

Electronic supplementary information

D-A-D-T type four-component radical-dual-difunctionalization and acylative azidation of two different alkenes and TMSN₃

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I. General information

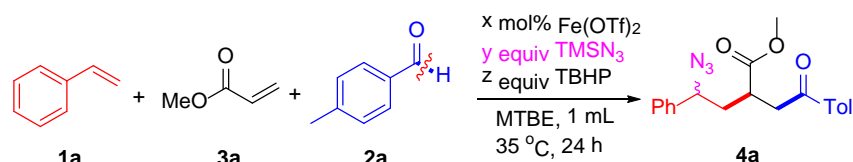
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents (methyl tertiary butyl ether, ethyl acetate, dichloroethane, acetonitrile, chlorobenzene, fluorobenzene) were used as purchased. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Melting points are uncorrected. Infrared spectrum (IR) was tested on a nicolet 6700 infrared spectrometer according to “case film technique” and the sample is loaded on the surface of a KBr plate by evaporation of sample solution. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane (TMS: $\delta=0$ ppm); while chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane (chloroform: δ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

The ratios of d.r. of products were roughly determined by HPLC analysis of crude reaction mixtures (with a UV detector by assuming the response of the two diastereoisomer was identical), since the diastereoisomer ratios might change during the purification procedure such as silica gel column chromatograph.

II. General experimental procedures

An oven-dried reaction vessel was successively charged with $\text{Fe}(\text{OTf})_2$ (3.0 mol%) in MTBE (1 mL, self-prepared solution), methyl acrylate (**3a**, 0.2 mmol, 1.0 equiv), styrene (**1a**, 0.4 mmol, 2.0 equiv), 4-methylbenzaldehyde (**2a**, 1.0 mmol, 5.0 equiv), *tert*-butyl hydroperoxide (TBHP, 70% in water, 0.6 mmol, 3.0 equiv) and trimethylsilyl azide (TMSN_3 , 0.8 mmol, 4.0 equiv). The vessel was sealed under air atmosphere and heated at 35 °C (oil bath temperature) for 24 h. Then the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum ether (30:1, $R_f = 0.4$) as eluent to give the product **4a**.

III. Optimization of the reaction conditions^a



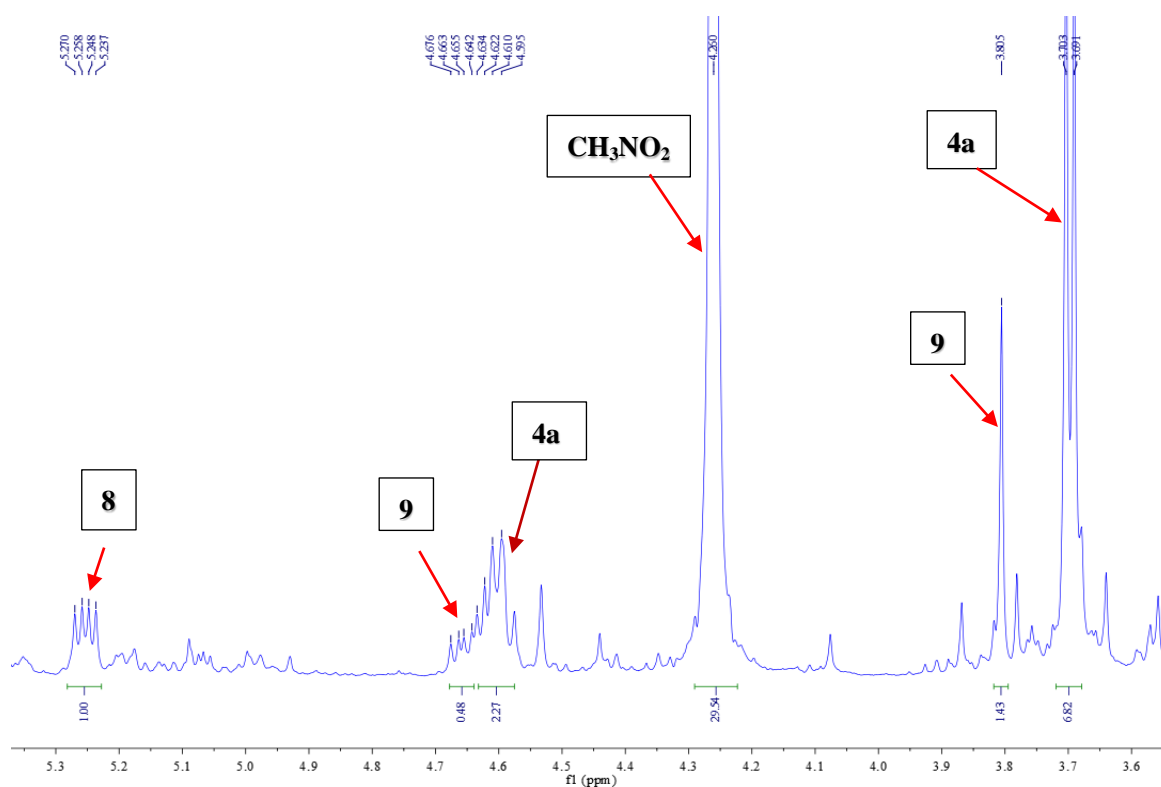
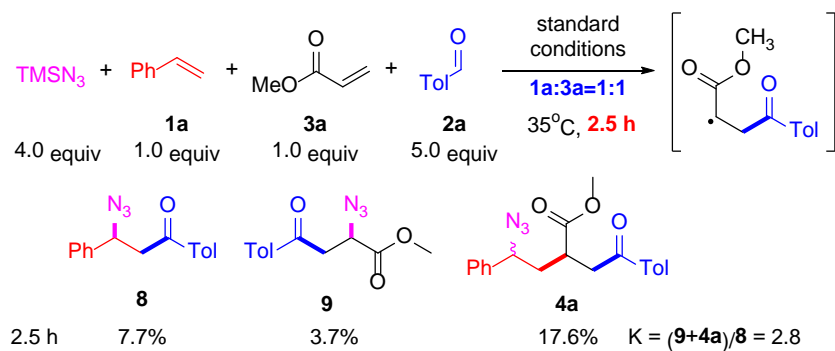
Entry	Cat. (mol%)	[O](equiv)	Ratio 3a:1a:2a:TMSN ₃	Sol. (1mL)	Yield of 4a [%] ^b
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1	Fe(OTf) ₃ (5)	TBHP(2.5)	1:2:5:4	MTBE	52
2	Fe(OTf) ₂ (5)	TBHP(2.5)	1:2:5:4	MTBE	56
3	Fe(acac) ₃ (5)	TBHP(2.5)	1:2:5:4	MTBE	15
4	Cu(OTf) ₂ (5)	TBHP(2.5)	1:2:5:4	MTBE	33
5	Fe(OTf) ₂ (2)	TBHP(2.5)	1:2:5:4	MTBE	61
6	Fe(OTf) ₂	TBHP(2.5)	1:2:5:4	MTBE	64
7	Fe(OTf) ₂ (3)	TBHP(2.5)	1:2:5:4	MTBE	68
8	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:4	MTBE	70
9	Fe(OTf) ₂ (3)	TBHP(3.5)	1:2:5:4	MTBE	70
10	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:4	Et ₂ O	48
11	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:4	THF	30
12	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:4	CH ₃ CN	42
13 ^c	Fe(OTf) ₂ (3)	TBHP(3) in oil	1:2:5:4	MTBE	67
14	Fe(OTf) ₂ (3)	DTBP(3)	1:2:5:4	MTBE	0
15	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:3	MTBE	62
16	Fe(OTf) ₂ (3)	TBHP(3)	1:2:4:4	MTBE	60
17	Fe(OTf) ₂ (3)	TBHP(3)	2:1:5:4	MTBE	33
18	Fe(OTf) ₂ (3)	TBHP(3)	1:1.5:5:4	MTBE	52
19 ^d	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:4	MTBE	61
20 ^e	Fe(OTf) ₂ (3)	TBHP(3)	1:2:5:4	MTBE	66

^a Conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (1.0 mmol, 5.0 equiv), **3a** (0.2 mmol, 1.0 equiv), TBHP (70% in H₂O, 0.6 mmol, 3.0 equiv), TMSN₃ (0.8 mmol, 4.0 equiv), Cat. (x mol %) in solvent (1 mL, prepared solution) stirred at 35 °C for 24 h. ^b isolated yield, ^c TBHP (5.5 mol/L in decane), ^d at 30°C, ^e at 40 °C.

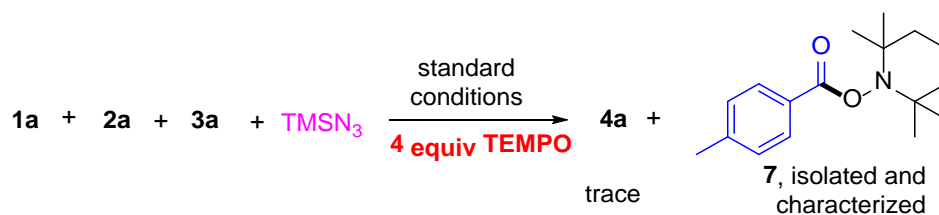
IV. The relative reaction rate of two different alkenes

To explore the relative reaction rate of acyl radical with the two different alkenes (methyl acrylate **3a** vs styrene **1a**), An *equal amount* of two different alkenes was added and shorten the reaction time to 2.5 hour. The detailed operations are as follows: an oven-dried reaction vessel was charged with Fe(OTf)₂ (3.0 mol%) in MTBE (1 mL, self-prepared solution), methyl acrylate (**3a**, 0.2 mmol, 1.0 equiv), styrene (**1a**, 0.2 mmol, 1.0 equiv), 4-methylbenzaldehyde (**2a**, 1.0 mmol, 5.0 equiv), *tert*-butyl hydroperoxide (TBHP, 70% in water, 0.6 mmol, 3.0 equiv) and trimethylsilyl azide (TMSN₃, 0.8 mmol, 4.0 equiv). The vessel was sealed and heated at 35 °C (oil bath temperature) for 2.5 hour. Then, the reaction mixture was carefully isolated by column chromatography and preparative TLC, three products (**8**, **9** and **4a**) were obtained and characterized. Their yields were determined by the ¹H NMR of reaction mixture using CH₃NO₂ (9.3 mg) as the internal standard.



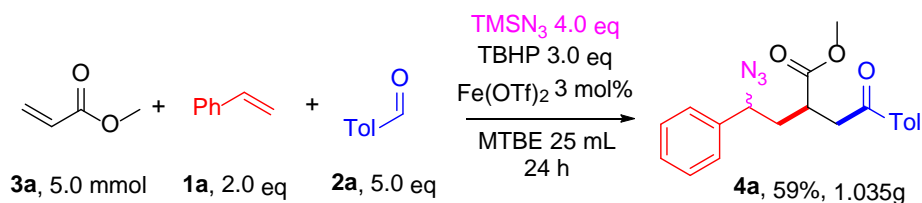
V. Radical inhibition experiments

To further understand this reaction, radical inhibition experiment was carried out in the presence of TEMPO. We found that: in the presence of TEMPO (2,2,6,6-tetramethyl piperidine-1-oxyl, 4.0 equiv), this reaction was completely inhibited and the 2,2,6,6-tetramethylpiperidin-1-yl 4-methylbenzoate **7** was isolated (ethyl ether/petroleum ether = 1:50, $R_f = 0.6$) and characterized.

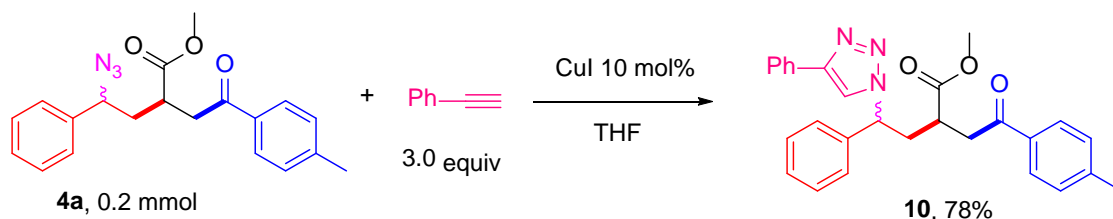


VI. Scaled-up reaction and post-transformation of product

An oven-dried reaction vessel was successively charged with $\text{Fe}(\text{OTf})_2$ (3.0 mol%) in MTBE (25 mL, self-prepared solution), methyl acrylate (**3a**, 5.0 mmol, 1.0 equiv), styrene (**1a**, 10.0 mmol, 2.0 equiv), 4-methylbenzaldehyde (**2a**, 25.0 mmol, 5.0 equiv), *tert*-butyl hydroperoxide (TBHP, 70% in water, 15.0 mmol, 3.0 equiv) and trimethylsilyl azide (TMSN_3 , 20.0 mmol, 4.0 equiv). The vessel was sealed and heated at 35 °C (oil bath temperature) for 24 h. Then 20 mL aqueous 5% NaHCO_3 was added, which was next extracted with CH_2Cl_2 , dried with Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum ether (30:1, $R_f = 0.4$) as eluent to give the product **4a** (1.035g, 59%).



To an oven-dried glass tube, **4a** (0.2 mmol, 1.0 equiv) was dissolved in THF (1.0 mL), then phenylacetylene (0.6 mmol, 3.0 equiv) and CuI (0.02 mmol, 0.1 equiv) were added. The reaction was performed at 60 °C for 12 h, and the resulting solution was concentrated under vacuum. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum ether (15:1, $R_f = 0.3$) to afford the white solid product **10** (70.1 mg, 78%).

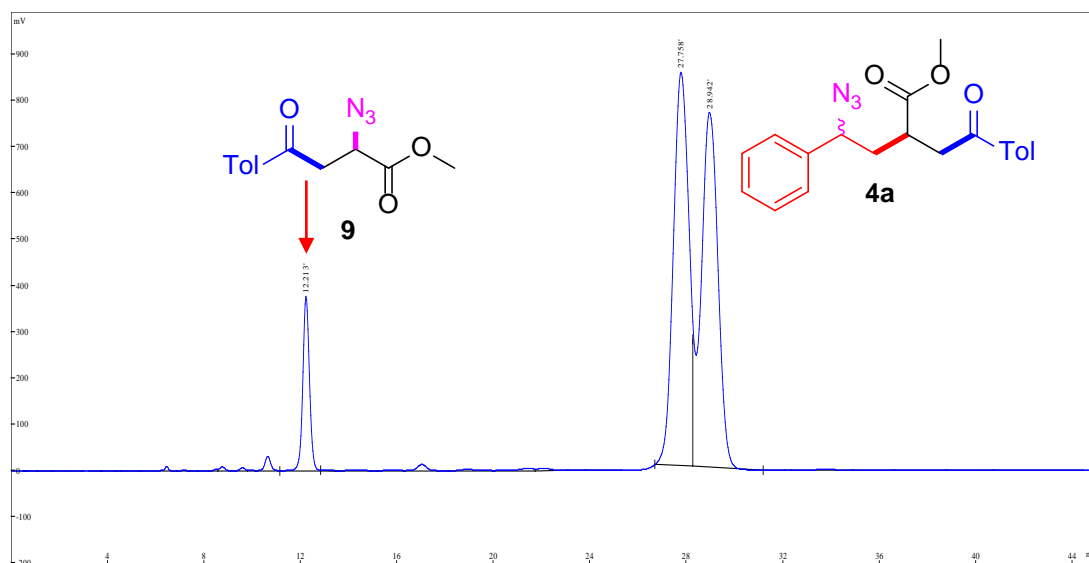


VII. Determination of d.r. value by HPLC for the diastereoisomers of 4a

The d.r. values of products were roughly determined by HPLC analysis of crude reaction mixtures (with a UV detector by assuming the responses of the two diastereoisomers were identical), since the diastereoisomer ratio might change during the purification procedure such as silica gel column chromatography.

With the model reaction and product **4a** as an example, the crude reaction mixture was analyzed using HPLC on a C-18 column, eluted by CH₃CN:H₂O=60:40, the two diastereoisomers could be separated as two peak (retention time 27-28 min), with almost the same peak area. At the same time, the acylative azidation product of the single alkene - methyl acrylate (**3a**) was also detected by the HPLC.

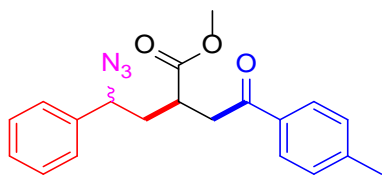
The d.r. values of other products were determined similarly, which were indicated in Tables 2-4 and the HPLC spectrum copied in pages S129-S156.



序号	保留时间	浓度	峰面积
	retention time	peak percentage	peak area
1	12.213	8.885	7279889
2	27.758	45.99	37692931
3	28.942	45.12	36964602
总计 (total)		100	81937422

VIII. Spectra data of products 4a-4o, 5b-5s, 6b-6j, 7, 8, 9, 10.

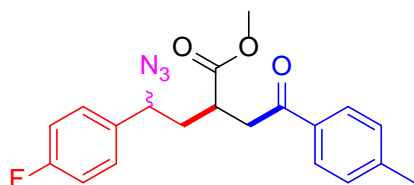
(4a) methyl-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (49.1 mg, 70%).

^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.83 (m, 2H), 7.41 – 7.33 (m, 5H), 7.28 – 7.26 (m, 2H), 4.63 – 4.57 (m, 1H), 3.73 – 3.72 (m, 3H), 3.47 – 3.40 (m, 1H), 3.32 – 3.29 (m, 0.4 \times 1H), 3.20 – 3.04 (m, 1.6 \times 1H), 2.42 (s, 3H), 2.34 – 2.26 (m, 0.6 \times 1H), 2.21 – 2.14 (m, 0.4 \times 1H), 2.03 – 1.95 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.16, 197.12, 175.30, 144.32, 139.37, 138.84, 134.05, 129.42, 128.73, 128.59, 128.25, 128.23, 127.19, 126.92, 64.67, 63.40, 52.15, 40.72, 40.37, 38.67, 38.07, 38.02, 37.92, 21.751. IR (cm^{-1}): 3059, 3027, 2950, 2921, 1734, 1684, 1635, 1608, 1570, 1449, 1334, 815, 754, 701, 551. HRMS: calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 374.1475; Found: 374.1481.

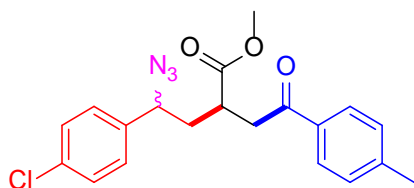
(4b) methyl-4-azido-4-(4-fluorophenyl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-fluoro-4-vinylbenzene (**1b**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (49.5 mg, 67%).

^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.81 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H), 7.10 – 7.04 (m, 2H), 4.62 – 4.56 (m, 1H), 3.71 – 3.70 (m, 3H), 3.45 – 3.39 (m, 1H), 3.30 – 3.23 (m, 0.4 \times 1H), 3.19 – 3.09 (m, 1H), 3.04 – 2.97 (m, 0.6 \times 1H), 2.40 (s, 3H), 2.30 – 2.22 (m, 0.6 \times 1H), 2.16 – 2.10 (m, 0.4 \times 1H), 1.98 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.00, 196.97, 175.14, 175.10, 162.71 (d, J = 246.0 Hz), 162.18 (d, J = 246.0 Hz), 135.21 (d, J = 3.2 Hz), 134.62 (d, J = 3.2 Hz), 133.96, 133.92, 129.38, 128.98, 128.89, 128.66, 128.58, 128.18, 128.16, 115.93 (d, J = 11.5 Hz), 115.87 (d, J = 11.5 Hz), 63.91, 63.60, 52.11, 40.66, 40.32, 38.66, 37.99, 37.86, 37.76, 21.67. ^{19}F NMR (376 MHz, CDCl_3) δ (-113.06, -113.31). IR (cm^{-1}): 3341, 3034, 2952, 2474, 2101, 1898, 1734, 1682, 1509, 1439, 1099, 1006, 838, 736, 537, 462. HRMS: calcd. for $\text{C}_{20}\text{H}_{20}\text{FN}_3\text{O}_3\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 392.1381; Found: 392.1391.

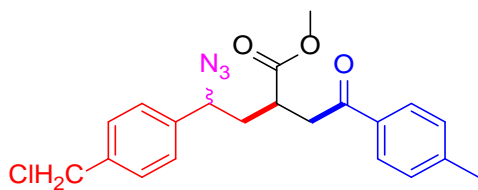
(4c) methyl-4-azido-4-(4-chlorophenyl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-chloro-4-vinylbenzene (**1c**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (47.7 mg, 62%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.38 – 7.34 (m, 2H), 7.29 – 7.24 (m, 4H), 4.61 – 4.55 (m, 1H), 3.72 – 3.71 (m, 3H), 3.44 – 3.38 (m, 1H), 3.31 – 3.24 (m, 0.3×1H), 3.19 – 3.08 (m, 1H), 3.03 – 2.96 (m, 0.7×1H), 2.41 (s, 3H), 2.29 – 2.21 (m, 0.7×1H), 2.16 – 2.09 (m, 0.3×1H), 1.96 – 1.88 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.04, 197.00, 175.21, 175.16, 144.44, 144.42, 137.98, 137.34, 134.53, 134.35, 133.94, 133.92, 129.45, 129.27, 129.21, 128.60, 128.28, 128.24, 128.22, 63.99, 63.69, 52.24, 40.73, 40.39, 38.67, 37.96, 37.87, 37.74, 21.78. IR (cm⁻¹): 3031, 2951, 2922, 2099, 1735, 1682, 1606, 1573, 1492, 1427, 1408, 1092, 1014, 810, 737, 528. HRMS: calcd. for C₂₀H₂₀ClN₃O₃Na⁺ [M+ Na]⁺: 408.1085; Found: 408.1095.

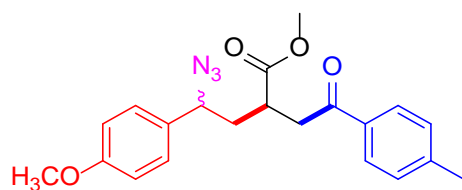
(4d) methyl-4-azido-4-(4-(chloromethyl)phenyl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-(chloromethyl)-4-vinylbenzene (**1d**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as pale yellow oil (48.7 mg, 61%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.24 (m, 2H), 4.63 – 4.58 (m, 3H), 3.71 – 3.70 (m, 3H), 3.44 – 3.38 (m, 1H), 3.31 – 3.26 (m, 0.4×1H), 3.17 – 3.00 (m, 1.6×1H), 2.40 (s, 3H), 2.31 – 2.23 (m, 0.6×1H), 2.18 – 2.11 (m, 0.4×1H), 1.98 – 1.92 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.12, 197.07, 175.24, 144.40, 144.38, 139.68, 139.09, 137.91, 137.79, 133.94, 133.93, 129.43, 129.27, 129.25, 128.23, 128.22, 127.57, 127.30, 64.28, 63.99, 52.22, 45.78, 40.72, 40.37, 38.66, 38.01, 37.93, 37.80, 21.78. IR (cm⁻¹): 3031, 2951, 2100, 1731, 1681, 1607, 1573, 1513, 1436, 1102, 1000, 810, 737, 682, 636, 560, 463. HRMS: calcd. for C₂₁H₂₂ClN₃O₃Na⁺ [M+ Na]⁺: 422.1242; Found: 422.1254.

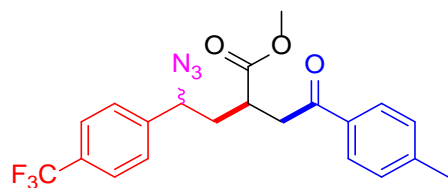
(4e) methyl-4-azido-4-(4-methoxyphenyl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-vinylbenzene (**1e**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:15, R_f = 0.4) as colorless oil (36.6 mg, 48%).

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.81 (m, 2H), 7.28 – 7.24 (m, 4H), 6.92 – 6.89 (m, 2H), 4.56 – 4.50 (m, 1H), 3.81 (s, 3H), 3.72 – 3.70 (m, 3H), 3.49 – 3.38 (m, 1H), 3.28 – 3.21 (m, 0.4×1H), 3.17 – 3.07 (m, 1H), 3.08 – 2.98 (m, 0.6×1H), 2.41 (s, 3H), 2.30 – 2.23 (m, 0.6×1H), 2.17 – 2.10 (m, 0.4×1H), 2.01 – 1.90 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.21, 175.38, 159.82, 159.74, 144.32, 134.03, 134.01, 131.23, 130.71, 129.42, 128.51, 128.24, 114.37, 114.33, 64.16, 63.91, 55.39, 52.17, 40.65, 40.41, 38.48, 37.99, 37.91, 21.78. IR (cm⁻¹): 3000, 2952, 2838, 2094, 1731, 1681, 1608, 1513, 1438, 1406, 1113, 1033, 833, 810, 736, 545, 461. HRMS: calcd. for C₂₁H₂₃N₃O₄Na⁺ [M+ Na]⁺: 404.1581; Found: 404.1590.

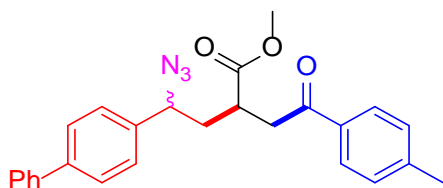
(4f) methyl-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)-4-(4-(trifluoromethyl)phenyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-(trifluoromethyl)-4-vinylbenzene (**1f**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (35.2 mg, 42%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.67 – 7.63 (m, 2H), 7.49 – 7.45 (m, 2H), 7.26 – 7.24 (m, 2H), 4.72 – 4.65 (m, 1H), 3.72 – 3.71 (m, 3H), 3.46 – 3.39 (m, 1H), 3.33 – 3.27 (m, 0.5×1H), 3.14 (td, *J* = 17.6, 6.0 Hz, 1H), 3.04 – 2.98 (m, 0.5×1H), 2.41 (s, 3H), 2.32 – 2.24 (m, 0.6×1H), 2.19 – 2.12 (m, 0.5×1H), 2.00 – 1.89 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.99, 196.93, 175.15, 175.07, 163.77, 139.36, 138.83, 130.83 (q, *J* = 32.3 Hz), 130.67 (q, *J* = 32.3 Hz), 129.59, 129.03, 128.99, 128.70, 128.56, 127.17, 126.89, 126.79 (q, *J* = 3.7 Hz), 126.02 (q, *J* = 3.8 Hz), 123.99 (d, *J* = 270.5 Hz), 113.86, 64.65, 64.39, 55.56, 52.12, 40.47, 40.13, 38.66, 38.06, 37.95. ¹⁹F NMR (376 MHz, CDCl₃) δ (-61.05, -62.65, -62.67, -64.29). IR (cm⁻¹): 3032, 2953, 2924, 2102, 1732, 1682, 1607, 1573, 1437, 1325, 1068, 1017, 841, 810, 603, 551. HRMS: calcd. for C₂₁H₂₀F₃N₃O₃Na⁺ [M+ Na]⁺: 442.1349; Found: 442.1359.

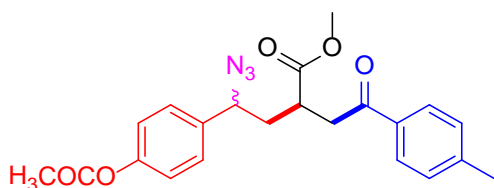
(4g) methyl-4-([1,1'-biphenyl]-4-yl)-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 4-vinyl-1,1'-biphenyl (**1g**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:25, R_f = 0.3) as colorless oil (55.5 mg, 65%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.61 – 7.56 (m, 4H), 7.45 – 7.34 (m, 5H), 7.23 – 7.21 (m, 2H), 4.67 – 4.61 (m, 1H), 3.72 – 3.70 (m, 3H), 3.46 – 3.40 (m, 1H), 3.32 – 3.28 (m, 0.4×1H), 3.18 – 3.04 (m, 1.6×1H), 2.38 – 2.37 (m, 3H), 2.35 – 2.28 (m, 0.6×1H), 2.23 – 2.16 (m, 0.4×1H), 2.05 – 1.97 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.10, 197.04, 175.23, 144.26, 141.54, 141.42, 140.46, 138.30, 137.75, 134.00, 133.98, 129.37, 128.87, 128.20, 128.18, 127.69, 127.65, 127.59, 127.33, 127.14, 64.35, 64.10, 52.12, 40.65, 40.35, 38.56, 37.99, 37.85, 21.69. IR (cm⁻¹): 3030, 2950, 2099, 1732, 1682, 1606, 1573, 1486, 1437, 1407, 1077, 840, 766, 736, 698, 564, 511. HRMS: calcd. for C₂₆H₂₅N₃O₃Na⁺ [M+ Na]⁺: 450.1788; Found: 450.1797.

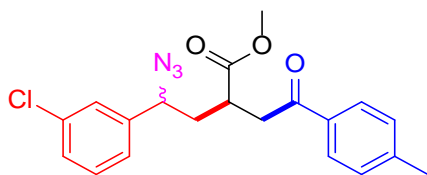
(4h) methyl-4-(4-acetoxyphenyl)-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 4-vinylphenyl acetate (**1h**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:15, R_f = 0.3) as colorless oil (49.1 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.21 (m, 2H), 7.37 – 7.33 (m, 2H), 7.27 – 7.24 (m, 2H), 7.13 – 7.10 (m, 2H), 4.63 – 4.57 (m, 1H), 3.71 – 3.70 (m, 3H), 3.45 – 3.39 (m, 1H), 3.31 – 3.27 (m, 0.5×1H), 3.18 – 3.05 (m, 1.5×1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.28 – 2.23 (m, 0.5×1H), 2.16 – 2.10 (m, 0.5×1H), 1.98 – 1.91 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.11, 197.06, 175.24, 169.43, 169.38, 150.74, 150.63, 144.34, 137.06, 136.49, 133.93, 130.24, 129.41, 129.25, 128.21, 127.95, 122.16, 122.13, 64.08, 63.78, 52.20, 40.74, 40.32, 38.80, 38.13, 37.95, 37.81, 21.75, 21.22. IR (cm⁻¹): 3033, 2952, 2100, 1732, 1682, 1607, 1573, 1508, 1369, 1109, 1016, 911, 847, 811, 736, 542. HRMS: calcd. for C₂₂H₂₃N₃O₅Na⁺ [M+ Na]⁺: 432.1530; Found: 432.1540.

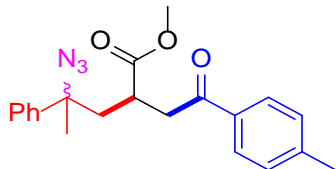
(4i) methyl-4-azido-4-(3-chlorophenyl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-chloro-3-vinylbenzene (**1i**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as reddish brown oil (46.2 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.82 (m, 2H), 7.33 – 7.30 (m, 3H), 7.26 – 7.20 (m, 3H), 4.62 – 4.55 (m, 1H), 3.73 – 3.72 (m, 3H), 3.46 – 3.39 (m, 1H), 3.32 – 3.25 (m, 0.4×1H), 3.20 – 3.10 (m, 1H), 3.06 – 3.00 (m, 0.6×1H), 2.40 (s, 3H), 2.29 – 2.21 (m, 0.6×1H), 2.16 – 2.09 (m, 0.4×1H), 1.96 – 1.87 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.01, 196.96, 175.13, 175.10, 144.40, 141.65, 141.02, 134.92, 134.88, 133.94, 130.34, 130.30, 129.43, 128.88, 128.69, 128.22, 127.30, 127.01, 125.37, 125.03, 64.11, 63.81, 52.21, 40.75, 40.34, 38.76, 38.03, 37.89, 37.75, 21.75. IR (cm⁻¹): 3031, 2951, 2922, 2100, 1713, 1681, 1606, 1573, 1477, 1435, 999, 880, 810, 737, 697, 561. HRMS: calcd. for C₂₀H₂₀ClN₃O₃Na⁺ [M+ Na]⁺: 408.1085; Found: 408.1094.

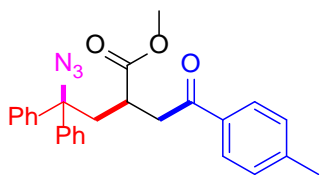
(4j) methyl-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)-4-phenylpentanoate



The title compound was prepared according to the general procedure described above by the reaction between prop-1-en-2-ylbenzene (**1j**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (40.9 mg, 56%).

¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.69 (m, 2H), 7.42 – 7.33 (m, 4H), 7.28 – 7.19 (m, 3H), 3.60 – 3.55 (m, 3H), 3.31 – 3.25 (m, 0.6×1H), 3.13 – 2.92 (m, 2.4×1H), 2.44 – 2.38 (m, 4H), 2.04 – 1.99 (m, 1H), 1.77(s, 1.8×1H), 1.75 (s, 1.2×1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.24, 175.75, 175.68, 144.21, 144.16, 142.82, 142.75, 134.10, 134.03, 129.38, 129.33, 128.75, 128.72, 128.22, 128.19, 127.68, 127.65, 125.73, 125.72, 66.37, 66.35, 52.09, 52.03, 43.94, 43.82, 41.36, 41.10, 37.04, 26.06, 25.89, 21.75. IR (cm⁻¹): 3029, 2949, 2107, 1737, 1682, 1607, 1537, 1494, 1445, 1407, 1030, 810, 765, 700, 645, 563. HRMS: calcd. for C₂₁H₂₃N₃O₃Na⁺ [M+ Na]⁺: 388.1632; Found: 388.1640.

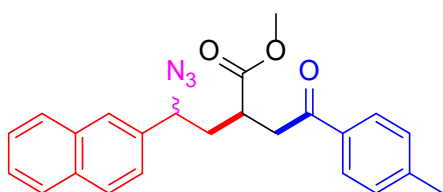
(4k) methyl-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)-4,4-diphenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between ethene-1,1-diyldibenzene (**1k**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3) as pale yellow oil (57.2 mg, 67%).

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 10H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.59 (s, 3H), 3.20 – 3.07 (m, 2H), 3.00 – 2.94 (m, 2H), 2.60 (dd, *J* = 10.0, 4.8 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.18, 175.67, 144.13, 142.39, 142.24, 133.93, 129.30, 128.52, 128.48, 128.18, 127.92, 127.74, 127.31, 127.08, 71.98, 52.14, 41.08, 40.06, 36.88, 21.73. IR (cm⁻¹): 3058, 3029, 2949, 2108, 1775, 1732, 1682, 1607, 1493, 1446, 1032, 977, 810, 736, 700, 656, 563. HRMS: calcd. for C₂₆H₂₅N₃O₃Na⁺ [M+ Na]⁺: 450.1788; Found: 450.1794.

(4l) methyl-4-azido-4-(naphthalen-2-yl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate

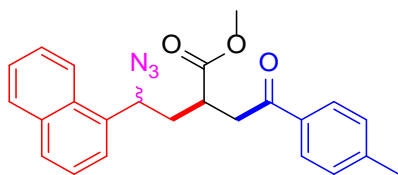


The title compound was prepared according to the general procedure described above by the reaction between 2-vinylnaphthalene (**1l**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3) as colorless oil (49.7 mg, 62%).

¹H NMR (400 MHz, CDCl₃) 7.89 – 7.77 (m, 6H), 7.53 – 7.43 (m, 3H), 7.26 – 7.22 (m, 2H), 4.79 – 4.74 (m, 1H), 3.72 – 3.69 (m, 3H), 3.47 – 3.40 (m, 1H), 3.36 – 3.30 (m, 0.4×1H), 3.21 – 3.04 (m, 1.6×1H), 2.40 – 2.33 (m, 3.6×1H), 2.16 – 2.09 (m, 0.4×1H), 2.10 – 2.02 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.16, 197.13, 175.34, 144.34, 136.74, 136.16, 133.98, 133.41, 133.33, 133.24, 129.41, 129.18, 129.09, 128.25, 128.23, 128.19, 128.14, 127.85, 127.84, 126.73, 126.63, 126.56, 126.51, 126.19, 124.40, 124.35, 64.90, 64.64, 52.22, 40.76, 40.43, 38.64, 38.05, 37.99, 37.94, 21.76. IR (cm⁻¹): 3056, 2950, 2098, 1731, 1682, 1606, 1573, 1508, 1436, 1407, 894, 858, 811, 748, 559, 479. HRMS: calcd. for C₂₄H₂₃N₃O₃Na⁺ [M+ Na]⁺: 424.1632; Found: 424.1640.

(4m) methyl-4-azido-4-(naphthalen-1-yl)-2-(2-oxo-2-(p-tolyl)ethyl)butanoate

The two diastereoisomers were separated by column chromatograph.



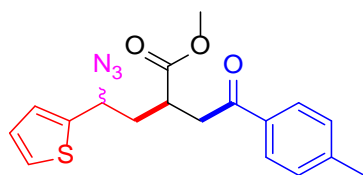
The title compound was prepared according to the general procedure described above by the reaction between 1-vinylnaphthalene (**1m**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3~0.35, the R_f gap between **4m** and **4m'**) as colorless oil (**4m** + **4m'** = 52.2 mg, 65%).

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 3H), 7.61 – 7.47 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.45 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.78 (s, 3H), 3.48 – 3.40 (m, 2H), 3.22 – 3.16 (m, 1H), 2.40 (s, 3H), 2.37 – 2.31 (m, 1H), 2.05 – 1.98 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.10, 175.50, 144.37, 135.41, 134.09, 134.01, 130.52, 129.44, 129.17, 129.00, 128.26, 126.83, 126.04, 125.51, 124.11, 122.92, 61.52, 52.27, 40.93, 38.44, 38.04, 21.79. IR (cm⁻¹): 3051, 2950, 2922, 2104, 1732, 1682, 1606, 1509, 1437, 1260, 1180, 802, 779, 750, 560. HRMS: calcd. for C₂₄H₂₃N₃O₃Na⁺ [M+ Na]⁺: 424.1632; Found: 424.1631.

(**4m'**)

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 3H), 7.60 – 7.47 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 2H), 5.41 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.71 (s, 3H), 3.50 – 3.41 (m, 2H), 3.24 – 3.16 (m, 1H), 2.49 – 2.43 (m, 1H), 2.40 (s, 3H), 2.33 – 2.17 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.23, 175.44, 144.37, 134.49, 134.09, 134.18, 134.20, 130.73, 129.44, 129.30, 129.23, 128.25, 126.75, 126.05, 125.44, 124.81, 123.05, 61.42, 52.24, 40.38, 38.58, 37.29, 21.79. IR (cm⁻¹): 3050, 2950, 2923, 2103, 1734, 1682, 1606, 1573, 1510, 1436, 1224, 1168, 804, 780, 560. HRMS: calcd. for C₂₄H₂₃N₃O₃Na⁺ [M+ Na]⁺: 424.1632; Found: 424.1632.

(**4n**) methyl-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)-4-(thiophen-2-yl)butanoate

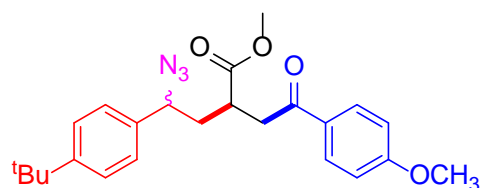


The title compound was prepared according to the general procedure described above by the reaction between 2-vinylthiophene (**1n**), 4-methylbenzaldehyde (**2a**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:25, R_f = 0.3) as brown oil (33.6 mg, 47%).

¹H NMR (400 MHz, CDCl₃) 7.86 – 7.82 (m, 2H), 7.32– 7.29 (m, 1H), 7.27 – 7.24 (m, 2H), 7.09 – 7.08 (m, 1H), 7.02 – 6.99 (m, 1H), 4.88 – 4.83 (m, 1H), 3.72 – 3.71 (m, 3H), 3.49 – 3.40 (m, 1H),

3.32 – 3.29 (m, 0.5×1H), 3.20 – 3.06 (m, 1.6×1H), 2.40 (s, 3H), 2.38 – 2.25 (m, 1H), 2.10 – 2.01 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.03, 197.00, 175.07, 144.33, 144.31, 142.10, 141.54, 133.99, 133.97, 129.40, 128.23, 128.22, 126.99, 126.94, 126.39, 126.10, 125.83, 125.80, 59.69, 59.54, 52.18, 40.54, 40.30, 38.75, 38.39, 37.95, 37.73, 21.73. IR (cm⁻¹): 3341, 3031, 2951, 2922, 2102, 1731, 1682, 1607, 1573, 1436, 1407, 1108, 1000, 810, 707, 560. HRMS: calcd. for C₁₈H₁₉N₃O₃Na⁺ [M+ Na]⁺: 380.1039; Found: 380.1044.

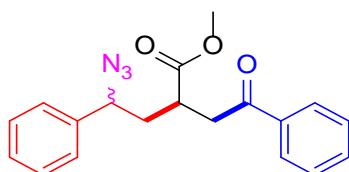
(4o) methyl-4-azido-4-(4-(tert-butyl)phenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)butanoate



The title compound was prepared according to the general procedure described above by the reaction between 1-(*tert*-butyl)-4-vinylbenzene (**1o**), 4-methoxybenzaldehyde (**2c**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as pale yellow oil (59.3 mg, 70%).

¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.89 (m, 2H), 7.40 – 7.38 (m, 2H), 7.27 – 7.24 (m, 2H), 6.93 – 6.90 (m, 2H), 4.58 – 4.52 (m, 1H), 3.85 (s, 3H), 3.71 – 3.69 (m, 3H), 3.42 – 3.36 (m, 1H), 3.29 – 3.24 (m, 0.4×1H), 3.14 – 3.01 (m, 1.6×1H), 2.31 – 2.24 (m, 0.6×1H), 2.17 – 2.12 (m, 0.4×1H), 2.02 – 1.93 (m, 1H), 1.31 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 196.05, 195.97, 175.37, 175.34, 163.72, 151.58, 151.48, 136.26, 135.77, 130.36, 129.59, 129.57, 126.81, 126.58, 125.88, 125.84, 64.33, 64.10, 55.52, 52.07, 40.40, 40.12, 38.51, 38.10, 38.01, 37.96, 34.65, 31.33. IR (cm⁻¹): 3056, 2962, 2841, 2096, 1713, 1680, 1600, 1575, 1511, 1462, 1438, 1110, 1030, 992, 831, 737, 703, 608, 572. HRMS: calcd. for C₂₄H₂₉N₃O₄Na⁺ [M+ Na]⁺: 446.2050; Found: 446.2054.

(5b) methyl-4-azido-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate

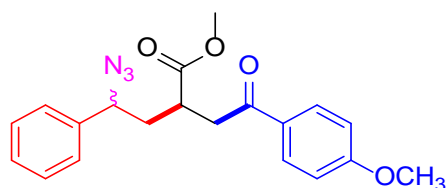


The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), benzaldehyde (**2b**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3) as colorless oil (43.1 mg, 64%).

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.91 (m, 2H), 7.58 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.31 (m, 5H), 4.62 – 4.56 (m, 1H), 3.71 – 3.70 (m, 3H), 3.48 – 3.42 (m, 1H), 3.32 – 3.26 (m,

0.4×1H), 3.20 – 3.03 (m, 1.6×1H), 2.32 – 2.25 (m, 0.6×1H), 2.20 – 2.13 (m, 0.4×1H), 2.02 – 1.94 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.52, 197.48, 175.17, 163.72, 139.33, 138.80, 136.51, 133.43, 129.04, 129.01, 128.72, 128.58, 128.10, 128.09, 127.16, 126.89, 64.65, 64.36, 52.13, 40.80, 40.44, 38.63, 38.03, 37.97, 37.89. IR (cm⁻¹): 3062, 3030, 2951, 2099, 1732, 1686, 1597, 1493, 1449, 1219, 1168, 1001, 846, 757, 701, 560. HRMS: calcd. for C₁₉H₁₉N₃O₃Na⁺ [M+ Na]⁺: 360.1319; Found: 360.1319.

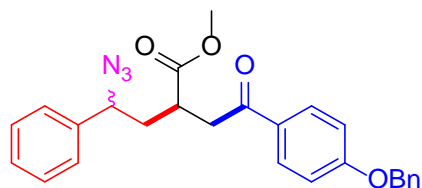
(5c) methyl-4-azido-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methoxybenzaldehyde (**2c**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as colorless oil (47.7 mg, 65%).

¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.89 (m, 2H), 7.41 – 7.31 (m, 5H), 6.93 – 6.91 (m, 2H), 4.61 – 4.55 (m, 1H), 3.85 (s, 3H), 3.71 – 3.70 (m, 3H), 3.43 – 3.36 (m, 1H), 3.30 – 3.24 (m, 0.3×1H), 3.15 – 3.01 (m, 1.7×1H), 2.32 – 2.24 (m, 0.7×1H), 2.19 – 2.12 (m, 0.3×1H), 2.01 – 1.93 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 195.99, 195.95, 175.34, 163.77, 139.36, 138.83, 130.38, 129.59, 129.03, 128.99, 128.70, 128.56, 127.17, 126.89, 113.86, 64.65, 64.39, 55.56, 52.12, 40.47, 40.13, 38.66, 38.06, 37.95. IR (cm⁻¹): 2951, 2841, 2099, 1732, 1677, 1600, 1575, 1420, 1362, 1169, 831, 760, 702, 610, 561, 526. HRMS: calcd. for C₂₀H₂₁N₃O₄Na⁺ [M+ Na]⁺: 390.1424; Found: 390.1426.

(5d) methyl-4-azido-2-(2-(4-(benzyloxy)phenyl)-2-oxoethyl)-4-phenylbutanoate

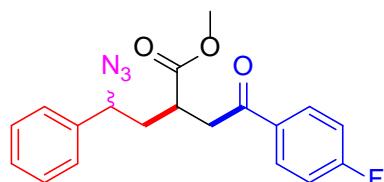


The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-(benzyloxy)benzaldehyde (**2d**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as colorless oil (56.7 mg, 64%).

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.88 (m, 2H), 7.42 – 7.30 (m, 10H), 6.99 – 6.97 (m, 2H), 5.10 (s, 2H), 4.60 – 4.54 (m, 1H), 3.69 – 3.68 (m, 3H), 3.41 – 3.34 (m, 1H), 3.28 – 3.23 (m, 0.4×1H), 3.13 – 3.01 (m, 1.6×1H), 2.31 – 2.23 (m, 0.6×1H), 2.18 – 2.11 (m, 0.4×1H), 2.00 – 1.92

(m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.93, 195.89, 175.27, 162.86, 139.33, 138.81, 136.18, 130.37, 129.76, 129.00, 128.96, 128.75, 128.67, 128.53, 128.30, 127.51, 127.14, 126.87, 114.70, 70.18, 64.62, 64.35, 52.08, 40.44, 40.10, 38.61, 38.03, 37.92. IR (cm^{-1}): 3063, 3032, 1950, 2098, 1731, 1681, 1600, 1575, 1509, 1455, 1114, 991, 916, 830, 739, 700, 649, 561. HRMS: calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_4\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 466.1737; Found: 466.1739.

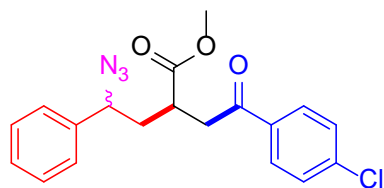
(5e) methyl-4-azido-2-(2-(4-fluorophenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-fluorobenzaldehyde (**2e**), methyl acrylate (**3a**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (45.4 mg, 64%).

^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.94 (m, 2H), 7.40 – 7.31 (m, 5H), 7.15 – 7.10 (m, 2H), 4.62 – 4.56 (m, 1H), 3.72 – 3.71 (m, 3H), 3.46 – 3.40 (m, 1H), 3.32 – 3.26 (m, 0.4 \times 1H), 3.17 – 3.02 (m, 1.6 \times 1H), 2.32 – 2.25 (m, 0.6 \times 1H), 2.19 – 2.12 (m, 0.4 \times 1H), 2.01 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.01, 195.97, 175.20, 165.99 (d, J = 254.0 Hz), 139.39, 138.75, 132.92, 132.89, 132.79 (d, J = 9.3 Hz), 129.10, 129.06, 128.80, 128.66, 127.18, 126.90, 115.89 (d, J = 21.8 Hz), 64.65, 64.31, 52.26, 40.73, 40.34, 38.66, 38.06, 37.94, 37.87. ^{19}F NMR (376 MHz, CDCl_3) δ (-104.60, -104.63). IR (cm^{-1}): 3064, 3032, 2952, 2470, 2096, 1731, 1682, 1597, 1507, 1437, 1410, 1100, 995, 833, 738, 701, 602, 560. HRMS: calcd. for $\text{C}_{19}\text{H}_{18}\text{FN}_3\text{O}_3\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 378.1224; Found: 378.1225.

(5f) methyl-4-azido-2-(2-(4-chlorophenyl)-2-oxoethyl)-4-phenylbutanoate

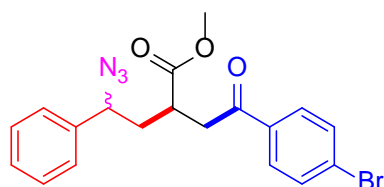


The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-chlorobenzaldehyde (**2f**), methyl acrylate (**3a**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (40.9 mg, 55%).

^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.85 (m, 2H), 7.44 – 7.31 (m, 7H), 4.62 – 4.55 (m, 1H), 3.71 – 3.70 (m, 3H), 3.45 – 3.38 (m, 1H), 3.32 – 3.25 (m, 0.4 \times 1H), 3.15 – 3.02 (m, 1.6 \times 1H), 2.32 – 2.25 (m, 0.6 \times 1H), 2.19 – 2.12 (m, 0.4 \times 1H), 2.01 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ

196.40, 196.36, 175.12, 139.93, 139.24, 138.71, 134.73, 129.54, 129.52, 129.08, 129.06, 128.79, 128.64, 127.15, 126.87, 64.60, 64.26, 52.25, 40.74, 40.34, 38.60, 38.01, 37.88, 37.82. IR (cm⁻¹): 3031, 2951, 3923, 2099, 1732, 1687, 1589, 1490, 1437, 1401, 1217, 1169, 1092, 994, 820, 762, 701, 527. HRMS: calcd. for C₁₉H₁₈ClN₃O₃Na⁺ [M+ Na]⁺: 394.0929; Found: 394.0932.

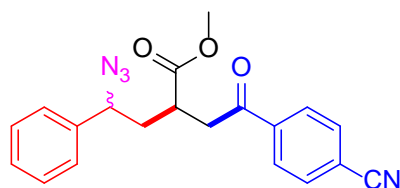
(5g) methyl-4-azido-2-(2-(4-bromophenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-bromobenzaldehyde (**2g**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (39.8 mg, 48%).

¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.77 (m, 2H), 7.61 – 7.58 (m, 2H), 7.42 – 7.31 (m, 5H), 4.61 – 4.55 (m, 1H), 3.72 – 3.71 (m, 3H), 3.45 – 3.38 (m, 1H), 3.32 – 3.25 (m, 0.4×1H), 3.15 – 3.02 (m, 1.6×1H), 2.32 – 2.24 (m, 0.6×1H), 2.19 – 2.12 (m, 0.4×1H), 2.01 – 1.93 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.63, 175.13, 139.26, 138.73, 135.16, 132.09, 129.65, 129.11, 129.09, 128.82, 128.72, 128.67, 127.17, 126.90, 64.63, 64.29, 52.29, 40.75, 40.35, 38.63, 38.04, 37.90, 37.84. IR (cm⁻¹): 3031, 2951, 2923, 2099, 1734, 1686, 1585, 1437, 1398, 1217, 1169, 1070, 1009, 816, 763, 701. HRMS: calcd. for C₁₉H₁₈BrN₃O₃Na⁺ [M+ Na]⁺: 438.0424; Found: 438.0425.

(5h) methyl-4-azido-2-(2-(4-cyanophenyl)-2-oxoethyl)-4-phenylbutanoate

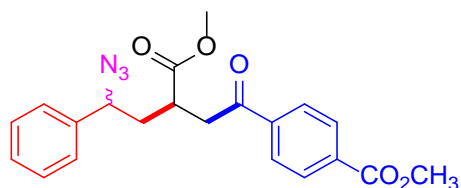


The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-formylbenzotrile (**2h**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as colorless oil (18.1 mg, 25%).

¹H NMR (400 MHz, CDCl₃) δ 8.03 – 8.00 (m, 2H), 7.79 – 7.60 (m, 2H), 7.43 – 7.31 (m, 5H), 4.63 – 4.56 (m, 1H), 3.73 – 3.72 (m, 3H), 3.51 – 3.44 (m, 1H), 3.33 – 3.30 (m, 0.5×1H), 3.18 – 3.05 (m, 1.5×1H), 2.33 – 2.26 (m, 0.5×1H), 2.20 – 2.13 (m, 0.5×1H), 2.02 – 1.94 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.44, 196.39, 174.89, 139.34, 139.15, 138.63, 132.66, 129.13, 129.10, 128.86, 128.73, 128.55, 127.13, 126.86, 117.96, 116.70, 64.60, 64.18, 52.35, 41.01, 40.54, 38.55, 37.95, 37.81. IR (cm⁻¹): 3031, 2952, 2230, 2100, 1732, 1693, 1606, 1493, 1437, 1403, 1216,

1169, 1108, 955, 828, 738, 720, 569. HRMS: calcd. for $C_{20}H_{19}N_4O_3Na^+$ $[M+Na]^+$: 385.1271; Found: 385.1274.

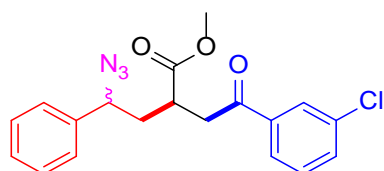
(5i) methyl 4-(5-azido-3-(methoxycarbonyl)-5-phenylpentanoyl)benzoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), methyl 4-formylbenzoate (**2i**), methyl acrylate (**3a**), with TBHP and $TMSN_3$, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as colorless oil (27.7 mg, 35%).

1H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 2H), 7.99 – 7.96 (m, 2H), 7.40 – 7.32 (m, 5H), 4.63 – 4.57 (m, 1H), 3.94 (s, 3H), 3.72 – 3.71 (m, 3H), 3.54 – 3.45 (m, 1H), 3.34 – 3.27 (m, 0.4×1H), 3.22 – 3.04 (m, 1.6×1H), 2.34 – 2.26 (m, 0.6×1H), 2.20 – 2.13 (m, 0.4×1H), 2.03 – 1.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.14, 197.09, 175.02, 166.19, 139.55, 139.19, 138.67, 134.14, 129.92, 129.05, 129.02, 128.76, 128.62, 128.01, 127.12, 126.84, 64.55, 64.21, 52.56, 52.23, 41.08, 40.66, 38.55, 37.96, 37.82, 37.76. IR (cm^{-1}): 3031, 2952, 2100, 1727, 1690, 1503, 1436, 1407, 1281, 1109, 995, 956, 839, 801, 701, 560, 528. HRMS: calcd. for $C_{21}H_{21}N_3O_5Na^+$ $[M+Na]^+$: 418.1373; Found: 418.1374.

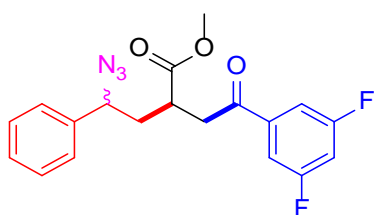
(5j) methyl 4-azido-2-(2-(3-chlorophenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 3-chlorobenzaldehyde (**2j**), methyl acrylate (**3a**), with TBHP and $TMSN_3$, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3) as colorless oil (39.3 mg, 53%).

1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.89 (m, 1H), 7.82 – 7.79 (m, 1H), 7.56 – 7.53 (m, 1H), 7.43 – 7.31 (m, 6H), 4.62 – 4.56 (m, 1H), 3.72 – 3.71 (m, 3H), 3.46 – 3.39 (m, 1H), 3.31 – 3.26 (m, 0.3×1H), 3.16 – 3.03 (m, 1.7×1H), 2.33 – 2.25 (m, 0.7×1H), 2.19 – 2.12 (m, 0.3×1H), 2.01 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.37, 196.33, 175.01, 139.26, 138.74, 138.01, 135.11, 133.39, 130.11, 129.11, 129.08, 128.82, 128.68, 128.29, 128.27, 127.18, 126.91, 126.20, 64.64, 64.29, 52.25, 40.87, 40.46, 38.59, 38.00, 37.88, 37.83. IR (cm^{-1}): 3065, 3031, 2951, 2099, 1732, 1692, 1572, 1436, 1214, 1169, 998, 787, 763, 701, 682, 526. HRMS: calcd. for $C_{19}H_{18}ClN_3O_3Na^+$ $[M+Na]^+$: 394.0929; Found: 394.0929.

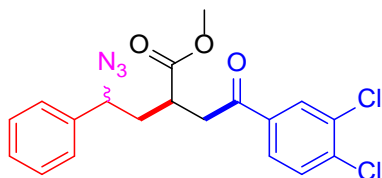
(5k) methyl-4-azido-2-(2-(3,5-difluorophenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 3,5-difluorobenzaldehyde (**2k**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3) as colorless oil (43.3 mg, 58%).

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.31 (m, 7H), 7.04 – 7.00 (m, 1H), 4.62 – 4.56 (m, 1H), 3.72 – 3.71 (m, 3H), 3.44 – 3.37 (m, 1H), 3.32 – 3.27 (m, 0.4×1H), 3.12 – 3.01 (m, 1.6×1H), 2.32 – 2.25 (m, 0.6×1H), 2.19 – 2.12 (m, 0.4×1H), 2.01 – 1.92 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 195.19, 195.15, 174.85, 174.84, 163.18 (d, *J* = 249.7 Hz), 163.06 (d, *J* = 249.6 Hz), 139.18, 138.66, 139.29 (t, *J* = 7.5 Hz), 129.12, 129.09, 128.84, 128.70, 127.15, 126.87, 111.12 (d, *J* = 11.6 Hz), 111.11 (d, *J* = 25.9 Hz), 108.75 (t, *J* = 25.2 Hz), 64.59, 64.20, 52.29, 40.89, 40.43, 38.52, 37.94, 37.80, 37.79. ¹⁹F NMR (376 MHz, CDCl₃) δ (-107.77, -107.78). IR (cm⁻¹): 3067, 3035, 2953, 2470, 2092, 1734, 1685, 1598, 1509, 1439, 1415, 1100, 992, 843, 744, 705, 600, 555. HRMS: calcd. for C₁₉H₁₇F₂N₃O₃Na⁺ [M+ Na]⁺: 396.1130; Found: 396.1150.

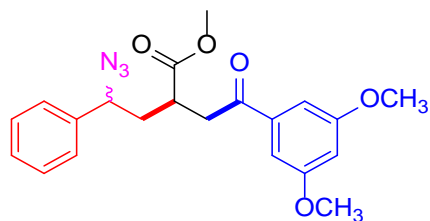
(5l) methyl-4-azido-2-(2-(3,4-dichlorophenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 3,4-dichlorobenzaldehyde (**2l**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.3) as colorless oil (46.1 mg, 54%).

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.99 (m, 1H), 7.76 – 7.73 (m, 1H), 7.55 – 7.53 (m, 1H), 7.43 – 7.31 (m, 5H), 4.62 – 4.56 (m, 1H), 3.72 – 3.71 (m, 3H), 3.44 – 3.37 (m, 1H), 3.32 – 3.25 (m, 0.4×1H), 3.13 – 3.02 (m, 1.6×1H), 2.32 – 2.25 (m, 0.6×1H), 2.19 – 2.12 (m, 0.4×1H), 2.01 – 1.92 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 195.47, 195.43, 174.93, 139.19, 138.67, 138.08, 135.96, 133.47, 130.90, 130.18, 130.16, 129.12, 129.09, 128.84, 128.71, 127.16, 126.89, 64.60, 64.22, 52.31, 40.74, 40.30, 38.55, 37.97, 37.84, 37.80. IR (cm⁻¹): 3068, 3036, 2958, 2095, 1736, 1697, 1572, 1439, 1214, 1175, 998, 785, 767, 705, 687, 528. HRMS: calcd. for C₁₉H₁₇Cl₂N₃O₃Na⁺ [M+ Na]⁺: 428.0539; Found: 428.0559.

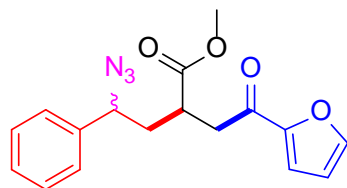
(5m) methyl-4-azido-2-(2-(3,5-dimethoxyphenyl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 3,5-dimethoxybenzaldehyde (**2m**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:10, R_f = 0.4) as colorless oil (50.0 mg, 63%).

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.31 (m, 5H), 7.07 – 7.05 (m, 2H), 6.65 (s, 1H), 4.61 – 4.55 (m, 1H), 3.82 – 3.81 (m, 6H), 3.72 – 3.71 (m, 3H), 3.44 – 3.37 (m, 1H), 3.29 – 3.25 (m, 0.4×1H), 3.16 – 3.01 (m, 1.6×1H), 2.32 – 2.24 (m, 0.6×1H), 2.19 – 2.11 (m, 0.4×1H), 2.00 – 1.92 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.27, 197.23, 175.21, 160.99, 139.34, 138.81, 138.37, 129.09, 129.05, 128.78, 128.63, 127.20, 126.92, 105.93, 105.76, 64.65, 64.36, 55.72, 52.22, 40.96, 40.58, 38.65, 38.02, 37.91. IR (cm⁻¹): 2955, 2846, 2099, 1732, 1679, 1605, 1576, 1428, 1368, 1162, 826, 755, 708, 615, 557, 524. HRMS: calcd. for C₂₁H₂₃N₃O₅Na⁺ [M+ Na]⁺:420.1530; Found:420.1547.

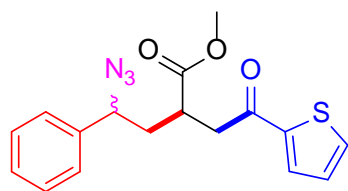
(5n) methyl-4-azido-2-(2-(furan-2-yl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), furan-2-carbaldehyde (**2n**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:25, R_f = 0.3) as brown oil (26.2 mg, 40%).

¹H NMR (400 MHz, CDCl₃) δ 7.58 (s, 1H), 7.40 – 7.31 (m, 5H), 7.20 – 7.19 (m, 1H), 6.54 – 6.53 (m, 1H), 4.60 – 4.55 (m, 1H), 3.71 – 3.70 (m, 3H), 3.34 – 3.22 (m, 1.5×1H), 3.08 – 2.99 (m, 1.5×1H), 2.31 – 2.23 (m, 0.5×1H), 2.18 – 2.11 (m, 0.5×1H), 2.01 – 1.91 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 186.64, 174.96, 152.39, 146.60, 139.23, 138.72, 129.06, 129.02, 128.75, 128.61, 127.16, 126.90, 117.35, 112.47, 64.51, 64.27, 52.22, 40.39, 40.00, 38.51, 37.95, 37.61, 37.52. IR (cm⁻¹): 3134, 3031, 2952, 2100, 1733, 1677, 1569, 1469, 1396, 1234, 1165, 1018, 883, 763, 702, 595. HRMS: calcd. for C₁₇H₁₇N₃O₄Na⁺ [M+ Na]⁺: 350.1111; Found: 350.1111.

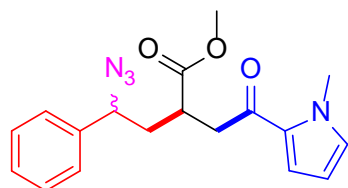
(5o) methyl-4-azido-2-(2-oxo-2-(thiophen-2-yl)ethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), thiophene-2-carbaldehyde (**2o**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:25, R_f = 0.3) as brown oil (33.0 mg, 48%).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.70 (m, 1H), 7.64 – 7.63 (m, 1H), 7.41 – 7.31 (m, 5H), 7.13 – 7.11 (m, 1H), 4.61 – 4.55 (m, 1H), 3.71 – 3.70 (m, 3H), 3.40 – 3.33 (m, 1H), 3.31 – 3.24 (m, 0.4×1H), 3.14 – 3.02 (m, 1.6×1H), 2.32 – 2.25 (m, 0.6×1H), 2.19 – 2.12 (m, 0.4×1H), 2.02 – 1.94 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 190.34, 174.96, 143.62, 139.26, 138.73, 134.02, 132.19, 129.06, 129.02, 128.76, 128.61, 128.25, 127.16, 126.91, 64.58, 64.34, 52.20, 41.29, 40.93, 38.54, 38.08, 37.96, 37.94. IR (cm⁻¹): 3030, 2951, 2099, 1732, 1662, 1558, 1416, 1355, 1224, 1168, 1058, 857, 728, 702, 581, 559. HRMS: calcd. for C₁₇H₁₇N₃O₃SNa⁺ [M+ Na]⁺: 366.0883; Found: 366.0883.

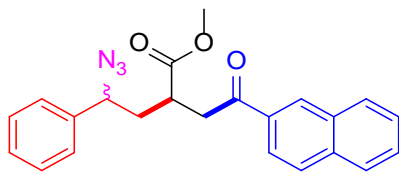
(5p) methyl-4-azido-2-(2-(1-methyl-1H-pyrrol-2-yl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 1-methyl-1H-pyrrole-2-carbaldehyde (**2p**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as sepia oil (24.5 mg, 36%).

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.31 (m, 5H), 6.95 – 6.93 (m, 1H), 6.80 – 6.79 (m, 1H), 6.12 – 6.10 (m, 1H), 4.60 – 4.53 (m, 1H), 3.90 – 3.88 (m, 3H), 3.71 – 3.70 (m, 3H), 3.28 – 3.20 (m, 1.4×1H), 3.04 – 2.95 (m, 1.6×1H), 2.31 – 2.23 (m, 0.6×1H), 2.15 – 2.09 (m, 0.4×1H), 1.97 – 1.88 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 187.85, 187.81, 175.43, 139.40, 138.86, 131.31, 130.22, 130.21, 129.00, 128.95, 128.67, 128.51, 127.15, 126.88, 119.28, 108.18, 64.61, 64.38, 52.11, 40.96, 40.63, 38.63, 38.17, 38.07, 38.01, 37.75, 37.73. IR (cm⁻¹): 3109, 3062, 3030, 2951, 2099, 1731, 1651, 1527, 1409, 1316, 1243, 1064, 957, 743, 702, 607, 559, 528. HRMS: calcd. for C₁₈H₂₀N₄O₃Na⁺ [M+ Na]⁺: 363.1428; Found: 363.1427.

