Rhodium-catalyzed synthesis of N-substituted 3-acylpyrroles from enaminones and vinylene carbonate

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Supporting Information

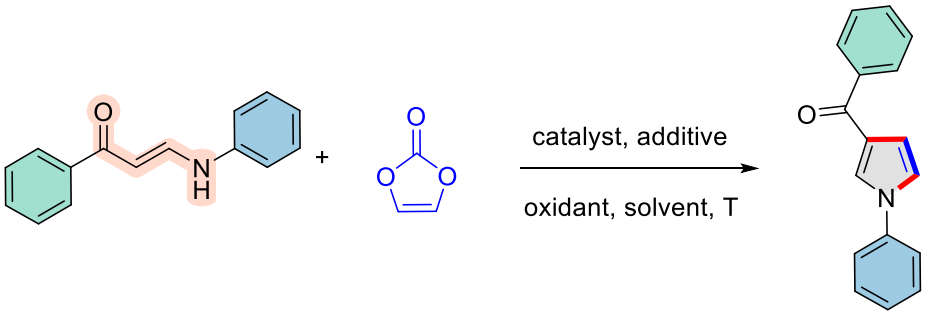
1. General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX500 or DRX600. Chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated DMSO-d_6 or $CDCl_3$ or acetone-d_6 was used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument.

Unless otherwise noted, all reactions in standard conditions were carried out under air atmosphere. All the other chemicals used in the experiment were purchased from commercial sources and were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). Enaminones **1** were prepared according to the previously mentioned literature[1-4].

2. Optimization of reaction conditions

Table S1. Optimization of the *N*-substituted 3-carbonypyrroles synthesis.[a]



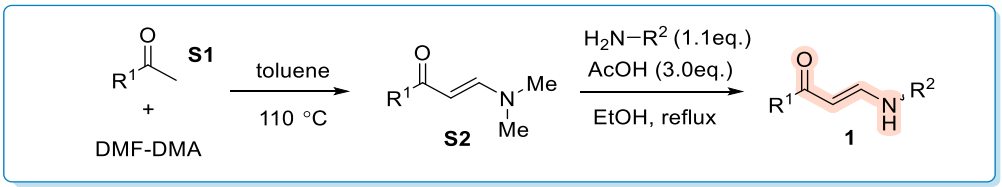
1d **2** **3d**

entry	solvent	catalyst (5 mol%)	Additive 1(10% mol) / Additive 2 (2equiv.)	oxidant (20 mol%)	T (°C)	Yield (%)[b]
1	DCE	$[Cp^*RuCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	51
2	DCE	$[Cp^*RhCl_2]_2$	Ag_2CO_3/NaOAc	$Cu(OAc)_2$	100	23
3	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/$Zn(OAc)_2$	$Cu(OAc)_2$	100	61
4	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/TEA	$Cu(OAc)_2$	100	45
5	**DCE**	**$[Cp^*RhCl_2]_2$**	**$AgSbF_6$/NaOAc**	**$Cu(OAc)_2$**	**100**	**90**
6	toluene	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	56
7	MeCN	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	trace
8	HFIP	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	trace
9	DCM	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	58
10	EtOH	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	trace
11	PEG200	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	trace
12[c]	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	61
13[d]	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	78
14	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	rt	32
15	toluene	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	rt	19
16	DCM	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	rt	24
17	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	90	76
18	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	110	85
19[e]	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	79
20[f]	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	62
21[g]	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	55
22	DCE	-	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	nr
23	DCE	$[Cp^*RhCl_2]_2$	-/NaOAc	$Cu(OAc)_2$	100	29
24	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/-	$Cu(OAc)_2$	100	trace
25	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	-	100	38
26[h]	DCE	$[Cp^*RhCl_2]_2$	$AgSbF_6$/NaOAc	$Cu(OAc)_2$	100	84

[a]Reaction conditions: **1d** (0.3 mmol), **2** (0.45 mmol), catalyst (5 mol%), additive **1** (10 mol%), additive **2** (2 equiv.), oxidant (20 mol%), solvent (1.0 mL), under air atmosphere, 36h. [b]Isolated yield. [c]Reaction under Ar. [d]Reaction under O_2. [e]DCE (2.0 mL). [f]DCE (3.0 mL). [g]DCE (4.0 mL). [h] $AgSbF_6$ = 20 mol%. nr = no reaction.

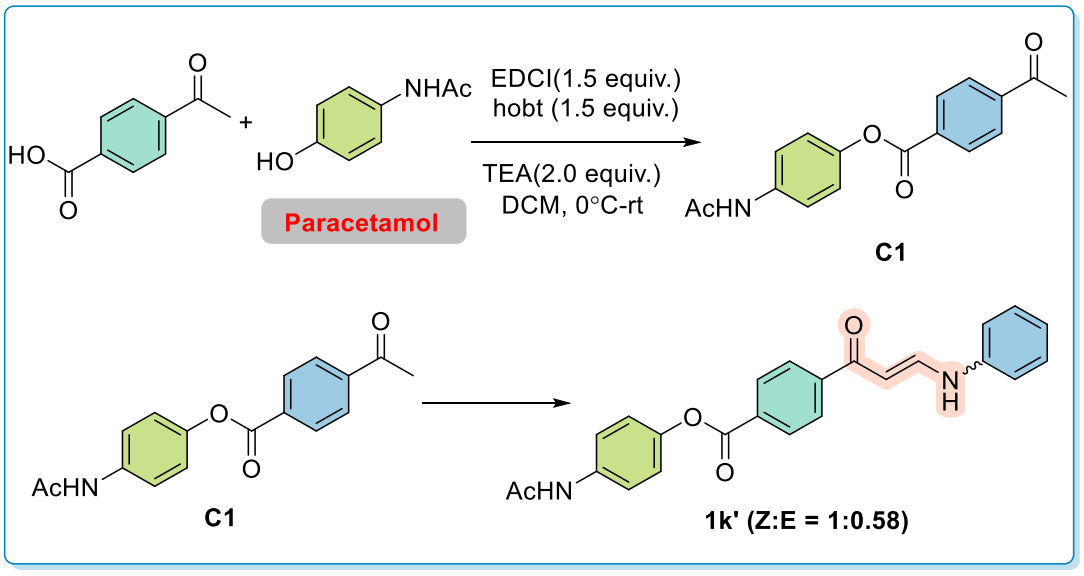
3. General Procedure

3.1 General synthesis of N-substituent enaminones 1.



To a 100 mL round flask charged with ketones **S1**(20 mmol), *N,N*-dimethylformamide dimethyl acetal (30 mmol) and toluene (20 mL). The mixture was stirred at 110℃ (oil bath) for 12 h until ketones **S1** were completely consumed as monitored by TLC. Then, the resulting mixture were cooled to room temperature and the solvent (toluene) was removed up about of 5 mL under vacuum, the filtration of the crystal produced the yellow crystalline *N,N*-dimethyl enaminones **S2** in good yields. Afterward, to a 50 mL round bottom flask charged with *N,N*-dimethyl enaminones **S2** (10 mmol), amines (12mmol), AcOH(30mmol) and ethyl alcohol (20mL), and the reaction was held at reflux for about 12 h until the reaction was complete consumed. The reaction was cooled to room temperature and the ethyl alcohol was removed under vacuum and residue was purified by column chromatography or crystallisation to obtained *N*-substituent enaminones **1**.

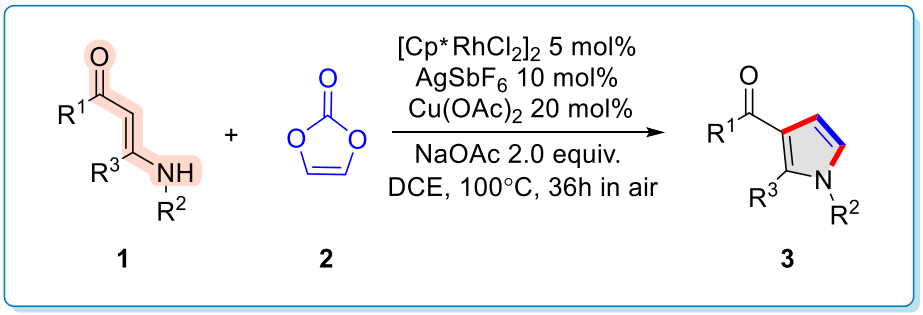
Substrate 1k' synthesis:



To a 50 mL round flask charged with ketones (10 mmol), EDCI (1.5 equiv.), hobt (1.5 equiv.), TEA (2 equiv.) and DCM (20 mL). Then the paracetamol (1.2 equiv.) were added into the above reaction under an ice water bath.Then, the mixture was vigorously stirred at rt for 3 h. until ketones were completely consumed as monitored by TLC and

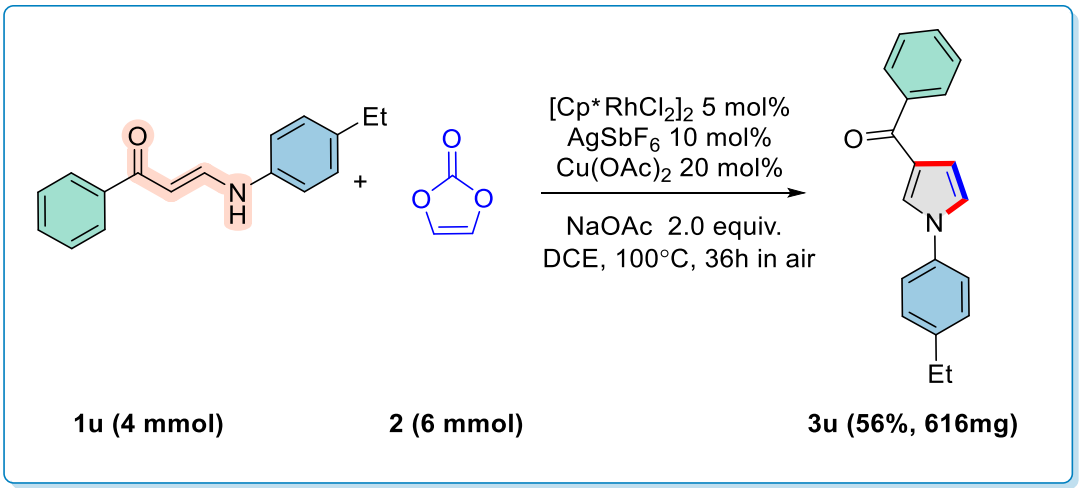
extracted with DCM, dired over anhydrous Na_2SO_4. The combined organic layers were evaporated to afford the residue. The crude product purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1) to afford **C1** with 90% yield. Then, enaminone **1k′** were prepared according to the above-mentioned.

3.2 synthesis of *N*-substituted 3-carbonypyrroles 3.



To a 10 mL Schlenk tube equipped with magnetic stir bar was charged with enaminones **1** (0.3 mmol, 1.0 equiv.), vinylene carbonate **2** (0.45 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgSbF_6$ (10.0 mol%), $Cu(OAc)_2$ (20.0 mol%), NaOAc (2.0 equiv.) and DCE (1.0 mL) under an air atmosphere. The mixture was stirred at rt for 2 min for proper mixing of the reactants, and then heated at 100℃ (oil bath) under air for 36h. After the mixture was completed (monitored by TLC), the mixture were cooled to rt, diluted with ethyl acetate, washed with brine, then combined organic phase were evaporated under vacuum. The crude product was separated by flash column chromatography to afford *N*-substituted 3-carbonypyrroles **3**.

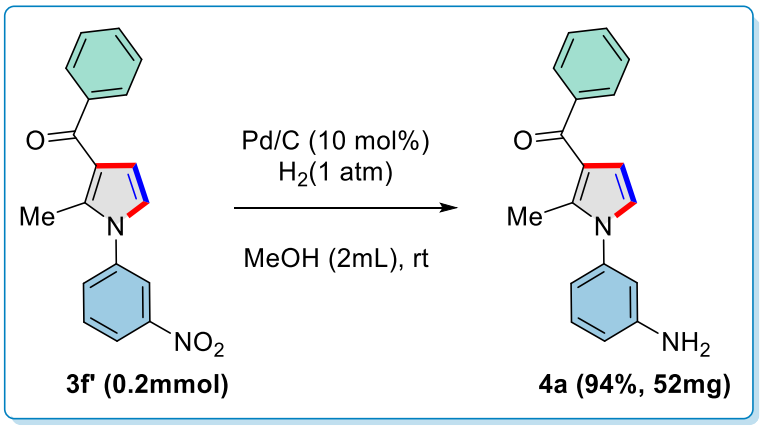
3.3 Gram-scale synthesis of *N*-substituted 3-carbonypyrroles 3u.



To a 50 mL Schlenk tube was charged with enaminones **1u** (4 mmol, 1.0 equiv.), vinylene carbonate **2** (6 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgSbF_6$ (10.0 mol%), $Cu(OAc)_2$ (20.0 mol%), NaOAc (2.0 equiv.) and DCE (12 mL) under an air

atmosphere. The mixture was stirred at rt for 2 min for proper mixing of the reactants, and then heated at 100℃ (oil bath) under air for 36h. After the mixture was completed (monitored by TLC), the mixture were cooled to rt, diluted with ethyl acetate, washed with brine, dired over anhydrous Na_2SO_4, then combined organic phase were evaporated under vacuum. The crude product was separated by flash column chromatography to afford *N*-substituted 3-carbonypyrroles **3u** (56%,616mg).

3.4 Further Synthetic Applications.

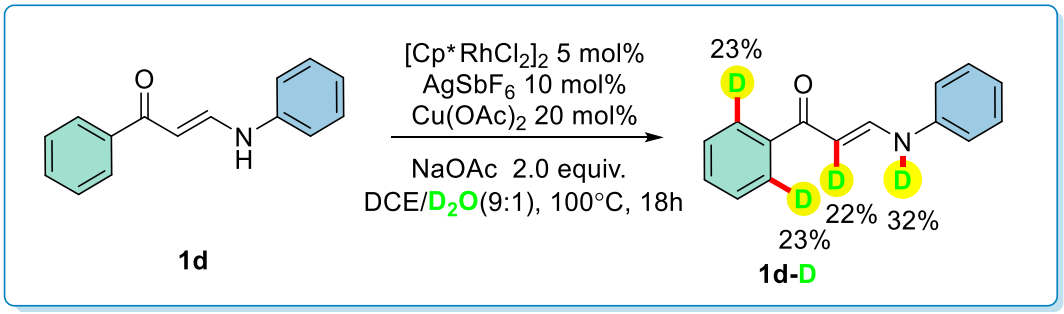


3f' (0.2mmol) **4a (94%, 52mg)**

To a 10 mL round flask charged with **3f'** (0.2 mmol, 1.0 equiv.), Pd/C (10 mol%) and MeOH (2 mL) under an air atmosphere. Then the round flask was purged with hydrogen. Then the mixture was stirred at room temperature for 4 h. Filtered through a short pad of Celite, concentrated in vacuo to afford **4a** in 94% yields.

3.5 Mechanistic studies.

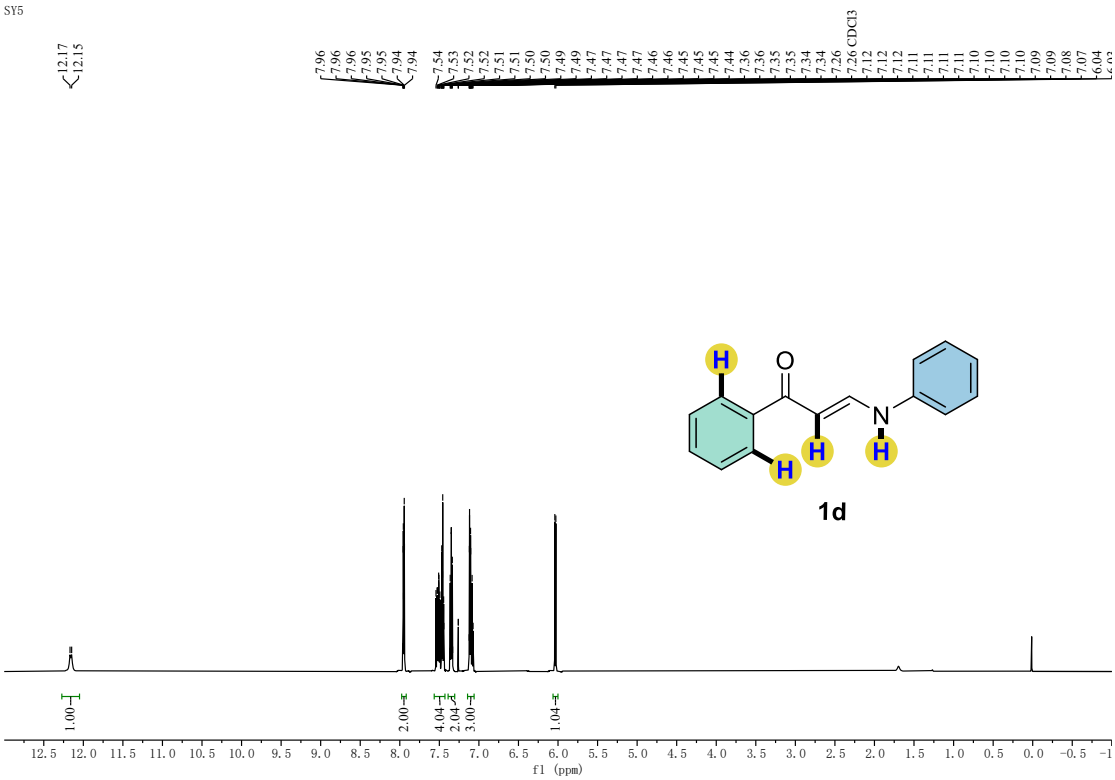
(1) H/D Exchange experiment



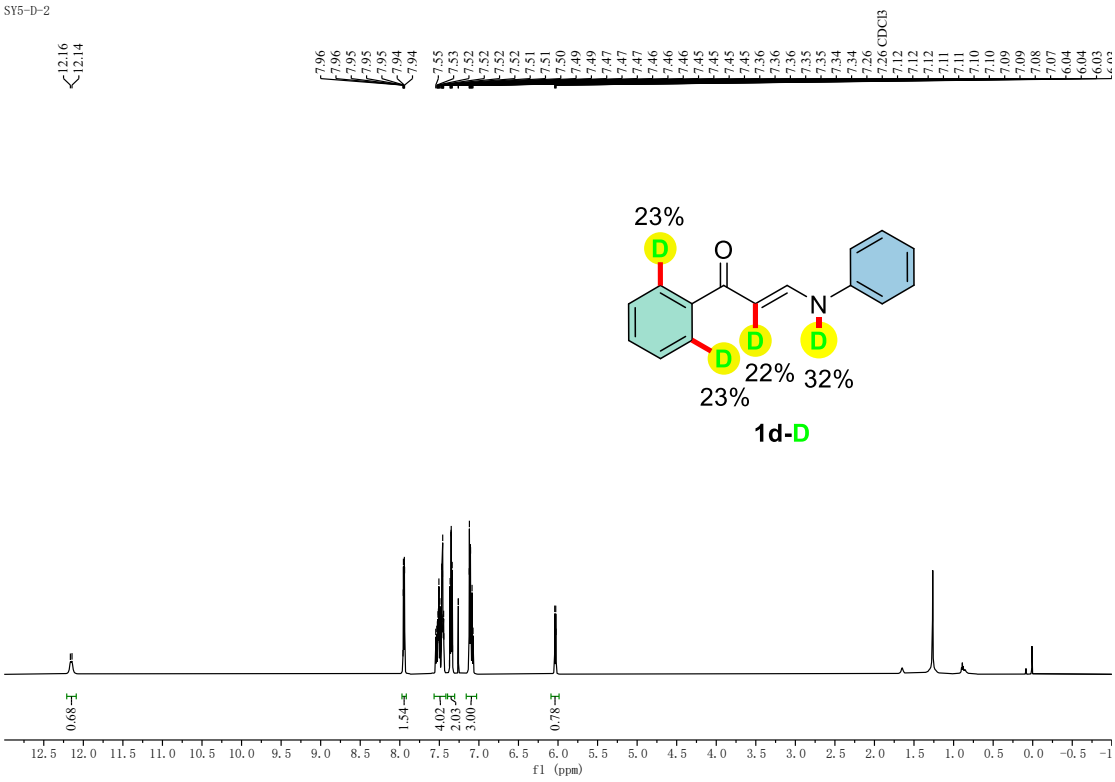
1d **1d-D**

To a 10 mL Schlenk tube equipped with magnetic stir bar was charged with enaminones **1d** (0.3 mmol, 1.0 equiv.), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgSbF_6$ (10.0 mol%), $Cu(OAc)_2$ (20.0 mol%), NaOAc (2.0 equiv.) and DCE (0.9 mL) and D_2O (0.1 mL) under an air atmosphere. The mixture was stirred at rt for 2 min for proper mixing of the reactants, and then heated at 100℃ (oil bath) under air for 18h, the mixture were cooled to rt, diluted with ethyl acetate, washed with brine, dired over anhydrous Na_2SO_4,

then combined organic phase were evaporated under vacuum. The crude product was separated by flash column chromatography on silica gel with petroleum ether/ethyl acetate. The deuterium ratio of 22% deuteration of the olefinic C-H bond was observed and 23% deuteration incorporation was estimated at each *ortho*-position of the aryl C-H bonds by ^{1}H NMR spectra analysis.

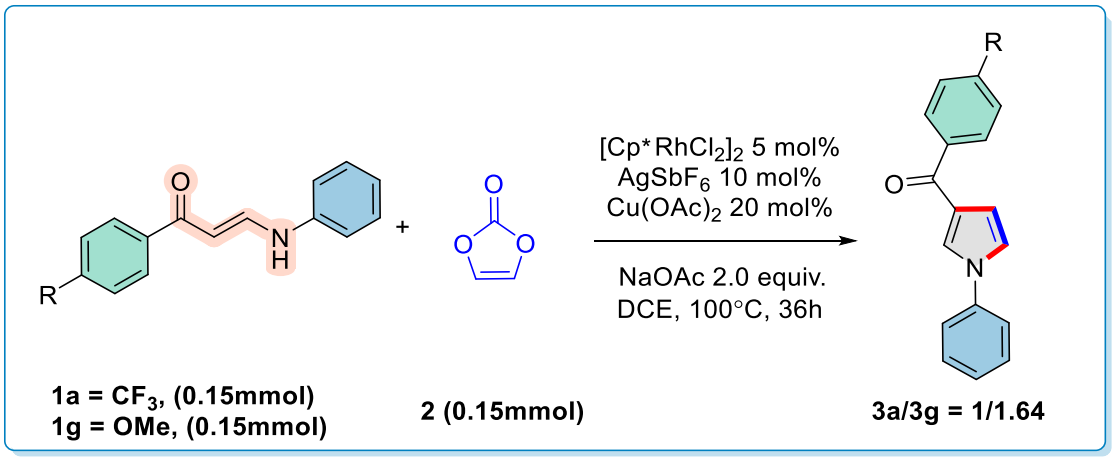


^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.14 (d, *J* = 12.2 Hz, 1H), 7.99–7.91 (m, 2H), 7.56–7.41 (m, 4H), 7.38–7.29 (m, 2H), 7.14–7.02 (m, 3H), 6.02 (d, *J* = 7.8 Hz, 1H).



^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.15 (d, *J* = 12.4 Hz, 0.68 H), 7.99–7.89 (m, 1.54 H), 7.57–7.42 (m, 4H), 7.40–7.31 (m, 2H), 7.16–7.03 (m, 3H), 6.03 (dd, *J* = 7.9, 1.8 Hz, 0.78 H).

(2) Competition experiment

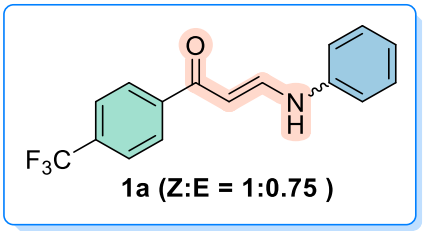


To a 10 mL Schlenk tube equipped with magnetic stir bar was charged with **1a** (0.15 mmol,1.0 equiv.), **1g** (0.15 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.0 equiv.) $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgSbF_6$ (10.0 mol%), $Cu(OAc)_2$ (20.0 mol%), NaOAc (2.0 equiv.) and DCE (1.0 mL) under an air atmosphere. The mixture was stirred at rt for 2 min for proper mixing of the reactants, and then heated at 100℃ (oil bath) under air for

36h. After the mixture was completed (monitored by TLC), the mixture were cooled to rt, diluted with ethyl acetate, washed with brine, dired over anhydrous Na_2SO_4, then combined organic phase were evaporated under vacuum, and the residue was purified by flash column chromatography on silica gel to afford **3a** and **3g** in a ratio 1:1.64.

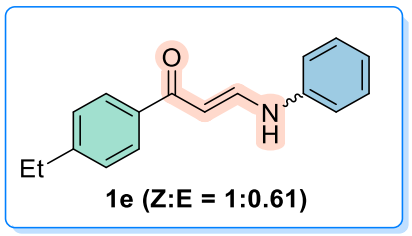
4. Spectroscopic Data

3-(phenylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1a)



Yellow solid ; **Mp**: 136.9-137.4 °C; **IR** (KBr) 3360, 3244, 3212, 2955, 1478, 1339, 1248, 1118, 904, 826, 777, 670, 638 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.13 (d, J = 12.6 Hz, 1H), 8.19–7.97 (m, 3H), 7.92–7.76 (m, 2H), 7.45–7.30 (m, 3H), 7.25–6.97 (m, 2H), 6.18 (d, J = 7.7 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 188.3, 147.5, 140.2, 131.7 (d , J_2 = 32.5 Hz), 130.2, 128.4, 128.4, 126.1 (d , J_3 = 3.75 Hz), 126.0(d , J_3 = 3.75 Hz), 125.5 (d , J_1 = 275 Hz), 124.3, 117.1, 93.6; **^{19}F NMR** (470 MHz, DMSO-d_6) δ -61.3; **HRMS** (TOF ES^+): m/z calcd for $C_{16}H_{13}F_3NO[(M+H)^+]$, 292.0944; found, 292.0943.

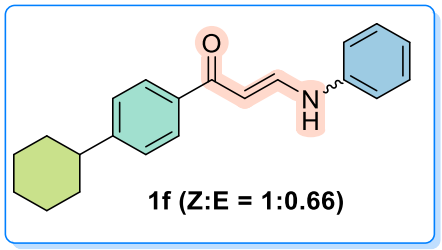
1-(4-ethylphenyl)-3-(phenylamino)prop-2-en-1-one (1e)



Yellow solid ; **Mp**: 113.5-114.0 °C; **IR** (KBr) 3211, 2891, 2769, 1636, 1475, 1290, 1109, 807, 749, 696 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.07 (d, J = 12.4 Hz, 1H), 7.90 (dt, J = 7.9, 6.0 Hz, 2H), 7.84–7.78 (m, 1H), 7.41–7.29 (m, 5H), 7.20–6.97 (m, 2H), 6.12 (d, J = 7.8 Hz, 1H), 2.67 (qd, J = 7.7, 2.0 Hz, 2H), 1.20 (td, J = 7.6, 2.5 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 189.8, 148.4, 146.0, 140.6,

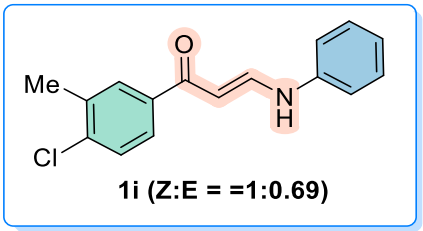
136.8, 130.1, 128.4, 127.8, 123.8, 116.6, 93.7, 28.6, 15.7; **HRMS** (TOF ES$^+$): m/z calcd for $C_{17}H_{18}NO[(M+H)^+]$, 252.1383; found, 252.1387.

1-(4-cyclohexylphenyl)-3-(phenylamino)prop-2-en-1-one (1f)



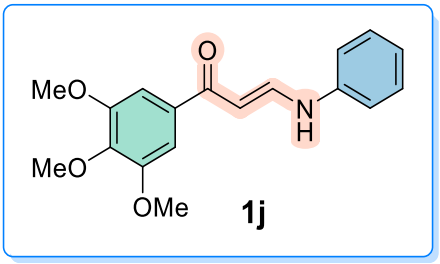
Yellow solid ; **Mp**: 151.2-151.7 °C; **IR** (KBr) 3383, 3049, 2835, 1891, 1830, 1724, 1598, 1545, 1280, 910, 750, 548 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 12.05 (d, J = 12.3 Hz, 1H), 7.95–7.84 (m, 2H), 7.83–7.76 (m, 1H), 7.34 (dt, J = 9.3, 7.3 Hz, 5H), 7.18–7.12 (m, 1H), 7.07 (tt, J = 7.0, 1.3 Hz, 1H), 6.11 (d, J = 7.9 Hz, 1H), 2.57 (t, J = 11.2 Hz, 1H), 1.88–1.74 (m, 4H), 1.75–1.65 (m, 1H), 1.49–1.30 (m, 4H), 1.26 (td, J = 12.1, 3.1 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 189.8, 152.1, 146.0, 140.6, 137.0, 130.2, 127.8, 127.4, 123.8, 116.6, 93.7, 44.2, 34.1, 26.7, 26.0; **HRMS** (TOF ES$^+$): m/z calcd for $C_{21}H_{24}NO[(M+H)^+]$, 306.1852; found, 306.1858.

3-((5-hydroxynaphthalen-1-yl)amino)-1-(4-methoxyphenyl)prop-2-en-1-one (1i)



Yellow solid ; **Mp**: 123.0-123.5 °C; **IR** (KBr) 3554, 3225, 3088, 2884, 2649, 1643, 1472, 1289, 1219, 1148, 847, 719, 690, 539 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 12.07 (d, *J* = 12.5 Hz, 1H), 8.25–7.88 (m, 2H), 7.86–7.76 (m, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.41–7.30 (m, 3H), 7.22–6.98 (m, 2H), 6.13 (d, *J* = 7.8 Hz, 1H), 2.41 (d, *J* = 1.6 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 188.7, 146.7, 140.4, 137.9, 137.3, 136.3, 130.2, 129.6, 126.8, 124.0, 116.8, 93.6, 20.1; **HRMS** (TOF ES$^+$): m/z calcd for $C_{16}H_{15}ClNO[(M+H)^+]$, 272.0837; found, 272.0841.

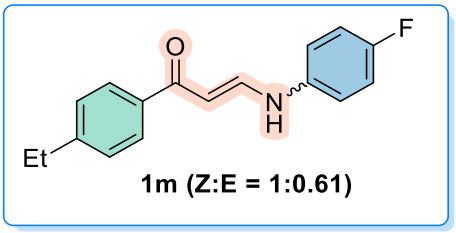
3-(phenylamino)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (1j)



1j

Yellow solid ; **Mp**: 81.8-82.3 °C; **IR** (KBr) 2953, 1630, 1594, 1553, 1478, 1328, 1290, 1206, 1168, 1126, 824, 761, 640, 491 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 12.12 (d, J = 12.3 Hz, 1H), 7.52 (dd, J = 12.3, 7.8 Hz, 1H), 7.39–7.31 (m, 2H), 7.21 (s, 2H), 7.10 (dd, J = 7.5, 5.0 Hz, 3H), 5.98 (d, J = 7.8 Hz, 1H), 3.94 (s, 6H), 3.92 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.0, 153.1, 144.9, 141.3, 140.2, 134.6, 129.8, 123.8, 116.3, 104.7, 93.5, 61.0, 56.3; **HRMS** (TOF ES^{+}): m/z calcd for $C_{18}H_{20}NO_4[(M+H)^{+}]$, 314.1387; found, 314.1391.

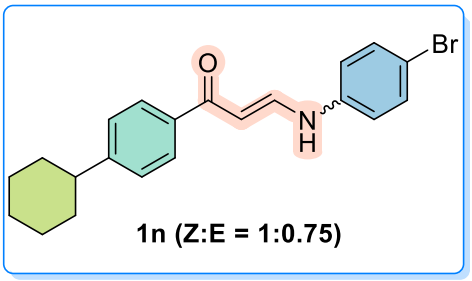
1-(4-ethylphenyl)-3-((4-fluorophenyl)amino)prop-2-en-1-one (1m)



1m (Z:E = 1:0.61)

Yellow solid ; **Mp**: 130.6-131.4 °C; **IR** (KBr) 3390, 3200, 3042, 1754, 1494, 1423, 1244, 1057, 927, 705, 756, 605, 530 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.04 (d, J = 12.4 Hz, 1H), 8.12–7.75 (m, 3H), 7.43–7.29 (m, 3H), 7.25–7.13 (m, 3H), 6.10 (d, J = 7.8 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.21 (td, J = 7.6, 1.2 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 189.7, 158.9 (d, J_1 = 245.0 Hz), 146.4, 137.6, 136.8, 128.4, 127.8, 116.7 (d, J_2 = 25.0 Hz), 118.5 (d, J_3 = 8.1 Hz), 93.6, 28.6, 15.7; **^{19}F NMR** (470 MHz, DMSO-d_6) δ -120.1; **HRMS** (TOF ES^{+}): m/z calcd for $C_{17}H_{17}FNO[(M+H)^{+}]$, 270.1289; found, 270.1292.

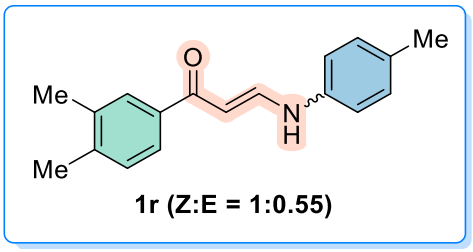
3-((4-bromophenyl)amino)-1-(4-cyclohexylphenyl)prop-2-en-1-one (1n)



1n (Z:E = 1:0.75)

Yellow solid ; **Mp**: 132.6-133.1 °C; **IR** (KBr) 3440, 2927, 1759, 1662, 1635, 1550, 1240, 779, 529 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-*d*$_6$) δ 11.97 (d, *J* = 12.3 Hz, 1H), 8.13–7.75 (m, 3H), 7.50 (dd, *J* = 24.2, 8.3 Hz, 2H), 7.33 (dd, *J* = 14.3, 8.1 Hz, 3H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H), 2.57 (t, *J* = 11.4 Hz, 1H), 1.75 (dd, *J* = 52.3, 12.3 Hz, 5H), 1.58–1.09 (m, 5H); **^{13}C NMR** (150 MHz, DMSO-*d*$_6$) δ 190.0, 152.2, 145.6, 144.0, 138.8, 132.8, 127.8, 127.4, 127.3, 118.8, 94.3, 44.2, 34.1, 26.7, 26.0; **HRMS** (TOF ES$^+$): m/z calcd for $C_{21}H_{23}BrNO[(M+H)^+]$, 384.0958; found, 384.0962.

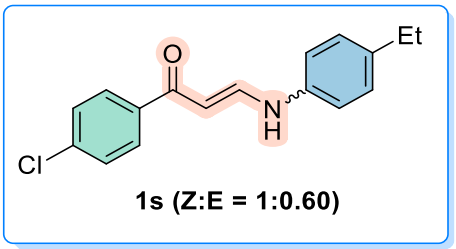
1-(3,4-dimethylphenyl)-3-(p-tolylamino)prop-2-en-1-one (1r)



1r (Z:E = 1:0.55)

Yellow solid ; **Mp**: 130.0-130.5 °C; **IR** (KBr) 3660, 3290, 3264, 2928, 2006, 1774, 1634, 1581, 1461, 1392, 1335, 1292, 1244, 1158, 1057, 866, 809, 580 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 12.07 (d, J = 12.4 Hz, 1H), 7.83 (dd, J = 12.4, 7.8 Hz, 1H), 7.74 (d, J = 1.9 Hz, 1H), 7.71–7.64 (m, 1H), 7.26–7.11 (m, 4H), 7.08–7.02 (m, 1H), 6.07 (d, J = 7.8 Hz, 1H), 2.27 (dd, J = 10.4, 8.5 Hz, 9H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 189.8, 146.0, 141.0, 138.2, 137.0, 136.9, 132.9, 130.6, 130.1, 128.6, 125.2, 116.6, 93.3, 20.8, 19.9; **HRMS** (TOF ES$^+$): m/z calcd for $C_{18}H_{20}NO[(M+H)^+]$, 266.1539; found, 266.1541.

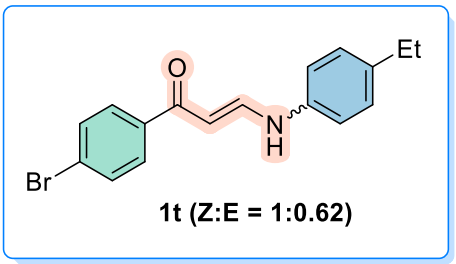
1-(4-chlorophenyl)-3-((4-ethylphenyl)amino)prop-2-en-1-one (1s)



1s (Z:E = 1:0.60)

Yellow solid ; **Mp**: 167.5-168.0 °C; **IR** (KBr) 3530, 3233, 1762, 1652, 1542, 1475, 1244, 1122, 872, 835, 770, 720 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.09 (d, J = 12.6 Hz, 1H), 8.21–7.82 (m, 3H), 7.55 (d, J = 8.3 Hz, 2H), 7.33–7.03 (m, 4H), 6.09 (d, J = 7.8 Hz, 1H), 2.62–2.52 (m, 2H), 1.16 (td, J = 7.6, 4.2 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 188.2, 147.1, 139.8, 138.2, 137.9, 136.9, 129.4, 129.4, 129.1, 116.9, 93.0, 28.0, 16.1 ; **HRMS** (TOF ES^+): m/z calcd for $C_{17}H_{16}ClNO[(M+Na)^+]$, 308.0813; found, 308.0812.

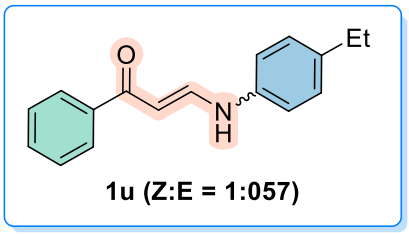
1-(4-bromophenyl)-3-((4-ethylphenyl)amino)prop-2-en-1-one (1t)



1t (Z:E = 1:0.62)

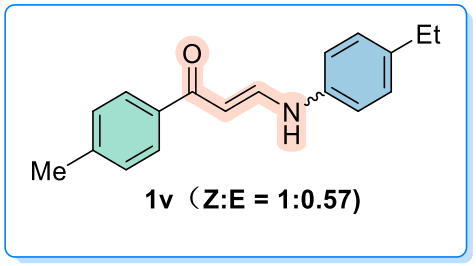
Yellow solid ; **Mp**: 188.1-188.6 °C; **IR** (KBr) 3529, 3264, 2889, 2782, 2473, 1756, 1659, 1573, 1462, 1316, 1251, 1183, 1110, 961, 885, 832, 770, 656, 567 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.09 (d, J = 12.6 Hz, 1H), 7.97–7.86 (m, 2H), 7.83–7.76 (m, 1H), 7.74–7.64 (m, 2H), 7.31–7.05 (m, 4H), 6.08 (d, J = 7.7 Hz, 1H), 2.62–2.52 (m, 2H), 1.16 (td, J = 7.6, 4.4 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 188.3, 147.1, 139.8, 138.1, 132.1, 129.7, 129.6, 129.4, 125.9, 117.0, 93.0, 28.0, 16.1; **HRMS** (TOF ES^+): m/z calcd for $C_{17}H_{17}BrNO[(M+H)^+]$, 330.0488; found, 330.0494.

3-((4-ethylphenyl)amino)-1-phenylprop-2-en-1-one (1u)



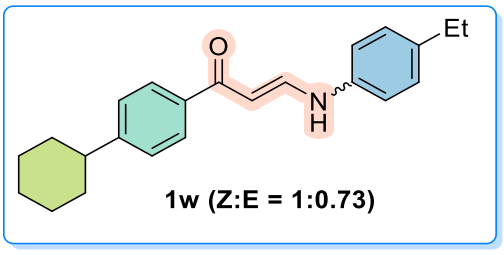
Yellow solid ; **Mp**: 145.2-145.7 °C; IR (KBr) 3650, 3355, 2898, 1633, 1544, 1500, 1472, 1296, 1115, 866, 760, 704, 661, 606 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.11 (d, J = 12.5 Hz, 1H), 7.99–7.82 (m, 3H), 7.59–7.53 (m, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.25 (d, J = 8.2 Hz, 1H), 7.24–7.14 (m, 2H), 7.09 (d, J = 8.2 Hz, 1H), 6.11 (d, J = 7.8 Hz, 1H), 2.56 (p, J = 7.9 Hz, 2H), 1.16 (td, J = 7.6, 3.7 Hz, 3H).**^{13}C NMR** (125 MHz, DMSO-d_6) δ 189.7, 146.6, 139.6, 139.2, 138.3, 132.1, 129.4, 129.0, 127.5, 116.8, 93.2, 28.0, 16.1; **HRMS** (TOF ES$^+$): m/z calcd for $C_{17}H_{18}NO[(M+H)^+]$, 252.1383; found, 252.1385.

3-((4-ethylphenyl)amino)-1-(p-tolyl)prop-2-en-1-one (1v)



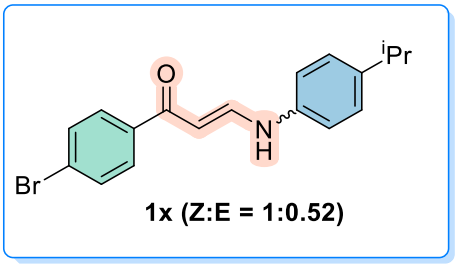
Yellow solid ; **Mp**: 141.6-142.1 °C; **IR** (KBr) 3450, 2950, 1625, 1571, 1289, 1182, 777, 620 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.08 (d, J = 12.5 Hz, 1H), 7.90–7.81 (m, 2H), 7.80–7.73 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.26–7.14 (m, 3H), 7.11–7.04 (m, 1H), 6.07 (d, J = 7.8 Hz, 1H), 2.56 (p, J = 7.7 Hz, 2H), 2.37 (s, 3H), 1.16 (td, J = 7.6, 3.2 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 189.5, 146.2, 142.2, 139.4, 138.4, 136.6, 129.6, 129.4, 127.6, 116.7, 93.2, 28.0, 21.5, 16.1; **HRMS** (TOF ES$^+$): m/z calcd for $C_{18}H_{20}NO[(M+H)^+]$, 266.1539; found, 266.1541.

1-(4-cyclohexylphenyl)-3-((4-ethylphenyl)amino)prop-2-en-1-one (1w)



Yellow solid ; **Mp**: 112.3-112.8 °C; **IR** (KBr) 3546, 3289, 2776, 1769, 1635, 1520, 1369, 1283, 1240, 1041, 960, 780 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.06 (d, J = 12.4 Hz, 1H), 7.83 (dd, J = 41.2, 8.0 Hz, 3H), 7.33 (d, J = 7.9 Hz, 2H), 7.28–7.13 (m, 3H), 7.07 (d, J = 8.0 Hz, 1H), 6.07 (d, J = 7.8 Hz, 1H), 2.56 (p, J = 7.6 Hz, 3H), 1.87–1.65 (m, 5H), 1.39 (dt, J = 28.6, 12.1 Hz, 4H), 1.31–1.12 (m, 4H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 189.6, 152.0, 146.2, 139.4, 138.4, 137.8, 129.4, 127.8, 127.7, 127.3, 127.2, 116.7, 93.2, 44.2, 34.1, 27.9, 26.7, 26.0, 16.1; **HRMS** (TOF ES$^+$): m/z calcd for $C_{23}H_{28}NO[(M+H)^+]$, 334.2165; found, 334.2171.

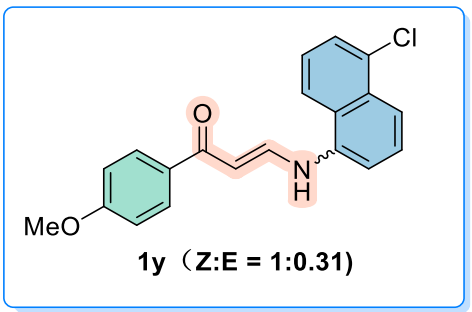
1-(4-bromophenyl)-3-((4-isopropylphenyl)amino)prop-2-en-1-one (1x)



1x (Z:E = 1:0.52)

Yellow solid ; **Mp**: 149.9-150.4 °C; **IR** (KBr) 3238, 3178, 3117, 3018, 2747, 1905, 1527, 1264, 1185, 984, 917, 781, 530 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.09 (d, J = 12.6 Hz, 1H), 8.30–7.48 (m, 5H), 7.35–7.14 (m, 3H), 7.10 (d, J = 8.1 Hz, 1H), 6.08 (d, J = 7.8 Hz, 1H), 3.00–2.68 (m, 1H), 1.19 (dd, J = 6.9, 4.5 Hz, 6H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 188.3, 147.2, 144.4, 139.1, 138.2, 132.1, 129.6, 127.9, 125.9, 117.0, 93.0, 33.3, 24.4; **HRMS** (TOF ES$^+$): m/z calcd for $C_{18}H_{19}BrNO[(M+H)^+]$, 344.0645; found, 344.0651.

3-((5-chloronaphthalen-1-yl)amino)-1-(4-methoxyphenyl)prop-2-en-1-one (1y)

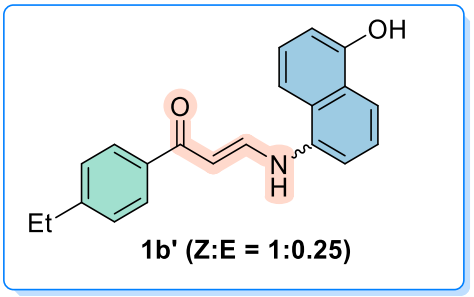


1y（Z:E = 1:0.31)

Yellow solid ; **Mp**: 189.8-190.3 °C; **IR** (KBr) 3539, 3309, 3051, 1710, 1587, 1529, 1481, 1419, 1303, 1269, 1077, 974, 874, 540 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-

d$_6$) δ 13.20 (d, J = 11.4 Hz, 1H), 8.37–7.43 (m, 9H), 7.06 (d, J = 7.9 Hz, 2H), 6.34 (d, J = 7.7 Hz, 1H), 3.85 (d, J = 10.1 Hz, 3H); **^{13}C NMR** (150 MHz, DMSO-*d*$_6$) δ 190.0, 146.4, 136.9, 132.1, 131.5, 130.0, 129.8, 128.5, 127.6, 127.3, 120.2, 119.2, 114.4, 114.3, 112.0, 95.3, 55.9; **HRMS** (TOF ES$^+$): m/z calcd for $C_{20}H_{17}ClNO_2$[(M+H)$^+$], 338.0942; found, 338.0940.

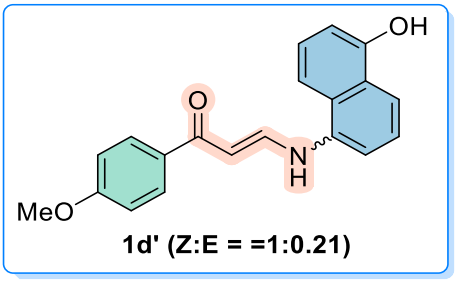
1-(4-ethylphenyl)-3-((5-hydroxynaphthalen-1-yl)amino)prop-2-en-1-one (1b')



1b' (Z:E = 1:0.25)

Yellow solid ; **Mp**: 130.1-130.6 °C; **IR** (KBr) 3524, 3434, 3310, 1731, 1468, 1354, 1269, 1202, 1090, 1024, 831, 806, 721 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 13.14 (d, J = 11.7 Hz, 1H), 10.35 (s, 1H), 8.15 (dd, J = 11.7, 7.7 Hz, 1H), 8.07–7.85 (m, 3H), 7.63–7.57 (m, 1H), 7.57–7.31 (m, 5H), 6.99 (dd, J = 6.8, 1.6 Hz, 1H), 6.29 (d, J = 7.6 Hz, 1H), 2.68 (p, J = 7.5 Hz, 2H), 1.21 (td, J = 7.6, 4.3 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 190.5, 154.4, 148.6, 147.0, 136.7, 135.7, 128.5, 127.9, 127.9, 126.0, 125.5, 125.2, 118.1, 111.3, 110.7, 109.3, 94.7, 28.6, 15.7; **HRMS** (TOF ES$^+$): m/z calcd for $C_{21}H_{20}NO_2$[(M+H)$^+$], 318.1487; found, 318.1490.

1-(4-chloro-3-methylphenyl)-3-(phenylamino)prop-2-en-1-one (1d')

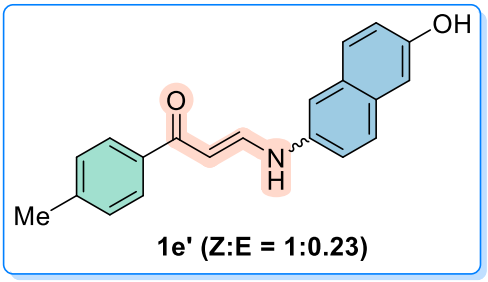


1d' (Z:E = =1:0.21)

Yellow solid ; **Mp**: 180.3-180.8 °C; **IR** (KBr) 3452, 3282, 2915, 2773, 1634, 1490, 1400, 1240, 1161, 1061, 960, 919, 828, 760, 726, 497 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 13.11 (d, J = 11.7 Hz, 1H), 10.35 (s, 1H), 8.19–8.07 (m, 1H), 8.06–

7.98 (m, 2H), 7.93 (d, J = 8.2 Hz, 1H), 7.62–7.42 (m, 4H), 7.05 (dd, J = 9.0, 2.2 Hz, 2H), 6.99 (dd, J = 7.0, 1.5 Hz, 1H), 6.27 (d, J = 7.8 Hz, 1H), 3.84 (d, J = 6.1 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 189.7, 162.8, 154.4, 146.4, 135.8, 131.7, 129.9, 127.8, 126.0, 125.5, 125.2, 117.9, 114.3, 111.0, 110.7, 109.3, 94.5, 55.9; **HRMS** (TOF ES$^+$): m/z calcd for $C_{20}H_{18}NO_3$[(M+H)$^+$], 320.1281; found, 320.1284.

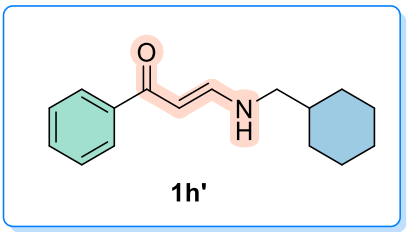
3-((6-hydroxynaphthalen-2-yl)amino)-1-(p-tolyl)prop-2-en-1-one (1e')



1e' (Z:E = 1:0.23)

Yellow solid ; **Mp**: 115.9-116.4 °C; **IR** (KBr) 3108, 2910, 2457, 1768, 1627, 1615, 1422, 1380, 1240, 1065, 892, 845, 789, 765, 621 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 13.14 (d, J = 11.7 Hz, 1H), 10.35 (s, 1H), 8.15 (dd, J = 11.8, 7.6 Hz, 1H), 7.94 (dd, J = 8.1, 5.7 Hz, 3H), 7.60 (d, J = 7.5 Hz, 1H), 7.57–7.28 (m, 5H), 6.99 (dd, J = 6.8, 1.6 Hz, 1H), 6.29 (d, J = 7.6 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 190.4, 154.4, 147.0, 142.5, 136.4, 135.7, 129.7, 129.5, 127.8, 126.0, 125.5, 125.2, 118.1, 111.3, 110.7, 109.3, 94.6, 21.6; **HRMS** (TOF ES$^+$): m/z calcd for $C_{20}H_{18}NO_2$[(M+H)$^+$], 304.1332; found, 304.1328.

3-((cyclohexylmethyl)amino)-1-phenylprop-2-en-1-one(1h')

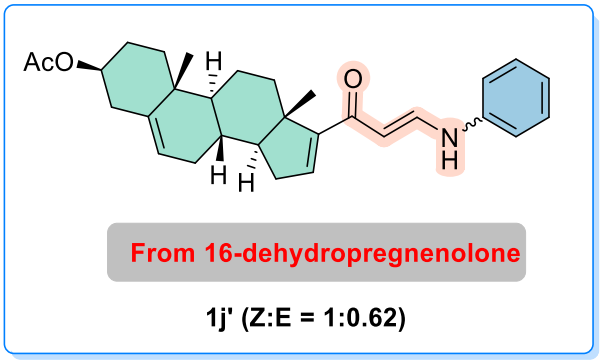


1h'

Yellow oil ; **IR** (KBr) 2924, 2851, 1632, 1585, 1500, 1281, 1214, 1049, 734 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 10.45 (s, 1H), 7.91–7.84 (m, 2H), 7.47–7.36 (m, 3H), 6.90 (dd, *J* = 12.8, 7.3 Hz, 1H), 5.68 (d, *J* = 7.3 Hz, 1H), 3.09 (t, *J* = 6.6 Hz, 2H), 1.80–1.64 (m, 5H), 1.50 (m, 1H), 1.32–1.09 (m, 3H), 0.95 (m, 2H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.8, 154.9, 139.9, 130.9, 128.3, 127.1, 89.8, 56.2, 39.3, 30.6,

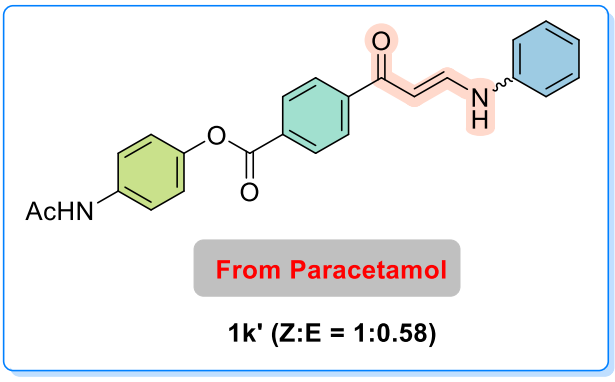
26.3, 25.9; **HRMS** (TOF ES$^+$): m/z calcd for $C_{16}H_{22}NO[(M+H)^+]$, 244.1696; found, 244.1701.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-(3-(phenylamino)acryloyl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (1j')



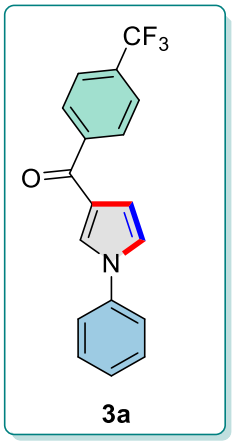
Yellow solid ; **Mp**: 112.4-112.9 °C; **IR** (KBr) 3589, 2930, 2859, 1660, 1532, 1510, 1261, 1213, 1076, 895, 760, 691, 560 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.61 (d, J = 12.2 Hz, 1H), 7.62 (dd, J = 12.3, 8.0 Hz, 1H), 7.39–7.16 (m, 3H), 7.10–6.85 (m, 2H), 6.67 (s, 1H), 5.70 (d, J = 8.0 Hz, 1H), 5.37 (d, J = 5.0 Hz, 1H), 4.45 (qd, J = 9.5, 8.2, 4.6 Hz, 1H), 2.39 (d, J = 12.1 Hz, 1H), 2.26 (dd, J = 22.9, 7.8 Hz, 3H), 1.98 (s, 5H), 1.88–1.72 (m, 2H), 1.70–1.47 (m, 5H), 1.33 (dddd, J = 47.1, 17.7, 11.8, 7.0 Hz, 2H), 1.13–0.98 (m, 5H), 0.94 (d, J = 9.4 Hz, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 190.1, 170.2, 155.7, 143.5, 142.2, 140, 140, 130.1, 122.3, 116.2, 95.5, 73.7, 56.4, 40.4, 40.1, 40.0, 39.9, 38.2, 36.8, 35.0, 32.2, 30.2, 27.8, 21.5, 20.8, 19.4, 16.4; **HRMS** (TOF ES$^+$): m/z calcd for $C_{30}H_{38}NO[(M+H)^+]$, 460.2846; found, 460.2849.

4-acetamidophenyl-4-(3-(phenylamino)acryloyl)benzoate (1k')



Yellow solid ; **Mp**: 110.3-110.8 °C; **IR** (KBr) 3784, 2959, 2863, 1733, 1633, 1605, 1557, 1281, 1250, 1223, 1050, 810, 650, 620 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.17 (d, J = 12.6 Hz, 1H), 10.06 (s, 1H), 8.37–7.93 (m, 5H), 7.67 (d, J = 8.4 Hz, 2H), 7.50–7.15 (m, 6H), 7.17–6.97 (m, 1H), 6.21 (d, J = 7.7 Hz, 1H), 2.07 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 188.6, 168.8, 164.8, 147.5, 146.1, 140.3, 137.7, 131.8, 131.6, 130.5, 130.2, 128.0, 124.4, 122.4, 120.4, 117.1, 93.9, 24.4; **HRMS** (TOF ES^{+}): m/z calcd for $C_{24}H_{21}N_2O_4[(M+H)^{+}]$, 401.1496; found, 401.1496.

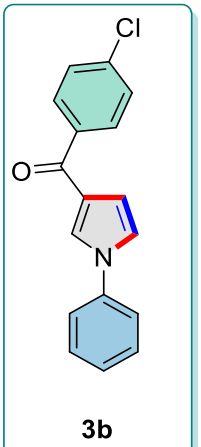
(1-phenyl-1H-pyrrol-3-yl)(4-(trifluoromethyl)phenyl)methanone (3a)



3a

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 56%, 53mg); **IR** (KBr) 3441, 3327, 2599, 1646, 1516, 1327, 1274, 1172, 1129, 1065, 857, 763, 650, 510 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 1.9 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.37–7.31 (m, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 2.6 Hz, 1H), 6.78 (dd, *J* = 3.0, 1.7 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 188.4, 141.9, 138.5, 132.0 (q , J_2 = 32.5 Hz), 128.9, 128.1, 126.3, 125.3, 124.7, 124.3 (q , J_3 = 3.8 Hz), 122.8 (d , J_1 = 270.0 Hz), 120.7, 120.2, 111.2; **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -62.8; **HRMS** (TOF ES^+): m/z calcd for $C_{18}H_{12}F_3NNaO[(M+Na)^+]$, 338.0763; found, 338.0765.

(4-chlorophenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3b)

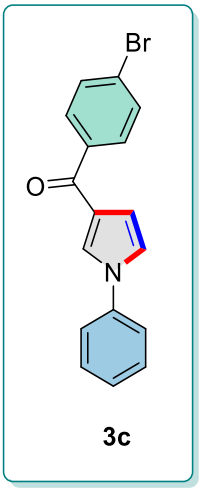


3b

Yellow oil (V $_{\text{petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 69%, 58mg); **IR** (KBr) 3556, 3372, 2920, 1948, 1679, 1625, 1286, 855, 760 cm^{-1}; **^{1}H NMR** (500 MHz,

Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.43–7.30 (m, 6H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 2.6 Hz, 1H), 6.75 (t, *J* = 2.3 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 188.3, 138.6, 137.0, 136.8, 129.3, 128.8, 127.5, 126.2, 125.0, 124.8, 120.4, 120.1, 111.3. **HRMS** (TOF ES$^+$): m/z calcd for $C_{17}H_{13}ClNO[(M+H)^+]$, 282.0680; found, 282.0687.

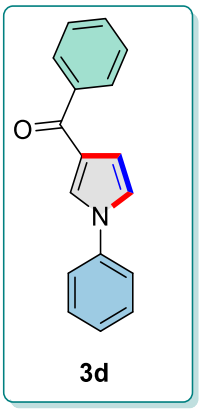
(4-bromophenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3c)



3c

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 53%, 52mg); **IR** (KBr) 3454, 3386, 3291, 2898, 1635, 1586, 1512, 1275, 1171, 1074, 860, 760, 580 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.79–7.73 (m, 2H), 7.66–7.57 (m, 3H), 7.51–7.45 (m, 2H), 7.45–7.40 (m, 2H), 7.38–7.33 (m, 1H), 7.12 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.84 (dd, *J* = 3.1, 1.7 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.5, 139.7, 138.5, 131.6, 130.5, 129.9, 127.3, 126.4, 126.1, 125.9, 121.4, 121.2, 112.3. **HRMS** (TOF ES$^+$): m/z calcd for $C_{17}H_{12}BrNNaO[(M+Na)^+]$, 347.9994; found, 348.0000.

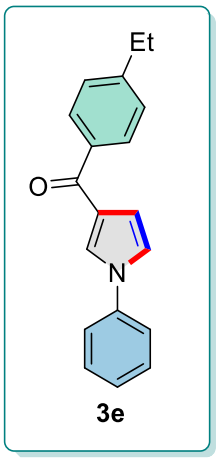
Phenyl(1-phenyl-1H-pyrrol-3-yl)methanone (3d)



3d

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 90%, 67mg); **IR** (KBr) 3689, 2934, 1941, 1772, 1634, 1511, 1423, 1281, 1050, 870, 720, 544 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92–7.86 (m, 2H), 7.62 (t, *J* = 2.0 Hz, 1H), 7.58–7.53 (m, 1H), 7.47 (dtd, *J* = 8.2, 6.7, 1.6 Hz, 4H), 7.44–7.39 (m, 2H), 7.37–7.31 (m, 1H), 7.11 (t, *J* = 2.6 Hz, 1H), 6.88 (dd, *J* = 3.1, 1.7 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.8, 139.8, 139.8, 131.6, 129.9, 129.0, 128.3, 127.1, 126.2, 126.2, 121.2, 121.2, 112.4. **HRMS** (TOF ES^+): m/z calcd for $C_{17}H_{14}NO[(M+H)^+]$, 248.1070; found, 248.1076.

(4-ethylphenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3e)

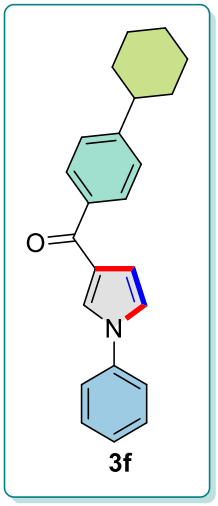


3e

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 87%, 72mg); **IR** (KBr) 3741, 3281, 3176, 2881, 2094, 1876, 1521, 1464, 1403, 1219, 1171, 1072, 940, 860, 580 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.55 (s, 1H), 7.45–7.29 (m, 4H), 7.23 (m, 3H), 7.03 (s, 1H), 6.80 (s, 1H), 2.65 (d, *J* = 9.1 Hz, 2H), 1.20 (t, *J* = 7.9 Hz, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 190.5, 148.4, 139.8, 137.3, 129.8, 129.2, 127.8, 127.0, 126.4, 125.9, 121.1, 121.1, 112.4, 28.9,

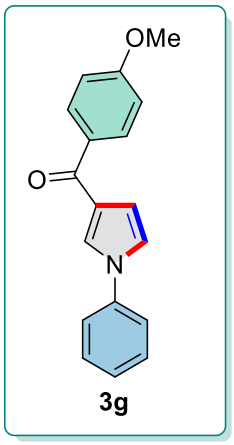
15.4. **HRMS** (TOF ES^+): m/z calcd for $C_{19}H_{18}NO[(M+H)^+]$, 276.1383; found, 276.1389.

(4-cyclohexylphenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3f)



Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 65%, 64mg); **IR** (KBr) 3682, 3353, 2924, 2366, 1636, 1510, 1281, 1174, 860, 838, 686, 640 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.85–7.80 (m, 2H), 7.63 (t, *J* = 2.0 Hz, 1H), 7.49–7.40 (m, 4H), 7.36–7.28 (m, 3H), 7.10 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.88 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.58 (m, 1H), 1.94–1.84 (m, 4H), 1.77 (dtt, *J* = 12.8, 3.3, 1.5 Hz, 1H), 1.53–1.35 (m, 5H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.5, 152.1, 139.8, 137.4, 129.8, 129.2, 127.0, 126.8, 126.3, 125.9, 121.1, 121.0, 112.4, 44.7, 34.3, 26.8, 26.1. **HRMS** (TOF ES^+): m/z calcd for $C_{23}H_{24}NO_2[(M+H)^+]$, 330.1850; found, 330.1856.

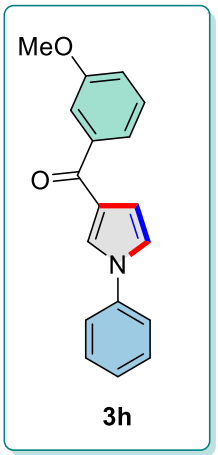
(4-methoxyphenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3g)



3g

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 85%, 71mg); **IR** (KBr) 3829, 3784, 3567, 3412, 2972, 2844, 2575, 1632, 1505, 1260, 1163, 1030, 890, 840, 760, 690 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.86–7.81 (m, 2H), 7.53 (t, *J* = 1.9 Hz, 1H), 7.40–7.32 (m, 4H), 7.26–7.22 (m, 1H), 7.01 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.91–6.87 (m, 2H), 6.76 (dd, *J* = 3.0, 1.7 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 189.5, 162.6, 139.8, 132.4, 131.3, 129.8, 127.0, 126.4, 125.5, 121.1, 120.9, 113.5, 112.5, 55.4. **HRMS** (TOF ES^+): m/z calcd for $C_{18}H_{16}NO_2[(M+H)^+]$, 278.1176; found, 278.1182.

(3-methoxyphenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3h)

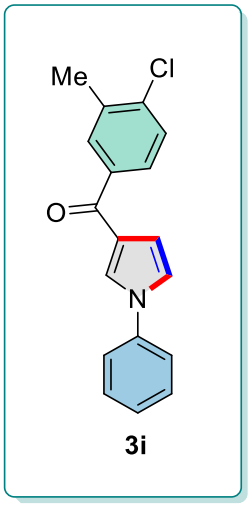


3h

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 53%, 44mg); **IR** (KBr) 3516, 3284, 2953, 1516, 1278, 1086, 1038, 889, 751, 650 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.62 (t, *J* = 2.0 Hz, 1H), 7.49–7.44 (m, 3H), 7.43–7.40 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.36–7.32 (m, 1H), 7.12–7.07 (m, 2H), 6.88 (dd, *J* = 3.1, 1.7 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 190.4, 159.6,

141.1, 139.8, 129.8, 129.2, 127.1, 126.2, 121.5, 121.2, 121.2, 117.9, 113.6, 112.4, 55.5. **HRMS** (TOF ES^+): m/z calcd for $C_{18}H_{15}NNaO_2[(M+Na)^+]$, 300.0995; found, 300.0998.

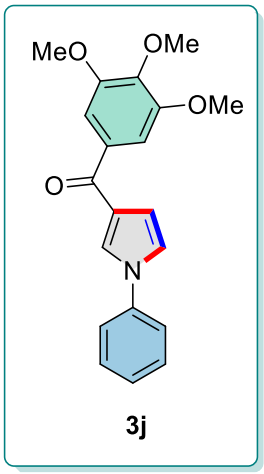
(4-chloro-3-methylphenyl)(1-phenyl-1H-pyrrol-3-yl)methanone (3i)



3i

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 76%, 67mg); **IR** (KBr) 3768, 2977, 2798, 1636, 1596, 1512, 1290, 1265, 1211, 1057, 936, 752, 636, 570, 520 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.4 Hz, 1H), 7.67–7.58 (m, 2H), 7.51–7.39 (m, 5H), 7.38–7.32 (m, 1H), 7.11 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.84 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.7, 139.7, 138.2, 138.0, 136.3, 131.4, 129.9, 128.9, 127.7, 127.2, 126.0, 126.0, 121.3, 121.2, 112.4, 20.2. **HRMS** (TOF ES^+): m/z calcd for $C_{18}H_{14}ClNNaO[(M+Na)^+]$, 318.0656; found, 318.0662.

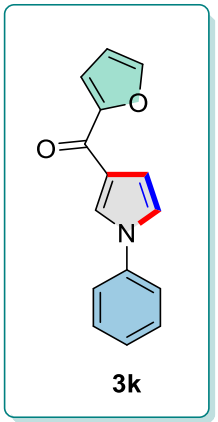
(1-phenyl-1H-pyrrol-3-yl)(3,4,5-trimethoxyphenyl)methanone (3j)



3j

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 88%, 89mg); **IR** (KBr) 3749, 3457, 2939, 2843, 1737, 1636, 1583 1510, 1412, 1328, 1228, 1130, 760, 607, 503 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (m, 1H), 7.52–7.39 (m, 4H), 7.39–7.31 (m, 1H), 7.17 (d, *J* = 1.0 Hz, 2H), 7.13 (td, *J* = 2.7, 2.2, 1.1 Hz, 1H), 6.87 (dt, *J* = 2.9, 1.4 Hz, 1H), 3.93 (dd, *J* = 7.5, 1.2 Hz, 9H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.7, 152.9, 141.3, 139.7, 134.9, 129.9, 127.1, 126.0, 125.7, 121.2, 121.1, 112.5, 106.6, 61.0, 56.3. **HRMS** (TOF ES^{+}): m/z calcd for $C_{20}H_{20}NO_4$[(M+H)$^{+}$], 338.1387; found, 338.1391.

furan-2-yl(1-phenyl-1H-pyrrol-3-yl)methanone (3k)

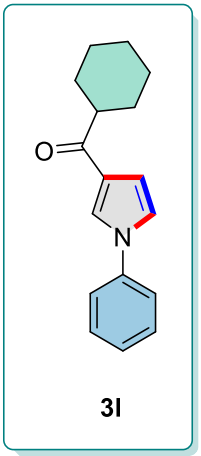


3k

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 79%, 56mg); **IR** (KBr) 3403, 3160. 2948, 1732, 1622, 1569, 1511, 1469, 1266, 1200, 1056, 835, 760, 497 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.95 (t, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 1.7 Hz, 1H), 7.41–7.33 (m, 4H), 7.28–7.22 (m, 2H), 7.00 (t, *J* = 2.7 Hz, 1H), 6.96 (dd, *J* = 3.0, 1.7 Hz, 1H), 6.48 (dd, *J* = 3.6, 1.7 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-

d) δ 175.1, 152.9, 144.4, 138.8, 128.8, 126.0, 124.7, 124.0, 120.1, 120.0, 116.2, 111.1, 110.9. **HRMS** (TOF ES^+): m/z calcd for $C_{15}H_{12}NO[(M+H)^+]$, 238.0863; found, 238.0868.

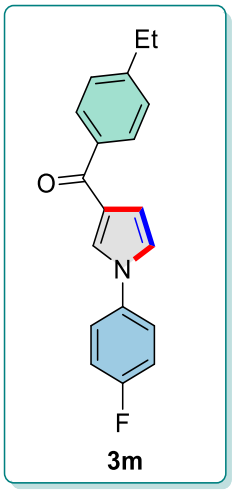
Cyclohexyl(1-phenyl-1H-pyrrol-3-yl)methanone (3l)



3l

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 65%, 49mg); **IR** (KBr) 3589, 2930, 2859, 1660, 1532, 1510, 1261, 1213, 1076, 895, 760, 691, 560 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (t, *J* = 1.9 Hz, 1H), 7.50–7.39 (m, 4H), 7.36–7.29 (m, 1H), 7.07–7.02 (m, 1H), 6.77 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.96 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.87 (dddd, *J* = 23.5, 12.7, 5.1, 2.4 Hz, 4H), 1.72 (dddd, *J* = 12.6, 5.1, 3.2, 1.6 Hz, 1H), 1.55 (qd, *J* = 12.4, 3.1 Hz, 2H), 1.41–1.24 (m, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 199.7, 139.9, 129.8, 127.0, 126.5, 123.7, 121.1, 121.1, 110.9, 47.6, 29.6, 26.0. **HRMS** (TOF ES^+): m/z calcd for $C_{17}H_{20}NO[(M+H)^+]$, 254.1539; found, 254.1544.

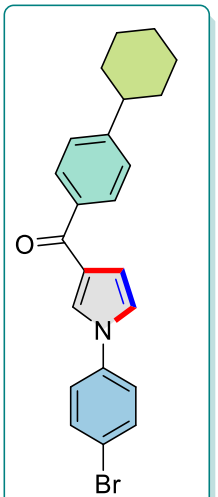
(4-ethylphenyl)(1-(4-fluorophenyl)-1H-pyrrol-3-yl)methanone (3m)



3m

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 73%, 64mg); **IR** (KBr) 3747, 3276, 3169, 2976, 1630, 1520, 1277, 931, 877, 759 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.85–7.79 (m, 2H), 7.55 (t, *J* = 1.9 Hz, 1H), 7.43–7.35 (m, 2H), 7.33–7.28 (m, 2H), 7.19–7.12 (m, 2H), 7.03 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.86 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.4, 161.4 (d, J_1 = 246 Hz), 148.4, 137.2, 136.2(d, J_4=3.75Hz), 129.2, 127.8, 126.4, 126.1, 123.0 (d, J_3 = 28.75 Hz), 121.3, 116.7 (d, J_2 = 22.5 Hz), 112.5, 28.9, 15.3; **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -114.7; **HRMS** (TOF ES^+): m/z calcd for $C_{19}H_{16}FNNaO[(M+Na)^+]$, 316.1108; found, 316.1111.

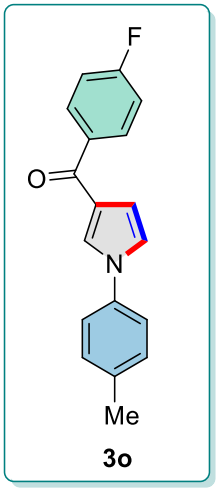
(1-(4-bromophenyl)-1H-pyrrol-3-yl)(4-cyclohexylphenyl)methanone (3n)



3n

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 59%, 72mg); **IR** (KBr) 3305, 2929, 2866, 1633, 1508, 1275, 1191, 831, 703, 631, 545 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.87–7.77 (m, 2H), 7.62–7.52 (m, 3H), 7.31 (dd, *J* = 8.6, 2.1 Hz, 4H), 7.06 (t, *J* = 2.7 Hz, 1H), 6.88 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.58 (ddd, *J* = 11.5, 8.1, 3.3 Hz, 1H), 1.96–1.80 (m, 4H), 1.81–1.73 (m, 1H), 1.51–1.36 (m, 4H), 1.27 (dt, *J* = 12.5, 3.5 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.3, 152.3, 138.8, 137.2, 132.9, 129.2, 129.1, 126.8, 126.7, 125.6, 122.6, 120.8, 120.4, 112.8, 44.7, 34.2, 26.8, 26.1. **HRMS** (TOF ES^{+}): m/z calcd for $C_{23}H_{23}BrNO[(M+H)^{+}]$, 408.0958; found, 408.0959.

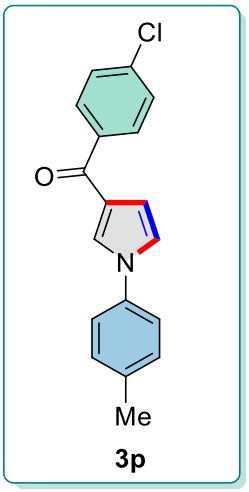
(4-fluorophenyl)(1-(p-tolyl)-1H-pyrrol-3-yl)methanone (3o)



3o

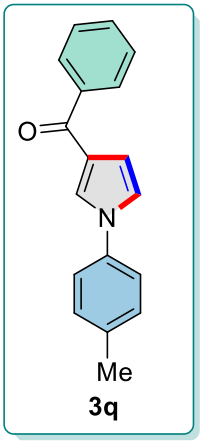
Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 74%, 62mg); **IR** (KBr) 3580, 3571, 2999, 1767, 1640, 1520, 1242, 1055, 761, 720 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88–7.81 (m, 2H), 7.50 (t, *J* = 1.9 Hz, 1H), 7.27–7.21 (m, 2H), 7.20 (d, *J* = 6.6 Hz, 2H), 7.12–7.05 (m, 2H), 7.01 (dd, *J* = 3.0, 2.2 Hz, 1H), 6.76 (dd, *J* = 3.0, 1.7 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.3, 164.9 (d, J_1 = 250 Hz), 137.4, 137.2, 136.0 (d, J_4 = 3.8 Hz), 131.4 (d, J_3 = 8.8 Hz), 130.3, 126.0, 125.7, 121.4, 121.1, 115.3 (d, J_2 = 22.5 Hz), 112.2, 21.0; **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -107.9; **HRMS** (TOF ES^{+}): m/z calcd for $C_{18}H_{15}FNO[(M+H)^{+}]$, 280.1132; found, 280.1128.

