Electronic Supplementary Information

Triflic acid-promoted cycloisomerization of 2-alkynylphenyl isothiocyanates and isocyanates: a novel synthetic method for a variety of indole derivatives

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1. Synthesis

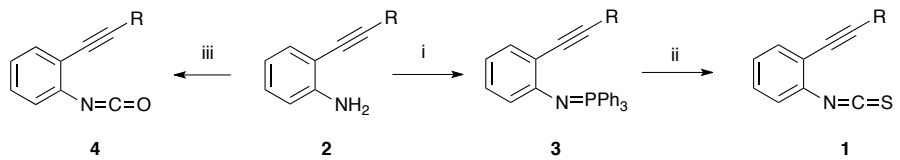
1.1 General Information

All melting points were determined on a Yanaco melting point apparatus MP-500 and are uncorrected. Infrared spectra were recorded on a Horiba FT-710 model spectrophotometer. ^{1}H and ^{13}C NMR spectral data were obtained with a Bruker Avance-600, a JEOL JNM-LA 500, or a JEOL JNM-AL 300 instrument and chemical shifts are reported in ppm down field from tetramethylsilane (TMS) using an internal standard of TMS and $CDCl_3$. Accurate mass was measured by high-resolution electrospray ionization (ESI) mass to determine an elemental formula by comparing calculated exact mass. The elemental analyses (C, H, and N) were performed with Yanaco CHN coder MT-6. The starting materials, 2-alkynylanilines **2a**–**c**,**f**,**h**–**k**,[S1–S5] iminophosphoranes **3a**–**c**,**j**,**k**,[S1,S6,S7] 2-(alkyn-1-yl)phenyl isothiocyanates **1a**,**b**,**j**,**k**,[S1,S8,S9] and 2-(alkyn-1-yl)phenyl isocyanates **4a**–**c**,**f**–**i**,**k**[S10–S13] were synthesized according to procedures previously described in the literature. The other new compounds **1**–**4** were synthesized in similar ways.

Table S1. Preparation of 2-(alkyn-1-yl)phenyl isothiocyanates **1** and isocyanates **4**.

		2 → **3**		**3** (**2**)[a] → **1**		**2** → **4**	
Entry	R	Time/h	Yield/%	Time/h	Yield/%	Time/h	Yield/%
a	*t*-Bu	6	85	24	99	2	89
b	*i*-Pr	12	86	24	99	6	99
c	*n*-Pr	6	79	24	99	4	76
d		12	79	24	86	6	81
e		24	78	24	82	1	99
f		18	74	24	99	3	99
g		18	76	24	96	3	86
h		12	87	24	99	3	86
i		18	72	24	99	6	83
j	TMS	6	76	24	99	4	89
k	Ph	6	78	24	94	3	76
l	CPh_3	24	50 (**2**, 23%)	12	96[a]	3	–[b]

a) Isothiocyanate **1l** was prepared from the reaction of **2l** with di(1*H*-imidazol-1-yl)methanethione.[S9]
b) Isocyanate **4l** was used without isolation because of its highly hygroscopic property.



Scheme S1. Preparation of 2-(alkyn-1-yl)phenyl isothiocyanates **1** and isocyanates **4**.
Reagent and conditions (i) PPh_3 (1.2 equiv), C_2Cl_6 (1.2 equiv), Et_3N (2.4 equiv), CH_2Cl_2, rt, 4 h; (ii) CS_2, rt, 12 h; (iii) triphosgene (0.37–1.1 equiv), Et_3N (2.0 equiv), toluene, 0 °C → rt.

1.2 Preparation of 2-(alkyn-1-yl)phenyl isothiocyanates 1 and isocyanates 4.

The key substrates, 2-(alkyn-1-yl)phenyl isothiocyanates **1** and isocyanates **4**, were prepared from 2-alkynylanilines **2** as outlined in Scheme S1. 2-Alkynylanilines **2**, which were readily synthesized from commercially available 2-iodoaniline and alkynes via the Sonogashira coupling, were converted to the corresponding iminophosphoranes **3**. The aza-Wittig reaction of **3** with carbon disulfide gave 2-(alkyn-1-yl)phenyl isothiocyanates **1a**–**k** in almost quantitative yields (Table S1). Isothiocyanate **1l** was conveniently prepared in high yield (96%) from the reaction of **2l** with di(1*H*-imidazol-1-yl)methanethione, as the aza-Wittig reaction of **3l** gave a moderate yield of **1l**. 2-(Alkyn-1-yl)phenyl isocyanates **4** were prepared in good to excellent yields by treatment of anilines **2** with triphosgene (Table S1). Trityl-substituted isocyanate **4l** (R = CPh_3) was highly hygroscopic and was used in one pot for the next reaction without isolation.

1.2.1 Typical procedure for synthesis of 2-(alkyn-1-yl)phenyl isothiocyanates 1

Iminophosphorane **3a** (R = *t*Bu; 1.00 g, 2.3 mmol) was dissolved into carbon disulfide (20 mL) and the mixture was stirred at room temperature for a day. After removal of the carbon disulfide, the residue was purified by silica gel column chromatography with hexane as an eluant to give 2-(3,3-dimethyl-1-butynyl)phenyl isothiocyanate (**1a**)[S1] (500 mg, 99%) as a colorless oil; IR (neat) 2900, 2028, 1440, 746 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.35 (s, 9H), 7.07–7.09 (m, 1H), 7.14–7.20 (m, 2H), 7.37 (dd, J = 7.7, 7.7 Hz, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 28.3 (C), 30.6 ($3CH_3$), 74.7 (C), 106.5 (C), 123.6 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.2 (C), 132.7 (CH), 136.4 (C); LRMS–EI (*m/z*): 215 (M^+, 99%), 200 (100); HRMS–ESI (*m/z*): calcd for $C_{13}H_{13}NS$ [M^+]: 215.0769, found: 215.0771.

2-Isothiocyanate-2-(3-methylbut-1-yn-1-yl)benzene (1b)[S1]

Colorless oil; IR (neat): 2969, 2069, 1450, 757 cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 1.33 (d, J = 7.0 Hz, 6H), 2.87 (sextet, J = 7.0 Hz, 1H), 7.12 (dd, J = 7.7, 7.7 Hz, 1H), 7.18–7.24 (m, 2H), 7.41 (dd, J = 7.7, 7.7 Hz, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 21.5 (CH), 22.5 ($2CH_3$), 75.5 (C), 104.1 (C), 123.6 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.5 (CH), 132.6 (C), 137.4 (C); LRMS–EI (*m/z*): 200 (M^+, 100%), 186 (90); HRMS–EI (*m/z*): calcd for $C_{12}H_{11}NS$ $(M)^+$: 201.0613, found: 201.0612.

1-Isothiocyanato-2-(pent-1-yn-1-yl)benzene (1c)

Colorless oil; IR (neat): 3062.4 (m), 2044.8 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.07 (t, J = 7.4 Hz, 3H), 1.69 (tq, J = 7.1, 7.4 Hz, 2H), 2.46 (t, J = 7.1 Hz, 2H), 7.08 (dd, J = 1.8, 7.9 Hz, 1H), 7.16 (ddd, J = 1.8, 7.6, 7.6 Hz, 1H), 7.20 (ddd, J = 1.4, 7.6, 7.9 Hz, 1H), 7.38 (dd, J = 1.8, 7.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.6 (CH_3), 21.71 (CH_2), 21.73 (CH_2), 76.5 (C), 99.0 (C), 123.4 (C), 124.4 (CH), 126.7 (CH), 128.1 (CH), 132.3 (CH), 132.9 (C), 132.8 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{11}NSNa$: 224.0504, found: 224.0503.

1-Isothiocyanato-2-(3-methoxy-3-methylbut-1-yn-1-yl)benzene (1d)

Pale yellow oil; IR (neat): 2985.3 (w), 2065.3 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.60 (s, 6H), 3.46 (s, 3H), 7.13 (dd, J = 1.6, 8.1 Hz, 1H), 7.20 (ddd, J = 1.4, 7.6, 8.1 Hz, 1H), 7.26 (ddd, J = 1.6, 7.7, 7.8 Hz, 1H), 7.43 (dd, J = 1.4, 7.8 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 27.9 ($2CH_3$), 51.9 (CH_3), 71.0 (C), 79.6 (C), 98.5 (C), 121.8 (C), 124.8 (CH), 126.8 (CH), 128.9 (CH), 132.4 (C), 132.8 (CH), 136.5 (C); LRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{13}NNaOS$: 254.0610, found: 254.0602.

1-Isothiocyanato-2-[(1-methylcyclohexyl)ethynyl]benzene (1e)

Colorless oil; IR (neat): 2931.3 (s), 2854.1 (w), 2067.3 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.12–1.31 (m, 3H), 1.33 (s, 3H), 1.58–1.78 (m, 5H), 1.88–1.94 (m, 2H), 7.12 (dd, J = 1.7, 7.3 Hz, 1H), 7.17 (ddd, J = 1.5, 7.3, 7.4 Hz, 1H), 7.20 (ddd, J = 1.7, 7.4, 7.6 Hz, 1H), 7.40 (dd, J = 1.5, 7.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.4 ($2CH_2$), 25.8 (CH_2), 29.7 (CH_3), 33.6 (C), 39.1 ($2CH_2$), 77.2 (C), 104.7 (C), 123.3 (C), 124.9 (CH), 126.7 (CH), 128.0 (CH), 132.1 (C), 132.8 (CH), 135.8 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{17}NSNa$: 278.0974, found: 278.0976.

1-(Cyclohexylethynyl)-2-isothiocyanatobenzene (1f)
Colorless oil; IR (neat): 2931.3 (s), 2854.1 (m), 2059.6 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.31–1.41 (m, 3H), 1.52–1.66 (m, 3H), 1.73–1.82 (m, 2H), 1.89–1.99 (m, 2H), 2.66 (tt, J = 4.0, 8.9 Hz, 1H), 7.10 (dd, J = 1.4, 7.7 Hz, 1H), 7.15–7.23 (m, 2H), 7.39 (dd, J = 1.7, 7.3 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.8 ($2CH_2$), 25.8 (CH_2), 29.9 (CH), 32.0 ($2CH_2$), 76.1 (C), 102.6 (C), 123.4 (C), 124.4 (CH), 126.6 (CH), 128.0 (CH), 132.4 (C + CH), 132.5 (C), 137.1 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{15}NSNa$: 264.0817, found: 264.0819.

1-(Cyclopentylethynyl)-2-isothiocyanatobenzene (1g)
Colorless oil; IR (neat): 2954.4 (m), 2051.9 (s) cm^{-1}; ^1H NMR (300.4 MHz, $CDCl_3$) δ 1.56–1.67 (m, 2H), 1.76–1.85 (m, 4H), 1.99–2.07 (m, 2H), 2.90 (tt, J = 7.7, 7.7 Hz, 1H), 7.09 (dd, J = 1.6, 7.6 Hz, 1H), 7.14–7.22 (m, 2H), 7.38 (dd, J = 1.9, 7.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.2 ($2CH_2$), 31.0 (CH), 33.4 ($2CH_2$), 75.8 (C), 103.1 (C), 123.6 (C), 124.4 (CH), 126.8 (CH), 128.1 (CH), 132.5 (CH), 132.6 (C), 137.3 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{13}NSNa$: 250.0661, found: 250.0664.

1-(Cyclopropylethynyl)-2-isothiocyanatobenzene (1h)
Light yellow oil; IR (neat): 2229.3 (w), 2059.6 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 0.88–0.94 (m, 2H), 0.94–1.00 (m, 2H), 1.51 (tt, J = 5.0, 8.3 Hz, 1H), 7.05 (dd, J = 1.6, 7.7 Hz, 1H), 7.14 (ddd, J = 1.6, 7.4, 7.7 Hz, 1H), 7.18 (ddd, J = 1.8, 7.6, 7.7 Hz, 1H), 7.35 (dd, J = 1.8, 7.4 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 0.4 (CH), 8.5 ($2CH_2$), 71.5 (C), 101.9 (C), 123.5 (C), 124.3 (CH), 126.7 (CH), 128.0 (CH), 132.3 (CH), 132.5 (C), 137.7 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_9NSNa$: 222.0348, found: 222.0344.

1-(Cyclohex-1-enylethynyl)-2-isothiocyanatobenzene (1i)
Light yellow oil; IR (neat): 2931.3 (s), 2861.4 (m), 2059.6 (s), 1627.6 (w) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.58–1.66 (m, 2H), 1.66–1.73 (m, 2H), 2.14–2.20 (m, 2H), 2.26–2.32 (m, 2H), 6.38 (ddd, J = 1.8, 4.0, 5.9 Hz, 1H), 7.10 (dd, J = 1.5, 7.7 Hz, 1H), 7.15–7.23 (m, 2H), 7.40 (dd, J = 1.3, 7.2 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.4 (CH_2), 22.2 (CH_2), 25.8 (CH_2), 28.7 (CH_2), 82.3 (C), 99.0 (C), 120.4 (C), 123.3 (C), 124.5 (CH), 126.8 (CH), 128.3 (CH), 132.1 (C), 132.3 (CH), 136.7 (CH), 137.5 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{13}NSNa$: 262.0661, found: 262.0659.

2-Isothiocyanato-1-(trimethylsilylethynyl)benzene (1j)[S1]
Colorless oil; IR (neat): 3070, 2960, 2898, 2537, 2038, 1592, 1477, 1444, 1409, 1249, 1103, 935, 844, 756 cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 0.30 (s, 9H), 7.09–7.12 (m, 1H), 7.16–7.28 (m, 2H), 7.43–7.46 (m, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 0.39 ($3CH_3$), 99.7 (C), 102.9 (C), 122.5 (C), 124.6 (CH), 126.8 (CH), 129.2 (CH), 132.8 (C), 132.9 (CH), 137.3 (C); LRMS–EI (*m/z*): 231 (M^+, 32%), 216 (100); HRMS–EI (*m/z*): calcd for $C_{12}H_{13}NSSi$ $(M)^+$: 231.0538, found: 231.0540.

2-Isothiocyanato-1-(2-phenyl-1-ethynyl)benzene (1k) [S8]
Colorless oil; ^1H NMR (300.4 MHz, $CDCl_3$): δ 7.09–7.12 (m, 1H), 7.17–7.26 (m, 2H), 7.34–7.36 (m, 3H), 7.48–7.51 (m, 1H), 7.63–7.66 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 84.9 (C), 96.9 (C), 122.4 (C),

122.7 (C), 124.5 (CH), 126.9 (CH), 128.3 (2CH), 128.8 (CH), 128.9 (CH), 131.6 (2CH), 132.4 (C), 132.5 (CH), 137.8 (C).

1-(2-isothiocyanatophenyl)-2-tritylethyne (1l)
Colorless crystals; mp 136.4–137.1 °C; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 7.11–7.41 (m, 18H), 7.48 (d, J = 7.5 Hz, 1H); IR (KBr): 3062.4 (m), 3023.8 (w), 2113.6 (s), 1689.3 (m) cm^{-1}; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 56.4 (C), 80.8 (C), 102.4 (C), 121.3 (C), 126.0 (CH), 126.7 (CH), 126.9 (3CH), 128.1 (6CH), 128.9 (CH), 129.2 (6CH), 132.6 (C), 133.0 (CH), 136.1 (C), 144.7 (3C); HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{28}H_{19}NSNa$: 424.1130, found: 424.1132; Anal. calcd for $C_{28}H_{19}NS$: C 83.76, H 4.77, N 3.49, found: C 84.11., H 4.98, N 3.46.

1.2.2 Typical Procedure for Synthesis of 2-(alkyn-1-yl)phenyl isocyanates 4
2-(3-Methylbut-1-yn-1-yl)phenylamine **3b** (306 mg, 1.92 mmol) and triethylamine (0.5 mL, 3.84 mmol) were dissolved into dry toluene (20 mL) and the mixture was cooled to 0 ˚C with stirring. A toluene solution (5 mL) of triphosgene (211 mg, 0.71 mmol) was added dropwise with stirring at 0 ˚C and then at room temperature for 1 hour. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified using flash column chromatography on silica gel with hexane as an eluant to give 1-isocyanato-2-(3-methylbut-1-yn-1-yl)benzene (**4b**)[S10] (356 mg, 99%) as a colorless oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.29 (d, J = 6.9 Hz, 6H), 2.83 (septet, J = 6.9 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.05 (dd, J = 8.0, 7.7 Hz, 1H), 7.14 (dd, J = 7.7, 7.9 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.4 (CH), 22.3 ($2CH_3$), 75.4 (C), 104.4 (C), 121.6 (C), 123.2 (CH), 125.1 (CH), 127.3 (C), 128.4 (CH), 132.1 (CH), 134.9 (C).

1-(3,3-Dimethyl-but-1-yn-1-yl)-2-isocyanatobenzene (4a) [S10]
Colorless oil; ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 1.35 (s, 9H), 6.96 (d, J = 8.1 Hz, 1H), 7.06 (dd, J = 7.5, 8.1 Hz, 1H), 7.16 (dd, J = 7.5, 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 28.4 (C), 30.4 ($3CH_3$), 74.7 (C), 106.9 (C), 121.7 (C), 123.3 (CH), 125.2 (CH), 128.3 (C), 128.4 (CH), 132.3 (CH), 134.6 (C).

1-Isocyanato-2-pent-1-yn-1-ylbenzene (4c) [S10]
Colorless oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.05 (t, J = 7.4 Hz, 3H), 1.67 (tq, J = 7.0, 7.4 Hz, 2H), 2.45 (t, J = 7.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 1H), 7.08 (dd, J = 7.6, 7.6 Hz, 1H), 7.18 (dd, J = 7.6, 8.0 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.4 (CH_3), 21.6 (CH_2), 21.7 (CH_2), 76.4 (C), 99.5 (C), 121.6 (C), 123.3 (CH), 125.2 (CH), 127.4 (C), 128.5 (CH), 132.0 (CH), 135.2 (C).

1-Isocyanato-2-(3-methoxy-3-methylbut-1-yn-1-yl)benzene (4d)
Yellow oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.58 (s, 6H), 3.43 (s, 3H), 7.00 (dd, J = 1.2, 8.0 Hz, 1H), 7.11 (ddd, J = 1.1, 7.7, 7.8 Hz, 1H), 7.23 (ddd, J = 1.6, 7.8, 8.0 Hz, 1H), 7.42 (dd, J = 1.6, 7.8 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 27.7 ($2CH_3$), 51.7 (CH_3), 71.0 (C), 79.6 (C), 99.1 (C), 120.3 (C), 123.5 (CH), 125.3 (CH), 126.6 (C), 129.2 (CH), 132.6 (CH), 134.7 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{13}NNaO$: 238.0838, found: 238.0834.

1-Isocyanato-2-(1-methylcyclohexylethynyl)benzene (4e)
Colorless oil; IR (neat): 2931.3 (s), 2854.1 (m), 2260.2 (s) cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.13–1.30 (m, 3H), 1.31 (s, 3H), 1.59–1.72 (m, 5H), 1.86–1.92 (m, 2H), 6.99 (dd, J = 1.1, 7.7 Hz, 1H), 7.09 (ddd, J = 1.5, 7.6, 7.6 Hz, 1H), 7.18 (ddd, J = 1.5, 7.6, 7.6 Hz, 1H), 7.40 (dd, J = 1.5, 7.7 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.3 ($2CH_2$), 25.8 (CH_2), 29.5 (CH_3), 33.6 (C), 39.0 ($2CH_2$), 77.2 (C),

105.4 (C), 121.8 (C), 123.4 (CH), 125.2 (CH), 126.7 (C), 128.3 (CH), 132.6 (CH), 134.5 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{18}NO$: 240.1383, found: 240.1383.

1-Cyclohexylethynyl-2-isocyanatobenzene (4f) [S11]
Colorless oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.29–1.39 (m, 3H), 1.51–1.62 (m, 3H), 1.70–1.80 (m, 2H), 1.88–1.98 (m, 2H), 2.64 (tt, J = 3.7, 9.6 Hz, 1H), 6.98 (dd, J = 1.3, 8.0 Hz, 1H), 7.09 (ddd, J = 1.3, 7.6, 7.6 Hz, 1H), 7.18 (ddd, J = 1.6, 7.6, 7.9 Hz, 1H), 7.37 (dd, J = 1.6, 7.7 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.0 ($2CH_2$), 25.8 (CH_2), 30.0 (CH), 32.1 ($2CH_2$), 76.0 (C), 103.3 (C), 121.7 (C), 123.3 (CH), 125.2 (CH), 127.1 (C), 128.4 (CH), 132.3 (CH), 134.8 (C).

1-Cyclopentylethynyl-2-isocyanatobenzene (4g) [S12]
Colorless oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.50–1.68 (m, 2H), 1.68–1.86 (m, 4H), 1.94–2.09 (m, 2H), 2.88 (tt, J = 7.7, 7.7 Hz, 1H), 6.96 (dd, J = 1.4, 7.8 Hz, 1H), 7.06 (ddd, J = 1.5, 7.6, 7.6 Hz, 1H), 7.15 (ddd, J = 1.7, 7.6, 7.7 Hz, 1H), 7.35 (dd, J = 1.7, 7.6 Hz, 1H); ^{13}C NMR (125.65 MHz, $CDCl_3$): δ 25.1 ($2CH_2$), 30.9 (CH), 33.3 ($2CH_2$), 75.7 (C), 103.5 (C), 121.7 (C), 123.2 (CH), 125.2 (CH), 127.3 (C), 128.4 (CH), 132.1 (CH), 134.8 (C).

1-Cyclopropylethynyl-2-isocyanatobenzene (4h) [S13]
Colorless oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 0.84–0.94 (m, 4H), 1.49 (tt, J = 5.3, 8.2 Hz, 1H), 6.94 (d, J = 7.9 Hz, 1H), 7.05 (dd, J = 7.6, 7.7 Hz, 1H), 7.14 (dd, J = 7.7, 7.9 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H); ^{13}C NMR (125.65 MHz, $CDCl_3$): δ 0.26 (CH), 8.3 ($2CH_2$), 71.5 (C), 102.3 (C), 121.5 (C), 123.2 (CH), 125.2 (CH), 127.4 (C), 128.3 (CH), 132.0 (CH), 134.9 (C).

1-Cyclohex-1-enylethynyl-2-isocyanatobenzene (4i) [S14]
Yellow oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.54–1.74 (m, 4H), 2.11–2.21 (m, 2H), 2.21–2.33 (m, 2H), 6.33 (ddd, J = 1.8, 4.0, 5.9 Hz, 1H), 6.99 (dd, J = 1.4, 7.8 Hz, 1H), 7.10 (ddd, J = 1.4, 7.6, 7.6 Hz, 1H), 7.19 (ddd, J = 1.7, 7.6, 7.8 Hz, 1H), 7.39 (dd, J = 1.7, 7.7 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.4 (CH_2), 22.2 (CH_2), 25.8 (CH_2), 28.5 (CH_2), 82.1 (C), 99.4 (C), 120.3 (C), 121.5 (C), 123.4 (CH), 125.3 (CH), 127.2 (C), 128.7 (CH), 132.1 (CH), 134.5 (C), 136.5 (CH).

(2-Isocyanatophenylethynyl)trimethylsilane (4j)
Colorless oil; IR (neat): 2962, 2268, 2160, 1597, 1419, 1250, 864, 756 cm^{-1}; ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 0.28 (s, 9H), 6.97 (d, J = 8.0 Hz, 1H), 7.08 (dd, J = 7.6, 7.7 Hz, 1H), 7.21 (dd, J = 7.6, 8.0 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ –0.5 ($3CH_3$), 99.8 (C), 103.6 (C), 120.7 (C), 123.5 (CH), 125.2 (CH), 126.9 (C), 129.5 (CH), 132.5 (CH), 135.2 (C).

1-Isocyanato-2-(2-phenylethynyl)benzene (4k) [S10]
Colorless oil; ^{1}H-NMR (500.0 MHz, $CDCl_3$): δ 7.06 (d, J = 7.9 Hz, 1H), 7.16 (dd, J = 7.2, 7.7 Hz, 1H), 7.26 (dd, J = 7.7, 7.9 Hz, 1H), 7.34–7.40 (m, 3H), 7.52 (d, J = 7.3 Hz, 1H), 7.59–7.66 (m, 2H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ 84.8 (C), 97.4 (C), 121.0 (C), 122.4 (C), 123.6 (CH), 125.5 (CH), 127.3 (C), 128.4 (2CH), 128.9 (CH), 129.3 (CH), 131.5 (2CH), 132.3 (CH), 134.8 (C).

Starting materials 2 and 3
2-(3-Methoxy-3-methylbut-1-ynyl)phenylamine (2d)
Yellow solid; mp 43.1–44.0 °C; IR (KBr): 3463.5 (m), 3371.0 (m), 2977.6 (m), 2931.3 (m), 2206.2 (w), 1612.2 (s) cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.55 (s, 6H), 3.42 (s, 3H), 4.13–4.24 (br. s, 2H), 6.61–6.67 (m, 2H), 7.08 (ddd, J = 1.5, 7.9, 8.4 Hz, 1H), 7.25 (dd, J = 1.5, 8.0 Hz, 1H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ 28.4 ($2CH_3$), 51.5 (CH_3), 70.9 (C), 80.7 (C), 96.3 (C), 107.1 (C), 114.0 (CH), 117.5 (CH),

129.5 (CH), 132.0 (CH), 147.7 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO$: 212.1046, found: 212.1046.

2-(1-Methylcyclohexylethynyl)phenylamine (2e)
Yellow oil; IR (neat): 3471.2 (w), 3378.7 (w), 2923.6 (s), 2854.1 (m), 1612.2 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.11–1.29 (m, 3H), 1.30 (s, 3H), 1.57–1.75 (m, 5H), 1.79–1.84 (m, 2H), 4.00–4.23 (br. s, 2H), 6.61–6.66 (m, 2H), 7.04 (dd, J = 7.2, 8.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.5 ($2CH_2$), 25.8 (CH_2), 30.5 (CH_3), 33.4 (C), 39.4 ($2CH_2$), 78.0 (C), 102.1 (C), 108.9 (C), 114.0 (CH), 117.7 (CH), 128.6 (CH), 131.9 (CH), 147.4 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{20}N$: 214.1590, found: 214.1595.

2-Cyclopentylethynylphenylamine (2g)
Yellow oil; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.54–1.66 (m, 2H), 1.66–1.84 (m, 4H), 1.95–2.06 (m, 2H), 2.87 (tt, J = 7.5, 7.5 Hz, 1H), 4.02–4.24 (br. s, 2H), 6.64–6.68 (m, 2H), 7.05 (dd, J = 7.4, 7.8 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.9 ($2CH_2$), 31.0 (CH), 34.1 ($2CH_2$), 76.4 (C), 100.0 (C), 118.9 (C), 114.0 (CH), 117.7 (CH), 128.6 (CH), 131.8 (CH), 147.4 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{16}N$: 186.1277, found: 186.1276.

2-Triphenylprop-1-ynylphenylamine (2l)
Colorless crystals; mp 132.7–134.4 °C; IR (KBr): 3448.1 (w), 3363.3 (w), 3023.8 (w), 1604.5 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 3.94–4.21 (br. s, 2H), 6.60–6.70 (m, 2H), 7.07 (dd, J = 7.4, 7.9 Hz, 1H), 7.20–7.38 (m, 16H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 56.4 (C), 82.1 (C), 101.1 (C), 108.2 (C), 114.2 (CH), 117.8 (CH), 126.9 (3CH), 128.1 (6CH), 129.1 (6CH), 129.4 (CH), 132.1 (CH), 145.8 (3C), 148.2 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{27}H_{21}Na$: 382.1562, found: 382.1562.

Iminophosphorane 3a[S1,S6,S7]
Colorless solid; mp 109–110 °C; ^1H NMR (300.4 MHz, $CDCl_3$): δ 1.38 (s, 9H), 6.42 (d, J = 6.2 Hz, 1H), 6.54 (dd, J = 7.0, 7.5 Hz, 1H), 6.77 (dd, J = 7.0, 7.5 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.41–7.50 (m, 9H), 7.81–7.87 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 28.2 (C), 31.5 ($3CH_3$), 79.8 (C), 100.3 (C), 117.0 (d, J = 1.1 Hz, CH), 119.4 (d, J = 22.6 Hz, C), 121.3 (d, J = 9.0 Hz, CH), 127.6 (CH), 128.4 (d, J = 12.5 Hz, 6CH), 131.46 (d, J = 100.0 Hz, 3C), 131.48 (d, J = 2.7 Hz, 3CH), 132.7 (d, J = 9.5 Hz, 6CH), 133.2 (d, J = 1.3 Hz, CH), 152.1 (C).

Iminophosphorane 3b [S1]
Colorless solid; mp 128–129 °C; IR (KBr): 2964, 1580, 682 cm^{-1}; ^1H NMR (300.4 MHz, $CDCl_3$): δ 1.328 (d, J = 6.9 Hz, 3H), 1.331 (d, J = 6.9 Hz, 3H), 2.90 (sextet, J = 6.9 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 6.55 (dd, J = 7.4, 7.4 Hz, 1H), 6.75–6.81 (m, 1H), 7.28–7.32 (m, 1H), 7.38–7.53 (m, 9H), 7.80–7.87 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.6 ($2CH_3$), 23.4 (CH), 80.6 (C), 97.6 (C), 117.0 (d, J = 1.1 Hz, CH), 119.3 (d, J = 22.4 Hz, C), 121.3 (d, J = 9.3 Hz, CH), 127.6 (CH), 128.4 (d, J = 11.8 Hz, 6CH), 131.4 (d, J = 100.1 Hz, 3C), 131.5 (d, J = 3.0 Hz, 3CH), 132.7 (d, J = 10.0 Hz, 6CH), 133.0 (d, J = 1.7 Hz, CH), 152.3 (C); LRMS–EI (*m/z*): 419 (M^+, 100%), 418 (40), 183 (42); HRMS-EI (*m/z*): calcd for $C_{29}H_{26}NP$ $(M)^+$: 419.1804, found: 419.1811.

Iminophosphorane 3c [S6]
Colorless solid; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.06 (t, J = 7.4 Hz, 3H), 1.69 (tq, J = 7.2, 7.4 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 6.46 (d, J = 7.9 Hz, 1H), 6.56 (dd, J = 7.3, 7.9 Hz, 1H), 6.79 (dd, J = 7.3, 7.5 Hz, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.39–7.49 (m, 6H), 7.48–7.53 (m, 3H), 7.80–7.86 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.8 (CH_3), 22.1 (CH_2), 22.6 (CH_2), 81.6 (C), 92.2 (C), 117.1 (CH), 119.4 (d, J =

21.7 Hz, C), 121.5 (d, J = 9.3 Hz, CH), 127.6 (CH), 128.4 (d, J = 11.9 Hz, 6CH), 131.49 (d, J = 2.9 Hz, 3CH), 131.50 (d, J = 100.4 Hz, 3C), 132.7 (d, J = 9.3 Hz, 6CH), 133.0 (CH), 152.7 (C); HRMS–ESI (*m/z*): calcd for $C_{29}H_{27}NP$: 420.1876, found: 420.1866; Anal. calcd for $C_{29}H_{26}NP$: C 83.03, H 6.25, N 3.34, found: C 83.27, H 6.40, N 3.02.

Iminophosphorane 3d
Yellow oil; IR (KBr): 3062.4 (w), 2213.9 (w), 1589.1 (m) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.60 (s, 6H), 3.42 (s, 3H), 6.45 (d, J = 8.1 Hz, 1H), 6.50 (dd, J = 7.5, 7.6 Hz, 1H), 6.76 (dd, J = 7.5, 8.1 Hz, 1H), 7.29–7.41 (m, 10H), 7.46–7.84 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 28.5 ($2CH_3$), 51.2 (CH_3), 70.9 (C), 85.4 (C), 92.5 (C), 116.6 (CH), 117.8 (d, J = 23.0 Hz, C), 120.9 (d, J = 9.3 Hz, CH), 128.10 (CH), 128.13 (d, J = 11.9 Hz, 6CH), 130.9 (d, J = 100.1 Hz, 3C), 131.3 (3CH), 132.0 (d, J = 10.1 Hz, 6CH), 133.0 (CH), 152.5 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{29}NOP$: 450.1981, found: 450.1977.

Iminophosphorane 3e
Colorless crystals; mp 135.2–137.7 °C; IR (KBr): 2923.6 (m), 1581.3 (w) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.07–1.20 (m, 1H), 1.21–1.30 (m, 2H), 1.35 (s, 3H), 1.47–1.55 (m, 2H), 1.56–1.64 (m, 1H), 1.75–1.84 (m, 2H), 1.85–1.93 (m, 2H), 6.41 (d, J = 7.9 Hz, 1H), 6.56 (dd, J = 7.6, 7.9 Hz, 1H), 6.77 (dd, J = 7.6, 7.9 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.40–7.45 (m, 6H), 7.47–7.53 (m, 3H), 7.81–7.88 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.4 (CH_2), 26.1 (CH_2), 30.6 (CH_3), 33.4 (C), 39.9 (CH_2), 82.5 (C), 98.5 (C), 117.1 (C), 119.7 (C), 119.9 (C), 121.3 (CH), 121.4 (CH), 127.5 (CH), 128.4 (d, J = 12.0 Hz, 6CH), 131.5 (d, J = 2.3 Hz, 3CH), 131.6 (d, J = 99.6 Hz, 3C), 132.7 (d, J = 10.1 Hz, 6CH), 133.4 (CH), 152.1 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{33}H_{33}NP$: 474.2345, found: 474.2343.

Iminophosphorane 3f
Colorless crystals; mp 121.3–122.8 °C; IR (KBr): 3054.7 (w), 2931.3 (s), 2854.1 (m), 1581.3 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$) δ 1.23–1.36 (m, 3H), 1.46–1.56 (m, 1H), 1.56–1.67 (m, 2H), 1.71–1.82 (m, 2H), 1.92–2.02 (m, 2H), 2.61–2.72 (m, 1H), 6.47 (d, J = 7.7 Hz, 1H), 6.48 (d, J = 7.7 Hz, 1H), 6.72 (dd, J = 7.7, 7.7 Hz, 1H), 7.23–7.38 (m, 10H), 7.75–7.85 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 24.7 ($2CH_2$), 25.7 (CH_2), 30.0 (CH), 32.8 ($2CH_2$), 81.2 (C), 95.8 (C), 116.6 (CH), 119.0 (d, J = 22.0 Hz, C), 120.9 (d, J = 9.8 Hz, CH), 127.2 (CH), 128.0 (d, J = 12.4 Hz, 6CH), 131.0 (d, J = 99.6 Hz, 3C), 131.2 (d, J = 1.8 Hz, 3CH), 132.2 (d, J = 9.8 Hz, 6CH), 132.7 (CH), 152.0 (C); Anal. calcd for $C_{32}H_{30}NP$: C 83.63, H 6.58, N 3.05, found: C 83.37, H 6.70, N 3.00.

Iminophosphorane 3g
Colorless crystals; mp 149.0–151.0 °C; IR (KBr): 3070.1 (m), 2954.4 (s), 2869.6 (m), 1581.3 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.52–1.64 (m, 2H), 1.72–1.83 (m, 4H), 1.98–2.09 (m, 2H), 2.93 (tt, J = 7.3, 7.3 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 6.54 (dd, J = 7.4, 7.9 Hz, 1H), 6.77 (dd, J = 7.4, 7.9 Hz, 1H), 7.23 (d, J = 7.4 Hz, 1H), 7.36–7.43 (m, 6H), 7.44–7.50 (m, 3H), 7.78–7.85 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.1 ($2CH_2$), 31.4 (CH), 34.1 ($2CH_2$), 81.0 (C), 96.3 (C), 117.0 (CH), 119.4 (d, J = 22.2 Hz, C), 121.3 (d, J = 9.1 Hz, CH), 127.5 (CH), 128.3 (d, J = 12.2 Hz, 6CH), 131.14 (d, J = 100.4 Hz, 3C), 131.44 (d, J = 2.3 Hz, 3CH), 132.6 (d, J = 10.4 Hz, 6CH), 132.9 (CH), 152.3 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{31}H_{29}NP$: 446.2032, found: 446.2036; Anal. calcd for $C_{31}H_{28}NP$: C 83.57, H 6.33, N 3.14, found: C 83.20, H 6.30, N 2.90.

Iminophosphorane 3h
Colorless crystals; mp 163.0–166.4 °C; IR (KBr): 3054.7 (m), 3008.4 (m), 1581.3 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 0.85 (d, J = 6.7 Hz, 4H), 1.55 (tt, J = 6.7, 6.7 Hz, 1H), 6.45 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 7.6, 7.6 Hz, 1H), 6.78 (dd, J = 7.6, 8.2 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.39–7.44 (m, 6H),

7.46–7.51 (m, 3H), 7.78–7.85 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 0.8 (CH), 8.4 ($2CH_2$), 76.9 (C), 95.1 (C), 117.0 (CH), 119.1 (d, J = 22.2 Hz, C), 121.3 (d, J = 9.3 Hz, CH), 127.6 (CH), 128.4 (d, J = 12.2 Hz, 6CH), 131.4 (d, J = 100.4 Hz, 3C), 131.5 (d, J = 2.3 Hz, 3CH), 132.6 (d, J = 10.1 Hz, 6CH), 132.9 (CH), 152.6 (C); Anal. calcd for $C_{29}H_{24}NP$: C 83.43, H 5.79, N 3.36, found: C 83.27, H 5.94, N 3.09.

Iminophosphorane 3i
Yellow crystals; mp 137.2–139.8 °C; IR (KBr): 3054.7 (m), 2923.6 (m), 1581.3 (s) cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.59–1.66 (m, 2H), 1.66–1.73 (m, 2H), 2.12–2.19 (m, 2H), 2.29–2.35 (m, 2H), 6.21 (t, J = 4.0 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 6.56 (dd, J = 7.6, 7.9 Hz, 1H), 6.79 (dd, J = 7.6, 7.9 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.36–7.44 (m, 6H), 7.45–7.51 (m. 3H), 7.79–7.87 (m. 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.7 (CH_2), 22.6 (CH_2), 25.8 (CH_2), 29.6 (CH_2), 88.4 (C), 93.7 (C), 119.0 (d, J = 22.8 Hz, C), 121.2 (CH), 121.3 (CH), 121.9 (C), 127.9 (CH), 128.4 (d, J = 12.0 Hz, 6CH), 131.3 (d, J = 100.4 Hz, 3C), 131.5 (CH), 134.5 (CH), 132.7 (d, J = 9.3 Hz, 6CH), 132.8 (d, J = 6.2 Hz, 3CH), 152.5 (C); HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{32}H_{29}NP$: 458.2032, found: 458.2030.

Iminophosphorane 3j [S1a,S2b]
Colorless solid; mp 109–110 °C; ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 0.29 (s, 9H), 6.42 (d, J = 8.2 Hz, 1H), 6.55 (dd, J = 7.4, 7.4 Hz, 1H), 6.81 (ddd, J = 1.7, 7.3, 7.7 Hz, 1H), 7.35–7.54 (m, 10H), 7.79–7.86 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 0.4 ($3CH_3$), 95.5 (C), 106.9 (C), 116.9 (CH), 118.3 (d, J = 22.9 Hz, C), 121.3 (d, J = 9.8 Hz, CH), 128.5 (d, J = 12.1 Hz, 6CH), 128.7 (CH), 131.1 (d, J = 99.8 Hz, 3C), 131.6 (d, J = 2.7 Hz, 3CH), 132.7 (d, J = 9.7 Hz, 6CH), 133.7 (CH), 153.3 (C).

Iminophosphorane 3k [S1a, S2b]
Colorless solid; mp 143–145 °C; ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 6.49 (d, J = 7.6 Hz, 1H), 6.61 (dd, J = 7.6, 7.6 Hz, 1H), 6.85 (dd, J = 7.6, 7.6 Hz, 1H), 7.24–7.50 (m, 14H), 7.58 (dd, J = 1.2, 7.9 Hz, 1H), 7.81–7.88 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 91.4 (C), 91.9 (C), 117.1 (CH), 121.3 (d, J = 9.3 Hz, CH), 124.9 (C), 127.2 (2CH), 128.2 (d, J = 23.2 Hz, 6CH), 128.54 (CH), 128.56 (C), 128.6 (CH), 131.3 (d, J = 100.3 Hz, 3C), 131.4 (2CH), 131.6 (d, J = 3.1 Hz, 3CH), 132.6 (d, J = 22.9 Hz, 6CH), 132.9 (d, J = 1.8 Hz, CH), 152.9 (C).

Iminophosphorane 3l
Colorless crystals; mp 197.8–198.9 °C; IR (KBr): 3054.7 (s), 3016.1 (s), 1581.3 (s) cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 6.37 (d, J = 8.2 Hz, 1H), 6.57 (dd, J = 7.5, 7.6 Hz, 1H), 6.78 (dd, J = 7.5, 8.2 Hz, 1H), 7.10–7.17 (m, 9H), 7.20–7.27 (m, 6H), 7.37–7.44 (m, 10H), 7.69–7.77 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 56.5 (C), 86.5 (C), 97.5 (C), 117.0 (CH), 119.1 (d, J = 21.7 Hz, C), 121.0 (d, J = 8.5 Hz, CH), 126.3 (3CH), 127.7 (6CH), 128.1 (CH), 128.4 (d, J = 12.2 Hz, 6CH), 129.4 (6CH), 131.4 (d, J = 2.8 Hz, 3CH), 131.4 (d, J = 100.1 Hz, 3C), 132.6 (d, J = 9.6 Hz, 6CH), 133.2 (CH), 146.1 (3C), 152.9 (C); Anal. calcd for $C_{45}H_{34}NP$: C 87.21, H 5.53, N 2.26, found: C 86.90, H 5.63, N 2.25.

1.3 Physical and spectral data of migration products from isothiocyanates 1

1,2,3,5-Tetrahydrocyclopenta[4,5]thieno[2,3-*b*]indole (7)
Colorless crystals; mp 201.0–202.9 °C; IR (KBr): 3371.0 (s), 2923.6 (s) cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.34–1.44 (m, 1H), 1.54–1.71 (m, 4H), 1.73–1.81 (m, 1H), 1.93–2.09 (m, 2H), 2.56–2.63 (m, 1H), 2.69–2.77 (m, 1H), 6.96–7.06 (m, 3H), 7.23–7.33 (br. s, 1H), 7.36 (dd, J = 3.7, 6.3 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 26.5 (CH_2), 27.8 (CH_2), 28.1 (CH_2), 32.3 (CH_2), 33.4 (CH_2), 110.6 (CH), 114.8 (C), 116.2 (C), 118.1 (CH), 119.5 (CH), 121.5 (CH), 127.9 (C), 128.9 (C), 135.6 (C), 145.2 (C); Anal. calcd for $C_{15}H_{15}NS$: C 74.65, H 6.26, N 5.80, found: C 74.51, H 6.64, N 5.41.

2,3,4,6-Tetrahydro-1*H*-benzo[4,5]thieno[2,3-*b*]indole (8)
Colorless crystals; mp 259.6–261.6 °C; IR (KBr): 3455.8 (s), 3378.7 (s), 2946.7 (s) cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 1.66–1.73 (m, 2H), 1.73–1.82 (m, 1H), 1.82–1.91 (m, 1H), 2.10 (dt, J = 6.8, 15.9 Hz, 1H), 2.24 (dt, J = 7.2, 15.9 Hz, 1H), 2.53–2.66 (m, 2H) 7.01–7.08 (m, 3H), 7.40 (dd, J = 3.0, 5.5 Hz, 1H), 7.43–7.51 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 26.8 (CH_2), 27.1 (CH_2), 32.8 (CH_2), 33.4 (CH_2), 110.7 (CH), 113.8 (C), 117.1 (C), 118.2 (CH), 119.5 (CH), 121.6 (CH), 127.1 (C), 128.4 (C), 135.7 (C), 150.0 (C); Anal. calcd for $C_{14}H_{13}NS$: C 73.97, H 5.76, N 6.16, found: C 74.08, H 5.84, N 6.12.

2,3-Diphenylspiro[indene-1,3'-indoline]-2'-thione (9) (see X-Ray crystallographic data & Fig. 1)
Colorless crystals; mp 248.0–248.8 °C; IR (KBr): 3178.1 (s), 1951.6 (w), 1619.9 (s) cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$) δ 6.84–6.89 (m, 3H), 6.93–7.08 (m, 6H), 7.16 (dd, J = 7.5, 7.5 Hz, 1H), 7.23 (dd, J = 7.6, 7.8 Hz, 1H), 7.31–7.35 (m, 2H), 7.36–7.43 (m, 3H), 7.45–7.48 (m, 2H), 10.17–10.53 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 77.5 (C), 110.3 (CH), 121.3 (CH), 122.3 (CH), 124.3 (CH), 124.5 (CH), 126.9 (CH), 127.3 (CH), 127.76 (CH), 127.84 (2CH), 128.1 (CH), 128.5 (2CH), 128.8 (CH), 129.1 (2CH), 129.6 (2CH), 133.9 (C), 134.3 (C), 134.5 (C), 143.3 (C), 144.0 (C), 144.9 (C), 145.7 (C), 147.3 (C), 206.0 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{28}H_{19}NSNa$: 424.1130, found: 424.1129; Anal. calcd for $C_{28}H_{19}NS$: C 83.76, H 4.77, N 3.49, found: C 83.71, H 4.91, N 3.42.

1.4 Physical and spectral data of migration products from isocyanates 4

2,2-Dimethyl-2*H*-furo[2,3-*b*]indole (12)
Yellow solid; mp 188.3–190.2 °C; IR (KBr): 1589.1 (s), 1619.9 (s), 2931.3 (w), 2969.8 (w) cm^{-1}; ^1H NMR (600.0 MHz, $CDCl_3$): δ 1.66 (s, 6H), 6.98 (s, 1H), 7.05 (ddd, J = 1.4, 7.2, 7.2 Hz, 1H), 7.33 (ddd, J = 1.2, 7.2, 7.2 Hz, 1H), 7.36 (dd, J = 1.2, 7.2, 1H), 7.52 (dd, J = 1.4, 7.2 Hz, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 25.2 ($2CH_3$), 103.0 (C), 119.3 (CH), 122.4 (CH), 122.5 (C), 123.8 (CH), 130.9 (CH), 132.7 (C), 141.2 (CH), 163.8 (C), 183.2 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{12}NO$: 186.0913, found: 186.0914.

