Supporting Information

A Stereoselective Thiocyanate Conjugate Addition to Electron Deficient Alkynes and Concomitant Cyclization to N, S-Heterocycles

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I. General Information and methods.

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 400 MHz spectrometers for ^{1}H NMR, 100 MHz for ^{13}C NMR Chemical shifts δ are given in ppm relative to the residual signals of tetramethylsilane in $CDCl_3$ and $CDCl_3$/DMSO-d_6 for ^{1}H and ^{13}C NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), broad singlet (bs). HRMS were obtained using the electro spray ionization (ESI) technique and a time-of-flight (TOF) analyzer. Column chromatography was performed using silica gel (100-200 mesh) as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). The characterizations of these compounds were further established using HR/ESI Mass spectroscopy. Melting points were measured on a capillary melting point apparatus and are uncorrected.

II. X-Ray Data Collection and Structure Refinement Details

X-Ray data for compound 2k

A good quality single crystal of size 0.38 x 0.26 x 0.24 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **2k** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5^{o} steps at 293(2) K. Cell determination, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24[1] software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by

the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

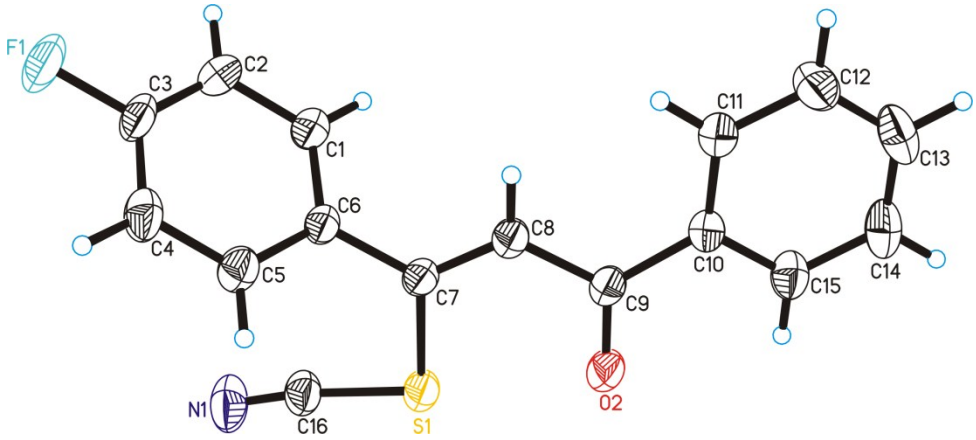


Figure S1 ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **2k** determined at 293 K.

Crystallization: Crystal of compound **2k** was grown from the solvents MeCN+DCM by slow evaporation method.

Table S1 Crystal data and structure refinement details for **2k**.

Compound	**2k**
Empirical formula	$C_{16}H_{10}FNOS$
Formula weight	283.31
Crystal System	Triclinic
Space group	*P* -1
a (Å)	9.129(2)
b (Å)	9.271(3)
c (Å)	9.583(4)
α (°)	89.47(2)
β (°)	78.65(2)
γ (°)	63.696(13)
V (Å^3)	710.0(4)
Z	2
D_c (g/cm^3)	1.325
F_{000}	292
μ (mm^{-1})	0.233
θ_{max} (°)	25.43
Total reflections	4746
Unique reflections	2396

Reflections [$I > 2\sigma(I)$]	1717
Parameters	181
R_{int}	0.0323
Goodness-of-fit	0.995
R [$F^2 > 2\sigma(F^2)$]	0.0415
wR (F^2, all data)	0.1111
CCDC No.	1556460

X-Ray data for compound 3f

A good quality single crystal of size 0.42 x 0.34 x 0.24 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **3f** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5^{o} steps at 293(2) K. Cell determinations, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24[1] software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

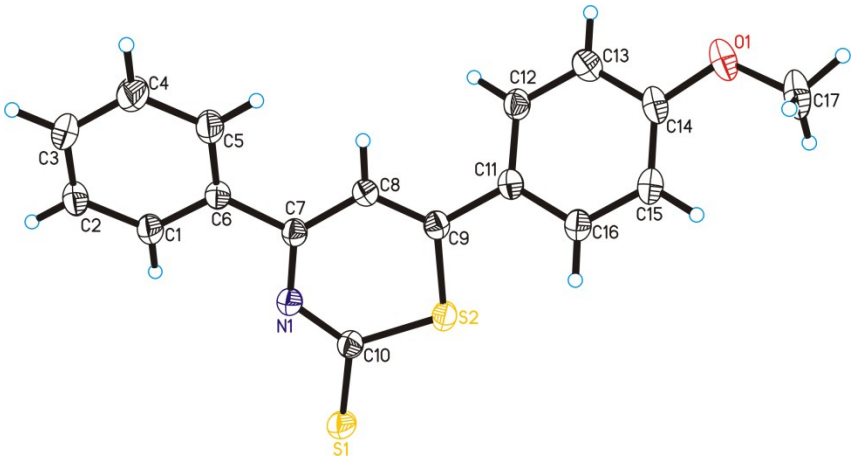


Figure S2 ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **3f** determined at 293 K.

Crystallization: Crystal of compound **3f** was grown from the solvent MeCN+DCM by slow evaporation method.

Table S2 Crystal data and structure refinement details for **3f.**

Compound	**3f**
Empirical formula	$C_{17}\,H_{13}\,N\,O\,S_2$
Formula weight	311.40
Crystal System	Monoclinic
Space group	$P\,2_1/c$
a (Å)	14.435(4)
b (Å)	7.4188(17)
c (Å)	14.492(4)
α (°)	90.00
β (°)	106.001(5)
γ (°)	90.00
V (Å^3)	1491.8(7)
Z	4
D_c (g/cm^3)	1.386
F_{000}	648
μ (mm^{-1})	0.354
θ_{max} (°)	25.35
Total reflections	9681
Unique reflections	2679
Reflections [$I > 2\sigma(I)$]	2179
Parameters	190
R_{int}	0.0375
Goodness-of-fit	1.065
R [$F^2 > 2\sigma(F^2)$]	0.0367
wR (F^2, all data)	0.1018
CCDC No.	1556445

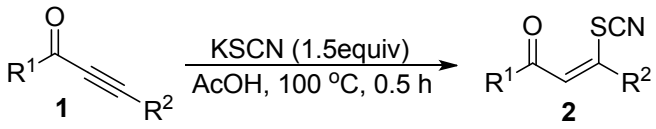
References

1. CrystalClear 2.1, Rigaku Corporation, Tokyo, Japan
2. Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112–122.

III. General Procedure for the preparation of starting materials and final compounds and chareteristic data of compounds

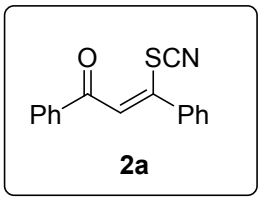
All the starting materials used *i.e.* ynones, ynoates, ynal, ynamides and sulfonyl acetylene were prepared according to the literature procedures. Yields were not optimized and data matches with the reported compounds.[1]

General procedure A for the synthesis of 2a-2bb from 1a-1bb.



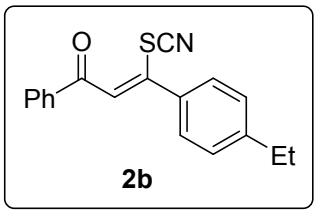
A mixture of alkynones **1** (0.5 mmol) and potassium thiocyanate (0.75 mmol) was stirred in AcOH (4 ml) at 70 °C for 0.5 h. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched by saturated sodium bicarbonate solution and extracted with EtOAc. Combined organic layers was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel, 6-8% EtOAc in Hexanes) to get pure final products **2a-2bb**.

(*Z*)-1,3-Diphenyl-3-thiocyanatoprop-2-en-1-one (2a):



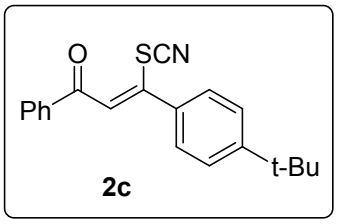
Pale yellow solid; mp 97-99 °C; R_f = 0.44 (15% ethyl acetate/hexane); Yield = 118 mg (89%); FT-IR (KBr) *v* 3396, 3038, 2148, 1637, 1552, 1244, 760, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.64-7.61 (m, 1H), 7.54-7.49 (m, 7H), 7.41 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 152.9, 137.6, 136.4, 133.9, 130.8, 129.1, 128.9, 128.6, 128.5, 122.2, 111.0 ppm; HRMS(ESI) calcd for $C_{16}H_{12}NOS$ $[M + H]^+$ 266.0640 found 266.0640.

(*Z*)-3-(4-Ethylphenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2b):



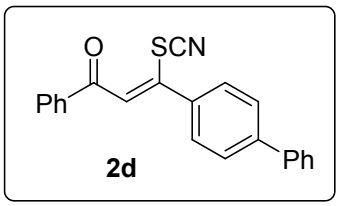
Pale yellow solid; mp 85-87 ^{o}C; R_f = 0.40 (15% ethyl acetate/hexane); Yield = 123 mg (84%); FT-IR (KBr) *v* 3390, 3040, 2136, 1639, 1558, 1237, 758, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.39 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 153.1, 147.4, 136.5, 134.9, 133.9, 129.1, 128.6, 128.4, 121.9, 111.2, 28.8, 15.3 ppm; HRMS(ESI) calcd for $C_{18}H_{16}NOS$ [M + H] 294.0953 found 294.0935.

(*Z*)-3-(4-(*tert*-Butyl)phenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2c):



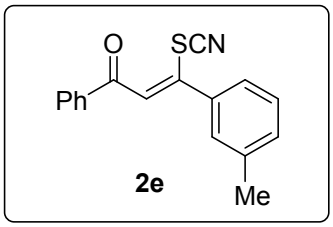
Pale yellow solid, mp 161-163 ^{o}C; R_f = 0.40 (15% ethyl acetate/hexane); Yield = 140 mg (87%); FT-IR (KBr) *v* 3382, 2960, 2156, 1638, 1597, 1244, 781, 658 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02-7.97 (m, 2H), 7.64-7.59 (m, 1H), 7.59-7.48 (m, 4H), 7.47-7.42 (m, 2H), 7.39 (s, 1H), 1.36 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 183.9, 149.5, 148.1, 131.7, 129.8, 129.0, 124.2, 123.7, 123.5, 121.0, 117.1, 106.3, 30.2, 26.4 ppm; HRMS (ESI-TOF) calcd for $C_{20}H_{20}NOS$ [M + H]$^{+}$ 322.1266 found 322.1258.

(*Z*)-3-([1,1'-Biphenyl]-4-yl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2d):



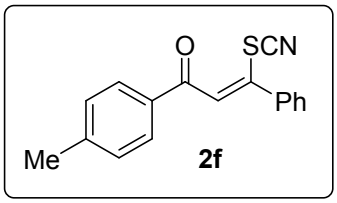
Pale yellow solid; mp 144-146 ^{o}C; R_f = 0.38 (15% ethyl acetate/hexane); Yield = 129 mg (76%); FT-IR (KBr) *v* 3356, 2922, 2156, 1636, 1549, 1246, 762, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.01 (m, 2H), 7.76-7.73 (m, 2H), 7.66-7.58 (m, 5H), 7.55-7.46 (m, 4H), 7.46 (s, 1H), 7.43-7.38 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 152.6, 143.8, 139.9, 136.5, 136.3, 134.0, 129.2, 129.1, 129.0, 128.6, 128.2, 127.6, 127.4, 122.2, 111.2 ppm; HRMS(ESI) calcd for $C_{22}H_{16}NOS$ [M + H] 342.0953 found 342.0945.

(*Z*)-1-Phenyl-3-thiocyanato-3-(m-tolyl)prop-2-en-1-one (2e):



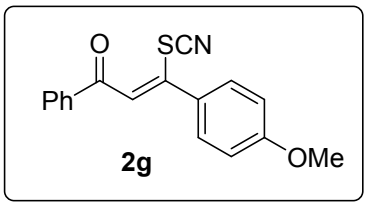
Pale yellow solid; mp 111-113 ^{o}C; R_f = 0.40 (15% ethyl acetate/hexane); Yield = 125 mg (90%); FT-IR (KBr) *v* 3365, 2995, 2140, 1642, 1554, 1239, 776, 656 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.04-7.97 (m, 2H), 7.64-7.59 (m, 1H), 7.55-7.49 (m, 2H), 7.43-7.37 (m, 2H), 7.34-7.27 (m, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 188.7, 153.0, 138.7, 137.4, 136.3, 133.8, 131.4, 128.9, 128.8, 128.7, 128.4, 125.5, 121.8, 110.9, 21.4 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{14}NOS$ $[M + H]^+$ 280.0796 found 280.0789.

(*Z*)-3-Phenyl-3-thiocyanato-1-(p-tolyl)prop-2-en-1-one (2f):



Pale yellow solid; mp 117-119 ^{o}C; R_f = 0.42 (15% ethyl acetate/hexane); Yield = 114 mg (82%); FT-IR (KBr) *v* 3379, 3011, 2156, 1635, 1553, 1247, 763, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.53-7.48 (m, 5H), 7.39 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.5, 152.3, 145.2, 137.7, 133.9, 130.7, 129.8, 128.9, 128.8, 128.6, 122.2, 111.2, 21.9 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NOS$ [M + H] 280.0796 found 280.0801.

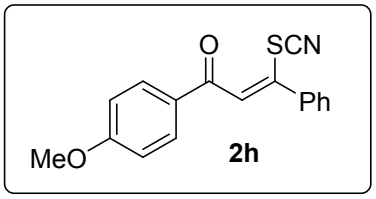
(*Z*)-3-(4-Methoxyphenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2g):



Pale yellow solid; mp 119-121 ^{o}C; R_f = 0.34 (15% ethyl acetate/hexane); Yield = 136 mg (92%); FT-IR (KBr) *v* 3359, 3020, 2159, 1636, 1550, 1254, 759, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.4 Hz, 2H), 7.69-7.65 (m, 3H), 7.62-7.58 (m, 1H), 7.54-7.51 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 161.7,

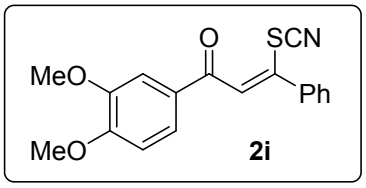
152.8, 136.6, 133.9, 130.2, 129.9, 129.1, 128.6, 121.7, 114.3, 111.4, 55.6 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NO_2S$ $[M + H]^+$ 296.0745 found 296.0754.

(*Z*)-1-(4-Methoxyphenyl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (2h):



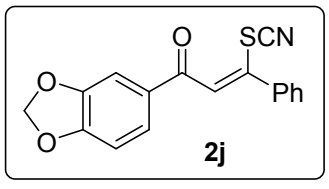
Pale yellow solid; mp 104-106 ^oC; R_f = 0.36 (15% ethyl acetate/hexane); Yield = 113 mg (77%); FT-IR (KBr) *v* 3378, 3042, 2135, 1643, 1599, 1216, 757, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.52-7.48 (m, 5H), 7.36 (s, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 164.4, 151.7, 137.7, 131.1, 130.7, 129.4, 128.9, 128.6, 122.2, 114.4, 11.4, 55.7 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NO_2S$ $[M + H]^+$ 296.0745 found 296.0746.

(*Z*)-1-(3,4-Dimethoxyphenyl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (2i):



Pale yellow solid; mp 128-130 ^oC; R_f = 0.32 (15% ethyl acetate/hexane); Yield = 113 mg (72%); FT-IR (KBr) *v* 3388, 3048, 2139, 1664, 1591, 1263, 729, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 2H), 7.53-7.47 (m, 5H), 7.37 (s, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2, 154.3, 151.8, 149.7, 137.7, 130.7, 129.6, 128.9, 128.6, 123.4, 121.9, 111.3, 110.6, 110.3, 56.3, 56.2 ppm; HRMS(ESI) calcd for $C_{18}H_{16}NO_3S$ $[M + H]^+$ 326.0851 found 326.0869.

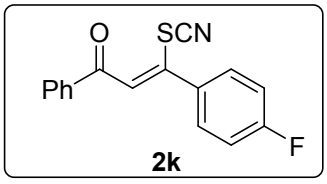
(*Z*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (2j):



Pale yellow solid; mp 138-140 ^oC; R_f = 0.36 (15% ethyl acetate/hexane); Yield = 117 mg (76%); FT-IR (KBr) *v* 3345, 2919, 2141, 1624, 1544, 1253, 759, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 1H), 7.52-7.48 (m, 6H), 7.31 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 152.7, 152.0, 148.8, 137.6, 131.2, 130.7, 128.9, 128.5,

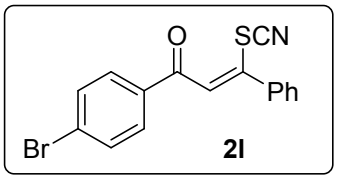
125.2, 122.1, 111.2, 108.3, 108.2, 102.3 ppm; HRMS(ESI) calcd for $C_{17}H_{12}NO_3S$ $[M + H]^+$ 310.0538 found 310.0528.

(*Z*)-3-(4-Fluorophenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2k):



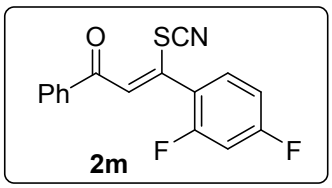
Pale yellow solid; mp 133-135 ^oC; R_f = 0.38 (15% ethyl acetate/hexane); Yield = 105 mg (74%); FT-IR (KBr) *v* 3378, 3066, 2158, 1638, 1544, 1229, 778, 637 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.65-7.61 (m, 1H), 7.54-7.48 (m, 4H), 7.39 (s, 1H), 7.26-7.19 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 164.1 (d, *J* = 250.5 Hz), 151.8, 136.3, 134.1, 133.6 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 8.7 Hz), 129.2, 128.6, 122.4, 116.3 (d, *J* = 22.1 Hz), 111.0 ppm; HRMS(ESI) calcd for $C_{16}H_{11}NOSF$ [M + H] 284.0545 found 284.0533.

(*Z*)-1-(4-Bromophenyl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (2l):



Pale yellow solid; mp 149-151 ^oC; R_f = 0.38 (15% ethyl acetate/hexane); Yield = 144 mg (84%); FT-IR (KBr) *v* 3355, 3030, 2159, 1603, 1550, 1284, 759, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.53-7.47 (m, 5H), 7.34 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 153.8, 137.3, 135.1, 132.4, 130.8, 129.9, 129.2, 128.9, 128.4, 121.5, 110.7 ppm; HRMS(ESI) calcd for $C_{16}H_{11}NOSBr$ $[M + H]^+$ 343.9745 found 343.9744.

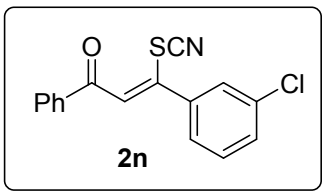
(*Z*)-3-(2,4-Difluorophenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2m):



Pale yellow solid; mp 144-146 ^oC; R_f = 0.38 (15% ethyl acetate/hexane); Yield = 108 mg (72%); FT-IR (KBr) *v* 3315, 2995, 2159, 1639, 1499, 1234, 758, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.65-7.62 (m, 1H), 7.54-7.50 (m, 2H), 7.42 (s, 1H), 7.39-7.36 (m, 1H), 7.06-6.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 146.3, 136.1, 134.3, 131.6

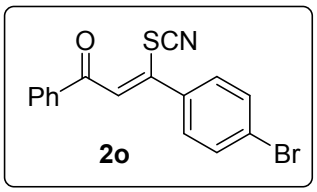
(d, *J* = 6.9 Hz), 129.2, 128.7, 123.4, 112.5 (d, J = 3.8 Hz), 112.2, 110.8, 105.5, 105.2, 104.9 ppm; HRMS(ESI) calcd for $C_{16}H_{10}NOSF_2$ $[M + H]^+$ 302.0451 found 302.0458.

(*Z*)-3-(3-Chlorophenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2n):



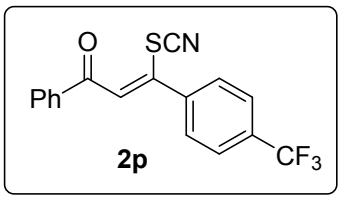
Pale yellow solid; mp 119-121 °C; R_f = 0.38 (15% ethyl acetate/hexane); Yield = 120 mg (80%); FT-IR (KBr) *v* 3386, 3040, 2127, 1646, 1478, 1245, 729, 627 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.00 (d, *J* = 7.4 Hz, 2H), 7.66-7.60 (m, 1H), 7.56-7.45 (m, 5H), 7.42-7.36 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 188.6, 150.9, 138.8, 136.1, 134.8, 134.0, 130.7, 130.1, 129.0, 128.5, 128.3, 126.8, 122.5, 110.5 ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{11}NOSCl$ $[M + H]^+$ 300.0250 found 300.0240.

(*Z*)-3-(4-Bromophenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2o):



Pale yellow solid; mp 129-131 °C; R_f = 0.36 (15% ethyl acetate/hexane); Yield = 131 mg (76%); FT-IR (KBr) *v* 3342, 3019, 2151, 1653, 1424, 1245, 741, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.01-7.97 (m, 2H), 7.68-7.60 (m, 3H), 7.55-7.49 (m, 2H), 7.40-7.34 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 188.6, 151.4, 136.2, 136.1, 134.0, 132.1, 129.9, 129.0, 128.5, 125.3, 122.3, 110.7 ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{11}NOSBr$ $[M + H]^+$ 343.9745 found 343.9741.

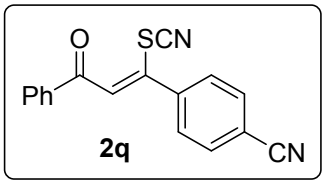
(*Z*)-1-Phenyl-3-thiocyanato-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (2p):



Pale yellow solid; mp 141-143 °C; R_f = 0.36 (15% ethyl acetate/hexane); Yield = 118 mg (71%); FT-IR (KBr) *v* 3364, 3040, 2138, 1636, 1426, 1230, 726, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.03-7.93 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.68-7.59 (m, 3H), 7.56-7.50 (m, 2H), 7.42 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 188.6, 150.9, 140.6, 136.0, 134.1, 132.5 (q, *J* =

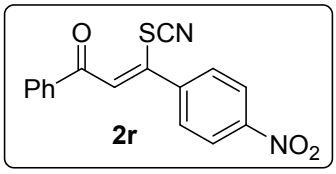
33.0 Hz), 129.1, 128.9, 128.5, 125.9 (q, J = 3.7 Hz), 123.6 (d, J = 272.8 Hz), 122.7, 110.5 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{11}NOSF_3$ $[M + H]^+$ 334.0513 found 334.0504.

(*Z*)-4-(3-Oxo-3-phenyl-1-thiocyanatoprop-1-en-1-yl)benzonitrile (2q):



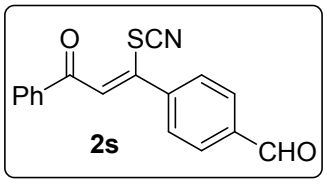
Pale yellow solid; mp 177-179 °C; R_f = 0.36 (15% ethyl acetate/hexane); Yield = 106 mg (73%); FT-IR (KBr) ν 3384, 3037, 2284, 1685, 1429, 1242, 743, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02-7.97 (m, 2H), 7.84-7.79 (m, 2H), 7.67-7.59 (m, 2H), 7.56-7.50 (m, 2H), 7.42 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 145.5, 136.6, 131.1, 129.5, 127.9, 124.5, 124.3, 123.8, 118.1, 113.0, 109.8, 105.6 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{11}N_2OS$ $[M + H]^+$ 291.0592 found 291.0586.

(*Z*)-3-(4-Nitrophenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2r):



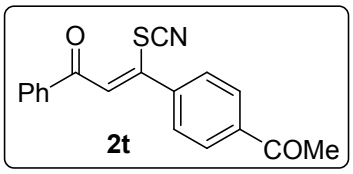
Pale yellow solid; mp 189-191 °C; R_f = 0.34 (15% ethyl acetate/hexane); Yield = 107 mg (69%); FT-IR (KBr) ν 3403, 3058, 2146, 1631, 1445, 1230, 729, 649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41-8.35 (m, 2H), 8.04-7.97 (m, 2H), 7.70-7.62 (m, 2H), 7.45 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 149.9, 148.9, 143.0, 135.8, 134.3, 129.6, 129.1, 128.5, 124.1, 123.0, 110.3 ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{11}N_2O_3S$ $[M + H]^+$ 311.0490 found 311.0475.

(*Z*)-4-(3-Oxo-3-phenyl-1-thiocyanatoprop-1-en-1-yl)benzaldehyde (2s):



Pale yellow solid; mp 168-170 °C; R_f = 0.36 (15% ethyl acetate/hexane); Yield = 95 mg (65%); FT-IR (KBr) ν 3384, 3019, 2149, 1650, 1484, 1263, 749, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.06-7.97 (m, 4H), 7.69-7.62 (m, 2H), 7.44 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 188.6, 151.0, 142.6, 137.4, 136.0, 134.0, 129.2, 129.1, 128.5, 122.6, 110.5 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{12}NO_2S$ $[M + H]^+$ 294.0589 found 294.0571.

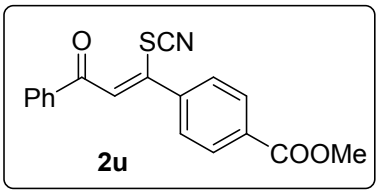
***Z*)-3-(4-Acetylphenyl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2t):**



2t

Pale yellow solid; mp 186-188 ^{o}C; R_f = 0.32 (15% ethyl acetate/hexane); Yield = 104 mg (68%); FT-IR (KBr) ν 3387, 3020, 2126, 1645, 1424, 1255, 776, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.06 (m, 2H), 8.03-7.96 (m, 2H), 7.66-7.58 (m, 3H), 7.56-7.49 (m, 2H), 7.42 (s, 1H), 2.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 188.6, 151.3, 141.4, 138.4, 136.0, 134.0, 129.0, 128.8, 128.7, 128.5, 122.5, 110.6, 26.7 ppm; HRMS (ESI-TOF) calcd for $C_{18}H_{14}N_2OS$ $[M + H]^+$ 308.0745 found 308.0734.

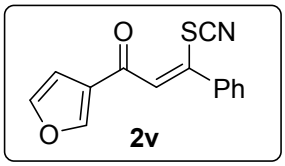
Methyl (*Z*)-4-(3-oxo-3-phenyl-1-thiocyanatoprop-1-en-1-yl)benzoate (2u):



2u

Pale yellow solid; mp 125-127 ^{o}C; R_f = 0.34 (15% ethyl acetate/hexane); Yield = 106 mg (66%); FT-IR (KBr) ν 3348, 3066, 2140, 1680, 1423, 1274, 739, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.16 (m, 2H), 8.03-7.97 (m, 2H), 7.66-7.61 (m, 1H), 7.59-7.49 (m, 4H), 7.42 (s, 1H), 3.95 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 166.0, 151.5, 141.4, 136.0, 134.0, 132.0, 130.1, 129.0, 128.5, 122.4, 110.6, 52.4 ppm; HRMS (ESI-TOF) calcd for $C_{18}H_{14}NO_3S$ $[M + H]^+$ 324.0694 found 324.0688.

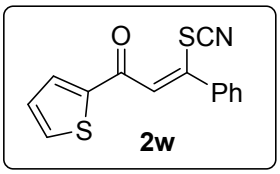
(*Z*)-1-(Furan-3-yl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (2v):



2v

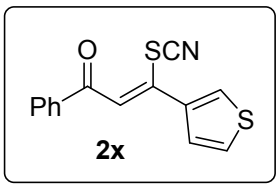
Pale yellow solid; mp 120-122 ^{o}C; R_f = 0.38 (15% ethyl acetate/hexane); Yield = 104 mg (82%); FT-IR (KBr) ν 3402, 3048, 2139, 1626, 1416, 1235, 728, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.08 (m, 1H), 7.53-7.48 (m, 4H), 7.47-7.43 (m, 2H), 6.97 (s, 1H), 6.85 (dd, J = 1.8, 0.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 151.4, 147.6, 144.9, 137.1, 130.6, 128.8, 128.3, 127.6, 123.0, 110.6, 108.6 ppm; HRMS (ESI-TOF) calcd for $C_{14}H_{10}NO_2S$ $[M + H]^+$ 256.0432 found 256.0424.

(*Z*)-3-Phenyl-3-thiocyanato-1-(thiophen-2-yl)prop-2-en-1-one (2w):



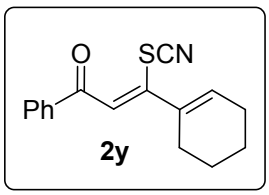
Pale yellow solid; mp 96-98 ^{o}C; R_f = 0.40 (15% ethyl acetate/hexane); Yield = 123 mg (91%); FT-IR (KBr) *v* 3388, 3052, 2157, 1667, 1485, 1249, 721, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.82-7.71 (m, 2H), 7.57-7.44 (m, 5H), 7.23-7.15 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 181.0, 151.9, 143.5, 137.2, 135.3, 132.6, 130.7, 128.8, 128.6, 128.3, 122.2, 110.6 ppm; HRMS (ESI-TOF) calcd for $C_{14}H_{10}NOS_2$ $[M + H]^+$ 272.0204 found 272.0198.

(*Z*)-1-Phenyl-3-thiocyanato-3-(thiophen-3-yl)prop-2-en-1-one (2x):



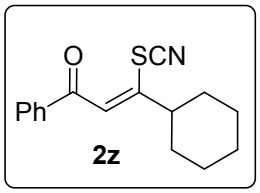
Pale yellow solid; mp 93-95 ^{o}C; R_f = 0.38 (10% ethyl acetate/hexane); Yield = 116 mg (86%); FT-IR (KBr) *v* 3372, 3027, 2157, 1635, 1448, 1231, 775, 643 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.98 (m, 2H), 7.65-7.61 (m, 1H), 7.55-7.51 (m, 5H), 7.21-7.18 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.6, 143.7, 137.5, 136.4, 134.0, 131.3, 129.1, 128.6, 128.4, 123.1, 110.9 ppm; HRMS(ESI) calcd for $C_{14}H_{10}NOS_2$ [M + H] 272.0204 found 272.0209.

(*Z*)-3-(Cyclohex-1-en-1-yl)-1-phenyl-3-thiocyanatoprop-2-en-1-one (2y):



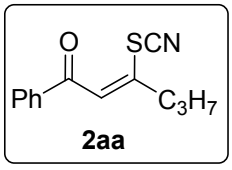
Brown oil; R_f = 0.42 (15% ethyl acetate/hexane); Yield = 118 mg (88%); FT-IR (neat) *v* 3342, 2932, 2161, 1636, 1451, 1235, 721, 664 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.62-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.25 (s, 1H), 6.04-6.03 (m, 1H), 2.34-2.32 (m, 2H), 2.27-2.25 (m, 2H), 1.85-1.79 (m, 2H), 1.73-1.67 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 155.8, 136.8, 136.6, 133.8, 132.1, 129.0, 128.5, 119.3, 111.9, 28.9, 25.4, 22.3, 21.5 ppm; HRMS(ESI) calcd for $C_{16}H_{16}NOS$ $[M + H]^+$ 270.0953 found 270.0945.

(*Z*)-3-Cyclohexyl-1-phenyl-3-thiocyanatoprop-2-en-1-one (2z):



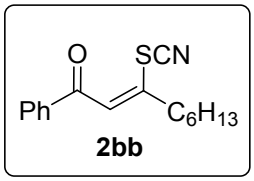
Pale yellow solid; mp 82-84 °C; R_f = 0.40 (15% ethyl acetate/hexane); Yield = 108 mg (80%); FT-IR (KBr) *v* 3326, 3021, 2121, 1642, 1419, 1244, 727, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.63-7.56 (m, 1H), 7.54-7.46 (m, 2H), 7.24 (s, 1H), 2.91-2.80 (m, 1H), 2.22-2.13 (m, 2H), 1.96-1.87 (m, 2H), 1.85-1.77 (m, 1H), 1.53-1.35 (m, 4H), 1.33-1.22 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 159.6, 136.6, 133.5, 128.8, 128.3, 116.8, 111.4, 47.3, 33.8, 26.3, 25.8 ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{18}NOS$ $[M + H]^+$ 272.1109 found 272.1107.

(*Z*)-1-Phenyl-3-thiocyanatohex-2-en-1-one (2aa):



Pale yellow solid; mp 66-68 °C; R_f = 0.42 (15% ethyl acetate/hexane); Yield = 96 mg (83%); FT-IR (KBr) *v* 3335, 3019, 2142, 1645, 1420, 1246, 738, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.63-7.57 (m, 1H), 7.53-7.47 (m, 1H), 7.29 (s, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 1.88-1.77 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 248.8 Hz), 188.8, 154.4, 136.4, 133.6, 128.9, 128.3, 119.1, 111.3, 41.4, 22.5, 13.3 ppm; HRMS (ESI-TOF) calcd for $C_{13}H_{14}NOS$ $[M + H]^+$ 232.0796 found 232.0783.

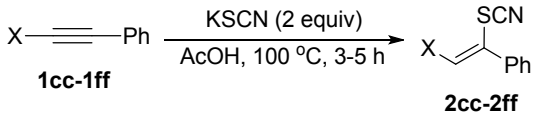
(*Z*)-1-Phenyl-3-thiocyanatonon-2-en-1-one (2bb):



Pale yellow solid; mp 44-46 °C; R_f = 0.40 (15% ethyl acetate/hexane); Yield = 116 mg (85%); IR (KBr) *v* 3341, 3038, 2152, 1665, 1419, 1244, 726, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.92 (m, 2H), 7.63-7.57 (m, 1H), 7.54-7.47 (m, 2H), 7.28 (s, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.83-1.73 (m, 2H), 1.49-1.30 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 154.8, 136.4,

133.6, 128.9, 128.3, 119.0, 111.3, 39.6, 31.3, 29.2, 28.6, 22.4, 13.9 ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{20}NOS$ $[M + H]^+$ 274.1266 found 274.1258.

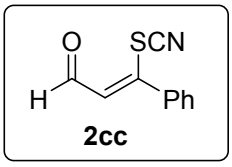
General procedure B for the synthesis of electron deficient tethered alkynes (2cc-2ff) from 1cc-1ff.



1cc-1ff **2cc-2ff**

A mixture of alkynones **1** (0.5 mmol) and potassium thiocyanate (1 mmol) was stirred in AcOH (4 ml) at 100 °C for 3-5 h. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched by saturated sodium bicarbonate solution and extracted with EtOAc. Combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel, 10-15% EtOAc in Hexanes) to get pure final products (**2cc-2ff)**.

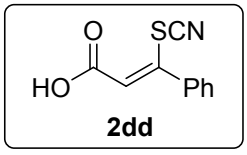
(*Z*)-3-Phenyl-3-thiocyanatoacrylaldehyde (2cc):



2cc

Pale yellow solid; mp 82-84 °C; R_f = 0.30 (15% ethyl acetate/hexane); Yield = 70 mg (74%); IR (KBr) *v* 3329, 3041, 2149, 1645, 1424, 1248, 720, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.88 (d, *J* = 2.8 Hz, 1H), 7.58-7.46 (m, 5H), 6.70 (d, *J* = 2.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.5, 150.5, 136.2, 131.6, 129.2, 128.5, 126.9, 109.1 ppm; HRMS(ESI) calcd for $C_{10}H_7NOSNa$ $[M + H]^+$ 212.0146 found 212.0143.