(4-chlorophenyl)(1-(p-tolyl)-1H-pyrrol-3-yl)methanone (3p)



Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 59%, 52mg); **IR** (KBr) 3507, 3241, 3019, 2406, 1633, 1525, 1276, 1089, 1053, 714, 638, 582, 470 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.85–7.80 (m, 2H), 7.56 (t, *J* = 2.0 Hz, 1H), 7.48–7.42 (m, 2H), 7.33–7.28 (m, 2H), 7.28–7.24 (m, 2H), 7.07 (dd, *J* = 3.0, 2.2 Hz, 1H), 6.82 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.4, 138.1, 137.8, 137.3, 137.2, 130.4, 130.3, 128.6, 126.1, 125.7, 121.5, 121.1, 112.1, 21.0. **HRMS** (TOF ES^{+}): m/z calcd for $C_{18}H_{14}ClNNaO[(M+Na)^{+}]$, 318.0656; found, 318.0663.

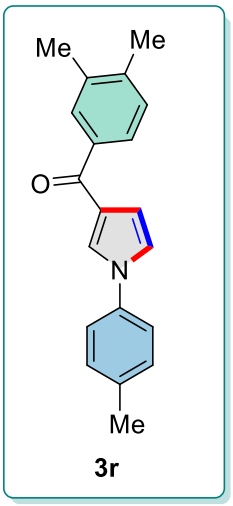
Pphenyl(1-(p-tolyl)-1H-pyrrol-3-yl)methanone (3q)



Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 88%, 69 mg); **IR** (KBr) 3553, 3180, 1633, 1526, 1278, 1172, 824, 709, 675 cm^{-1}; **^{1}H NMR** (600 MHz, Acetone-d_6) δ 7.92–7.87 (m, 2H), 7.77 (t, *J* = 2.0 Hz, 1H), 7.61–7.57 (m, 1H), 7.52 (ddd, *J* = 8.7, 4.2, 2.4 Hz, 4H), 7.34 (dd, *J* = 3.1, 2.1 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.2 Hz,

2H), 6.80 (dd, J = 3.1, 1.7 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR** (150 MHz, Acetone-d_6) δ 189.1, 140.0, 137.4, 136.7, 131.4, 130.3, 128.8, 128.7, 128.4, 128.3, 125.9, 125.7, 121.2, 120.7, 111.7, 20.0. **HRMS** (TOF ES$^+$): m/z calcd for $C_{18}H_{16}NO[(M+H)^+]$, 262.1226; found, 262.1221.

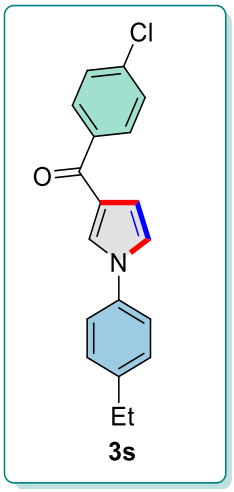
(3,4-dimethylphenyl)(1-(p-tolyl)-1H-pyrrol-3-yl)methanone (3r)



3r

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 77%, 67mg); **IR** (KBr) 3495, 3261, 2940, 1634, 1526, 1269, 813, 625 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.68 (d, J = 1.8 Hz, 1H), 7.63 (dd, J = 7.7, 1.9 Hz, 1H), 7.58 (t, J = 1.9 Hz, 1H), 7.32–7.28 (m, 2H), 7.27–7.24 (m, 2H), 7.23 (d, J = 7.7 Hz, 1H), 7.06 (dd, J = 3.0, 2.2 Hz, 1H), 6.85 (dd, J = 3.0, 1.7 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 6H); **^{13}C NMR** (125 MHz, Chloroform-d) δ 190.7, 140.8, 137.6, 137.5, 136.9, 136.7, 130.3, 130.2, 129.4, 126.8, 126.2, 125.9, 121.1, 121.0, 112.2, 20.9, 19.9, 19.8. **HRMS** (TOF ES$^+$): m/z calcd for $C_{20}H_{19}NNaO[(M+Na)^+]$, 312.1359; found, 312.1360.

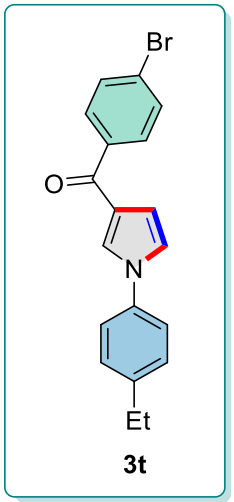
(4-chlorophenyl)(1-(4-ethylphenyl)-1H-pyrrol-3-yl)methanone (3s)



3s

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 66%, 61mg); **IR** (KBr) 3627, 3141, 2962, 2851, 1637, 1586, 1525, 1274, 1090, 881, 760, 640 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.85–7.78 (m, 2H), 7.56 (t, *J* = 2.0 Hz, 1H), 7.47–7.41 (m, 2H), 7.34–7.30 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.07 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.82 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.4, 143.6, 138.1, 137.8, 137.5, 130.4, 129.2, 128.5, 126.1, 125.6, 121.5, 121.2, 112.1, 28.3, 15.6. **HRMS** (TOF ES^{+}): m/z calcd for $C_{19}H_{16}ClNNaO[(M+Na)^{+}]$, 332.0813; found, 332.0815.

(4-bromophenyl)(1-(4-ethylphenyl)-1H-pyrrol-3-yl)methanone (3t)

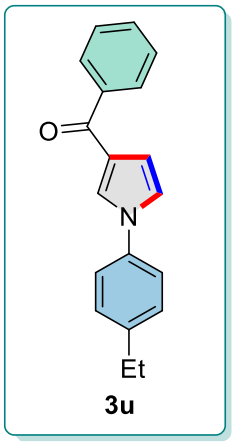


3t

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 66%, 70mg); **IR** (KBr) 3404, 3266, 3115, 1637, 1583, 1520, 1271, 918, 686, 629 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73–7.61 (m, 2H), 7.57–7.52 (m, 2H), 7.49 (t, *J* = 2.0 Hz, 1H),

7.30–7.15 (m, 4H), 7.00 (dd, J = 3.0, 2.2 Hz, 1H), 6.75 (dd, J = 3.1, 1.7 Hz, 1H), 2.62 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 188.5, 142.6, 137.5, 136.4, 130.5, 129.5, 128.1, 125.3, 125.1, 124.6, 120.5, 120.2, 111.1, 27.3, 14.5. **HRMS** (TOF ES$^+$): m/z calcd for $C_{19}H_{17}BrNO[(M+H)^+]$, 354.0488; found, 354.0496.

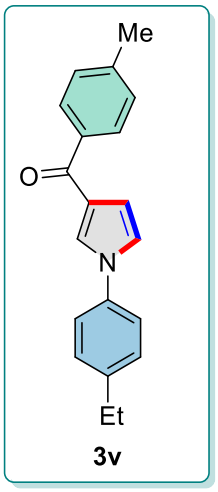
(1-(4-ethylphenyl)-1H-pyrrol-3-yl)(phenyl)methanone (3u)



3u

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 86%, 71mg); **IR** (KBr) 3614, 3470, 3346, 3262, 3059, 2969, 1732, 1640, 1520, 1275, 1050, 720 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81–7.76 (m, 2H), 7.49 (t, J = 2.0 Hz, 1H), 7.48–7.43 (m, 1H), 7.41–7.35 (m, 2H), 7.25–7.21 (m, 2H), 7.21–7.15 (m, 2H), 6.98 (dd, J = 3.0, 2.2 Hz, 1H), 6.77 (dd, J = 3.1, 1.7 Hz, 1H), 2.59 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.8, 143.4, 139.9, 137.6, 131.5, 129.2, 129.0, 128.3, 126.3, 126.0, 121.3, 121.2, 112.2, 28.4, 15.6. **HRMS** (TOF ES$^+$): m/z calcd for $C_{19}H_{18}NO[(M+H)^+]$, 276.1383; found, 276.1389.

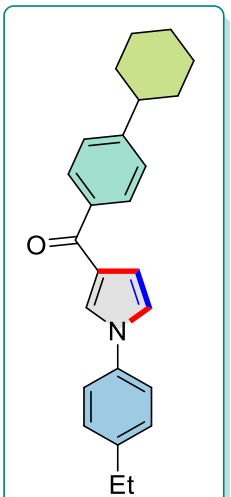
(1-(4-ethylphenyl)-1H-pyrrol-3-yl)(p-tolyl)methanone (3v)



3v

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 83%, 72mg); **IR** (KBr) 3413, 2971, 1635, 1515, 1275, 1049, 885, 835, 749, 515, 472 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.84–7.76 (m, 2H), 7.58 (t, *J* = 2.0 Hz, 1H), 7.34–7.25 (m, 6H), 7.07 (dd, *J* = 3.0, 2.2 Hz, 1H), 6.85 (dd, *J* = 3.0, 1.7 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.5, 143.4, 142.1, 137.7, 137.2, 129.2, 129.1, 128.9, 126.1, 126.0, 121.2, 121.1, 112.2, 28.3, 21.6, 15.6. **HRMS** (TOF ES^{+}): m/z calcd for $C_{20}H_{20}NO[(M+H)^{+}]$, 290.1539; found, 290.1546.

(4-cyclohexylphenyl)(1-(4-ethylphenyl)-1H-pyrrol-3-yl)methanone (3w)

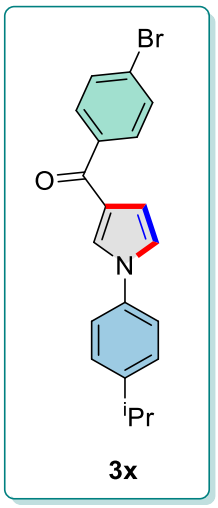


3w

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 75%, 80mg); **IR** (KBr) 3536, 3053, 2929, 2857, 1637, 1611, 1523, 1275, 837, 766, 712, 469 cm^{-1}; **^{1}H NMR** (500

MHz, Chloroform-*d*) δ 7.79–7.68 (m, 2H), 7.51 (t, *J* = 1.9 Hz, 1H), 7.29–7.13 (m, 6H), 6.98 (dd, *J* = 3.0, 2.2 Hz, 1H), 6.78 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.54–2.44 (m, 1H), 1.86–1.74 (m, 4H), 1.68 (dtt, *J* = 12.0, 3.2, 1.6 Hz, 1H), 1.44–1.27 (m, 4H), 1.18 (t, *J* = 7.6 Hz, 4H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.5, 152.0, 143.3, 137.7, 137.5, 129.2, 129.1, 126.8, 126.1, 126.0, 121.2, 112.2, 44.7, 34.3, 28.3, 26.8, 26.1, 15.6. **HRMS** (TOF ES$^+$): m/z calcd for $C_{25}H_{28}NO[(M+H)^+]$, 358.2165; found, 358.2170.

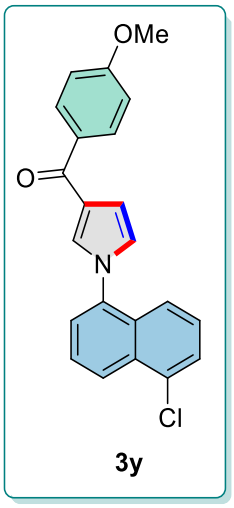
(4-bromophenyl)(1-(4-isopropylphenyl)-1H-pyrrol-3-yl)methanone (3x)



3x

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 55%, 61mg); **IR** (KBr) 3526, 3272, 3167, 1766, 1525, 1244, 895, 744, 640, 406 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78–7.72 (m, 2H), 7.64–7.59 (m, 2H), 7.56 (t, *J* = 1.9 Hz, 1H), 7.36–7.30 (m, 4H), 7.08 (dd, *J* = 3.1, 2.2 Hz, 1H), 6.82 (dd, *J* = 3.0, 1.7 Hz, 1H), 2.96 (hept, *J* = 7.0 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.5, 148.2, 138.6, 137.5, 131.5, 130.5, 127.8, 126.3, 126.2, 125.6, 121.6, 121.2, 112.1, 33.7, 24.0. **HRMS** (TOF ES$^+$): m/z calcd for $C_{20}H_{18}BrNNaO[(M+Na)^+]$, 390.0464; found, 390.0459.

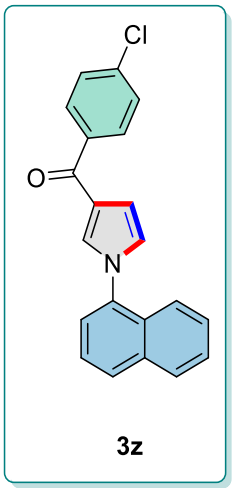
(1-(5-chloronaphthalen-1-yl)-1H-pyrrol-3-yl)(4-methoxyphenyl)methanone (3y)



3y

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 68%, 74mg); **IR** (KBr) 3439, 3277, 3074, 2933, 1739, 1600, 1504, 1258, 1168, 1033, 793, 759, 694, 605, 580 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.69–7.55 (m, 4H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.6, 7.4 Hz, 1H), 7.02–6.91 (m, 4H), 3.87 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 189.5, 162.6, 137.2, 132.6, 132.4, 131.6, 131.3, 130.9, 129.3, 127.3, 126.3, 125.7, 125.5, 124.8, 124.5, 121.9, 113.5, 111.5, 55.4. **HRMS** (TOF ES^{+}): m/z calcd for $C22H_{16}ClNNaO_2$[(M+Na)$^{+}$], 384.0762; found, 384.0766.

(1-(6-hydroxynaphthalen-2-yl)-1H-pyrrol-3-yl)(p-tolyl)methanone (3z)

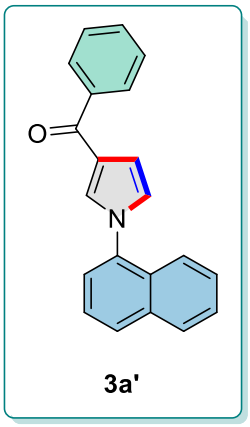


3z

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 63%, 63mg); **IR** (KBr) 3556, 3303, 2909, 1634, 1523, 1276, 1018, 876, 742, 651 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.68 (d,

J = 8.3 Hz, 1H), 7.60–7.47 (m, 5H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.03 (t, *J* = 2.5 Hz, 1H), 6.93 (t, *J* = 2.3 Hz, 1H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 189.4, 138.2, 137.8, 136.7, 134.2, 130.4, 129.8, 129.4, 129.1, 128.5, 128.4, 127.6, 127.0, 125.2, 125.1, 125.1, 123.5, 122.5, 111.2. **HRMS** (TOF ES$^+$): m/z calcd for $C_{21}H_{15}ClNO[(M+H)^+]$, 332.0837; found, 332.0840.

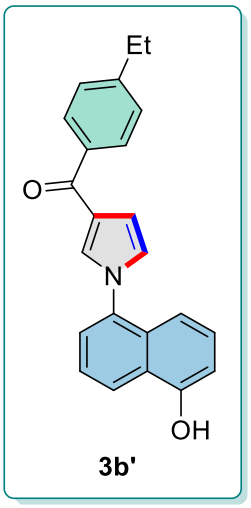
(1-(naphthalen-1-yl)-1H-pyrrol-3-yl)(phenyl)methanone (3a')



3a'

Yellow oil ($V_{\text{Petroleum ether}}/V_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 89%, 79mg); **IR** (KBr) 3590, 2963, 2893, 1636, 1531, 1464, 1281, 1017, 937, 880, 774, 728, 704, 527, 464 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.97–7.88 (m, 4H), 7.70 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.59–7.49 (m, 6H), 7.48–7.42 (m, 2H), 7.04–7.01 (m, 1H), 6.96 (dd, *J* = 2.9, 1.7 Hz, 1H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.8, 139.9, 136.9, 134.2, 131.5, 129.9, 129.4, 129.0, 129.0, 128.3, 128.2, 127.5, 126.9, 125.4, 125.2, 124.9, 123.5, 122.6, 111.2. **HRMS** (TOF ES$^+$): m/z calcd for $C_{21}H_{16}NO[(M+H)^+]$, 298.1226; found, 298.1233.

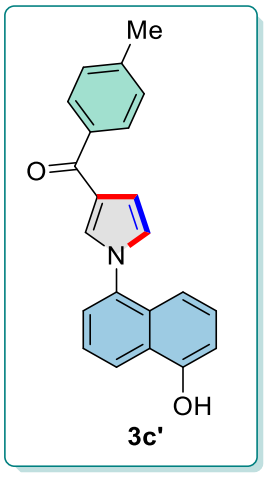
(4-ethylphenyl)(1-(5-hydroxynaphthalen-1-yl)-1H-pyrrol-3-yl)methanone (3b')



3b'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 64%, 66mg); **IR** (KBr) 3566, 3263, 2903, 1607, 1522, 1448, 1425, 1378, 1277, 1050, 878, 790, 641, 480 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.30 (dd, *J* = 6.7, 3.1 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 1.9 Hz, 1H), 7.44–7.36 (m, 2H), 7.31–7.18 (m, 4H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.96–6.87 (m, 3H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.5, 151.5, 147.6, 136.1, 135.4, 129.7, 129.4, 128.4, 126.8, 126.7, 124.6, 124.1, 124.1, 123.1, 122.9, 122.3, 113.4, 110.2, 108.5, 27.9, 14.3. **HRMS** (TOF ES^{+}): m/z calcd for $C_{23}H_{19}NNaO_2$[(M+Na)$^{+}$], 364.1308; found, 364.1308.

(1-(5-hydroxynaphthalen-1-yl)-1H-pyrrol-3-yl)(phenyl)methanone (3c')

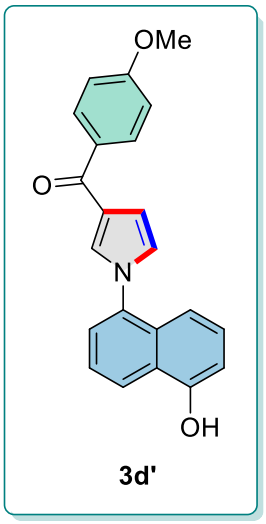


3c'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 70%, 69mg); **IR** (KBr) 3884, 3760, 3425, 2914, 1603, 1411, 1086, 794, 734, 646, 508 cm^{-1}; **^{1}H NMR** (500 MHz,

Chloroform-*d*) δ 8.34 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.55–7.46 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.00 (t, *J* = 2.6 Hz, 1H), 6.97–6.89 (m, 2H), 6.26 (s, 1H), 2.41 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.9, 152.1, 142.2, 137.1, 136.6, 130.8, 130.0, 129.2, 128.9, 127.6, 125.5, 125.3, 125.0, 124.3, 124.1, 123.1, 114.9, 111.2, 109.5, 21.6. **HRMS** (TOF ES$^+$): m/z calcd for $C_{22}H_{18}NO_2$ [(M+H)$^+$], 328.1332; found, 328.1333.

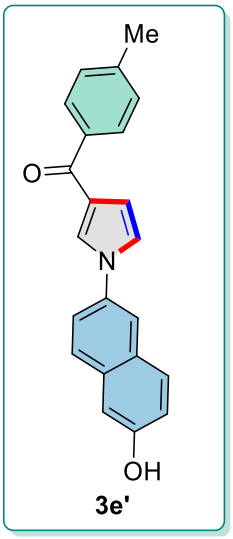
(1-(5-hydroxynaphthalen-1-yl)-1H-pyrrol-3-yl)(4-methoxyphenyl)methanone (3d')



3d'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 71%, 73mg); **IR** (KBr) 3647, 3269, 2943, 2878, 2762, 1602, 1424, 1262, 1169, 1047, 797, 720, 696, 620, 565 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.35 (dd, *J* = 7.2, 2.5 Hz, 1H), 8.01–7.91 (m, 2H), 7.57–7.43 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.00 (t, *J* = 2.5 Hz, 1H), 6.98–6.91 (m, 4H), 6.62 (br, 1H), 3.87 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.1, 162.6, 152.2, 136.6, 132.3, 131.4, 130.8, 129.7, 127.6, 125.5, 125.2, 124.9, 124.2, 124.0, 123.1, 114.8, 113.5, 111.3, 109.5, 55.4. **HRMS** (TOF ES$^+$): m/z calcd for $C_{22}H_{18}NO_3$[(M+H)$^+$], 344.1281; found, 344.1287.

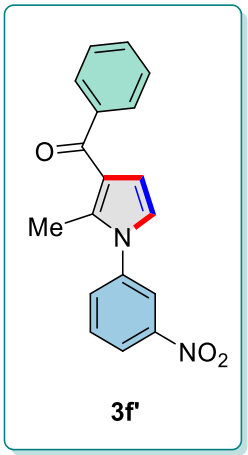
(4-chlorophenyl)(1-(naphthalen-1-yl)-1H-pyrrol-3-yl)methanone (3e')



3e'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 67%, 66mg); **IR** (KBr) 3505, 3216, 2957, 1638, 1500, 1279, 1002, 795, 710, 553, 428 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.48 (s, 1H), 8.38 (dq, *J* = 7.2, 3.6 Hz, 1H), 7.83 (dd, *J* = 8.1, 3.0 Hz, 2H), 7.54–7.39 (m, 3H), 7.34–7.30 (m, 1H), 7.26 (dd, *J* = 8.3, 2.7 Hz, 2H), 7.15 (dd, *J* = 8.6, 3.1 Hz, 1H), 7.04–6.96 (m, 2H), 6.92 (q, *J* = 2.7 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.6, 153.7, 142.0, 137.2, 136.4, 130.8, 129.9, 129.1, 128.9, 127.9, 126.0, 125.2, 124.9, 123.7, 123.7, 123.5, 113.3, 110.9, 109.2, 21.5. **HRMS** (TOF ES$^+$): m/z calcd for $C_{22}H_{18}NO_2$[$(M+H)^+$], 328.1332; found, 328.1337.

(2-methyl-1-(3-nitrophenyl)-1H-pyrrol-3-yl)(phenyl)methanone (3f')

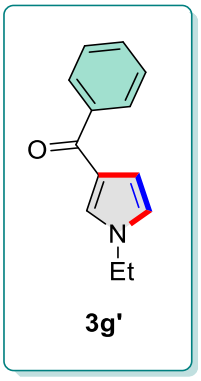


3f'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 59%, 54mg); **IR** (KBr) 3422, 3211, 2967, 1635, 1530, 1425, 1351, 1280, 881, 699, 536, 431 cm^{-1}; **^{1}H NMR** (500

MHz, Chloroform-*d*) δ 8.32 (dt, *J* = 7.5, 2.1 Hz, 1H), 8.25 (t, *J* = 2.0 Hz, 1H), 7.88–7.82 (m, 2H), 7.75–7.68 (m, 2H), 7.58–7.51 (m, 1H), 7.51–7.44 (m, 2H), 6.76 (d, *J* = 3.2 Hz, 1H), 6.56 (d, *J* = 3.2 Hz, 1H), 2.52 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 192.4, 148.8, 140.2, 140.0, 136.5, 132.0, 131.6, 130.4, 129.2, 128.2, 122.9, 122.0, 121.3, 120.8, 113.3, 12.8. **HRMS** (TOF ES$^+$): m/z calcd for $C_{18}H_{15}N_2O_3$[(M+H)$^+$], 307.1077; found, 307.1080.

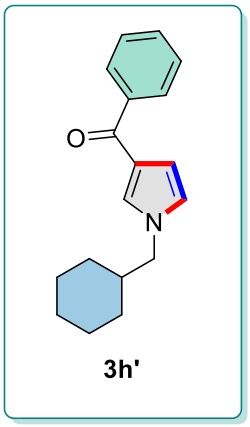
(1-ethyl-1H-pyrrol-3-yl)(phenyl)methanone (3g')



3g'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 82%, 49mg); **IR** (KBr) 2978, 1631, 1521, 1383, 1237, 1212, 1075, 878, 723 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.84–7.79 (m, 2H), 7.53–7.49 (m, 1H), 7.44 (ddt, *J* = 8.3, 6.6, 1.2 Hz, 2H), 7.24 (t, *J* = 2.0 Hz, 1H), 6.68 (m, 2H), 3.95 (q, *J* = 7.4 Hz, 2H), 1.45 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 190.7, 140.3, 131.3, 128.9, 128.2, 127.5, 124.4, 121.8, 111.0, 44.9, 16.4. **HRMS** (TOF ES$^+$): m/z calcd for $C_{13}H_{14}NO$[(M+H)$^+$], 200.1070; found, 200.1075.

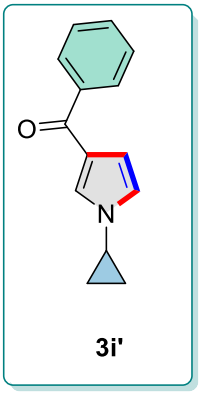
(1-(cyclohexylmethyl)-1H-pyrrol-3-yl)(phenyl)methanone (3h')



3h'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 86%, 69mg); **IR** (KBr) 2926, 2852, 1632, 1525, 1449, 1260, 1148, 877, 721 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85–7.78 (m, 2H), 7.54–7.48 (m, 1H), 7.47–7.41 (m, 2H), 7.18 (t, *J* = 2.0 Hz, 1H), 6.68–6.60 (m, 2H), 3.70 (d, *J* = 7.2 Hz, 2H), 1.75–1.59 (m, 6H), 1.26–1.11 (m, 3H), 0.92 (m, 2H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.7, 140.3, 131.3, 129.0, 128.5, 128.2, 124.2, 122.8, 110.8, 56.9, 39.6, 30.7, 26.3, 25.7; **HRMS** (TOF ES^{+}): m/z calcd for $C_{18}H_{22}NO[(M+H)^{+}]$, 268.1694; found, 268.1701.

(1-cyclopropyl-1H-pyrrol-3-yl)(phenyl)methanone (3i')

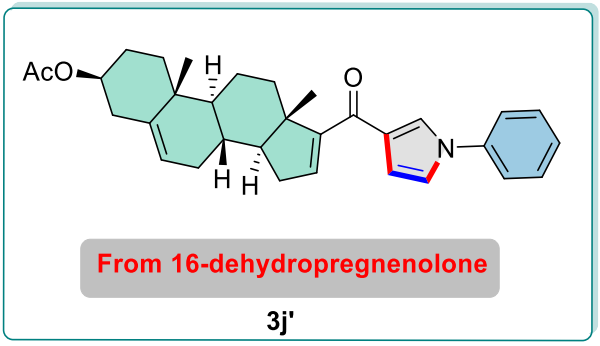


3i'

Yellow oil (V $_{\text{Petroleum ether}}$/V $_{\text{Ethyl acetate}}$ = 30:1 to 10:1, 87%, 55mg); **IR** (KBr) 3744, 3613, 3252, 3021, 2954, 1635, 1525, 1320, 1269, 1212, 1074, 775, 720, 665, 595, 470 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.75–7.71 (m, 2H), 7.46–7.41 (m, 1H), 7.37 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.22 (t, *J* = 1.9 Hz, 1H), 6.71–6.67 (m, 1H), 6.56 (dd, *J* = 3.0, 1.7 Hz, 1H), 3.31 (tt, *J* = 6.5, 4.3 Hz, 1H), 0.89 (dtd, *J* = 7.6, 3.9, 3.3, 2.1 Hz, 4H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 190.6, 140.1, 131.3, 128.8, 128.5, 128.2, 124.3, 123.0, 110.7, 30.6, 6.5. **HRMS** (TOF ES^{+}): m/z calcd for

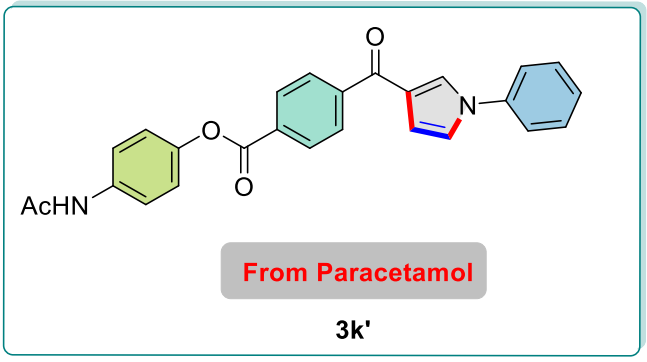
$C_{14}H_{14}NO[(M+H)^+]$, 212.1070; found, 212.1075.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-(1-phenyl-1H-pyrrole-3-carbonyl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (3j')



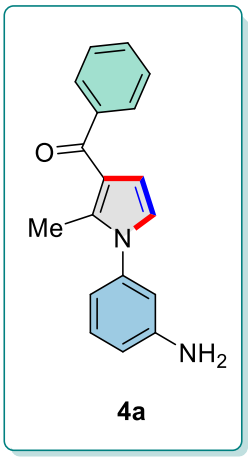
Yellow oil ($V_{\text{Petroleum ether}}/V_{\text{Ethyl acetate}}$ = 20:1 to 5:1, 79%, 115mg); **IR** (KBr) 3524, 3381, 2890, 1737, 1660, 1514, 1285, 1204, 1085, 956, 872, 780, 540, 510 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.54 (t, *J* = 1.9 Hz, 1H), 7.46 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.43–7.38 (m, 2H), 7.32 (td, *J* = 7.2, 1.5 Hz, 1H), 7.05 (t, *J* = 2.6 Hz, 1H), 6.77 (dd, *J* = 3.1, 1.7 Hz, 1H), 6.56 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.41 (d, *J* = 4.9 Hz, 1H), 4.62 (tdd, *J* = 10.6, 6.2, 4.2 Hz, 1H), 2.34 (dddd, *J* = 24.5, 12.3, 6.8, 3.4 Hz, 4H), 2.15–2.00 (m, 5H), 1.88 (dt, *J* = 14.1, 3.9 Hz, 2H), 1.80–1.47 (m, 6H), 1.44–1.34 (m, 1H), 1.19–1.10 (m, 4H), 1.08 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 188.4, 170.5, 155.1, 141.0, 140.3, 139.9, 129.8, 127.9, 126.9, 124.5, 122.1, 121.1, 120.9, 111.4, 73.9, 56.3, 50.6, 47.5, 38.2, 36.9, 36.9, 34.2, 32.6, 31.7, 30.2, 27.8, 21.4, 20.7, 19.3, 16.4. **HRMS** (TOF ES^+): m/z calcd for $C_{32}H_{38}NO_3[(M+H)^+]$, 484.2846; found, 484.2841.

4-acetamidophenyl 4-(1-phenyl-1H-pyrrole-3-carbonyl)benzoate (3k')



Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1 to 5:1, 87%, 111mg); **IR** (KBr) 3689, 3121, 2860, 2616, 2007, 1935, 1732, 1622, 1601, 1591, 1472, 1200, 990, 740 cm^{-1}; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.34–8.27 (m, 2H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.62 (t, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.51–7.46 (m, 2H), 7.46–7.40 (m, 2H), 7.41–7.33 (m, 2H), 7.22–7.16 (m, 2H), 7.14 (t, *J* = 2.6 Hz, 1H), 6.88 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 189.9, 168.3, 164.7, 147.0, 144.2, 139.6, 135.8, 131.8, 130.2, 129.9, 128.9, 127.4, 126.5, 125.9, 122.1, 121.7, 121.2, 120.9, 112.3, 24.6. **HRMS** (TOF ES$^+$): m/z calcd for $C_{26}H_{21}N_2O_4[(M+H)^+]$, 425.1496; found, 425.1499.

(1-(3-aminophenyl)-2-methyl-1H-pyrrol-3-yl)(phenyl)methanone (4a)



4a

Yellow oil ($V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1 to 10:1, 94%, 52mg); **IR** (KBr) 3437, 3228, 3170, 2717, 1628, 1616, 1502, 1325, 1241, 1107, 883, 710, 530 cm^{-1}; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81–7.72 (m, 2H), 7.47–7.41 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.16 (dd, *J* = 14.4, 6.5 Hz, 1H), 6.67–6.57 (m, 3H), 6.53 (t, *J* = 2.1 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 3.80 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 191.5, 146.4, 139.7, 138.9, 136.1, 130.1, 129.0, 128.1, 127.0, 120.0, 119.9, 115.1, 113.6, 111.6, 111.2, 11.9. **HRMS** (TOF ES$^+$): m/z calcd for $C_{18}H_{17}N_2O[(M+H)^+]$, 277.1335; found, 277.1337.

5. X-ray Structure and Data of 3q

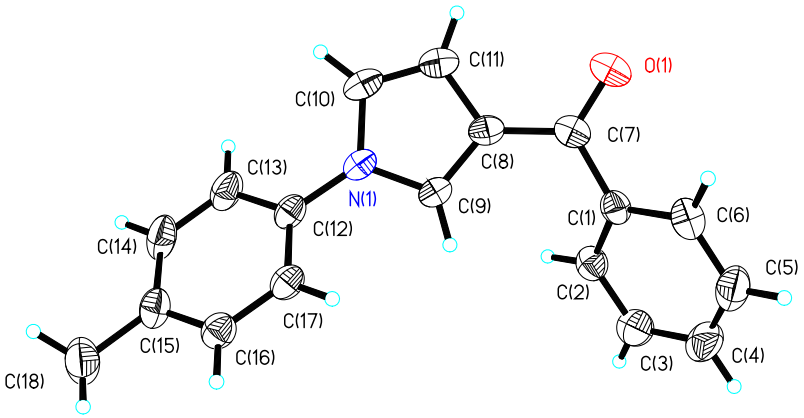


Figure S1. X-Ray crystal structure of **3q**, ellipsoid is drawn at the 30% probability level.

Table S2. Crystal data and structure refinement for **3q**

Identification code	mo_240117A	
Chemical formula	$C_{18}H_{15}NO$	
Formula weight	261.31 g/mol	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.200 x 0.260 mm	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 9.5331(3) Å	α = 90°
	b = 11.0505(3) Å	β = 90°
	c = 26.8472(8) Å	γ = 90°
Volume	2828.23(14) $Å^3$	
Z	8	
Density (calculated)	1.227 g/cm^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	1104	
Theta range for data collection	2.62 to 28.34°	
Index ranges	-12<=h<=12, -14<=k<=14, -35<=l<=35	
Reflections collected	33019	
Independent reflections	3523 [R(int) = 0.0787]	
Max. and min. transmission	0.7457 and 0.7047	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL 2018/3 (Sheldrick, 2015)	
Function minimized	$\Sigma w(Fo^2 - Fc^2)^2$	
Data / restraints / parameters	3523 / 0 / 182	

Goodness-of-fit on F2	1.143
Final R indices	2100 data; I>2σ(I) R1 = 0.0661, wR2 = 0.1300
	all data R1 = 0.1212, wR2 = 0.1545
Weighting scheme	$w=1/[\sigma^2(Fo^2)+(0.0513P)^2+0.5898P]$
	where $P=(Fo^2+2Fc^2)/3$
Largest diff. peak and hole	0.156 and -0.195 $eÅ^{-3}$
R.M.S. deviation from mean	0.036 $eÅ^{-3}$

Table S3. Bond Lengths for **3q**

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
O1	C7	1.227(2)		N1	C9	1.362(2)
N1	C10	1.387(2)		N1	C12	1.429(3)
C1	C2	1.385(3)		C1	C6	1.389(3)
C1	C7	1.487(3)		C2	H2	0.93
C2	C3	1.376(3)		C3	H3	0.93
C3	C4	1.374(4)		C4	H4	0.93
C4	C5	1.367(4)		C5	H5	0.93
C5	C6	1.377(3)		C6	H6	0.93
C7	C8	1.454(3)		C8	C9	1.379(3)
C8	C11	1.421(3)		C9	H9	0.93
C10	H10	0.93		C10	C11	1.345(3)
C11	H11	0.93		C12	C13	1.382(3)
C12	C17	1.378(3)		C13	H13	0.93
C13	C14	1.379(3)		C14	H14	0.93
C14	C15	1.385(3)		C15	C16	1.375(3)
C15	C18	1.504(3)		C16	H16	0.93
C16	C17	1.381(3)		C17	H17	0.93
C18	H18A	0.96		C18	H18B	0.96
C18	H18C	0.96				

Table S4. Bond Angles for **3q**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C9	N1	C10	108.13(18)		C9	N1	C12	125.32(16)
C10	N1	C12	126.53(17)		C2	C1	C6	118.9(2)
C2	C1	C7	121.72(19)		C6	C1	C7	119.2(2)
C1	C2	H2	119.9		C3	C2	C1	120.2(2)
C3	C2	H2	119.9		C2	C3	H3	119.8
C4	C3	C2	120.3(2)		C4	C3	H3	119.8
C3	C4	H4	120		C5	C4	C3	120.0(2)
C5	C4	H4	120		C4	C5	H5	119.9
C4	C5	C6	120.2(2)		C6	C5	H5	119.9
C1	C6	H6	119.8		C5	C6	C1	120.3(2)
C5	C6	H6	119.8		O1	C7	C1	119.0(2)
O1	C7	C8	120.3(2)		C8	C7	C1	120.68(18)
C9	C8	C7	127.59(18)		C9	C8	C11	106.09(18)
C11	C8	C7	126.03(19)		N1	C9	C8	108.99(17)
N1	C9	H9	125.5		C8	C9	H9	125.5
N1	C10	H10	125.8		C11	C10	N1	108.48(18)
C11	C10	H10	125.8		C8	C11	H11	125.8
C10	C11	C8	108.31(19)		C10	C11	H11	125.8
C13	C12	N1	120.95(18)		C17	C12	N1	119.92(17)
C17	C12	C13	119.1(2)		C12	C13	H13	120.1
C14	C13	C12	119.8(2)		C14	C13	H13	120.1
C13	C14	H14	119		C13	C14	C15	122.0(2)
C15	C14	H14	119		C14	C15	C18	122.0(2)
C16	C15	C14	117.1(2)		C16	C15	C18	120.9(2)
C15	C16	H16	119		C15	C16	C17	122.0(2)
C17	C16	H16	119		C12	C17	C16	120.01(19)
C12	C17	H17	120		C16	C17	H17	120
C15	C18	H18A	109.5		C15	C18	H18B	109.5
C15	C18	H18C	109.5		H18A	C18	H18B	109.5
H18A	C18	H18C	109.5		H18B	C18	H18C	109.5