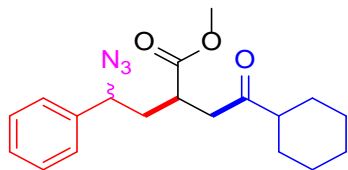
(5q) methyl-4-azido-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 2-naphthaldehyde (**2q**), methyl acrylate (**3a**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:25, R_f = 0.3) as colorless oil (52.6 mg, 68%).

^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 8.00 – 7.92 (m, 2H), 7.87 – 7.84 (m, 2H), 7.60 – 7.51 (m, 2H), 7.41 – 7.31 (m, 5H), 4.65 – 4.59 (m, 1H), 3.73 – 3.71 (m, 3H), 3.61 – 3.55 (m, 1H), 3.38 – 3.22 (m, 1.5 \times 1H), 3.15 – 3.08 (m, 0.5 \times 1H), 2.36 – 2.29 (m, 0.5 \times 1H), 2.23 – 2.16 (m, 0.5 \times 1H), 2.07 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.44, 197.40, 175.27, 139.29, 138.77, 135.72, 133.73, 132.47, 129.87, 129.63, 129.04, 129.00, 128.72, 128.68, 128.58, 127.85, 127.16, 126.93, 126.89, 123.71, 123.68, 64.61, 64.33, 52.19, 40.83, 40.48, 38.64, 38.06, 38.03, 37.92. IR (cm^{-1}): 3060, 3031, 2950, 2098, 1732, 1681, 1627, 1436, 1360, 1168, 1124, 1027, 942, 822, 749, 701, 477. HRMS: calcd. for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_3\text{Na}^+$ [$\text{M} + \text{Na}$] $^+$: 410.1475; Found: 410.1475.

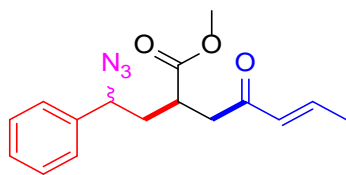
(5r) methyl-4-azido-2-(2-cyclohexyl-2-oxoethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), cyclohexanecarbaldehyde (**2r**), methyl acrylate (**3a**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:40, R_f = 0.4) as colorless oil (37.1 mg, 54%).

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.29 (m, 5H), 4.55 – 4.48 (m, 1H), 3.69 – 3.68 (m, 3H), 3.11 – 3.06 (m, 0.4 \times 1H), 2.91 – 2.87 (m, 1.6 \times 1H), 2.64 – 2.58 (m, 1H), 2.35 – 2.27 (m, 1H), 2.21 – 2.14 (m, 0.6 \times 1H), 2.08 – 2.01 (m, 0.4 \times 1H), 1.89 – 1.76 (m, 5H), 1.33 – 1.17 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 211.51, 211.46, 175.24, 139.36, 138.83, 129.07, 129.03, 128.75, 128.60, 127.17, 126.89, 64.64, 64.37, 52.12, 50.82, 50.78, 42.59, 42.19, 38.58, 37.96, 37.62, 37.54, 28.49, 25.91, 25.69. IR (cm^{-1}): 2925, 2847, 2097, 1738, 1448, 1686, 1597, 1448, 1240, 816, 756, 691. HRMS: calcd. for $\text{C}_{19}\text{H}_{25}\text{N}_3\text{O}_3\text{Na}^+$ [$\text{M} + \text{Na}$] $^+$: 366.1969; Found: 366.1787.

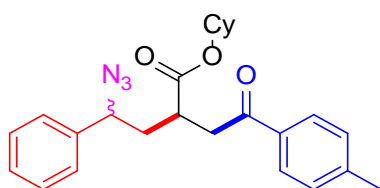
(5r) methyl (E)-2-(2-azido-2-phenylethyl)-4-oxohept-5-enoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), (E)-but-2-enal (**2r**), methyl acrylate (**3a**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:40, R_f = 0.4) as colorless oil (28.4 mg, 44%).

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.29 (m, 5H), 6.91 – 6.81 (m, 1H), 6.13 – 6.07 (m, 1H), 4.56 – 4.50 (m, 1H), 3.70 – 3.69 (m, 3H), 3.17 – 3.11 (m, 0.5×1H), 3.03 – 2.97 (m, 1H), 2.94 – 2.88 (m, 0.5×1H), 2.76 – 2.67 (m, 1H), 2.24 – 2.17 (m, 0.5×1H), 2.11 – 2.04 (m, 0.5×1H), 1.93 – 1.84 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 197.33, 197.31, 175.20, 143.59, 139.29, 138.76, 129.01, 128.97, 128.69, 128.55, 127.13, 126.86, 64.52, 64.28, 52.12, 38.51, 37.93, 37.71, 37.61, 18.41. IR (cm⁻¹): 2925, 2848, 2098, 1732, 1688, 1630, 1448, 1335, 1266, 1210, 1035, 1008, 893, 756, 688. HRMS: calcd. for C₁₆H₁₉N₃O₃Na⁺ [M+ Na]⁺: 324.1319; Found: 324.1331.

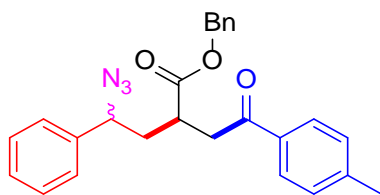
(6b) cyclohexyl-4-azido-2-[2-oxo-2-(p-tolyl)ethyl]-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methylbenzaldehyde (**2a**), cyclohexyl acrylate (**3b**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (53.5 mg, 64%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.41 – 7.30 (m, 5H), 7.26 – 7.23 (m, 2H), 4.85 – 4.77 (m, 1H), 4.66 – 4.57 (m, 1H), 3.43 – 3.36 (m, 1H), 3.30 – 3.23 (m, 0.3×1H), 3.14 – 3.04 (m, 1H), 3.00 – 2.93 (m, 0.7×1H), 2.40 (s, 3H), 2.32 – 2.24 (m, 0.7×1H), 2.16 – 2.09 (m, 0.3×1H), 1.99 – 1.92 (m, 1H), 1.87 – 1.84 (m, 2H), 1.72 – 1.70 (m, 2H), 1.54 – 1.51 (m, 1H), 1.48 – 1.31 (m, 4H), 1.29 – 1.21 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 197.19, 197.17, 174.14, 144.15, 139.65, 138.82, 134.12, 129.34, 128.99, 128.96, 128.65, 128.46, 128.19, 128.17, 127.20, 126.76, 73.20, 64.66, 64.34, 40.73, 40.45, 38.98, 38.31, 38.19, 38.02, 31.69, 31.60, 31.53, 31.51, 25.39, 23.79, 23.75, 21.71. IR (cm⁻¹): 3086, 3031, 2937, 2859, 2098, 1724, 1683, 1607, 1453, 1222, 1179, 1015, 811, 701, 559. HRMS: calcd. for C₂₅H₂₉N₃O₃Na⁺ [M+ Na]⁺: 442.2101; Found: 442.2100.

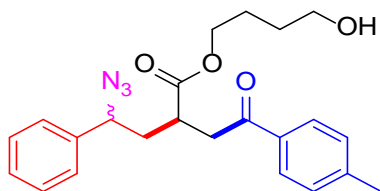
(6c) benzyl-4-azido-2-[2-oxo-2-(p-tolyl)ethyl]-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methylbenzaldehyde (**2a**), benzyl acrylate (**3c**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (51.2 mg, 60%).

^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.80 (m, 2H), 7.37 – 7.30 (m, 8H), 7.25 – 7.18 (m, 4H), 5.23 – 5.10 (m, 2H), 4.53 – 4.46 (m, 1H), 3.45 – 3.30 (m, 1.4×1H), 3.16 – 3.03 (m, 1.6×1H), 2.40 (s, 3H), 2.32 – 2.24 (m, 0.6×1H), 2.16 – 2.09 (m, 0.4×1H), 2.00 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.10, 174.66, 174.64, 144.32, 144.30, 129.42, 129.02, 128.97, 128.71, 128.68, 128.61, 128.53, 128.49, 128.42, 128.41, 128.26, 128.24, 127.22, 126.83, 66.83, 66.78, 64.41, 64.28, 40.71, 40.37, 38.94, 38.14, 37.97, 21.78. IR (cm^{-1}): 3063, 3032, 2952, 2922, 2098, 1731, 1682, 1607, 1495, 1455, 1252, 1162, 1002, 809, 751, 699. HRMS: calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_3\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 450.1788; Found: 450.1785.

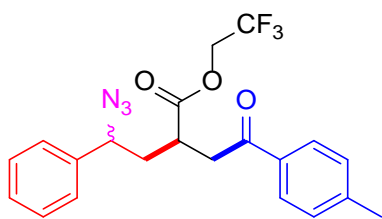
(6d) 4-hydroxybutyl-4-azido-2-[2-oxo-2-(p-tolyl)ethyl]-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methylbenzaldehyde (**2a**), 4-hydroxybutyl acrylate (**3d**), with TBHP and TMSN_3 , and purified by flash column chromatography (ethyl ether/petroleum ether = 1:10, R_f = 0.3) as colorless oil (42.5 mg, 52%).

^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.80 (m, 2H), 7.41 – 7.31 (m, 5H), 7.26 – 7.23 (m, 2H), 4.63 – 4.56 (m, 1H), 4.21 – 4.15 (m, 1H), 4.13 – 4.07 (m, 1H), 3.66 – 3.63 (m, 2H), 3.45 – 3.38 (m, 1H), 3.29 – 3.23 (m, 0.5×1H), 3.17 – 3.07 (m, 1H), 3.05 – 2.98 (m, 0.5×1H), 2.40 (s, 3H), 2.32 – 2.25 (m, 0.5×1H), 2.18 – 2.11 (m, 0.5×1H), 2.00 – 1.92 (m, 2H), 1.76 – 1.70 (m, 2H), 1.65 – 1.57 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.35, 197.33, 174.85, 144.36, 139.34, 138.76, 133.92, 129.39, 129.02, 128.98, 128.70, 128.55, 128.20, 128.18, 127.14, 126.82, 64.82, 64.59, 64.29, 62.23, 40.73, 40.34, 38.71, 38.12, 38.01, 37.98, 29.13, 25.07, 25.05, 21.72. IR (cm^{-1}): 3440, 3060, 3032, 2947, 2480, 2096, 1731, 1681, 1606, 1493, 1039, 810, 737, 701, 560. HRMS: calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_3\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 432.1894; Found: 432.1896.

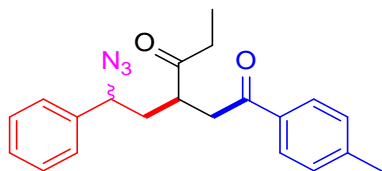
(6e) 2,2,2-trifluoroethyl-4-azido-2-(2-oxo-2-(p-tolyl)ethyl)-4-phenylbutanoate



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methylbenzaldehyde (**2a**), 2,2,2-trifluoroethyl acrylate (**3e**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:30, R_f = 0.4) as colorless oil (52.9 mg, 63%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.80 (m, 2H), 7.42 – 7.30 (m, 5H), 7.26 – 7.24 (m, 2H), 4.65 – 4.53 (m, 2H), 4.49 – 4.38 (m, 1H), 3.48 – 3.40 (m, 1H), 3.37 – 3.34 (m, 0.4×1H), 3.25 – 3.15 (m, 1H), 3.12 – 3.08 (m, 0.6×1H), 2.40 (s, 3H), 2.33 – 2.26 (m, 0.6×1H), 2.18 – 2.11 (m, 0.4×1H), 2.03 – 1.95 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.73, 196.69, 173.37, 173.30, 144.56, 139.12, 138.46, 133.70, 129.46, 129.12, 129.07, 128.85, 128.68, 128.21, 128.18, 127.14, 126.81, 123.06 (d, *J* = 275.5 Hz), 64.34, 64.11, 60.62 (q, *J* = 36.3 Hz), 60.52 (q, *J* = 36.3 Hz), 40.59, 40.23, 38.59, 37.81, 37.73, 37.59, 21.73. ¹⁹F NMR (376 MHz, CDCl₃) δ (-73.49, -73.51). IR (cm⁻¹): 3059, 3032, 2955, 2923, 1734, 1686, 1635, 1602, 1573, 1450, 1334, 809, 758, 710, 556. HRMS: calcd. for C₂₁H₂₀F₃N₃O₃Na⁺ [M+ Na]⁺: 442.1349; Found: 442.1355.

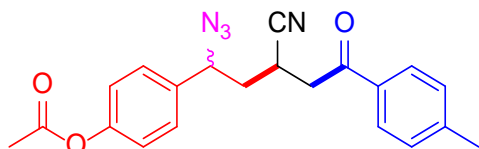
(6f) 3-(2-azido-2-phenylethyl)-1-(p-tolyl)hexane-1,4-dione



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**), 4-methylbenzaldehyde (**2a**), pent-1-en-3-one (**3f**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.4) as colorless oil (31.4 mg, 45%).

¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.80 (m, 2H), 7.42 – 7.29 (m, 5H), 7.26 – 7.23 (m, 2H), 4.53 – 4.44 (m, 1H), 3.48 – 3.40 (m, 1H), 3.33 – 3.28 (m, 1H), 3.10 – 3.03 (m, 1H), 2.80 – 2.70 (m, 1H), 2.65 – 2.51 (m, 1H), 2.40 (s, 3H), 2.20 – 2.04 (m, 1H), 1.95 – 1.89 (m, 0.4×1H), 1.81 – 1.76 (m, 0.6×1H), 1.09 – 1.04 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 213.70, 213.42, 197.79, 197.68, 144.35, 139.03, 138.94, 134.02, 133.96, 129.43, 129.16, 129.14, 128.82, 128.77, 128.25, 127.00, 126.96, 64.49, 64.43, 43.70, 43.38, 41.13, 40.59, 38.32, 37.88, 36.34, 35.98, 21.79, 7.80, 7.76. IR (cm⁻¹): 3059, 3038, 2923, 2098, 1766, 1681, 1651, 1606, 1368, 1201, 1123, 813, 773, 702, 559. HRMS: calcd. for C₂₁H₂₃N₃O₂Na⁺ [M+ Na]⁺: 372.1682; Found: 372.1685.

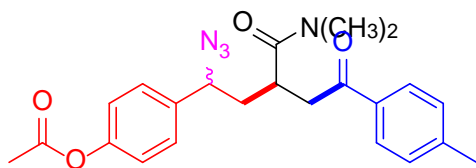
(6g) 4-[1-azido-3-cyano-5-oxo-5-(p-tolyl)pentyl]phenyl acetate



The title compound was prepared according to the general procedure described above by the reaction between 4-vinylphenyl acetate (**1h**), 4-methylbenzaldehyde (**2a**), acrylonitrile (**3g**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:20, R_f = 0.3) as colorless oil (30.1 mg, 40%).

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.43 – 7.37 (m, 2H), 7.29 – 7.27 (m, 2H), 7.20 – 7.13 (m, 2H), 4.84 – 4.75 (m, 1H), 3.66 – 3.59 (m, 0.5×1H), 3.43 – 3.21 (m, 2H), 3.11 – 3.05 (m, 0.5×1H), 2.42 (s, 3H), 2.32 – 2.31 (m, 3H), 2.23 – 2.15 (m, 0.5×1H), 2.11 – 1.95 (m, 1.5×1H). ¹³C NMR (100 MHz, CDCl₃) δ 194.44, 194.38, 169.37, 169.27, 151.12, 150.88, 145.04, 145.01, 136.13, 134.93, 130.20, 129.58, 129.23, 128.32, 128.20, 128.18, 127.95, 122.47, 122.36, 121.07, 120.95, 63.34, 40.37, 38.88, 37.48, 24.21, 23.82, 21.77, 21.19, 21.16. IR (cm⁻¹): 3347, 3037, 2924, 2242, 2102, 1766, 1682, 1606, 1508, 1410, 1368, 1205, 1016, 912, 810, 737. HRMS: calcd. for C₂₁H₂₀N₄O₃Na⁺ [M+ Na]⁺: 399.1428; Found: 399.1432.

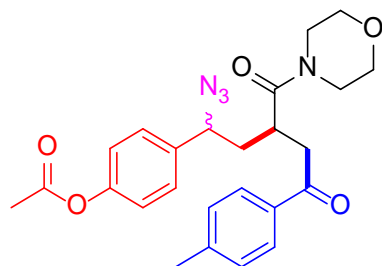
(6h) 4-[1-azido-3-(dimethylcarbamoyl)-5-oxo-5-(p-tolyl)pentyl]phenyl acetate



The title compound was prepared according to the general procedure described above by the reaction between 4-vinylphenyl acetate (**1h**), 4-methylbenzaldehyde (**2a**), *N,N*-dimethylacrylamide (**3h**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:4, R_f = 0.3) as colorless oil (52.3 mg, 62%).

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.81 (m, 2.30×1H), 7.35 – 7.33 (m, 2.30×1H), 7.28 – 7.23 (m, 2.30×1H), 7.15 – 7.10 (m, 2.30×1H), 4.53 (dd, *J* = 8.0, 6.8 Hz, 0.5×1H), 4.40 (dd, *J* = 10.0, 4.4 Hz, 0.65×1H), 3.66 – 3.61 (m, 0.65×1H), 3.55 – 3.41 (m, 1.65×1H), 3.22 (s, 1.95H), 3.12 – 3.11 (m, 0.34×1H), 3.07 – 3.04 (m, 0.50×1H), 3.01 – 3.00 (m, 0.31×1H), 3.01 – 3.00 (m, 3.45×1H), 2.92 (s, 1.50×1H), 2.32 – 2.31 (m, 3H), 2.40 (s, 3.45×1H), 2.31 – 2.30 (m, 3.45×1H), 2.24 – 2.17 (m, 0.50×1H), 2.15 – 2.08 (m, 0.65×1H), 1.96 – 1.89 (m, 1.15×1H). ¹³C NMR (100 MHz, CDCl₃) 198.09, 197.96, 174.59, 174.44, 169.34, 169.30, 150.81, 150.65, 144.24, 137.06, 136.41, 134.14, 134.06, 129.37, 128.26, 128.24, 128.18, 127.96, 122.23, 122.07, 63.96, 63.55, 42.34, 41.30, 39.99, 38.31, 37.65, 37.44, 36.01, 35.90, 33.74, 33.72, 21.73, 21.20. IR (cm⁻¹): 3053, 2927, 2100, 1766, 1681, 1607, 1506, 1401, 1367, 1015, 912, 813, 736, 702, 552. HRMS: calcd. for C₂₃H₂₆N₄O₄Na⁺ [M+ Na]⁺: 445.1846; Found: 445.1853.

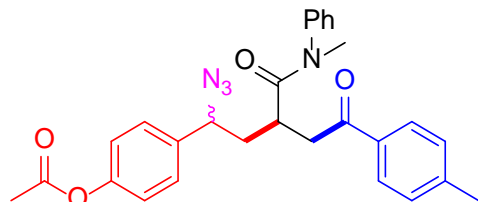
(6i) 4-[1-azido-3-(morpholine-4-carbonyl)-5-oxo-5-(p-tolyl)pentyl]phenyl acetate



The title compound was prepared according to the general procedure described above by the reaction between 4-vinylphenyl acetate (**1h**), 4-methylbenzaldehyde (**2a**), 1-morpholinoprop-2-en-1-one (**3i**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:4, R_f = 0.3) as colorless oil (59.4 mg, 64%).

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.81 (m, 2H), 7.35 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 7.15 – 7.10 (m, 2H), 4.53 (dd, *J* = 8.0, 6.4 Hz, 0.5×1H), 4.40 (dd, *J* = 10.4, 4.4 Hz, 0.5×1H), 3.85 – 3.78 (m, 1H), 3.72 – 3.53 (m, 8H), 3.42 – 3.31 (m, 1H), 3.11 – 2.98 (m, 1H), 2.40 (s, 3H), 2.31 – 2.30 (m, 3H), 2.25 – 2.17 (m, 0.5×1H), 2.16 – 2.09 (m, 0.5×1H), 1.96 – 1.89 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) 197.87, 197.74, 173.28, 173.14, 169.29, 169.25, 150.88, 150.72, 144.35, 136.85, 136.18, 134.05, 133.96, 129.39, 128.27, 128.25, 128.15, 127.92, 122.33, 122.15, 67.00, 66.92, 66.87, 66.71, 63.81, 63.49, 46.78, 46.31, 42.55, 42.41, 41.33, 40.09, 38.45, 33.28, 33.06, 21.72, 21.17. IR (cm⁻¹): 3054, 2966, 2922, 2858, 2100, 1766, 1681, 1634, 1507, 1441, 1115, 1031, 911, 735, 552. HRMS: calcd. for C₂₃H₂₆N₄O₄Na⁺ [M+ Na]⁺: 487.1952; Found: 487.1956.

(6j) 4-[1-azido-3-(methyl(phenyl)carbamoyl)-5-oxo-5-(p-tolyl)pentyl]phenyl acetate

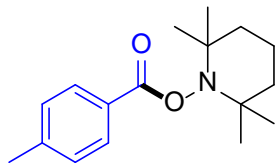


The title compound was prepared according to the general procedure described above by the reaction between 4-vinylphenyl acetate (**1h**), 4-methylbenzaldehyde (**2a**), *N*-methyl-*N*-phenylacrylamide (**3j**), with TBHP and TMSN₃, and purified by flash column chromatography (ethyl ether/petroleum ether = 1:8, R_f = 0.4) as colorless oil (46.5 mg, 48%).

¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.75 (m, 2H), 7.43 – 7.33 (m, 4H), 7.27 – 7.21 (m, 5H), 7.10 – 7.07 (m, 2H), 7.01 – 7.00 (m, 1H), 4.36 – 4.29 (m, 1H), 3.51 – 3.39 (m, 1H), 3.28 – 3.26 (s, 3H), 3.23 – 3.16 (m, 1H), 3.00 – 2.93 (m, 1H), 2.4 (s, 3H), 2.29 – 2.28 (m, 3H), 2.17 – 2.10 (m, 0.6×1H), 2.01 – 1.96 (m, 0.4×1H), 1.89 – 1.79 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) 197.66, 174.10, 169.26, 169.21, 150.64, 150.50, 144.02, 143.47, 143.38, 136.35, 136.27, 134.04, 129.83, 129.27, 128.19, 128.15, 128.11, 127.96, 127.80, 127.57, 127.52, 122.10, 122.00, 63.68, 63.21, 40.76, 40.64, 38.13, 37.80, 37.67, 37.36, 35.38, 35.27, 21.66, 21.15. IR (cm⁻¹): 3059, 3038, 2923,

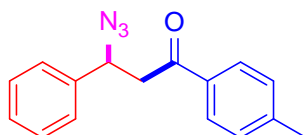
2098, 1766, 1681, 1651, 1507, 1495, 1392, 1368, 911, 773, 702, 559. HRMS: calcd. for $C_{28}H_{29}N_4O_4Na^+$ $[M+Na]^+$: 507.2003; Found: 507.2010.

(7) 2,2,6,6-tetramethylpiperidin-1-yl 4-methylbenzoate¹



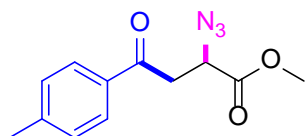
White solid. M.p. 54.0-55.0 °C, (ethyl ether/petroleum ether = 1:50, R_f = 0.6). 1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 1.81 – 1.67 (m, 3H), 1.60 – 1.57 (m, 2H), 1.48 – 1.48 (m, 1H), 1.27 (s, 6H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.50, 143.56, 129.63, 129.19, 126.90, 60.38, 39.05, 31.98, 21.69, 20.88, 17.04. IR (cm^{-1}): 2974, 2933, 1407, 1378, 1176, 1132, 954, 748, 688.

(8) 3-azido-3-phenyl-1-(p-tolyl)propan-1-one



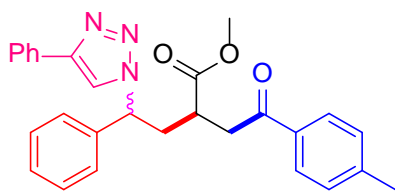
colorless oil, (ethyl ether/petroleum ether = 1:50, R_f = 0.4). 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.40 – 7.39 (m, 4H), 7.35 – 7.31 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 5.26 (d, J = 8.8, 4.8 Hz, 1H), 3.53 (dd, J = 17.2, 8.8 Hz, 1H), 3.22 (dd, J = 17.2, 4.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.23, 144.55, 139.46, 134.12, 129.49, 129.04, 128.53, 128.36, 126.94, 61.65, 45.20, 21.78. IR (cm^{-1}): 3059, 3036, 2098, 1686, 815, 754, 701, 551. HRMS: calcd. for $C_{16}H_{15}N_3ONa^+$ $[M+Na]^+$: 288.1107; Found: 288.1114.

(9) methyl 2-azido-4-oxo-4-(p-tolyl)butanoate



colorless oil, (ethyl ether/petroleum ether = 1:30, R_f = 0.4). 1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.63 (dd, J = 7.2, 5.6 Hz, 1H), 3.84 (s, 3H), 3.52 (dd, J = 18.0, 5.2 Hz, 1H), 3.22 (dd, J = 17.6, 7.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.36, 170.53, 144.92, 133.57, 129.58, 128.39, 58.08, 53.11, 40.06, 21.86. IR (cm^{-1}): 3059, 2098, 1738, 1688, 1636, 754, 701, 551. HRMS: calcd. for $C_{12}H_{13}N_3ONa^+$ $[M+Na]^+$: 270.0849; Found: 270.0862.

(10) methyl-4-oxo-2-(2-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-4-(p-tolyl)butanoate

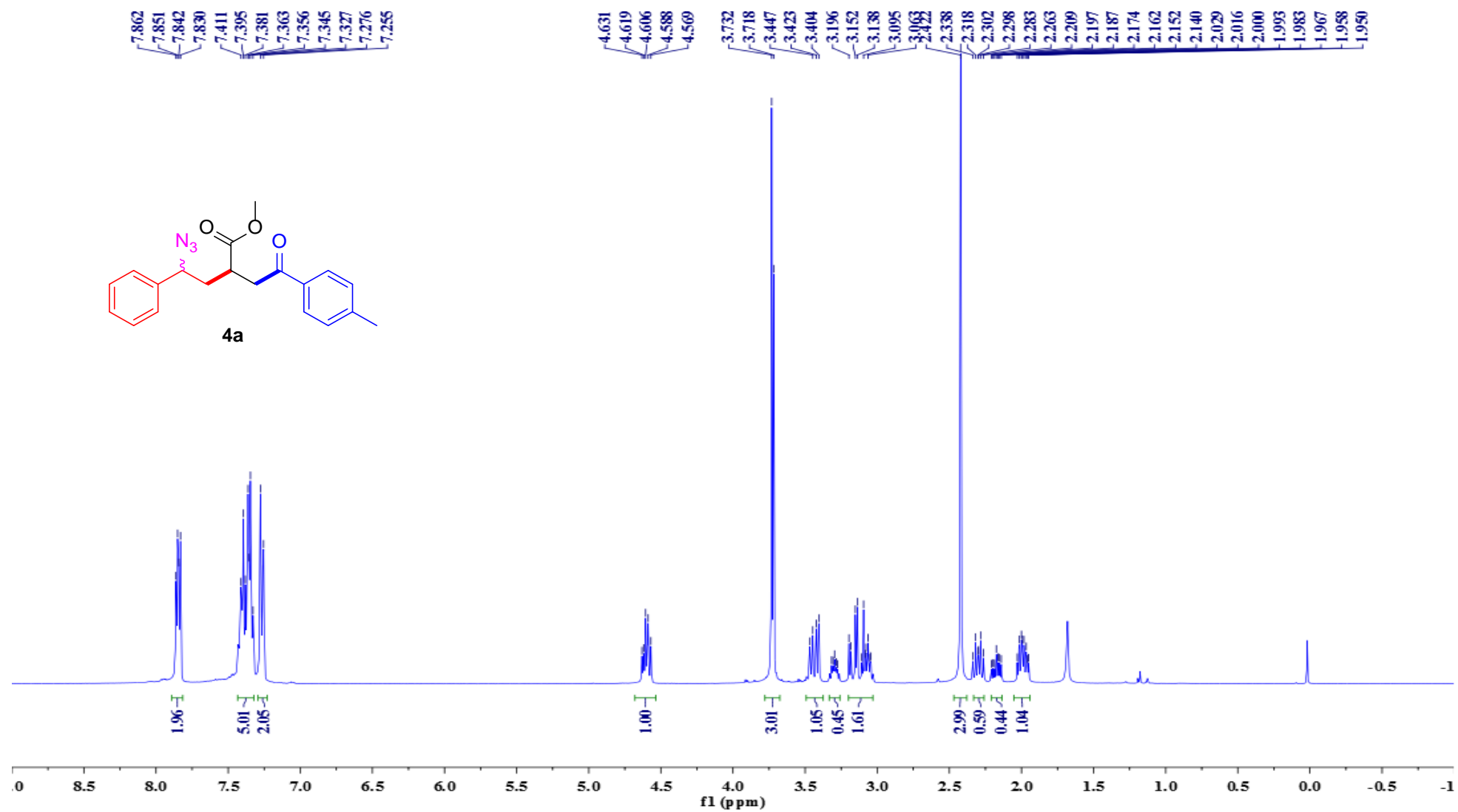


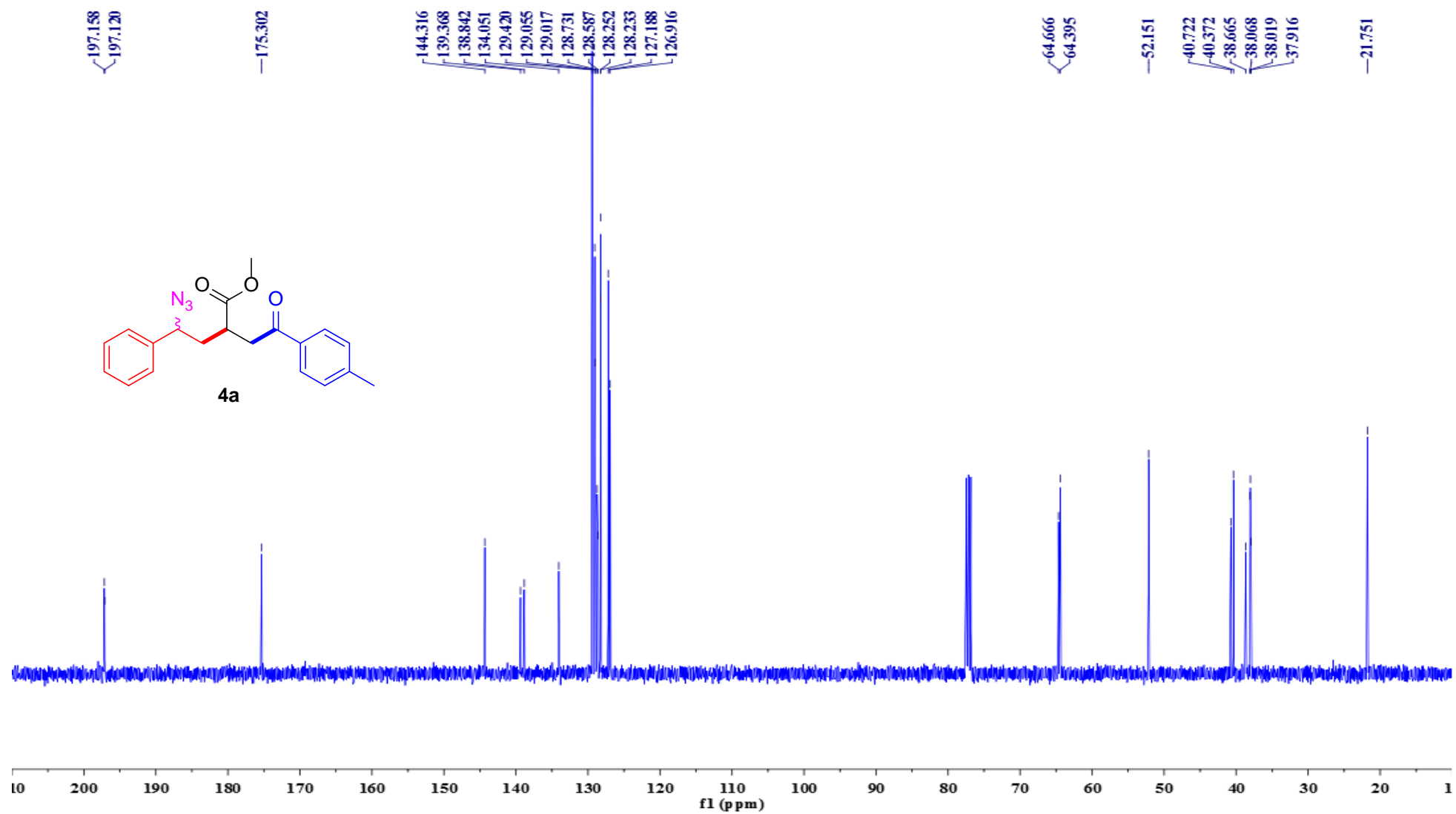
White solid. M.p. 60.0-61.0 °C (ethyl ether/petroleum ether = 1:15, $R_f = 0.3$). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 0.5×1H), 7.83 – 7.72 (m, 4H), 7.71 (s, 0.5×1H), 7.44 – 7.30 (m, 8H), 7.23 – 7.21 (m, 1H), 5.91 – 5.81 (m, 1H), 3.68 – 3.66 (m, 3H), 3.47 – 3.40 (m, 1H), 3.28 – 3.17 (m, 1H), 3.03 – 2.93 (m, 1.5×1H), 2.88 – 2.81 (m, 0.5×1H), 2.74 – 2.64 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.04, 197.01, 174.92, 174.77, 147.90, 144.42, 139.11, 138.15, 133.79, 133.75, 130.58, 130.53, 129.41, 129.24, 129.13, 129.00, 128.86, 128.84, 128.70, 128.20, 127.31, 126.68, 125.77, 125.75, 119.84, 119.09, 63.64, 63.29, 52.28, 52.25, 40.67, 40.14, 37.69, 37.59, 37.20, 36.60, 21.76. IR (cm^{-1}): 3134, 3084, 2953, 2924, 1732, 1681, 1606, 1507, 1455, 1362, 839, 809, 776, 697. HRMS: calcd. for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_3\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 476.1945; Found: 476.1945.

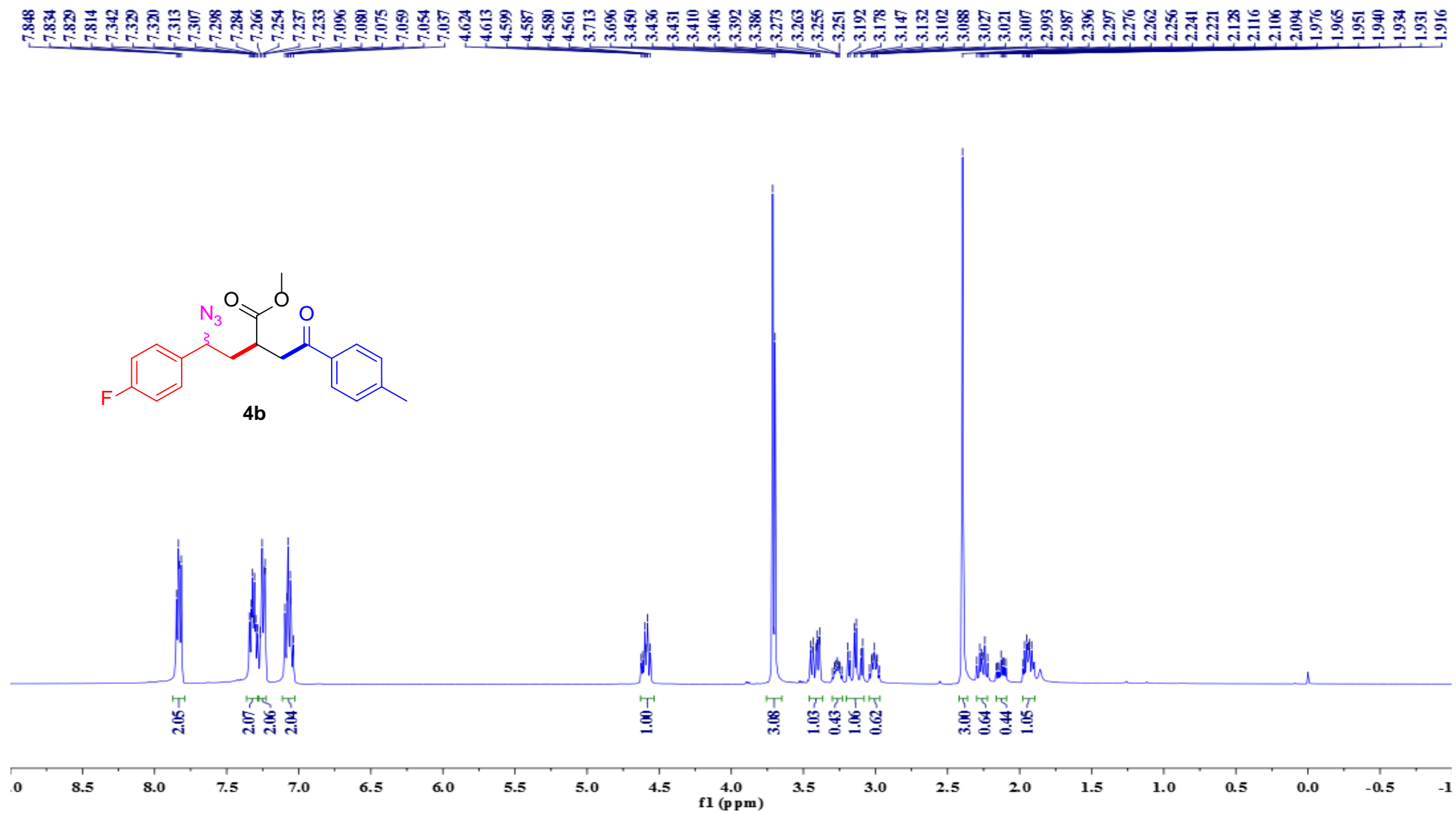
IX. References

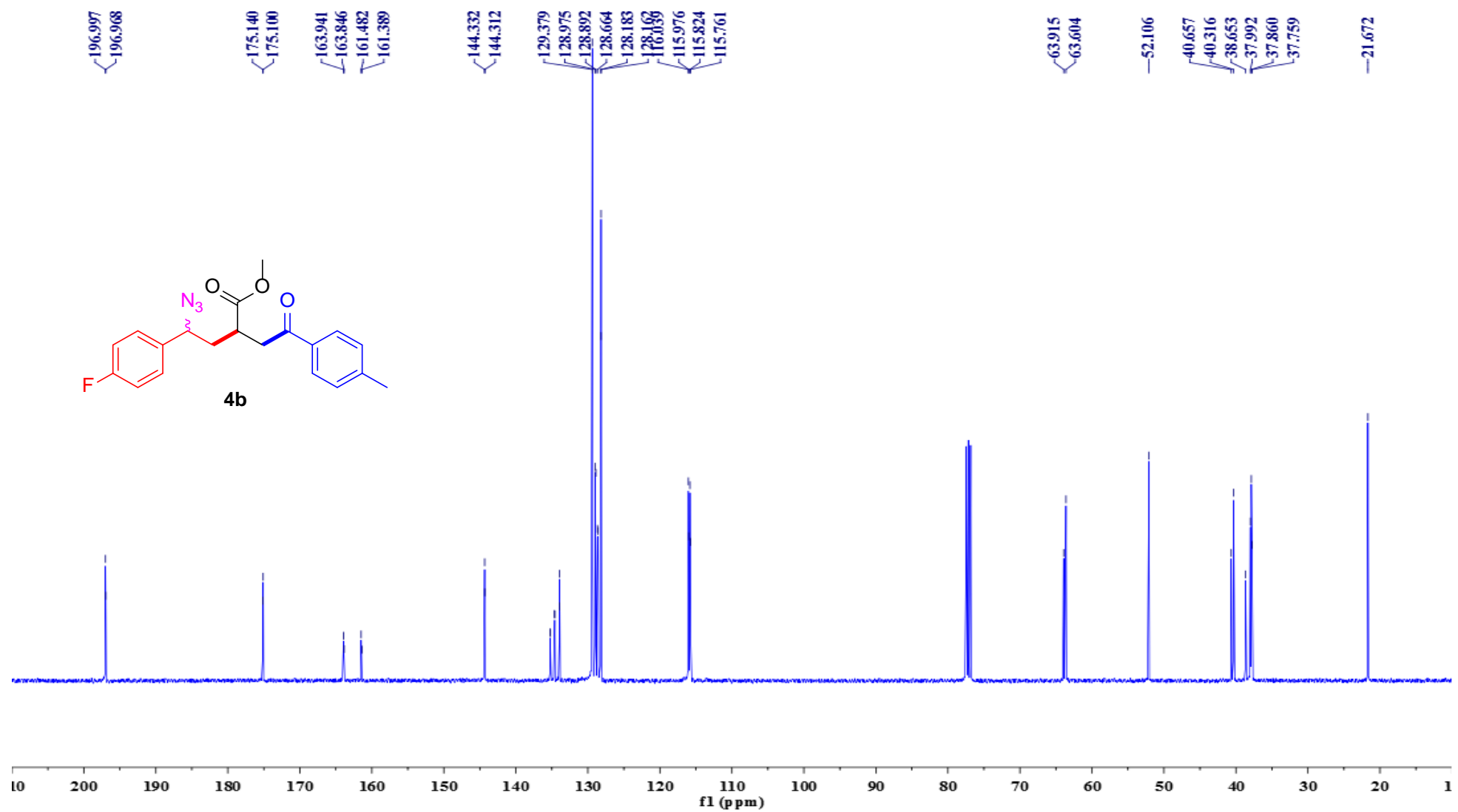
¹ M. Ociepa, O. Baka, J. Narodowiec and D. Gryko, *Adv. Synth. Catal.* 2017, **359**, 3560-3565.

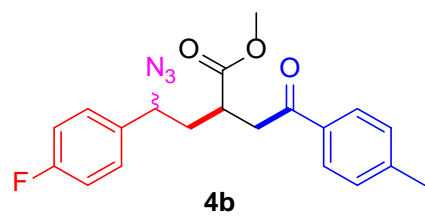
X. Copies of ^1H and ^{13}C NMR spectra of products 4a-4o, 5b-5s, 6b-6j, 7, 8, 9, 10.



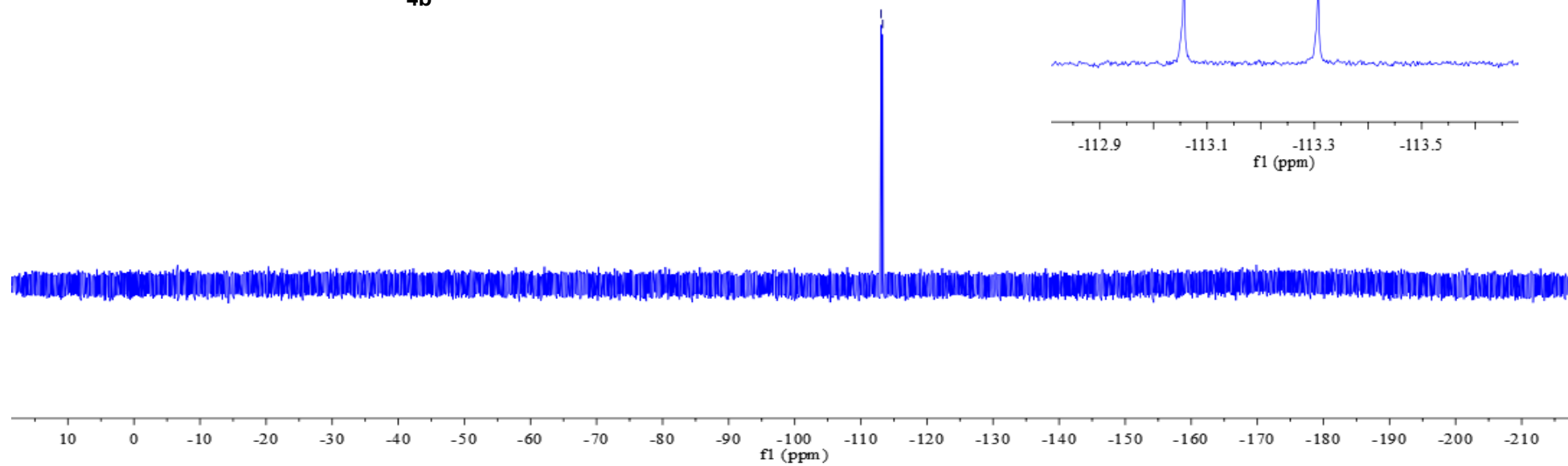
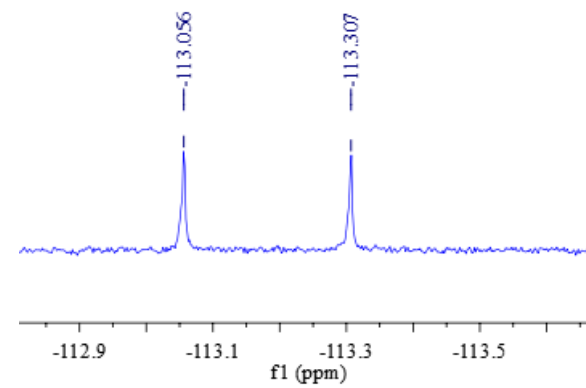


