Silver-catalysed intramolecular hydroamination of alkynes with trichloroacetimidates

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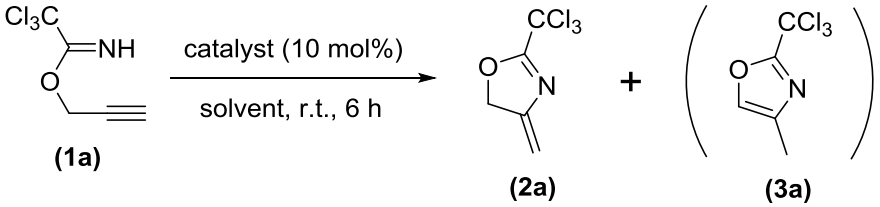
Supporting information

General

Solvents were dried by passing through the columns of molecular sieves in a solvent purification system (Innovative Technology Inc.). Unless otherwise stated, materials obtained from commercial suppliers were used without purification. Preparative separations were performed on silica gel by column chromatography. TLCs were performed using silica gel 60 F_{254} aluminium sheets and visualised with $KMnO_4$ solution or exposure to UV light (λ = 254 nm). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded at 25 °C on Bruker Avance™ 400 spectrometers. Chemical shifts (δ) were reported in ppm, and *J* values in Hz. ^{1}H NMR spectra were referenced to residual proton resonances in deuterated $CDCl_3$ (δ_H = 7.26), and ^{13}C NMR spectra to $CDCl_3$ (δ_C = 77.0). High-resolution mass spectra (HRMS) were performed by the Mass Spectroscopy Service of Imperial College London on Micromass Autospec Premier, Micromass LCT Premier, or VG Platform II spectrometers. Elemental analyses were performed by the Analytical Services at London Metropolitan University, U.K.

Table S1. Optimization of catalytic conditions.



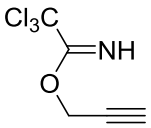
(1a) (2a) (3a)

Entry	Catalyst	Solvent	Conversion (%)	Yield of 2a (%)	Yield of 3a (%)
1	AgOAc	DCE	51	21	-
2	AgTFA	DCE	100	14	15
3	Ag_2CO_3	DCE	NR	-	-
4	Ag_2O	DCE	NR	-	-
5	$AgNO_3$	DCE	NR	-	-
6	Ag_2SO_4	DCE	NR	-	-
7	$AgSbF_6$	DCE	100	54	-
8	$AgPF_6$	DCE	37	13	-
9	$AgBF_4$	DCE	100	-	16
10	AgOTf	DCE	100	-	46
11	AgOTs	DCE	100	5	26
12	[Ag(phen)][OTf]	DCE	NR	-	-
13	$[Ag(py)_2][OTf]$	DCE	100	83	-
14	TfOH	DCE	NR	-	-
15	AgOAc	MeCN	36	8	-
16	AgTFA	MeCN	100	76	-

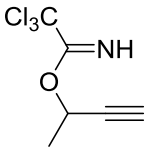
17	Ag_2CO_3	MeCN	NR	-	-
18	Ag_2O	MeCN	NR	-	-
19	$AgNO_3$	MeCN	NR	-	-
20	Ag_2SO_4	MeCN	NR	-	-
21	$AgSbF_6$	MeCN	100	28	-
22	$AgPF_6$	MeCN	49	16	-
23	$AgBF_4$	MeCN	100	-	36
24	AgOTf	MeCN	100	18	15
25	AgOTs	MeCN	91	9	8
26	[Ag(phen)][OTf]	MeCN	NR	-	-
27	$[Ag(py)_2][OTf]$	MeCN	100	83	-
28	AgOAc	acetone	30	9	-
29	AgTFA	acetone	62	22	-
30	Ag_2CO_3	acetone	NR	-	-
31	Ag_2O	acetone	NR	-	-
32	$AgNO_3$	acetone	NR	-	-
33	Ag_2SO_4	acetone	NR	-	-
34	$AgSbF_6$	acetone	82	37	-
35	$AgPF_6$	acetone	27	5	-
36	$AgBF_4$	acetone	100	37	5
37	AgOTf	acetone	100	40	-
38	AgOTs	acetone	68	28	-
39	[Ag(phen)][OTf]	acetone	NR	-	-
40	$[Ag(py)_2][OTf]$	acetone	100	87	-
41	TfOH	acetone	NR	-	-
42	AgOAc	CH_2Cl_2	51	26	-
43	AgTFA	CH_2Cl_2	100	10	28
44	Ag_2CO_3	CH_2Cl_2	NR	-	-
45	Ag_2O	CH_2Cl_2	NR	-	-
46	$AgNO_3$	CH_2Cl_2	NR	-	-
47	Ag_2SO_4	CH_2Cl_2	NR	-	-
48	$AgSbF_6$	CH_2Cl_2	100	13	35
49	$AgPF_6$	CH_2Cl_2	40	15	-
50	$AgBF_4$	CH_2Cl_2	100	12	22
51	AgOTf	CH_2Cl_2	100	-	52
52	AgOTs	CH_2Cl_2	100	-	38
53	[Ag(phen)][OTf]	CH_2Cl_2	NR	-	-
54	$[Ag(py)_2][OTf]$	CH_2Cl_2	100	83	-
55	AgOAc	THF	46	9	-
56	AgTFA	THF	73	15	-
57	Ag_2CO_3	THF	66	4	-
58	Ag_2O	THF	NR	-	-
59	$AgNO_3$	THF	NR	-	-
60	Ag_2SO_4	THF	NR	-	-
61	$AgSbF_6$	THF	77	35	-
62	$AgPF_6$	THF	26	3	-

63	$AgBF_4$	THF	57	16	-
64	AgOTf	THF	96	51	-
65	AgOTs	THF	79	28	-
66	[Ag(phen)][OTf]	THF	NR	-	-
67	$[Ag(py)_2][OTf]$	THF	100	75	-

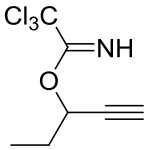
General Procedure for the Synthesis of the Propargylic Trichloroacetimidates (1a-c, 1e-g):
A solution of propargylic alcohol (1 equiv.) and trichloroacetonitrile (1.2 equiv.) in CH_2Cl_2 (2.5 mL per mmol of propargylic alcohol) was cooled to 0 °C in an ice bath and DBU (0.1 equiv.) was added dropwise. The reaction mixture was allowed to stir at 0 °C for (t_1) min, then warmed to room temperature and stirred for another (t_2) min. The solvent was removed in vacuo, and the residue was purified by column chromatography.



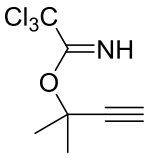
Prop-2-ynyl 2,2,2-trichloroacetimidate (1a): [1]
t_1 = 60, t_2 = 30. Purified by column chromatography (petroleum ether/ethyl acetate, 8:1), 3.11 g (78%) of **1a** was obtained as a colourless oil from 1.16 mL (20 mmol) of propargyl alcohol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 4.91 (d, *J* = 2.4, 2H), 2.55 (t, *J* = 2.4, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.82, 90.70, 77.06, 75.06, 56.57. MS [CI]: *m/z* (%) = 198 (100) $[M-H]^+$.



1-Methylprop-2-ynyl 2,2,2-trichloroacetimidate (1b): [1]
t_1 = 60, t_2 = 60. Purified by column chromatography (petroleum ether/ethyl acetate, 10:1), 3.43 g (80%) of **1b** was obtained as a colourless oil from 1.57 mL (20 mmol) of 3-butyn-2-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1 H), 5.54 (dq, *J* = 6.7, 2.1, 1H), 2.52 (d, *J* = 2.1, 1H), 1.64 (d, *J* = 6.7, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.43, 91.06, 81.36, 73.59, 64.92, 20.83. MS [CI]: *m/z* (%) = 214 (100) $[M+H]^+$.

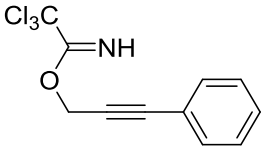


1-Ethylprop-2-ynyl 2,2,2-trichloroacetimidate (1c):
t_1 = 60, t_2 = 120. Purified by column chromatography (petroleum ether/ethyl acetate, 8:1), 1.42 g (52%) of **1c** was obtained as a colourless oil from 1.00 g (11.9 mmol) of 1-pentyn-3-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 5.39 (td, *J* = 6.4, 2.2, 1H), 2.52 (d, *J* = 2.2, 1H), 1.97 (m, 2H), 1.10 (t, *J* = 7.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.63, 91.19, 80.29, 74.14, 69.76, 27.81, 9.26. MS [CI]: *m/z* (%) = 228 (100) $[M+H]^+$.



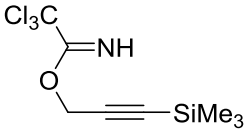
1,1-Dimethylprop-2-ynyl 2,2,2-trichloroacetimidate (1e): [1]

t_1 = 60, t_2 = 300. Purified by column chromatography (petroleum ether/ethyl acetate, 10:1), 1.22 g (27%) of **1e** was obtained as a colourless oil from 1.94 mL (20 mmol) of 2-methyl-3-butyn-2-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 2.61 (s, 1H), 1.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.82, 91.94, 83.89, 75.34, 73.28, 28.56 ppm. MS [CI]: *m/z* (%) = 228 (100) $[M+H]^+$.



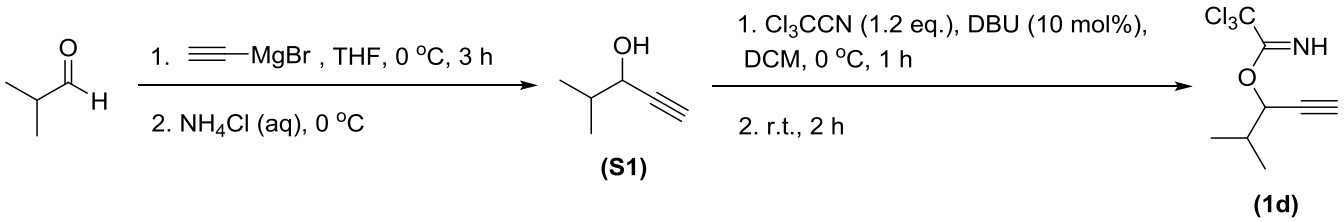
3-Phenylprop-2-ynyl 2,2,2-trichloroacetimidate (1f):

t_1 = 60, t_2 = 90. Purified by column chromatography (petroleum ether/ethyl acetate, 8:1), 1.72g (78%) of **1f** was obtained as a colourless oil from 1.0 mL (8.0 mmol) of 3-phenyl-2-propyn-1-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 7.49 (dd, *J* = 7.5, 2.2, 2H), 7.37-7.29 (m, 3H), 5.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.98, 131.98, 128.87, 128.33, 122.10, 90.95, 87.23, 82.29, 57.58. MS [CI]: *m/z* (%) = 229 (100), 133 (86), 246 (62). (M^+ not observed)



3-(Trimethylsilyl)prop-2-ynyl 2,2,2-trichloroacetimidate (1g):

t_1 = 60, t_2 = 60. Purified by column chromatography (petroleum ether/ethyl acetate, 8:1), 1.97 g (93%) of **1g** was obtained as a colourless oil from 1.0 g (7.8 mmol) of 3-(trimethylsilyl)propargyl alcohol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 4.91 (s, 2H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.87, 98.22, 92.99, 90.86, 54.73, -0.30. MS [CI]: *m/z* (%) = 272 (100) $[M+H]^+$.

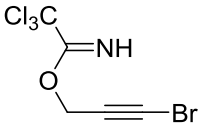


1-Methyl-4-pentyn-3-ol (S1): [2]

A solution of isobutyraldehyde (0.91 mL, 10 mmol, 1.0 equiv.) in dry THF (25 mL) and added to a solution of ethynylmagnesium bromide (0.5 M in THF, 30 mL, 15 mmol) at 0 °C. After 3 h, the reaction was quenched by addition of saturated aq. NH_4Cl solution (50 mL) at 0 °C. Volatile components of the reaction mixture were removed under reduced pressure, and Et_2O (50 mL) was then added. The organic layer was separated, washed with brine (50 mL) and dried over Na_2SO_4. The solvent was removed in vacuo, to furnish 1-methyl-4-pentyn-3-ol (S1) as an orange oil, which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (dd, *J* = 5.8, 2.1, 1H), 2.48 (d, *J* = 2.1, 1H), 1.96-1.86 (m, 1H), 1.80 (br s, 1H), 1.04 (dd, *J* = 7.8, 6.8, 6H).

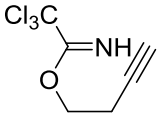
1-(1-Methylethyl)-prop-2-ynyl 2,2,2-trichloroacetimidate (1d):

A mixture of S1 (0.60 g, 6.11 mmol) and trichloroacetonitrile (0.74 mL, 7.34 mmol, 1.2 equiv.) dissolved in CH_2Cl_2 (15 mL) was cooled to 0 °C in an ice bath, to which DBU (90 µL, 0.61 mmol, 0.1 equiv.) was added dropwise. The reaction mixture was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for another 2 h. The mixture was evaporated, and the resulting brown oil residue was chromatographed on silica using petroleum ether/ethyl acetate (8:1) as eluting solvent. 0.75 g (50%) of **1d** was obtained as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 5.26 (dd, *J* = 5.6, 2.2, 1H), 2.50 (d, *J* = 2.2, 1H), 2.25-2.13 (m, 1H), 1.10 (dd, *J* = 9.3, 6.7, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.69, 91.27, 79.16, 74.65, 73.59, 32.42, 17.92, 17.66. MS [CI]: *m/z* (%) = 242 (28) $[M+H]^+$.

