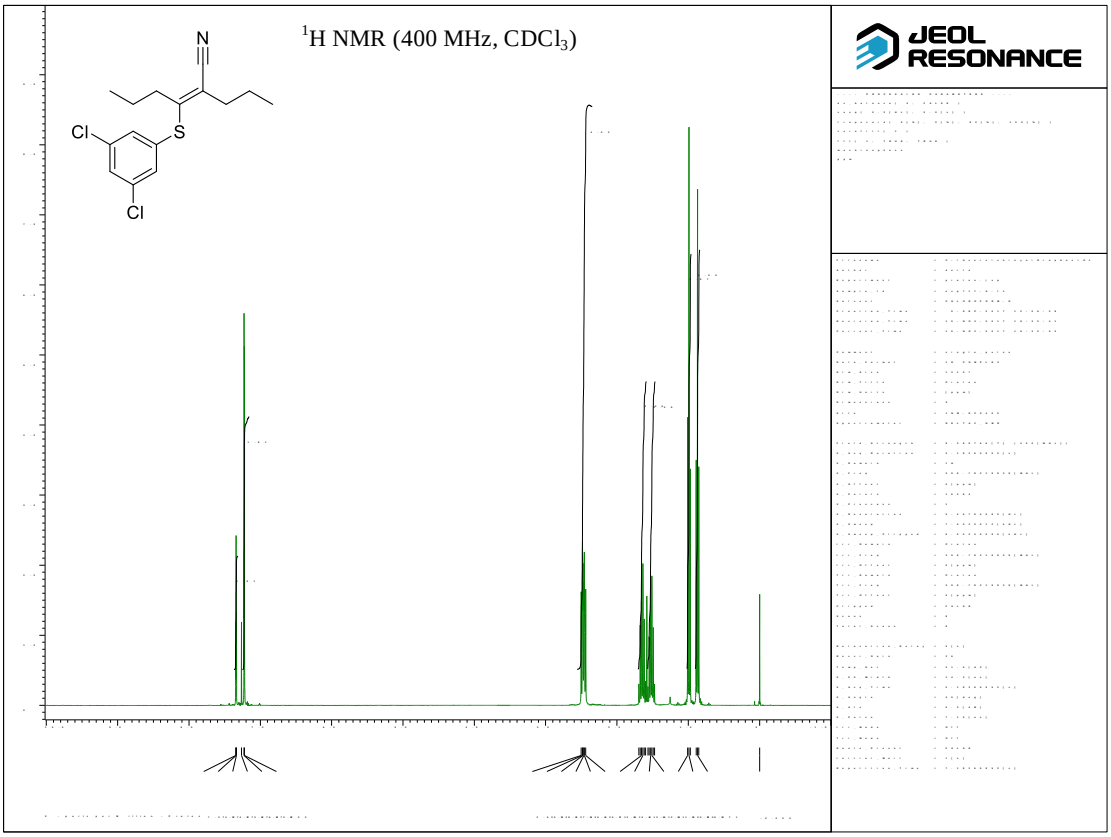

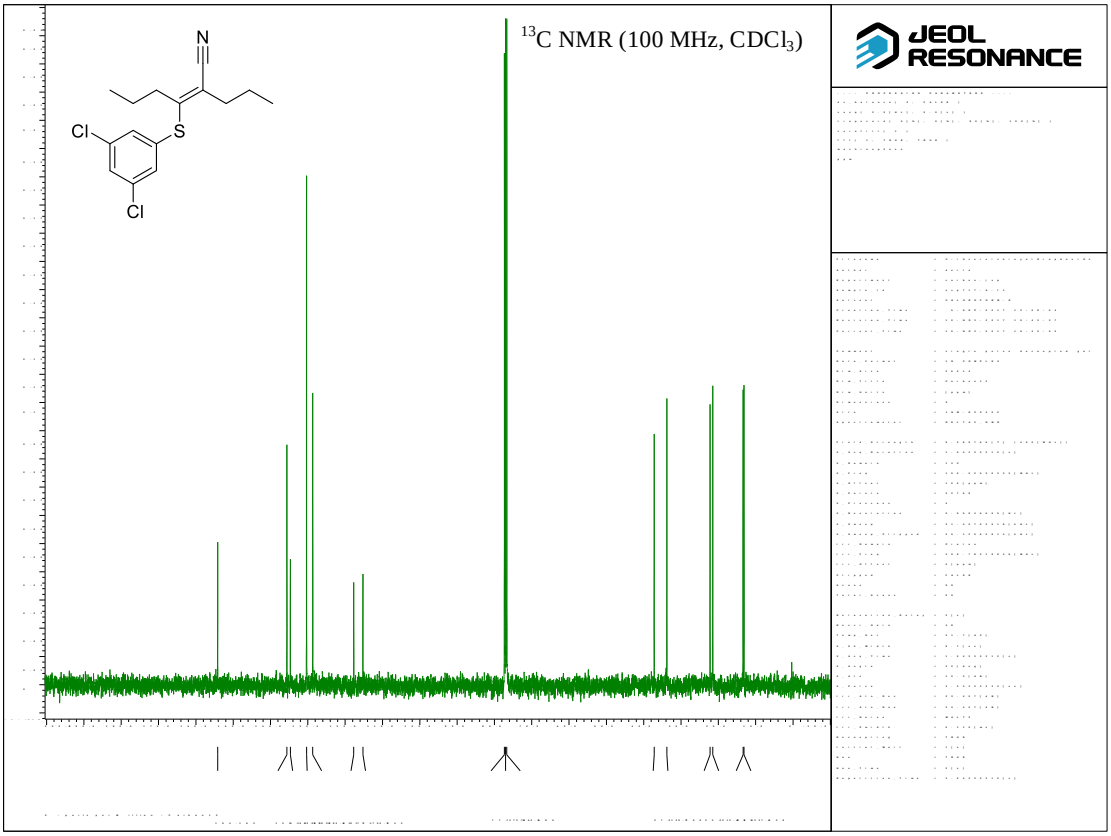

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