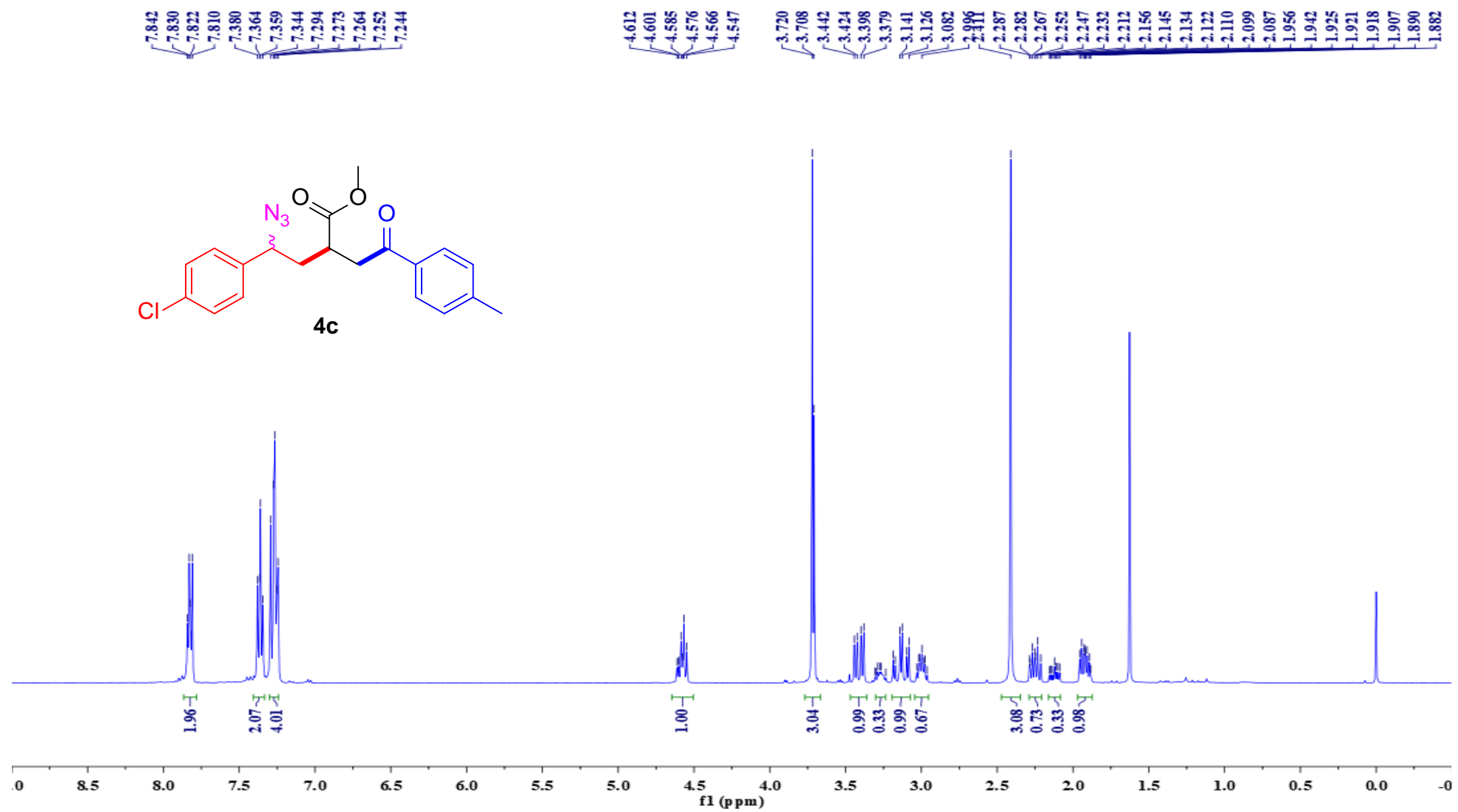


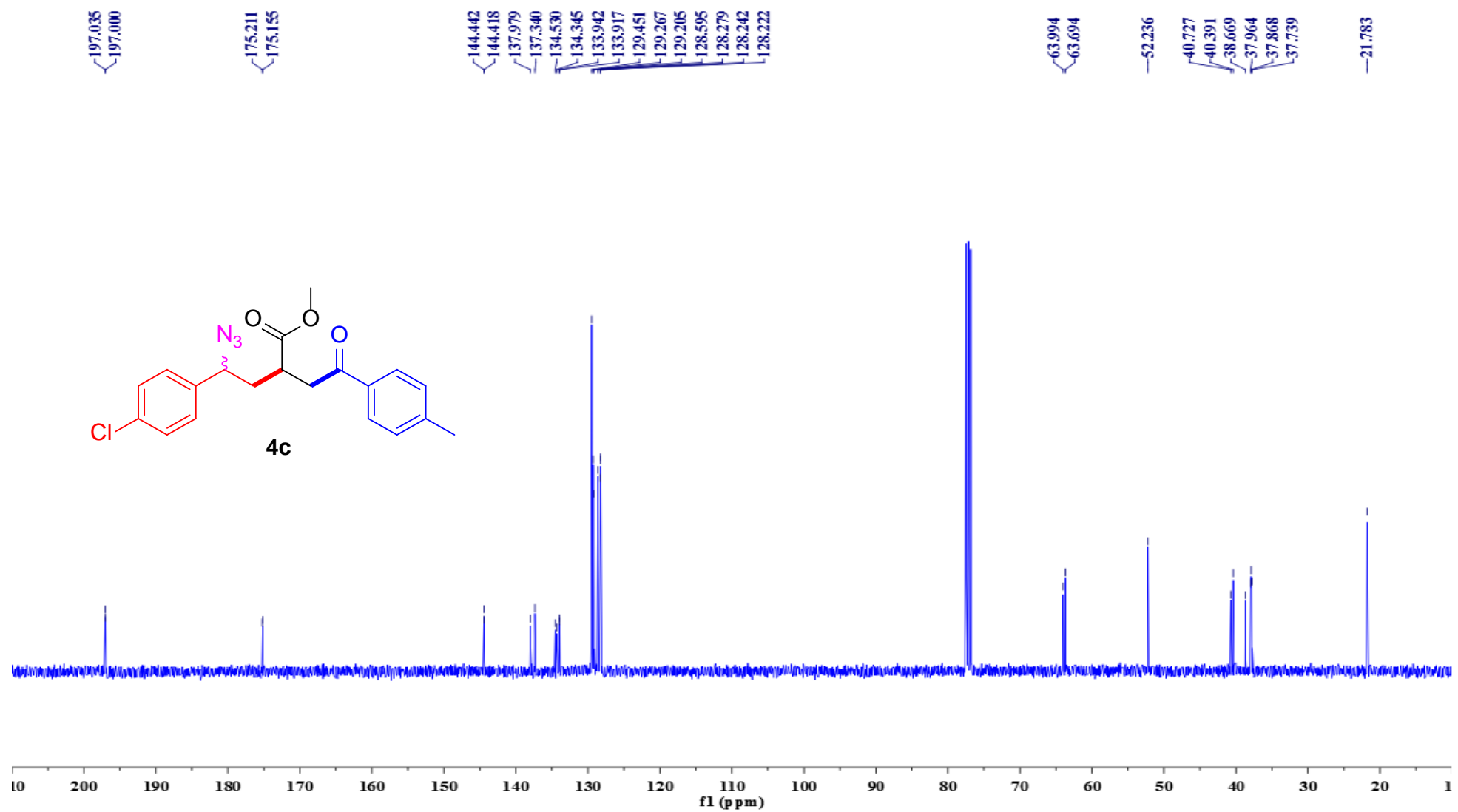


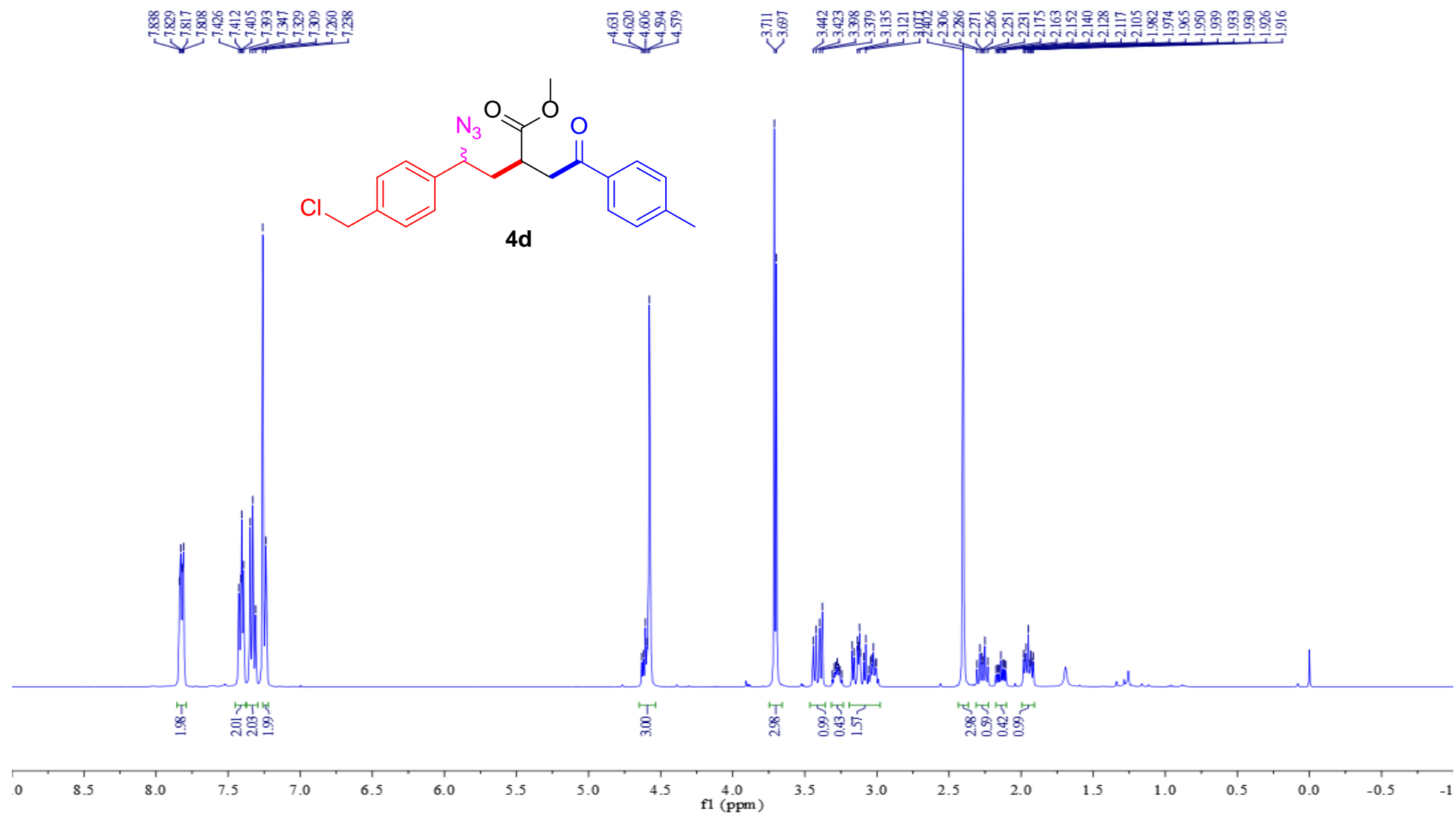


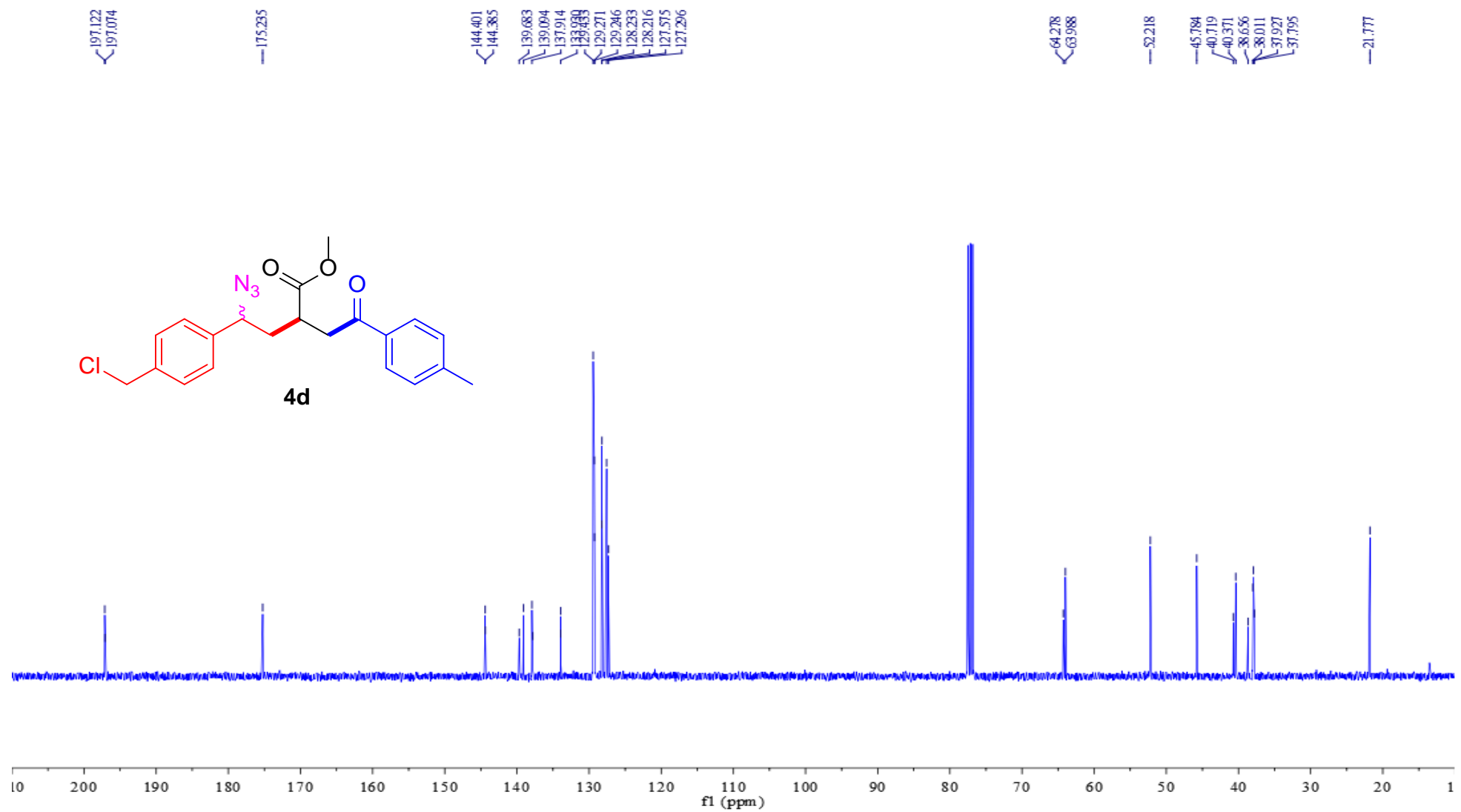
113.056
113.307

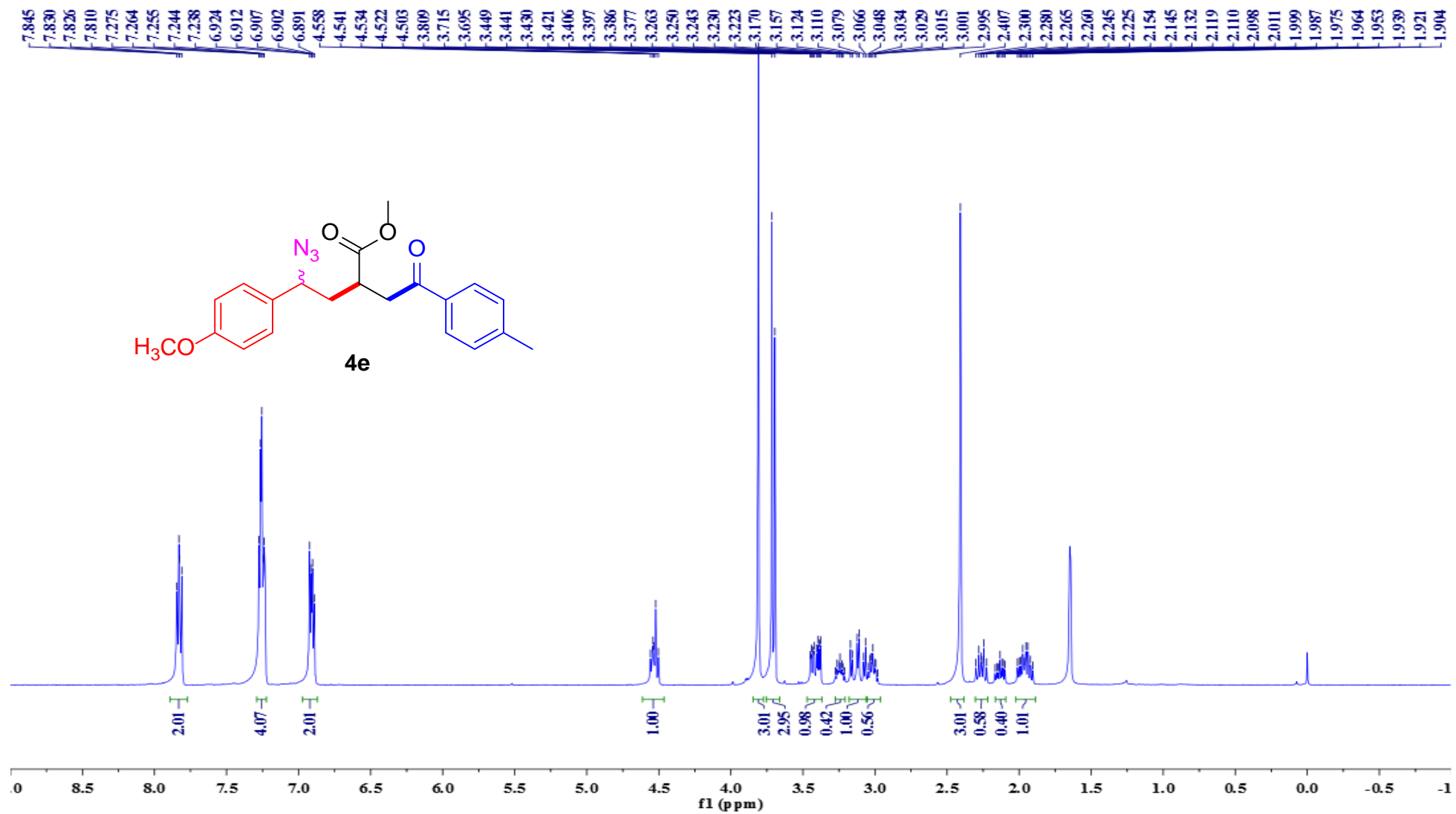


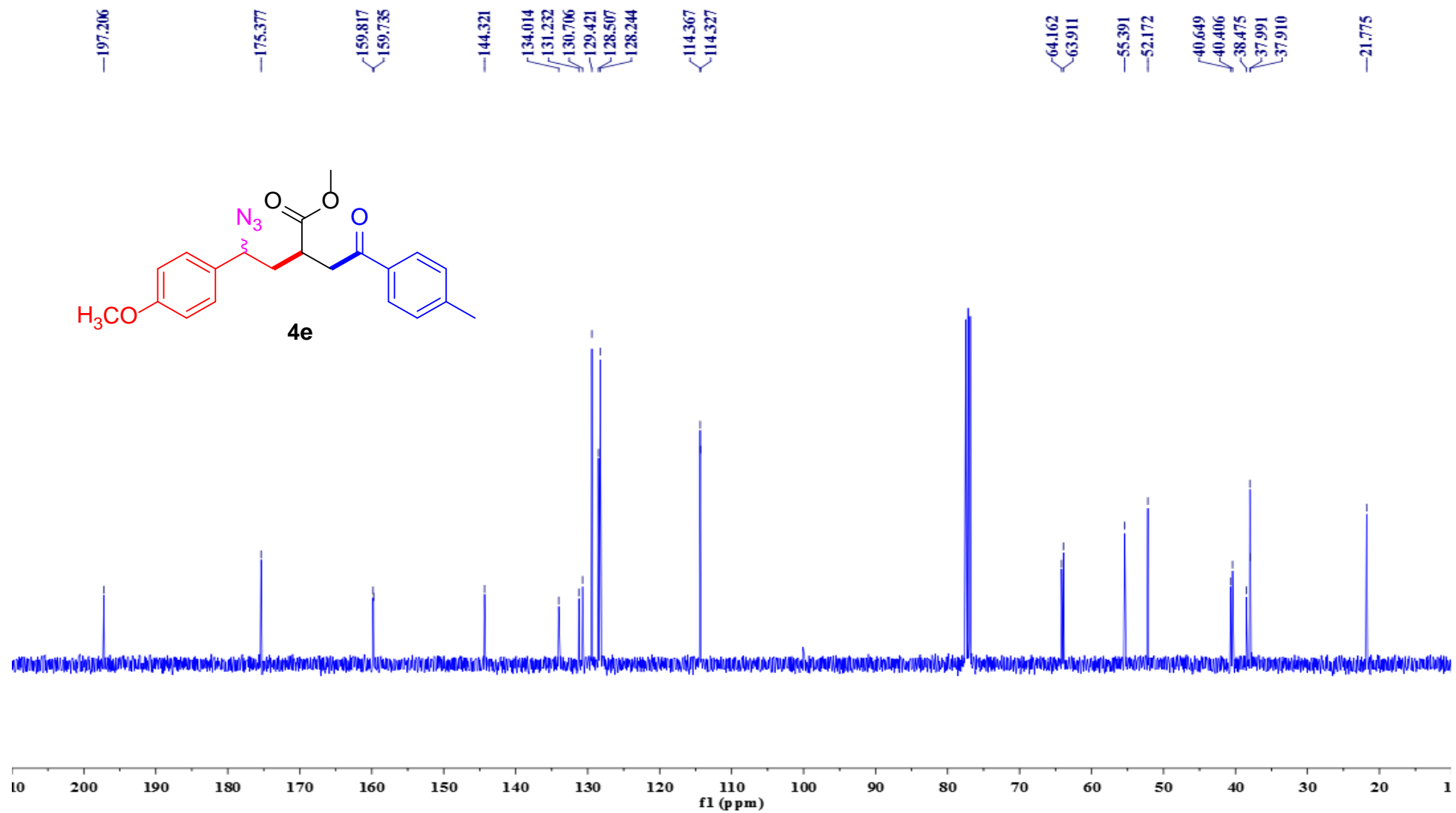


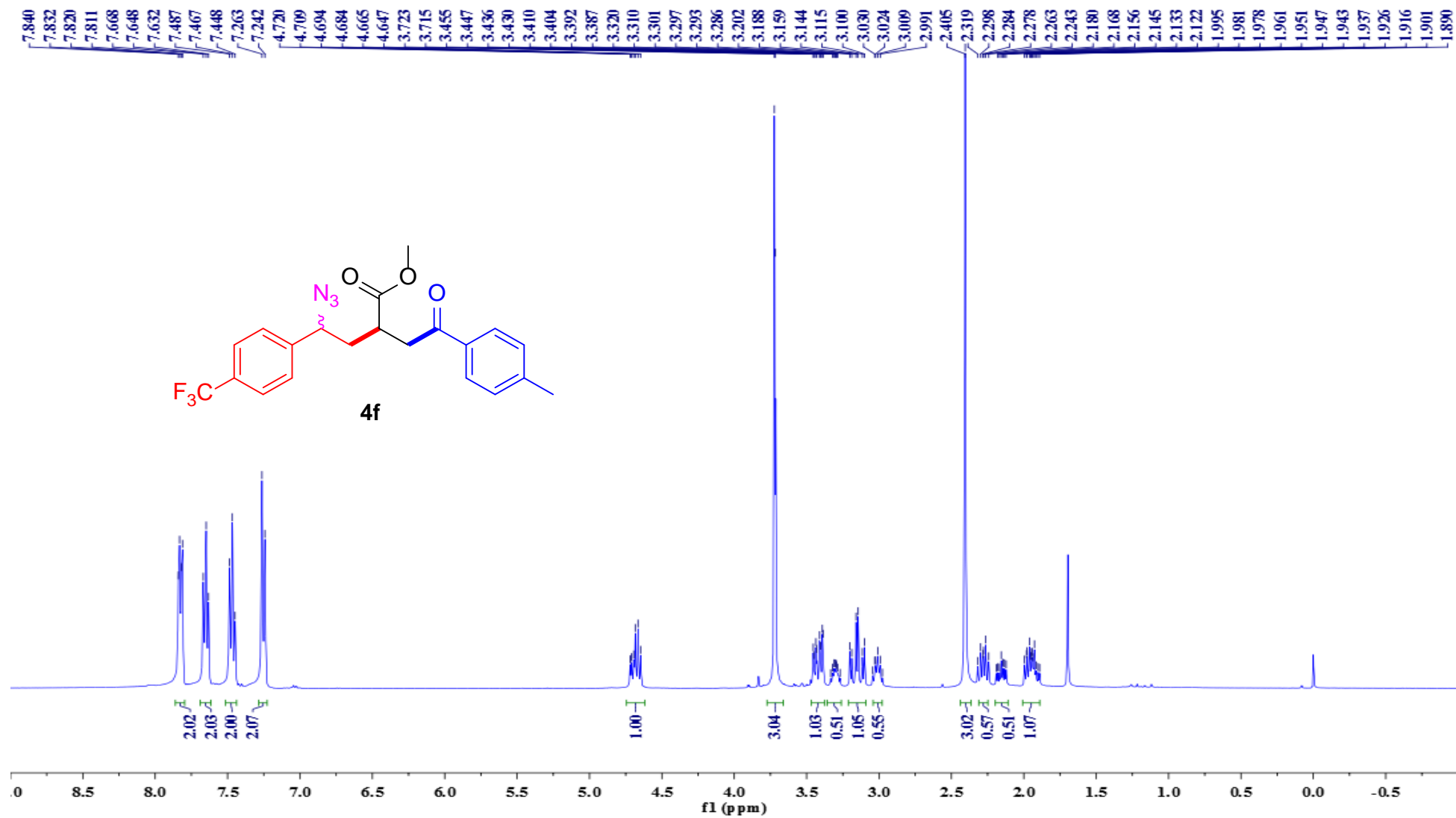


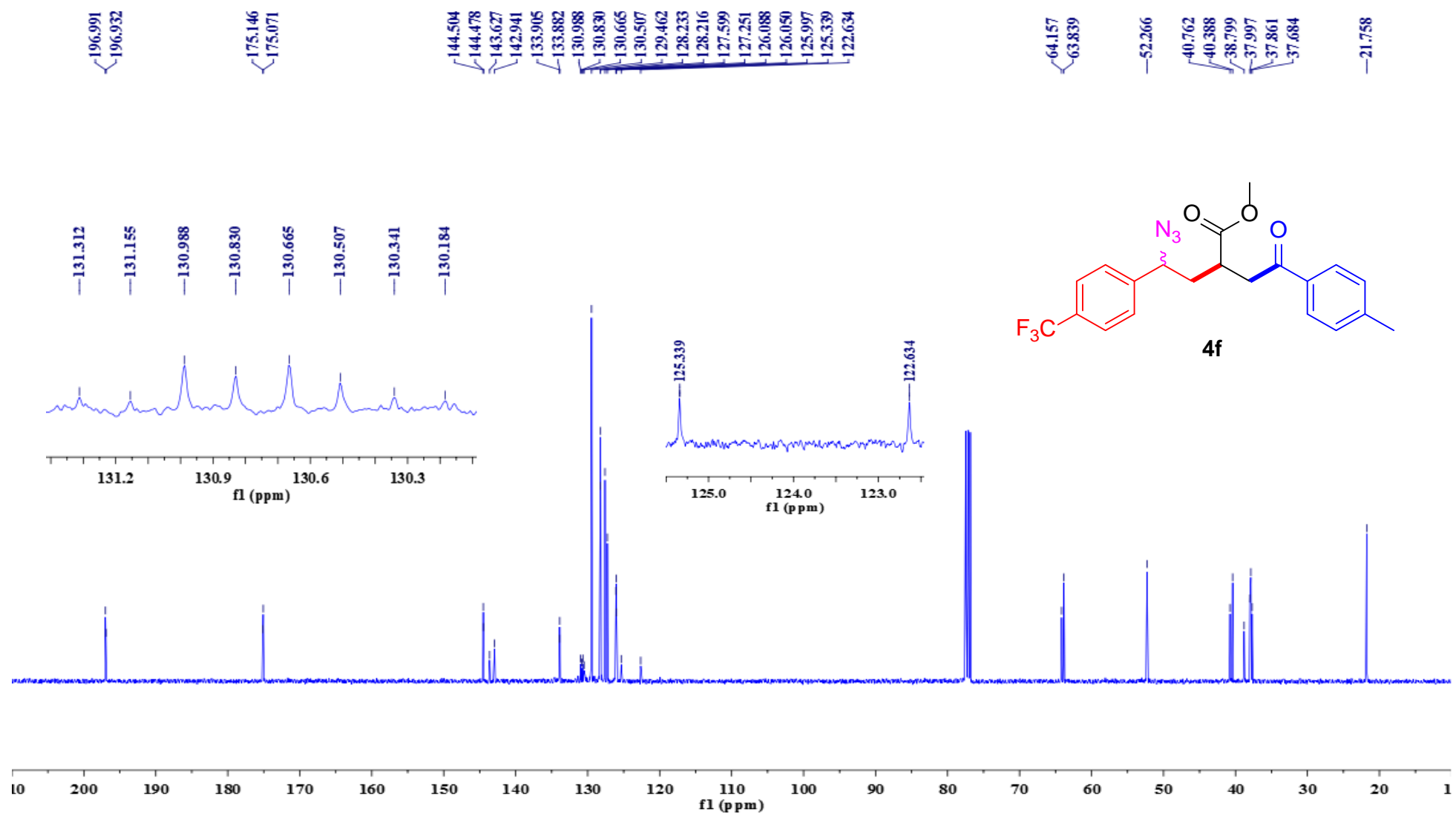


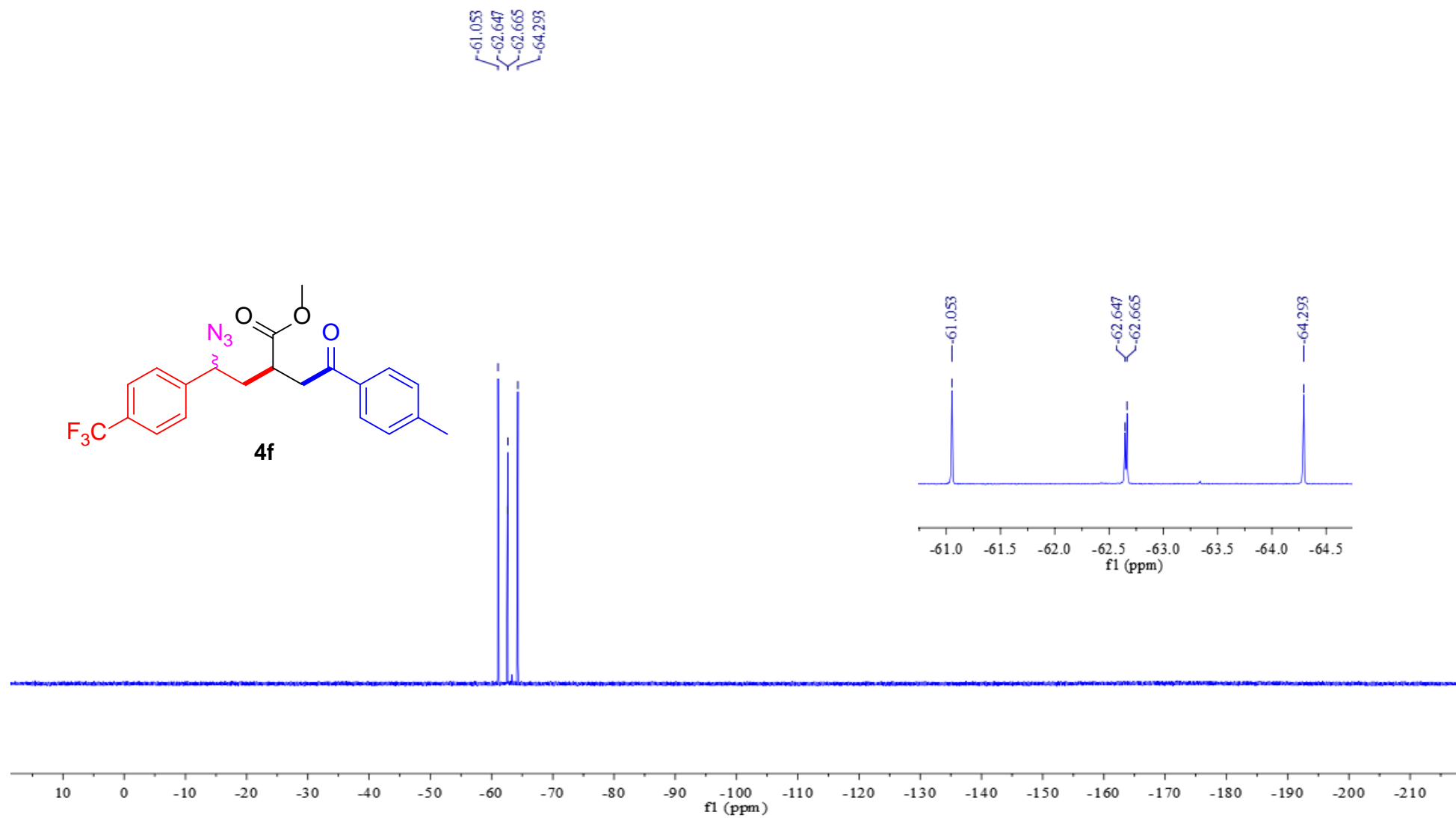


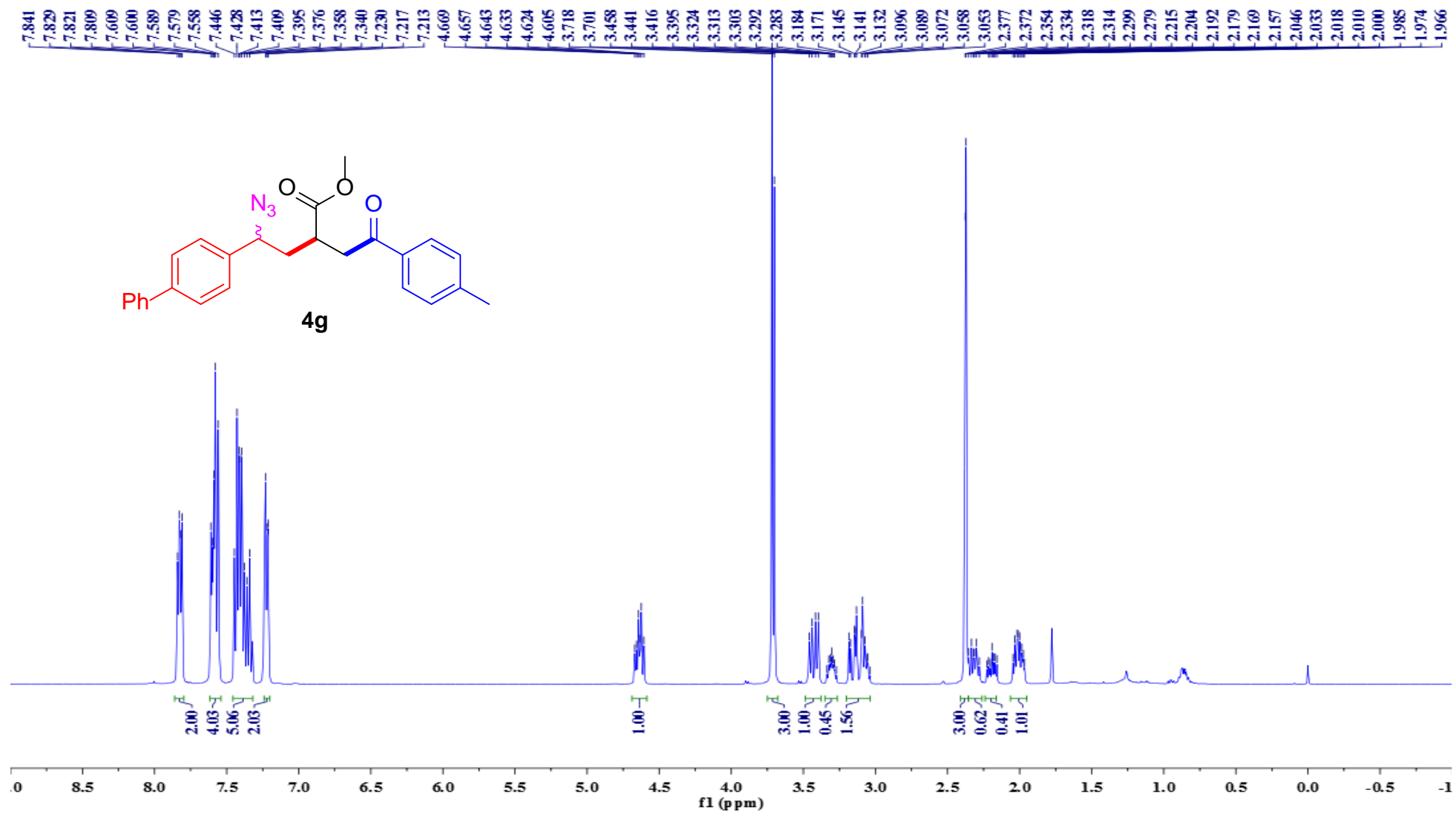


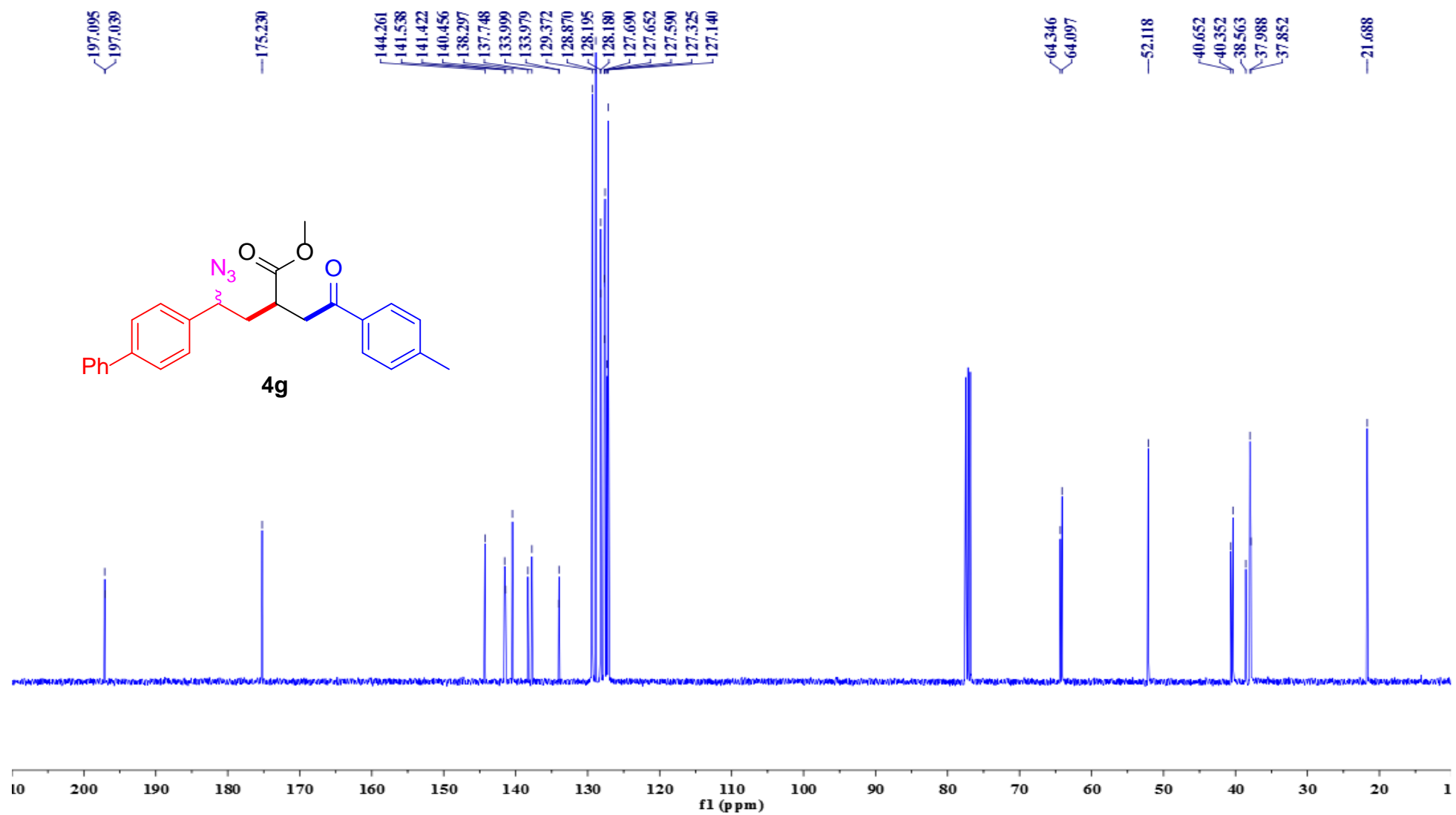


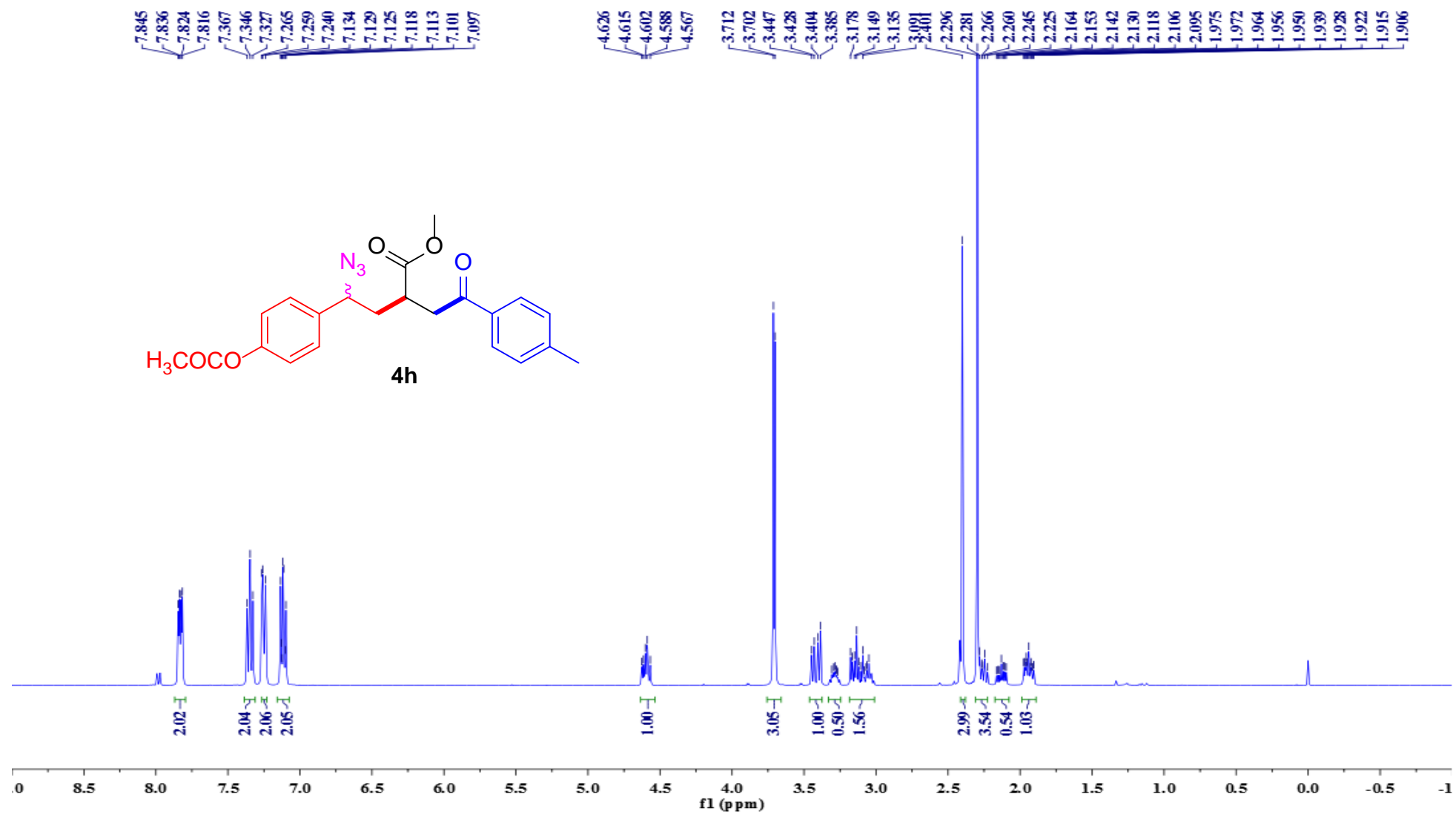


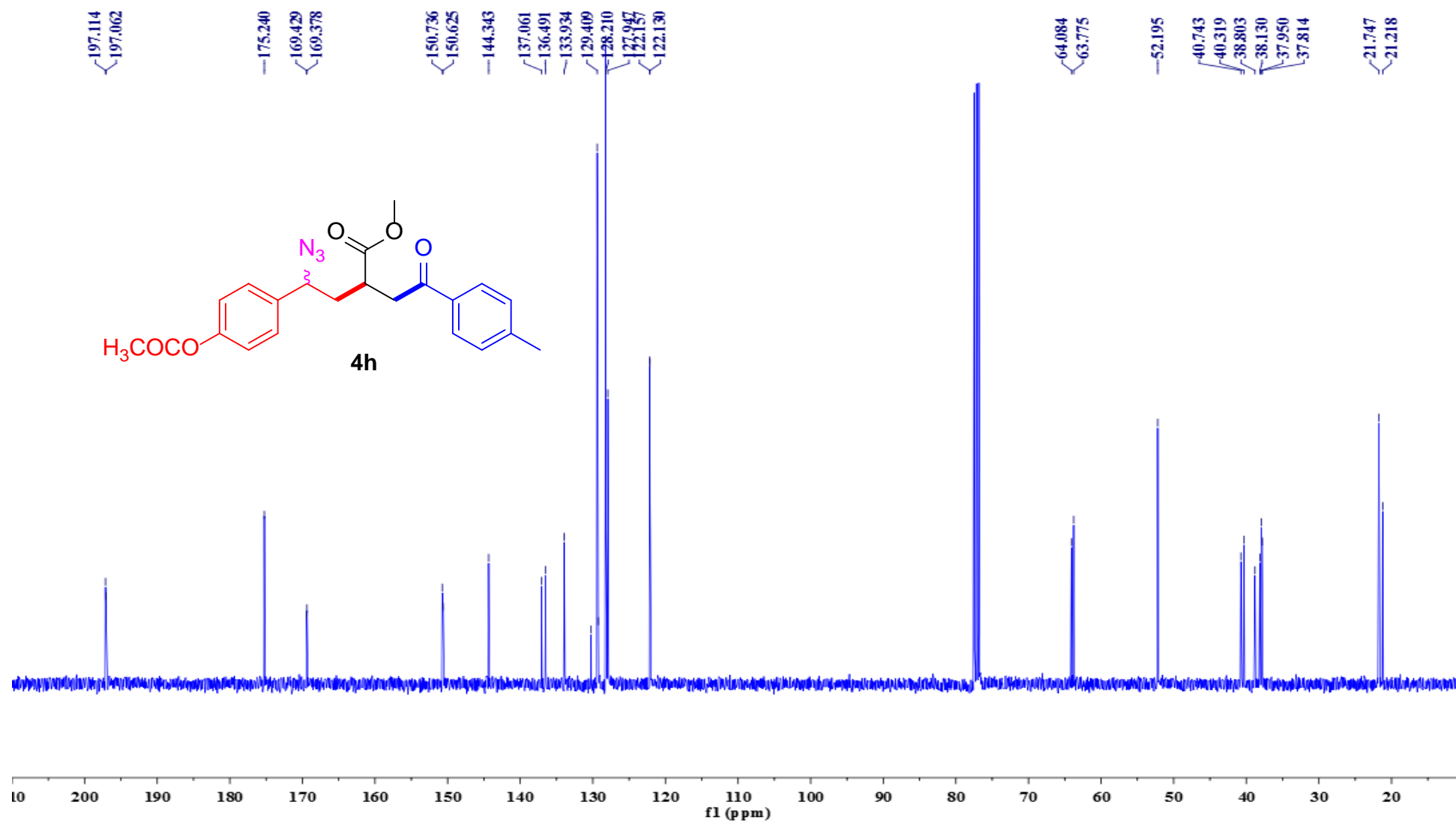


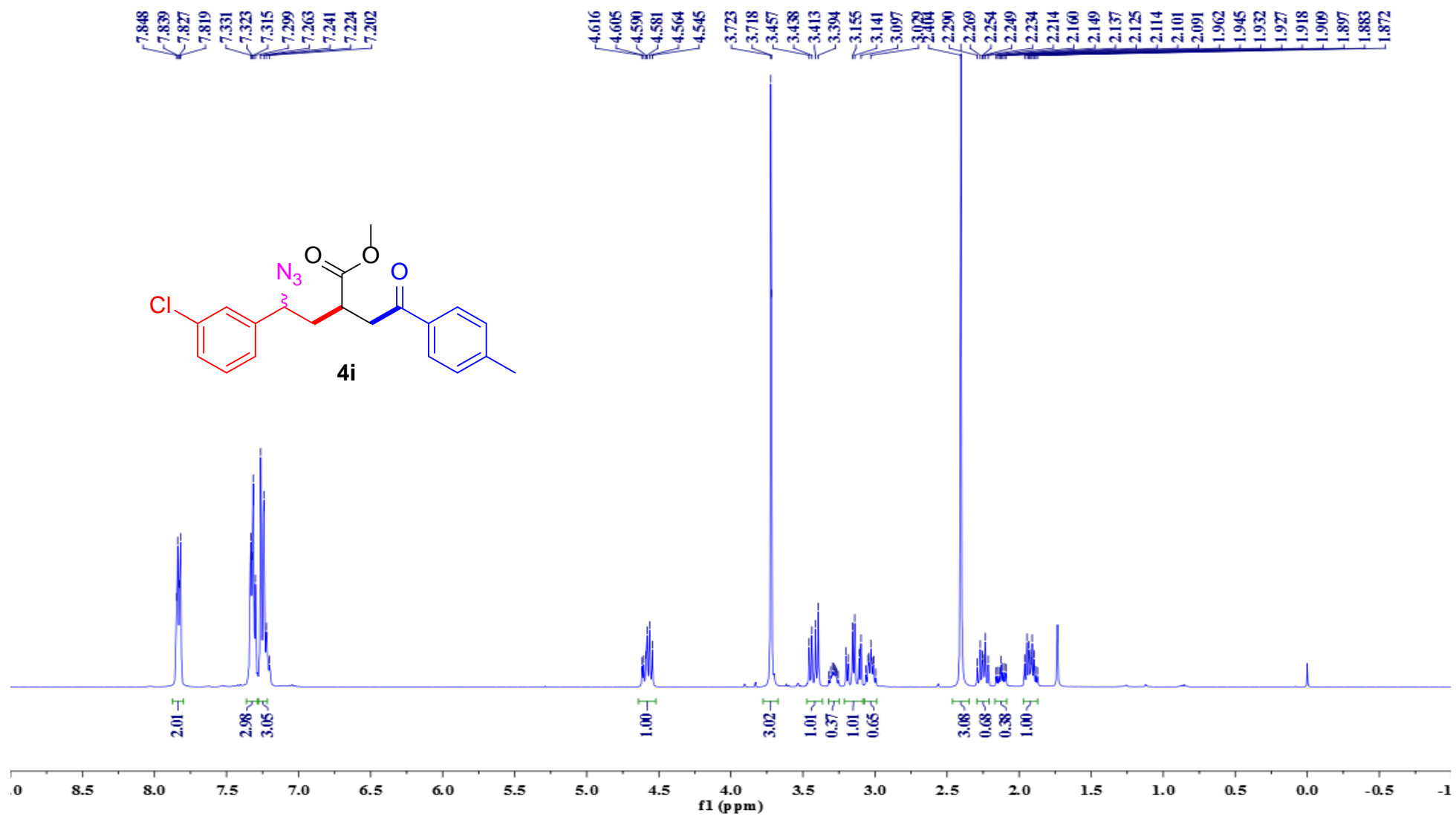


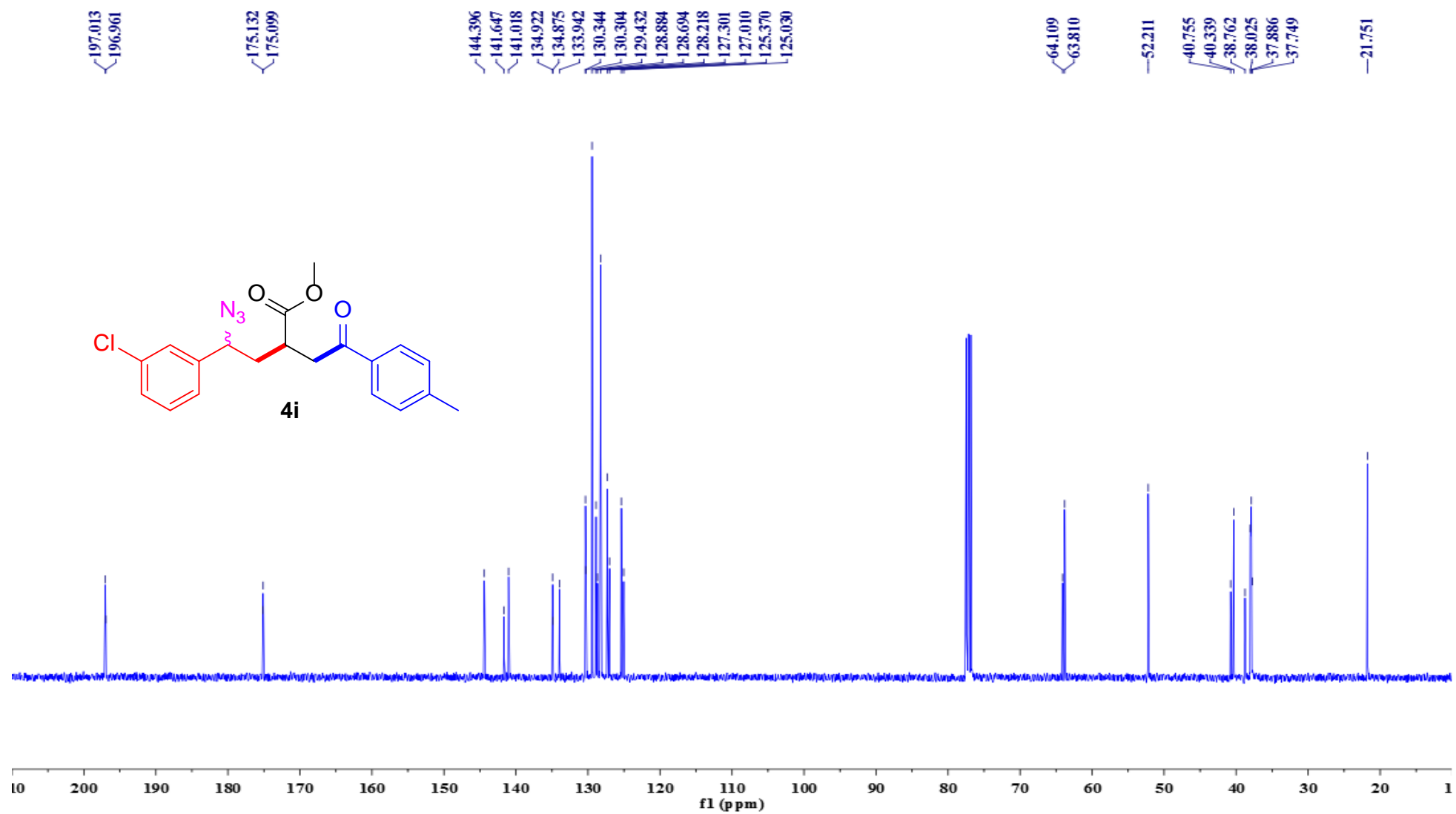


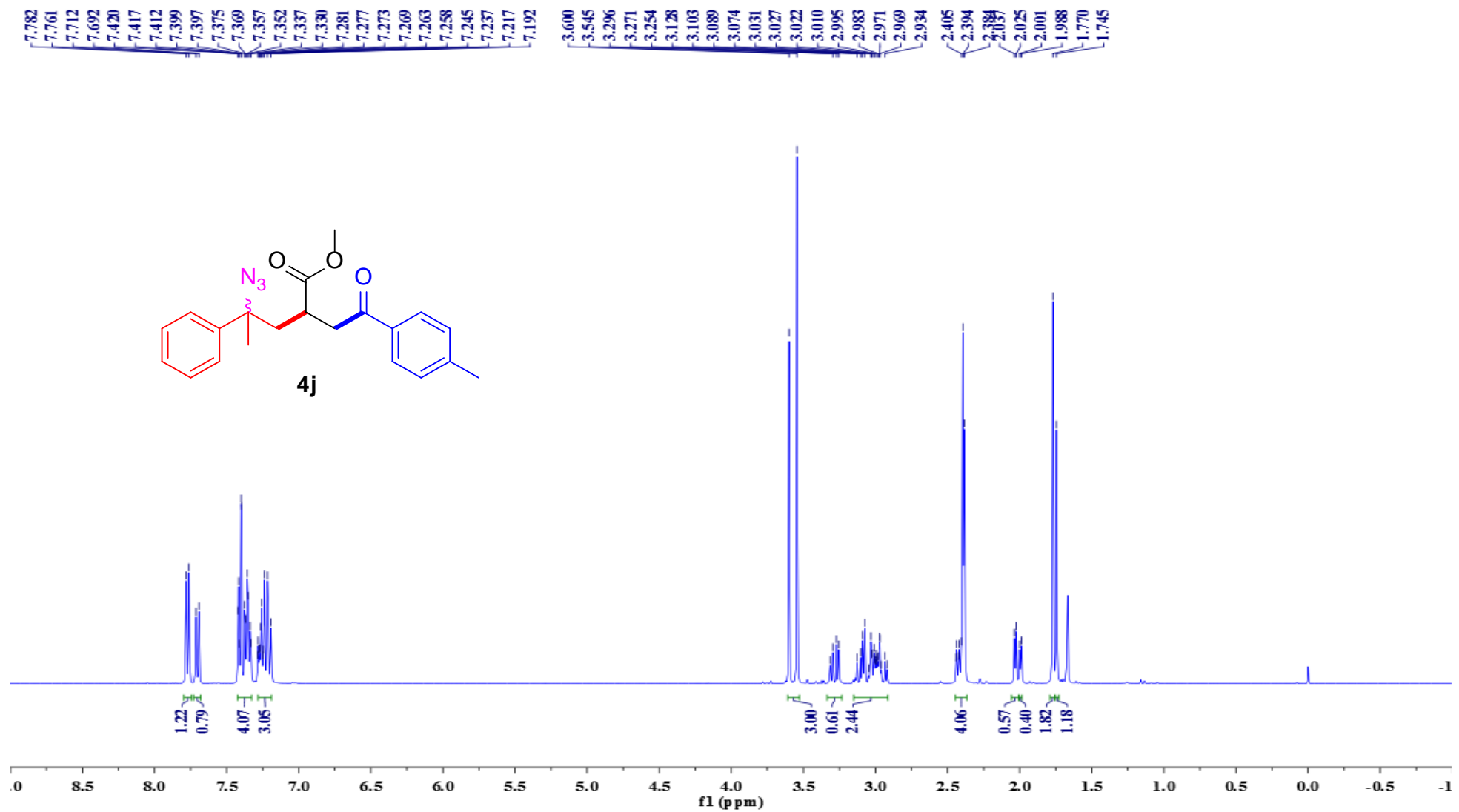


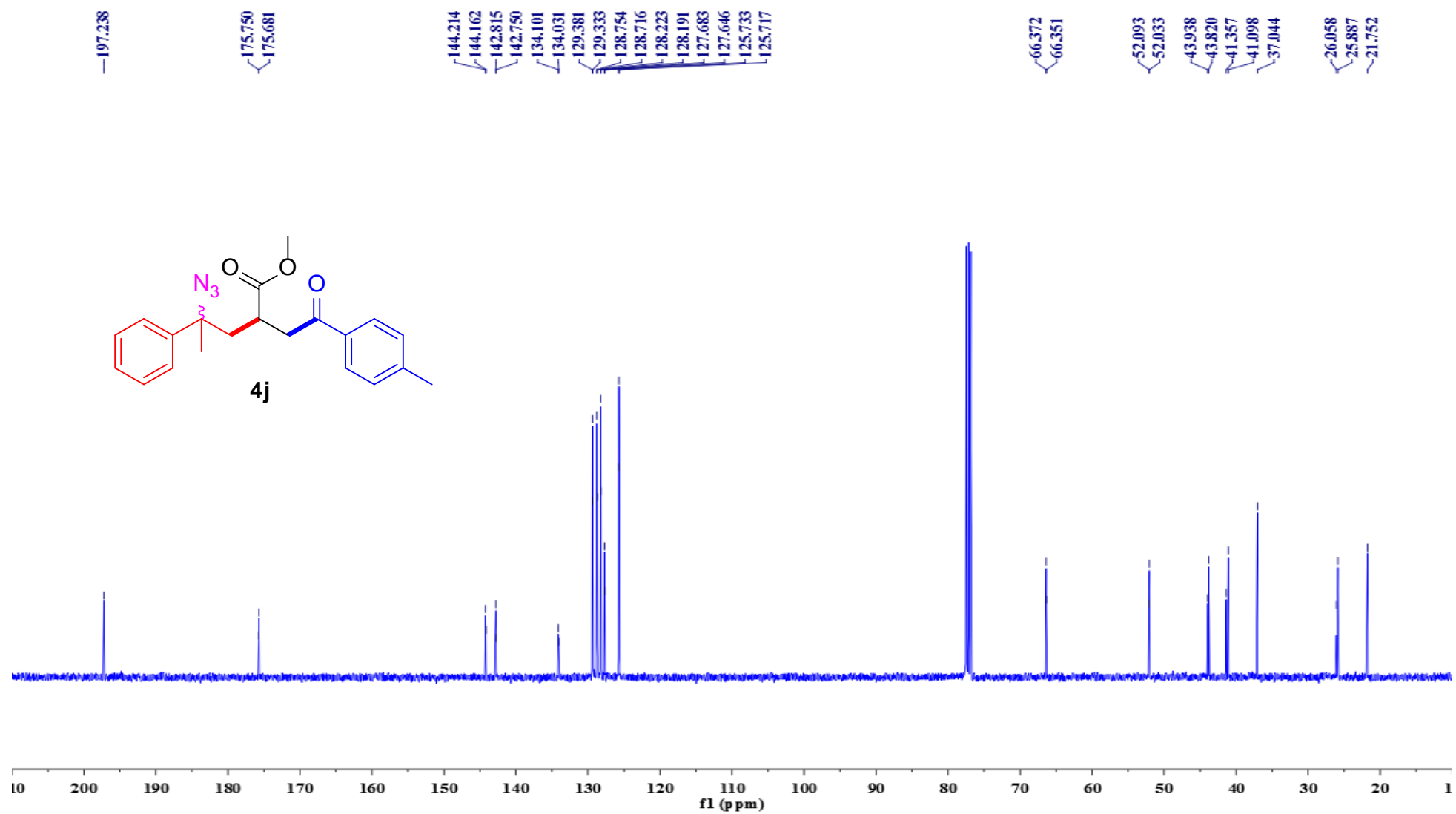


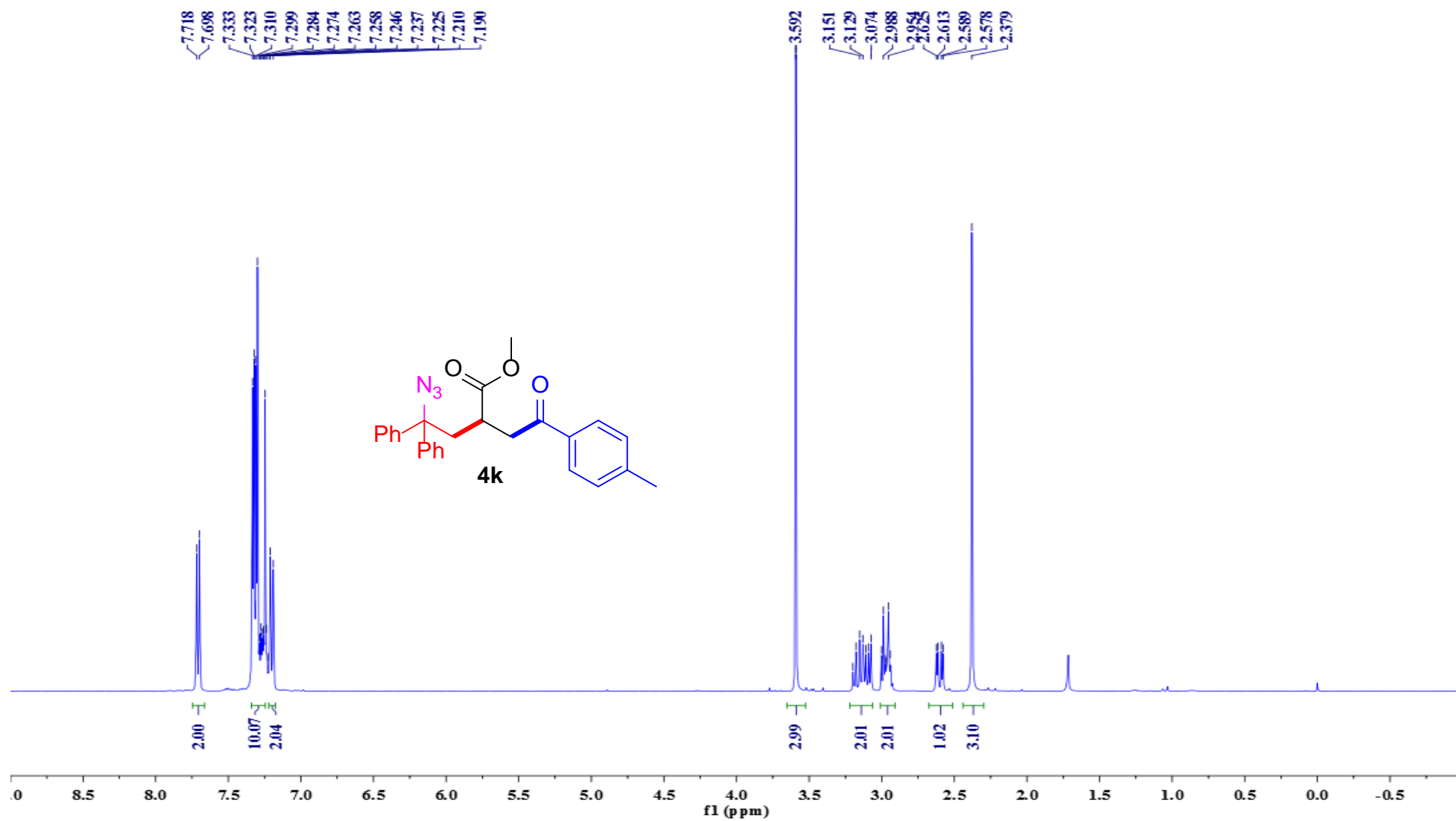


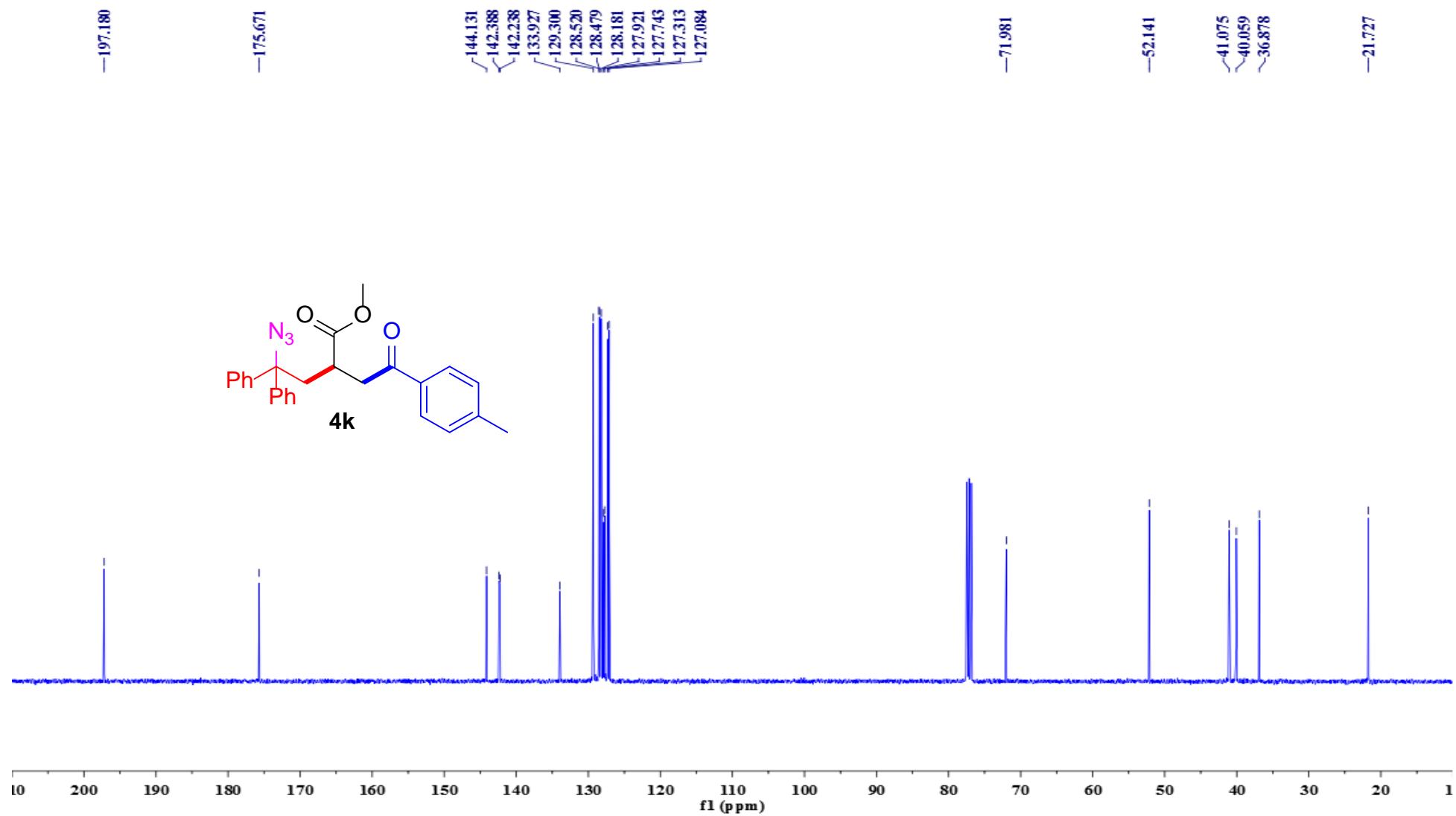


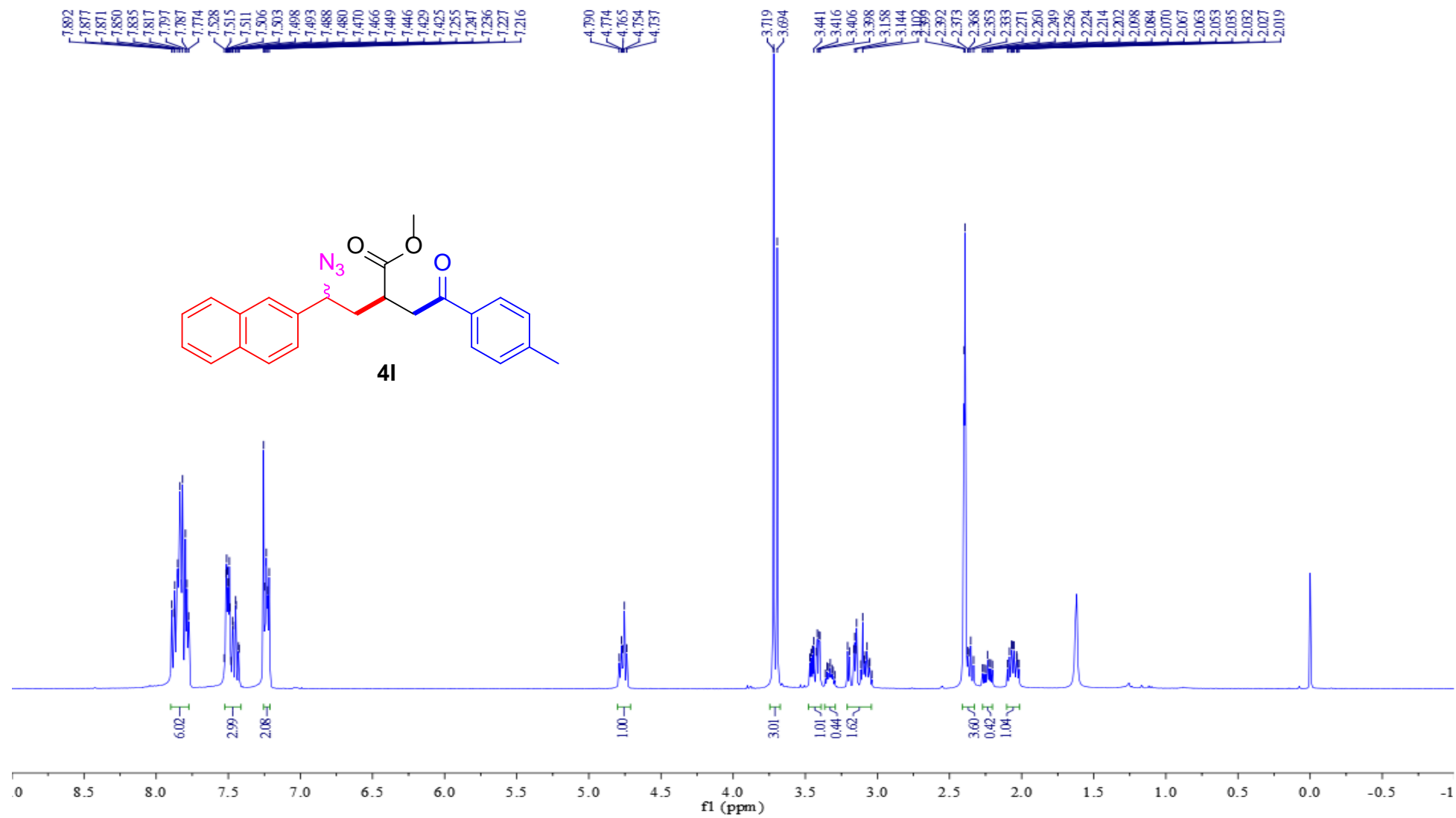


