Supporting Information

Synthesis of *N*-β-brominated alkenyl isothiocyanates via dehydrogenation of alkyl isothiocyanates

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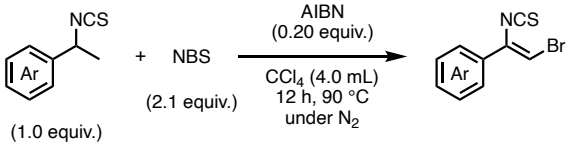
1. General Experimental Details

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. NBS and tetrachloromethane were purchased from Wako chemicals. AIBN was purchased from TCI. All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using Chem Scene HPTLC Silica Gel 60 GF254. Flash column chromatography was performed with Kanto Silica Gel 60 N (spherical, neutral) (40–50 μm). Silica-gel column chromatography was performed on an Isolera Spektra instrument equipped with a Biotage SNAP Ultra 10 g cartridge for 0.20 mmol scale reactions. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9260 II NEXT instrument equipped with JAIGEL-2HR columns using chloroform as an eluent. High-resolution mass spectra were recorded on a Bruker Daltonic microTOF spectrometer (APCI) and JEOL JMS-T100LC spectrometer for electrospray ionization (ESI). Nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECX-500 (^{1}H 500 MHz, ^{13}C 126 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. Experimental Procedures

Procedure for the dehydrogenation with bromination of alkyl isothiocyanate



General procedure A: AIBN (6.6 mg, 0.040 mmol, 0.20 equiv.), NBS (75 mg, 0.42 mmol, 2.1 equiv.) and substrate (0.20 mmol, 1.0 equiv. if solid) were added to a dried reaction tube with a stirring bar. The tube was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). Tetrachloromethane (4.0 mL) and substrate (0.20 mmol, 1.0 equiv. if liquid) were added to the tube and the mixture was stirred for 12 h at 90 °C. The crude mixture was quenched with saturated $Na_2S_2O_3$ *aq.* and extracted with $CHCl_3$ (3 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel provided the desired product.

3. Proposed Mechanism

A proposed mechanism of the dehydrogenative bromination is illustrated in Figure S 1. Firstly, the C–H bond at the α-position of isothiocyanate is abstracted by bromo radical, generated from bromine. Then, Wohl–Ziegler bromination gives the α-bromo isothiocyanate **A**. However, intermediate **A** is unstable, and the bromo group is eliminated, resulting the formation of vinyl isothiocyanate **B**. Vinyl isothiocyanate **B** is rapidly converted to the desired *N*-β-brominated alkenyl isothiocyanate **E** or **F** through the cation intermediates **C** or **D**. We consider that the stereoselectivity is determined by the steric effect between the bromo group and aryl group. Intermediate **C** is more favored because the bromo group locates far from the bulky aryl group. On the other hand, sterically congested intermediate **D** is disfavored. Therefore, *Z*-isomers were obtained selectively.

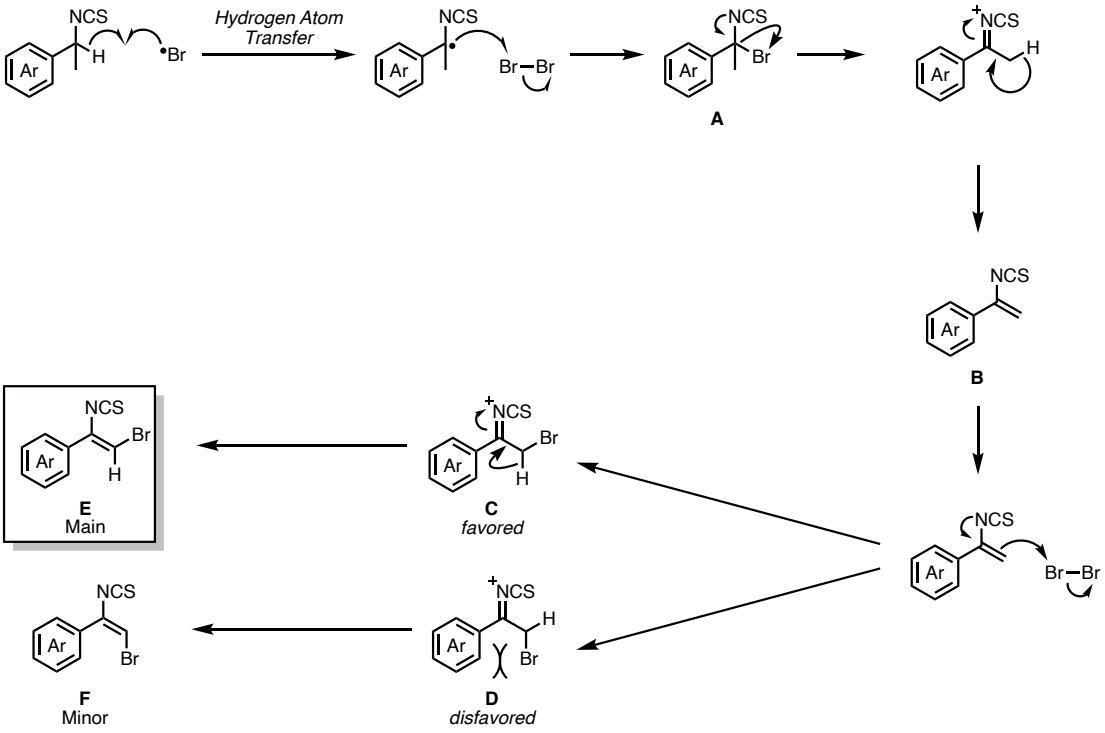


Figure S 1. Proposed mechanism of dehydrogenation with bromination.

4. Preparation of Substrates

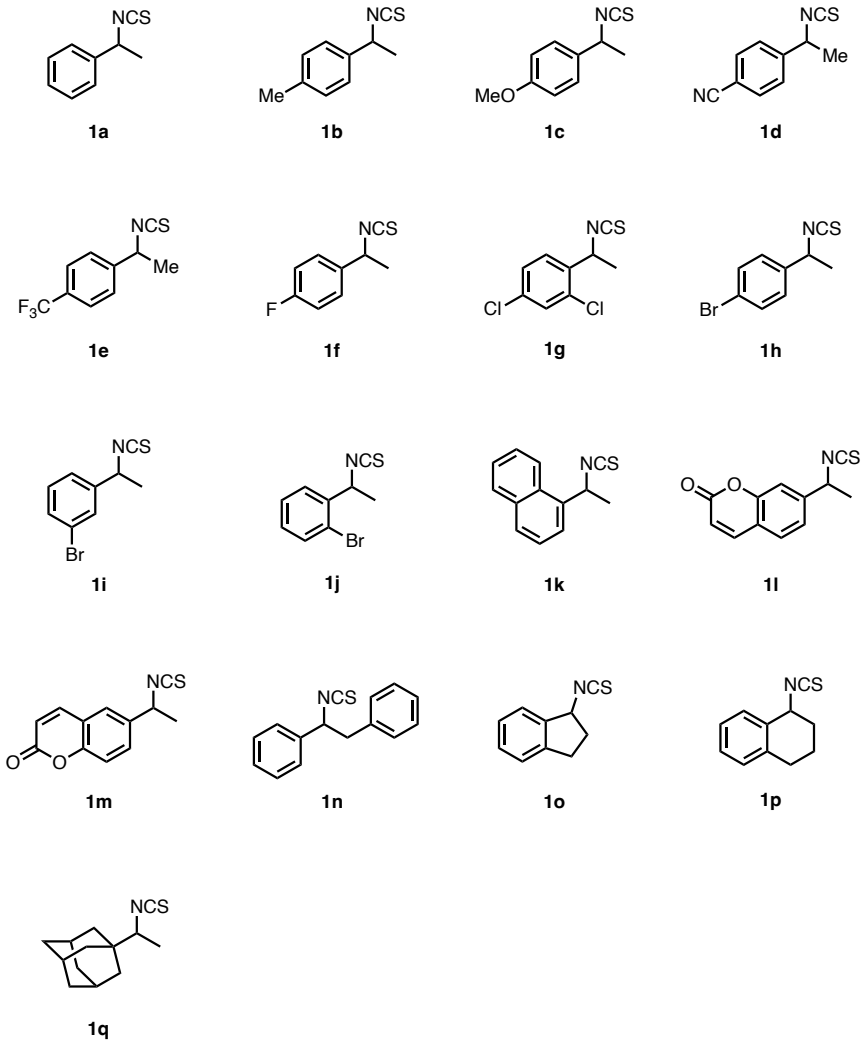
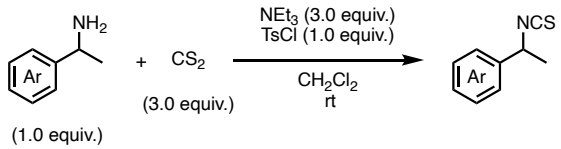
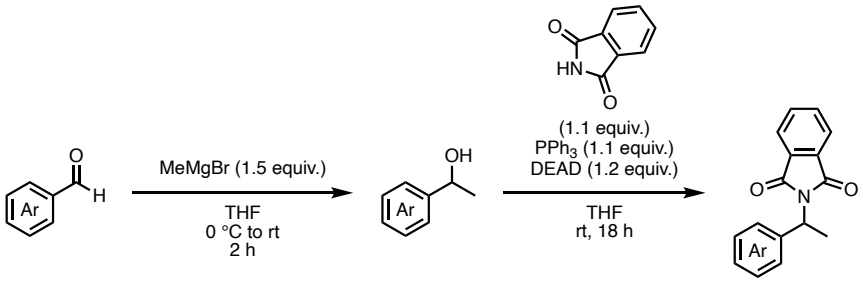


Figure S 2. The list of substrates.

Procedure of isothiocyanates synthesis

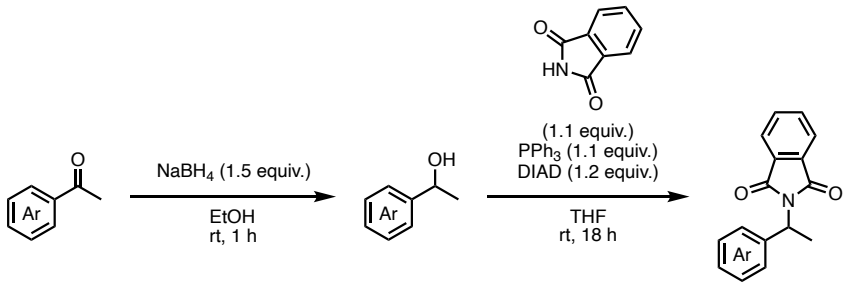


General procedure B: Dichloromethane, benzylamine (1.0 equiv.), NEt_3 (3.0 equiv.) and CS_2 (3.0 equiv.) were added to a round bottom flask with a stirring bar and the mixture was stirred for 1 h. TsCl (1.0 equiv.) was then added to the mixture. The reaction mixture was stirred for 4 h. Then, $CHCl_3$ was added to the crude mixture, and the organic layer was washed with 1 M HCl *aq*. × 2 and $NaHCO_3$ *aq*. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel provided the corresponding isothiocyanates.



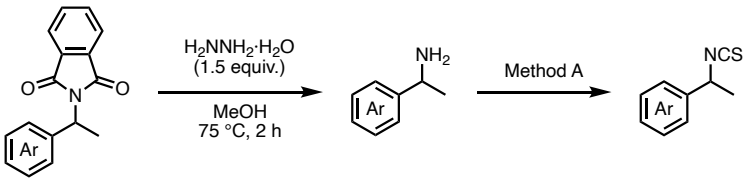
General procedure C: Aldehyde (1.0 equiv.) and a stirring bar were added to the 100 mL round bottom flask. Then, the flask was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). THF was then added to the flask. The mixture was stirred at 0 °C, and MeMgBr (3 M in Et_2O, 1.5 equiv.) was added dropwise. The mixture was warmed up to rt and stirred for 2 h. NH_4Cl *aq.* was added to the flask and extracted with EtOAc × 3. The organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. If the desired benzyl alcohol was sufficiently pure, the second step was conducted without further purification. When, the product was not pure, the benzyl alcohol was purified by chromatography on silica gel provided the corresponding benzyl alcohol.

The resulting benzyl alcohol (1.0 equiv.), THF, phthalimide (1.1 equiv.), and PPh_3 (1.1 equiv.) were added to a 100 mL round bottom flask with a stirring bar. Then, DEAD (2.2 M in toluene, 1.2 equiv.) or diisopropyl azodicarboxylate (1.9 M in toluene, 1.2 equiv.) was added dropwise, and the mixture was stirred overnight. H_2O was added to the crude mixture and extracted with EtOAc × 3. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc) provided the corresponding phthalimide compound.

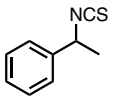


General procedure D: Ketone (1.0 equiv.) and a stirring bar were added to the 100 mL round bottom flask. Then, EtOH was added to the flask and $NaBH_4$ (1.5 equiv.) was added slowly. The mixture was stirred for 1 h. H_2O was added to the flask and extracted with EtOAc × 3. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The desired benzyl alcohol was sufficiently pure, the second step was conducted without further purification.

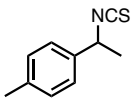
The resulting benzyl alcohol (1.0 equiv.), THF, phthalimide (1.1 equiv.), and PPh_3 (1.1 equiv.) were added to a 100 mL round bottom flask with a stirring bar. Then, diisopropyl azodicarboxylate (1.9 M, in toluene, 1.2 equiv.) was added dropwise, and the mixture was stirred overnight. The organic layer was concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc) provided the corresponding phthalimide compound.



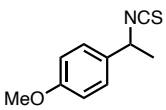
General procedure E: The resulting benzyl phthalimide compound (1.0 equiv.), MeOH, and $H_2NNH_2 \cdot H_2O$ (1.5 equiv.) were added to a test tube with a stirring bar and the mixture was stirred for 2 h at 75 °C. 1 M HCl *aq*. was added to the crude mixture and filtered. The filtrate was neutralized with 1 M NaOH *aq.* and the desired compound was extracted with EtOAc × 3. The organic layer was dried by Na_2SO_4 and concentrated *in vacuo*, then, the benzylamine compound was obtained without further purification. Next, according to Method A, benzyl isothiocyanates were synthesized from the obtained benzylamine.



(1-isothiocyanatoethyl)benzene (**1a**) [S1]: The title compound was synthesized according to General procedure B from the starting amine (4.8 g, 40 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) provided **1a** (5.89 g, 36.1 mmol, 90%) as a colorless oil.

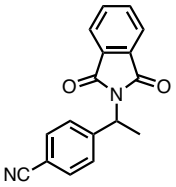


1-(1-isothiocyanatoethyl)-4-methylbenzene (**1b**) [S2]: The title compound was synthesized according to General procedure B from the starting amine (276 mg, 2.0 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1b** (284 mg, 1.60 mmol, 78%) as a colorless oil.



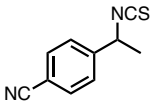
1-(1-isothiocyanatoethyl)-4-methoxybenzene (**1c**) [S2]: The title compound was synthesized according to General procedure B from the starting amine (631 mg, 4.17 mmol). Purified by flash

column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1c** (603 mg, 3.12 mmol, 75%) as a pale yellow oil.



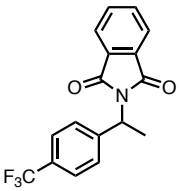
4-(1-(1,3-dioxoisoindolin-2-yl)ethyl)benzonitrile: The title compound was synthesized according to General procedure C with DEAD from the starting aldehyde (393 mg, 3.0 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) afforded 4-(1-(1,3-dioxoisoindolin-2-yl)ethyl)benzonitrile (479 mg, 1.74 mmol, 57% (two step)) as a white solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.93 (d, J = 7.5 Hz, 3H), 5.59 (q, J = 7.5 Hz, 1H), 7.59–7.64 (m, 4H), 7.73 (dd, J = 5.5, 3.0 Hz, 2H), 7.82 (dd, J = 5.5, 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 17.3, 49.1, 111.7, 118.7, 123.5, 128.3, 131.8, 132.5, 134.3, 145.4, 168.0; HRMS (APCI, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{13}N_2O_2$ 277.0972; Found 277.0973.



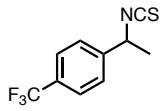
4-(1-isothiocyanatoethyl)benzonitrile (**1d**): The title compound was synthesized according to General procedure E from 4-(1-(1,3-dioxoisoindolin-2-yl)ethyl)benzonitrile (414 mg, 1.5 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1d** (210 mg, 1.11 mmol, 76% (two step)) as a white solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.70 (d, J = 7.0 Hz, 3H), 5.00 (q, J = 7.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 24.7, 56.5, 111.9, 118.2, 126.2, 132.7, 134.2, 145.1; HRMS (APCI, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{10}H_9N_2S$ 189.0481; Found 189.0483.



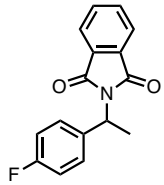
2-(1-(4-(trifluoromethyl)phenyl)ethyl)isoindoline-1,3-dione: The title compound was synthesized according to General procedure C with diisopropyl azodicarboxylate from the starting aldehyde (875 mg, 5.0 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) afforded 2-(1-(4-(trifluoromethyl)phenyl)ethyl)isoindoline-1,3-dione (693 mg, 2.17 mmol, 43% (two step)) as a pale yellow oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.94 (d, J = 7.0 Hz, 3H), 5.61 (q, J = 7.0 Hz, 1H), 7.57–7.63 (m, 4H), 7.71 (dd, J = 5.0, 3.0 Hz, 2H), 7.82 (dd, J = 5.0, 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 17.5, 49.2, 123.5, 124.1 (q, J = 272 Hz), 125.6, 128.0, 130.0 (q, J = 32.5 Hz), 131.9, 134.3, 144.2, 168.2; HRMS (APCI, positive) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3NO_2$ 320.0893; Found 320.0890.

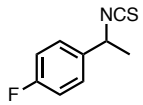


1-(1-isothiocyanatoethyl)-4-(trifluoromethyl)benzene (**1e**): The title compound was synthesized according to General procedure E from 2-(1-(4-(trifluoromethyl)phenyl)ethyl)isoindoline-1,3-dione (480 mg, 1.5 mmol).. Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1e** (109 mg, 0.470 mmol, 31% (two step)) as a pale yellow oil.

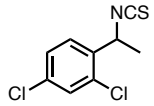
^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.70 (d, J = 7.0 Hz, 3H), 5.00 (q, J = 7.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 25.1, 56.7, 124.0 (q, J = 273 Hz), 126.0, 126.1 (q, J = 3.5 Hz), 130.6 (q, J = 32.4 Hz), 134.0, 144.2; HRMS (APCI, positive) m/z: $[M-NCS]^+$ Calcd for $C_9H_8F_3$ 173.0573; Found 173.0572.



2-(1-(4-fluorophenyl)ethyl)isoindoline-1,3-dione[S3]: The title compound was synthesized according to General procedure D from the starting ketone (689 mg, 4.99 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) afforded 2-(1-(4-fluorophenyl)ethyl)isoindoline-1,3-dione (605 mg, 2.25 mmol, 45% (two step)) as a white solid.

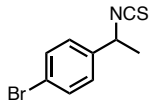


1-fluoro-4-(1-isothiocyanatoethyl)benzene (**1f**)[S2]: The title compound was synthesized according to General procedure E from 2-(1-(4-fluorophenyl)ethyl)isoindoline-1,3-dione (412 mg, 1.53 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1f** (106 mg, 0.584 mmol, 38% (two step)) as a pale yellow oil.

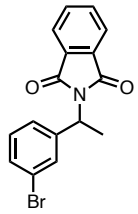


2,4-dichloro-1-(1-isothiocyanatoethyl)benzene (**1g**): The title compound was synthesized according to General procedure B from the starting amine (383 mg, 2.02 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1g** (158 mg, 0.682 mmol, 34%) as a colorless oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.65 (d, J = 6.5 Hz, 3H), 5.33 (q, J = 6.5 Hz, 1H), 7.32 (dd, J = 8.5, 2.5 Hz, 1H), 7.39 (d, J = 2.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 23.6, 53.9, 127.8, 128.0, 129.7, 132.2, 134.0, 134.7, 136.4; HRMS (APCI, positive) m/z: $[M]^+$ Calcd for $C_9H_7Cl_2NS$ 230.9671; Found 230.9671.

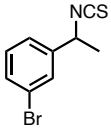


1-bromo-4-(1-isothiocyanatoethyl)benzene (**1h**)[S2]: The title compound was synthesized according to General procedure B from the starting amine (402 mg, 2.01 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **1h** (276 mg, 1.14 mmol, 57%) as a colorless oil.

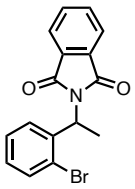


2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione: The title compound was synthesized according to General procedure D from the starting ketone (928 mg, 5.02 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) afforded 2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione (1.05 g, 3.19 mmol, 64% (two step)) as a colorless oil.

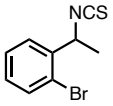
^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.90 (d, J = 7.5 Hz, 3H), 5.52 (q, J = 7.5 Hz, 1H), 7.18–7.22 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.63–7.65 (m, 1H), 7.69–7.73 (m, 2H), 7.80–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 17.6, 49.1, 122.7, 123.5, 126.2, 130.2, 130.8, 131.0, 132.0, 134.2, 142.6, 168.1; HRMS (APCI, positive) m/z: $[M]^+$ Calcd for $C_{16}H_{12}BrNO_2$ 329.0046; Found 329.0048.



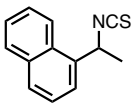
1-bromo-3-(1-isothiocyanatoethyl)benzene (1i)[S4]: The title compound was synthesized according to General procedure E from 2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione (661 mg, 2.00 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:20 to 80:20) afforded **1i** (424 mg, 1.75 mmol, 88% (two step)) as a pale yellow oil.



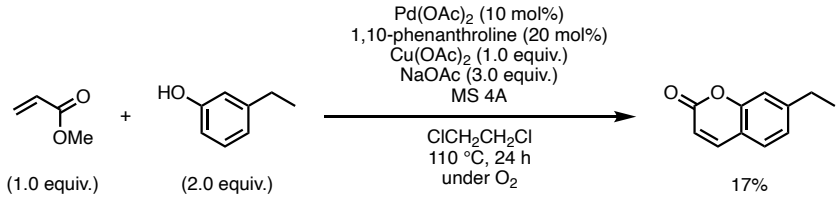
2-(1-(2-bromophenyl)ethyl)isoindoline-1,3-dione: The title compound was synthesized according to General procedure D from the starting ketone (997 mg, 5.01 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) afforded 2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione (828 mg, 2.51 mmol, 50%) as a white solid. The product was contained byproduct. Although the product was contaminated with several byproducts, the product was directly used in the next step without further purification.
(^{1}H NMR and ^{13}C NMR of this compound are attached in Figure S 34, Figure S 35.)



1-bromo-2-(1-isothiocyanatoethyl)benzene (1j)[S4]: The title compound was synthesized according to General procedure E from 2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione (496 mg, 1.5 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded 1-bromo-2-(1-isothiocyanatoethyl)benzene (150 mg, 0.619 mmol, 41% (two step)) as a colorless oil.

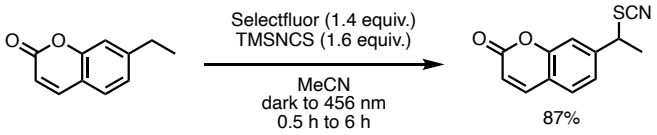


1-(1-isothiocyanatoethyl)naphthalene (1k)[S4]: The title compound was synthesized according to General procedure B from the starting amine (856 mg, 5.00 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded 1-bromo-2-(1-isothiocyanatoethyl)benzene (905 mg, 4.24 mmol, 85%) as a colorless oil.



7-ethyl-2*H*-chromen-2-one: $Cu(OAc)_2$ (2.18 g, 12 mmol, 1.0 equiv.), NaOAc (2.96 g, 36 mmol, 3.0 equiv.), 1,10-phenanthroline (432 mg, 2.4 mmol, 20 mol%), $Pd(OAc)_2$ (270 mg, 1.2 mmol, 10 mol%) and activated MS 4A (1.58 g) were added to a 300 mL two-neck round bottom flask with a stirring bar. The flask was filled with oxygen by employing the usual Schlenk technique (evacuate-refill cycle). Dichloroethane (100 mL), 3-ethylphenol (2.99 g, 24 mmol, 2.0 equiv.), and methyl acetate (1.04 g, 12 mmol, 1.0 equiv.) were added to the flask and the mixture was stirred for 24 h at 110 °C. The crude mixture was filtered by celite with EtOAc and the organic layer was concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 97:3 to 75:25) and GPC provided 7-ethyl-2*H*-chromen-2-one (363 mg, 2.09 mmol, 17%) as an orange solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.28 (t, J = 7.5 Hz, 3H), 2.75 (q, J = 7.5 Hz, 2H), 6.36 (d, J = 9.5 Hz, 1H), 7.13 (dd, J = 7.5, 1.5 Hz, 1H), 7.17 (s, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 15.3, 29.1, 115.6, 116.0, 116.8, 124.6, 127.8, 143.5, 149.5, 154.4, 161.3; HRMS (APCI, positive) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}O_2$ 175.0754; Found 175.0752.

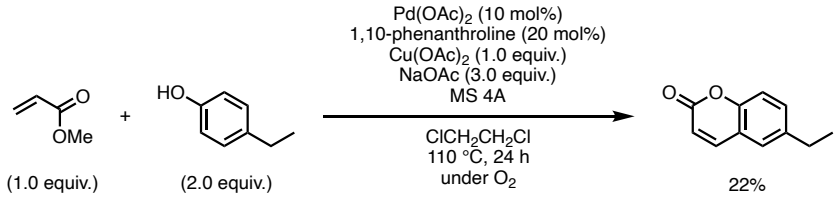


7-(1-thiocyanatoethyl)-2*H*-chromen-2-one: 7-Ethyl-2*H*-chromen-2-one (363 mg, 2.09 mmol, 1.0 equiv.) and Selectfluor (1.06 g, 3.00 mmol, 1.4 equiv.) were added to a 50 mL round bottom flask with a stirring bar. The flask was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). Acetonitrile (10 mL) and TMSNCS (428 mg, 3.26 mmol, 1.6 equiv.) were added to the flask and the mixture was stirred under dark for 0.5 h followed by blue light irradiation and a cooling fan for 6 h. The reaction temperature was 25 °C at the beginning and gradually increased to 65 °C by irradiation of blue light. The crude mixture was passed through a short pad of silica gel and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 90:10 to 0:100) provided 7-(1-thiocyanatoethyl)-2*H*-chromen-2-one (419 mg, 1.81 mmol, 87%) as a pale yellow solid.

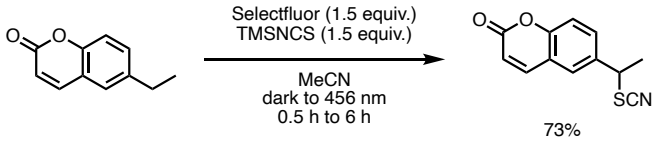
^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.90 (d, J = 7.0 Hz, 3H), 4.65 (q, J = 7.0 Hz, 1H), 6.46 (d, J = 9.5 Hz, 1H), 7.32–7.36 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 21.6, 47.6, 111.0, 115.5, 117.5, 119.2, 123.3, 128.7, 142.8, 143.7, 154.2, 160.3; HRMS (APCI, positive) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO_2S$ 232.0427; Found 232.0427.

7-(1-isothiocyanatoethyl)-2*H*-chromen-2-one (**1l**): 7-(1-Thiocyanatoethyl)-2*H*-chromen-2-one (347 mg, 1.50 mmol, 1.0 equiv.), $MeNO_2$ (15 mL) and $ZnCl_2$ (409 mg, 3.0 mmol, 2.0 equiv.) were added to a 50 mL round bottom flask with a stirring bar and the mixture was stirred for 3 h at 60 °C. H_2O (15 mL) was added to the crude mixture and extracted with $CHCl_3$. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) provided **1l** (233 mg, 1.01 mmol, 67%) as a white solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.72 (d, J = 7.0 Hz, 3H), 5.02 (q, J = 7.0 Hz, 1H), 6.45 (d, J = 9.5 Hz, 1H), 7.26–7.30 (m, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 25.1, 56.7, 114.2, 117.2, 118.7, 121.7, 128.7, 134.5, 142.9, 144.7, 154.4, 160.5; HRMS (APCI, positive) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO_2S$ 232.0427; Found 232.0428.



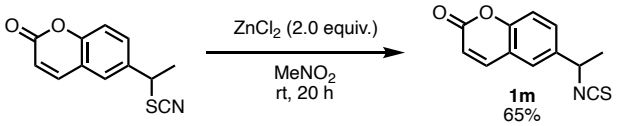
6-ethyl-2*H*-chromen-2-one[S5]: $Cu(OAc)_2$ (2.19 g, 12 mmol, 1.0 equiv.), NaOAc (2.96 g, 36 mmol, 3.0 equiv.), 1,10-phenanthroline (432 mg, 2.4 mmol, 20 mol%), $Pd(OAc)_2$ (270 mg, 1.2 mmol, 10 mol%), 4-ethylphenol (2.93 g, 24 mmol, 2.0 equiv.) and activated MS 4A (1.58 g) were added to a 300 mL two-neck round bottom flask with a stirring bar. The flask was filled with oxygen by employing the usual Schlenk technique (evacuate-refill cycle). Dichloroethane (100 mL) and methyl acetate (1.05 g, 12 mmol, 1.0 equiv.) were added to the flask and the mixture was stirred for 24 h at 110 °C. The crude mixture was filtered by celite with EtOAc and the organic layer was concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 97:3 to 75:25) and GPC provided 6-ethyl-2*H*-chromen-2-one (476 mg, 2.73 mmol, 22%) as a pale yellow solid.



6-(1-thiocyanatoethyl)-2H-chromen-2-one: 6-Ethyl-2*H*-chromen-2-one (686 mg, 3.94 mmol, 1.0 equiv.) and Selectfluor (2.13 g, 6.01 mmol, 1.5 equiv.) were added to a 50 mL round bottom flask with a stirring bar. The flask was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). Acetonitrile (20 mL) and TMSNCS (775 mg, 5.91 mmol, 1.5 equiv.) were added to the flask and the mixture was stirred under dark for 0.5 h followed by blue light irradiation and a cooling fan for 6 h. The reaction temperature was 25 °C at the beginning and gradually increased to 65 °C by irradiation of blue light. The crude mixture was passed through a short pad of

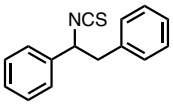
silica gel and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 90:10 to 0:100) provided 6-(1-thiocyanatoethyl)-2*H*-chromen-2-one (661 mg, 2.86 mmol, 73%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.91 (d, *J* = 7.5 Hz, 3H), 4.64 (q, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 9.5 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.57 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.72 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 21.8, 47.4, 111.2, 117.5, 117.7, 119.0, 126.5, 130.6, 135.8, 143.0, 154.0, 160.2; HRMS (APCI, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{10}NO_2S$ 232.0427; Found 232.0427.



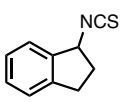
6-(1-isothiocyanatoethyl)-2*H*-chromen-2-one (**1m**): 6-(1-Thiocyanatoethyl)-2*H*-chromen-2-one (231 mg, 1.00 mmol, 1.0 equiv.), $MeNO_2$ (10 mL) and $ZnCl_2$ (280 mg, 2.0 mmol, 2.0 equiv.) were added to a 50 mL round bottom flask with a stirring bar and the mixture was stirred for 20 h at rt. H_2O (15 mL) was added to the crude mixture and extracted with $CHCl_3$ × 3. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) provided **1m** (149 mg, 0.646 mmol, 65%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.73 (d, *J* = 7.0 Hz, 3H), 5.01 (q, *J* = 7.0 Hz, 1H), 6.48 (d, *J* = 10.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.47–7.49 (m, 2H), 7.73 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 25.1, 56.3, 117.4, 117.6, 119.0, 124.8, 129.1, 133.8, 136.7, 143.1, 153.7, 160.4; HRMS (APCI, positive) *m*/*z*:$[M+H]^+$ Calcd for $C_{12}H_{10}NO_2S$ 232.0427; Found 232.0426.

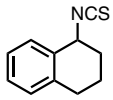


1n: The title compound was synthesized according to General procedure B from the starting amine (985 mg, 4.99 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) two times afforded **1n** (305 mg, 1.28 mmol, 26%) as a colorless oil.

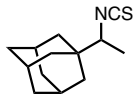
^{1}H NMR ($CDCl_3$ 500 MHz) δ 3.13–3.21 (m, 2H), 4.93–4.96 (m, 1H), 7.14 (d, *J* = 7.0 Hz, 2H), 7.24–7.39 (m, 8H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 45.8, 63.4, 126.2, 127.4, 128.5, 128.7, 128.9, 129.6, 132.9, 136.3, 138.6; HRMS (APCI, positive) *m*/*z*: $[M-NCS]^+$ Calcd for $C_{14}H_{13}$ 181.1012; Found 181.1014.



1-isothiocyanato-2,3-dihydro-1*H*-indene (1o)[S2]: The title compound was synthesized according to General procedure B from the starting amine (670 mg, 5.03 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded 1-isothiocyanato-2,3-dihydro-1*H*-indene (697 mg, 3.98 mmol, 79%) as a brown oil.

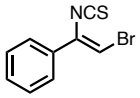


1-isothiocyanato-1,2,3,4-tetrahydronaphthalene (1p)[S2]: The title compound was synthesized according to General procedure B from the starting amine (740 mg, 5.03 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded 1-isothiocyanato-1,2,3,4-tetrahydronaphthalene (929 mg, 4.91 mmol, 98%) as a yellow oil.



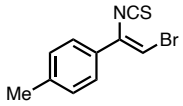
1q[S6]: The title compound was synthesized according to General procedure B from the starting amine (357 mg, 1.99 mmol). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 70:30) afforded **1q** (337 mg, 1.52 mmol, 76%) as a colorless oil.

5. Characterization Data



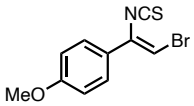
(*Z*)-(2-bromo-1-isothiocyanatovinyl)benzene (**2a**): The title compound was synthesized according to General procedure A from **1a** (31.8 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/$CHCl_3$ = 100:0 to 80:20) afforded **2a** (40.2 mg, 0.167 mmol, 86%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.72 (s, 1H), 7.39–7.42 (m, 3H), 7.46–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 104.6, 125.4, 129.1, 129.9, 133.6, 134.5, 138.5; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for C_9H_6BrNS 238.9399; Found 238.9399.



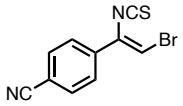
(*Z*)-1-(2-bromo-1-isothiocyanatovinyl)-4-methylbenzene (**2b**): The title compound was synthesized according to General procedure A from **1b** (36.1 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/$CHCl_3$ = 100:0 to 80:20) afforded **2b** (29.4 mg, 0.116 mmol, 57%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 2.36 (s, 3H), 6.64 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 21.4, 103.6, 125.4, 129.8, 130.9, 134.5, 138.4, 140.1; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{10}H_8BrNS$ 252.9555; Found 252.9556.



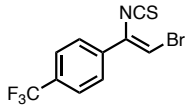
(*Z*)-1-(2-bromo-1-isothiocyanatovinyl)-4-methoxybenzene (**2c**): The title compound was synthesized according to General procedure A from **1c** (39.2 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/$CHCl_3$ = 100:0 to 80:20) afforded **2c** (21.7 mg, 0.0803 mmol, 40%) as a colorless oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 3.83 (s, 3H), 6.57 (s, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) 55.6, 102.5, 114.4, 126.3, 126.9, 134.2, 138.3, 160.8; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{10}H_8NOS$ 268.9504; Found 268.9505.



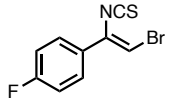
(*Z*)-4-(2-bromo-1-isothiocyanatovinyl)benzonitrile (**2d**): The title compound was synthesized according to General procedure A from **1d** (37.5 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **2d** (33.8 mg, 0.128 mmol, 64%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.93 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 108.4, 113.4, 118.2, 126.0, 132.9, 133.3, 137.6, 140.0; HRMS (APCI, positive) m/z: $[M]^+$ Calcd for $C_{10}H_5BrN_2S$ 263.9351; Found 263.9351.



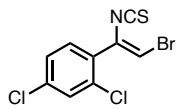
(*Z*)-1-(2-bromo-1-isothiocyanatovinyl)-4-(trifluoromethyl)benzene (**2e**): The title compound was synthesized according to General procedure A from **1e** (47.0 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) and GPC afforded **2e** (23.8 mg, 0.0772 mmol, 38%) as a colorless oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.86 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 107.0, 123.8 (q, J = 273 Hz), 125.9, 126.2 (q, J = 3.7 Hz), 131.7 (q, J = 33.6 Hz), 133.6, 137.0, 139.7; HRMS (APCI, positive) m/z: $[M]^+$ Calcd for $C_{10}H_5BrF_3NS$ 306.9273; Found 306.9272.