(*Z*)-3-[1-(Cyclohex-1-en-1-yl)ethylidene]-1,3-dihydroindol-2-one (13)
Yellow solid; mp 172.0–173.8 °C; IR (KBr) : 3178.1 (w), 2923.6 (w), 1689.3 (s), 1612.2 (s) cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 1.69–1.87 (m, 4H), 2.09–2.27 (m, 4H), 2.56 (s, 3H), 5.65–5.70 (m, 1H), 6.82 (d, J = 7.7 Hz, 1H), 6.92 (dd, J = 7.7, 7.7 Hz, 1H), 7.14 (dd, J = 7.7, 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.91–8.03 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 20.7 (CH_3), 21.8 (CH_2), 22.7 (CH_2), 25.0 (CH_2), 25.8 (CH_2), 109.1 (CH), 121.41 (C), 120.44 (CH), 123.2 (CH), 123.8 (C), 124.3 (CH), 127.7 (CH), 139.2 (C), 139.9 (C), 159.3 (C), 170.0 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{17}NONa$: 262.1202, found: 262.1203.

3'-Methylspiro[cyclohexane-1,2'-furo[2,3-*b*]indole] (14)
Yellow oil; IR (neat): 2931.3 (s), 2854.1 (w), 1704.8 (s), 1612.2 (m) cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 1.24–1.33 (m, 1H), 1.60–1.65 (m, 2H), 1.75–1.89 (m, 7H), 2.27 (s, 3H), 7.04 (ddd, J = 0.9, 7.2, 7.5 Hz, 1H), 7.29 (ddd, J = 1.2, 7.5, 7.7 Hz, 1H), 7.37 (dd, J = 0.9, 7.7 Hz, 1H), 7.52 (dd, J = 1.2, 7.2 Hz, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 13.0 (CH_3), 22.4 ($2CH_2$), 24.5 (CH_2), 33.0 ($2CH_2$), 105.0 (C), 119.1 (CH), 121.8 (CH), 122.8 (CH), 123.2 (C), 128.2 (C), 130.0 (CH), 155.3 (C), 163.1 (C), 182.3 (C); HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{18}NO$: 240.1383, found: 240.1386.

6a-Methyl-6a,7,8,9,10,11-hexahydrocyclohepta[4,5]furo[2,3-*b*]indole (15)

Yellowish oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.33–1.43 (m, 1H), 1.55–1.76 (m, 4H), 1.66 (s, 3H), 1.94–2.03 (m, 2H), 2.20 (ddd, J = 2.1, 9.3, 14.7 Hz, 1H), 2.53 (ddd, J = 4.1, 9.3, 13.6 Hz, 1H), 3.18 (ddd, J = 4.3, 7.3, 11.6 Hz, 1H), 7.04 (ddd, J = 0.9, 7.3, 7.6 Hz, 1H), 7.30 (ddd, J = 1.2, 7.6, 7.7 Hz, 1H), 7.36 (dd, J = 0.9, 7.8 Hz, 1H), 7.49 (dd, J = 1.2, 7.3 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 23.8 (CH_2), 24.4 (CH_3), 29.3 (CH_2), 27.6 (CH_2), 29.7 (CH_2), 37.6 (CH_2), 106.9 (C), 119.1 (CH), 121.9 (CH), 122.7 (CH), 123.1 (C), 128.4 (C), 129.6 (CH), 160.0 (C), 162.8 (C), 182.6 (C).

(*E*)-3-Cyclohex-1-enylmethylene-1,3-dihydroindol-2-one (*E*-17)[S15]
Yellow crystals; mp 124.7–126.5 °C; IR (KBr): 3139.5 (m), 1697.1 (s), 1604.5 (s) cm^{-1}; ^{1}H NMR (600.1 MHz, $CDCl_3$) δ 1.68–1.74 (m, 2H), 1.74–1.80 (m, 2H), 2.26–2.31 (m, 2H), 2.33–2.38 (m, 2H), 6.41–6.45 (m, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.94 (dd, J = 7.8, 7.9 Hz, 1H), 7.18 (dd, J = 7.6, 7.9 Hz, 1H), 7.23 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 9.05–9.44 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 21.7 (CH_2), 22.5 (CH_2), 26.1 (CH_2), 28.5 (CH_2), 110.2 (CH), 121.6 (CH), 122.3 (C), 123.7 (CH), 124.6 (C), 128.9 (CH), 134.4 (C), 135.1 (CH), 141.1 (CH), 141.5 (C), 171.3 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{15}NNaO$: 248.1046, found: 248.1046.

(*Z*)-3-Cyclohex-1-enylmethylene-1,3-dihydro-indol-2-one (*Z*-17) [S15]
Yellow crystals; mp 200.2–201.0 °C; IR (KBr): 3131.8 (w), 1697.1 (s), 1589.1 (s) cm^{-1}; ^{1}H NMR (600.1 MHz, $CDCl_3$) δ 1.63–1.69 (m, 2H), 1.69–1.74 (m, 2H), 2.31–2.36 (m, 2H), 2.68–2.74 (m, 2H), 6.61–6.66 (m, 1H), 6.79 (d, J = 7.4 Hz, 1H), 6.98 (dd, J = 7.2, 7.7 Hz, 1H), 7.05 (s, 1H), 7.16 (dd, J = 7.4, 7.7 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.59–7.73 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 21.5 (CH_2), 22.7 (CH_2), 27.2 (CH_2), 28.4 (CH_2), 109.1 (CH), 118.8 (CH), 121.5 (CH), 123.0 (C), 125.9 (C), 128.1 (CH), 136.1 (C), 139.1 (C), 141.0 (CH), 141.7 (CH), 167.4 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{15}NNaO$: 248.1046, found: 248.1046.

3-Cyclohexylidenemethylene-1,3-dihydroindol-2-one (**18**)
Yellow oil; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 1.51–1.72 (m, 4H), 1.80–1.90 (m, 2H), 2.30–2.38 (m, 2H), 2.38–2.47 (m, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.98 (dd, J = 7.5, 7.7 Hz, 1H), 7.15 (dd, J = 7.7, 7.8 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 9.97–10.07 (br. s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.6 (CH_2), 27.4 ($2CH_2$), 30.3 ($2CH_2$), 98.7 (C), 110.2 (CH), 112.6 (C), 121.4 (CH), 121.7 (CH), 123.1 (C), 138.0 (CH), 139.4 (C), 170.9 (C), 200.7 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{15}NNaO$: 248.1046, found: 248.1044.

(*Z*)-3-(Cyclohex-2-en-1-ylidene)indolin-2-one (21) (major)
^{1}H NMR (600.1 MHz, $CDCl_3$): δ 1.95 (tt, J = 6.3, 6.6 Hz, 2H), 2.33 (ddt, J = 1.8, 4.4, 6.3 Hz, 2H), 2.97 (t, J = 6.6 Hz, 2H), 6.53 (dt, J = 4.4, 10.2 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 7.00 (dd, J = 7.7, 7.8 Hz, 1H), 7.18 (dd, J = 7.7, 7.8 Hz, 1H), 7.55 (d, J = 7.8 Hz,1H) 8.31 (dt, J = 1.8, 10.2 Hz, 1H), 8.71–8.80 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 21.9 (CH_2), 25.3 (CH_2), 28.7 (CH_2), 109.5 (CH), 119.5 (C), 121.5 (CH), 124.3 (CH), 124.5 (C), 125.9 (CH), 127.7 (CH), 140.0 (C), 141.0 (CH), 150.2 (C), 170.0 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{13}NNaO$: 234.0889, found: 234.0896.
(*E*)-isomer was identified by comparisons of ^{1}H and ^{13}C NMR spectra between *Z*-isomer **21** and a *Z,E*-mixture (*Z:E* = 8:2) of **21**.

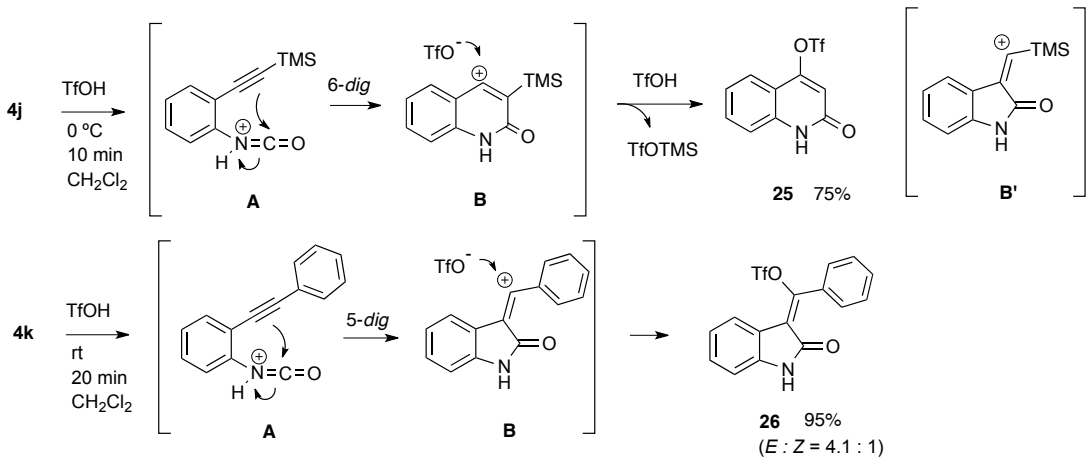
3-Cyclopent-1-enylmethylene-1,3-dihydro-indol-2-one (22) (see X-Ray crystallographic data and Fig. 2)
Yellow crystals, mp 160.8–162.1 °C; IR (KBr): 3425.0 (w), 3070.1 (w), 2831.0 (w), 1697.1 (s), 1596.8 (s) cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 2.02 (tt, J = 7.7, 7.7 Hz, 2H), 2.54 (dt, J = 2.7, 7.7 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H), 6.70 (t, J = 2.7 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.97 (dd, J = 7.6, 7.6 Hz, 1H), 7.16 (dd, J = 7.6, 7.6 Hz, 1H), 7.26 (s, 1H), 7.38 (d, J = 7.6 Hz, 1H), 8.22–8.43 (br. s, 1H); ^{13}C NMR

(125.7 MHz, $CDCl_3$): δ 24.5 (CH_2), 33.5 (CH_2), 34.9 (CH_2), 109.3 (CH), 119.0 (CH), 121.5 (CH), 124.1 (C), 125.5 (C), 128.3 (CH), 132.7 (CH), 139.6 (C), 141.9 (C), 146.3 (CH), 168.0 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{13}NNaO$: 234.0899, found: 234.0895.

3-(2-Hydroxy-cyclobutylidene)-1,3-dihydroindol-2-one (23)
Yellow crystals; mp 142.7–144.3 °C; IR (KBr): 3409.5 (br. m), 2923 (w), 1712.5 (s), 1619.9 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 2.24–2.33 (m, 1H), 2.55–2.63 (m, 1H), 2.84 (ddd, J = 10.2, 18.1, 18.1 Hz, 1H), 2.99–3.07 (m, 1H), 5.34 (ddd, J = 4.4, 7.3, 8.9 Hz, 1H), 5.62 (s, 1H), 6.87 (d, J = 7.9 Hz, 1H), 7.04 (dd, J = 7.5, 8.6 Hz, 1H), 7.22 (dd, J = 7.9, 8.6 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.66–7.81 (br.s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 23.6 (CH_2), 26.8 (CH_2), 71.6 (CH), 110.0 (CH), 121.7 (CH), 122.3 (CH), 122.6 (CH), 123.1 (C), 128.5 (C), 140.0 (C), 163.8 (C), 169.5 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{11}NNaO_2$: 224.0682, found: 224.0680.

2,3-Diphenylspiro[indene-1,3'-indoline]-2'-one (24)
Colorless crystals; mp 216.8–218.2 °C; IR (KBr): 3185.8 (w), 3062.4 (w), 1704.8 (s) cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 6.86–6.96 (m, 5H), 6.97–7.07 (m, 4H), 7.15–7.22 (m, 2H), 7.30–7.48 (m, 7H), 8.60–8.99 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 68.4 (C), 110.3 (CH), 121.4 (CH), 122.2 (CH), 123.1 (CH), 123.9 (CH), 126.6 (CH), 127.3 (CH), 127.7 (CH), 128.0 (2CH), 128.1 (CH), 128.5 (2CH), 128.6 (CH), 128.8 (2CH), 129.6 (2CH, C) 134.45 (C), 134.49 (C), 142.0 (C), 142.3 (C), 144.6 (C), 145.4 (C), 145.6 (C), 177.6 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{28}H_{19}NNaO$: 408.1359, found: 408.1360.

In the reactions of trimethylsilyl- and phenyl- substituted isocyanates **4j** and **4k**, the triflated quinolinone **25**[S17] (75% yield) and the triflated 3-methylene-oxindole **26** (95%) were obtained, in which no rearrangement reaction was involved. The difference in the cyclization modes can be explained by considering the stability of the intermediary carbocation **B** that formed. In the former case (from **4j**), the cation **B** can be more stabilized by resonance than the alternative cation **B′** because the cation is placed in a benzylic position in **B**. In the latter case (from **4k**), the carbocation **B** is also stabilized by the phenyl group. Although no skeletal rearrangement was involved in these cases, we found that both the triflated heterocycles (**25** and **26**) underwent a coupling reaction, such as Suzuki or Sonogashira coupling, and nucleophilic substitution reaction (with, e.g., an amine) to give a variety of substituted quinolin-2-one and 3-methylene-oxindole derivatives. These findings will be reported elsewhere.



Scheme S2 (17) Reaction of isocyanates **4j** and **4k** to produce triflated quinolone **25** and indole **26**.

2-Oxo-1,2-dihydroquinolin-4-yl trifluoromethanesulfonate (25)[S16]
Colorless solid; mp 221–223 °C; IR (KBr) : 3471, 2861.8 (w), 1666.2 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$) δ 6.78 (s, 1H), 7.37 (ddd, J = 0.9, 7.3, 8.1 Hz, 1H), 7.52 (dd, J = 1.2, 8.1 Hz, 1H), 7.67 (ddd, J = 1.2, 7.3, 8.4 Hz, 1H), 7.79 (dd, J = 0.9, 8.4 Hz, 1H), 12.83–12.89 (br. s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 111.4 (CH), 114.3 (C), 116.6 (CH), 118.6 (q, J_{CF3} = 320.4 Hz, C), 122.1 (CH), 123.9 (CH), 132.9 (CH), 138.7 (C), 155.6 (C), 164.1 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_6F_3NNaO_4S$: 315.9862, found: 315.9852.

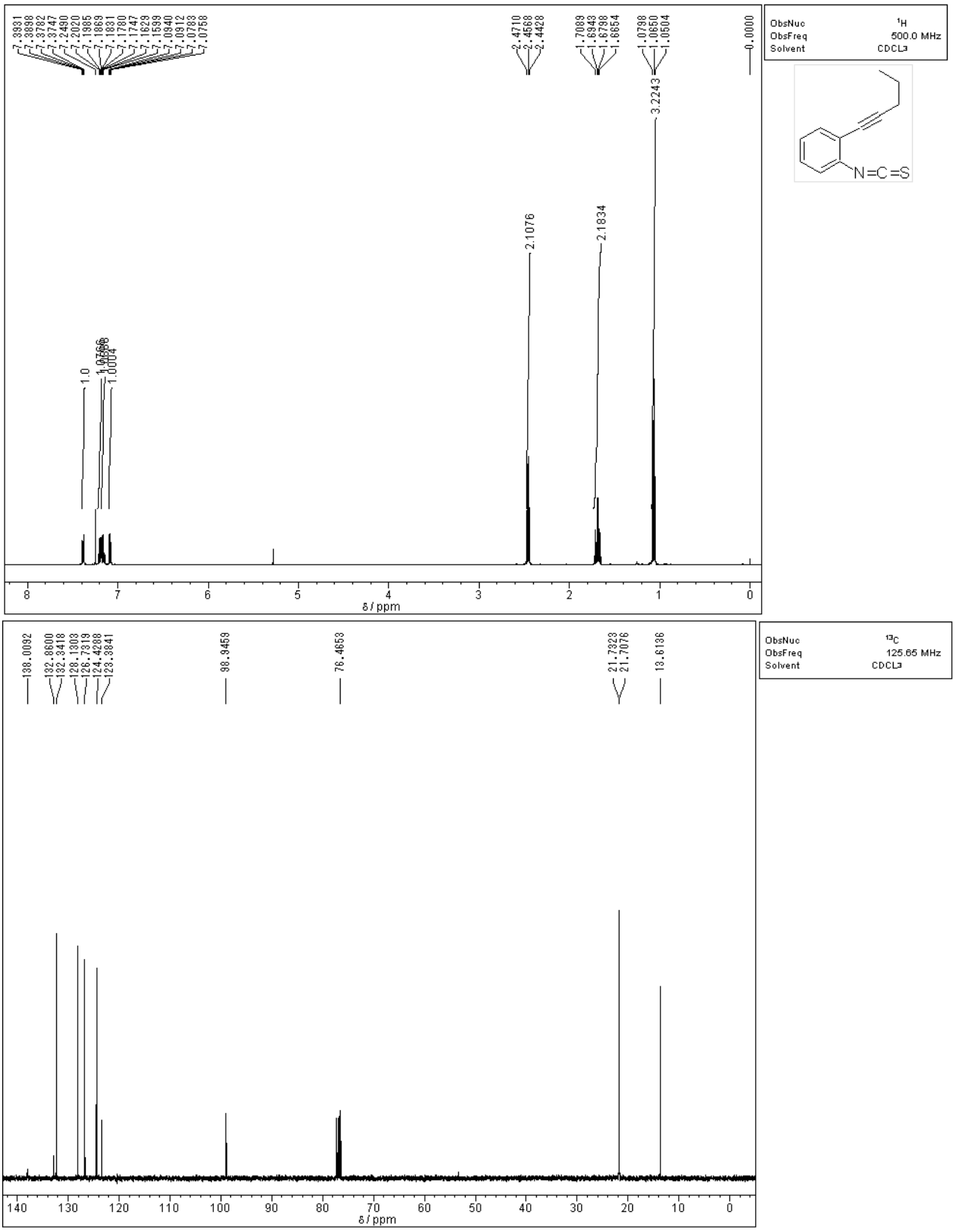
(*E*)-(2-Oxoindolin-3-ylidene)(phenyl)methyl trifluoromethanesulfonate (*E*-26)
Yellow crystals; mp 146.3–148.1 °C; IR (KBr): 3162.7 (w), 1720.2 (s), 1612.2 (m) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 6.67 (dd, J = 0.9, 7.8 Hz, 1H), 7.09 (ddd, J = 0.9, 7.9, 8.8 Hz, 1H), 7.27 (ddd, J = 1.1, 7.9, 8.8 Hz, 1H), 7.46–7.51 (m, 2H), 7.55 (dddd, J = 1.4, 1.4, 6.3, 6.3 Hz, 1H), 7.58–7.62 (m, 2H), 7.95 (dd, J = 1.1, 7.9 Hz, 1H), 8.34–8.48 (br. s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 110.1 (CH), 118.0 (q, J_{CF3} = 314.0 Hz, C), 120.0 (C), 120.7 (C), 122.9 (CH), 125.4 (CH), 128.1 (2CH), 130.07 (C), 130.15 (2CH), 131.1 (CH), 131.6 (CH), 140.7 (C), 153.7 (C), 166.9 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{10}F_3NNaO_4S$: 392.0175, found: 392.0175.

(*Z*)-(2-Oxoindolin-3-ylidene)(phenyl)methyltrifluoromethanesulfonate (*Z*-26)
Yellow crystals; mp 159.1–160.8 °C; IR (KBr): 3193.5 (w), 1712.5 (s), 1612.2 (s) cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$) δ 6.67 (d, J = 7.5 Hz, 1H), 6.74 (dd, J = 7.9, 8.5 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 7.23 (dd, J = 7.5, 8.5 Hz, 1H), 7.54–7.60 (m, 2H), 7.60–7.67 (m, 3H), 9.81–10.0 (br. s, H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 110.6 (CH), 118.1 (q, J_{CF3} = 320.8 Hz, C), 119.8 (C), 121.5 (C), 122.0 (CH), 123.0 (CH), 129.34 (2CH), 129.36 (2CH), 131.2 (CH), 131.4 (C), 132.1 (CH), 141.0 (C), 150.1 (C), 166.7 (C); HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{10}F_3NNaO_4S$: 392.0175, found: 392.0175.

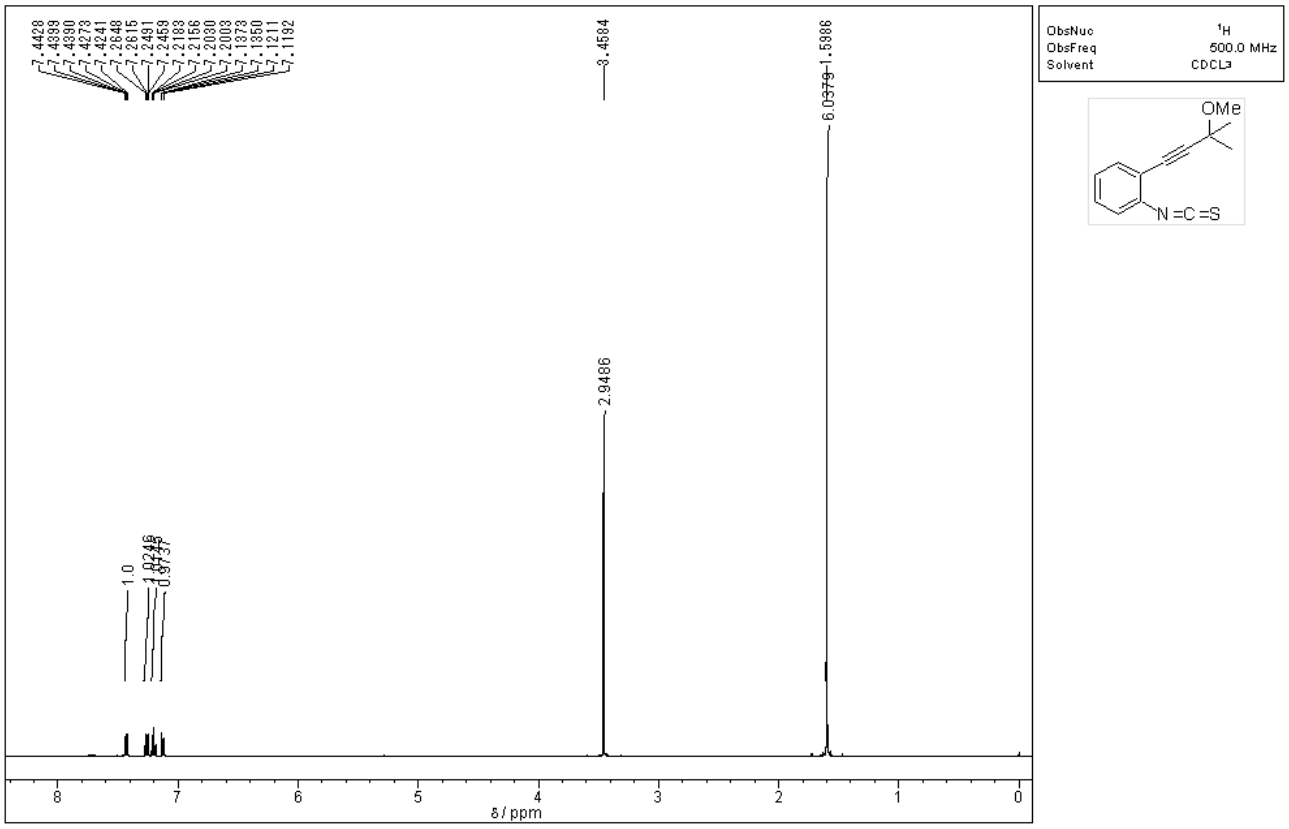
The reactions of the other isocyanates **4c**, **4d**, and **4i** under optimal or similar reaction conditions were unsuccessful, resulting in the formation of mixtures of unidentified products.

2. ^{1}H- and ^{13}C-NMR spectra of new compounds

1c



1d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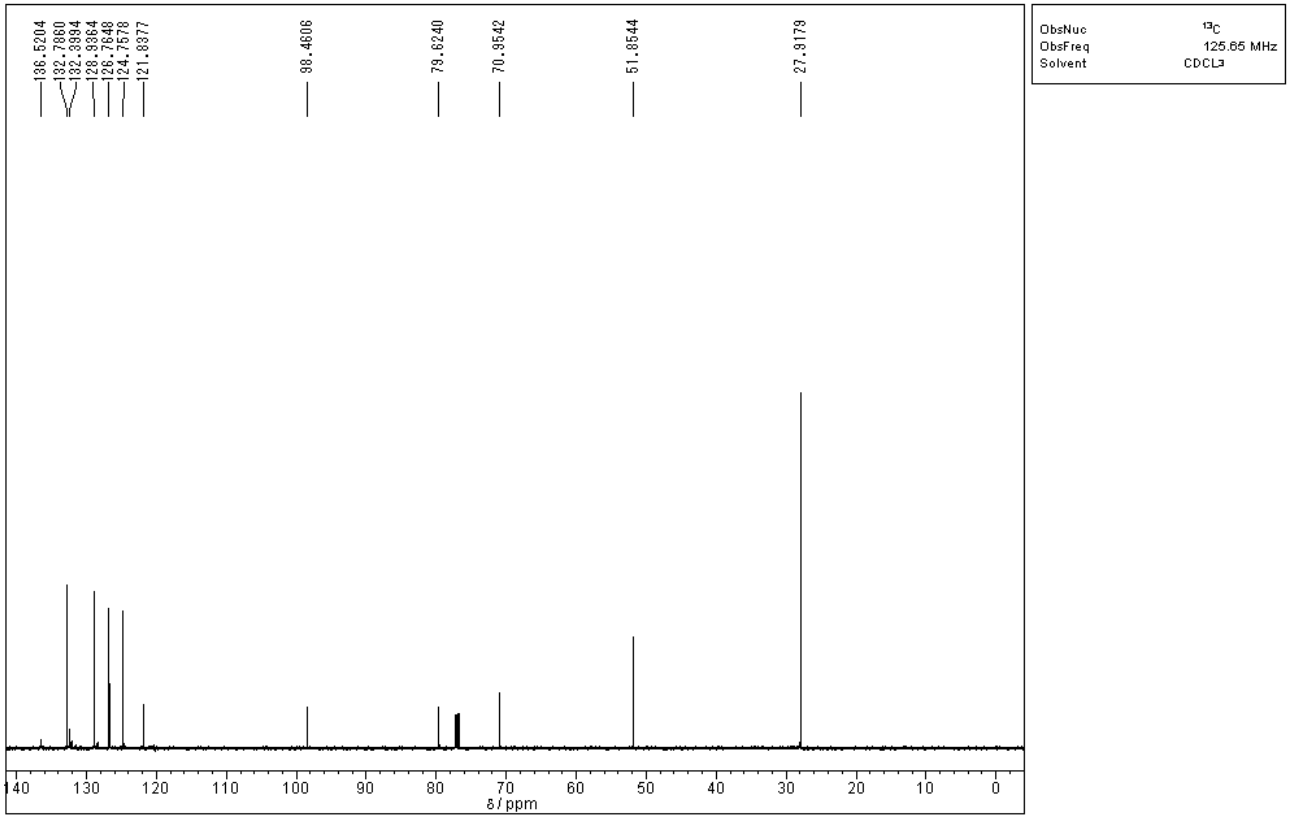
OMe
N=C=S
δ / ppm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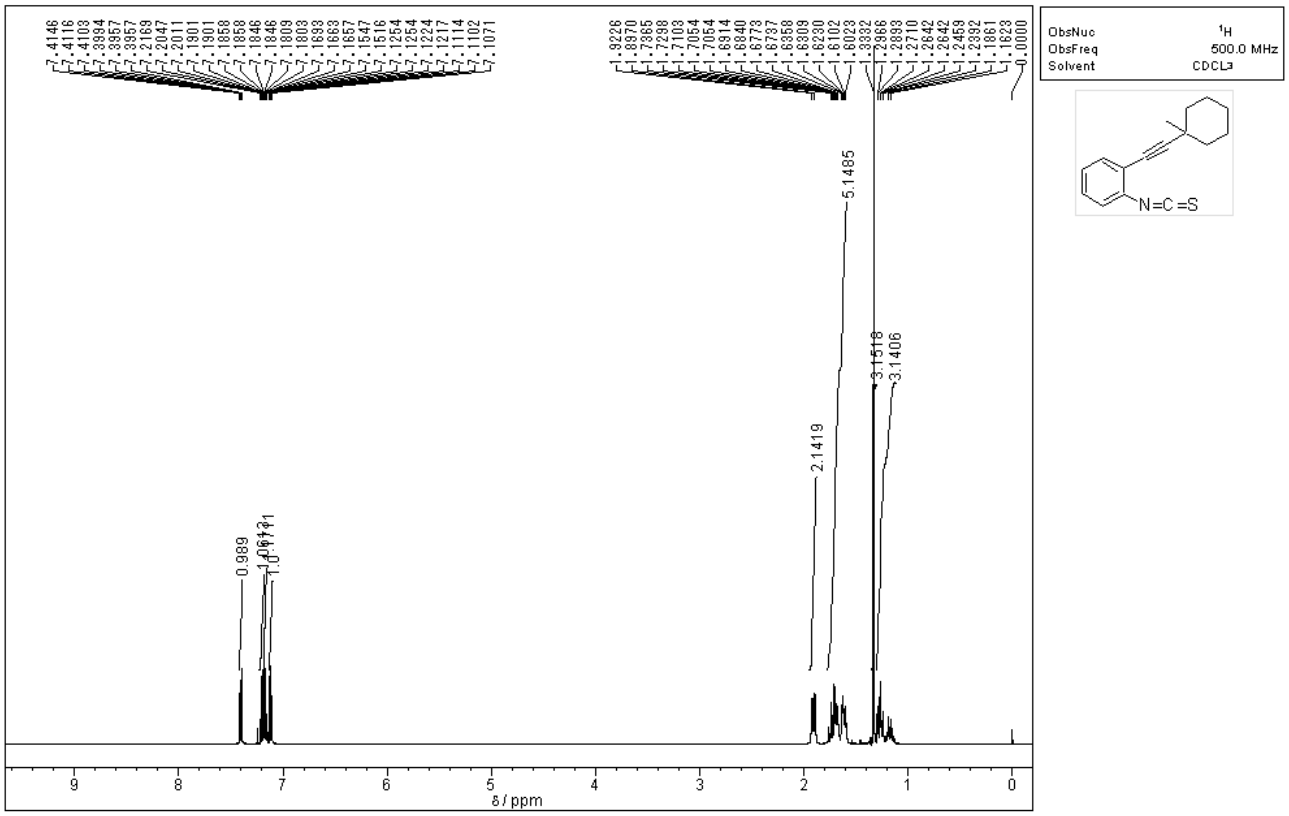
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

1e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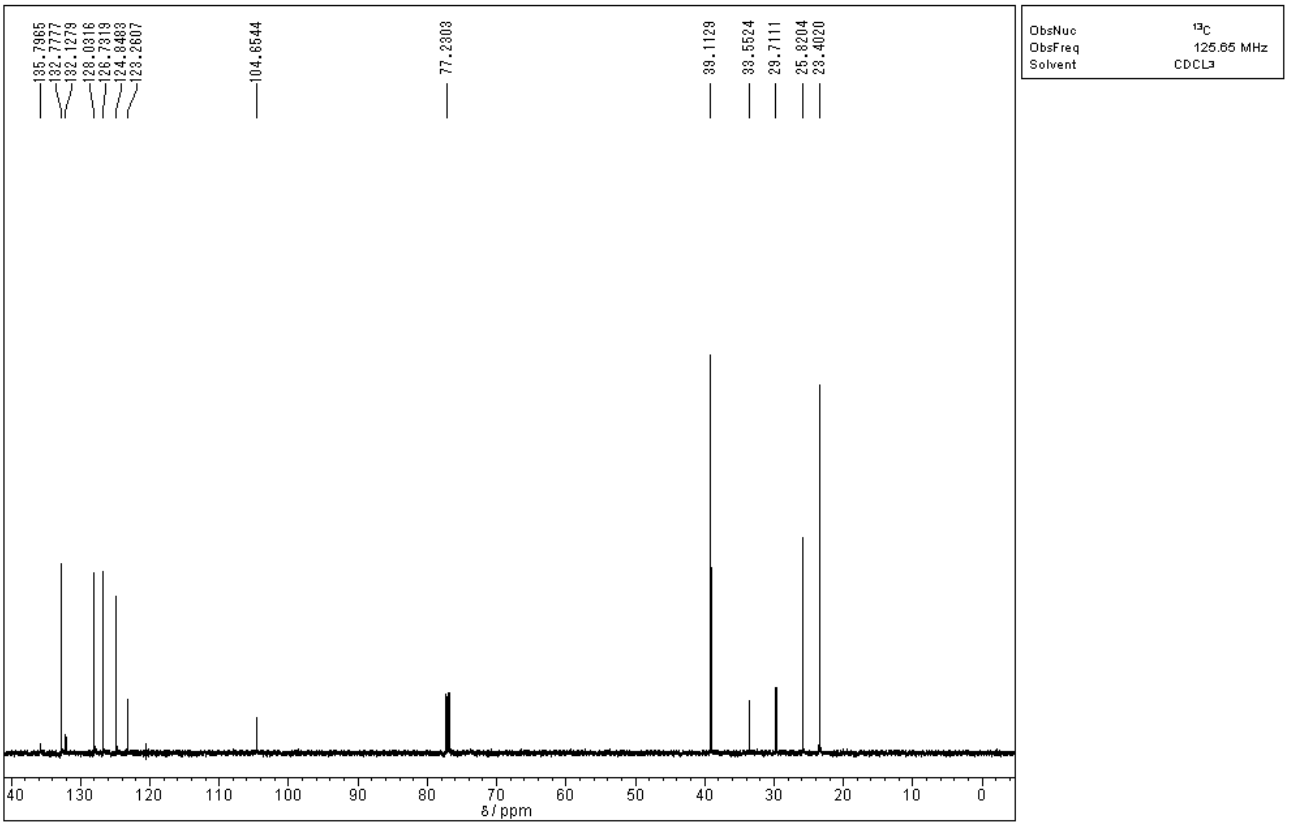
3.1406
2.1419
0.989
δ / ppm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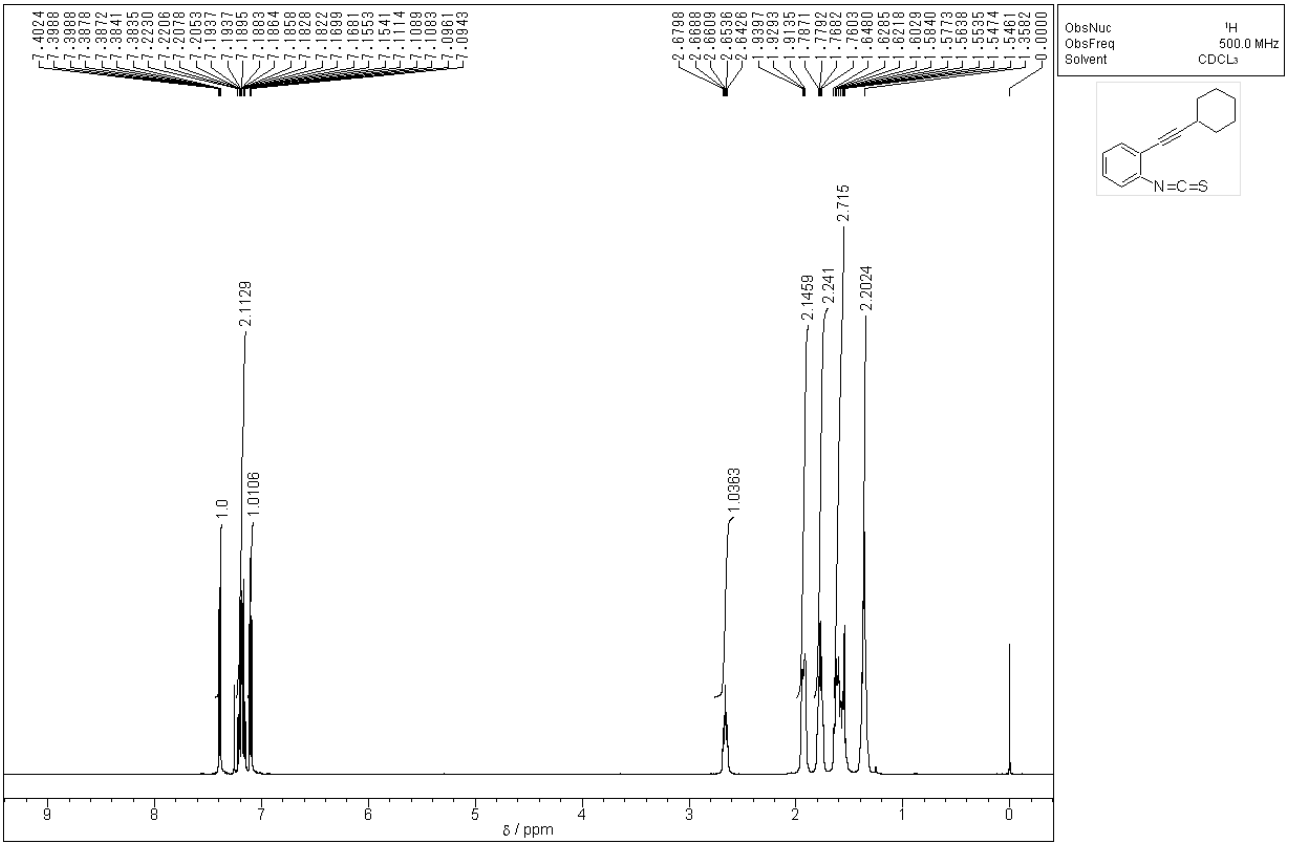
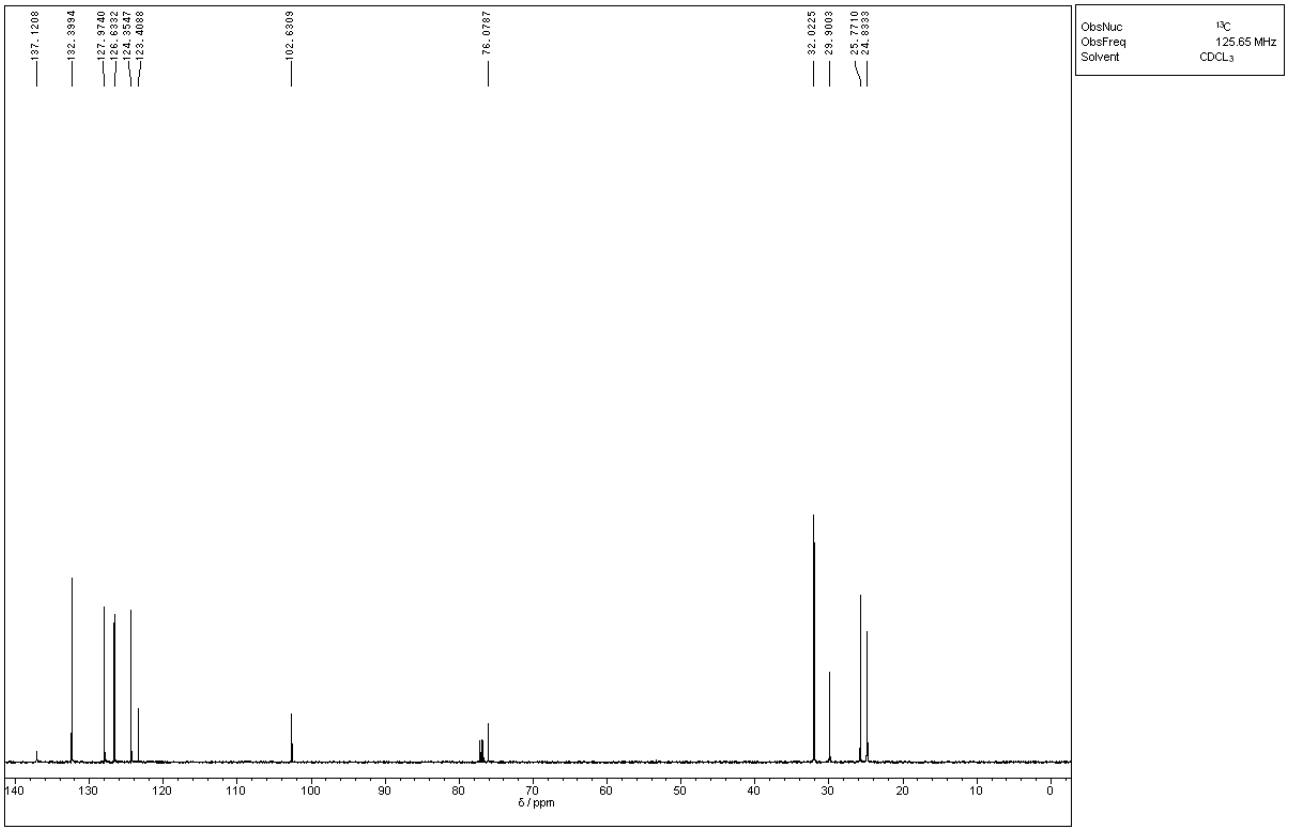
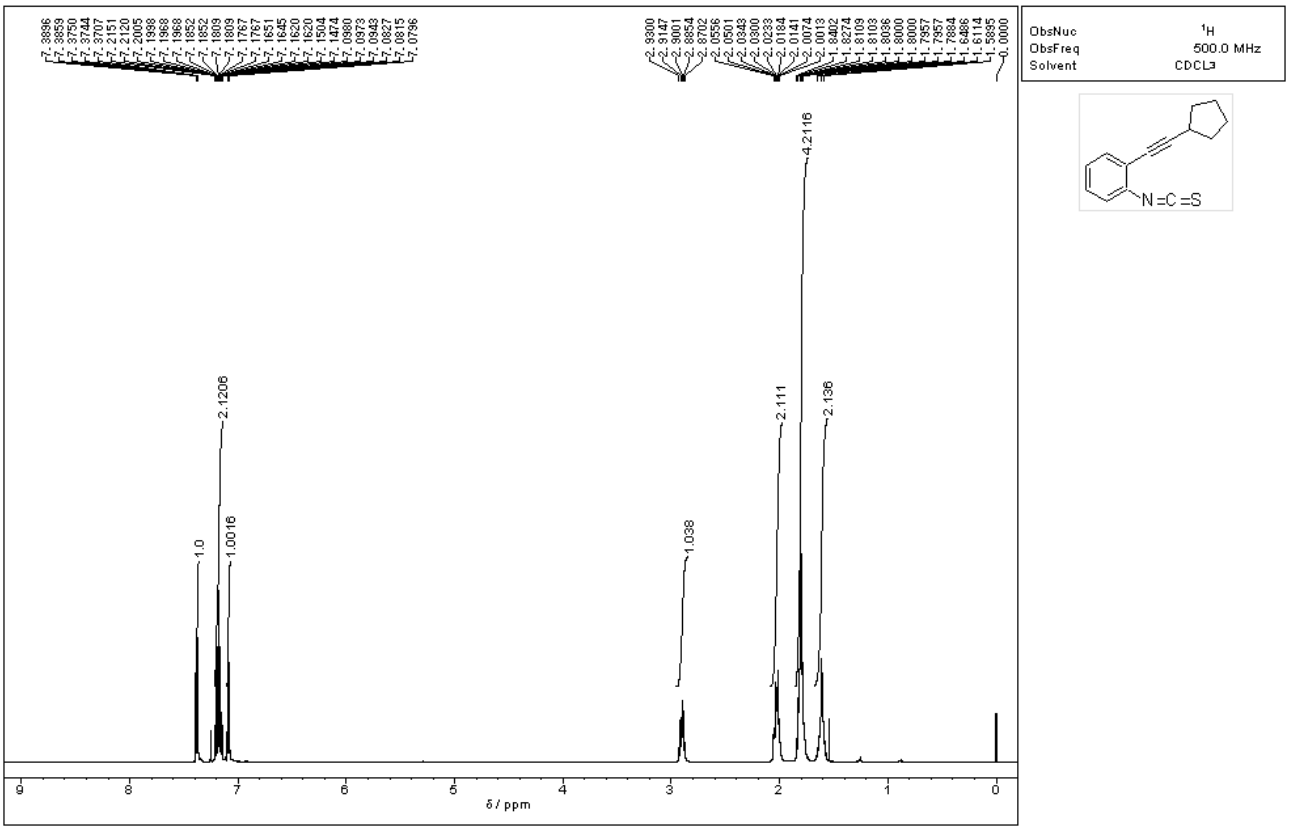
Solvent CDCL3
135.7965
132.7777
132.1279
128.0316
126.7319
124.8483
123.2607
104.6544
77.2303
39.1129
33.5524
29.7111
25.8204
23.4020
δ / ppm