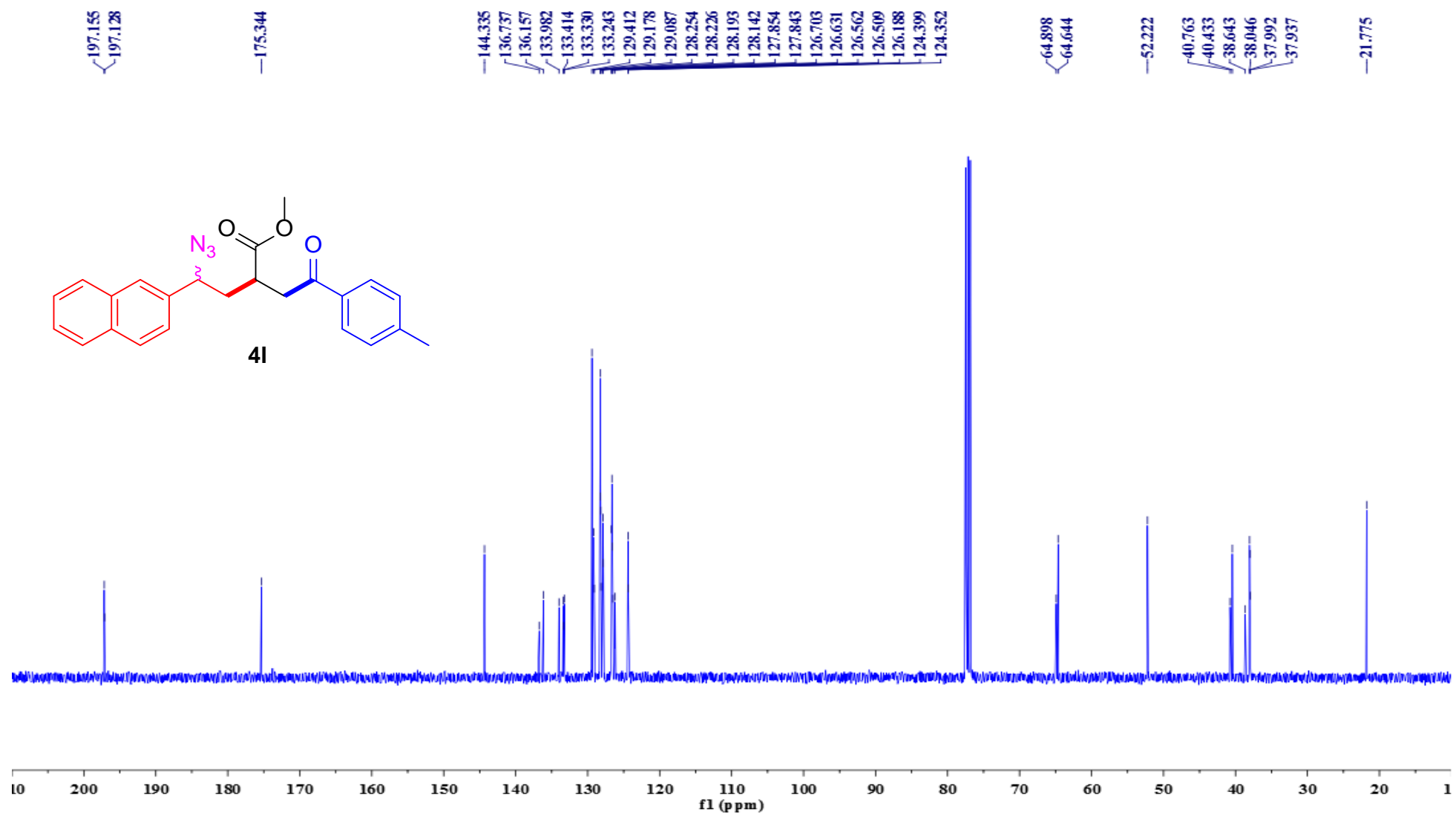


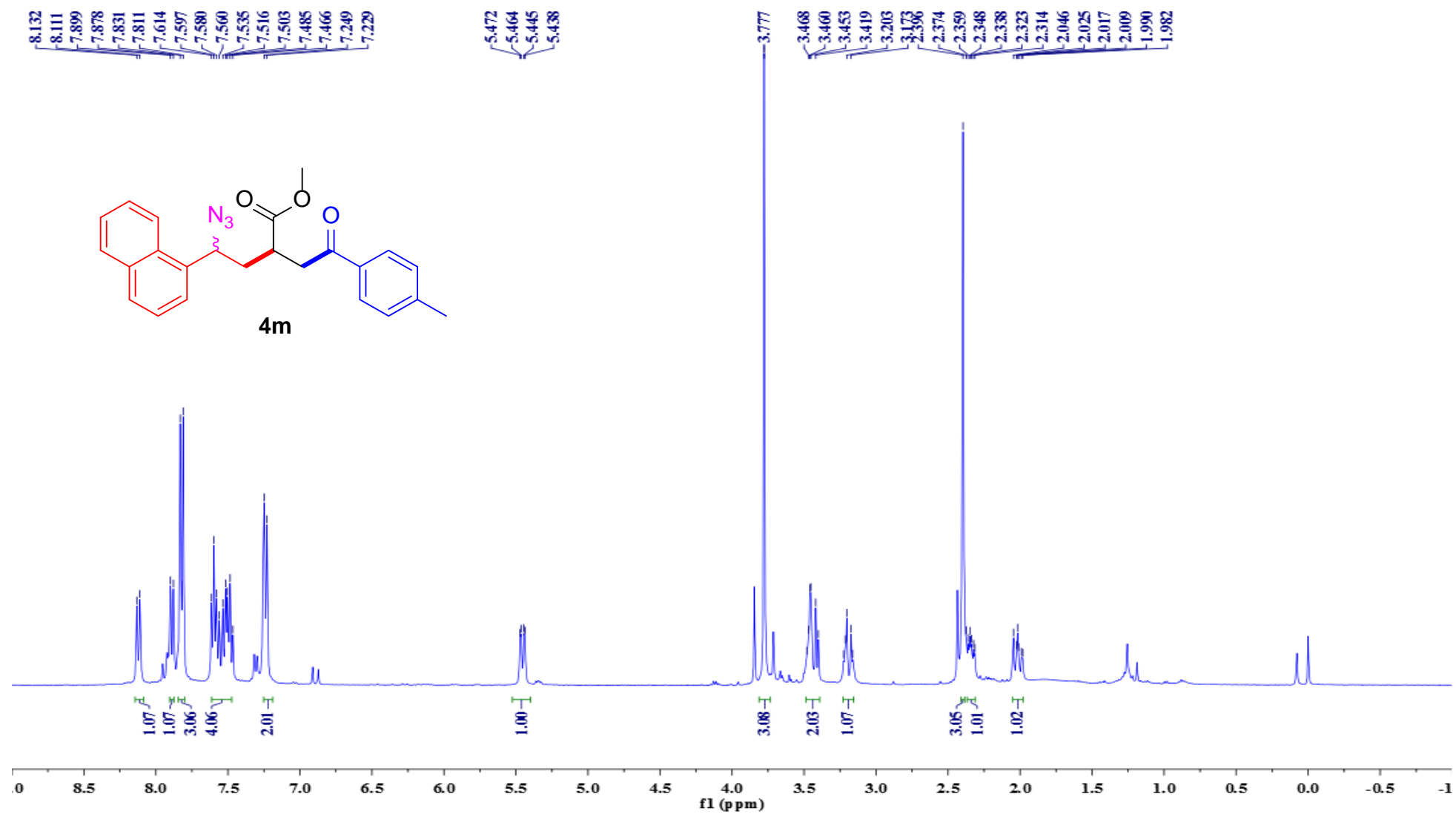


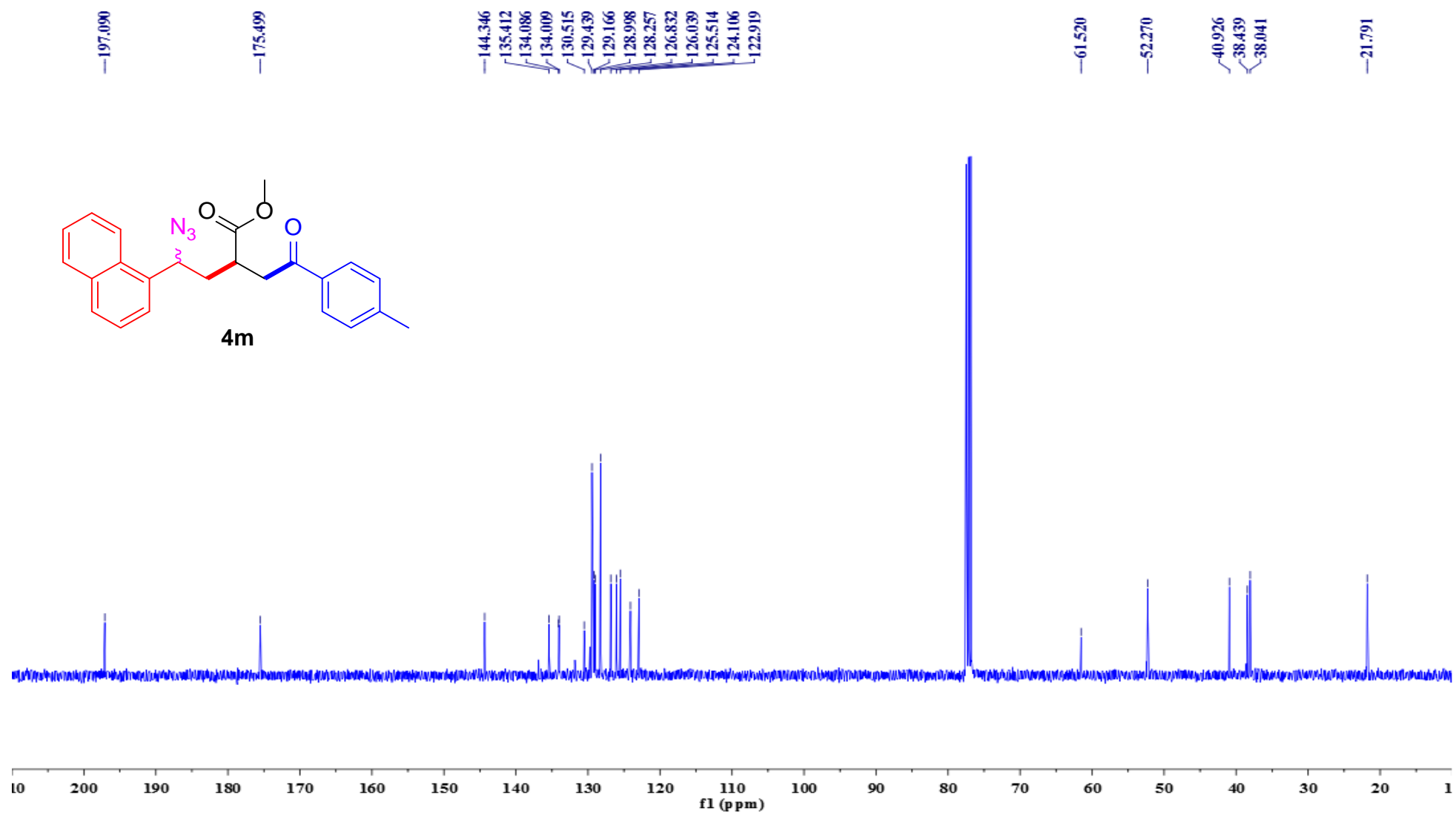


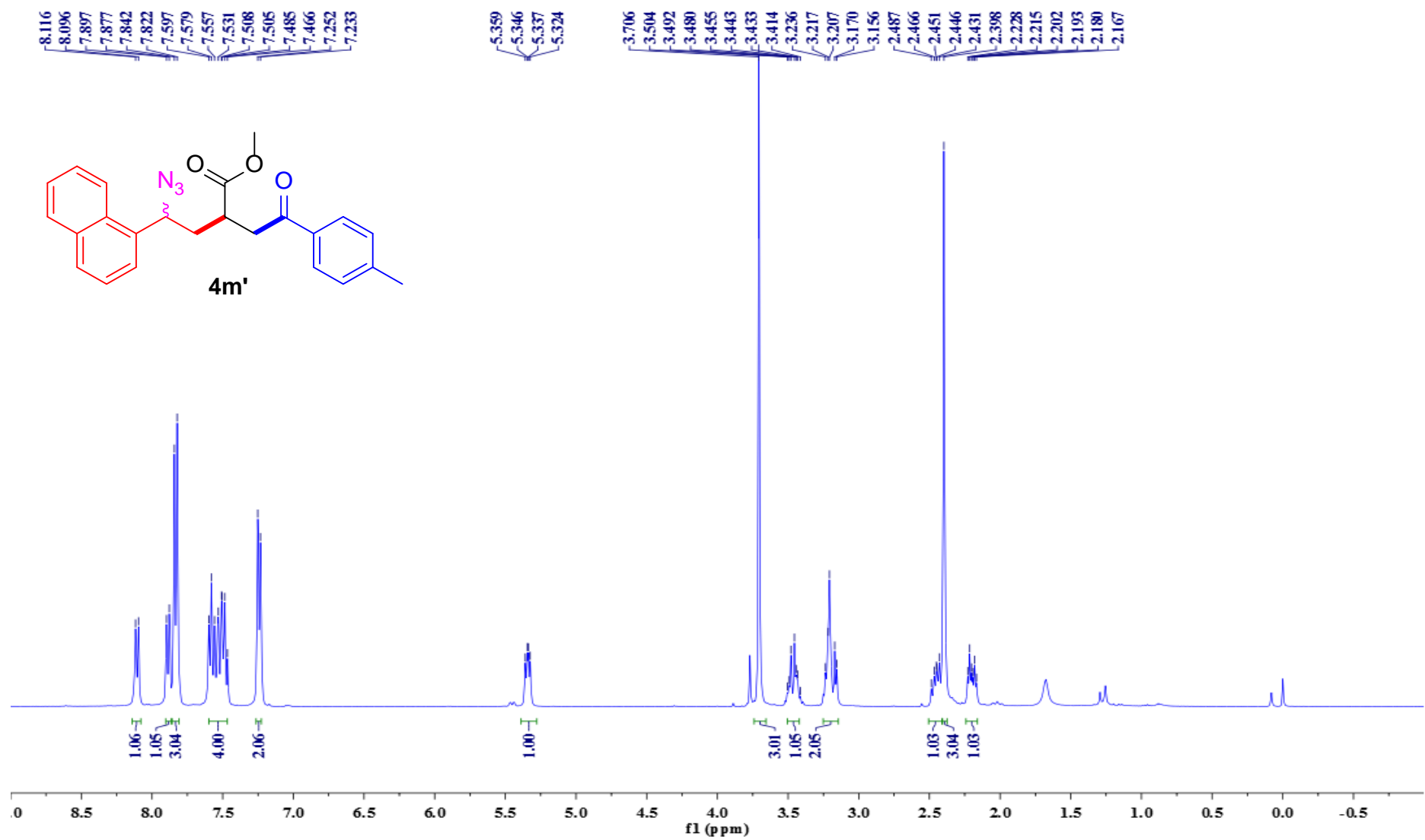


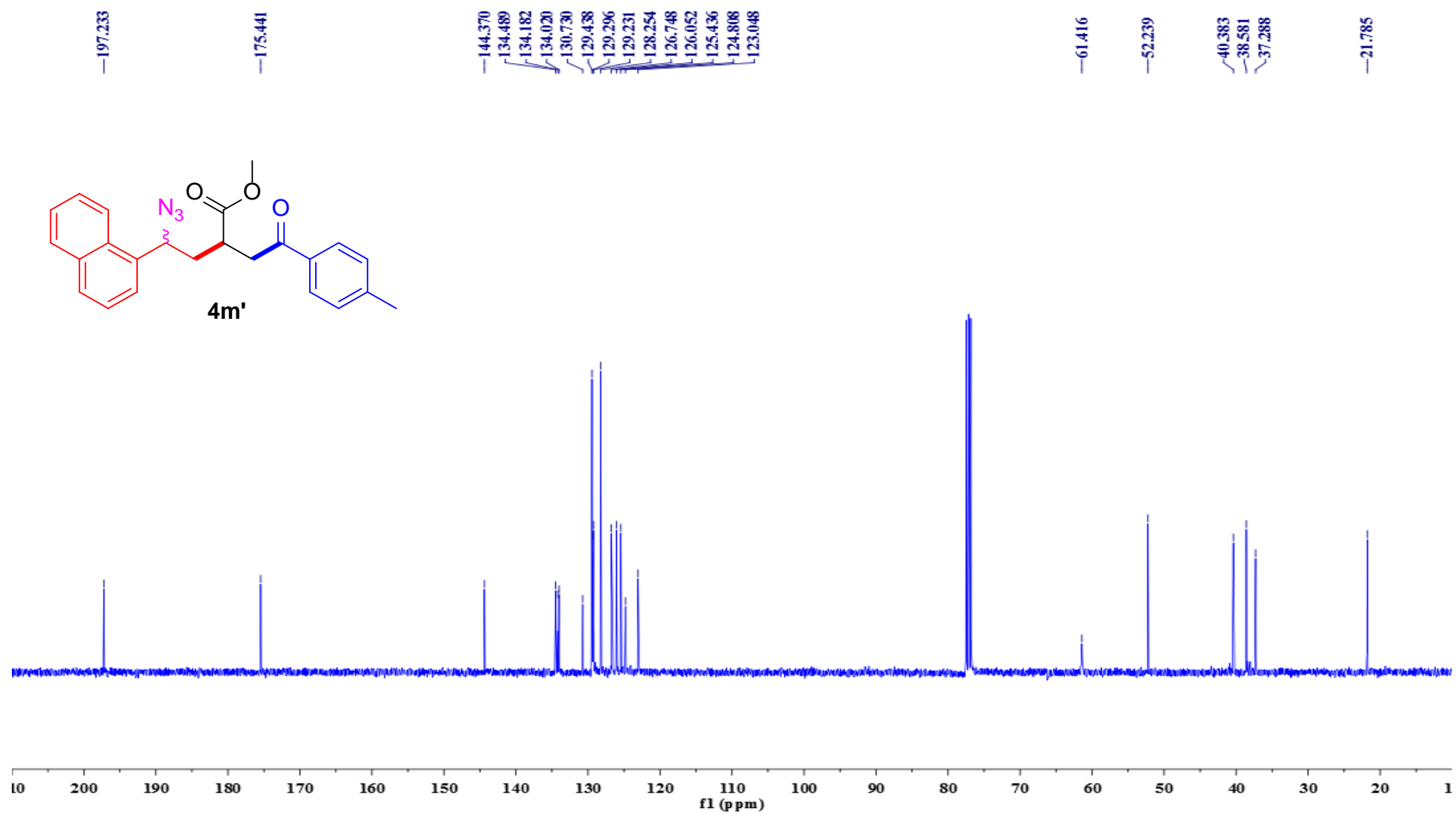


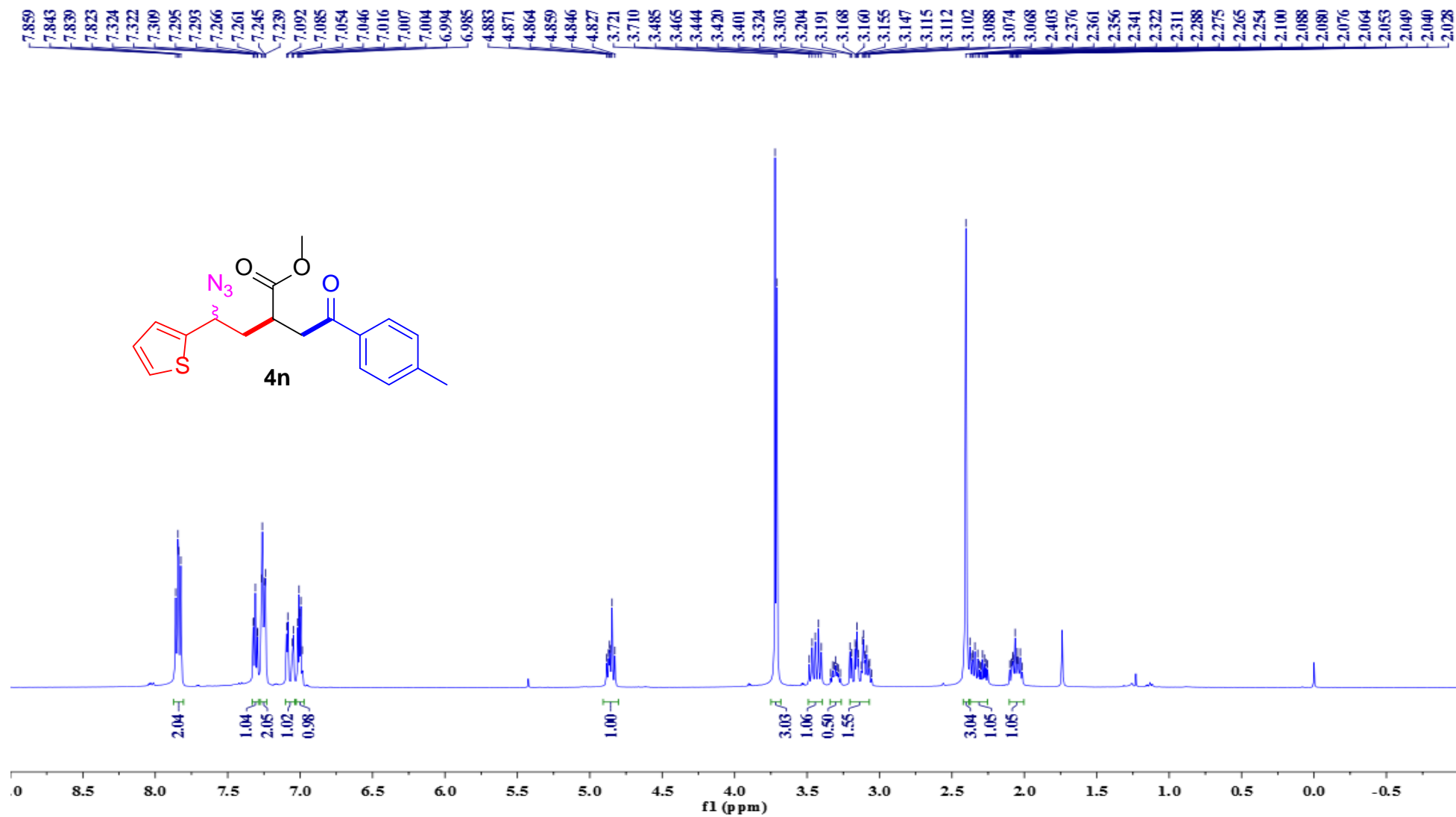


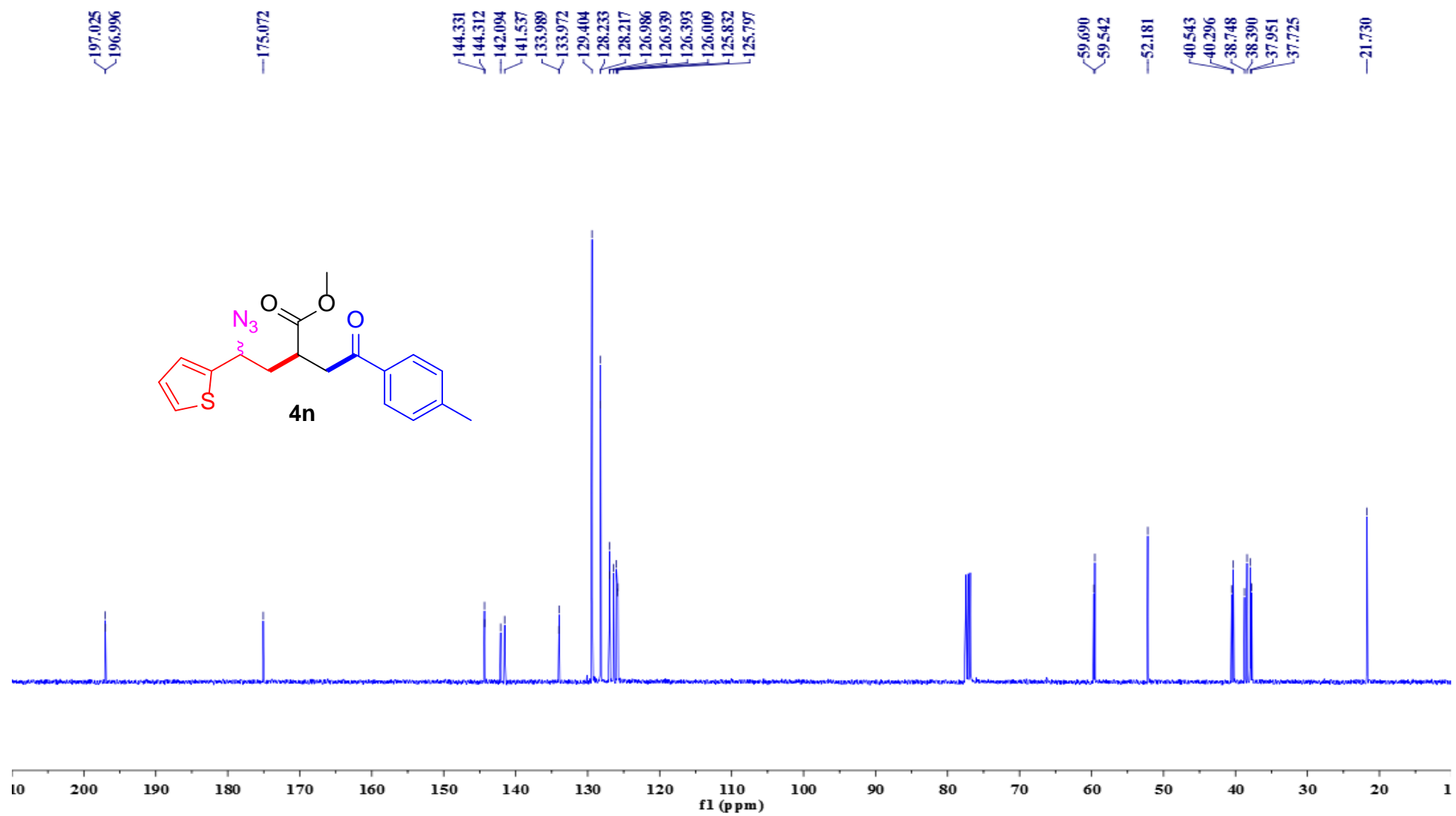


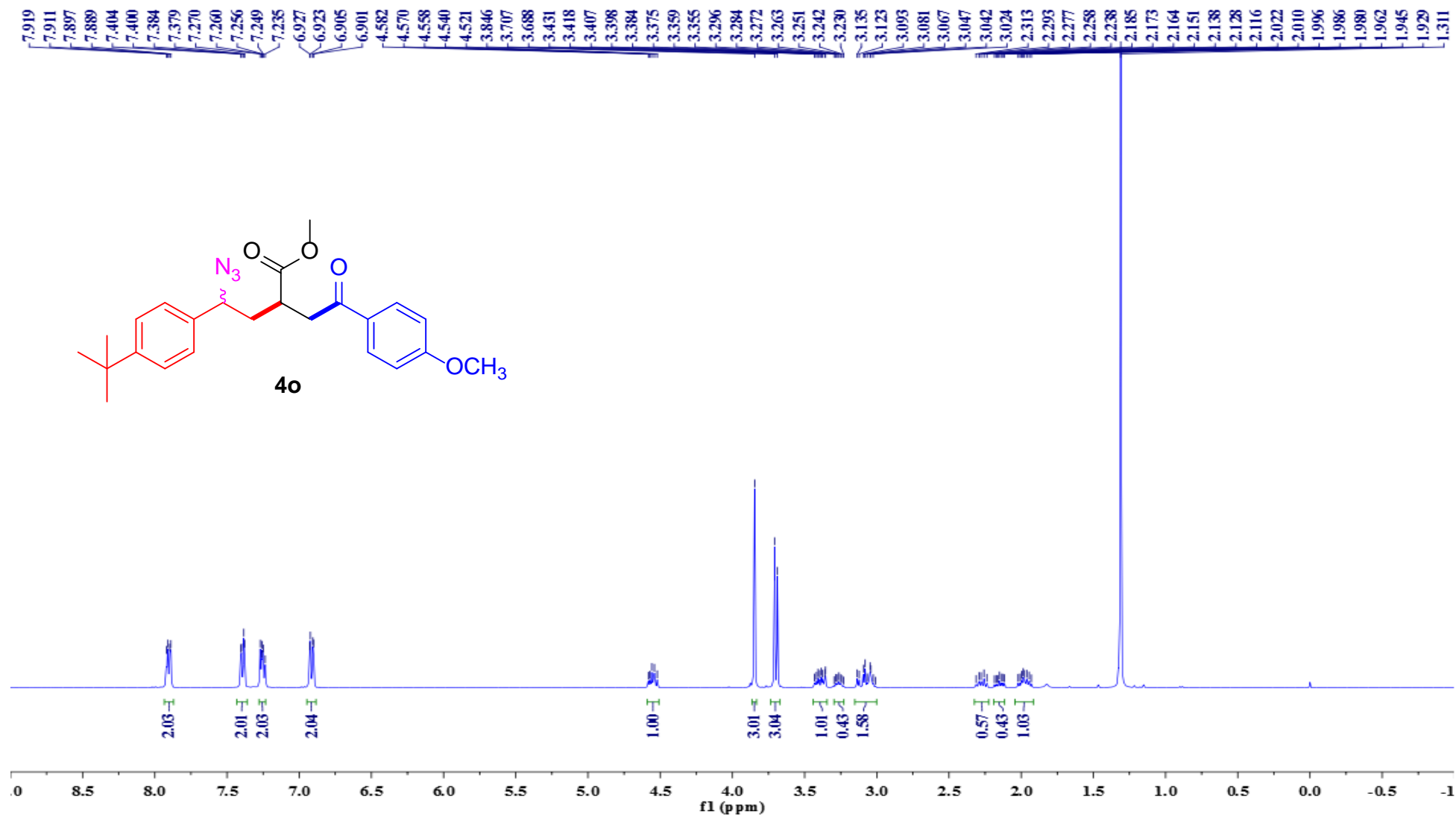


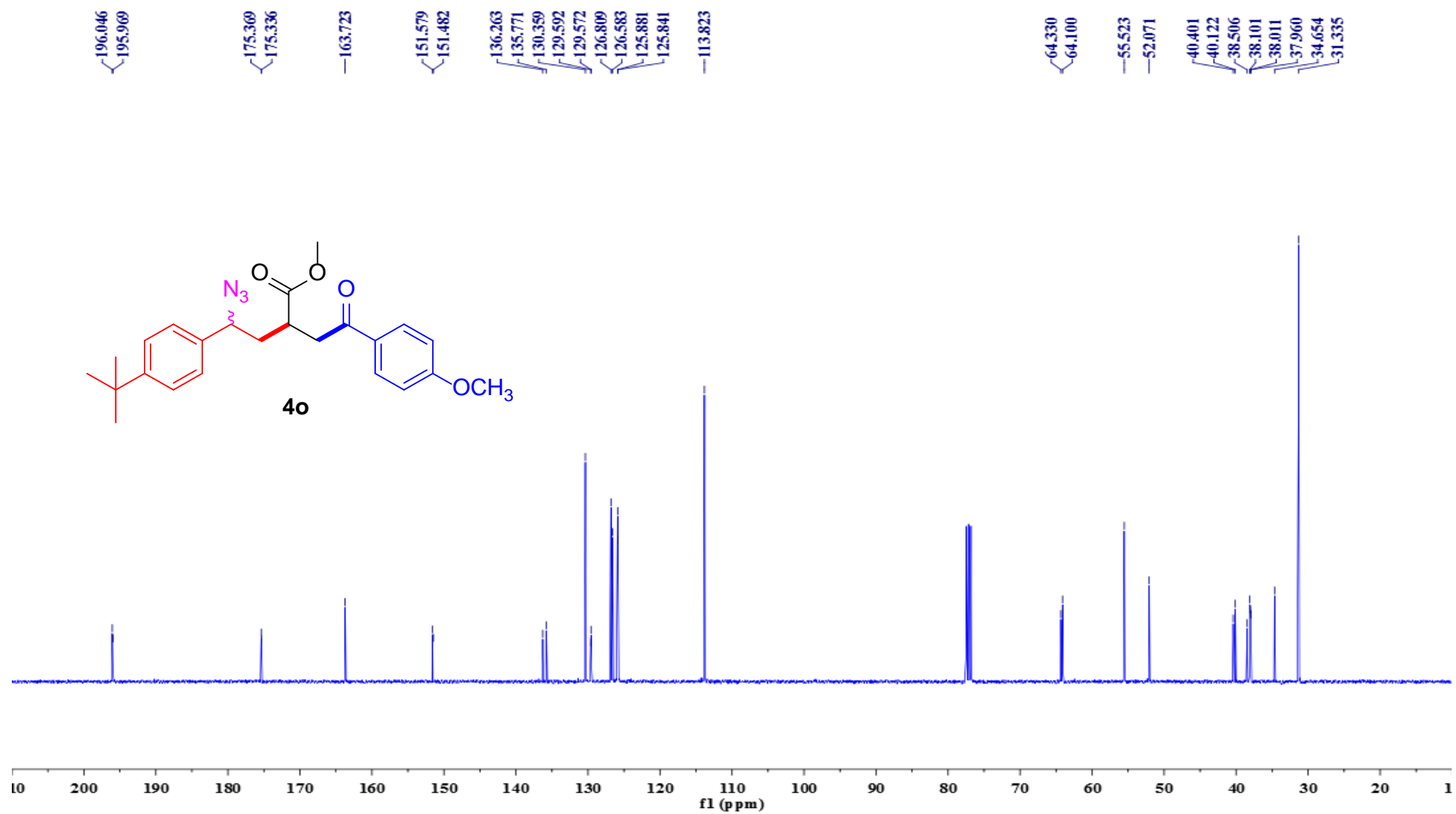


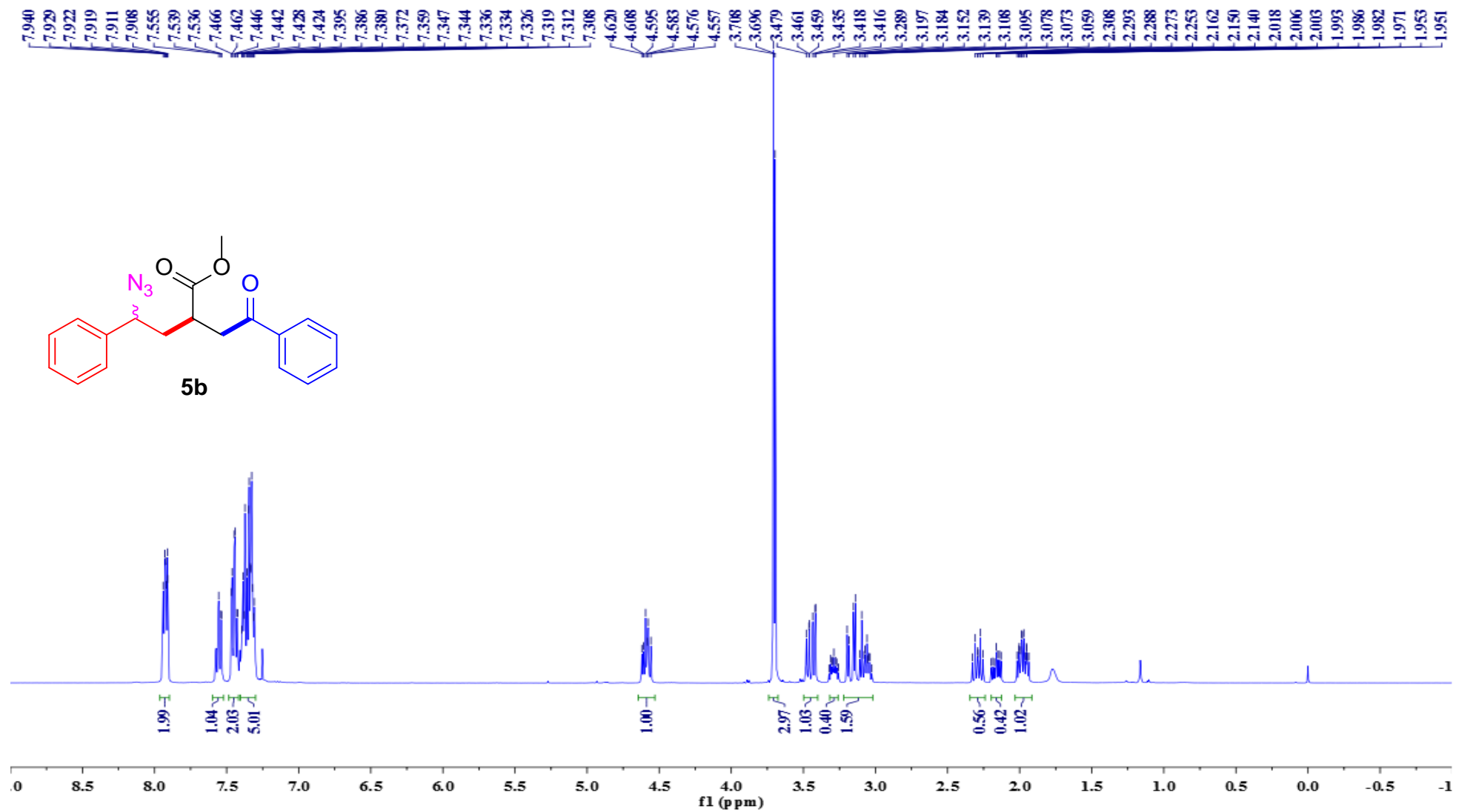


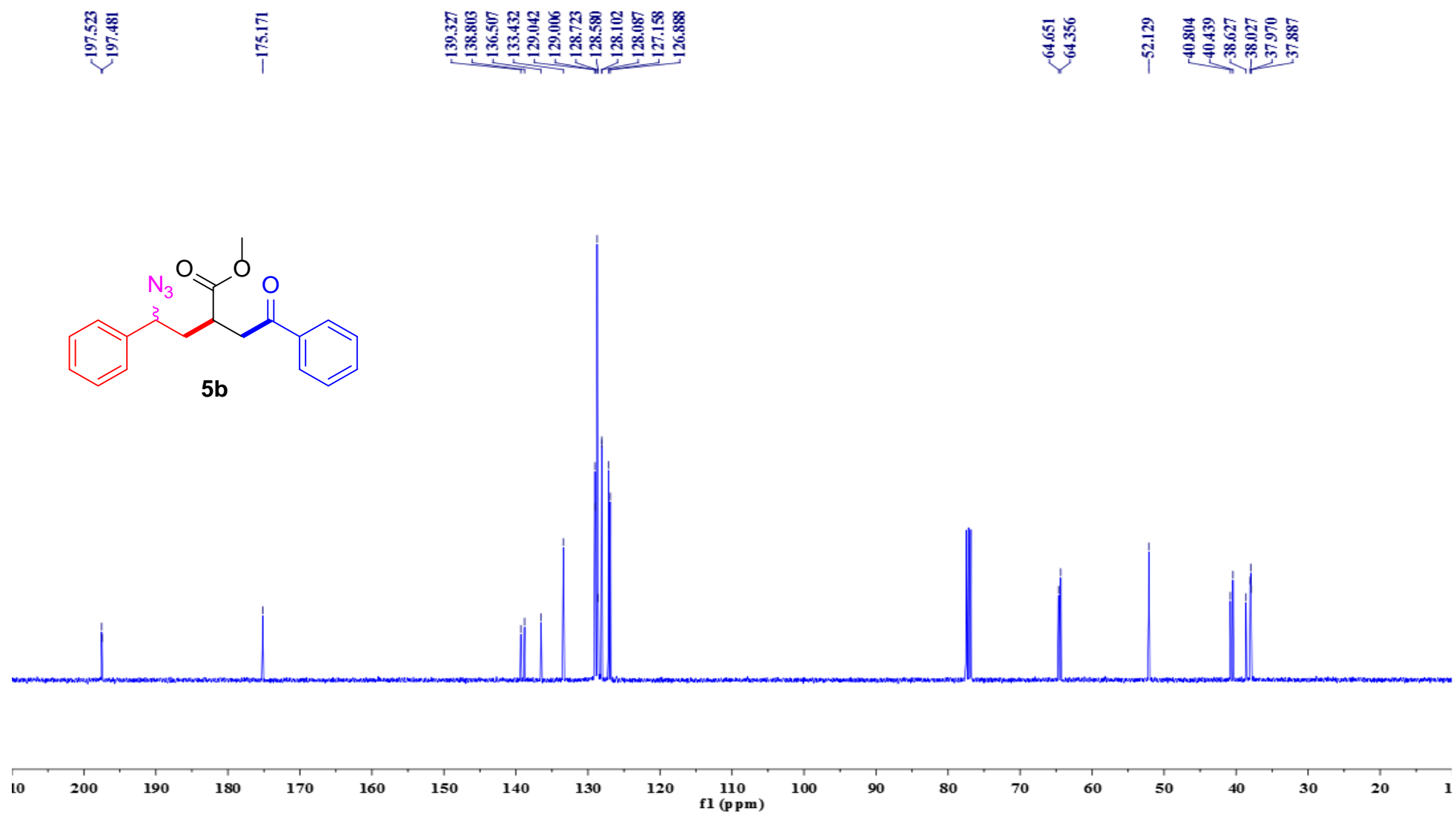


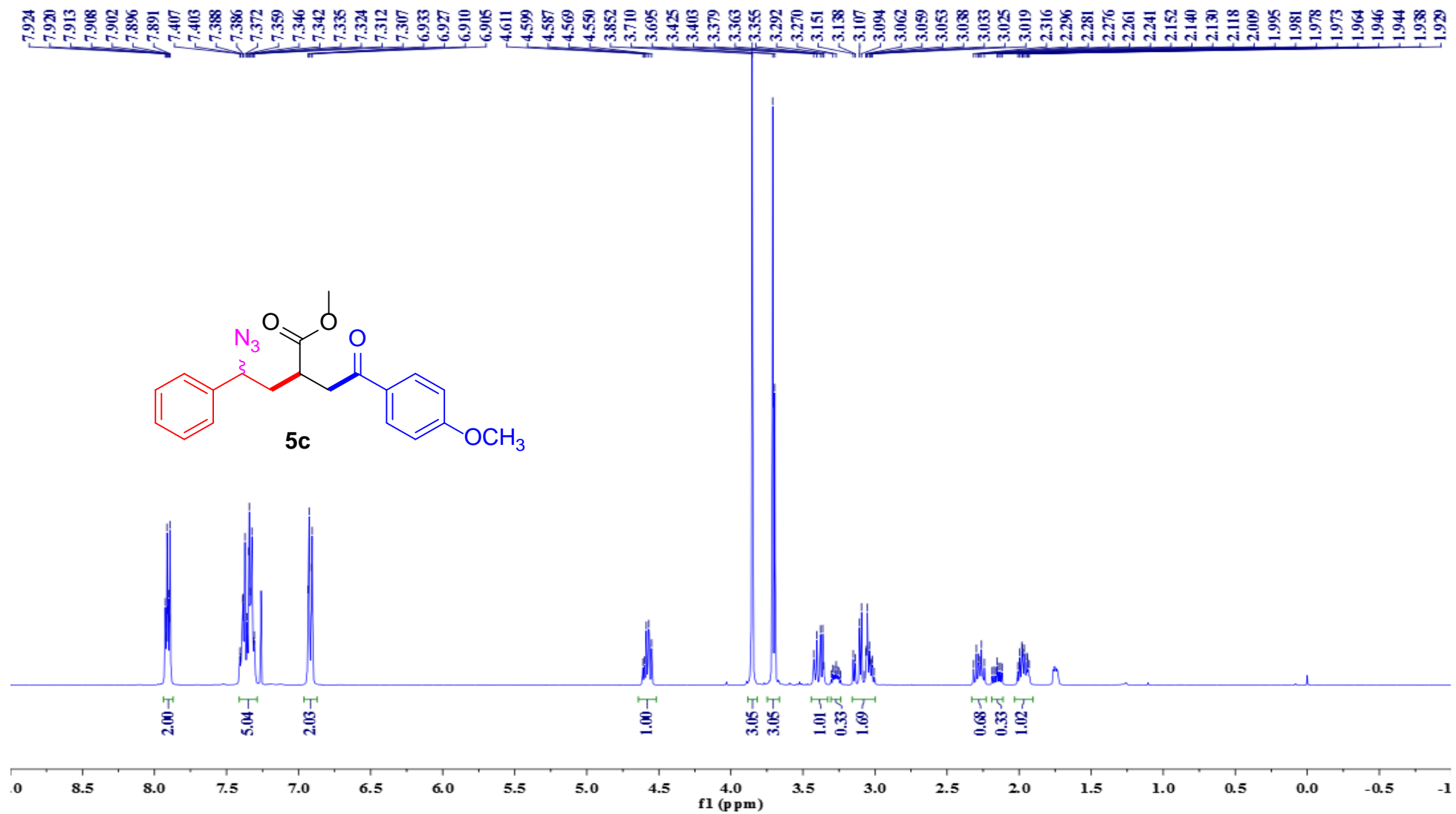


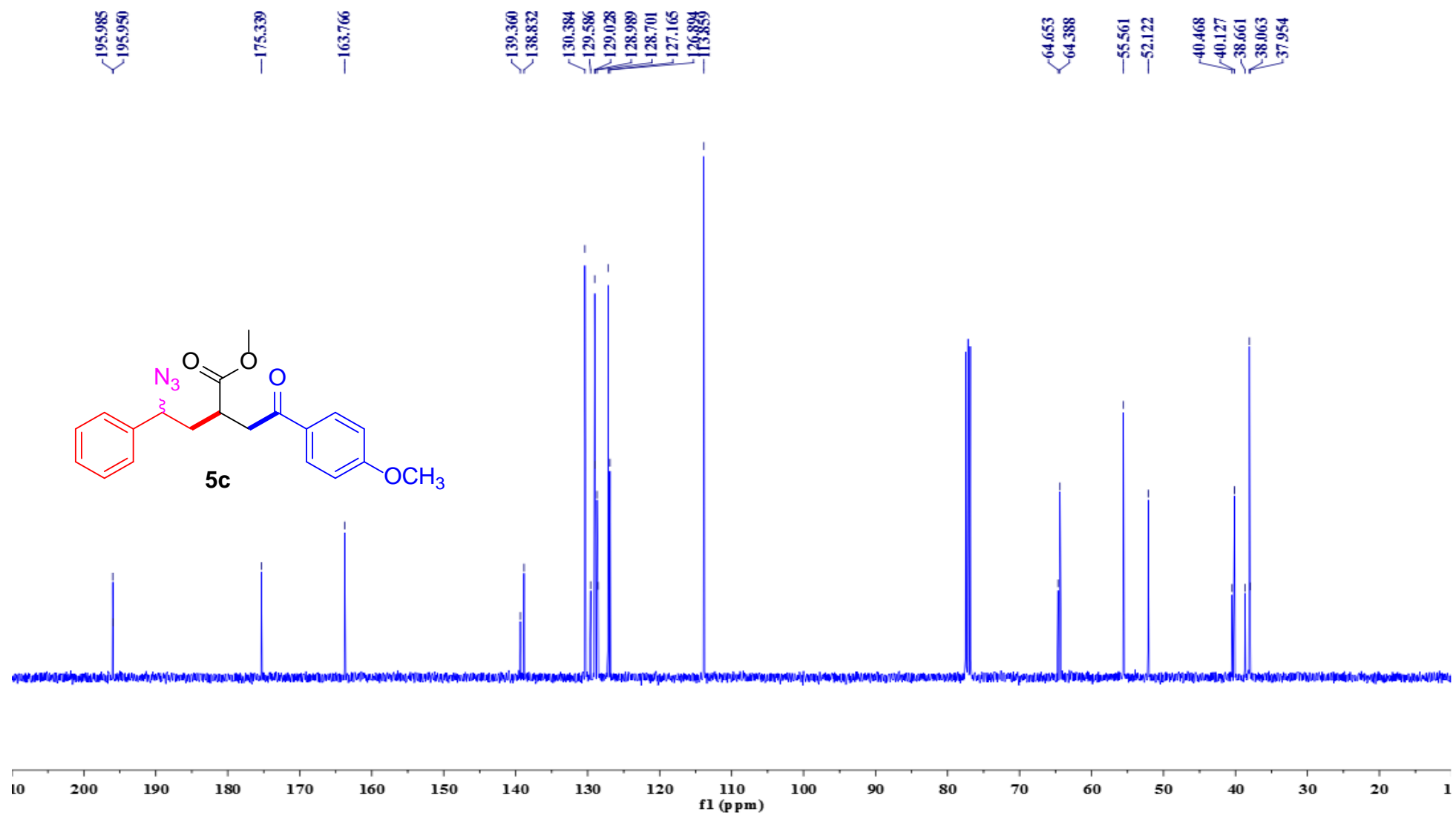


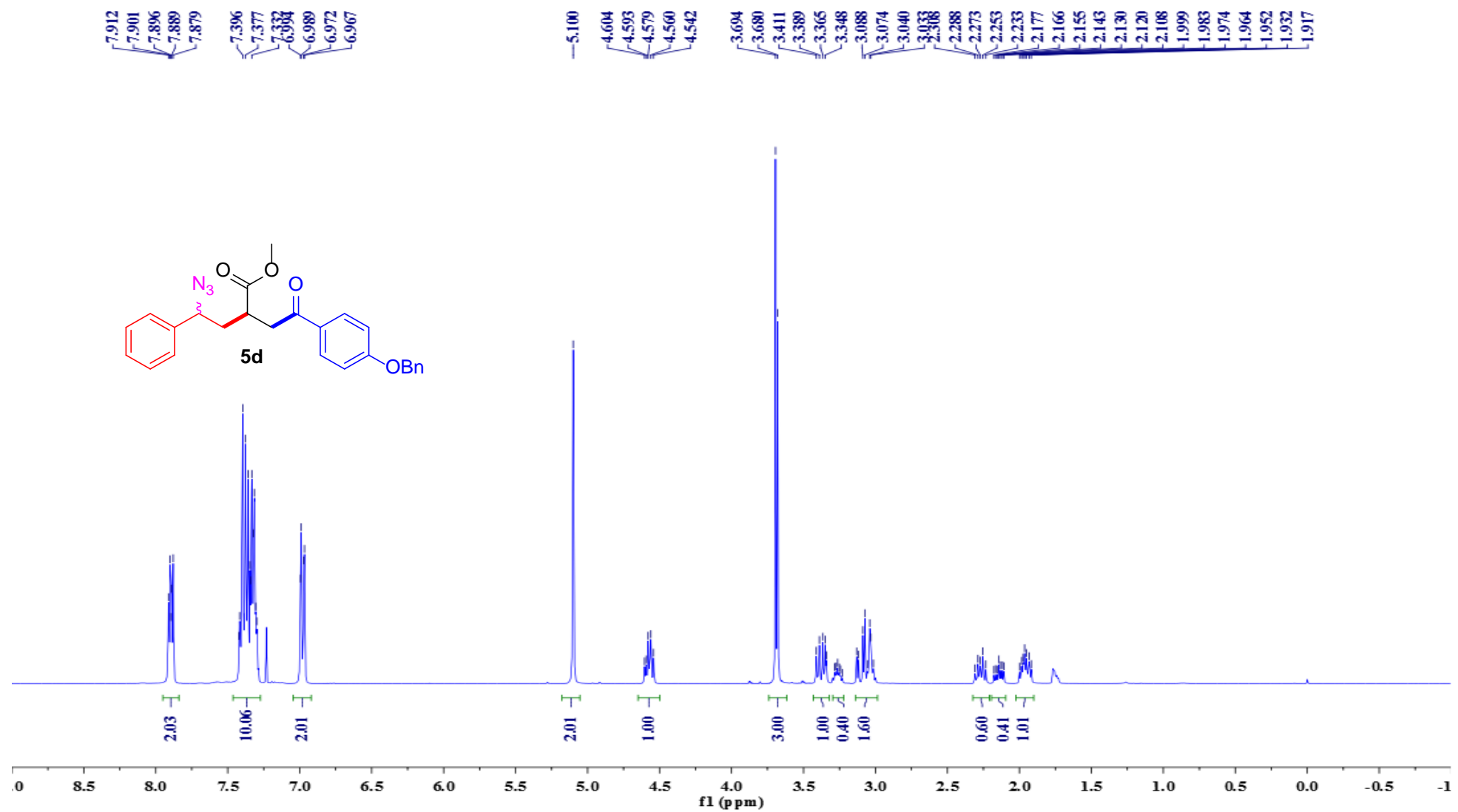


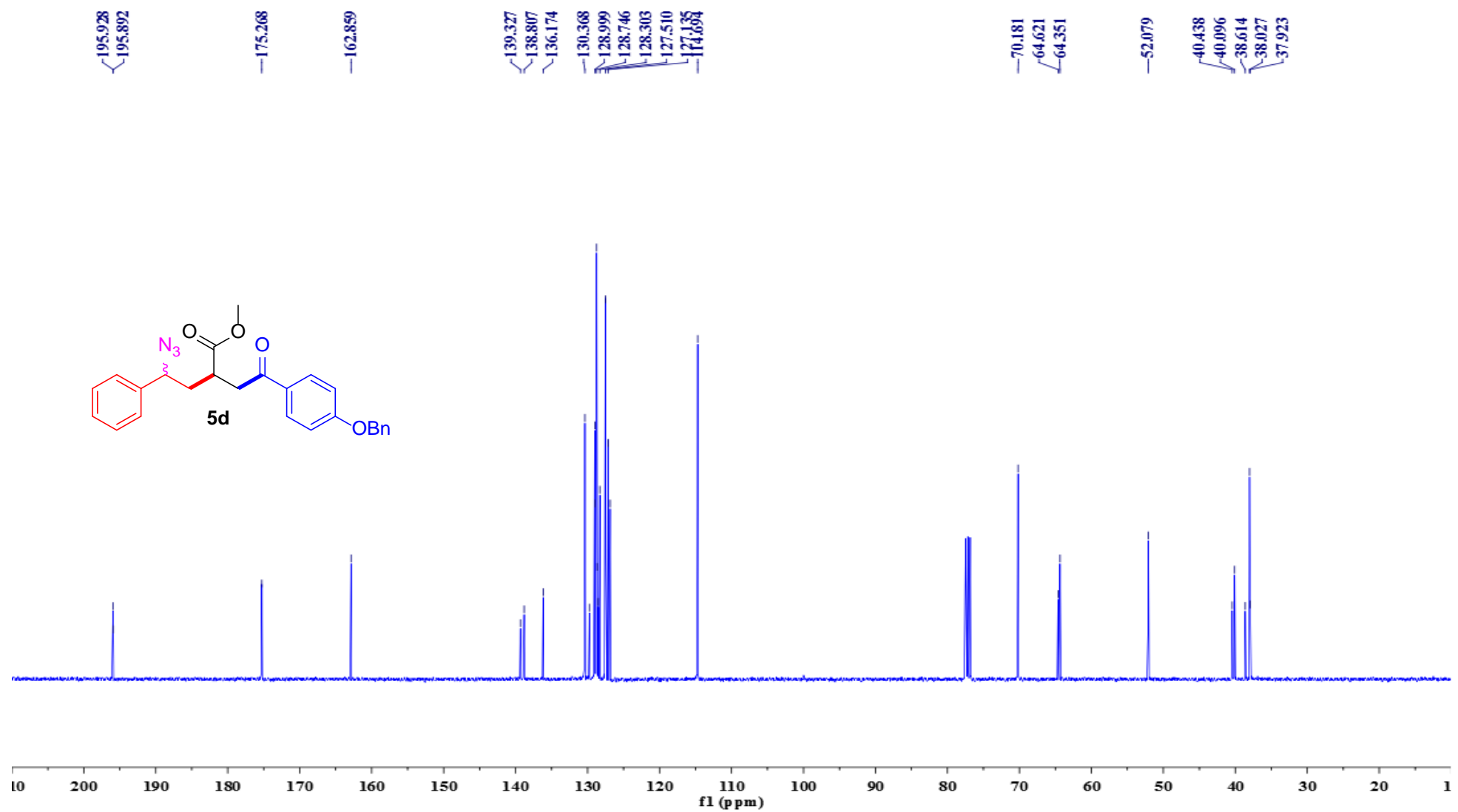


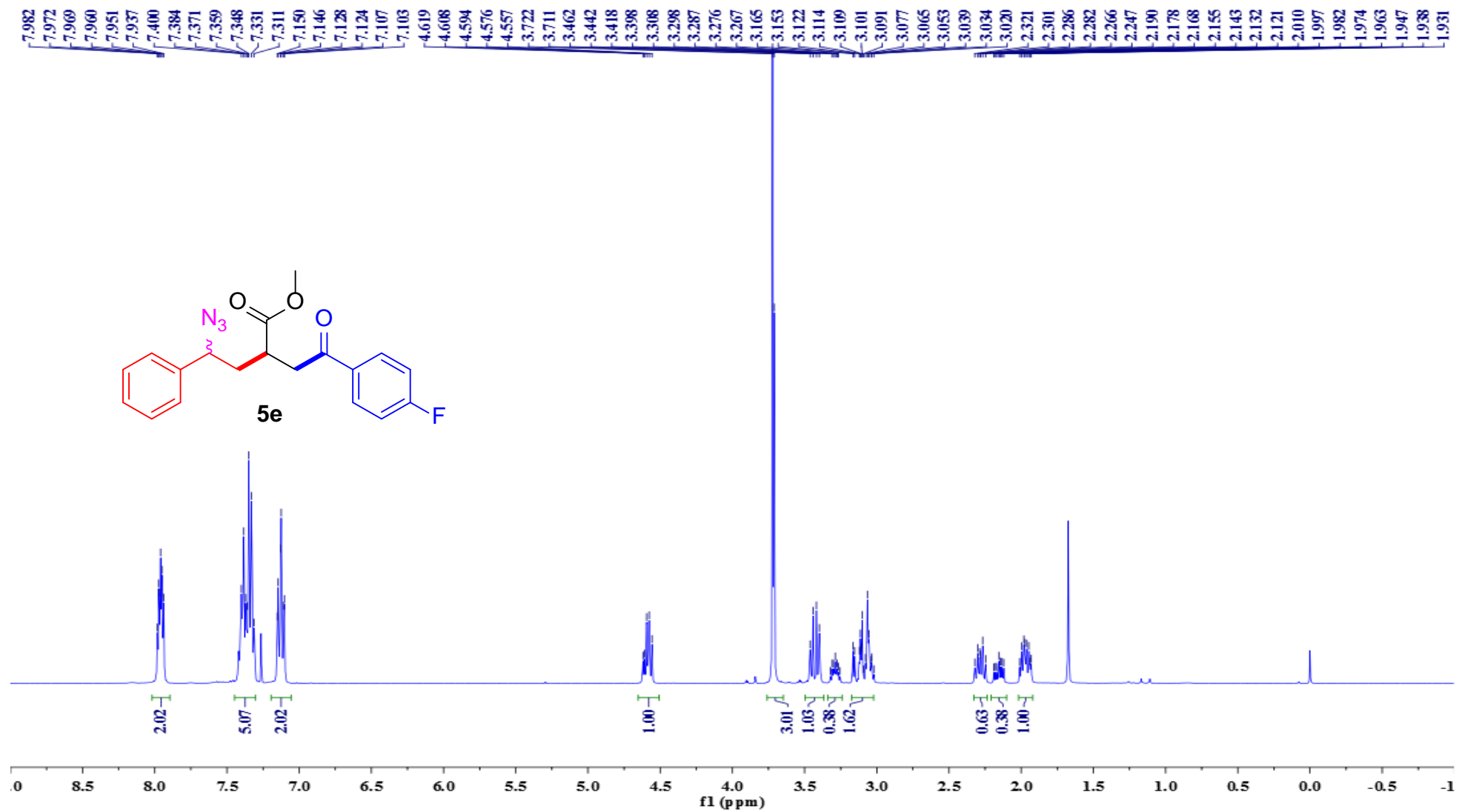


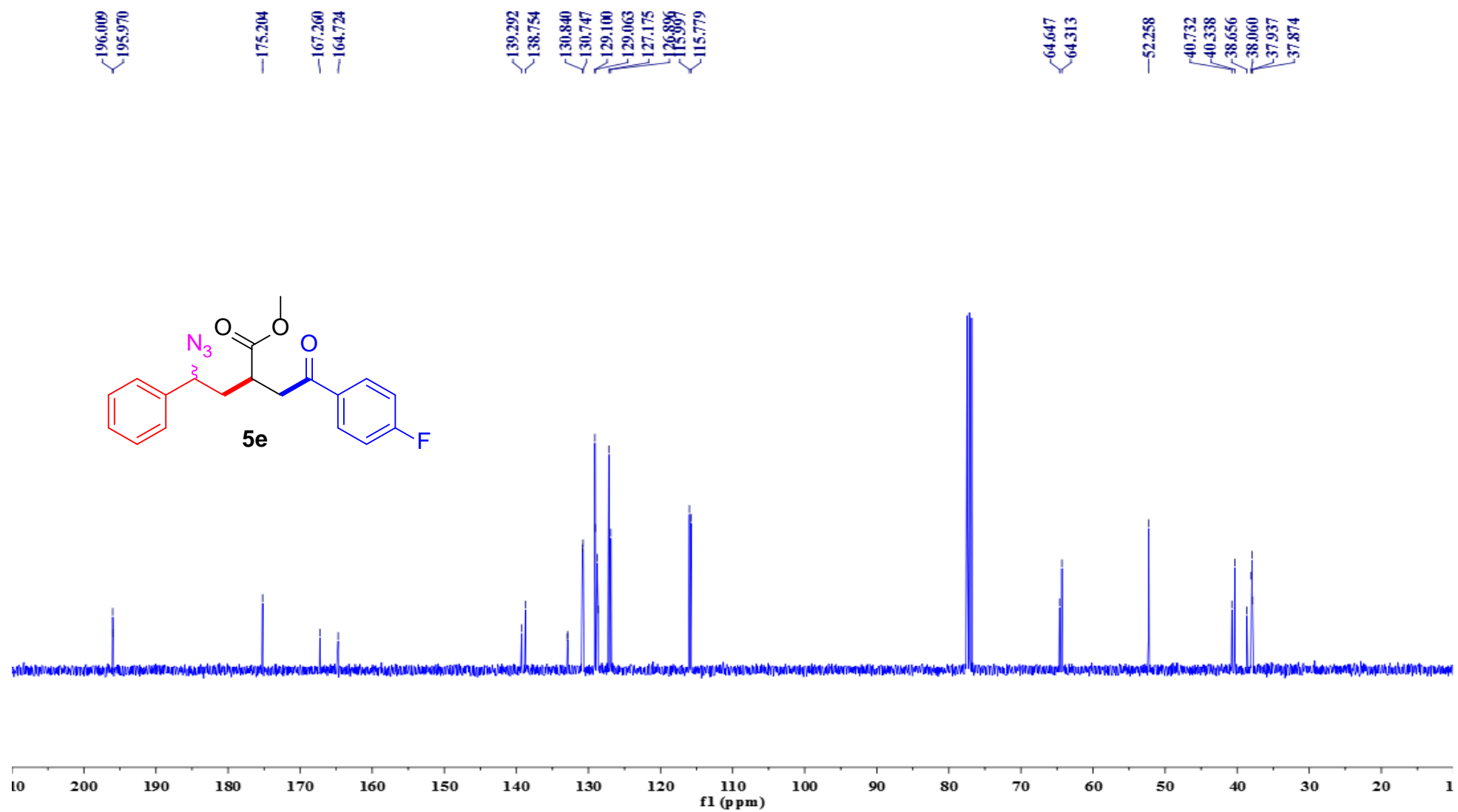


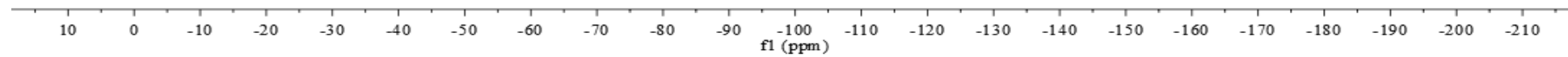
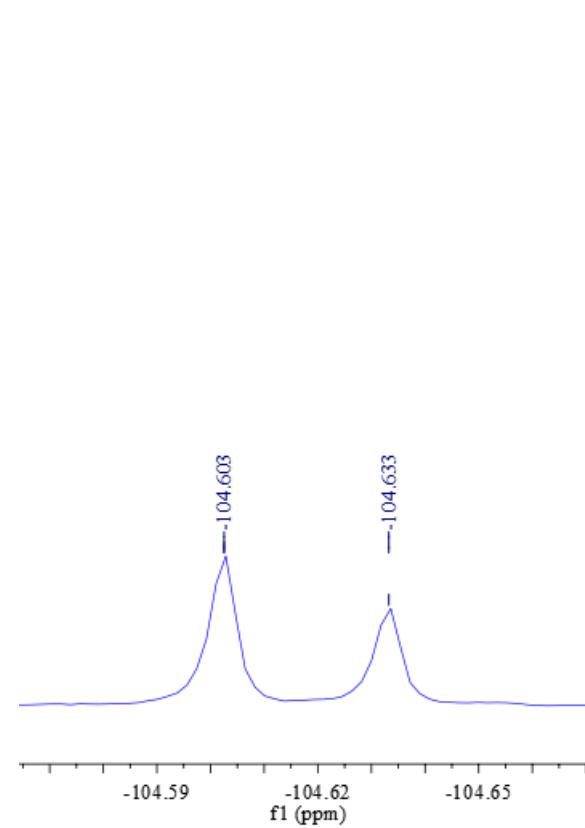
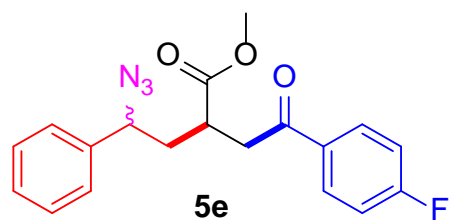