6. ^{1}H NMR and ^{13}C NMR spectra for spectroscopic date

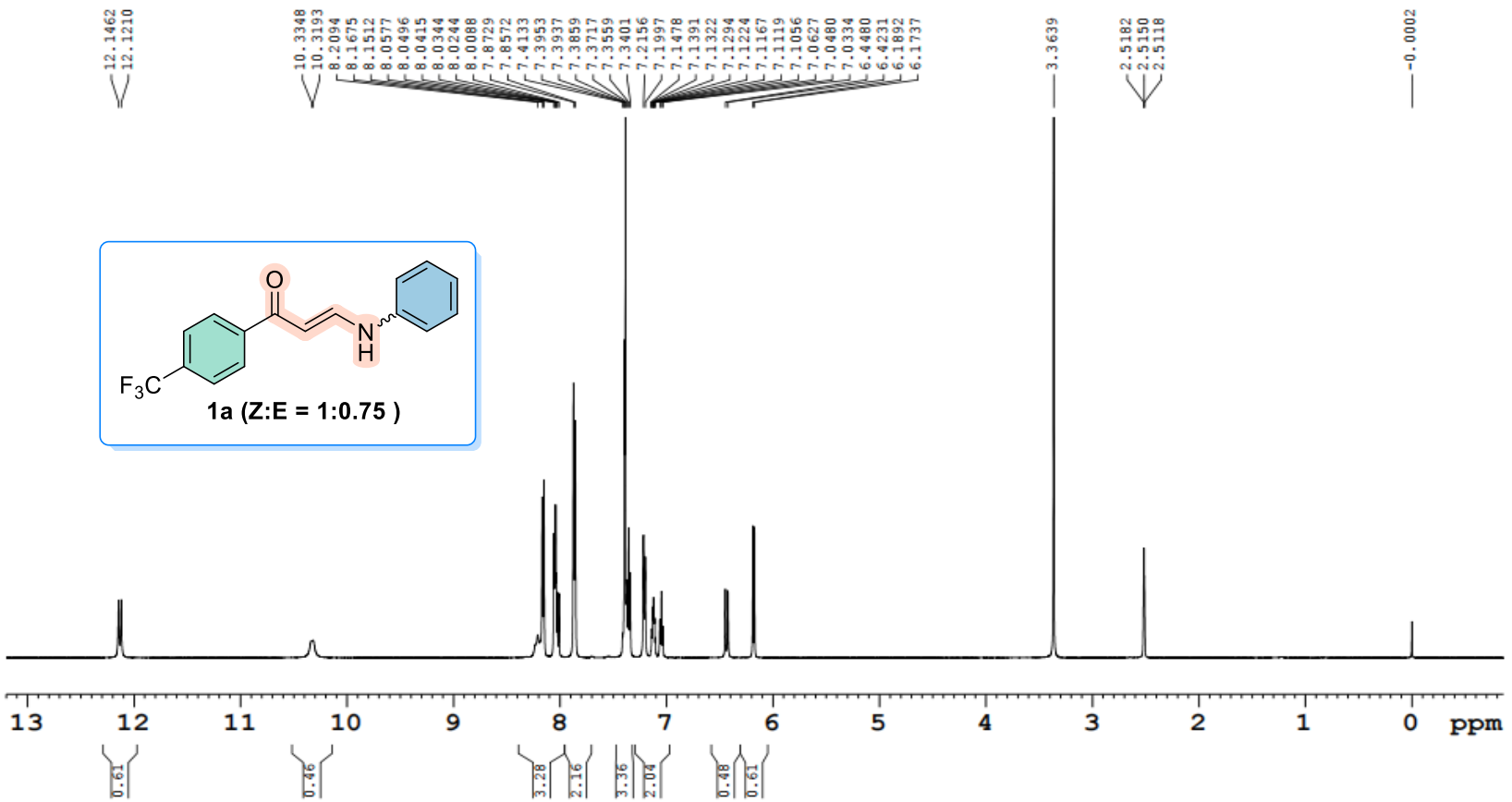


Figure S2. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1a**

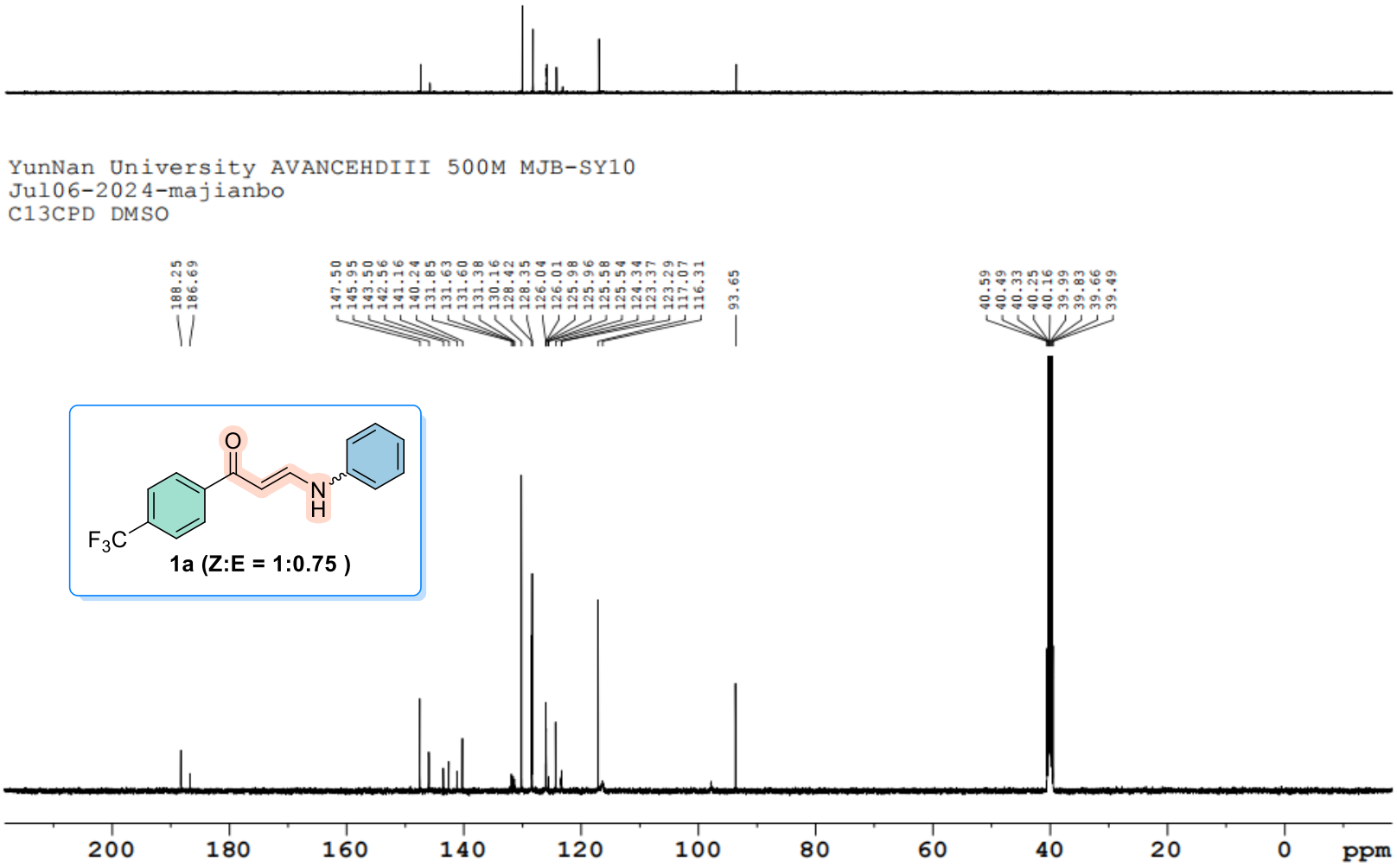


Figure S3. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1a**

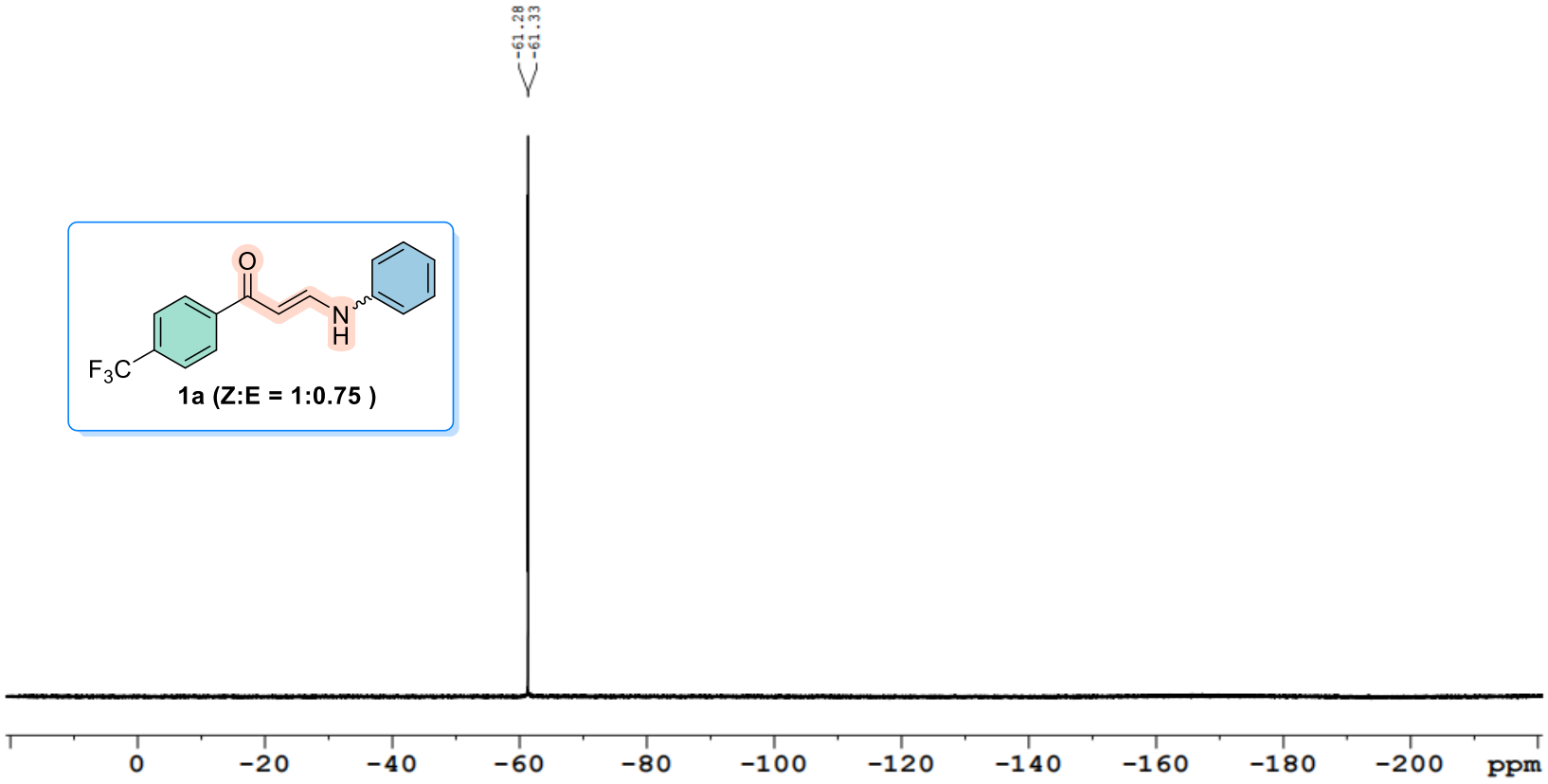


Figure S4. ^{19}F NMR (470 MHz, DMSO-d_6) spectra of compound **1a**

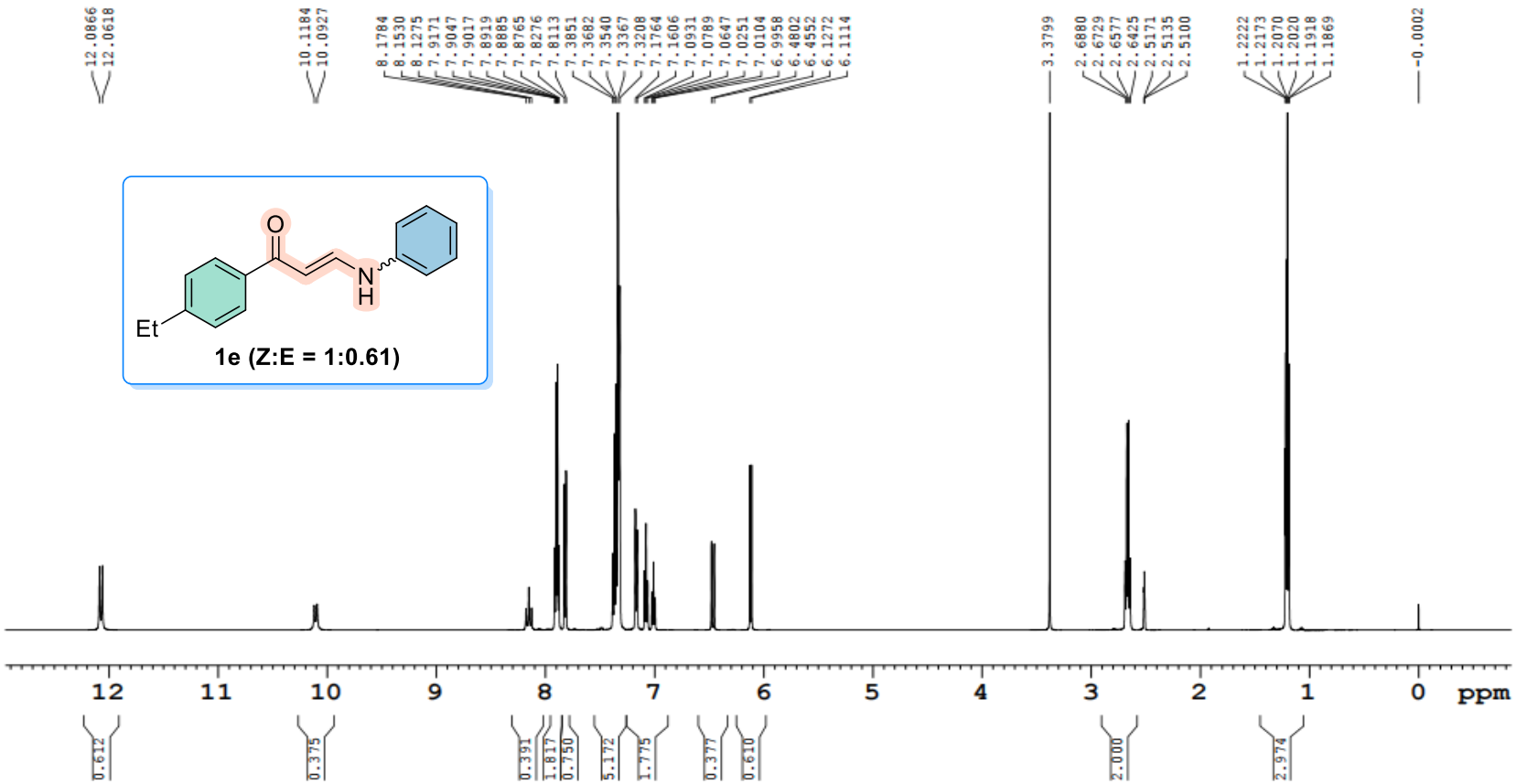


Figure S5. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1e**

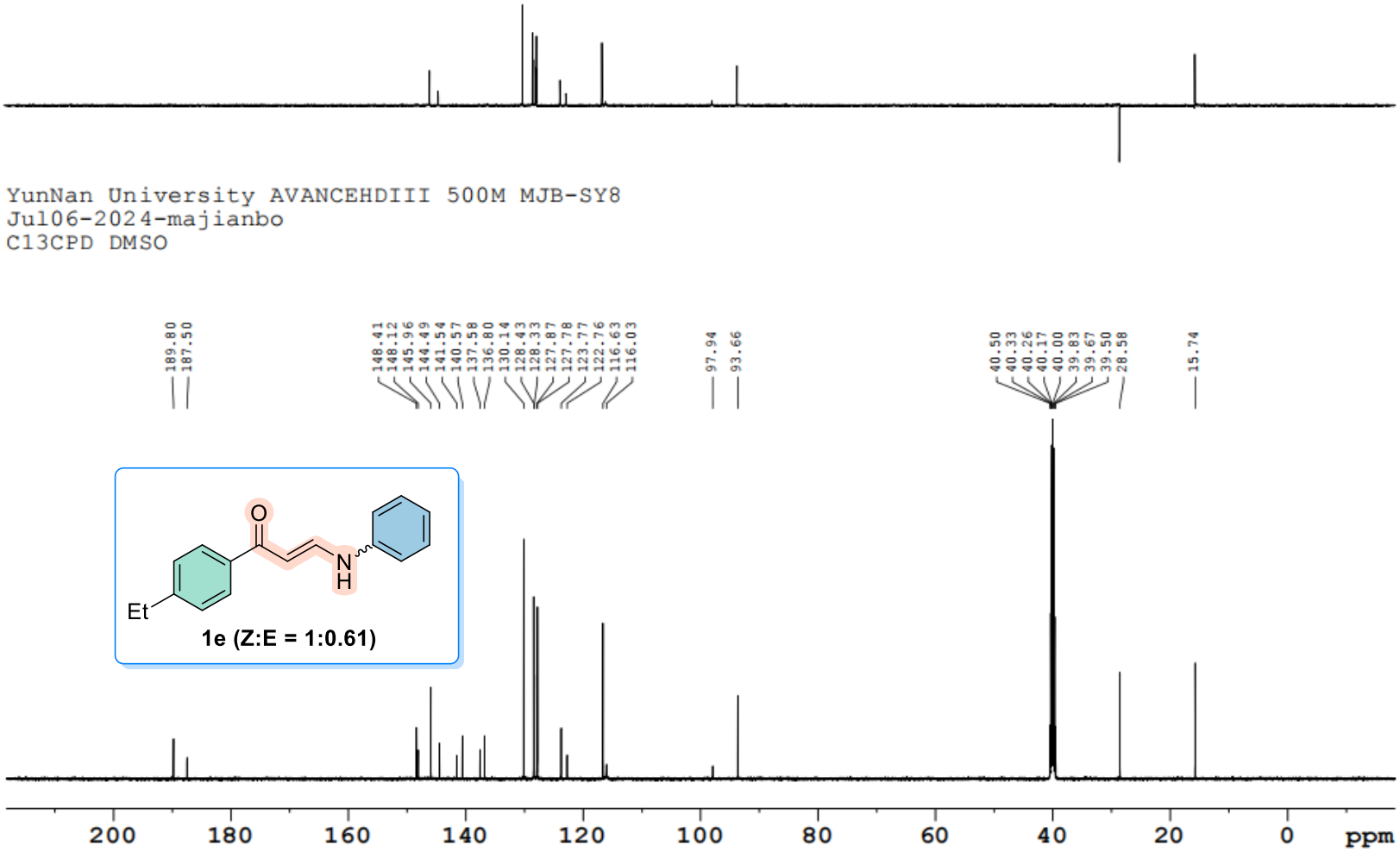


Figure S6. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1e**

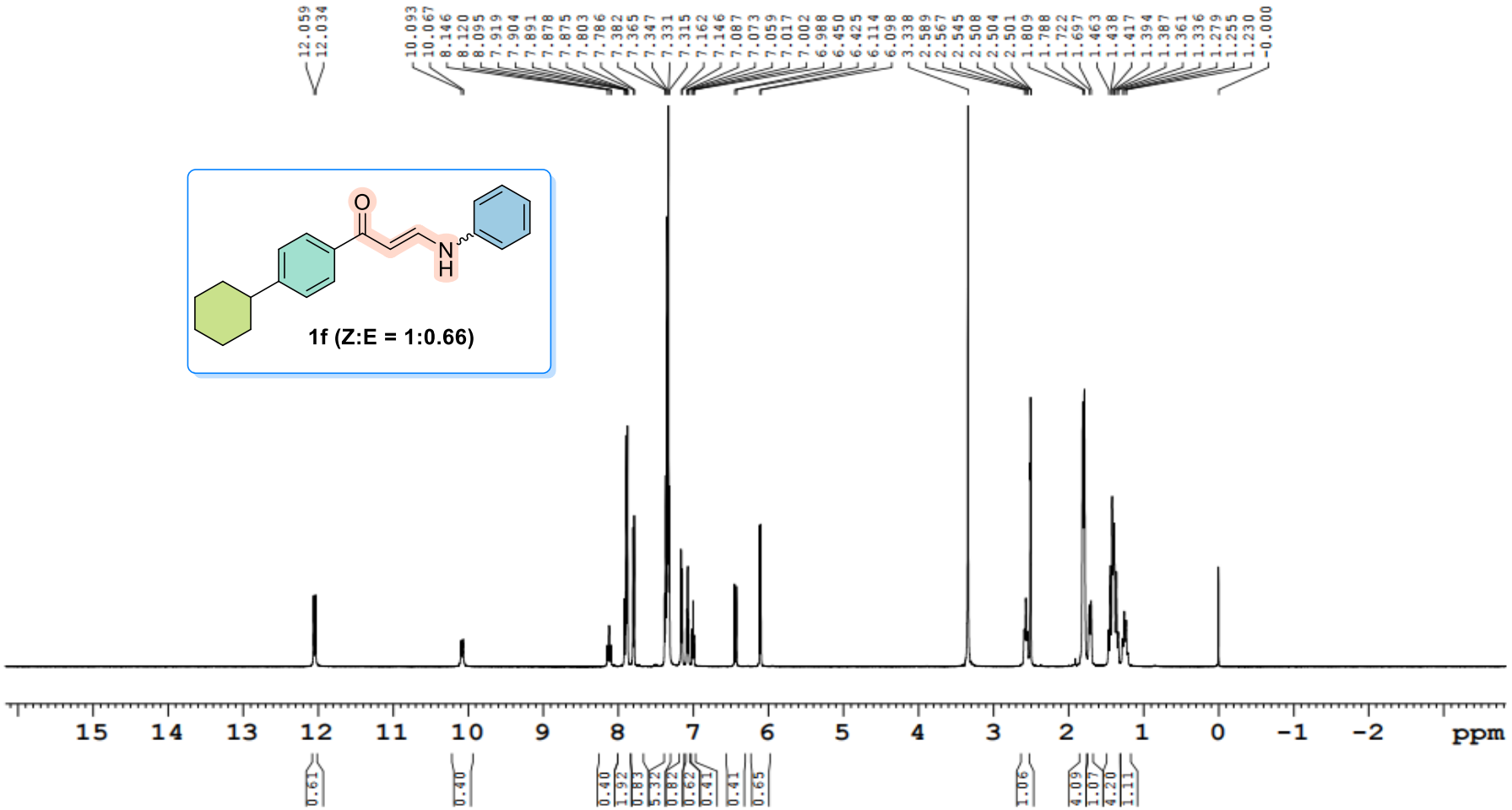


Figure S7. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1f**

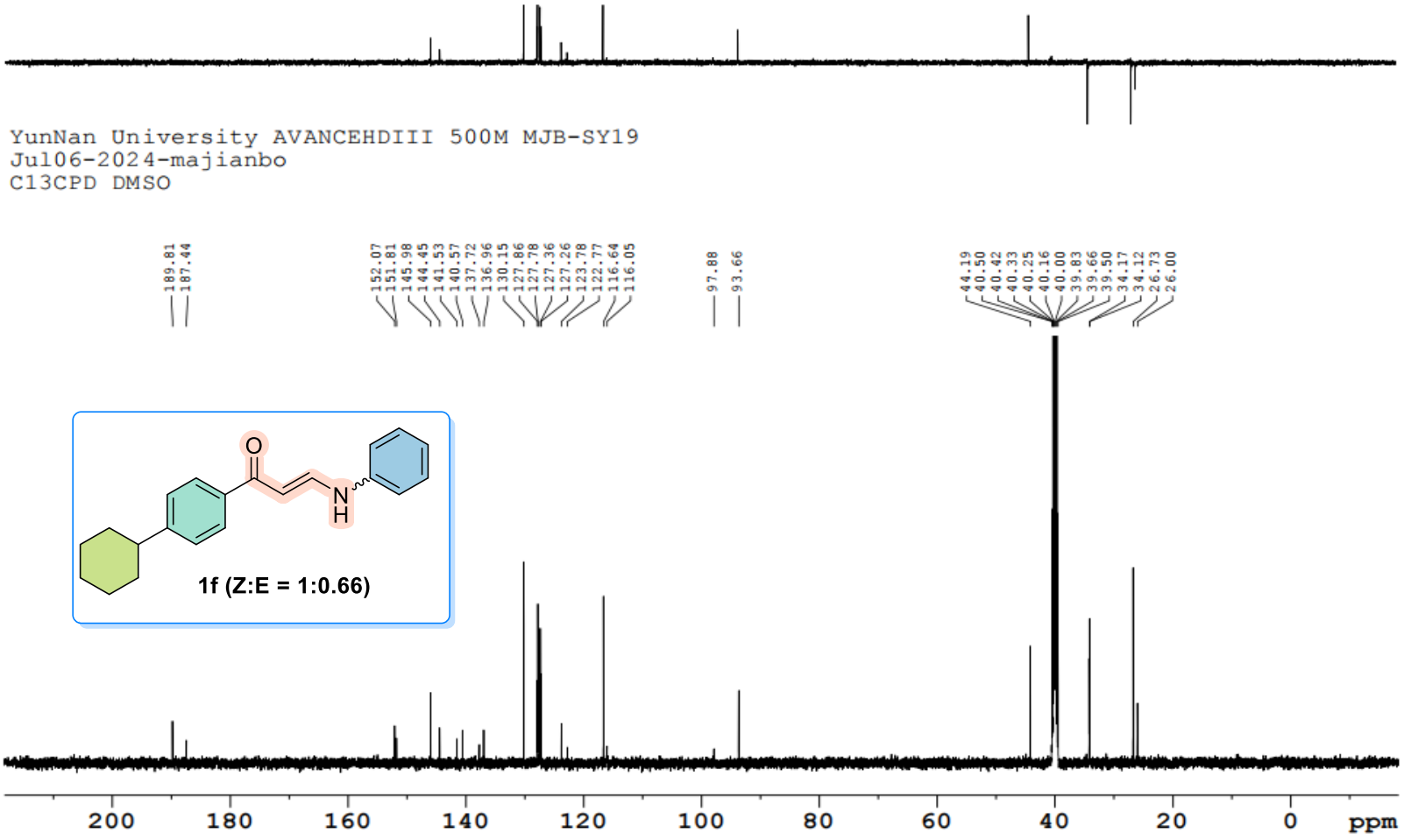


Figure S8. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1f**

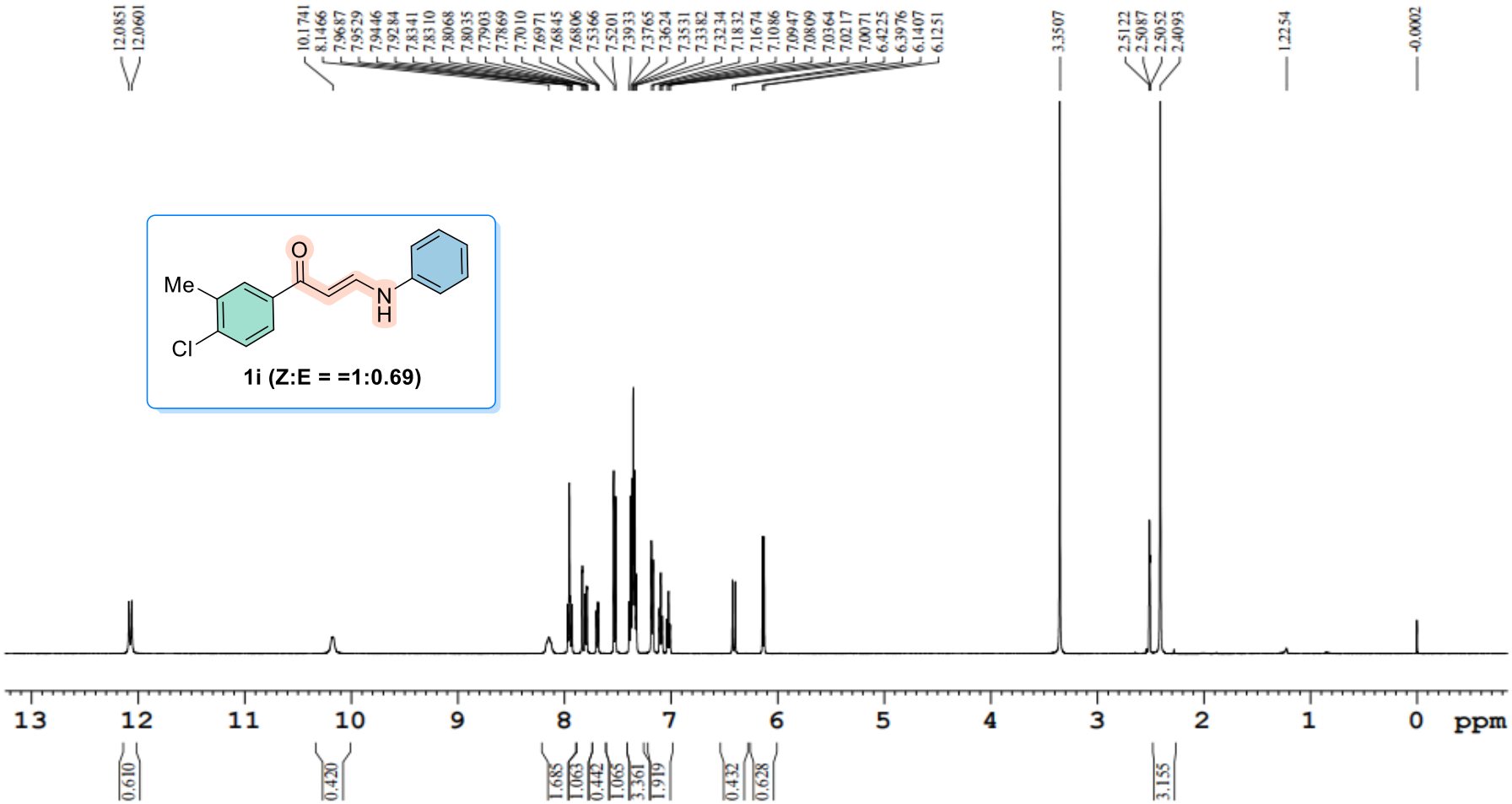


Figure S9. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1i**

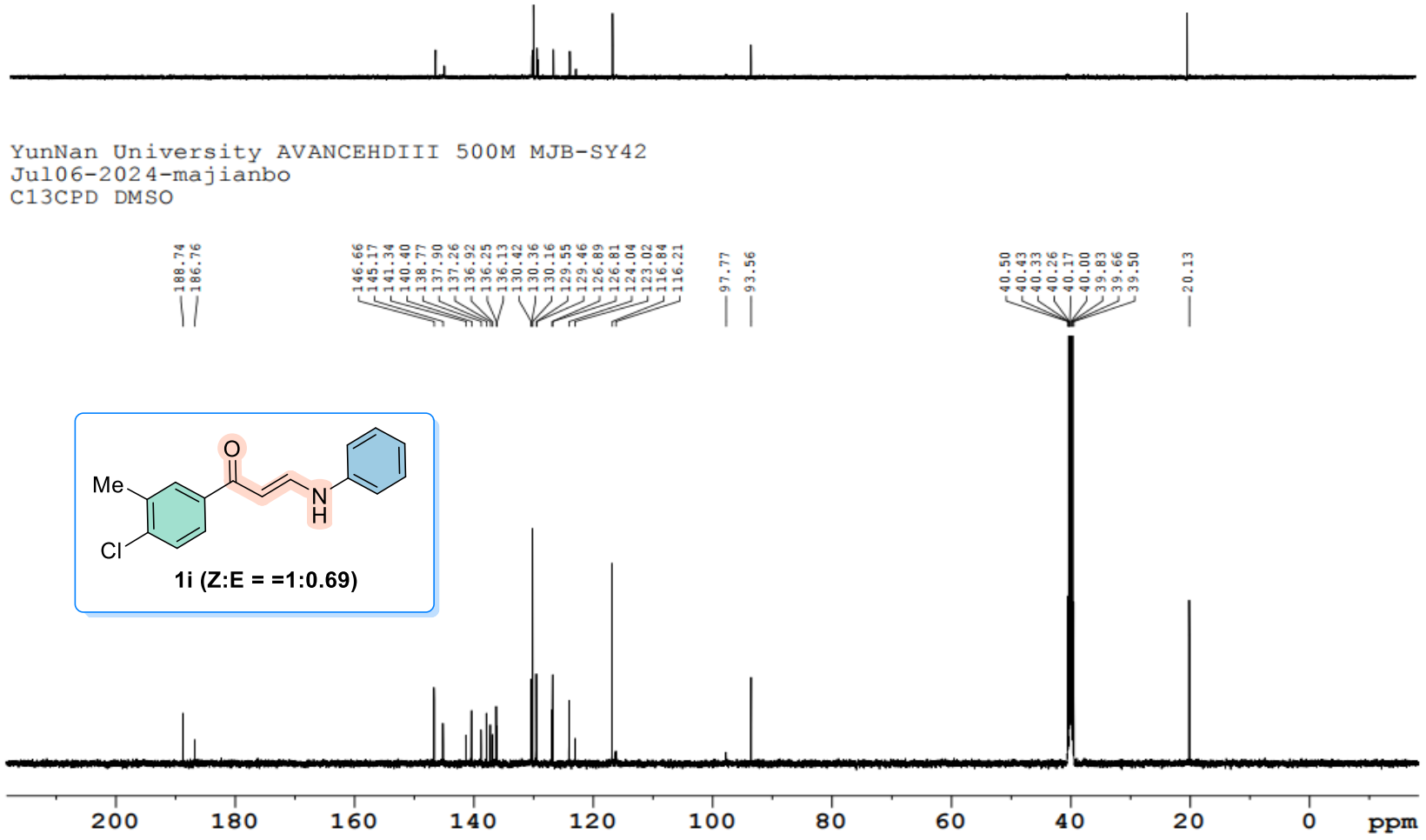


Figure S10. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1i**

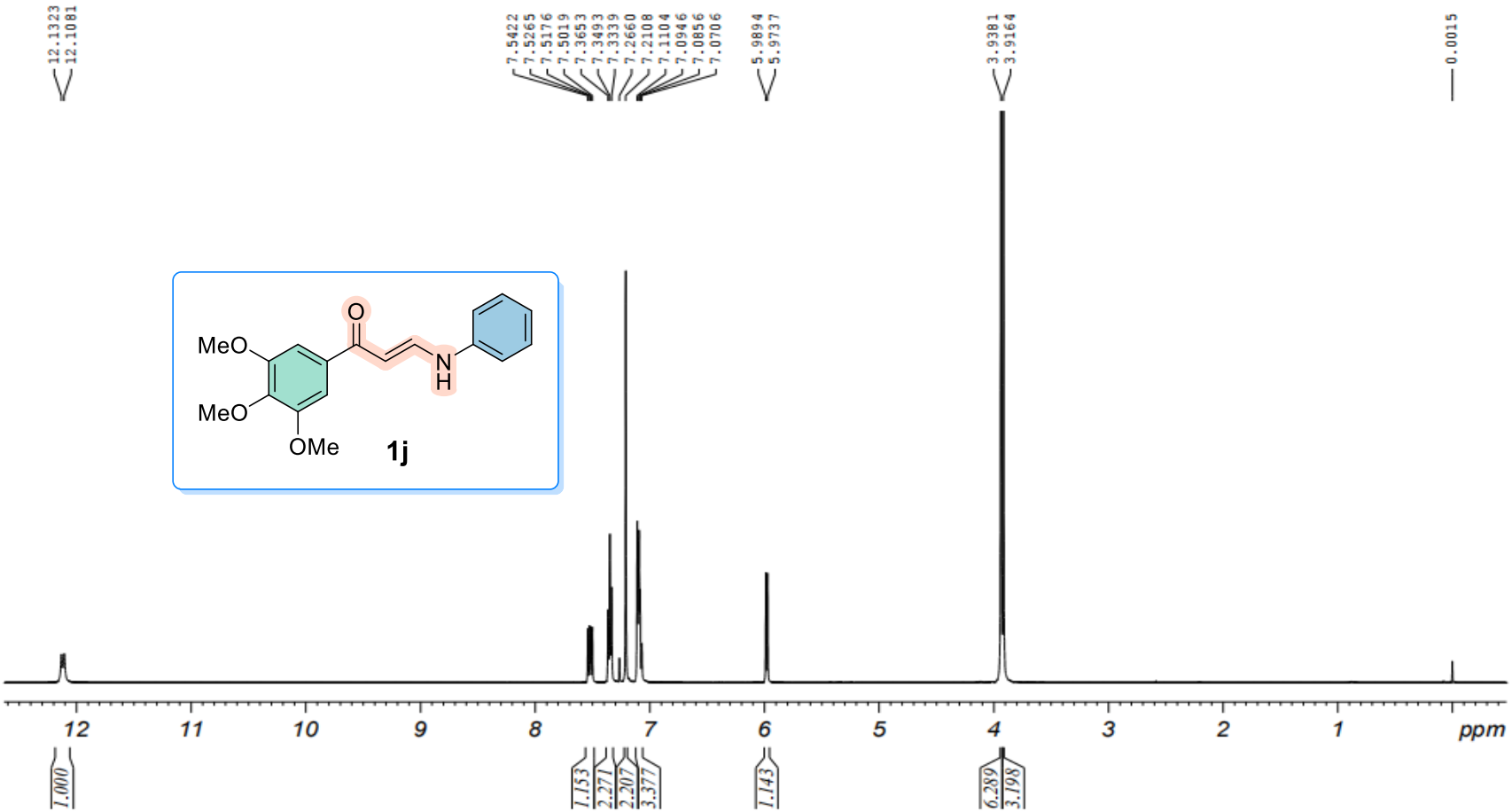


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **1j**

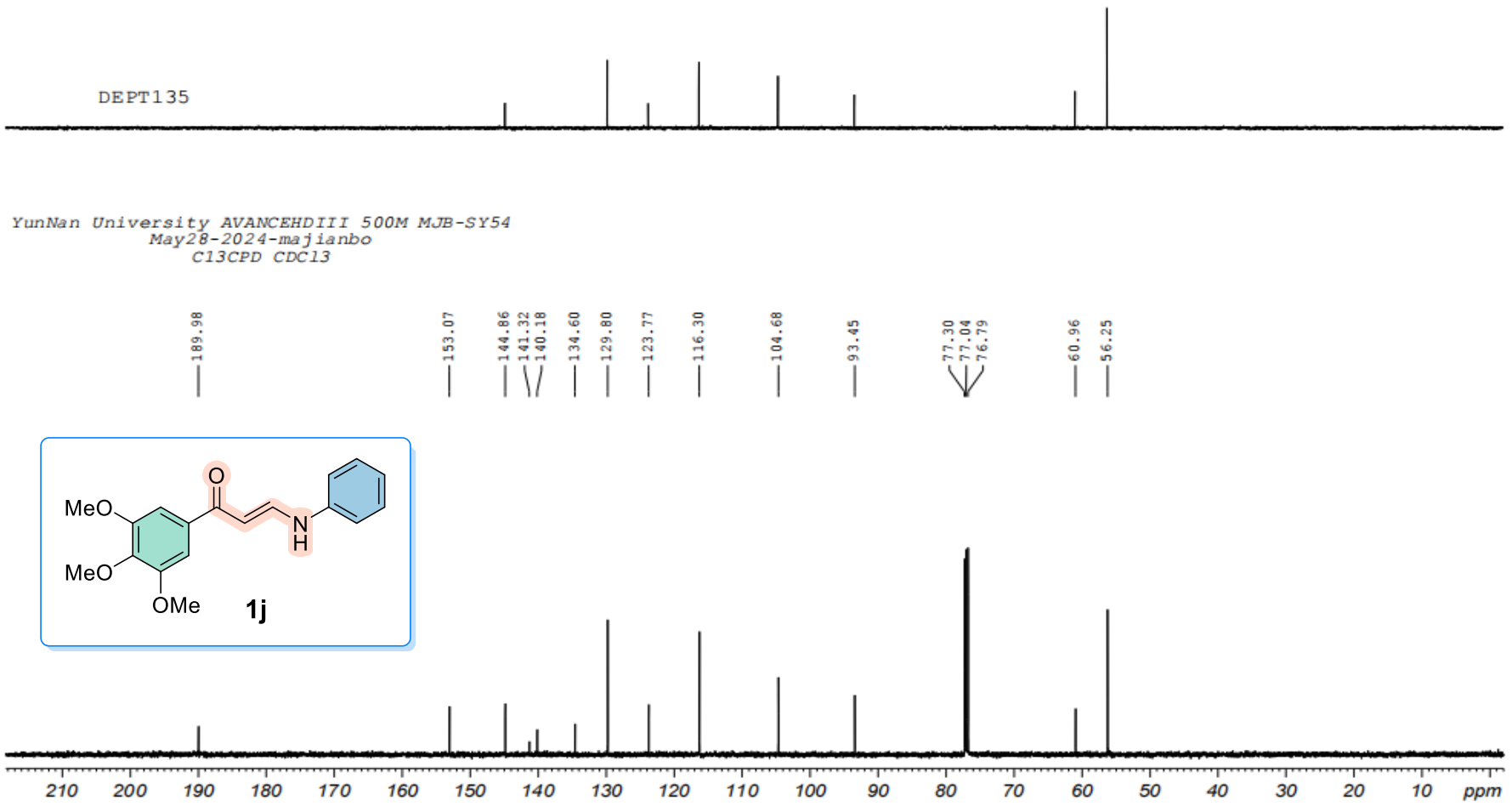


Figure S12. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **1j**

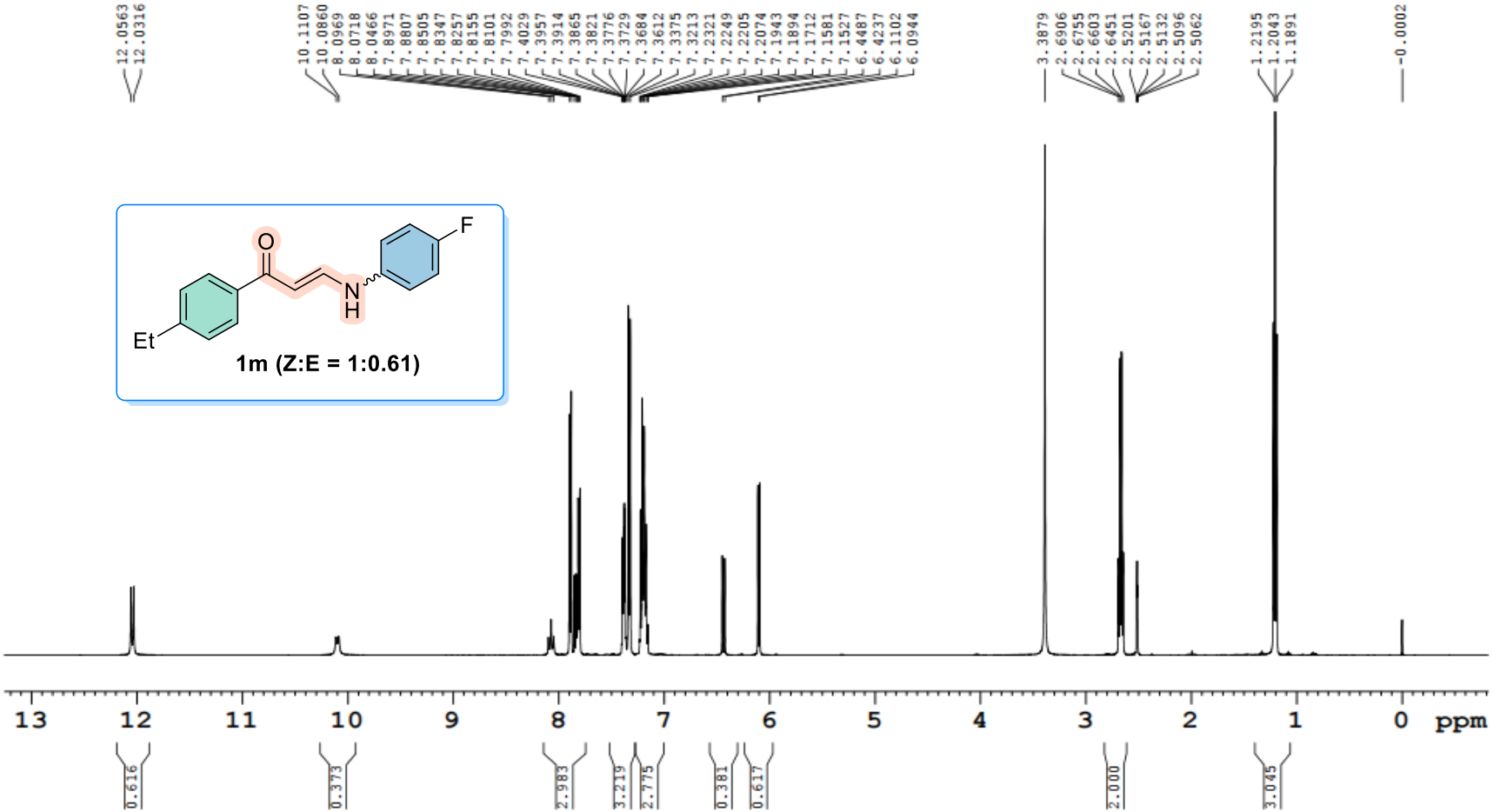


Figure S13. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1m**

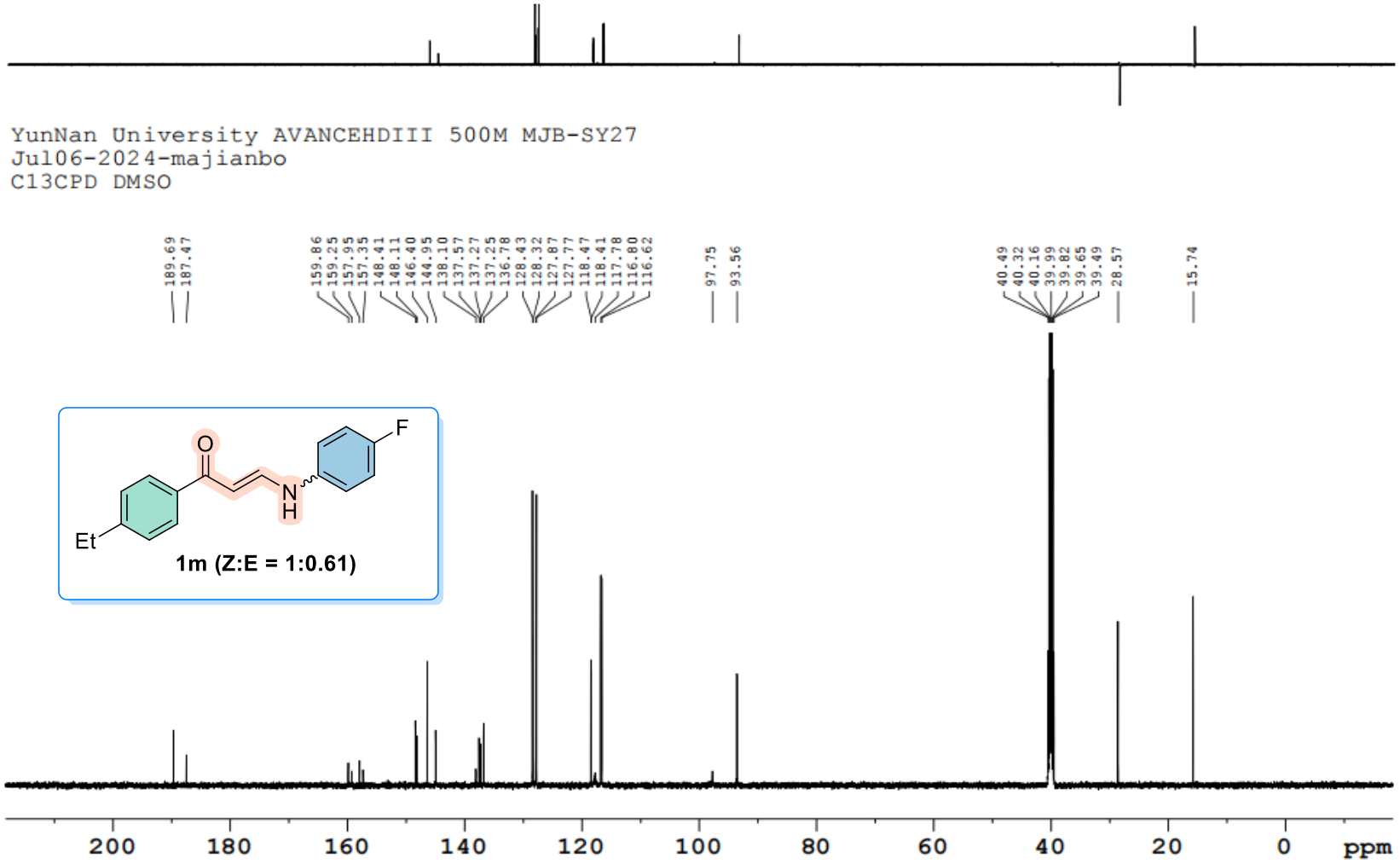


Figure S14. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1m**

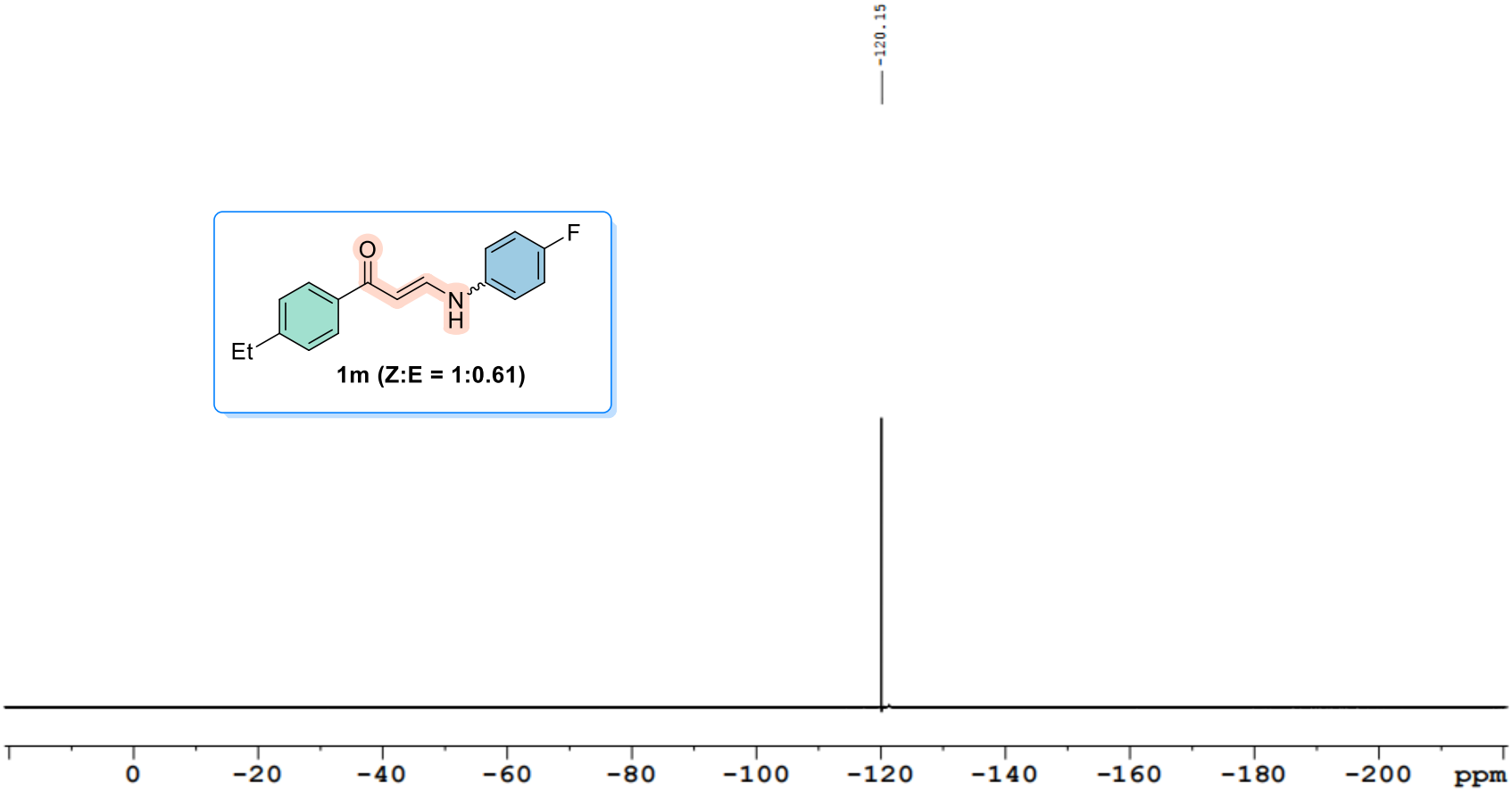


Figure S15. ^{19}F NMR (470 MHz, DMSO-d_6) spectra of compound **1m**

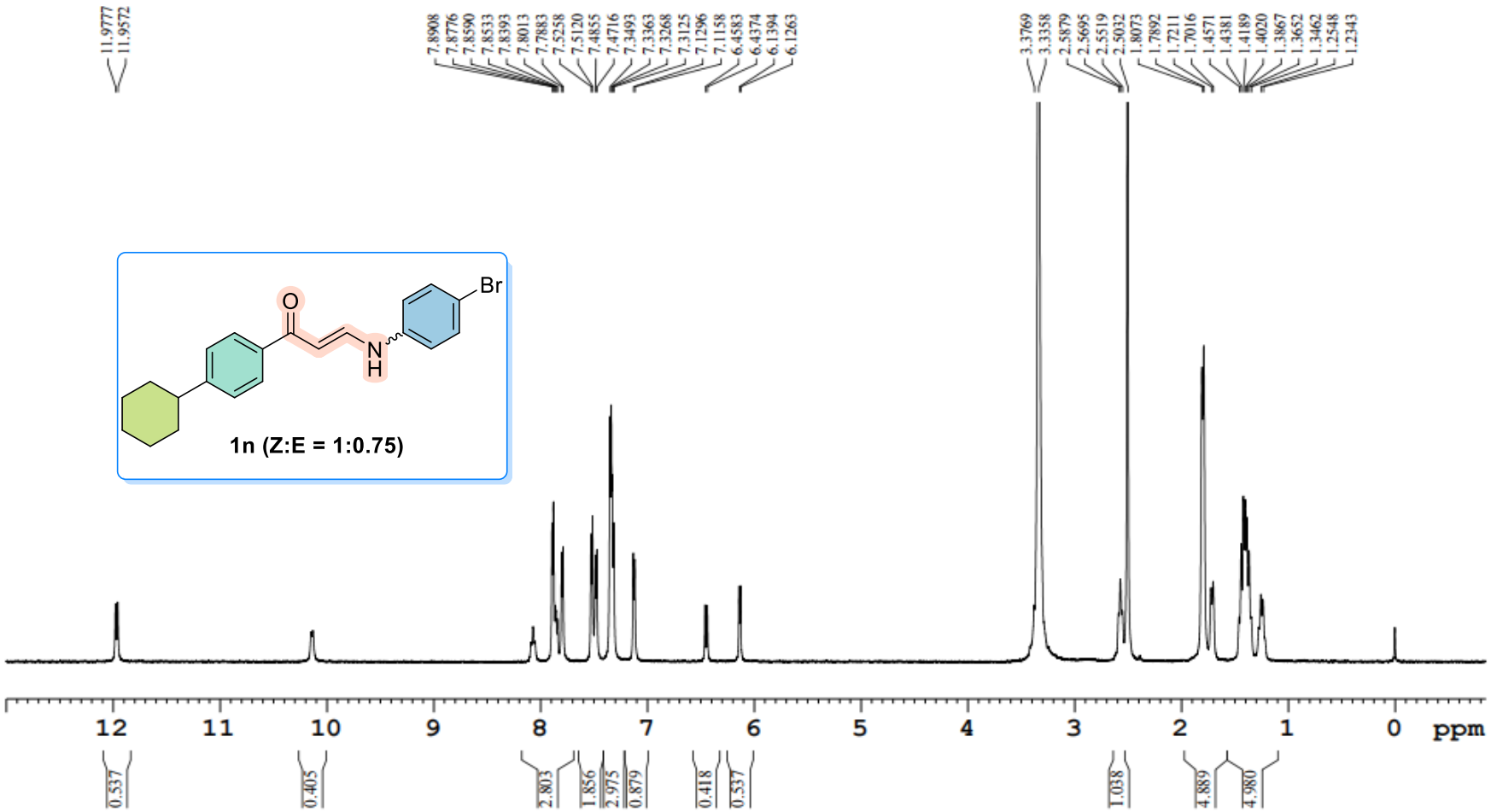


Figure S16. [1]H NMR (600 MHz, DMSO-d_6) spectra of compound **1n**

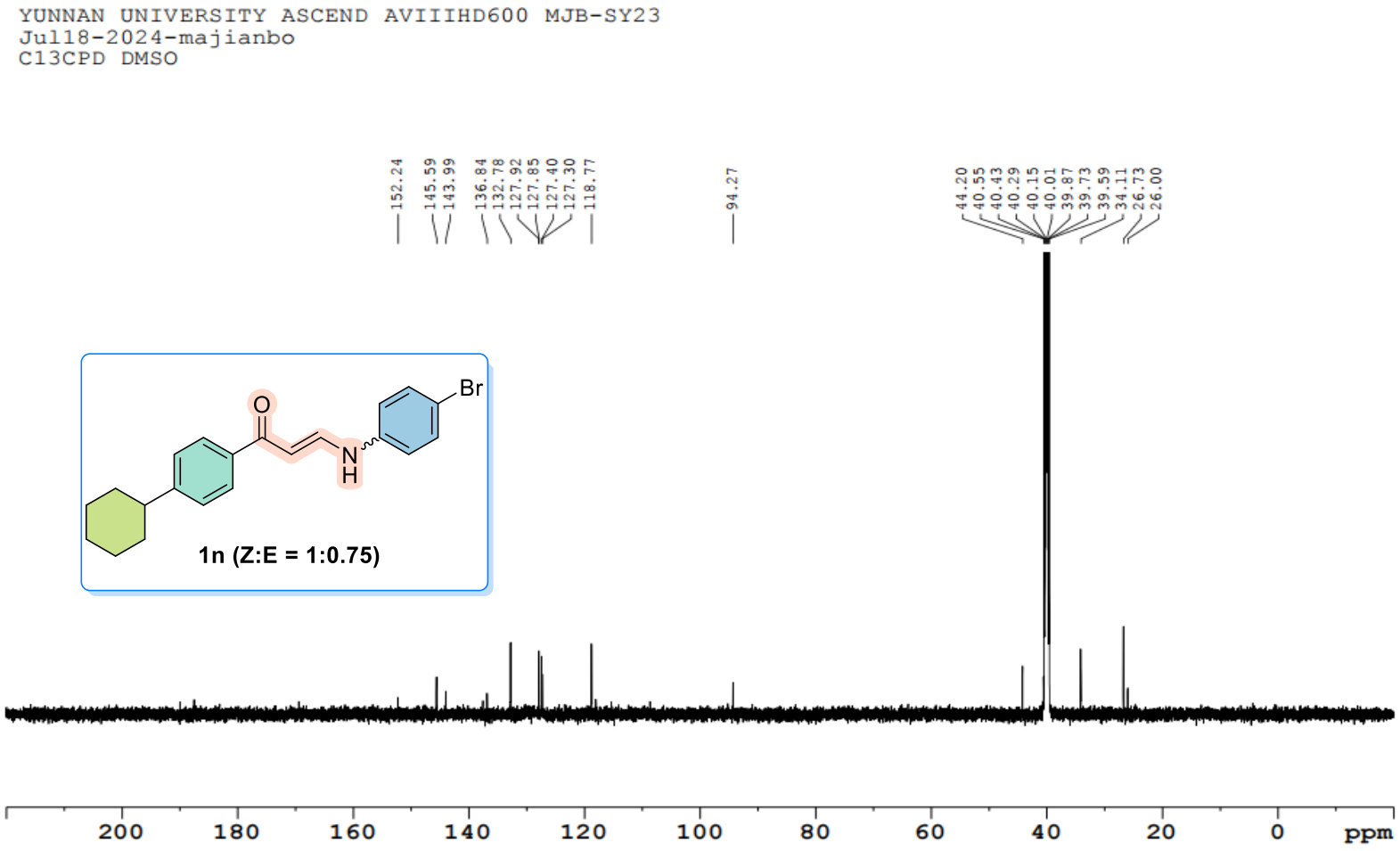


Figure S17. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **1n**

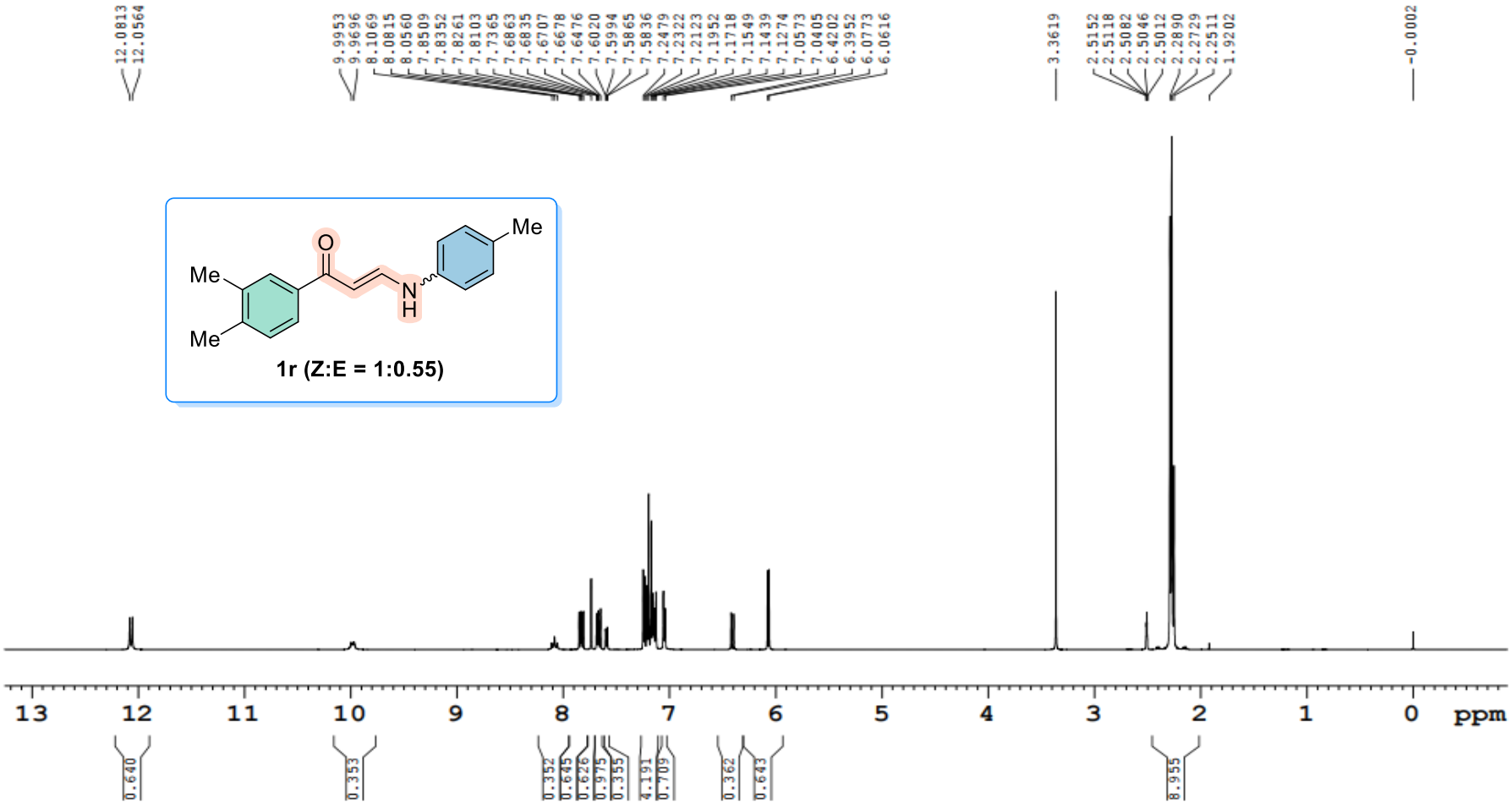


Figure S18. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1r**

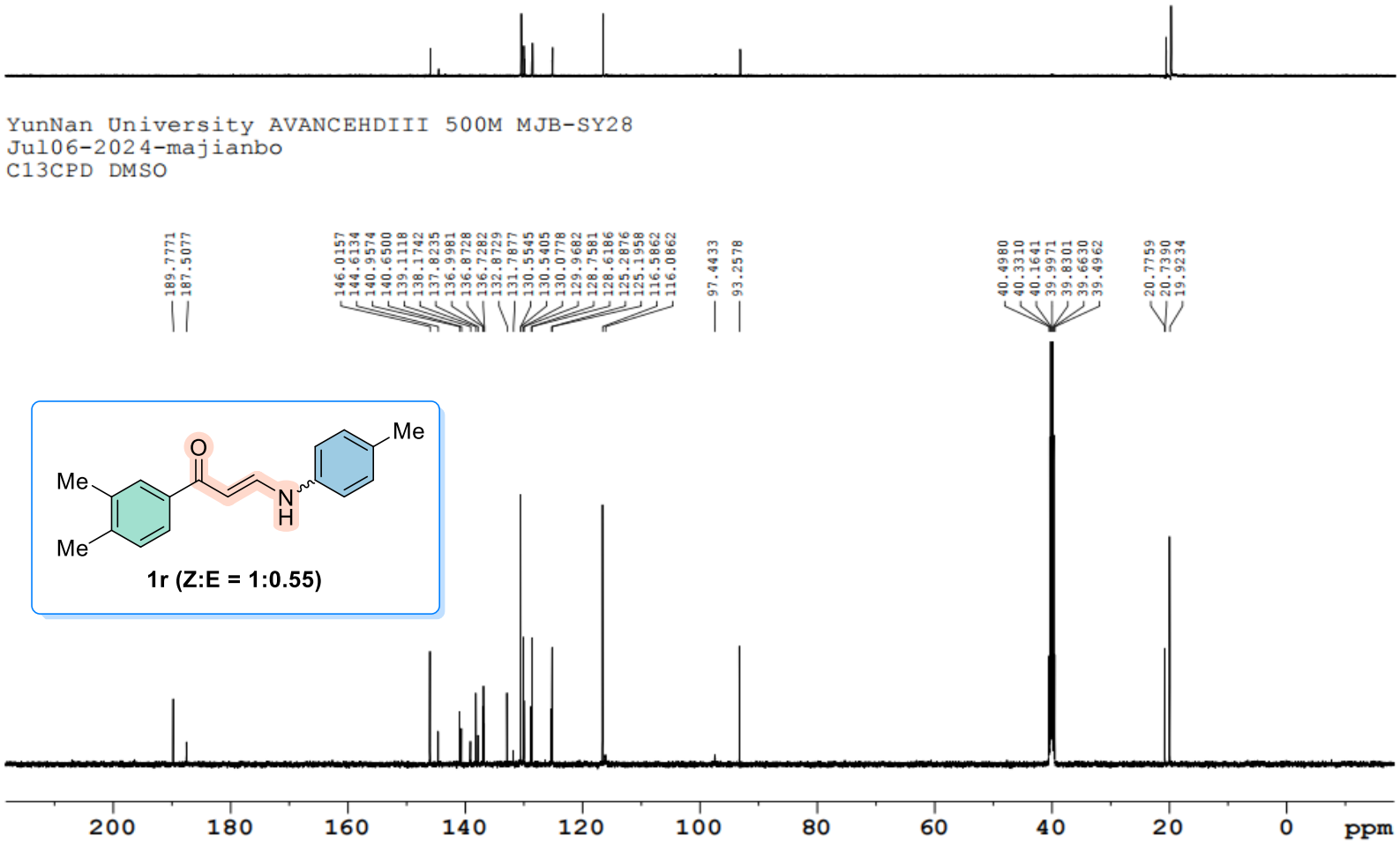


Figure S19. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1r**

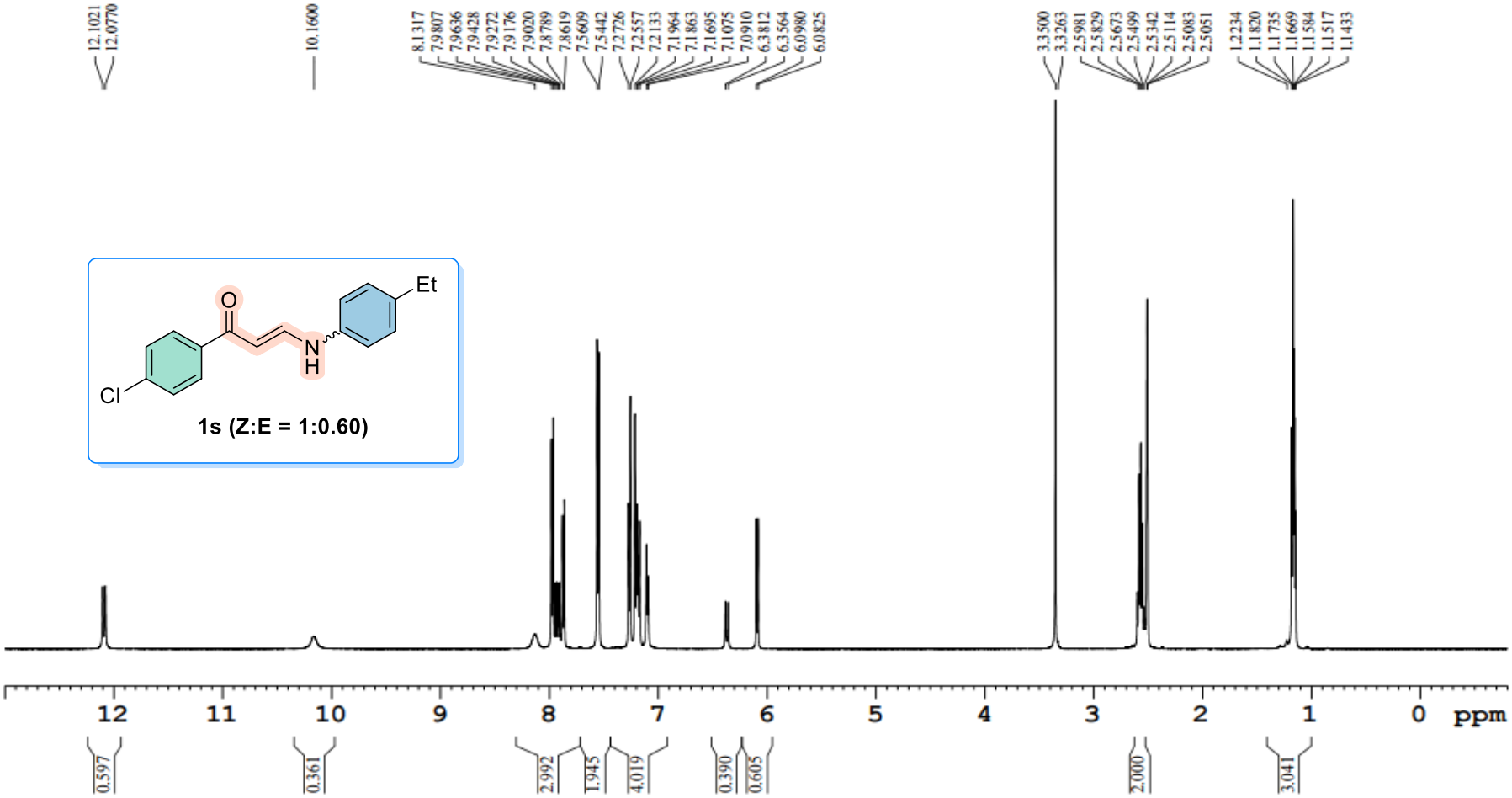


Figure S20. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1s**

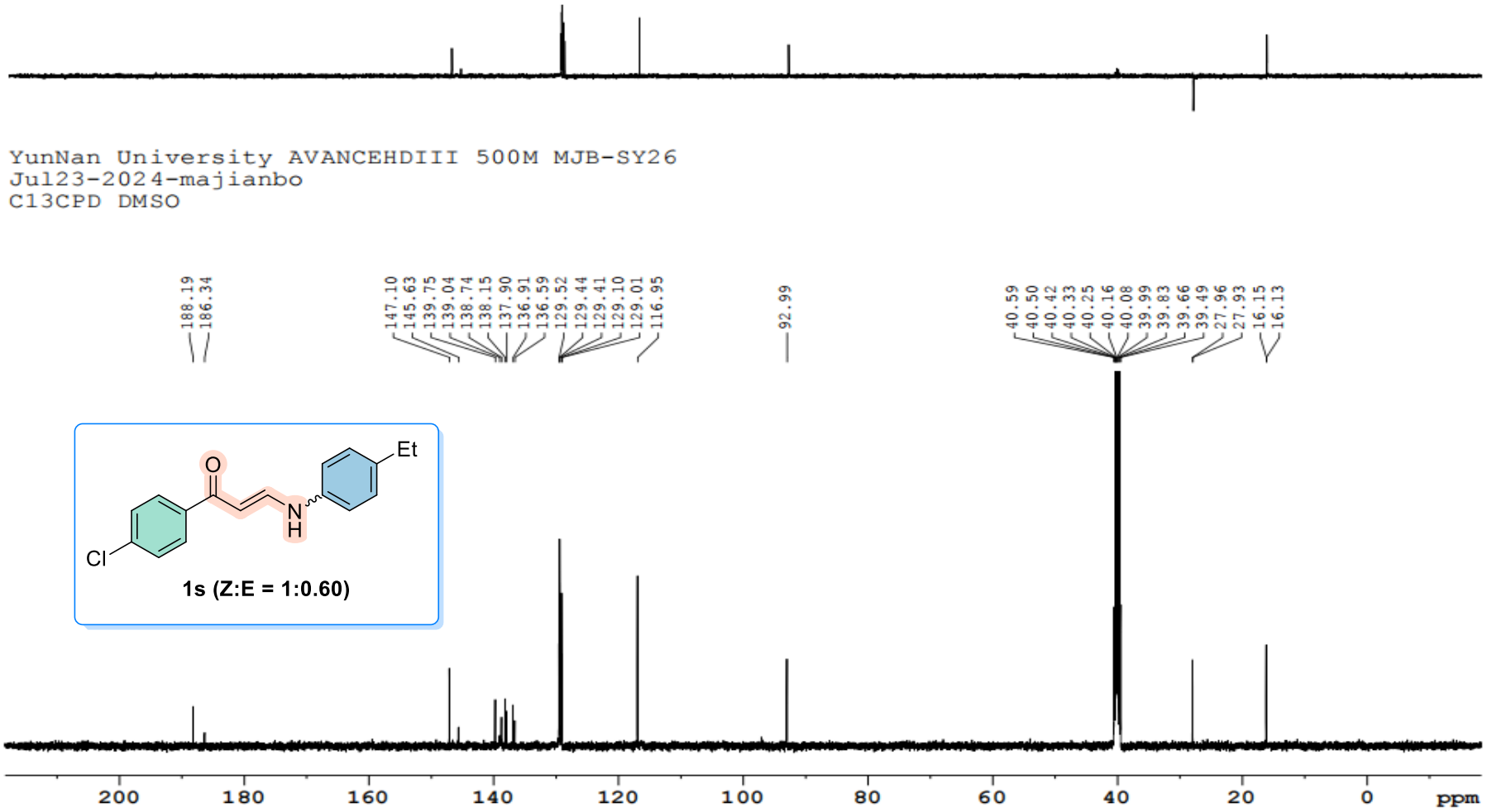


Figure S21. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1s**

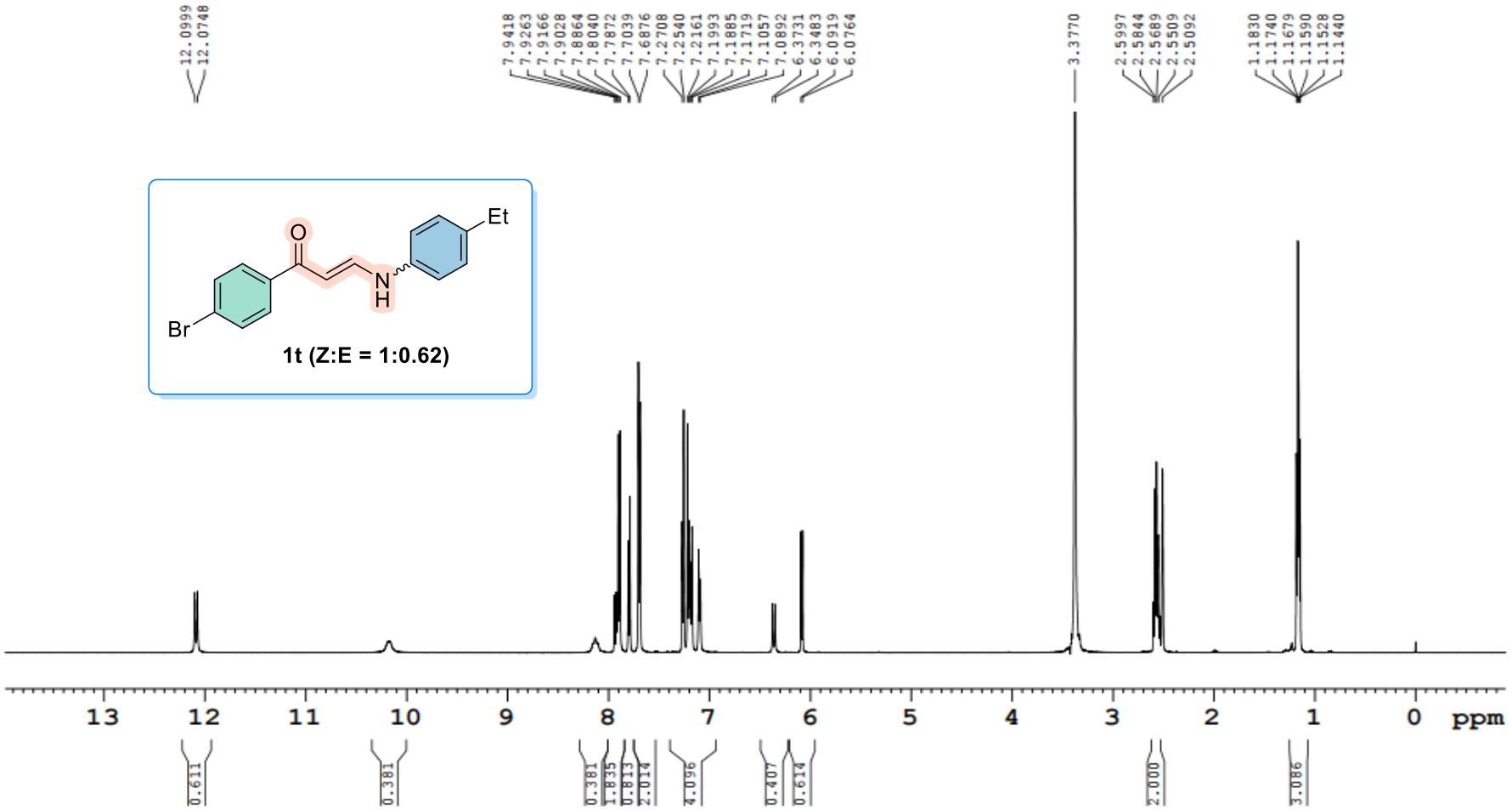


Figure S22. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1t**

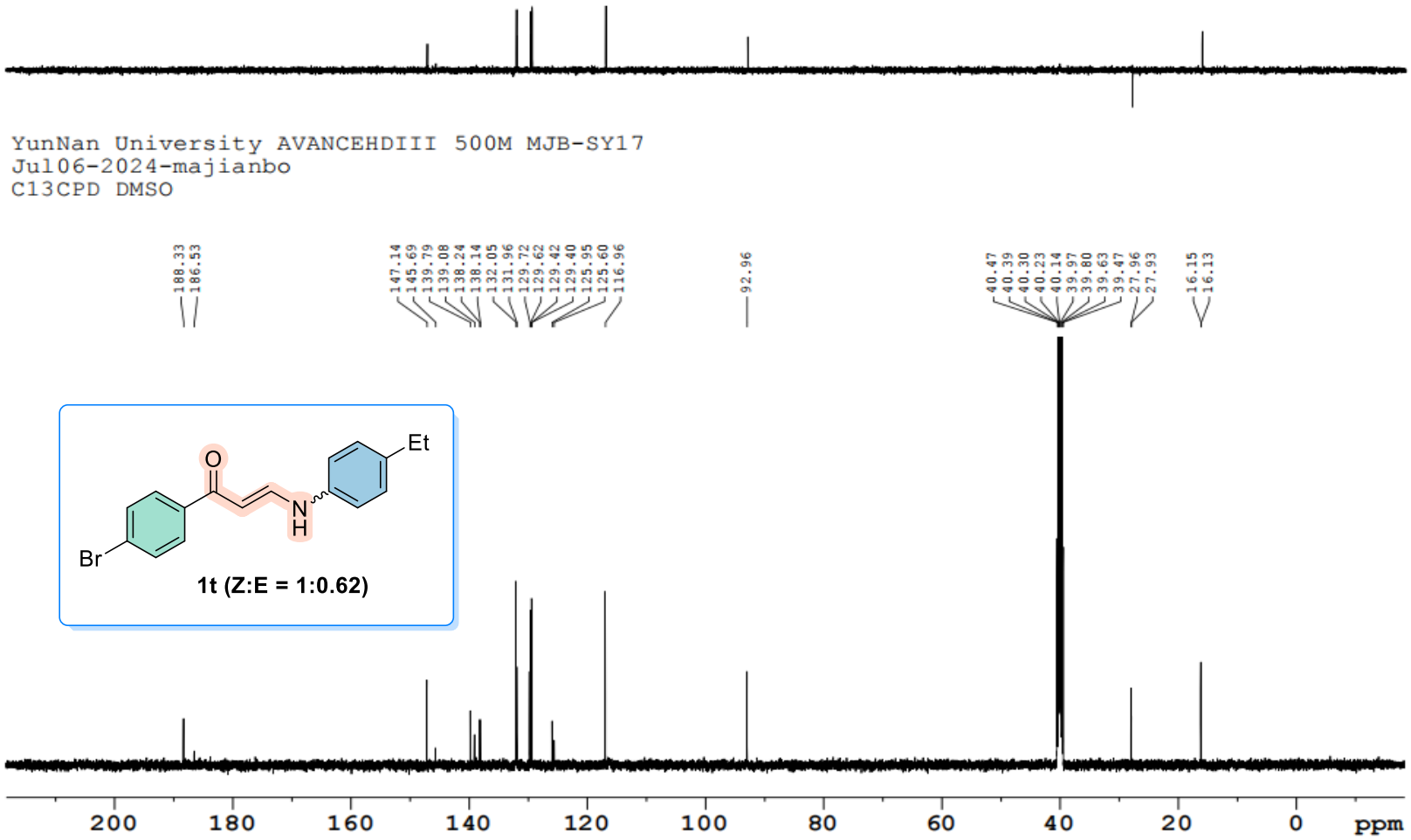


Figure S23. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1t**

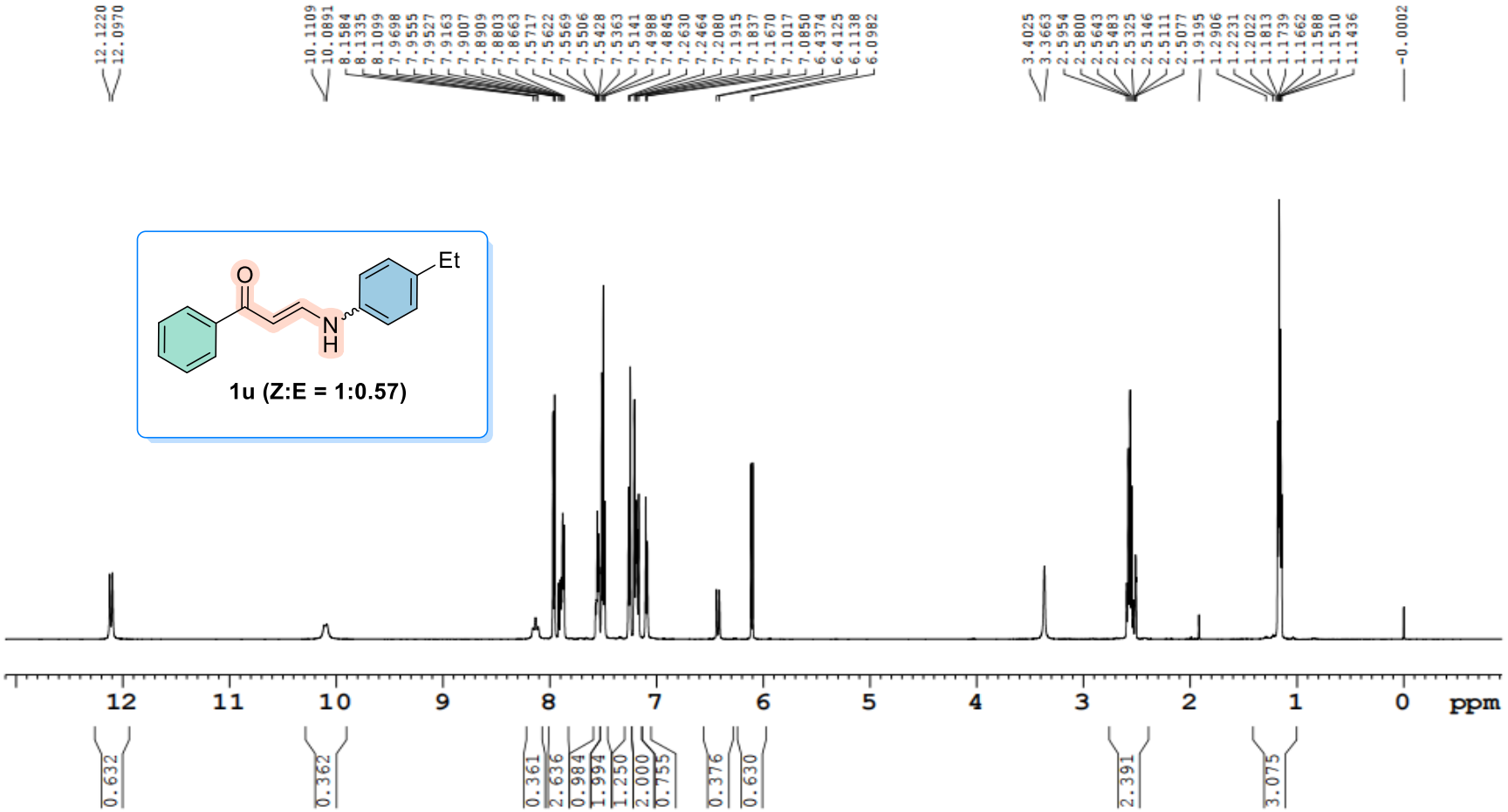