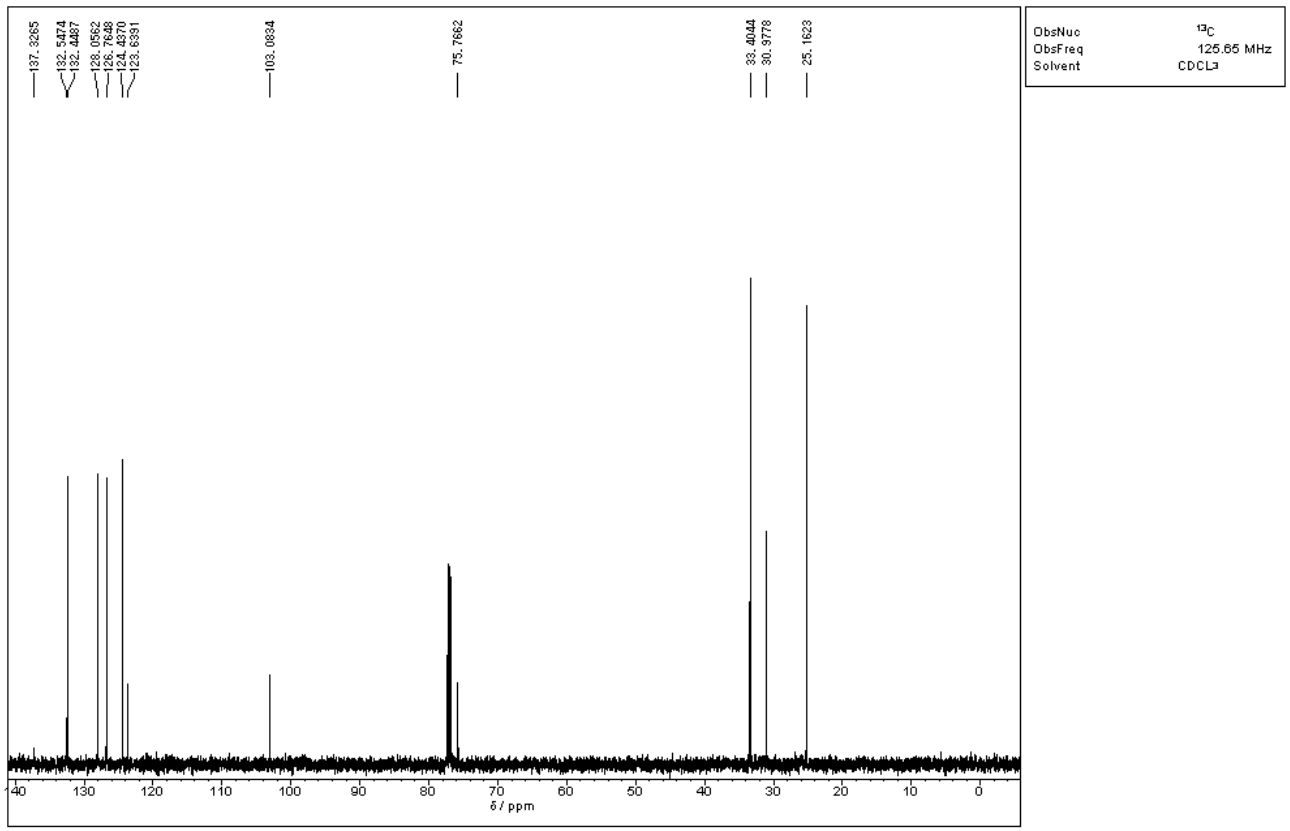
1f


ObsNuc ¹H
ObsFreq 500.0 MHz
Solvent CDCL₃
N=C=S
δ / ppm

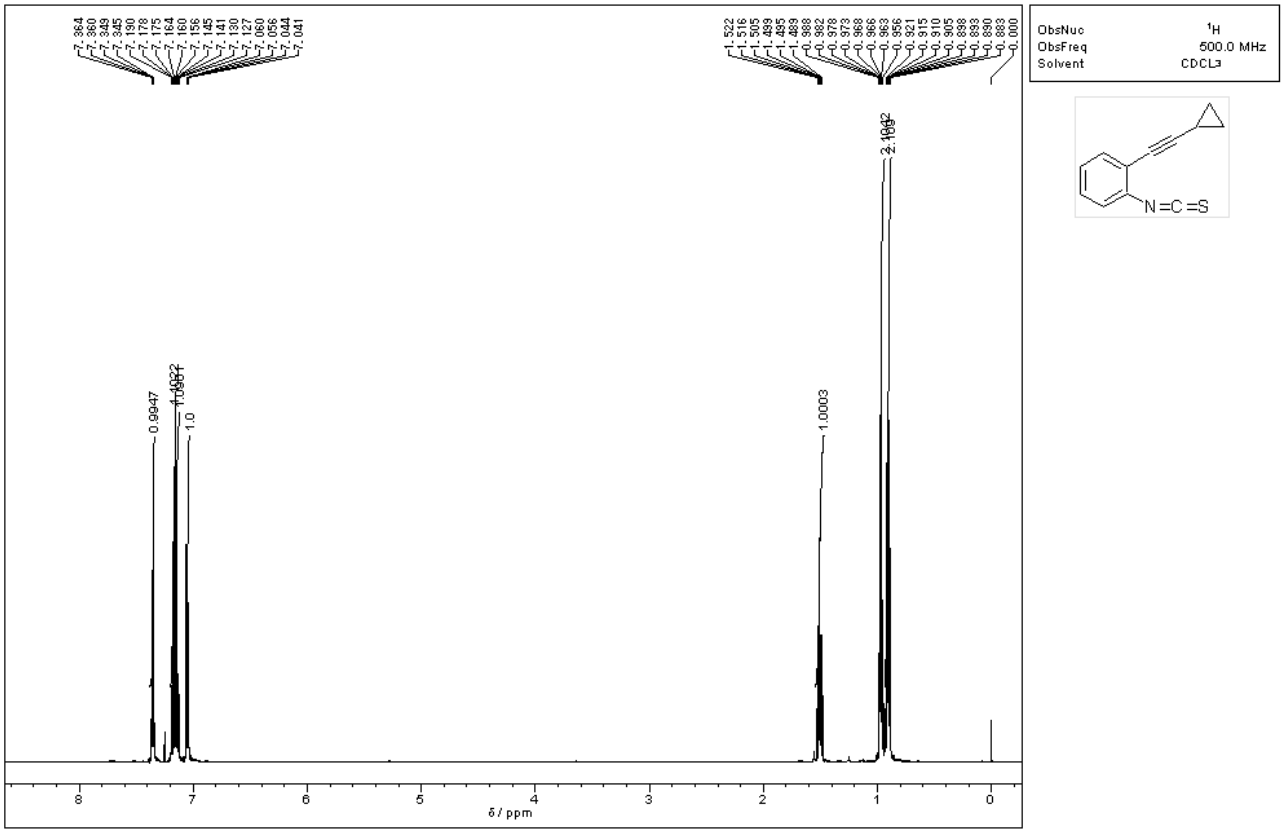

ObsNuc ¹³C
ObsFreq 125.65 MHz
Solvent CDCL₃
δ / ppm

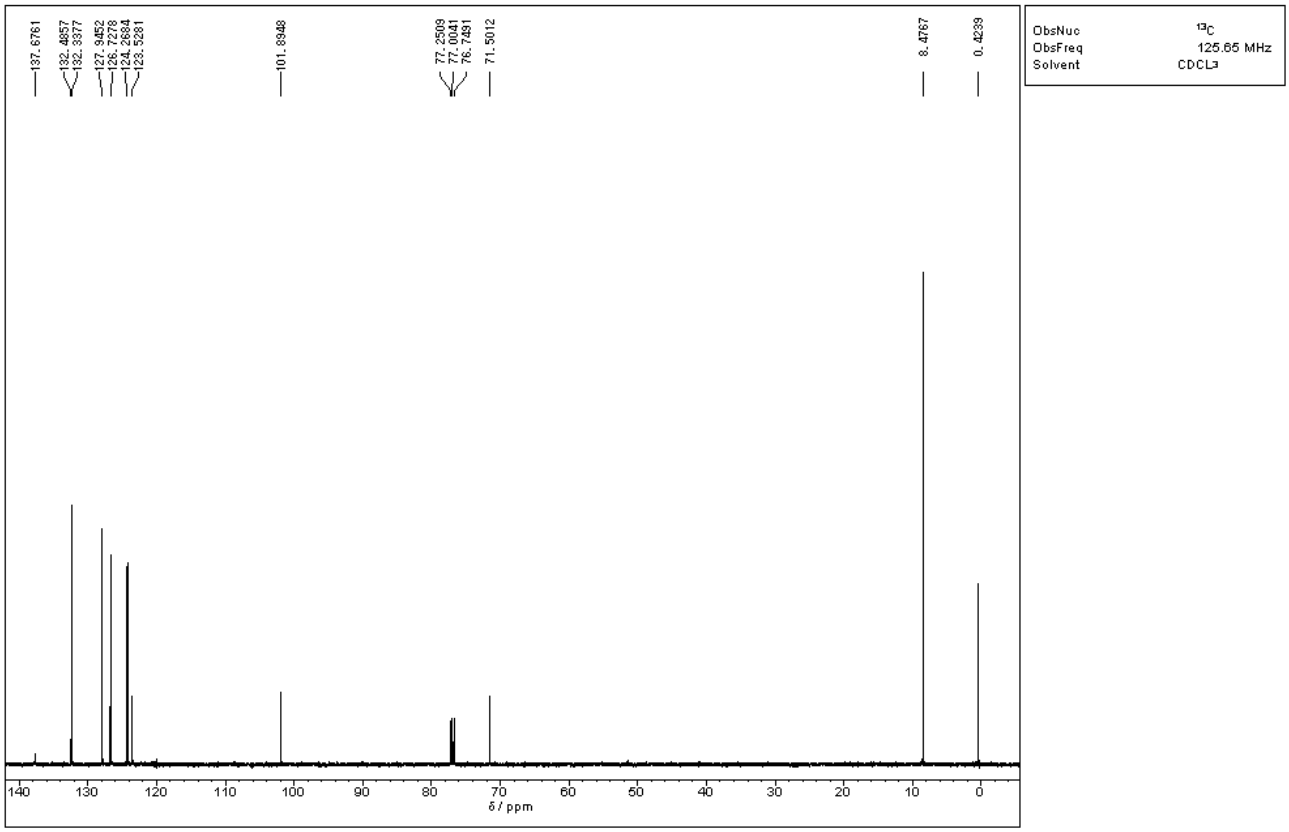
1g


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=C=S
1.0
2.1206
1.0016
1.038
2.111
4.2116
2.136
δ / ppm

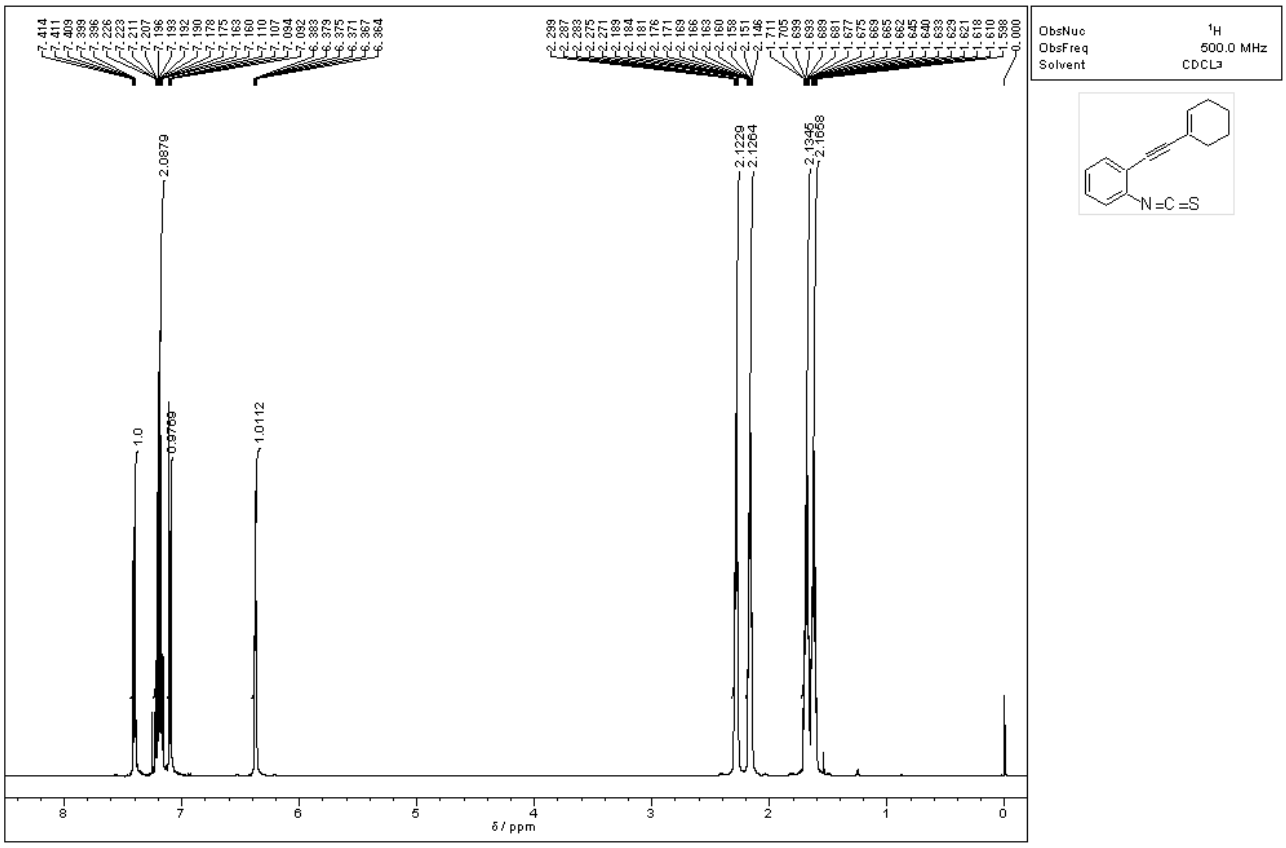

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
137.3265
132.5474
132.4467
128.0562
126.7648
124.4370
123.8391
103.0834
75.7662
33.4044
30.9778
25.1623
δ / ppm

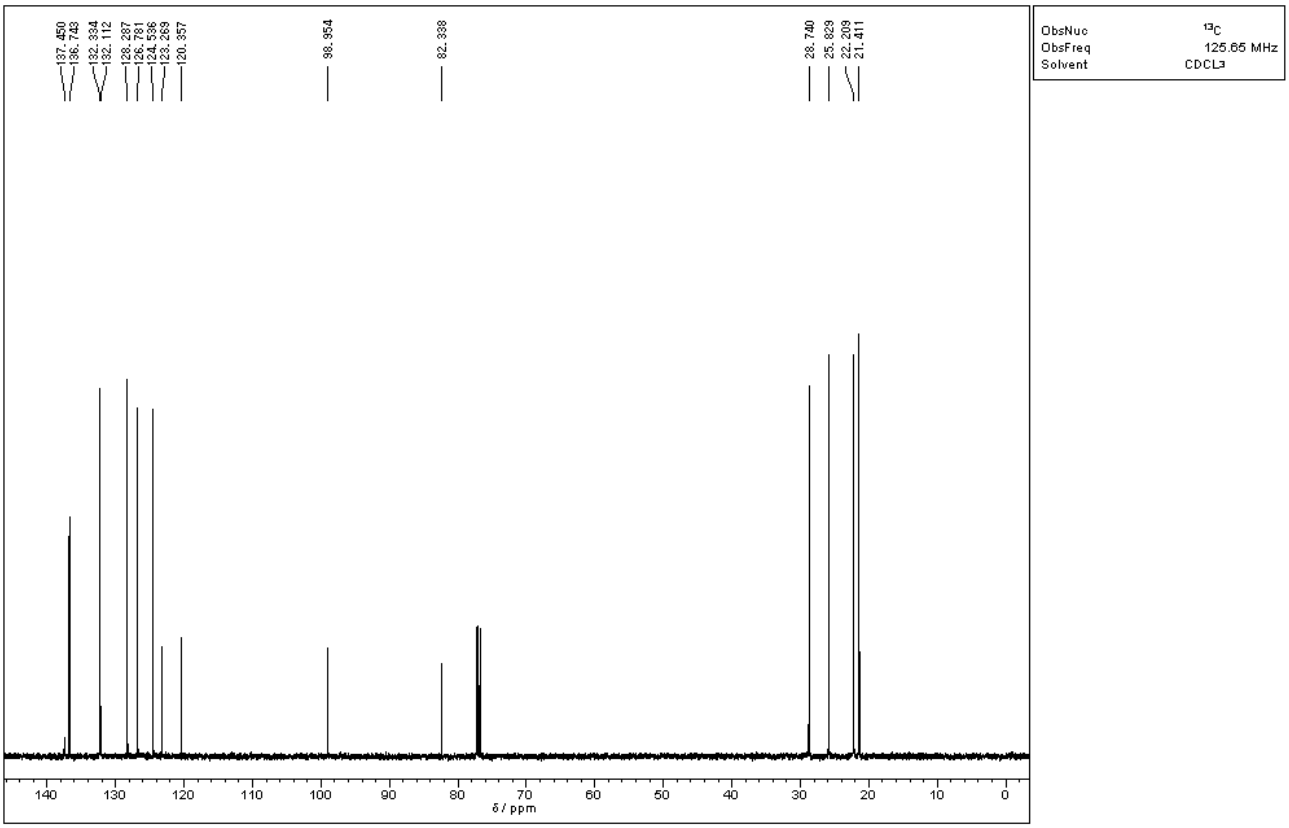
1h


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=C=S
δ / ppm

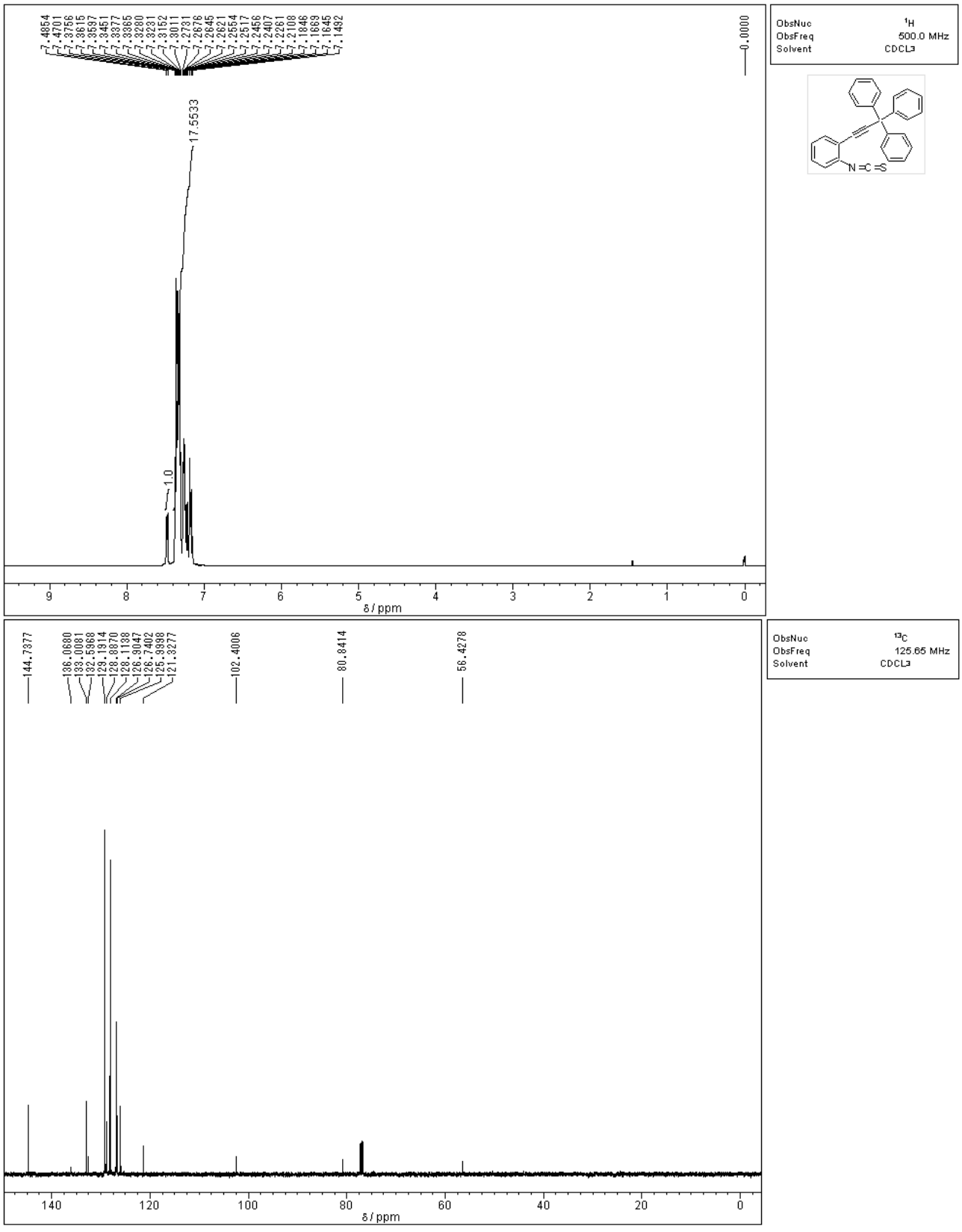

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

1i

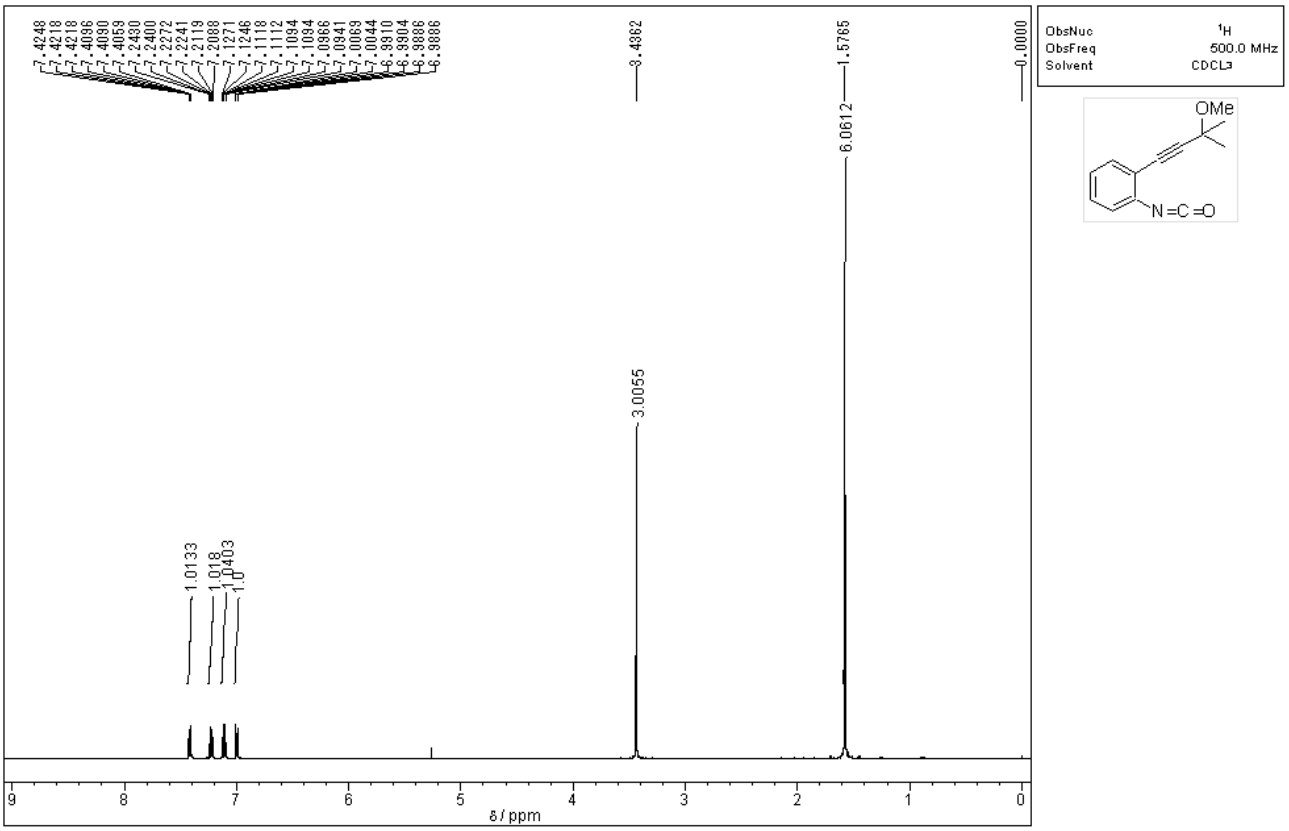

ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=C=S
δ / ppm

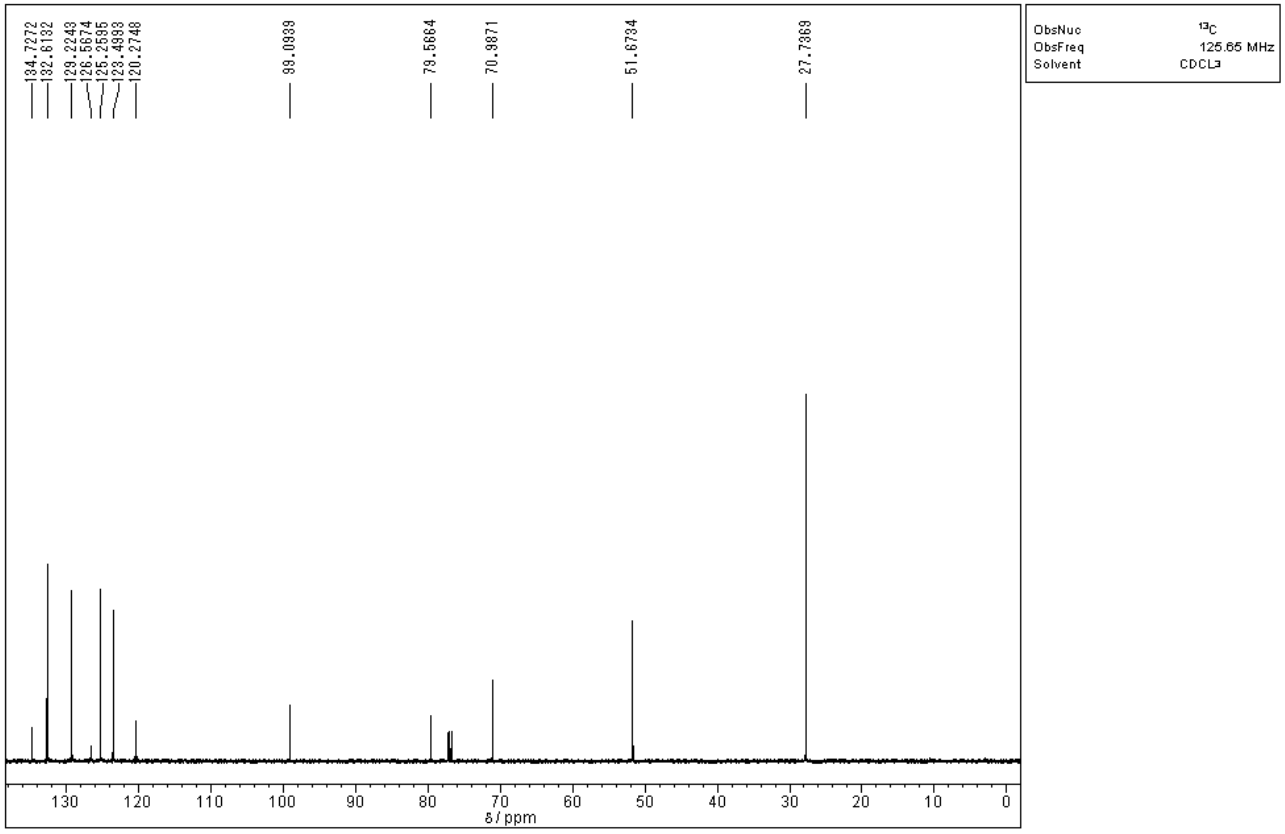

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

1l

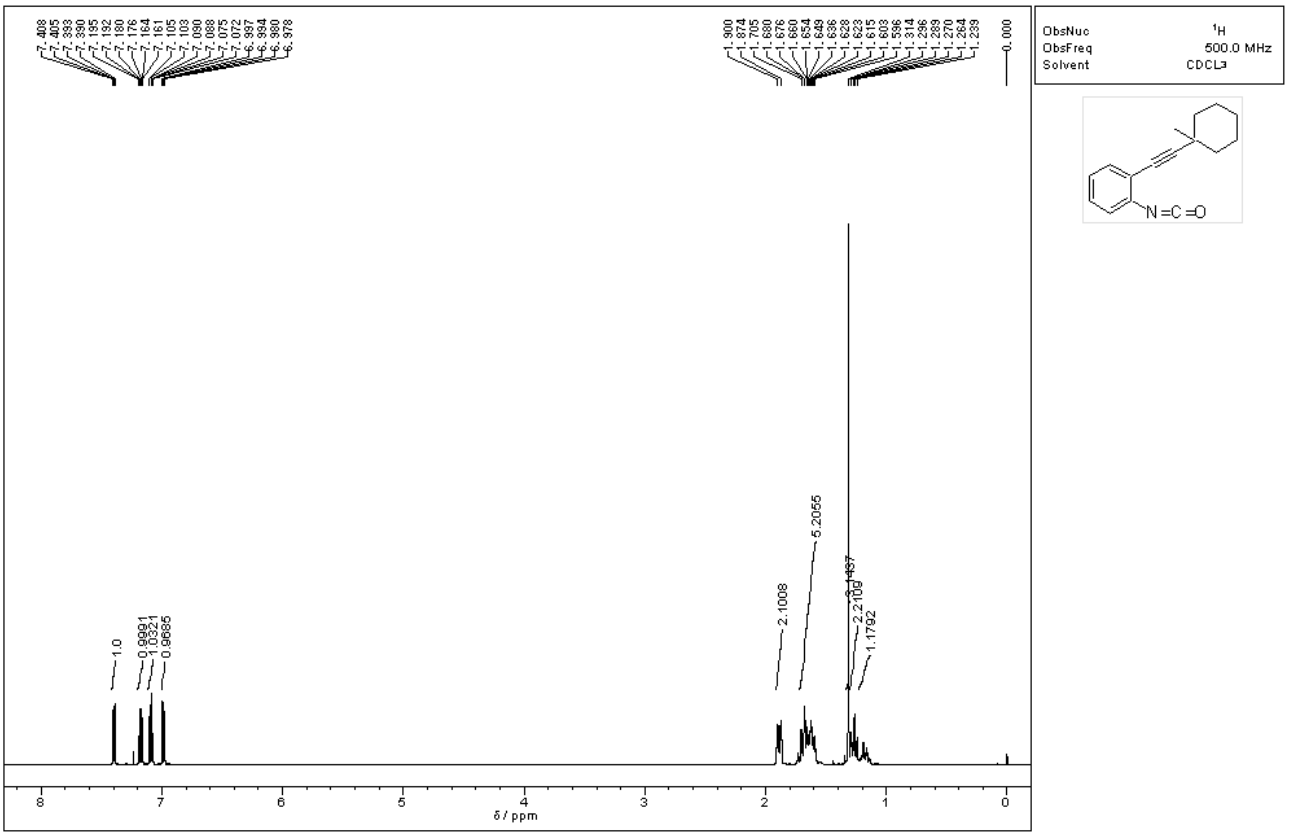

7.4954
7.4701
7.3756
7.3615
7.3597
7.3451
7.3377
7.3385
7.3280
7.3231
7.3152
7.3011
7.2731
7.2676
7.2645
7.2621
7.2554
7.2517
7.2456
7.2407
7.2261
7.2108
7.1846
7.1669
7.1645
7.1482
0.0000
17.5533
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=C=S
144.7877
136.0680
133.0081
132.5968
129.1914
128.8870
128.1138
126.9047
126.7402
125.8998
121.8277
102.4006
80.8414
56.4278
140
120
100
80
60
40
20
0
δ / ppm
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3

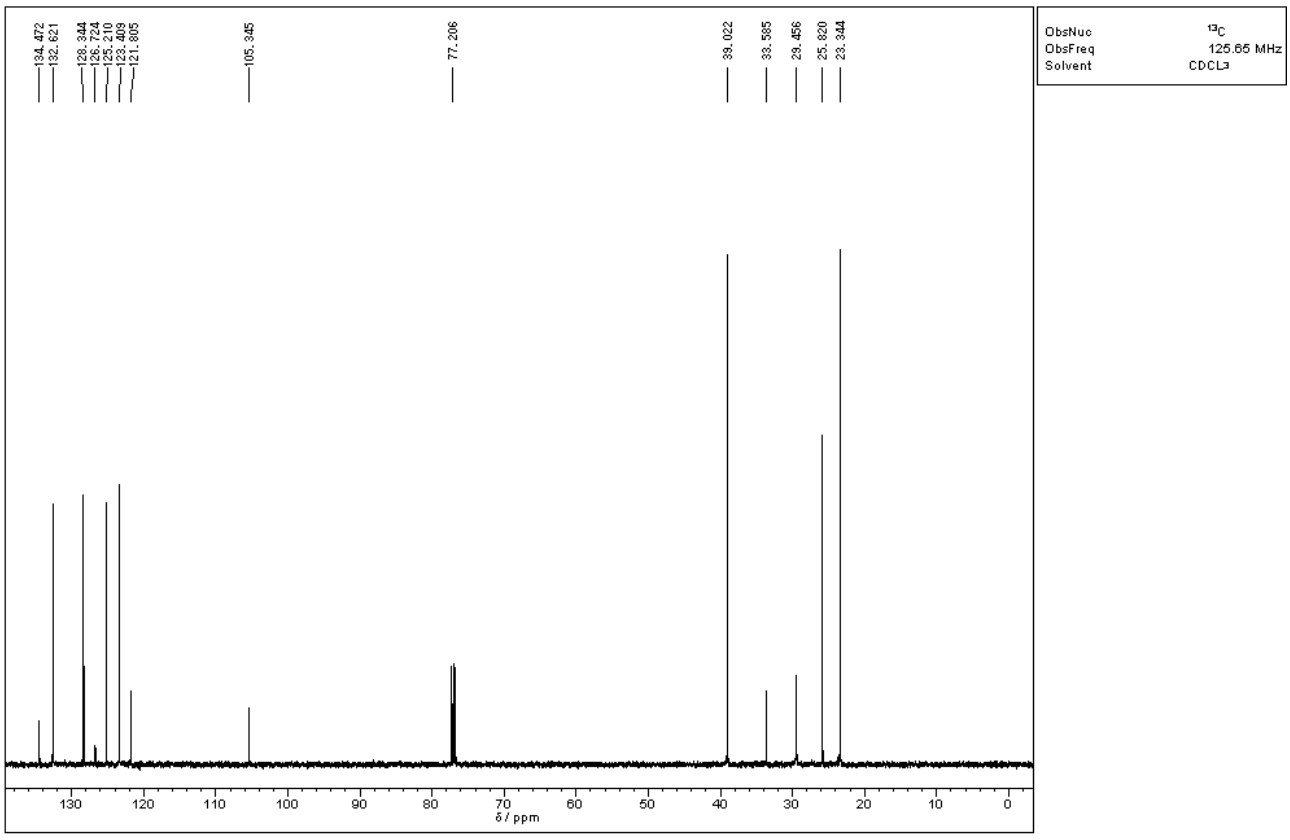
4d


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
OMe
N=C=O
δ / ppm

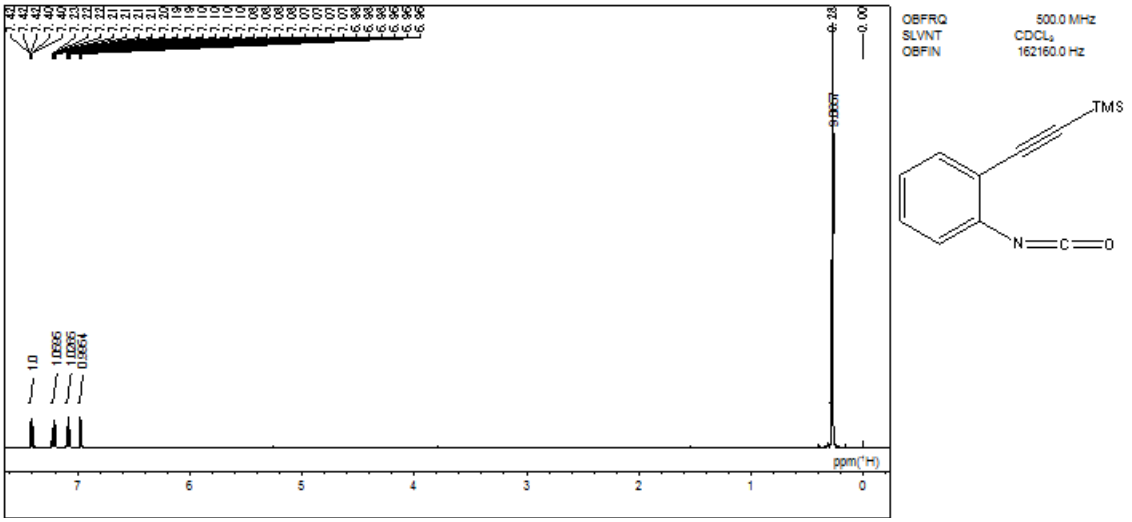

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

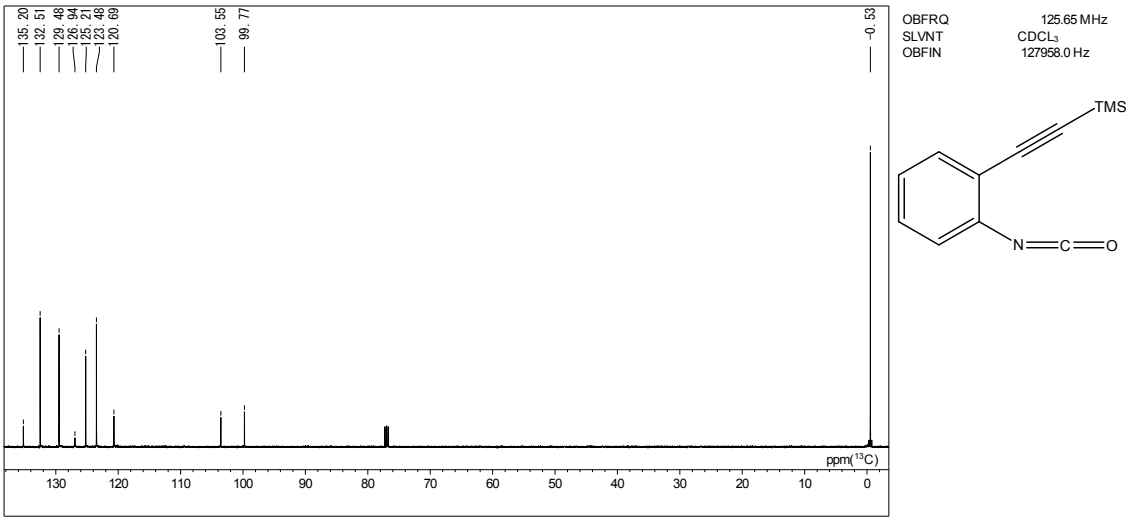
4e


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=C=O
δ / ppm

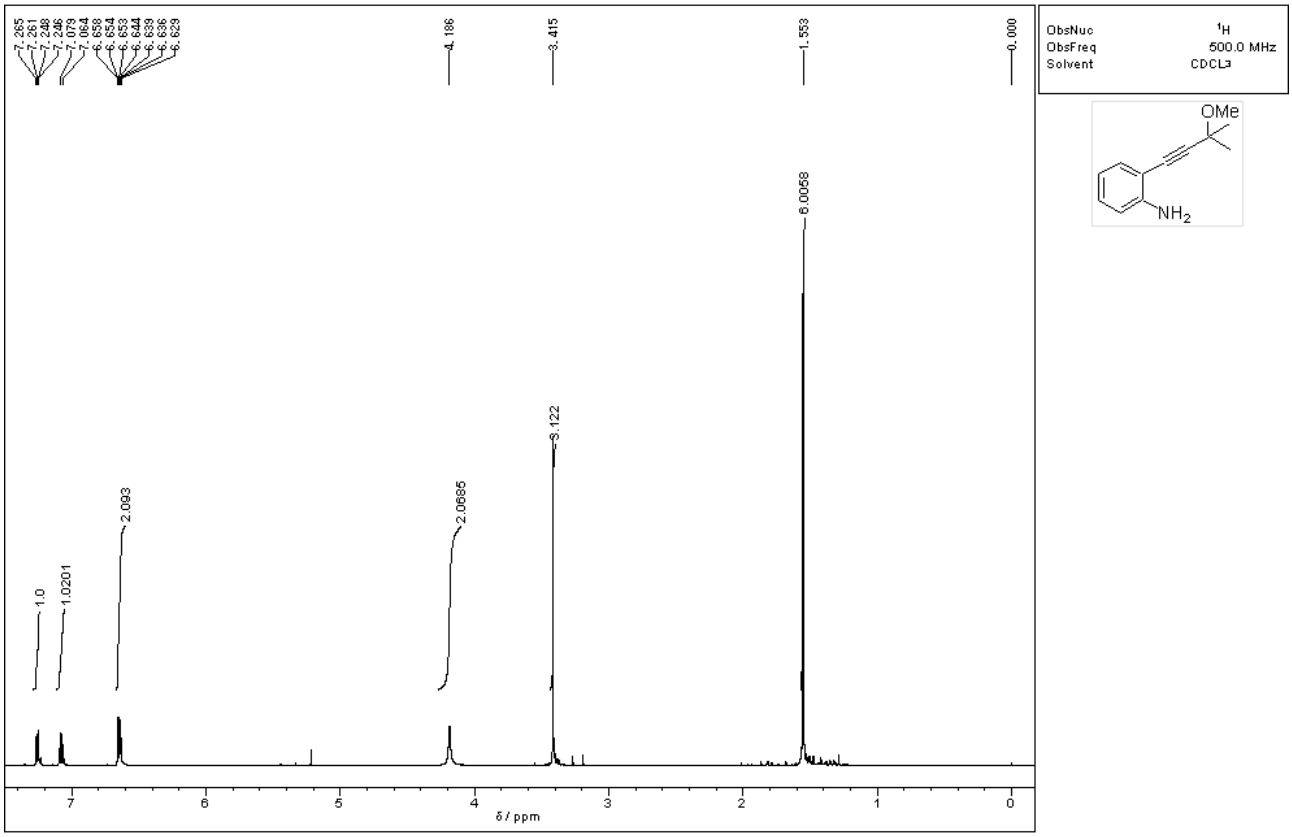

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

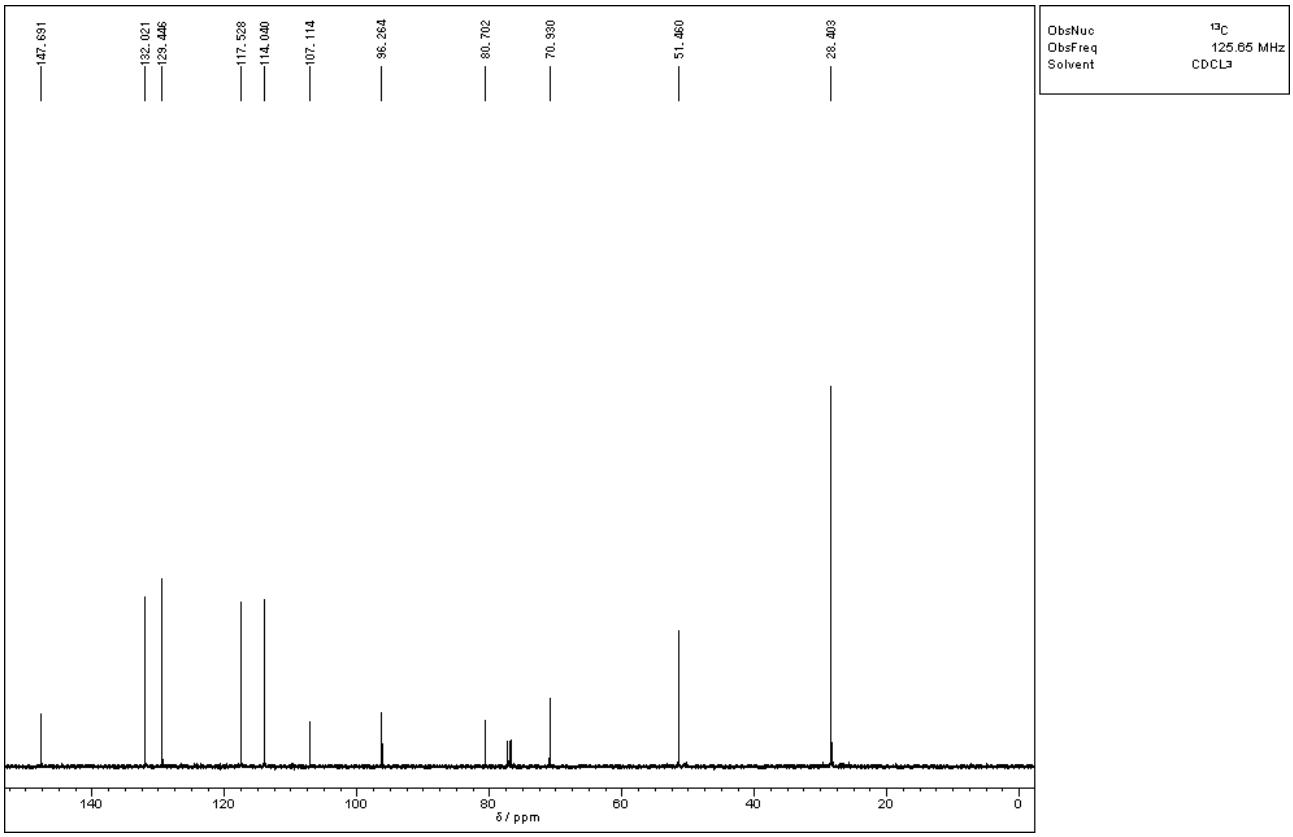
4j


OBFRQ 500.0 MHz
SLVNT CDCl3
OBFIN 162160.0 Hz
TMS
N=C=O
ppm(1H)

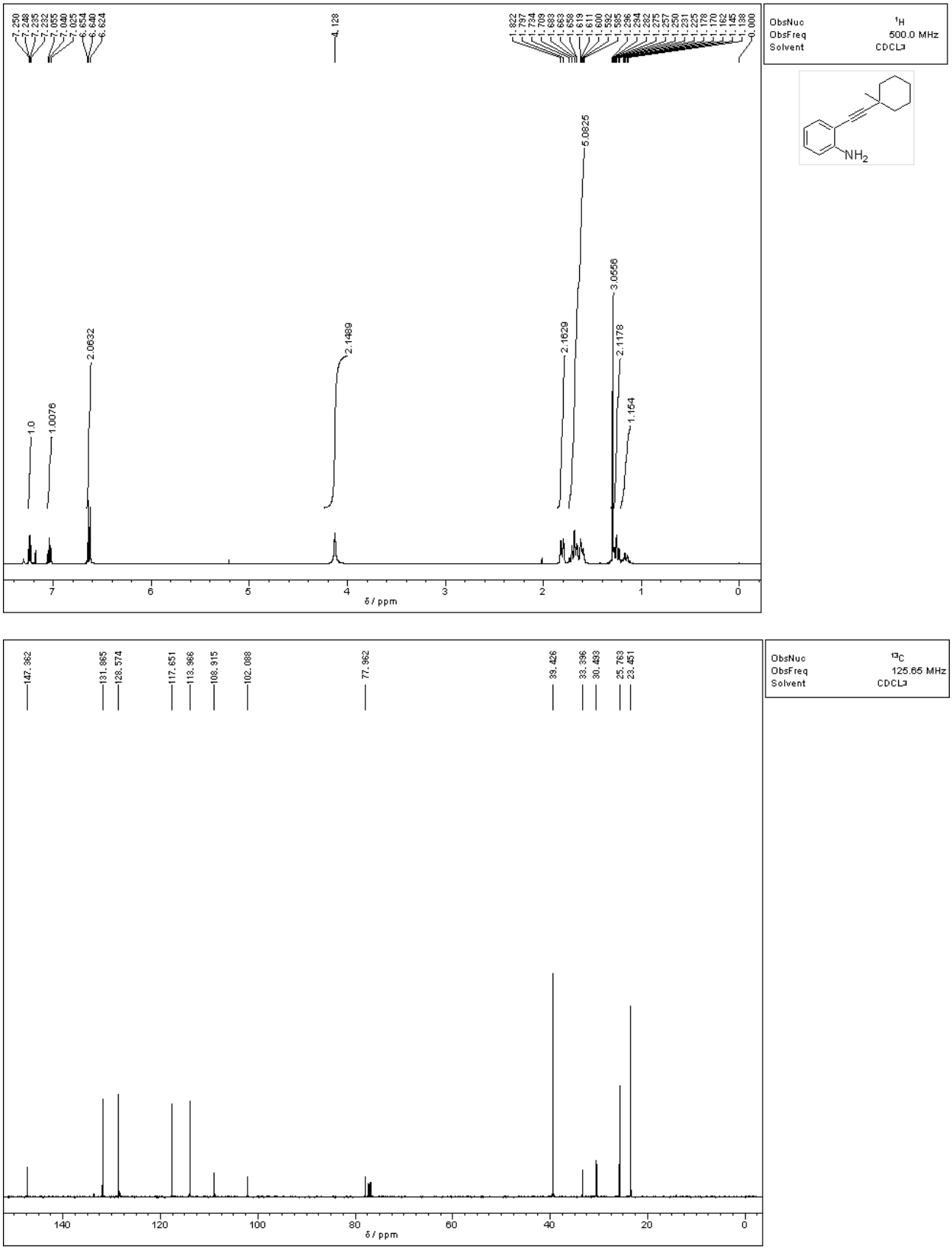

OBFRQ 125.65 MHz
SLVNT CDCl3
OBFIN 127958.0 Hz
TMS
N=C=O
ppm(13C)

2d

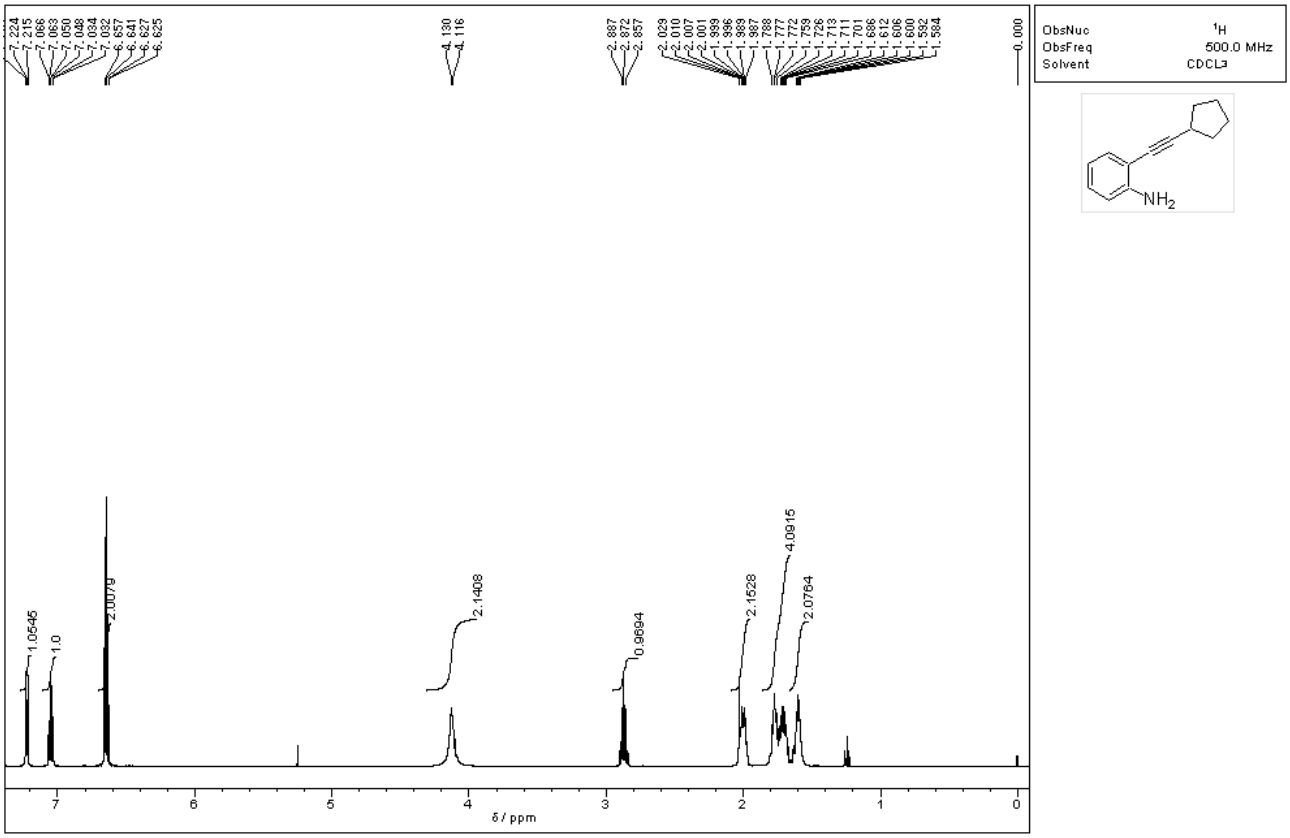

7.265
7.261
7.248
7.246
7.079
7.064
6.658
6.654
6.653
6.644
6.639
6.636
6.629
4.186
3.415
1.553
0.000
6.0058
3.122
2.093
2.0685
1.0
1.0201
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
OMe
NH2
δ / ppm

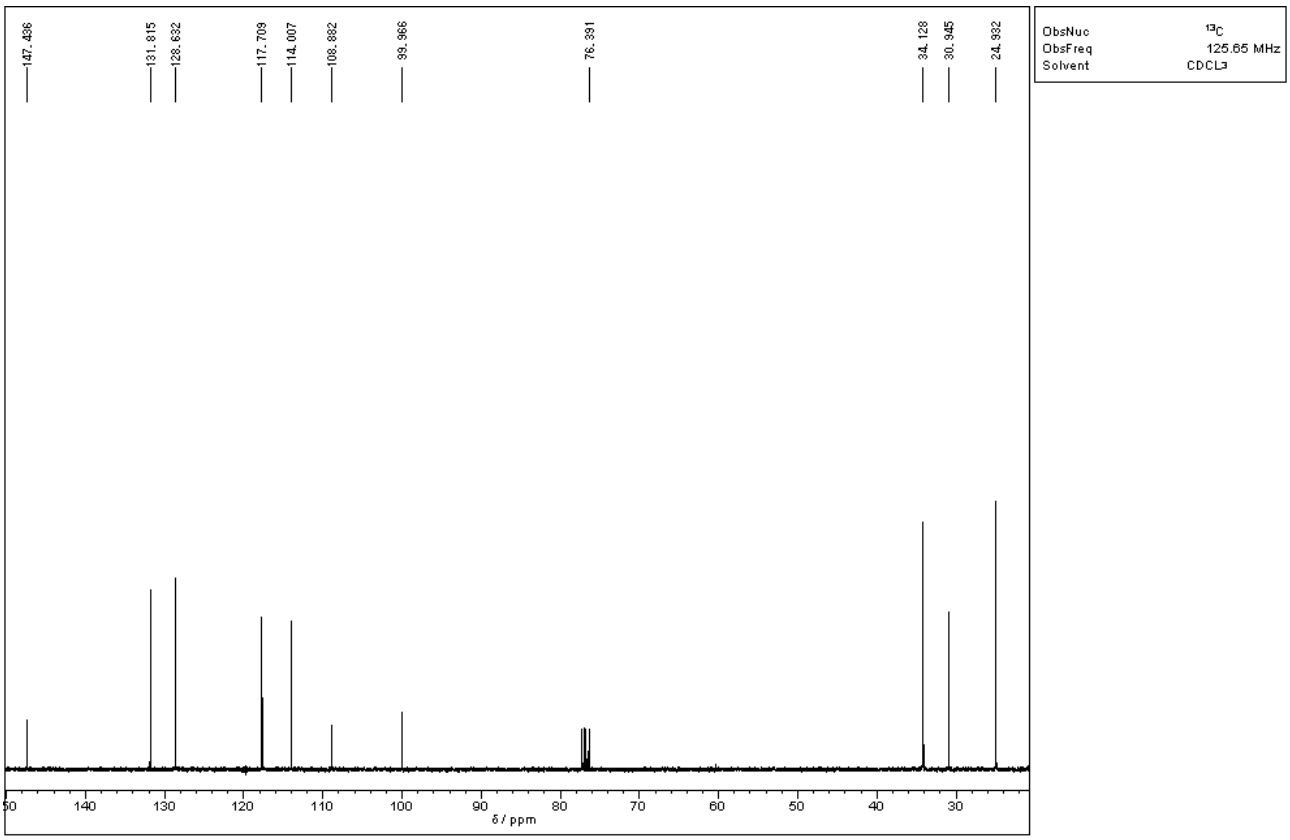

147.631
132.021
129.446
117.528
114.040
107.114
96.264
80.702
70.930
51.460
28.403
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

2e

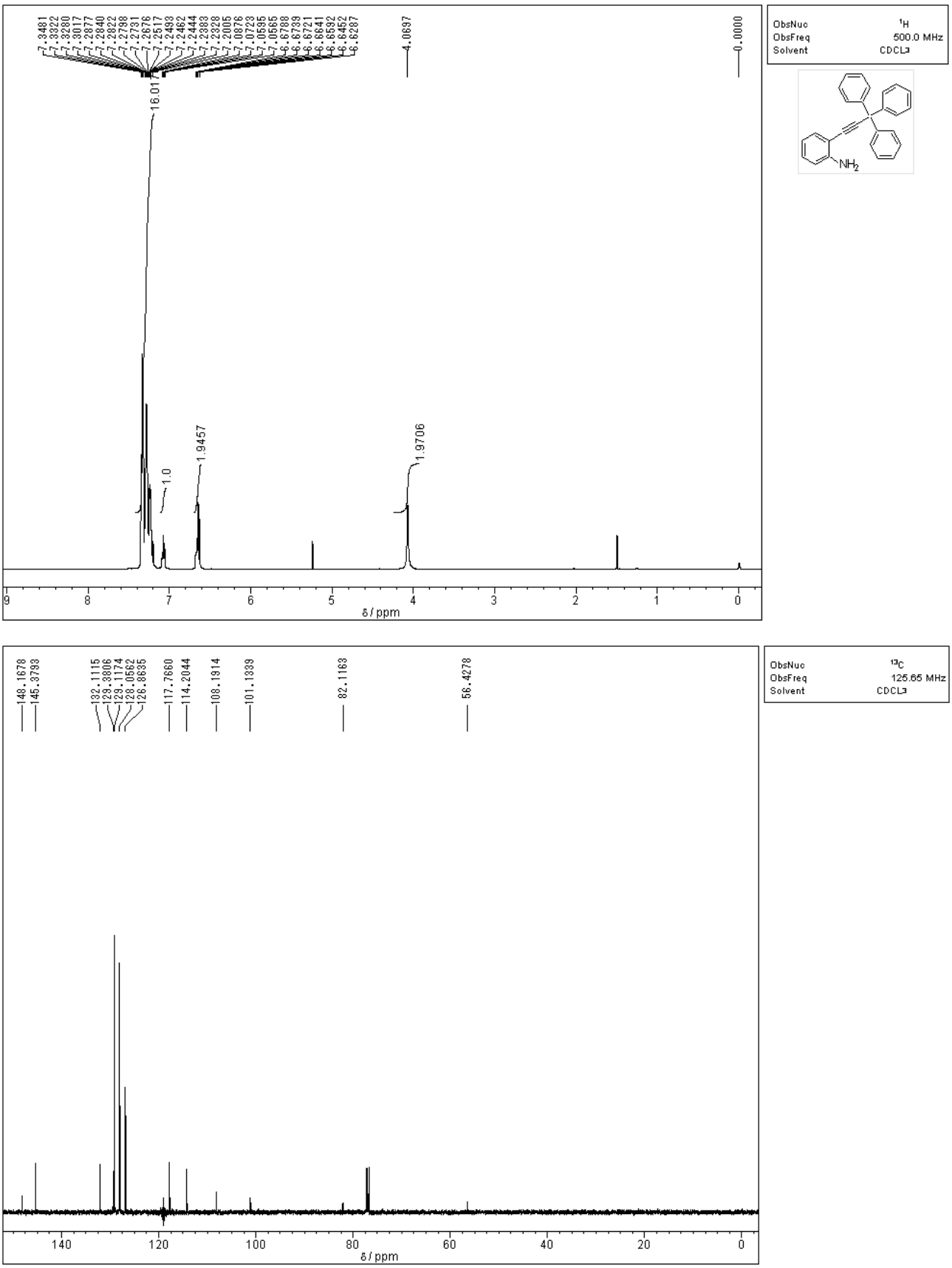

ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
NH2
δ / ppm
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

2g


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
NH2
δ / ppm


ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

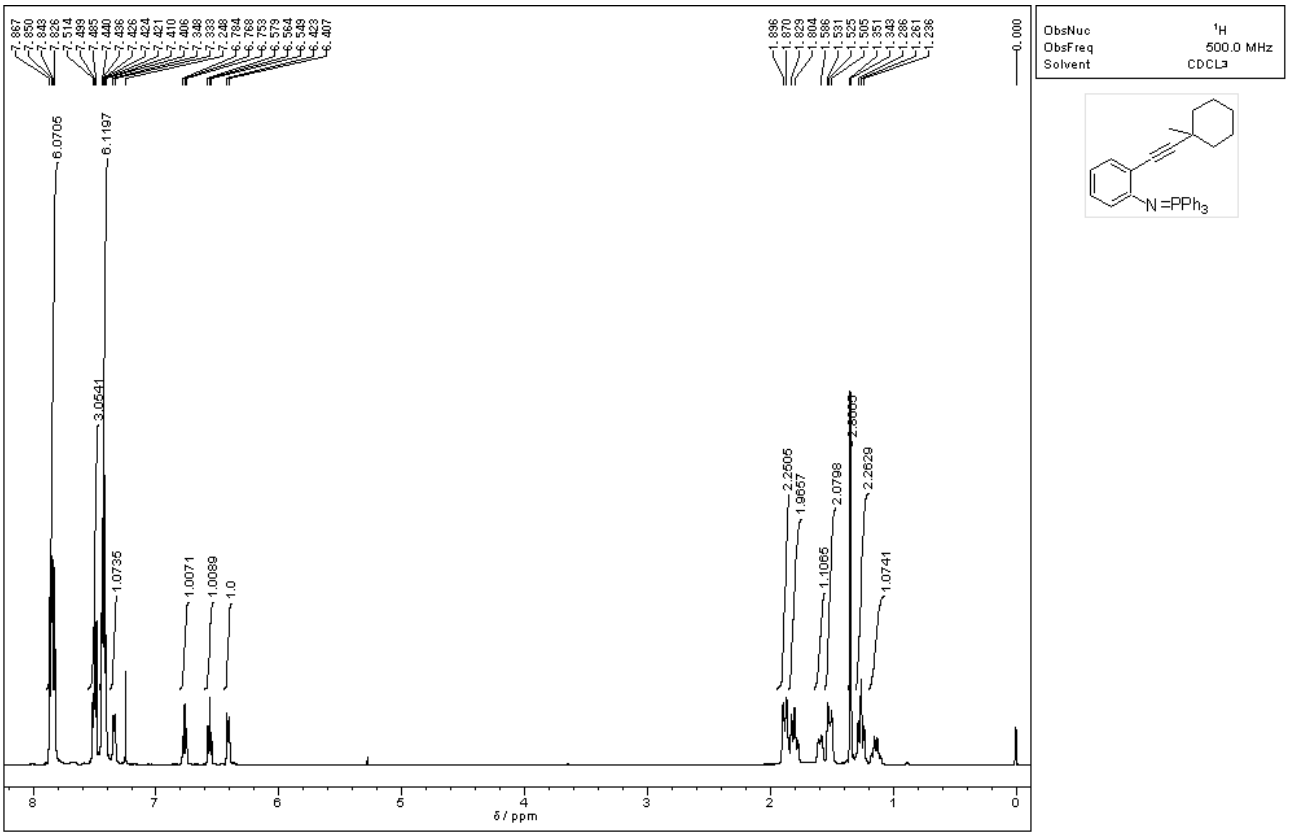
2l

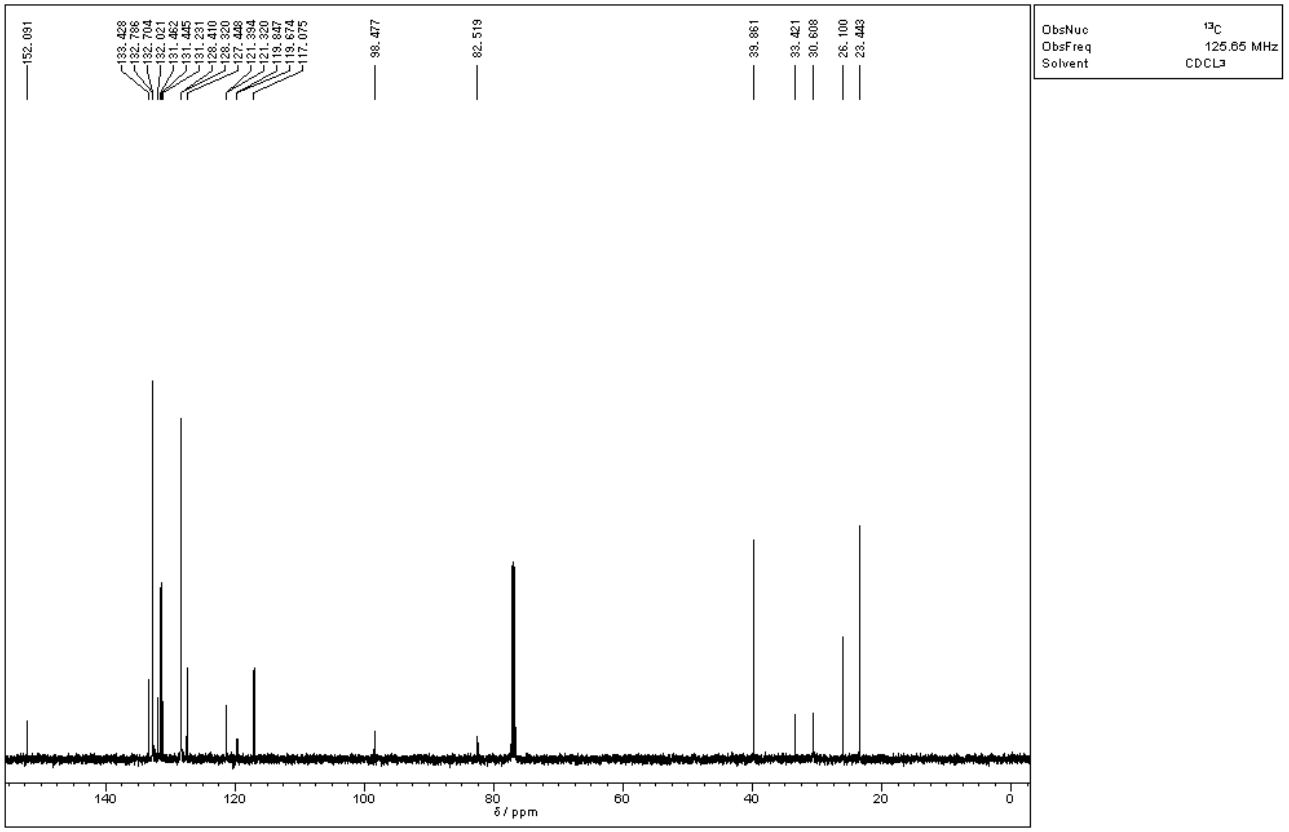

7.3481
7.3322
7.3280
7.3017
7.2877
7.2840
7.2822
7.2798
7.2731
7.2676
7.2517
7.2493
7.2462
7.2444
7.2388
7.2328
7.2005
7.0876
7.0723
7.0595
7.0565
6.6788
6.6739
6.6721
6.6641
6.6592
6.6452
6.6287
4.0697
0.0000
16.01
1.0
1.9457
1.9706
9
8
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
NH2
148.1678
145.3798
132.1115
128.3806
128.1174
128.0562
126.8635
117.7660
114.2044
108.1814
101.1399
82.1163
56.4278
140
120
100
80
60
40
20
0
δ / ppm
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3

3d

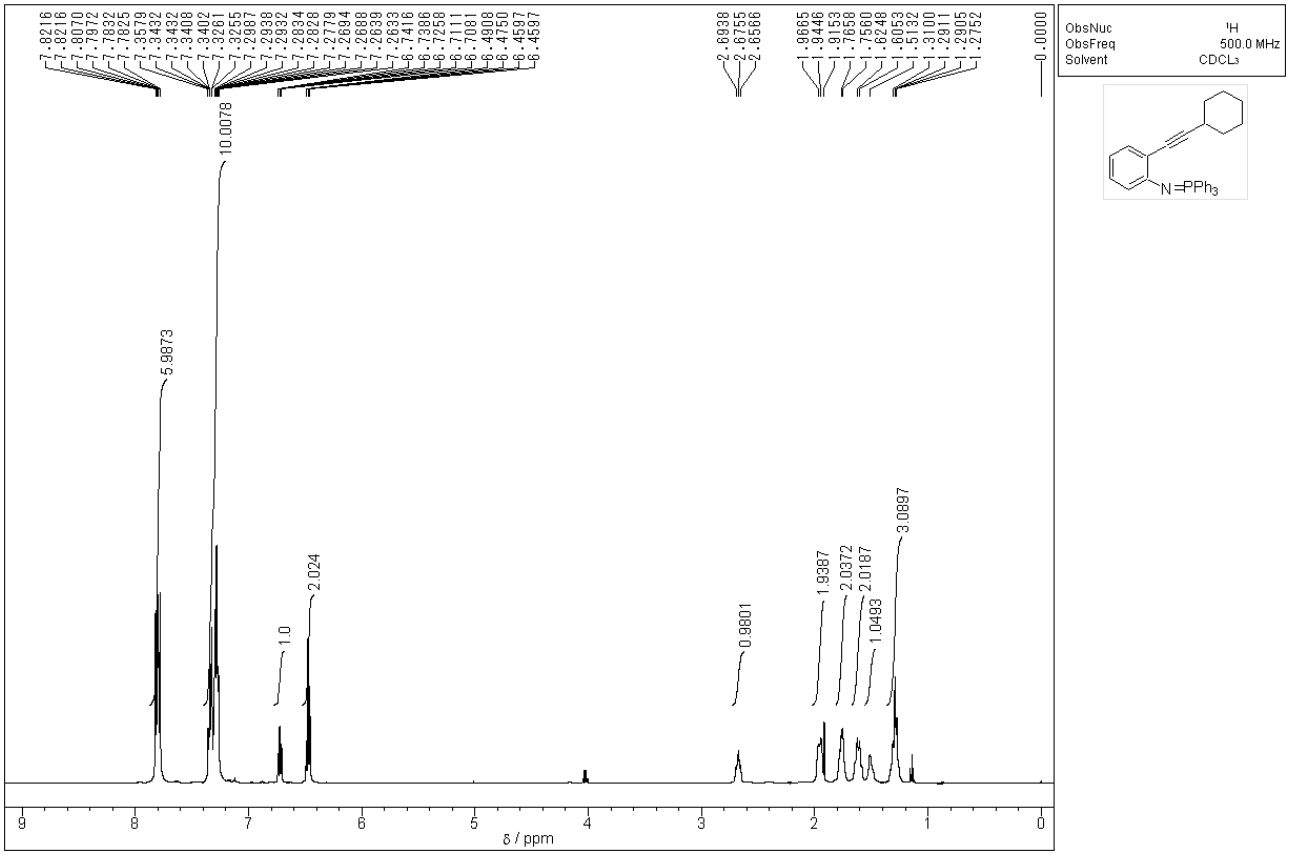

ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
OMe
N=PPh3
δ / ppm
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

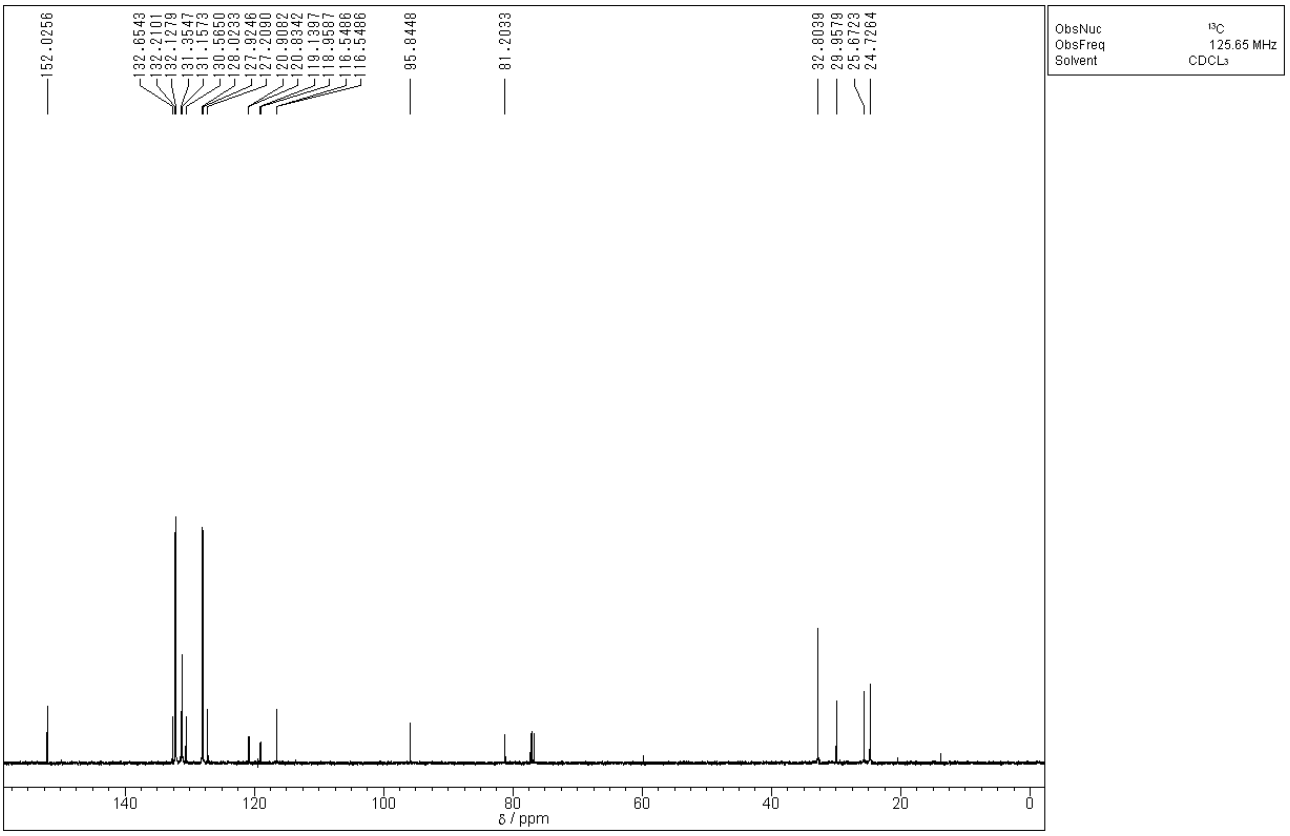
3e


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=PPh3
δ / ppm

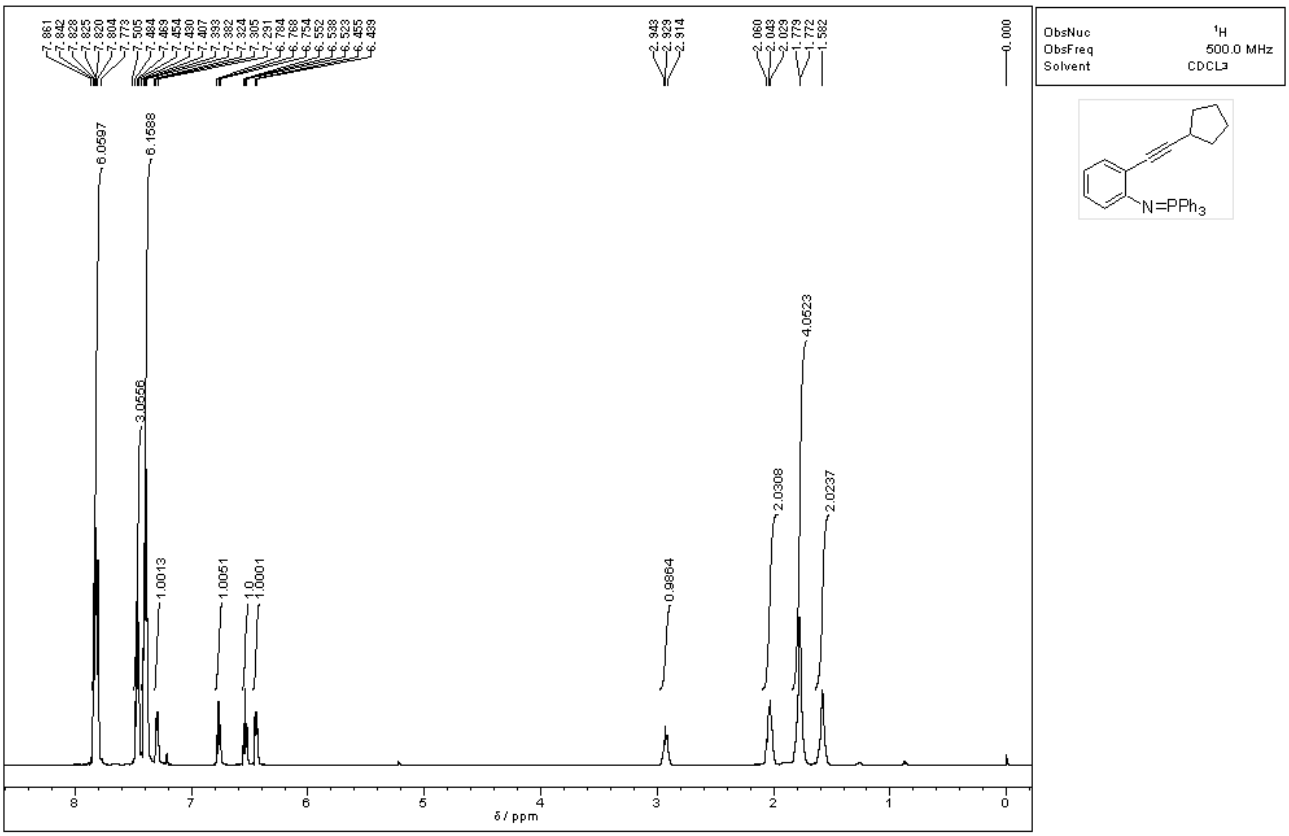

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

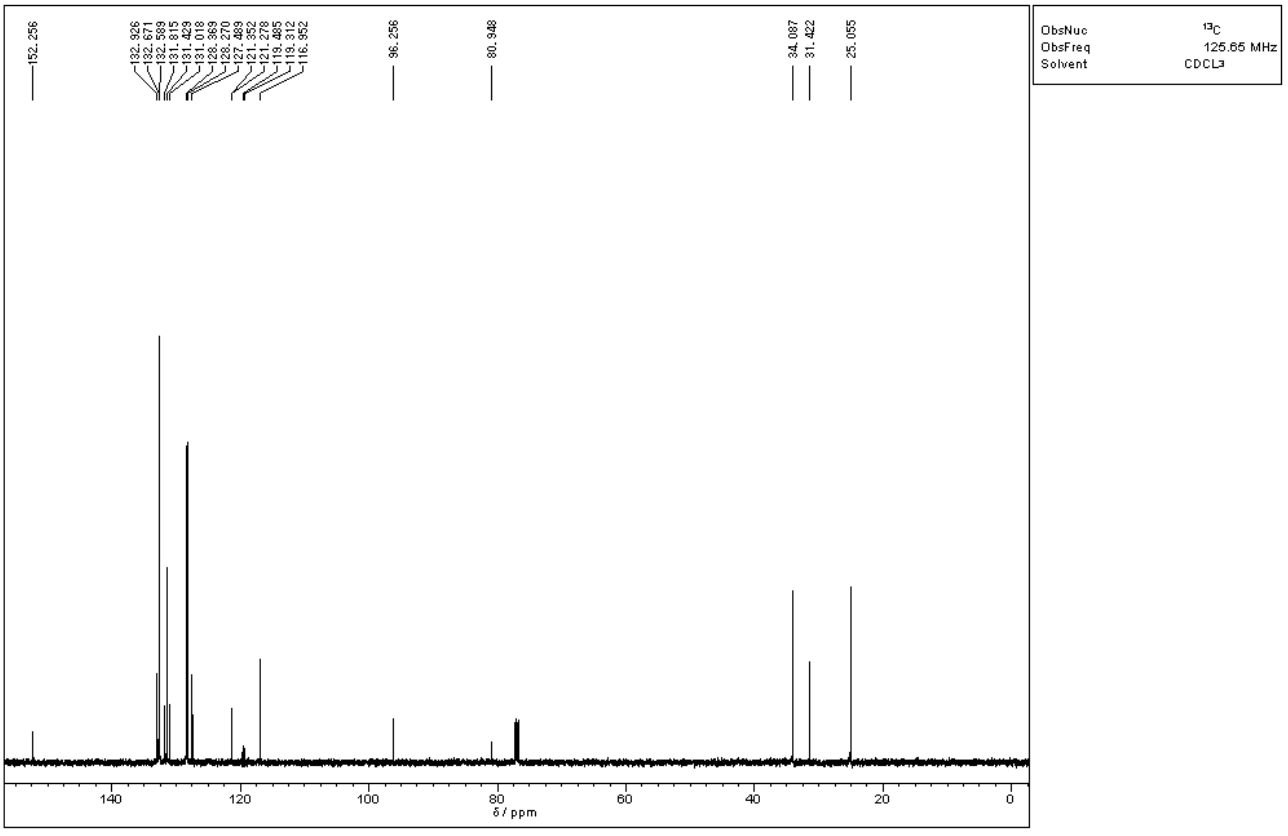
3f


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=PPh3
δ / ppm

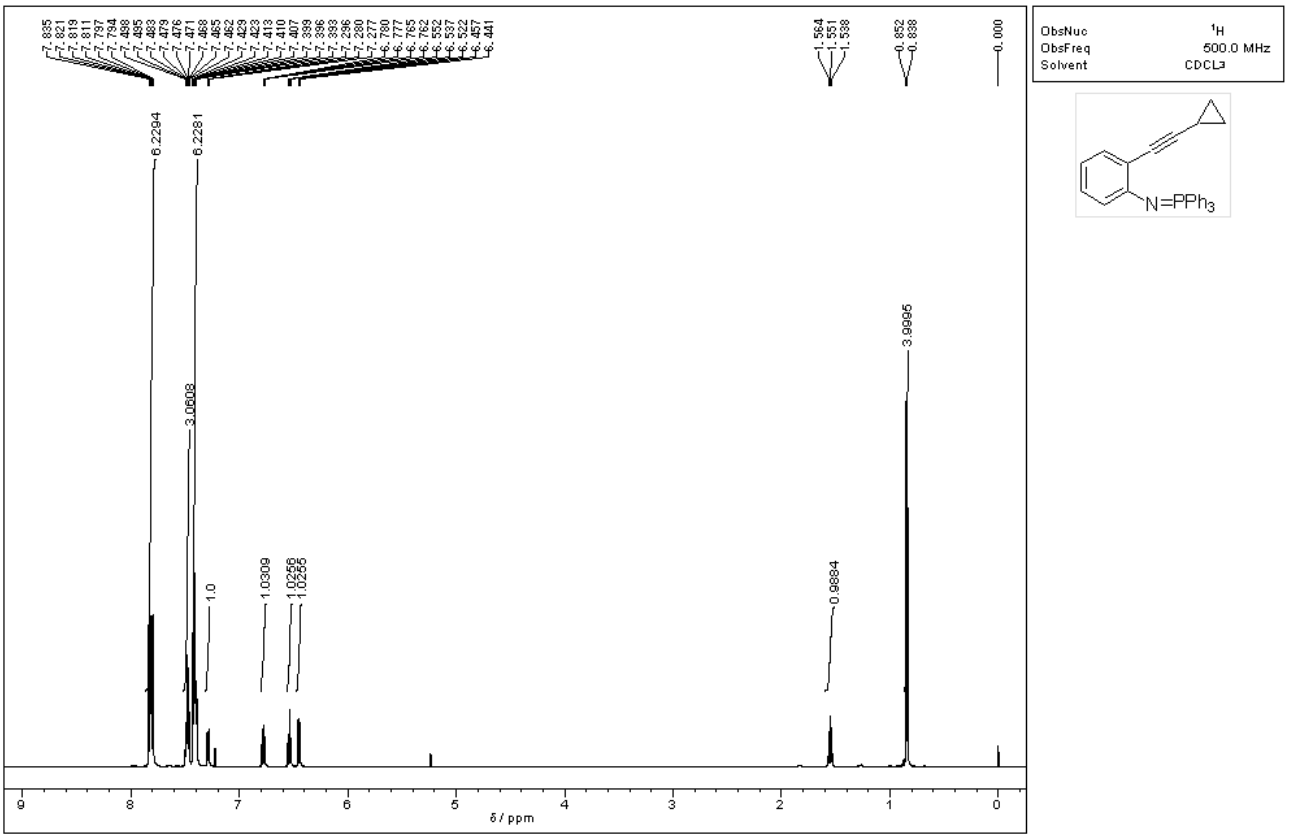

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

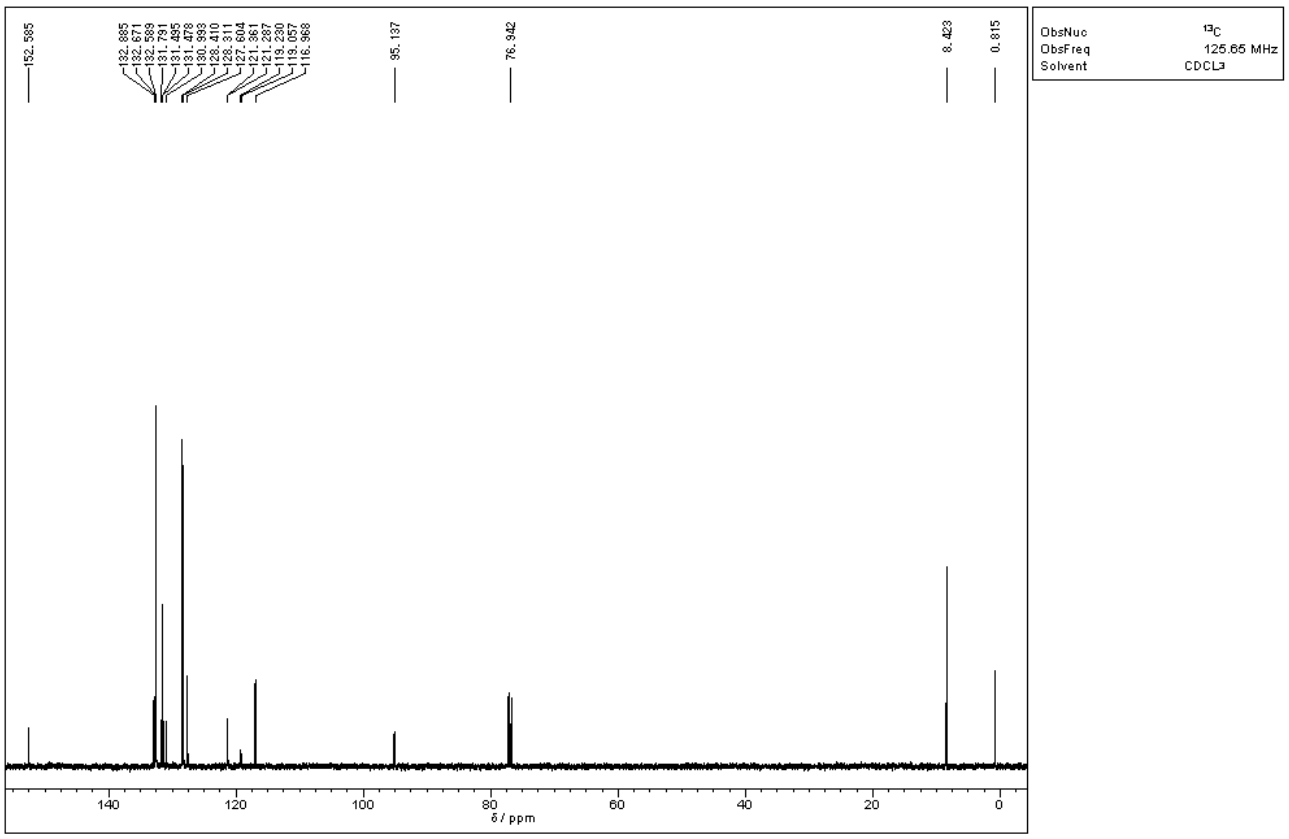
3g


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=PPh3
δ / ppm

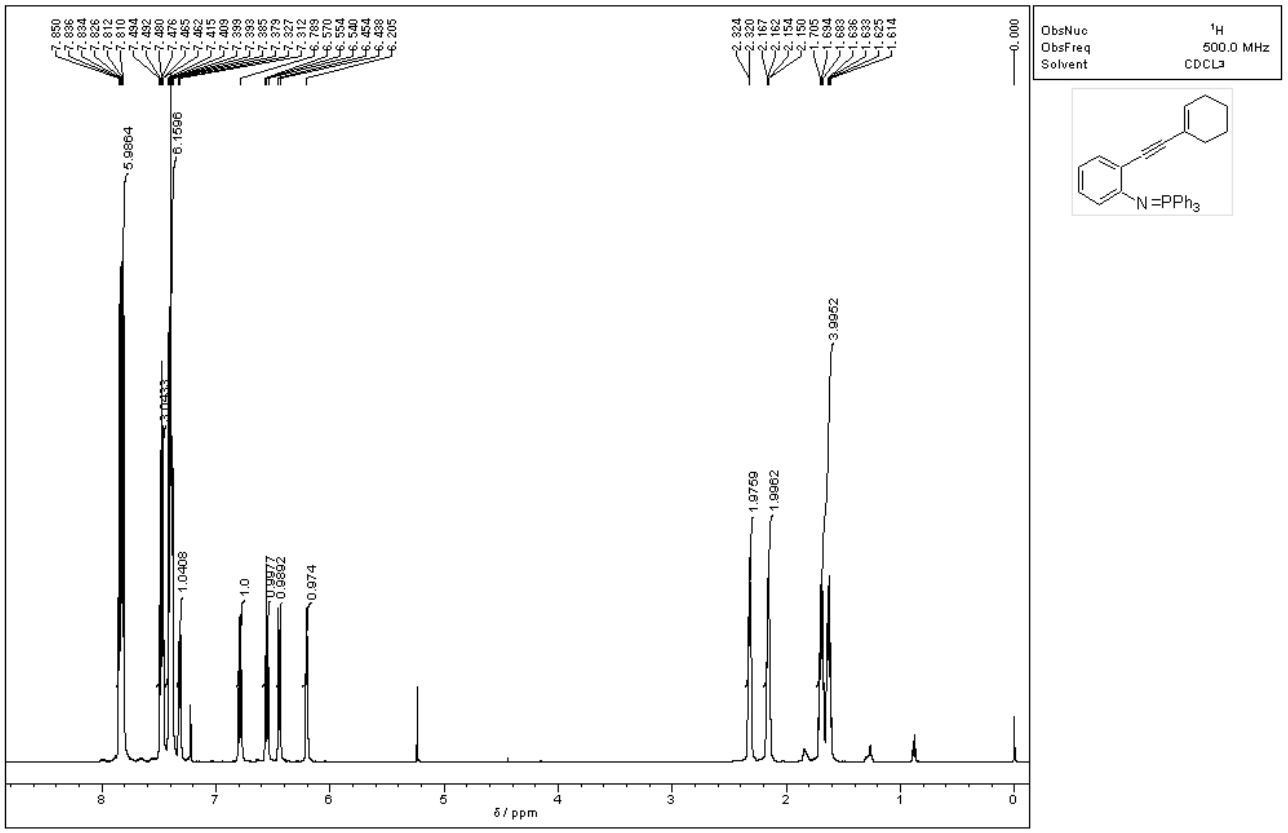

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

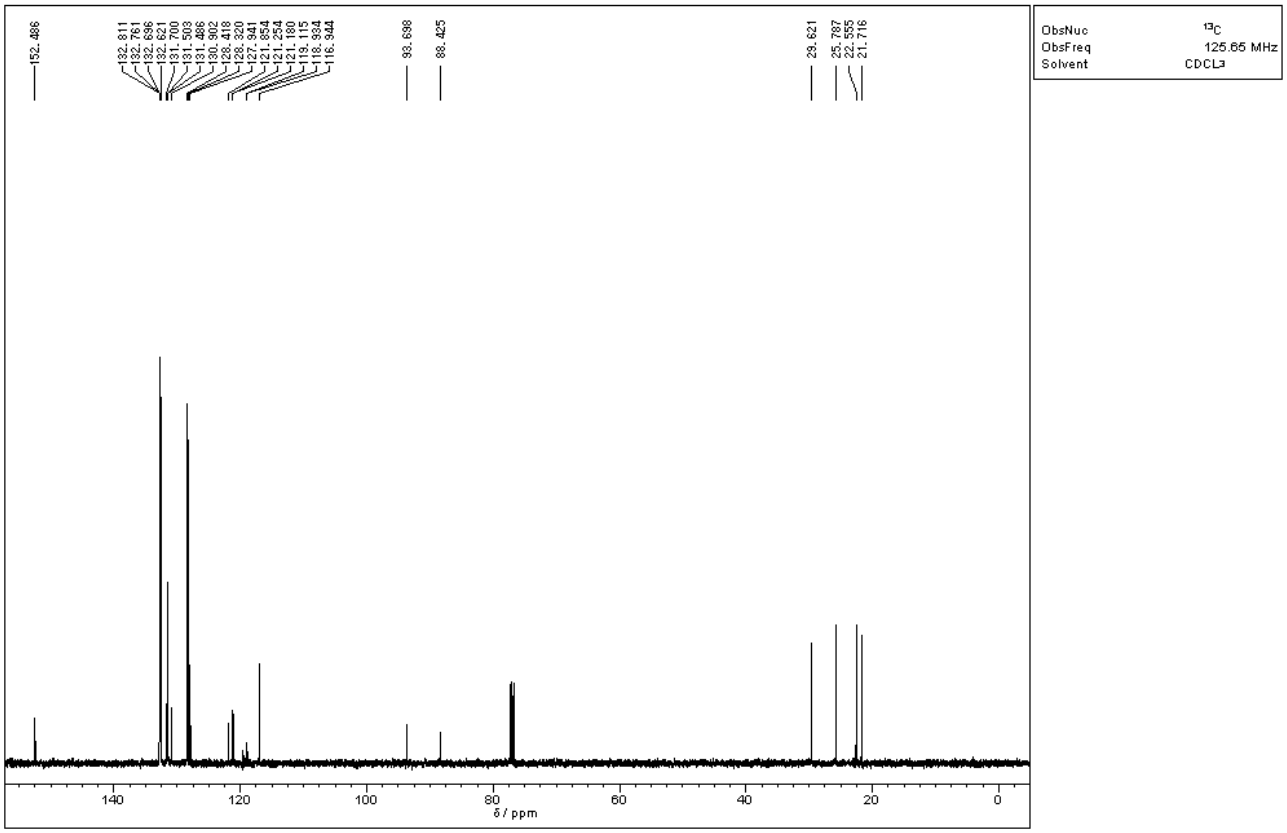
3h


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=PPh3
δ / ppm

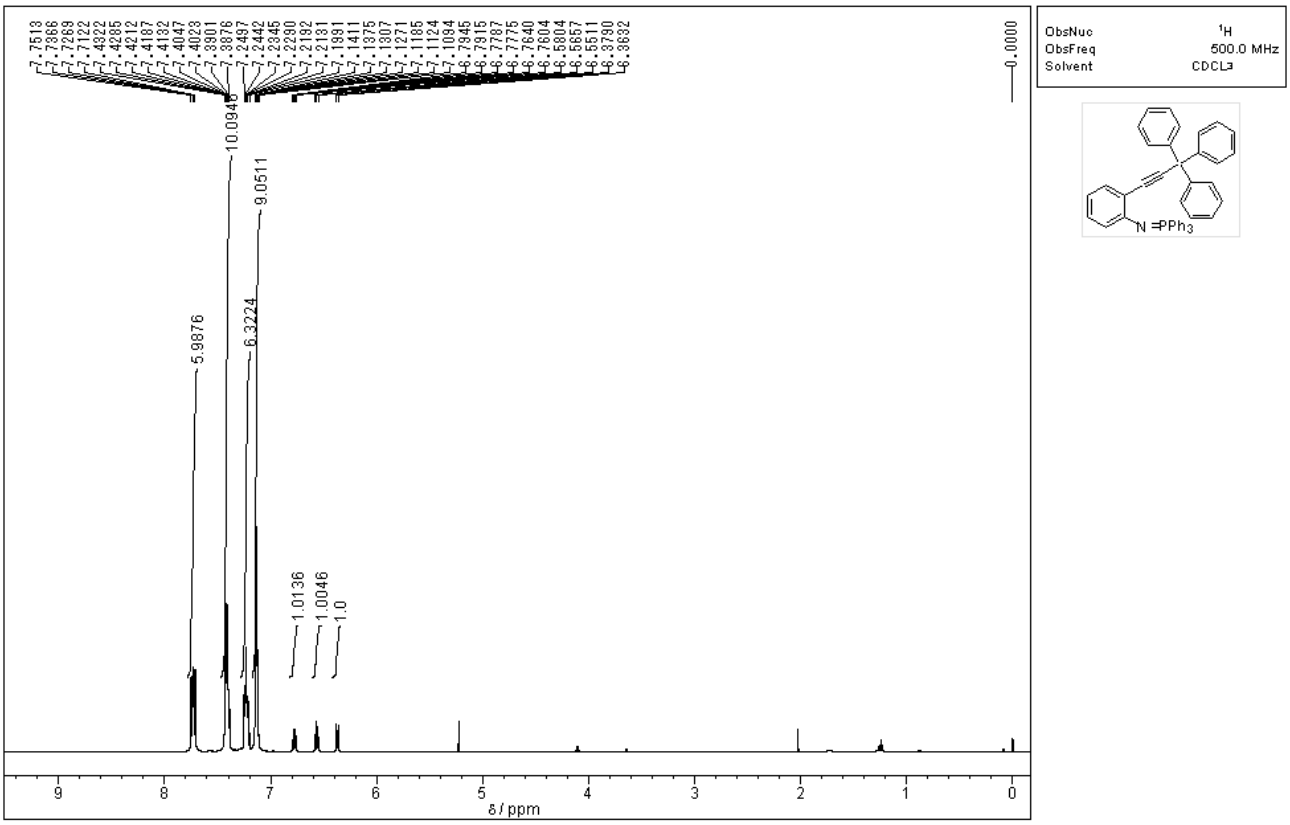

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

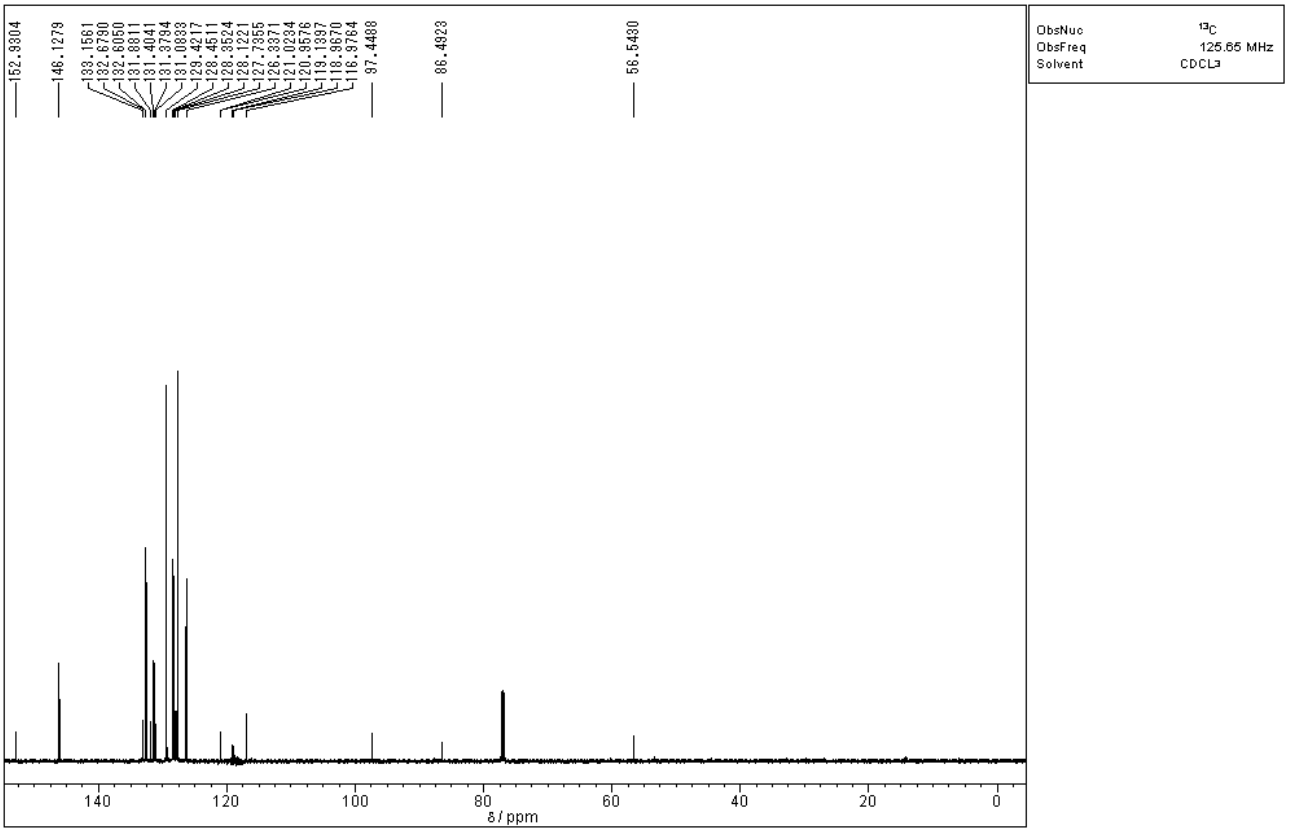
3i


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N=PPh3
δ / ppm

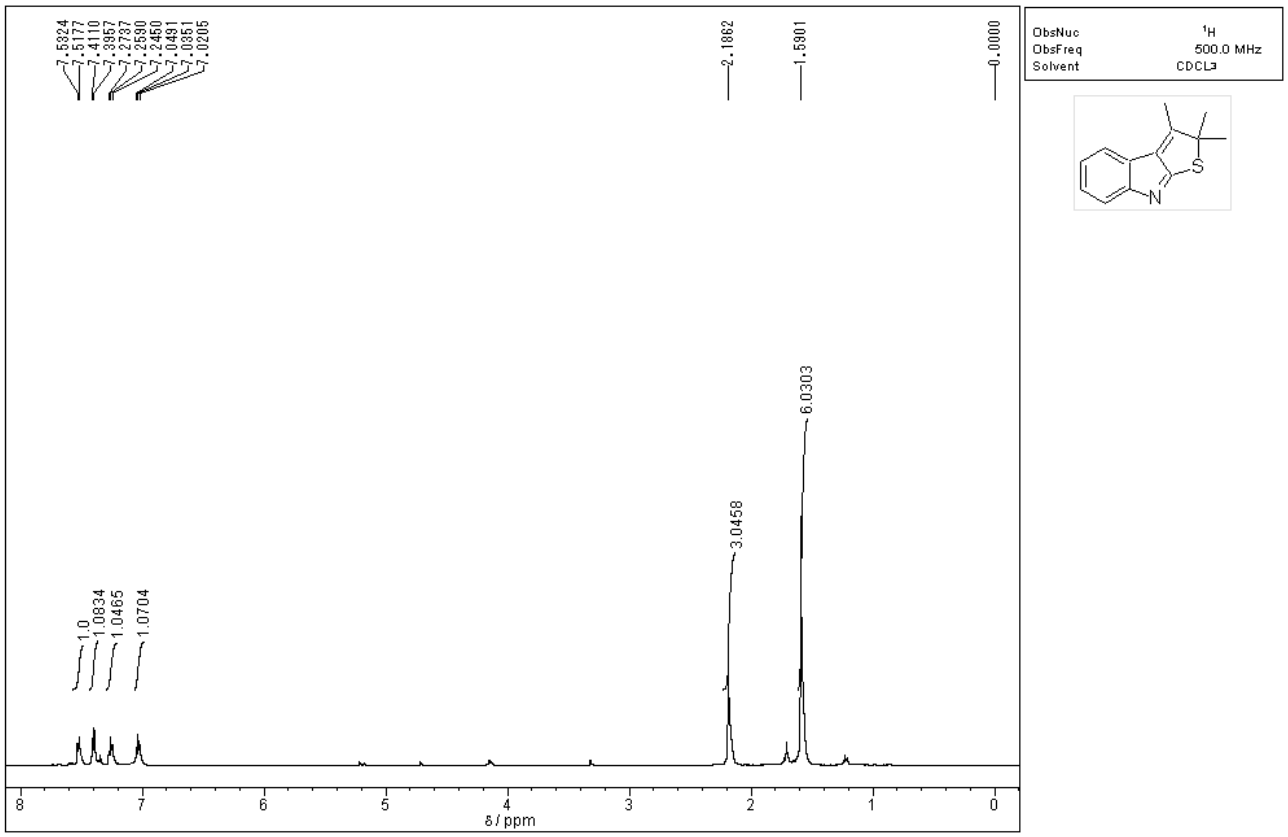

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

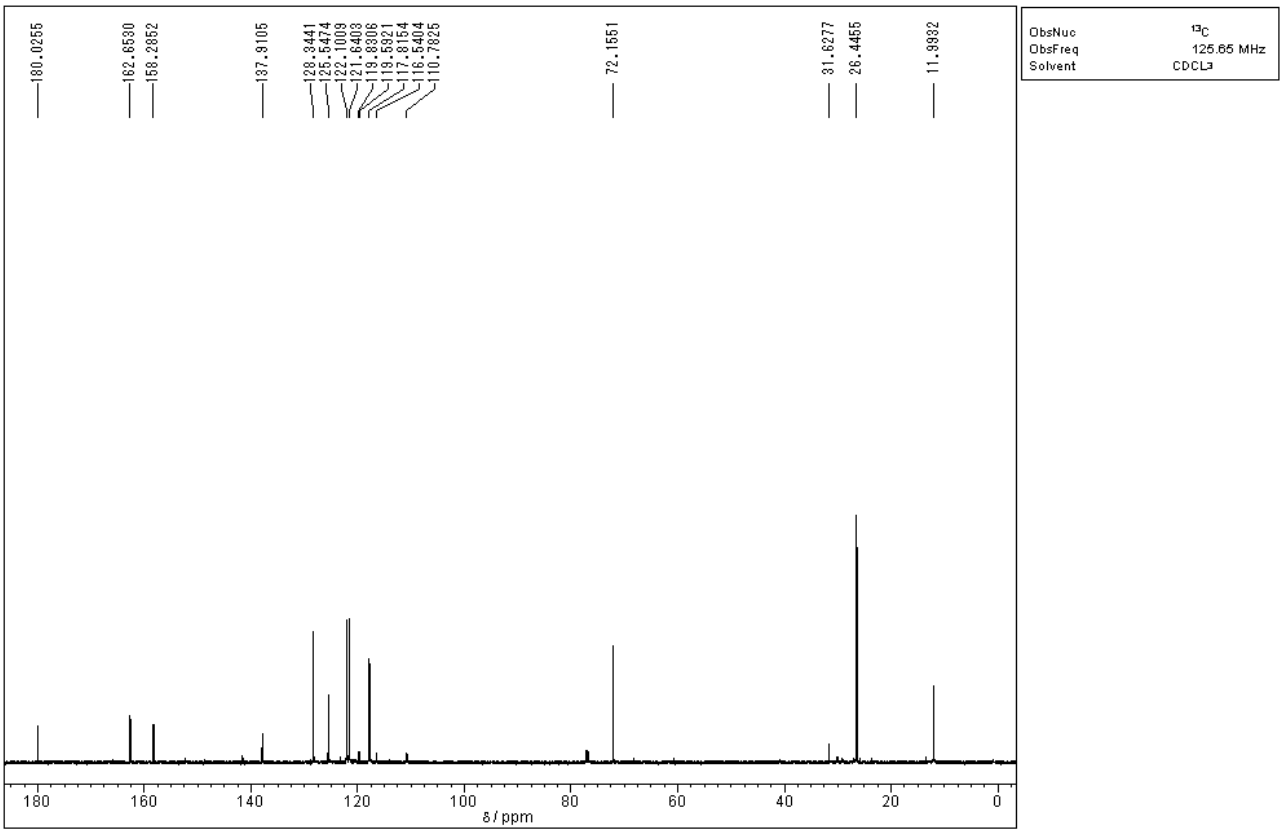
3l


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
N =PPh3
δ / ppm

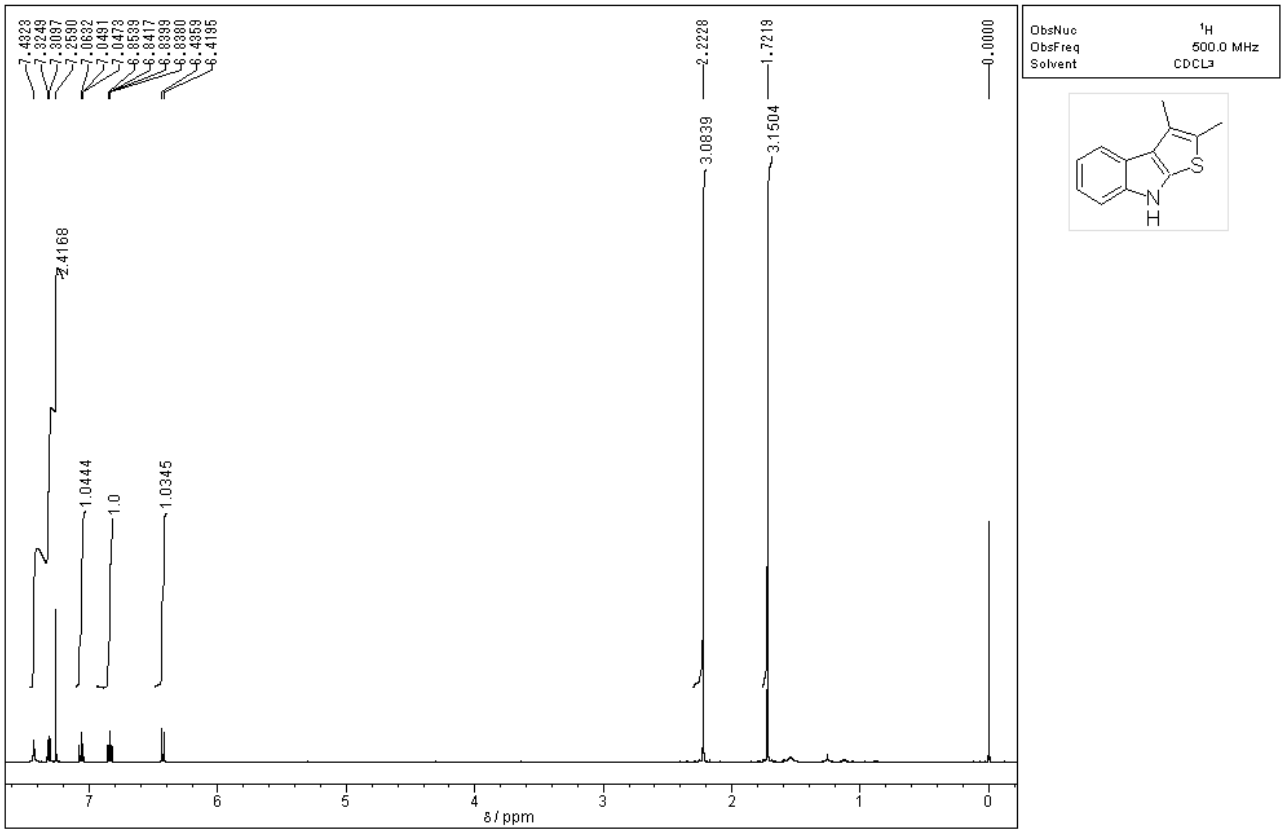

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

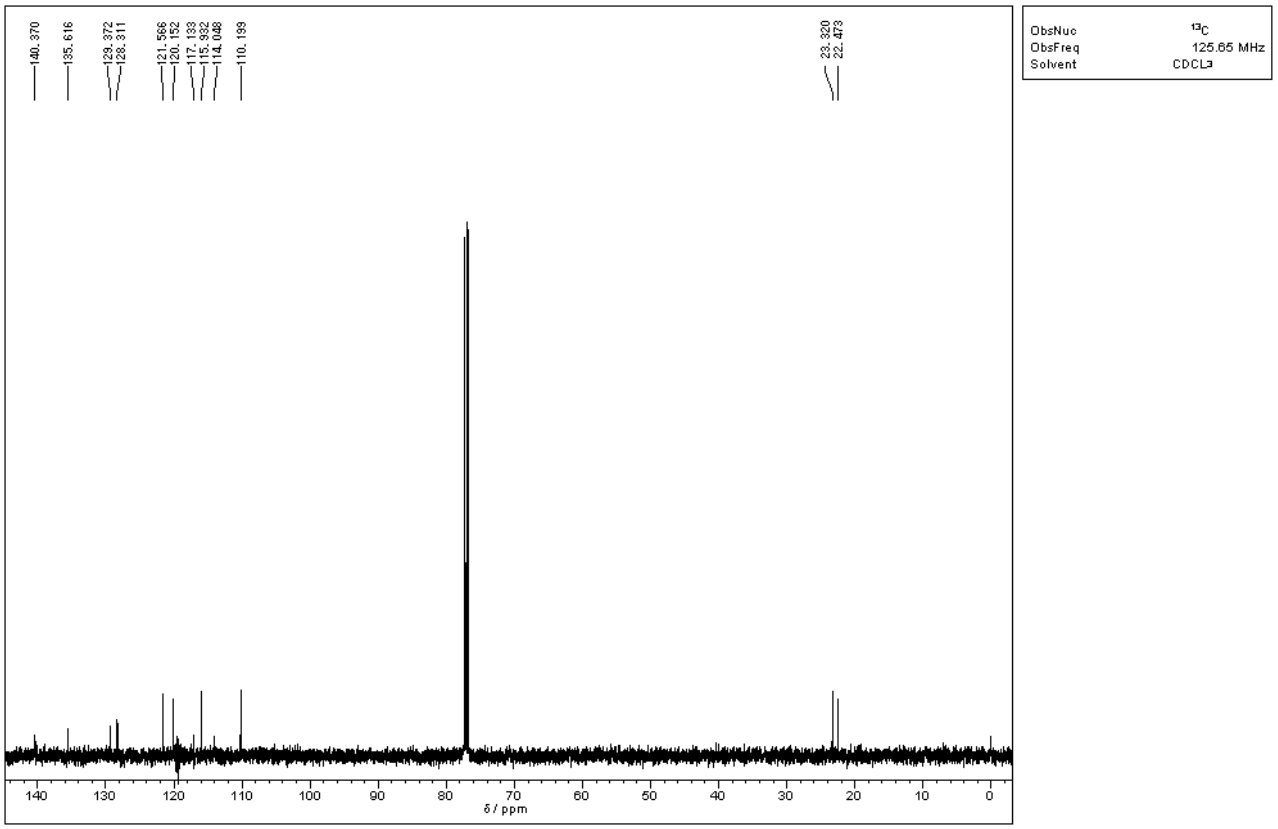
5


7.5324
7.5177
7.4110
7.3957
7.2737
7.2590
7.2450
7.1041
7.0861
7.0205
2.1862
1.5801
0.0000
6.0303
3.0458
1.0
1.0834
1.0465
1.0704
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
δ / ppm

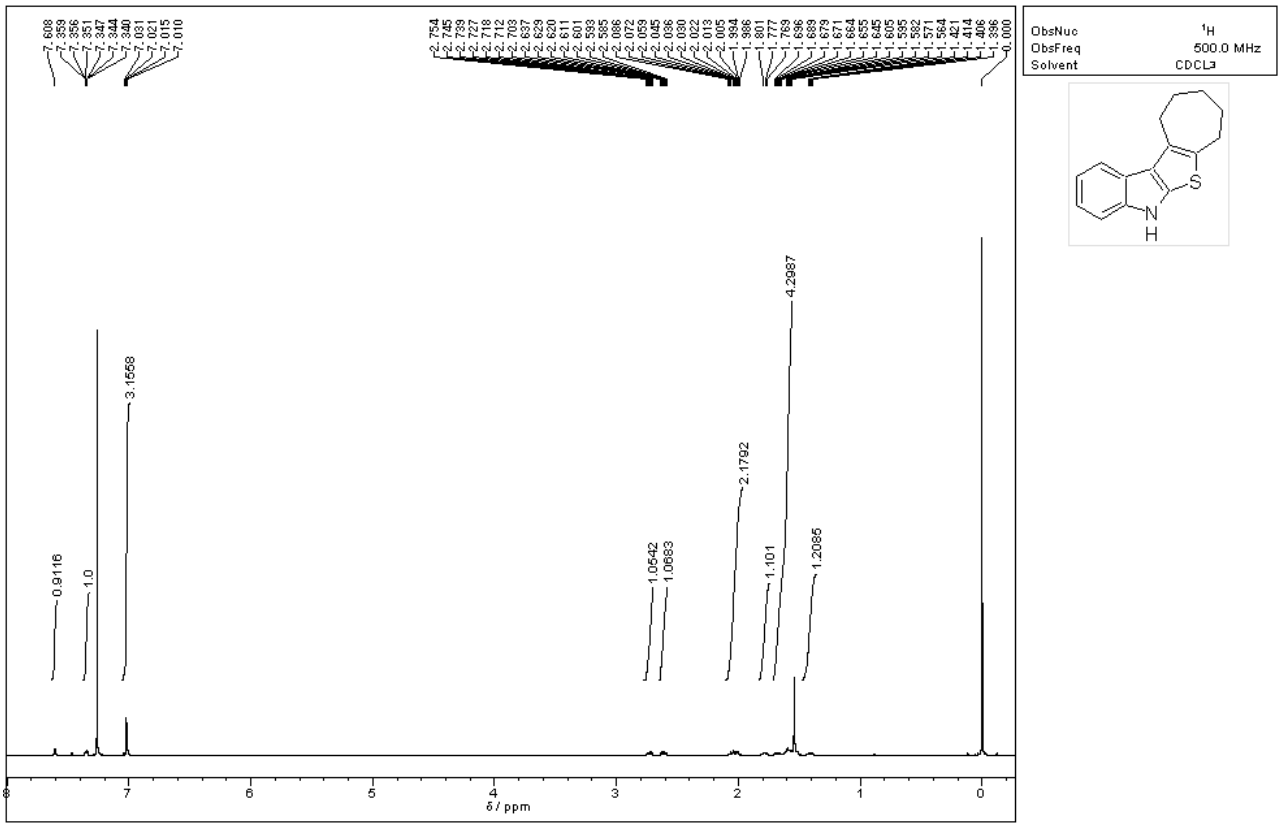

180.0255
162.8530
158.2852
137.9105
128.3441
125.6474
122.1009
121.6403
119.8306
119.5921
117.8154
116.5404
110.7825
72.1551
31.6277
28.4455
11.9932
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

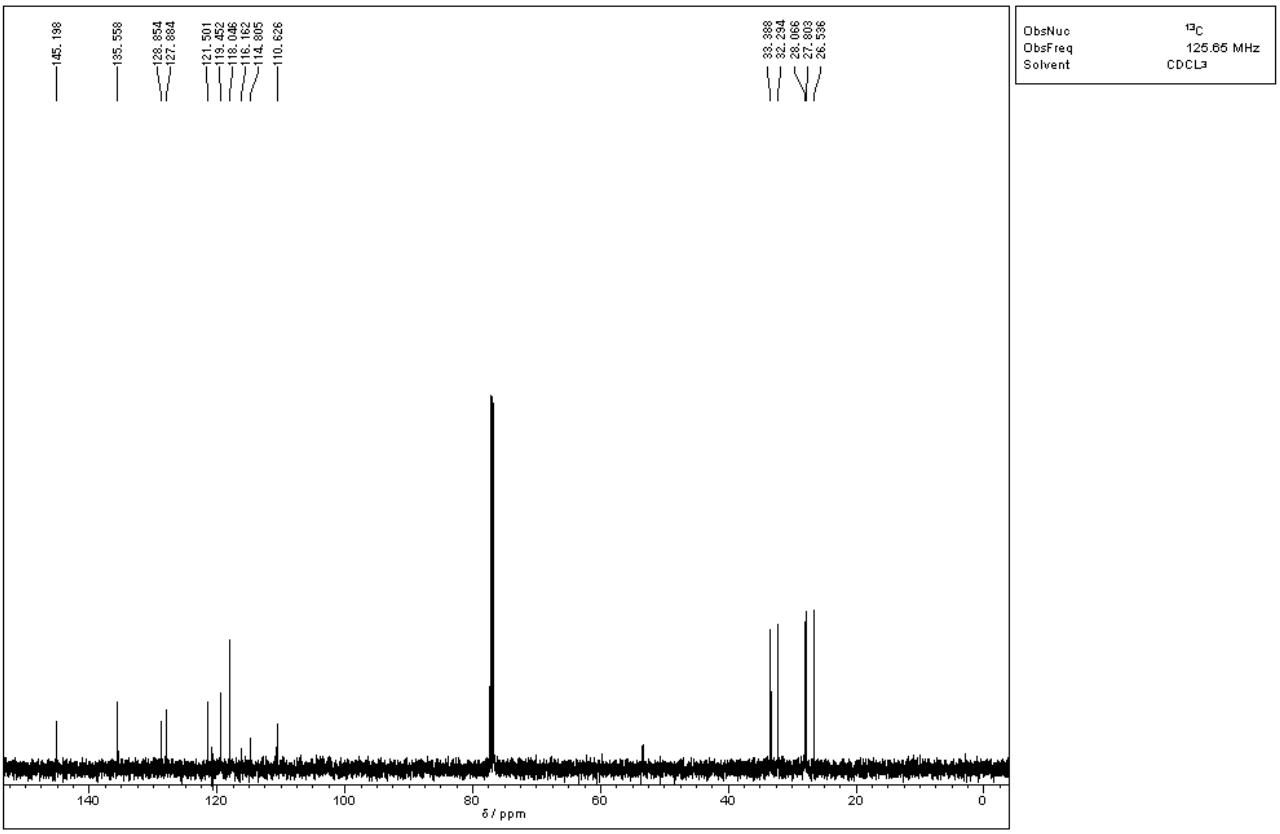
6


7.4823
7.3249
7.3097
7.2590
7.0632
7.0491
7.0473
6.8539
6.8417
6.8399
6.8380
6.4359
6.4195
2.2228
1.7218
0.0000
3.0839
3.1504
2.4168
1.0444
1.0
1.0345
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3

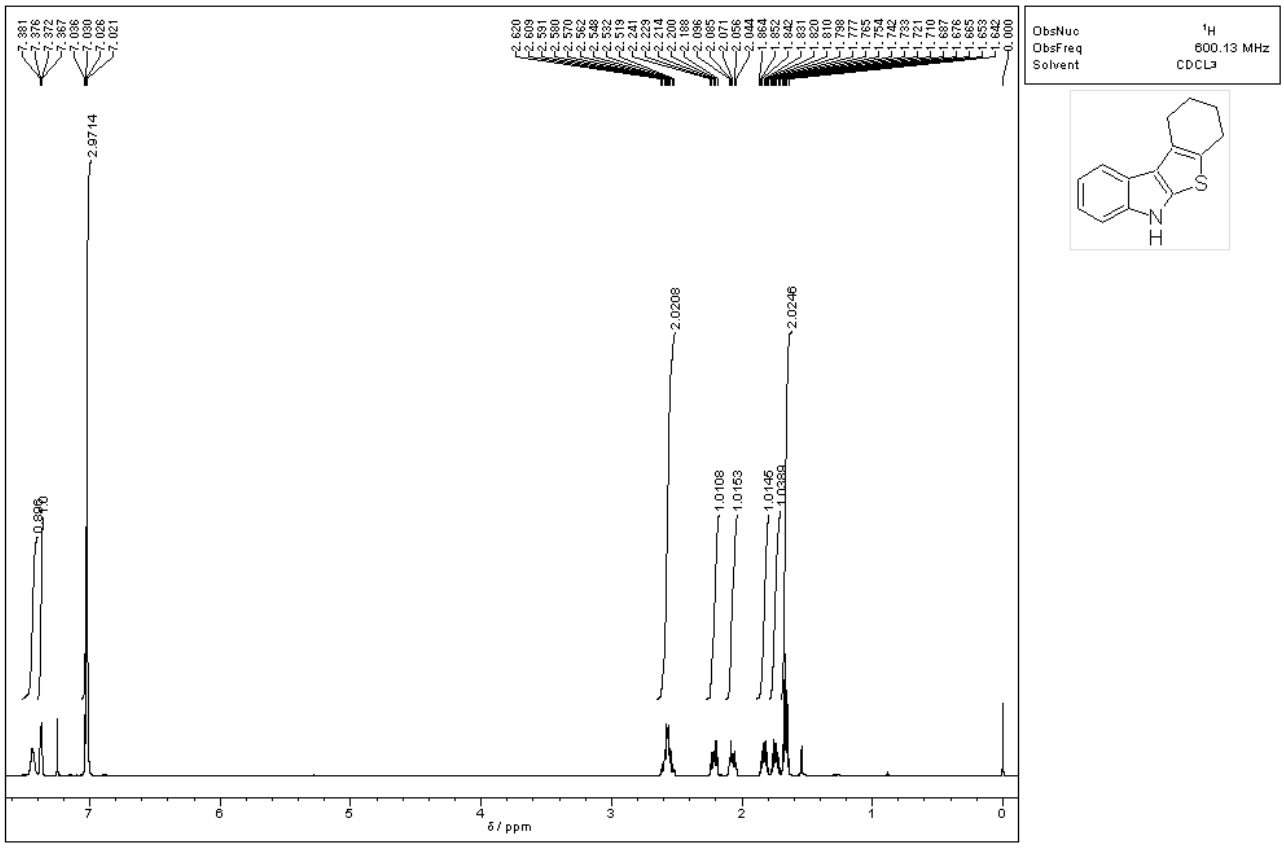

140.370
135.616
129.372
128.311
121.566
120.152
117.133
115.932
114.048
110.199
23.320
22.473
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3

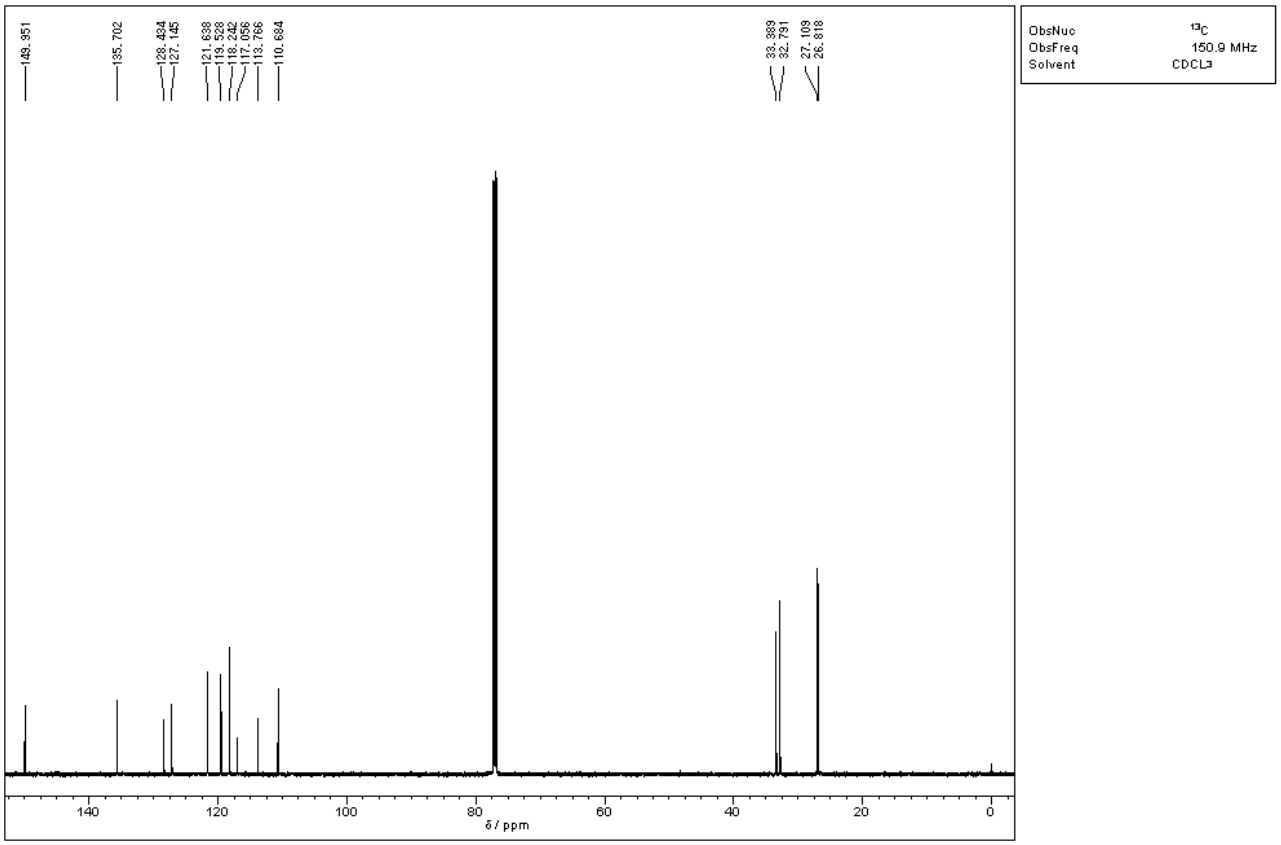
7


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
7.608 7.358 7.356 7.351 7.347 7.344 7.340 7.031 7.021 7.015 7.010
2.754 2.745 2.739 2.727 2.718 2.712 2.703 2.637 2.629 2.620 2.611 2.601 2.593 2.585 2.086 2.072 2.059 2.045 2.036 2.030 2.022 2.013 2.005 1.994 1.986 1.801 1.777 1.769 1.696 1.689 1.679 1.671 1.664 1.655 1.645 1.605 1.595 1.582 1.571 1.564 1.421 1.414 1.406 1.396 0.000
0.9116
1.0
3.1558
1.0542
1.0683
2.1792
1.101
4.2987
1.2085
δ / ppm

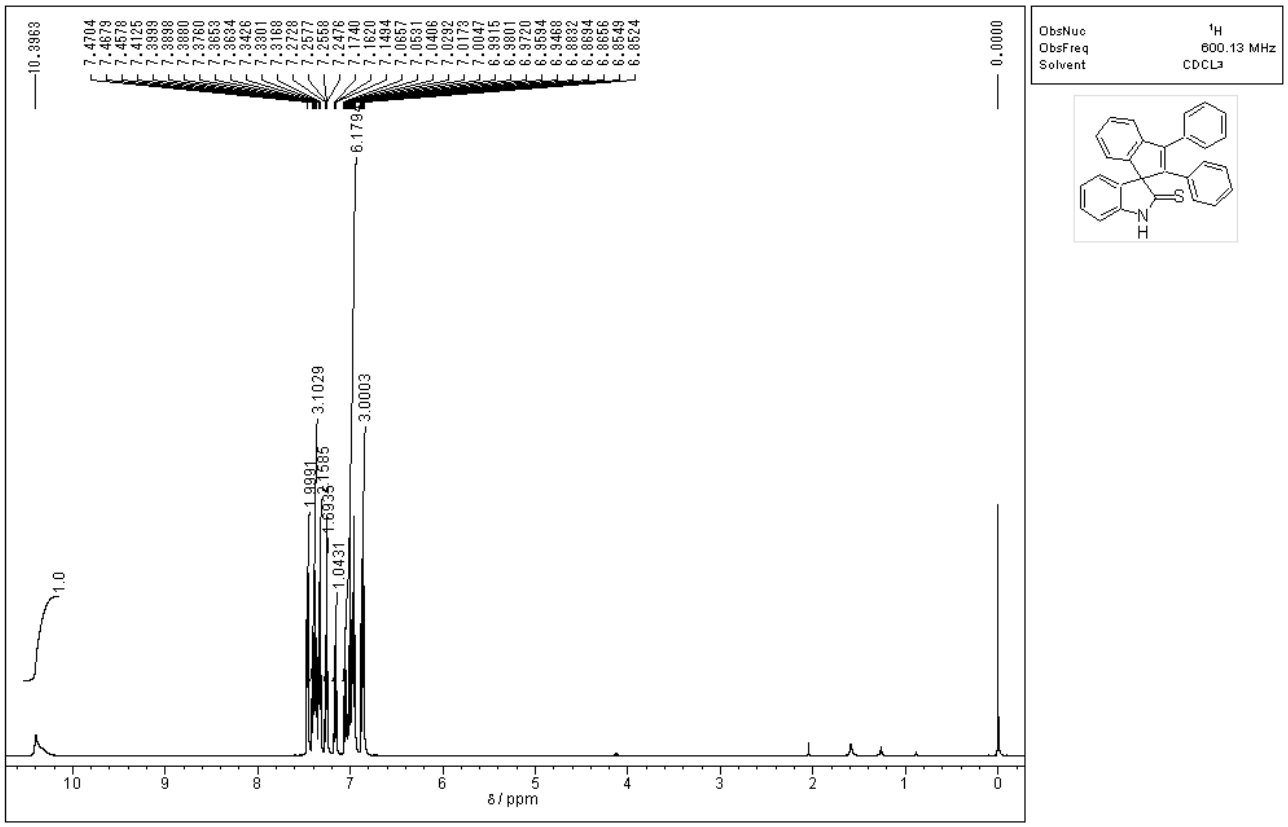

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
145.198
135.558
128.854
127.884
121.501
119.452
118.046
116.162
114.805
110.626
33.388
32.294
28.066
27.803
26.536
δ / ppm

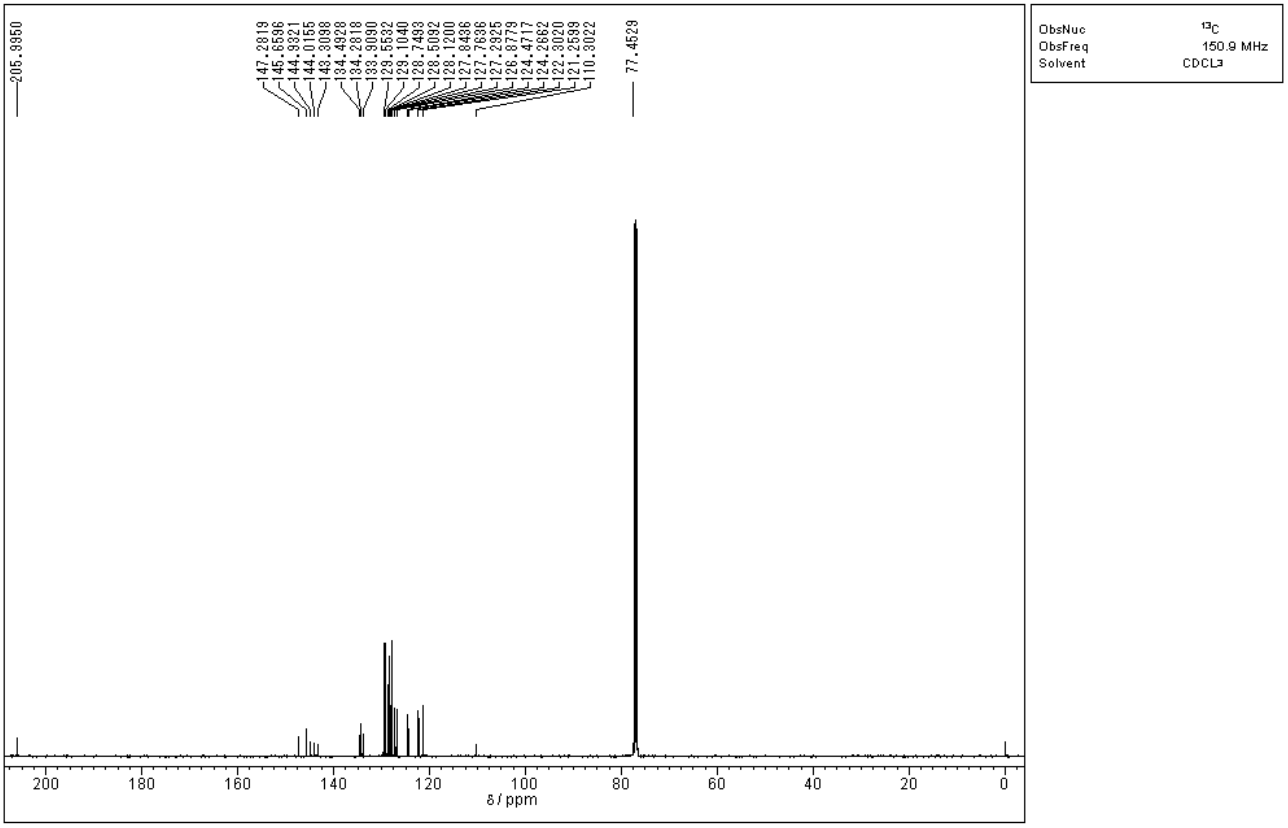
8


ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
7.381
7.376
7.372
7.367
7.036
7.030
7.026
7.021
2.620
2.609
2.591
2.580
2.570
2.562
2.548
2.532
2.519
2.241
2.229
2.214
2.200
2.188
2.096
2.085
2.071
2.056
2.044
1.864
1.852
1.842
1.831
1.820
1.810
1.798
1.777
1.765
1.754
1.742
1.733
1.721
1.710
1.697
1.676
1.665
1.653
1.642
0.000
2.9714
0.8996
0.8976
2.0208
1.0108
1.0153
1.0145
1.0389
2.0246
S
N
H
7
6
5
4
3
2
1
0
δ / ppm

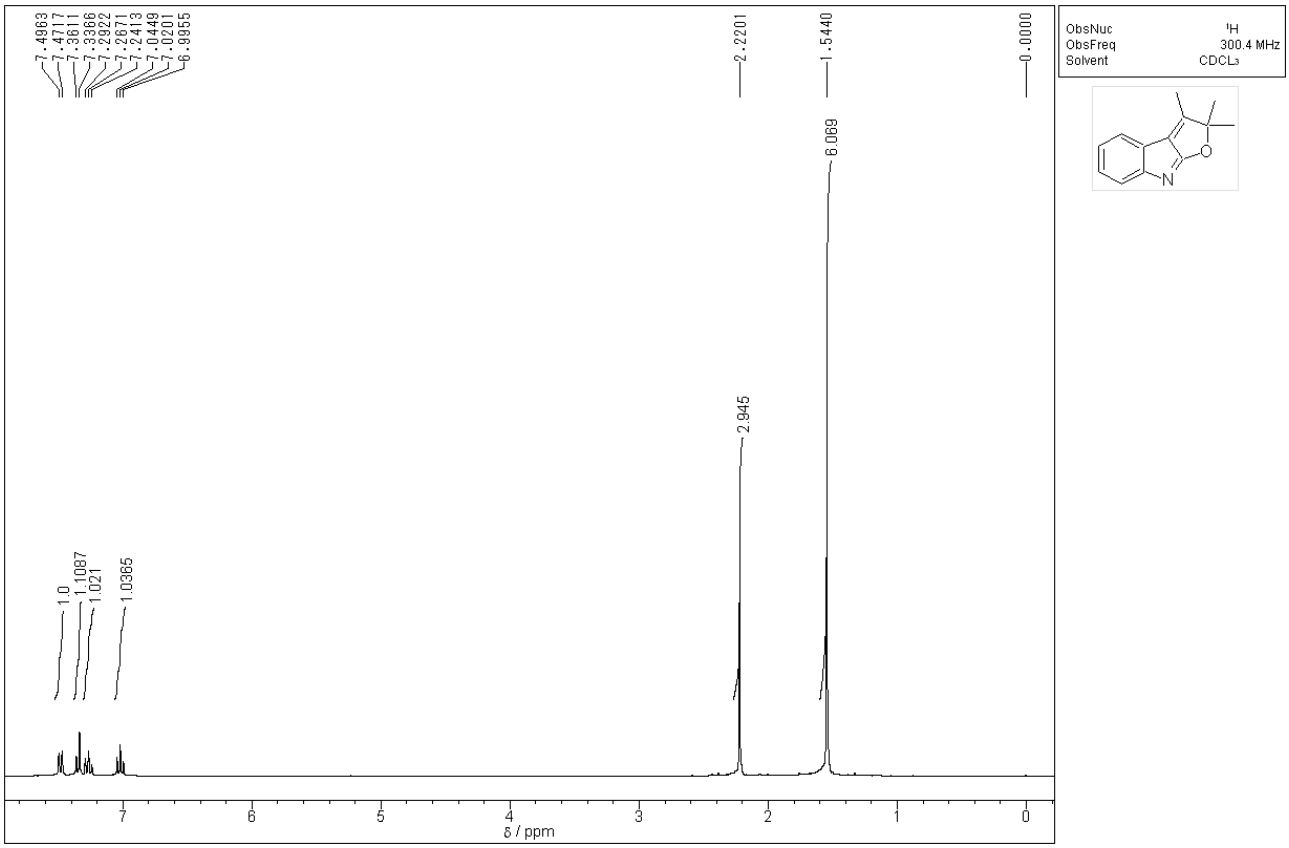

ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
149.951
135.702
128.434
127.145
121.638
119.528
118.242
117.056
113.766
110.684
33.389
32.791
27.109
26.818
140
120
100
80
60
40
20
0
δ / ppm