(*Z*)-3-Phenyl-3-thiocyanatoacrylic acid (2dd):

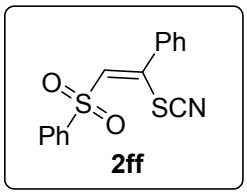


2dd

Pale yellow solid; mp 188-190 °C; R_f = 0.30 (20% ethyl acetate/hexane); Yield = 70 mg (68%); IR (KBr) *v* 3341, 3029, 2136, 1638, 1422, 1256, 724, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 10.2 (bs, 1H), 7.58-7.48 (m, 5H),

6.80 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 161.6, 157.0, 133.1, 132.3, 129.8, 126.5, 115.0 ppm; HRMS(ESI) calcd for $C_{10}H_9NO_3S$ $[M + H_2O]^+$ 223.0303 found 223.0331.

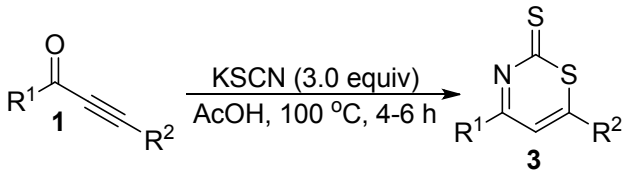
(*Z*)-((2-Phenyl-2-thiocyanatovinyl)sulfonyl)benzene (2ff):



2ff

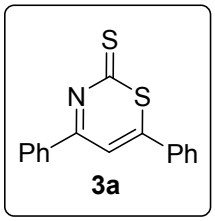
Off white solid; mp 75-77 °C; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 116 mg (77%); IR (KBr) *v* 3327, 3019, 2147, 1626, 1442, 1244, 728, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.01 (m, 2H), 7.75-7.71 (m, 1H), 7.65-7.61 (m, 2H), 7.49-7.42 (m, 3H), 7.38-7.36 (m, 2H), 6.67 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 139.7, 135.3, 134.6, 131.6, 130.1, 129.8, 129.1, 128.2, 127.7, 108.1 ppm; HRMS(ESI) calcd for $C_{15}H_{12}NO_2S_2$ $[M + H]^+$ 302.0309 found 302.0303.

Synthesis of Thiazine-2-thiones (3a-3r) from alkynones (1) using General procedure C:



A mixture of alkynones **1** (0.5 mmol) and KSCN (1.5 mmol) was stirred in AcOH (6 ml) at 100 °C for 4-6 h. After completion of reaction a red spot was visualised on TLC at 0.2-0.4 R_f in 15% EtOAc/Hexanes. Reaction mixture was then quenched by saturated sodium bicarbonate solution and extracted with EtOAc. Combined organic layers was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel, 10-20% EtOAc in Hexanes) to get pure final product **3a-3r**.

4,6-Diphenyl-2*H*-1,3-thiazine-2-thione (3a):

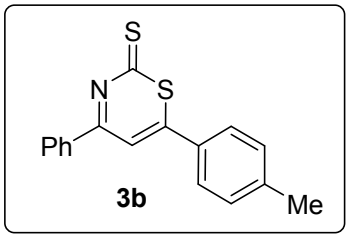


3a

Reddish brown solid; mp 152-154 °C; R_f = 0.36 (20% ethyl acetate/hexane); Yield = 119 mg (85%); IR (KBr) *v* 3343, 3026, 1622, 1357, 1248, 714, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.70-7.65 (m,

2H), 7.63-7.60 (m, 2H), 7.56-7.52 (m, 2H), 7.23-7.21 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 164.7, 160.3, 137.5, 136.9, 133.3, 131.7, 129.6, 129.5, 129.3, 129.2, 109.1 ppm; HRMS(ESI) calcd for $C_{16}H_{12}NS_2$ [M + H] 282.0411 found 282.0392.

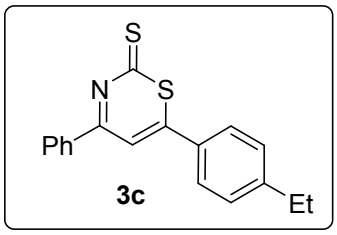
4-Phenyl-6-(*p*-tolyl)-2*H*-1,3-thiazine-2-thione (3b):



3b

Reddish brown solid; mp 151-153 ^{o}C; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 119 mg (81%); IR (KBr) *v* 3356, 3019, 1636, 1348, 1239, 728, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.3 Hz, 1H), 8.17 (d, *J* = 7.3 Hz, 1H), 7.69 (s, 1H), 7.63-7.59 (m, 3H), 7.55-7.51 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 164.6, 143.9, 137.1, 133.2, 133.0, 131.9, 130.4, 129.1, 128.9, 126.8, 126.6, 110.9, 109.5, 21.7 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NS_2$ [M + H]$^{+}$ 296.0568 found 296.0565.

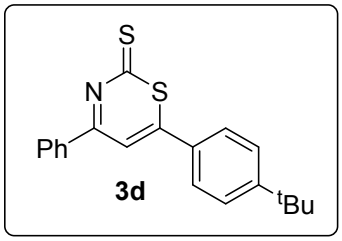
6-(4-Ethylphenyl)-4-phenyl-2*H*-1,3-thiazine-2-thione (3c):



3c

Reddish brown solid; mp 109-111 ^{o}C; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 122 mg (79%); IR (KBr) *v* 3348, 3036, 1641, 1329, 1214, 734, 642 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8.21 (m, 2H), 7.69 (s, 1H), 7.63-7.61 (m, 3H), 7.55-7.51 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 168.7, 164.5, 150.1, 137.0, 133.2, 132.1, 129.4, 129.3, 129.2, 126.8, 110.9, 29.0, 15.3 ppm; HRMS (ESI) calcd for $C_{18}H_{16}NS_2$ [M + H] 310.0724 found 310.0731.

6-(4-(*tert*-Butyl)phenyl)-4-phenyl-2*H*-1,3-thiazine-2-thione (3d):

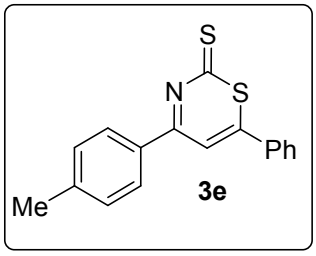


3d

Reddish brown solid; mp 161-163 ^{o}C; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 128 mg (76%); IR (KBr) *v* 3356, 3024, 1624, 1330, 1219, 726, 631 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ

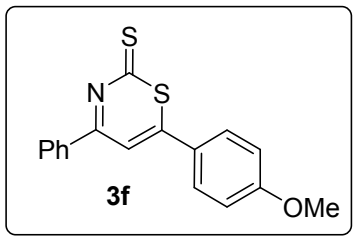
8.23-8.21 (m, 2H), 7.70 (s, 1H), 7.66-7.65 (m, 1H), 7.64-7.63 (m, 1H), 7.62-7.59 (m, 1H), 7.57-7.52 (m, 4H), 1.36 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 168.7, 164.6, 157.0, 137.1, 133.2, 131.8, 129.3, 129.2, 126.9, 125.6, 110.9, 35.3, 31.2 ppm; HRMS(ESI) calcd for $C_{20}H_{20}NS_2$ [M + H] 338.1037 found 338.1039.

6-Phenyl-4-(*p*-tolyl)-2*H*-1,3-thiazine-2-thione (3e):



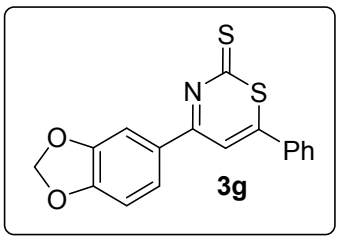
Reddish brown solid; mp 124-126 °C; R_f = 0.36 (20% ethyl acetate/hexane); Yield = 108 mg (73%); IR (KBr) *v* 3350, 3034, 1634, 1310, 1224, 729, 624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.69-7.67 (m, 2H), 7.62-7.52 (m, 3H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 168.0, 164.2, 144.7, 134.8, 133.9, 132.6, 130.1, 129.8, 129.5,126.8, 111.3, 21.9 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NS_2$ [M + H]$^+$ 296.0568 found 296.0563.

6-(4-Methoxyphenyl)-4-phenyl-2*H*-1,3-thiazine-2-thione (3f):



Reddish brown solid; mp 164-166 °C; R_f = 0.30 (20% ethyl acetate/hexane); Yield = 115 mg (74%); IR (KBr) *v* 3348, 3042, 1618, 1315, 1264, 719, 623 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2H), 7.63-7.59 (m, 1H), 7.53-7.49 (m, 2H), 7.48-7.44 (m, 2H), 7.34 (s, 1H), 7.03-7.00 (m, 2H), 3.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 168.3, 164.6, 163.1, 137.0, 133.0, 129.1, 129.0, 128.9, 128.4, 128.3, 126.8, 115.2, 114.9, 109.8, 108.4, 55.7 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NOS_2$ [M + H]$^+$ 312.0517 found 312.0522.

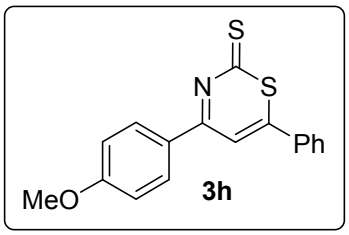
4-(Benzo[d][1,3]dioxol-5-yl)-6-phenyl-2*H*-1,3-thiazine-2-thione (3g):



Reddish brown solid; mp 168-170 °C; R_f = 0.30 (20% ethyl acetate/hexane); Yield = 100 mg (62%); IR (KBr) *v* 3319, 3024, 1631, 1348, 1224, 749, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ

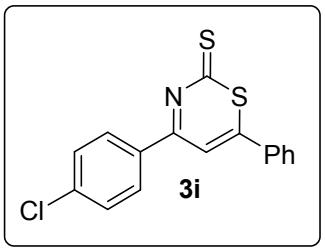
7.85 (dd, J_1 = 8.3 Hz, J_2 = 1.8 Hz, 1H), 7.78-7.79 (m, 1H), 7.67-7.65 (m, 2H), 7.62 (s, 1H), 7.59-7.57 (m, 1H), 7.55-7.51 (m, 2H), 6.94, (d, J = 8.3 Hz, 1H), 6.09 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d^6): δ 200.5, 167.4, 164.5, 163.6, 152.9, 148.9, 134.3, 133.3, 130.6, 129.9, 127.5, 127.1, 111.9, 109.3, 109.2, 103.0 ppm; HRMS(ESI) calcd for $C_{17}H_{12}NO_2S_2$ $[M + H]^+$ 326.0309 found 326.0298.

4-(4-Methoxyphenyl)-6-phenyl-2*H*-1,3-thiazine-2-thione (3h):



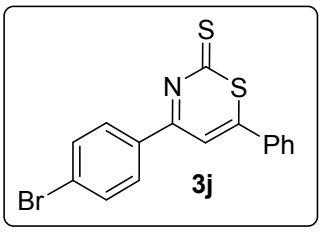
Reddish brown solid; mp 133-135 ^{o}C; R_f = 0.28 (20% ethyl acetate/hexane); Yield = 101 mg (65%); IR (KBr) *v* 3329, 3041, 1629, 1344, 1223, 724, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.9 Hz, 2H), 7.70-7.63 (m, 3H), 7.61-7.52 (m, 3H), 7.02 (d, J = 8.9 Hz, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 167.5, 164.4, 163.4, 134.9, 132.5, 131.8, 131.2, 129.8, 129.6, 128.9, 126.9, 126.7, 114.8, 110.9, 55.8 ppm; HRMS(ESI) calcd for $C_{17}H_{14}NOS_2$ $[M + H]^+$ 312.0517 found 312.0521.

4-(4-Chlorophenyl)-6-phenyl-2*H*-1,3-thiazine-2-thione (3i):



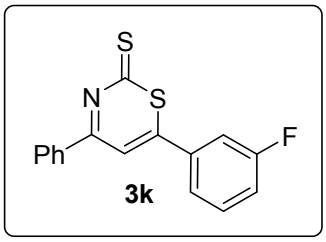
Reddish brown solid; mp 137-139 ^{o}C; R_f = 0.32 (20% ethyl acetate/hexane); Yield = 107 mg (68%); IR (KBr) *v* 3341, 3021, 1624, 1341, 1223, 721, 630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (t, J = 1.8 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.70-7.68 (m, 2H), 7.63-7.62 (m, 1H), 7.62-7.61 (m, 1H), 7.59-7.54 (m, 3H), 7.48 (t, J = 7.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 169.3, 163.1, 138.8, 135.6, 134.5, 133.1, 133.0, 130.4, 129.9, 129.1, 127.2, 126.8, 111.3 ppm; HRMS(ESI) calcd for $C_{16}H_{11}NS_2Cl$ $[M + H]^+$ 316.0021 found 316.0028.

4-(4-Bromophenyl)-6-phenyl-2*H*-1,3-thiazine-2-thione (3j):



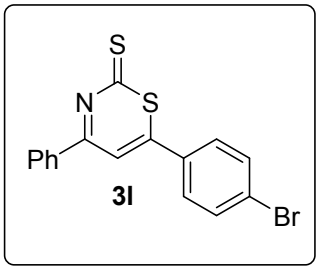
Reddish brown solid; mp 196-198 ^{o}C; R_f = 0.30 (20% ethyl acetate/hexane); Yield = 112 mg (62%); IR (KBr) *v* 3329, 3032, 1631, 1342, 1219, 744, 628 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.69-7.66 (m, 4H), 7.64 (s, 1H), 7.60-7.53 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 169.0, 163.3, 135.7, 134.6, 132.9, 132.6, 130.7, 129.9, 128.6, 126.8, 111.0 ppm; HRMS(ESI) calcd for $C_{16}H_{11}NS_2Br$ $[M + H]^+$ 359.9516 found 359.9503.

6-(3-Fluorophenyl)-4-phenyl-2*H*-1,3-thiazine-2-thione (3k):



Reddish brown solid; mp 132-134 ^{o}C; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 95 mg (64%); IR (KBr) *v* 3318, 3024, 1626, 1319, 1224, 728, 646 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (t, *J* = 7.2 Hz, 2H), 7.69-7.61 (m, 2H), 7.56-7.49 (m, 4H), 7.41-7.37 (m, 1H), 7.32-7.26 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 165.3 (d, *J* = 200.1 Hz), 136.7, 133.5, 131.6 (d, *J* = 8.0 Hz), 129.3, 122.6, 119.6 (d, *J* = 21.3 Hz), 113.8 (d, *J* = 24.1 Hz), 112.0 ppm; HRMS(ESI) calcd for $C_{16}H_{11}NFS_2$ [M + H] 300.317 found 300.0320.

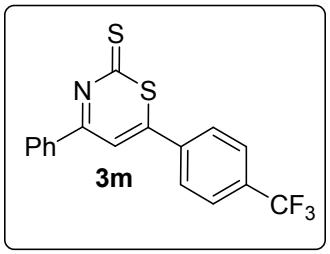
6-(4-Bromophenyl)-4-phenyl-2*H*-1,3-thiazine-2-thione (3l):



Reddish brown solid; mp 164-166 ^{o}C; R_f = 0.32 (20% ethyl acetate/hexane); Yield = 104 mg (58%); IR (KBr) *v* 3329, 3017, 1630, 1324, 1235, 730, 627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.19 (m, 2H), 7.69-7.66 (m, 3H), 7.64-7.60 (m, 1H), 7.56-7.51 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 166.7, 164.3, 136.7, 133.5, 133.1, 129.3,

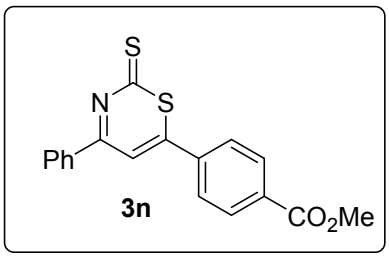
129.2, 128.1, 127.6, 111.5 ppm; HRMS(ESI) calcd for $C_{16}H_{11}NS_2Br$ $[M + H]^+$ 359.9516 found 359.9492.

4-Phenyl-6-(4-(trifluoromethyl)phenyl)-2*H*-1,3-thiazine-2-thione (3m):



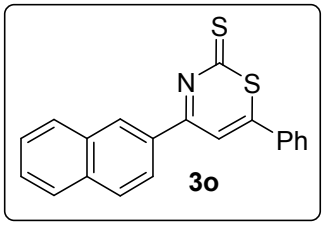
Reddish brown solid; mp 165-167 ^oC; R_f = 0.32 (20% ethyl acetate/hexane); Yield = 86 mg (49%); IR (KBr) *v* 3324, 3036, 1617, 1334, 1226, 734, 655 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.22-8.20 (m, 2H), 7.82-7.77 (m, 4H), 7.69 (s, 1H), 7.65-7.61 (m, 1H), 7.56-7.52 (m, 2H), 7.57-7.52 (m, 4H), 1.36 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 165.8, 164.1, 137.9, 136.5, 134.1 (d, J = 32.8 Hz), 133.6, 129.3, 127.3, 126.8 (q, J = 3.6 Hz), 123.5 (d, J = 271.1 Hz), 112.6 ppm; HRMS(ESI) calcd for $C_{17}H_{11}NS_2F_3$ $[M + H]^+$ 350.0285 found 350.0279.

Methyl 4-(4-phenyl-2-thioxo-2*H*-1,3-thiazin-6-yl)benzoate (3n):



Reddish brown gum; R_f = 0.30 (20% ethyl acetate/hexane); Yield = 86 mg (51%); IR (neat) *v* 3344, 3028, 1624, 1349, 1229, 725, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23-8.18 (m, 4H), 7.75-7.72 (m, 3H), 7.64-7.61 (m, 1H), 7.56-7.52 (m, 2H), 3.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 166.4, 165.8, 164.1, 138.4, 136.5, 133.6, 133.4, 130.8, 129.2, 126.7, 112.2, 52.6 ppm; HRMS(ESI) calcd for $C_{18}H_{14}NO_2S_2$ [M + H] 340.0466 found 340.0454.

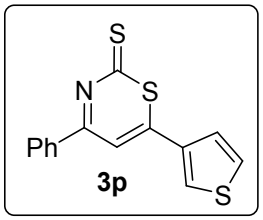
4-(Naphthalen-2-yl)-6-phenyl-2*H*-1,3-thiazine-2-thione (3o):



Reddish brown solid; mp 135-137 ^oC; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 86 mg (52%); IR (KBr) *v* 3354, 3019, 1636, 1329, 1227, 744, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.27 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 8.01-7.93 (m, 2H), 7.88

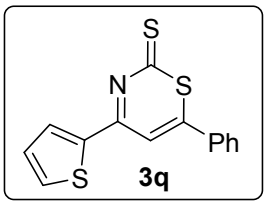
(d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H), 7.72-7.70 (m, 2H), 7.64-7.54 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 168.2, 164.2, 135.8, 134.8, 134.1, 133.1, 132.7, 131.0, 129.9, 129.8, 129.1, 129.0, 127.9, 127.2, 126.8, 124.9, 111.6 ppm; HRMS(ESI) calcd for $C_{20}H_{14}NS_2$ [M + H] 332.0568 found 332.0563.

4-Phenyl-6-(thiophen-3-yl)-2*H*-1,3-thiazine-2-thione (3p):



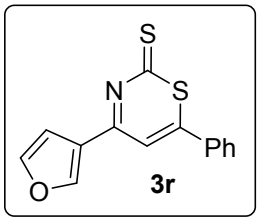
Reddish brown solid; mp 131-133 °C; R_f = 0.34 (20% ethyl acetate/hexane); Yield = 99 mg (69%); IR (KBr) *v* 3328, 3031, 1624, 1325, 1224, 734, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.70-7.65 (m, 2H), 7.63-7.60 (m, 2H), 7.56-7.52 (m, 2H), 7.23-7.21 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 164.7, 160.3, 137.5, 136.9, 133.3, 131.7, 129.6, 129.5, 129.3, 129.2, 109.1 ppm; HRMS(ESI) calcd for $C_{14}H_{10}NS_3$ [M + H] 287.9975 found 287.9973.

6-Phenyl-4-(thiophen-2-yl)-2*H*-1,3-thiazine-2-thione (3q):



Reddish brown solid; mp 122-124 °C; R_f = 0.36 (20% ethyl acetate/hexane); Yield = 95 mg (66%); IR (KBr) *v* 3344, 3020, 1626, 1319, 1244, 741, 655 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.04 (m, 1H), 7.80-7.79 (m, 1H), 7.66-7.64 (m, 2H), 7.61-7.57 (m, 2H), 7.55-7.51 (m, 2H), 7.25-7.22 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 167.6, 158.4, 143.5, 136.4, 134.5, 132.9, 132.7, 129.8, 129.5, 126.6, 110.2 ppm; HRMS(ESI) calcd for $C_{14}H_{10}NS_3$ $[M + H]^+$ 287.9975 found 287.9976.

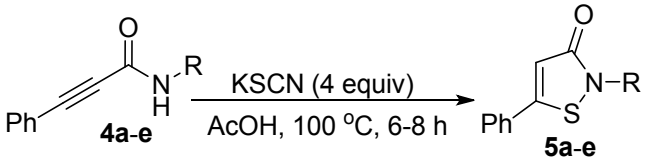
4-(Furan-3-yl)-6-phenyl-2*H*-1,3-thiazine-2-thione (3r):



Reddish brown solid; mp 132-134 °C; R_f = 0.36 (20% ethyl acetate/hexane); Yield = 83 mg (61%); IR (KBr) *v* 3331, 3019, 1630, 1324, 1249, 736, 648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.65-7.63 (m, 2H), 7.59-7.51 (m, 4H), 7.36 (s, 1H), 7.07 (s, 1H) ppm; ^{13}C

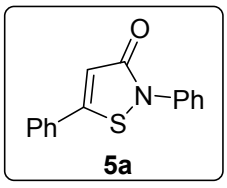
NMR (100 MHz, $CDCl_3$): δ 202.2, 167.9, 159.2, 148.2, 145.2, 134.4, 132.7, 129.8, 127.1, 126.6, 111.3, 109.3 ppm; HRMS(ESI) calcd for $C_{14}H_{10}NOS_2$ $[M + H]^+$ 272.0204 found 272.0197.

General procedure D for the synthesis of Isothiazolones (5a-e) from ynamide (4a-4e).



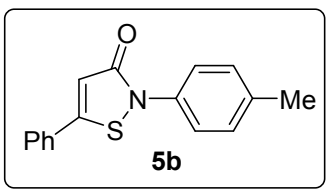
A mixture of ynamide **4** (0.5 mmol) and KSCN (2 mmol) was stirred in AcOH (6 ml) at 100 °C for 6-8 h. After completion of reaction a red spot was visualised on TLC at 0.2-0.5 R_f in 20% EtOAc/Hexanes. Reaction mixture was then quenched by saturated sodium bicarbonate solution and extracted with EtOAc. Combined organic layers was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel, 10-20% EtOAc in Hexanes) to get pure final product (**5a-e**).

2,5-Diphenylisothiazol-3(2*H*)-one (5a)[2]:



Off white solid; mp 92-94 °C; R_f = 0.22 (20% ethyl acetate/hexane); Yield = 107 mg (85%); IR (KBr) *v* 3344, 3028, 1628, 1424, 1215, 728, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.56-7.44 (m, 7H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 156.1, 136.9, 131.3, 130.1, 129.6, 129.5, 127.4, 126.0, 124.7, 110.8 ppm; HRMS(ESI) calcd for $C_{15}H_{12}NOS$ $[M + H]^+$ 254.0640 found 254.0638.

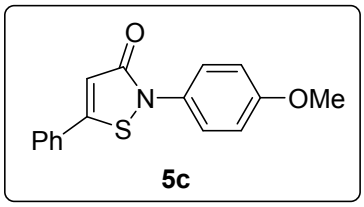
5-Phenyl-2-(p-tolyl)isothiazol-3(2*H*)-one (5b):



Off white solid; mp 108-110 °C; R_f = 0.20 (20% ethyl acetate/hexane); Yield = 111 mg (83%); IR (KBr) *v* 3346, 3019, 1619, 1428, 1216, 725, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ

7.56-7.48 (m, 7H), 7.28-7.26 (m, 2H), 6.57 (s, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 155.9, 137.4, 134.1, 131.1, 130.1, 129.9, 129.4, 125.9, 124.7, 110.6, 21.1 ppm; HRMS(ESI) calcd for $C_{16}H_{14}NOS$ $[M + H]^+$ 268.0796 found 268.0788.

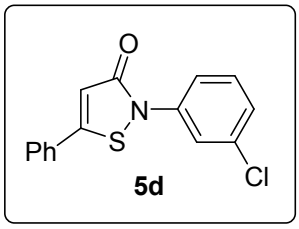
2-(4-Methoxyphenyl)-5-phenylisothiazol-3(2*H*)-one (5c):



5c

Off white solid; mp 119-121 °C; R_f = 0.28 (30% ethyl acetate/hexane); Yield = 115 mg (81%); IR (KBr) *v* 3341, 3025, 1626, 1415, 1242, 726, 628 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 7H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 158.9, 155.9, 131.1, 130.1, 129.4, 129.2, 126.8, 125.8, 114.6, 110.4, 55.6 ppm; HRMS(ESI) calcd for $C_{16}H_{14}NO_2S$ $[M + H]^+$ 284.0745 found 284.0741.

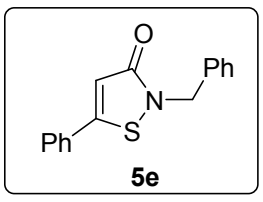
2-(3-Chlorophenyl)-5-phenylisothiazol-3(2*H*)-one (5d):



5d

Pale yellow solid; mp 101-103 °C; R_f = 0.24 (20% ethyl acetate/hexane); Yield = 109 mg (76%); IR (KBr) *v* 3338, 3026, 1636, 1425, 1238, 724, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 2.0 Hz, 1H), 7.62-7.52 (m, 6H), 6.41 (t, *J* = 8.1 Hz, 1H), 7.33-7.30 (m, 1H), 6.59 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 156.2, 137.9, 135.0, 131.4, 130.3, 129.5, 127.2, 125.9, 124.3, 122.2, 110.5 ppm; HRMS(ESI) calcd for $C_{15}H_{11}NOSCl$ $[M + H]^+$ 288.0250 found 288.0243.

2-Benzyl-5-phenylisothiazol-3(2*H*)-one (5e):

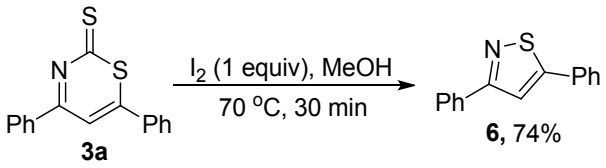


5e

Pale yellow solid; mp 154-156 °C; R_f = 0.22 (20% ethyl acetate/hexane); Yield = 96 mg (72%); IR (KBr) *v* 3346, 3054, 1629, 1419, 1224, 735, 620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 5H), 7.40-7.35 (m, 5H), 6.55 (s, 1H), 5.01 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 156.3, 136.3, 130.9,

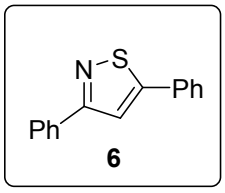
130.2, 129.3, 128.9, 128.4, 128.3, 125.8, 110.0, 47.4 ppm; HRMS(ESI) calcd for $C_{16}H_{14}NOS$ [M + H]$^+$ 268.0796 found 268.0795.

General procedure E for the synthesis of Isothiazole (6) from 4,6-diphenyl-2H-1,3-thiazine-2-thione (3a) .



A mixture of **3a** (0.5 mmol) and I_2 (0.5 mmol) was stirred in MeOH (3 ml) at 70 ^{o}C for 0.5 h. After completion of the reaction (as indicated by TLC), the reaction mixture was concentrated under reduced pressure and extracted with EtOAc after addition of water. Combined organic layers was dried with anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel, 6-8% EtOAc in Hexanes) to get pure final product **6**.

3,5-Diphenylisothiazole (6)[3]:



Orange solid; mp 82-84 ^{o}C; R_f = 0.24 (20% ethyl acetate/hexane); Yield = 88 mg (74%); IR (KBr) *v* 3328, 3025, 1614, 1422, 1242, 728, 676 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2H), 7.76 (s, 1H), 7.67-7.65 (m, 2H), 7.50-7.40 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 168.4, 135.0, 131.2, 129.7, 129.4, 128.9, 127.0, 126.8, 117.7 ppm; HRMS(ESI) calcd for $C_{15}H_{12}NS$ [M + H]$^+$ 238.0690 found 238.0687.

References

1. (a) S. Cai, K. Yang, D. Z. Wang, *Org. Lett.,* 2014, **16**, 2606-2609. (b) K. Okamoto, T. Shimbayashi, E. Tamura, K. Ohe, *Org. Lett.,* 2015, **17**, 5843-5845. (c) C. E. Song, D. Jung, S. Y. Choung, E. J. Roh, S. G. Lee, *Angew. Chem. Int. Ed.,* 2004, **43**, 6183-6185. (d) D. Qiana, J. Zhang, *Chem. Commun.,* 2012, **48**, 7082-7084. (e) J. Meesin, P. Katrun, C. Pareseecharoen, M. Pohmakotr, V. Reutrakul, D. Soorukram, C. Kuhakarn, *J. Org. Chem*., 2016, **81**, 2744.
2. S. W. Wright, J. J. Petraitis, B. Freimark, J. V. Giannaras, M. A. Pratta, S. R. Sherk, J. M. Williams, R. L. Magolda and E. C. Arner, *Bioorg. Med. Chem.,* 1996, **4**, 851.
3. I. C. Christoforou and P. A. Koutentis, *Org. Biomol. Chem*., 2007, **5**, 1381.

