

# Palladium-catalyzed Regioselective Synthesis of Mono and Bis(arylthiol) Alkene from Propargyl Carbonate and Thiophenol

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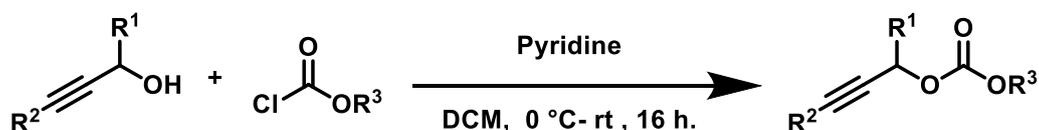
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## 1. General experimental

Unless otherwise noted, all materials including solvents and reagents were obtained from commercial suppliers and were used without further purification. All dry reactions were carried out under argon or nitrogen atmosphere in dried glassware. All work-up and purification were carried out with reagent-grades solvents in air. Analytical TLC was performed using  $2.5 \times 5$  cm plates coated with a 0.25 mmol thickness of silica gel (60F-254); visualization was accomplished under UV lamp. NMR spectra were recorded on 400 MHz spectrometer for  $^1\text{H}$  NMR 100 MHz for  $^{13}\text{C}$  NMR spectroscopy and chemical shift for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are expressed in parts per million(ppm) relative to the solvent. Chemical shifts are reported relative to the residual signals of either tetramethyl silane in  $\text{CDCl}_3$  or deuterated DMSO for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift assignments are based on two-dimensional NMR experiments including  $^1\text{H}$ -COSY, NOESY, HSQC and HMBC. All  $^{13}\text{C}$  spectra are  $^1\text{H}$  decoupled. NMR data is represented as follows chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, app. dd, = apparent doublet of doublets, app. t = apparent triplet), coupling constant (J) in Hertz (Hz), integration. HRMS were recorded by using Q-TOF mass spectrometer. Mass spectra were recorded using electron spray ionization (ESI-MS) using argon FAB gas. Column chromatography was performed with silica gel (100-200 mesh) as the stationary state. All reaction was monitored by TLC.

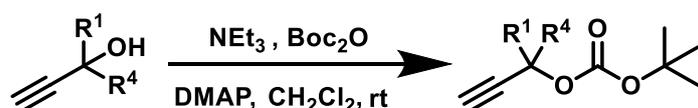
## 2. Synthetic Details

### General Procedure 1 (GP1) for the preparation of 1a, 1c-1d and 1k-1l:



As per literature procedure<sup>1</sup> a 250 ml schlenk flask was placed under an argon atmosphere and charged with functionalised propargyl alcohol (1 equiv.) and 0.2 M DCM, then stirred for 5 min at rt. After that pyridine (2 equiv.) was added to the solution and the mixture was stirred for 15 min. The solution was then cooled to 0°C using an ice water bath followed by the dropwise addition of functionalised chloroformate (2 equiv.) over few mins. Then resulting mixture was allowed to stir for 1h at 0°C and warmed to rt and stirred for 16 h. The reaction was quenched with the saturated solution of ammonium chloride and extracted into DCM and washed with water then brine. The crude product was dried over sodium sulphate and concentrated under reduced pressure. Then the liquid product (1a, 1c-1d and 1k-1l) was obtained by column- chromatography.

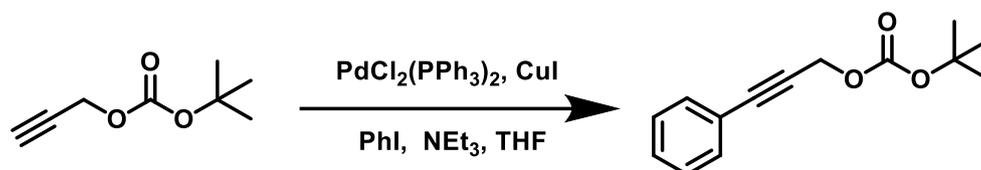
### General Procedure 2 (GP2) for the preparation of 1b, 1e, 1g and 1i-1j:



According to the literature procedure<sup>2</sup> to a solution of alcohol (1 equiv.) in DCM (0.5 M) was added  $\text{NEt}_3$  (1.1 equiv.),  $\text{Boc}_2\text{O}$  (1 equiv.) and DMAP (0.05 equiv.). The mixture was stirred

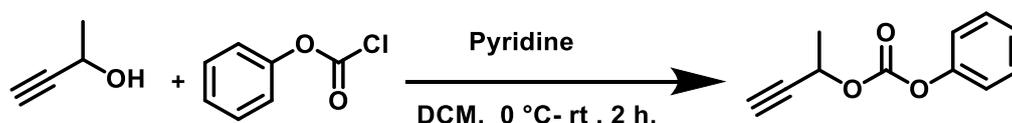
at rt and followed periodically by TLC. Upon completion, the reaction was quenched with water and extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure. The crude was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether) to give the protected alcohol (1b, 1e, 1g and 1i-1j).

**Procedure 1 (P1) for the preparation of 1h:<sup>3</sup>**



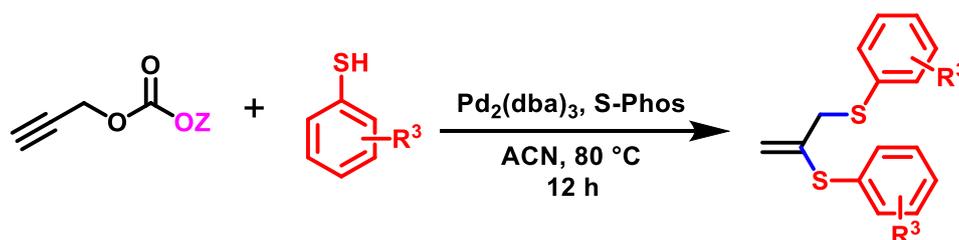
To a solution of alkyne (1 equiv.) in THF (0.1 M), PhI (1.2 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.03 equiv.), CuI (0.05 equiv.) and NEt<sub>3</sub> (10 equiv.) were successively added. The reaction mixture was allowed to react at rt overnight. Upon completion, it was diluted with diethyl ether and filtered through silica, and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether) to afford the desired product (1h).

**Procedure 2 (P2) for the preparation of 1f:**



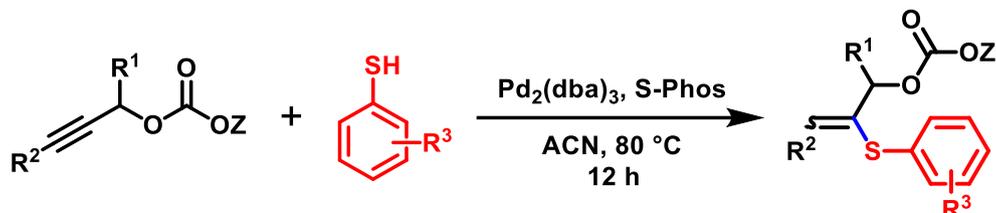
As per literature procedure<sup>4</sup> a 250 ml schlenk flask was placed under an argon atmosphere and charged with but-3-yn-2-ol (1 equiv.) and 0.2 M DCM, then stirred for 5 min at rt. After that pyridine (2 equiv.) was added to the solution and the mixture was stirred for 15 min. The solution was then cooled to 0°C using an ice water bath followed by the dropwise addition of phenyl chloroformate (2 equiv.) over few mins. Then resulting mixture was allowed to stir for 1h at 0°C and warmed to rt and stirred for an additional hour. The reaction was quenched with the saturated solution of ammonium chloride and extracted into DCM and washed with water then brine. The crude product was dried over sodium sulphate and concentrated under reduced pressure. Then the colourless liquid product (1f) was obtained through column-chromatography.

**General Procedure 3 (GP3) for the preparation of 3a-3g & 8a:**



A Schlenk tube equipped with a stir bar was evacuated, backfilled with nitrogen and charged with substrate (2.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2 mol%) and S-phos (5 mol%) before propargyl carbonate (1.1 mmol) in acetonitrile (0.2 M with respect to the substrate) was added. The reaction was stirred at 80°C in an oil bath for 12 h. The suspension was filtered through a Celite pad and the resulting solution was concentrated in vacuo and the crude product was purified by flash column chromatography.

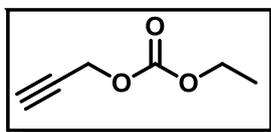
#### General Procedure 4 (GP4) for the preparation of 4a-4z',4a' & 4i':



A Schlenk tube equipped with a stir bar was evacuated, backfilled with nitrogen and charged with substrate (1.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2 mol%) and S-phos (5 mol%) before propargyl carbonate (1.1 mmol) in acetonitrile (0.2 M with respect to the substrate) was added. The reaction was stirred at 80°C in an oil bath for 12 h. The suspension was filtered through a Celite pad and the resulting solution was concentrated in vacuo and the crude product was purified by flash column chromatography to produce the products 4a- 4z' & 4a'.

### 3. Experimental section:

#### Ethyl prop-2-yn-1-yl carbonate (1a)



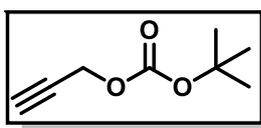
Colourless liquid. Synthesised by GP1 (87%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.72 (d, *J* = 2.34 Hz, 2H), 4.23 (q, *J* = 7.13 Hz, 2H), 2.55 (t, *J* = 2.44 Hz, 1H), 1.32 (t, *J* = 7.08 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 154.47, 75.49, 64.48, 63.67, 54.97, 14.12.

HRMS (*m/z*): calculated for C<sub>6</sub>H<sub>9</sub>O<sub>3</sub> [*M* + H]<sup>+</sup>, 129.0546; found, 129.0538.

#### Tert-butyl prop-2-yn-1-yl carbonate (1b)<sup>3</sup>

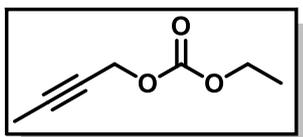


Pale yellow liquid. Synthesised by GP2 (91%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 4.66 (d,  $J$  = 2.53 Hz, 2H), 2.49 (t,  $J$  = 2.44 Hz, 1H), 1.49 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 152.73, 82.98, 77.38, 75.18, 54.28, 27.68.

**But-2-yn-1-yl ethyl carbonate (1c)<sup>1</sup>**

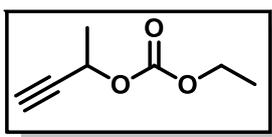


Colourless liquid. Synthesised by GP1 (95%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 4.68-4.67 (m, 2H), 4.21 (q,  $J$  = 7.14 Hz, 2H), 1.86-1.84 (m, 3H), 1.30 (t,  $J$  = 7.12 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 154.52, 83.46, 72.65, 63.99, 55.62, 13.94, 3.18.

**But-3-yn-2-yl ethyl carbonate (1d)<sup>5</sup>**

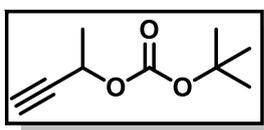


Yellow liquid. Synthesised by GP1 (97%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 5.27 (dq,  $J$  = 2.14 Hz,  $J$  = 6.70 Hz, 1H), 4.19 (q,  $J$  = 7.16 Hz, 2H), 2.48 (d,  $J$  = 2.14 Hz, 1H), 1.52 (d,  $J$  = 6.75 Hz, 3H), 1.29 (t,  $J$  = 7.15 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 154.12, 81.45, 73.64, 64.26, 63.69, 21.86, 14.17.

**But-3-yn-2-yl tert-butyl carbonate (1e)**



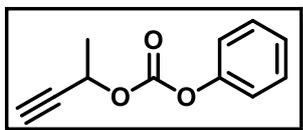
Yellow liquid. Synthesised by GP2 (93%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 5.19 (dq,  $J$  = 2.10 Hz,  $J$  = 6.73 Hz, 1H), 2.44 (d,  $J$  = 2.12 Hz, 1H), 1.49 (d,  $J$  = 6.72 Hz, 3H), 1.45 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 152.37, 82.67, 81.76, 73.31, 62.76, 27.69, 21.19.

**HRMS** (m/z): calculated for C<sub>9</sub>H<sub>15</sub>O<sub>3</sub> [M + H]<sup>+</sup>, 171.1016; found, 171.1023.

**But-3-yn-2-yl phenyl carbonate (1f)**



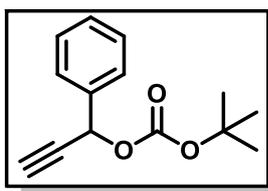
Colourless liquid. Synthesised by P2 (94%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.40-7.33 (m, 2H), 7.24-7.15 (m, 3H), 5.37 (dq, *J* = 2.12 Hz, *J* = 6.73 Hz, 1H), 2.53 (d, *J* = 2.14 Hz, 1H), 1.60 (d, *J* = 6.72 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 152.71, 151.05, 129.50, 126.14, 120.99, 81.00, 74.33, 64.85, 21.22.

**HRMS** (m/z): calculated for C<sub>11</sub>H<sub>11</sub>O<sub>3</sub> [M + H]<sup>+</sup>, 191.0703; found, 191.0708.

**Tert-butyl (1-phenylprop-2-yn-1-yl) carbonate (1g)<sup>3</sup>**

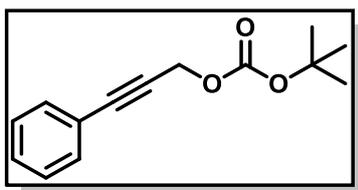


Colourless liquid. Synthesised by GP2 (88%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.55-7.53 (m, 2H), 7.40-7.34 (m, 3H), 6.23 (d, *J* = 2.29, 1H), 2.68 (d, *J* = 2.32 Hz, 1H), 1.48 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 152.47, 136.25, 129.15, 128.69, 127.70, 83.16, 80.04, 76.00, 68.21, 27.76.

**Tert-butyl (3-phenylprop-2-yn-1-yl) carbonate (1h)<sup>3</sup>**

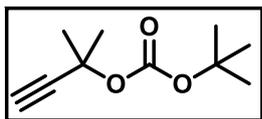


Colourless liquid. Synthesised by P1 (76%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.45-7.43 (m, 2H), 7.33-7.27 (m, 3H), 4.89 (s, 2H), 1.50 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 152.88, 131.85, 128.72, 128.27, 122.19, 86.84, 82.88, 82.65, 55.26, 27.73.

**Tert-butyl (2-methylbut-3-yn-2-yl) carbonate (1i)<sup>3</sup>**

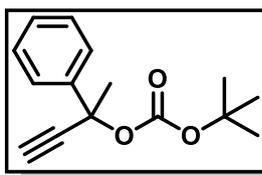


Colourless liquid. Synthesised by GP2 (89%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.54 (s, 1H), 1.69 (s, 6H), 1.49 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 151.35, 84.47, 82.22, 72.81, 72.41, 28.86, 27.79.

**Tert-butyl (2-phenylbut-3-yn-2-yl) carbonate (1j)<sup>6</sup>**

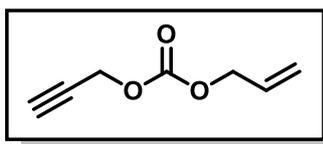


Colourless liquid. Synthesised by GP2 (90%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.60-7.58 (m, 2H), 7.37-7.33 (m, 2H), 7.31-7.27 (m, 1H), 2.81 (s, 1H), 1.88 (s, 3H), 1.40 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.88, 142.19, 128.39, 127.96, 124.68, 82.83, 82.63, 75.70, 32.59, 27.71.

**Allyl prop-2-yn-1-yl carbonate (1k)**



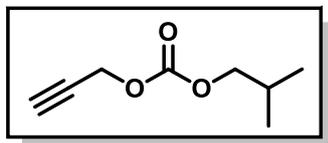
Colourless liquid. Synthesised by GP1 (95%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 5.98-5.88 (m, 1H), 5.39-5.35 (m, 1H), 5.29-5.26 (m, 1H), 4.73(d,  $J$  = 2.47 Hz, 2H), 4.67-4.64 (m, 2H), 2.54 (t,  $J$  = 2.45 Hz, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ =154.34, 131.26, 119.04, 75.65, 68.83, 55.21.

**HRMS (m/z):** calculated for C<sub>7</sub>H<sub>9</sub>O<sub>3</sub> [M + H]<sup>+</sup>, 141.0546; found, 141.0532.

**Isobutyl prop-2-yn-1-yl carbonate (11)**



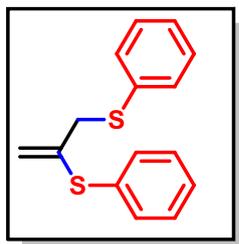
Colourless liquid. Synthesised by GP1 (90%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 4.72 (d, *J* = 2.45 Hz, 2H), 3.96 (d, *J* = 6.67 Hz, 2H), 2.53 (t, *J* = 2.46 Hz, 1H), 2.03-1.93 (m, 1H), 0.96 (d, *J* = 6.74 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ =154.67, 75.52, 74.54, 73.89, 55.06, 27.73, 18.79.

**HRMS (m/z):** calculated for C<sub>8</sub>H<sub>13</sub>O<sub>3</sub> [M + H]<sup>+</sup>, 157.0859; found, 157.0847.

**Prop-2-ene-1,2-diylbis(phenylsulfane) (3a)**



Pale yellow oil. Synthesised by GP3 (76%).

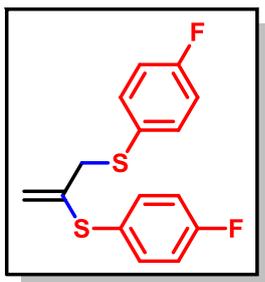
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.42-7.41 (m, 2H), 7.34-7.27 (m, 6H), 7.24 (s, 1H), 7.22-7.17 (m, 1H), 5.37 (s, 1H), 5.07 (s, 1H), 3.65 (s, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 141.13, 133.09, 132.69, 130.76, 130.35, 129.24, 128.84, 128.02, 126.61, 116.94, 40.21.

**IR ν (cm<sup>-1</sup>):** 3740, 3419, 2921, 1635, 1068, 738, 688.

**HRMS (m/z):** calculated for C<sub>15</sub>H<sub>15</sub>S<sub>2</sub> [M + H]<sup>+</sup>, 259.0610; found, 259.0618.

**Prop-2-ene-1,2-diylbis((4-fluorophenyl)sulfane) (3b)**



Pale yellow oil. Synthesised by GP3 (82%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.42-7.35 (m, 4H), 7.05-6.96 (m, 4H), 5.17 (s, 1H), 4.88 (s, 1H), 3.56 (s, 2H).

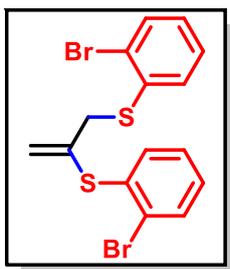
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 164.15 (d,  $J_{\text{C-F}}$  = 249.17 Hz), 163.50 (d,  $J_{\text{C-F}}$  = 248.14 Hz), 161.67 (d,  $J_{\text{C-F}}$  = 249.17 Hz), 161.08 (d,  $J_{\text{C-F}}$  = 248.14 Hz), 141.91, 135.90 (d,  $J_{\text{C-F}}$  = 8.43 Hz), 135.82 (d,  $J_{\text{C-F}}$  = 8.43 Hz), 133.87 (d,  $J_{\text{C-F}}$  = 8.18 Hz), 133.79 (d,  $J_{\text{C-F}}$  = 8.18 Hz), 130.17 (d,  $J_{\text{C-F}}$  = 3.28 Hz), 130.14 (d,  $J_{\text{C-F}}$  = 3.28 Hz), 127.40 (d,  $J_{\text{C-F}}$  = 3.99 Hz), 127.37 (d,  $J_{\text{C-F}}$  = 3.99 Hz), 116.57 (d,  $J_{\text{C-F}}$  = 27.79 Hz), 116.36 (d,  $J_{\text{C-F}}$  = 27.79 Hz), 116.08 (d,  $J_{\text{C-F}}$  = 21.84 Hz), 115.86 (d,  $J_{\text{C-F}}$  = 21.84 Hz), 115.45, 41.49.

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):** -112.59 (s, 1F), -114.37 (s, 1F).

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3838, 3436, 2064, 1635, 1065, 668.

**HRMS** ( $m/z$ ): calculated for  $\text{C}_{15}\text{H}_{13}\text{F}_2\text{S}_2$  [ $\text{M} + \text{H}$ ] $^+$ , 295.0421; found, 295.0422.

### Prop-2-ene-1,2-diylbis((2-bromophenyl)sulfane) (3c)



Colourless oil. Synthesised by GP3 (84%).

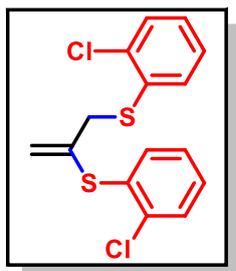
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.62-7.60 (m, 1H), 7.55-7.53 (m, 1H), 7.44-7.42 (m, 1H), 7.30-7.21 (m, 3H), 7.15-7.12 (m, 1H), 7.06-7.02 (m, 1H), 5.58 (s, 1H), 5.17 (s, 1H), 3.71 (s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 138.41, 136.63, 134.22, 133.73, 133.60, 133.02, 130.13, 129.23, 128.04, 127.73, 127.46, 127.31, 124.60, 119.38, 38.85$ .

IR  $\nu$  ( $\text{cm}^{-1}$ ): 3433, 2921, 1634, 1444, 1105, 742.

HRMS (m/z): calculated for  $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{S}_2$   $[\text{M} + \text{H}]^+$ , 416.8820; found 416.8824.

### Prop-2-ene-1,2-diylbis((2-chlorophenyl)sulfane) (3d)



Colourless oil. Synthesised by GP3 (85%).

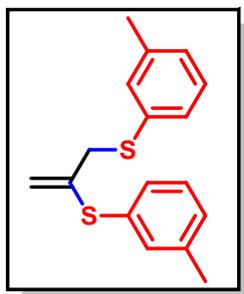
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.45\text{-}7.42$  (m, 2H), 7.37-7.35 (m, 1H), 7.33-7.30 (m, 1H), 7.24-7.20 (m, 2H), 7.19-7.11 (m, 2H), 5.52 (s, 1H), 5.13 (s, 1H), 3.71 (s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 138.46, 136.95, 134.63, 134.50, 134.07, 132.02, 130.68, 130.26, 129.71, 129.24, 127.46, 127.37, 127.07, 118.76, 38.54$ .

IR  $\nu$  ( $\text{cm}^{-1}$ ): 3430, 2922, 1633, 1450, 1034, 744.

HRMS (m/z): calculated for  $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{S}_2$   $[\text{M} + \text{H}]^+$ , 326.9830; found, 326.9837.

### Prop-2-ene-1,2-diylbis(m-tolylsulfane) (3e)



Pale yellow oil. Synthesised by GP3 (65%).

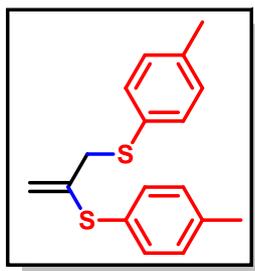
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.25\text{-}7.24$  (m, 1H), 7.22-7.20 (m, 2H), 7.15-7.13 (m, 3H), 7.12-7.09 (m, 1H), 7.01-6.99 (m, 1H), 5.39 (s, 1H), 5.10 (s, 1H), 3.65 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  =141.17, 139.07, 138.57, 135.50, 133.58, 132.39, 130.77, 130.03, 129.03, 128.82, 128.67, 127.39, 127.10, 116.87, 40.05, 21.31, 21.25.

**IR  $\nu$  ( $\text{cm}^{-1}$ ):** 3839, 3740, 3422, 2921, 1634, 1064, 771.

**HRMS (m/z):** calculated for  $\text{C}_{17}\text{H}_{19}\text{S}_2$   $[\text{M} + \text{H}]^+$ , 287.0923; found, 287.0932.

**Prop-2-ene-1,2-diylbis(p-tolylsulfane) (3f)**



Colourless oil. Synthesised by GP3 (68%).

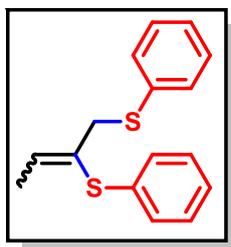
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.33-7.30 (m, 2H), 7.26-7.25 (m, 2H), 7.14-7.12 (m, 2H), 7.08-7.05 (m, 2H), 5.24 (s, 1H), 4.95 (s, 1H), 3.59 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  =142.01, 138.32, 136.76, 133.67, 132.39, 131.96, 131.07, 130.01, 129.59, 115.28, 40.77, 21.17, 21.05.

**IR  $\nu$  ( $\text{cm}^{-1}$ ):** 3432, 2921, 2316, 1634, 1490, 1091, 804.

**HRMS (m/z):** calculated for  $\text{C}_{17}\text{H}_{19}\text{S}_2$   $[\text{M} + \text{H}]^+$ , 287.0923; found, 287.0928.

**But-2-ene-1,2-diylbis(phenylsulfane) (3g)**



Pale yellow oil. Synthesised by GP3 (56%).

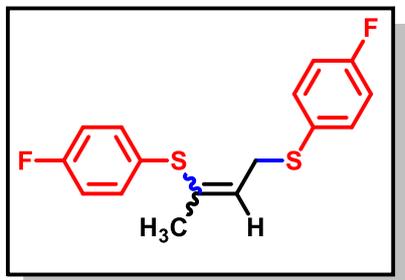
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.33-7.26 (m, 5H), 7.25-7.15 (m, 5H), 6.11 (q,  $J$  = 6.76 Hz 1H), 3.62 (s, 2H), 1.85 (d,  $J$  = 6.79 Hz, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 136.14, 134.77, 134.25, 130.90, 130.60, 129.84, 129.13, 128.88, 126.58, 126.46, 42.01, 15.91.

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3394, 2920, 1456, 1068.

**HRMS** ( $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{17}\text{S}_2$  [ $\text{M} + \text{H}$ ] $^+$ , 273.0766; found, 273.0765.

**But-2-ene-1,3-diylbis((4-fluorophenyl)sulfane) (8a)**



Colourless oil. Synthesised by GP3 (62%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.38-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.01-6.97 (m, 4H), 5.56 (qt,  $J$  = 8.00 Hz,  $J$  = 1.24 Hz, 1H), 3.49 (d,  $J$  = 7.98 Hz, 2H), 1.64 (s, 3H).

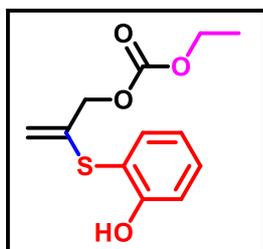
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 163.79 (d,  $J_{\text{C-F}}$  = 248.20 Hz), 163.64 (d,  $J_{\text{C-F}}$  = 247.87 Hz), 161.30 (d,  $J_{\text{C-F}}$  = 248.20 Hz), 161.18 (d,  $J_{\text{C-F}}$  = 247.87 Hz), 134.79, 134.69 (d,  $J_{\text{C-F}}$  = 5.03 Hz), 134.64 (d,  $J_{\text{C-F}}$  = 5.03 Hz), 134.61 (d,  $J_{\text{C-F}}$  = 5.14 Hz), 134.56 (d,  $J_{\text{C-F}}$  = 5.14 Hz), 130.03 (d,  $J_{\text{C-F}}$  = 4.12 Hz), 129.99 (d,  $J_{\text{C-F}}$  = 4.12 Hz), 128.26 (d,  $J_{\text{C-F}}$  = 2.64 Hz), 128.24 (d,  $J_{\text{C-F}}$  = 2.64 Hz), 125.20, 116.31 (d,  $J_{\text{C-F}}$  = 21.87 Hz), 116.09 (d,  $J_{\text{C-F}}$  = 21.87 Hz), 116.05 (d,  $J_{\text{C-F}}$  = 21.70 Hz), 115.83 (d,  $J_{\text{C-F}}$  = 21.70 Hz), 34.31, 17.38.

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):** -113.67 (s, 1F), -114.19 (s, 1F).

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3379, 2920, 1384, 1225, 1080.

**HRMS** ( $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{15}\text{F}_2\text{S}_2$  [ $\text{M} + \text{H}$ ] $^+$ , 309.0578; found, 309.0574.

**Ethyl 2-((2-hydroxyphenyl)thio)allyl carbonate (4a)**



Pale yellow oil. Synthesised by GP4 (82%).

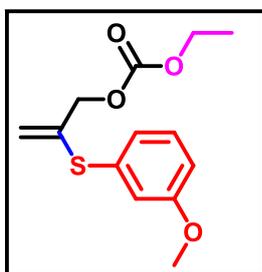
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.47-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.03-7.01 (m, 1H), 6.94-6.89 (m, 1H), 6.39 (s, 1H), 5.41 (s, 1H), 4.97 (s, 1H), 4.64 (s, 2H), 4.22 (q, *J* = 7.13 Hz, 2H), 1.32 (t, *J* = 7.13 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 157.14, 154.69, 138.39, 136.61, 132.40, 121.20, 115.71, 115.04, 114.55, 68.36, 64.47, 14.25.

**IR** ν (cm<sup>-1</sup>): 3396, 2923, 1743, 1647, 1382, 1260, 1020, 767.

**HRMS** (m/z): calculated for C<sub>12</sub>H<sub>15</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 255.0686; found, 255.0682.

**Ethyl (2-((3-methoxyphenyl)thio)allyl) carbonate (4b)**



Yellow oil. Synthesised by GP4 (74%).

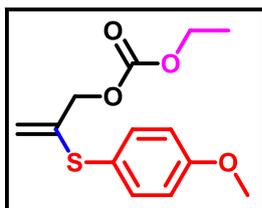
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.23-7.21 (m, 1H), 7.01-6.97 (m, 2H), 6.83-6.81 (m, 1H), 5.60 (s, 1H), 5.39 (s, 1H), 4.65 (s, 2H), 4.20 (q, *J* = 7.12 Hz, 2H), 3.80 (s, 3H), 1.31 (t, *J* = 7.14 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 160.07, 154.67, 138.30, 130.04, 124.15, 118.63, 116.95, 113.92, 68.33, 64.30, 55.33, 14.24.

**IR** ν (cm<sup>-1</sup>): 3391, 2921, 1617, 1383, 1051, 771.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 269.0842; found, 269.0835.

**Ethyl (2-((4-methoxyphenyl)thio)allyl) carbonate (4c)**



Pale yellow oil. Synthesised by GP4 (70%).

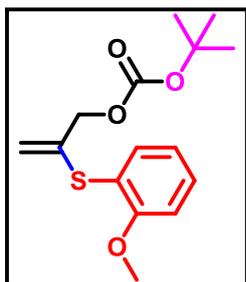
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.42-7.39 (m, 2H), 6.89-6.87 (m, 2H), 5.39 (s, 1H), 5.05 (s, 1H), 4.63 (s, 2H), 4.23-4.18 (q, *J* = 7.14 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J* = 7.13 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 160.15, 154.73, 140.69, 135.67, 121.74, 114.95, 114.42, 68.48, 64.27, 55.35, 14.26.

**IR** v (cm<sup>-1</sup>): 3407, 2924, 1743, 1383, 1246, 1021, 753.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 269.0842; found, 269.0840.

#### Tert-butyl (2-((2-methoxyphenyl)thio)allyl) carbonate (4d)



Colourless oil. Synthesised by GP4 (72%).

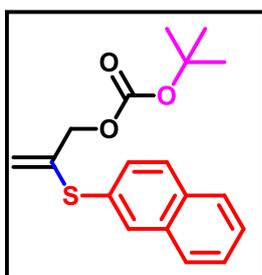
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.40-7.38 (m, 1H), 7.30-7.25 (m, 1H), 6.95-6.88 (m, 2H), 5.55 (s, 1H), 5.27 (s, 1H), 4.59 (s, 2H), 3.86 (s, 3H), 1.48 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 158.41, 153.00, 137.89, 133.35, 129.47, 121.50, 121.30, 120.43, 117.29, 111.18, 82.38, 67.68, 55.90, 27.76.

**IR** v (cm<sup>-1</sup>): 3781, 3409, 2921, 2854, 2042, 1739, 1616, 1582, 1465, 1374, 1251, 1155, 1093, 1029, 943, 855, 751, 673, 578, 497.

**HRMS** (m/z): calculated for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 297.1155; found, 297.1155.

#### Tert-butyl (2-(naphthalen-2-ylthio)allyl) carbonate (4e)



Colourless oil. Synthesised by GP4 (74%).

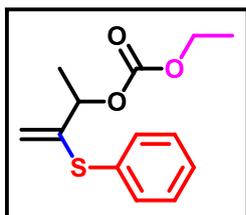
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.93 (s, 1H), 7.82-7.76 (m, 3H), 7.49-7.47 (m, 3H), 5.59 (s, 1H), 5.35 (s, 1H), 4.62 (s, 2H), 1.47 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 152.98, 138.99, 133.76, 132.65, 131.44, 129.62, 129.30, 128.90, 127.74, 127.55, 126.63, 126.52, 117.83, 67.80, 27.74.

**IR** ν (cm<sup>-1</sup>): 3391, 2923, 2854, 1743, 1646, 1381, 1275, 1160, 745.

**HRMS** (m/z): calculated for C<sub>18</sub>H<sub>21</sub>O<sub>3</sub>S [M + H]<sup>+</sup>, 317.1206; found, 317.1213.

**Ethyl (3-(phenylthio)but-3-en-2-yl) carbonate (4f)**



Pale yellow oil. Synthesised by GP4 (88%).

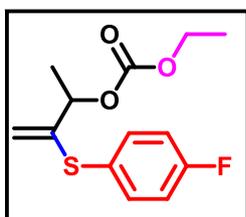
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.47-7.45 (m, 2H), 7.36-7.27 (m, 3H), 5.52 (s, 1H), 5.22 (q, *J* = 6.56 Hz, 1H), 5.07 (s, 1H), 4.18 (q, *J* = 7.11 Hz, 2H), 1.51 (d, *J* = 6.57 Hz, 3H), 1.30 (t, *J* = 7.14 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.19, 145.26, 132.97, 132.22, 129.25, 128.01, 114.77, 75.60, 64.04, 20.27, 14.25.

**IR** ν (cm<sup>-1</sup>): 3381, 2923, 1744, 1379, 1257, 1068, 771.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>17</sub>O<sub>3</sub>S [M + H]<sup>+</sup>, 253.0893; found, 253.0902.

**Ethyl (3-((4-fluorophenyl)thio)but-3-en-2-yl) carbonate (4g)**



Yellow oil. Synthesised by GP4 (88%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.47-7.43 (m, 2H), 7.06-7.02 (m, 2H), 5.46 (s, 1H), 5.20 (q, *J* = 6.55 Hz, 1H), 4.96 (s, 1H), 4.18 (q, *J* = 7.19 Hz, 2H), 1.50 (d, *J* = 6.59 Hz, 3H), 1.30 (t, *J* = 7.18 Hz, 3H).

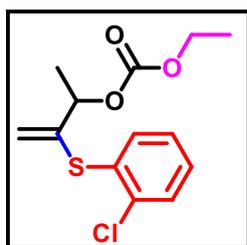
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 164.11 (d, *J*<sub>C-F</sub> = 248.56 Hz), 161.64 (d, *J*<sub>C-F</sub> = 248.56 Hz), 154.17, 145.88, 135.65 (d, *J*<sub>C-F</sub> = 8.38 Hz), 135.57 (d, *J*<sub>C-F</sub> = 8.38 Hz), 127.03 (d, *J*<sub>C-F</sub> = 3.49 Hz), 126.99 (d, *J*<sub>C-F</sub> = 3.49 Hz), 116.58 (d, *J*<sub>C-F</sub> = 22.11 Hz), 116.36 (d, *J*<sub>C-F</sub> = 22.11 Hz), 113.67, 75.46, 64.06, 20.24, 14.23.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** -112.85 (s, 1F).

**IR** ν (cm<sup>-1</sup>): 3383, 2984, 1745, 1590, 1488, 1377, 1258, 1069, 831.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>16</sub>FO<sub>3</sub>S [M + H]<sup>+</sup>, 271.0799; found, 271.0804.

### 3-((2-chlorophenyl)thio)but-3-en-2-yl ethyl carbonate (4h)



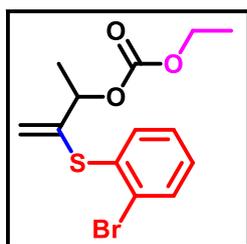
Yellow oil. Synthesised by GP4 (90%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.52-7.50 (m, 1H), 7.42-7.40 (m, 1H), 7.25-7.20 (m, 2H), 5.65 (s, 1H), 5.22 (q, *J* = 6.56 Hz, 1H), 5.15 (s, 1H), 4.19 (q, *J* = 7.13 Hz, 2H), 1.53 (d, *J* = 6.58 Hz, 3H), 1.30 (t, *J* = 7.15 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.18, 142.88, 136.06, 133.59, 132.05, 130.15, 128.91, 127.34, 117.43, 75.50, 64.09, 20.21, 14.26.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>16</sub>ClO<sub>3</sub>S [M + H]<sup>+</sup>, 287.0503; found, 287.0519.

### 3-((2-bromophenyl)thio)but-3-en-2-yl ethyl carbonate (4i)



Colourless oil. Synthesised by GP4 (92%).

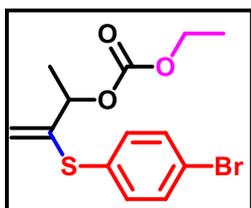
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.60-7.58 (m, 1H), 7.52-7.50 (m, 1H), 7.30-7.26 (m, 1H), 7.14-7.10 (m, 1H), 5.68 (s, 1H), 5.22 (q, *J* = 6.53 Hz, 1H), 5.18 (s, 1H), 4.19 (q, *J* = 7.12 Hz, 2H), 1.53 (d, *J* = 6.52 Hz, 3H), 1.31 (t, *J* = 7.18 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.19, 143.02, 134.28, 133.46, 133.25, 128.88, 127.99, 126.25, 117.90, 75.46, 64.11, 20.25, 14.27.

**IR** ν (cm<sup>-1</sup>): 3391, 2926, 1744, 1615, 1446, 1378, 1258, 1023, 753.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>16</sub>BrO<sub>3</sub>S [M + H]<sup>+</sup>, 330.9998; found, 330.9987.

### 3-((4-bromophenyl)thio)but-3-en-2-yl ethyl carbonate (4j)



Pale yellow oil. Synthesised by GP4 (90%).

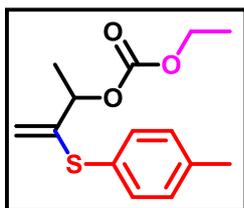
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.47-7.43 (m, 2H), 7.33-7.29 (m, 2H), 5.57 (s, 1H), 5.19 (q, *J* = 6.57 Hz, 1H), 5.15 (s, 1H), 4.17 (q, *J* = 7.15 Hz, 2H), 1.49 (d, *J* = 6.56 Hz, 3H), 1.30 (t, *J* = 7.16 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.15, 144.48, 134.05, 132.37, 131.71, 122.16, 116.35, 75.47, 64.11, 20.21, 14.25.

**IR** ν (cm<sup>-1</sup>): 3388, 1743, 1382, 1259, 1066, 765.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>16</sub>BrO<sub>3</sub>S [M + H]<sup>+</sup>, 330.9998; found, 330.9995.

### Ethyl (3-(p-tolylthio)but-3-en-2-yl) carbonate (4k)



Colourless oil. Synthesised by GP4 (60%).

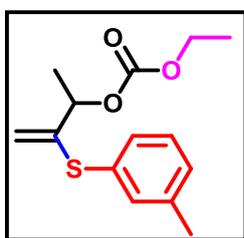
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.35 (d,  $J$  = 8.09 Hz, 2H), 7.15 (d,  $J$  = 7.94 Hz, 2H), 5.43 (s, 1H), 5.21 (q,  $J$  = 6.58 Hz, 1H), 4.95 (s, 1H), 4.18 (q,  $J$  = 7.08 Hz, 2H), 2.34 (s, 3H), 1.51 (d,  $J$  = 6.54 Hz, 3H), 1.30 (t,  $J$  = 7.13 Hz, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 146.06, 138.38, 133.62, 130.08, 128.18, 113.04, 75.58, 64.02, 21.18, 20.31, 14.26.

**IR  $\nu$  ( $\text{cm}^{-1}$ ):** 3386, 2922, 1633, 1383, 1060, 770.

**HRMS ( $m/z$ ):** calculated for  $\text{C}_{14}\text{H}_{19}\text{O}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ , 267.1049; found, 267.1061.

**Ethyl (3-(*m*-tolylthio)but-3-en-2-yl) carbonate (4l)**



Colourless oil. Synthesised by GP4 (65%).

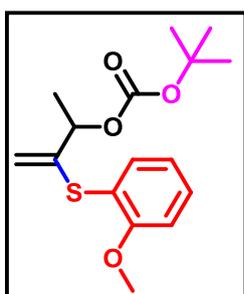
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.28-7.20 (m, 3H), 7.11-7.09 (m, 1H), 5.50 (s, 1H), 5.22 (q,  $J$  = 6.54 Hz, 1H), 5.05 (s, 1H), 4.18 (q,  $J$  = 7.18 Hz, 2H), 2.33 (s, 3H), 1.51 (d,  $J$  = 6.56 Hz, 3H), 1.30 (t,  $J$  = 7.10 Hz, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 154.19, 145.41, 139.11, 133.58, 131.79, 130.02, 129.06, 128.87, 114.40, 75.61, 64.02, 21.21, 20.31, 14.25.

**IR  $\nu$  ( $\text{cm}^{-1}$ ):** 3396, 1744, 1383, 1258, 1058, 771.

**HRMS ( $m/z$ ):** calculated for  $\text{C}_{14}\text{H}_{19}\text{O}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ , 267.1049; found, 267.1055.

**Tert-butyl (3-((2-methoxyphenyl)thio)but-3-en-2-yl) carbonate (4m)**



Pale yellow oil. Synthesised by GP4 (78%).

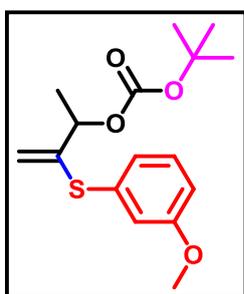
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.45-7.43 (m, 1H), 7.31-7.27 (m, 1H), 6.95-6.88 (m, 2H), 5.49 (s, 1H), 5.17 (q, *J* = 6.55 Hz, 1H), 4.99 (s, 1H), 3.85 (s, 3H), 1.50 (d, *J* = 6.55 Hz, 3H), 1.48 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 158.60, 152.56, 144.38, 134.35, 129.62, 121.23, 120.58, 114.06, 111.25, 82.13, 74.76, 55.89, 27.81, 20.34.

**IR** ν (cm<sup>-1</sup>): 3380, 2927, 1739, 1580, 1471, 1375, 1266, 1161, 1085, 761.

**HRMS** (m/z): calculated for C<sub>16</sub>H<sub>23</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 311.1312; found, 311.1327.

**Tert-butyl (3-((3-methoxyphenyl)thio)but-3-en-2-yl) carbonate (4n)**



Pale yellow oil. Synthesised by GP4 (80%).

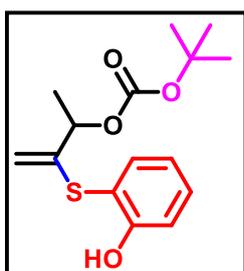
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.25-7.18 (m, 1H), 7.08-7.00 (m, 2H), 6.83-6.74 (m, 1H), 5.54 (s, 1H), 5.17 (q, *J* = 6.58 Hz, 1H), 5.14 (s, 1H), 3.80 (s, 3H), 1.48 (d, *J* = 6.54 Hz, 3H), 1.48 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 160.03, 152.53, 145.09, 133.71, 129.96, 124.65, 117.29, 115.27, 114.12, 82.25, 74.65, 55.31, 27.80, 20.29.

**IR** ν (cm<sup>-1</sup>): 3380, 2928, 1740, 1585, 1380, 1261, 1160, 1087, 773.

**HRMS** (m/z): calculated for C<sub>16</sub>H<sub>23</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 311.1312; found, 311.1316.

**Tert-butyl (3-((2-hydroxyphenyl)thio)but-3-en-2-yl) carbonate (4o)**



Yellow oil. Synthesised by GP4 (84%).

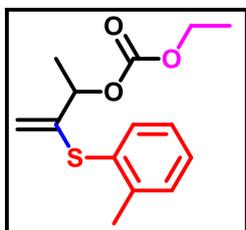
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.46-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.03-7.01 (m, 1H), 6.94-6.89 (m, 1H), 6.44 (s, 1H), 5.31 (m, 1H), 5.18 (q, *J* = 6.57 Hz, 1H), 4.61 (s, 1H), 1.52-1.50 (m, 12H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 157.16, 152.87, 144.83, 136.78, 132.28, 121.07, 115.82, 114.70, 110.29, 82.78, 74.85, 27.79, 20.37.

**IR** ν (cm<sup>-1</sup>): 3413, 2923, 1737, 1382, 1264, 1160, 1090, 767.

**HRMS** (m/z): calculated for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 297.1155; found, 297.1159.

#### Ethyl (3-(*o*-tolylthio)but-3-en-2-yl) carbonate (4p)



Yellow oil. Synthesised by GP4 (66%).

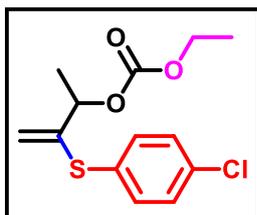
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.49 (d, *J* = 7.44 Hz, 1H), 7.26-7.25 (m, 2H), 7.20-7.16 (m, 1H), 5.36 (s, 1H), 5.26-5.22 (q, *J* = 6.55 Hz, 1H), 4.65 (s, 1H), 4.22-4.17 (q, *J* = 7.12 Hz, 2H), 2.40 (s, 3H), 1.54 (d, *J* = 6.55 Hz, 3H), 1.31 (t, *J* = 7.12 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.23, 145.15, 141.74, 135.29, 130.76, 130.32, 129.03, 126.78, 111.13, 75.74, 64.05, 20.36, 14.27.

**IR** ν (cm<sup>-1</sup>): 3417, 2924, 1744, 1630, 1379, 1256, 1054, 766.

**HRMS** (m/z): calculated for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub>S [M + H]<sup>+</sup>, 267.1049; found, 267.1042.

#### 3-((4-chlorophenyl)thio)but-3-en-2-yl ethyl carbonate (4q)



Yellow oil. Synthesised by GP4 (88%).

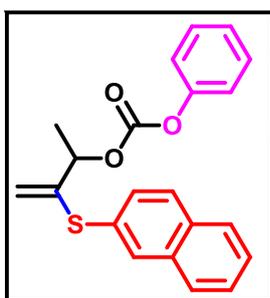
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.39-7.37 (m, 2H), 7.31-7.29 (m, 2H), 5.56 (s, 1H), 5.22-5.17 (q, *J* = 6.53 Hz, 1H), 5.12 (s, 1H), 4.20-4.14 (m, 2H), 1.50 (d, *J* = 6.53 Hz, 3H), 1.30 (t, *J* = 7.14 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.16, 144.74, 134.17, 133.97, 130.92, 129.44, 115.90, 75.48, 64.11, 20.21, 14.23.

**IR** ν (cm<sup>-1</sup>): 3425, 2926, 1744, 1634, 1381, 1257, 1076, 821.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>16</sub>ClO<sub>3</sub>S [M + H]<sup>+</sup>, 287.0503; found, 287.0508.

### 3-(naphthalen-2-ylthio)but-3-en-2-yl phenyl carbonate (4r)



Colourless oil. Synthesised by GP4 (70%).

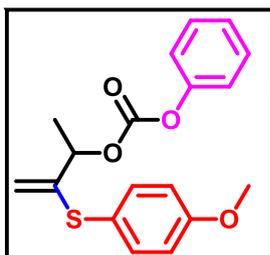
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.99 (s, 1H), 7.81-7.77 (m, 2H), 7.52-7.47 (m, 2H), 7.39-7.34 (m, 3H), 7.28-7.18 (m, 3H), 7.14-7.12 (m, 3H), 5.63 (s, 1H), 5.41-5.36 (m, 1H), 5.18 (s, 1H), 1.64-1.61 (m, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 152.72, 151.05, 144.76, 133.80, 132.76, 132.19, 129.81, 129.50, 129.45, 129.01, 127.77, 127.62, 126.65, 126.15, 126.01, 121.03, 120.99, 115.69, 64.85, 20.24.

**IR** ν (cm<sup>-1</sup>): 3401, 2924, 1759, 1383, 1250, 1078, 759.

**HRMS** (m/z): calculated for C<sub>21</sub>H<sub>19</sub>O<sub>3</sub>S [M + H]<sup>+</sup>, 351.1049; found, 351.1052.

### 3-((4-methoxyphenyl)thio)but-3-en-2-yl phenyl carbonate (4s)



Colourless oil. Synthesised by GP4 (73%).

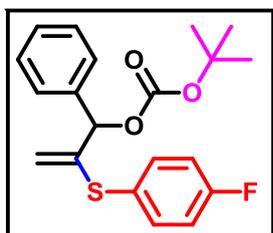
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.40-7.36 (m, 5H), 7.28-7.18 (m, 4H), 6.83 (s, 1H), 6.82 (s, 1H), 5.40 (q, *J* = 6.72 Hz, 1H), 3.79 (s, 3H), 1.63 (d, *J* = 6.72 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 159.94, 152.71, 151.04, 132.68, 129.50, 128.46, 126.14, 120.98, 114.63, 64.84, 55.37, 21.23.

**IR** ν (cm<sup>-1</sup>): 3403, 2922, 1384, 1218, 1062, 770.

**HRMS** (m/z): calculated for C<sub>18</sub>H<sub>19</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 331.0999; found, 331.1004.

**Tert-butyl (2-((4-fluorophenyl)thio)-1-phenylallyl) carbonate (4t)**



Colourless oil. Synthesised by GP4 (70%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.56-7.54 (m, 1H), 7.41-7.32 (m, 7H), 7.03-6.99 (m, 1H), 6.02 (s, 1H), 5.56 (s, 1H), 5.10 (s, 1H), 1.47 (s, 9H).

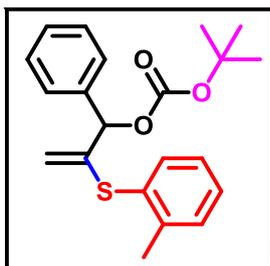
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 164.09 (d, *J*<sub>C-F</sub> = 248.51 Hz), 161.62 (d, *J*<sub>C-F</sub> = 248.51 Hz), 152.42, 144.82, 135.68 (d, *J*<sub>C-F</sub> = 8.38 Hz), 135.60 (d, *J*<sub>C-F</sub> = 8.38 Hz), 129.15, 128.69, 128.43, 127.70, 127.42, 127.24 (d, *J*<sub>C-F</sub> = 2.68 Hz), 127.22 (d, *J*<sub>C-F</sub> = 2.68 Hz), 116.51 (d, *J*<sub>C-F</sub> = 21.94 Hz), 116.29 (d, *J*<sub>C-F</sub> = 21.94 Hz), 114.91, 82.69, 79.27, 27.76.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** -112.92 (s, 1F).

**IR** ν (cm<sup>-1</sup>): 3406, 2923, 1741, 1382, 1258, 1157, 1079, 755.

**HRMS** (m/z): calculated for C<sub>20</sub>H<sub>22</sub>FO<sub>3</sub>S [M + H]<sup>+</sup>, 361.1268; found, 361.1274.

**Tert-butyl (1-phenyl-2-(o-tolylthio)allyl) carbonate (4u)**



Pale yellow oil. Synthesised by GP4 (72%).

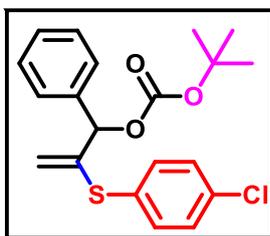
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.44-7.30 (m, 7H), 7.26-7.13 (m, 3H), 6.05 (s, 1H), 5.45 (s, 1H), 4.79 (s, 1H), 2.26 (s, 3H), 1.47 (s, 9H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 152.48, 144.26, 141.87, 137.56, 135.38, 130.71, 130.51, 129.00, 128.48, 128.36, 127.35, 126.71, 112.28, 82.59, 79.44, 27.80, 20.31.

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3420, 1742, 1626, 1458, 1376, 1263, 1159, 1083, 875, 760.

**HRMS** ( $m/z$ ): calculated for  $\text{C}_{21}\text{H}_{25}\text{O}_3\text{S}$   $[\text{M} + \text{H}]^+$ , 357.1519; found, 357.1522.

**Tert-butyl 2-((4-chlorophenyl)thio)-1-phenylallyl carbonate (4v)**



Pale yellow oil. Synthesised by GP4 (68%).

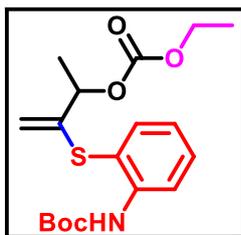
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.37-7.31 (m, 6H), 7.30-7.28 (m, 3H), 6.01 (s, 1H), 5.65 (s, 1H), 5.24 (s, 1H), 1.46 (s, 9H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 152.40, 143.76, 137.21, 134.02, 131.12, 129.39, 128.62, 128.44, 127.70, 127.44, 116.91, 79.29, 75.97, 27.77.

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3411, 1741, 1383, 1259, 1158, 1085.

**HRMS** ( $m/z$ ): calculated for  $\text{C}_{20}\text{H}_{22}\text{ClO}_3\text{S}$   $[\text{M} + \text{H}]^+$ , 377.0973; found, 377.0978.

**Tert-butyl 2-((3-((ethoxycarbonyl)oxy)but-1-en-2-yl)thio)phenyl)carbamate (4w)**



Colourless oil. Synthesised by GP4 (55%).

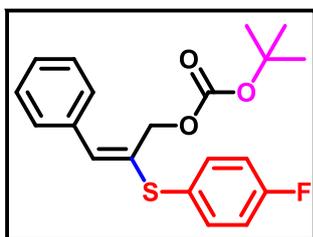
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 8.17 (d,  $J$  = 8.04 Hz, 1H), 7.54-7.48 (m, 1H), 7.44 (s, 1H), 7.41- 7.37 (m, 1H), 7.04- 7.00 (m, 1H), 5.31 (s, 1H), 5.28-5.23 (q,  $J$  = 6.49 Hz, 1H), 4.58 (s, 1H), 4.24-4.18 (m, 2H), 1.57-1.55 (m, 3H), 1.51 (s, 9H), 1.32 (t,  $J$  = 7.14 Hz, 3H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 154.19, 144.46, 140.65, 136.83, 131.15, 123.13, 119.31, 117.04, 110.53, 80.68, 75.52, 64.17, 28.28, 20.40, 14.26.

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3780, 3397, 2920, 1736, 1638, 1508, 1453, 1382, 1254, 1073, 948, 755, 668.

**HRMS** ( $m/z$ ): calculated for  $\text{C}_{18}\text{H}_{26}\text{NO}_5\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ , 368.1526; found, 368.1528.

**Tert-butyl (2-((4-fluorophenyl)thio)-3-phenylallyl) carbonate (4x)**



Pale yellow oil. Synthesised by GP4 (72%).

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.60 (d,  $J$  = 7.73 Hz, 2H), 7.39-7.34 (m, 4H), 7.30-7.27 (m, 1H), 7.02 (s, 1H), 7.00-6.96 (m, 2H), 4.59 (s, 2H), 1.47 (s, 9H).

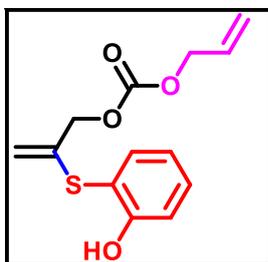
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 163.45 (d,  $J_{\text{C-F}}$  = 248.17 Hz), 161.48 (d,  $J_{\text{C-F}}$  = 248.17 Hz), 152.91, 135.34, 134.32, 133.72 (d,  $J_{\text{C-F}}$  = 8.12 Hz), 133.66 (d,  $J_{\text{C-F}}$  = 8.12 Hz), 129.50, 129.20, 128.16, 128.12, 127.78 (d,  $J_{\text{C-F}}$  = 3.46 Hz), 127.75 (d,  $J_{\text{C-F}}$  = 3.46 Hz), 116.36 (d,  $J_{\text{C-F}}$  = 22.21 Hz), 116.18 (d,  $J_{\text{C-F}}$  = 22.21 Hz), 82.49, 69.16, 27.76.

**$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):** -113.84 (s, 1F).

**IR**  $\nu$  ( $\text{cm}^{-1}$ ): 3778, 3399, 3300, 2921, 2853, 1757, 1590, 1246, 1171, 1090, 1028, 918, 825, 756, 682, 526.

**HRMS** (m/z): calculated for C<sub>20</sub>H<sub>22</sub>FO<sub>3</sub>S [M + H]<sup>+</sup>, 361.1268; found, 361.1276.

**Allyl (2-((2-hydroxyphenyl)thio)allyl) carbonate (4y)**



Colourless oil. Synthesised by GP4 (65%).

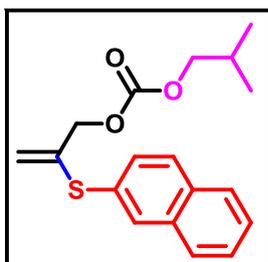
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.47-7.32 (m, 2H), 7.04-6.92 (m, 2H), 6.38 (s, 1H), 5.99-5.89 (m, 1H), 5.41-5.27 (m, 3H), 4.98 (s, 1H), 4.66 (s, 4H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 157.14, 154.52, 138.27, 136.62, 132.43, 131.35, 121.22, 119.17, 115.71, 115.17, 68.83, 68.55.

**IR** ν (cm<sup>-1</sup>): 3777, 3417, 2923, 1744, 1627, 1458, 1384, 1254, 1101, 767.

**HRMS** (m/z): calculated for C<sub>13</sub>H<sub>15</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 267.0686; found, 267.0681.

**Isobutyl (2-(naphthalen-2-ylthio)allyl) carbonate (4z)**



Colourless oil. Synthesised by GP4 (63%).

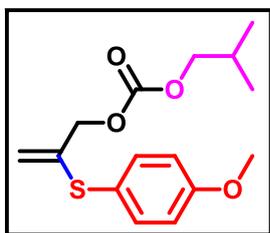
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.94-7.93 (m, 1H), 7.82-7.76 (m, 3H), 7.50-7.47 (m, 3H), 5.61 (s, 1H), 5.37 (s, 1H), 4.69 (s, 2H), 3.91-3.90 (d, *J* = 6.72 Hz, 2H), 1.99-1.92 (m, 1H), 0.94-0.93 (d, *J* = 6.73 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 154.89, 138.79, 133.77, 132.68, 131.47, 129.52, 129.27, 128.94, 127.76, 127.55, 126.66, 126.56, 118.17, 74.37, 68.53, 27.77, 18.86.

**IR** ν (cm<sup>-1</sup>): 3835, 3737, 3388, 2923, 2856, 2350, 1747, 1617, 1456, 1384, 1250, 1153, 1064, 816, 747, 476.

**HRMS** (m/z): calculated for C<sub>18</sub>H<sub>21</sub>O<sub>3</sub>S [M + H]<sup>+</sup>, 317.1206; found, 317.1204.

**Isobutyl (2-((4-methoxyphenyl)thio)allyl) carbonate (4z')**



Colourless oil. Synthesised by GP4 (75%).

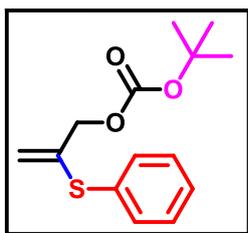
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.41-7.38 (m, 2H), 6.89-6.81 (m, 2H), 5.39 (s, 1H), 5.06(s, 1H), 4.63 (s, 2H), 3.93 (d, *J* = 6.72 Hz, 2H), 3.80 (s, 3H), 2.03-1.93 (m, 1H), 0.95 (d, *J* = 6.72 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 160.14, 154.92, 140.72, 135.66, 132.66, 121.75, 114.94, 114.40, 74.33, 68.50, 55.34, 27.78, 18.88.

**IR** ν (cm<sup>-1</sup>): 3917, 3777, 3413, 2924, 2304, 1744, 1598, 1490, 1459, 1383, 1247, 1101, 1032, 827, 765, 628.

**HRMS** (m/z): calculated for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>S [M + H]<sup>+</sup>, 297.1155; found, 297.1164.

**Tert-butyl (2-(phenylthio)allyl) carbonate (4a')**



Colourless oil. Synthesised by GP4 (86%).

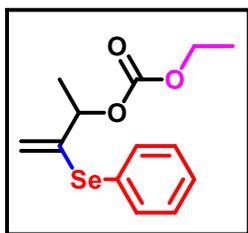
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.45-7.42 (m, 2H), 7.35-7.28 (m, 3H), 5.55 (s, 1H), 5.29 (s, 1H), 4.58 (s, 2H), 1.48 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 152.99, 139.07, 132.37, 132.27, 129.26, 127.89, 117.47, 82.49, 67.69, 27.76.

**IR** ν (cm<sup>-1</sup>): 3782, 2921, 1740, 1382, 1260, 1070.

**HRMS** (m/z): calculated for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub>S [M + H]<sup>+</sup>, 267.1049; found, 267.1057.

### Ethyl (3-(phenylselanyl)but-3-en-2-yl) carbonate (7)



Pale yellow oil. The compound (7) was Synthesized by follow the same procedure GP4 (75%).

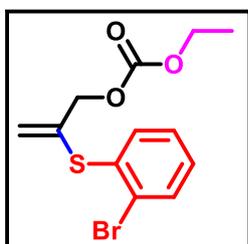
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.58-7.56 (m, 2H), 7.31-7.29 (m, 3H), 5.84 (s, 1H), 5.27-5.23 (m, 2H), 4.19-4.13 (m, 2H), 1.49 (d,  $J$  = 6.54 Hz, 3H), 1.29 (t,  $J$  = 7.14 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 154.15, 142.35, 134.59, 132.46, 129.35, 128.20, 128.04, 118.31, 115.66, 64.03, 20.52, 14.25.

**IR**  $\nu$  (cm<sup>-1</sup>): 3781, 3397, 2921, 2854, 1742, 1603, 1449, 1381, 1256, 1154, 1063, 1026, 883, 831, 739, 689.

**HRMS** ( $m/z$ ): calculated for C<sub>13</sub>H<sub>17</sub>O<sub>3</sub>Se [M + H]<sup>+</sup>, 301.0337; found, 301.0335.

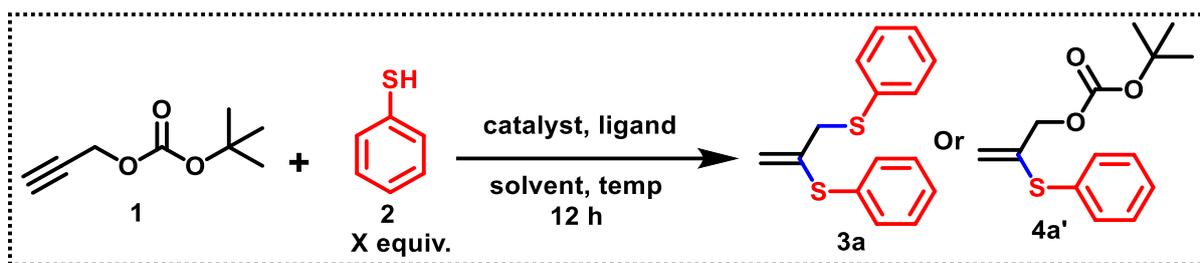
### Ethyl (2-((2-bromophenyl)thio)allyl) carbonate (4i')



Colourless oil. Synthesised by GP4.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.60-7.57 (m, 1H), 7.44-7.42 (m, 1H), 7.30-7.26 (m, 1H), 7.14- 7.09 (m, 1H), 5.76 (s, 1H), 5.47 (s, 1H), 4.66 (s, 1H), 4.21 (q,  $J$  = 7.16 Hz, 2H), 1.32 (t,  $J$  = 7.14 Hz, 3H).

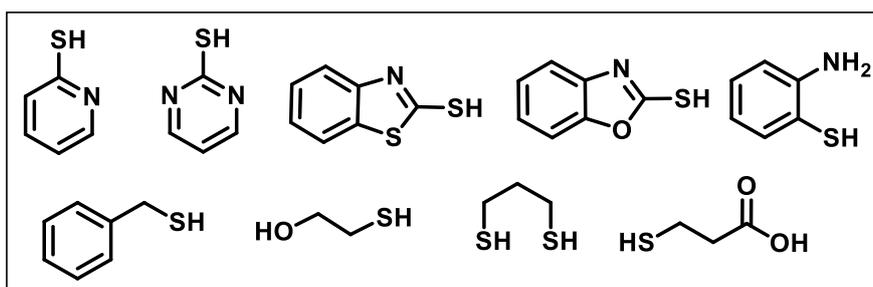
### Table 1. Optimization of the reaction conditions<sup>a</sup>



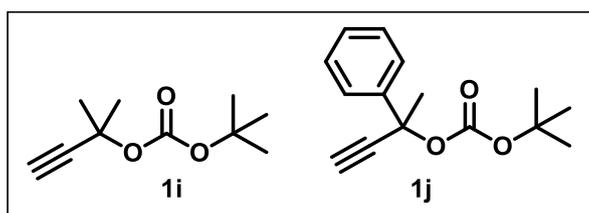
Entry	Catalyst	ligand	solvent	X(equiv)	Temp.	Yield <sup>b</sup> (%)
1.	Pd <sub>2</sub> (dba) <sub>3</sub>	dppb	DMF	2	80°C	52
2.	Pd(OAc) <sub>2</sub>	dppb	DMF	2	80°C	n.r.
3.	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dppb	DMF	2	80°C	40
4.	Ni(Cod) <sub>2</sub>	dppb	DMF	2	80°C	22
5.	Pd <sub>2</sub> (dba) <sub>3</sub>	dppb	ACN	2	80°C	63
6.	Pd <sub>2</sub> (dba) <sub>3</sub>	dppe	ACN	2	80°C	54
7.	Pd <sub>2</sub> (dba) <sub>3</sub>	none	ACN	2	80°C	30
8.	Pd <sub>2</sub> (dba) <sub>3</sub>	Xantphos	ACN	2	80°C	64
9.	Pd <sub>2</sub> (dba) <sub>3</sub>	X-phos	ACN	2	80°C	66
10.	<b>Pd<sub>2</sub>(dba)<sub>3</sub></b>	<b>S-phos</b>	<b>ACN</b>	<b>2</b>	<b>80°C</b>	<b>76</b>
11.	Pd <sub>2</sub> (dba) <sub>3</sub>	Me-phos	ACN	2	80°C	72
12.	Pd <sub>2</sub> (dba) <sub>3</sub>	S-phos	Toluene	2	110°C	62
13.	Pd <sub>2</sub> (dba) <sub>3</sub>	S-phos	1,4-dioxane	2	100°C	70
14 <sup>c</sup> .	Pd <sub>2</sub> (dba) <sub>3</sub>	S-phos	ACN	1	80°C	86 <sup>d</sup>

<sup>a</sup>Reaction Conditions: propargyl carbonate (1.1 mmol), thiophenol (2.0 mmol), catalyst (2 mol%), ligand (5 mol%), 0.2 M, 12 h. <sup>b</sup>Determined by <sup>1</sup>H NMR, <sup>c</sup>propargyl carbonate (1.1 mmol), thiophenol (1.0 mmol), catalyst (2 mol%), ligand (5 mol%), 0.2 M, 80°C, 12 h. <sup>d</sup>4a' formed.

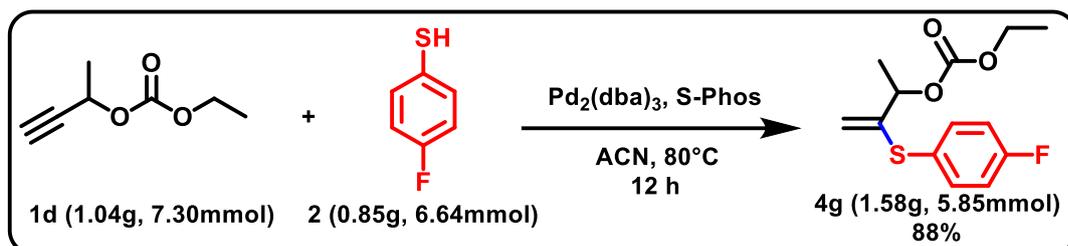
## Unreactive thiols



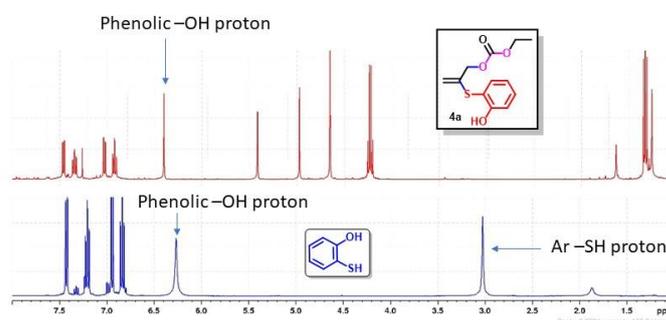
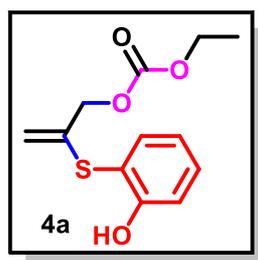
## Unreactive propargyl carbonates



## Gram scale synthesis



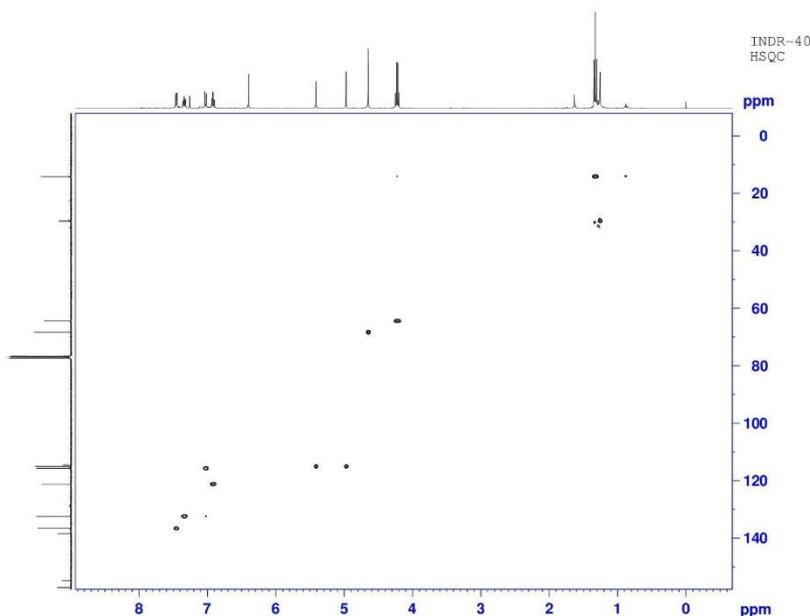
## Confirmation of structure **4a** through 1-D & 2-D NMR spectrum



**Fig 1: comparison of  $^1\text{H}$  NMR between SM (2-mercapto phenol) and product (**4a**).**

mono(arylthiol) alkene (**4a**) having free -OH group was observed in a higher yield by using 2-mercapto phenol as a nucleophile. The structure **4a** was identified by 1D and 2D NMR spectrum. We have performed  $^1\text{H}$  NMR of 2-mercapto phenol (blue colour spectrum) and our compound **4a** (red colour spectrum). (**Fig 1**). For 2-mercapto phenol, the phenolic -OH proton comes around  $\delta$  value 6.26 (s, 1H) and -SH proton around  $\delta$  3.02 (s, 1H). In our compound **4a**, there are no peak around  $\delta$  value 3.00-4.00, that proves -SH proton is not present in this compound. In 2-mercapto phenol, the phenolic -OH proton is coming around  $\delta$  value 6.26 and

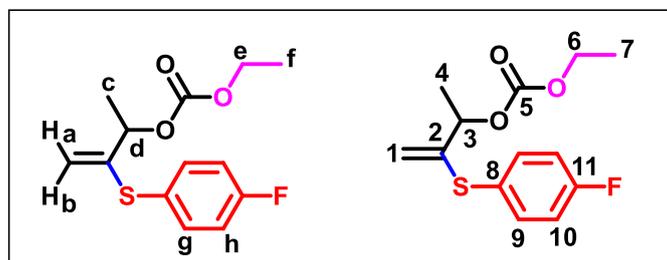
after formation of mono(arylthiol) alkene (**4a**) that proton is coming in the same region ( $\delta$  value 6.39). In compound **4a**,  $\delta$  value 6.39 in proton



**Fig 2: 2D HSQC spectrum of product (4a).**

NMR corresponds no carbon which show in HSQC spectrum (**Fig 2**), that proves this is phenolic -OH proton. In our novel methodology, mono(arylthiol) alkenes were formed via newly C-S bond formation through single attack by soft thio nucleophile without any decarboxylation. The phenolic -OH does not react as a nucleophile in our case, that may be more electronegativity of O than S. Another point is that why phenolic -OH group does not react as a second nucleophile by using 2-mercapto phenol as substrate, whereas external thiol attack as a second nucleophile by using 2 equiv. of thiophenol, and intramolecular -SH group attack as a second nucleophile when 2-mercapto thiophenol is used instead of 2-mercapto phenol. This may be -SH group of thiophenol is more reactive as compare to aromatic -OH group.

## Confirmation of structure **4g** for mono(arylthiol) alkene product through 1-D & 2-D NMR spectrum

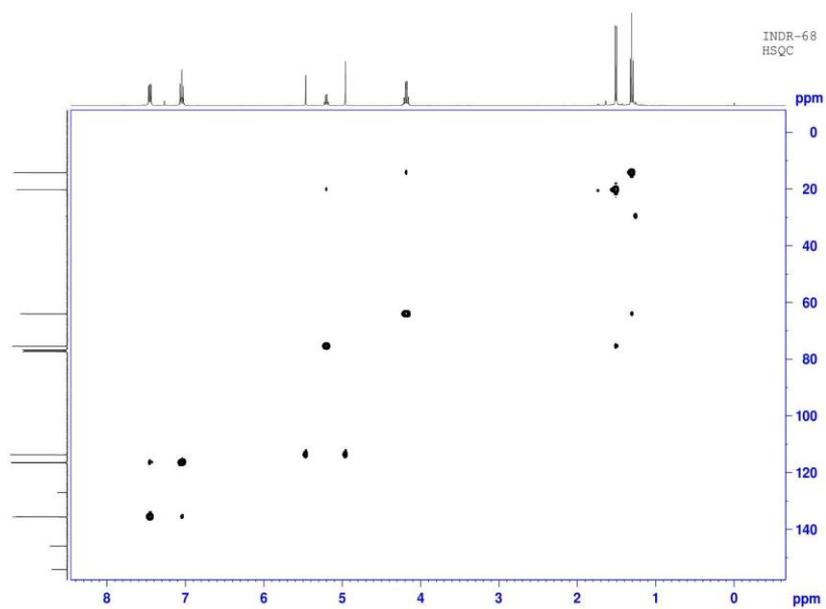


**Fig 3: Protons and carbon numbering of compound (4g).**

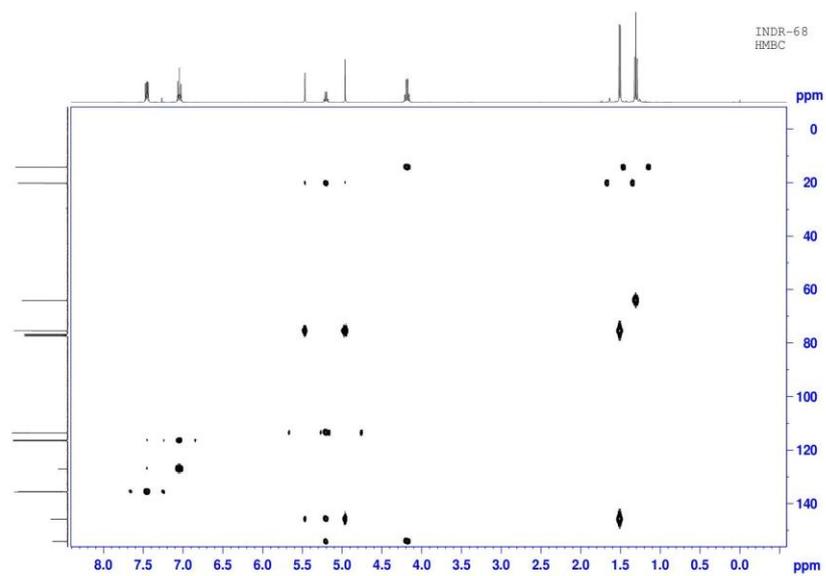
The structure **4g** for mono(arylthiol) alkene product was identified and all protons and carbons are assigned by using 1D (<sup>1</sup>H and <sup>13</sup>C) and 2D NMR (COSY, NOESY, HSQC, HMBC) spectrum. In aromatic region two **g** protons are most downfielded, which comes around 7.47-7.43 (m, 2H). After that, two remaining aromatic protons (**h**) are appeared at 7.06-7.02 (m, 2H). Two olefinic protons are identified by NOESY and HSQC. In NOESY spectrum has some weak correlation between  $\delta$  value 5.46 and  $\delta$  value 5.20 and strong correlation between  $\delta$  value 5.46 and  $\delta$  value 4.96. In HSQC spectrum shows  $\delta$  value 5.46 and 4.96 corresponds same carbon. That proves 5.46 (s, 1H) is proton **a**, 5.20 (q,  $J = 6.55$  Hz, 1H) is proton **d** and 4.96 (s, 1H) is proton **b**. In <sup>1</sup>H spectrum same  $J$  values and coupling nature shows that 1.50 is coming doublet for 3H **c** protons, 4.18 (q,  $J = 7.19$  Hz, 2H) for **e** protons and 1.30 (t,  $J = 7.18$  Hz, 3H) for **f** protons. All carbons of compound **4g** are assigned by DEPT, HSQC and HMBC spectrum.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta = 7.47-7.43$  (m, 2H, **g**), 7.06-7.02 (m, 2H, **h**), 5.46 (s, 1H, **a**), 5.20 (q,  $J = 6.55$  Hz, 1H, **d**), 4.96 (s, 1H, **b**), 4.18 (q,  $J = 7.19$  Hz, 2H, **e**), 1.50 (d,  $J = 6.59$  Hz, 3H, **c**), 1.30 (t,  $J = 7.18$  Hz, 3H, **f**).

