Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Triflic acid catalysed intermolecular hydroamination of alkenes with Fmoc-NH_2 as the amine source

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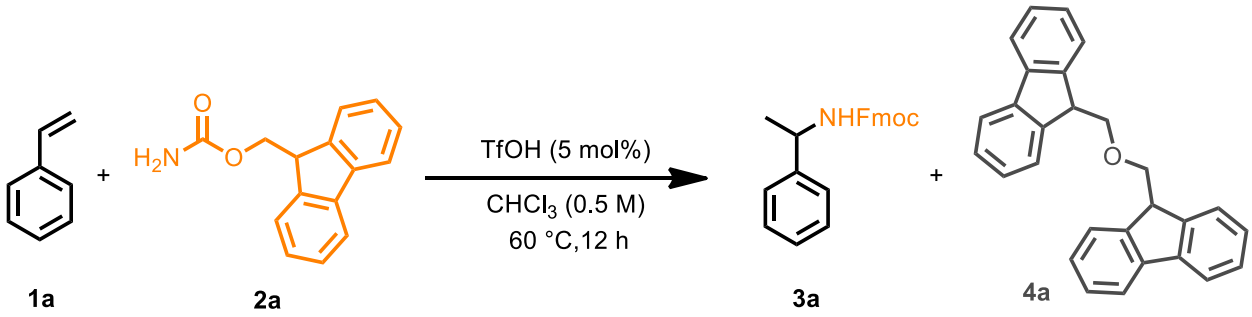
1. General information

All starting materials were purchased from BLD Pharmatech (India) Pvt.Ltd., Tokyo Chemical Industry (India) Pvt.Ltd, and Sigma Aldrich Chemicals Pvt.Ltd and were used as received. All reactions were carried out in oven-dried (110 °C) glassware. Reactions were monitored by thin layer chromatography (TLC) using silica gel TLC plates (aluminum sheets coated with silica gel, Merck) and visualized by UV lamp (λ = 254 nm) and/or stained using vanillin or $KMnO_4$. The products were purified by column chromatography using petether/ethyl acetate binary solvent as the eluent and silica gel as the stationary phase (100–200 mesh or 200–400 mesh). Melting points were determined on a BK-programmable melting point apparatus (max = 320 °C) and were uncorrected. ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ NMR spectra were recorded on Bruker ASCEND™ 400 MHz spectrometer instrument in $CDCl_3$ (purchased from SynNMR) or D_2O solvent at 25 °C until and otherwise mentioned. All spectra were processed using TopSpin 4.4.1 software. Chemical shift (δ) values were reported in ppm (parts per million) from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ = 7.26 ppm for ^{1}H NMR, 77.16 ppm for $^{13}C\{^{1}H\}$ NMR; D_2O = 4.79 ppm for ^{1}H NMR). NMR signals are reported as follows: chemical shift (ppm), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (*J*) in Hz, and integration value. The VT-NMR analysis was carried out in a screw cap NMR tube. A capillary containing 0.1M C_6F_6 in $CDCl_3$ was used as a reference for $^{19}F\{^{1}H\}$ NMR. HPLC analysis was conducted using a reverse phase C18 column (100 mm × 2.1 mm i.d., 3 µm), maintained at 25 °C, using the following method file: overall running time = 6 minutes, acetonitrile – 80% and water – 20% as an isocratic mixture; flow rate = 0.2 mL/minute; injection volume = 1 µL. A photodiode array (PDA) detector set at 254 nm. The obtained data was further plotted in OriginLab software 2024. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific-Exactive mass spectrometer operated in Time-of-flight mass spectrometry (TOF-MS) mode upon dissolving in acetonitrile at IISER Berhampur.

2. Experimental Section

2.1 Reaction method development

General procedure for reaction optimization and NMR yield calculation



In an oven-dried 10 mL screw cap reaction vial, styrene (**1a**, 40 μL, 0.344 mmol) and Fmoc-NH_2 (**2a**, 83.3 mg, 0.344 mmol) in $CHCl_3$ (690 μL, 0.5 M) were taken, and triflic acid (1.56 μL, 0.017 mmol, 5 mol%) was added to the mixture and stirred at 60 °C for 12 h in a preheated metal block. The reaction progress was monitored by TLC. After 12 h, to the reaction mixture, 1,3,5-trimethoxy benzene (TMB) (57.9 mg, 0.344 mmol) was added as an NMR standard and stirred for 5 minutes at RT. An aliquot amount (50 μL) was taken in an NMR tube, and 550 μL $CDCl_3$ was added, then ^{1}H NMR was recorded. The percentage of NMR yield was calculated from the crude ^{1}H NMR using the following method.

Procedure followed to isolate the product:

After reaction completion, the reaction mixture was concentrated under reduced pressure. After removal of solvent, the residue was purified by column chromatography on silica gel (200 – 400 mesh) using pet ethers: ethyl acetate binary solvent mixture (100% pet ether to 20% ethyl acetate in pet ethers) to get the (9H-fluoren-9-yl)methyl(1-phenylethyl)carbamate product (**3a**) and 9-(((2,3-dihydro-1H-inden-1-yl)methoxy)methyl)-9H-fluorene product (**4a**).

NMR yield for (9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate (3a):

Molar ratio of the compounds (Product **3a** / TMB) = [(observed integral of **3a** /1) / (observed integral of TMB / 9)].

The molar amount of product **3a** = [molar ratio of the compounds (**3a** / TMB) × mmol of TMB].

Percentage Yield Calculation

NMR yield = molar amount of product **3a** × molecular weight of the product

Percent yield of product = (observed NMR yield / Theoretical yield) × 100

Example of NMR spectrum for yield calculation:

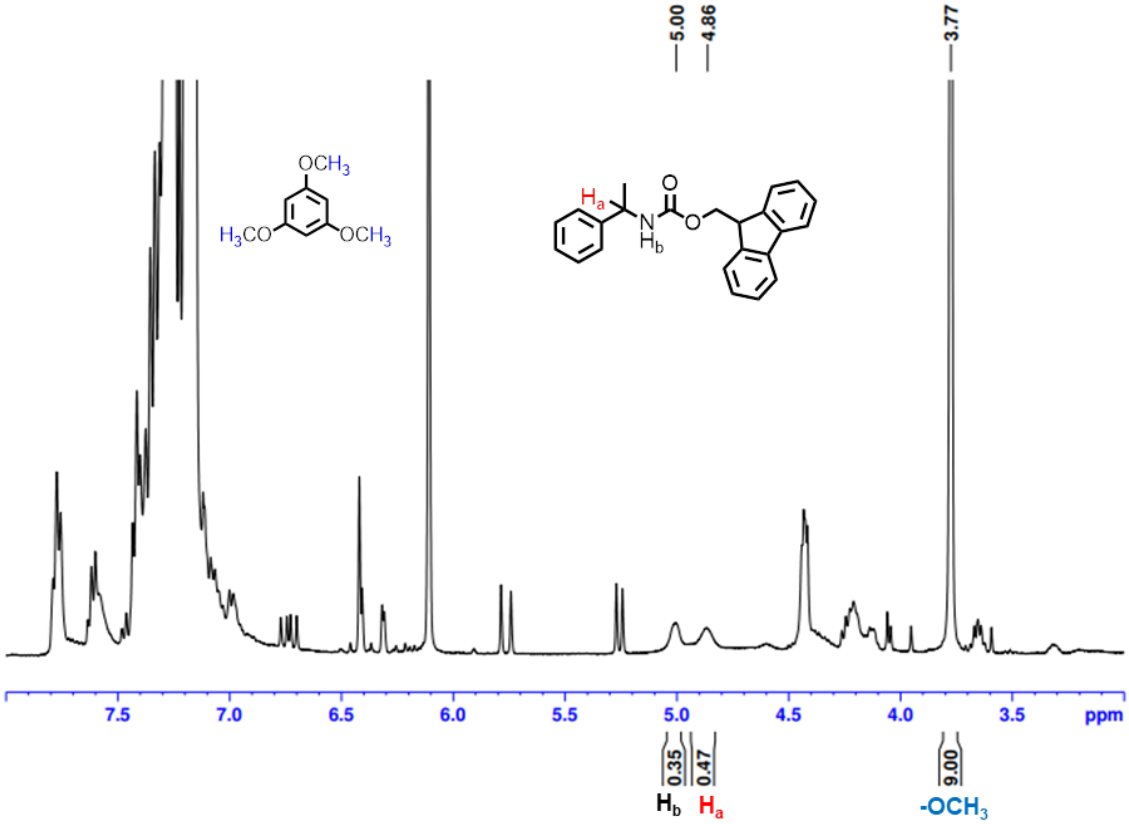


Figure S1: Representative crude ^{1}H NMR analysis of the reaction mixture with 1,3,5-trimethoxybenzene as the internal standard to calculate yield. Styrene: Fmoc-NH_2 = 1:1 at 0.344 mmol scale.

Calculated NMR yield for (9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate (3a):

Molar ratio of the compounds (Product **3a** / TMB) = [(0.47 /1) / (9 / 9)]

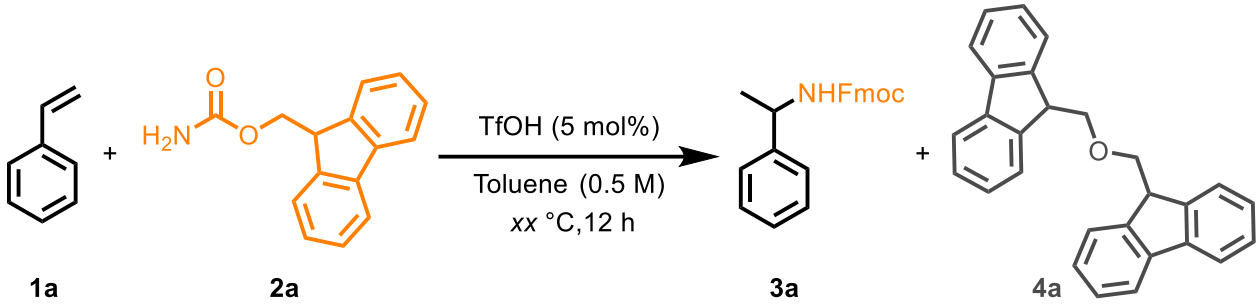
The molar amount of product **3a** = [0.47 × 0.344]

Percentage yield Calculation:

NMR yield = 0.1616 × 343.1572 = 55.61 mg

Percent yield of product = (55.61/118) × 100 = 47%

Table S1. Temperature screening

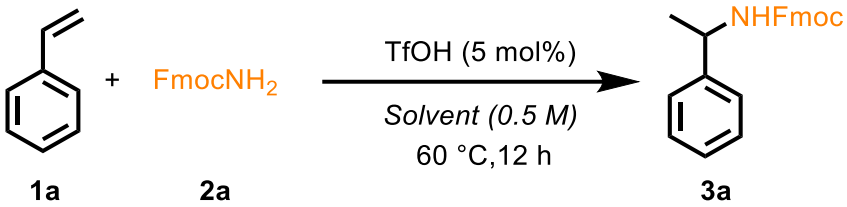


Entry	Temperature (°C)	Time (h)	Yield[a] (%)	
			3a	4a
1.	40	12	0[b]	0
2.	**60**	**12**	**35**	**4[c]**
3.	80	4	47	6[c]
4.	100	12	0	-
5	100	0.5	37	8[c]

Styrene: Fmoc-NH_2 = 1:1 at 0.344 mmol scale. [a] Yield determined by ^{1}H NMR spectroscopy. 1,3,5-trimethoxybenzene was used as an internal standard. [b] Starting material **2a** was not consumed.

[c] Isolated yield after column chromatography.

Table S2. Solvent screening

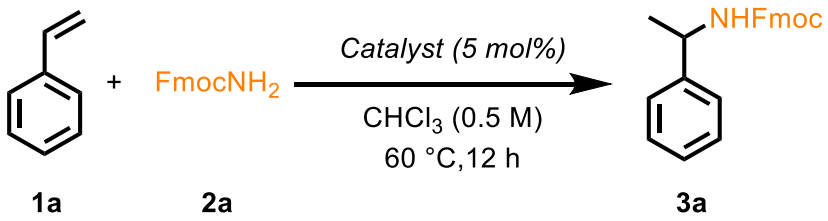


Entry	Solvent	Yield[a] (%)
1.	1,4–Dioxane	0[b]
2.	THF	0[b]
3.	ACN	0[b]
4.	Toluene	35
5.	Cyclohexane	24
6.	DCM[c]	25[d]
7.	*p*-Xylene	33
8.	1,2–DCE	35
9.	**$CHCl_3$**	**47**

Styrene: Fmoc-NH_2 = 1:1 at 0.344 mmol scale. [a] Yield determined by ^1H NMR spectroscopy. 1,3,5-trimethoxybenzene was used as an internal standard. [b] Starting material **2a** was not consumed.

[c] Reaction at room temperature. [d] Isolated yield after column chromatography

Table S3. Catalyst screening



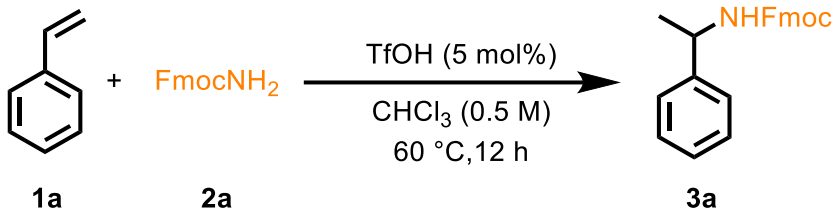
1a **2a** **3a**

Entry	Catalyst	Yield[a] (%)
1.	CF_3COOH	0[b]
2.	CH_3COOH	0[b]
3.	HCOOH	0[b]
4.	$(C_6H_5)_2P(O)OH$	0[b]
5.	*p*-TSA	Trace
6.	1 M $HCl{\cdot}Et_2O$	0[b]
7.	CH_3SO_3H	15
8.	H_2SO_4	31
9.	$(CF_3SO_2)_2NH$	29[c]
10.	**TfOH**	**47**

Styrene: Fmoc-NH_2 = 1:1 at 0.344 mmol scale. [a] Yield determined by ^1H NMR spectroscopy. 1,3,5-trimethoxybenzene was used as an internal standard. [b] Starting material **2a** was not consumed.

[c] **4a** by-product formation was observed and 6% isolated after column purification.

Table S4. Reagent equivalent screening

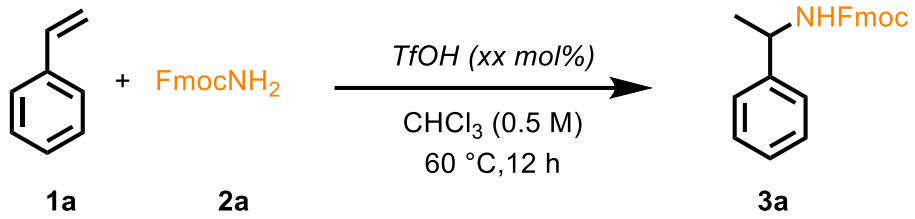


1a **2a** **3a**

Entry	Condition[a] (Styrene: Fmoc-NH_2)	Yield[b] (%)
1.	1:1	47
2.	**3:1**	**63**
3.	4:1	56
4.	1:3	43
5.	3:1	64[c]

[a] Styrene: Fmoc-NH_2 ratio at 0.344 mmol. [b] Yield determined by ^{1}H NMR spectroscopy. 1,3,5-trimethoxybenzene was used as an internal standard. [c] Reaction was conducted under an argon atmosphere and molecular sieves.

Table S5. Catalyst loading screening

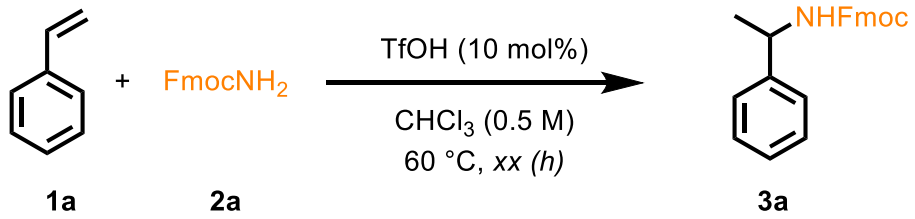


1a **2a** **3a**

Entry	Catalyst Loading	Yield (%)
2.	1 mol %	Trace
3.	5 mol %	47[a]
4.	**10 mol %**	**81[b]**
5.	20 mol %	86[b]

Styrene: Fmoc-NH_2 ratio 3:1 at 0.344 mmol of Fmoc-NH_2. [a] Yield determined by ^{1}H NMR spectroscopy. 1,3,5-trimethoxybenzene was used as an internal standard. [b] Isolated yield after column chromatography.

Table S6. Reaction time screening

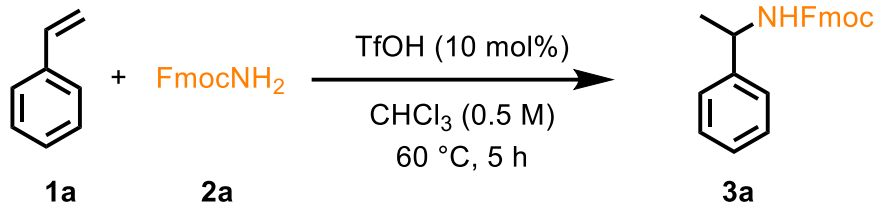


1a **2a** **3a**

Entry	Time (h)	Yield[a] (%)
1.	4	82
2.	**5**	**91**
3.	6	85
4.	7	83
5.	12	81

Styrene: Fmoc-NH_2 = 3:1 at 0.344 mmol scale of Fmoc-NH_2. [a] Yield determined by ^1H NMR spectroscopy. 1,3,5-trimethoxybenzene was used as an internal standard.

Table S7. Control reaction



1a **2a** **3a**

Entry	Condition	Result [a]
1.	Without styrene	No product formation
2.	Without Fmoc-NH_2	No product formation
3.	Without catalyst	No product formation

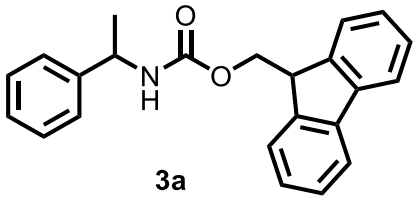
Styrene: Fmoc-NH_2 = 3:1 at 0.344 mmol scale. [a] Adjudged by the TLC.

2.2 Substrate Scope and Characterization Data

General procedure for the substrate scope (GPS-1)

To an oven-dried 10 mL screw cap vial with a PTFE-coated magnetic stir bar (10 mm × 6 mm), Fmoc-NH_2 (**2a**, 121 mg, 0.5 mmol, 1 equiv) and vinyl arene (1.5 mmol, 3 equiv) were added. Then, $CHCl_3$ (0.5 M, 1 mL) was added. Finally, TfOH (0.05 mmol, 10 mol%, 5 μL) was added using a 50 μL glass syringe. Then the vial was closed with a PTFE screw cap and stirred (500 rpm) at 60 °C (pre-heated metal block) for 5 h. After 5 h, TLC was checked using 20% ethyl acetate in hexane. Further, it was purified by silica gel column chromatography (200 – 400 mesh) using 100% pet ether to 20% ethyl acetate in pet ether as a mobile phase.

(9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate (3a):



3a

Procedure: Synthesized from styrene (1.5 mmol, 174 μL) by following the GPS-1 for 5 h.

Large scale reaction: $FmocNH_2$ (1.0 g, 4.14 mmol), styrene (1.5 mL, 12.4 mmol), TfOH (37.4 μL, 0.414 mmol).

TLC profile: 20% ethyl acetate in hexane; R_f = 0.45[1].

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 158 mg; 91% (Large scale: 1.26 g; 89%).

Physical state: White crystalline solid.

Melting point: 79 °C (156°C)[2].

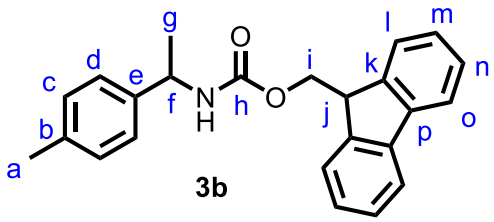
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.59 (br d, *J* = 7.3 Hz, 2H), 7.43–7.29 (m, 9H), 5.06 (br s, 1H), 4.88 (br t, *J* = 6.6 Hz, 1H), 4.43 (br d, *J* = 6.8 Hz, 2H), 4.22 (br t, *J* = 6.9 Hz, 1H), 1.51 (br d, *J* = 5.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.1, 141.4, 128.8, 127.8, 127.5, 127.1, 126.1, 125.1, 125.1, 120.1, 66.6, 50.8, 47.4, 22.5.

Spectral data matches with previously reported literature[1].

MS (HRMS,TOF-MS $[M+Na]^+$): Calcd for $[C_{23}H_{21}NO_2Na]^+$: 366.1470; Found: 366.1482.

(9H-fluoren-9-yl)methyl(1-(p-tolyl)ethyl)carbamate (3b):



3b

Procedure: Synthesized from 4-methyl styrene (1.5 mmol, 198 μL) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.55.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 130 mg; 73%.

Physical state: White crystalline solid.

Melting point: 132 °C.

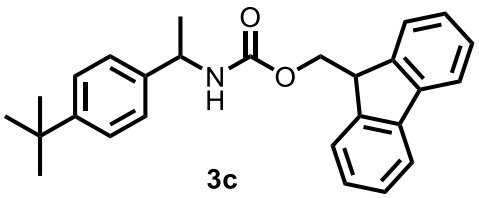
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 2H; H_l), 7.61 (br d, *J* = 7.1 Hz, 2H; H_o), 7.42 (t, *J* = 7.3 Hz, 2H; H_m), 7.33 (br t, *J* = 8.1 Hz, 2H; H_n), 7.22–7.13 (m, 4H; $H_{c\ \&\ d}$), 5.08 (br s, 1H; *NH*), 4.86 (br t, *J* = 7.6 Hz, 1H; H_f), 4.43 (d, *J* = 6.4 Hz, 2H; H_i), 4.22 (br t, *J* = 6.2 Hz, 1H; H_j), 2.37 (s, 3H; H_a), 1.50 (d, *J* = 5.9 Hz, 3H; H_g).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7 (C_h), 144.1 (C_k), 141.4 (C_p), 140.6 (C_e), 137.1 (C_b), 129.4 (C_d), 127.7 (C_m), 127.1 (C_n), 126.0 (C_c), 125.1 (C_o), 120.0 (C_l), 66.6 (C_i), 50.5 (C_f), 47.4 (C_j), 22.4 (C_g), 21.2 (C_a).

Hydrogen and carbon peaks were assigned with the help of DEPT-135 and 2D NMR.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{24}H_{23}NO_2Na]^+$: 380.1621; Found: 380.1641.

(9H-fluoren-9-yl)methyl (1-(4-(tert-butyl)phenyl)ethyl)carbamate (3c):



3c

Procedure: Synthesized from 4-*tert*-butyl styrene (1.5 mmol, 275 μL) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.45.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 162 mg; 81%.

Physical state: obtained as a pale-yellow oil, which turns to a yellowish-white puffy solid while drying under a high vacuum.

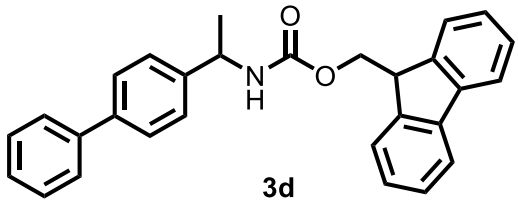
Melting point: 59 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.59 (br d, *J* = 6.6 Hz, 2H), 7.42–7.38 (m, 4H), 7.36–7.31 (br s, 2H), 7.26–7.24 (m, 2H; merges with $CDCl_3$), 5.01 (br s, 1H), 4.86 (br s, 1H), 4.42 (d, *J* = 6.7 Hz, 2H), 4.21 (t, *J* = 6.7 Hz, 1H), 1.50 (d, *J* = 6.1 Hz, 3H), 1.33 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 150.4, 144.1, 141.4, 140.4, 127.8, 127.2, 125.9, 125.7, 125.2, 125.2, 120.1, 66.6, 50.4, 47.4, 34.6, 31.5, 22.3.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{27}H_{29}NO_2Na]^+$: 422.2096; Found: 422.2105.

(9H-fluoren-9-yl)methyl (1-([1,1'-biphenyl]-4-yl)ethyl)carbamate (3d):



3d

Procedure: Synthesized from 4-phenyl styrene (1.5 mmol, 270 mg) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.39.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 132 mg; 63%.

Physical state: obtained as a colorless oil, which turns into a white puffy solid while drying under a high vacuum.

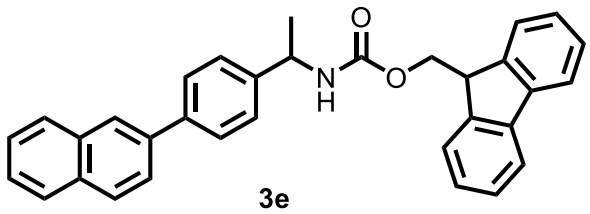
Melting point: 83 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (br s, 2H), 7.63–7.50 (m, 6H), 7.48–7.35 (m, 9H), 5.13 (br s, 1H), 4.95 (br s, 1H), 4.48 (br d, *J* = 6.1 Hz, 2H), 4.25 (br s, 1H), 1.55 (br d, *J* = 5.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.0, 142.6, 141.4, 140.9, 140.4, 128.9, 127.8, 127.5, 127.4, 127.2, 127.1, 126.5, 125.1, 120.1, 66.6, 50.5, 47.4, 22.5.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{29}H_{25}NO_2Na]^+$: 442.1783; Found: 442.1797.

(9H-fluoren-9-yl)methyl (1-(naphthalen-2-yl)ethyl)carbamate (3e):



3e

Procedure: Synthesized from 2-(4-vinylphenyl)naphthalene (1.5 mmol, 316 μL) by following the GPS-1 for 3 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.44.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 135 mg; 57%.

Physical state: White solid.

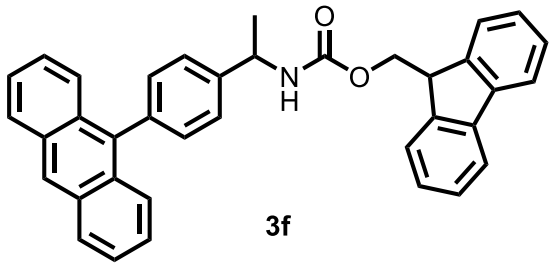
Melting point: 108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.95–7.88 (m, 4H), 7.78–7.71 (m, 5H), 7.63 (br s, 2H), 7.52 (br s, 2H), 7.42 (br s,3H), 7.34 (br s, 2H), 5.13 (br s, 1H), 4.96 (br s, 1H), 4.48 (d, *J* = 4.2 Hz, 2H), 4.25 (br s, 1H), 1.55 (d, *J* = 5.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.0, 142.7, 141.4, 140.3, 138.2, 133.8, 132.7, 128.6, 128.3, 127.8, 127.2, 126.6, 126.4, 126.3, 126.1, 125.8, 125.6, 125.1, 125.1, 120.1, 66.6, 50.5, 47.4, 22.5.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{33}H_{27}NO_2Na]^+$: 492.1939; Found: 492.1943.

(9H-fluoren-9-yl)methyl (1-(4-(anthracen-9-yl)phenyl)ethyl)carbamate (3f):



3f

Procedure: Synthesized from 9-(4-vinylphenyl)anthracene (1.5 mmol, 465 μL) by following the GPS-1 for 4 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.43.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 135 mg; 52%.

Physical state: Yellow solid.

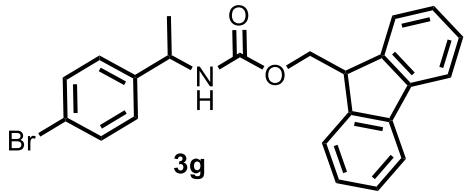
Melting point: 144 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.68–7.66 (m, 4H), 7.48–7.44 (m, 4H), 7.42–7.41 (m, 4H), 7.35–7.33 (m, 4H), 5.16 (br s, 1H), 5.06 (br s, 1H), 4.52 (d, *J* = 4.6 Hz, 2H), 4.27 (br s, 1H), 1.63 (br s, 3H; merges with H_2O peak).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.9, 144.1, 144.1, 141.5, 137.9, 136.7, 131.7, 131.5, 130.4, 128.5, 127.8, 127.2, 127.0, 126.7, 126.1, 125.5, 125.2, 125.1, 120.1, 66.7, 50.7, 47.5, 22.6.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{37}H_{29}NO_2Na]^+$: 542.2096; Found: 542.2103.

(9H-fluoren-9-yl)methyl (1-(4-bromophenyl)ethyl)carbamate (3g):



3g

Procedure: Synthesized from 4-bromostyrene (1.5 mmol, 200 μL) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.42.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ethers).

Yield: 154 mg; 73%.

Physical state: White solid.

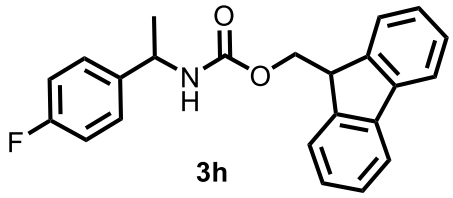
Melting point: 156 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.8 Hz, 2H), 7.57 (br s, 2H), 7.46–7.39 (m, 4H), 7.31–7.29 (br s, 2H), 7.16 (d, *J* = 5.9 Hz, 2H), 5.01 (br s, 1H), 4.80 (br s, 1H), 4.43 (br s, 2H), 4.19 (br s, 1H), 1.45 (br d, *J* = 4.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.6, 143.9, 142.7, 141.4, 131.8, 127.8, 127.2, 125.0, 121.2, 120.1, 120.1, 66.6, 50.3, 47.4, 22.4.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{23}H_{20}BrNO_2Na]^+$: 444.0575; Found: 444.0578.

(9H-fluoren-9-yl)methyl (1-(4-fluorophenyl)ethyl)carbamate (3h):



3h

Procedure: Synthesized from 4-fluorostyrene (1.5 mmol, 180 μL) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.50.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 123 mg; 68%.

Physical state: Obtained as white oil and crystallizes slowly.

Melting point: 80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.58 (br s, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.35–7.26 (m, 4H; merges with $CDCl_3$), 7.02 (t, *J* = 8.6 Hz, 2H), 5.03 (br s, 1H), 4.84 (br s, 1H), 4.44 (d, *J* = 6.0 Hz, 2H), 4.20 (br s, 1H), 1.47 (br d, *J* = 4.9 Hz, 3H).

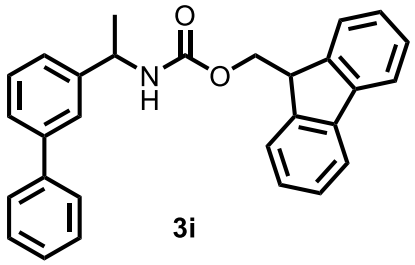
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.5 Hz), 155.7, 144.0, 144.0, 141.5, 127.8, 127.7 (d, *J* = 8.7 Hz; *partially overlaps with 127.8 peak*), 127.2, 125.1, 120.1, 115.6 (d, *J* = 21.3 Hz), 66.6, 50.2, 47.4, 22.5.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ –115.4.

Some minor peaks were also in ^{19}F{^{1}H} *observed that could not be identified.*

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{23}H_{20}FNO_2Na]^+$: 384.1376; Found: 384.1382.

(9H-fluoren-9-yl)methyl (1-([1,1'-biphenyl]-3-yl)ethyl)carbamate (3i):



3i

Procedure: Synthesized from 3-vinyl-1,1'-biphenyl (1.5 mmol, 193 μL) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.45.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 80 mg; 38%.

Physical state: obtained as an off-white gel, which turns to an off-white puffy solid while drying under a high vacuum.

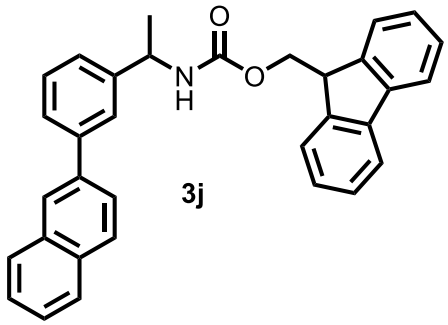
Melting point: 136 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (br d, *J* = 6.2 Hz, 2H), 7.66–7.64 (m, 3H), 7.56 (br d,*J* = 7.5 Hz, 2H), 7.52–7.40 (m, 8H), 7.34 (br d, *J* = 6.9 Hz , 2H), 5.27 (d, *J* = 5.8 Hz, 1H), 5.00 (br s, 1H), 4.50 (d, *J* = 6.2 Hz 2H), 4.26 (br s, 1H), 1.56 (d, *J* = 3.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.0, 141.7, 141.4, 141.1, 129.2, 128.8, 128.8, 127.7, 127.5, 127.3, 127.1, 126.3, 125.1, 125.0, 124.9, 120.0, 66.6, 50.8, 47.3, 22.5.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{29}H_{25}NO_2Na]^+$: 442.1783; Found: 442.1793.

(9H-fluoren-9-yl)methyl(1-(3-(naphthalen-2-yl)phenyl)ethyl)carbamate (3j):



3j

Procedure: Synthesized using 2-(3-vinylphenyl)naphthalene (1.5 mmol, 346 mg) by following the GPS-1 for 5 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.43.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 98 mg; 42%.

Physical state: White solid, obtained as an off-white gel, given a pet ether wash and drying on high vacuum, obtained as a puffy white solid.

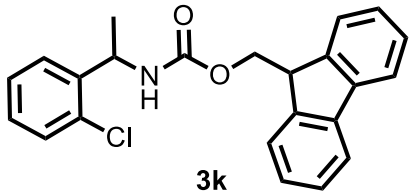
Melting point: 134 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.95–7.88 (m, 3H), 7.78–7.75 (m, 3H), 7.68 (br s, 1H), 7.64–7.61 (m, 2H), 7.53–7.46 (m, 4H), 7.39–7.36 (br s, 2H), 7.34–7.31 (m, 3H), 5.17 (br s, 1H), 4.99 (br s, 1H), 4.47 (d, *J* = 4.2 Hz, 2H), 4.24 (br s, 1H), 1.59 (d, *J* = 5.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.2, 144.0, 141.7, 141.4, 138.5, 133.8, 132.8, 132.7, 129.4, 128.6, 128.3, 127.8, 127.2, 126.6, 126.5, 126.1, 126.0, 125.7, 125.1, 125.1, 124.8, 120.1, 66.7, 50.9, 47.4, 22.7.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{33}H_{27}NO_2Na]^+$: 492.1939; Found: 492.1930.

(9H-fluoren-9-yl)methyl (1-(2-chlorophenyl)ethyl)carbamate (3k):



3k

Procedure: Synthesized using 1-chloro-2-vinylbenzene (1.5 mmol, 193 μL) by following the GPS-1 for 8 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.45.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 27 mg; 14%.

Physical state: obtained as an off-white gel, which turns to an off-white solid while drying under vacuum.

Melting point: 82 °C.

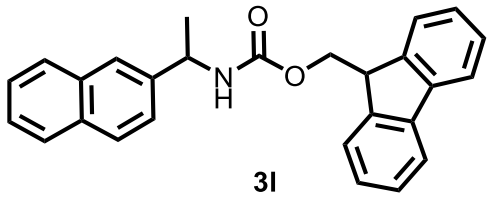
Note: *Undergoes slow decomposition during high vacuum or heat.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (br d, *J* = 7.64 Hz, 2H), 7.60 (d, *J* = 6.12 Hz, 2H), 7.42–7.35 (m, 3H), 7.34–7.30 (m, 3H), 7.24–7.21 (m, 2H; merges with $CDCl_3$), 5.25–5.18 (m, 2H), 4.41 (d, *J* = 6.70 Hz, 2H), 4.21 (br s, 1H), 1.49 (d, *J* = 5.88 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.4, 144.0, 141.4, 130.2, 128.5, 127.8, 127.5, 127.3, 127.1, 126.9, 125.1, 120.1, 119.9, 66.7, 48.8, 47.4, 21.4.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{23}H_{20}ClNO_2Na]^+$: 400.1080; Found: 400.1089.

(9H-fluoren-9-yl)methyl (1-(naphthalen-2-yl)ethyl)carbamate (3l):



3l

Procedure: Synthesized using 2-vinylnaphthalene (1.5 mmol, 232 mg) by following the GPS-1 for 4 h.

TLC profile: 20% ethyl acetate in hexane; R_f = 0.45.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 114 mg; 58%

Physical state: obtained as an off-white gel, which turns to an off-white solid while drying under a high vacuum.

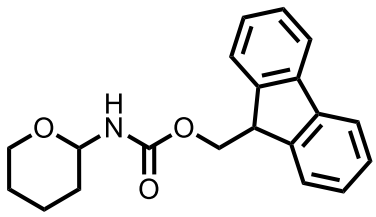
Melting point: 98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.0 Hz, 1H), 7.59–7.56 (m, 5H), 7.46–7.33 (m, 9H), 5.05 (br s, 1H), 4.91 (br d, *J* = 5.3 Hz, 1H), 4.44 (br d, *J* = 6.5 Hz, 2H), 4.22 (br s, 1H), 1.53 (d, *J* = 4.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.1, 141.4, 133.5, 132.9, 128.7, 128.7, 128.5, 128.1, 127.8, 127.1, 126.3, 126.0, 125.5, 125.1, 124.5, 120.1, 66.7, 50.9, 47.4, 22.5.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{27}H_{23}NO_2Na]^+$: 416.1626; Found: 416.1629.

9H-Fluoren-9-ylmethyl (tetrahydropyran-2-yl)carbamate (3m):



3m

Procedure: Synthesized using 3,4-dihydro-2H-pyran (1.5 mmol, 140 μL) by following the GPS-1 for 10 min.

Large scale reaction: $FmocNH_2$ (1.0 g, 4.14 mmol), 3,4-dihydro-2H-pyran (1.2 mL, 12.4 mmol), TfOH (37.4 μL, 0.414 mmol).

TLC profile: 20% ethyl acetate in hexane; R_f = 0.32.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in pet ether).

Yield: 117 mg; 72% (Large scale: 1 g; 74%).

Physical state: White solid.

Melting point: 136 °C.

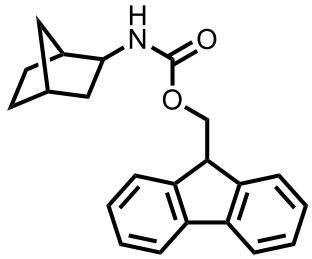
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 5.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 5.52 (br d, *J* = 7.1 Hz, 1H), 4.90 (br s, 1H), 4.41 (br s, 2H), 4.22 (s, 1H), 3.98 (d, *J* = 10.9 Hz, 1H), 3.58 (br s, 1H), 1.88–1.79 (m, 3H), 1.57–1.51 (m, 2H; *merges with H_2O*), 1.41–1.38 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.6, 144.0, 141.4, 127.8, 127.2, 125.2, 120.1, 80.1, 67.3, 67.1, 47.2, 31.5, 25.1, 23.0.

Spectral data matches with previously reported literature[3].

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{20}H_{21}NO_3Na]^+$: 346.1419; Found: 346.1437.

(9H-fluoren-9-yl)methyl (1S,4R)-bicyclo[2.2.1]heptan-2-ylcarbamate (3n):



3n

Procedure: Synthesized using (1R,4S)-bicyclo[2.2.1]hept-2-ene (1.5 mmol, 141 mg) by following the GPS-1 for 5 h.

TLC profile: 20% Ethyl acetate in hexane; R_f = 0.45.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% Ethylacetate in pet ether).

Yield: 103 mg; 62%.

Physical state: white crystalline solid.

Melting point: 135 °C.

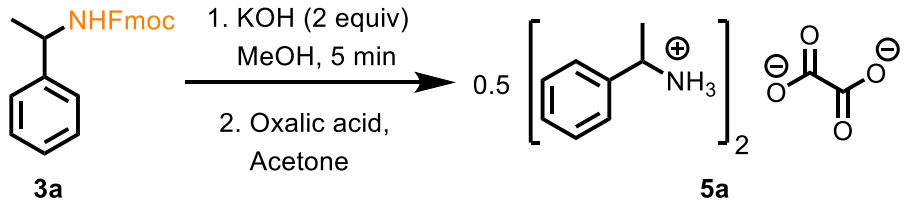
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 4.63 (br s, 1H), 4.40 (d, *J* = 5.1 Hz, 2H), 4.21 (br s, 1H), 3.53 (br s, 1H), 2.24 (t, *J* = 13.2 Hz, 2H), 1.78 (d, *J* = 8.3 Hz, 1H), 1.48–1.43 (m, 2H), 1.30–1.26 (m, 2H), 1.14–1.12 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.8, 144.2, 141.5, 127.8, 127.1, 125.2, 120.1, 66.5, 54.5, 47.5, 42.5, 40.5, 35.8, 35.5, 28.3, 26.4.

MS (HRMS, TOF-MS $[M+Na]^+$): Calcd for $[C_{22}H_{23}NO_2Na]^+$: 356.1627; Found: 356.1639.

2.3 Deprotection of hydroamination product

Deprotection of (9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate (3a)



3a **5a**

In a 10 mL RB, (9H-fluoren-9-yl)methyl (1-phenylmethyl)carbamate (**3a**, 180 mg, 0.524 mmol) was taken in methanol (0.25 M), and 2 equiv KOH (58.8 mg, 1.05 mmol) were added and stirred at RT for 5 min, after the completion of the reaction (monitored by TLC, 20% ethyl acetate in hexane) reaction mixture was concentrated under reduced pressure. Water was added to the residue, and the organic compound was extracted with DCM. The organic layers combined and were concentrated under reduced pressure. The crude product was dissolved in acetone (0.5 M), and an acetone solution (0.5 M) of 1.5 equiv of oxalic acid (70.8 mg, 0.786 mmol) was added dropwise into it. Resulted precipitate was filtered out and washed with acetone to remove the excess oxalic acid.

1-Phenylethylamineoxalate (5a)

Yield: 64 mg; 58%.

Physical state: White solid.

Melting point: 178 °C.

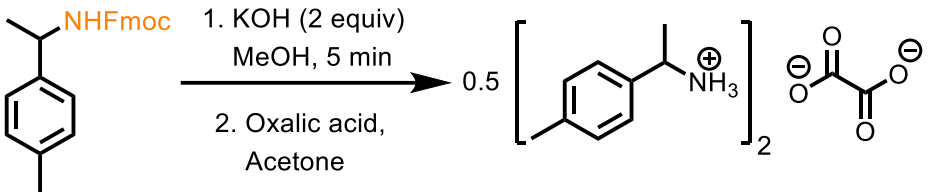
^{1}H NMR (400 MHz, D_2O) δ 7.51–7.47 (m, 5H), 4.55 (q, *J* = 6.8 Hz, 1H), 1.66 (3H, d, *J* = 7.2 Hz).

^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 173.3, 137.8, 129.3, 129.2, 126.5, 51.0, 19.3.

Spectral data matches with previously reported literature[4]*.*

MS (HRMS, TOF-MS): Cacld for $[M–C_2O_4NH_3]^+ = [C_8H_9]^+$: 105.0704, Found: 105.0707.

Deprotection of (9H-fluoren-9-yl)methyl (1-(*p*-tolyl)ethyl)carbamate (3b)



3b **5b**

In a 10 mL RB (9H-fluoren-9-yl)methyl (1-(*p*-tolyl)ethyl)carbamate (187 mg, 0.524 mmol) was taken in Methanol (0.25 M), and 2 equiv KOH (58.8 mg, 1.05 mmol) were added and stirred at RT for 5 min. After the completion of the reaction (monitored by TLC, 20 % ethyl acetate in hexane), the reaction mixture was concentrated under reduced pressure, and a water workup was done with DCM. The organic layer collected was concentrated under reduced pressure. The crude product was dissolved in acetone (0.5 M), and an acetone solution (0.5 M) of 1.5 equiv of oxalic acid (70.8 mg, 0.786 mmol) was added dropwise into it. Resulted precipitate was filtered out and washed with acetone to remove the excess oxalic acid

1-(*p*-tolyl)ethanaminium oxalate (5b):

Yield: 94 mg; 80%.

Physical state: White solid.

Melting point: 198 °C.

^{1}H NMR (400 MHz, D_2O) δ 7.36–7.30 (m, 4H), 4.49 (q, J = 6.8 Hz, 1H), 2.33 (s, 3H), 1.61 (d, J = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 167.9, 139.5, 134.8, 129.7, 126.5, 50.7, 20.1, 19.2.

MS (HRMS, TOF-MS): Cacld for $[M–C_2O_4NH_3]^+ = [C_9H_{11}]^+$: 119.0861, Found: 119.0870.