VI. Copies of 1H and 13C NMR spectra

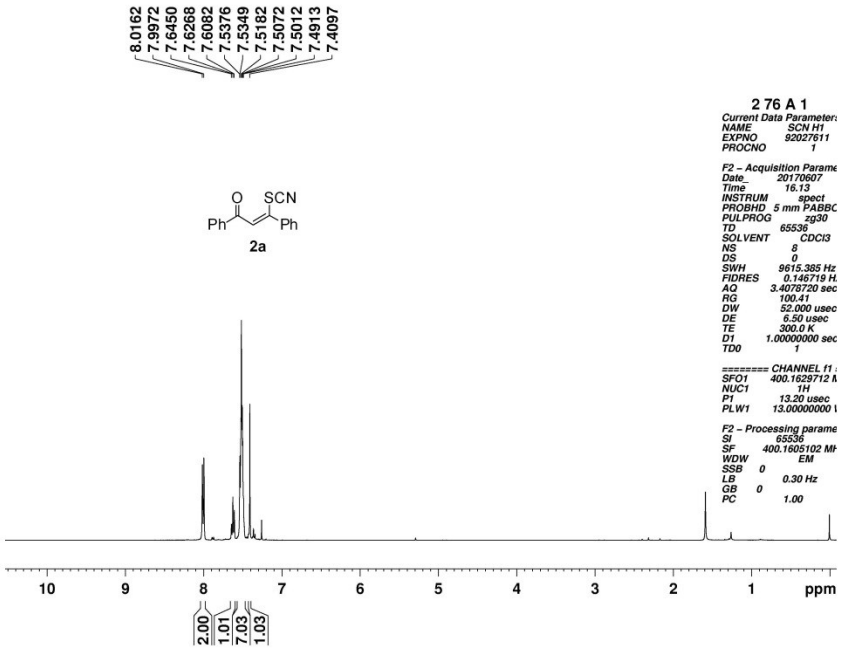


Fig. S3: ^{1}H NMR of 2a

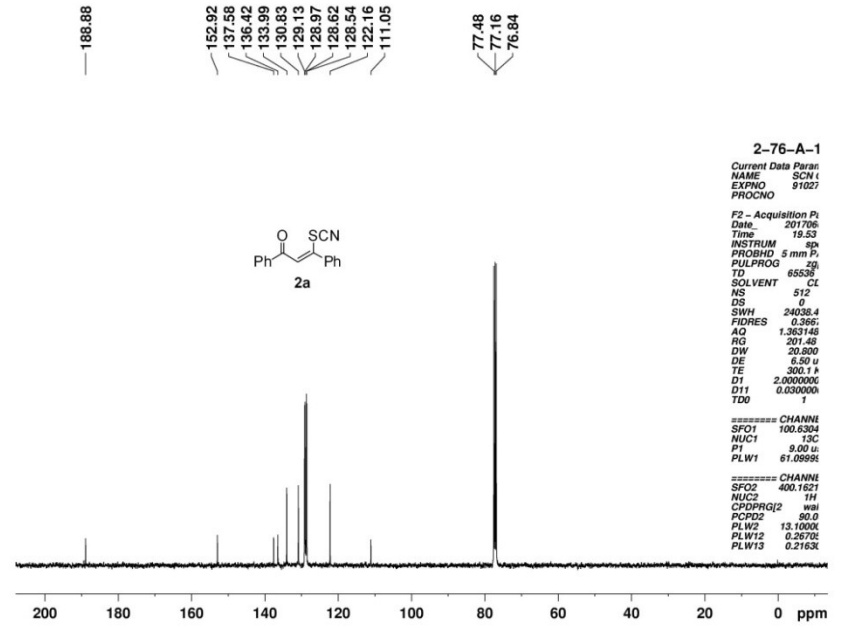


Fig. S4: ^{13}C NMR of 2a

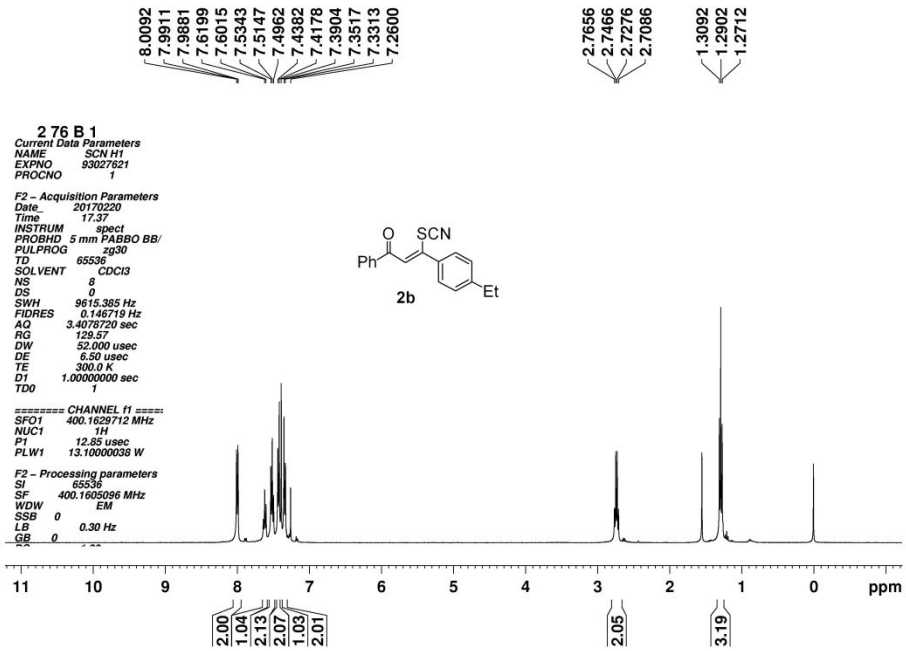


Fig. S5: ^{1}H NMR of 2b

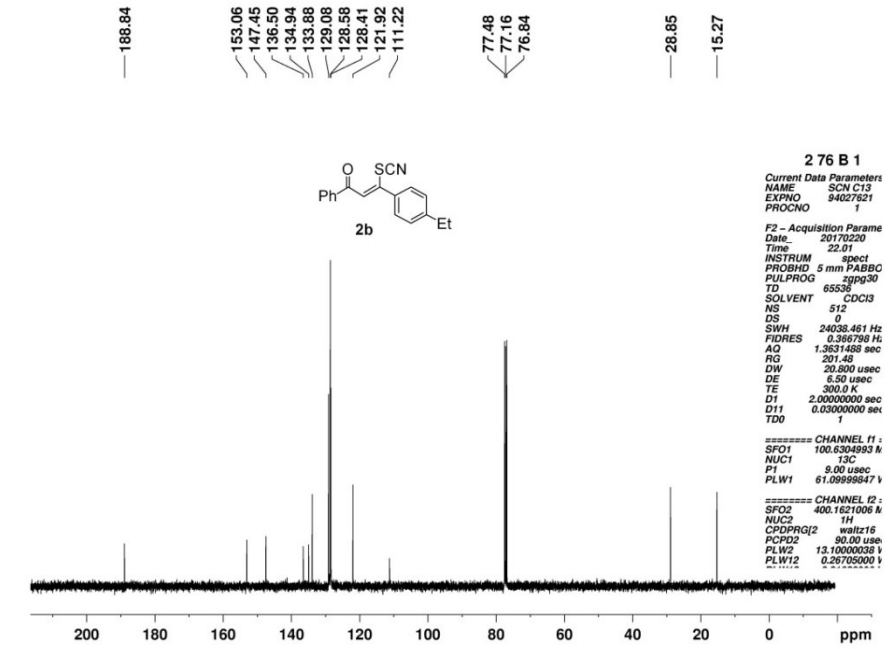


Fig. S6: ^{13}C NMR of 2b

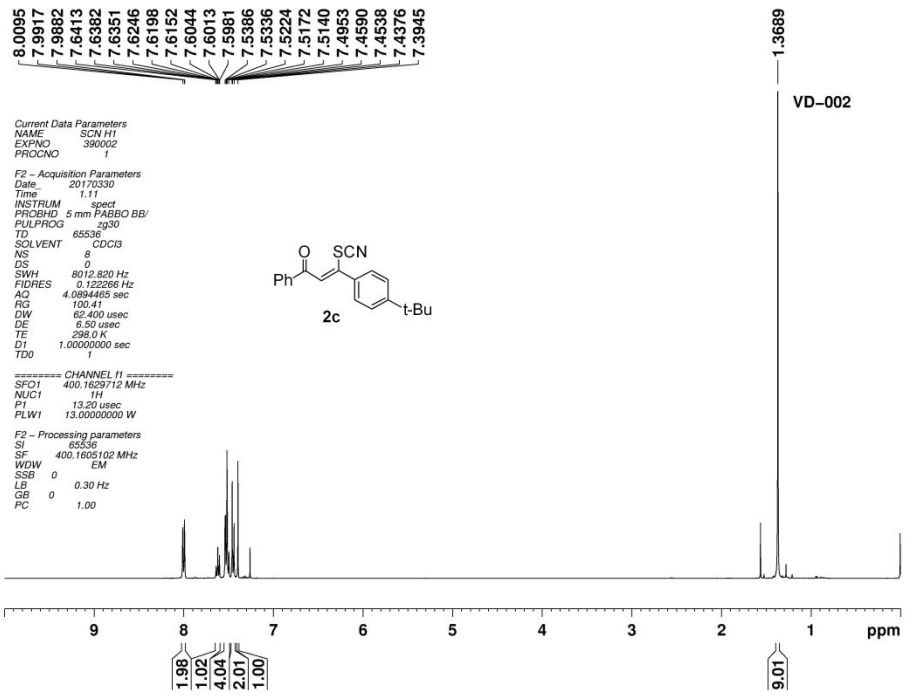


Fig. S7: ^{1}H NMR of 2c

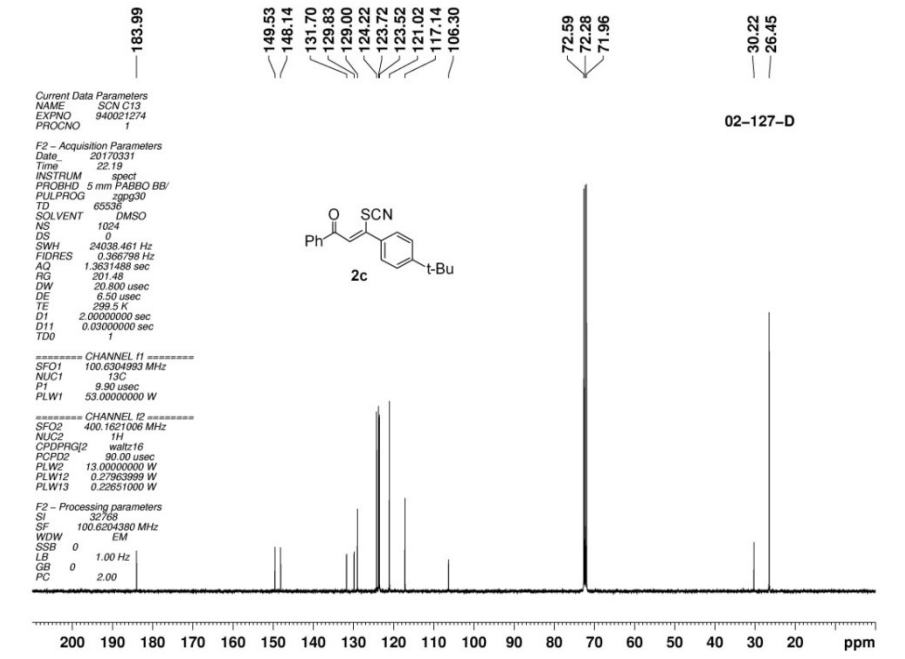


Fig. S8: ^{13}C NMR of 2c

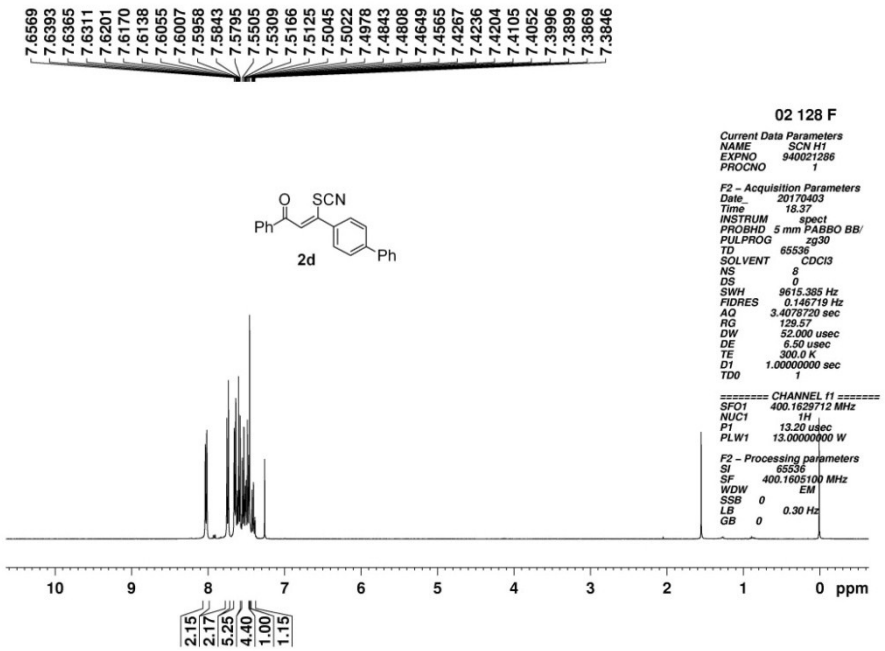


Fig. S9: ^{1}H NMR of 2d

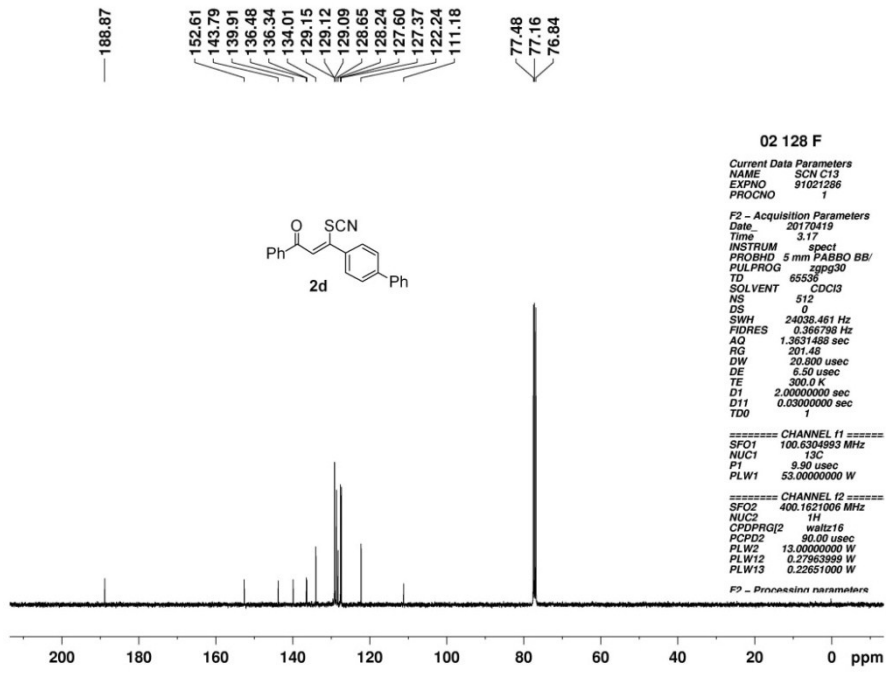


Fig. S10: ^{13}C NMR of 2d

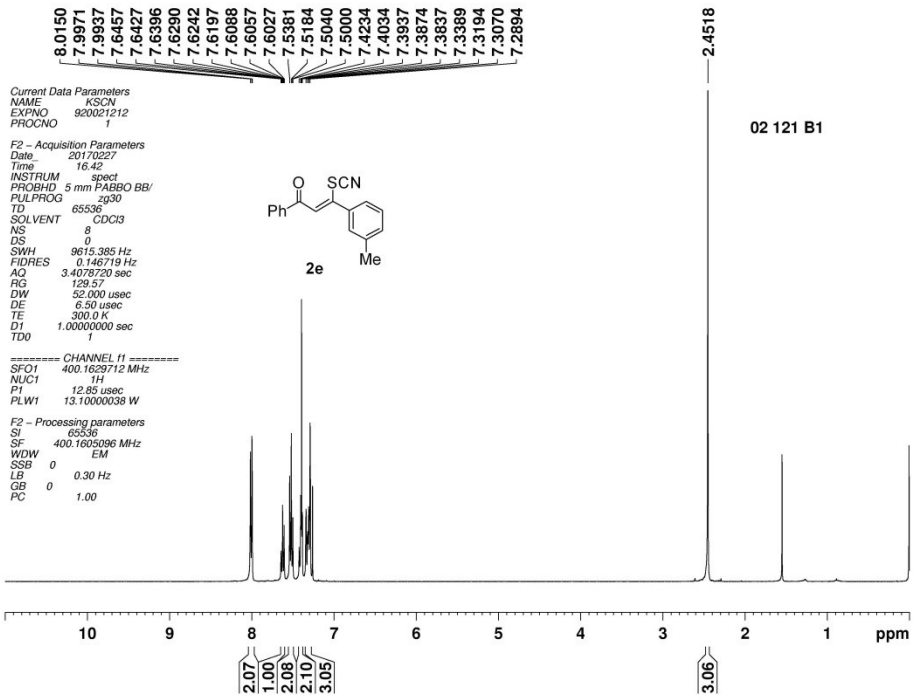


Fig. S11: ^{1}H NMR of 2e

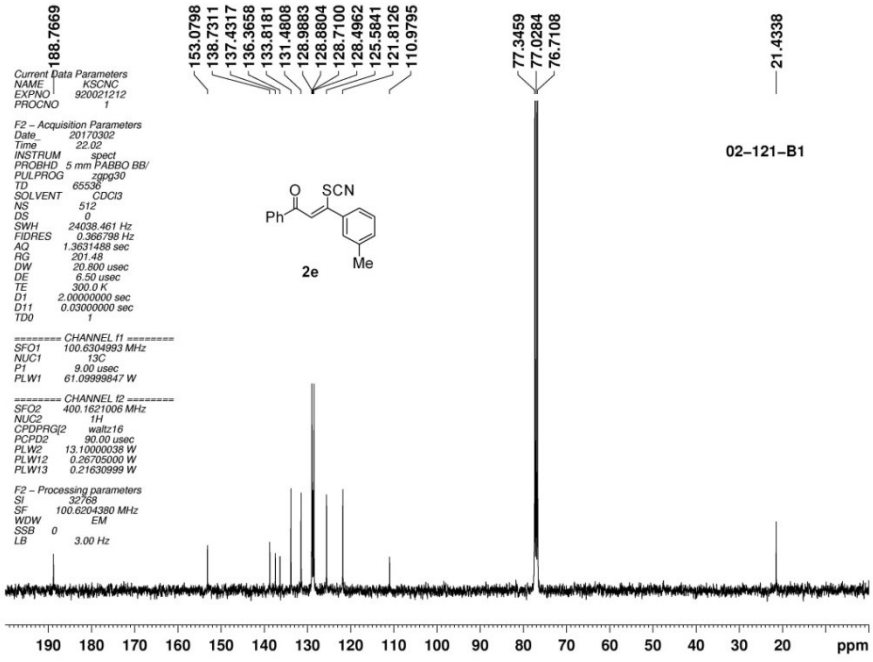


Fig. S12: ^{13}C NMR of 2e

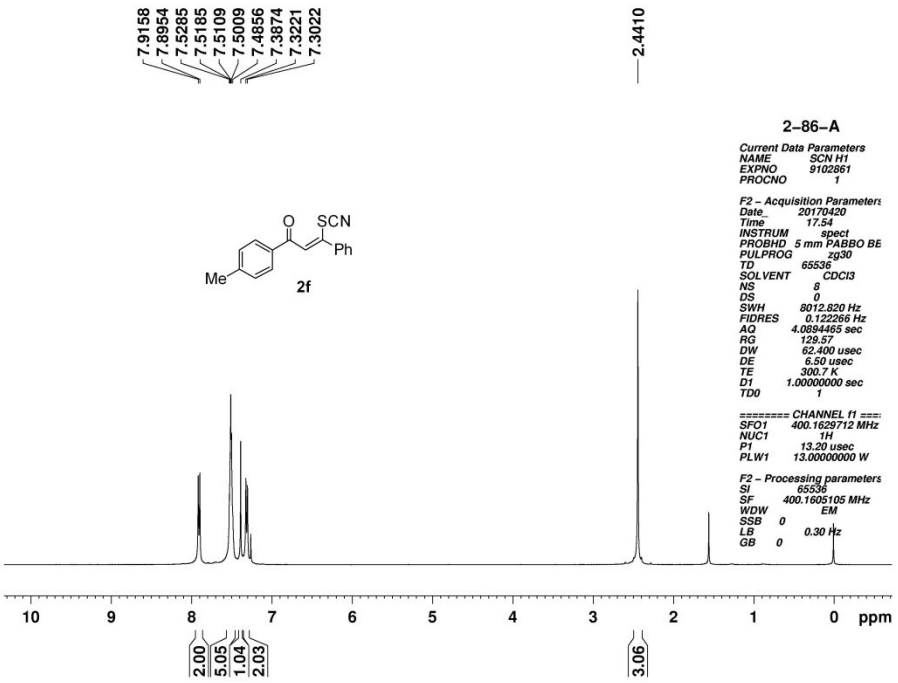


Fig. S13: ^{1}H NMR of 2f

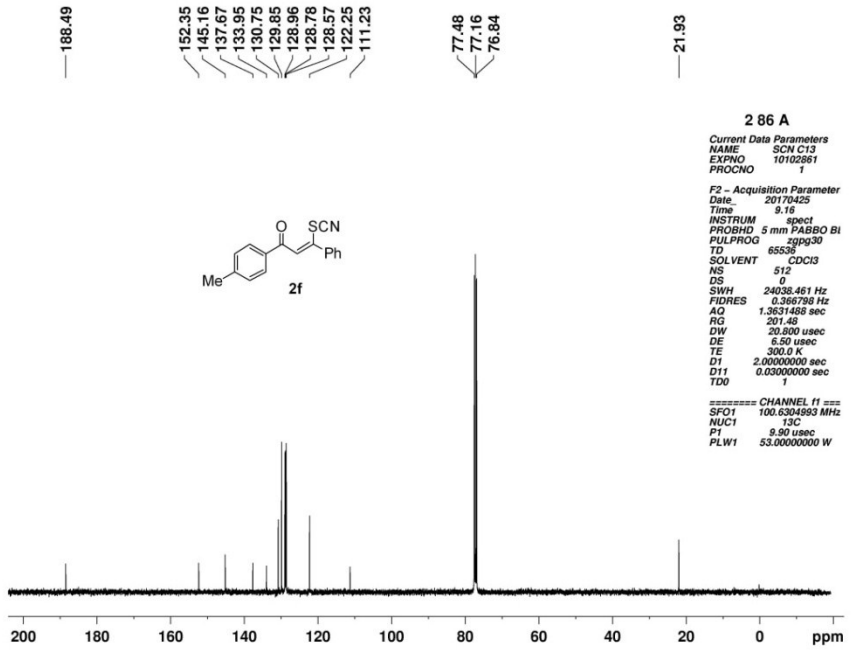


Fig. S14: ^{13}C NMR of 2f

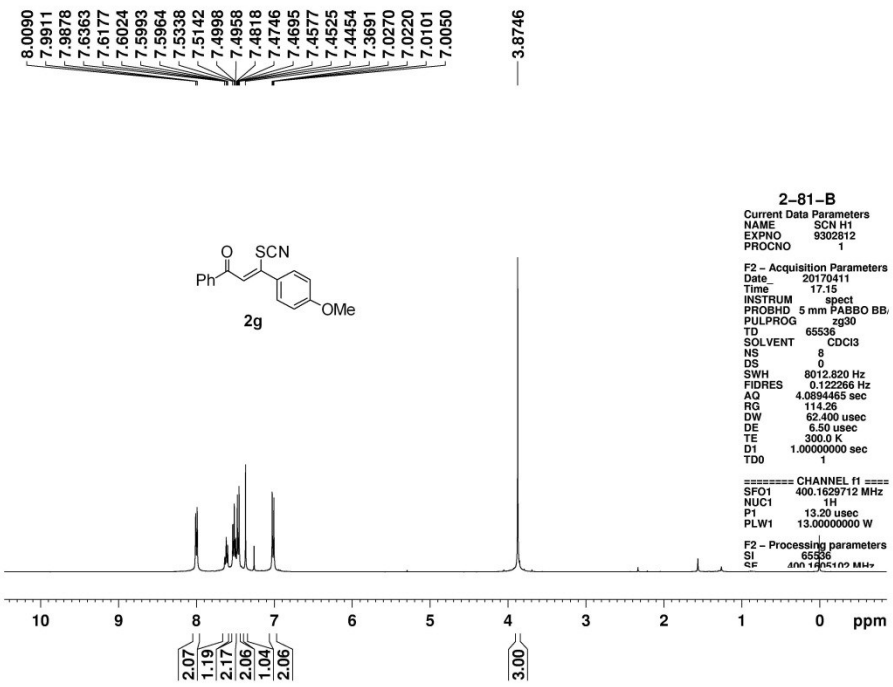


Fig. S15: ^{1}H NMR of 2g

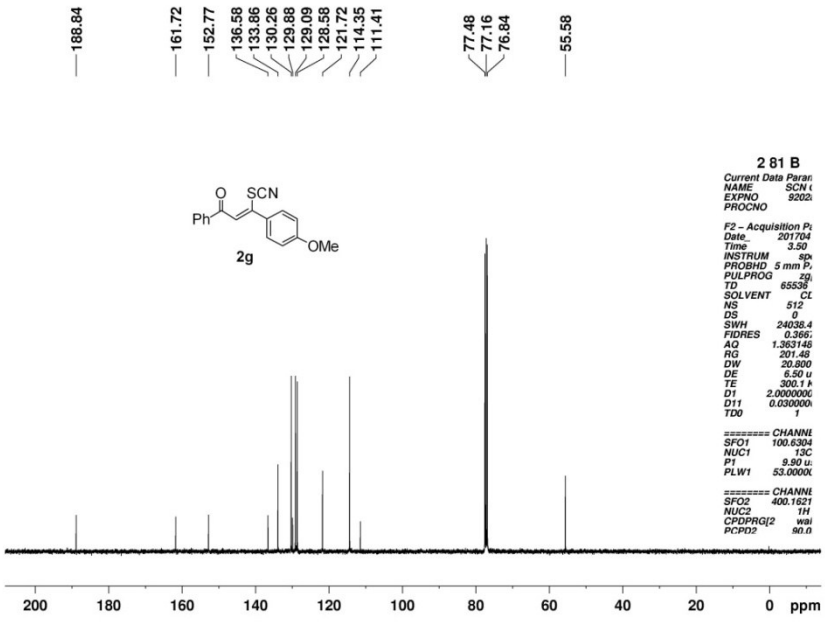


Fig. S16: ^{13}C NMR of 2g

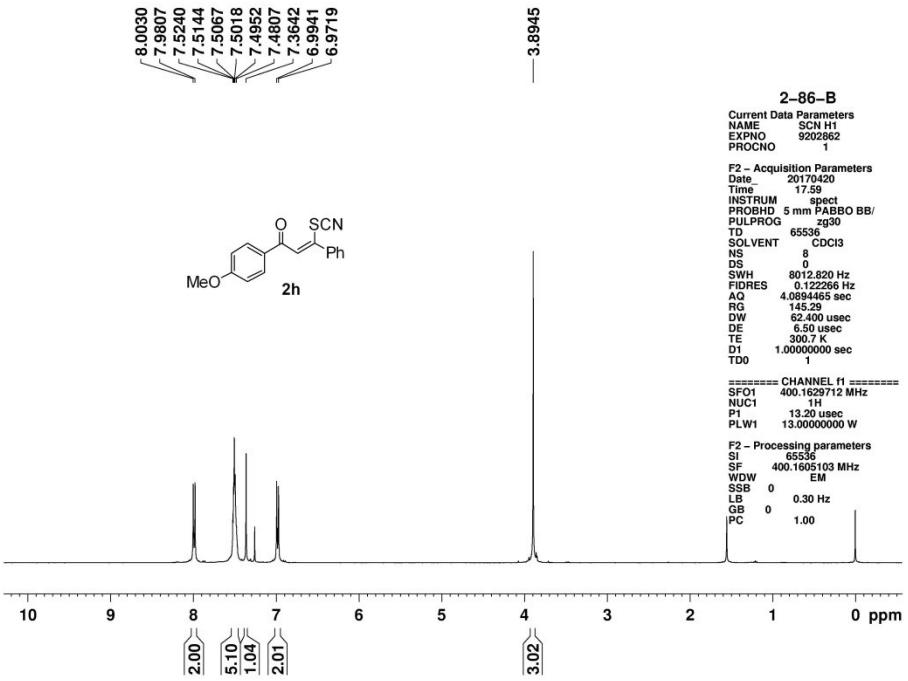


Fig. S17: ^{1}H NMR of 2h

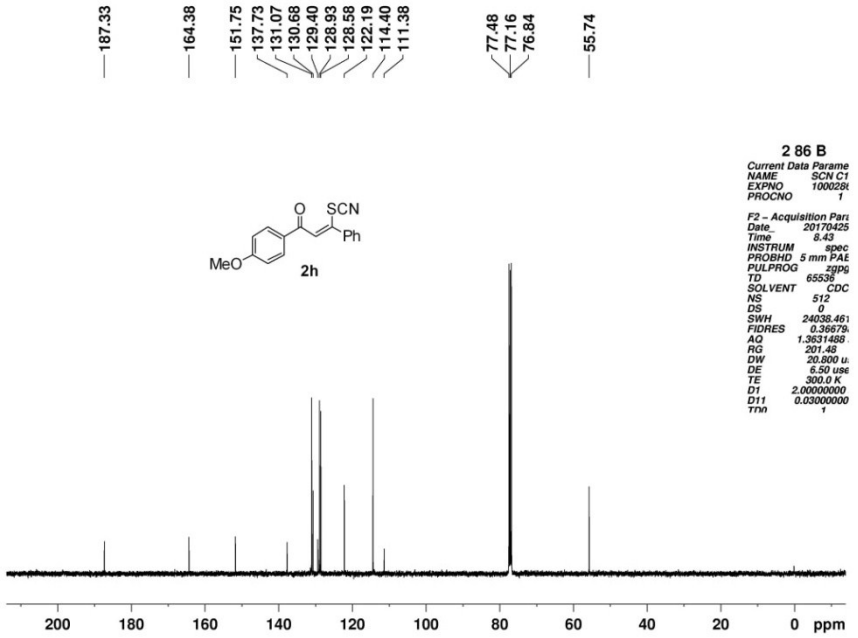


Fig. S18: ^{13}C NMR of 2h

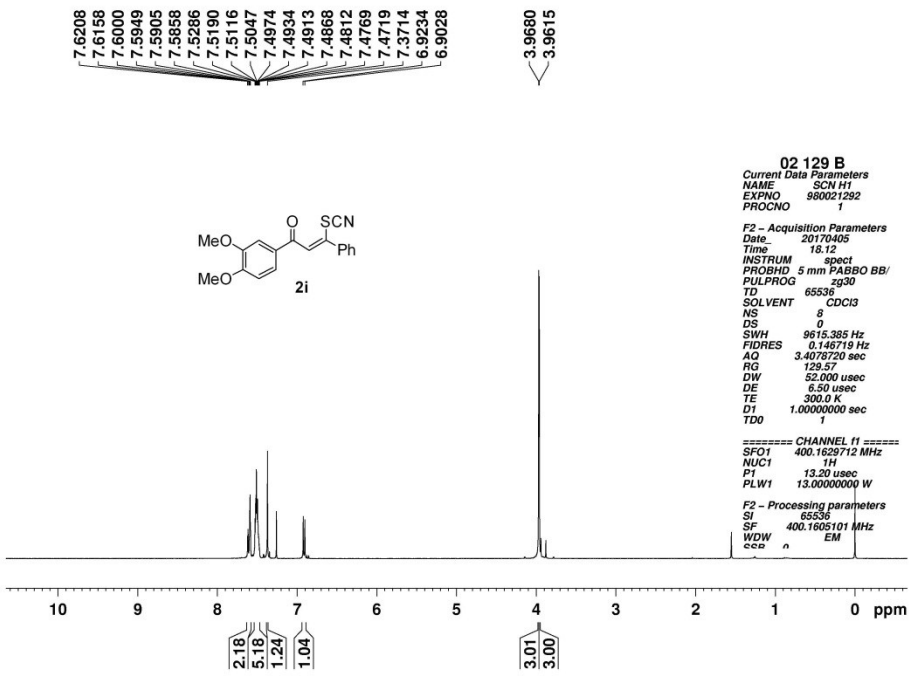


Fig. S19: ^{1}H NMR of 2i

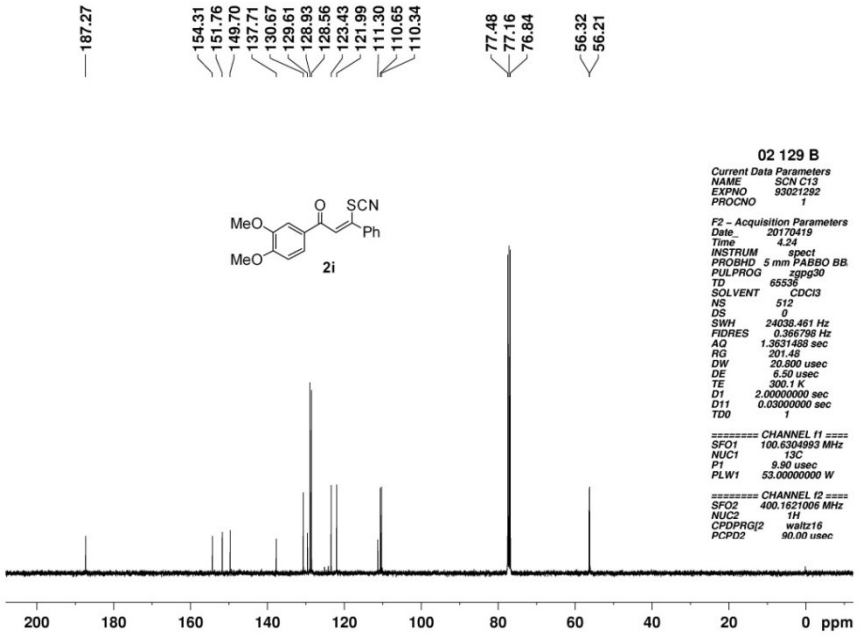


Fig. S20: ^{13}C NMR of 2i