Figure S24. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1u**

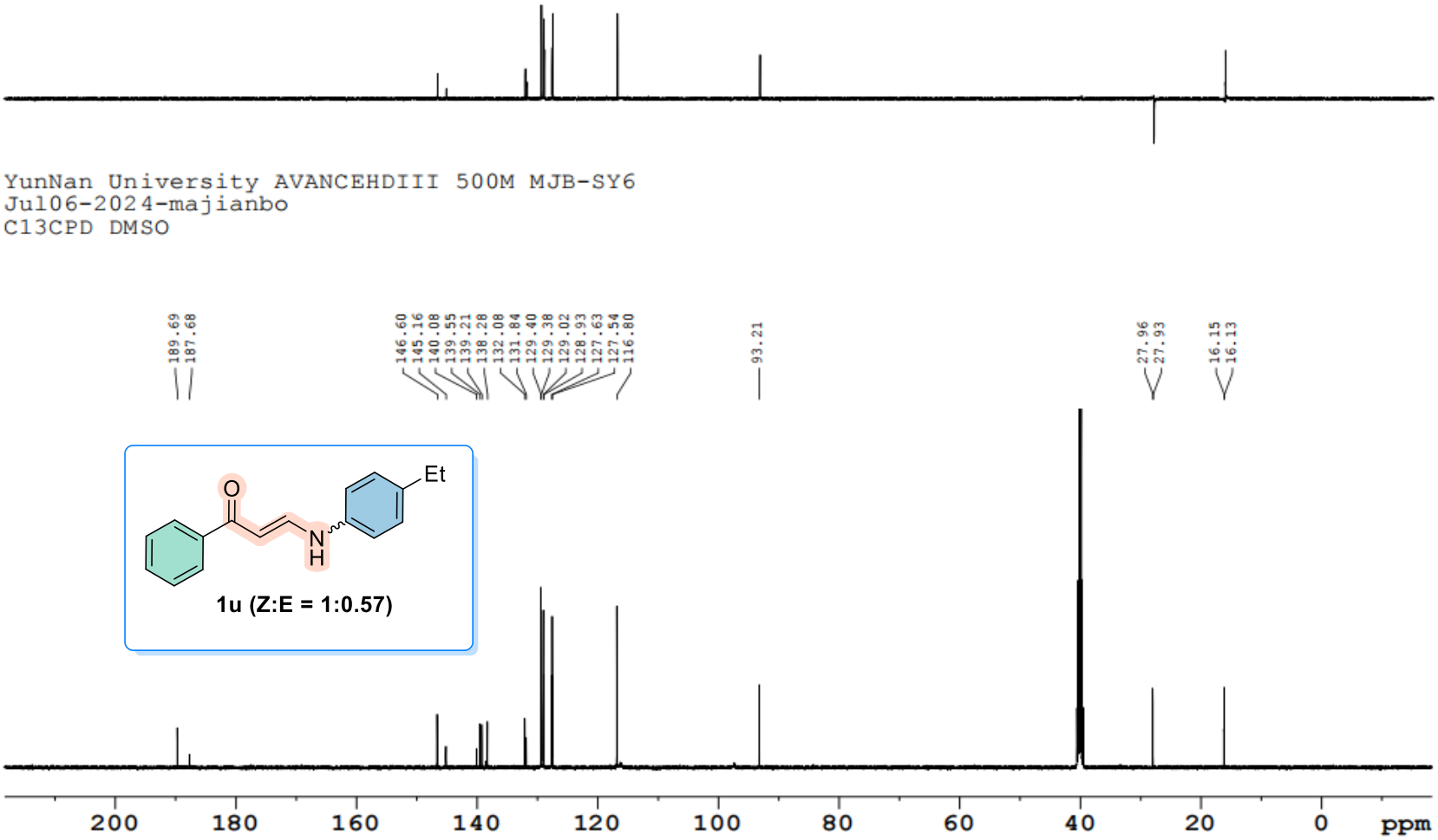


Figure S25. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1u**

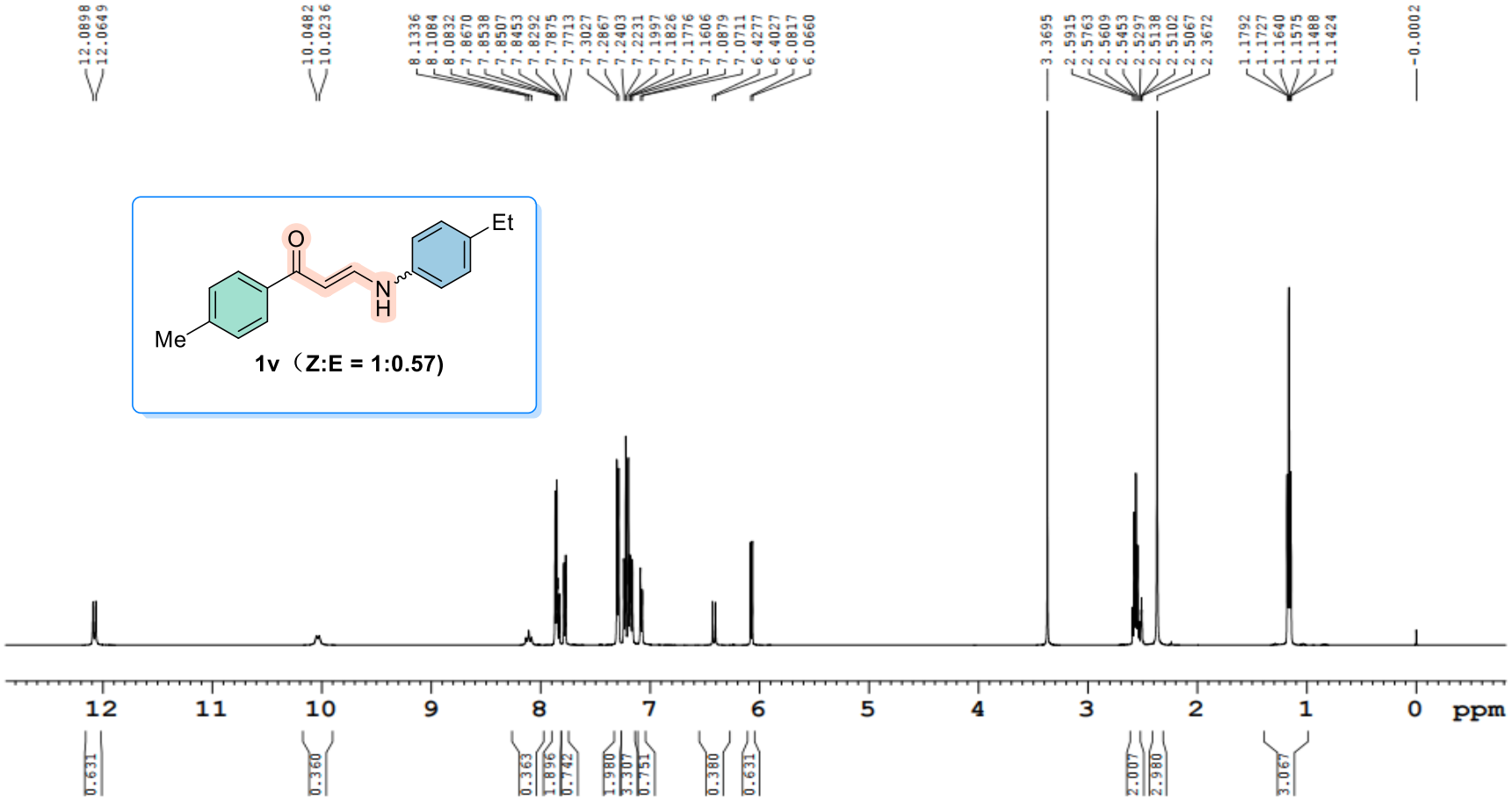


Figure S26. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1v**

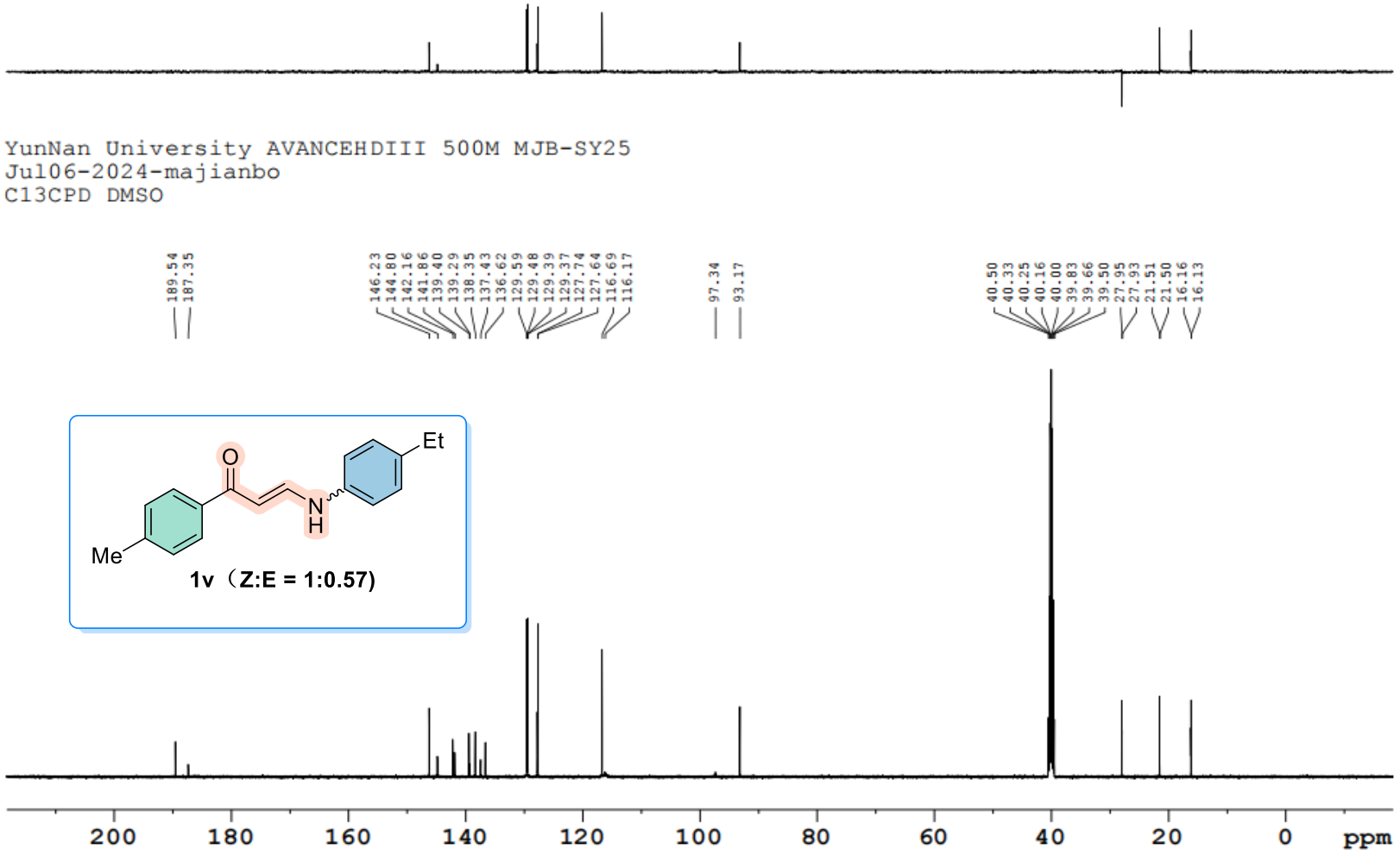


Figure S27. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1v**

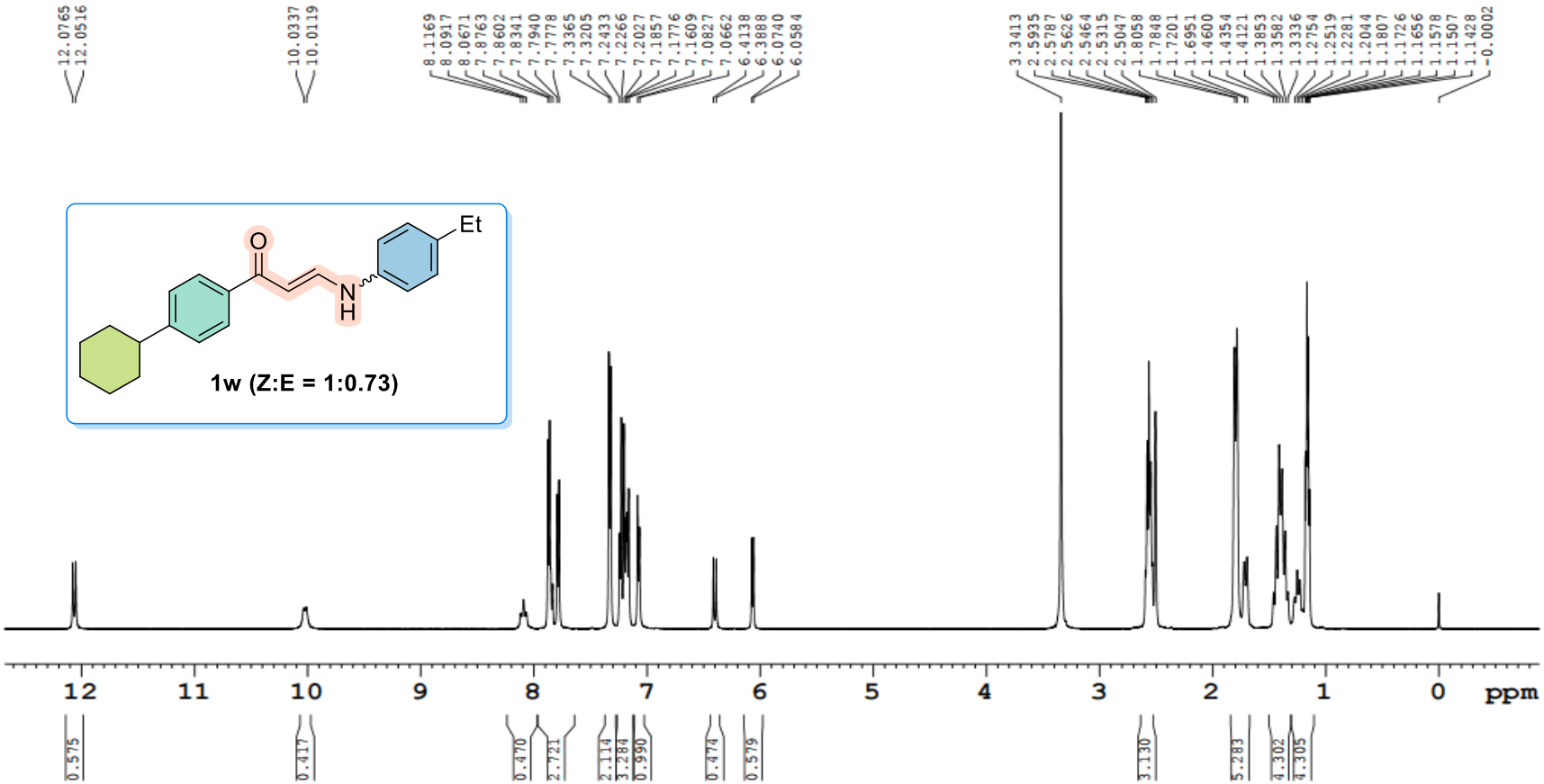


Figure S28. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1w**

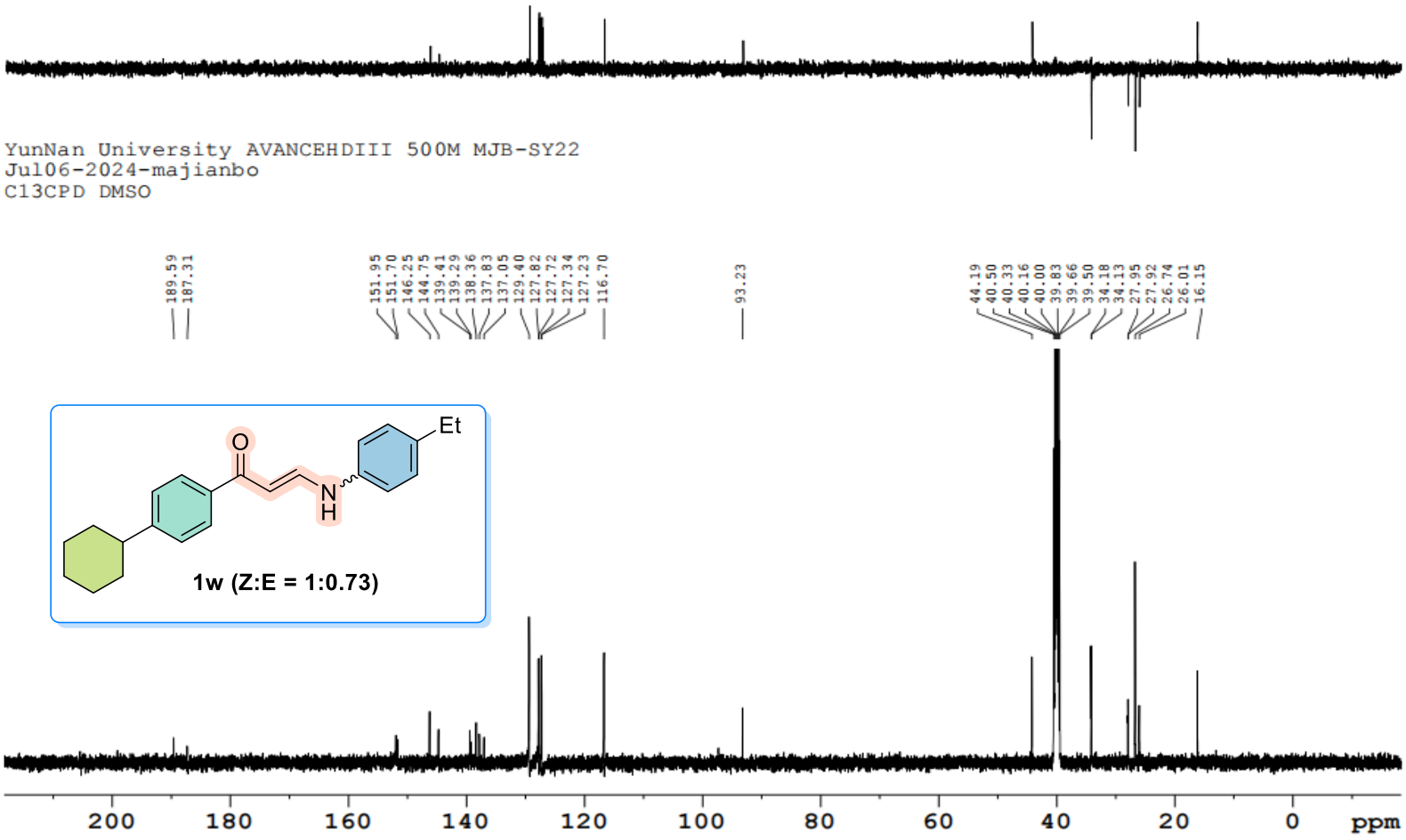


Figure S29. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1w**

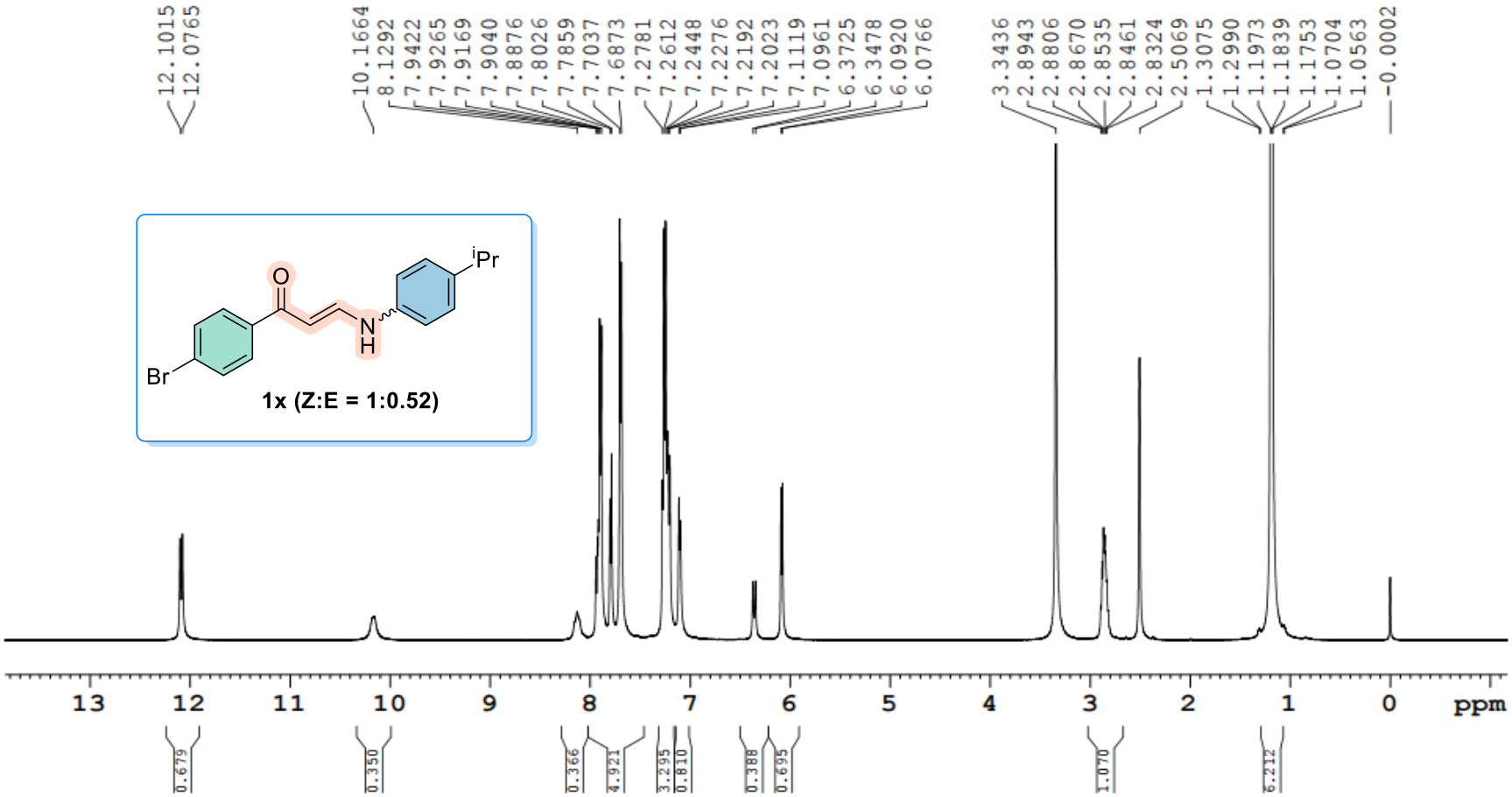


Figure S30. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1x**

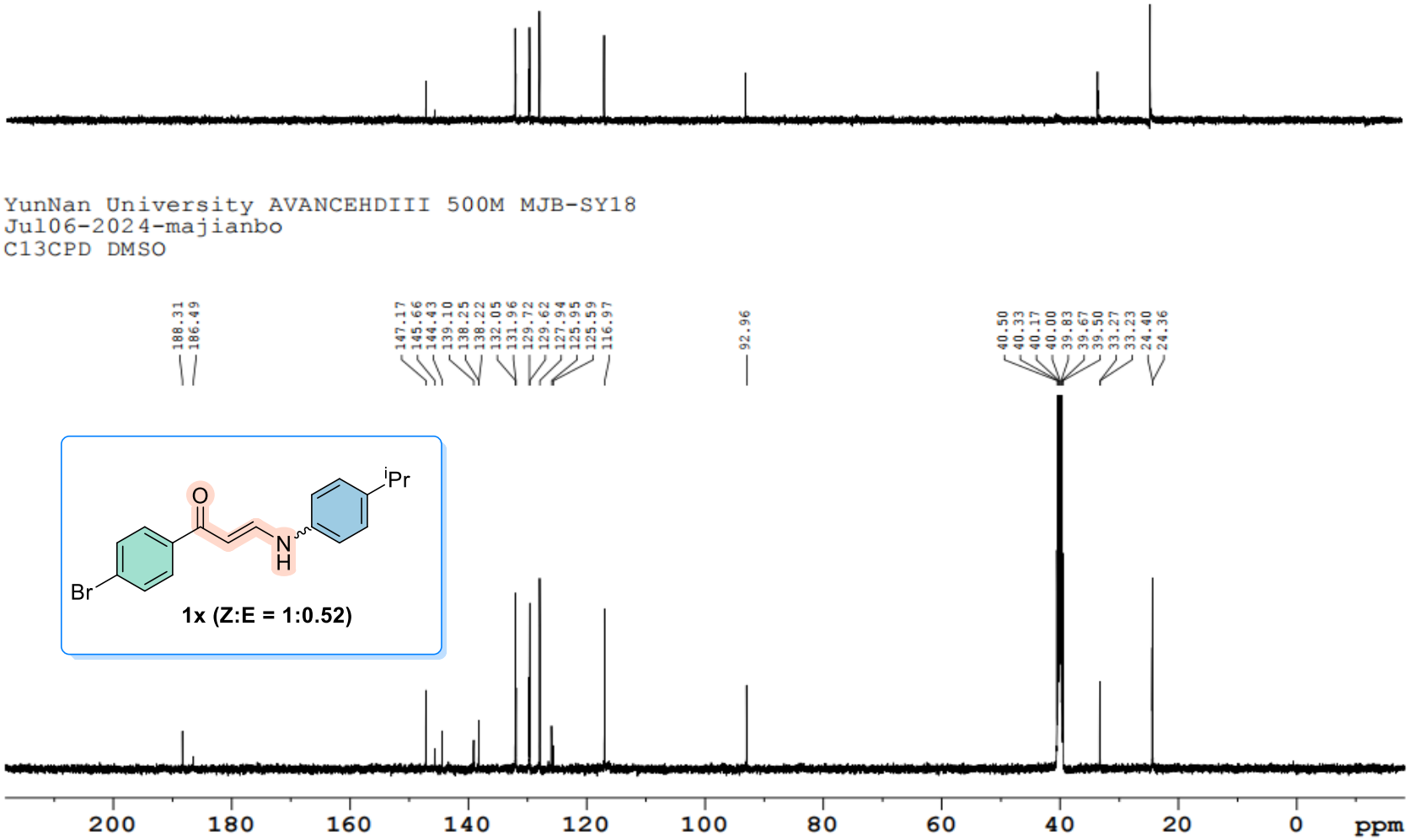


Figure S31. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1x**

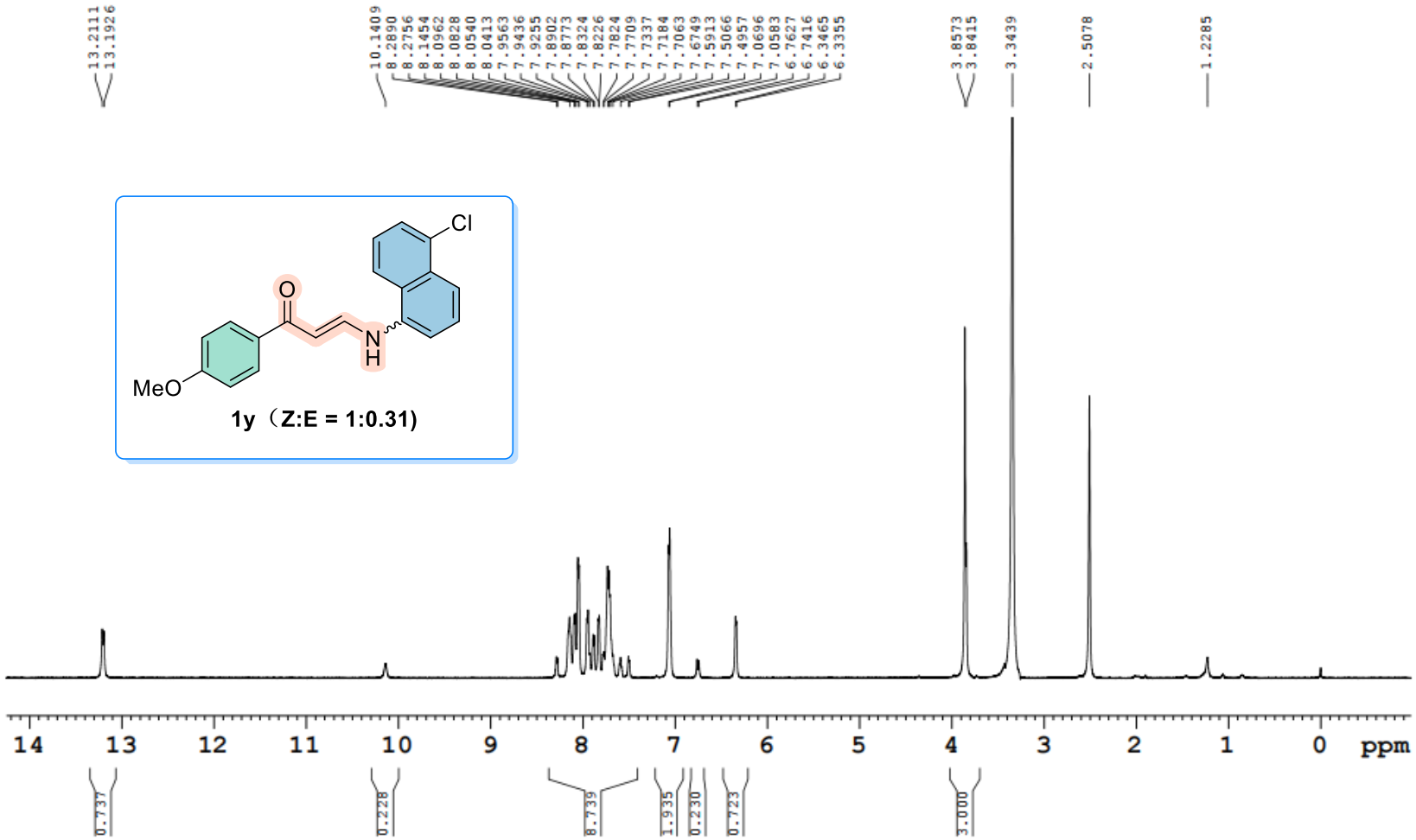


Figure S32. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **1y**

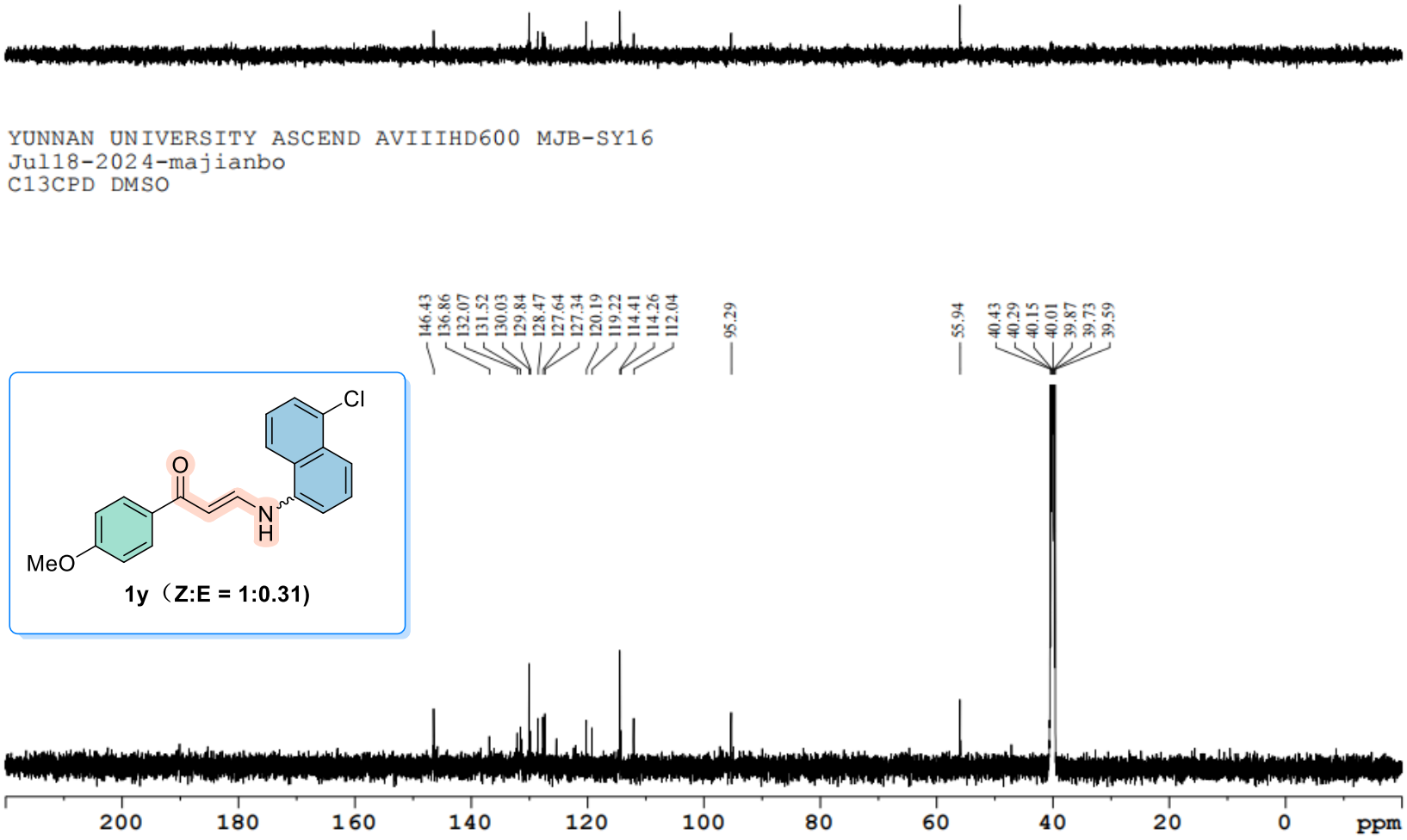


Figure S33. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **1y**

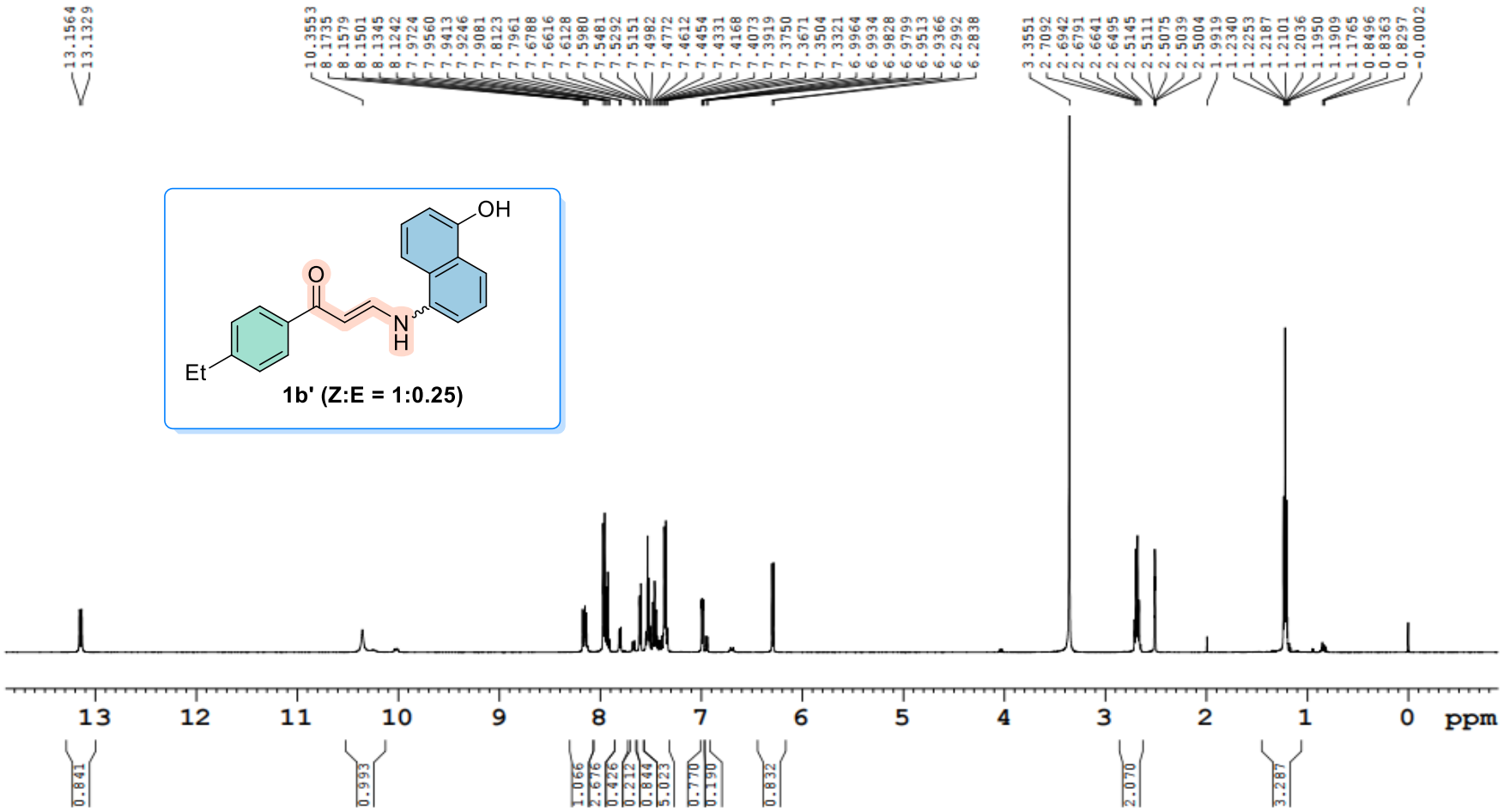


Figure S34. [1]H NMR (500 MHz, DMSO-d_6) spectra of compound **1b'**

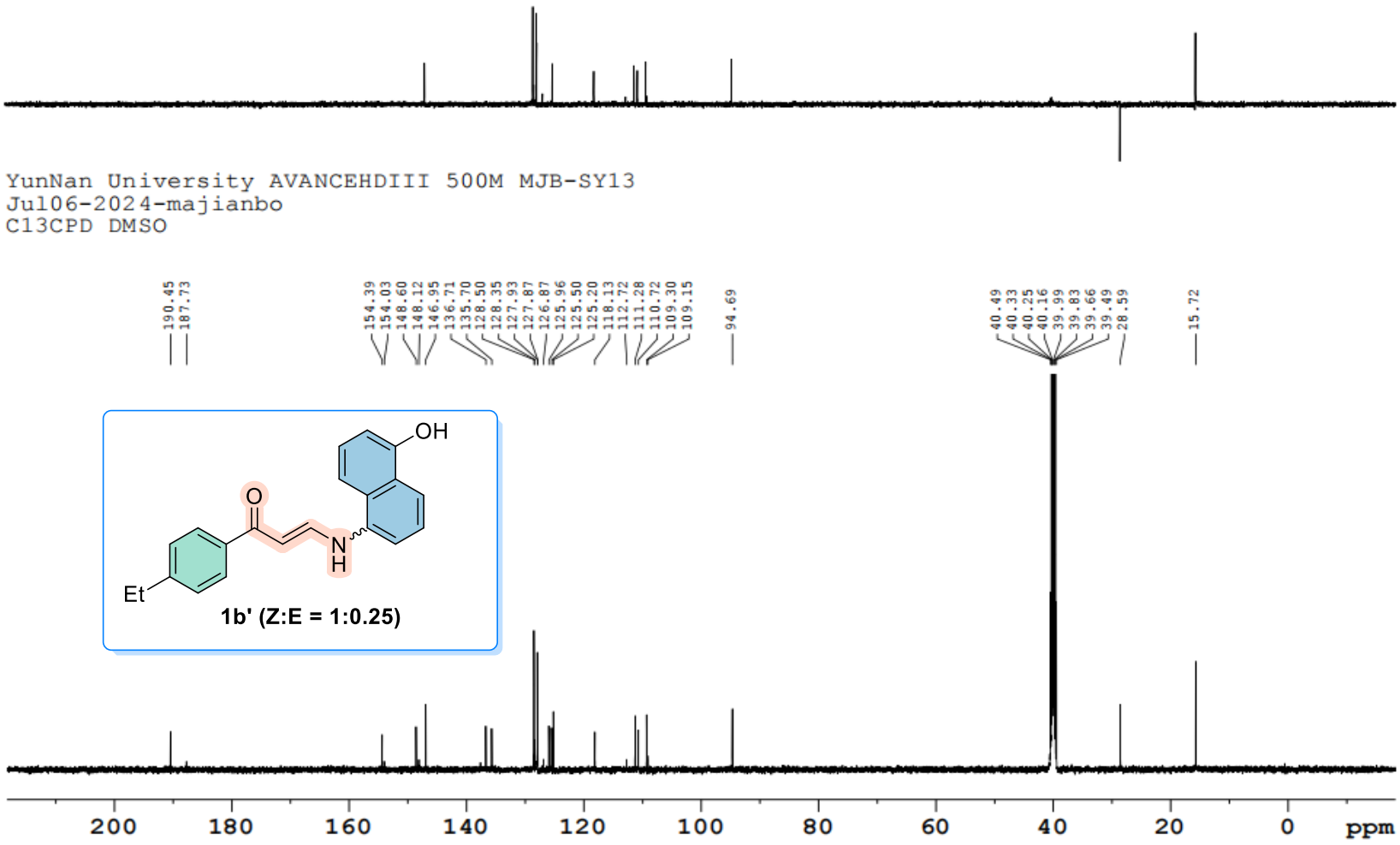


Figure S35. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1b'**

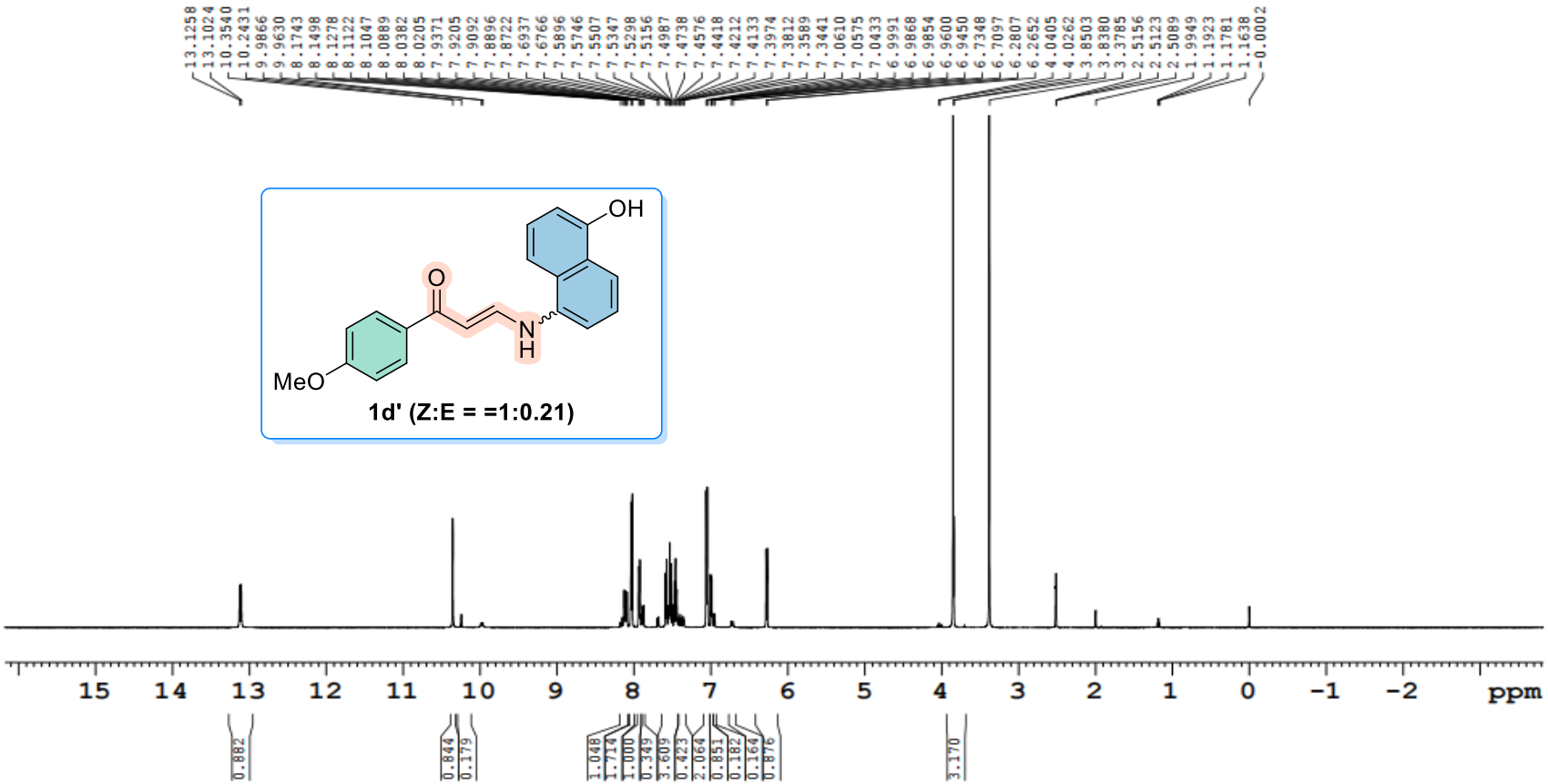


Figure S36. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1d'**

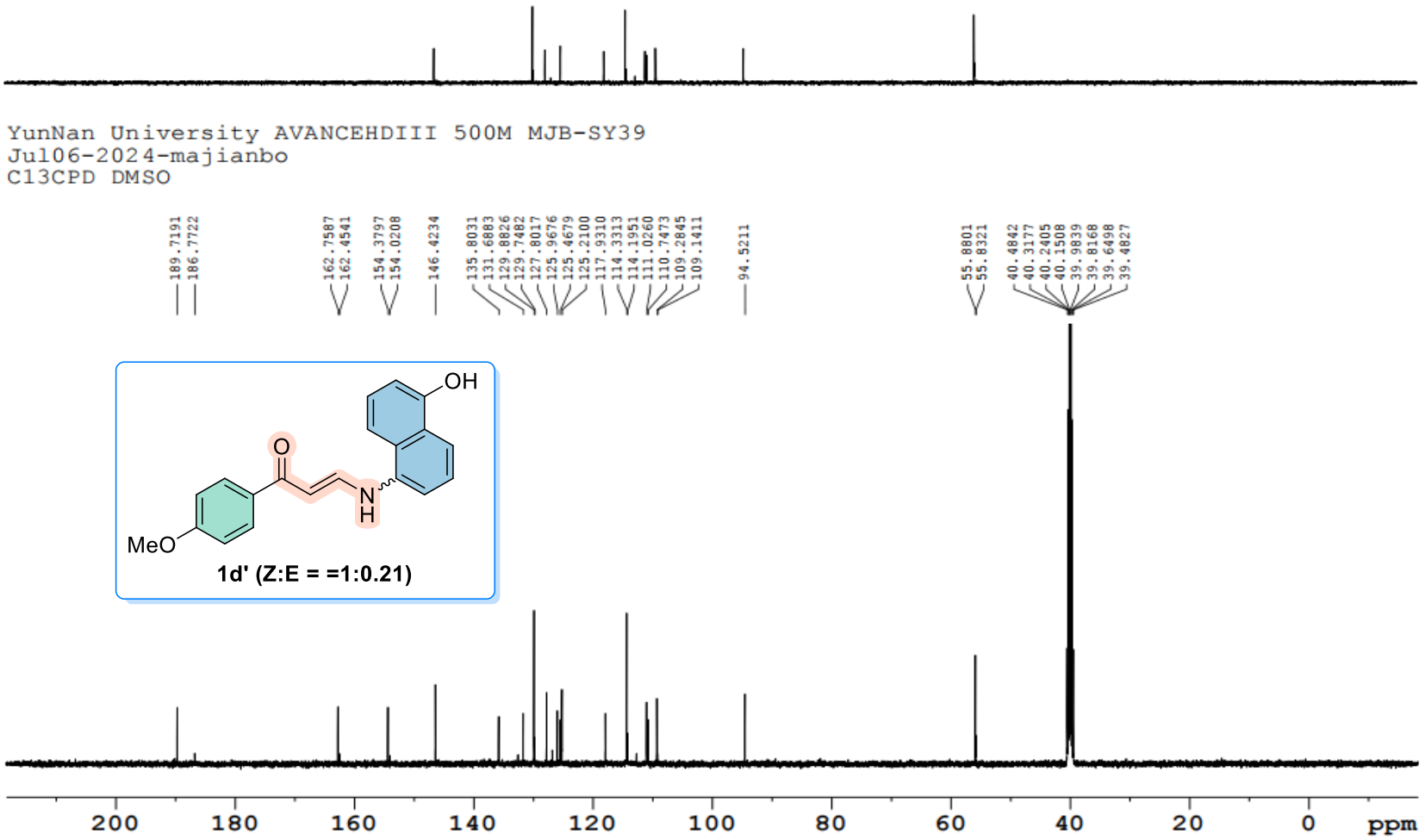


Figure S37. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1d'**

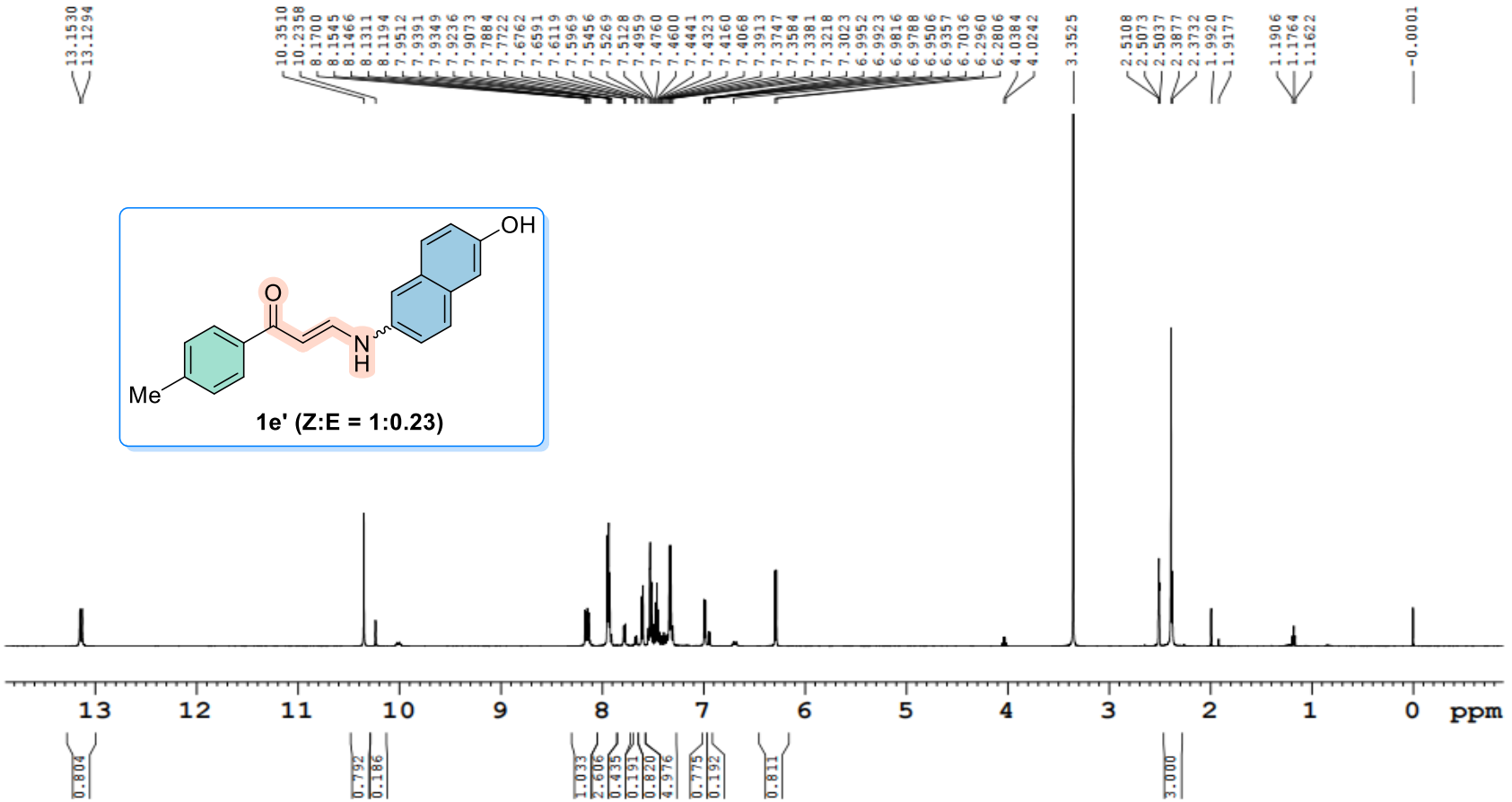


Figure S38. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1e'**

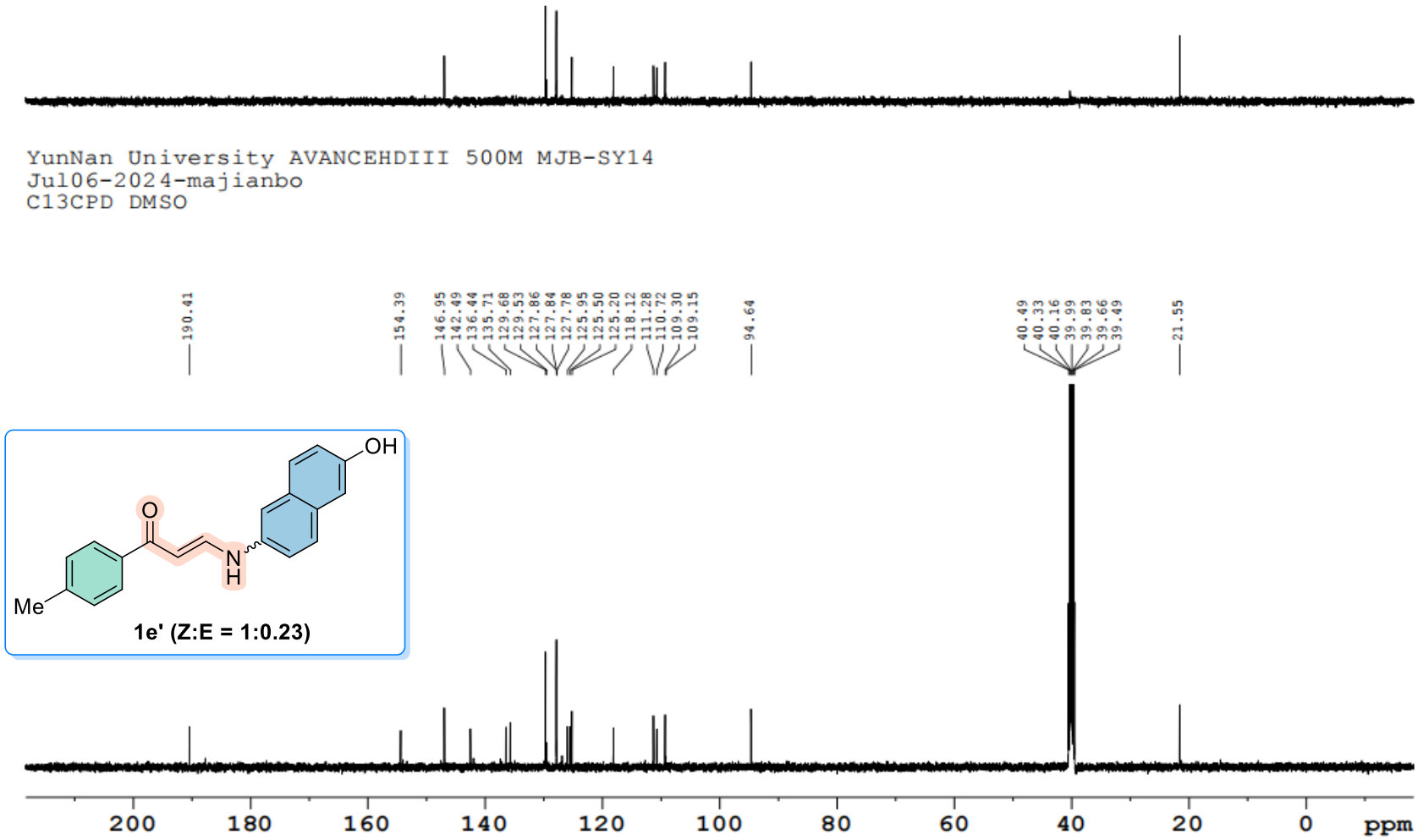


Figure S39. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1e'**

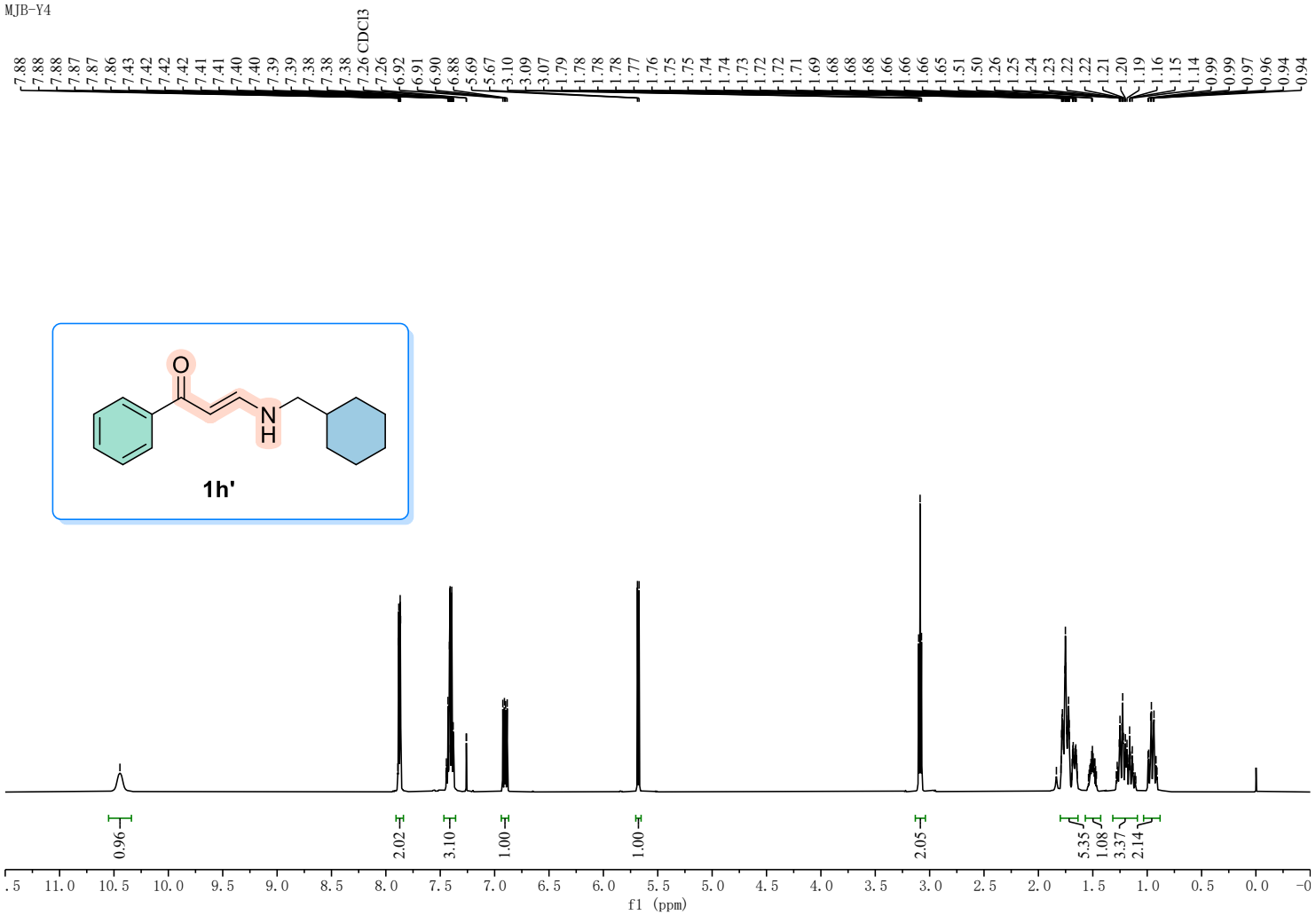


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **1h'**

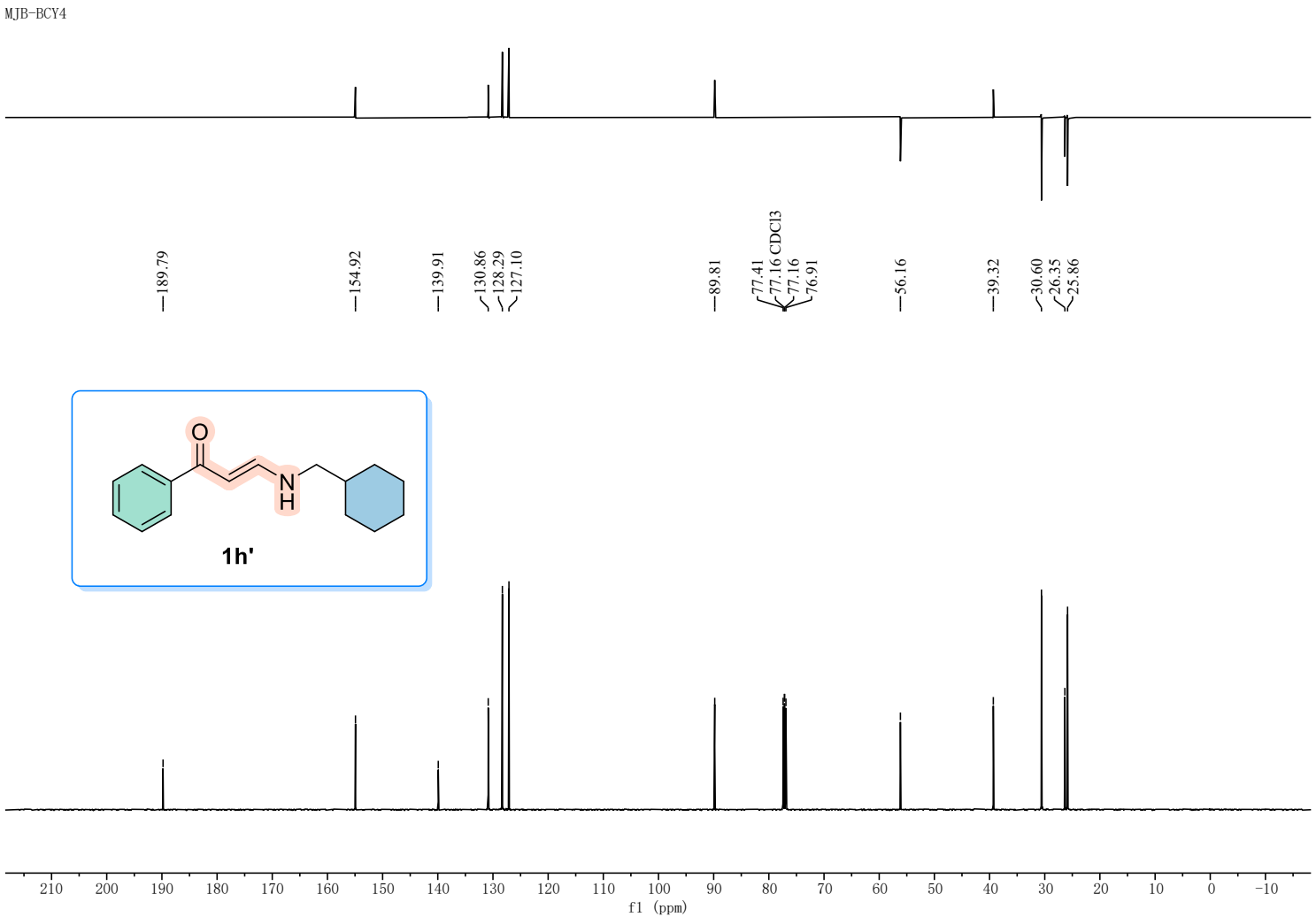


Figure S41. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **1h'**

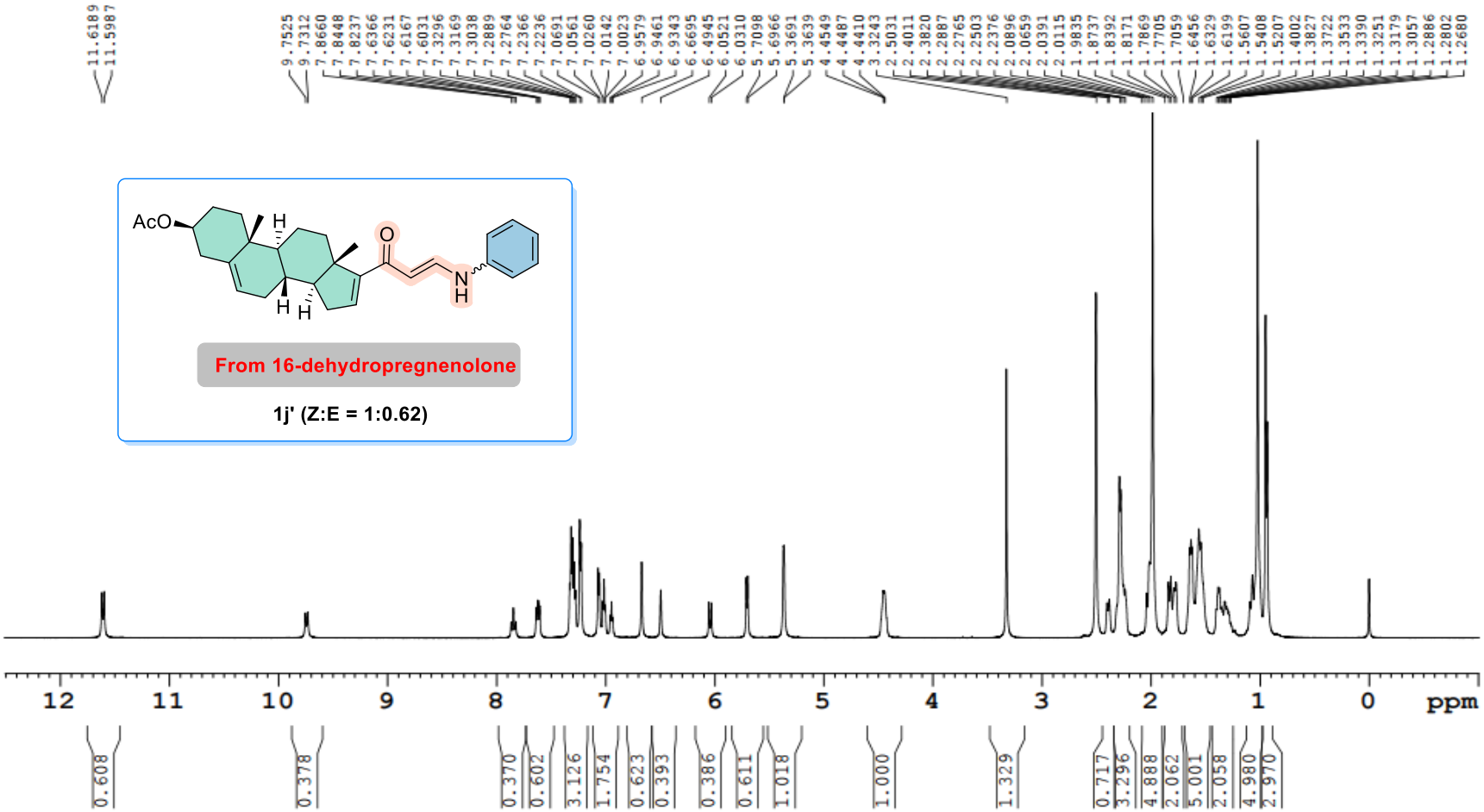


Figure S42. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **1j'**

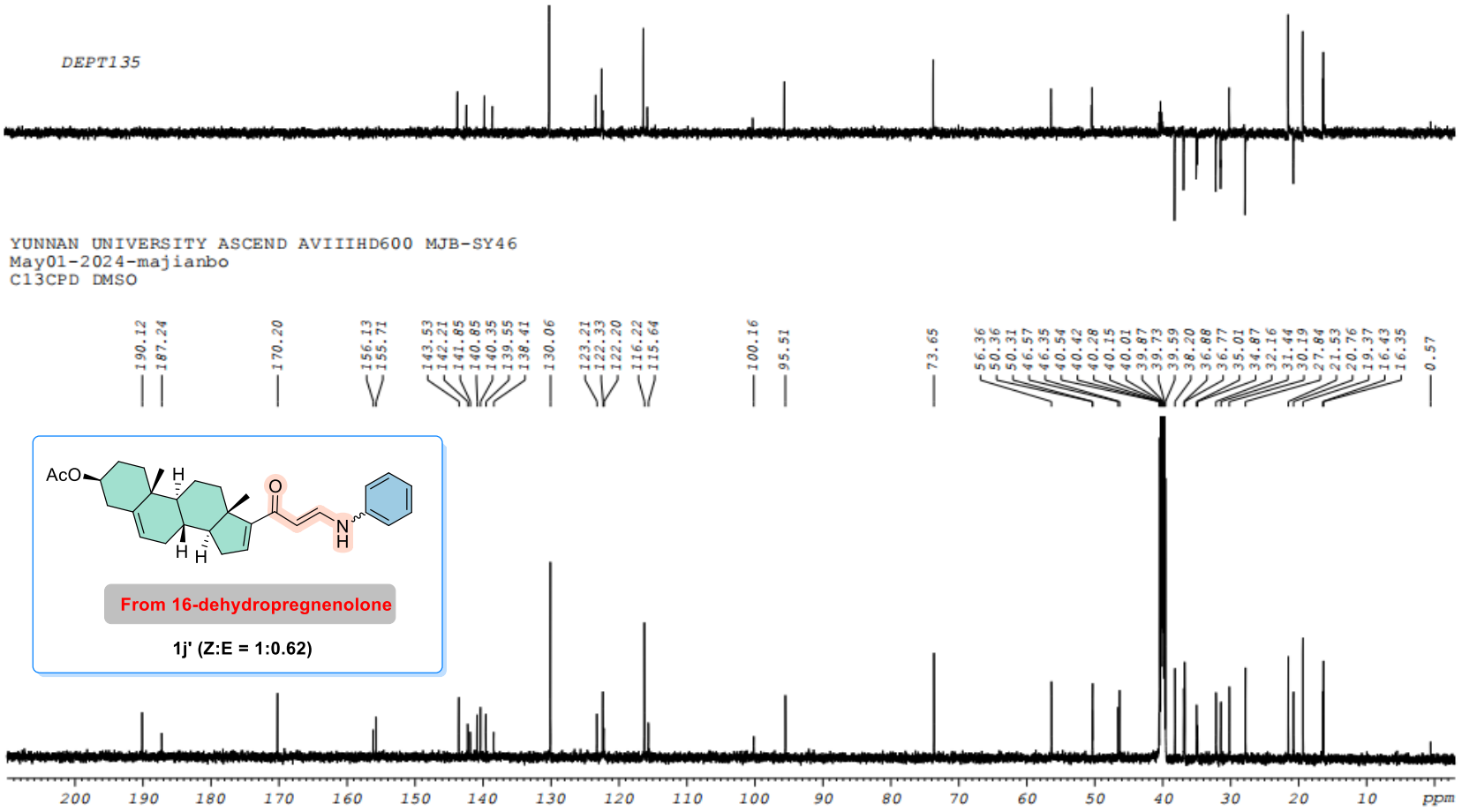


Figure S43. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **1j'**

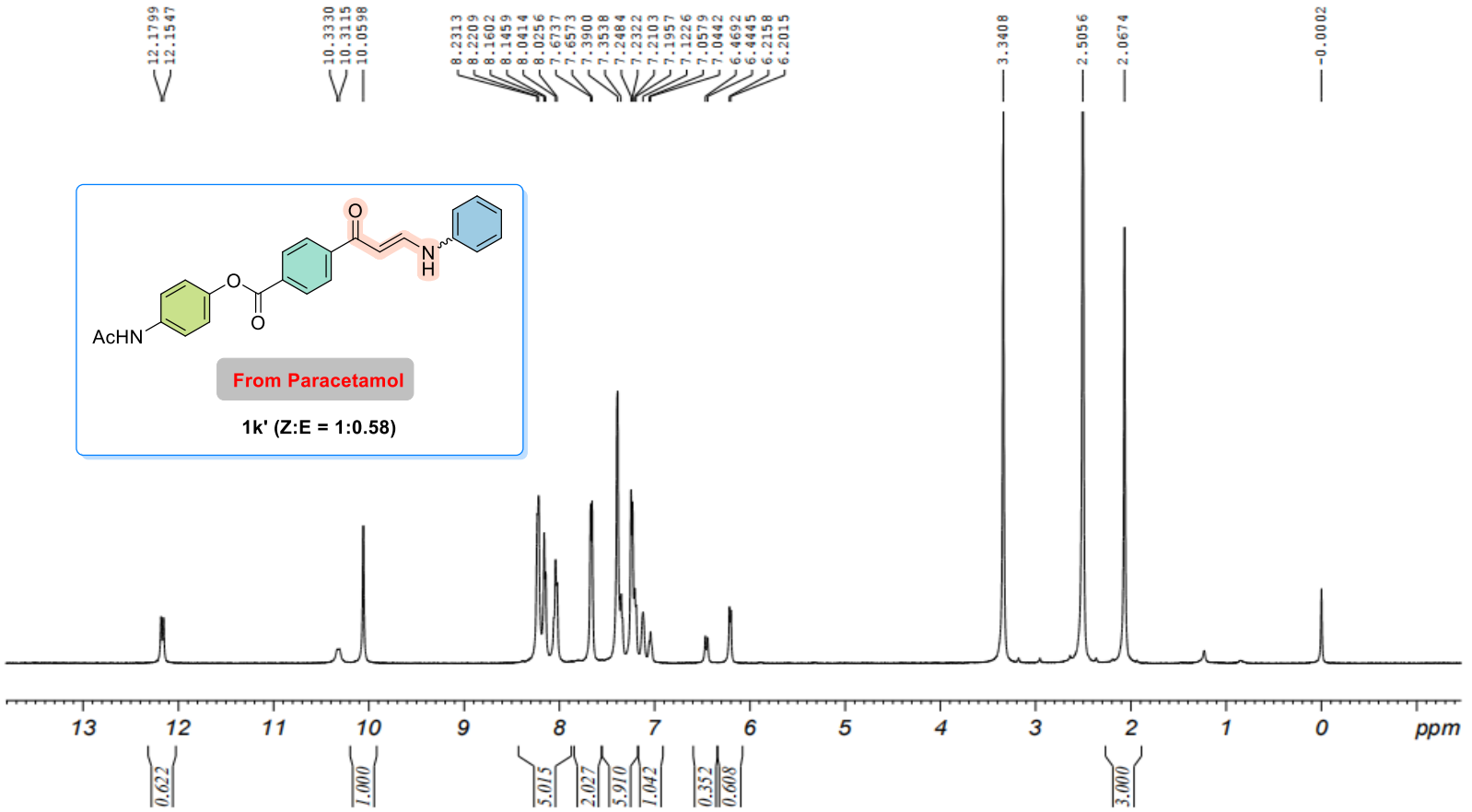


Figure S44. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **1k'**

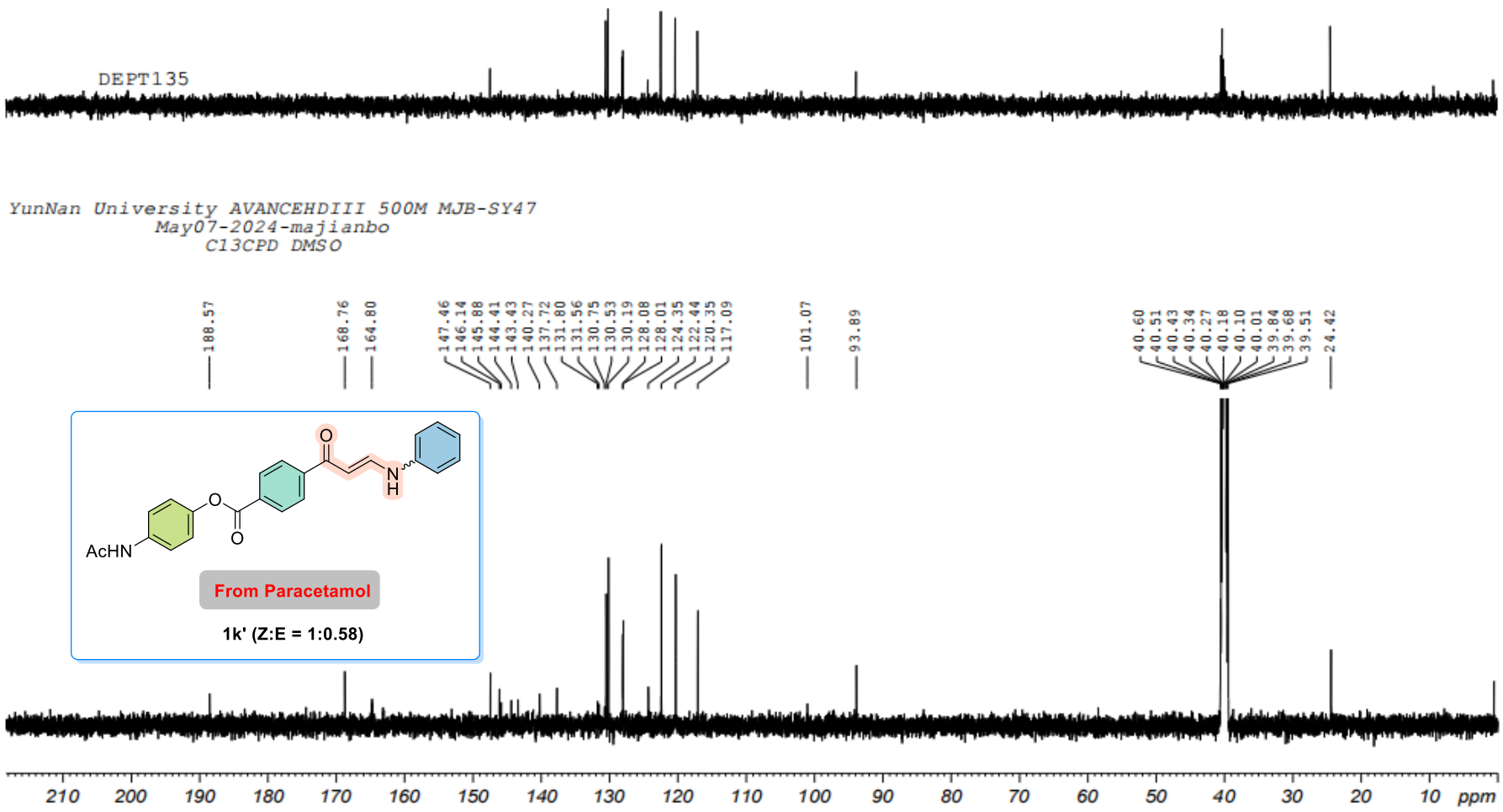


Figure S45. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **1k'**

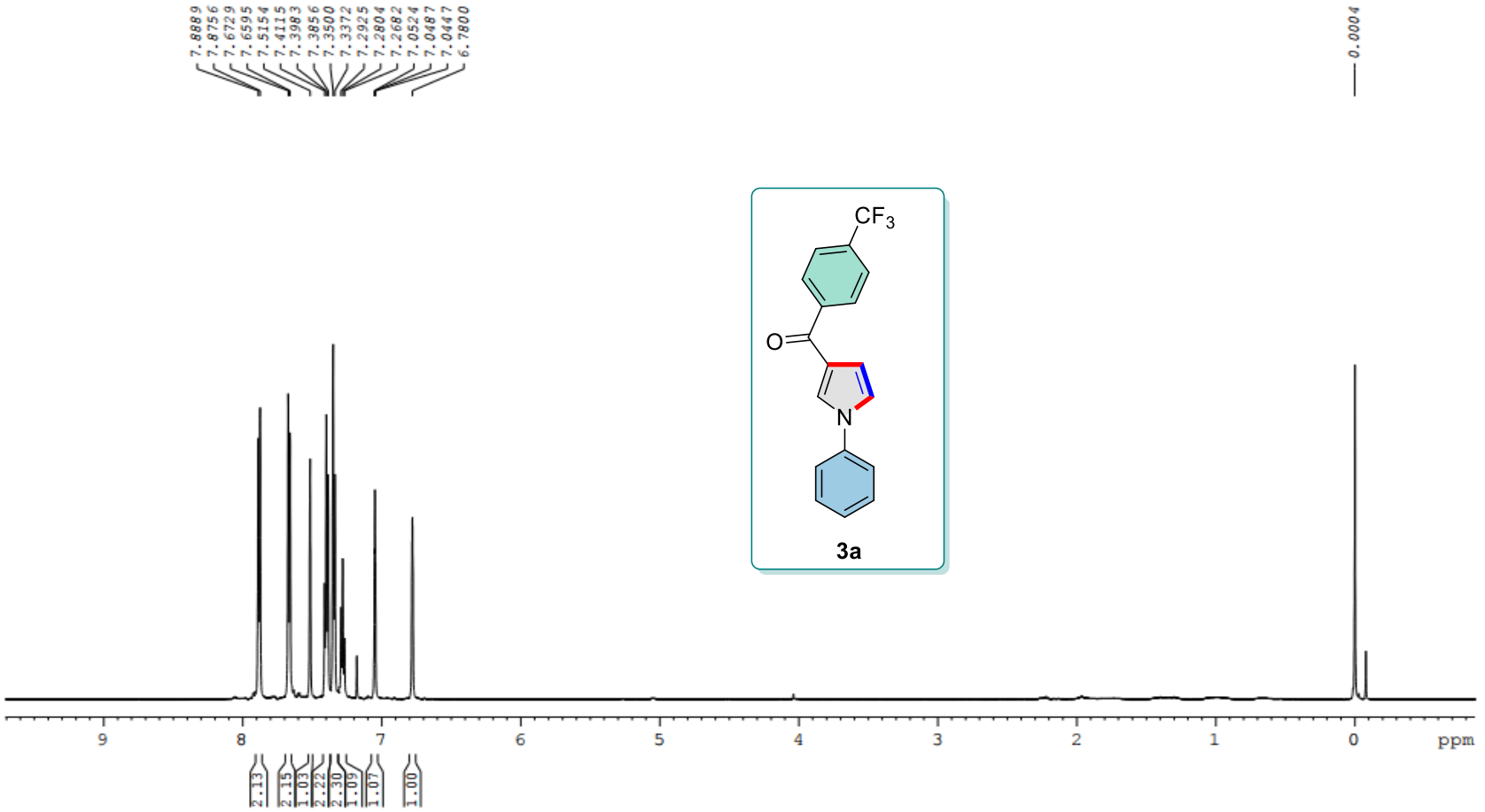


Figure S46. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3a**