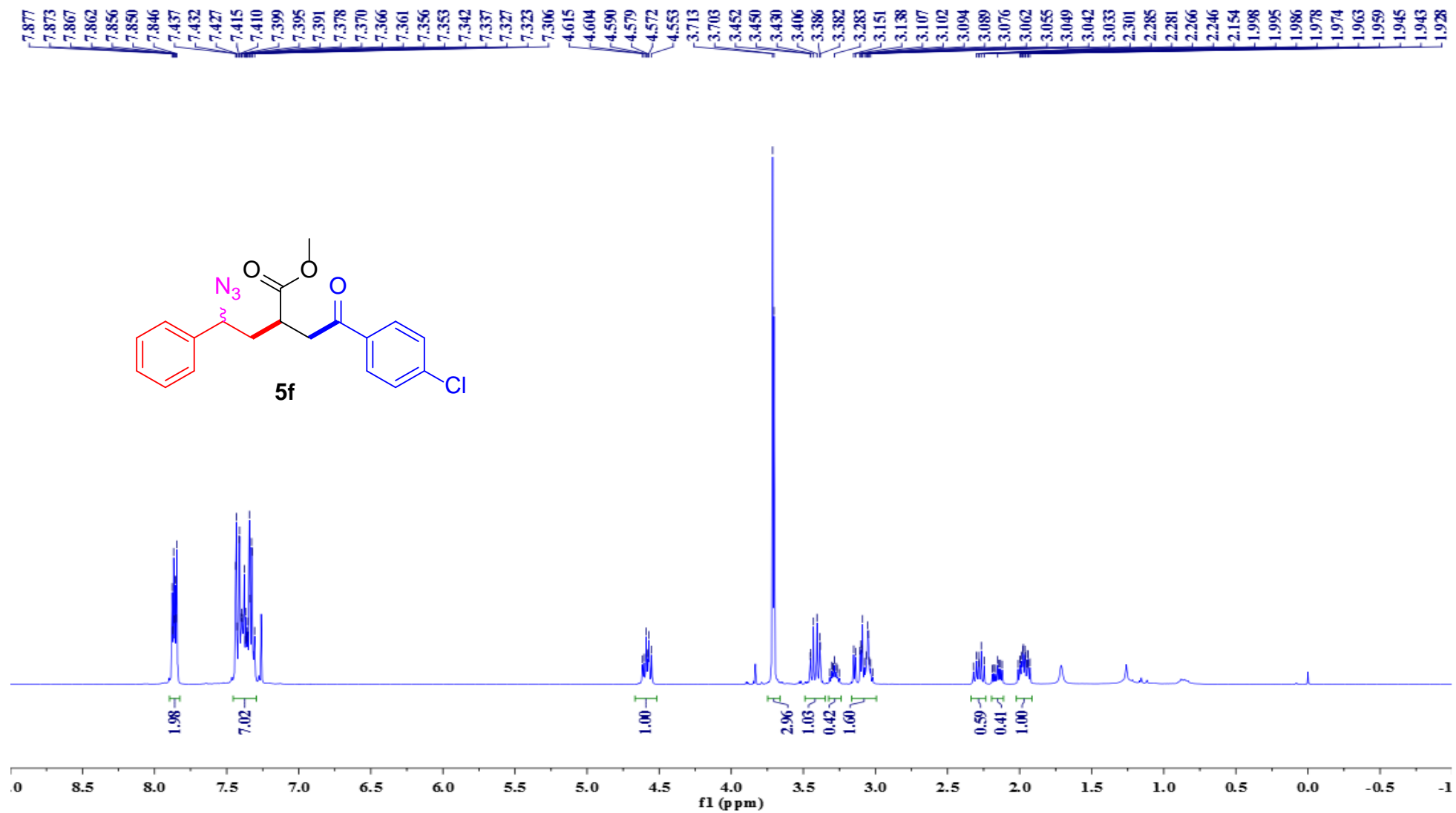


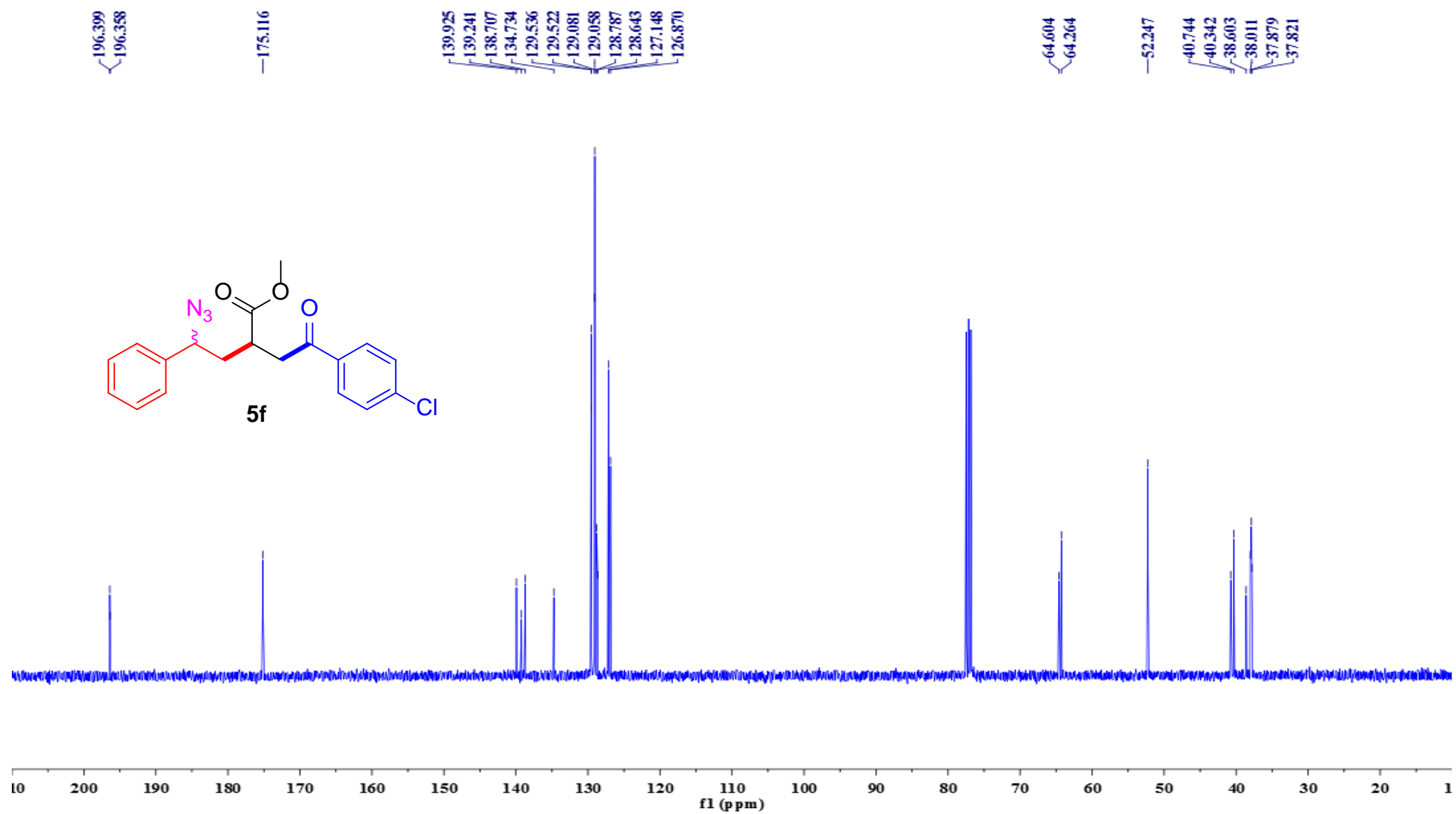


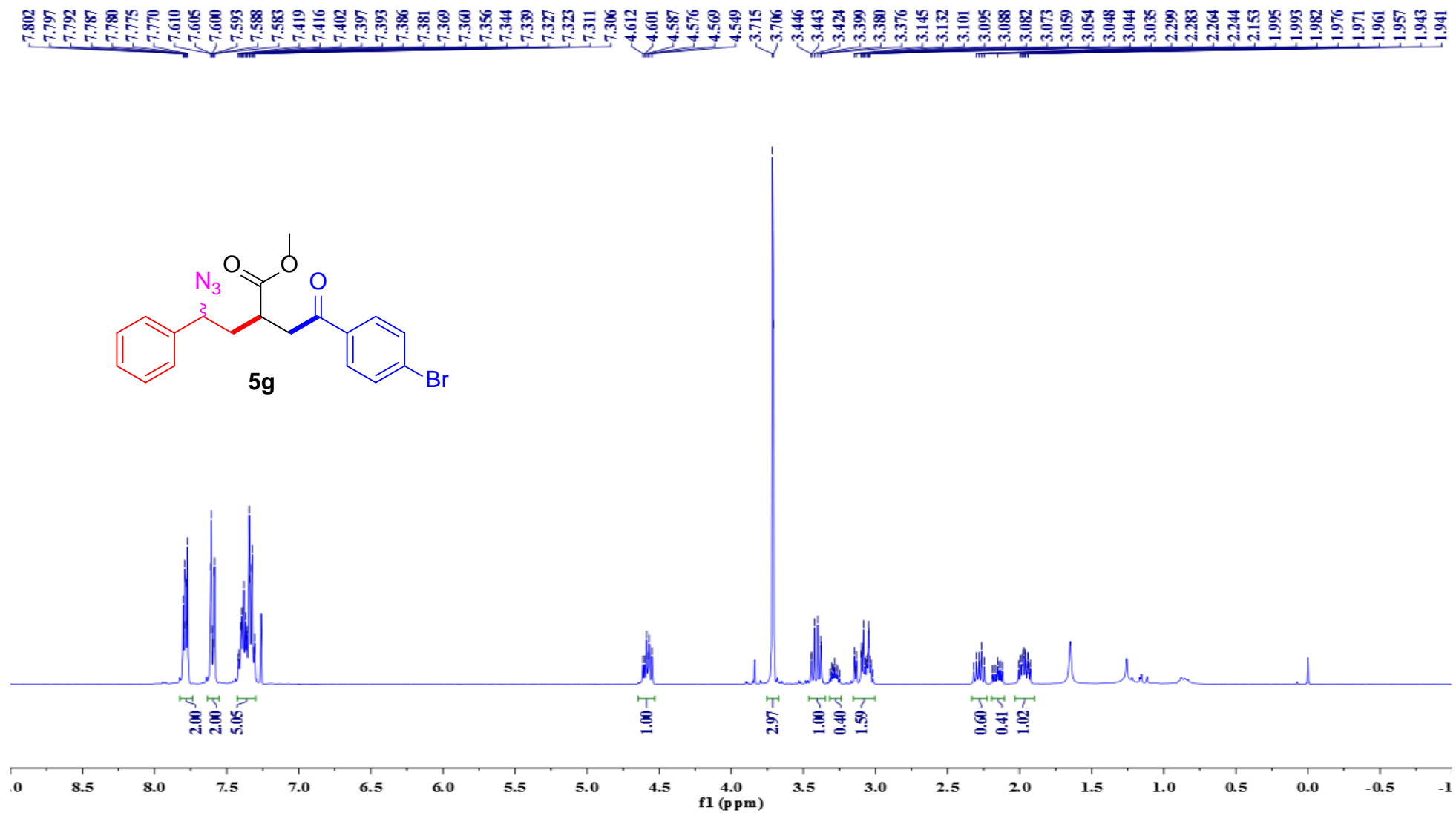


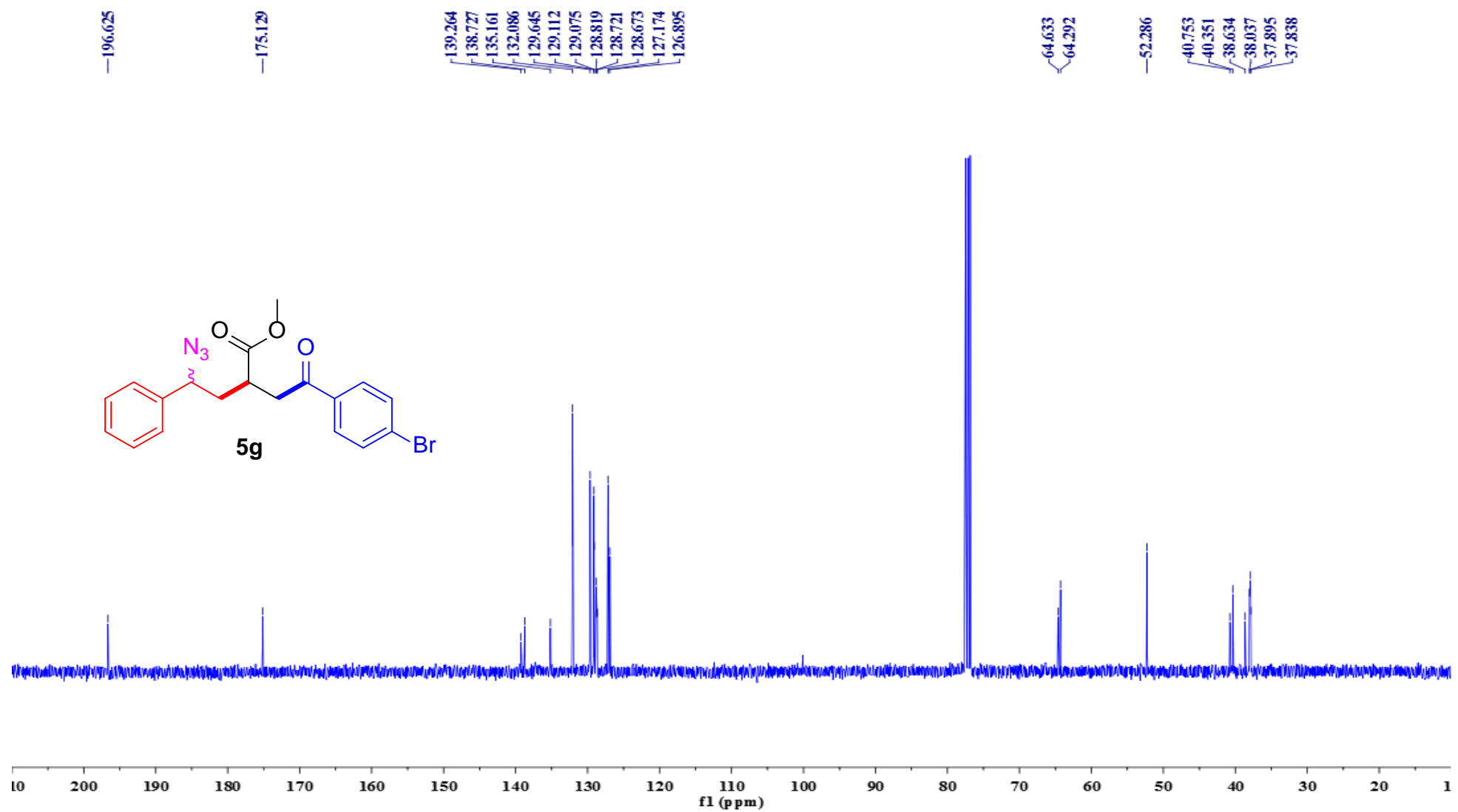


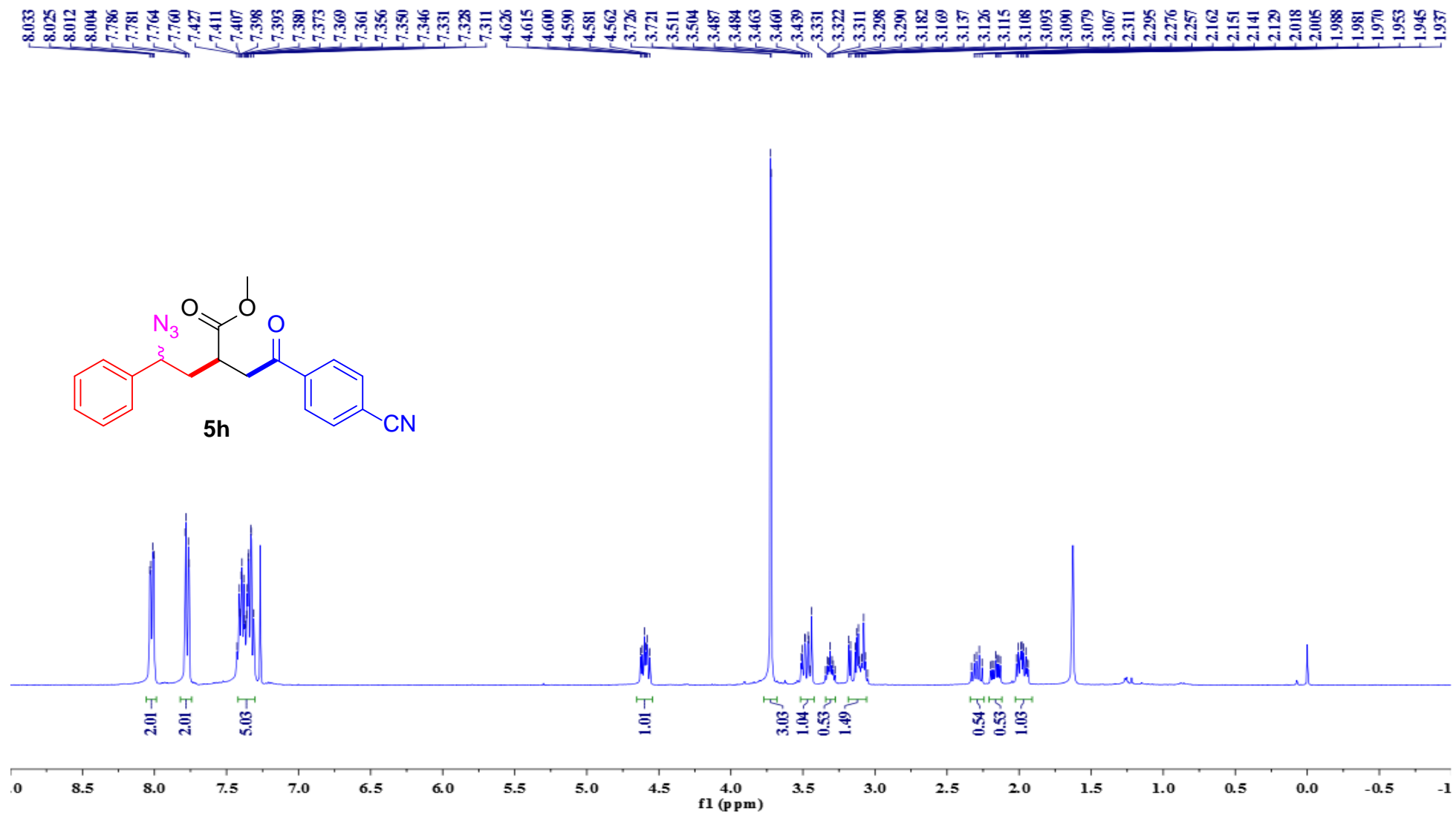


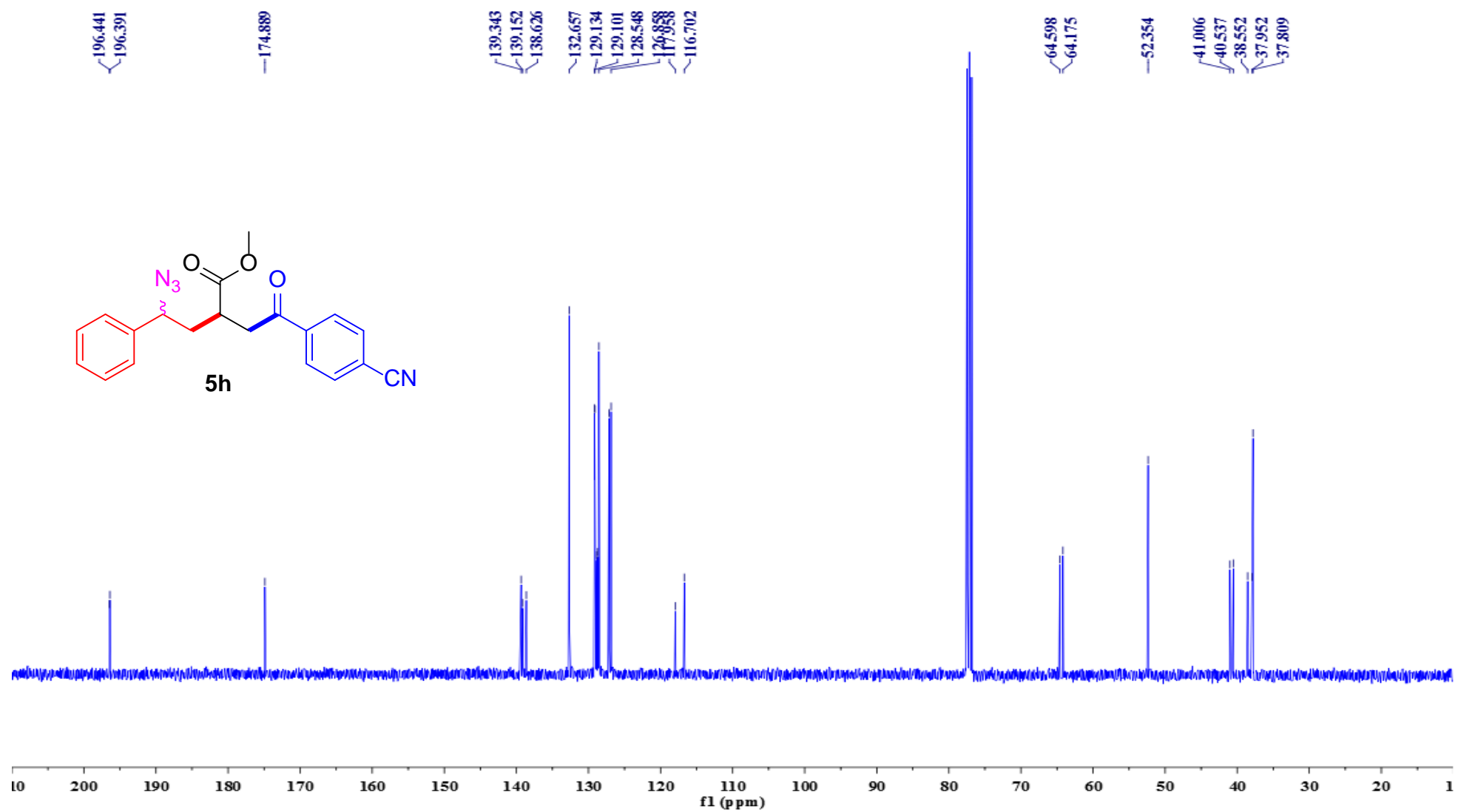


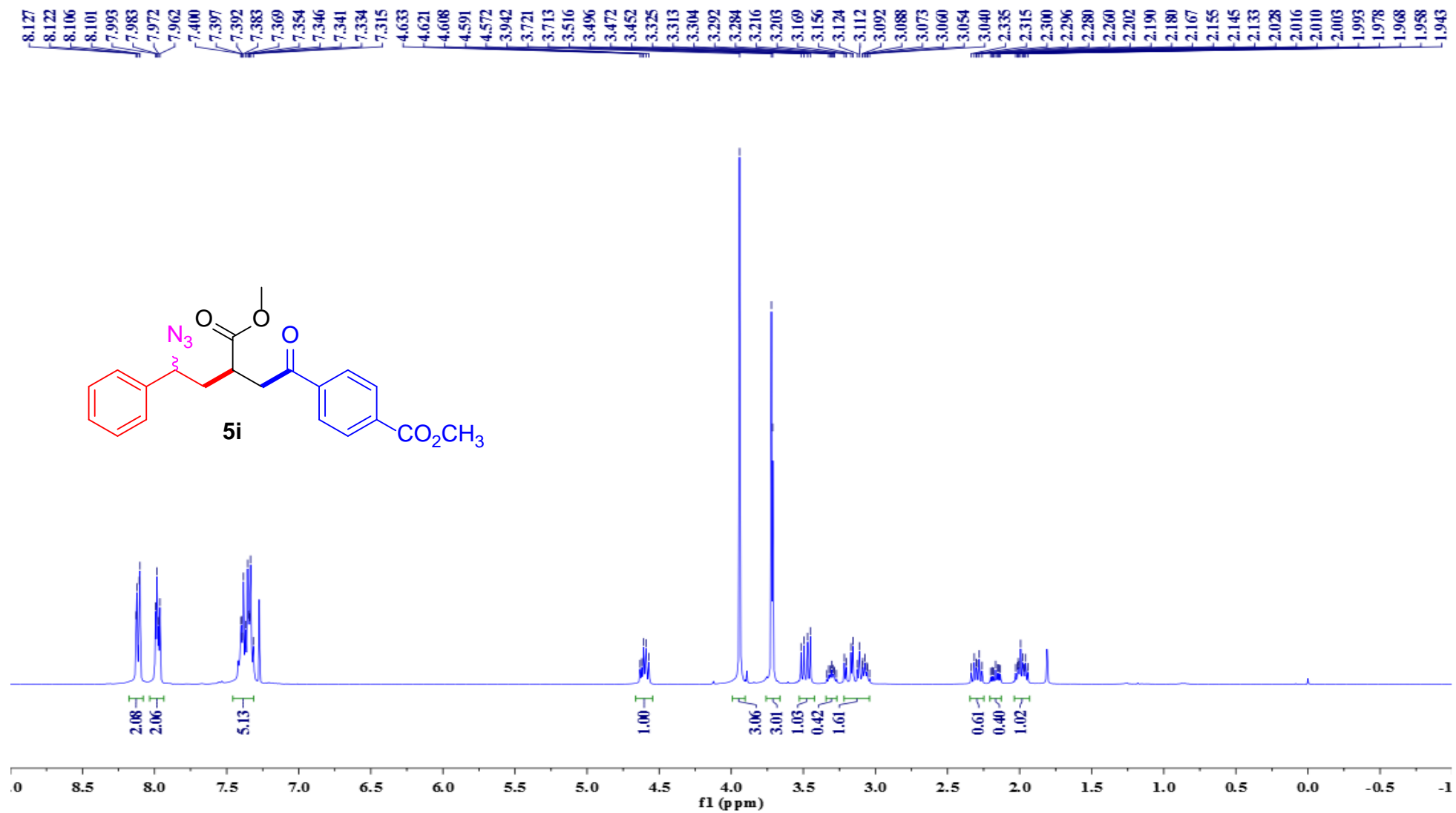


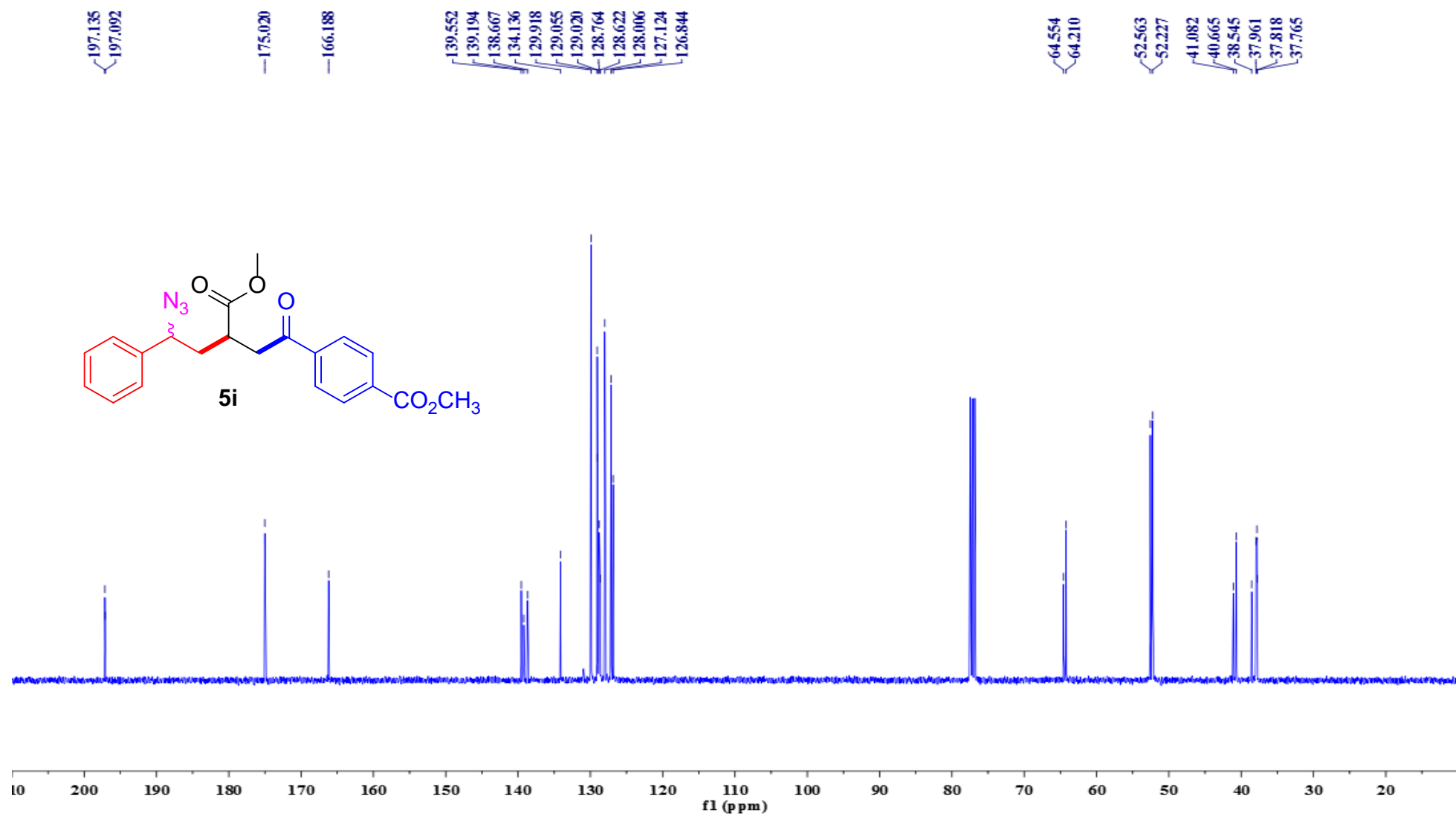


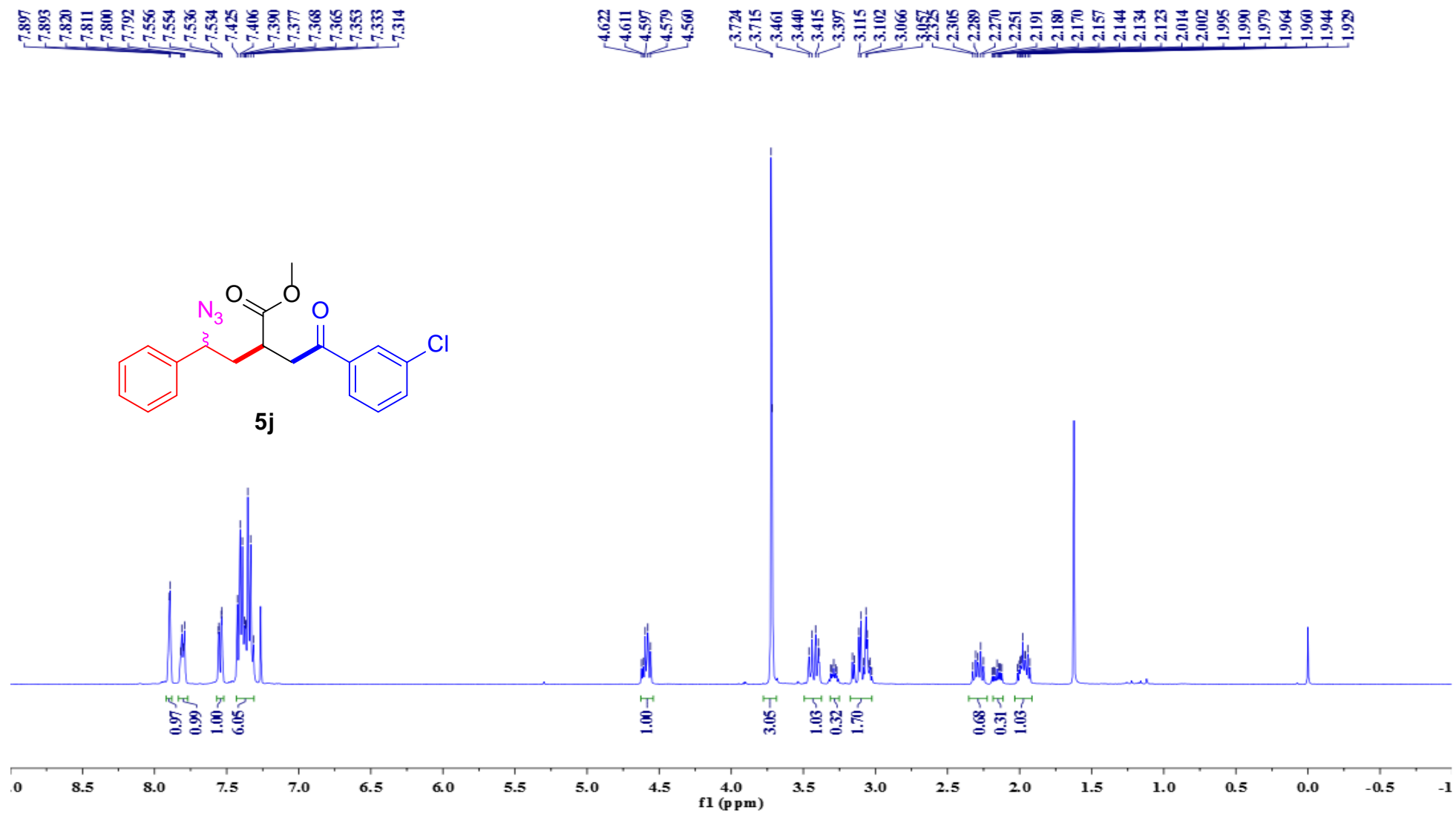


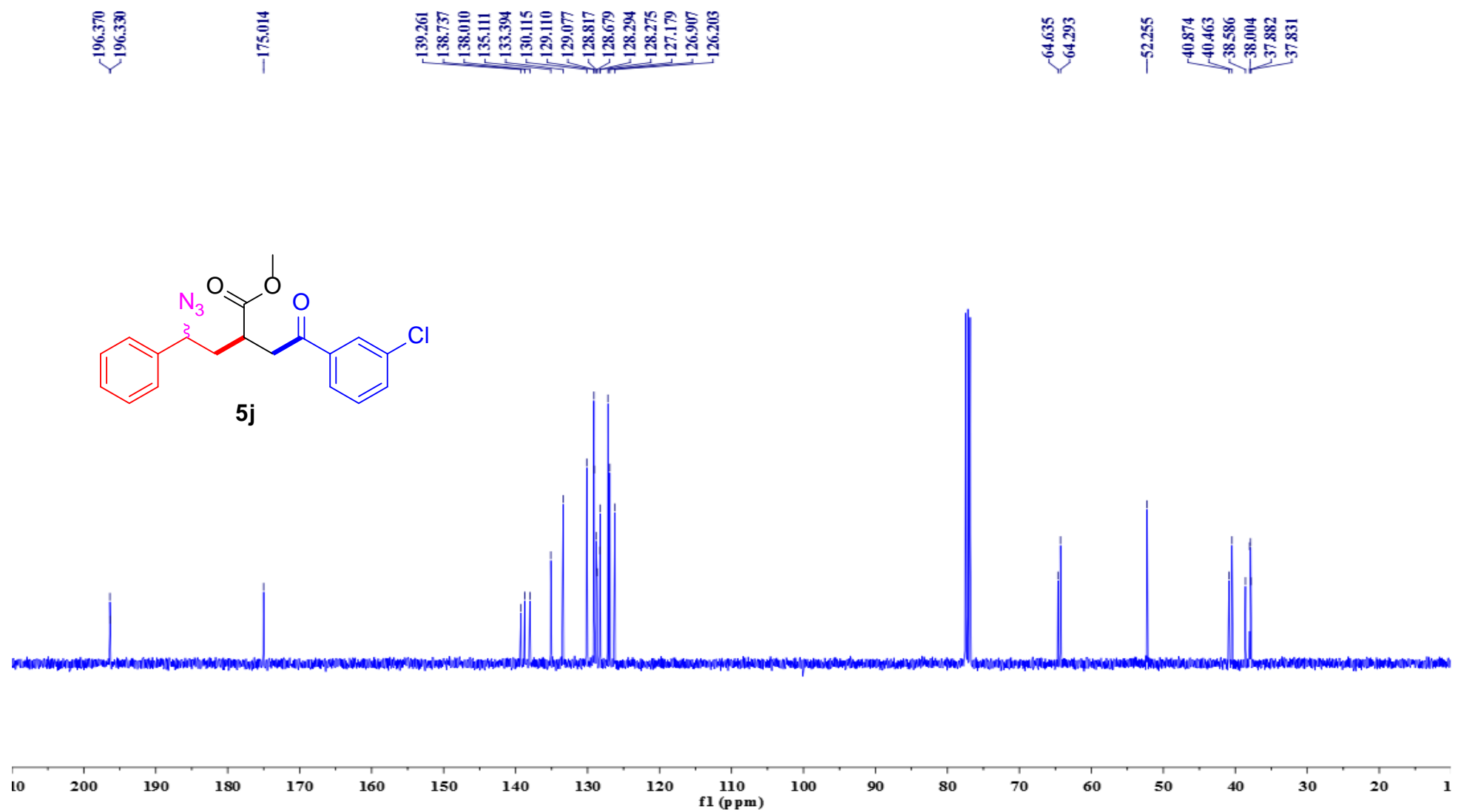


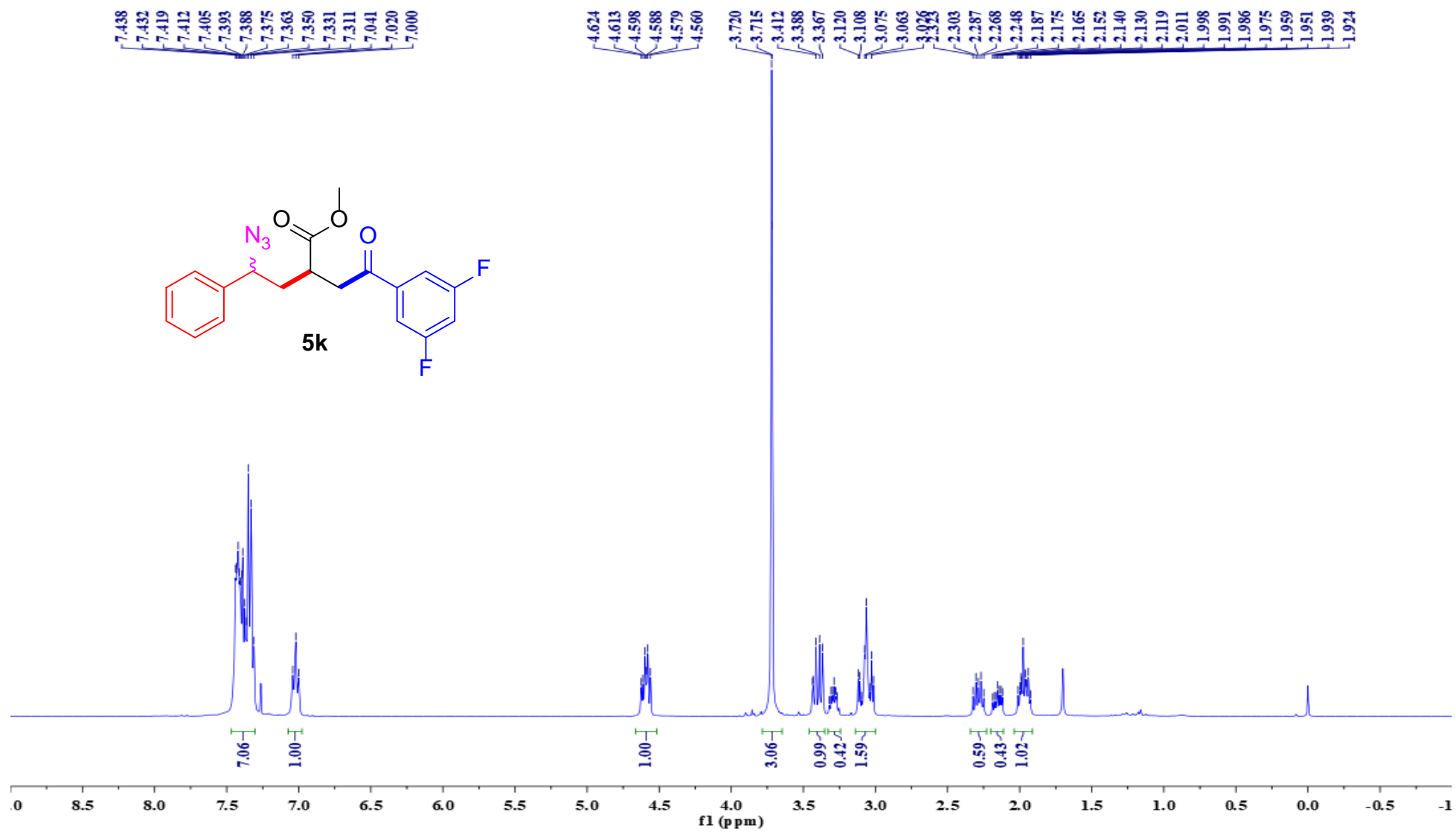


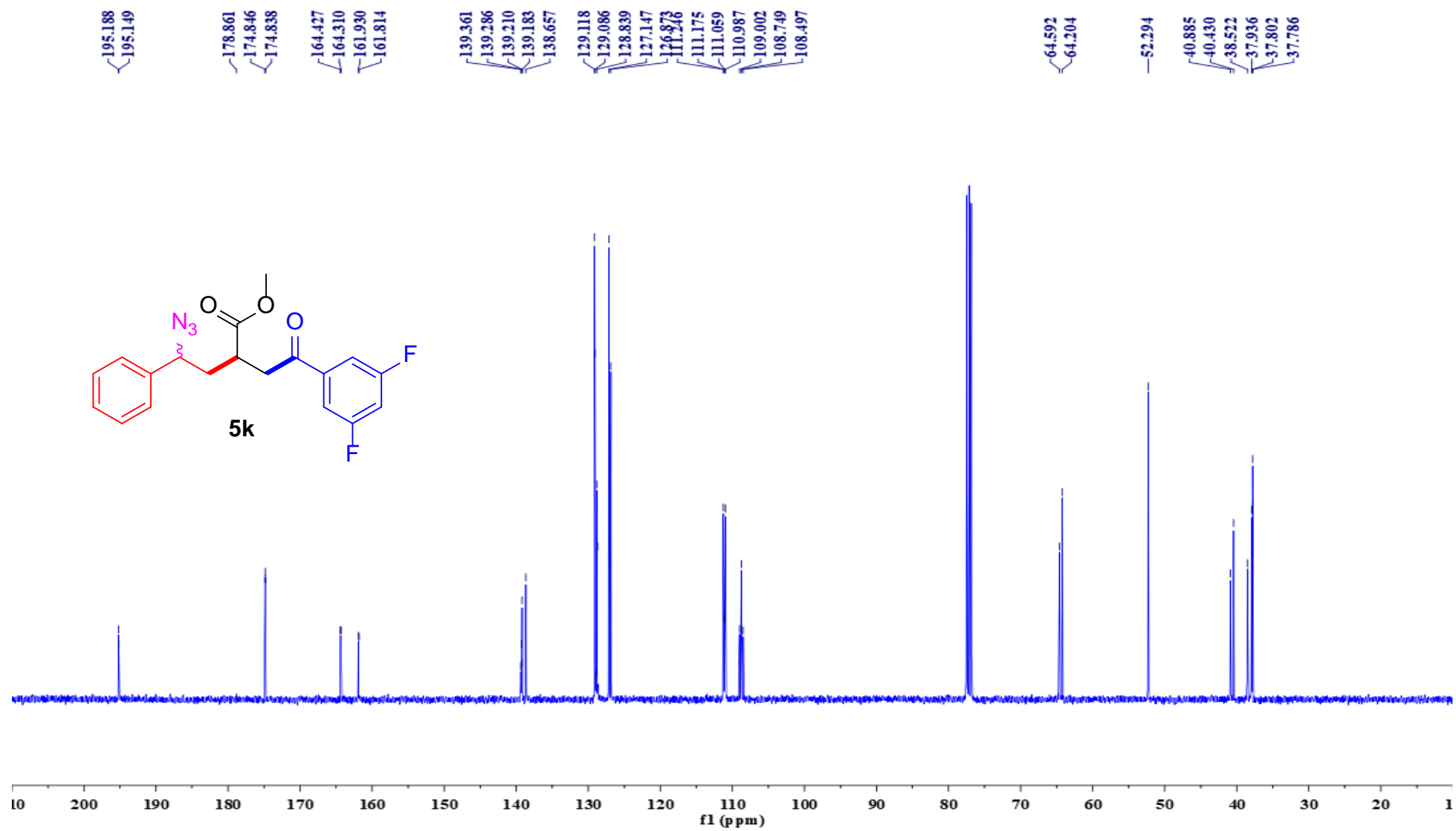


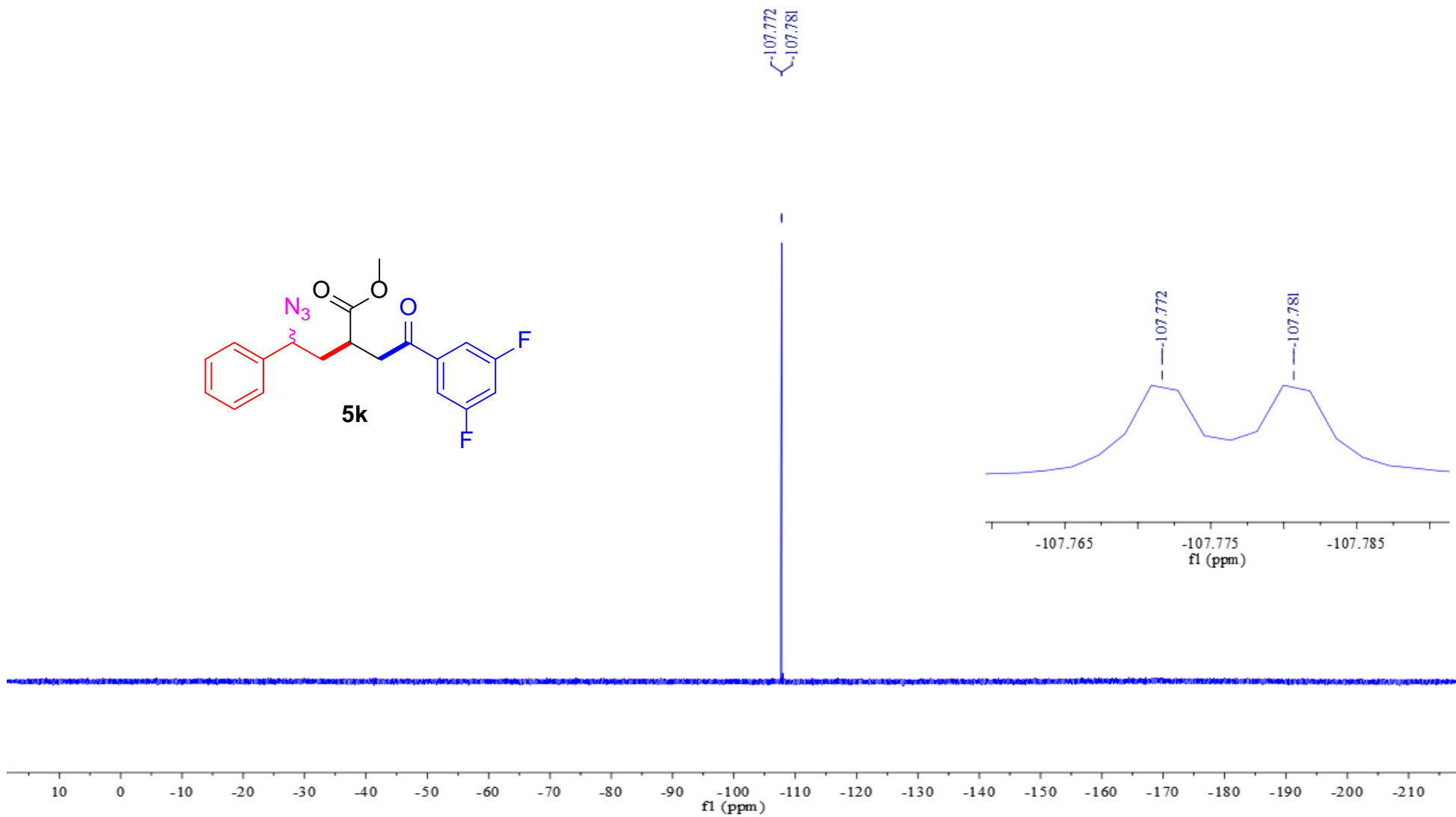
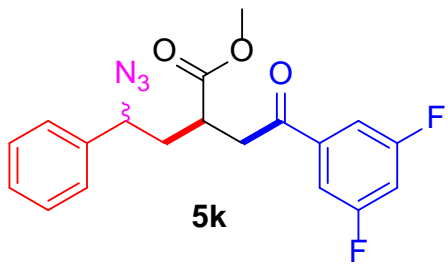