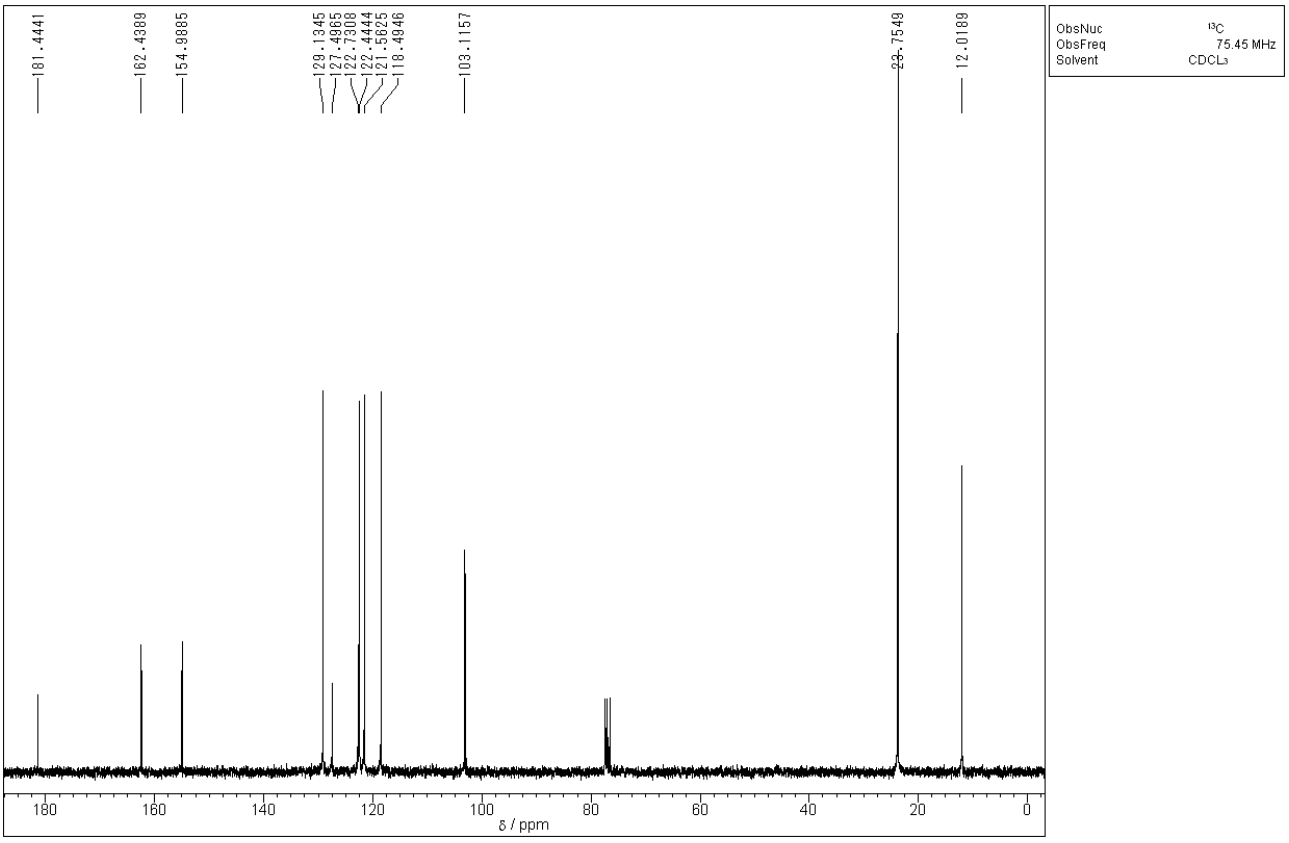
9


ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
10.3963
7.4704
7.4679
7.4578
7.4125
7.3999
7.3898
7.3880
7.3760
7.3653
7.3634
7.3426
7.3301
7.3168
7.2728
7.2577
7.2568
7.2476
7.1740
7.1620
7.1494
7.0657
7.0531
7.0406
7.0292
7.0173
7.0047
6.9915
6.9801
6.9720
6.9594
6.9468
6.8832
6.8694
6.8656
6.8549
6.8524
0.0000
6.1794
3.1029
3.0003
1.9991
1.9935
1.9585
1.0431
1.0
δ / ppm

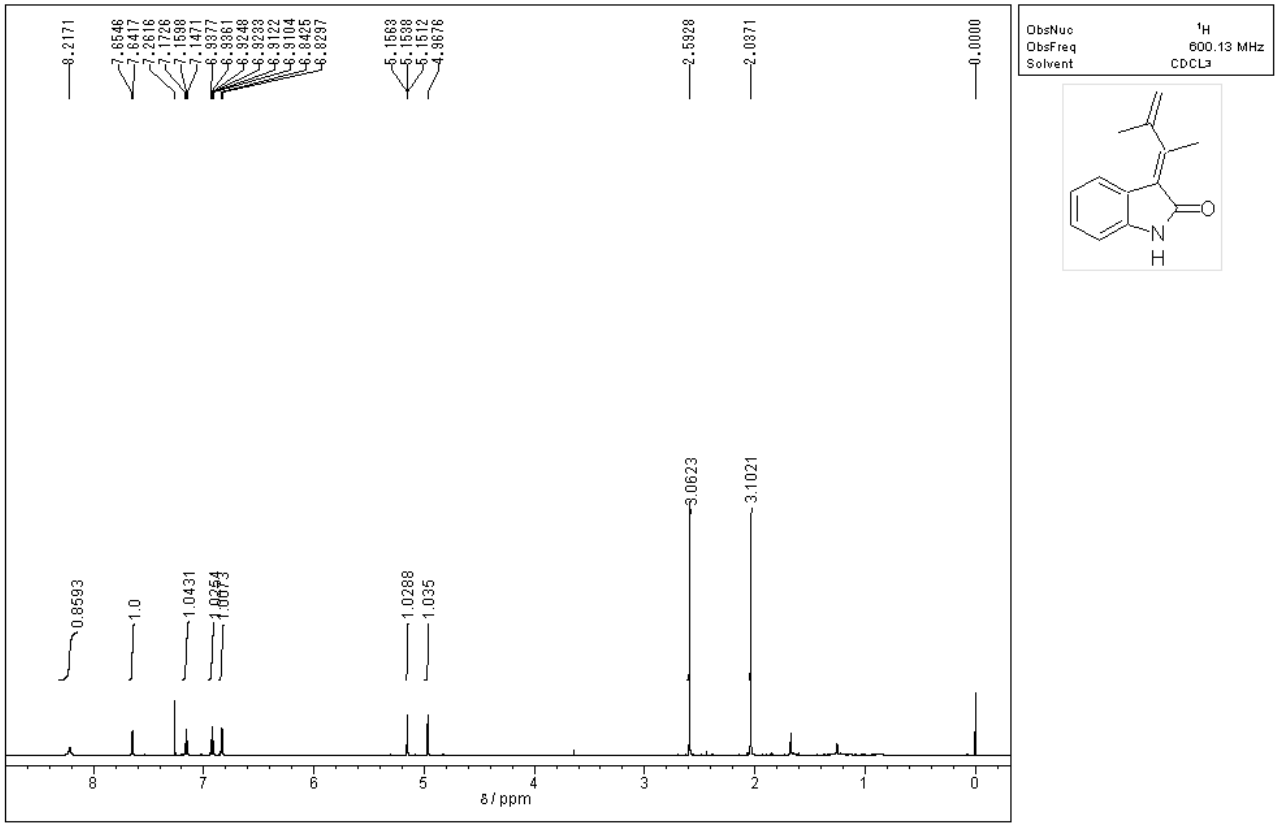

ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
205.9850
147.2819
145.6596
144.9321
144.0155
143.3098
134.4828
134.2818
133.9090
129.5532
129.1040
128.7493
128.5092
128.1200
127.8488
127.7698
127.2925
126.8779
124.4717
124.2662
122.3020
121.2599
110.3022
77.4529
δ / ppm

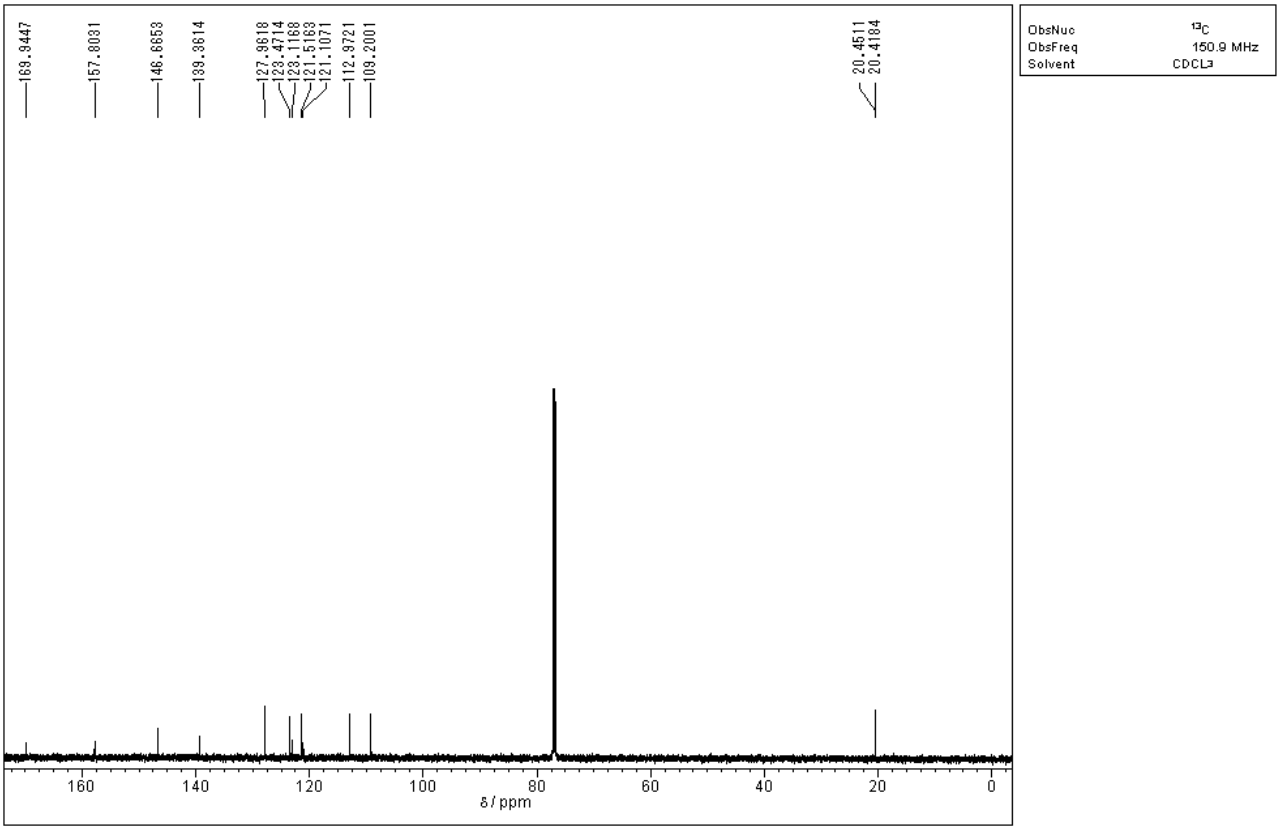
10


7.4963
7.4717
7.3611
7.3366
7.2922
7.2671
7.2413
7.0449
7.0201
6.9855
2.2201
1.5440
0.0000
6.069
2.945
1.0
1.1087
1.021
1.0365
ObsNuc 1H
ObsFreq 300.4 MHz
Solvent CDCL3
δ / ppm

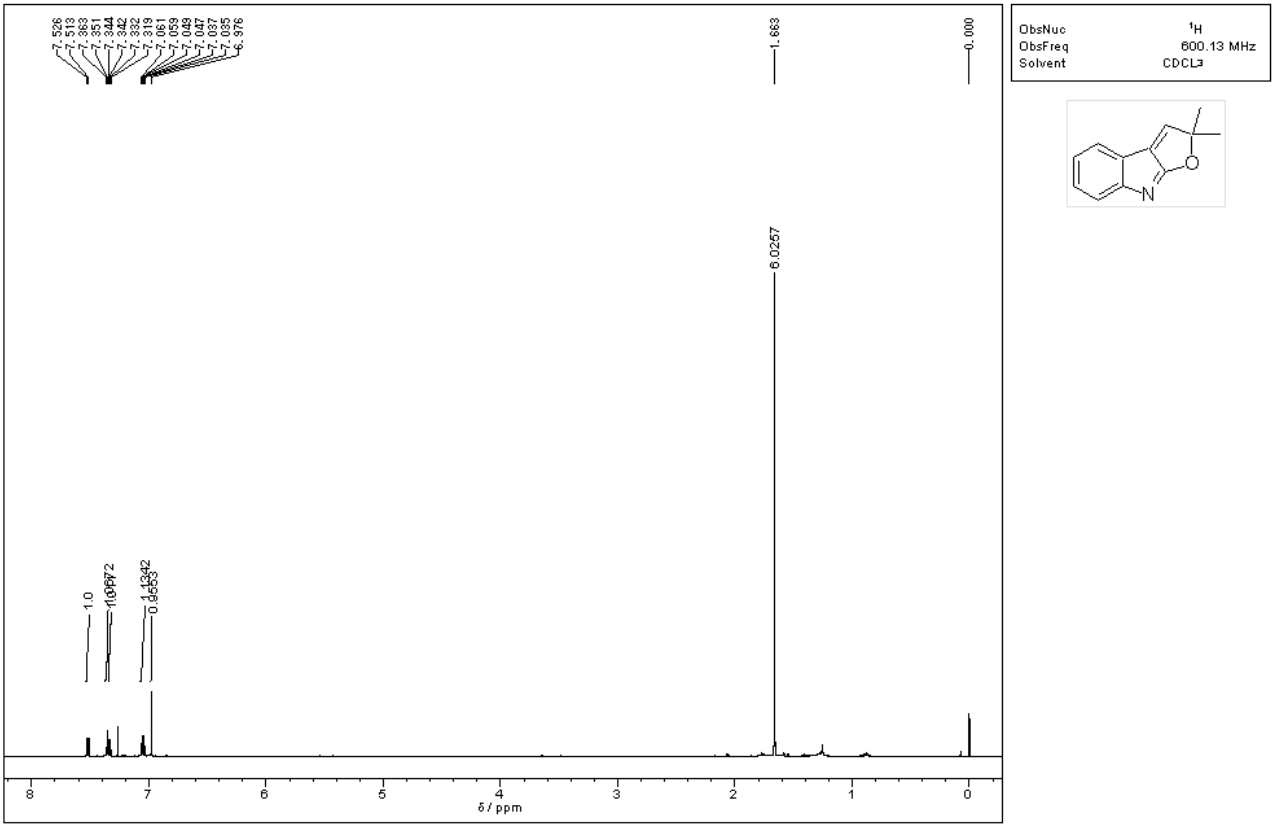

181.4441
162.4389
154.9885
129.1345
127.4865
122.7308
122.4444
121.5625
118.4946
103.1157
23.7549
12.0189
ObsNuc 13C
ObsFreq 75.45 MHz
Solvent CDCL3
δ / ppm

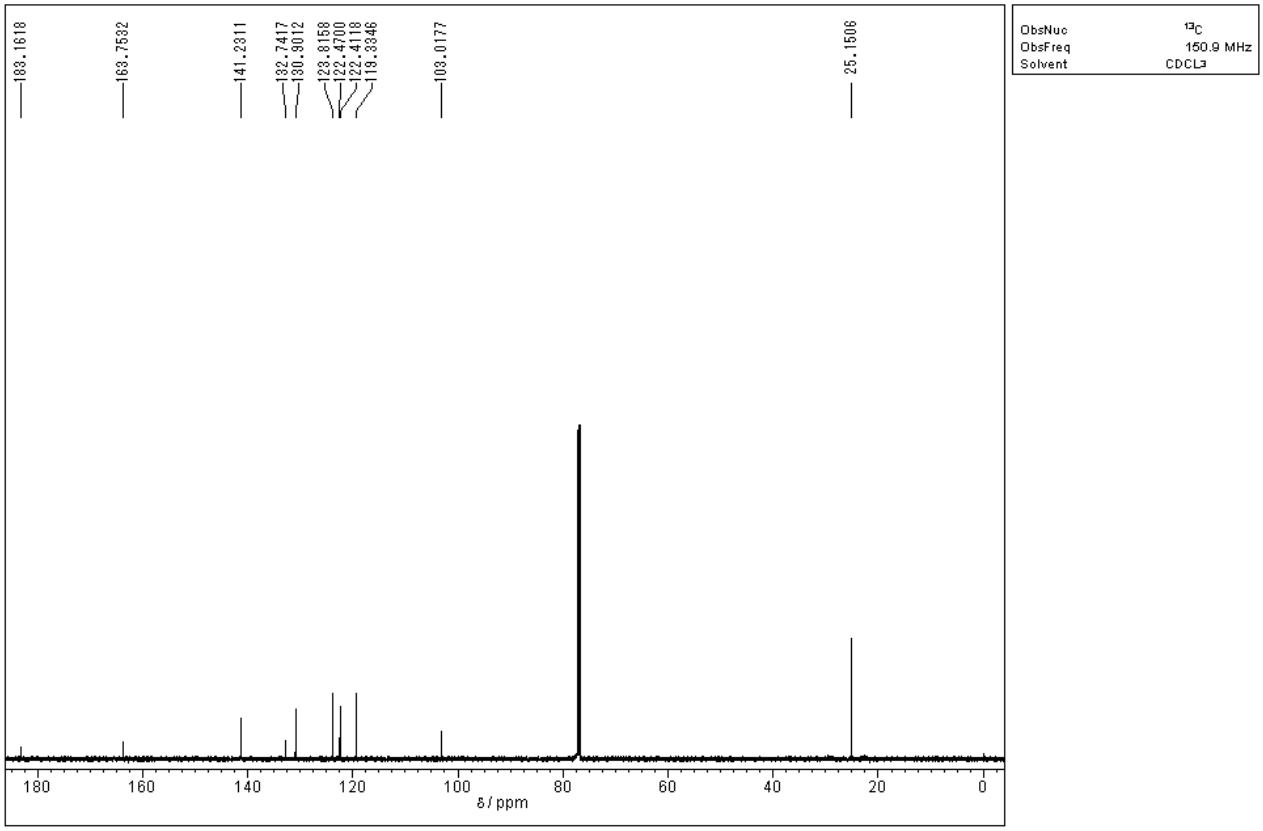
11


8.2171
7.6546
7.6417
7.2616
7.1726
7.1598
7.1471
6.9377
6.8861
6.8248
6.9233
6.9122
6.9104
6.8425
6.8297
5.1563
5.1538
5.1512
4.9878
2.5928
2.0871
0.0000
3.0623
3.1021
0.8593
1.0
1.0431
1.0254
1.0673
1.0288
1.035
δ / ppm
ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3

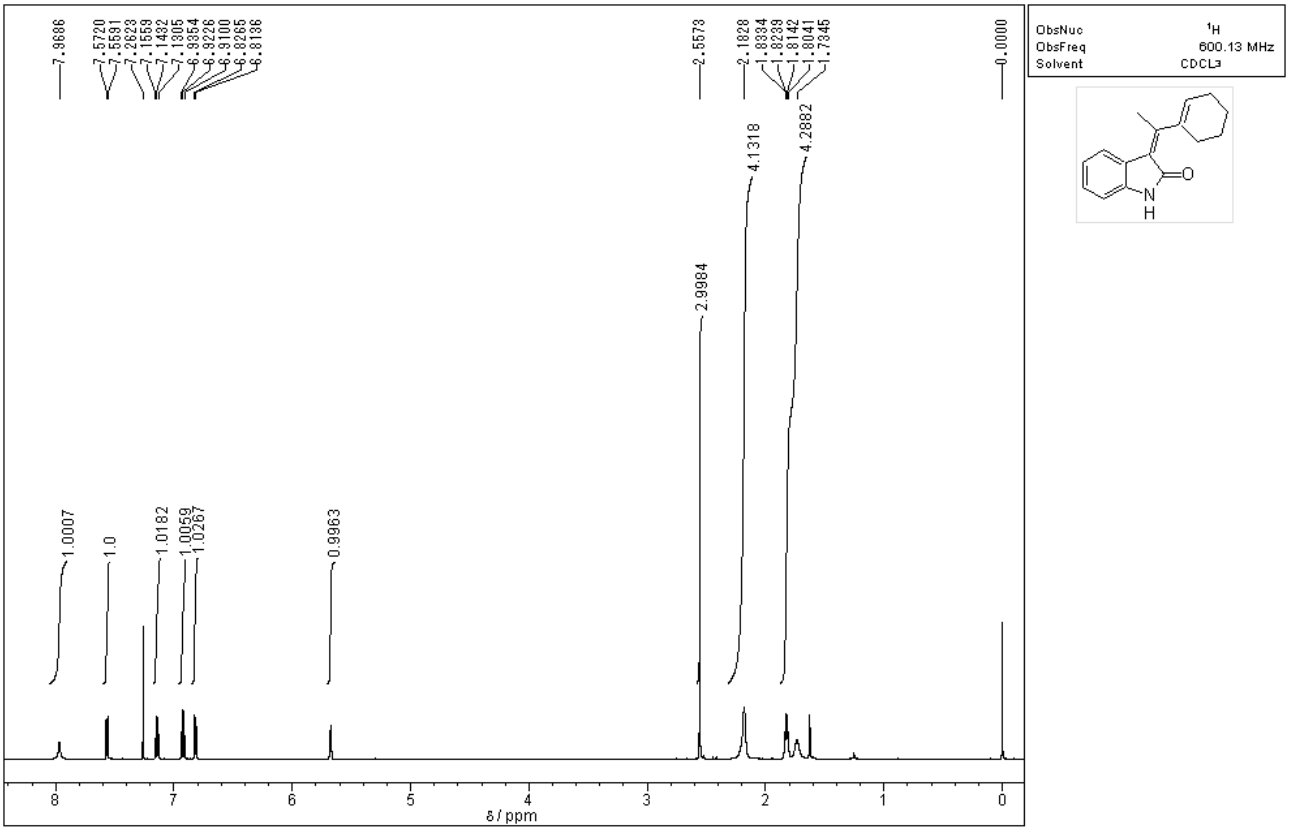

169.9447
157.8031
146.6653
139.3614
127.9618
123.4714
123.1168
121.5163
121.1071
112.9721
109.2001
20.4511
20.4184
δ / ppm
ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3

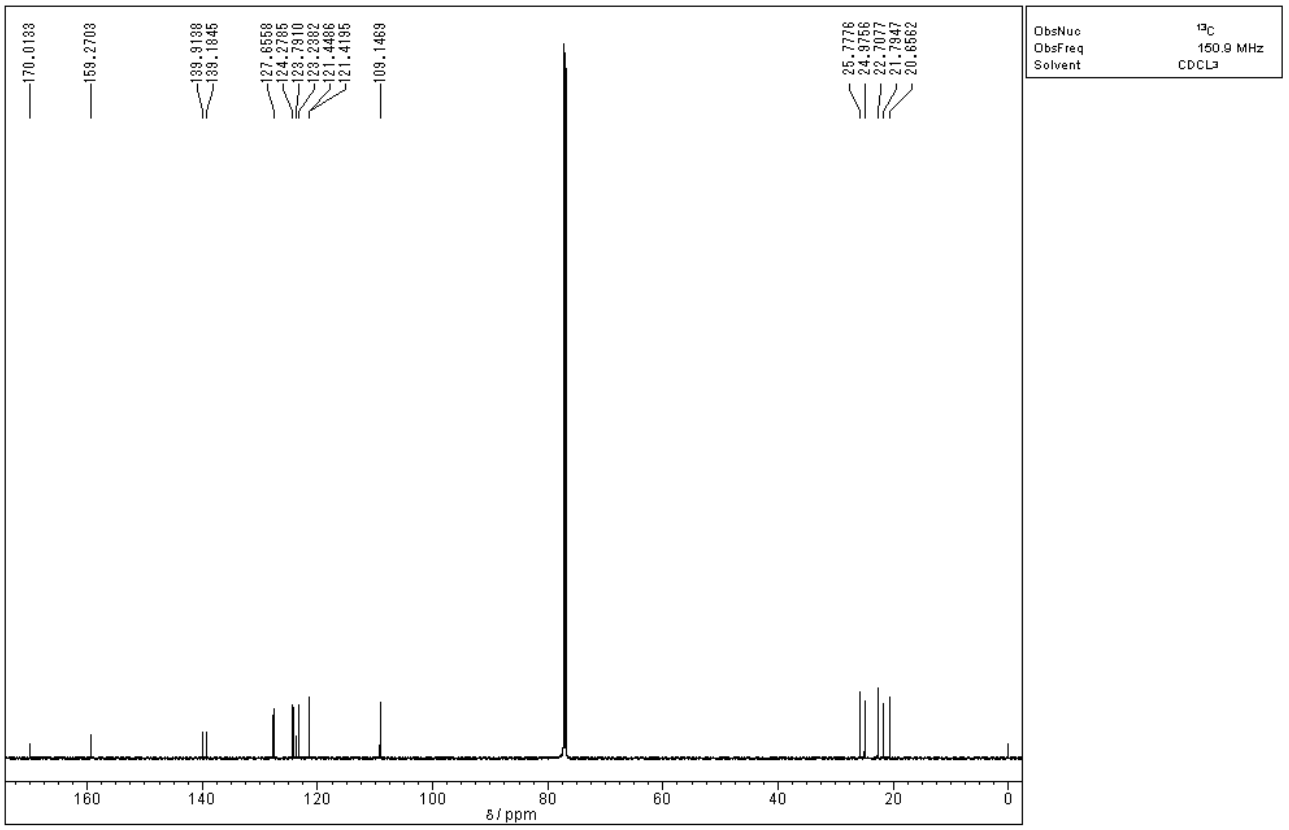
12


7.526
7.513
7.363
7.351
7.344
7.342
7.332
7.319
7.061
7.059
7.049
7.047
7.037
7.035
6.976
1.663
0.000
6.0257
1.0
1.0972
1.1342
0.4553
8
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
O
N

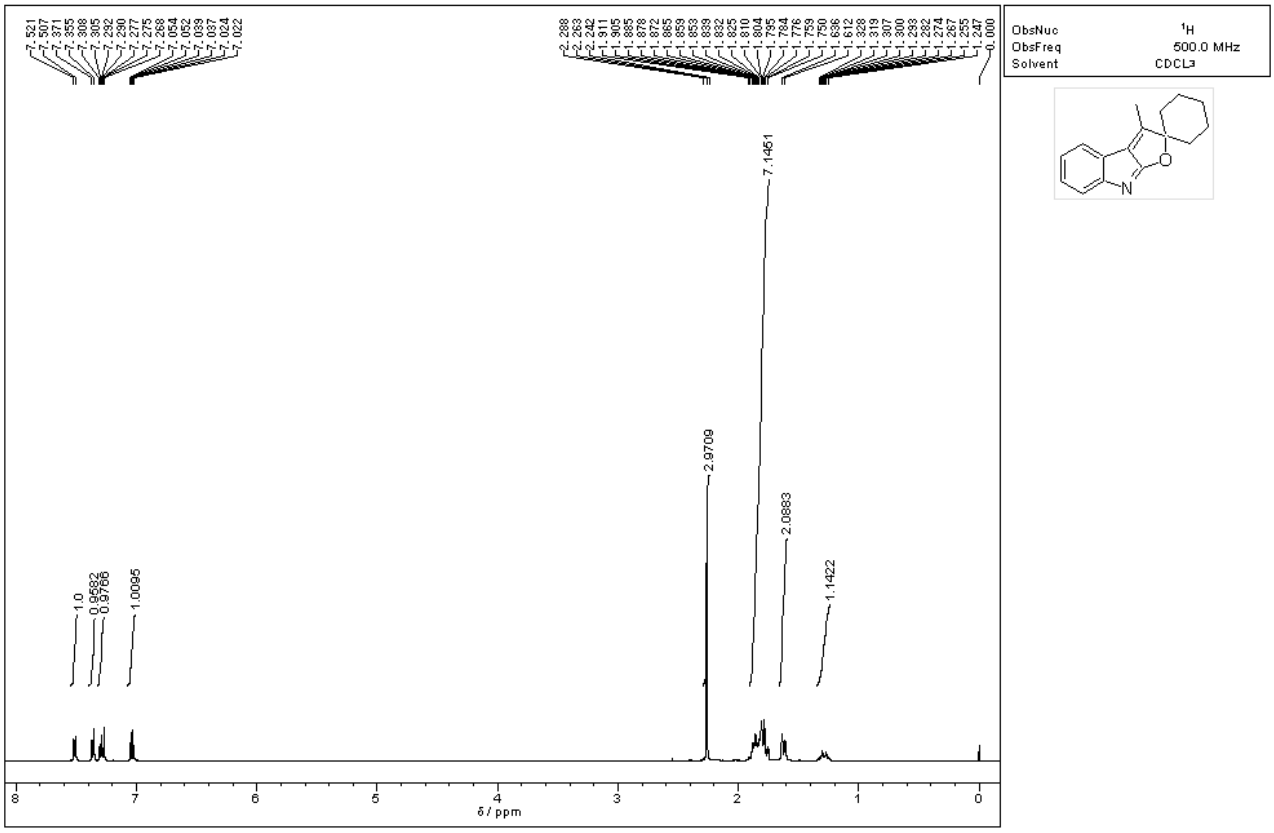

183.1618
163.7532
141.2311
132.7417
130.9012
123.8158
122.4700
122.4118
119.3346
103.0177
25.1508
180
160
140
120
100
80
60
40
20
0
δ / ppm
ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3

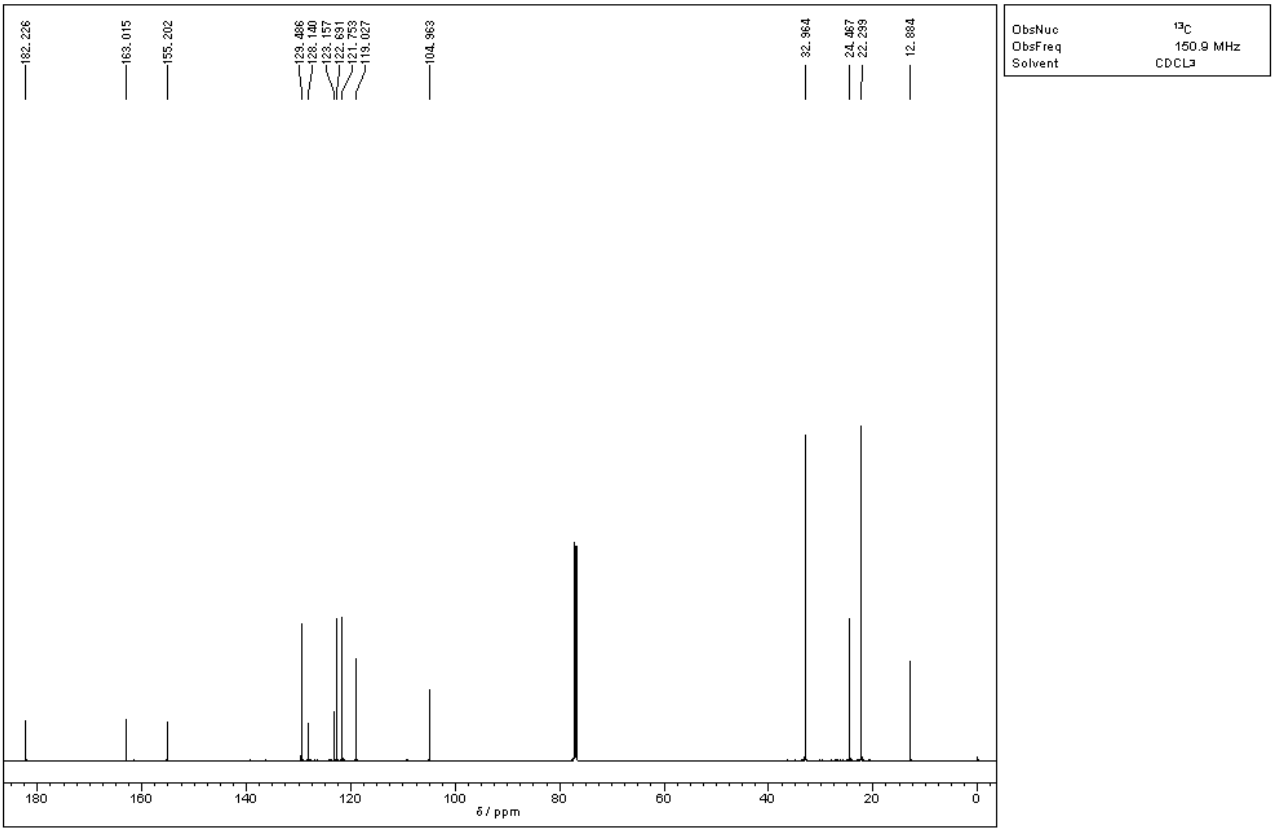
13


7.8686
7.5720
7.5591
7.2823
7.1569
7.1432
7.1305
6.8854
6.8226
6.9100
6.8265
6.8138
2.5573
2.1828
1.8334
1.8238
1.8142
1.8041
1.7345
0.0000
4.1318
4.2882
2.9984
1.0007
1.0
1.0182
1.0059
1.0267
0.9963
ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
δ / ppm

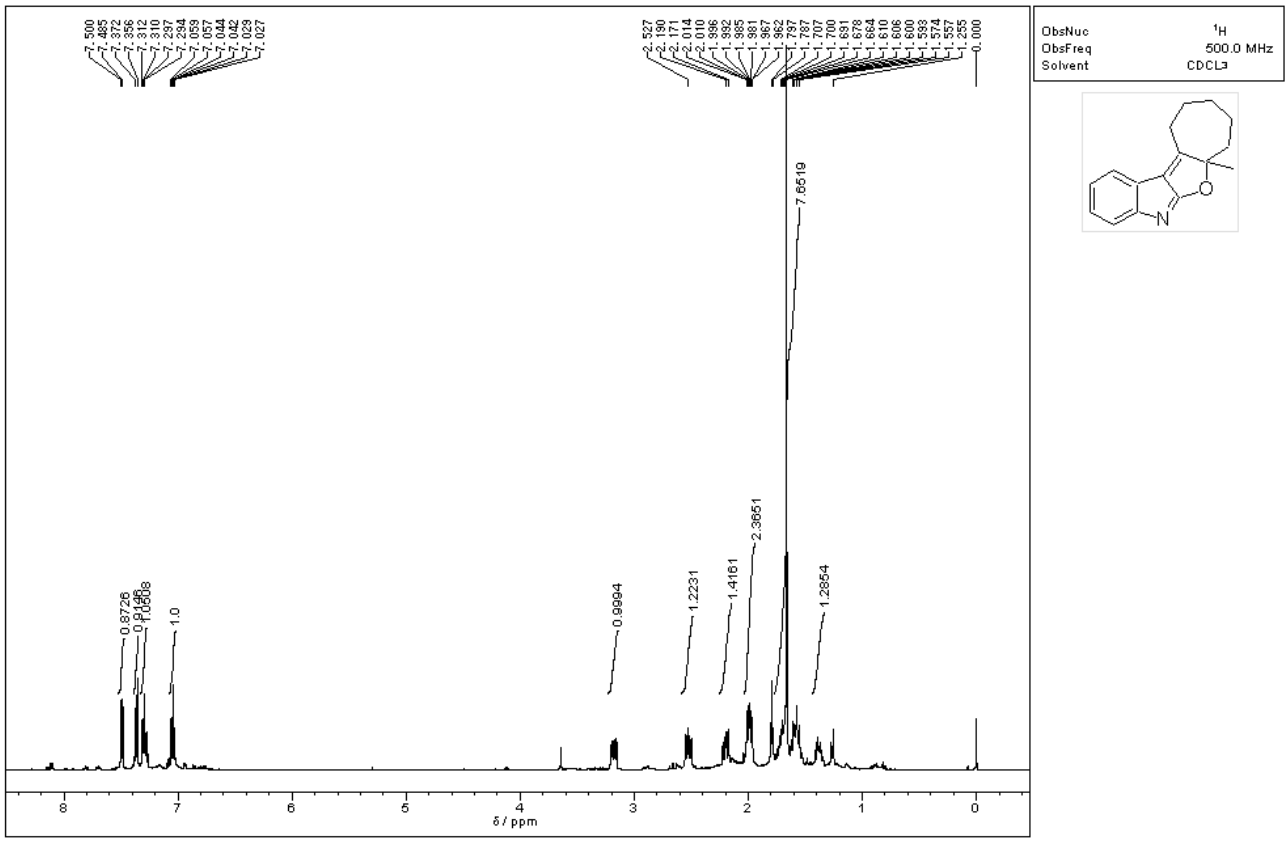

170.0133
159.2703
139.9138
139.1845
127.6558
124.2785
123.7910
120.2382
121.4486
121.4195
109.1469
25.7776
24.9756
22.7077
21.7947
20.6562
ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
δ / ppm

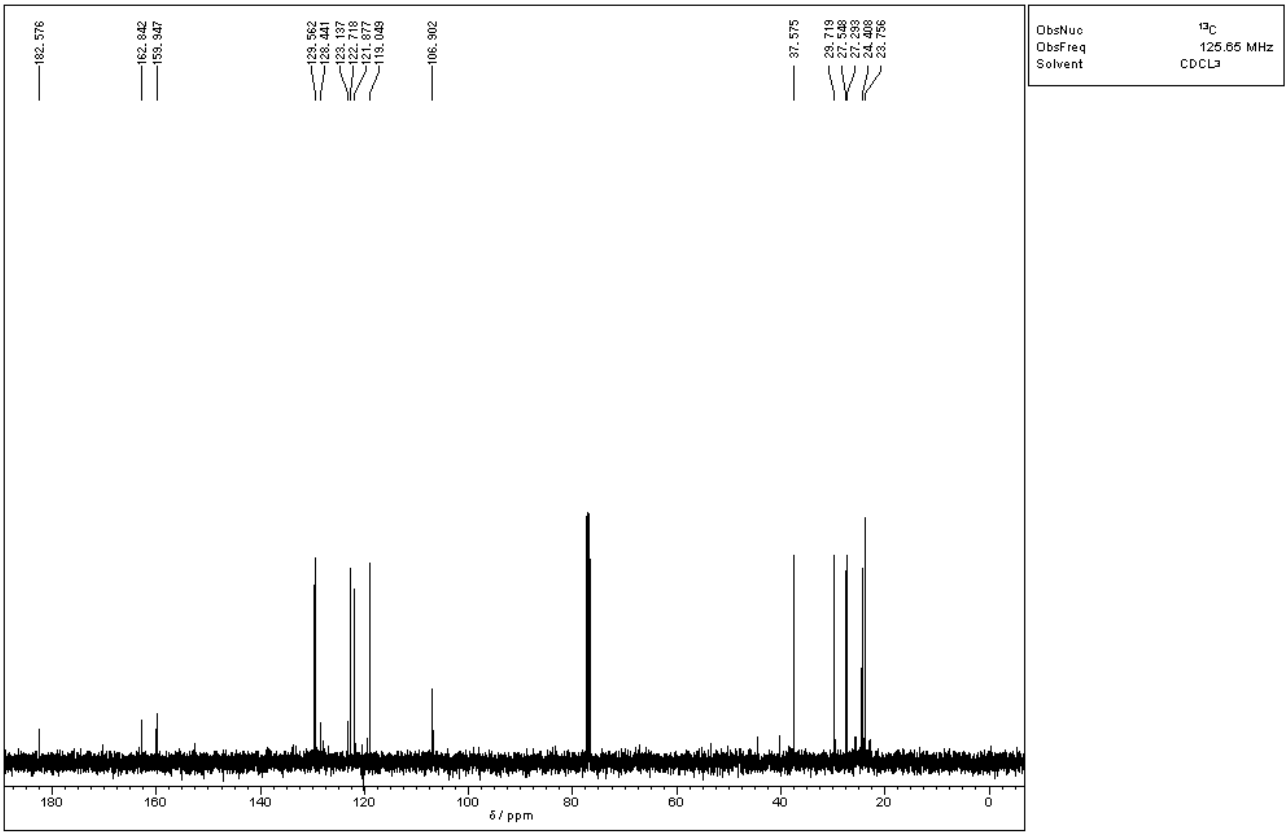
14


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
7.1451
2.9709
2.0883
1.1422
1.0
0.9582
0.9766
1.0095
δ / ppm

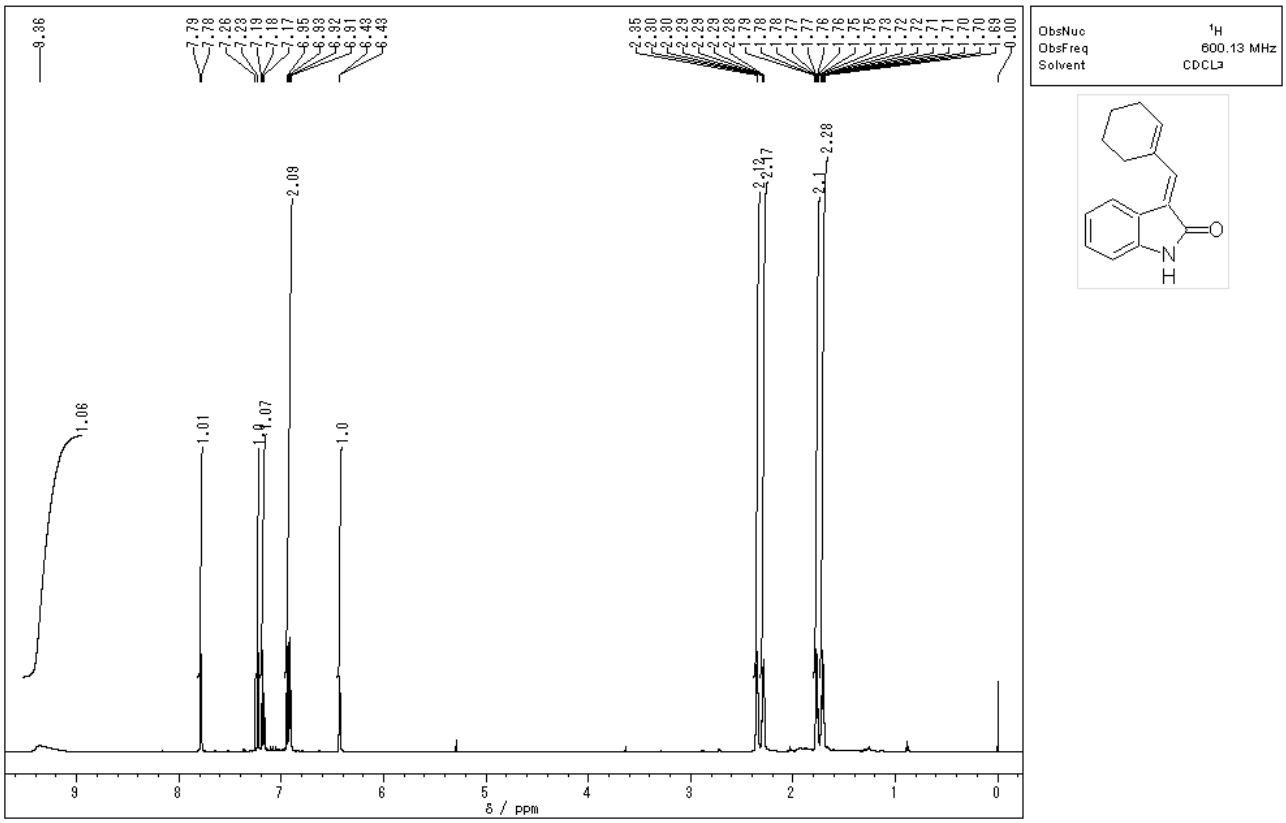

ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
182.226
163.015
155.202
129.488
128.140
123.157
122.691
121.753
119.027
104.963
32.964
24.467
22.239
12.884
δ / ppm