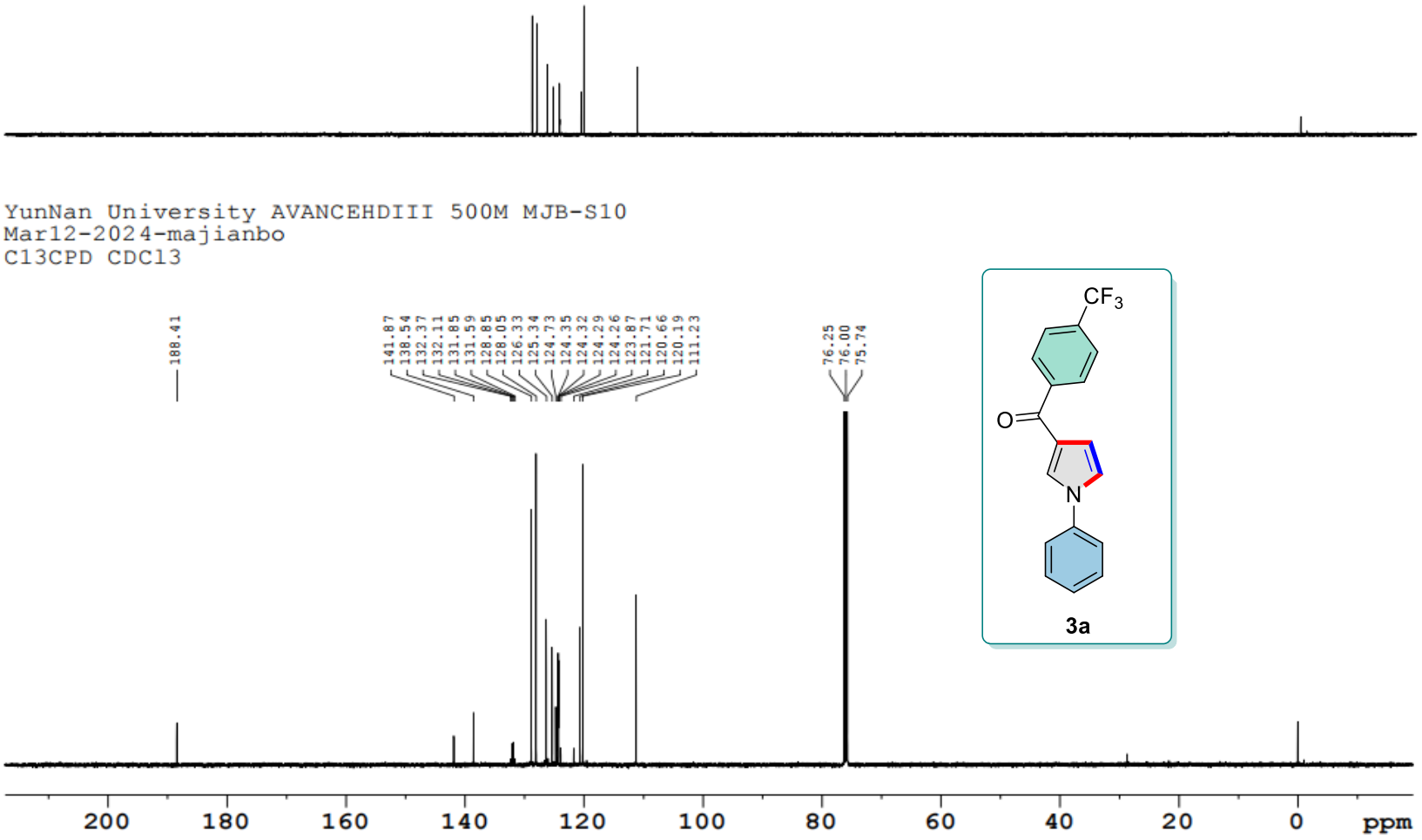


Figure S47. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3a**

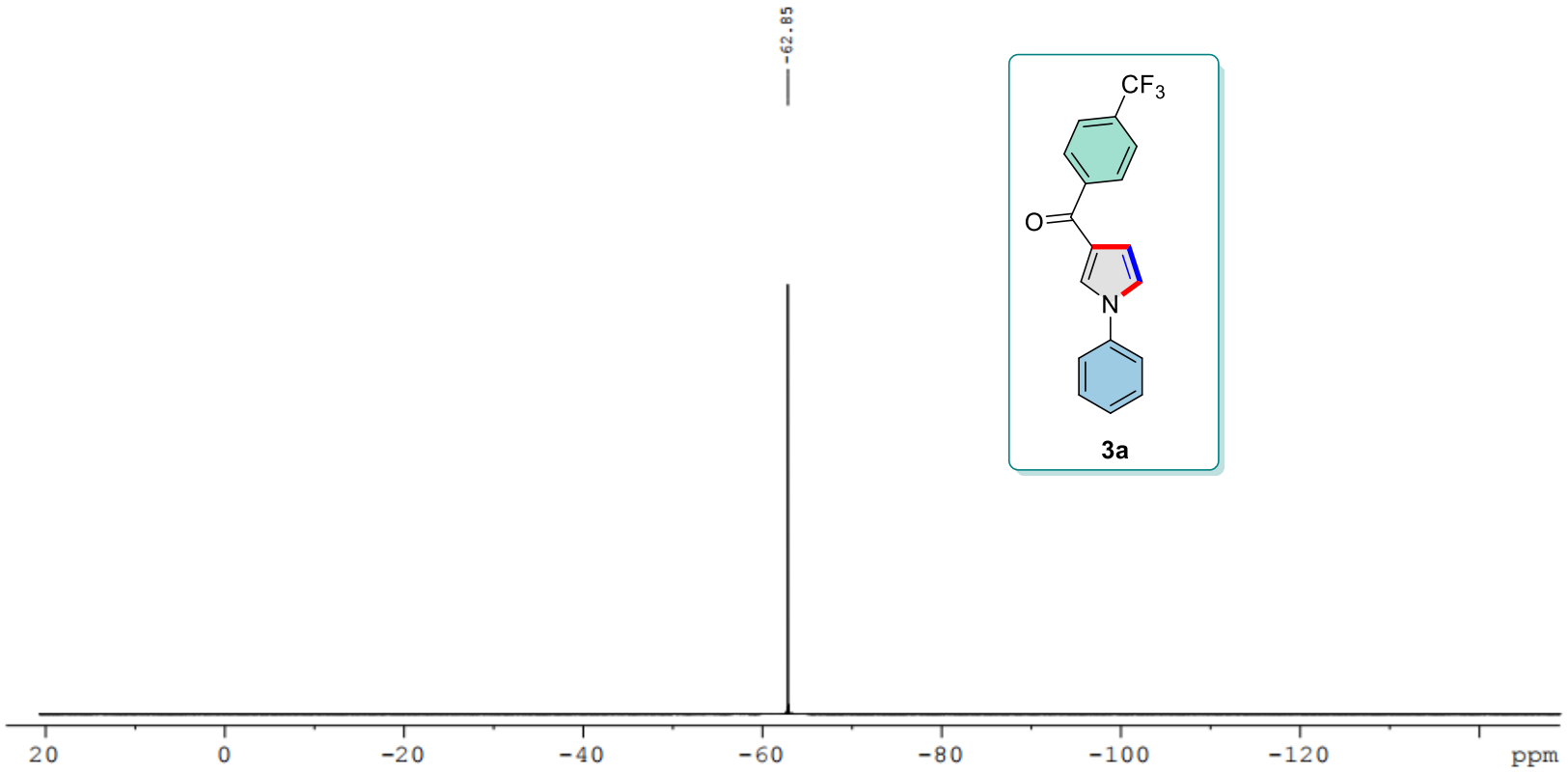


Figure S48. ^{19}F NMR (470 MHz, $CDCl_3$-d_1) spectra of compound **3a**

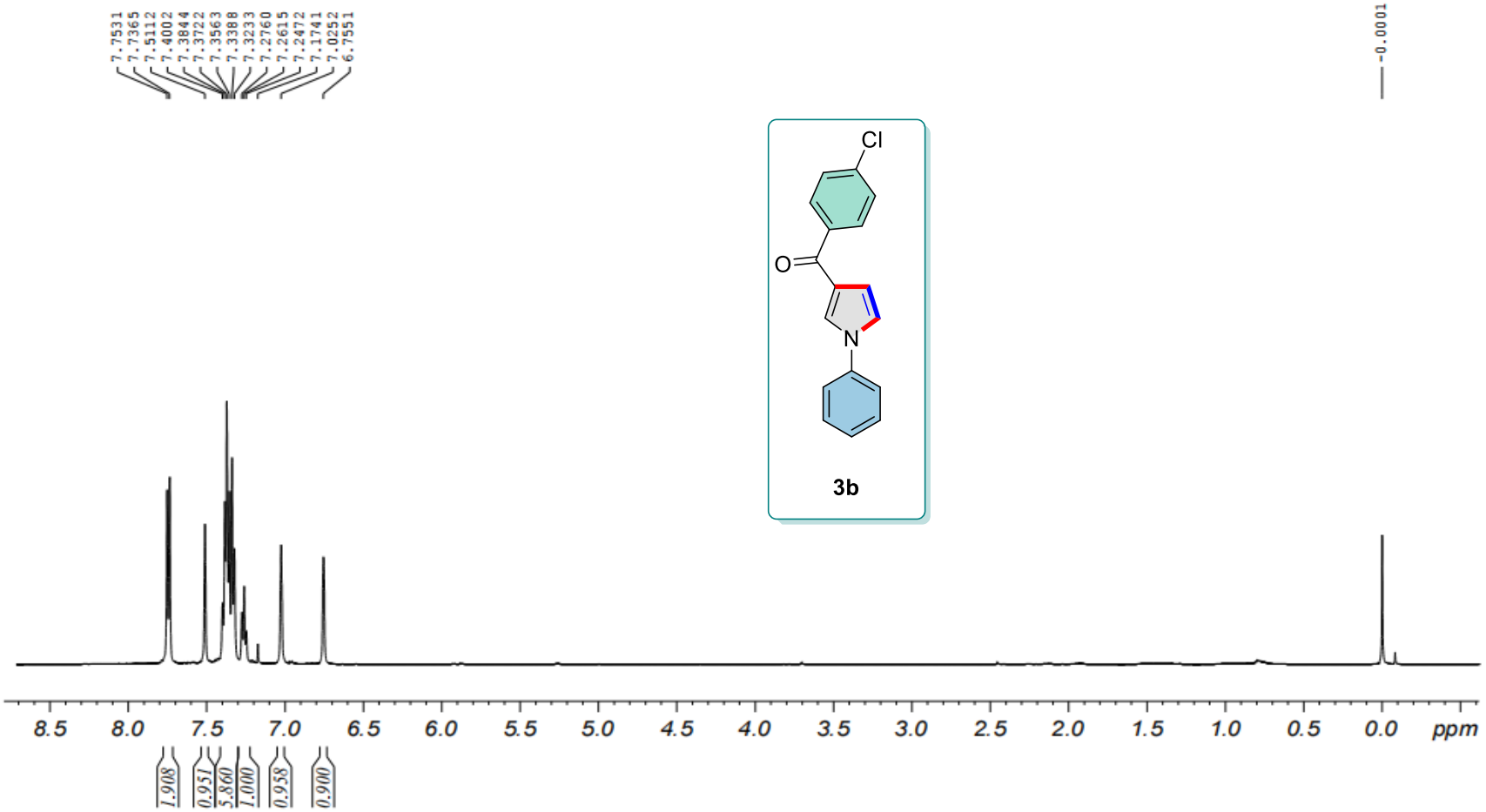


Figure S49. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3b**

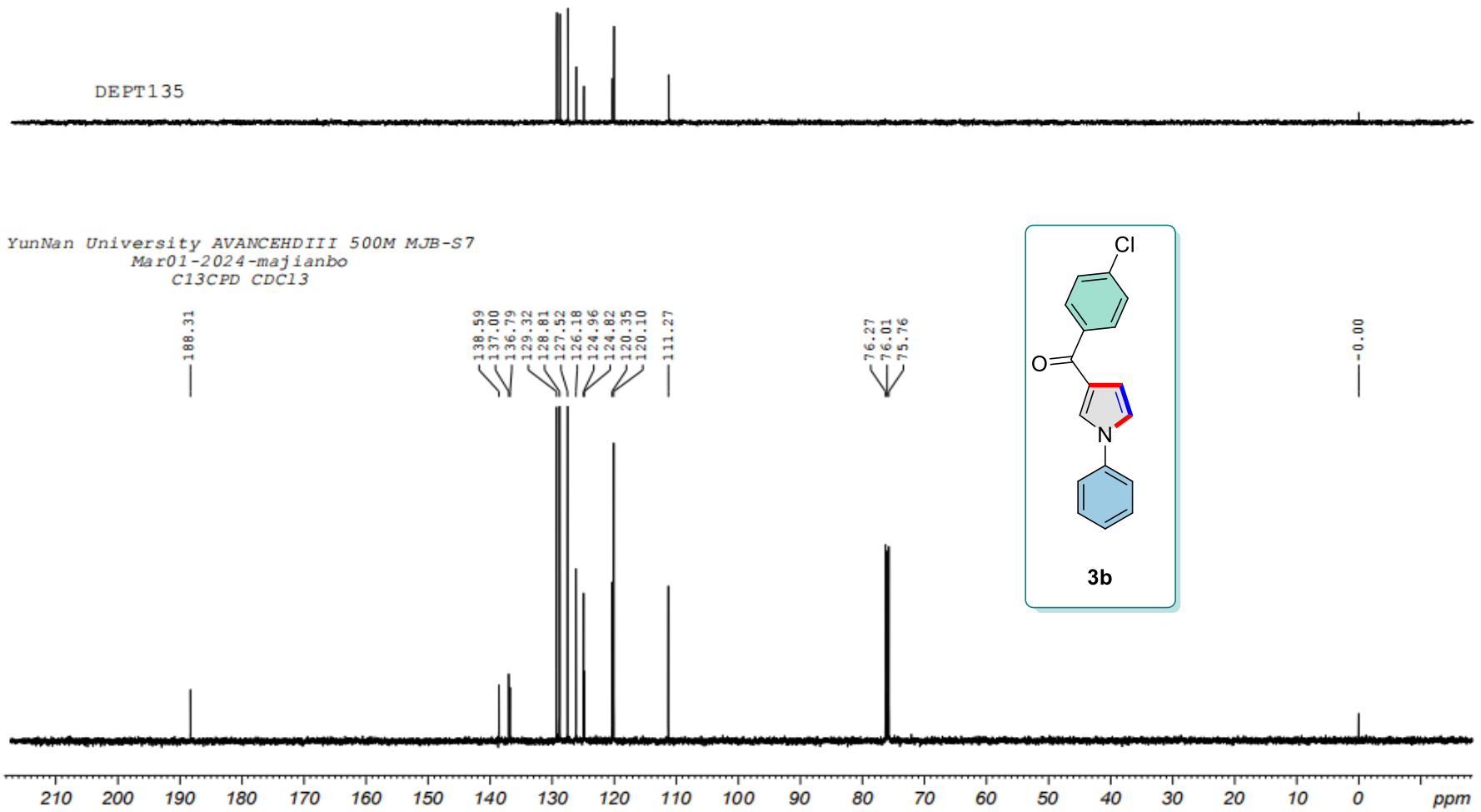


Figure S50. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3b**

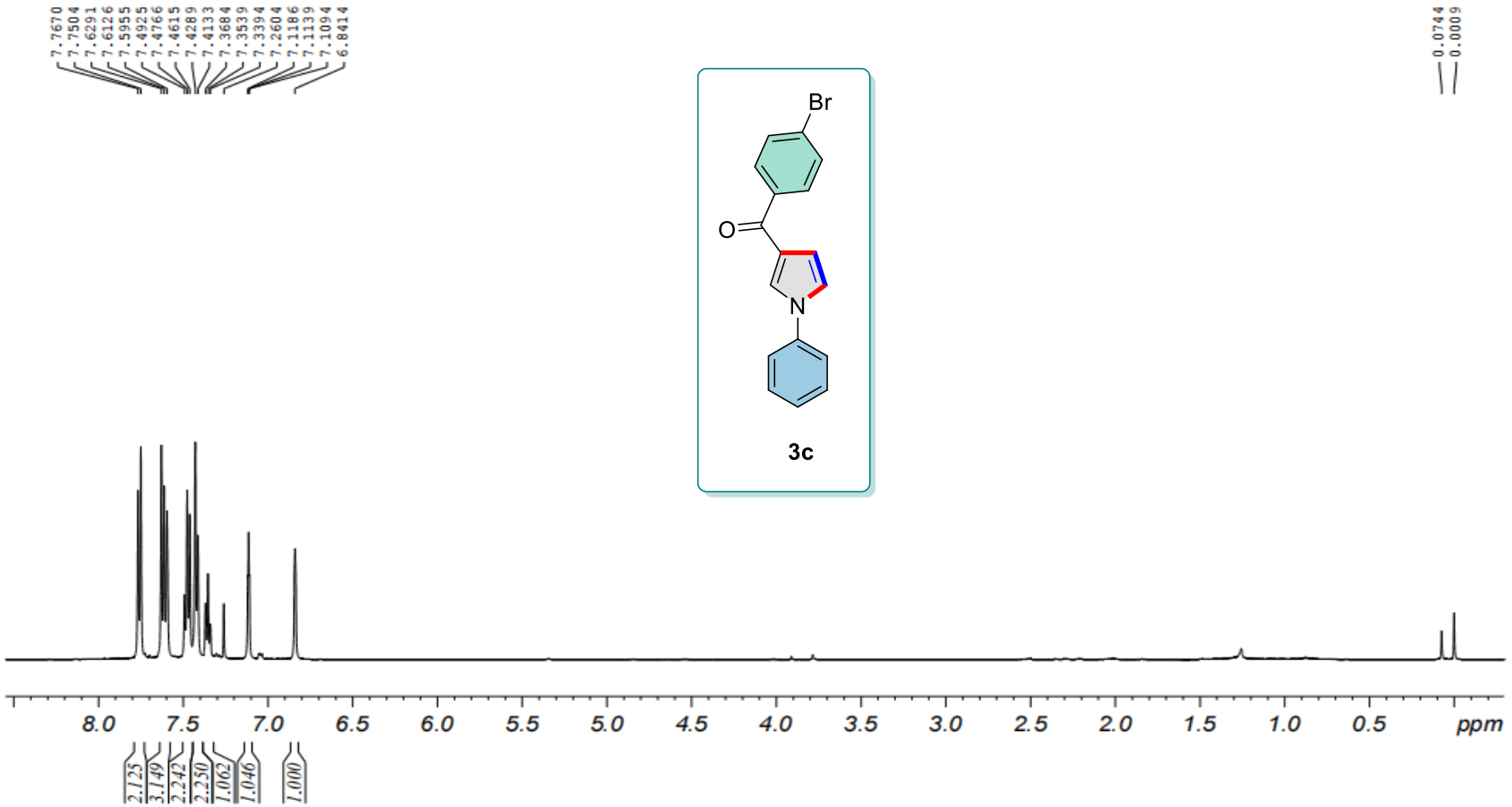


Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3c**

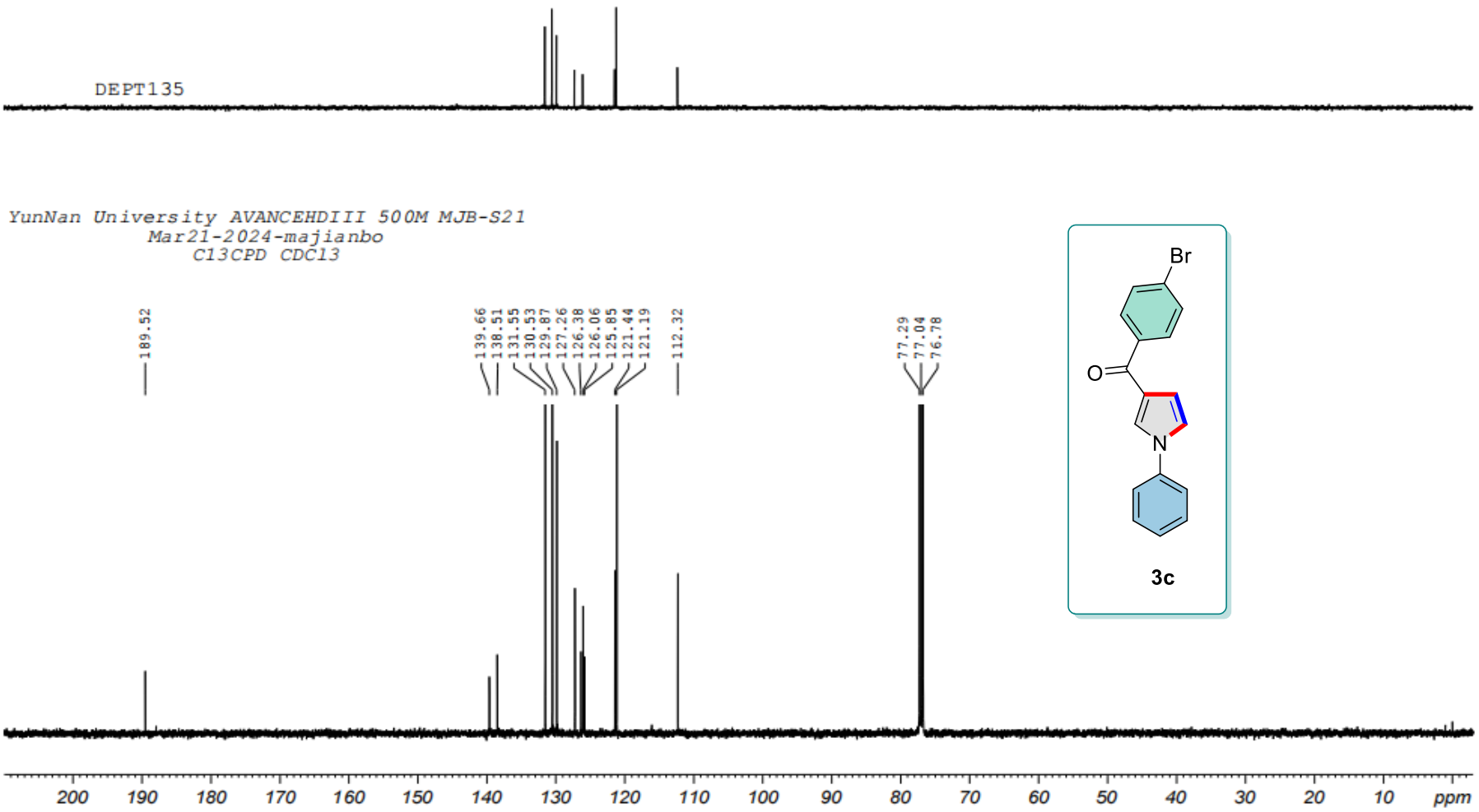


Figure S52. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3c**

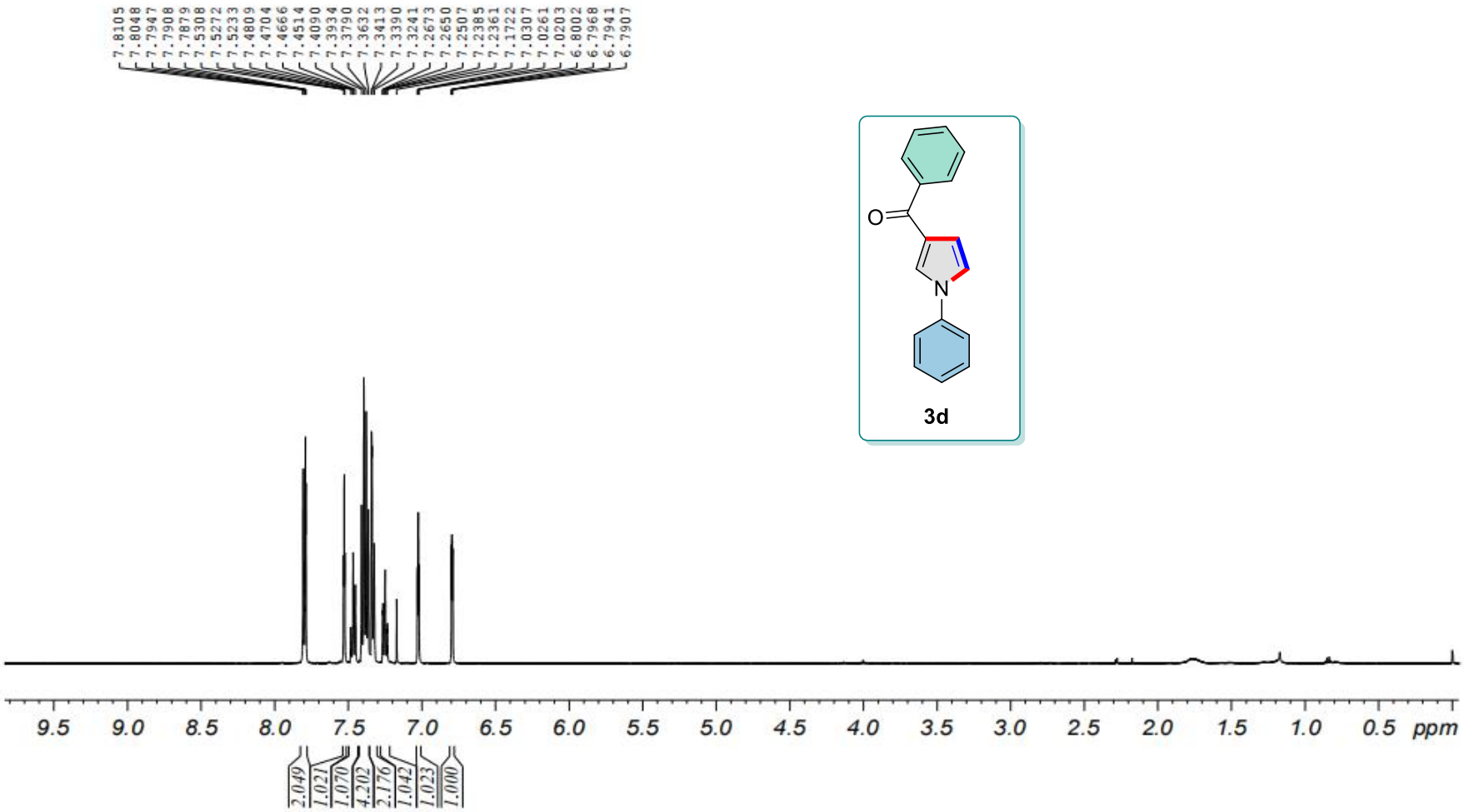


Figure S53. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3d**

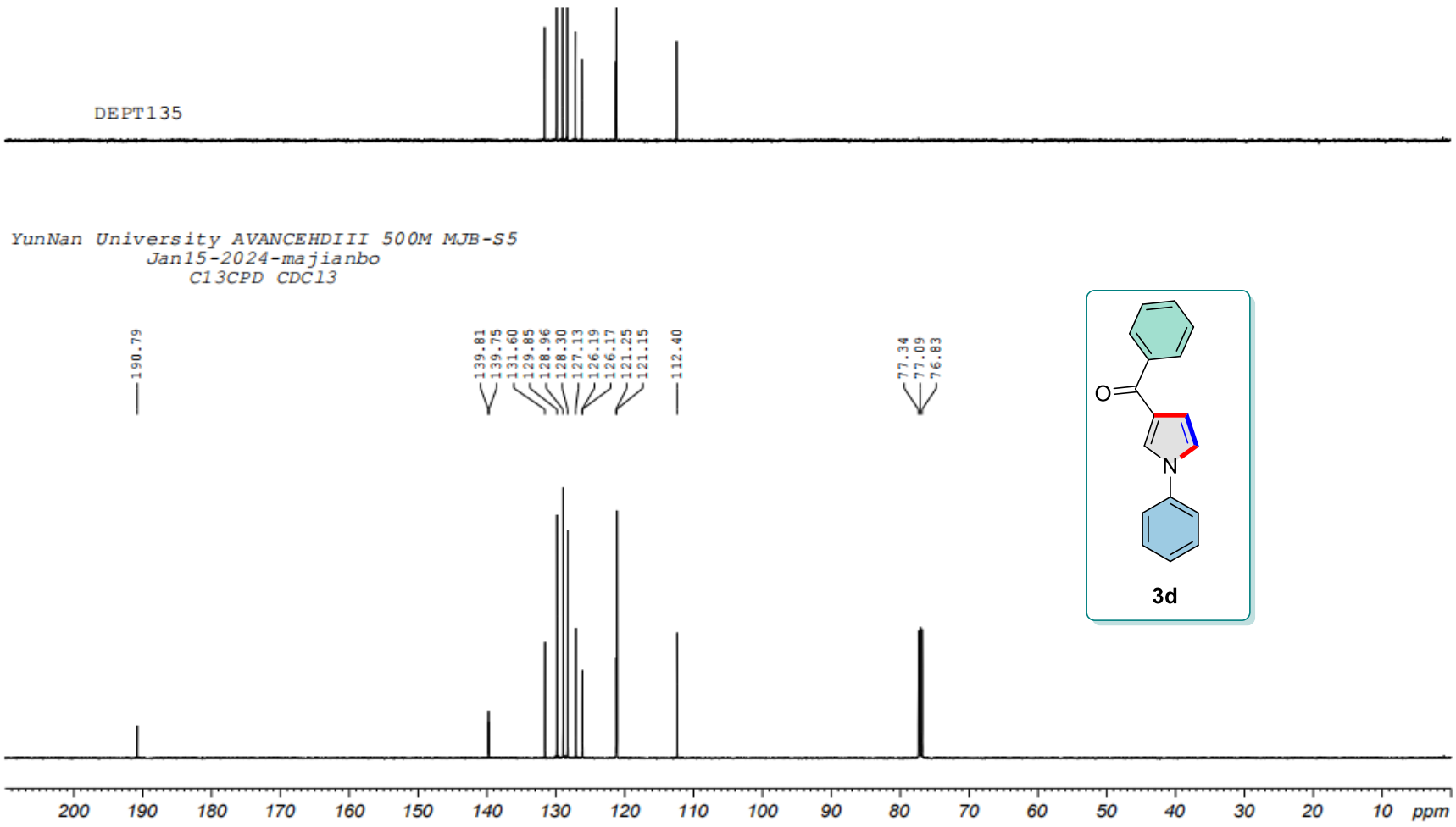


Figure S54. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3d**

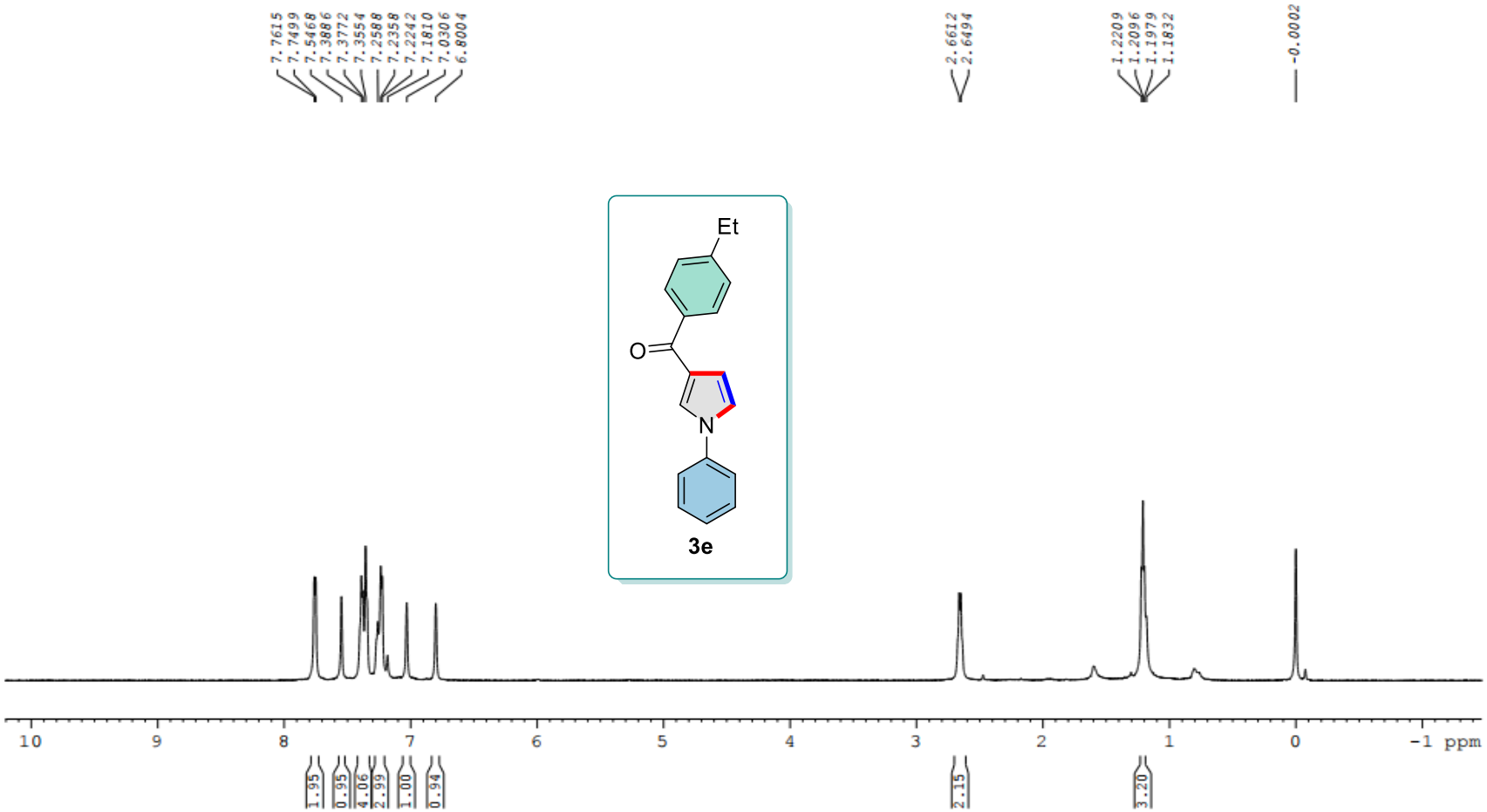


Figure S55. ^{1}H NMR (600 MHz, $CDCl_3$-d_1) spectra of compound **3e**

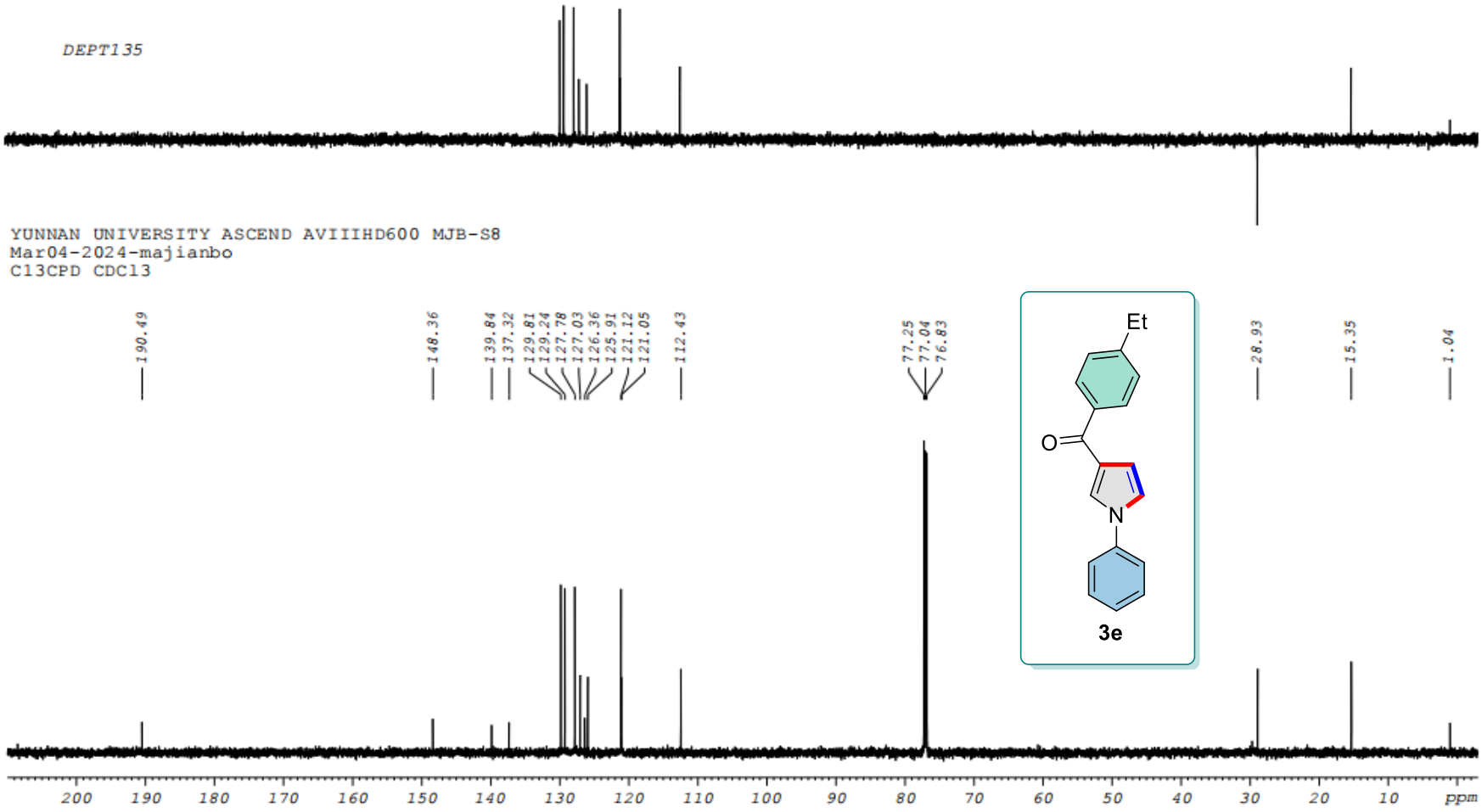


Figure S56. ^{13}C NMR (150 MHz, CDCl3-d_1) spectra of compound **3e**

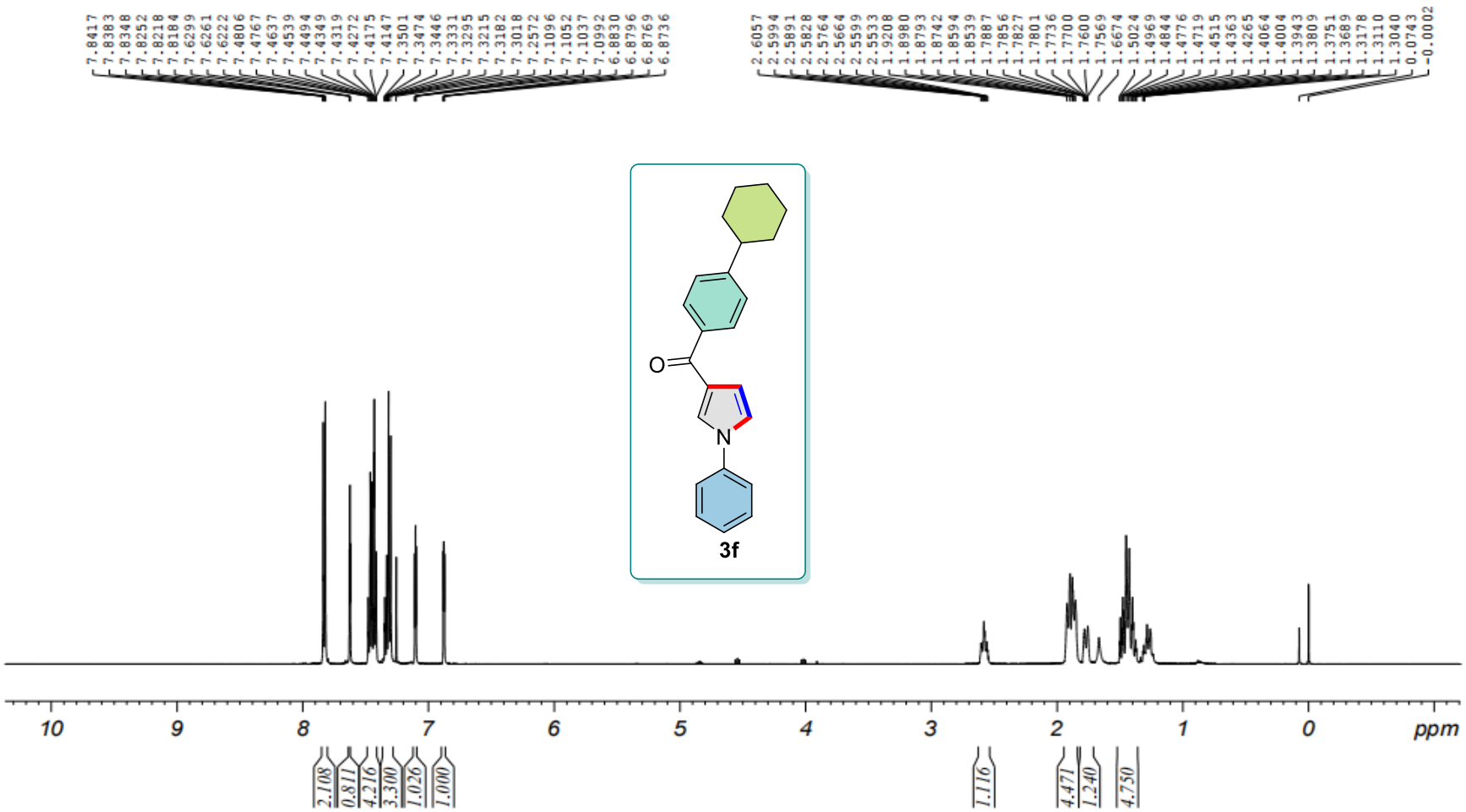


Figure S57. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3f**

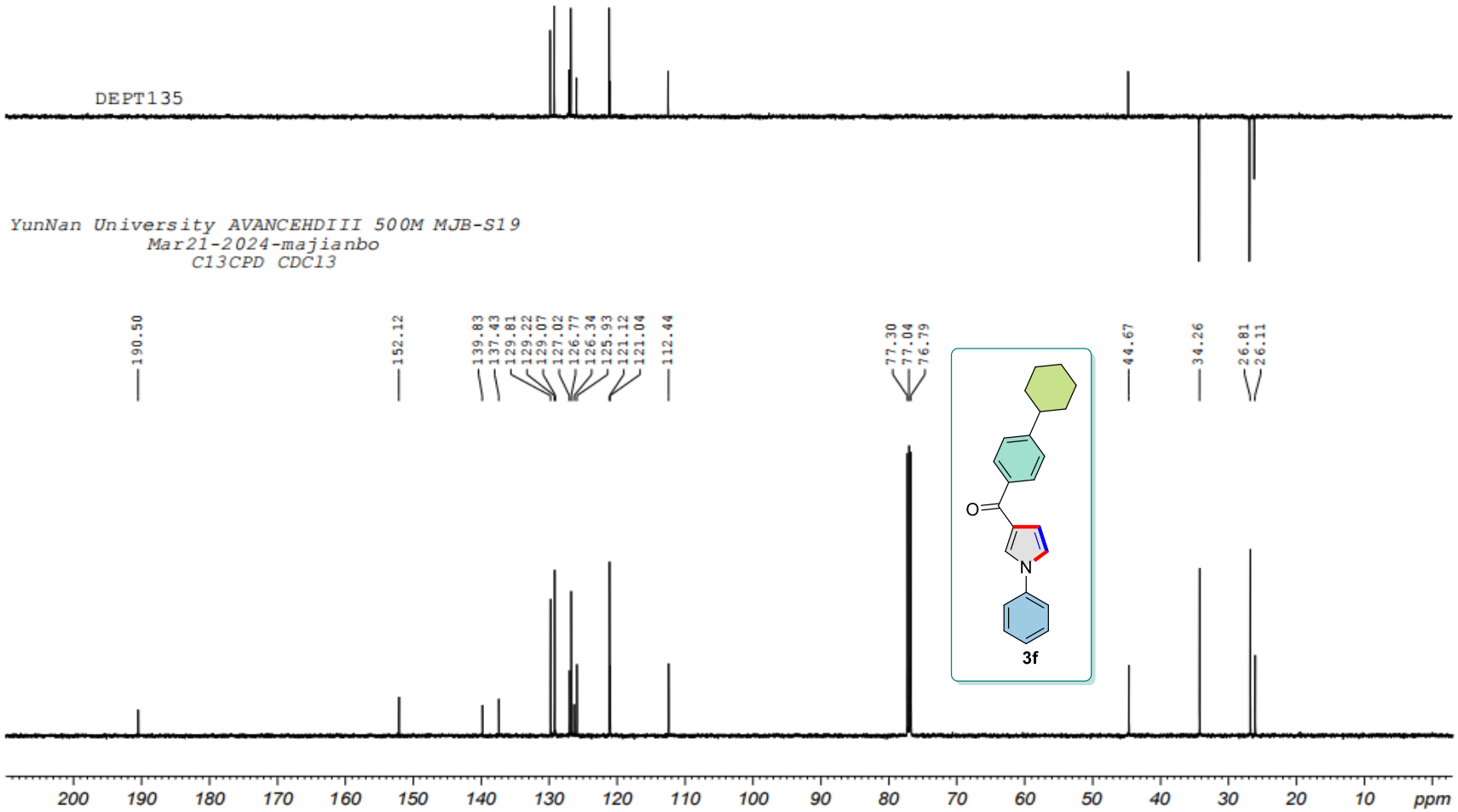


Figure S58. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3f**

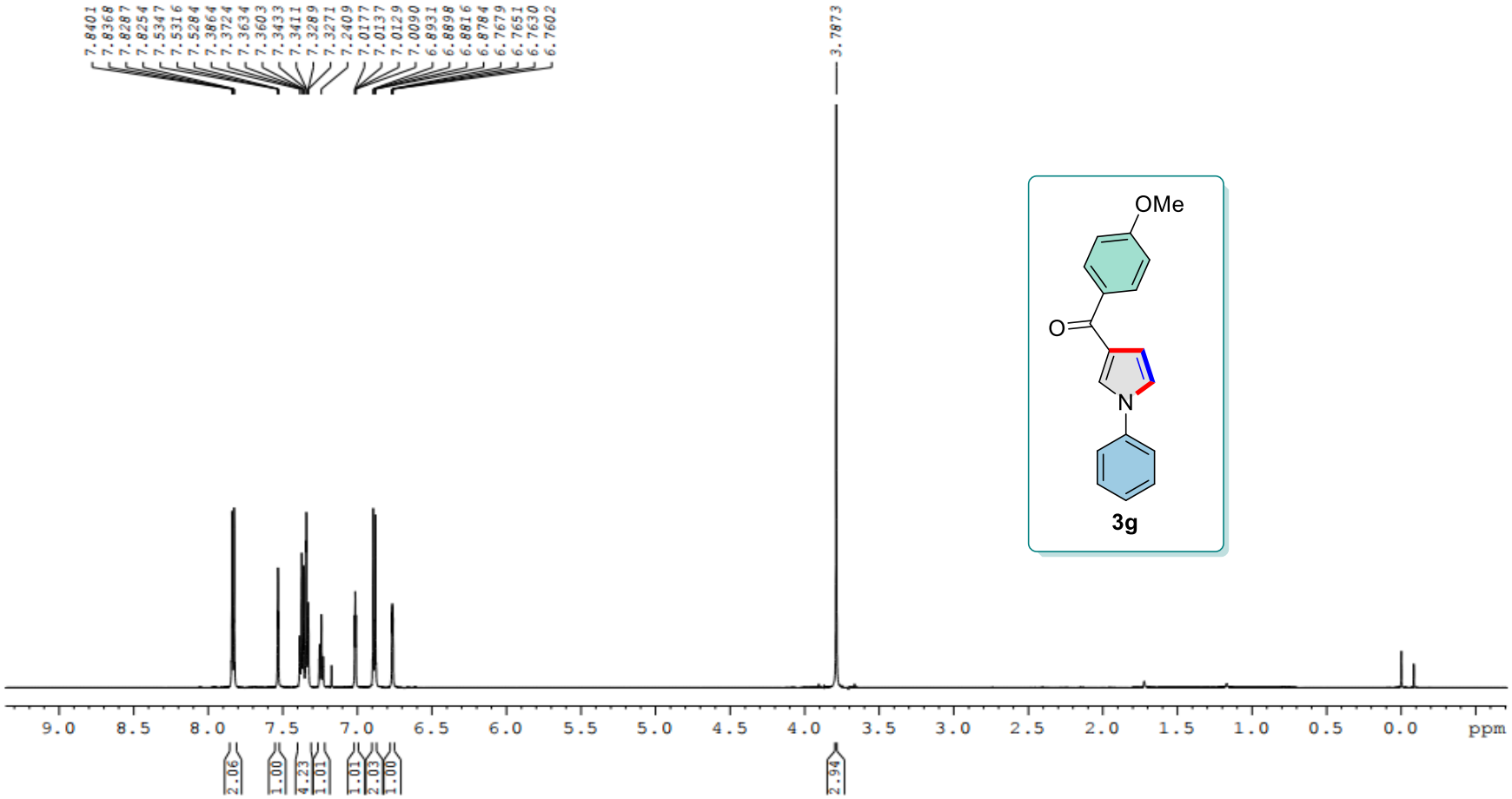


Figure S59. ^{1}H NMR (600 MHz, $CDCl_3$-d_1) spectra of compound **3g**

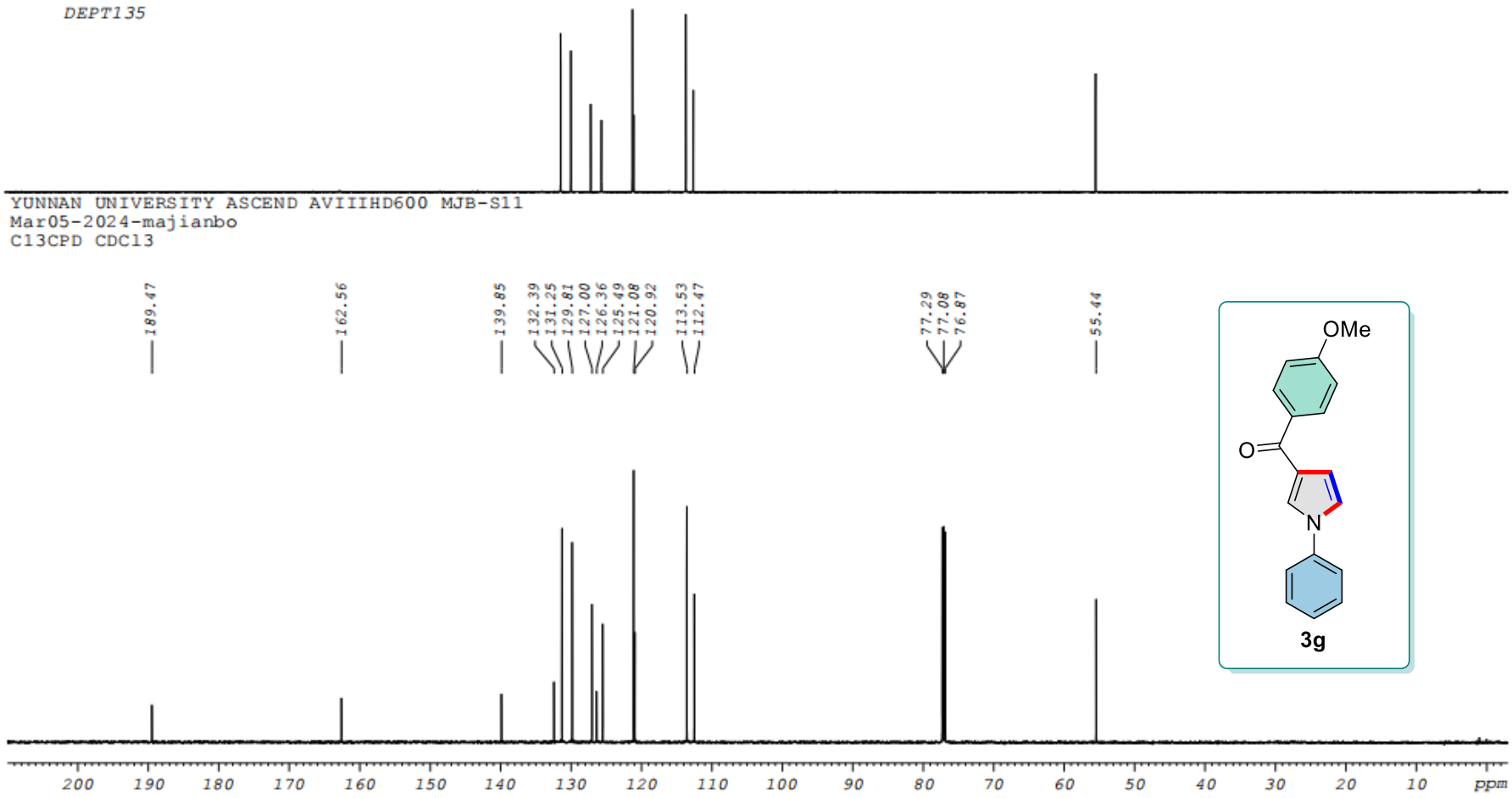


Figure S60. ^{13}C NMR (150 MHz, $CDCl_3$-d_1) spectra of compound **3g**

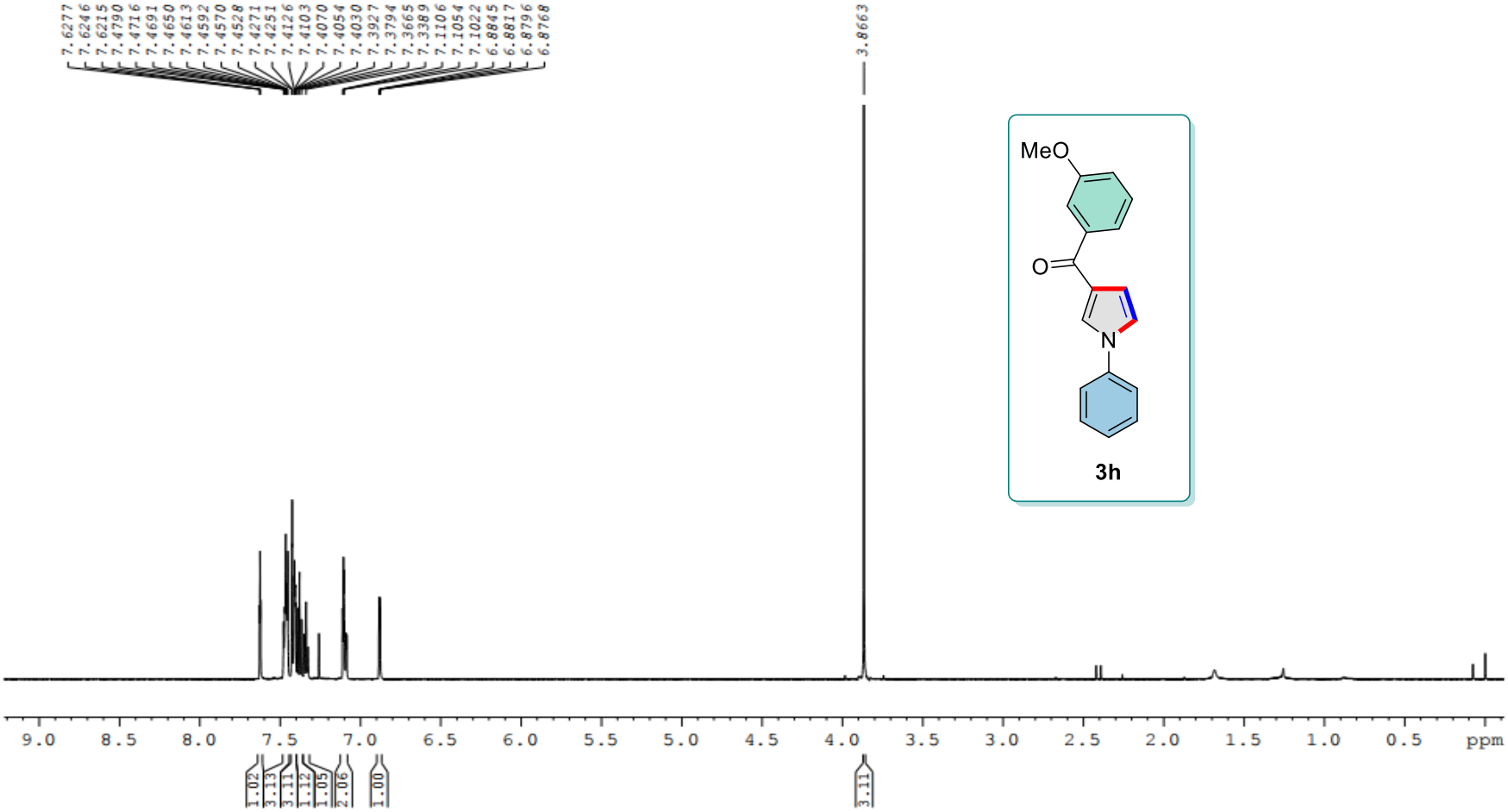


Figure S61. ^{1}H NMR (600 MHz, $CDCl_3$-d_1) spectra of compound **3h**

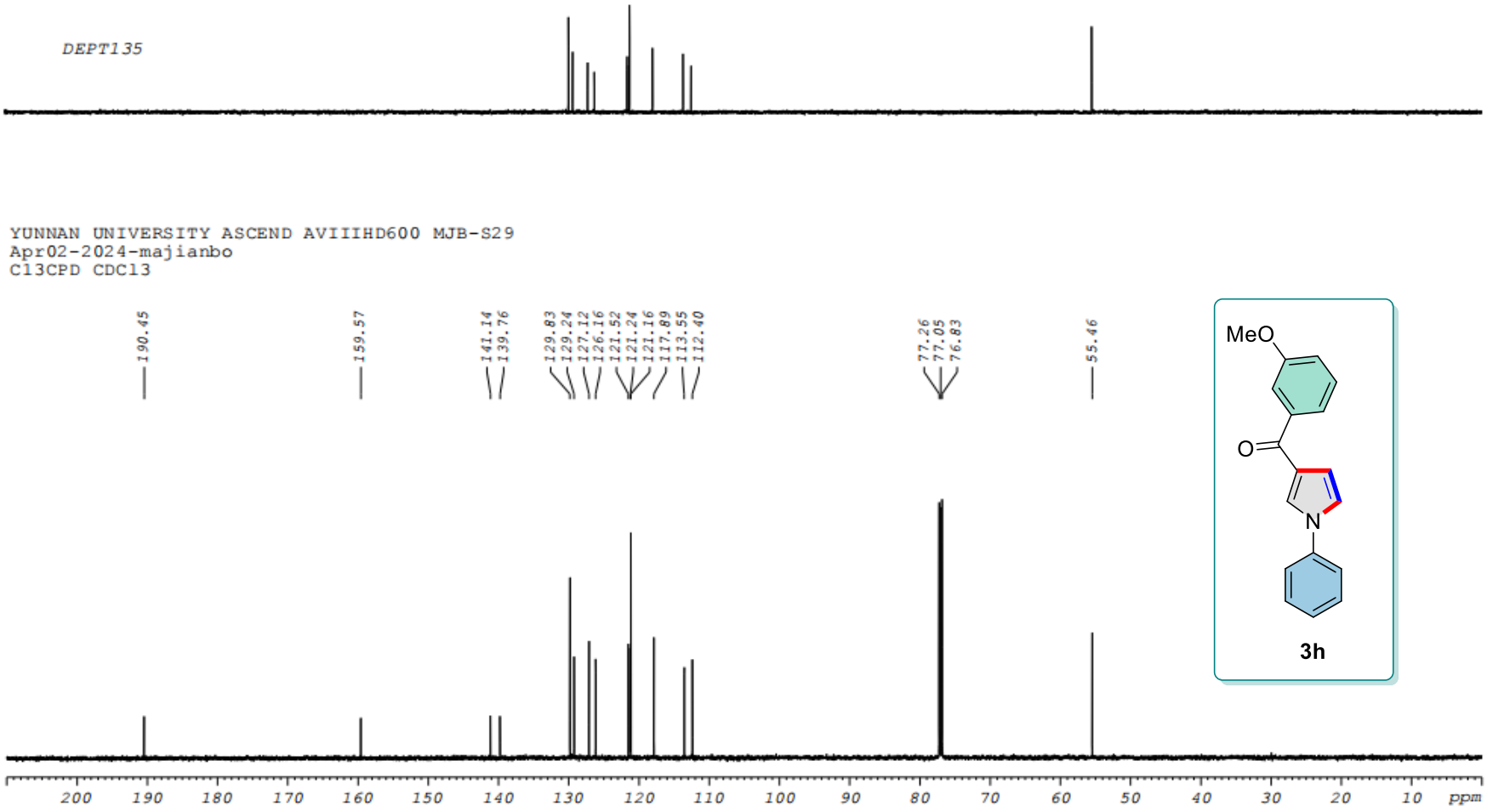


Figure S62. ^{13}C NMR (150 MHz, $CDCl_3$-d_1) spectra of compound **3h**

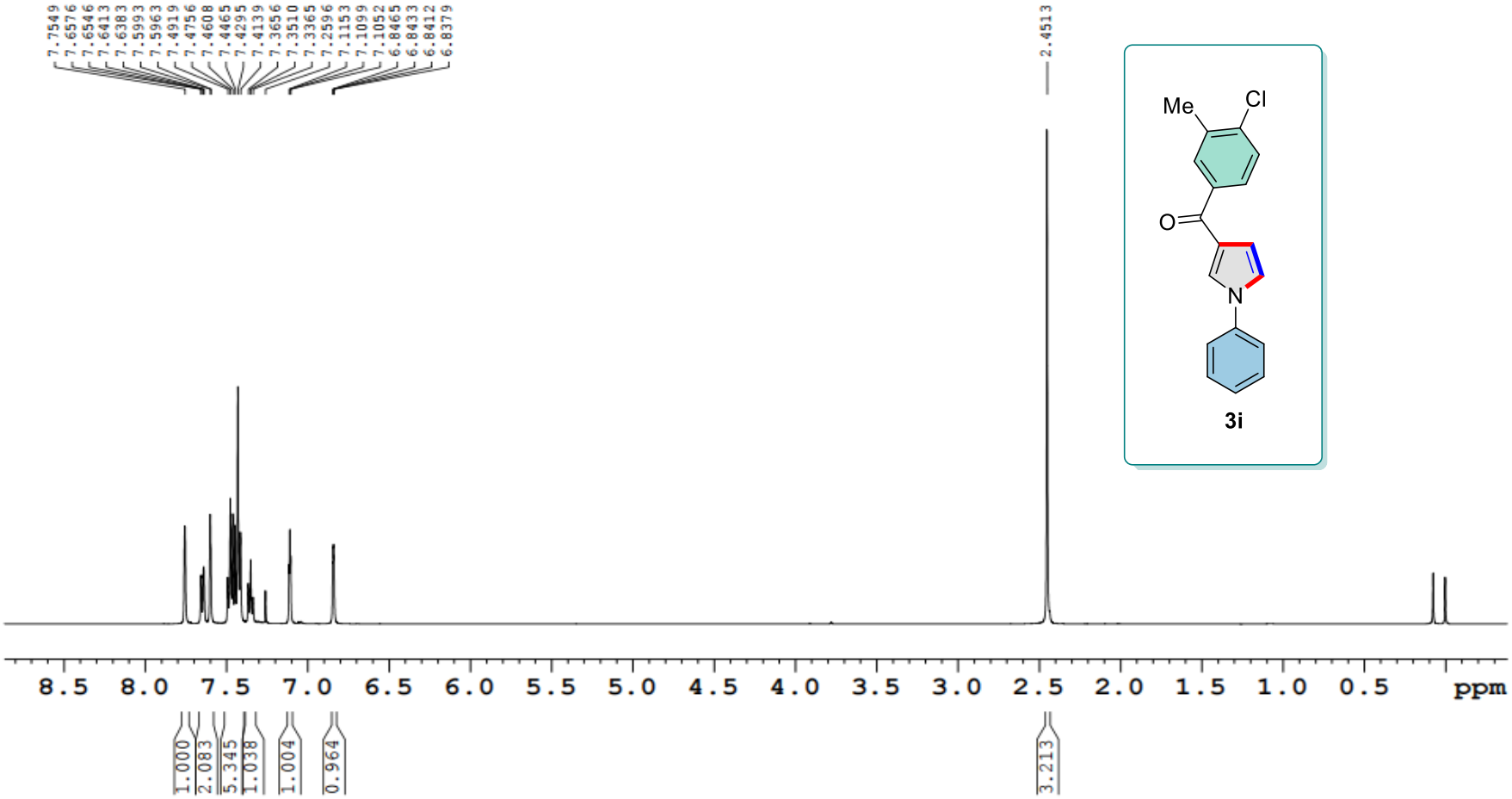


Figure S63. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3i**

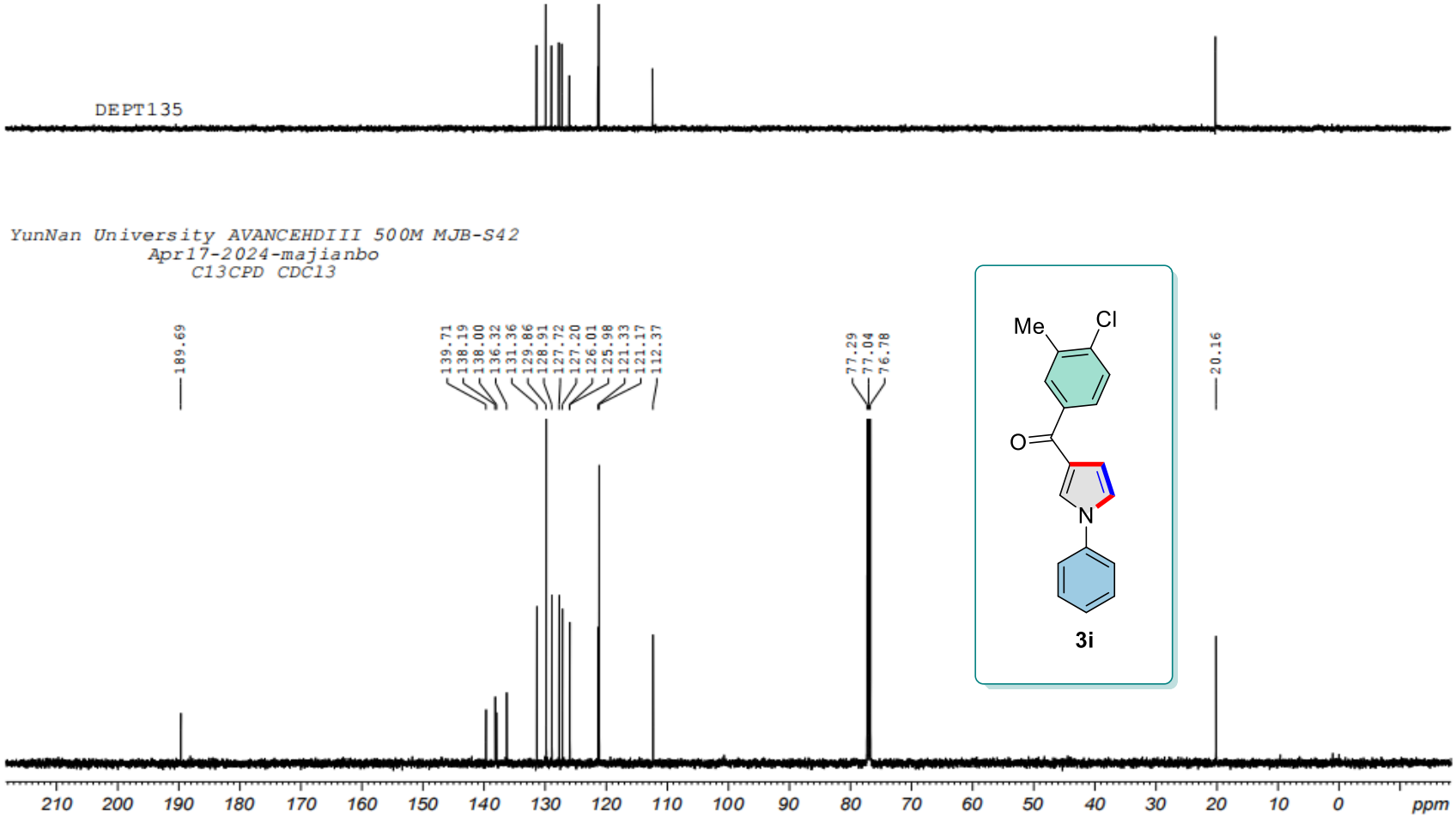


Figure S64. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3i**

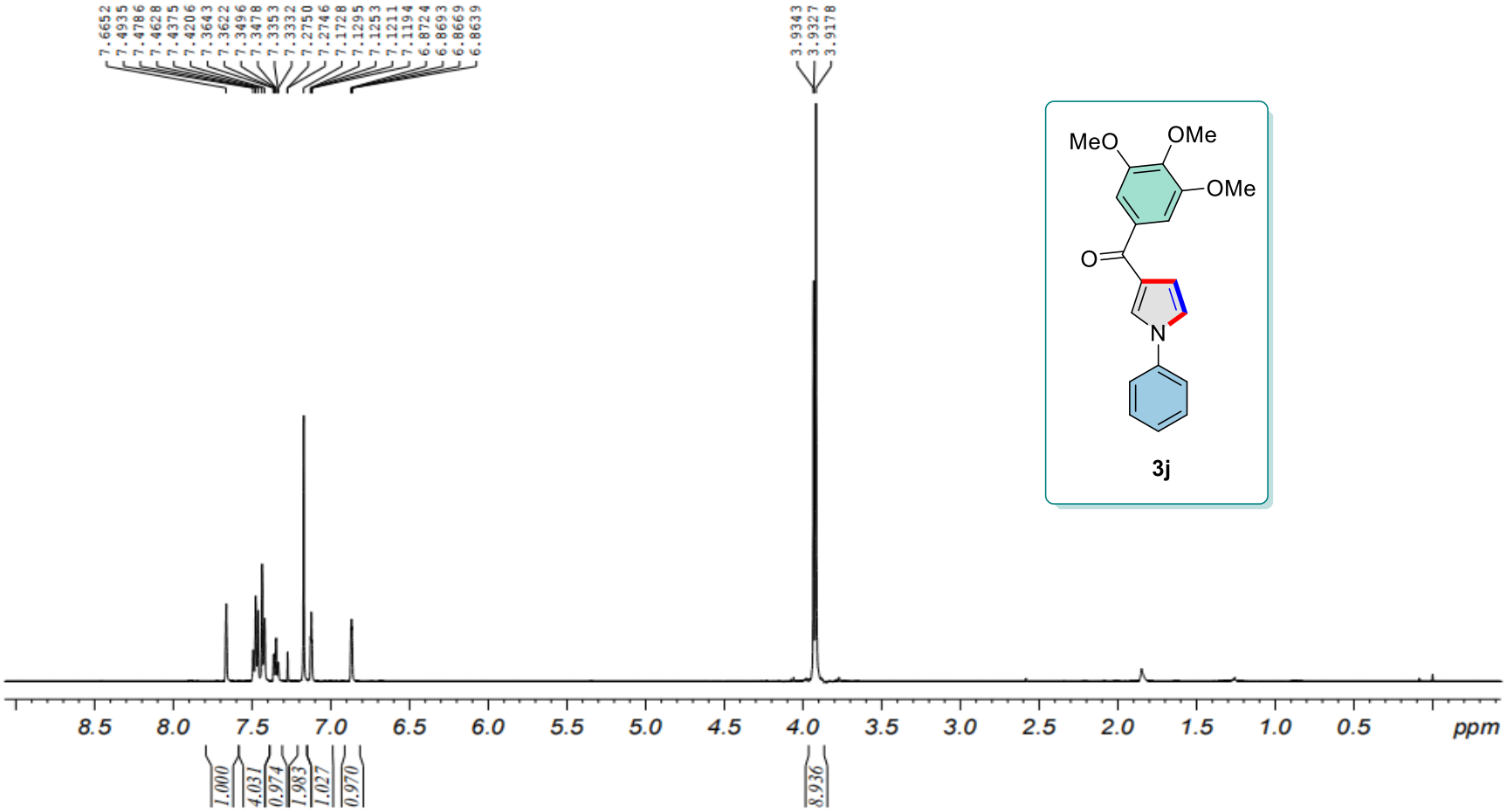


Figure S65. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3j**

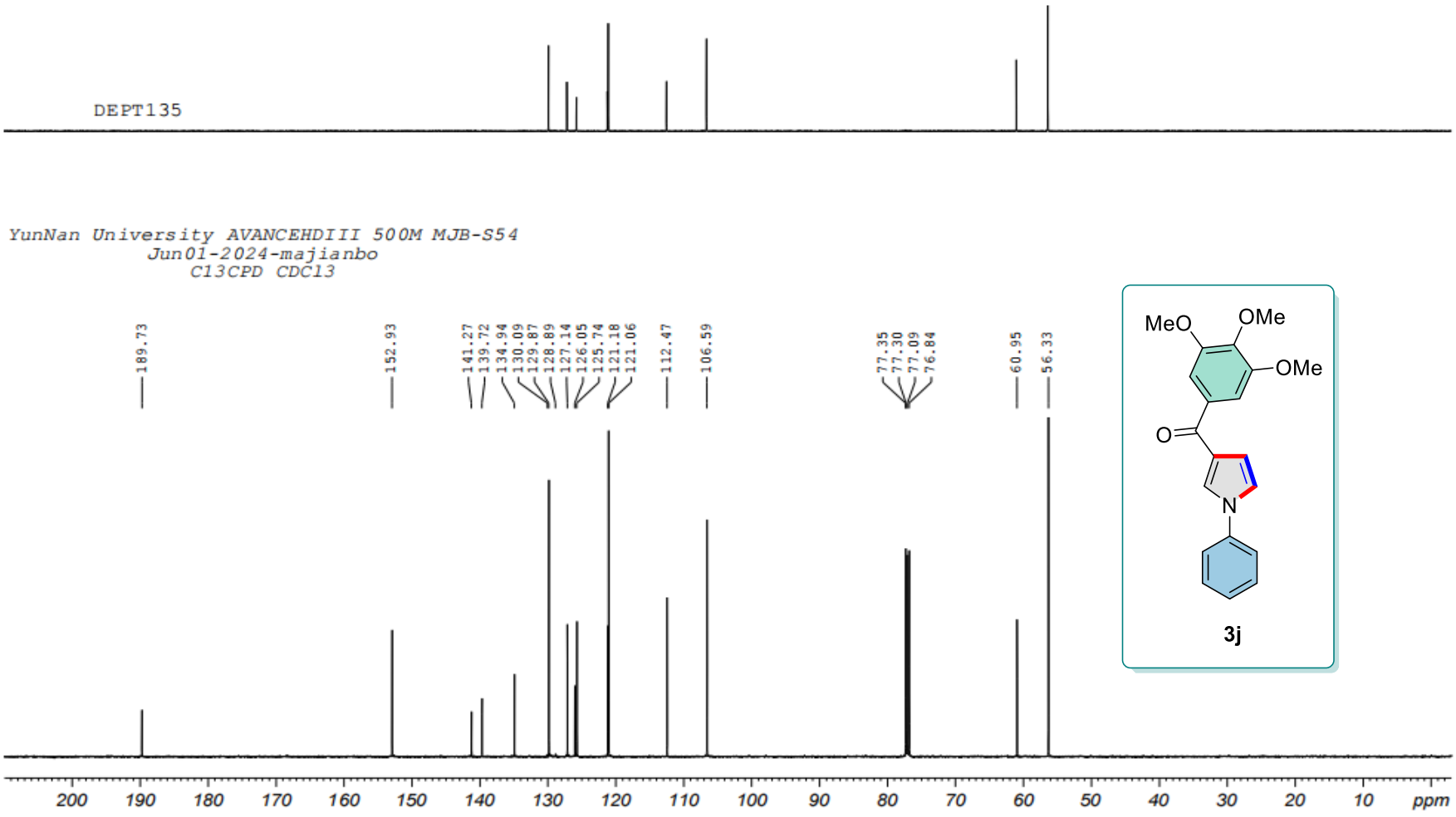


Figure S66. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3j**

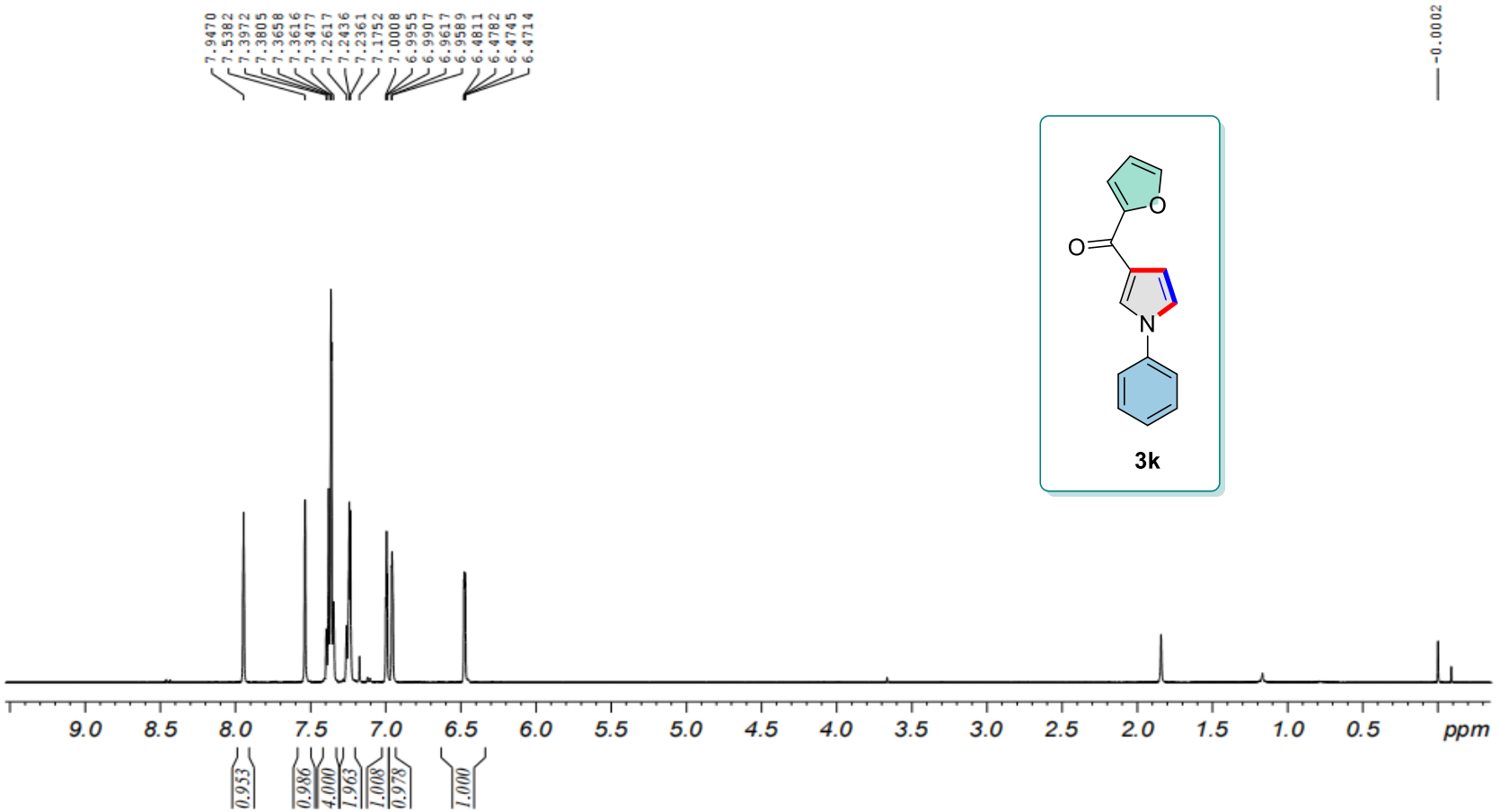


Figure S67. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3k**

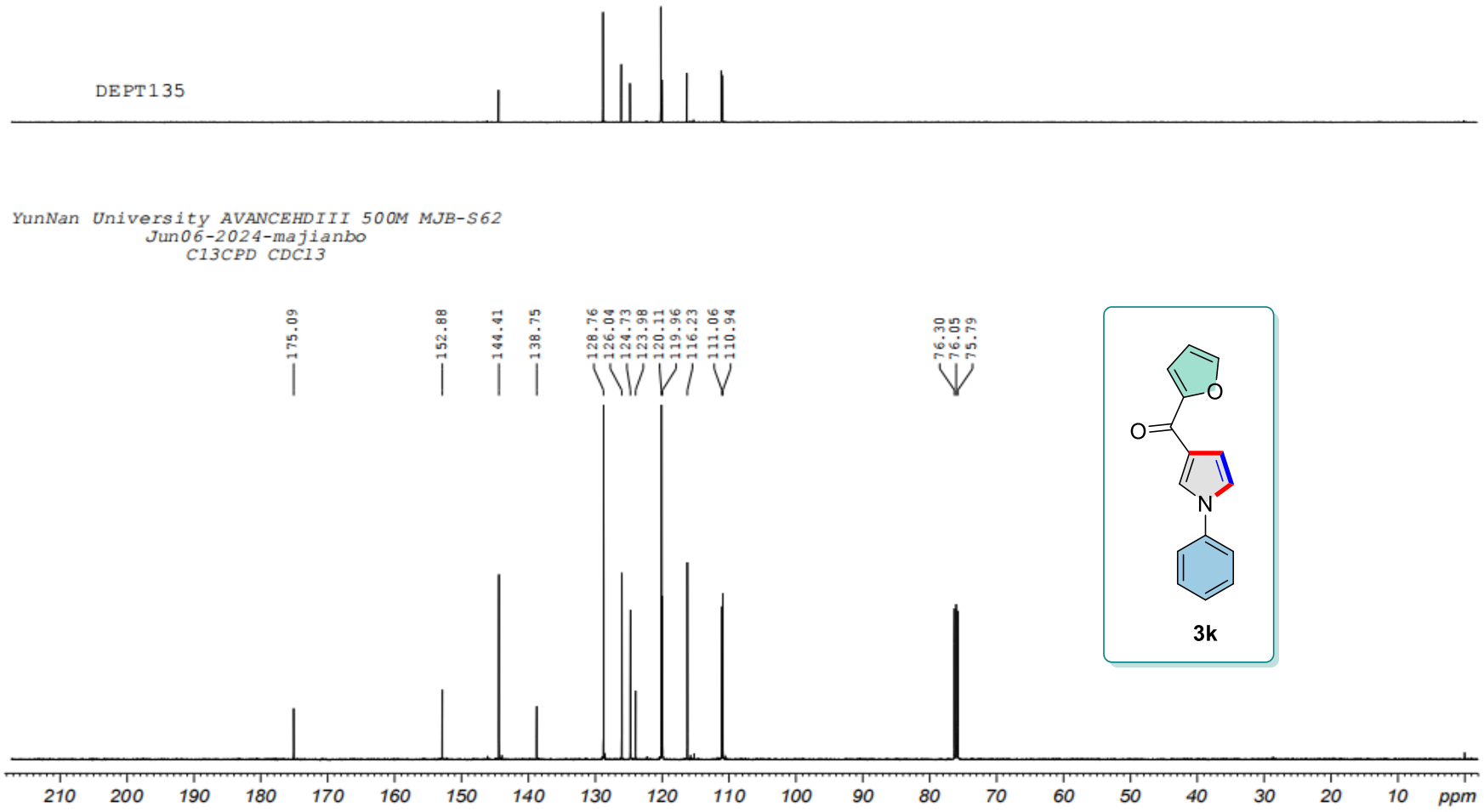


Figure S68. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3k**

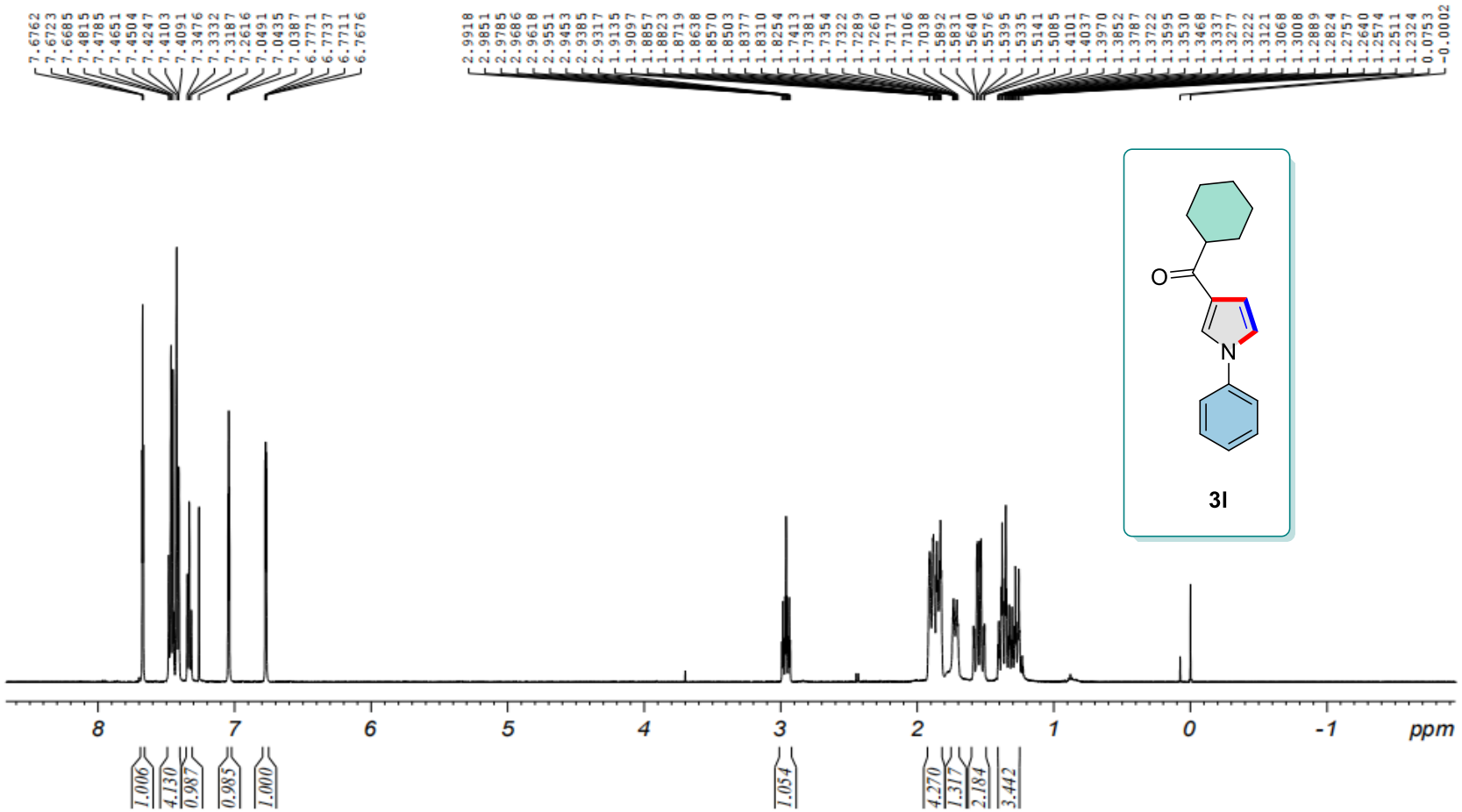