2.4 Reaction mechanistic analysis:

NMR analysis

$^{19}F\{^{1}H\}$ NMR analysis:

To an oven-dried screw cap NMR tube containing C_6F_6 (0.1 M in $CDCl_3$) in a closed capillary, 0.5 mL $CDCl_3$ was added, followed by TfOH (50 μL,1 equiv) (*Note: white turbidity was observed*). After recording $^{19}F\{^{1}H\}$ NMR, Fmoc-NH_2 (**2a**; 6 mg; × 10 times) / hydroamination product (**3a**; 8.9 mg × 10 times) was added portion-wise (0.1 equiv to 1 equiv; like titration), and $^{19}F\{^{1}H\}$ NMR was recorded.

Note: The NMR tube was carefully tilted up and down to get a proper mixing, and C_6F_6 was used as a reference –165 ppm.

a) After adding 0.2 equiv Fmoc-NH_2, a new peak was observed at –80.6 ppm, and the TfOH peak (–79.1 ppm) completely disappeared[5]. Adding 0.5 equiv. and 1 equiv. Fmoc-NH_2 resulted in a slight shift (–81.4 and –81.7 ppm)

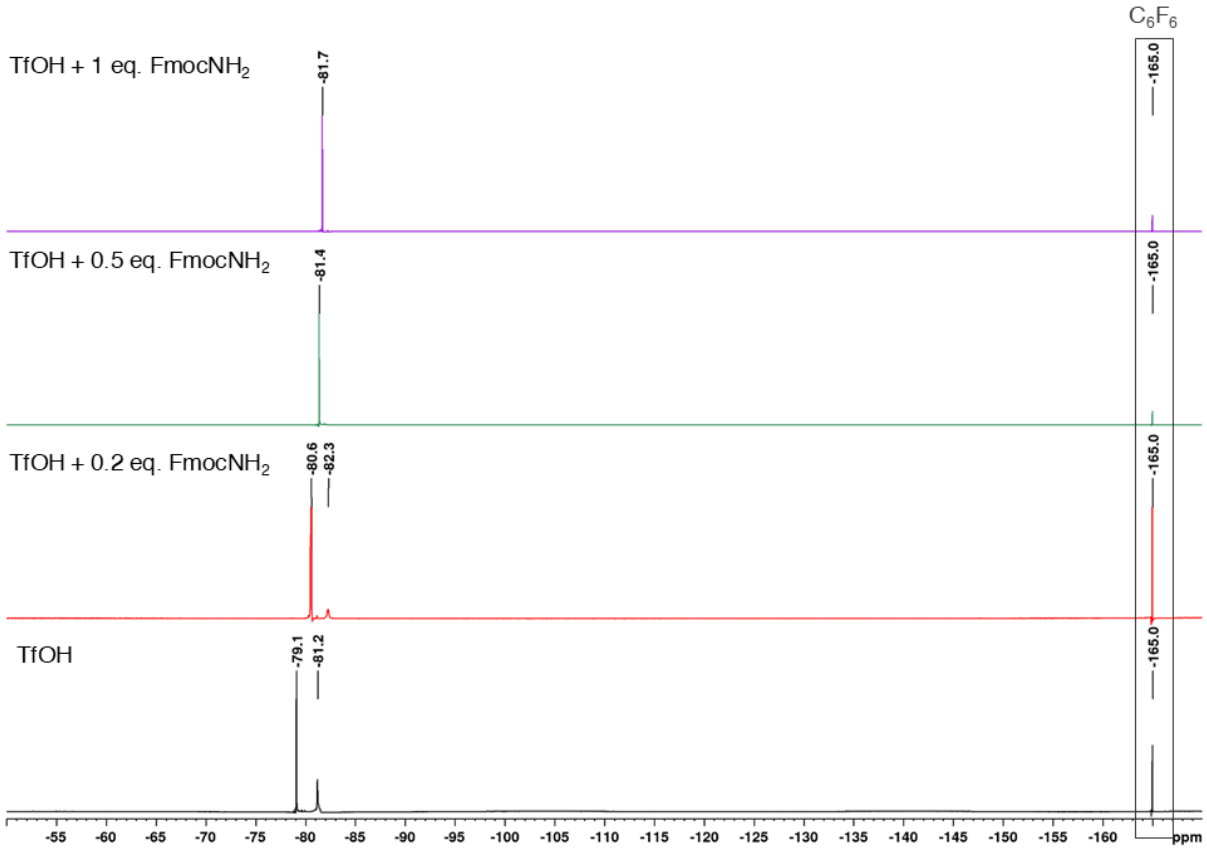


Figure S2: $^{19}F\{^{1}H\}$ NMR analysis of Fmoc-NH_2 with gradually added TfOH (0.2 eq., 0.5 eq., and 1 eq.)

b) After adding 0.2 equiv **3a,** a new peak was observed at –80.4, and the TfOH peak (–79.1 ppm) disappeared completely[5]. Adding 0.5 equiv. and 1 equiv. **3a**, resulted in a slight shift (–81.0 and –81.6 ppm).

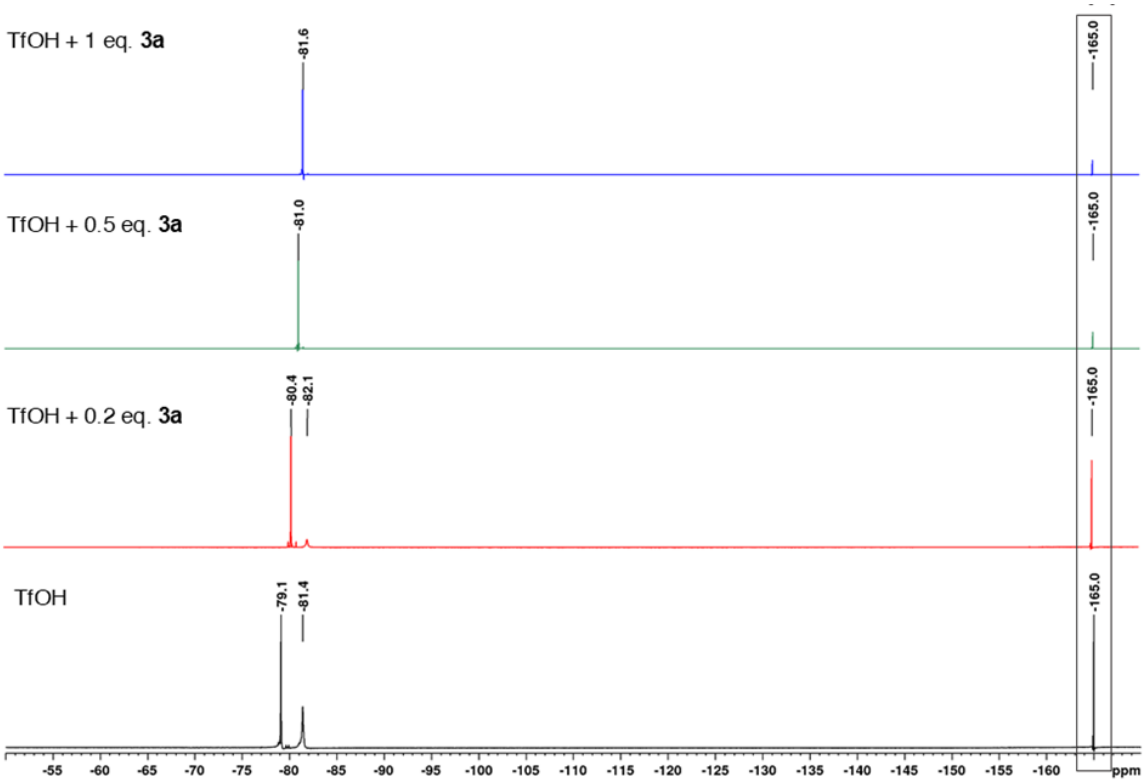
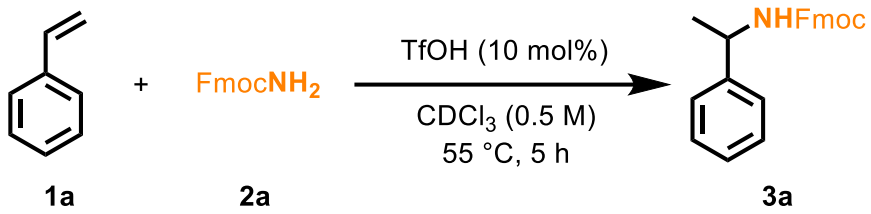


Figure S3: $^{19}F\{^{1}H\}$ NMR analysis of **3a** with gradually added TfOH (0.2 eq., 0.5 eq., and 1 eq.)

.

$^{19}F\{^{1}H\}$ NMR reaction monitoring at 55 °C:



To an oven-dried screw cap NMR tube containing C_6F_6 (0.1 M in $CDCl_3$) in a closed capillary, $CDCl_3$ (0.5 M, 0.5 mL) was added using an oven-dried needle with a glass syringe, followed by TfOH (0.025 mmol, 10 mol%, 2.5 μL). After recording ^{1}H and $^{19}F\{^{1}H\}$ NMR, Fmoc-NH_2 (**2a**, 60.5 mg, 0.25 mmol, 1 equiv) was added, and ^{1}H and $^{19}F\{^{1}H\}$ NMR were recorded. At last, styrene (**1a**, 0.75 mmol, 3 equiv, 87 μL) was added, and ^{1}H and $^{19}F\{^{1}H\}$ NMR were recorded.

Then, the NMR probe temperature was raised to 55 °C gradually, and $^{19}F\{^{1}H\}$ NMR was recorded every hour.

Note: Due to the limited solubility of Fmoc-NH_2 and shimming issues, ^{1}H NMR could not be recorded. Peaks were analyzed by keeping C_6F_6 as a reference at –165 ppm.

The addition of TfOH to $CDCl_3$ results in immediate white turbidity. In $^{19}F\{^{1}H\}$ NMR, two peaks were observed at –79.1 ppm, corresponding to homogenously dissolved TfOH, and a small broad peak at –82.4 ppm due to immediate moisture absorption. These data closely agreed with the previously reported chemical shift values and studies[5,6].

Adding Fmoc-NH_2 to this results in the interaction between Fmoc-NH_2 and TfOH. After adding styrene to this, no changes were observed in $^{19}F\{^{1}H\}$ NMR chemical shift values. The $^{19}F\{^{1}H\}$ NMR recorded each hour shows the overlapping of two peaks at –81.2 ppm. This showed that $FmocNH_2$ (**2a**) and hydroamination product (**3a**) have hydrogen bonding interaction with TfOH during the reaction, and no free TfOH was observed.

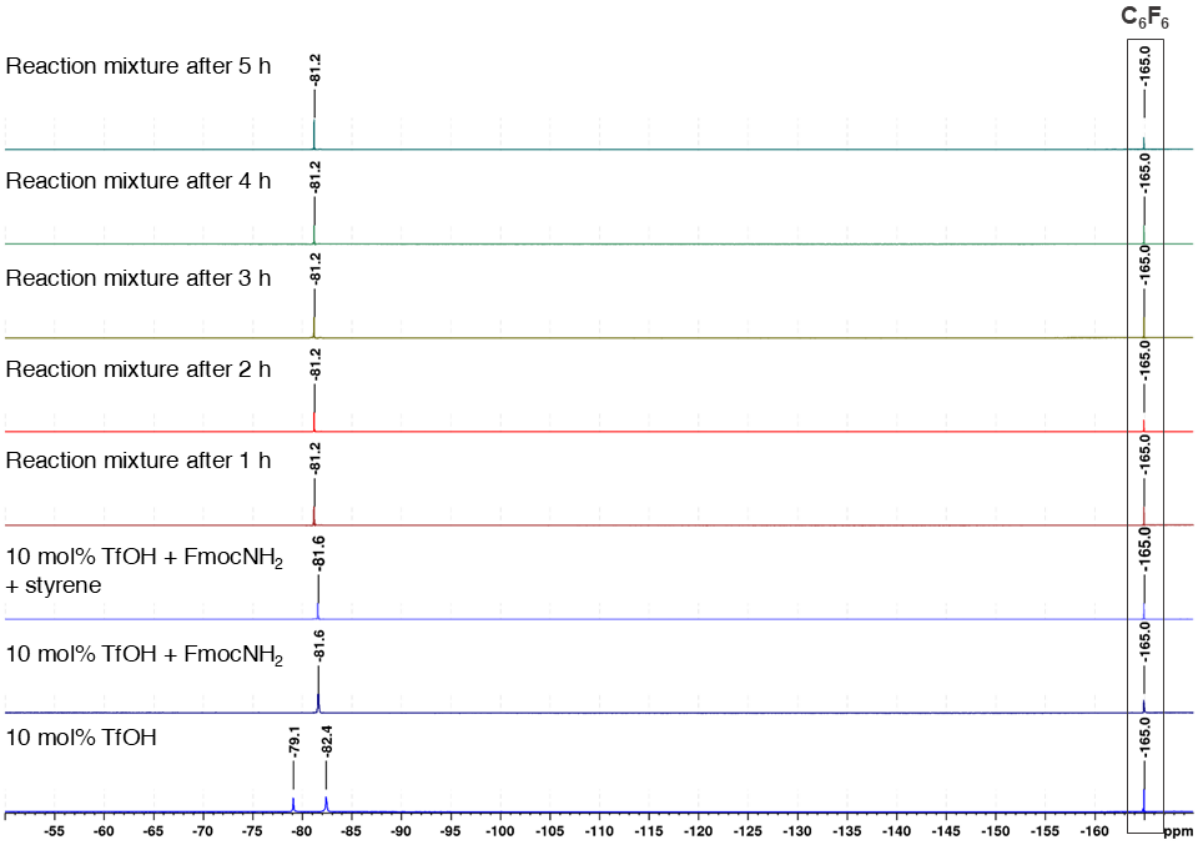


Figure S4: Stacked $^{19}F\{^{1}H\}$ NMR spectra of reaction monitored at 55 °C.

^{1}H NMR analysis:

To an oven-dried NMR tube (separate analysis), styrene (**1a**; 0.75 mmol, 3 equiv, 87 μL) / Fmoc-NH_2 (**2a**; 60.5 mg, 0.25 mmol, 1 equiv) / hydroamination product (**3a**; 89.2 mg, 0.25 mmol, 1 equiv)was added, followed by 0.5 mL $CDCl_3$. After recording ^{1}H NMR, TfOH was added gradually (0.1 equiv. to 1 equiv.), and ^{1}H was recorded after each addition.

Note: The NMR tube was carefully tilted up and down to get proper mixing.

a) After adding 0.1 equiv of TfOH (10 mol%) to the styrene, immediate decomposition and color change were observed (**Figure S5**). Adding further, TfOH did not show any further changes[7].

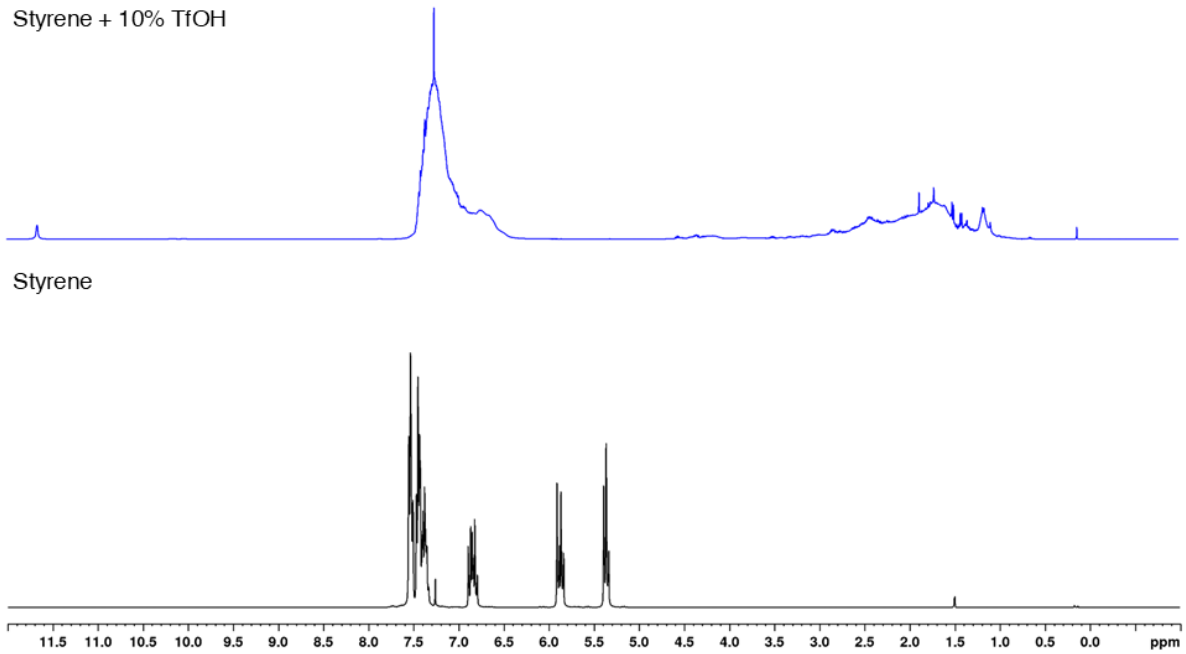


Figure S5: ^{1}H NMR analysis of styrene with TfOH

b) Adding 0.2 equiv of TfOH to Fmoc-NH_2 results in the disappearance of the NH peak at 4.71 ppm and a new broad peak at 8.69 ppm. Adding 0.5 equiv results in the peak shifting to 9.66 ppm and broadening. After reaching 1 equiv. of TfOH, a broad peak was observed at 13.03 ppm. Also, the CH_2 peak (doublet; 4.42 ppm) and CH peak (triplet; 4.24 ppm) showed considerable deshielding as they moved to 4.62 ppm and 4.25 ppm, respectively.

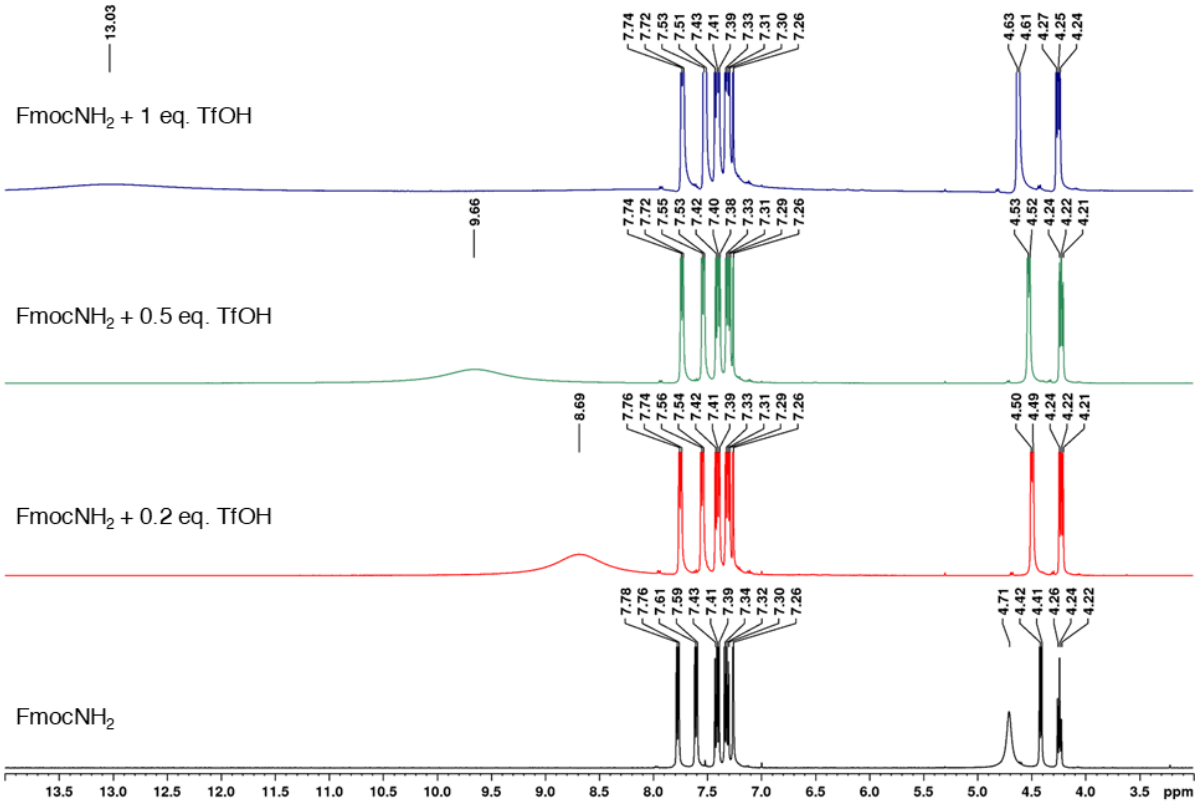
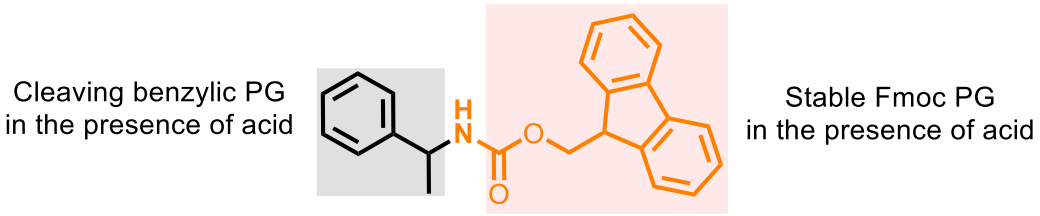


Figure S6: ^{1}H NMR analysis of Fmoc-NH_2 with TfOH

The CO group may also get protonated (like the protonation of carbamic acids), which is well known for carbamate groups[8–10]. However, the observed pattern shows that NH_2 peaks were immediately undergoing exchange, and slowly, C=O may get protonated reversibly.

c) Adding 0.1 equiv of TfOH to **3a** results in the partial disappearance of the NH peak at 5.24 ppm and a new broad peak at 10.07 ppm. Adding 0.2 equiv results in a complete conversion of the NH peak at 5.25 ppm and a new broad peak at 12.55 ppm. After reaching 0.5 equiv and 1 equiv of TfOH, a broad peak was observed at 13.67 ppm and 14.14 ppm, respectively. While the CH proton of benzylic carbon results in slow decomposition due to benzylic deprotection by strong acids[11].



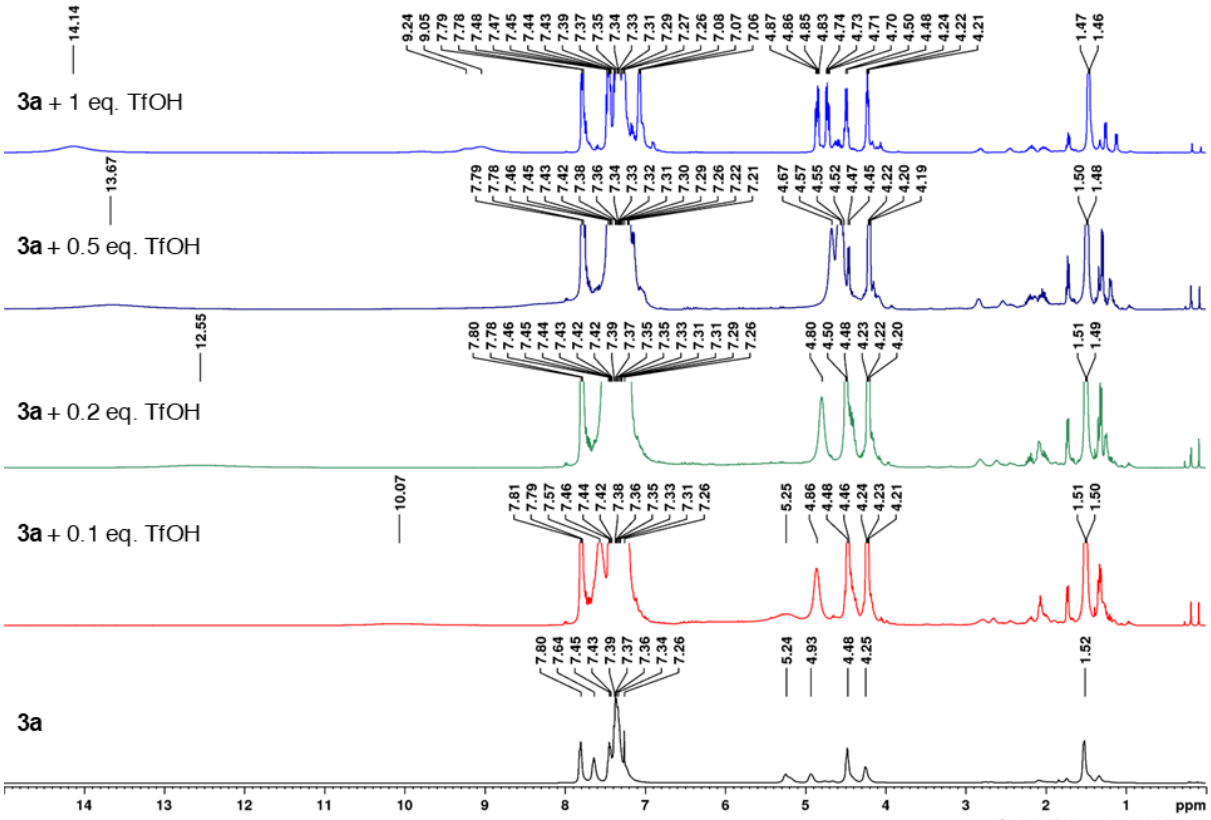


Figure S7: ^{1}H NMR analysis of **3a** with TfOH

The CO group may also get protonated (like the protonation of carbamic acids), which is well known for carbamate groups[8,9,12]. However, the NH proton's fast exchange was observed. Due to the decomposition and this competitive protonation, assigning becomes impractical.

Kinetic analysis[13–17]

The reaction progress was monitored by LC-MS instrument using the HPLC reverse phase C18 column (100 mm × 2.1 mm i.d., 3 µm), using the optimized method file mentioned below, and the photodiode array (PDA) detector set at 254 nm.

Overall running time: 6 minutes, acetonitrile – 80% and water – 20% as an isocratic mixture; flow rate = 0.2 mL/minute; injection volume = 1 µL.

General procedure followed for the kinetic analysis:

Reaction setup for the standard reaction:

To a 30 mL oven-dried reaction vial with a magnetic stir bar (15 mm × 6 mm), Fmoc-NH_2 (**2a**, 242 mg, 1 mmol, 1 equiv.) was added, followed by styrene (**1a**, 316 mg, 3 mmol, 3 equiv., 348 µL). 2 mL of CHCl3 (0.5 M) was added to the resulting white slurry. Finally, CF_3SO_3H (15.3 mg, 10 mol%, 9 µL)) was added using a 100 µL glass syringe. It was closed with a PTFE screw cap and placed in a pre-heated metal block at 60 °C for 6 hours with stirring (500 rpm).

The same procedure was followed for the different excess experiments of FmocNH_2, styrene, and catalyst loading. The reagent volume was recalculated according to the changes.

Sample preparation for HPLC analysis:

Every 30 minutes, the reaction vial was removed from the heating block and allowed to cool down for a minute. 10 µL of reaction crude aliquot was taken out using a 100 µL micropipette and diluted to 2 mL using acetonitrile in a vial. It was further analyzed after obtaining the data from HPLC analysis.

(Due to the limited solubility of Fmoc-NH_2, a tip was completely dipped into the bottom of the reaction mixture to take aliquot)

Concentration calculation and VTNA plotting:

The concentration of the formed product was calculated from the observed area in LC using a calibrated method file and linear fitting method. The obtained concentration was multiplied by the dilution factor to get the actual reaction mixture concentration. The obtained concentrations from all the reactions were plotted in the Variable Time Normalization Analysis (VTNA) Excel sheet developed by Prof. Jordi Burés and co-workers. The average time and obtained concentrations were used for the final plots and the error bar.

Note: Some samples showed a slight drift in the retention time. However, the MS(ESI) m/z data confirmed the presence of the compound.

Calibration curve for 1a, 2a and **3a:**

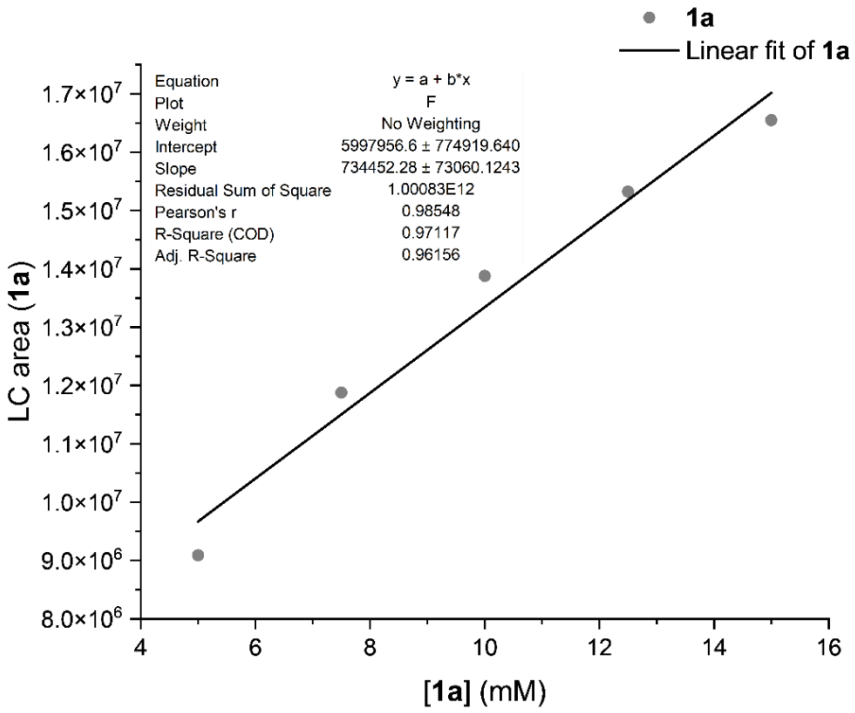


Figure S8: HPLC calibration curve of styrene (**1a)**

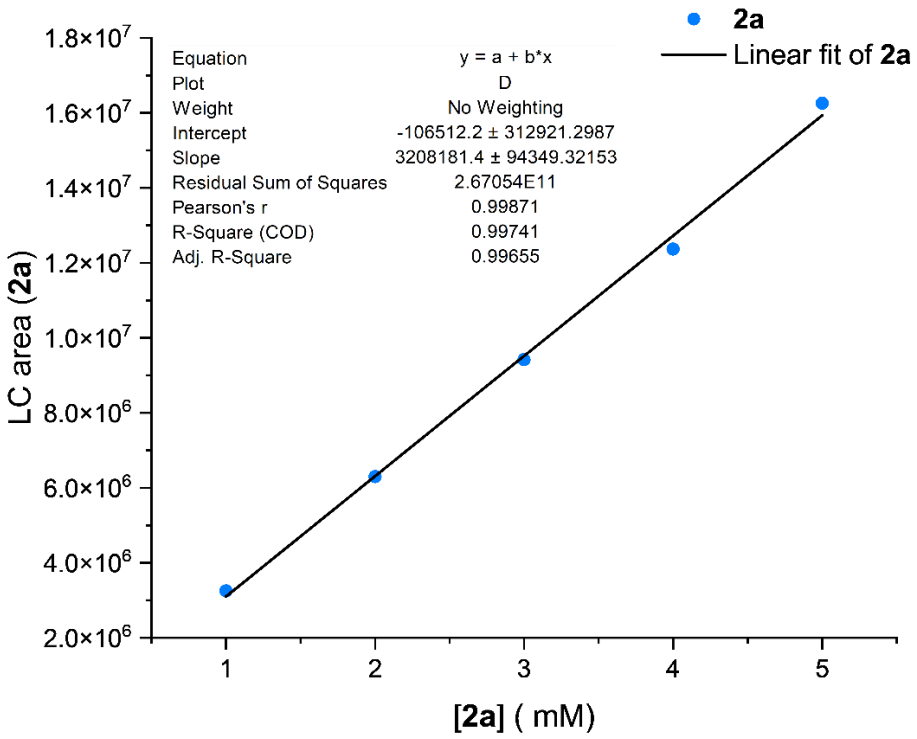


Figure S9: HPLC calibration curve of Fmoc-NH_2 (**2a**)

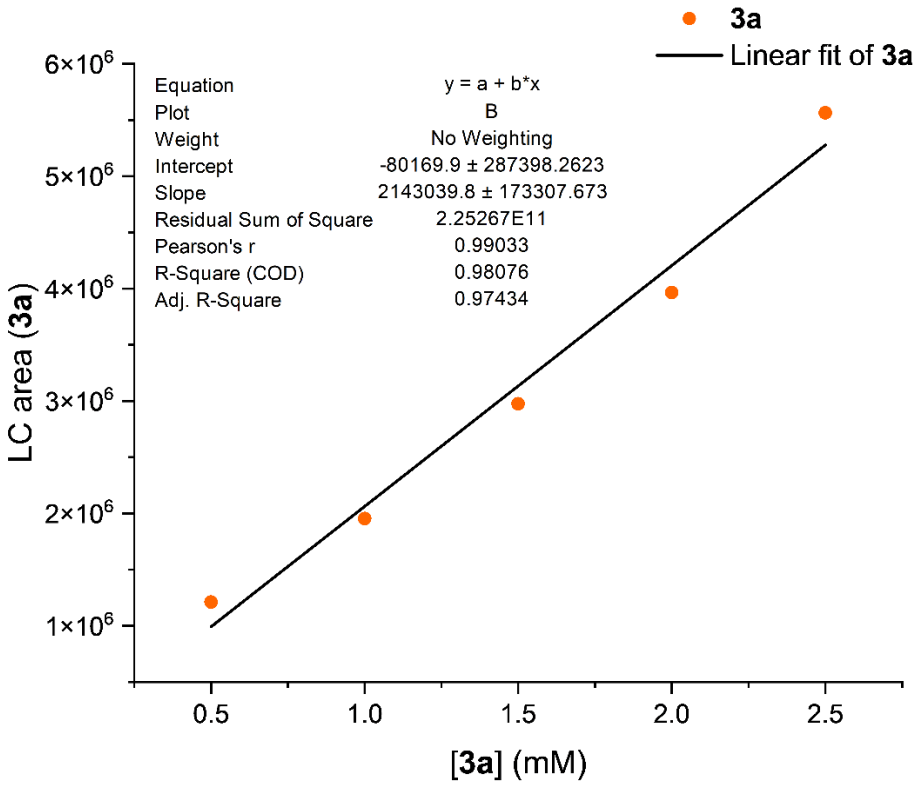


Figure S10: HPLC calibration curve of the product (**3a**)

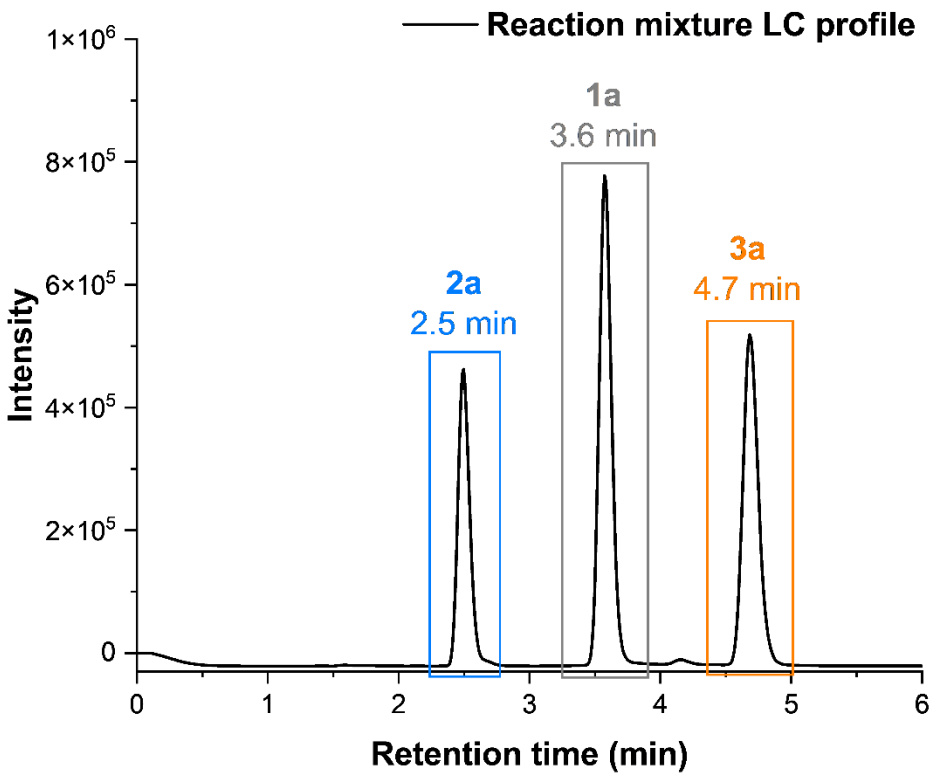


Figure S11:HPLC profile of **1a**, **2a** and **3a** with retention time

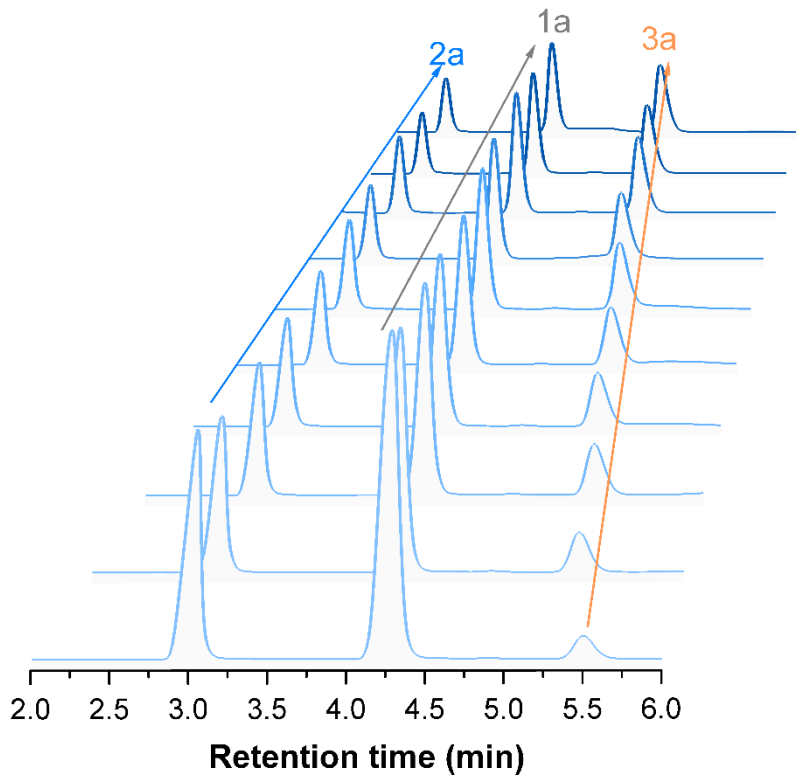


Figure S12: Reaction progress was monitored for 6 hours (*Retention time: 2 to 6 minutes was zoomed for clarity*). As the reaction goes on, the **1a** and **2a** areas decreased, and the **3a** area increased.

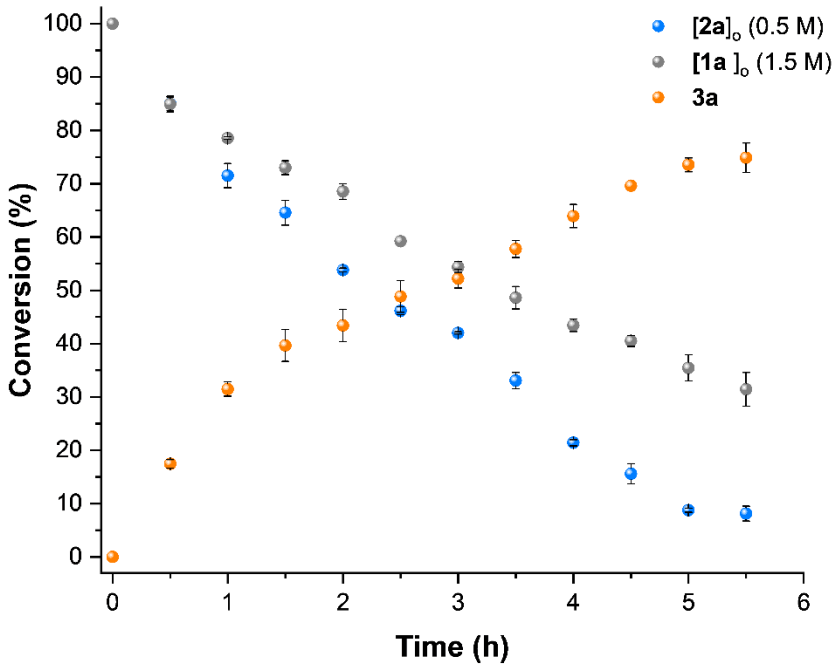
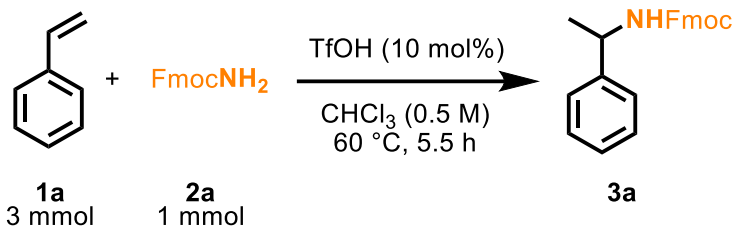


Figure S13: Conversion profile of **1a** and **2a** to **3a** (%). An acceptable mass balance is observed in the standard reaction.

Standard reaction monitoring:



Concentration details of the reactants in the reaction mixture:

Reactant	Amount added	Actual concentration in 2 mL $CHCl_3$
1a	348 μL (3 mmol)	1.5 M
2a	242 mg (1 mmol)	0.5 M
TfOH	9 μL (0.1 mmol; 10 mol%)	0.05 M

Concentration details of LCMS sample:

Reactant	Actual concentration in 2 mL $CHCl_3$	The final concentration of the LCMS sample (diluted with 2 mL CH_3CN; dilution factor is 200)
1a	1.5 M	10 μL × 1.5 M = x × 2 mL = 7.5 mM
2a	0.5 M	10 μL × 0.5 M = x × 2 mL = 2.5 mM
TfOH	0.05 M	10 μL × 0.05 M = x × 2 mL = 0.25 mM

The obtained HPLC concentration values were finally multiplied by 0.2, the dilution factor for mM to M.

Same excess and catalyst inhibition experiments:

The same excess reaction and reaction with the product were added to find out any possibility of catalytic deactivation or product inhibition.

Reaction condition	**Actual [M] in 2 mL $CHCl_3$ (Reaction mixture)**		**The final concentration of the LCMS sample (diluted with 2 mL CH_3CN)**
Standard reaction	**1a**	348 μL; 1.5 M	10 μL × 1.5 M = x × 2 mL = 7.5 mM
	2a	242 mg; 0.5 M	10 μL × 0.5 M = x × 2 mL = 2.5 mM
	TfOH	9 μL; 0.05 M	10 μL × 0.05 M = x × 2 mL = 0.25 mM
Same excess	**1a**	209 μL; 0.9 M	10 μL × 0.9 M = x × 2 mL = 4.5 mM
	2a	145 mg; 0.3 M	10 μL × 0.3 M = x × 2 mL = 1.5 mM
	TfOH	9 μL; 0.05 M	10 μL × 0.05 M = x × 2 mL = 0.25 mM
Product added	**1a**	209 μL; 0.9 M	10 μL × 0.9 M = x × 2 mL = 4.5 mM
	2a	145 mg; 0.3 M	10 μL × 0.3 M = x × 2 mL = 1.5 mM
	TfOH	9 μL; 0.05 M	10 μL × 0.05 M = x × 2 mL = 0.25 mM
	3a	137 mg; 0.2 M	10 μL × 0.2 M = x × 2 mL = 0.2 mM

Standard reaction (set 1)			**Standard reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.43938	0.08831538	0.50	0.4282	0.0860682
1.00	0.77324	0.15542124	1.00	0.79214	0.15922014
1.50	1.00717	0.20244117	1.50	0.96502	0.19396902
2.00	1.10098	0.22129698	2.00	1.05788	0.21263388
2.50	1.19371	0.23993571	2.50	1.23584	0.24840384
3.00	1.28546	0.25837746	3.00	1.31001	0.26331201
3.50	1.42528	0.28648128	3.50	1.44778	0.29100378
4.00	1.57421	0.31641621	4.00	1.60492	0.32258892
4.50	1.73101	0.34793301	4.50	1.73101	0.34793301
5.00	1.83804	0.36944604	5.00	1.81952	0.36572352
5.50	1.84221	0.37028421	5.50	1.88132	0.37814532

Time (h)	Average ([**3a**])	Standard deviation ([**3a**])
0.00	0	0
0.50	0.086758	0.001581091
1.00	0.156538	0.002672864
1.50	0.197219	0.00596091
2.00	0.215886	0.00609526
2.50	0.242955	0.005958082
3.00	0.259547	0.003471894
3.50	0.287306	0.003181981
4.00	0.317913	0.00434305
4.50	0.346202	0
5.00	0.365756	0.002619124
5.50	0.372353	0.005530989

Same excess (set 1)			**Same excess (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0.000	0	0.00	0.000	0
0.50	0.184	0.09175	0.50	0.178	0.08896
1.00	0.266	0.13275	1.00	0.258	0.12916
1.50	0.302	0.1512	1.50	0.316	0.15793
2.00	0.346	0.17281	2.00	0.369	0.18456
2.50	0.372	0.18608	2.50	0.412	0.2058
3.00	0.414	0.20719	3.00	0.441	0.22049
3.50	0.440	0.2198	3.50	0.471	0.23554
4.00	0.470	0.23497	4.00	0.509	0.25469
4.50	0.505	0.25252	4.50	0.542	0.27114
5.00	0.575	0.28735	5.00	0.590	0.2952
5.50	0.597	0.29851	5.50	0.608	0.30387

t (h)	**Time shift** Time+1.5 (h)	Average ([**3a**])	Standard deviation ([**3a**])
0.00	1.50	0	0
0.50	2.00	0.090355	0.001972828
1.00	2.50	0.130955	0.002538513
1.50	3.00	0.154565	0.004758829
2.00	3.50	0.178685	0.008308505
2.50	4.00	0.19594	0.013944146
3.00	4.50	0.21384	0.00940452
3.50	5.00	0.22767	0.011129861
4.00	5.50	0.24483	0.013944146
4.50	6.00	0.26183	0.013166328
5.00	6.5	0.291275	0.005550788
5.50	7.00	0.30119	0.003790092

Product (3a) added (set 1)			**Product (3a) added (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0.381	0.19032	0.00	0.370	0.18496
0.50	0.438	0.21909	0.50	0.430	0.21502
1.00	0.491	0.24539	1.00	0.493	0.2463
1.50	0.573	0.28674	1.50	0.560	0.28012
2.00	0.599	0.29942	2.00	0.592	0.29584
2.50	0.634	0.31684	2.50	0.630	0.31494
3.00	0.671	0.3355	3.00	0.699	0.34963
3.50	0.753	0.37625	3.50	0.762	0.3812
4.00	0.811	0.40574	4.00	0.783	0.3914
4.50	0.883	0.44137	4.50	0.845	0.42241
5.00	0.939	0.46938	5.00	0.916	0.45818
5.50	0.984	0.49183	5.50	0.964	0.48194

t (h)	**Time shift** Time+1.5 (h)	Average ([**3a**])	Standard deviation ([**3a**])
0.00	1.50	0.18764	0.003790092
0.50	2.00	0.217055	0.002877925
1.00	2.50	0.245845	0.000643467
1.50	3.00	0.28343	0.004681047
2.00	3.50	0.29763	0.002531442
2.50	4.00	0.31589	0.001343503
3.00	4.50	0.342565	0.009991419
3.50	5.00	0.378725	0.003500179
4.00	5.50	0.39857	0.010139911
4.50	6.00	0.43189	0.013406745
5.00	6.5	0.46378	0.007919596
5.50	7.00	0.486885	0.006993286

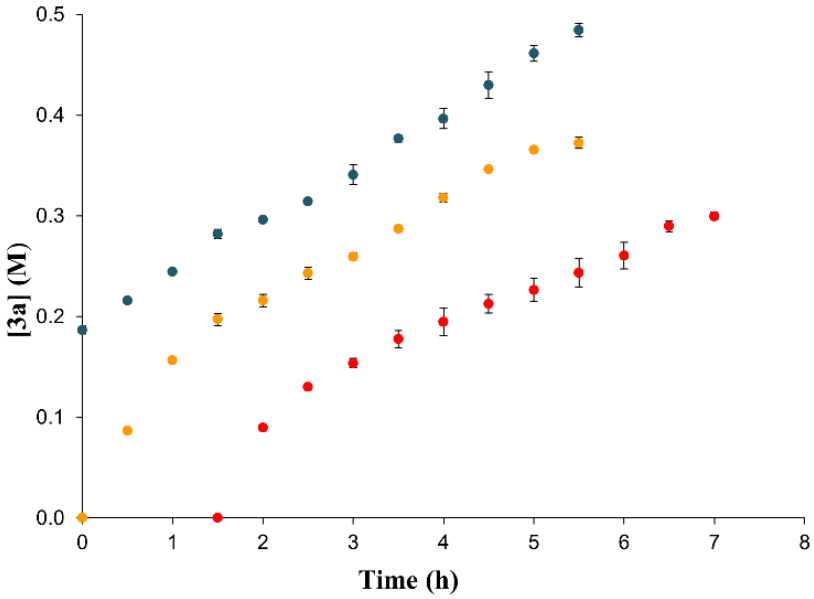


Figure S14: standard reaction (yellow color), same excess (shown in red color) with 1.5 h time shift and product added reaction (green color).

When time shift was adjusted to 1.5 h, the same excess experiment showed the expected deviation (Red), which strongly supports the product inhibition due to the interaction between TfOH and **2a** / **3a**.

Order of styrene (1a):

3 different reactions were analyzed to find out the order of styrene (**1a**).

1a loading	**Actual [1a] in 2 mL $CHCl_3$**	**The final concentration of the LCMS sample (diluted with 2 mL CH_3CN; dilution factor is 200)**
Standard reaction (3 mmol)	348 μL; 1.5 M	10 μL × 1.5 M = x × 2 mL = 7.5 mM
Higher loading (4 mmol)	464 μL; 2 M	10 μL × 2 M = x × 2 mL = 10 mM
Higher loading (5 mmol)	581 μL; 2.5 M	10 μL × 2.5 M = x × 2 mL = 12.5 mM

Standard reaction (set 1)			**Standard reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.43938	0.087876	0.50	0.4282	0.08564
1.00	0.77324	0.154648	1.00	0.79214	0.158428
1.50	1.00717	0.201434	1.50	0.96502	0.193004
2.00	1.10098	0.220196	2.00	1.05788	0.211576
2.50	1.19371	0.238742	2.50	1.23584	0.247168
3.00	1.28546	0.257092	3.00	1.31001	0.262002
3.50	1.42528	0.285056	3.50	1.44778	0.289556
4.00	1.57421	0.314842	4.00	1.60492	0.320984
4.50	1.73101	0.346202	4.50	1.73101	0.346202
5.00	1.83804	0.367608	5.00	1.81952	0.363904
5.50	1.84221	0.368442	5.50	1.88132	0.376264

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.086758	0.001581091
0.156538	0.002672864
0.197219	0.00596091
0.215886	0.00609526
0.242955	0.005958082
0.259547	0.003471894
0.287306	0.003181981
0.317913	0.00434305
0.346202	0
0.365756	0.002619124
0.372353	0.005530989

Higher 1a reaction (4 mmol) (set-1)			**Higher 1a reaction (4 mmol) (set-2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.46711	0.093422	0.50	0.48536	0.097072
1.00	0.98904	0.197808	1.00	0.88339	0.176678
1.50	1.23707	0.247414	1.50	1.2609	0.25218
2.00	1.45727	0.291454	2.00	1.38887	0.277774
2.50	1.64482	0.328964	2.50	1.53281	0.306562
3.00	1.77788	0.355576	3.00	1.71368	0.342736
3.50	1.90342	0.380684	3.50	1.87466	0.374932
4.00	1.99861	0.399722	4.00	1.96067	0.392134
4.50	1.96022	0.392044	4.50	1.99123	0.398246
5.00	2.06858	0.413716	5.00	2.0893	0.41786
5.50	2.10761	0.421522	5.50	2.10663	0.421326

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.095247	0.00258094
0.187243	0.014941166
0.249797	0.003370071
0.284614	0.009673221
0.317763	0.015840606
0.349156	0.009079251
0.377808	0.004067278
0.395928	0.005365526
0.395145	0.004385476
0.365756	0.002619124
0.372353	0.005530989

Higher 1a reaction (5 mmol) (set-1)			**Higher 1a reaction (5 mmol) (set-2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.52054	0.104108	0.50	0.50391	0.100782
1.00	1.00698	0.201396	1.00	0.97297	0.194594
1.50	1.26922	0.253844	1.50	1.15662	0.231324
2.00	1.51654	0.303308	2.00	1.39463	0.278926
2.50	1.69579	0.339158	2.50	1.67138	0.334276
3.00	1.88874	0.377748	3.00	1.81683	0.363366
3.50	1.95691	0.391382	3.50	1.93924	0.387848
4.00	2.03942	0.407884	4.00	2.0102	0.40204
4.50	2.1125	0.4225	4.50	2.11663	0.423326
5.00	2.07401	0.414802	5.00	1.93536	0.387072
5.50	1.9446	0.38892	5.50	1.85497	0.370994

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.102445	0.002351837
0.197995	0.00480974
0.242584	0.015924045
0.291117	0.017240678
0.336717	0.003452095
0.370557	0.01016961
0.389615	0.002498915
0.404962	0.004132332
0.422913	0.00058407
0.400937	0.019608071
0.379957	0.012675596

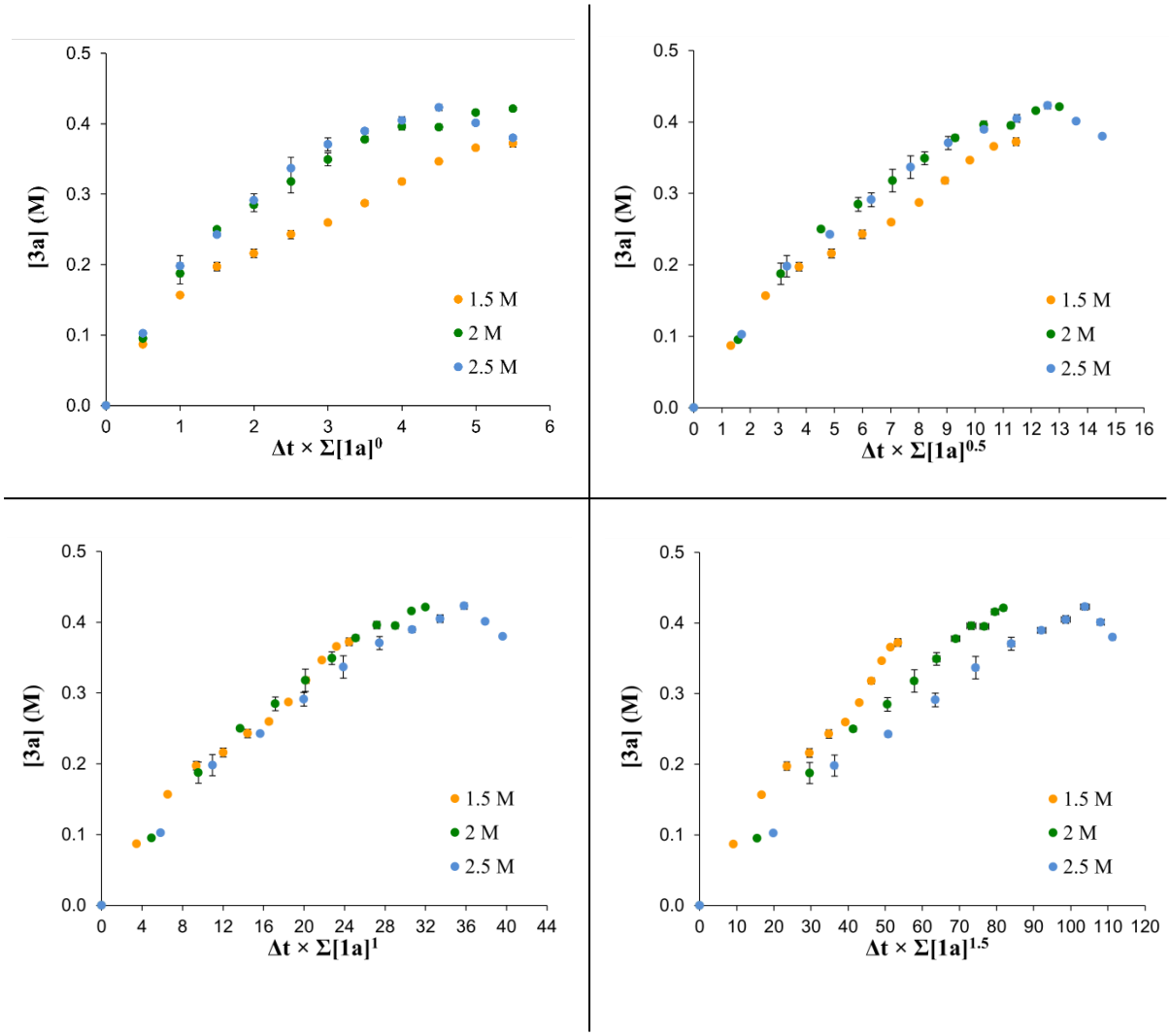


Figure S15: VTNA plots of **3a** with respect to 1.5 M, 2 M, and 2.5 M concentrations of **1a** having orders 0 to 1.5.

Applying the VTNA analysis, a significant overlap between the curves was obtained for an order of **1a**, equal to 1 with respect to **3a** formation. This exactly matches the expected styrene involvement in one catalytic cycle.

Order of Fmoc-NH_2 (2a):

3 different reactions were analyzed to find out the order of FmocNH_2 (**2a**).

2a loading	**Actual [2a] in 2 mL $CHCl_3$**	**The final concentration of the LCMS sample (diluted with 2 mL CH_3CN; dilution factor is 200)**
Standard reaction (1 mmol)	242 mg; 0.5 M	10 μL × 0.5 M = x × 2 mL = 2.5 mM
Lower loading (0.6 mmol)	145 mg; 0.3 M	10 μL × 0.3 M = x × 2 mL = 1.5 mM
Higher loading (1.4 mmol)	338 mg; 0.7 M	10 μL × 0.7 M = x × 2 mL = 3.5 mM

Standard reaction (set 1)			**Standard reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.43938	0.087876	0.50	0.4282	0.08564
1.00	0.77324	0.154648	1.00	0.79214	0.158428
1.50	1.00717	0.201434	1.50	0.96502	0.193004
2.00	1.10098	0.220196	2.00	1.05788	0.211576
2.50	1.19371	0.238742	2.50	1.23584	0.247168
3.00	1.28546	0.257092	3.00	1.31001	0.262002
3.50	1.42528	0.285056	3.50	1.44778	0.289556
4.00	1.57421	0.314842	4.00	1.60492	0.320984
4.50	1.73101	0.346202	4.50	1.73101	0.346202
5.00	1.83804	0.367608	5.00	1.81952	0.363904
5.50	1.84221	0.368442	5.50	1.88132	0.376264

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.086758	0.001581091
0.156538	0.002672864
0.197219	0.00596091
0.215886	0.00609526
0.242955	0.005958082
0.259547	0.003471894
0.287306	0.003181981
0.317913	0.00434305
0.346202	0
0.365756	0.002619124
0.372353	0.005530989

Lower 2a reaction (set 1)			**Lower 2a reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.23749	0.047498	0.50	0.29078	0.058156
1.00	0.64888	0.129776	1.00	0.63053	0.126106
1.50	0.81685	0.16337	1.50	0.7194	0.14388
2.00	0.93076	0.186152	2.00	0.8587	0.17174
2.50	1.00305	0.20061	2.50	1.00034	0.200068
3.00	1.09272	0.218544	3.00	1.10431	0.220862
3.50	1.11157	0.222314	3.50	1.13105	0.22621
4.00	1.14141	0.228282	4.00	1.17396	0.234792
4.50	1.2034	0.24068	4.50	1.22439	0.244878
5.00	1.21083	0.242166	5.00	1.22754	0.245508
5.50	1.2142	0.24284	5.50	1.23584	0.247168

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.052827	0.03768172
0.127941	0.012975409
0.153625	0.068907556
0.178946	0.050954115
0.200339	0.001916259
0.219703	0.008195368
0.224262	0.01377444
0.231537	0.023016326
0.242779	0.014842171
0.243837	0.011815754
0.245004	0.015301791

Higher 2a reaction (set 1)			**Higher 2a reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.49505	0.09901	0.50	0.49421	0.098842
1.00	0.81067	0.162134	1.00	0.88818	0.177636
1.50	1.12982	0.225964	1.50	1.0932	0.21864
2.00	1.27074	0.254148	2.00	1.26581	0.253162
2.50	1.38028	0.276056	2.50	1.51206	0.302412
3.00	1.5457	0.30914	3.00	1.64179	0.328358
3.50	1.72611	0.345222	3.50	1.77401	0.354802
4.00	1.83589	0.367178	4.00	1.90153	0.380306
4.50	1.92852	0.385704	4.50	2.10959	0.421918
5.00	2.00155	0.40031	5.00	2.26279	0.452558
5.50	2.05693	0.411386	5.50	2.27967	0.455934

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.098926	0.000118794
0.169885	0.010961569
0.222302	0.00517885
0.253655	0.000697207
0.289234	0.018636506
0.318749	0.013589178
0.350012	0.006774083
0.373742	0.009282898
0.403811	0.025607165
0.426434	0.036944915
0.43366	0.031500193

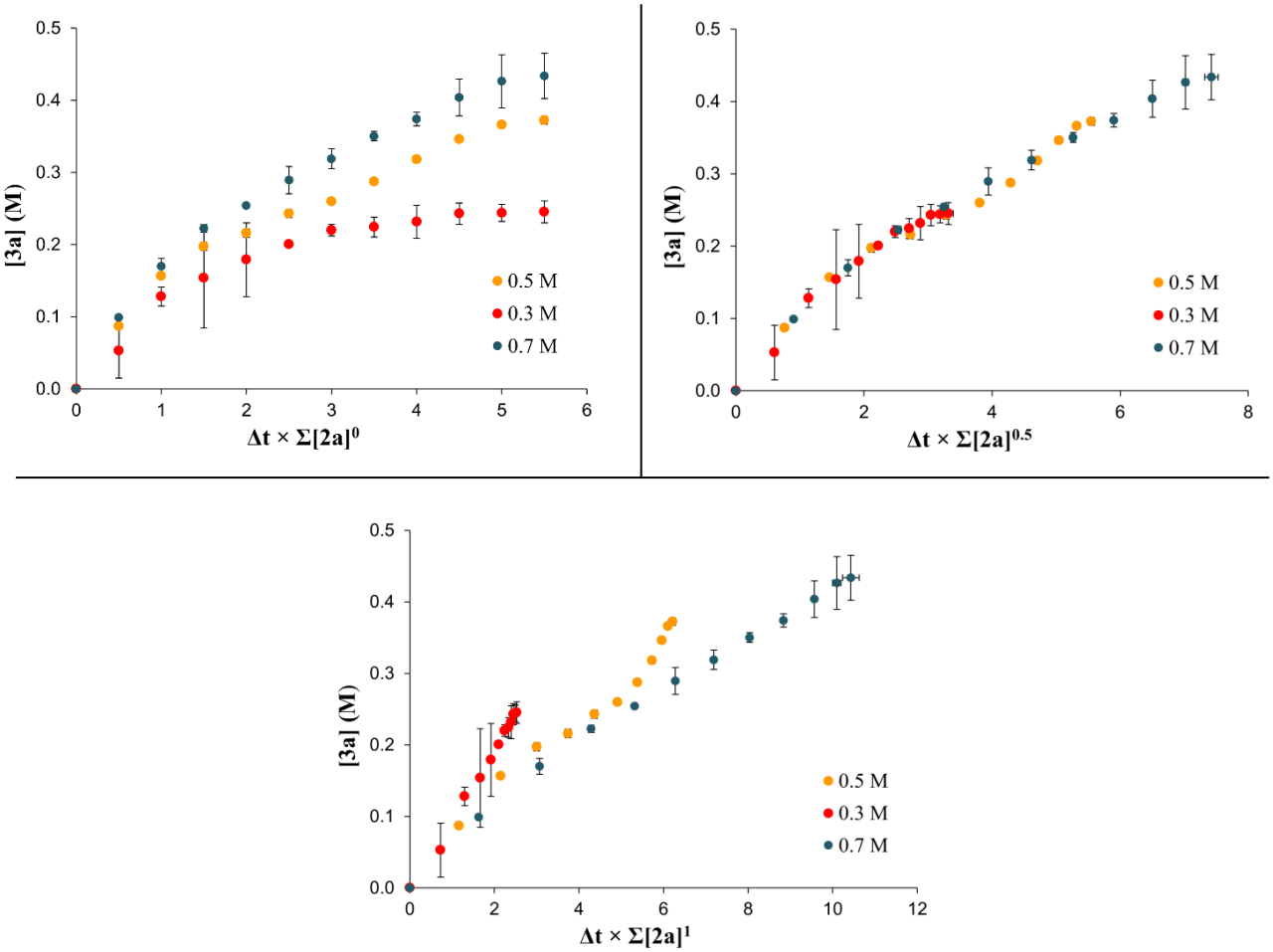


Figure S16: VTNA plots of **3a** using 1.5 M, 2 M, and 2.5 M concentrations of 2**a** having orders 0, 0.5, and 1.

Applying the VTNA analysis, a significant overlap between the curves was obtained for an order of **2a**, equal to 0.5, with respect to **3a** formation. The interaction with TfOH resulted in the fractional value of order (0.5).

Order of catalyst (TfOH):

3 different reactions were analyzed to find out the order of TfOH.

TfOH loading	**Actual [2a] in 2 mL $CHCl_3$**	**The final concentration of the LCMS sample (diluted with 2 mL CH_3CN; dilution factor is 200)**
Standard reaction (0.1 mmol; 10 mol%)	9 μL; 0.05 M	10 μL × 0.5 M = x × 2 mL = 0.25 mM
Higher loading (0.15 mmol; 15 mol%)	13.5 μL; 0.075 M	10 μL × 0.3 M = x × 2 mL = 0. 375mM
Higher loading (0.2 mmol; 20 mol%)	18 μL; 0.1 M	10 μL × 0.7 M = x × 2 mL = 0.5 mM

Standard reaction (set 1)			**Standard reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.43938	0.087876	0.50	0.4282	0.08564
1.00	0.77324	0.154648	1.00	0.79214	0.158428
1.50	1.00717	0.201434	1.50	0.96502	0.193004
2.00	1.10098	0.220196	2.00	1.05788	0.211576
2.50	1.19371	0.238742	2.50	1.23584	0.247168
3.00	1.28546	0.257092	3.00	1.31001	0.262002
3.50	1.42528	0.285056	3.50	1.44778	0.289556
4.00	1.57421	0.314842	4.00	1.60492	0.320984
4.50	1.73101	0.346202	4.50	1.73101	0.346202
5.00	1.83804	0.367608	5.00	1.81952	0.363904
5.50	1.84221	0.368442	5.50	1.88132	0.376264

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.086758	0.001581091
0.156538	0.002672864
0.197219	0.00596091
0.215886	0.00609526
0.242955	0.005958082
0.259547	0.003471894
0.287306	0.003181981
0.317913	0.00434305
0.346202	0
0.365756	0.002619124
0.372353	0.005530989

15 mol% TfOH reaction (set 1)			**15 mol% TfOH reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.28407	0.056814	0.50	0.35577	0.071154
1.00	0.93213	0.186426	1.00	0.69414	0.138828
1.50	1.13978	0.227956	1.50	0.90095	0.18019
2.00	1.32609	0.265218	2.00	1.12907	0.225814
2.50	1.57543	0.315086	2.50	1.24047	0.248094
3.00	1.67673	0.335346	3.00	1.38475	0.27695
3.50	1.77114	0.354228	3.50	1.54381	0.308762
4.00	1.8585	0.3717	4.00	1.74105	0.34821
4.50	1.9661	0.39322	4.50	1.81411	0.362822
5.00	2.01125	0.40225	5.00	1.85028	0.370056
5.50	2.02289	0.404578	5.50	1.96703	0.393406

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.063984	0.010139911
0.162627	0.033656869
0.204073	0.033775663
0.245516	0.027862836
0.28159	0.047370497
0.306148	0.041292208
0.331495	0.032149317
0.359955	0.016609938
0.378021	0.021494632
0.386153	0.022764596
0.398992	0.007899797

20 mol% TfOH reaction (set 1)			**20 mol% TfOH reaction (set 2)**		
t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)	t (h)	LC concentration [**3a**] (mM)	Reaction concentration [**3a**] (M)
0.00	0	0	0.00	0	0
0.50	0.44828	0.089656	0.50	0.49218	0.098436
1.00	0.90697	0.181394	1.00	0.78222	0.156444
1.50	1.17124	0.234248	1.50	1.04147	0.208294
2.00	1.32346	0.264692	2.00	1.26518	0.253036
2.50	1.51966	0.303932	2.50	1.45404	0.290808
3.00	1.67671	0.335342	3.00	1.68139	0.336278
3.50	1.81388	0.362776	3.50	1.84532	0.369064
4.00	1.9958	0.39916	4.00	1.99996	0.399992
4.50	2.04237	0.408474	4.50	2.05274	0.410548
5.00	2.00853	0.401706	5.00	2.03068	0.406136
5.50	2.02105	0.40421	5.50	2.02727	0.405454

Average ([**3a**])	Standard deviation ([**3a**])
0	0
0.094046	0.006208398
0.168919	0.017642314
0.221271	0.018352249
0.258864	0.008242037
0.29737	0.009280069
0.33581	0.000661852
0.36592	0.004446287
0.399576	0.000588313
0.409511	0.001466539
0.403921	0.003132483
0.404832	0.000879641

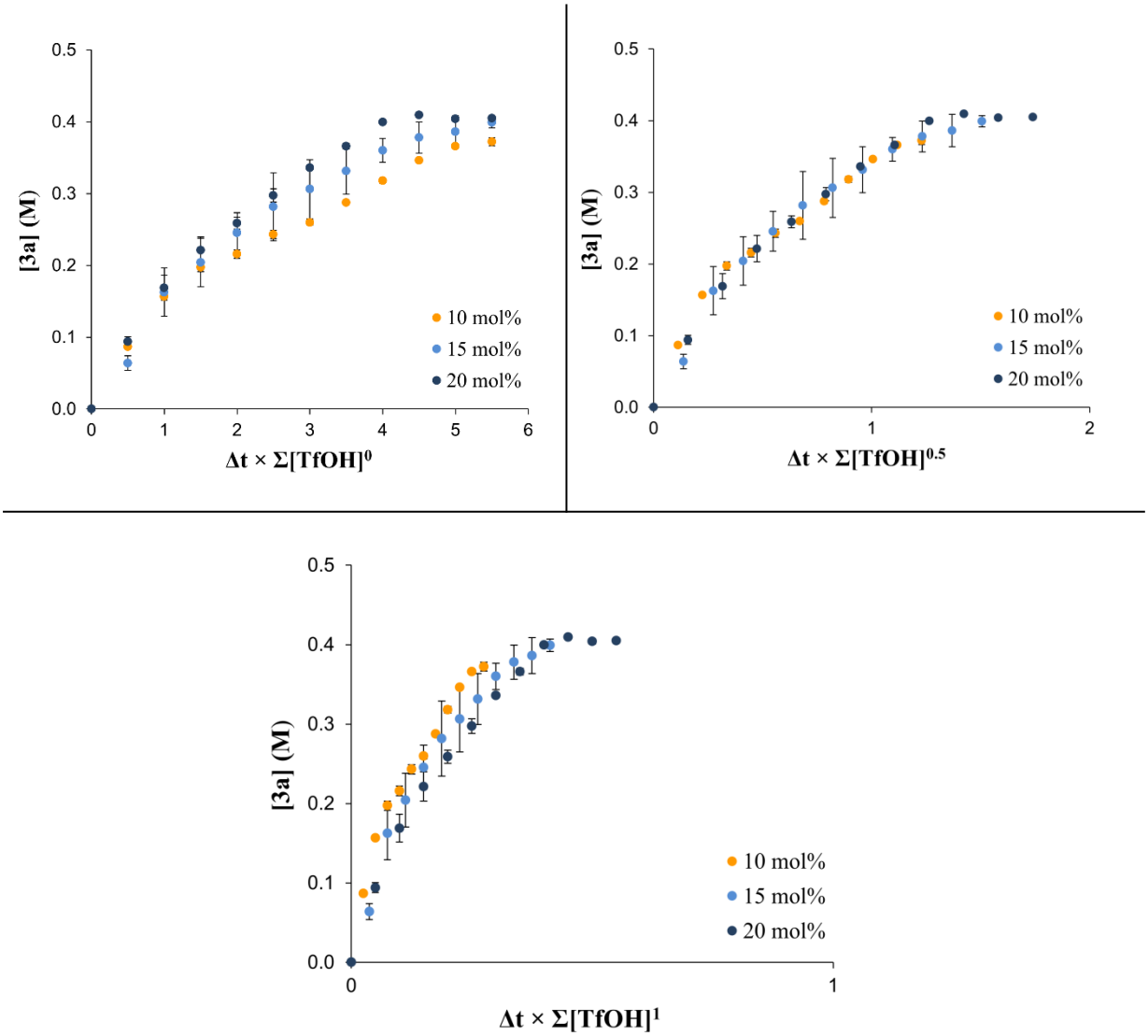
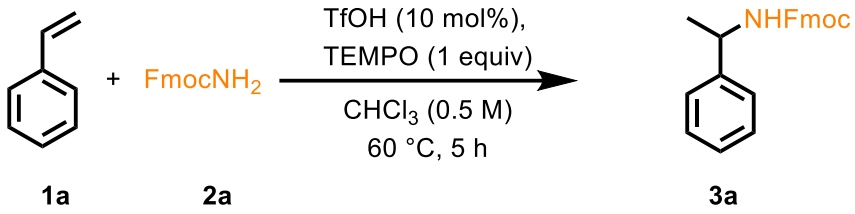


Figure S17: VTNA plots of **3a** using 10 mol%, 20 mol%, and 30 mol% of TfOH with the time normalized to 0, 0.5, and 1.

Applying the VTNA analysis, a significant overlap between the curves was obtained for an order of **TfOH**, equal to 0.5, with respect to **3a** formation. The interaction with $FmocNH_2$ resulted in the fractional value of order (0.5).

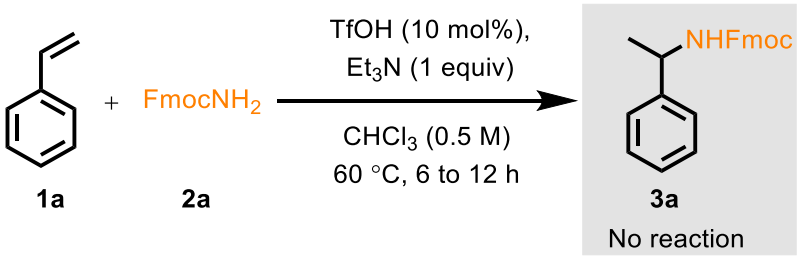
2.5 Control Experiments

Hydroamination with Fmoc-NH_2 in the presence of TEMPO



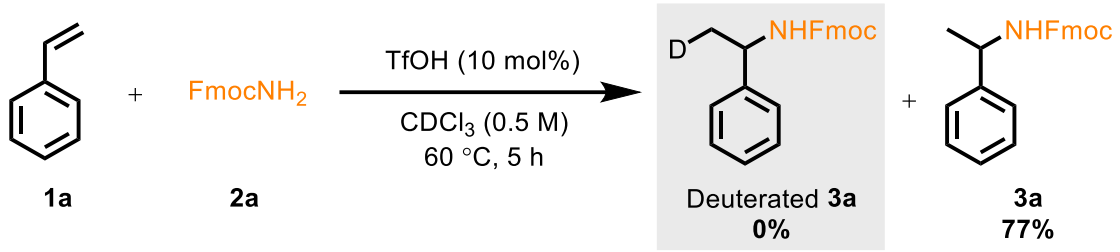
In a 5 ml screw-capped vial styrene (**1a**, 43.2 μL, 0.372 mmol) and Fmoc-NH_2 (**2a**, 30 mg, 0.124 mmol) were taken in $CHCl_3$ (0.5 M), and followed by triflic acid (1.12 μL, 0.012 mmol), TEMPO (19.4 mg, 0.124 mmol) was added into the vial and the mixture was stirred at 60 °C in a preheated metal block for 5 h. The reaction mixture was monitored by TLC. After the completion of the reaction, the crude mixture was concentrated under reduced pressure and purified using column chromatography on silica gel petether: ethyl acetate (95:5) binary solvent mixture to get the (9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate **3a** (35 mg; 83 %).

Hydroamination with Fmoc-NH_2 in the presence of a base (Et_3N):



In a 5 ml screw-capped vial, styrene (**1a**, 43.2 μL, 0.372 mmol) and Fmoc-NH_2 (**2a**, 30 mg, 0.124 mmol) were taken in $CHCl_3$ (0.5 M), and Et_3N (17.3 μL, 0.124 mmol) followed by triflic acid (1.12 μL, 0.012 mmol) were added into vial and the mixture was stirred at 60 °C in a preheated metal block for 6 h to 12 h. The progress of the reaction was monitored by TLC. No desired product formation was observed.

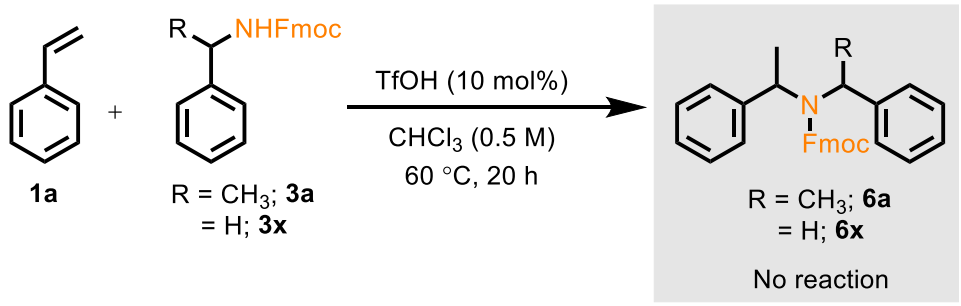
Hydroamination reaction in $CDCl_3$:



To an oven-dried 10 mL screw cap vial with a magnetic stir bar (10 mm × 6 mm), Fmoc-NH_2 (**2a**, 121 mg, 0.5 mmol, 1 equiv) and styrene (**1a**, 1.5 mmol, 3 equiv, 174 μL) were added. Then, $CDCl_3$ (0.5 M, 1 mL) was added using an oven-dried needle with a glass syringe. Finally, TfOH (0.05 mmol, 10 mol%, 5 μL) was added using a 50 μL glass syringe. Then the vial was closed with a PTFE screw cap and placed in the pre-heated metal block at 60 °C for 5 h with constant stirring (500 rpm). After 5 h, TLC was checked and purified as mentioned for substrate **3a** (133 mg; 78%).

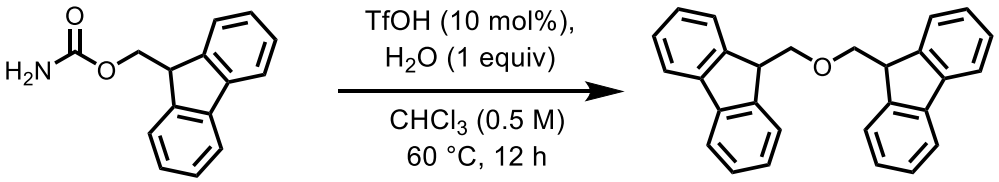
The integration value of the CH_3 peak at 1.51 ppm in ^1H NMR did not show any changes. The splitting pattern of the CH_3 peak at 22.5 ppm in $^{13}C\{^1H\}$ NMR remains as a singlet, and no triplet pattern was observed.

Hydroamination with Fmoc-protected amines:



In a 5 ml screw-capped vial with a stir bar, styrene (**1a**, 51 μL, 0.438 mmol) and **3a** (50 mg, 0.146 mmol) or **3x** (48 mg, 0.146 mmol) were taken in $CHCl_3$ (0.5 M), and followed by triflic acid (10 mol%). This mixture was stirred at 60 °C in a preheated metal block for 20 h. The reaction mixture was monitored by TLC. No desired product formation was observed.

Synthesis of 9-(((2,3-dihydro-1H-inden-1-yl)methoxy)methyl)-9H-fluorene (4a) from Fmoc-NH_2:



2a **4a**

In a 5 ml screw-capped vial, Fmoc-NH_2 (**2a**, 40 mg, 0.167 mmol) was taken in $CHCl_3$ (0.5 M), and triflic acid (1.49 μL, 0.016 mmol) and water (2.98 μL, 0.167 mmol) were added into the vial, and the mixture was stirred at 60 °C in a preheated metal block for 12 h. After 12 h, the crude reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using pet ether: ethyl acetate (90:6) binary solvent as eluent to give the corresponding 9-(((2,3-dihydro-1H-inden-1-yl)methoxy)methyl)-9H-fluorene.

9,9'-(oxybis(methylene))bis(9H-fluorene) (4a)[18]:

TLC profile: 20% ethyl acetate in hexane; R_f = 0.38.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 20% ethyl acetate in petether).

Yield: 24 mg; 38%.

Physical state: white solid.

Melting point: 101 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 2H), 4.00–3.98 (m, 1H), 3.92 (d, *J* = 6 Hz, 2H).

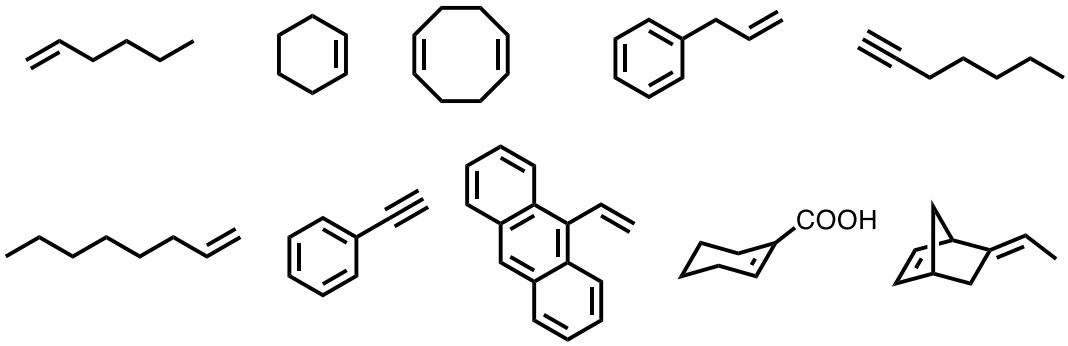
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5, 141.7, 127.7, 127.2, 124.8, 120.2, 65.3, 50.5

MS (HRMS, TOF-MS): Calcd for $[M–C_{14}H_{11}O]^+$: 179.0860; Found: 179.0873.

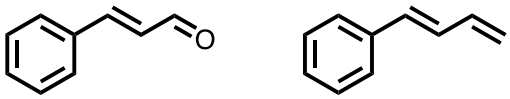
2.6 Table of unreacted substrates

The following substrates were tried for hydroamination reaction under the optimized condition. The progress of the reaction was monitored by TLC. No desired product formation was observed.

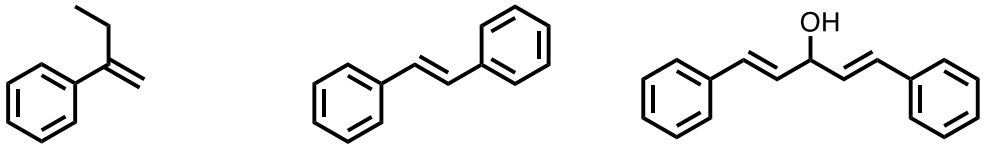
Non-activated alkenes and alkynes and activated alkenes



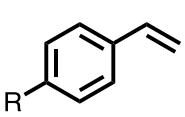
Conjugated vinyl arenes



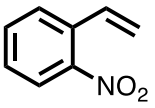
α, β substituted vinyl arenes

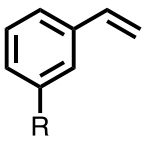


Vinylarenes with EWG and EDG



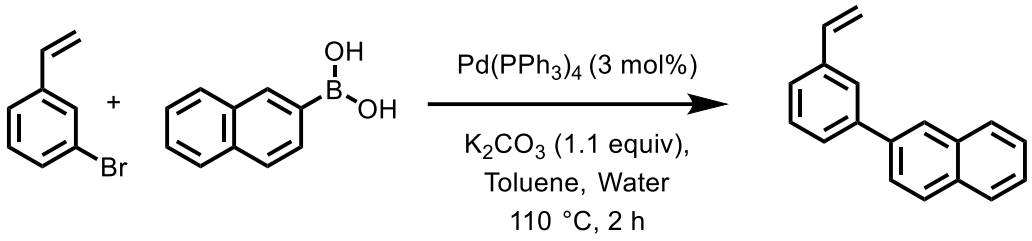
R = NO_2,
= CF_3,
= OMe
= NH_2





R = Br
= Cl (observed reaction in 8 h but the product underwent decomposition on isolation)

2.7 Synthesis of 2-(3-vinylphenyl)naphthalene



3-Bromostyrene (326 µl, 2.5 mmol) is charged into a 50 mL Schlenk tube equipped with a magnetic stirrer with naphthylboronic acid (320 mg, 2.75 mmol) and $Pd(PPh_3)_4$ (87 mg, 0.073 mmol) under argon. Argon sparge toluene (6 mL) and potassium carbonate (380mg, 2.75 mmol) dissolved in water (2 mL) were added using a syringe. The reaction mixture was stirred under reflux for 2 h. After the completion of the reaction, the reaction mixture was cooled and passed through celite using DCM (20 mL). The crude was washed with water, and the aqueous phase was extracted twice with DCM (2 × 5 mL). The combined organic layers were washed with water (15 mL), dried over anhydrous Na_2SO_4, filtered, and the solvents removed under reduced pressure. The residue was purified by column chromatography on silica gel using pet ether as eluent.

2-(3-vinylphenyl)naphthalene:

TLC profile: 6% Ethyl acetate in hexane; R_f = 0.60.

Purification: 200–400 mesh silica gel; column chromatography (eluent: 100% pet ether to 5% ethyl acetate in pet ether).

Yield: 414 mg; 72%.

Physical state: Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.99–7.92 (m, 3H), 7.83–7.81 (m, 2H), 7.68–7.67 (m, 1H), 7.58–7.51 (m, 4H), 6.94–6.86 (m, 1H), 5.93 (d, J = 17.5 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.6, 138.5, 138.3, 137.0, 133.8, 132.8, 129.1, 128.5, 128.3, 127.8, 127.1, 126.4, 126.1, 126.0, 125.7, 125.6, 125.2, 114.3.

MS (HRMS, TOF-MS $[M+H]^+$): Calcd. For $[C_{18}H_{15}]^+$: 231.1174; Found: 231.1201.

3. References

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4. $^{1}H/^{13}C$ {^{1}H} NMR and HRMS spectra of compounds

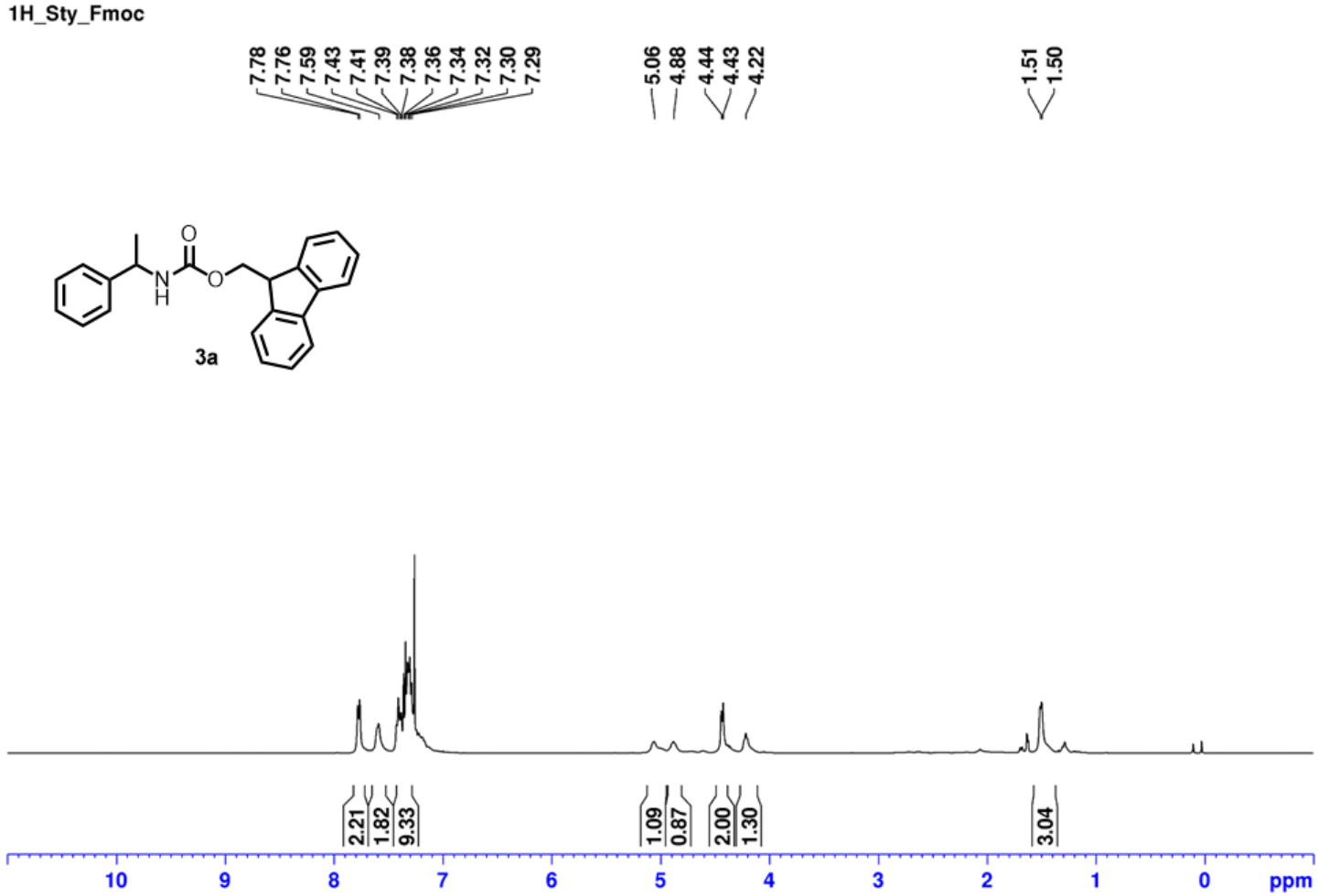


Figure S20: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate**

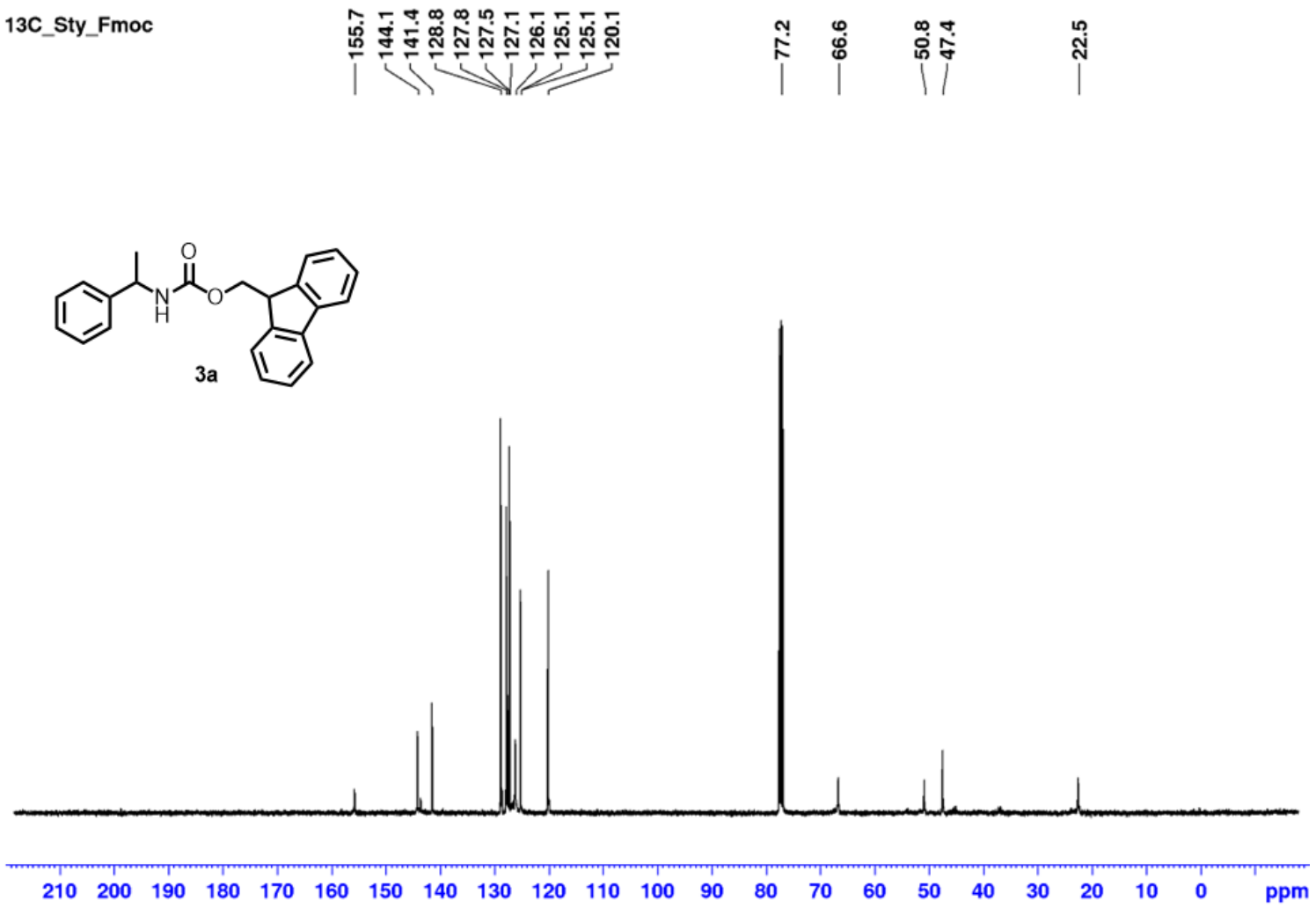


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-phenylethyl)carbamate**

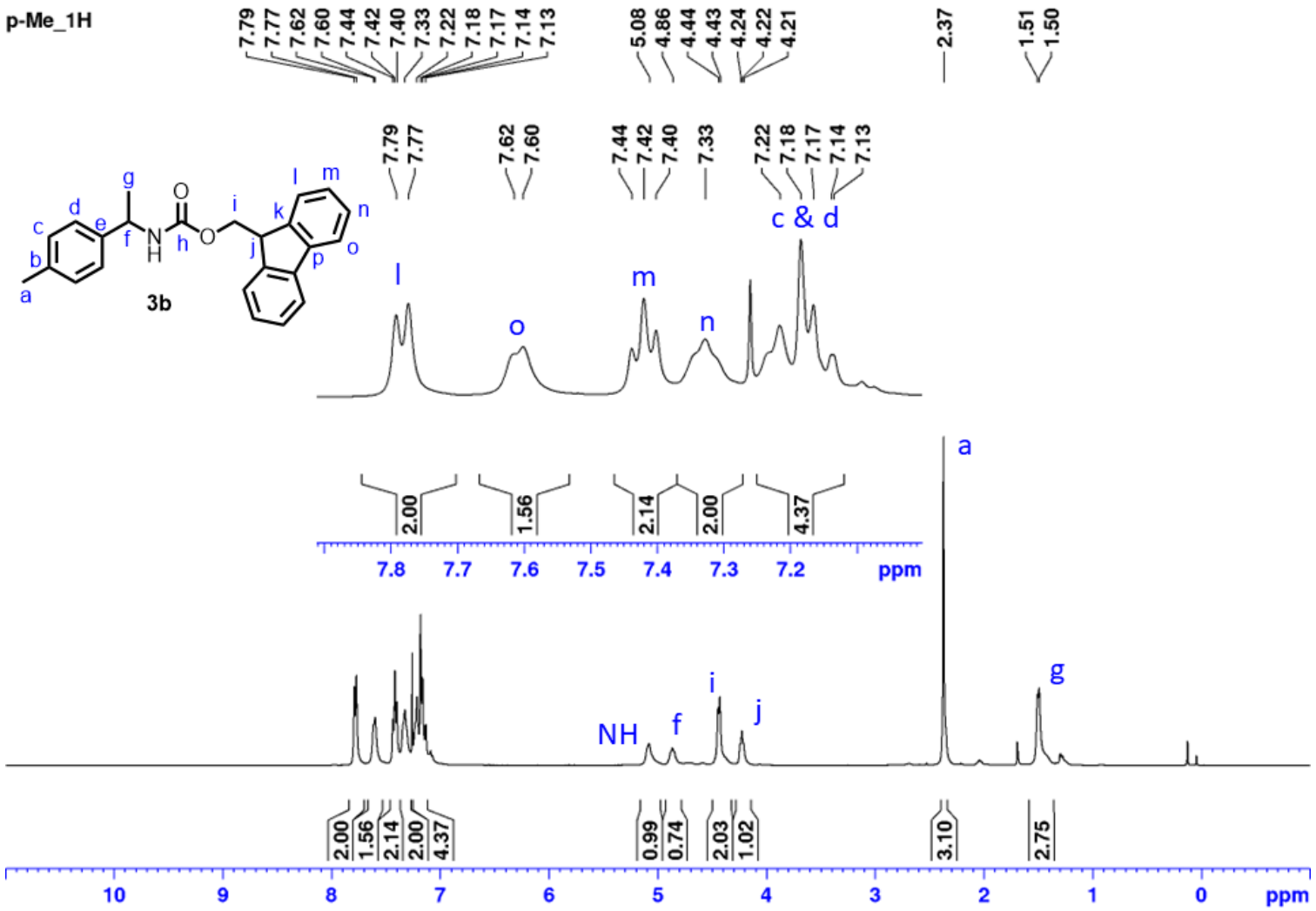


Figure S22: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(p-tolyl)ethyl)carbamate**

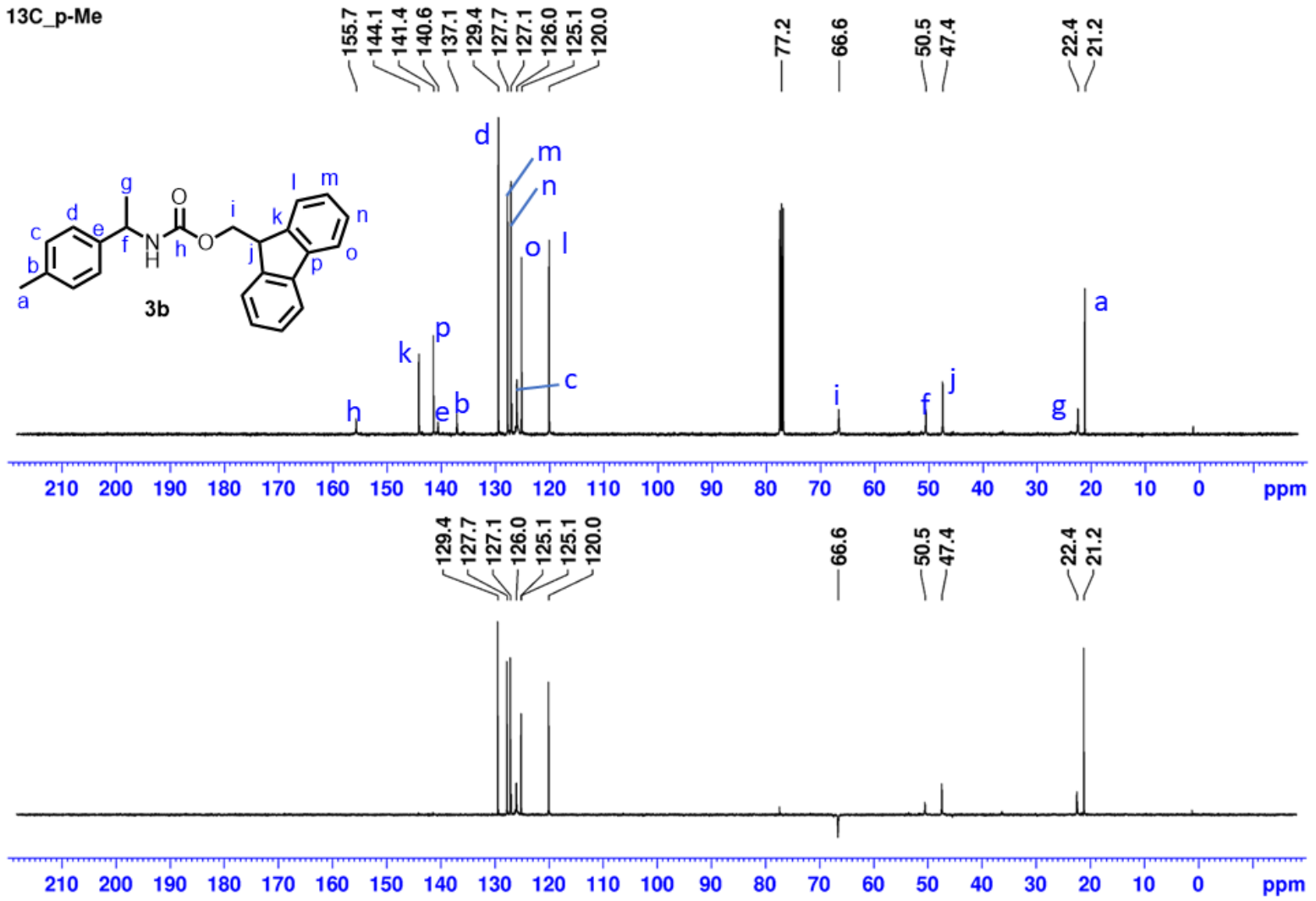
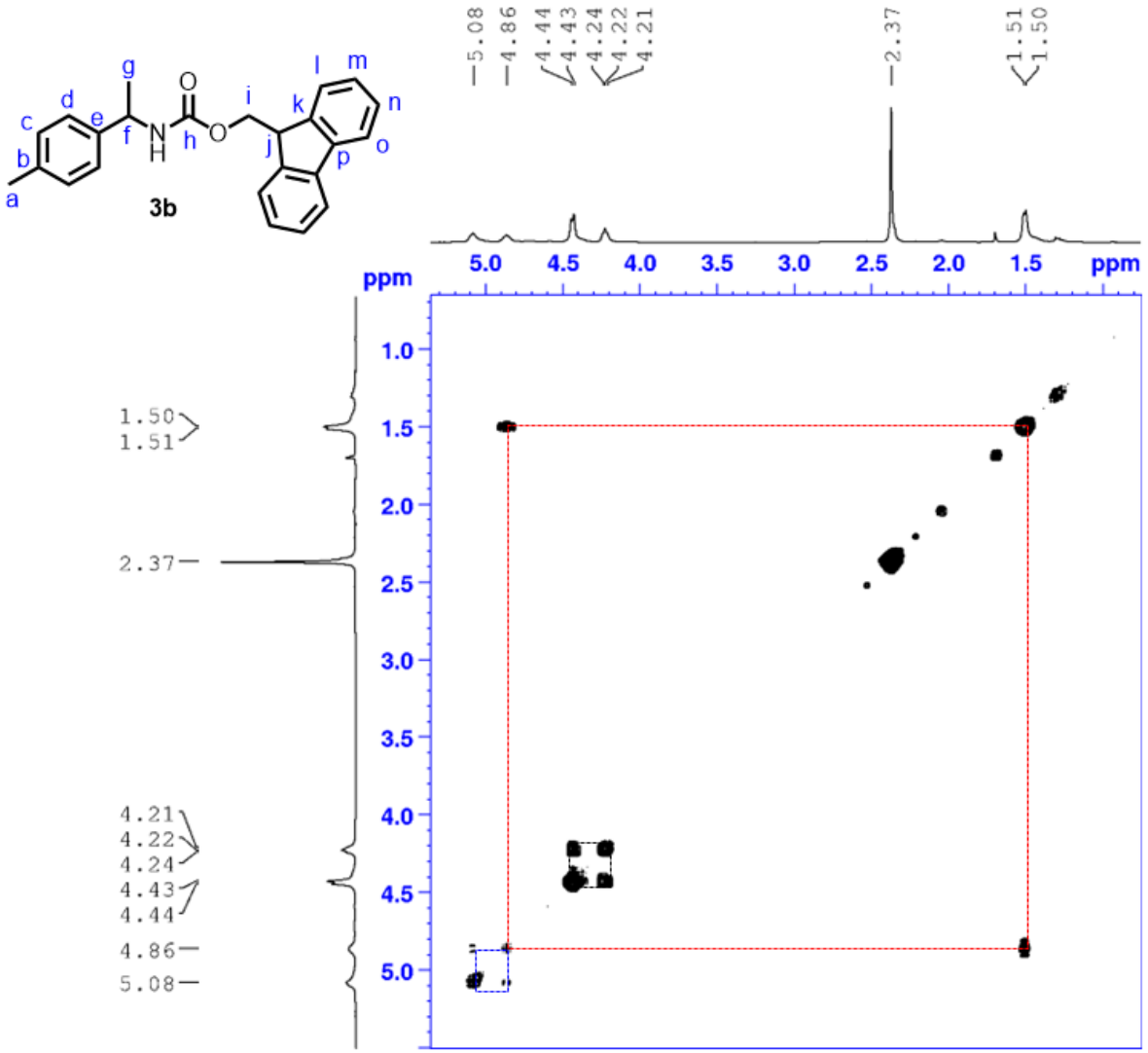


Figure S23: $^{13}C\{^{1}H\}$ and DEPT-135 NMR spectra of **(9H-fluoren-9-yl)methyl (1-(*p*-tolyl)ethyl)carbamate**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4.44
4.43
4.24
4.22
4.21
2.37
1.51
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ppm
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0

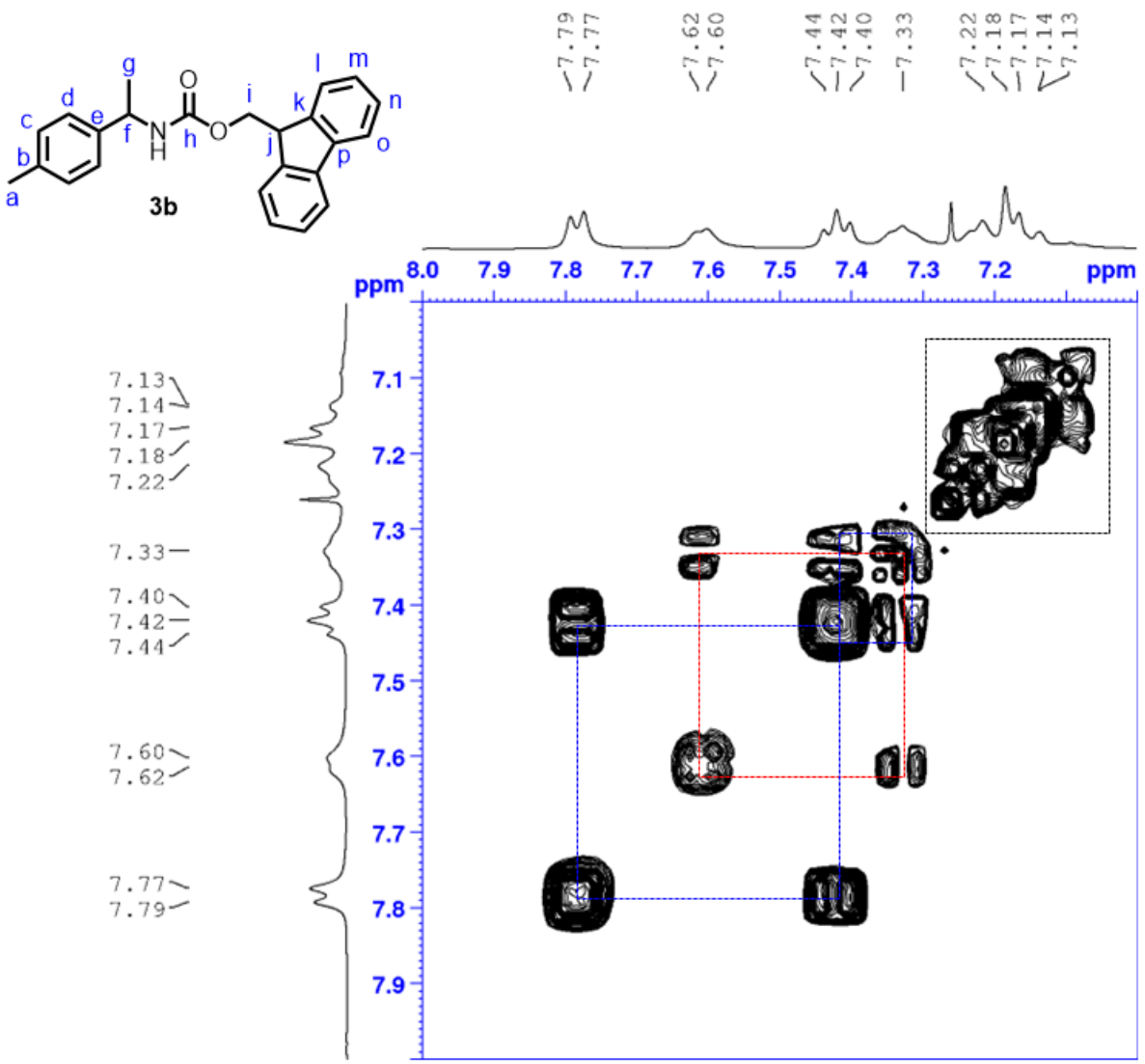
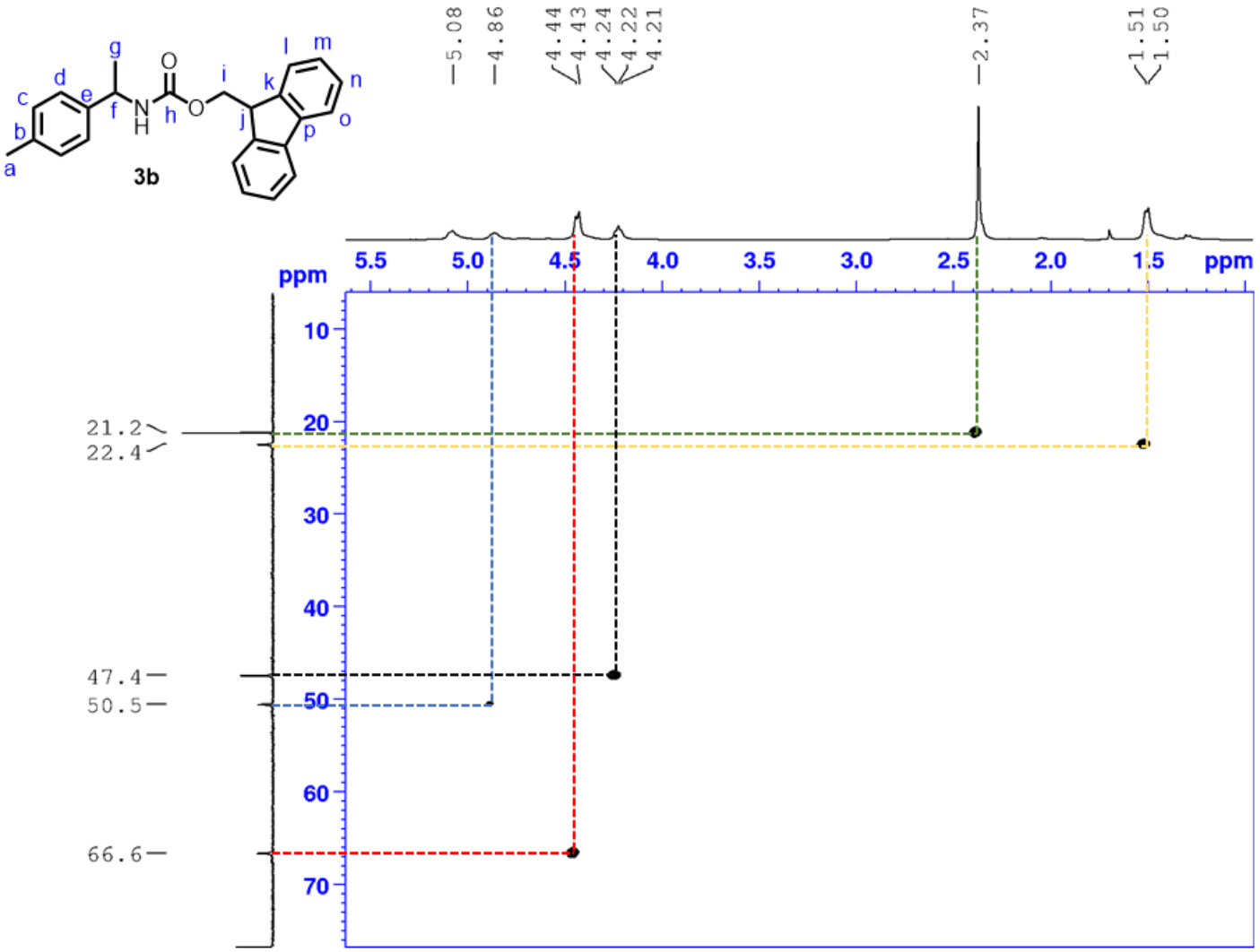


Figure S24: COSY of (9H-fluoren-9-yl)methyl(1-(p-tolyl)ethyl)carbamate **(3b)** in $CDCl_3$. Alkyl and aryl regions were zoomed separately.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1.50
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5.0
4.5
4.0
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3.0
2.5
2.0
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30
40
50
60
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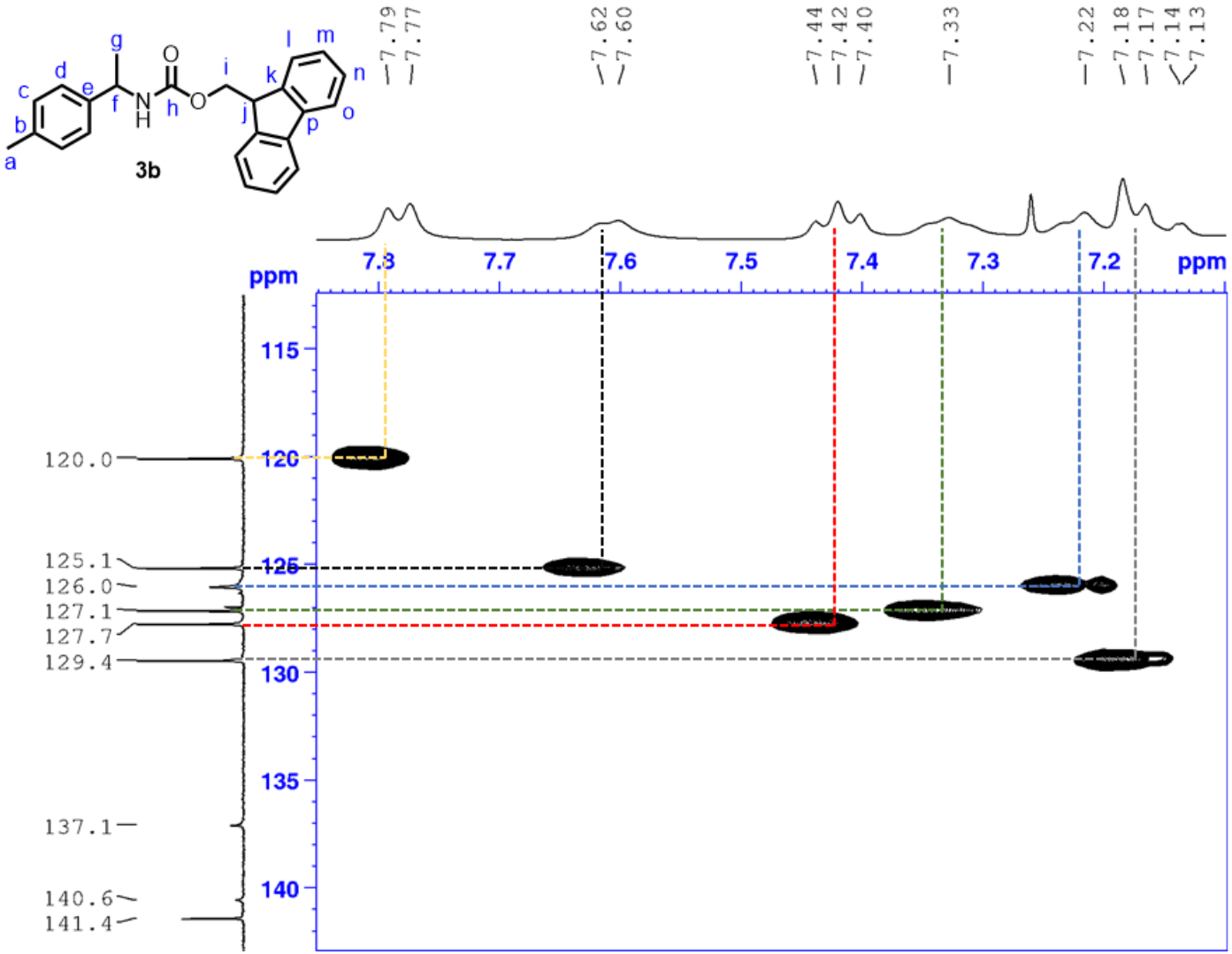


Figure S25: HSQC of (9H-fluoren-9-yl)methyl(1-(p-tolyl)ethyl)carbamate **(3b)** in $CDCl_3$. Alkyl and aryl regions were zoomed separately.

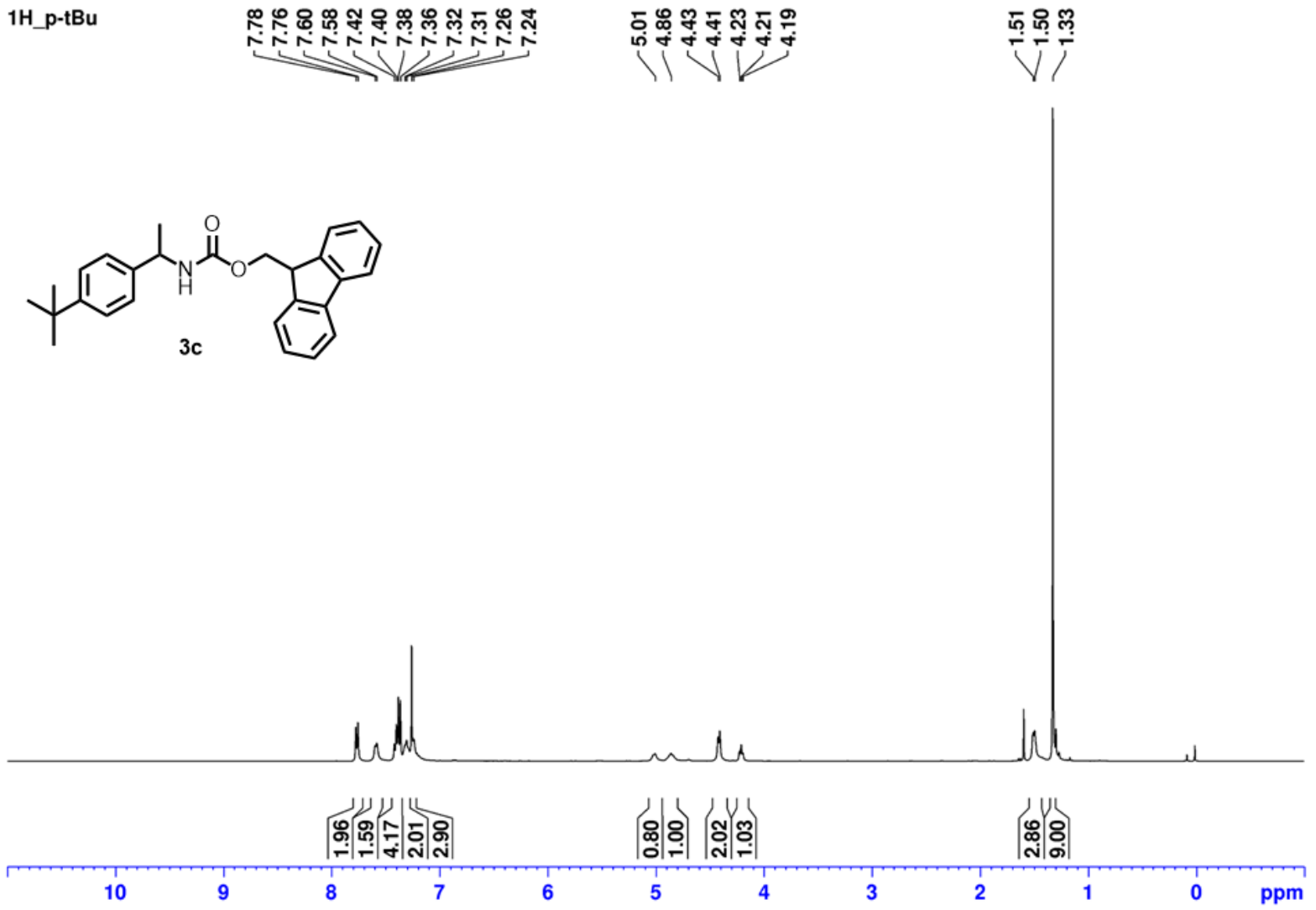


Figure S26: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-(tert-butyl)phenyl)ethyl)carbamate**

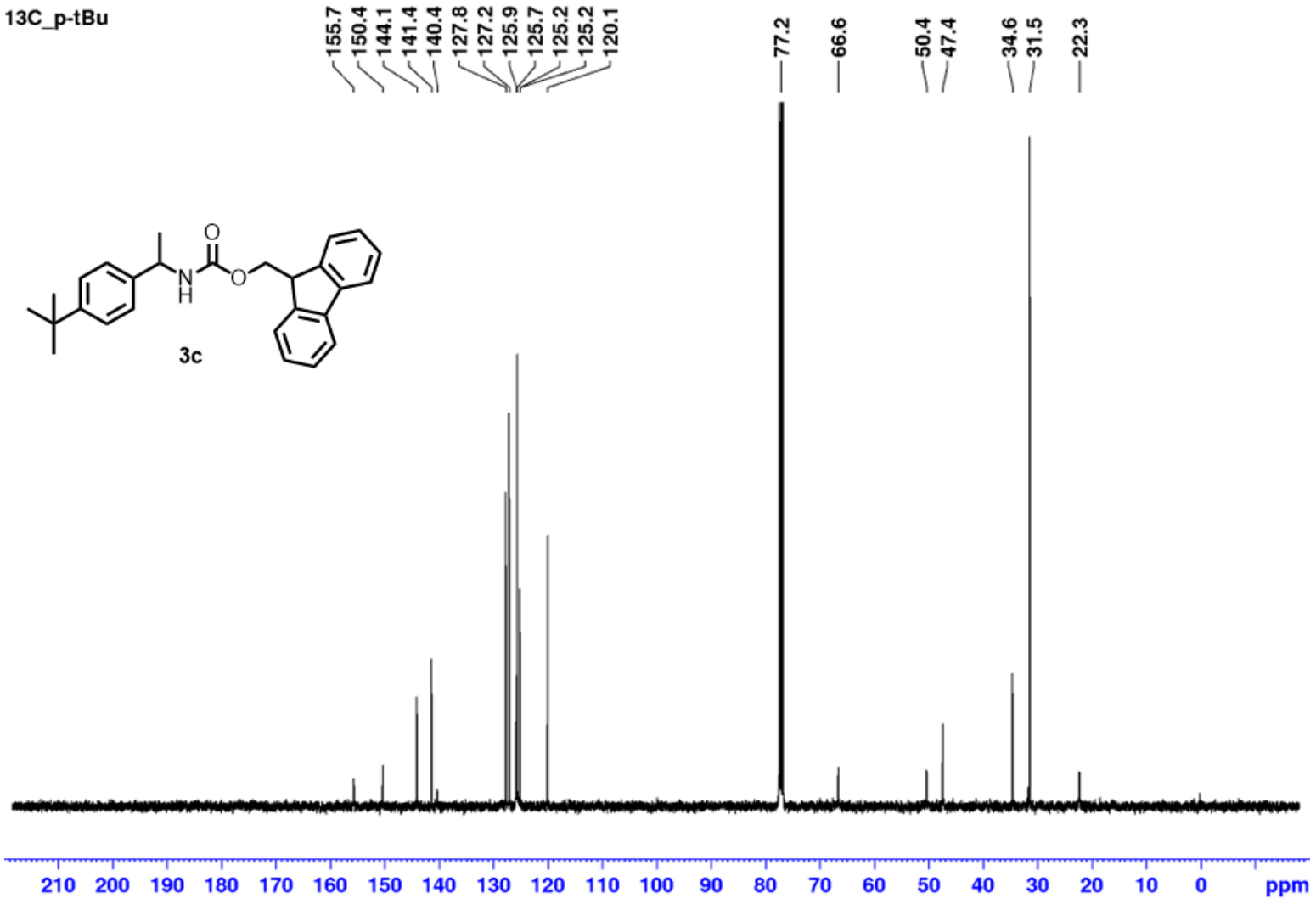


Figure S27: $^{13}C\{^{1}H\}$ spectrum of **(9H-fluoren-9-yl)methyl (1-(4-(tert-butyl)phenyl)ethyl)carbamate**

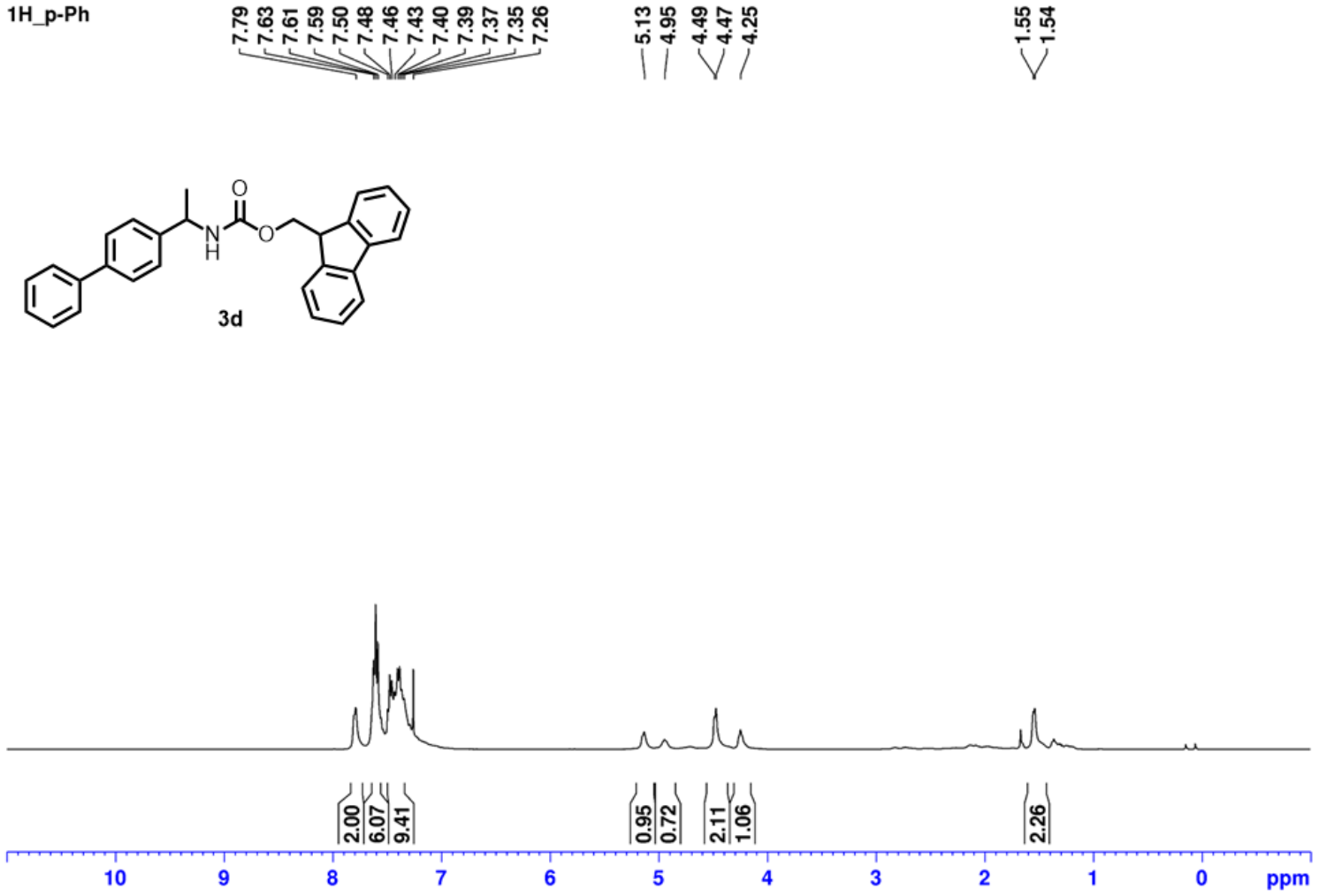


Figure S28: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-([1,1'-biphenyl]-4-yl)ethyl)carbamate**

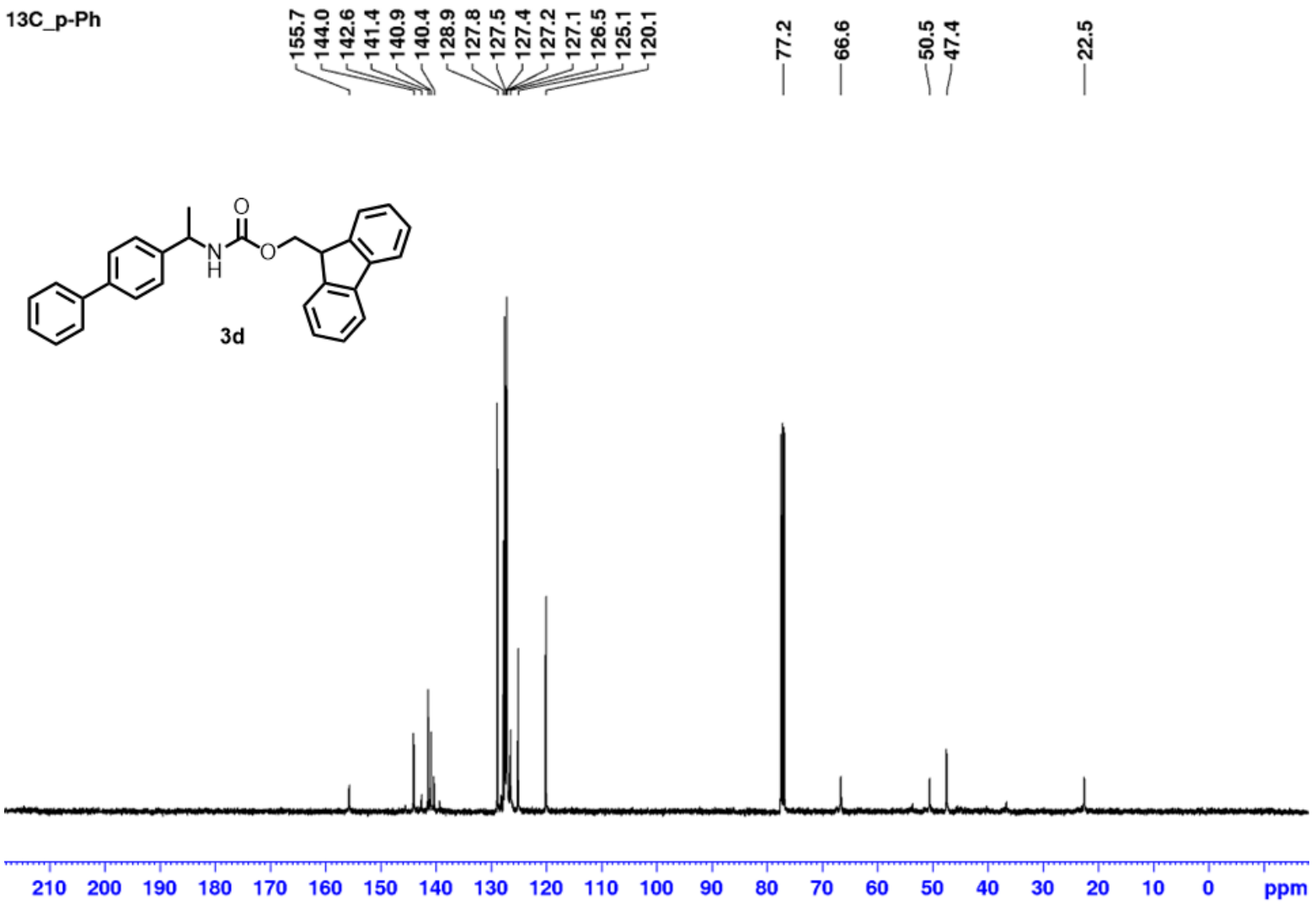


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-([1,1'-biphenyl]-4-yl)ethyl)carbamate**

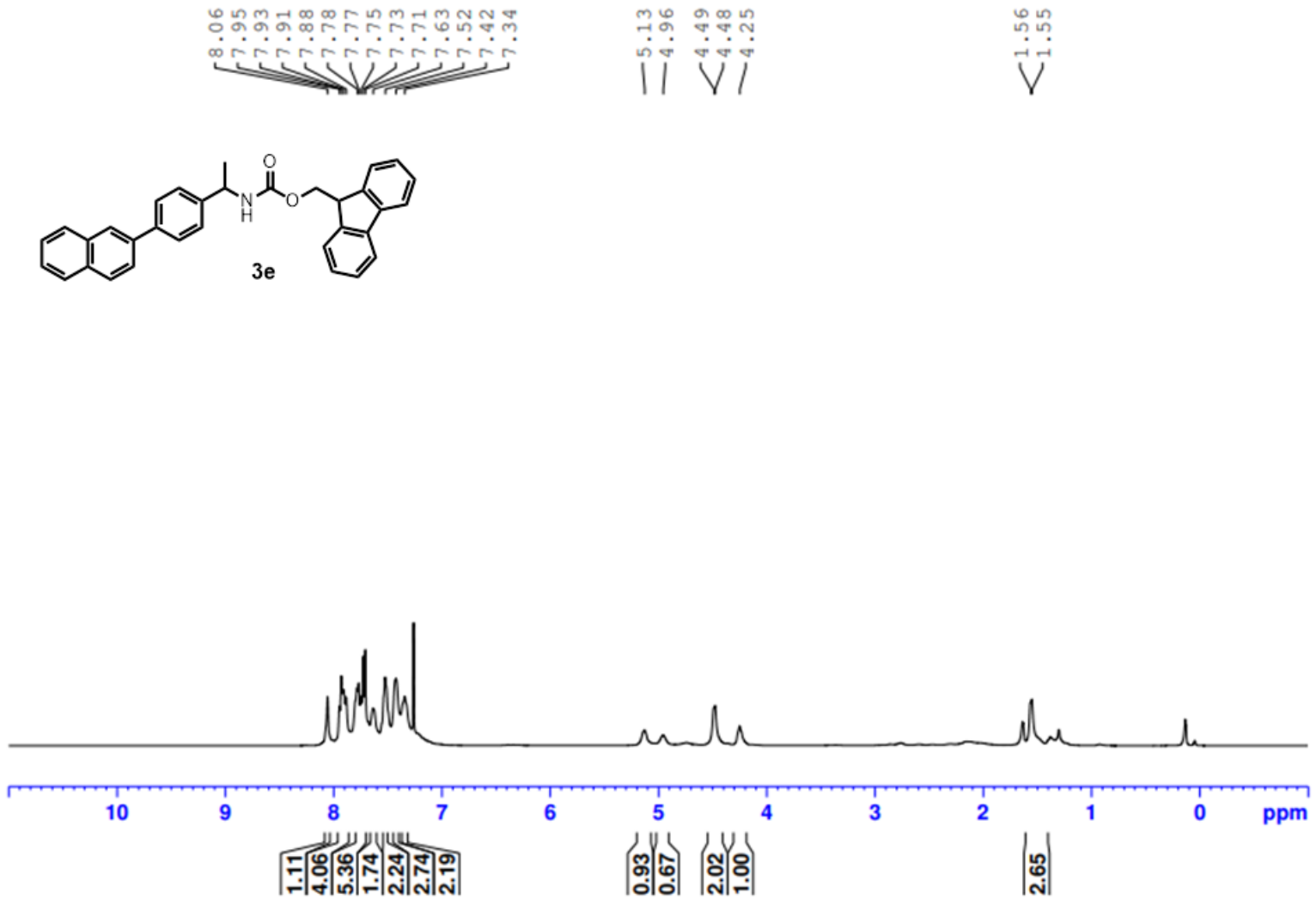


Figure S30: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(naphthalen-2-yl)ethyl)carbamate**

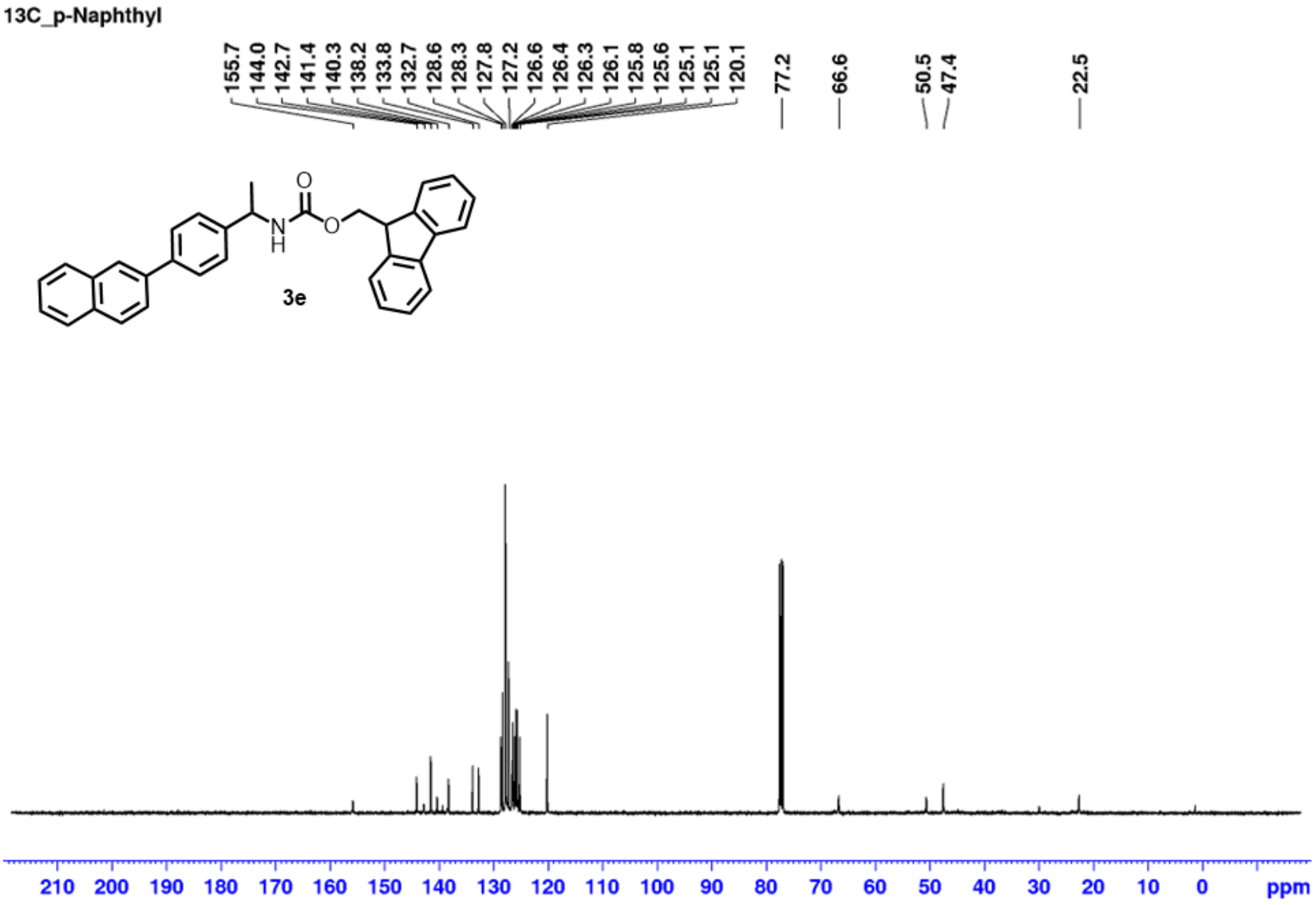


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(naphthalen-2-yl)ethyl)carbamate**

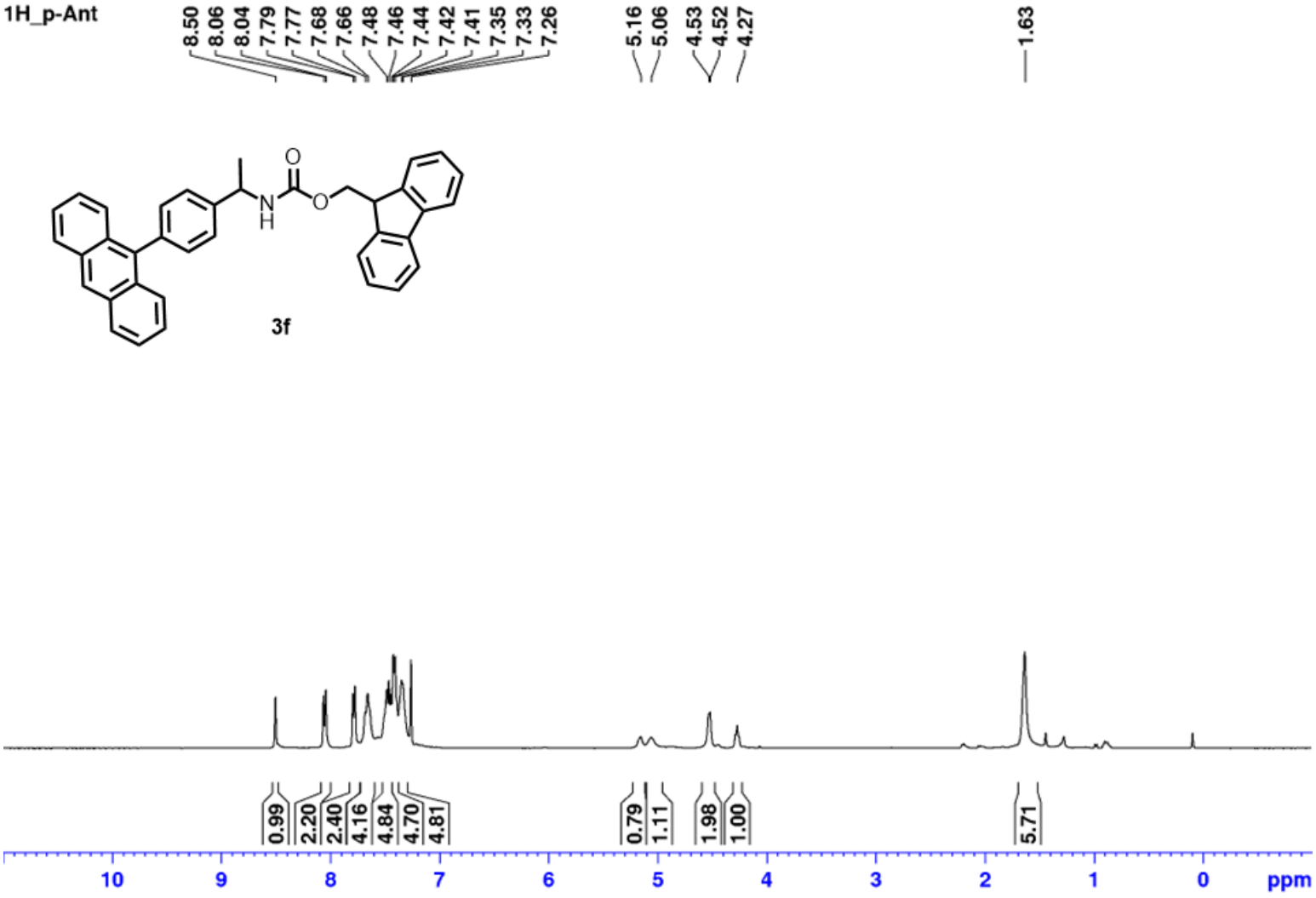


Figure S32: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-(anthracen-9-yl)phenyl)ethyl)carbamate**

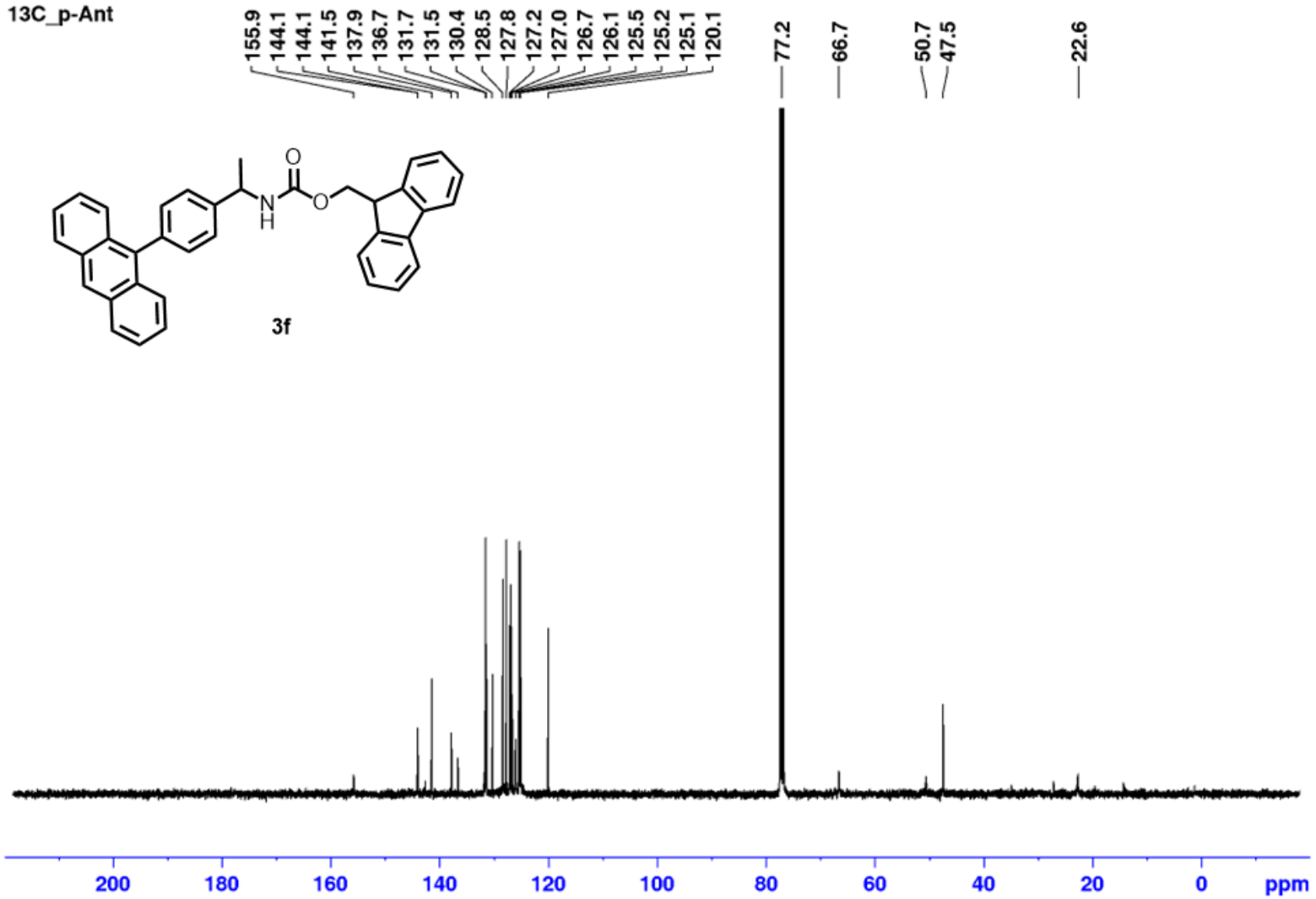


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-(anthracen-9-yl)phenyl)ethyl)carbamate**

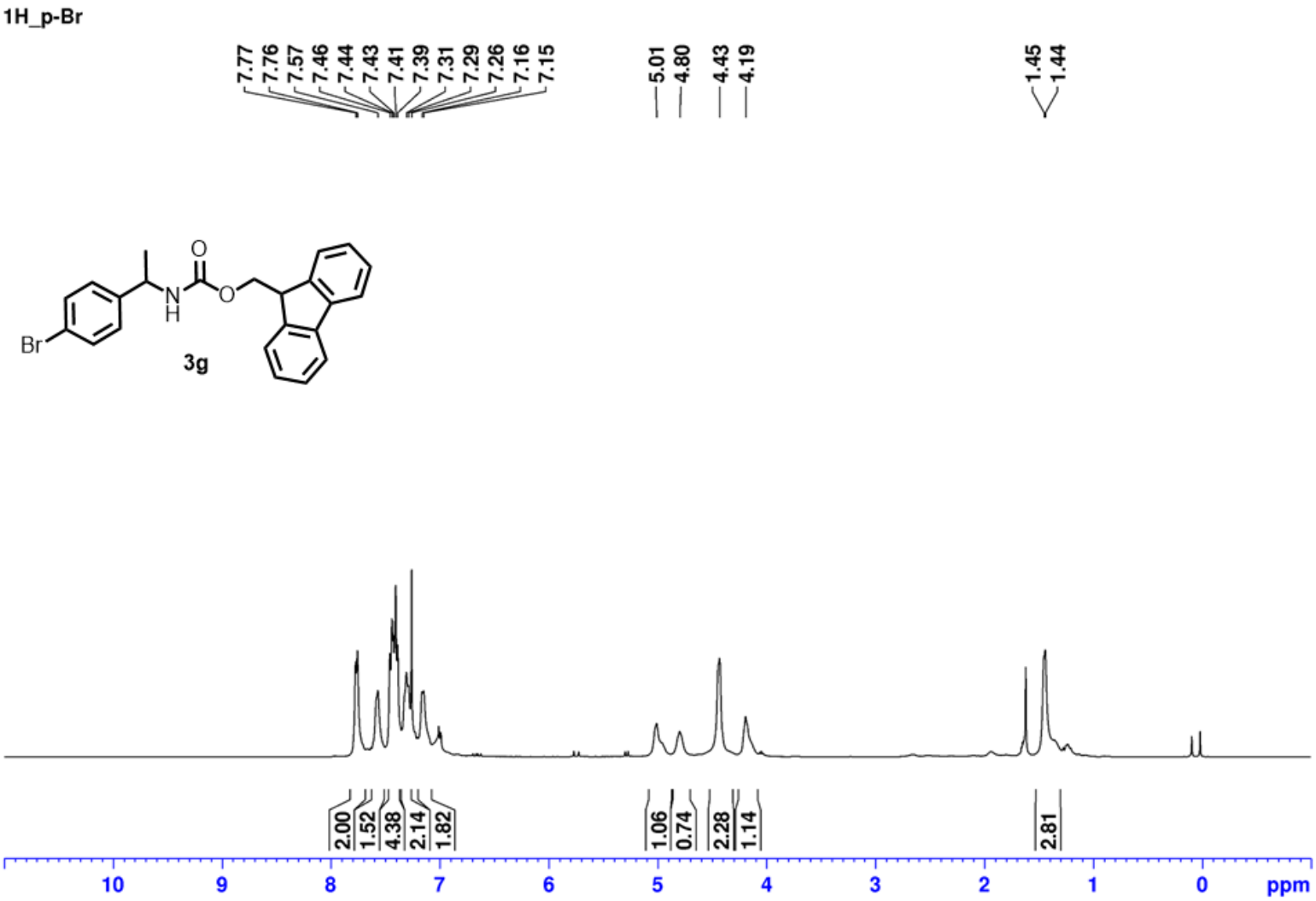


Figure S34: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-bromophenyl)ethyl)carbamate**

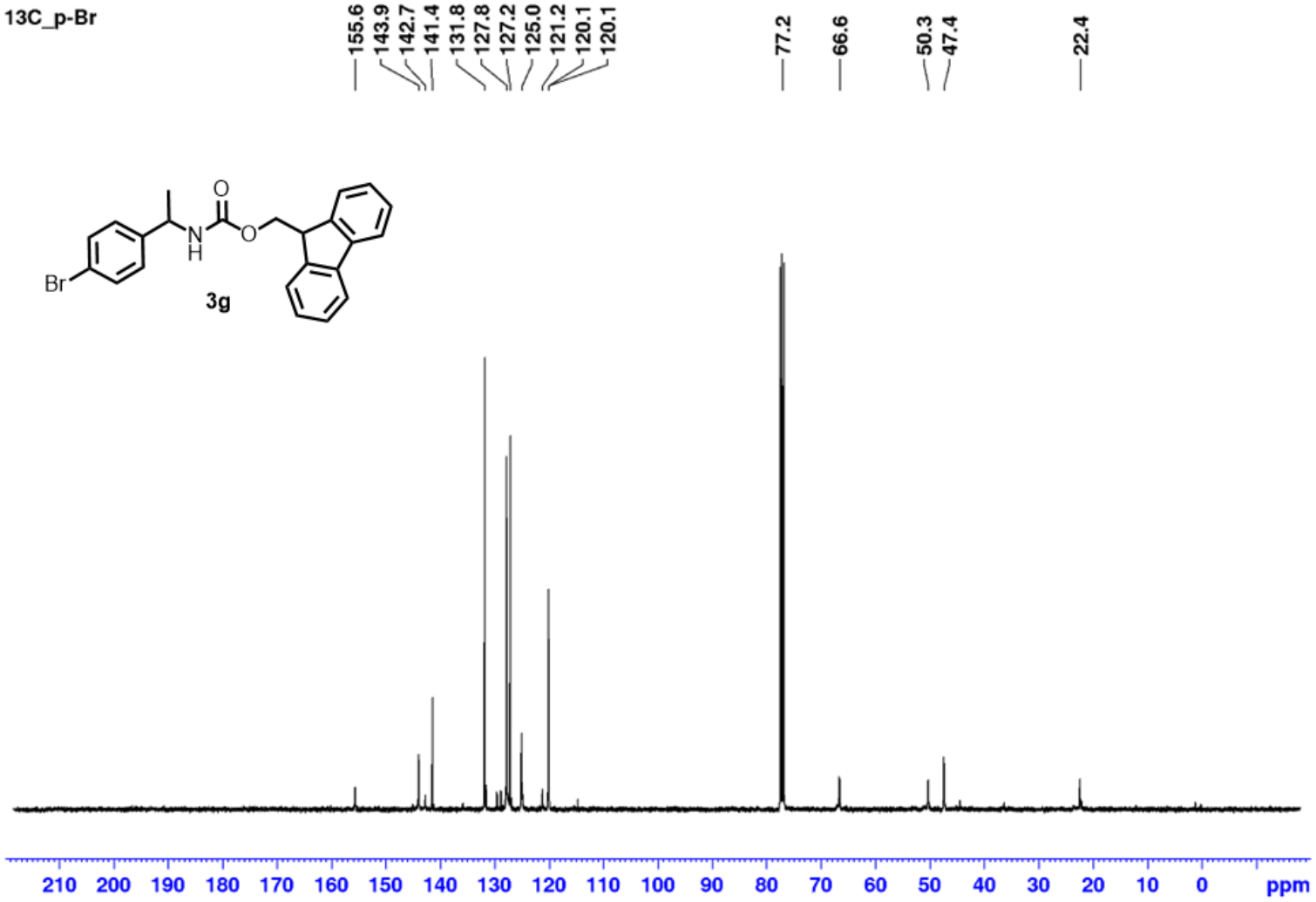


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-bromophenyl)ethyl)carbamate**

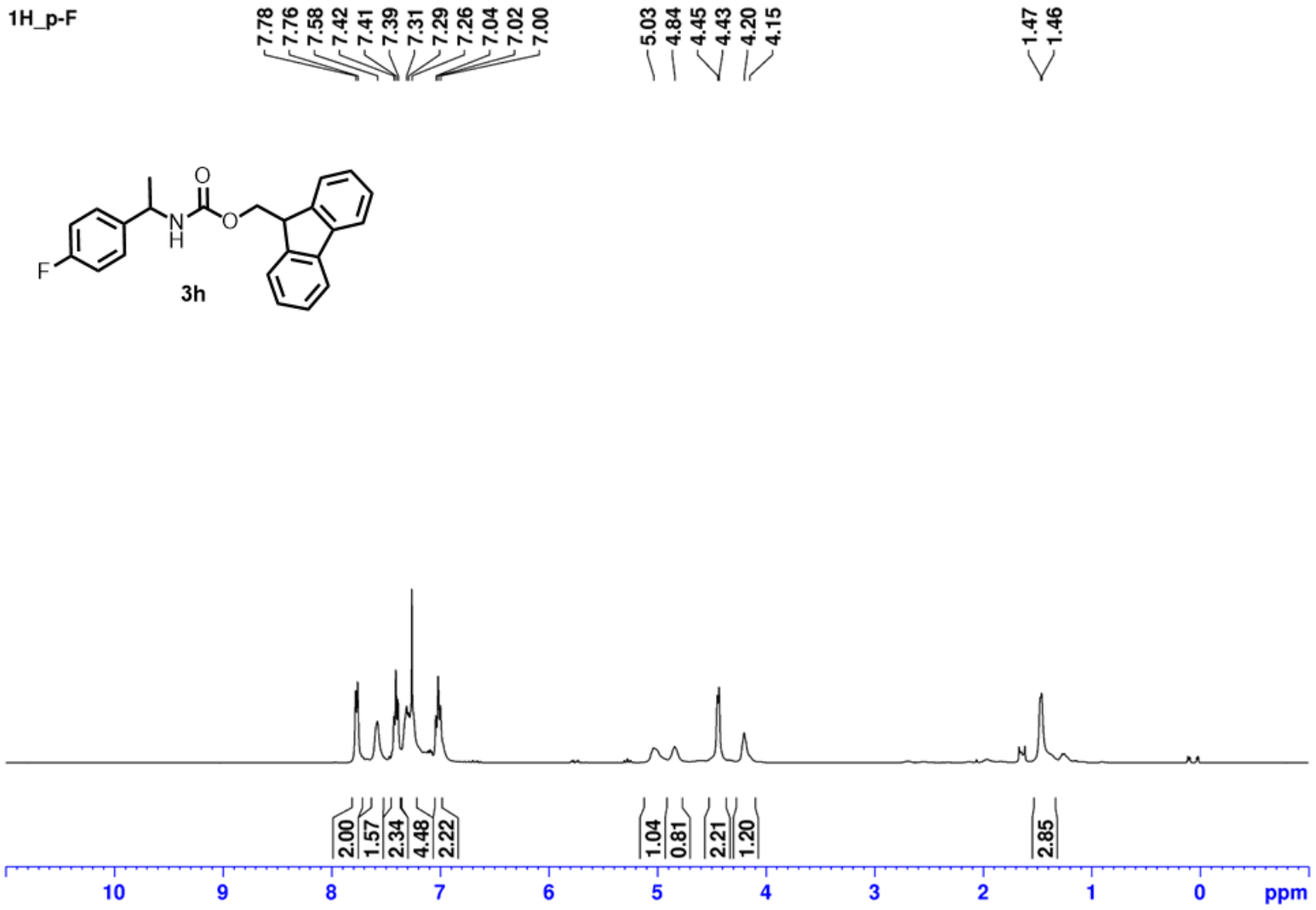


Figure S36: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-fluorophenyl)ethyl)carbamate**

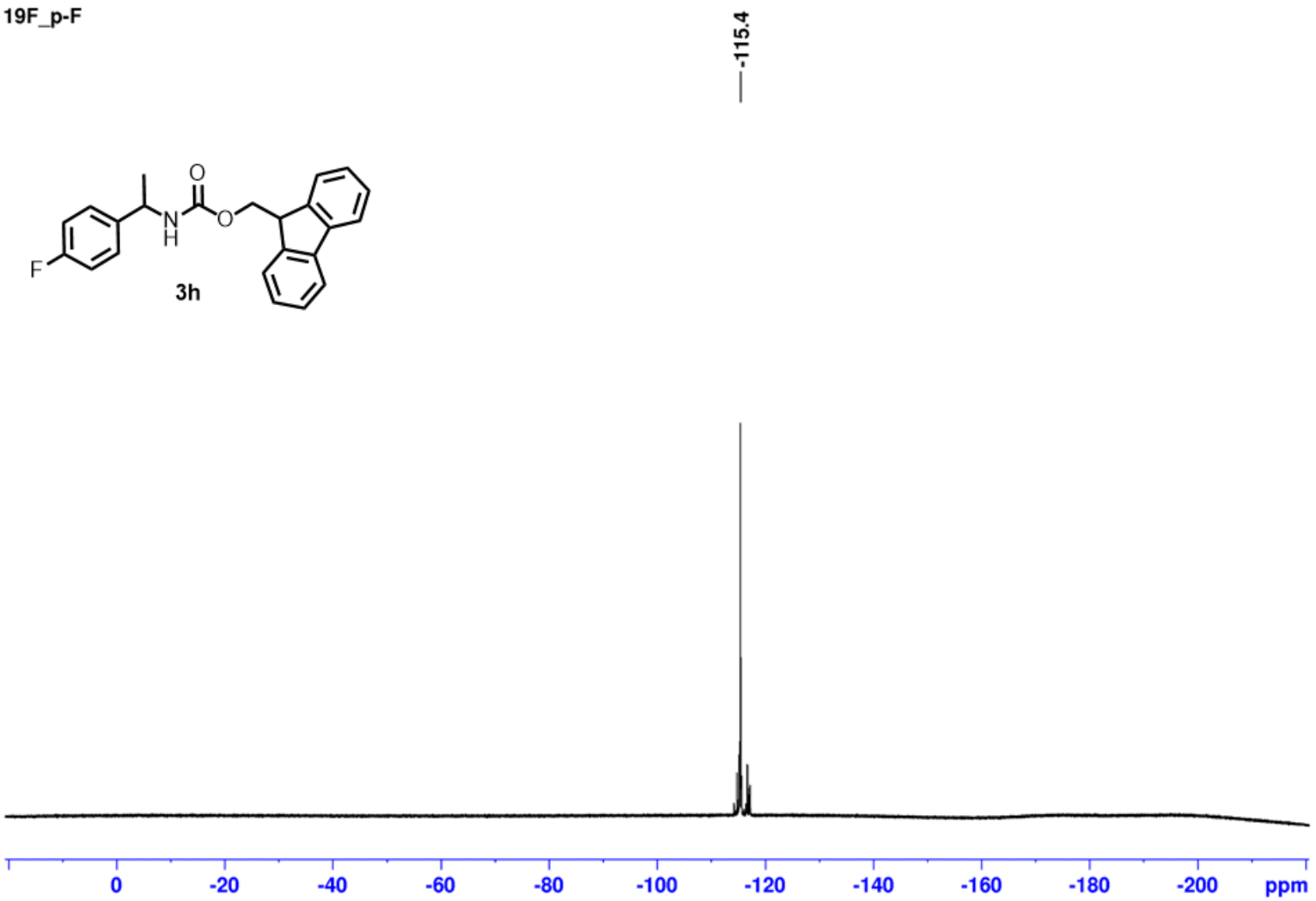


Figure S37: $^{19}F\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-fluorophenyl)ethyl)carbamate**

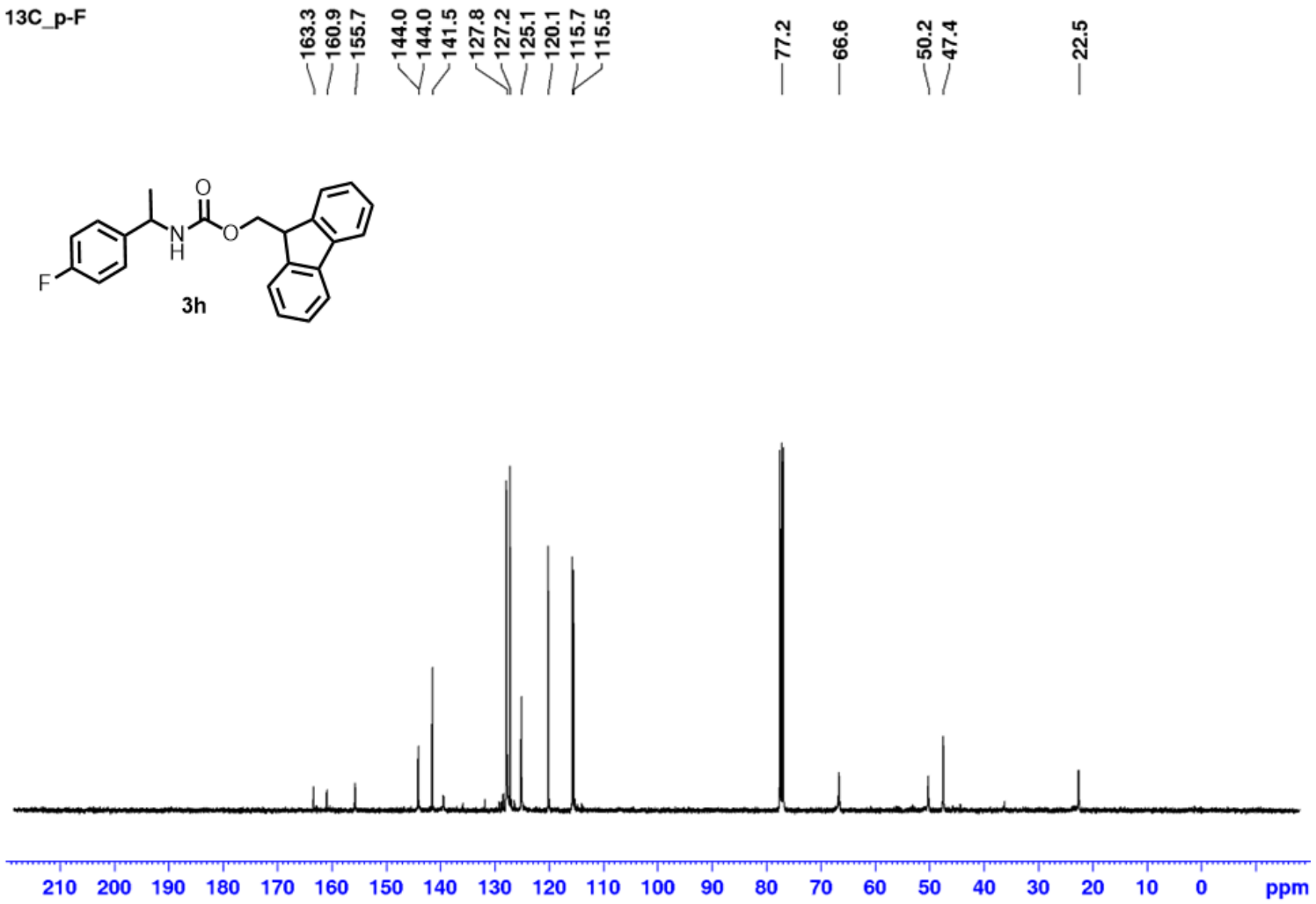


Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(4-fluorophenyl)ethyl)carbamate**

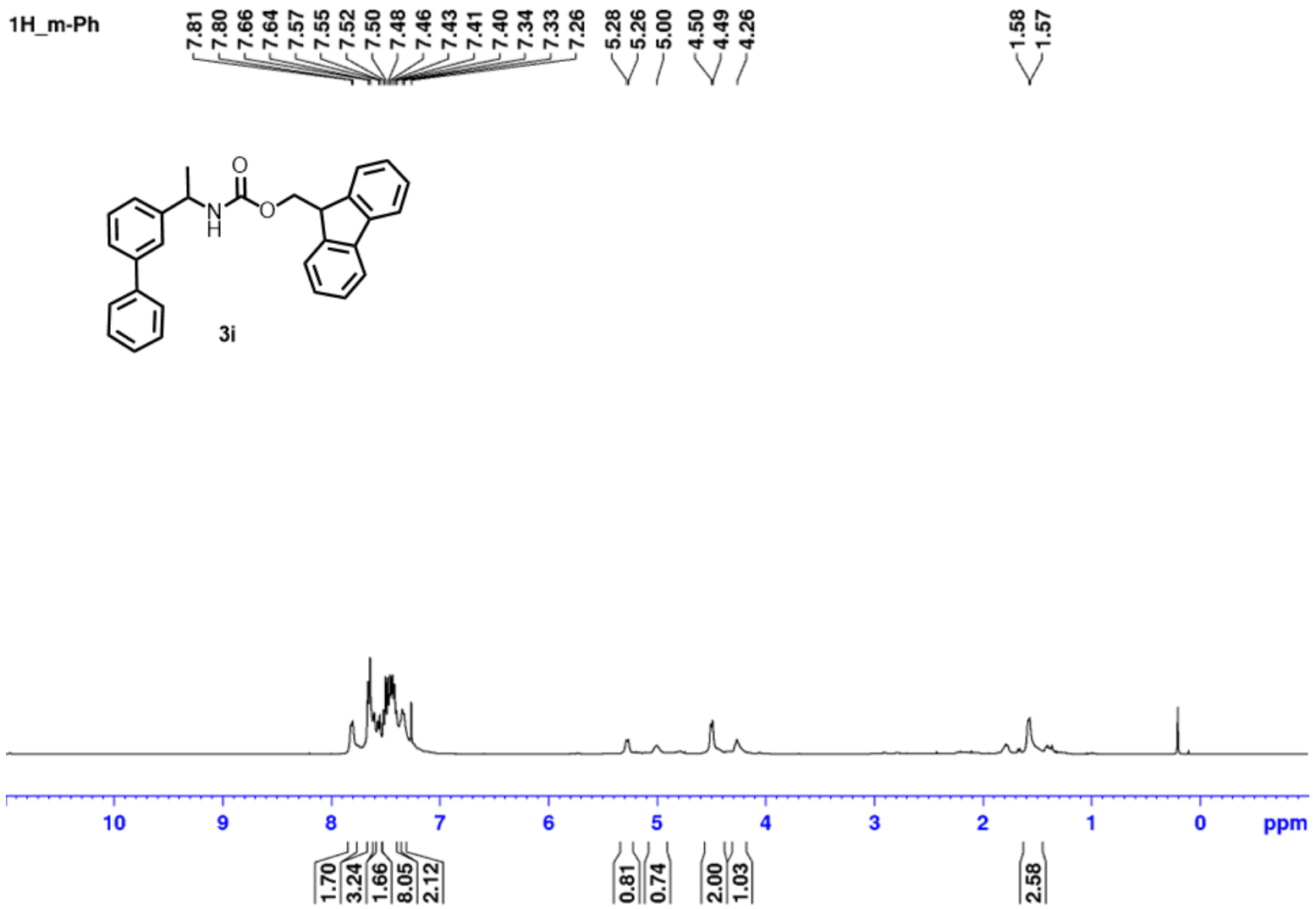


Figure S39: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-([1,1'-biphenyl]-3-yl)ethyl)carbamate**

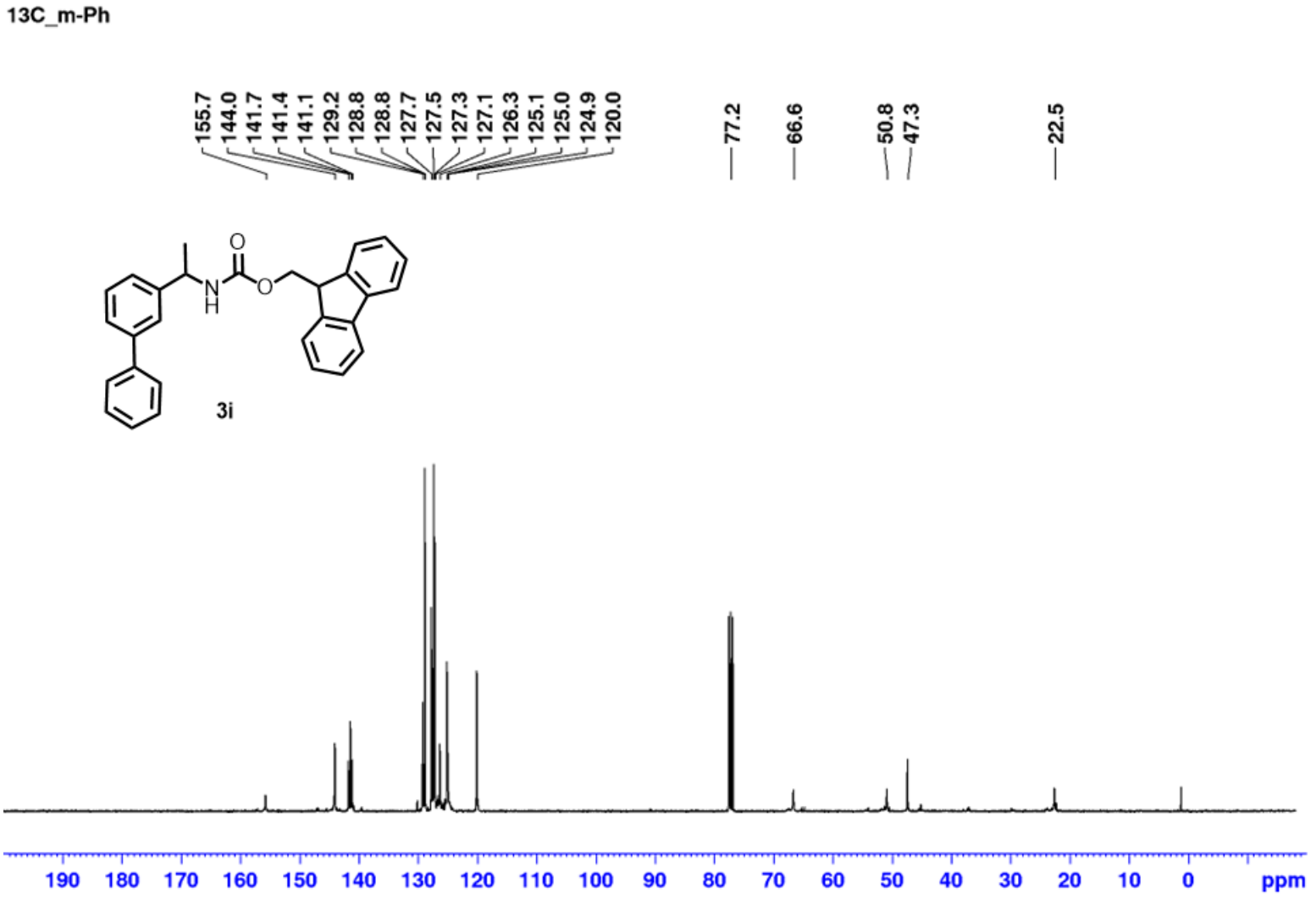


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum of **((9H-fluoren-9-yl)methyl (1-([1,1'-biphenyl]-3-yl)ethyl)carbamate**

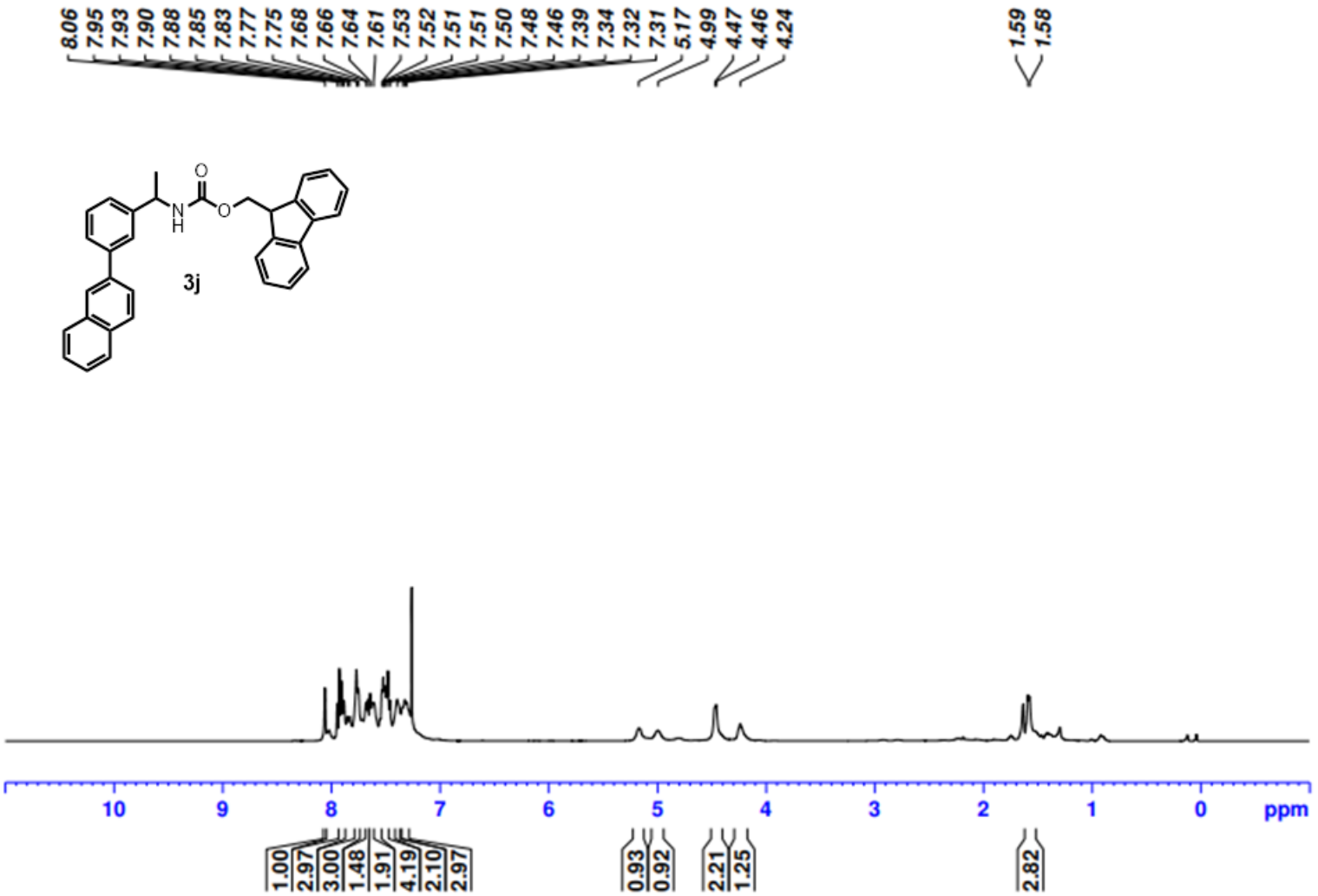


Figure S41: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(3-(naphthalen-2-yl)phenyl)ethyl)carbamate**

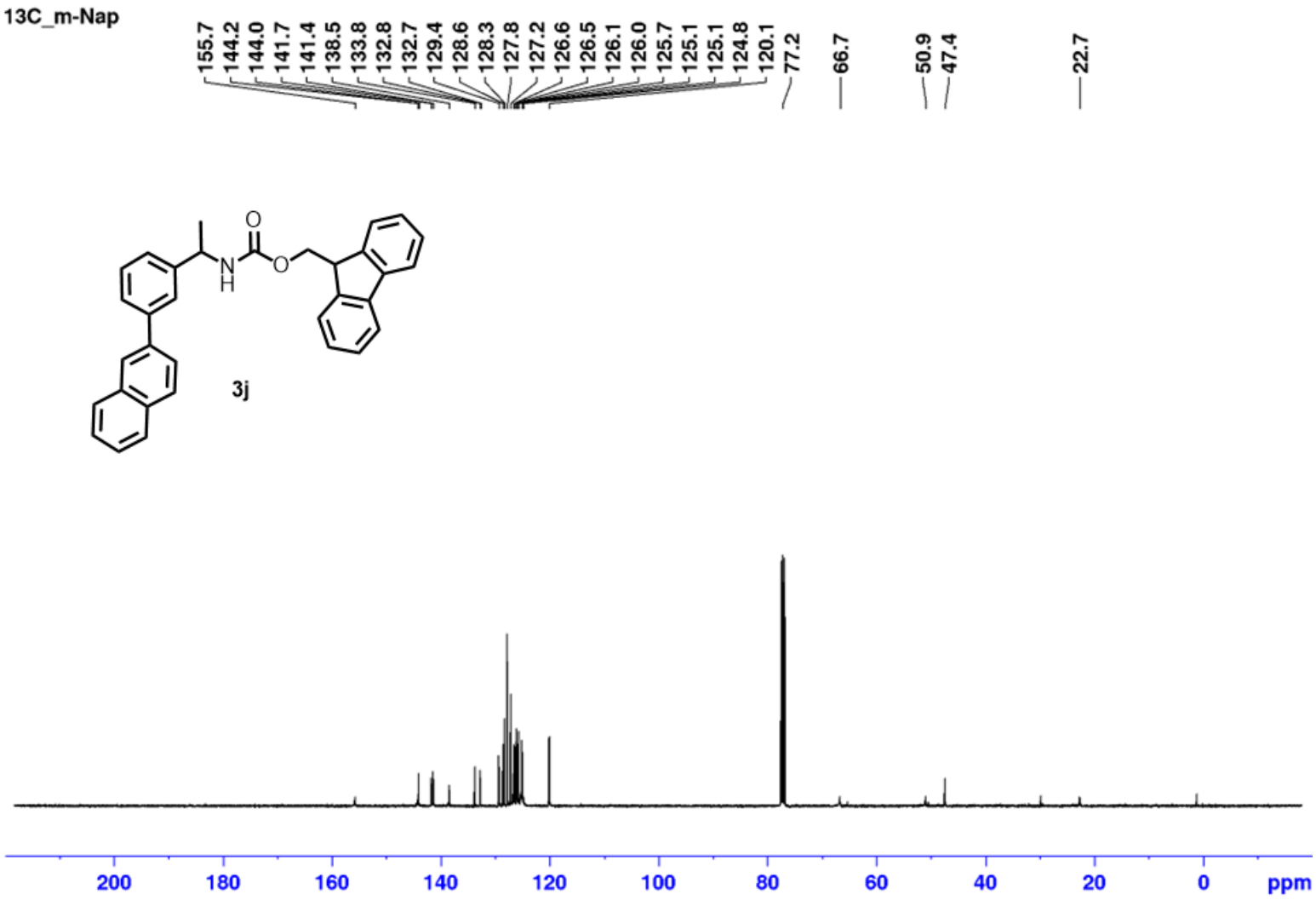


Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(3-(naphthalen-2-yl)phenyl)ethyl)carbamate**

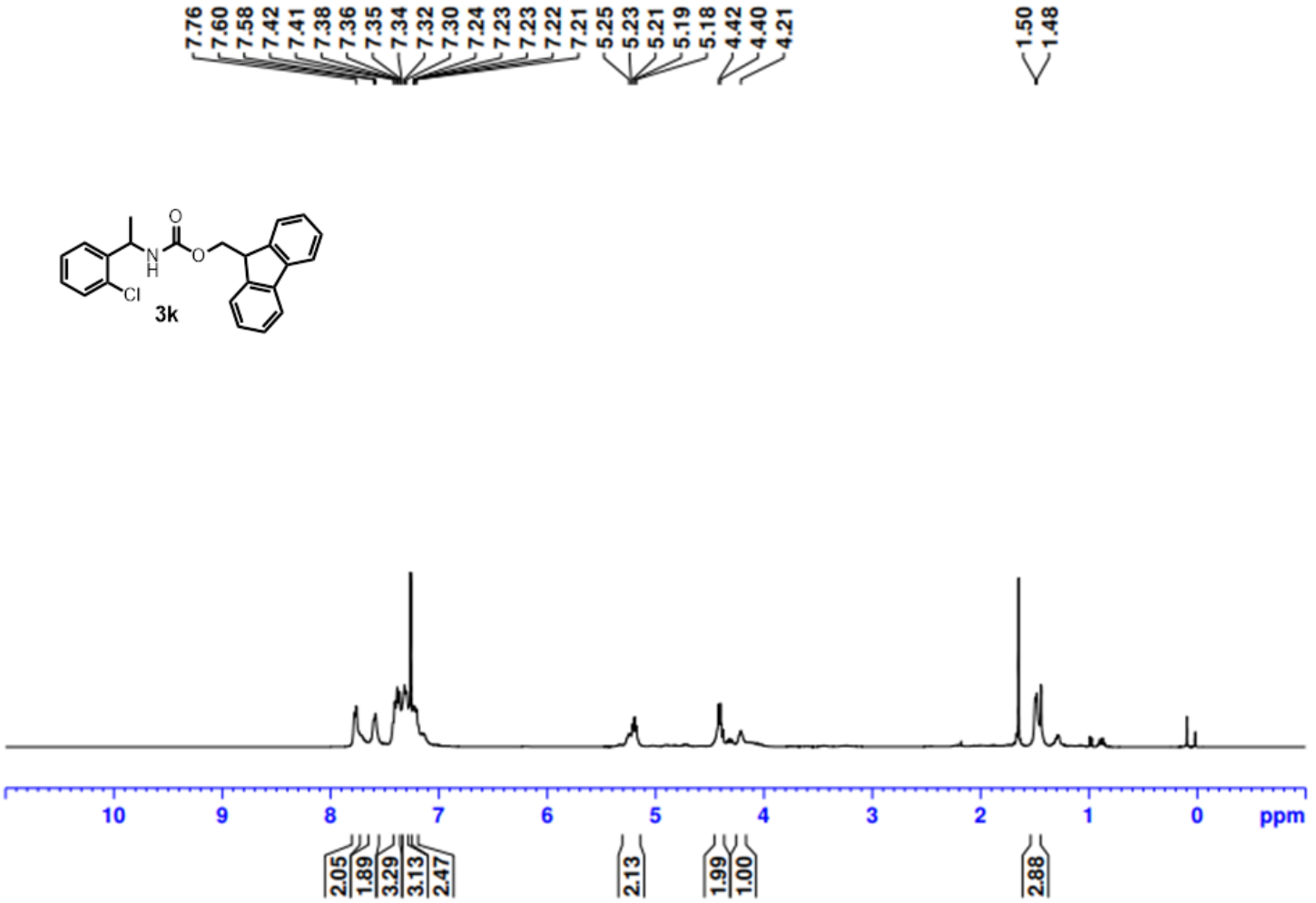


Figure S43: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(2-chlorophenyl)ethyl)carbamate**

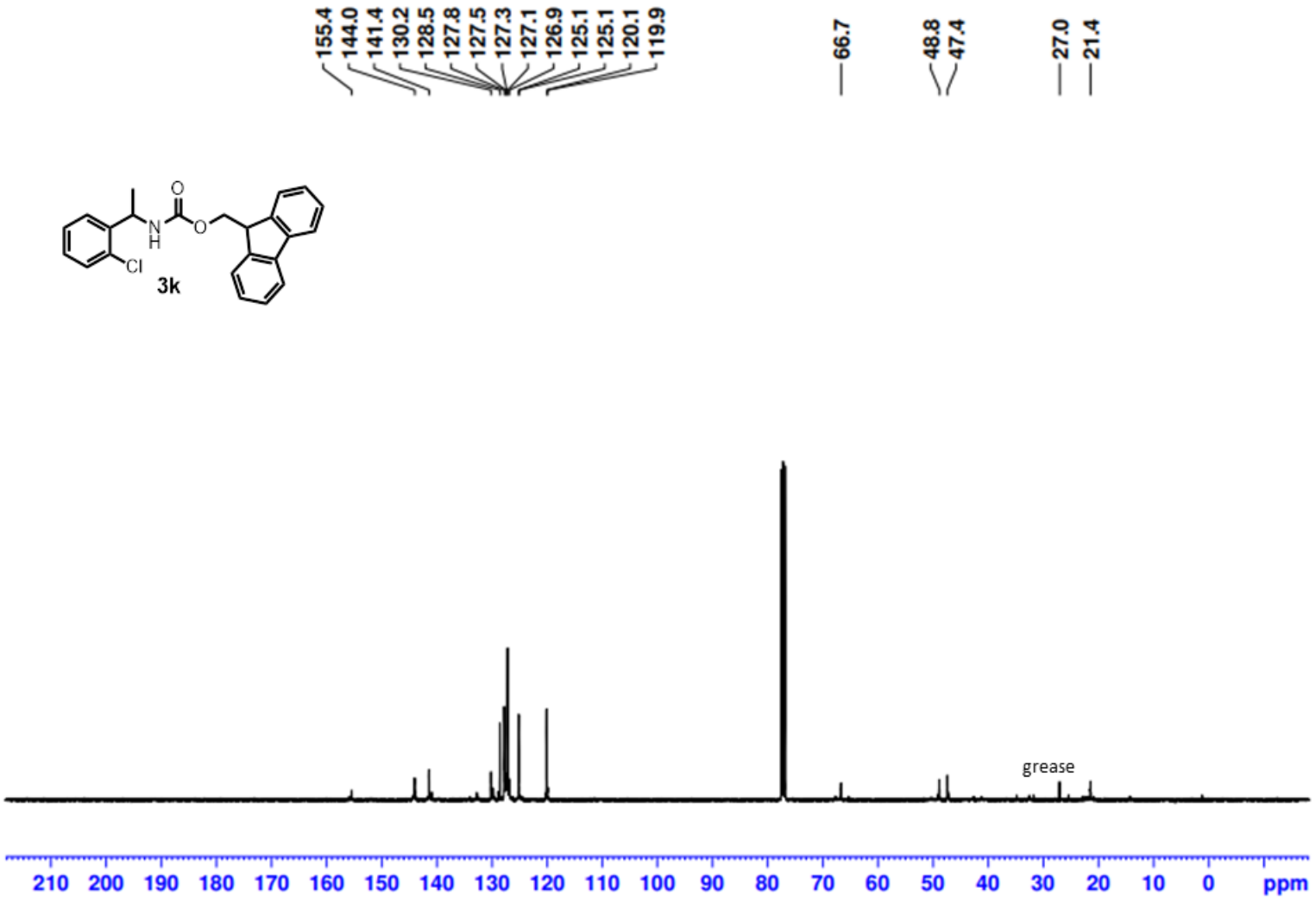


Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1-(2-chlorophenyl)ethyl)carbamate**

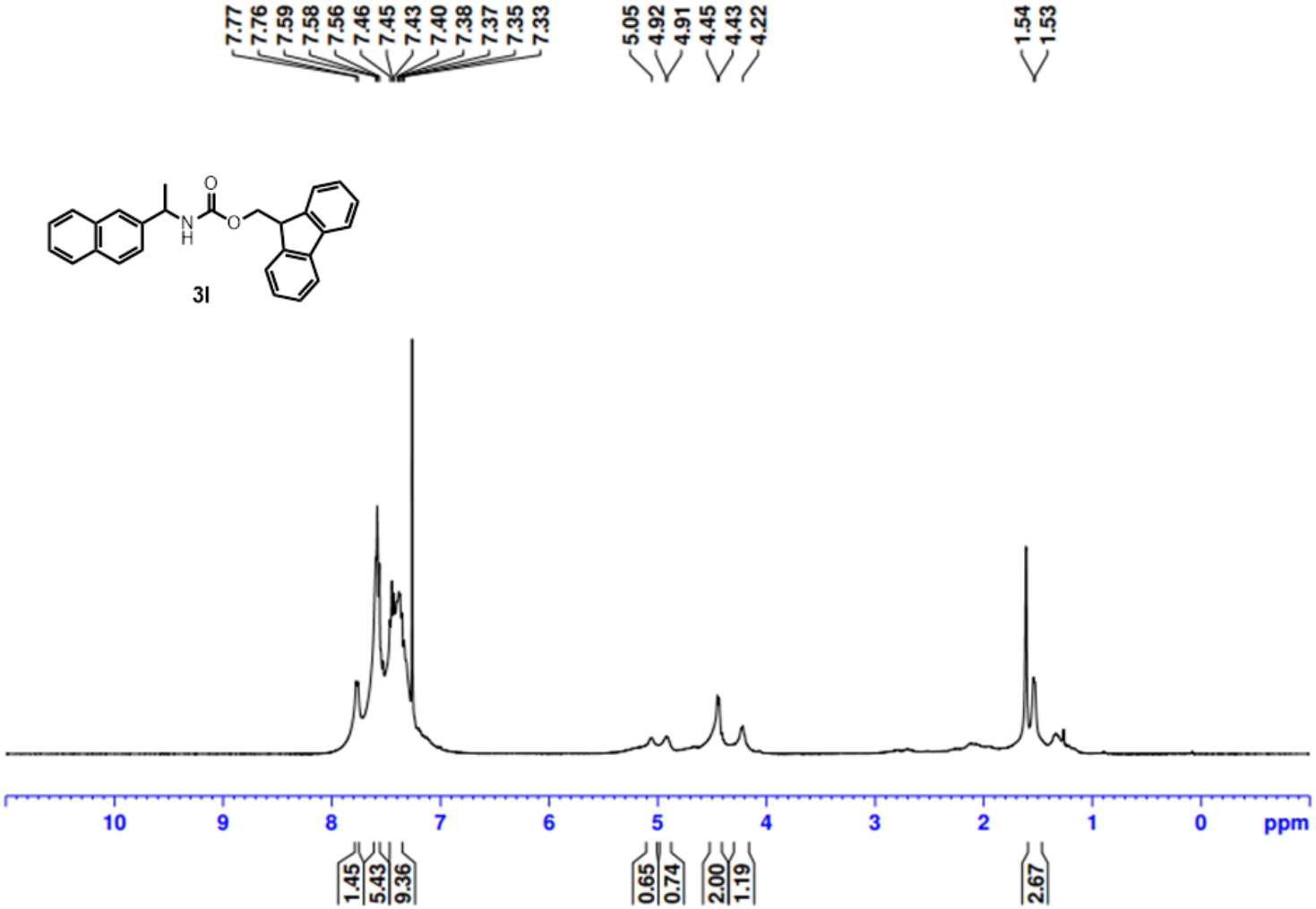


Figure S45: ^{1}H NMR spectrum of **9H-Fluoren-9-ylmethyl (tetrahydropyran-2-yl)carbamate**

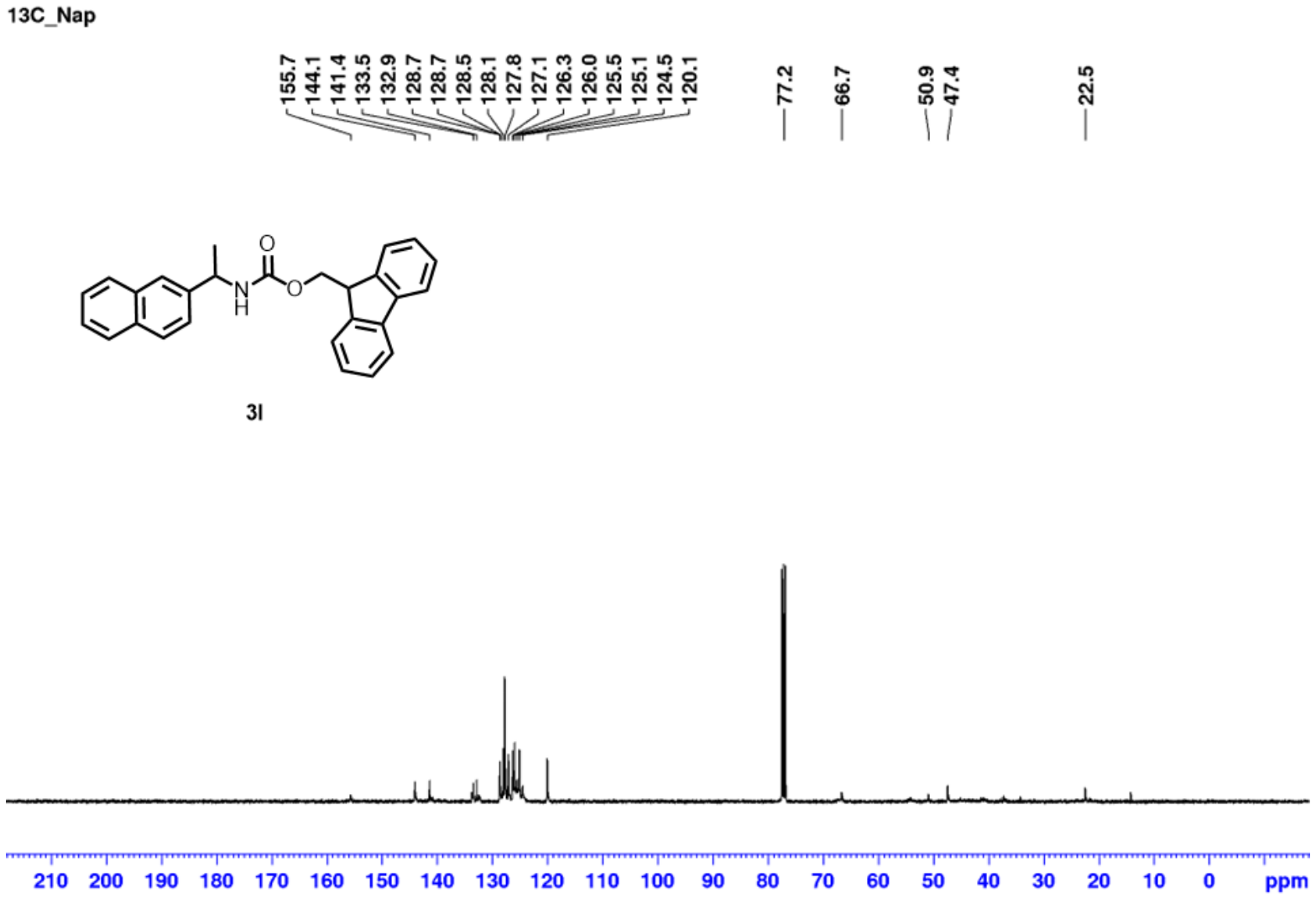


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of **9H-Fluoren-9-ylmethyl (tetrahydropyran-2-yl)carbamate**

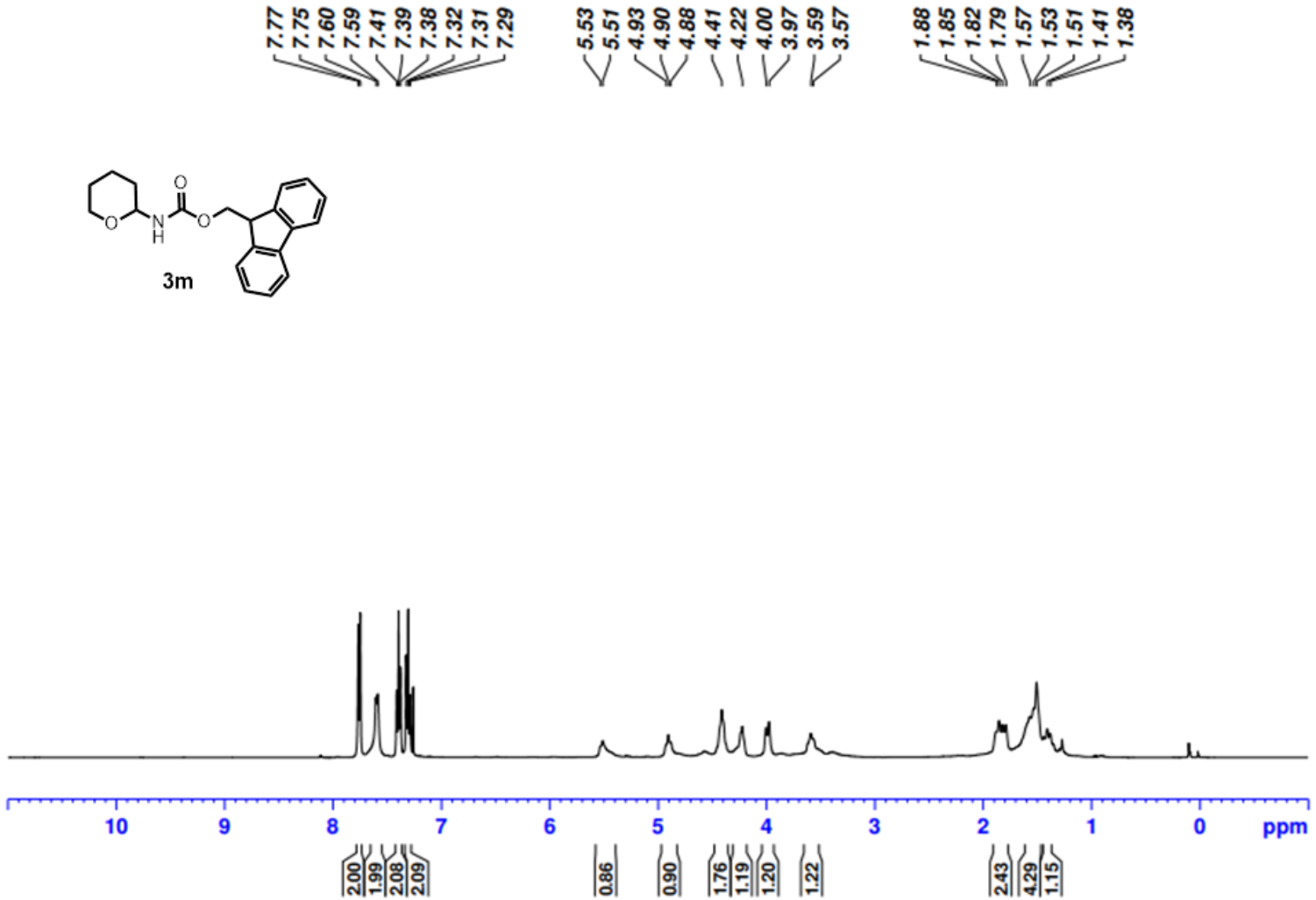


Figure S47: ^{1}H NMR spectrum of **9H-Fluoren-9-ylmethyl (tetrahydropyran-2-yl)carbamate**

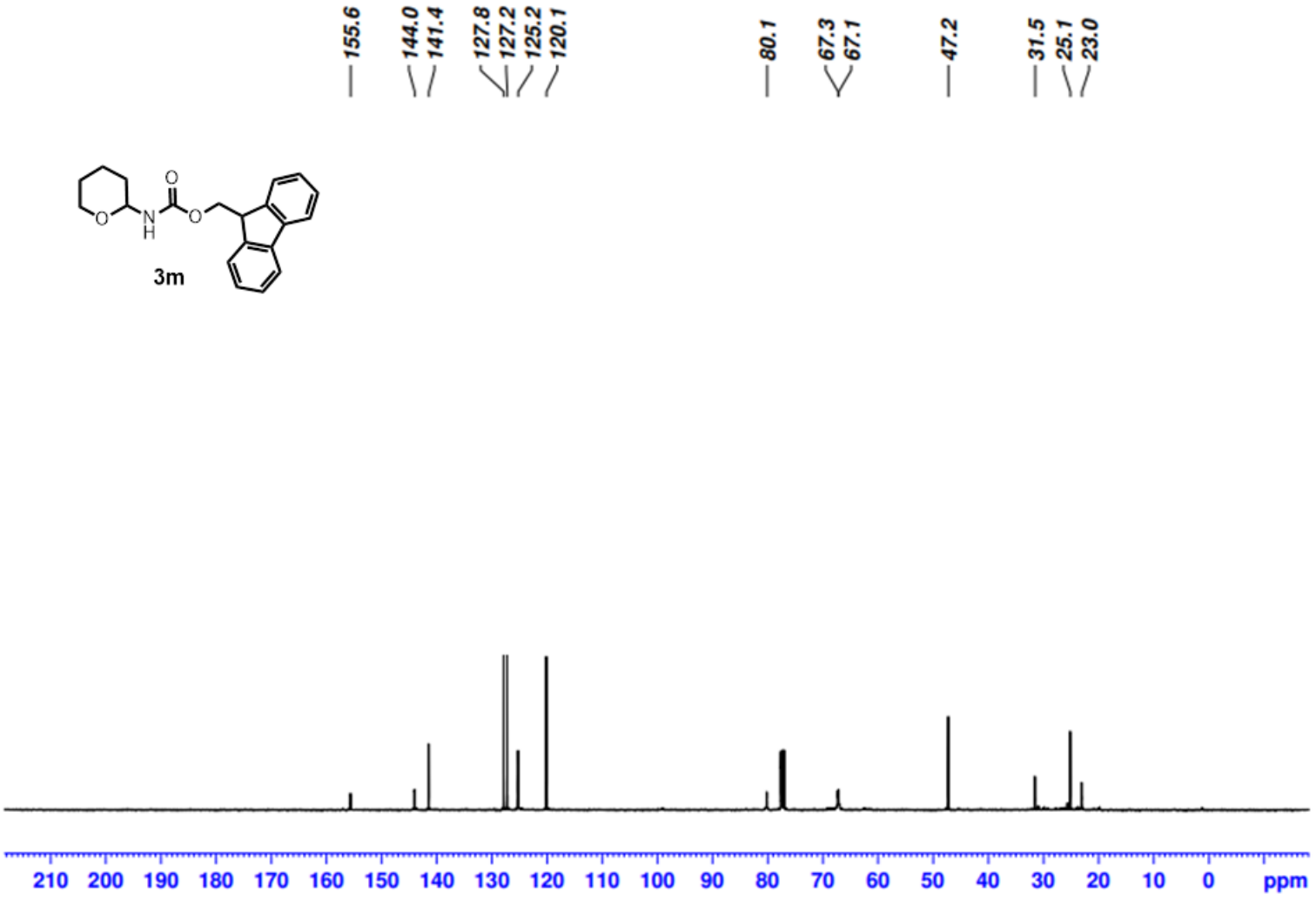


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of **9H-Fluoren-9-ylmethyl (tetrahydropyran-2-yl)carbamate**

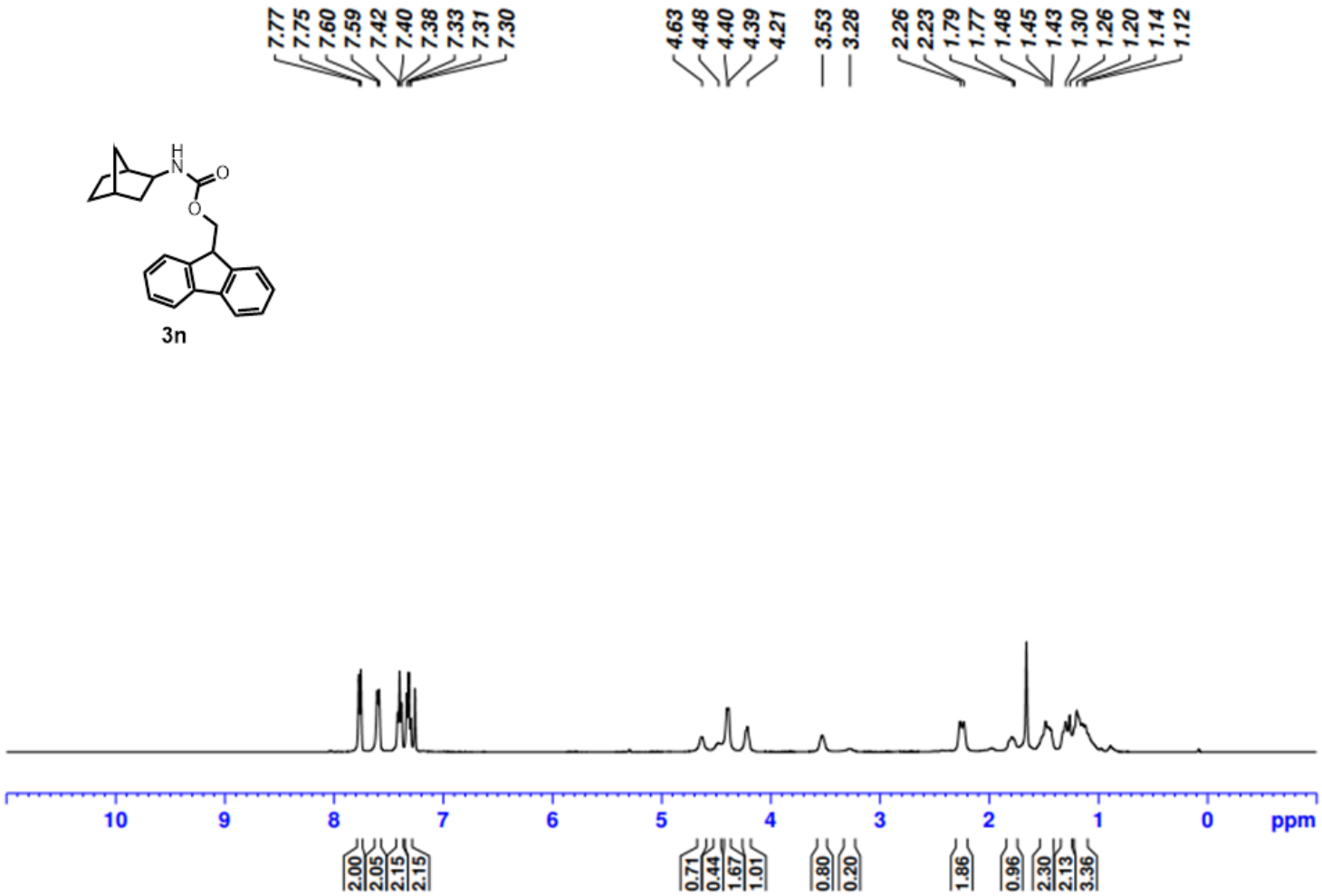


Figure S49: ^{1}H NMR spectrum of **(9H-fluoren-9-yl)methyl (1S,4R)-bicyclo[2.2.1]heptan-2-ylcarbamate**

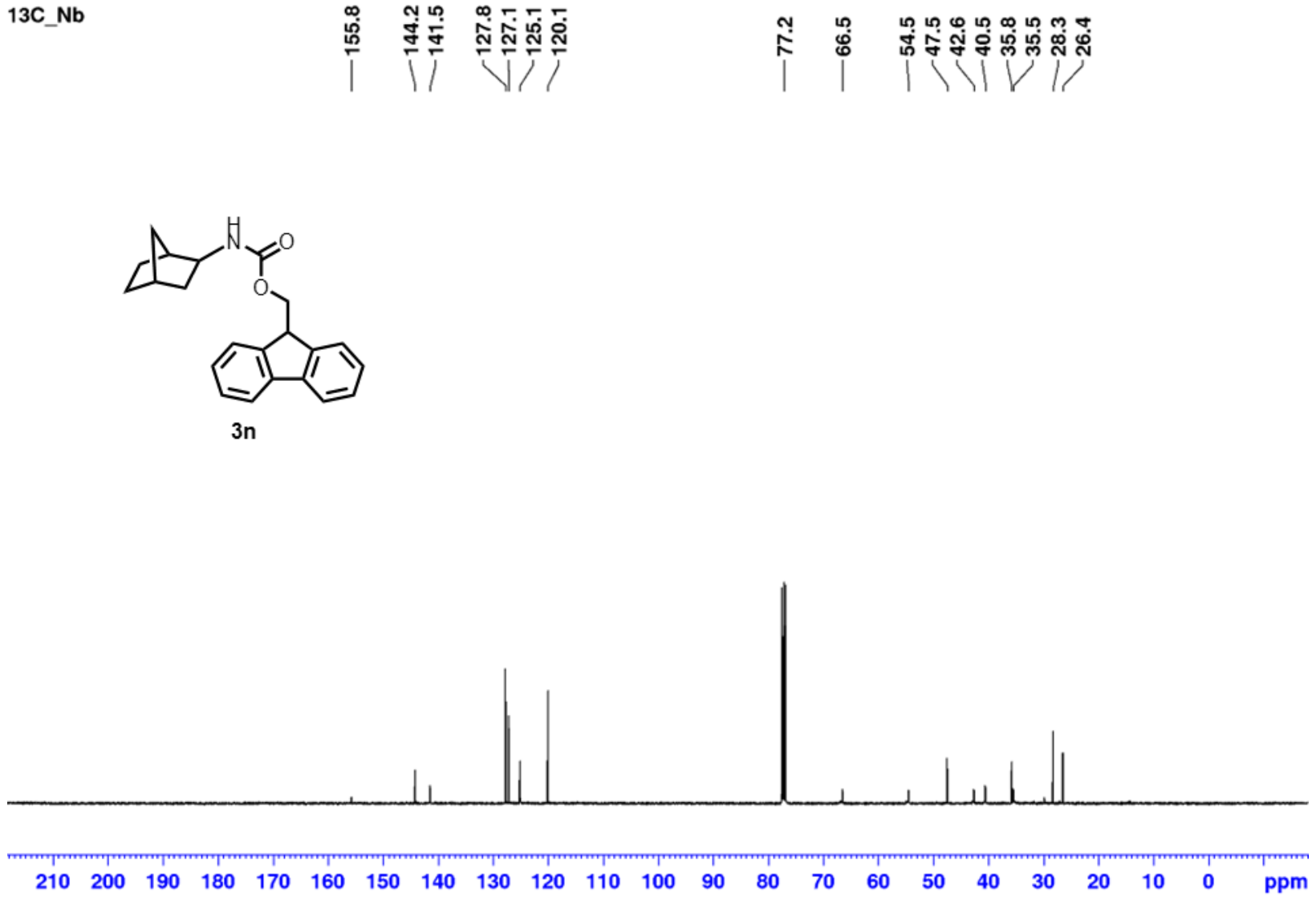


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of **(9H-fluoren-9-yl)methyl (1S,4R)-bicyclo[2.2.1]heptan-2-ylcarbamate**

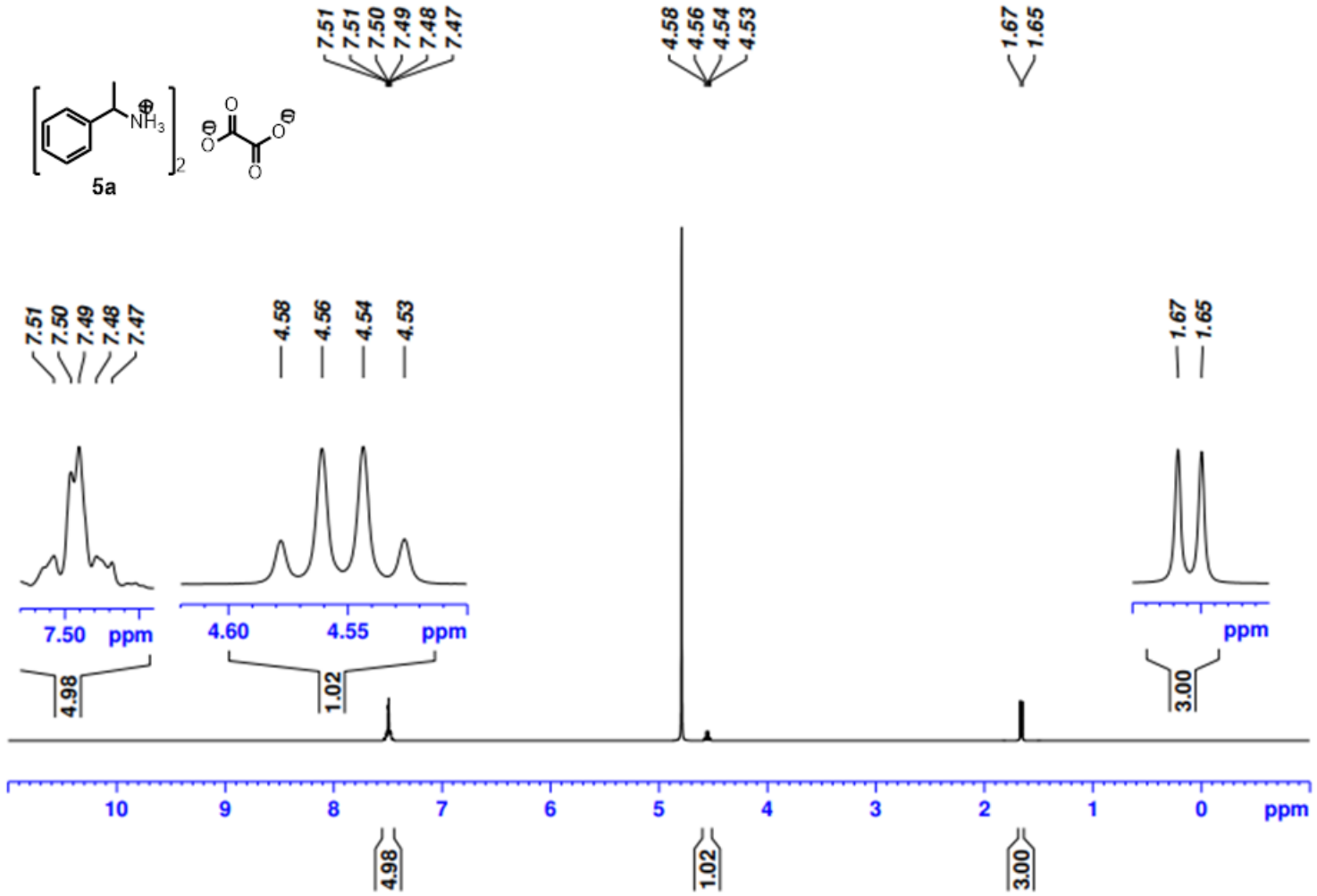


Figure S51: ^{1}H NMR spectrum of **1-Phenylethylamineoxalate**

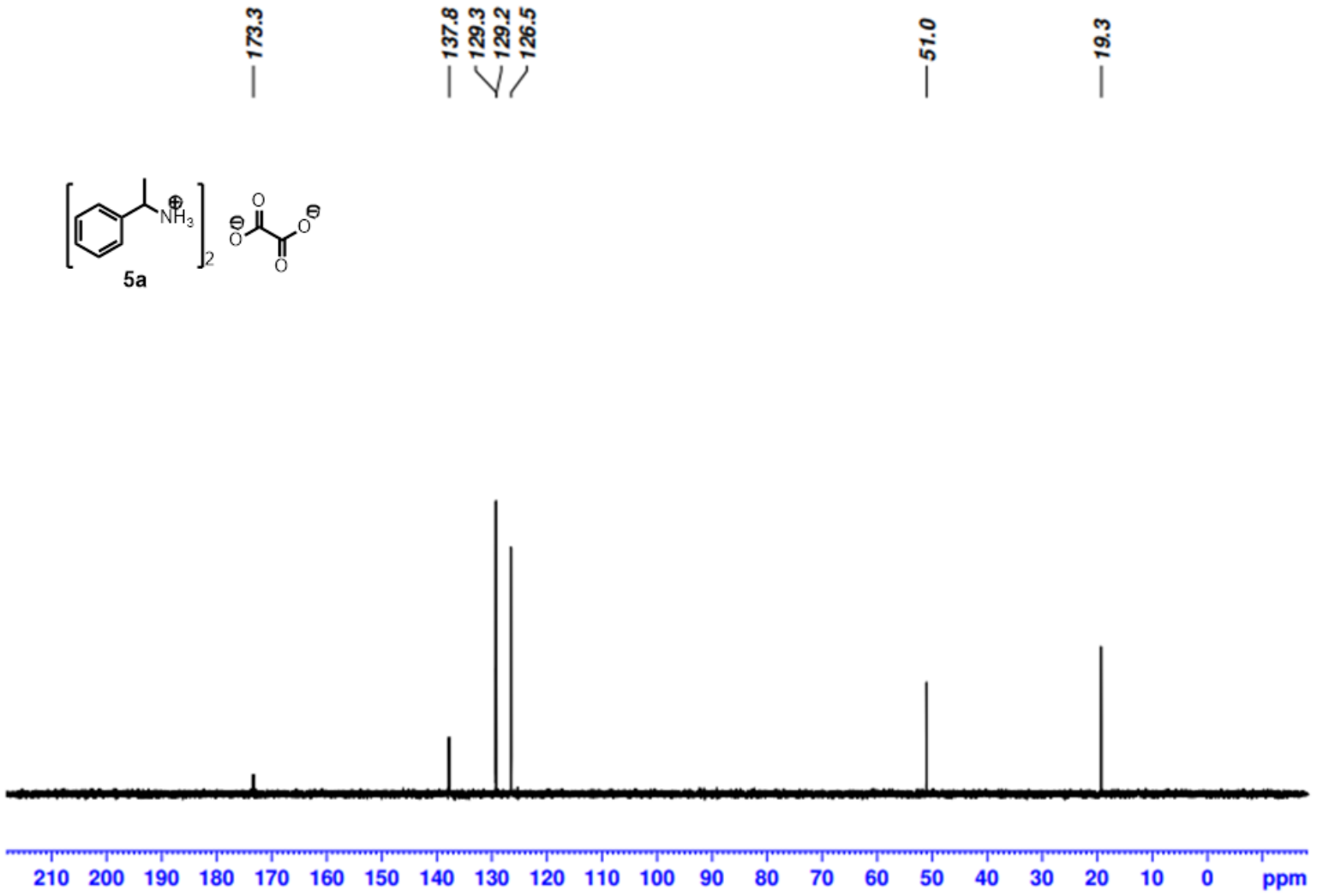


Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum of **1-Phenylethylamineoxalate**

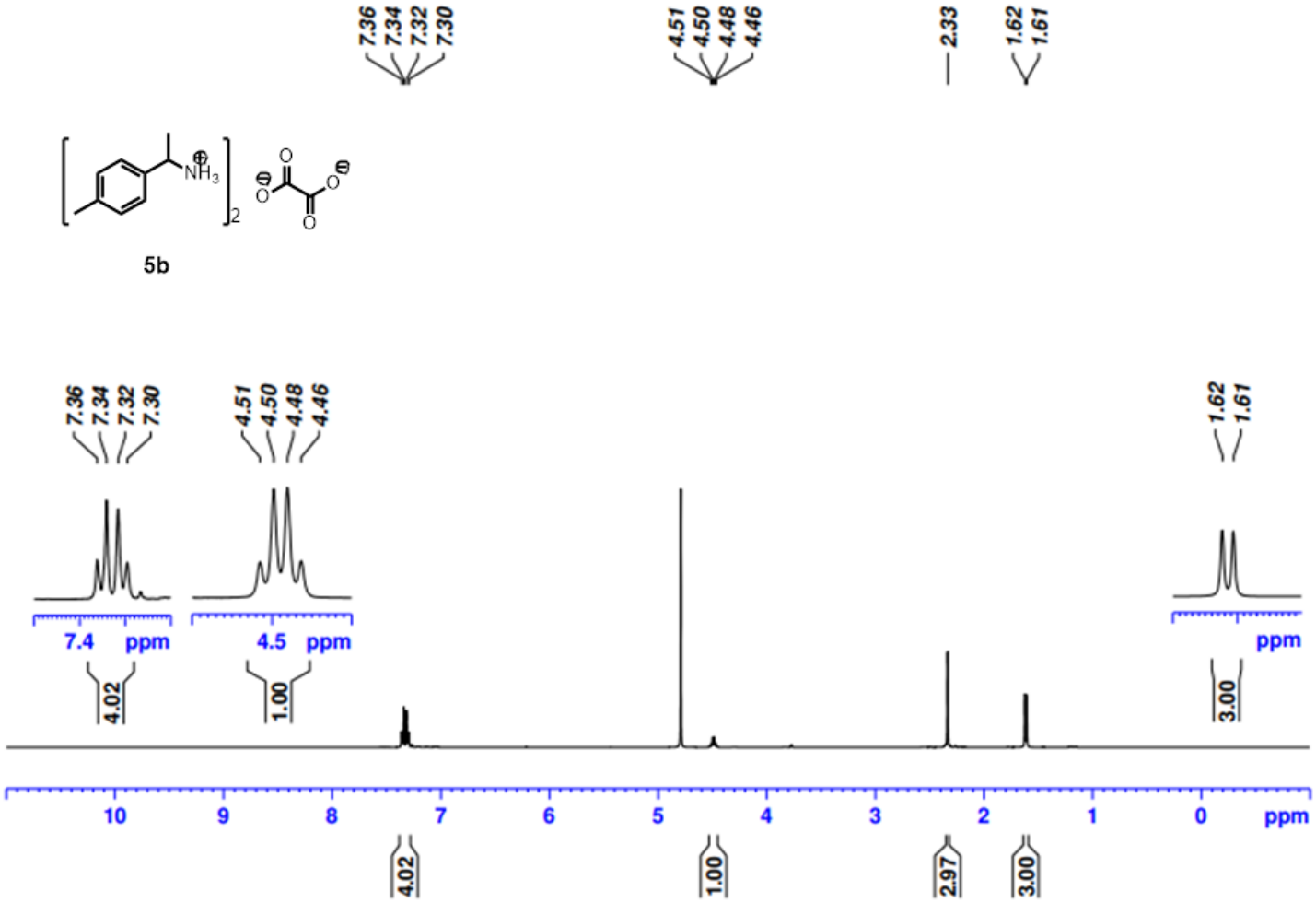


Figure S53: ^{1}H NMR spectrum of **1-(*p*-tolyl)ethanaminium oxalate**

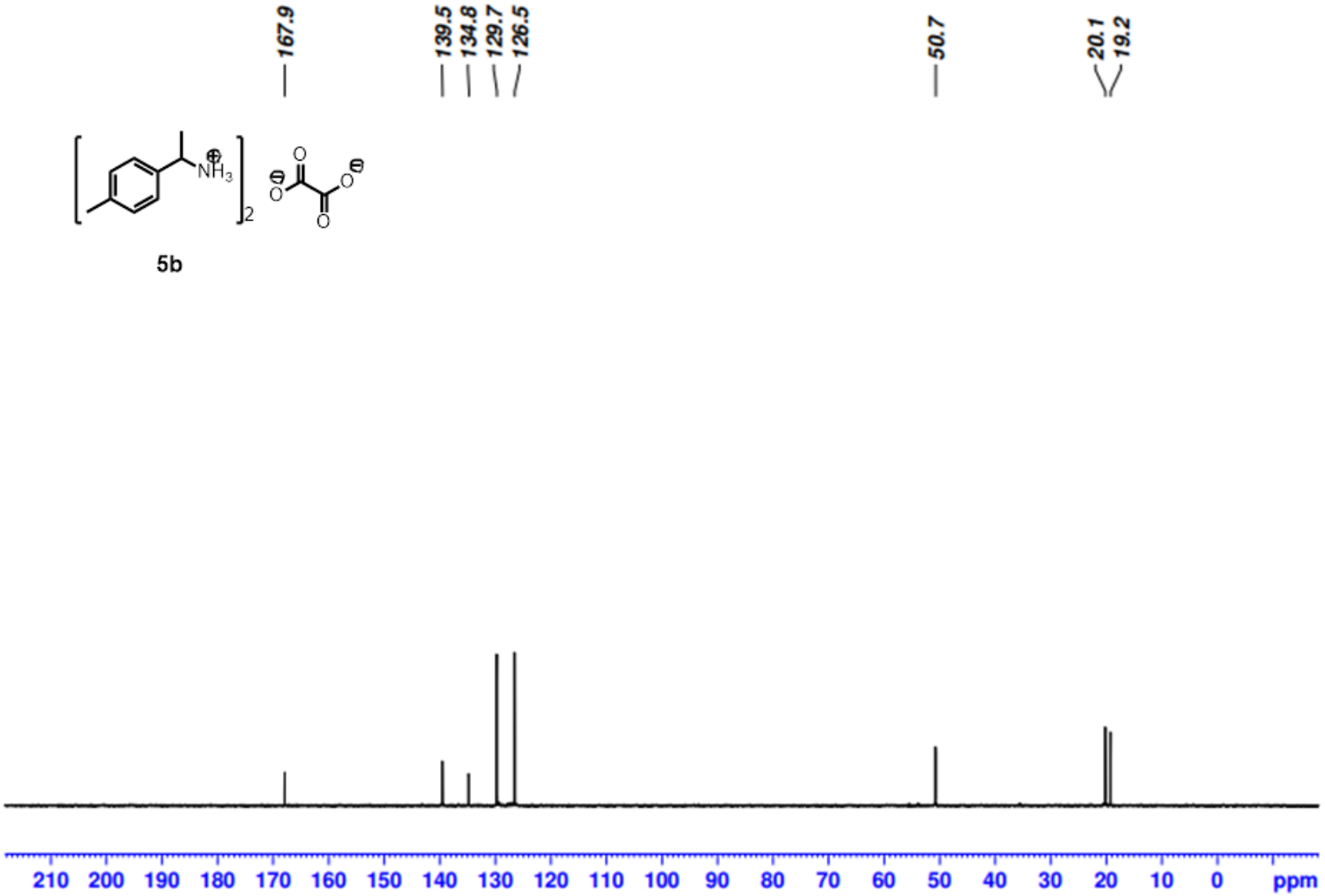


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of **1-(*p*-tolyl)ethanaminium oxalate**

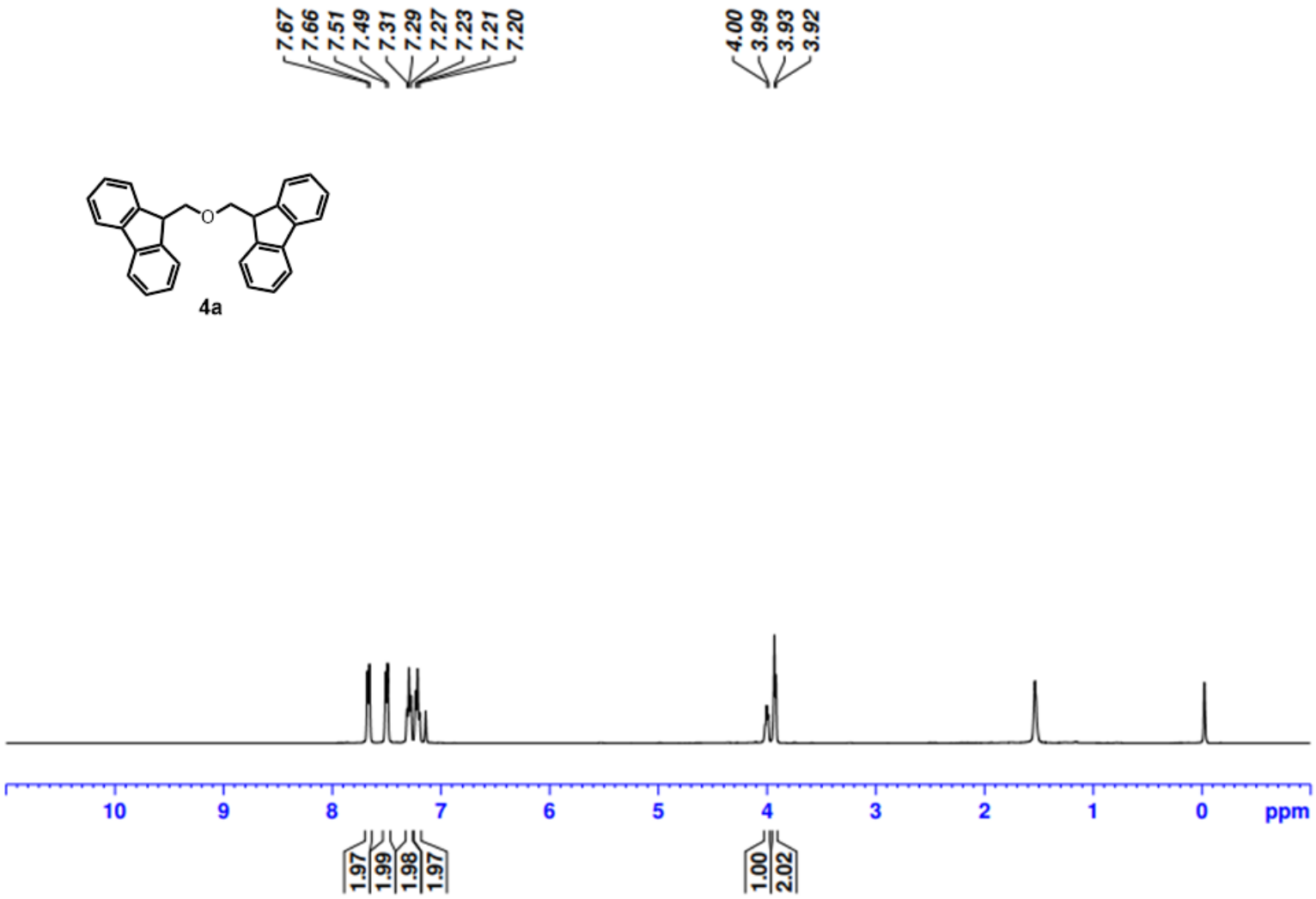


Figure S55: ^{1}H NMR spectrum of **9,9'-(oxybis(methylene))bis(9*H*-fluorene)**

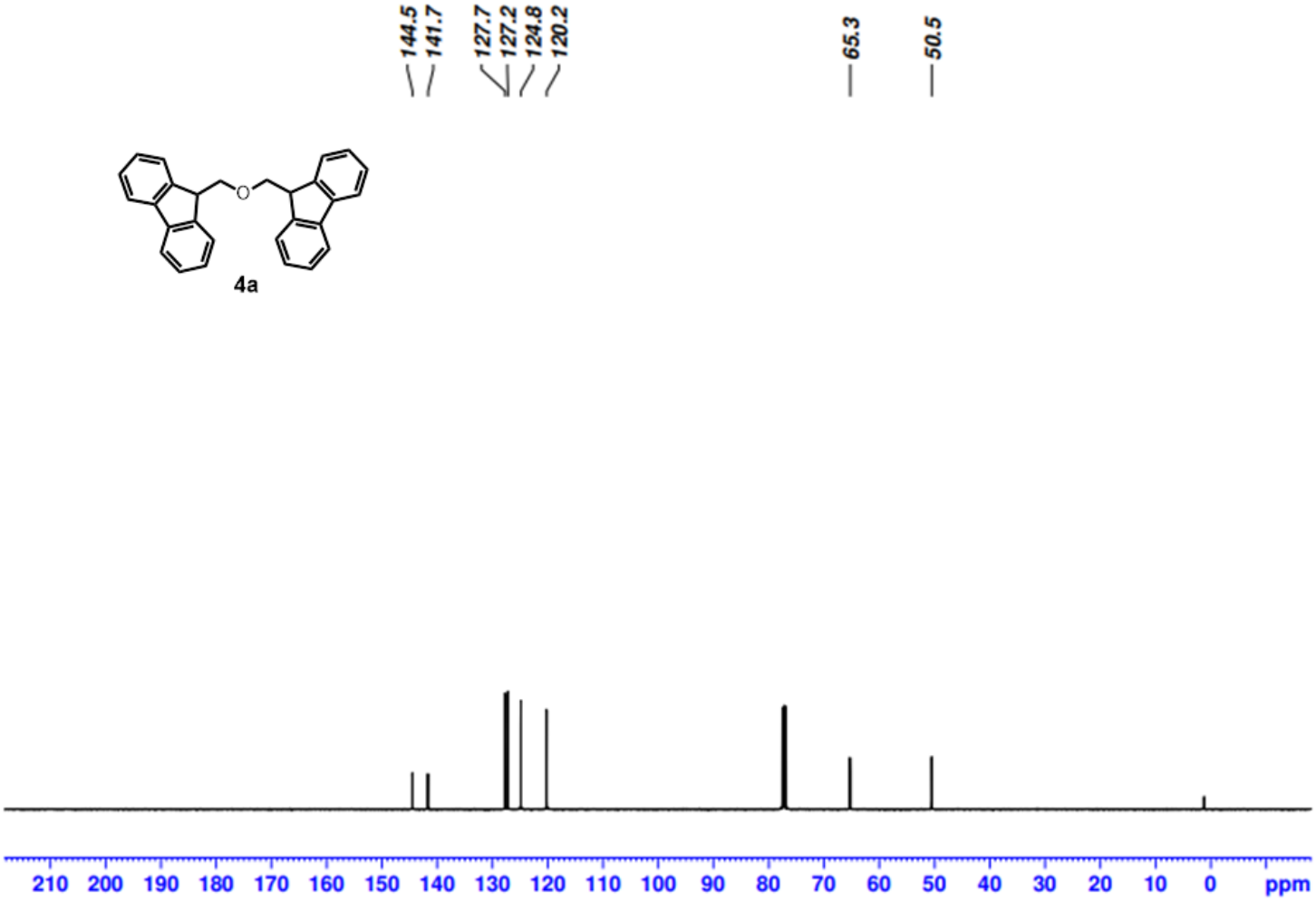


Figure S56: $^{13}C\{^{1}H\}$ NMR spectrum of **9,9'-(oxybis(methylene))bis(9*H*-fluorene)**

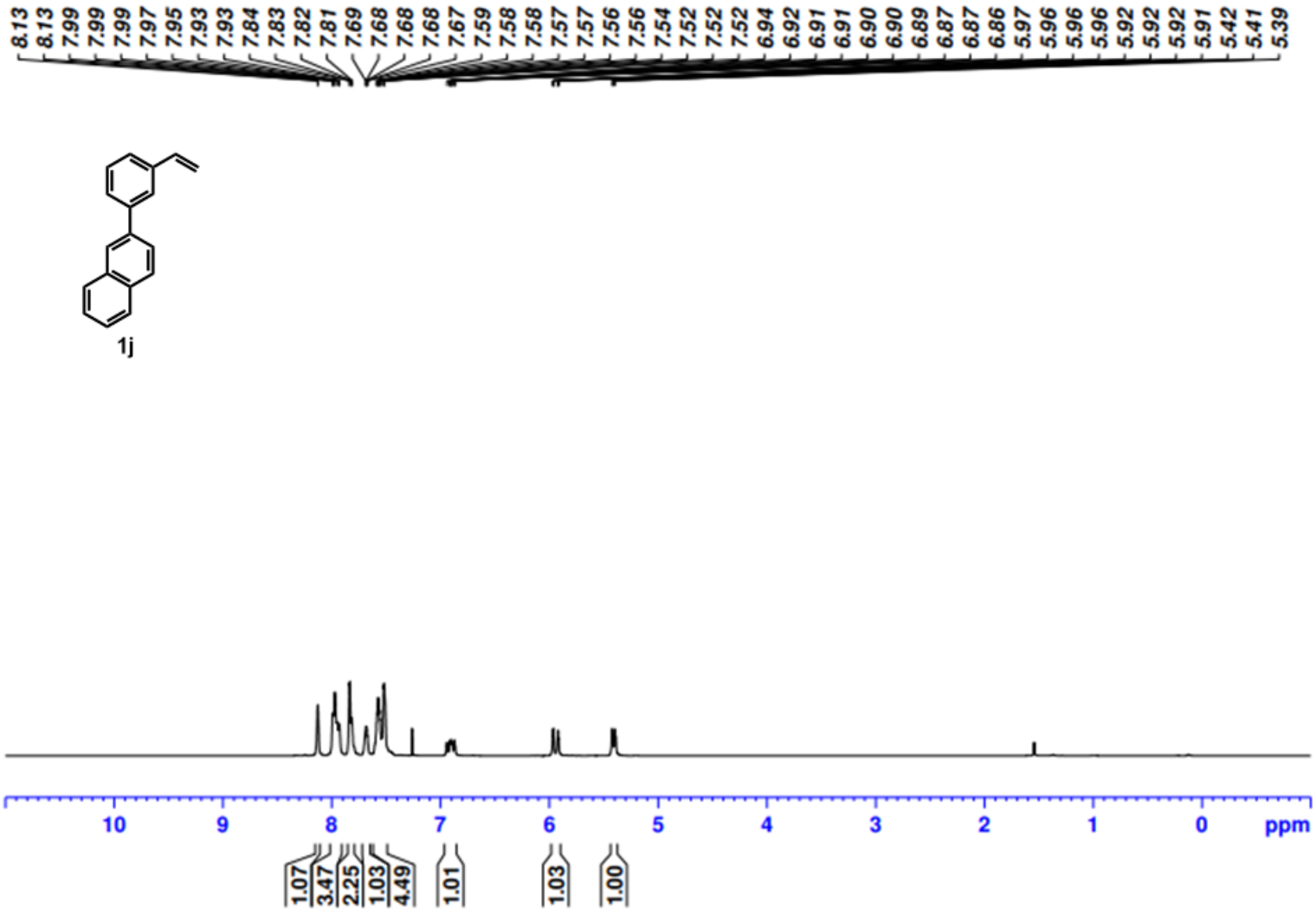


Figure S57: ^{1}H NMR spectrum of **2-(3-vinylphenyl)naphthalene**

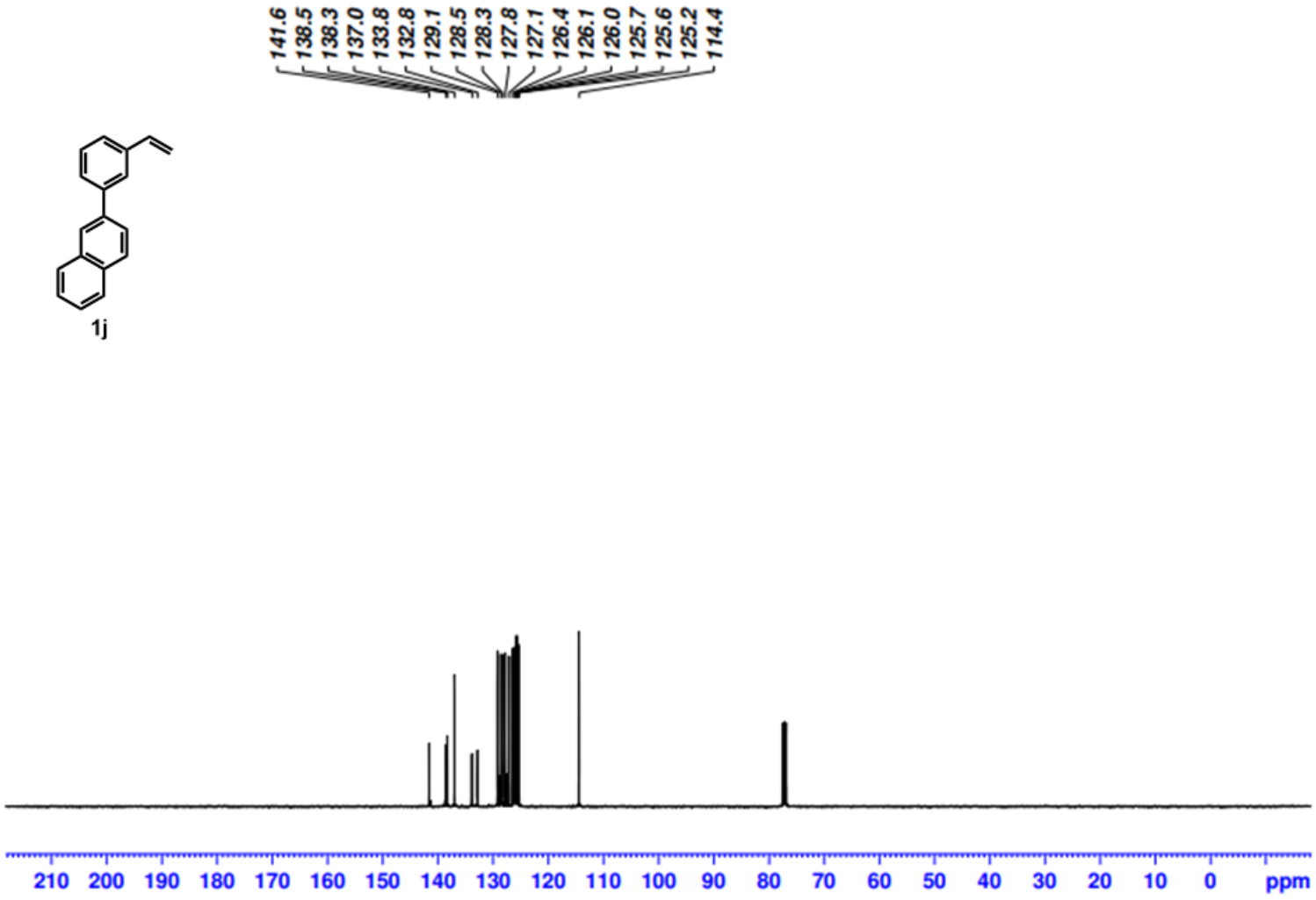
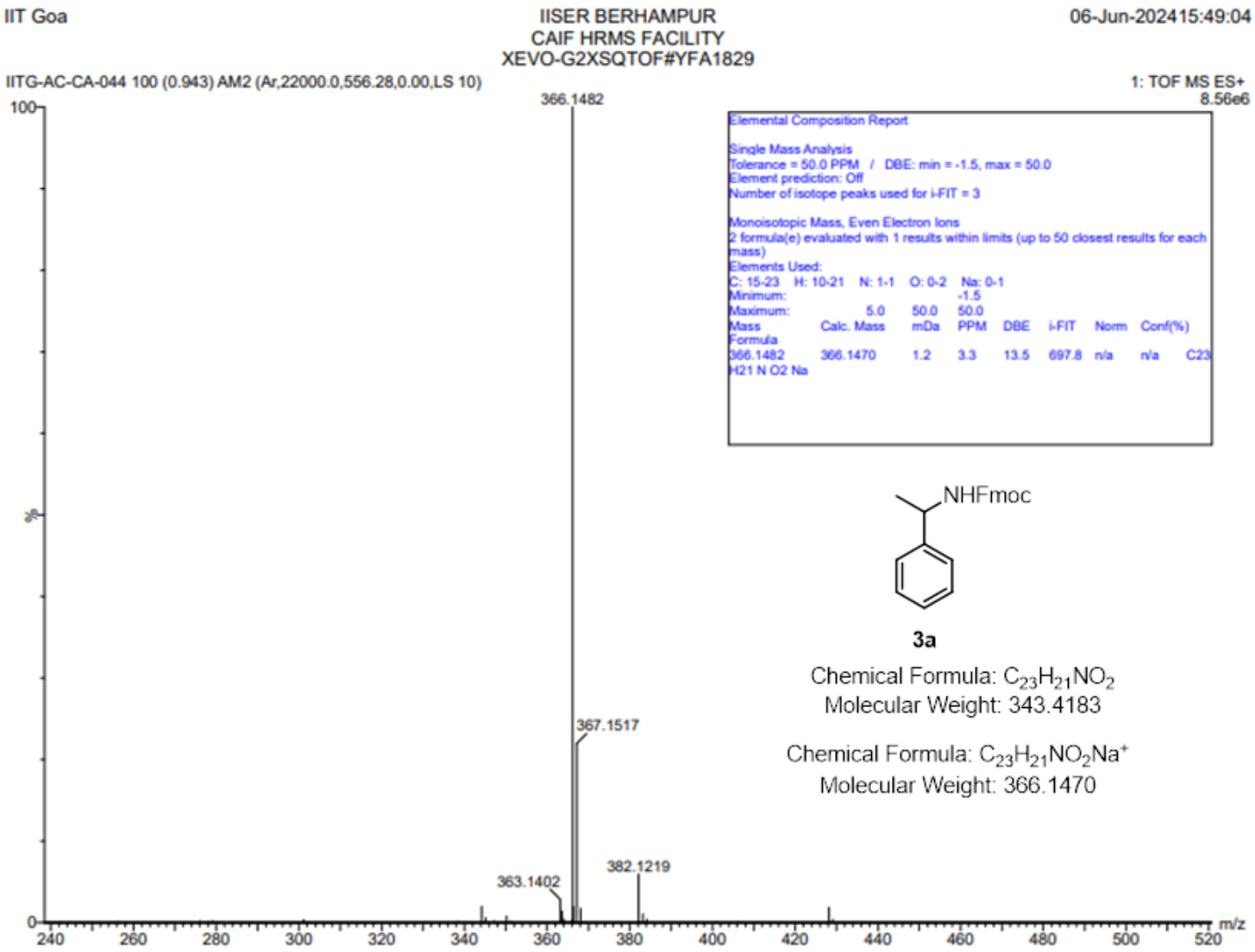
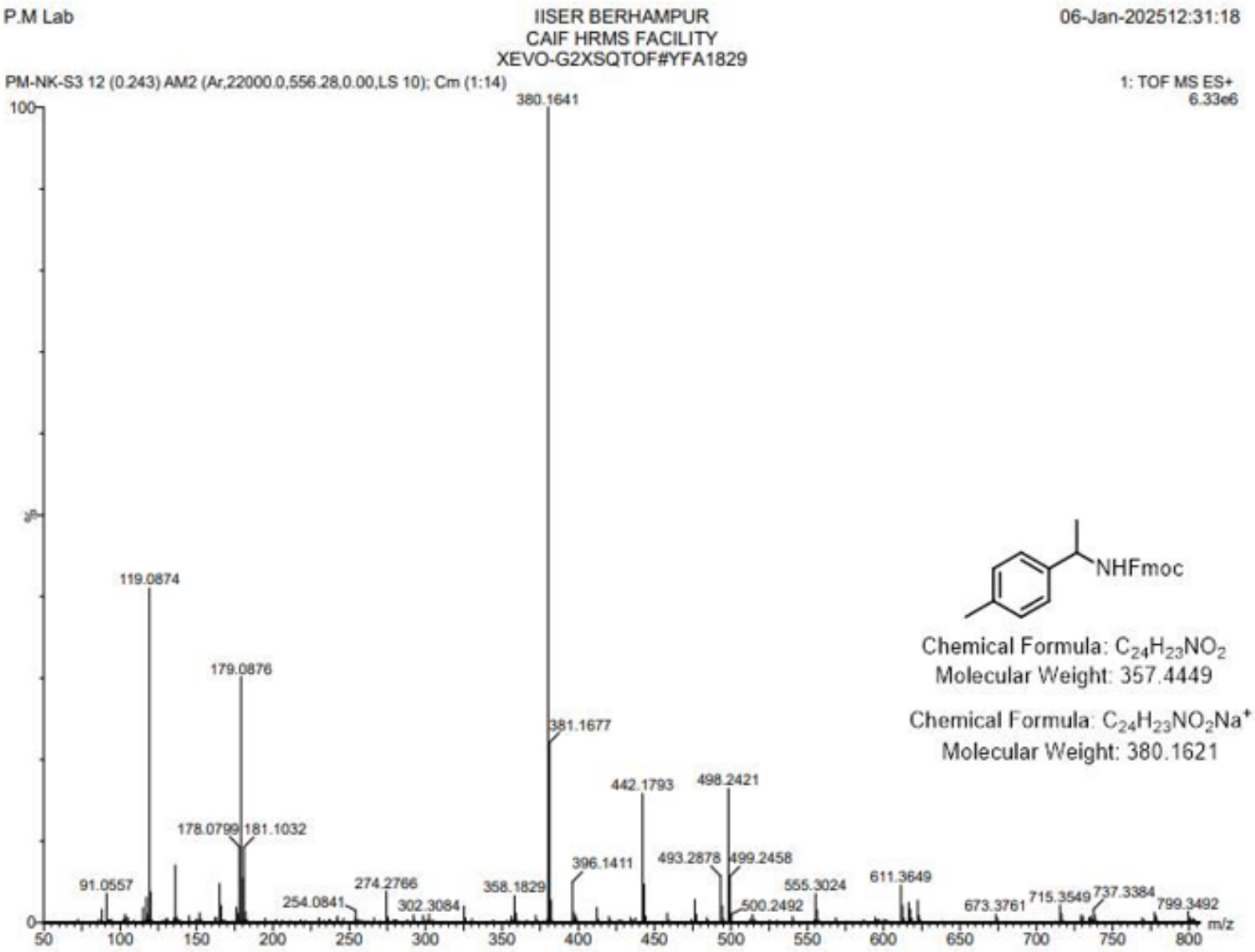
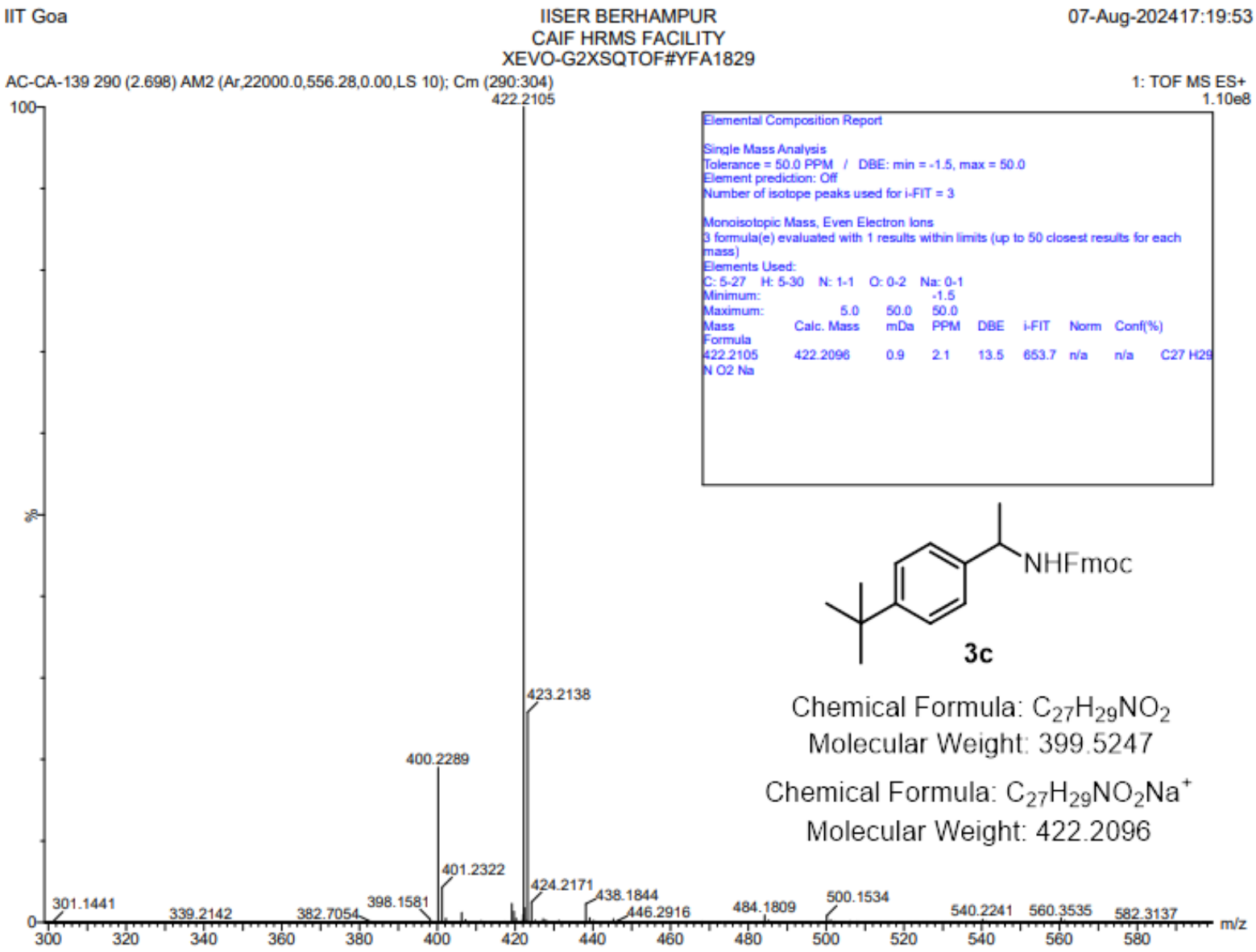


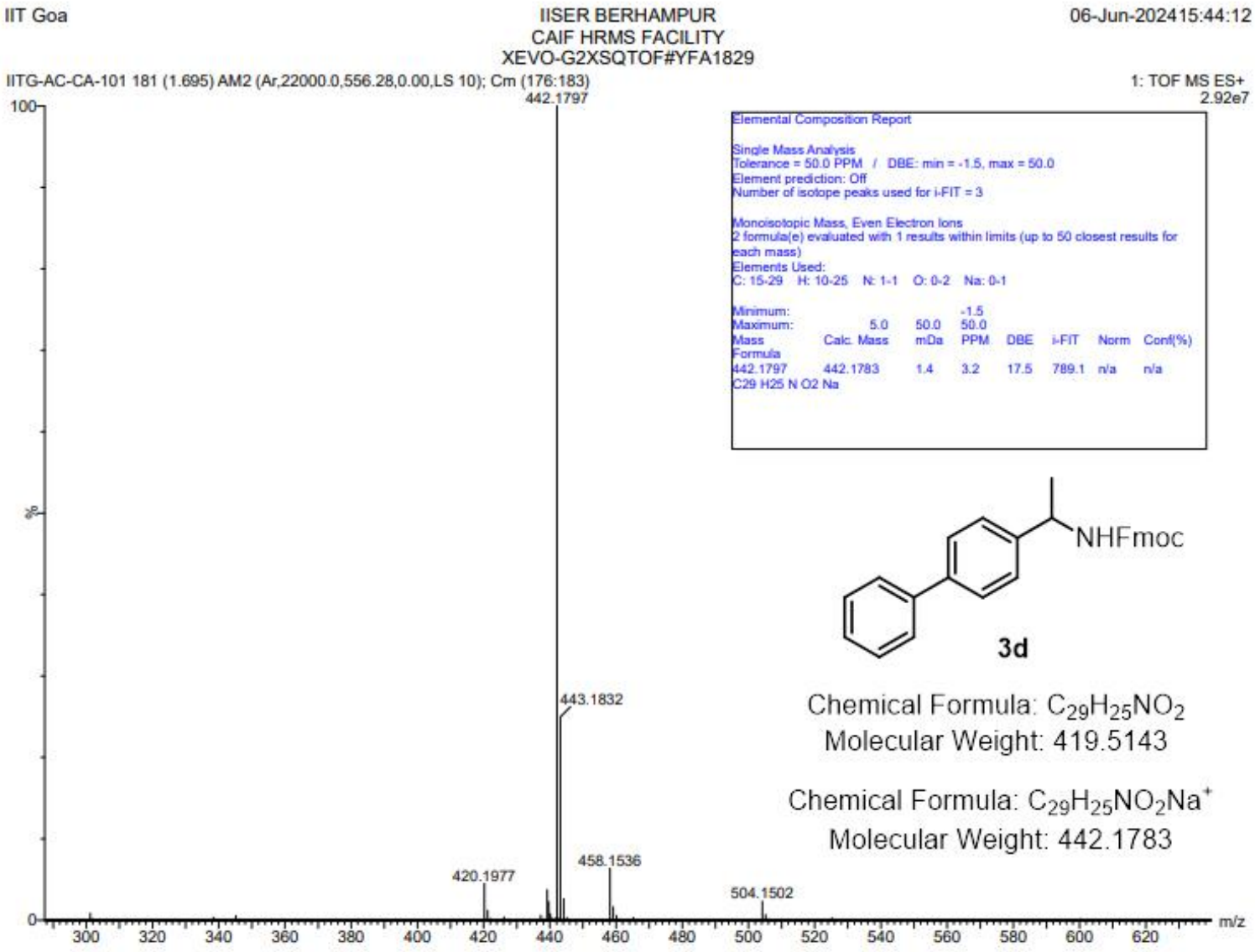
Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of **2-(3-vinylphenyl)naphthalene**

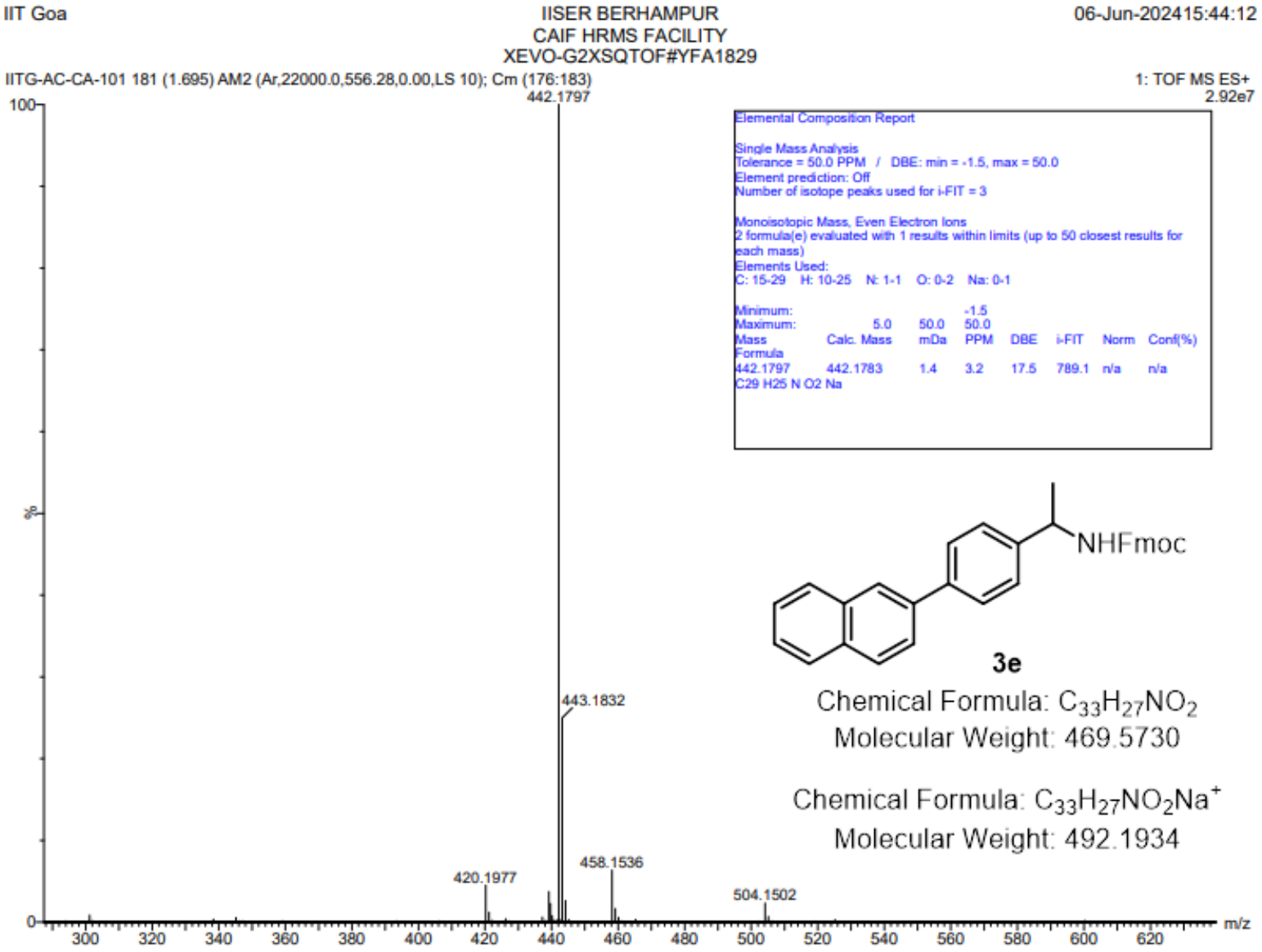
HRMS Spectra

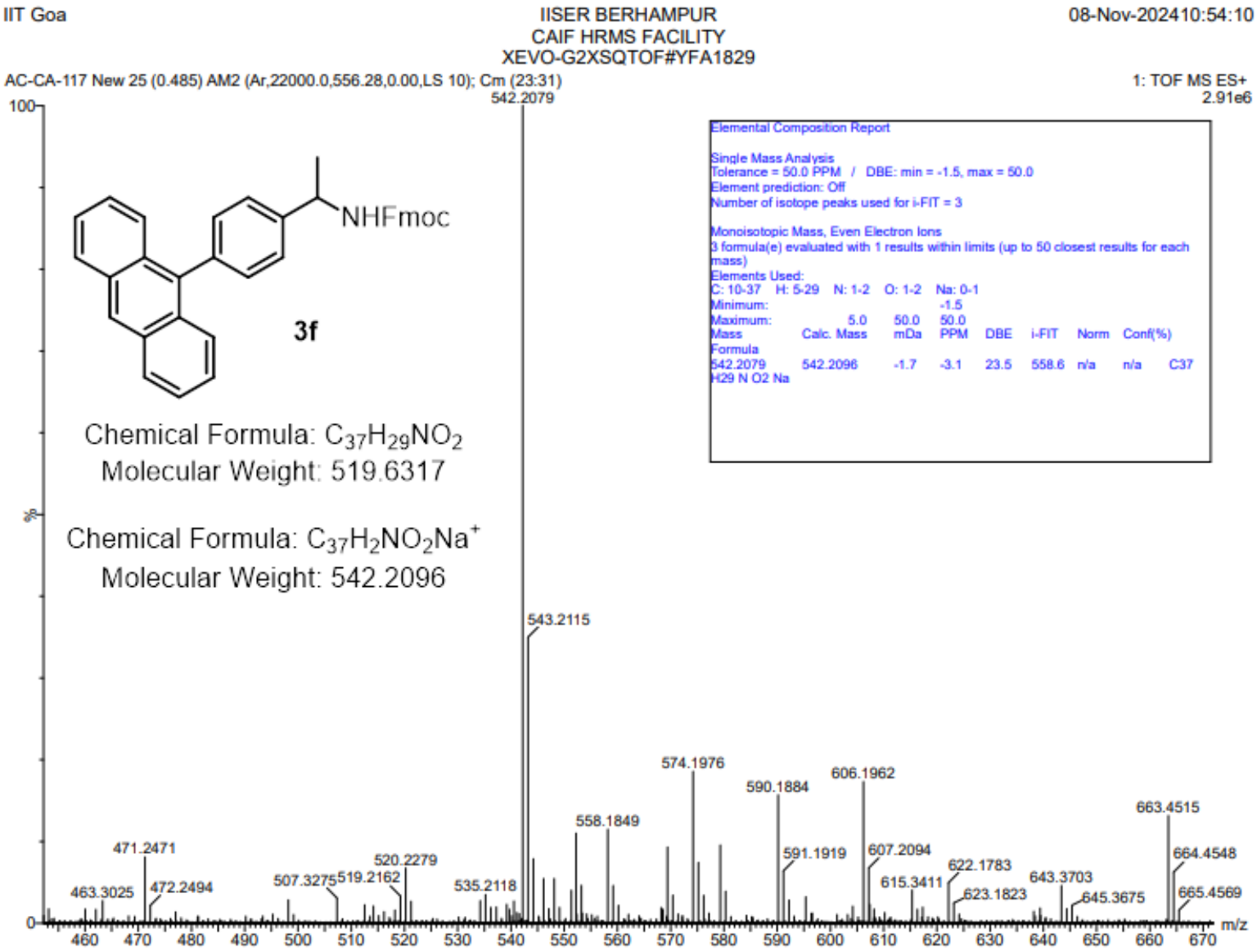


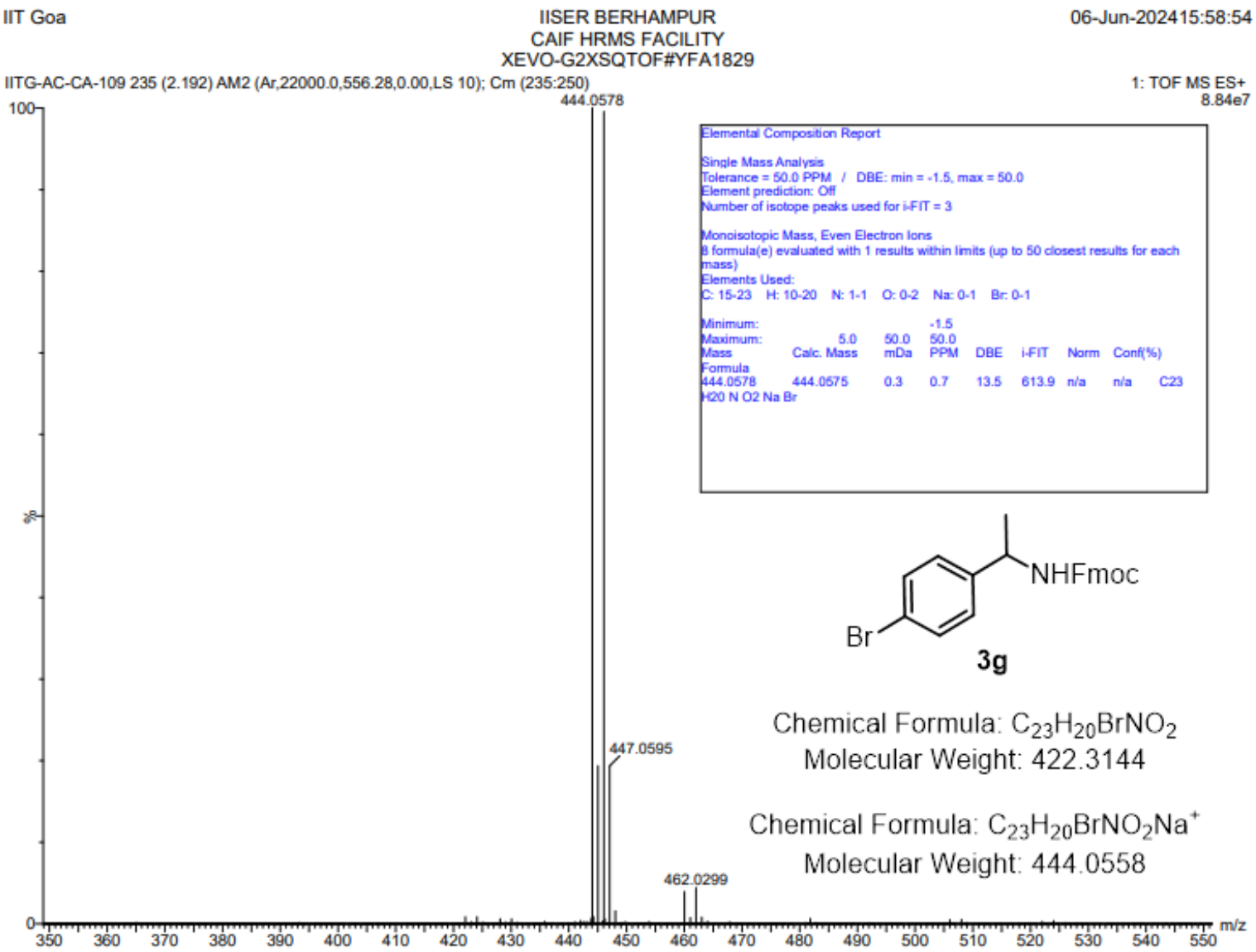

P.M Lab
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
06-Jan-202512:31:18
PM-NK-S3 12 (0.243) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (1:14)
1: TOF MS ES+
6.33e6
380.1641
119.0874
179.0876
381.1677
442.1793
498.2421
178.0799
181.1032
396.1411
493.2878
499.2458
91.0557
274.2766
254.0841
358.1829
555.3024
611.3649
302.3084
500.2492
673.3761
715.3549
737.3384
799.3492
m/z
NHFmoc
Chemical Formula: C24H23NO2
Molecular Weight: 357.4449
Chemical Formula: C24H23NO2Na+
Molecular Weight: 380.1621

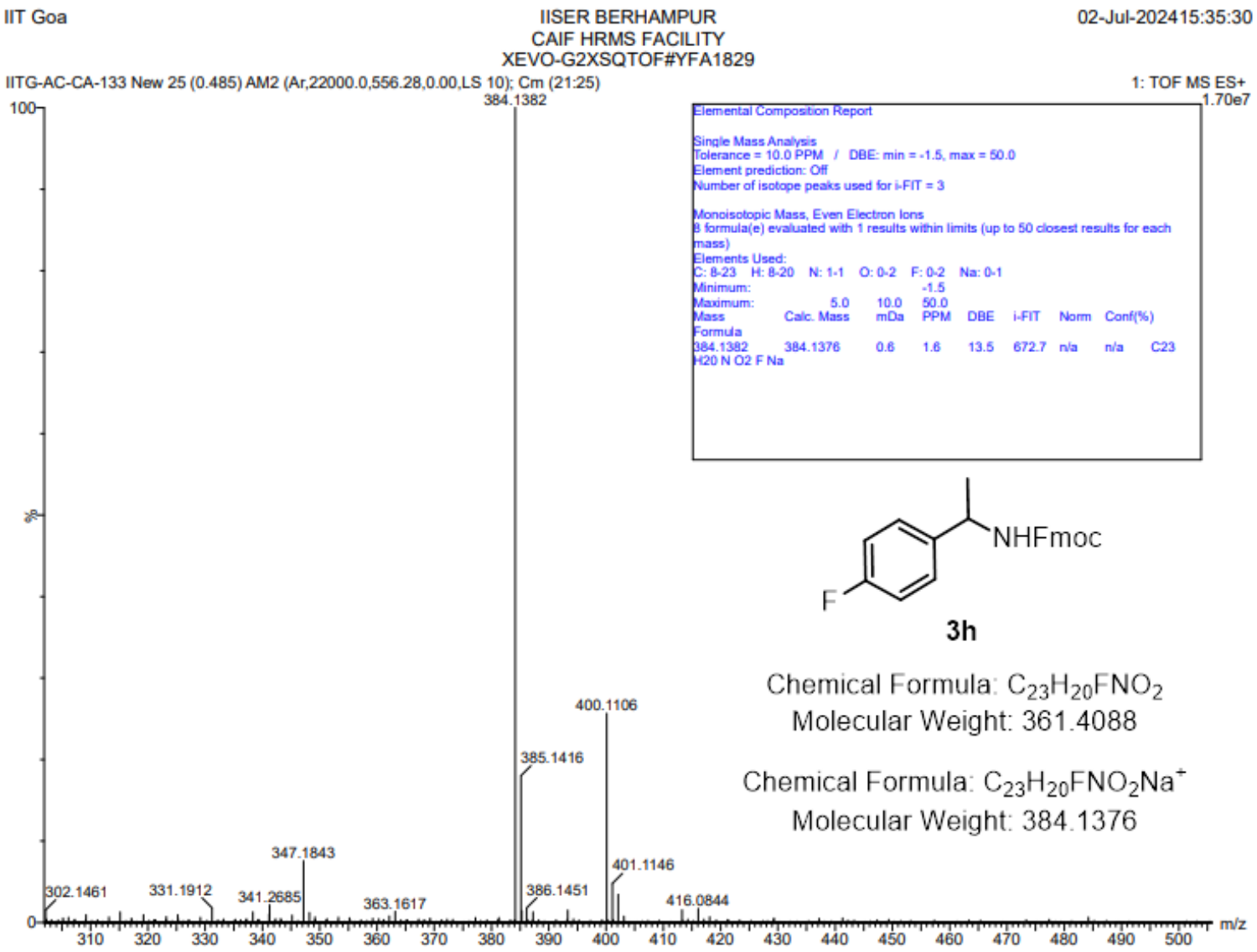

IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
07-Aug-202417:19:53
AC-CA-139 290 (2.698) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (290:304)
1: TOF MS ES+
1.10e8
Elemental Composition Report
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-27 H: 5-30 N: 1-1 O: 0-2 Na: 0-1
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
422.2105 422.2096 0.9 2.1 13.5 653.7 n/a n/a C27 H29 N O2 Na
NHFmoc
3c
Chemical Formula: C27H29NO2
Molecular Weight: 399.5247
Chemical Formula: C27H29NO2Na+
Molecular Weight: 422.2096
422.2105
423.2138
400.2289
401.2322
424.2171
438.1844
446.2916
484.1809
500.1534
540.2241
560.3535
582.3137
301.1441
339.2142
382.7054
398.1581
%
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
06-Jun-202415:44:12
IITG-AC-CA-101 181 (1.695) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (176:183)
1: TOF MS ES+
2.92e7
442.1797
443.1832
420.1977
458.1536
504.1502
Elemental Composition Report
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-29 H: 10-25 N: 1-1 O: 0-2 Na: 0-1
Minimum: -1.5
Maximum: 5.0 50.0 50.0
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%)
Formula
442.1797 442.1783 1.4 3.2 17.5 789.1 n/a n/a
C29 H25 N O2 Na
NHFmoc
3d
Chemical Formula: C29H25NO2
Molecular Weight: 419.5143
Chemical Formula: C29H25NO2Na+
Molecular Weight: 442.1783
100
%
0
300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
06-Jun-202415:44:12
IITG-AC-CA-101 181 (1.695) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (176:183)
1: TOF MS ES+
2.92e7
442.1797
443.1832
458.1536
420.1977
504.1502
Elemental Composition Report
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-29 H: 10-25 N: 1-1 O: 0-2 Na: 0-1
Minimum: -1.5
Maximum: 5.0 50.0 50.0
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%)
Formula
442.1797 442.1783 1.4 3.2 17.5 789.1 n/a n/a
C29 H25 N O2 Na
NHFmoc
3e
Chemical Formula: C33H27NO2
Molecular Weight: 469.5730
Chemical Formula: C33H27NO2Na+
Molecular Weight: 492.1934
%
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
08-Nov-202410:54:10
AC-CA-117 New 25 (0.485) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (23:31)
1: TOF MS ES+
2.91e6
NHFmoc
3f
Chemical Formula: C37H29NO2
Molecular Weight: 519.6317
Chemical Formula: C37H2NO2Na+
Molecular Weight: 542.2096
Elemental Composition Report
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 10-37 H: 5-29 N: 1-2 O: 1-2 Na: 0-1
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
542.2079 542.2096 -1.7 -3.1 23.5 558.6 n/a n/a C37 H29 N O2 Na
542.2079
543.2115
574.1976
590.1884
606.1962
558.1849
663.4515
471.2471
591.1919
607.2094
664.4548
520.2279
622.1783
643.3703
463.3025
472.2494
507.3275
519.2162
535.2118
615.3411
623.1823
645.3675
665.4569
%
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
06-Jun-202415:58:54
IITG-AC-CA-109 235 (2.192) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (235:250)
1: TOF MS ES+
8.84e7
444.0578
447.0595
462.0299
Elemental Composition Report
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-23 H: 10-20 N: 1-1 O: 0-2 Na: 0-1 Br: 0-1
Minimum: -1.5
Maximum: 5.0 50.0 50.0
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
444.0578 444.0575 0.3 0.7 13.5 613.9 n/a n/a C23 H20 N O2 Na Br
NHFmoc
Br
3g
Chemical Formula: C23H20BrNO2
Molecular Weight: 422.3144
Chemical Formula: C23H20BrNO2Na+
Molecular Weight: 444.0558
%
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
02-Jul-202415:35:30
IITG-AC-CA-133 New 25 (0.485) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (21:25)
1: TOF MS ES+
1.70e7
Elemental Composition Report
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-23 H: 8-20 N: 1-1 O: 0-2 F: 0-2 Na: 0-1
Minimum: -1.5
Maximum: 5.0 10.0 50.0
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
384.1382 384.1376 0.6 1.6 13.5 672.7 n/a n/a C23 H20 N O2 F Na
384.1382
400.1106
385.1416
347.1843
401.1146
302.1461
331.1912
341.2685
363.1617
386.1451
416.0844
100
%
0
310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
m/z
NHFmoc
F
3h
Chemical Formula: C23H20FNO2
Molecular Weight: 361.4088
Chemical Formula: C23H20FNO2Na+
Molecular Weight: 384.1376

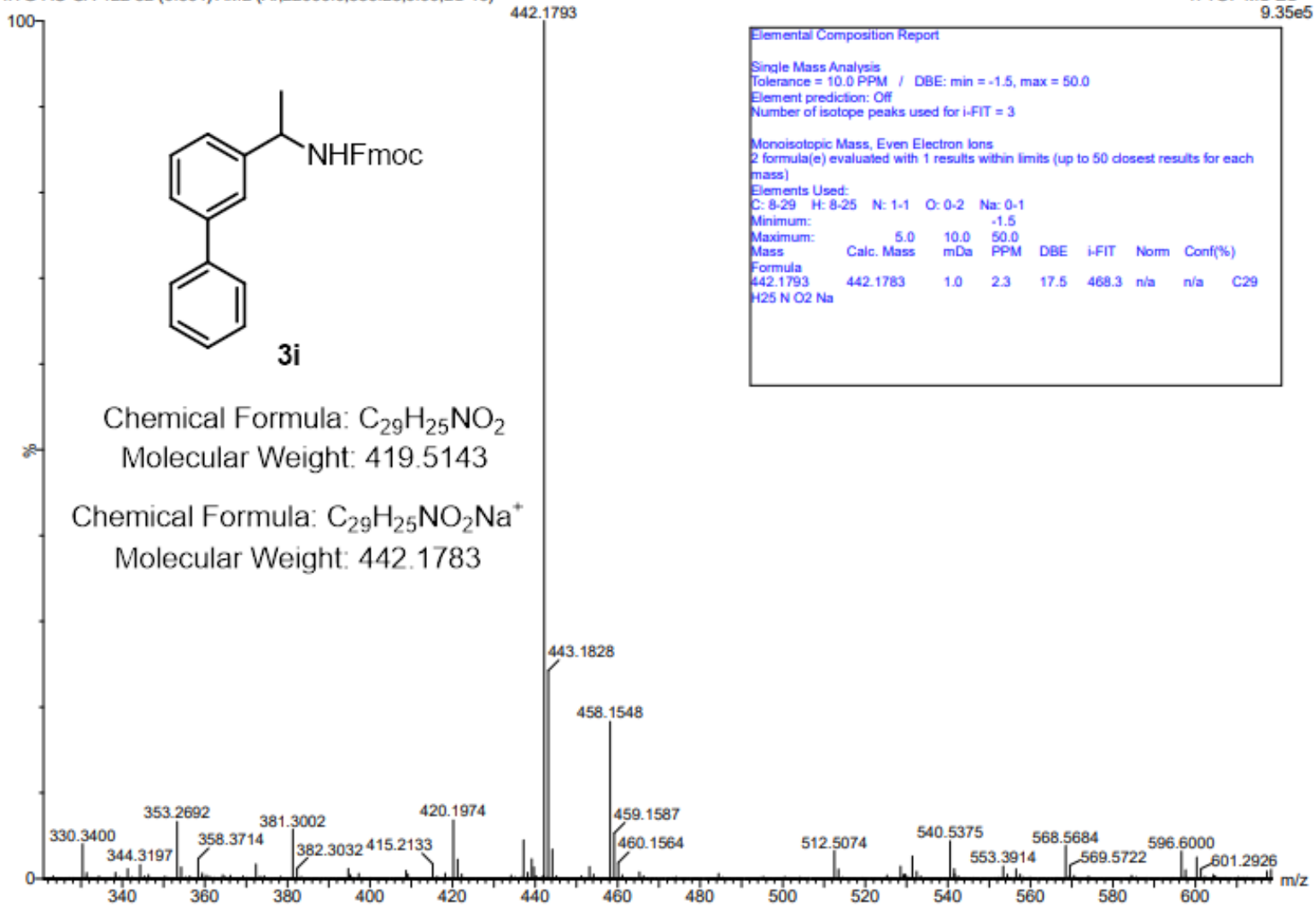
IIT Goa

IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829

02-Jul-202416:22:15

IITG-AC-CA-122 32 (0.604) AM2 (Ar,22000.0,556.28,0.00,LS 10)

1: TOF MS ES+
9.35e5

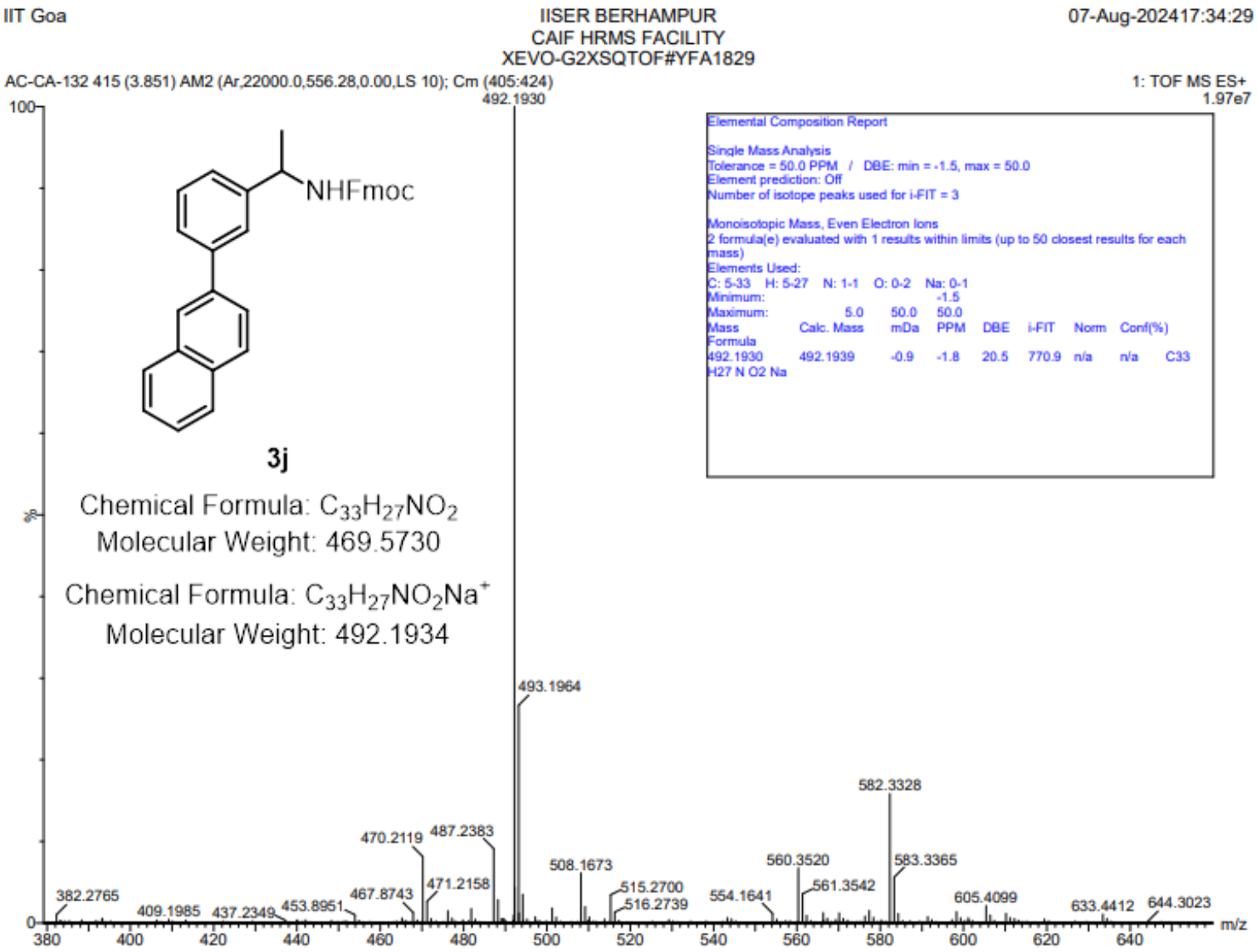


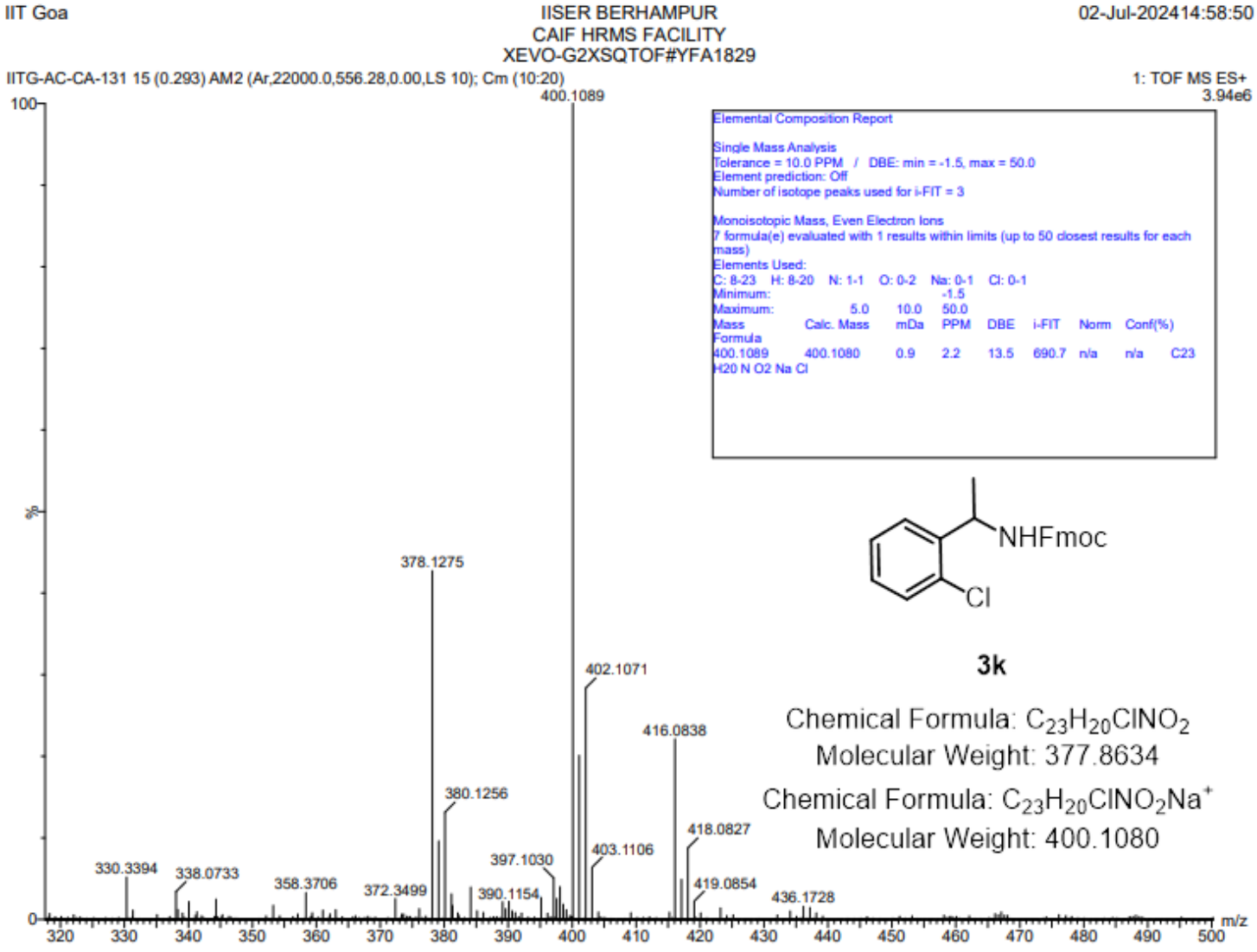
Elemental Composition Report

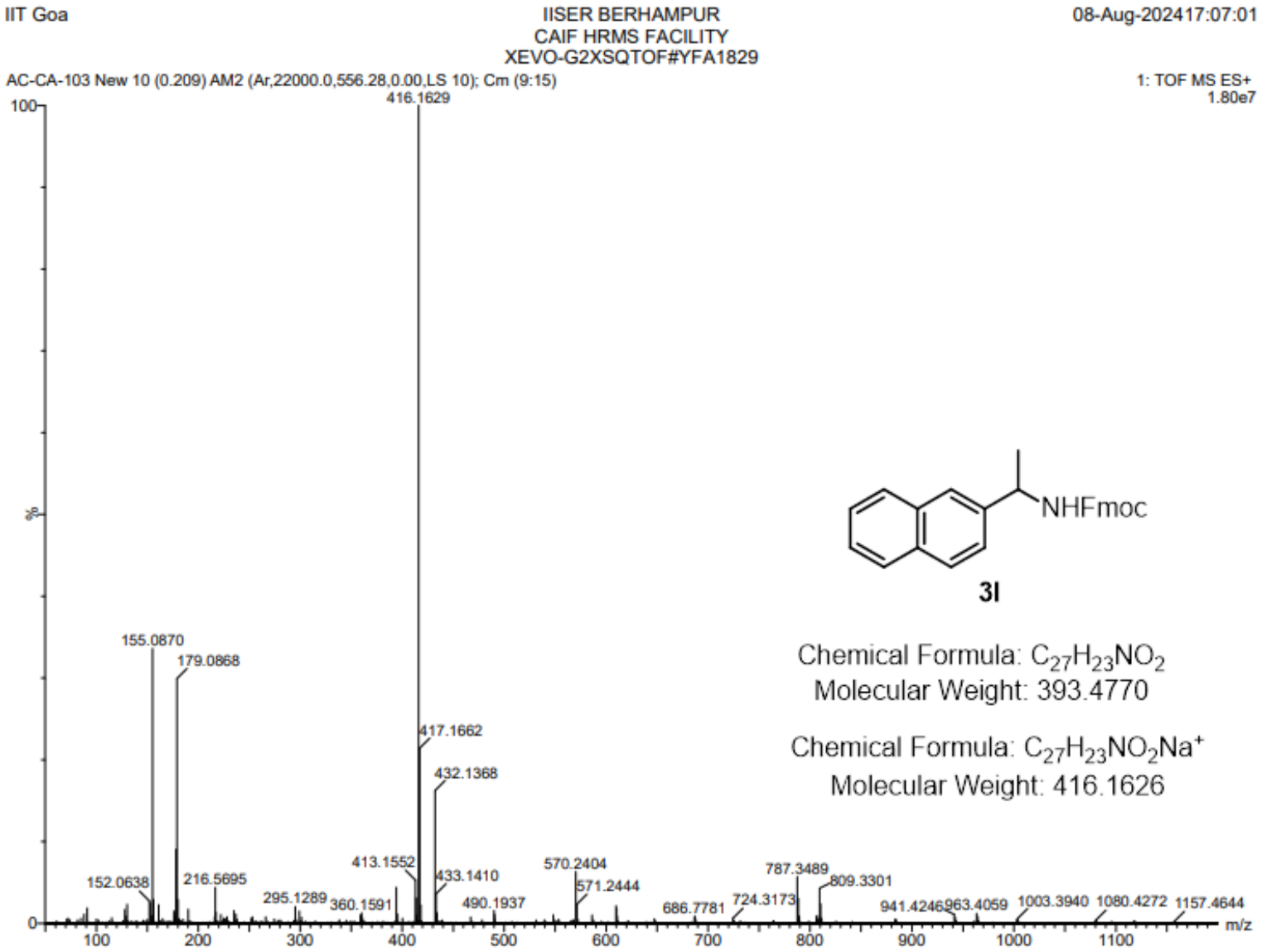
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-29 H: 8-25 N: 1-1 O: 0-2 Na: 0-1

Minimum:			-1.5					
Maximum:	5.0	10.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
442.1793	442.1783	1.0	2.3	17.5	468.3	n/a	n/a	C29 H25 N O2 Na


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
07-Aug-202417:34:29
AC-CA-132 415 (3.851) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (405:424)
1: TOF MS ES+
1.97e7
492.1930
NHFmoc
3j
Chemical Formula: C33H27NO2
Molecular Weight: 469.5730
Chemical Formula: C33H27NO2Na+
Molecular Weight: 492.1934
Elemental Composition Report
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-33 H: 5-27 N: 1-1 O: 0-2 Na: 0-1
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
492.1930 492.1939 -0.9 -1.8 20.5 770.9 n/a n/a C33 H27 N O2 Na
493.1964
582.3328
470.2119
487.2383
508.1673
560.3520
583.3365
471.2158
515.2700
561.3542
382.2765
467.8743
516.2739
554.1641
605.4099
409.1985
437.2349
453.8951
633.4412
644.3023
%
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
02-Jul-202414:58:50
IITG-AC-CA-131 15 (0.293) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (10:20)
1: TOF MS ES+
3.94e6
Elemental Composition Report
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-23 H: 8-20 N: 1-1 O: 0-2 Na: 0-1 Cl: 0-1
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
400.1089 400.1080 0.9 2.2 13.5 690.7 n/a n/a C23 H20 N O2 Na Cl
NHFmoc
Cl
3k
Chemical Formula: C23H20ClNO2
Molecular Weight: 377.8634
Chemical Formula: C23H20ClNO2Na+
Molecular Weight: 400.1080
400.1089
378.1275
402.1071
416.0838
380.1256
418.0827
403.1106
397.1030
419.0854
330.3394
338.0733
358.3706
372.3499
390.1154
436.1728
%
m/z


IIT Goa
IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829
08-Aug-202417:07:01
AC-CA-103 New 10 (0.209) AM2 (Ar,22000.0,556.28,0.00,LS 10); Cm (9:15)
1: TOF MS ES+
1.80e7
416.1629
155.0870
179.0868
417.1662
432.1368
152.0638
216.5695
295.1289
360.1591
413.1552
433.1410
490.1937
570.2404
571.2444
686.7781
724.3173
787.3489
809.3301
941.4246
963.4059
1003.3940
1080.4272
1157.4644
NHFmoc
3l
Chemical Formula: C27H23NO2
Molecular Weight: 393.4770
Chemical Formula: C27H23NO2Na+
Molecular Weight: 416.1626
%
m/z

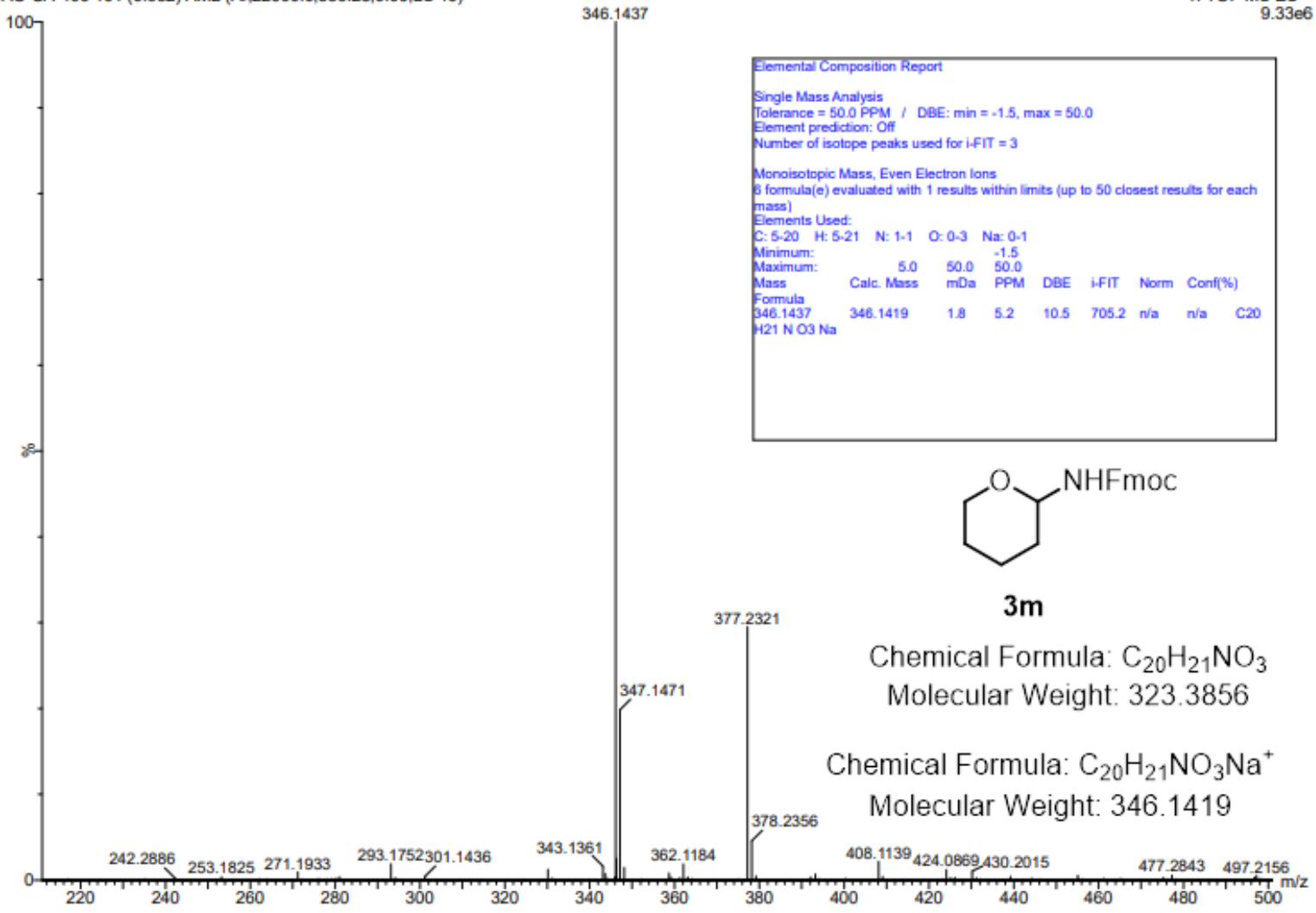
IIT Goa

IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829

07-Aug-202417:29:36

AC-CA-106 101 (0.952) AM2 (Ar,22000.0,556.28,0.00,LS 10)

1: TOF MS ES+
9.33e6



Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-20 H: 5-21 N: 1-1 O: 0-3 Na: 0-1

Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	
346.1437	346.1419	1.8	5.2	10.5	705.2	n/a	n/a	C20 H21 N O3 Na

3m

Chemical Formula: $C_{20}H_{21}NO_3$
Molecular Weight: 323.3856

Chemical Formula: $C_{20}H_{21}NO_3Na^+$
Molecular Weight: 346.1419

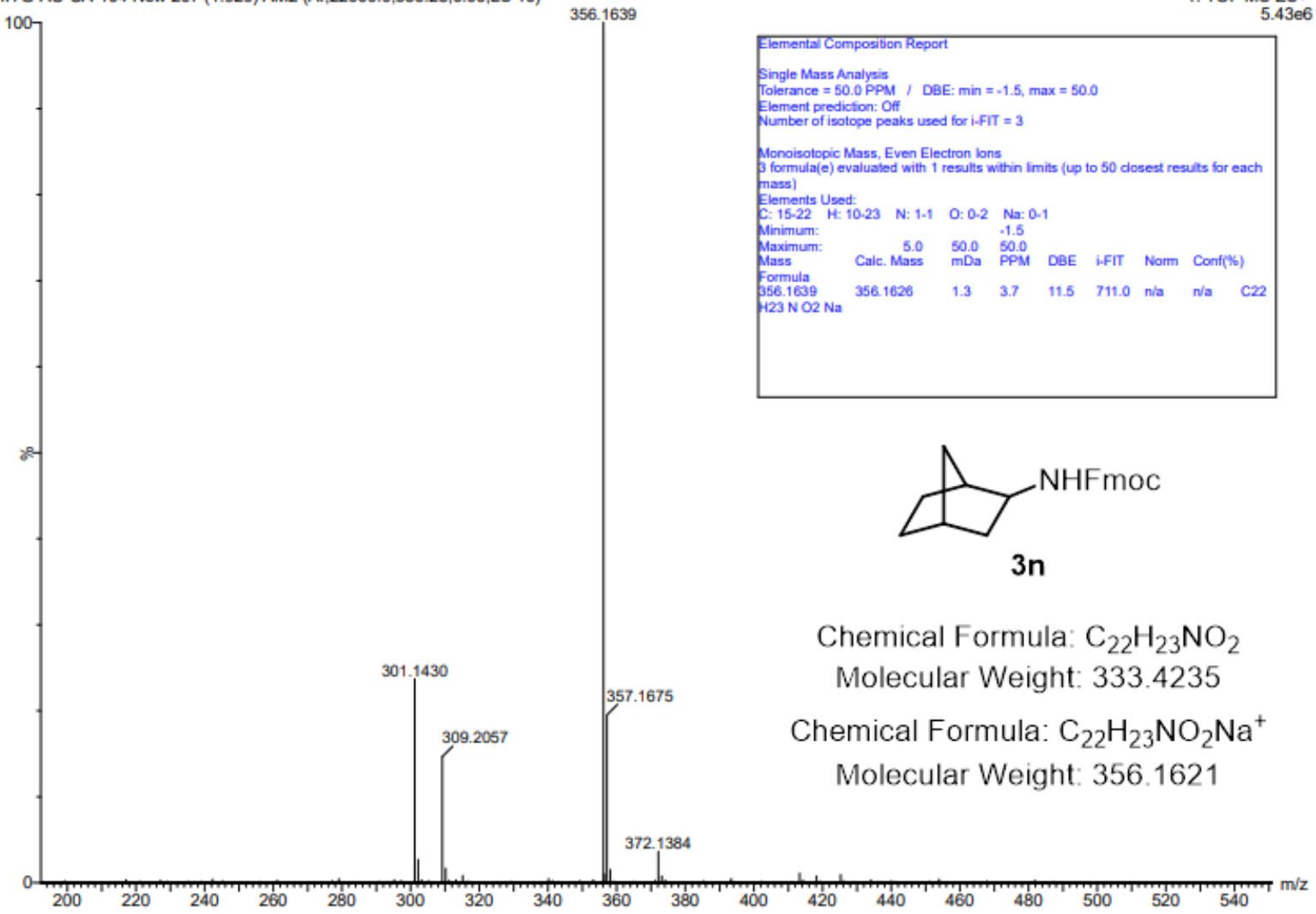
IIT Goa

IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829

06-Jun-202416:18:43

IITG-AC-CA-104 New 207 (1.929) AM2 (Ar,22000.0,556.28,0.00,LS 10)

1: TOF MS ES+
5.43e6



Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-22 H: 10-23 N: 1-1 O: 0-2 Na: 0-1

Minimum:			-1.5					
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
356.1639	356.1626	1.3	3.7	11.5	711.0	n/a	n/a	C22 H23 N O2 Na

3n

Chemical Formula: $C_{22}H_{23}NO_2$
Molecular Weight: 333.4235

Chemical Formula: $C_{22}H_{23}NO_2Na^+$
Molecular Weight: 356.1621

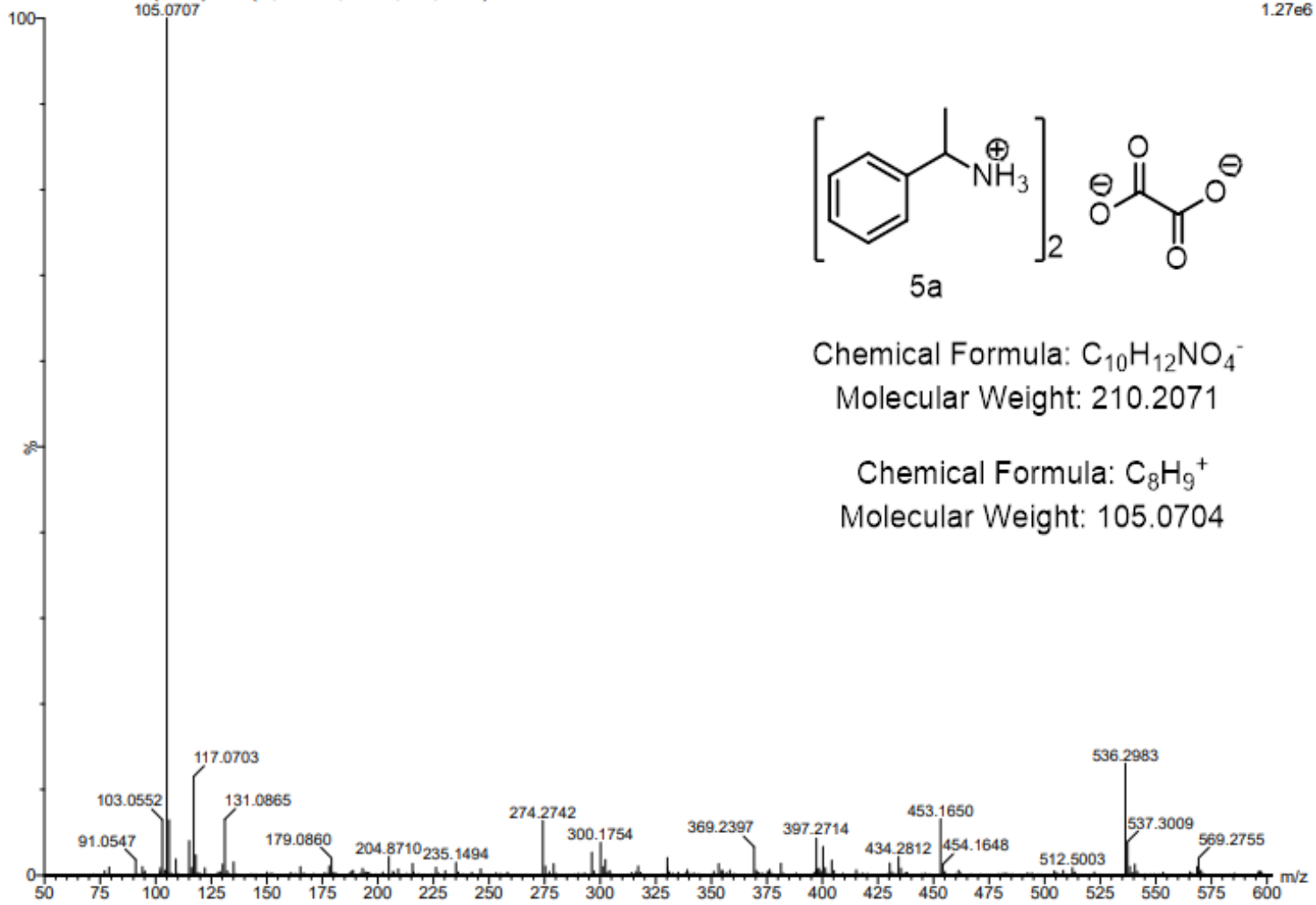
P.M Lab

IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829

14-Jan-202516:47:10

PM-NK-S1 New 37 (0.700) AM2 (Ar,22000.0,556.28,0.00,LS 10)

1: TOF MS ES+
1.27e6



5a

Chemical Formula: $C_{10}H_{12}NO_4^-$
Molecular Weight: 210.2071

Chemical Formula: $C_8H_9^+$
Molecular Weight: 105.0704

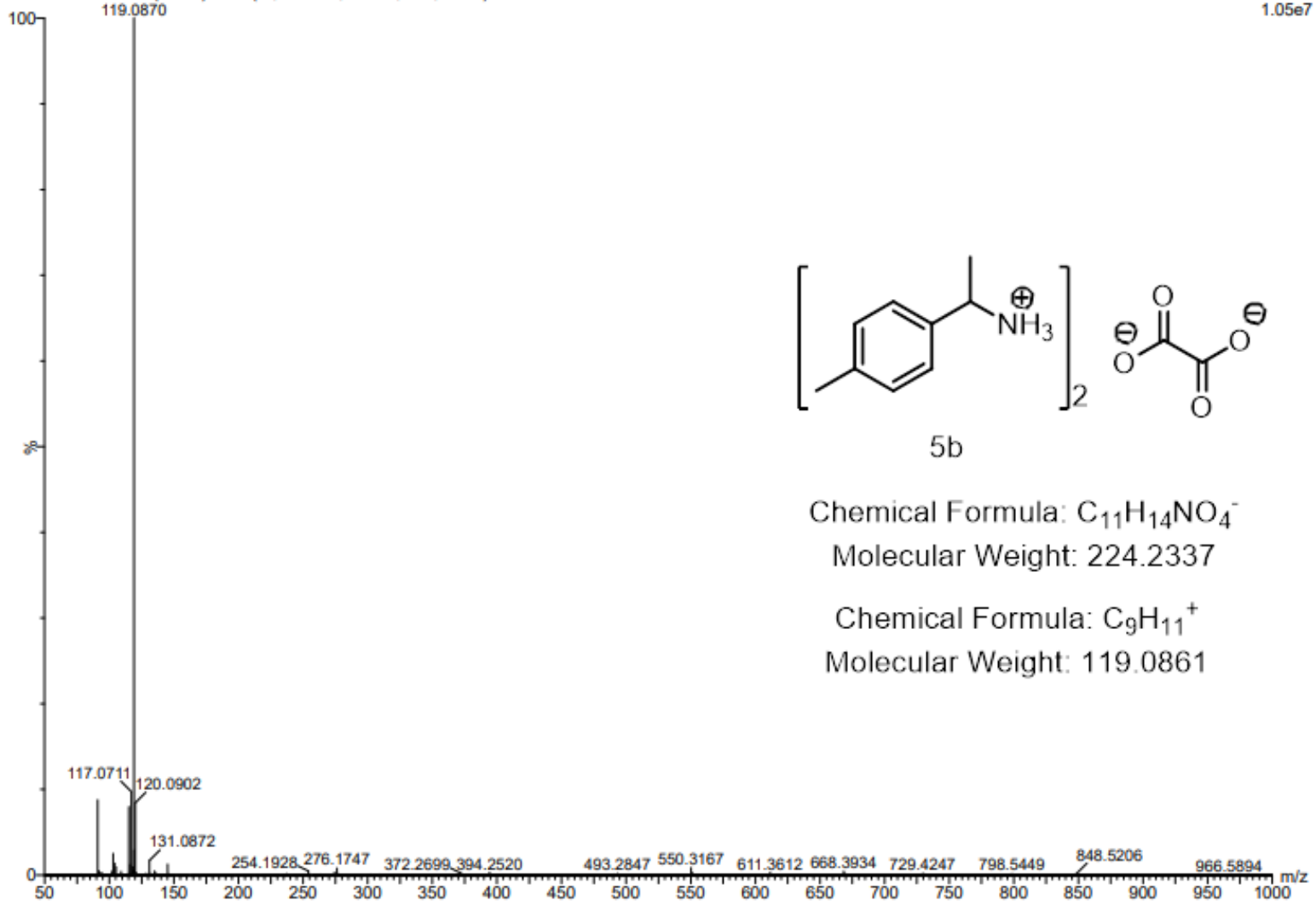
P.M Lab

IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829

14-Jan-202517:08:53

PM-NK-S2 New 17 (0.339) AM2 (Ar,22000.0,556.28,0.00,LS 10)

1: TOF MS ES+
1.05e7



5b

Chemical Formula: $C_{11}H_{14}NO_4^-$
Molecular Weight: 224.2337

Chemical Formula: $C_9H_{11}^+$
Molecular Weight: 119.0861