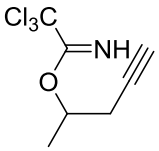


3-Bromoprop-2-ynyl 2,2,2-trichloroacetimidate (1h):
A mixture of propargyl alcohol (1.16 mL, 20 mmol, 1.0 equiv.), *N*-bromosuccinimide (3.92 g, 22 mmol, 1.1 equiv.) and silver nitrate (0.34 g, 2.0 mmol, 0.1 equiv.) in acetone (50 mL) was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue dissolved in water (50 mL). The resulting solution was extracted with Et_2O (2 × 50 mL), and the combined organic extracts washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the bromopropargylic alcohol as a colourless oil, to which CH_2Cl_2 (50 mL) and trichloroacetonitrile (2.4 mL, 24 mmol, 1.2 equiv.) were added. The solution was cooled to 0 °C in an ice bath, before DBU (0.3 mL, 2.0 mmol, 0.1 equiv.) was added dropwise. The reaction mixture was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for another 3 h. The solvent was then evaporated, and the resulting brown oil chromatographed on silica using petroleum ether/ethyl acetate (8:1) as eluting solvent, to furnish 3.34 g (60%) of **1h** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 4.93 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.77, 90.68, 73.48, 57.45, 48.18. MS [CI]: *m/z* (%) = 280 (83) $[M+H]^+$.

General procedure for the preparation of homopropargyl trichloroacetimidates (1i-k):
A solution of homopropargyl alcohol (1 equiv., 20 mmol) and trichloroacetonitrile (1.2 equiv., 24 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C in an ice bath and DBU (0.1 equiv., 2 mmol) was added dropwise. The reaction mixture was allowed to stir at 0 °C for (t_1) min, then warmed to room temperature and stirred for another (t_2) min. The solvent was removed in vacuo, and the residue chromatographed on silica.

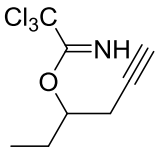


But-3-ynyl 2,2,2-trichloroacetimidate (1i):
This compound was previously reported by Shin *et al.*[3] but no experimental details and spectroscopic data were given. t_1 = 60, t_2 = 60. Purified by column chromatography (petroleum ether/ethyl acetate, 10:1) on silica, 3.28 g (76%) of **1i** was obtained as a colourless oil from 1.51 mL (20 mmol) of 3-butyn-1-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 4.40 (t, *J* = 7.0, 2H), 2.68 (td, *J* = 7.0, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.53, 91.19, 79.60, 70.14, 66.81, 18.50. MS [CI]: *m/z* (%) = 214 (100) $[M+H]^+$.



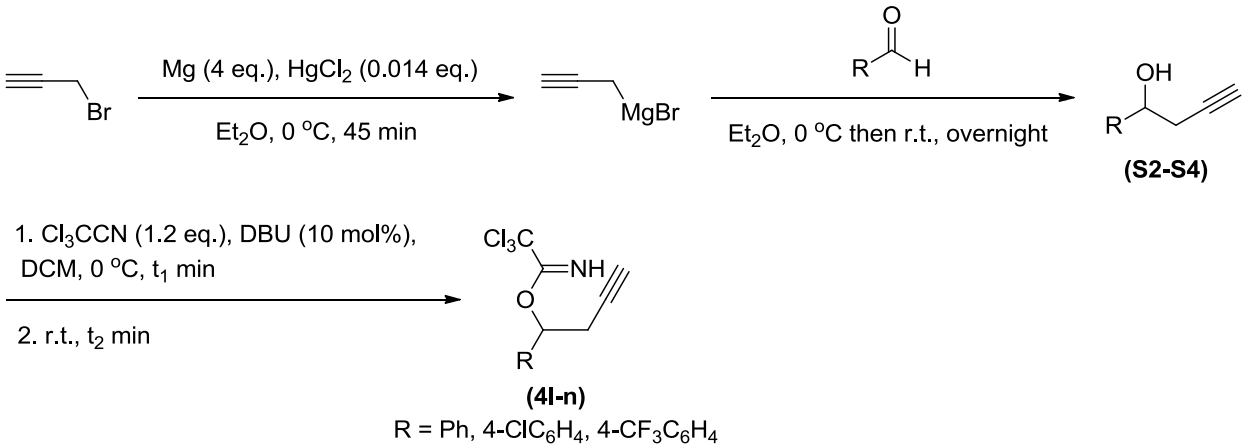
1-Methyl-but-3-ynyl 2,2,2-trichloroacetimidate (1j):

t_1 = 60, t_2 = 360. Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) on silica, 3.71 g (81%) of **1j** was obtained as a colourless oil from 1.90 mL (20 mmol) of 4-pentyn-2-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 5.17 - 5.09 (m, 1H), 2.68-2.54 (m, 2H), 2.02 (t, *J* = 2.7, 1H), 1.47 (d, *J* = 6.3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.94, 91.59, 79.47, 73.63, 70.62, 24.87, 18.33. MS [CI]: *m/z* (%) = 228 (100) $[M+H]^+$.



1-Ethyl-but-3-ynyl 2,2,2-trichloroacetimidate (1k):

t_1 = 60, t_2 = 60. Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) on silica, 2.37 g (96%) of **1k** was obtained as a colourless oil from 1.0 g (10.2 mmol) of 5-hexyn-3-ol. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 5.02-4.96 (m, 1H), 2.64 - 2.62 (m, 2H), 2.00 (t, *J* = 2.7, 1H), 1.91 - 1.86 (m, 2H), 1.01 (t, *J* = 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.27, 91.71, 79.47, 78.01, 70.48, 25.72, 22.50, 9.41. MS [CI]: *m/z* (%) = 242 (100) $[M+H]^+$.

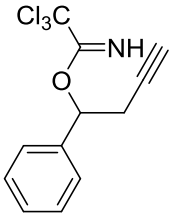


General procedure for the preparation of homopropargyl alcohols (S2-S4):

Propargylmagnesium bromide was prepared by a modified literature procedure:[4] A mixture of Mg turnings (1.94 g, 80 mmol) and $HgCl_2$ (75 mg) in dry Et_2O (20 mL) were stirred at room temperature for 30 min. Propargyl bromide (80% solution in toluene, 1.0 mL, 6.72 mmol) was added in one portion to initiate the reaction (indicated by a slight exotherm). The reaction mixture was cooled to 0 °C in an ice bath, and another 5.0 mL of propargyl bromide (80% solution in toluene, 33.6 mmol) was added dropwise over 30 min. Stirring was continued for another 45 min at 0 °C, after which the solution was decanted into a solution of the corresponding aldehyde (20 mmol) in Et_2O (15 mL) at 0 °C. The ice bath was removed, and reaction mixture stirred overnight at room temperature. The reaction was quenched by the addition of 40 mL of saturated aq. NH_4Cl at 0 °C. The aqueous layer was extracted with 3 × 40 mL of Et_2O, and the combined organic extracts washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude homopropargyl alcohols S2-S4 were obtained as orange oils, which were used in the next steps without further purification.

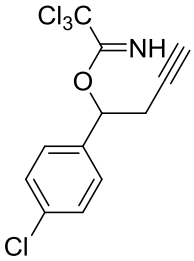
General Procedure for the synthesis of the homopropargyl trichloroacetimidates (1l-n):

A solution of homopropargyl alcohol S2-S4 (1 equiv., 10 mmol) and trichloroacetonitrile (1.2 equiv., 12 mmol) in CH_2Cl_2 (25 mL) was cooled to 0 °C in an ice bath and DBU (0.1 equiv., 1 mmol) was added dropwise. The reaction mixture was allowed to stir at 0 °C for 15 min, then warmed to room temperature and stirred for further 4 h. The solvent was removed in vacuo, and the residue chromatographed on silica.



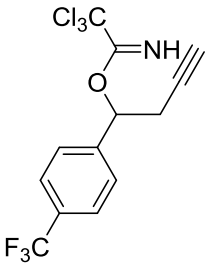
1-Phenyl-but-3-ynyl 2,2,2-trichloroacetimidate (1l):

Purified by column chromatography (petroleum ether/ethyl acetate, 6:1), 1.88 g (65%) of **1l** was obtained as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.49 - 7.46 (m, 2H), 7.41-7.32 (m, 3H), 5.99 (t, *J* = 6.6, 1H), 2.97 - 2.79 (m, 2H), 2.00 (t, *J* = 2.7, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.40, 138.48, 128.47, 126.34, 91.43, 79.22, 78.25, 70.88, 26.63 (CCl_3 was too broad to be detected). MS [CI]: *m/z* (%) = 257 (100), 274 (94), 145 (86). (M^+ not observed)



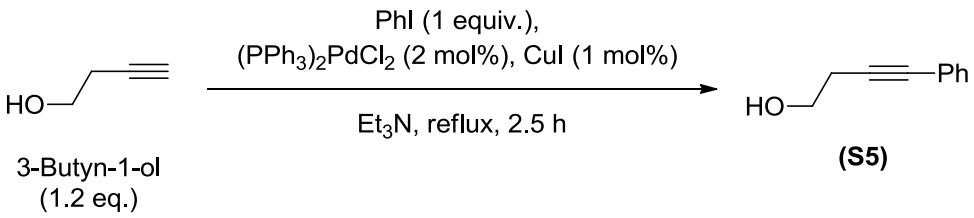
1-(4-Chlorophenyl)-but-3-ynyl 2,2,2-trichloroacetimidate (1m):

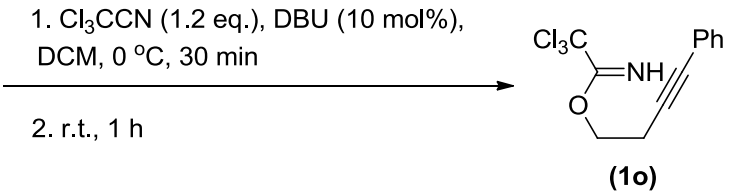
This compound was previously reported by Shin *et al.*[3] but no experimental details and spectroscopic data were given. Purified by column chromatography (petroleum ether/ethyl acetate, 10:1), 1.36 g (42%) of 1m was obtained as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.42 - 7.34 (m, 4H), 5.93 (t, *J* 6.6 Hz, 1H), 2.94-2.77 (m, 2H), 2.00 (t, *J* = 2.6, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.25, 136.89, 134.36, 128.69, 127.85, 91.24, 78.75, 71.22, 26.41 (CCl_3 was too broad to be detected). MS [CI]: *m/z* (%) = 181 (100), 164 (31), 364 (26). (M^+ not observed)



1-(4-Trifluoromethylphenyl)-but-3-ynyl 2,2,2-trichloroacetimidate (1n):

After column chromatography (petroleum ether/ethyl acetate, 10:1) on silica, 1.56 g (44%) of 1n was obtained as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.66-7.58 (m, 4H), 6.01 (t, *J* = 6.4, 1H), 2.97-2.80 (m, 2H), 2.01 (t, *J* = 2.7, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.21, 142.33, 130.63 (q, *J* = 32.4 Hz), 126.72, 125.50, 125.47, 122.64, 91.12, 78.46, 71.47, 26.40. MS [CI]: *m/z* (%) = 371 (100), 215 (34). (M^+ not observed)





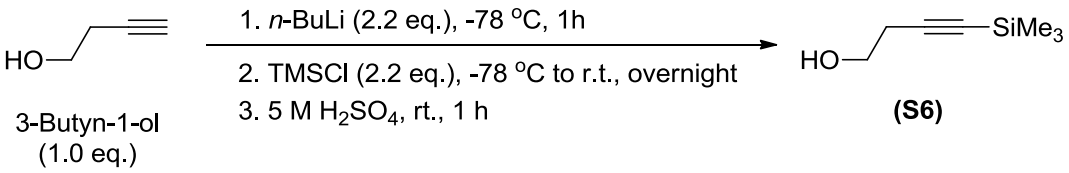
(1o)

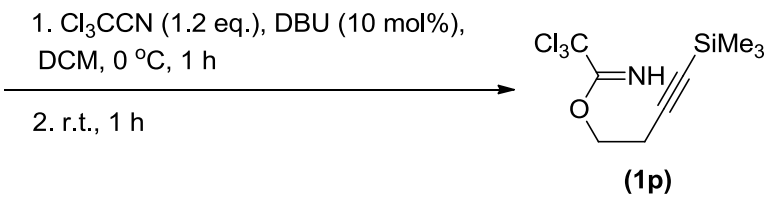
Preparation of 4-phenyl-3-butyn-1-ol (S5): [5]

A mixture of *bis*(triphenylphosphine)palladium(II) dichloride (0.0147 g, 0.02 mmol, 2 mol%), copper(I) iodide (0.0019 g, 0.01 mmol, 1 mol%), iodobenzene (0.11 mL, 1.0 mmol, 1 equiv.) and 3-butyn-1-ol (0.09 mL, 1.2 mmol, 1.2 equiv.) was dissolved in dry Et_3N (6 mL) and refluxed for 2.5 h. The dark brown solution was diluted with an ethyl acetate/water mixture (1:1.25 mL), and the resultant biphasic solution was separated. The organic layer was washed with water and then brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The resulting orange oil was and purified by column chromatography on silica gel to afford 0.86 g (59%) of S5 as a light yellow oil. ^{1}H NMR (400 MHz, CDCl3): δ = 7.48 - 7.40 (m, 2H), 7.36 - 7.27 (m, 3H), 3.84 (t, *J* = 6.3, 2H), 2.72 (t, *J* = 6.3, 2H), 1.82 (br s, 1H).

4-Phenyl-but-3-ynyl 2,2,2-trichloroacetimidate (1o):

A solution of S5 (0.86 g, 5.88 mmol, 1.0 equiv.) and trichloroacetonitrile (0.71 mL, 7.06 mmol, 1.2 equiv.) in CH_2Cl_2 (15 mL) was cooled to 0 °C in an ice bath, and DBU (88 μL, 0.59 mmol, 0.1 equiv.) was added dropwise. The reaction mixture was allowed to stir at 0 °C for 30 min, then warmed to room temperature and stirred for another 1 h. The solvent was evaporated, and the resultant brown oil chromatographed on silica using petroleum ether/ethyl acetate (6:1). 1.59 g (93%) of **1o** was obtained as a light yellow crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.41 - 7.37 (m, 3H), 7.30 - 7.28 (m, 2H), 4.49 (t, *J* = 7.0, 2H), 2.92 (t, *J* = 7.0, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.64, 131.64, 127.96, 123.38, 91.30, 85.04, 82.23, 67.07, 19.47. MS [CI]: *m/z* (%) = 290 (33) $[M+H]^+$.