Figure S69. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3l**

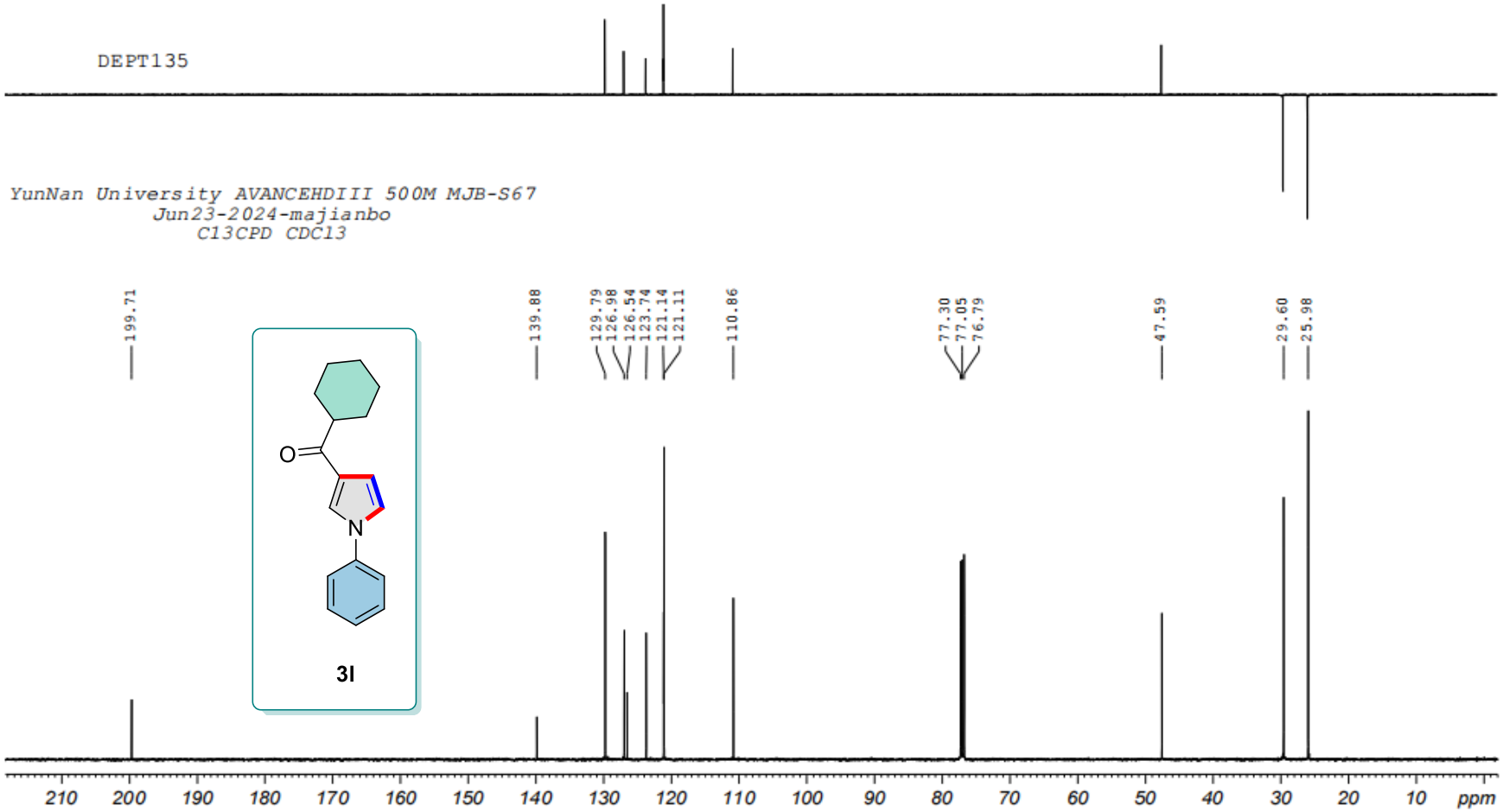


Figure S70. ^{13}F NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3l**

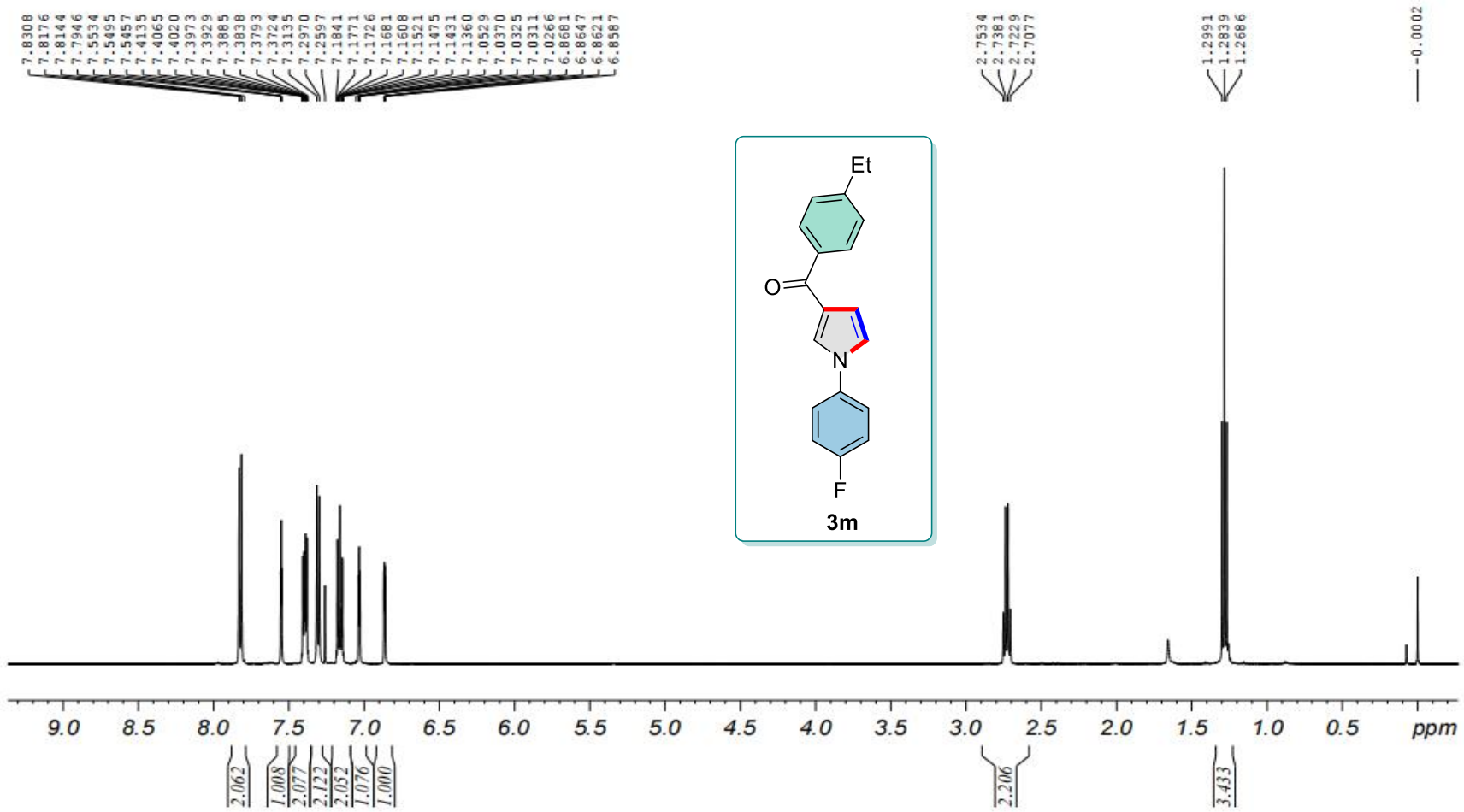


Figure S71. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3m**

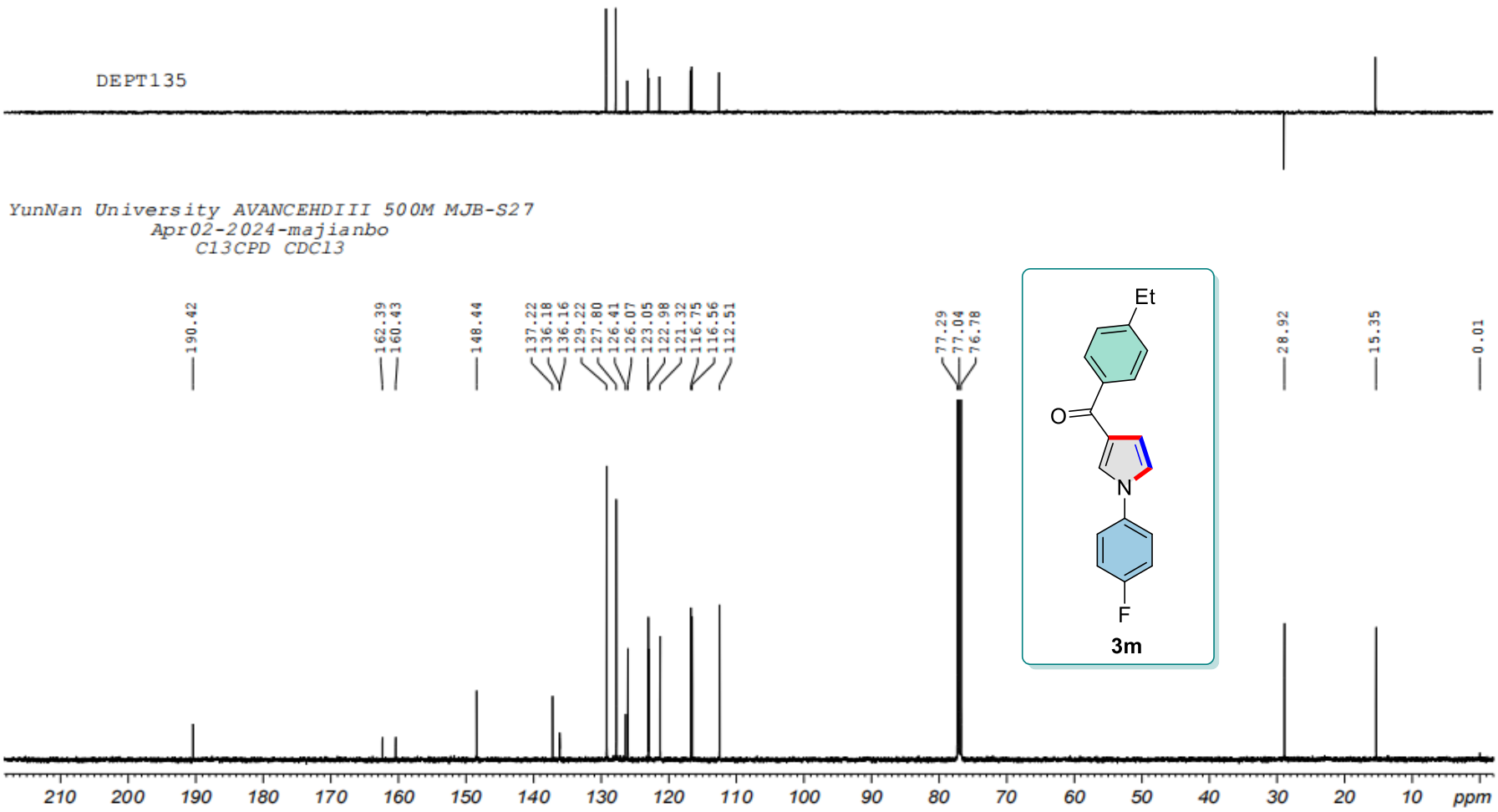


Figure S72. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3m**

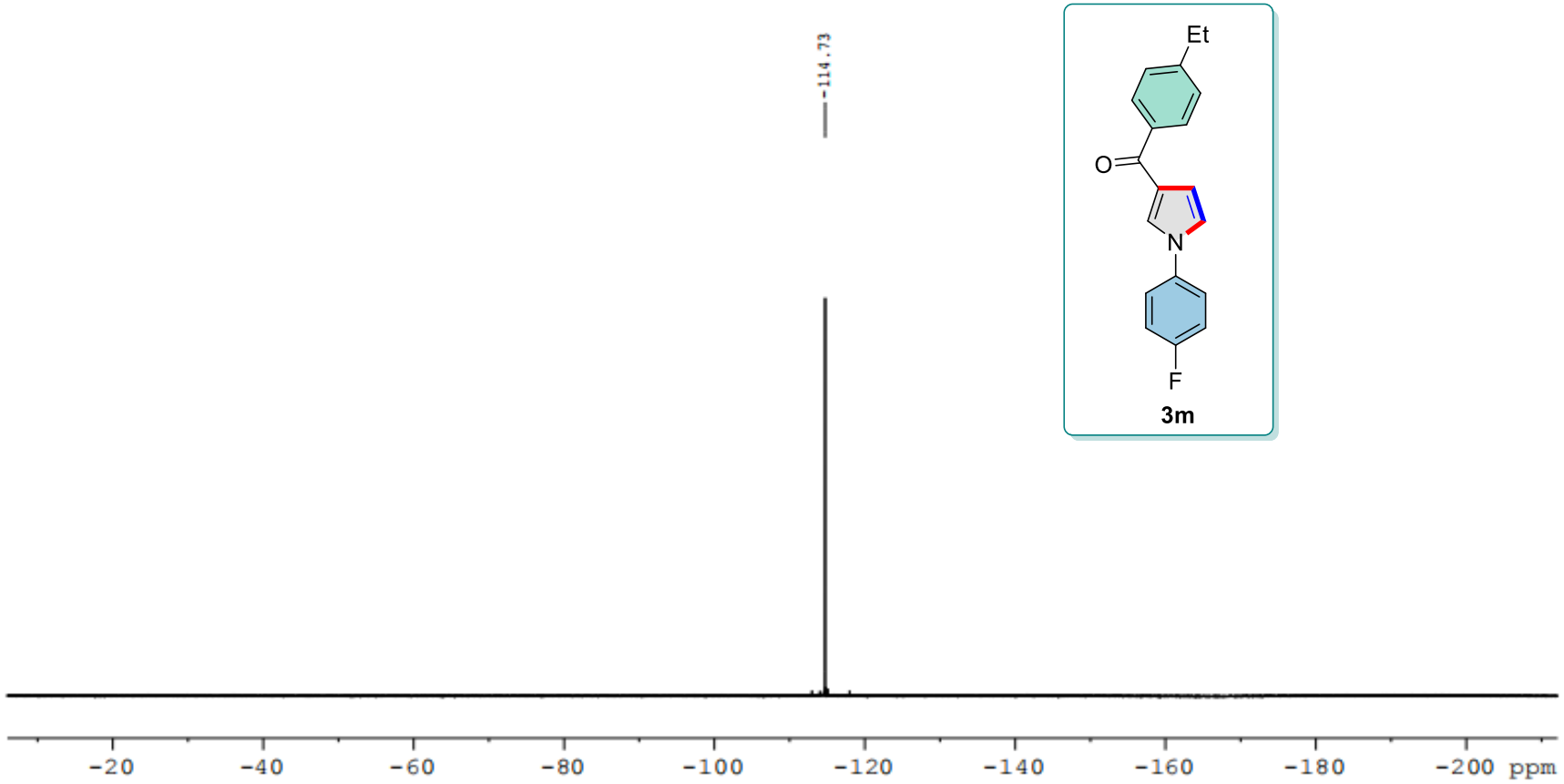


Figure S73. ^{19}F NMR (470 MHz, $CDCl_3$-d_1) spectra of compound **3m**

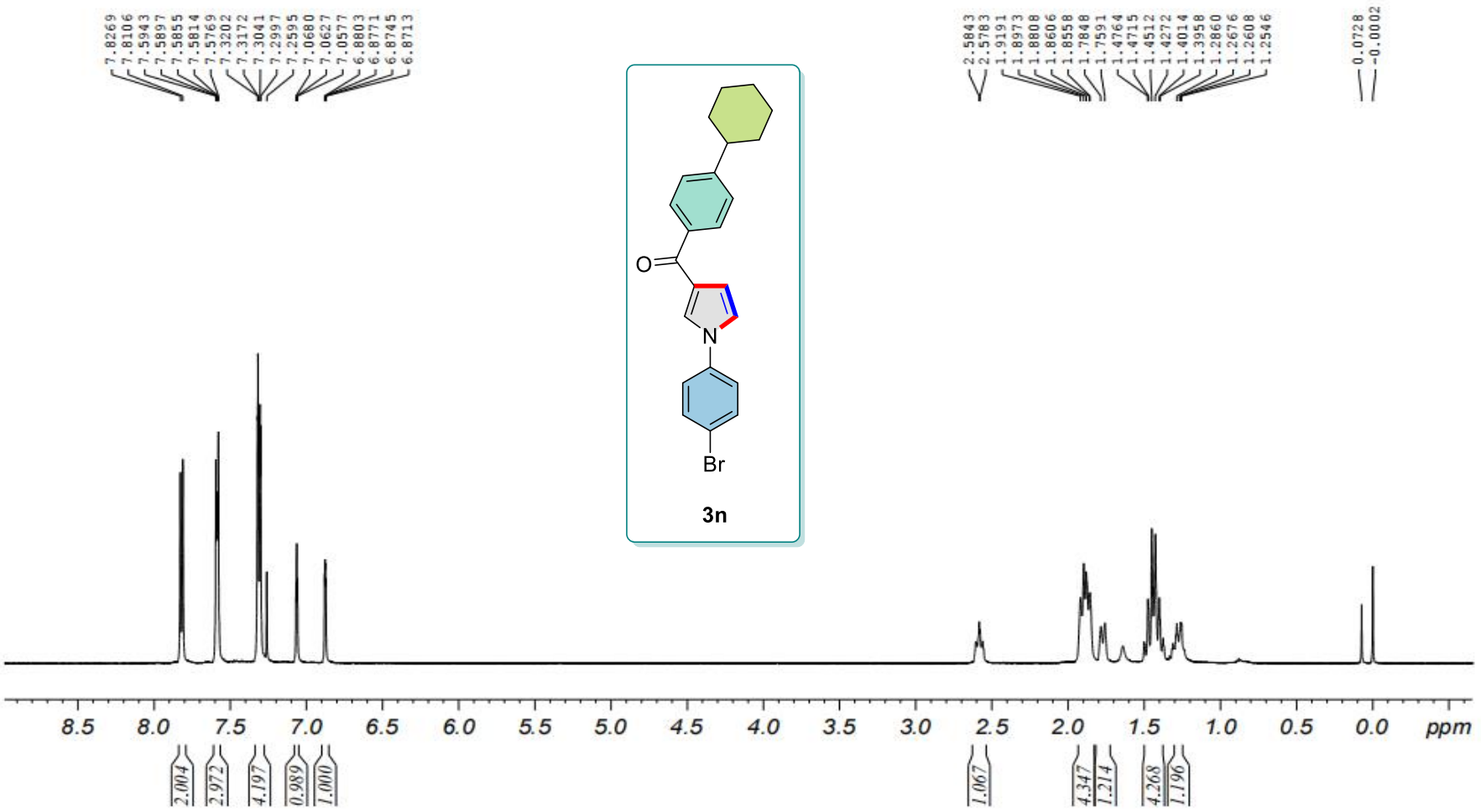


Figure S74. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3n**

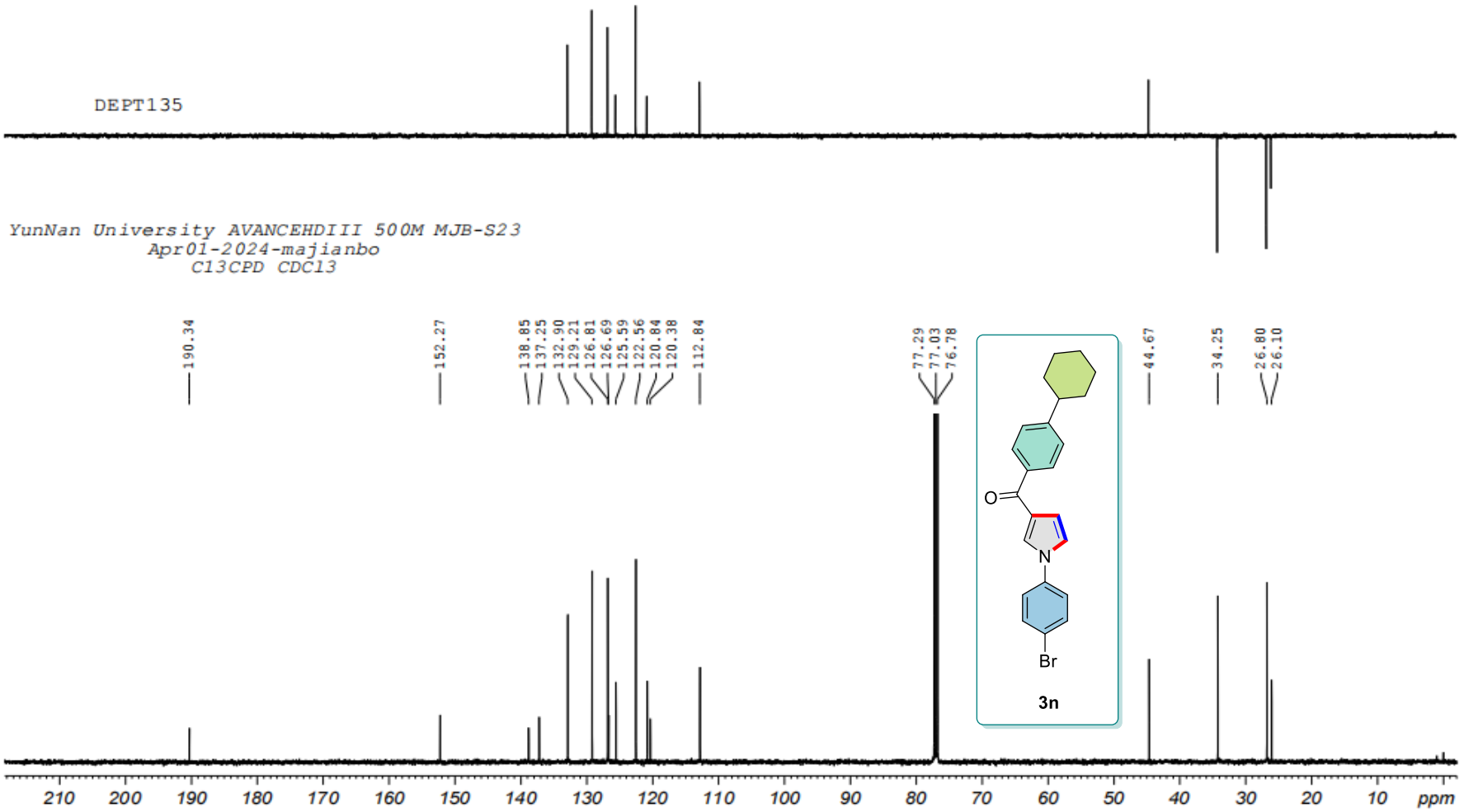


Figure S75. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3n**

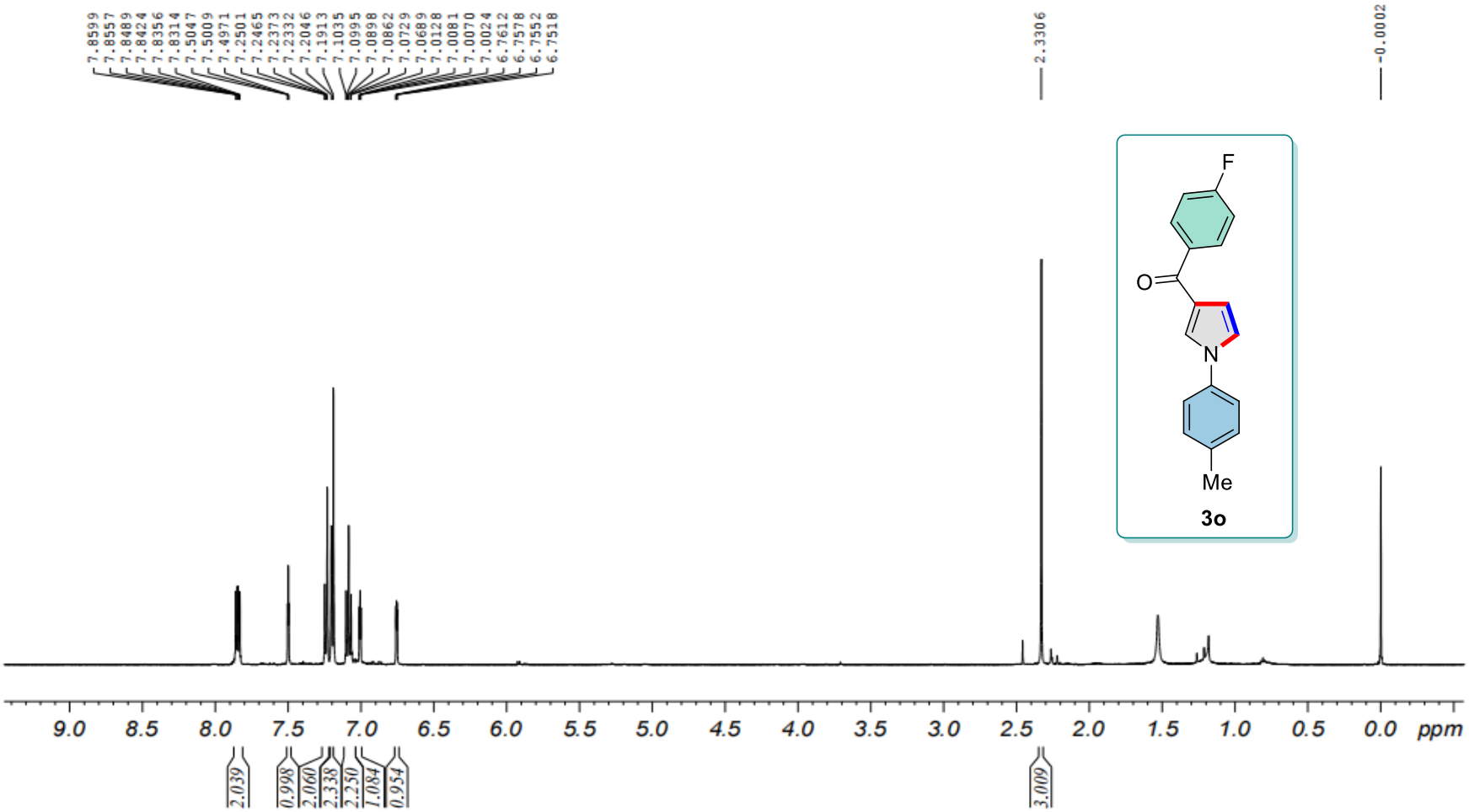


Figure S76. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3o**

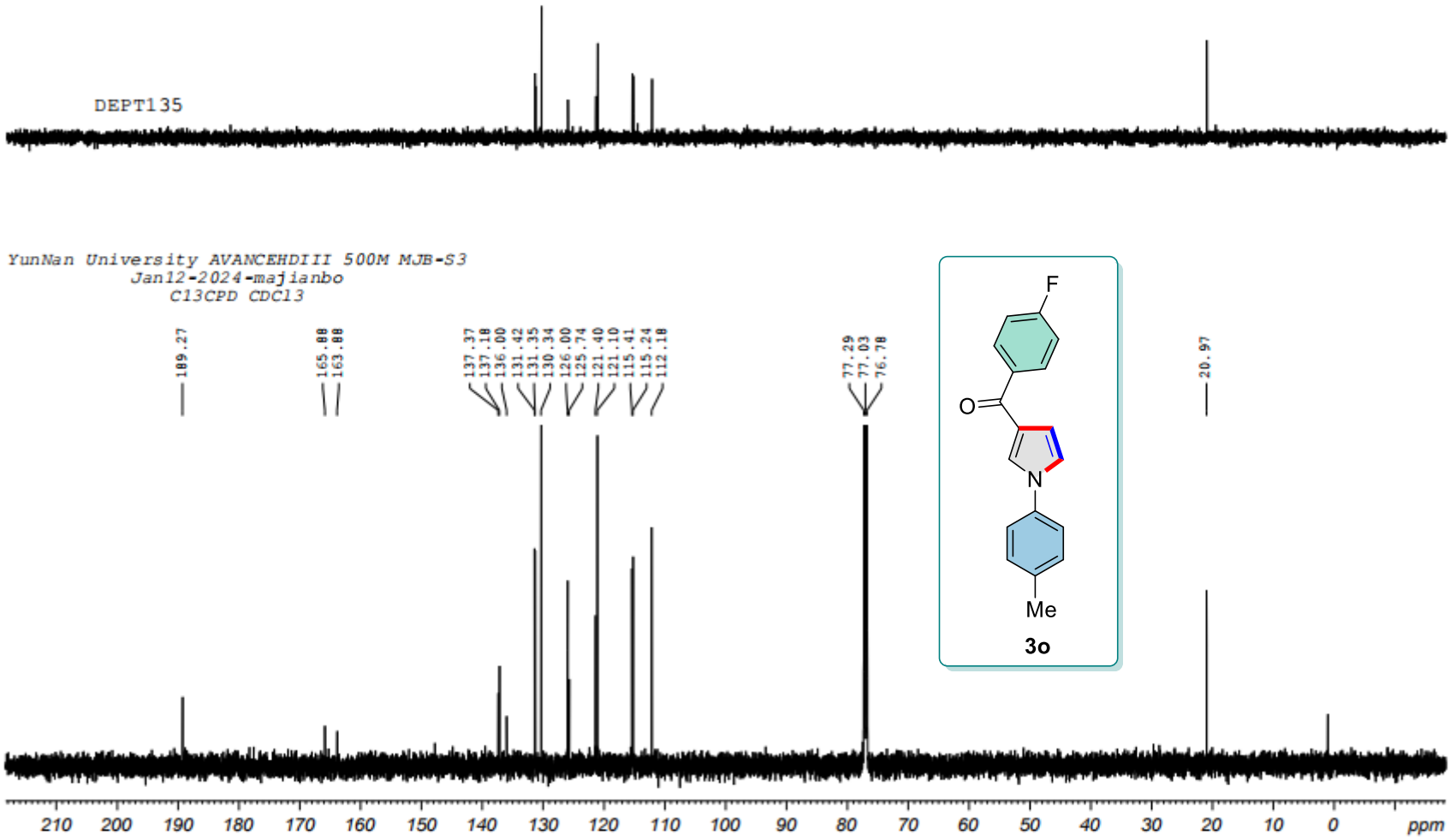


Figure S77. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3o**

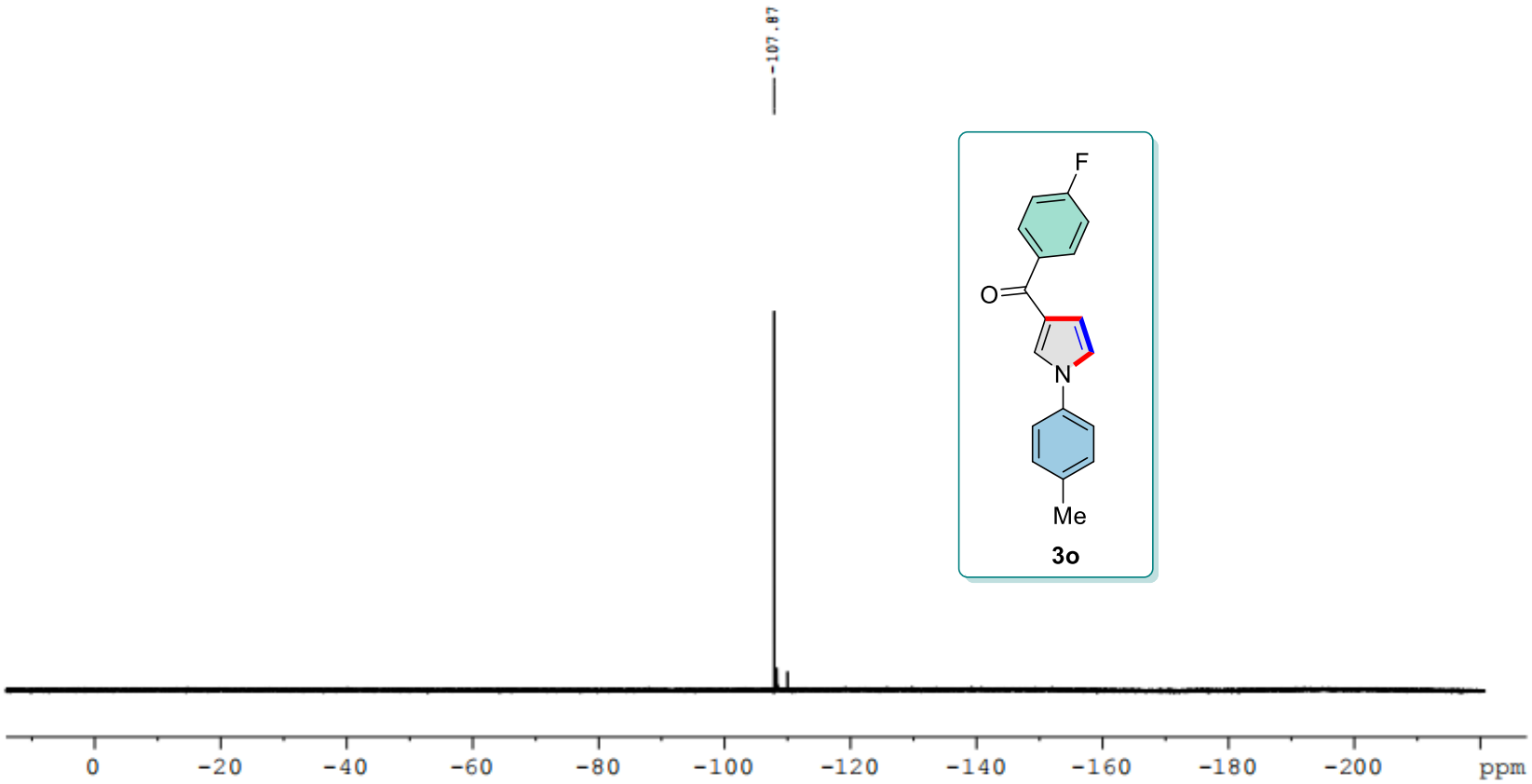


Figure S78. ^{19}F NMR (470 MHz, $CDCl_3$-d_1) spectra of compound **3o**

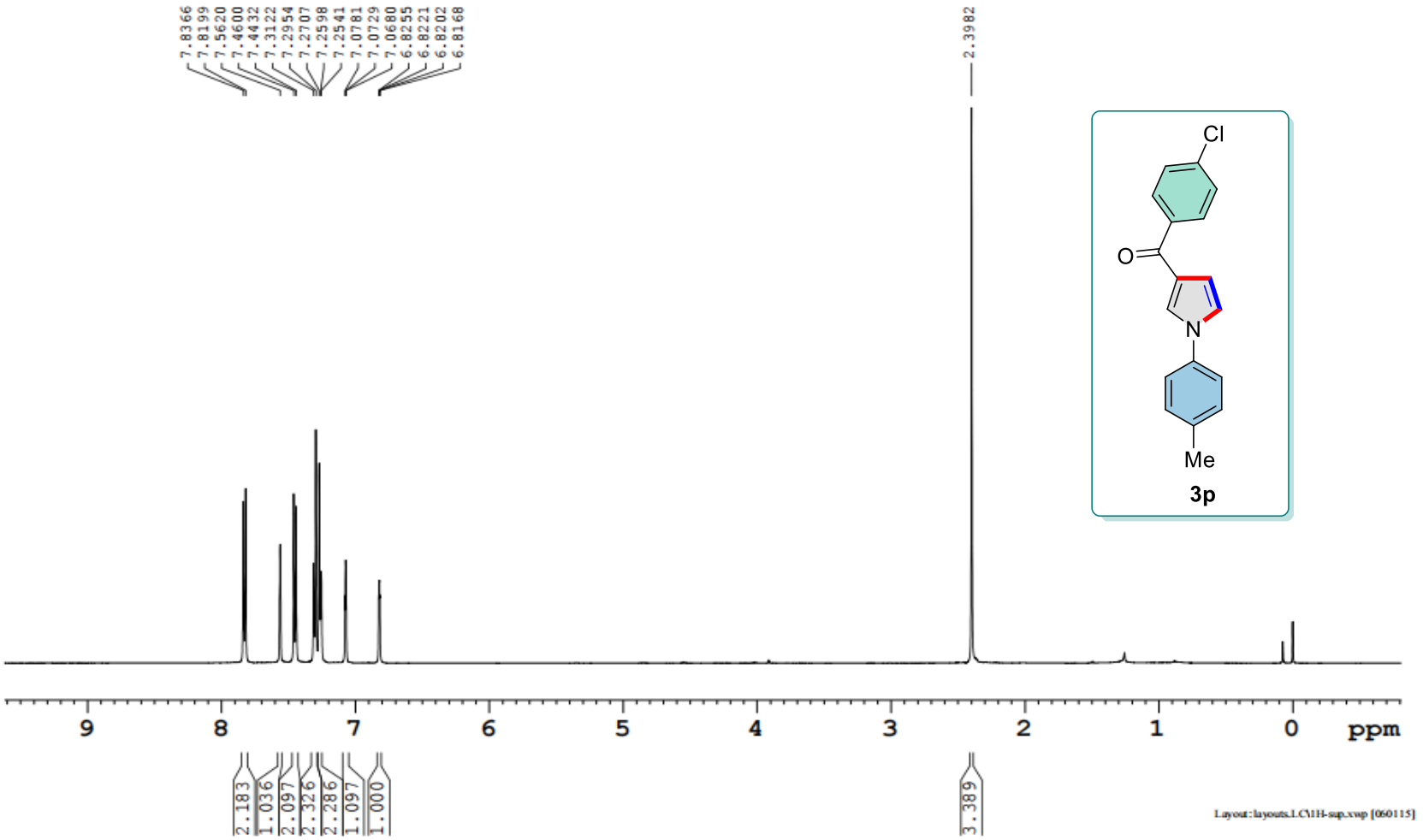


Figure S79. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3p**

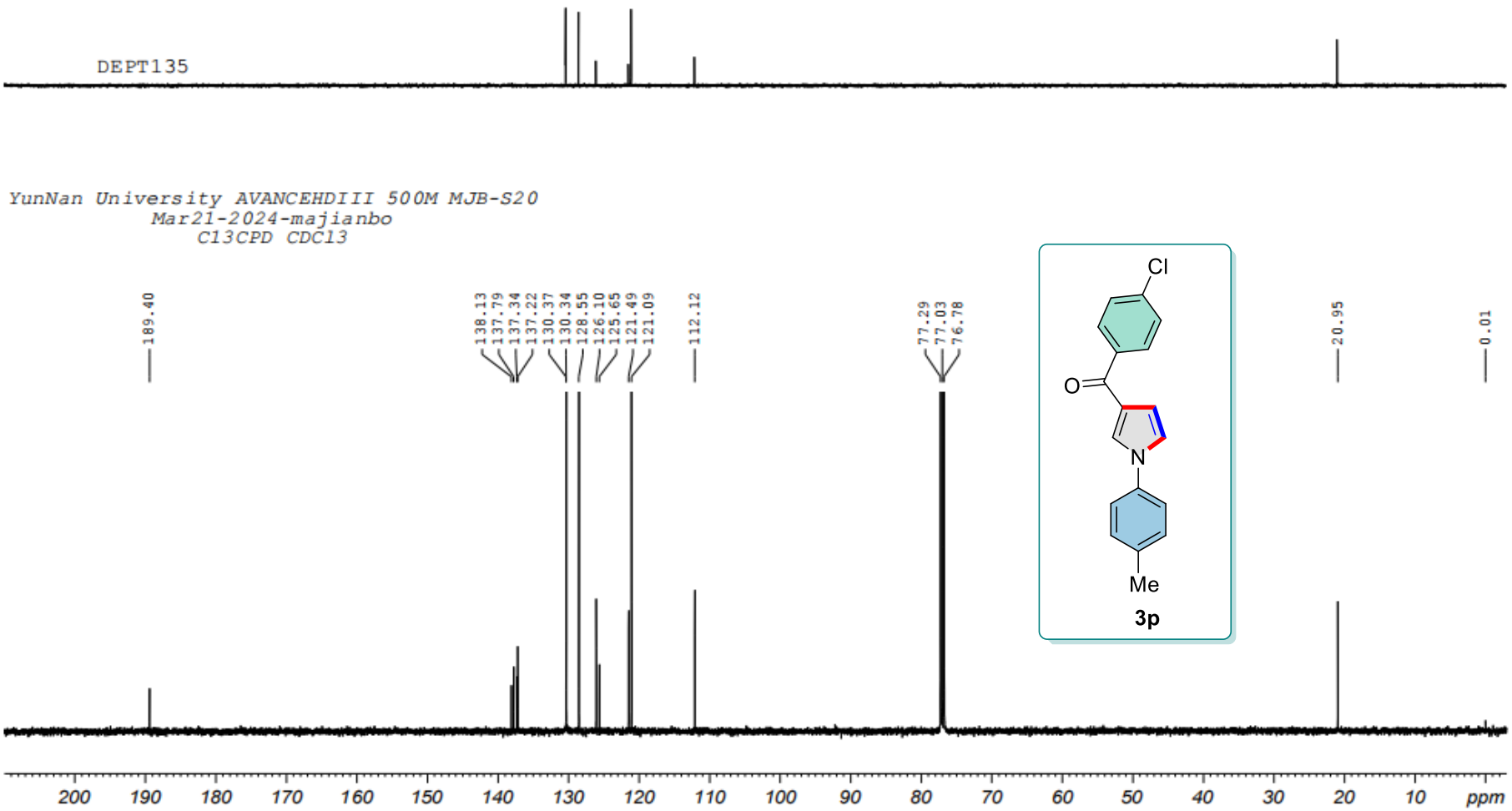


Figure S80. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3p**

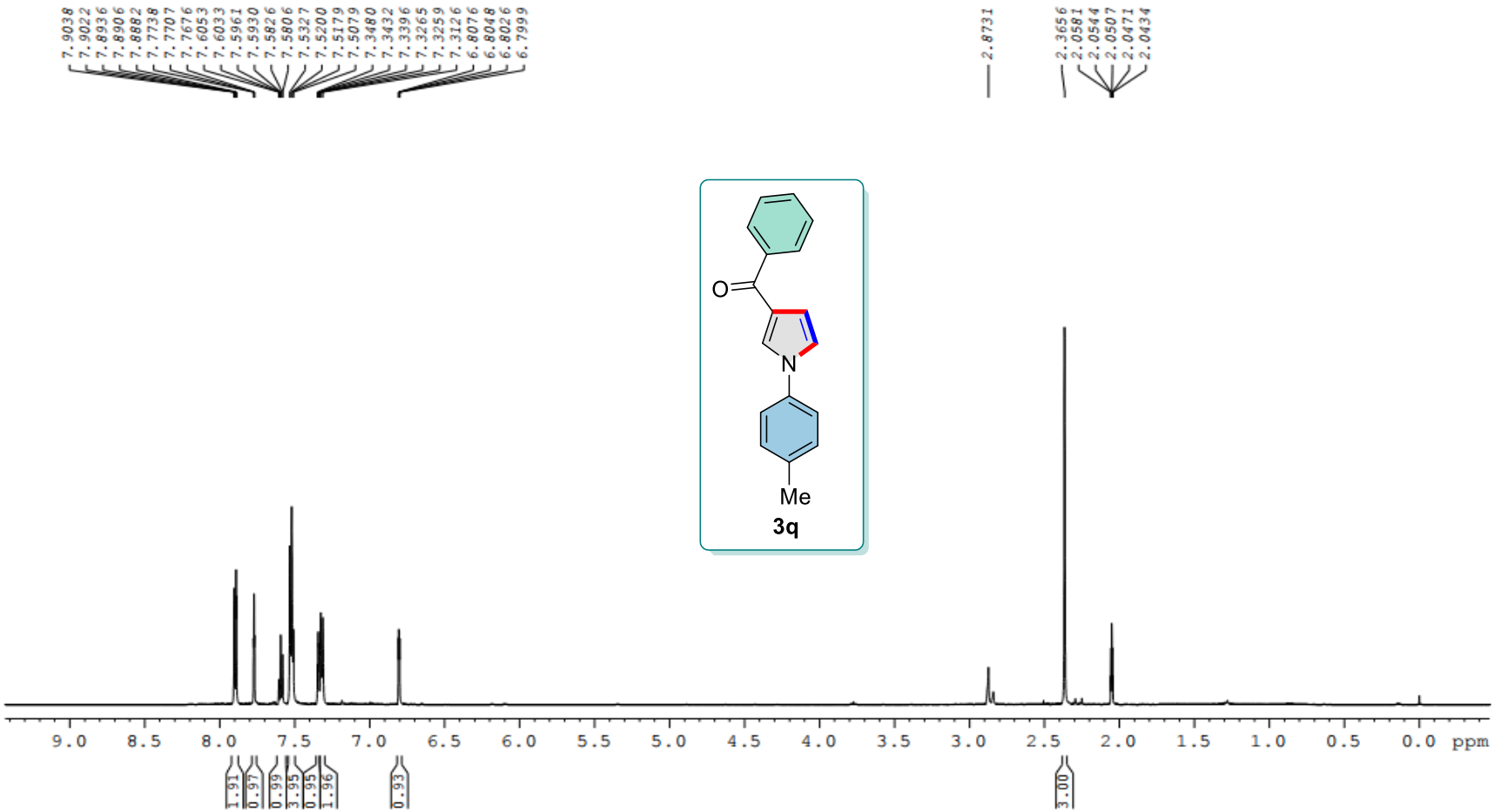


Figure S81. ^{1}H NMR (600 MHz, Acetone-d_6) spectra of compound **3q**

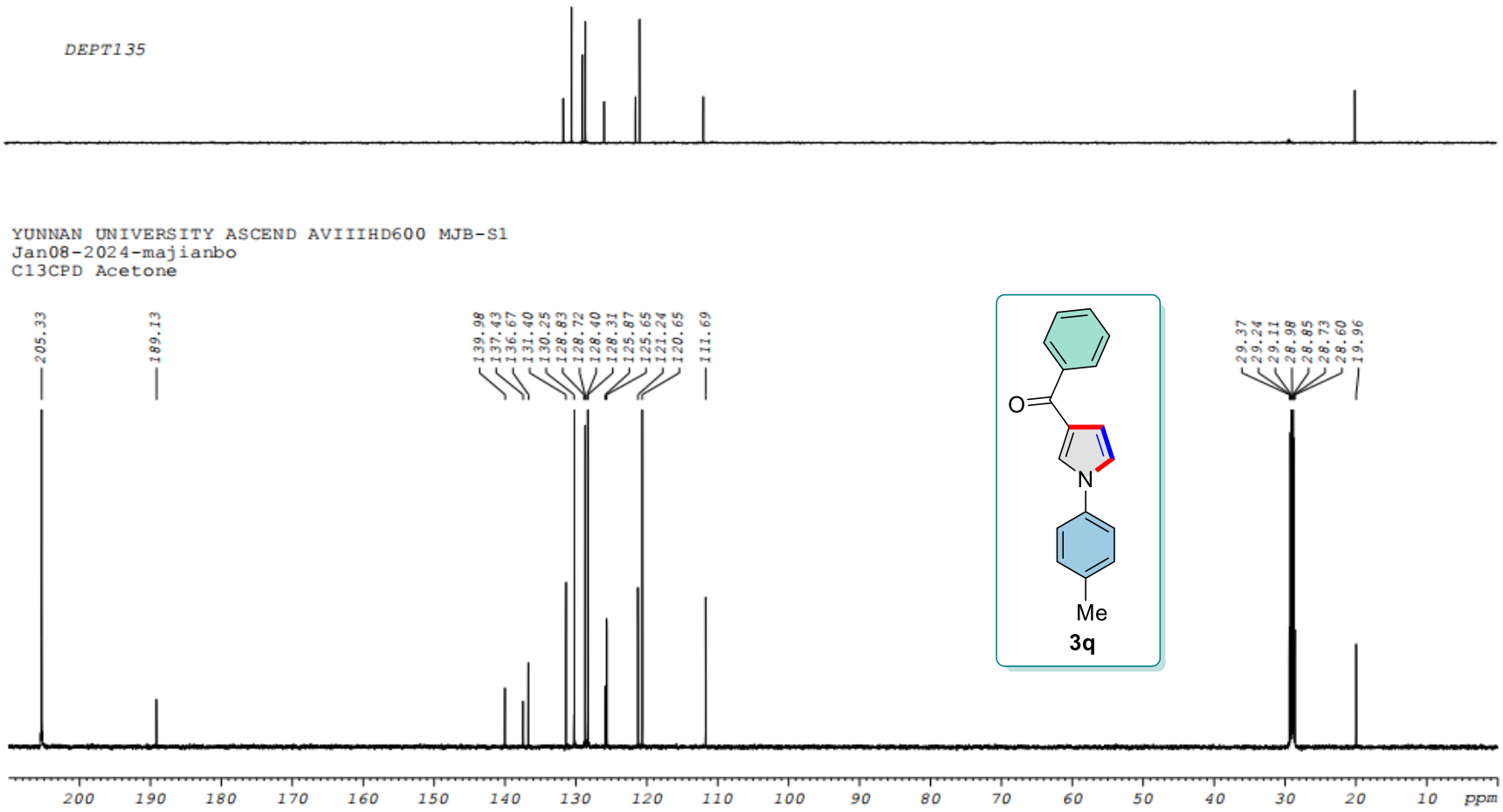


Figure S82. ^{13}C NMR (150 MHz, Acetone-d_6) spectra of compound **3q**

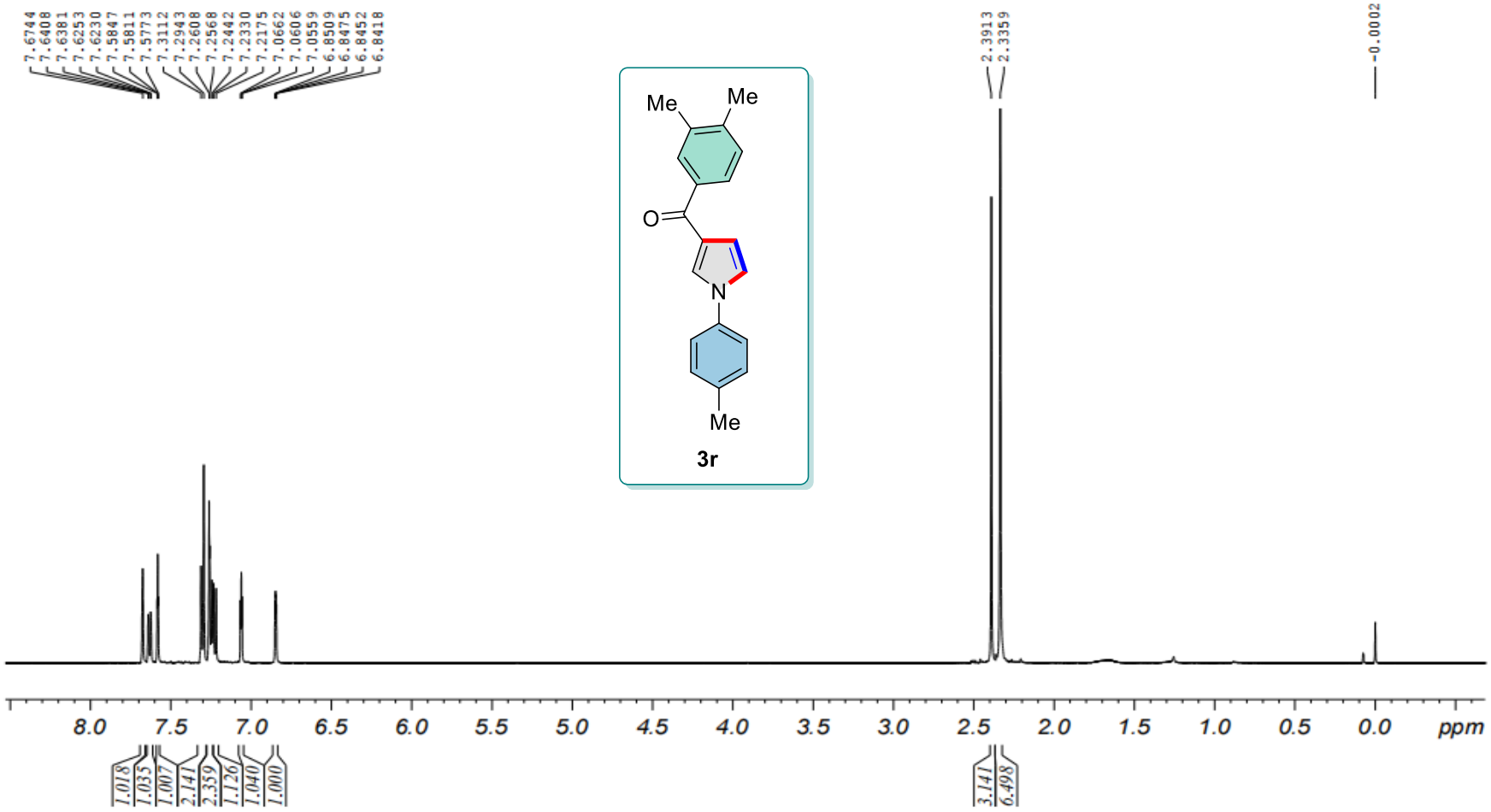


Figure S83. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3r**

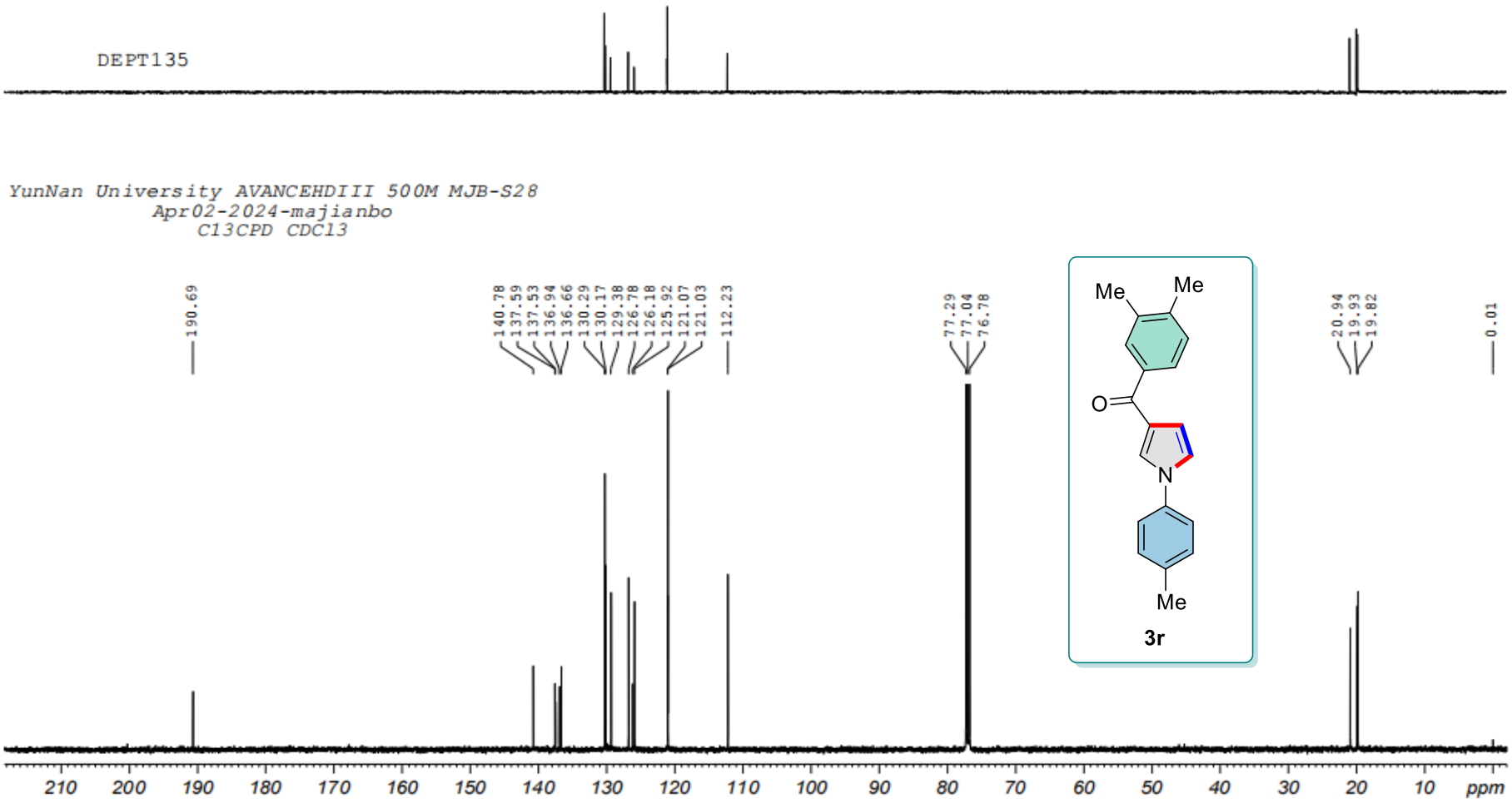


Figure S84. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3r**

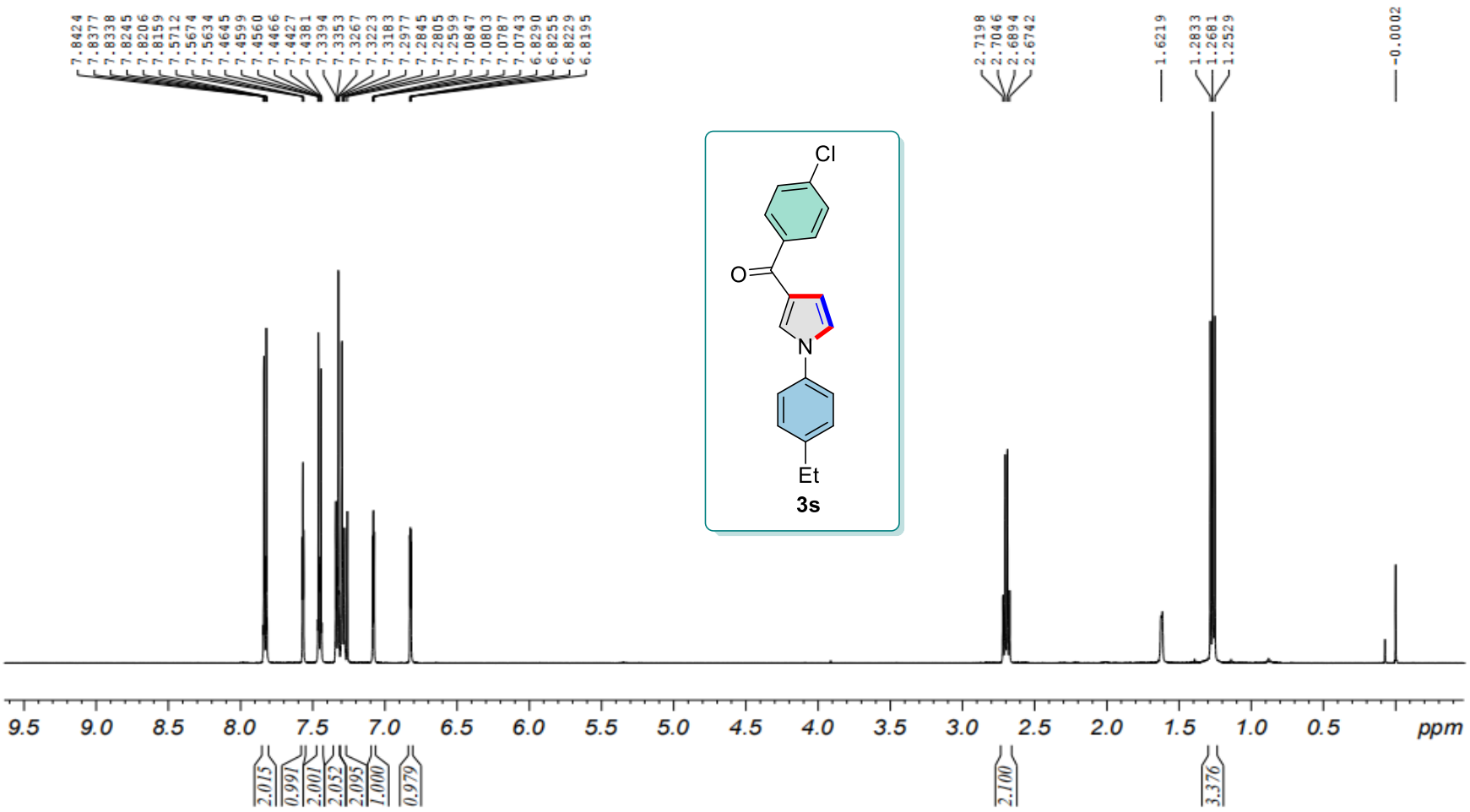


Figure S85. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3s**

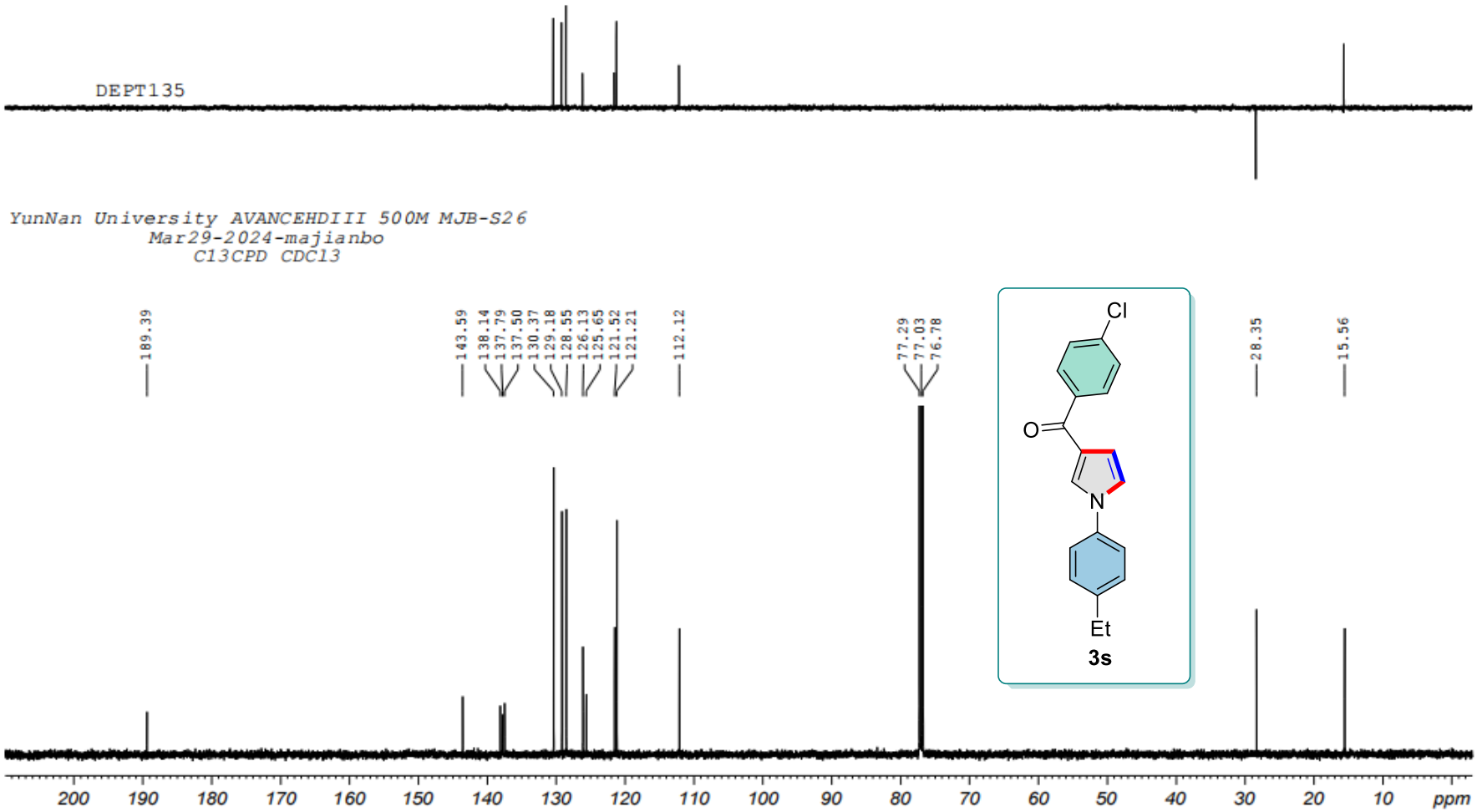


Figure S86. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3s**

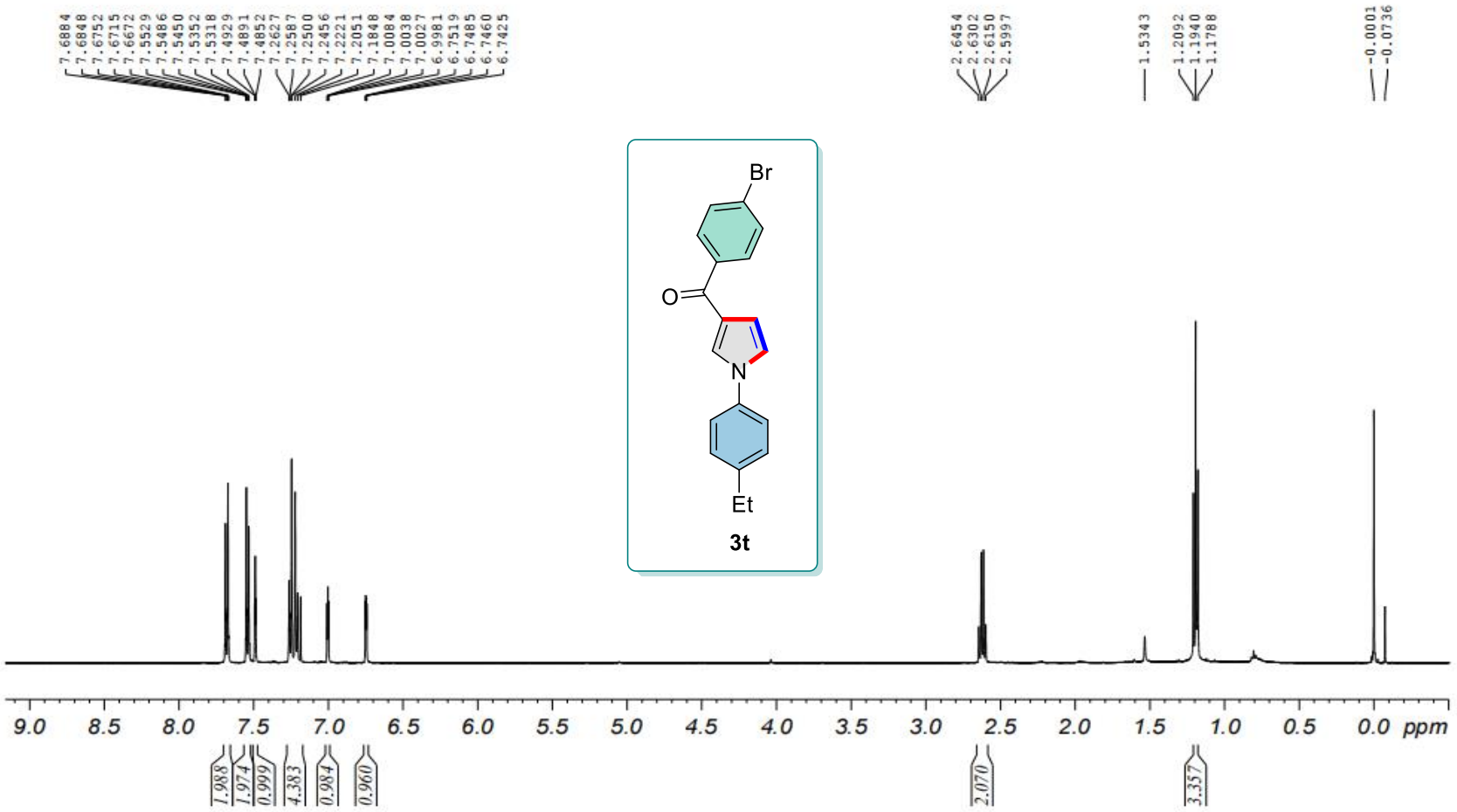


Figure S87. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3t**

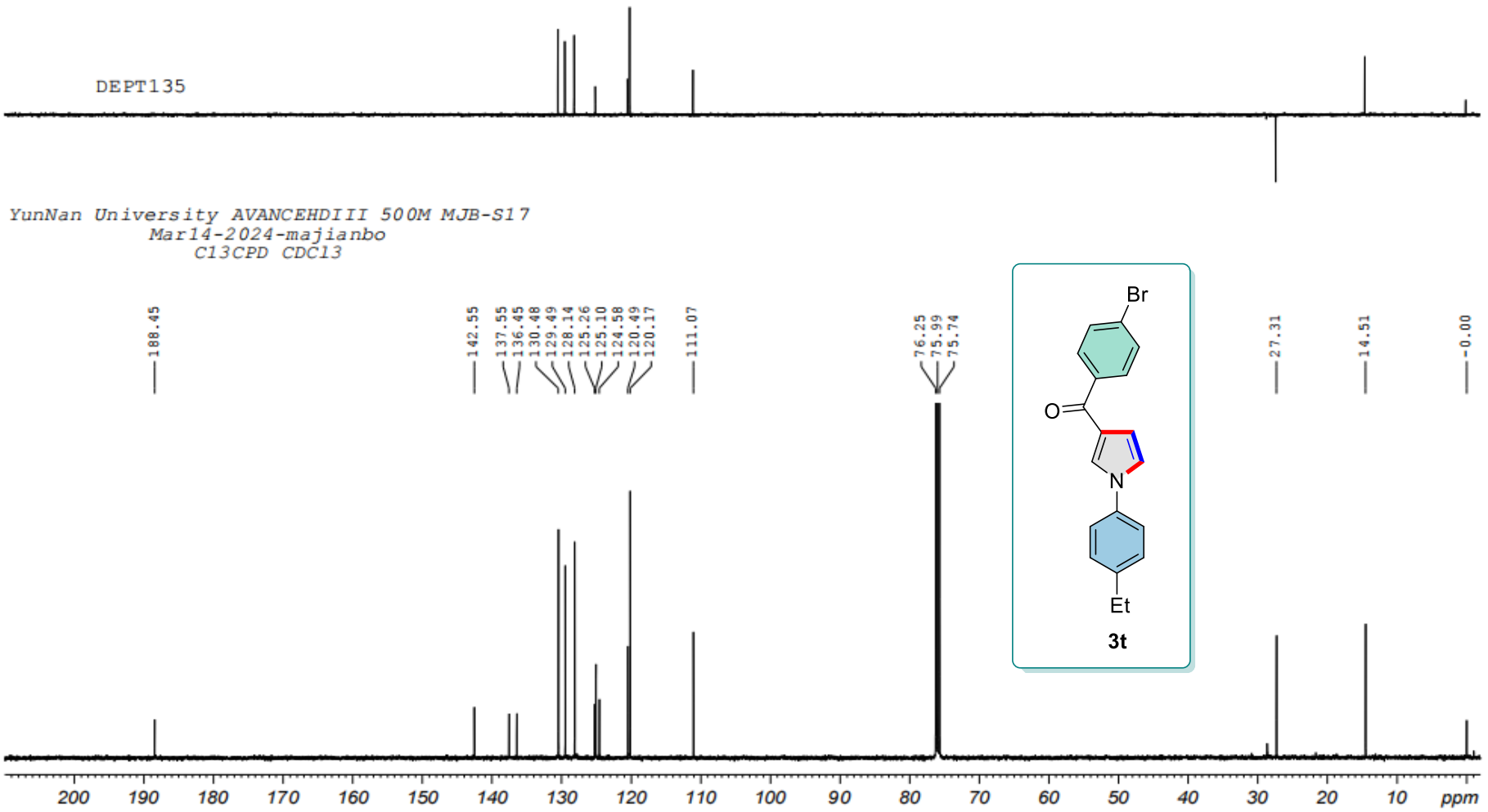


Figure S88. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3t**

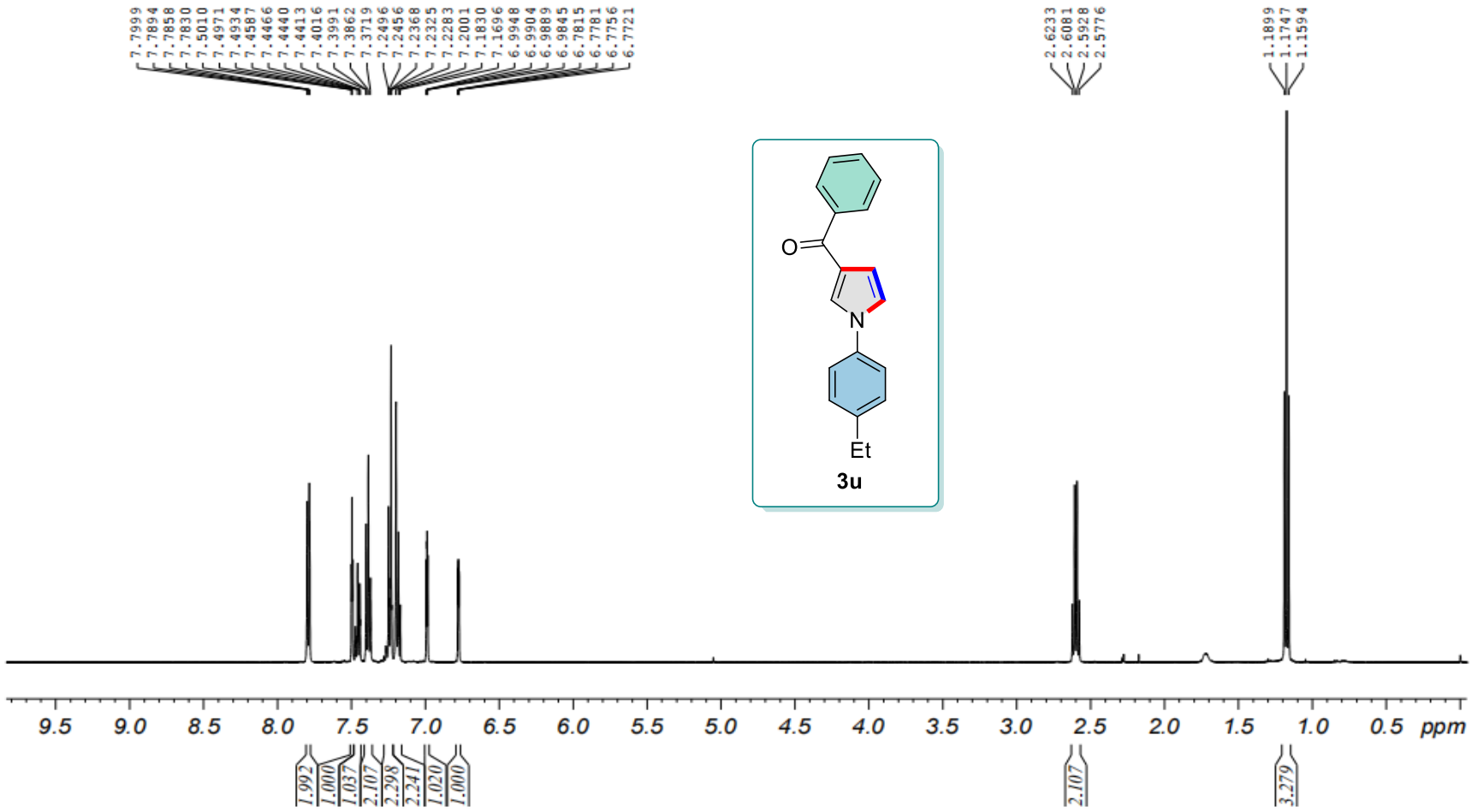


Figure S89. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3u**

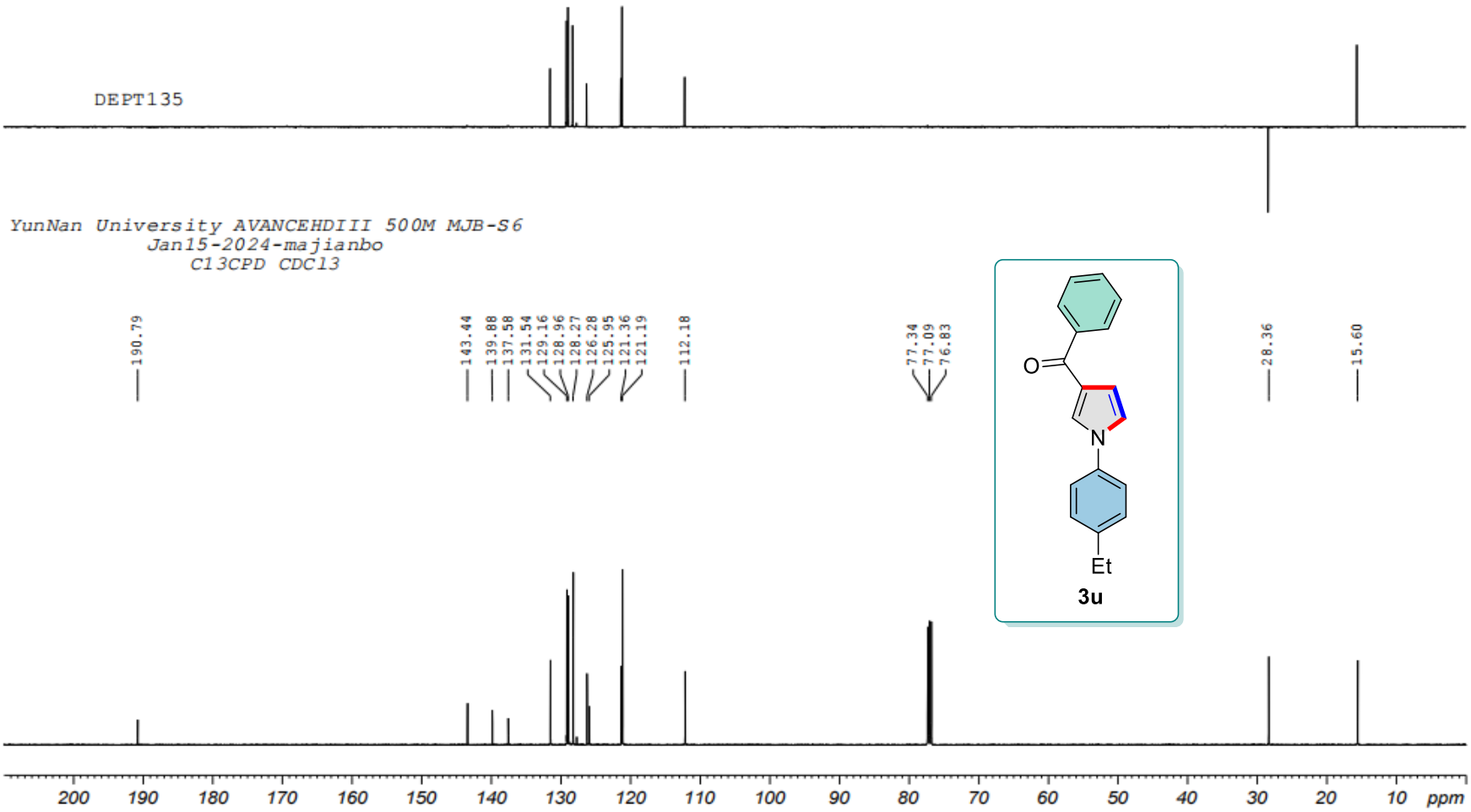


Figure S90. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3u**

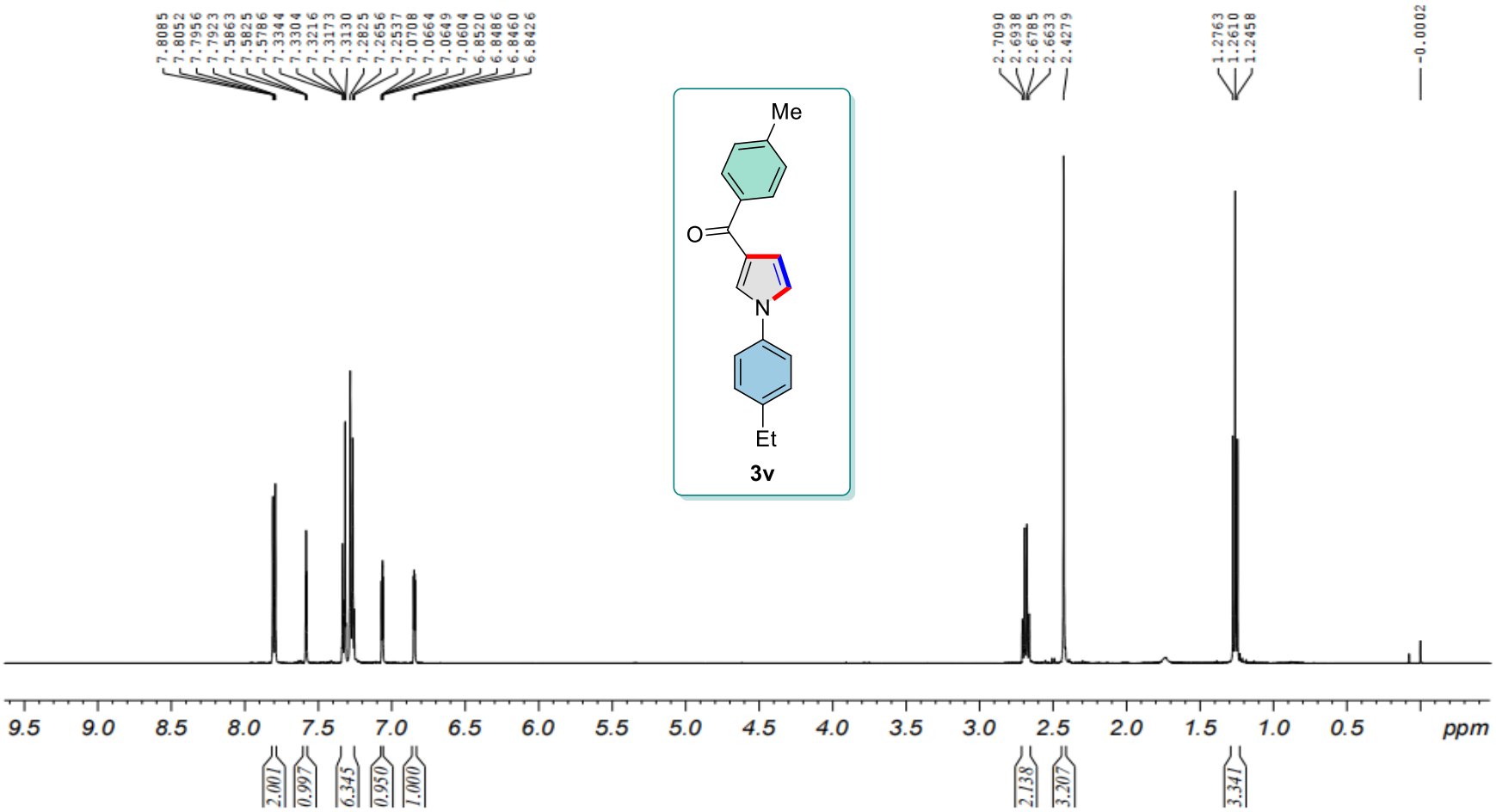