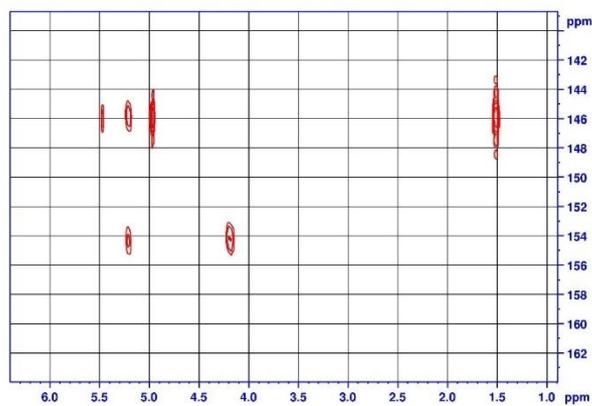
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta = 164.11$  (d,  $J_{C-F} = 248.56$  Hz, **C11**), 161.64 (d,  $J_{C-F} = 248.56$  Hz), 154.17 (**C5**), 145.88 (**C2**), 135.65 (d,  $J_{C-F} = 8.38$  Hz, **C9**), 135.57 (d,  $J_{C-F} = 8.38$  Hz), 127.03 (d,  $J_{C-F} = 3.49$  Hz, **C8**), 126.99 (d,  $J_{C-F} = 3.49$  Hz), 116.58 (d,  $J_{C-F} = 22.11$  Hz, **C10**), 116.36 (d,  $J_{C-F} = 22.11$  Hz), 113.67 (**C1**), 75.46 (**C3**), 64.06 (**C6**), 20.24 (**C4**), 14.23 (**C7**).



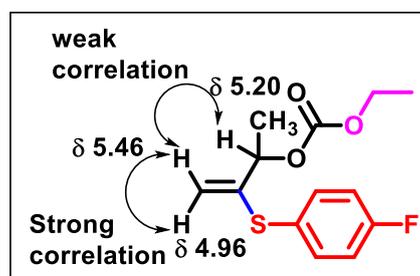
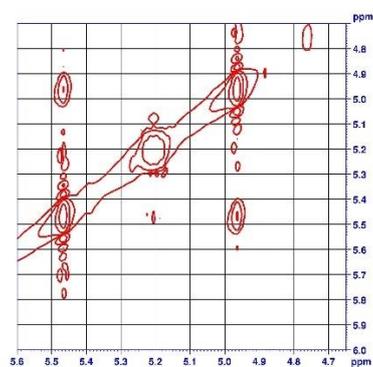
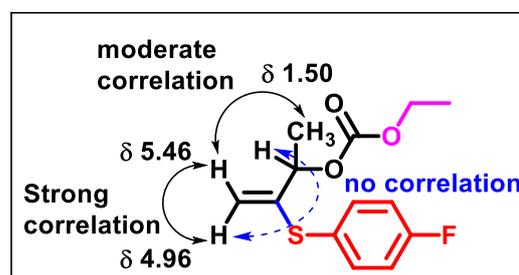
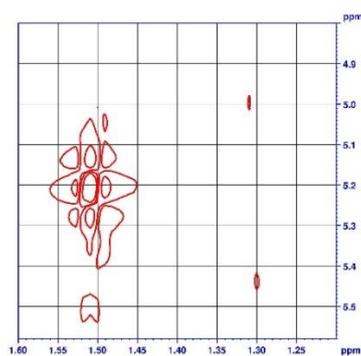
**Fig 4: 2D HSQC spectrum of product (4g).**



**Fig 5: 2D HMBC spectrum of product (4g).**



**Fig 6: Magnified 2D HMBC Spectrum of 4g.**



**Fig 7: Magnified 2D NOESY Spectrum of 4g.**

## Confirmation of structure 3a for bis(arylthiol) alkene product with literature-known compound<sup>7</sup> through 1-D NMR spectrum

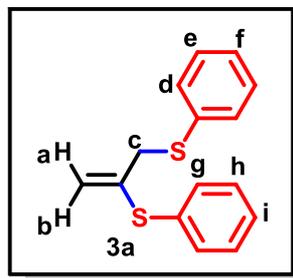


Fig 8: Protons numbering of compound (3a).

Our reported spectral data as follow

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.42-7.41 (m, 2H, **d,e,f,g,h,i**), 7.34-7.27 (m, 6H, **d,e,f,g,h,i**), 7.24 (s, 1H, **d,e,f,g,h,i**), 7.22-7.17 (m, 1H, **d,e,f,g,h,i**), 5.37 (s, 1H, **a,b**), 5.07 (s, 1H, **a,b**), 3.65 (s, 2H, **c**).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 141.13, 133.09, 132.69, 130.76, 130.35, 129.24, 128.84, 128.02, 126.61, 116.94, 40.21.

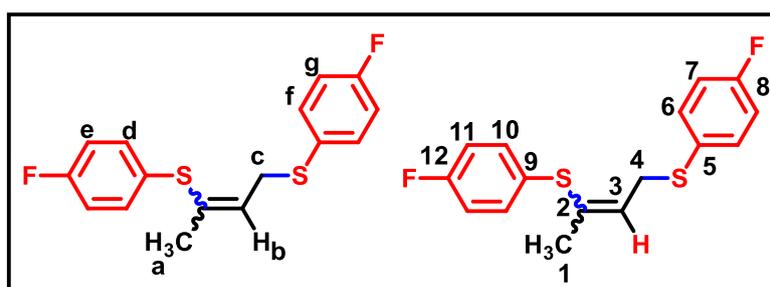
The same compound was reported by Cohen group<sup>7</sup> (Org. Lett., 2006, 8 (10), 2087-2090). The spectral data of this compound which reported in their manuscript are shown below.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 3.66 (s, 2H), 5.08 (s, 1H), 5.38 (s, 1H), 7.17-7.44 (m, 10H).

**<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):**  $\delta$  = 141.1, 135.7, 133.1, 132.7, 130.3, 129.2, 128.8, 128.0, 126.6, 116.9, 40.2.

## Confirmation of structure 8a through 1-D & 2-D NMR spectrum

The structure **8a** (1,3-dithiolated product) was identified and all protons and carbons are assigned by using 1D (<sup>1</sup>H and <sup>13</sup>C) and 2D NMR (COSY, NOESY, HSQC, HMBC) spectrum. All assigned protons and carbons are mentioned below.

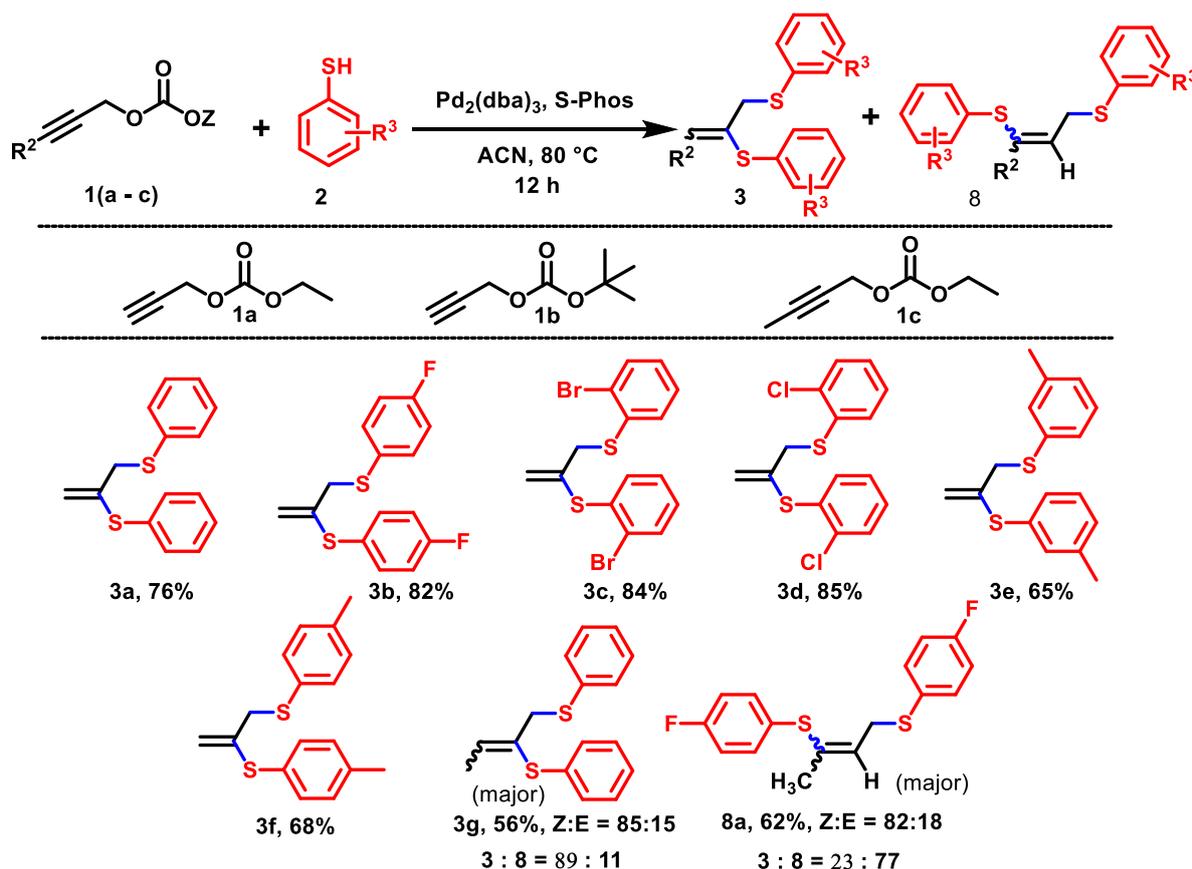


**Fig 9: Protons and carbon numbering of compound (8a).**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.38-7.35 (m, 2H, **d,e,f,g**), 7.25-7.21 (m, 2H, **d,e,f,g**), 7.01-6.97 (m, 4H, **d,e,f,g**), 5.56 (qt,  $J$  = 8.00 Hz,  $J$  = 1.24 Hz, 1H, **b**), 3.49 (d,  $J$  = 7.98 Hz, 2H, **c**), 1.64 (s, 3H, **a**).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 163.79 (d,  $J_{C-F}$  = 248.20 Hz, **C8**, **C12**), 163.64 (d,  $J_{C-F}$  = 247.87 Hz, **C8**, **C12**), 161.30 (d,  $J_{C-F}$  = 248.20 Hz), 161.18 (d,  $J_{C-F}$  = 247.87 Hz), 134.79 (**C2**), 134.69 (d,  $J_{C-F}$  = 5.03 Hz, **C6**, **C7**, **C10**, **C11**), 134.64 (d,  $J_{C-F}$  = 5.03 Hz), 134.61 (d,  $J_{C-F}$  = 5.14 Hz, **C6**, **C7**, **C10**, **C11**), 134.56 (d,  $J_{C-F}$  = 5.14 Hz), 130.03 (d,  $J_{C-F}$  = 4.12 Hz, **C5**, **C9**), 129.99 (d,  $J_{C-F}$  = 4.12 Hz), 128.26 (d,  $J_{C-F}$  = 2.64 Hz, **C5**, **C9**), 128.24 (d,  $J_{C-F}$  = 2.64 Hz), 125.20 (**C3**), 116.31 (d,  $J_{C-F}$  = 21.87 Hz, **C6**, **C7**, **C10**, **C11**), 116.09 (d,  $J_{C-F}$  = 21.87 Hz), 116.05 (d,  $J_{C-F}$  = 21.70 Hz, **C6**, **C7**, **C10**, **C11**), 115.83 (d,  $J_{C-F}$  = 21.70 Hz), 34.31 (**C4**), 17.38 (**C1**).

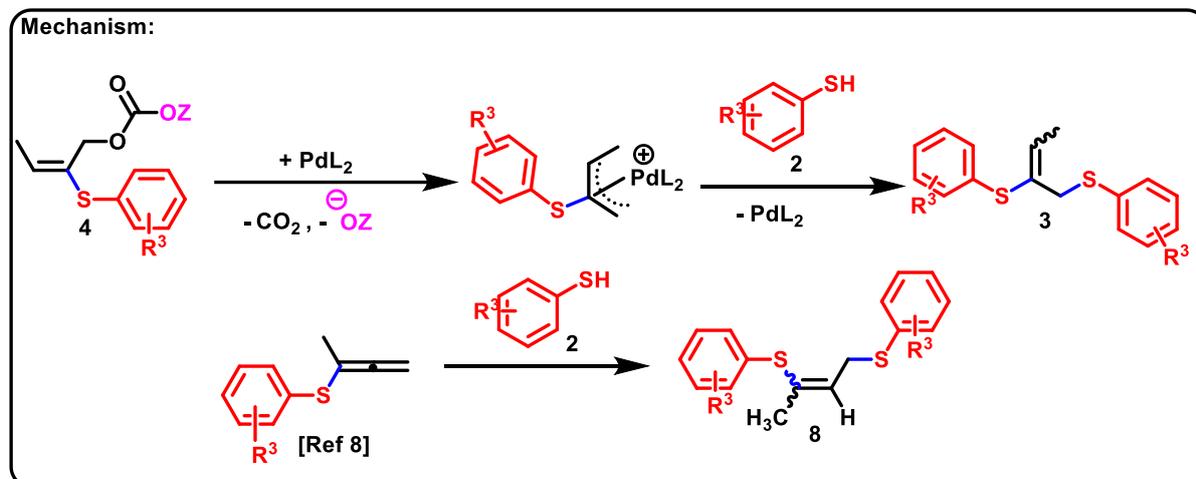
**Scheme S1** Substrates scope for Tsuji-Trost-type substitution <sup>a</sup>



<sup>a</sup>**Reaction Conditions:** propargyl carbonate (1.1 mmol), thiophenol (2.0 mmol), catalyst (2 mol%), ligand (5 mol%), 0.2 M, 12 h.

Without any substitution on terminal alkyne of propargyl carbonate, there was no possibility formation of regioisomer **8**. When the methyl group was present in the terminal alkyne of

propargylic carbonate (**1c**), two types of regioisomers were found and the yield of products (**3g** & **8a**) were comparatively poor.



**Fig 10: Plausible reaction mechanism of formation of regioisomer 3 and 8.**

By using normal thiophenol as nucleophile with the reaction of **1c**, the geminal disulfide **3g** was formed. Surprisingly electron withdrawing group containing thiophenol reacted with **1c** to produce another regioisomer **8a** as a major product. The probable reaction mechanism are shown in Fig. 10.

## References

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1. C. Q. O'Broin, P. J. Guiry, *Org. Lett.*, 2020, **22**, 879-883.
2. J. Stambask, A. V. Malkov, P. Kocovsk, *Collect. Czech. Chem. Commun.*, 2008, **73**, 705.
3. H. Yamamoto, M. Nishiyama, H. Imagawa, M. Nishizawa, *Tetrahedron Lett.*, 2006, **47**, 8369.
4. M. Yoshida, T. Okada, K. Shishido, *Tetrahedron.*, 2007, **63**, 6996-7002.
5. V. L. Ravalec, C. Fischmeister, C. Bruneau, *Advanced Synthesis & Catalysis*, 2009, **351**, 1115-1122.
6. A. K. Buzas, F. M. Istrate, F. Gagosz, *Tetrahedron.*, 2009, **65**, 1889-1901.
7. W. Chen, X. Zhao, L. Lu, T. Cohen, *Org. Lett.*, 2006, **8 (10)**, 2087-2090.
8. C. Q. O'Broin, P. J. Guiry, *J. Org. Chem.*, 2020, **85**, 10321-10333.

# **Palladium-catalyzed Regioselective Synthesis of Mono and Bis(arylthiol) Alkene from Propargyl Carbonate and Thiophenol.**

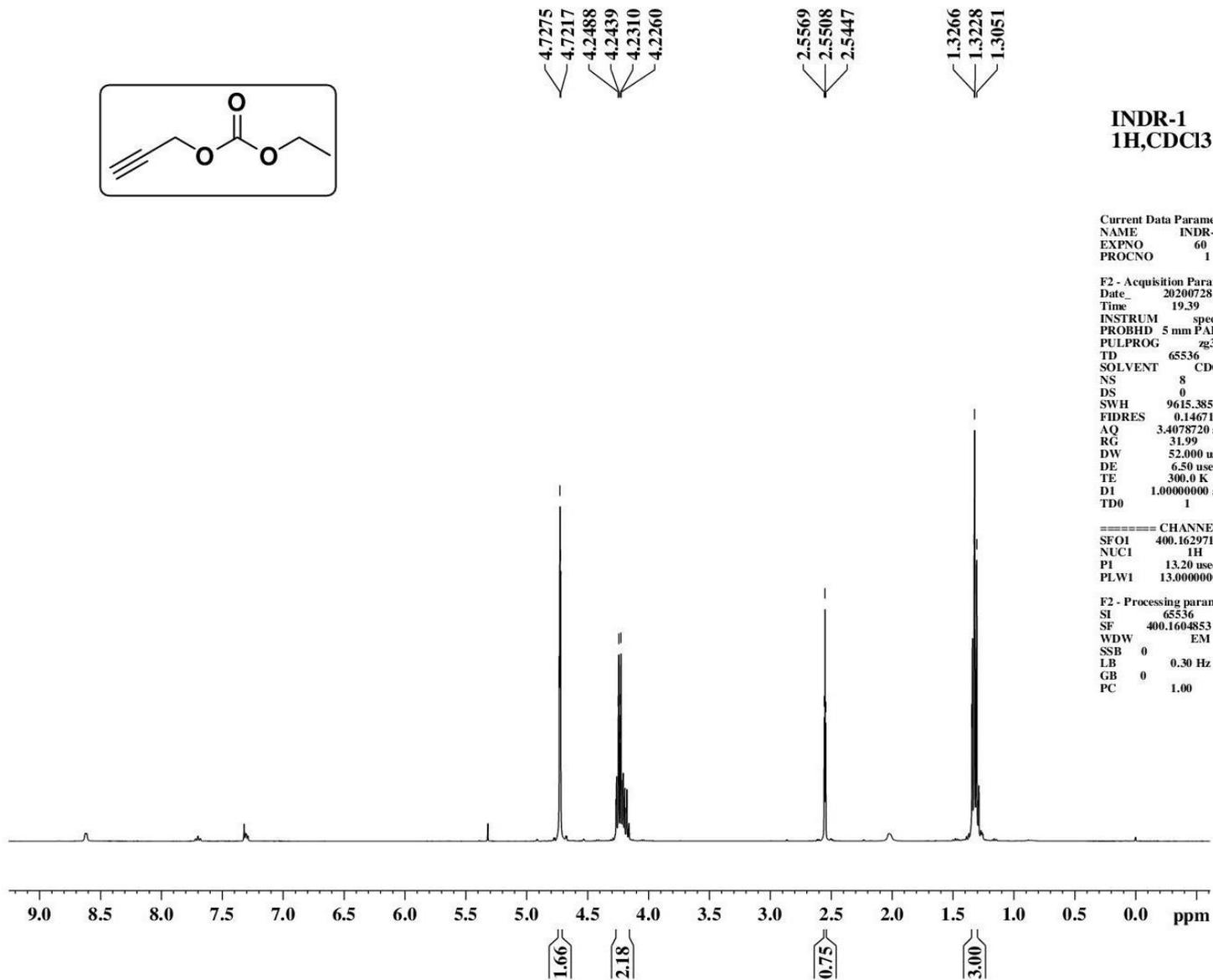
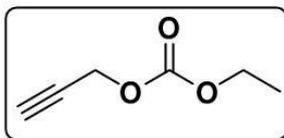
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Jankipuram extension, Sitapur Road, Lucknow 226031, UP, India

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Phone: 915222772450, ext 4659, Fax: 915222771941



**INDR-1**  
**<sup>1</sup>H,CDCl<sub>3</sub>**

Current Data Parameters

NAME INDR-1  
EXPNO 60  
PROCNO 1

F2 - Acquisition Parameters

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DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
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TE 300.0 K  
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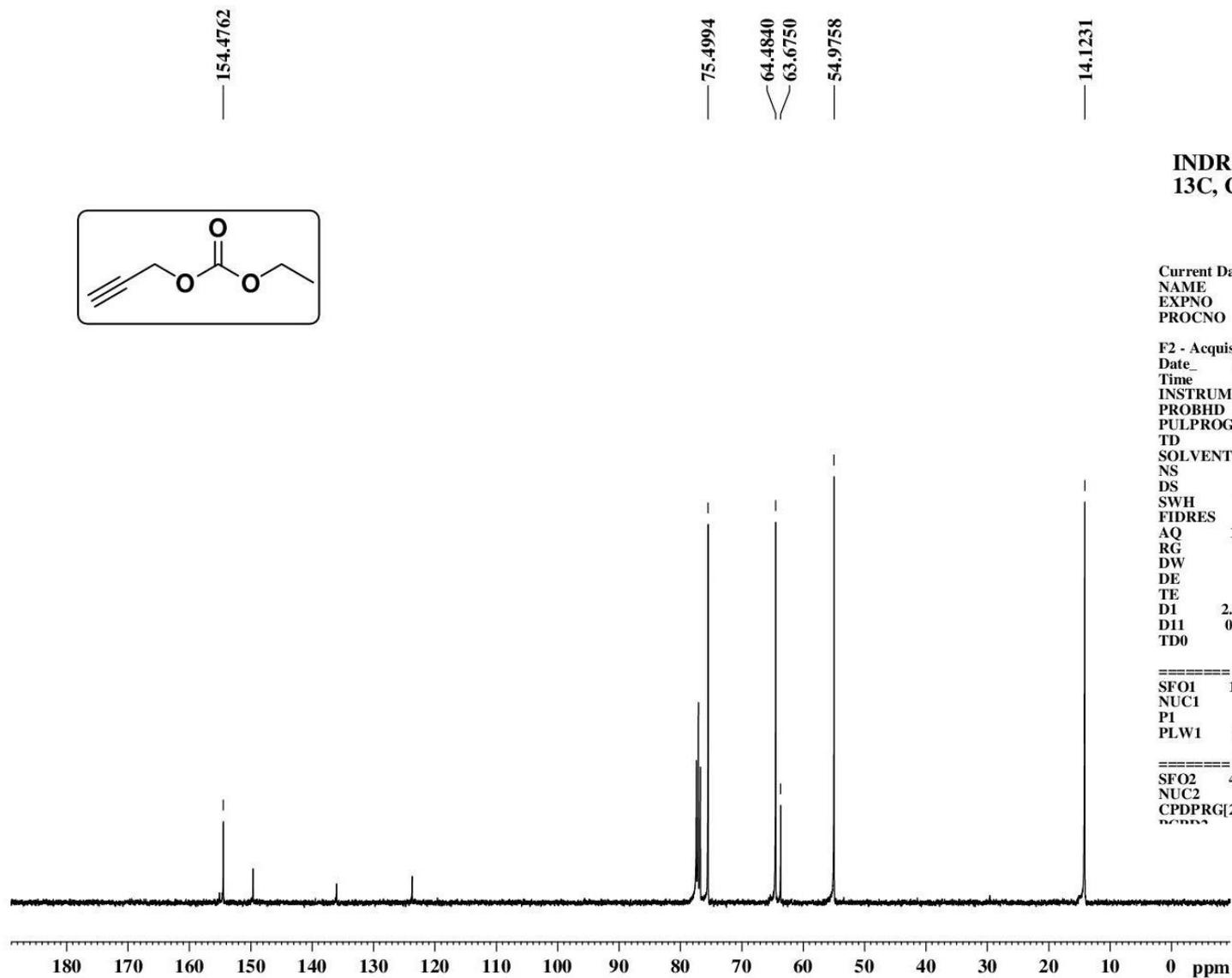
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F2 - Processing parameters

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SF 400.1604853 MHz  
WDW EM  
SSB 0  
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GB 0  
PC 1.00

**Fig.S1** <sup>1</sup>H NMR Spectrum of **1a**



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**13C, CDCl3**

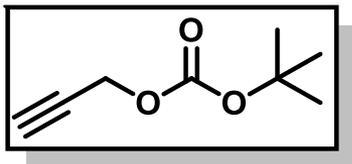
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SWH 24038.461 Hz  
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RG 201.48  
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TE 300.0 K  
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PLW1 53.00000000

==== CHANNEL 2  
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NUC2 1H  
CPDPRG2 waltz16  
NUC3 13C

**Fig.S2**  $^{13}\text{C}$  NMR Spectrum of **1a**



4.662  
4.657

2.500  
2.495  
2.490

1.498

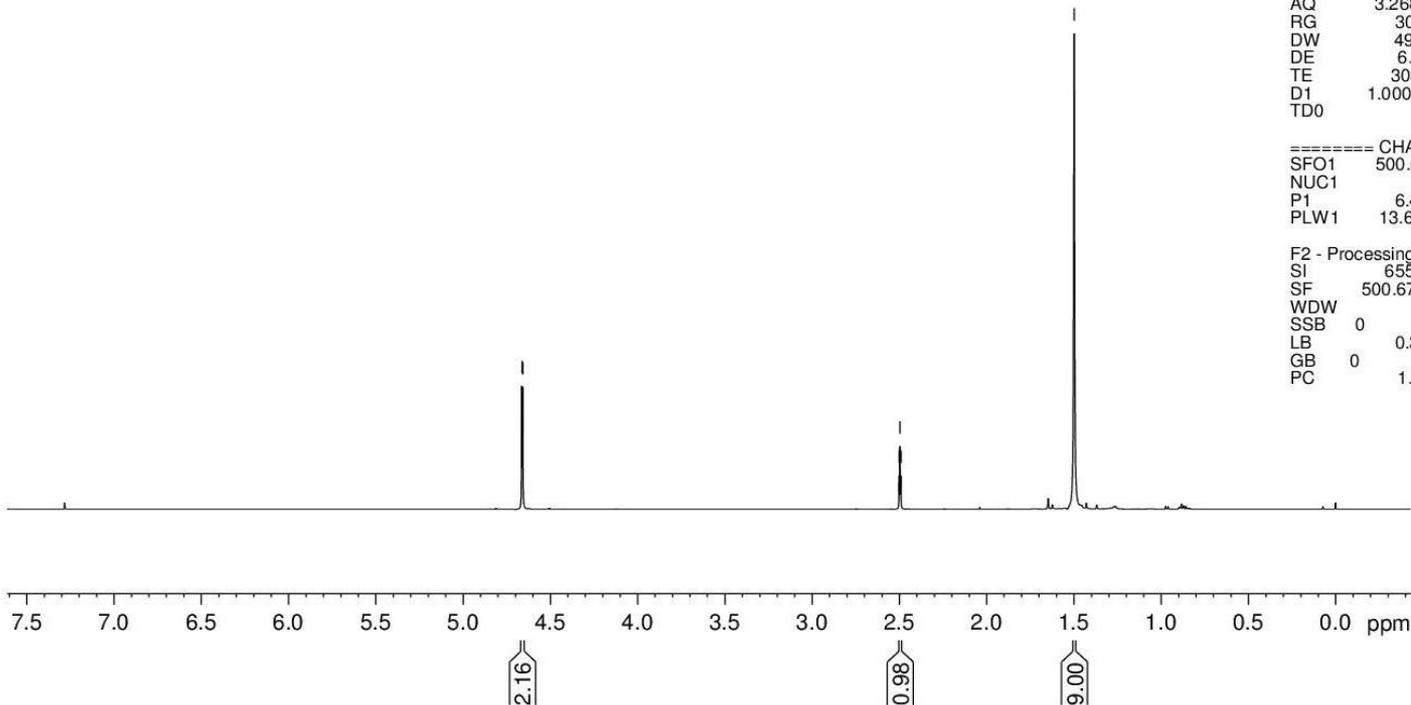
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**1H, CDCl3**

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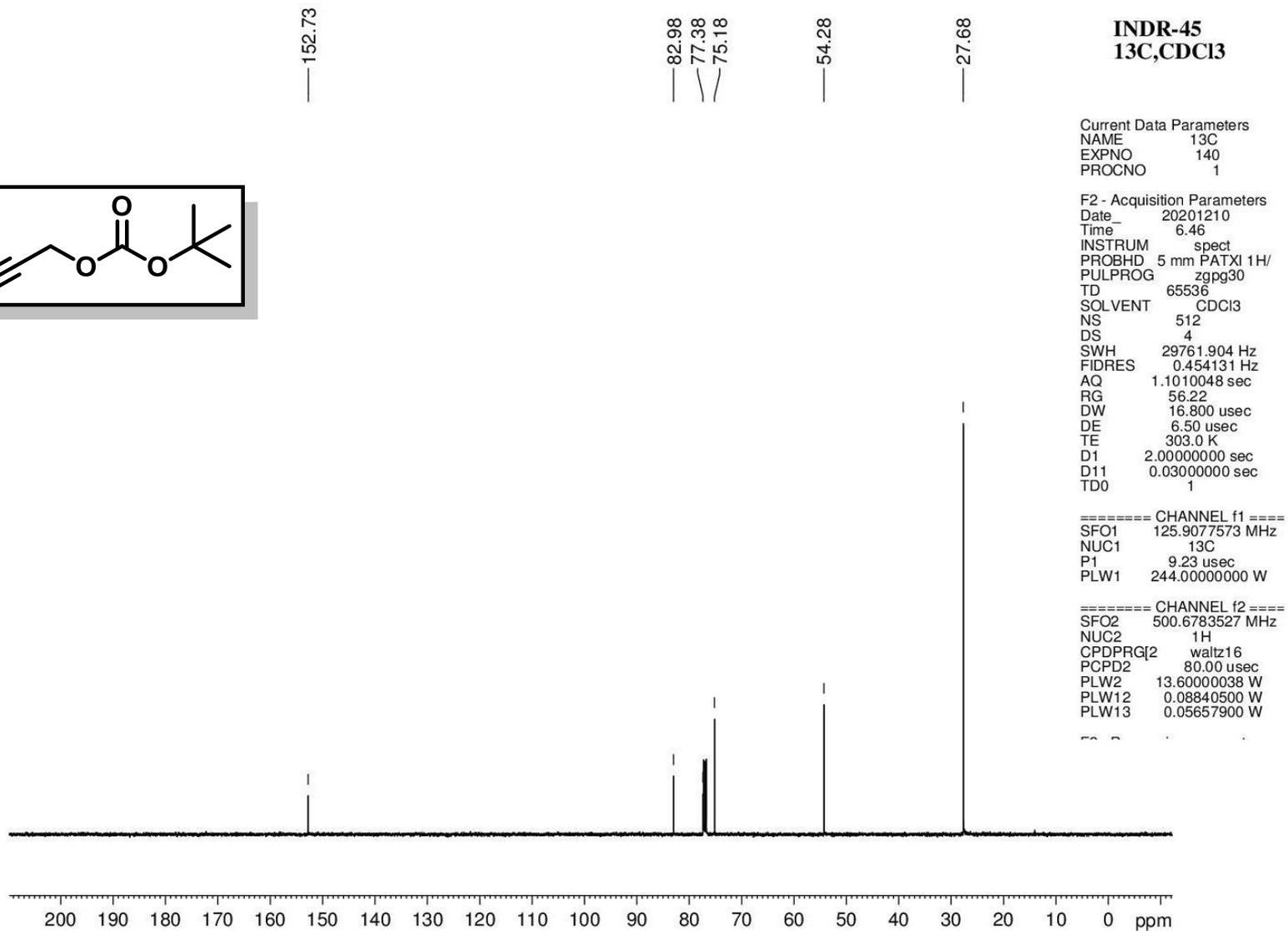
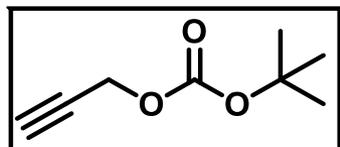
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PLW1 13.60000038 W

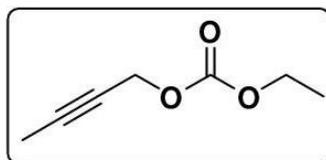
F2 - Processing parameters  
SI 65536  
SF 500.6763503 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Fig.S3** <sup>1</sup>H NMR Spectrum of **1b**



**Fig.S4** <sup>13</sup>C NMR Spectrum of **1b**



4.6840  
4.6814  
4.2282  
4.2256  
4.2239  
4.2213  
4.2195  
4.2103  
4.2076  
4.2061  
4.2035  
4.2016

1.8615  
1.8594  
1.8576  
1.8554  
1.8535  
1.3168  
1.3143  
1.3126  
1.3085

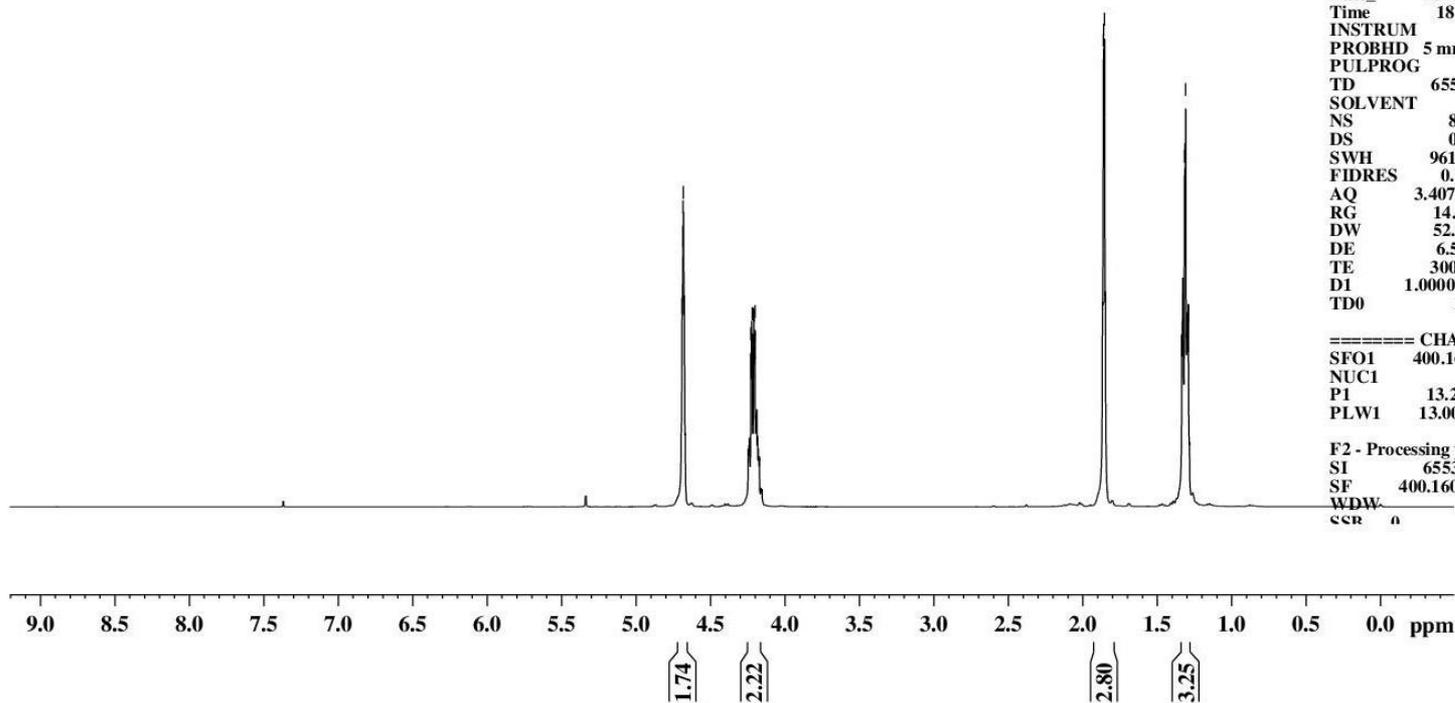
**INDR-5**  
**<sup>1</sup>H, CDCl<sub>3</sub>**

Current Data Parameters  
NAME 1H NMR  
EXPNO 20  
PROCNO 1

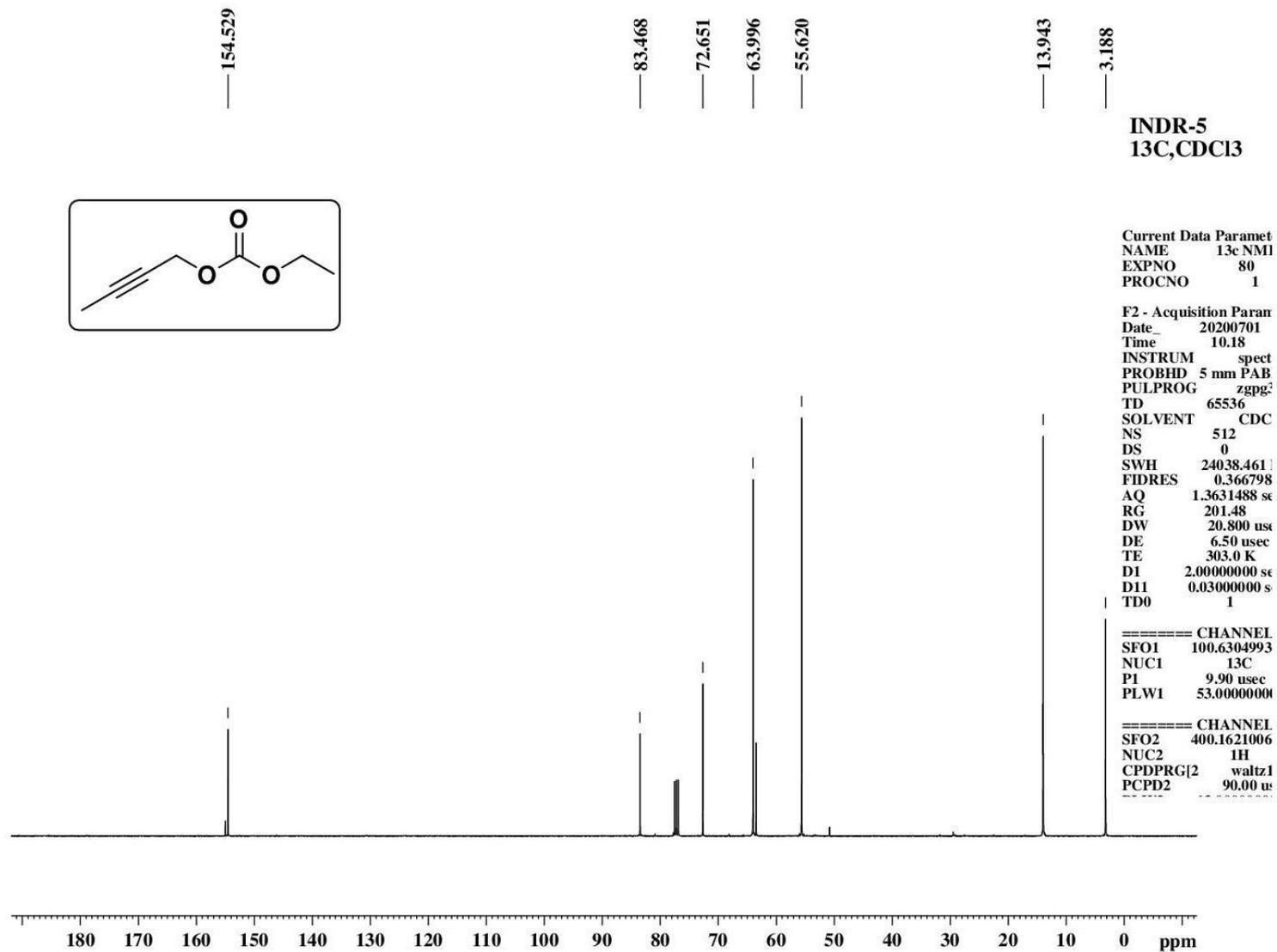
F2 - Acquisition Parameters  
Date\_ 20200619  
Time 18.57  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 14.41  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.0000000 sec  
TD0 1

==== CHANNEL f1 ====  
SFO1 400.1629712 MHz  
NUC1 1H  
P1 13.20 usec  
PLW1 13.0000000 W

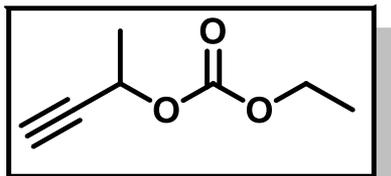
F2 - Processing parameters  
SI 65536  
SF 400.1604658 MHz  
WDW EM  
scr a



**Fig.S5** <sup>1</sup>H NMR Spectrum of **1c**



**Fig.S6** <sup>13</sup>C NMR Spectrum of **1c**



5.2930  
5.2888  
5.2796  
5.2753  
5.2661  
5.2619  
5.2527  
5.2485  
4.2176  
4.2034  
4.1891  
4.1747

2.4878  
2.4835

1.5355  
1.5220  
1.3063  
1.2921  
1.2778

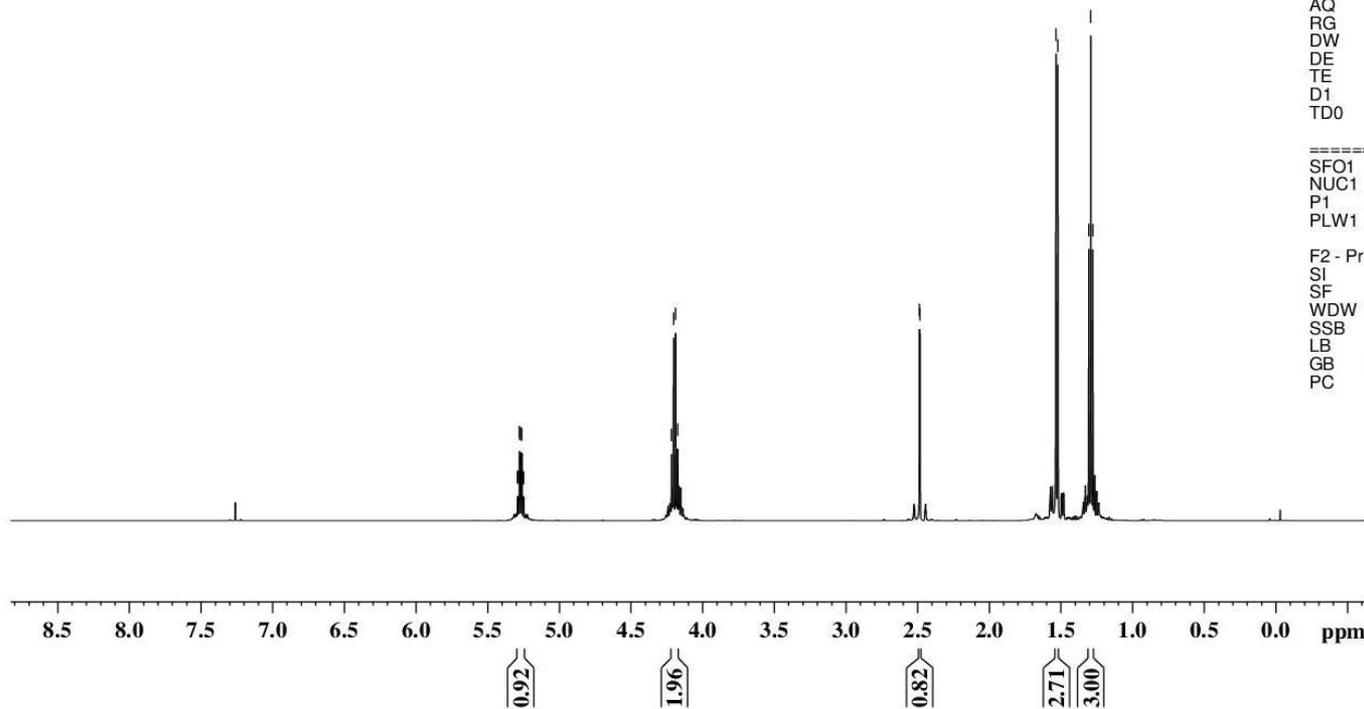
**INDR-66  
1H,CDCl3**

Current Data Parameters  
NAME 1H  
EXPNO 40  
PROCNO 1

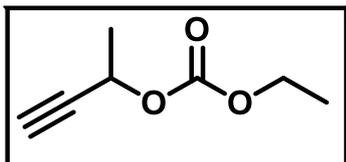
F2 - Acquisition Paramete  
Date\_ 20210222  
Time 8.32  
INSTRUM spect  
PROBHD 5 mm PATXI 1  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 2  
SWH 10026.738 Hz  
FIDRES 0.152996 Hz  
AQ 3.2680619 sec  
RG 30.83  
DW 49.867 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =  
SFO1 500.6794419 M  
NUC1 1H  
P1 6.45 usec  
PLW1 13.60000038 V

F2 - Processing paramete  
SI 65536  
SF 500.6763612 MH  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Fig.S7** <sup>1</sup>H NMR Spectrum of **1d**



— 154.13

— 81.46

— 73.65

— 64.26

— 63.69

— 21.19

— 14.18

**INDR 66**  
**<sup>13</sup>C, CDCI3**

Current Data Parameters

NAME 13C  
EXPNO 50  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20210224  
Time 3.29  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 201.48  
DW 20.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

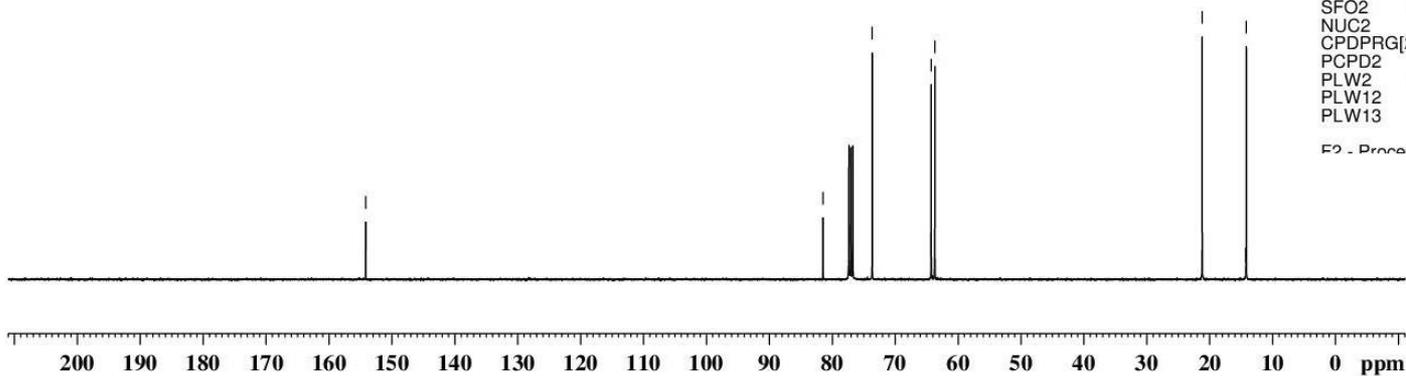
===== CHANNEL f1 =====

SFO1 100.6304993 MHz  
NUC1 13C  
P1 9.90 usec  
PLW1 53.00000000 W

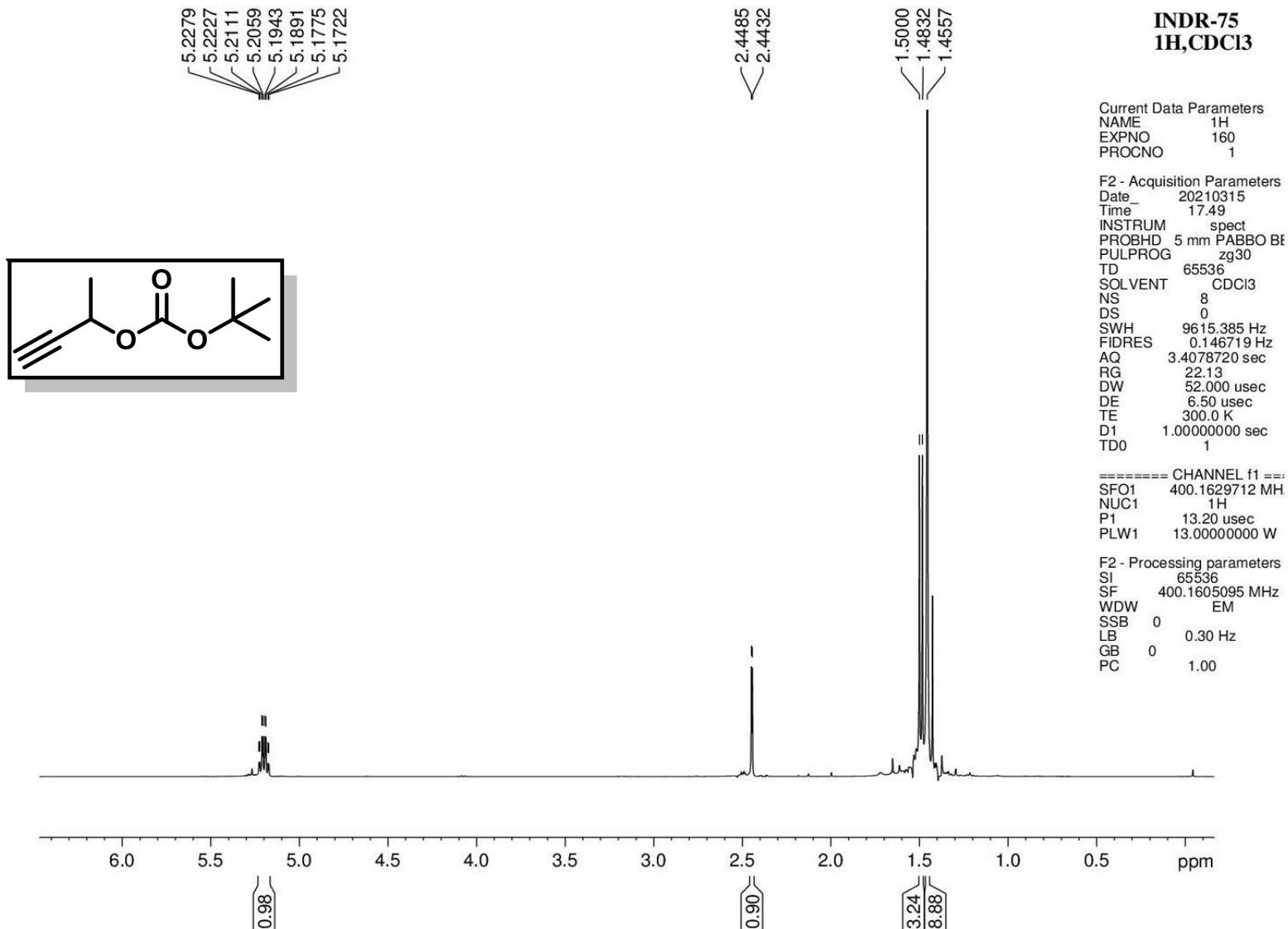
===== CHANNEL f2 =====

SFO2 400.1621006 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 13.00000000 W  
PLW12 0.27963999 W  
PLW13 0.22651000 W

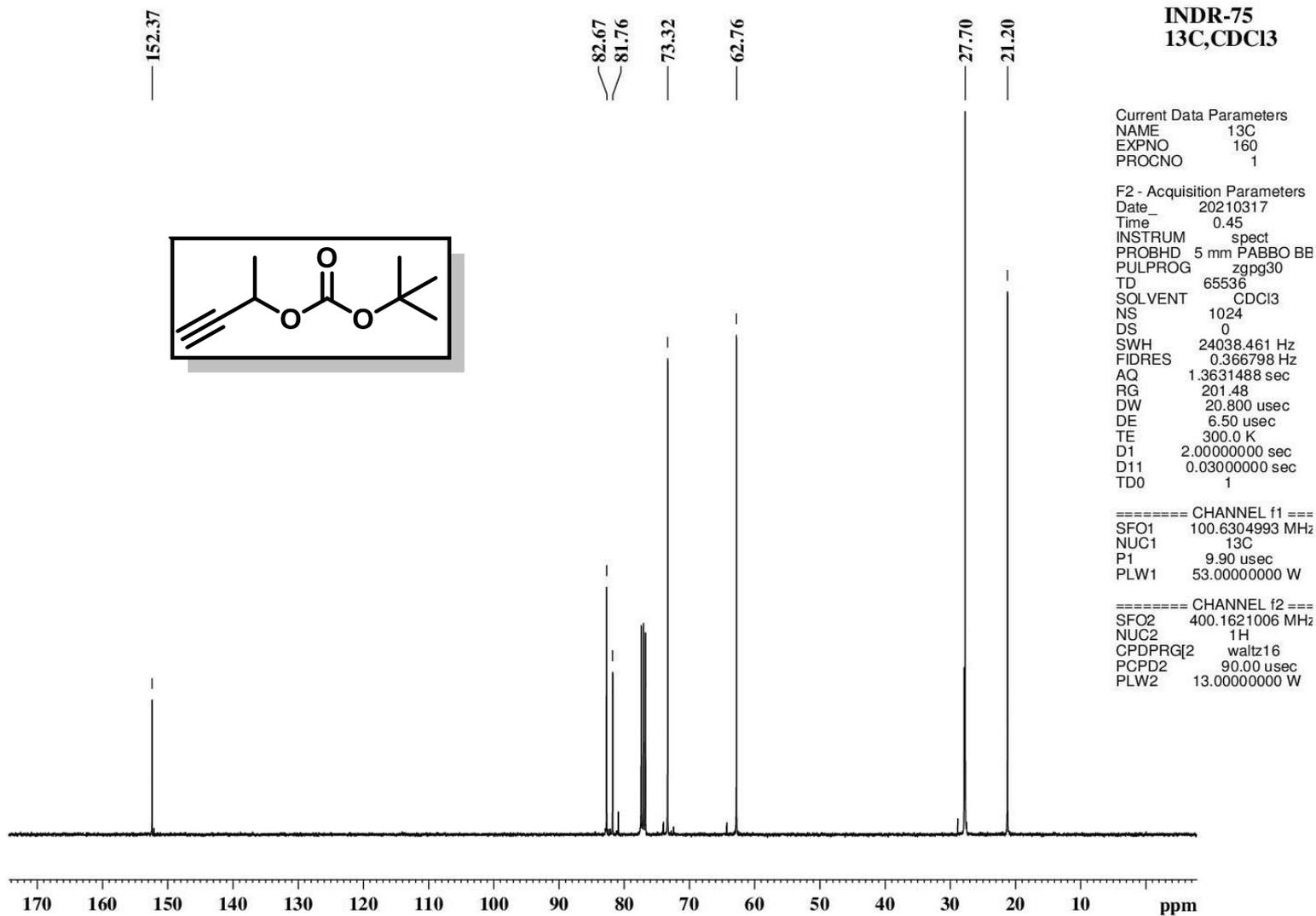
F2 - Processing parameters

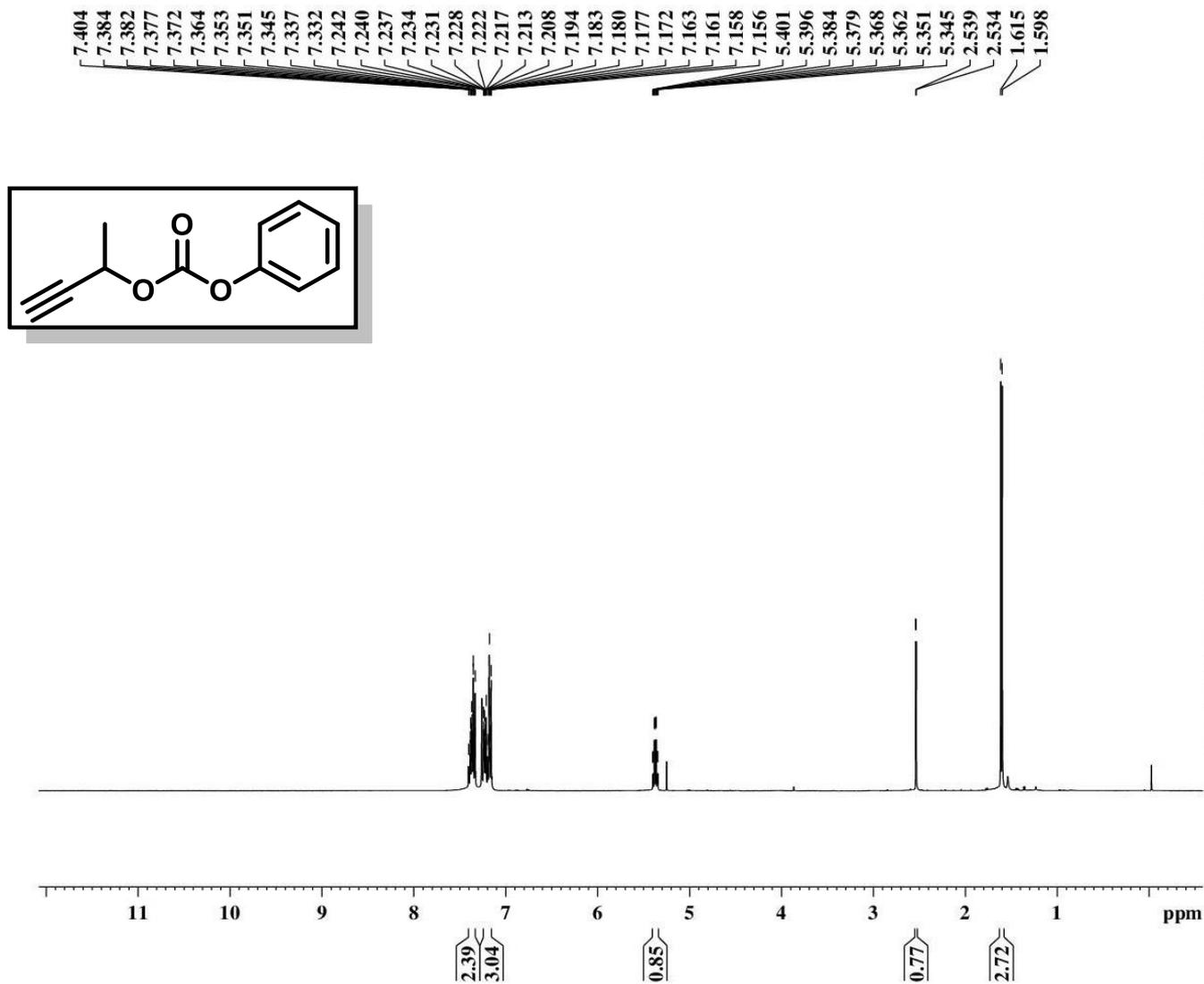


**Fig.S8** <sup>13</sup>C NMR Spectrum of **1d**



**Fig.S9**  $^1\text{H}$  NMR Spectrum of **1e**





**INDR-84**  
**1H, CDCI3**

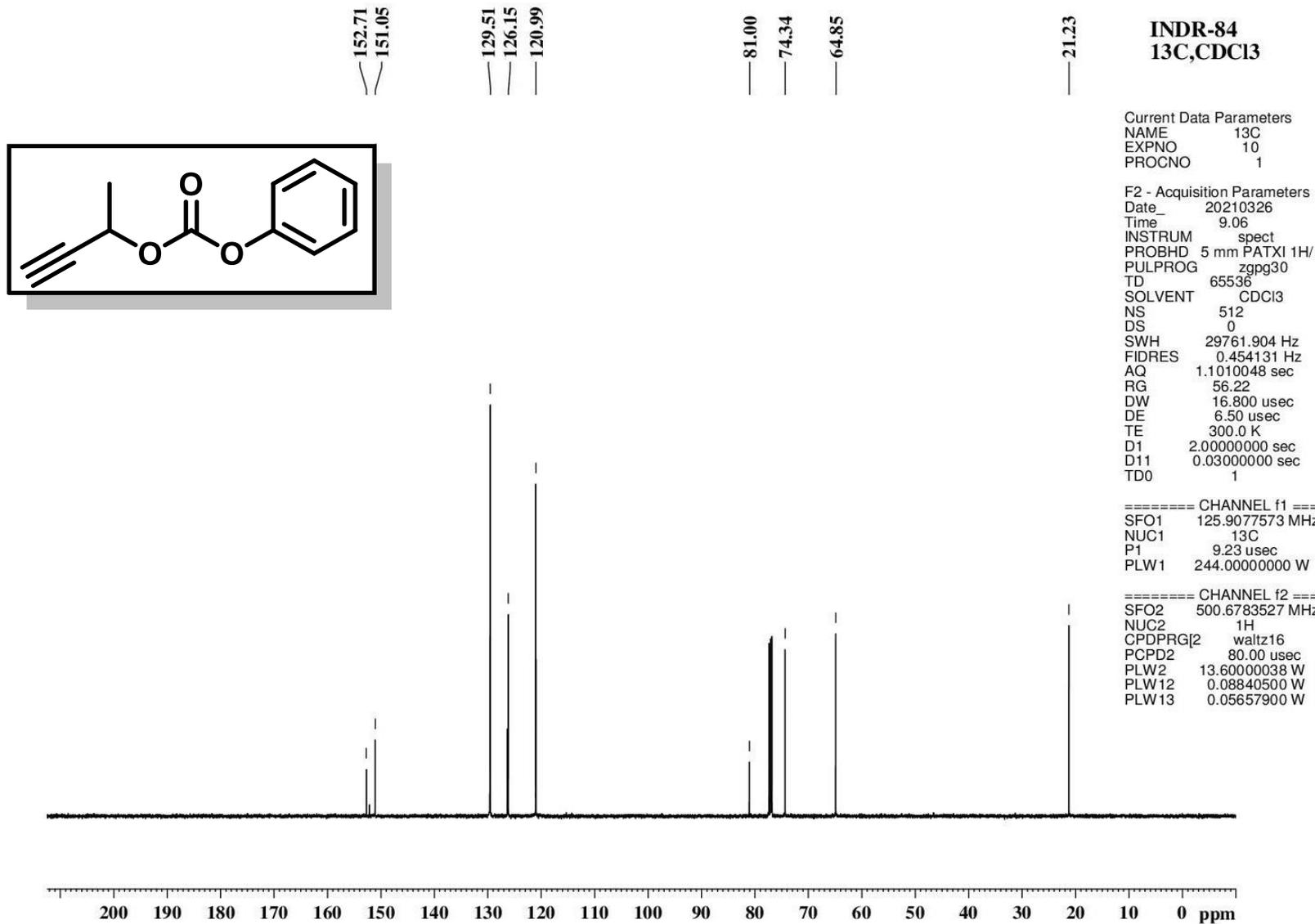
Current Data Parameters  
 NAME 1H  
 EXPNO 160  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20210322  
 Time 11.46  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 65.65  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

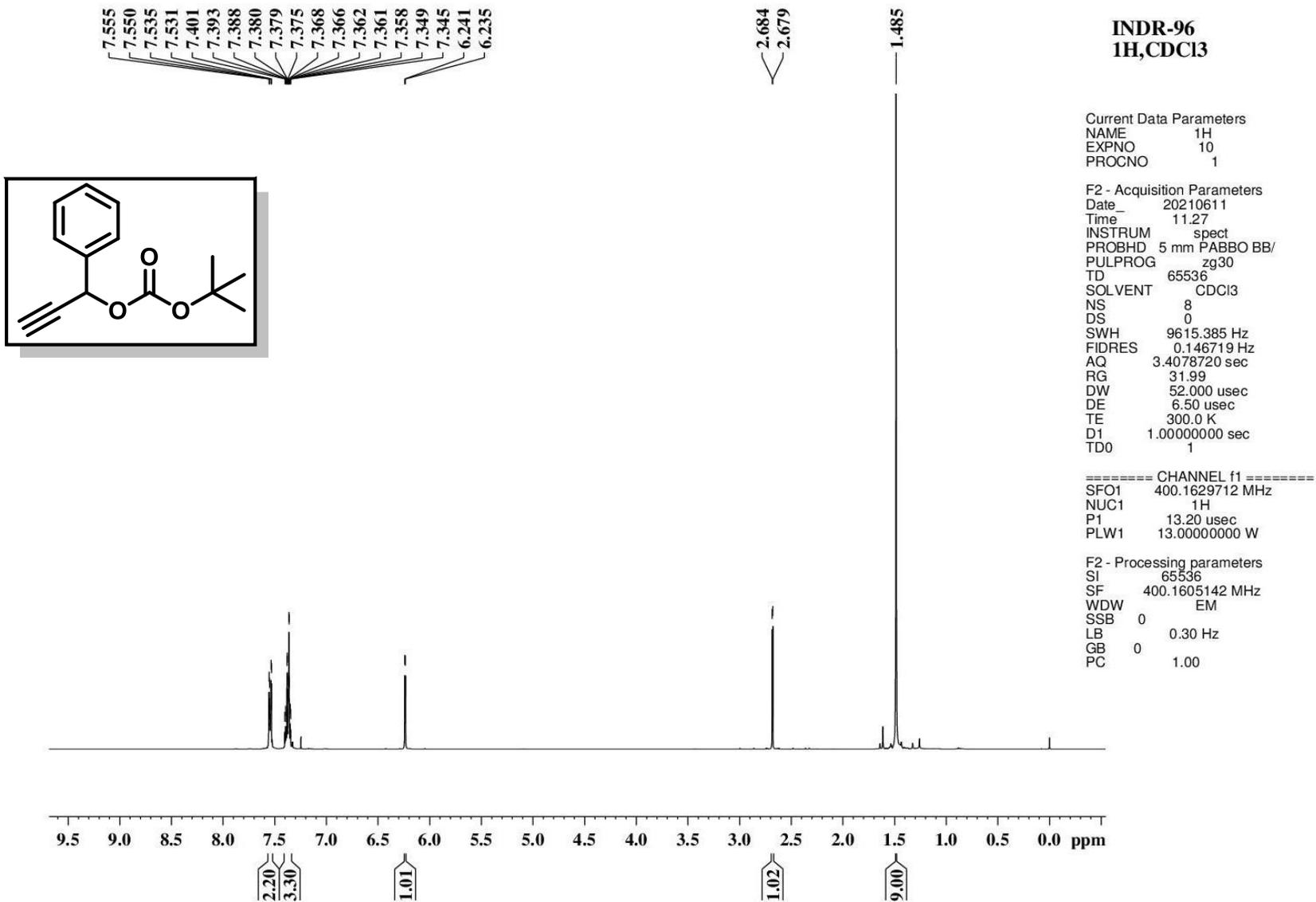
===== CHANNEL f1 =====  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 13.20 usec  
 PLW1 13.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 400.1605250 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

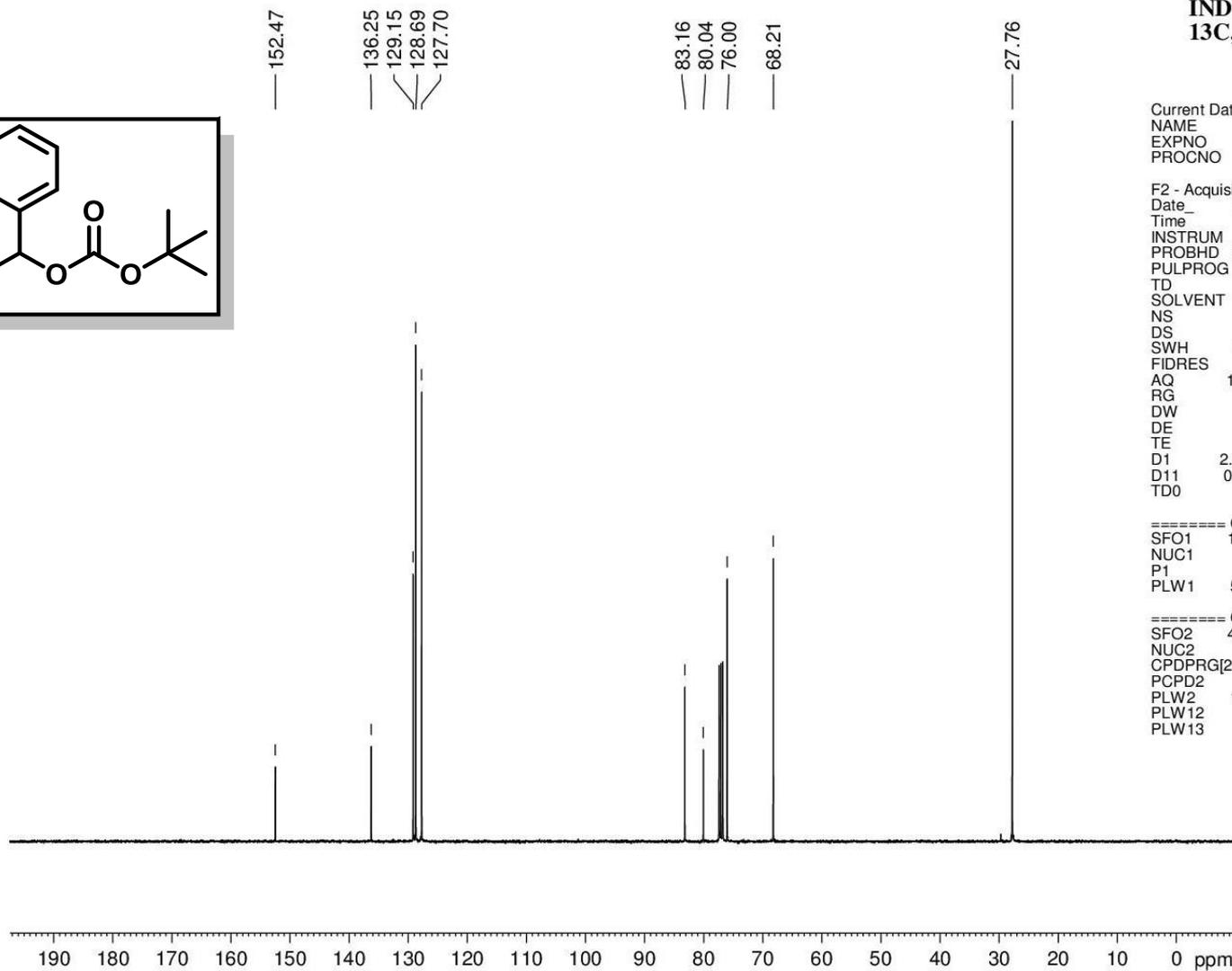
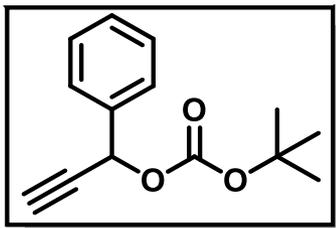
**Fig.S11** <sup>1</sup>H NMR Spectrum of **1f**



**Fig.S12**  $^{13}\text{C}$  NMR Spectrum of **1f**



**Fig.S13**  $^1\text{H}$  NMR Spectrum of **1g**



**INDR 96**  
**13C,CDCl3**

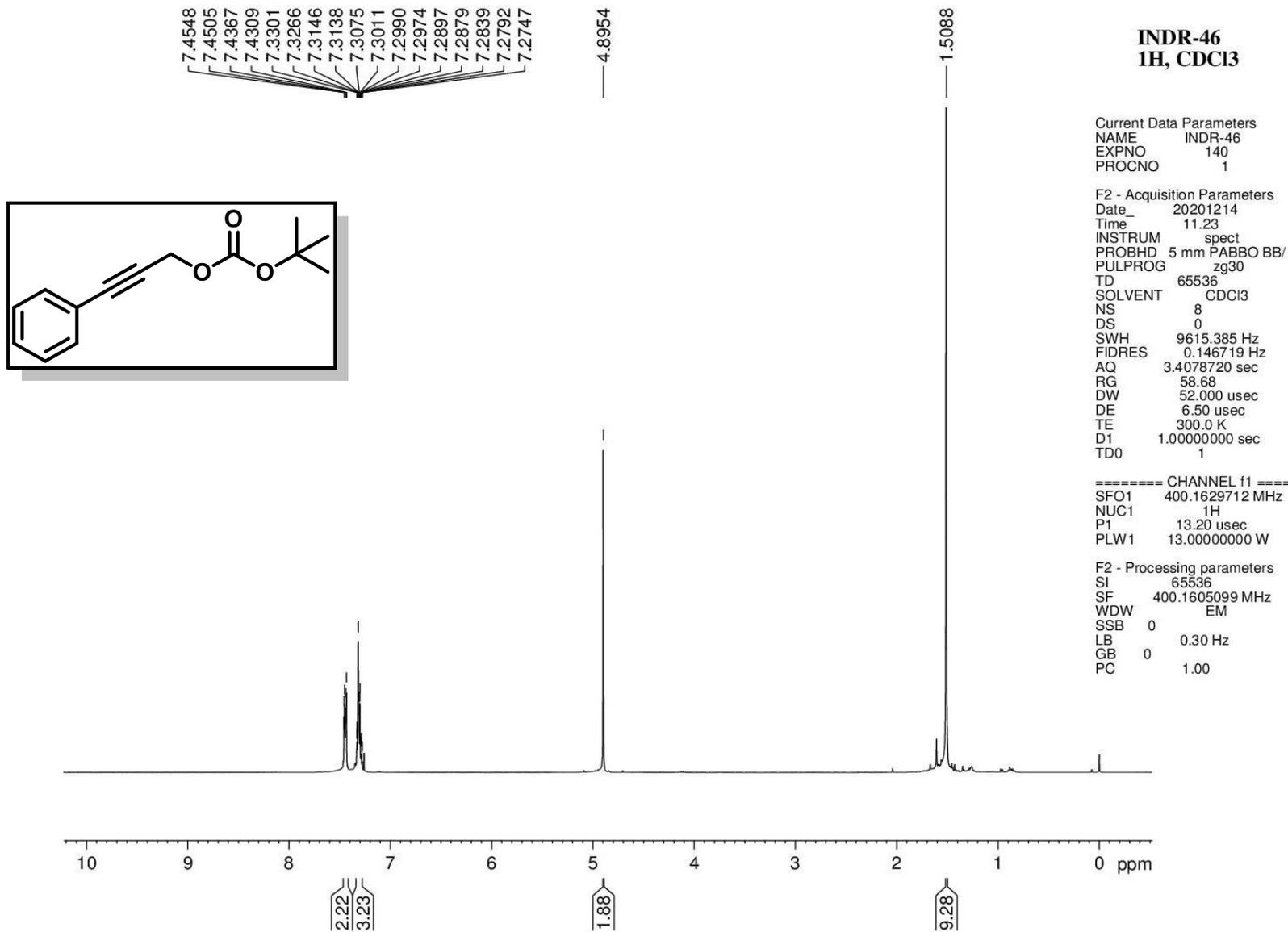
Current Data Parameters  
NAME 13C  
EXPNO 270  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210618  
Time 5.53  
INSTRUM spect  
PROBHD 5 mm PABBO BB  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 201.48  
DW 20.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.0000000 sec  
D11 0.03000000 sec  
TD0 1

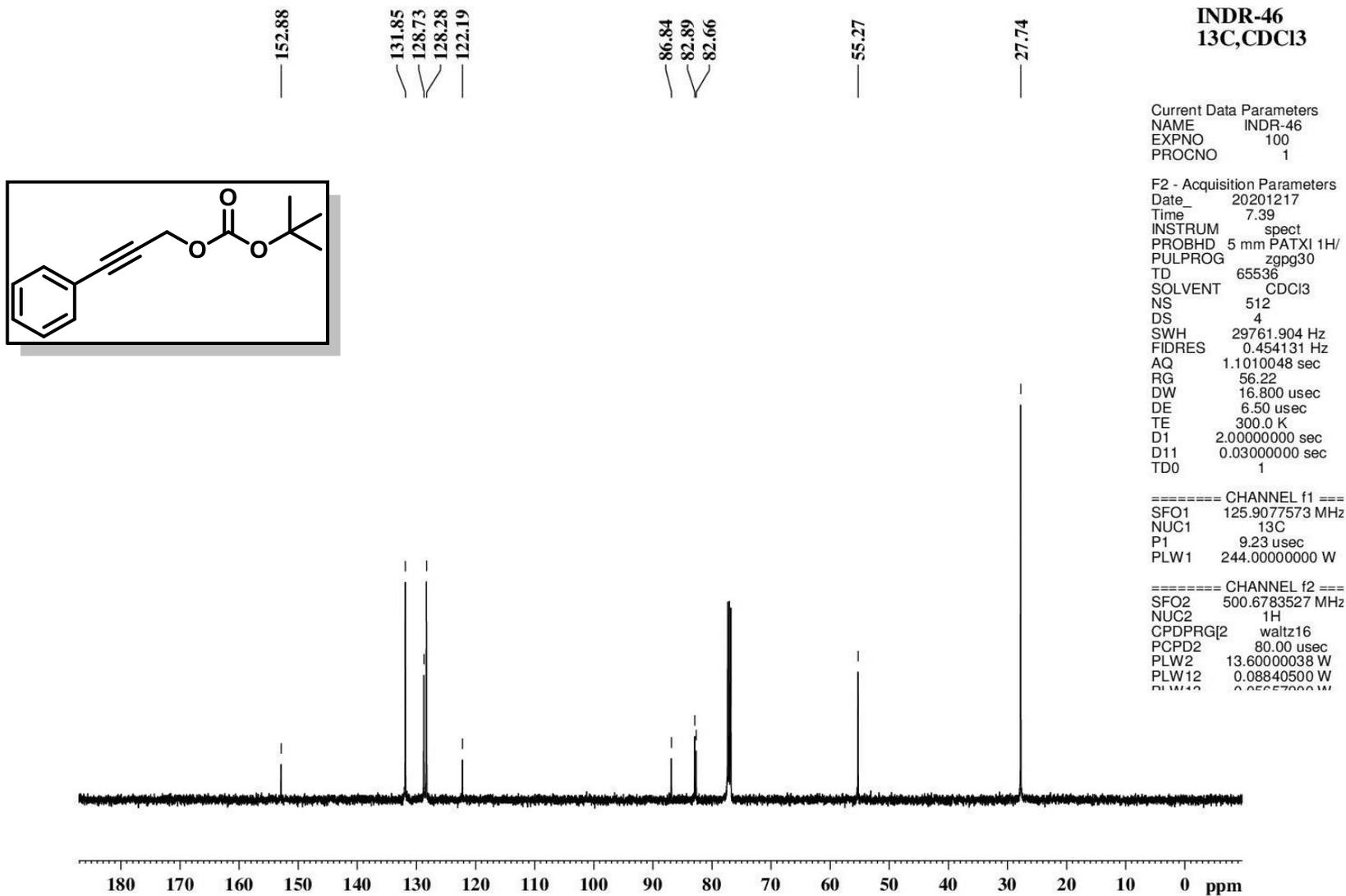
==== CHANNEL f1 ====  
SFO1 100.6304993 MHz  
NUC1 13C  
P1 9.90 usec  
PLW1 53.00000000 W