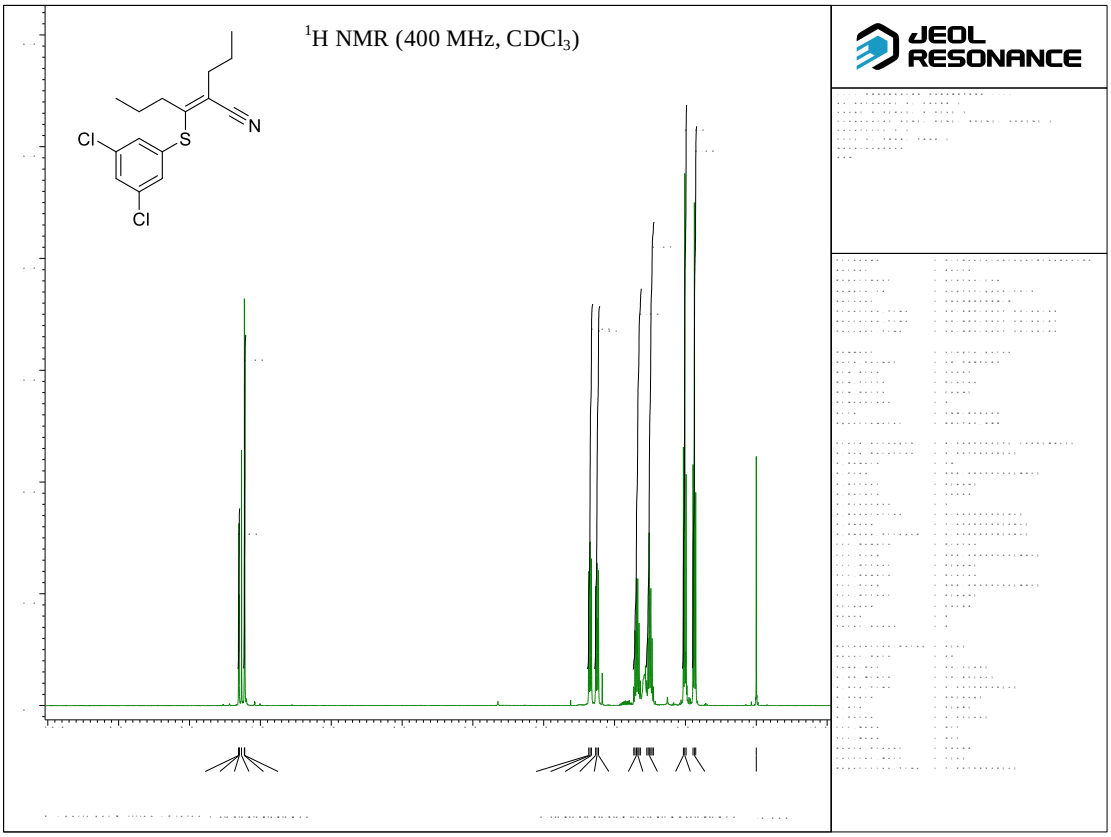
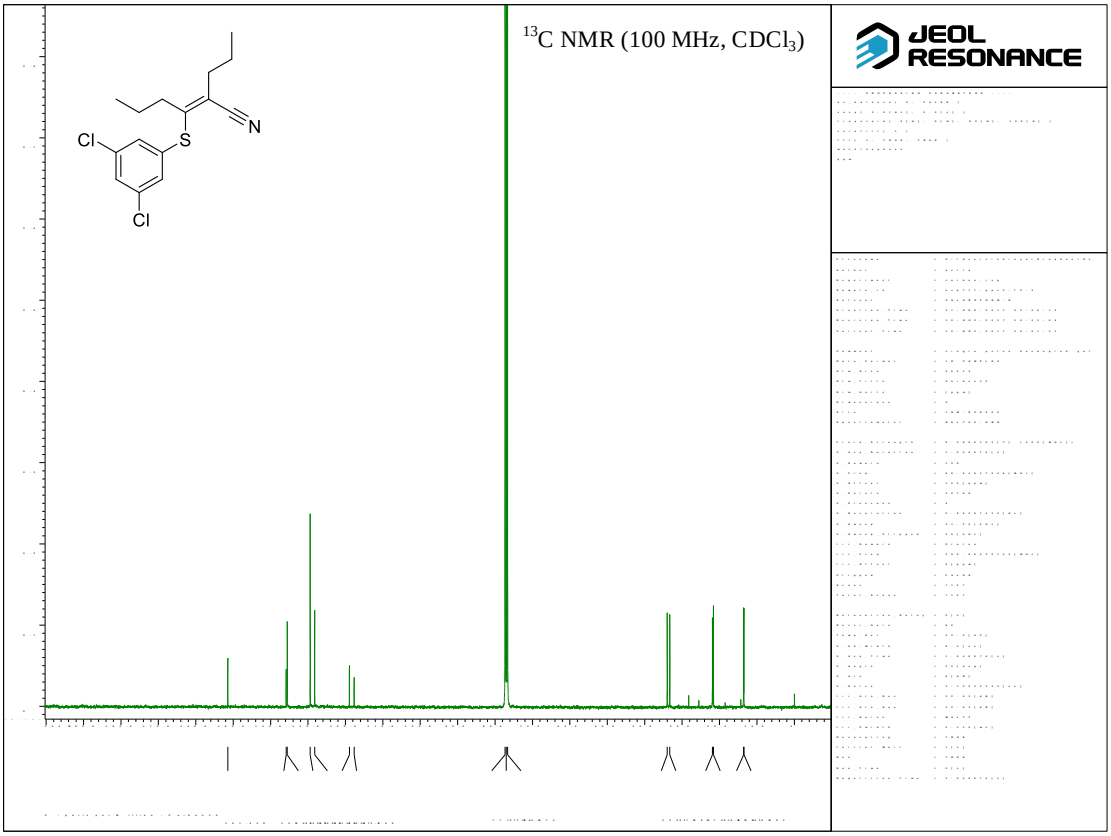
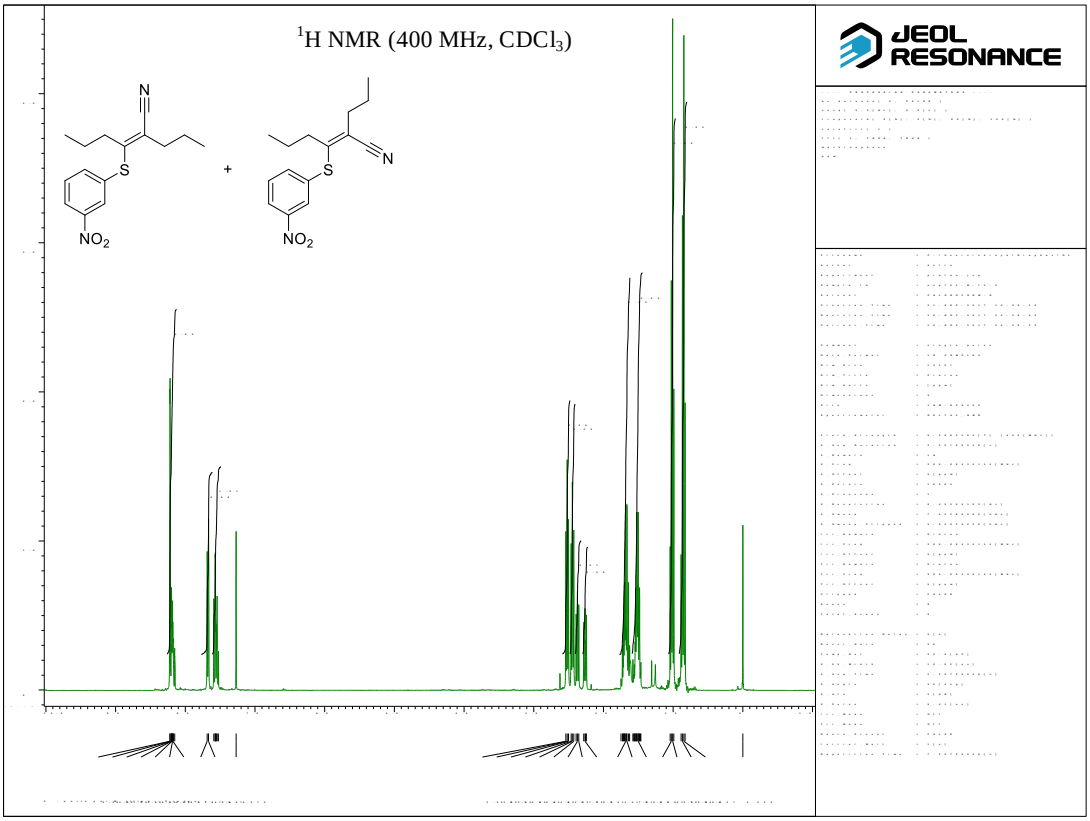