Figure S91. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3v**

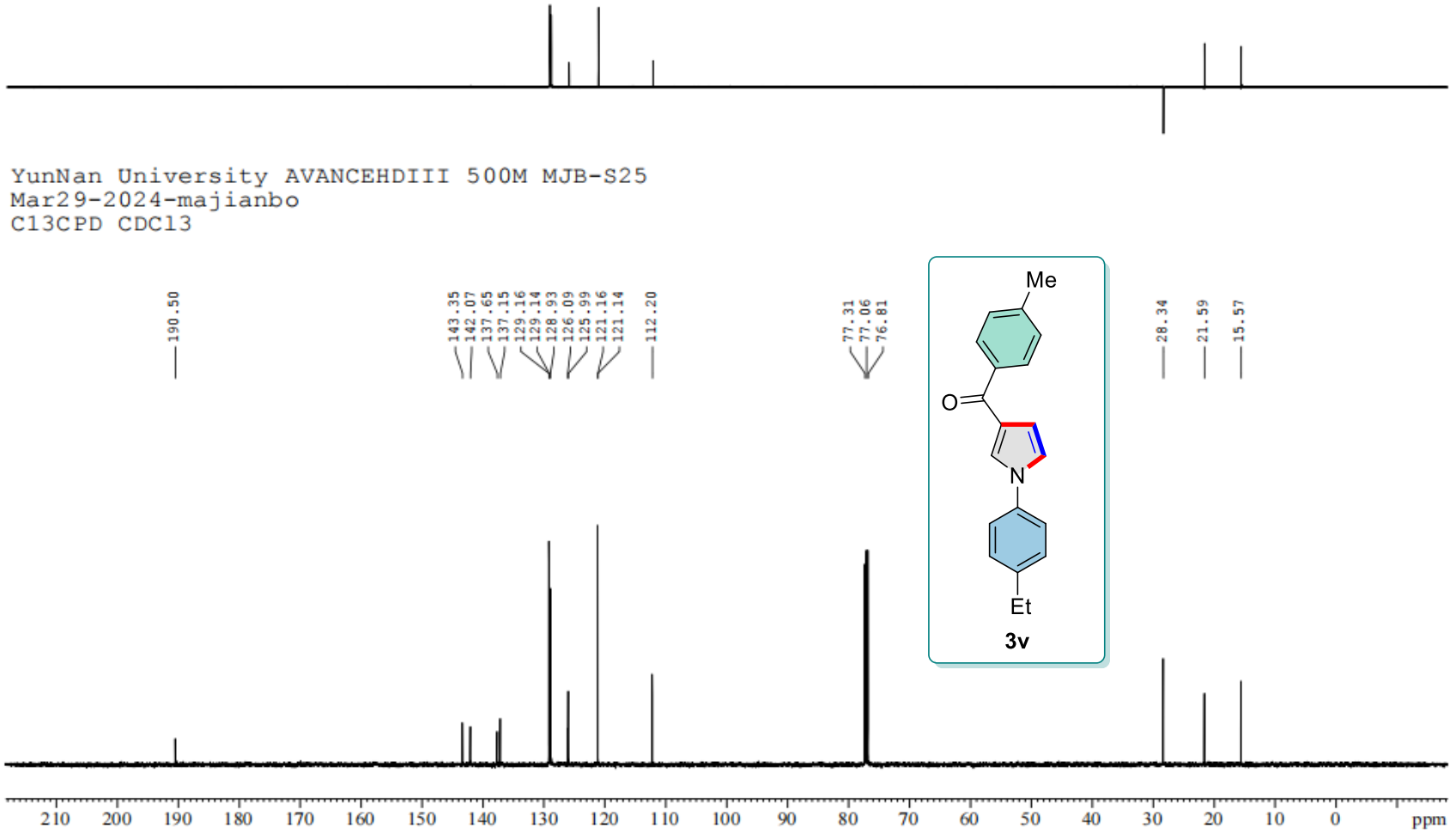


Figure S92. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3v**

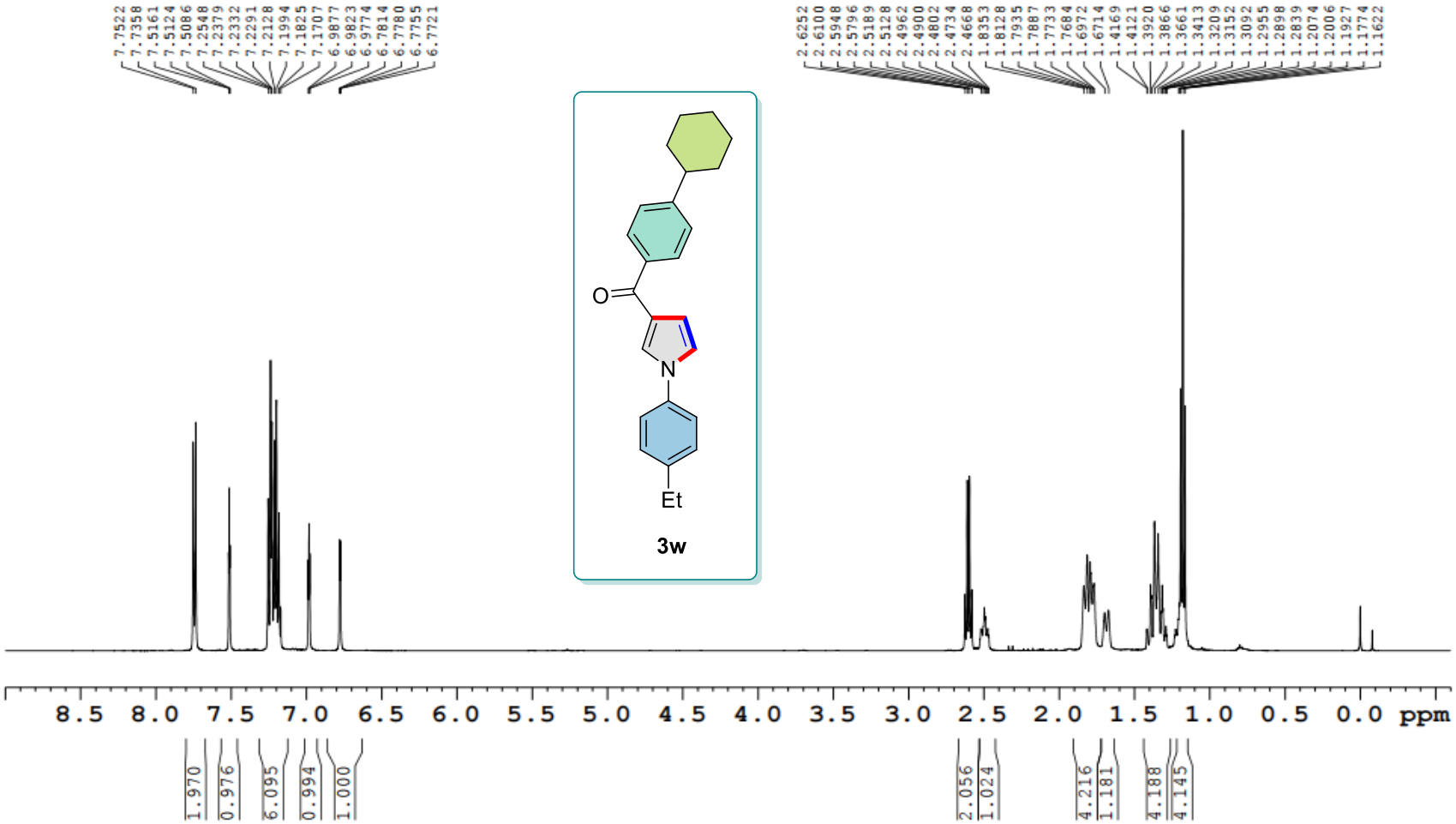


Figure S93. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3w**

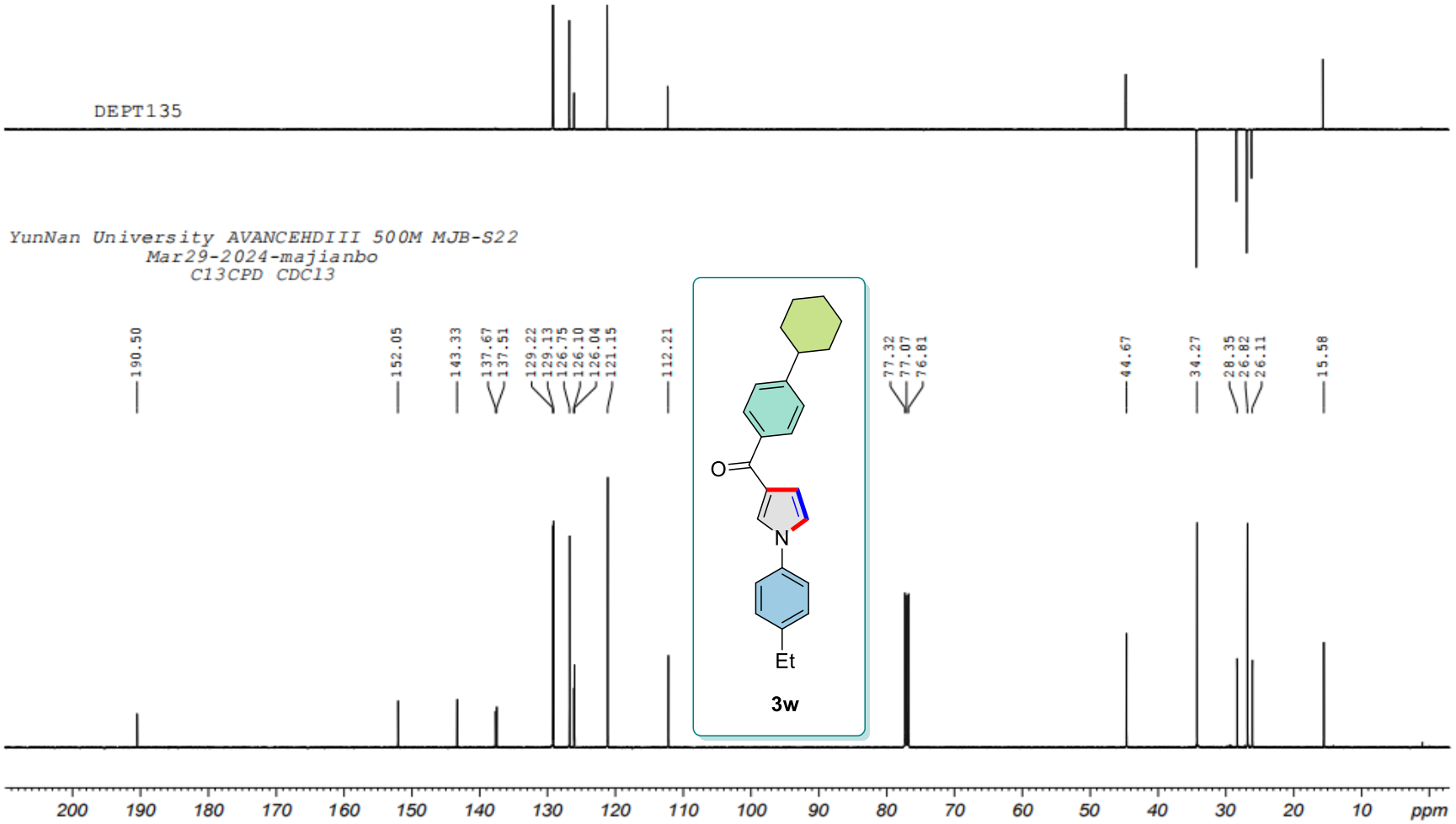


Figure S94. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3w**

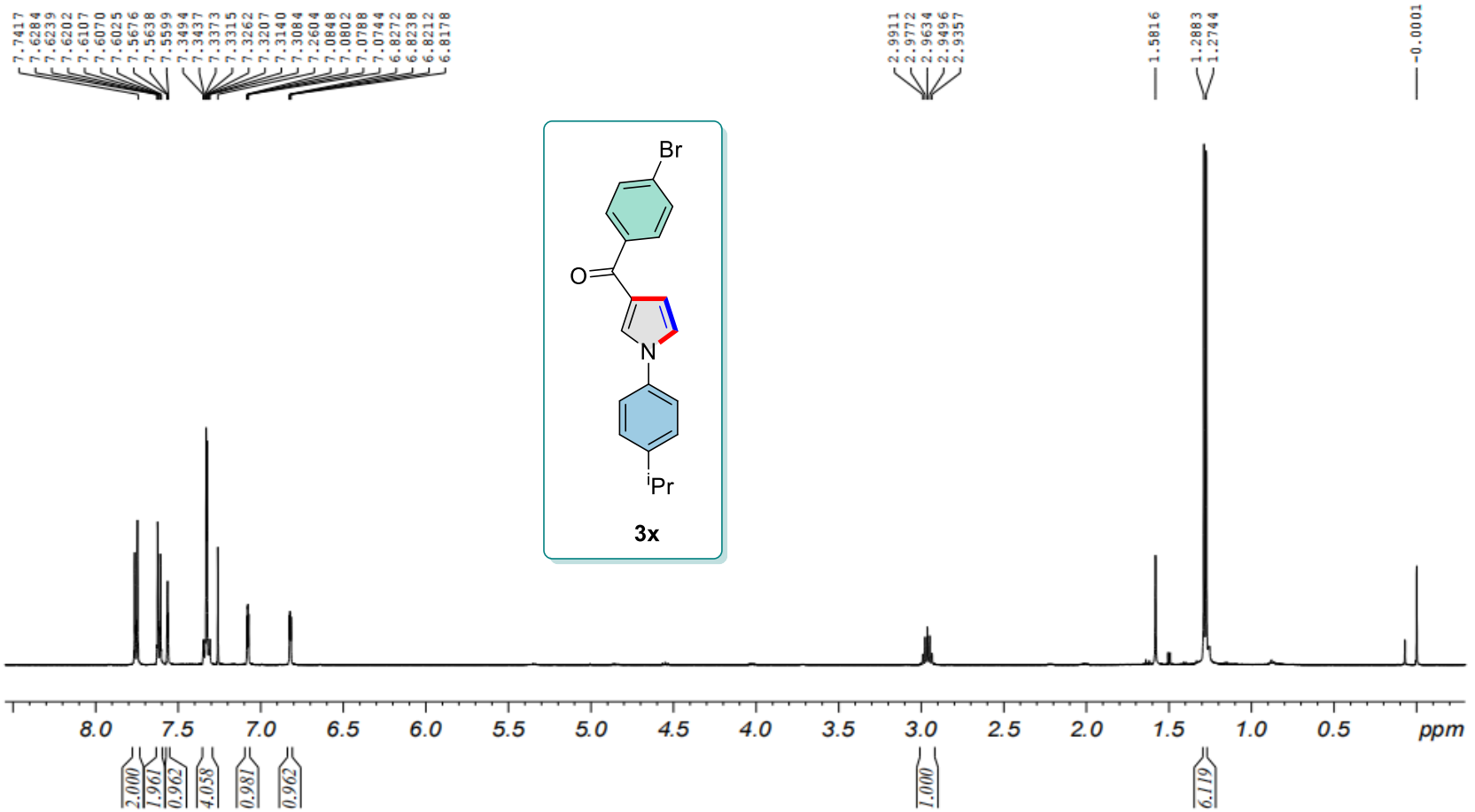


Figure S95. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3x**

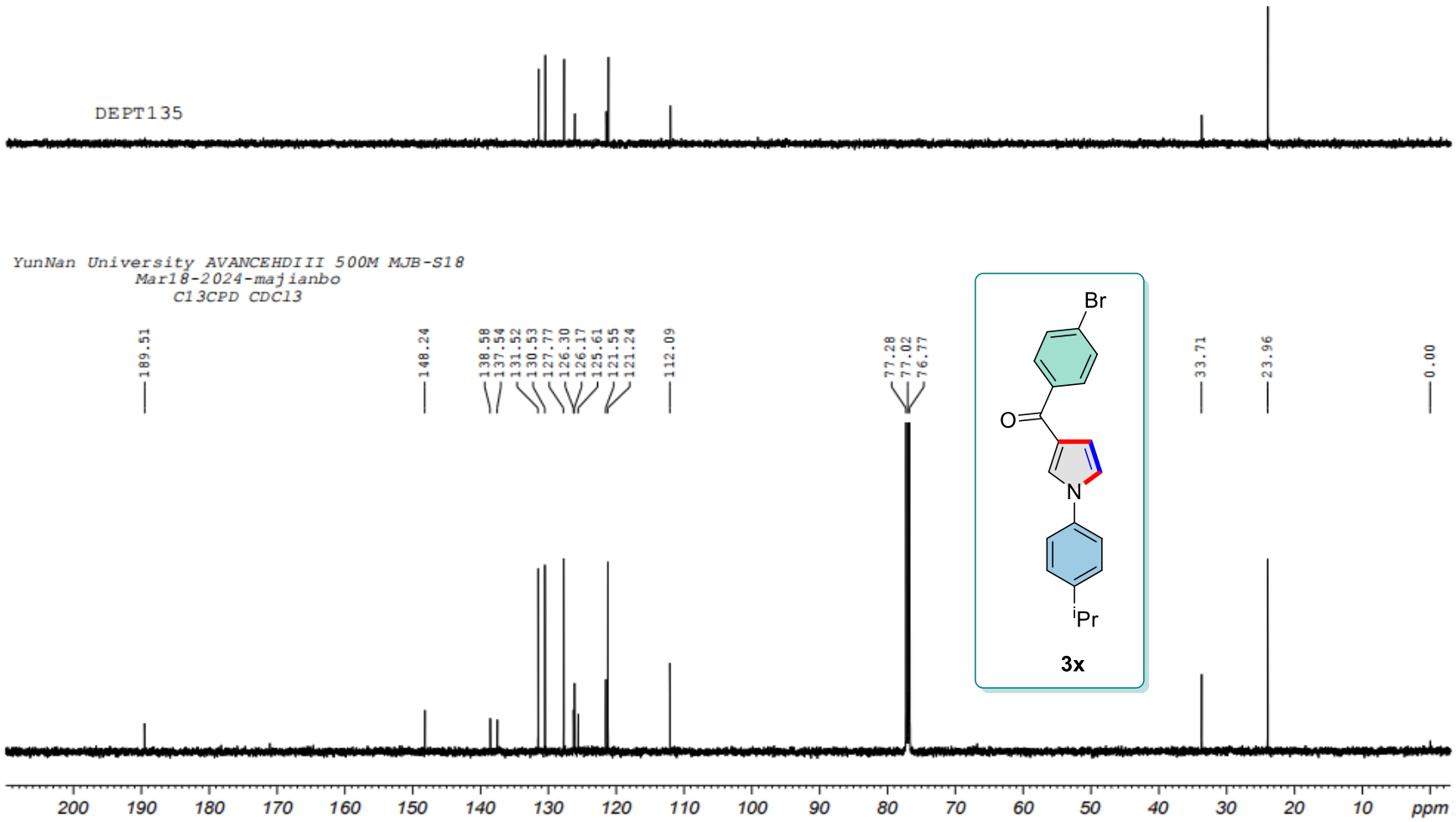


Figure S96. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3x**

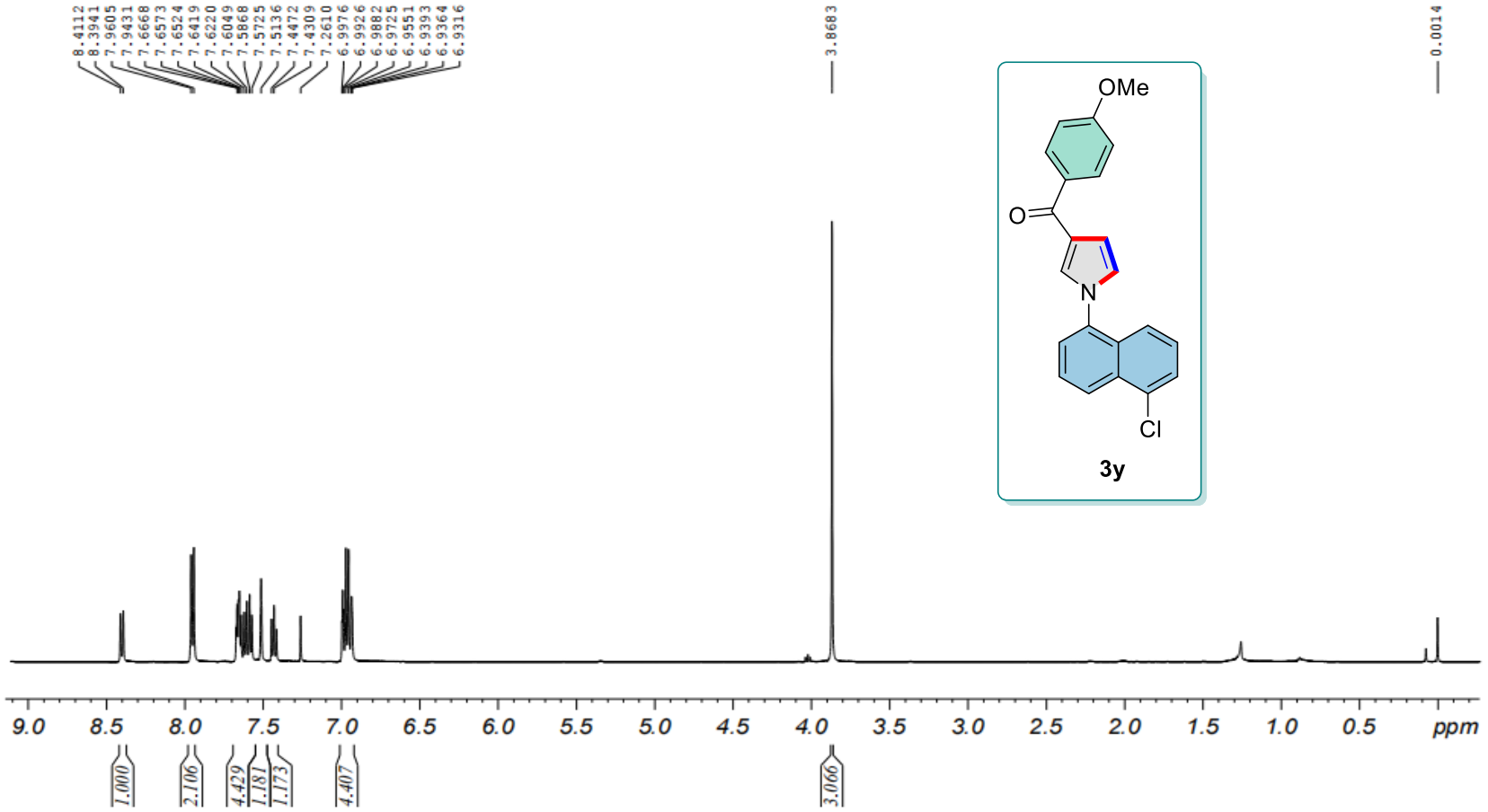


Figure S97. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3y**

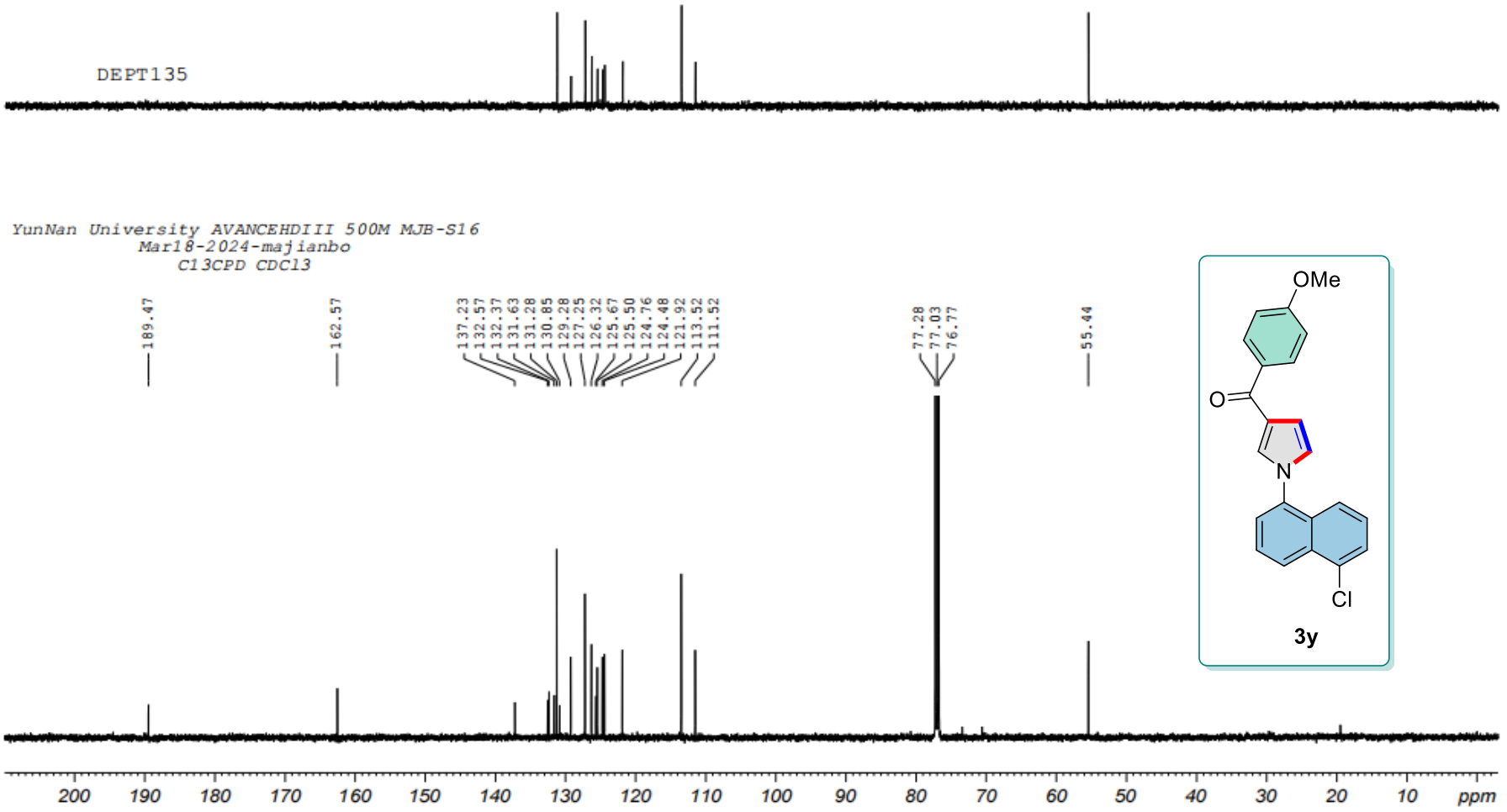


Figure S98. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3y**

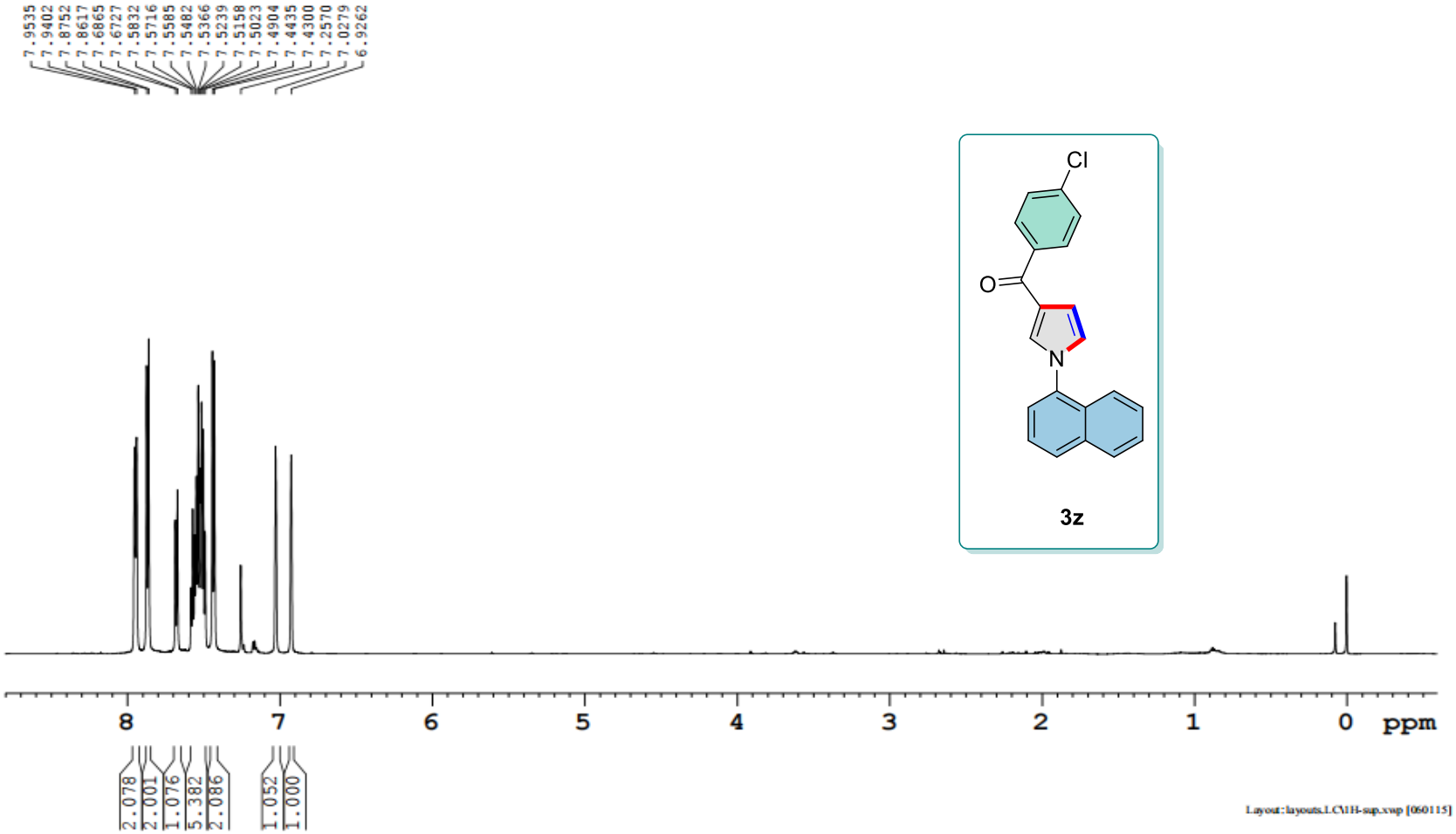


Figure S99. ^{1}H NMR (600 MHz, $CDCl_3$-d_1) spectra of compound **3z**

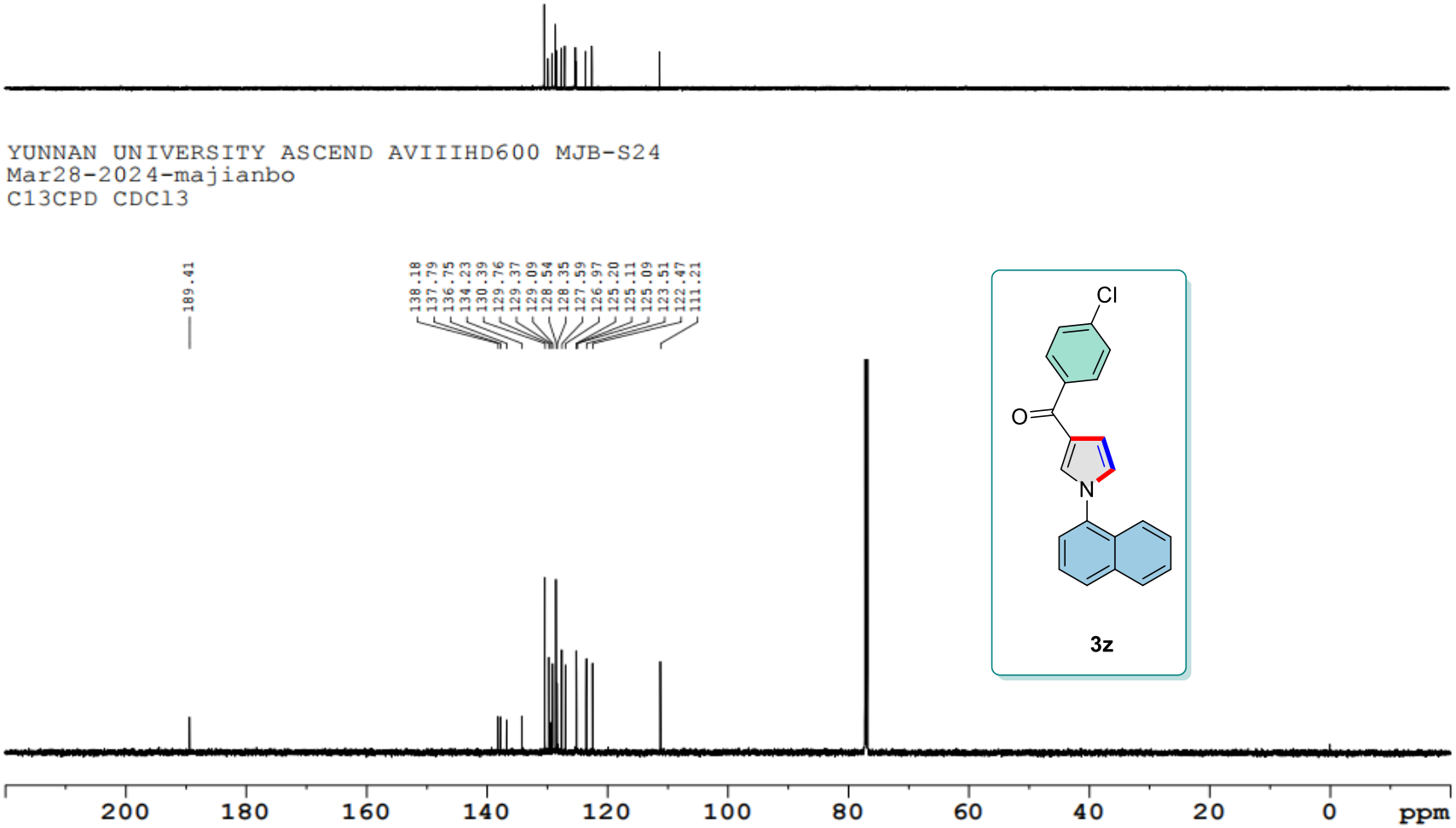


Figure S100. ^{13}C NMR (150 MHz, $CDCl_3$-d_1) spectra of compound **3z**

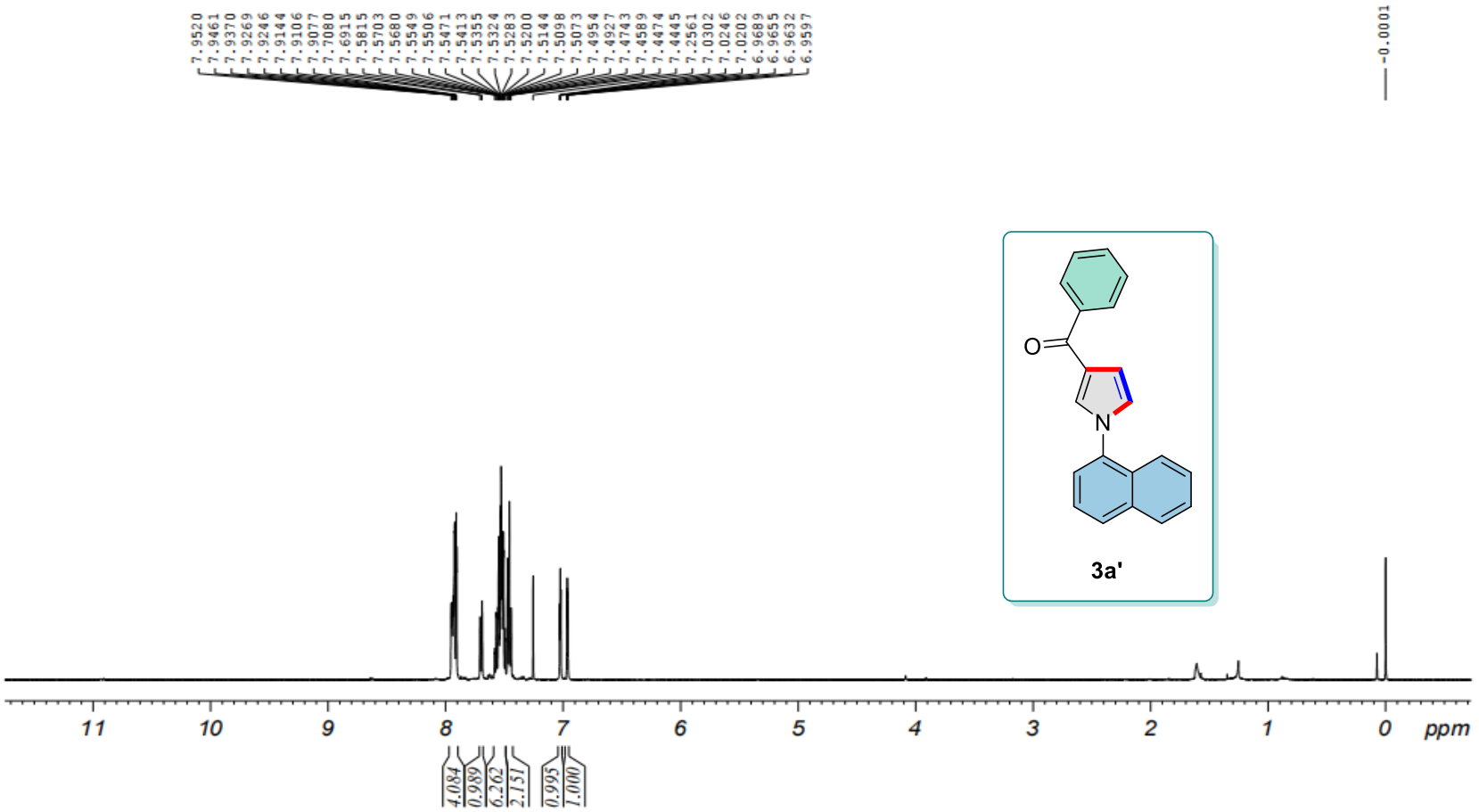


Figure S101. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3a'**

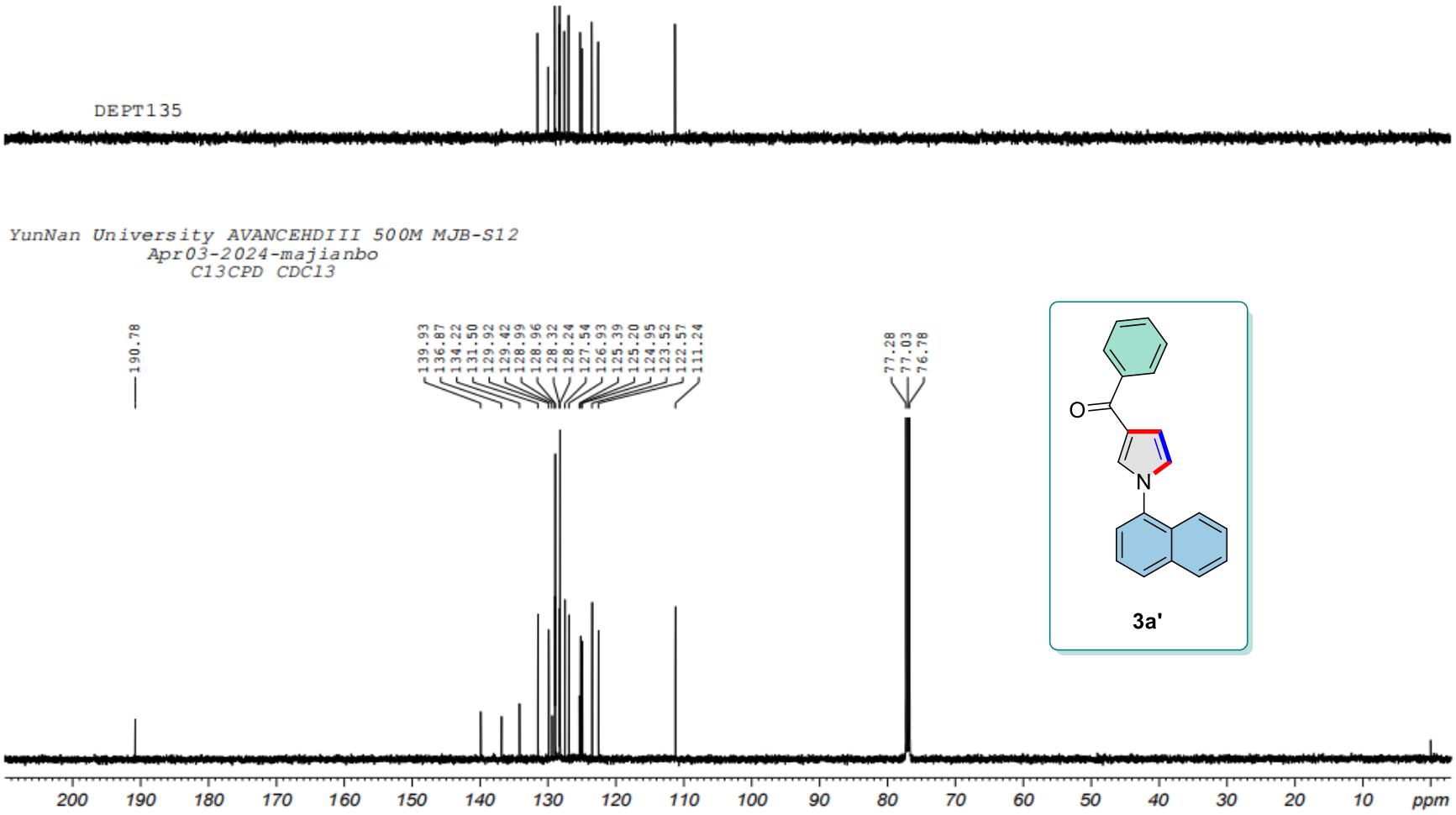


Figure S102. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3a'**

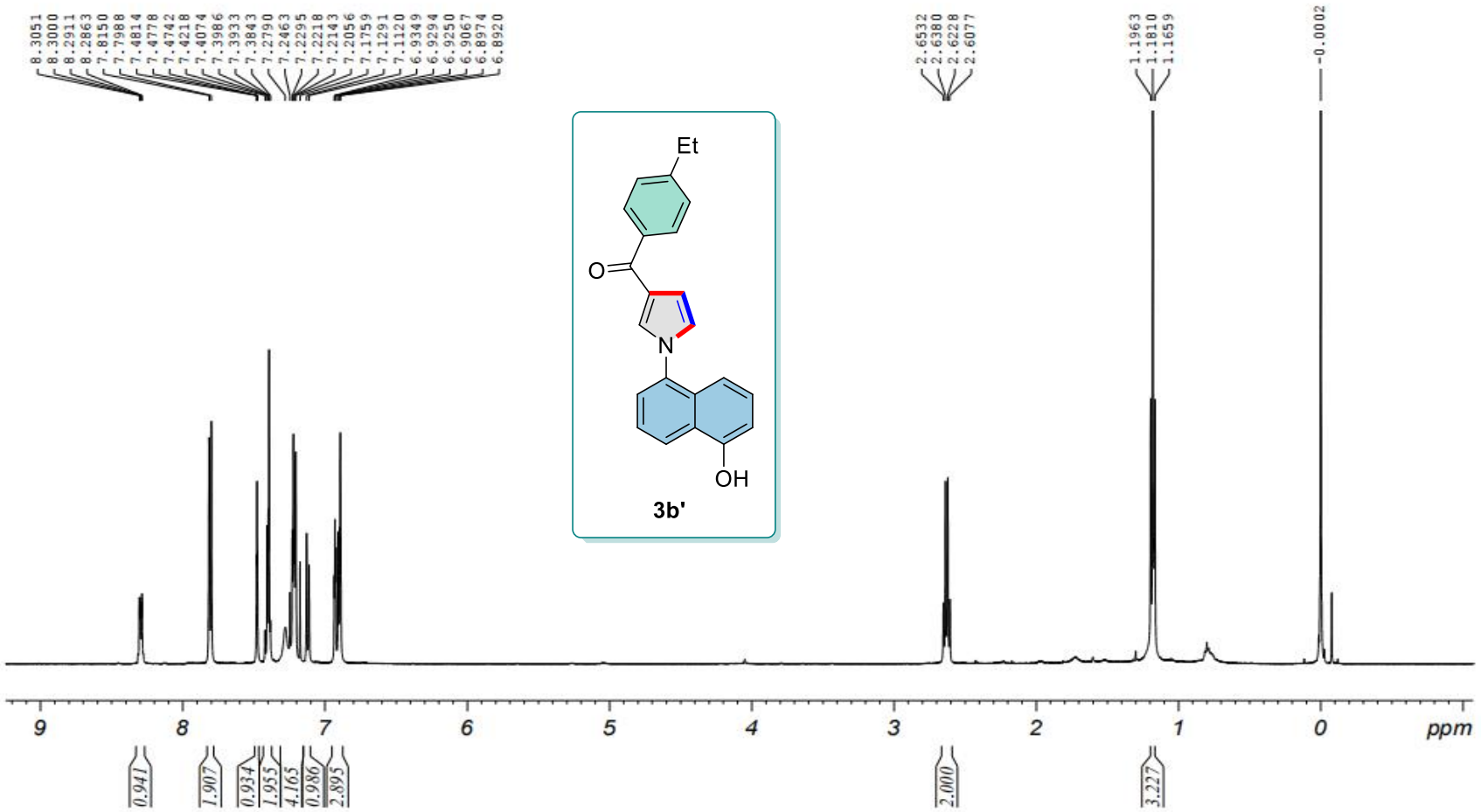


Figure S103. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3b'**

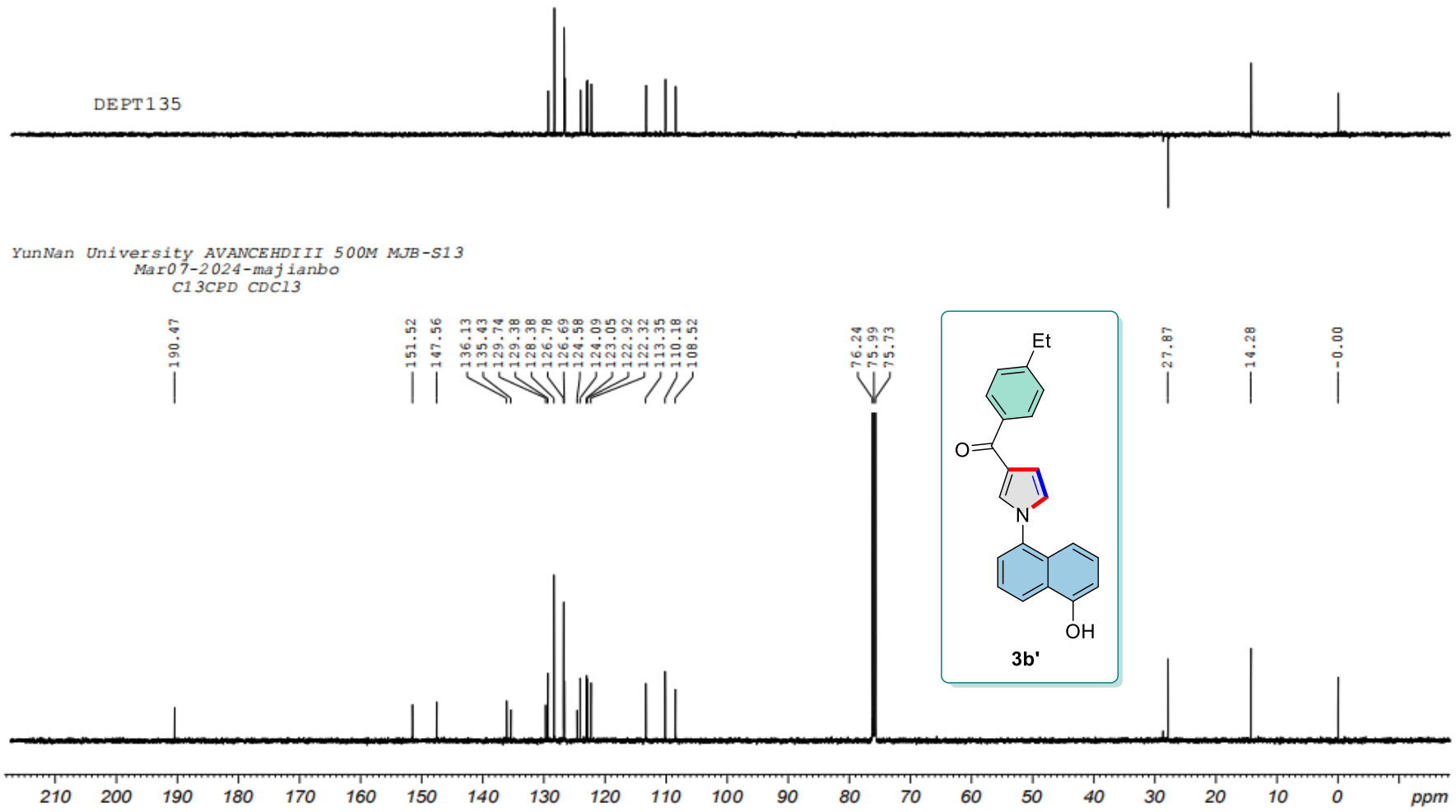


Figure S104. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3b'**

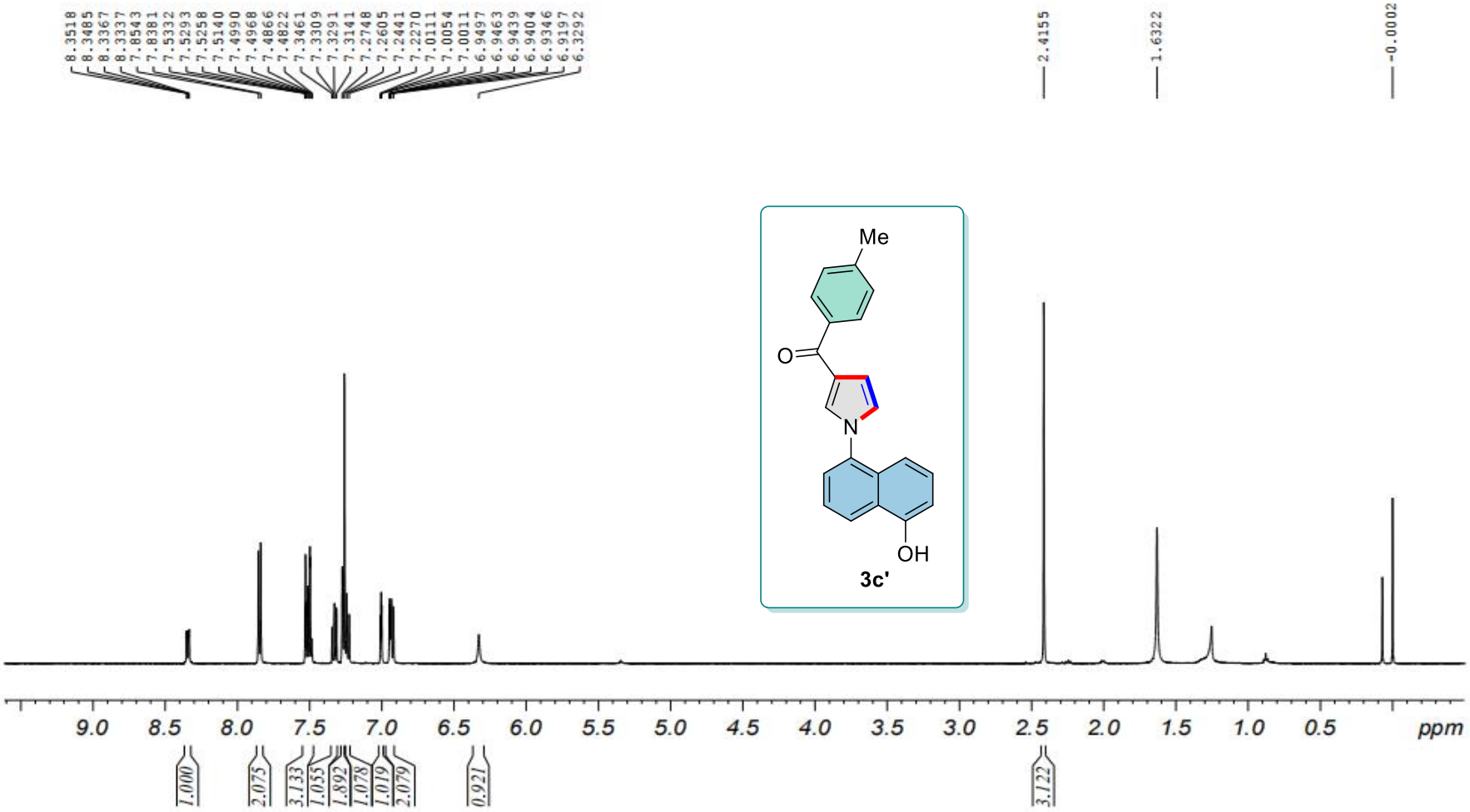


Figure S105. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3c'**

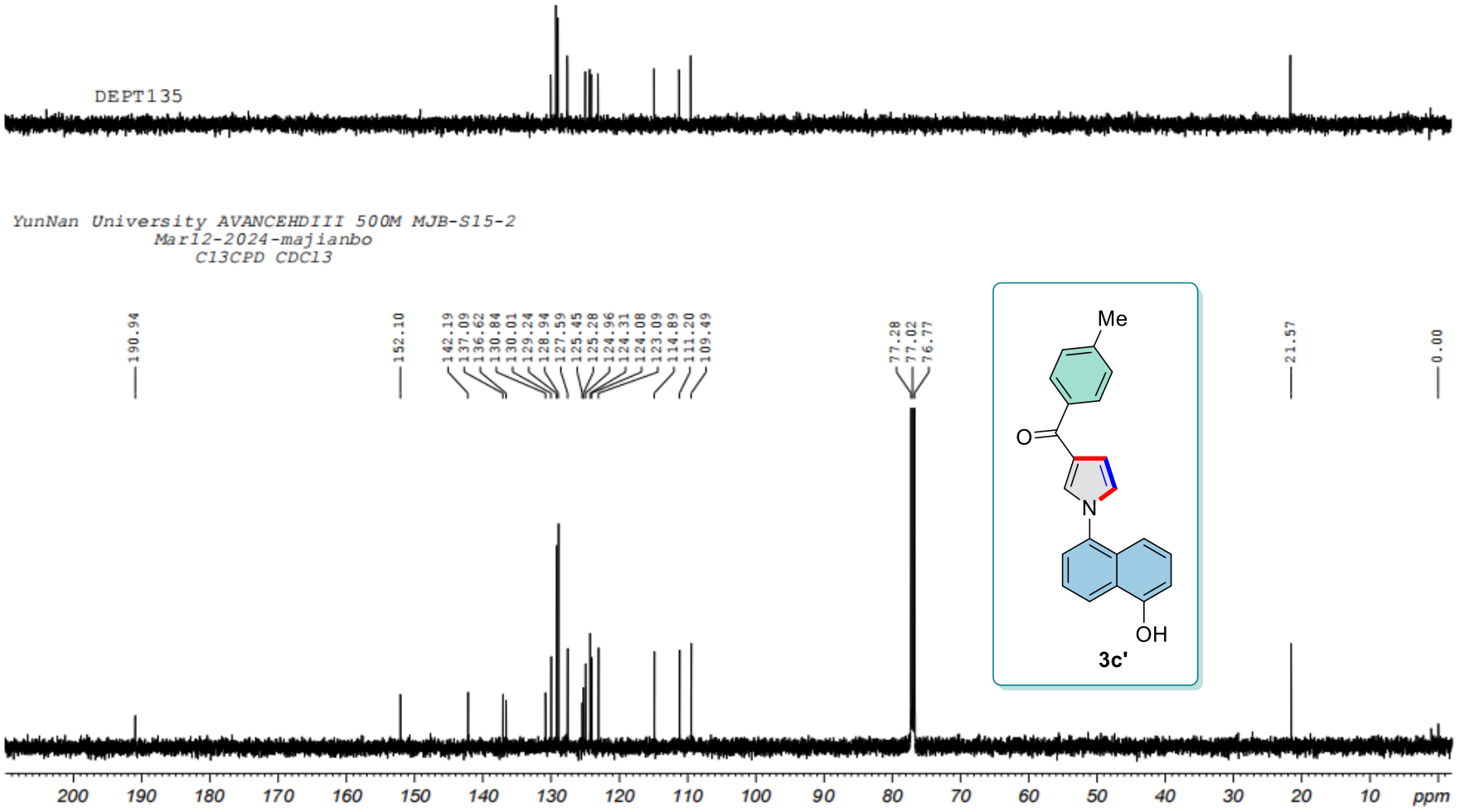


Figure S106. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3c'**

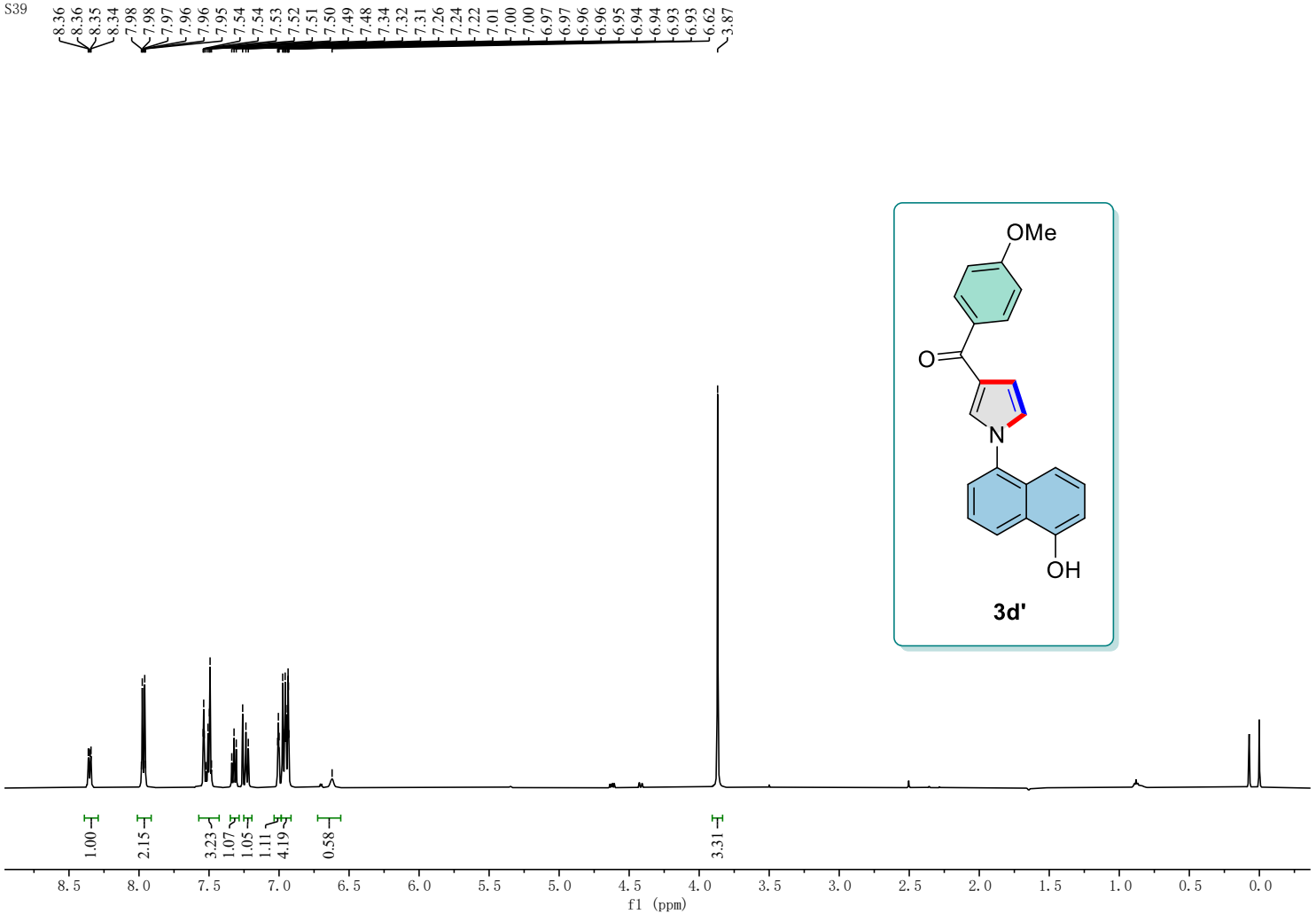


Figure S107. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3d'**

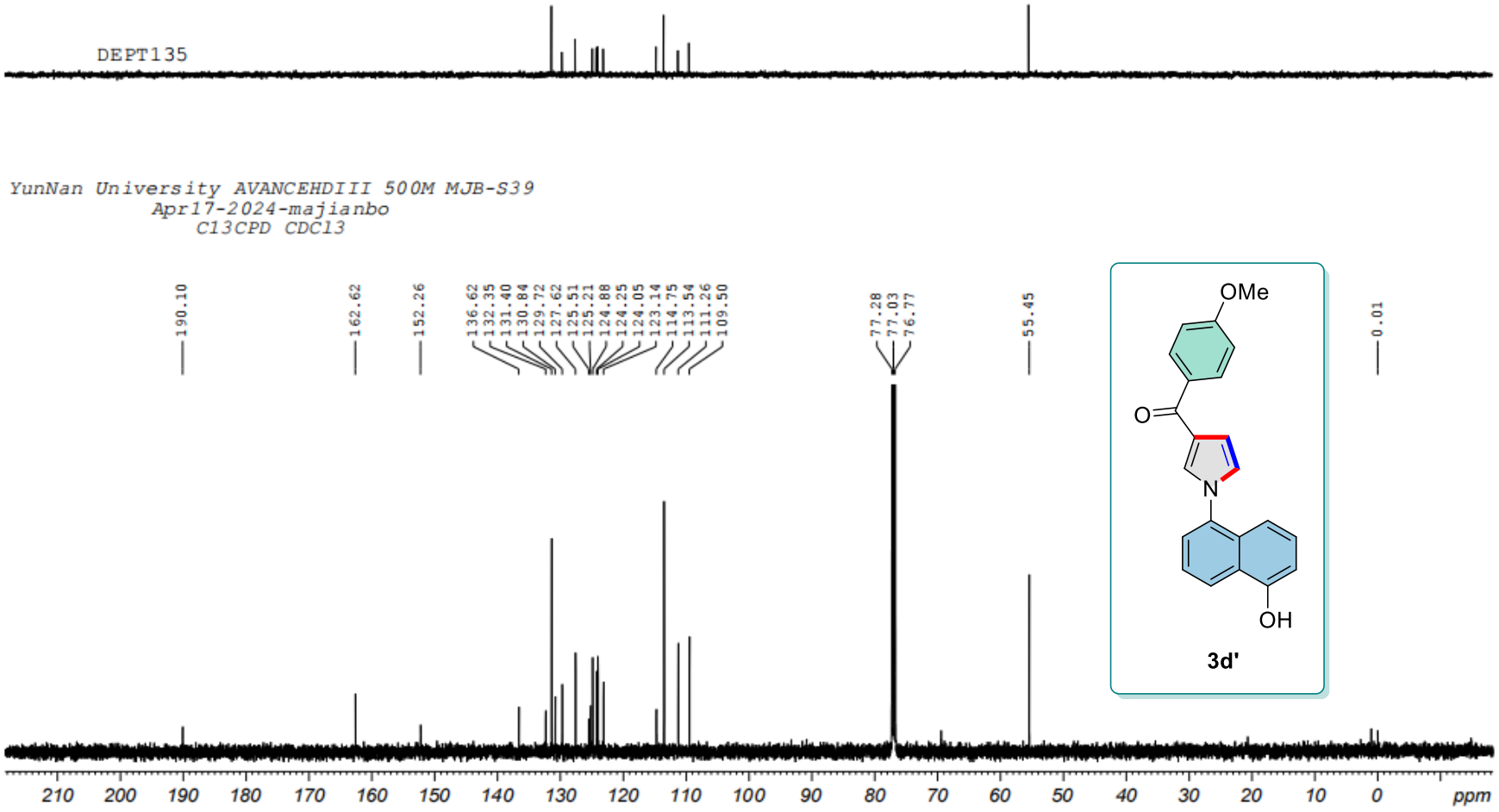


Figure S108. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3d'**

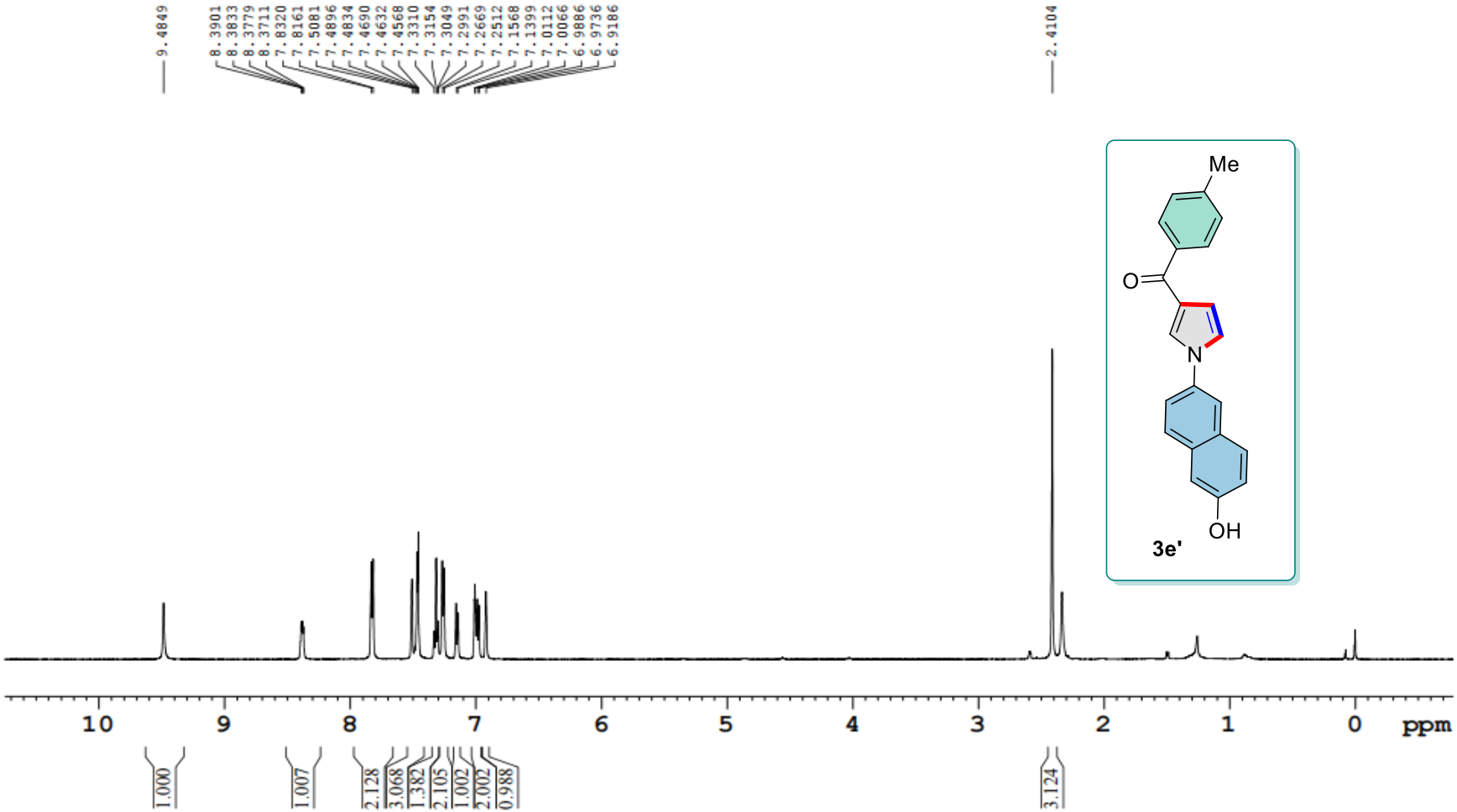


Figure S109. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3e'**

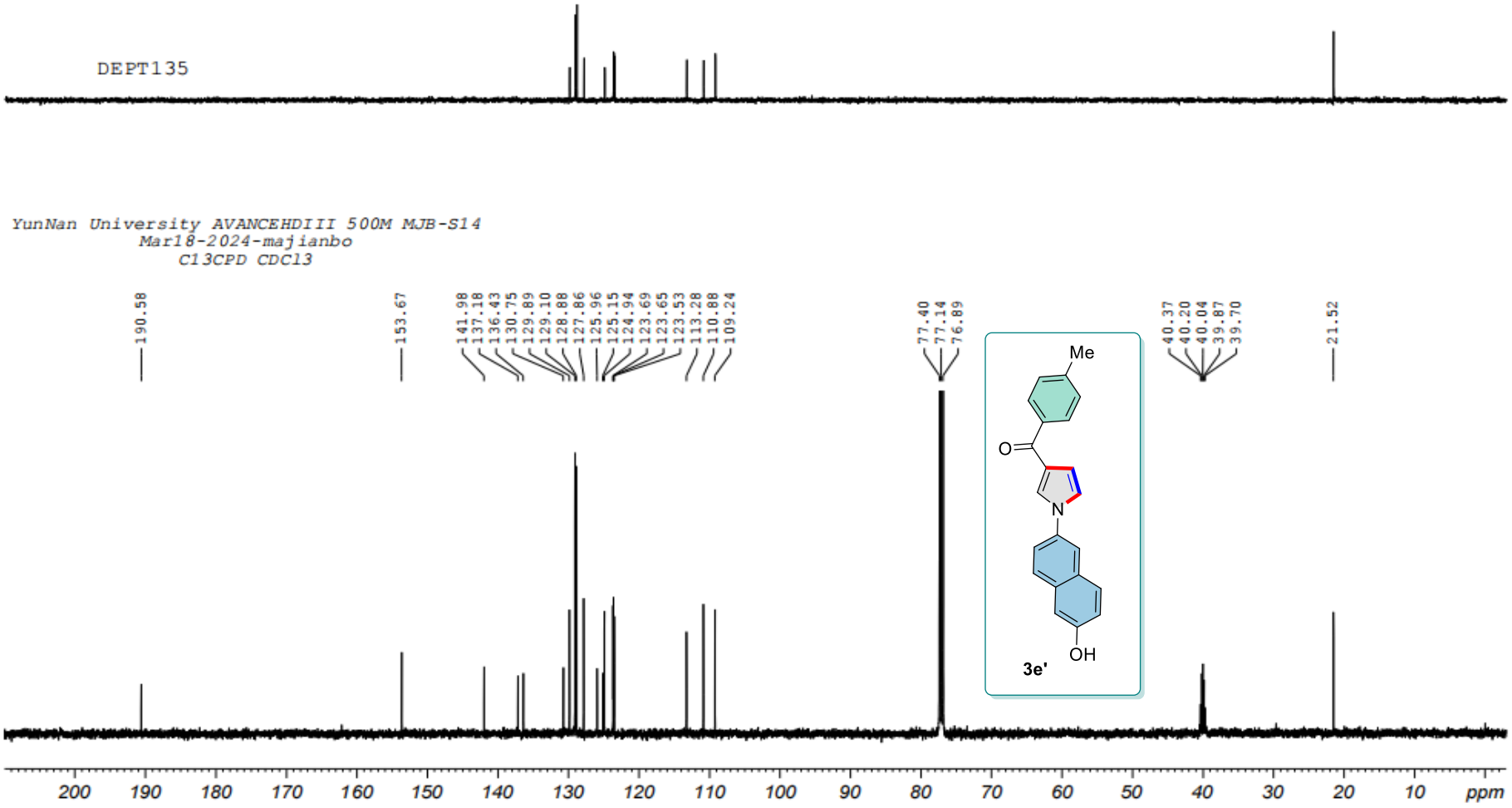


Figure S110. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3e'**

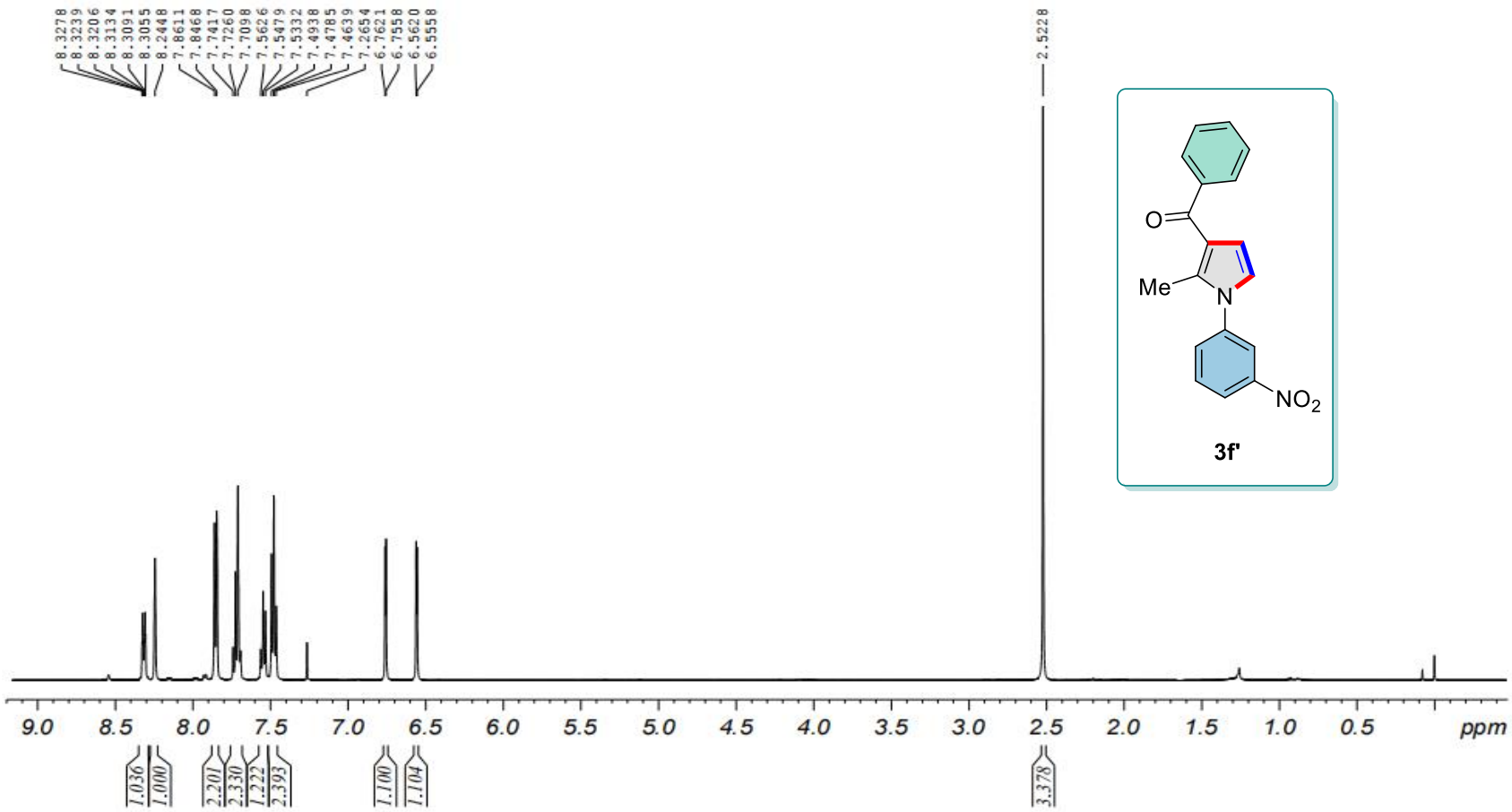


Figure S111. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3f'**

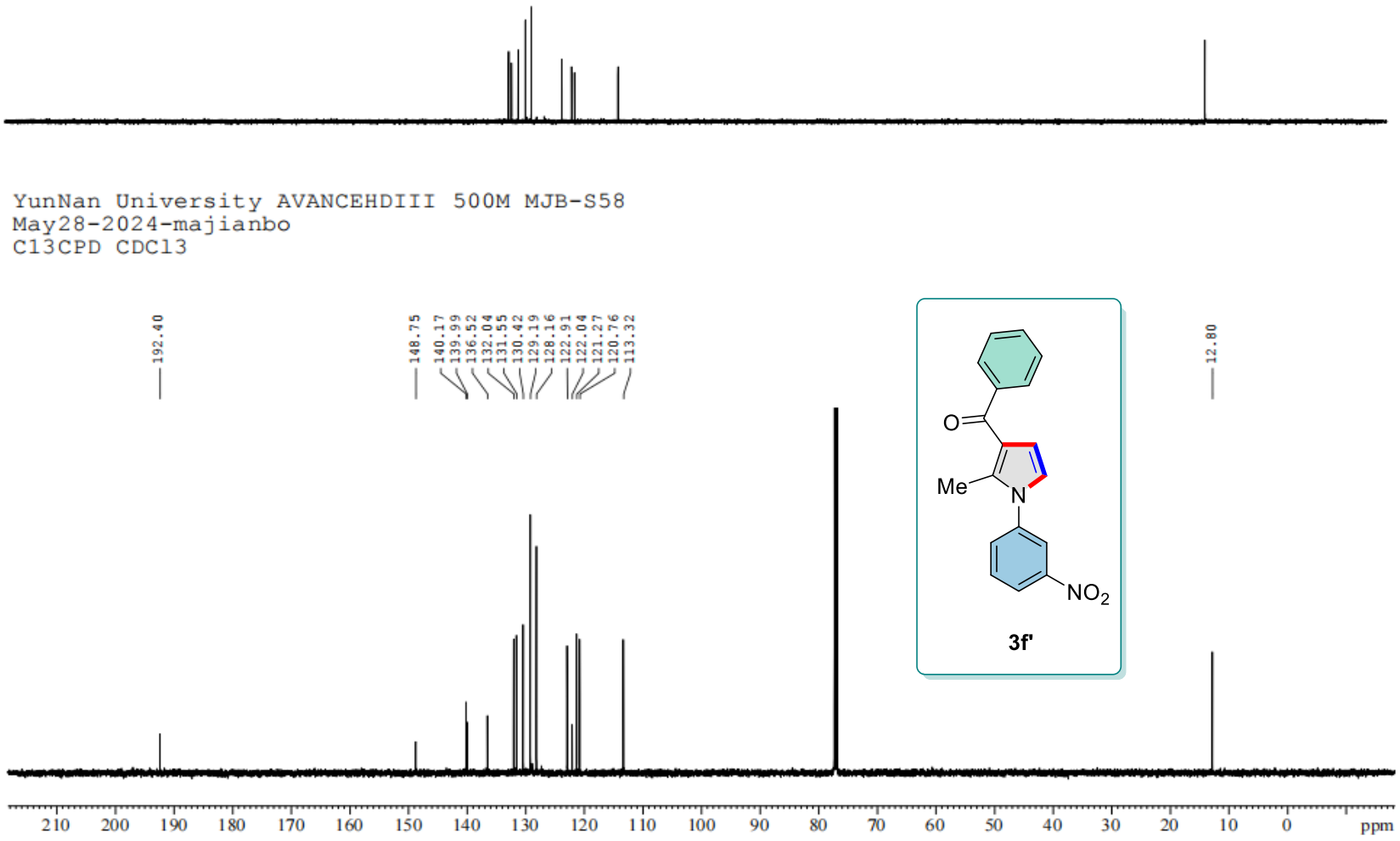


Figure S112. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3f'**

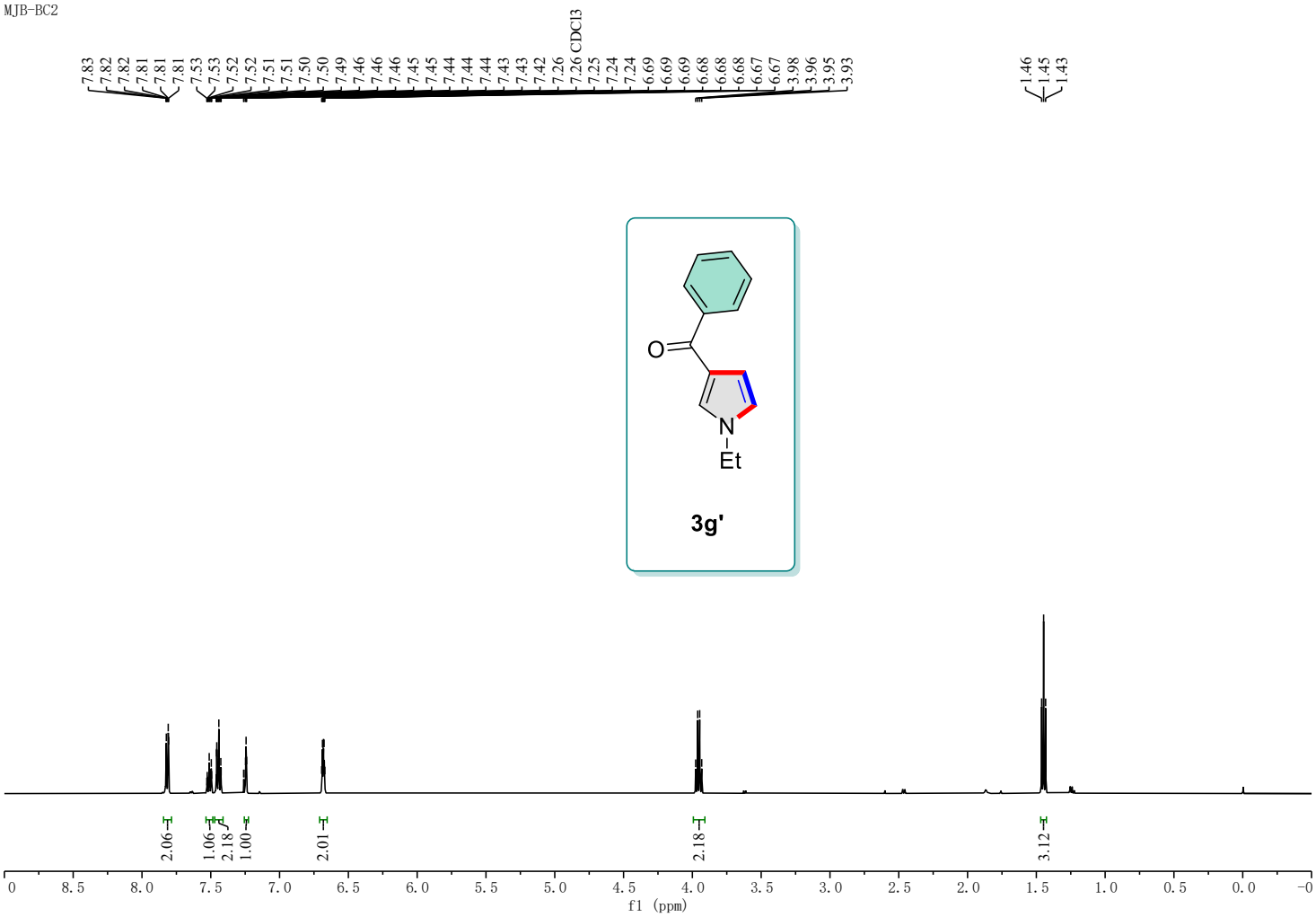


Figure S113. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3g'**