==== CHANNEL f2 ====  
SFO2 400.1621006 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 13.00000000 W  
PLW12 0.27963999 W  
PLW13 0.22651000 W

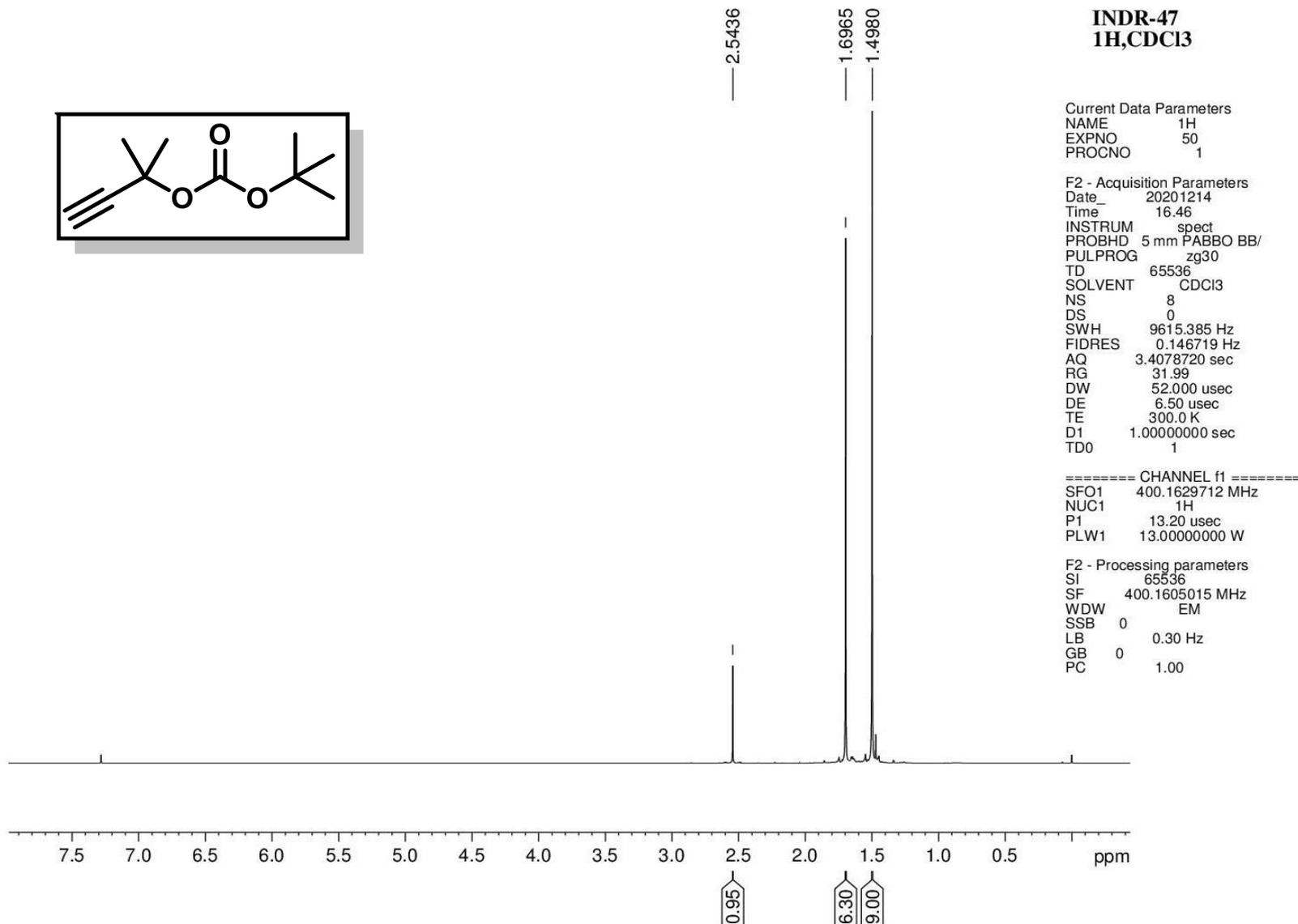
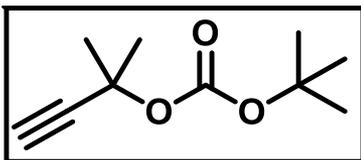
**Fig.S14**  $^{13}\text{C}$  NMR Spectrum of **1g**



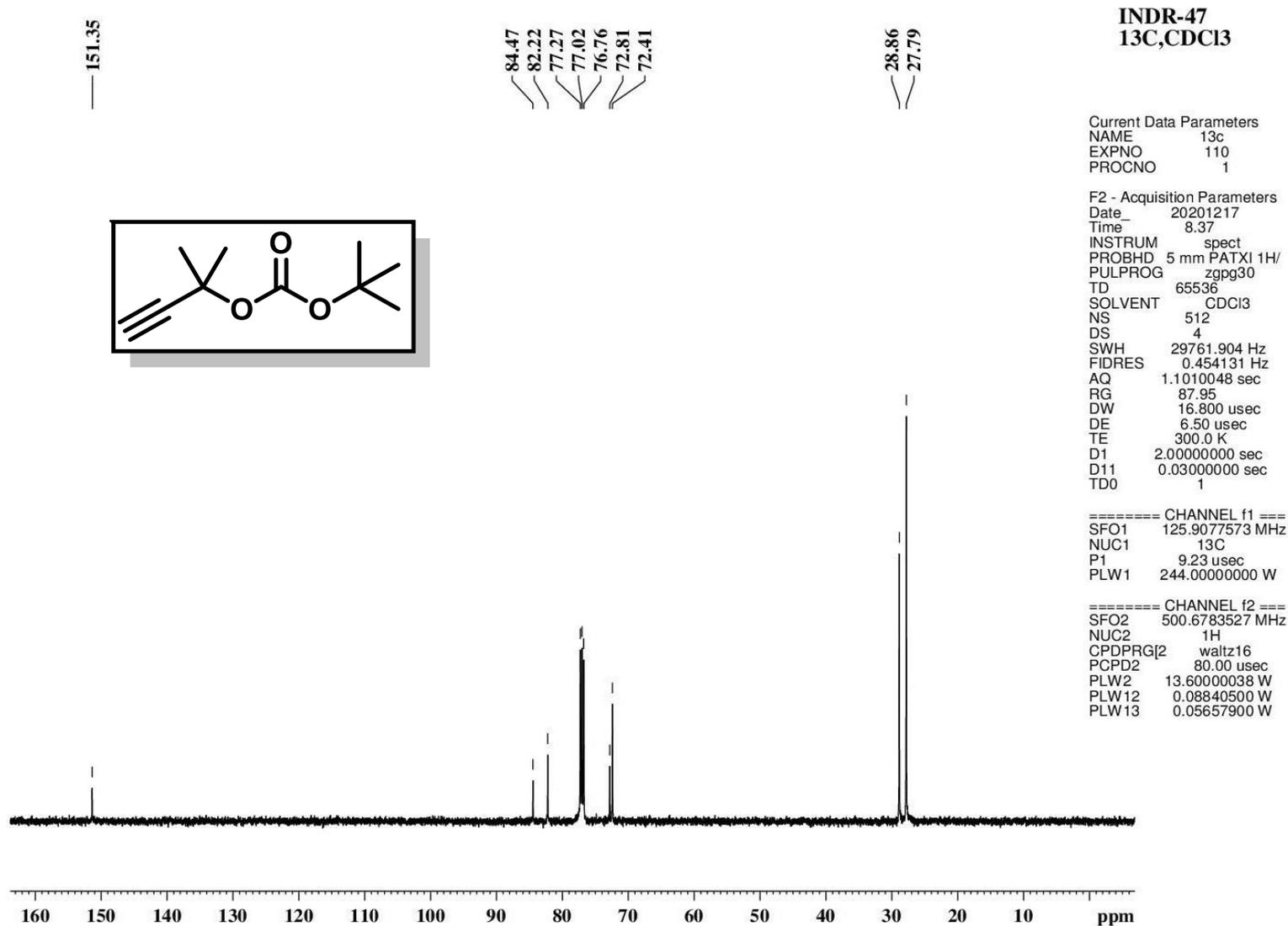
**Fig.S15** <sup>1</sup>H NMR Spectrum of **1h**



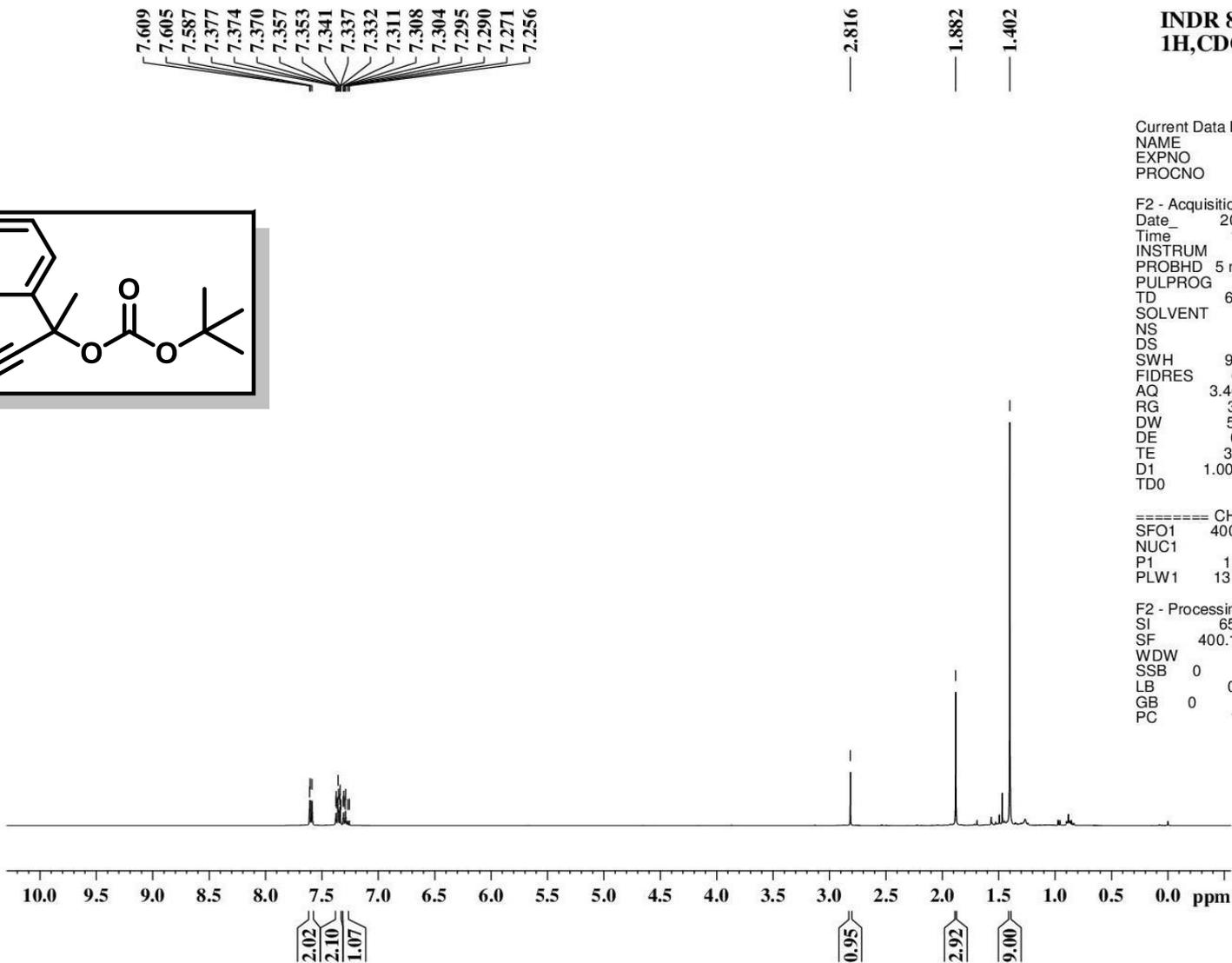
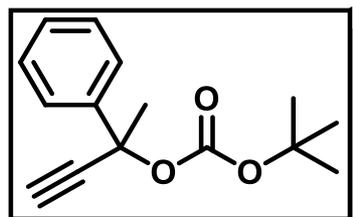
**Fig.S16** <sup>13</sup>C NMR Spectrum of **1h**



**Fig.S17** <sup>1</sup>H NMR Spectrum of **1i**



**Fig.S18** <sup>13</sup>C NMR Spectrum of **1i**



**INDR 80**  
**1H,CDCI3**

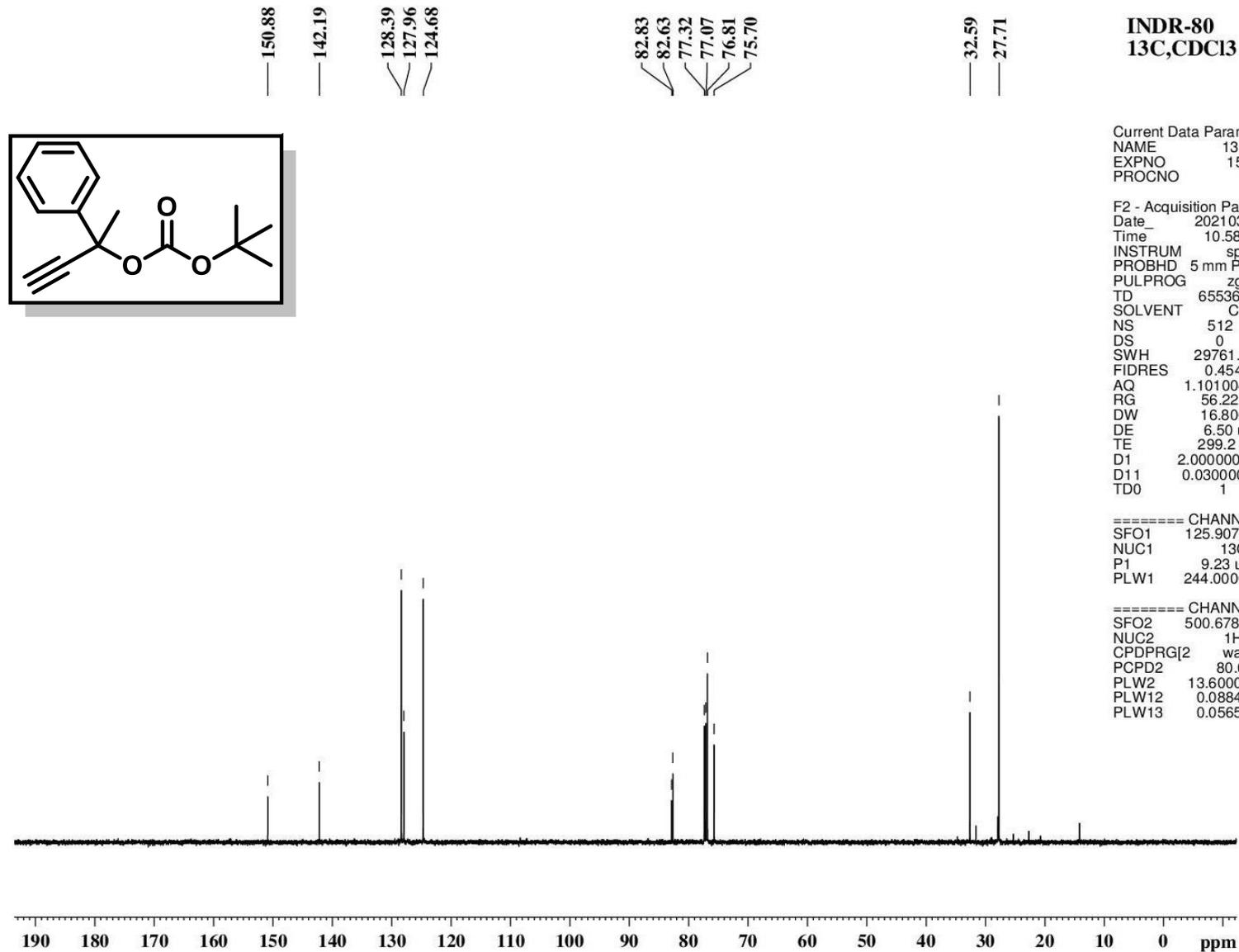
Current Data Parameters  
NAME 1H  
EXPNO 10  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210319  
Time 11.08  
INSTRUM spect  
PROBHD 5 mm PABBO BB  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 31.99  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.0000000 sec  
TDO 1

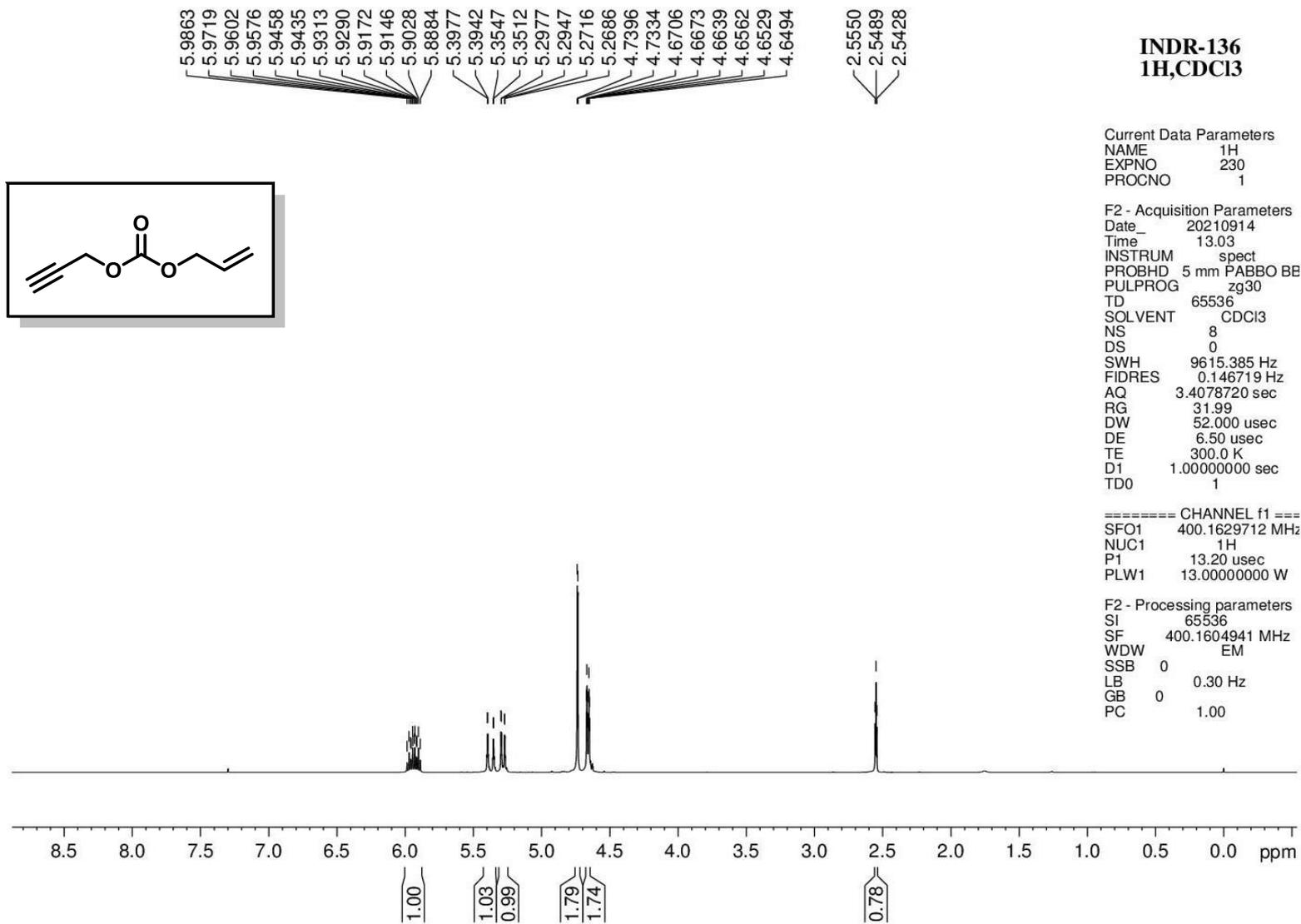
===== CHANNEL f1 =====  
SFO1 400.1629712 MHz  
NUC1 1H  
P1 13.20 usec  
PLW1 13.0000000 W

F2 - Processing parameters  
SI 65536  
SF 400.1605109 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

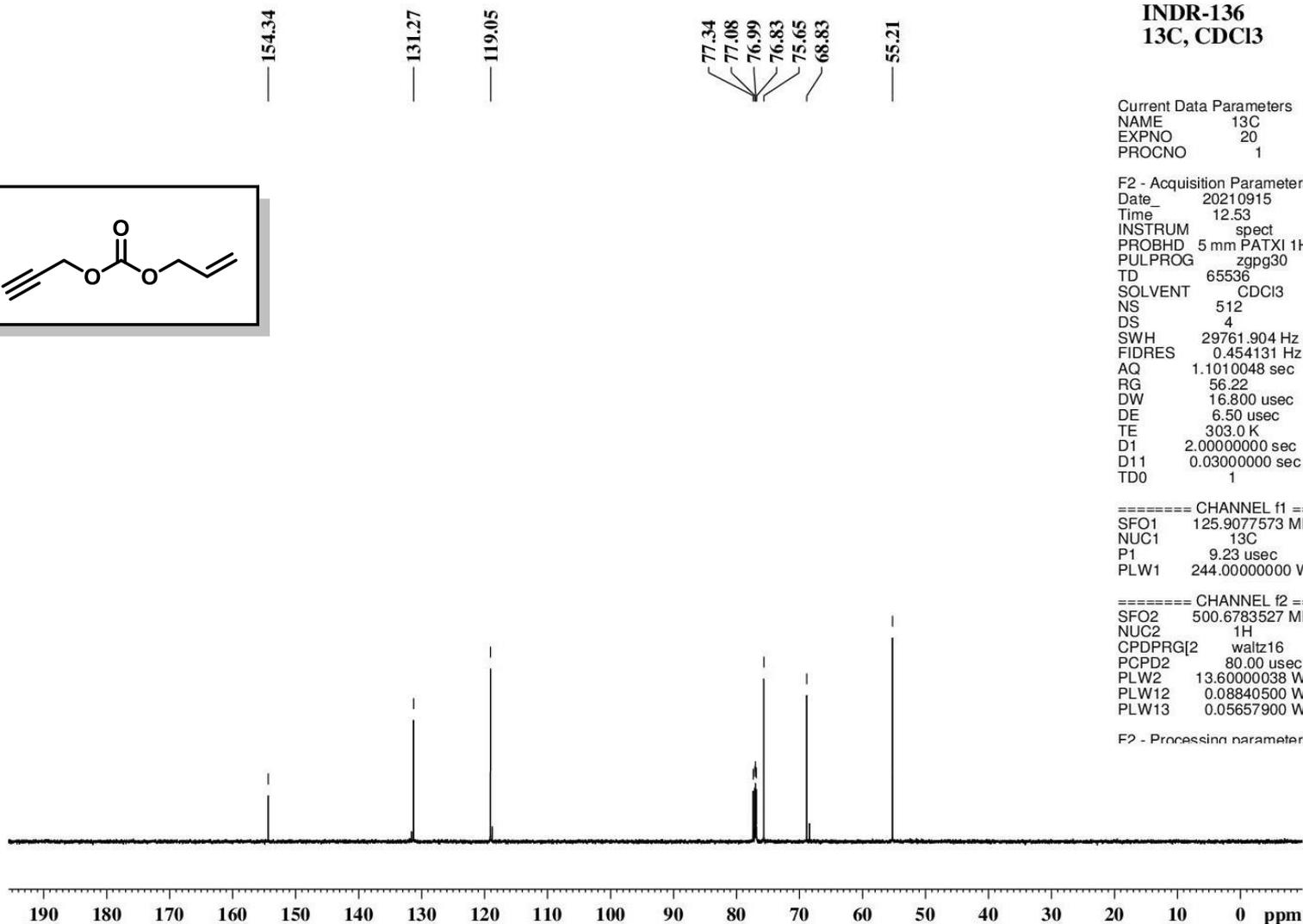
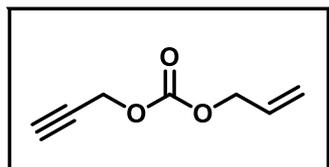
**Fig.S19** <sup>1</sup>H NMR Spectrum of **1j**



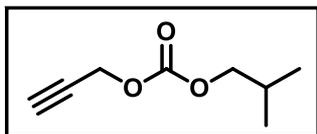
**Fig.S20**  $^{13}\text{C}$  NMR Spectrum of **1j**



**Fig.S21**  $^1\text{H}$  NMR Spectrum of **1k**



**Fig.S22** <sup>13</sup>C NMR Spectrum of **1k**



4.7295  
4.7234

3.9681  
3.9515

2.5383  
2.5321  
2.5260  
2.0380  
2.0212  
2.0147  
2.0044  
1.9979  
1.9876  
1.9810  
1.9708  
1.9642  
1.9541  
1.9474  
1.9373  
0.9666  
0.9497

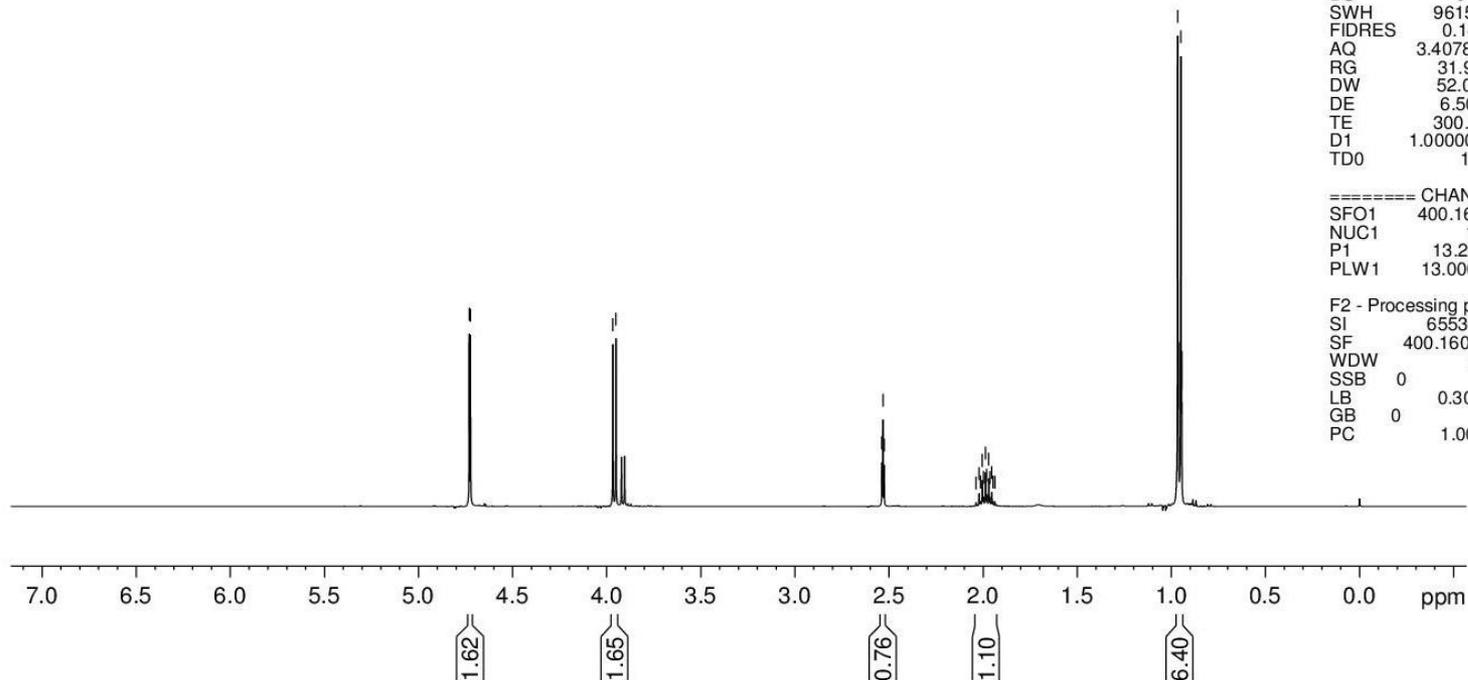
**INDR 137**  
**<sup>1</sup>H,CDCl<sub>3</sub>**

Current Data Parameters  
NAME 1H  
EXPNO 70  
PROCNO 1

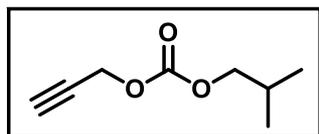
F2 - Acquisition Parameters  
Date\_ 20210915  
Time 13.59  
INSTRUM spect  
PROBHD 5 mm PABBO BE  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 31.99  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

==== CHANNEL f1 ====  
SFO1 400.1629712 MH  
NUC1 1H  
P1 13.20 usec  
PLW1 13.00000000 W

F2 - Processing parameters  
SI 65536  
SF 400.1604986 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Fig.S23** <sup>1</sup>H NMR Spectrum of **11**



— 154.68

75.52  
74.55  
73.90

— 55.06

— 27.74

— 18.80

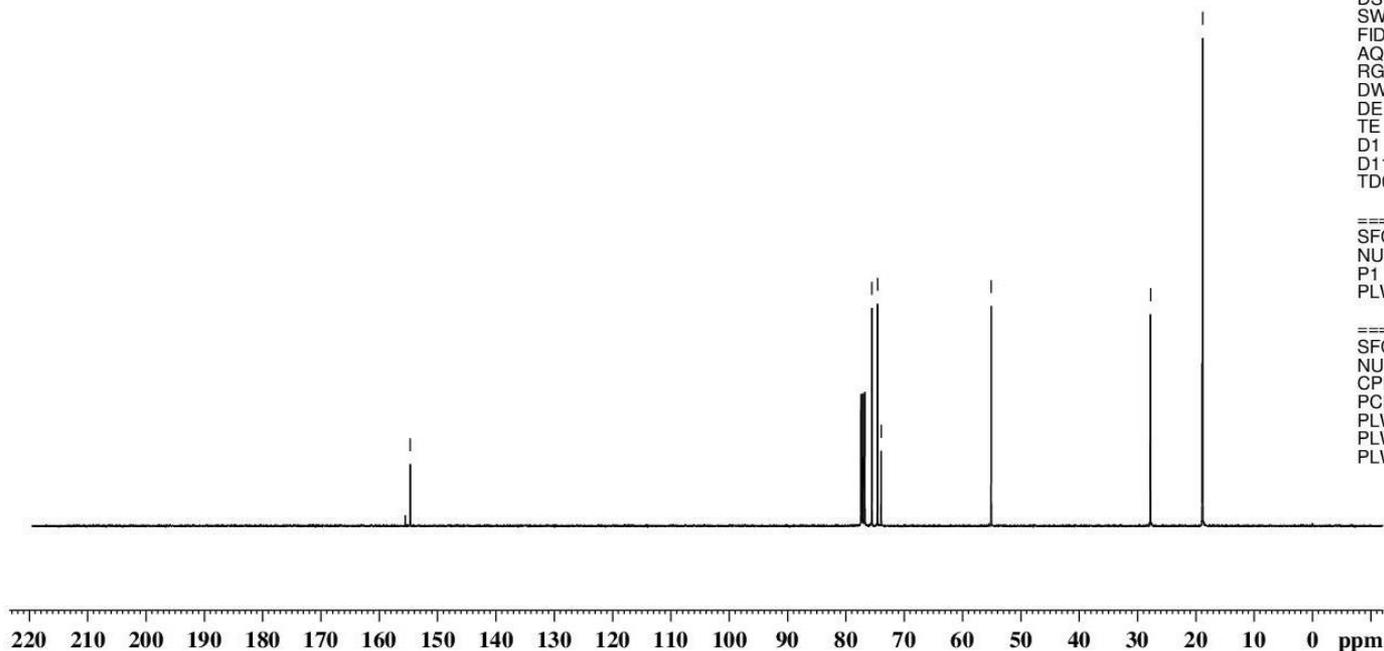
**INDR-137**  
**<sup>13</sup>C, CDCl<sub>3</sub>**

Current Data Parameters  
NAME 13C  
EXPNO 40  
PROCNO 1

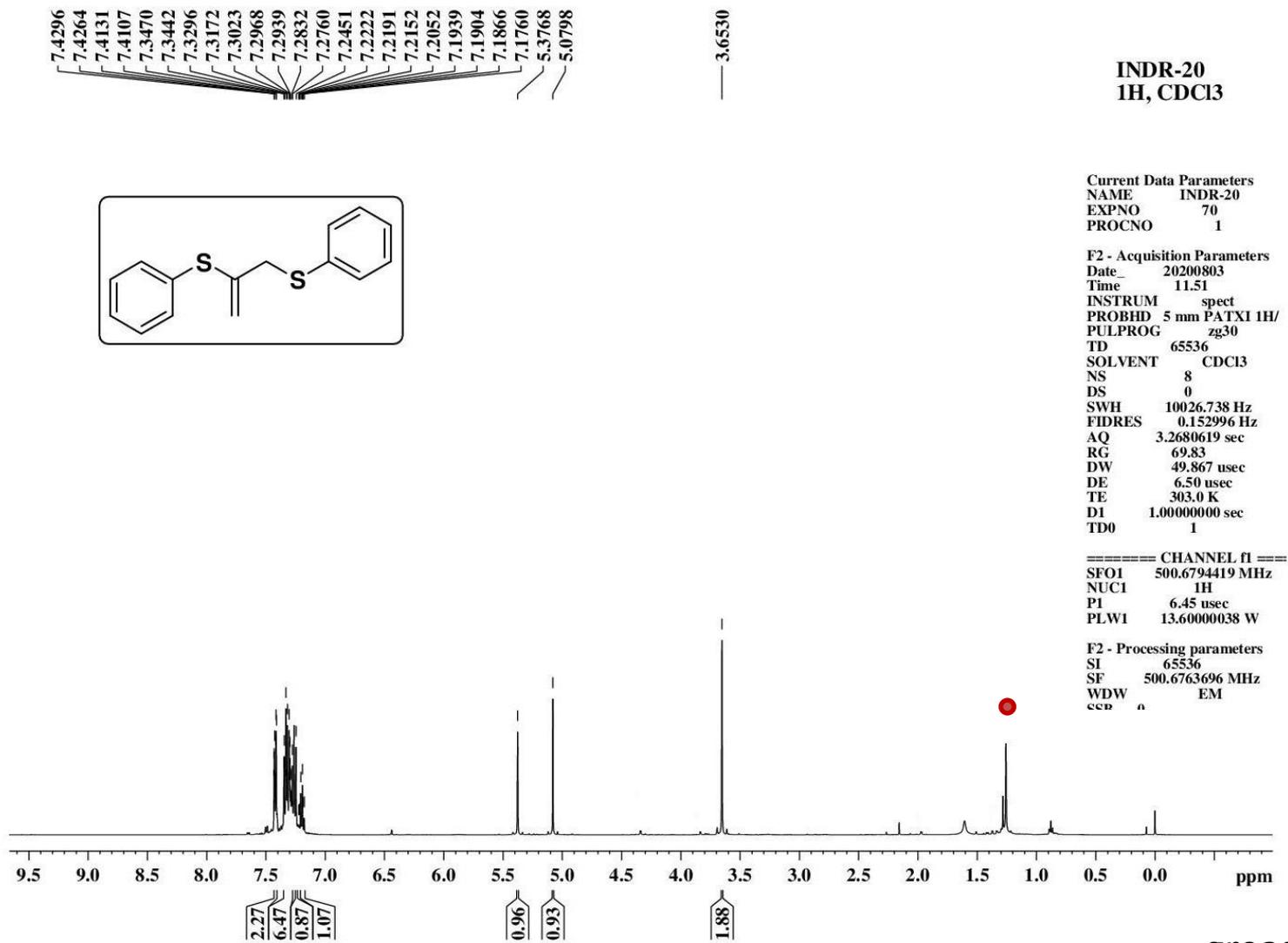
F2 - Acquisition Parameter  
Date\_ 20210918  
Time 9.55  
INSTRUM spect  
PROBHD 5 mm PABBO E  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 512  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 201.48  
DW 20.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

===== CHANNEL f1 =  
SFO1 100.6304993 MI  
NUC1 13C  
P1 9.90 usec  
PLW1 53.00000000 W

===== CHANNEL f2 =  
SFO2 400.1621006 MI  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 13.00000000 W  
PLW12 0.27963999 W  
PLW13 0.22651000 W



**Fig.S24** <sup>13</sup>C NMR Spectrum of **11**



**Fig.S25** <sup>1</sup>H NMR Spectrum of **3a**

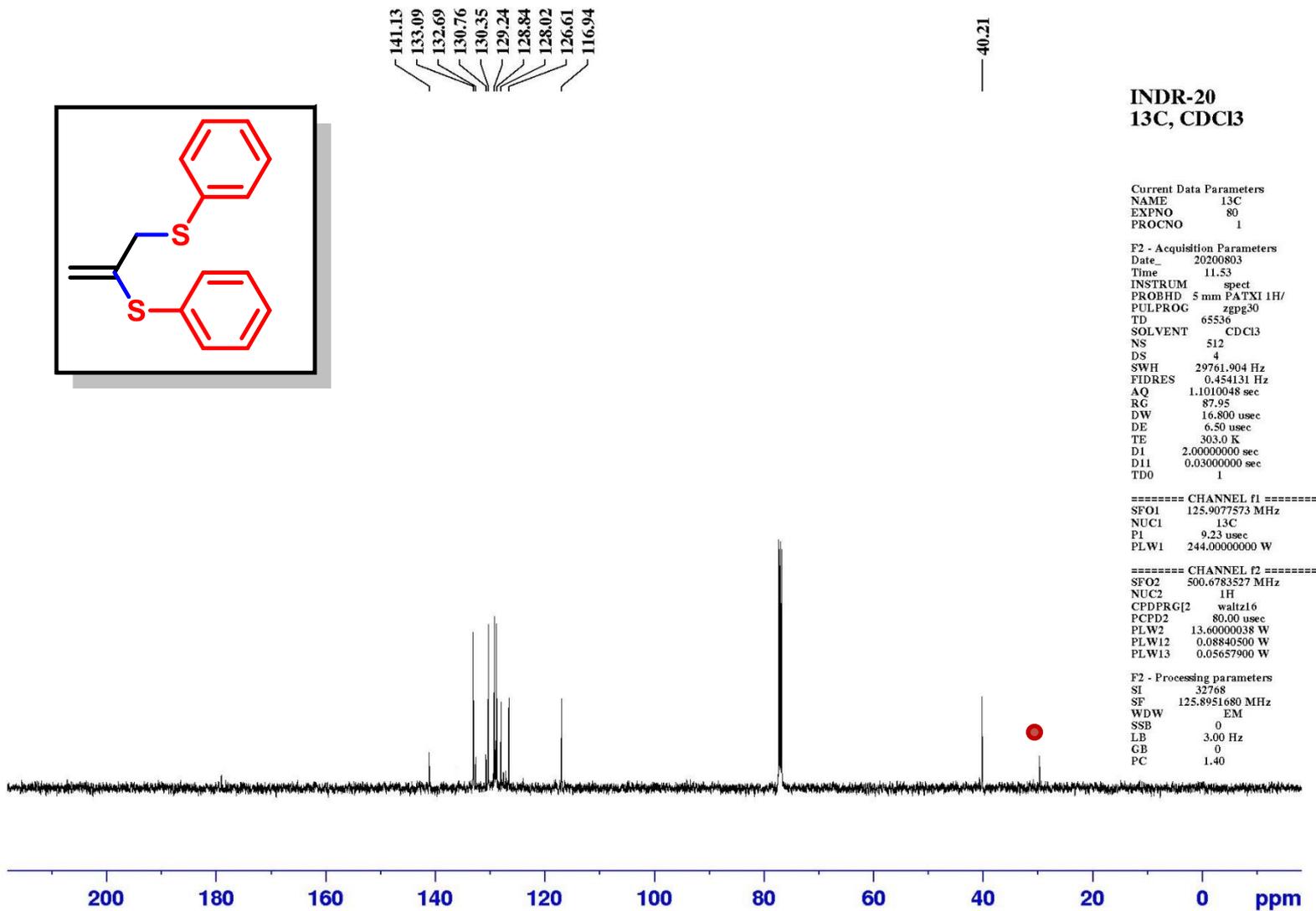
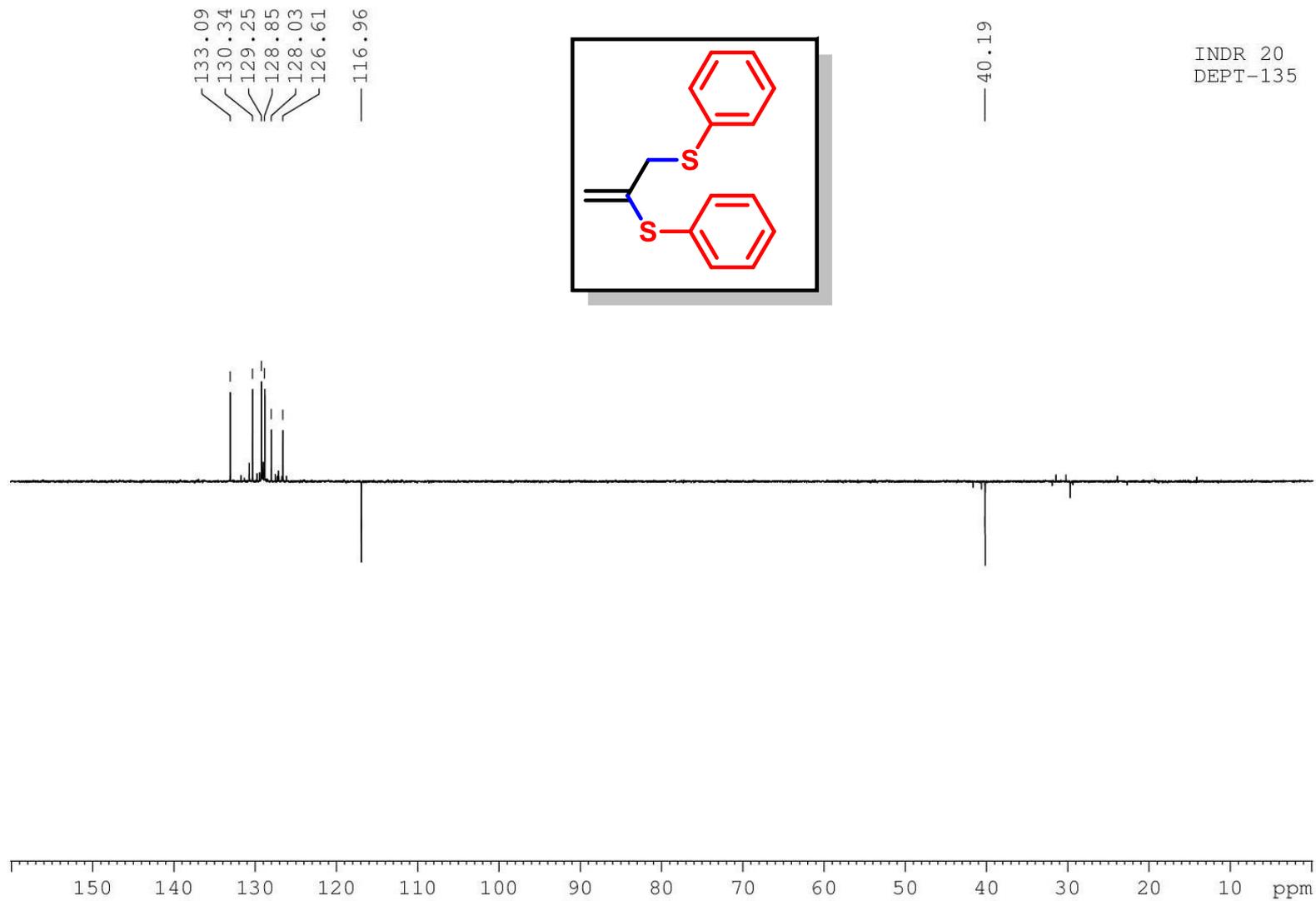


Fig.S26 <sup>13</sup>C NMR Spectrum of 3a



**Fig.S27** DEPT-135 Spectrum of **3a**

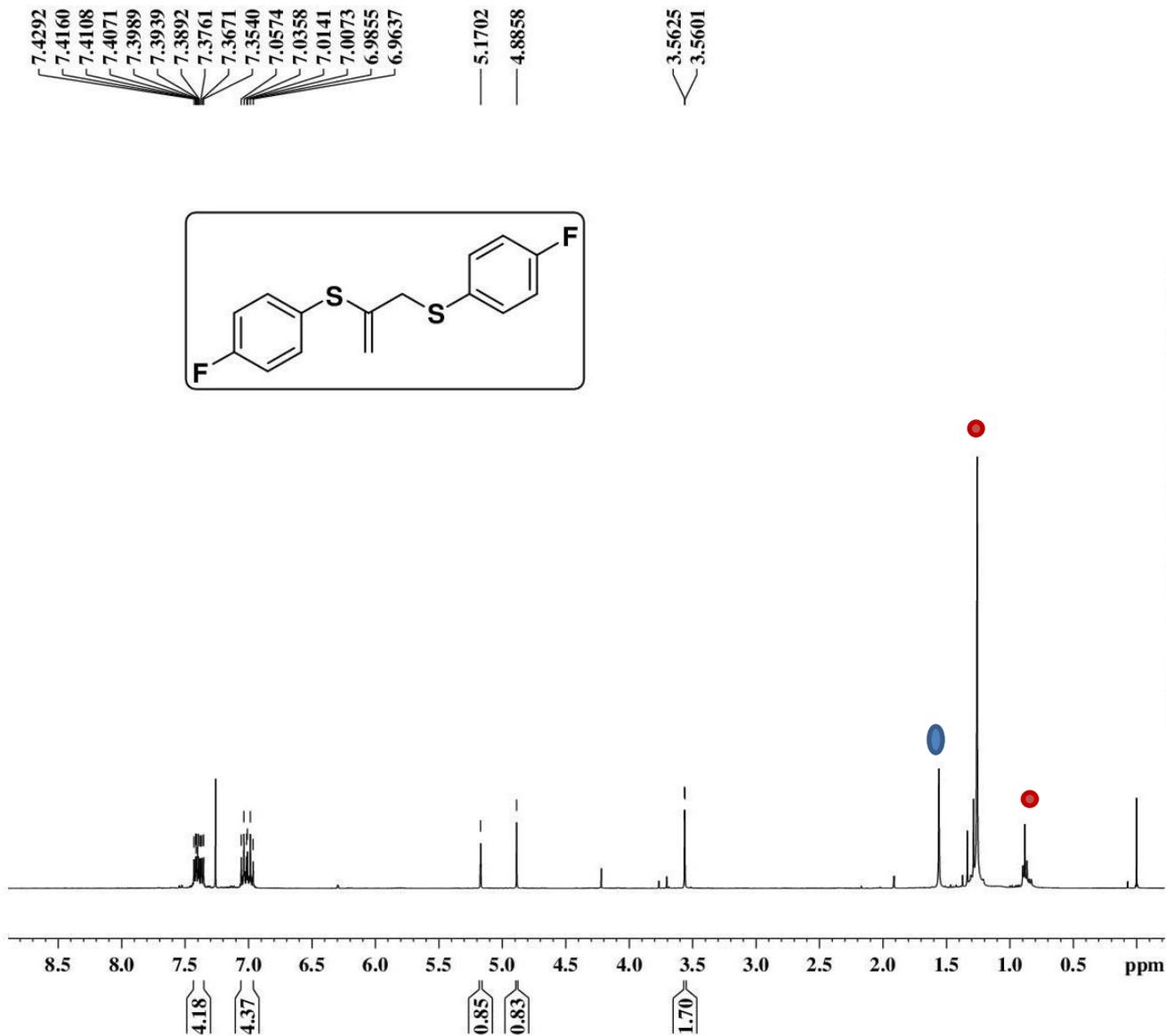


Fig.S28 <sup>1</sup>H NMR Spectrum of **3b**

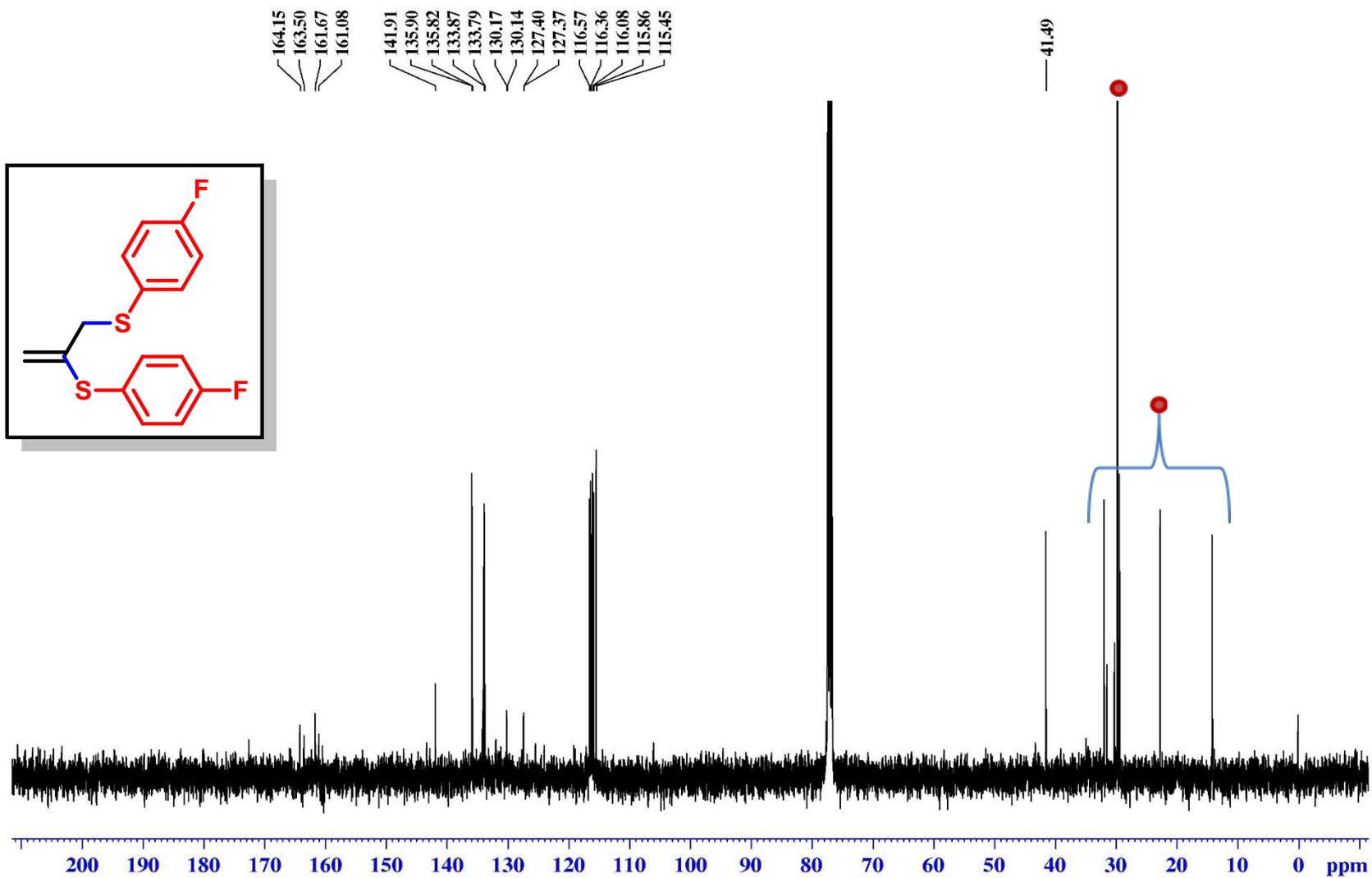
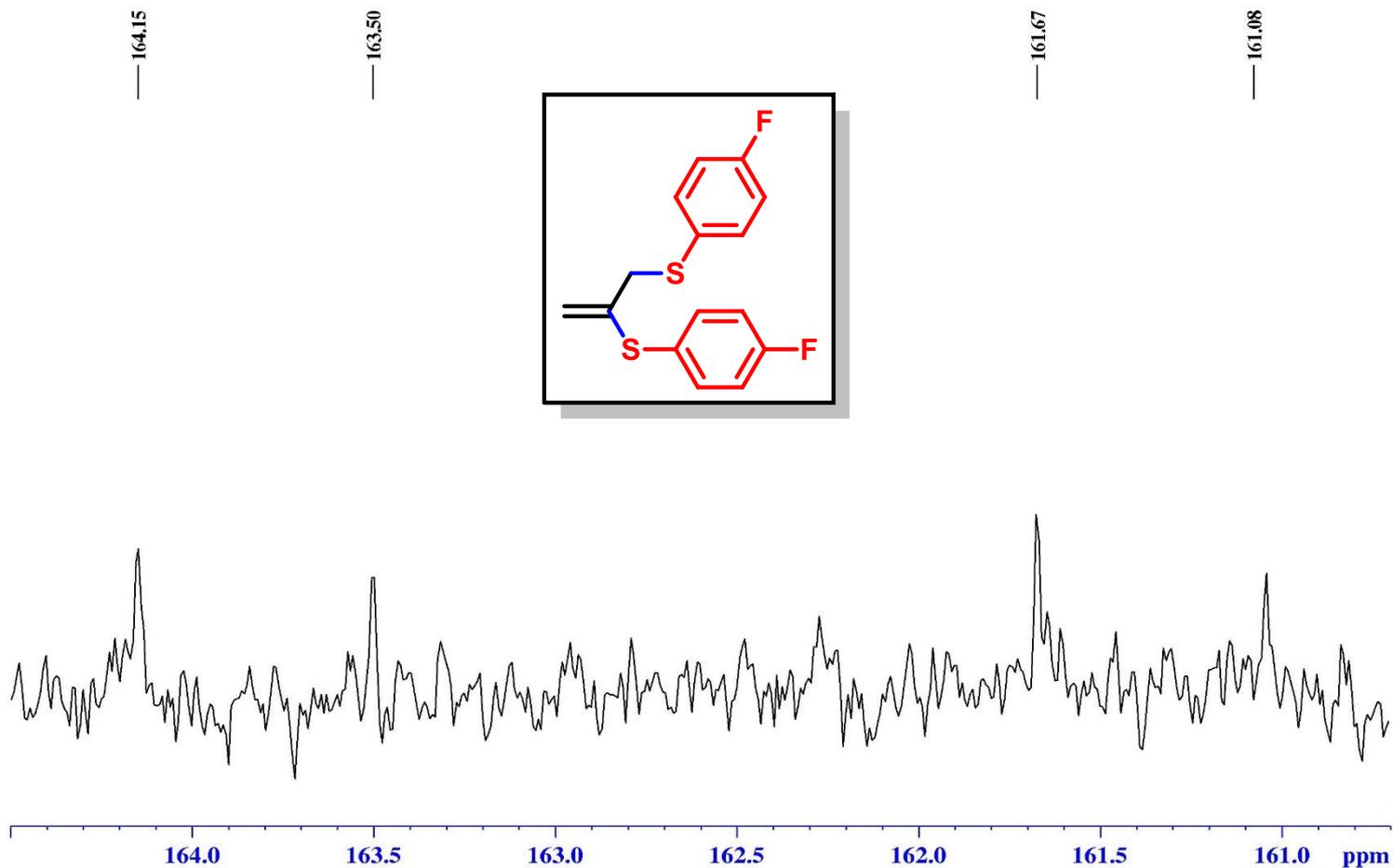
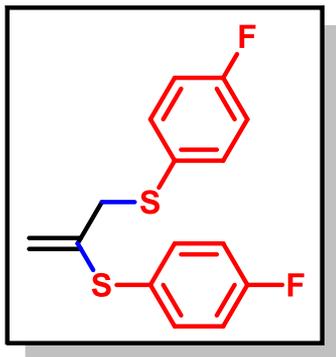


Fig.S29  $^{13}\text{C}$  NMR Spectrum of **3b**

• Hexane and grease



**Fig.S30**  $^{13}\text{C}$  NMR Spectrum of **3b** (magnified region between 164.5-160.7) S30



--112.59  
--114.37

INDR-28  
19F, CDCL3

Current Data Parameters  
NAME 19F  
EXPNO 30  
PROCNO 1

F2 - Acquisition Parameter  
Date\_ 20200814  
Time 14.13  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgfhigqn.2  
TD 131072  
SOLVENT CDCL3  
NS 16  
DS 4  
SWH 89285.711 Hz  
FIDRES 0.681196 Hz  
AQ 0.7340032 se  
RG 201.48  
DW 5.600 us  
DE 6.50 us  
TE 300.1 K  
D1 1.0000000 se  
D11 0.0300000 se  
D12 0.0000200 se  
TD0 1

===== CHANNEL f1 =====  
SFO1 376.4894122 MHz  
NUC1 19F  
P1 15.00 us  
PLW1 21.0000000 W

===== CHANNEL f2 =====  
SFO2 400.1621006 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 us  
PLW2 13.0000000 W  
PLW12 0.27963999 W

F2 - Processing parameters  
SI 65536  
SF 376.5270650 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz

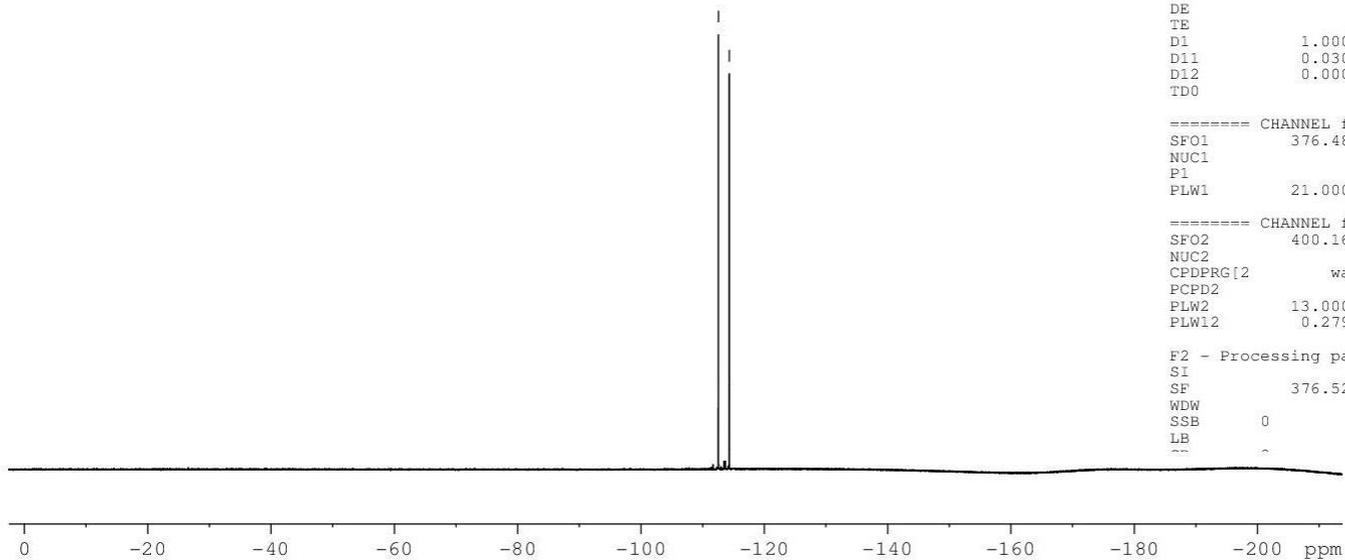
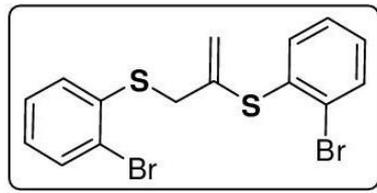


Fig.S31 <sup>19</sup>F NMR Spectrum of 3b

7.6218  
7.6194  
7.6059  
7.6035  
7.5504  
7.5481  
7.5346  
7.5322  
7.4485  
7.4454  
7.4329  
7.4299  
7.3004  
7.2975  
7.2847  
7.2817  
7.2785  
7.2757  
7.2631  
7.2607  
7.2528  
7.2476  
7.2453  
7.2304  
7.2281  
7.2150  
7.2125  
7.1569  
7.1537  
7.1412  
7.1386  
7.1262  
7.1230  
7.0609  
7.0577  
7.0452  
7.0428  
7.0304  
7.0273  
5.5807  
5.1782  
3.7171



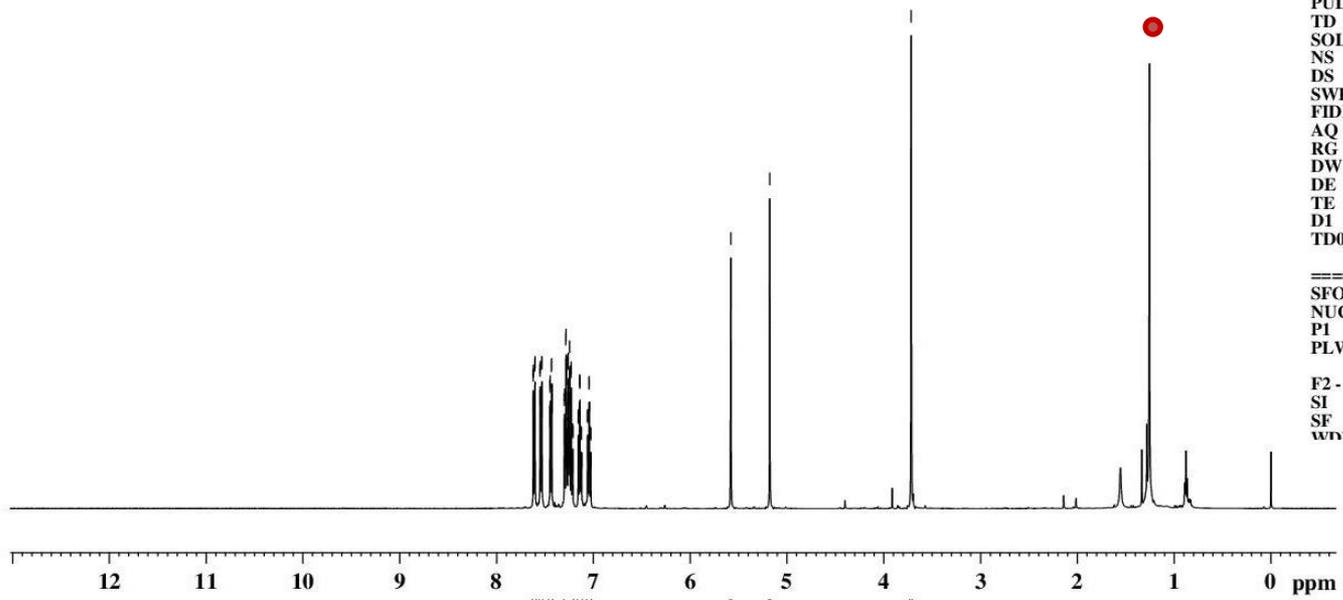
**INDR-32**  
**<sup>1</sup>H, CDCl<sub>3</sub>**

Current Data Parameters  
 NAME 1H  
 EXPNO 30  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20200911  
 Time 7.32  
 INSTRUM spect  
 PROBHD 5 mm PATXI 1H/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 16  
 DS 2  
 SWH 10026.738 Hz  
 FIDRES 0.152996 Hz  
 AQ 3.2680619 sec  
 RG 81.53  
 DW 49.867 usec  
 DE 6.50 usec  
 TE 303.0 K  
 D1 1.0000000 sec  
 TD0 1

==== CHANNEL f1 ====  
 SFO1 500.6794419 MHz  
 NUC1 1H  
 P1 6.45 usec  
 PLW1 13.60000038 W

F2 - Processing parameters  
 SI 65536  
 SF 500.6763651 MHz  
 wnw FM



● grease

**Fig.S32** <sup>1</sup>H NMR Spectrum of **3c**

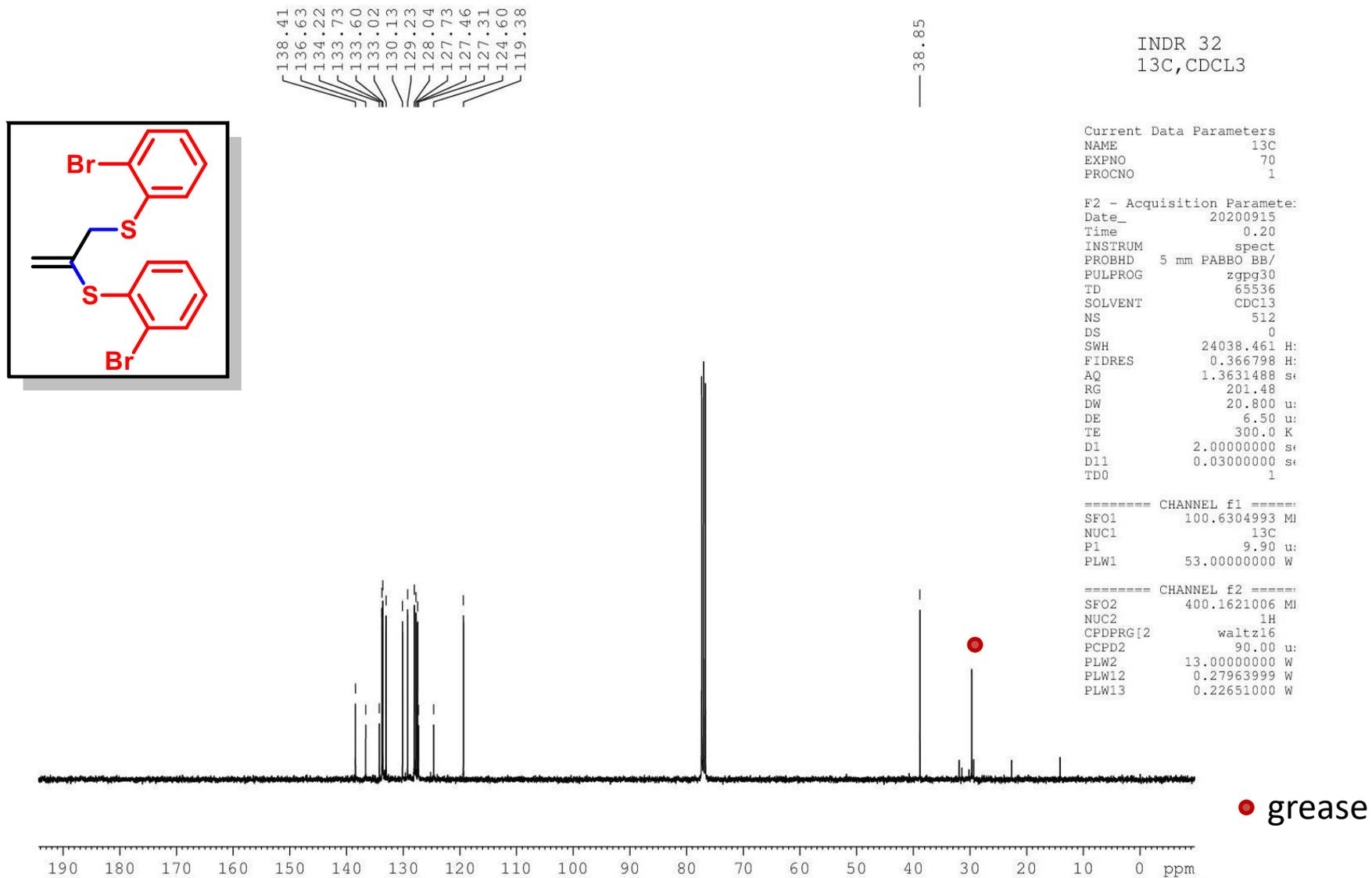
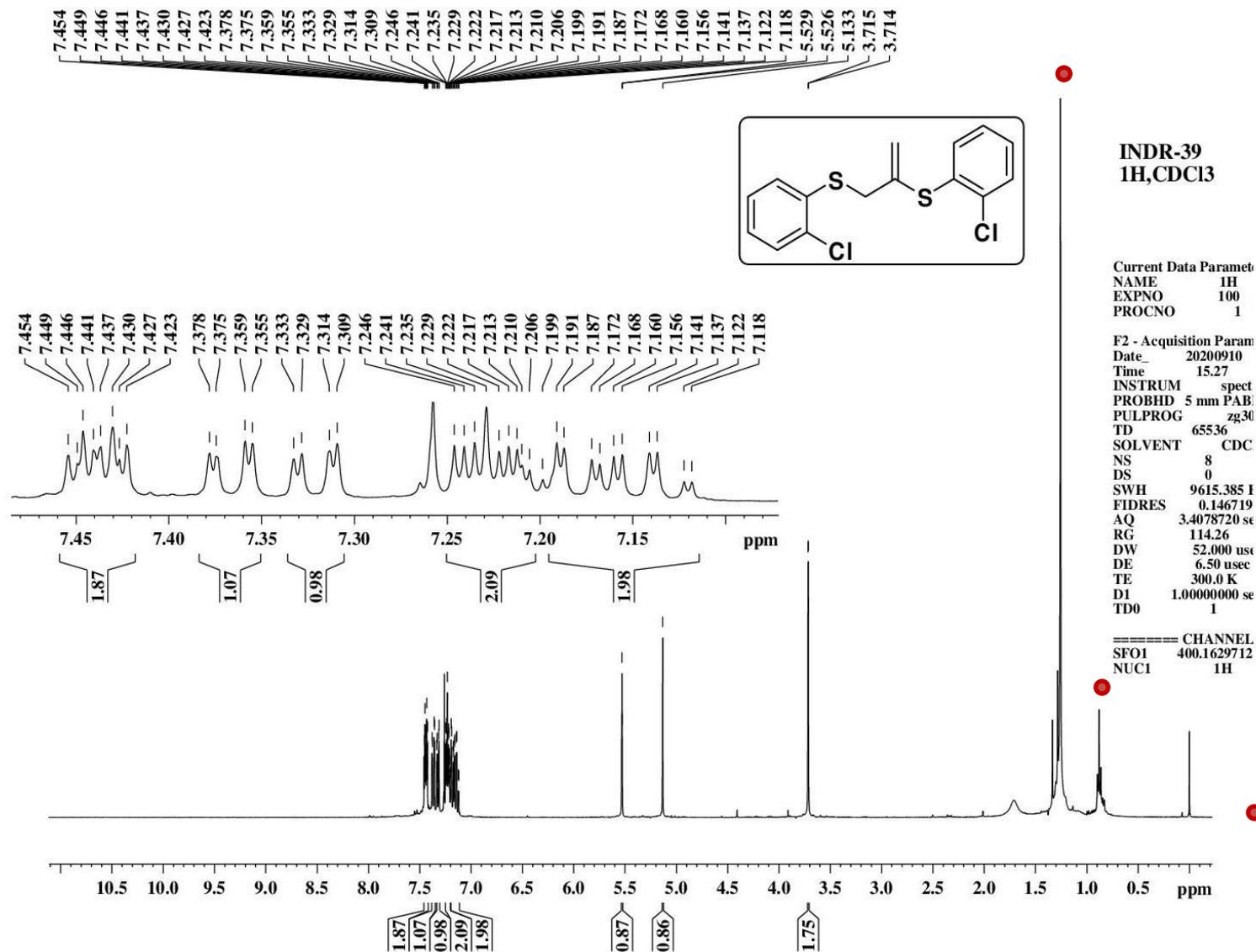
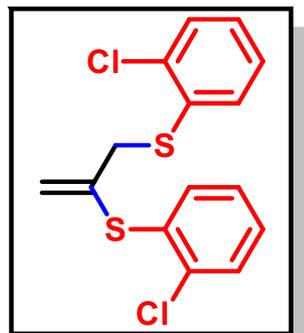


Fig.S33 <sup>13</sup>C NMR Spectrum of 3c



**Fig.S34** <sup>1</sup>H NMR Spectrum of **3d**



138.46  
136.95  
134.63  
134.50  
134.07  
132.02  
130.68  
130.26  
129.71  
129.24  
127.46  
127.37  
127.07  
118.76

38.54

INDR-39  
13C, CDCL3

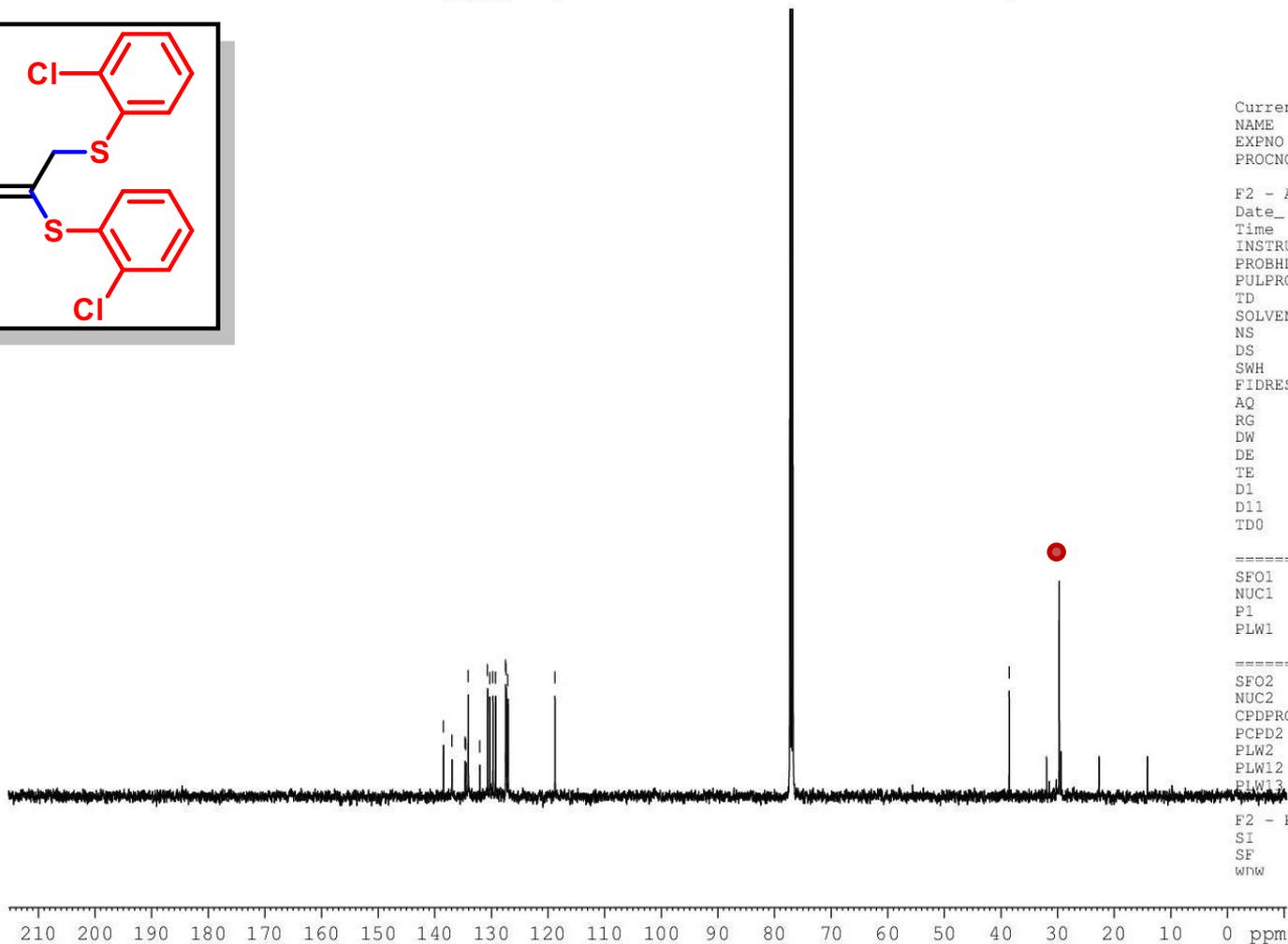
Current Data Parameters  
NAME 13C  
EXPNO 40  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20200911  
Time 8.26  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCL3  
NS 1024  
DS 4  
SWH 29761.904 H  
FIDRES 0.454131 H  
AQ 1.1010048 s  
RG 107.78  
DW 16.800 u  
DE 6.50 u  
TE 303.0 K  
D1 2.00000000 s  
D11 0.03000000 s  
TD0 1