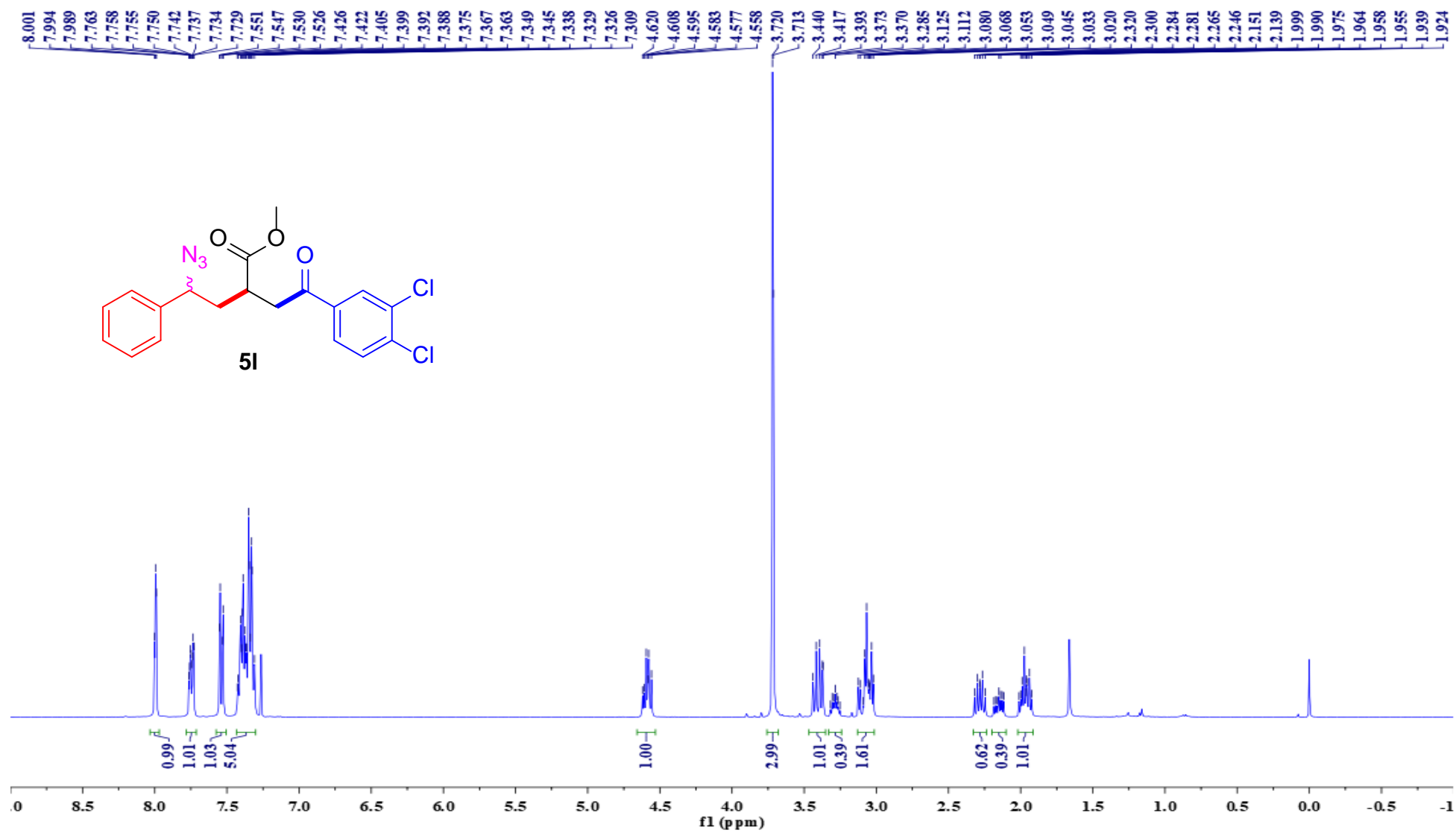


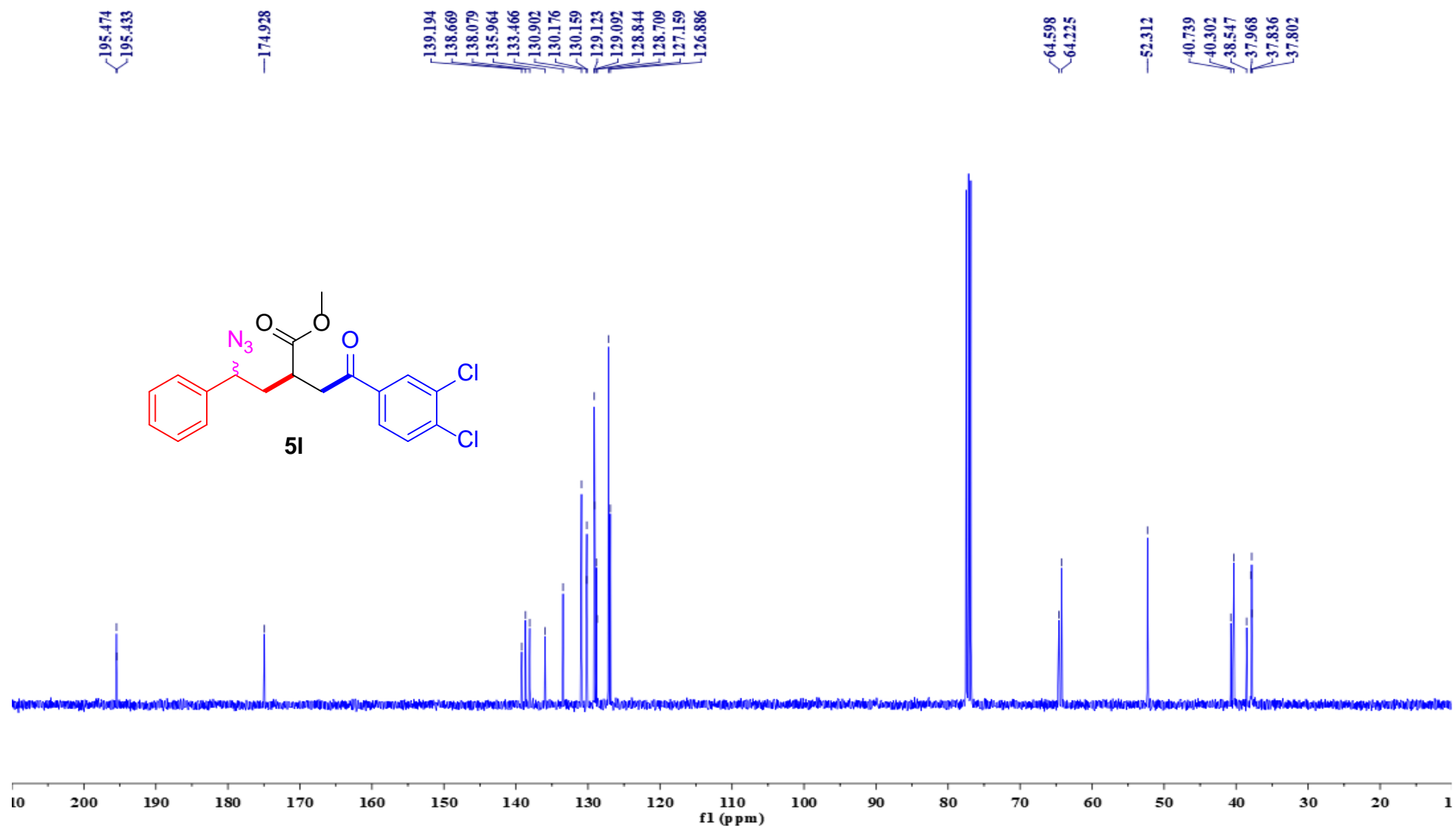


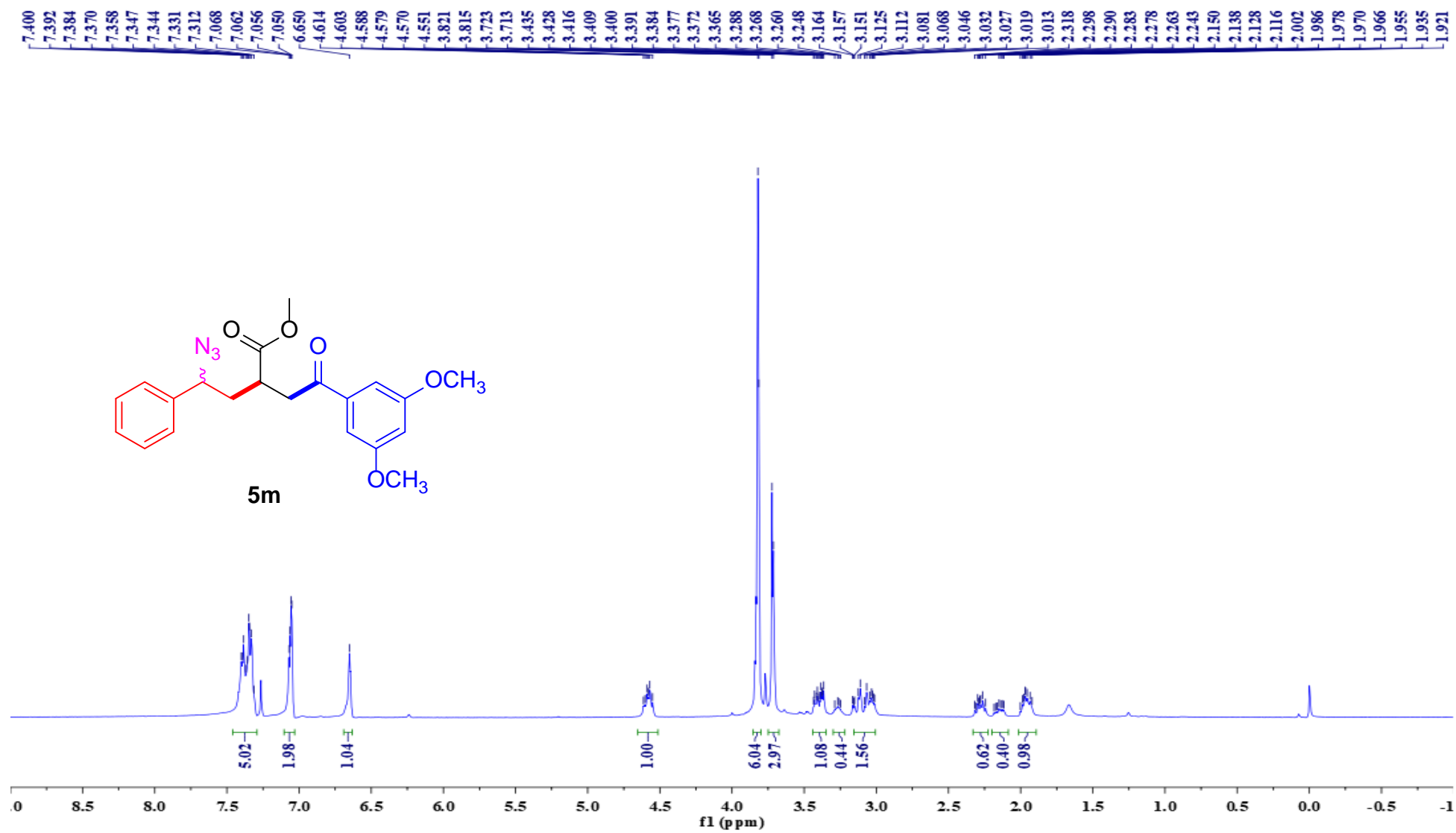


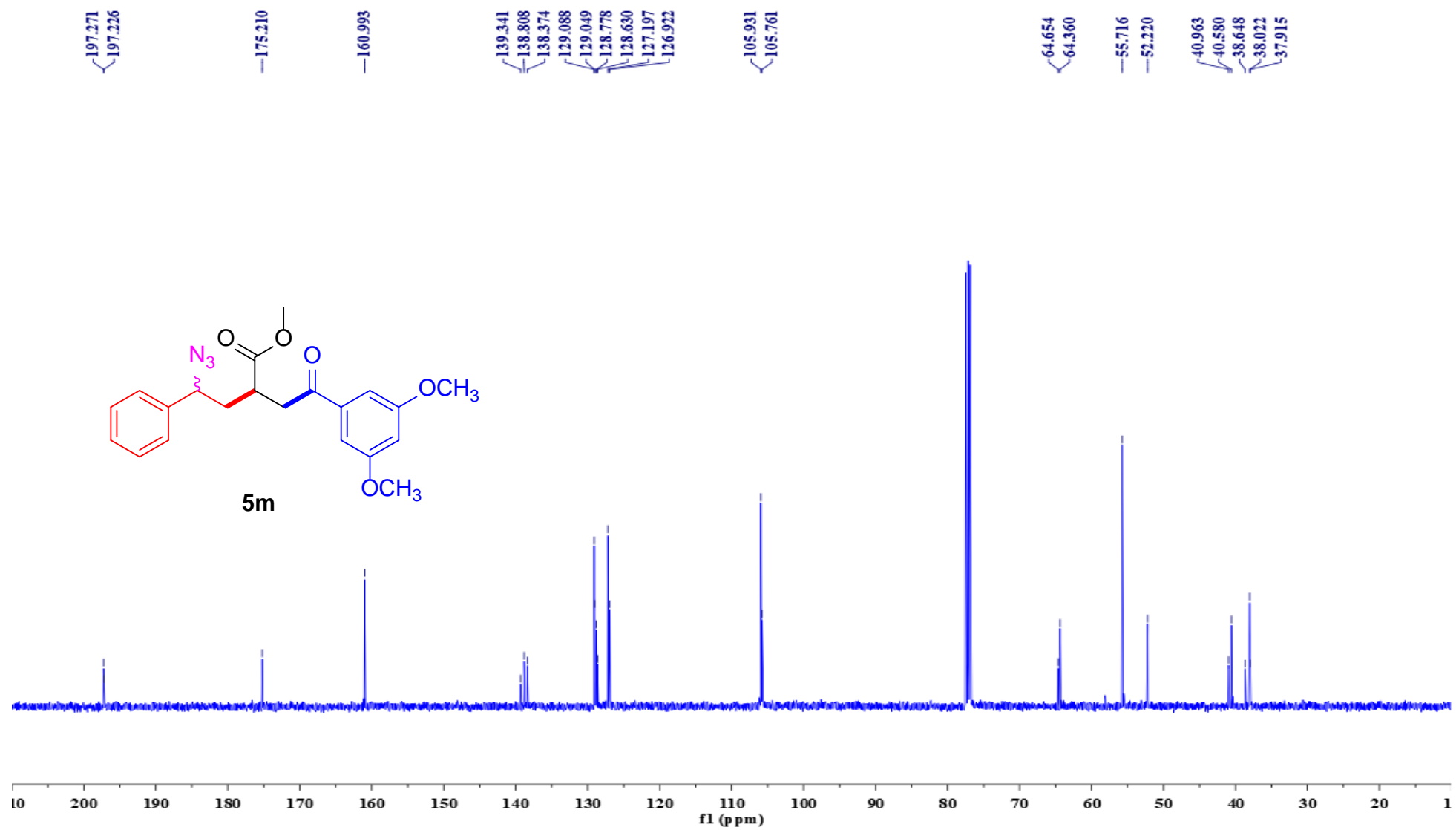


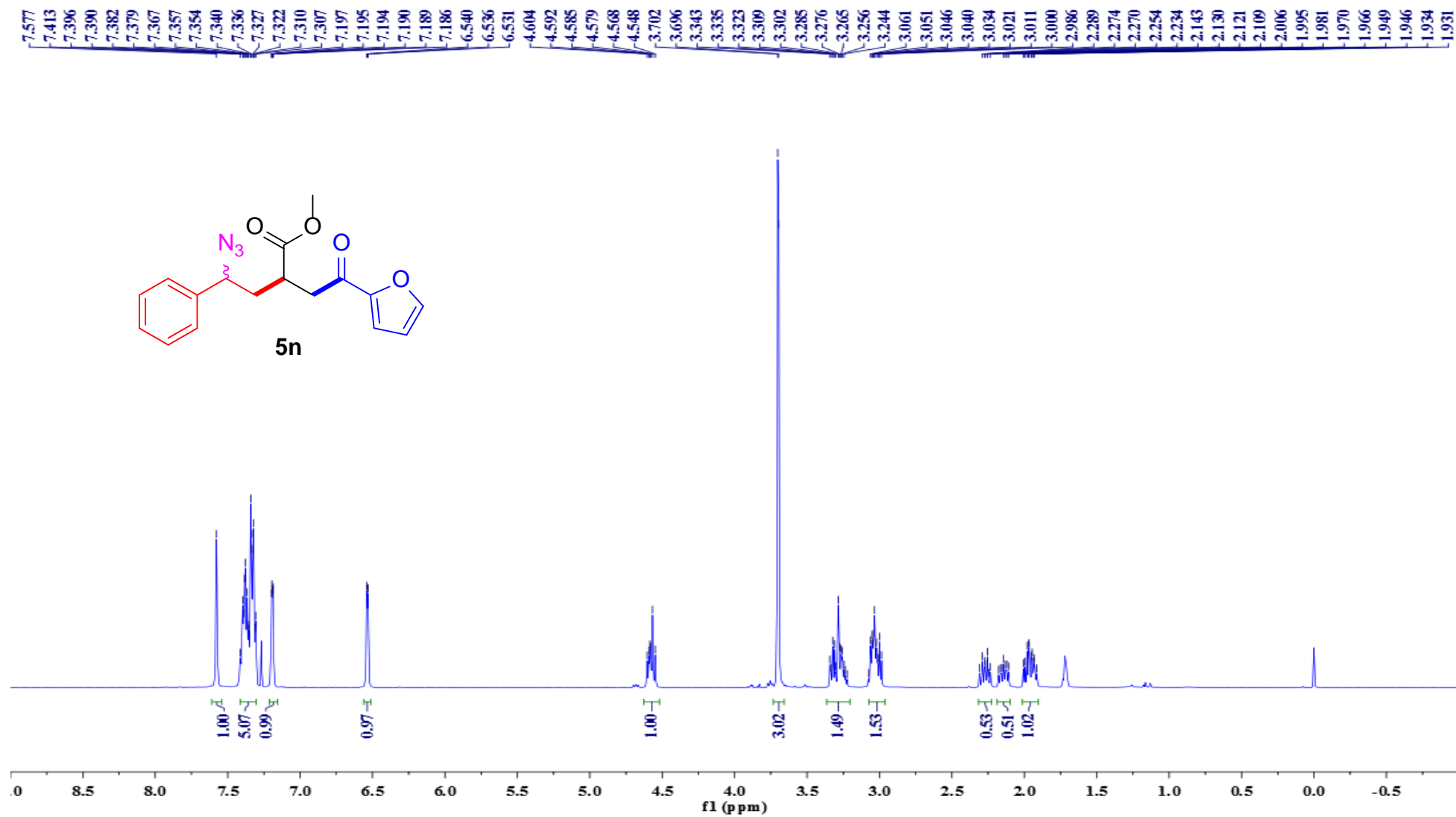


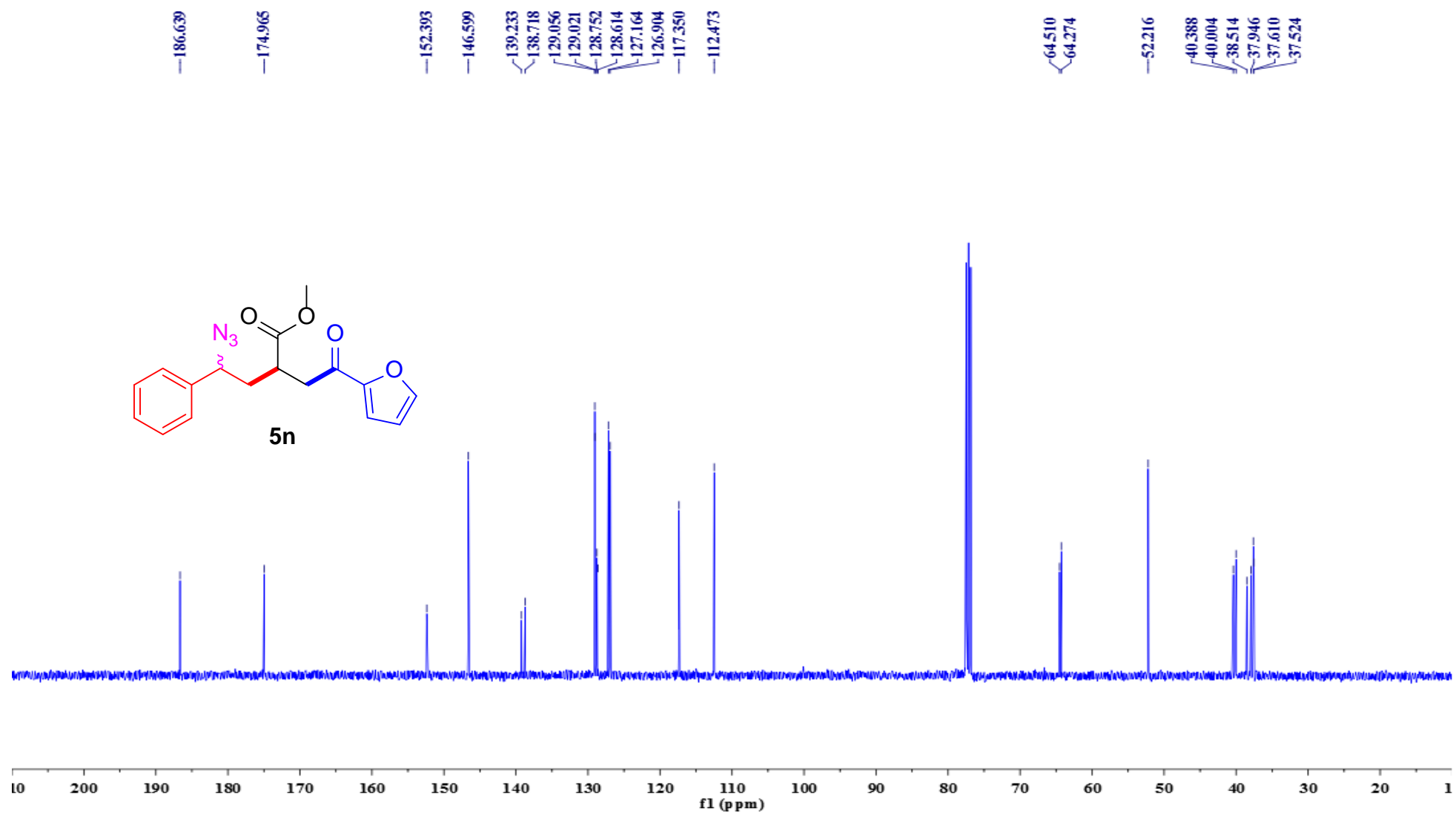


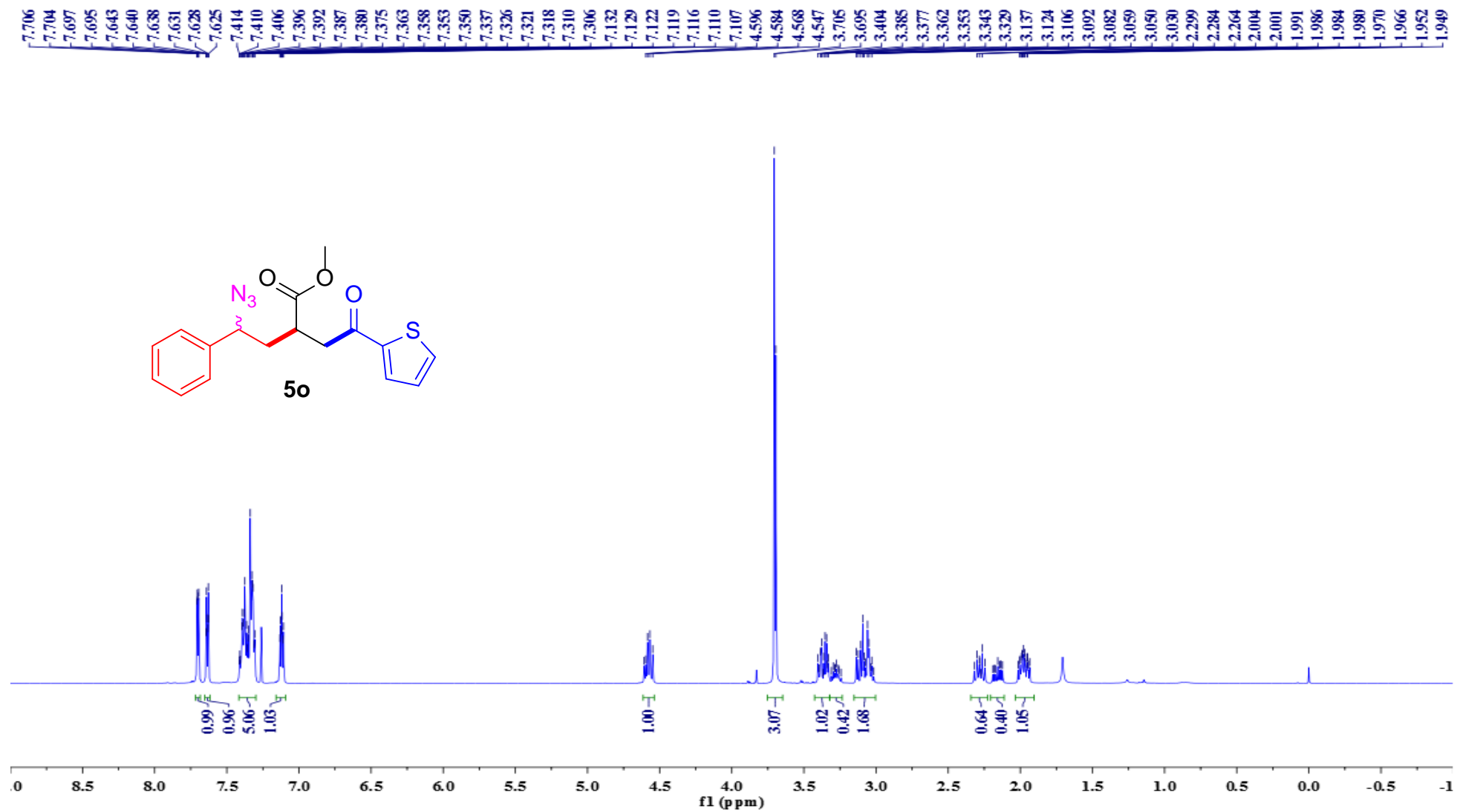


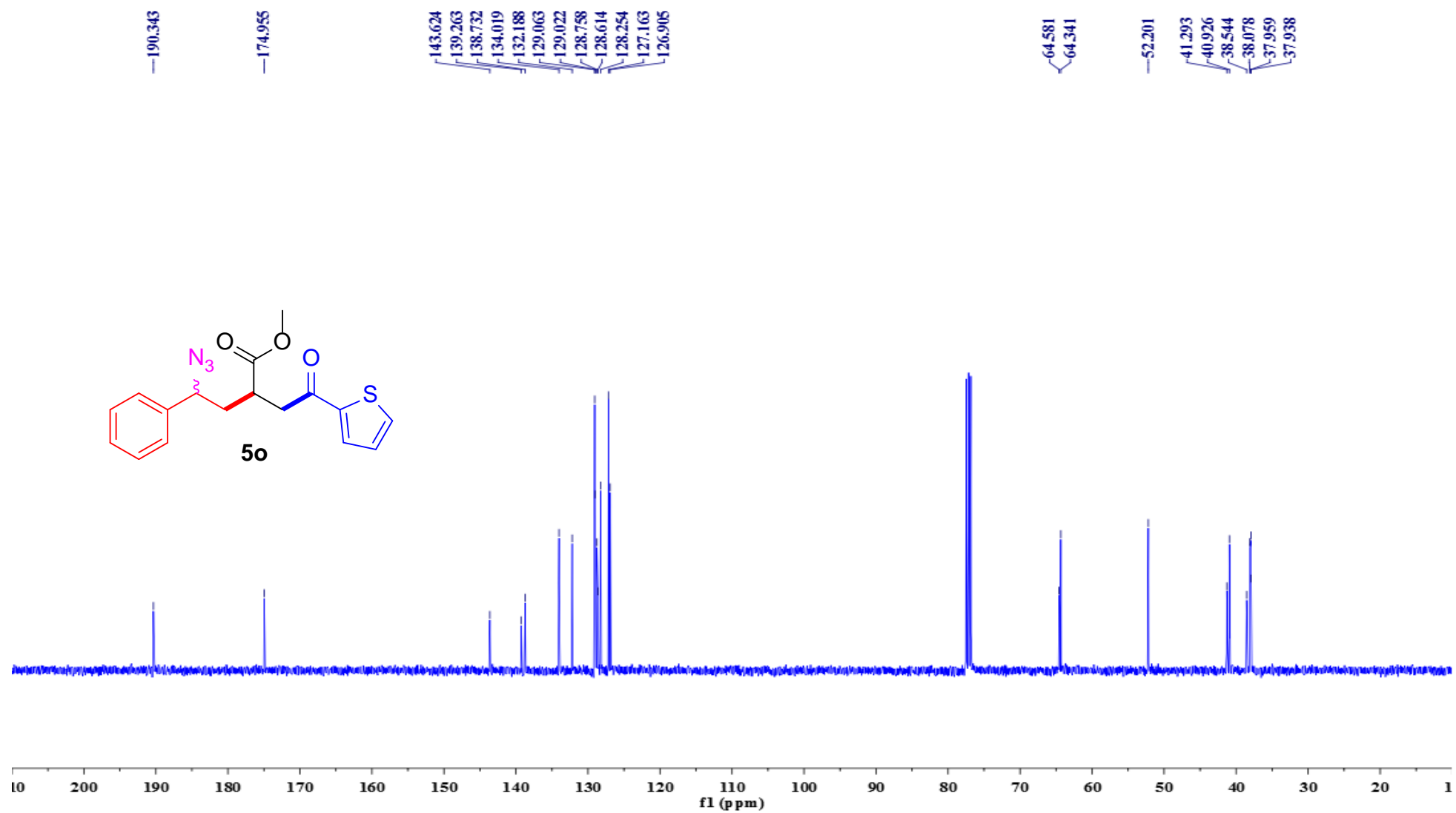


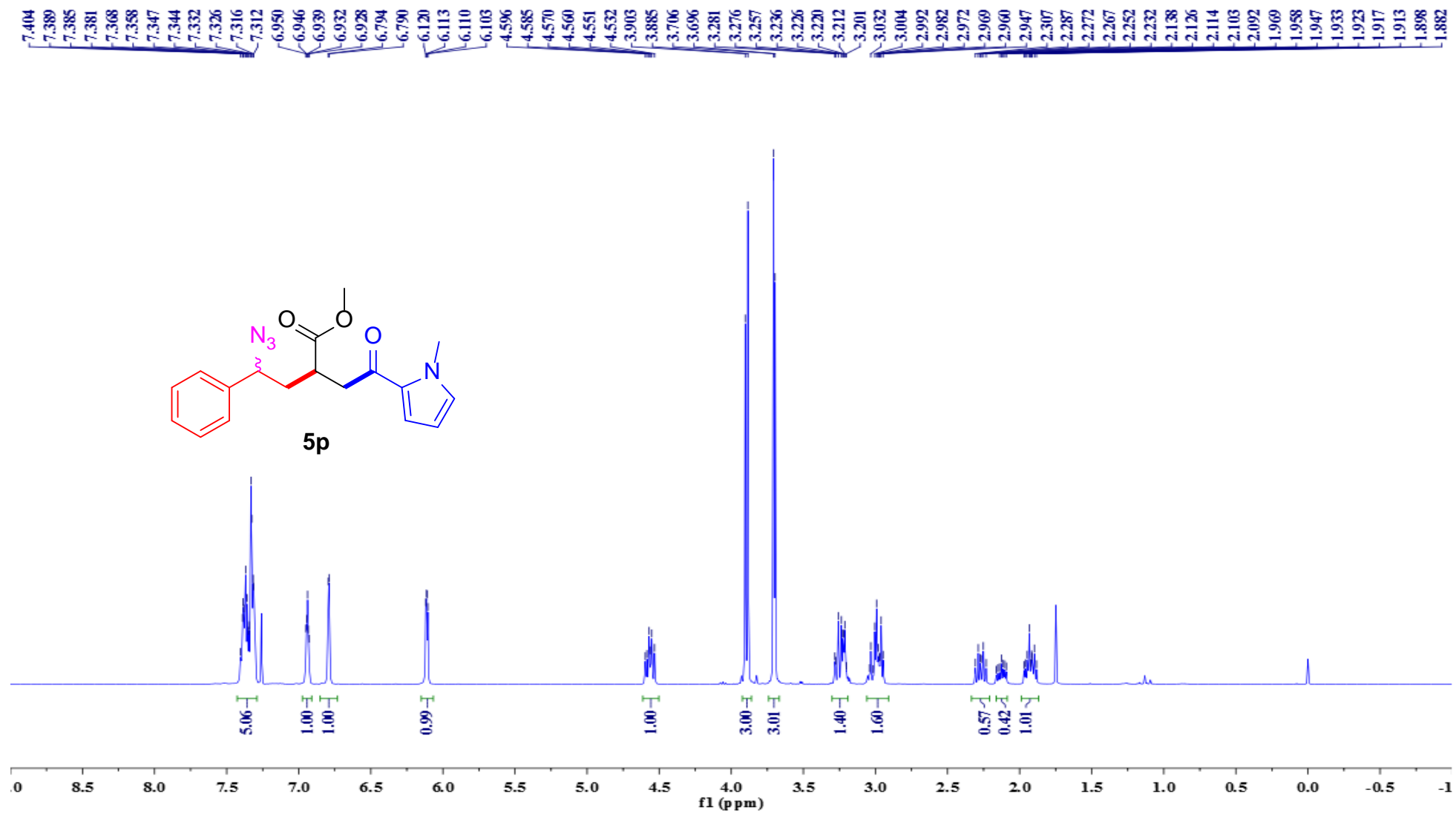


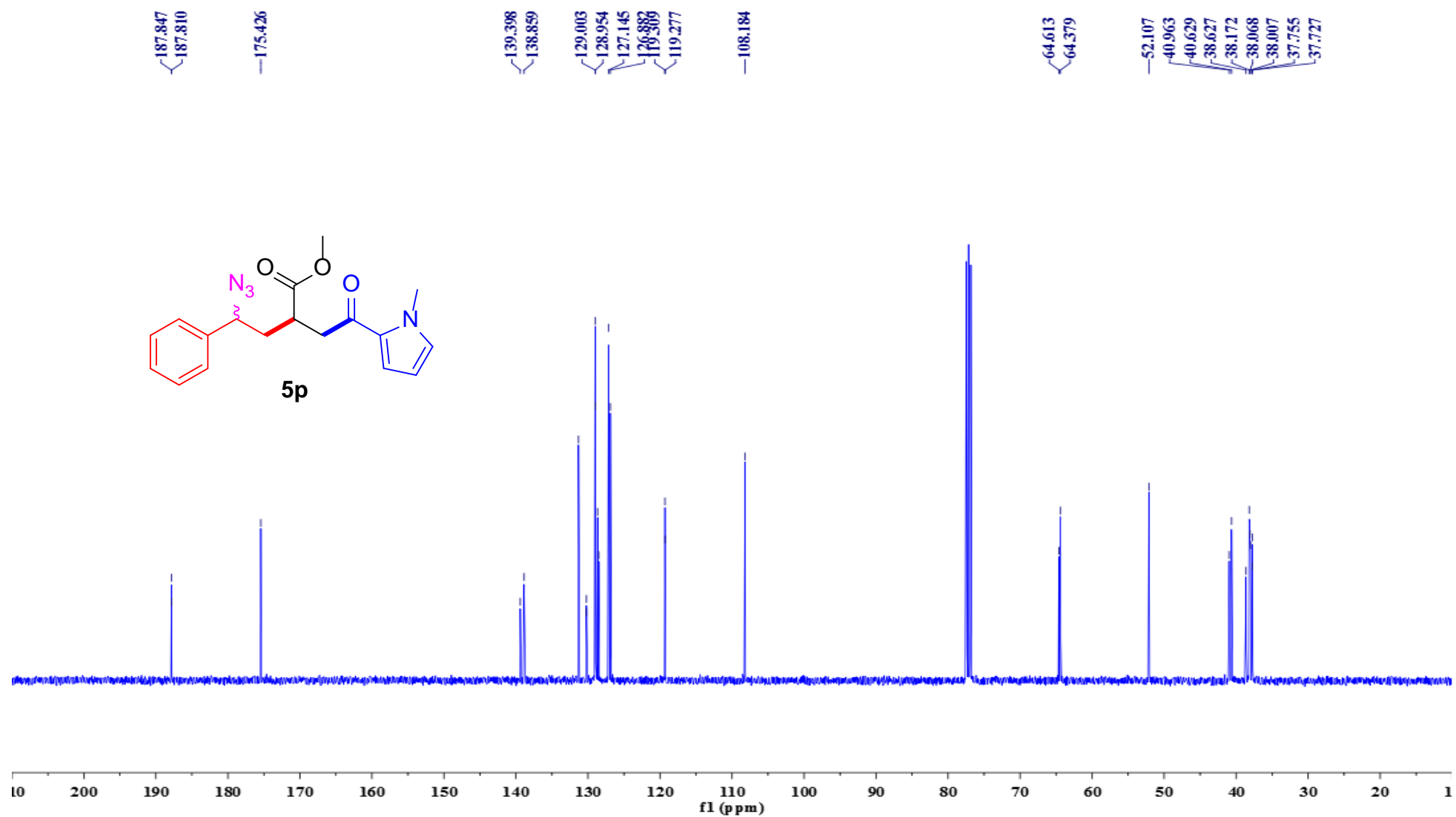


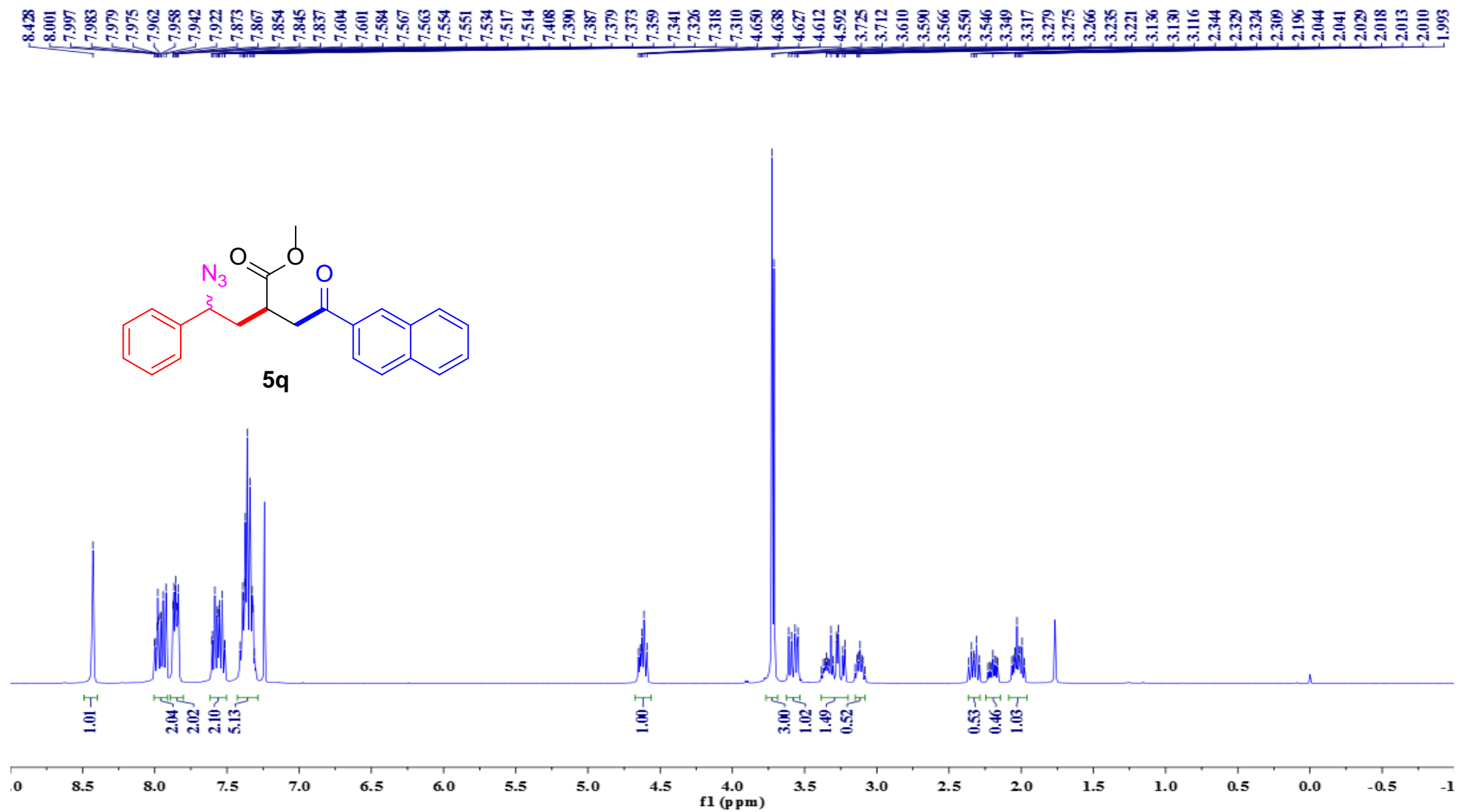


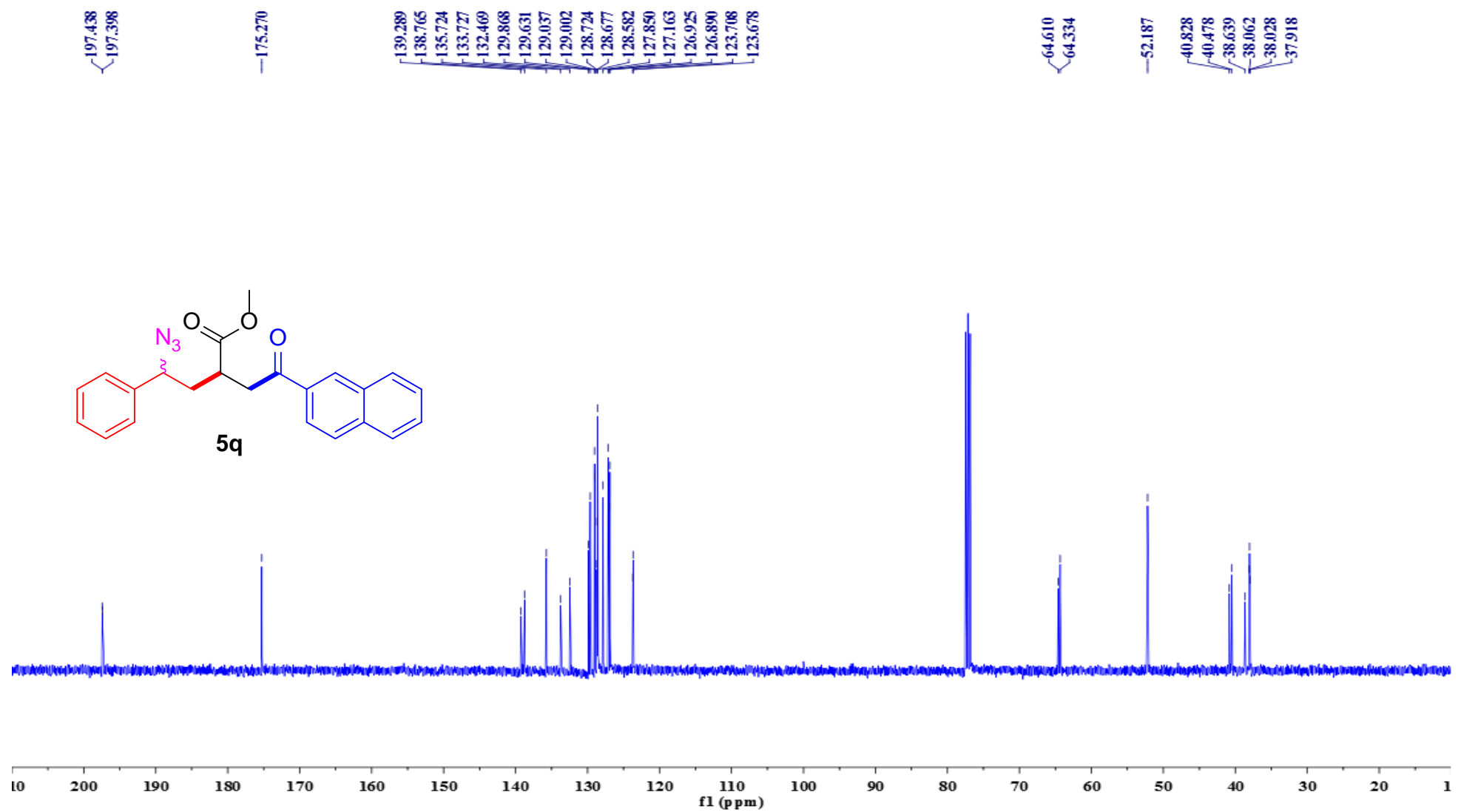


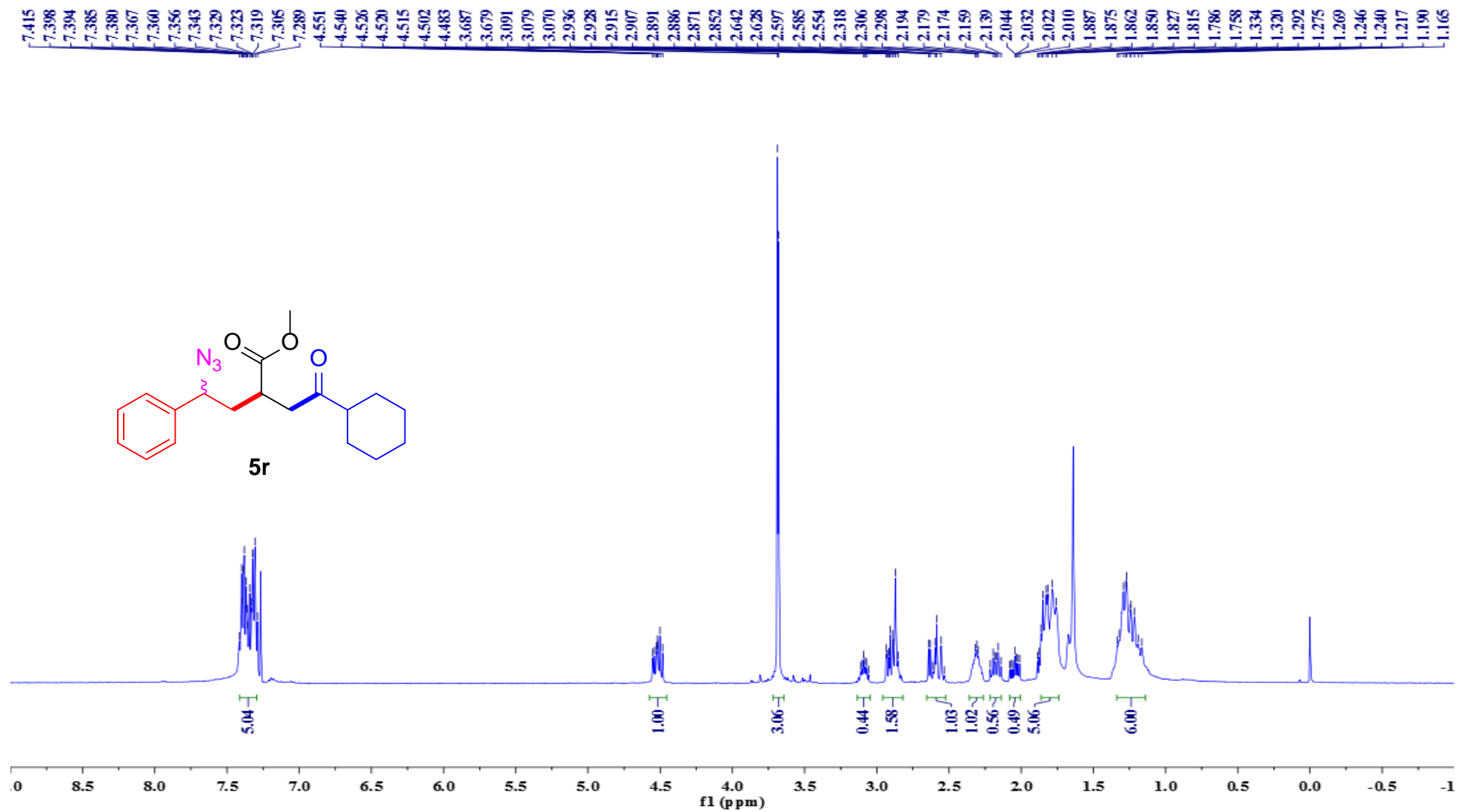


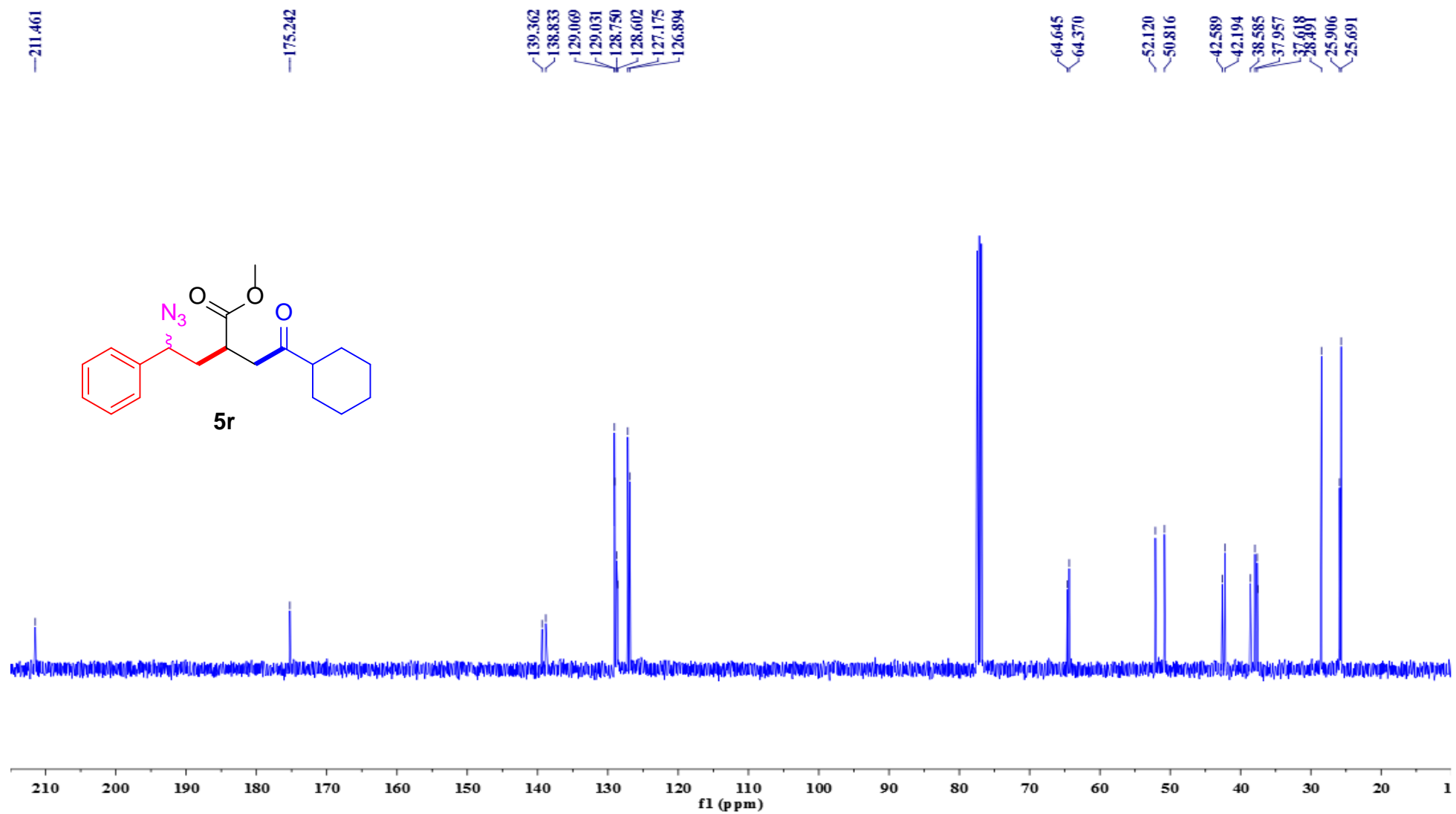


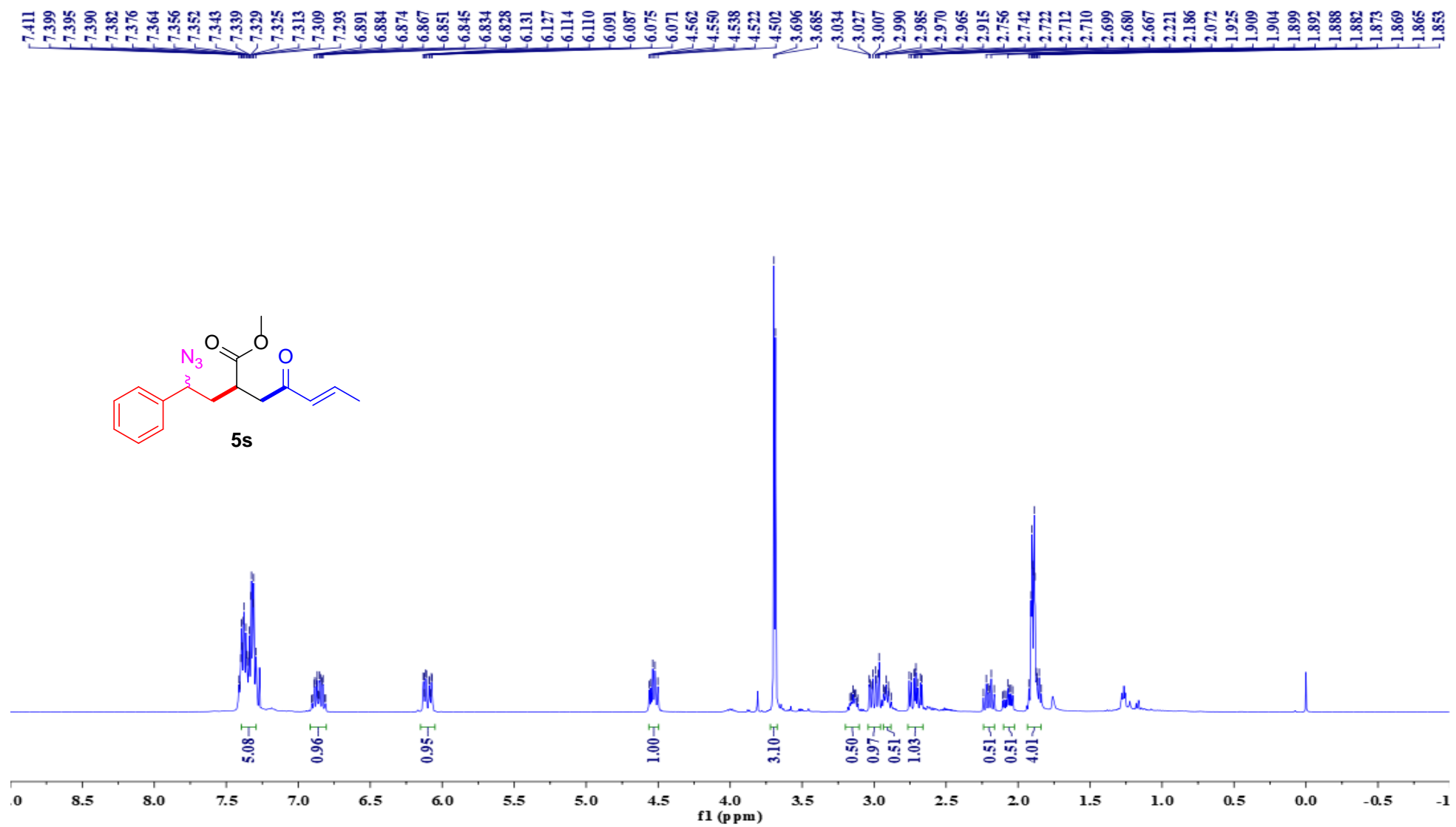


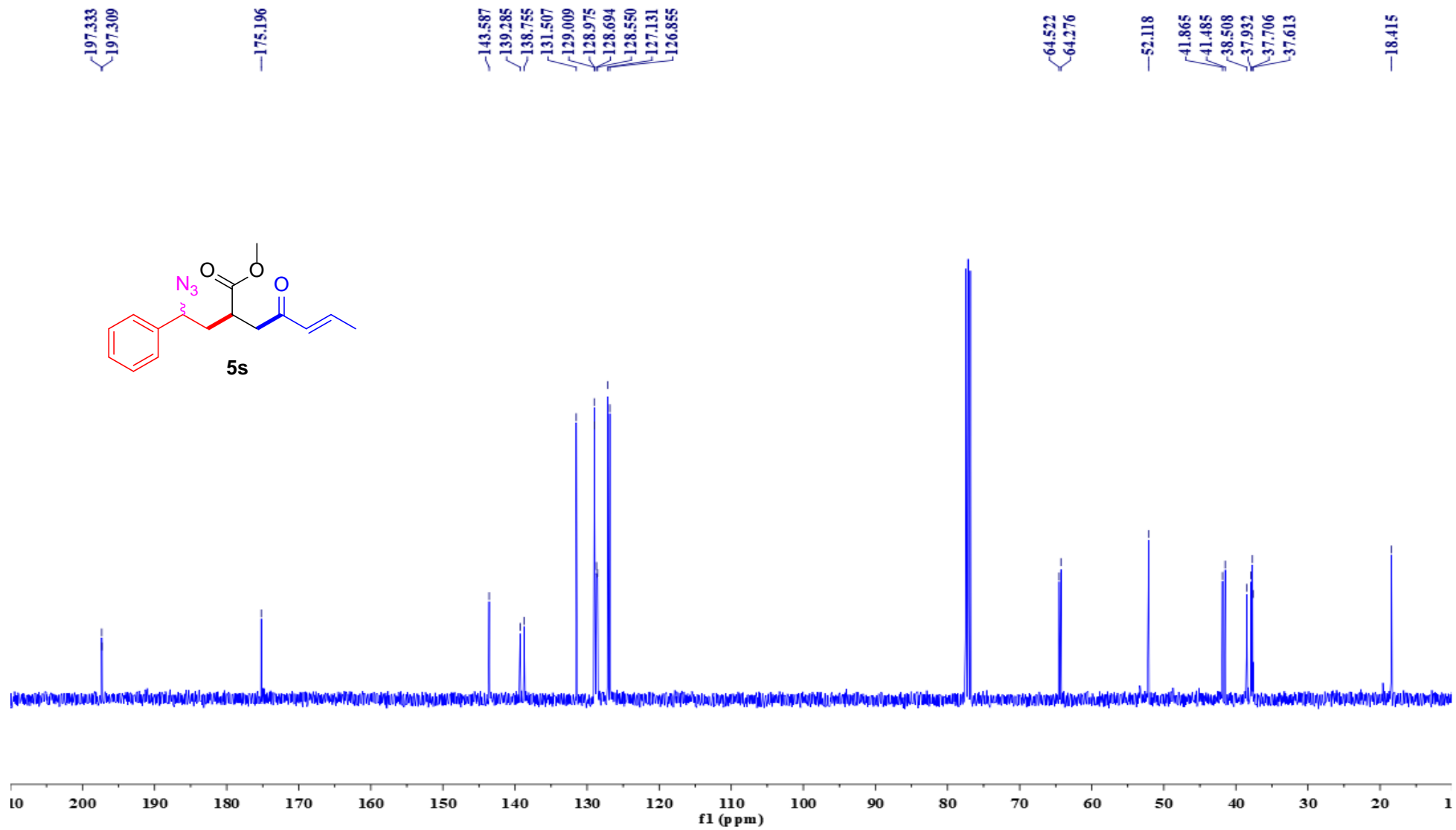
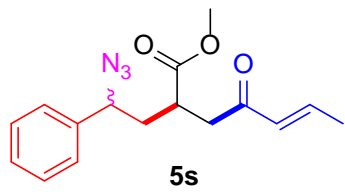


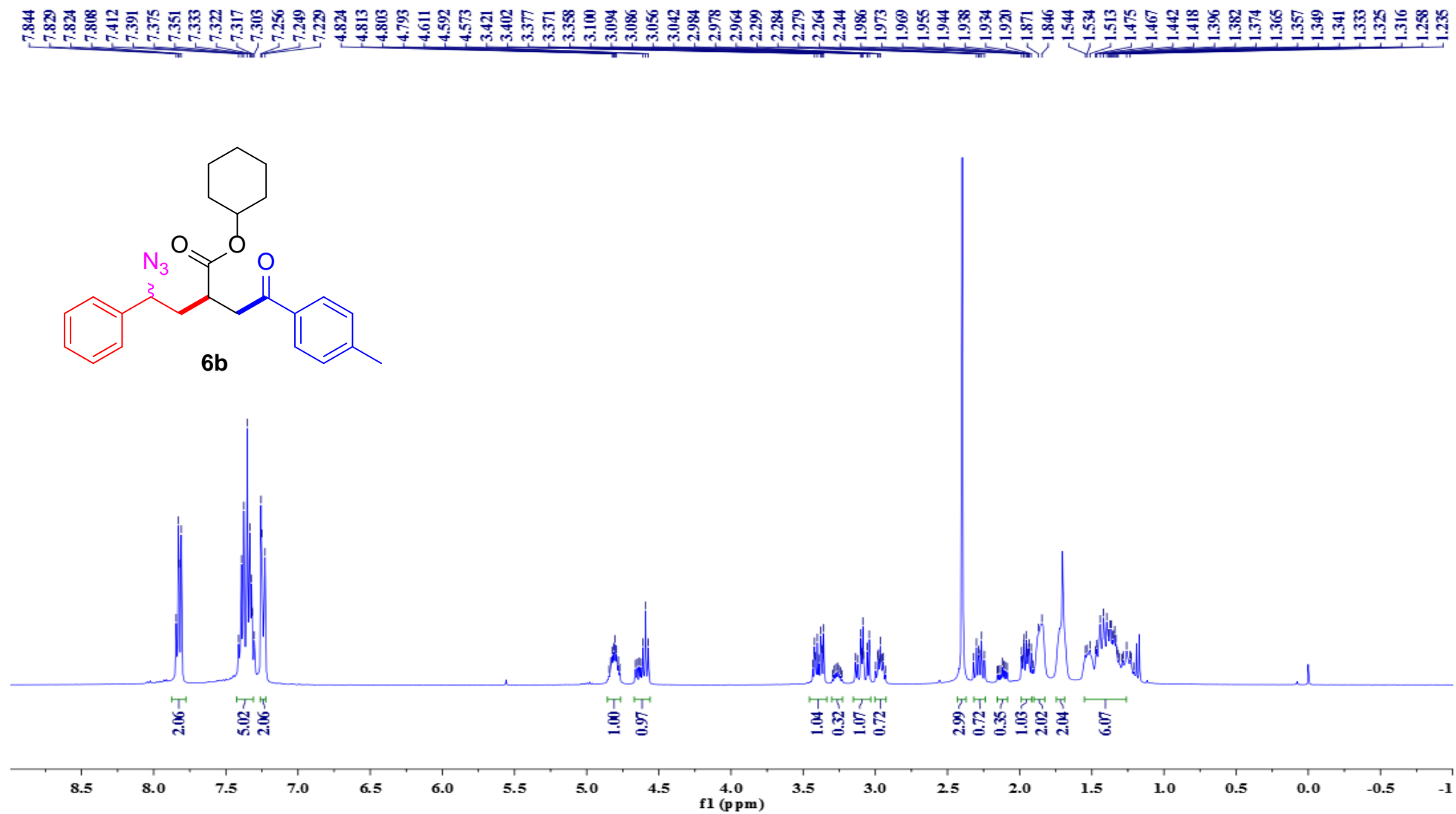


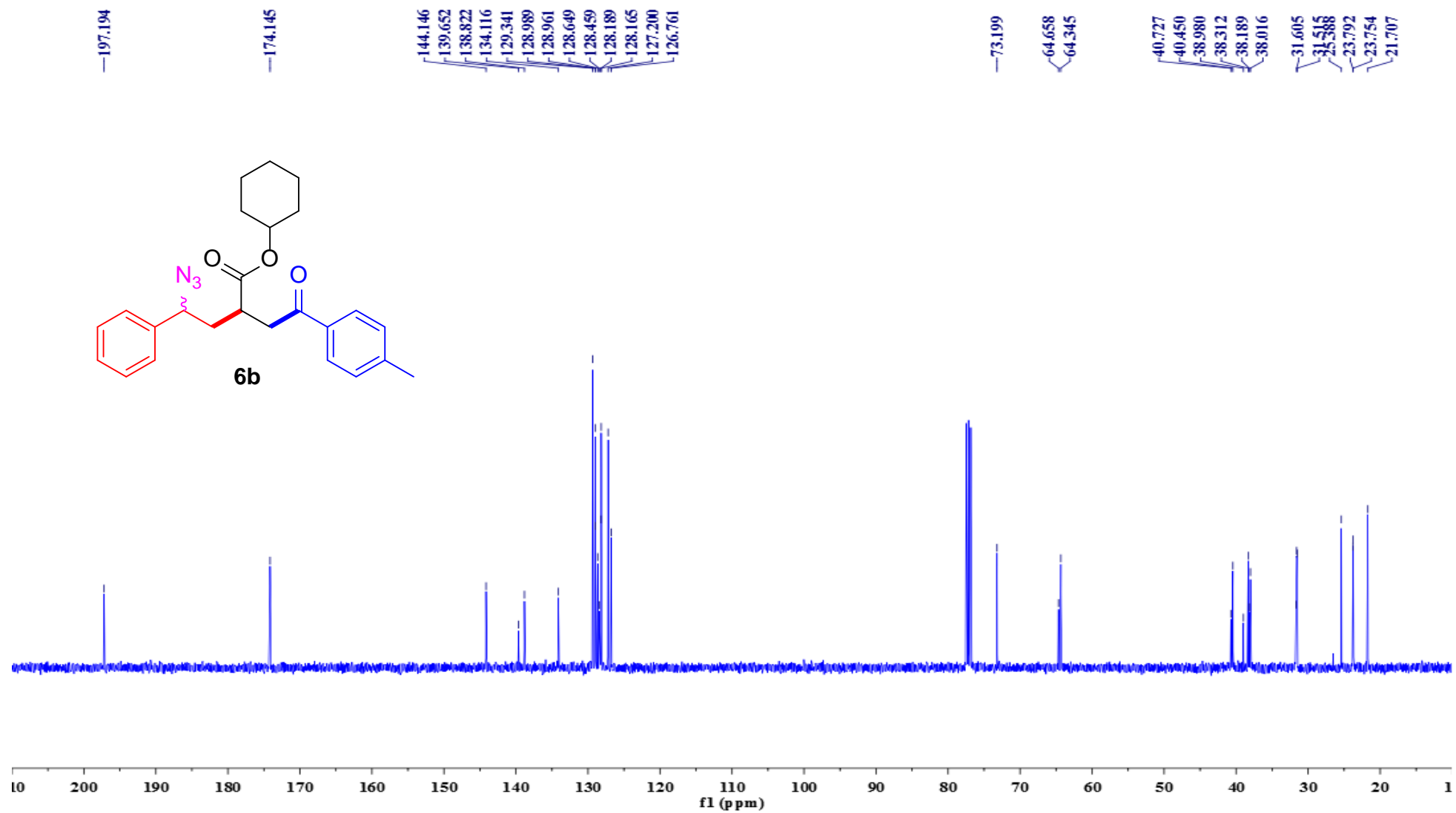


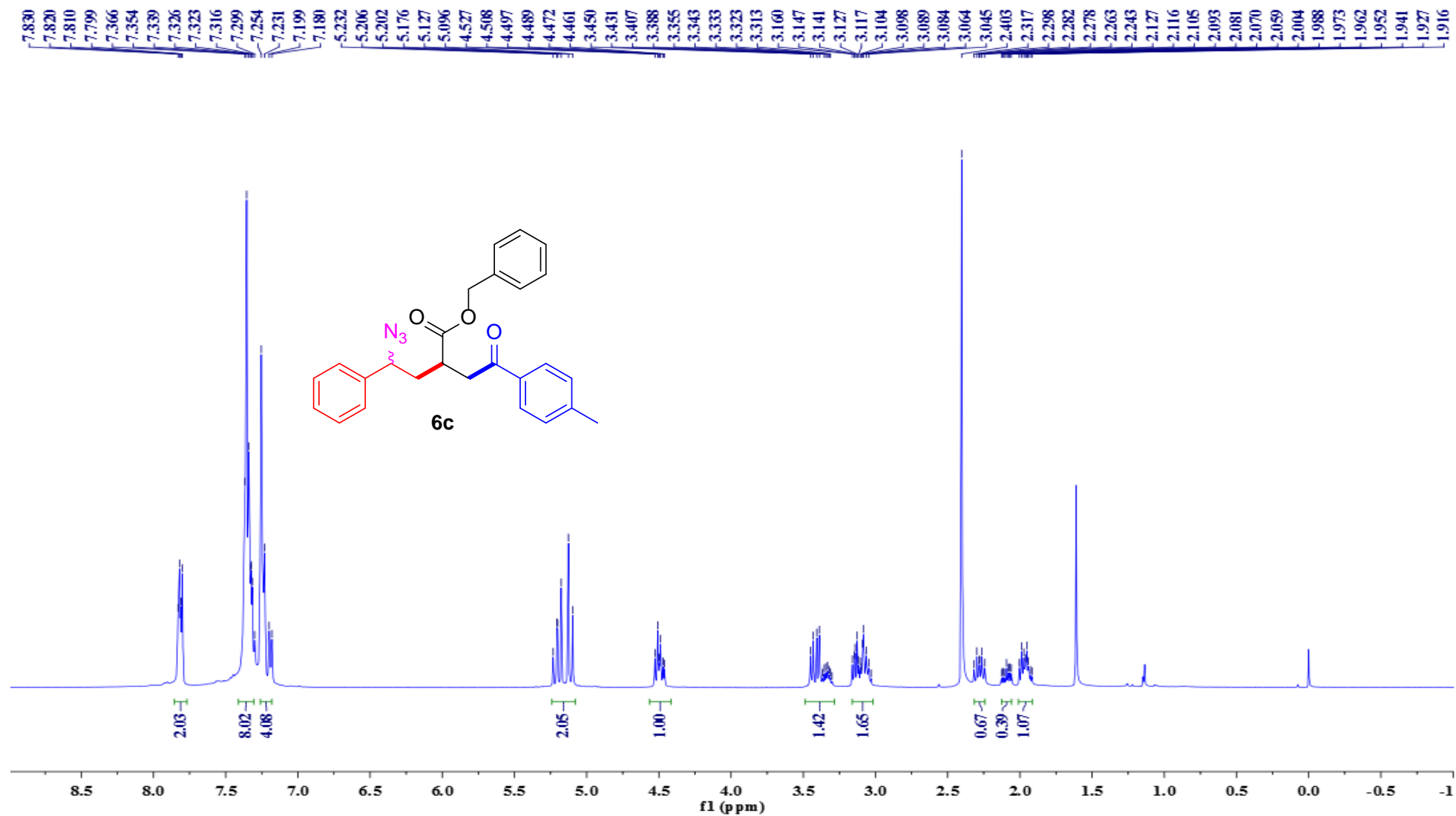




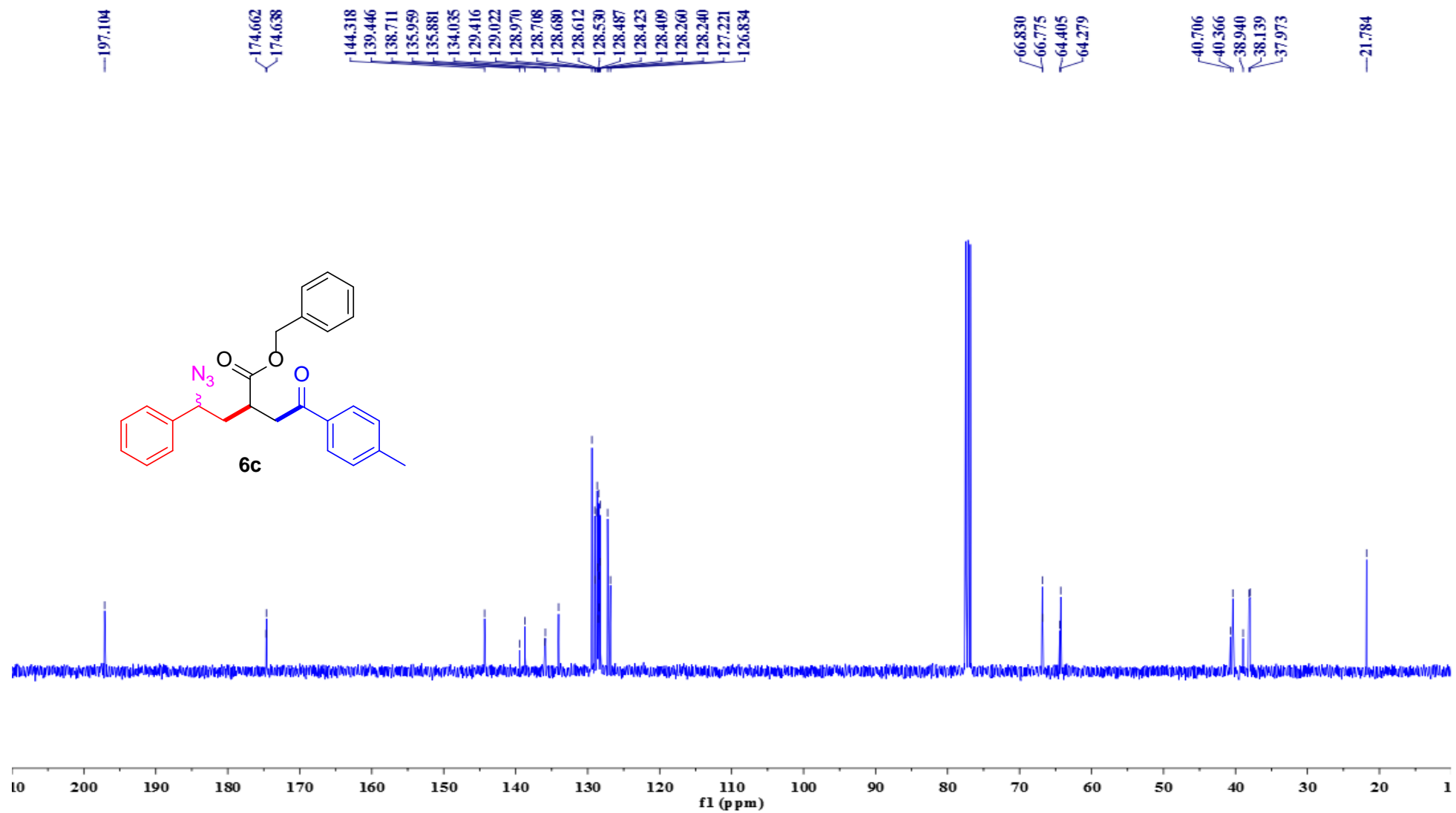


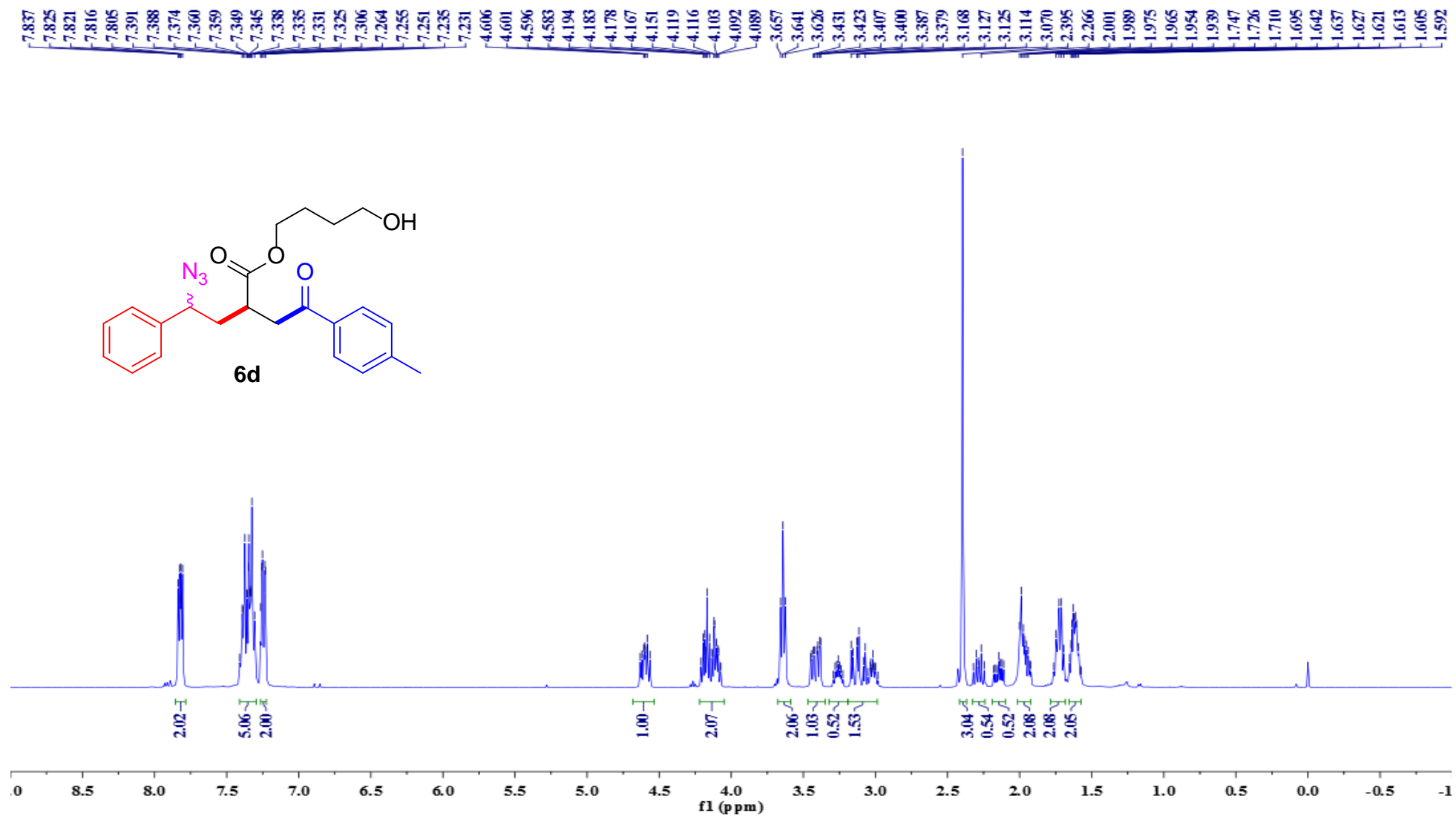




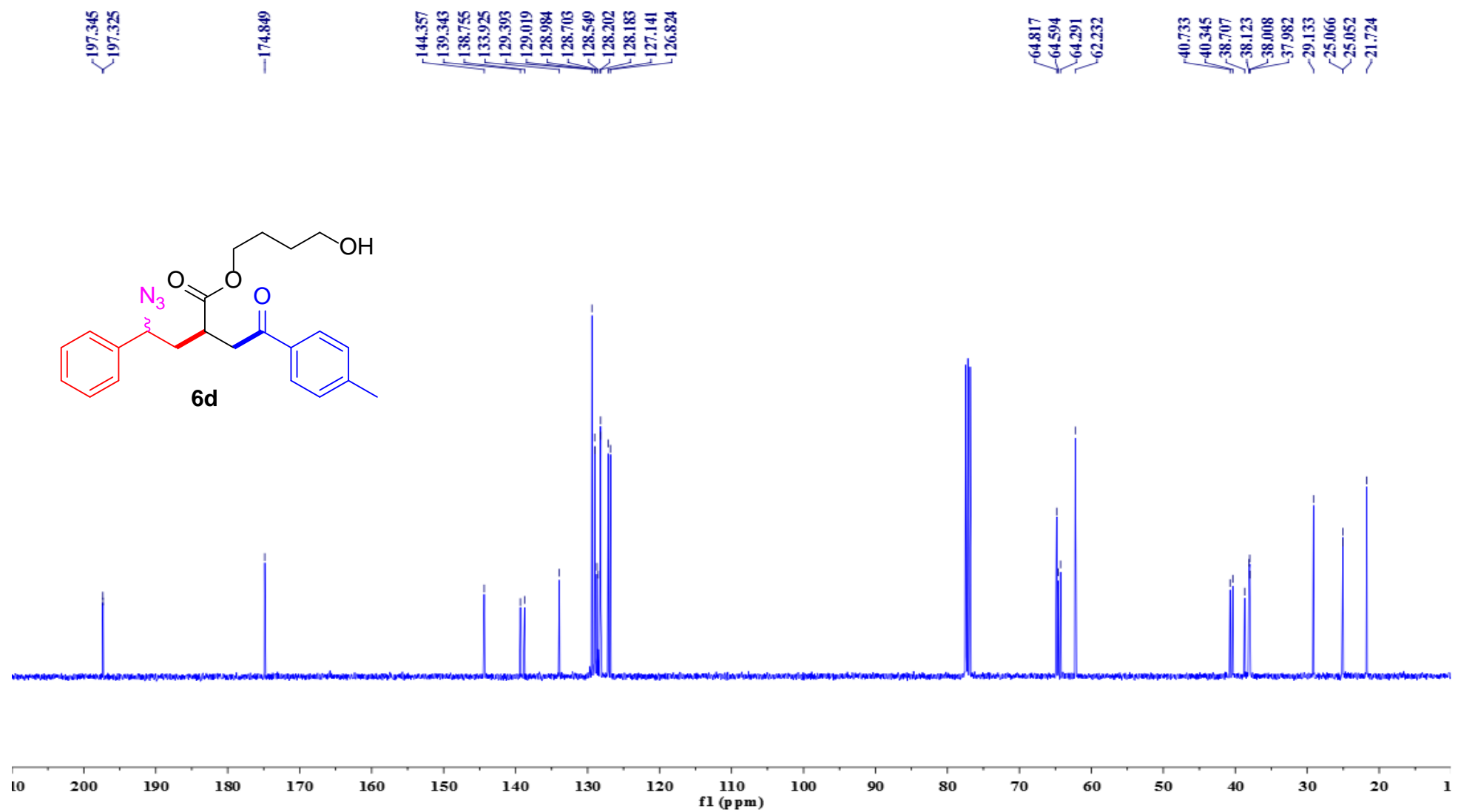


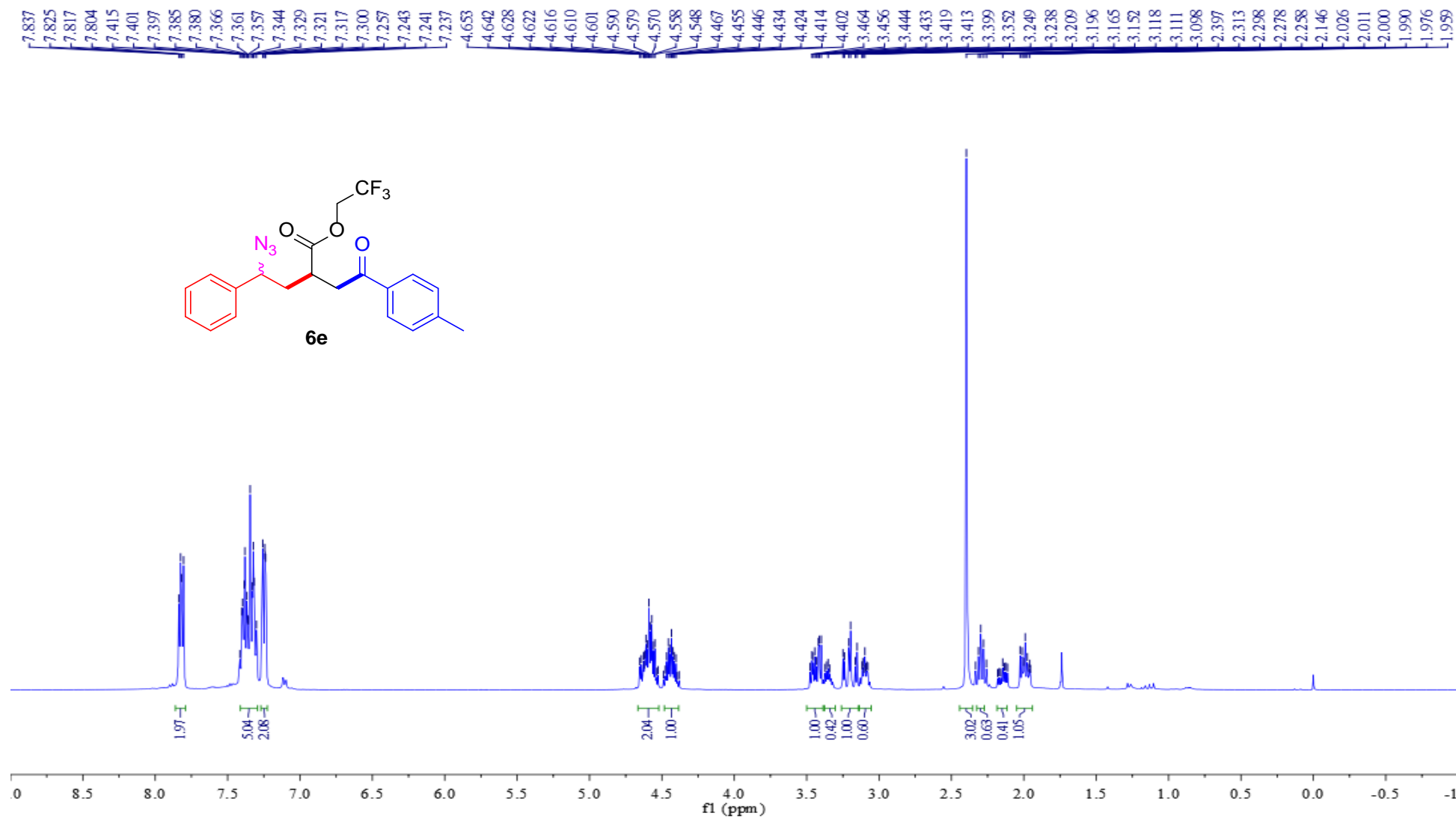
S104



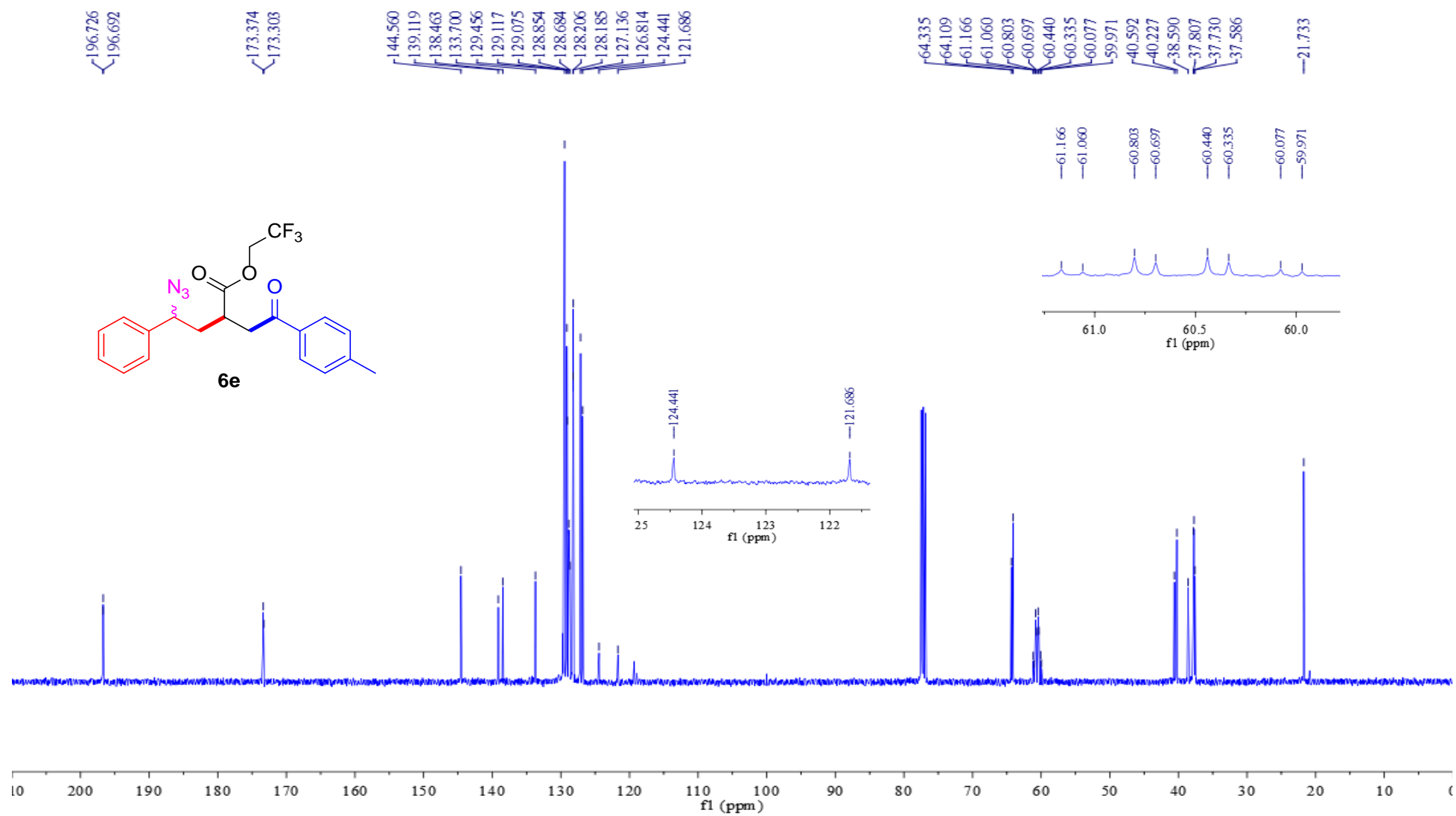


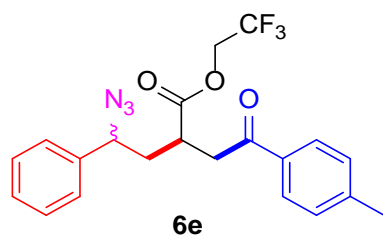
S106



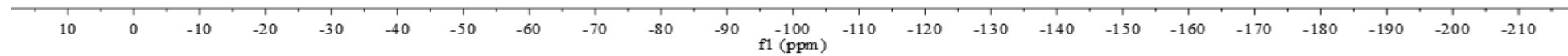
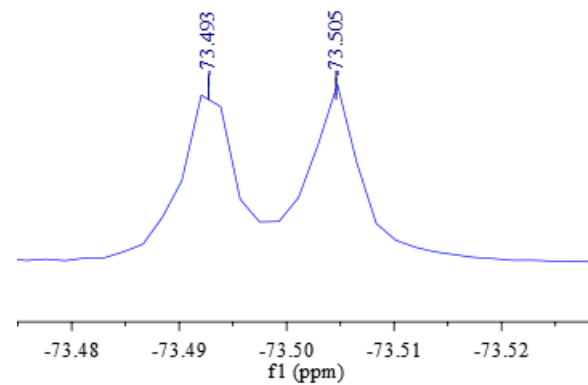


S108

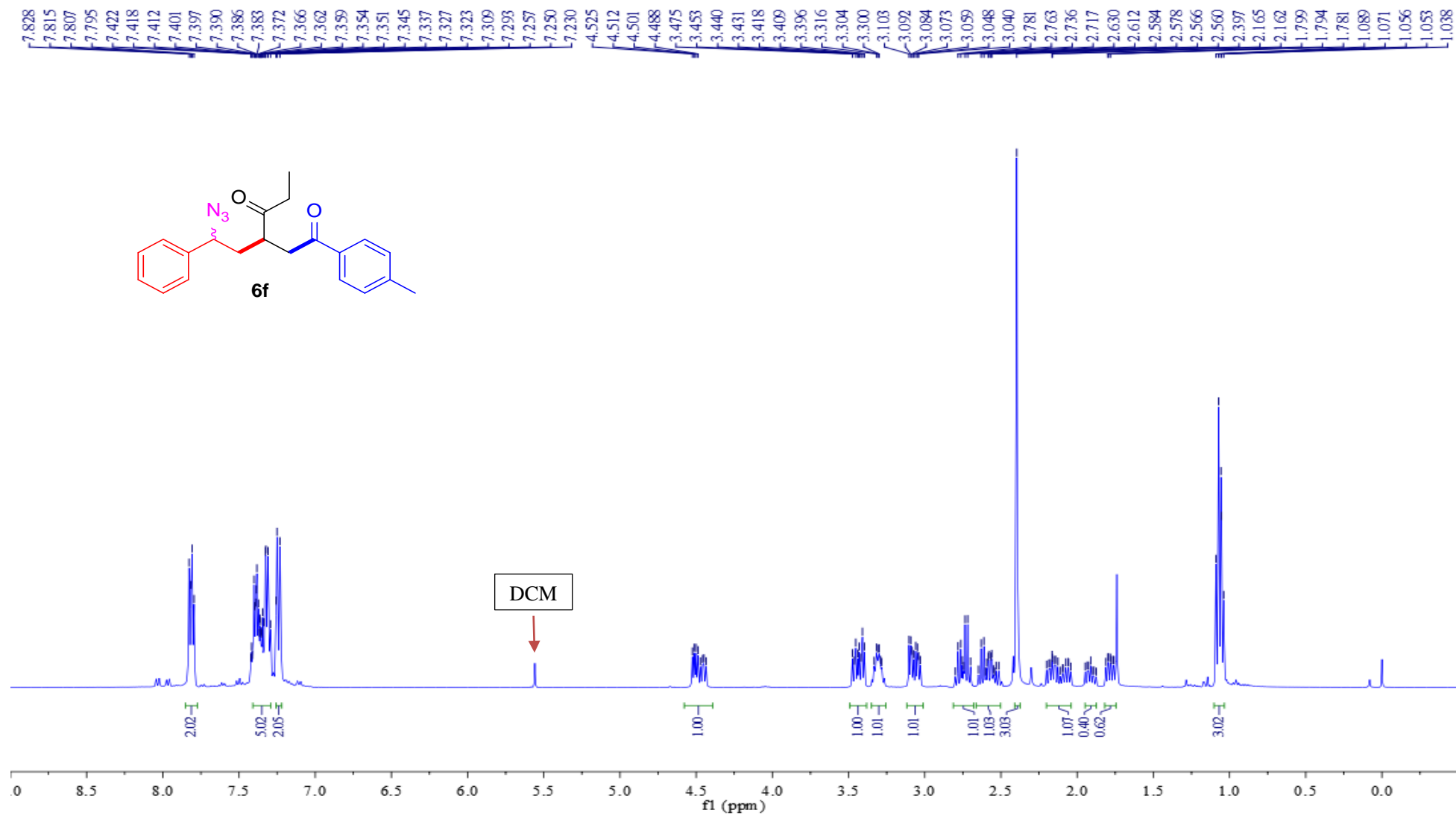


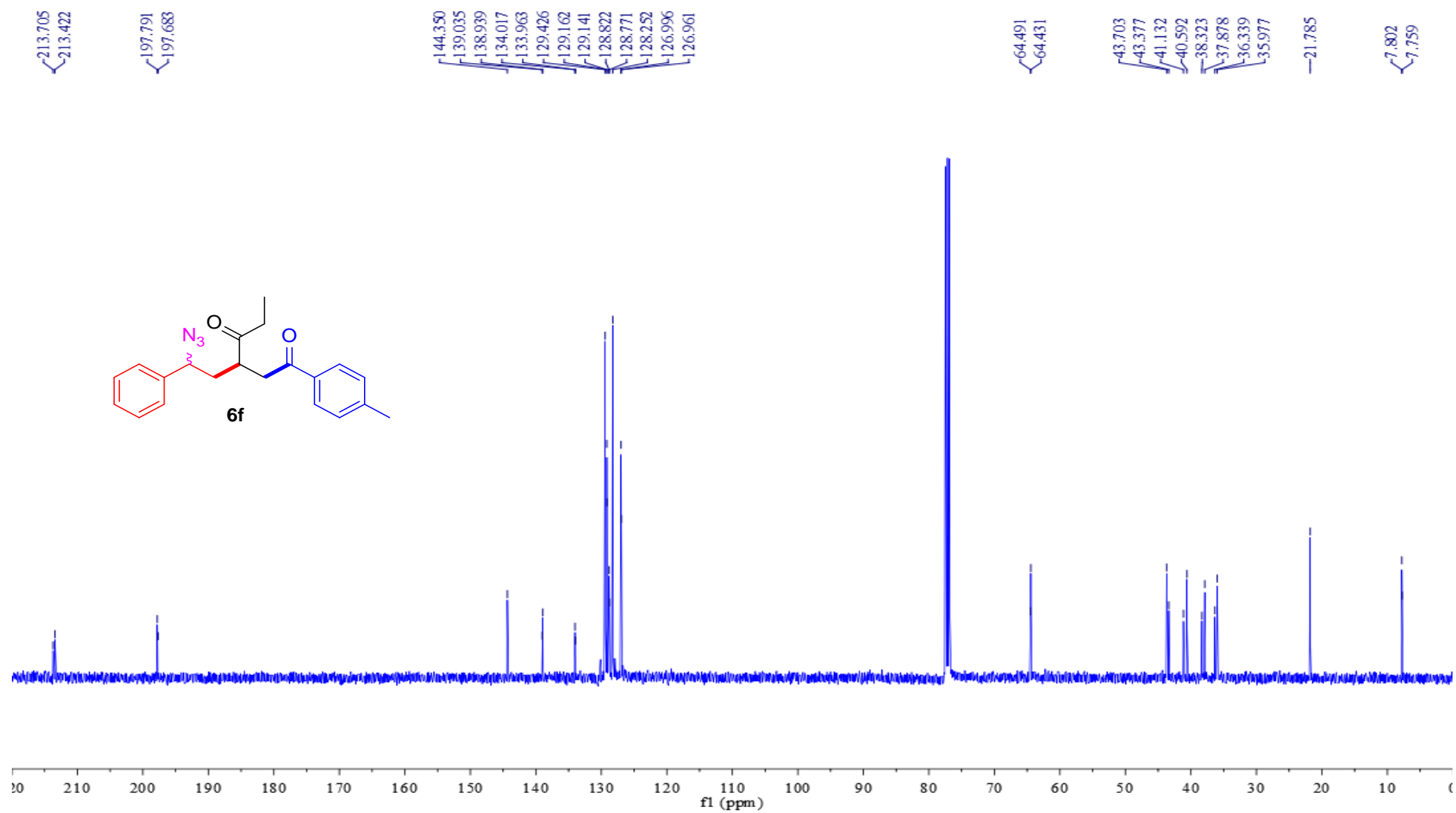


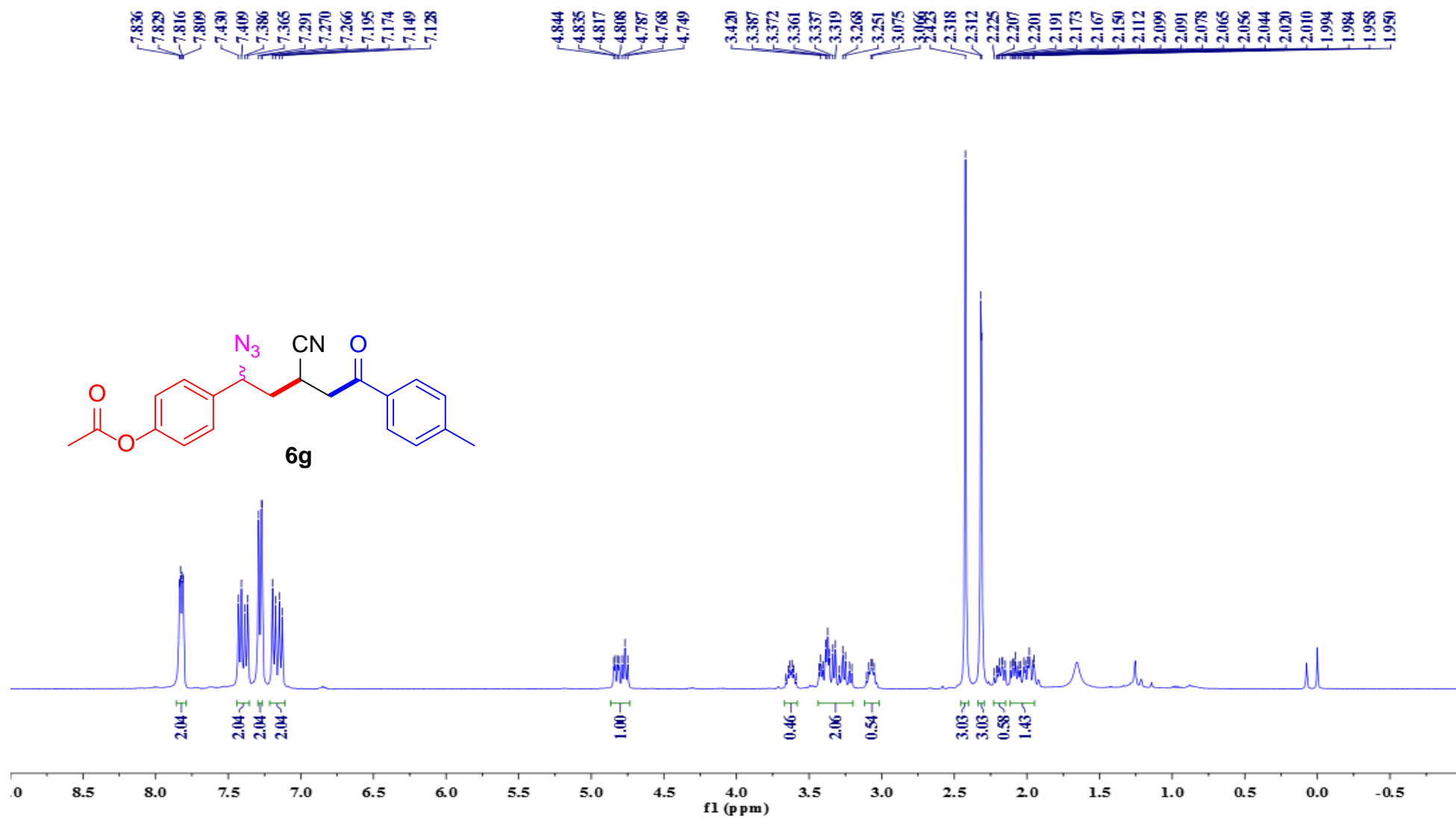
-73.493
-73.505

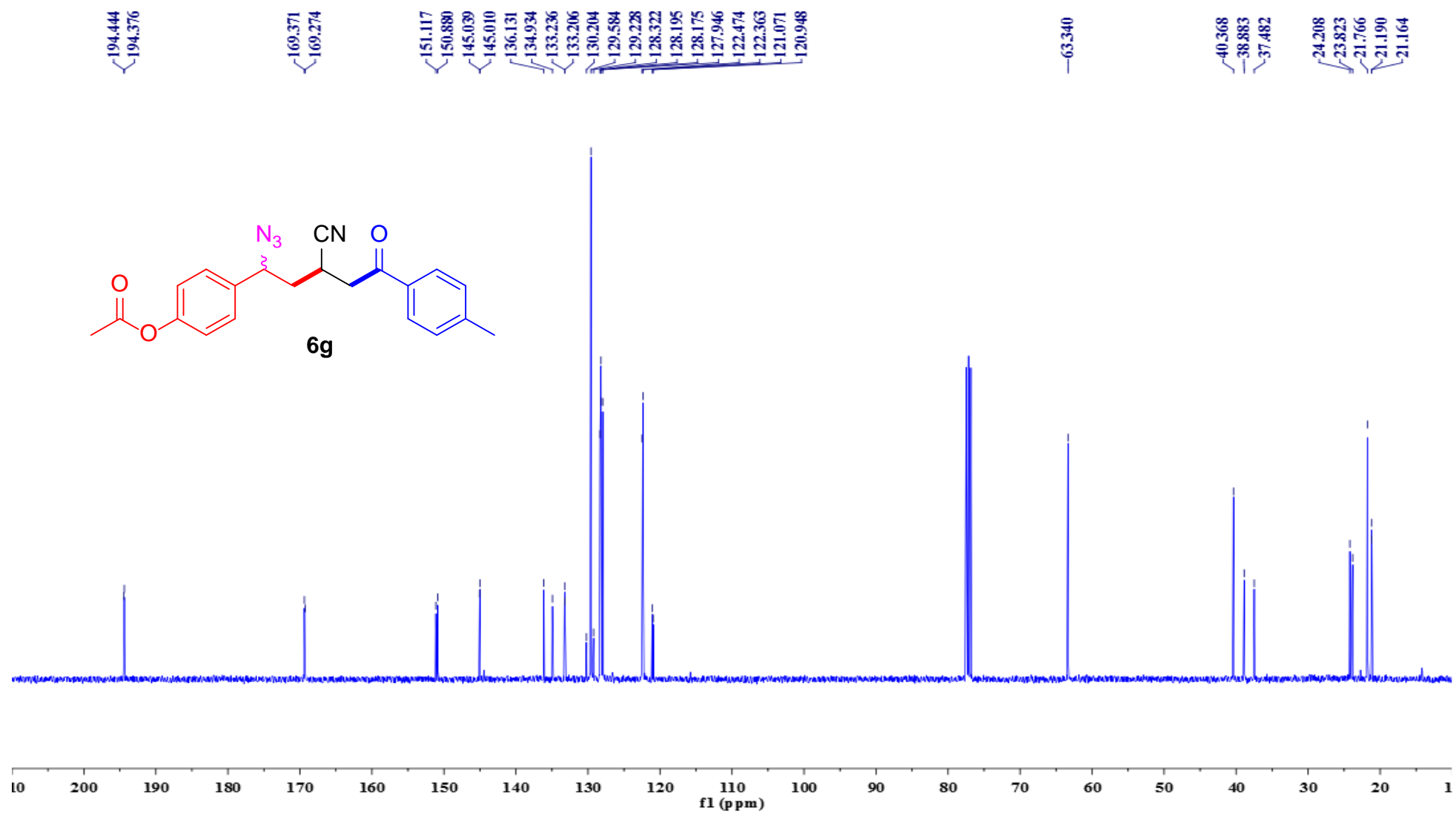


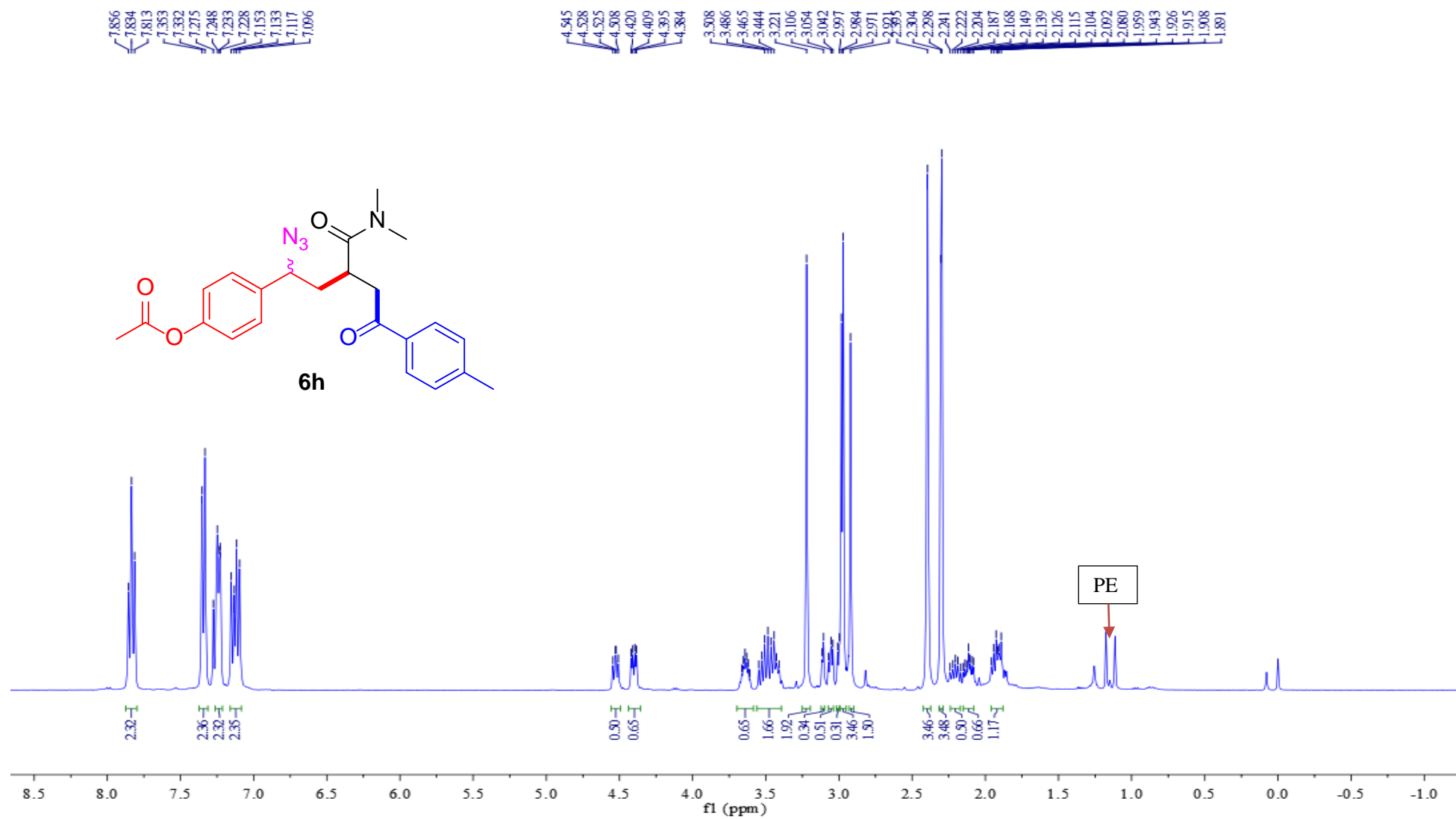
S110

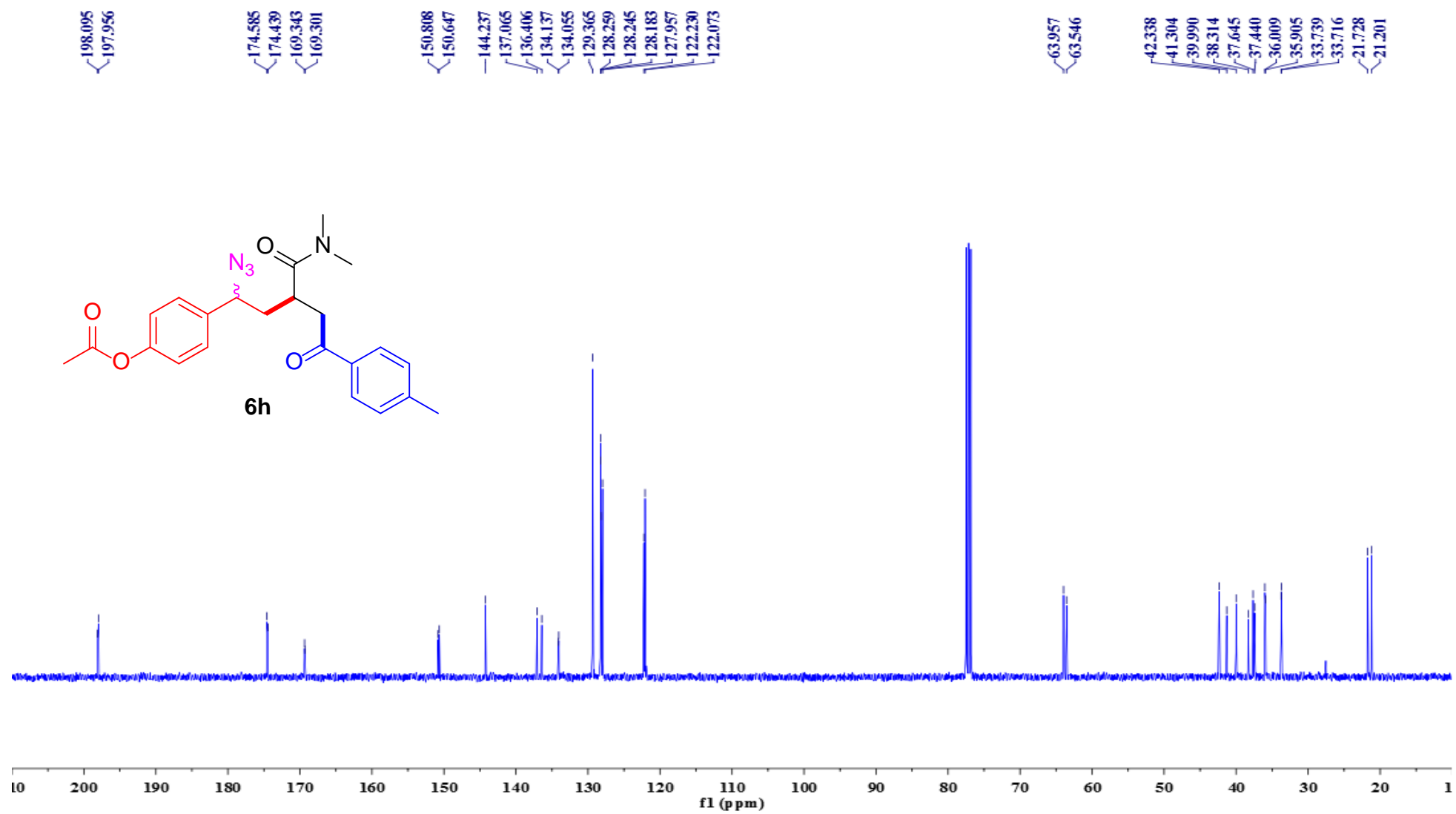


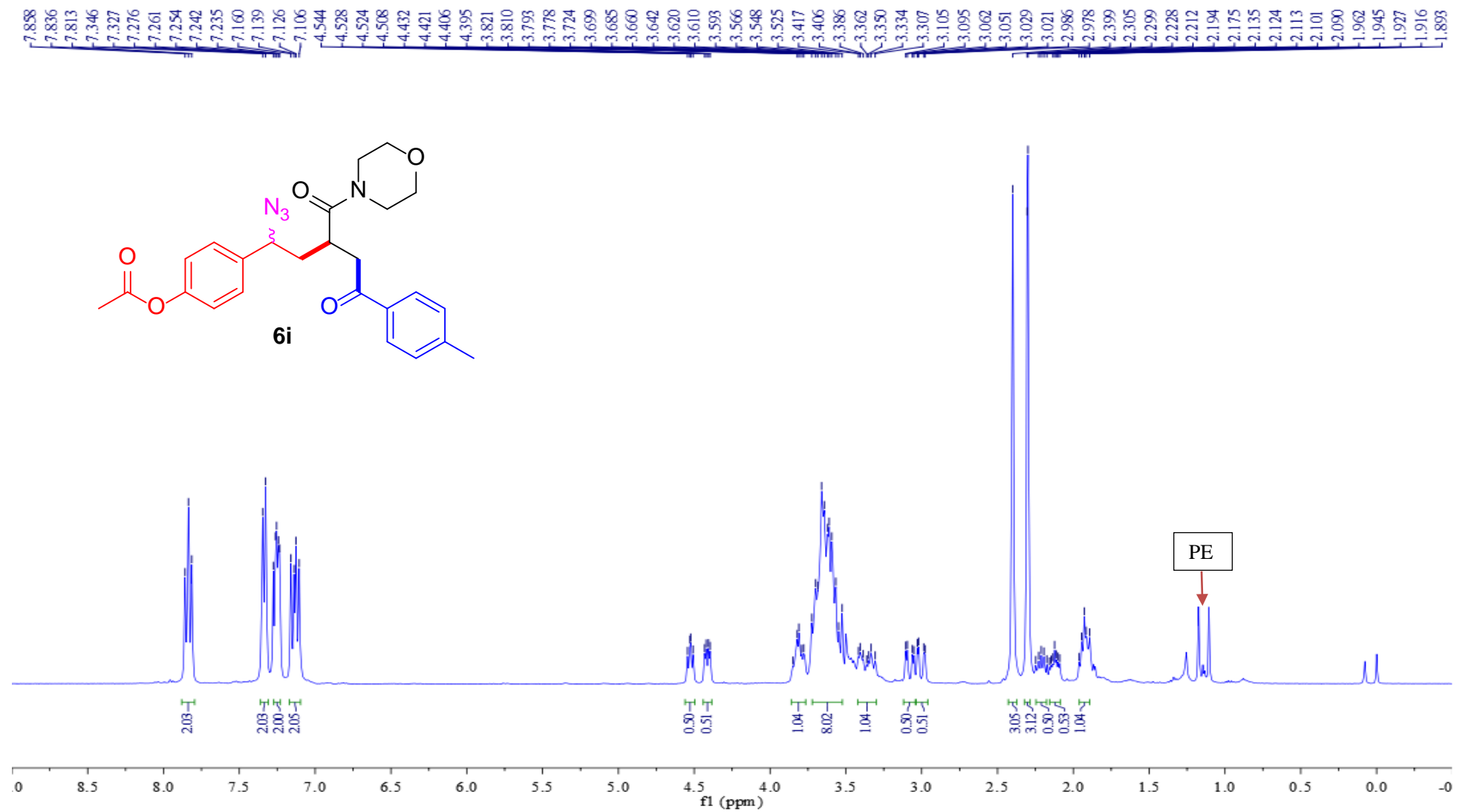


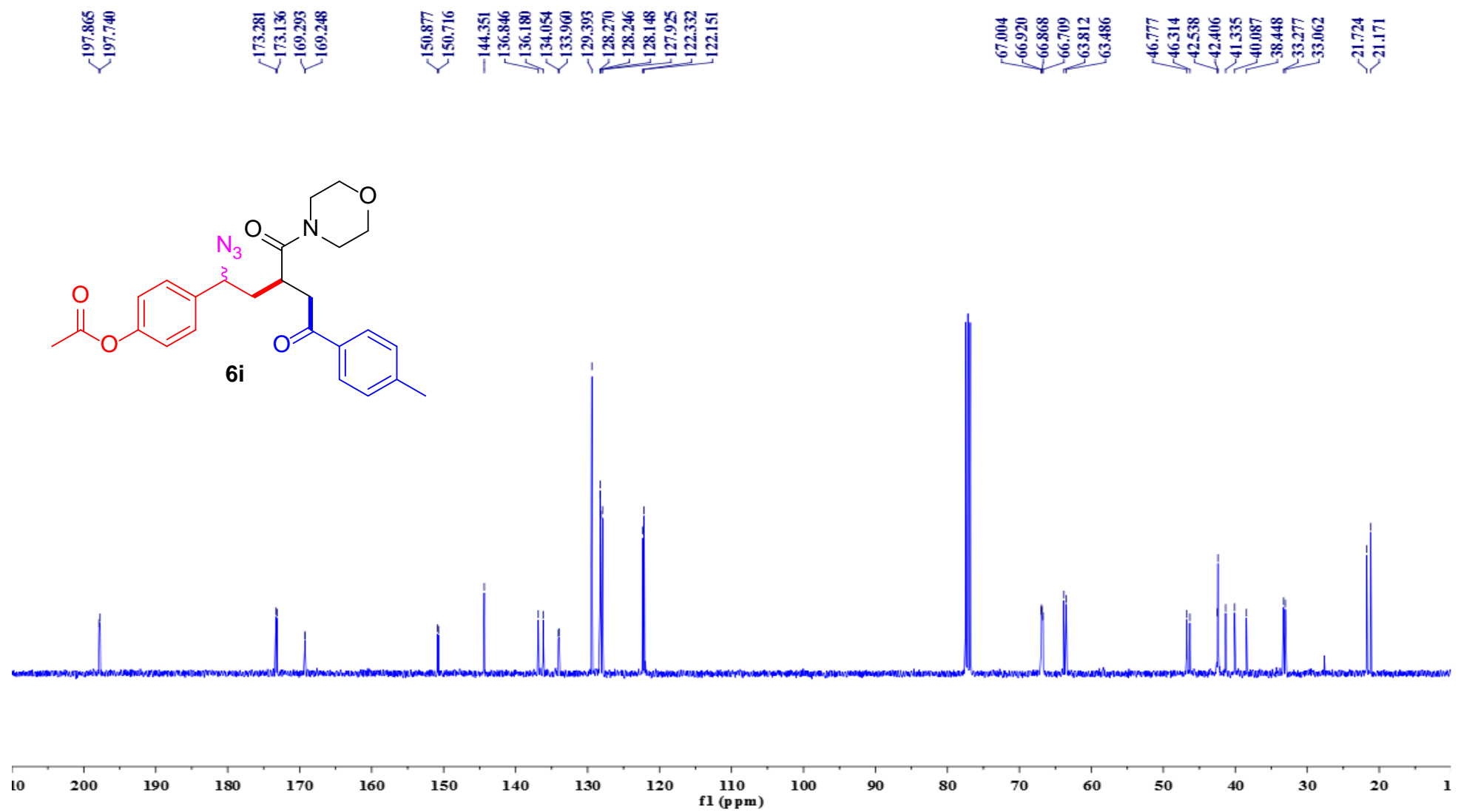


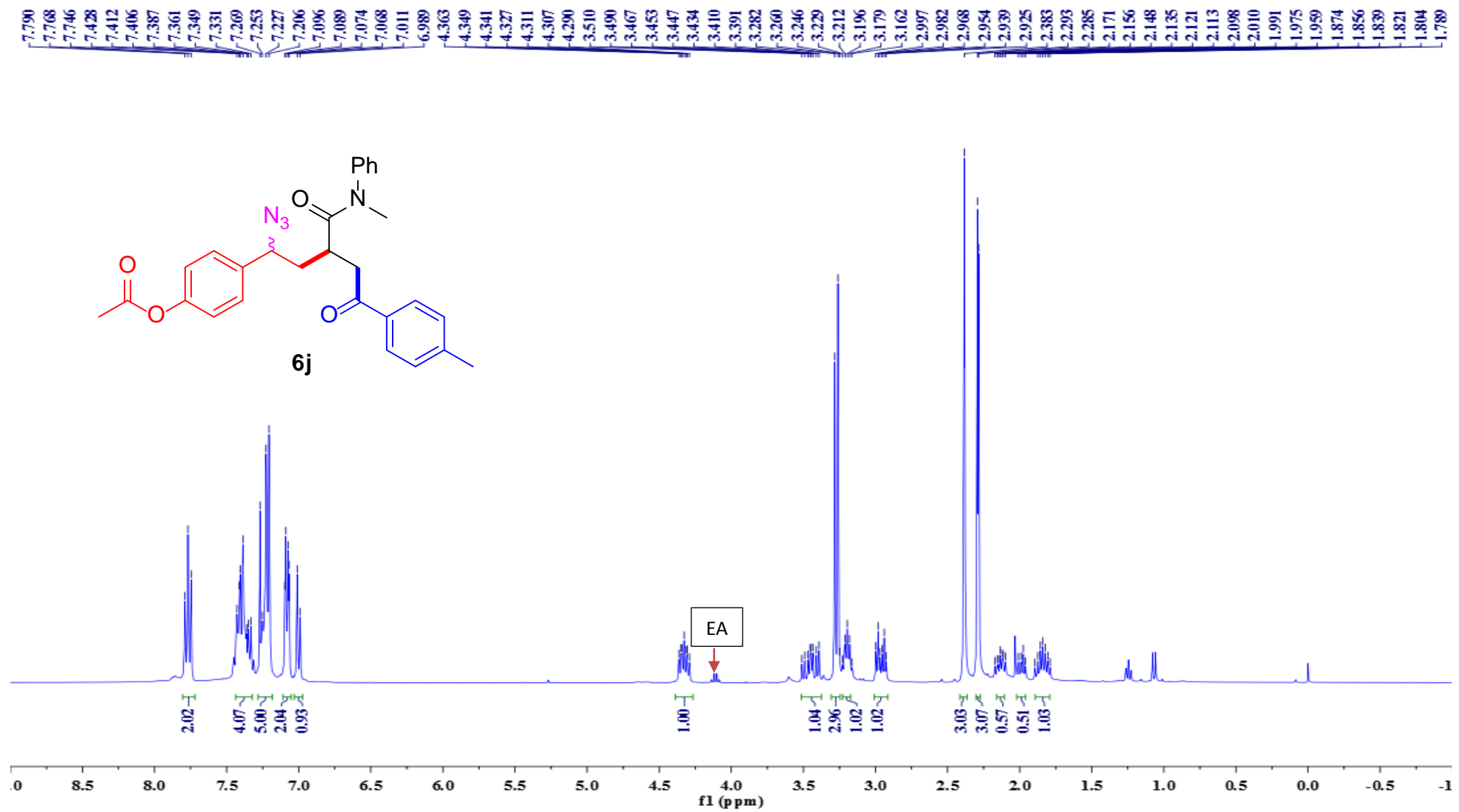


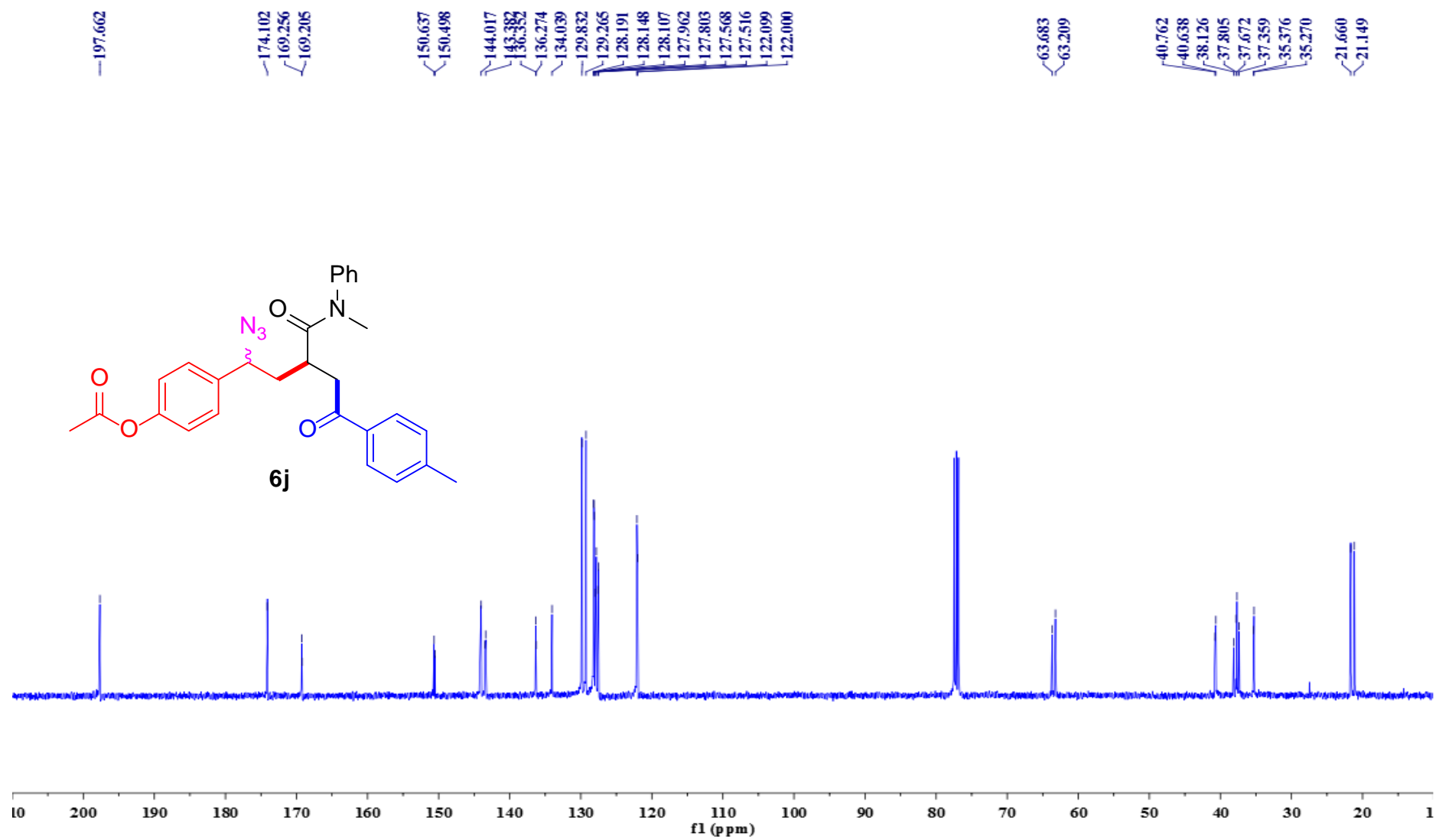


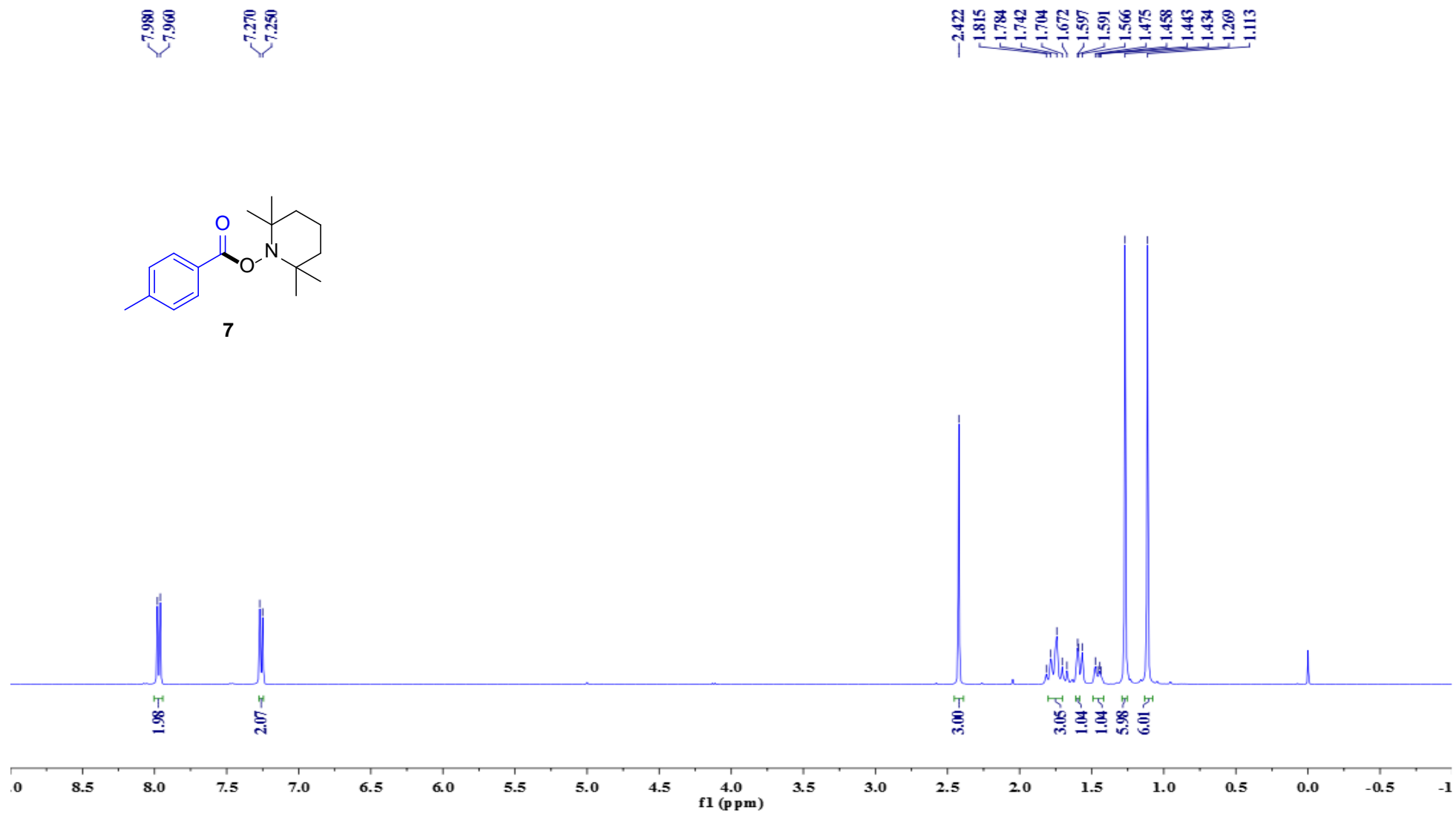
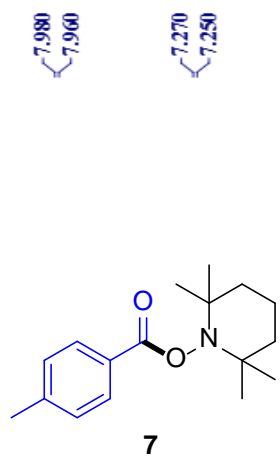


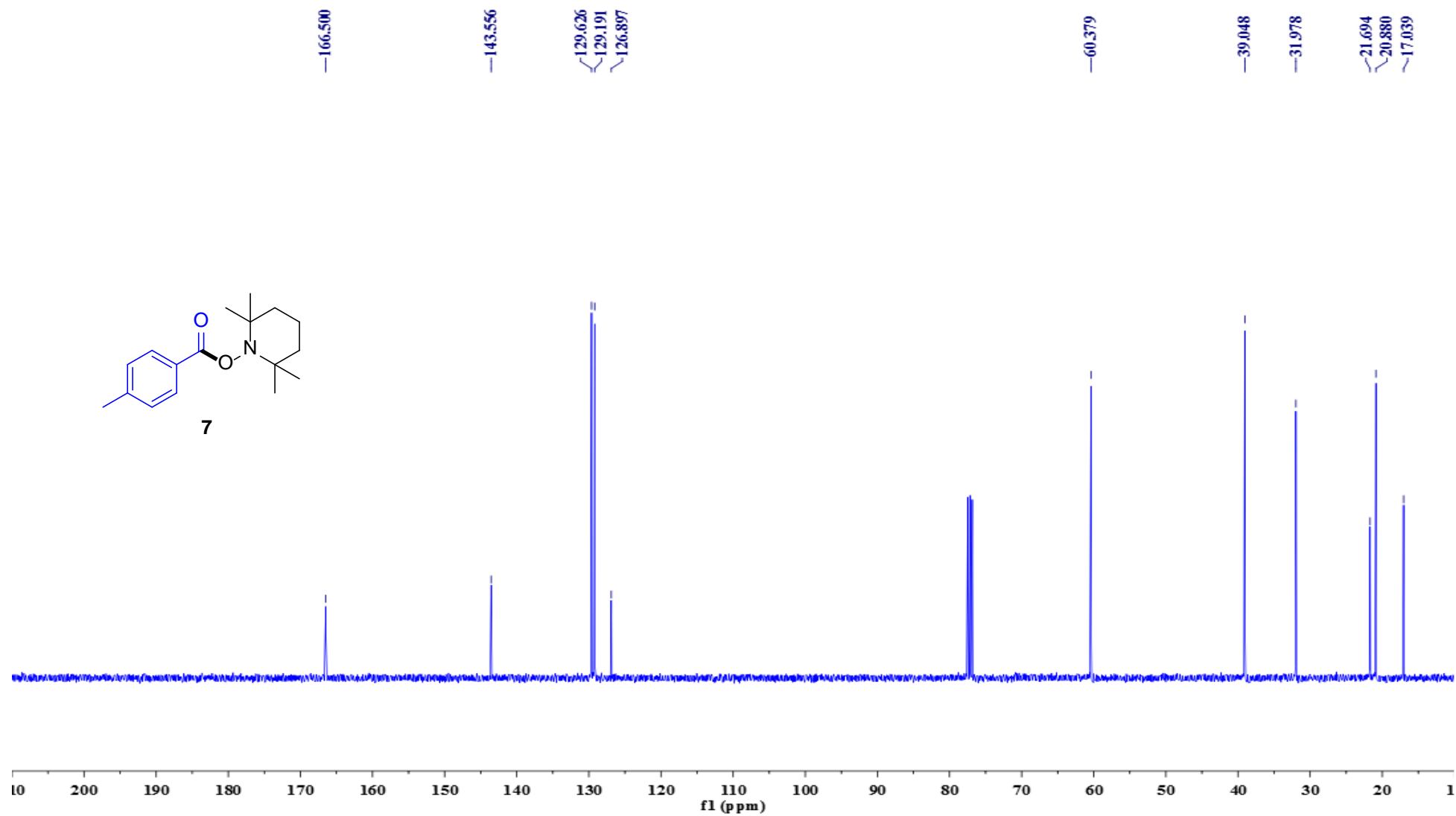
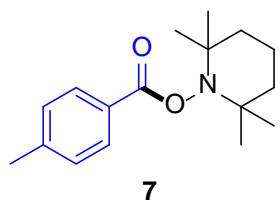


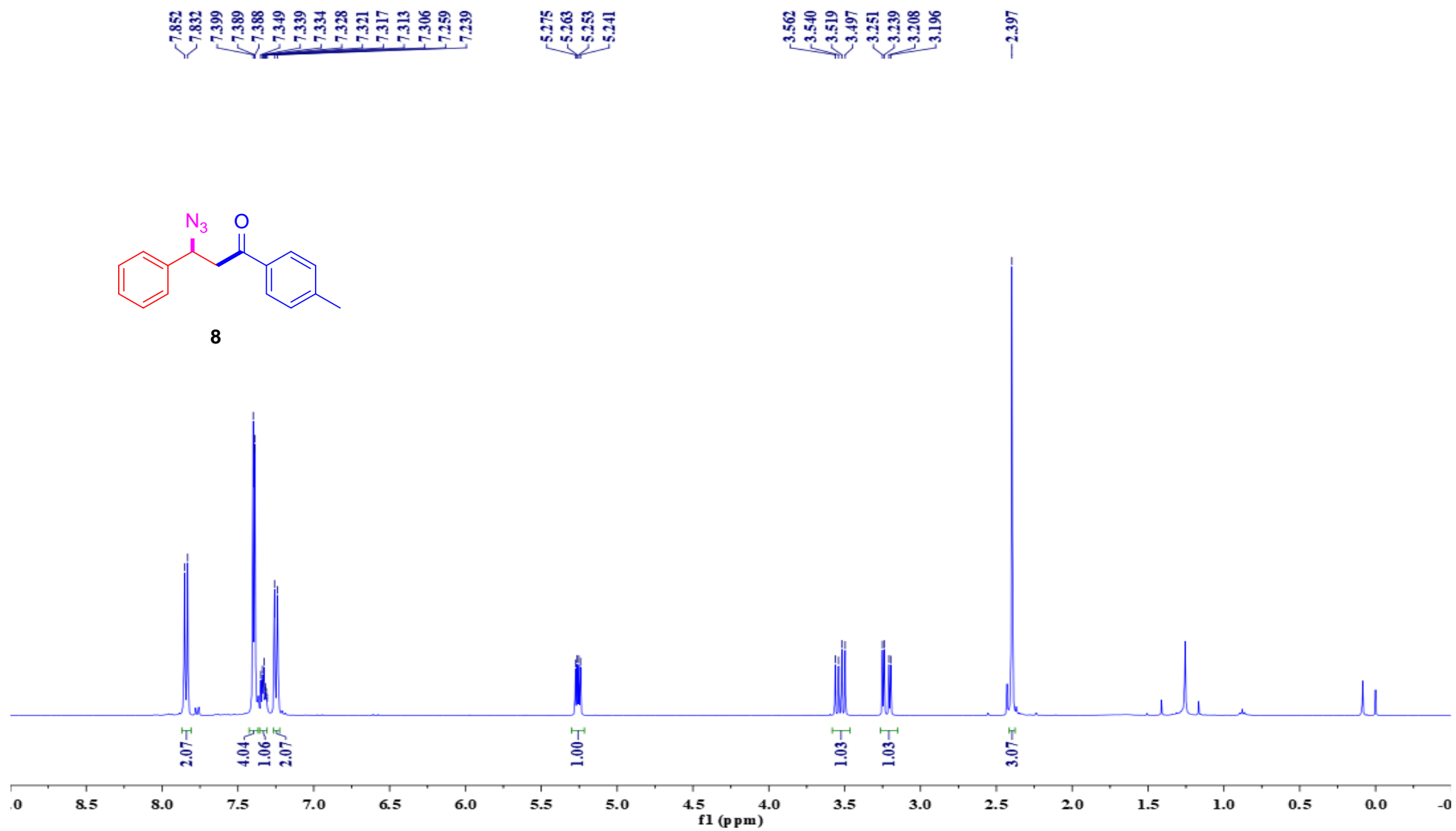
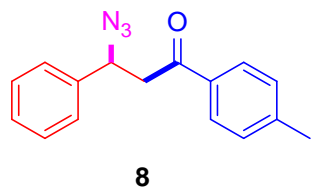


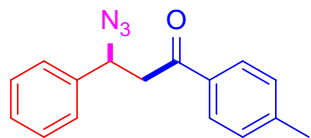




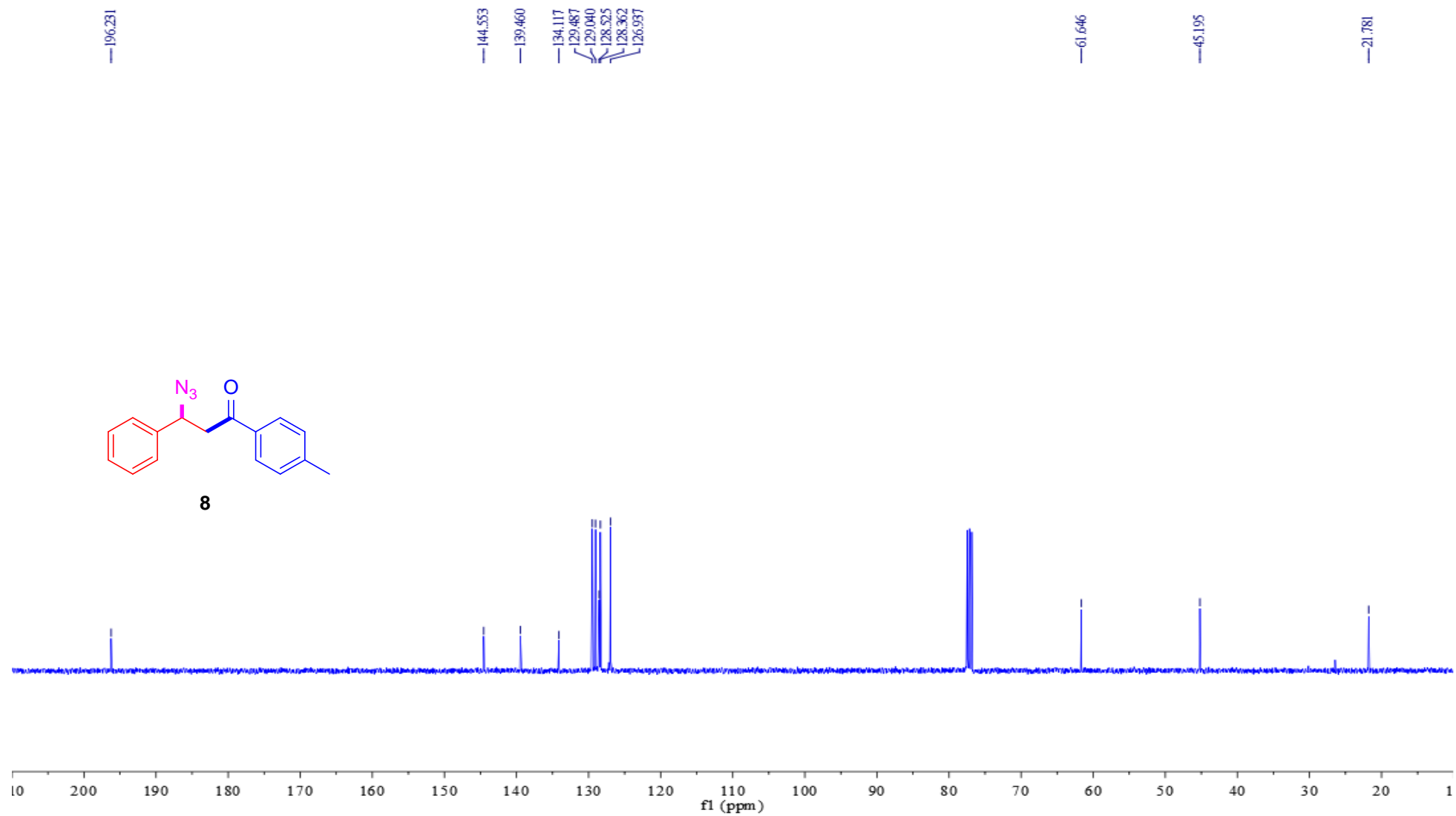




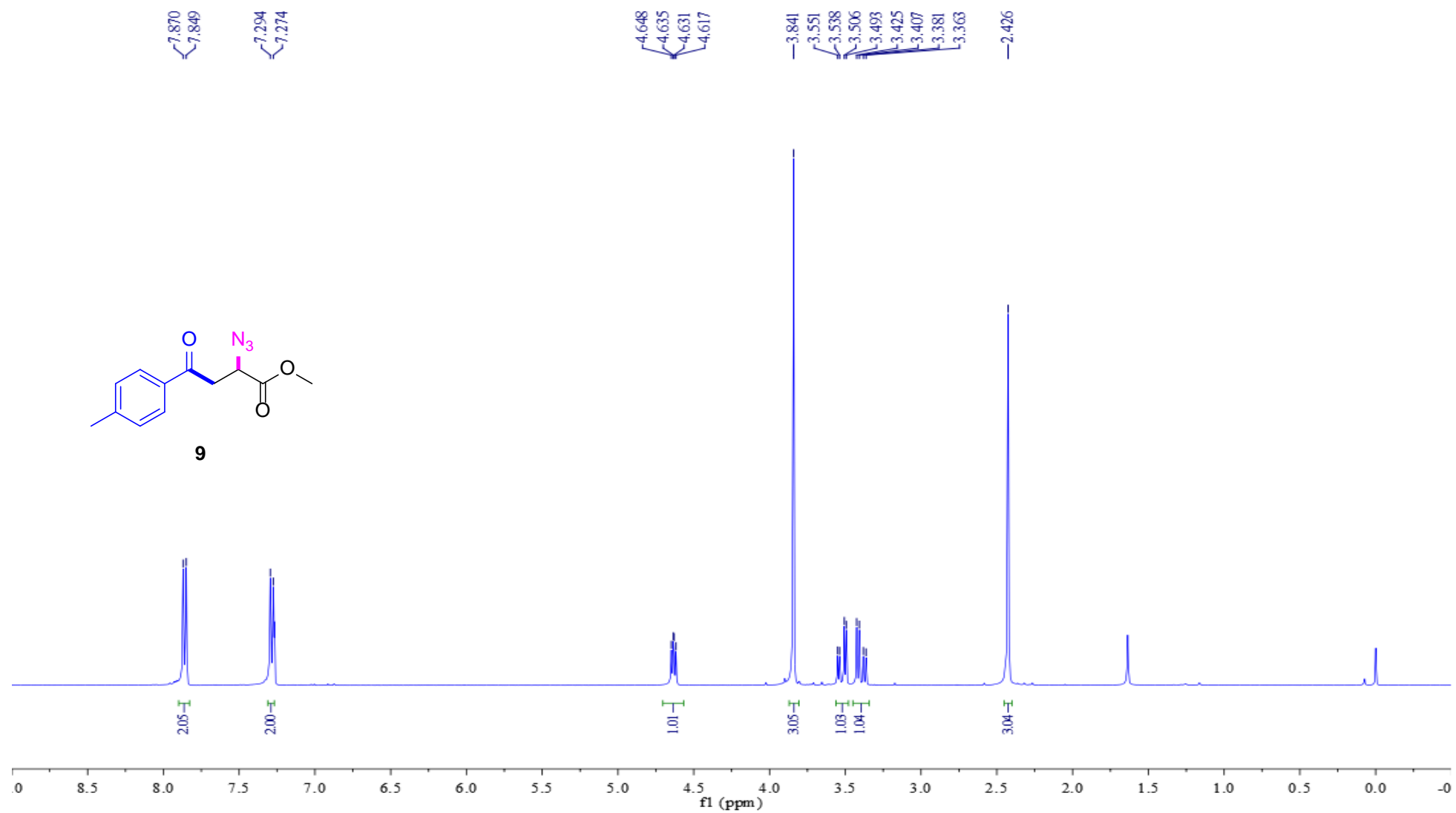


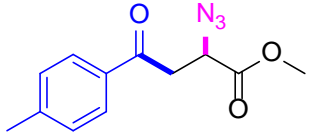


8

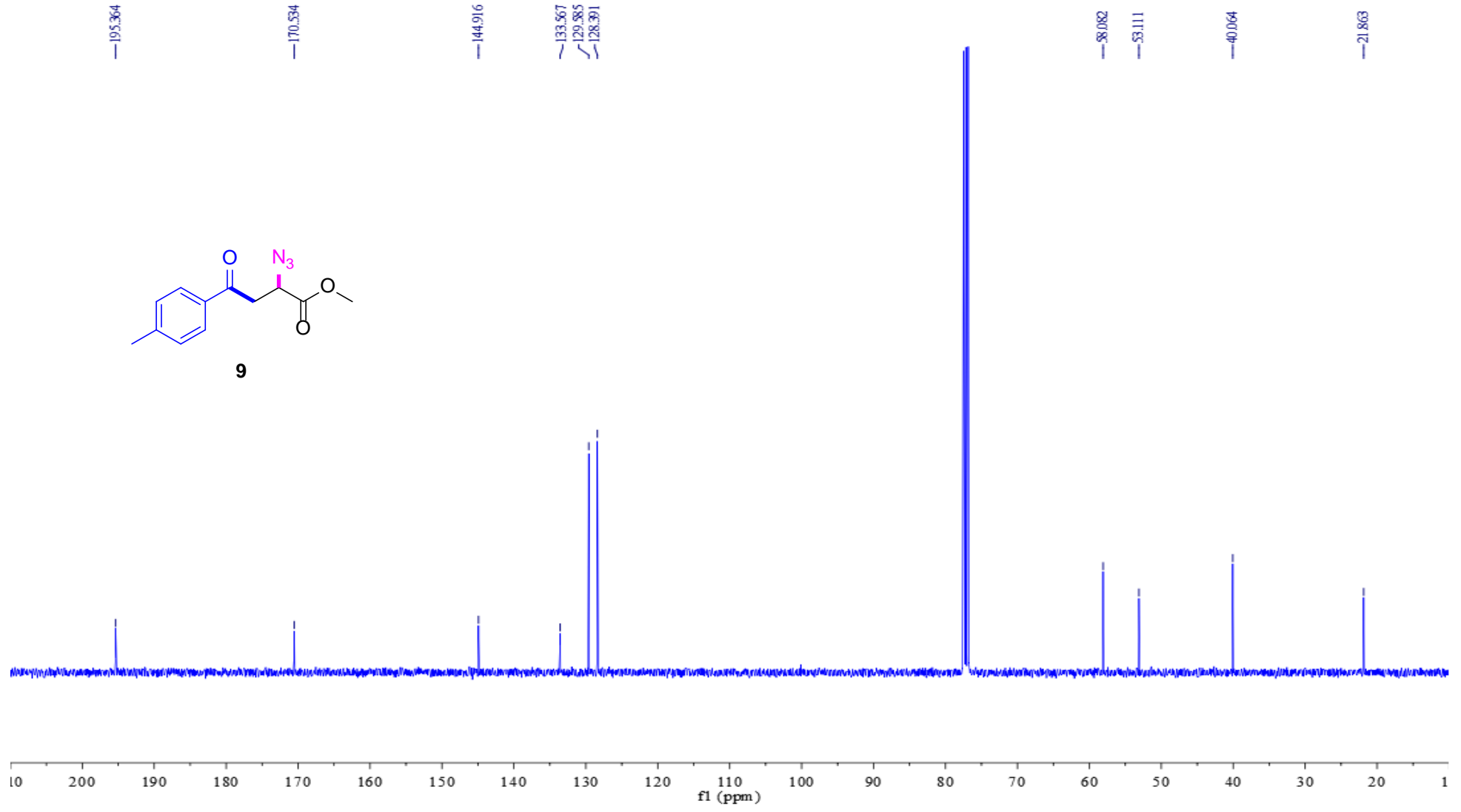


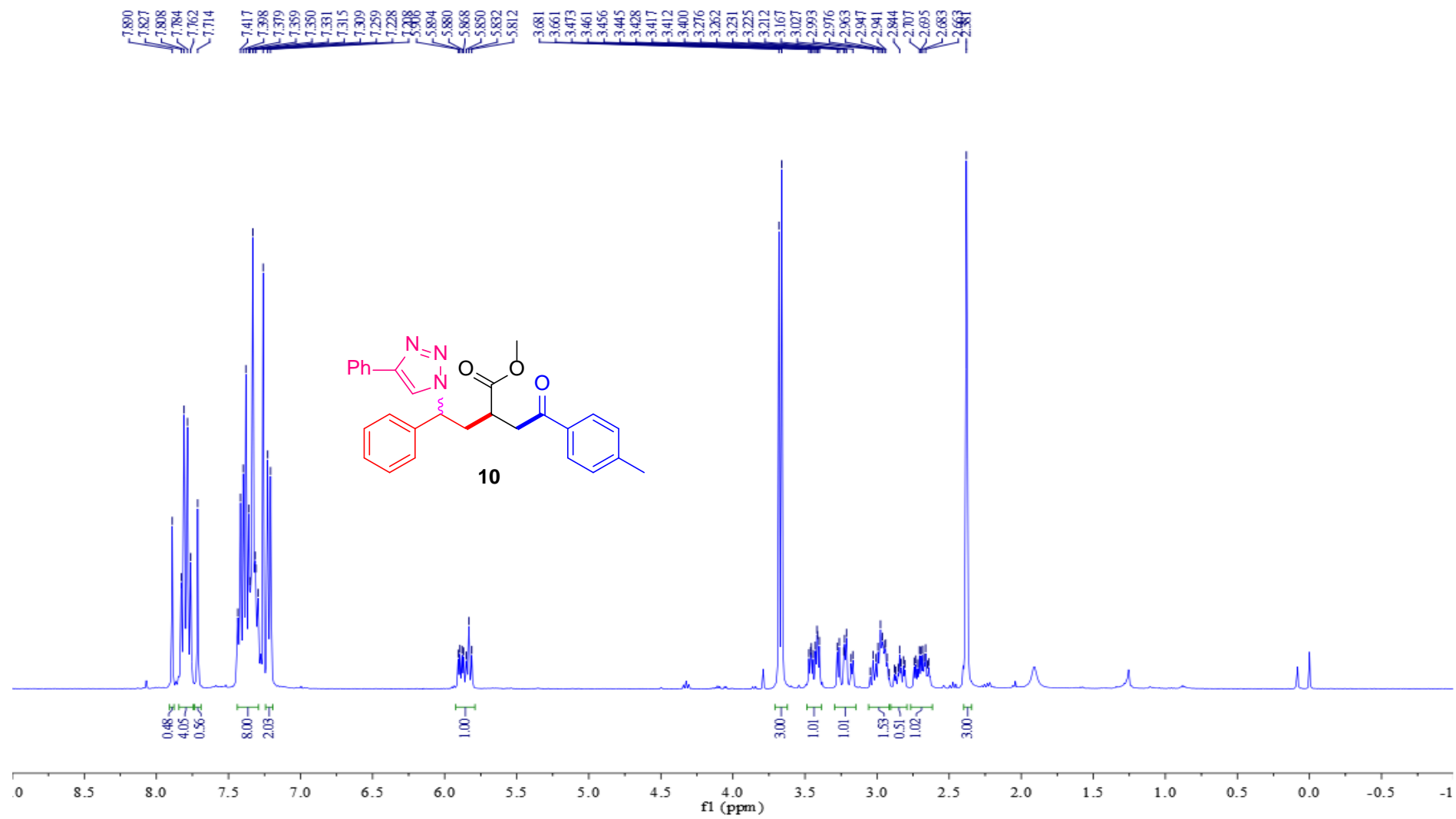
S124

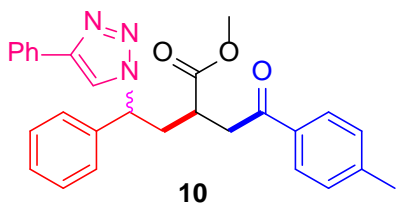
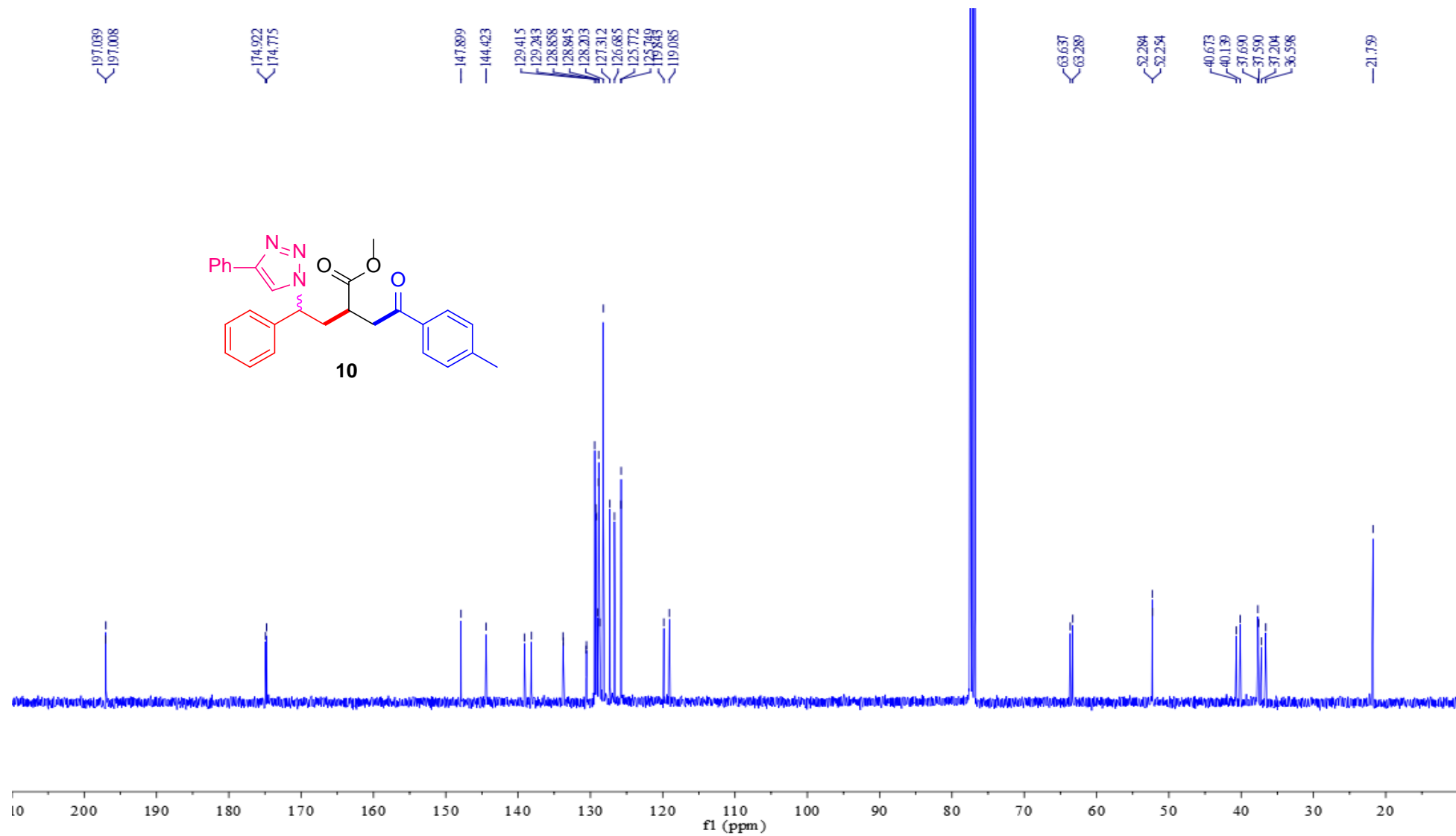