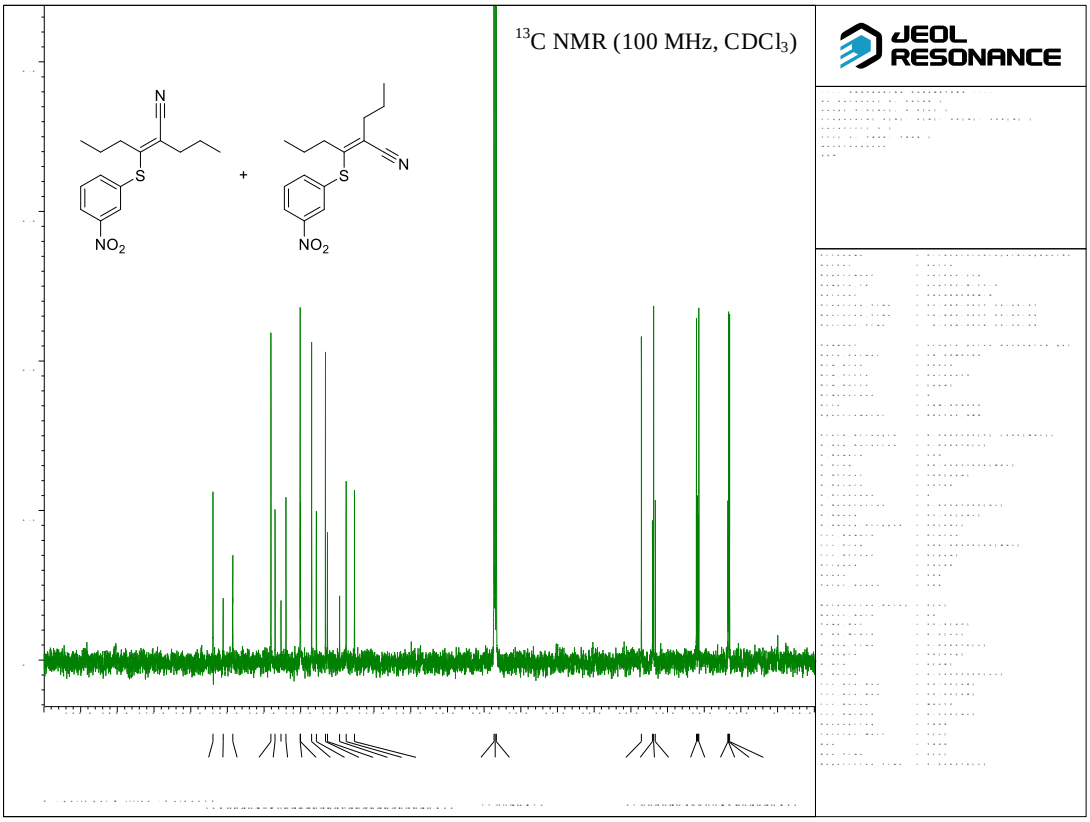




(E)-3-((3-Nitrophenyl)thio)-2-propylhex-2-enenitrile ((E)-4ag) and

(Z)-3-((3-Nitrophenyl)thio)-2-propylhex-2-enenitrile ((Z)-4ag)





(E)-3-(Cyclohexylthio)-2-propylhex-2-enenitrile ((E)-4ai) and

(Z)-3-(Cyclohexylthio)-2-propylhex-2-enenitrile ((Z)-4ai)