(1p)

Synthesis of 4-(trimethylsilyl)but-3-yn-1-ol (S6): [5], [6]

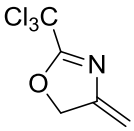
n-BuLi (1.6 M in hexane, 27.5 mL, 44 mmol, 2.2 equiv.) was added dropwise to a solution of 3-butyn-1-ol (1.5 mL, 20 mmol, 1.0 equiv.) in dry THF (25 mL) at -78°C. After stirring for 1 h, the yellow suspension was allowed to warm to room temperature, before cooling down again to -78 °C, whereupon trimethylchlorosilane (5.6 mL, 44 mmol, 2.2 equiv.) was added dropwise. The cooling bath was removed, and the reaction was stirred overnight at room temperature. The reaction was quenched by the dropwise

addition of 5M H_2SO_4 at 0 °C; stirring for 1 h to ensure complete hydrolysis of the TMS-ether. The aqueous layer was then separated and extracted with Et_2O (2 x 10mL). The combined organic layers was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give 1.89 g (66%) of S6 as a light yellow oil, which was used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71 (t, *J* = 6.3, 2H), 2.50 (t, *J* = 6.3 Hz, 2H), 1.74 (s, 1H), 0.16 (s, 9H).

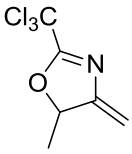
4-(Trimethylsilyl)but-3-ynyl 2,2,2-trichloroacetimidate (1p):
A solution of S6 (1.77 g, 12.4 mmol, 1.0 equiv.) and trichloroacetonitrile (1.50 mL, 14.9 mmol, 1.2 equiv.) in CH_2Cl_2 (30 mL) was cooled to 0 °C in an ice bath and DBU (0.18 mL, 1.24 mmol, 0.1 equiv.) was added dropwise. The reaction mixture was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for another 1 h. The solvent was evaporated, and the resulting brown oil chromatographed on silica using petroleum ether/ethyl acetate (8:1) as eluting solvent. 2.90 g (81%) of **1p** was obtained as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 4.38 (t, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 7.0 Hz, 2H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.59, 101.77, 91.27, 86.75, 66.94, 19.85, -0.02. MS [CI]: *m/z* (%) = 286 (100) $[M+H]^+$.

Synthesis of *bis*(pyridine)silver(I) trifluoromethane sulfonate [Ag(py)$_2$]OTf:
The complex was prepared using the general method published by Lee *et al.*:[7] A mixture of silver(I) trifluoromethanesulfonate (0.12 g, 0.5 mmol) and pyridine (5 mL) was stirred at room temperature overnight. The solvent was then evaporated and the residue dissolved in CH_2Cl_2 (10 mL) and filtered through a plug of Celite. The filtrate was evaporated, and Et_2O (20 mL) added to the residue, to precipitate the desired product as a white solid, which was collected by filtration and dried in vacuo (0.14 g, 69% yield). Spectroscopic data are in accordance with that reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (m, 4 H), 7.82 (m, 2 H), 7.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.01, 138.86, 125.25 ppm. Anal. Calc. for $C_{11}H_{10}AgF_3N_2O_3S$: C, 31.83; H, 2.43; N, 6.75%. Found: C, 31.83; H, 2.37; N, 6.68%.

General procedure for the Ag(I)-catalysed conversion of 1 to 2 or 4:
Substrate **1** (1 equiv.) was dissolved in acetone (2.5 mL per mmol of substrate) at room temperature and [Ag(py)$_2$]OTf (0.1 equiv.) was added. After the prescribed reaction time, the reaction mixture was filtered, and the filtrate concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/ethyl acetate).

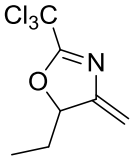


4-Methylene-2-(trichloromethyl)-4,5-dihydrooxazole (2a): [1], [3]
Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) on silica as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39 (td, *J* = 3.3, 1.6, 1H), 5.23 (t, *J* = 3.1, 2H), 4.87 (td, *J* = 3.3, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.55, 153.26, 102.11, 74.42. HRMS (ESI) calcd for $C_5H_4Cl_3NO$ $[M+H]^+$: 199.9437; found 199.9447.



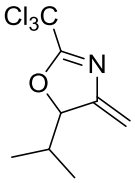
5-Methyl-4-methylene-2-(trichloromethyl)-4,5-dihydrooxazole (2b): [1]

Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46 (qt, *J* = 6.4, 3.0, 1H), 5.35 (dd, *J* = 3.4 1.5, 1H), 4.77-4.76 (m, 1H), 1.57 (d, *J* = 6.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.94, 158.48, 101.81, 83.35, 21.35. HRMS (ESI) calcd for $C_6H_6Cl_3NO$ $[M+H]^+$: 213.9593; found 213.9580.



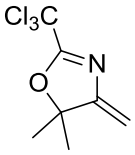
5-Ethyl-4-methylene-2-(trichloromethyl)-4,5-dihydrooxazole (2c):

Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.42-5.39 (m, 2H), 4.76 (t, *J* = 2.0, 1H), 2.05 - 1.95 (m, 1H), 1.81 - 1.71 (m, 1H), 1.01 (t, *J* = 7.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.31, 156.68, 102.06, 87.76, 28.51, 7.61. MS [CI]: *m/z* (%) = 228 (100) $[M+H]^+$.



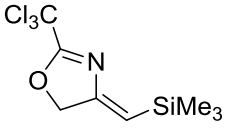
5-(1-Methylethyl)-4-methylene-2-(trichloromethyl)-4,5-dihydrooxazole (2d): [3]

Purified by column chromatography (petroleum ether/ethyl acetate, 10:1) to afford **2d** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.42 (dd, *J* = 1.4, 3.0, 1H), 5.26 (dd, *J* = 3.0, 5.8, 1H), 4.78 - 4.77 (m, 1H), 2.00 (m, 1H), 1.11 (d, *J* = 6.9, 3H), 0.95 (d, *J* = 6.9, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.43, 155.93, 102.61, 91.38, 33.84, 18.07, 14.77. HRMS (ESI) calcd for $C_8H_{10}Cl_3NO$ $[M+H]^+$: 241.9906; found 241.9911.



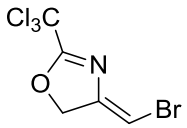
5,5-Dimethyl-4-methylene-2-(trichloromethyl)-4,5-dihydrooxazole (2e):

Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) to afford **2e** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (d, *J* = 1.5, 1H), 4.71 (d, *J* = 1.5, 1H), 1.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.27, 162.03, 100.86, 91.79, 27.74. HRMS (ESI) calcd for $C_7H_8Cl_3NO$ $[M+H]^+$: 229.9720; found 229.9730.

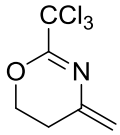


(*Z*)-4-Trimethylsilylmethylene-2-(trichloromethyl)-4,5-dihydrooxazole (2g):

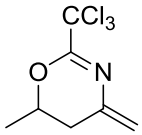
Purified by column chromatography (petroleum ether/ethyl acetate, 10:1) to afford **2g** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (t, *J* = 2.6, 1H), 5.14 (d, *J* = 2.6, 2H), 0.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.45, 159.23, 116.24, 75.65, -0.23. HRMS (ESI) calcd for $C_8H_{12}Cl_3NOSi$ $[M]^+$: 272.9724; found 272.9844.



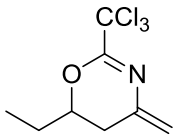
(*Z*)-4-Bromomethylene-2-(trichloromethyl)-4,5-dihydrooxazole (2h):
Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.92 (t, *J* = 2.8, 1H), 5.24 (d, *J* = 2.8, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.74, 149.81, 92.39, 74.79. HRMS (ESI) calcd for $C_5H_3BrCl_3NO$ $[M+H]^+$: 279.8521; found 279.8533.



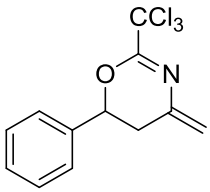
2-(Trichloromethyl)-4-methylene-5,6-dihydro-4*H*-1,3-oxazine (4a): [3]
Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.29 (s, 1H), 4.86 (s, 1H), 4.47 - 4.44 (m, 2H), 2.64 - 2.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.74, 140.99, 111.47, 67.40, 26.21. HRMS (ESI) calcd for $C_6H_6Cl_3NO$ $[M+H]^+$: 215.9564; found 215.9571.



2-(Trichloromethyl)-4-methylene-6-methyl-5,6-dihydro-1,3-oxazine (4b):
Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (s, 1H), 4.85 (s, 1H), 4.55 (dqd, *J* = 8.5, 6.4, 3.8, 1H), 2.65 (dd, *J* = 15.1, 3.8, 1H), 2.32 (ddt, *J* = 15.1, 8.5, 1.1, 1H), 1.42 (d, *J* = 6.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.91, 141.19, 111.76, 74.41, 32.98, 19.96. HRMS (ESI) calcd for $C_7H_8Cl_3NO$ $[M+H]^+$: 227.9750; found 227.9752.

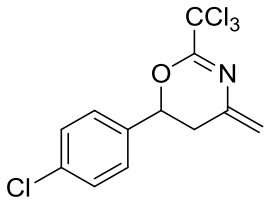


2-(Trichloromethyl)-4-methylene-6-ethyl-5,6-dihydro-1,3-oxazine (4c):
Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (s, 1H), 4.84 (s, 1H), 4.31 (dddd, *J* = 8.5, 7.6, 5.5, 3.9, 1H), 2.62 (dd, *J* = 15.1, 3.9, 1H), 2.34 (ddt, *J* = 15.1, 8.5, 1.5, 1H), 1.79-1.67 (m, 2H), 1.04 (t, *J* = 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.03, 141.38, 111.56, 79.25, 30.99, 27.23, 9.07. HRMS (ESI) calcd for $C_8H_{10}Cl_3NO$ $[M+H]^+$: 243.9877; found 243.9888.



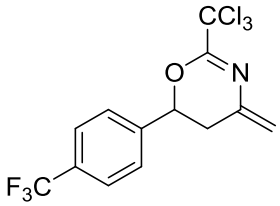
2-(Trichloromethyl)-4-methylene-6-phenyl-5,6-dihydro-1,3-oxazine (4d): [3]

Purified by column chromatography (petroleum ether/ethyl acetate, 5:1) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 - 7.37 (m, 5H), 5.38 (d, *J* = 1.7, 1H), 5.35 (dd, *J* = 10.6, 3.5, 1H), 4.92 (d, *J* = 1.7, 1H), 2.87 (dd, *J* = 15.2, 3.5, 1H), 2.62 (ddt, *J* = 15.2, 10.6, 1.7, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.20, 141.41, 138.23, 128.88, 125.74, 112.04, 92.01, 79.22, 34.08. HRMS (ESI) calcd for $C_{12}H_{10}Cl_3NO$ $[M+H]^+$: 289.9906; found 289.9894.



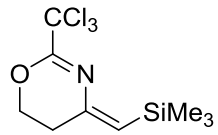
2-(Trichloromethyl)-4-methylene-6-(4-chlorophenyl)-5,6-dihydro-1,3-oxazine (4e): [3]

Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.38 (m, 2H), 7.33 - 7.30 (m, 2H), 5.39 (d, *J* = 1.6, 1H), 5.33 (dd, *J* = 10.4, 3.6, 1H), 4.93 (d, *J* = 1.6, 1H), 2.86 (dd, *J* = 15.2, 3.6 Hz, 1H), 2.59 (ddt, *J* = 15.2, 10.4, 1.6, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.88, 140.94, 136.69, 134.77, 129.11, 127.16, 112.44, 91.87, 78.43, 33.85. HRMS (ESI) calcd for $C_{12}H_9Cl_4NO$ $[M+H]^+$: 325.9487; found 325.9491.



2-(Trichloromethyl)-4-methylene-6-(4-trifluoromethylphenyl)-5,6-dihydro-1,3-oxazine (4f):

Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.2, 2H), 7.51 (d, *J* = 8.2, 2H), 5.44 - 5.40 (m, 2H), 4.95 (d, *J* = 1.7, 1H), 2.91 (dd, *J* = 15.2, 3.7 Hz, 1H), 2.60 (ddt, *J* = 15.2, 10.6, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.66, 142.12, 140.62, 131.04 (q, *J* = 33.0 Hz), 126.01, 125.94, 125.91, 125.20, 122.50, 112.72, 91.79, 78.28, 33.87. HRMS (ESI) calcd for $C_{13}H_9Cl_3F_3NO$ $[M+H]^+$: 357.9780; found 357.9776.



2-(Trichloromethyl)-4-(trimethylsilyl)methylene-5,6-dihydro-1,3-oxazine (4h):

Purified by column chromatography (petroleum ether/ethyl acetate, 8:1) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30 (t, *J* = 1.1 Hz, 1H), 4.44 (t, *J* = 6.1 Hz, 2H), 2.61 (td, *J* = 6.1, 1.1 Hz, 2H), 0.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.32, 146.94, 127.13, 92.39, 67.64, 28.84, -0.14. HRMS (ESI) calcd for $C_9H_{14}Cl_3NOSi$ $[M+H]^+$: 285.9988; found 285.9994.

References

[1] A. S. K. Hashmi, M. Rudolph, S. Schymura, J. Visus and W. Frey *Eur. J. Org. Chem.*, 2006, 4905–4909.

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[7] C. Y. Chen, J. Y. Zeng and H. M. Lee, *Inorg. Chim. Acta*, 2007, **360**, 21–30.