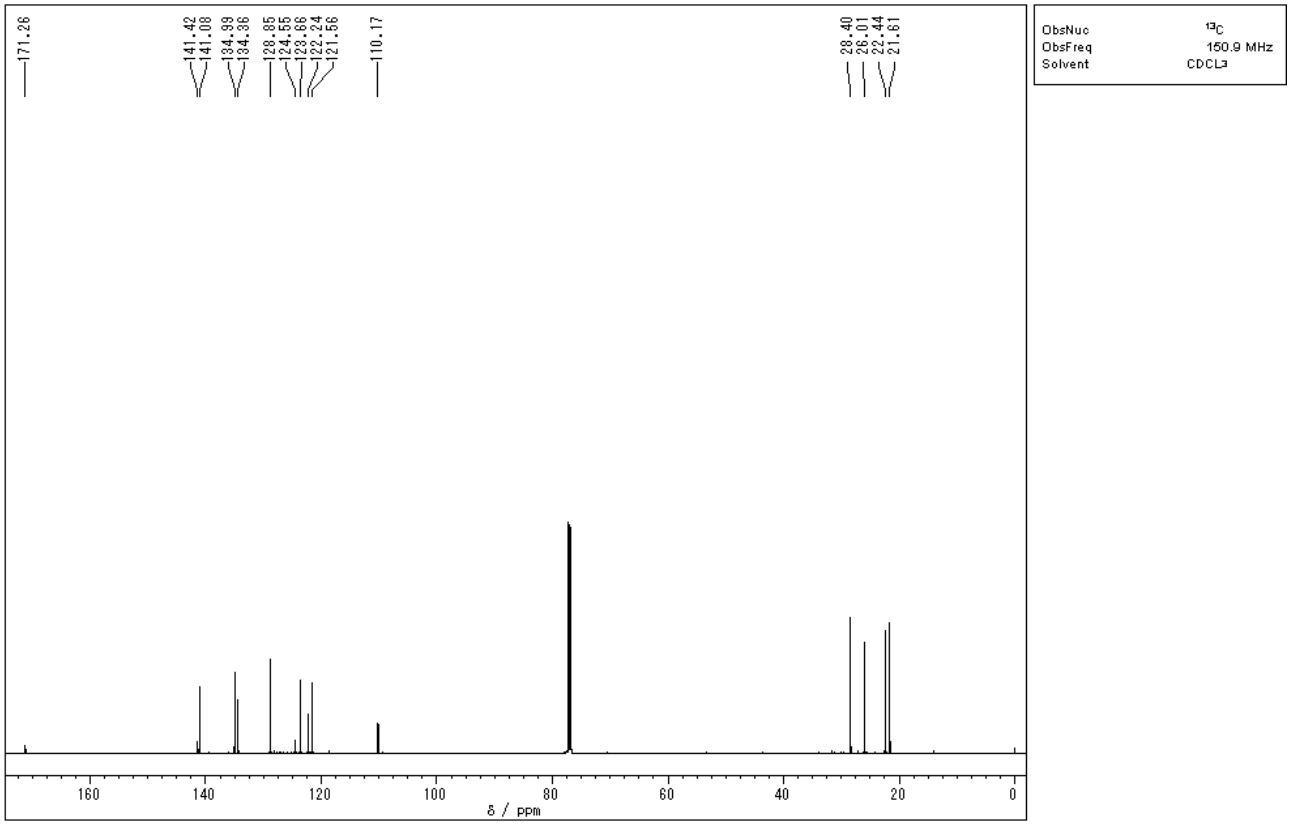
15


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
δ / ppm

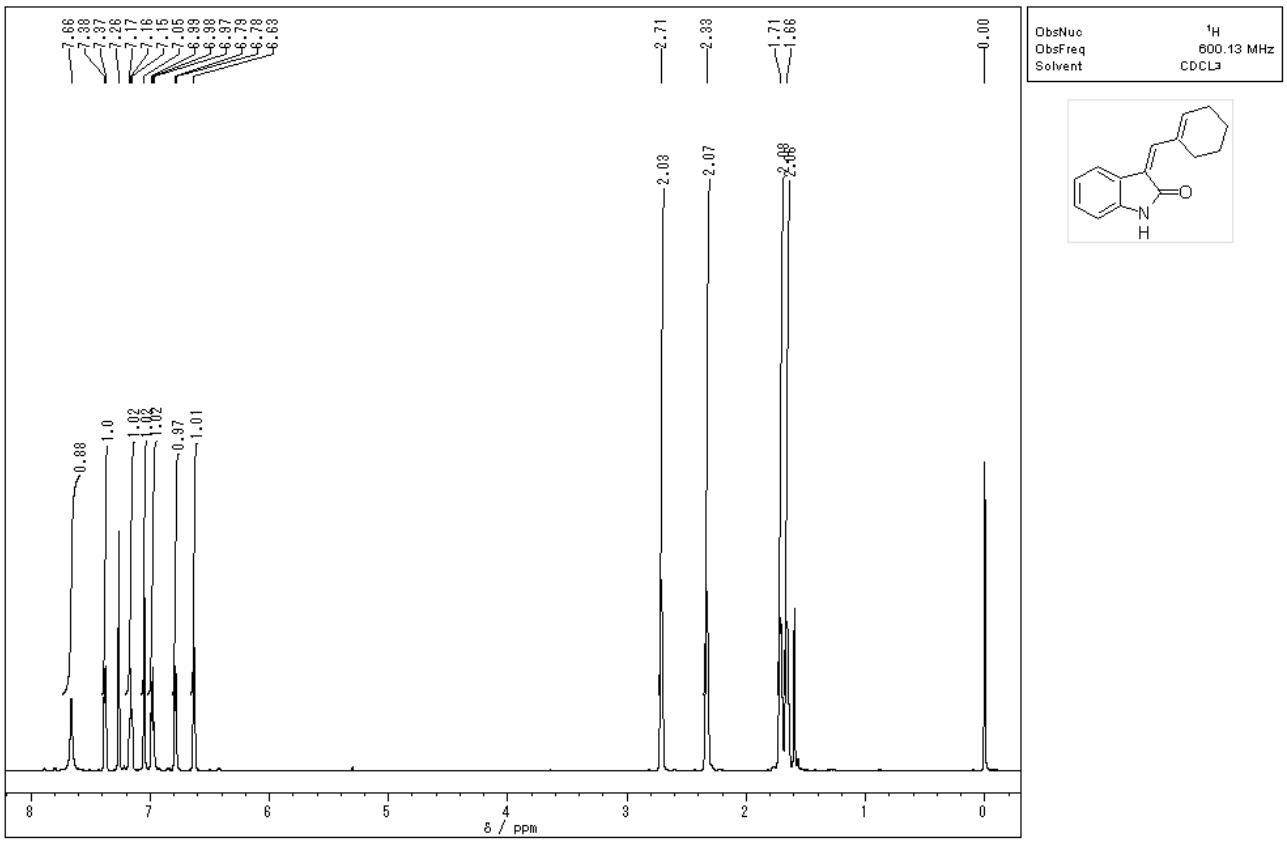

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

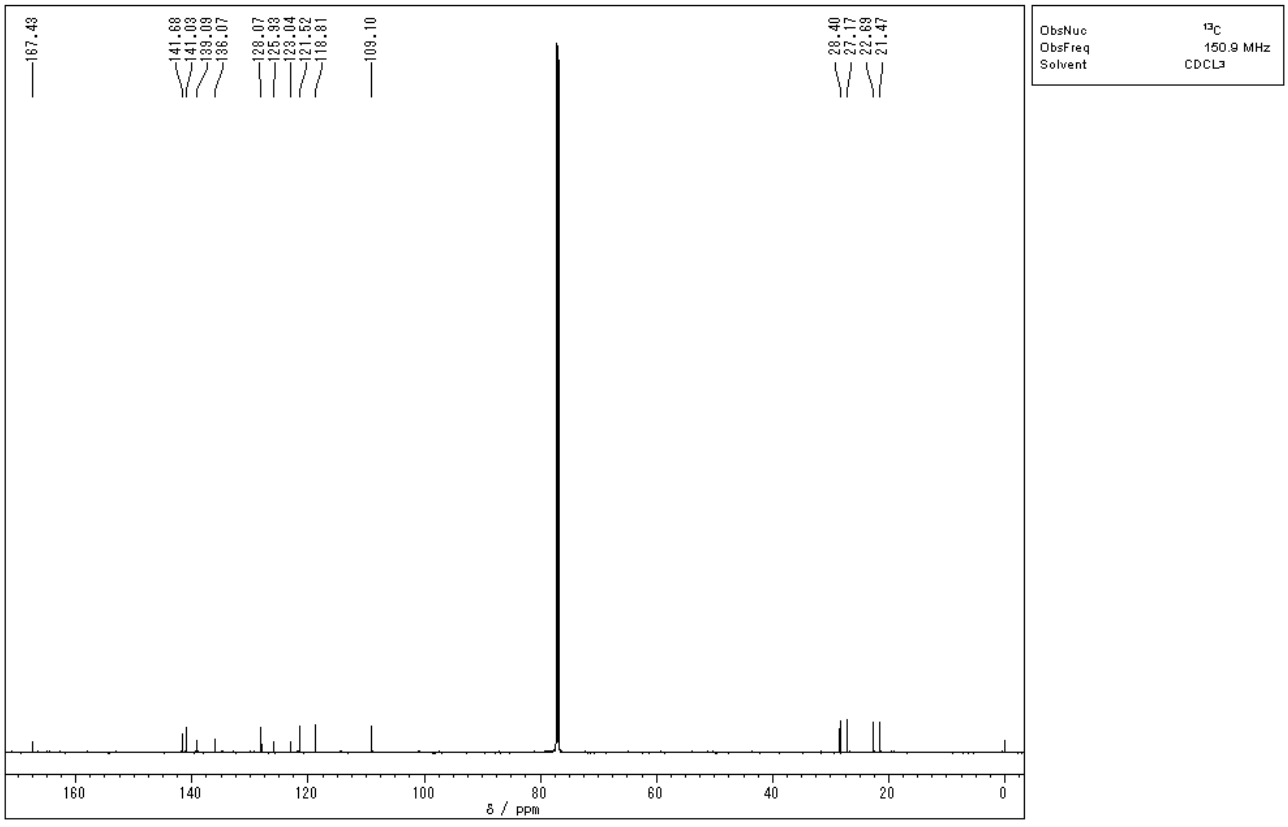
***E*-17**


ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
δ / ppm

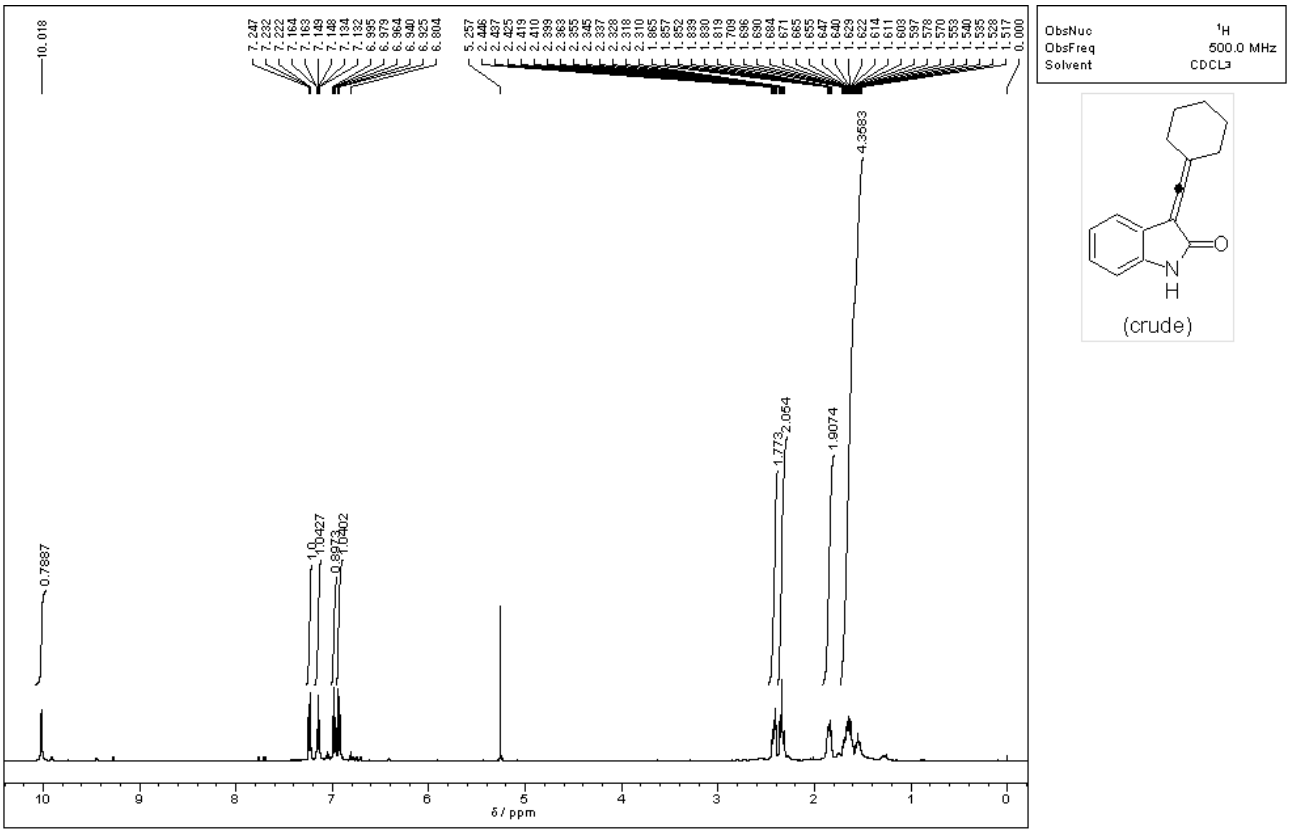

ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
δ / ppm

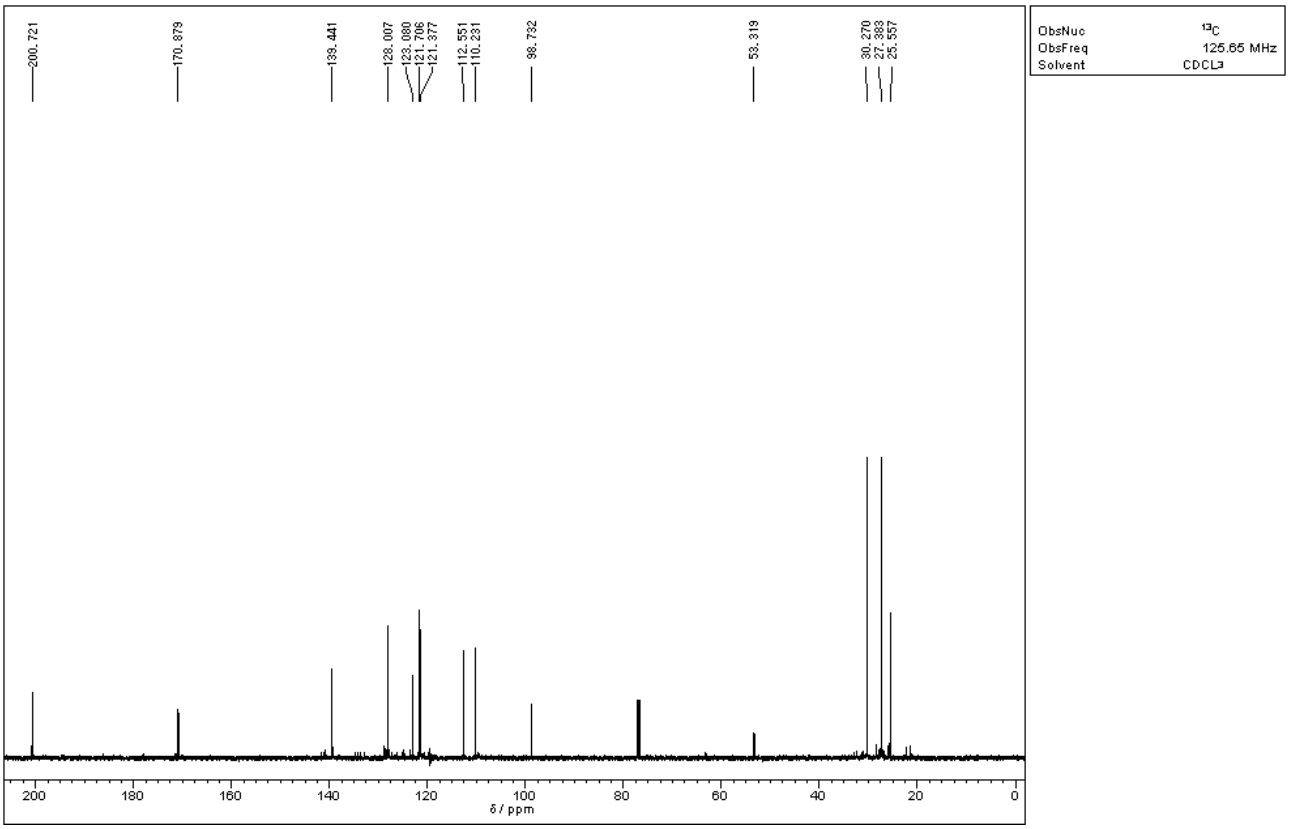
***Z*-17**


7.66
7.38
7.37
7.26
7.17
7.16
7.15
7.05
6.89
6.98
6.97
6.79
6.78
6.63
2.71
2.33
1.71
1.66
0.00
2.03
2.07
2.08
2.08
0.88
1.0
1.02
1.02
1.02
0.97
1.01
8
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
O
N
H

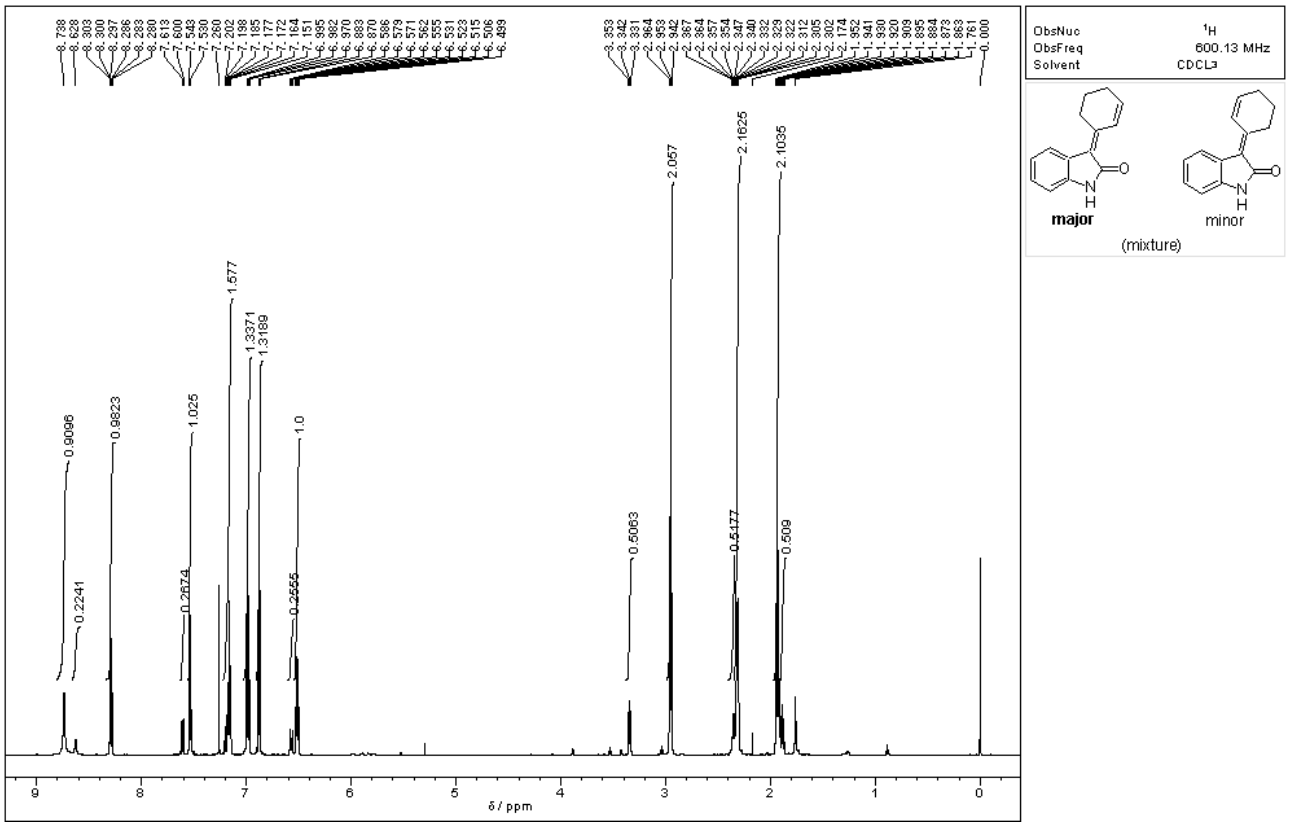

167.43
141.68
141.03
139.09
136.07
128.07
125.83
123.04
121.52
118.81
109.10
28.40
27.17
22.69
21.47
160
140
120
100
80
60
40
20
0
δ / ppm
ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3

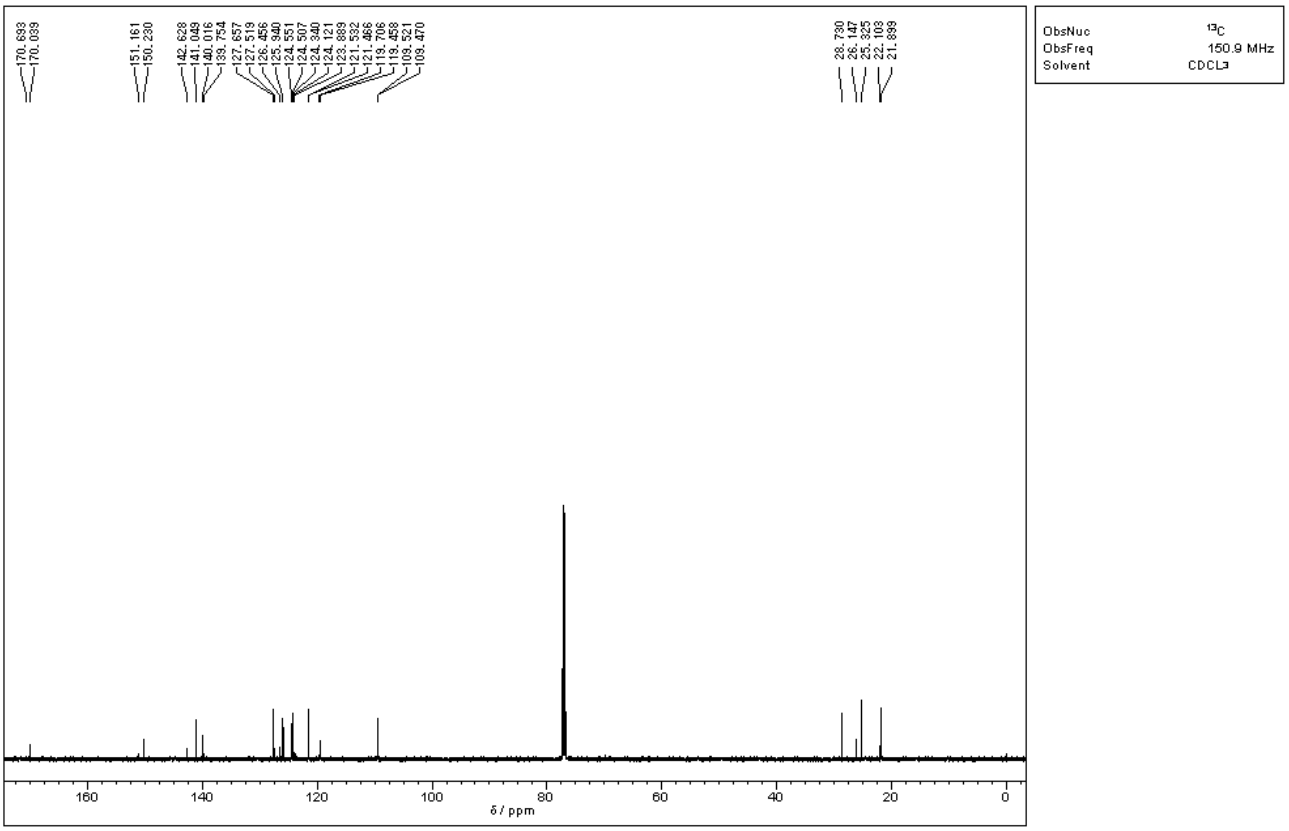
18


ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
(crude)
δ / ppm

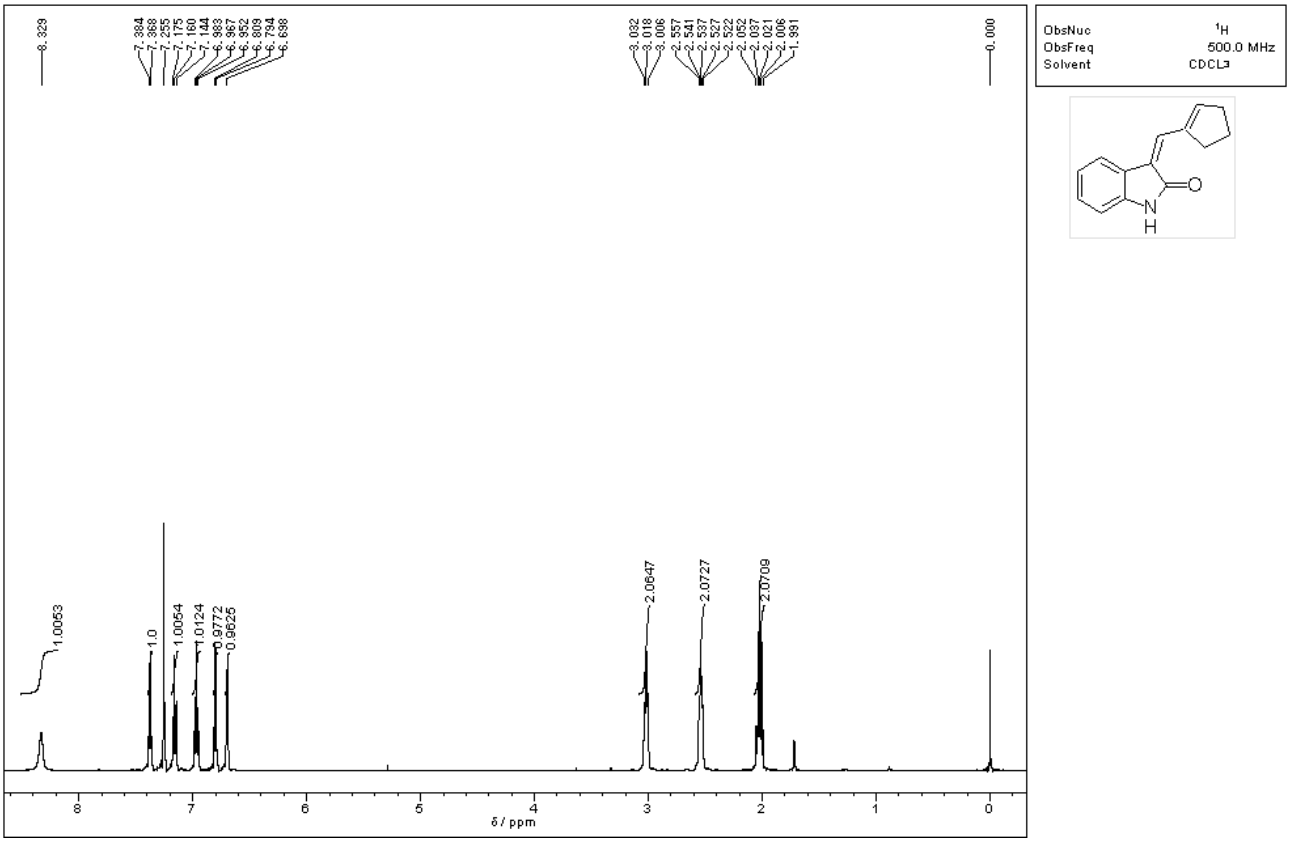

ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

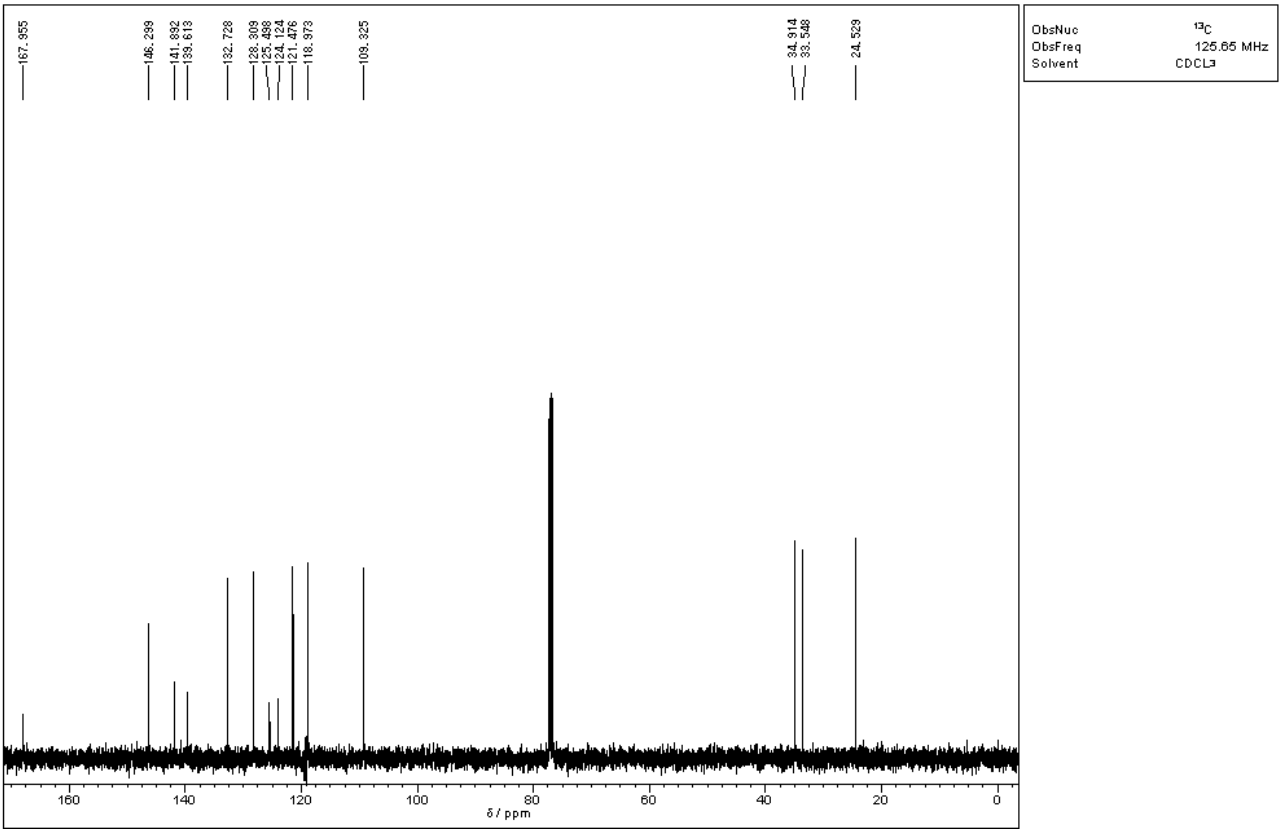
21


ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
major
minor
(mixture)
δ / ppm

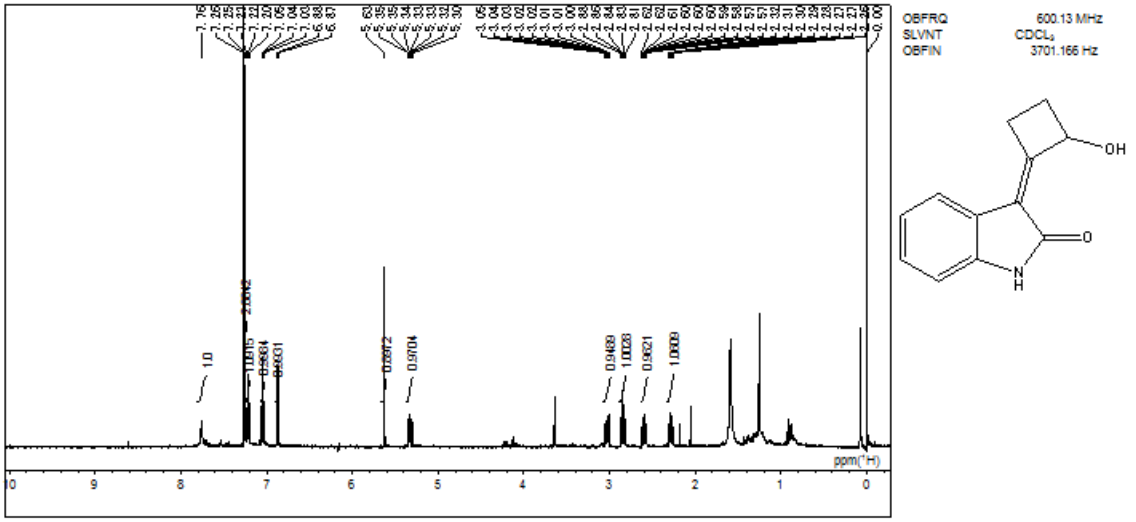

ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
δ / ppm

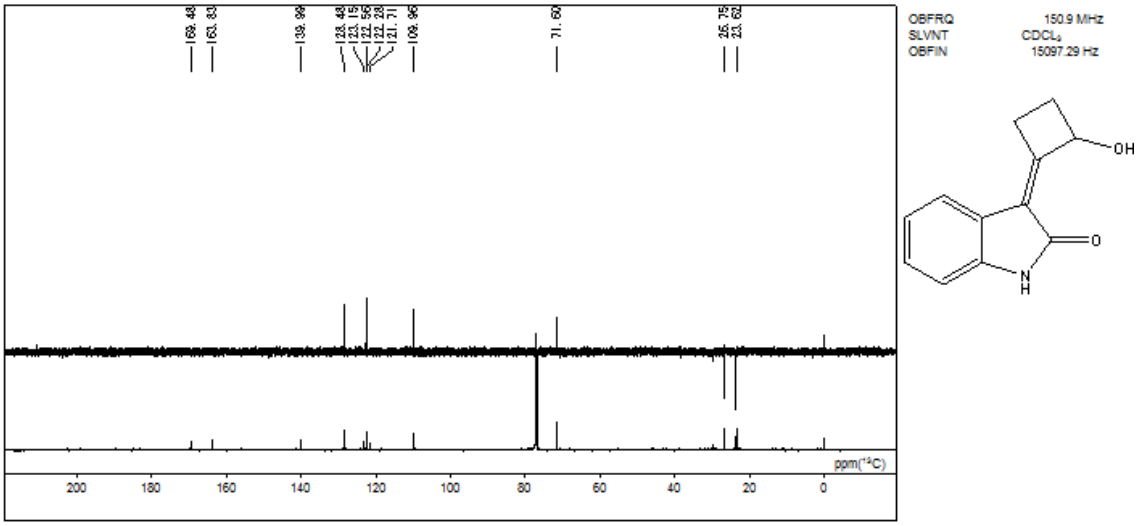
22Z


8.329
7.384
7.368
7.255
7.175
7.160
7.144
6.983
6.967
6.952
6.809
6.794
6.688
3.032
3.018
3.006
2.557
2.541
2.537
2.527
2.522
2.052
2.037
2.021
2.006
1.991
0.000
1.0053
1.0
1.0054
1.0124
0.9772
0.9625
2.0647
2.0727
2.0709
δ / ppm
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3

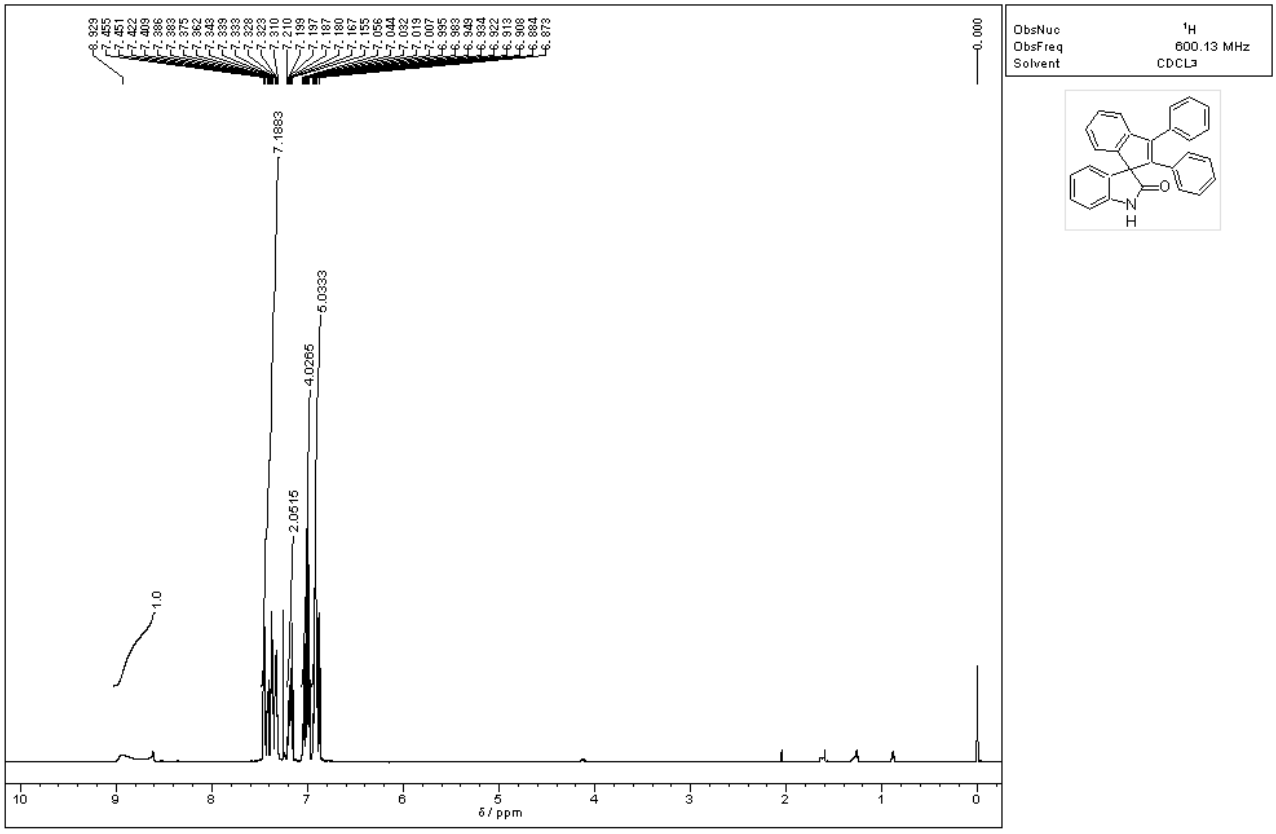

167.955
146.289
141.892
139.613
132.728
128.309
125.498
124.124
121.476
118.973
109.325
34.914
33.548
24.529
δ / ppm
ObsNuc 13C
ObsFreq 125.65 MHz
Solvent CDCL3

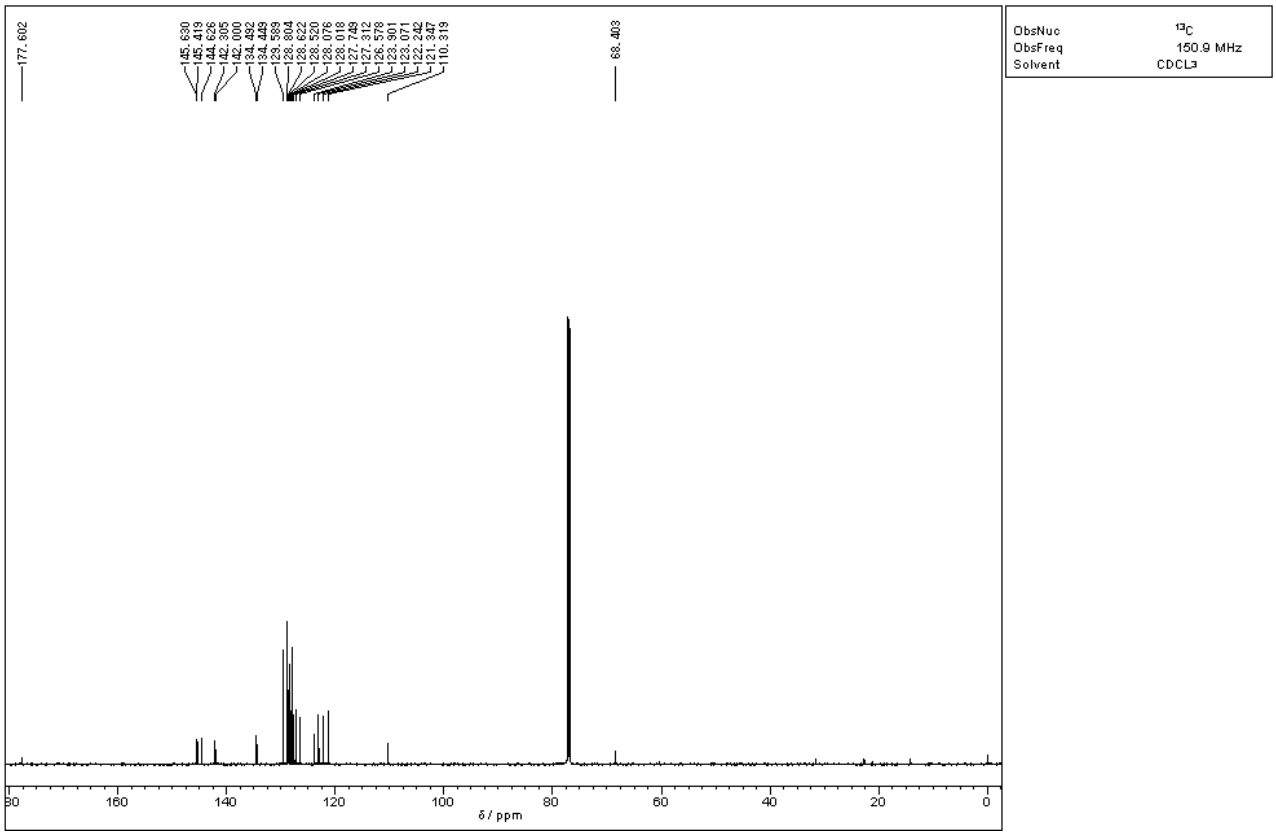
23


OBFRQ 600.13 MHz
SLVNT CDCl3
OBFIN 3701.166 Hz
OH
O
N
H
ppm(1H)

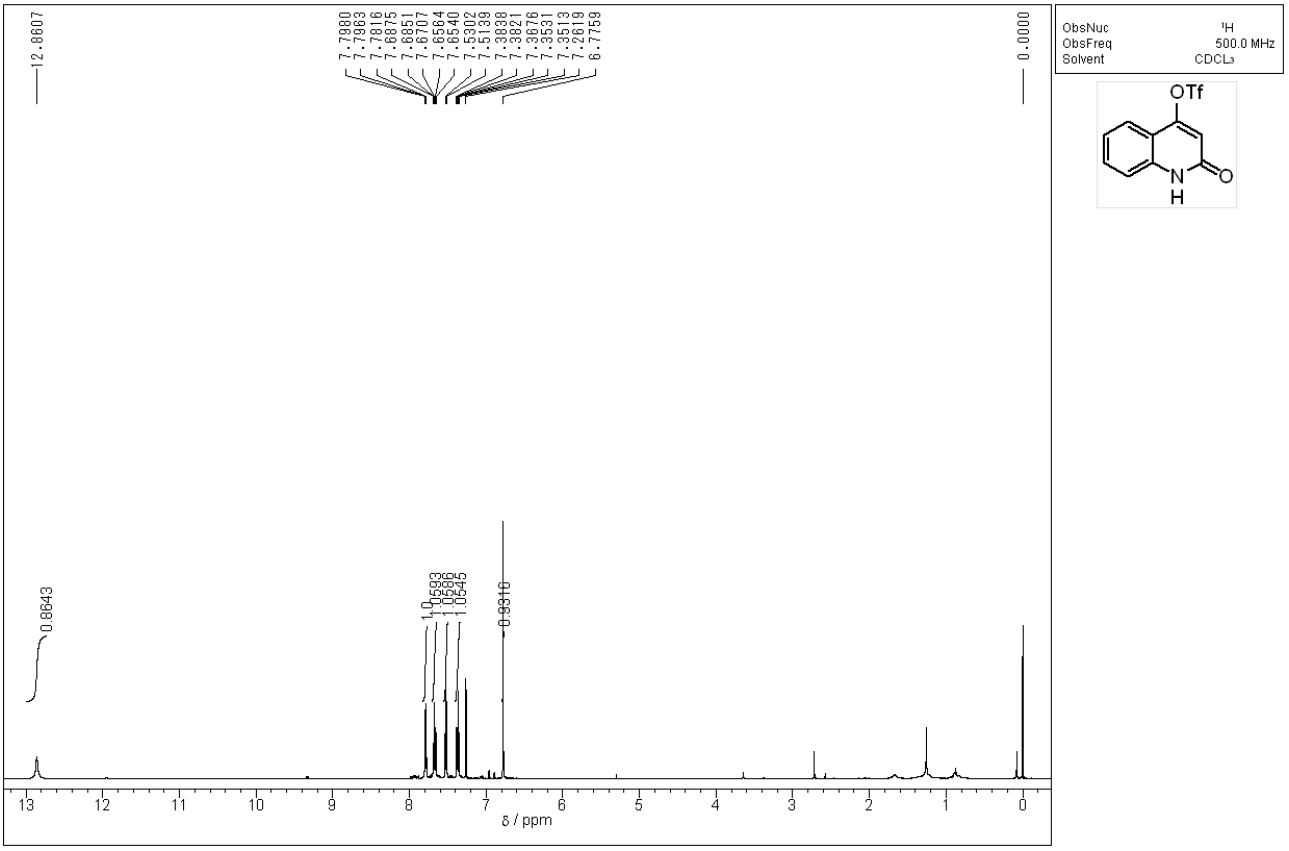

OBFRQ 150.9 MHz
SLVNT CDCl3
OBFIN 15097.29 Hz
OH
O
N
H
ppm(13C)

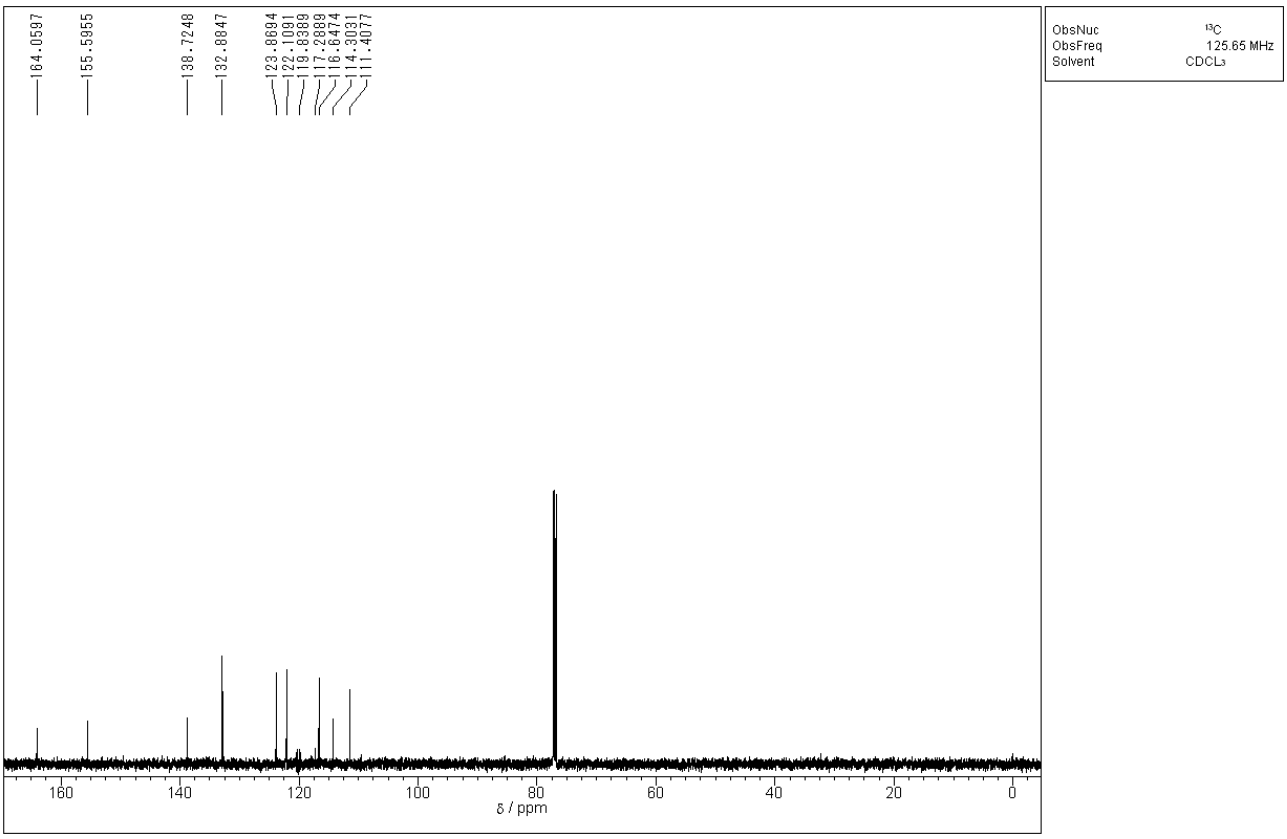
24


ObsNuc 1H
ObsFreq 600.13 MHz
Solvent CDCL3
7.1883
5.0333
4.0265
2.0515
1.0
δ / ppm

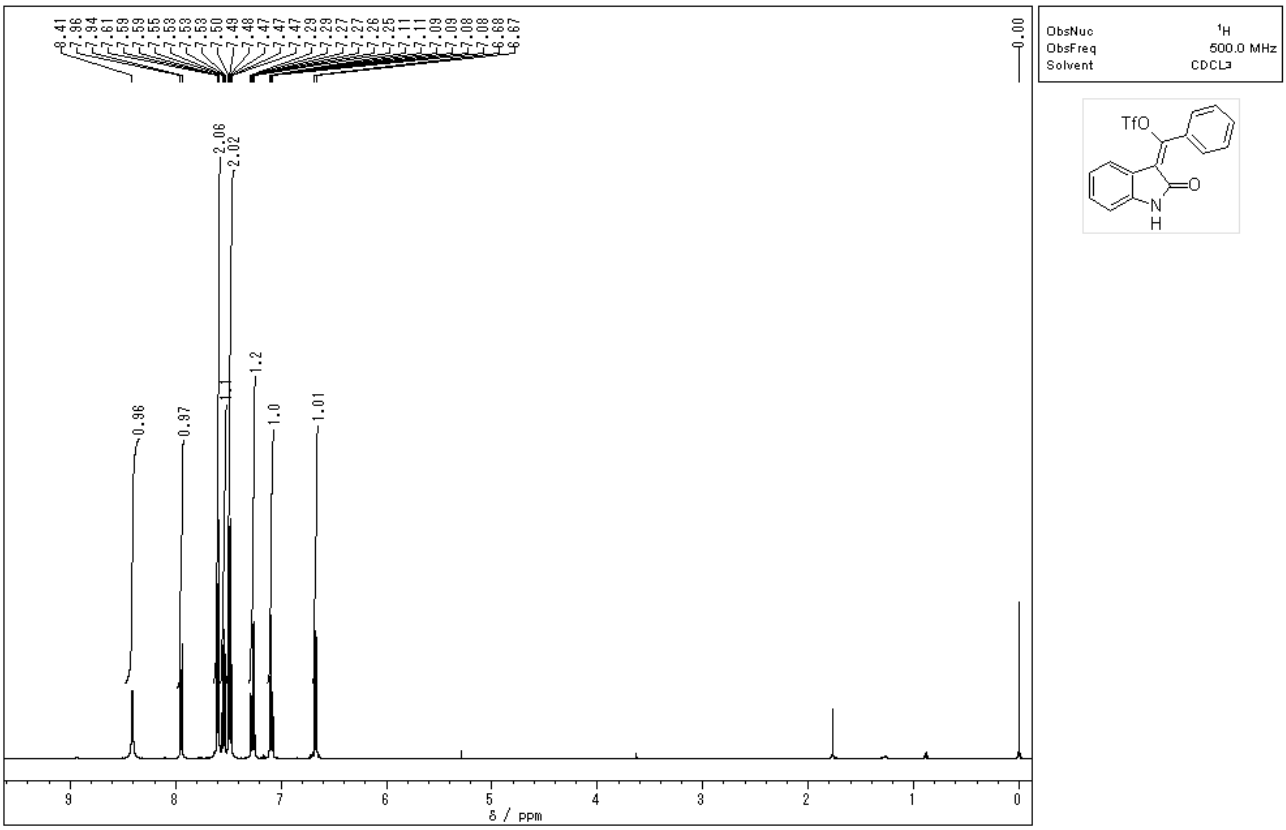

ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3
δ / ppm

25


12.8607
7.7980
7.7963
7.7816
7.6875
7.6851
7.6707
7.6564
7.6540
7.5302
7.5139
7.3838
7.3821
7.3676
7.3531
7.3513
7.2618
6.7759
0.0000
0.8643
1.0
1.0593
1.0566
1.0545
0.9316
13
12
11
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc ¹H
ObsFreq 500.0 MHz
Solvent CDCL₃
OTf
N
H
O


164.0597
155.5955
138.7248
132.8847
123.8694
122.1091
118.8389
117.2889
116.6474
114.3031
111.4077
160
140
120
100
80
60
40
20
0
δ / ppm
ObsNuc ¹³C
ObsFreq 125.65 MHz
Solvent CDCL₃

***E*-26**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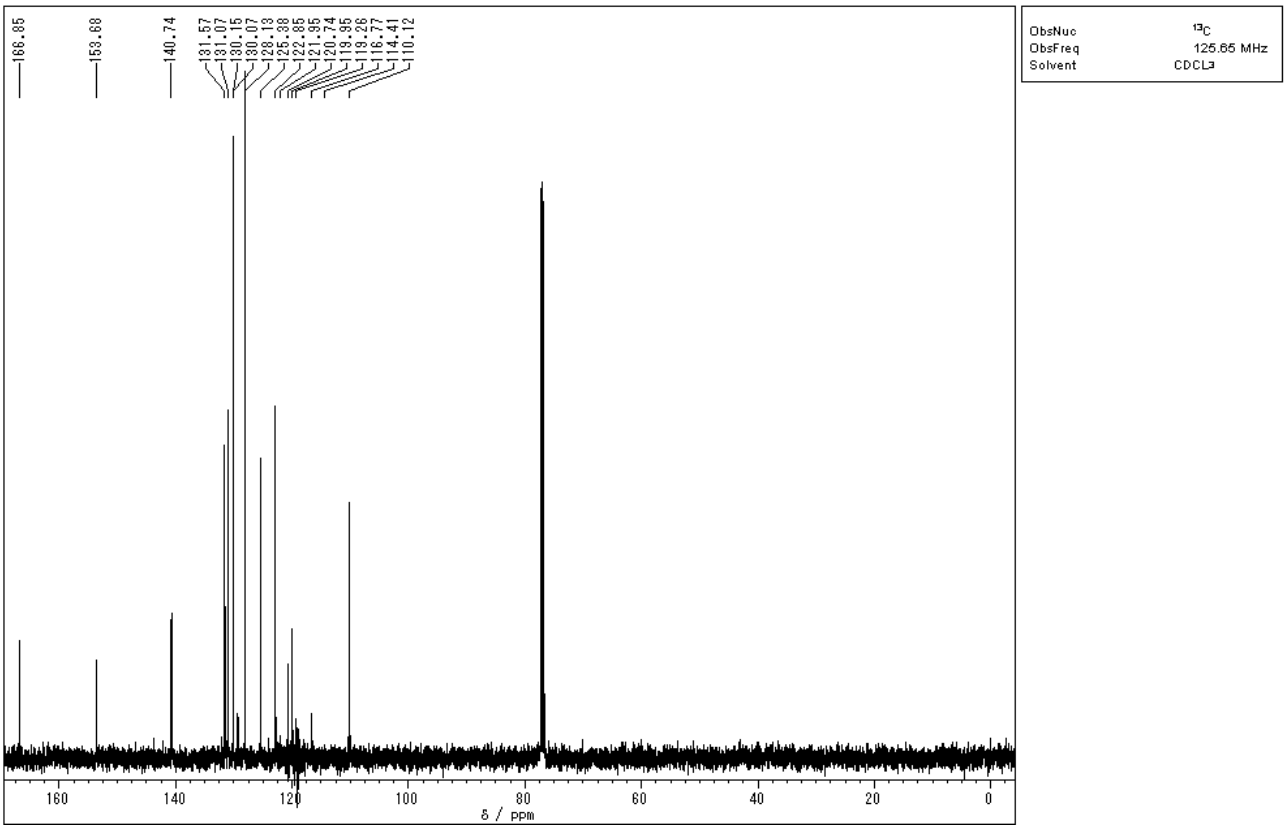
ObsFreq 500.0 MHz
Solvent CDCL3
TfO
O
N
H
δ / ppm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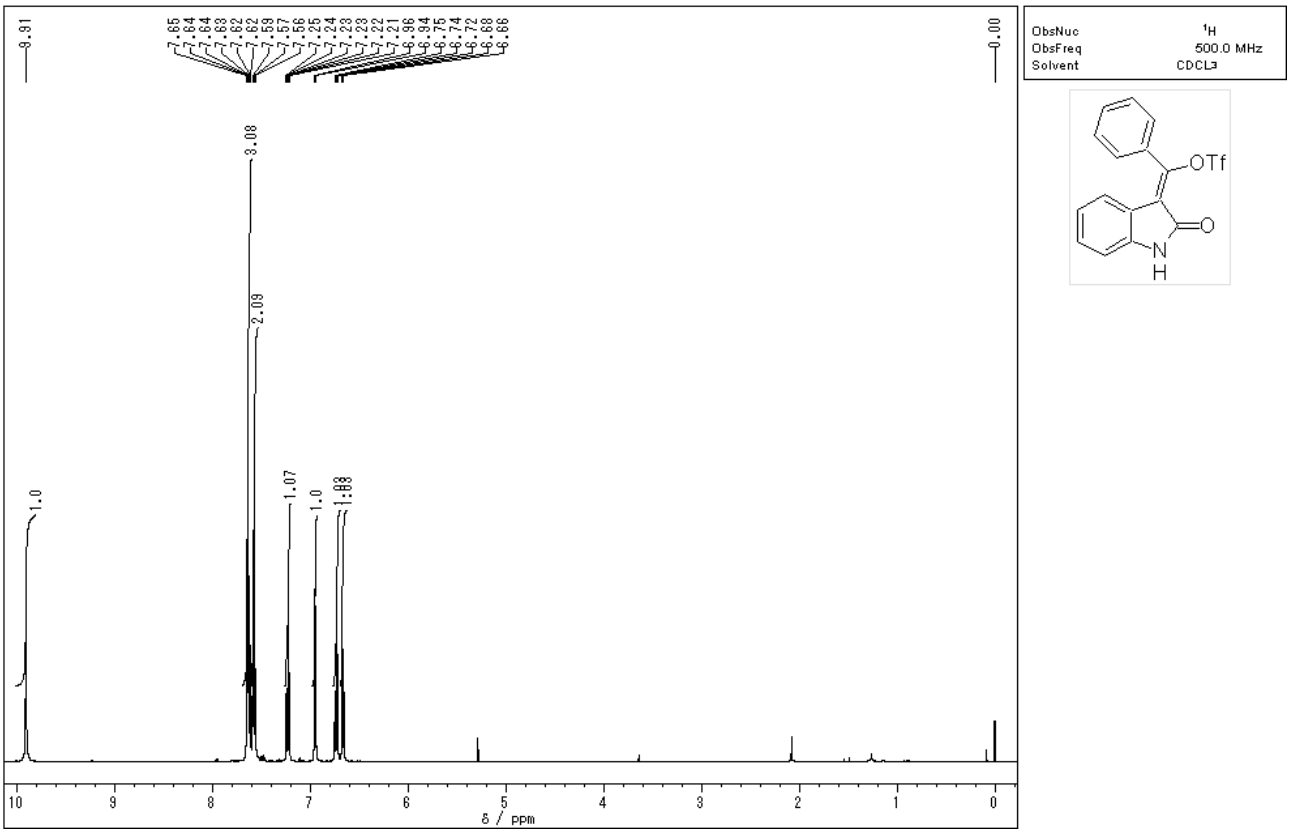
ObsFreq 125.65 MHz
Solvent CDCL3
δ / ppm

***Z*-26**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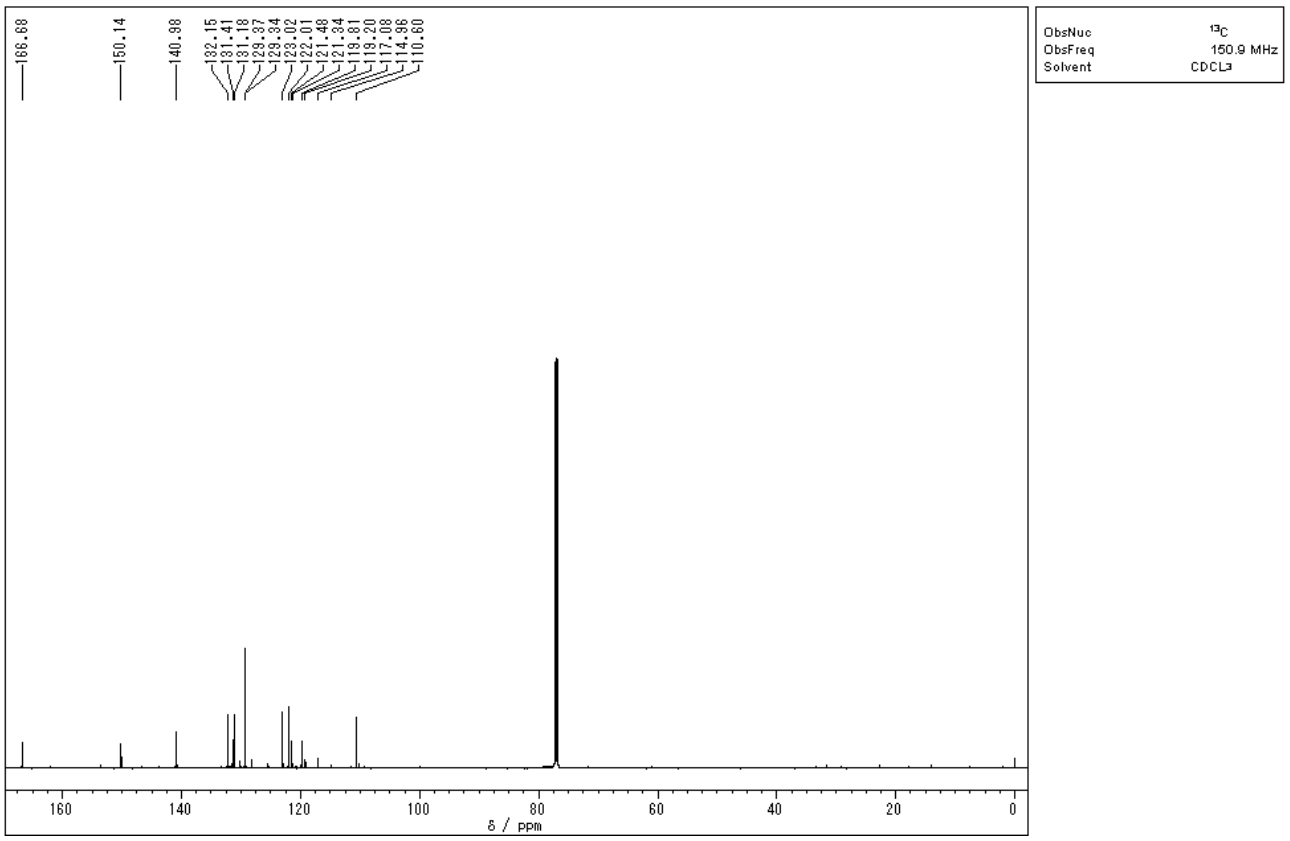
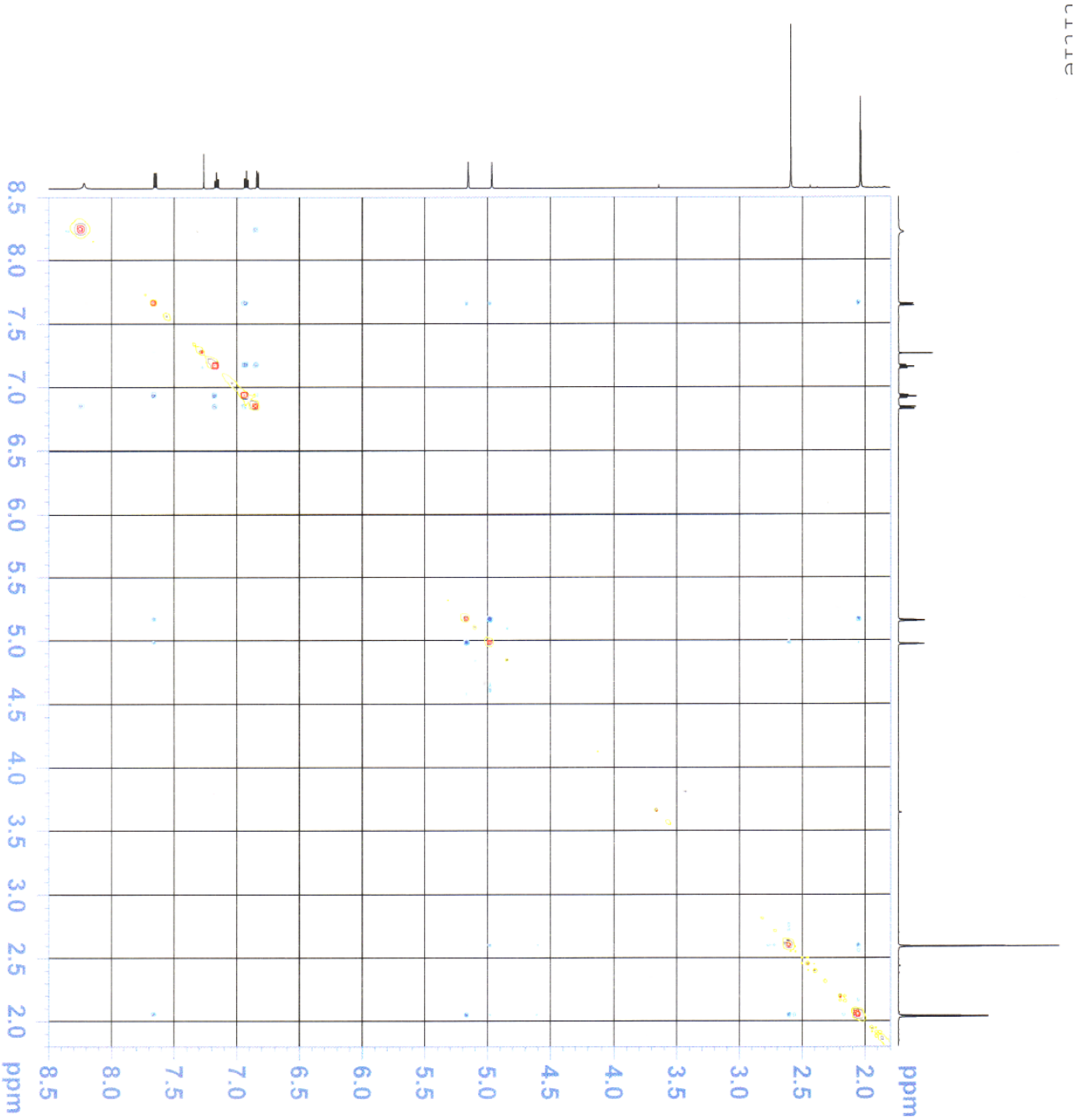
7.65
7.64
7.64
7.63
7.62
7.62
7.59
7.57
7.56
7.25
7.24
7.23
7.23
7.22
7.21
6.86
6.84
6.75
6.74
6.72
6.68
6.66
0.00
8.08
2.09
1.07
1.0
1.08
1.0
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
ObsNuc 1H
ObsFreq 500.0 MHz
Solvent CDCL3
OTf
O
N
H


166.68
150.14
140.98
132.15
131.41
131.18
129.37
129.34
123.02
122.01
121.48
121.34
119.81
118.20
117.08
114.96
110.60
160
140
120
100
80
60
40
20
0
δ / ppm
ObsNuc 13C
ObsFreq 150.9 MHz
Solvent CDCL3

3. NOESY NMR spectrum of 11



4. X-Ray crystallographic analysis for compounds 9 and 22

Table S2. Crystal data and structure refinement for **9**.

Empirical formula	$C_{28}H_{19}NS$	
Formula weight	401.50	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.0037(15) Å	a= 90°.
	b = 10.4097(6) Å	b= 98.5990(10)°.
	c = 15.2507(9) Å	g = 90°.
Volume	4081.8(4) $Å^3$	
Z	8	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.174 mm^{-1}	
F(000)	1680	
Crystal size	0.70 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.58 to 27.56°.	
Index ranges	-31<=h<=33, -13<=k<=12, -14<=l<=19	
Reflections collected	11394	
Independent reflections	4656 [R(int) = 0.0242]	
Completeness to theta = 27.56°	98.7 %	
Absorption correction	Analytical	
Max. and min. transmission	0.9661 and 0.8882	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4656 / 0 / 275	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0999	
R indices (all data)	R1 = 0.0424, wR2 = 0.1032	
Largest diff. peak and hole	0.343 and -0.392 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	9345(1)	5203(1)	2522(1)	20(1)
S(1)	9625(1)	4340(1)	1013(1)	23(1)
C(6)	8663(1)	7360(2)	3912(1)	33(1)
C(5)	8400(1)	8090(1)	3227(1)	32(1)
C(20)	8415(1)	8670(1)	-2693(1)	32(1)
C(14)	10090(1)	9114(2)	1408(1)	31(1)
C(21)	8885(1)	8156(1)	-2304(1)	29(1)
C(19)	7984(1)	8598(1)	-2263(1)	31(1)
C(12)	9422(1)	10478(1)	666(1)	29(1)
C(13)	9915(1)	10326(1)	1143(1)	29(1)
C(7)	8990(1)	6355(2)	3751(1)	28(1)
C(15)	9770(1)	8052(1)	1205(1)	26(1)
C(27)	7511(1)	4281(1)	-80(1)	27(1)
C(26)	7688(1)	3840(1)	773(1)	25(1)
C(4)	8432(1)	7794(1)	2341(1)	25(1)
C(18)	8021(1)	8020(1)	-1431(1)	25(1)
C(28)	7767(1)	5266(1)	-459(1)	24(1)
C(11)	9102(1)	9422(1)	455(1)	23(1)
C(22)	8925(1)	7570(1)	-1476(1)	23(1)
C(25)	8123(1)	4393(1)	1279(1)	22(1)
C(8)	9030(1)	6114(1)	2872(1)	20(1)
C(17)	8496(1)	7506(1)	-1030(1)	20(1)
C(16)	8547(1)	6864(1)	-154(1)	18(1)
C(23)	8201(1)	5820(1)	44(1)	18(1)
C(3)	8746(1)	6783(1)	2174(1)	18(1)
C(24)	8369(1)	5382(1)	907(1)	18(1)
C(10)	9272(1)	8189(1)	724(1)	18(1)
C(1)	9290(1)	5221(1)	1634(1)	17(1)
C(9)	8911(1)	7092(1)	565(1)	17(1)
C(2)	8841(1)	6164(1)	1312(1)	16(1)

Table S4. Bond lengths [Å] and angles [°] for **9**.

N(1)-C(1)	1.3411(15)
N(1)-C(8)	1.4099(16)
N(1)-H(1)	0.895(18)
S(1)-C(1)	1.6557(13)
C(6)-C(7)	1.392(2)
C(6)-C(5)	1.387(2)
C(6)-H(4)	0.9500
C(5)-C(4)	1.400(2)
C(5)-H(3)	0.9500
C(20)-C(21)	1.383(2)
C(20)-C(19)	1.384(2)
C(20)-H(13)	0.9500
C(14)-C(13)	1.381(2)
C(14)-C(15)	1.3898(19)
C(14)-H(9)	0.9500
C(21)-C(22)	1.3925(18)
C(21)-H(14)	0.9500
C(19)-C(18)	1.3943(18)
C(19)-H(12)	0.9500
C(12)-C(13)	1.385(2)
C(12)-C(11)	1.3877(18)
C(12)-H(7)	0.9500
C(13)-H(8)	0.9500
C(7)-C(8)	1.3836(17)
C(7)-H(5)	0.9500
C(15)-C(10)	1.3968(18)
C(15)-H(10)	0.9500
C(27)-C(26)	1.392(2)
C(27)-C(28)	1.3944(19)
C(27)-H(18)	0.9500
C(26)-C(25)	1.3945(18)
C(26)-H(17)	0.9500
C(4)-C(3)	1.3783(18)
C(4)-H(2)	0.9500
C(18)-C(17)	1.3984(18)
C(18)-H(11)	0.9500

C(28)-C(23)	1.3929(17)
C(28)-H(19)	0.9500
C(11)-C(10)	1.3992(17)
C(11)-H(6)	0.9500
C(22)-C(17)	1.3926(19)
C(22)-H(15)	0.9500
C(25)-C(24)	1.3787(17)
C(25)-H(16)	0.9500
C(8)-C(3)	1.3881(17)
C(17)-C(16)	1.4815(16)
C(16)-C(9)	1.3579(16)
C(16)-C(23)	1.4705(17)
C(23)-C(24)	1.3994(16)
C(3)-C(2)	1.5172(16)
C(24)-C(2)	1.5244(16)
C(10)-C(9)	1.4755(16)
C(1)-C(2)	1.5468(16)
C(9)-C(2)	1.5251(15)

C(1)-N(1)-C(8)	113.06(10)
C(1)-N(1)-H(1)	121.9(11)
C(8)-N(1)-H(1)	124.7(11)
C(7)-C(6)-C(5)	121.59(13)
C(7)-C(6)-H(4)	119.2
C(5)-C(6)-H(4)	119.2
C(6)-C(5)-C(4)	120.90(13)
C(6)-C(5)-H(3)	119.6
C(4)-C(5)-H(3)	119.6
C(21)-C(20)-C(19)	120.16(12)
C(21)-C(20)-H(13)	119.9
C(19)-C(20)-H(13)	119.9
C(13)-C(14)-C(15)	120.13(13)
C(13)-C(14)-H(9)	119.9
C(15)-C(14)-H(9)	119.9
C(20)-C(21)-C(22)	119.95(14)
C(20)-C(21)-H(14)	120.0
C(22)-C(21)-H(14)	120.0
C(20)-C(19)-C(18)	120.21(13)

C(20)-C(19)-H(12)	119.9
C(18)-C(19)-H(12)	119.9
C(13)-C(12)-C(11)	120.52(13)
C(13)-C(12)-H(7)	119.7
C(11)-C(12)-H(7)	119.7
C(12)-C(13)-C(14)	119.74(13)
C(12)-C(13)-H(8)	120.1
C(14)-C(13)-H(8)	120.1
C(8)-C(7)-C(6)	116.31(13)
C(8)-C(7)-H(5)	121.8
C(6)-C(7)-H(5)	121.8
C(10)-C(15)-C(14)	120.80(13)
C(10)-C(15)-H(10)	119.6
C(14)-C(15)-H(10)	119.6
C(26)-C(27)-C(28)	121.21(12)
C(26)-C(27)-H(18)	119.4
C(28)-C(27)-H(18)	119.4
C(27)-C(26)-C(25)	120.64(12)
C(27)-C(26)-H(17)	119.7
C(25)-C(26)-H(17)	119.7
C(3)-C(4)-C(5)	117.89(13)
C(3)-C(4)-H(2)	121.1
C(5)-C(4)-H(2)	121.1
C(17)-C(18)-C(19)	120.03(13)
C(17)-C(18)-H(11)	120.0
C(19)-C(18)-H(11)	120.0
C(27)-C(28)-C(23)	118.30(12)
C(27)-C(28)-H(19)	120.9
C(23)-C(28)-H(19)	120.9
C(12)-C(11)-C(10)	120.36(12)
C(12)-C(11)-H(6)	119.8
C(10)-C(11)-H(6)	119.8
C(17)-C(22)-C(21)	120.54(13)
C(17)-C(22)-H(15)	119.7
C(21)-C(22)-H(15)	119.7
C(24)-C(25)-C(26)	117.93(12)
C(24)-C(25)-H(16)	121.0
C(26)-C(25)-H(16)	121.0

C(7)-C(8)-C(3)	122.93(12)
C(7)-C(8)-N(1)	128.38(12)
C(3)-C(8)-N(1)	108.69(10)
C(22)-C(17)-C(18)	119.10(11)
C(22)-C(17)-C(16)	119.44(11)
C(18)-C(17)-C(16)	121.44(12)
C(9)-C(16)-C(23)	109.68(10)
C(9)-C(16)-C(17)	127.40(11)
C(23)-C(16)-C(17)	122.89(10)
C(28)-C(23)-C(24)	119.80(12)
C(28)-C(23)-C(16)	131.58(11)
C(24)-C(23)-C(16)	108.62(10)
C(4)-C(3)-C(8)	120.21(12)
C(4)-C(3)-C(2)	131.46(11)
C(8)-C(3)-C(2)	108.29(10)
C(25)-C(24)-C(23)	122.11(11)
C(25)-C(24)-C(2)	128.82(11)
C(23)-C(24)-C(2)	109.07(10)
C(15)-C(10)-C(11)	118.44(12)
C(15)-C(10)-C(9)	121.64(11)
C(11)-C(10)-C(9)	119.70(11)
N(1)-C(1)-C(2)	106.95(10)
N(1)-C(1)-S(1)	125.65(9)
C(2)-C(1)-S(1)	127.35(9)
C(16)-C(9)-C(10)	128.14(11)
C(16)-C(9)-C(2)	110.28(10)
C(10)-C(9)-C(2)	120.72(10)
C(3)-C(2)-C(24)	110.60(10)
C(3)-C(2)-C(9)	115.59(10)
C(24)-C(2)-C(9)	102.33(9)
C(3)-C(2)-C(1)	102.02(9)
C(24)-C(2)-C(1)	108.19(9)
C(9)-C(2)-C(1)	118.07(10)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	21(1)	22(1)	15(1)	4(1)	-1(1)	2(1)
S(1)	23(1)	26(1)	20(1)	-7(1)	-2(1)	4(1)
C(6)	34(1)	41(1)	25(1)	-11(1)	12(1)	-9(1)
C(5)	32(1)	28(1)	38(1)	-9(1)	15(1)	-2(1)
C(20)	51(1)	25(1)	15(1)	4(1)	-6(1)	-9(1)
C(14)	23(1)	34(1)	33(1)	2(1)	-4(1)	-9(1)
C(21)	40(1)	29(1)	18(1)	-1(1)	3(1)	-11(1)
C(19)	39(1)	24(1)	24(1)	4(1)	-11(1)	0(1)
C(12)	39(1)	18(1)	27(1)	1(1)	0(1)	-4(1)
C(13)	33(1)	27(1)	26(1)	-3(1)	3(1)	-14(1)
C(7)	28(1)	38(1)	16(1)	-1(1)	2(1)	-5(1)
C(15)	23(1)	24(1)	31(1)	5(1)	-3(1)	-3(1)
C(27)	20(1)	23(1)	36(1)	-5(1)	-4(1)	-4(1)
C(26)	22(1)	19(1)	35(1)	0(1)	4(1)	-4(1)
C(4)	24(1)	22(1)	30(1)	1(1)	6(1)	0(1)
C(18)	27(1)	23(1)	22(1)	1(1)	-4(1)	1(1)
C(28)	23(1)	22(1)	23(1)	-2(1)	-6(1)	0(1)
C(11)	26(1)	22(1)	21(1)	1(1)	-3(1)	-1(1)
C(22)	27(1)	22(1)	18(1)	-1(1)	-2(1)	-4(1)
C(25)	22(1)	19(1)	24(1)	2(1)	2(1)	-1(1)
C(8)	19(1)	23(1)	18(1)	-1(1)	1(1)	-3(1)
C(17)	26(1)	16(1)	15(1)	0(1)	-3(1)	-2(1)
C(16)	19(1)	17(1)	17(1)	1(1)	-1(1)	0(1)
C(23)	18(1)	18(1)	19(1)	-1(1)	-1(1)	1(1)
C(3)	19(1)	18(1)	18(1)	0(1)	2(1)	-4(1)
C(24)	16(1)	17(1)	19(1)	-1(1)	-1(1)	0(1)
C(10)	20(1)	19(1)	14(1)	1(1)	2(1)	-4(1)
C(1)	17(1)	16(1)	16(1)	1(1)	-2(1)	-2(1)
C(9)	18(1)	17(1)	16(1)	2(1)	0(1)	0(1)
C(2)	16(1)	16(1)	15(1)	1(1)	-1(1)	-1(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **9**.

	x	y	z	U(eq)
H(4)	8619	7551	4505	39
H(3)	8196	8800	3360	38
H(13)	8389	9074	-3257	38
H(9)	10429	9006	1729	37
H(14)	9180	8203	-2602	35
H(12)	7661	8945	-2535	37
H(7)	9302	11311	483	34
H(8)	10132	11053	1287	35
H(5)	9175	5863	4219	33
H(10)	9892	7222	1396	32
H(18)	7209	3904	-409	32
H(17)	7512	3155	1013	30
H(2)	8244	8275	1870	30
H(11)	7725	7974	-1137	30
H(19)	7647	5552	-1046	28
H(6)	8765	9536	125	28
H(15)	9247	7212	-1213	28
H(16)	8246	4097	1862	26
H(1)	9586(7)	4716(17)	2848(12)	31(4)

ORTEP view and numbering scheme of **9** with 50% probability displacement ellipsoids. H atoms are omitted for clarity.

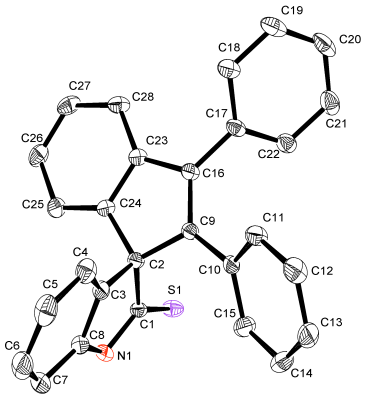


Table S7. Crystal data and structure refinement for **22**.

Empirical formula	$C_{14}H_{13}NO$	
Formula weight	211.25	
Temperature	291 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.8131(16) Å	a= 90°.
	b = 6.5022(10) Å	b= 105.352(2)°.
	c = 16.577(3) Å	g = 90°.
Volume	1123.9(3) $Å^3$	
Z	4	
Density (calculated)	1.248 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	448	
Crystal size	0.34 x 0.05 x 0.04 mm^3	
Theta range for data collection	1.95 to 27.50°.	
Index ranges	-13<=h<=13, -8<=k<=8, -21<=l<=15	
Reflections collected	6089	
Independent reflections	2526 [R(int) = 0.0273]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9969 and 0.9737	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2526 / 0 / 197	
Goodness-of-fit on F^2	0.895	
Final R indices [I>2sigma(I)]	R1 = 0.0659, wR2 = 0.1605	
R indices (all data)	R1 = 0.0994, wR2 = 0.1829	
Largest diff. peak and hole	0.170 and -0.280 $e.Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **22**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5711(2)	12471(4)	9604(1)	41(1)
C(2)	5823(2)	10408(3)	9233(1)	39(1)
C(3)	4700(2)	10258(3)	8506(1)	41(1)
C(4)	4254(2)	8722(4)	7924(2)	50(1)
C(5)	3143(3)	9086(5)	7291(2)	59(1)
C(6)	2503(3)	10940(5)	7242(2)	60(1)
C(7)	2931(2)	12489(4)	7819(2)	53(1)
C(8)	4029(2)	12105(3)	8447(1)	42(1)
C(9)	6715(2)	8918(4)	9494(2)	44(1)
C(10)	7889(2)	8805(4)	10161(2)	47(1)
C(11)	8536(3)	7025(5)	10318(2)	65(1)
C(12)	9717(3)	7168(6)	11024(2)	81(1)
C(13)	9814(3)	9430(6)	11240(3)	80(1)
C(14)	8564(3)	10443(5)	10746(2)	59(1)
N(1)	4660(2)	13398(3)	9098(1)	45(1)
O(1)	6386(2)	13234(3)	10246(1)	57(1)

Table S9. Bond lengths [Å] and angles [°] for **22**.

C(1)-O(1)	1.225(3)
C(1)-N(1)	1.362(3)
C(1)-C(2)	1.494(3)
C(2)-C(9)	1.355(3)
C(2)-C(3)	1.470(3)
C(3)-C(4)	1.384(3)
C(3)-C(8)	1.393(3)
C(4)-C(5)	1.390(4)
C(4)-H(4)	1.00(3)
C(5)-C(6)	1.382(4)
C(5)-H(5)	0.96(3)
C(6)-C(7)	1.382(4)
C(6)-H(6)	0.91(3)
C(7)-C(8)	1.379(3)
C(7)-H(7)	0.95(3)
C(8)-N(1)	1.395(3)
C(9)-C(10)	1.448(3)
C(9)-H(9)	0.95(3)
C(10)-C(11)	1.342(4)
C(10)-C(14)	1.494(4)
C(11)-C(12)	1.490(5)
C(11)-H(11)	0.92(3)
C(12)-C(13)	1.511(6)
C(12)-H(12A)	0.96(4)
C(12)-H(12B)	1.01(5)
C(13)-C(14)	1.532(4)
C(13)-H(13A)	0.98(4)
C(13)-H(13B)	0.95(4)
C(14)-H(14A)	1.01(4)
C(14)-H(14B)	0.97(3)
N(1)-H(1)	0.85(3)
O(1)-C(1)-N(1)	124.4(2)
O(1)-C(1)-C(2)	128.9(2)
N(1)-C(1)-C(2)	106.74(19)
C(9)-C(2)-C(3)	125.3(2)

C(9)-C(2)-C(1)	129.7(2)
C(3)-C(2)-C(1)	104.97(18)
C(4)-C(3)-C(8)	119.6(2)
C(4)-C(3)-C(2)	132.8(2)
C(8)-C(3)-C(2)	107.60(19)
C(3)-C(4)-C(5)	118.4(2)
C(3)-C(4)-H(4)	120.4(15)
C(5)-C(4)-H(4)	121.2(15)
C(6)-C(5)-C(4)	120.8(3)
C(6)-C(5)-H(5)	119.6(17)
C(4)-C(5)-H(5)	119.6(17)
C(7)-C(6)-C(5)	121.6(2)
C(7)-C(6)-H(6)	119.0(16)
C(5)-C(6)-H(6)	119.4(16)
C(8)-C(7)-C(6)	117.0(3)
C(8)-C(7)-H(7)	119.7(17)
C(6)-C(7)-H(7)	123.3(17)
C(7)-C(8)-C(3)	122.5(2)
C(7)-C(8)-N(1)	128.4(2)
C(3)-C(8)-N(1)	109.04(19)
C(2)-C(9)-C(10)	133.4(2)
C(2)-C(9)-H(9)	113.6(14)
C(10)-C(9)-H(9)	113.0(14)
C(11)-C(10)-C(9)	119.9(3)
C(11)-C(10)-C(14)	110.5(2)
C(9)-C(10)-C(14)	129.6(2)
C(10)-C(11)-C(12)	113.1(3)
C(10)-C(11)-H(11)	121(2)
C(12)-C(11)-H(11)	126.2(19)
C(11)-C(12)-C(13)	103.8(3)
C(11)-C(12)-H(12A)	109(2)
C(13)-C(12)-H(12A)	112(2)
C(11)-C(12)-H(12B)	110(3)
C(13)-C(12)-H(12B)	110(3)
H(12A)-C(12)-H(12B)	111(3)
C(12)-C(13)-C(14)	107.2(3)
C(12)-C(13)-H(13A)	109(2)
C(14)-C(13)-H(13A)	106(2)

C(12)-C(13)-H(13B)	112(3)
C(14)-C(13)-H(13B)	112(2)
H(13A)-C(13)-H(13B)	110(3)
C(10)-C(14)-C(13)	104.5(3)
C(10)-C(14)-H(14A)	111(2)
C(13)-C(14)-H(14A)	113(2)
C(10)-C(14)-H(14B)	112.8(18)
C(13)-C(14)-H(14B)	113.5(17)
H(14A)-C(14)-H(14B)	102(3)
C(1)-N(1)-C(8)	111.57(19)
C(1)-N(1)-H(1)	120.0(18)
C(8)-N(1)-H(1)	126.2(18)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **22**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42(1)	38(1)	42(1)	-1(1)	8(1)	0(1)
C(2)	43(1)	36(1)	38(1)	-2(1)	12(1)	0(1)
C(3)	45(1)	41(1)	38(1)	0(1)	13(1)	1(1)
C(4)	55(1)	51(2)	46(1)	-10(1)	15(1)	-1(1)
C(5)	60(2)	65(2)	48(2)	-16(1)	6(1)	-9(1)
C(6)	49(1)	79(2)	44(1)	-1(1)	-4(1)	0(1)
C(7)	49(1)	55(2)	49(1)	0(1)	6(1)	5(1)
C(8)	44(1)	43(1)	39(1)	-1(1)	12(1)	-1(1)
C(9)	48(1)	39(1)	46(1)	-5(1)	14(1)	2(1)
C(10)	44(1)	48(1)	51(1)	4(1)	16(1)	5(1)
C(11)	58(2)	56(2)	77(2)	6(2)	13(1)	13(1)
C(12)	61(2)	93(3)	81(2)	18(2)	8(2)	24(2)
C(13)	54(2)	98(3)	77(2)	-2(2)	-1(2)	9(2)
C(14)	49(1)	64(2)	58(2)	-2(1)	2(1)	3(1)
N(1)	51(1)	37(1)	45(1)	-4(1)	6(1)	6(1)
O(1)	55(1)	46(1)	58(1)	-15(1)	-4(1)	6(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **22**.

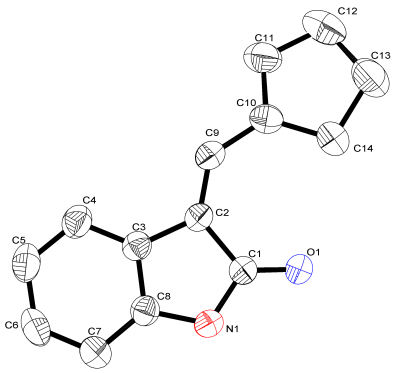
	x	y	z	U(eq)
H(1)	4350(20)	14470(50)	9265(17)	64(8)
H(4)	4750(20)	7410(40)	7943(16)	61(7)
H(5)	2820(30)	8040(40)	6884(17)	65(8)
H(6)	1790(20)	11150(40)	6821(16)	48(7)
H(7)	2510(30)	13780(50)	7797(17)	68(8)
H(9)	6560(20)	7710(40)	9161(14)	43(6)
H(11)	8230(30)	5870(50)	10014(19)	75(10)
H(12A)	10440(40)	6690(60)	10840(20)	115(13)
H(13A)	10500(40)	10050(60)	11040(30)	120(14)
H(14A)	8700(30)	11710(60)	10430(20)	99(11)
H(12B)	9610(40)	6340(70)	11520(30)	132(16)
H(13B)	9970(30)	9660(60)	11830(30)	114(14)
H(14B)	8050(30)	10990(50)	11098(18)	74(9)

Table S12. Torsion angles [°] for **22**.

O(1)-C(1)-C(2)-C(9)	-2.7(4)
N(1)-C(1)-C(2)-C(9)	179.0(2)
O(1)-C(1)-C(2)-C(3)	175.4(2)
N(1)-C(1)-C(2)-C(3)	-2.9(2)
C(9)-C(2)-C(3)-C(4)	-0.3(4)
C(1)-C(2)-C(3)-C(4)	-178.6(2)
C(9)-C(2)-C(3)-C(8)	-179.7(2)
C(1)-C(2)-C(3)-C(8)	2.0(2)
C(8)-C(3)-C(4)-C(5)	0.2(3)
C(2)-C(3)-C(4)-C(5)	-179.1(2)
C(3)-C(4)-C(5)-C(6)	0.4(4)
C(4)-C(5)-C(6)-C(7)	-0.6(4)
C(5)-C(6)-C(7)-C(8)	0.1(4)
C(6)-C(7)-C(8)-C(3)	0.6(4)
C(6)-C(7)-C(8)-N(1)	179.6(2)
C(4)-C(3)-C(8)-C(7)	-0.8(3)
C(2)-C(3)-C(8)-C(7)	178.7(2)
C(4)-C(3)-C(8)-N(1)	-180.0(2)
C(2)-C(3)-C(8)-N(1)	-0.5(2)
C(3)-C(2)-C(9)-C(10)	177.2(2)
C(1)-C(2)-C(9)-C(10)	-5.0(4)
C(2)-C(9)-C(10)-C(11)	174.2(3)
C(2)-C(9)-C(10)-C(14)	-6.2(5)
C(9)-C(10)-C(11)-C(12)	-179.8(3)
C(14)-C(10)-C(11)-C(12)	0.6(4)
C(10)-C(11)-C(12)-C(13)	-6.3(4)
C(11)-C(12)-C(13)-C(14)	9.2(4)
C(11)-C(10)-C(14)-C(13)	5.3(4)
C(9)-C(10)-C(14)-C(13)	-174.3(3)
C(12)-C(13)-C(14)-C(10)	-9.0(4)
O(1)-C(1)-N(1)-C(8)	-175.6(2)
C(2)-C(1)-N(1)-C(8)	2.8(2)
C(7)-C(8)-N(1)-C(1)	179.4(2)
C(3)-C(8)-N(1)-C(1)	-1.5(3)

Symmetry transformations used to generate equivalent atoms:

ORTEP view and numbering scheme of **22** with 50% probability displacement ellipsoids. H atoms are omitted for clarity.



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