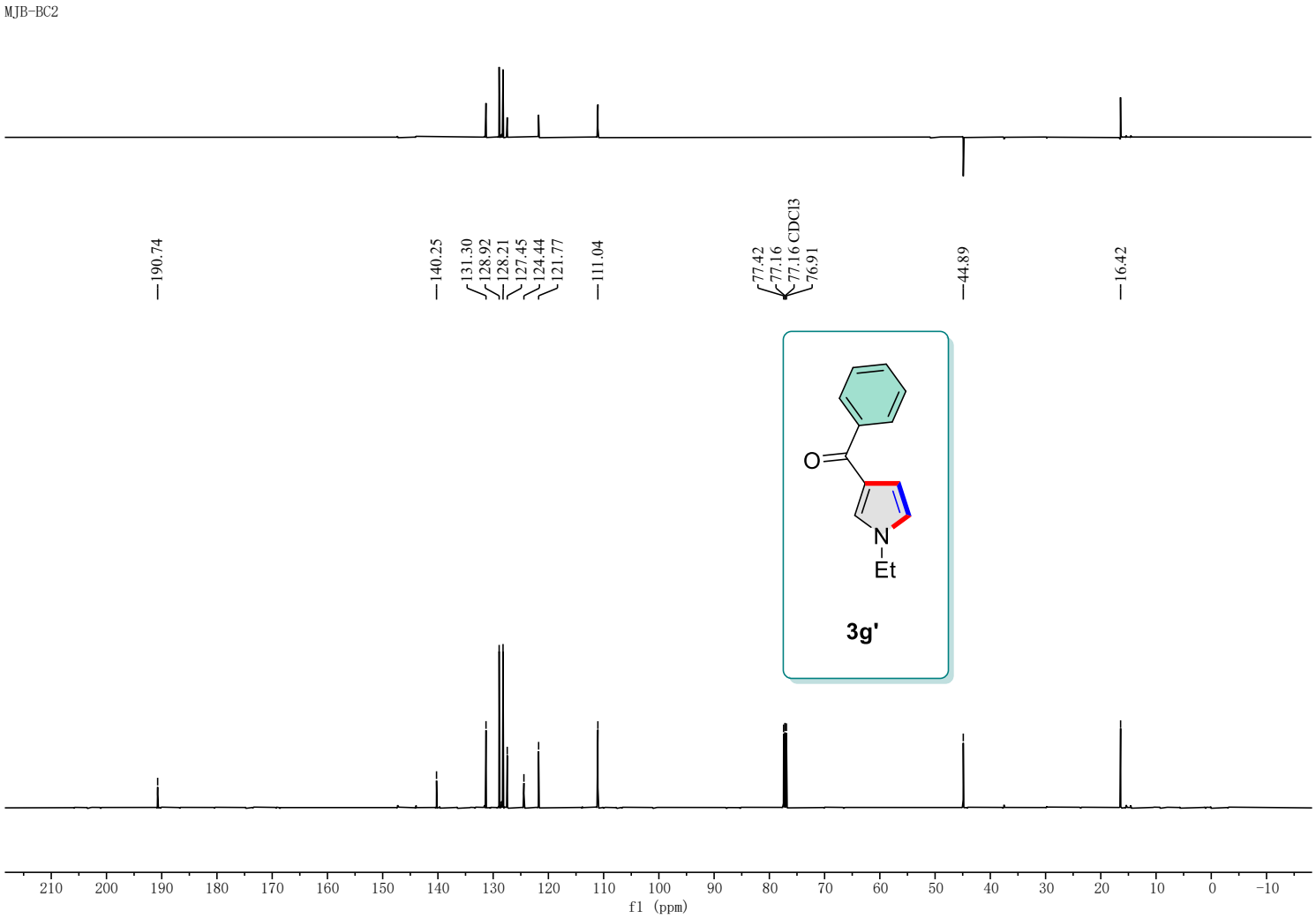


Figure S114. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3g'**

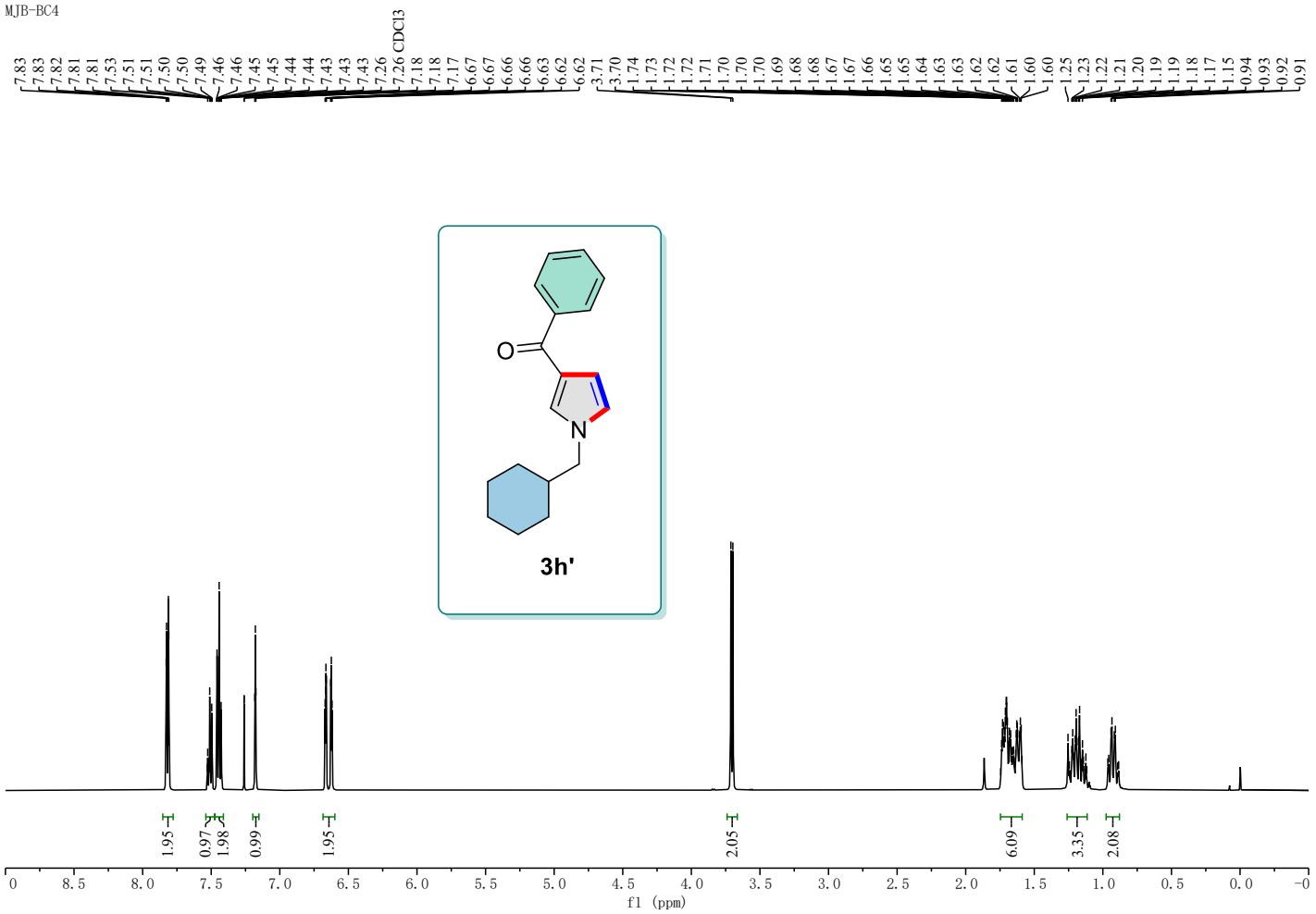


Figure S115. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3h'**

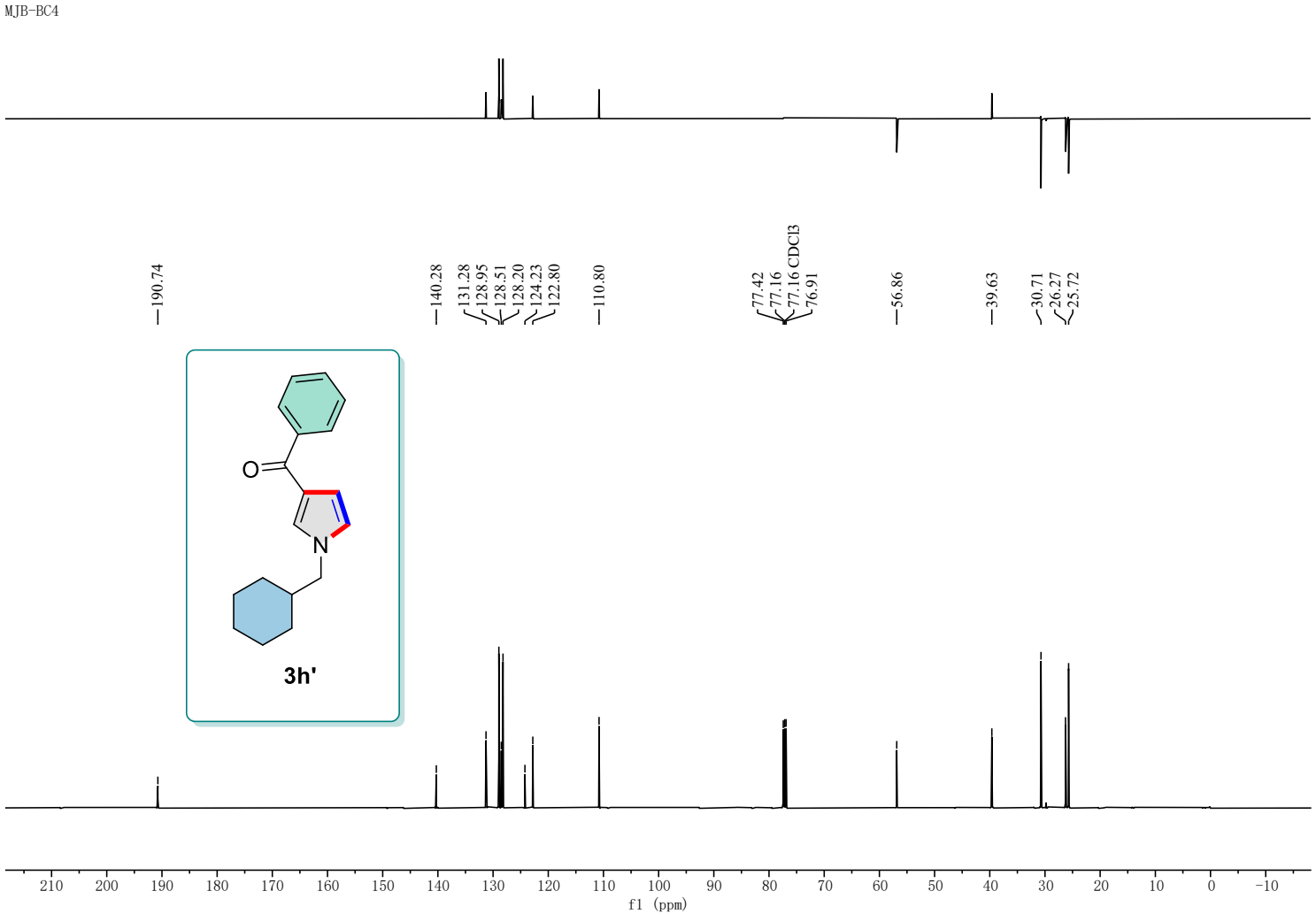


Figure S116. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3h'**

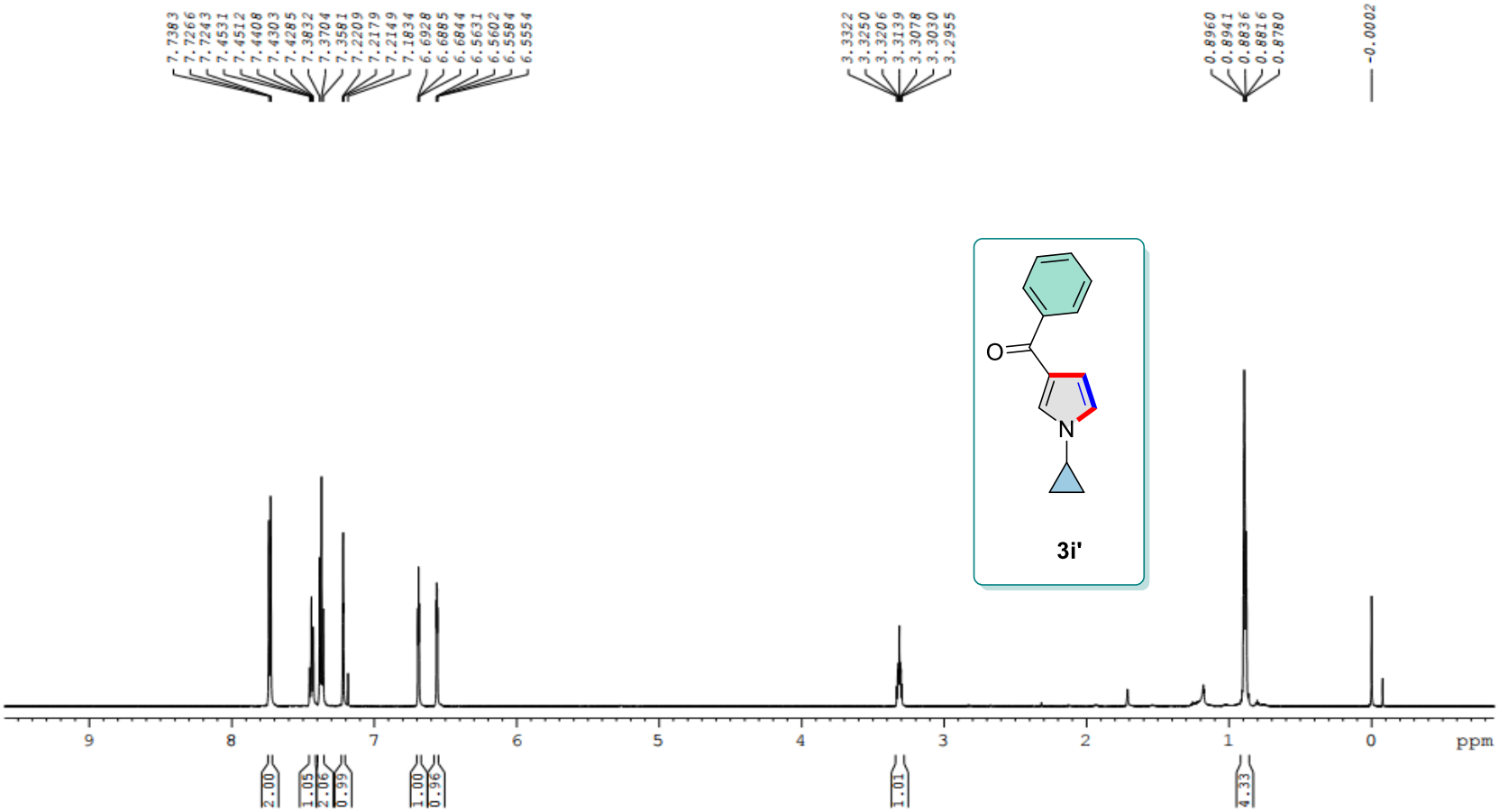


Figure S117. ^{1}H NMR (600 MHz, $CDCl_3$-d_1) spectra of compound **3i'**

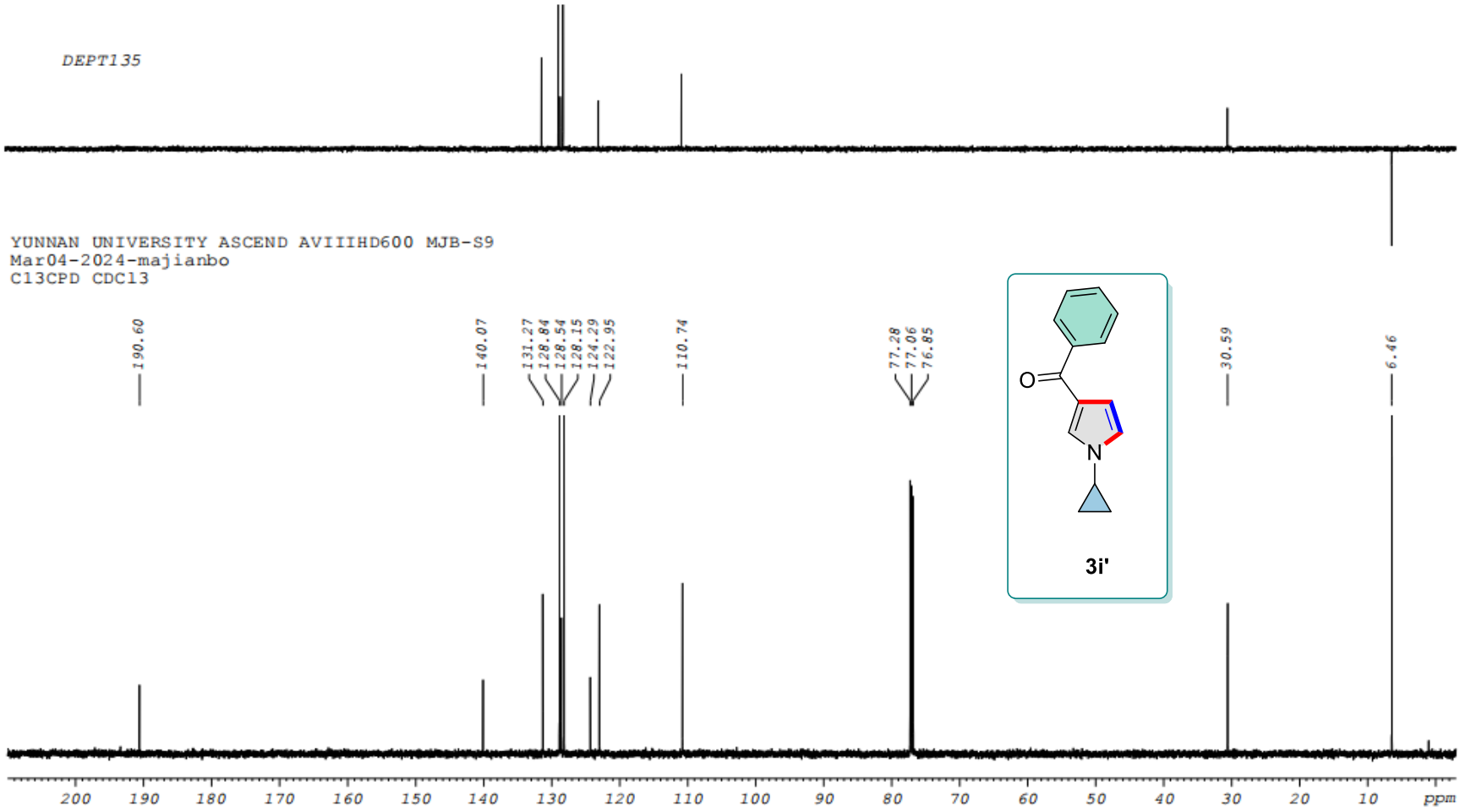


Figure S118. ^{13}C NMR (150 MHz, $CDCl_3$-d_1) spectra of compound **3i'**

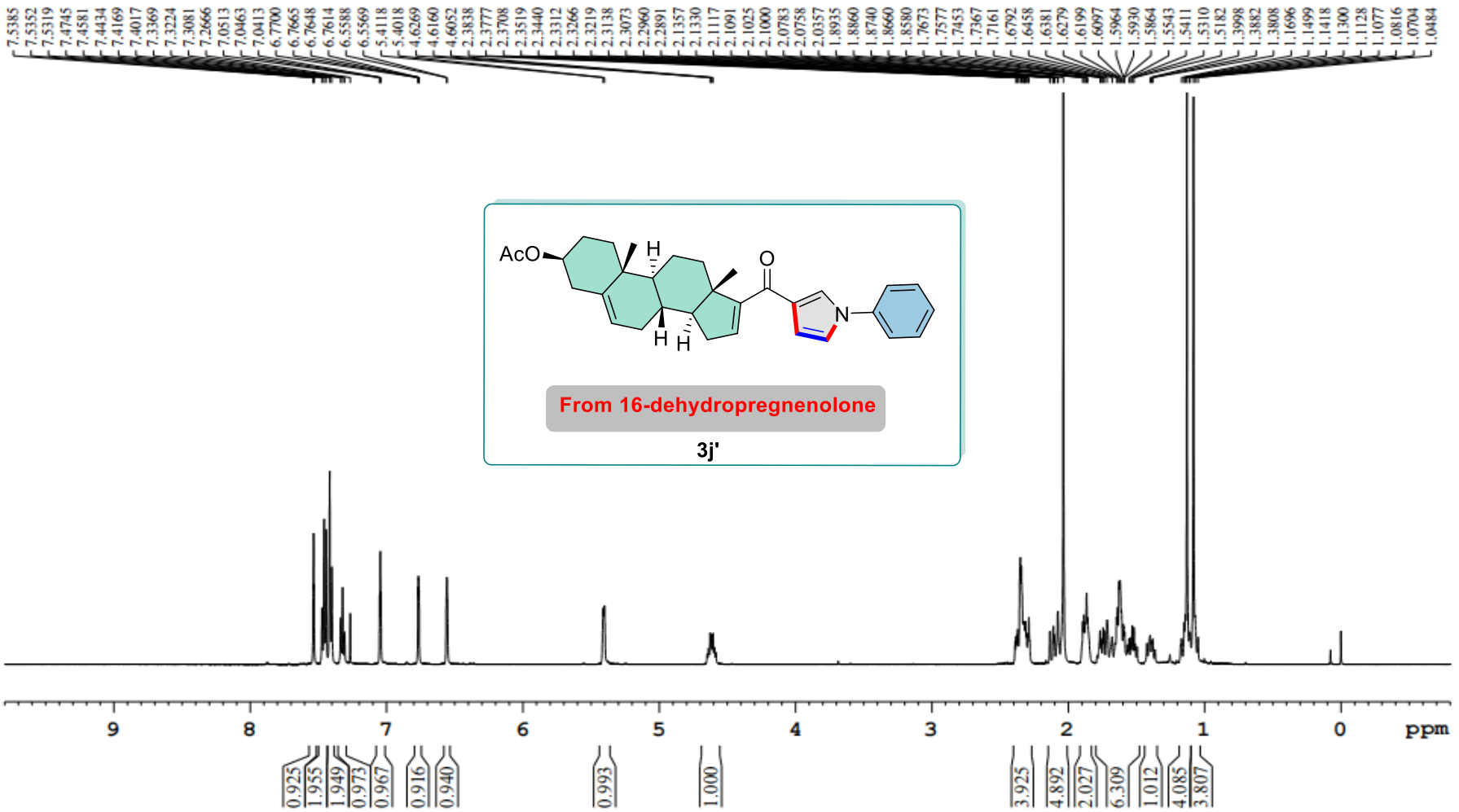


Figure S119. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **3j'**

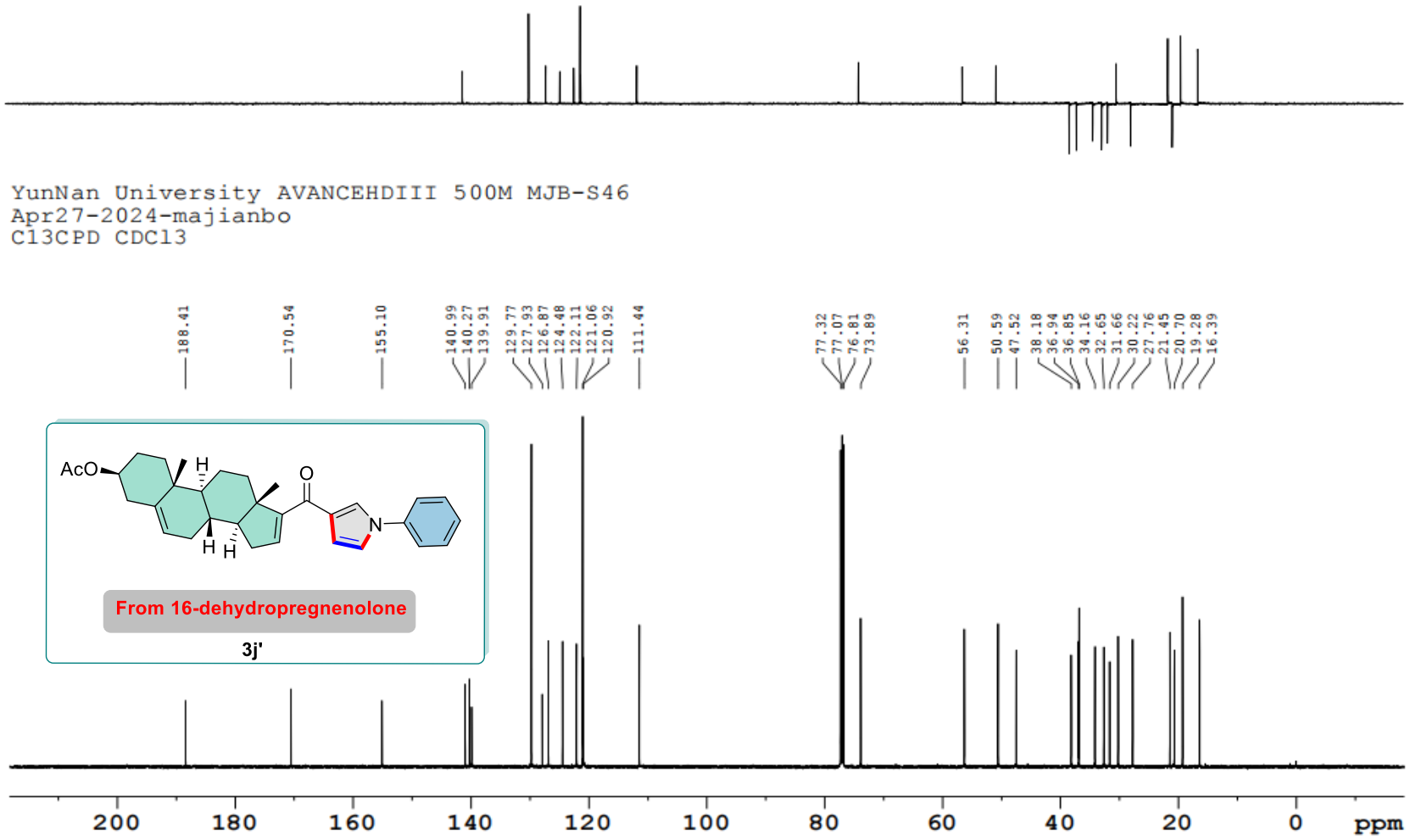


Figure S120. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **3j'**

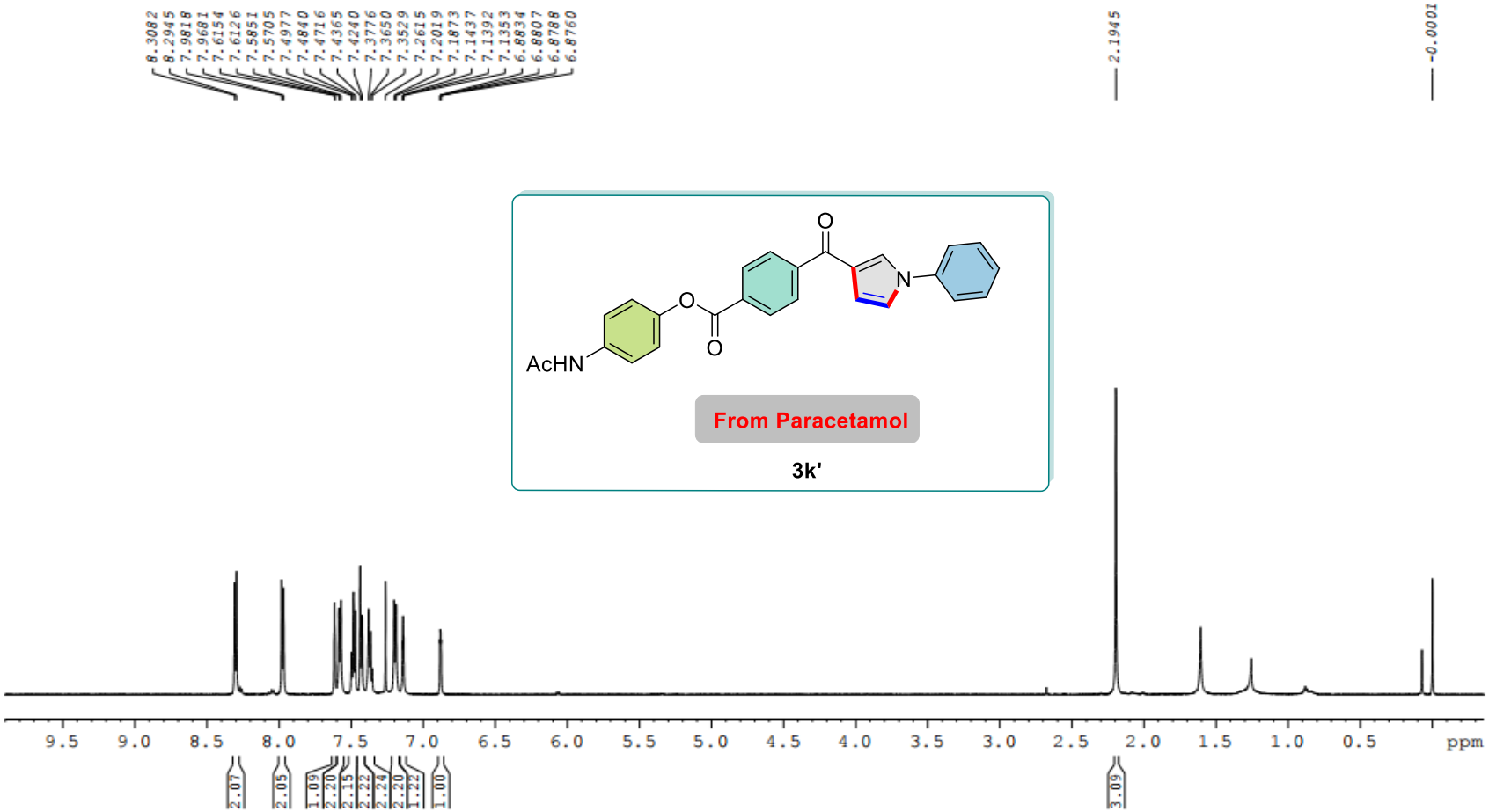


Figure S121. ^{1}H NMR (600 MHz, $CDCl_3$-d_1) spectra of compound **3k'**

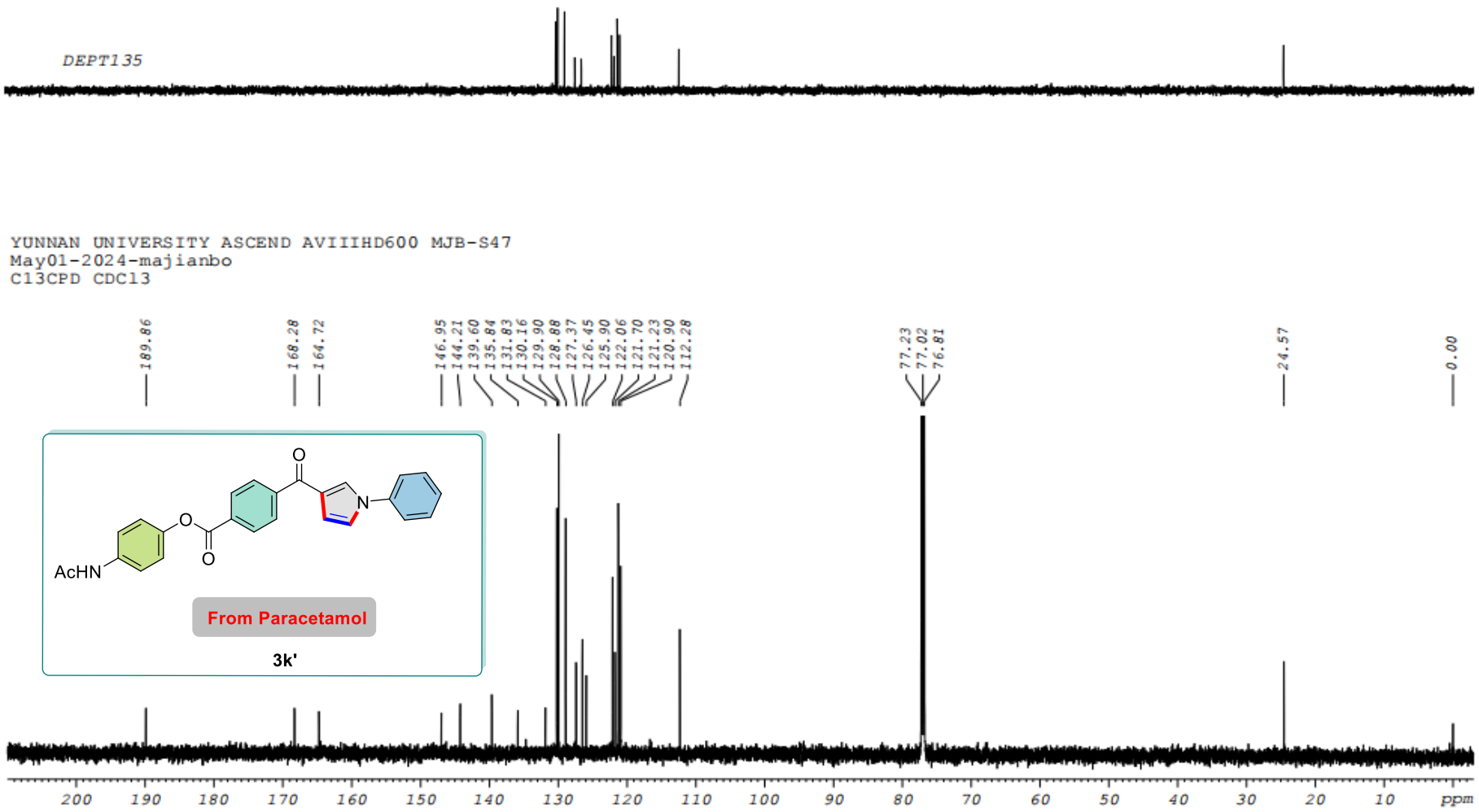


Figure S122. ^{13}C NMR (150 MHz, $CDCl_3$-d_1) spectra of compound **3k'**

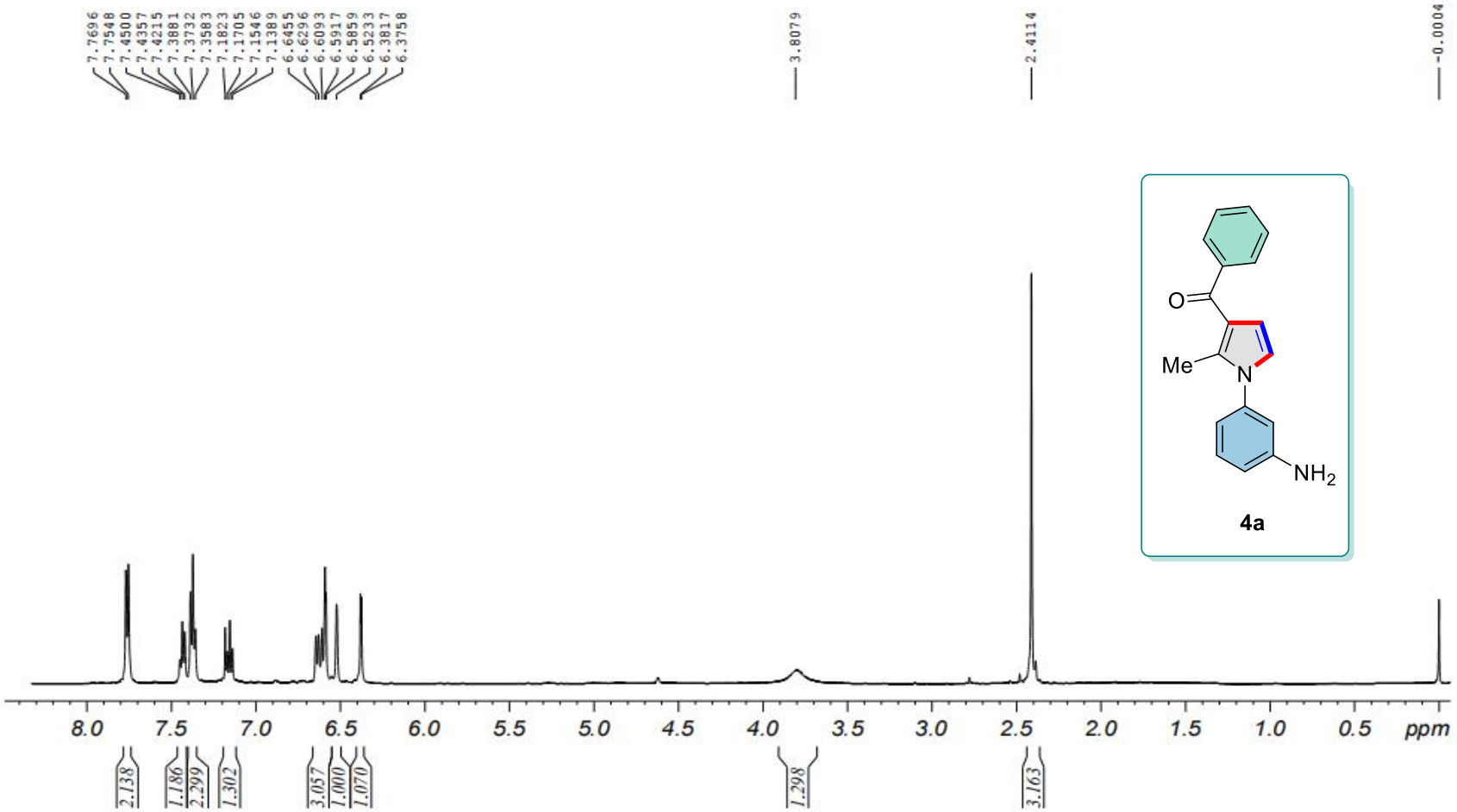


Figure S123. ^{1}H NMR (500 MHz, $CDCl_3$-d_1) spectra of compound **4a**

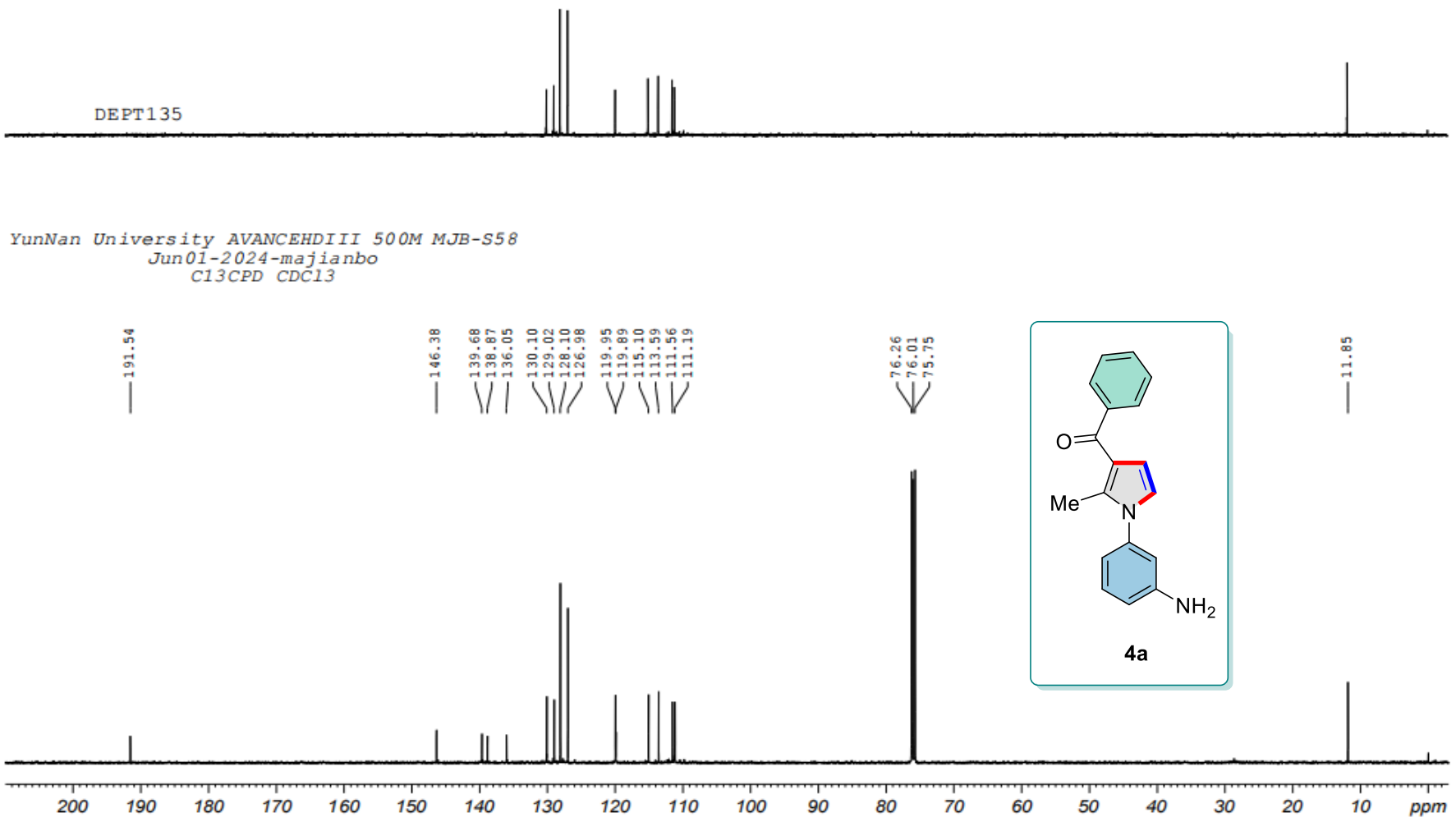
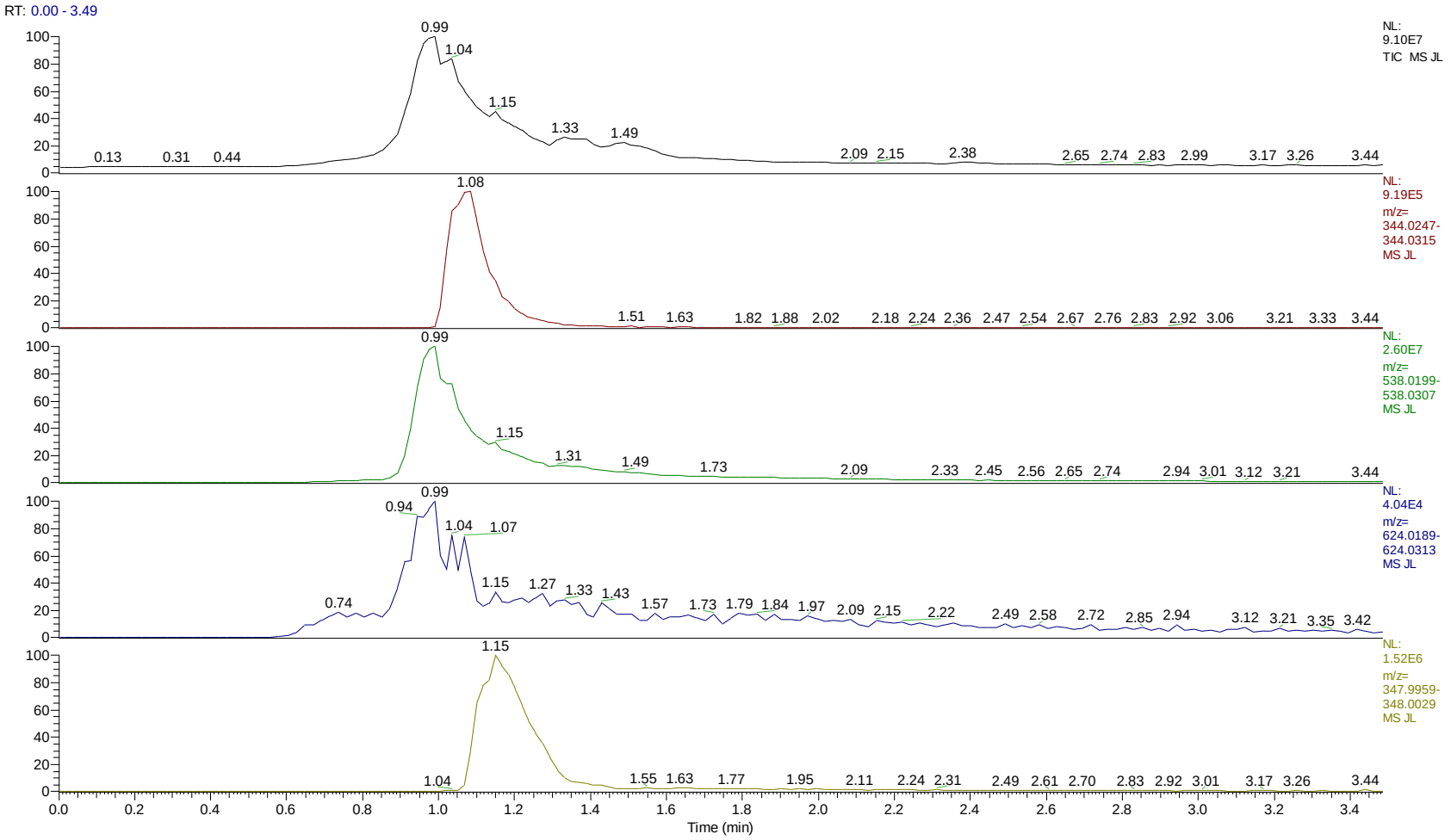


Figure S124. ^{13}C NMR (125 MHz, $CDCl_3$-d_1) spectra of compound **4a**

6. HPLC extracted ion flow diagrams of the reaction mixture and HRMS of substrate



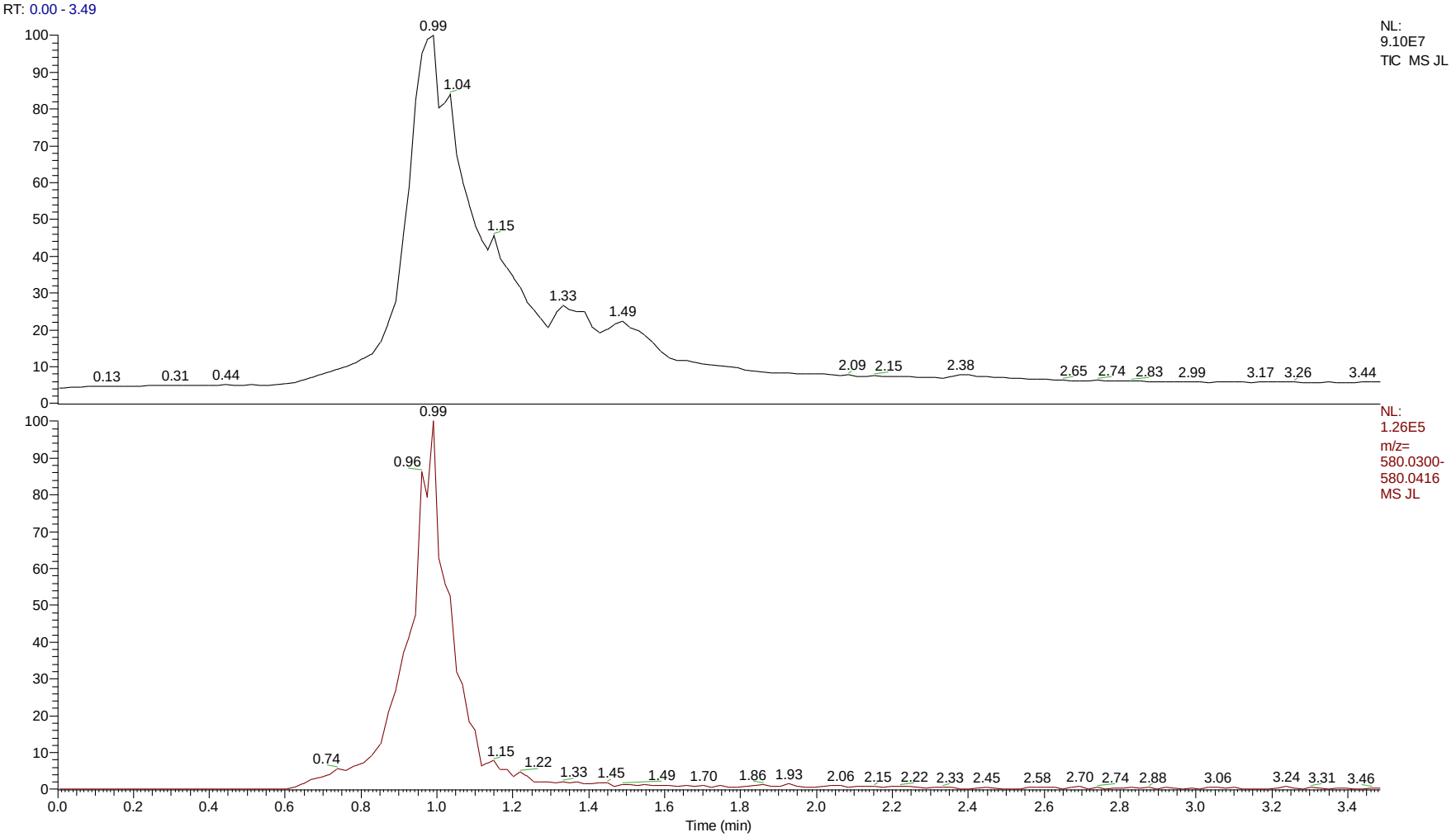


Figure S125. HPLC extracted ion flow diagrams of the reaction mixture

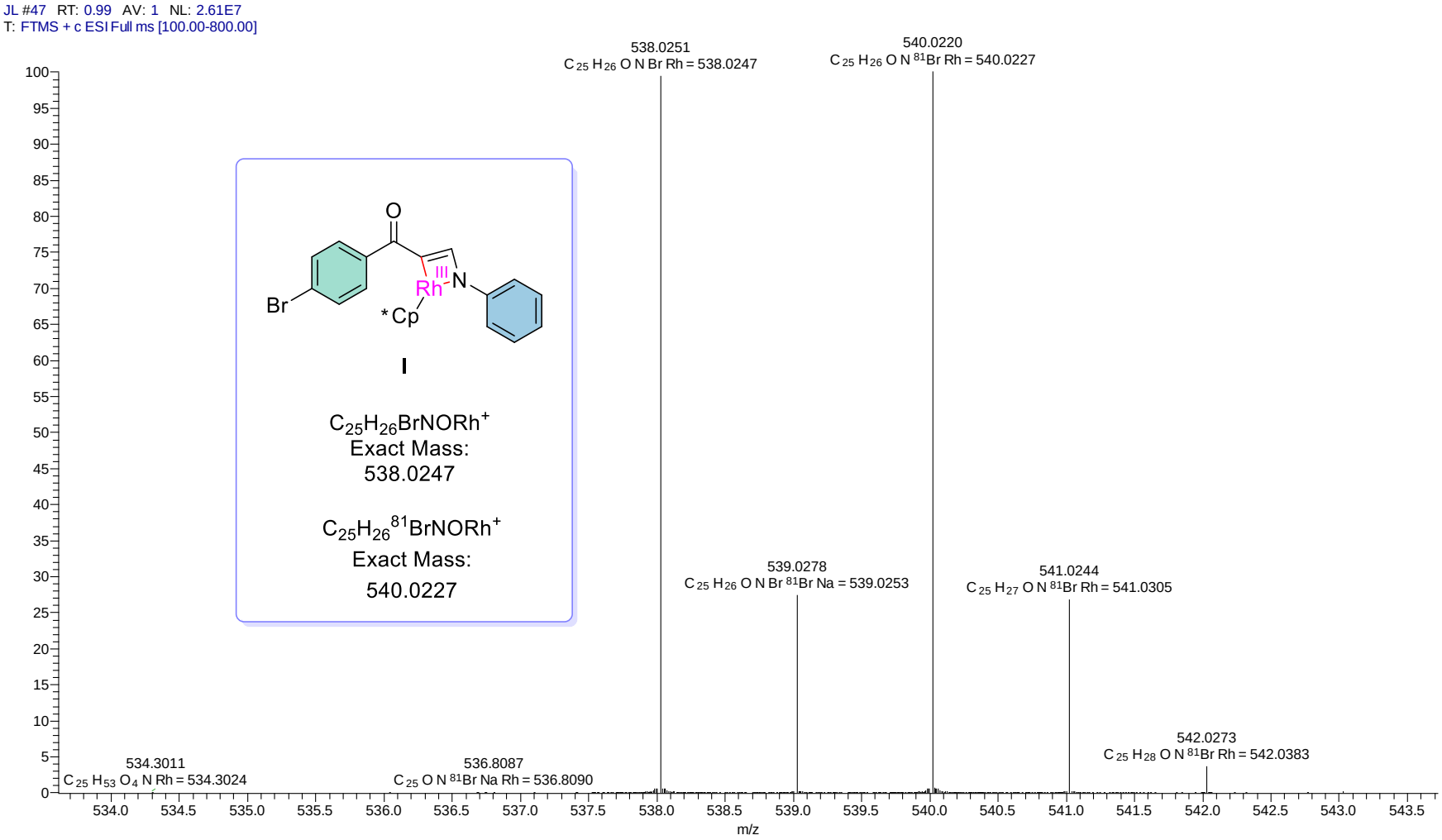


Figure S126. HRMS of substrate **I**

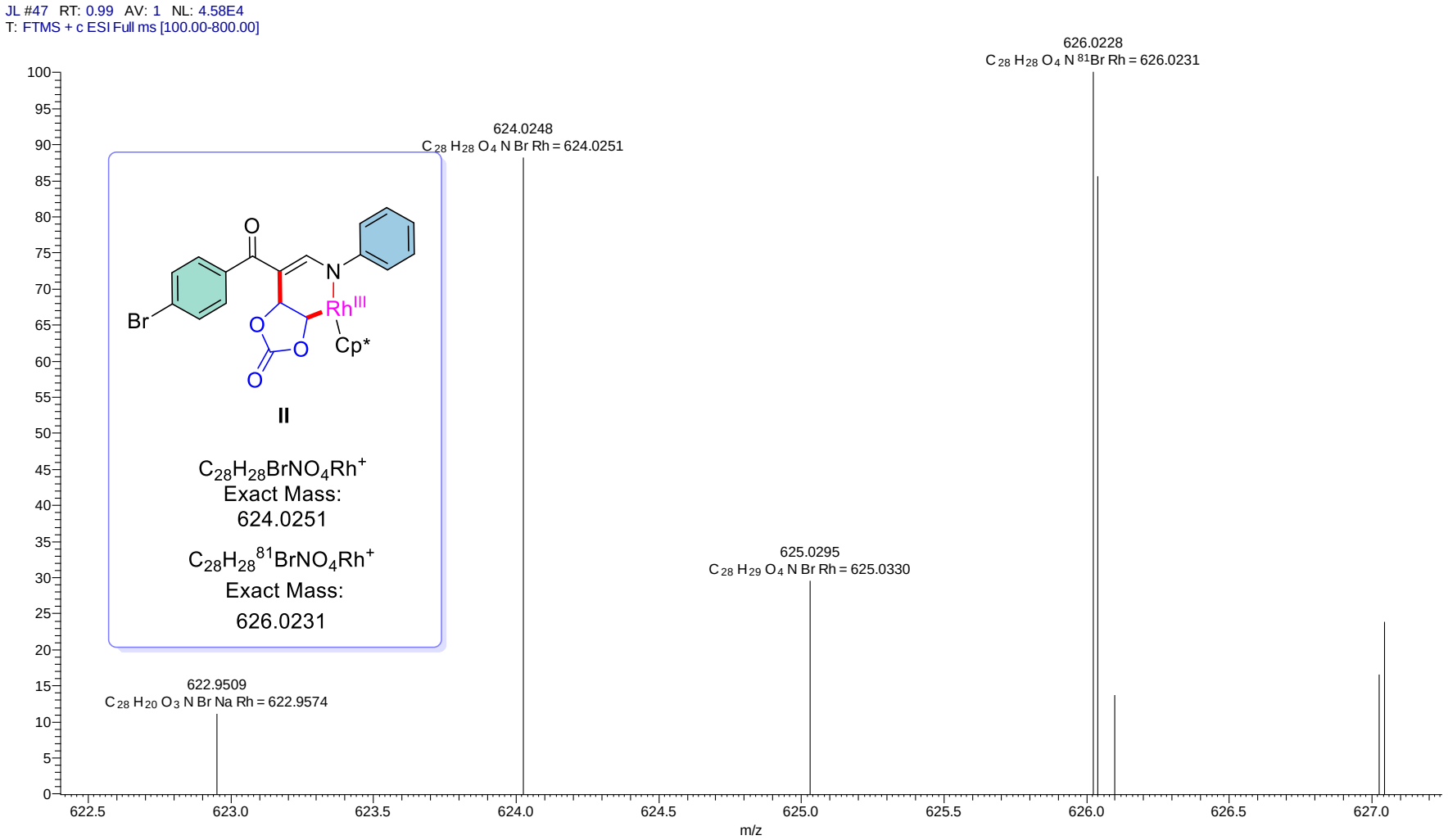


Figure S127. HRMS of substrate **II**

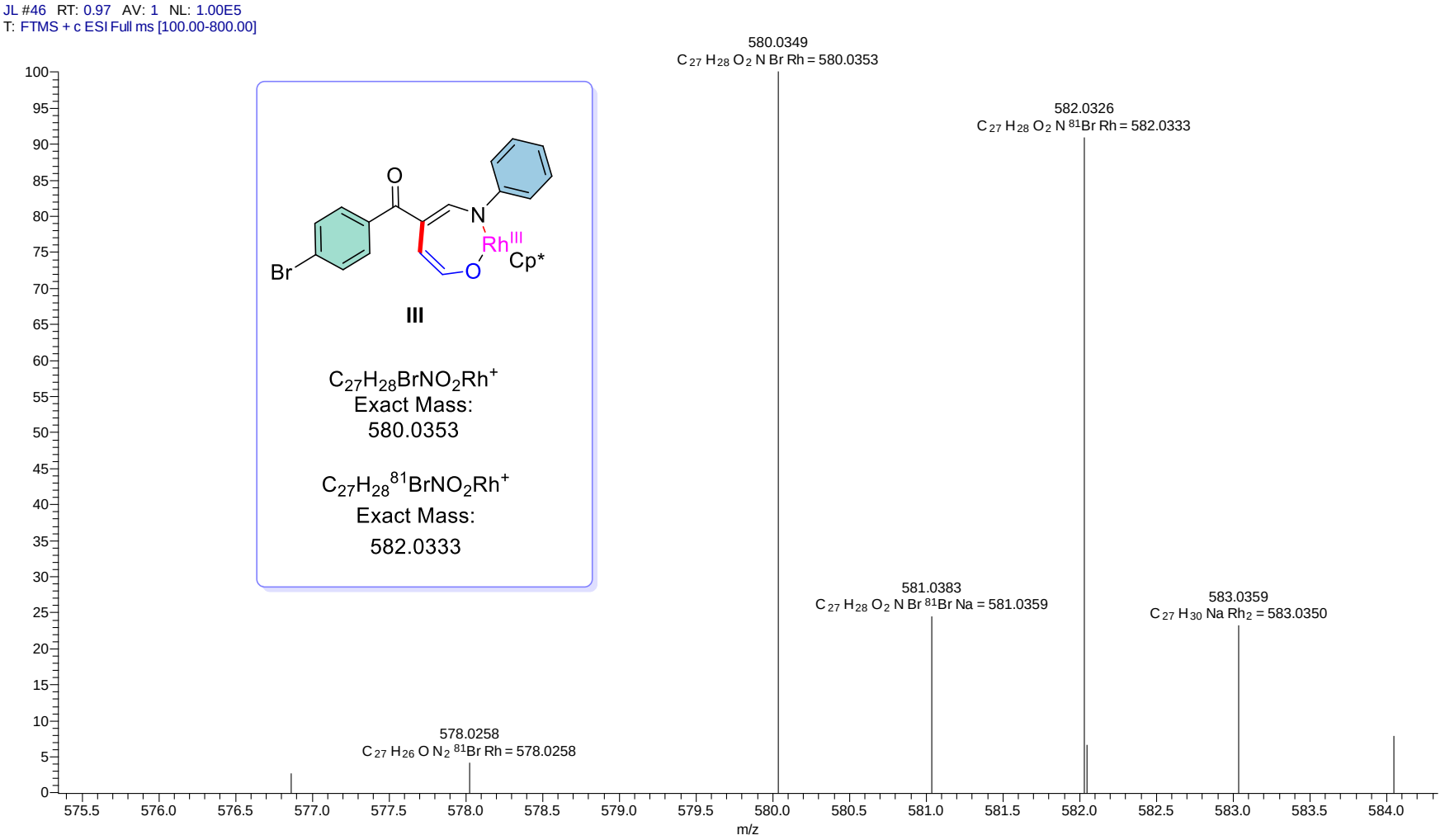


Figure S128. HRMS of substrate **III**

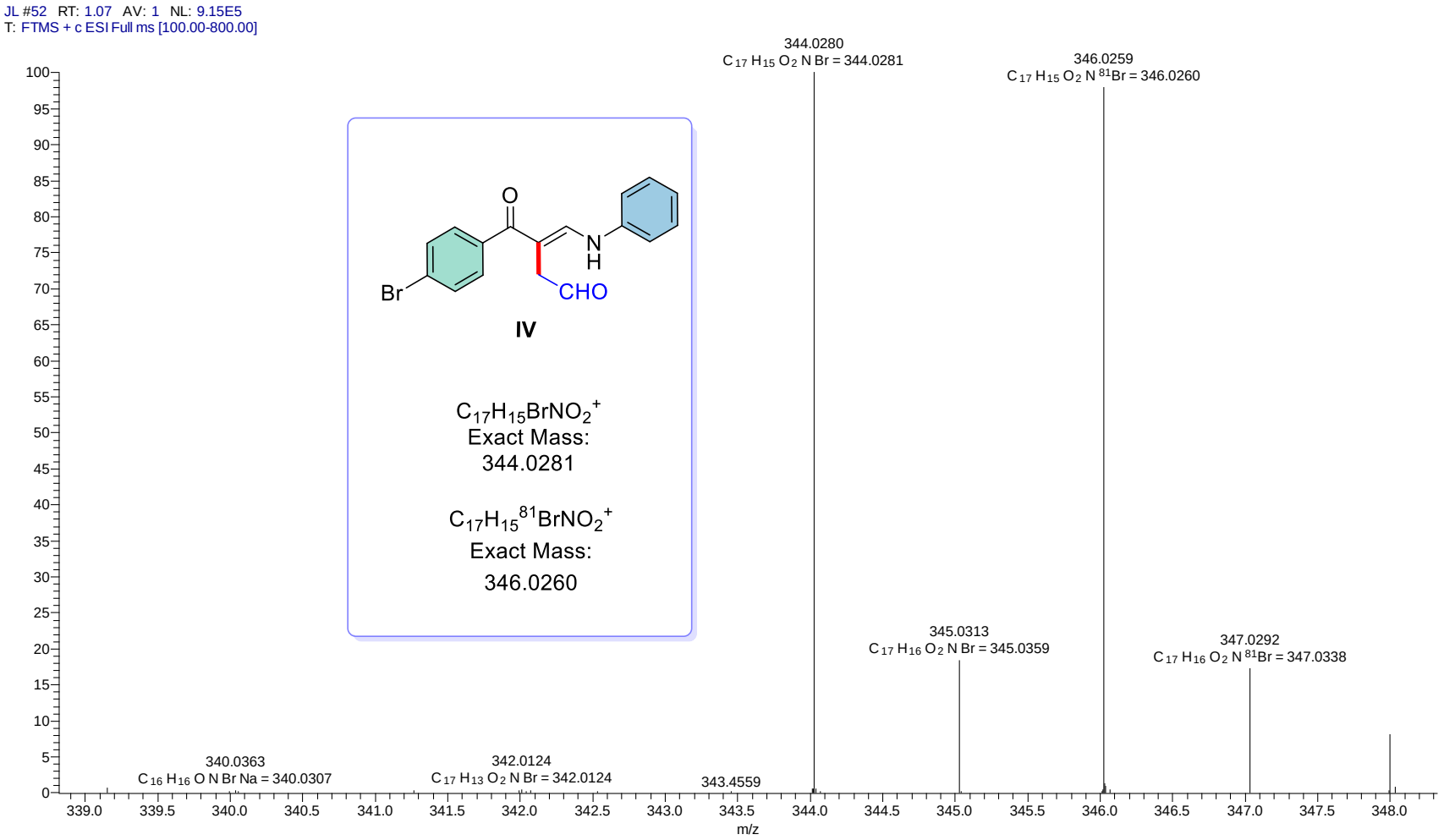


Figure S129. HRMS of substrate **IV**

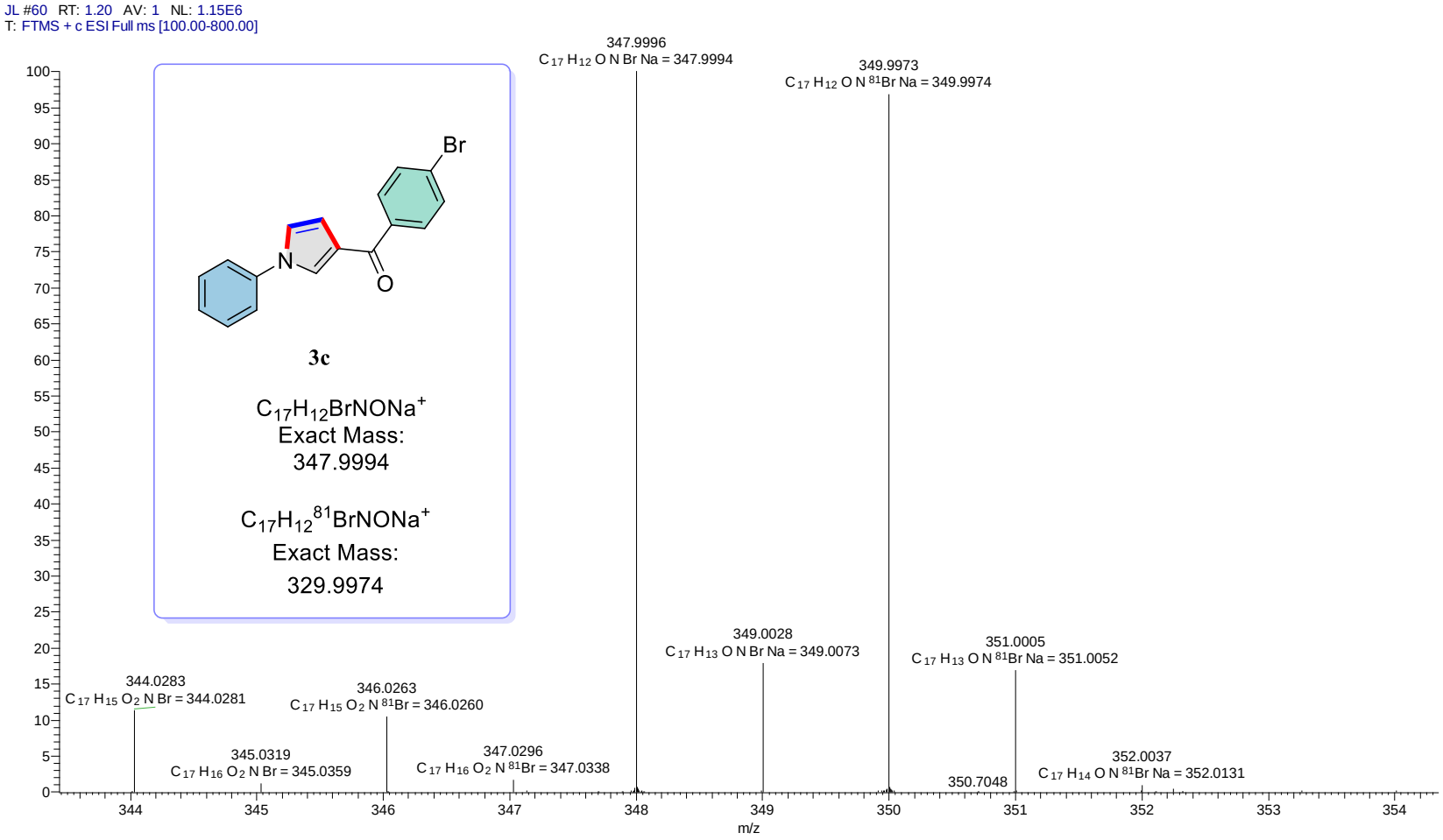


Figure S130. HRMS of substrate **3c**

8. References and Notes

1. X.-M. Hu, B. Zhou, C.-L. Yang, J. Lin and S.-J. Yan, *ACS Omega*, **2018**, *3*, 5994-6005.
2. X. Liang, P. Guo, W. Yang, M. Li, C. Jiang, W. Sun, T.-P. Loh and Y. Jiang, *Chem. Commun.* **2020**, *56*, 2043-2046.
3. M. Zhang, L. Chen, H. Sun, Z. Liu, S.-J. Yan and F. Yu, *Org. Lett.* **2023**, 25, 7214-7219.
4. E. M. Afsah, E. S. I. El‐Desoky, H. A. Etman, I. Youssef and A. M. Soliman, *J. Heterocycl. Che*m. **2018**, *55*, 2959-2970.
5. CCDC 2375576. contain the supplementary crystallographic data for compound **3q**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif