Supplementary Information (SI) for ChemComm.

Supporting information

Photoinduced benzylic C-H thiocyanation enabled by triphenylphosphine oxide and *N*-thiocyanophthalimide

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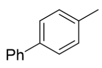
1. General Information

Commercial reagents and solvents were used as received, unless otherwise stated. Organic solution was concentrated under reduced pressure on a IKA rotary evaporator using an alcohol bath. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with $KMnO_4$. Flash chromatography was performed on silica gel 200-300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Energy Chemical® and Adamas-beta®). All ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on Bruker AV-400 or AV-600. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 (^{1}H NMR), δ = 77.16 (^{13}C NMR), or DMSO-*d*$_6$ defined at δ= 2.50 ppm (^{1}H NMR), δ= 39.52 ppm (^{13}C NMR). Coupling constants were quoted in Hz (*J*). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t) and quadruplet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m).

2. General procedure for the synthesis of starting materials



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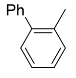

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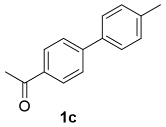

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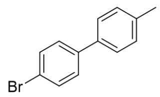

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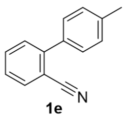

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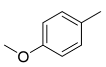

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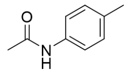

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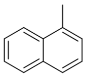

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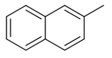

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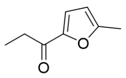

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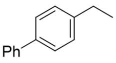

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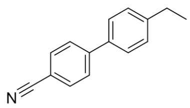

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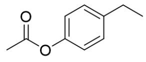

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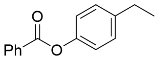

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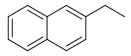

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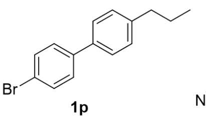

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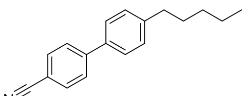

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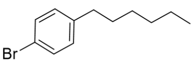

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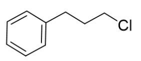

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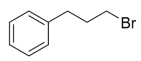

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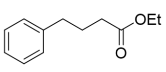

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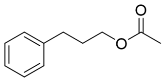

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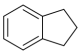

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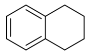

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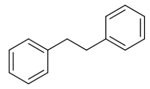

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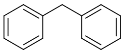

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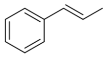

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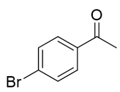

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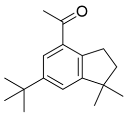

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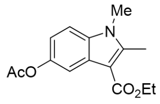

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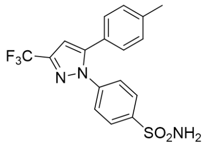

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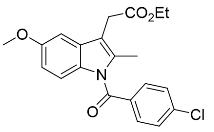

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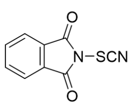

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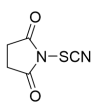

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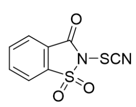

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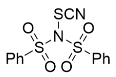


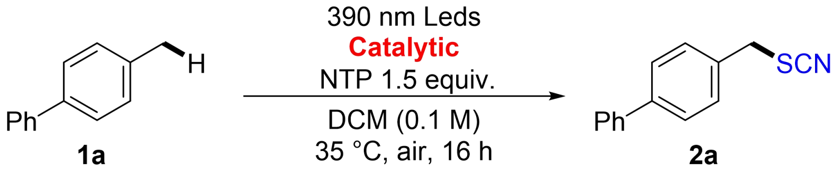
NTSI

1n[1], **NTP**[2], **NTS**[2], **NTSc**[2], **NTSI**[3] are known compounds and synthesized according to reported literatures. The other starting materials (from **1a** to **1m** and from

1o to **1af**) are commercially available.

3. The Optimization of Benzylic C-H Thiocyanation

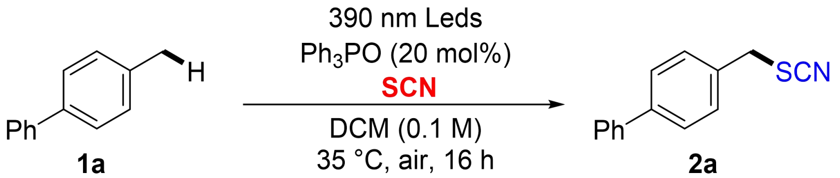
Table S1. The optimization of catalytic [a]

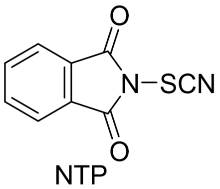


Entry	Catalytic	yield(2a) [b]
1	Ph_3PO (20 mol%)	62%
2	PCy_3O (20 mol%)	trace
3	Ph_2PCl (20 mol%)	47%
4	P(*t*-Bu)$_3$ 20 mol%)	14%
5	$(Ph)_2MePO$ (20 mol%)	36%
6	Ph_3P (20 mol%)	n.d. [c]
7	Ph_3PCl_2 (20 mol%)	34%
8	ClP(*t*-Bu)$_4$ (20 mol%)	trace
9	$(Ph)_2CyPO$ (20 mol%)	trace
10	PCy_3 (20 mol%)	trace
11	Ph_3PO (10 mol%)	59%
12	Ph_3PO (50 mol%)	41%
13	Ph_3PO (1.0 equiv)	44%

[a] Conditions employed 390 nm Leds, **1a** (0.2 mmol), catalytic (0.2-1 equiv.), NTP (1.5 equiv.), anhydrous DCM (2.0 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

Table S2. The optimization of SCN source [a]





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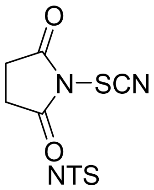

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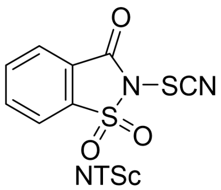
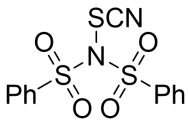


NTSc



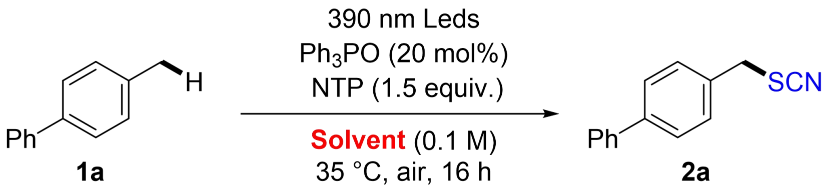
NTSI

Entry	SCN source	yield(2a) [b]
1	NTP (1.5 equiv.)	62%
2	NTS (1.5 equiv.)	53%
3	NTSc (1.5 equiv.)	Trace

4	NTSI (1.5 equiv.)	Trace
5	TMSNCS (1.5 equiv.)	n.d. [c]
6	NTP (1 equiv.)	33%
7	NTP (2 equiv.)	59%

[a] Conditions employed 390 nm Leds, **1a** (0.2 mmol), Ph_3PO (20 mol%), SCN (1-2 equiv.), anhydrous DCM (2.0 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 ℃, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

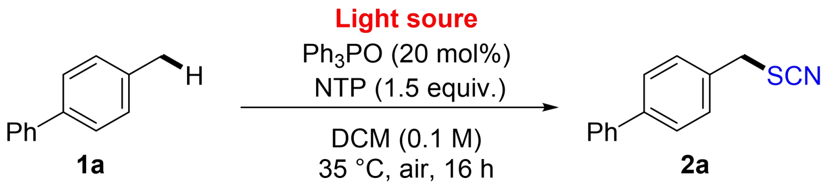
Table S3. The optimization of the solvent [a]



Entry	Solvent	yield(2a) [b]
1	DCM (0.1 M)	62%
2	DCE (0.1 M)	45%
3	CH_3CN (0.1 M)	30%
4	DMF (0.1 M)	n.d. [c]
5	DMSO (0.1 M)	n.d. [c]

[a] Conditions employed 390 nm Leds, **1a** (0.2 mmol), Ph_3PO (20 mol%), NTP (1.5 equiv.), anhydrous solvent (2.0 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 ℃, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

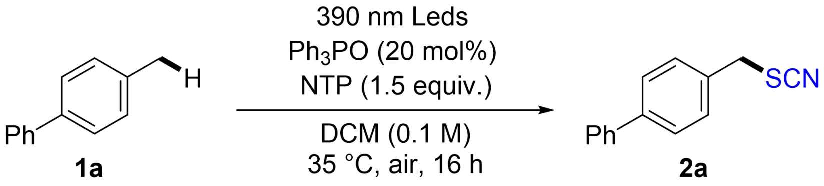
Table S4. The optimization of the light source [a]



Entry	Light source	yield(2a) [b]
1	390 nm Leds	62%
2	395 nm Leds	60%
3	12 W Blue Leds	trace

[a] Conditions employed light source, **1a** (0.2 mmol), Ph_3PO (20 mol%), NTP (1.5 equiv.), anhydrous DCM (2.0 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 ℃, 16 h, unless otherwise noted; [b] Isolated yields were reported.

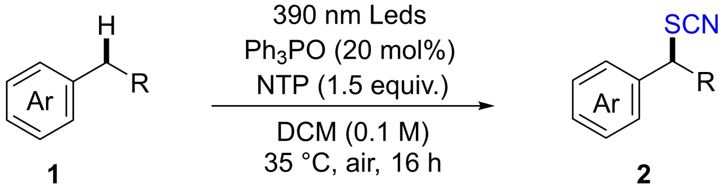
Table S5. Control Experiments [a]



Entry	Conditions	yield(2a) [b]
1	Standard	62%
2	No NTP	n.d. [c]
3	No Ph_3PO	25%
4	No Light	n.d. [c]
5	Under N_2	59%
6	Under O_2	54%
7	With NaN_3 (2.0 equiv.)	58%
8	With 1,4-dicyanobenzene (2.0 equiv.)	50%

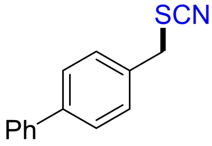
[a] Conditions employed 390 nm Leds, **1a** (0.2 mmol), Ph_3PO (20 mol%), NTP (1.5 equiv.), anhydrous DCM (2.0 mL), the reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with dry air (dried with anhydrous $CaCl_2$), 35 °C, 16 h, unless otherwise noted; [b] Isolated yields were reported; [c] Not detected.

4. Experiment Procedures and Product Characterization



General Procedure A: To a 5 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding benzylic C-H substrate (if solid, 0.2 mmol, 1.0 equiv.), Ph_3PO (20 mol%) and, NTP (1.5 equiv.). The vial was sealed and placed under dry air atmosphere, then anhydrous DCM (2.0 mL, 0.1 M), benzylic C-H substrate (if liquid, 0.2 mmol, 1.0 equiv.) were added into the vial via injection through the cap. The sealed vial was placed in 390 nm Leds and irradiated for 16 hours (maintain the temperature around 35 °C through fan cooling). When the reaction finished, the reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

General Procedure B: To a 5 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding benzylic C-H substrate (if solid, 0.2 mmol, 1.0 equiv.), Ph_3PO (20 mol%) and, NTP (2.5 equiv.). The vial was sealed and placed under dry air atmosphere, then anhydrous DCM (2.0 mL, 0.1 M), benzylic C-H substrate (if liquid, 0.2 mmol, 1.0 equiv.) were added into the vial via injection through the cap. The sealed vial was placed in 390 nm Leds and irradiated for 24 hours (maintain the temperature around 20 °C through air-conditioning). When the reaction finished, the reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



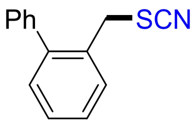
4-(chloromethyl)-1,1'-biphenyl (2a):

According to the general procedure A, the title compound was prepared from 4-methyl-1,1'-biphenyl (0.2 mmol) and it was obtained as a white solid 27.9 mg, 62% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.57 (m, 4H), 7.48 – 7.43 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 4.21 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 140.3, 133.4, 129.6, 129.0, 128.0, 127.8, 127.2, 112.1, 38.3.

Spectral data is in agreement with the literature.[4]



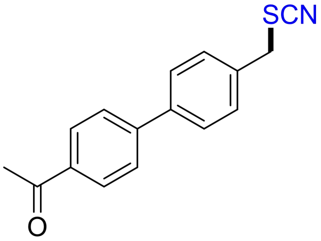
2-(thiocyanatomethyl)-1,1'-biphenyl (2b):

According to the general procedure B, the title compound was prepared from 2-methyl-1,1'-biphenyl (0.2 mmol) and it was obtained as a white solid 19.4 mg, 43% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.39 (m, 6H), 7.37 – 7.29 (m, 3H), 4.16 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 142.7, 139.9, 131.9, 130.8, 130.3, 129.2, 129.1, 128.7, 128.3, 127.9, 112.2, 36.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}NS$ 226.0690; Found 226.0686.



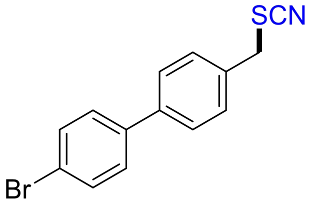
1-(4'-(thiocyanatomethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (2c):

According to the general procedure B, the title compound was prepared from 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (0.2 mmol) and it was obtained as a white solid 26.7 mg, 50% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.75 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 190.4, 147.5, 139.0, 136.4, 132.4, 129.9, 129.2, 127.5, 127.2, 112.0, 43.1, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}NOS$ 268.0796; Found 268.0790.



4-bromo-4'-(thiocyanatomethyl)-1,1'-biphenyl (2d):

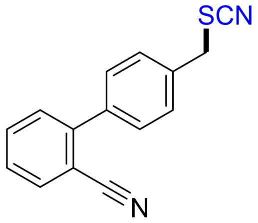
According to the general procedure A, the title compound was prepared from 4-bromo-4'-methyl-1,1'-biphenyl (0.2

mmol) and it was obtained as a white solid 29.7 mg, 49% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.59 – 7.54 (m, 4H), 7.47 – 7.42 (m, 4H), 4.20 (s, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 140.8, 139.2, 133.9, 132.1, 129.7, 128.8, 127.8, 122.2, 112.0, 38.2.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{14}H_{11}BrNS$ 303.9796; Found 303.9795.



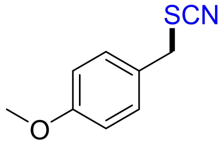
4'-(thiocyanatomethyl)-[1,1'-biphenyl]-2-carbonitrile (2e):

According to the general procedure A, the title compound was prepared from 4'-methyl-[1,1'-biphenyl]-2-carbonitrile (0.2 mmol) and it was obtained as a yellow oil 20.1 mg, 40% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.78 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.54 – 7.45 (m, 4H), 4.23 (s, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 144.6, 138.8, 135.1, 134.0, 133.1, 130.2, 129.7, 129.5, 128.1, 118.7, 112.0, 111.4, 38.1.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{11}N_2S$ 251.0643; Found 251.0637.



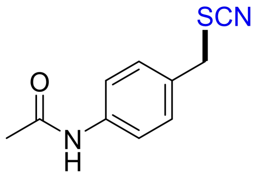
1-methoxy-4-(thiocyanatomethyl)benzene (2f):

According to the general procedure A, the title compound was prepared from 1-methoxy-4-methylbenzene (0.2 mmol) and it was obtained as a orange oil 16.7 mg, 47% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.31 – 7.27 (m, 2H), 6.92 – 6.88 (m, 2H), 4.14 (s, 2H), 3.81 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 160.2, 130.5, 126.4, 114.7, 112.3, 55.4, 38.4.

Spectral data is in agreement with the literature.[5]



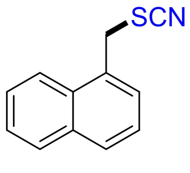
N-(4-(thiocyanatomethyl)phenyl)acetamide (2g):

According to the general procedure A, the title compound was prepared from *N*-(*p*-tolyl)acetamide (0.2 mmol) and it was obtained as a white solid 22.3 mg, 54% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, DMSO-d_6): δ 10.02 (s, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.31 (s, 2H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 168.4, 139.4, 130.3, 129.6, 119.1, 113.1, 37.0, 24.0.

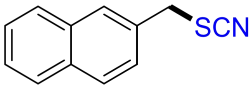
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{10}H_{11}N_2OS$ 207.0592; Found 207.0588.



1-(thiocyanatomethyl)naphthalene (2h):

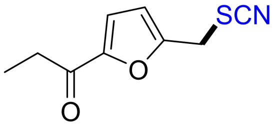
According to the general procedure A, the title compound was prepared from 1-methylnaphthalene (0.2 mmol) and it was obtained as a white solid 17.6 mg, 44% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.99 – 7.86 (m, 3H), 7.65 – 7.44 (m, 4H), 4.67 (s, 2H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 134.2, 130.8, 130.4, 129.6, 129.4, 128.8, 127.2, 126.5, 125.5, 122.9, 112.1, 36.6.
Spectral data is in agreement with the literature.[4]



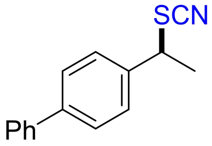
2-(thiocyanatomethyl)naphthalene (2i):

According to the general procedure B, the title compound was prepared from 2-methylnaphthalene (0.2 mmol) and it was obtained as a white solid 17.5 mg, 44% yield. (eluent: PE/EtOAc = 50/1).
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.89 – 7.81 (m, 4H), 7.55 – 7.44 (m, 3H), 4.33 (s, 2H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 133.4, 133.3, 131.7, 129.4, 128.5, 128.2, 127.9, 127.0, 126.9, 126.2, 112.1, 38.9.
Spectral data is in agreement with the literature.[6]



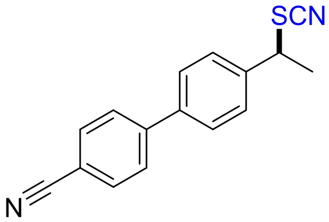
1-(5-(thiocyanatomethyl)furan-2-yl)propan-1-one (2j):

According to the general procedure B, the title compound was prepared from 1-(5-methylfuran-2-yl)propan-1-one (0.2 mmol) and it was obtained as a colourless oil 20.7 mg, 53% yield. (eluent: PE/EtOAc = 30/1).
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.13 (d, *J* = 3.5 Hz, 1H), 6.58 (d, *J* = 3.4 Hz, 1H), 4.21 (s, 2H), 2.85 (q, *J* = 7.4 Hz, 2H), 1.21 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 189.9, 153.3, 151.2, 117.7, 112.6, 111.0, 31.9, 30.6.
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_9H_{10}NO_2S$ 196.0432; Found 195.0358.



4-(1-thiocyanatoethyl)-1,1'-biphenyl (2k):

According to the general procedure A, the title compound was prepared from 4-ethyl-1,1'-biphenyl (0.2 mmol) and it was obtained as a white solid 37.6 mg, 79% yield. (eluent: PE/EtOAc = 50/1).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.67 – 7.57 (m, 4H), 7.52 – 7.44 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.66 (q, *J* = 7.0 Hz, 1H), 1.93 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 141.9, 140.2, 138.1, 128.9, 127.8, 127.6, 127.1, 111.8, 48.4, 22.0.
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{14}NS$ 240.0847; Found 240.0844.



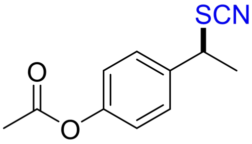
4'-(1-thiocyanatoethyl)-[1,1'-biphenyl]-4-carbonitrile (2l):

According to the general procedure A, the title compound was prepared from 4'-ethyl-[1,1'-biphenyl]-4-carbonitrile (0.2 mmol) and it was obtained as a white solid 25.9 mg, 49% yield. (eluent: PE/EtOAc = 50/1).
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H),

7.61 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 4.65 (q, *J* = 7.0 Hz, 1H), 1.91 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 144.8, 139.9, 132.8, 128.04, 128.02, 127.9, 118.9, 111.5, 48.2, 21.9.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{13}N2S$ 265.0799; Found 265.0796.



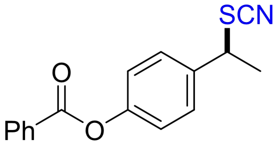
4-(1-thiocyanatoethyl)phenyl acetate (2m):

According to the general procedure A, the title compound was prepared from 4-ethylphenyl acetate (0.2 mmol) and it was obtained as a yellow oil 30.4 mg, 69% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 4.60 (q, *J* = 7.0 Hz, 1H), 2.30 (s, 3H), 1.86 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 169.3, 151.0, 136.7, 128.4, 122.4, 111.6, 48.0, 22.1, 21.2.

Spectral data is in agreement with the literature.[5]



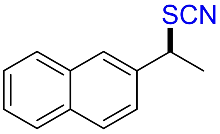
4-(1-thiocyanatoethyl)phenyl benzoate (2n):

According to the general procedure A, the title compound was prepared from 4-ethylphenyl benzoate (0.2 mmol) and it was obtained as a colourless oil 44.7 mg, 79% yield. (eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.23 – 8.17 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.43 (m, 4H), 7.28 – 7.22 (m, 2H), 4.64 (q, *J* = 7.0 Hz, 1H), 1.90 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 165.1, 151.4, 136.8, 133.9, 130.4, 129.4, 128.8, 128.5, 122.6, 111.6, 48.1, 22.2.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{14}NO_2S$ 284.0745; Found 284.0741.



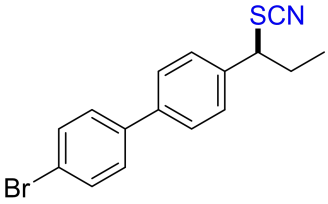
2-(1-thiocyanatoethyl)naphthalene (2o):

According to the general procedure A, the title compound was prepared from 2-ethylnaphthalene (0.2 mmol) and it was obtained as a white solid 27.8 mg, 65% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.90 – 7.81 (m, 4H), 7.56 – 7.45 (m, 3H), 4.78 (q, *J* = 7.0 Hz, 1H), 1.98 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 136.5, 133.5, 133.2, 129.3, 128.3, 127.9, 127.0, 126.9, 126.5, 124.6, 111.8, 49.0, 22.1.

Spectral data is in agreement with the literature.[5]



4-bromo-4'-(1-thiocyanatopropyl)-1,1'-biphenyl (2p):

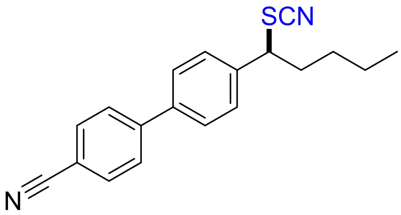
According to the general procedure A, the title compound was prepared from 4-bromo-4'-propyl-1,1'-biphenyl (0.2 mmol) and it was obtained as a colourless oil 36.8 mg, 56% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.59 – 7.55 (m, 4H), 7.46

– 7.39 (m, 4H), 4.32 – 4.28 (m, 1H), 2.30 – 2.14 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 140.6, 139.2, 137.8, 132.1, 128.8, 128.2, 127.6, 122.1, 111.7, 55.2, 29.1, 12.3.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{14}NO_2S$ 332.0109; Found 332.0105.



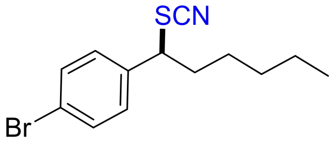
4'-(1-thiocyanatopentyl)-[1,1'-biphenyl]-4-carbonitrile (2q):

According to the general procedure A, the title compound was prepared from 4'-pentyl-[1,1'-biphenyl]-4-carbonitrile (0.2 mmol) and it was obtained as a colourless oil 44.3 mg, 72% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 4.40 – 4.35 (m, 1H), 2.23 – 2.11 (m, 2H), 1.44 – 1.27 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 144.7, 139.7, 139.3, 132.7, 128.3, 127.9, 127.8, 118.8, 111.6, 111.4, 53.3, 35.3, 29.6, 22.2, 13.9.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{19}N2S$ 307.1269; Found 307.1264.



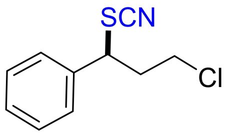
1-bromo-4-(1-thiocyanatohexyl)benzene (2r):

According to the general procedure A, the title compound was prepared from 1-bromo-4-hexylbenzene (0.2 mmol) and it was obtained as a yellow oil 54.4 mg, 76% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.27 (dd, *J* = 8.6, 6.9 Hz, 1H), 2.18 – 2.01 (m, 2H), 1.33 – 1.22 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 137.8, 132.4, 129.2, 123.0, 111.4, 53.1, 35.5, 31.2, 27.2, 22.4, 14.0.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{17}BrNS$ 298.0265; Found 298.0260.



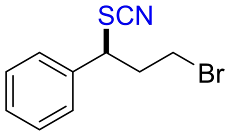
(3-chloro-1-thiocyanatopropyl)benzene (2s):

According to the general procedure A, the title compound was prepared from (3-chloropropyl)benzene (0.2 mmol) and it was obtained as a yellow oil 26.1 mg, 58% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.45 – 7.35 (m, 5H), 4.62 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.72 – 3.63 (m, 1H), 3.45 – 3.39 (m, 1H), 2.71 – 2.53 (m, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 137.1, 129.5, 127.6, 111.0, 50.0, 41.6, 38.0.

Spectral data is in agreement with the literature.[5]



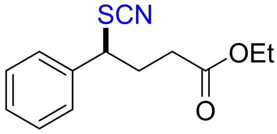
(3-bromo-1-thiocyanatopropyl)benzene (2t):

According to the general procedure A, the title compound was prepared from (3-bromopropyl)benzene (0.2 mmol) and it was obtained as a yellow oil 27.9 mg, 54% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.44 – 7.36 (m, 5H), 4.61 (dd, J = 8.5, 6.8 Hz, 1H), 3.51 – 3.46 (m, 1H), 3.27 – 3.23 (m, 1H), 2.74 – 2.62 (m, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 137.0, 129.5, 127.6, 110.9, 51.1, 38.0, 29.6.

Spectral data is in agreement with the literature.[5]



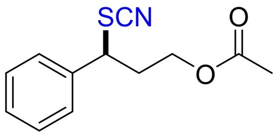
ethyl 4-phenyl-4-thiocyanatobutanoate (2u):

According to the general procedure A, the title compound was prepared from ethyl 4-phenylbutanoate (0.2 mmol) and it was obtained as a colourless oil 19.0 mg, 38% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.42 – 7.31 (m, 5H), 4.47 – 4.43 (m, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.56 – 2.30 (m, 4H), 1.24 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 172.0, 137.6, 129.4, 129.3, 127.6, 111.3, 60.9, 52.5, 31.8, 30.9, 14.3.

Spectral data is in agreement with the literature.[5]



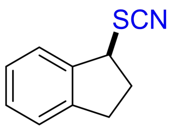
3-phenyl-3-thiocyanatopropyl acetate (2v):

According to the general procedure A, the title compound was prepared from 3-phenylpropyl acetate (0.2 mmol) and it was obtained as a colourless oil 18.5 mg, 39% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.42 – 7.32 (m, 5H), 4.50 – 4.45 (m, 1H), 4.20 – 4.15 (m, 1H), 4.02 – 3.96 (m, 1H), 2.55 – 2.44 (m, 2H), 2.01 (s, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 170.8, 137.5, 129.4, 129.4, 127.5, 111.2, 61.2, 50.2, 34.7, 20.9.

Spectral data is in agreement with the literature.[5]



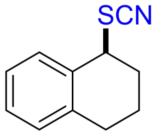
1-thiocyanato-2,3-dihydro-1*H*-indene (2w):

According to the general procedure A, the title compound was prepared from 2,3-dihydro-1*H*-indene (0.2 mmol) and it was obtained as a colourless oil 17.2 mg, 49% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.42 (d, J = 7.5 Hz, 1H), 7.32 – 7.23 (m, 3H), 4.92 (dd, J = 7.2, 2.9 Hz, 1H), 3.23 – 3.16 (m, 1H), 3.00 – 2.93 (m, 1H), 2.70 – 2.62 (m, 1H), 2.43 – 2.36 (m, 1H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 143.9, 139.5, 129.6, 127.4, 125.2, 125.1, 112.3, 53.5, 34.2, 30.6.

Spectral data is in agreement with the literature.[7]



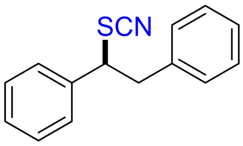
1-thiocyanato-1,2,3,4-tetrahydronaphthalene (2x):

According to the general procedure A, the title compound was prepared from 1,2,3,4-tetrahydronaphthalene (0.2 mmol) and it was obtained as a colourless oil 21.5 mg, 57% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.31 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 4.89 (t, *J* = 3.6 Hz, 1H), 2.91 – 2.75 (m, 2H), 2.41 – 1.88 (m, 4H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 138.0, 131.6, 130.4, 129.8 128.9, 126.5, 112.5, 49.8, 29.8, 28.7, 18.4.

Spectral data is in agreement with the literature.[7]



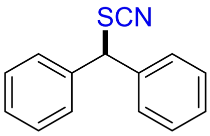
(1-thiocyanatoethane-1,2-diyl)dibenzene (2y):

According to the general procedure A, the title compound was prepared from 1,2-diphenylethane (0.2 mmol) and it was obtained as a colourless oil 31.1 mg, 65% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.36 – 7.28 (m, 5H), 7.26 – 7.07 (m, 5H), 4.53 (t, *J* = 7.7 Hz, 1H), 3.40 (d, *J* = 7.5 Hz, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 138.0, 136.7, 129.2, 129.1, 129.1, 128.7, 127.7, 127.3, 111.6, 55.1, 42.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NS$ 240.0847; Found 240.0844.



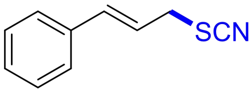
(thiocyanatomethylene)dibenzene (2z):

According to the general procedure A, the title compound was prepared from diphenylmethane (0.2 mmol) and it was obtained as a yellow oil 32.9 mg, 73% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ7.44 – 7.36 (m, 10H), 5.84 (s, 1H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 137.6, 129.2, 128.9, 128.35, 111.8, 57.6.

Spectral data is in agreement with the literature.[5]



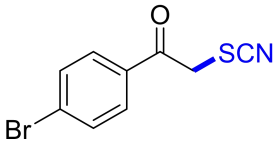
(3-thiocyanatoprop-1-en-1-yl)benzene (2aa):

According to the general procedure B, the title compound was prepared from prop-1-en-1-ylbenzene (0.2 mmol) and it was obtained as a yellow oil 15.8 mg, 45% yield. (eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.45 – 7.29 (m, 5H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.30 – 6.22 (m, 1H), 3.74 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 136.4, 135.5, 128.7, 128.6, 126.8, 121.3, 111.9, 37.0.

Spectral data is in agreement with the literature.[4]

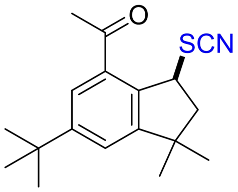


1-(4-bromophenyl)-2-thiocyanatoethan-1-one (2ab):

According to the general procedure B, the title compound was prepared from 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and it was obtained as a white solid 20.8 mg, 40% yield. (eluent: PE/EtOAc = 5/1).

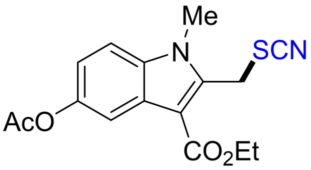
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 4.68 (s, 2H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 190.0, 132.8, 132.7, 130.5, 130.0, 111.6, 42.7.
Spectral data is in agreement with the literature.[8]

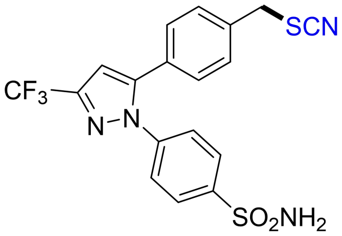


1-(6-(*tert*-butyl)-1,1-dimethyl-3-thiocyanato-2,3-dihydro-1*H*-inden-4-yl)ethan-1-one (2ac):

According to the general procedure A, the title compound was prepared from 1-(6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl)ethan-1-one (0.2 mmol) and it was obtained as a white solid 43.9 mg, 73% yield. (eluent: PE/EtOAc = 30/1).
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.76 (s, 1H), 7.40 (s, 1H), 5.55 (dd, *J* = 5.2, 4.4 Hz, 1H), 2.64 (s, 3H), 2.52 (d, *J* = 4.0 Hz, 2H), 1.46 (s, 3H), 1.37 (s, 9H), 1.35 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 199.7, 154.8, 154.1, 135.6, 133.4, 126.6, 124.3, 113.3, 50.7, 48.3, 43.2, 35.2, 31.5, 30.6, 30.1, 28.1.
Spectral data is in agreement with the literature.[5]



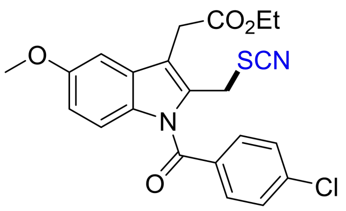
ethyl 5-acetoxy-1-methyl-2-(thiocyanatomethyl)-1*H*-indole-3-carboxylate (2ad):
According to the general procedure A, the title compound was prepared from ethyl 5-acetoxy-1,2-dimethyl-1*H*-indole-3-carboxylate (0.2 mmol) and it was obtained as a white solid 32.9 mg, 50% yield. (eluent: PE/EtOAc = 5/1).
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.81 (d, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.2 Hz, 1H), 4.72 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 170.3, 164.9, 146.6, 140.7, 135.0, 126.2, 118.4, 114.6, 112.0, 110.6, 106.4, 60.4, 30.39, 3.21, 21.2, 14.6.
Spectral data is in agreement with the literature.[9]



4-(5-(4-(thiocyanatomethyl)phenyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl) benzenesulfonamide (2ae):

Accoding to the general procedure B, the title compound was prepared from

4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (0.2 mmol) and it was obtained as a white solid 39.2 mg, 45% yield. (eluent: PE/EtOAc = 1/1).
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.52 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.28 (s, 1H), 4.38 (s, 2H).
^{13}C NMR (150 MHz, DMSO-d_6): δ 144.7, 144.1, 142.3 (q, *J* = 37.7 Hz), 141.0, 137.6, 129.5, 129.3, 128.1, 126.8, 126.0, 121.3 (d, *J* = 268.8 Hz), 112.9, 106.7, 36.4.
^{19}F NMR (376 MHz, DMSO-d_6): δ -60.94.
Spectral data is in agreement with the literature.[5]

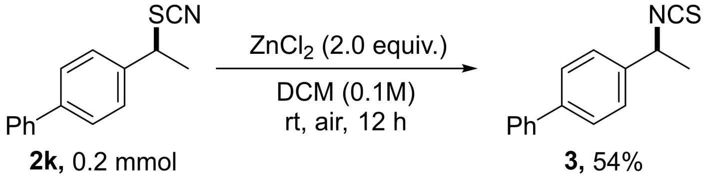


ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-(thiocyanatomethyl)-1*H*-indol-3-yl)acetate (2af):

According to the general procedure B, the title compound was prepared from methyl ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (0.2 mmol) and it was obtained as a white solid 32.7 mg, 37% yield. (eluent: PE/EtOAc = 5/1).
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.02 (s, 1H), 6.69 (d, *J* = 9.1 Hz, 1H), 6.40 (d, *J* = 9.1 Hz, 1H), 4.71 (s, 2H), 3.85 (d, *J* = 17.2 Hz, 5H), 3.74 (s, 3H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 170.6, 168.6, 156.6, 140.1, 133.2, 132.9, 131.3, 131.0, 130.0, 129.6, 117.45, 115.4, 114.3, 112.8, 102.3, 55.9, 52.7, 30.7, 30.1.
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{20}ClN_2O_2S$ 443.0832; Found 443.0827.

5. Synthetic application

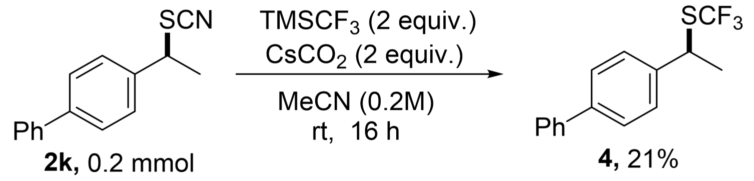
4-(1-isothiocyanatoethyl)-1,1'-biphenyl (3):



To an oven-dried Schlenk-tube (5 mL) was added 2k (45.1 mg, 0.2 mmol), ZnCl$_2$ (54.5 mg, 0.4 mmol), and 2 mL anhydrous DCM (2 mL). The resulting mixture was stirred for 12 h at room temperature and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using 2% hexane-ethyl acetate mixture to afford the title compound **3** (25.8 mg, 54% yield) as a yellow oil.
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.65 – 7.57 (m, 4H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.36 (m, 3H), 4.97 (q, *J* = 6.8 Hz, 1H), 1.72 (d, *J* = 6.8 Hz, 3H).

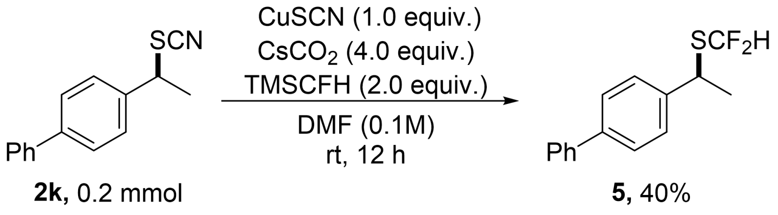
^{13}C NMR (150 MHz, CDCl$_3$): δ 141.4, 140.5, 139.3, 132.7, 129.0, 127.8, 127.7, 127.2, 126.0, 57.0, 25.1.
Spectral data is in agreement with the literature.[10]

(1-([1,1'-biphenyl]-4-yl)ethyl)(trifluoromethyl)sulfane (4):



To an oven-dried Schlenk-tube (10 mL) was added 2k (45.1 mg, 0.2 mmol), CsCO$_3$ (130.3 mg, 0.4 mmol) and MeCN (4 mL). Then trimethyl(trifluoromethyl)silane (60 uL, 0.4 mmol) was added at 0 °C. The resulting mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), the mixture was filtered through a short pad of celite and diluted with ethyl acetate (10 mL). Resulting organic layer was washed with water (5 mL), dried over sodium sulfate and concentrated under vacuum. The residue obtained was purified by a column chromatography on silica-gel using 1-2% hexane-ethyl acetate mixture to afford the title compound **4** (12.1 mg, 21% yield) as a white solid.
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.61 – 7.55 (m, 4H), 7.48 – 7.40 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 4.58 (q, J = 7.0 Hz, 1H), 1.78 (d, J = 7.0 Hz, 3H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 141.1, 140.6, 140.4, 130.6 (q, *J* = 307.4 Hz), 129.0, 127.9, 127.8, 127.6, 127.2, 44.4, 23.2.
^{19}F NMR (565 MHz, CDCl$_3$): δ -40.08.
Spectral data is in agreement with the literature.[11]

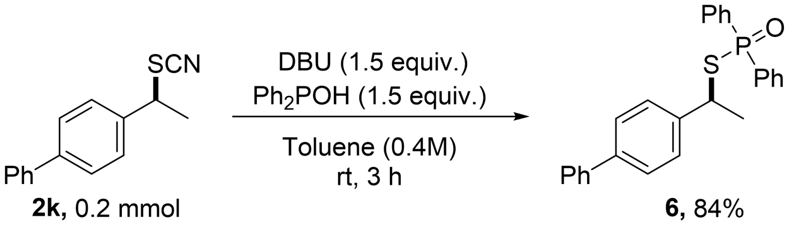
(1-([1,1'-biphenyl]-4-yl)ethyl)(difluoromethyl)sulfane (5):



An oven-dried 10 mL sealed tube with Teflon-coated stirrer bar was charged with the 2k (45.1 mg, 0.2 mmol), copper thiocyanate (24.3 mg, 0.2 mmol), Cs$_2$CO$_3$ (260.6 mg, 0.8 mmol) and DMF (2 mL) under Ar. Difluoromethyltrimethylsilane (48.8 mg, 0.4 mmol) was added and the suspension was stirred at room temperature for 12 h. The resulting organic solution was washed with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over MgSO4, filtered and concentrated. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (50:1) to afford the title compound **5** (21.2 mg, 40% yield) as a colourless oil.
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.62 – 7.56 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.61 (dd, *J* = 58.9, 55.4 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 1H), 1.73 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 141.3, 140.9, 140.7, 129.0, 127.7, 127.6, 127.2, 121.0 (dd, *J* = 274.6, 269.3 Hz), 42.2, 23.3.
^{19}F NMR (565 MHz, CDCl$_3$): δ -92.49 (d, *J* = 250.1 Hz), -95.88 (d, *J* = 250.8 Hz).
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{15}F_2S$ 265.0823; Found 265.0820.

(1-([1,1'-biphenyl]-4-yl)ethyl) diphenylphosphinothioate (6):

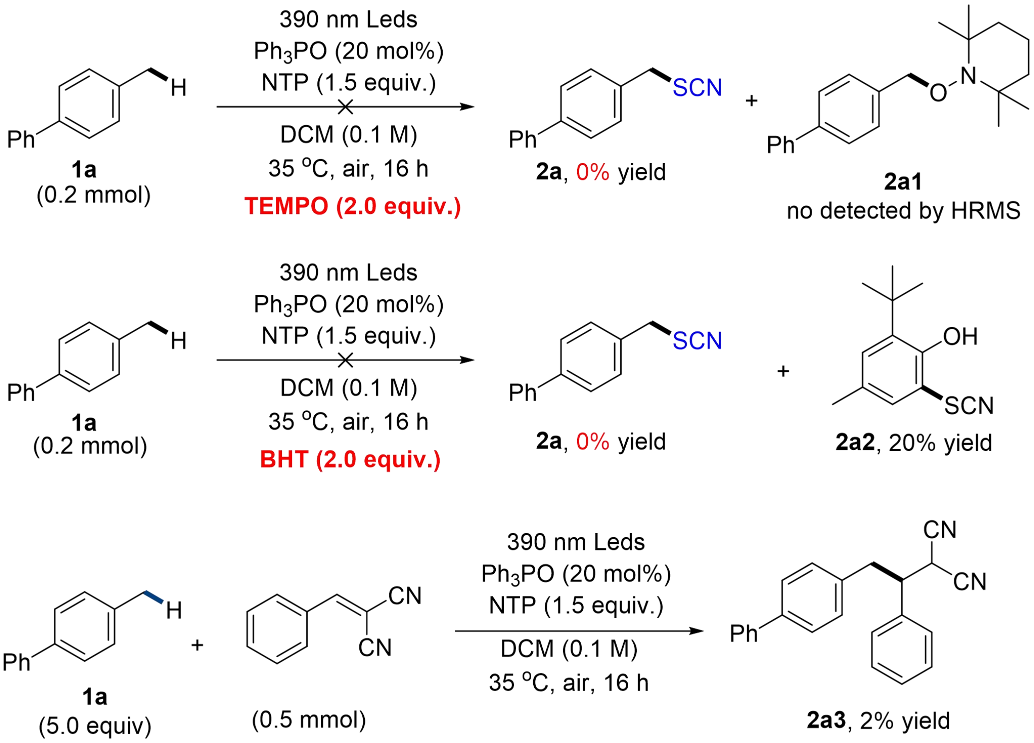


To an oven-dried Schlenk-tube (10 mL) was added 2k (45.1 mg, 0.2 mmol), diphenylphosphine oxide (62 mg, 0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7ene (DBU, 45 mg, 0.3 mmol) and toluene (8 mL). The resulting mixture was stirred for 3 h at room temperature and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using 50% hexane-ethyl acetate mixture to afford the title compound **6** (66.2 mg, 84% yield) as a white solid.
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.86 – 7.73 (m, 4H), 7.52 – 7.47 (m, 3H), 7.45 – 7.39 (m, 5H), 7.38 – 7.30 (m, 5H), 7.24 (d, J = 7.6 Hz, 2H), 4.62 – 4.56 (m, 1H), 1.76 (d, J = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, CDCl$_3$): δ 142.1 (d, *J* = 4.0 Hz), 140.5 (d, *J* = 73.5 Hz), 134.1 (d, *J* = 106.7 Hz), 132.8 (d, *J* = 106.9 Hz), 132.3 (d, *J* = 2.1 Hz), 132.00, 131.95 (d, *J* = 4.7 Hz), 131.2 (d, *J* = 10.0 Hz), 128.8, 128.7 (d, *J* = 12.9 Hz), 128.5 (d, *J* = 13.4 Hz), 127.6, 127.4, 127.2, 127.1, 44.2, 24.8 (d, *J* = 3.9 Hz).
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{26}H_{24}OPS$ 414.1207; Found 414.1212.

6. Mechanism Study

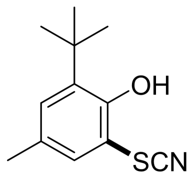
6.1 Radical Quenching Experiments

Scheme S1. The radical quenching experiments



Note: The detailed stepwise process for product **2a2** is as follows, a thiocyanato radical abstracts the phenolic hydrogen atom from BHT (2,6-*di*-*tert*-butyl-4-methylphenol), generating a stabilized phenoxyl radical and thiocyanic acid. The newly formed phenoxyl radical is highly stabilized by resonance, with the unpaired electron delocalized over the oxygen atom and the ortho/para positions of the benzene ring. One of the key contributing resonance structures places the radical character directly at an ortho carbon. This makes the ortho carbon strongly nucleophilic toward other radicals. A second SCN radical adds to the activated ortho carbon, forming a resonance-stabilized cyclohexadienyl radical intermediate. The cyclohexadienyl radical intermediate is non-aromatic and suffers from severe steric repulsion between the newly added SCN group and the adjacent bulky tert-butyl group. To relieve this strain and regain aromatic stability, the intermediate expels a tert-butyl radical, a stable tertiary carbon radical. This step yields the final product: a BHT derivative in which one ortho *tert*-butyl group is replaced by a thiocyanato group. The phenolic oxygen remains protonated because the initial hydrogen abstraction involved the hydroxylic hydrogen. The expelled tert-butyl radical may undergo subsequent reactions, such as hydrogen abstraction to form isobutane or coupling with other radicals in the system. The net result is the formal substitution of one tert-butyl group on BHT by a thiocyanato group, mediated by two thiocyanato radicals (one for H-abstraction and one for addition). This process provides strong evidence for the presence of thiocyanato radicals in the system.

The formation of product **2a3** is consistent with the proposed generation of a benzyl radical intermediate.



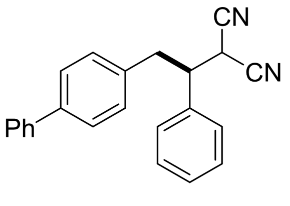
2-(tert-butyl)-4-methyl-6-thiocyanatophenol (2a2):

According to the general procedure, 4-methyl-1,1'-biphenyl (33.6 mg, 0.2 mmol, 1.0 equiv.), 2,6-di-tert-butyl-4-methylphenol (88.1 mg, 0.4 mmol, 2.0 equiv.), Ph_3PO (11.1 mg, 0.04 mmol, 0.2 equiv.), NTP (61.3 mg, 0.6 mmol, 1.5 equiv.) and 2.0 mL anhydrous DCM were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (9.0 mg, 20% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.05 (s, 1H), 6.54 (s, 1H), 4.94 (s, 1H), 2.29 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.7, 136.5, 129.3, 128.8, 126.8, 113.6, 34.7, 29.6, 17.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{16}NOS$ 222.3260; Found 222,3256.



2-(2-([1,1'-biphenyl]-4-yl)-1-phenylethyl)malononitrile (2a3):

According to the general procedure, 4-methyl-1,1'-biphenyl (420.5 mg, 2.5 mmol, 5.0 equiv.), 2-benzylidenemalononitrile (77 mg, 0.5 mmol, 1.0 equiv.), Ph_3PO (27.8 mg, 0.1 mmol, 0.2 equiv.), NTP (61.3 mg, 0.6 mmol, 1.5 equiv.) and 2.0 mL anhydrous DCM were used. After 16 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography (2 % ethyl acetate/petroleum ether) to provide the title compound as a colourless oil (3.2 mg, 2% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (t, J = 7.7 Hz, 4H), 7.47 – 7.38 (m, 7H), 7.35 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 3.90 (d, J = 5.2 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.35 – 3.27 (m, 2H).

^{13}C NMR (150MHz, $CDCl_3$): δ 140.7, 140.5, 136.5, 135.7, 129.5, 129.4, 129.3, 129.0, 128.2, 128.0, 127.7, 127.1, 112.1, 111.6, 48.4, 38.3, 28.7.

Spectral data is in agreement with the literature.[12]

6.2 UV/Vis-Absorption Spectra of the Reaction Components

Preparation of samples for the measurement of UV-Vis spectra.

Substrate 1a in DCM: 1a (0.20 mmol) was dissolved in anhydrous DCM (2.0 mL).

Ph_3PO in DCM: Ph_3PO (0.04 mmol) was dissolved in anhydrous DCM (2.0 mL).

NTP in DCM: NTP (0.30 mmol) was dissolved in anhydrous DCM (2.0 mL).

Substrate 1a and Ph_3PO in DCM: 1a (0.20 mmol) and Ph_3PO (0.04 mmol) were dissolved in anhydrous DCM (2.0 mL).

Substrate 1a and NTP in DCM: 1a (0.20 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL).

Ph_3PO and NTP in DCM: Ph_3PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL).

Substrate 1a, Ph_3PO and NTP in DCM: 1a (0.20 mmol), Ph_3PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL).

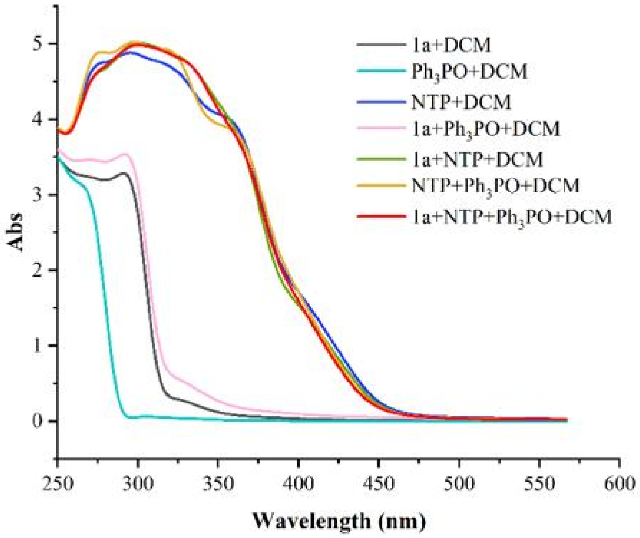


Figure S1. UV-Vis spectra of the reaction components (0 h).

Substrate 1a in DCM (4h): 1a (0.20 mmol) was dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

Ph_3PO in DCM (4h): Ph_3PO (0.04 mmol) was dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

NTP in DCM (4h): NTP (0.30 mmol) was dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

Substrate 1a and Ph_3PO in DCM (4h): 1a (0.20 mmol) and Ph_3PO (0.04 mmol) were dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

Substrate 1a and NTP in DCM (4h): 1a (0.20 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

Ph_3PO and NTP in DCM (4h): Ph_3PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

Substrate 1a, Ph_3PO and NTP in DCM (4h): 1a (0.20 mmol), Ph_3PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

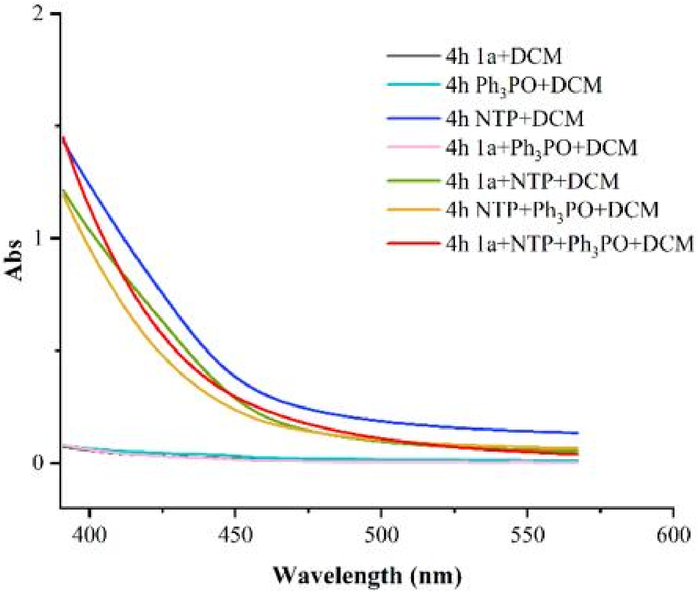


Figure S2. UV-Vis spectra of the reaction components (4 h).

Substrate 1a, Ph$_3$PO and NTP in DCM (0 h): 1a (0.20 mmol), Ph$_3$PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL).

Substrate 1a, Ph$_3$PO and NTP in DCM (4 h): 1a (0.20 mmol), Ph$_3$PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL), stirred for 4 h under 390nm Leds.

Substrate 1a, Ph$_3$PO and NTP in DCM (16 h): 1a (0.20 mmol), Ph$_3$PO (0.04 mmol) and NTP (0.30 mmol) were dissolved in anhydrous DCM (2.0 mL), stirred for 16 h under 390nm Leds.

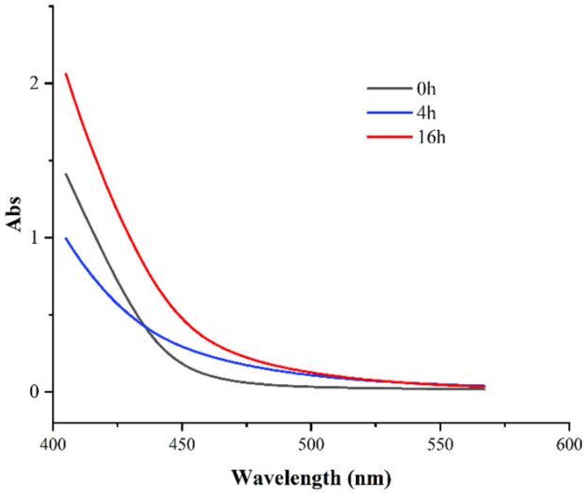


Figure S3. UV-Vis spectra of reaction at different reaction times.

Note: After 16 hours, a notable bathochromic shift in the absorption of the reaction solution was observed, which suggests that new species were generated.

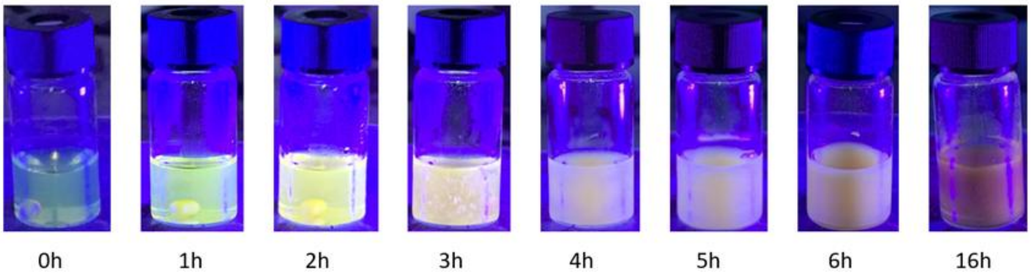


Figure S4. Benzylic C-H thiocyanation reaction mixture color changed as the reaction proceeded (0-16 h).

Note: After 2 hours of reaction, the formation of a visibly reflective material in the mixture provided preliminary evidence for the in situ generation of an electron donor-acceptor (EDA) complex.

6.3 ^{31}P-NMR Analysis

Preparation of samples for ^{31}P-NMR measurement: All samples containing $Ph_3P=O$ (0.04 mmol) and NTP in different proportions ranging from 1:0 to 1:12.5 with a total volume of 600 μL $CDCl_3$ were prepared in the nuclear magnetic tube and used for ^{31}P-NMR studies.

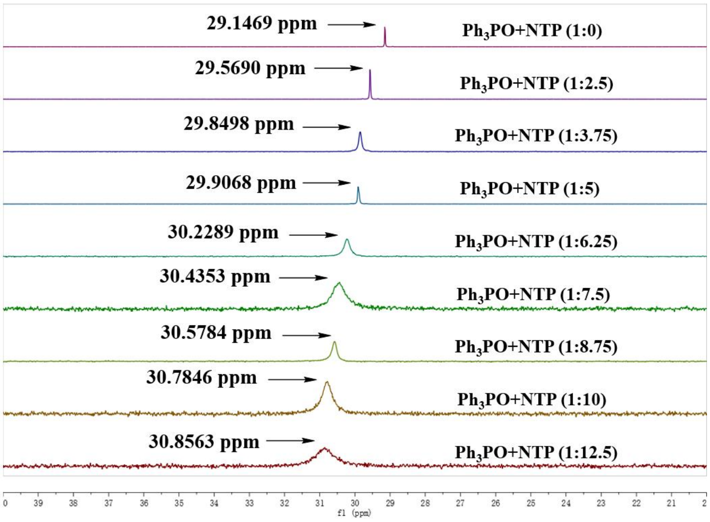


Figure S5. ^{31}P-NMR spectra of $Ph_3P=O$ and NTP with different ratios.

Note: The ^{31}P NMR chemical shift of triphenylphosphine oxide varied systematically with the molar ratio of NTP, confirming a specific molecular interaction between the two components.

6.4 Benesi-Hildebrand Plot[13]

In an NMR tube, the mixtures of Ph_3PO and NTP were dissolved in $CDCl_3$. The total volume of mixture was 600 μL, the concentration of Ph_3PO (0.04 mmol) was kept constant at 0.067 M, while that of NTP was varied from 0 to 0.833 M. The molar ratios of Ph_3PO: NTP were 1:0, 1:2.5, 1:3.75, 1:5, 1:6.25, 1:7.5, 1:8.75, 1:10, 1:12.5. **^{31}P-NMR** for each sample was recorded and the changes of chemical shift (Δδ) for -P group in Ph_3PO were used to draw the plot.The association constant of **Ph_3PO** with **NTP** (K_{EDA}) was alculated: $K_{EDA} = c/a = 0.066/0.3747 = 0.18\ M^{-1}$

Entry	Ph_3PO: NTP(mmol)	P(ppm)	Δppm	C(NTP), M	1/Δppm	1/C(NTP)
1	0.04:0.00	29.1469	0.0000	0.0000	-	-
2	0.04:0.10	29.5690	0.4221	0.1667	2.3691	6.0
3	0.04:0.15	29.8498	0.7029	0.2500	1.4227	4.0
4	0.04:0.20	29.9068	0.7599	0.3333	1.3160	3.0
5	0.04:0.25	30.2289	1.0820	0.4167	0.9242	2.4
6	0.04:0.30	30.4353	1.2884	0.5000	0.7762	2.0
7	0.04:0.35	30.5784	1.4315	0.5833	0.6986	1.7
8	0.04:0.40	30.7846	1.6377	0.6667	0.6106	1.5
9	0.04:0.50	30.8563	1.7094	0.8333	0.5850	1.2

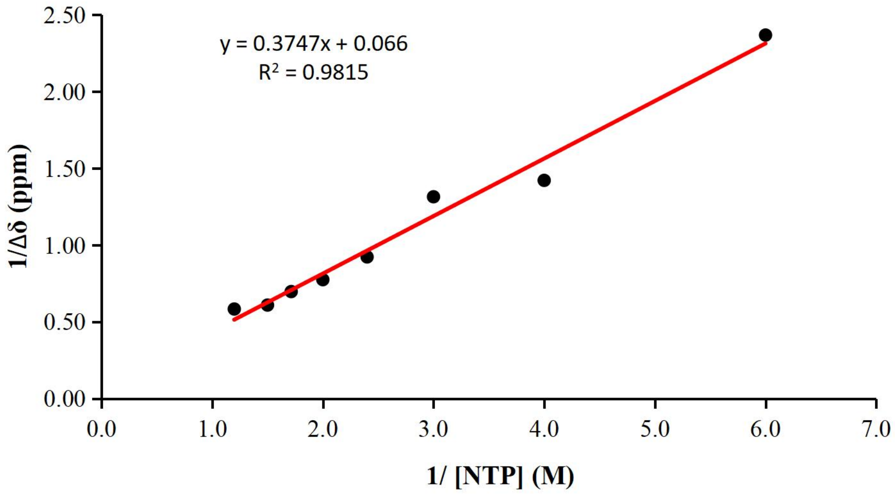


Figure S6. Benesi-Hildebrand Plot.

Note: The finite yet measurable equilibrium K_{EDA} unequivocally confirms the formation of the EDA complex, despite its modest magnitude.

7. References

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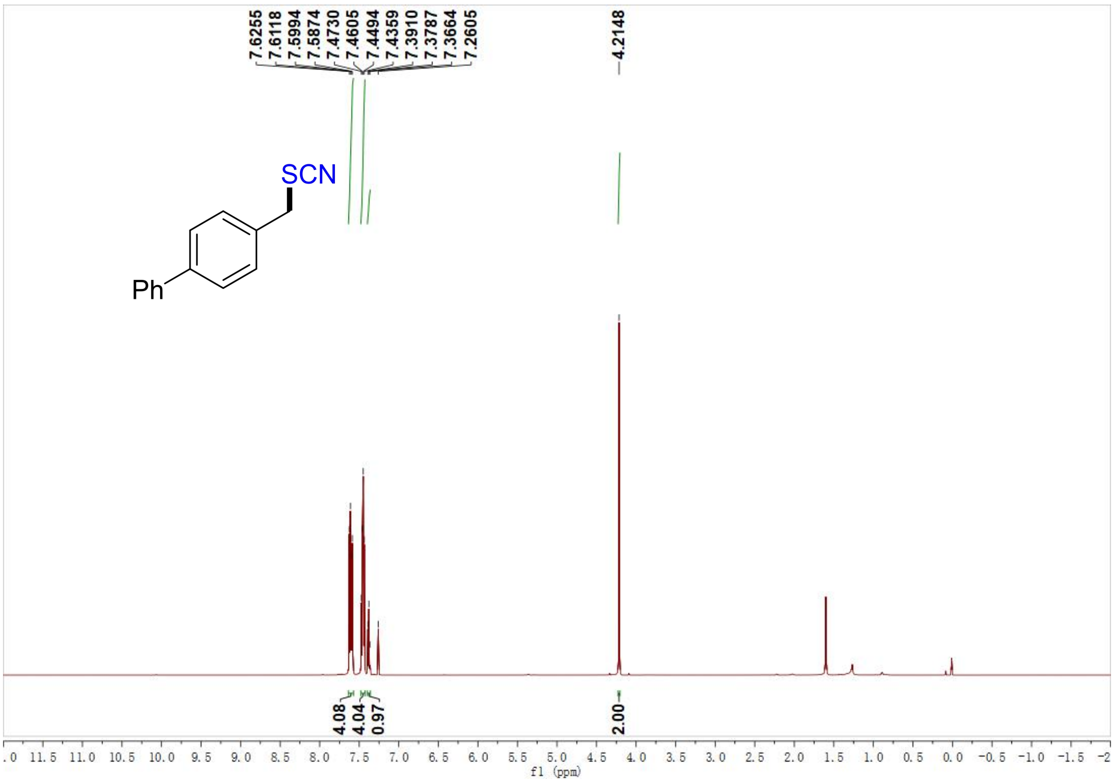
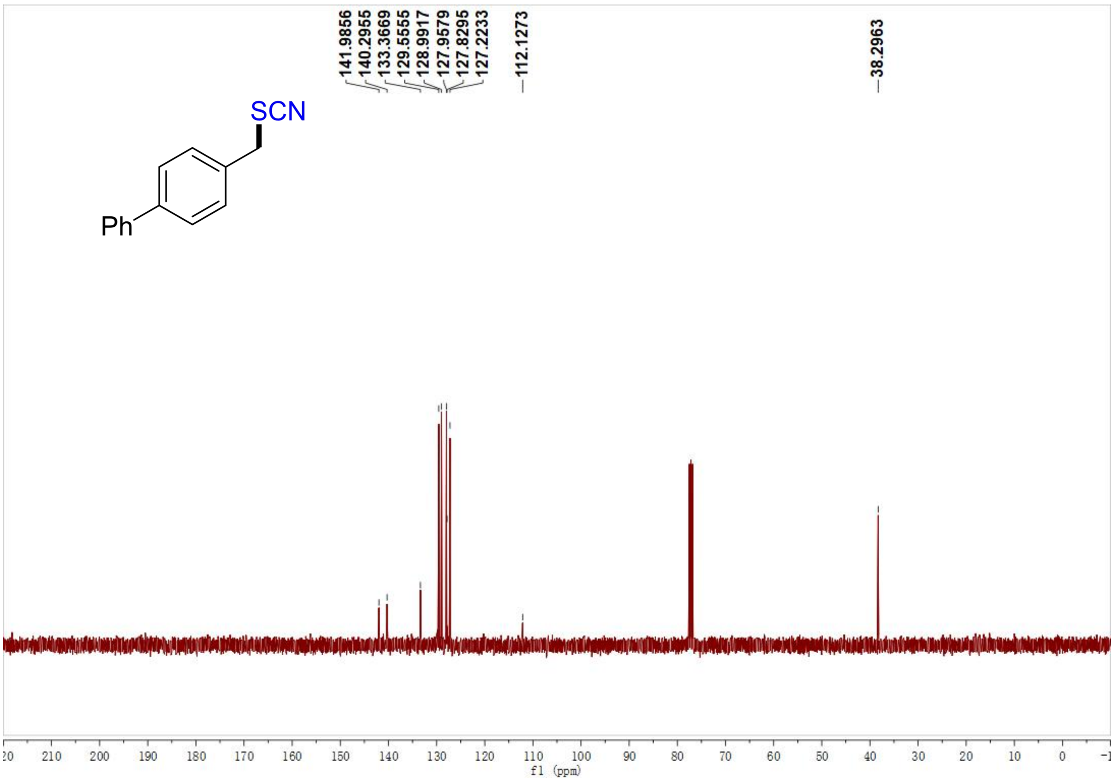
8. NMR spectra



^{1}H NMR (600 MHz, CDCl$_3$) of **2a**



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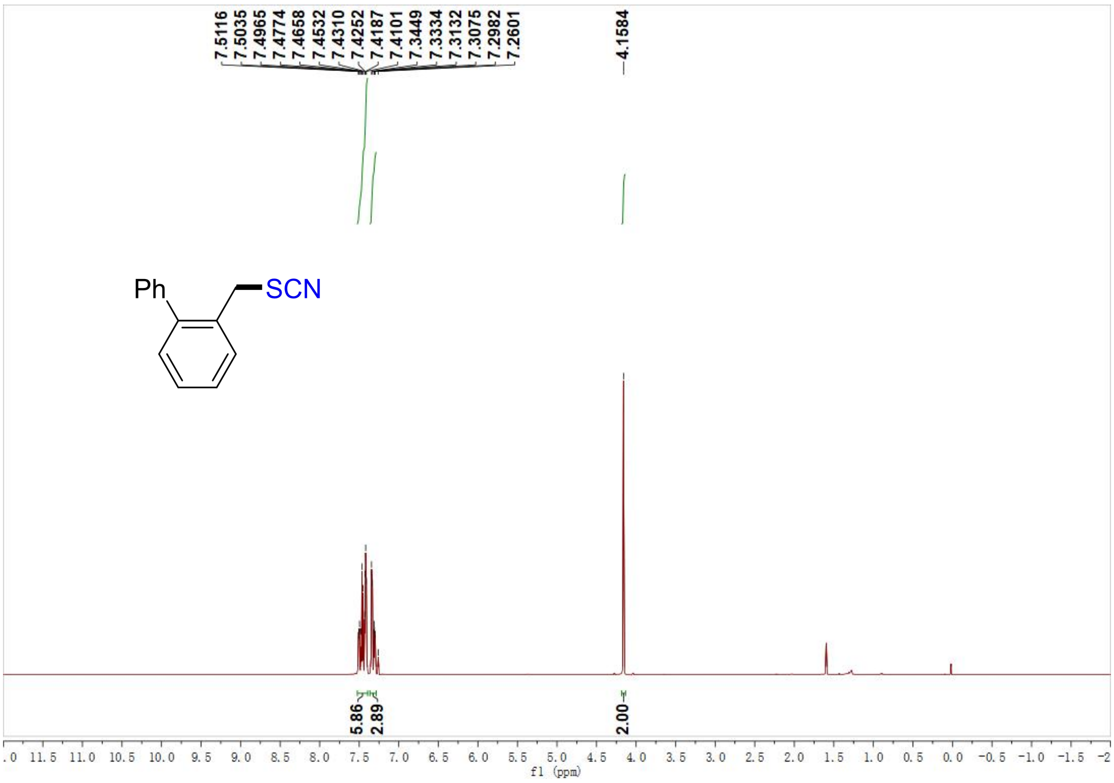

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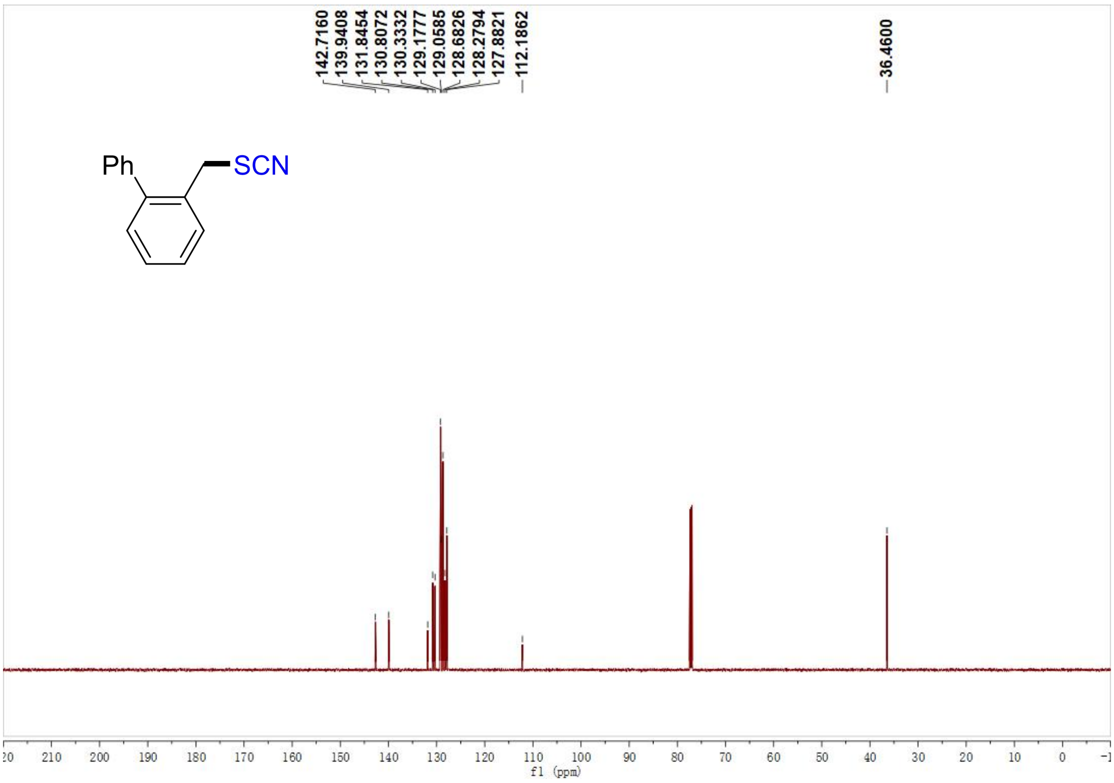

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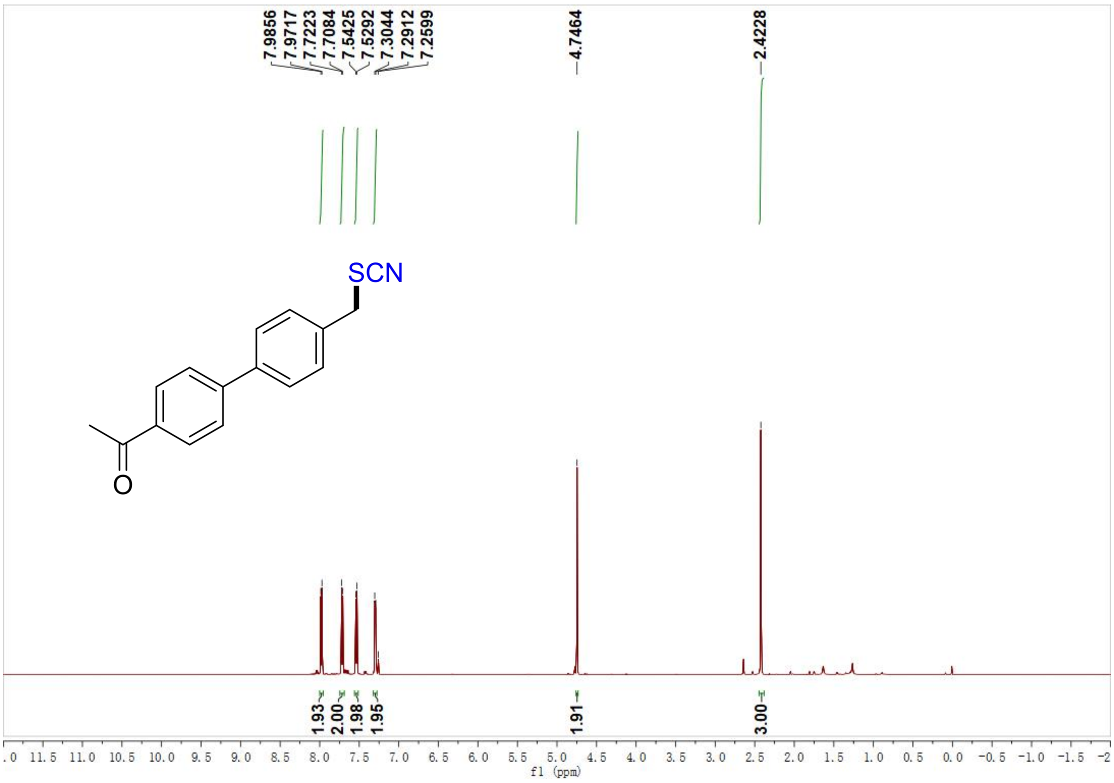
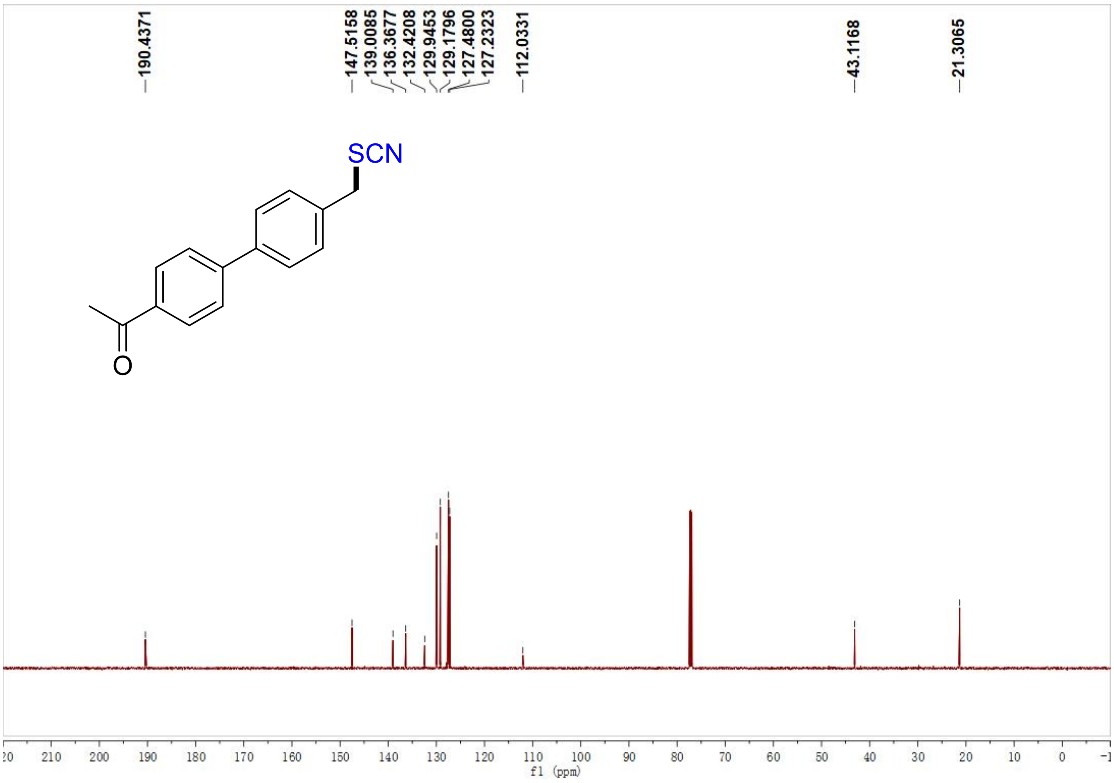
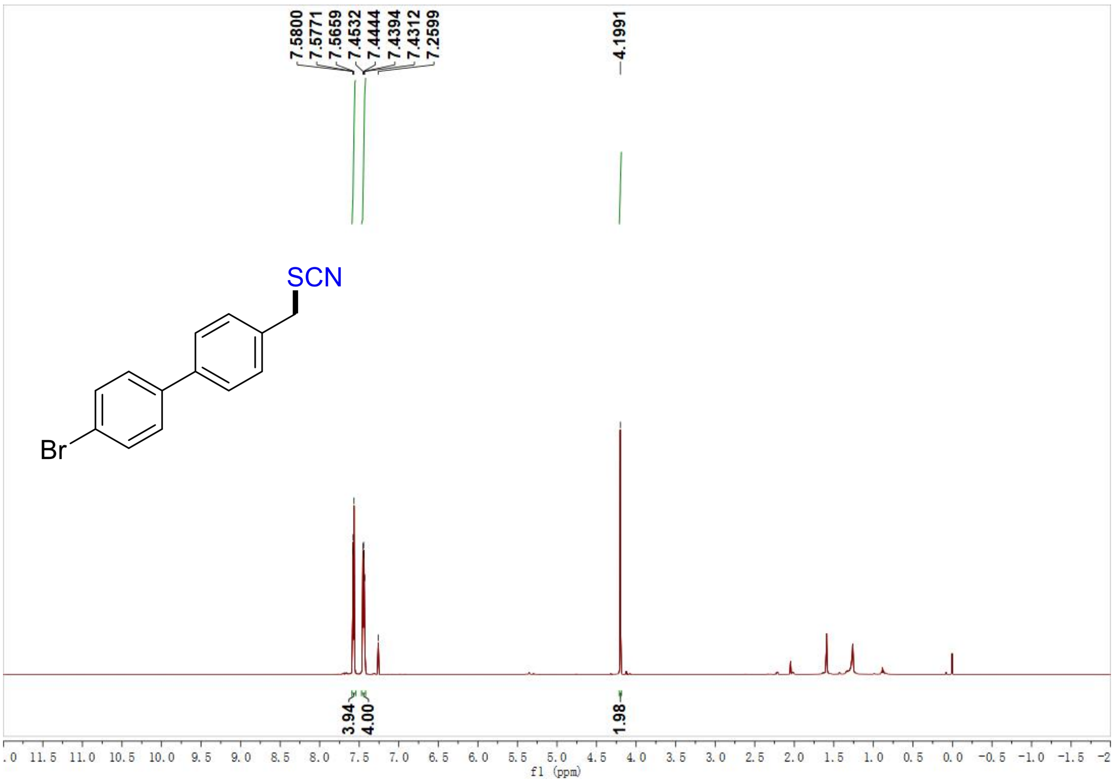


¹H NMR (600 MHz, $CDCl_3$) of **2c**



¹³C NMR (150 MHz, $CDCl_3$) of **2c**



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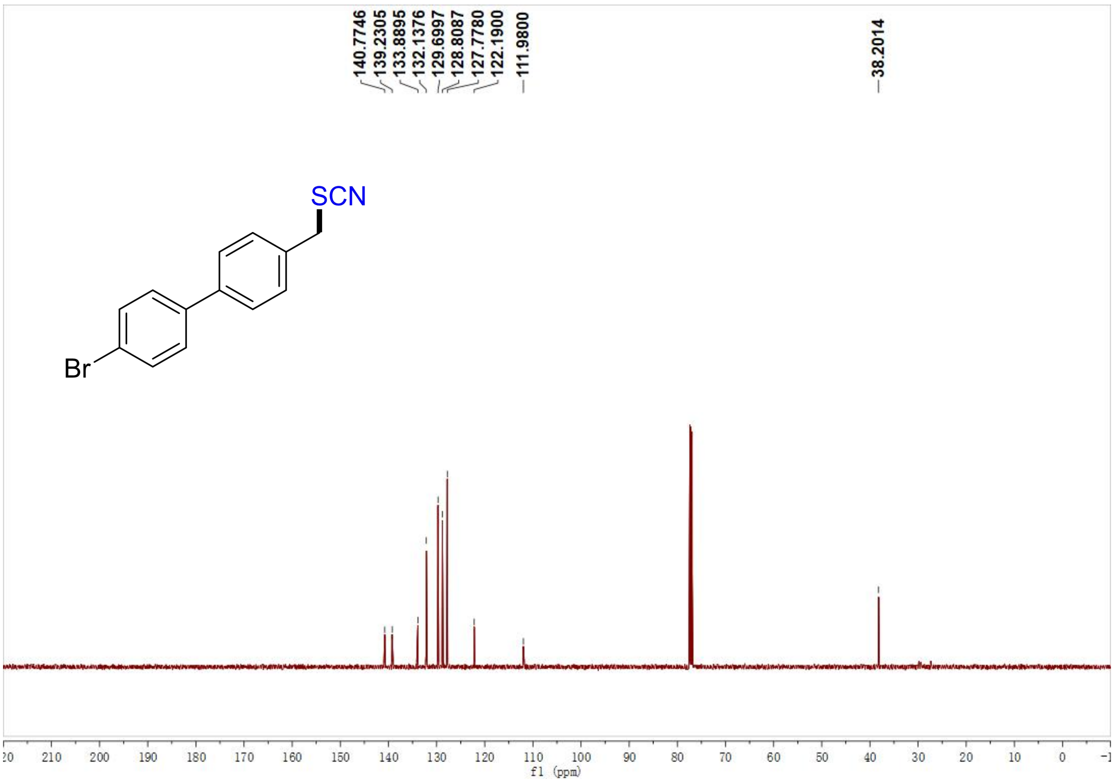
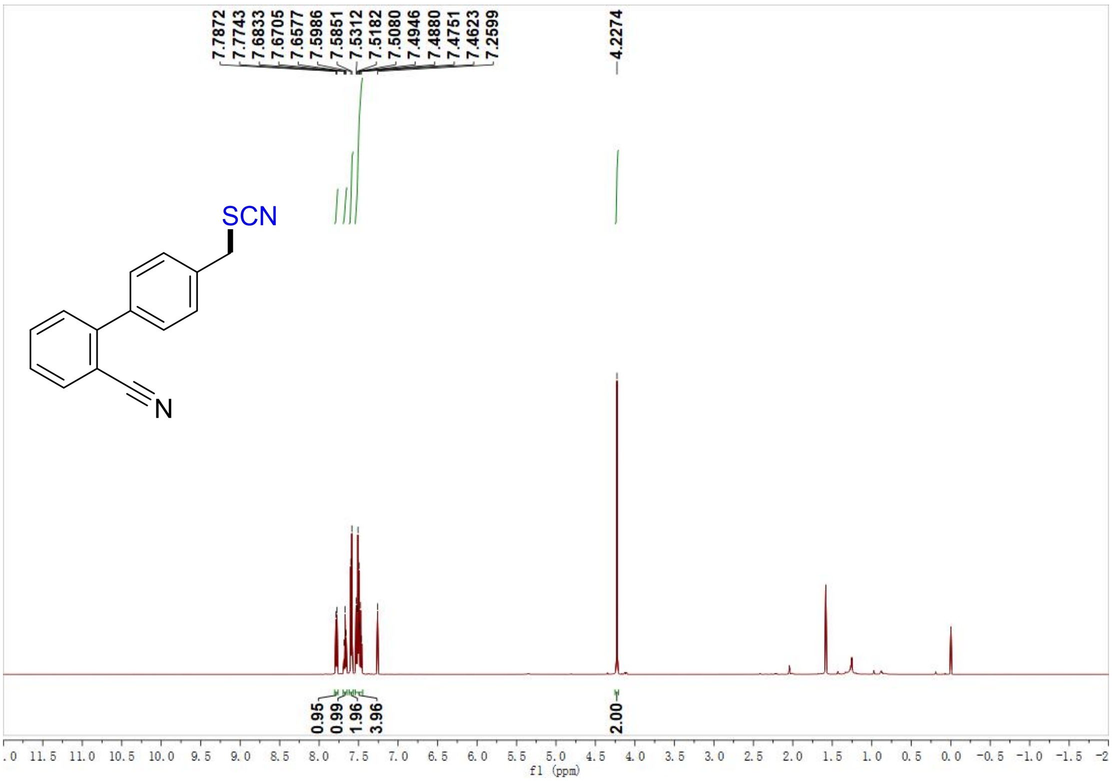


^{13}C NMR (150 MHz, CDCl$_3$) of **2d**



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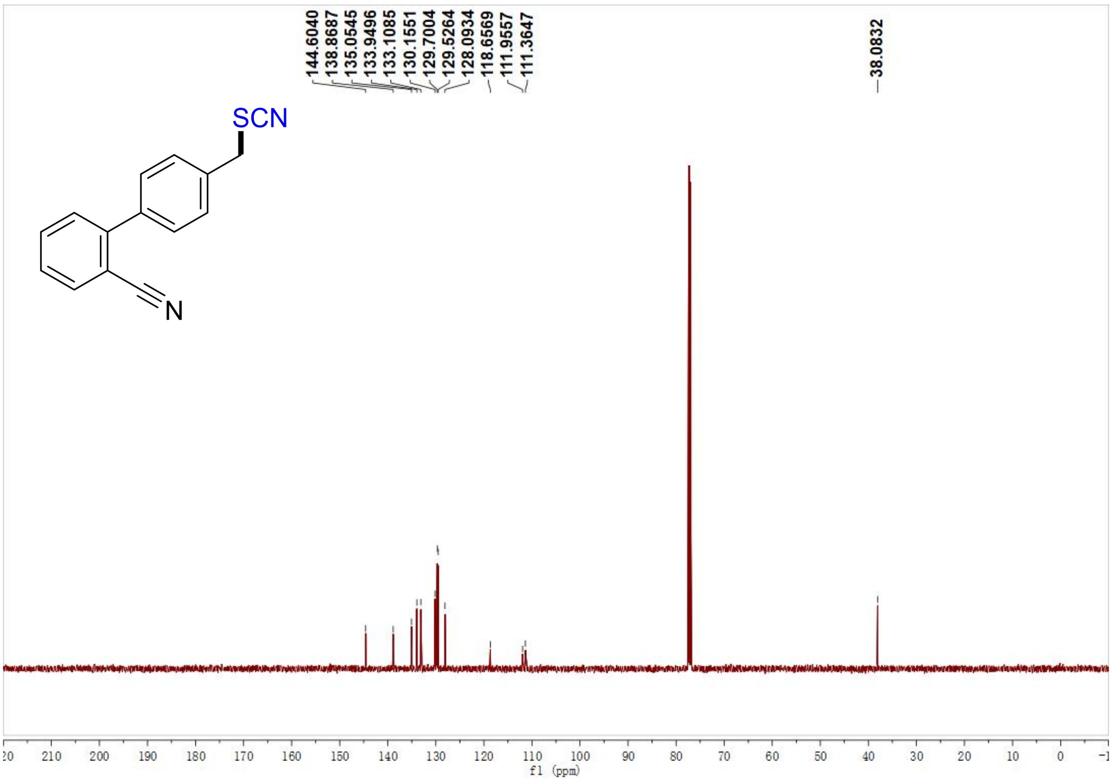

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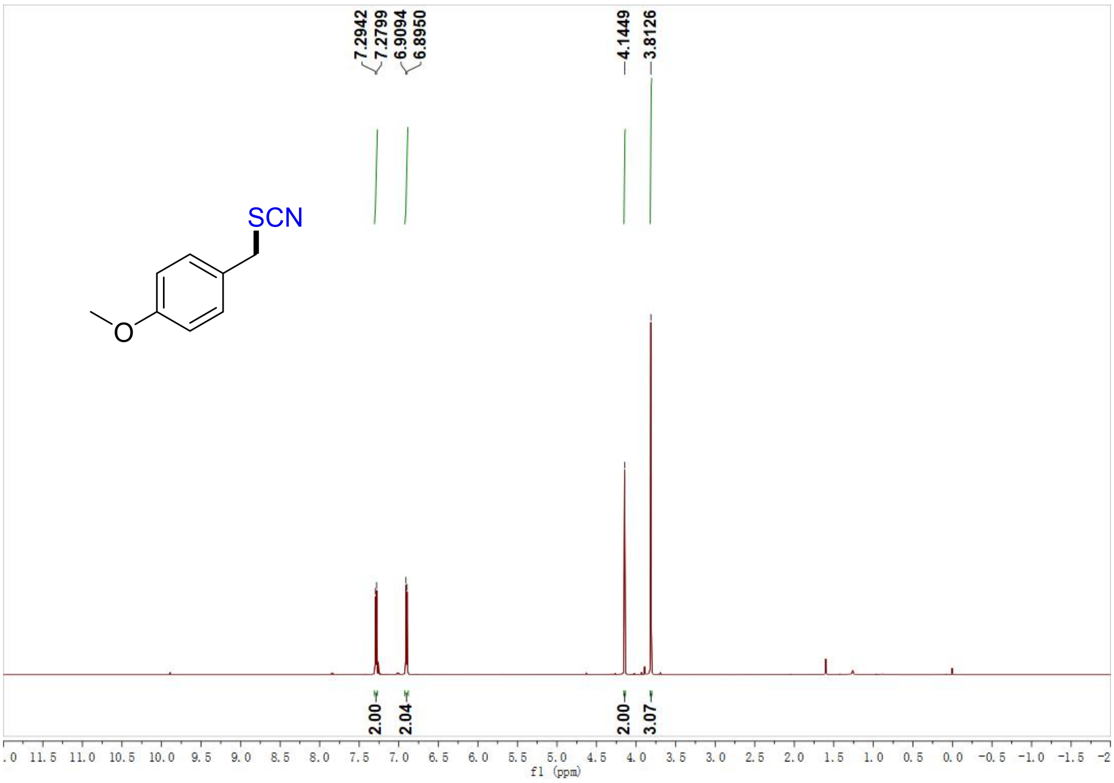

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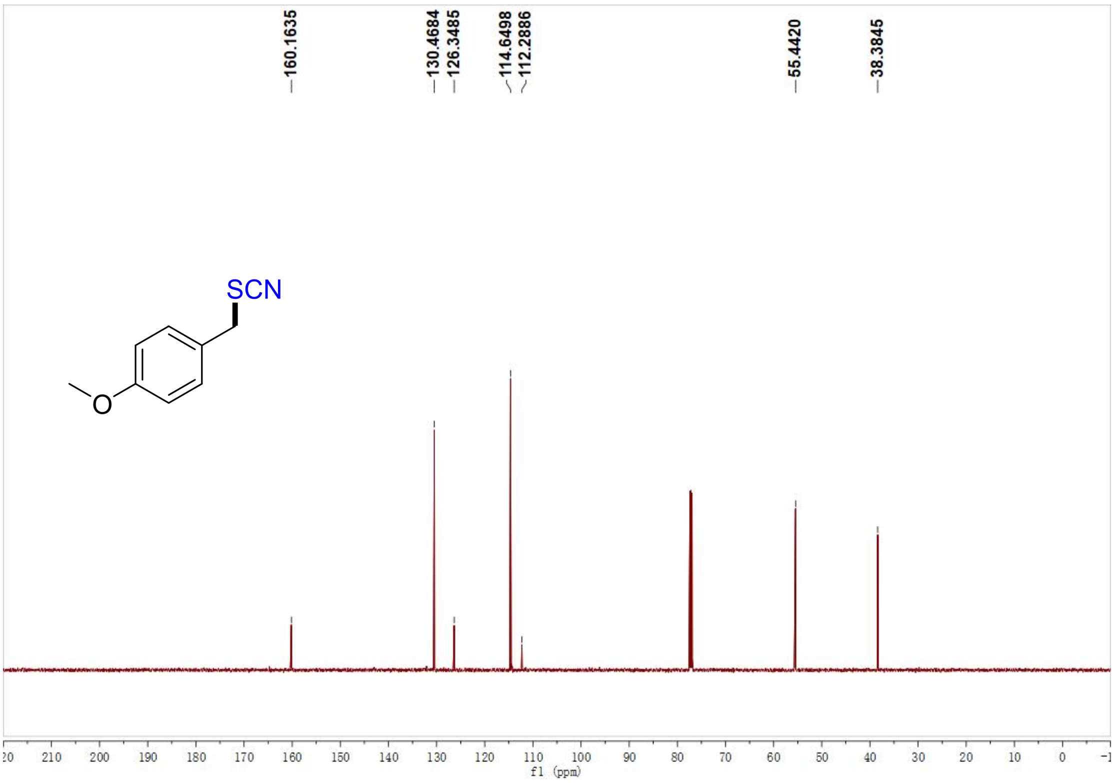

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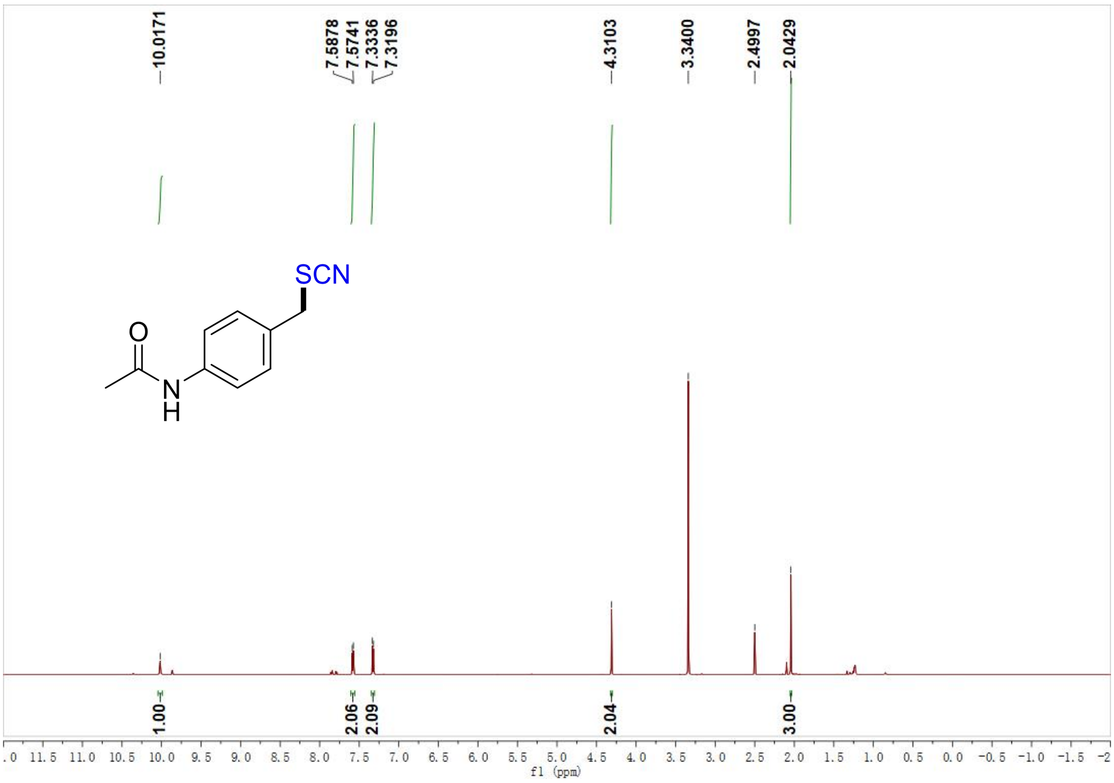

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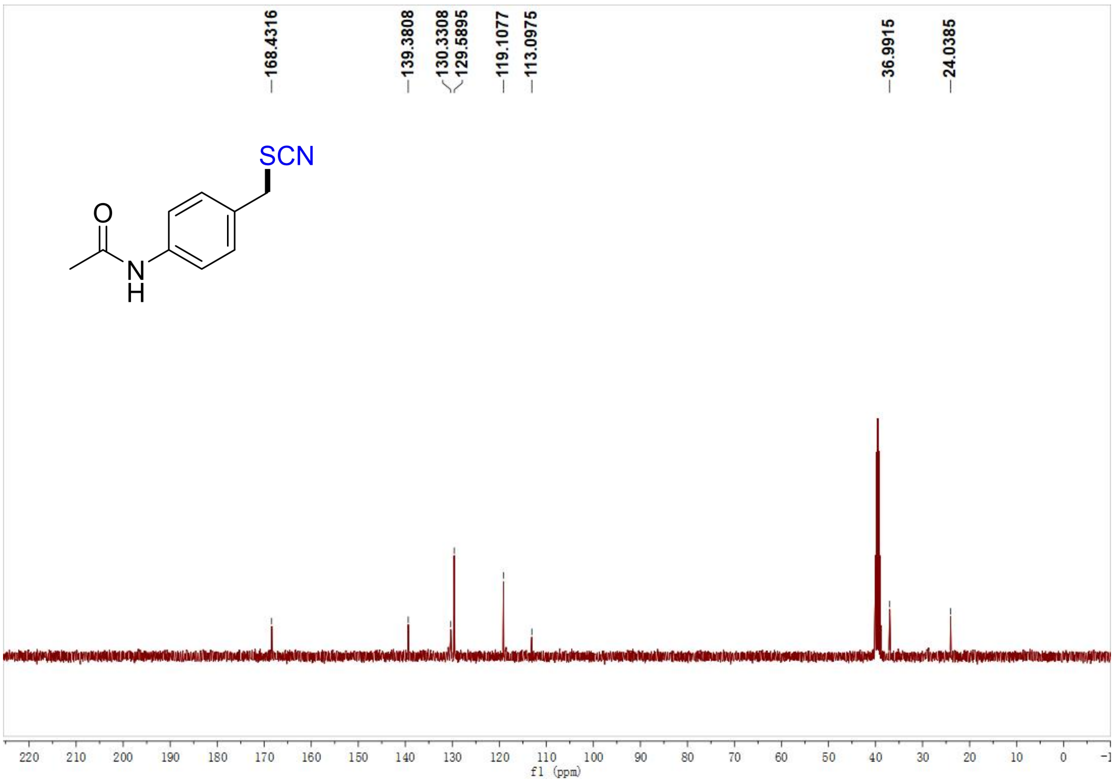

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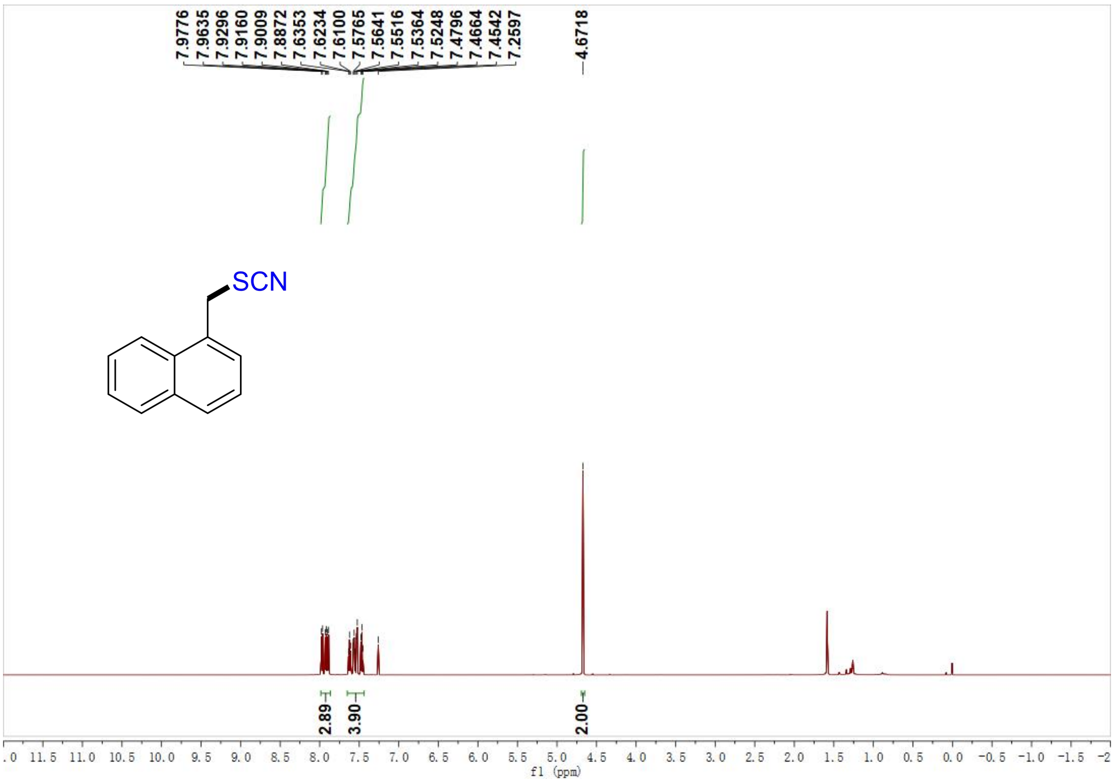

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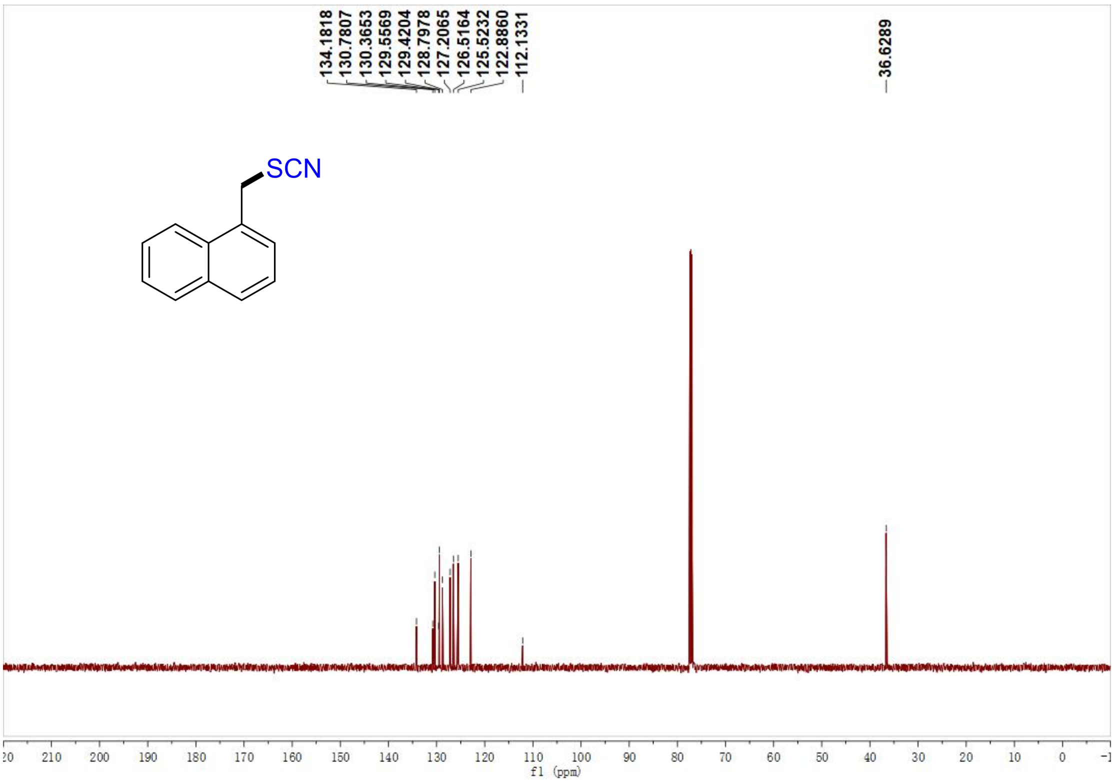

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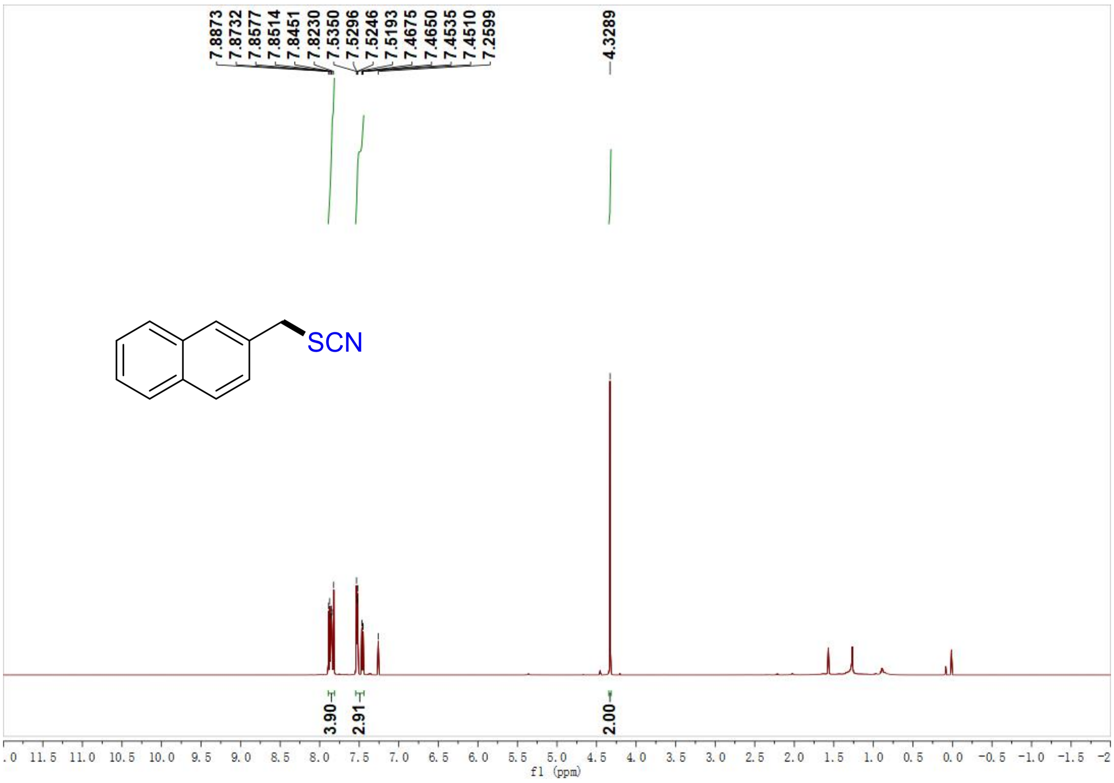

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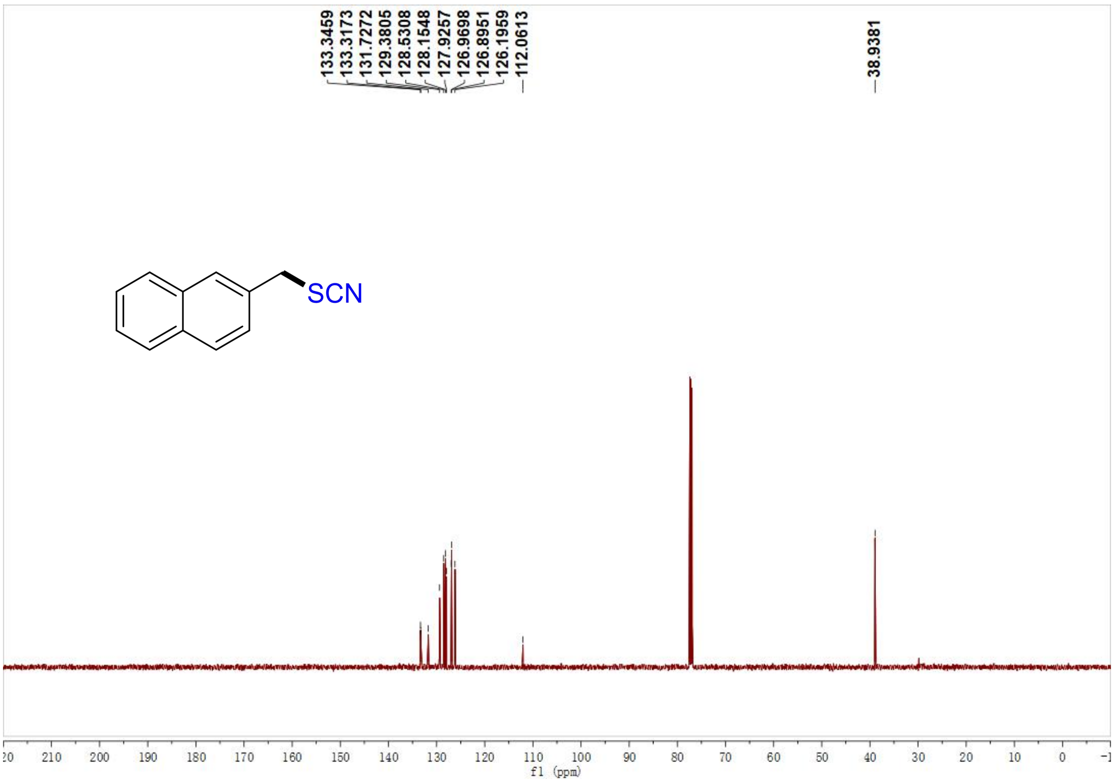

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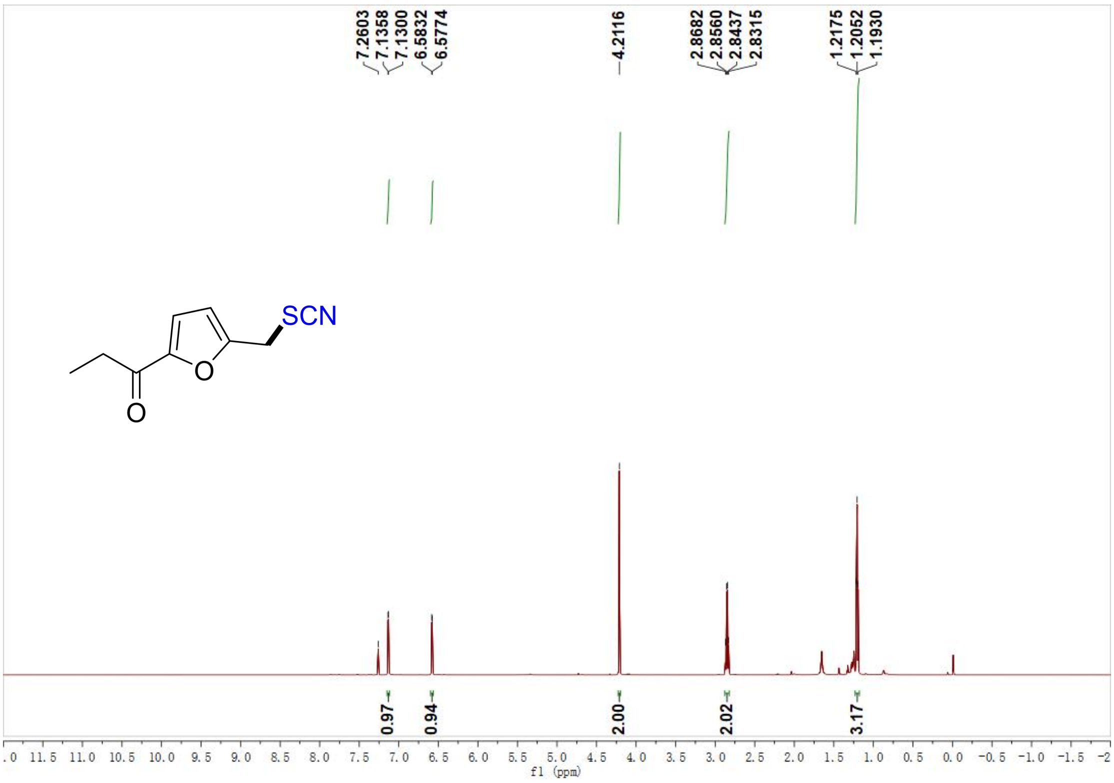

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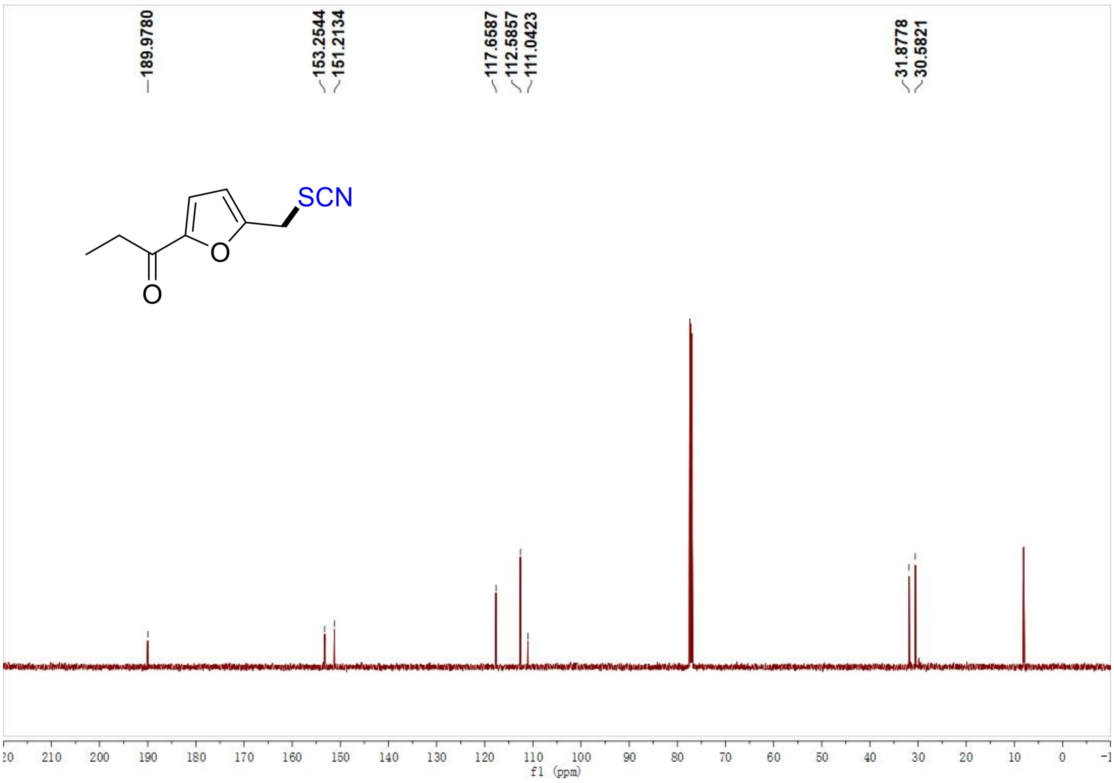

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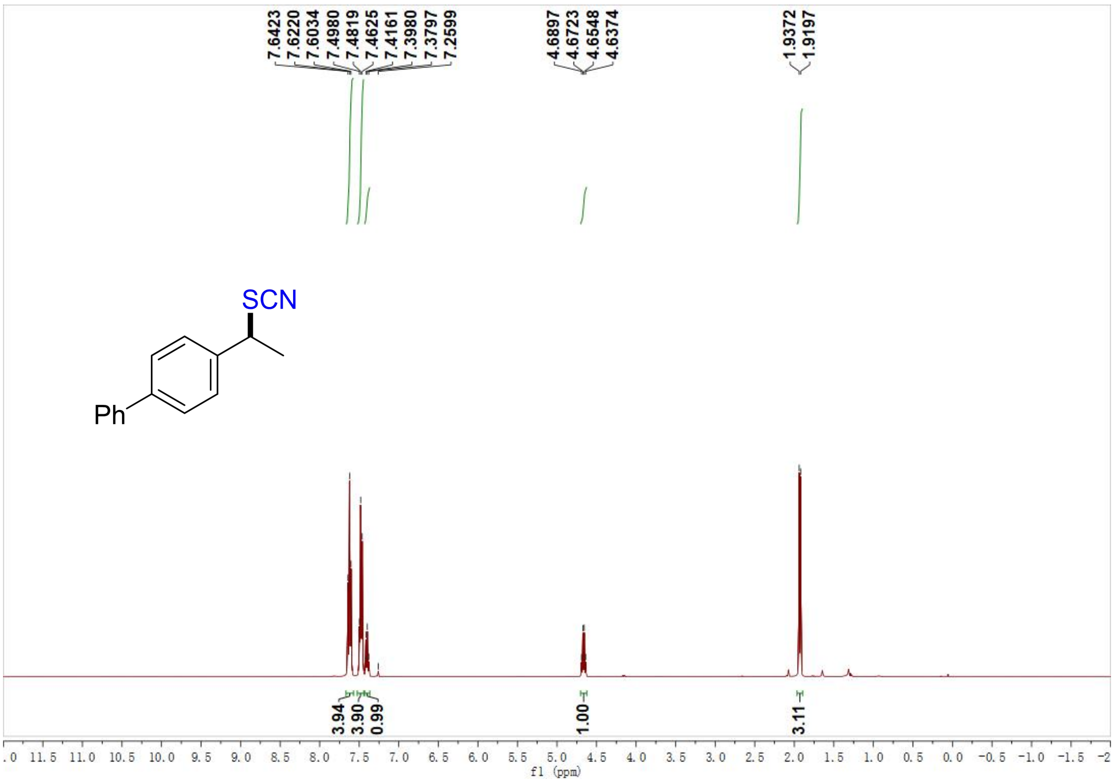

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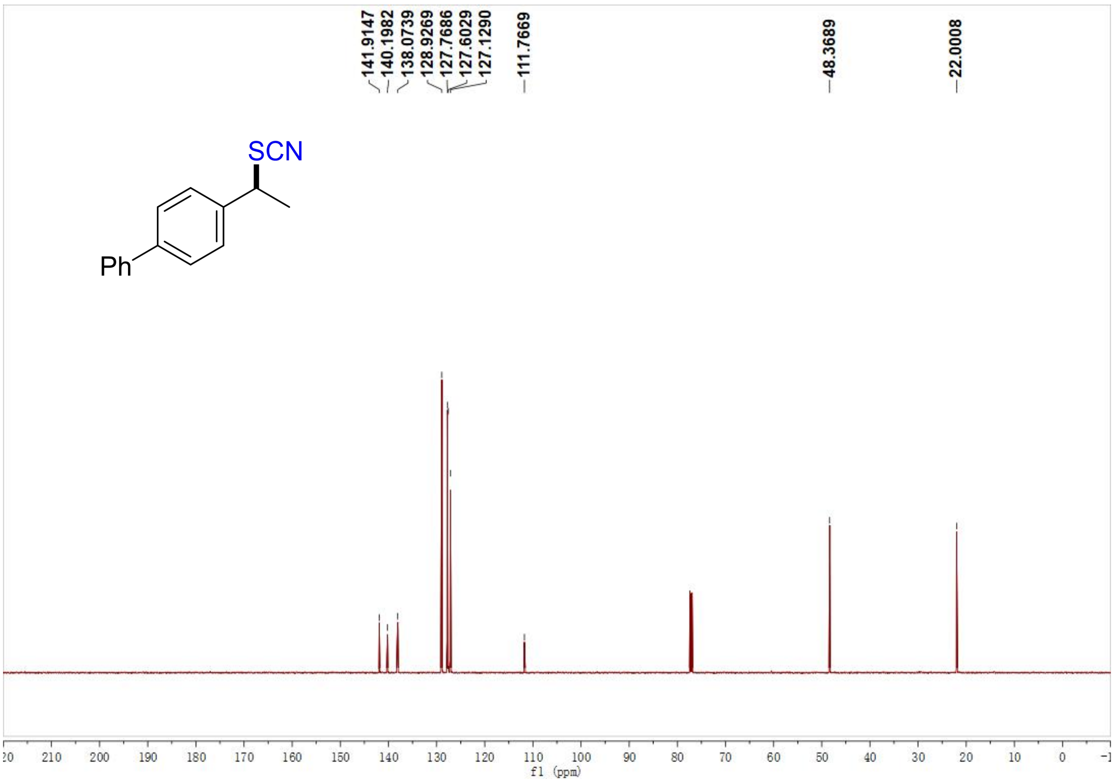

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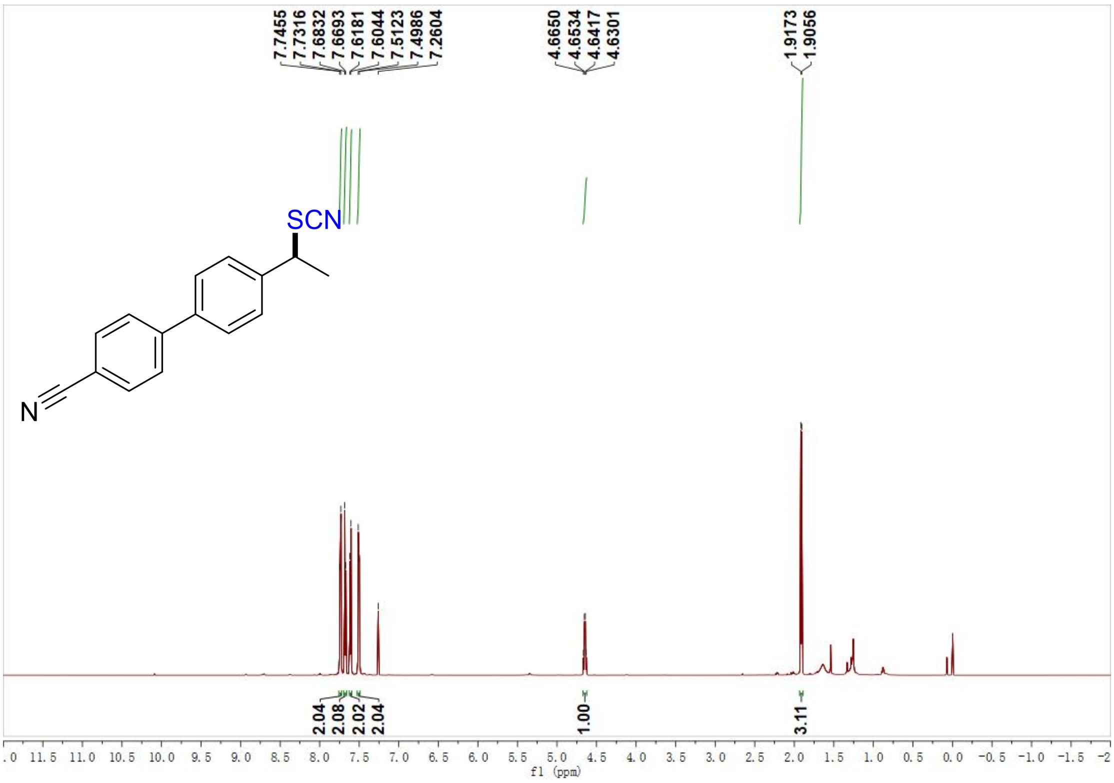

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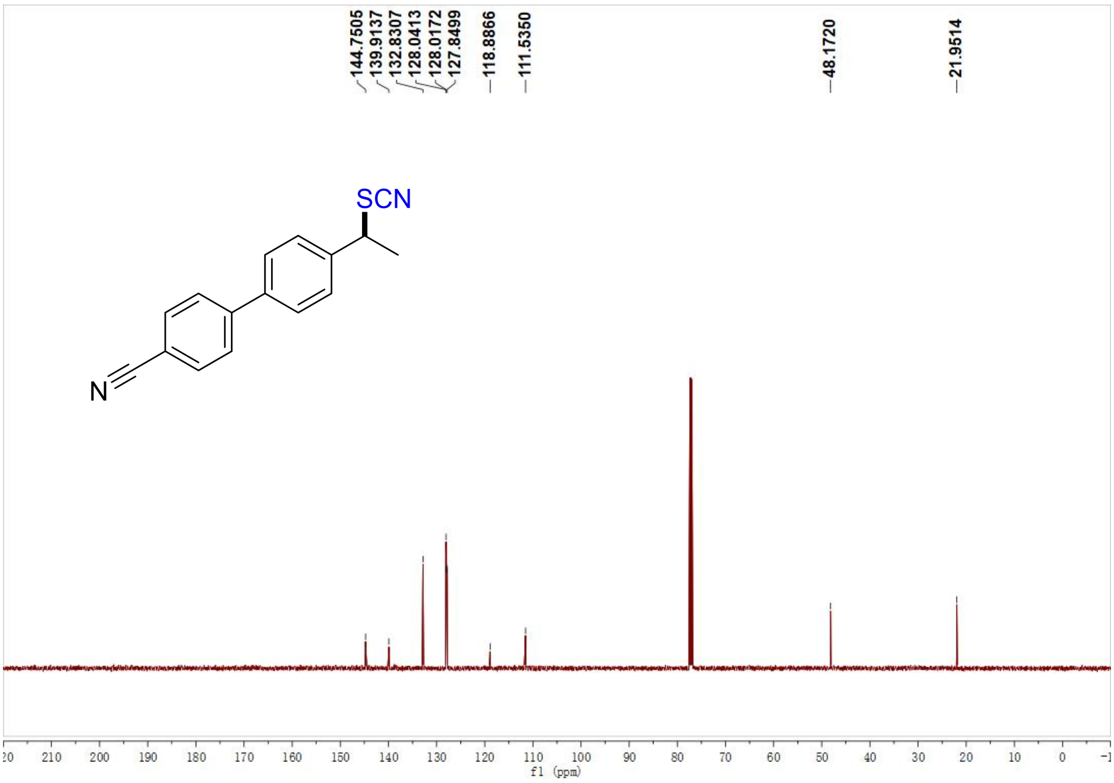

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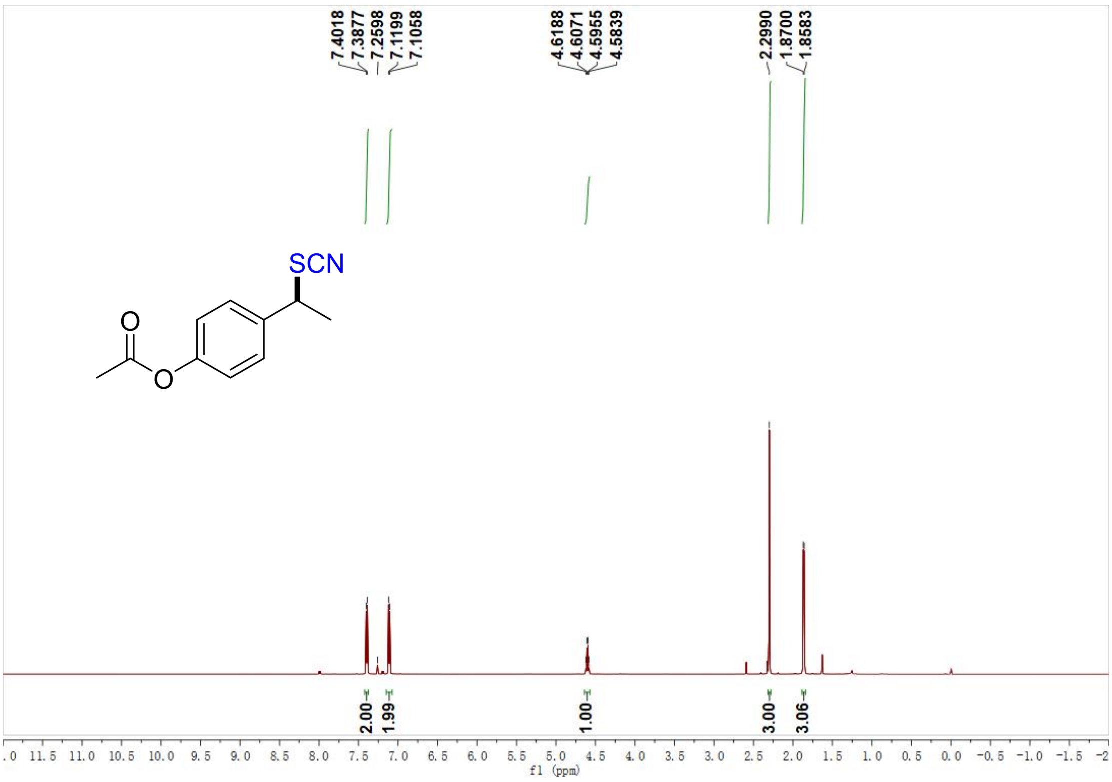

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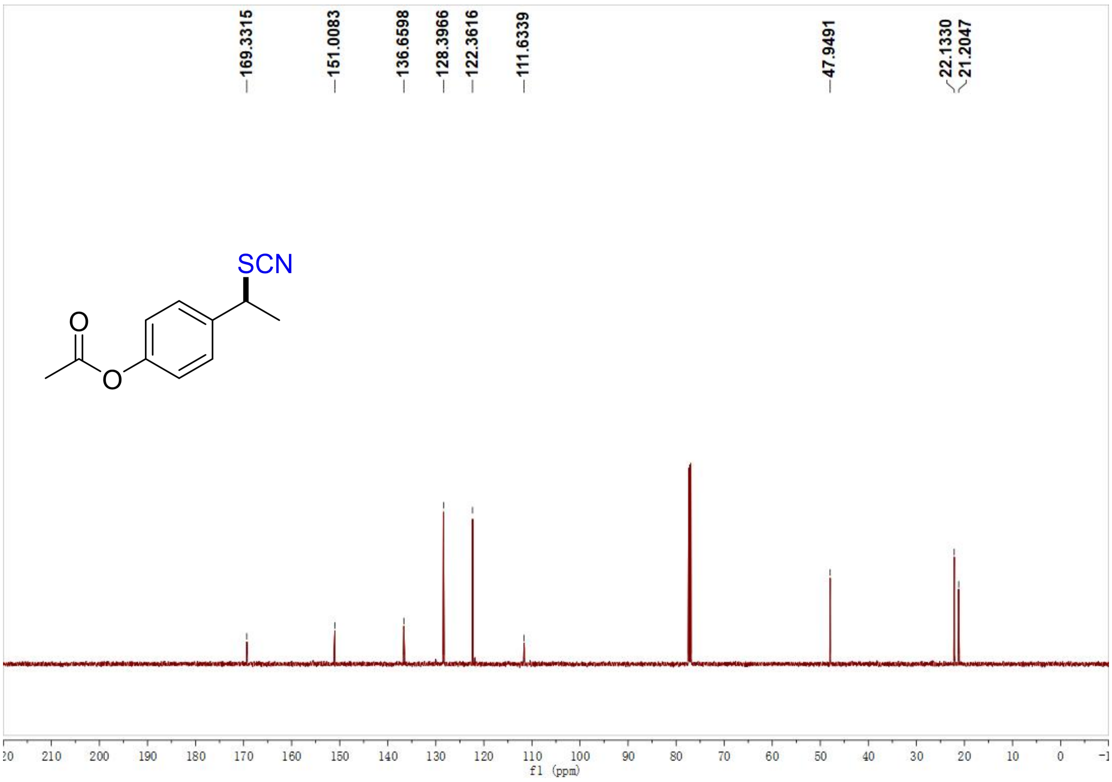

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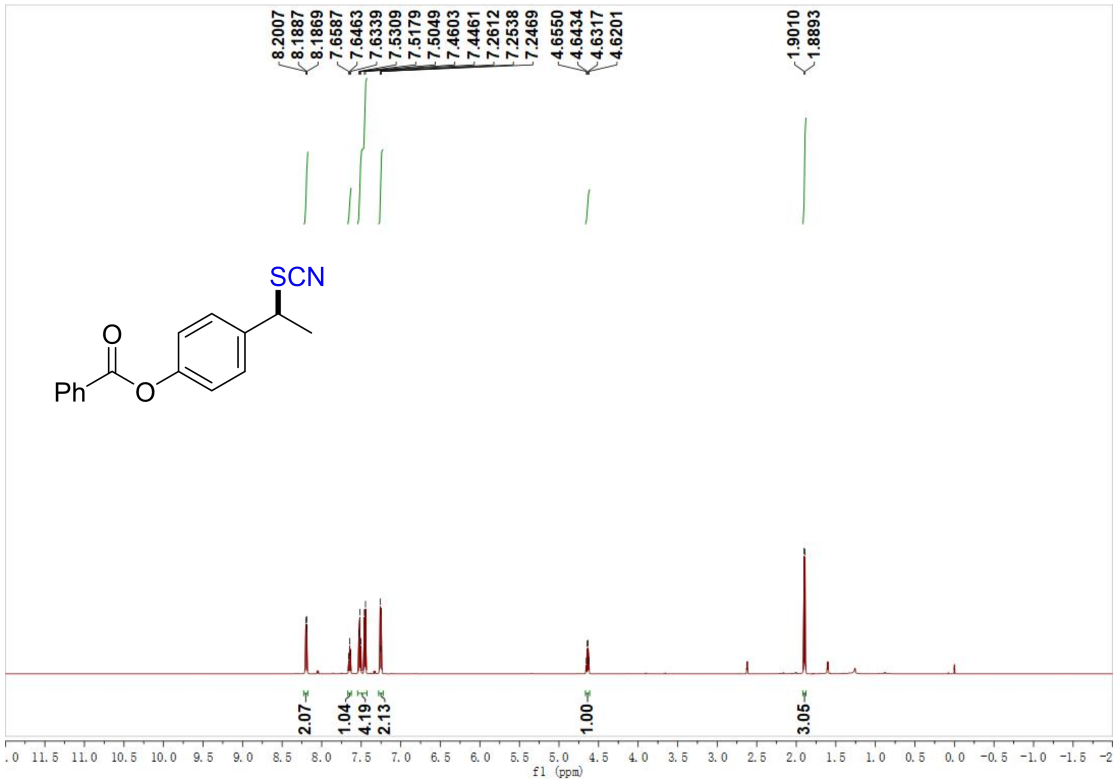

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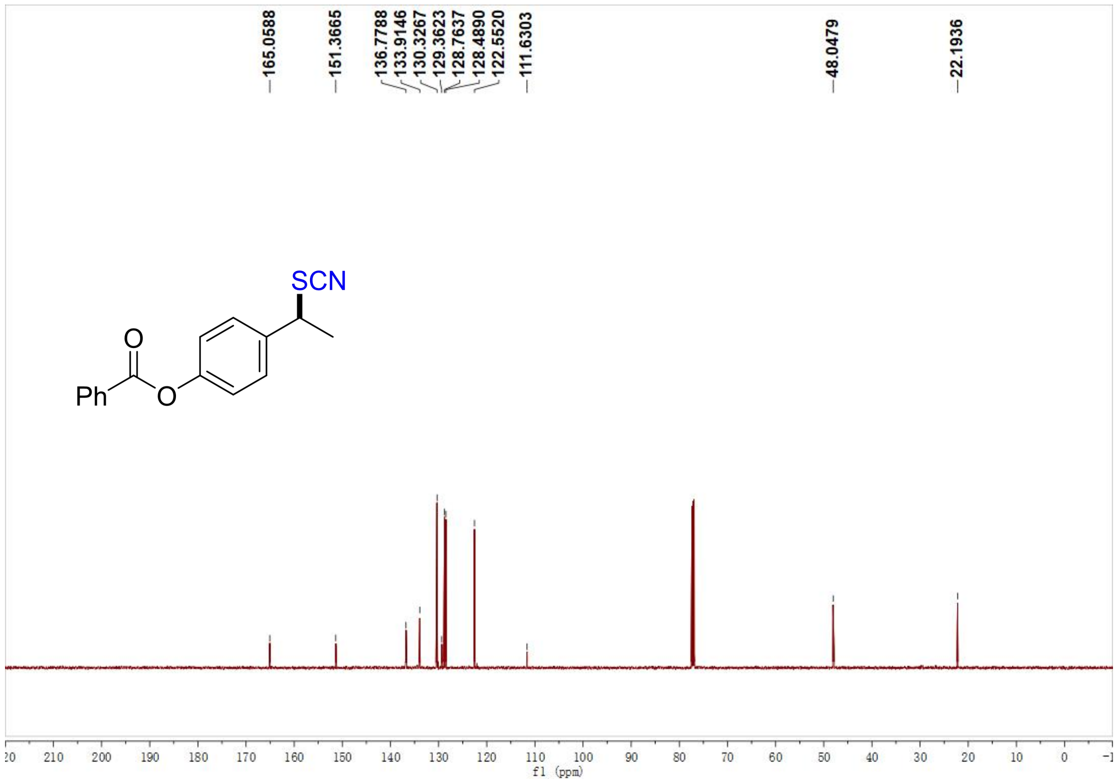

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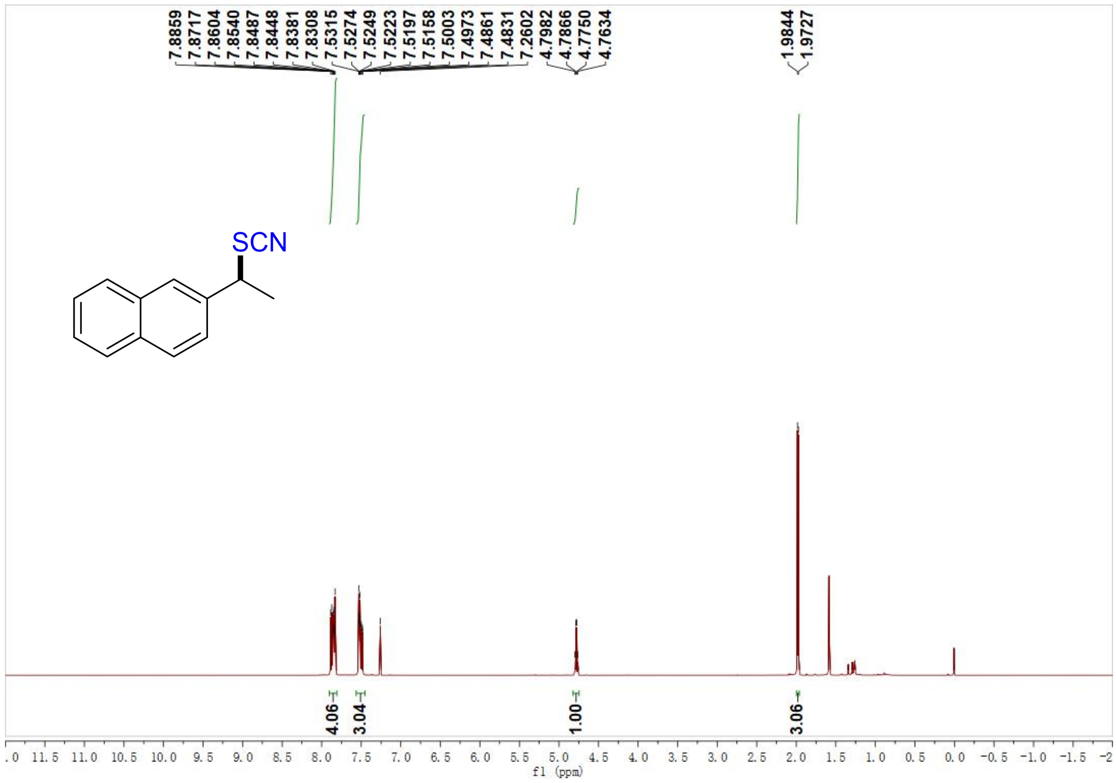

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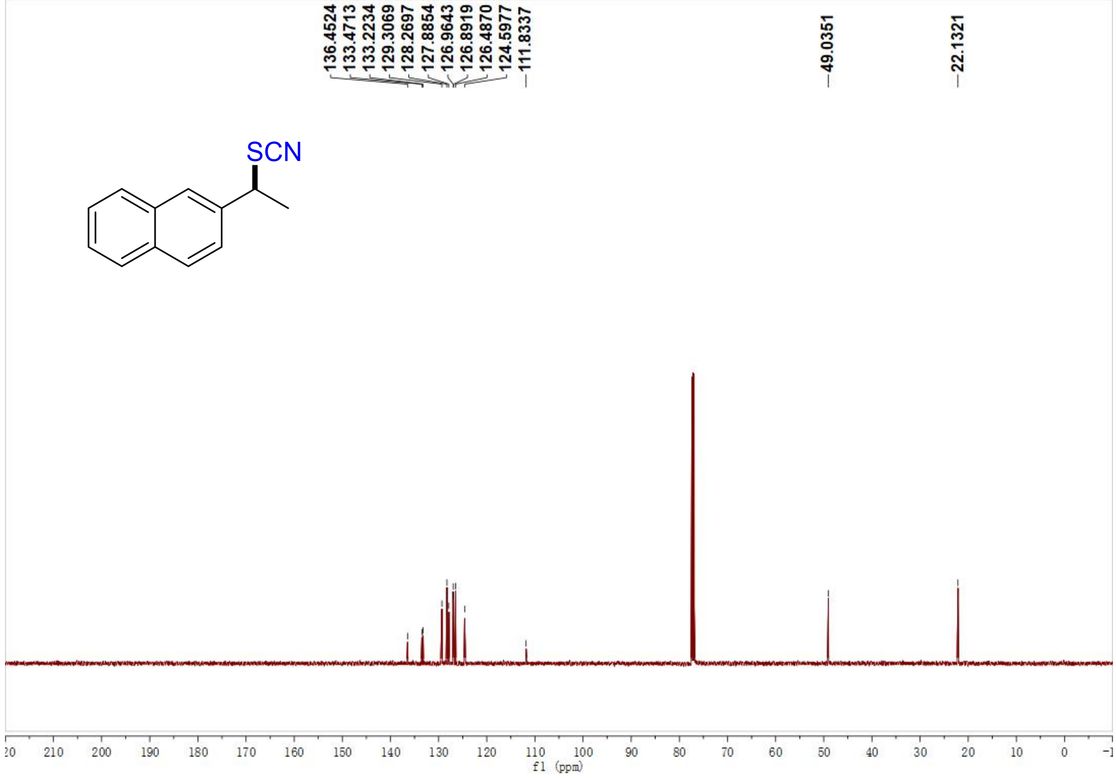

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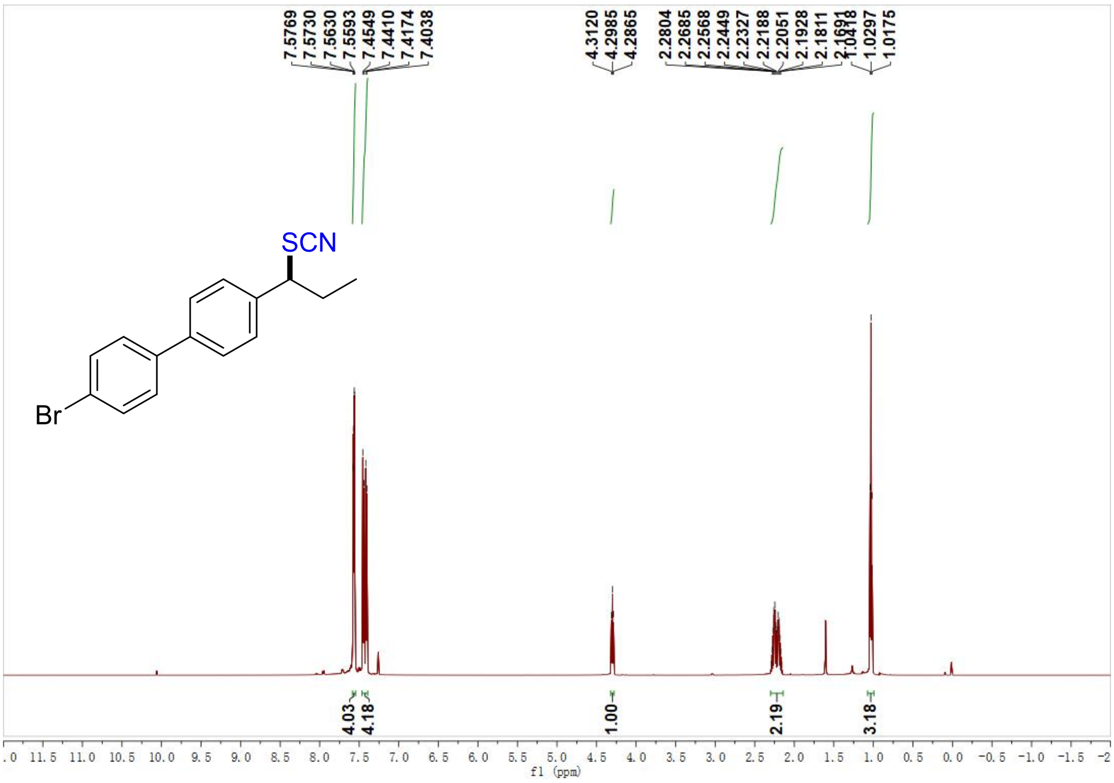

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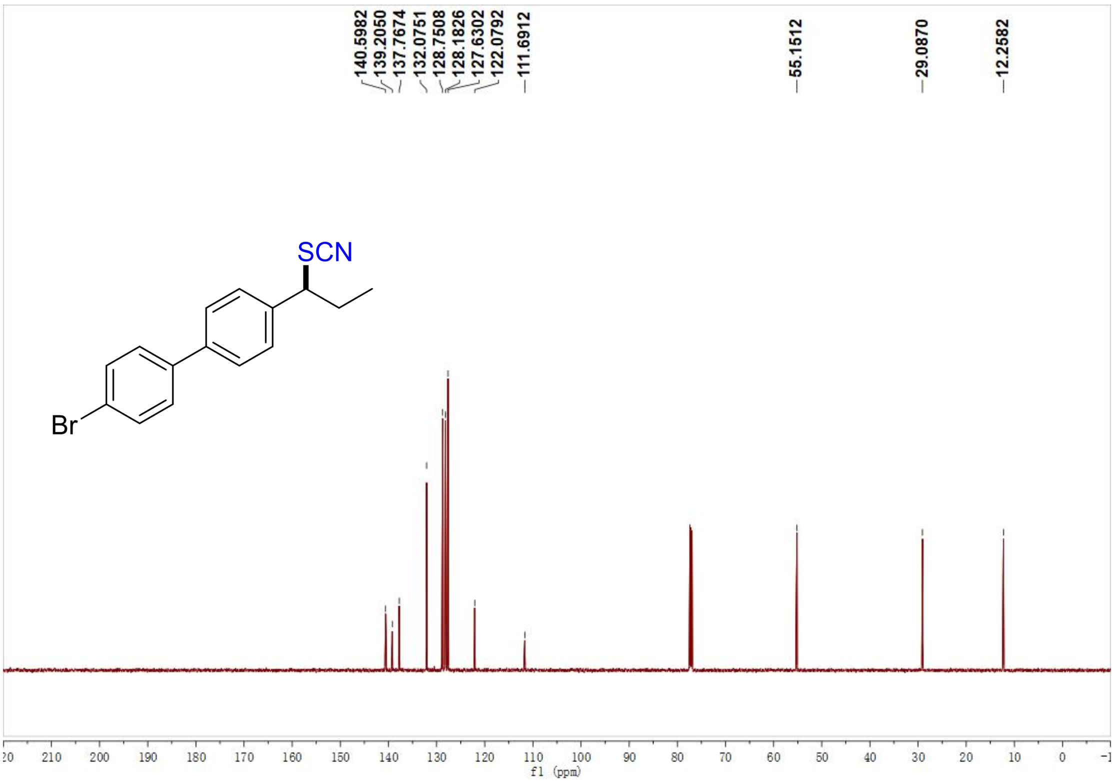

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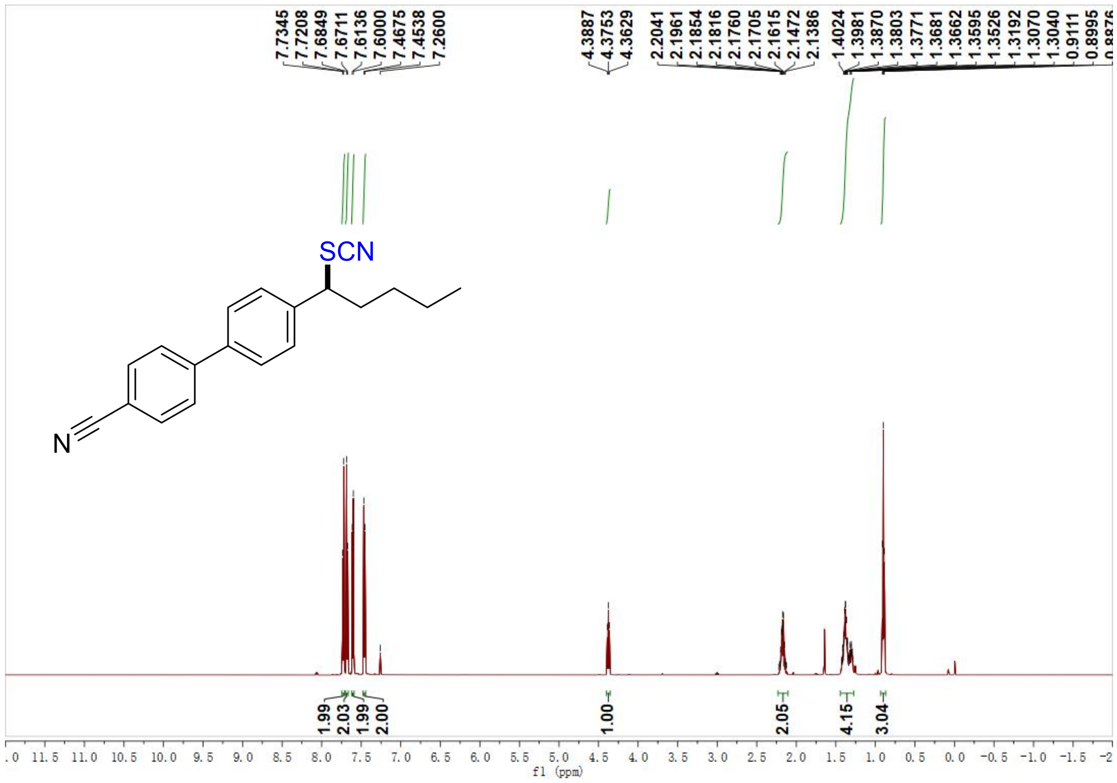

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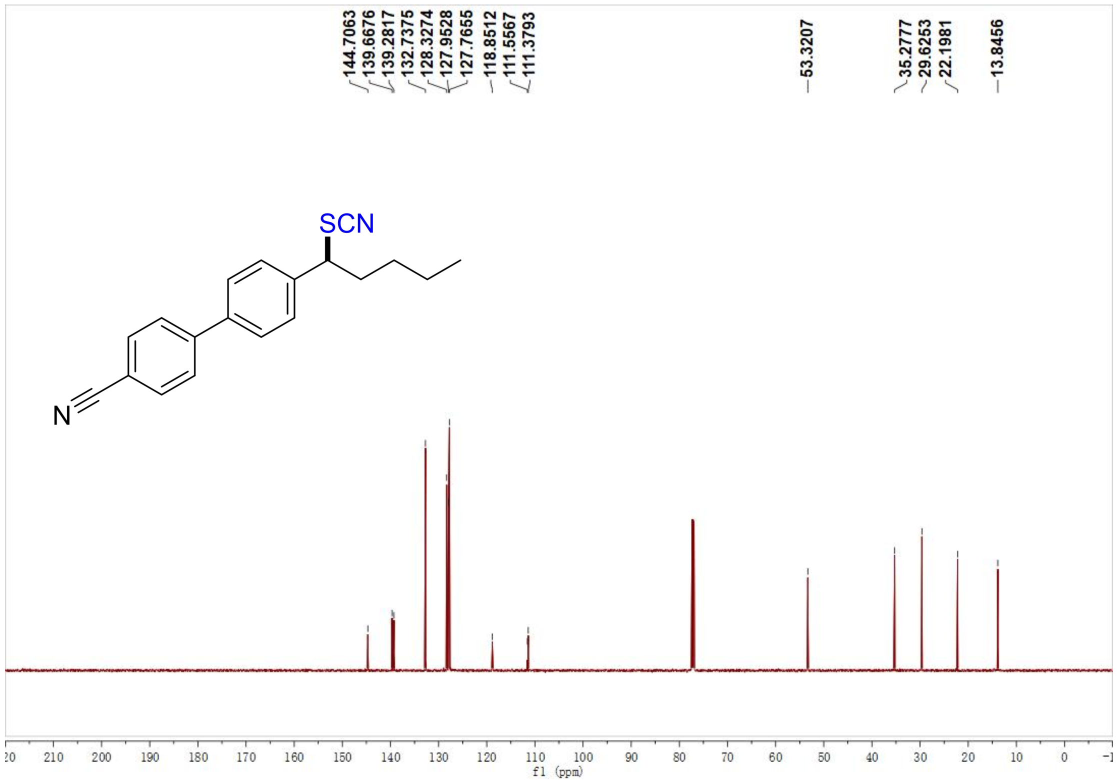

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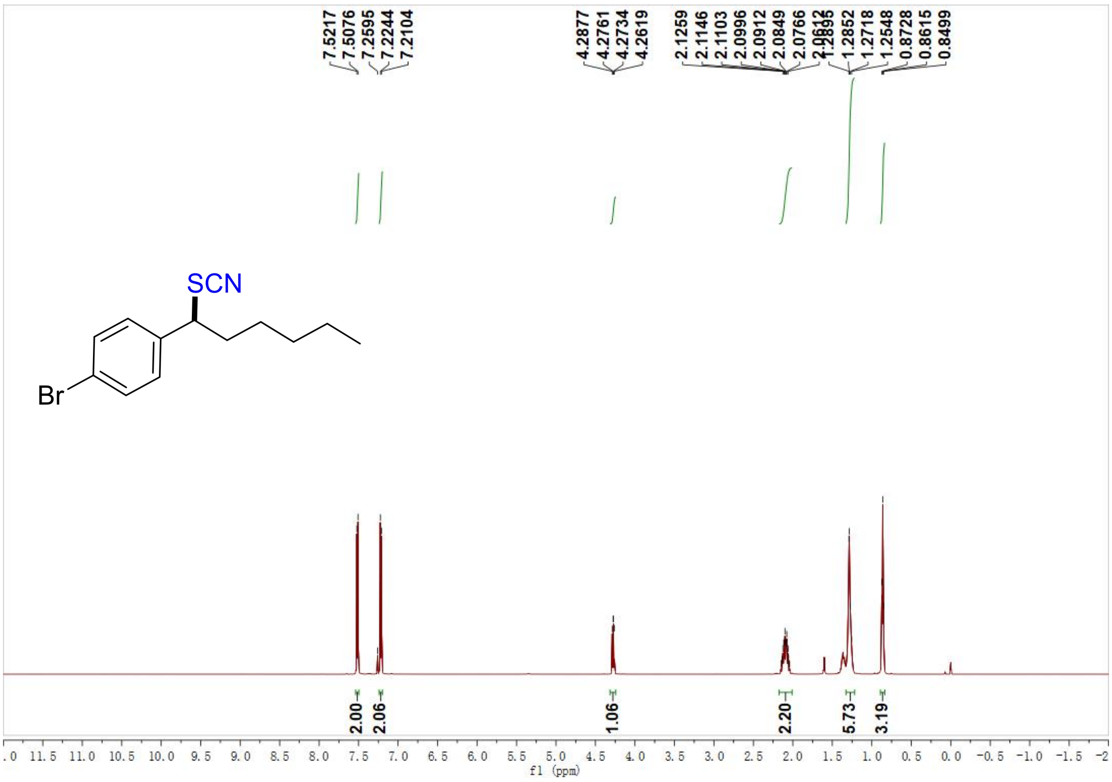

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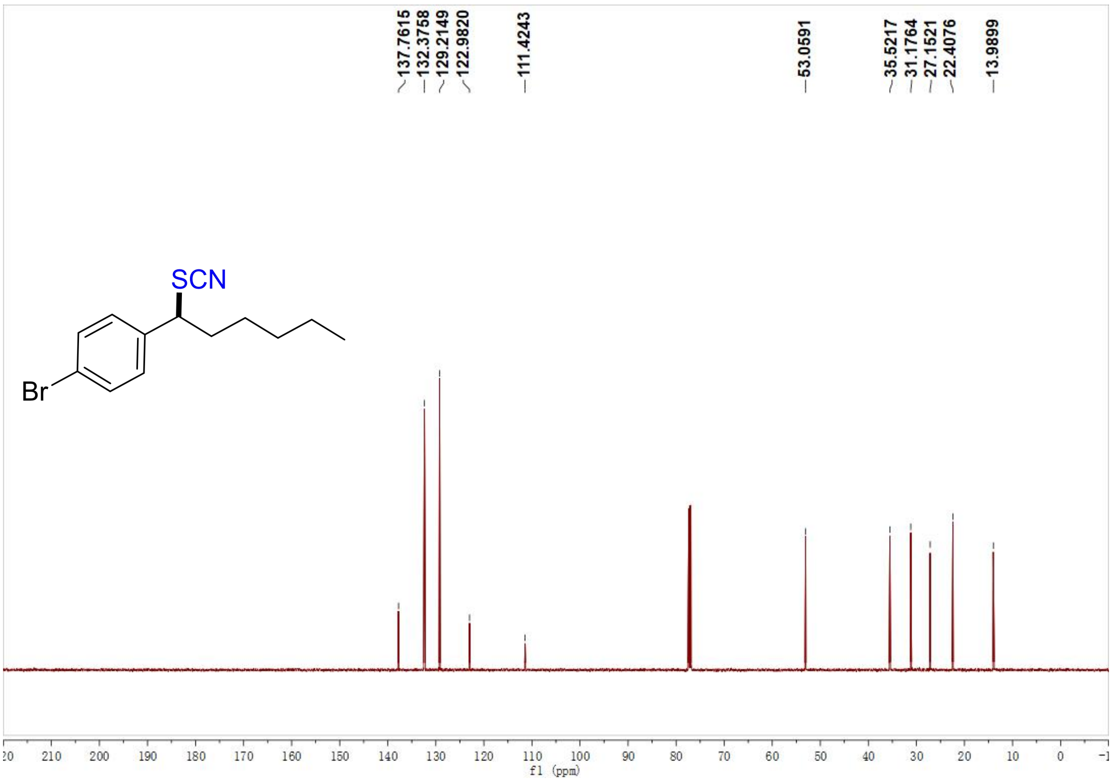

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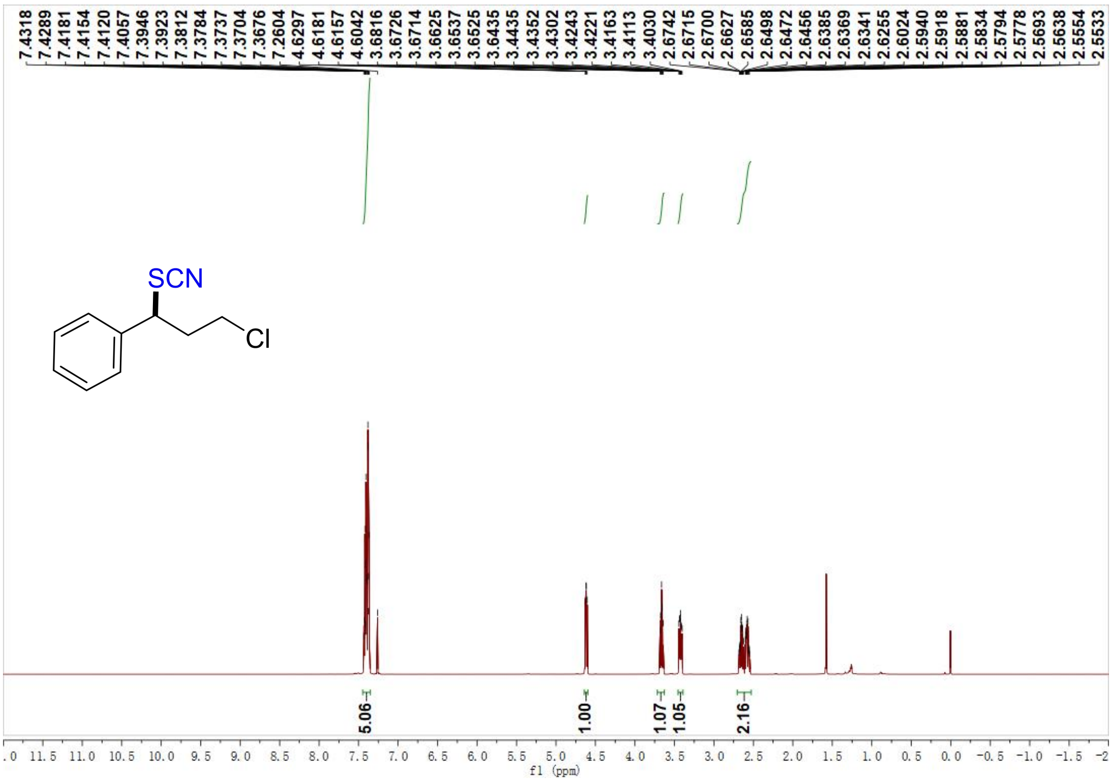

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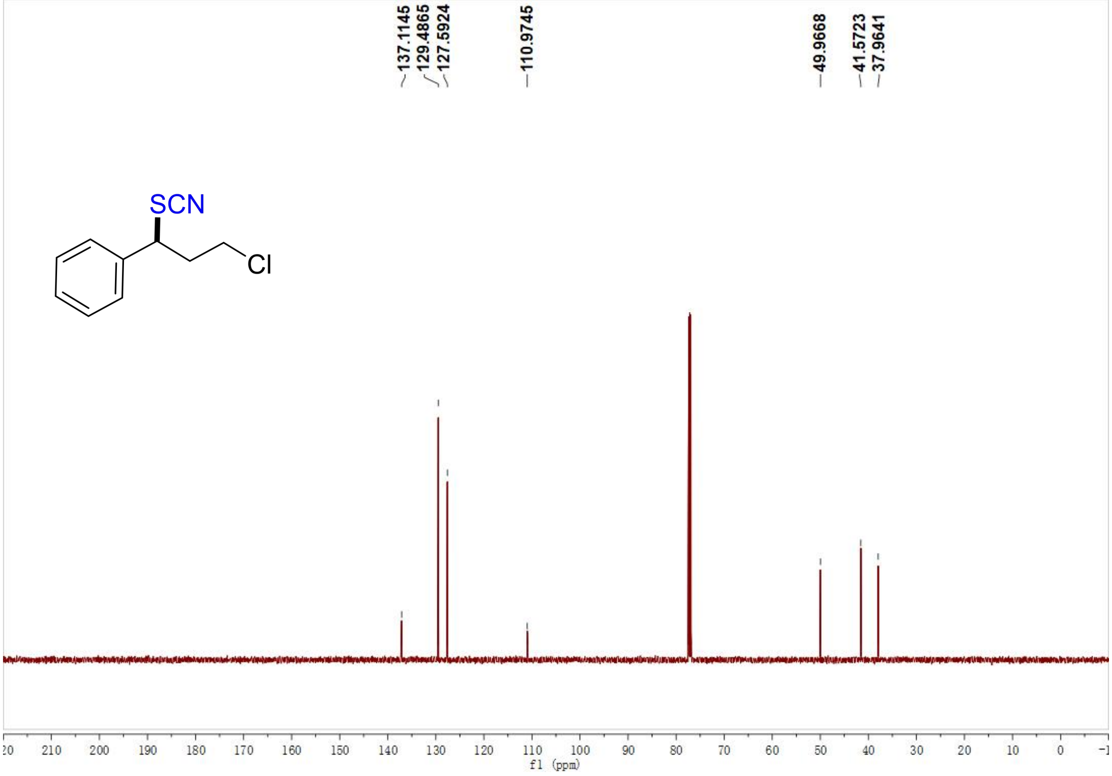

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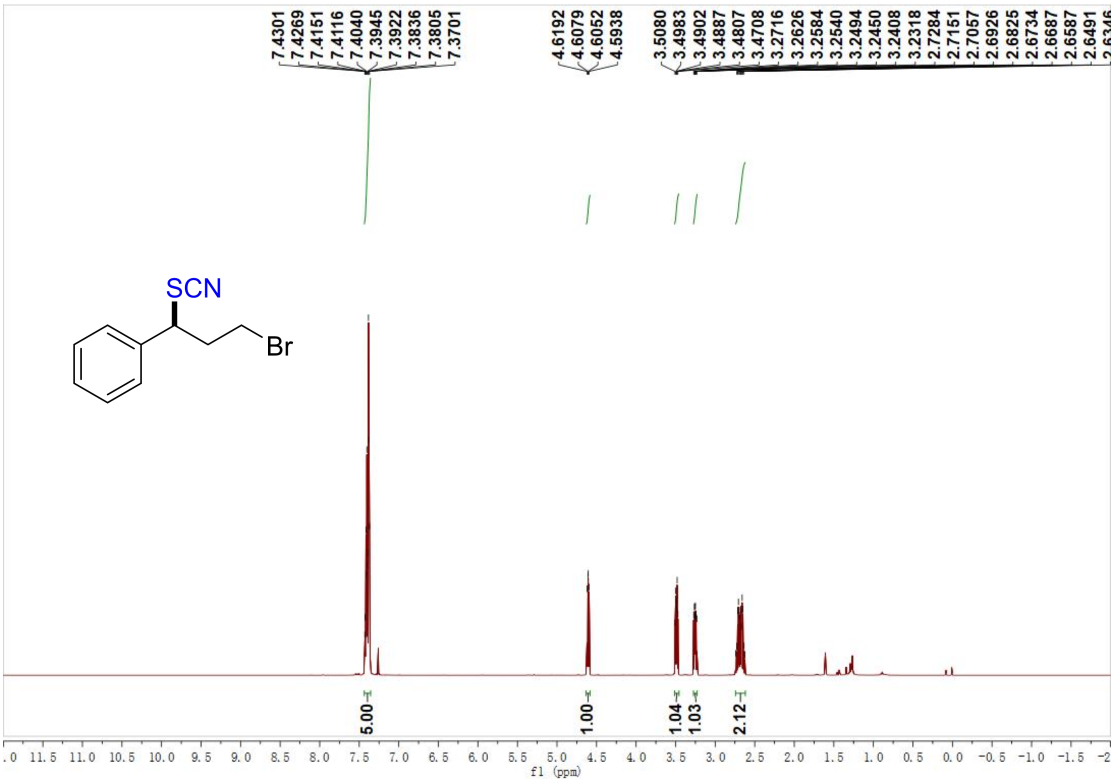

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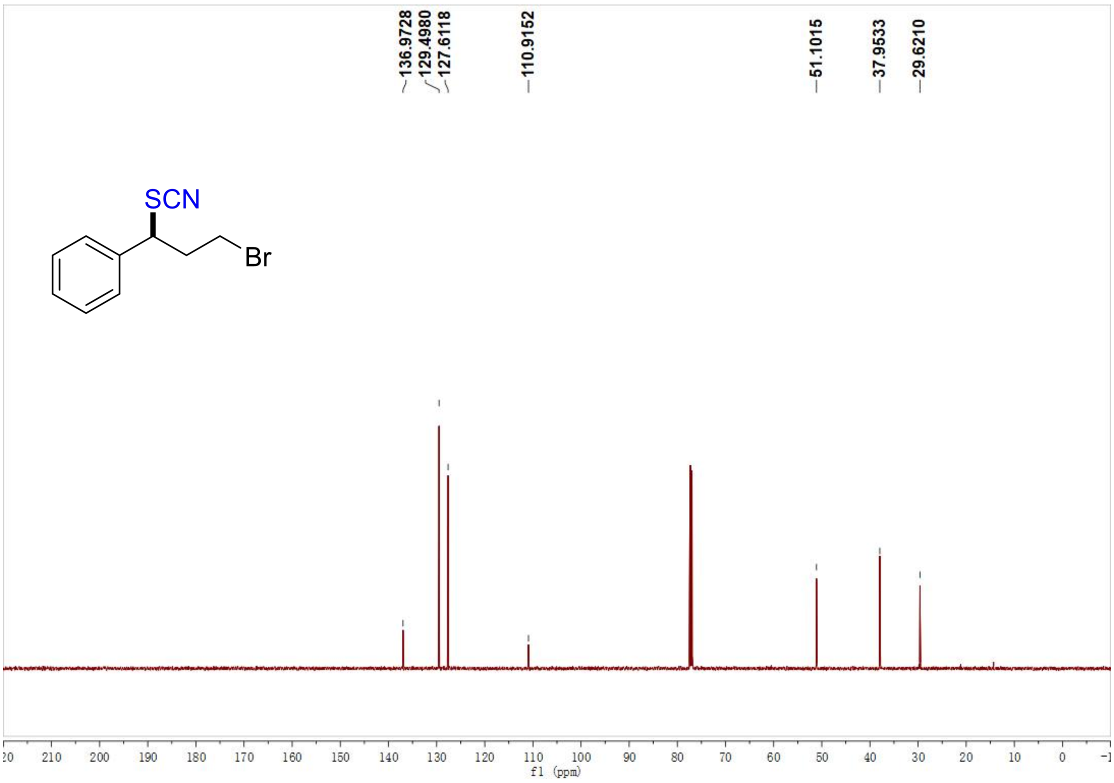

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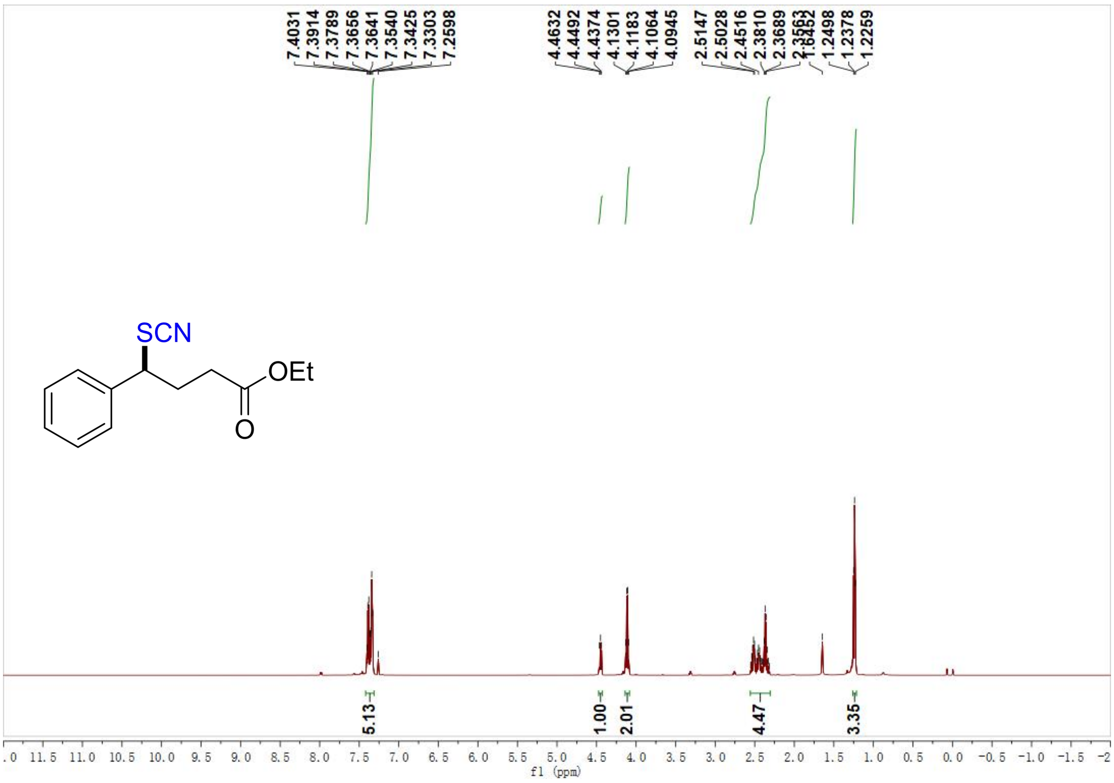

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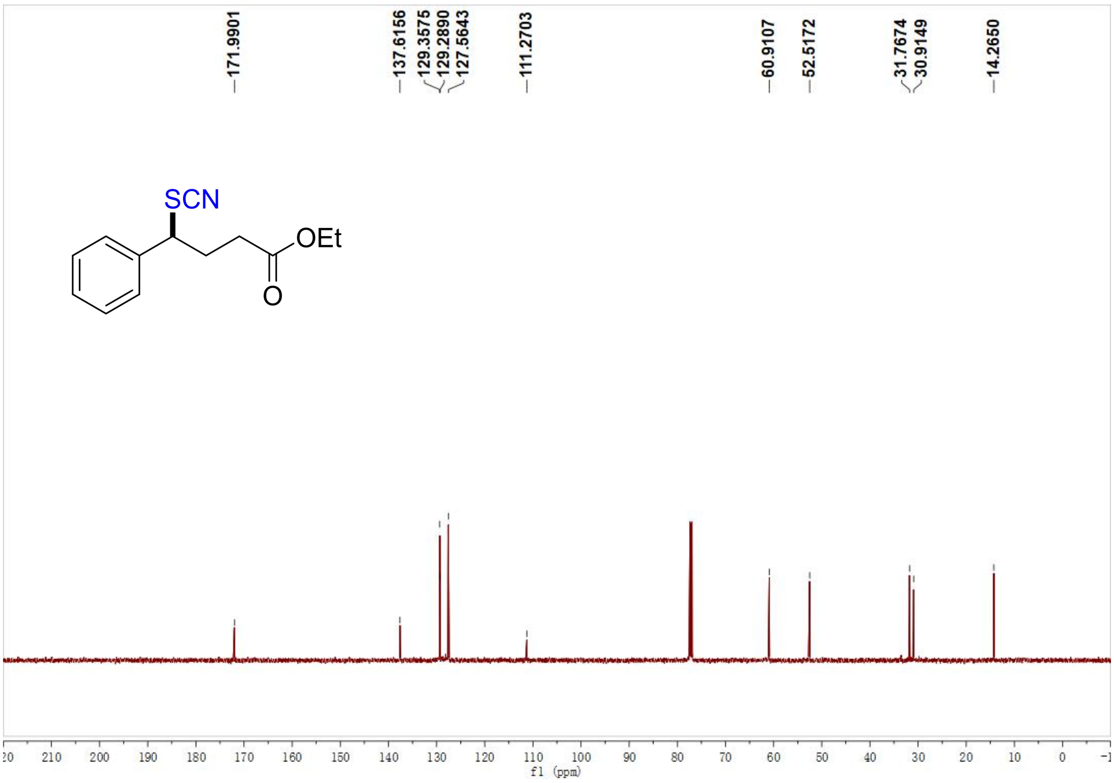
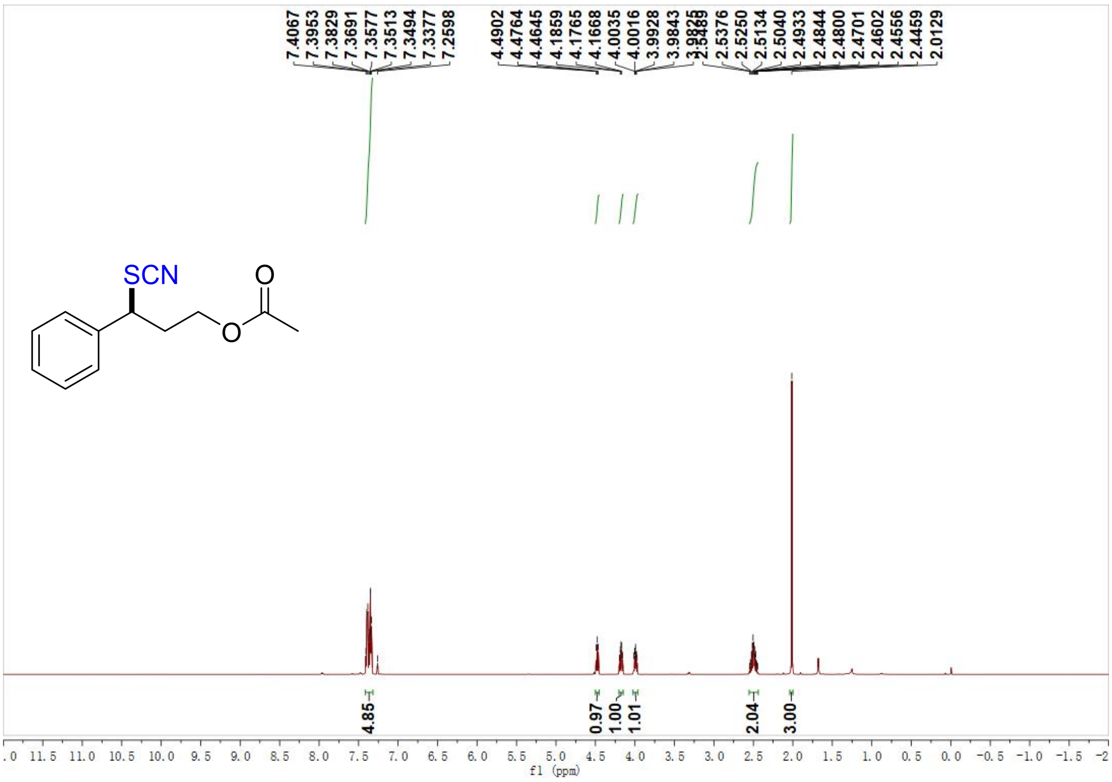
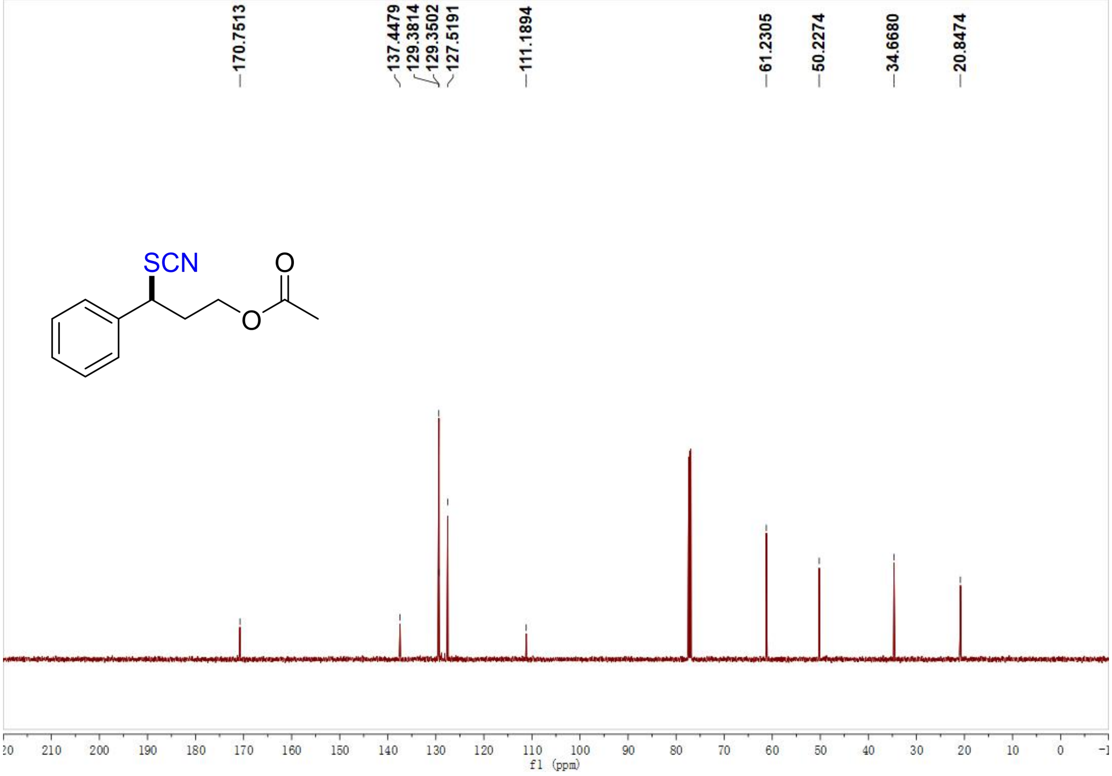


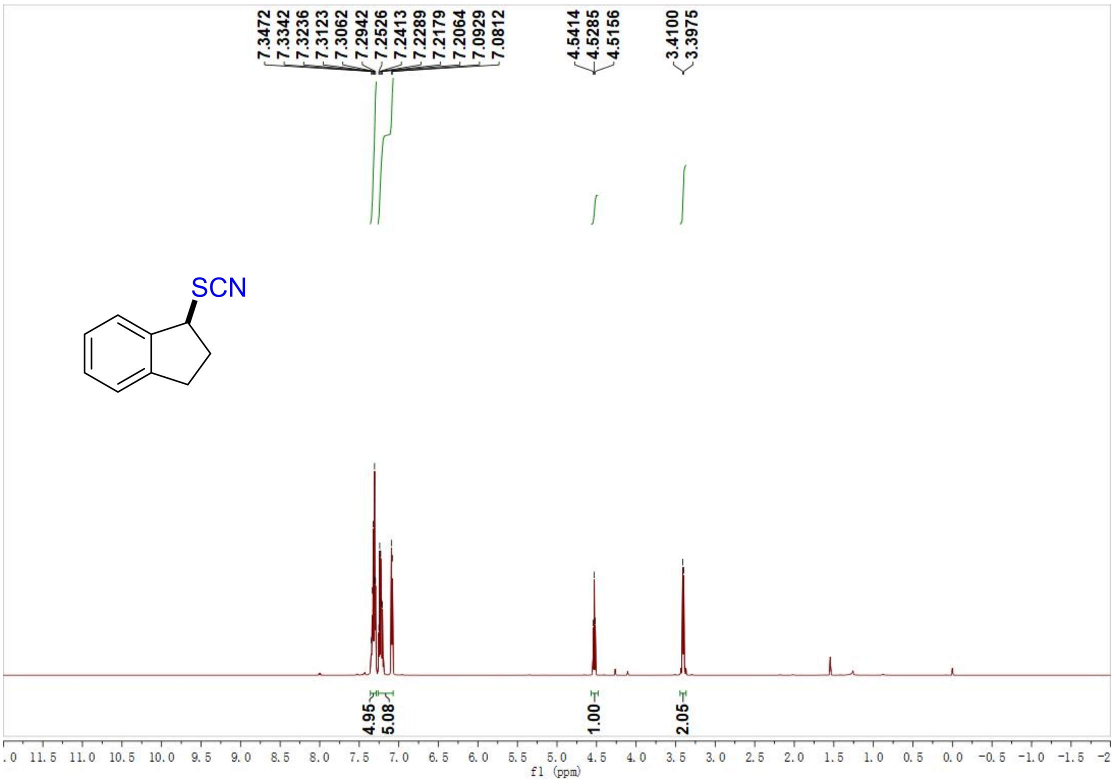
^{13}C NMR (150 MHz, CDCl$_3$) of **2u**



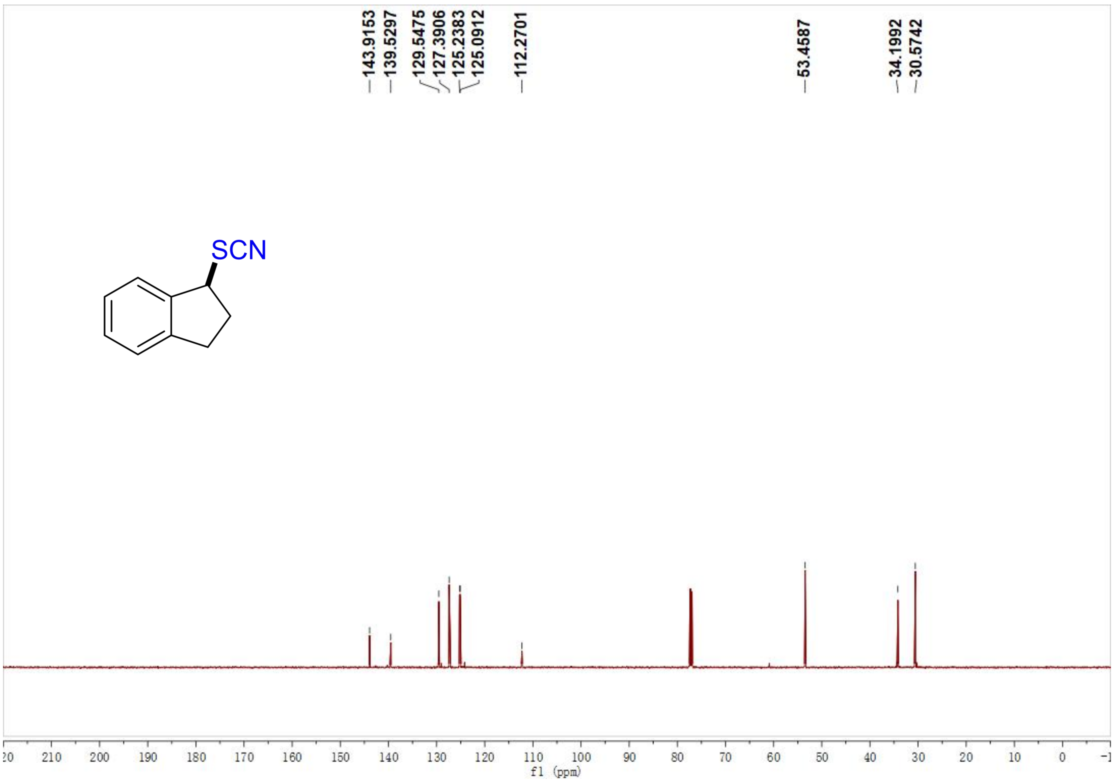
^{1}H NMR (600 MHz, CDCl$_3$) of **2v**



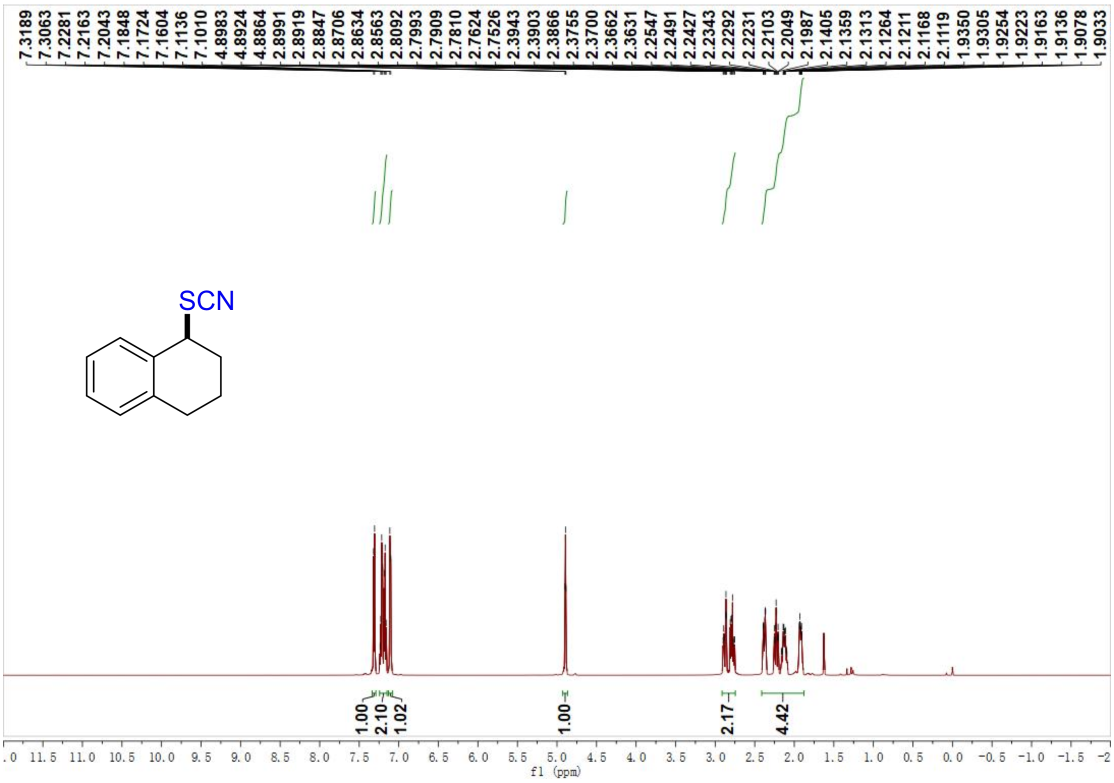
^{13}C NMR (150 MHz, CDCl$_3$) of **2v**



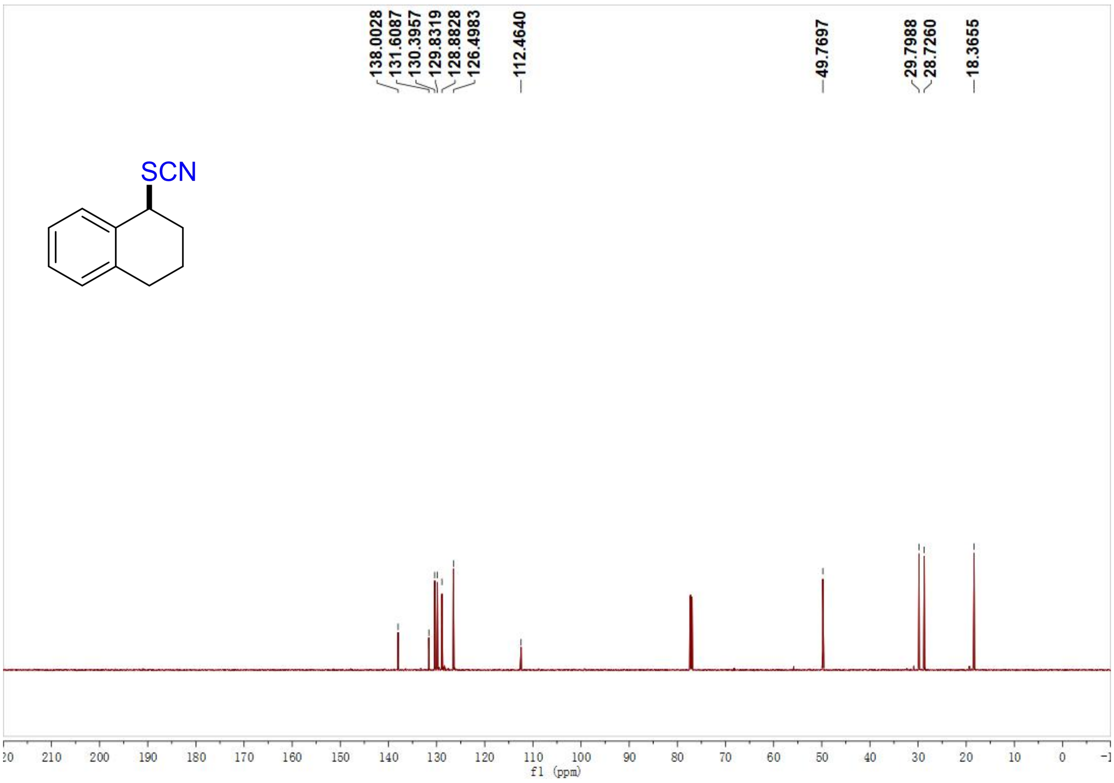
^{1}H NMR (600 MHz, $CDCl_3$) of **2w**



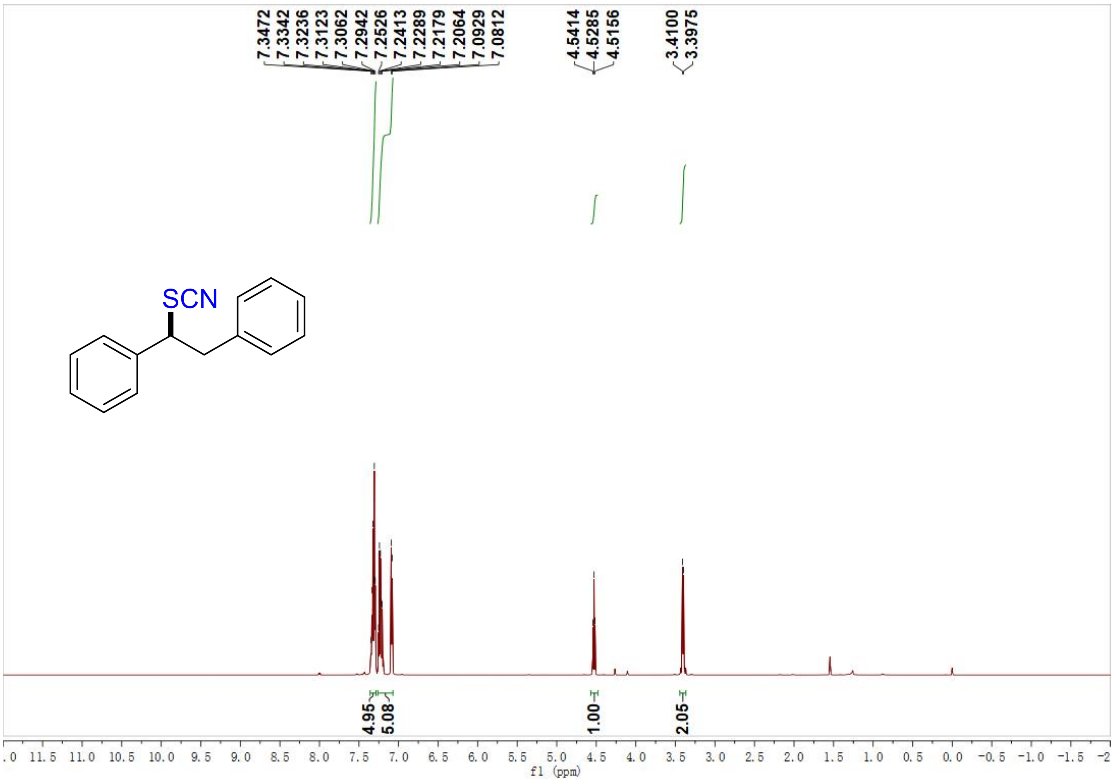
^{13}C NMR (150 MHz, $CDCl_3$) of **2w**



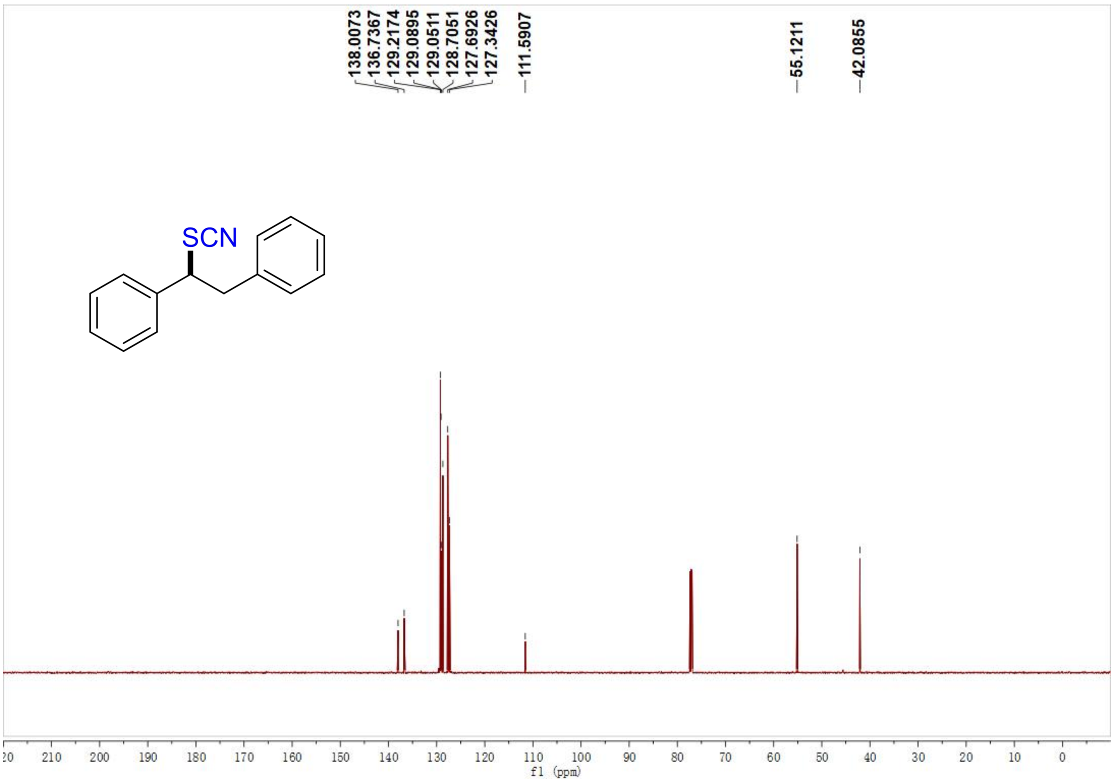
^{1}H NMR (600 MHz, CDCl$_3$) of **2x**



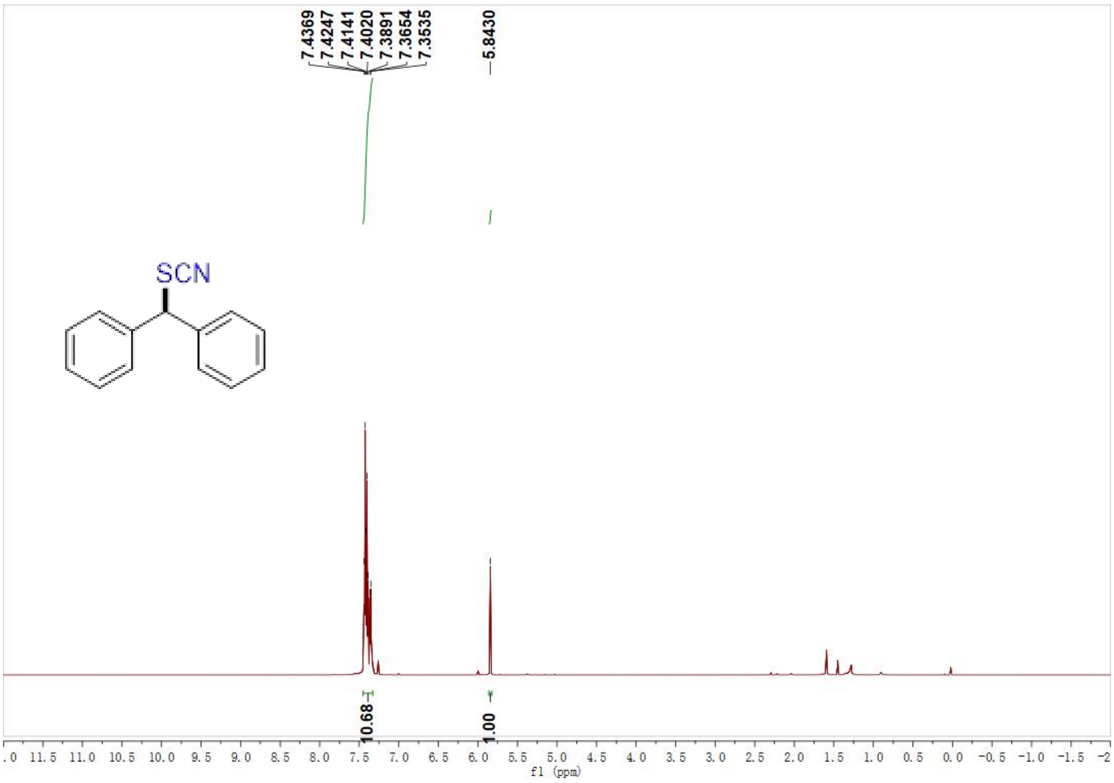
^{13}C NMR (150 MHz, CDCl$_3$) of **2x**



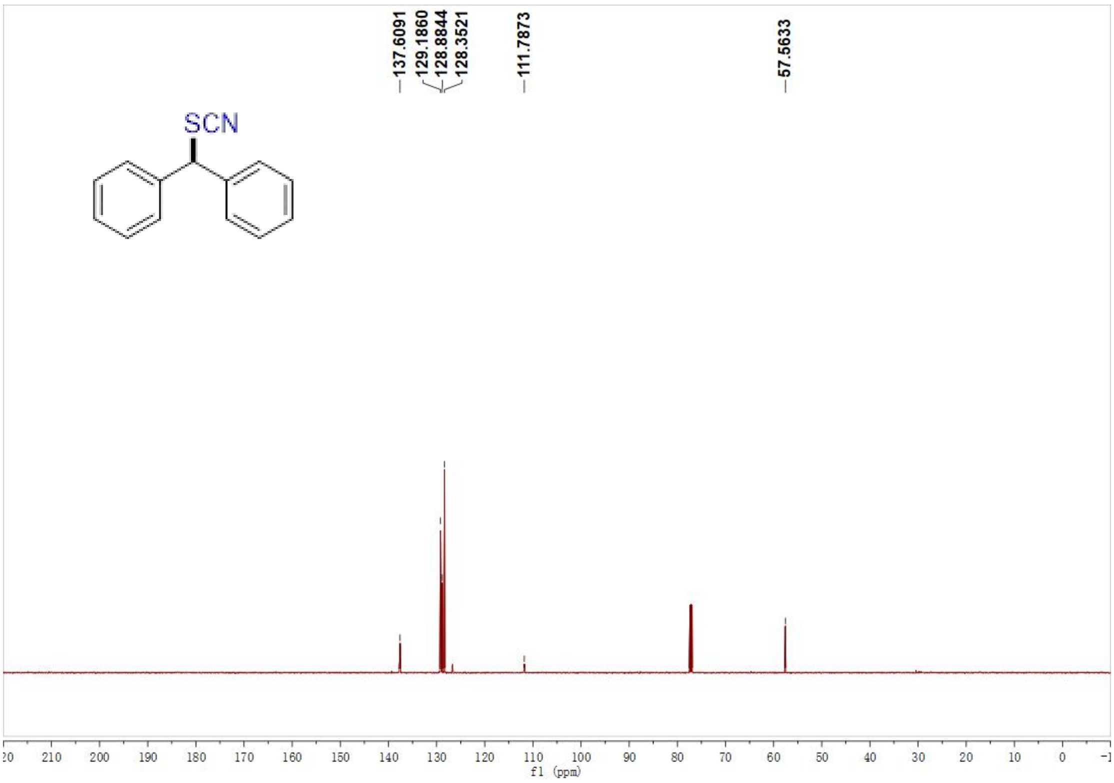
^{1}H NMR (600 MHz, CDCl$_3$) of **2y**



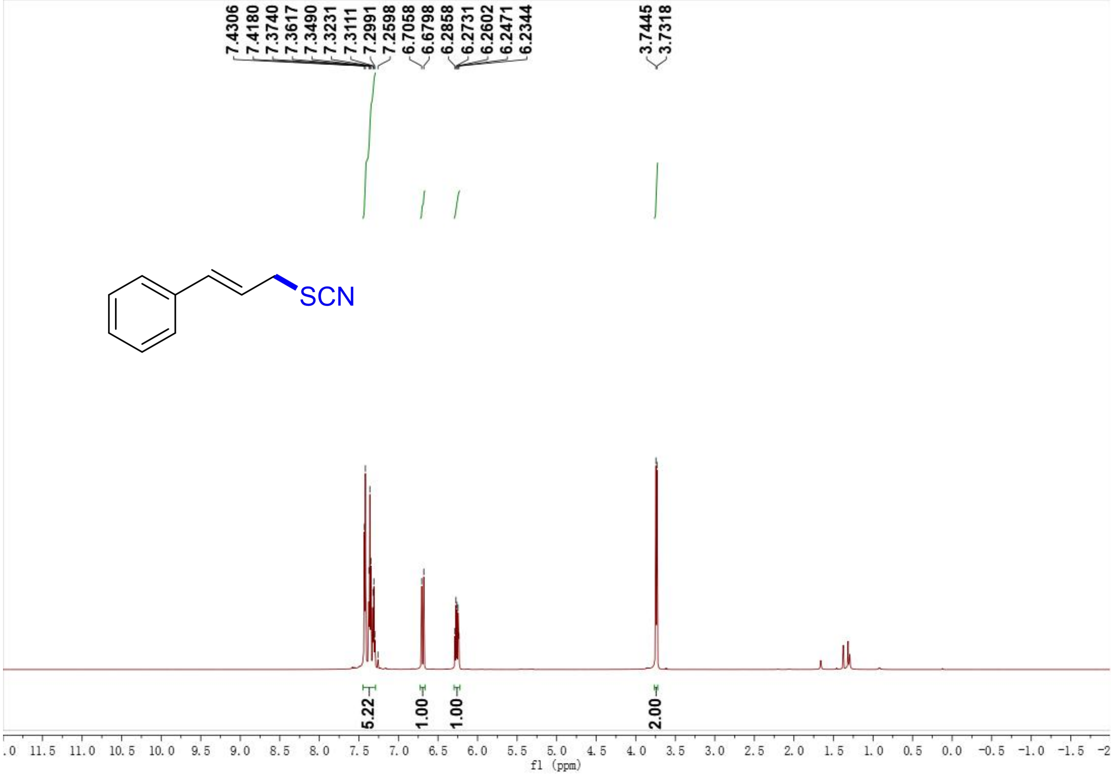
^{13}C NMR (150 MHz, CDCl$_3$) of **2y**



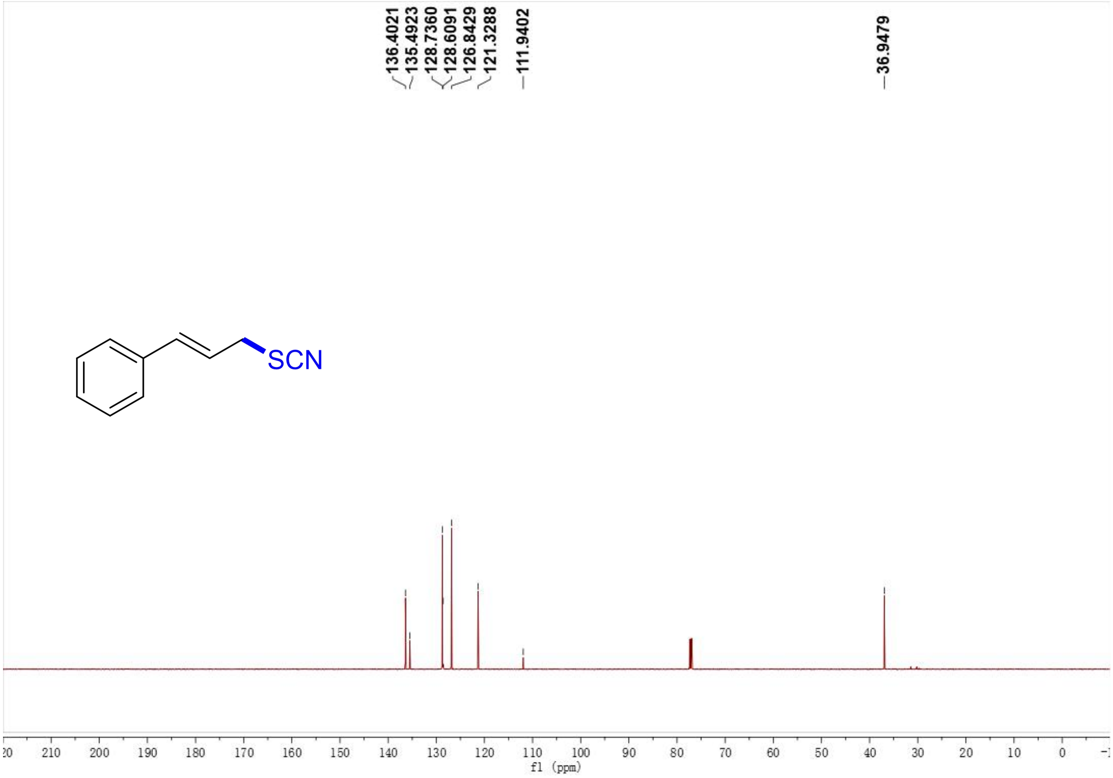
^{1}H NMR (600 MHz, CDCl$_3$) of **2z**



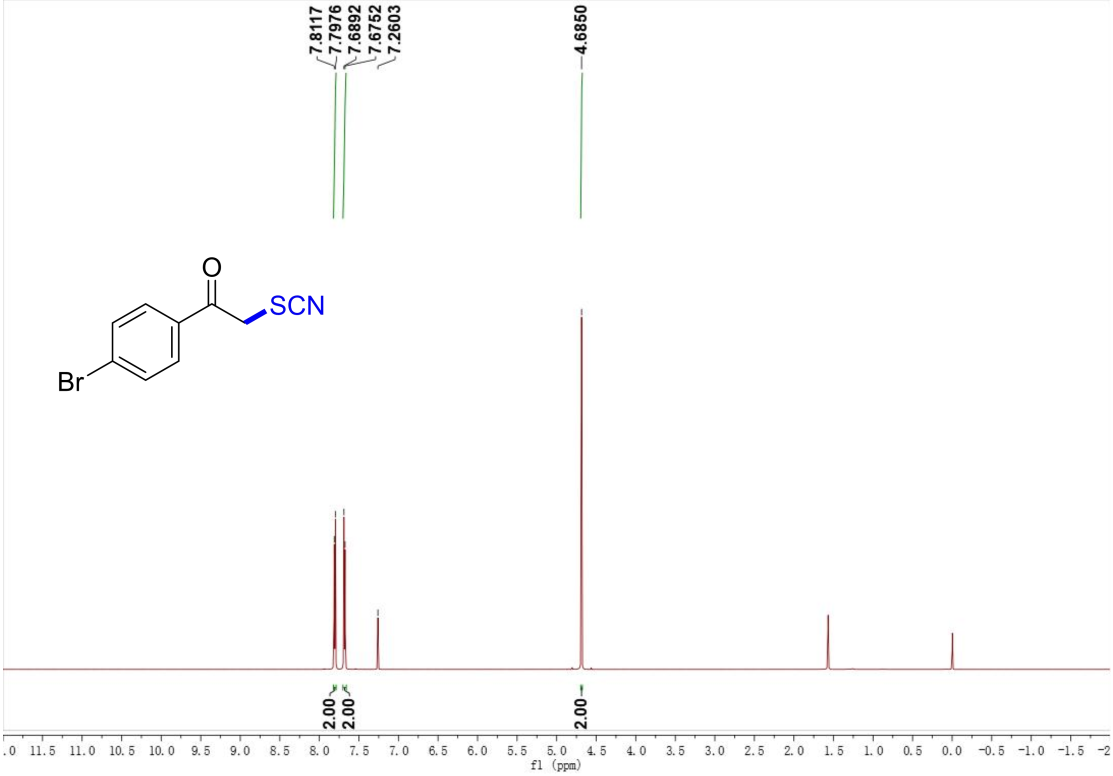
^{13}C NMR (150 MHz, CDCl$_3$) of **2z**



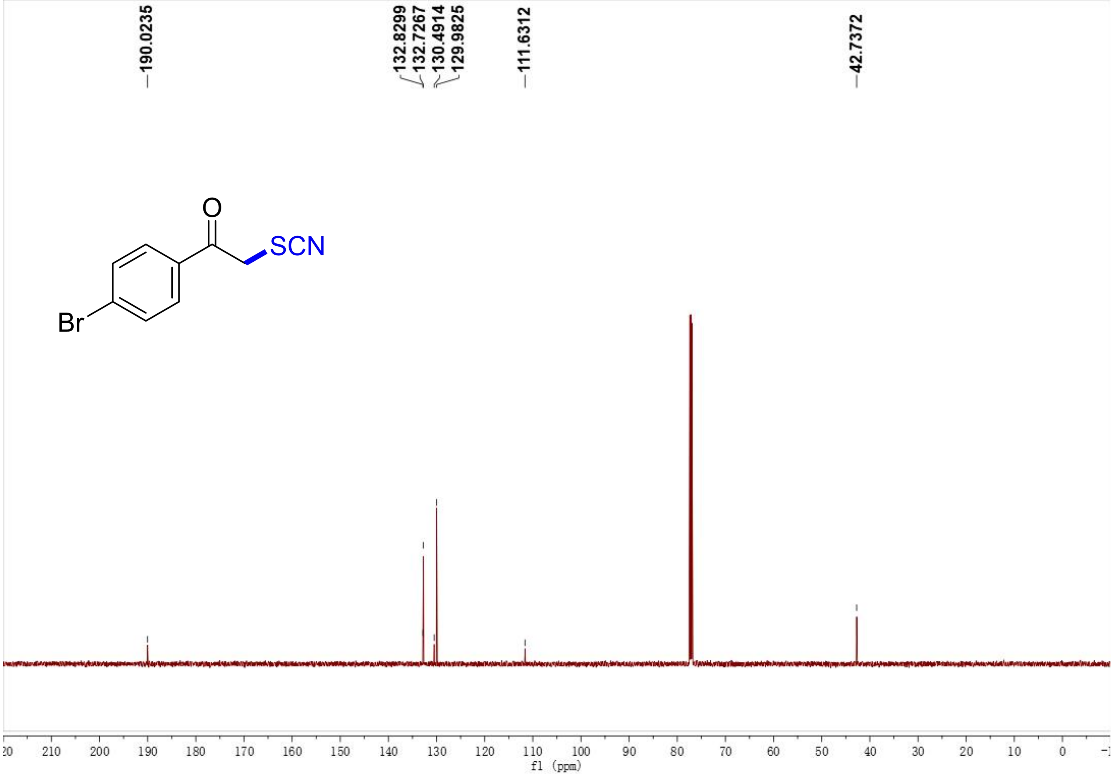
^{1}H NMR (600 MHz, CDCl$_3$) of **2aa**



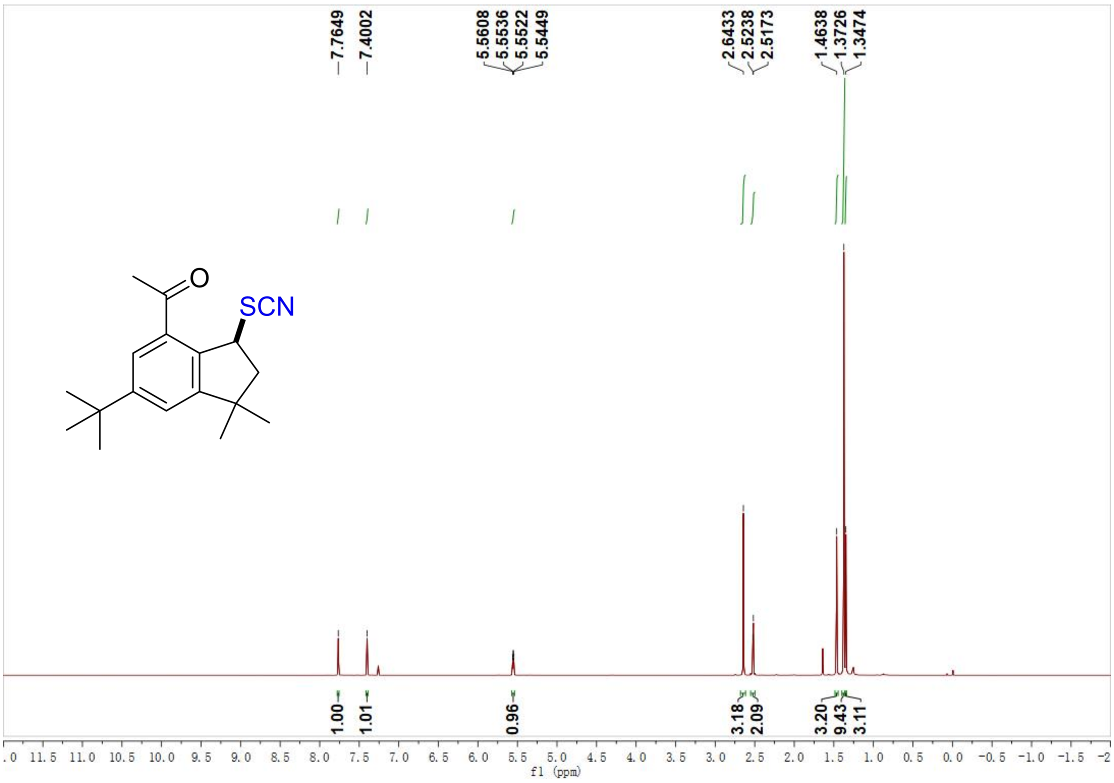
^{13}C NMR (150 MHz, CDCl$_3$) of **2aa**



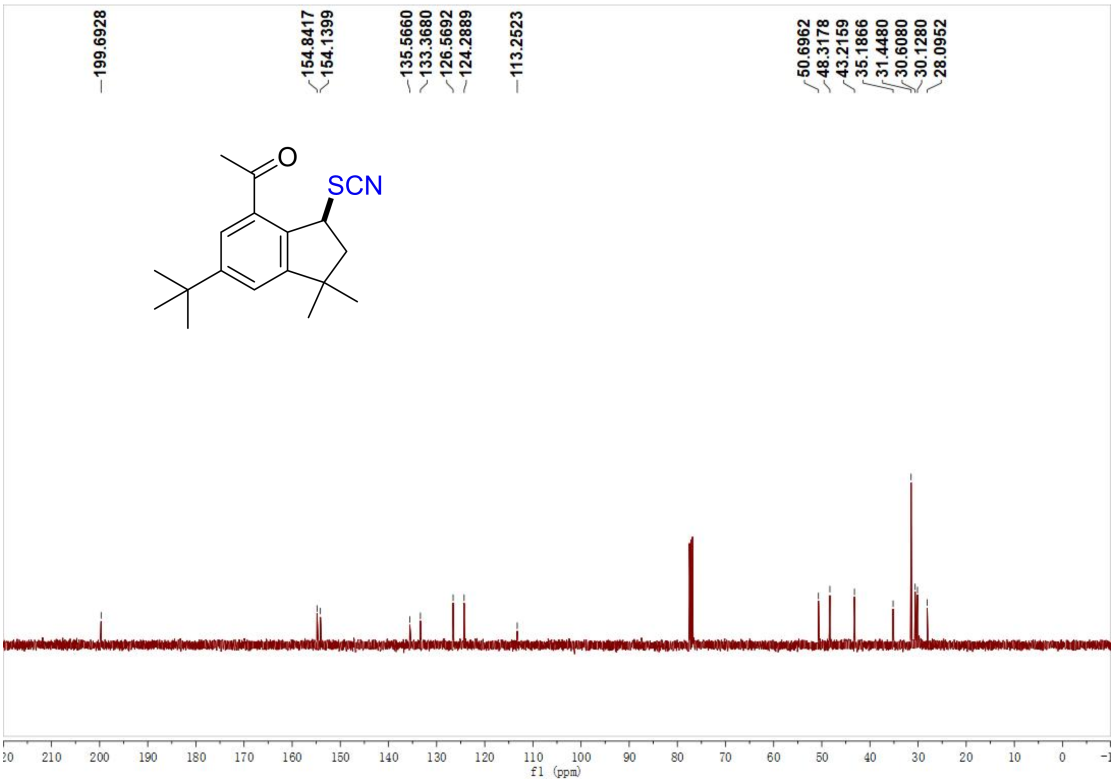
^{1}H NMR (600 MHz, $CDCl_3$) of **2ab**



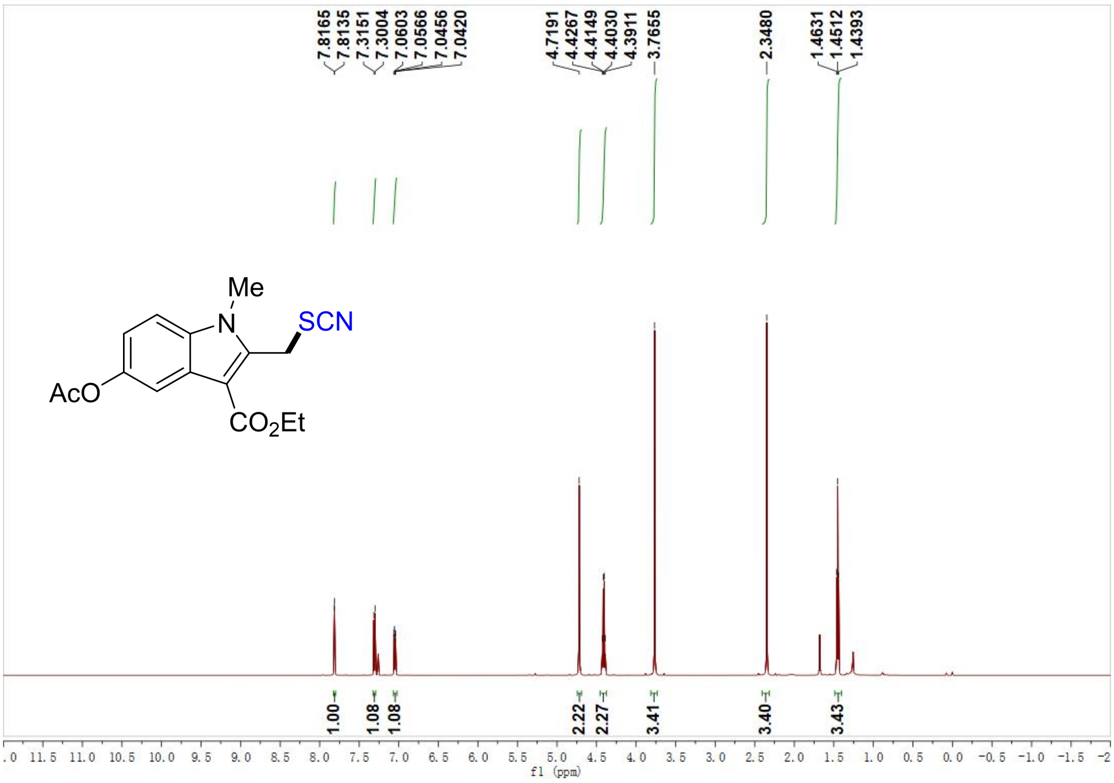
^{13}C NMR (150 MHz, $CDCl_3$) of **2ab**



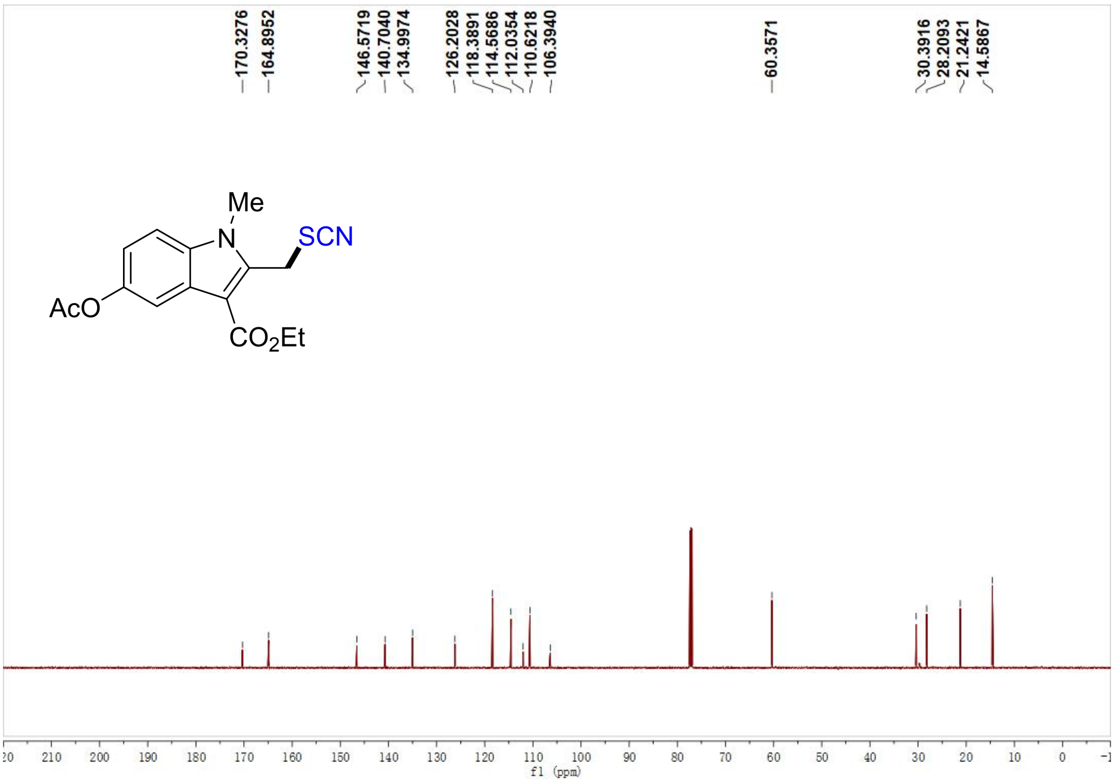
^{1}H NMR (600 MHz, CDCl$_3$) of **2ac**



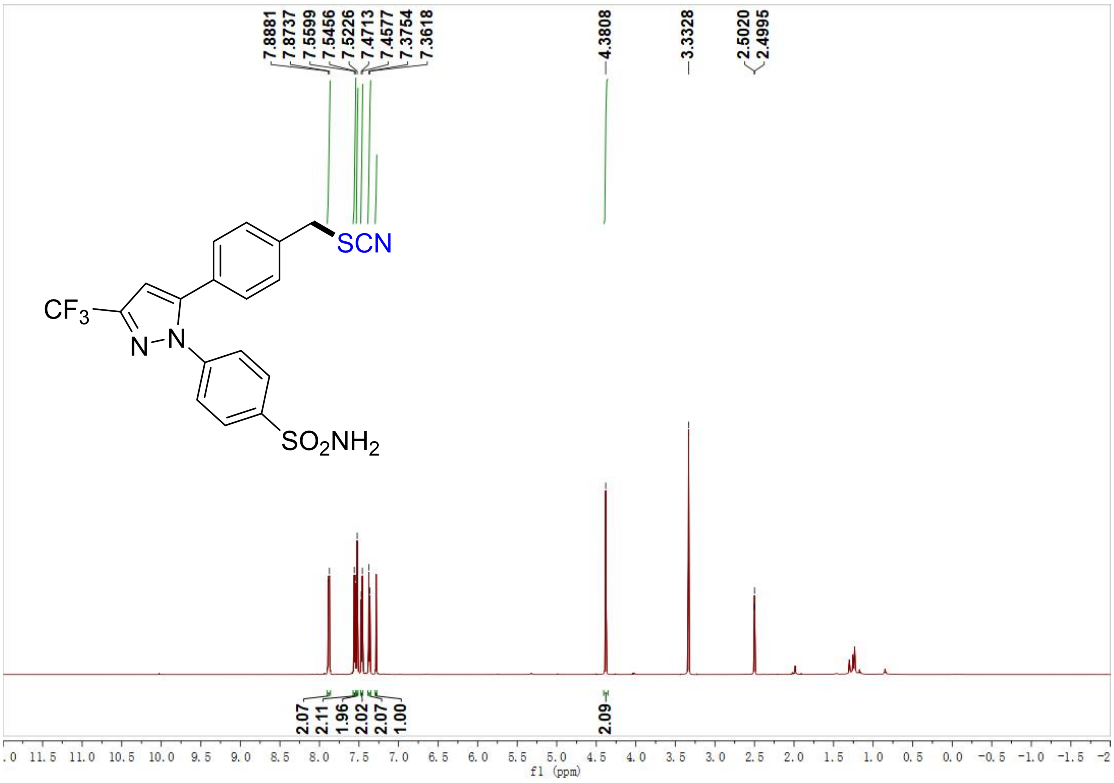
^{13}C NMR (150 MHz, CDCl$_3$) of **2ac**



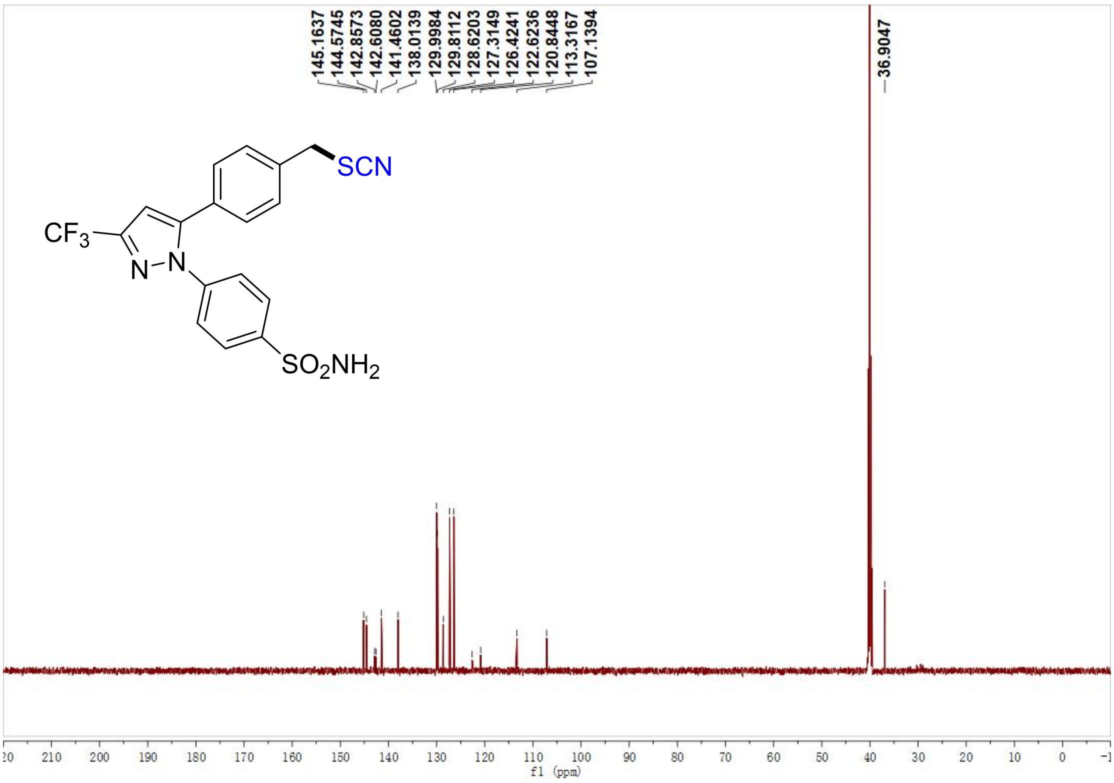
^{1}H NMR (600 MHz, CDCl$_3$) of **2ad**



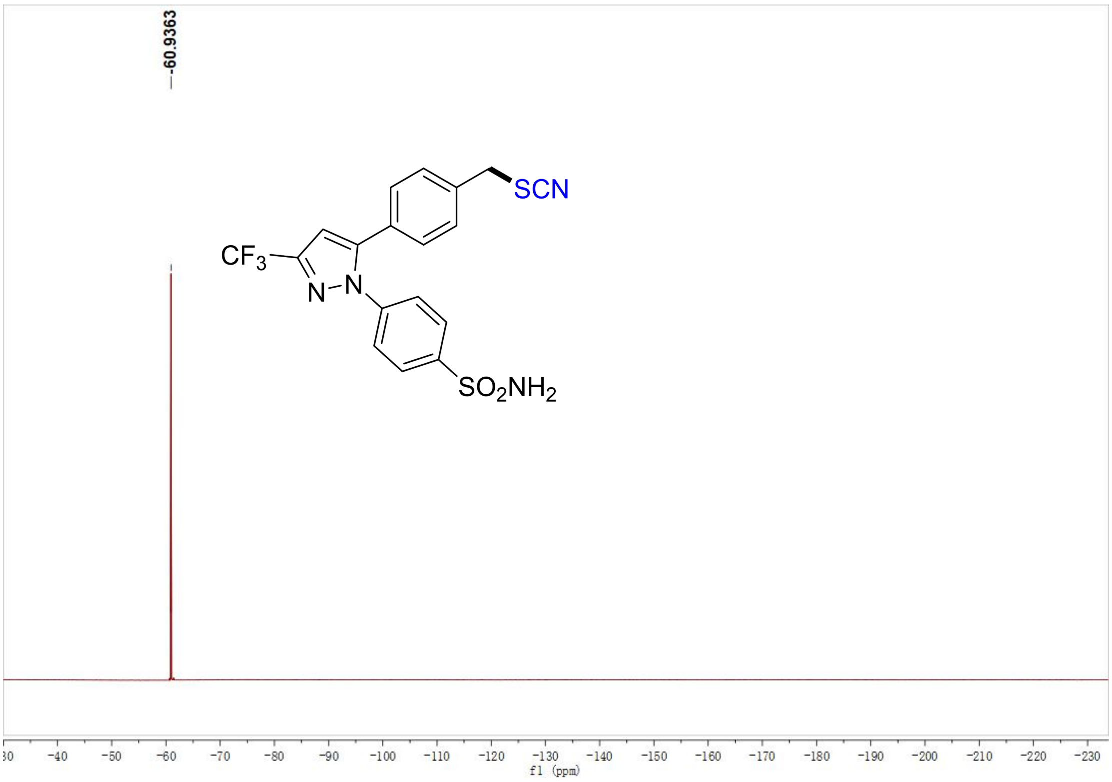
^{13}C NMR (150 MHz, CDCl$_3$) of **2ad**



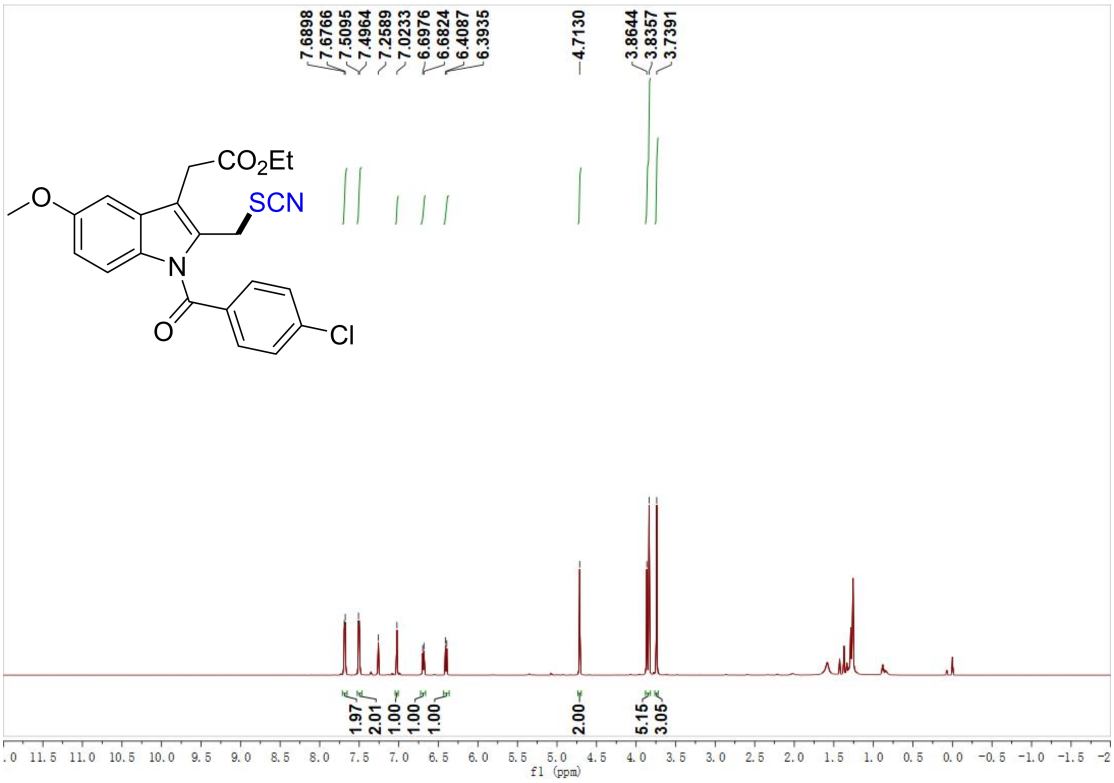
^{1}H NMR (600 MHz, DMSO-d_6) of **2ae**



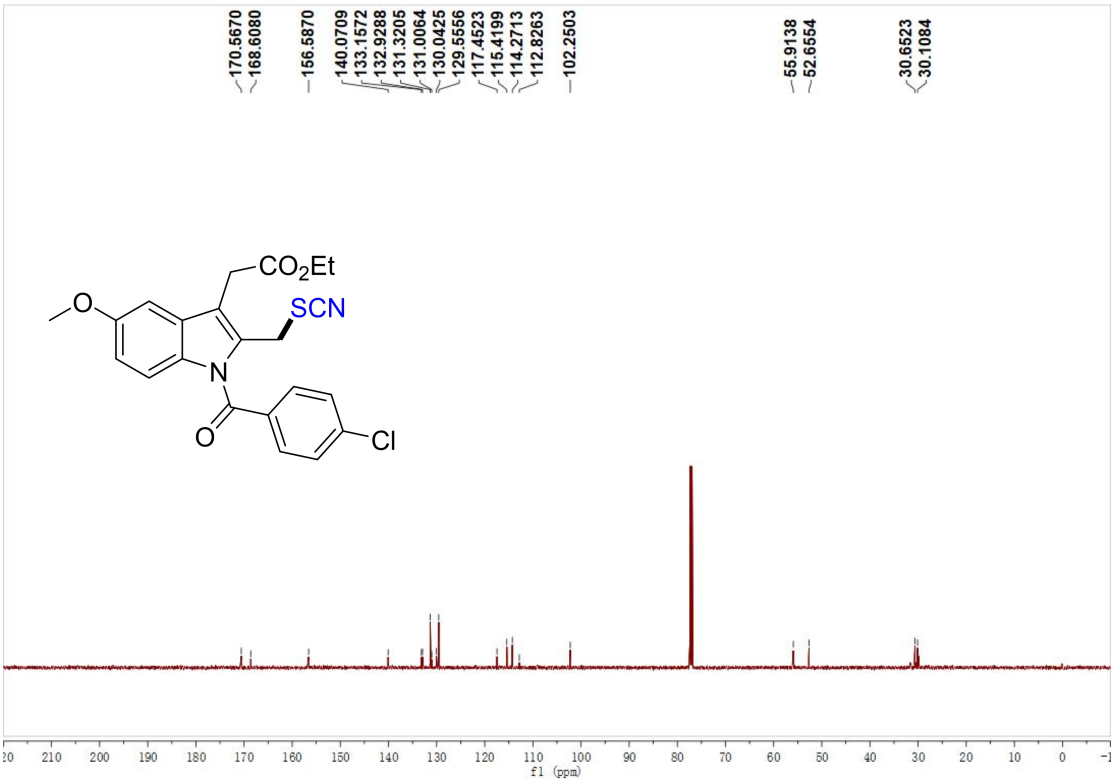
^{13}C NMR (150 MHz, DMSO-d_6) of **2ae**



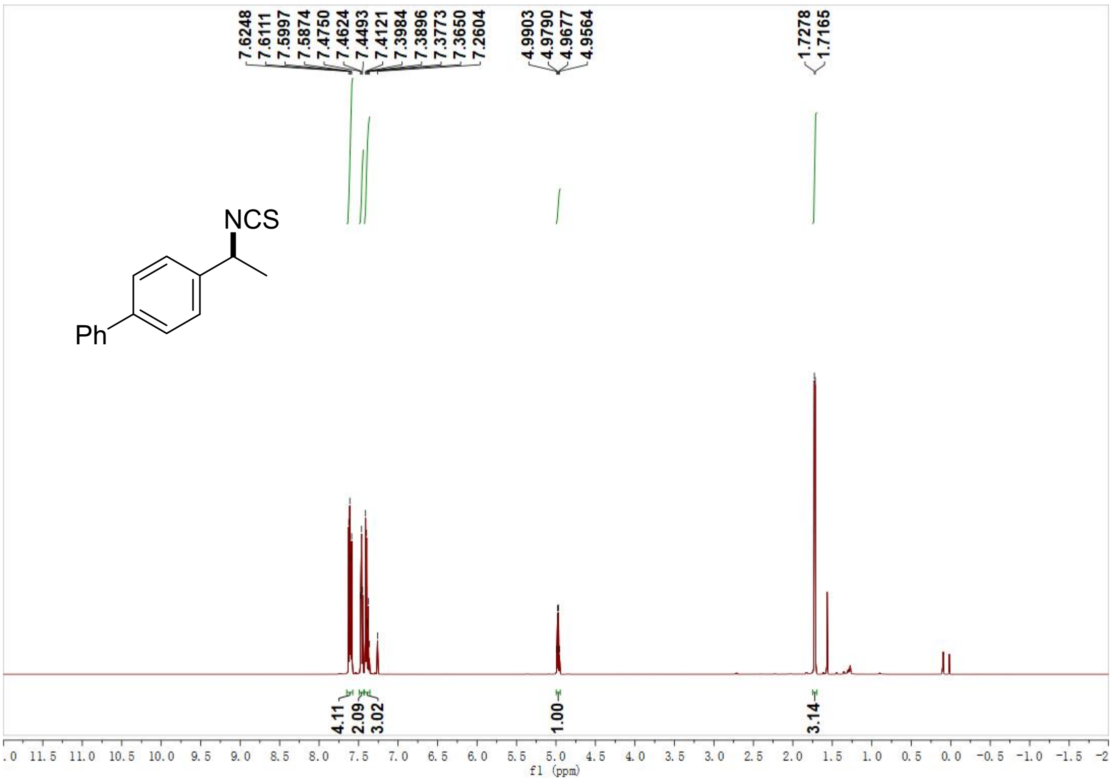
^{19}F NMR (376 MHz, DMSO-d_6) of **2ae**



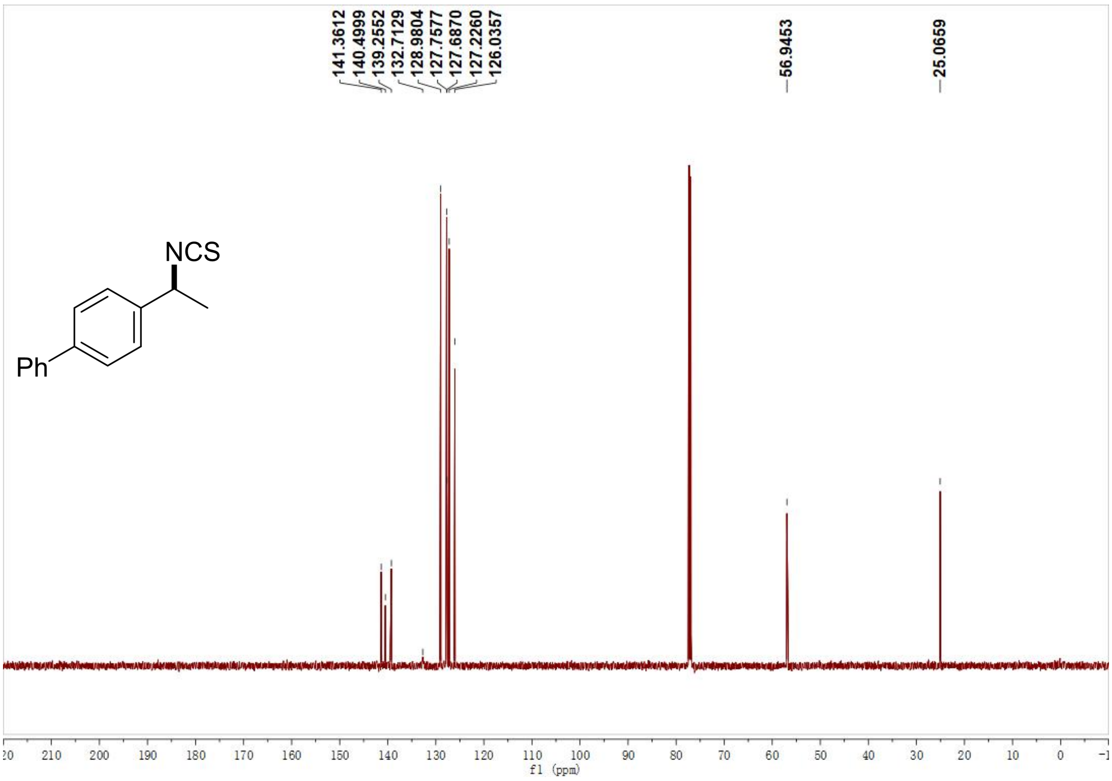
^{1}H NMR (600 MHz, CDCl$_3$) of **2af**



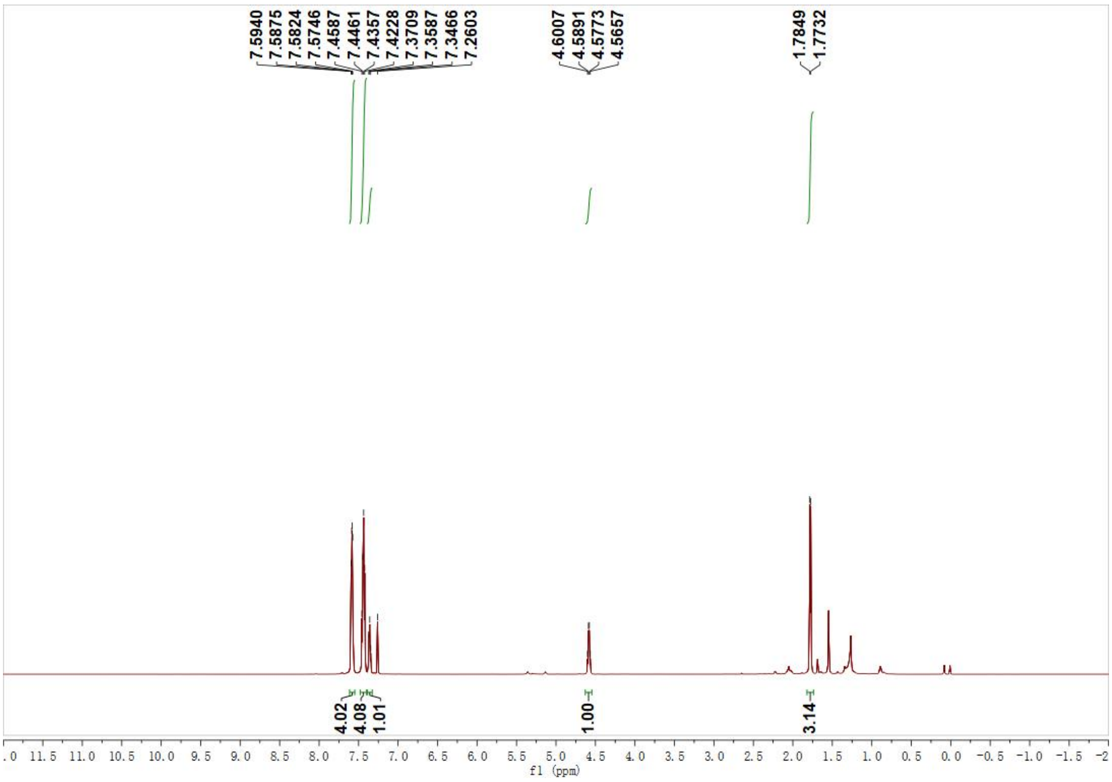
^{13}C NMR (150 MHz, CDCl$_3$) of **2af**



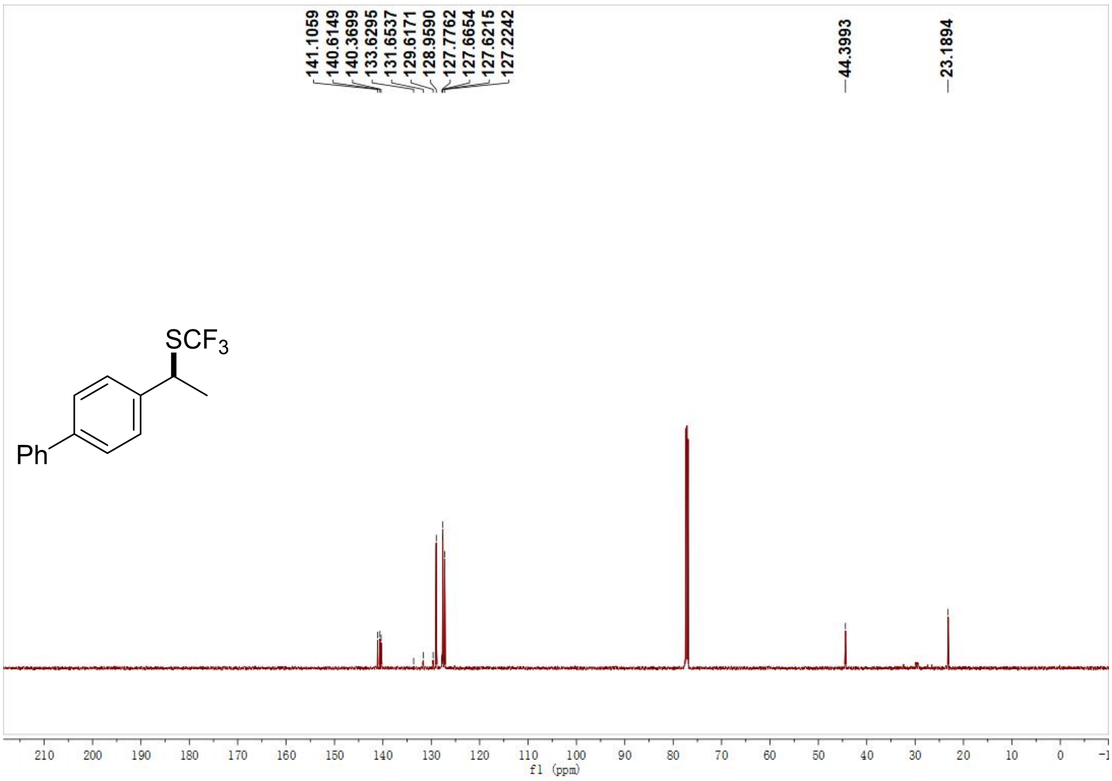
^{1}H NMR (600 MHz, CDCl$_3$) of **3**



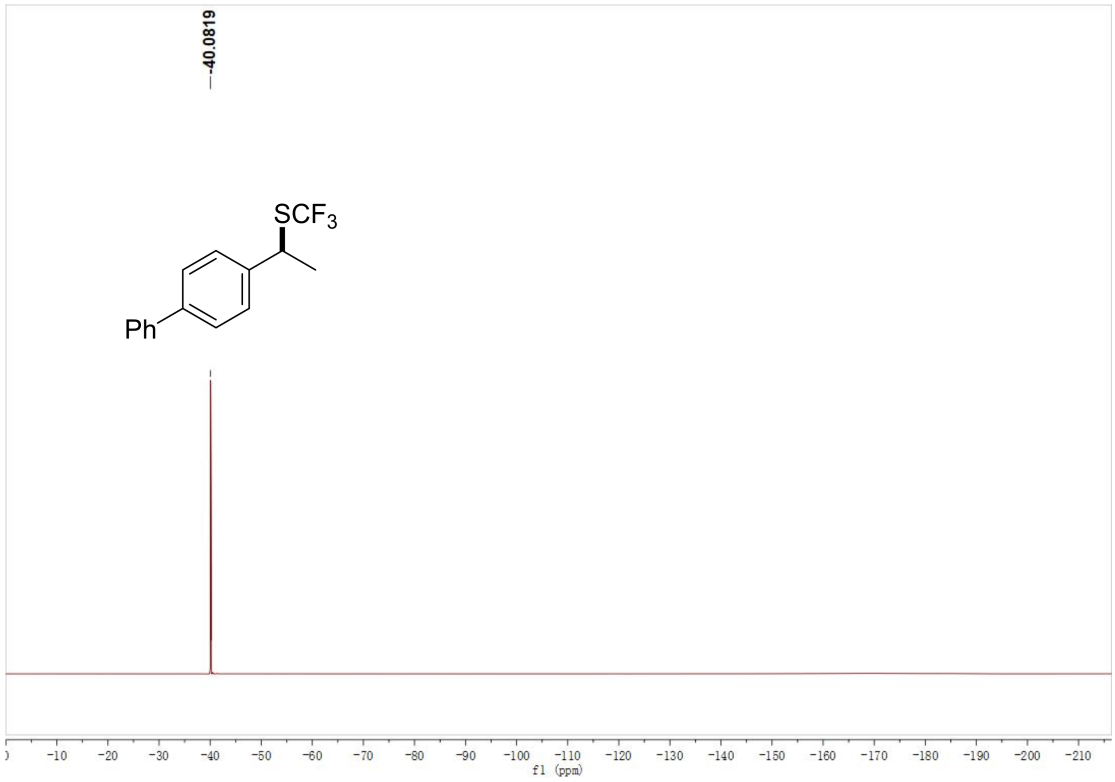
^{13}C NMR (150 MHz, CDCl$_3$) of **3**



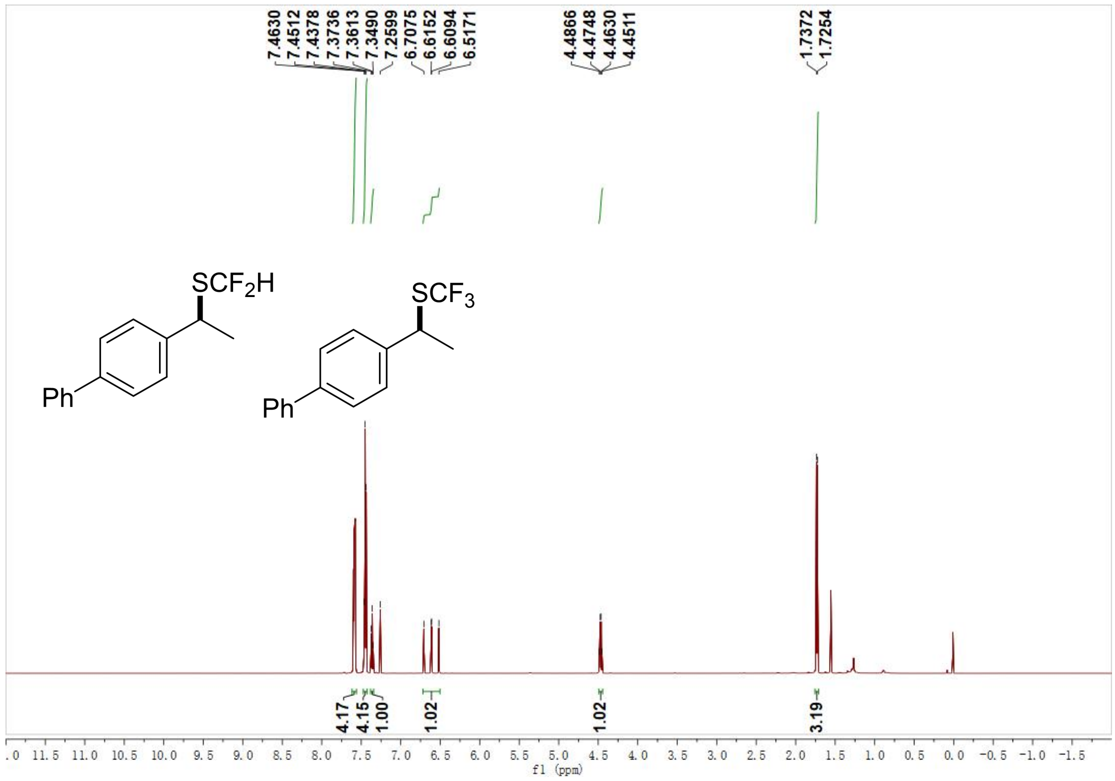
^{1}H NMR (600 MHz, $CDCl_3$) of **4**



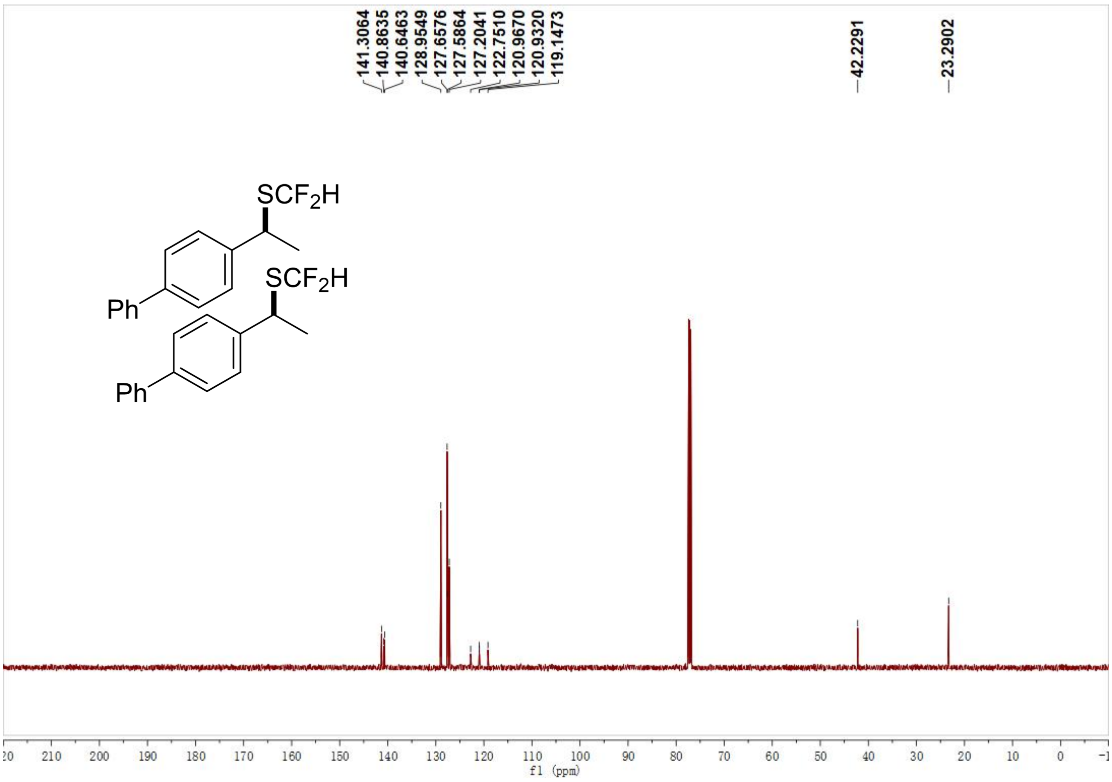
^{13}C NMR (150 MHz, $CDCl_3$) of **4**



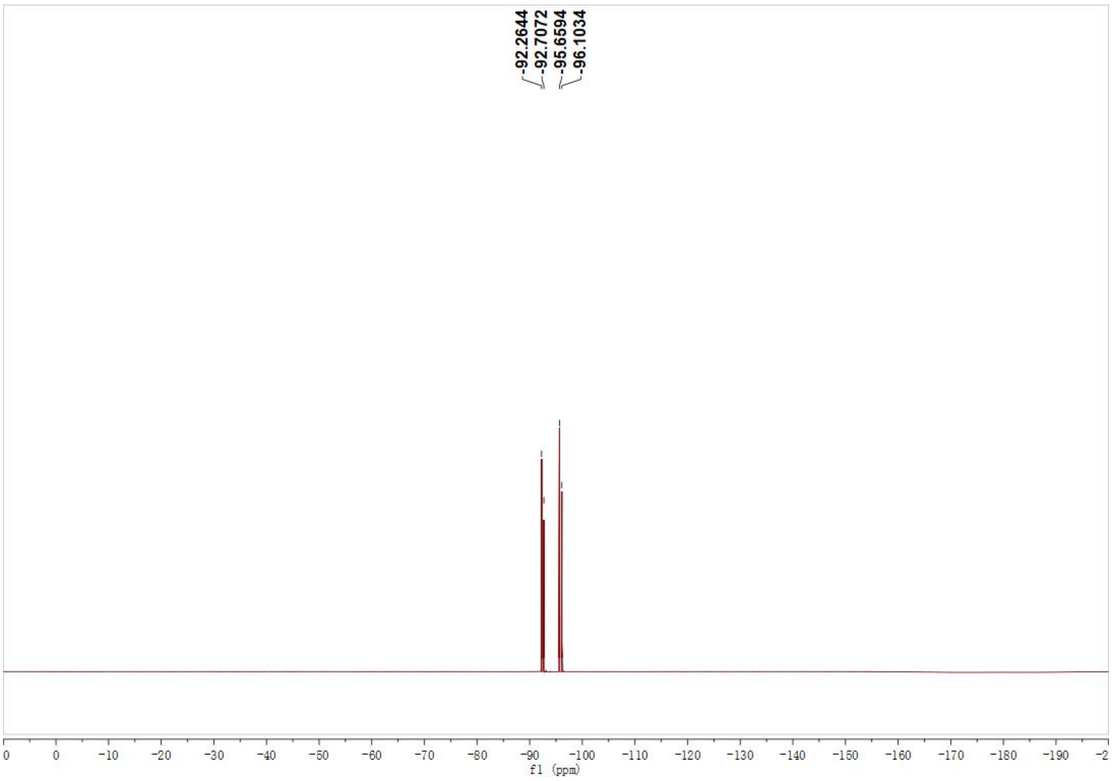
^{19}F NMR (565 MHz, CDCl$_3$) of **4**



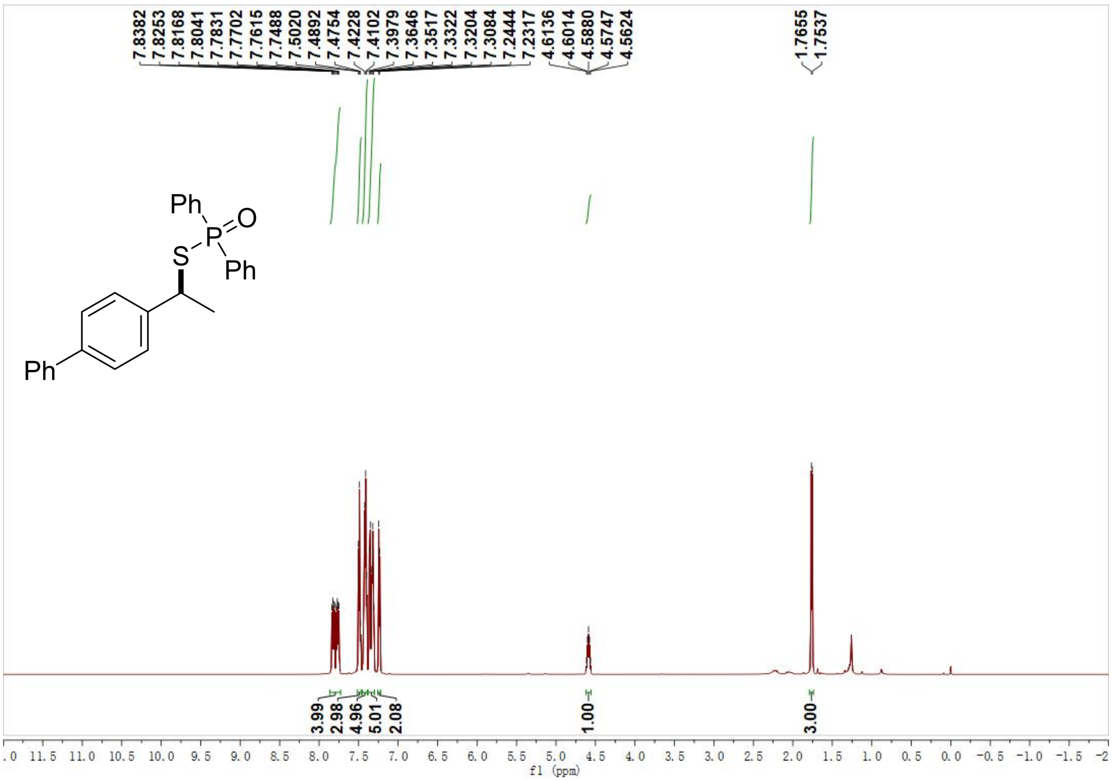
^{1}H NMR (600 MHz, CDCl$_3$) of **5**



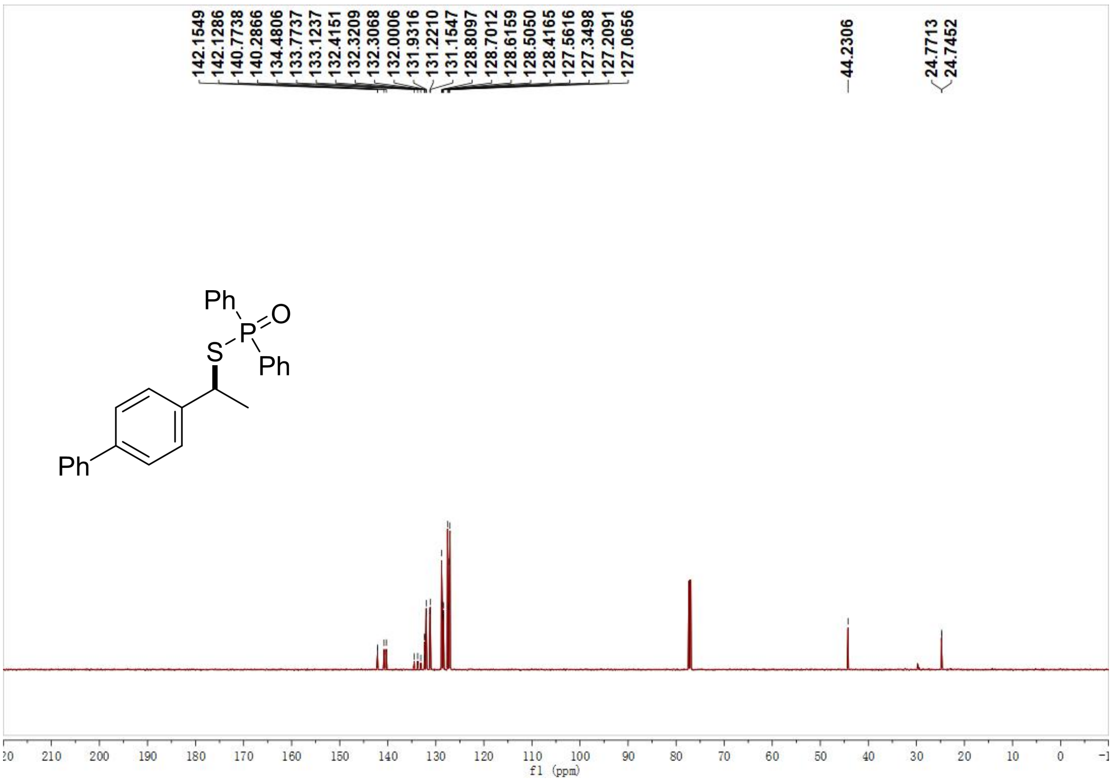
^{13}C NMR (150 MHz, CDCl$_3$) of **5**



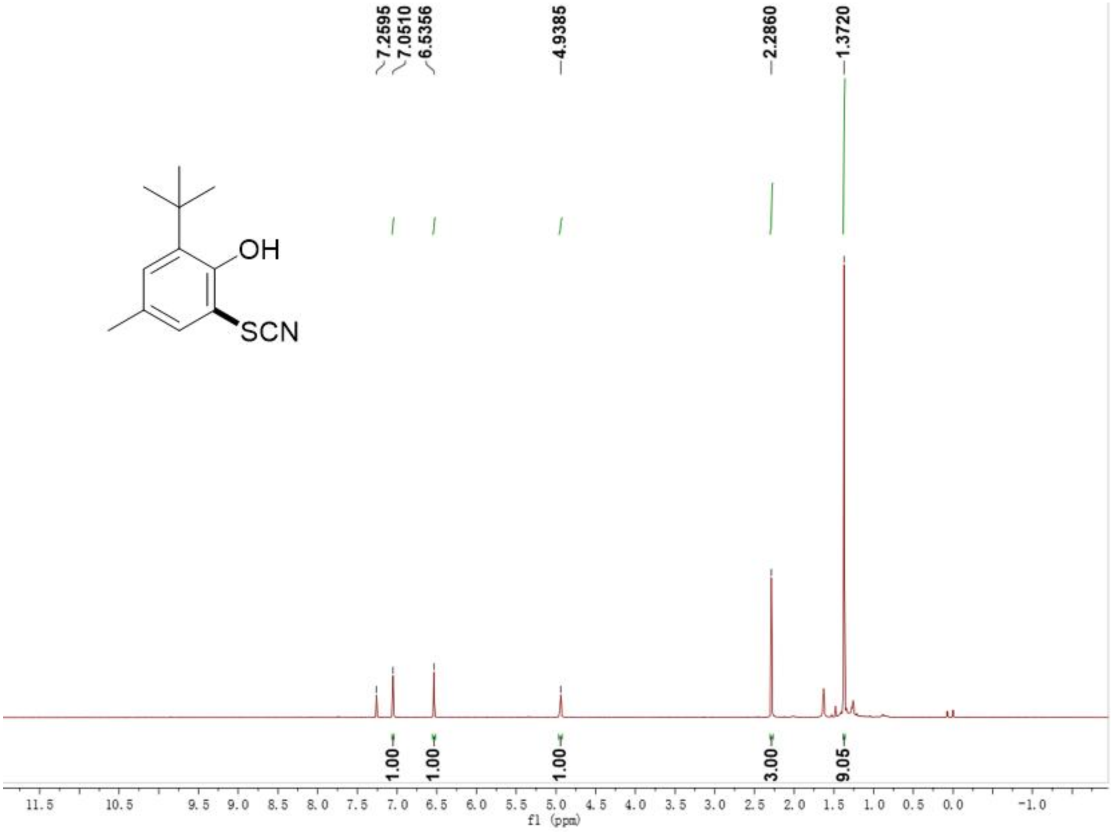
^{19}F NMR (565 MHz, CDCl$_3$) of **5**



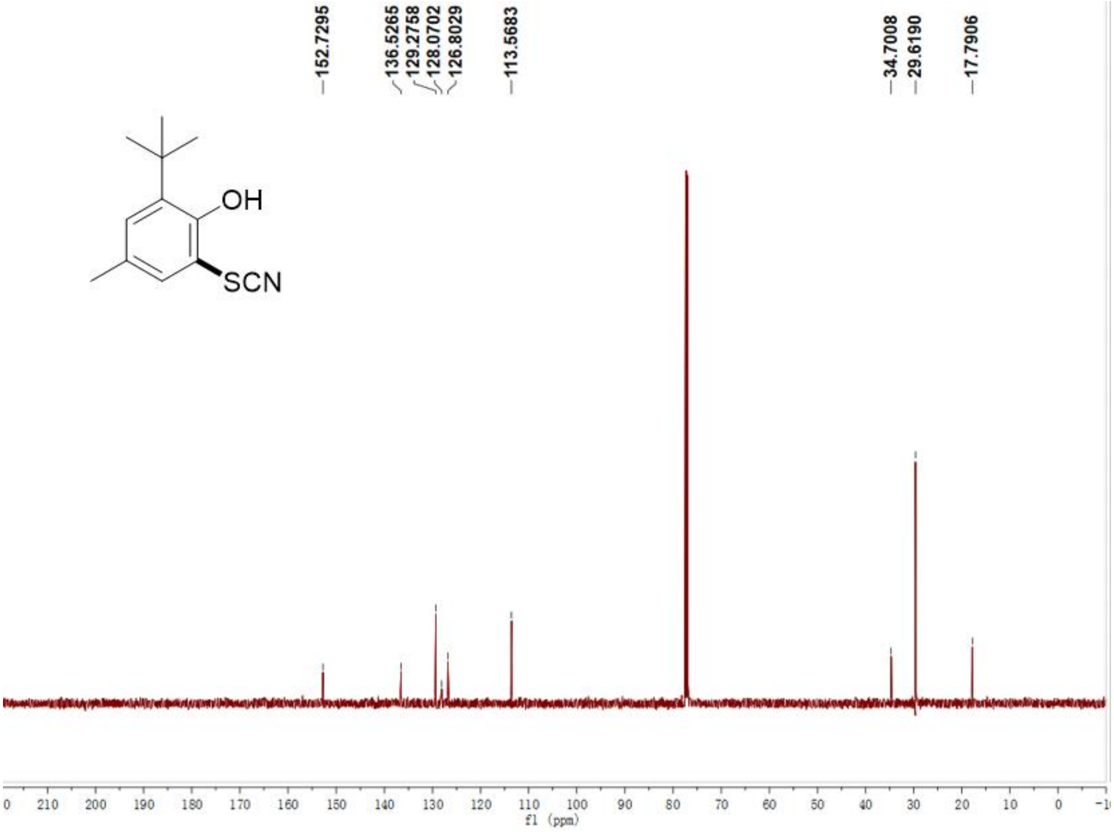
^{1}H NMR (600 MHz, CDCl$_3$) of **6**



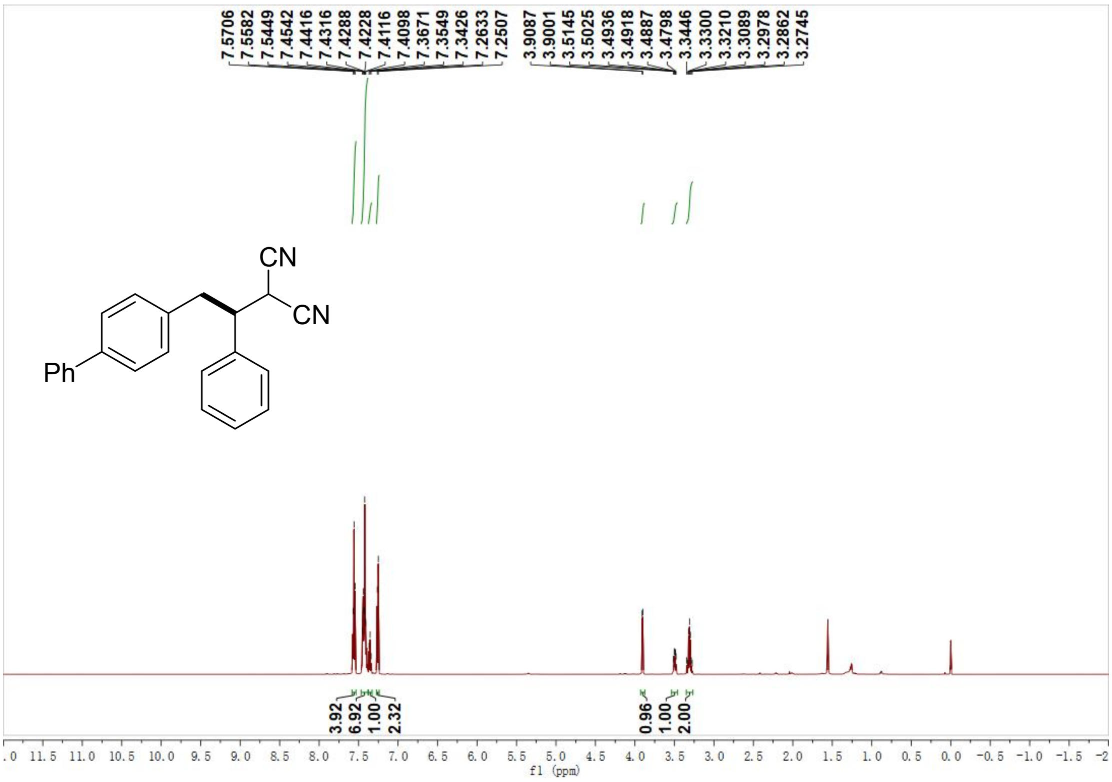
^{13}C NMR (150 MHz, CDCl$_3$) of **6**



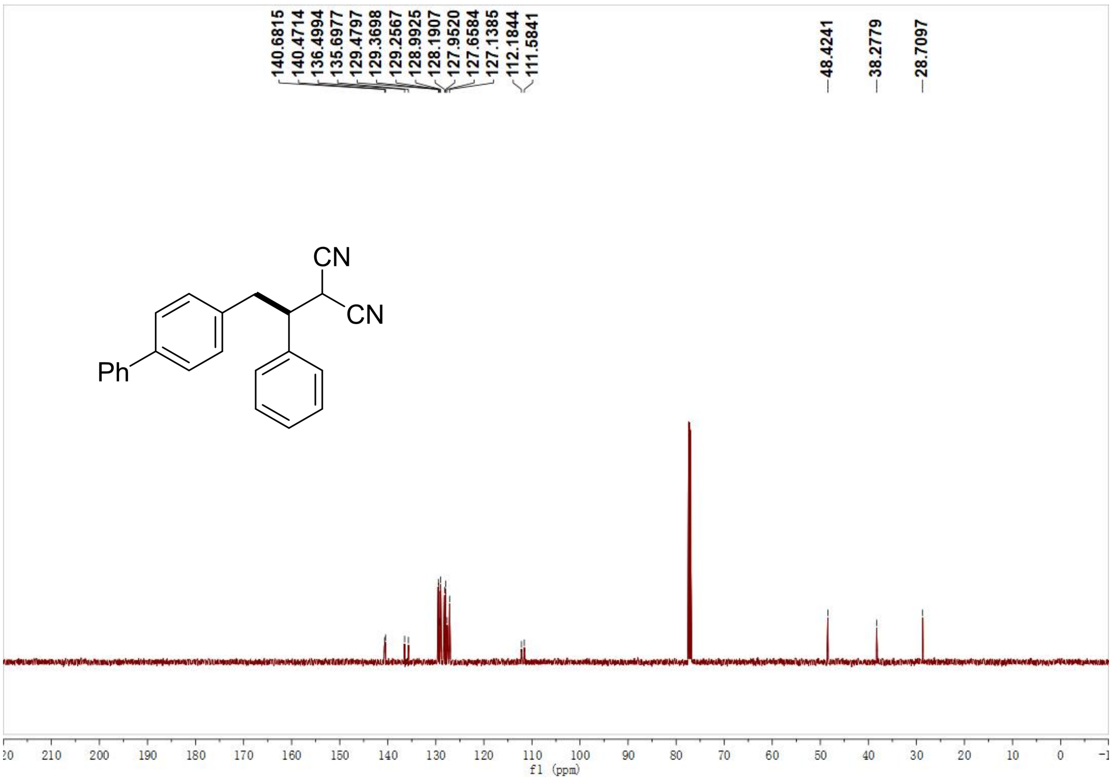
^{1}H NMR (600 MHz, CDCl$_3$) of **2a2**



^{13}C NMR (150 MHz, CDCl$_3$) of **2a2**



^{1}H NMR (600 MHz, CDCl$_3$) of **2a3**



^{13}C NMR (150 MHz, CDCl$_3$) of **2a3**