(*Z*)-1-(2-bromo-1-isothiocyanatovinyl)-4-fluorobenzene (**2f**): The title compound was synthesized according to General procedure A from **1f** (37.1 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) afforded **2f** (38.4 mg, 0.149 mmol, 73%) as a pale yellow oil.

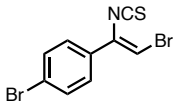
^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.66 (s, 1H), 7.07–7.12 (m, 2H), 7.44–7.49 (m, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 104.4, 116.2 (d, J = 21.7 Hz), 127.5 (d, J = 8.4 Hz), 129.9 (d, J = 3.7 Hz), 133.7, 139.0, 163.5 (d, J = 251 Hz); HRMS (APCI, positive) m/z: $[M]^+$ Calcd for C_9H_5BrFNS 256.9305; Found 256.9304.



(*Z*)-1-(2-bromo-1-isothiocyanatovinyl)-2,4-dichlorobenzene (**2g**): The title compound was synthesized according to General procedure A from **1g** (46.9 mg, 0.20 mmol scale). The

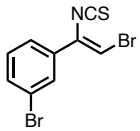
stereoselectivity was determined by ^{1}H NMR in the crude mixture. Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) and GPC afforded **2g** (36.8 mg, 0.119 mmol, 59%) as a white solid and (*E*)-1-(2-bromo-1-isothiocyanatovinyl)-2,4-dichlorobenzene (**2g'**) (4.7 mg, 0.0152 mmol, 8%) as a pale yellow oil.

2g: ^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.42 (s, 1H), 7.28–7.29 (m, 2H), 7.46 (t, *J* = 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 107.7, 127.7, 130.5, 131.3, 131.6, 132.0, 133.5, 136.6, 140.0; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_9H_4BrCl_2$ 306.8619; Found 306.8619.



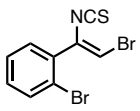
(*Z*)-1-bromo-4-(2-bromo-1-isothiocyanatovinyl)benzene (**2h**): The title compound was synthesized according to General procedure A from **1h** (51.1 mg, 0.21 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) afforded **2h** (53.3 mg, 0.167 mmol, 79%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.74 (s, 1H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 105.3, 124.1, 126.9, 132.3, 132.6, 133.7, 139.2; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_9H_5Br_2NS$ 316.8504; Found 316.8504.



(*Z*)-1-bromo-3-(2-bromo-1-isothiocyanatovinyl)benzene (**2i**): The title compound was synthesized according to General procedure A from **1i** (48.6 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **2i** (42.2 mg, 0.132 mmol, 66%) as a colorless oil.

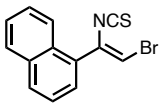
^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.77 (s, 1H), 7.26–7.29 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 106.2, 123.2, 124.1, 128.5, 130.6, 132.8, 133.3, 135.5, 139.4; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_9H_5Br_2NS$ 316.8504; Found 316.8503.



(*Z*)-1-bromo-2-(2-bromo-1-isothiocyanatovinyl)benzene (**2j**): The title compound was synthesized according to General procedure A from **1j** (48.4 mg, 0.20 mmol scale). The

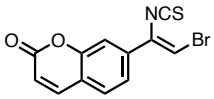
stereoselectivity was determined by ^{1}H NMR in the crude mixture. Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) and GPC afforded **2j** (24.6 mg, 0.0771 mmol, 40%) as a colorless oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.38 (s, 1H), 7.26–7.30 (m, 1H), 7.32–7.37 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 107.0, 122.1, 127.9, 130.9, 131.3, 133.8, 133.9, 135.6, 139.8; HRMS (APCI, positive) m/z: $[M]^+$ Calcd for $C_9H_5Br_2NS$ 316.8504; Found 316.8504.



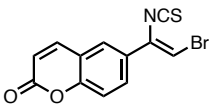
(*Z*)-1-(2-bromo-1-isothiocyanatovinyl)naphthalene (**2k**): The title compound was synthesized according to General procedure A from **1k** (47.0 mg, 0.22 mmol scale). The stereoselectivity was determined by ^{1}H NMR in crude mixture. Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 95:5) afforded the target product as the *E*/*Z* mixture (54.9 mg, 0.189 mmol, 86%). Furthermore, GPC afforded **2k** (30.6 mg, 0.106 mmol, 48%) as a white solid and (*E)*-1-(2-bromo-1-isothiocyanatovinyl)naphthalene (**2k'**) (3.0 mg, 0.0103 mmol, 5%) as a pale yellow oil.

2k: ^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.41 (s, 1H), 7.42–7.48 (m, 2H), 7.52–7.62 (m, 2H), 7.87–7.92 (m, 2H), 8.02 (d, J = 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 106.0, 124.6, 125.2, 126.7, 127.3, 127.5, 128.8, 130.4, 130.6, 132.3, 133.8, 134.1, 139.8; HRMS (APCI, positive) m/z: $[M + H]^+$ Calcd for $C_{13}H_9BrNS$ 289.9634; Found 289.9634.



(*Z*)-7-(2-bromo-1-isothiocyanatovinyl)-2*H*-chromen-2-one (**2l**): The title compound was synthesized according to General procedure A from **1l** (46.8 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) and GPC afforded **2l** (40.7 mg, 0.132 mmol, 65%) as a white solid.

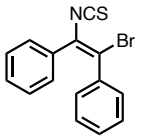
^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.48 (d, J = 9.5 Hz, 1H), 6.92 (s, 1H), 7.41 (dd, J = 8.0, 1.5 Hz, 1H), 7.45 (d, J = 1.5 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 107.6, 113.8, 117.9, 119.7, 121.3, 128.6, 133.4, 136.8, 139.8, 142.6, 154.3, 160.2; HRMS (APCI, positive) m/z: $[M + H]^+$ Calcd for $C_{13}H_9BrNS$ 307.9375; Found 307.9376.



(*Z*)-6-(2-bromo-1-isothiocyanatovinyl)-2*H*-chromen-2-one (**2m**): The title compound was synthesized according to General procedure A from **1m** (46.4 mg, 0.20 mmol scale). Purified by

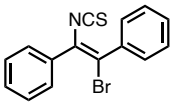
flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) and GPC afforded **2m** (34.0 mg, 0.110 mmol, 55%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.50 (d, *J* = 9.5 Hz, 1H), 6.80 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.61–7.65 (m, 2H), 7.74 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 105.7, 117.9, 118.0, 119.2, 124.9, 128.6, 130.2, 133.1, 139.6, 142.9, 154.6, 160.0; HRMS (APCI, positive) *m*/*z*: $[M + H]^+$ Calcd for $C_{13}H_9BrNS$ 307.9375; Found 307.9376.



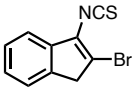
(*E*)-(1-bromo-2-isothiocyanatoethene-1,2-diyl)dibenzene (**2n**): The title compound was synthesized according to General procedure A from **1n** (45.8 mg, 0.19 mmol scale). The stereoselectivity was determined by ^{1}H NMR in crude mixture. Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 95:5) afforded the target products as *E*/*Z* mixture (50.6 mg, 0.160 mmol, 84%). Furthermore, GPC afforded **2n** (26.7 mg, 0.0844 mmol, 44%) as a white solid and (*Z*)-(1-bromo-2-isothiocyanatoethene-1,2-diyl)dibenzene (**2n'**) (6.8 mg, 0.0218 mmol, 11%) as a white solid. The stereoselectivity was determined by the yield of each compound.

2n: ^{1}H NMR ($CDCl_3$ 500 MHz) δ 7.15–7.26 (m, 10H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 121.3, 128.4, 128.6, 128.9, 129.1, 129.2, 129.9, 130.3, 134.6, 137.1, 137.5; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{15}H_{10}BrNS$ 314.9712; Found 314.9712.



(*Z*)-(1-bromo-2-isothiocyanatoethene-1,2-diyl)dibenzene (**2n'**):

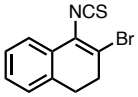
^{1}H NMR ($CDCl_3$ 500 MHz) δ 7.36–7.50 (m, 6H), 7.58–7.64 (m, 4H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 122.6, 128.2, 128.4, 128.6, 128.7, 129.3, 129.6, 130.3, 136.6, 137.1, 137.9; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{15}H_{10}BrNS$ 314.9712; Found 314.9712.



2-bromo-3-isothiocyanato-1*H*-indene (**2o**): AIBN (6.6 mg, 0.040 mmol, 0.20 equiv.) and NBS (72.4 mg, 0.407 mmol) were added to a dried reaction tube with a stirring bar. The tube was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). Tetrachloromethane (4.0 mL) and **1o** (106 mg, 0.60 mmol, 3.0 equiv.) were added to the tube and the mixture was stirred for 12 h at 90 °C. The crude mixture was quenched by saturated $Na_2S_2O_3$ *aq.* and extracted with

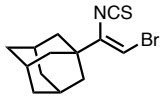
$CHCl_3$ (3 mL × 3). The organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) and GPC provided **2o** (23.6 mg, 0.0936 mmol, 46%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 3.64 (s, 2H), 7.25–7.29 (m, 1H), 7.32–7.38 (m, 2H), 7.42 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 42.5, 117.8, 118.3, 123.9, 126.6, 127.4, 130.9, 139.4, 140.3, 141.0; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{10}H_6BrNS$ 250.9399; Found 250.9400.



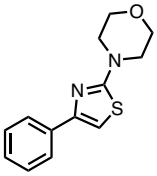
3-bromo-4-isothiocyanato-1,2-dihydronaphthalene (**2p**): AIBN (6.5 mg, 0.040 mmol, 0.20 equiv.) and NBS (71.9 mg, 0.404 mmol) were added to a dried reaction tube with a stirring bar. The tube was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). Tetrachloromethane (4.0 mL) and **1p** (113 mg, 0.60 mmol, 3.0 equiv.) were added to the tube and the mixture was stirred for 12 h at 90 °C. The crude mixture was quenched by saturated $Na_2S_2O_3$ *aq.* and extracted with $CHCl_3$ (3 mL × 3). The organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) and GPC provided **2p** (8.4 mg, 0.0316 mmol, 16%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 2.87–2.97 (m, 4H), 7.13 (d, J = 6.0 Hz, 1H), 7.24–7.30 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 28.6, 33.8, 122.1, 122.9, 127.3, 127.8, 128.9, 130.3, 133.9 (Two sp^2 signals were not observed because of overlapping); HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{11}H_8BrNS$ 264.9555; Found 264.9554.



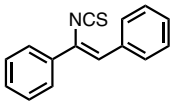
2q: The title compound was synthesized according to General procedure A from **1q** (44.9 mg, 0.20 mmol scale). Purified by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 80:20) afforded **2q** (37.2 mg, 0.125 mmol, 61%) as a white solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 1.64–1.69 (m, 3H), 1.72–1.76 (m, 9H), 2.07 (brs, 3H), 6.03 (s, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 28.2, 36.4, 40.1, 41.0, 101.9, 136.7, 144.0; HRMS (APCI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{13}H_{16}BrNS$ 297.0181; Found 297.0182.



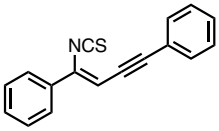
4-(4-phenylthiazol-2-yl)morpholine (**3**)[S7]: Alkenyl isothiocyanate **2a** (51.5 mg, 0.21 mmol, 1.0 equiv.) and MeCN (1.0 mL) were added to a dried reaction tube with a stirring bar. Then, morpholine (17.4 mg, 0.20 mmol, 1.0 equiv.) and DIPEA (53.1 mg, 0.41 mmol, 2.0 equiv.) in MeCN (1.0 mL) were added to the tube slowly and the mixture was stirred for 10 min at rt. The crude mixture was quenched by H_2O and extracted with EtOAc (3 mL × 3). The organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 95:5 to 50:50) afforded **3** (15.7 mg, 0.0637 mmol, 32%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 3.54 (t, *J* = 5.0 Hz, 4H), 3.85 (t, *J* = 5.0 Hz, 4H) 6.80 (s, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.36–7.39 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 48.7, 66.4, 101.8, 126.2, 127.8, 128.7, 135.1, 152.0, 171.3; HRMS (ESI, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2OS$ 247.0905; Found 247.0903.



(*Z*)-(1-isothiocyanatoethene-1,2-diyl)dibenzene (**4**): To a dried reaction tube with a stirring bar was added $Pd(dba)_2$ (5.3 mg, 0.0092 mmol, 5.0 mol%), PPh_3 (5.6 mg, 0.021 mmol, 10 mol%), $NaHCO_3$ (50.6 mg, 0.60 mmol, 3.0 equiv.), and phenylboronic acid (36.4 mg, 0.30 mmol, 1.5 equiv.). The tube was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle). Toluene (1.0 mL), EtOH (0.20 mL), and H_2O (0.30 mL) and **2a** (48.9 mg, 0.20 mmol, 1.0 equiv.) were added to the tube and the mixture was stirred for 7 h at 80 °C. The crude mixture was quenched by H_2O and extracted with EtOAc (3 mL × 3). The organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/$CHCl_3$ = 100:0 to 90:10) provided **4** (32.6 mg, 0.137 mmol, 67%) as a pale yellow oil.

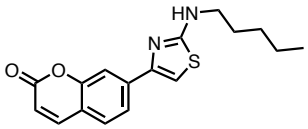
^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.75 (s, 1H), 7.31–7.46 (m, 6H), 7.60–7.62 (m, 2H), 7.70 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 124.4, 125.5, 126.9, 128.86, 128.88, 128.92, 129.0, 129.2, 134.4, 135.5, 136.3; HRMS (APCI, positive) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{12}NS$ 238.0685; Found 238.0684.



(*Z*)-(1-isothiocyanatobut-1-en-3-yne-1,4-diyl)dibenzene (**5**): To a dried reaction tube with a stirring bar was added $Pd(PPh_3)_4$ (11.0 mg, 0.0095 mmol, 5.0 mol%), PPh_3 (10.7 mg, 0.041 mmol, 20 mol%), K_2CO_3 (57.8 mg, 0.42 mmol, 2.0 equiv.), and CuI (3.7 mg, 0.019 mmol, 10 mol%). The tube was filled with nitrogen by employing the usual Schlenk technique (evacuate-refill cycle).

Dioxane (1.0 mL), **2a** (48.5 mg, 0.20 mmol, 1.0 equiv.), and phenylacetylene (41.7 mg, 0.408 mmol, 2.0 equiv.) were added to the tube and the mixture was stirred for 16 h at 60 °C. The crude mixture was passed through a short pad of silica gel and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/$CHCl_3$ = 100:0 to 80:20) afforded **5** (15.9 mg, 0.0608 mmol, 30%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 6.42 (s, 1H), 7.35–7.42 (m, 6H), 7.57–7.62 (m, 4H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 86.1, 101.9, 106.9, 122.9, 125.2, 128.6, 129.0, 129.1, 130.0, 131.7, 133.2, 137.4, 139.6; HRMS (APCI, positive) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{12}NS$ 262.0685; Found 262.0685.



7-(2-(pentylamino)thiazol-4-yl)-2*H*-chromen-2-one (**6**): Alkenyl isothiocyanate **2m** (61.9 mg, 0.20 mmol, 1.0 equiv.) and CH_2Cl_2 (1.0 mL) were added to a dried reaction tube with a stirring bar. Then, DIPEA (52.8 mg, 0.41 mmol, 2.0 equiv.) and pentane-1-amine (21.7 mg, 0.25 mmol, 1.2 equiv.) were added to the tube slowly and the mixture was stirred for 1 h at rt. The crude mixture was concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/EtOAc = 85:15 to 50:50) and ($CHCl_3$/EtOAc = 95:5 to 80:20) afforded **6** (19.5 mg, 0.0620 mmol, 31%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 0.92 (t, *J* = 7.5 Hz, 3H), 1.32–1.43 (m, 4H), 1.64–1.71 (m, 2H), 3.28–3.33 (m, 2H), 5.34 (t, *J* = 4.5 Hz, 1H), 6.39 (d, *J* = 9.0 Hz, 1H), 6.86 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.68–7.73 (m, 2H), 7.78 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 14.1, 22.5, 29.1, 29.2, 46.2, 103.6, 114.1, 116.1, 118.1, 122.2, 128.0, 138.7, 143.3, 149.8, 154.6, 161.2, 169.8. HRMS (APCI, positive) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2S$ 315.1162; Found 315.1161.

6. Photophysical Study

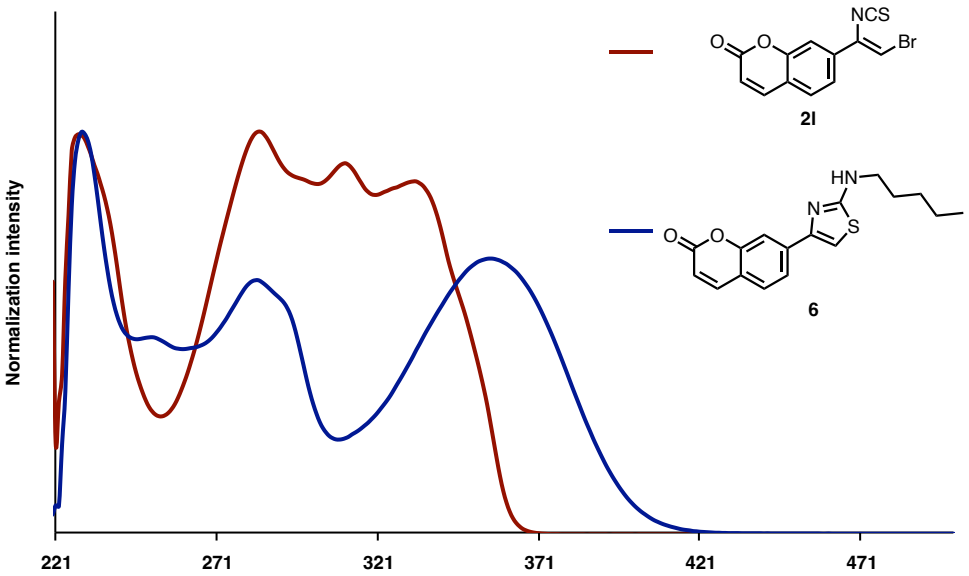


Figure S 3. UV-Vis absorption spectra of **2l** (red line) and **6** (blue line).

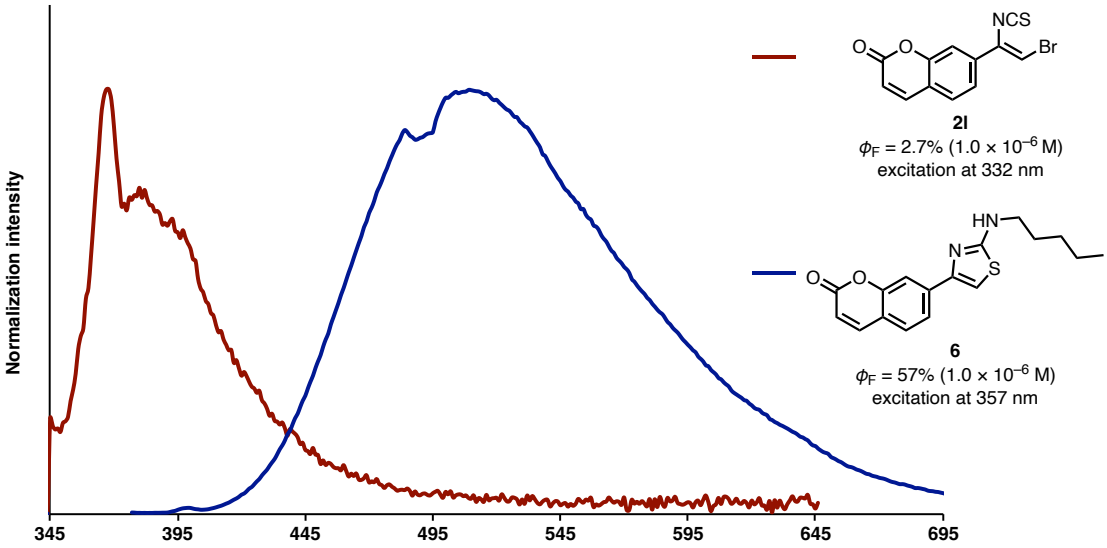


Figure S 4. Fluorescence spectra of **2l** (red line) and **6** (blue line).

7. X-ray Crystallographic Analysis

Single crystal X-ray diffraction (SCXRD)

SCXRD data was collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix6000HE hybrid photon counting detector using Cu Kα radiation (λ = 1.54184 Å). The diffraction profiles were integrated using the CrysAlisPro software. Crystal structures were solved via direct methods using the SHELXT program and refined with SHELXL.[S8,S9] All non-H atoms were refined using anisotropic thermal parameters. All calculations were performed using the Olex2 crystallographic software package.[S10]

Table S1. Crystallographic data and refinement details for **2k**.

	2k
CCDC	2343587
formula	$C_{13}H_8BrNS$
fw	290.17
T (K)	150
λ (A)	1.54184
cryst syst	Monoclinic
space group	$P2_1/c$
a (Å)	11.7154(2)
b (Å)	14.3463(3)
c (Å)	7.0036(1)
α (deg)	90
β (deg)	102.820(2)
γ (deg)	90
V (Å^3)	1147.77(4)
Z	4
D_{calc} (g / cm^3)	1.679
μ (mm^{-1})	6.314
F(000)	576.0
cryst size (mm)	0.50 × 0.05 × 0.05
GOF on F^2	1.114
$R1$, wR_2 [$I>2\sigma(I)$]	0.0363, 0.0985
$R1$, wR_2 [all data]	0.0380, 0.0999

ORTEP drawing

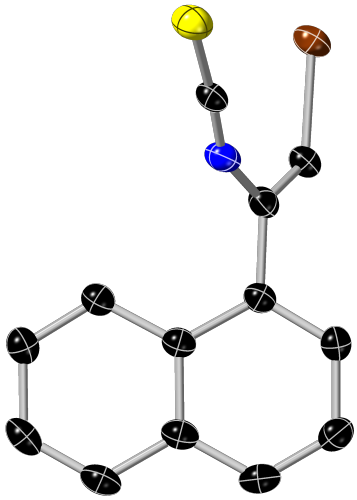


Figure S 5. ORTEP drawing of **2k**.

Table S2. Crystallographic data and refinement details for **2n**.

	2n
CCDC	2343588
formula	$C_{15}H_{10}BrNS$
fw	316.21
T (K)	150
λ (A)	1.54184
cryst syst	Orthorhombic
space group	*Pbca*
a (Å)	7.4897(2)
b (Å)	18.6819(4)
c (Å)	19.2474(4)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2693.13(11)
Z	8
D_{calc} (g / cm^3)	1.560
μ (mm^{-1})	5.435
F(000)	1264.0
cryst size (mm)	0.3 × 0.3 × 0.01
GOF on F^2	0.977
$R1$, wR_2 [$I>2\sigma(I)$]	0.0365, 0.0392
$R1$, wR_2 [all data]	0.1118, 0.1163

ORTEP drawing

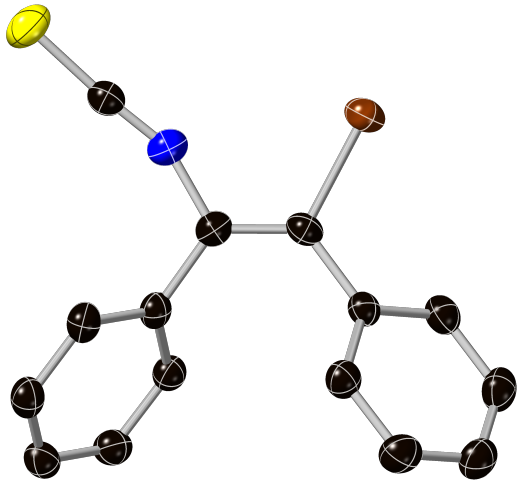


Figure S 6. ORTEP drawing of **2n**.

8. Labelling of Phosphatidylethanolamine within Biomembranes by 2l

General

Unless otherwise noted, all commercial reagents were used as received. Phospholipids used for membrane studies were purchased from Avanti Polar Lipids, Inc. D-Glucose used for membrane studies was purchased from FUJIFILM Wako Pure Chemical Co. $CHCl_3$ and CH_3OH used for membrane studies were purchased from Kanto Chemical Co. Phase-contrast and fluorescence microscopy observations were performed on an Olympus model IX73 inverted microscope, using a U-FUW mirror unit (excitation filter: λ = 340–390 nm, emission filter: λ = 420 nm) for fluorescence imaging. A coverslip was placed over the specimen through a 0.1 mm thick silicon-based spacer on a microscope slide. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed in the reflector mode on a JEOL model JMS-S3000 spectrometer using α-cyano-4-hydroxycinnamic (Tokyo Chemical Industry Co.) as a matrix.

Methods

Preparation of giant unilamellar vesicles for phase-contrast and fluorescence microscopy

To a CH_3Cl dispersion (20 μL) of 1,2-dihexadecanoyl-*sn*-glycero-3-phosphoethanolamine (DPPE, 10 nmol) and **2l** (10 nmol) were added *N*,*N*-diisopropylethylamine (1.0 μL, 5.7 μmol) and the mixture was incubated for 40 min at room temperature. The organic solvent was removed by the N_2 gas flow, and the resulting film was redispersed in CH_3OH (10 μL). Then, 1.0 μL of the dispersion was mixed with a CH_3Cl dispersion (19 μL) of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC, 38 nmol) and a CH_3OH solution (10 μL) of D-glucose (40 nmol). The mixture was slowly evaporated to dryness under the N_2 gas flow at room temperature, and the resulting film was further dried under vacuum for 2 h. A lipid thin film developed on the interior surface of the test tube was hydrated with distilled water (5.0 μL) for 10 min at 55 °C. Then, distilled water (195 μL) was added to the test tube and the mixture was further incubated for 15 h at 37 °C to obtain a dispersion of giant unilamellar vesicles (GUVs) ([DOPC] = 190 μM, [DPPE] = 10 μM, [**2l**] = 10 μM, [D-glucose] = 200 μM).

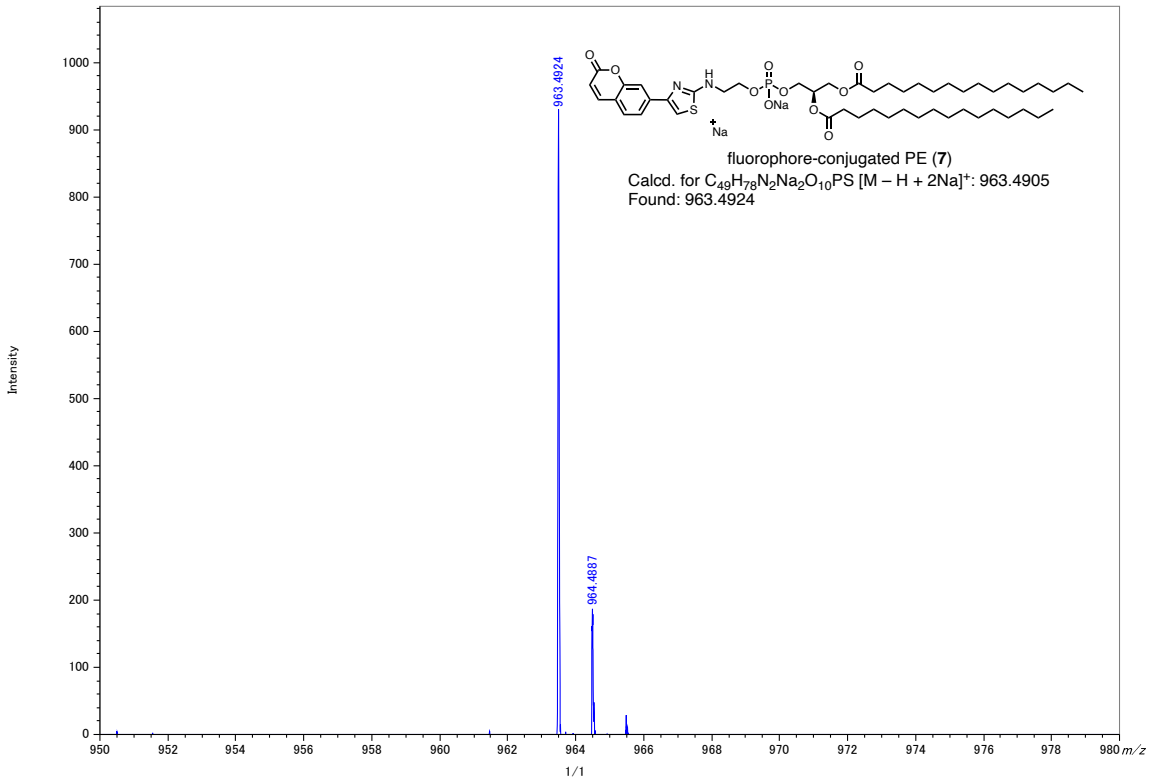


Figure S 7. High-resolution MALDI-TOF mass spectrum of fluorophore-conjugated PE (**7**) using α-cyano-4-hydroxycinnamic as a matrix.

9. Reference

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10. ^{1}H and ^{13}C NMR Spectra

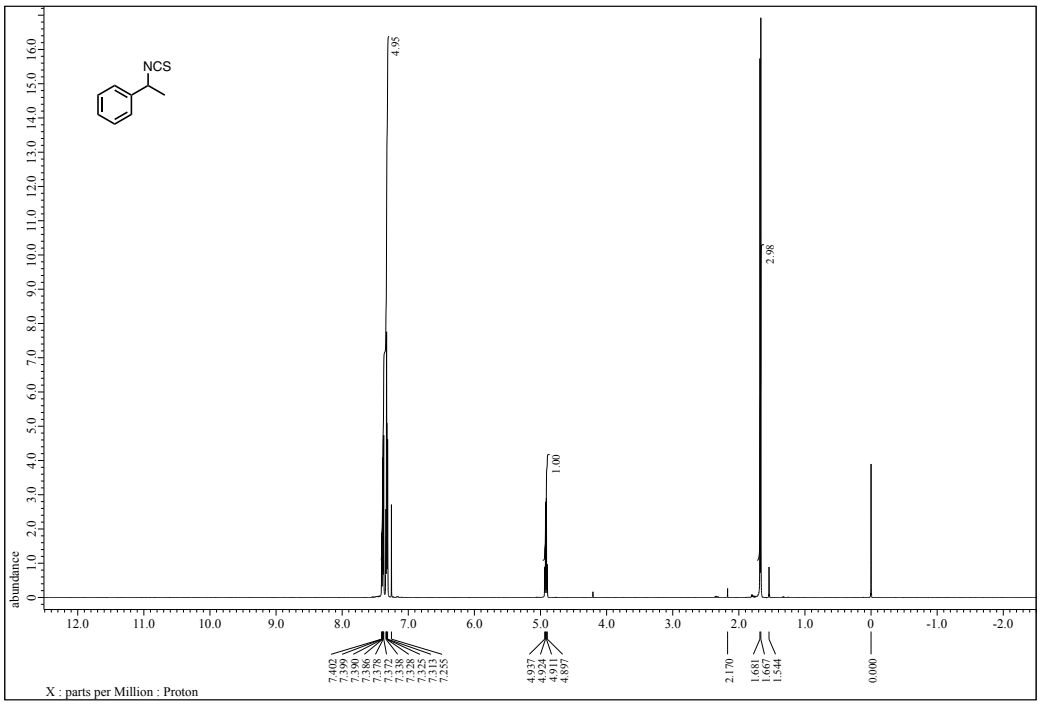

Figure S 8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1a**.

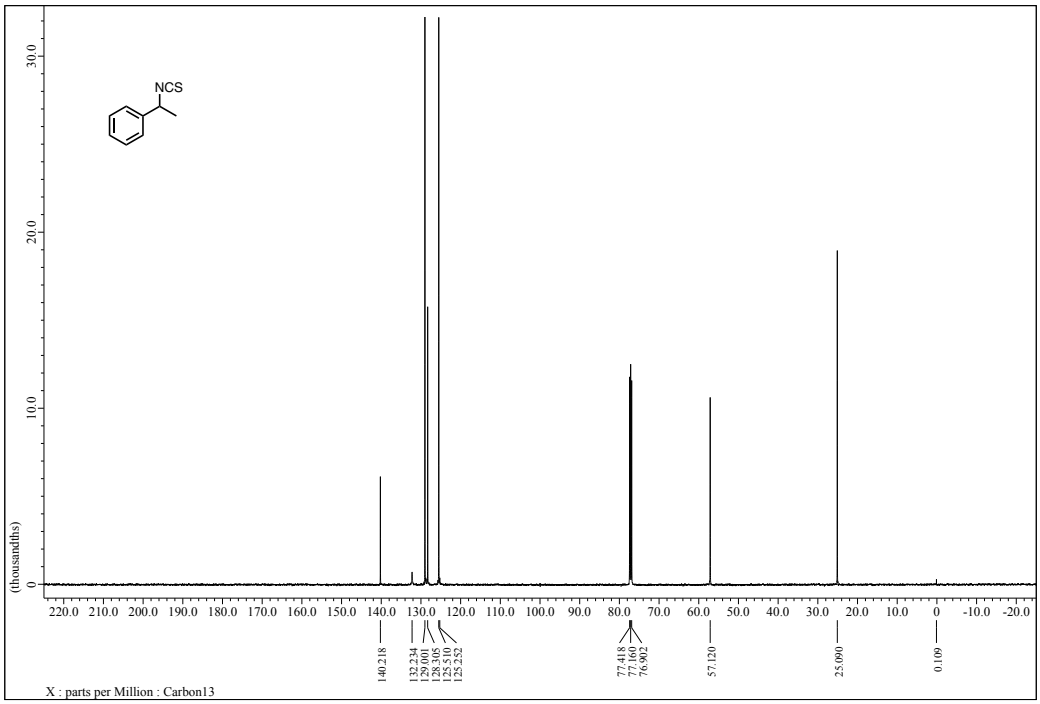

Figure S 9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1a**.

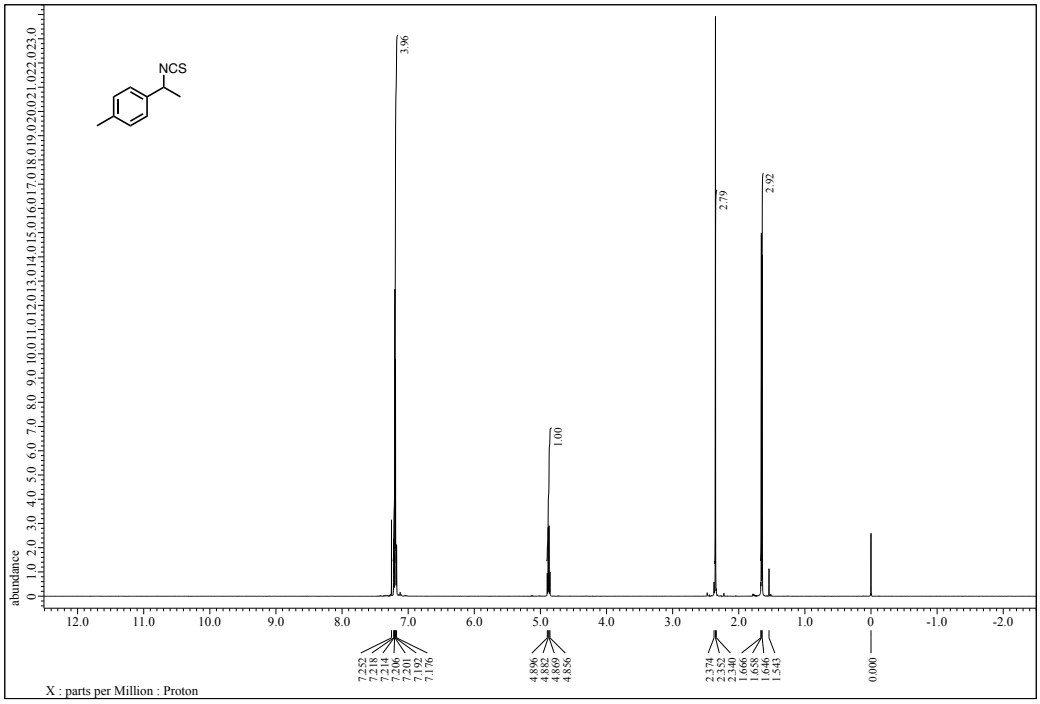

Figure S 10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1b**.