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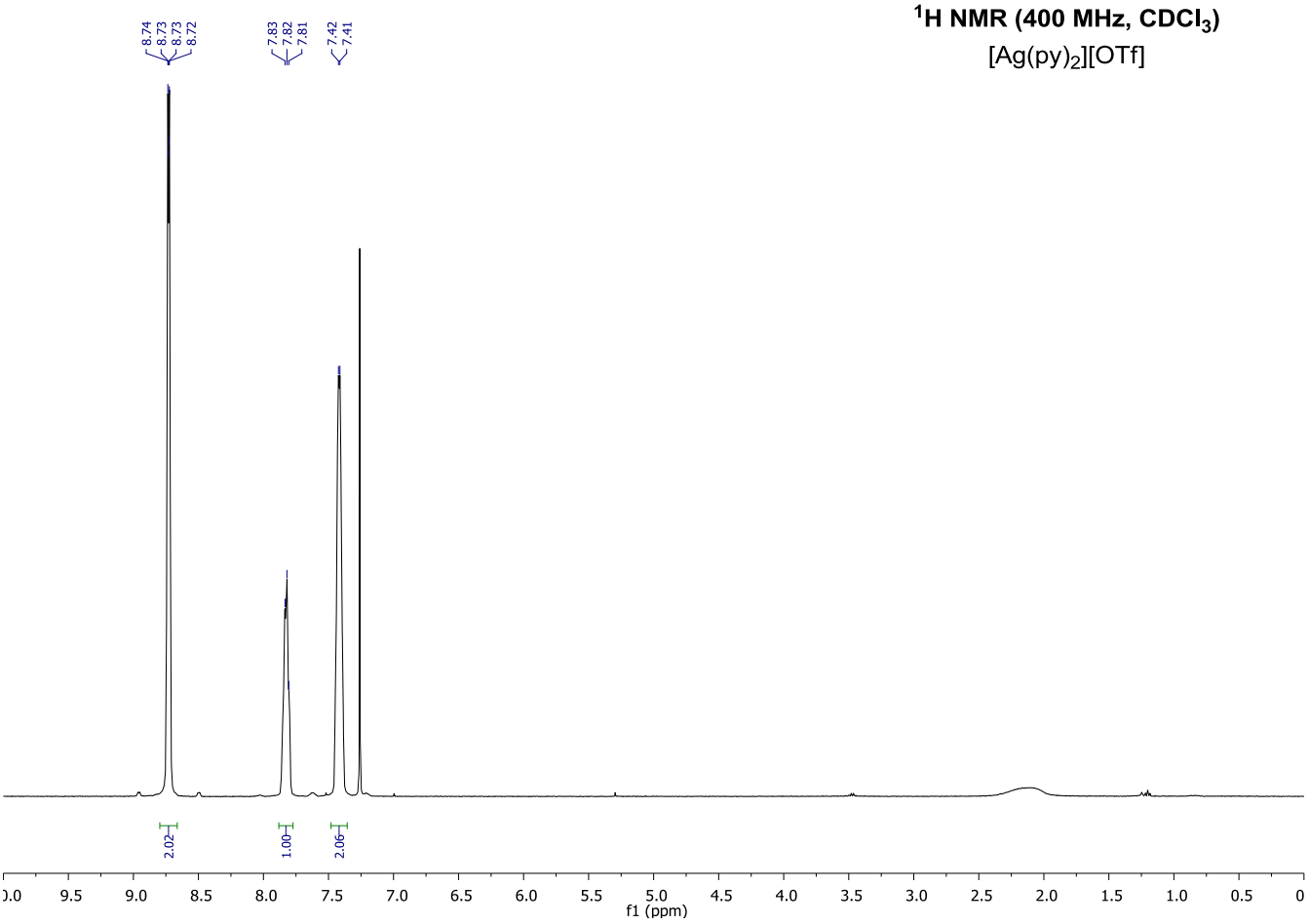
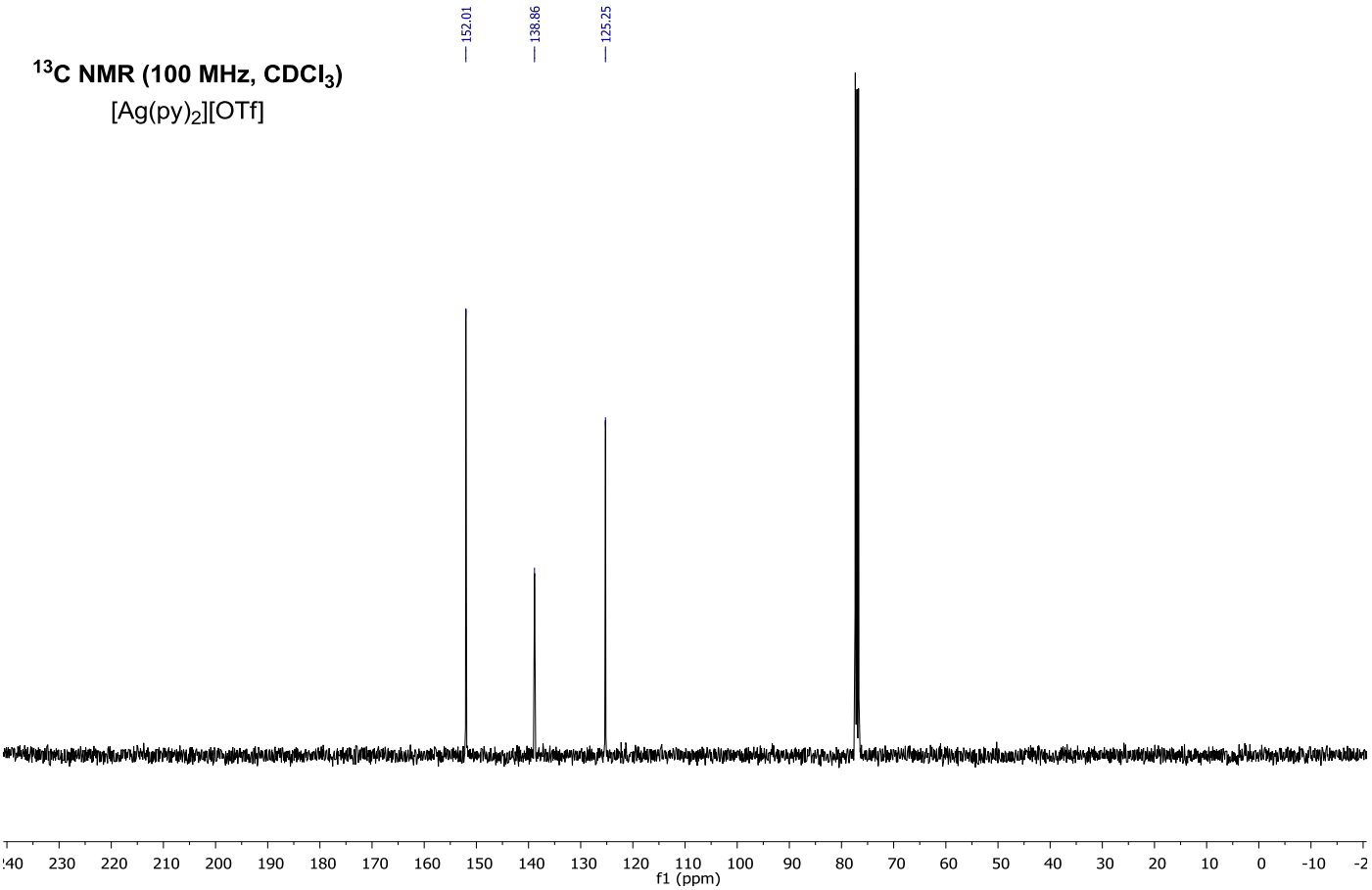
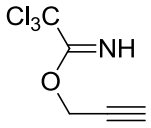
^{1}H NMR (400 MHz, $CDCl_3$)
$[Ag(py)_2][OTf]$



^{13}C NMR (100 MHz, $CDCl_3$)
$[Ag(py)_2][OTf]$

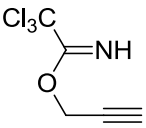


^{1}H NMR (400 MHz, $CDCl_3$)



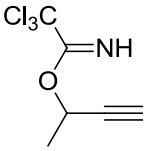
(1a)

^{13}C NMR (100 MHz, $CDCl_3$)



(1a)

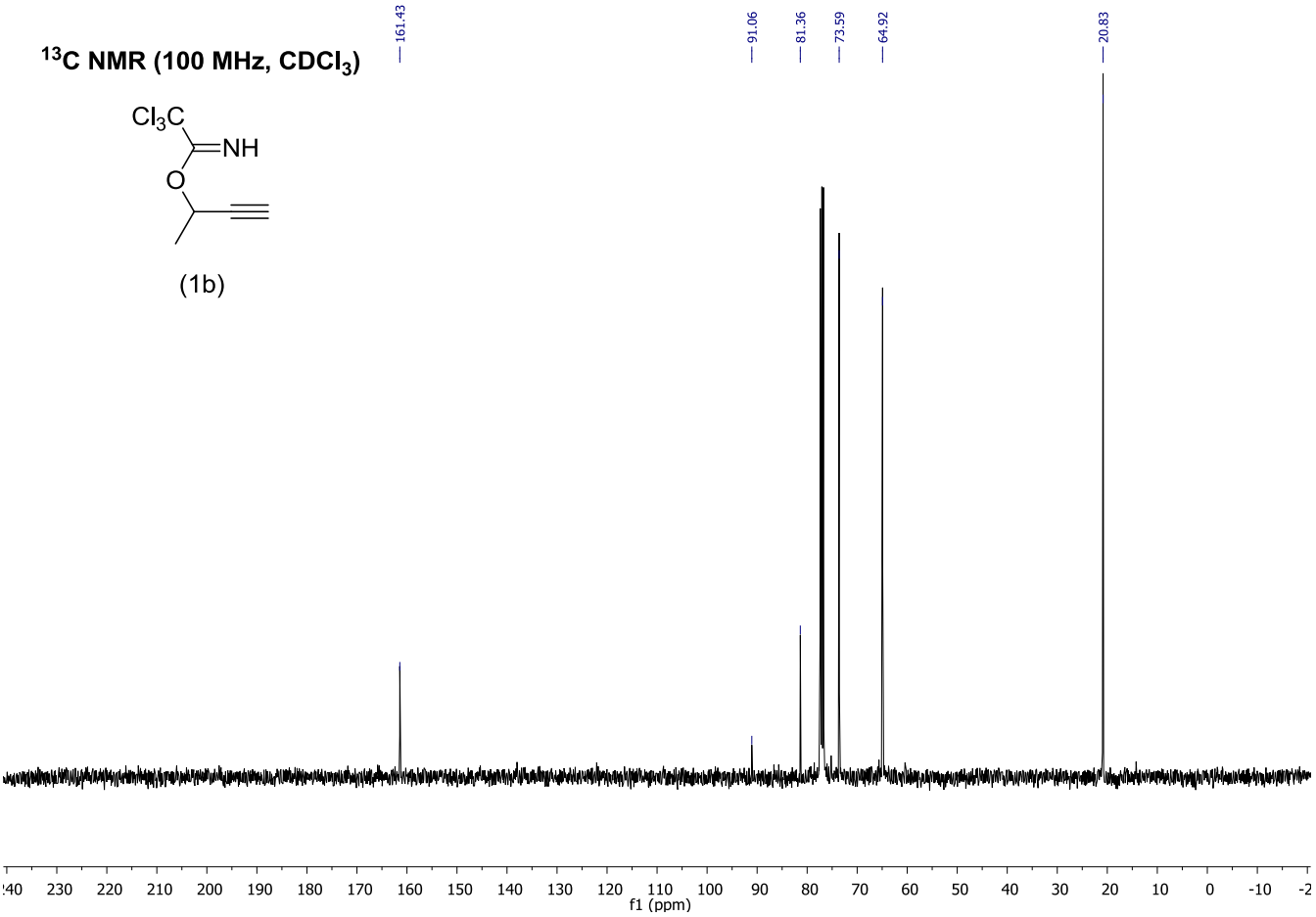
^{1}H NMR (400 MHz, $CDCl_3$)



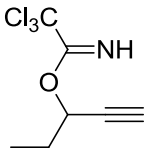
(1b)

^{13}C NMR (100 MHz, $CDCl_3$)

(1b)

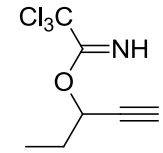


^{1}H NMR (400 MHz, $CDCl_3$)



(1c)

^{13}C NMR (100 MHz, $CDCl_3$)



(1c)

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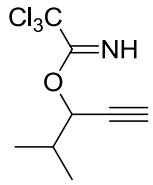

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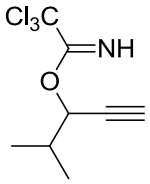
^{13}C NMR (100 MHz, $CDCl_3$)



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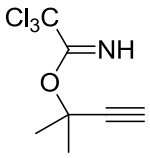
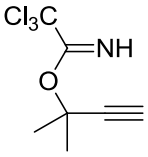
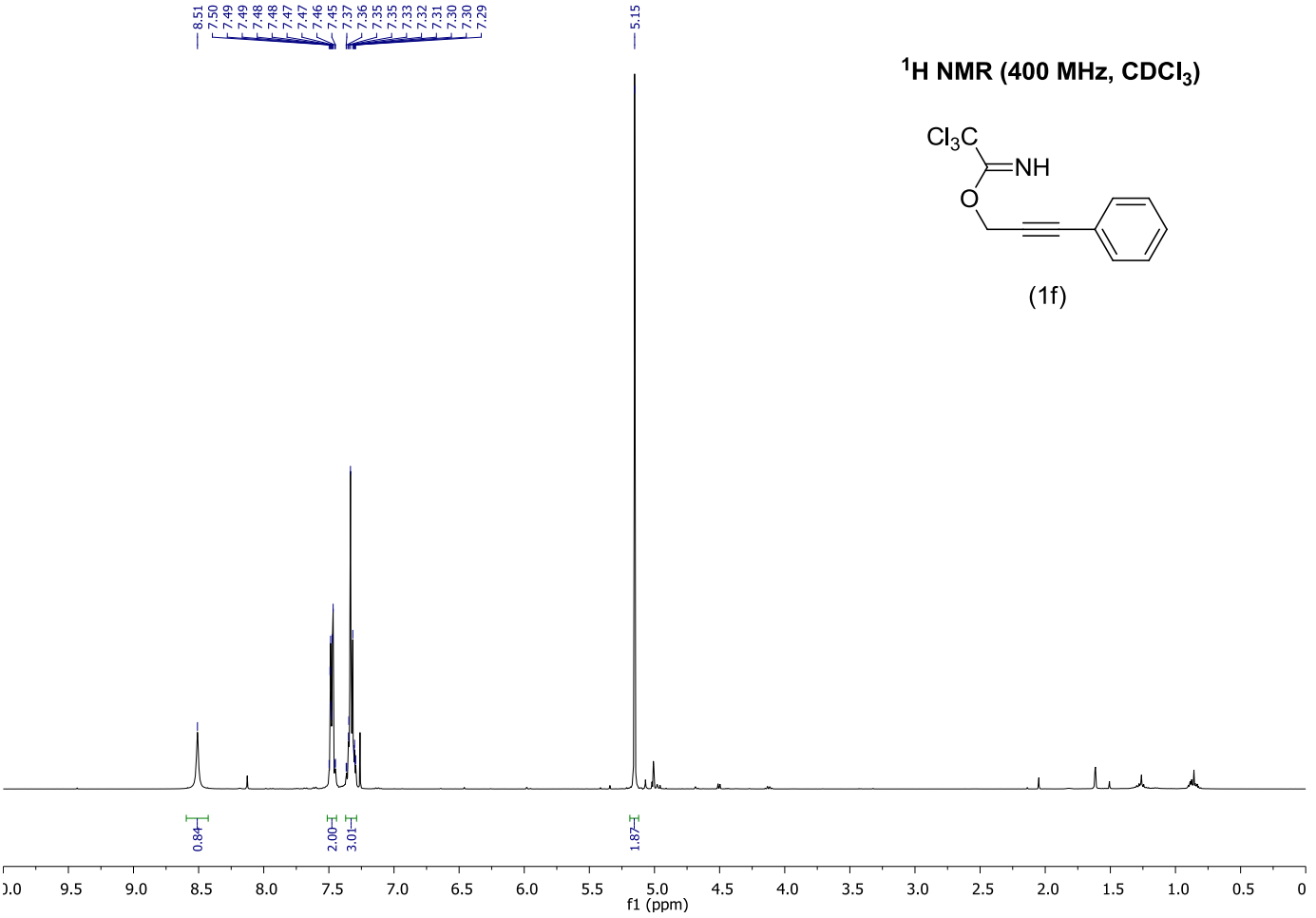


(1e)

^{13}C NMR (100 MHz, $CDCl_3$)



(1e)



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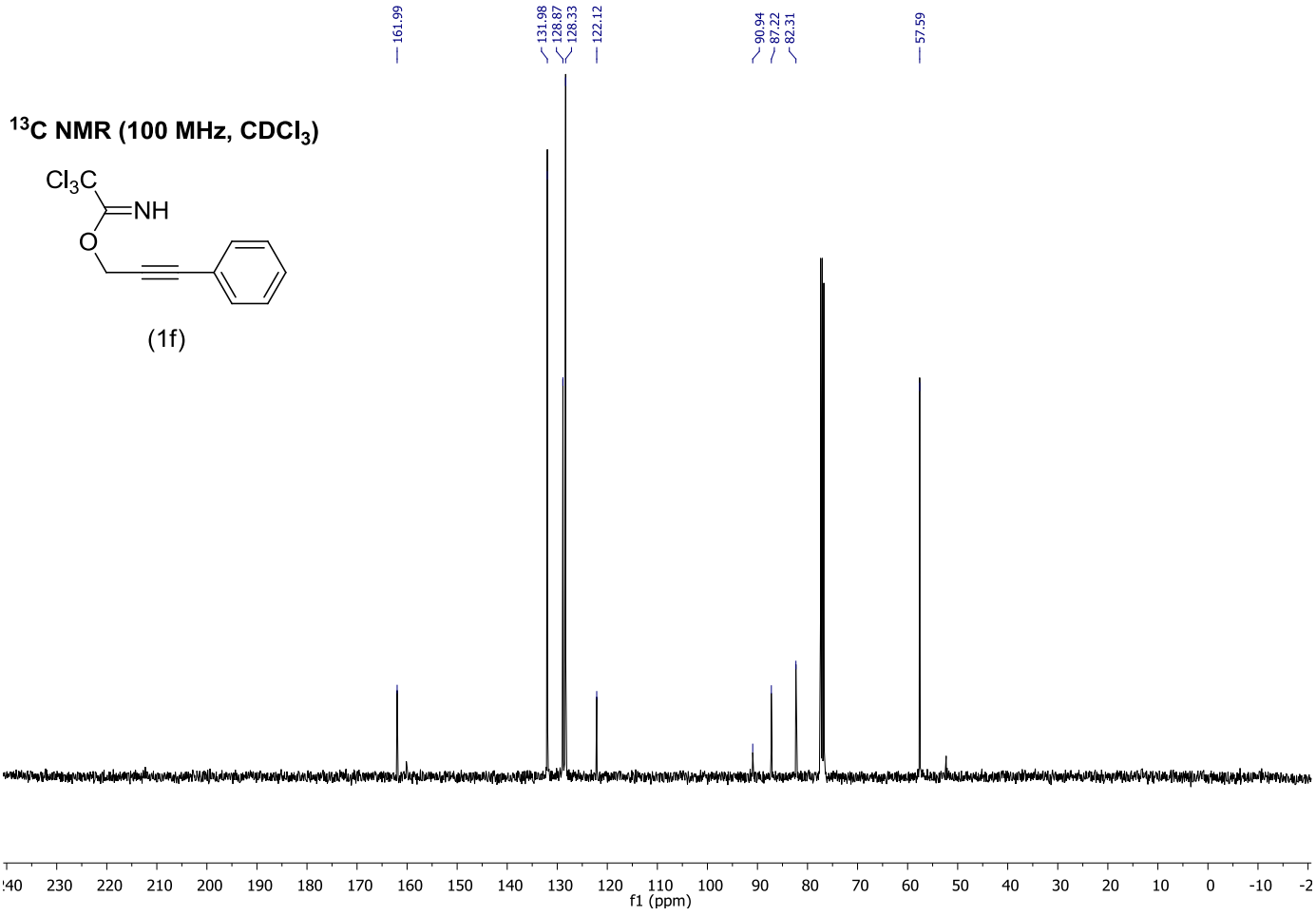
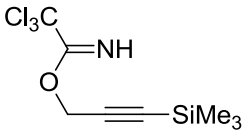
(1f)



^{13}C NMR (100 MHz, $CDCl_3$)

(1f)

^{1}H NMR (400 MHz, $CDCl_3$)



(1g)

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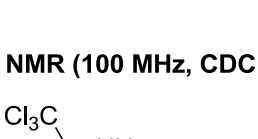

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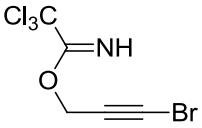

(1h)

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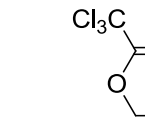

(1h)

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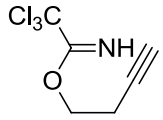

(1i)

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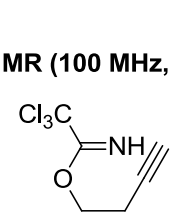

(1i)

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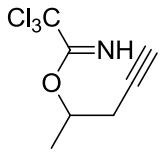

(1j)

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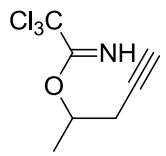

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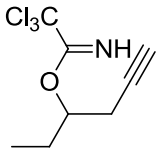

(1k)

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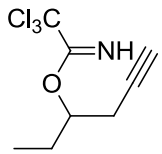

(1k)

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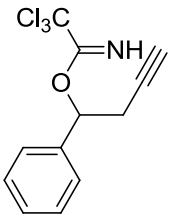
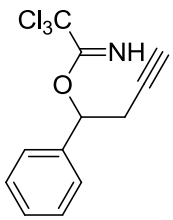
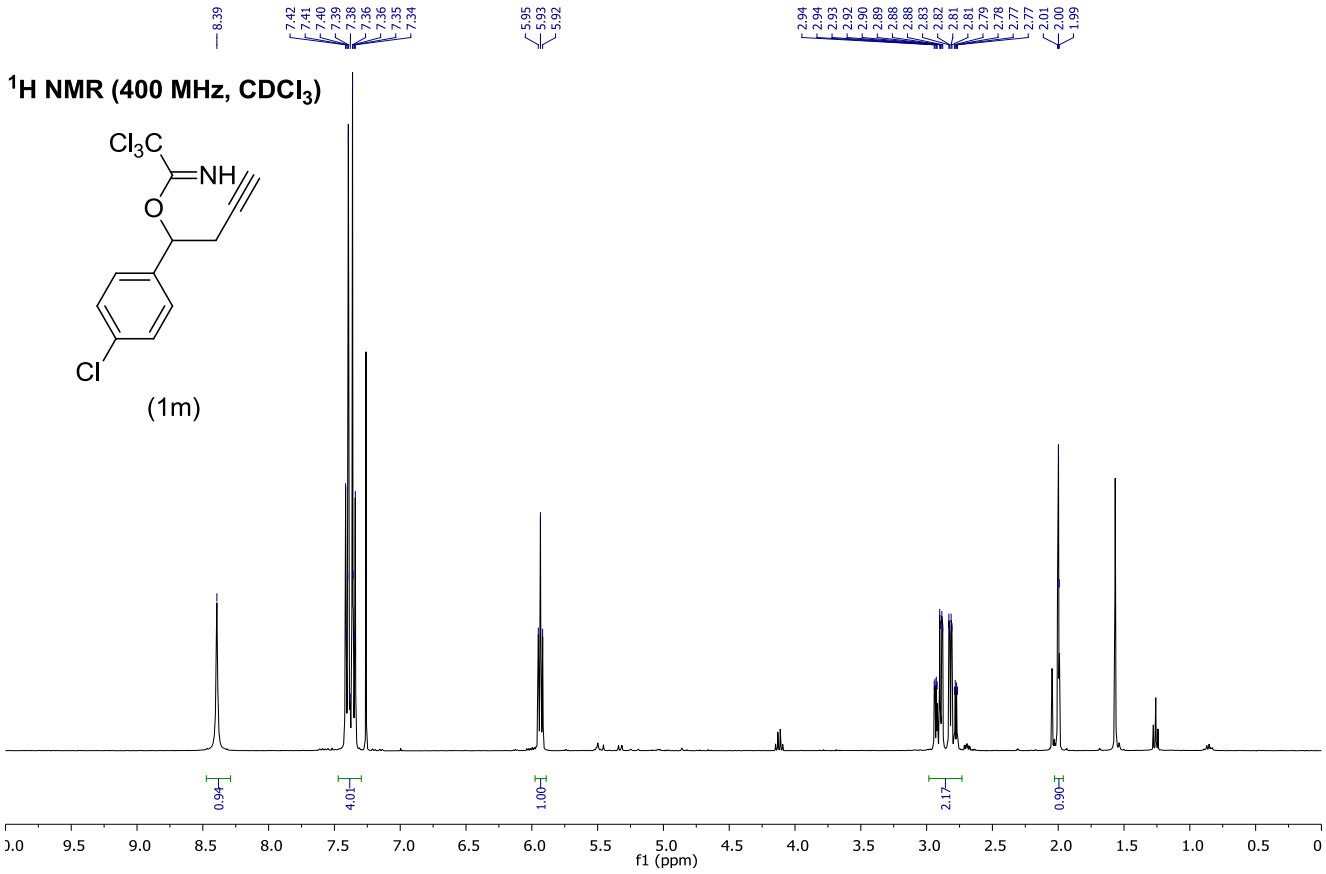


(1l)

^{13}C NMR (100 MHz, $CDCl_3$)



(1l)



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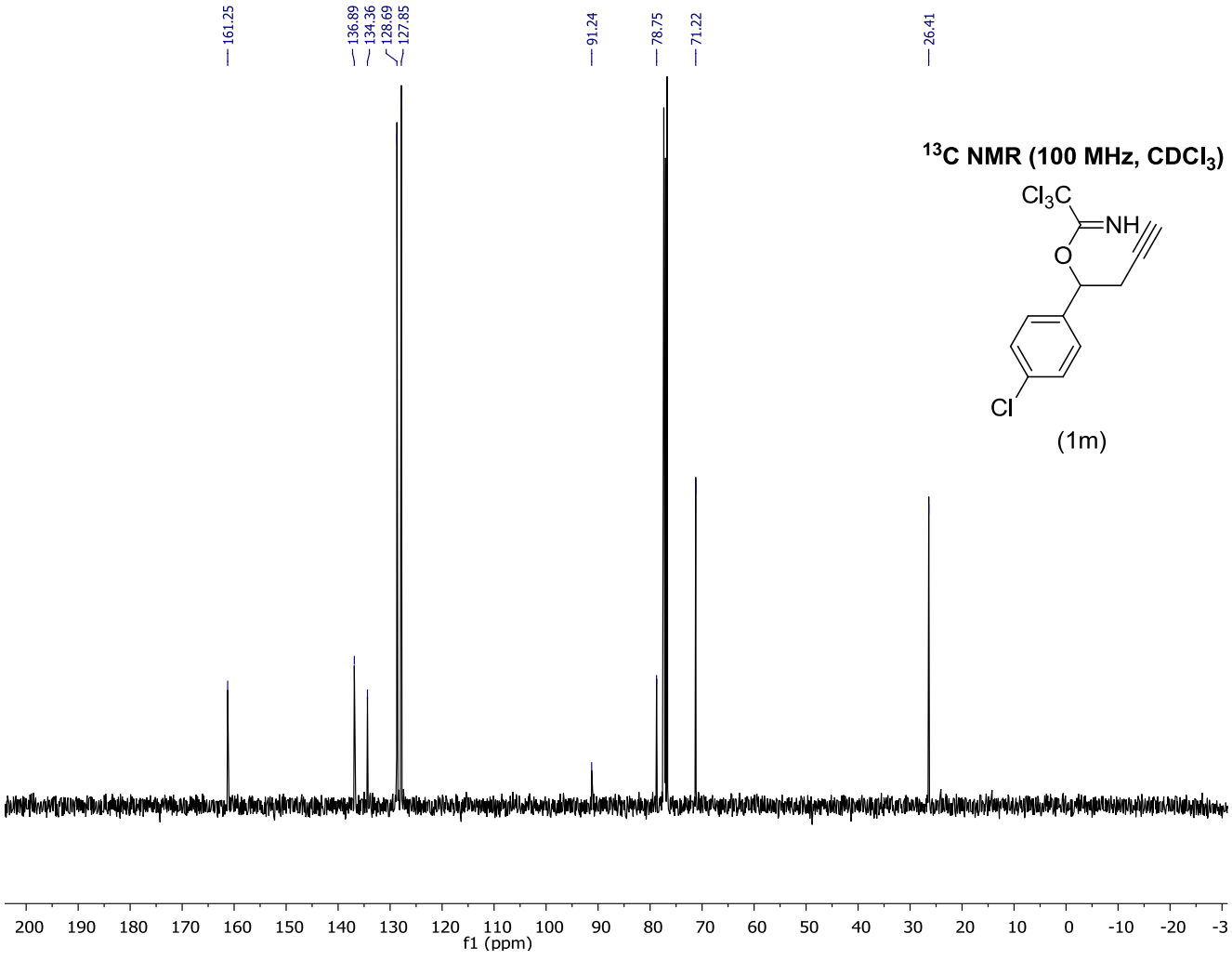
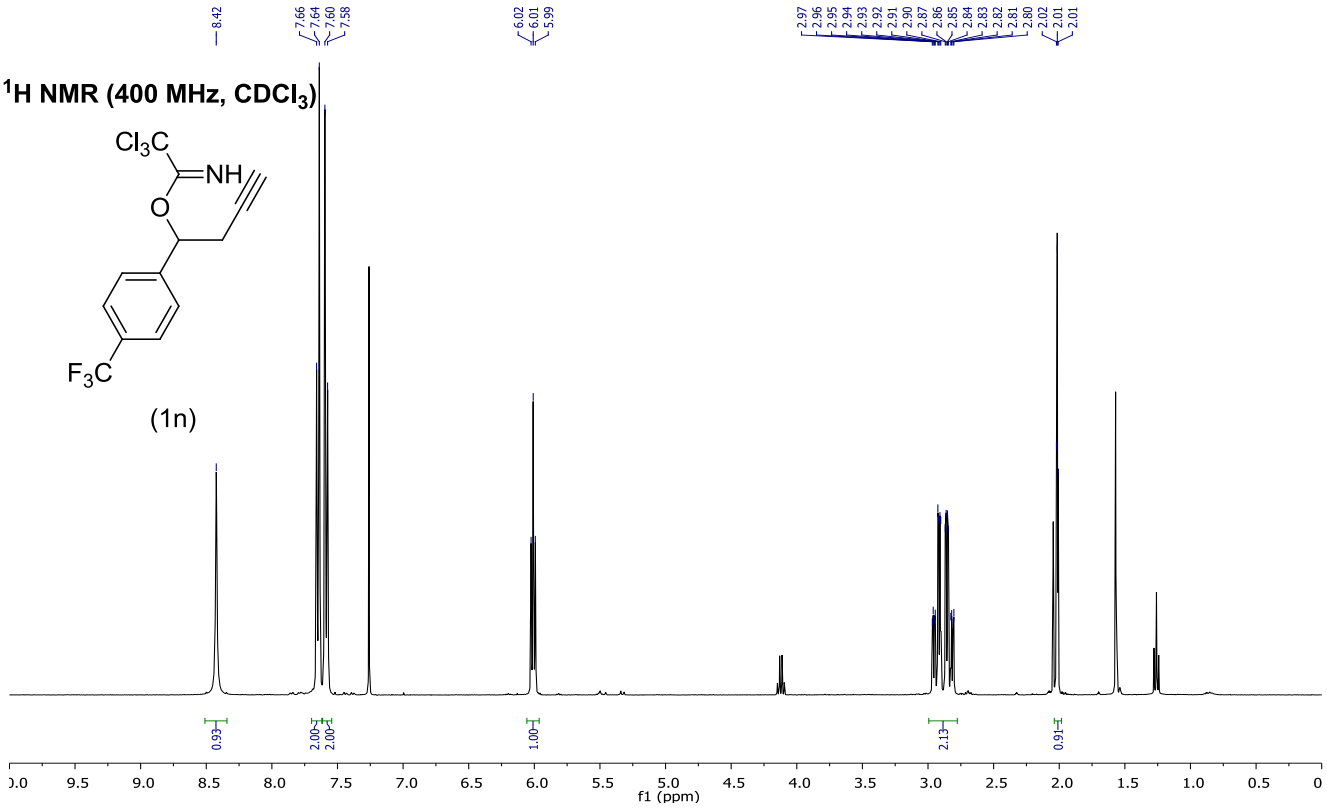
(1m)



^{13}C NMR (100 MHz, $CDCl_3$)

(1m)

^{1}H NMR (400 MHz, $CDCl_3$)



(1n)

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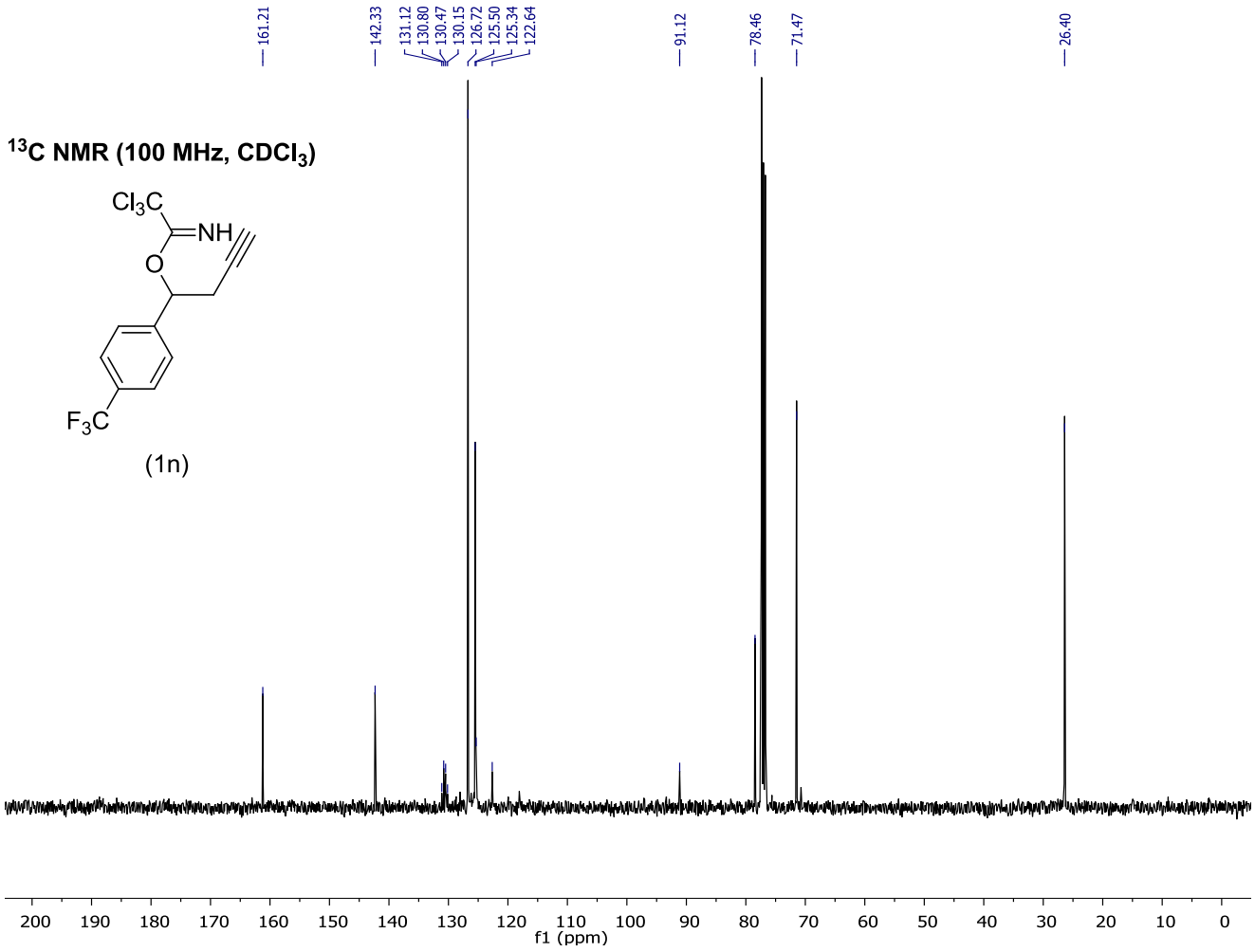

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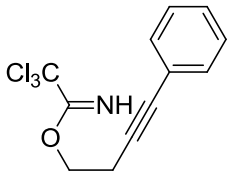

(1o)

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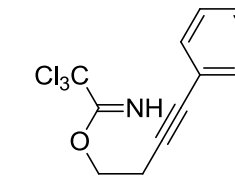

(1o)

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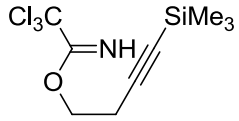
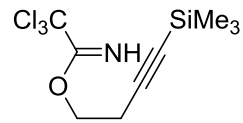


(1p)

^{13}C NMR (100 MHz, $CDCl_3$)



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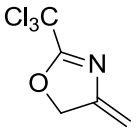
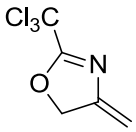


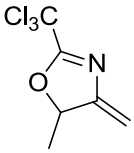
(2a)

^{13}C NMR (100 MHz, $CDCl_3$)



(2a)

^{1}H NMR (400 MHz, $CDCl_3$)



(2b)

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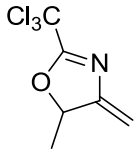

(2b)

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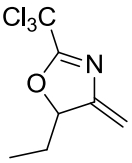

(2c)

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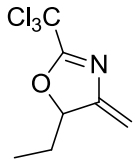

(2c)

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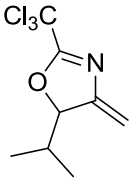

(2d)

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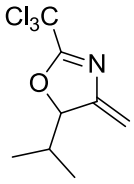

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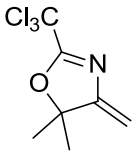

(2e)

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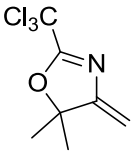

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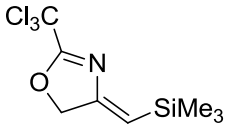
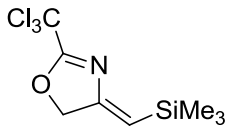


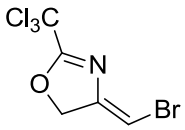
(2g)

^{13}C NMR (100 MHz, $CDCl_3$)



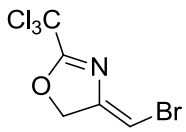
(2g)

^{1}H NMR (400 MHz, $CDCl_3$)



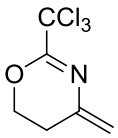
(2h)

^{13}C NMR (100 MHz, $CDCl_3$)

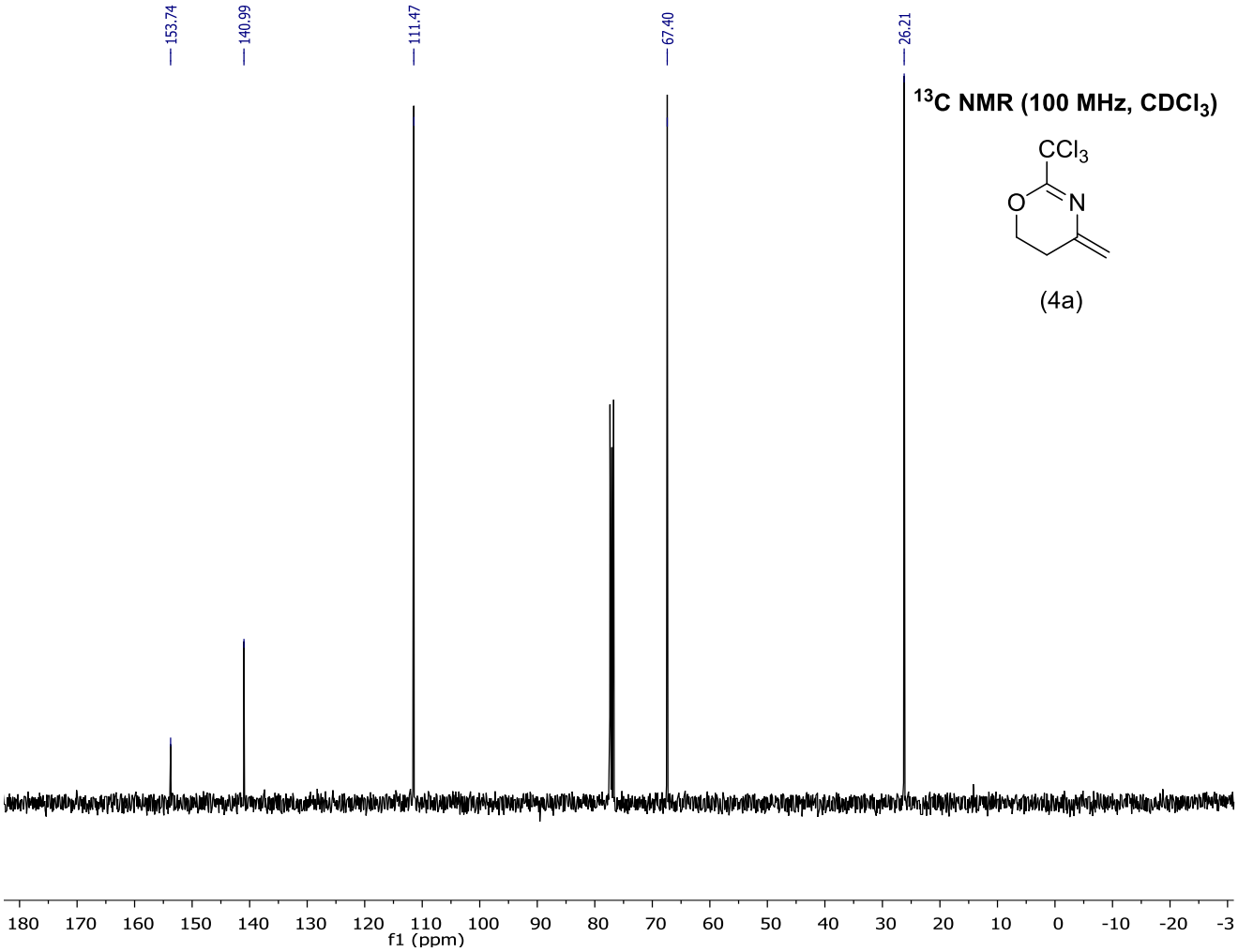


(2h)

^{1}H NMR (400 MHz, $CDCl_3$)



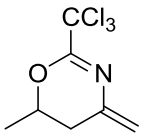
(4a)



^{13}C NMR (100 MHz, $CDCl_3$)

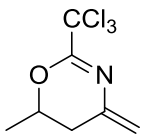
(4a)

^{1}H NMR (400 MHz, $CDCl_3$)



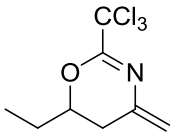
(4b)

^{13}C NMR (100 MHz, $CDCl_3$)



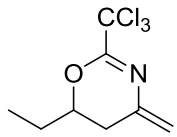
(4b)

^{1}H NMR (400 MHz, $CDCl_3$)

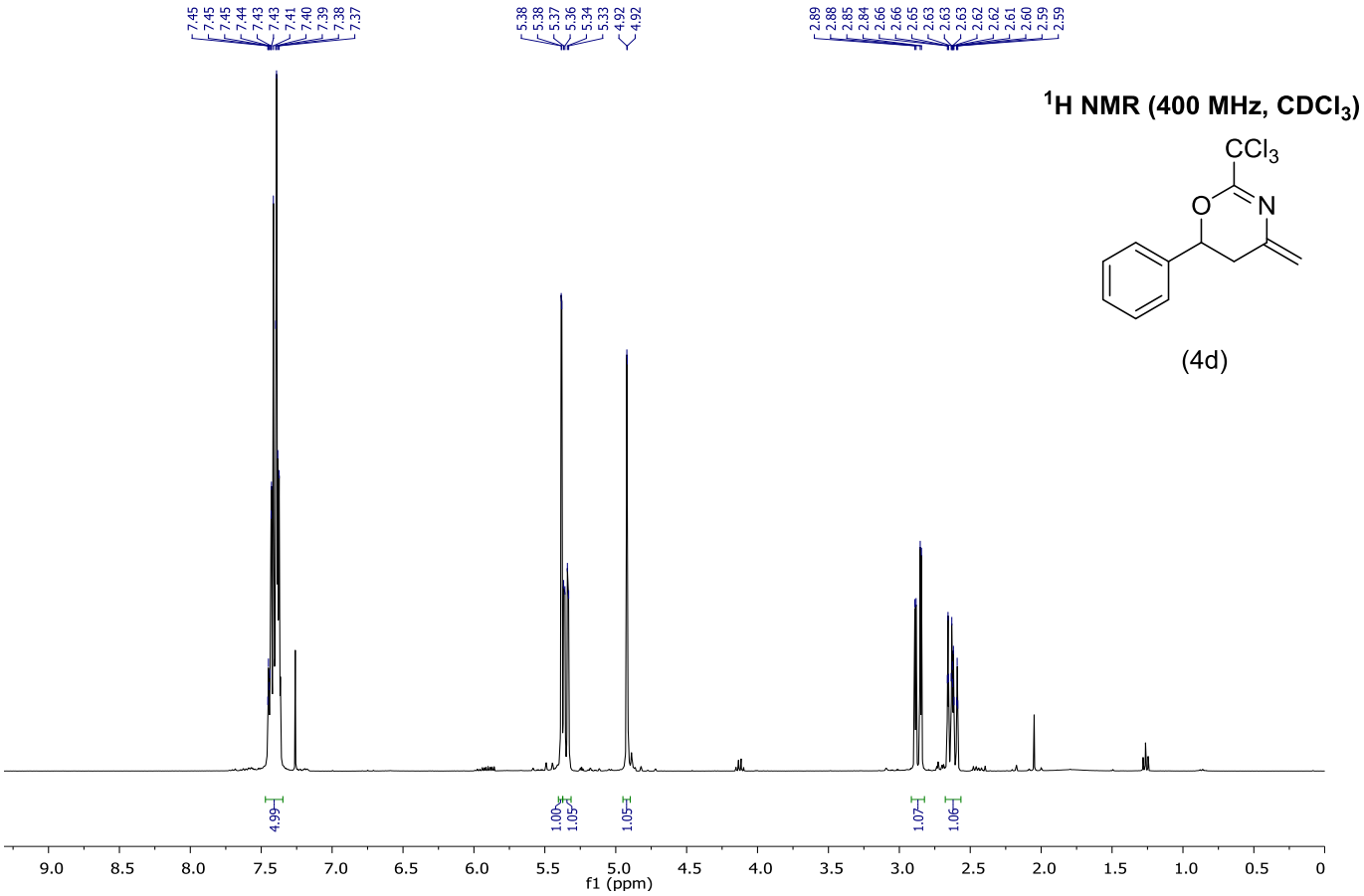


(4c)

^{13}C NMR (100 MHz, $CDCl_3$)

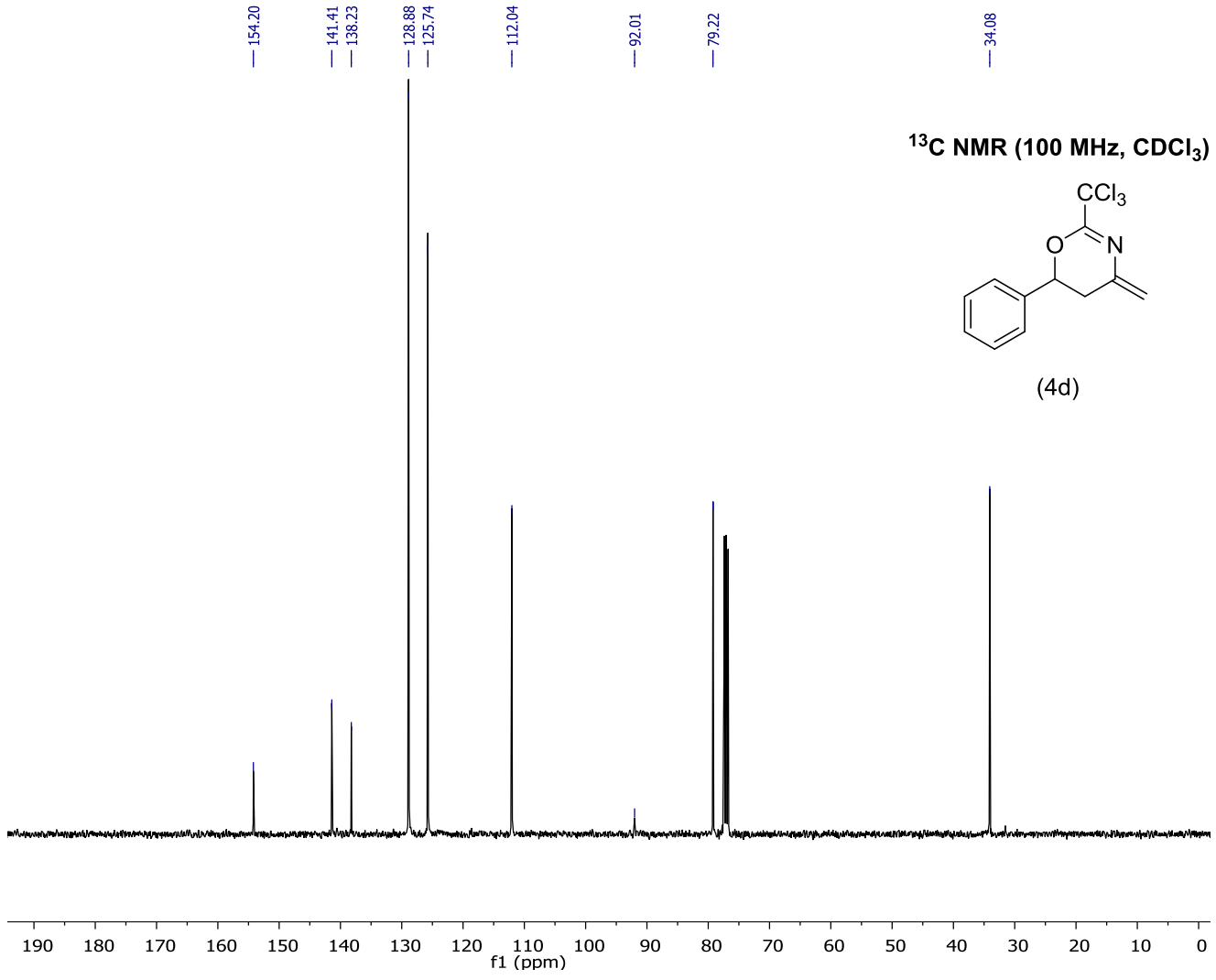


(4c)



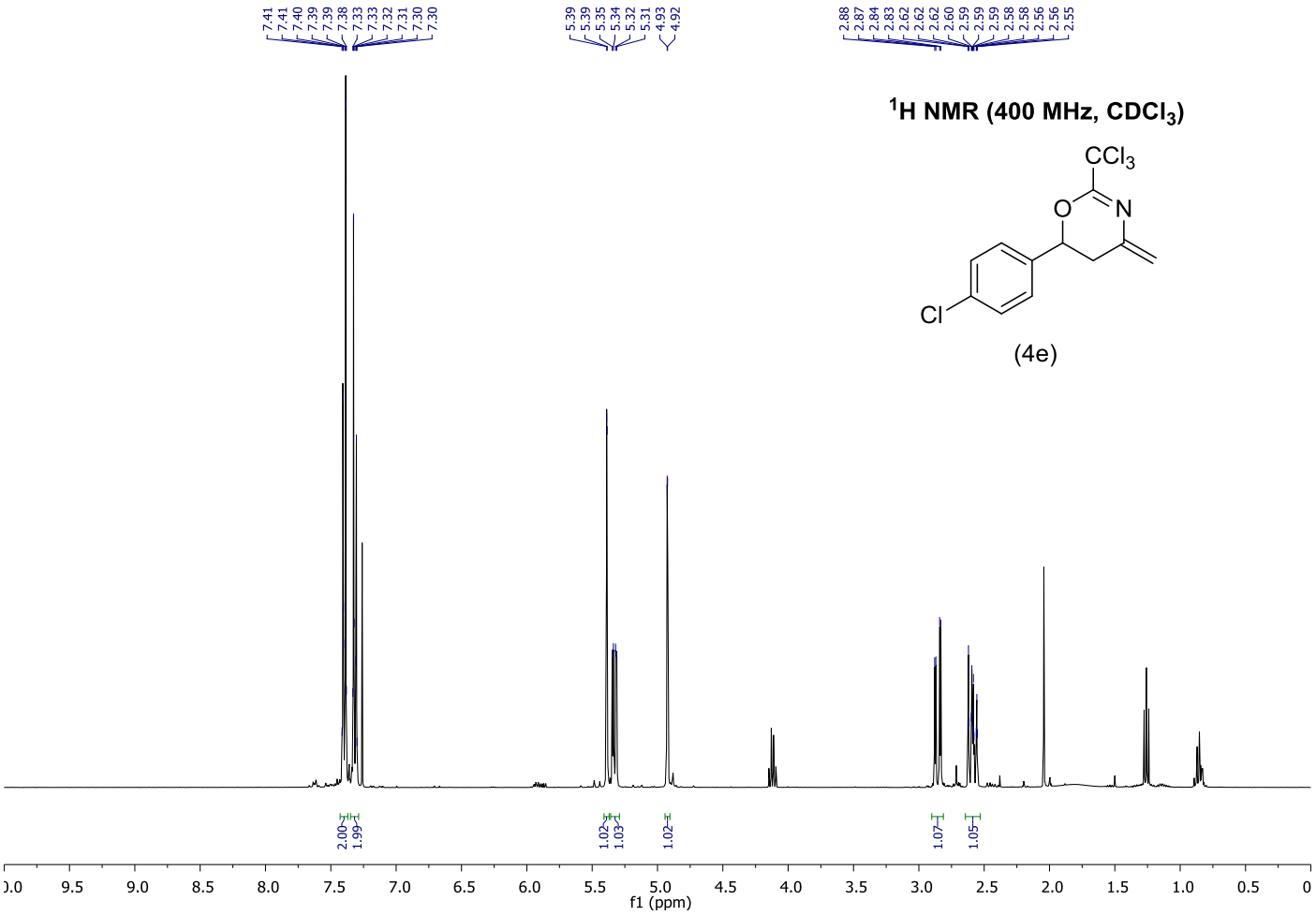
^{1}H NMR (400 MHz, $CDCl_3$)

(4d)



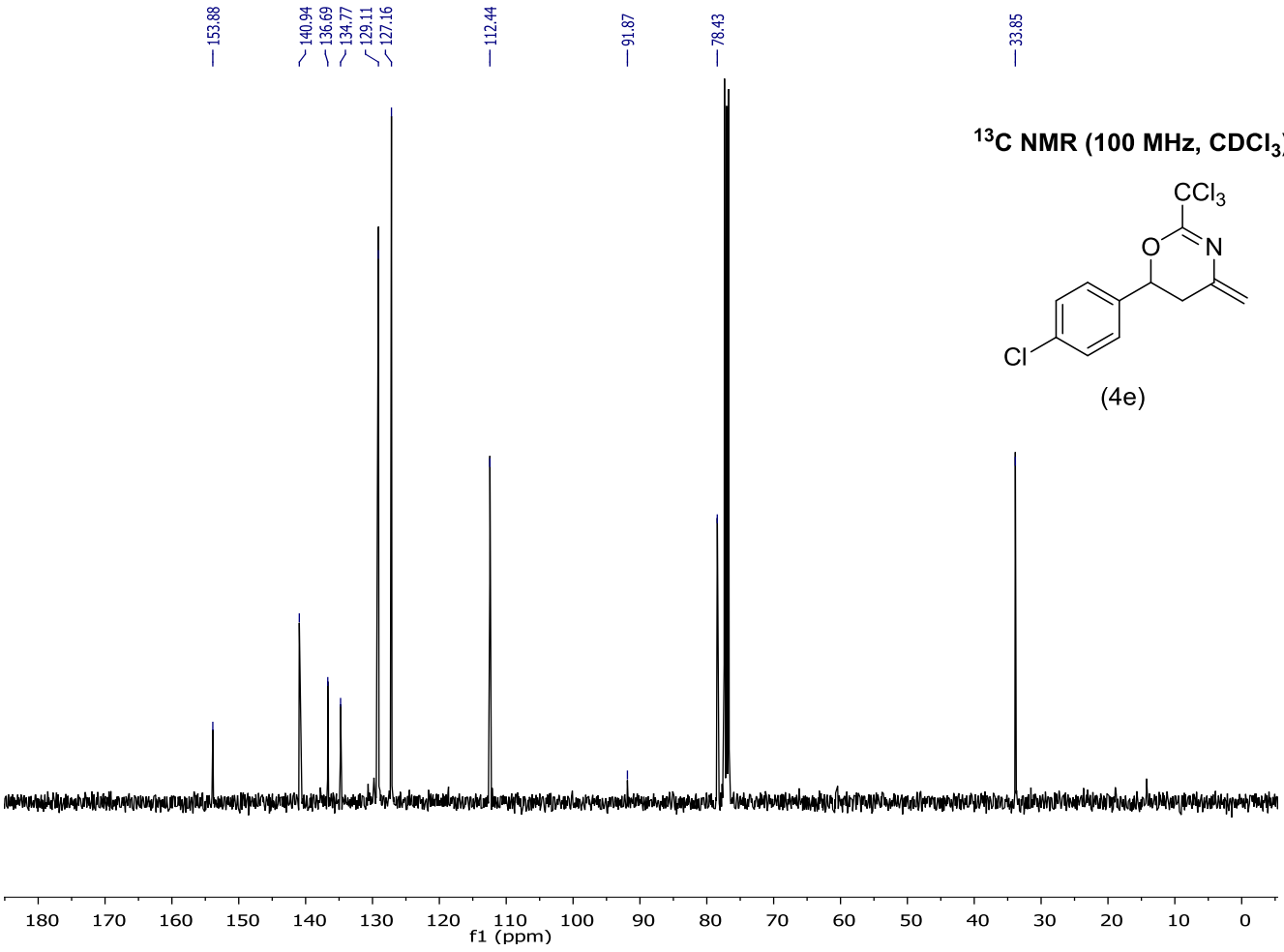
^{13}C NMR (100 MHz, $CDCl_3$)

(4d)



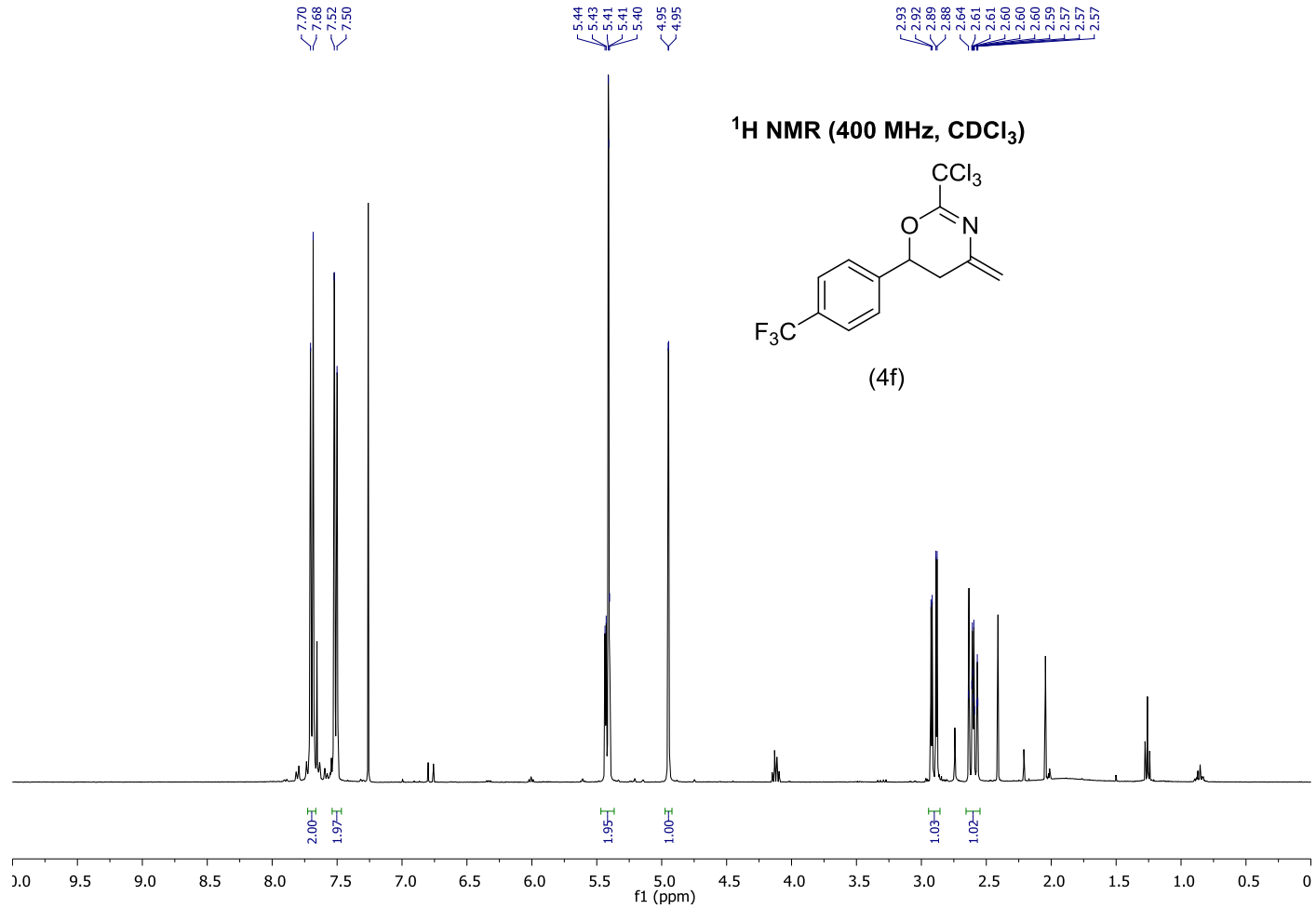
^{1}H NMR (400 MHz, $CDCl_3$)

(4e)



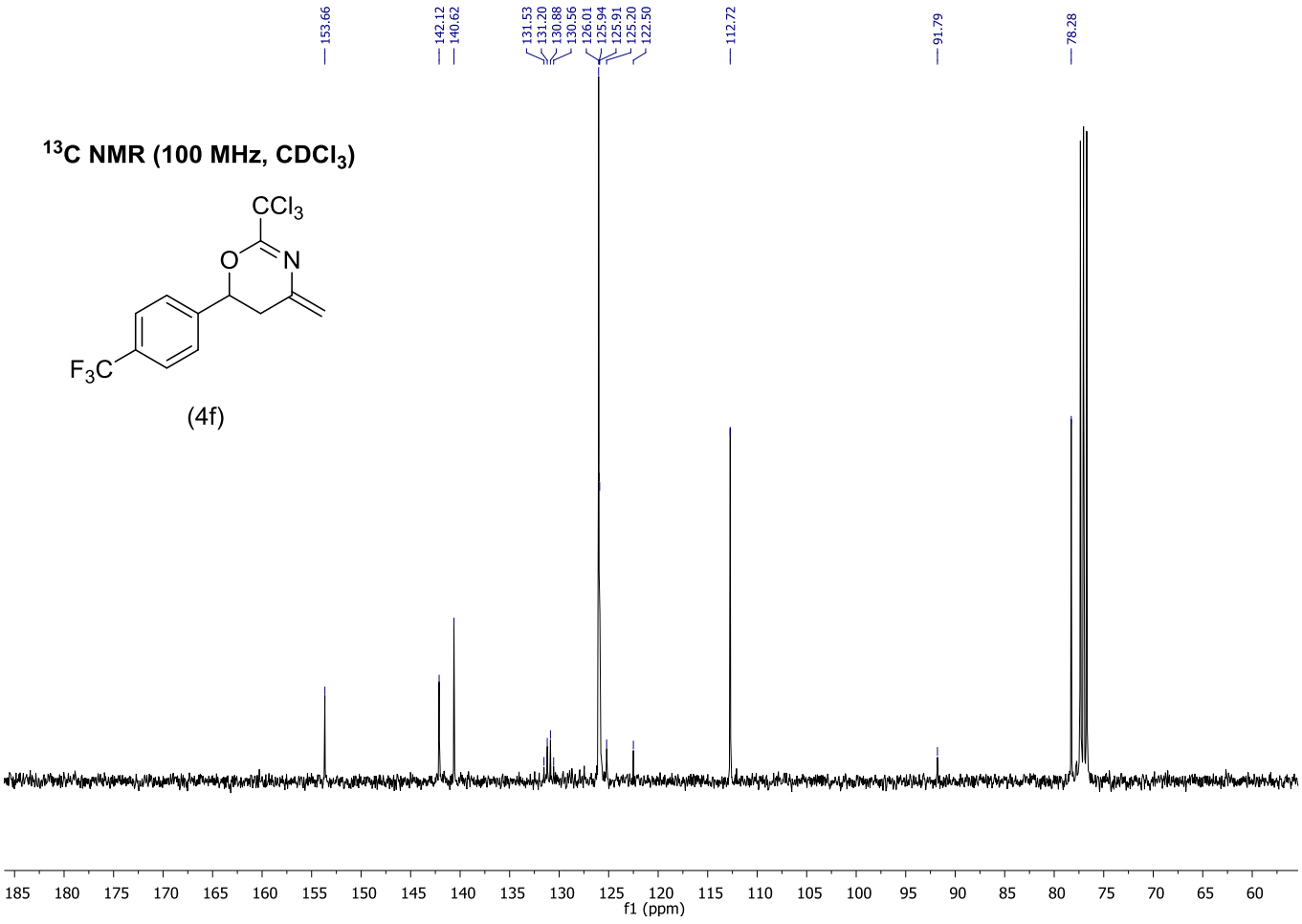
^{13}C NMR (100 MHz, $CDCl_3$)

(4e)



^{1}H NMR (400 MHz, $CDCl_3$)

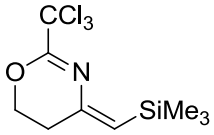
(4f)



^{13}C NMR (100 MHz, $CDCl_3$)

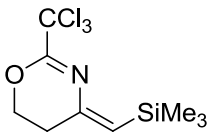
(4f)

^{1}H NMR (400 MHz, $CDCl_3$)

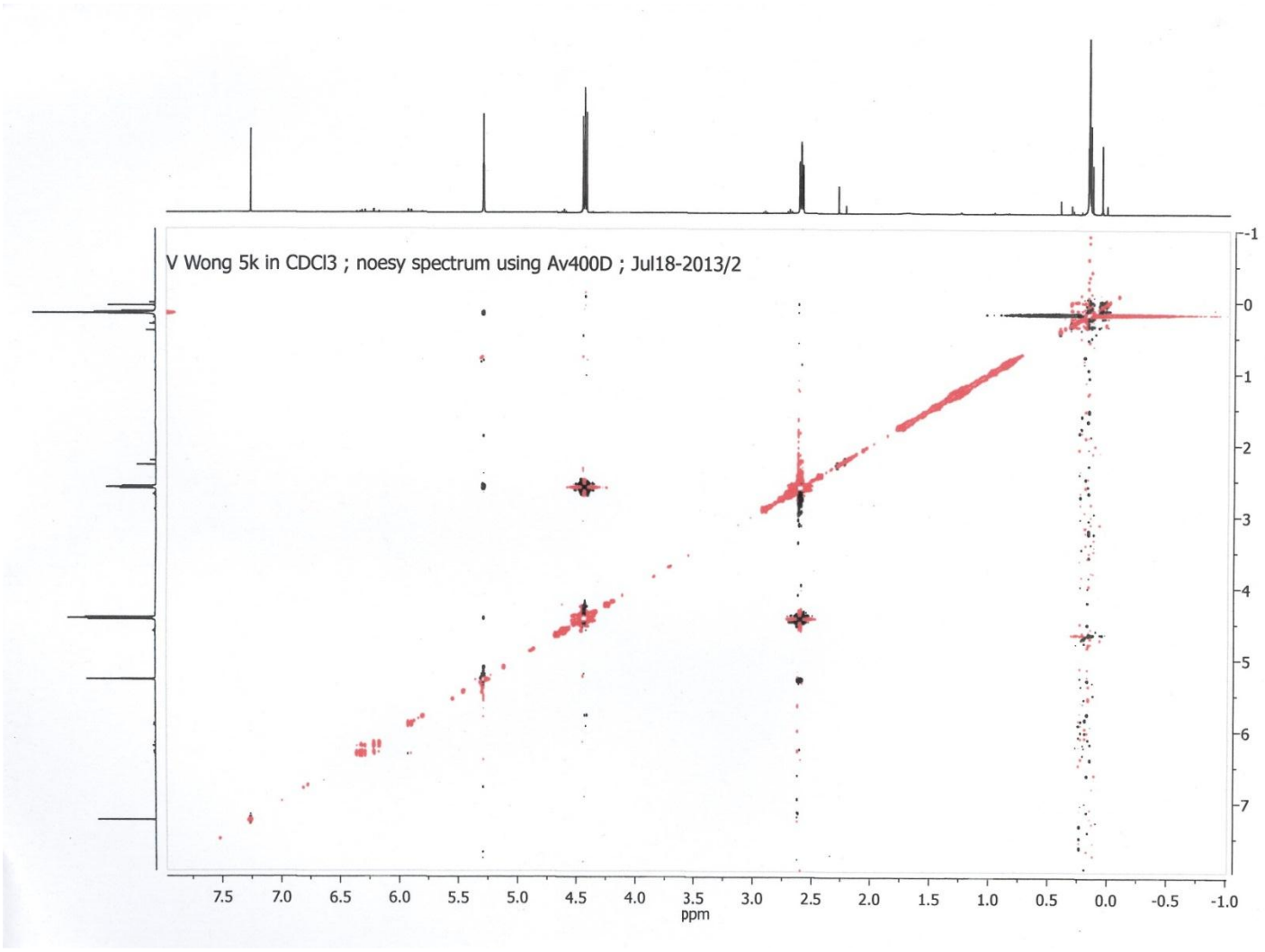


(**4h**)

^{13}C NMR (100 MHz, $CDCl_3$)



(**4h**)



NOESY spectrum for compound **4h**, showing distinct cross peaks between the alkenyl proton with TMS and methylene protons in the heterocyclic ring.