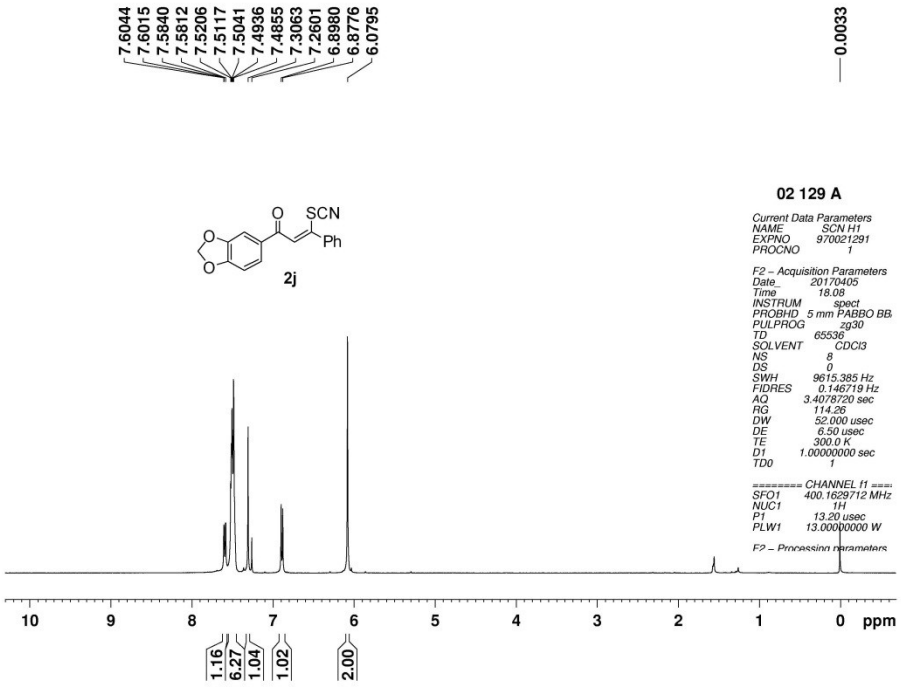


Fig. S21: ^{1}H NMR of 2j

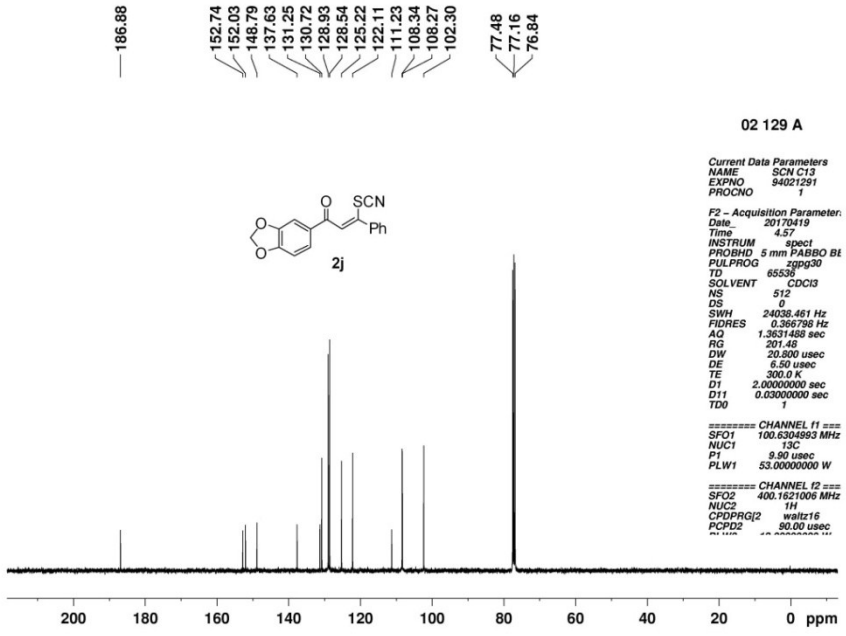


Fig. S22: ^{13}C NMR of 2j

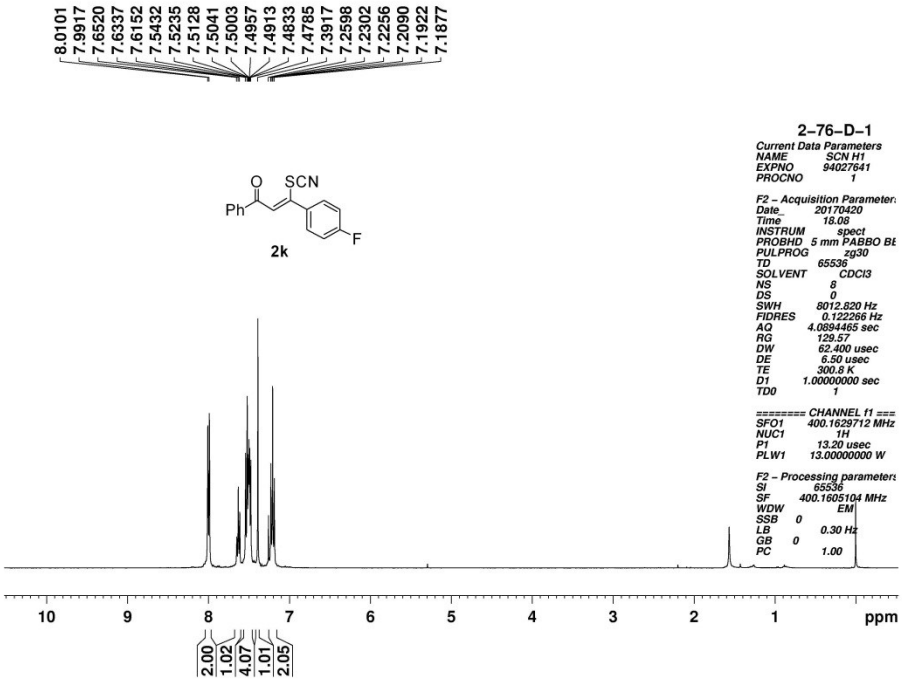


Fig. S23: ^{1}H NMR of 2k

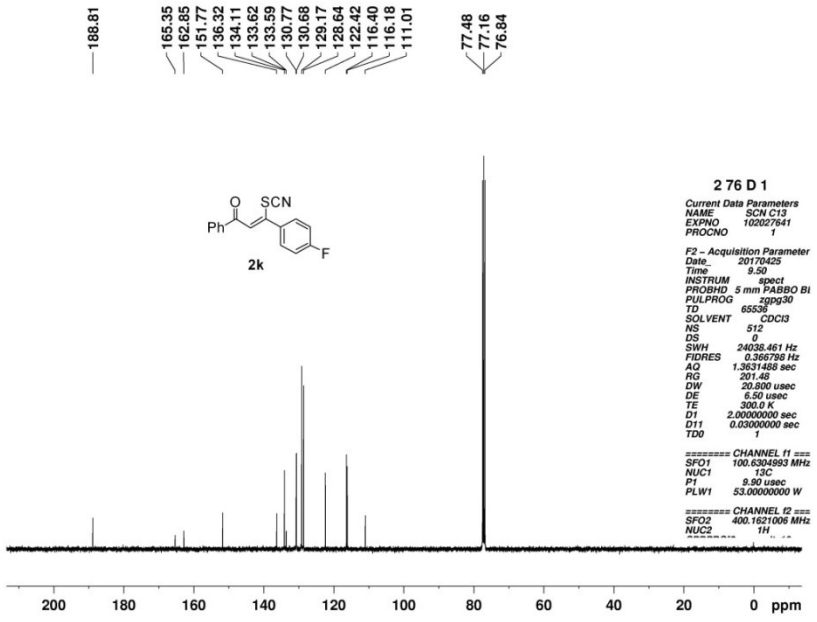


Fig. S24: ^{13}C NMR of 2k

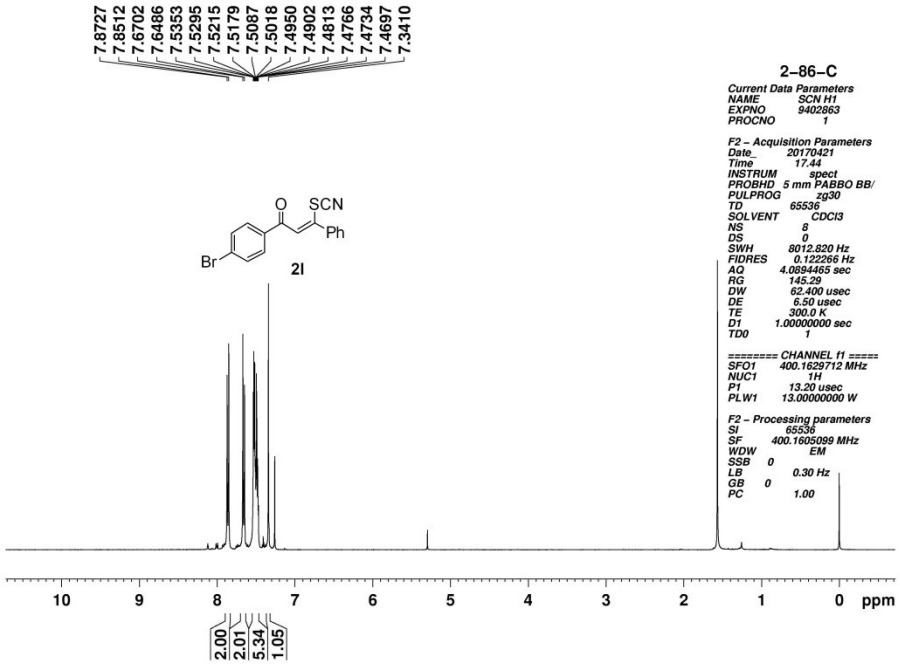


Fig. S25: ^{1}H NMR of 2l

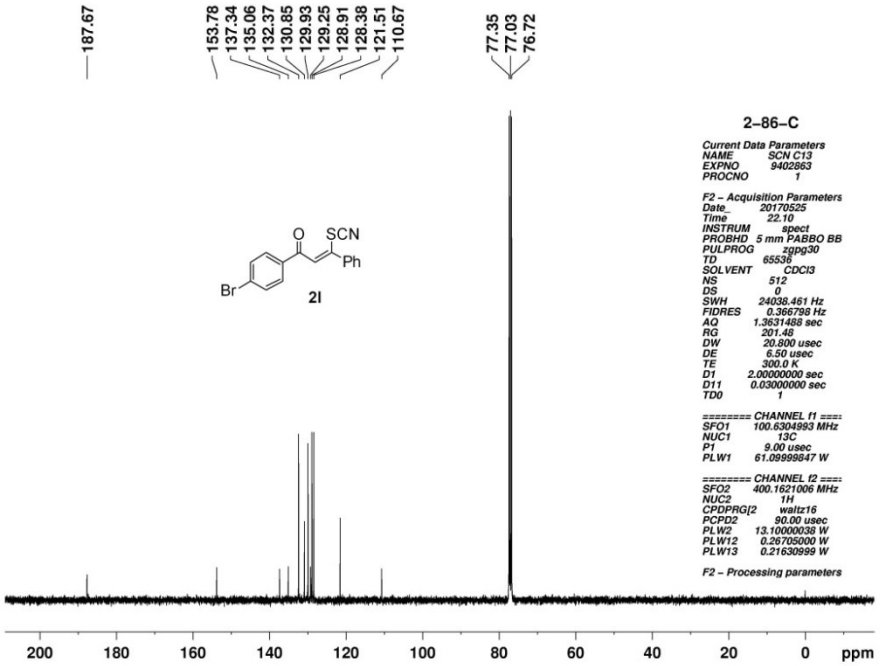


Fig. S26: ^{13}C NMR of 2l

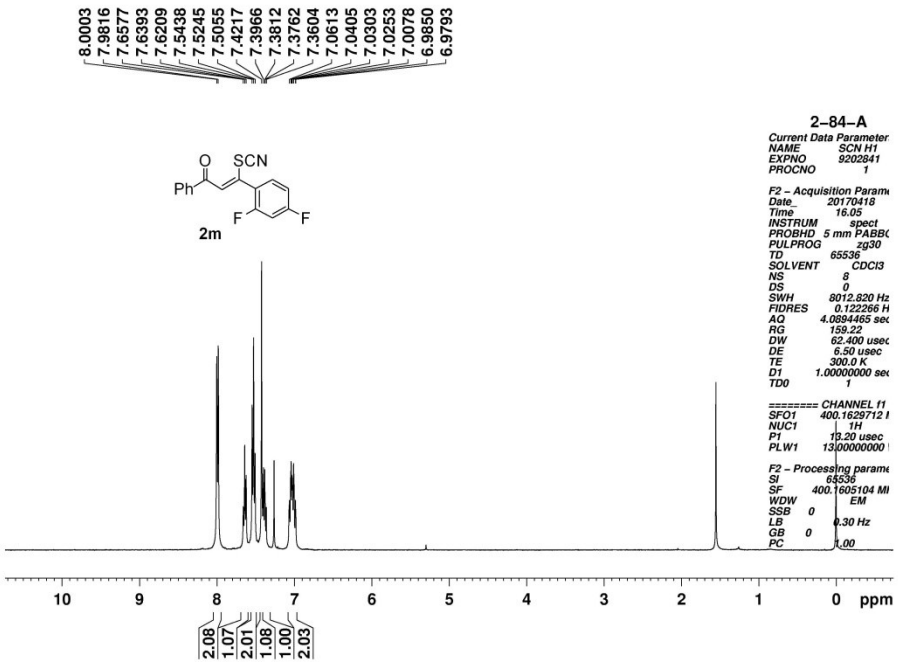


Fig. S27: ^{1}H NMR of 2m

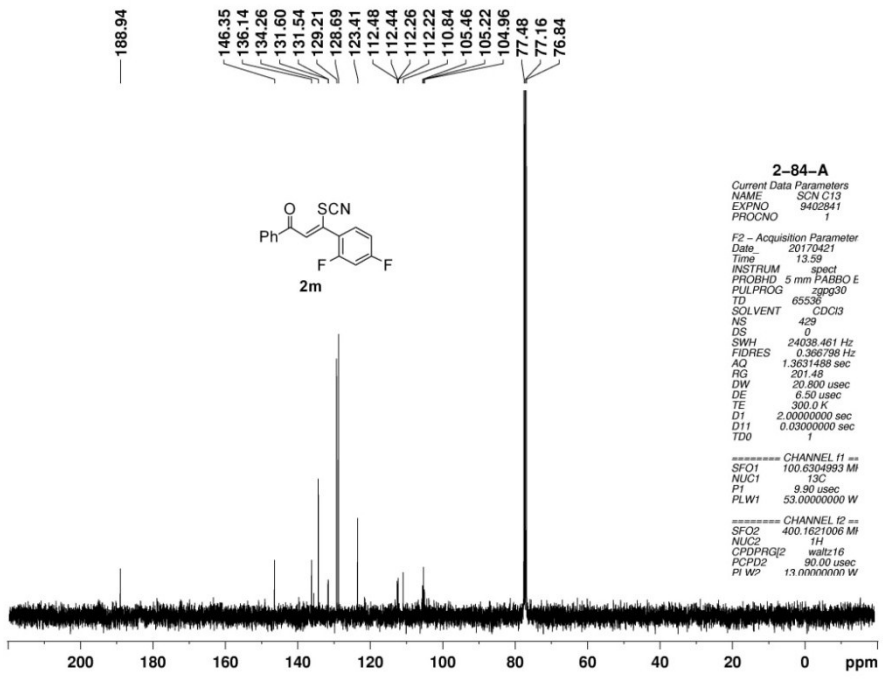


Fig. S28: ^{13}C NMR of 2m

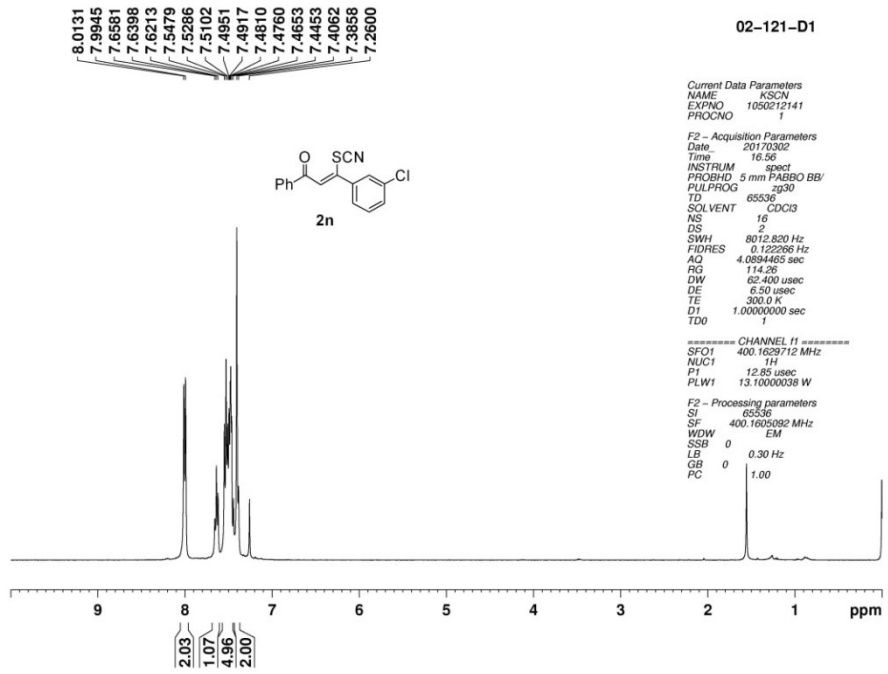


Fig. S29: ^{1}H NMR of 2n

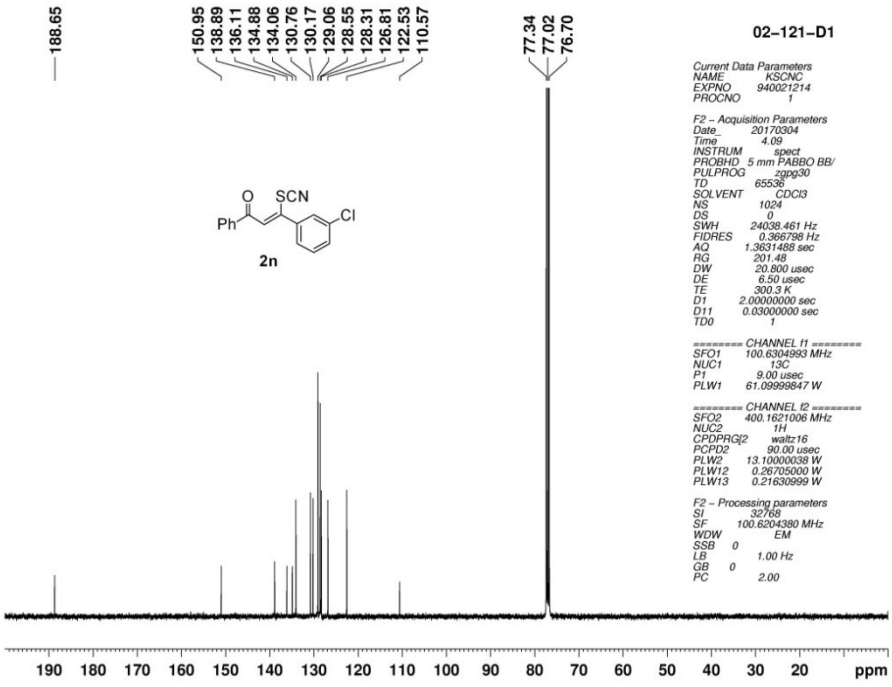


Fig. S30: ^{13}C NMR of 2n

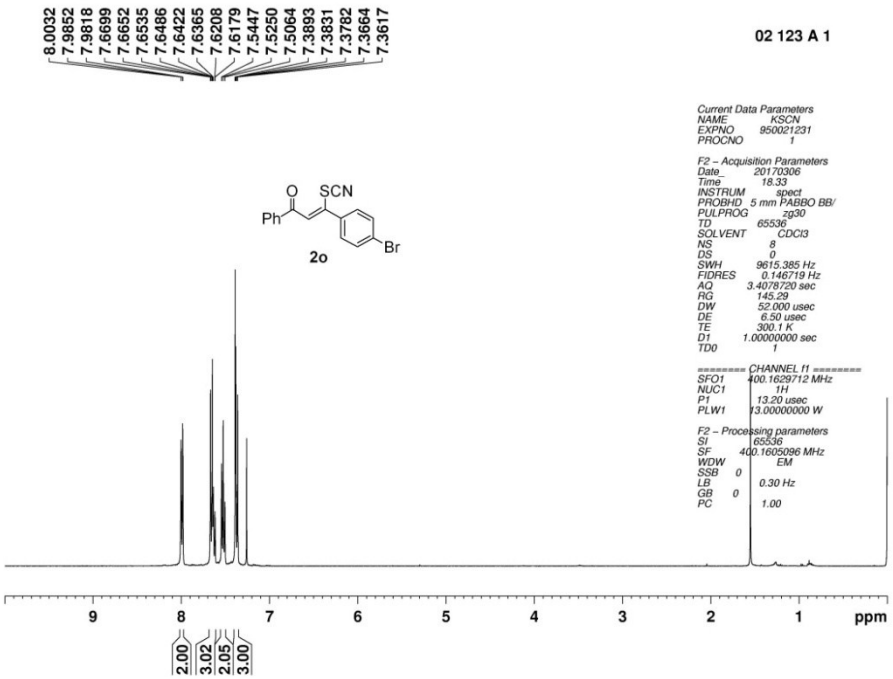


Fig. S31: ^{1}H NMR of 2o

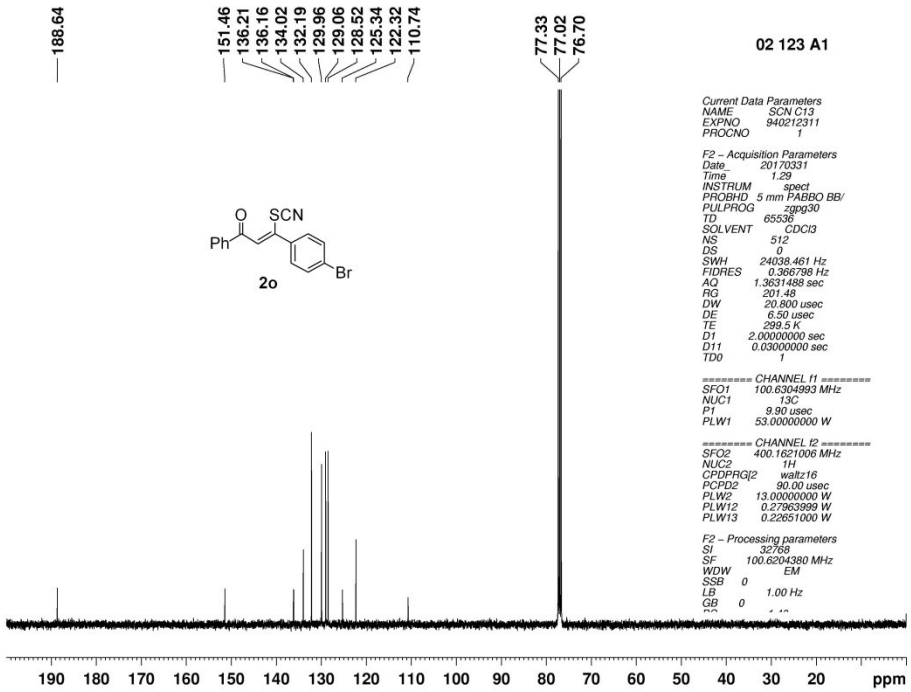


Fig. S32: ^{13}C NMR of 2o

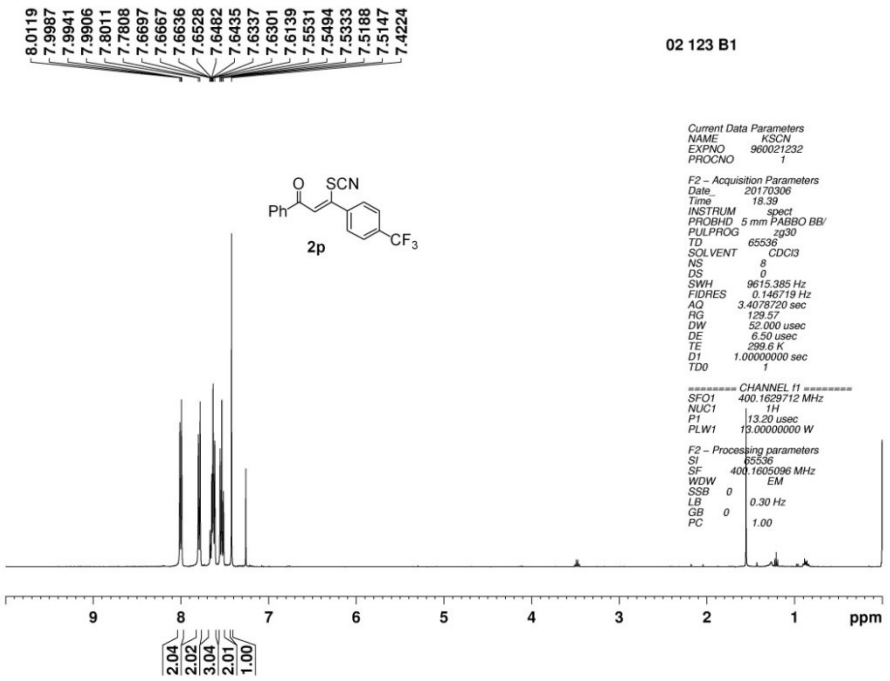


Fig. S33: ^{1}H NMR of 2p

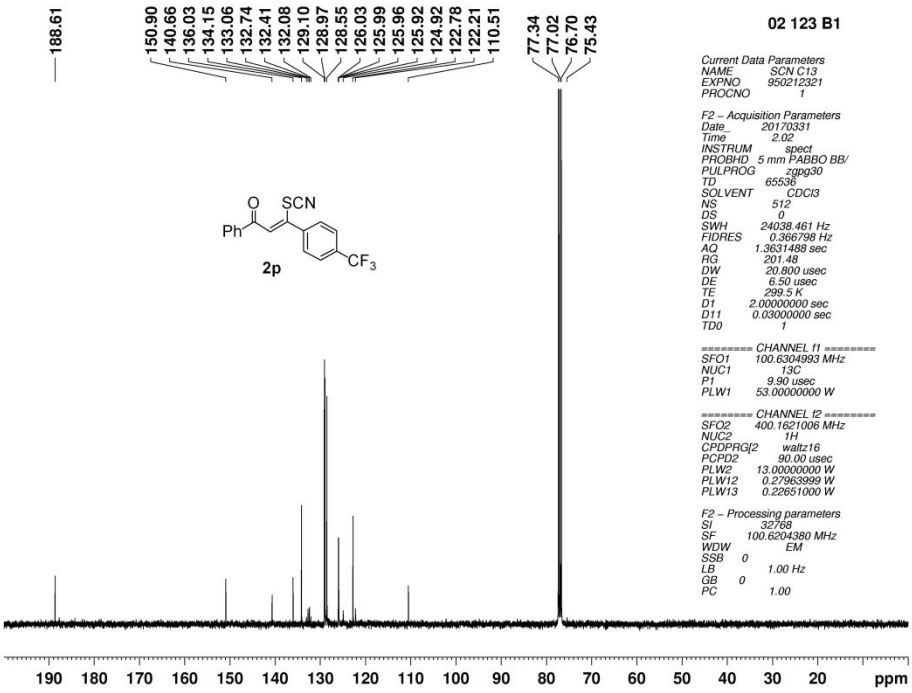


Fig. S34: ^{13}C NMR of 2p

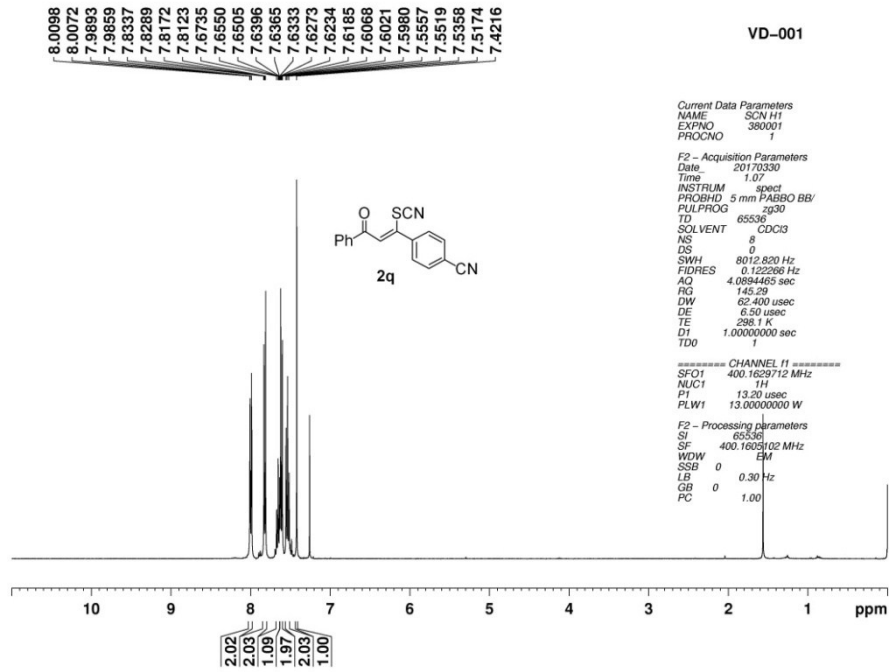


Fig. S35: ^{1}H NMR of 2q

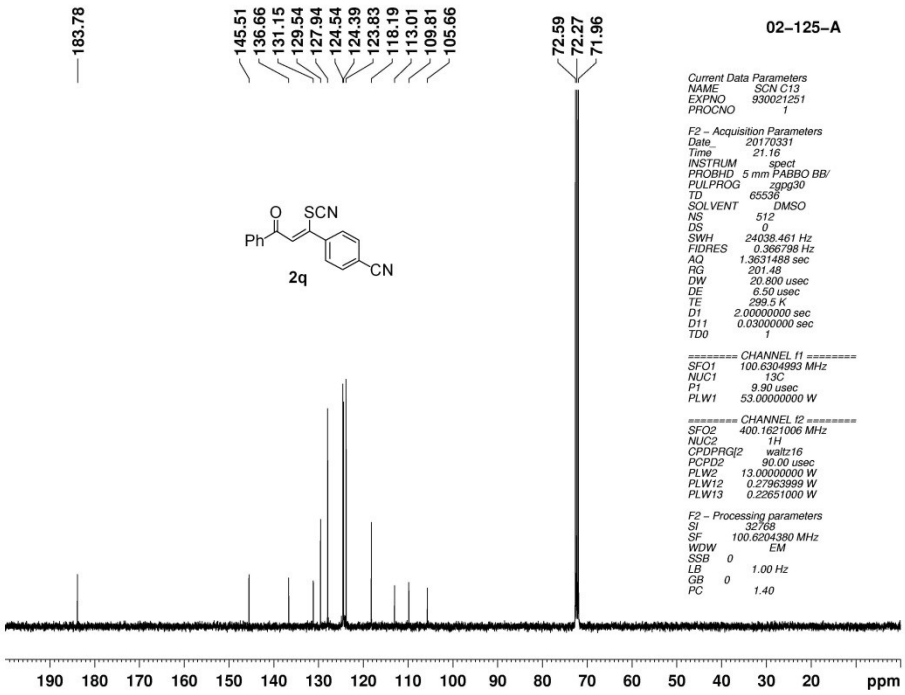


Fig. S36: ^{13}C NMR of 2q

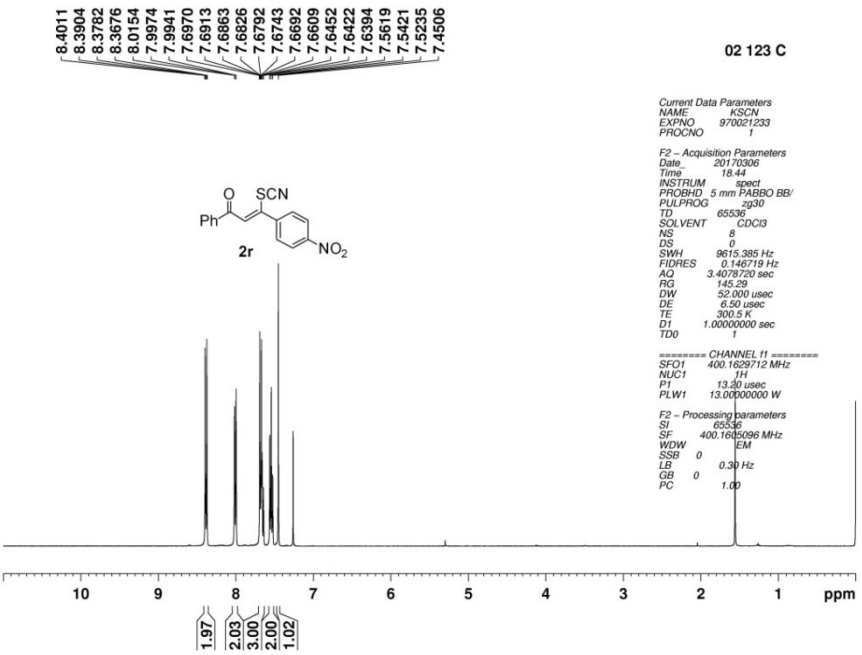


Fig. S37: ^{1}H NMR of 2r

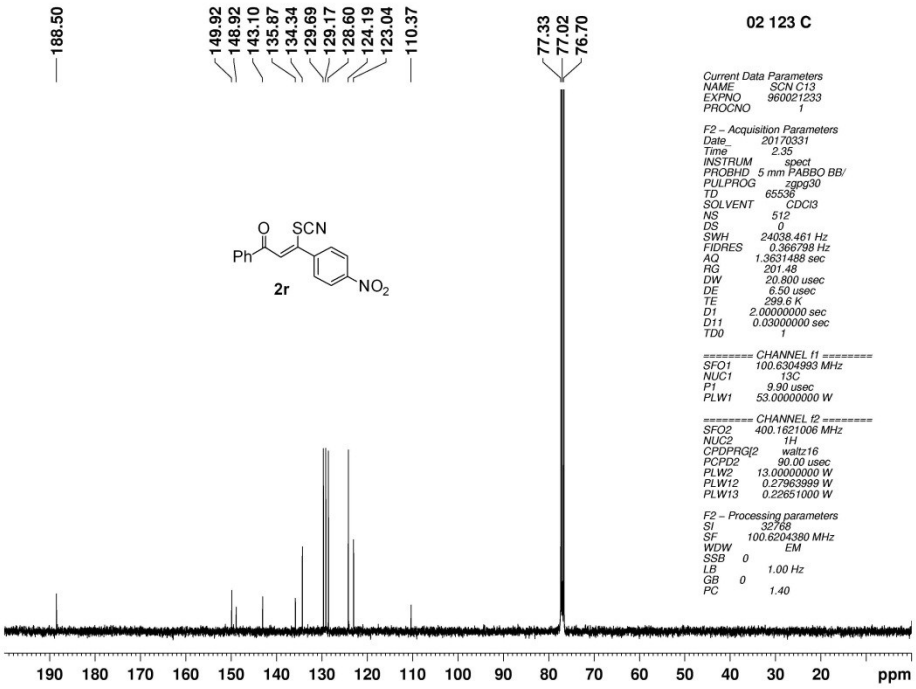


Fig. S38: ^{13}C NMR of 2r

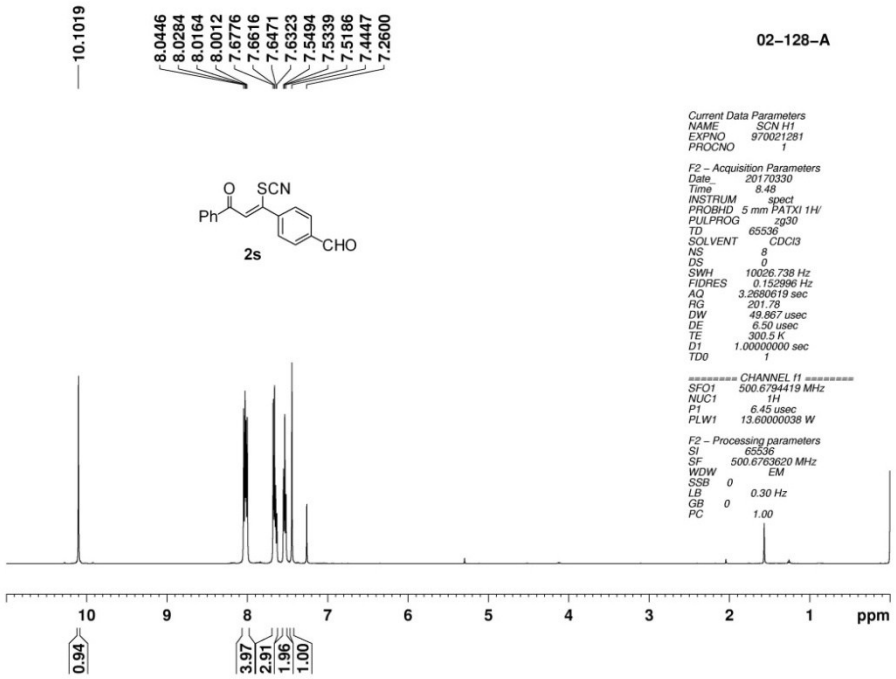