===== CHANNEL f1 =====  
SFO1 125.9077573 M  
NUC1 13C  
P1 9.23 u  
PLW1 244.00000000 W

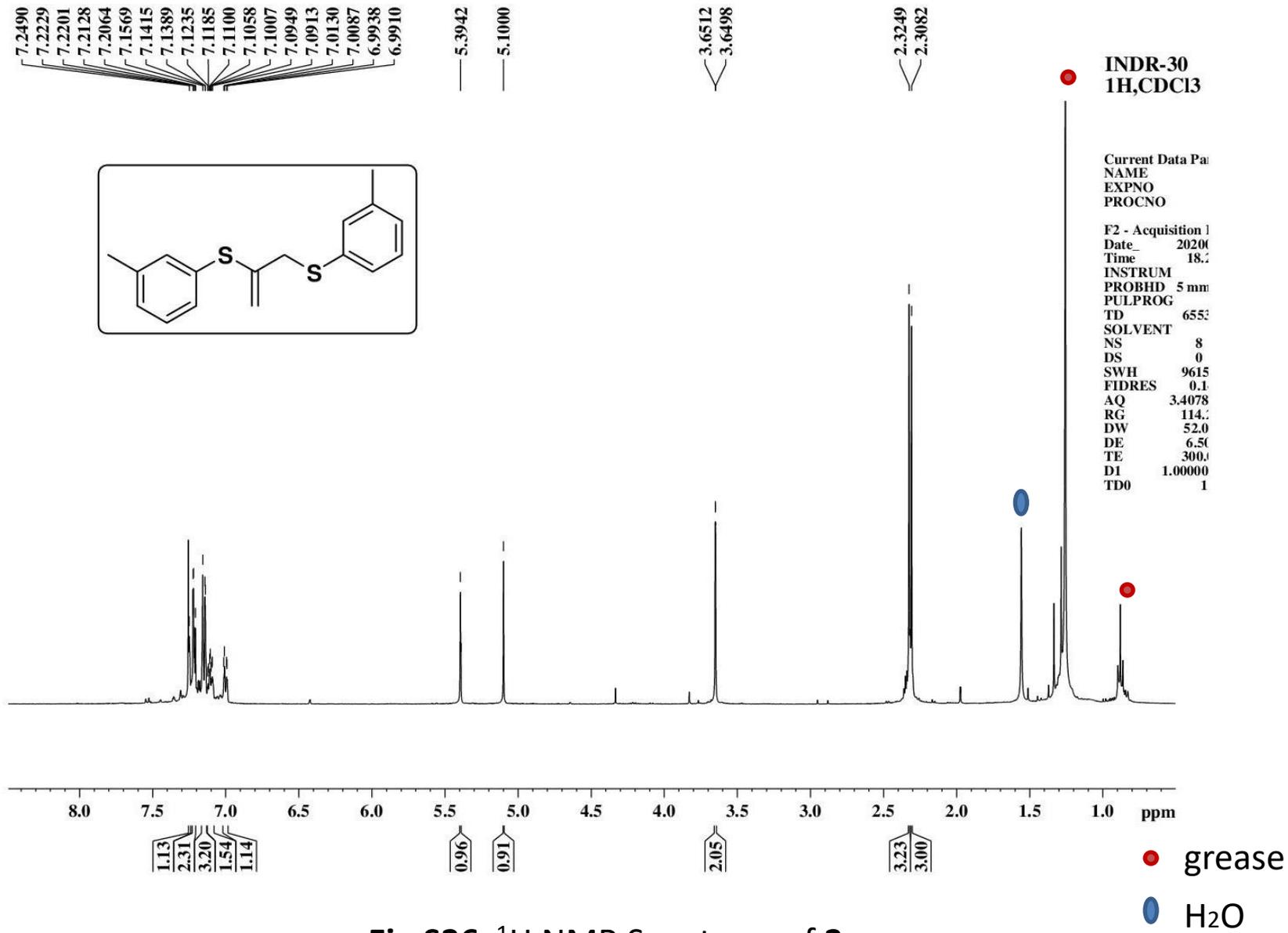
===== CHANNEL f2 =====  
SFO2 500.6783527 M  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 80.00 u  
PLW2 13.60000038 W  
PLW12 0.08840500 W  
PLW13 0.05657900 W

F2 - Processing parameter  
SI 32768  
SF 125.8951680 M  
whw FM

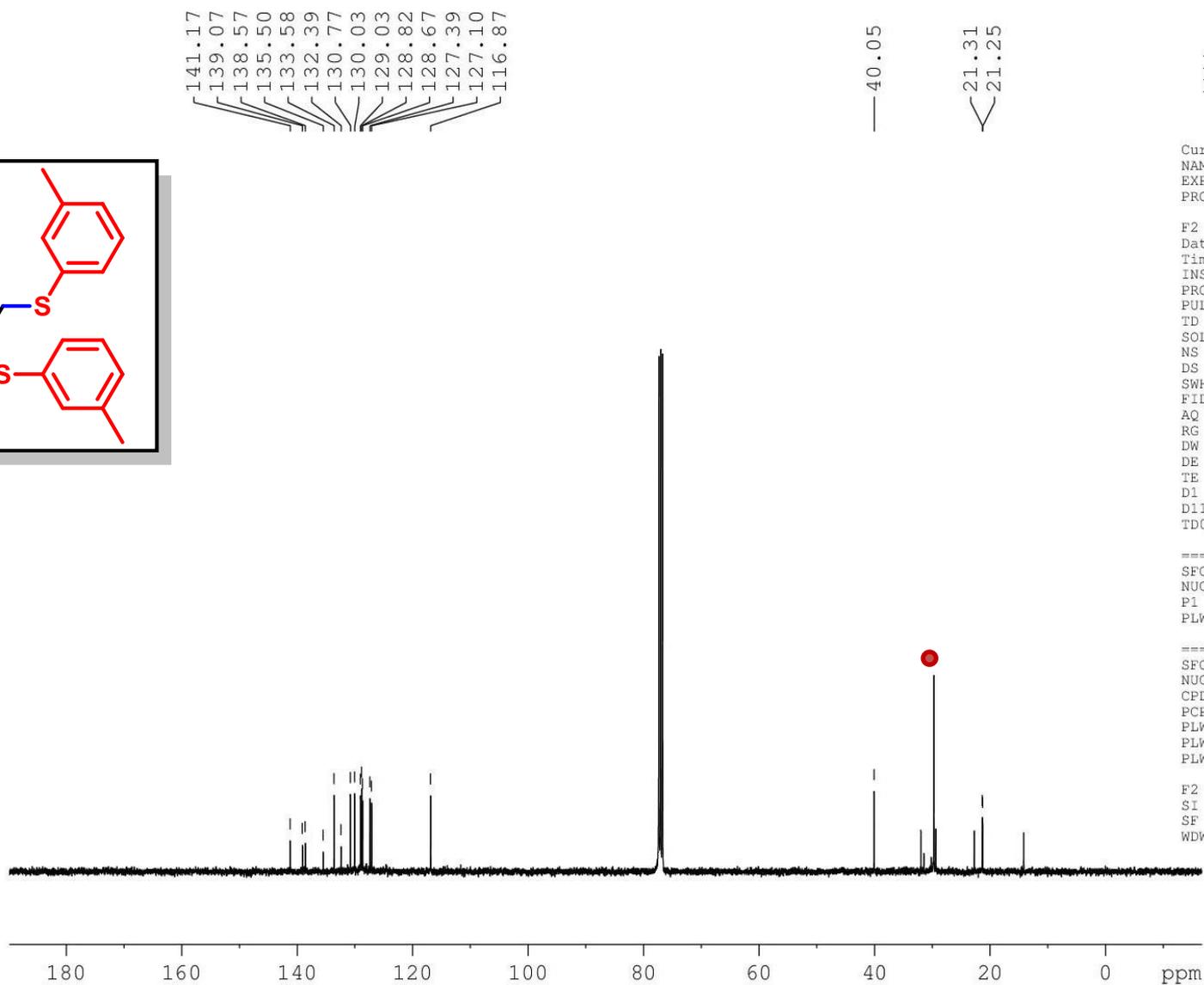
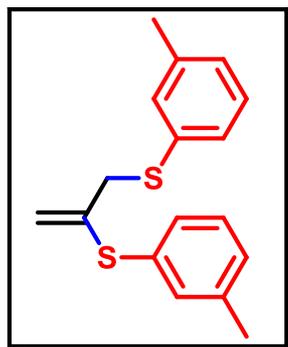


• grease

Fig.S35 <sup>13</sup>C NMR Spectrum of 3d



**Fig.S36** <sup>1</sup>H NMR Spectrum of **3e**



INDR-30  
13C, CDCL3

Current Data Parame  
NAME  
EXPNO  
PROCNO

F2 - Acquisition Pa  
Date\_ 2020  
Time 1  
INSTRUM s  
PROBHD 5 mm PABBO  
PULPROG zg  
TD 6  
SOLVENT C  
NS  
DS  
SWH 24038  
FIDRES 0.36  
AQ 1.363  
RG 20  
DW 20  
DE  
TE 3  
D1 2.0000  
D11 0.0300  
TD0

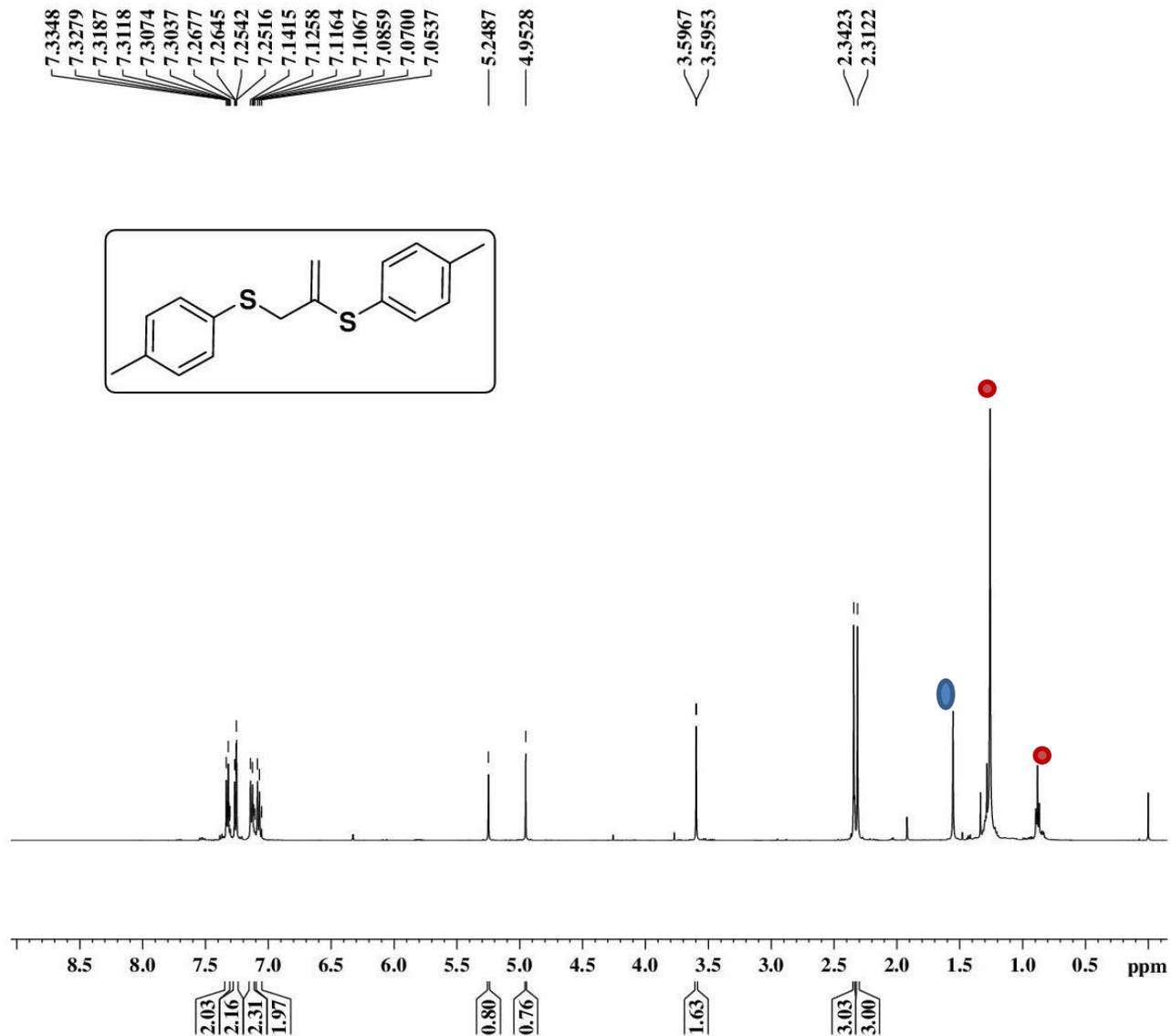
==== CHANNEL f1  
SFO1 100.630  
NUC1  
P1  
PLW1 53.0000

==== CHANNEL f2  
SFO2 400.162  
NUC2  
CPDPRG[2] wal  
PCPD2 9  
PLW2 13.0000  
PLW12 0.2796  
PLW13 0.2265

F2 - Processing par  
SI 3  
SF 100.620  
WDW

● grease

Fig.S37 <sup>13</sup>C NMR Spectrum of 3e



**INDR-33**  
**1H,CDC13**

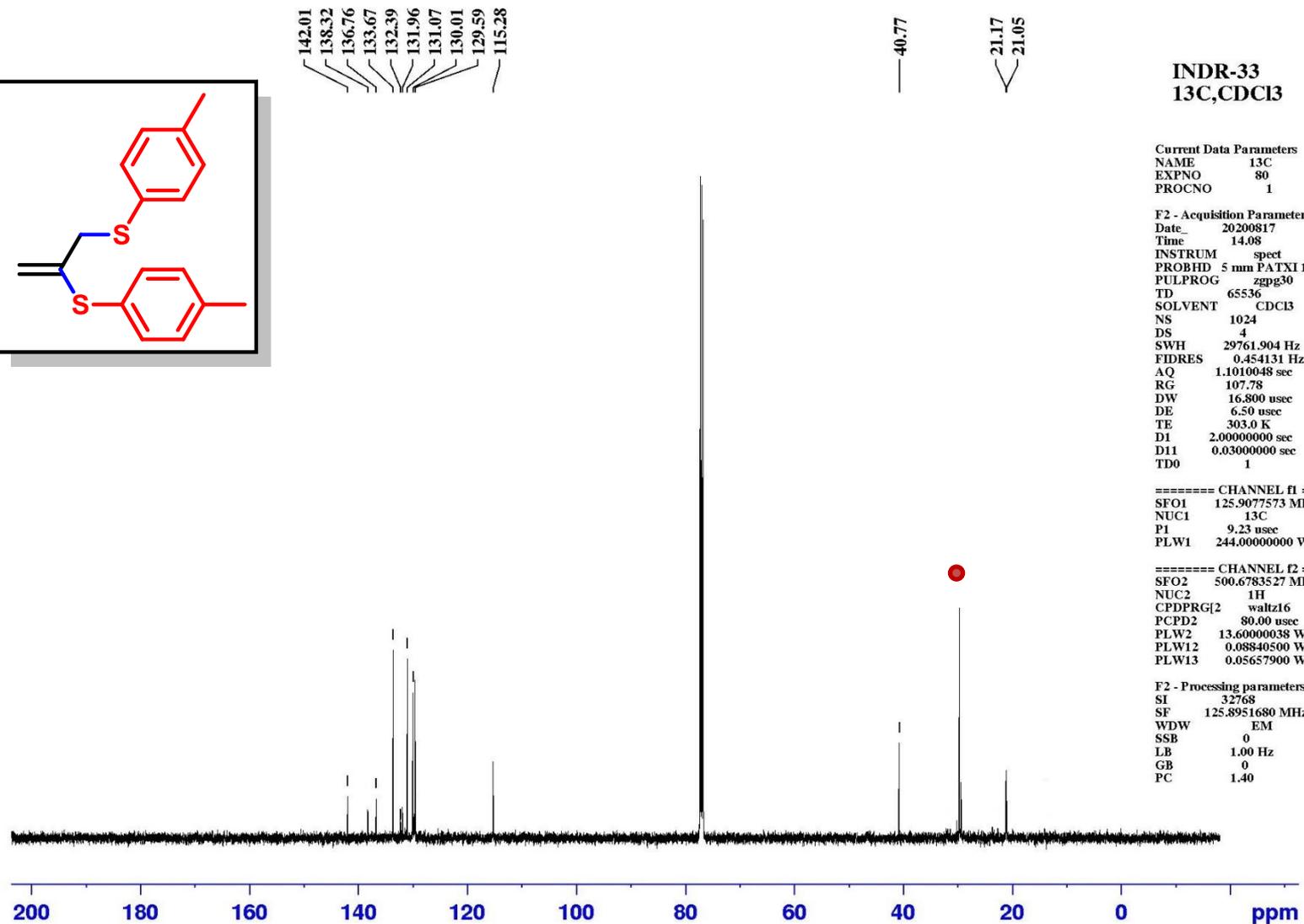
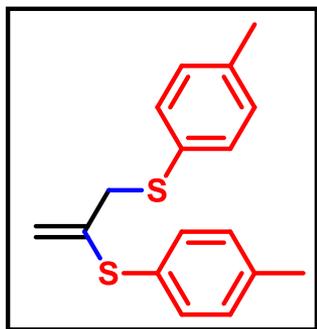
Current Data Parameters  
NAME 1H  
EXPNO 70  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20200817  
Time 13.12  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10026.738 Hz  
FIDRES 0.152996 Hz  
AQ 3.2680619 sec  
RG 107.78  
DW 49.867 usec  
DE 6.50 usec  
TE 303.0 K  
D1 1.00000000 sec  
TD0 1

==== CHANNEL f1 ====  
SFO1 500.6794419 MHz  
NUC1 1H  
P1 6.45 usec  
PLW1 13.60000038 W

F2 - Processing parameters  
SI 65536  
SF 500.6763647 MHz  
WDW EM

**Fig.S38** <sup>1</sup>H NMR Spectrum of **3f**



INDR-33  
13C, CDCl3

Current Data Parameters  
NAME 13C  
EXPNO 80  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20200817  
Time 14.08  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 1024  
DS 4  
SWH 29761.904 Hz  
FIDRES 0.454131 Hz  
AQ 1.1010048 sec  
RG 107.78  
DW 16.800 usec  
DE 6.50 usec  
TE 303.0 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

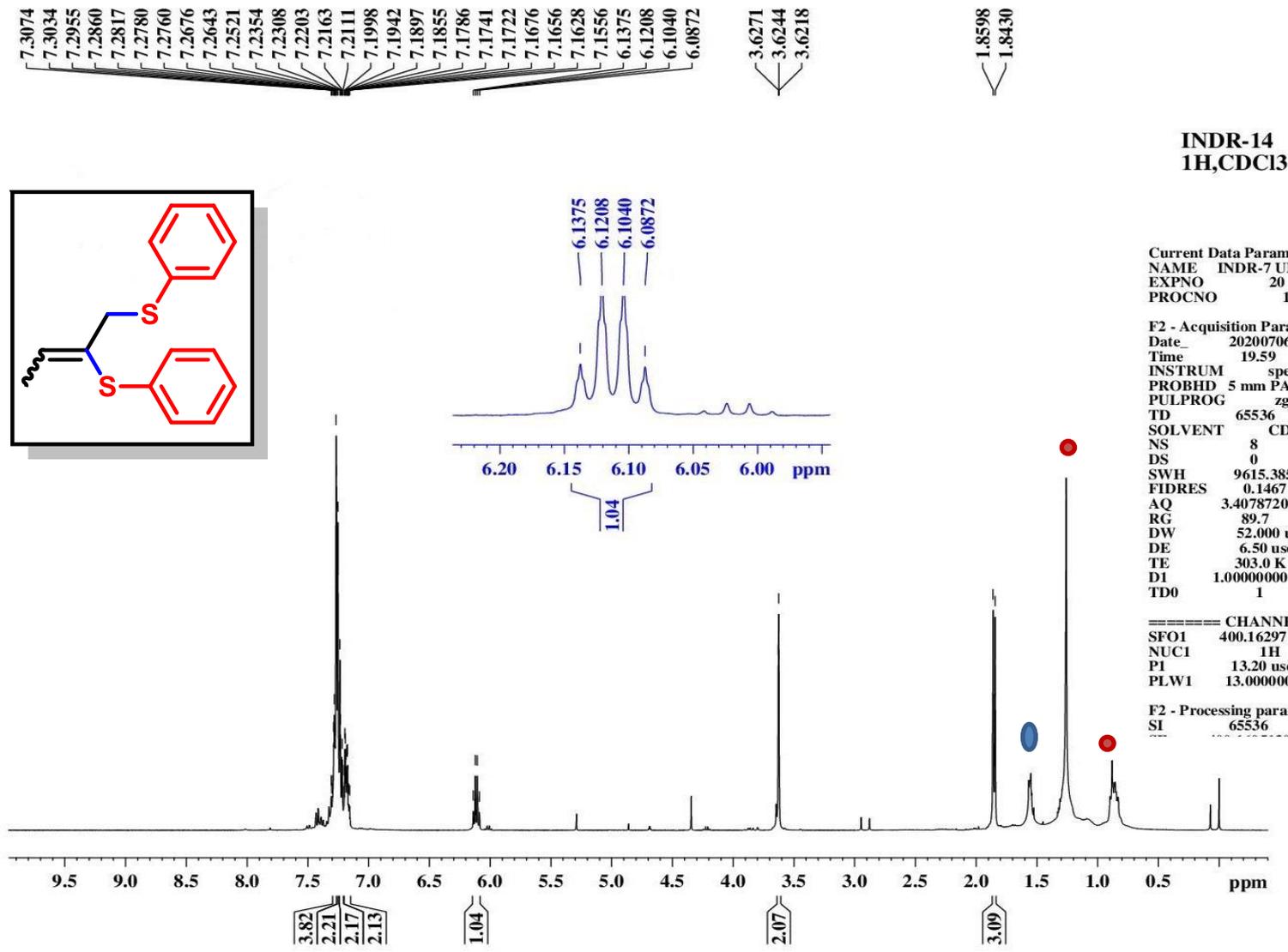
===== CHANNEL f1 =====  
SFO1 125.9077573 MHz  
NUC1 13C  
P1 9.23 usec  
PLW1 244.00000000 W

===== CHANNEL f2 =====  
SFO2 500.6783527 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 80.00 usec  
PLW2 13.60000038 W  
PLW12 0.08840500 W  
PLW13 0.05657900 W

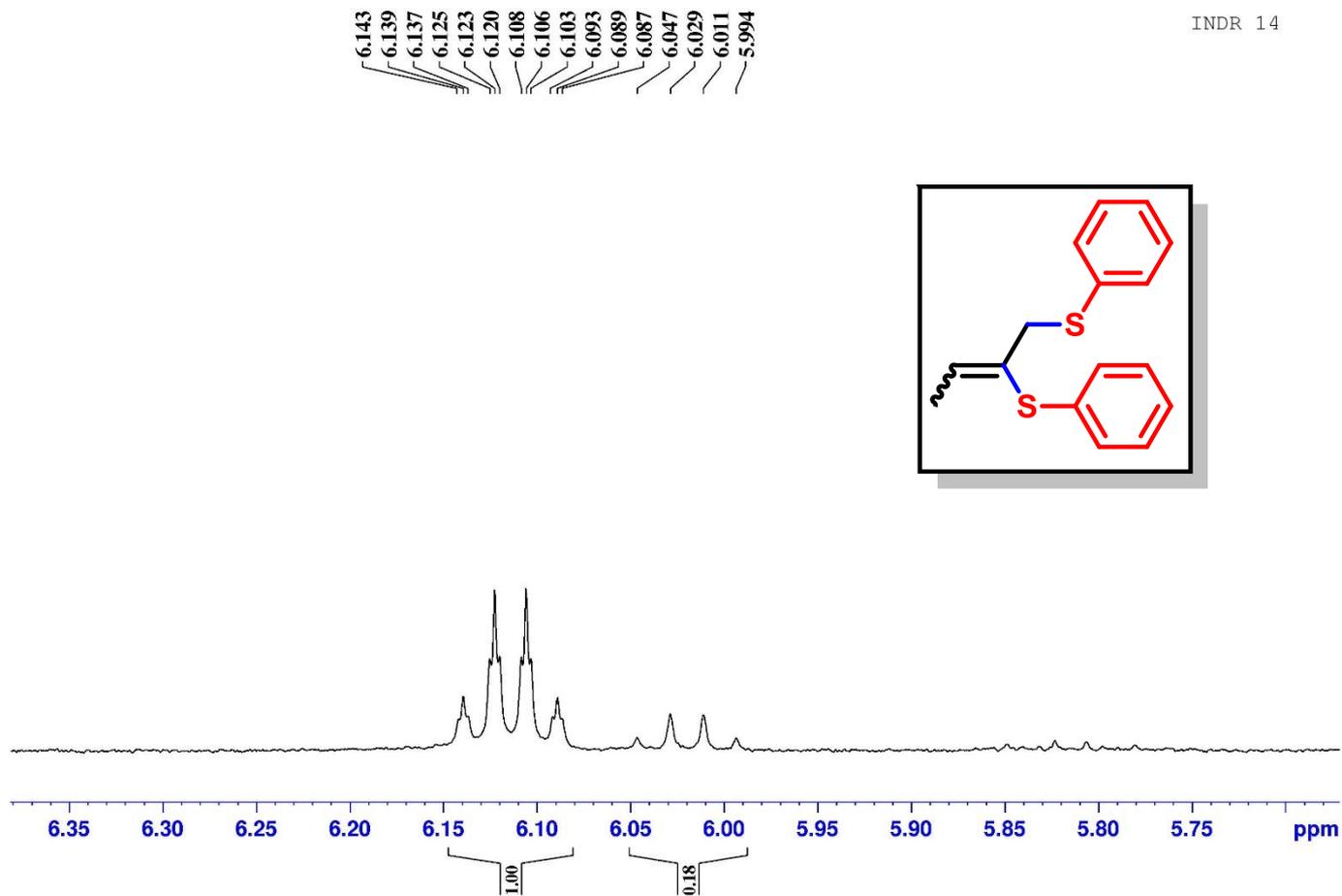
F2 - Processing parameters  
SI 32768  
SF 125.8951680 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

● grease

Fig.S39 <sup>13</sup>C NMR Spectrum of 3f



**Fig.S40** <sup>1</sup>H NMR Spectrum of **3g**



**Fig.S41** <sup>1</sup>H NMR Spectrum of isomeric mixture of **3g** ( magnified region between 6.35-5.75)

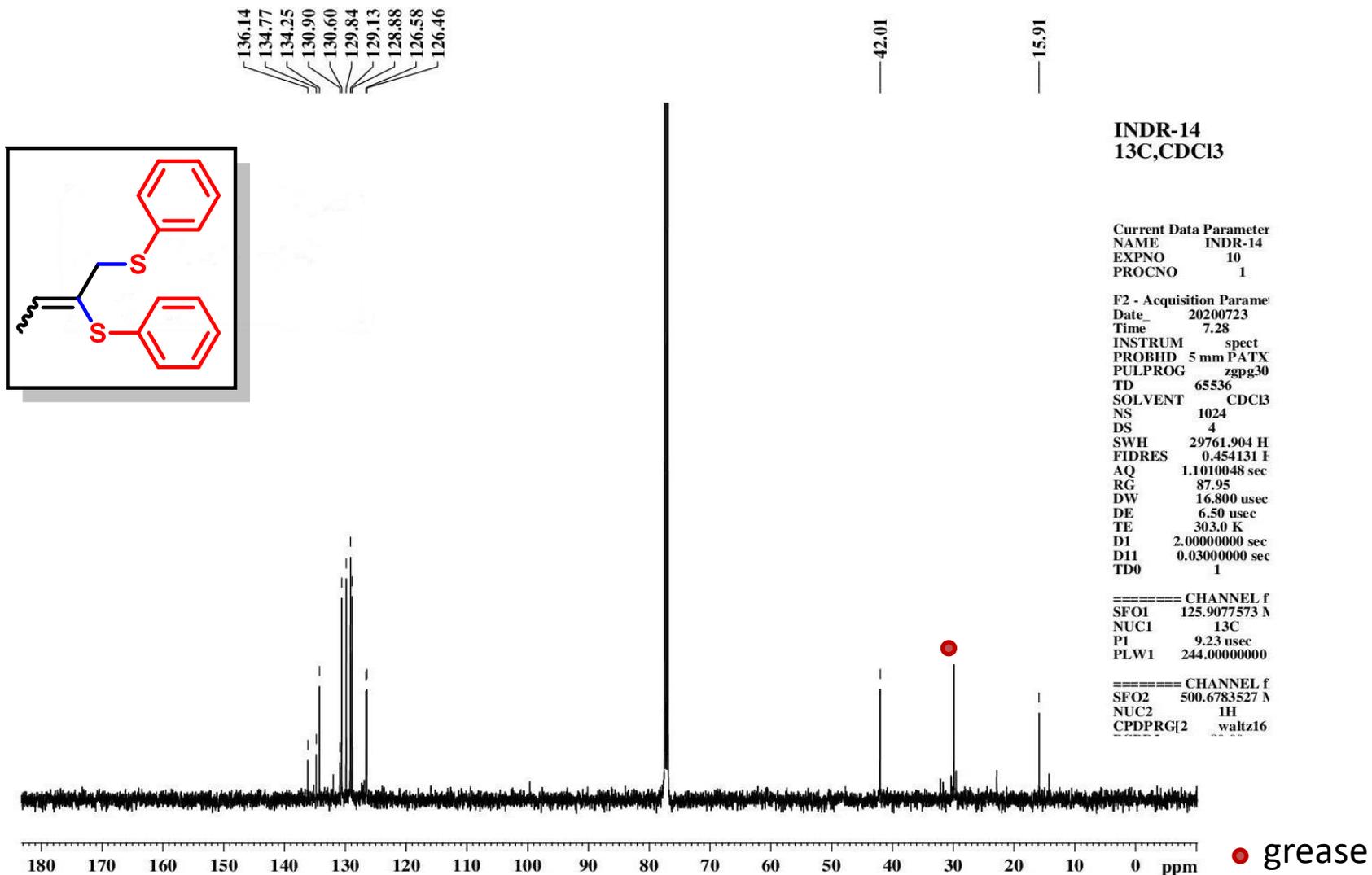
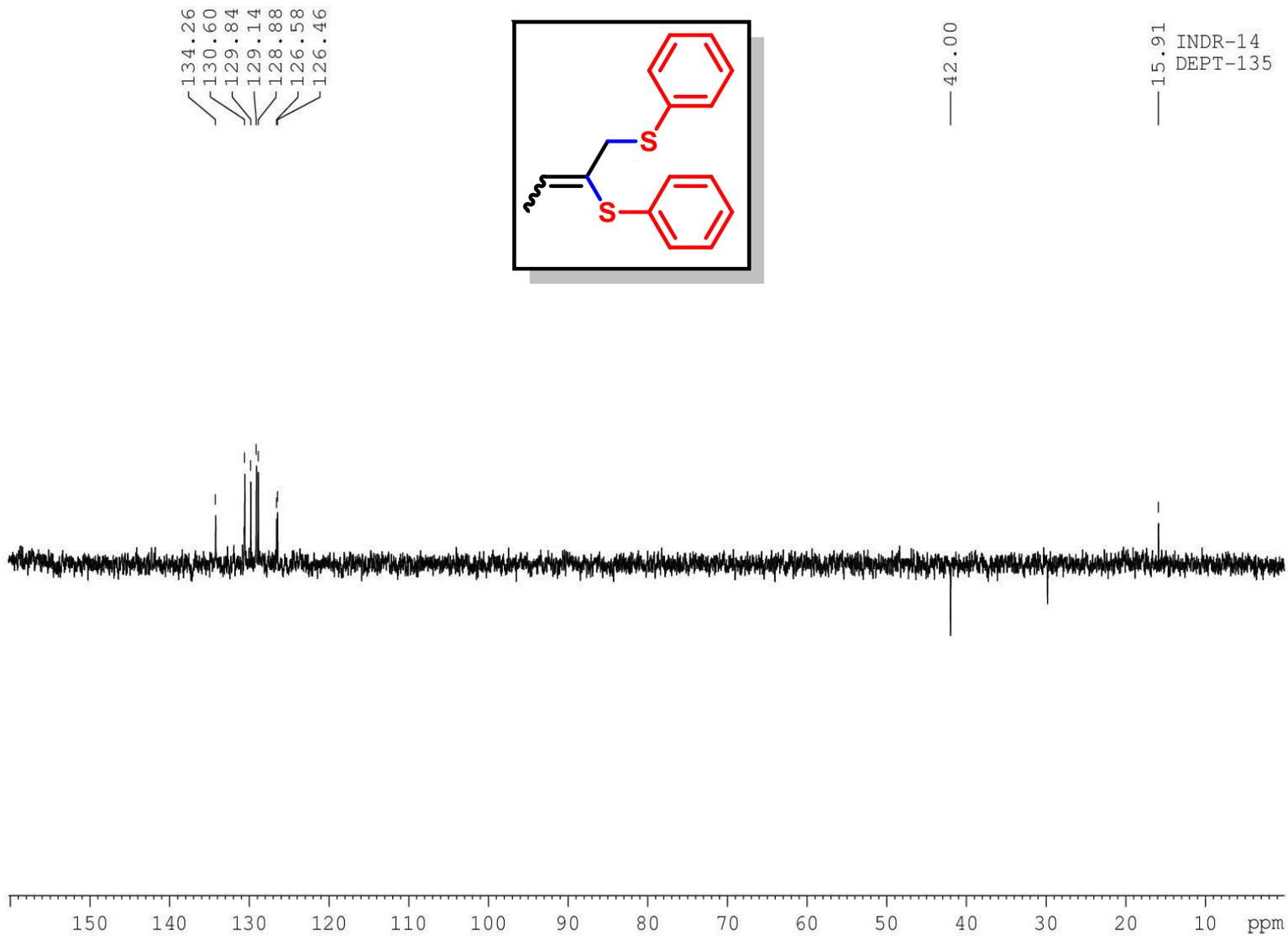


Fig.S42 <sup>13</sup>C NMR Spectrum of **3g**



**Fig.S43** DEPT-135 Spectrum of **3g**

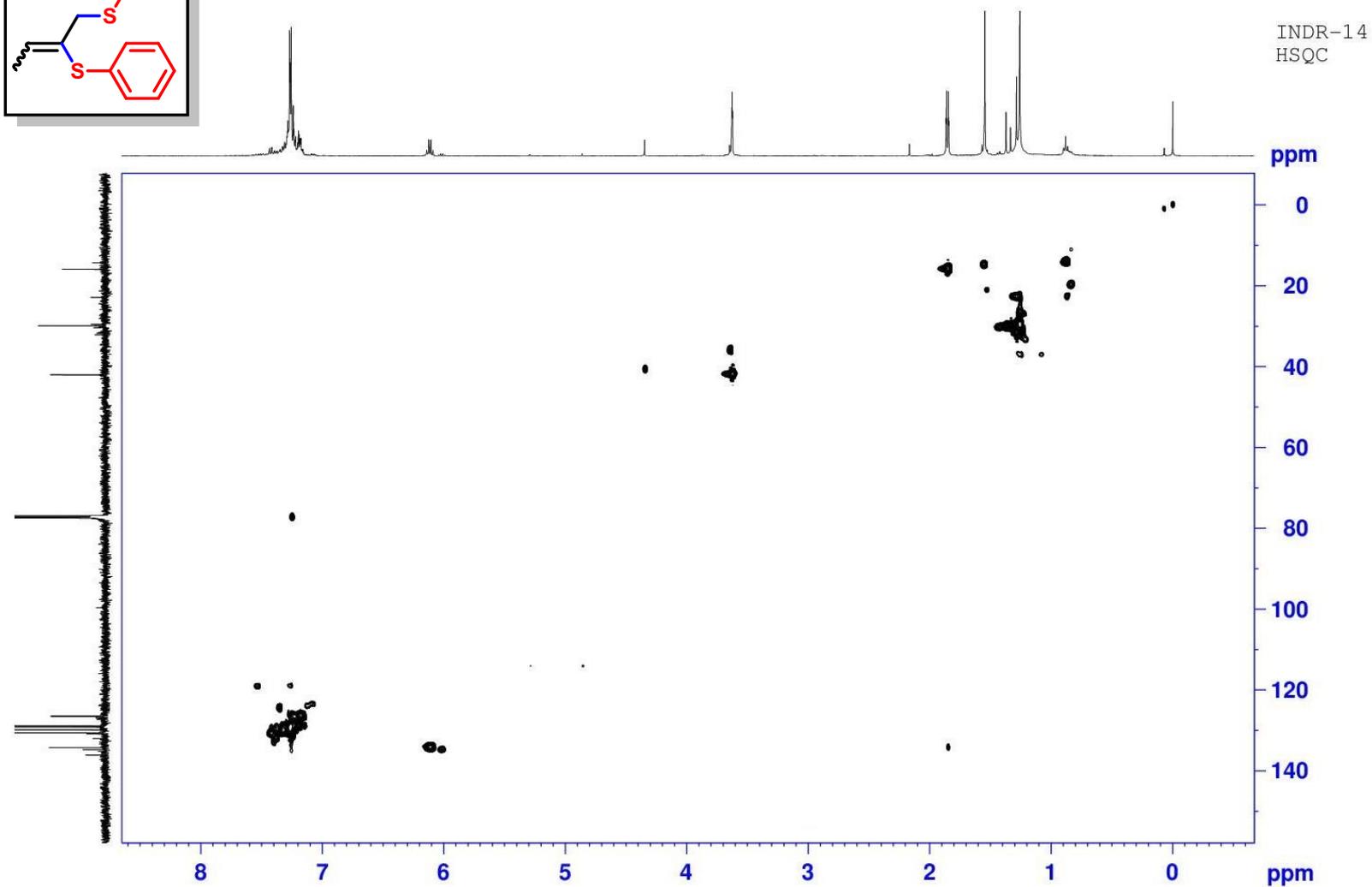
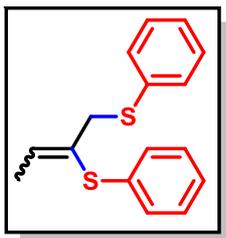
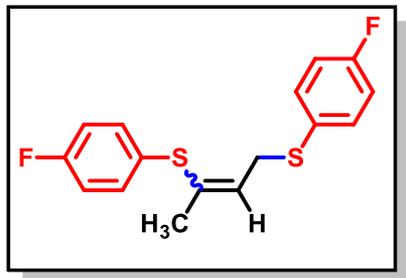
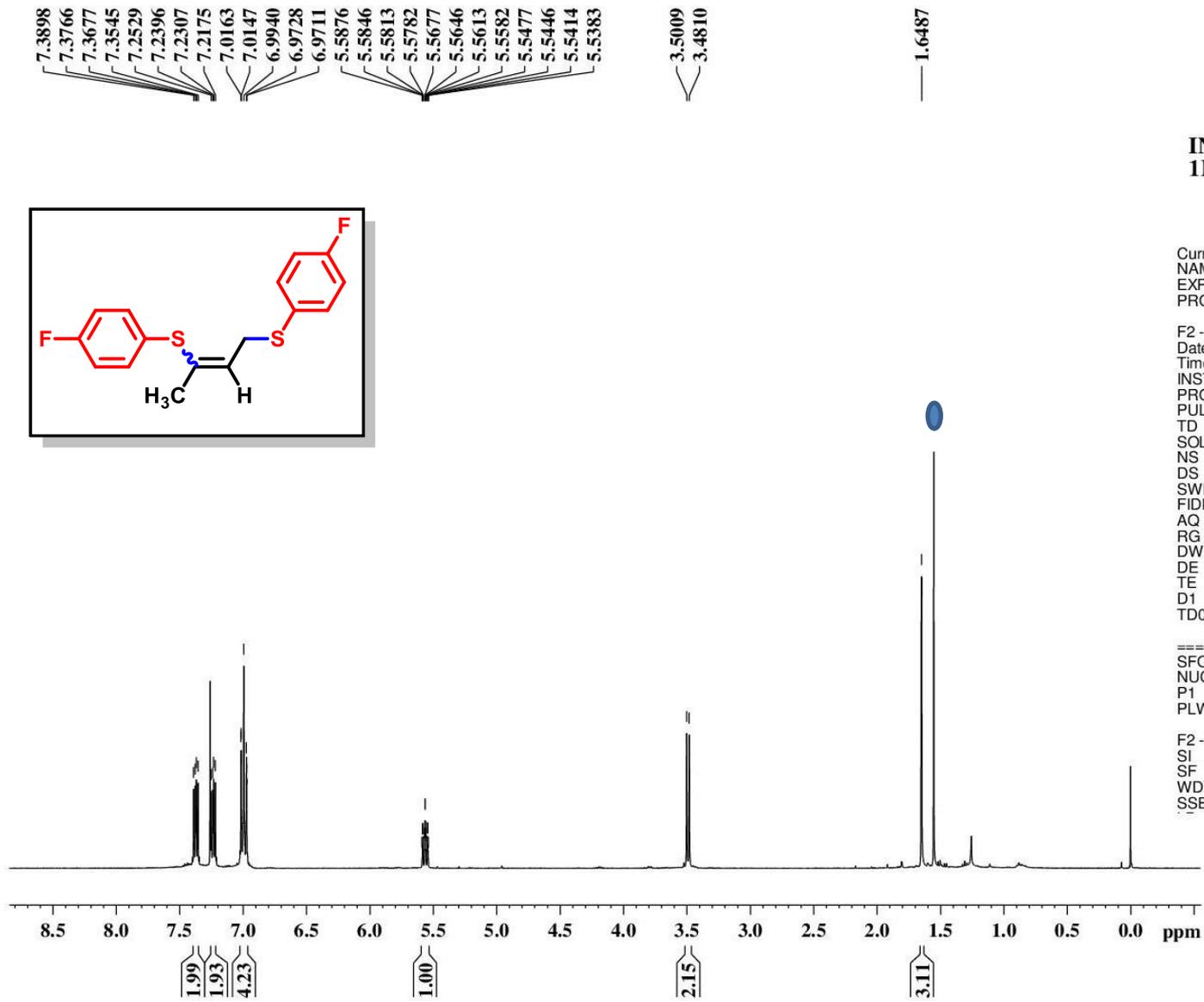


Fig.S44 HSQC Spectrum of **3g**



**INDR-67  
1H, CDCl3**

Current Data Parameters  
 NAME 1H  
 EXPNO 90  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20210304  
 Time 11.34  
 INSTRUM spect  
 PROBHD 5 mm PABBO I  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 145.29  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

==== CHANNEL f1 =  
 SFO1 400.1629712 M  
 NUC1 1H  
 P1 13.20 usec  
 PLW1 13.00000000 W

F2 - Processing parameter  
 SI 65536  
 SF 400.1605098 MH  
 WDW EM  
 SSB 0

H2O

**Fig.S45** <sup>1</sup>H NMR Spectrum of **8a**

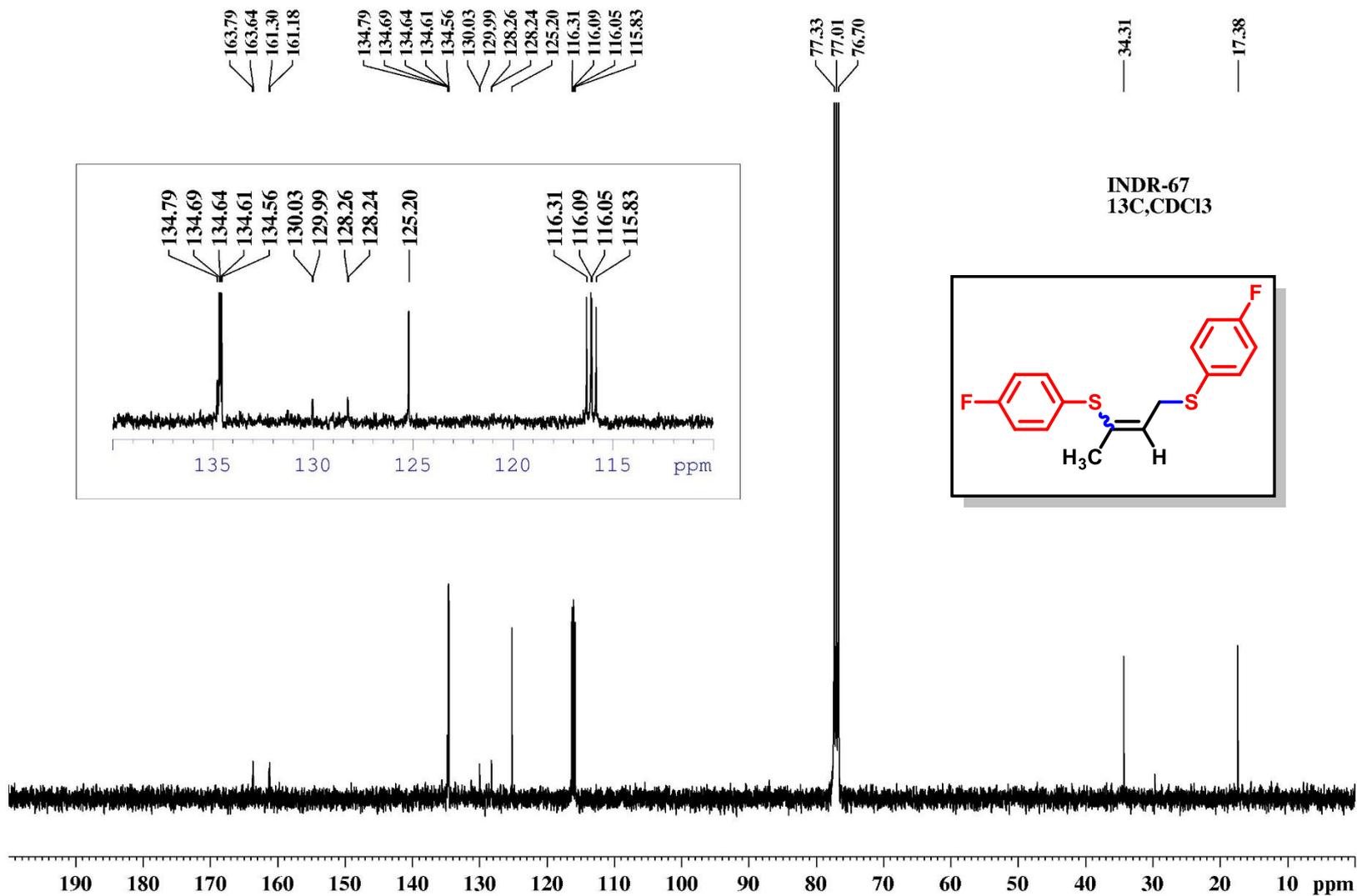
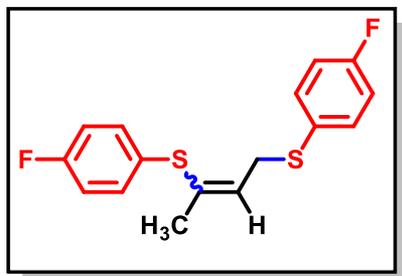


Fig.S46 <sup>13</sup>C NMR Spectrum of 8a



-113.6790  
-114.1932

INDR-67  
19F,CDCI3

Current Data Parameters  
NAME 19F  
EXPNO 100  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210310  
Time 17.04  
INSTRUM spect  
PROBHD 5 mm PABBC  
PULPROG zgfhgqn.2  
TD 131072  
SOLVENT CDCI3  
NS 16  
DS 4  
SWH 89285.711 H  
FIDRES 0.681196 H  
AQ 0.7340032 sec  
RG 201.48  
DW 5.600 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.0000000 sec  
D11 0.03000000 se  
D12 0.00002000 se  
TDO 1

===== CHANNEL f1  
SFO1 376.4894122 M  
NUC1 19F  
P1 15.00 usec  
PLW1 21.00000000'

===== CHANNEL f2  
SFO2 400.1621006 M  
NUC2 1H  
CPDPRG2 waltz16  
PCPD2 90.00 usec  
PLW2 13.00000000'  
PLW12 0.27963999'

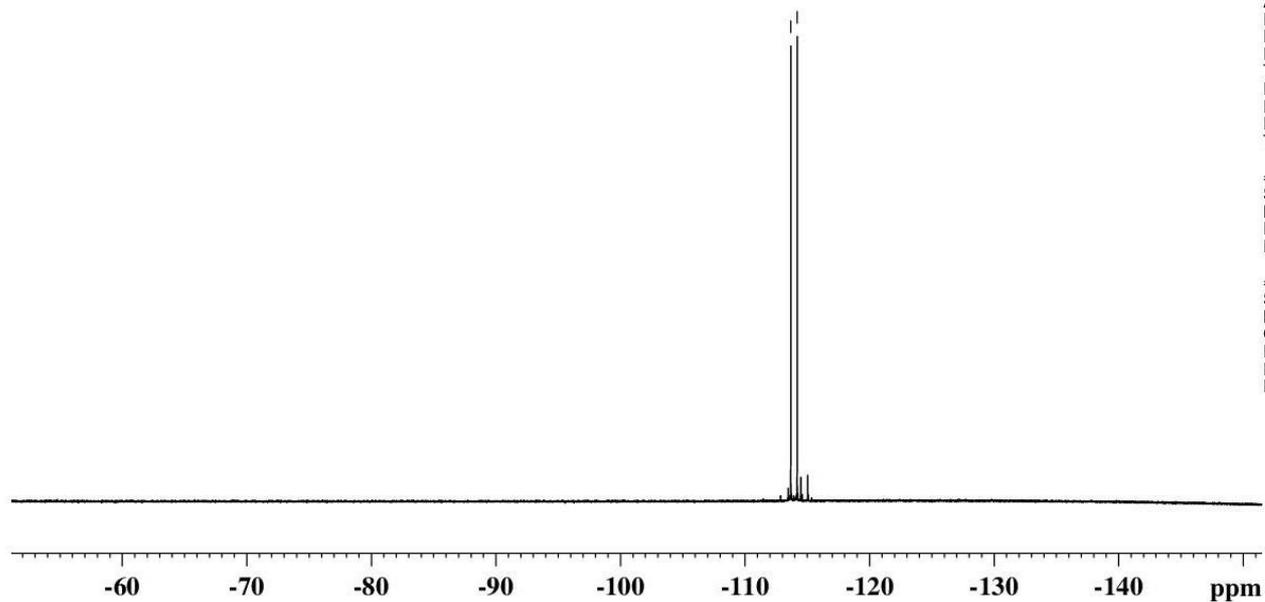
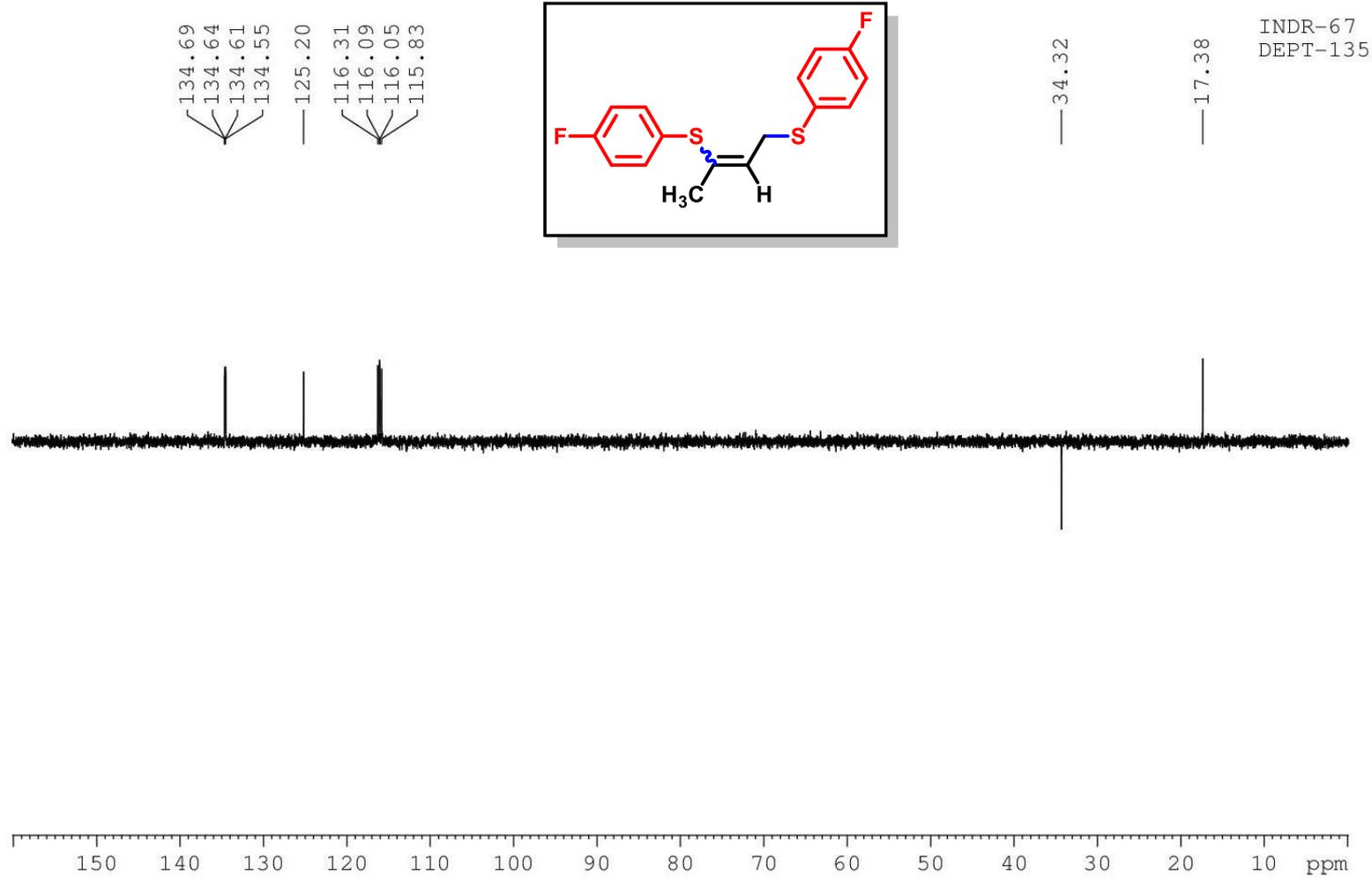
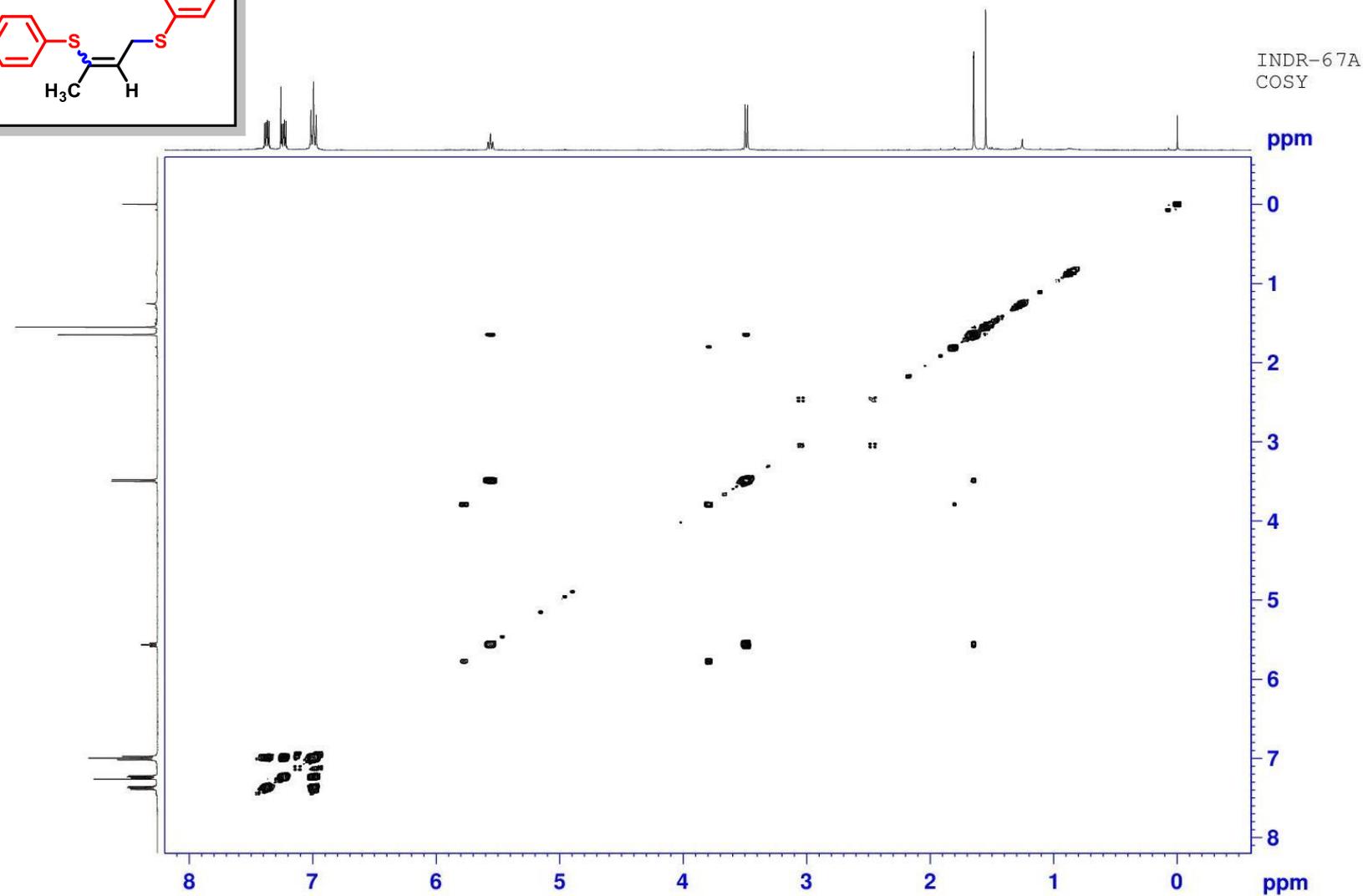
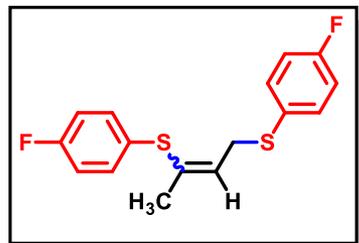


Fig.S47 <sup>19</sup>F NMR Spectrum of 8a



**Fig.S48** DEPT-135 Spectrum of **8a**



**Fig.S49** COSY Spectrum of **8a**

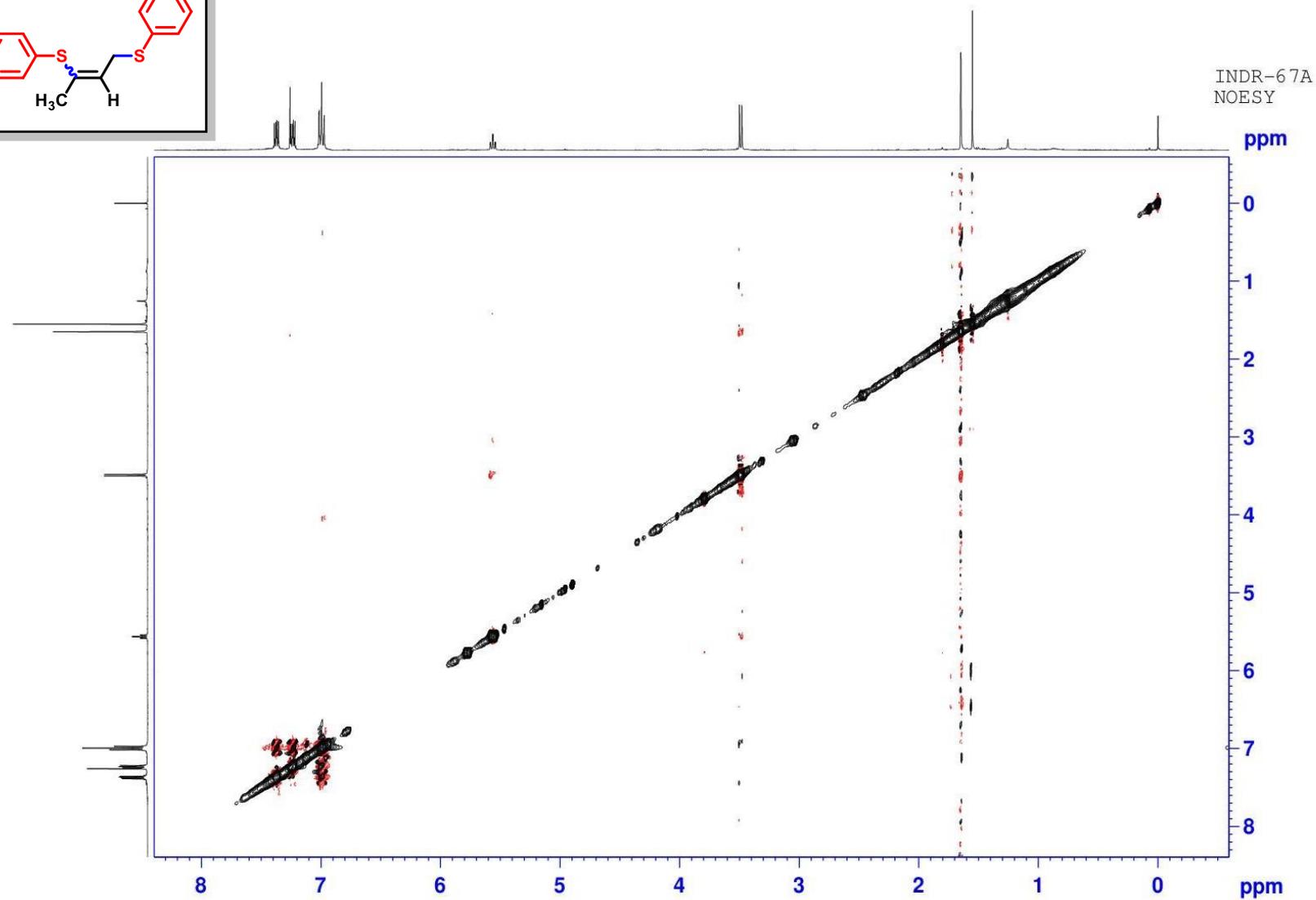
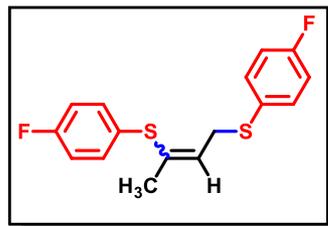
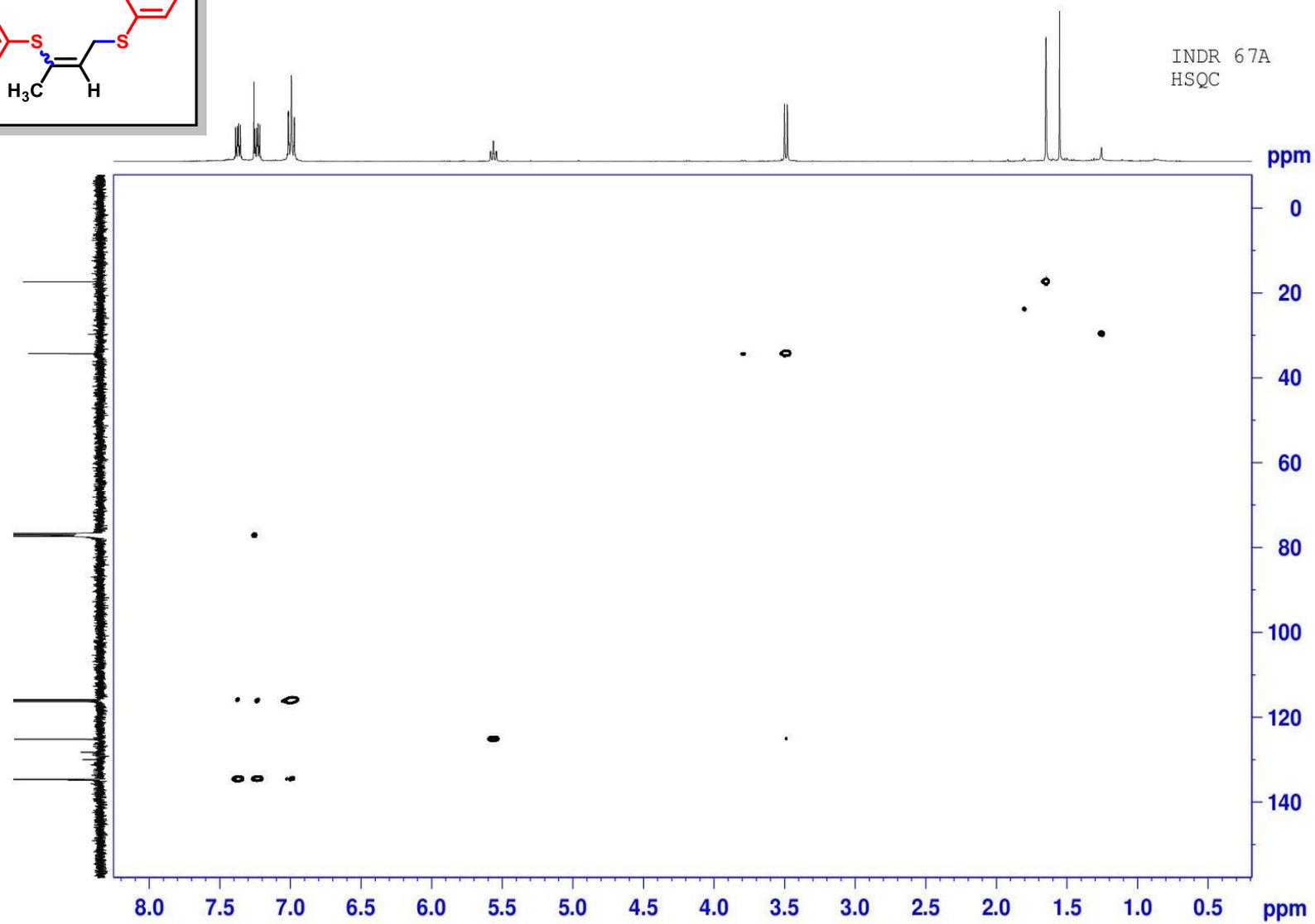
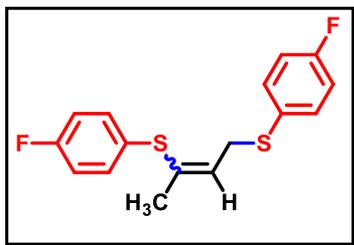


Fig.S50 NOESY Spectrum of 8a



**Fig.S51** HSQC Spectrum of **8a**

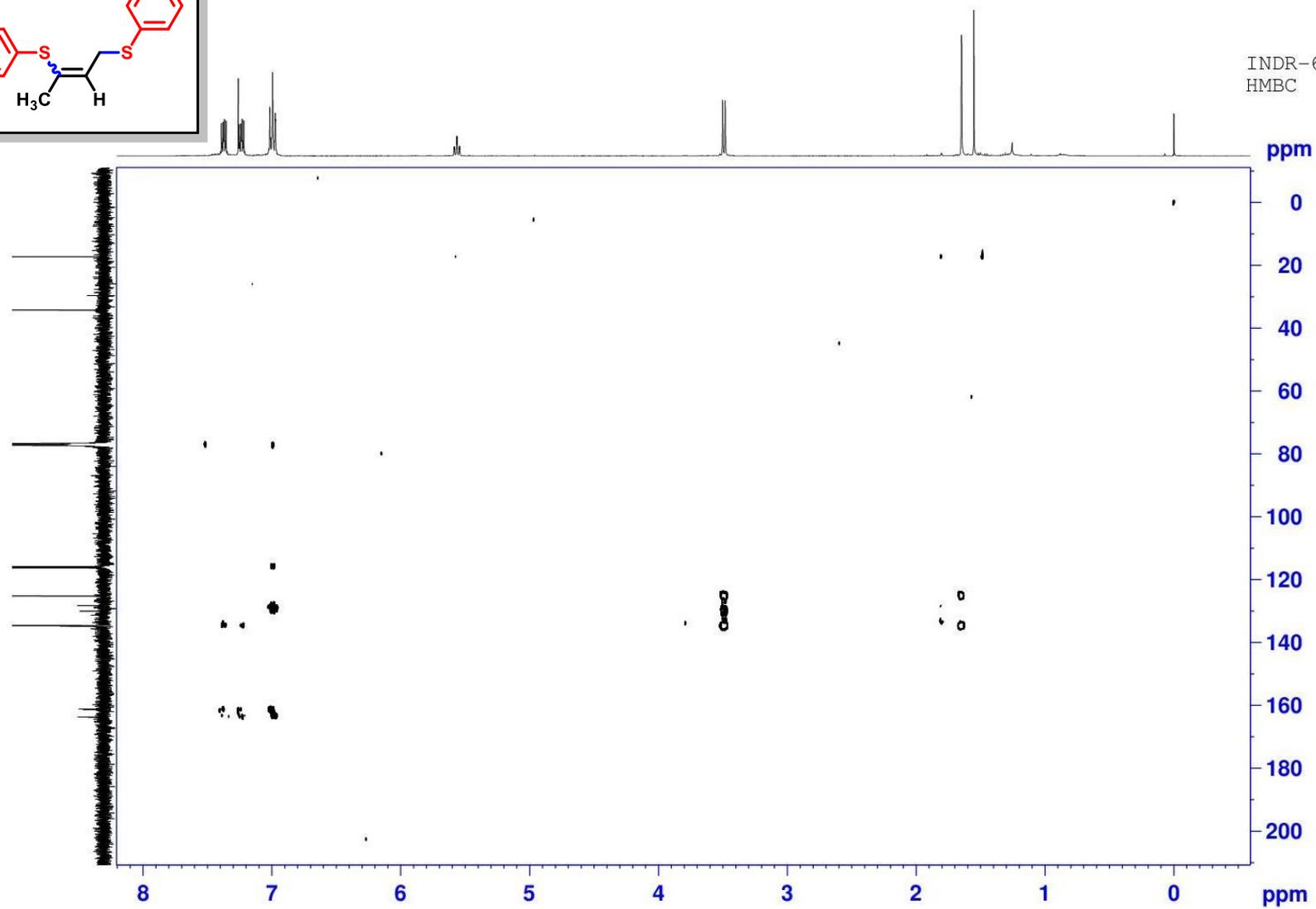
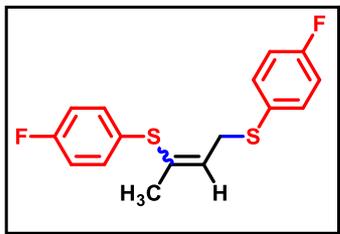
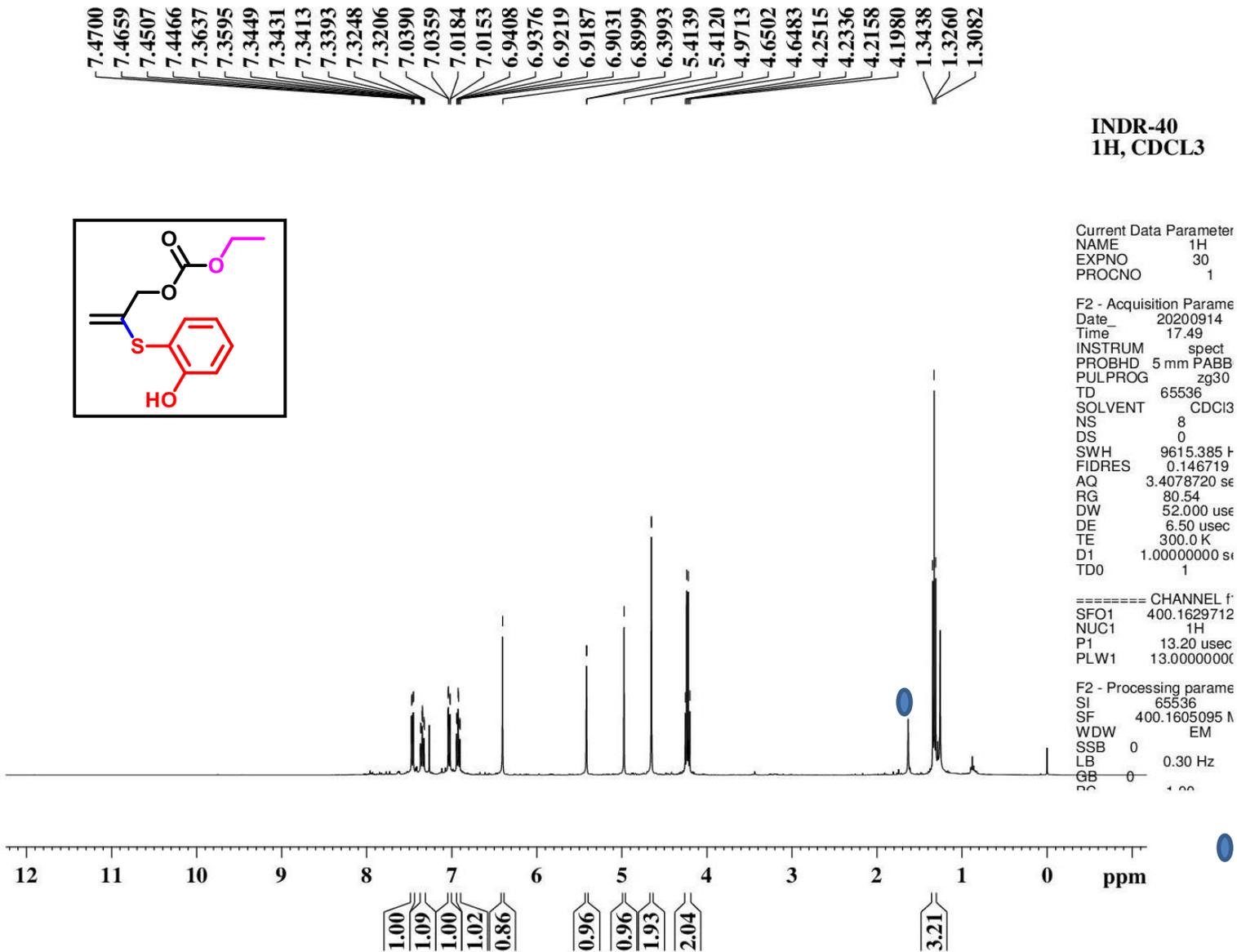


Fig.S52 HMBC Spectrum of 8a



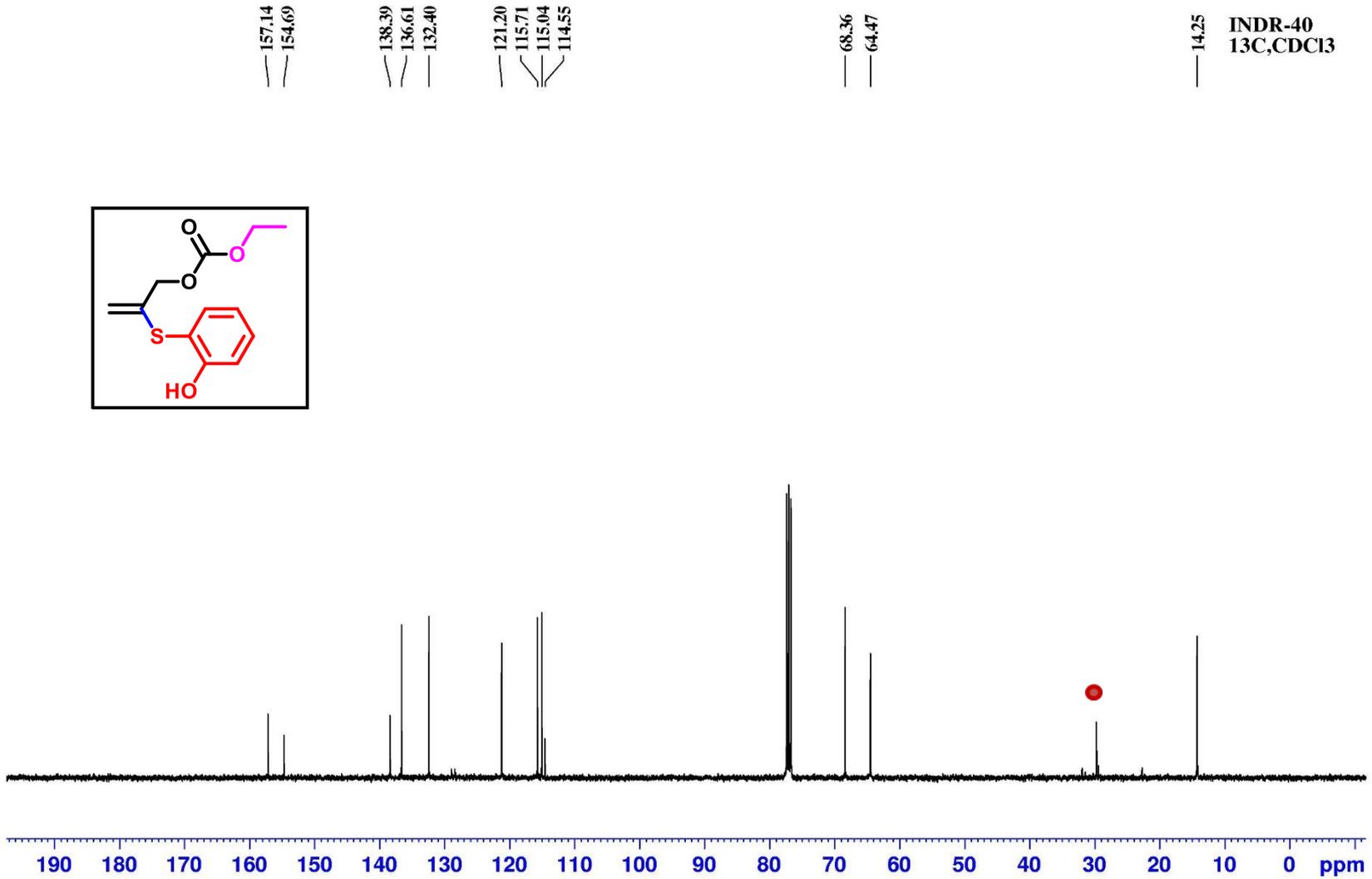
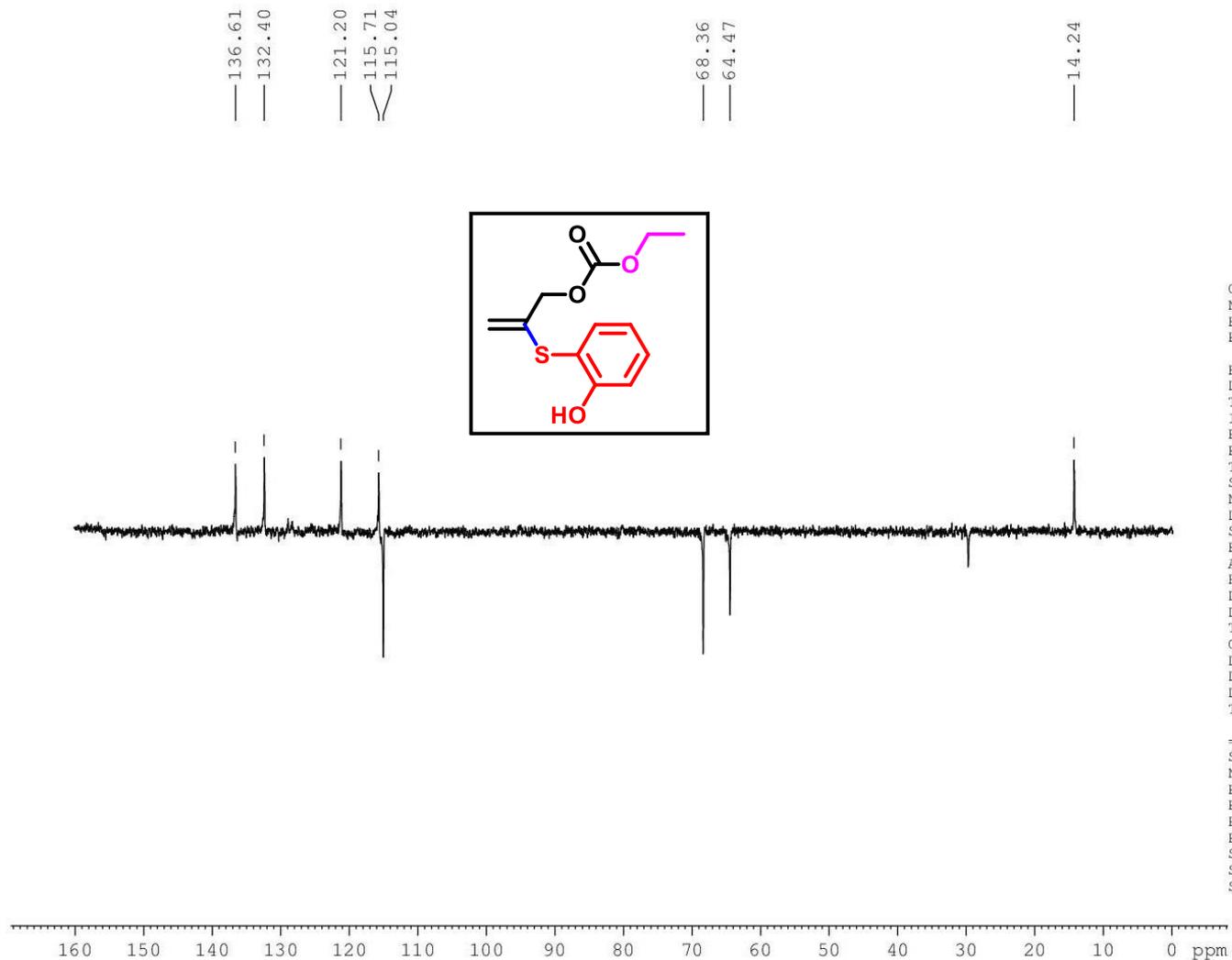


Fig.S54 <sup>13</sup>C NMR Spectrum of 4a



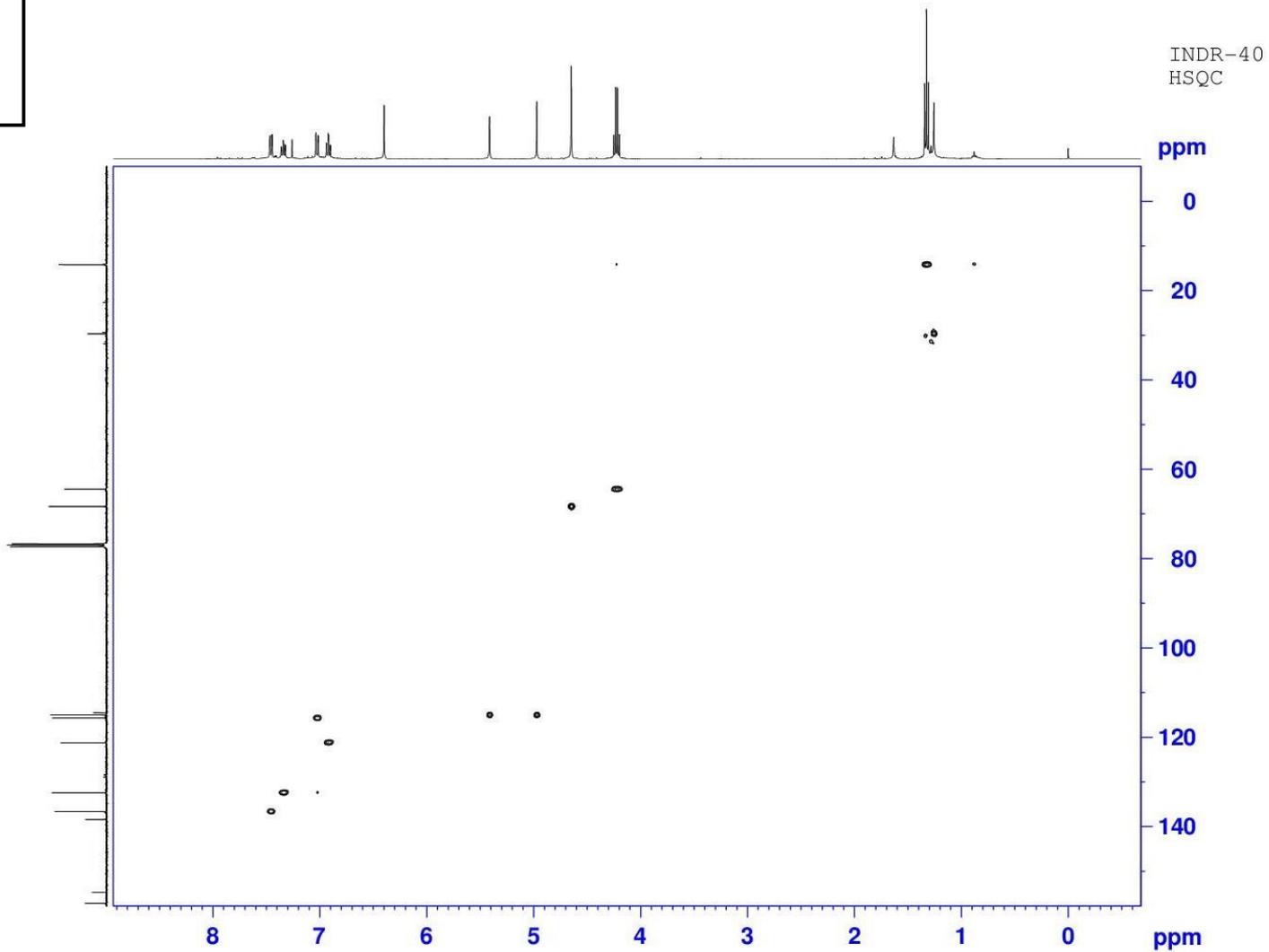
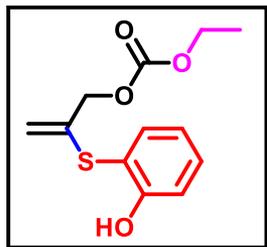
INDR-40  
DEPT-135

Current Data Paramete  
NAME DEPT-1  
EXPNO 1  
PROCNO

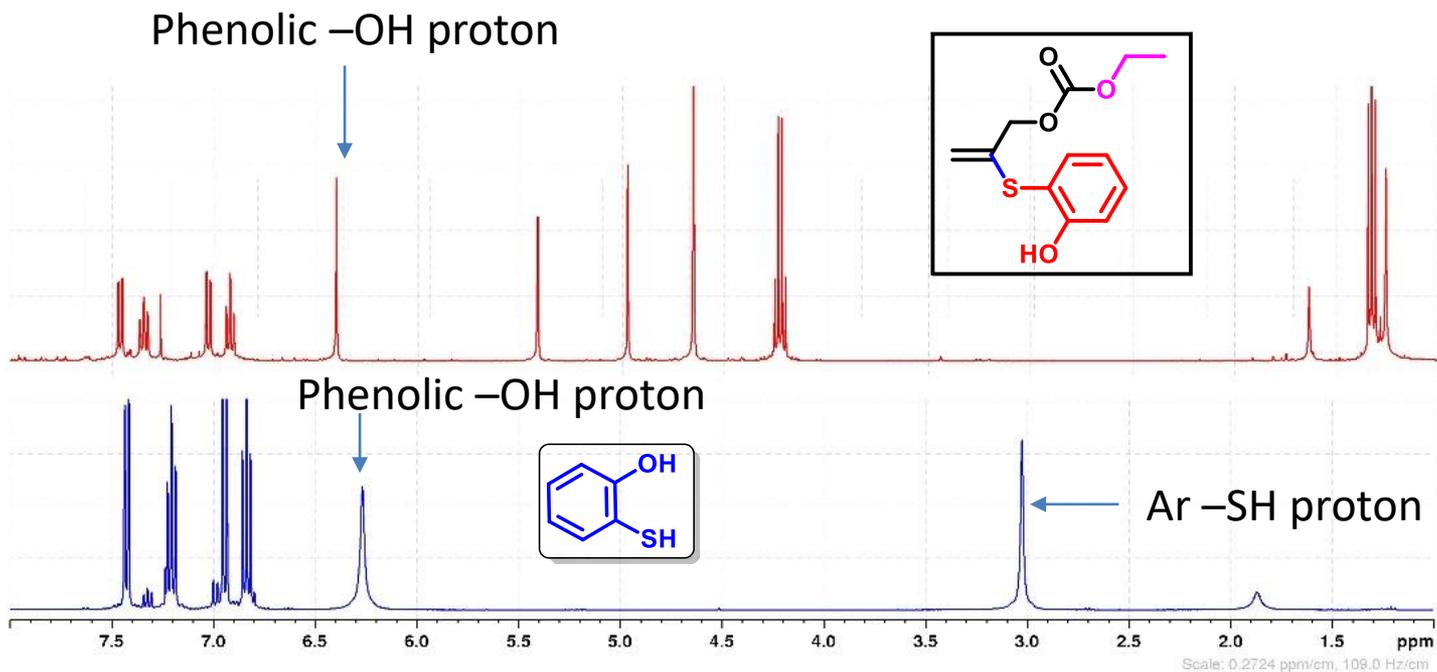
F2 - Acquisition Para  
Date\_ 202009  
Time 16.  
INSTRUM spe  
PROBHD 5 mm PABBO B  
PULPROG deptsp1  
TD 655  
SOLVENT CDC  
NS 2  
DS  
SWH 16129.0  
FIDRES 0.2461  
AQ 2.03161  
RG 201.  
DW 31.0  
DE 6.  
TE 300  
CNST2 145.00000  
D1 2.000000  
D2 0.003448  
D12 0.000020  
TD0

===== CHANNEL f1 =  
SFO1 100.62848  
NUC1 1  
P1 9.  
P13 2000.  
PLW0 0 W  
PLW1 53.000000  
SPNAM[5] Crp60comp  
SPOAL5 0.5  
SPOFFS5 0 Hz

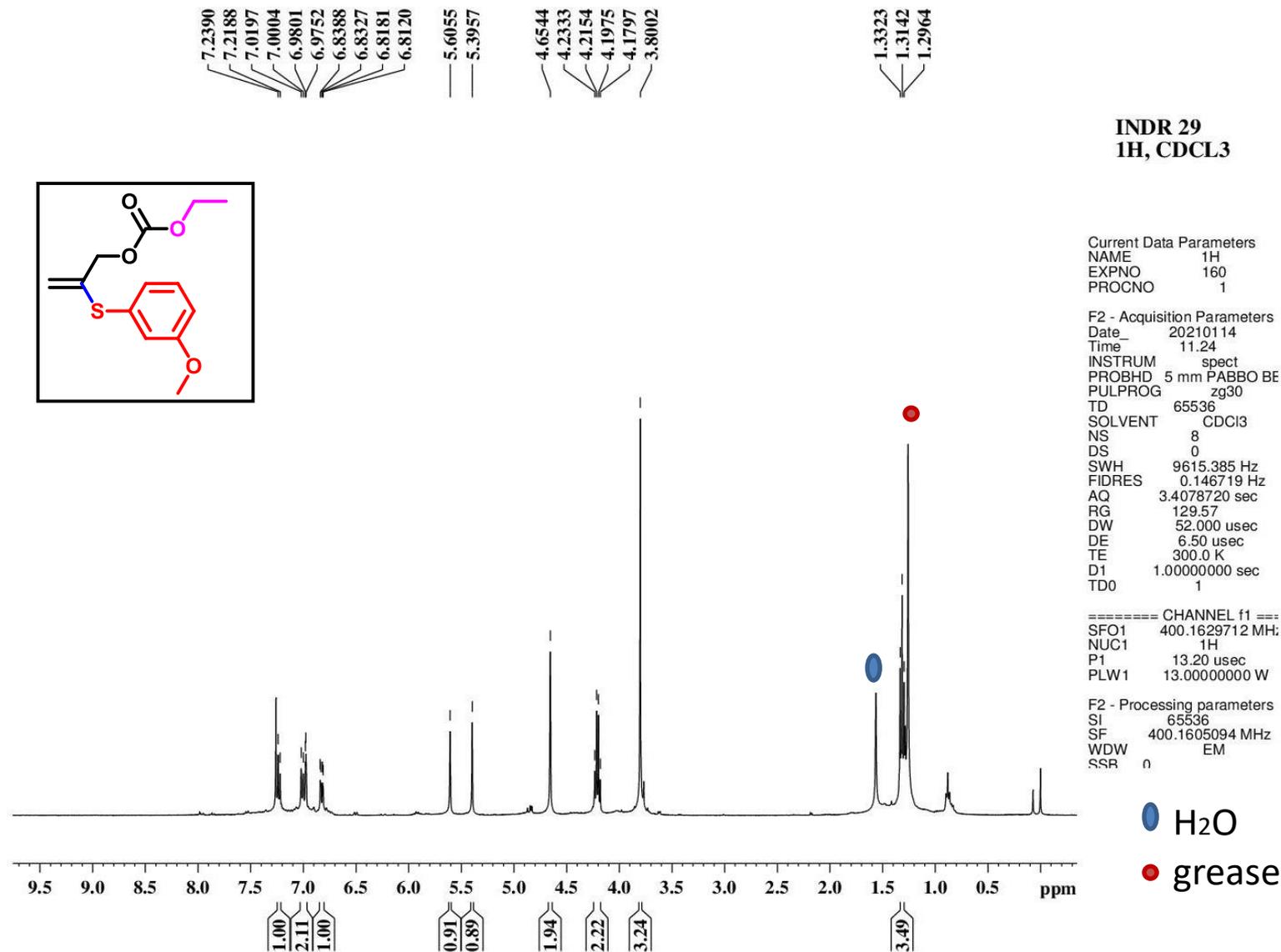
Fig.S55 DEPT-135 Spectrum of 4a



**Fig.S56** HSQC Spectrum of **4a**



**Fig.S57 comparison of <sup>1</sup>H NMR between SM (2-mercapto phenol) and product (4a).**



**Fig.S58** <sup>1</sup>H NMR Spectrum of **4b**

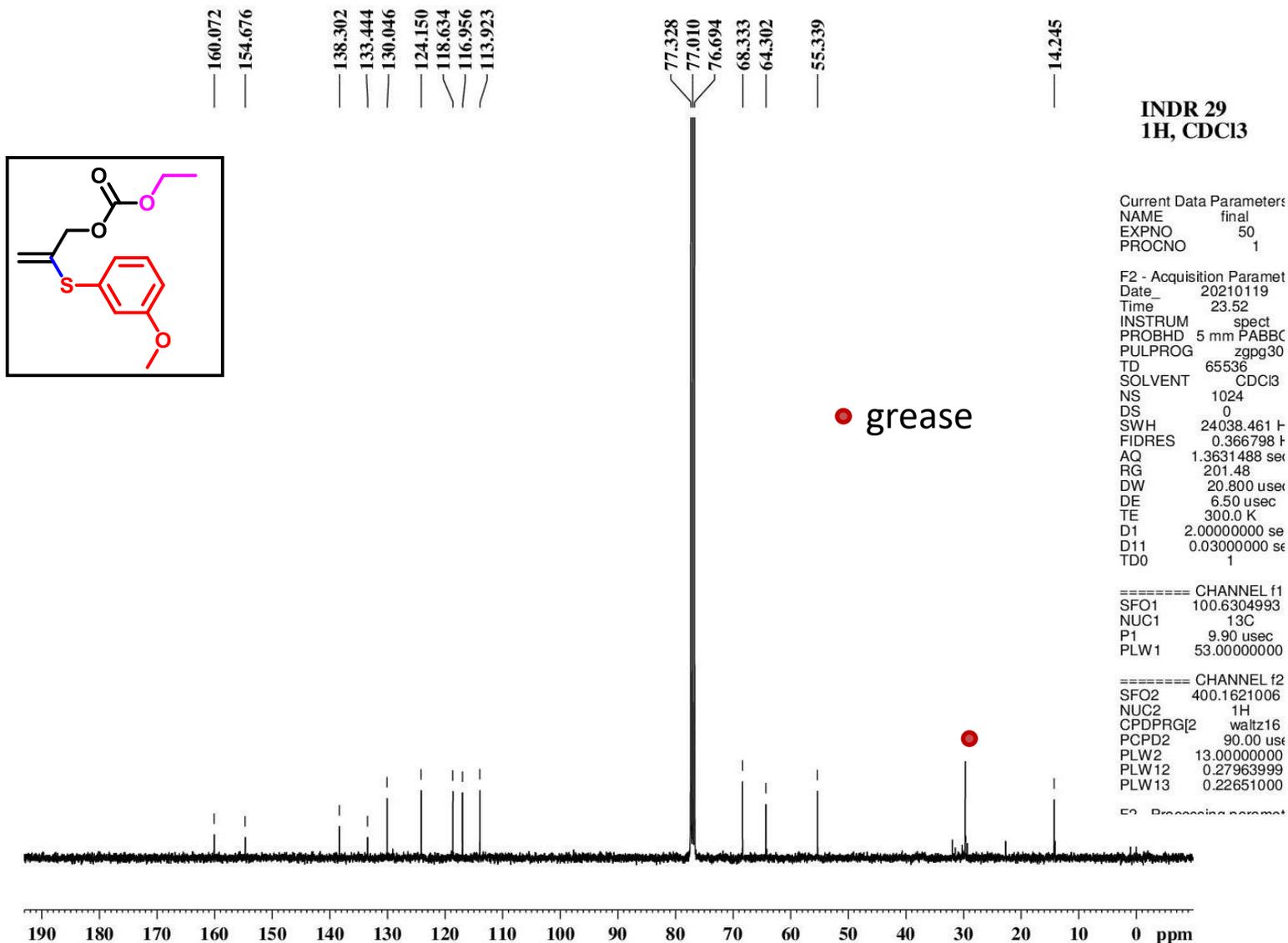
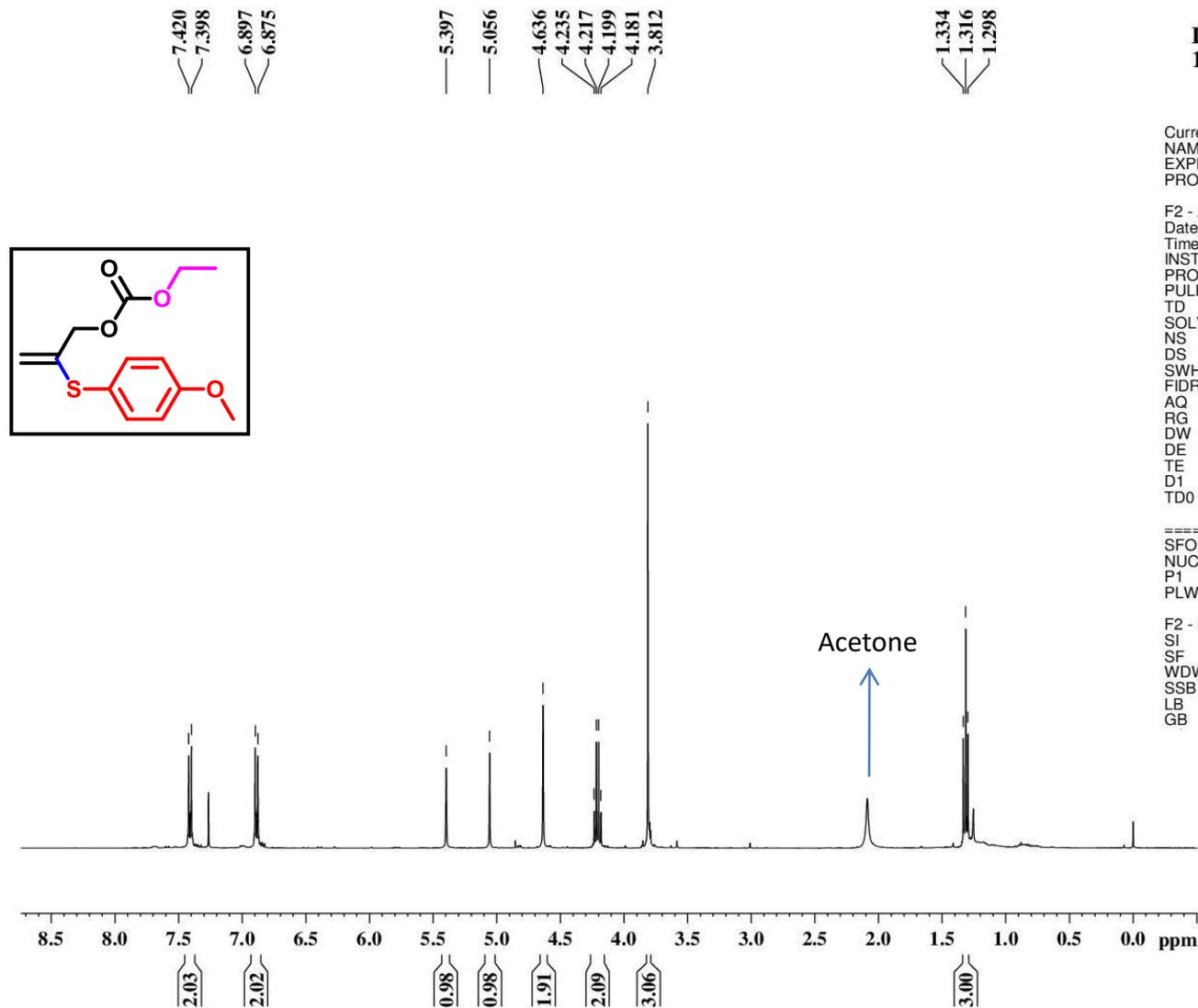


Fig.S59 <sup>13</sup>C NMR Spectrum of 4b



**Fig.S60** <sup>1</sup>H NMR Spectrum of **4c**

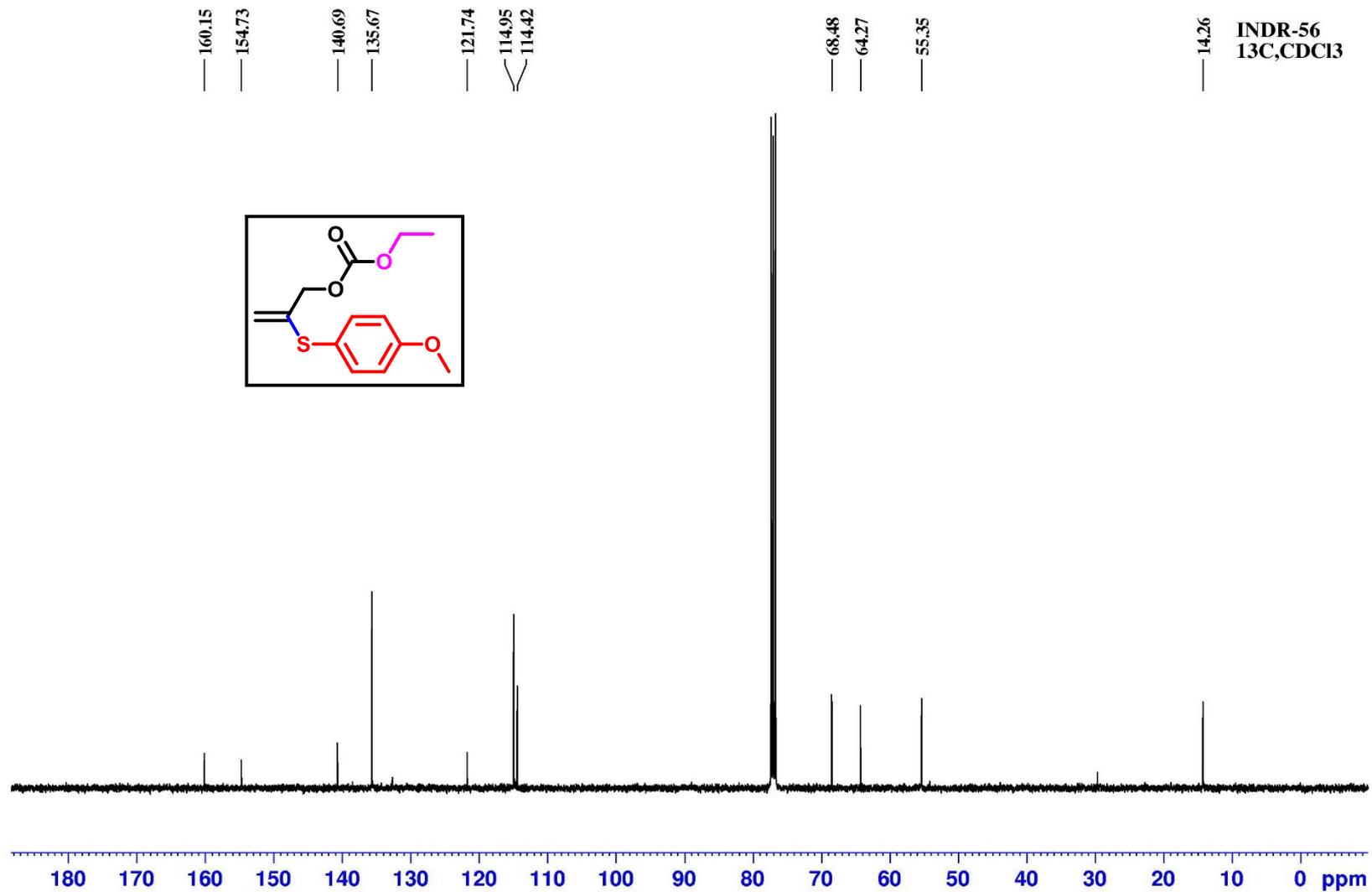
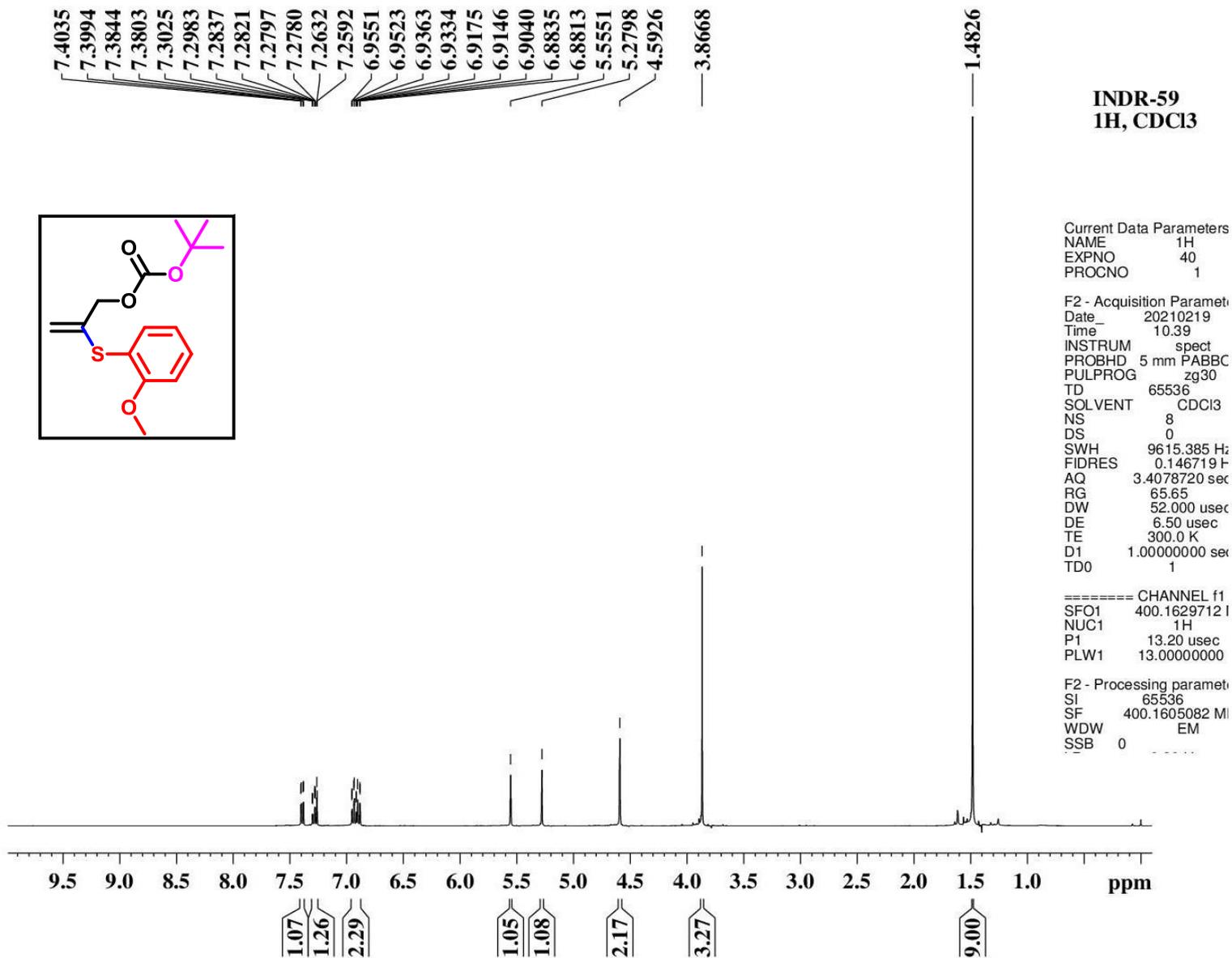
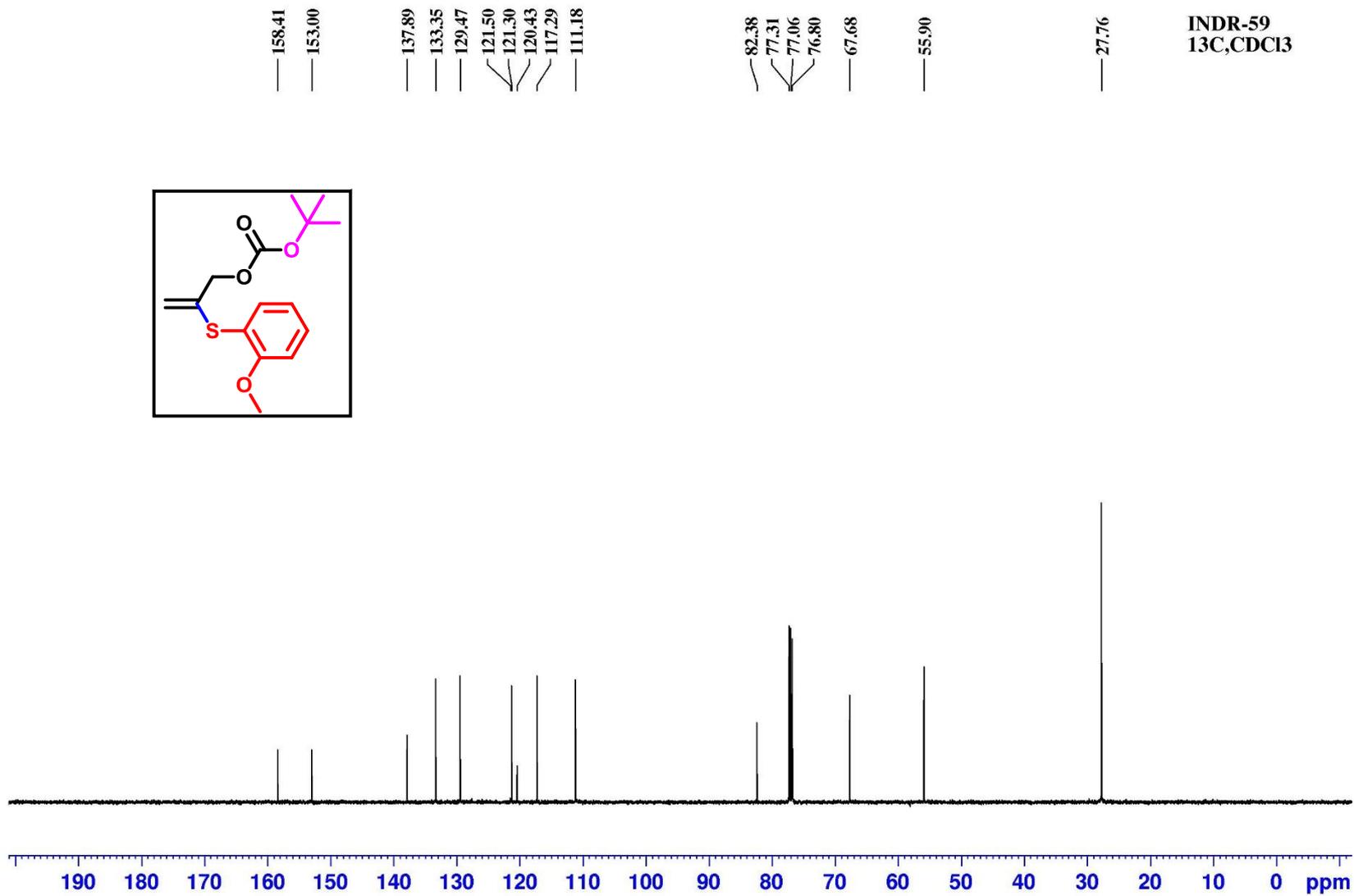


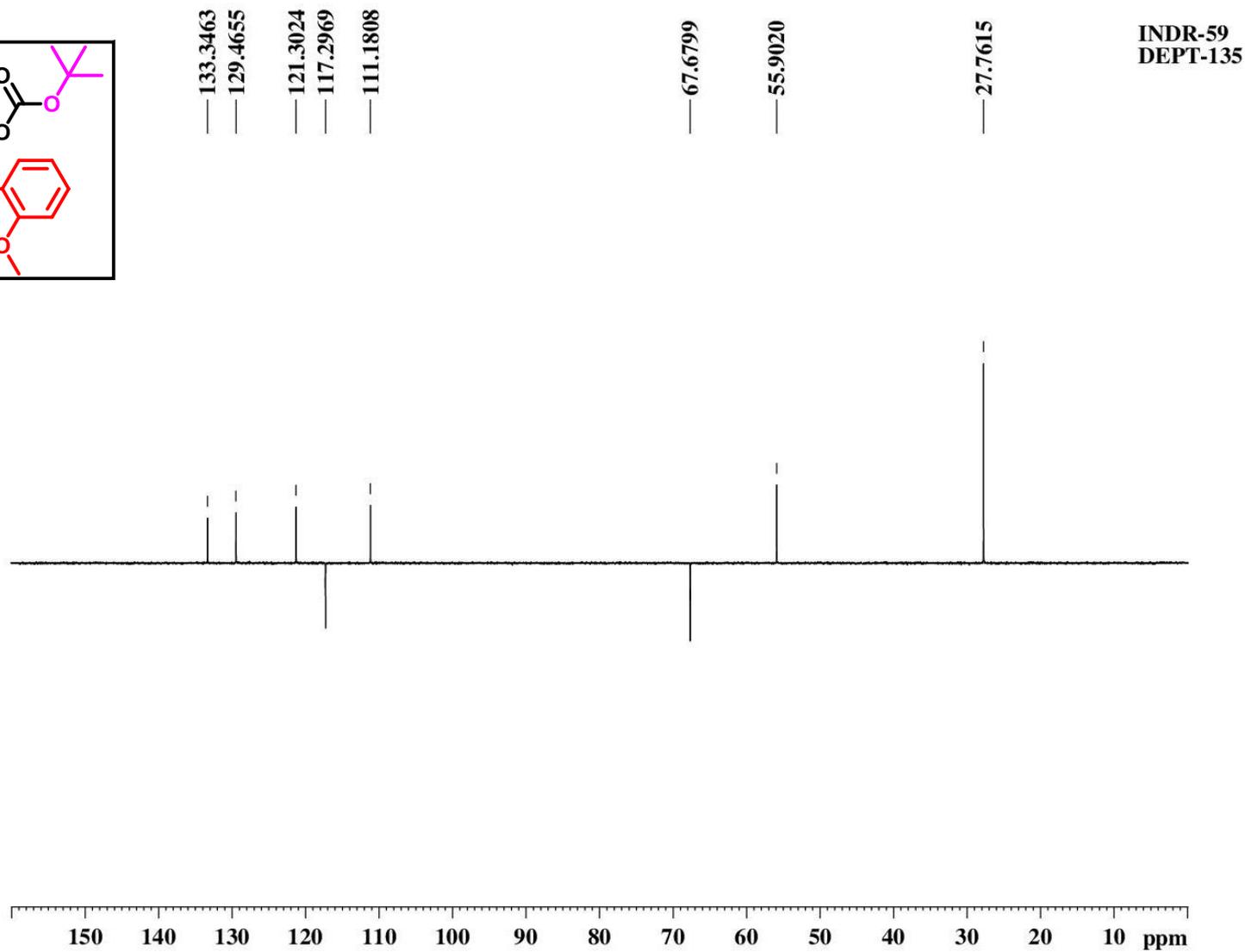
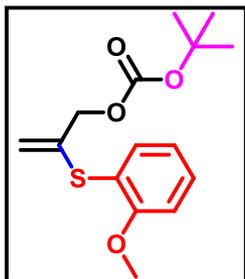
Fig.S61  $^{13}\text{C}$  NMR Spectrum of 4c



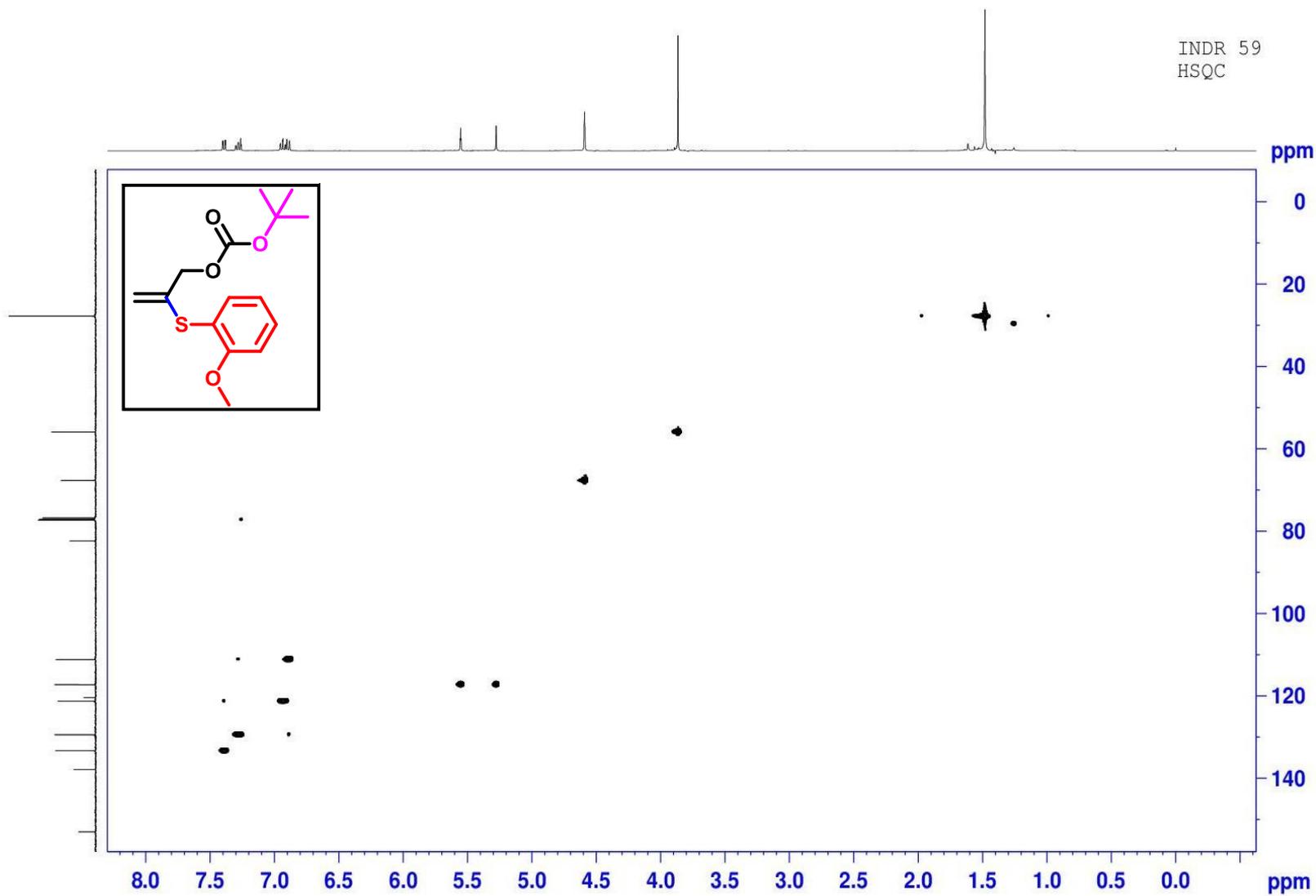
**Fig.S62** <sup>1</sup>H NMR Spectrum of **4d**



**Fig.S63**  $^{13}\text{C}$  NMR Spectrum of **4d**

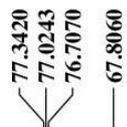
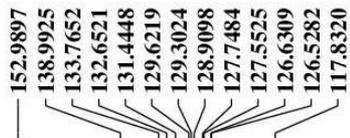
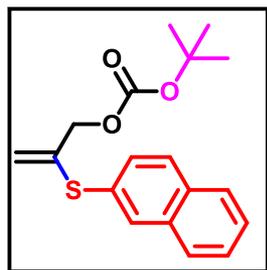


**Fig.S64** DEPT-135 Spectrum of **4d**



**Fig.S65** HSQC Spectrum of **4d**





INDR-52  
13C, CDCl3

Current Data Parameters  
NAME 13C  
EXPNO 180  
PROCNO 1

F2 - Acquisition Parameter  
Date\_ 20210112  
Time 15.58  
INSTRUM spect  
PROBHD 5 mm PABBO E  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 20.148  
DW 20.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.0000000 sec  
D11 0.0300000 sec  
TD0 1

===== CHANNEL f1 =  
SFO1 100.6304993 M  
NUC1 13C  
P1 9.90 usec  
PLW1 53.0000000 W

===== CHANNEL f2 =  
SFO2 400.1621006 M  
NUC2 1H  
CPDPRG2 waltz16  
PCPD2 90.00 usec  
PLW2 13.0000000 W  
PLW12 0.27963999 W  
PLW13 0.22651000 W

F2 - Processing parameter

● grease

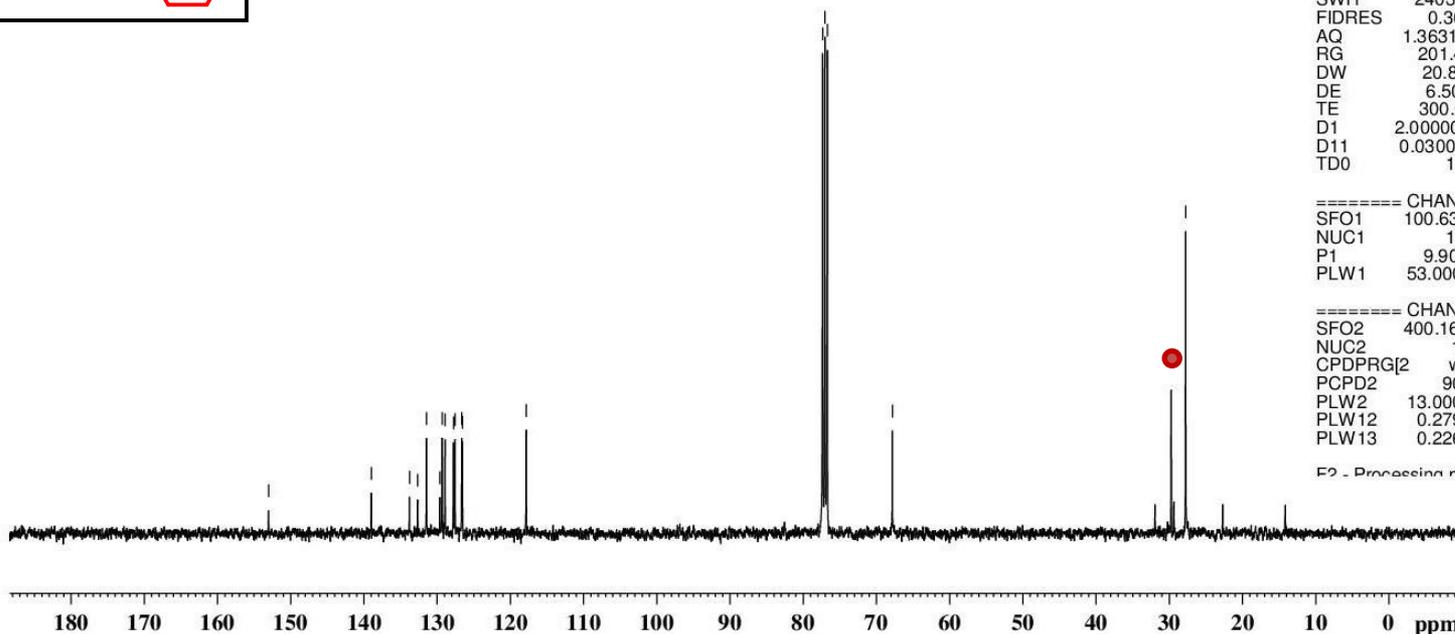


Fig.S67 <sup>13</sup>C NMR Spectrum of 4e

**INDR-78**  
**<sup>1</sup>H, CDCl<sub>3</sub>**

Current Data Parameters  
NAME 1H  
EXPNO 50  
PROCNO 1

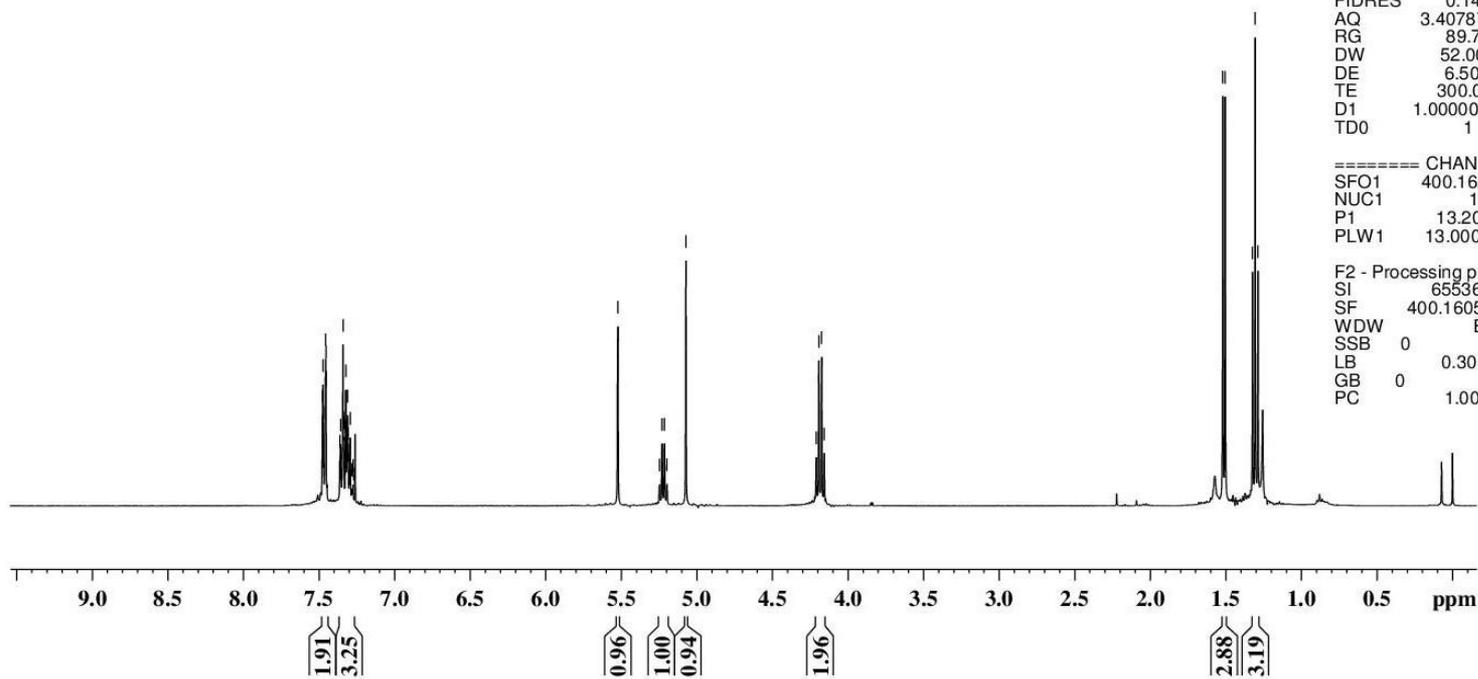
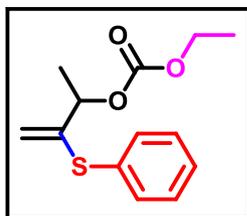
F2 - Acquisition Parameter  
Date\_ 20210317  
Time 16.08  
INSTRUM spect  
PROBHD 5 mm PABBO I  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 89.7  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =  
SFO1 400.1629712 M  
NUC1 <sup>1</sup>H  
P1 13.20 usec  
PLW1 13.00000000 V

F2 - Processing parameter  
SI 65536  
SF 400.1605101 MH  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

7.4755  
7.4715  
7.4587  
7.4548  
7.4516  
7.3606  
7.3557  
7.3513  
7.3391  
7.3353  
7.3341  
7.3242  
7.3205  
7.3132  
7.3093  
7.3055  
7.2988  
7.2918  
7.2832  
7.2772  
7.2736  
7.2703  
5.5220  
5.2462  
5.2298  
5.2134  
5.1971  
5.0722  
4.2092  
4.1914  
4.1736  
4.1559

1.5199  
1.5035  
1.3230  
1.3052  
1.2873



**Fig.S68** <sup>1</sup>H NMR Spectrum of **4f**

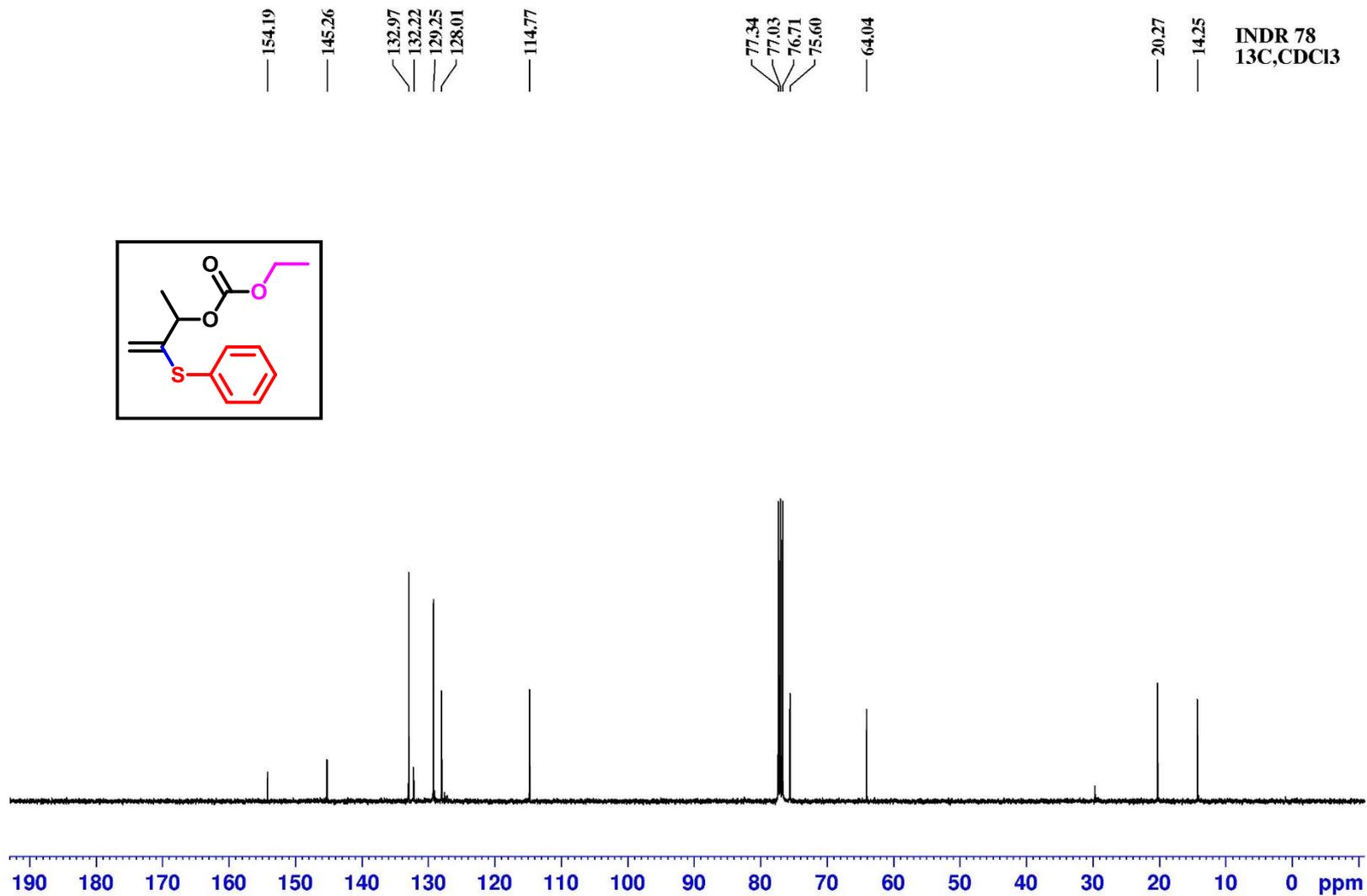
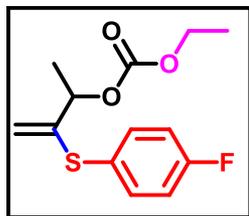


Fig.S69  $^{13}\text{C}$  NMR Spectrum of 4f



7.4725  
7.4594  
7.4504  
7.4372  
7.0693  
7.0478  
7.0259

5.4687  
5.4677  
5.2297  
5.2134  
5.1970  
5.1805  
4.9617  
4.2125  
4.1946  
4.1767  
4.1588

1.5171  
1.5006  
1.3245  
1.3067  
1.2888

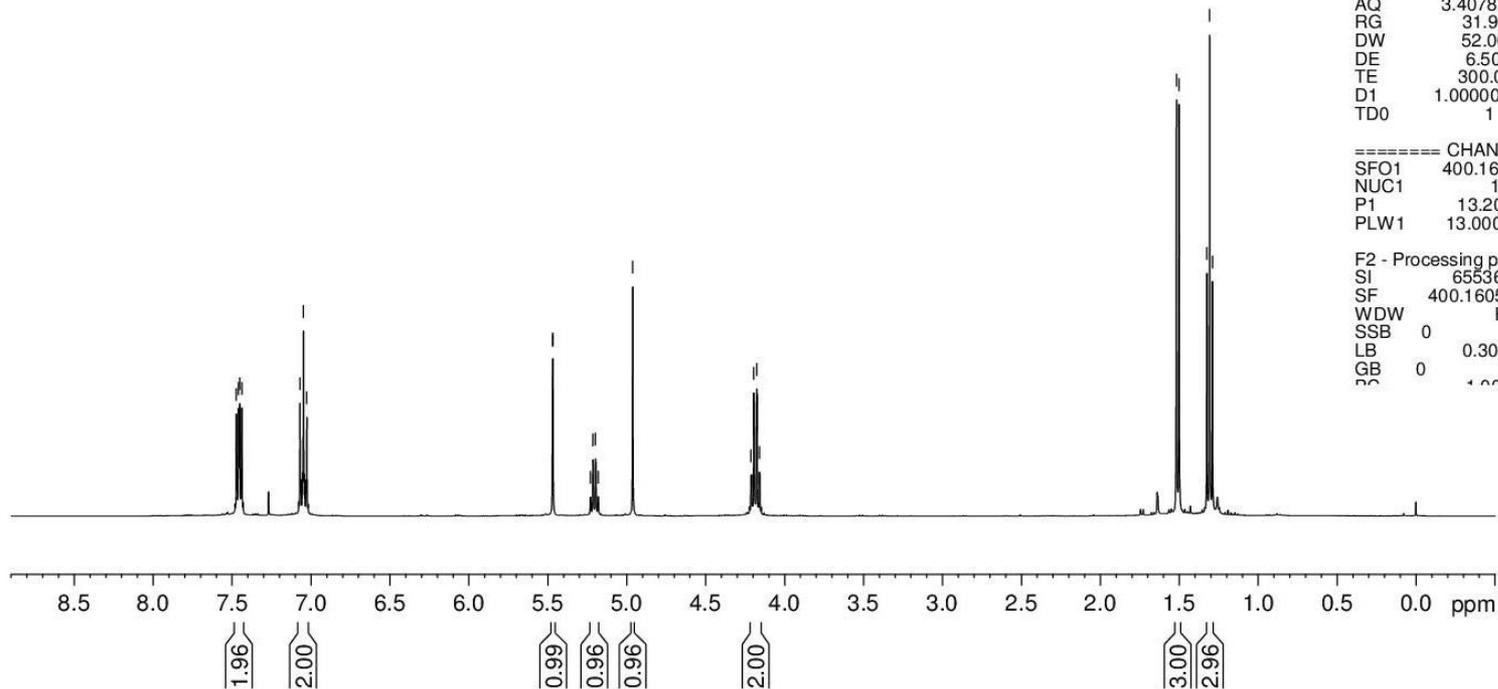
**INDR 68**  
**1H, CDCl3**

Current Data Parameters  
NAME 1H  
EXPNO 130  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210303  
Time 11.18  
INSTRUM spect  
PROBHD 5 mm PABBC  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 31.99  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1  
SFO1 400.1629712 MHz  
NUC1 1H  
P1 13.20 usec  
PLW1 13.00000000

F2 - Processing parameters  
SI 65536  
SF 400.1605061 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Fig.S70** <sup>1</sup>H NMR Spectrum of **4g**

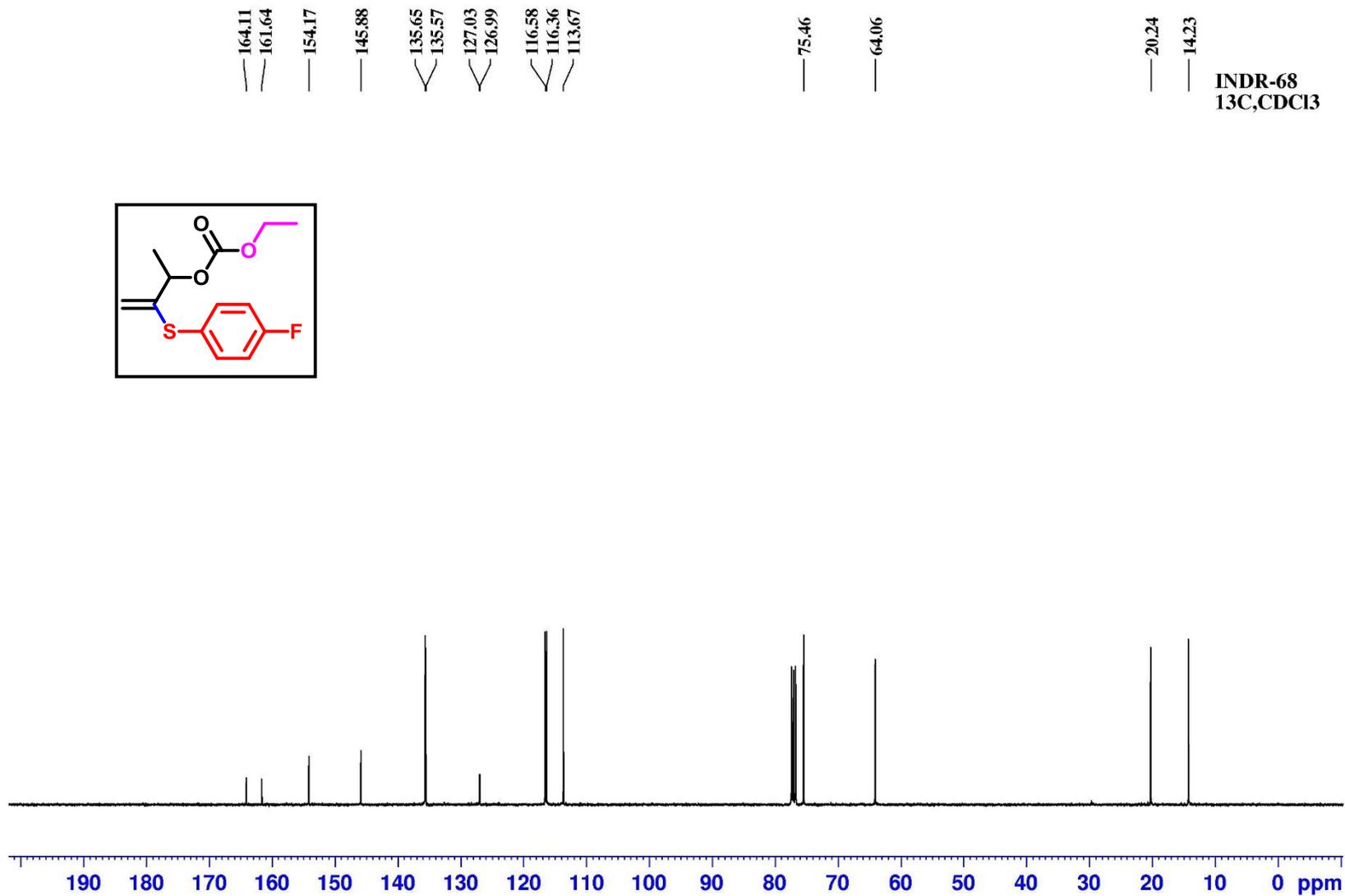
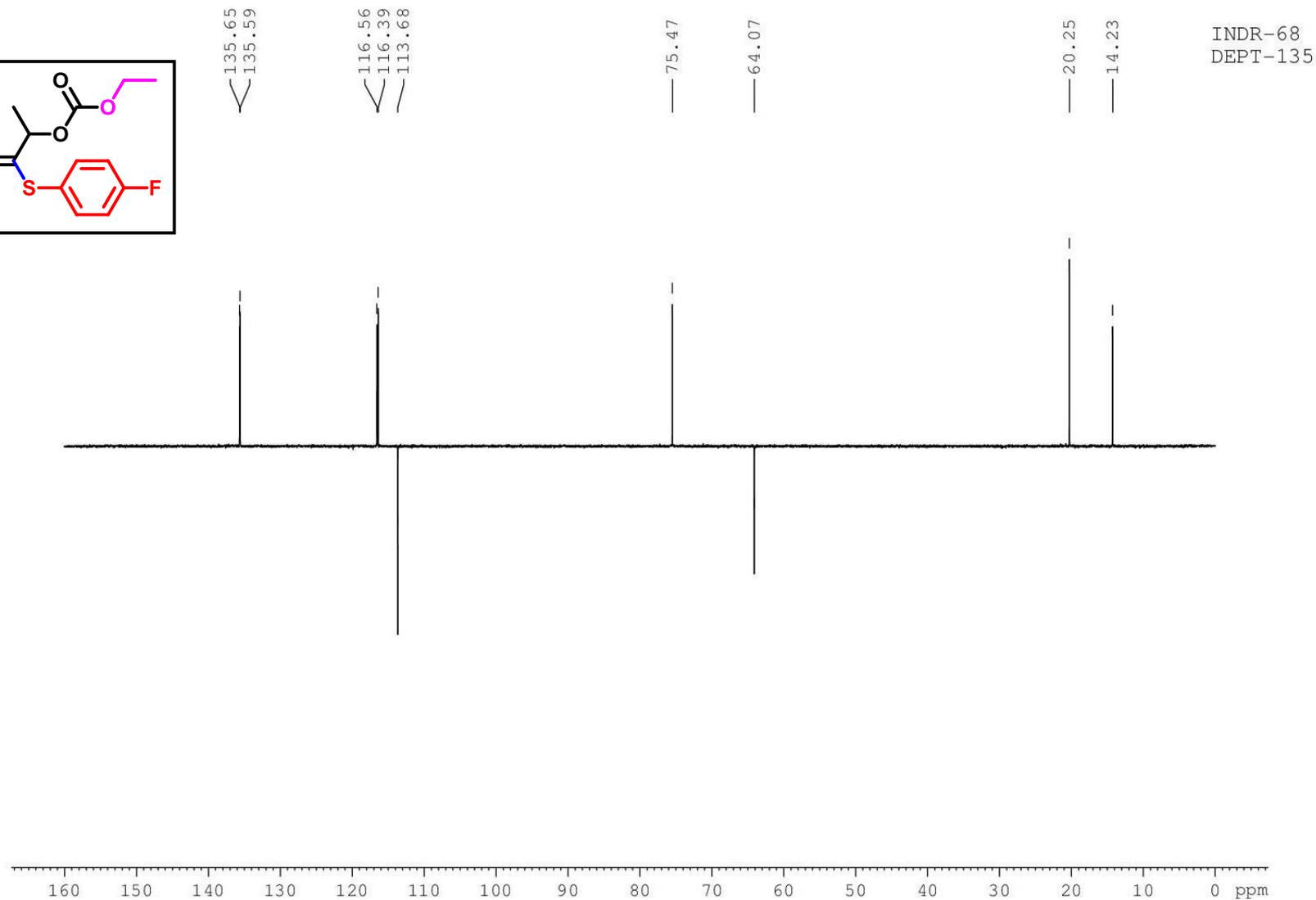
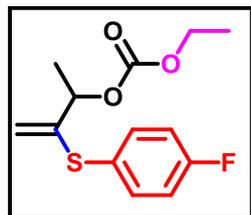
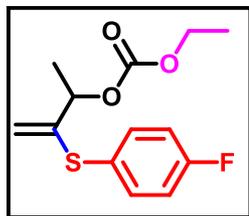


Fig.S71 <sup>13</sup>C NMR Spectrum of 4g



**Fig.S72** DEPT-135 Spectrum of **4g**



-112.8578

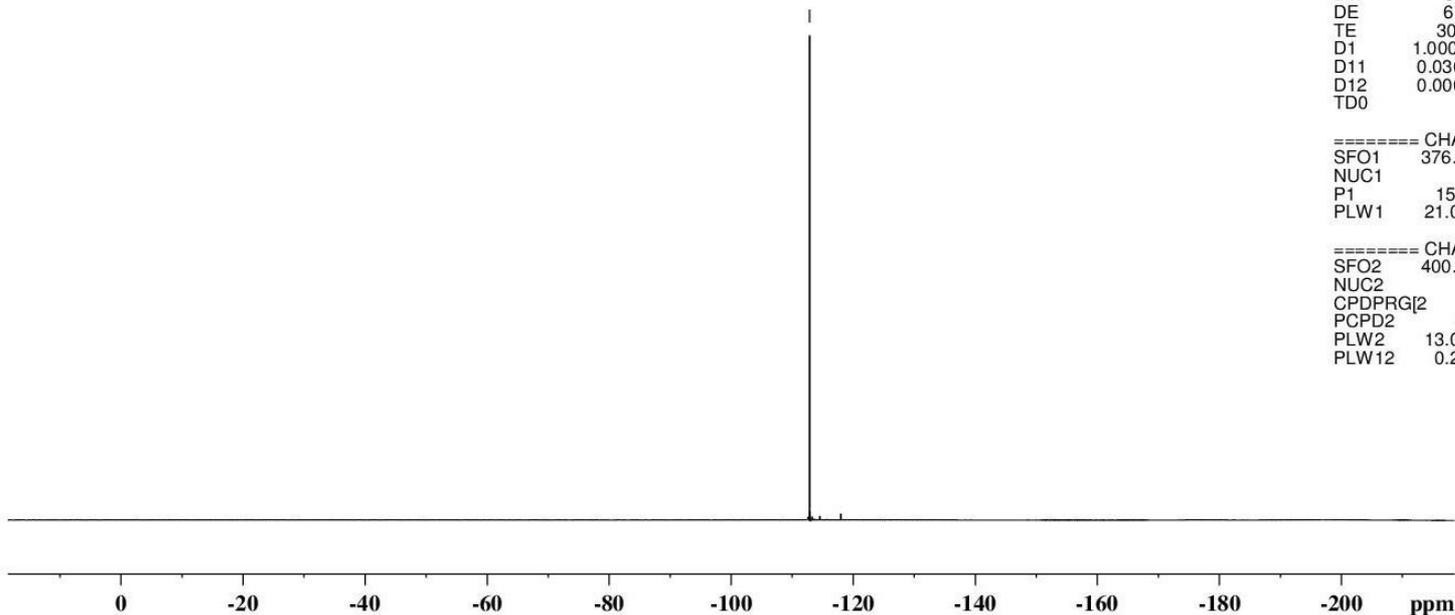
**INDR-68**  
**19F,CDCl3**

Current Data Parameters  
NAME 19F  
EXPNO 60  
PROCNO 1

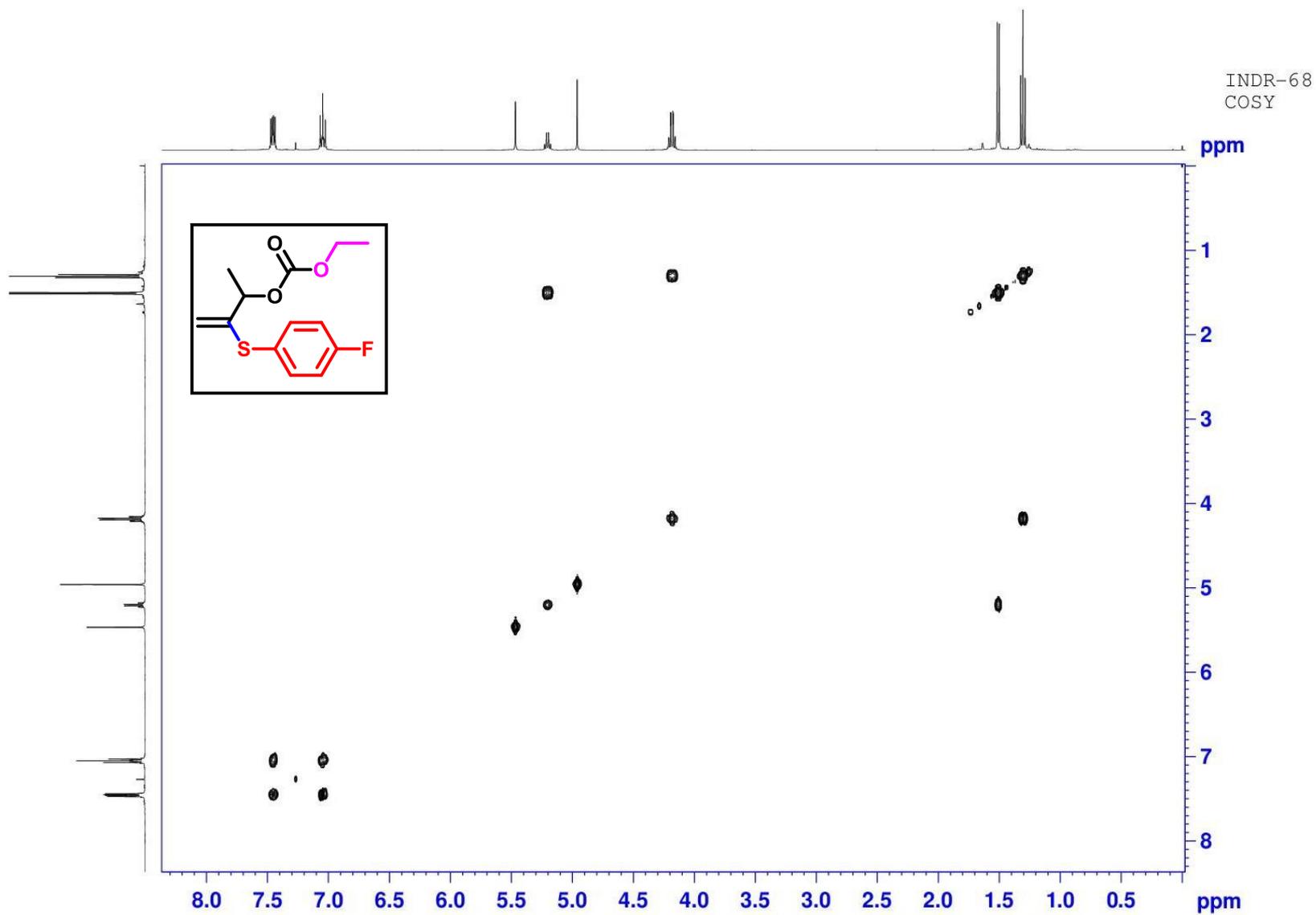
F2 - Acquisition Parameters  
Date\_ 20210310  
Time 10.47  
INSTRUM spect  
PROBHD 5 mm PABBO  
PULPROG zgfgigqn.2  
TD 131072  
SOLVENT CDCl3  
NS 16  
DS 4  
SWH 89285.711 Hz  
FIDRES 0.681196 Hz  
AQ 0.7340032 sec  
RG 201.48  
DW 5.600 usec  
DE 6.50 usec  
TE 300.1 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
D12 0.00002000 sec  
TD0 1

=====  
CHANNEL f1 :  
SFO1 376.4894122 MHz  
NUC1 19F  
P1 15.00 usec  
PLW1 21.00000000 V

=====  
CHANNEL f2 :  
SFO2 400.1621006 MHz  
NUC2 1H  
CPDPRG2 waltz16  
PCPD2 90.00 usec  
PLW2 13.00000000 V  
PLW12 0.27963999 V



**Fig.S73** <sup>19</sup>F NMR Spectrum of **4g**



**Fig.S74** COSY Spectrum of **4g**

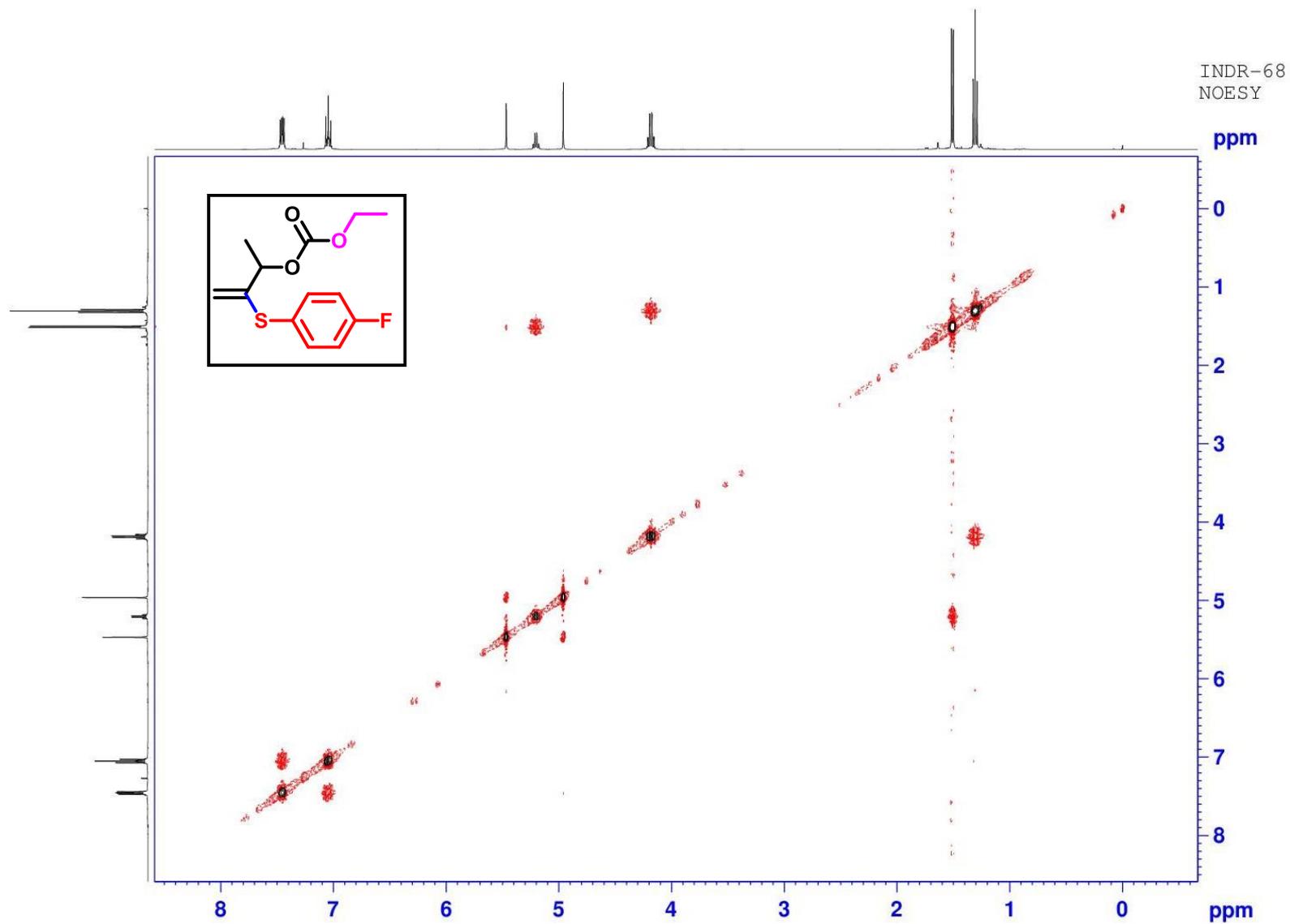
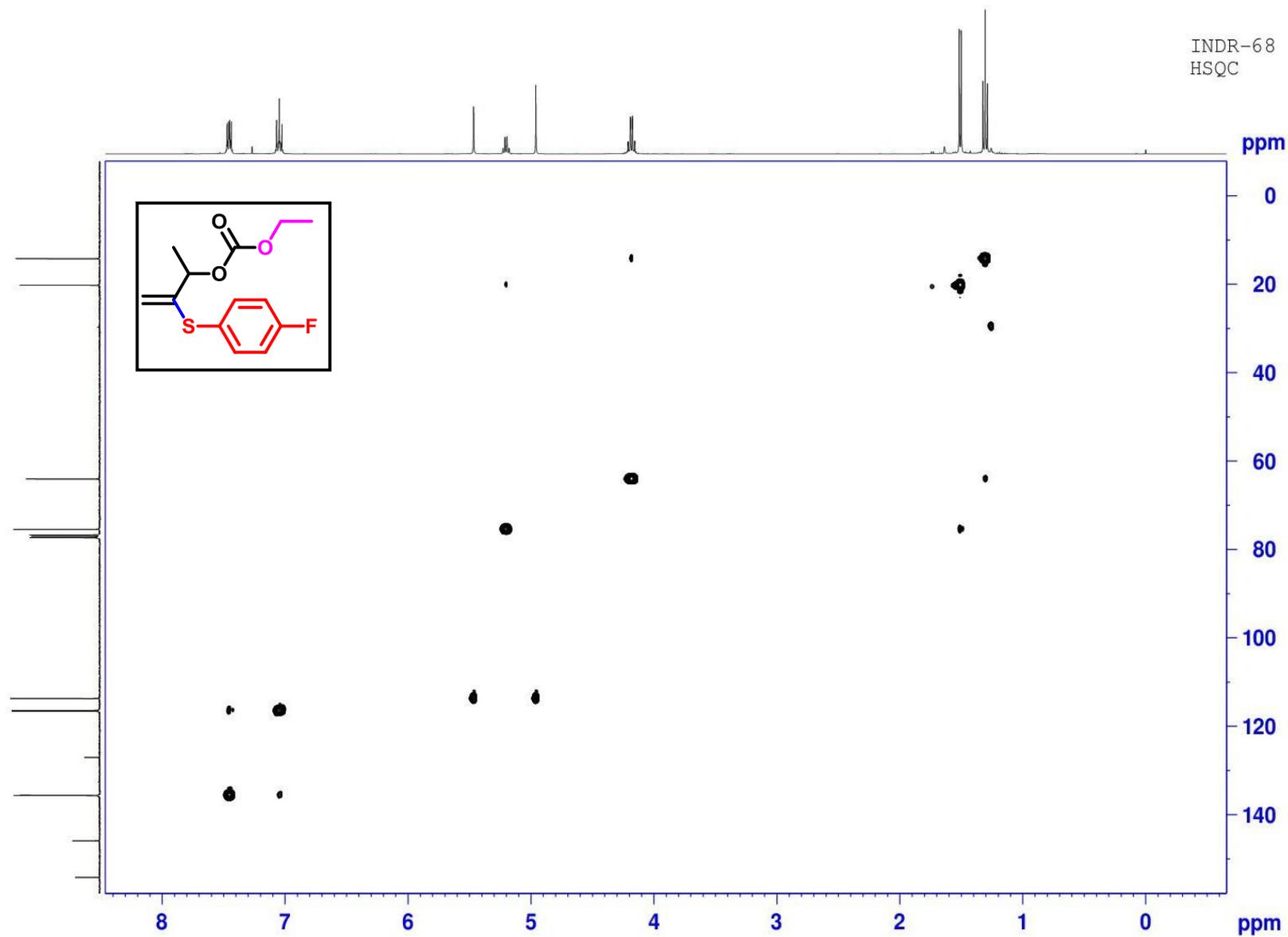
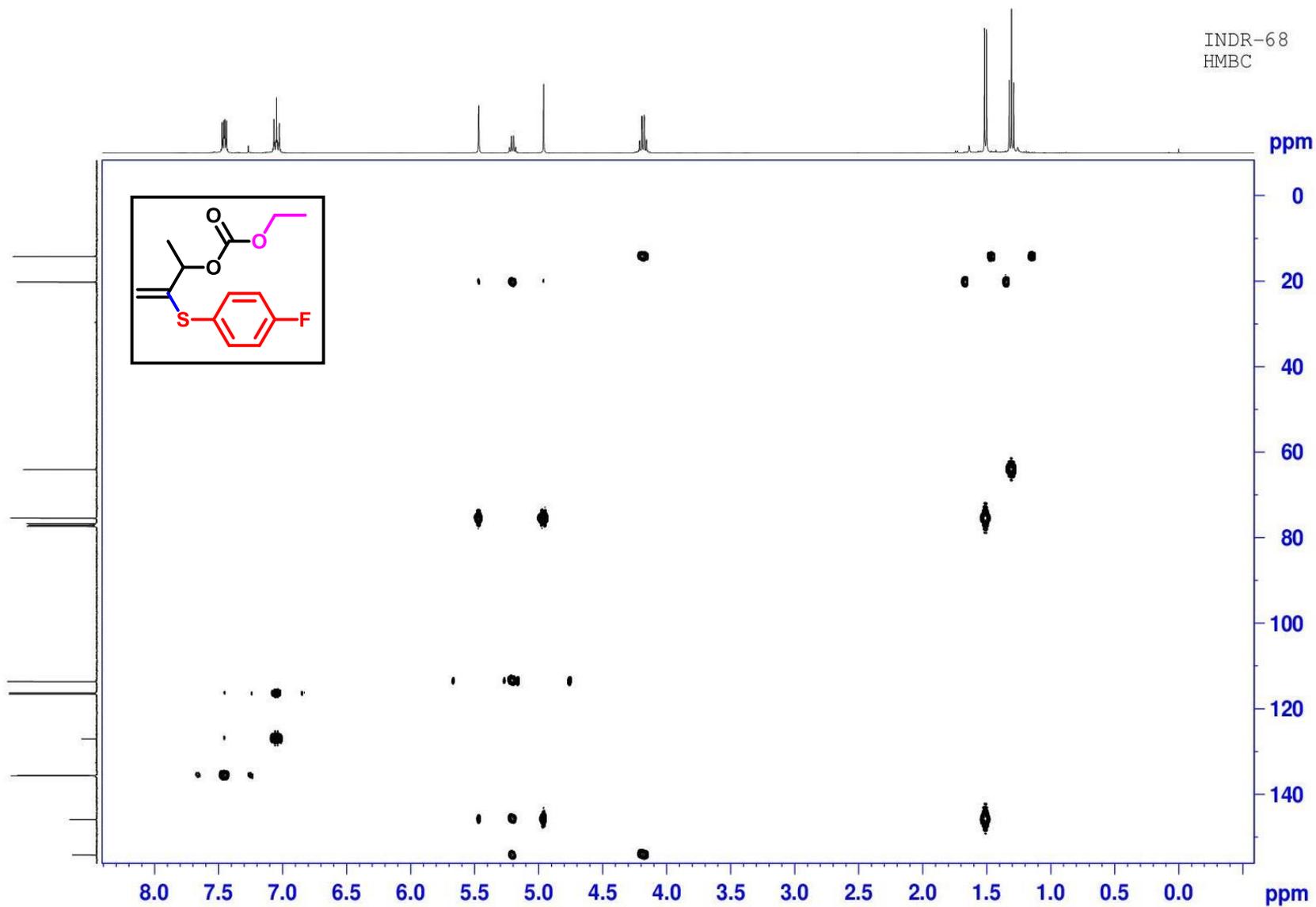


Fig.S75 NOESY Spectrum of **4g**



**Fig.S76** HSQC Spectrum of **4g**

INDR-68  
HMBC



**Fig.S77** HMBC Spectrum of **4g**

**INDR-70  
1H, CDCl3**

Current Data Parameters  
 NAME 1H  
 EXPNO 60  
 PROCNO 1

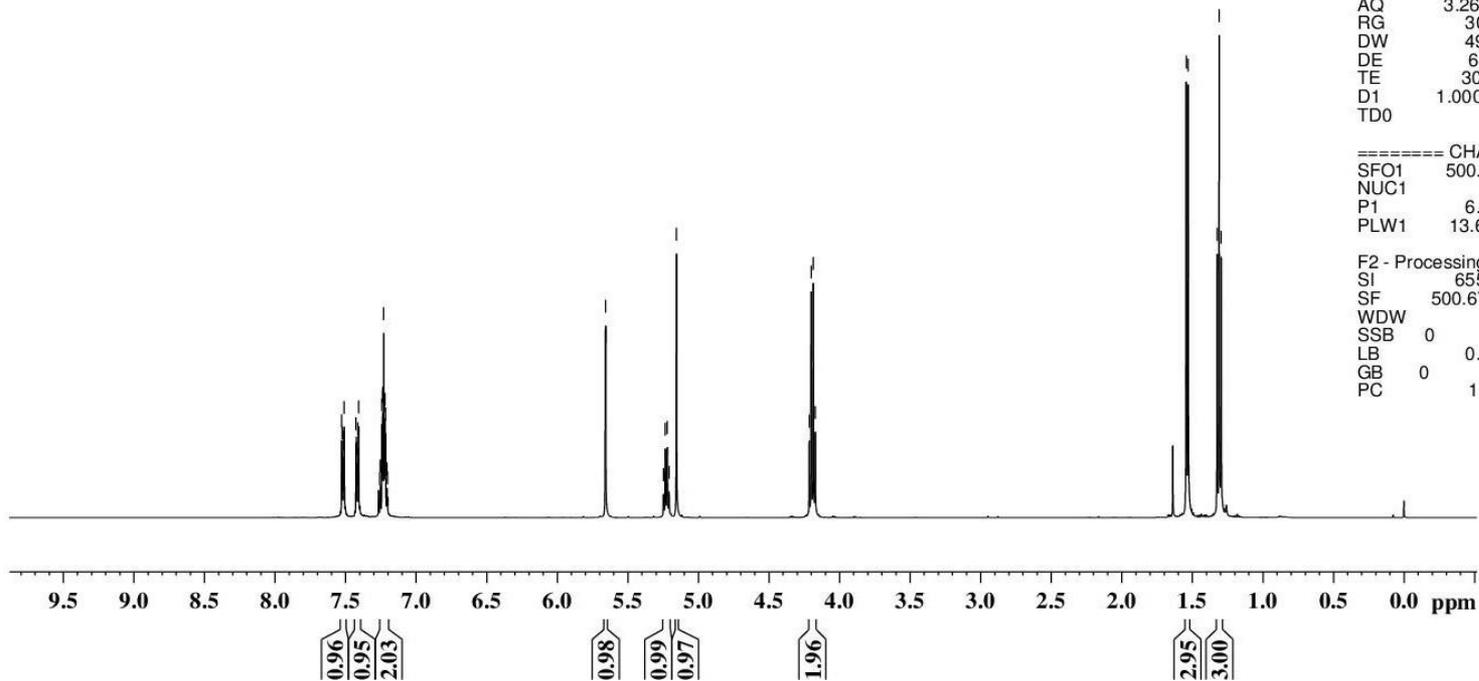
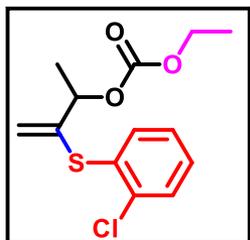
F2 - Acquisition Parameters  
 Date\_ 20210308  
 Time 12.18  
 INSTRUM spect  
 PROBHD 5 mm PATXI 1H/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10026.738 Hz  
 FIDRES 0.152996 Hz  
 AQ 3.2680619 sec  
 RG 30.83  
 DW 49.867 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 SFO1 500.6794419 MHz  
 NUC1 1H  
 P1 6.45 usec  
 PLW1 13.60000038 W

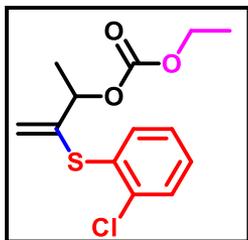
F2 - Processing parameters  
 SI 65536  
 SF 500.6763582 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

7.5280  
7.5232  
7.5158  
7.5130  
7.5092  
7.4263  
7.4226  
7.4199  
7.4121  
7.4076  
7.2572  
7.2532  
7.2424  
7.2384  
7.2358  
7.2297  
7.2237  
7.2211  
7.2169  
7.2063  
7.2021  
5.6571  
5.2464  
5.2341  
5.2210  
5.2079  
5.1553  
4.2139  
4.1997  
4.1854  
4.1712

1.5422  
1.5291  
1.3234  
1.3092  
1.2949



**Fig.S78** <sup>1</sup>H NMR Spectrum of **4h**



— 154.1829  
 — 142.8815  
 — 136.0641  
 — 133.5985  
 — 132.0573  
 — 130.1501  
 — 128.9135  
 — 127.3421  
 — 117.4303

77.3137  
 77.0601  
 76.8063  
 75.5046  
 — 64.0932

— 20.2182  
 — 14.2611

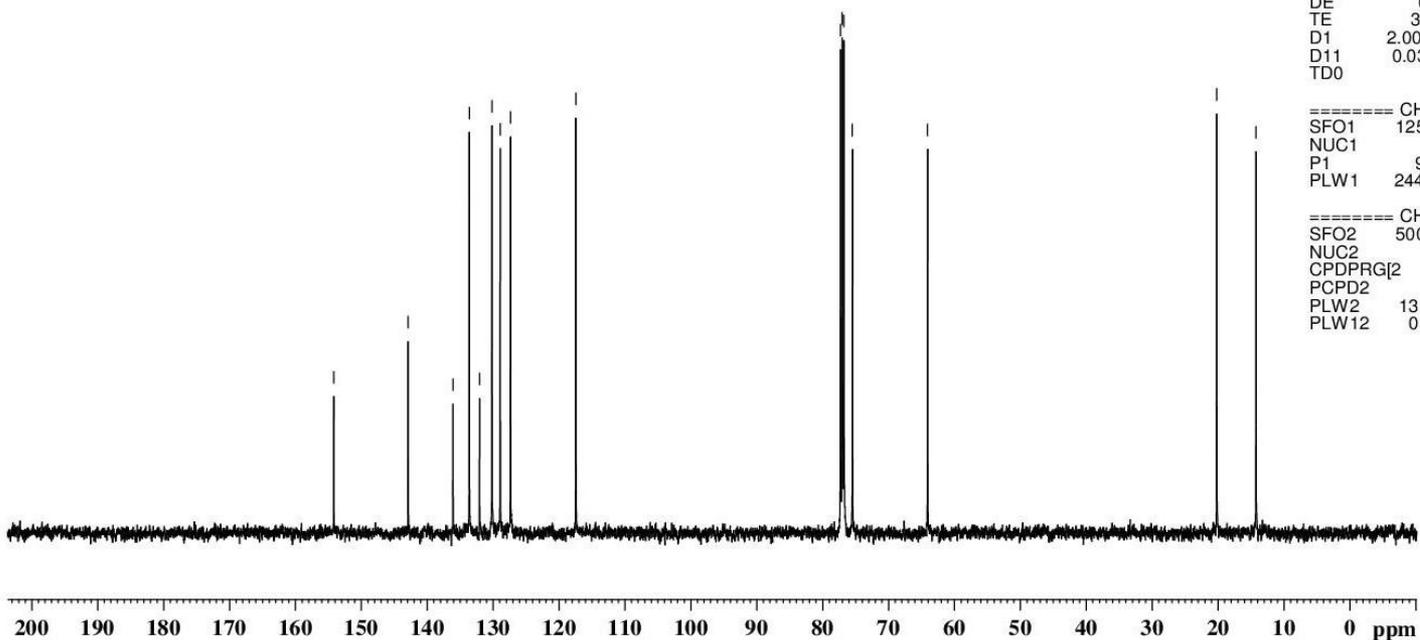
**INDR-70**  
**13C,CDCl3**

Current Data Parameters  
 NAME 13C  
 EXPNO 70  
 PROCNO 1

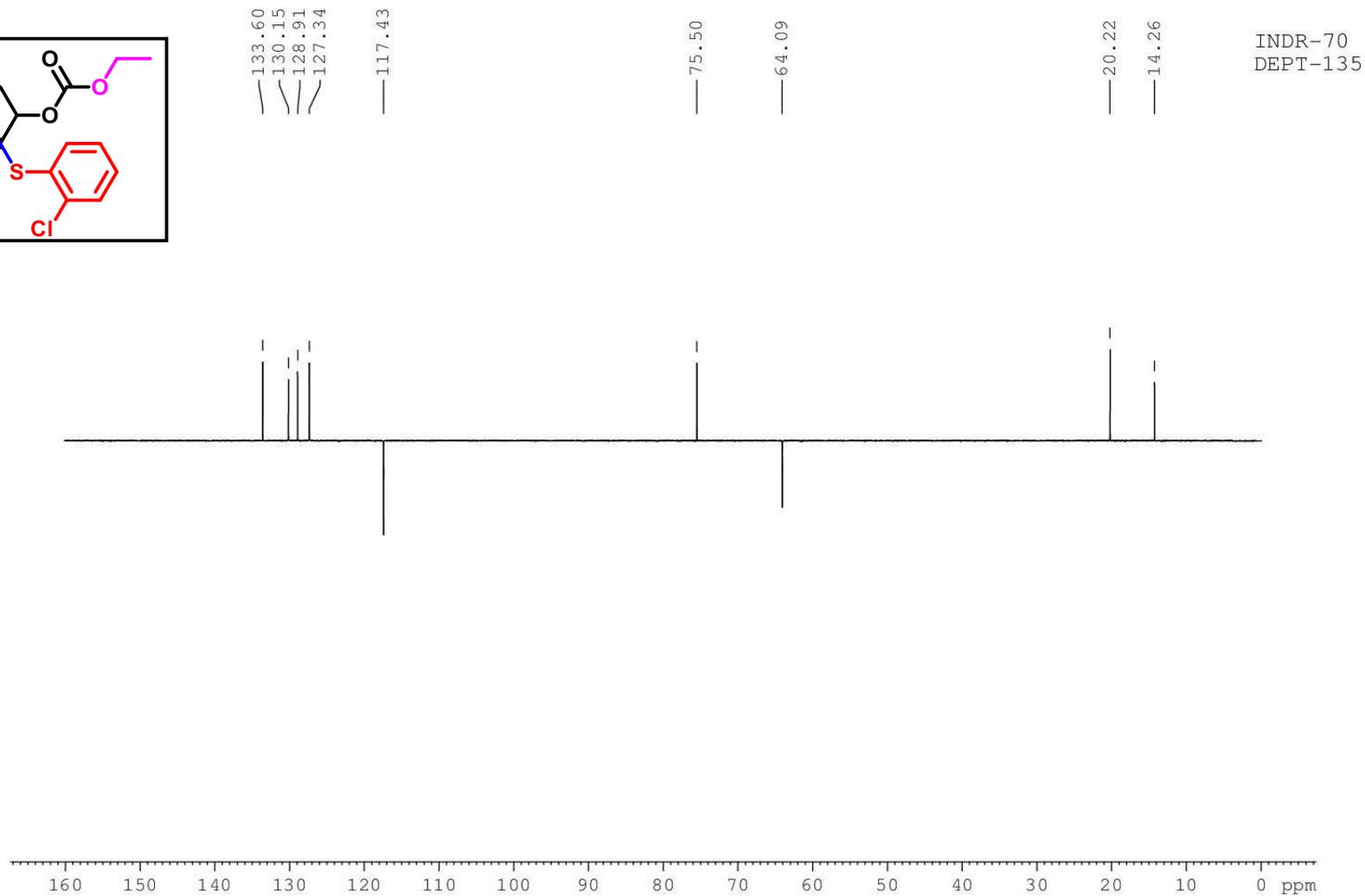
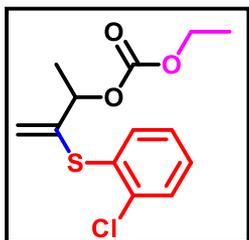
F2 - Acquisition Parameters  
 Date\_ 20210308  
 Time 12.32  
 INSTRUM spect  
 PROBHD 5 mm PATX1 1H/  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 512  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 107.78  
 DW 16.800 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TDO 1

==== CHANNEL f1 ===  
 SFO1 125.9077573 MH  
 NUC1 13C  
 P1 9.23 usec  
 PLW1 244.0000000 W

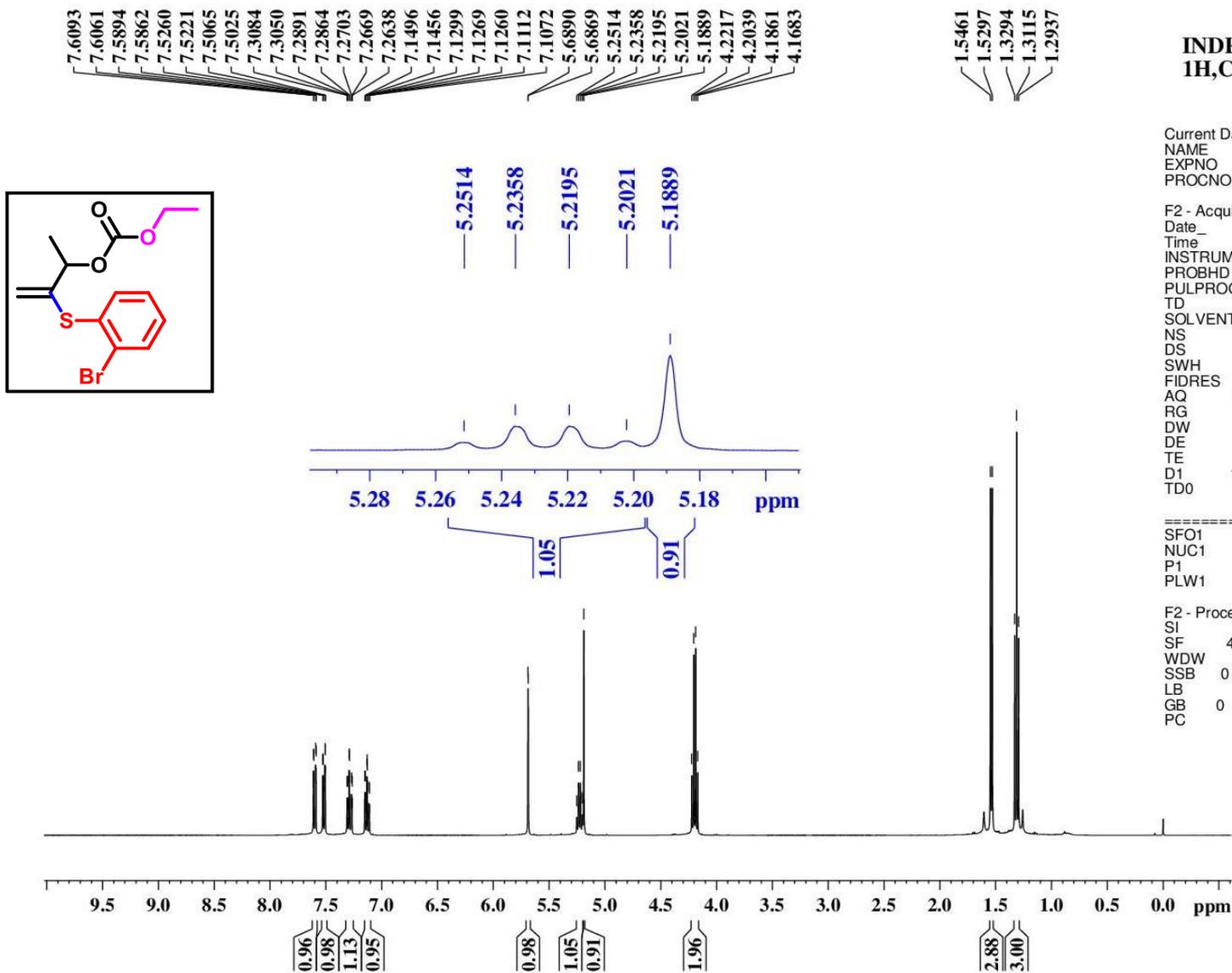
==== CHANNEL f2 ===  
 SFO2 500.6783527 MH  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 13.60000038 W  
 PLW12 0.08840500 W



**Fig.S79** <sup>13</sup>C NMR Spectrum of **4h**



**Fig.S80** DEPT-135 Spectrum of **4h**



**Fig.S81** <sup>1</sup>H NMR Spectrum of **4i**

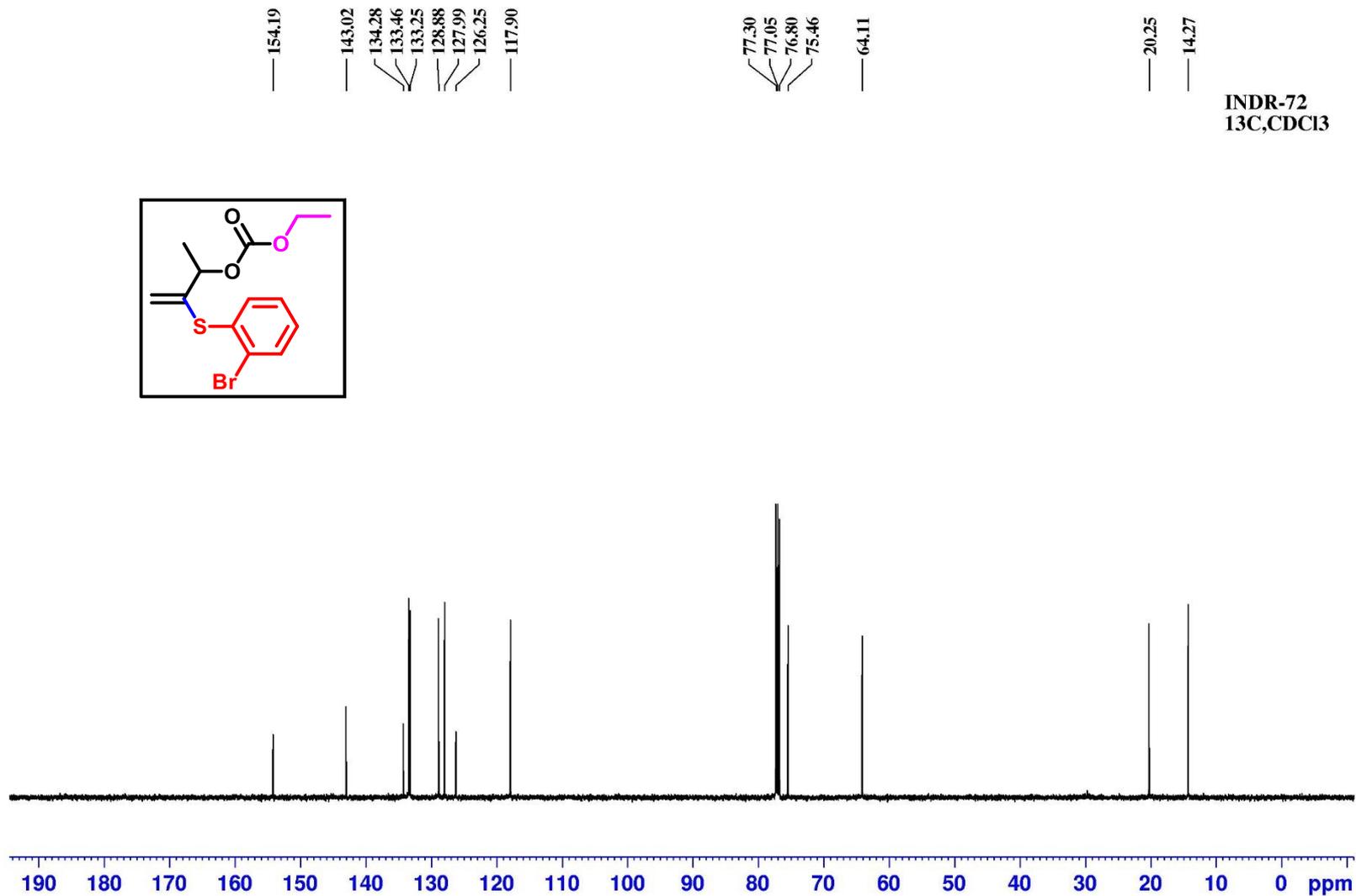
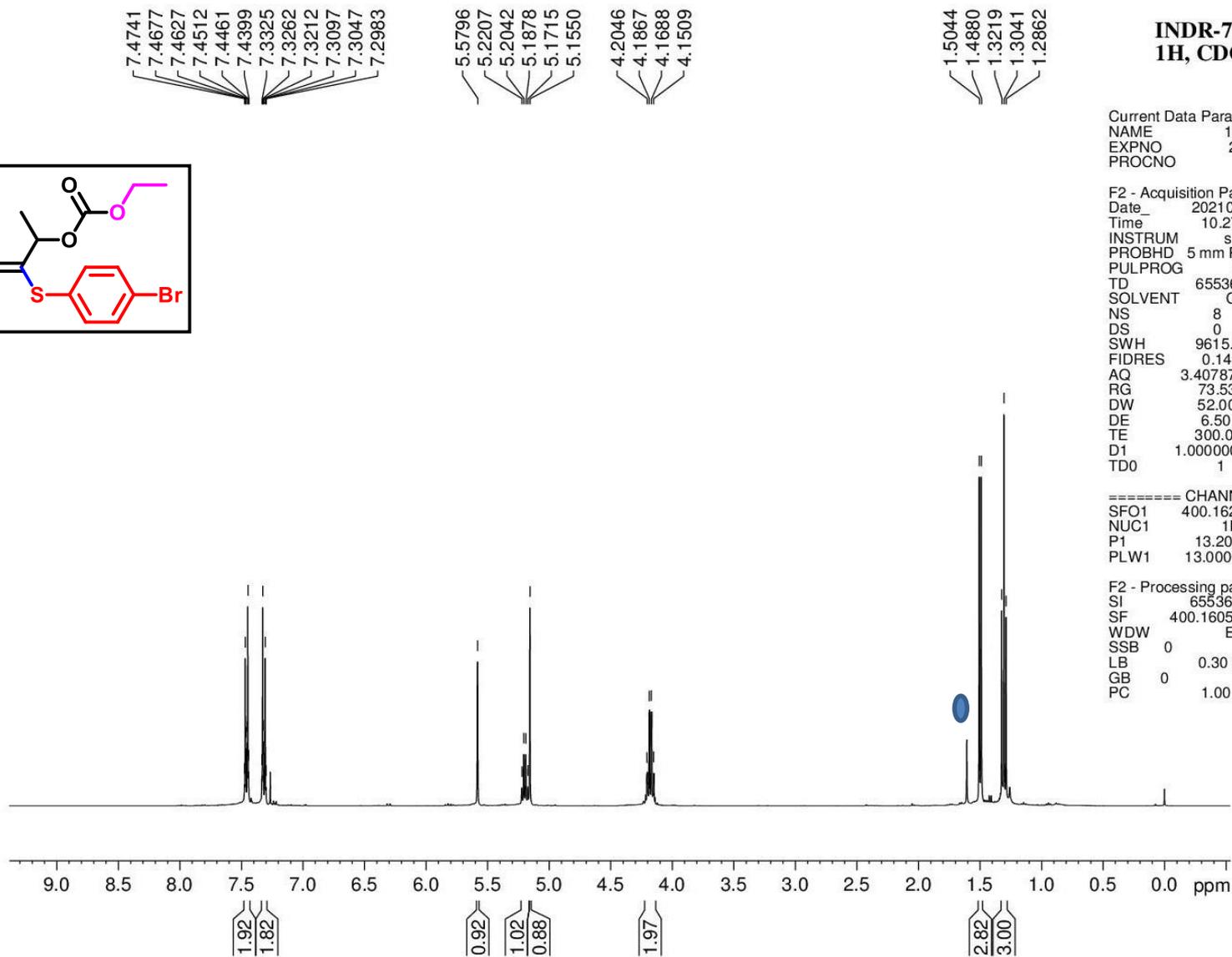
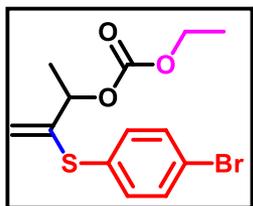


Fig.S82 <sup>13</sup>C NMR Spectrum of 4i



**Fig.S83** <sup>1</sup>H NMR Spectrum of **4j**

— 154.15  
— 144.48  
134.05  
132.37  
131.71  
— 122.16  
— 116.35  
77.30  
77.05  
76.79  
75.47  
— 64.11  
— 20.21  
— 14.25  
INDR-73  
13C, CDCl3

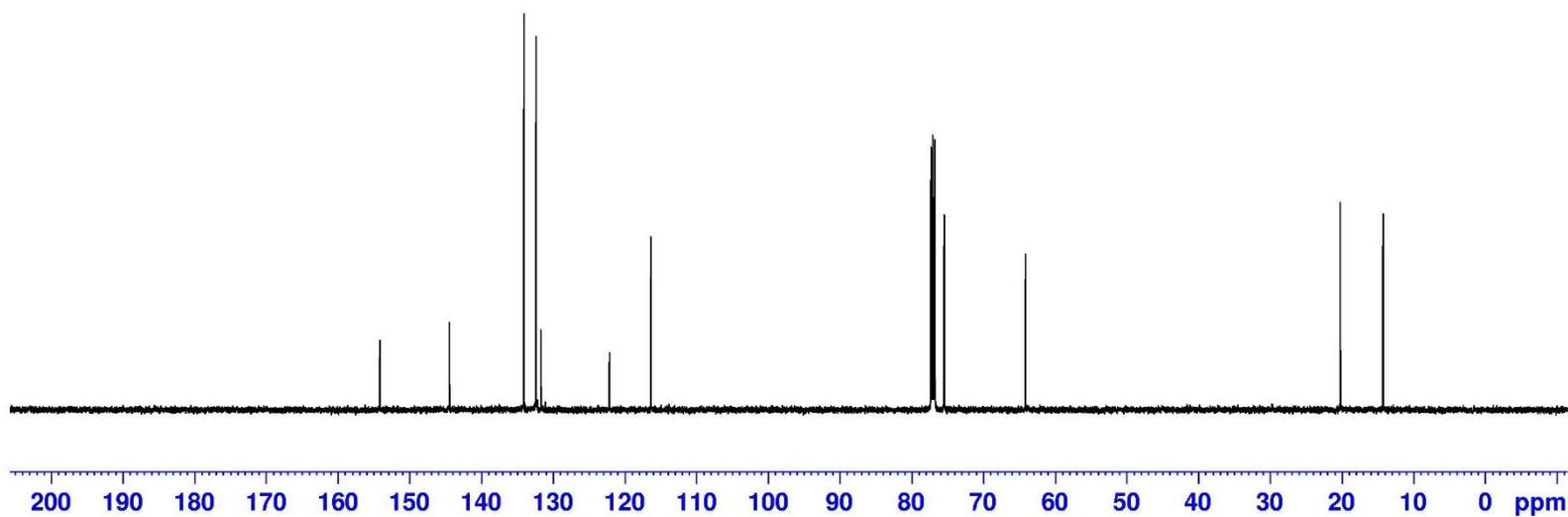
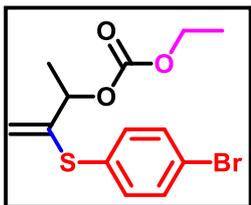
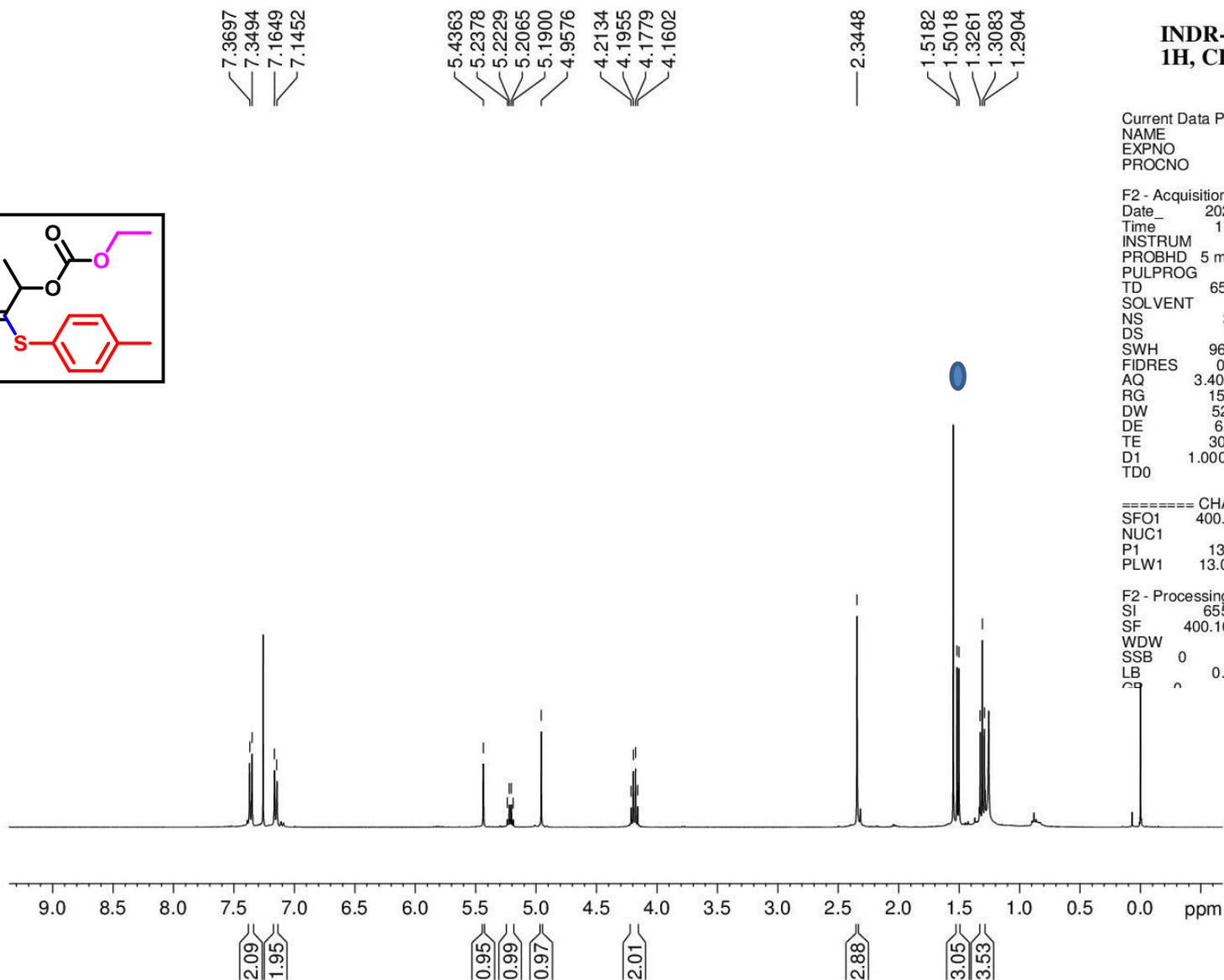
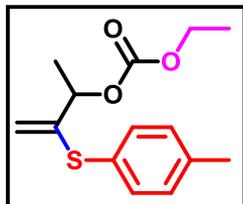


Fig.S84 <sup>13</sup>C NMR Spectrum of 4j



**INDR-76**  
**1H, CDCl<sub>3</sub>**

Current Data Parameters  
NAME 1H  
EXPNO 120  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210315  
Time 11.43  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 32  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 159.22  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.0000000 sec  
TD0 1

==== CHANNEL f1 ====  
SFO1 400.1629712 MHz  
NUC1 1H  
P1 13.20 usec  
PLW1 13.00000000 W

F2 - Processing parameters  
SI 65536  
SF 400.1605098 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz

● H<sub>2</sub>O

**Fig.S85** <sup>1</sup>H NMR Spectrum of **4k**

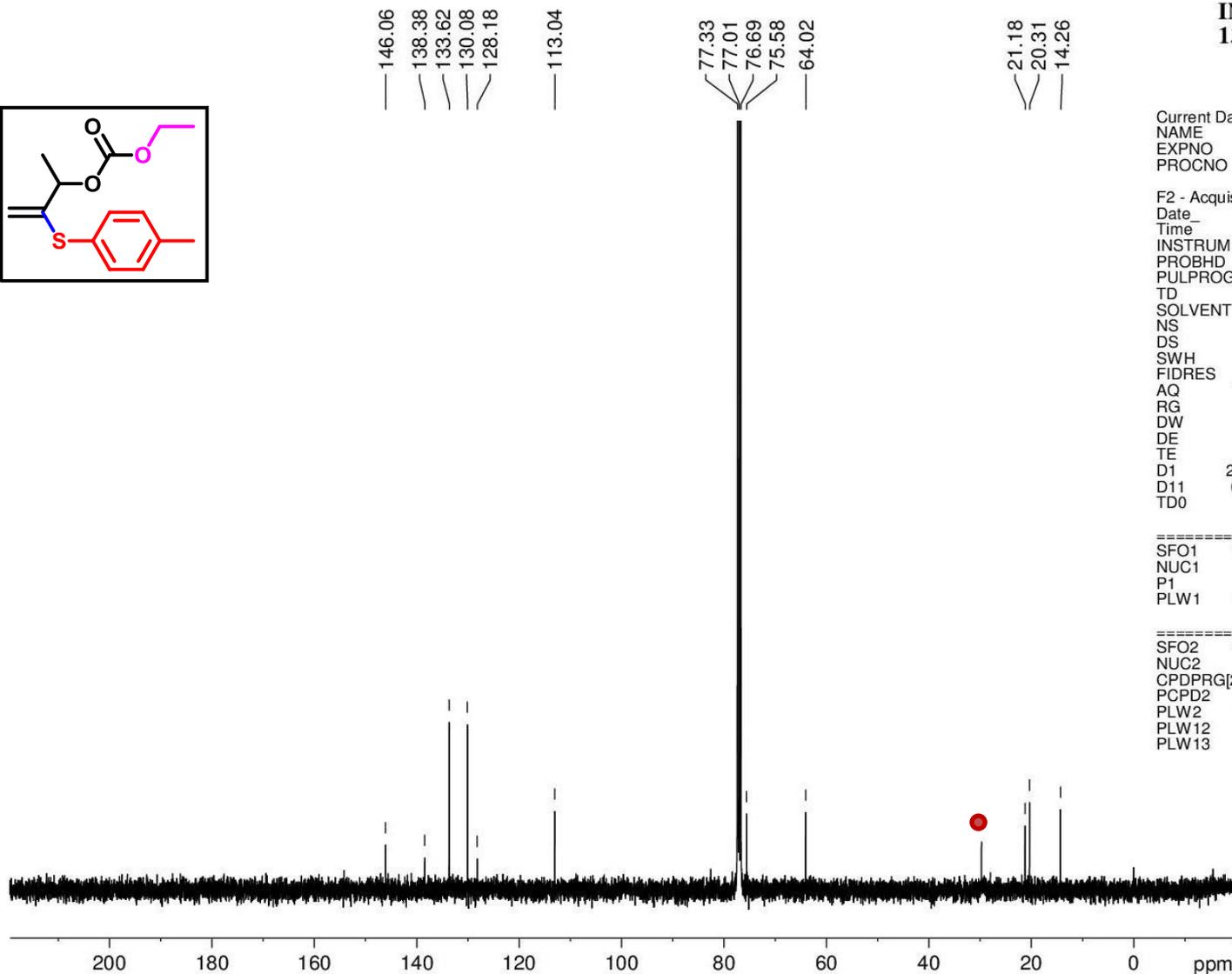
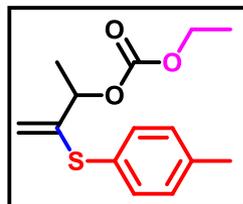
**INDR-76**  
**<sup>13</sup>C, CDCl<sub>3</sub>**

Current Data Parameters  
NAME 13C  
EXPNO 170  
PROCNO 1

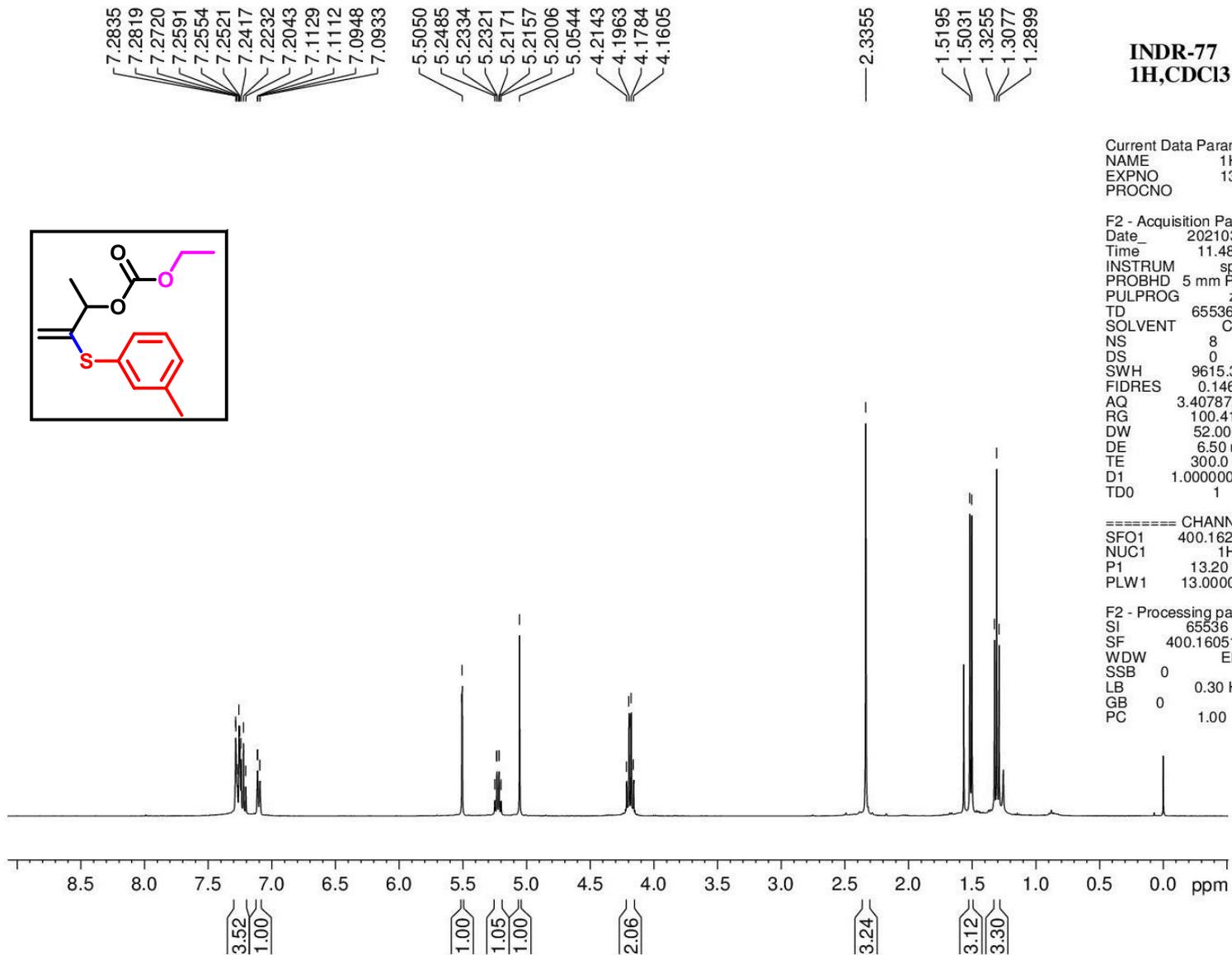
F2 - Acquisition Parameters  
Date\_ 20210317  
Time\_ 4.52  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 1024  
DS 0  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631488 sec  
RG 201.48  
DW 20.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.0000000 sec  
D11 0.0300000 sec  
TD0 1

===== CHANNEL f1 =====  
SFO1 100.6304993 MHz  
NUC1 <sup>13</sup>C  
P1 9.90 usec  
PLW1 53.0000000 W

===== CHANNEL f2 =====  
SFO2 400.1621006 MHz  
NUC2 <sup>1</sup>H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 13.0000000 W  
PLW12 0.27963999 W  
PLW13 0.22651000 W



**Fig.S86** <sup>13</sup>C NMR Spectrum of **4k**



**Fig.S87**  $^1\text{H}$  NMR Spectrum of **4I**

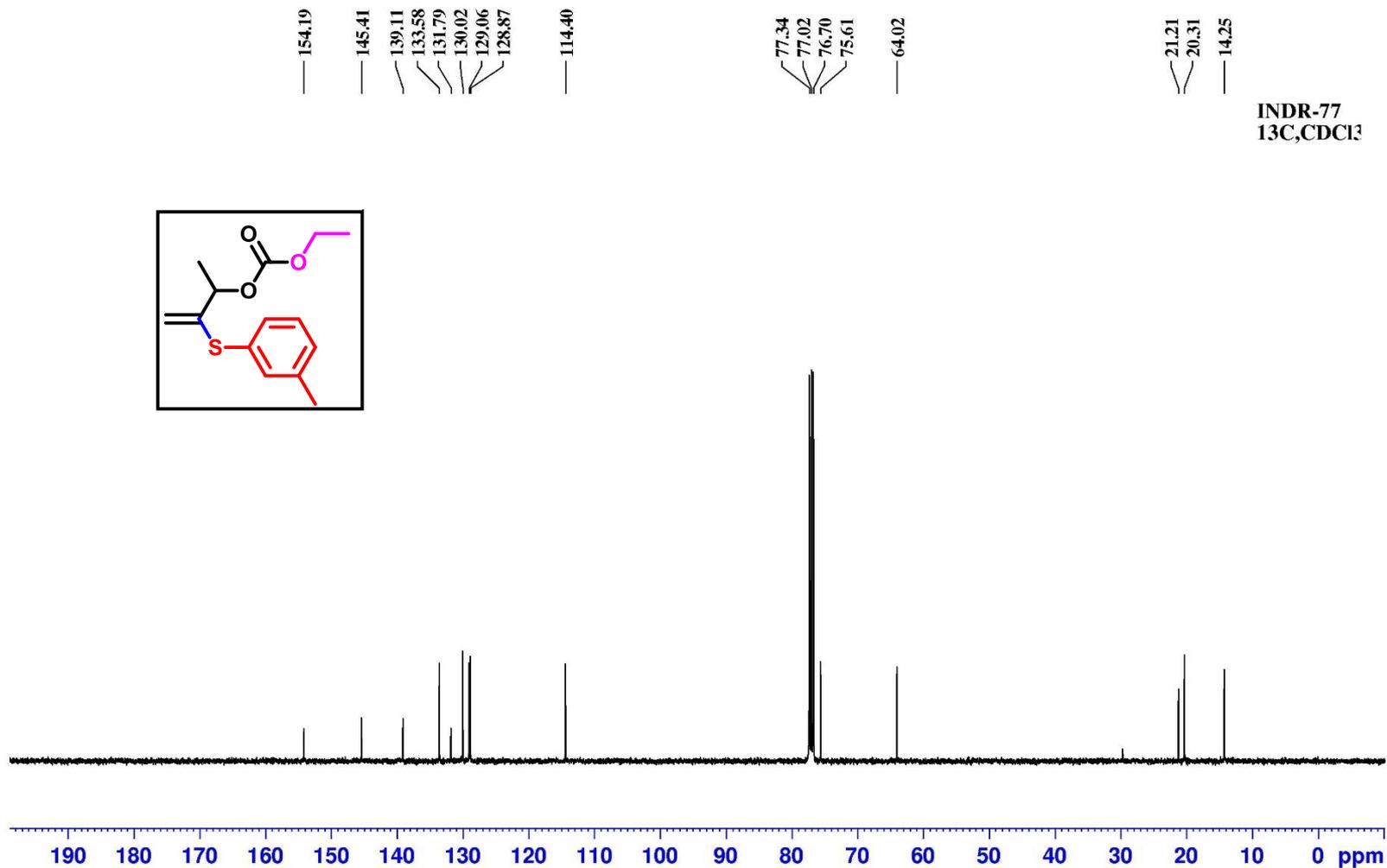
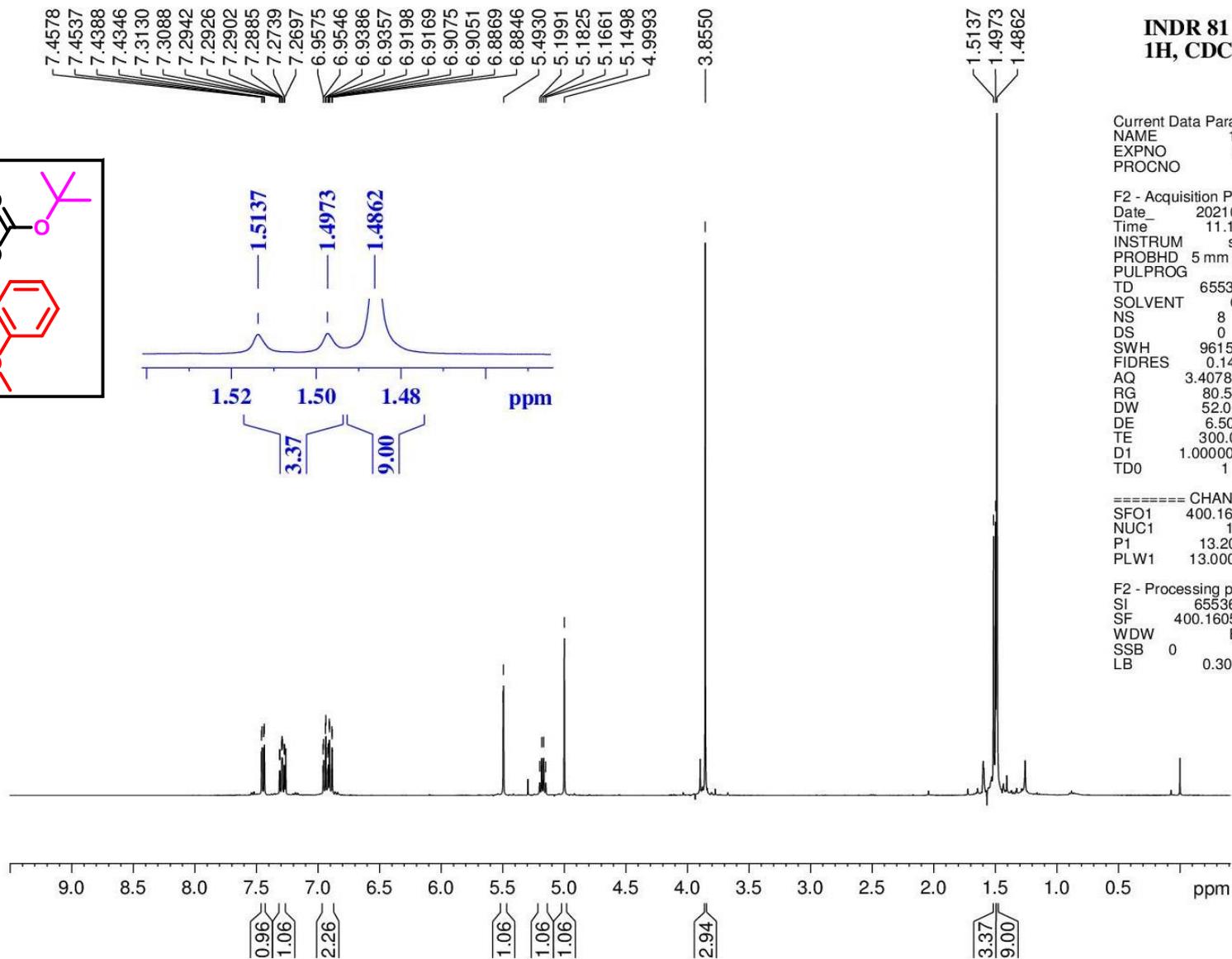
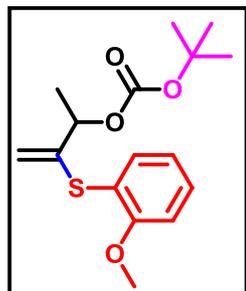


Fig.S88 <sup>13</sup>C NMR Spectrum of 4I



**INDR 81  
1H, CDCl3**

Current Data Parameters  
 NAME 1H  
 EXPNO 20  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20210319  
 Time 11.13  
 INSTRUM spect  
 PROBHD 5 mm PABBO  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 80.54  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 :  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 13.20 usec  
 PLW1 13.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 400.1605088 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz

**Fig.S89** <sup>1</sup>H NMR Spectrum of **4m**

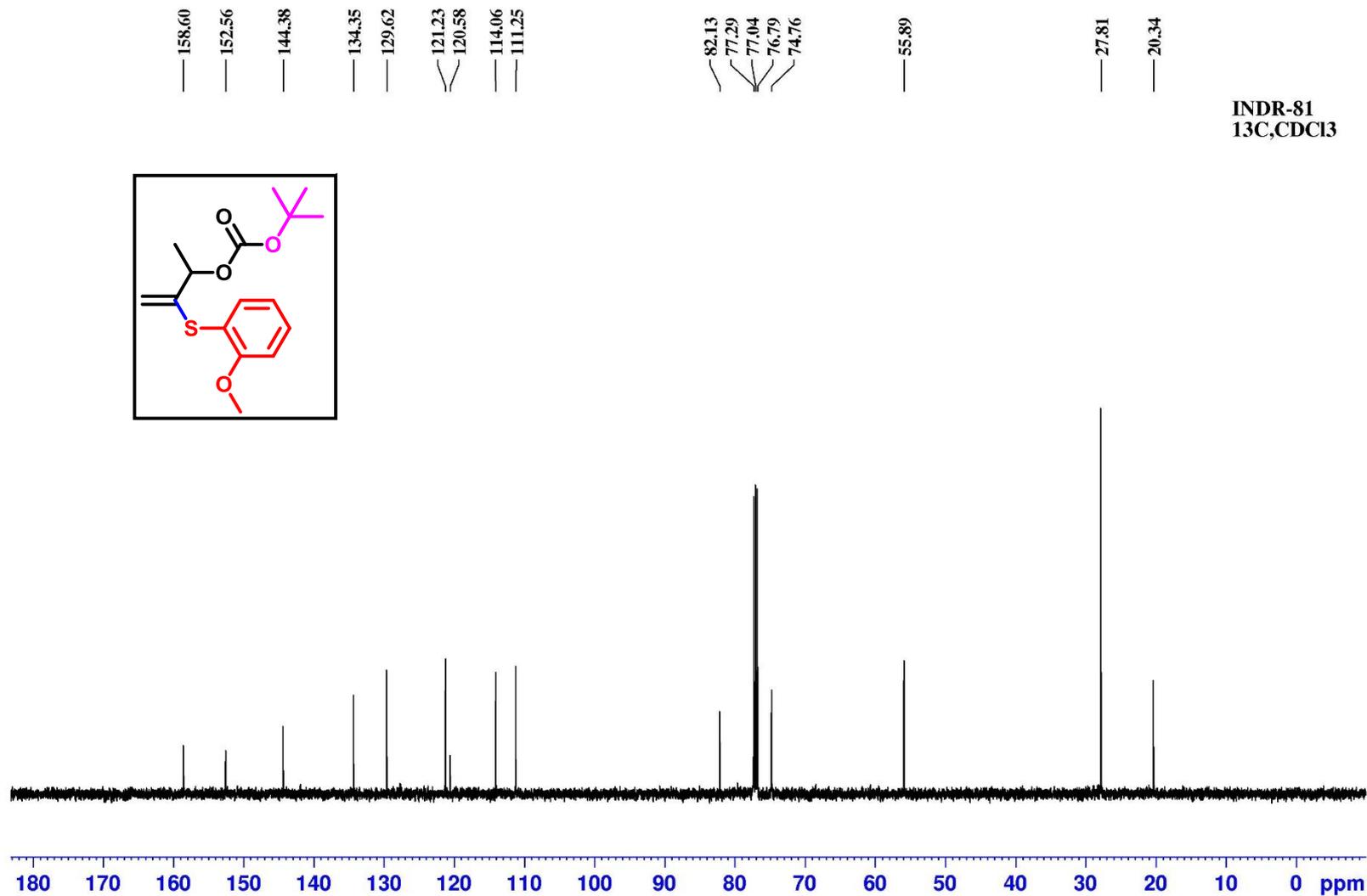
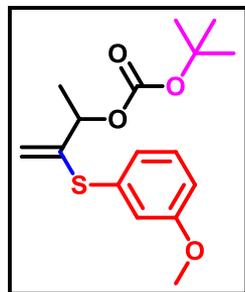


Fig.S90 <sup>13</sup>C NMR Spectrum of 4m





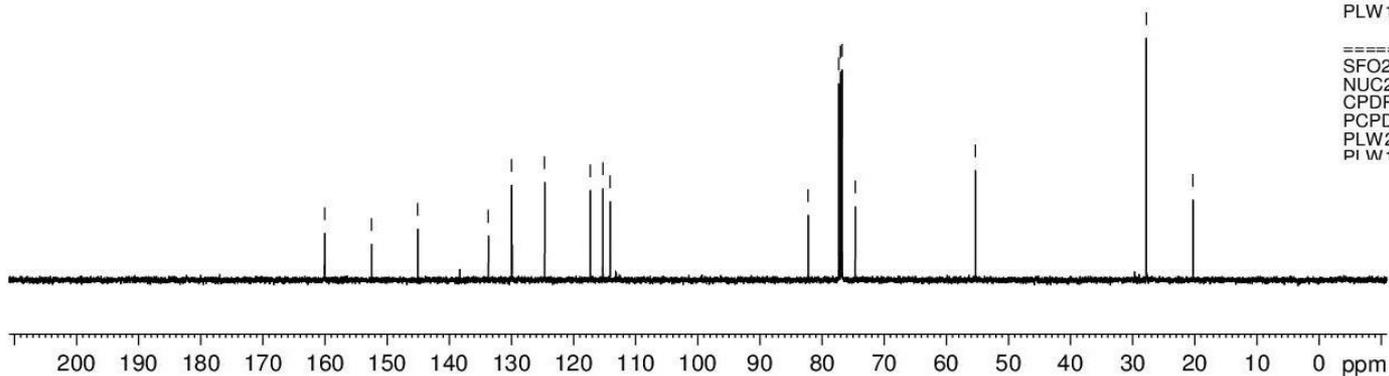
**INDR-82  
13C, CDCl<sub>3</sub>**

Current Data Parameters  
 NAME 13C  
 EXPNO 170  
 PROCNO 1

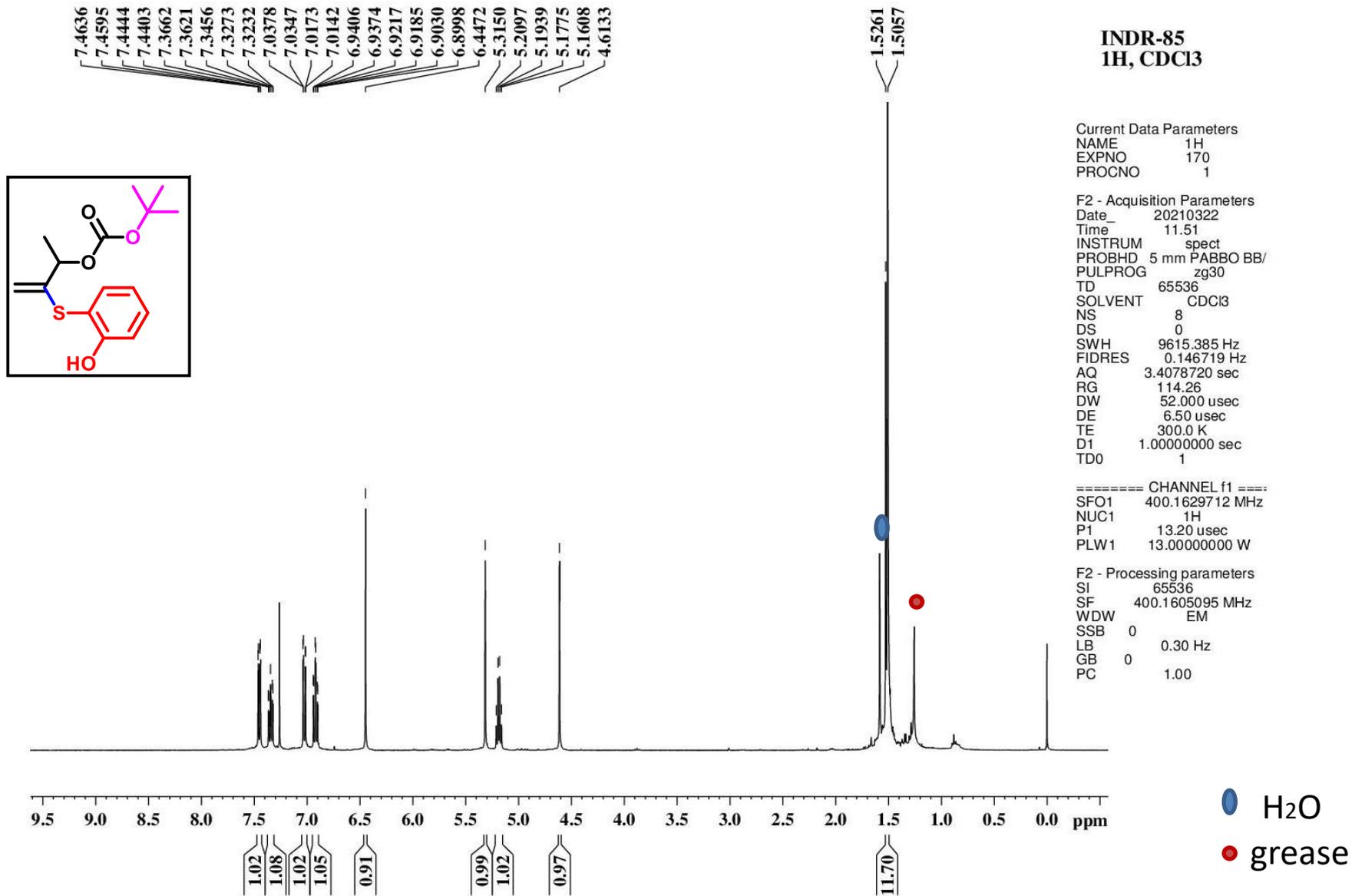
F2 - Acquisition Parameters  
 Date\_ 20210324  
 Time 11.19  
 INSTRUM spect  
 PROBHD 5 mm PATXI 1H  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 1024  
 DS 0  
 SWH 29761.904 Hz  
 FIDRES 0.454131 Hz  
 AQ 1.1010048 sec  
 RG 56.22  
 DW 16.800 usec  
 DE 6.50 usec  
 TE 299.1 K  
 D1 2.0000000 sec  
 D11 0.0300000 sec  
 TD0 1

===== CHANNEL f1 ==  
 SFO1 125.9077573 MHz  
 NUC1 13C  
 P1 9.23 usec  
 PLW1 244.0000000 W

===== CHANNEL f2 ==  
 SFO2 500.6783527 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 80.00 usec  
 PLW2 13.60000038 W  
 P1 W1? 0.08840500 W



**Fig.S92** <sup>13</sup>C NMR Spectrum of **4n**



**Fig.S93** <sup>1</sup>H NMR Spectrum of **4o**

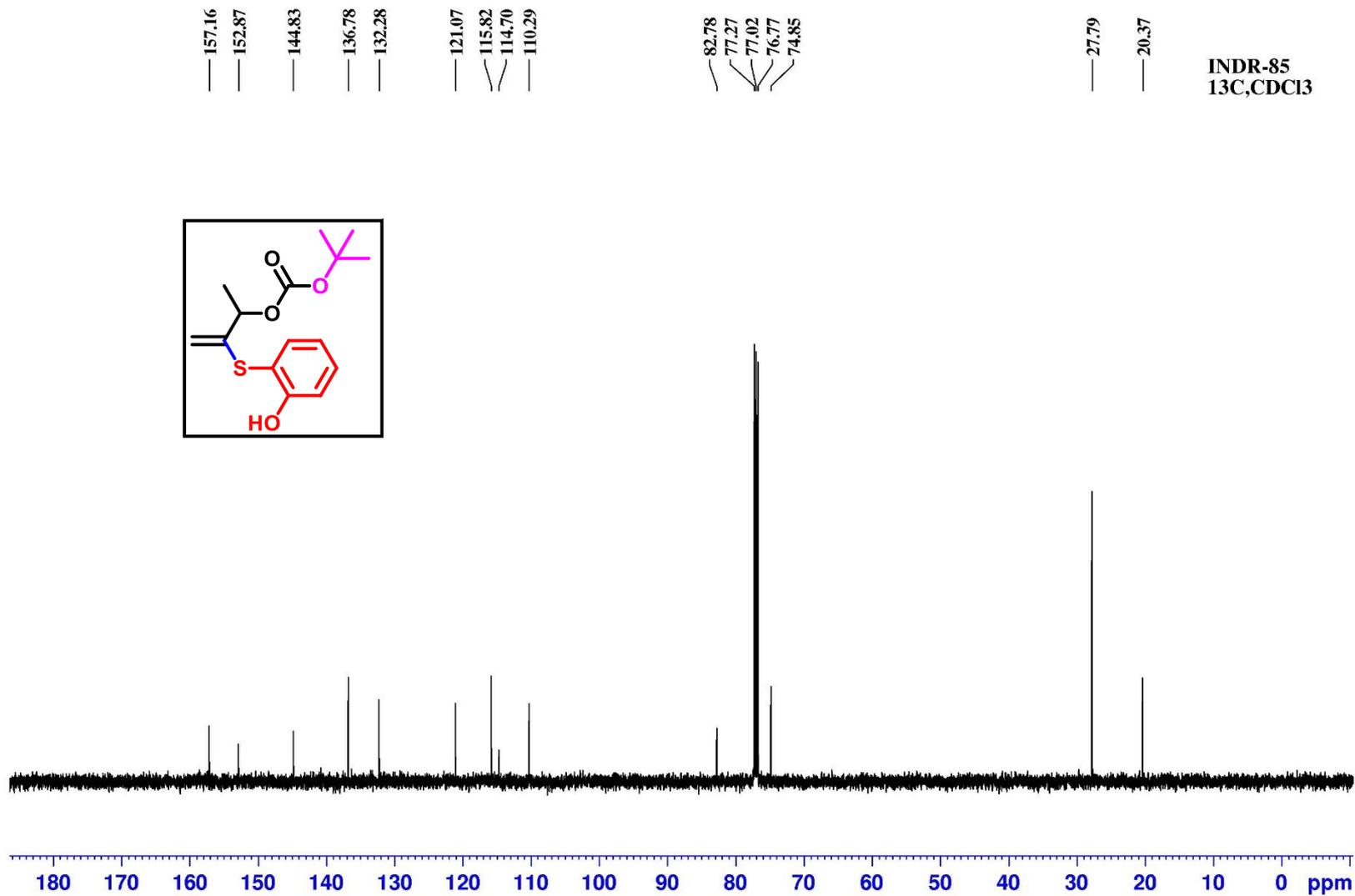
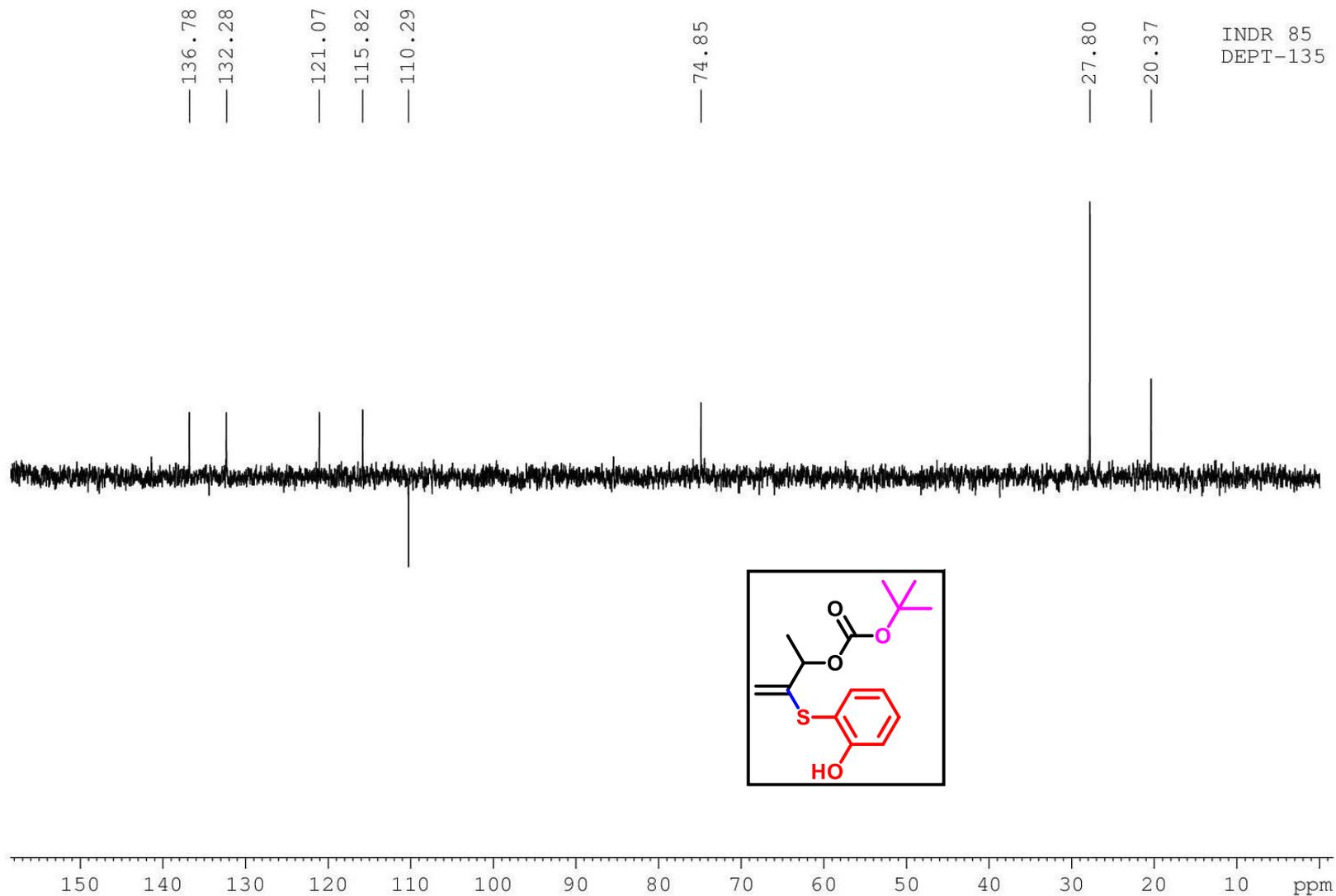


Fig.S94  $^{13}\text{C}$  NMR Spectrum of **4o**



**Fig.S95** DEPT-135 Spectrum of **4o**

INDR-85  
HSQC

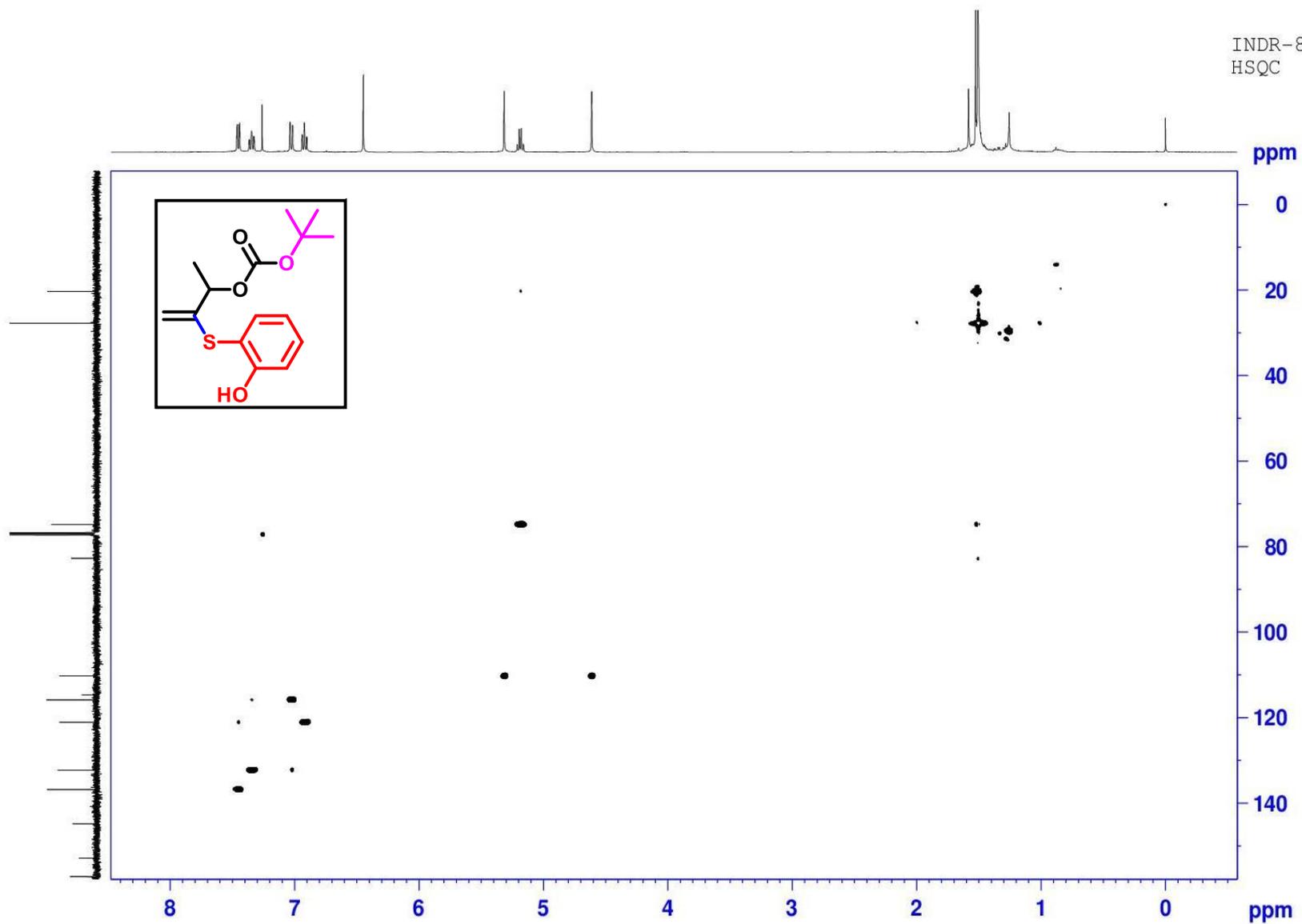


Fig.S96 HSQC Spectrum of **4o**

**INDR-107  
1H, CDCl3**

Current Data Parameters

NAME 1H  
EXPNO 30  
PROCNO 1

F2 - Acquisition Parameters

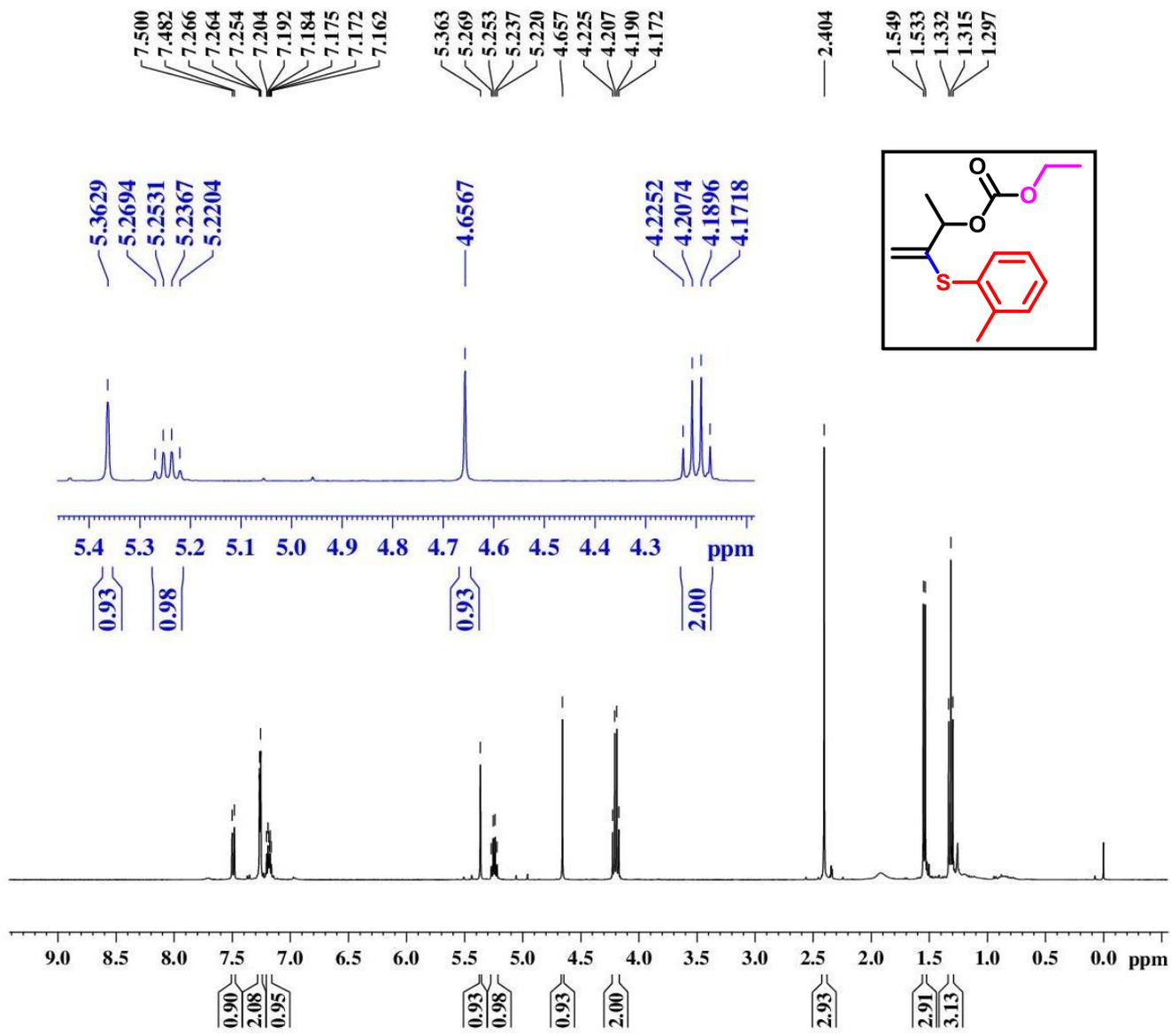
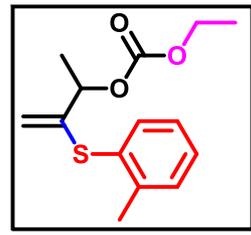
Date\_ 20210628  
Time 11.12  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 89.7  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====

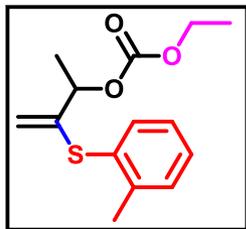
SFO1 400.1629712 MHz  
NUC1 1H  
P1 13.20 usec  
PLW1 13.00000000 W

F2 - Processing parameters

SI 65536  
SF 400.1605096 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Fig.S97** <sup>1</sup>H NMR Spectrum of **4p**



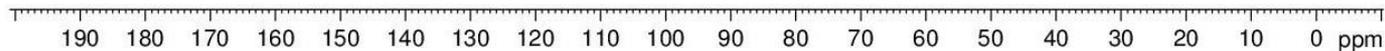
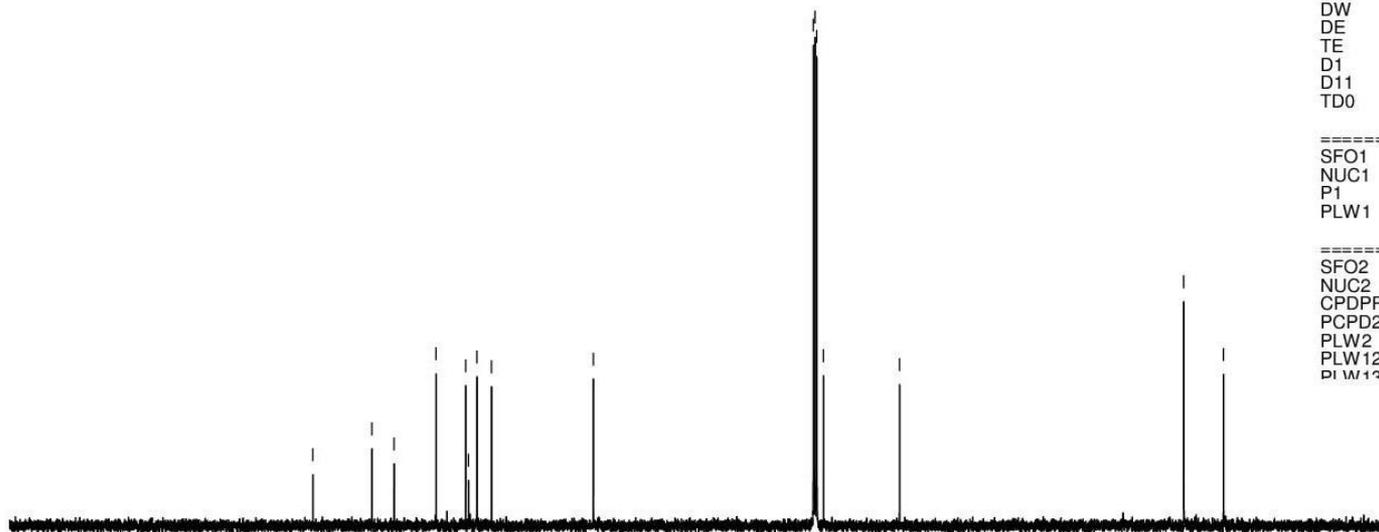
**IND-107**  
**<sup>13</sup>C, CDCl<sub>3</sub>**

Current Data Parameters  
NAME 13C  
EXPNO 110  
PROCNO 1

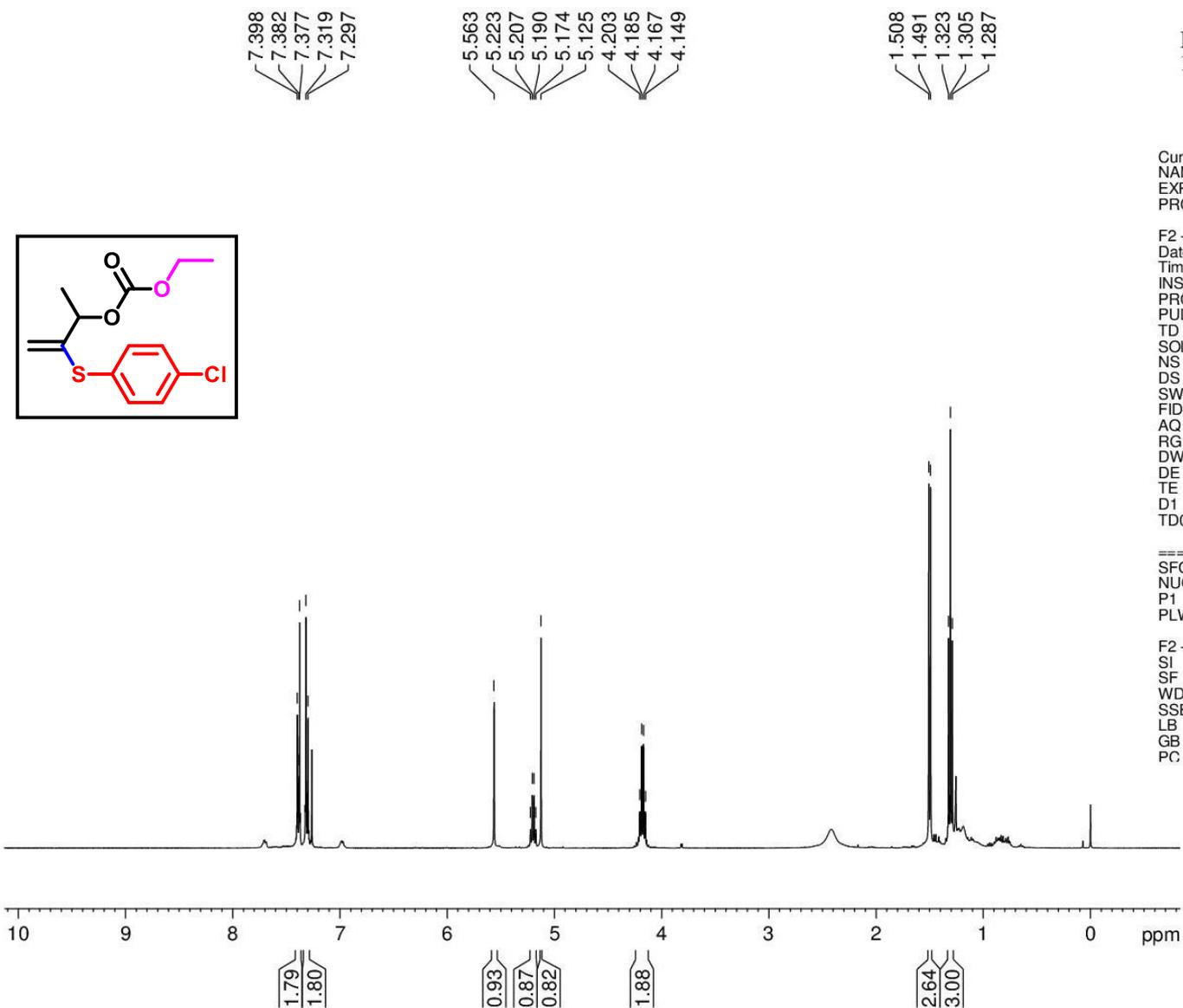
F2 - Acquisition Parameters  
Date\_ 20210630  
Time 9.32  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 1024  
DS 4  
SWH 29761.904 Hz  
FIDRES 0.454131 Hz  
AQ 1.1010048 sec  
RG 81.53  
DW 16.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1

==== CHANNEL f1 ====  
SFO1 125.9077573 MHz  
NUC1 <sup>13</sup>C  
P1 9.23 usec  
PLW1 244.0000000 W

==== CHANNEL f2 ====  
SFO2 500.6783527 MHz  
NUC2 <sup>1</sup>H  
CPDPRG2 waltz16  
PCPD2 80.00 usec  
PLW2 13.60000038 W  
PLW12 0.08840500 W  
PLW13 0.05667900 W



**Fig.S98** <sup>13</sup>C NMR Spectrum of **4p**



**INDR-113**  
**1H, CDCl3**

Current Data Parameters  
NAME 1H  
EXPNO 70  
PROCNO 1

F2 - Acquisition Parameter  
Date\_ 20210705  
Time 10.51  
INSTRUM spect  
PROBHD 5 mm PABBO E  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 114.26  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =:  
SFO1 400.1629712 MI  
NUC1 1H  
P1 13.20 usec  
PLW1 13.00000000 W

F2 - Processing parameter  
SI 65536  
SF 400.1605086 MH:  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**Fig.S99** <sup>1</sup>H NMR Spectrum of **4q**

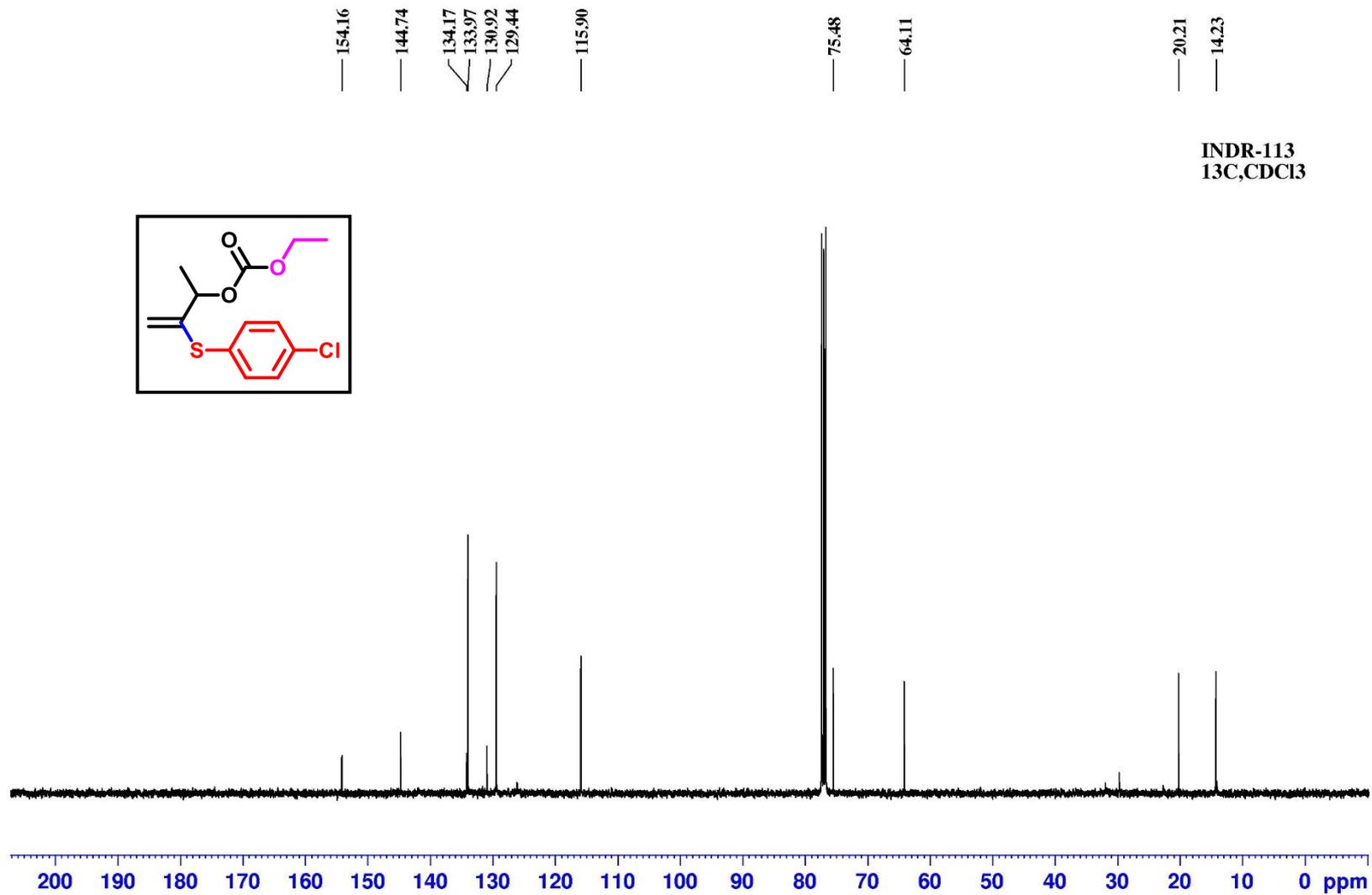
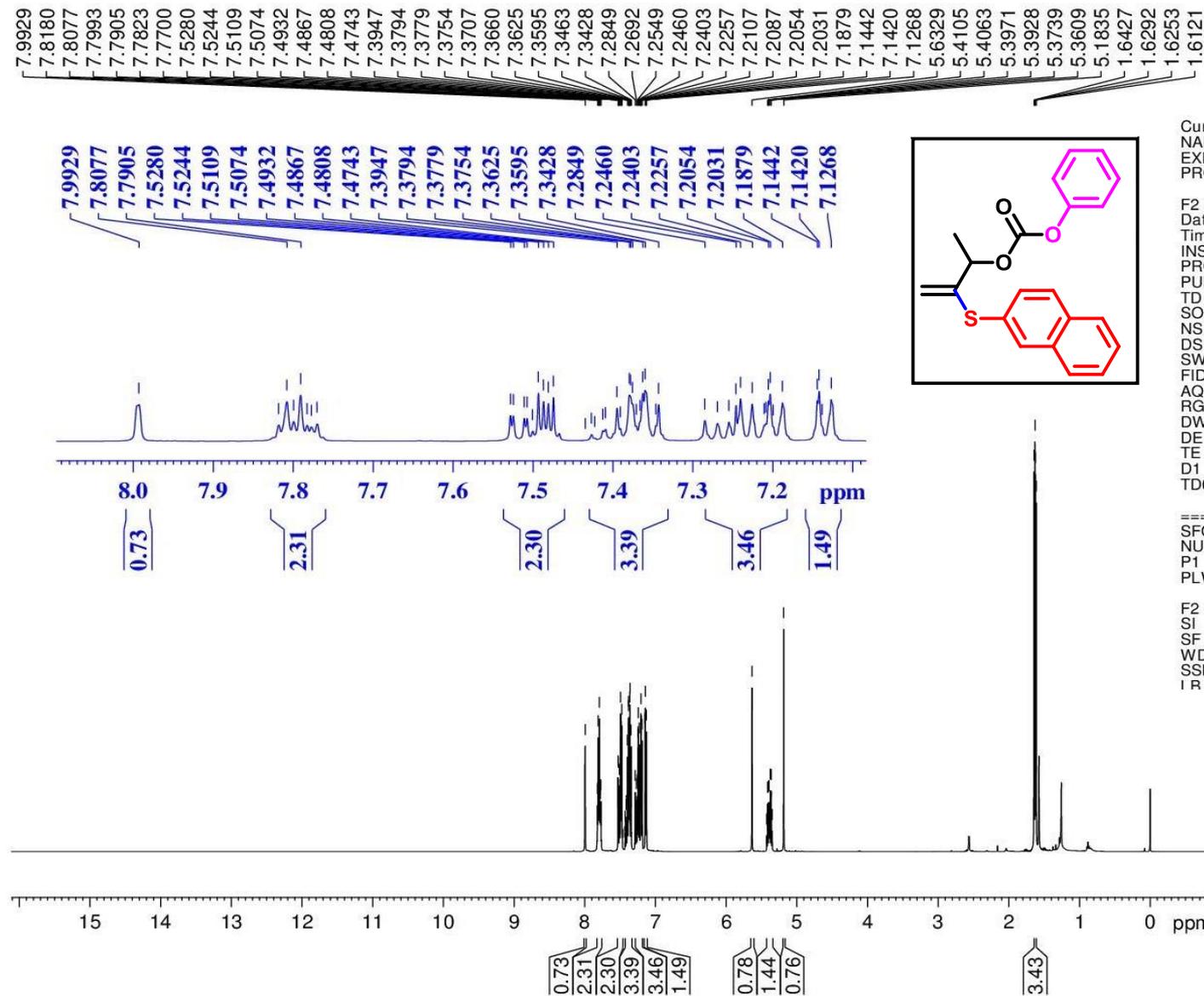


Fig.S100 <sup>13</sup>C NMR Spectrum of 4q



**INDR 87**  
**1H,CDCl3**

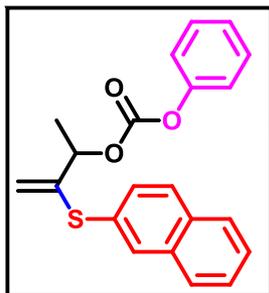
Current Data Parameters  
NAME 1H  
EXPNO 40  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210326  
Time 3.08  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10026.738 Hz  
FIDRES 0.152996 Hz  
AQ 3.2680619 sec  
RG 69.83  
DW 49.867 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

==== CHANNEL f1 ====  
SFO1 500.6794419 MHz  
NUC1 1H  
P1 6.45 usec  
PLW1 13.60000038 W

F2 - Processing parameters  
SI 65536  
SF 500.6763685 MHz  
WDW EM  
SSB 0  
IR 0.30 Hz

**Fig.S101** <sup>1</sup>H NMR Spectrum of **4r**



152.72  
151.05  
144.76  
133.80  
132.76  
132.19  
129.81  
129.50  
129.45  
129.01  
127.77  
127.62  
126.65  
126.15  
126.01  
121.03  
120.99  
115.69

77.30  
77.05  
76.79  
64.85

20.24

INDR 87  
13C, CDCl3

Current Data Parameters  
NAME 13C  
EXPNO 60  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210331  
Time 8.40  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 512  
DS 4  
SWH 29761.904 Hz  
FIDRES 0.454131 Hz  
AQ 1.1010048 sec  
RG 87.95  
DW 16.800 usec  
DE 6.50 usec  
TE 300.0 K  
D1 2.0000000 sec  
D11 0.0300000 sec  
TDO 1

==== CHANNEL f1 ===  
SFO1 125.9077573 MH;  
NUC1 13C  
P1 9.23 usec  
PLW1 244.0000000 W

==== CHANNEL f2 ===  
SFO2 500.6783527 MH;  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 80.00 usec  
PLW2 13.60000038 W  
PLW12 0.08840500 W  
PLW13 0.05657900 W

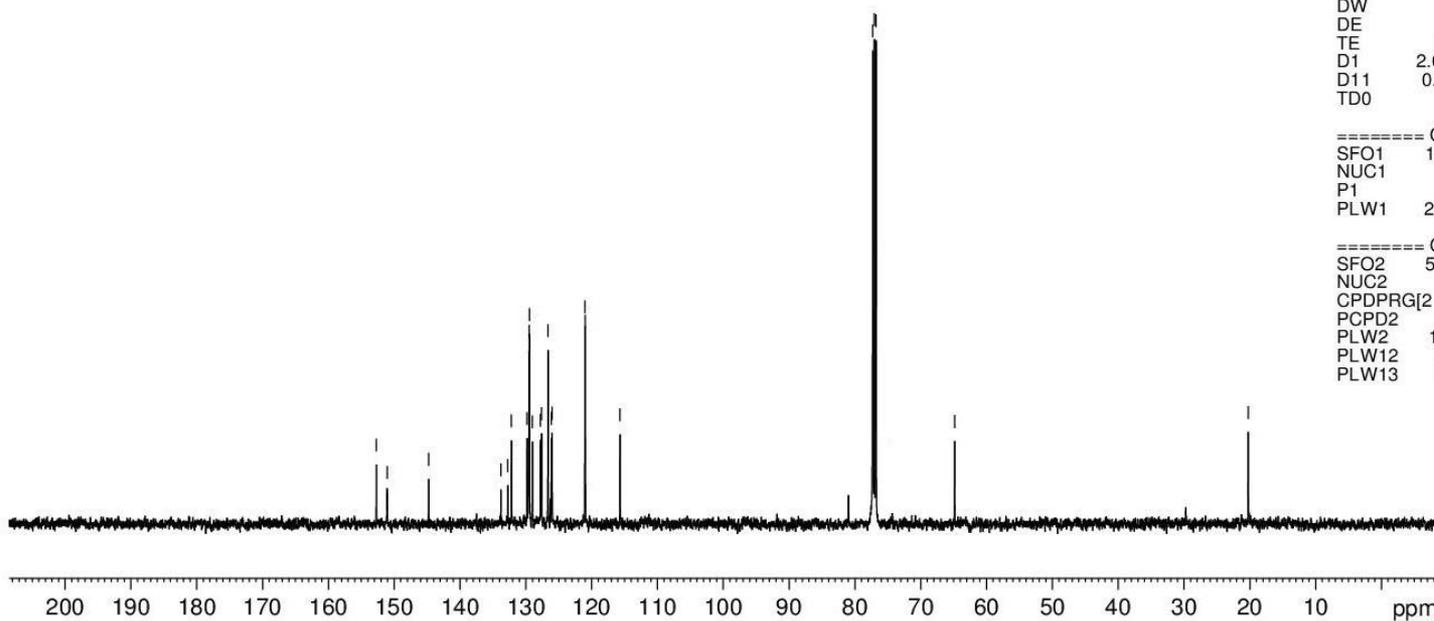
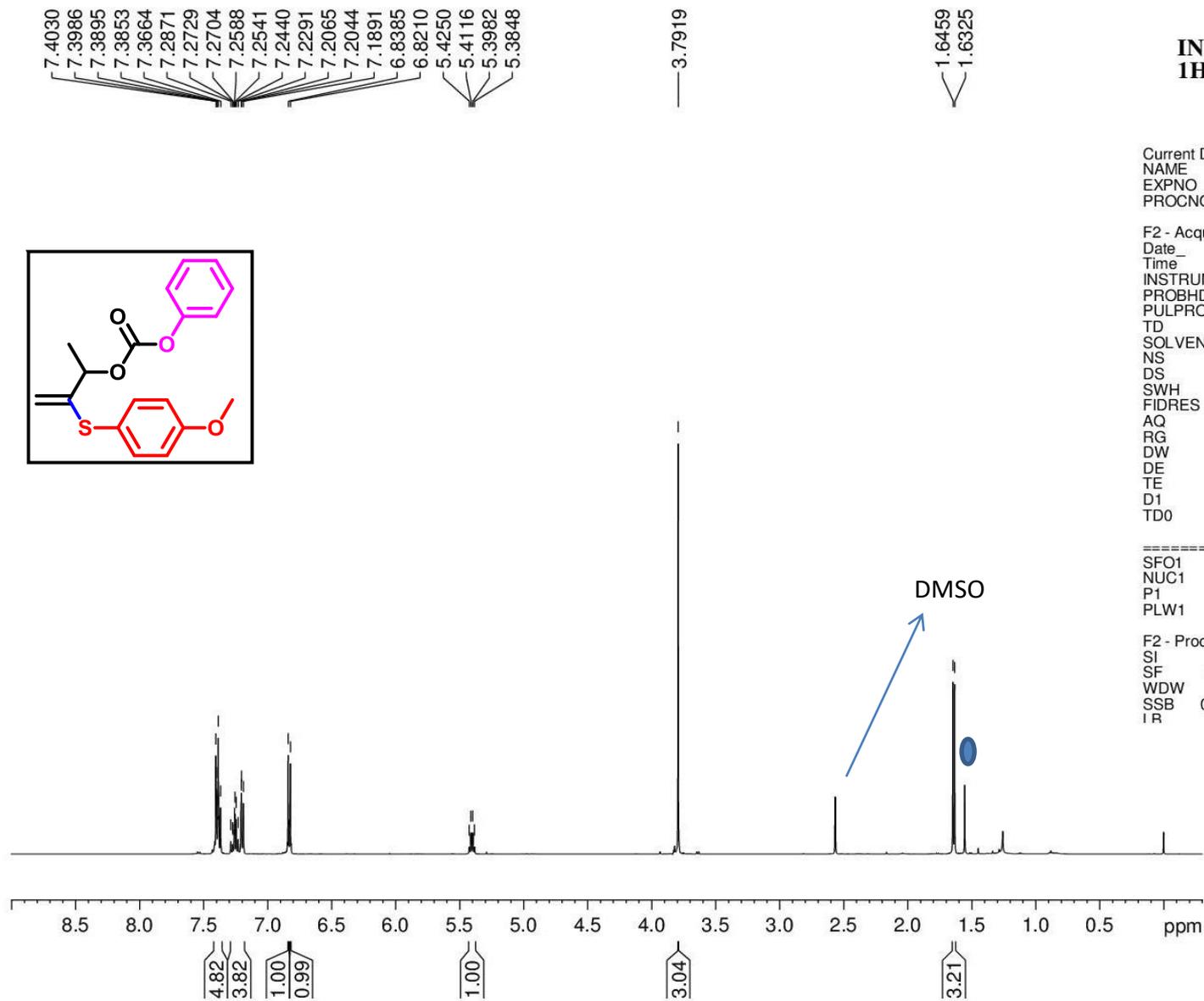


Fig.S102 <sup>13</sup>C NMR Spectrum of 4r



**INDR 88  
1H,CDCI3**

Current Data Parameters

NAME 1H  
EXPNO 50  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20210326  
Time 3.13  
INSTRUM spect  
PROBHD 5 mm PATXI 1H/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10026.738 Hz  
FIDRES 0.152996 Hz  
AQ 3.2680619 sec  
RG 99.13  
DW 49.867 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====

SFO1 500.6794419 MHz  
NUC1 1H  
P1 6.45 usec  
PLW1 13.60000038 W

F2 - Processing parameters

SI 65536  
SF 500.6763646 MHz  
WDW EM  
SSB 0  
IR 0.30 Hz

**Fig.S103** <sup>1</sup>H NMR Spectrum of **4s**

● H<sub>2</sub>O

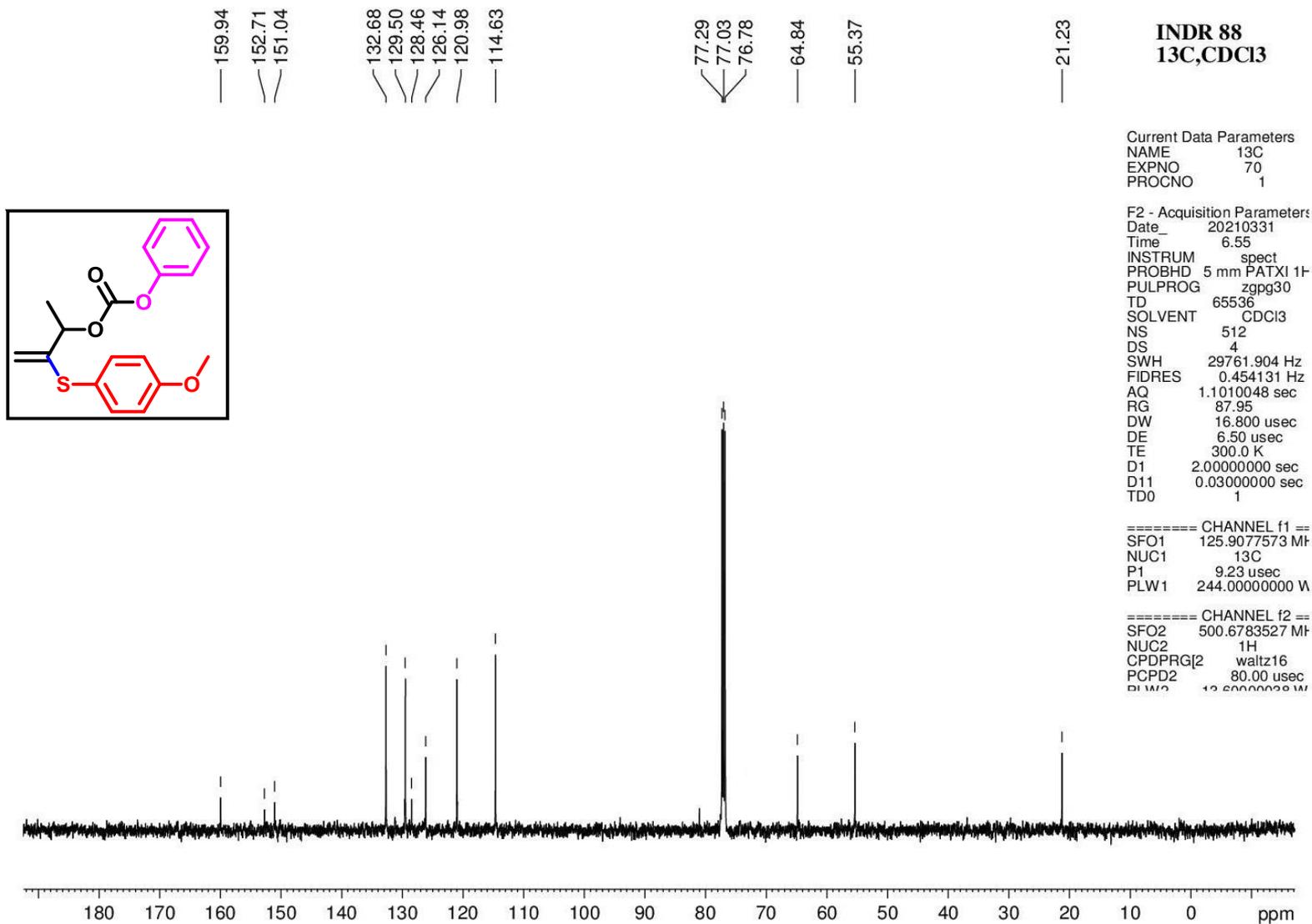


Fig.S104 <sup>13</sup>C NMR Spectrum of 4s

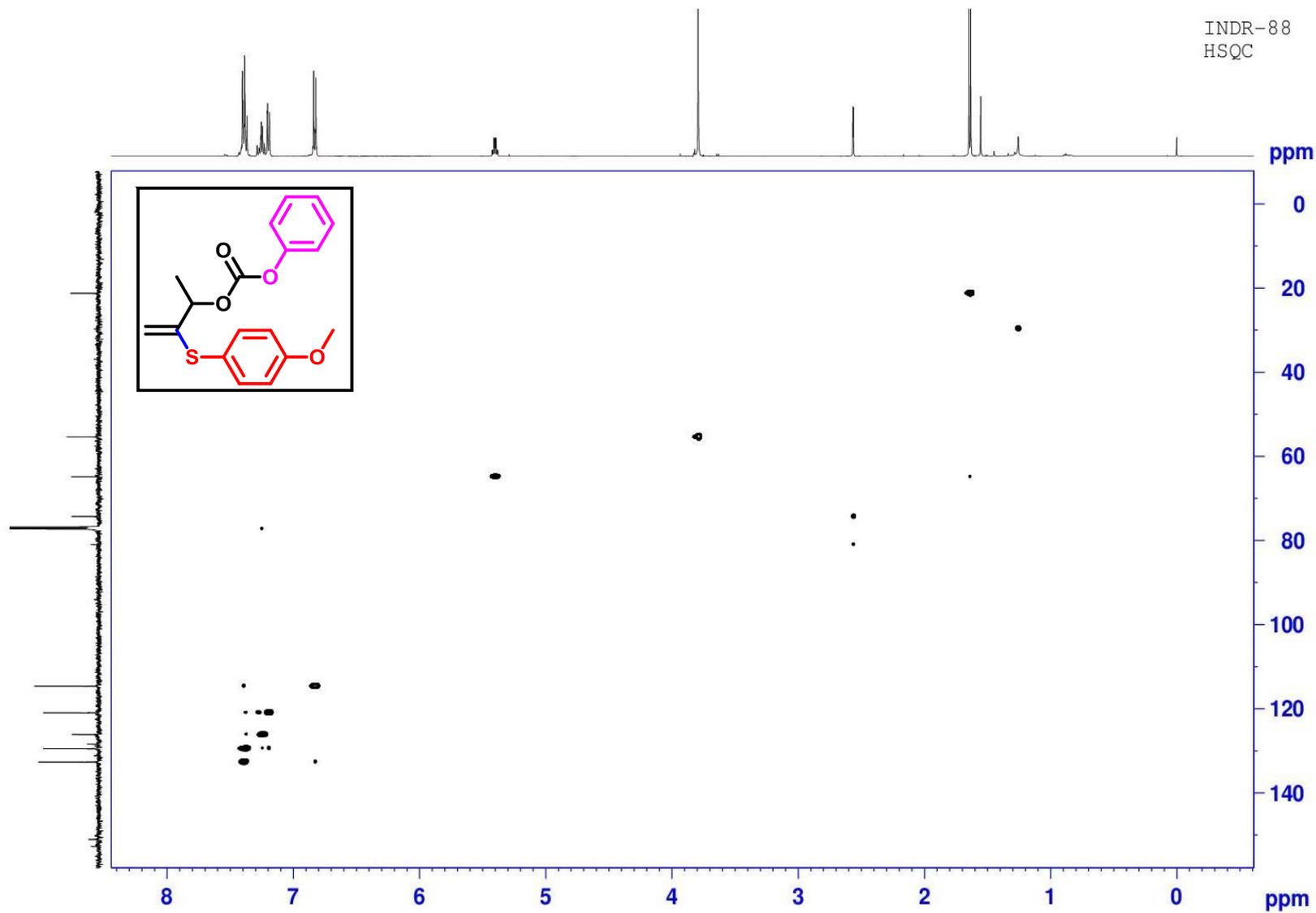
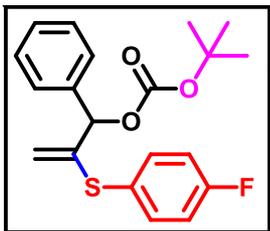
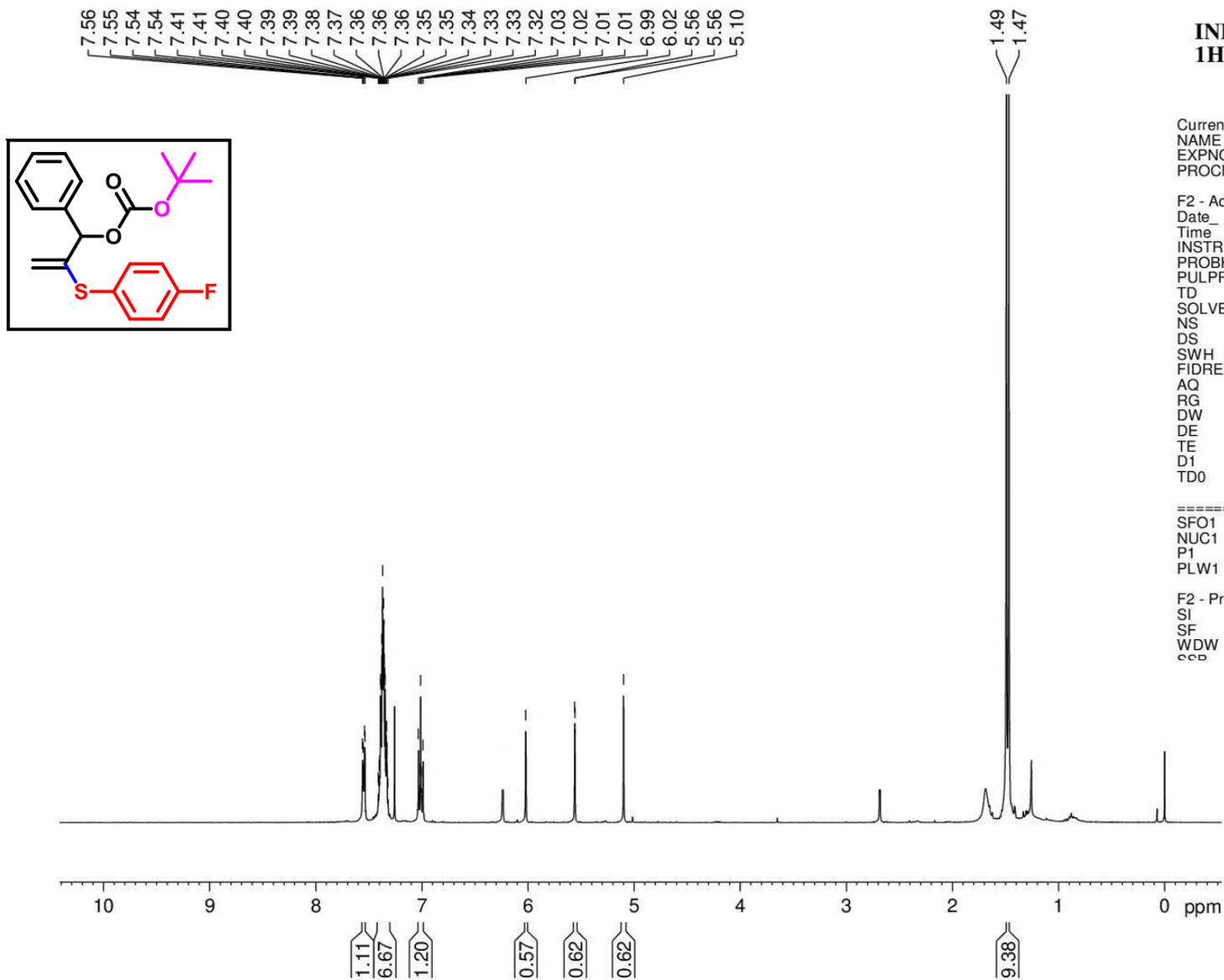


Fig.S105 HSQC Spectrum of 4s



**INDR 103  
1H, CDCI3**

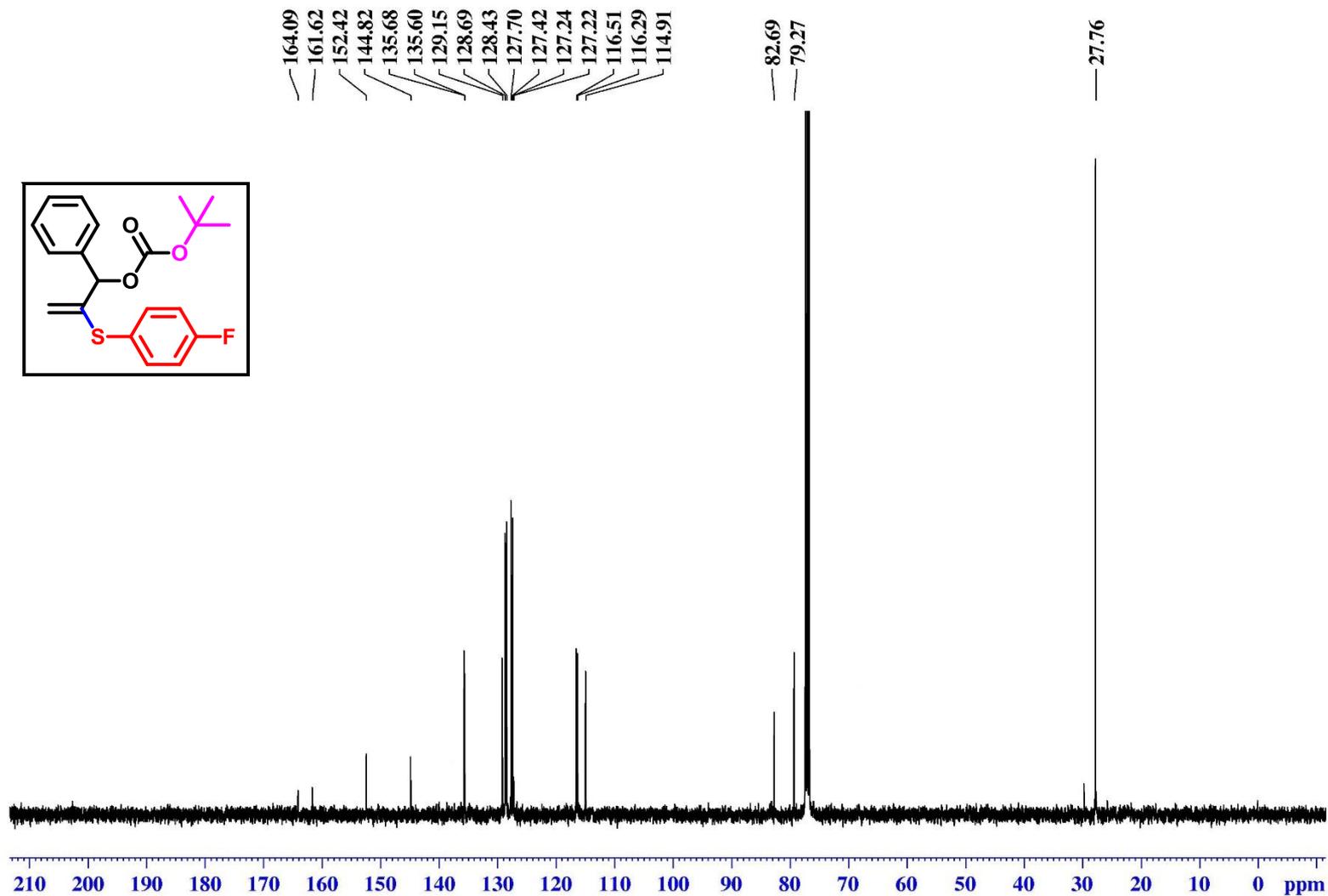
Current Data Parameters  
 NAME 1H  
 EXPNO 130  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20210629  
 Time 14.06  
 INSTRUM spect  
 PROBHD 5 mm PABBO E  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 100.41  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

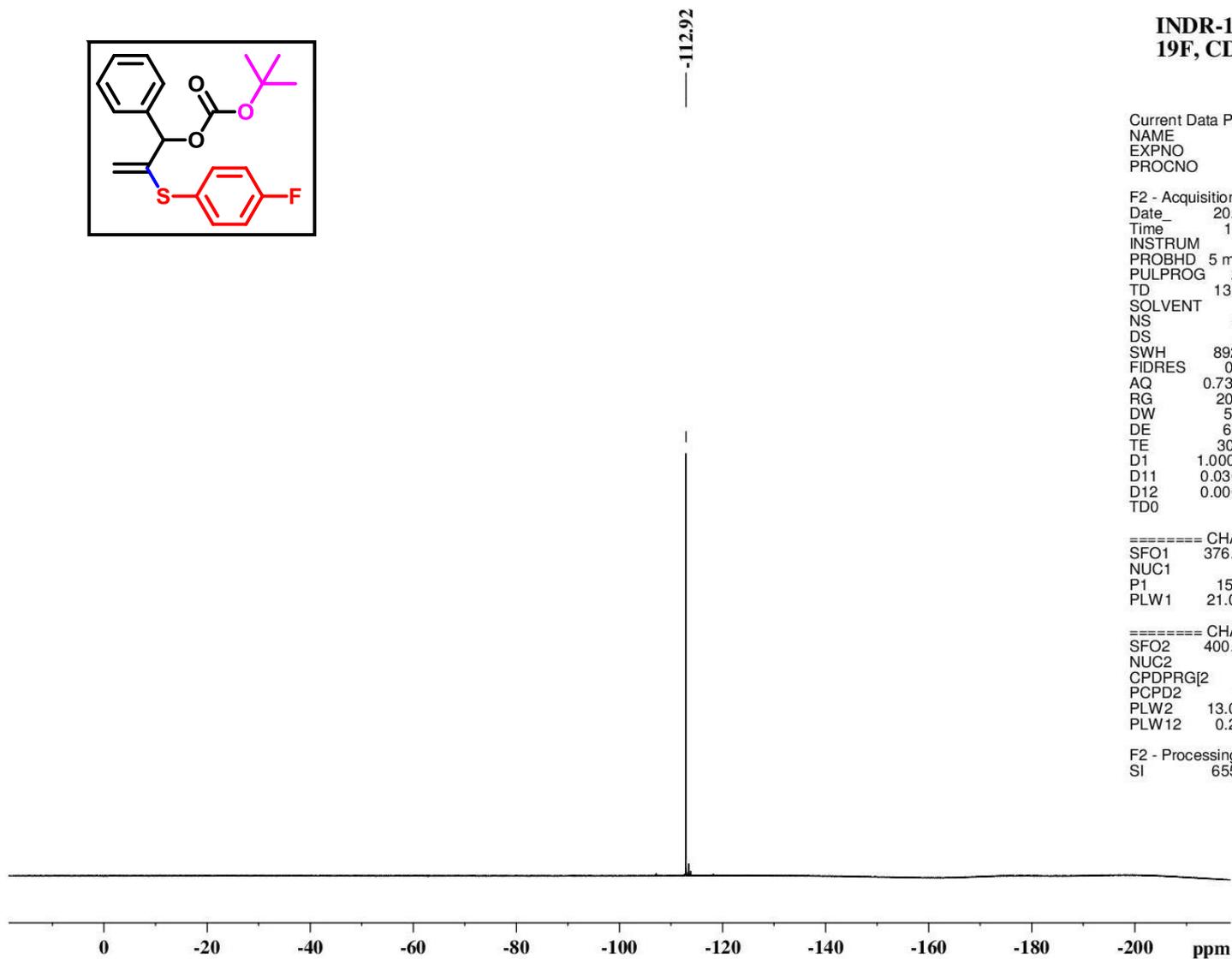
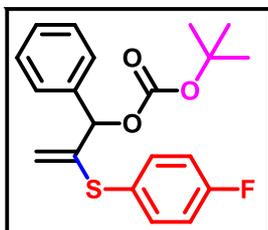
===== CHANNEL f1 ==  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 13.20 usec  
 PLW1 13.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 400.1605106 MHz  
 WDW EM  
 SSB 0

**Fig.S106** <sup>1</sup>H NMR Spectrum of **4t**



**Fig.S107**  $^{13}\text{C}$  NMR Spectrum of **4t**



**INDR-103**  
**19F, CDCI3**

Current Data Parameters  
NAME 19F  
EXPNO 90  
PROCNO 1

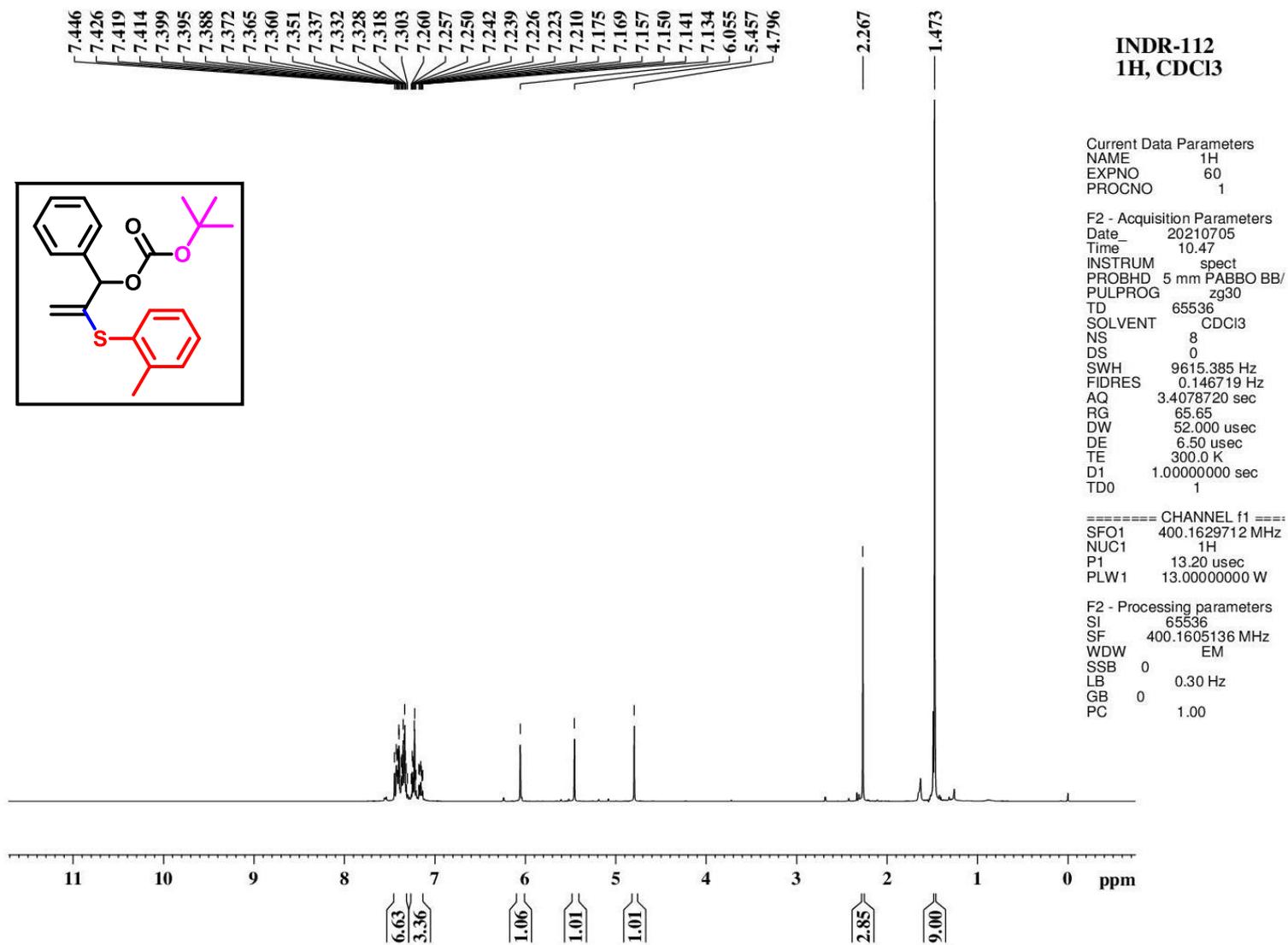
F2 - Acquisition Parameters  
Date\_ 20210705  
Time 11.02  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgfhgqn.2  
TD 131072  
SOLVENT CDCI3  
NS 16  
DS 4  
SWH 89285.711 Hz  
FIDRES 0.681196 Hz  
AQ 0.7340032 sec  
RG 201.48  
DW 5.600 usec  
DE 6.50 usec  
TE 300.1 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
D12 0.00002000 sec  
TD0 1

===== CHANNEL f1 =====  
SFO1 376.4894122 MHz  
NUC1 19F  
P1 15.00 usec  
PLW1 21.00000000 W

===== CHANNEL f2 =====  
SFO2 400.1621006 MHz  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 13.00000000 W  
PLW12 0.27963999 W

F2 - Processing parameters  
SI 65536

**Fig.S108** <sup>19</sup>F NMR Spectrum of **4t**



**Fig.S109** <sup>1</sup>H NMR Spectrum of **4u**

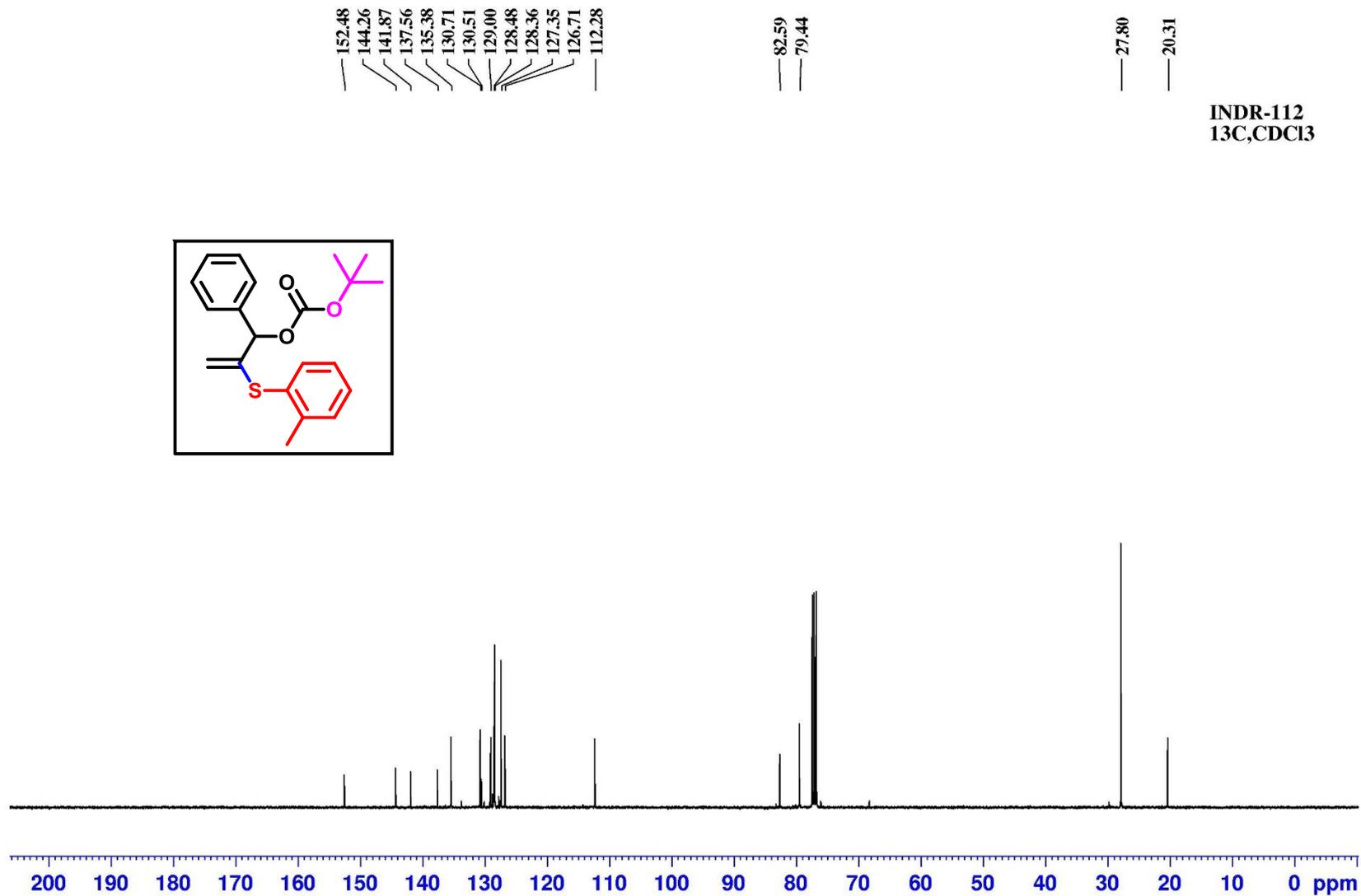


Fig.S110  $^{13}\text{C}$  NMR Spectrum of 4u

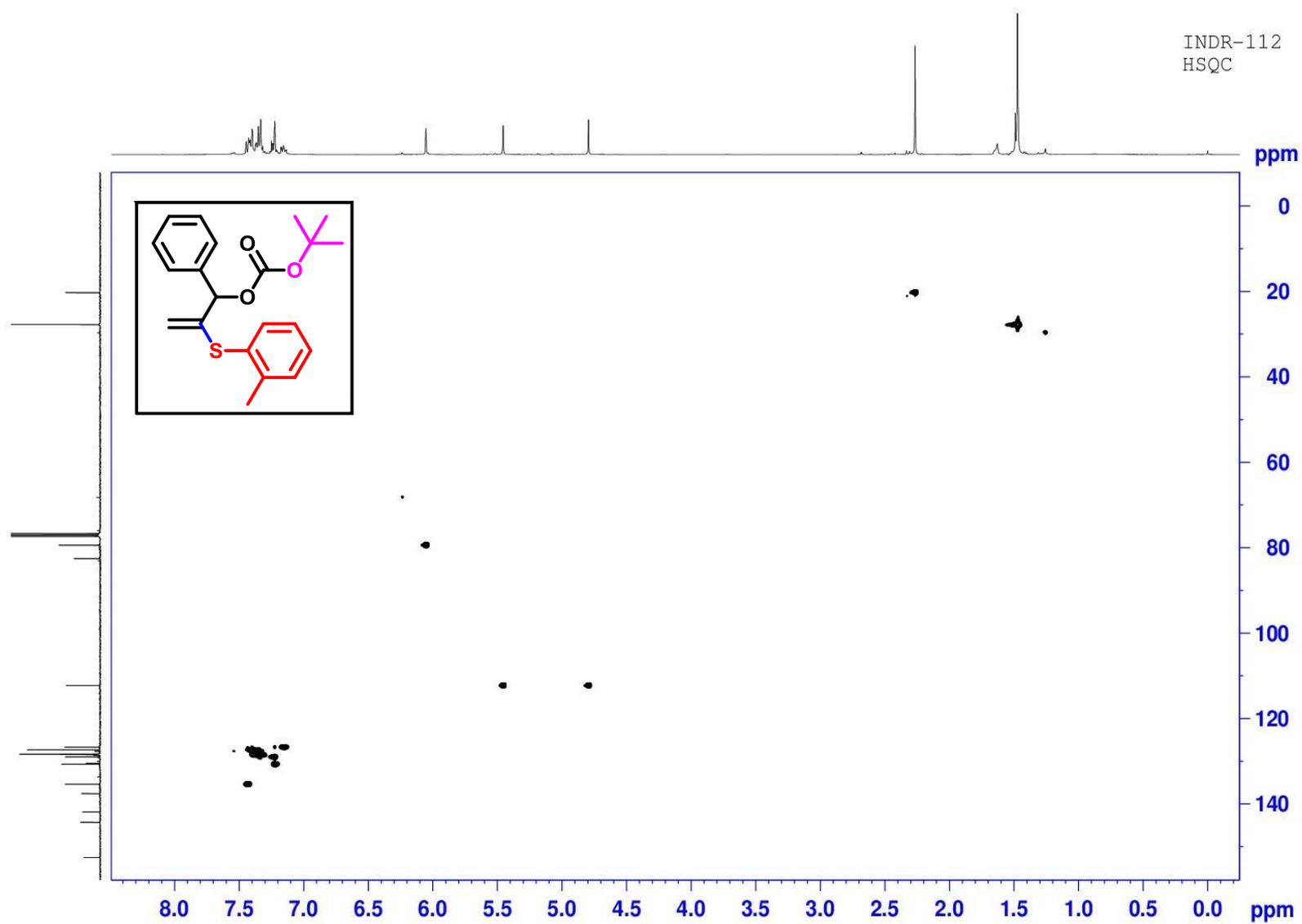
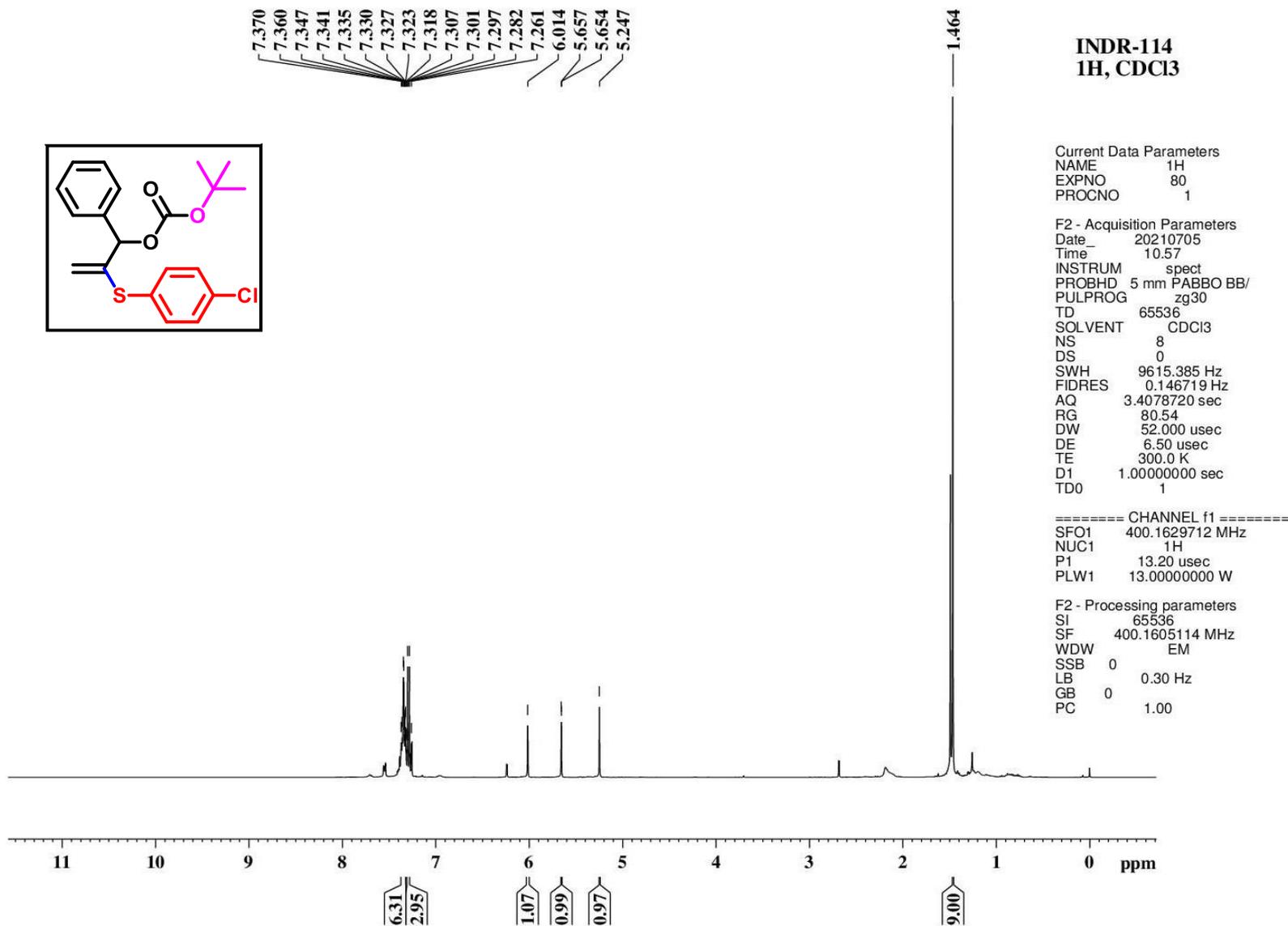


Fig.S111 HSQC Spectrum of 4u



**Fig.S112** <sup>1</sup>H NMR Spectrum of **4v**

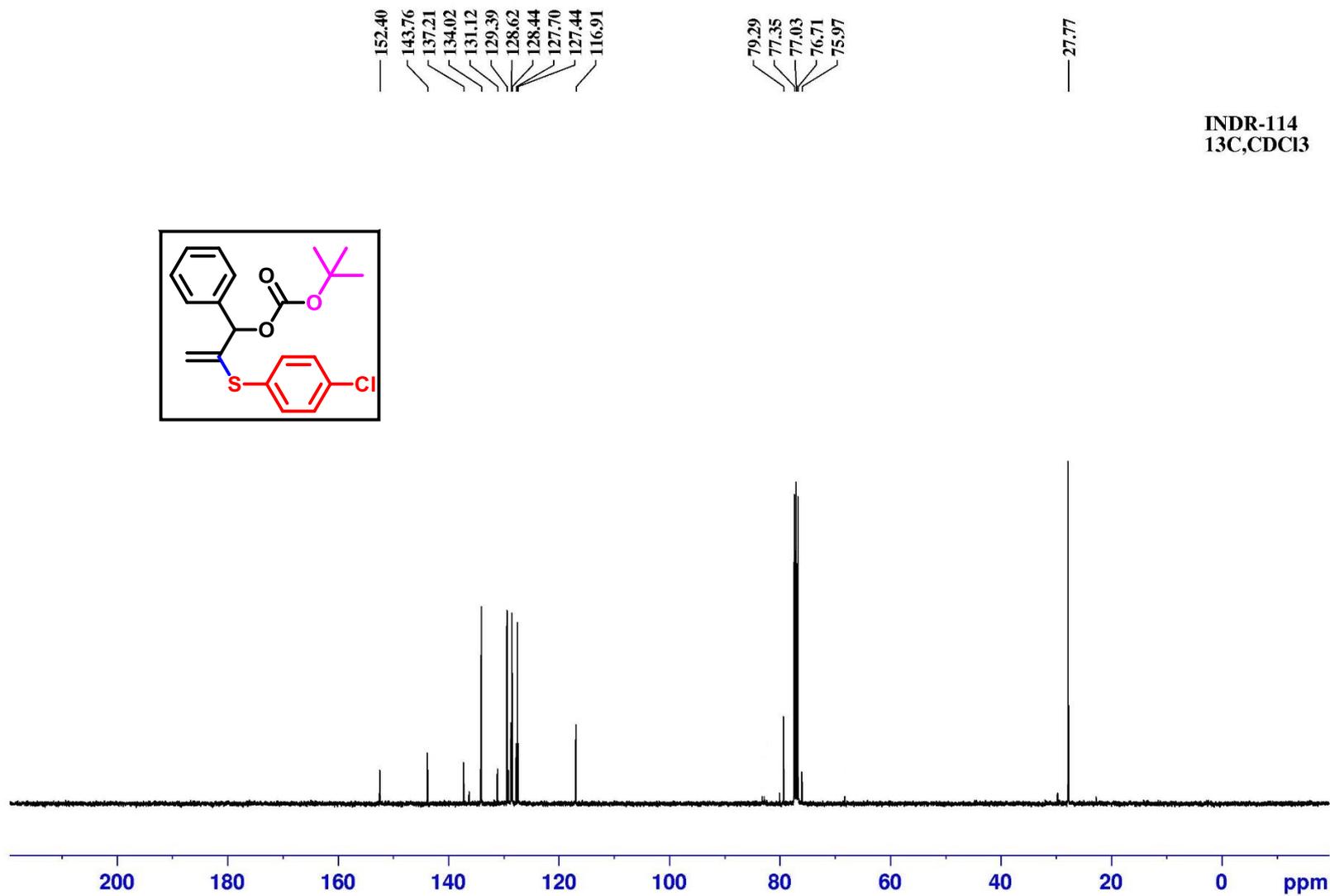
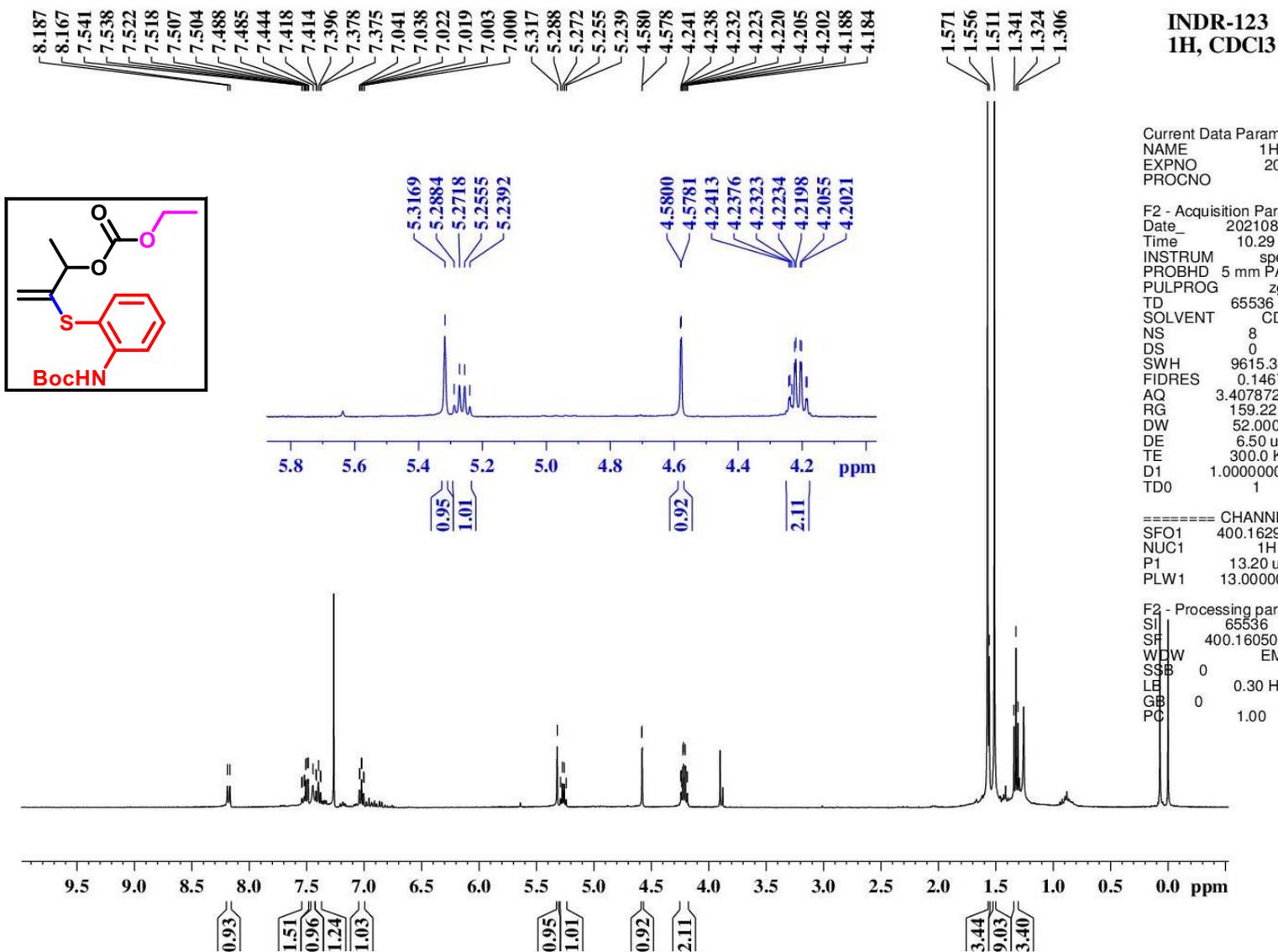
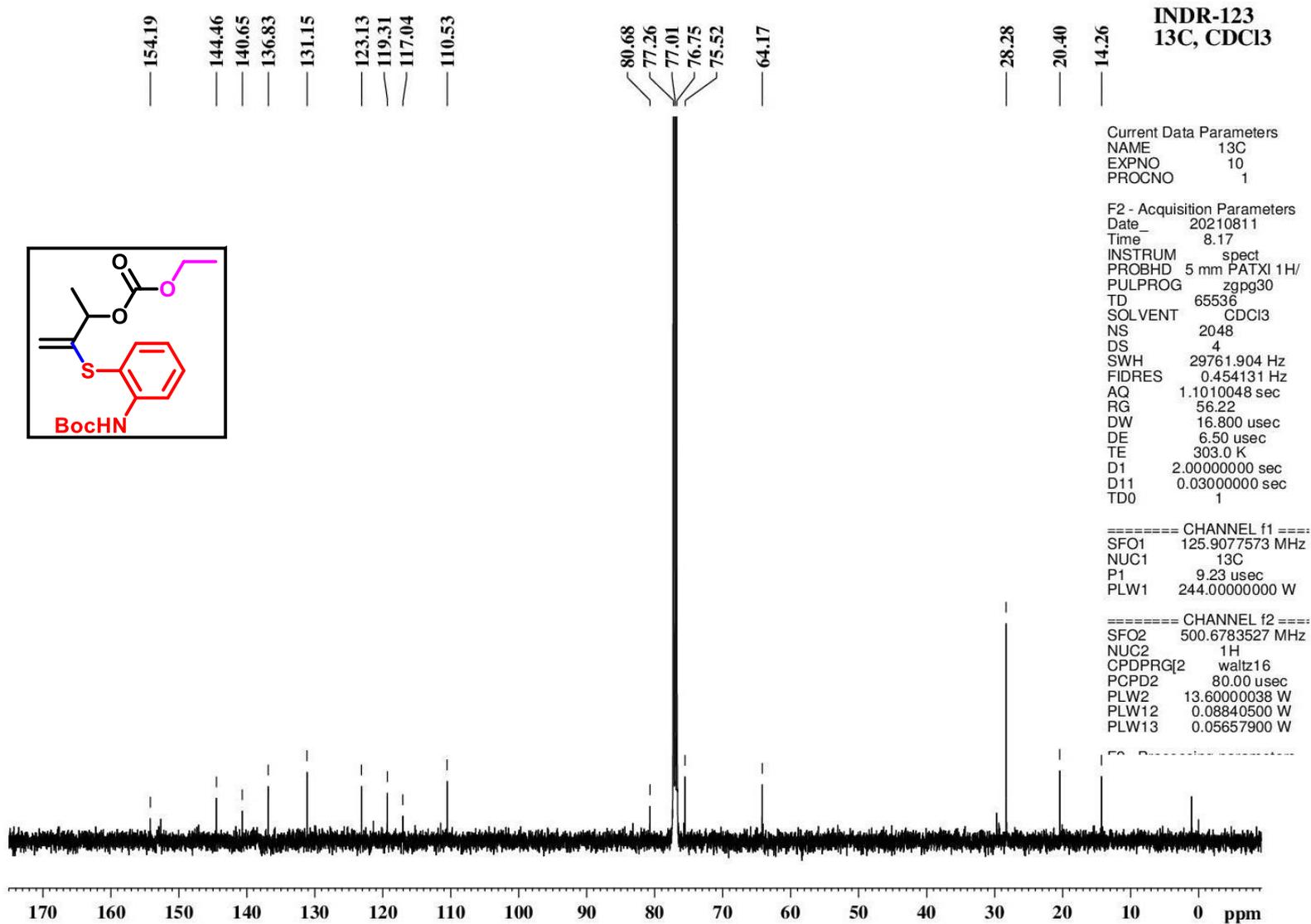


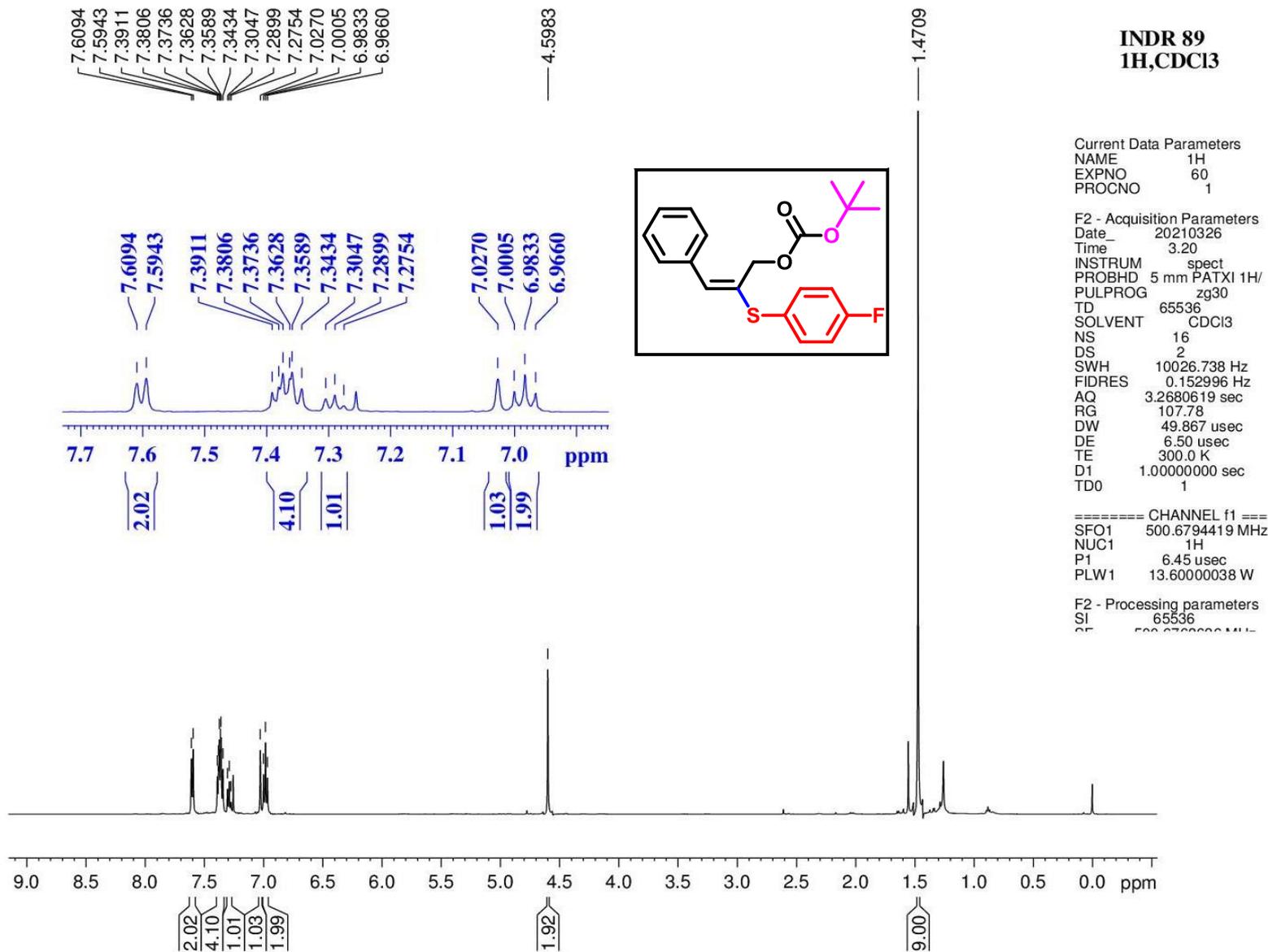
Fig.S113 <sup>13</sup>C NMR Spectrum of 4v



**Fig.S114**  $^1\text{H}$  NMR Spectrum of **4w**



**Fig.S115** <sup>13</sup>C NMR Spectrum of **4w**



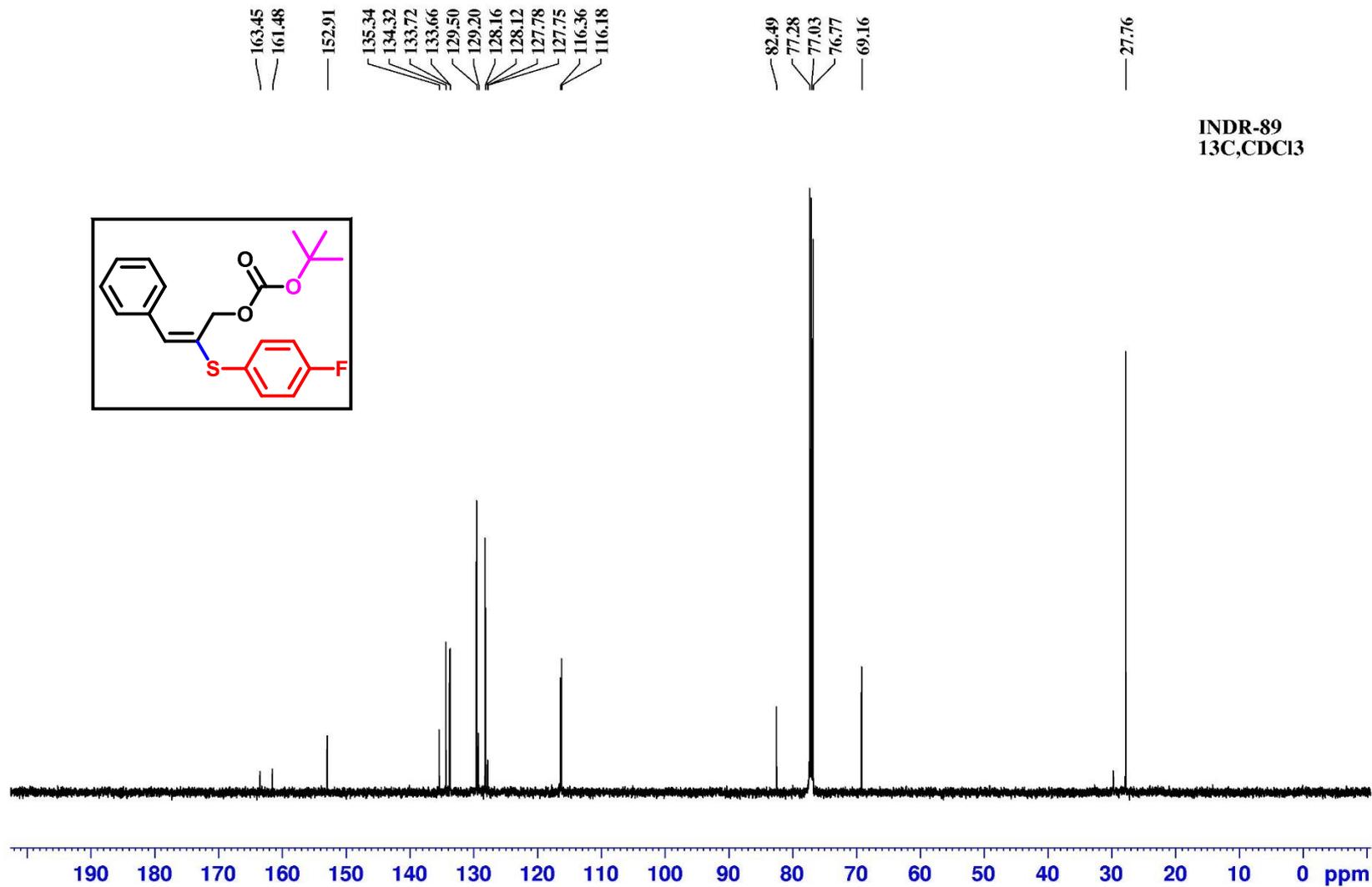
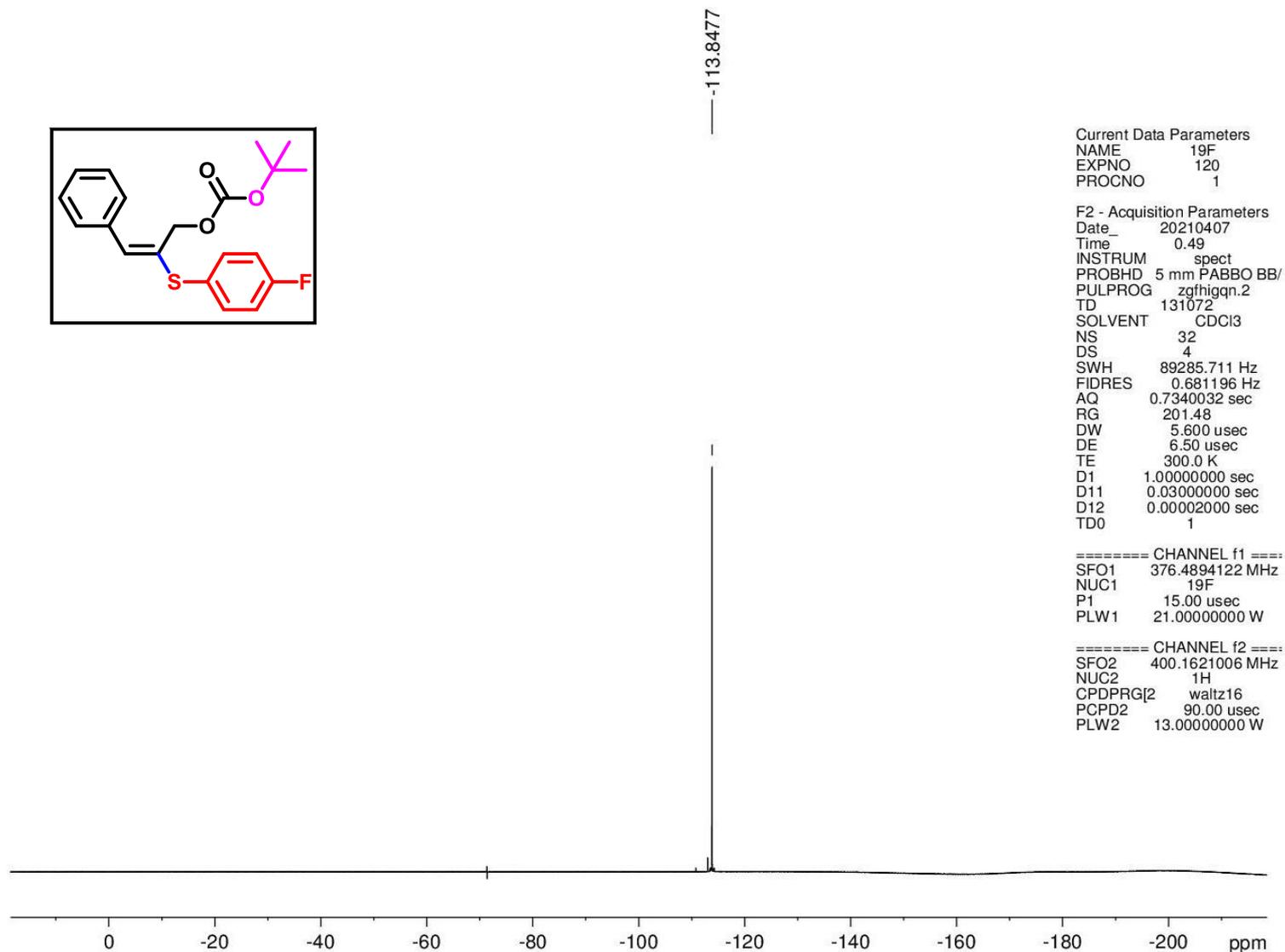


Fig.S117 <sup>13</sup>C NMR Spectrum of 4x



**Fig.S118**  $^{19}\text{F}$  NMR Spectrum of **4x**

INDR 89  
HSQC

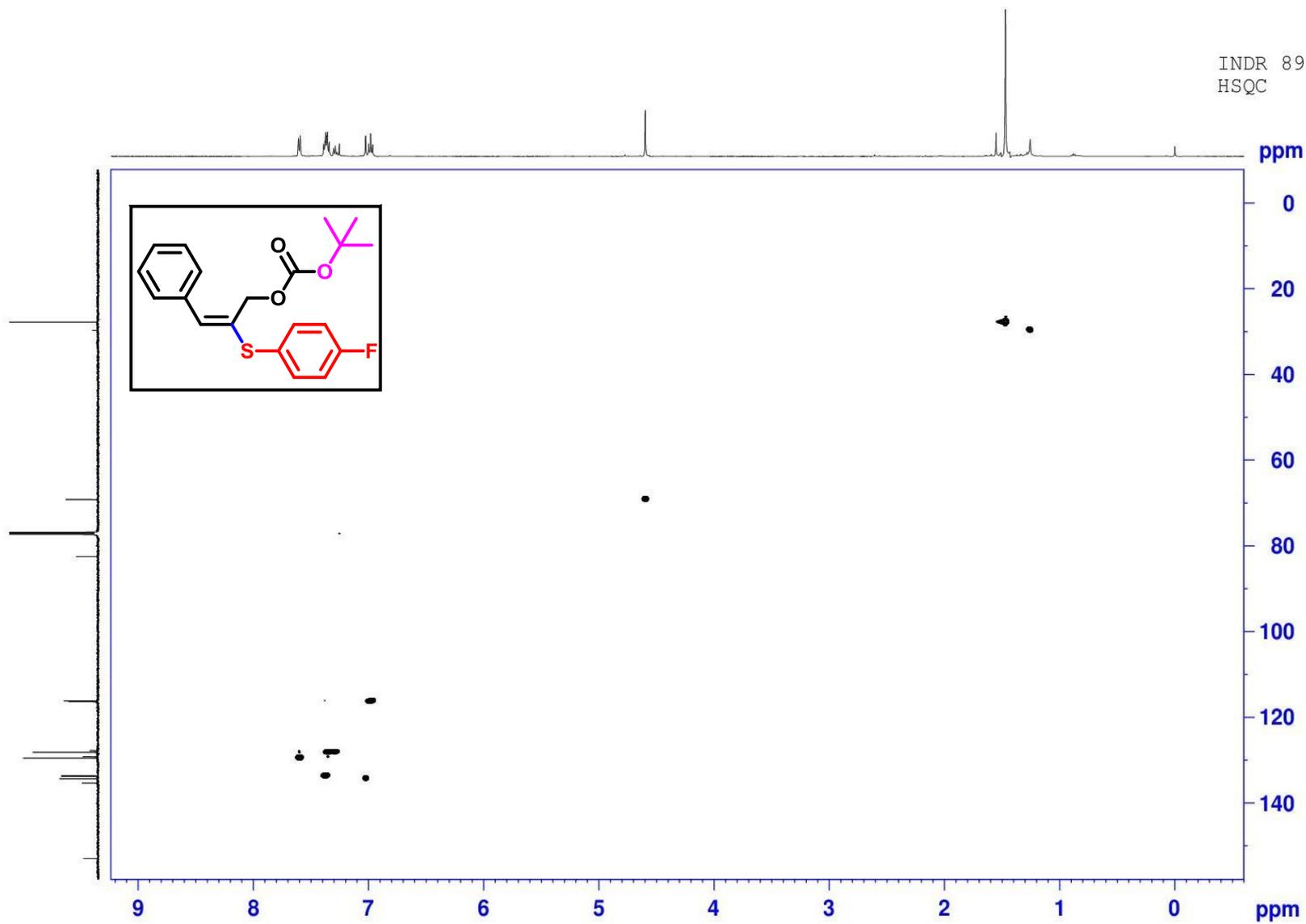


Fig.S119 HSQC Spectrum of 4x

7.4702  
7.4668  
7.4510  
7.4476  
7.3662  
7.3629  
7.3457  
7.3275  
7.0400  
7.0197  
6.9425  
6.9398  
6.9236  
6.3852  
5.9937  
5.9792  
5.9649  
5.9529  
5.9364  
5.9241  
5.9220  
5.9101  
5.8956  
5.4195  
5.4047  
5.4016  
5.3616  
5.3586  
5.3051  
5.3027  
5.2792  
4.9822  
4.6619

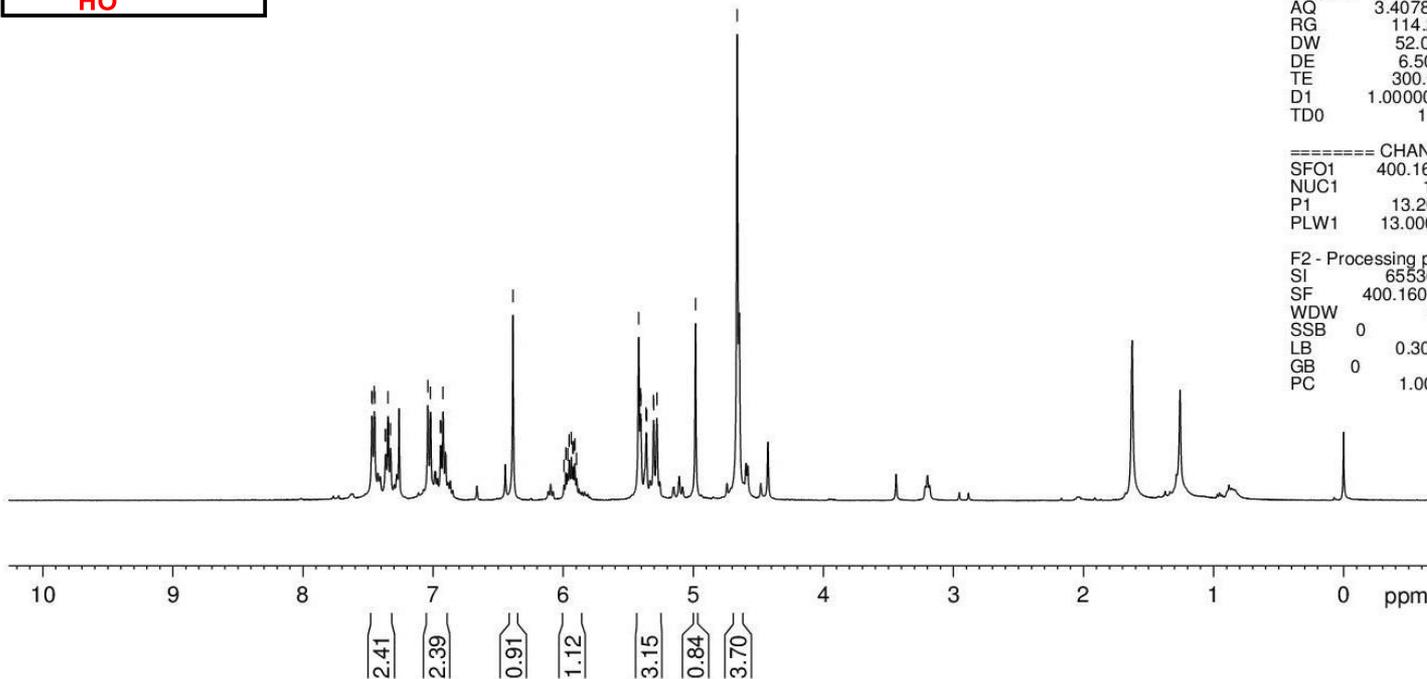
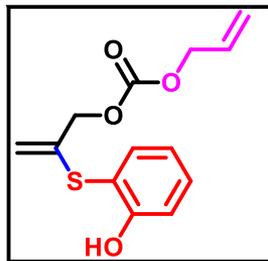
**INDR 142**  
**1H, CDCI3**

Current Data Parameters  
NAME 1H  
EXPNO 230  
PROCNO 1

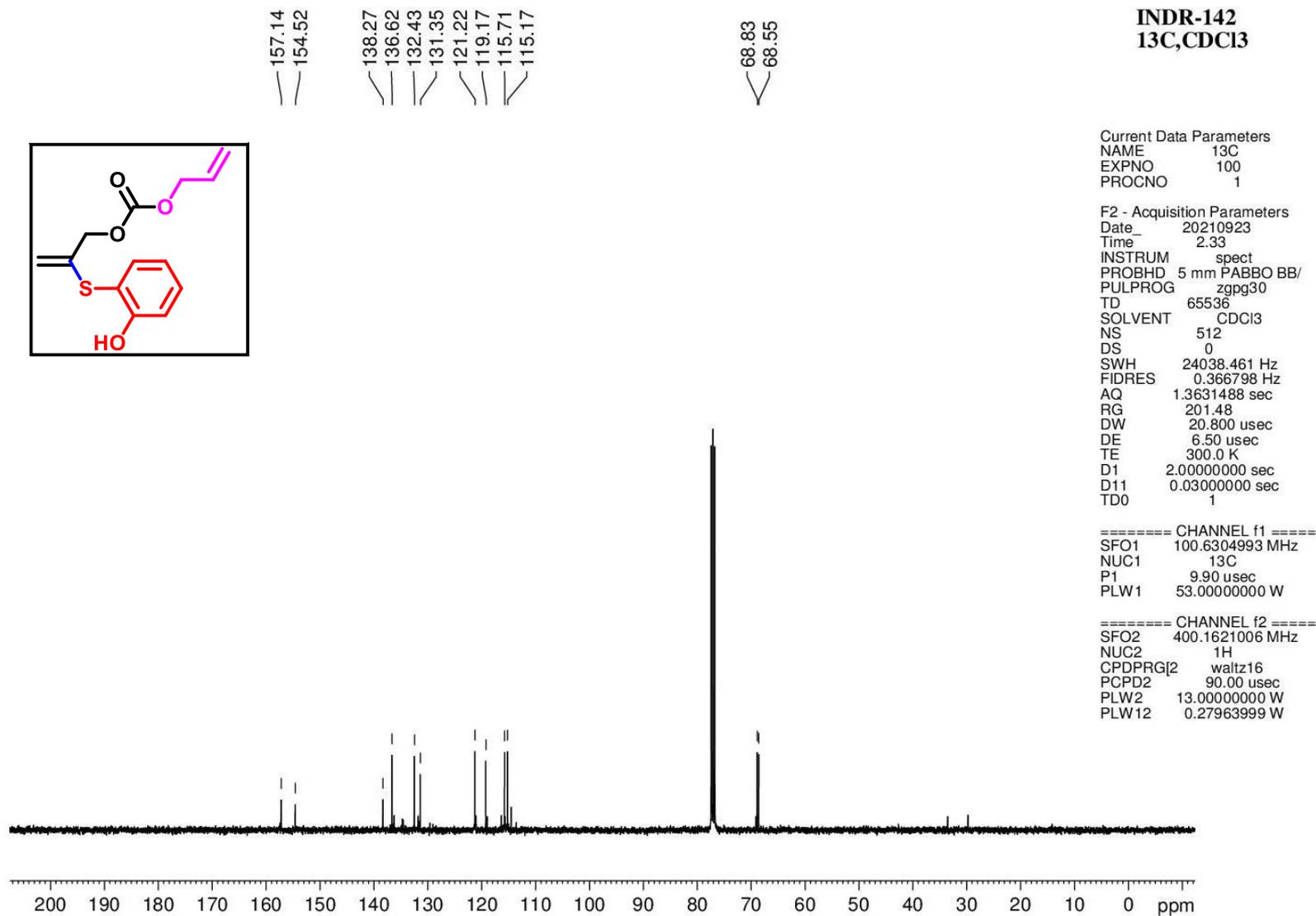
F2 - Acquisition Parameters  
Date\_ 20210920  
Time 21.48  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 0  
SWH 9615.385 Hz  
FIDRES 0.146719 Hz  
AQ 3.4078720 sec  
RG 114.26  
DW 52.000 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
SFO1 400.1629712 MHz  
NUC1 1H  
P1 13.20 usec  
PLW1 13.00000000 W

F2 - Processing parameters  
SI 65536  
SF 400.1605093 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**Fig.S120** <sup>1</sup>H NMR Spectrum of **4y**



**Fig.S121** <sup>13</sup>C NMR Spectrum of **4y**

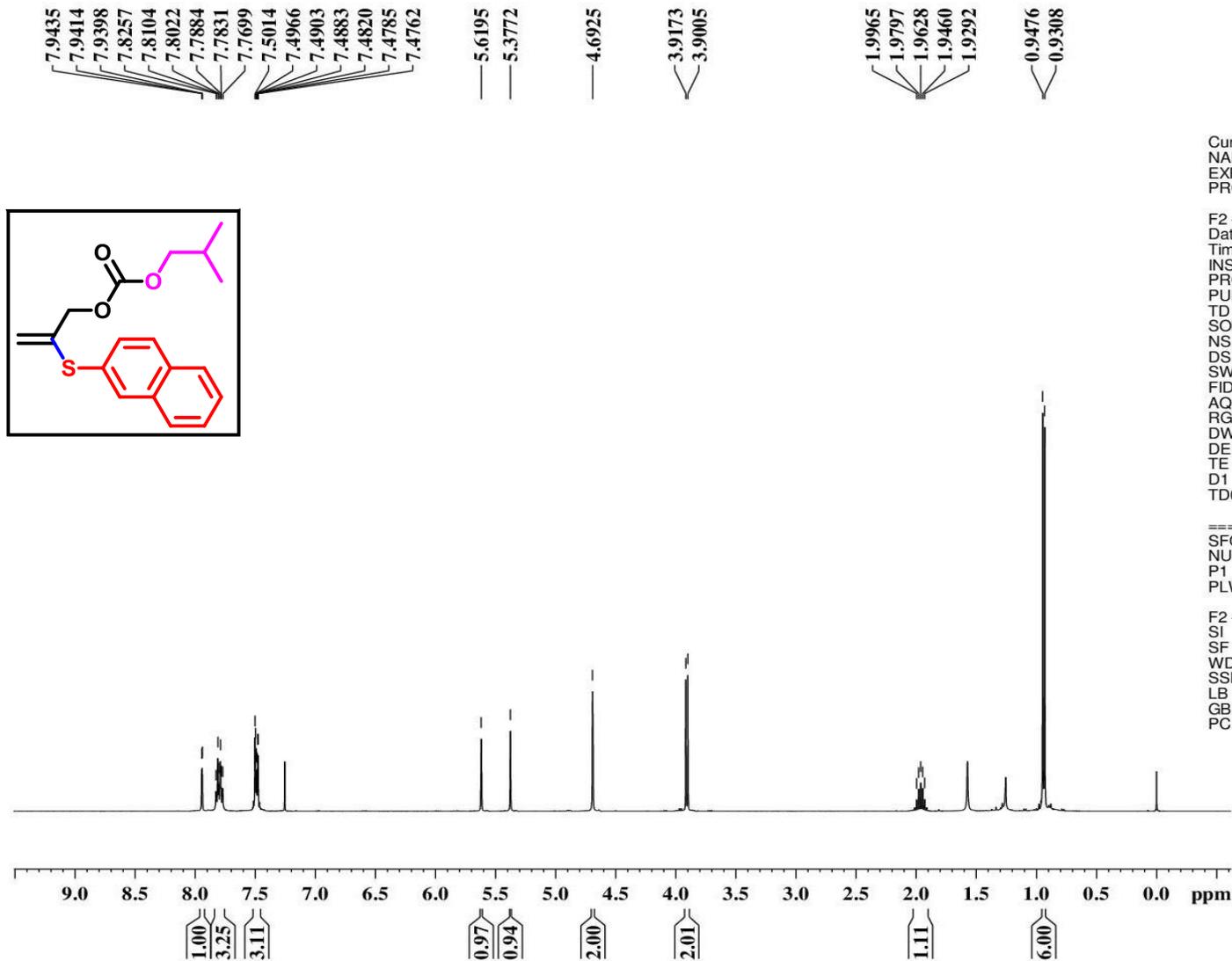
**INDR-146  
1H, CDCl3**

Current Data Parameters  
 NAME 1H  
 EXPNO 150  
 PROCNO 1

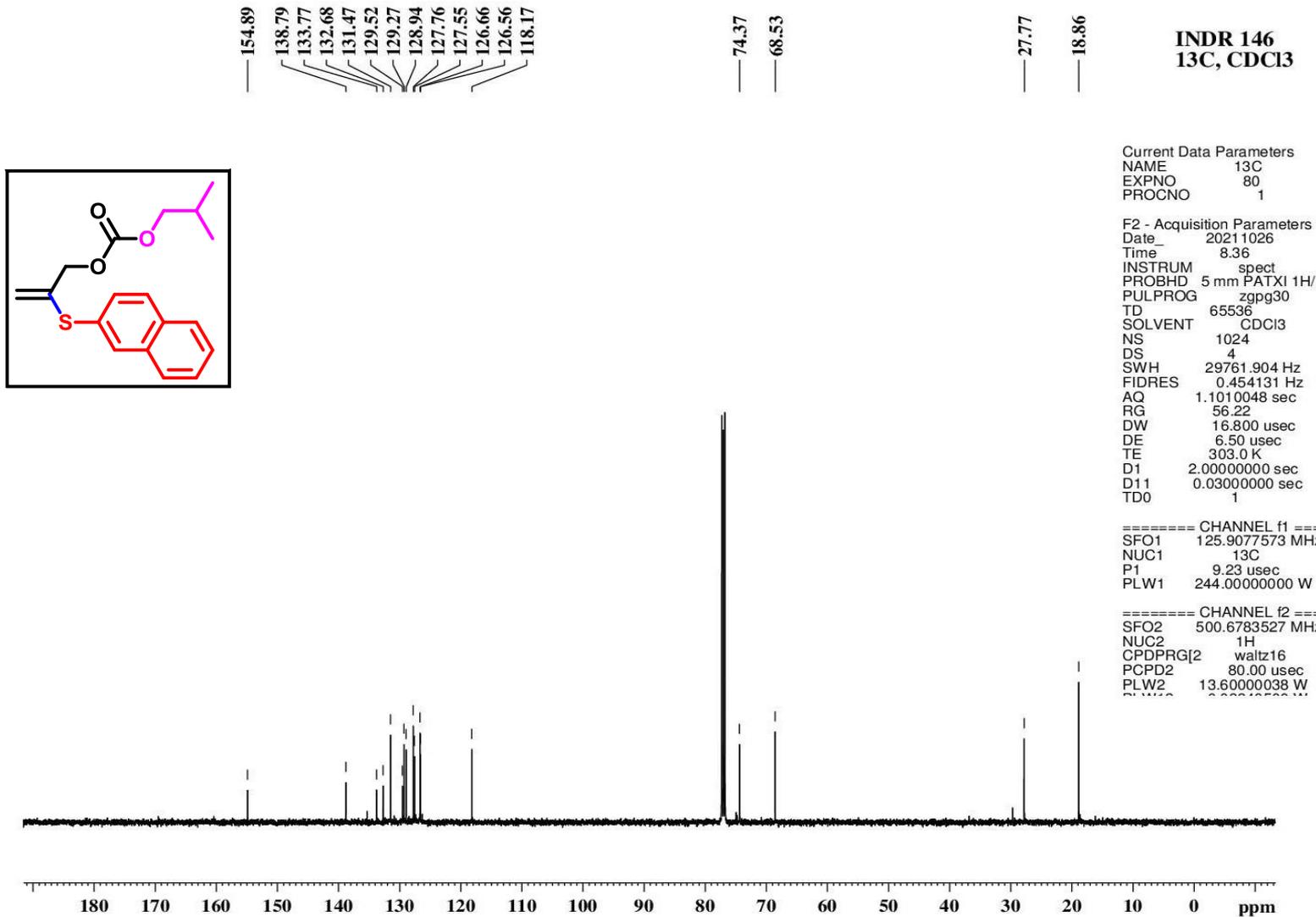
F2 - Acquisition Parameters  
 Date\_ 20211004  
 Time 14.10  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 100.41  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 13.20 usec  
 PLW1 13.00000000 W

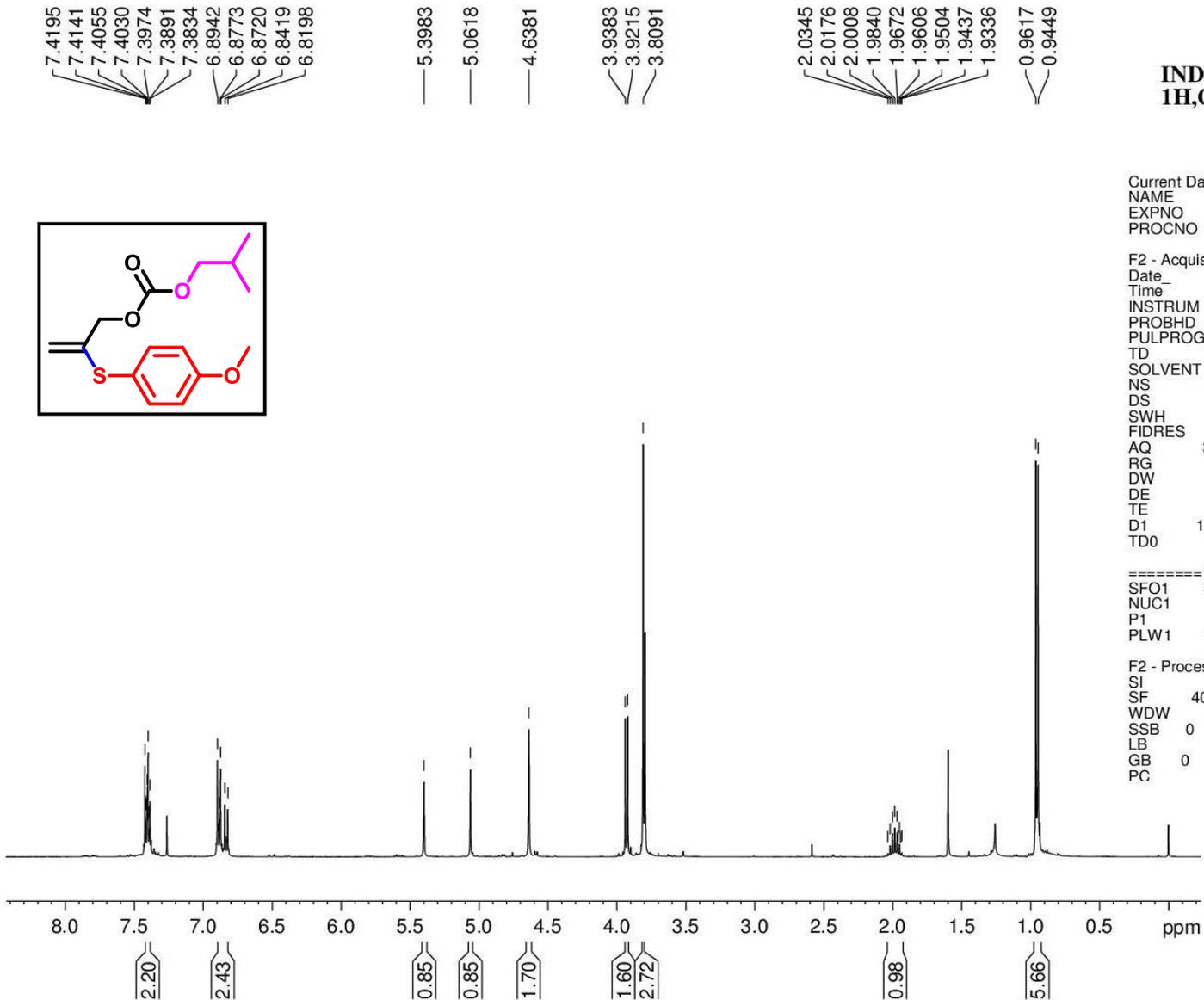
F2 - Processing parameters  
 SI 65536  
 SF 400.1605111 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



**Fig.S122** <sup>1</sup>H NMR Spectrum of **4z**



**Fig.S123**  $^{13}\text{C}$  NMR Spectrum of **4z**



**INDR-141  
1H,CDCl3**

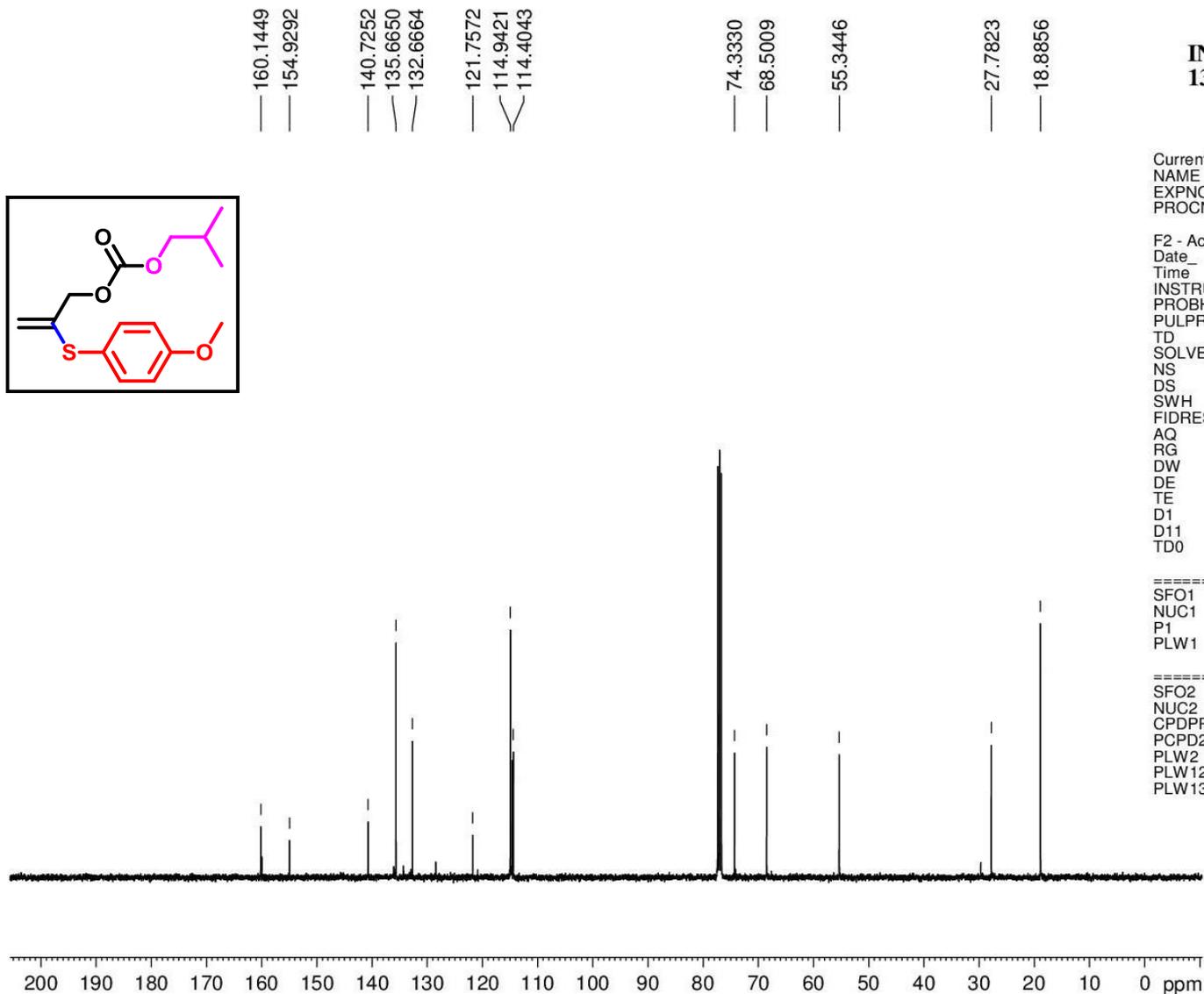
Current Data Parameters  
 NAME 1H  
 EXPNO 190  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20210920  
 Time 11.48  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 9615.385 Hz  
 FIDRES 0.146719 Hz  
 AQ 3.4078720 sec  
 RG 80.54  
 DW 52.000 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TD0 1

==== CHANNEL f1 ====  
 SFO1 400.1629712 MHz  
 NUC1 1H  
 P1 13.20 usec  
 PLW1 13.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 400.1605094 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

**Fig.S124** <sup>1</sup>H NMR Spectrum of 4z'



**INDR-141**  
**<sup>13</sup>C, CDCl<sub>3</sub>**

Current Data Parameters  
 NAME 13C  
 EXPNO 90  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20210923  
 Time 2.05  
 INSTRUM spect  
 PROBHD 5 mm PABBO BI  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 512  
 DS 0  
 SWH 24038.461 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 201.48  
 DW 20.800 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 ==  
 SFO1 100.6304993 MH  
 NUC1 13C  
 P1 9.90 usec  
 PLW1 53.00000000 W

==== CHANNEL f2 ==  
 SFO2 400.1621006 MH  
 NUC2 1H  
 CPDPRG[2] waltz16  
 PCPD2 90.00 usec  
 PLW2 13.00000000 W  
 PLW12 0.27963999 W  
 PLW13 0.22651000 W

**Fig.S125** <sup>13</sup>C NMR Spectrum of **4z'**

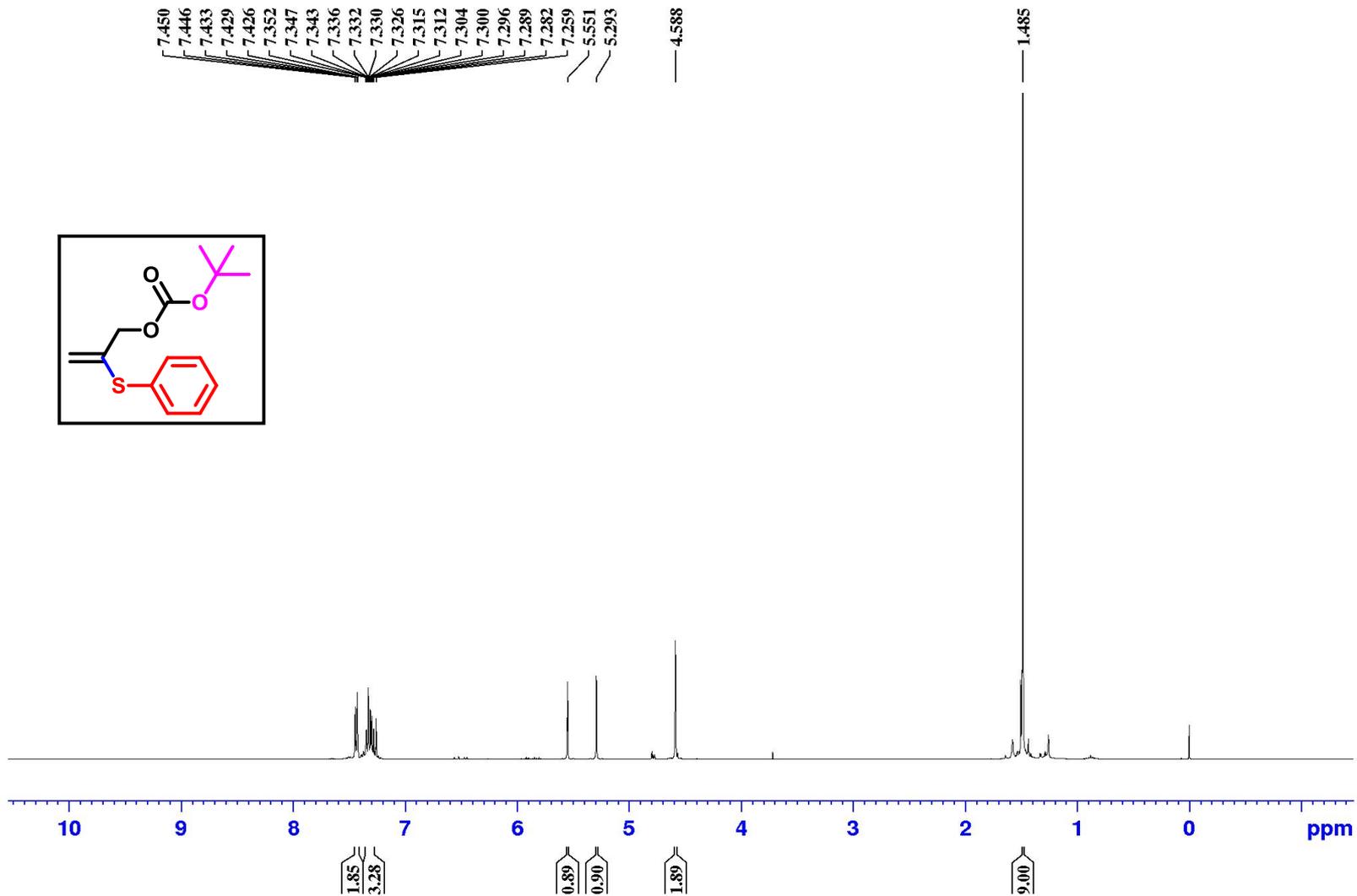
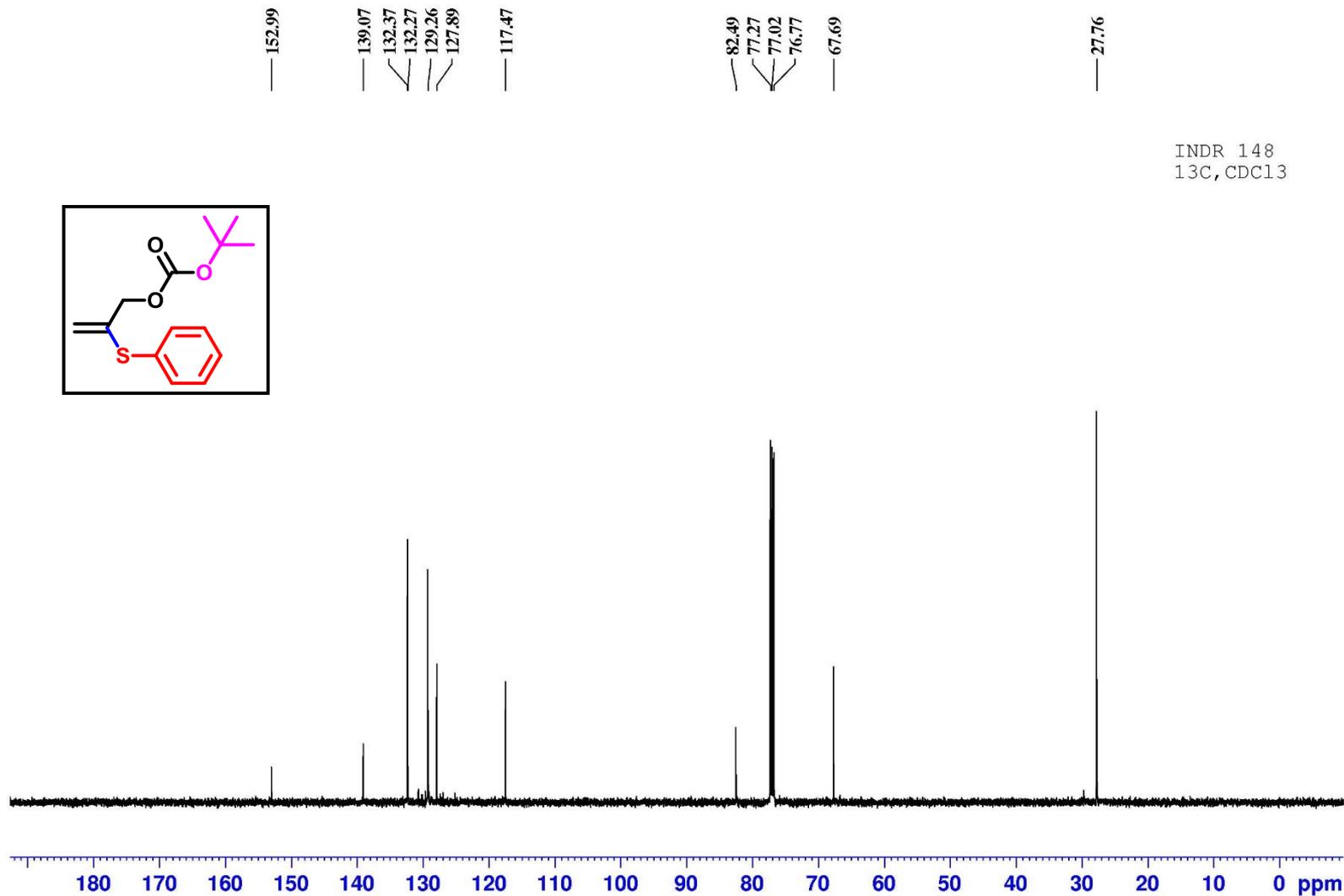
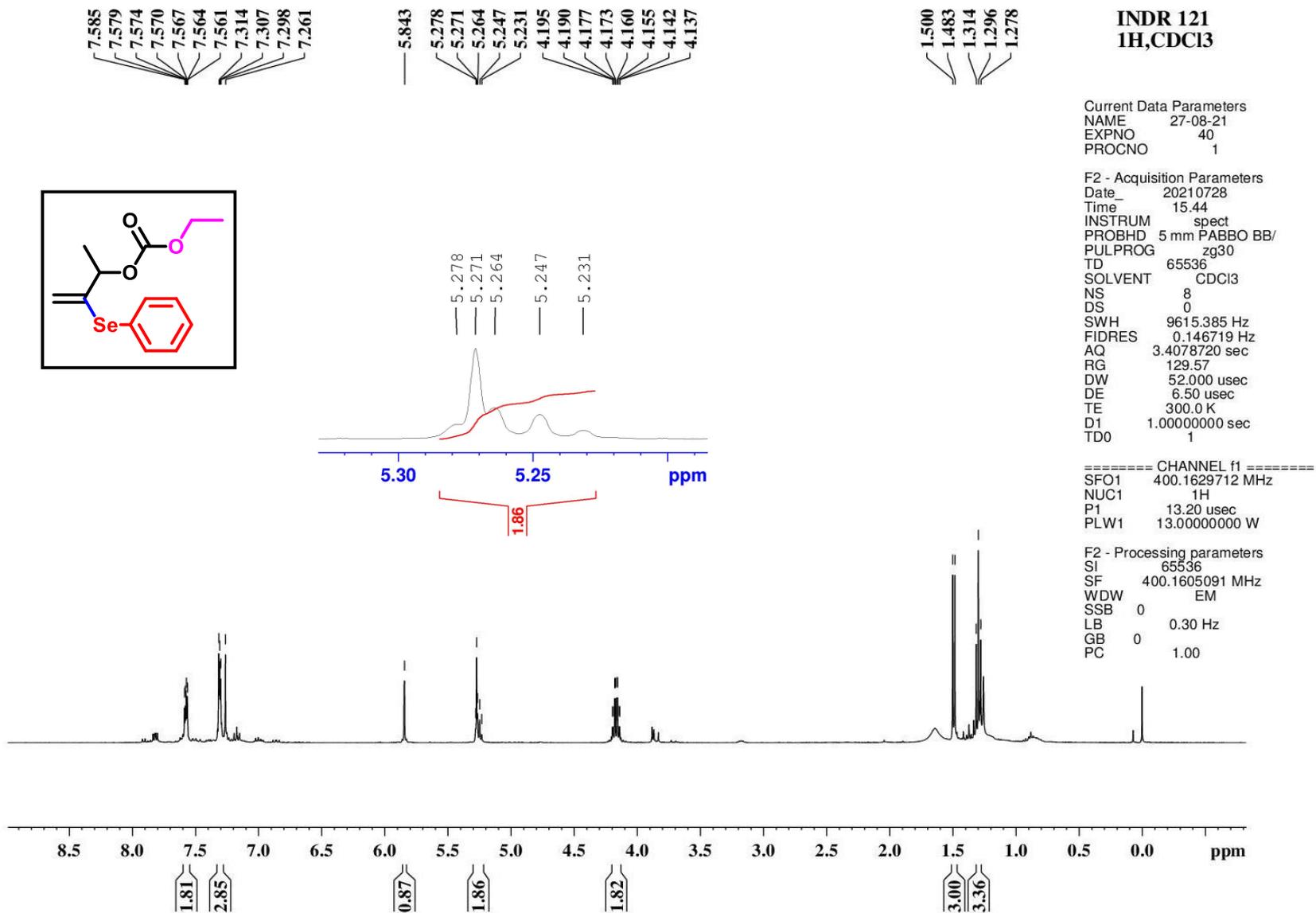


Fig.S126 <sup>1</sup>H NMR Spectrum of 4a'



INDR 148  
13C, CDC13

Fig.S127 <sup>13</sup>C NMR Spectrum of 4a'



**Fig.S128** <sup>1</sup>H NMR Spectrum of **7**

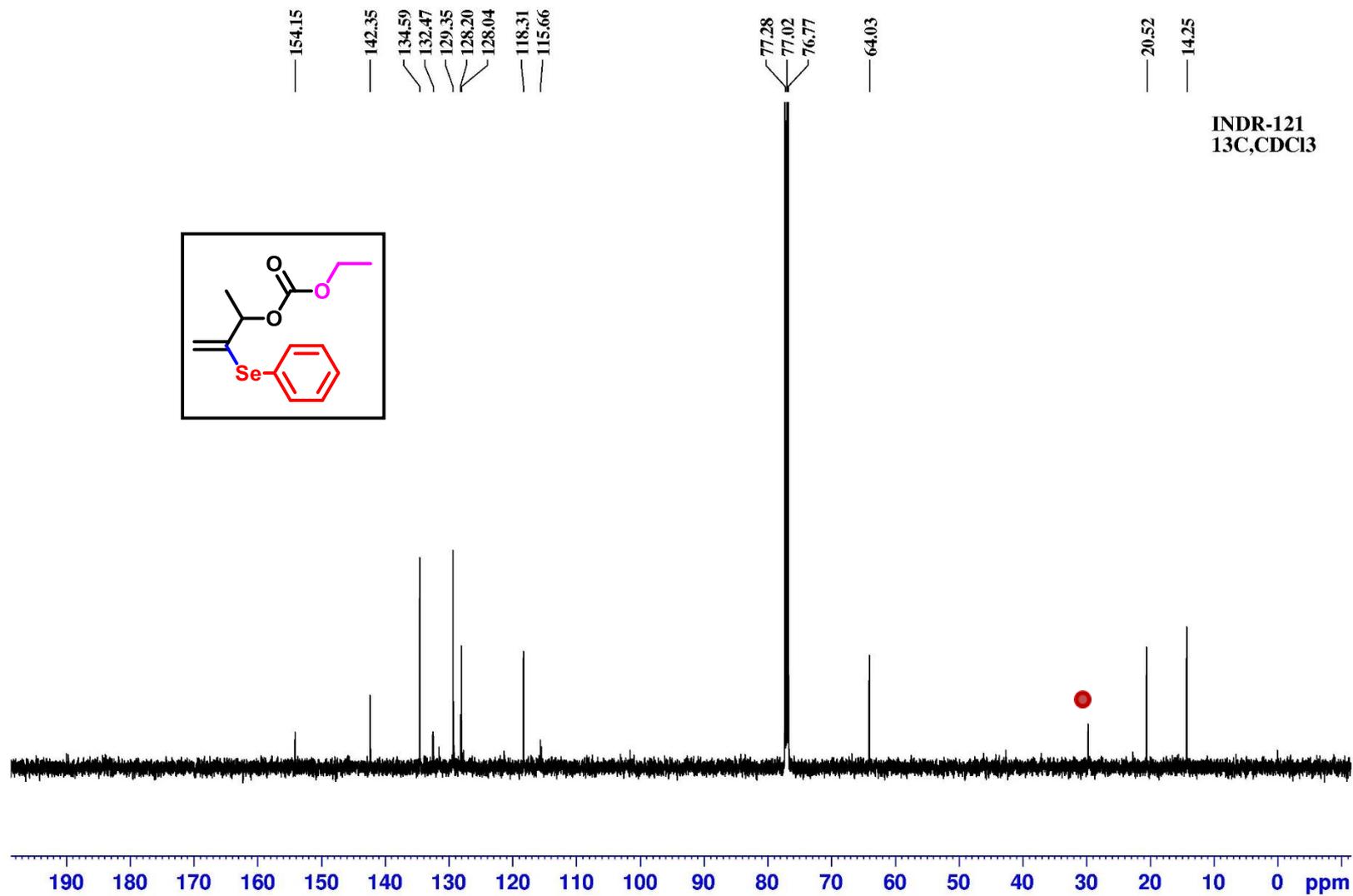


Fig.S129 <sup>13</sup>C NMR Spectrum of 7

● grease

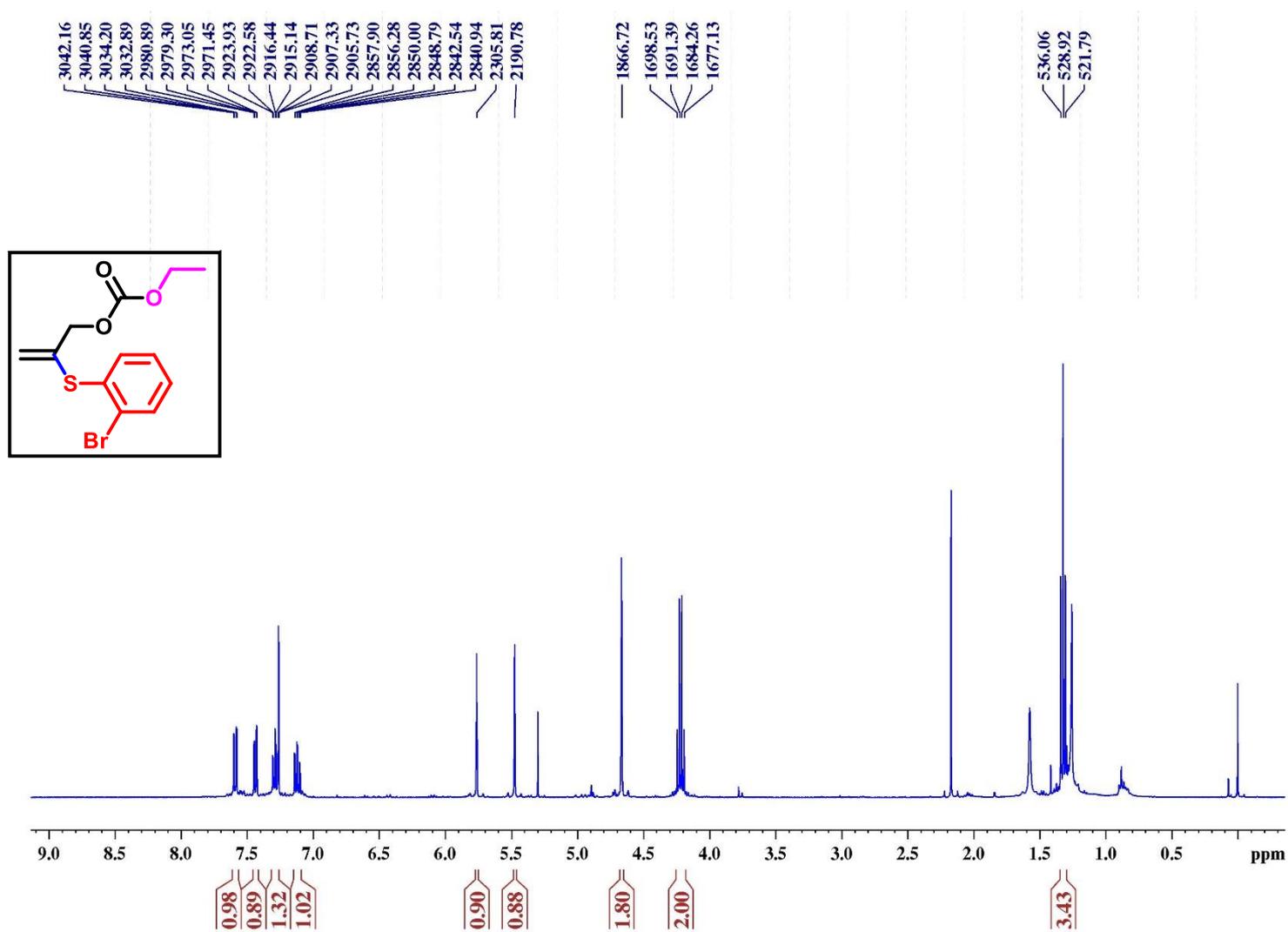
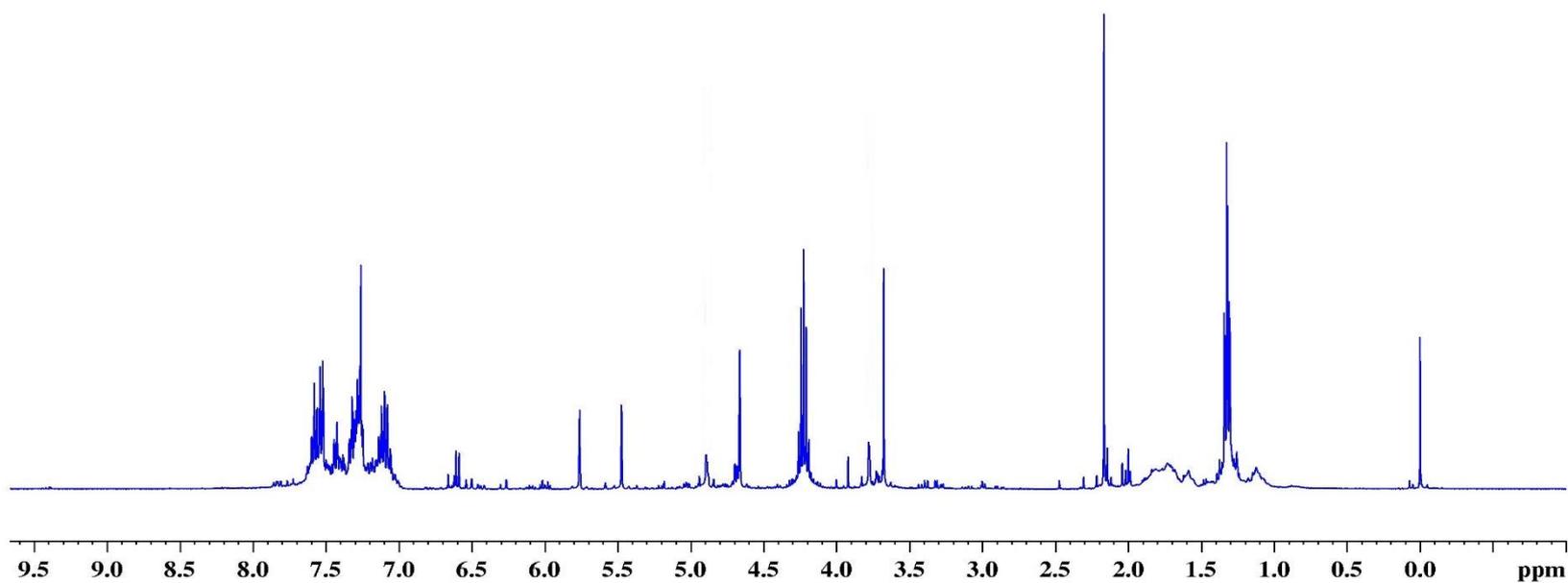
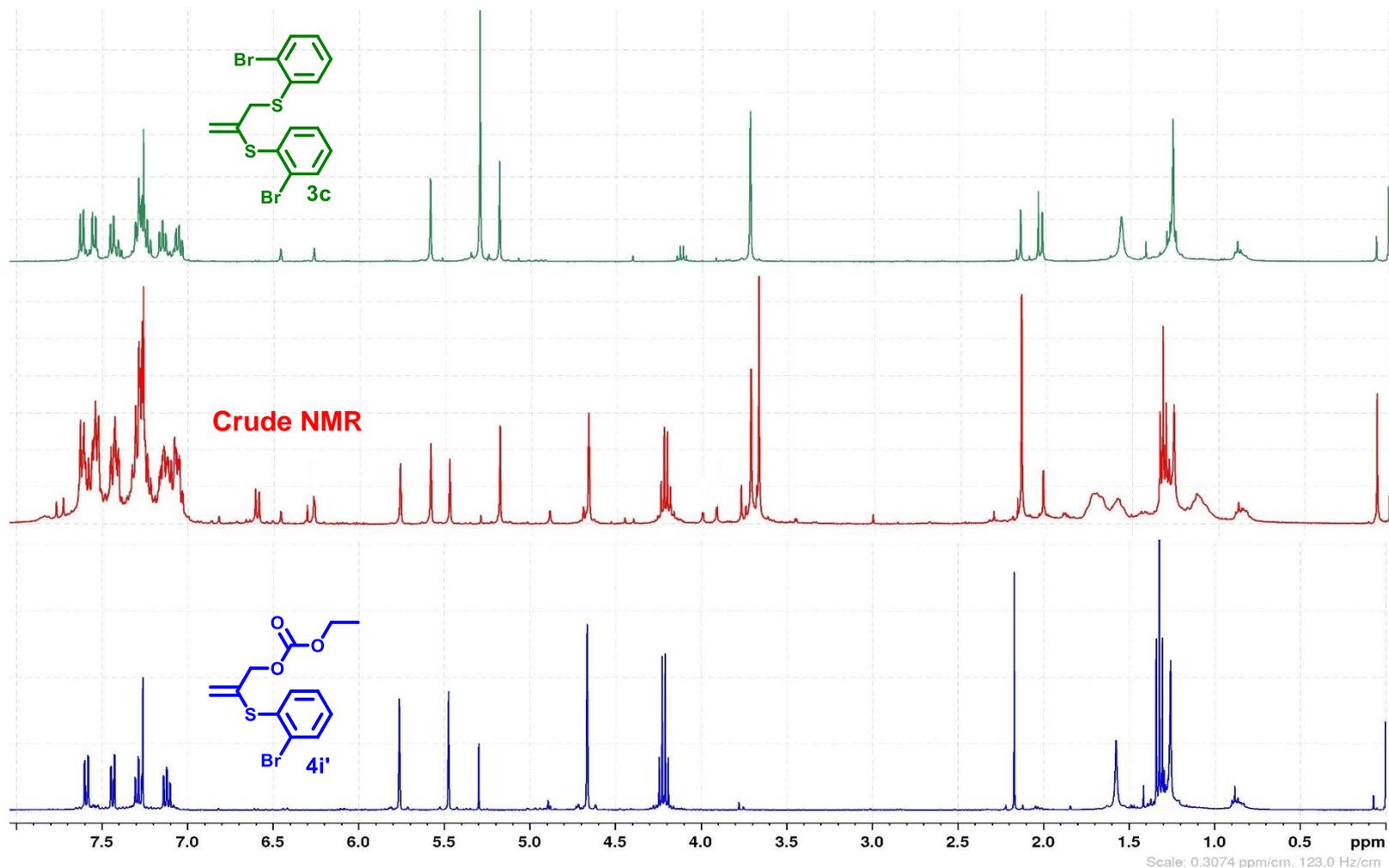


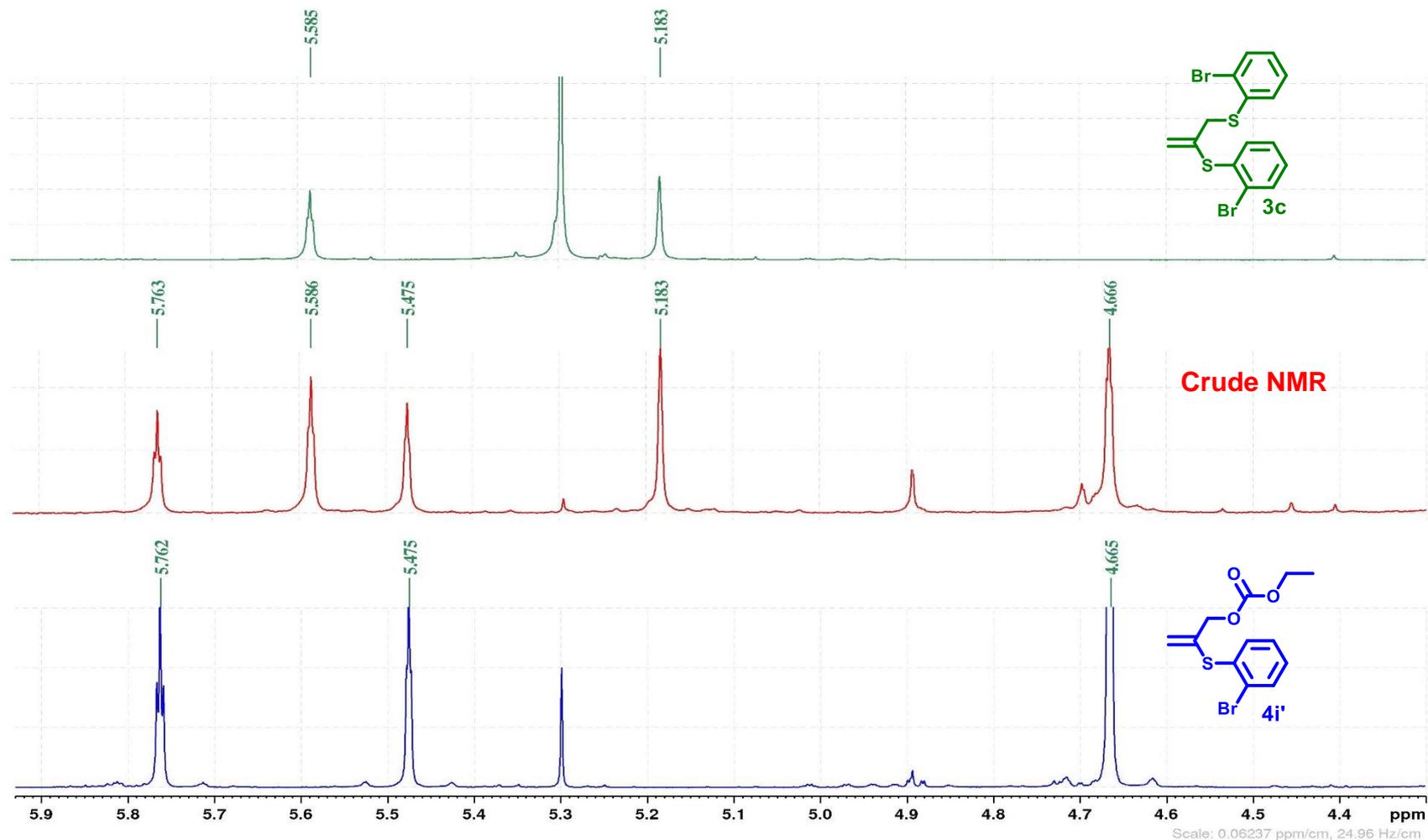
Fig.S130 <sup>1</sup>H NMR Spectrum of 4i'



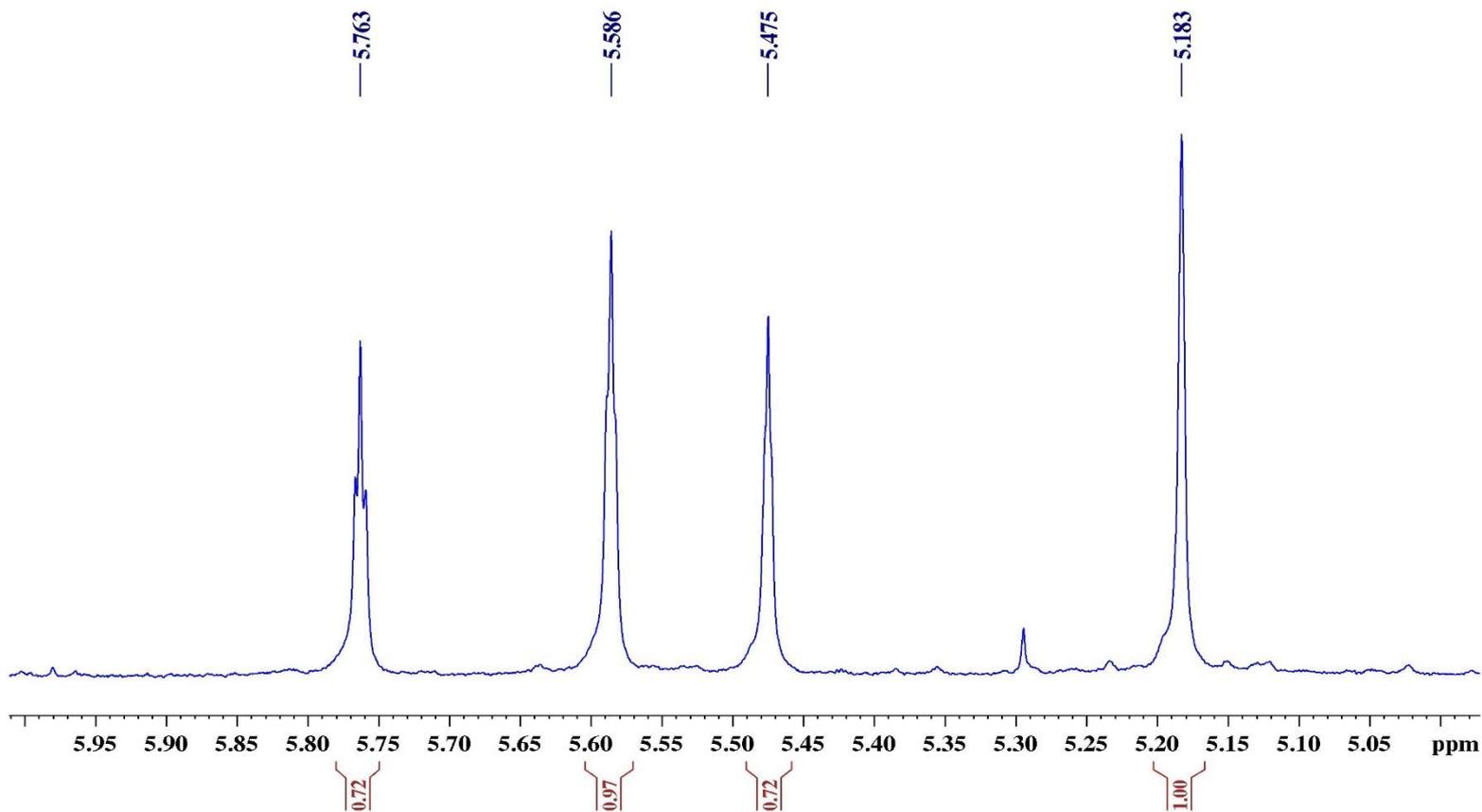
**Fig.S131** <sup>1</sup>H NMR Spectrum (Crude) of the reaction between propargyl carbonate (1.1 mmol) and 2-bromothiophenol (1.0 mmol) for preparation of mono(arylthiol) alkene **4i'**



**Fig.S132** Comparison between crude <sup>1</sup>H NMR Spectrum of the reaction between propargyl carbonate (1.0 mmol) and 2-bromothiophenol (1.5 mmol) under optimized reaction condition and <sup>1</sup>H NMR of purified mono(arylthiol) alkene **4i'** as well as bis(arylthiol) alkene **3c**



**Fig.S133** Magnified region of crude  $^1\text{H}$  NMR Spectrum of the reaction between propargyl carbonate (1.0 mmol) and 2-bromothiophenol (1.5 mmol) under optimized reaction condition and  $^1\text{H}$  NMR of purified mono(arylthiol) alkene **4i'** as well as bis(arylthiol) alkene **3c**



**Fig.S134** Distribution of products (**3c** and **4i'**) from magnified region of crude <sup>1</sup>H NMR Spectrum of reaction mixture of propargyl carbonate (1.0 mmol) and 2-bromothiophenol (1.5 mmol) under optimized reaction condition