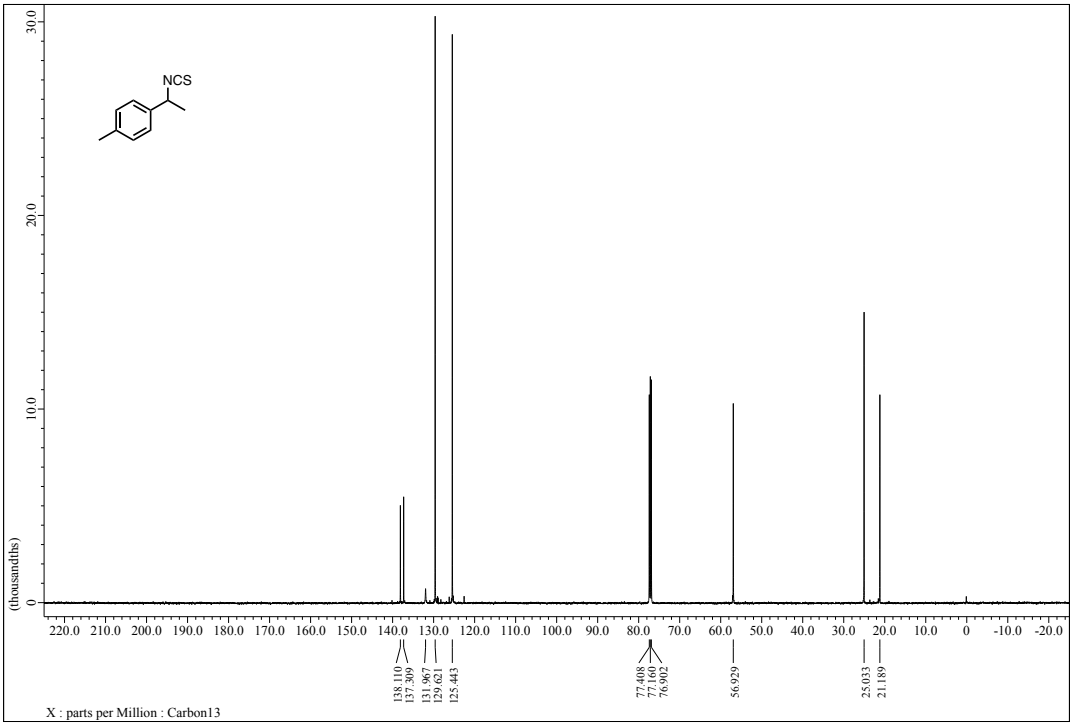

Figure S 11. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1b**.

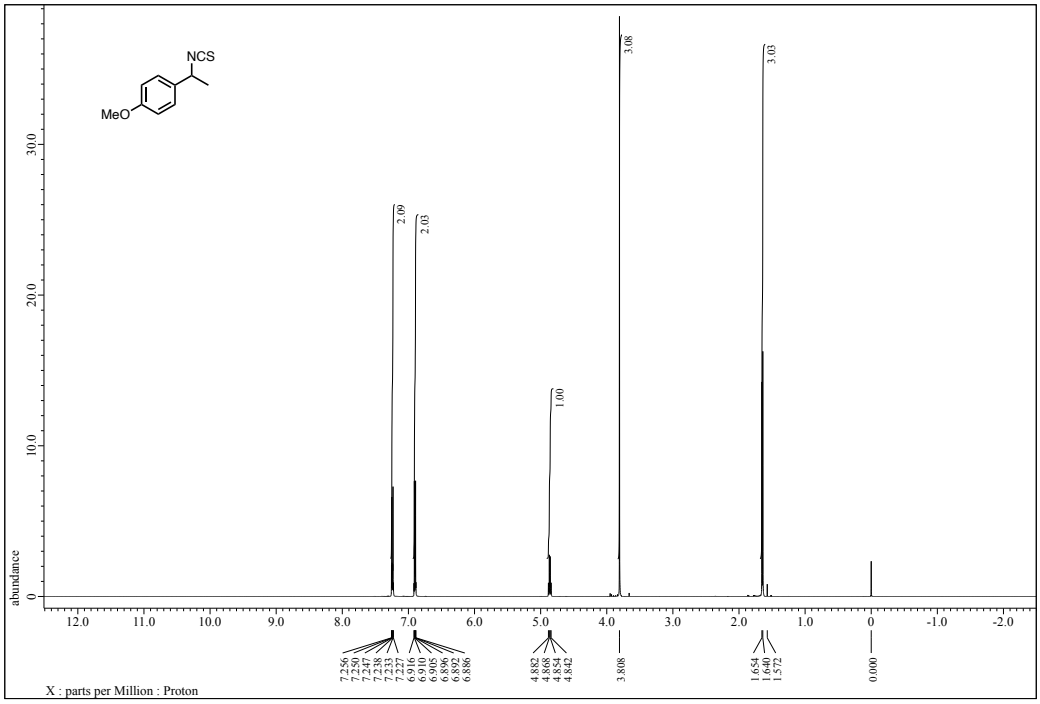

Figure S 12. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1c**.

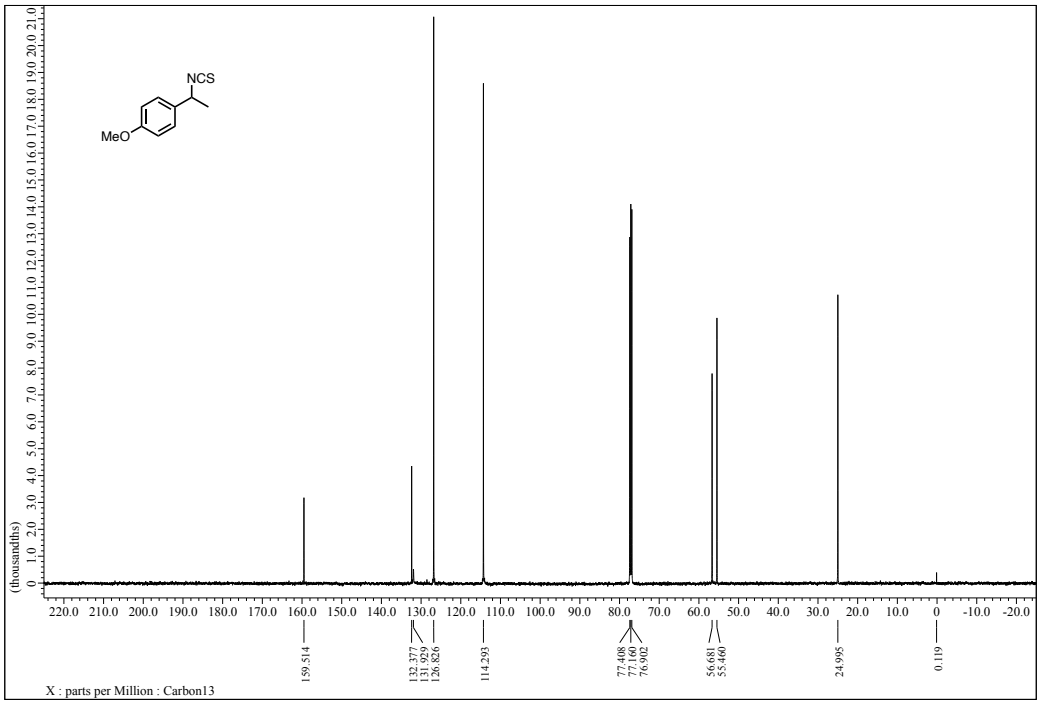

Figure S 13. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1c**.

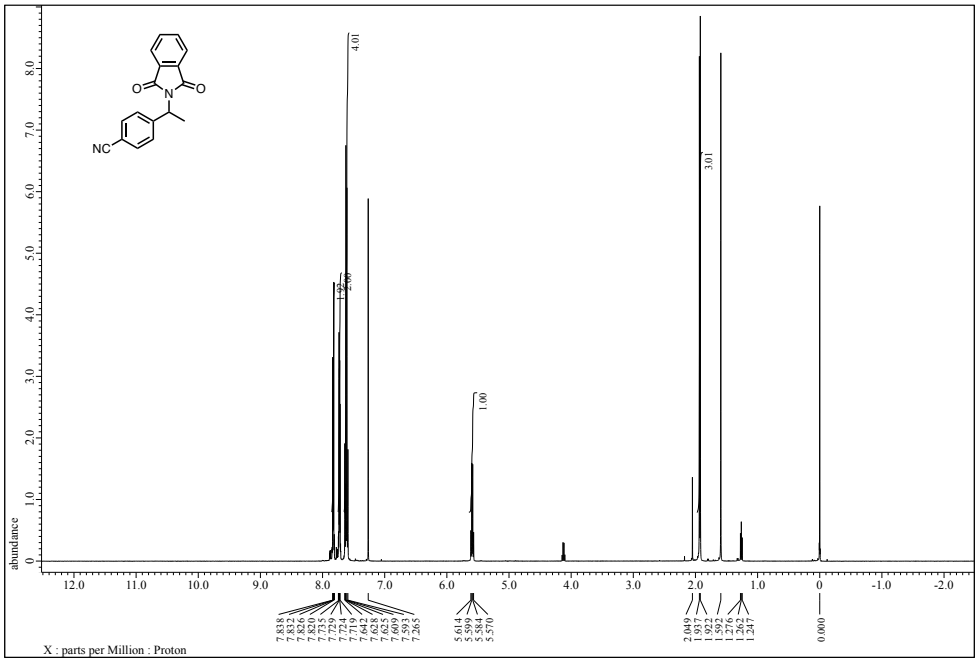

Figure S 14. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-(1-(1,3-dioxoisoindolin-2-yl)ethyl)benzonitrile.

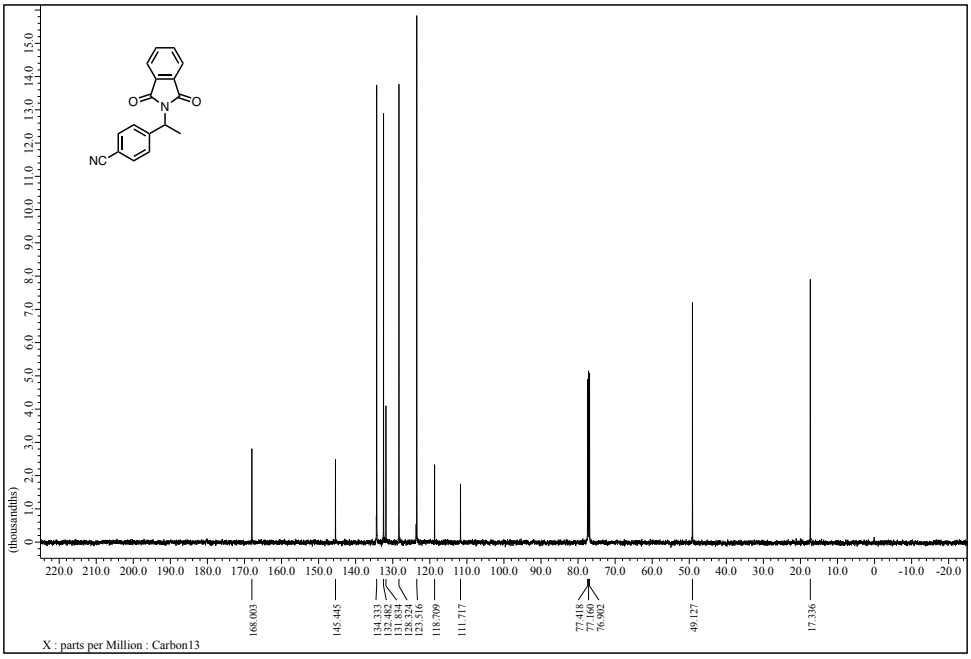

Figure S 15. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-(1-(1,3-dioxoisoindolin-2-yl)ethyl)benzonitrile.

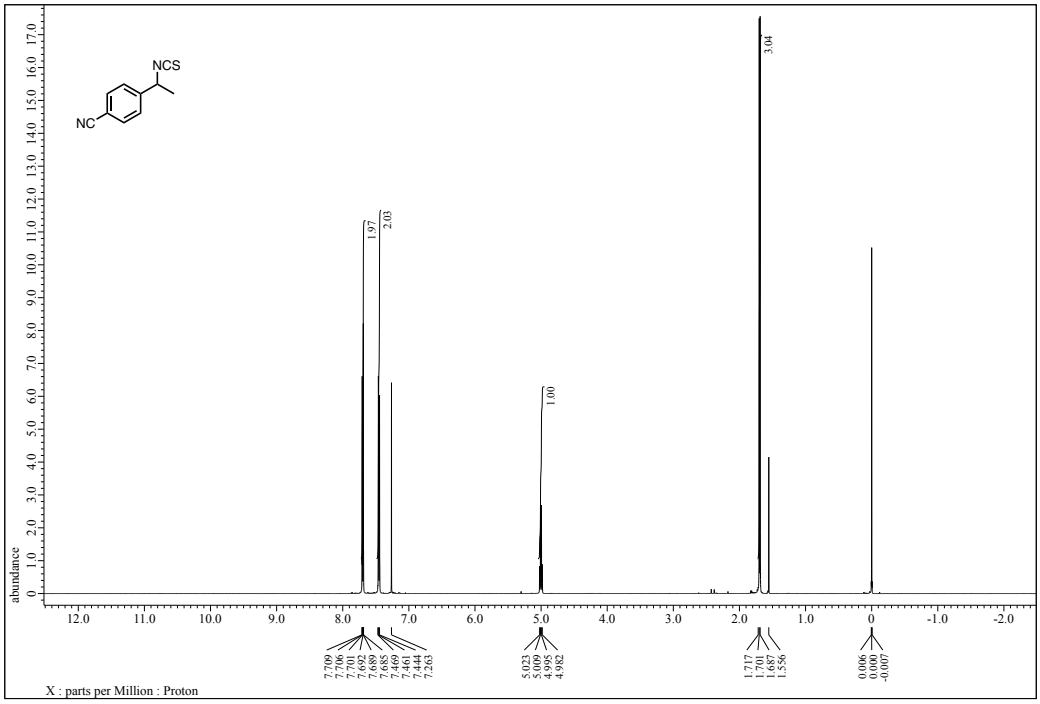

Figure S 16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1d**.

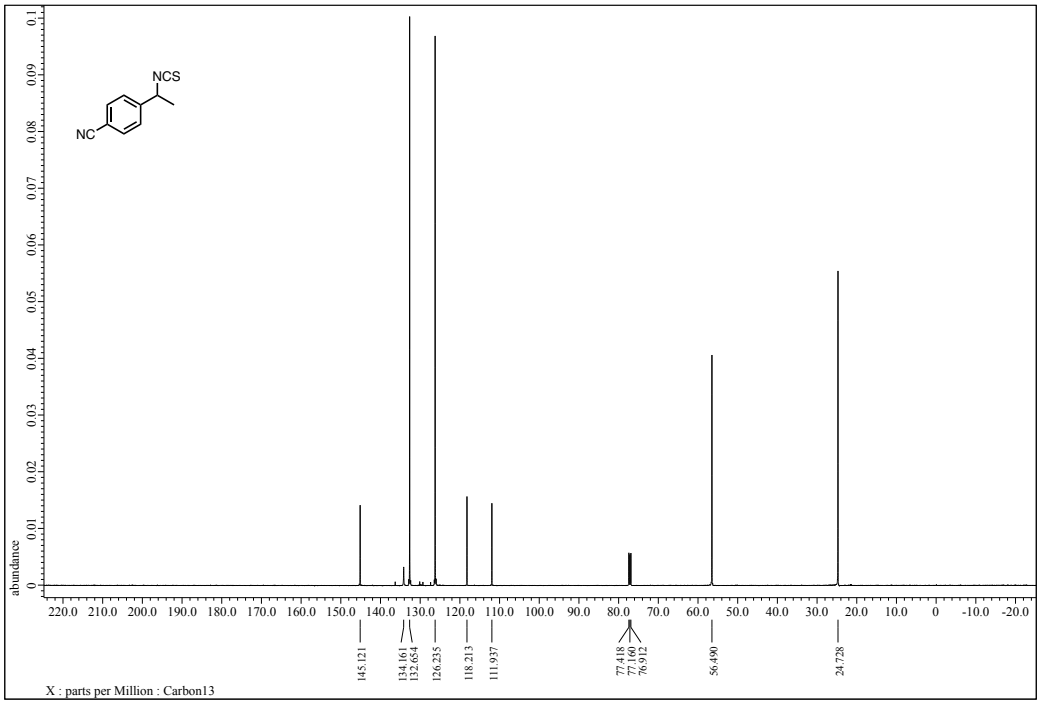

Figure S 17. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1d**.

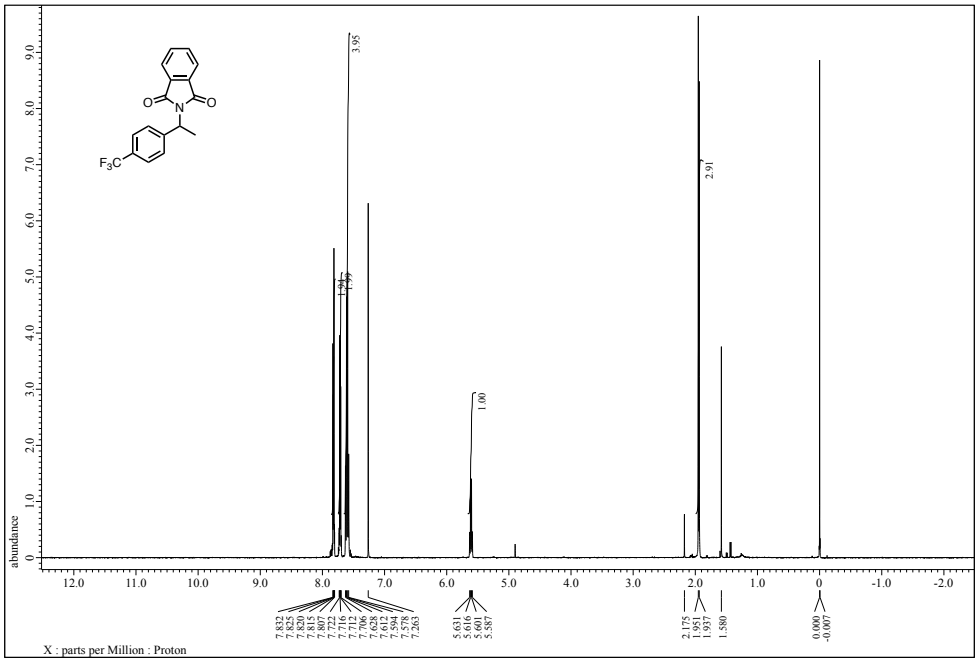

Figure S 18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2-(1-(4-(trifluoromethyl)phenyl)ethyl)isoindoline-1,3-dione.

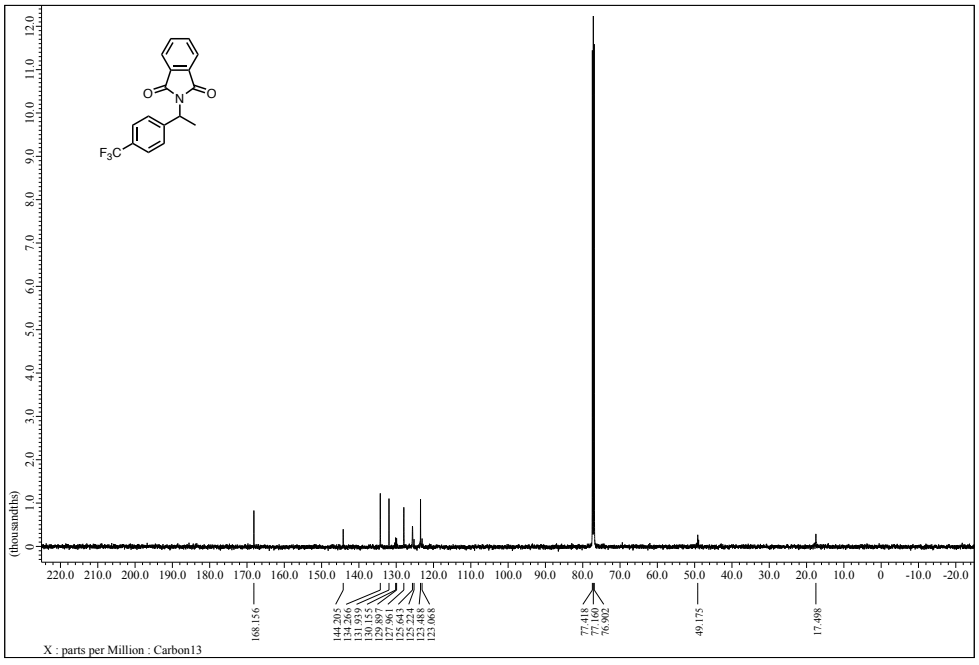

Figure S 19. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2-(1-(4-(trifluoromethyl)phenyl)ethyl)isoindoline-1,3-dione.

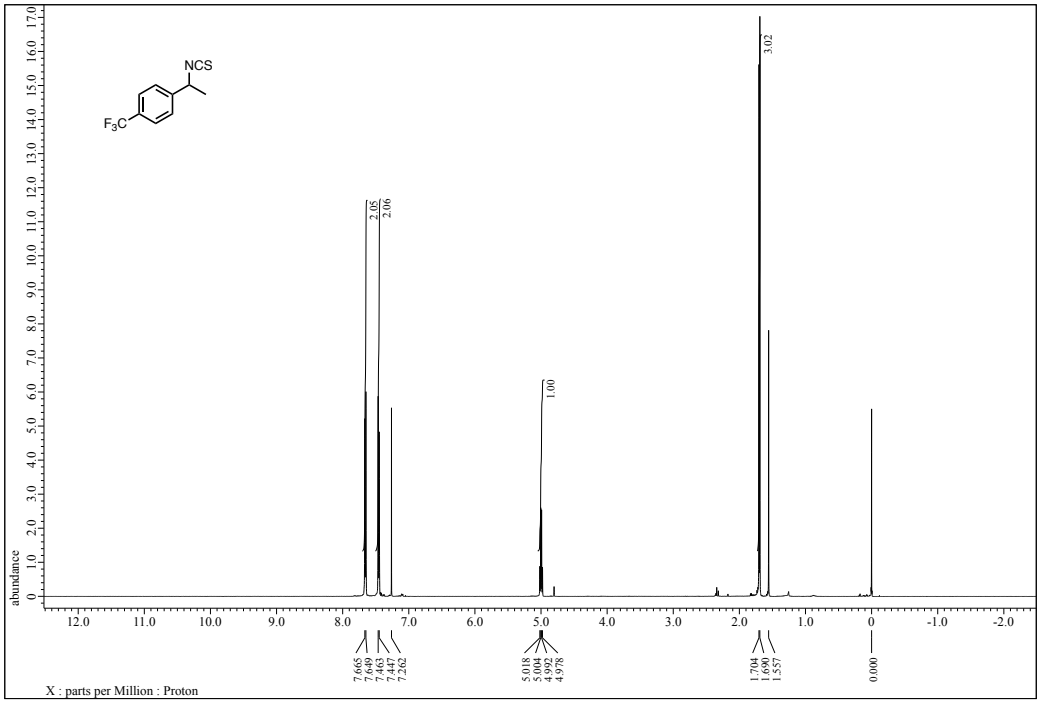

Figure S 20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1e**.

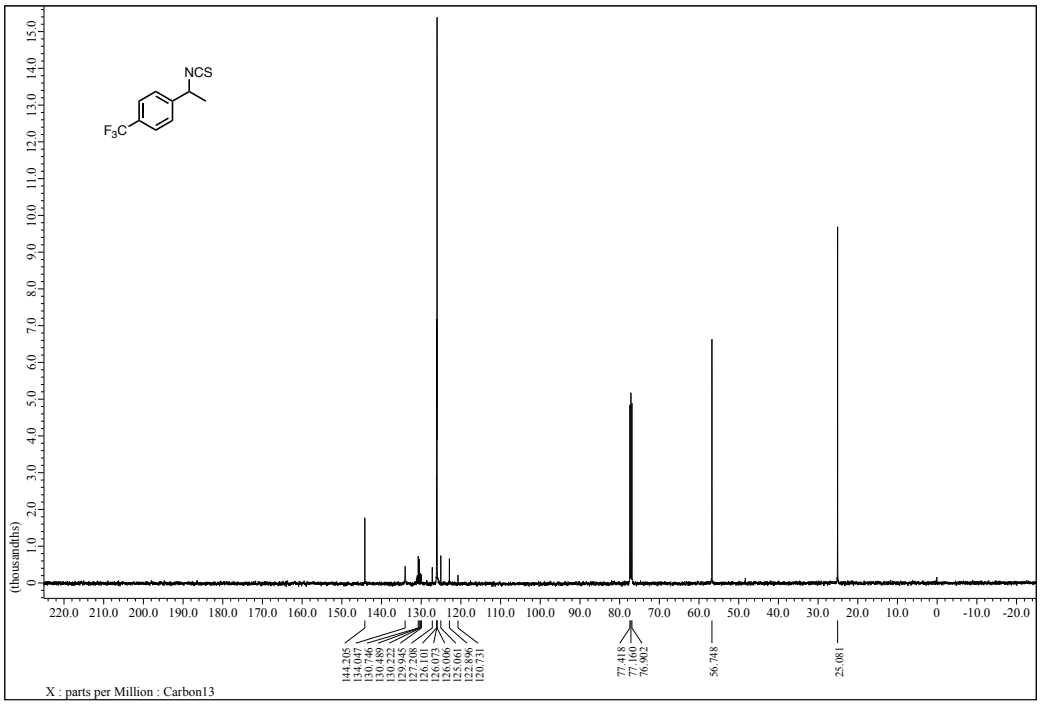

Figure S 21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1e**.

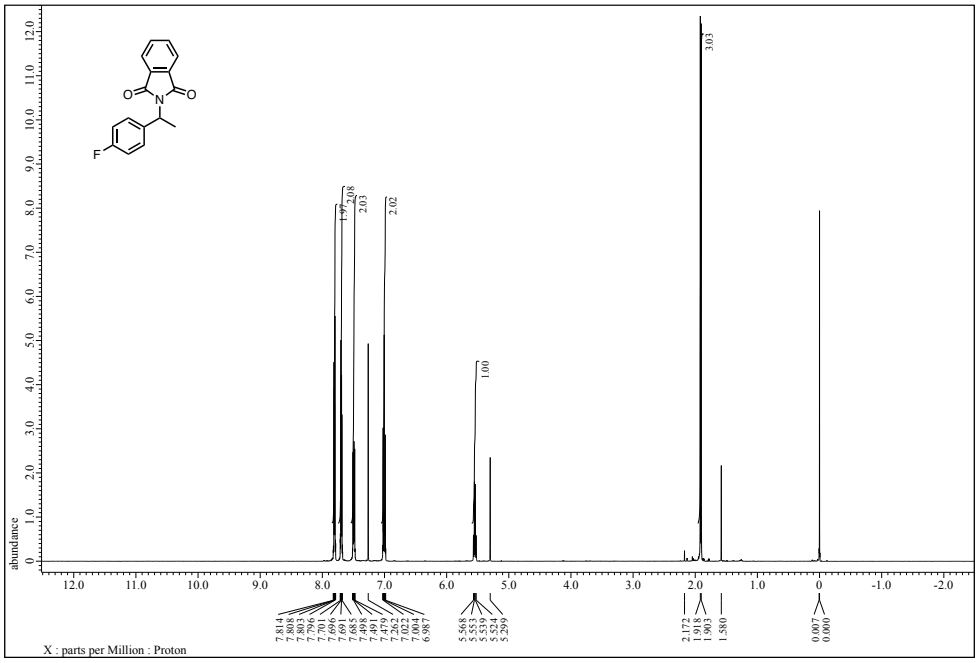

Figure S 22. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2-(1-(4-fluorophenyl)ethyl)isoindoline-1,3-dione.

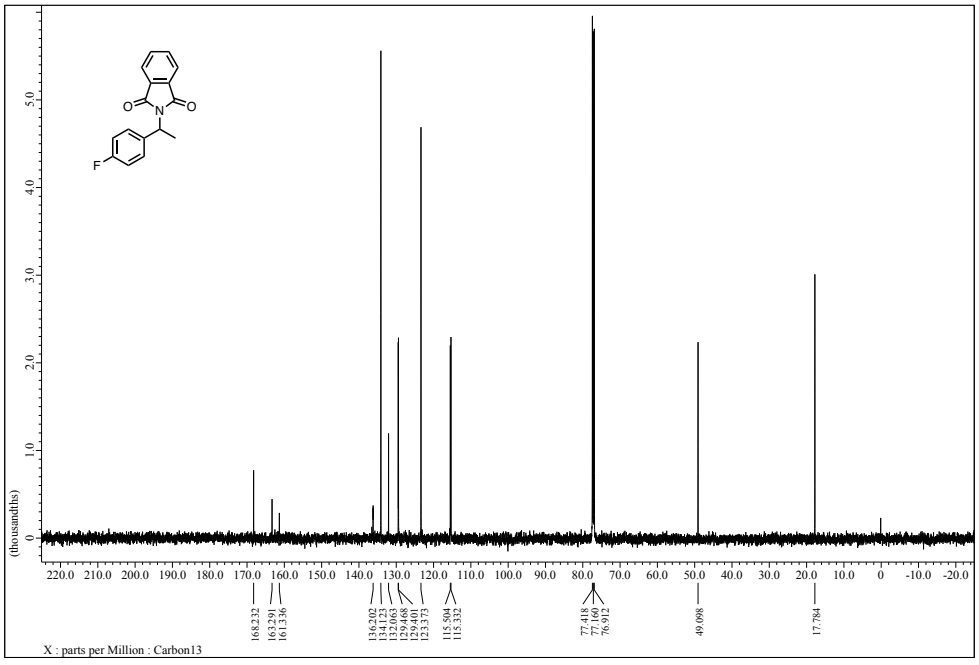

Figure S 23. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2-(1-(4-fluorophenyl)ethyl)isoindoline-1,3-dione.

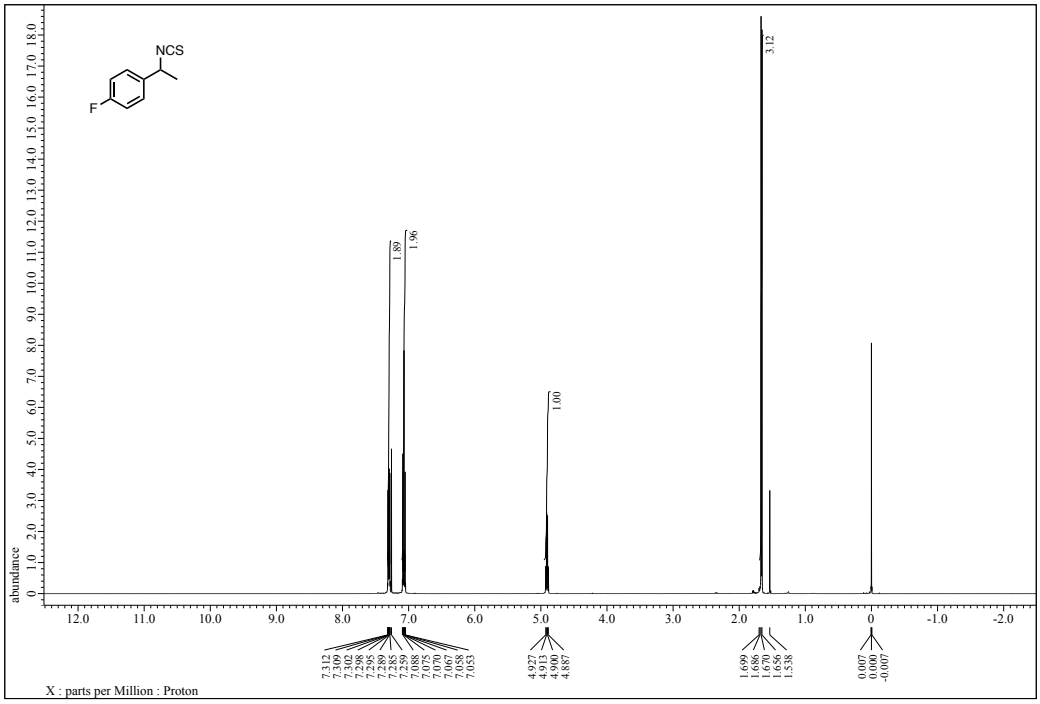

Figure S 24. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1f**.

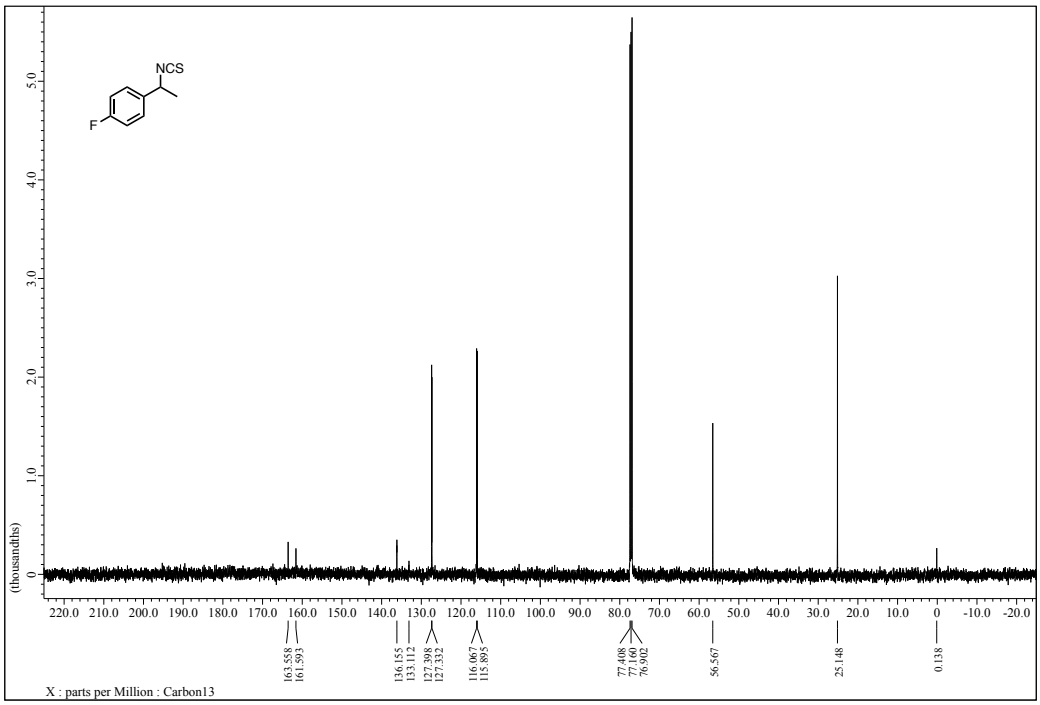

Figure S 25.^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1f**.

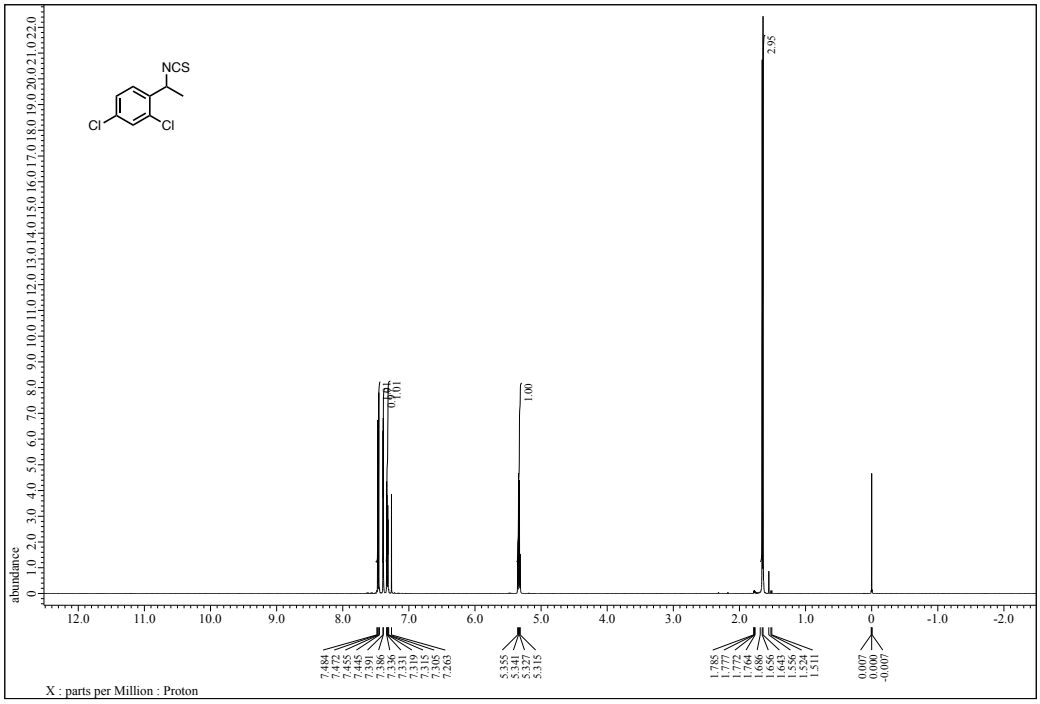

Figure S 26. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1g**.