Fig. S39: ^{1}H NMR of 2s

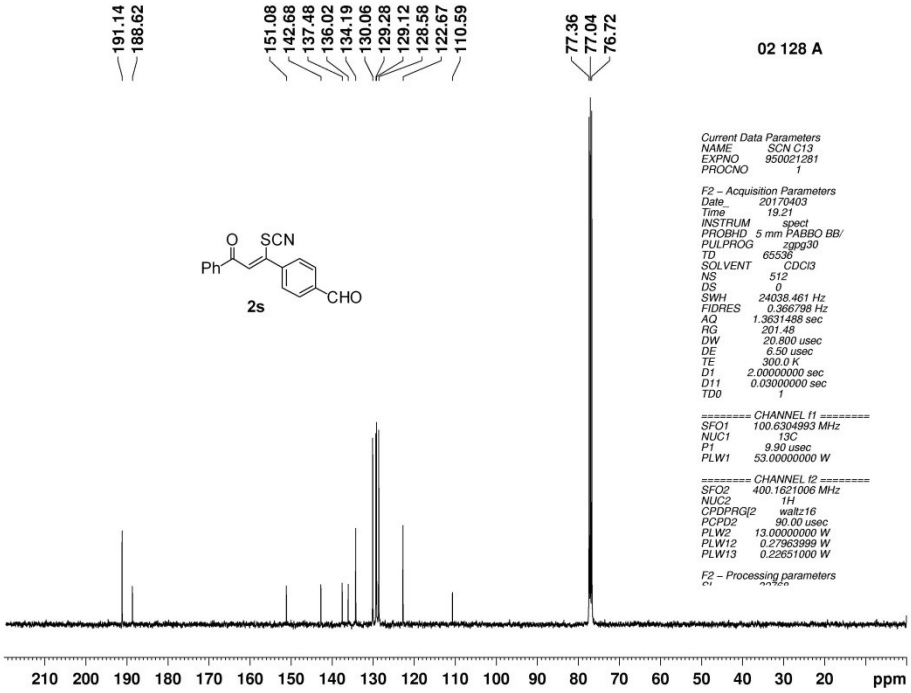


Fig. S40: ^{13}C NMR of 2s

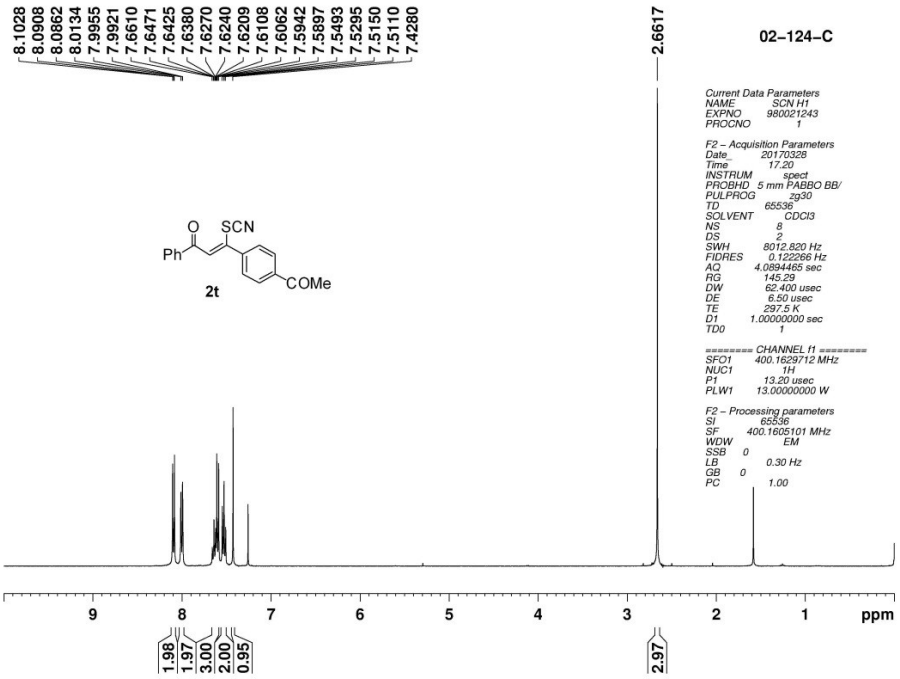


Fig. S41: ^{1}H NMR of 2t

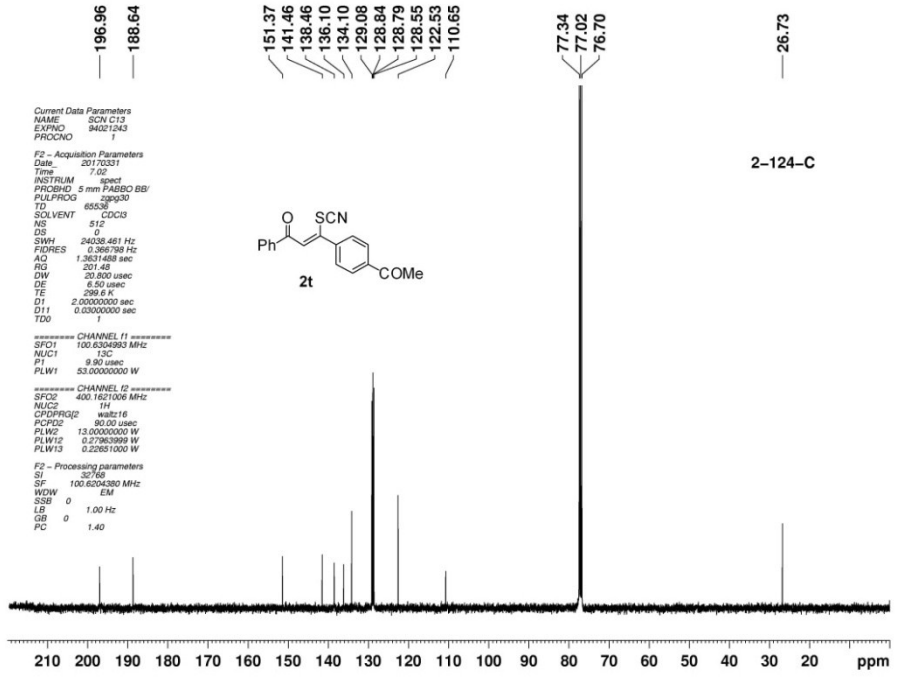


Fig. S42: ^{13}C NMR of 2t

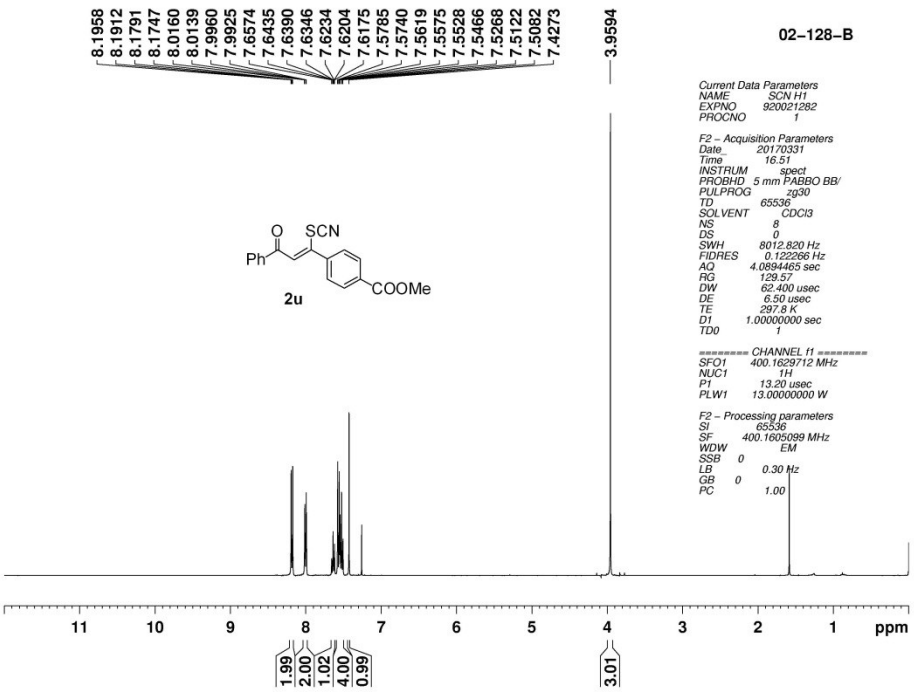


Fig. S43: ^{1}H NMR of 2u

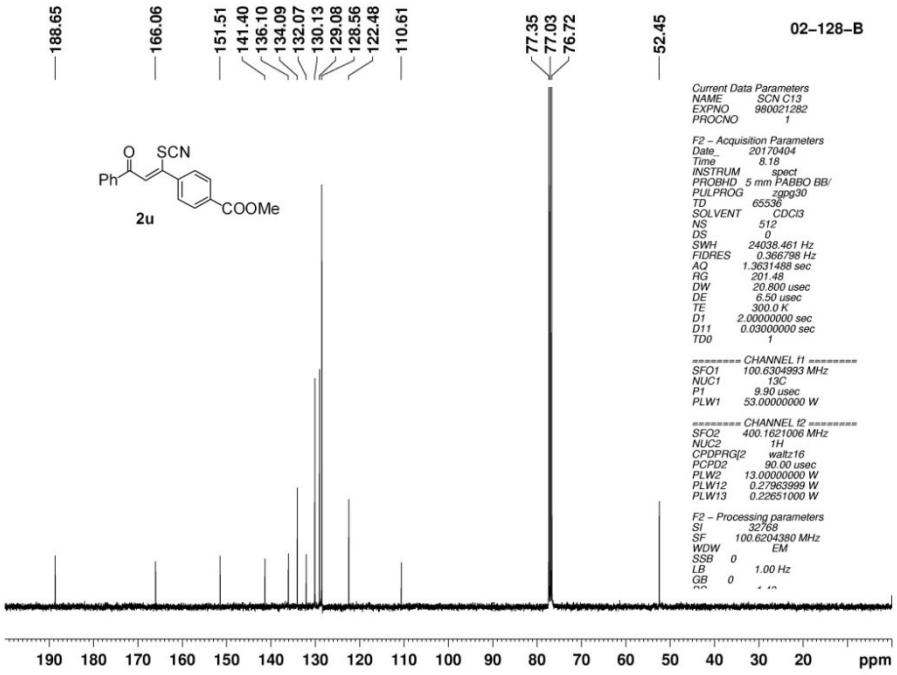


Fig. S44: ^{13}C NMR of 2u

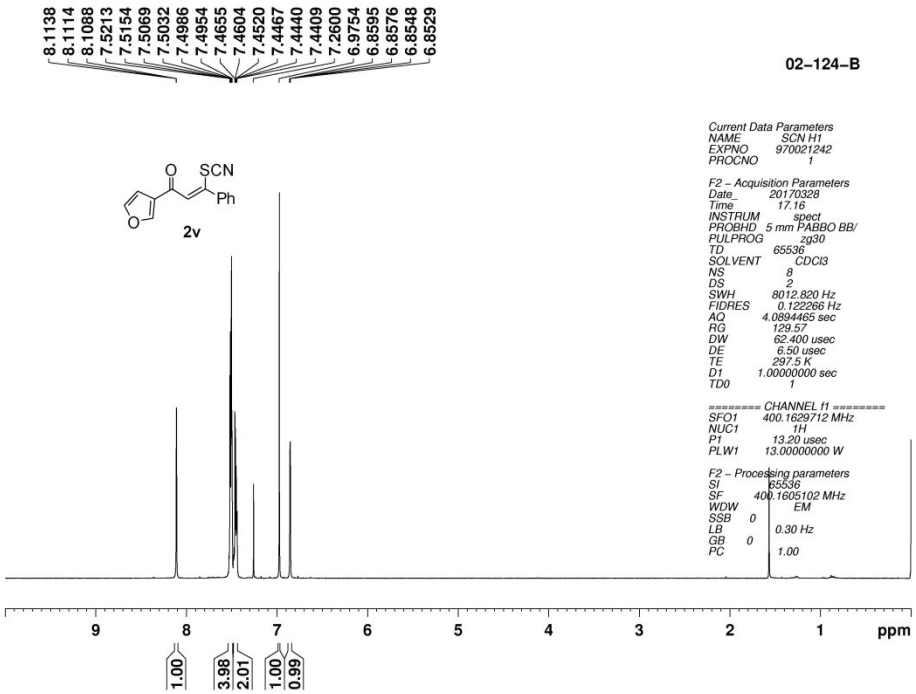


Fig. S45: ^{1}H NMR of 2v

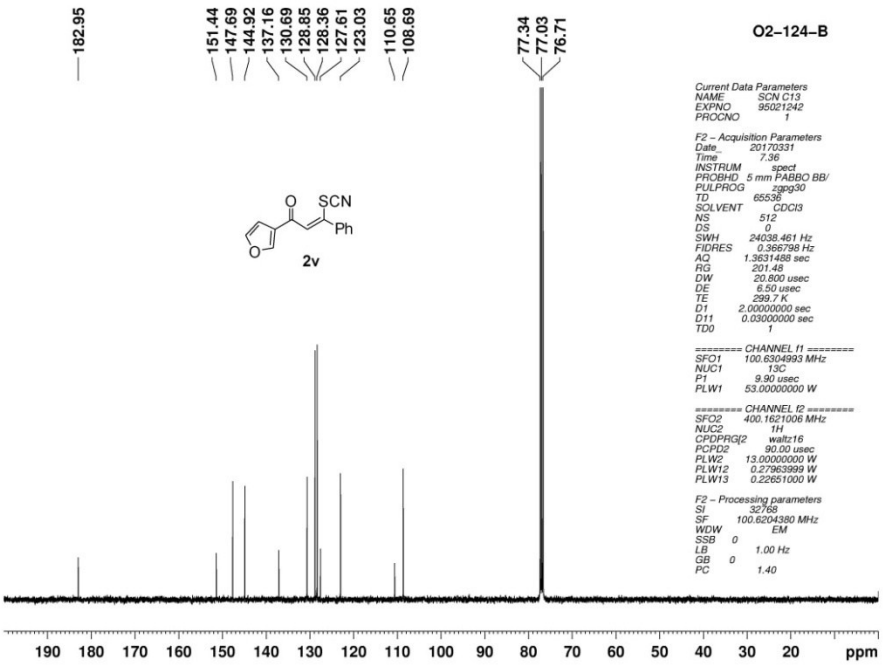


Fig. S46: ^{13}C NMR of 2v

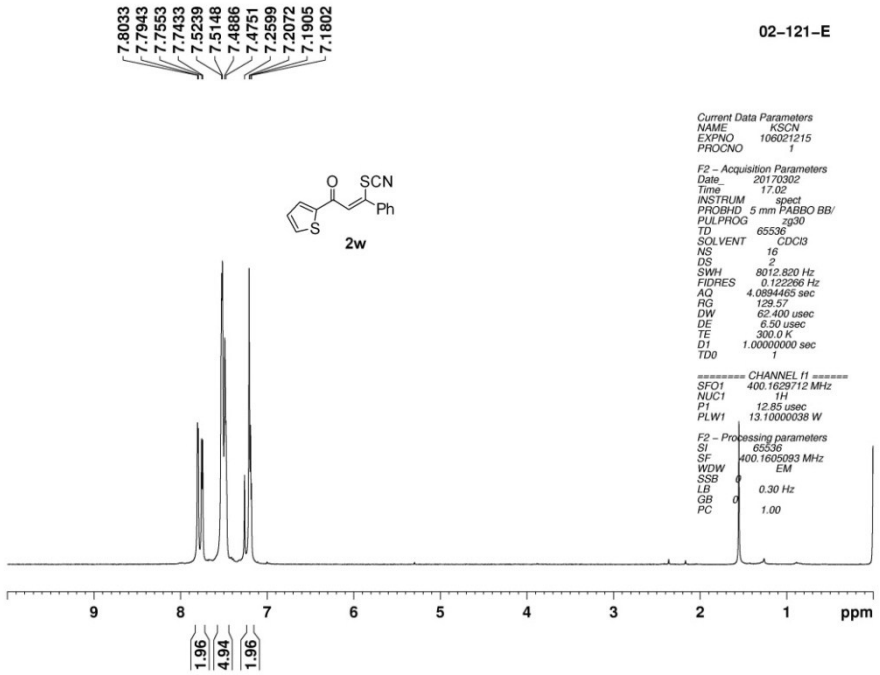


Fig. S47: ^{1}H NMR of 2w

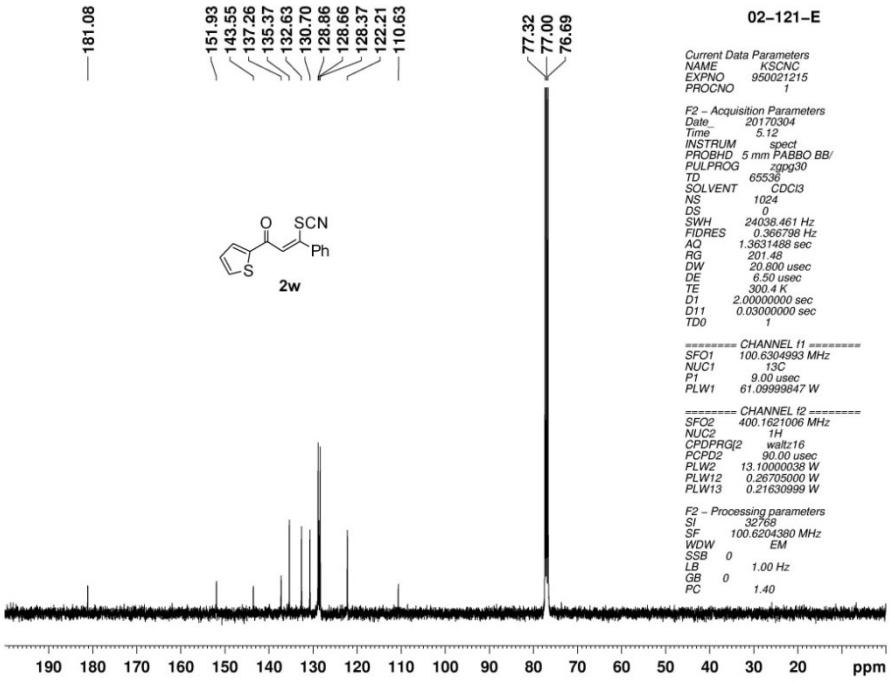


Fig. S48: ^{13}C NMR of 2w

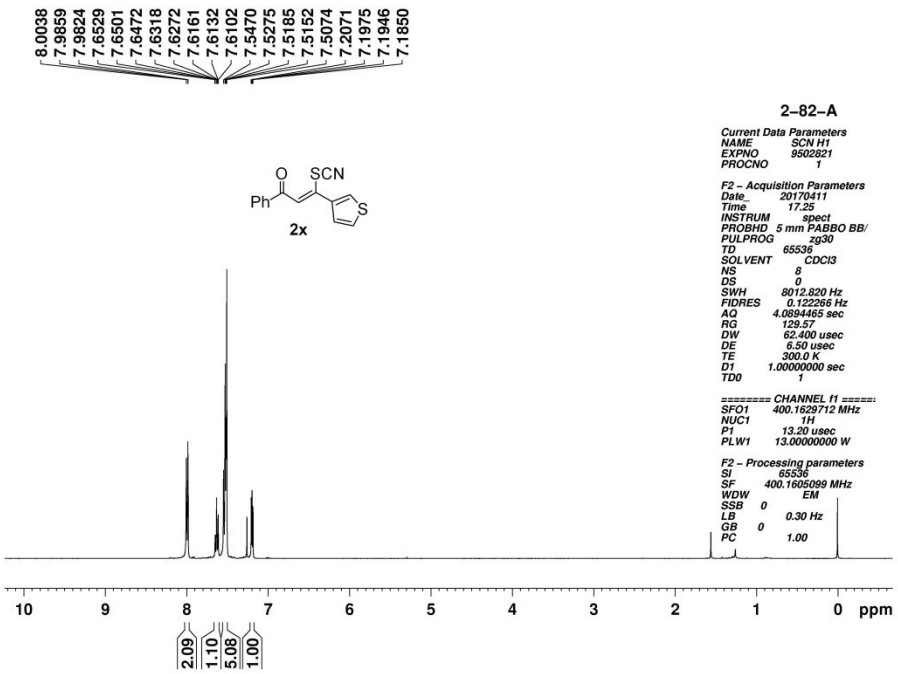


Fig. S49: ^{1}H NMR of 2x

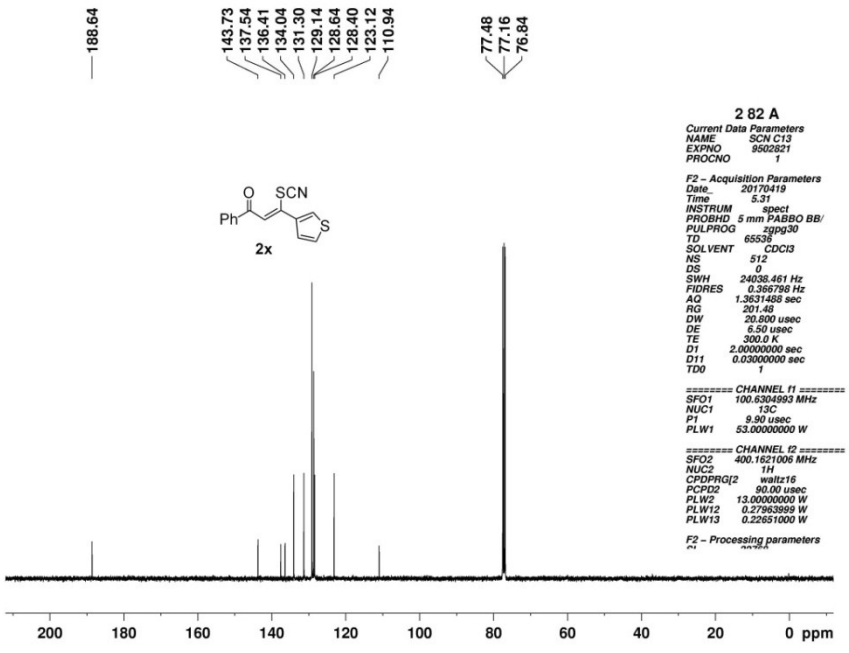


Fig. S50: ^{13}C NMR of 2x

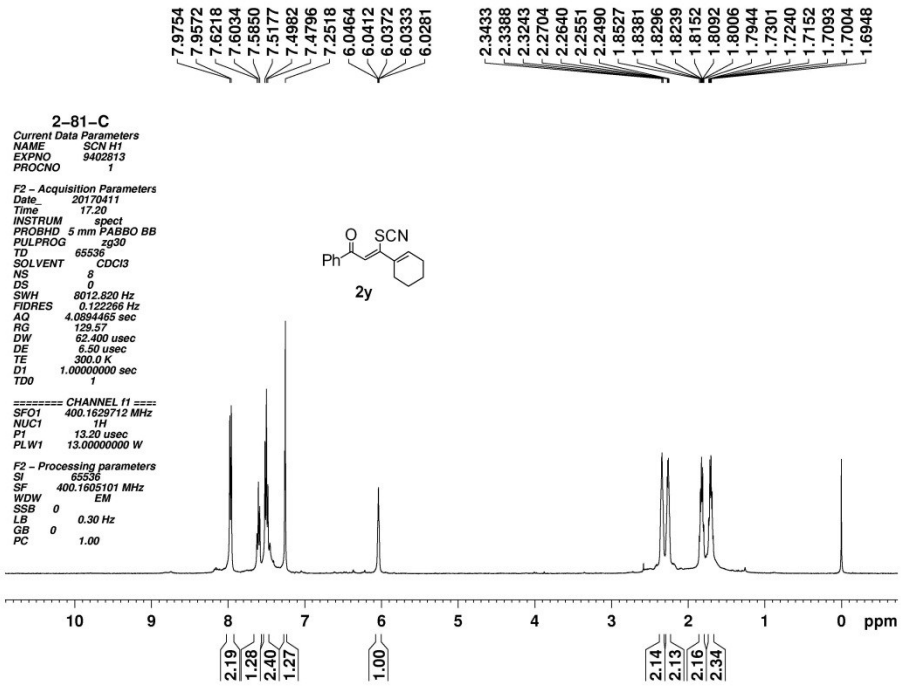


Fig. S51: ^{1}H NMR of 2y

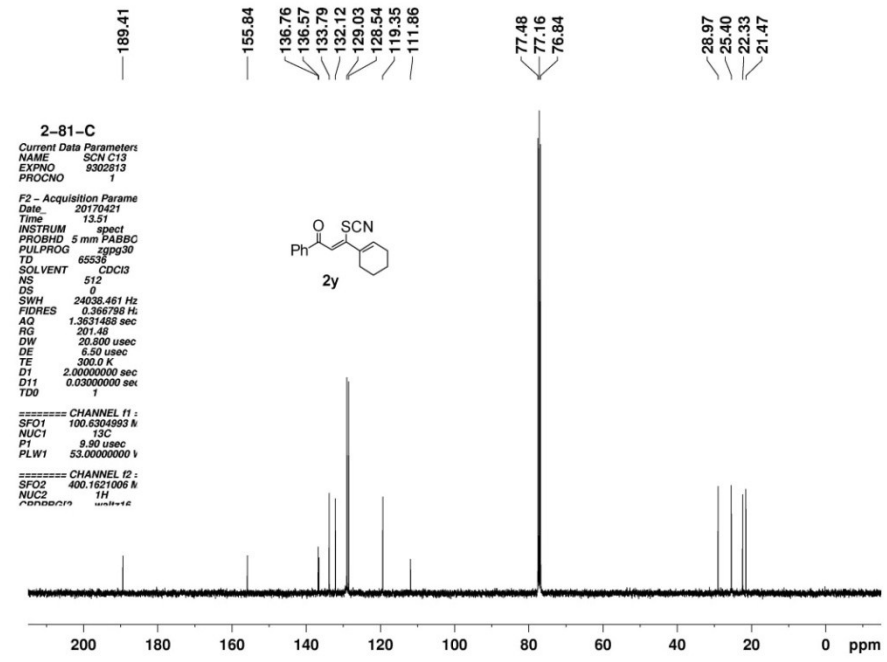


Fig. S52: ^{13}C NMR of 2y

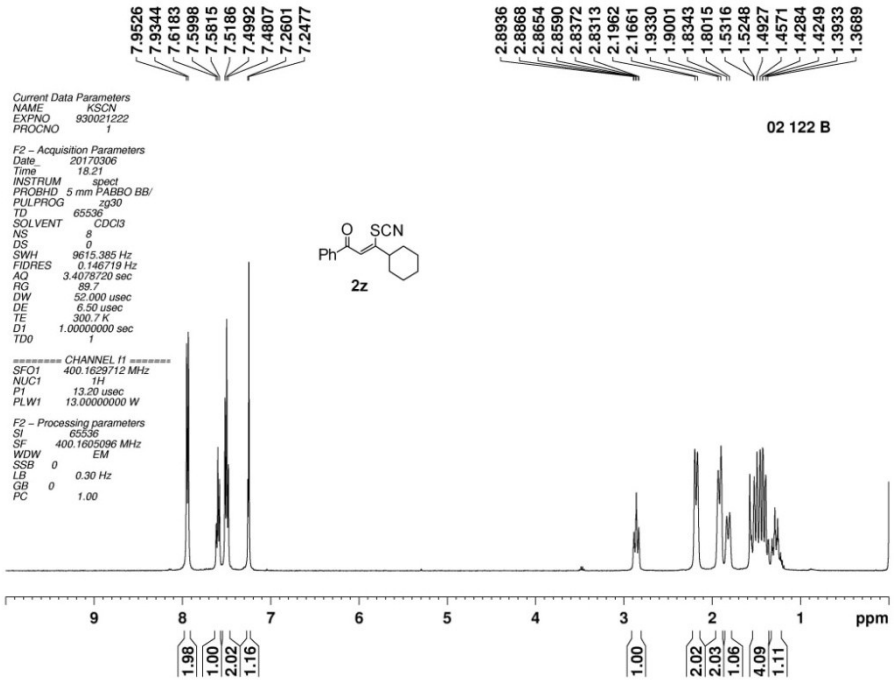


Fig. S53: ^{1}H NMR of 2z

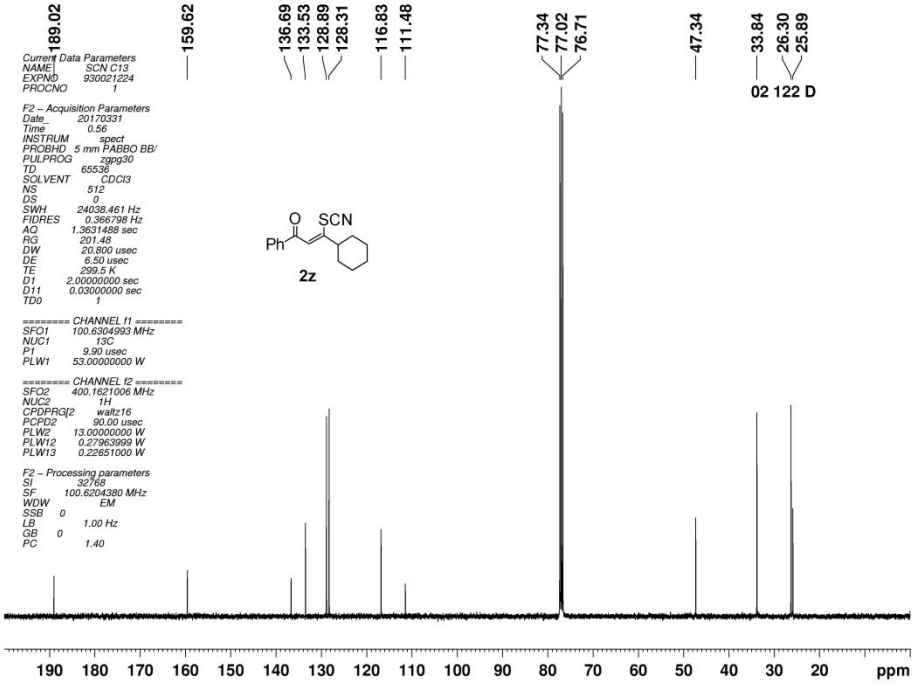


Fig. S54: ^{13}C NMR of 2z

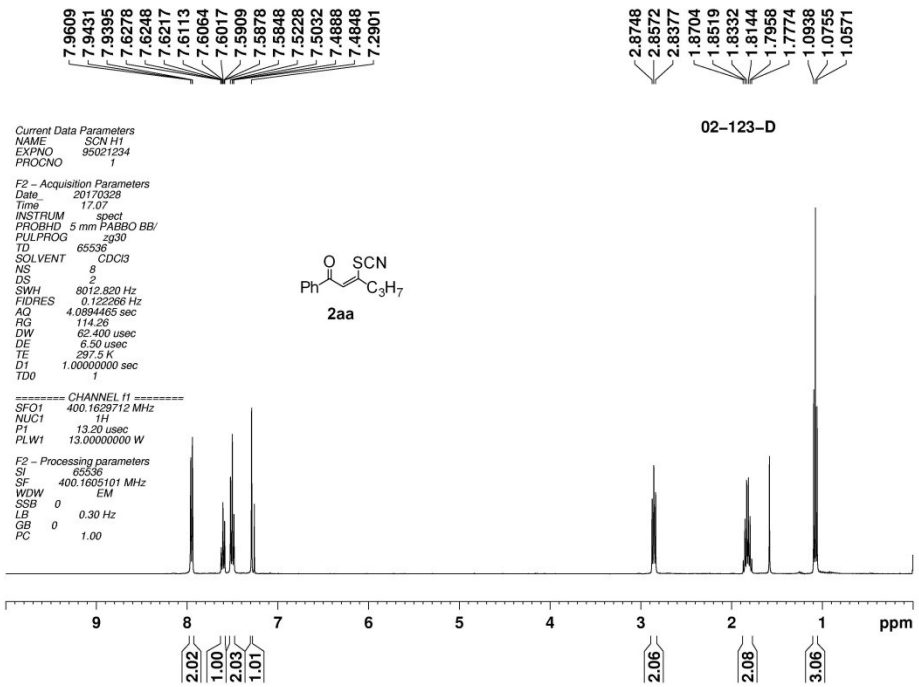


Fig. S55: ^{1}H NMR of 2aa

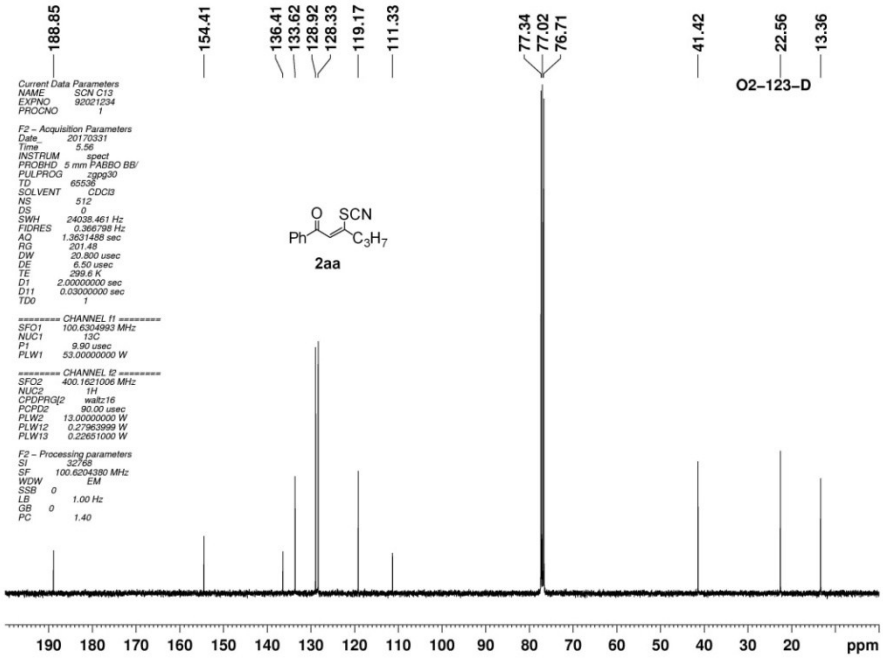


Fig. S56: ^{13}C NMR of 2aa

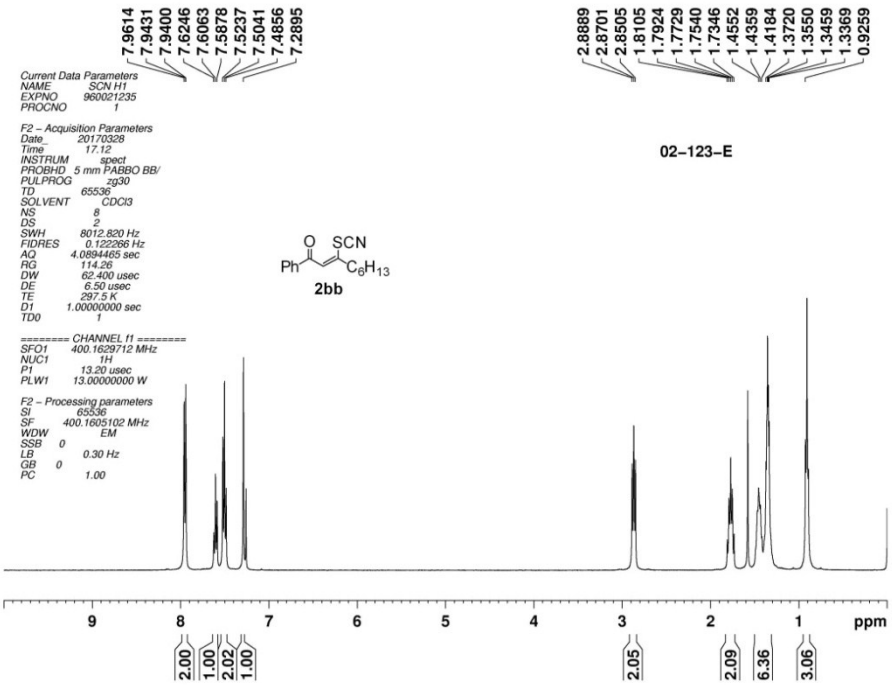


Fig. S57: ^{1}H NMR of 2bb

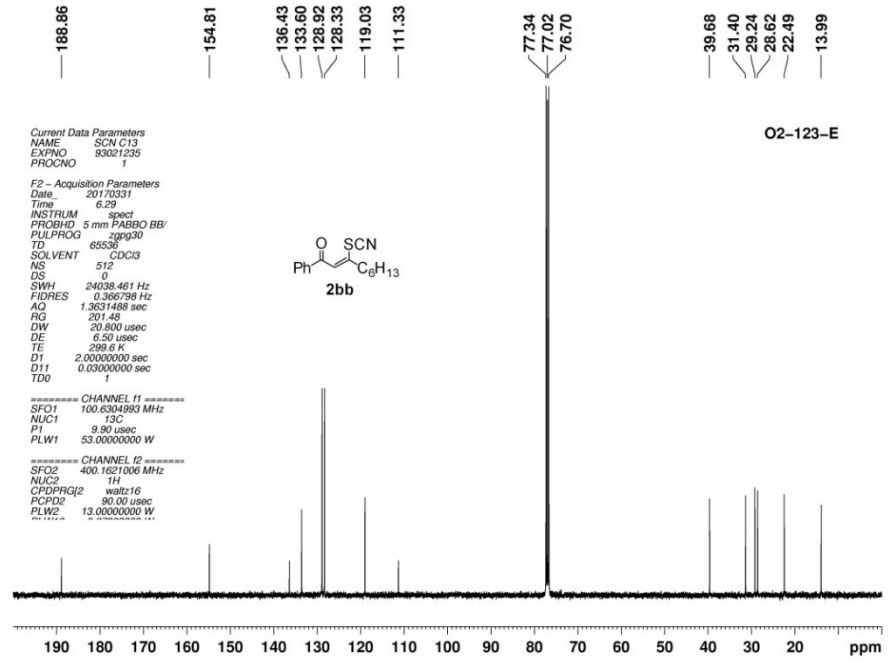


Fig. S58: ^{13}C NMR of 2bb

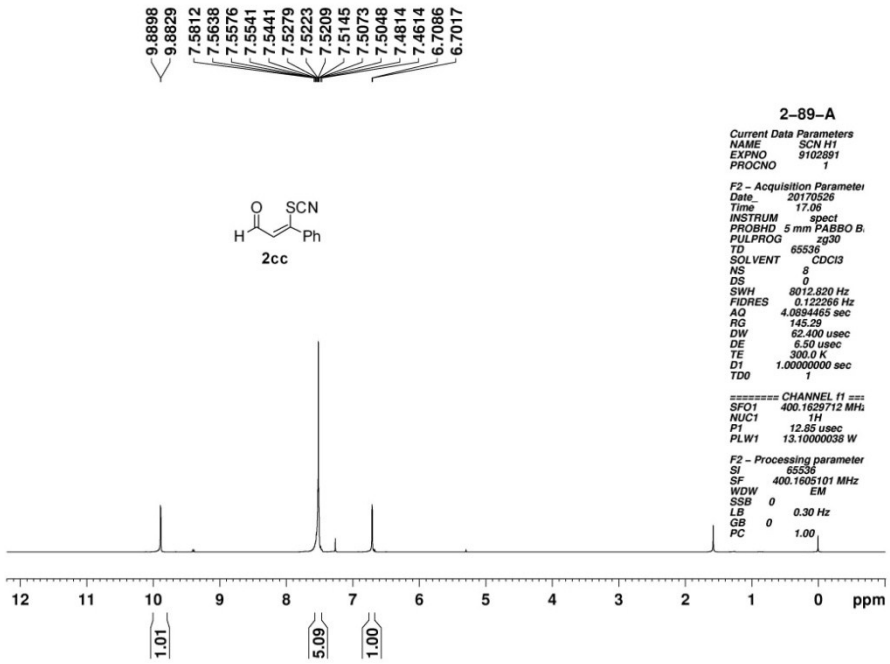


Fig. S59: ^{1}H NMR of 2cc

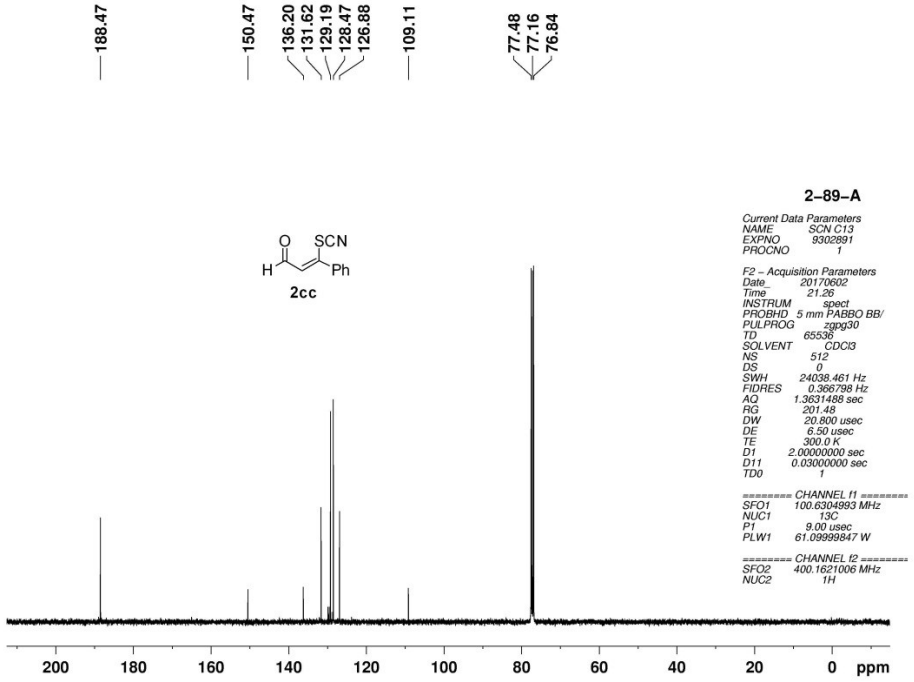


Fig. S60: ^{13}C NMR of 2cc

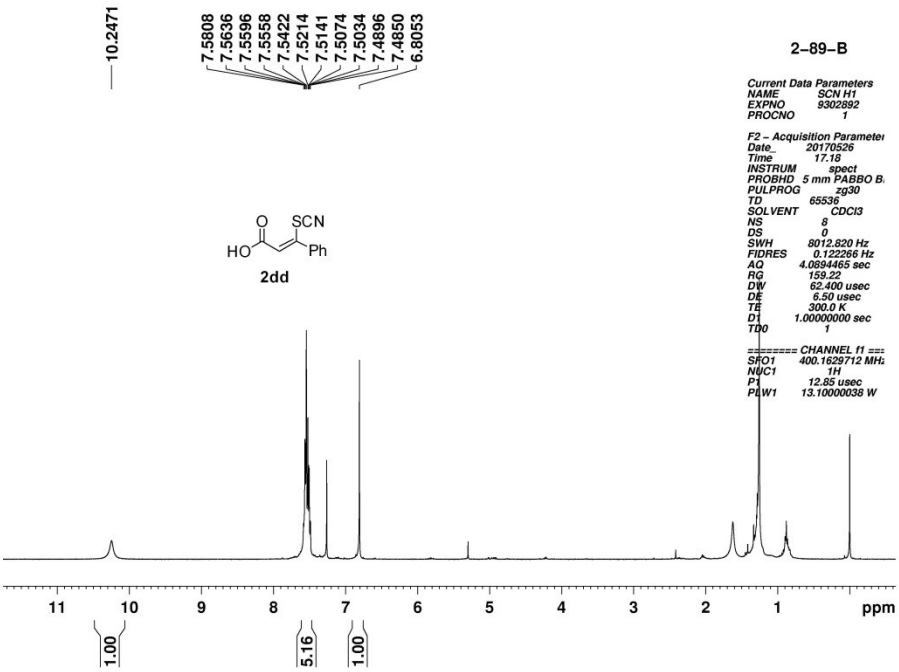


Fig. S61: ^{1}H NMR of 2dd

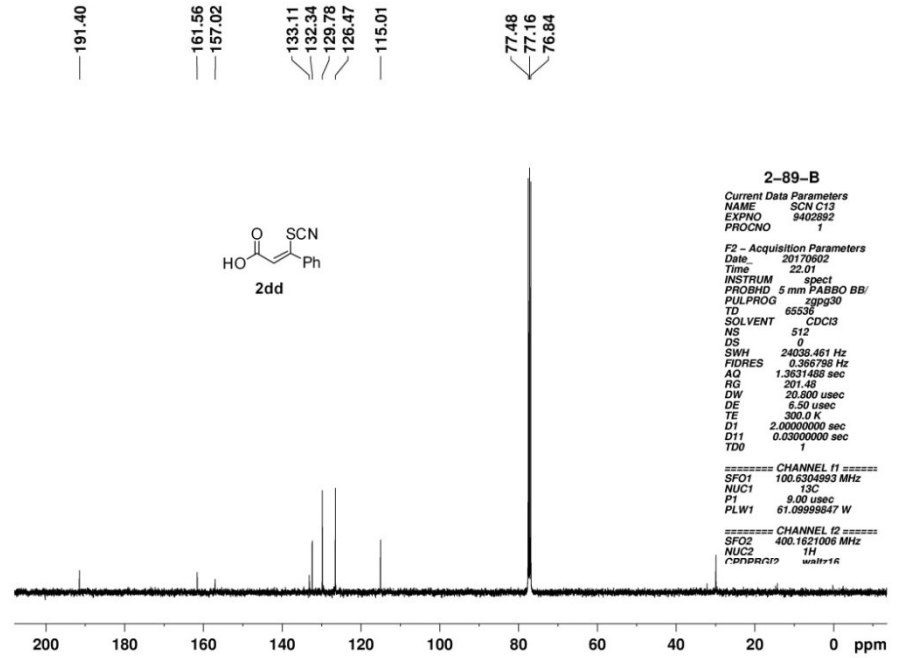


Fig. S62: ^{13}C NMR of 2dd

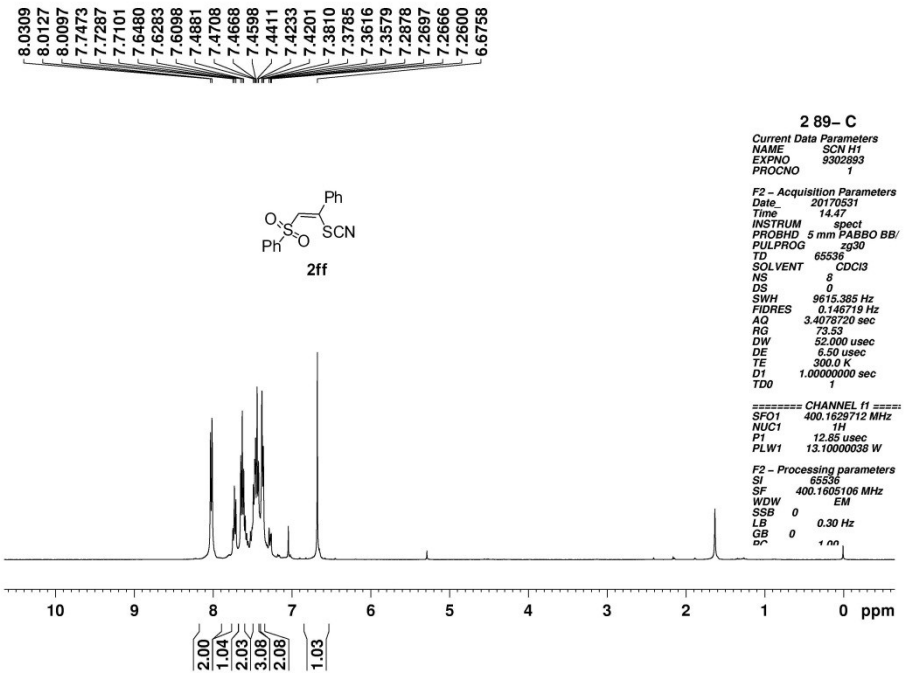


Fig. S63: ^{1}H NMR of 2ff

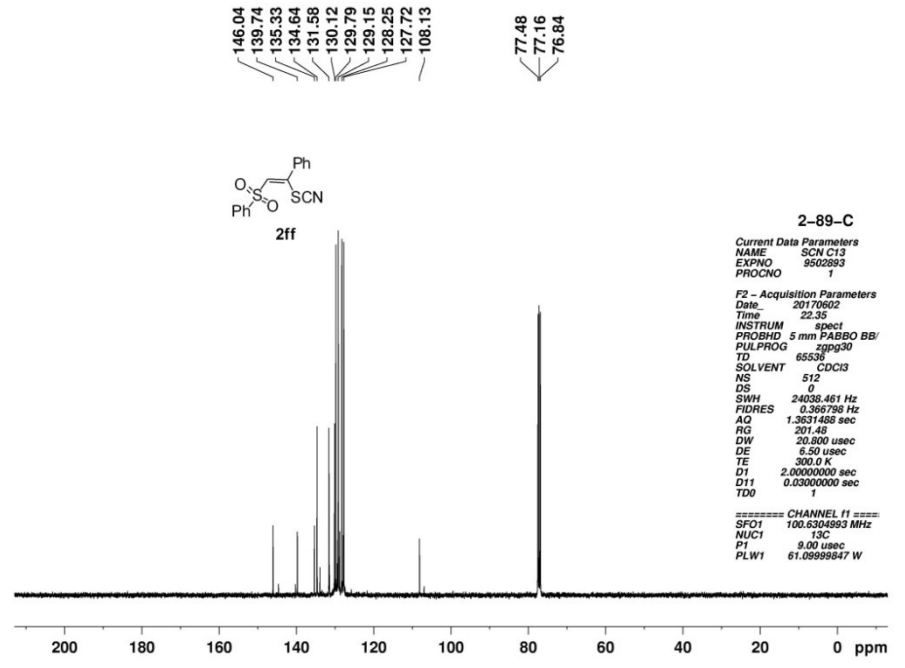


Fig. S64: ^{13}C NMR of 2ff

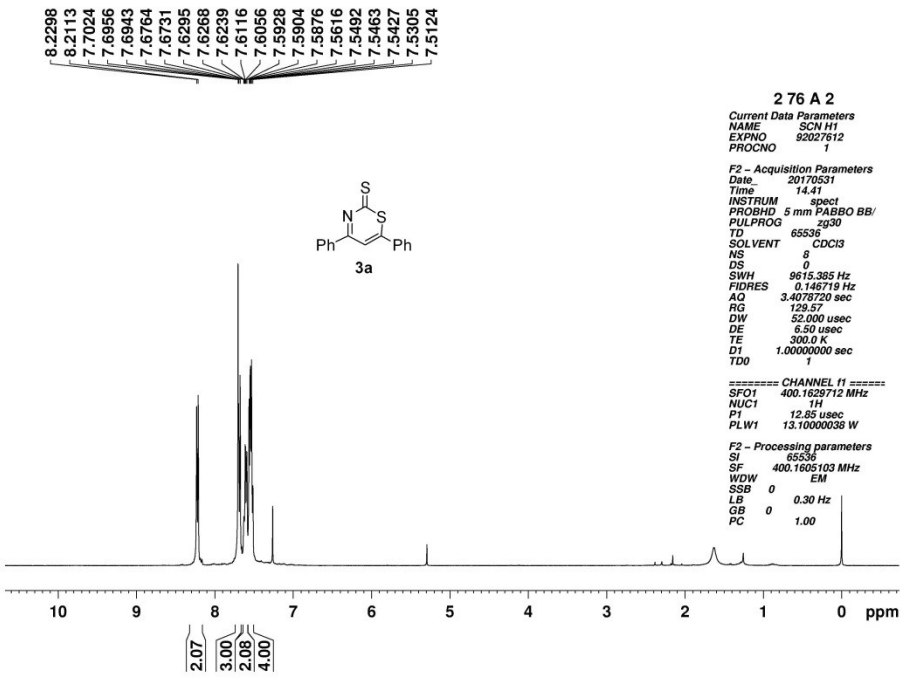


Fig. S65: ^{1}H NMR of 3a

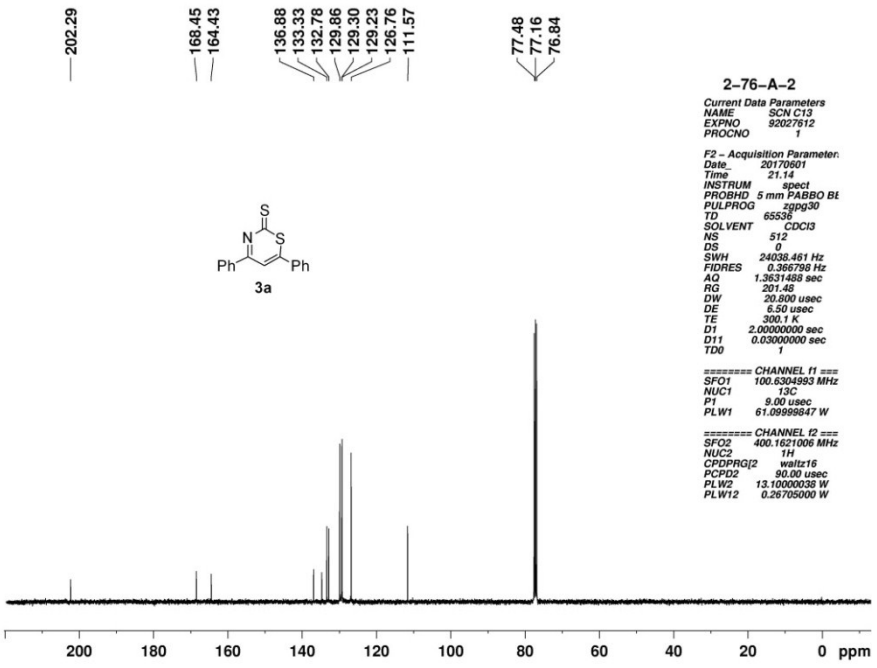


Fig. S66: ^{13}C NMR of 3a

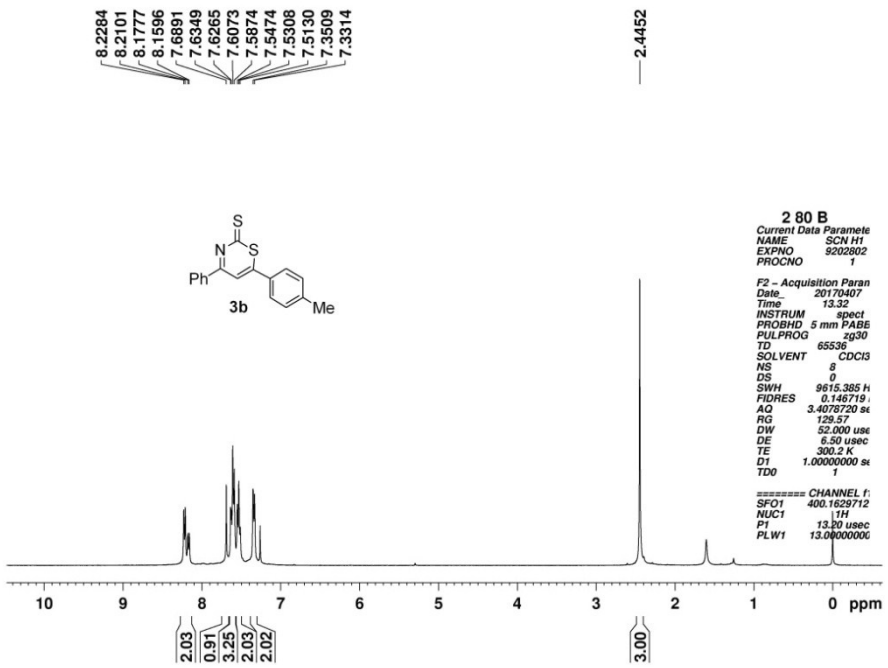


Fig. S67: ^{1}H NMR of 3b

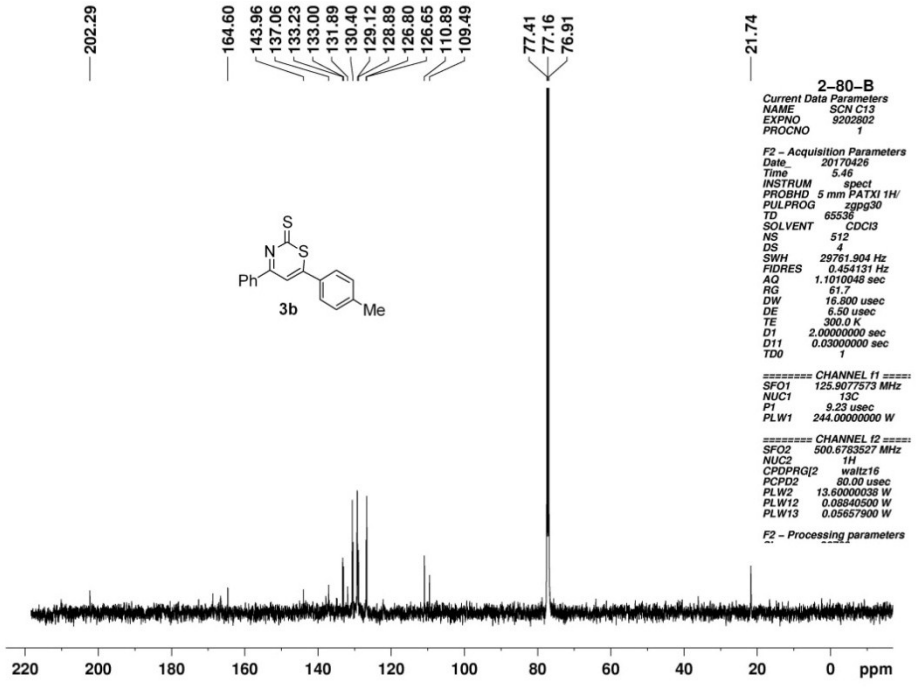


Fig. S68: ^{13}C NMR of 3b

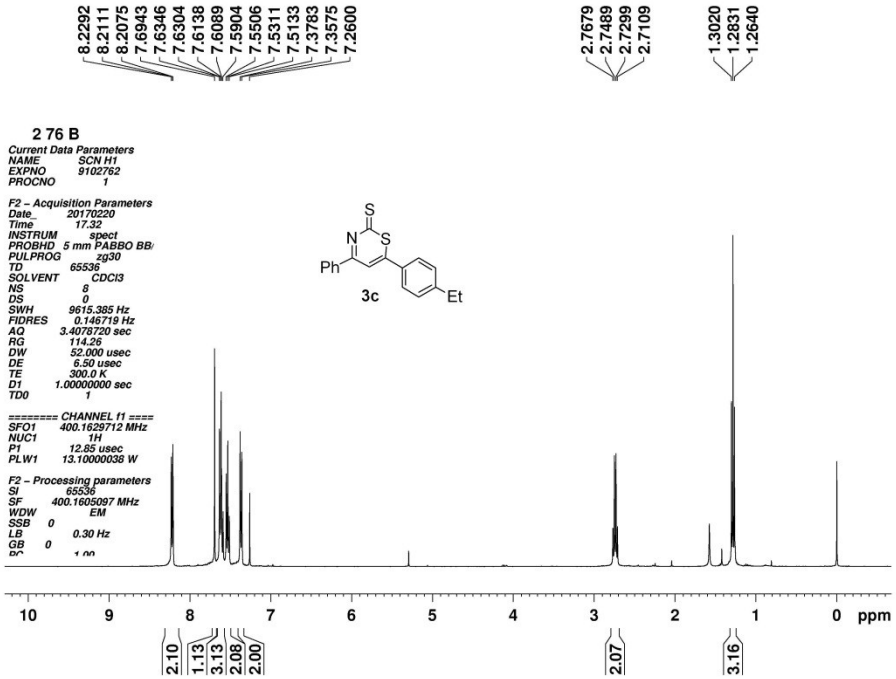


Fig. S69: ^{1}H NMR of 3c

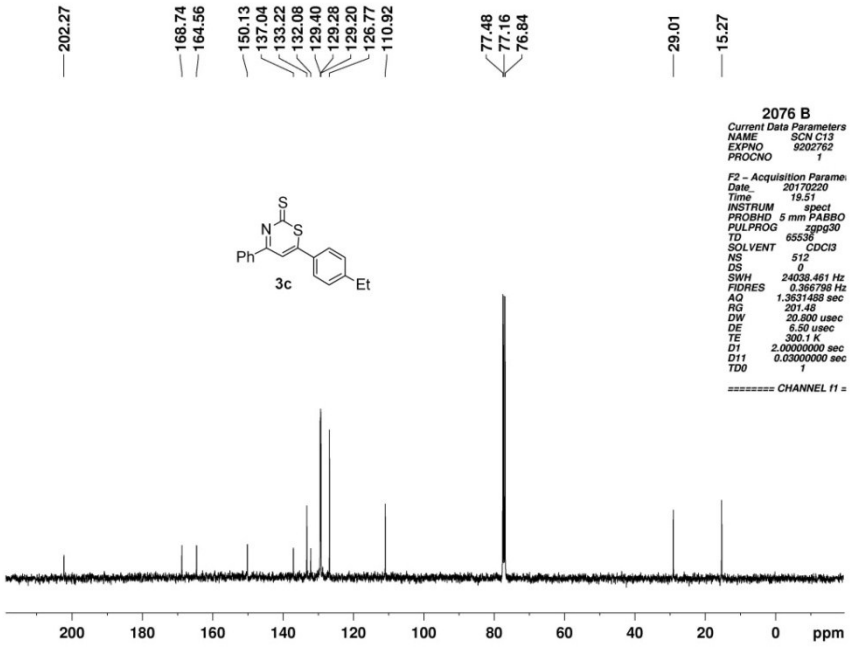


Fig. S70: ^{13}C NMR of 3c

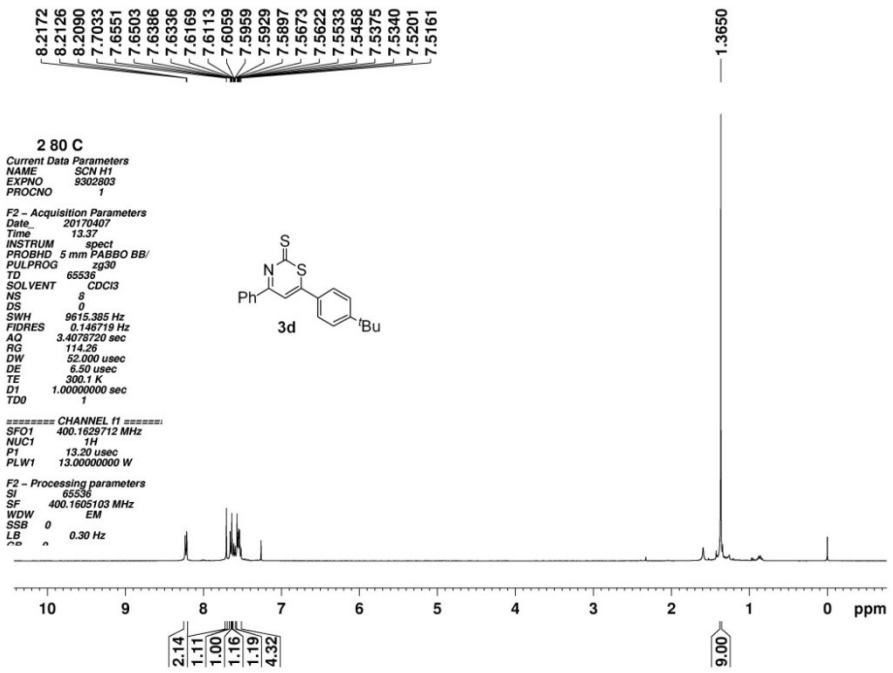


Fig. S71: ^{1}H NMR of 3d

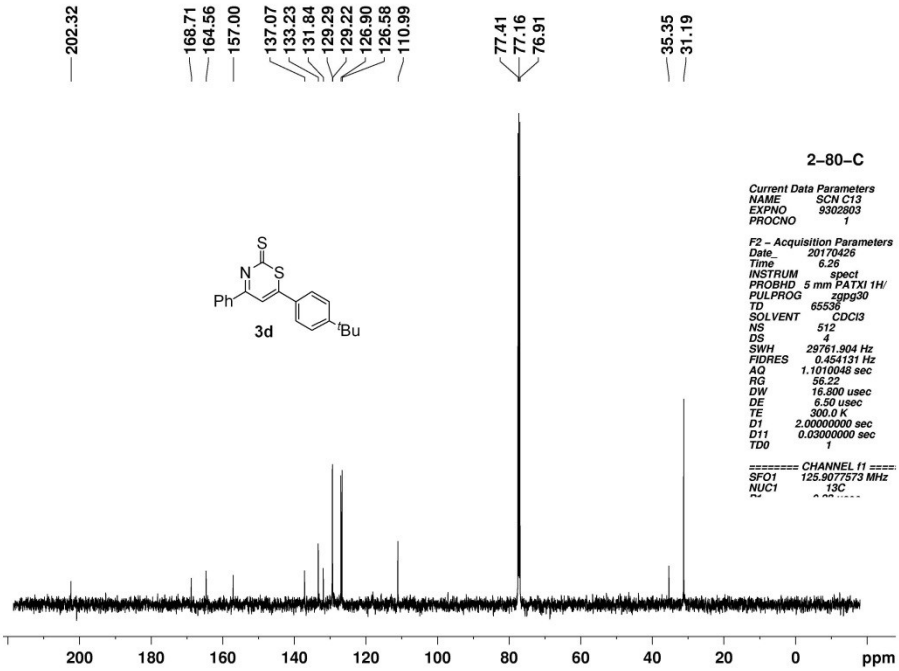


Fig. S72: ^{13}C NMR of 3d

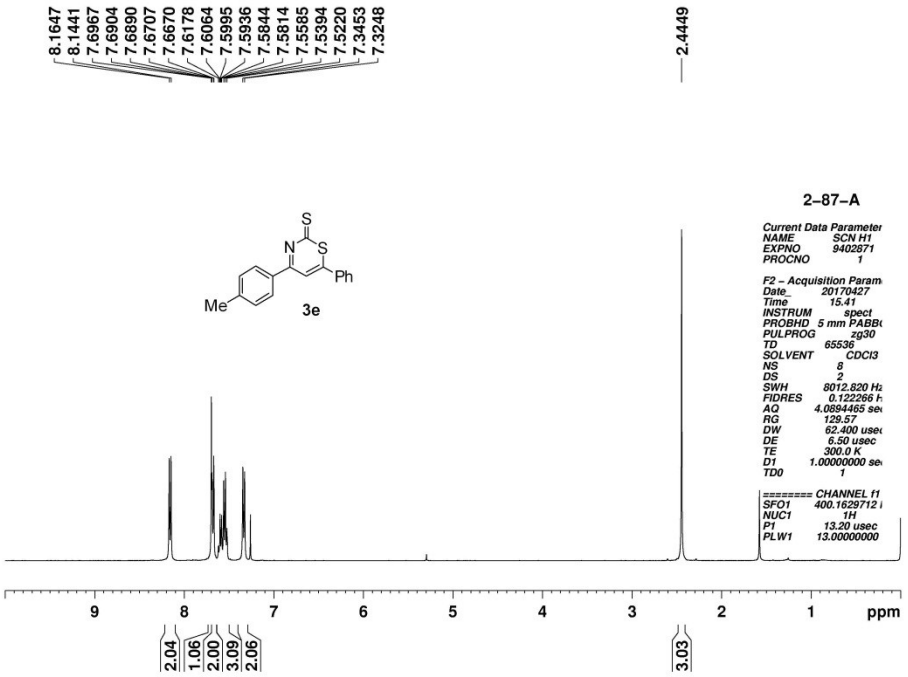


Fig. S73: ^{1}H NMR of 3e

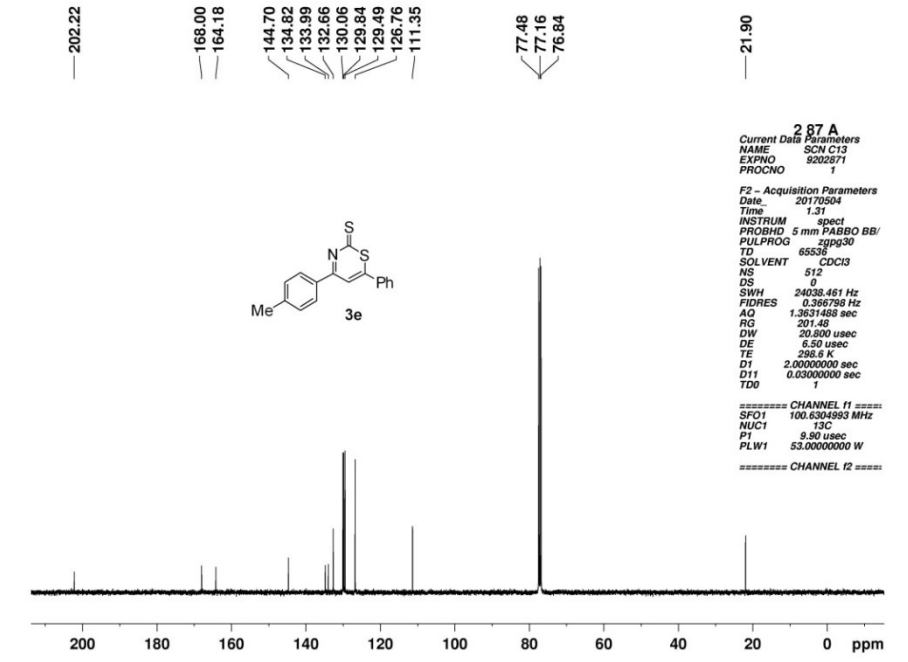


Fig. S74: ^{13}C NMR of 3e

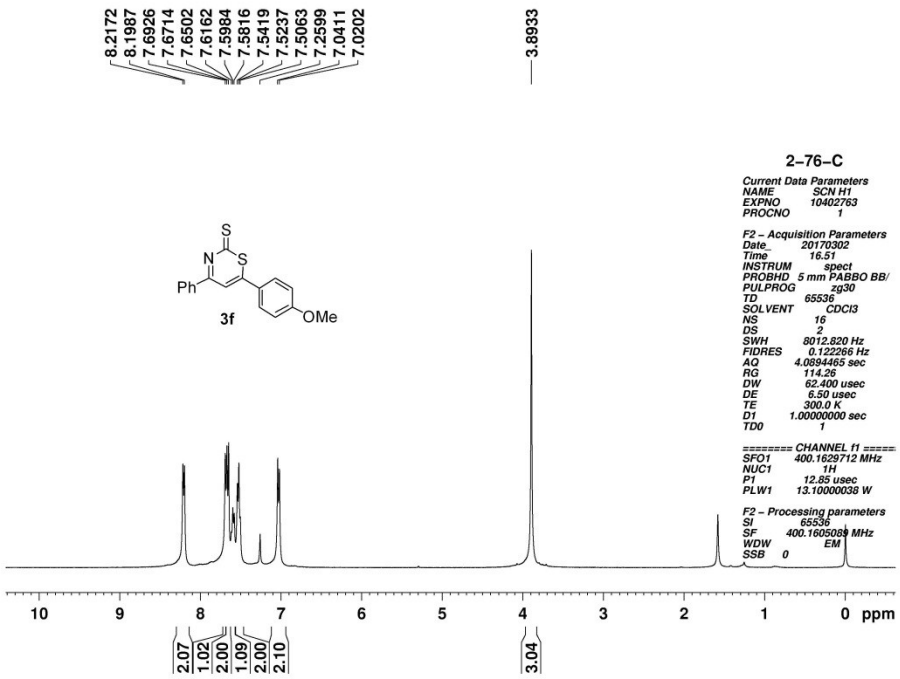


Fig. S75: ^{1}H NMR of 3f

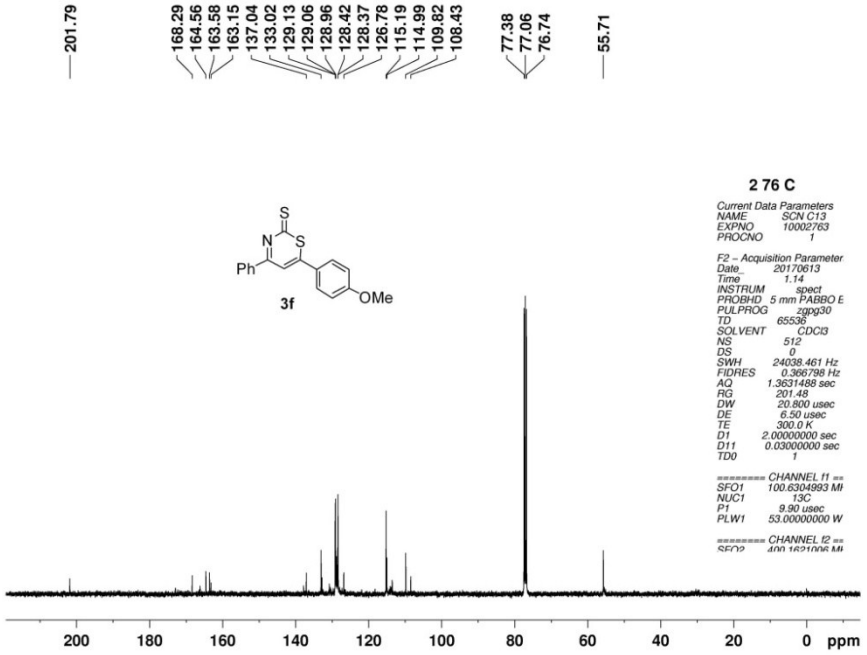


Fig. S76: ^{13}C NMR of 3f

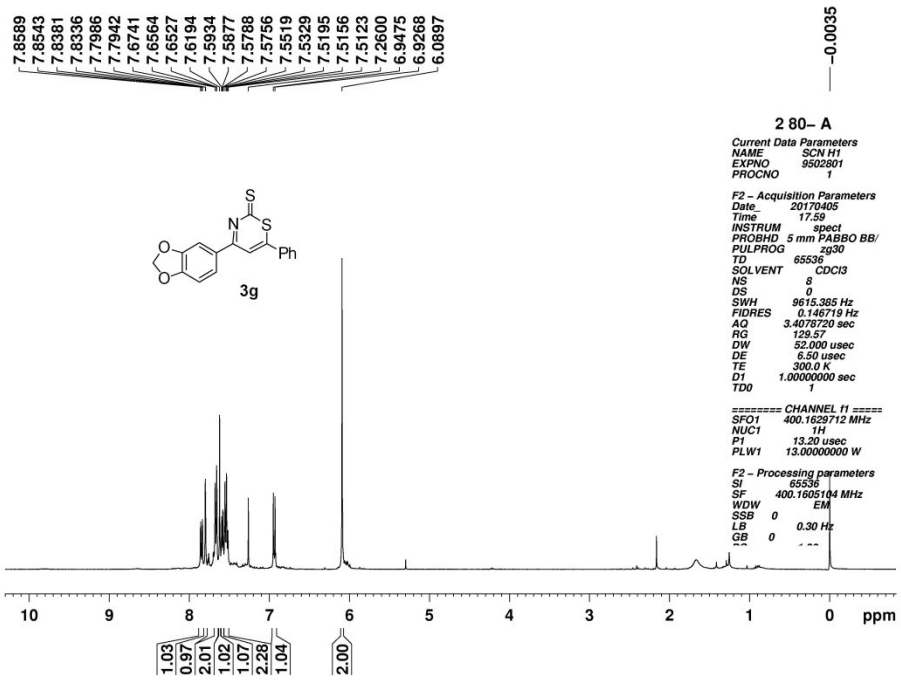


Fig. S77: ^{1}H NMR of 3g

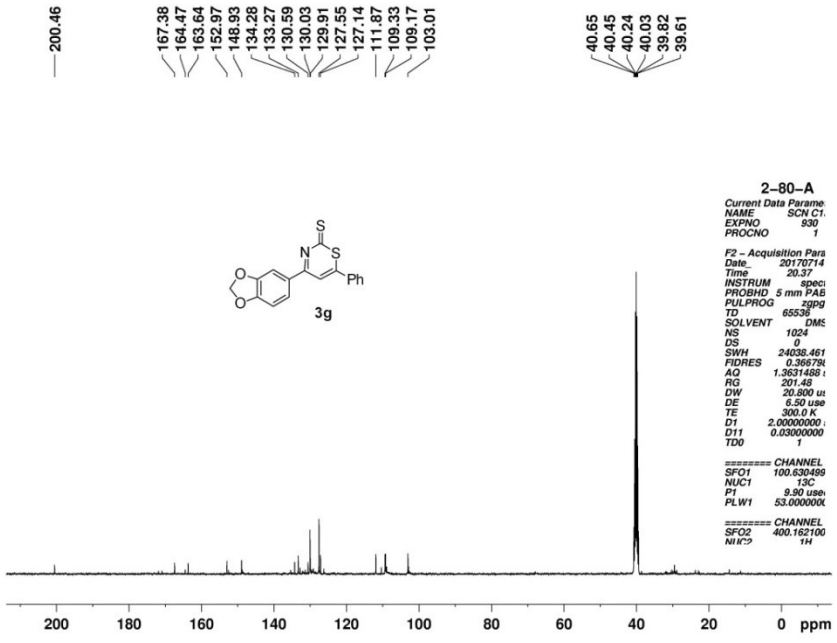


Fig. S78: ^{13}C NMR of 3g

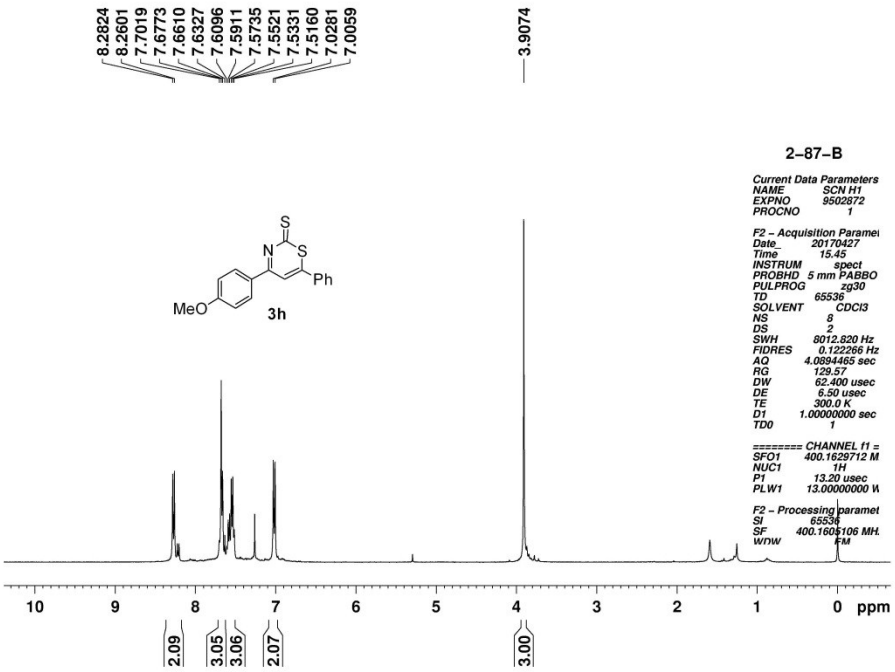


Fig. S79: ^{1}H NMR of 3h

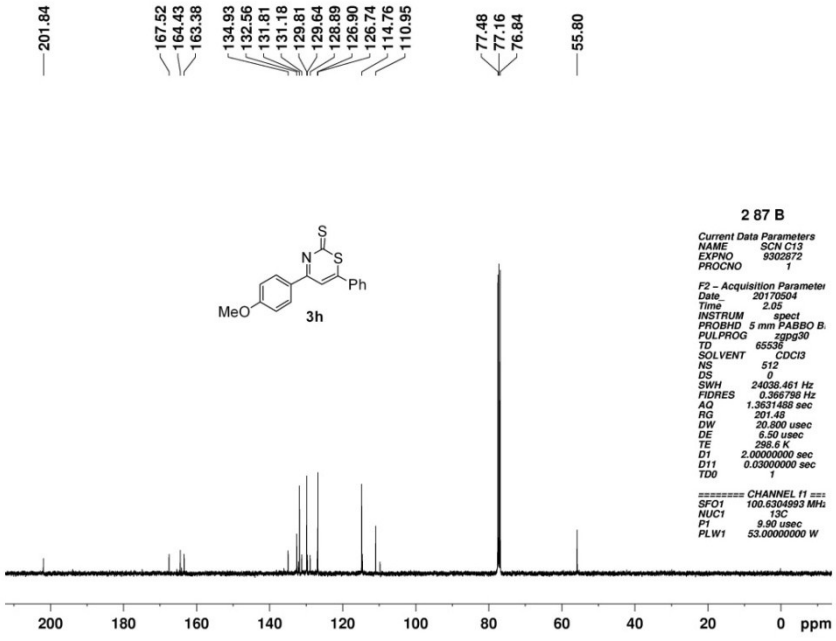


Fig. S80: ^{13}C NMR of 3h

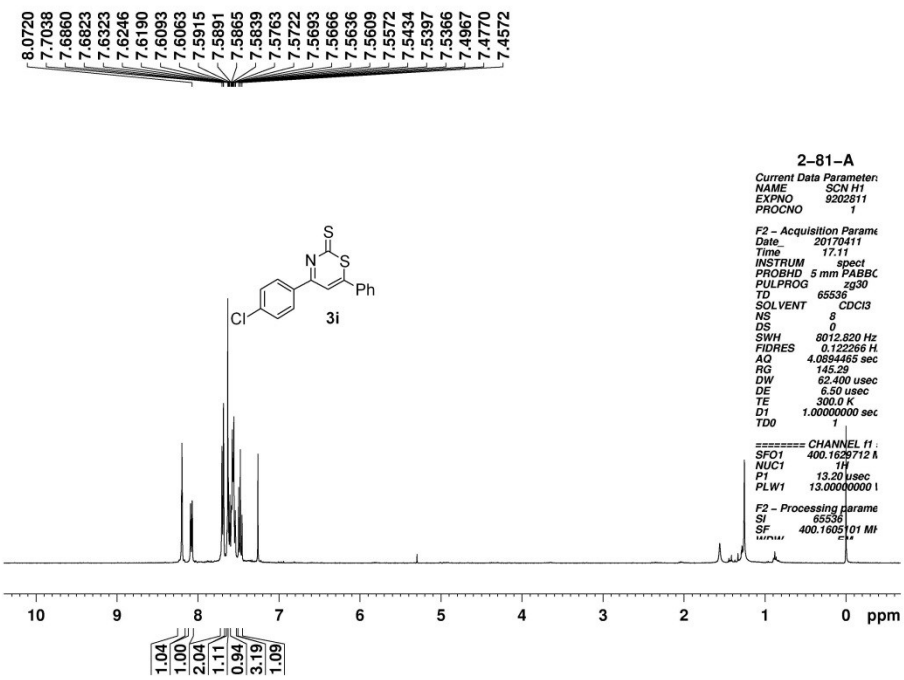


Fig. S81: ^{1}H NMR of 3i

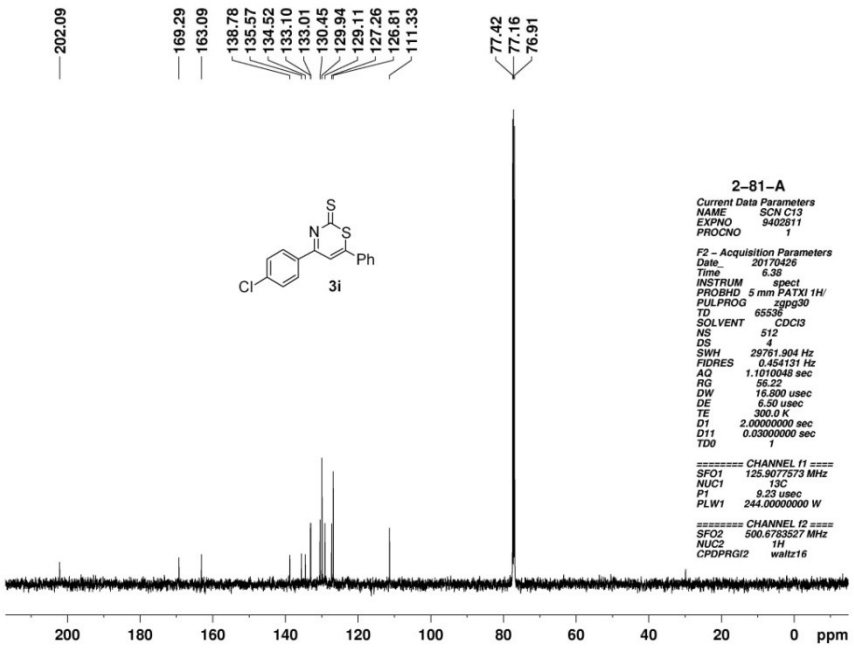


Fig. S82: ^{13}C NMR of 3i

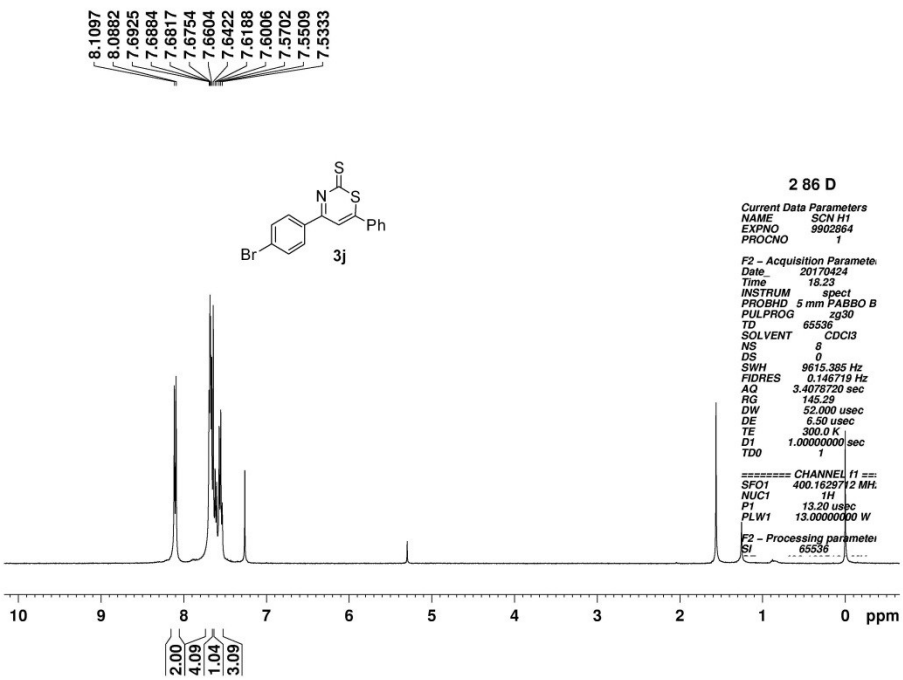


Fig. S83: ^{1}H NMR of 3j

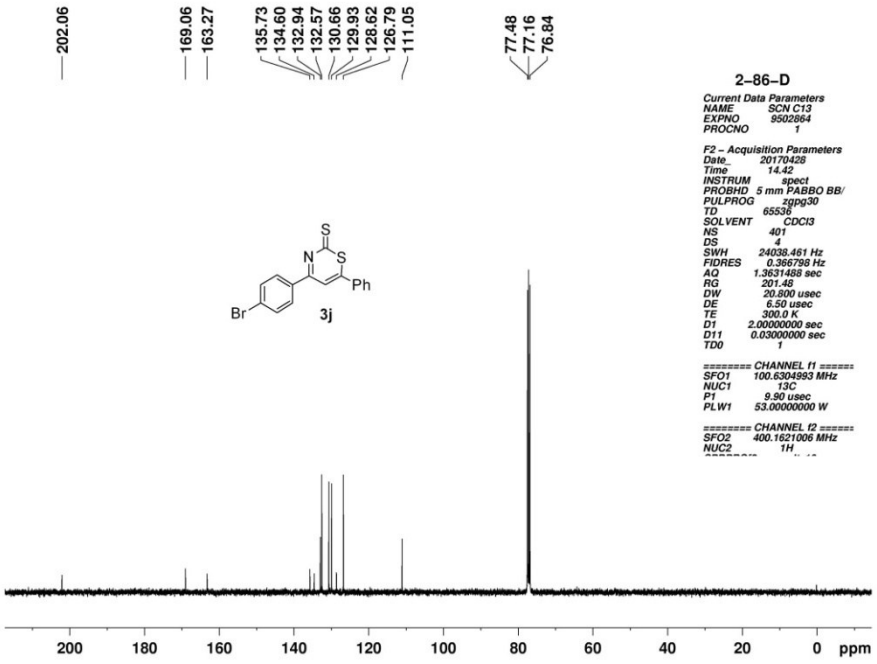


Fig. S84: ^{13}C NMR of 3j

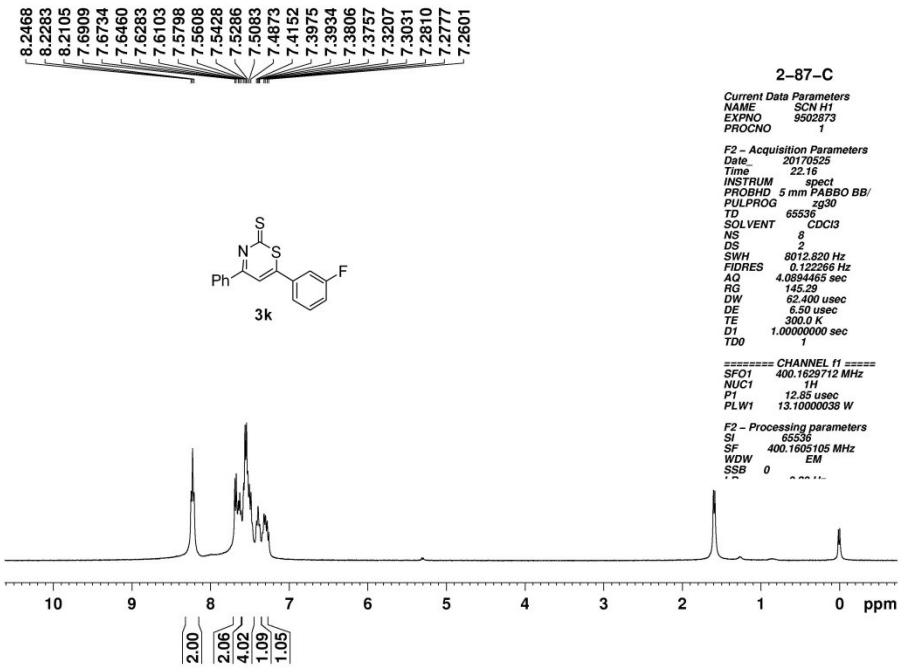


Fig. S85: ^{1}H NMR of 3k

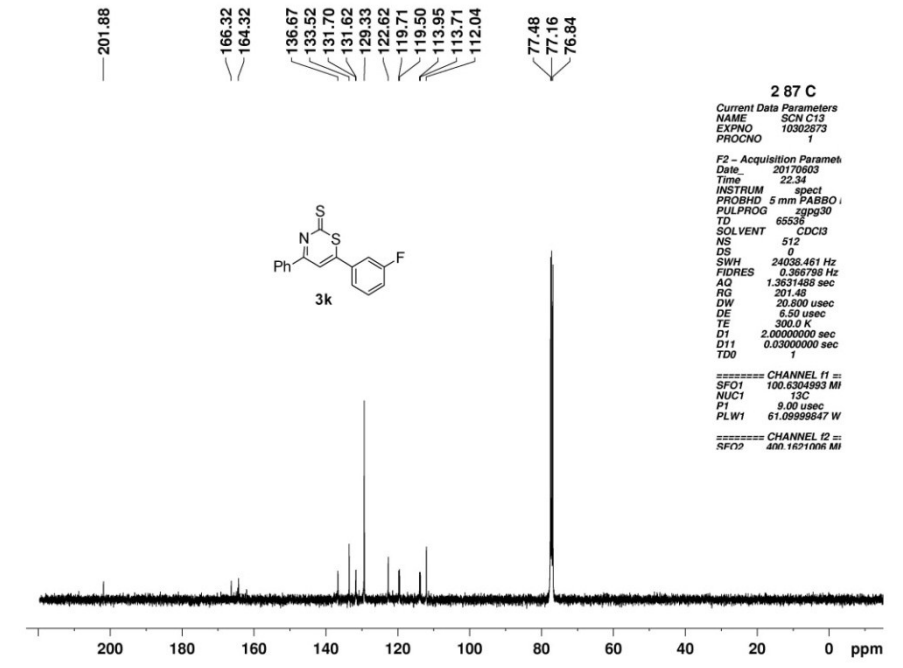


Fig. S86: ^{13}C NMR of 3k

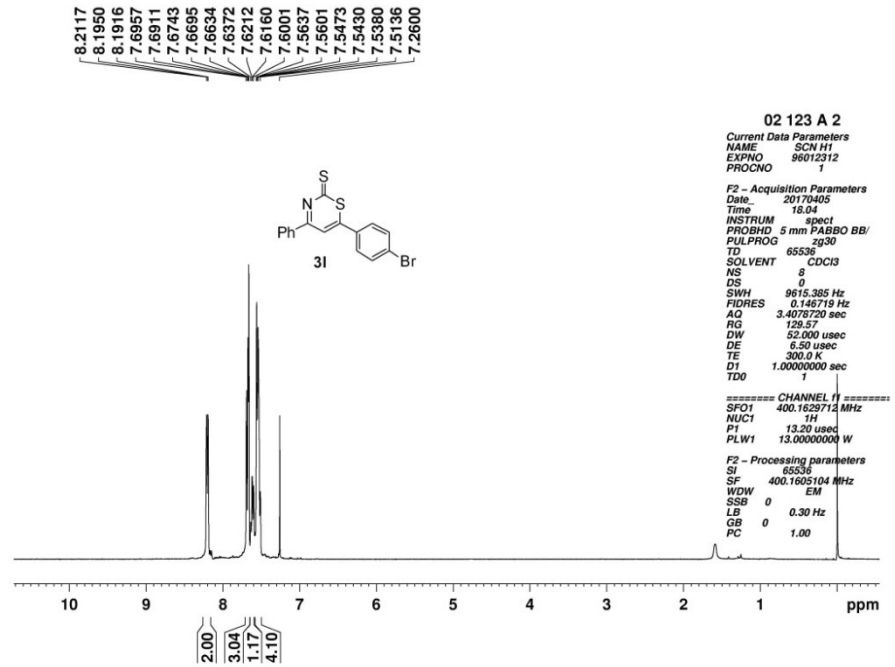


Fig. S87: ^{1}H NMR of 3l

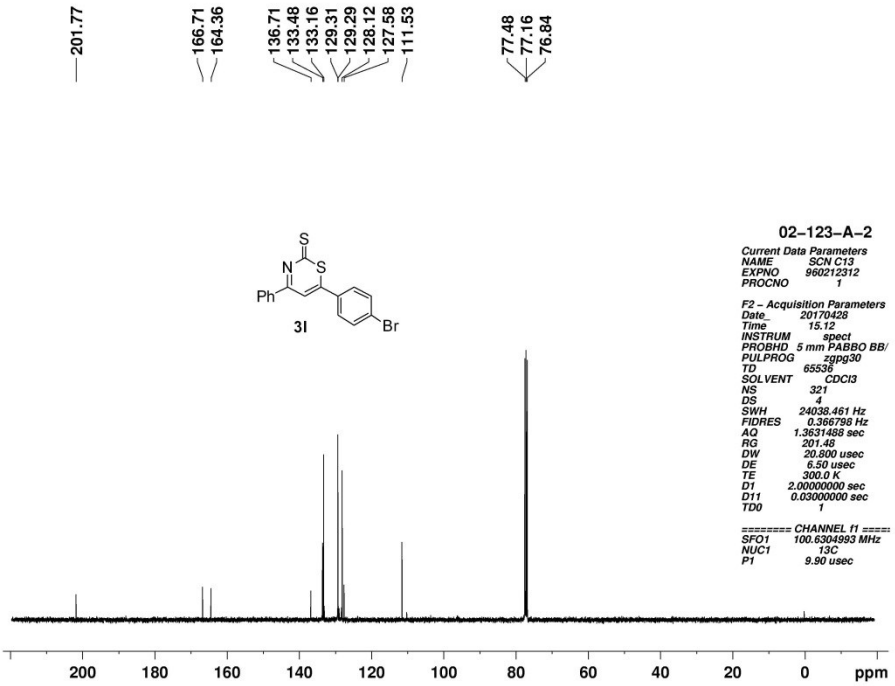


Fig. S88: ^{13}C NMR of 3l

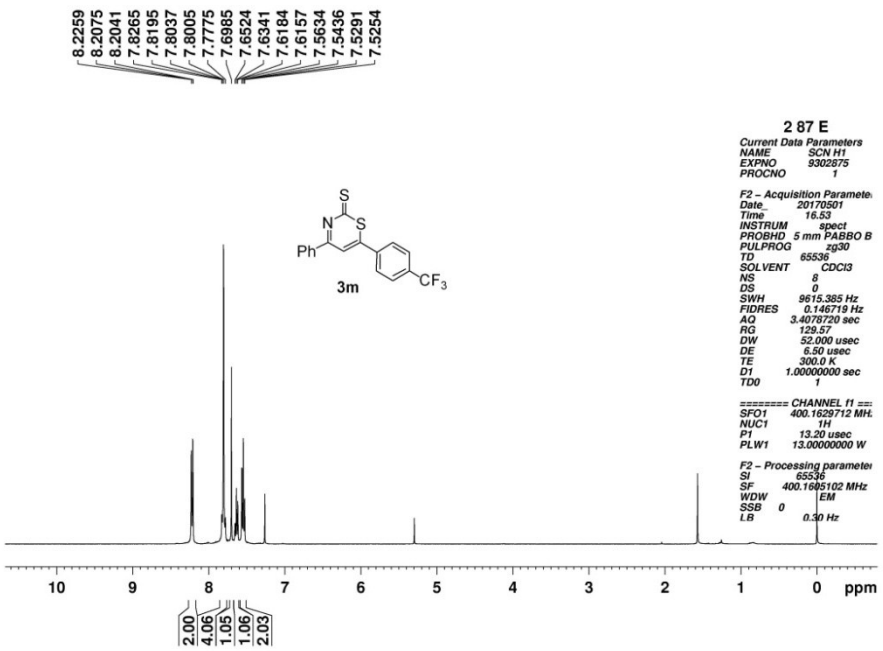


Fig. S89: ^{1}H NMR of 3m

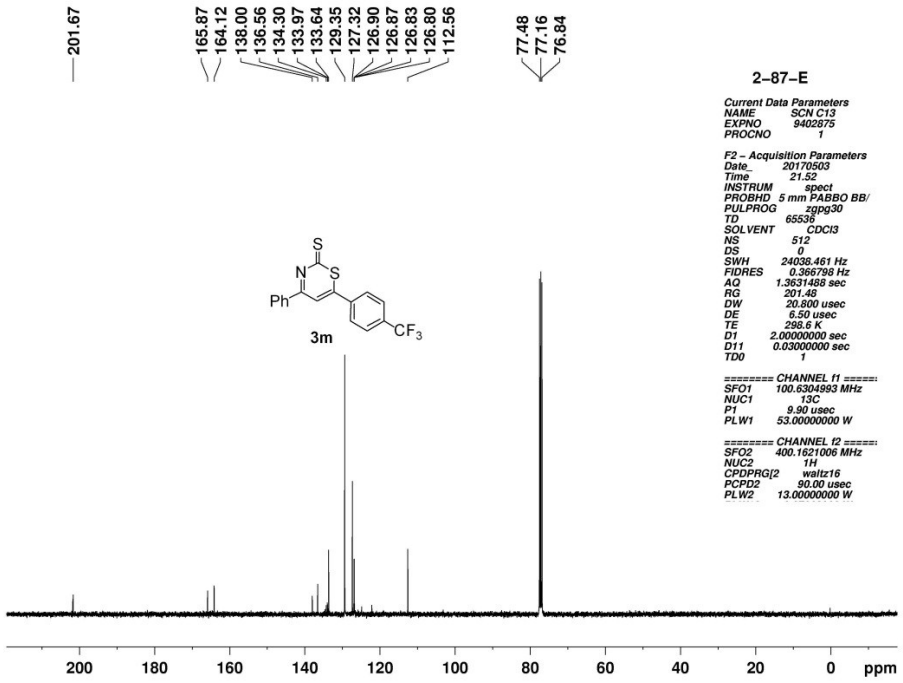


Fig. S90: ^{13}C NMR of 3m

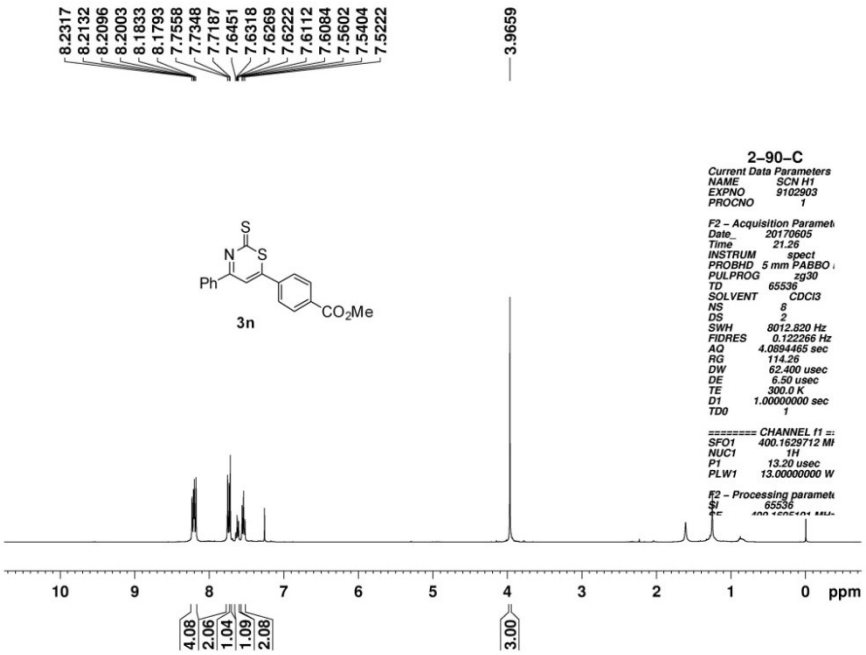


Fig. S91: ^{1}H NMR of 3n

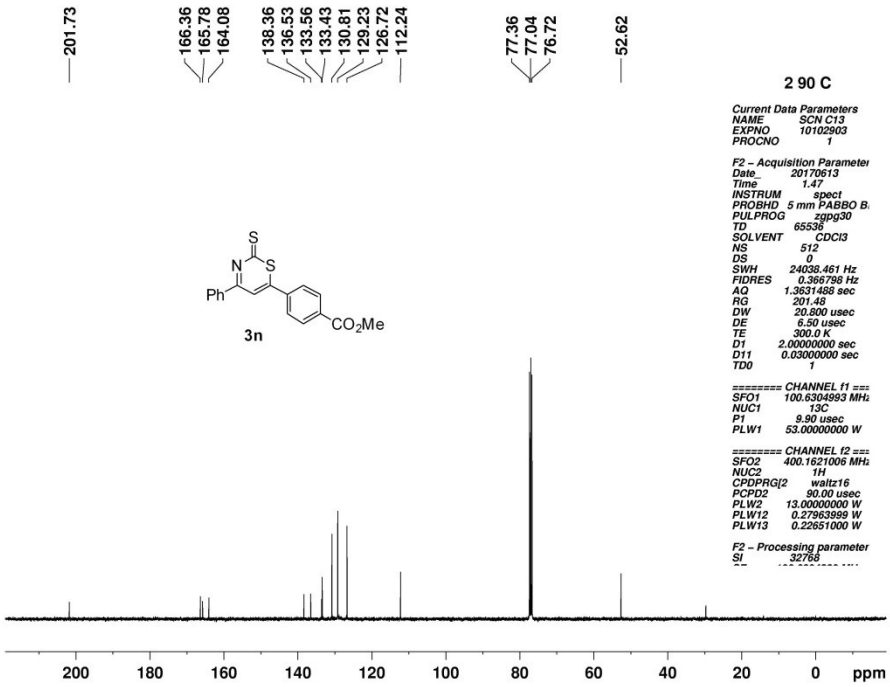


Fig. S92: ^{13}C NMR of 3n

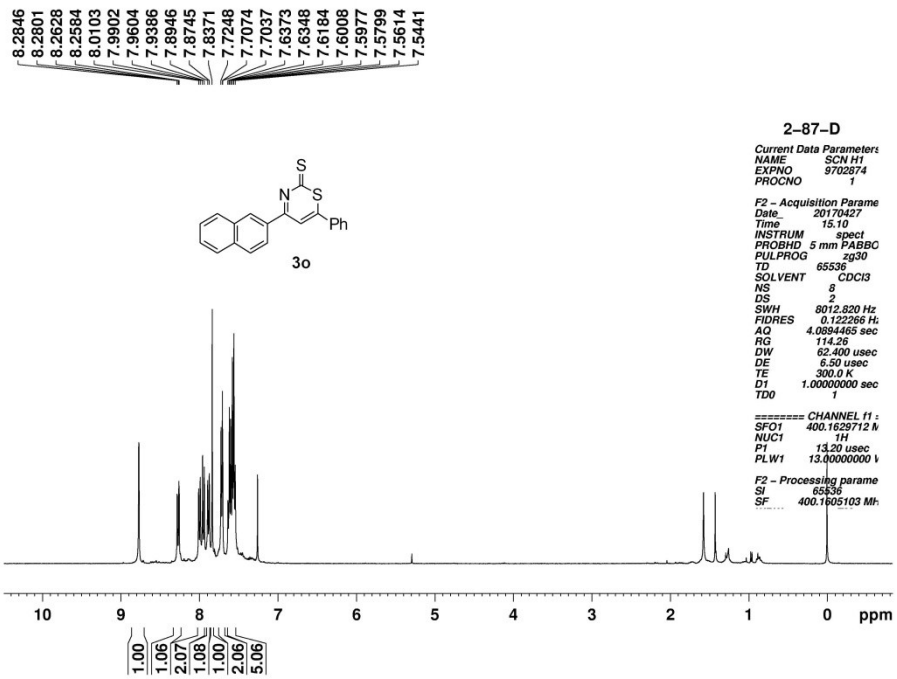


Fig. S93: ^{1}H NMR of 3o

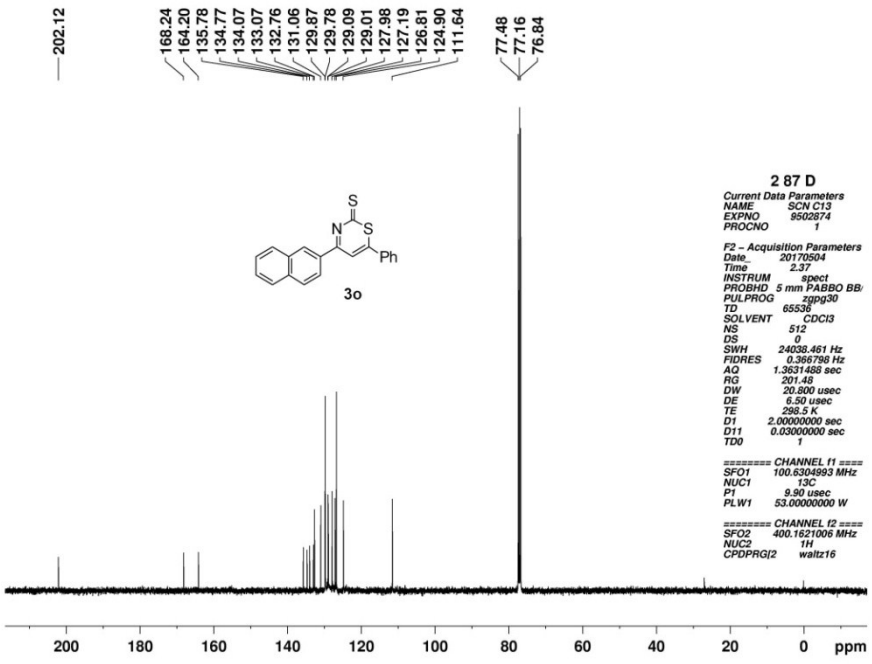


Fig. S94: ^{13}C NMR of 3o

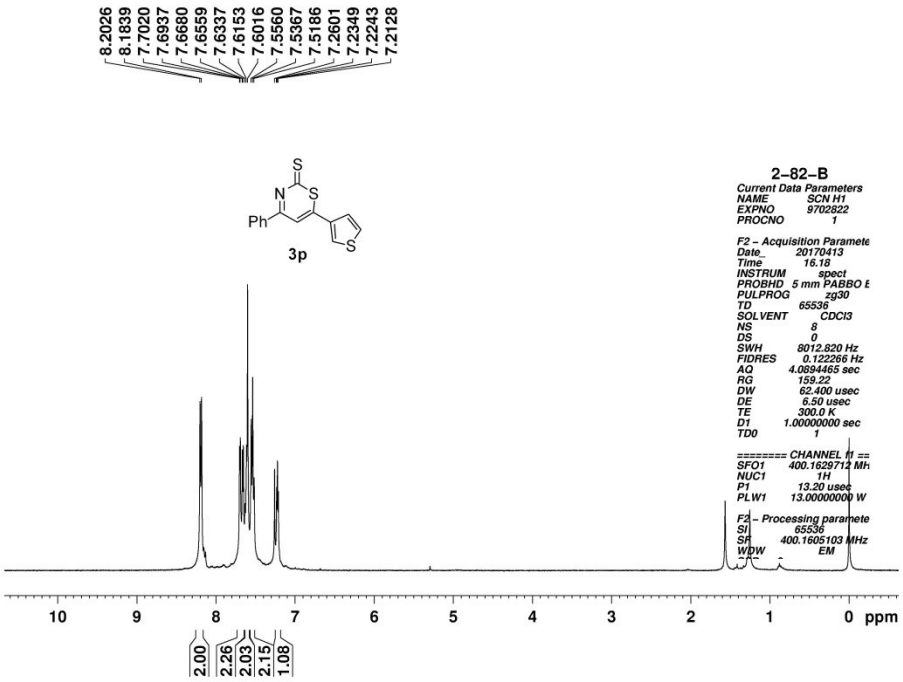


Fig. S95: ^{1}H NMR of 3p

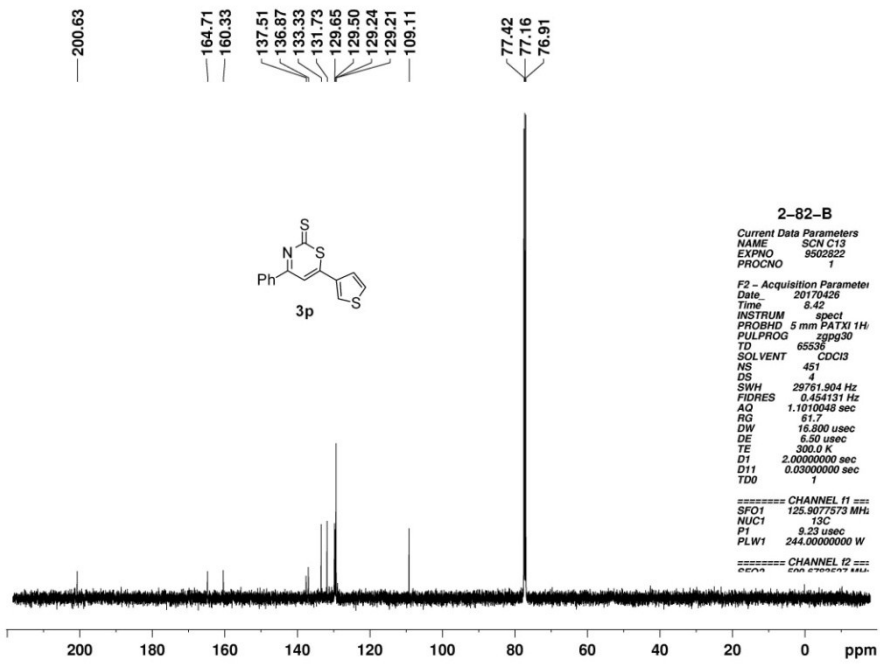


Fig. S96: ^{13}C NMR of 3p

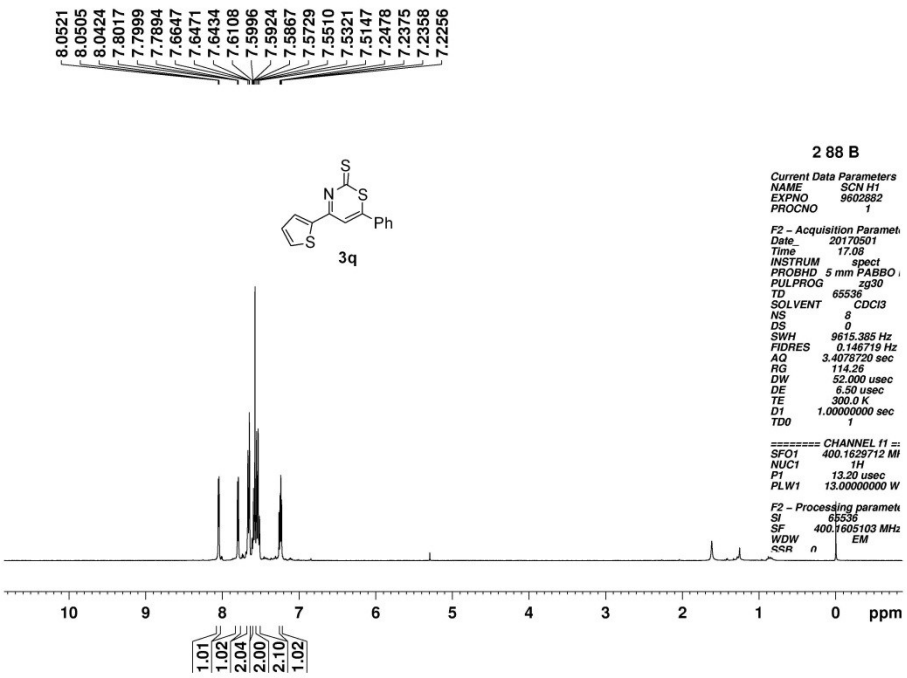


Fig. S97: ^{1}H NMR of 3q

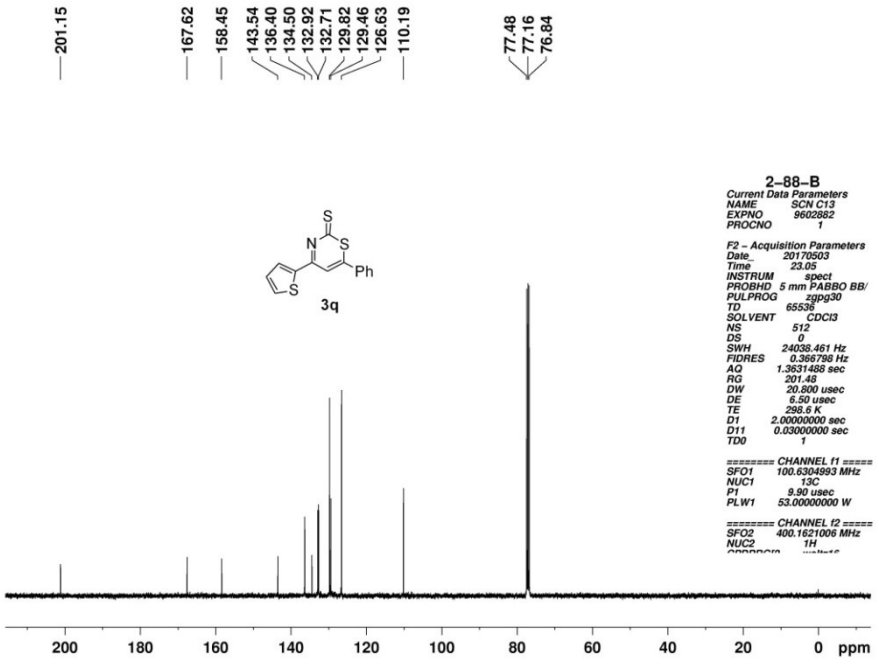


Fig. S98: ^{13}C NMR of 3q

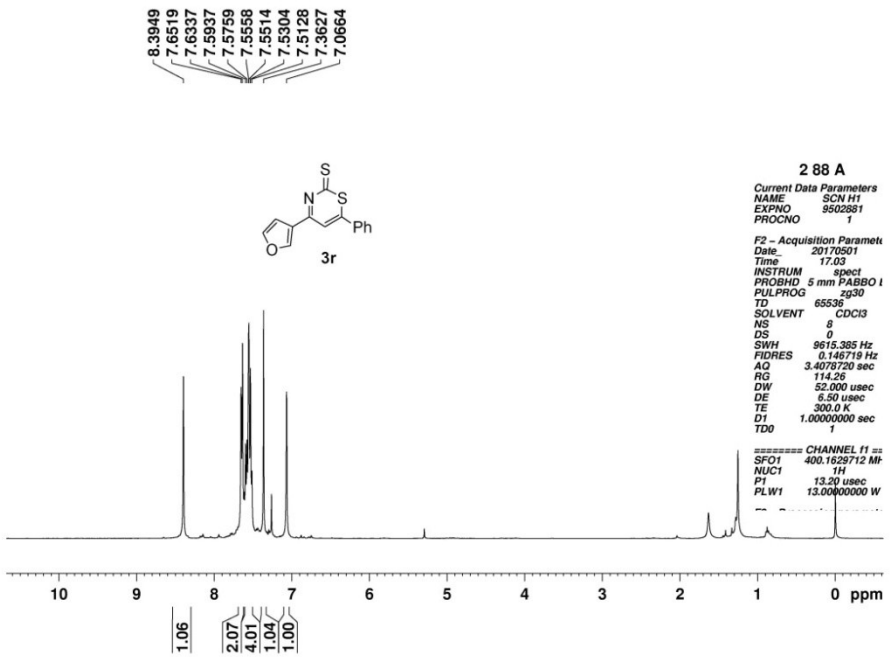


Fig. S99: ^{1}H NMR of 3r

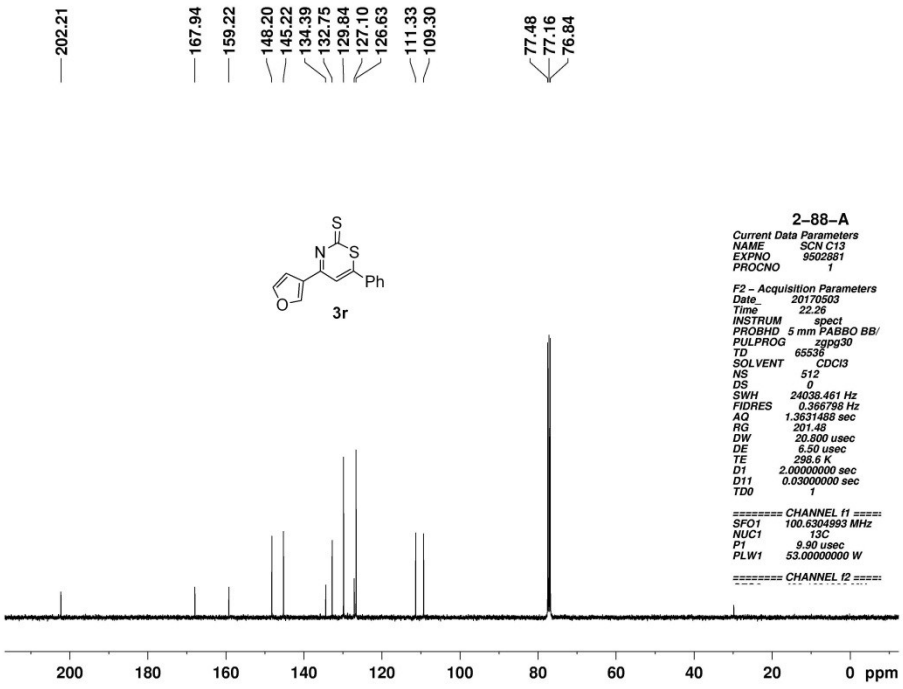


Fig. S100: ^{13}C NMR of 3r

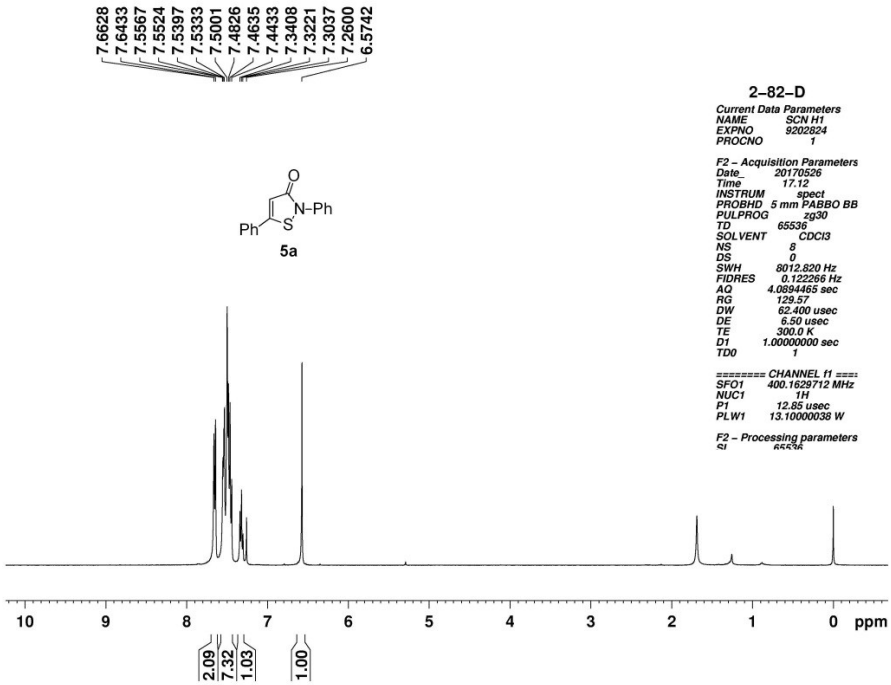


Fig. S101: ^{1}H NMR of 5a

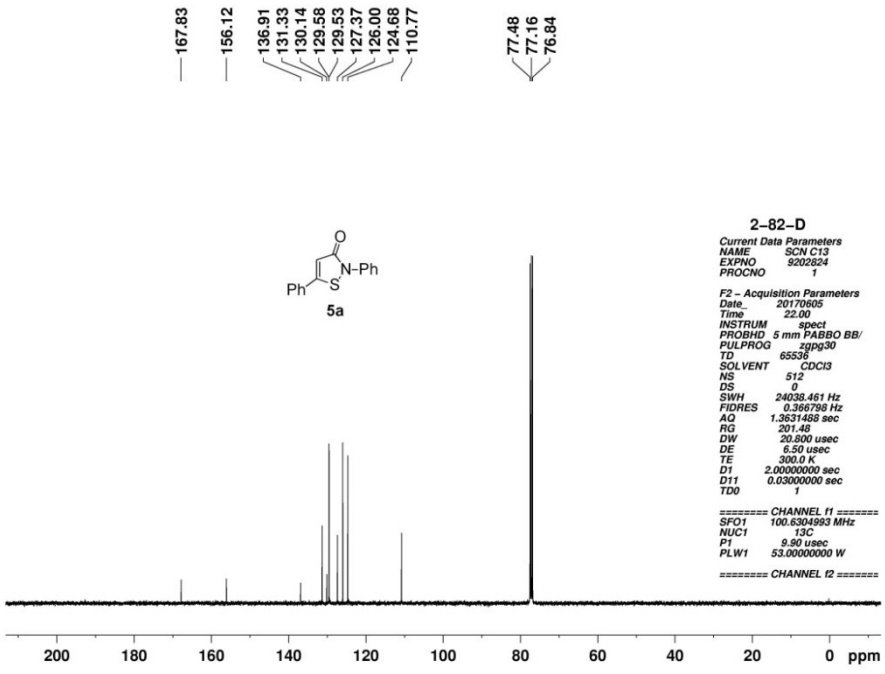


Fig. S102: ^{13}C NMR of 5a

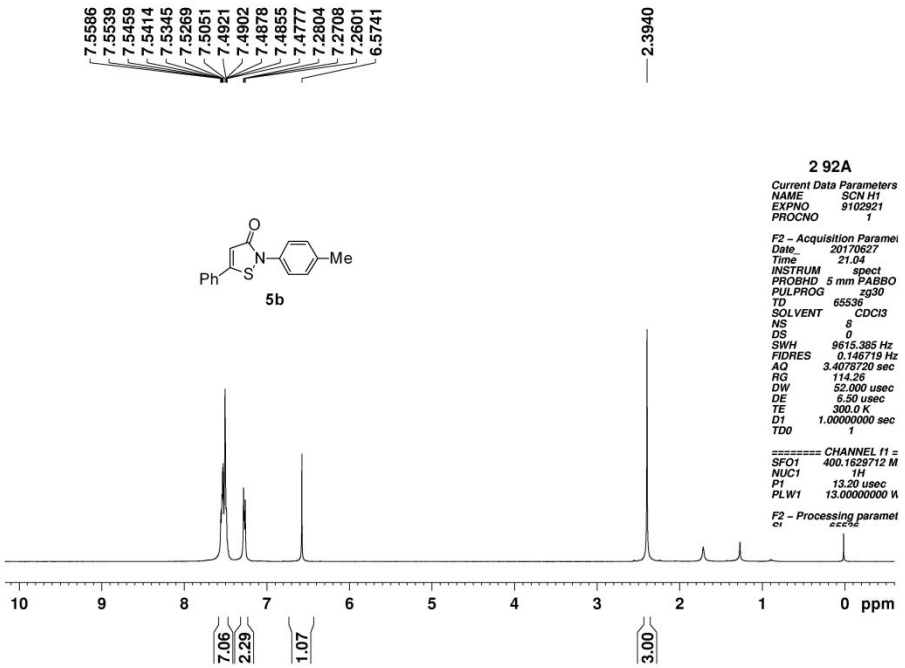


Fig. S103: ^{1}H NMR of 5b

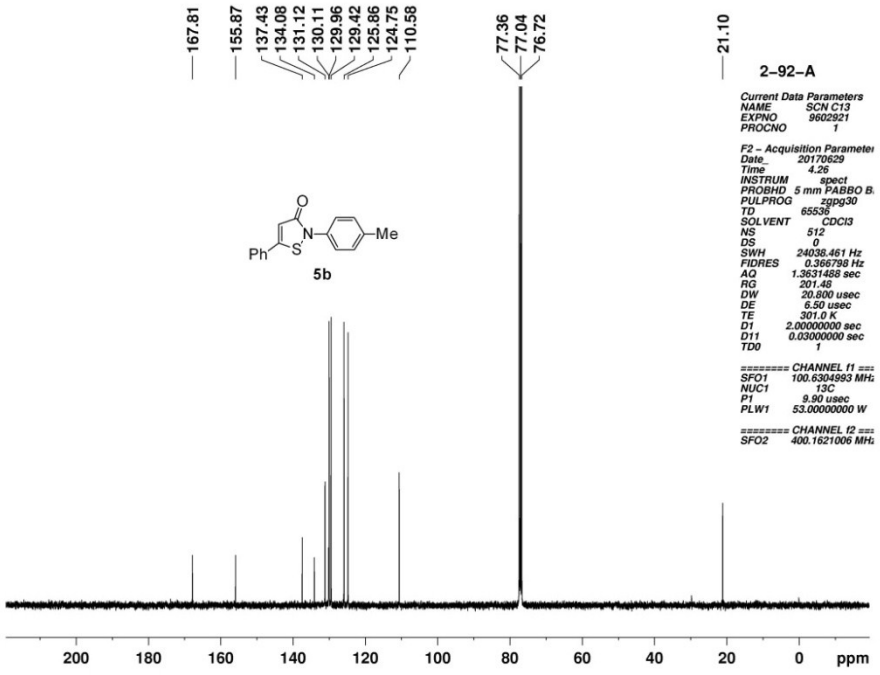


Fig. S104: ^{13}C NMR of 5b

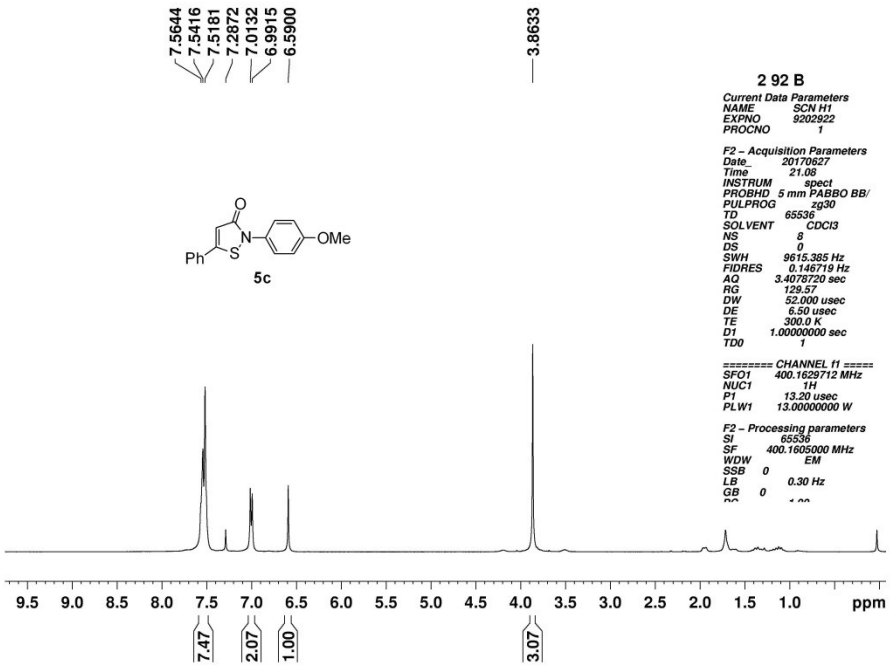


Fig. S105: ^{1}H NMR of 5c

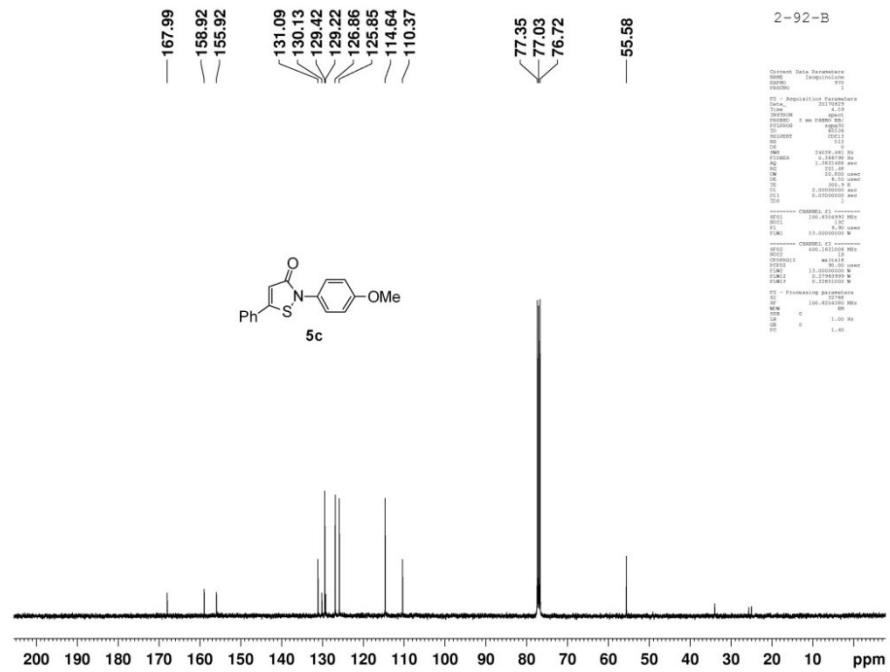


Fig. S106: ^{13}C NMR of 5c

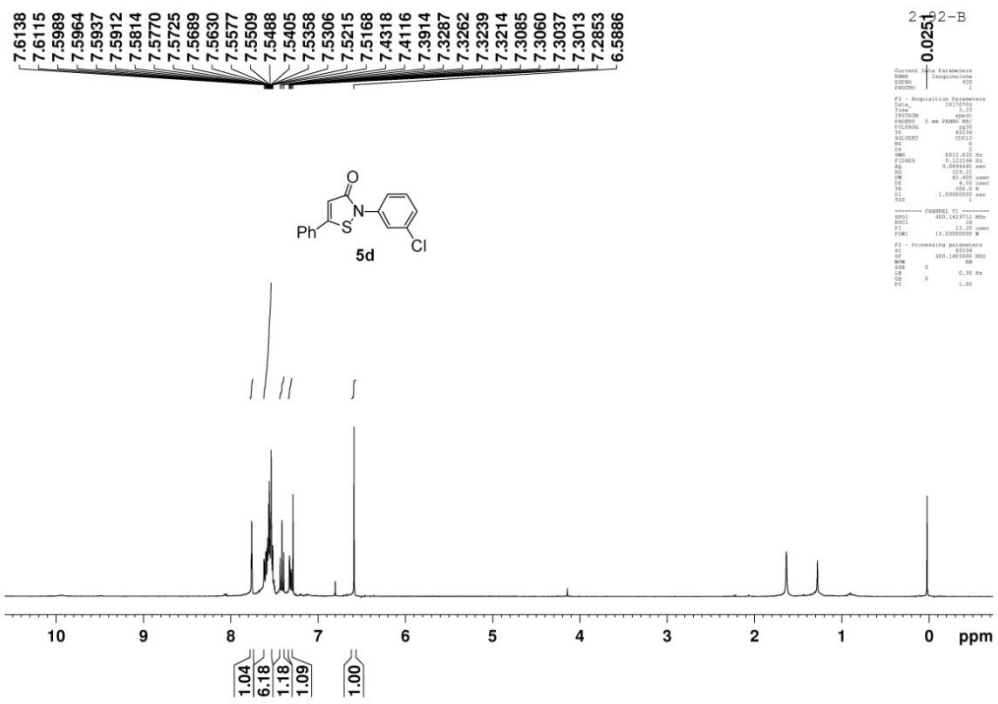


Fig. S107: ^{1}H NMR of 5d

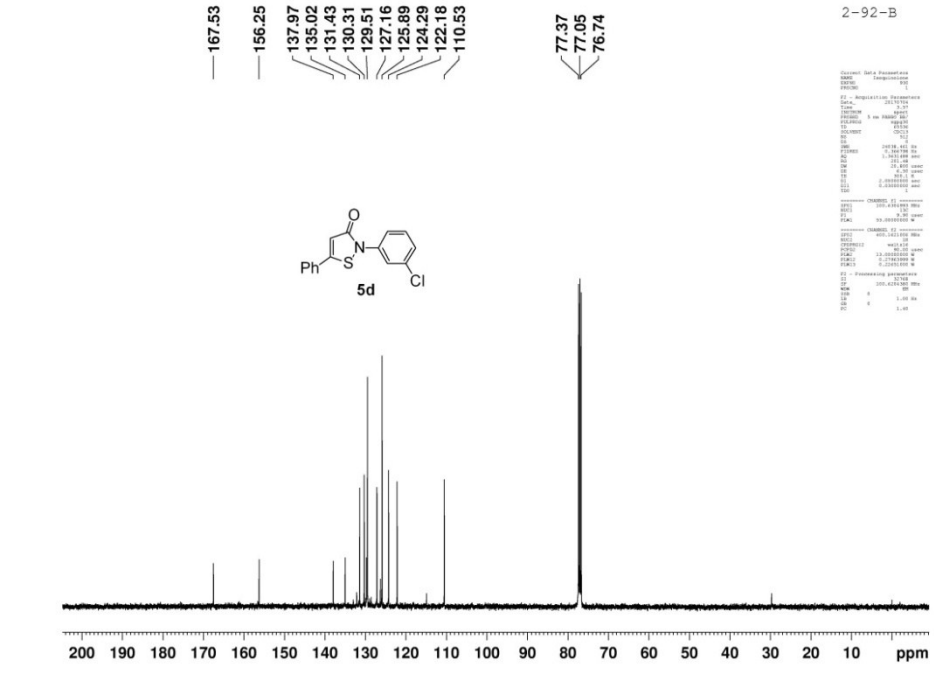


Fig. S108: ^{13}C NMR of 5d

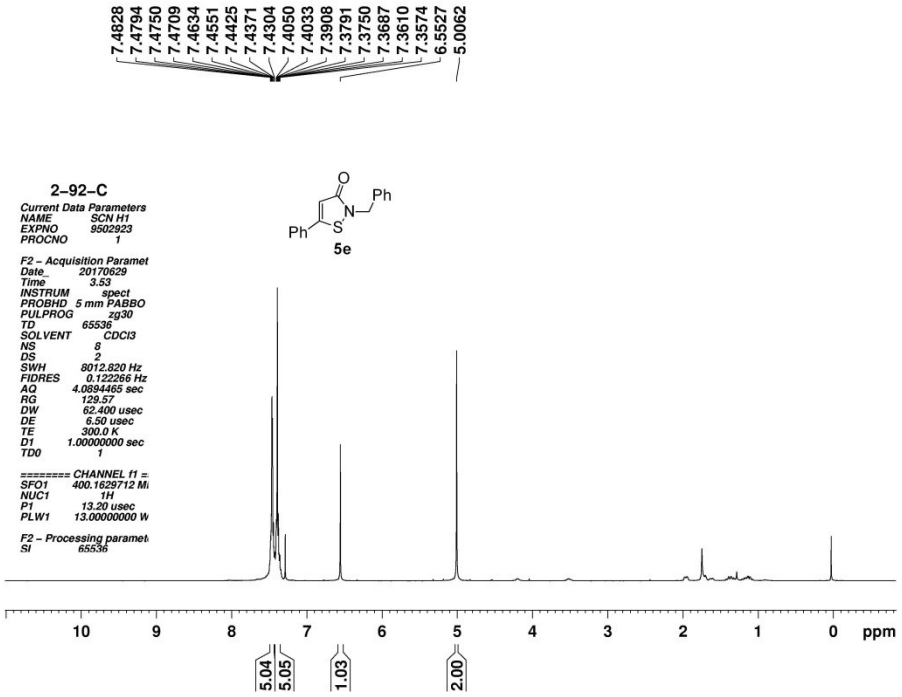


Fig. S109: ^{1}H NMR of 5e

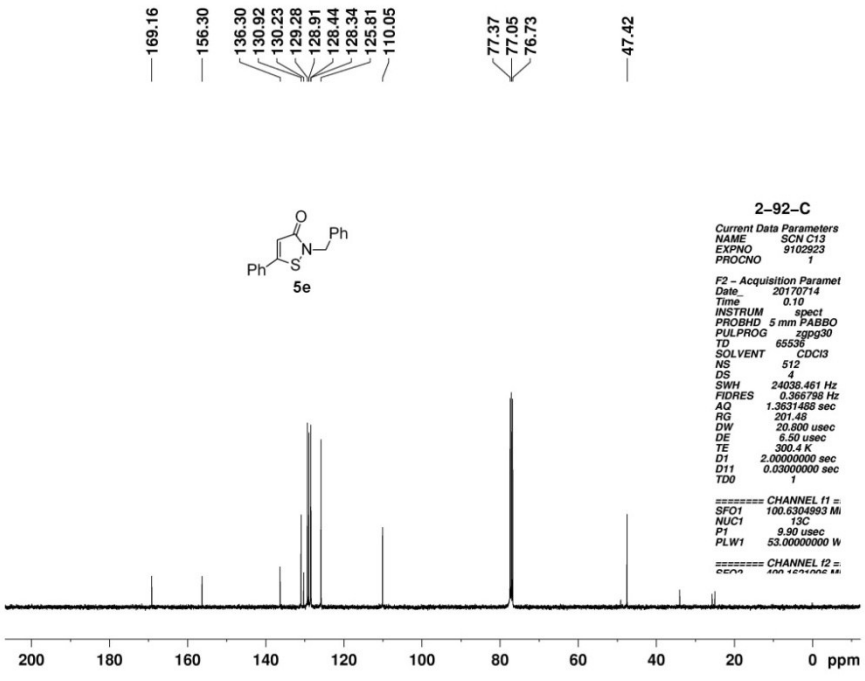


Fig. S110: ^{13}C NMR of 5e

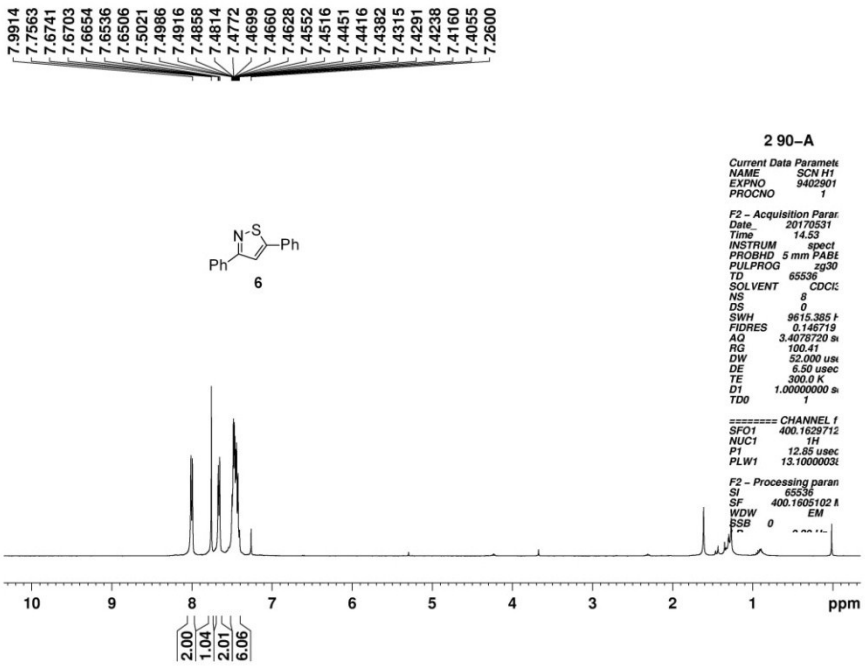


Fig. S111: ^{1}H NMR of 6

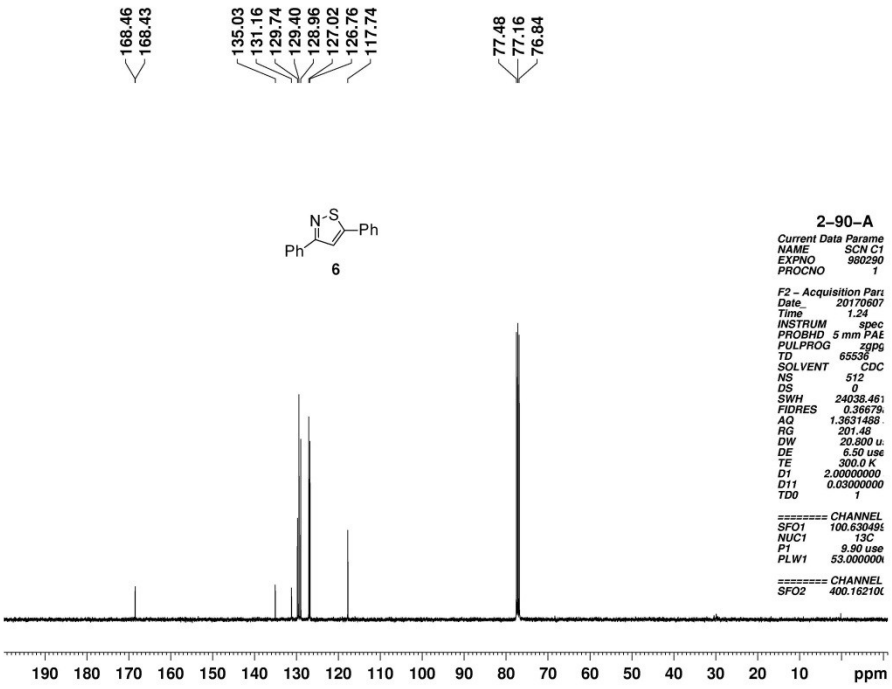


Fig. S112: ^{13}C NMR of 6