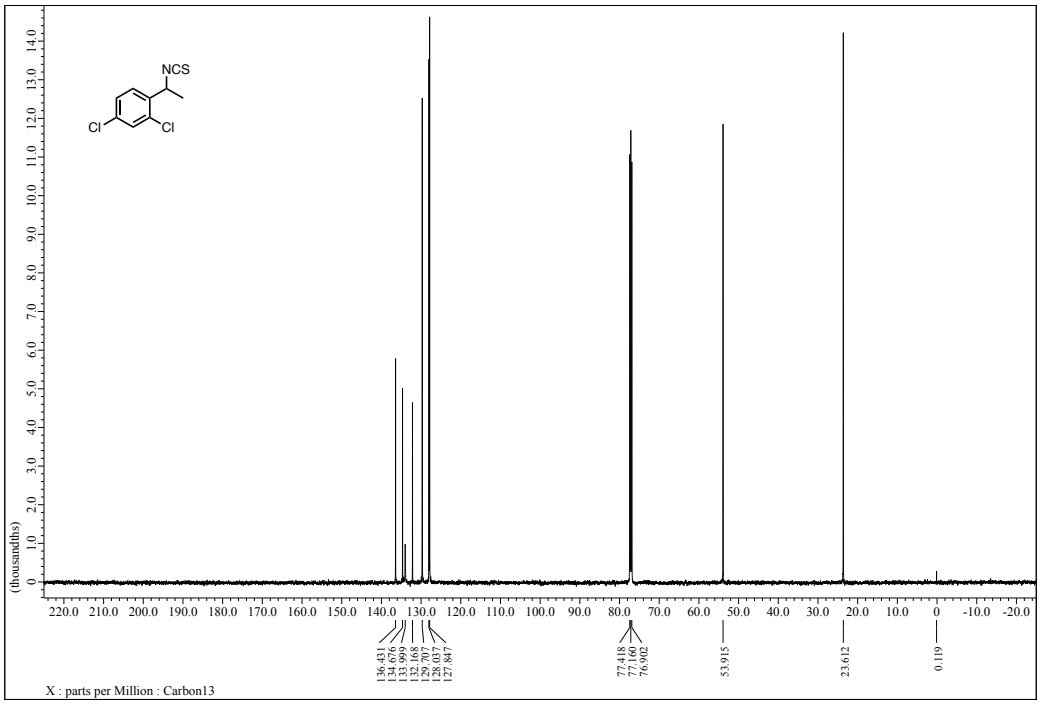

Figure S 27. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1g**.

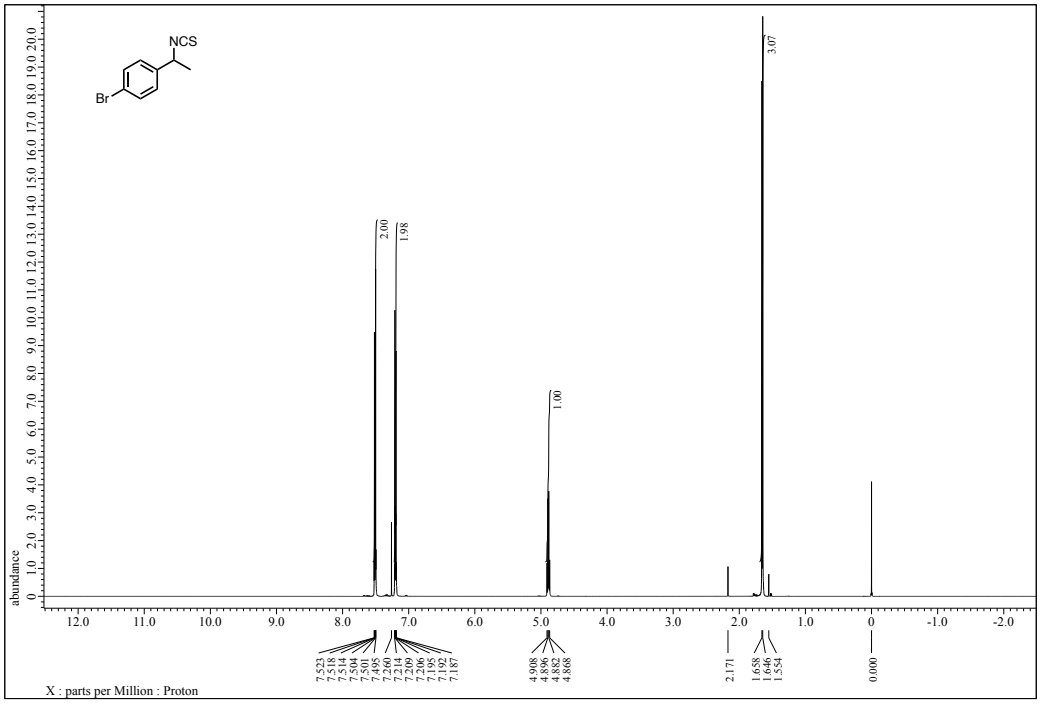

Figure S 28. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1h**.

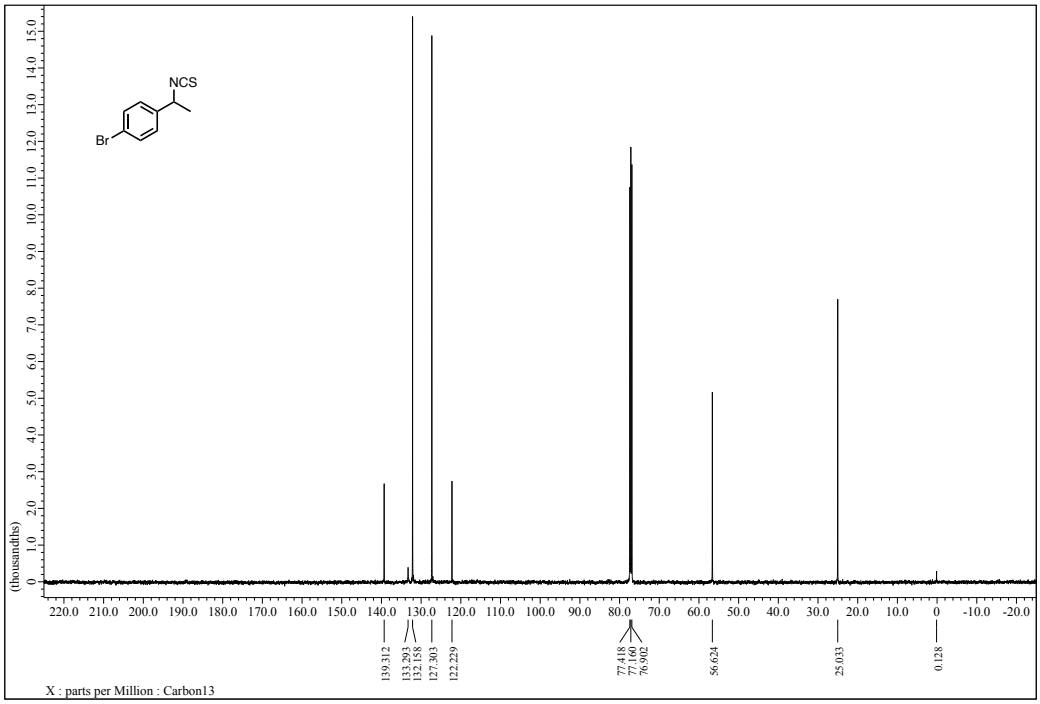

Figure S 29. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1h**.

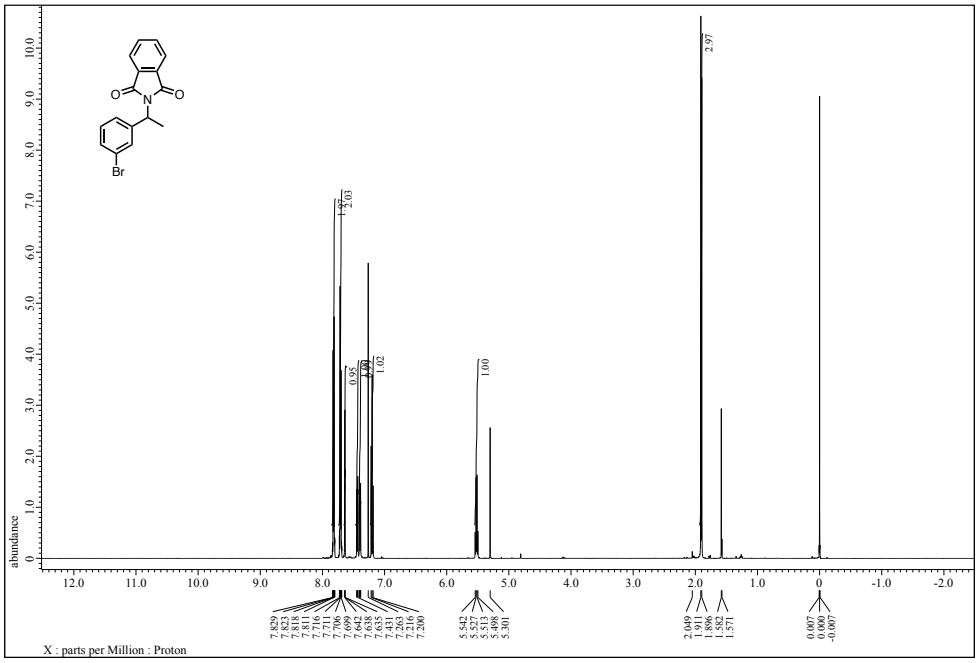

Figure S 30. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione.

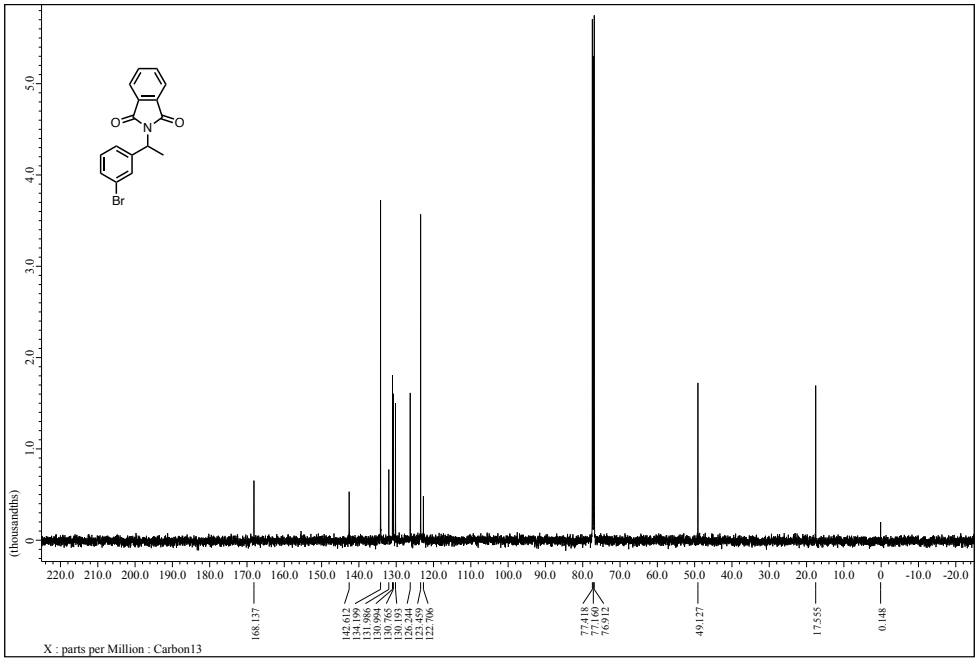

Figure S 31. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2-(1-(3-bromophenyl)ethyl)isoindoline-1,3-dione.

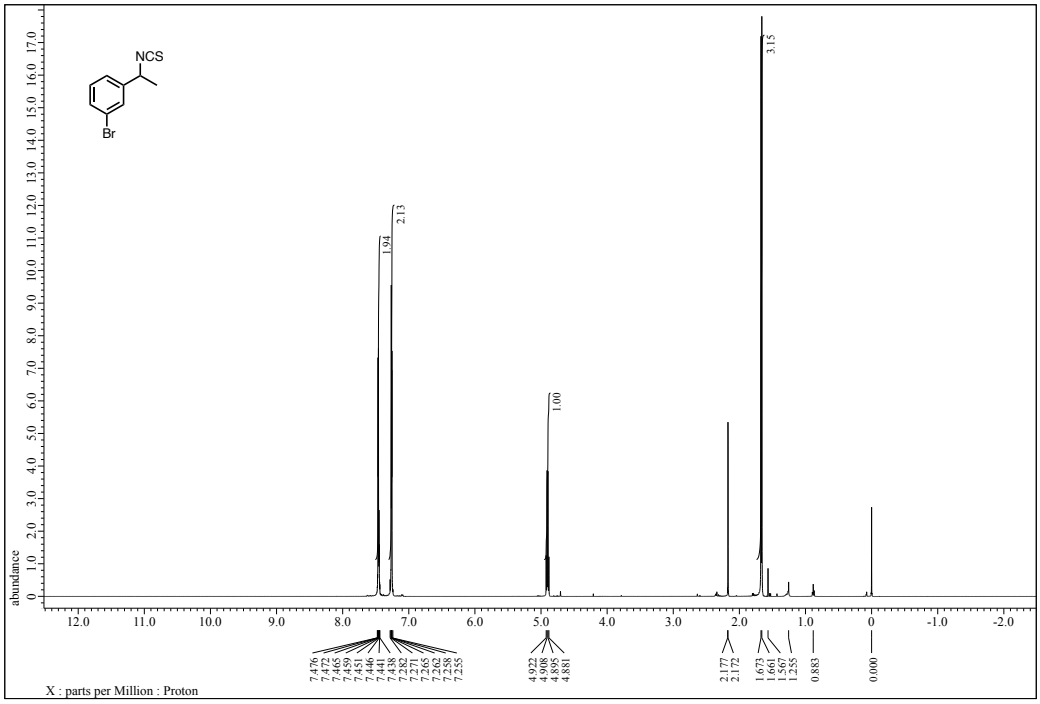

Figure S 32. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1i**.

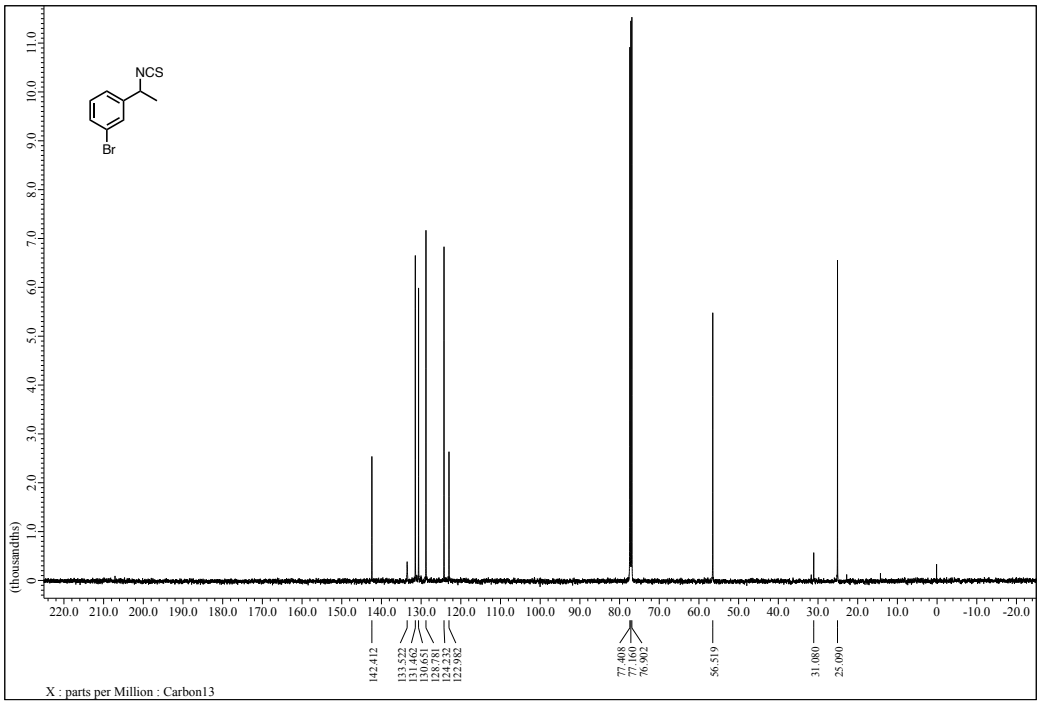

Figure S 33. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1i**.

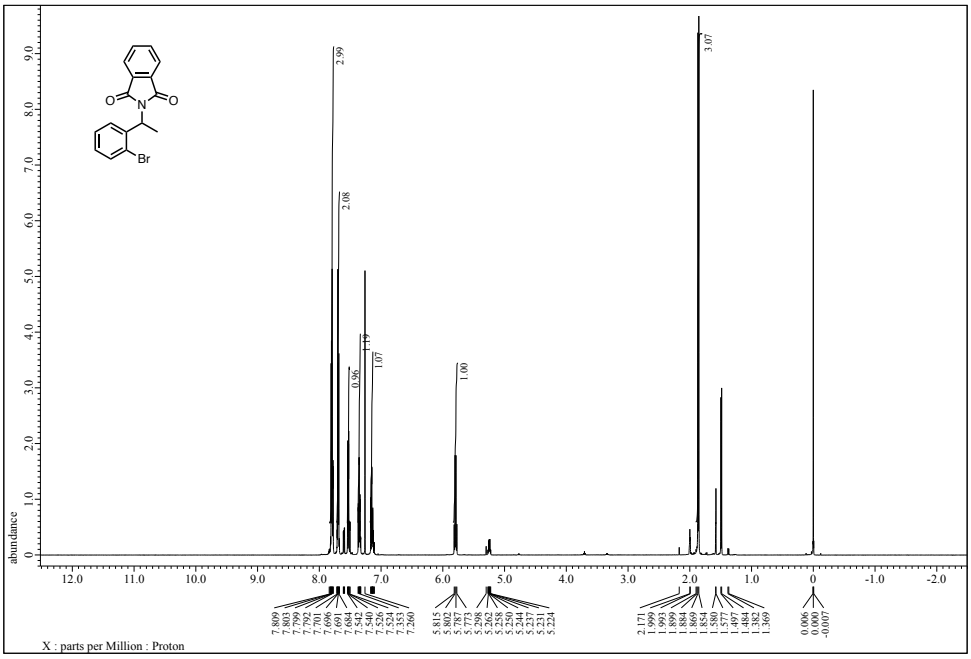

Figure S 34. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2-(1-(2-bromophenyl)ethyl)isoindoline-1,3-dione.

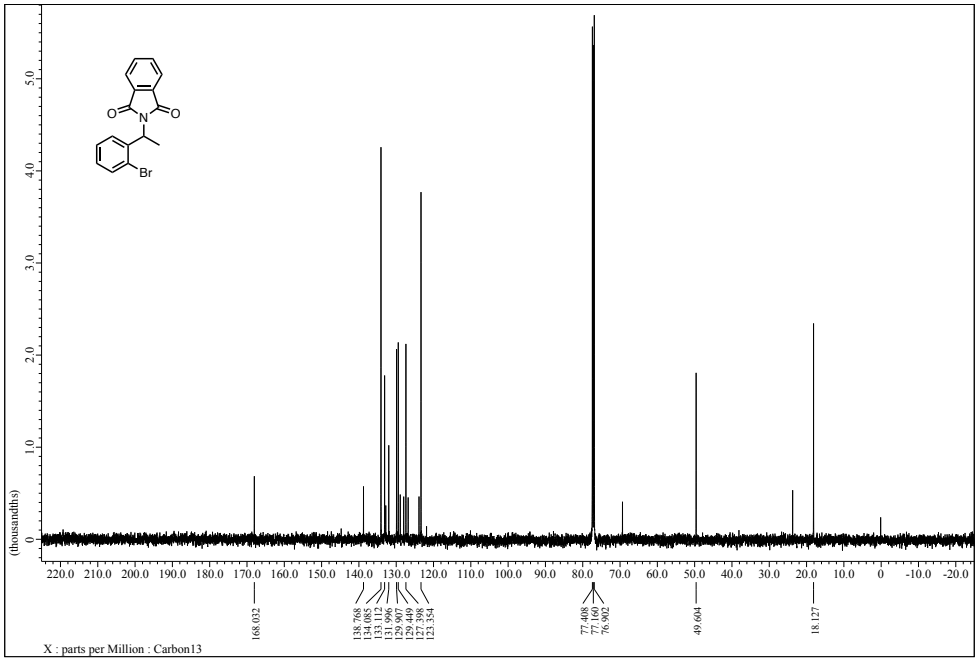

Figure S 35. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2-(1-(2-bromophenyl)ethyl)isoindoline-1,3-dione.

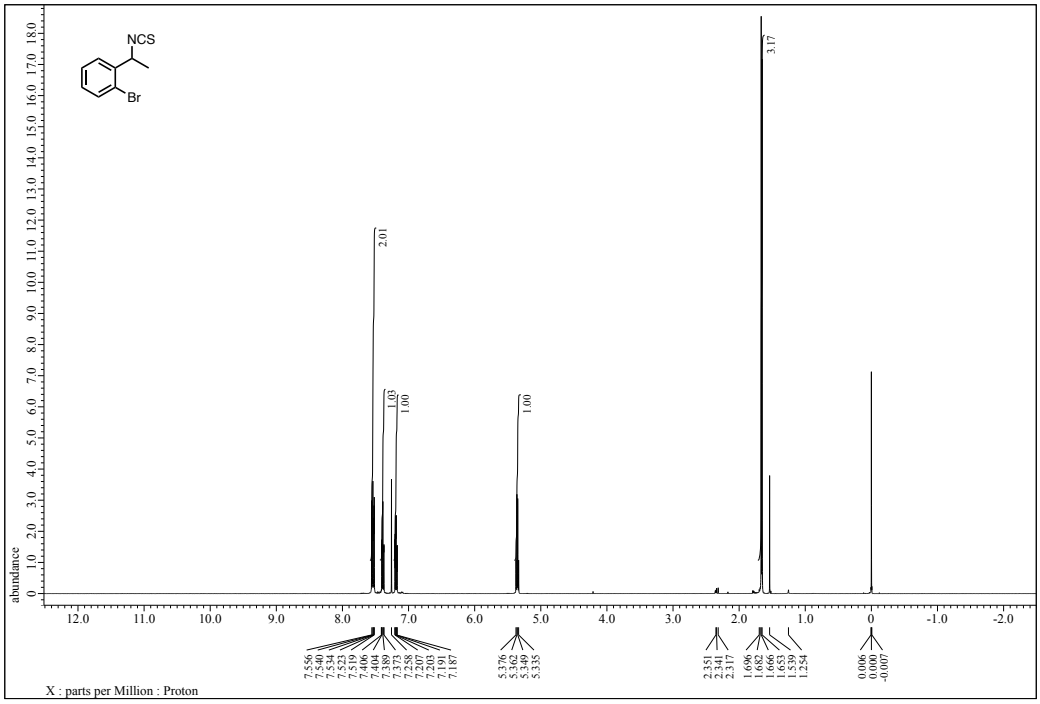

Figure S 36. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1j**.

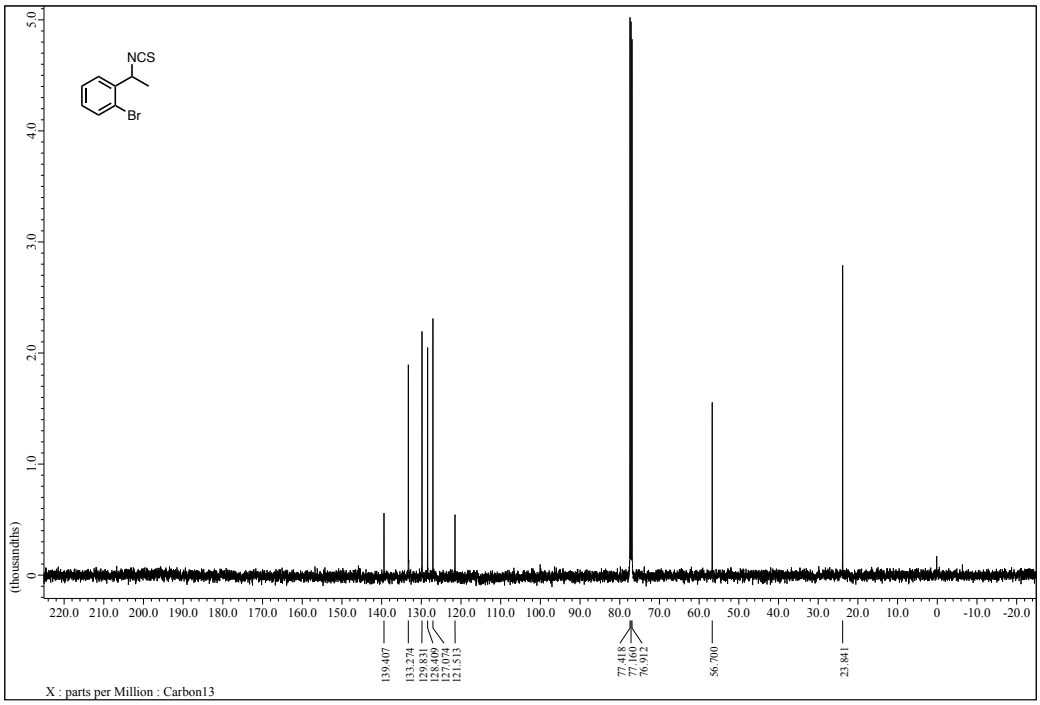

Figure S 37. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1j**.

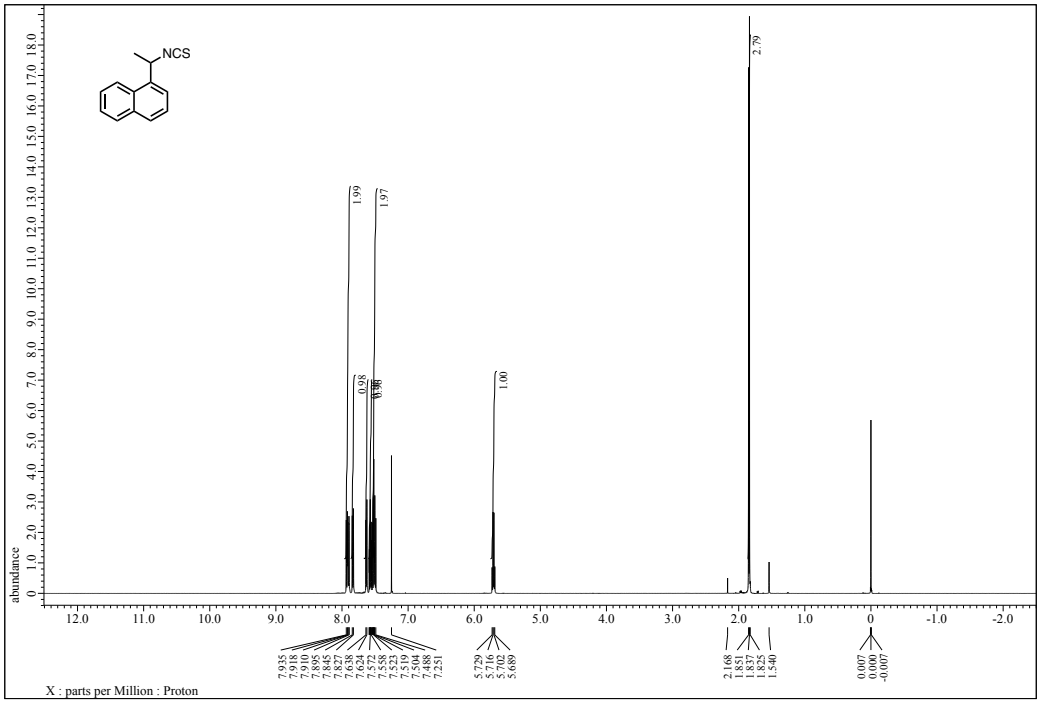

Figure S 38. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1k**.

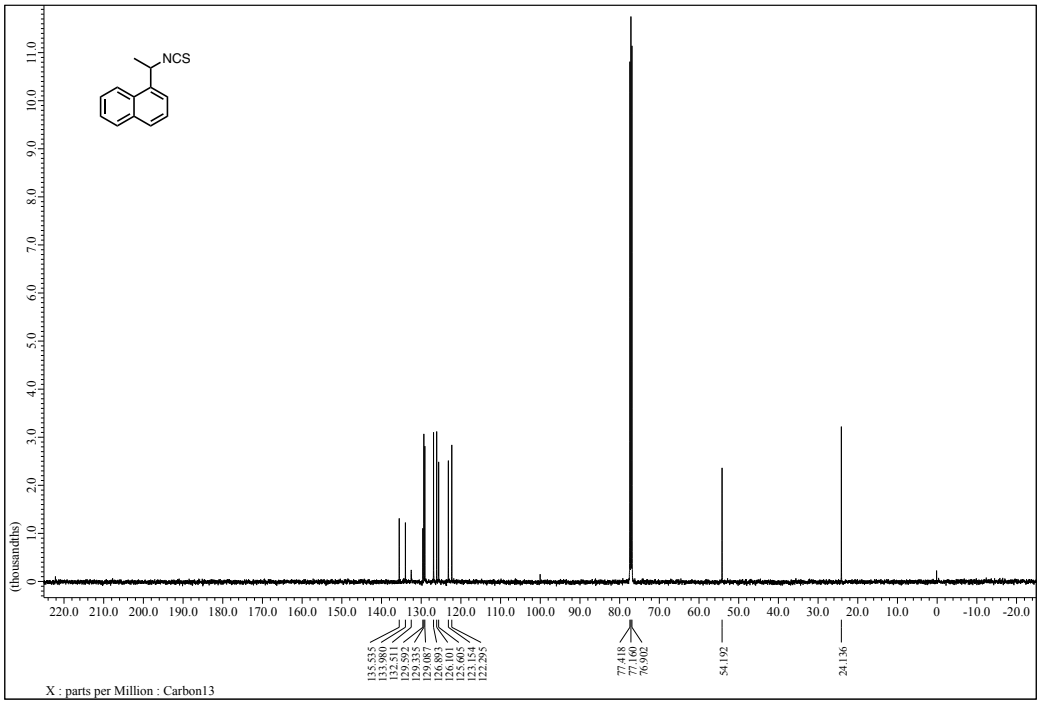

Figure S 39. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1k**.

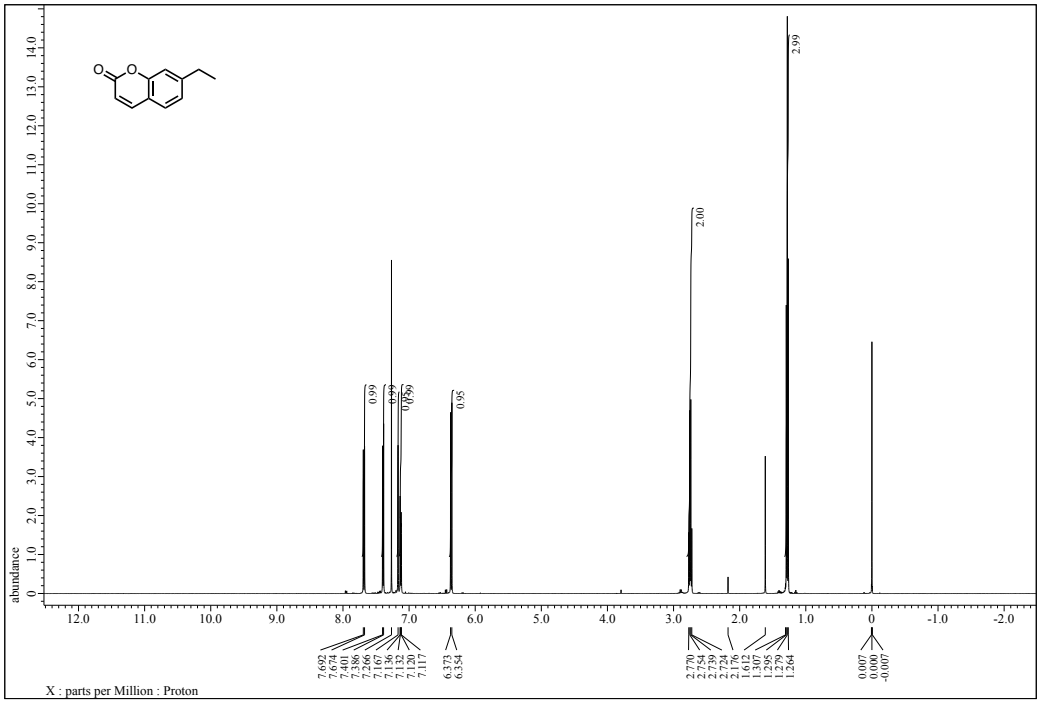

Figure S 40. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 7-ethyl-2*H*-chromen-2-one.

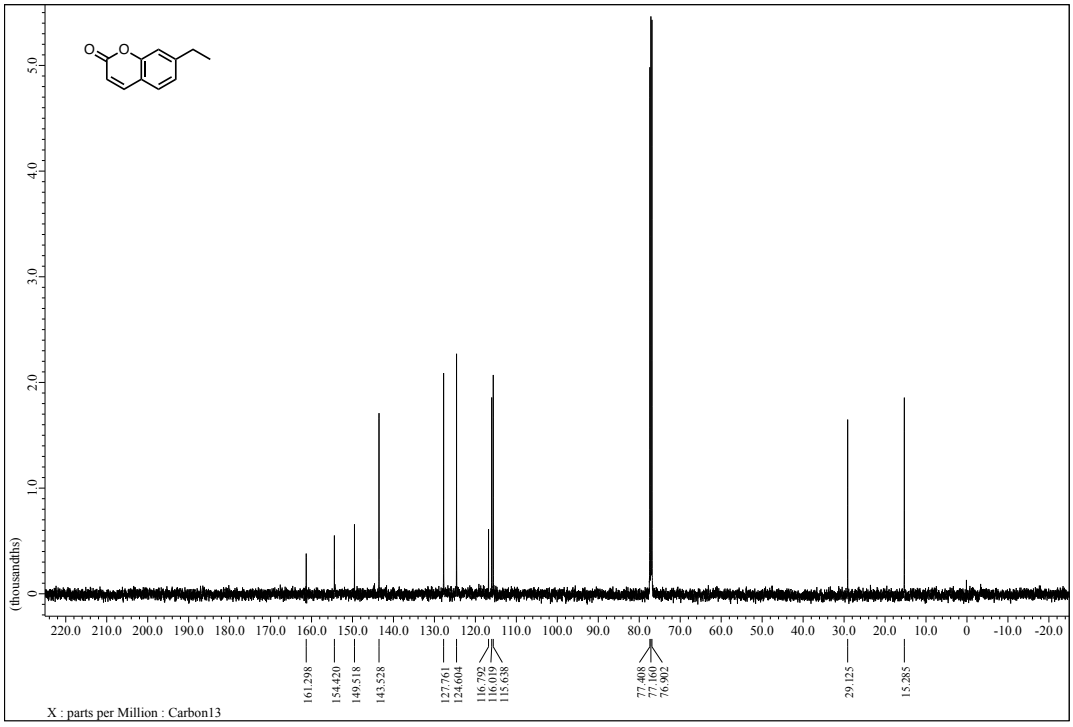

Figure S 41. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 7-ethyl-2*H*-chromen-2-one.

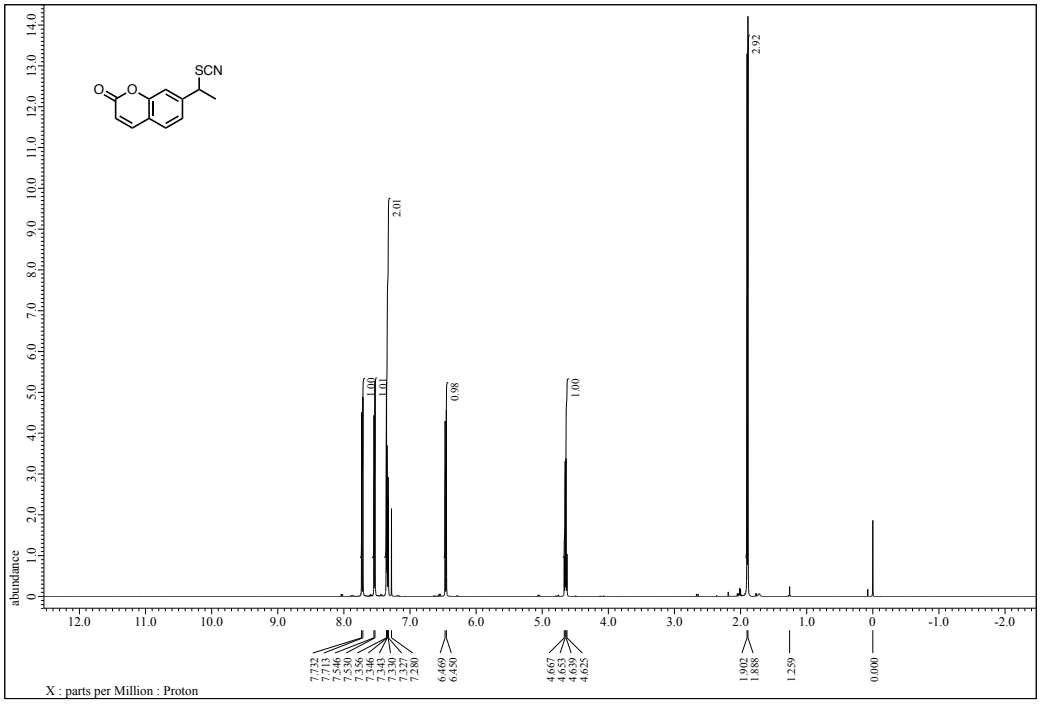

Figure S 42. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 7-(1-thiocyanatoethyl)-2*H*-chromen-2-one.

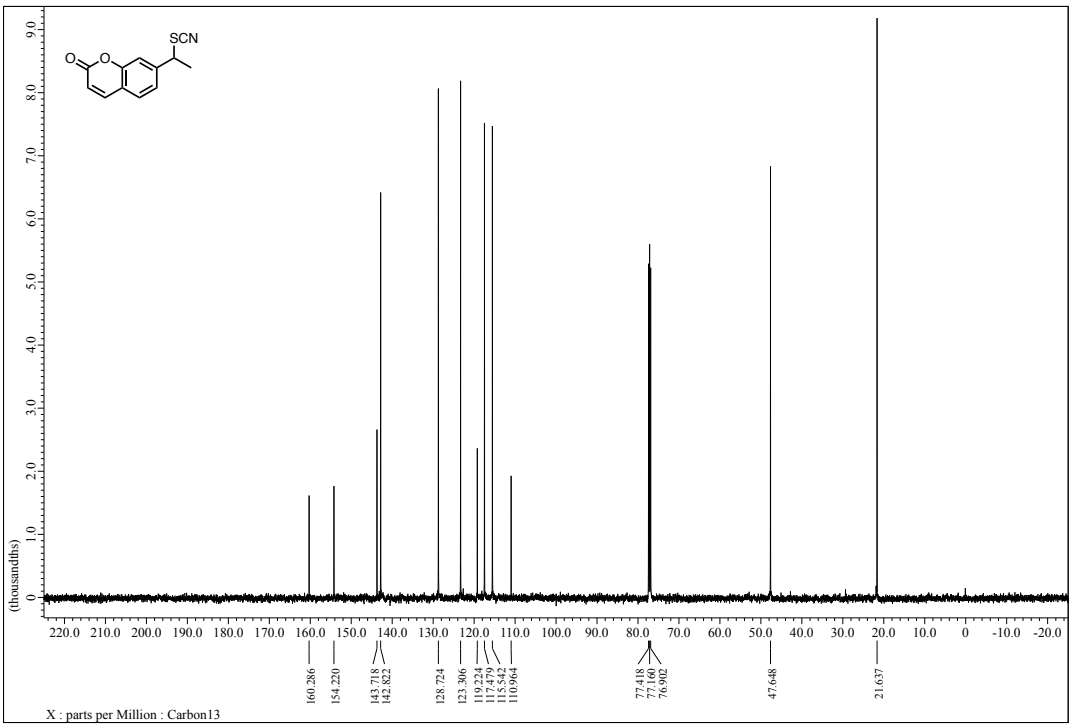

Figure S 43. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 7-(1-thiocyanatoethyl)-2*H*-chromen-2-one.

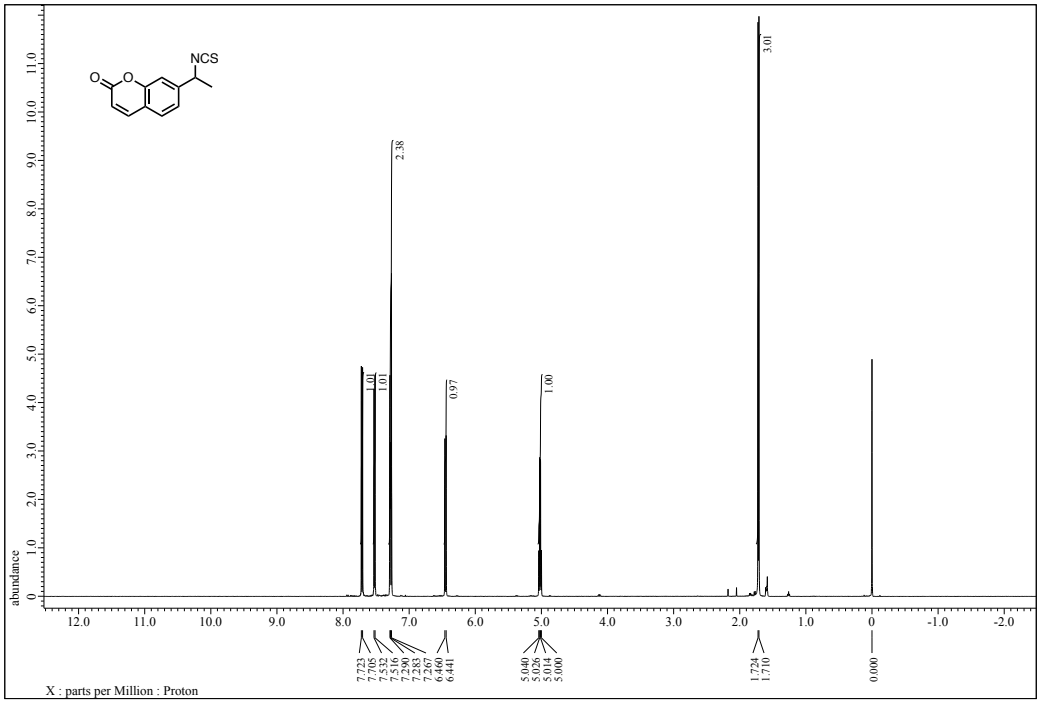

Figure S 44. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1l**.

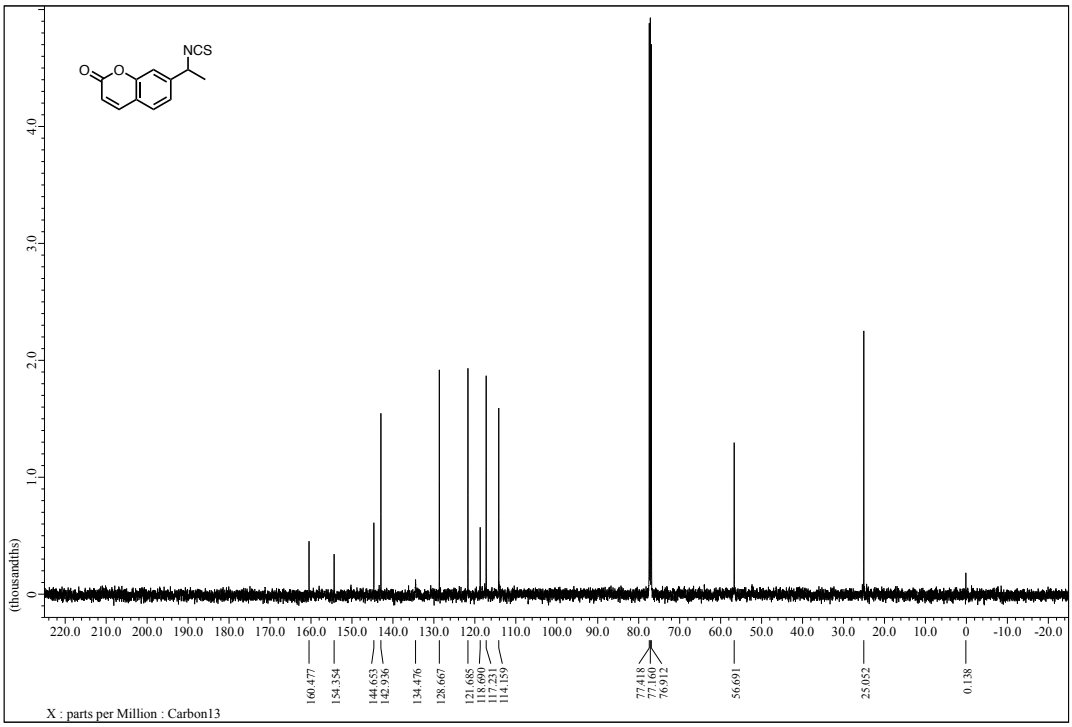

Figure S 45. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1l**.

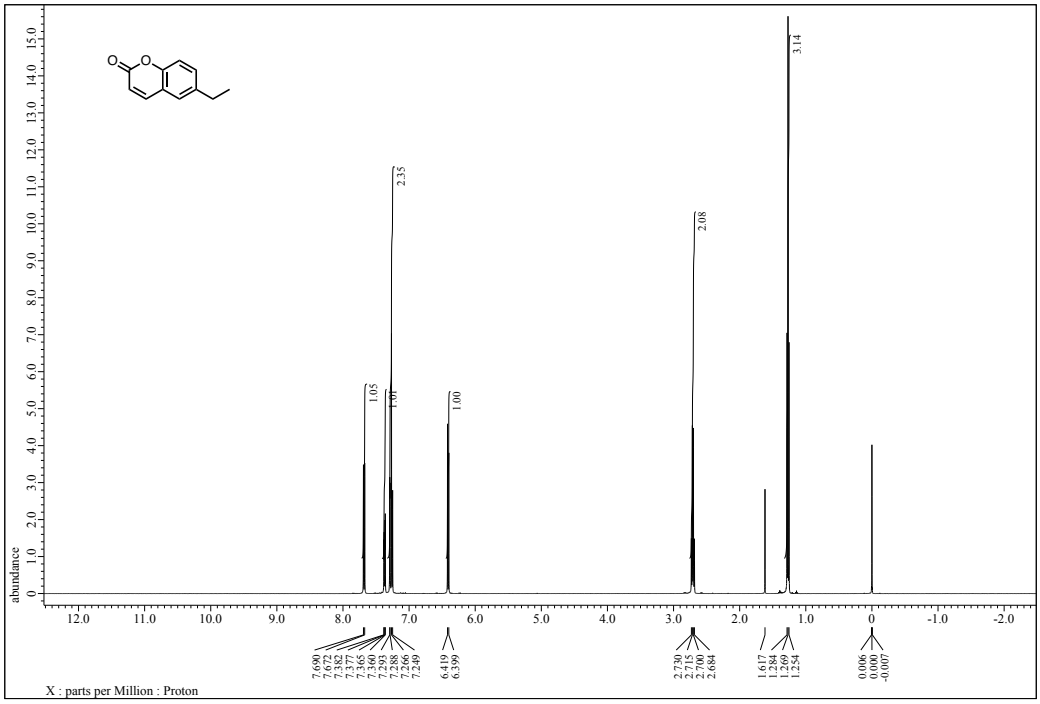

Figure S 46. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6-ethyl-2*H*-chromen-2-one.

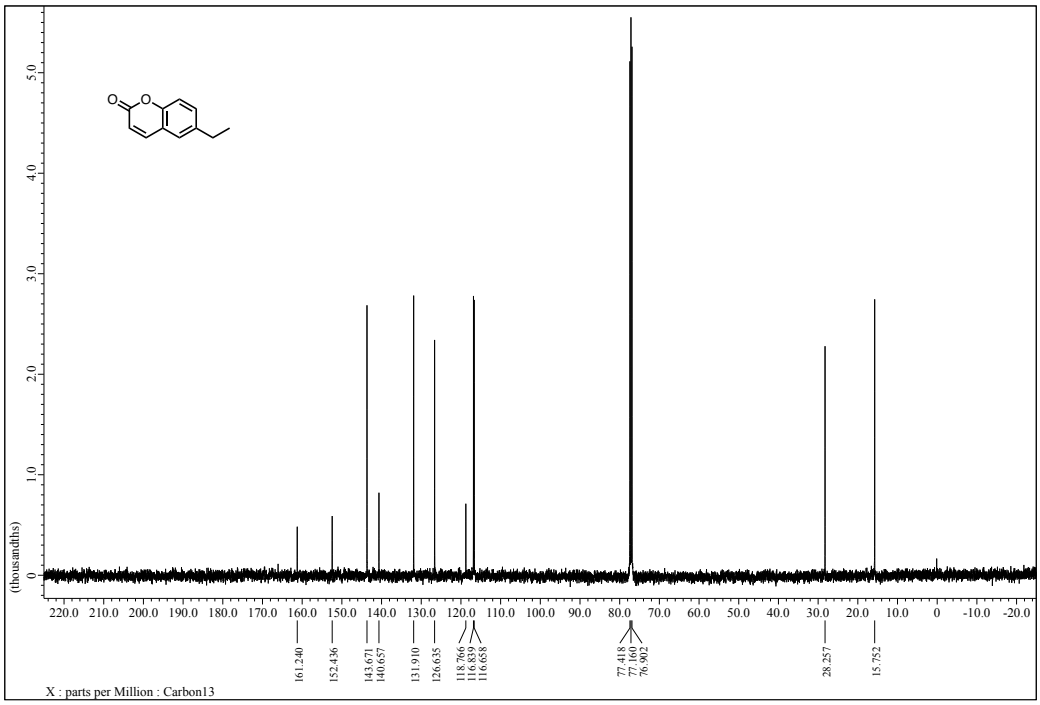

Figure S 47. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6-ethyl-2*H*-chromen-2-one.

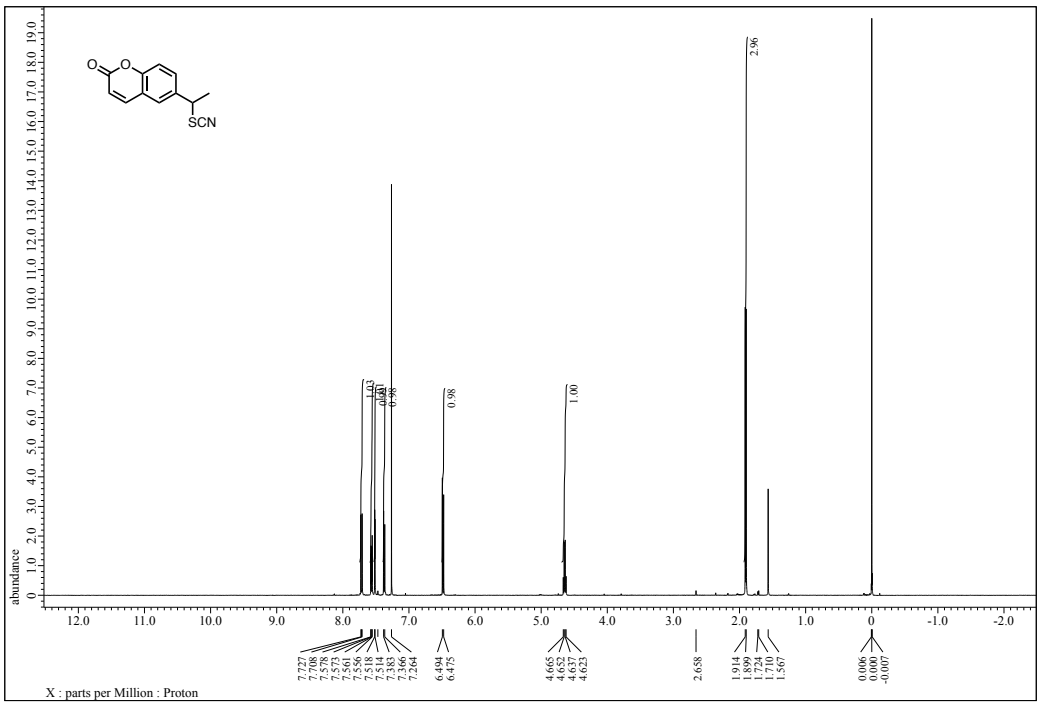

Figure S 48. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6-(1-thiocyanatoethyl)-2*H*-chromen-2-one.

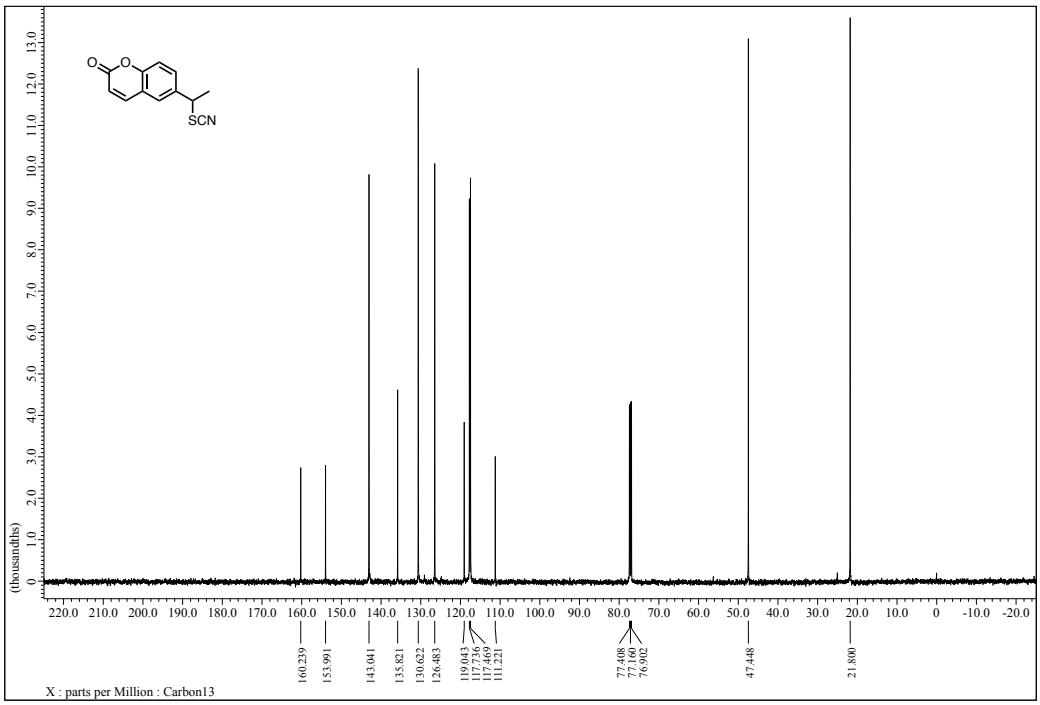

Figure S 49. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6-(1-thiocyanatoethyl)-2*H*-chromen-2-one.

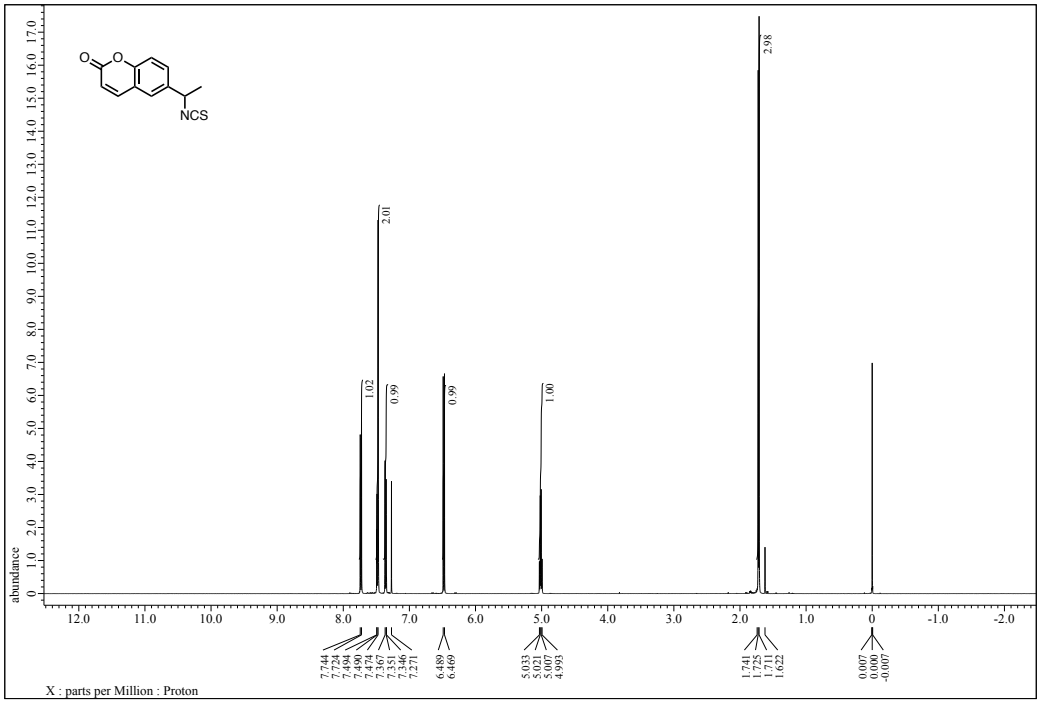

Figure S 50. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1m**.

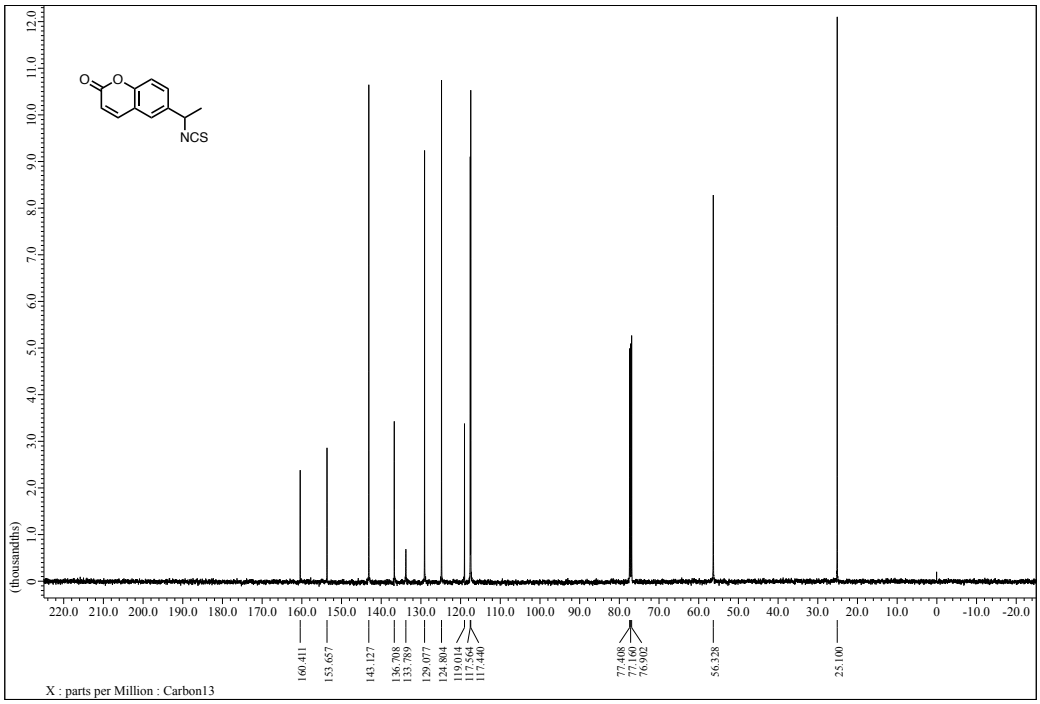

Figure S 51. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1m**.

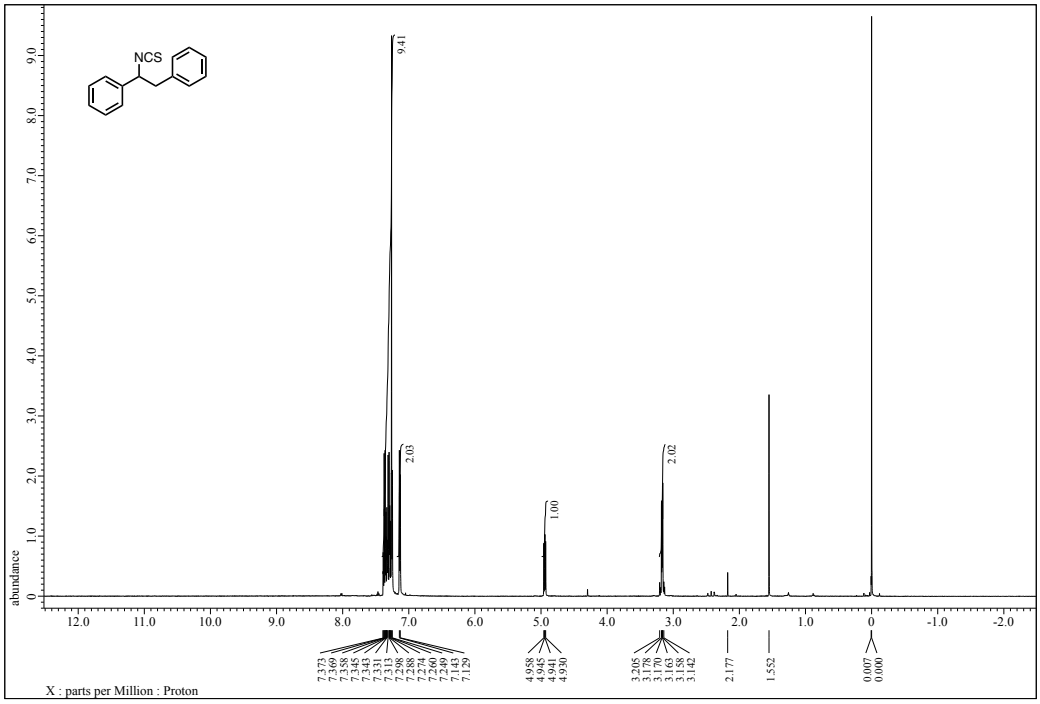

Figure S 52. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1n**.

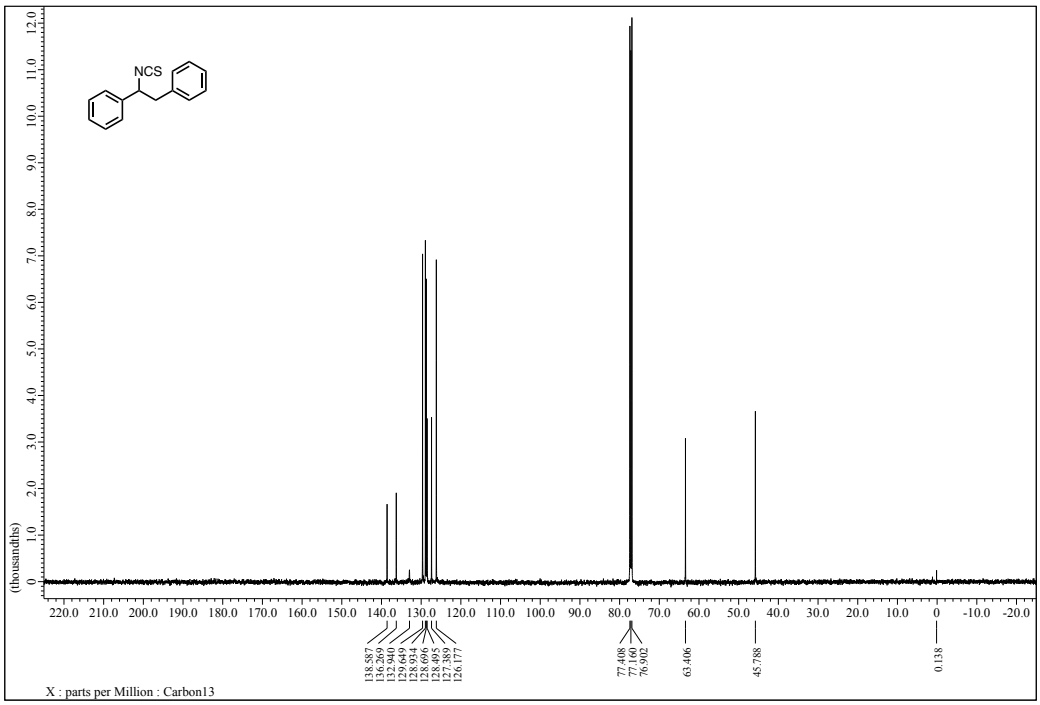

Figure S 53. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1n**.

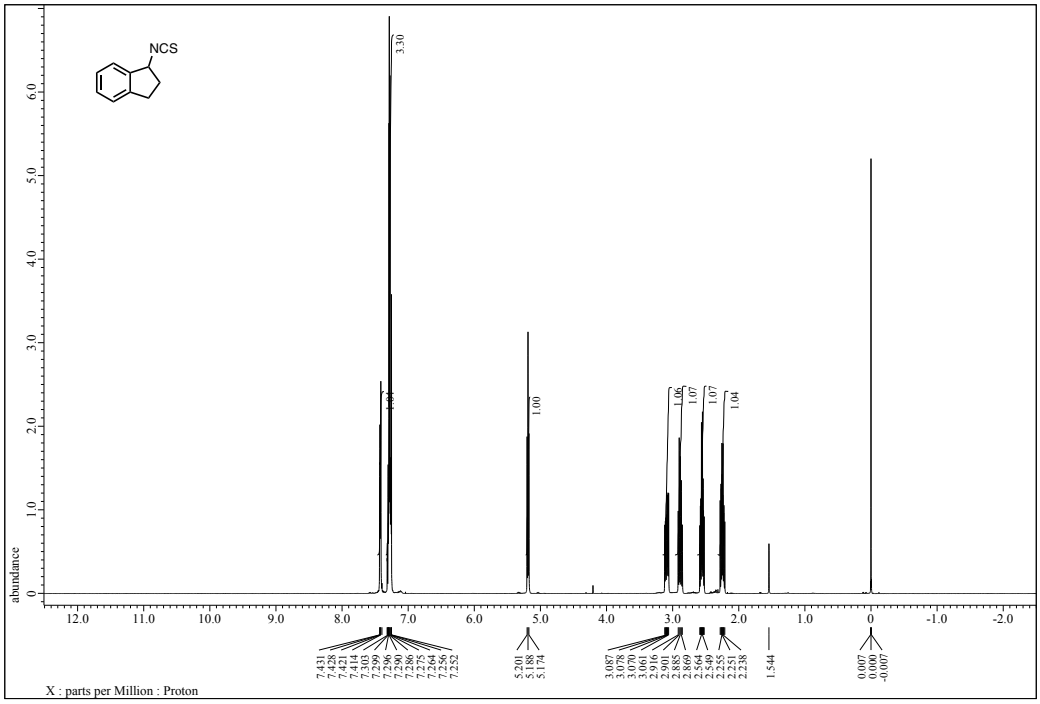

Figure S 54. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1o**.

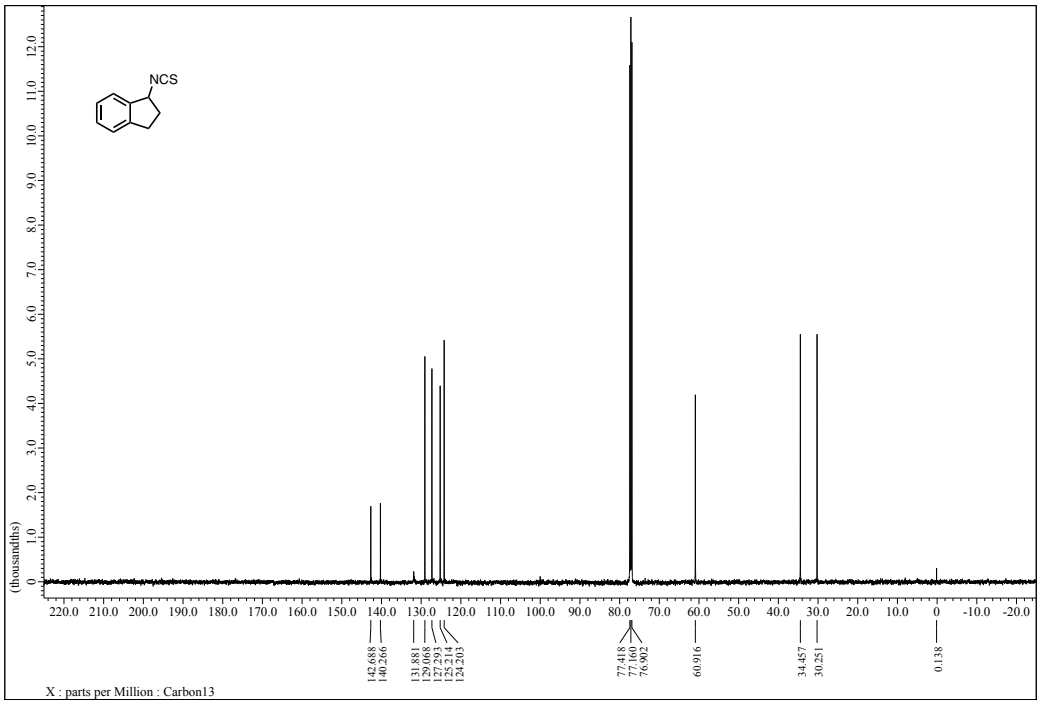

Figure S 55. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1o**.

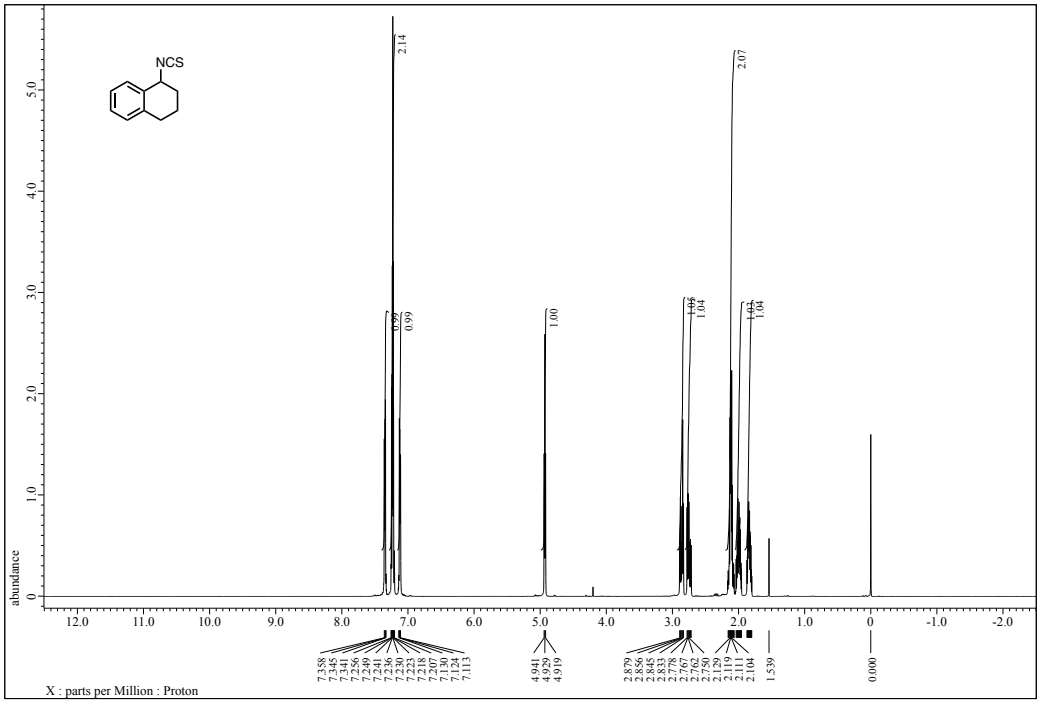

Figure S 56. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1p**.

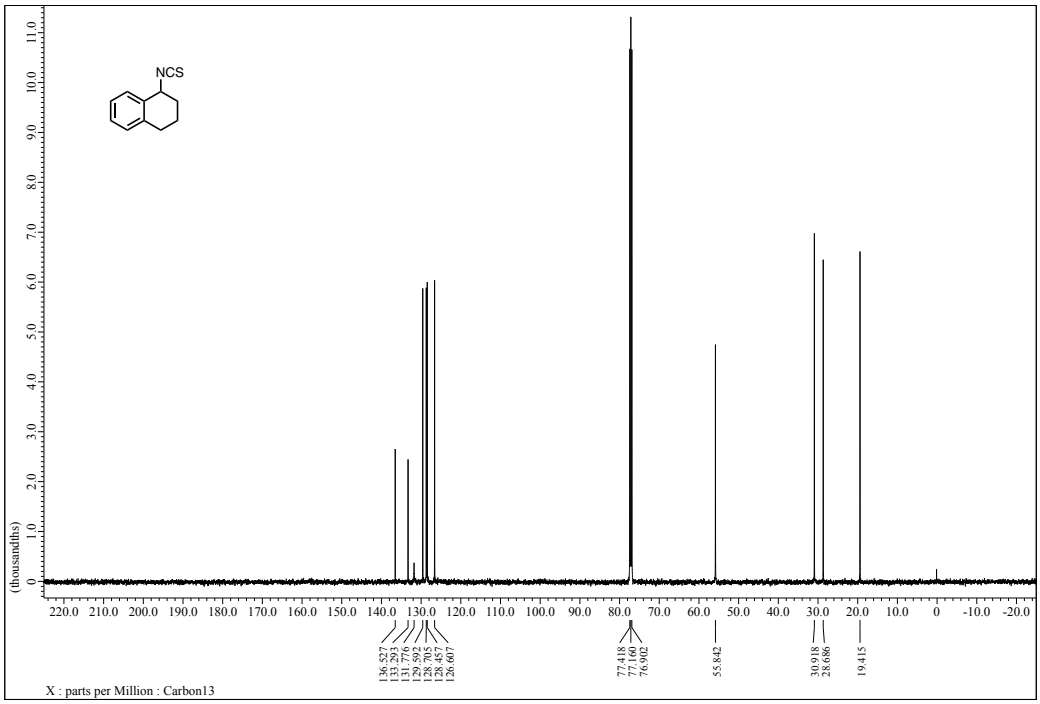

Figure S 57. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1p**.

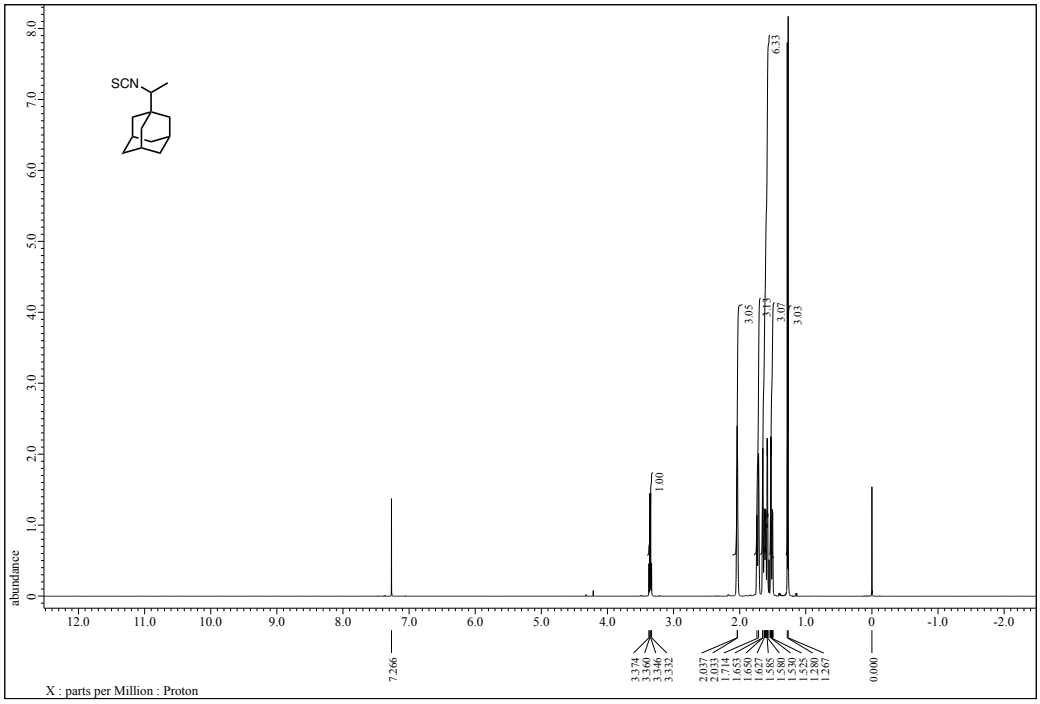

Figure S 58. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1q**.

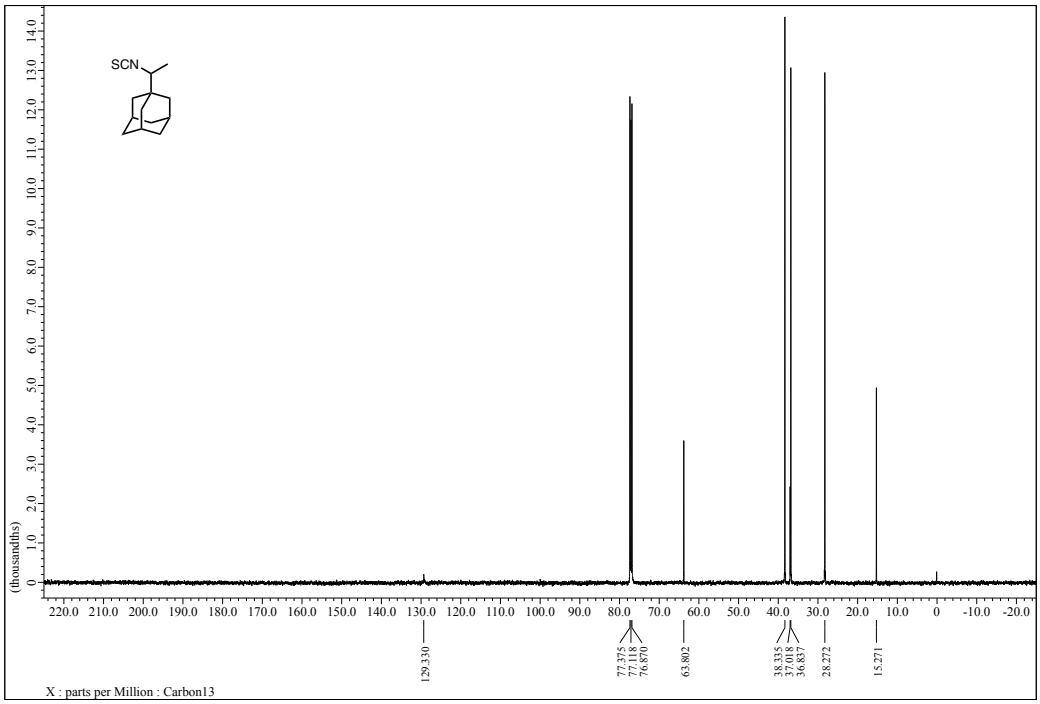

Figure S 59. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1q**.

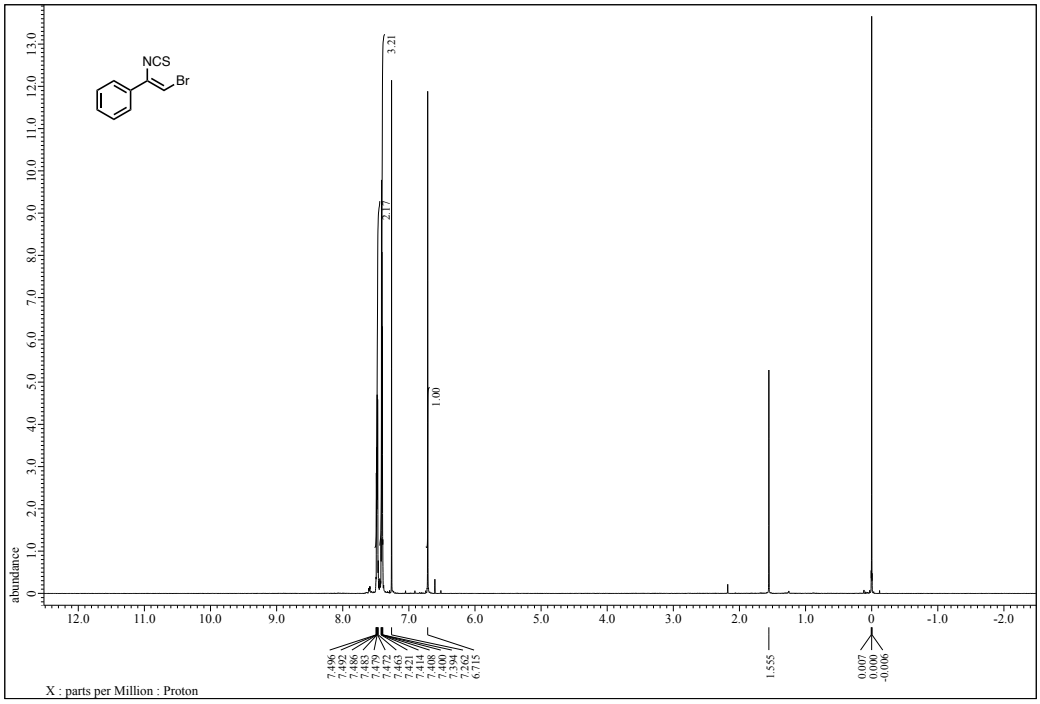

Figure S 60. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2a**.

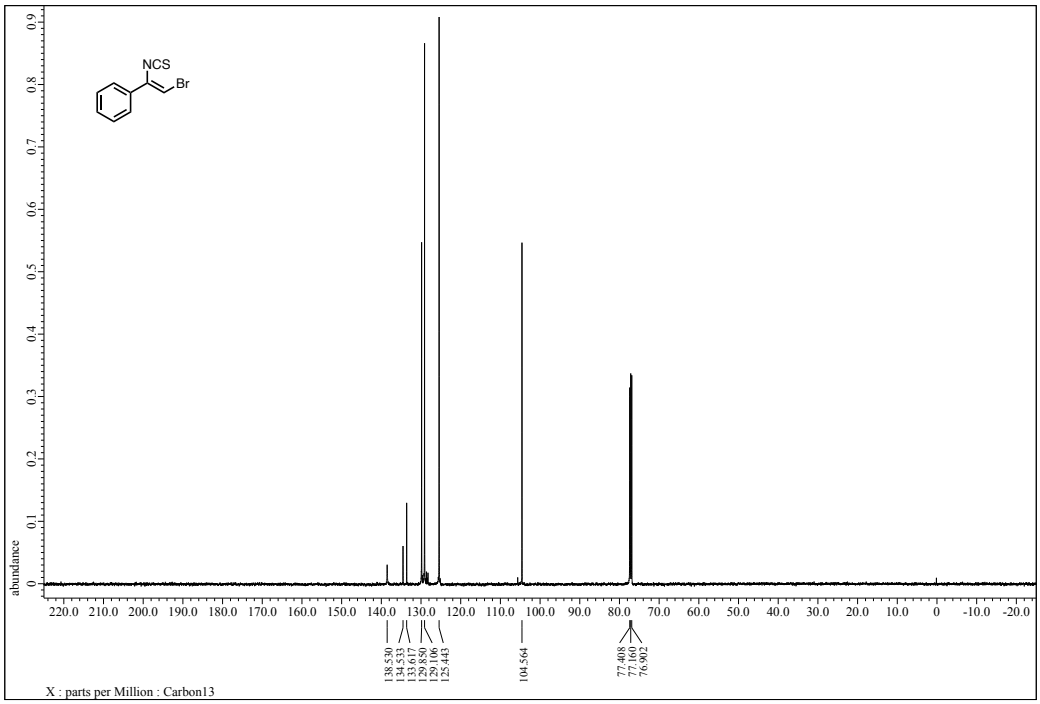

Figure S 61. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2a**.

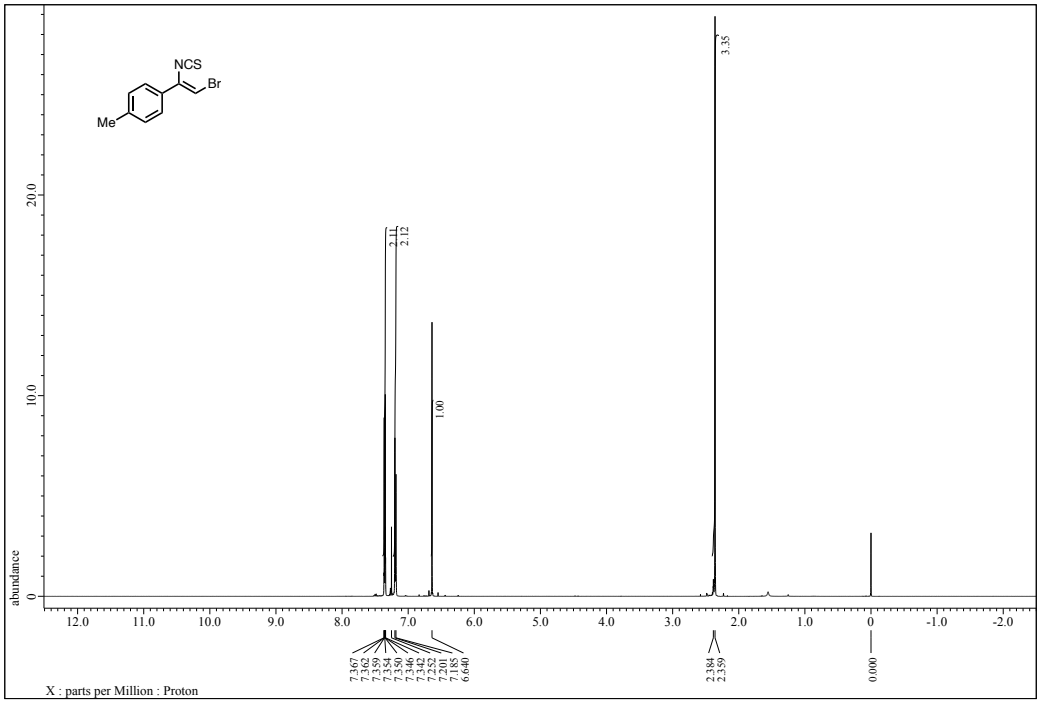

Figure S 62. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2b**.

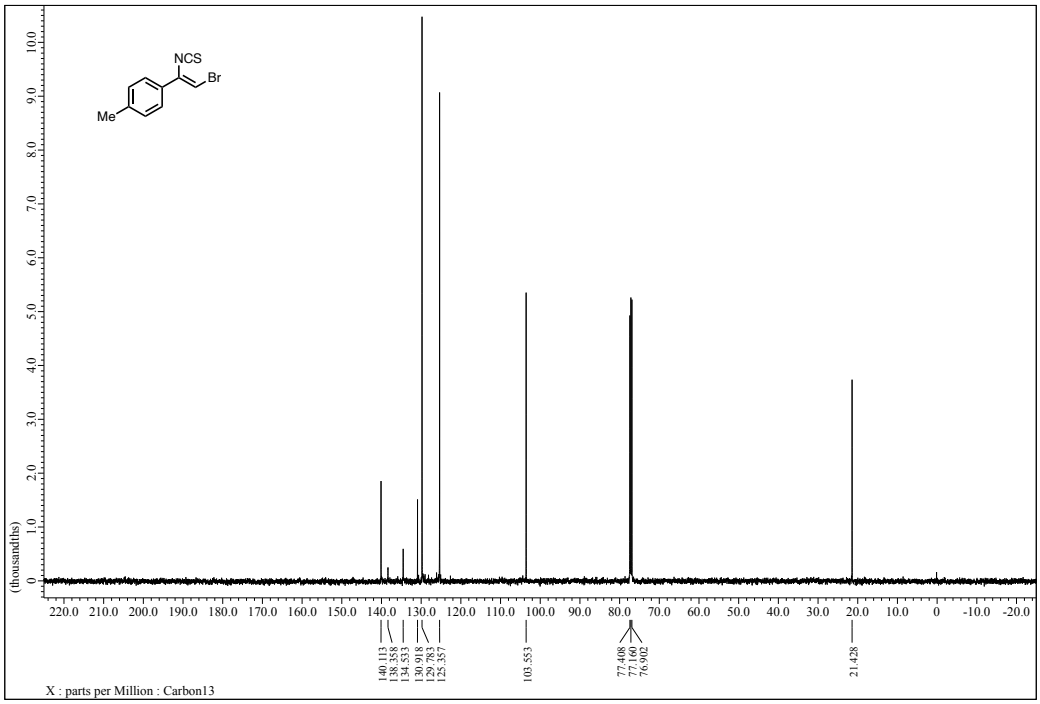

Figure S 63. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2b**.

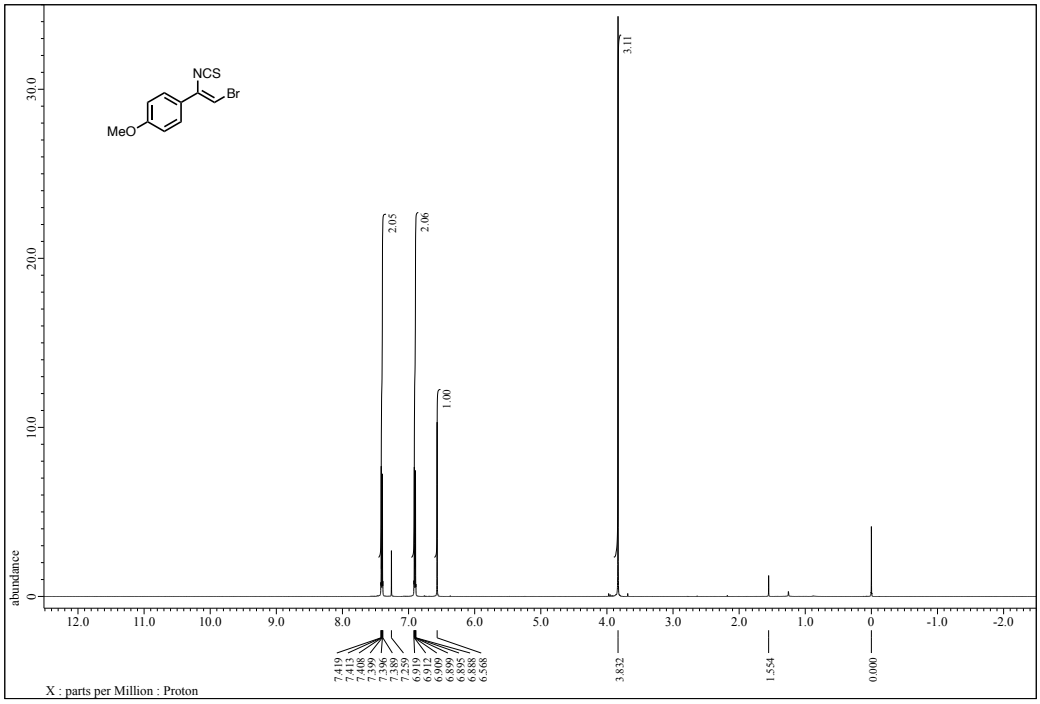

Figure S 64. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2c**.

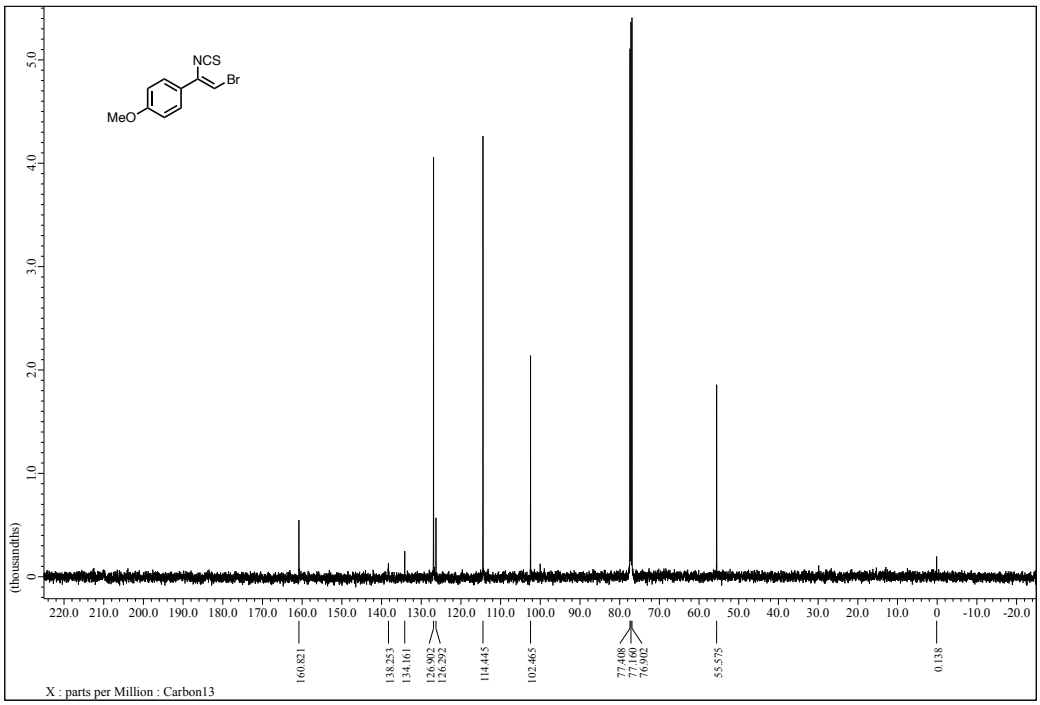

Figure S 65. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2c**.

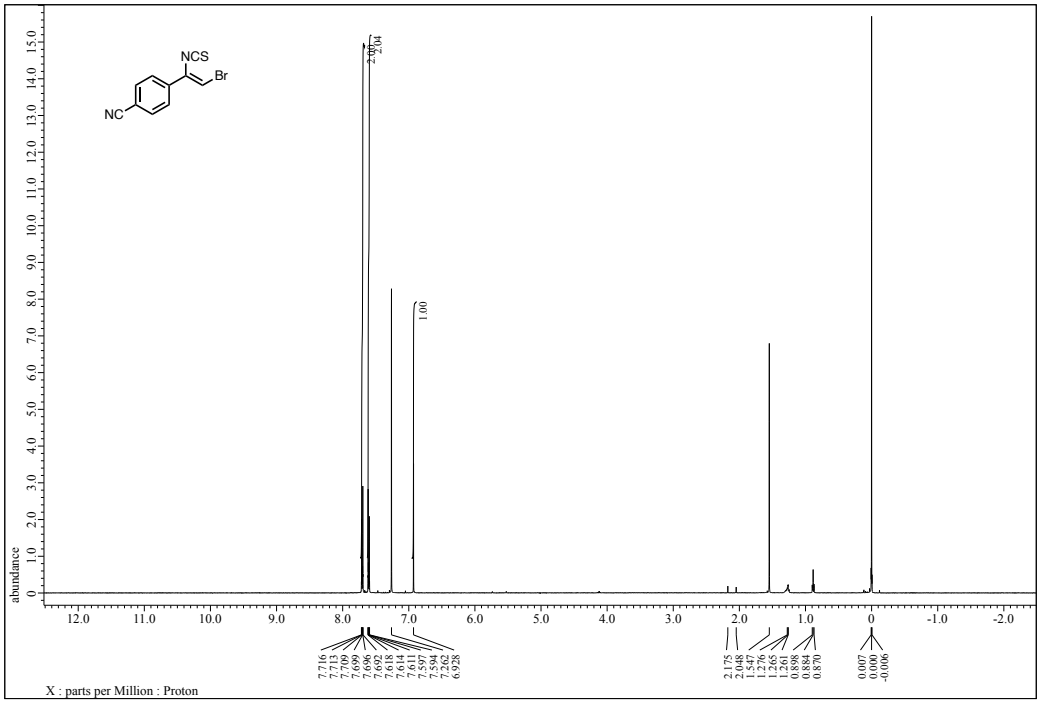

Figure S 66. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2d**.

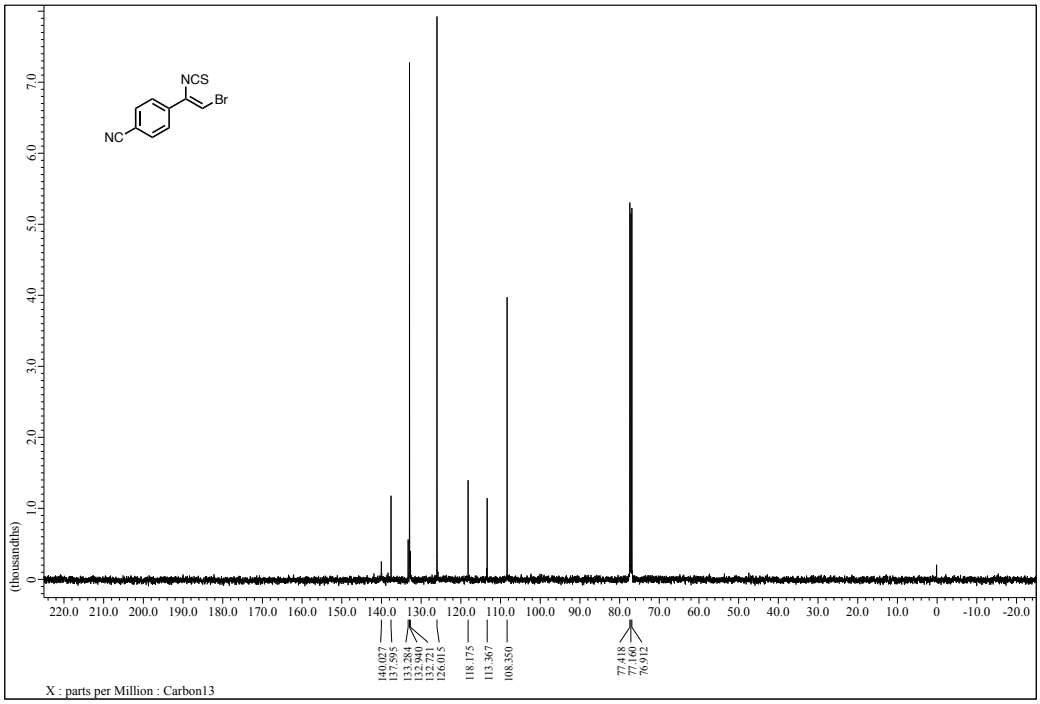

Figure S 67. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2d**.

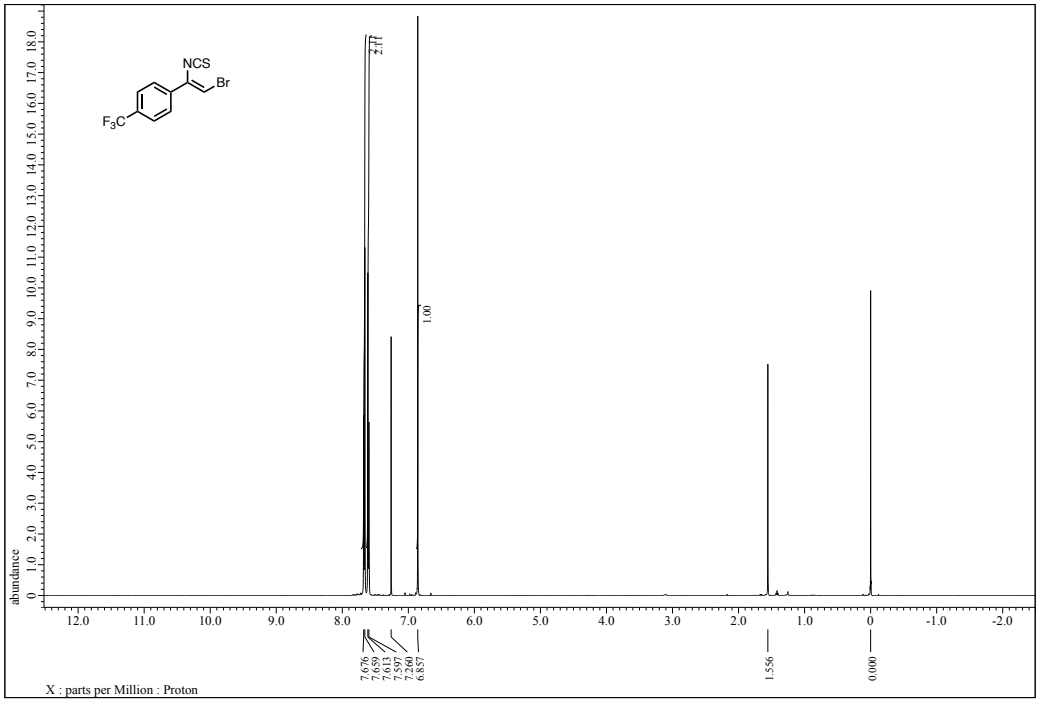

Figure S 68. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2e**.

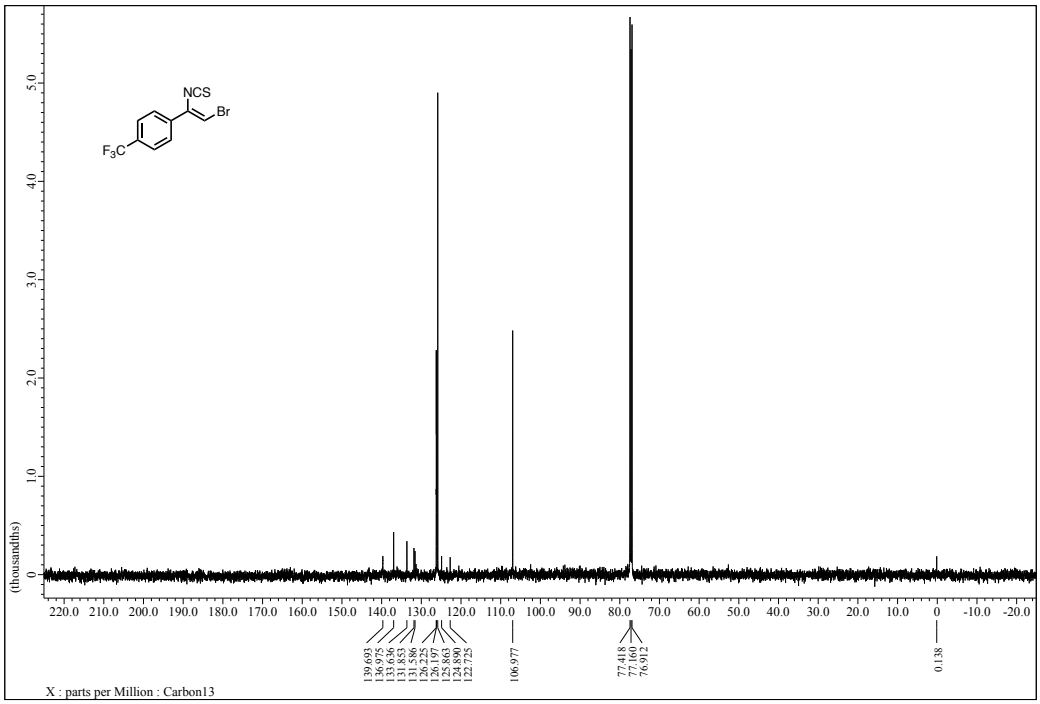

Figure S 69. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2e**.

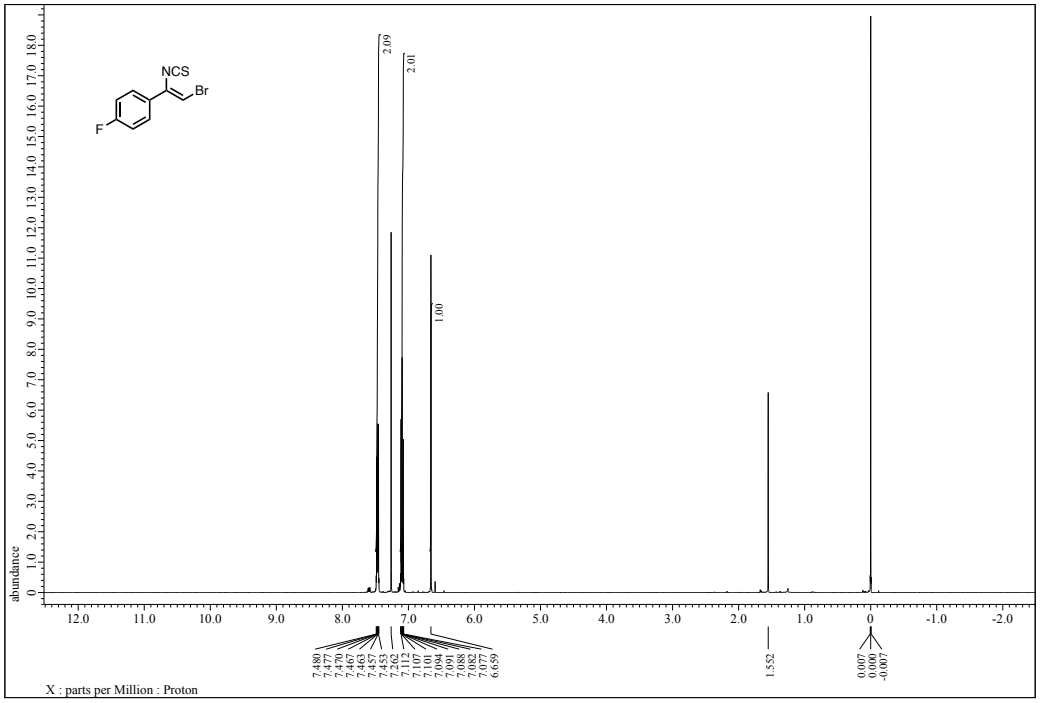

Figure S 70. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2f**.

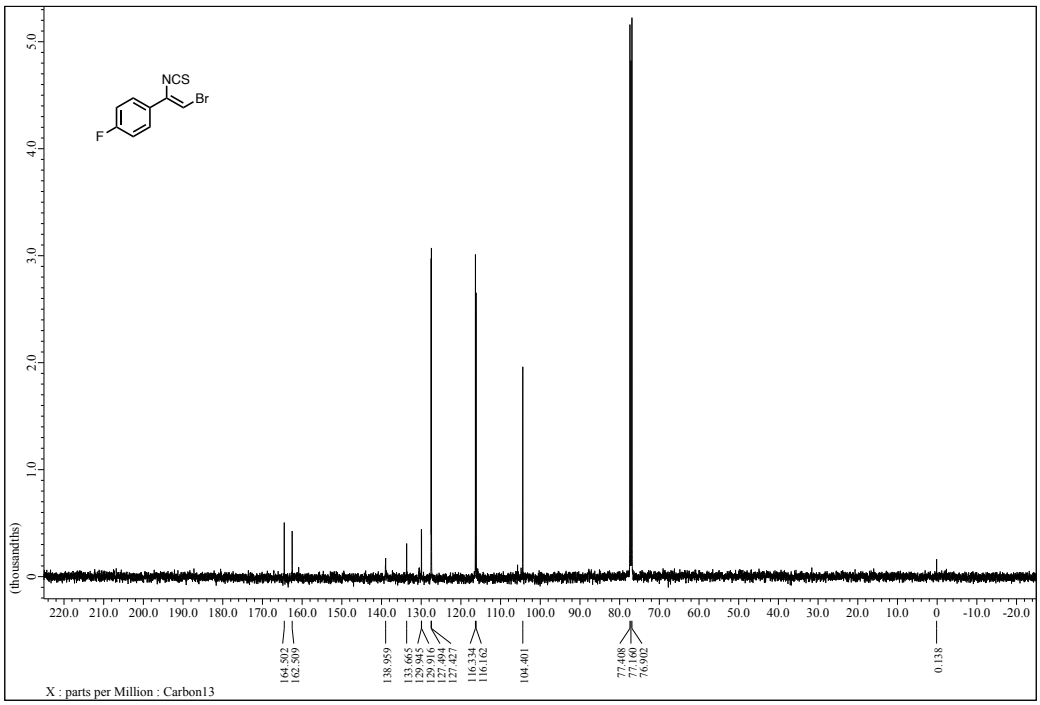

Figure S 71. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2f**.

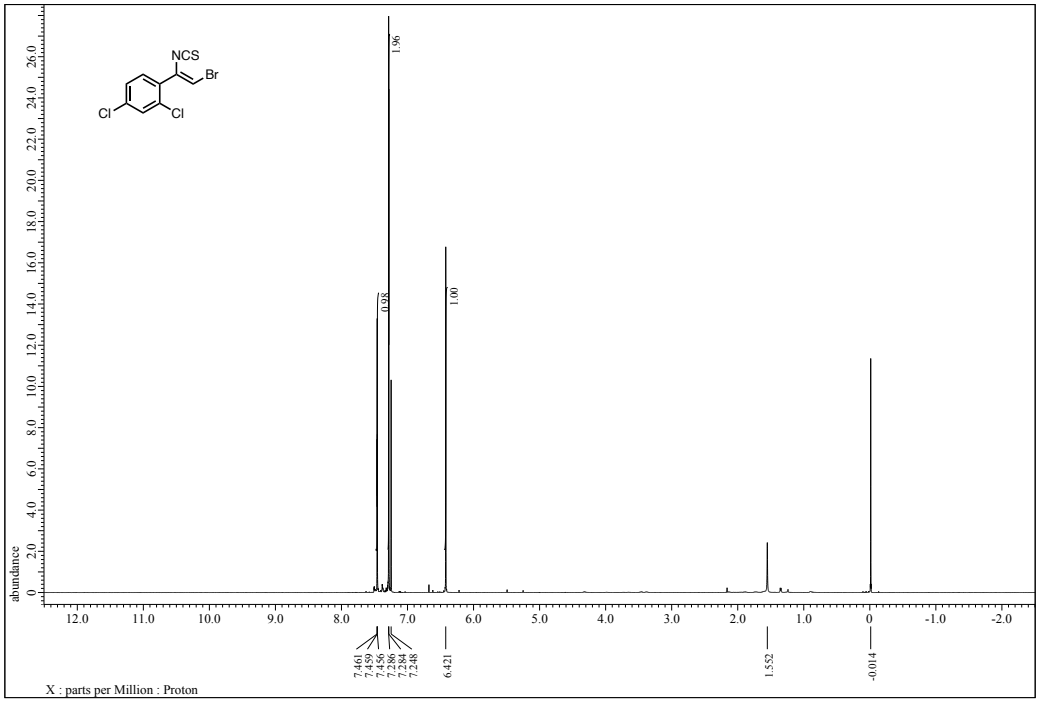

Figure S 72. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2g**.

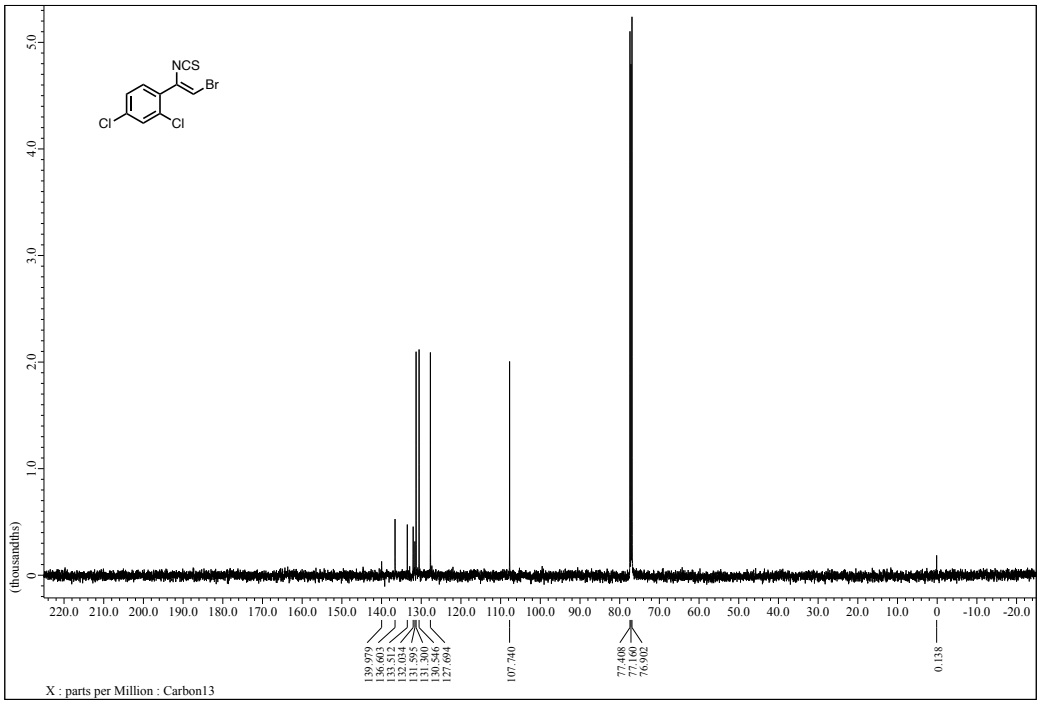

Figure S 73. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2g**.

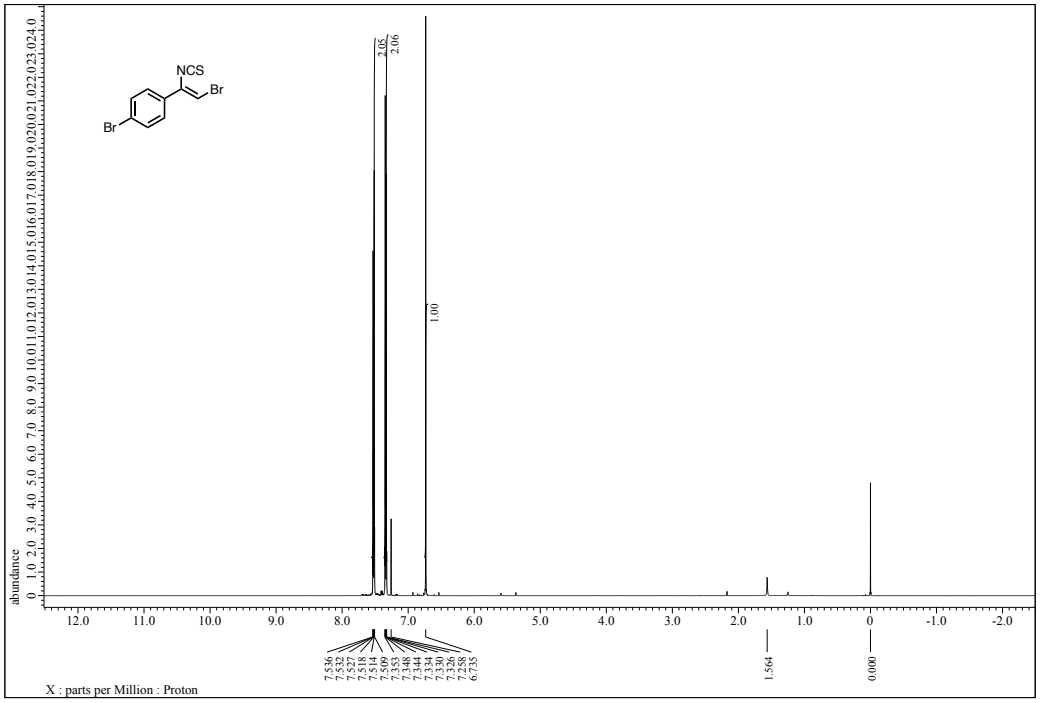

Figure S 74. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2h**.

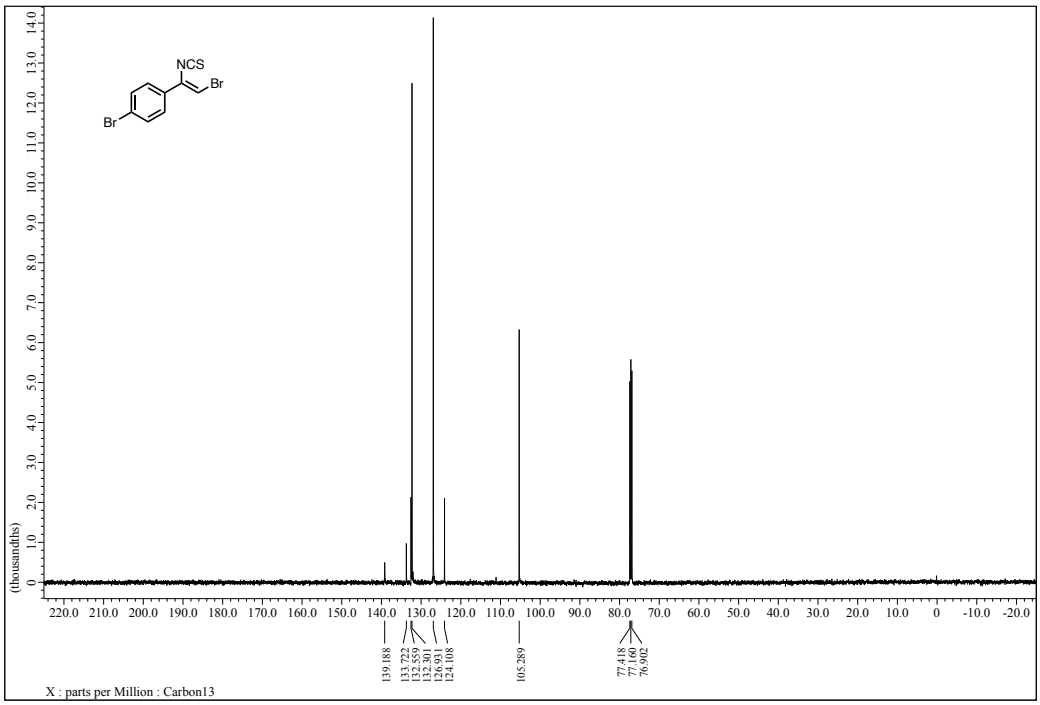

Figure S 75. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2h**.

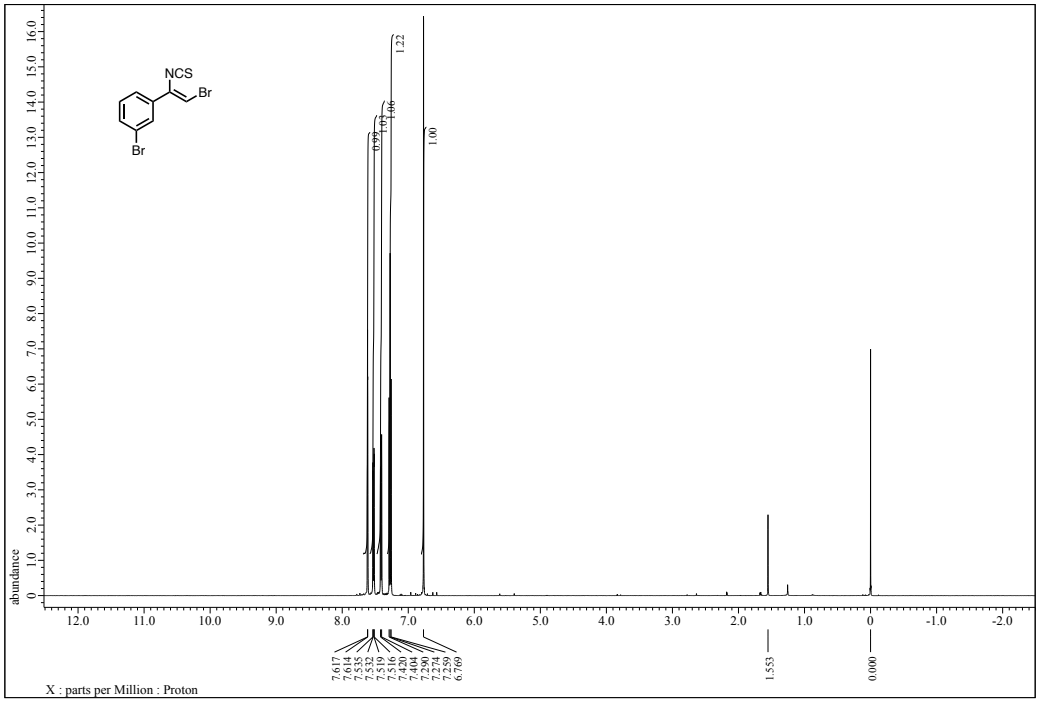

Figure S 76. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2i**.

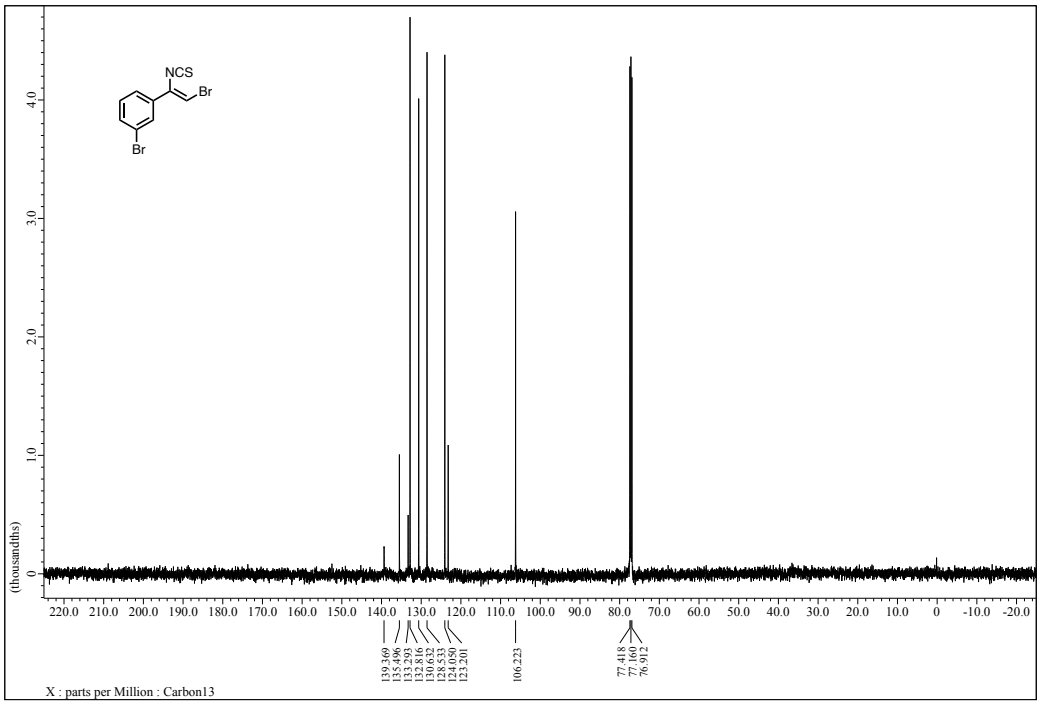

Figure S 77. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2i**.

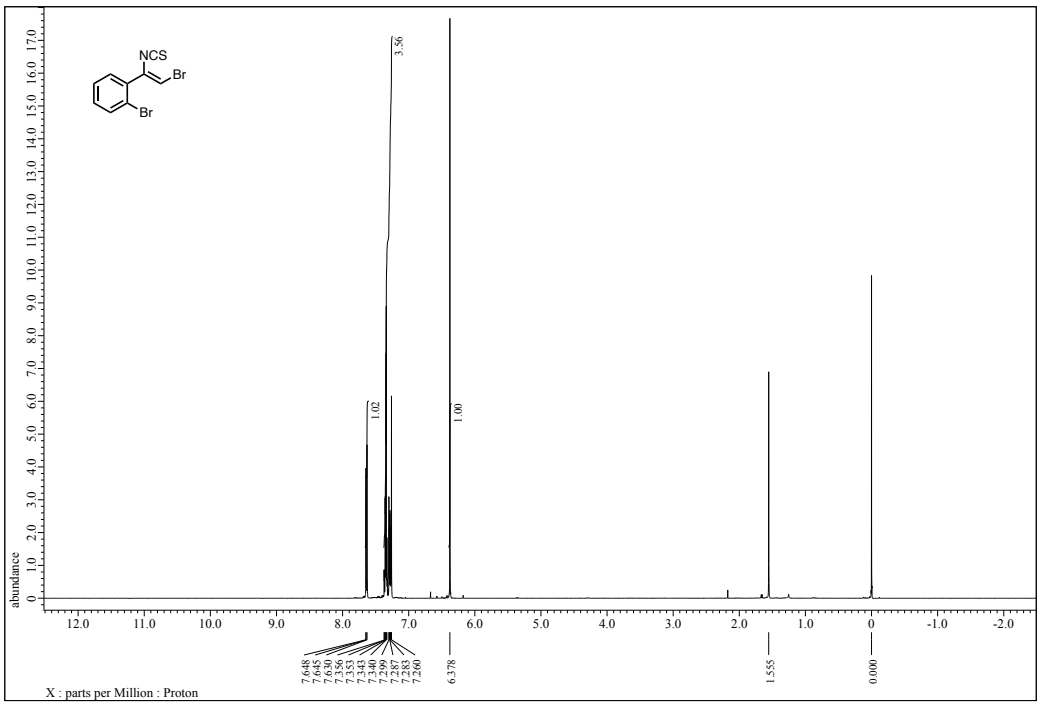

Figure S 78. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2j**.

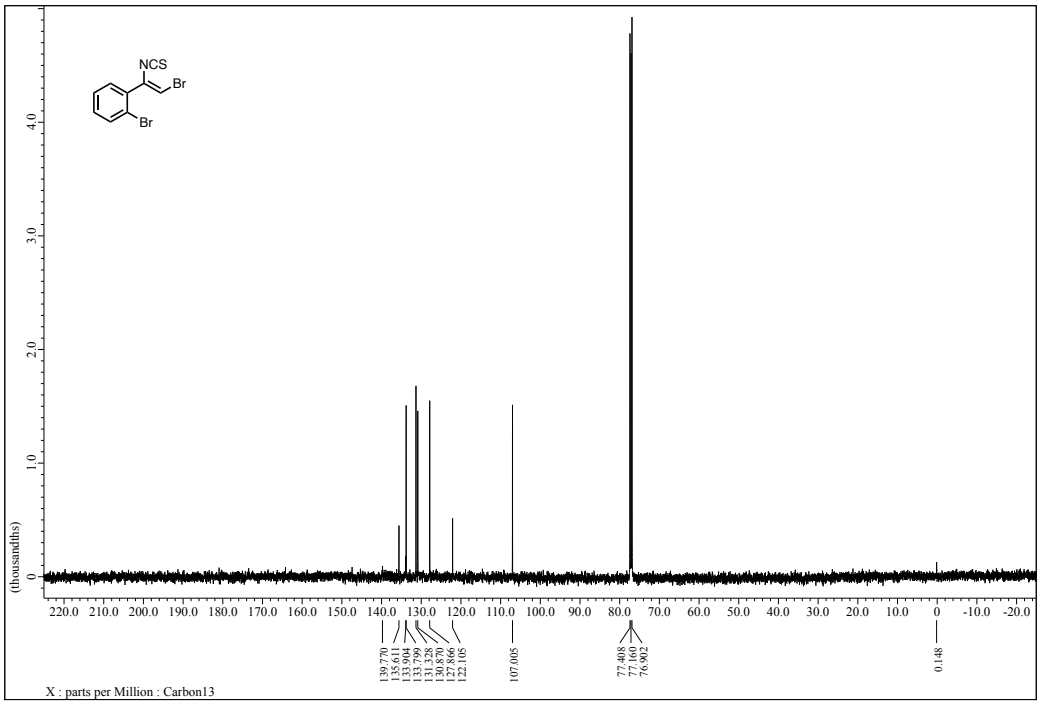

Figure S 79. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2j**.

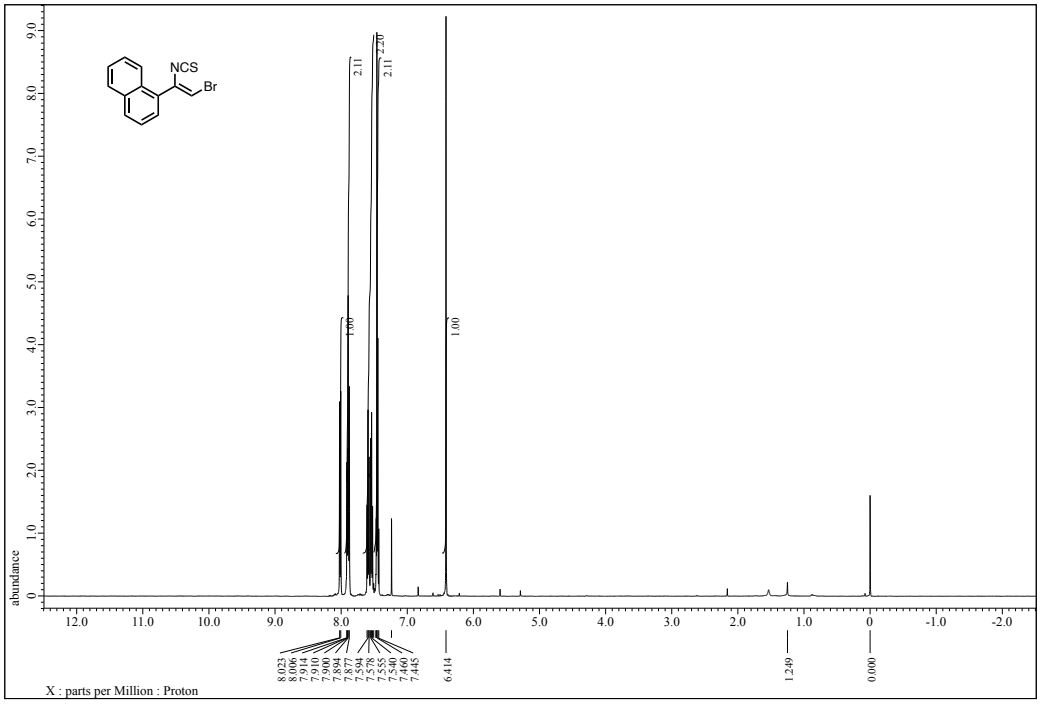

Figure S 80. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2k**.

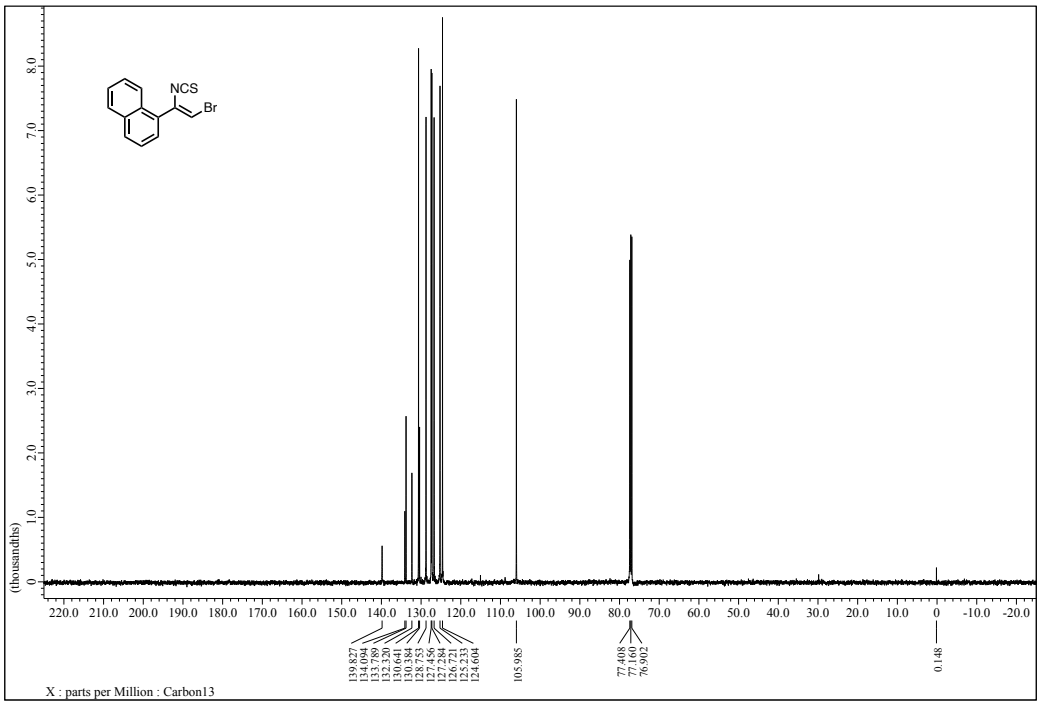

Figure S 81. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2k.**

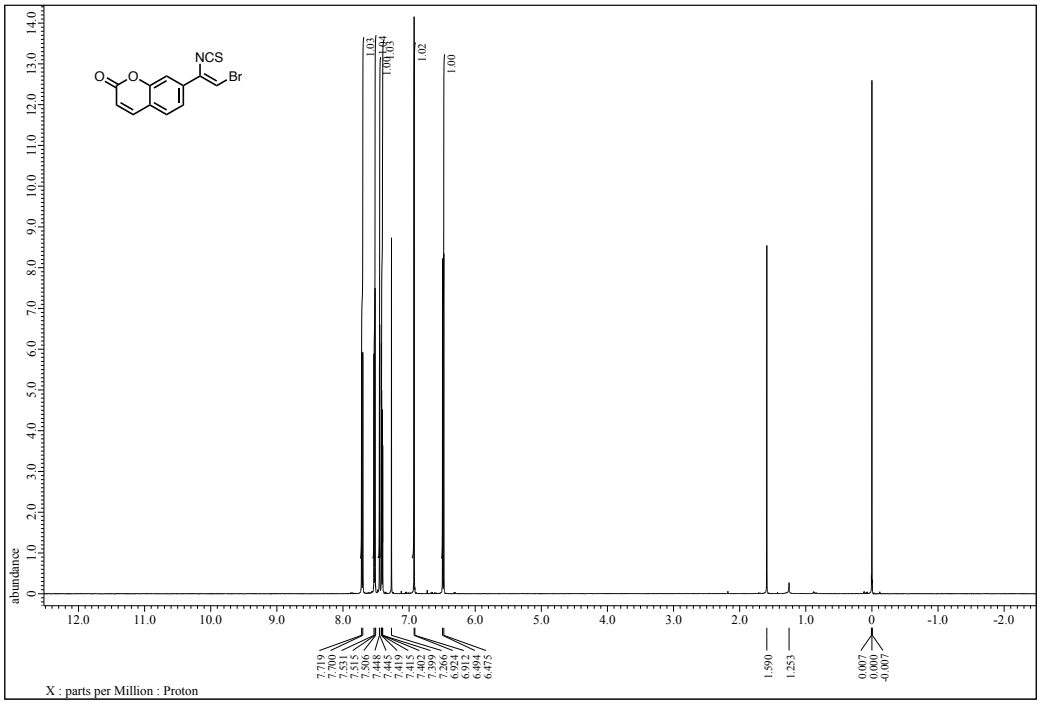

Figure S 82. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2l**.

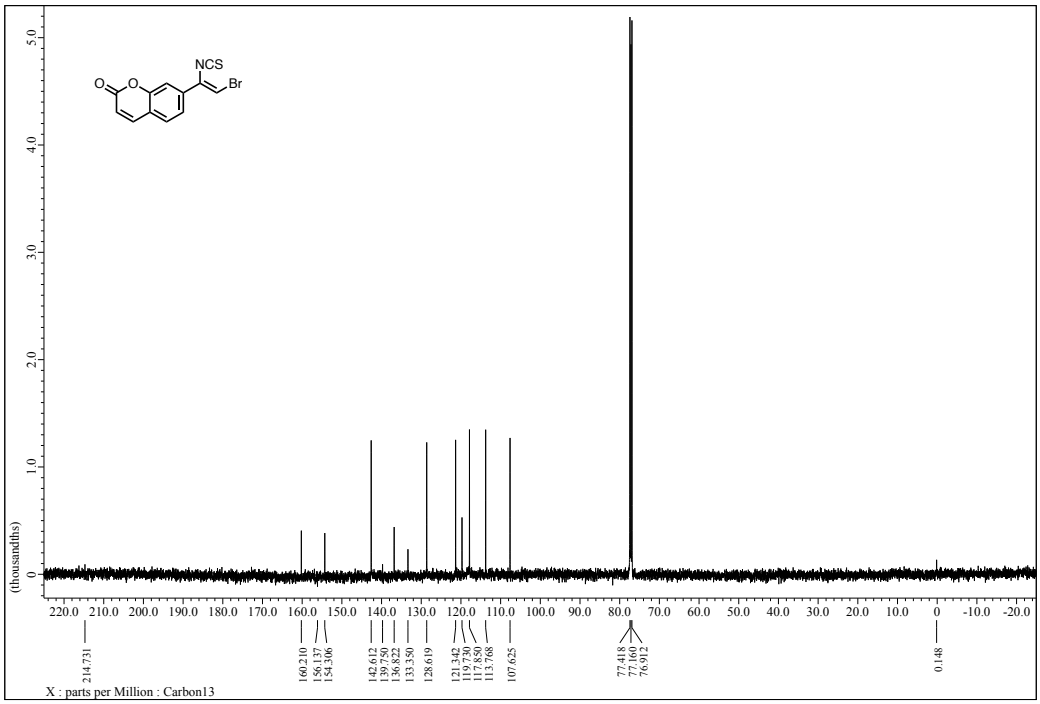

Figure S 83. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2l**.

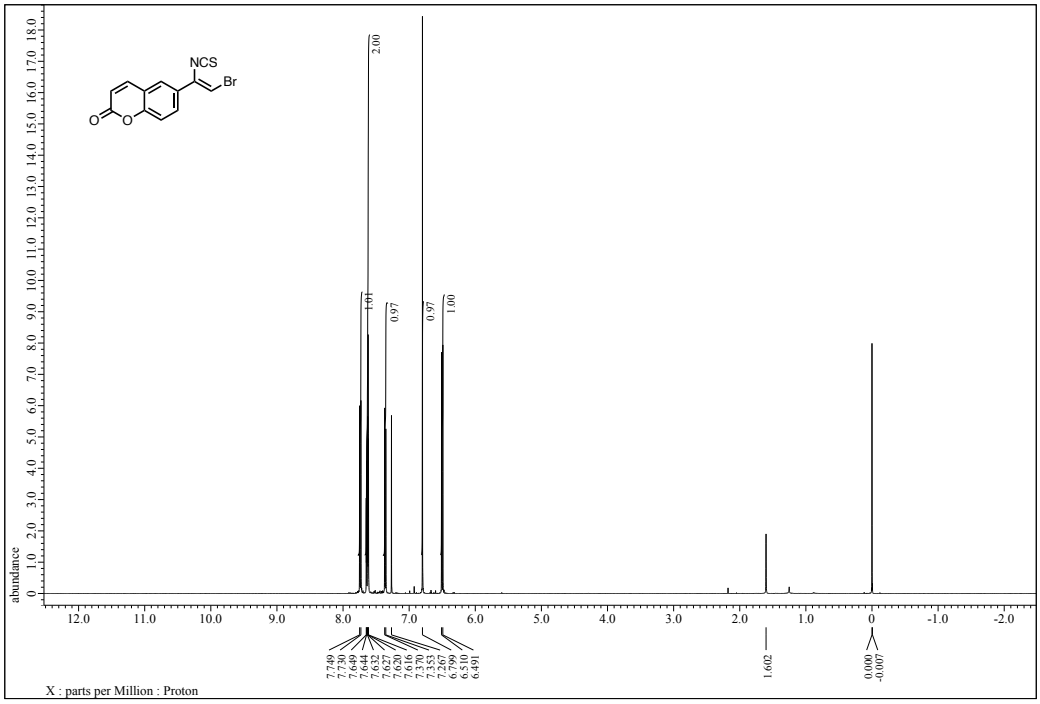

Figure S 84. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2m**.

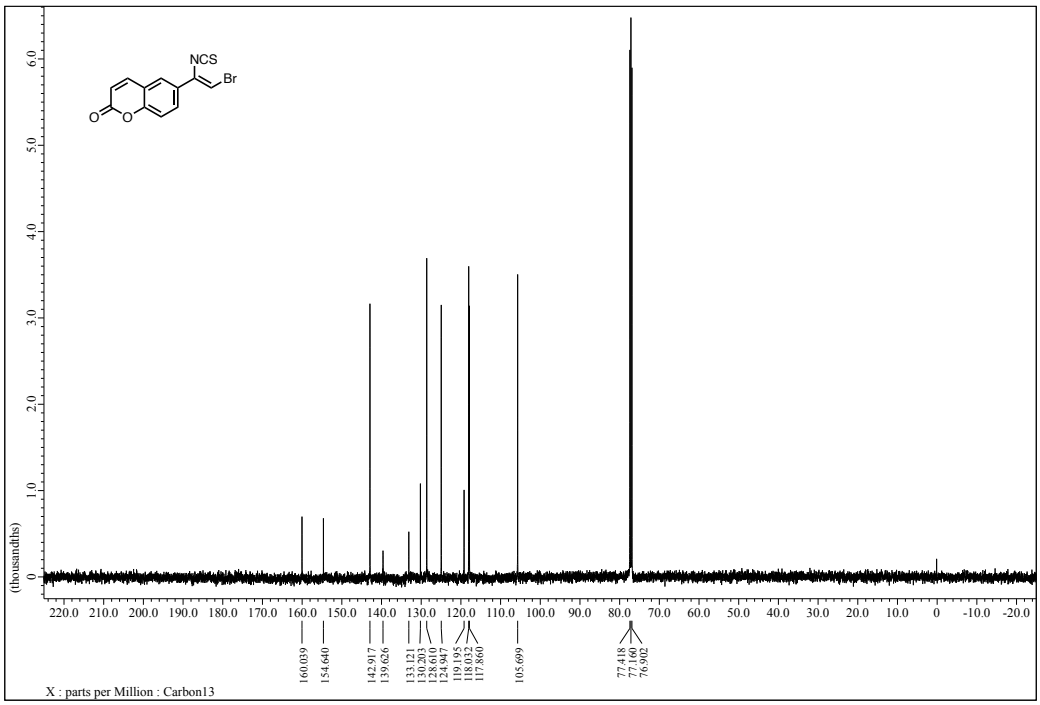

Figure S 85. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2m**.

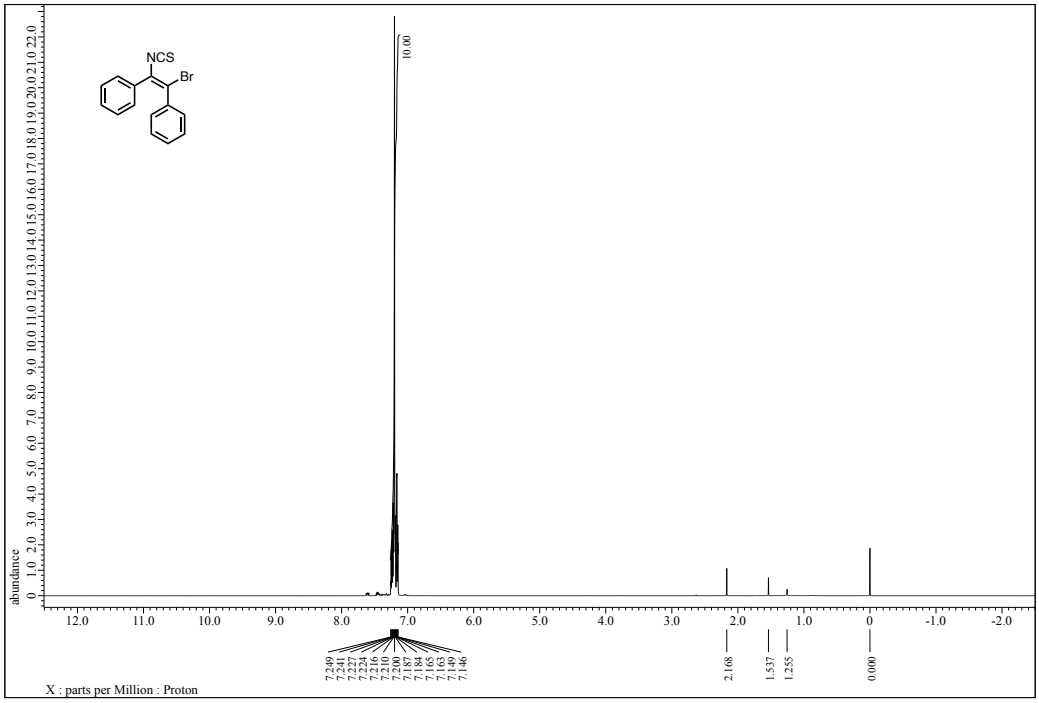

Figure S 86. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2n**.

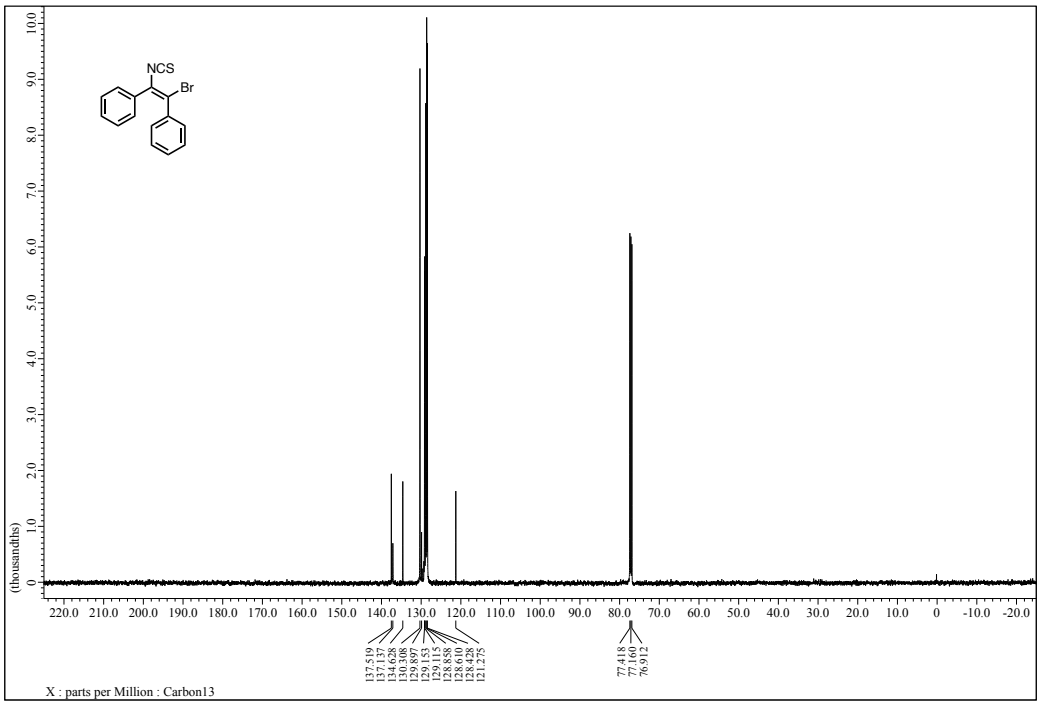

Figure S 87. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2n**.

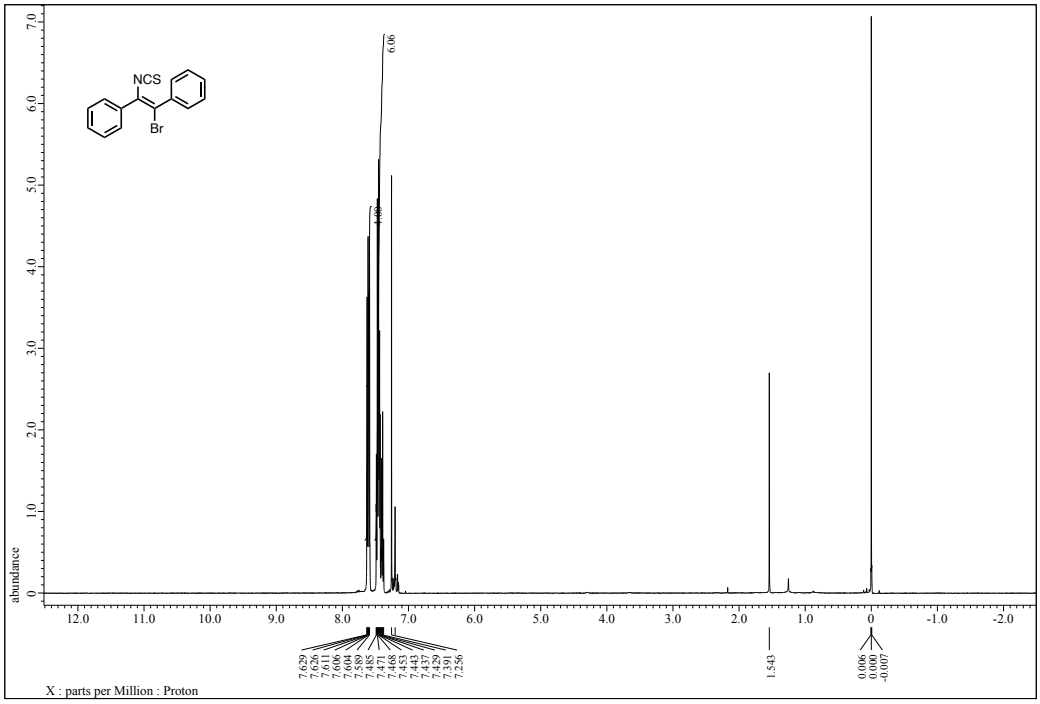

Figure S 88. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2n'**.

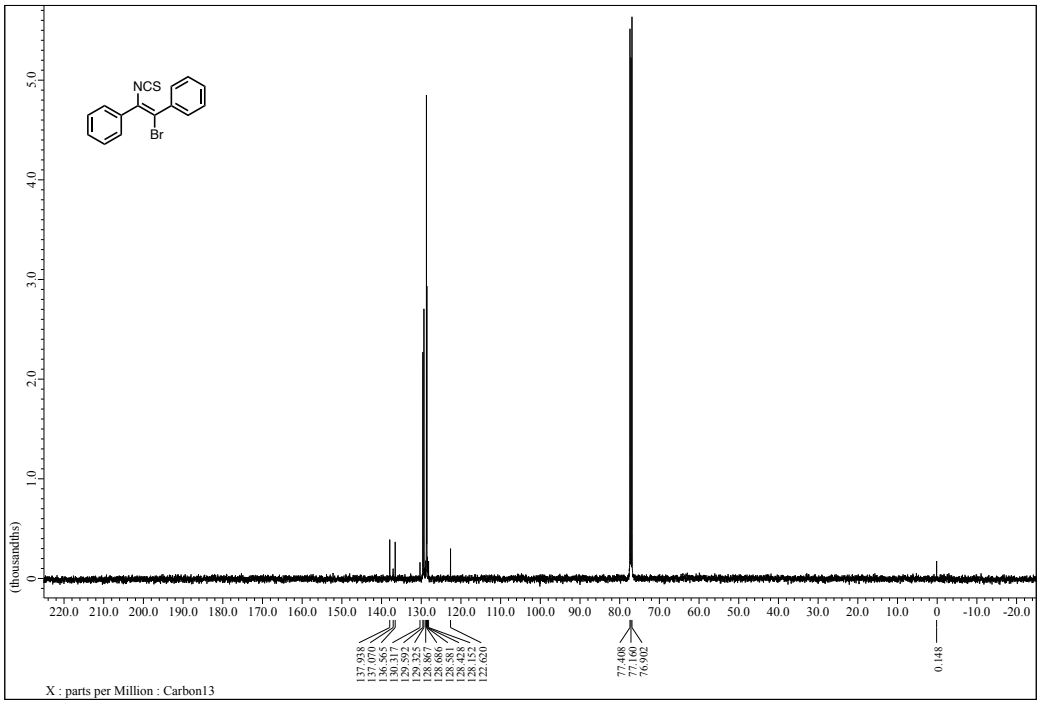

Figure S 89. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2n'**.

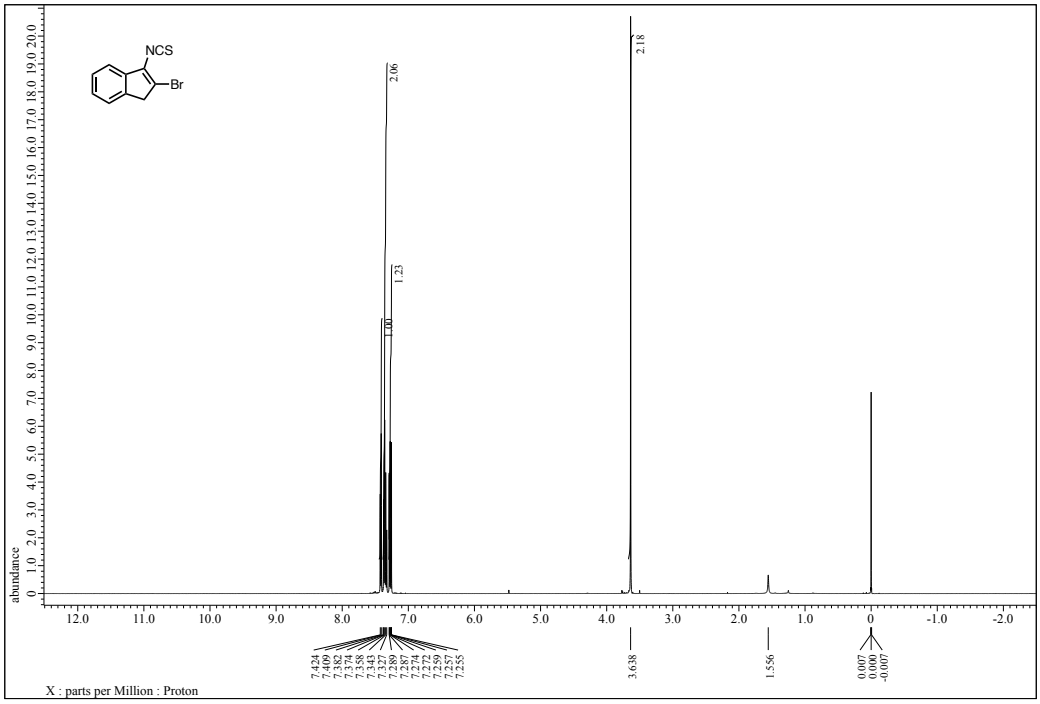

Figure S 90. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2o**.

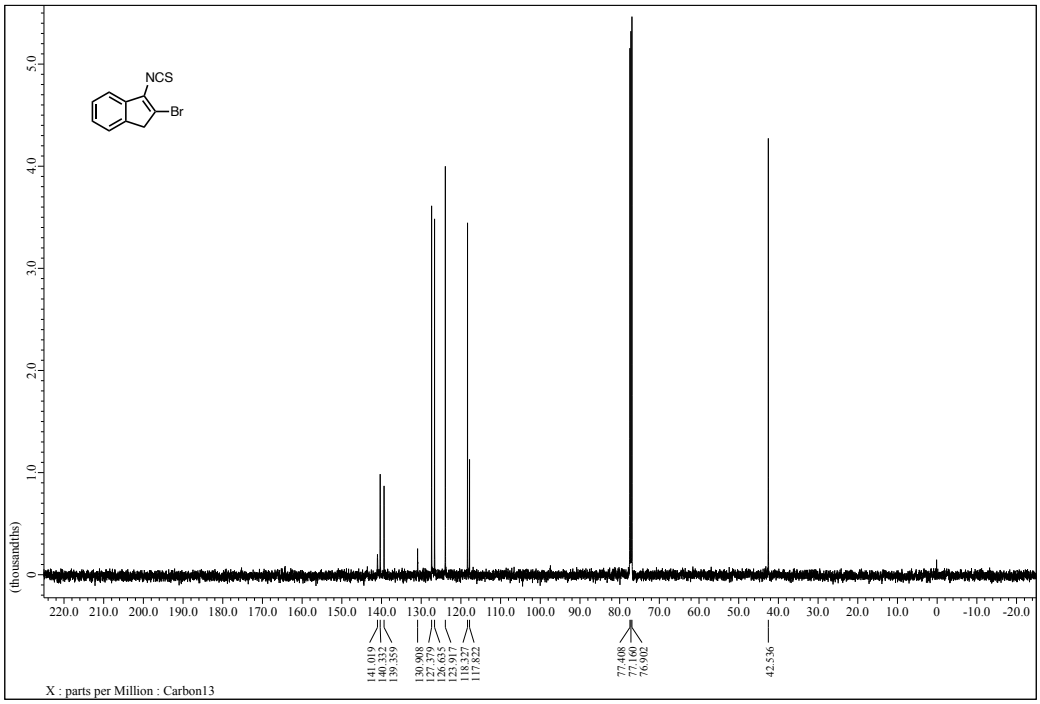

Figure S 91. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2o**.

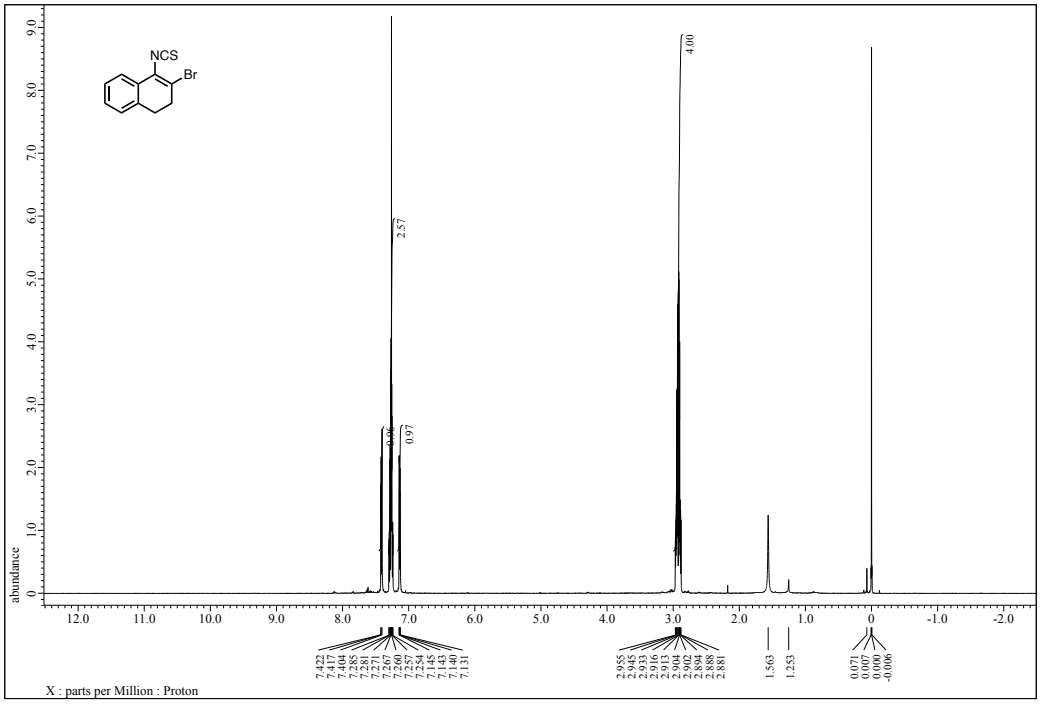

Figure S 92. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2p**.

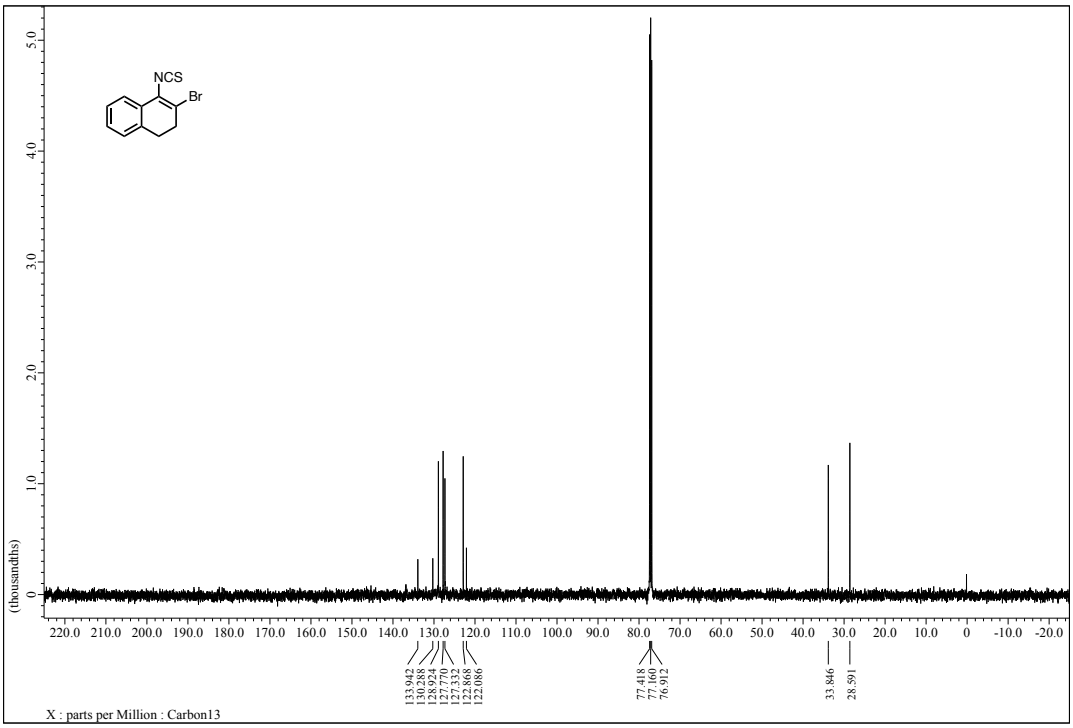

Figure S 93. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2p**.

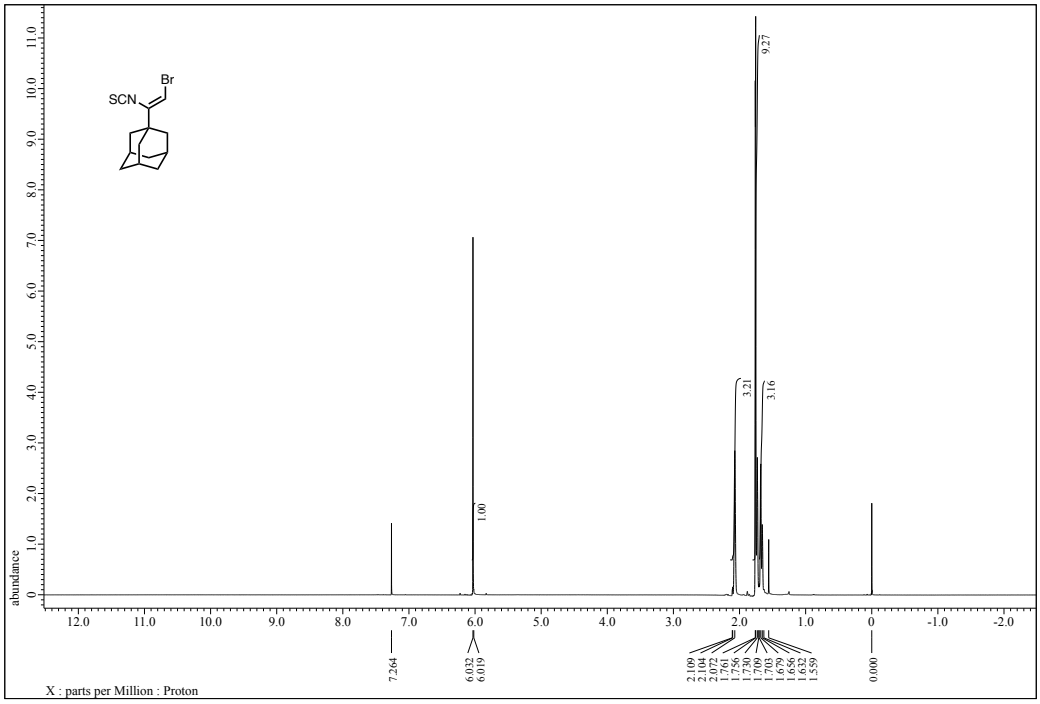

Figure S 94. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2q**.

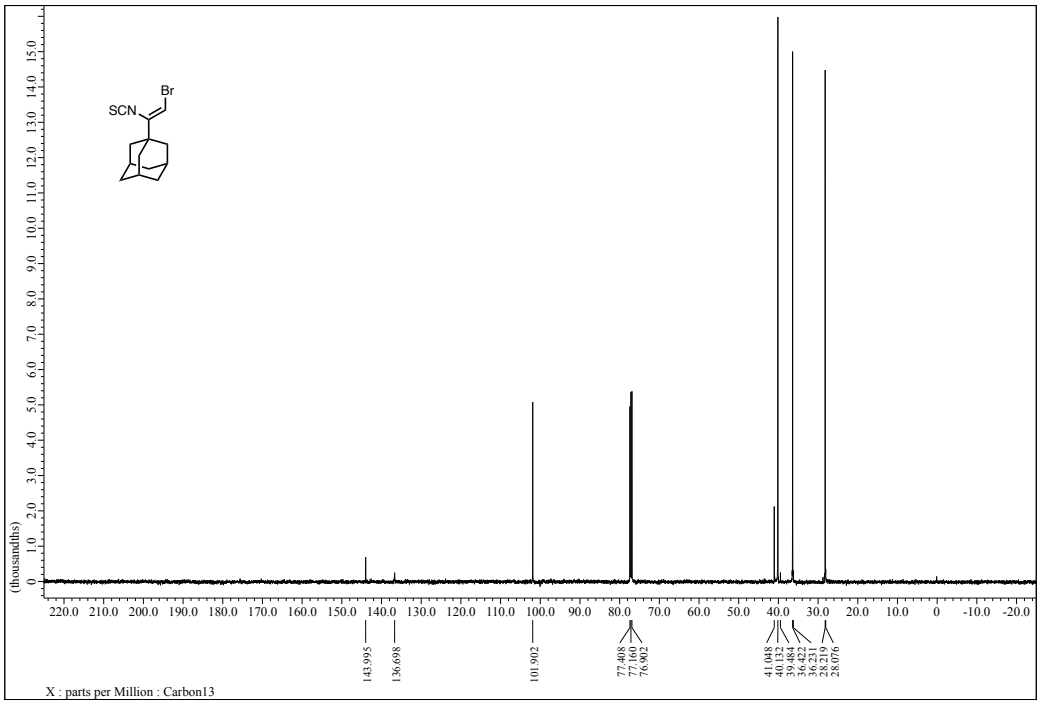

Figure S 95. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2q**.

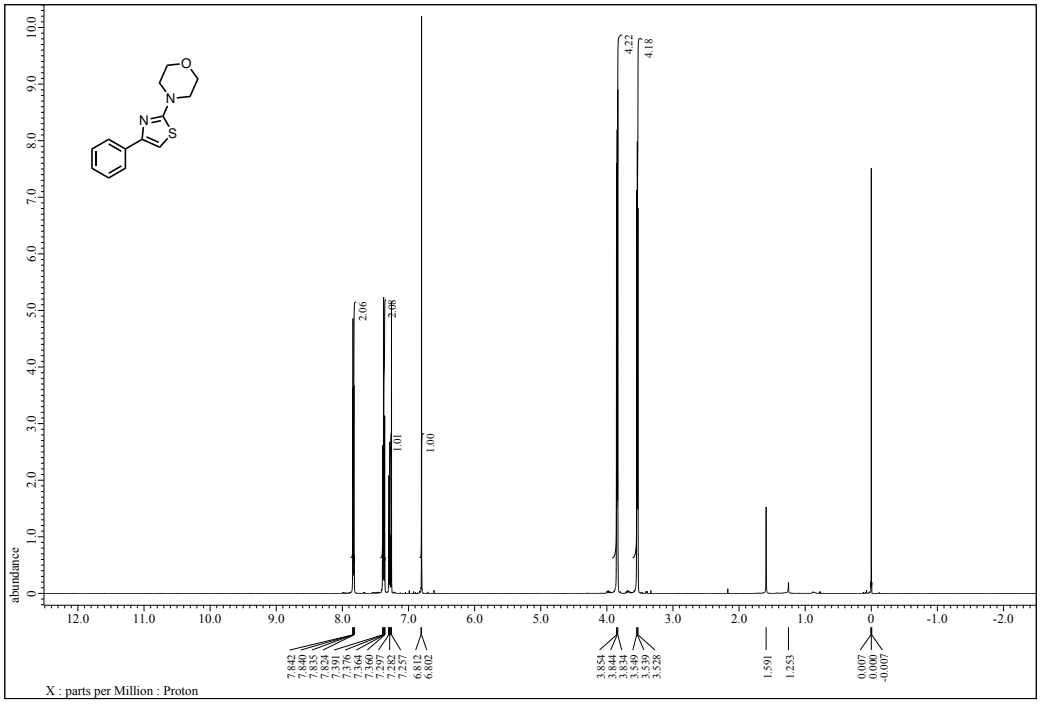

Figure S 96. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3**.

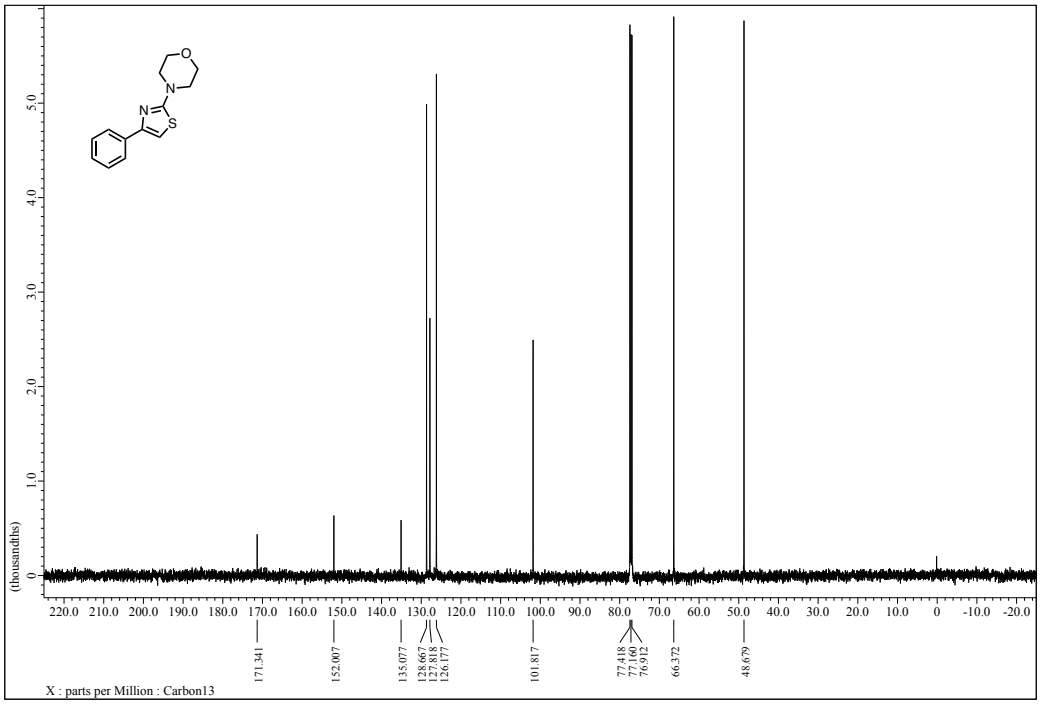

Figure S 97. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3**.

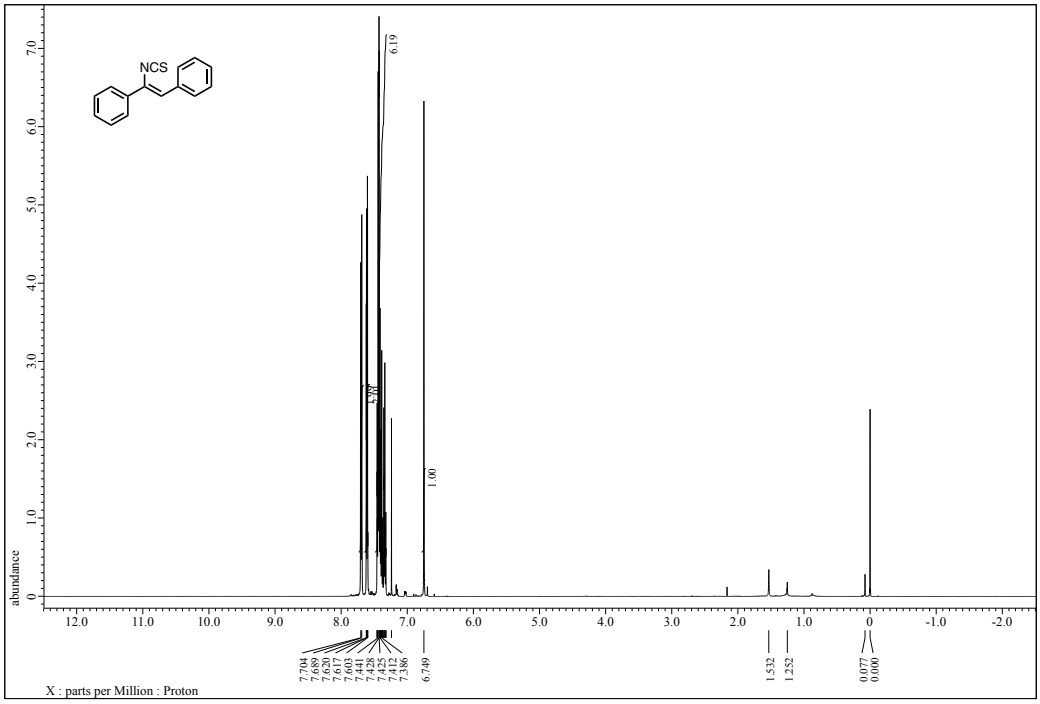

Figure S 98. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4**.

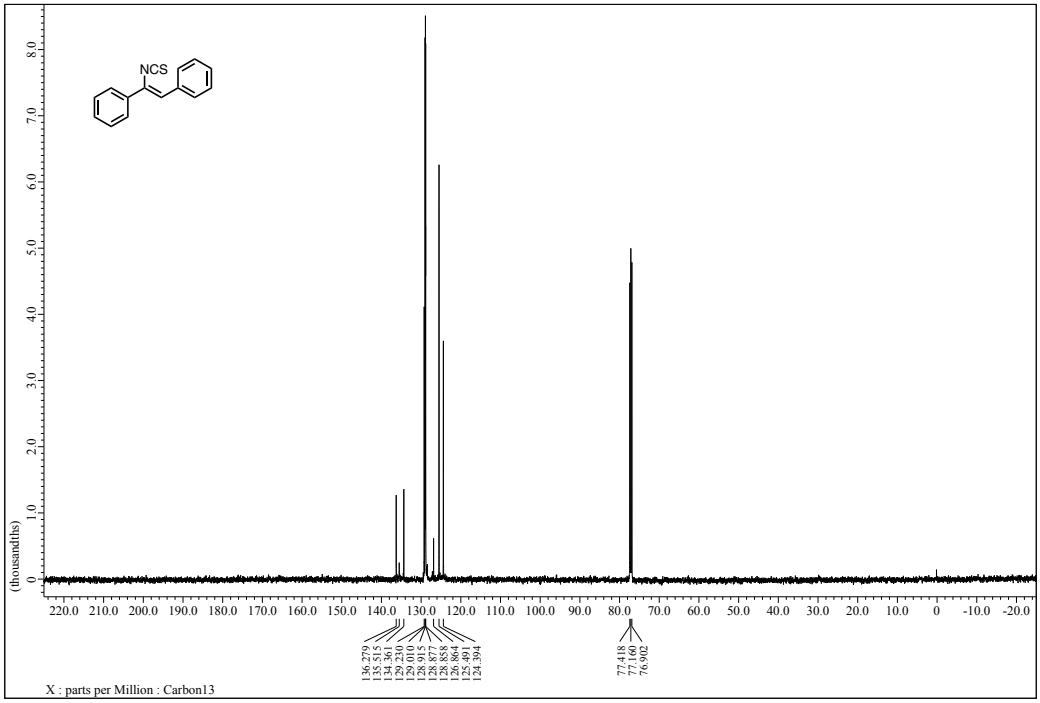

Figure S 99. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4**.

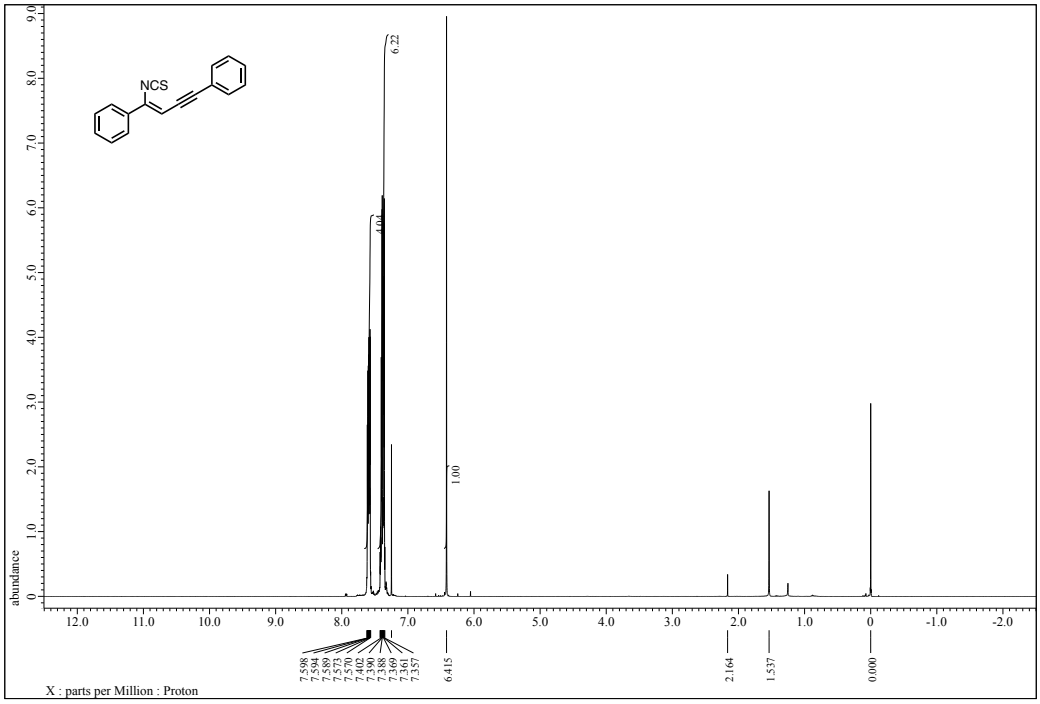

Figure S 100. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5**.

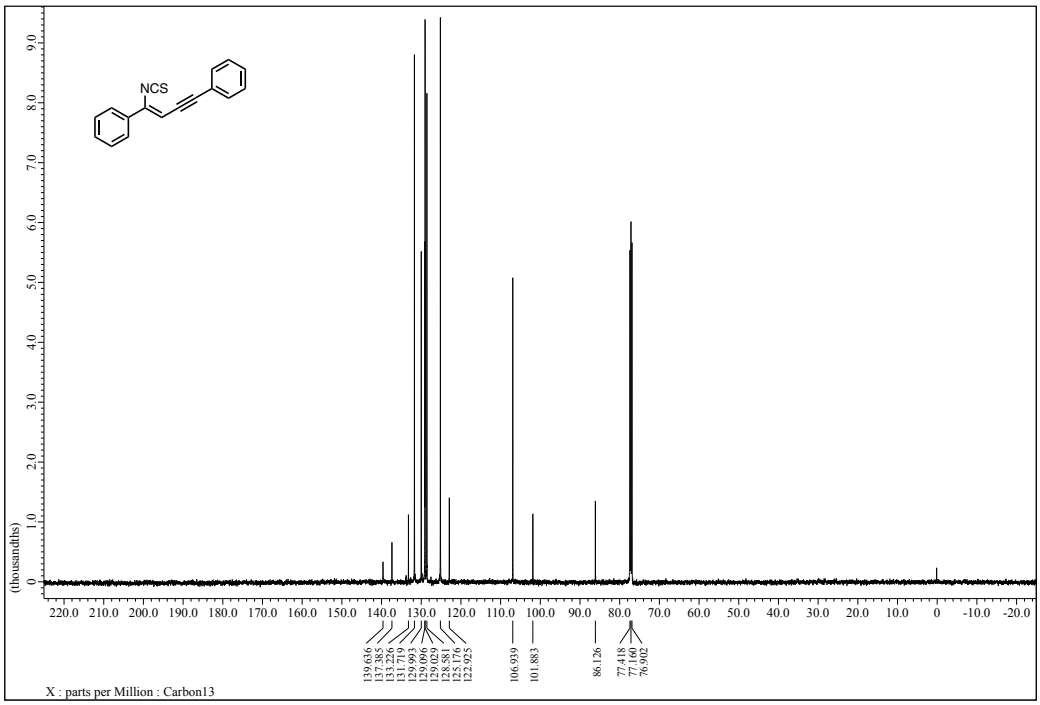

Figure S 101. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5**.

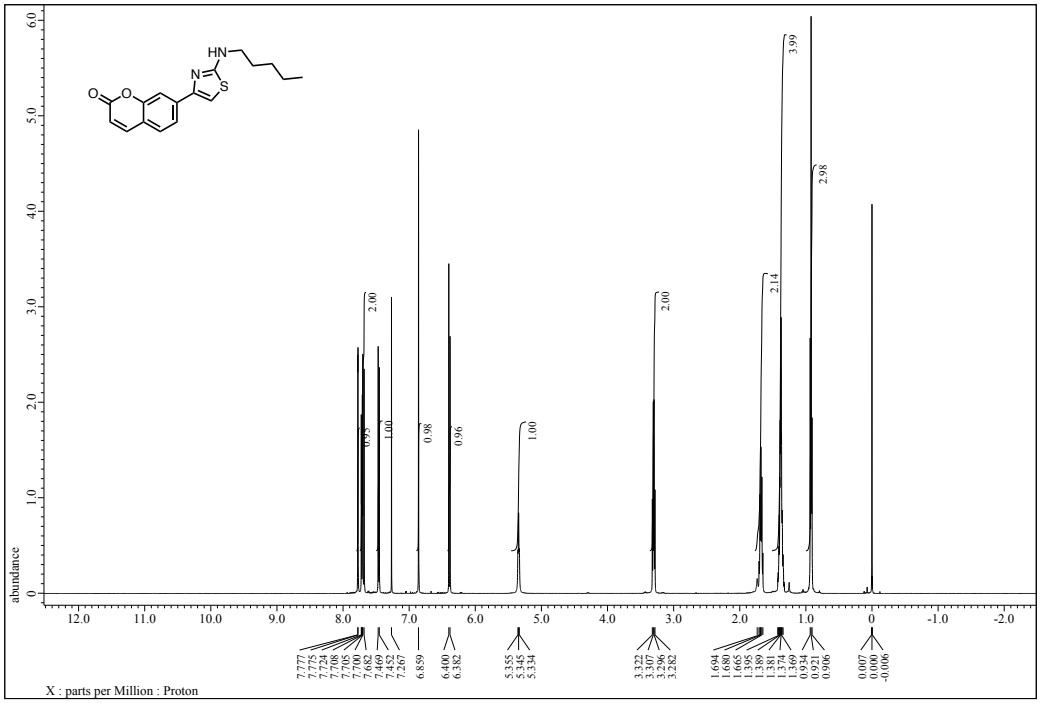

Figure S 102. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6**.

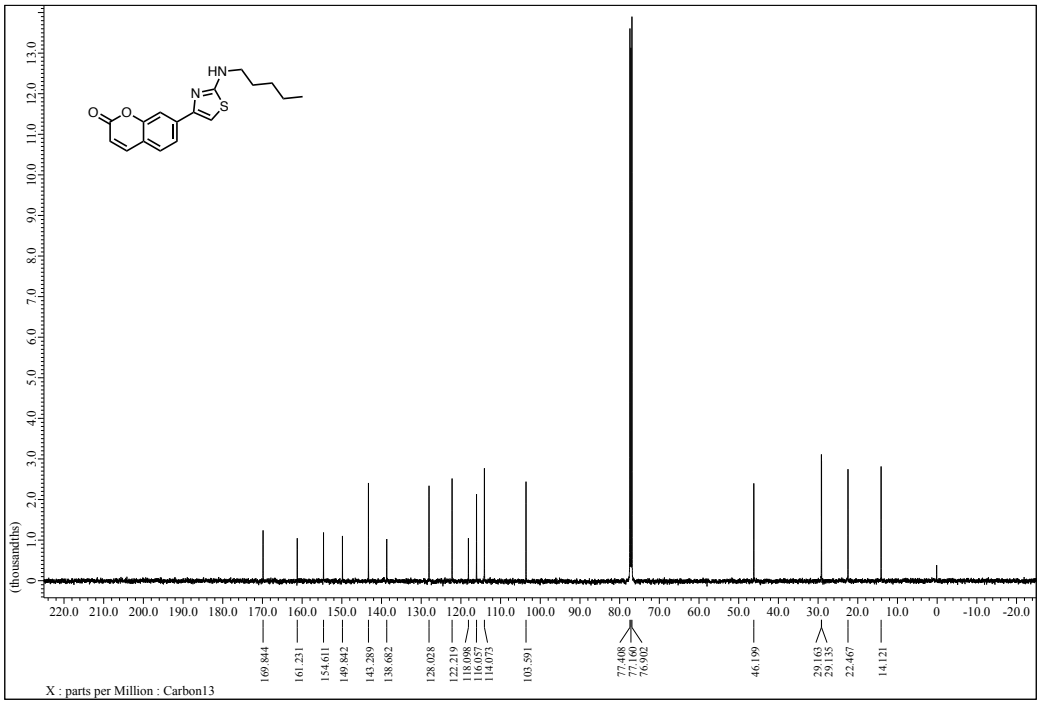

Figure S 103. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **6**.