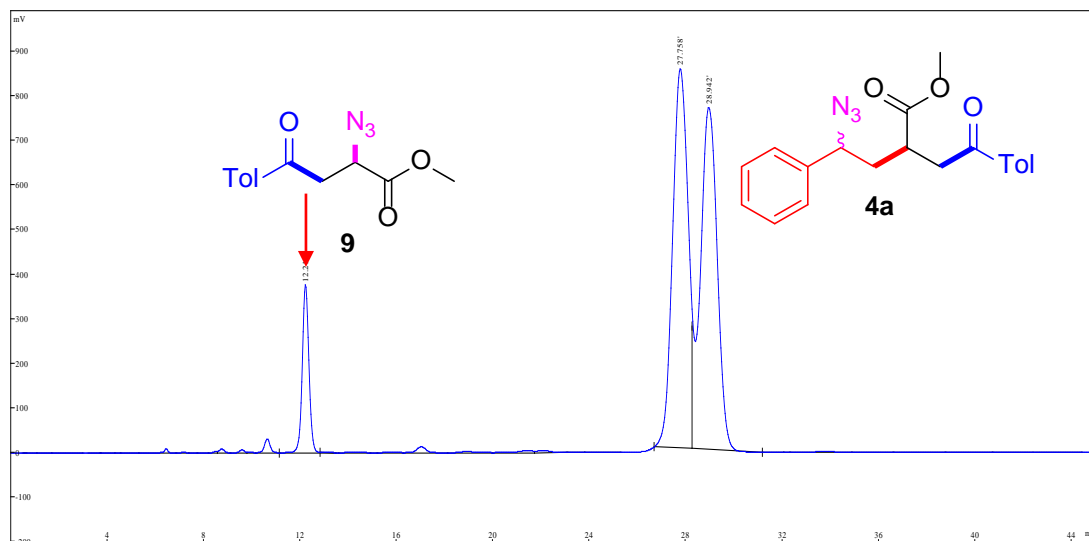
9





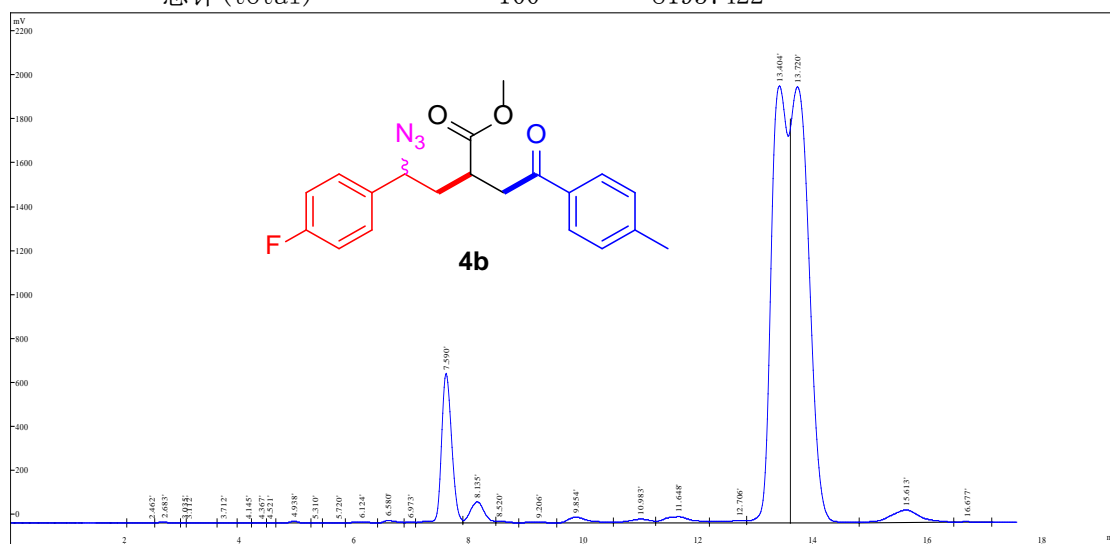


XI. Copies of HPLC spectra of products



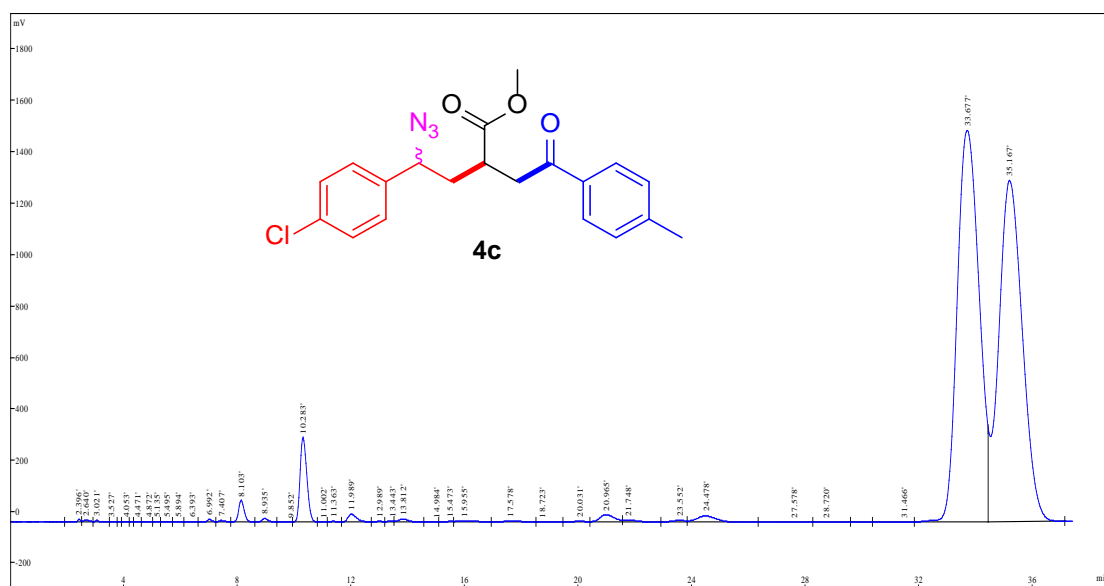
eluted by CH₃CN:H₂O=60:40

序号	保留时间	浓度	峰面积
	retention time	peak percentage	peak area
1	12.213	8.885	7279889
2	27.758	45.99	37692931
3	28.942	45.12	36964602
总计(total)		100	81937422



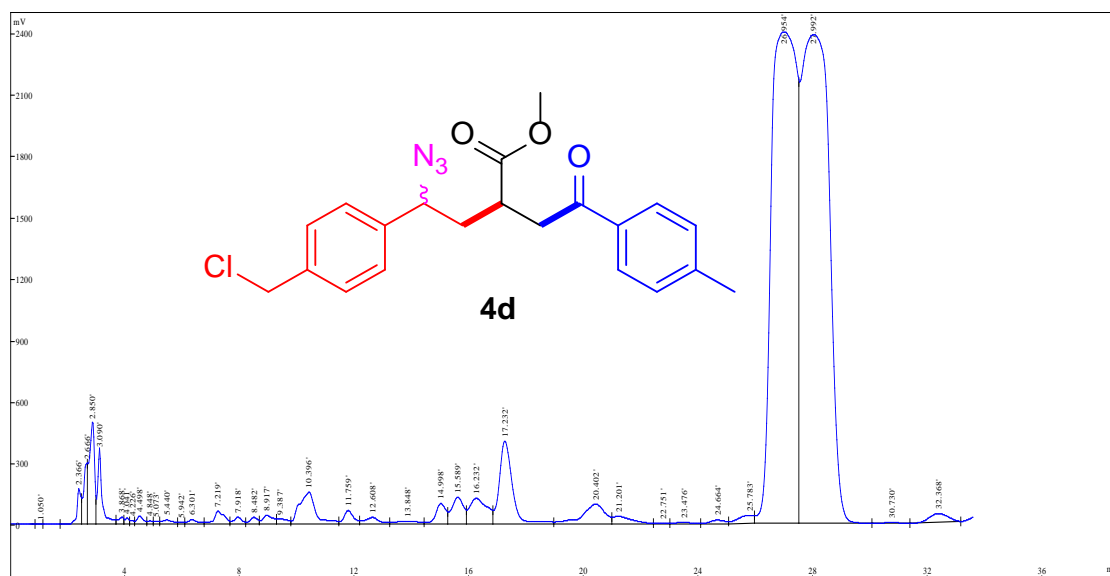
eluted by CH₃CN:H₂O=70:30

序号	保留时间	名称	浓度	峰面积
23	13.404		42.94	42777120
24	13.720		41.73	41576198



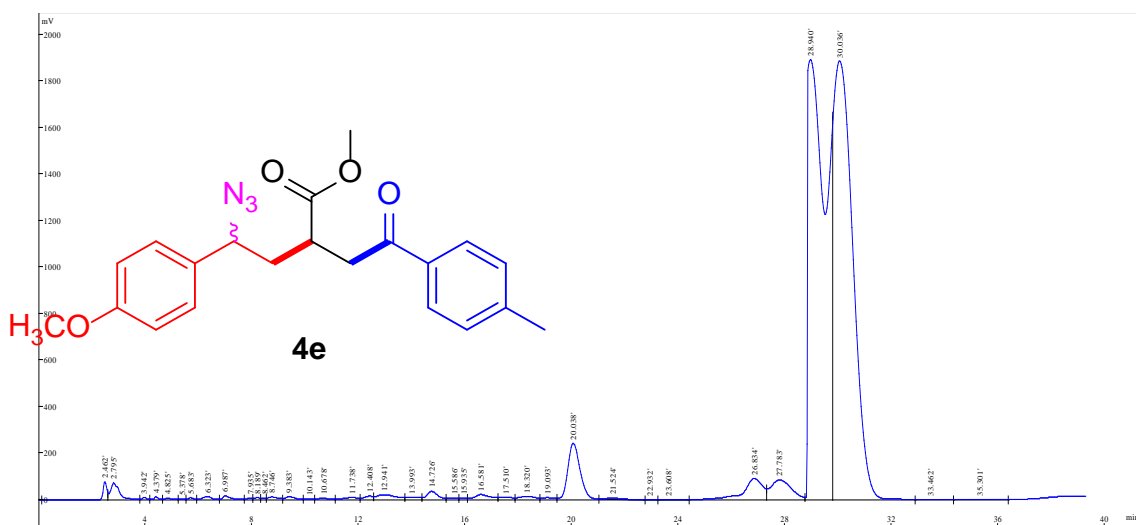
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
37	33.677		48.19	82215123
38	35.167		44.1	75243974



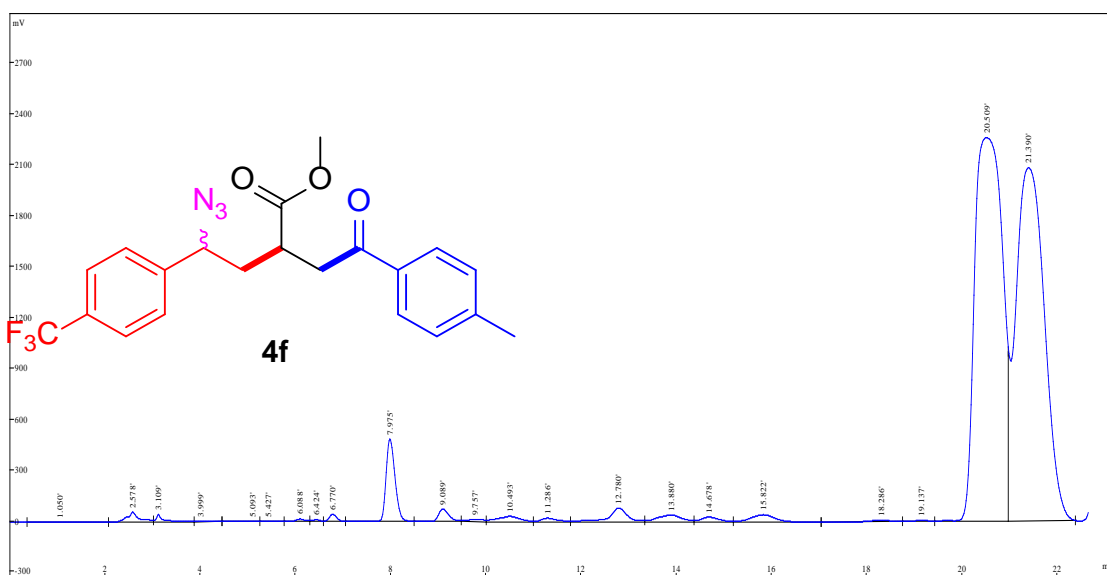
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
34	26.954		39.83	150429619
35	27.992		41.87	158133683



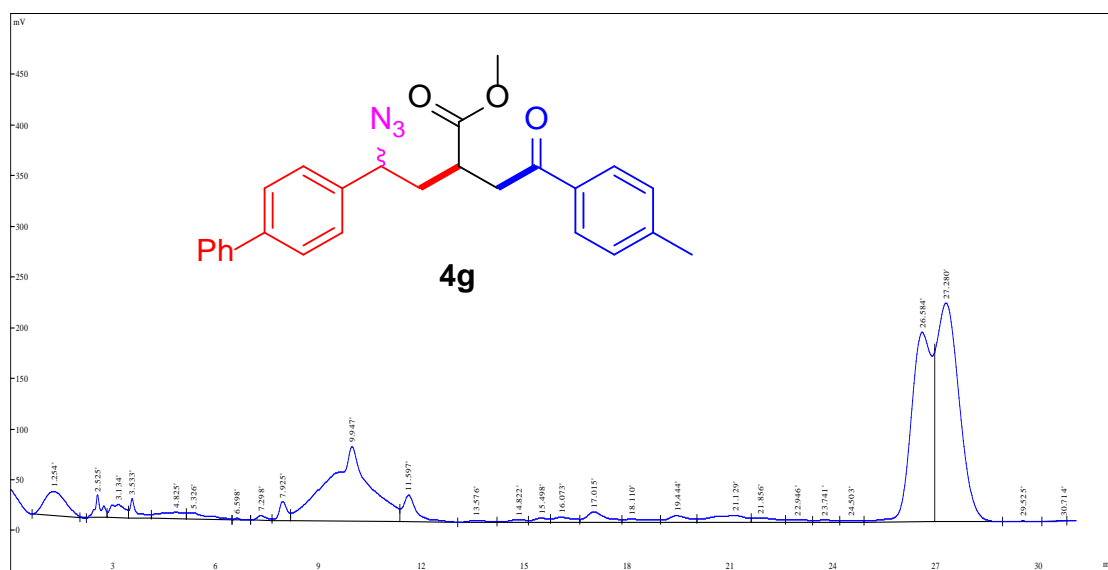
eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
34	28.940		42.54	90164819
35	30.036		43.61	92466362



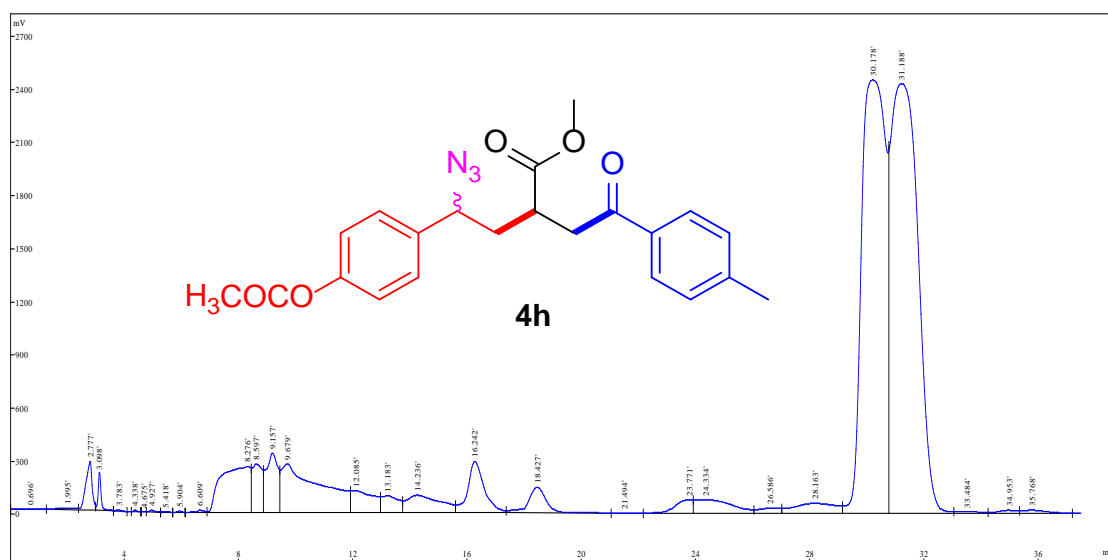
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
21	20.509		46.36	90872966
22	21.390		44.44	87113005



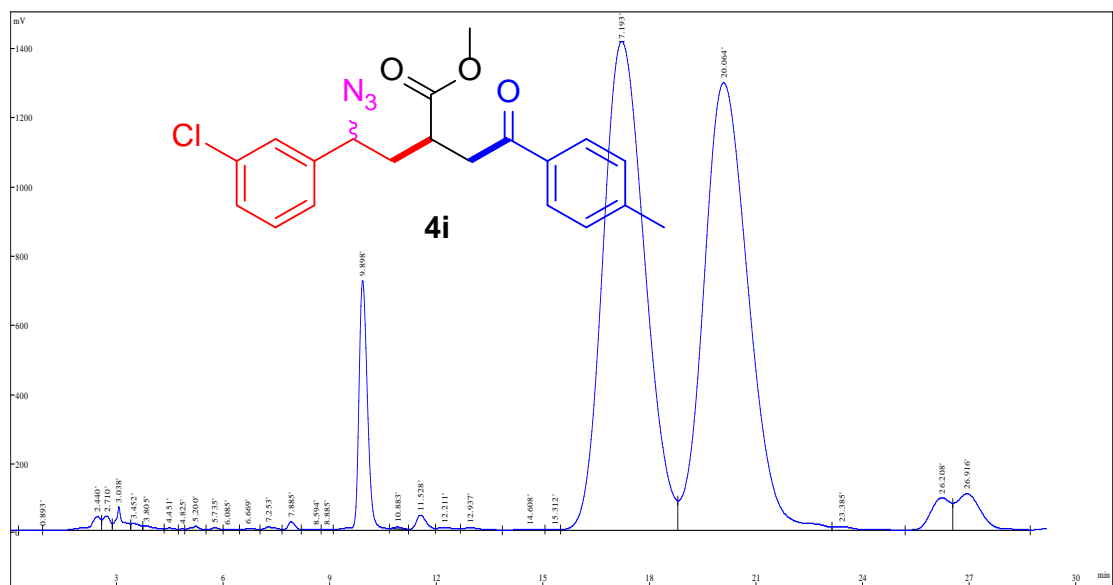
eluted by CH3CN:H2O=60:40

序号	保留时间	名称	浓度	峰面积
24	26.584		27.66	8244071
25	27.280		31.96	9523237



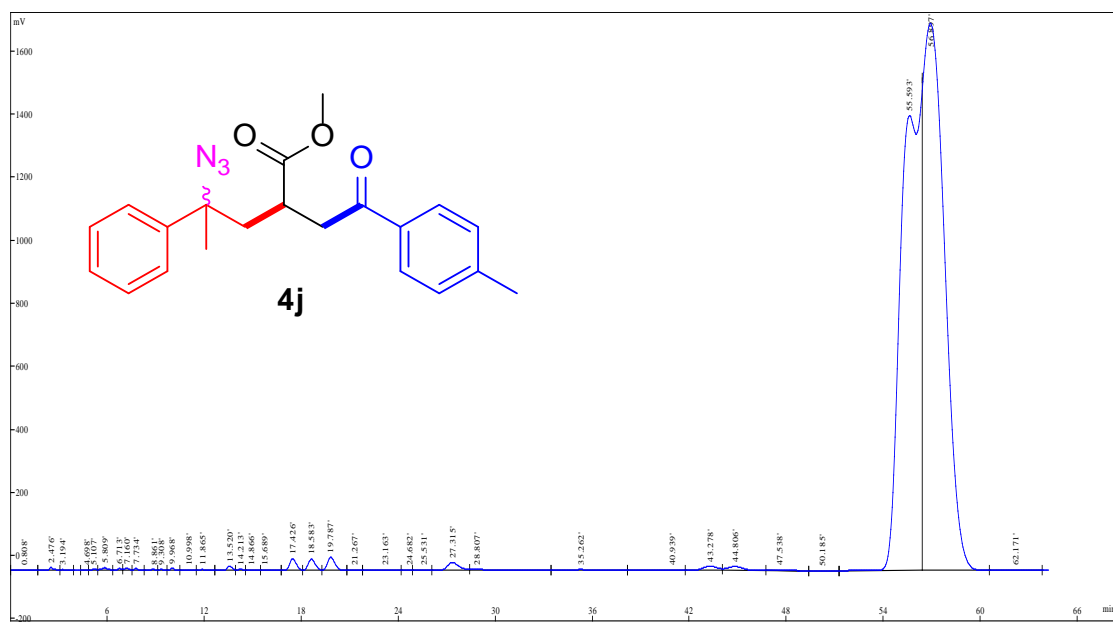
eluted by CH3CN:H2O=50:50

序号	保留时间	名称	浓度	峰面积
26	30.178		34.24	148424602
27	31.188		35.92	155720858



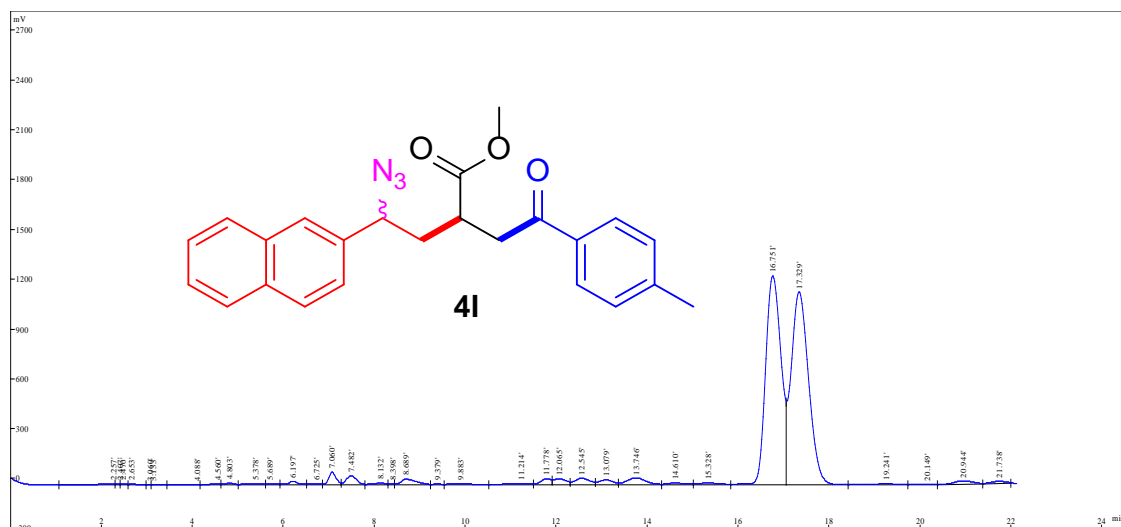
eluted by CH₃CN:H₂O=70:30

序号	保留时间	名称	浓度	峰面积
24	17.193		45.2	114895514
25	20.064		43.81	111353958



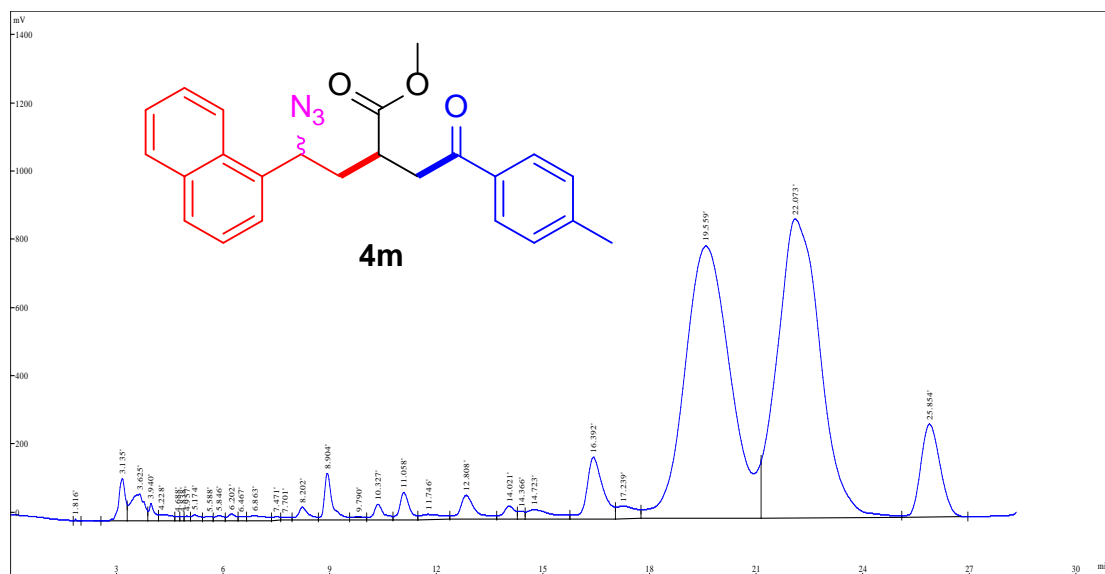
eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
34	55.593		41.92	126548851
35	56.897		50.7	153045094



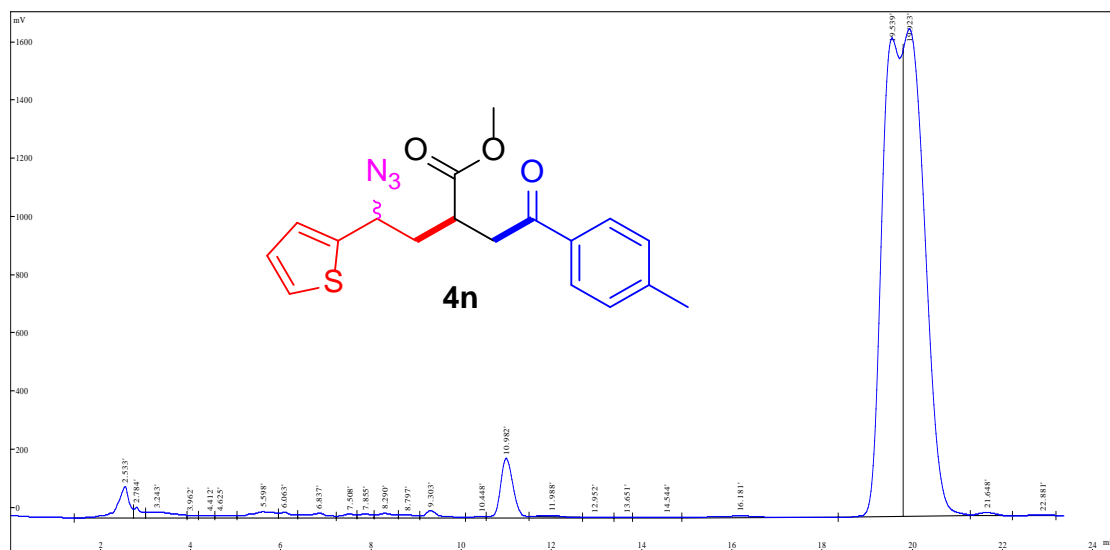
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
29	16.751		42.07	29790410
30	17.329		43.66	30921952



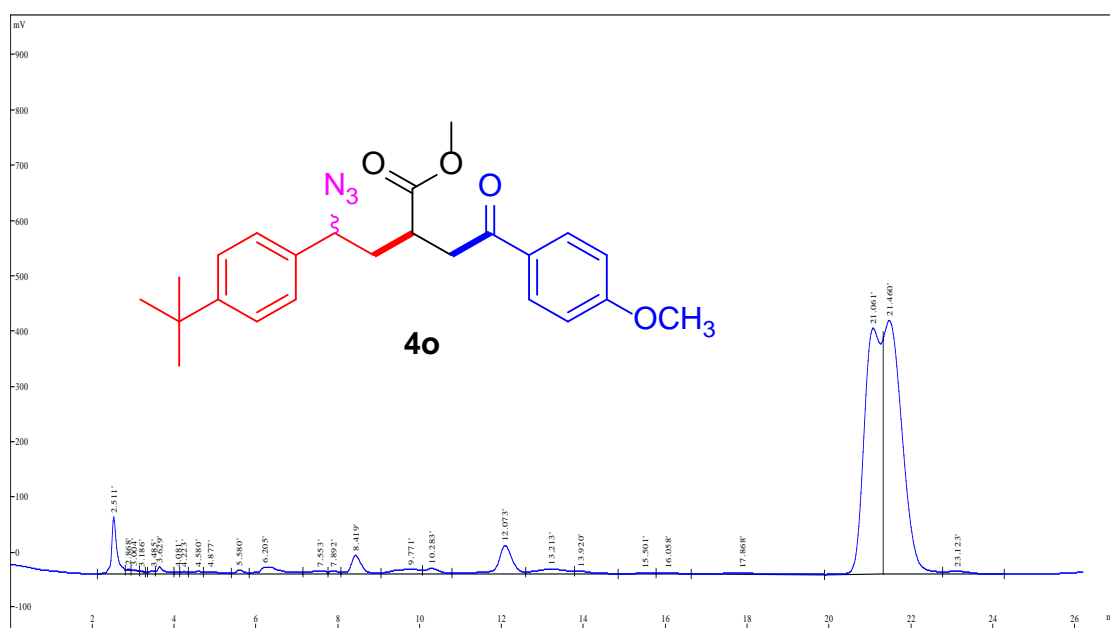
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
29	19.559		39.24	71321869
30	22.073		40.41	73447571



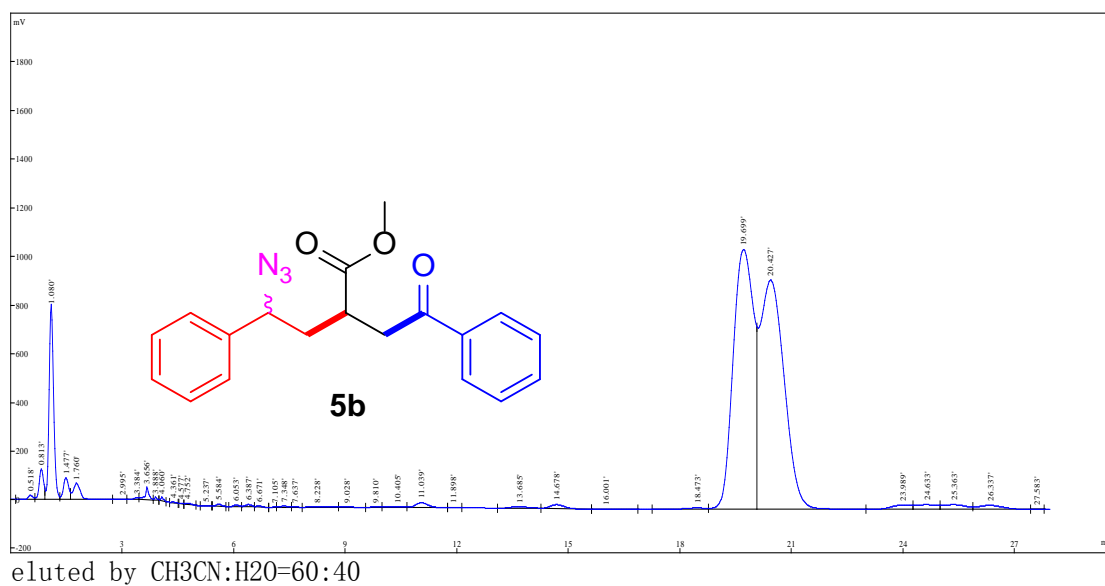
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
22	19.539		43.46	51702736
23	19.923		45.12	53685510

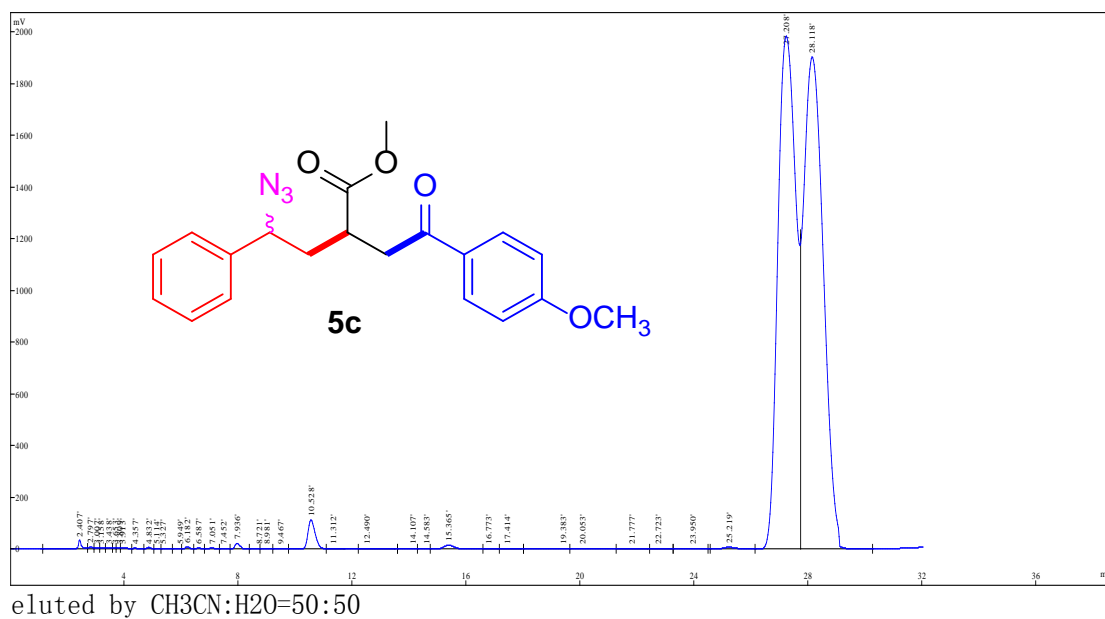


eluted by CH₃CN:H₂O=60:40

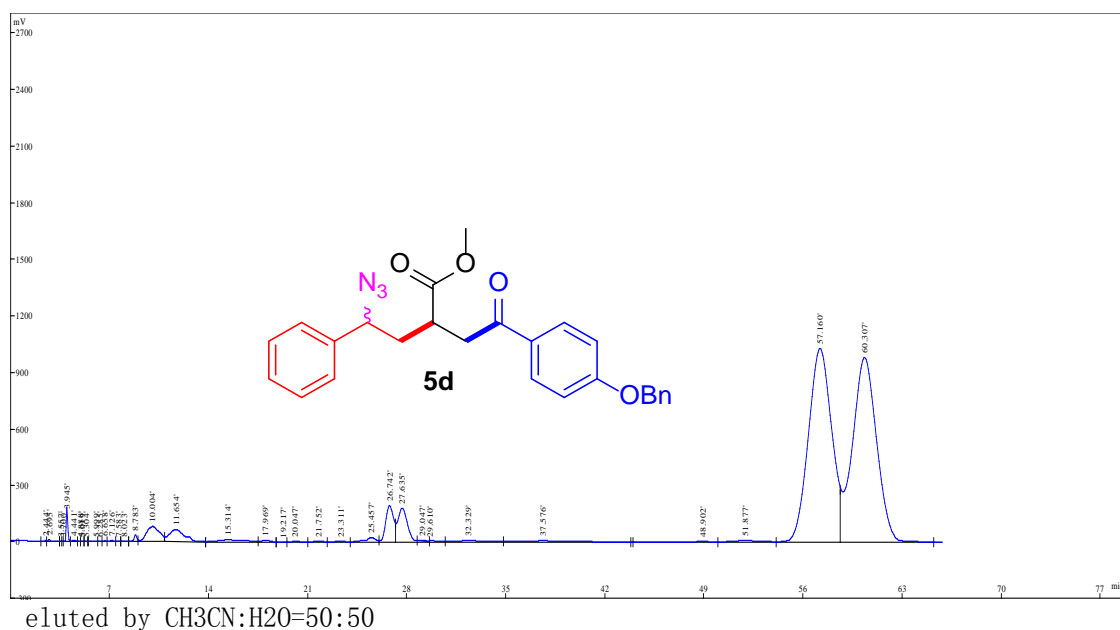
序号	保留时间	名称	浓度	峰面积
24	21.061		40.23	13616904
25	21.460		40.74	13783984



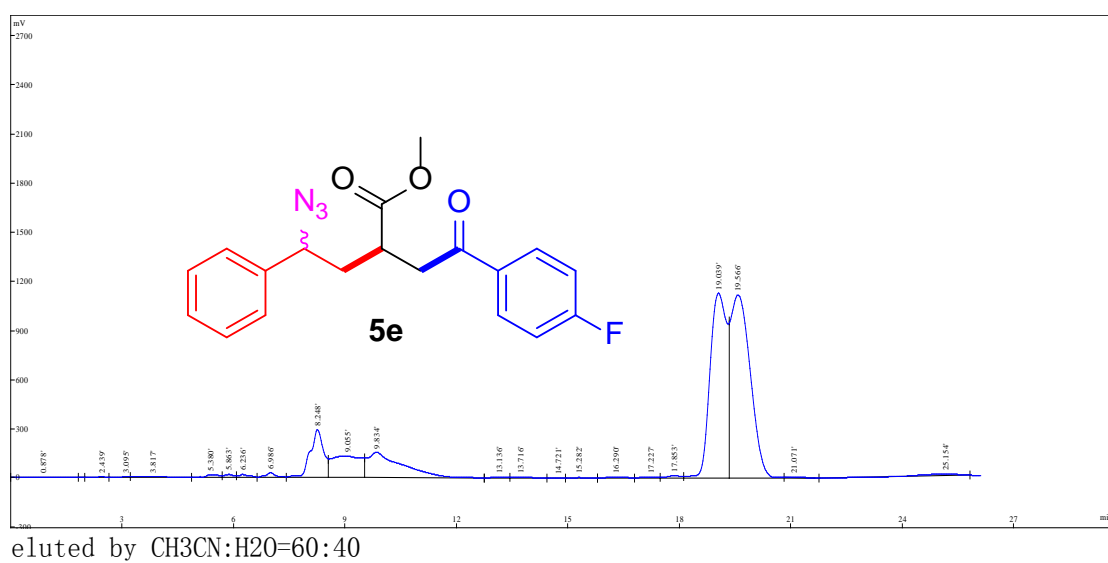
序号	保留时间	名称	浓度	峰面积
32	19.699		41.33	41492576
33	20.427		42.37	42533322



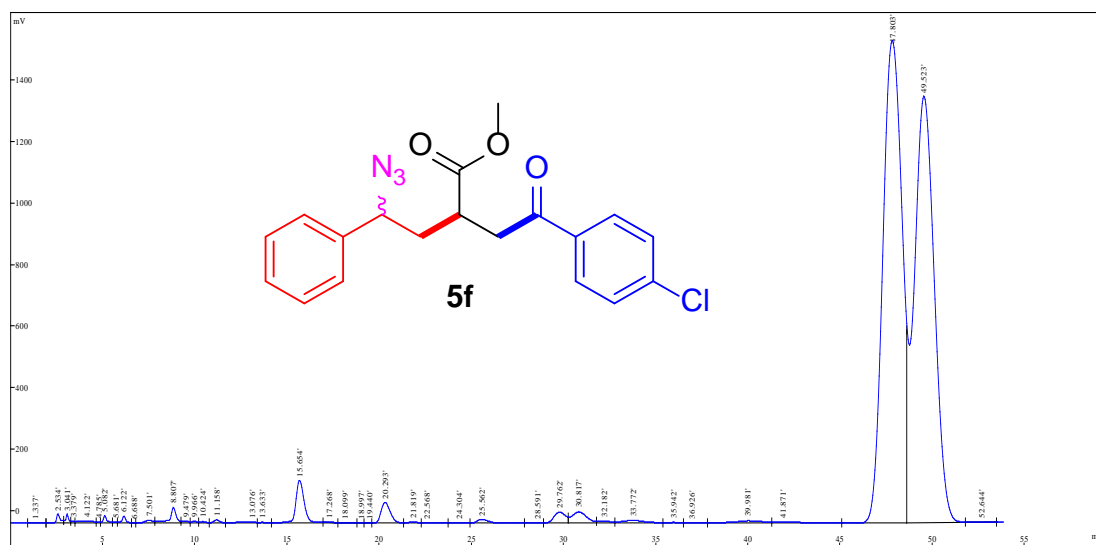
序号	保留时间	名称	浓度	峰面积
36	27.208		48.97	91073715
37	28.118		47.84	88985702



序号	保留时间	名称	浓度	峰面积
34	57.160		43.21	117925939
35	60.307		42.65	116411699

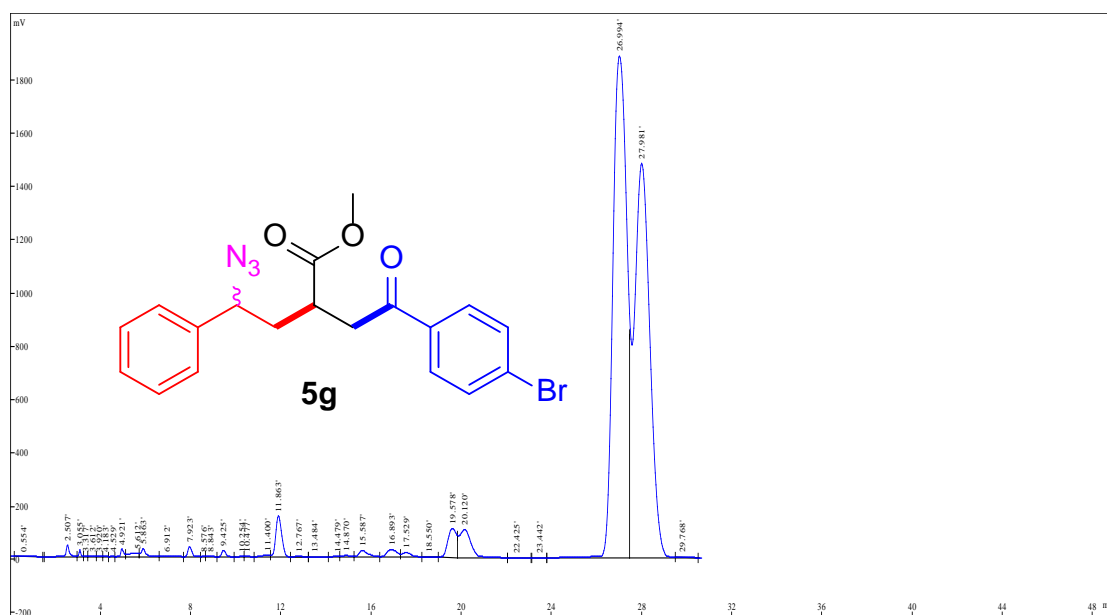


序号	保留时间	名称	浓度	峰面积
19	19.039		34.72	37550038
20	19.566		36.49	39460355



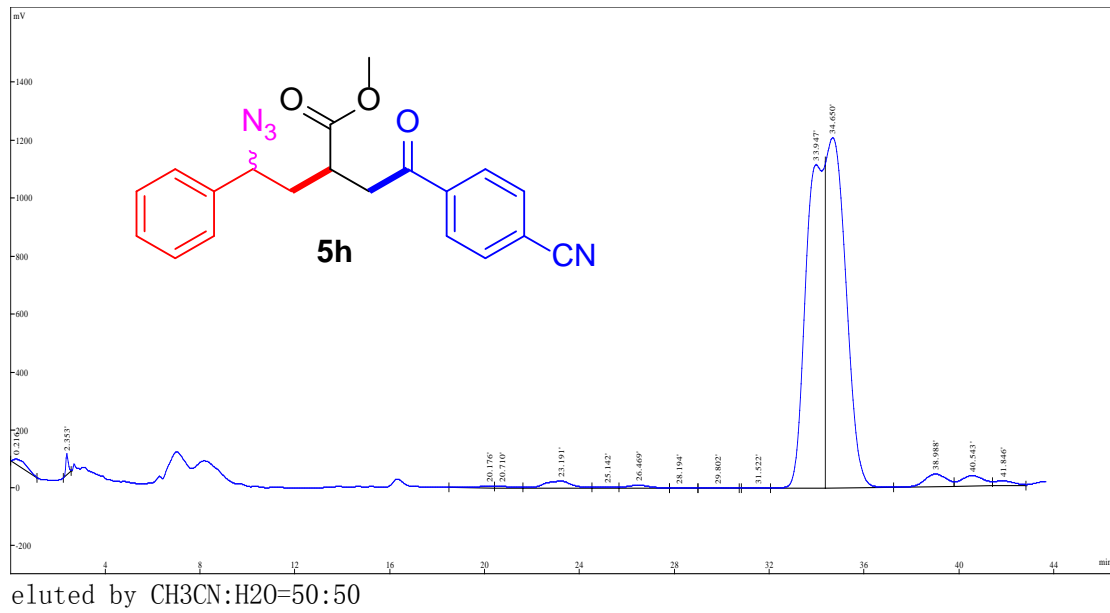
eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
38	47.803		46.67	111726182
39	49.523		44.37	106242291

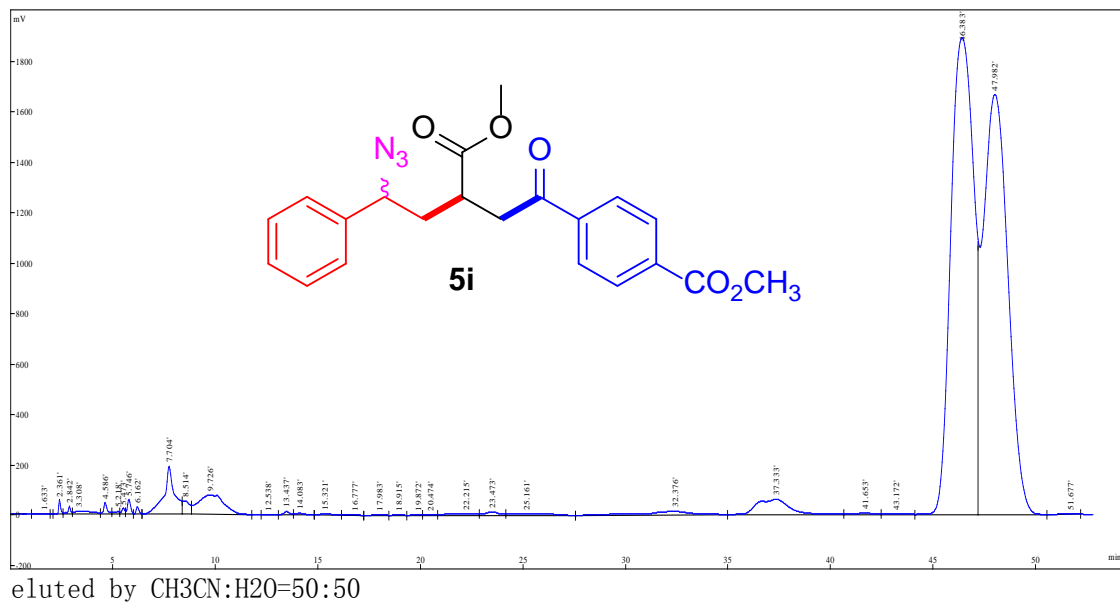


eluted by CH₃CN:H₂O=60:40

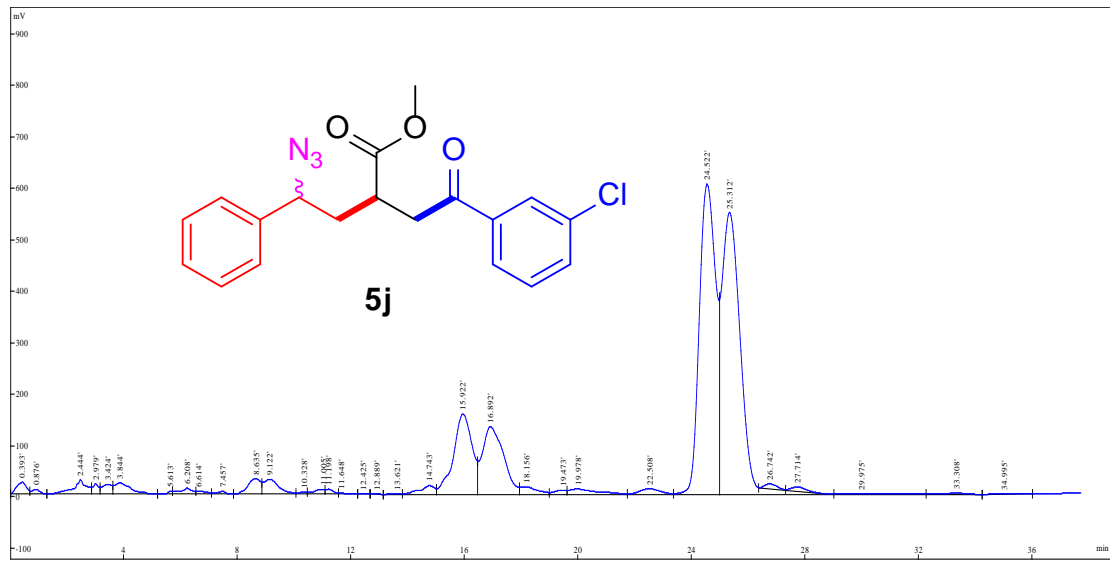
序号	保留时间	名称	浓度	峰面积
33	26.994		47.37	80765549
34	27.981		41.65	71043034



序号	保留时间	名称	浓度	峰面积
11	33.947		45.03	63649491
12	34.650		47.87	67661773

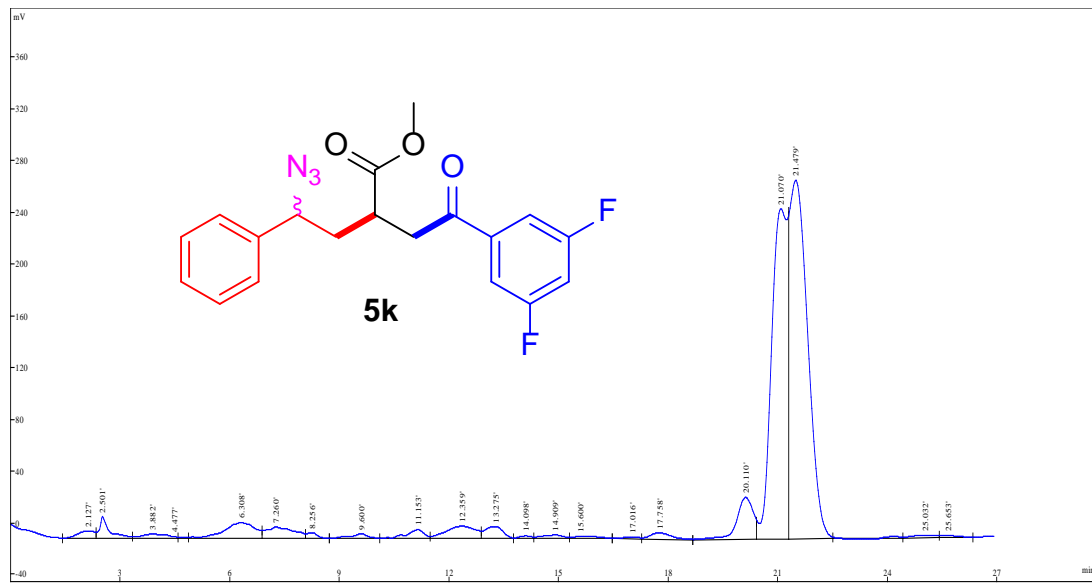


序号	保留时间	名称	浓度	峰面积
29	46.383		45.91	148551181
30	47.982		42.94	138892480



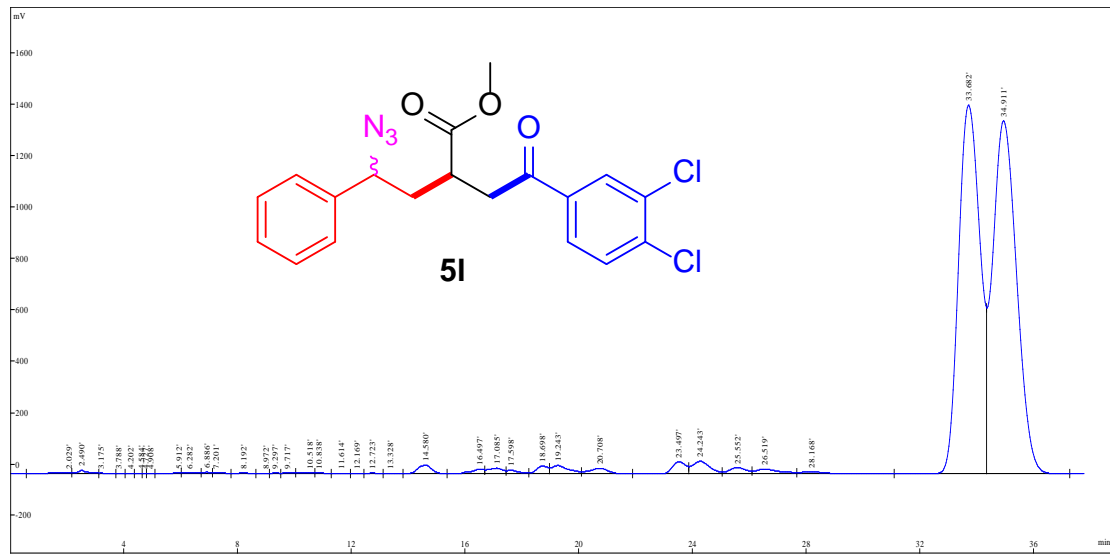
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
27	24.522		32.76	24911237
28	25.312		33.29	25315405



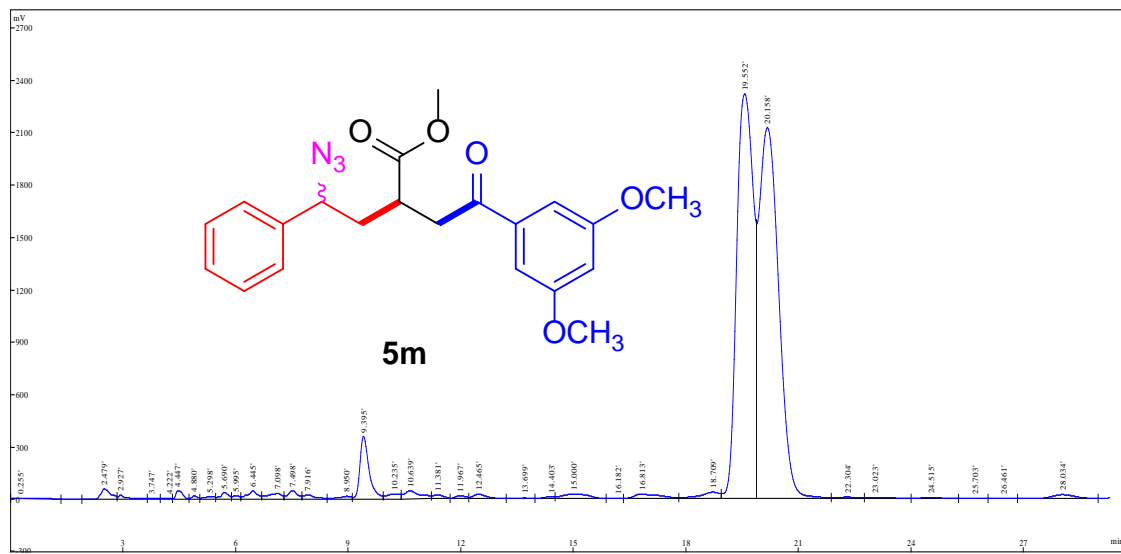
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
18	21.070		37.16	8182904
19	21.479		41.27	9084936



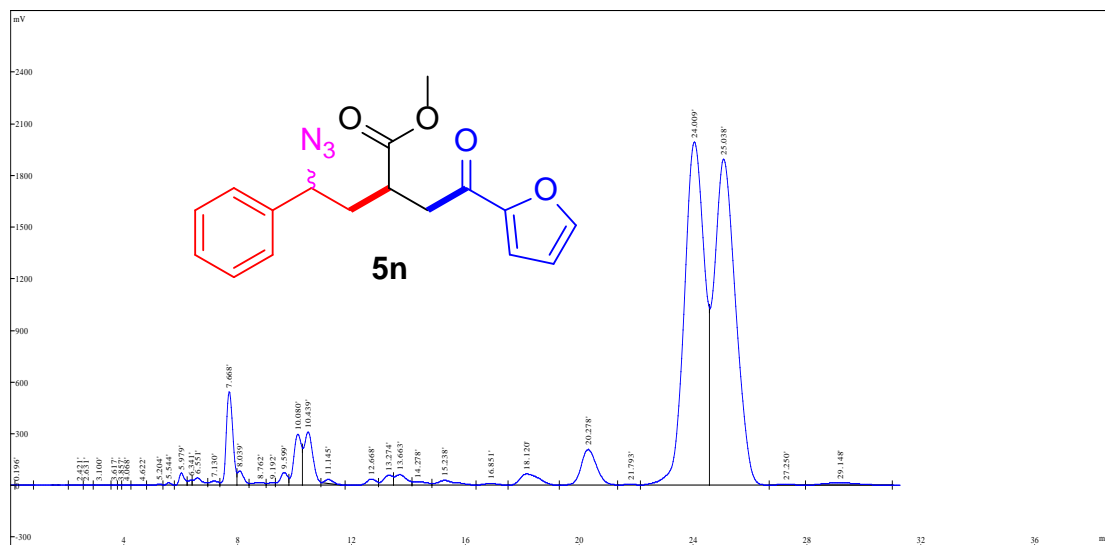
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
35	33.682		46.7	80043334
36	34.911		44.23	75807501



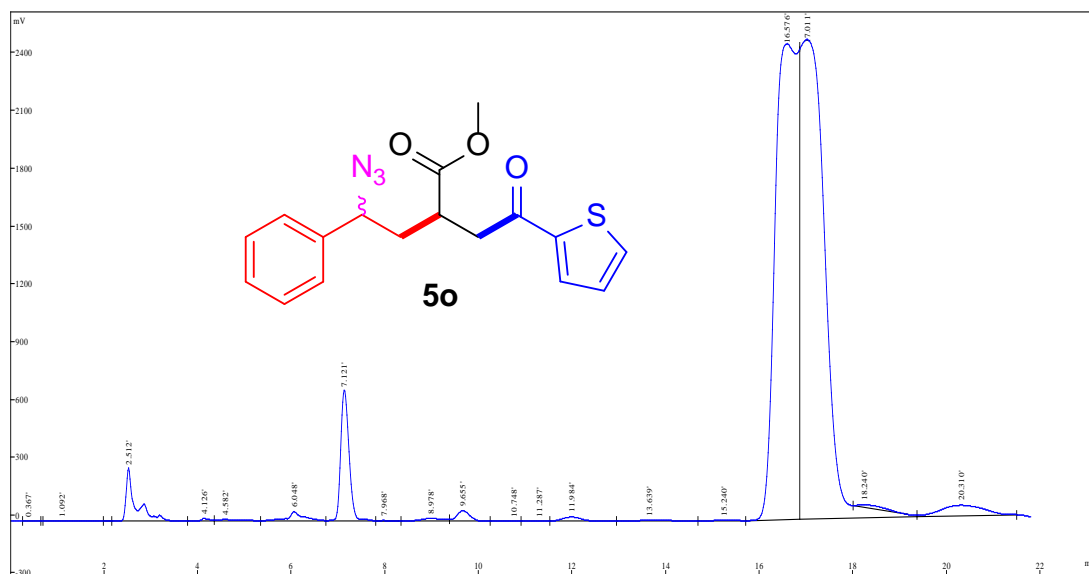
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
28	19.852		40.93	72734874
29	20.158		43.96	78099718



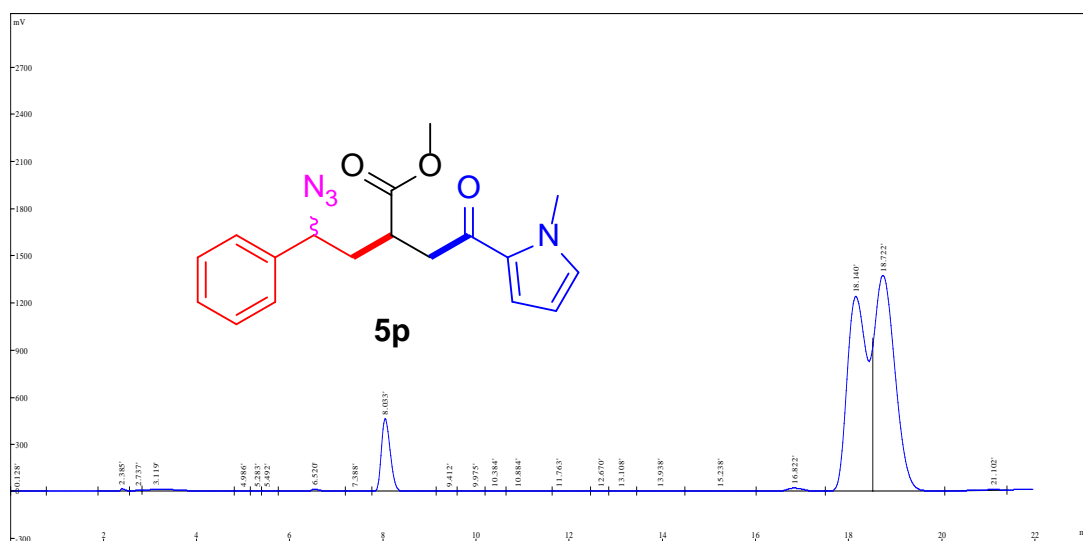
eluted by CH3CN:H2O=60:40

序号	保留时间	名称	浓度	峰面积
32	24.009		40.13	98738246
33	25.038		40.17	98854323



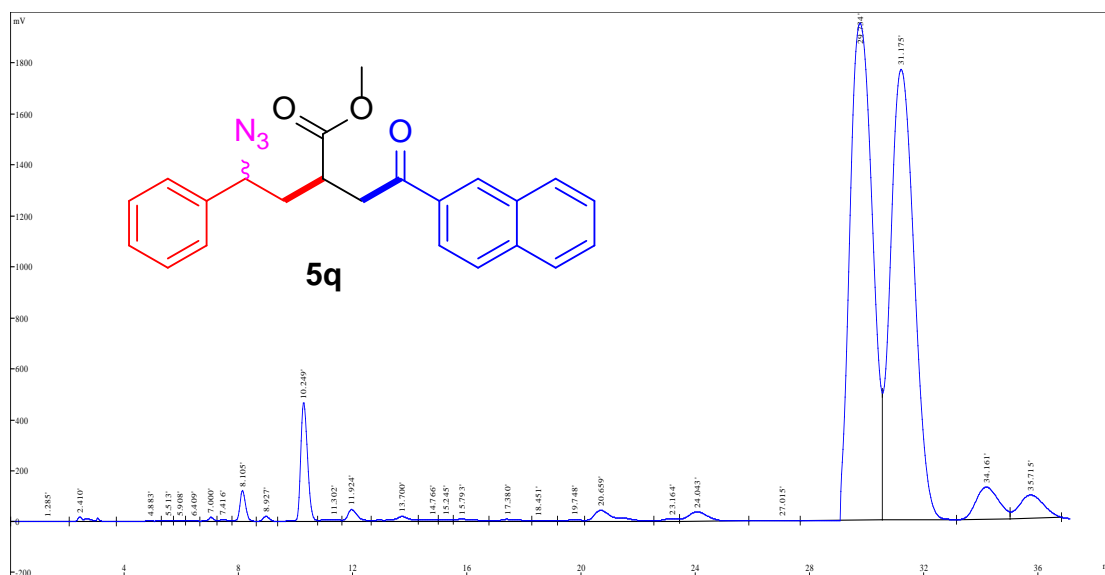
eluted by CH3CN:H2O=60:40

序号	保留时间	名称	浓度	峰面积
16	16.576		43.8	86339834
17	17.011		44.36	87468742



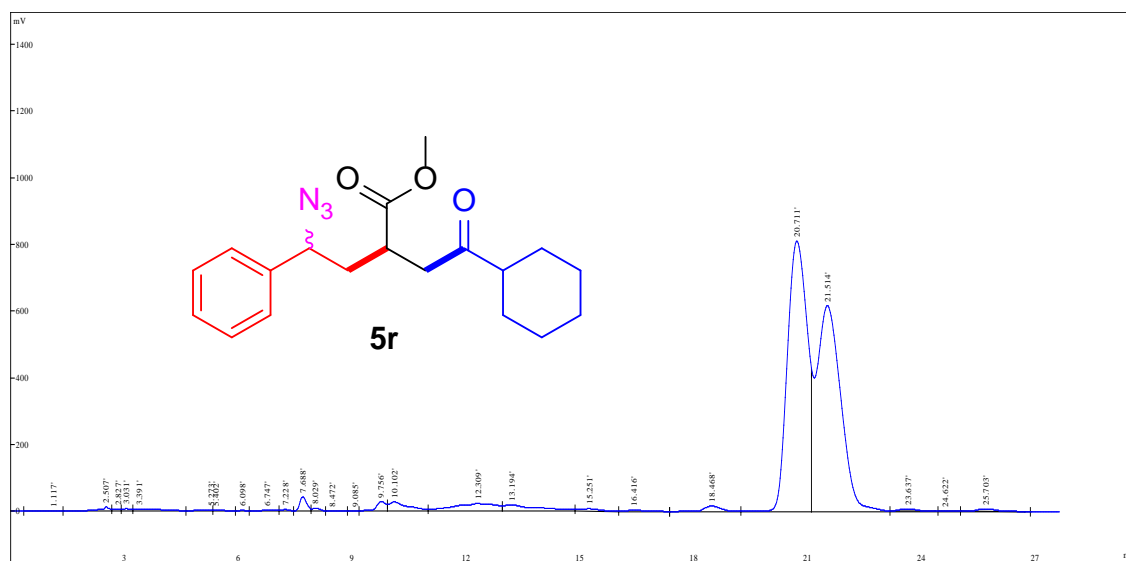
eluted by CH3CN:H2O=60:40

序号	保留时间	名称	浓度	峰面积
21	18.140		43.34	38660022
22	18.722		45.21	40329760



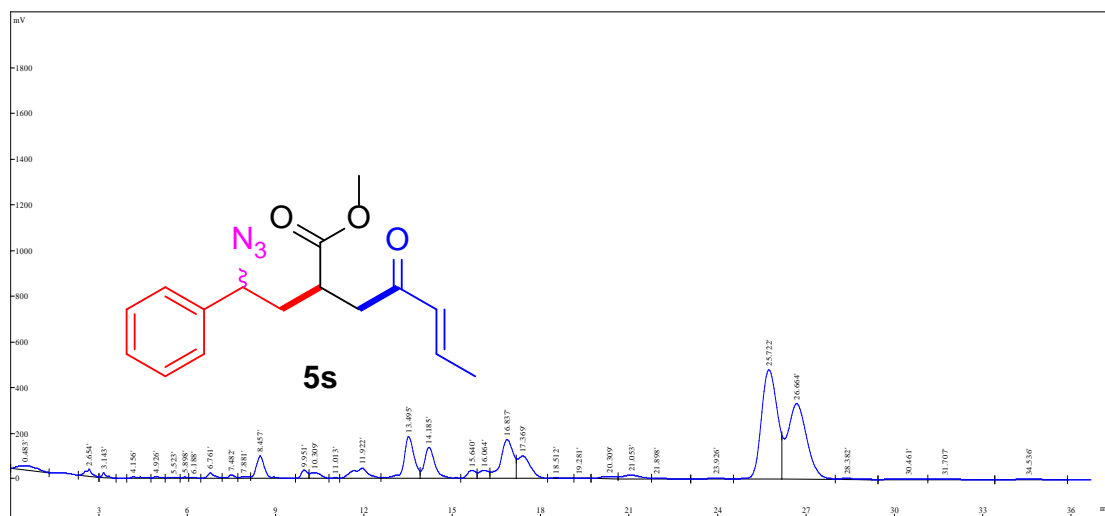
eluted by CH3CN:H2O=60:40

序号	保留时间	名称	浓度	峰面积
25	29.734		44.38	106708192
26	31.175		42.46	102114970



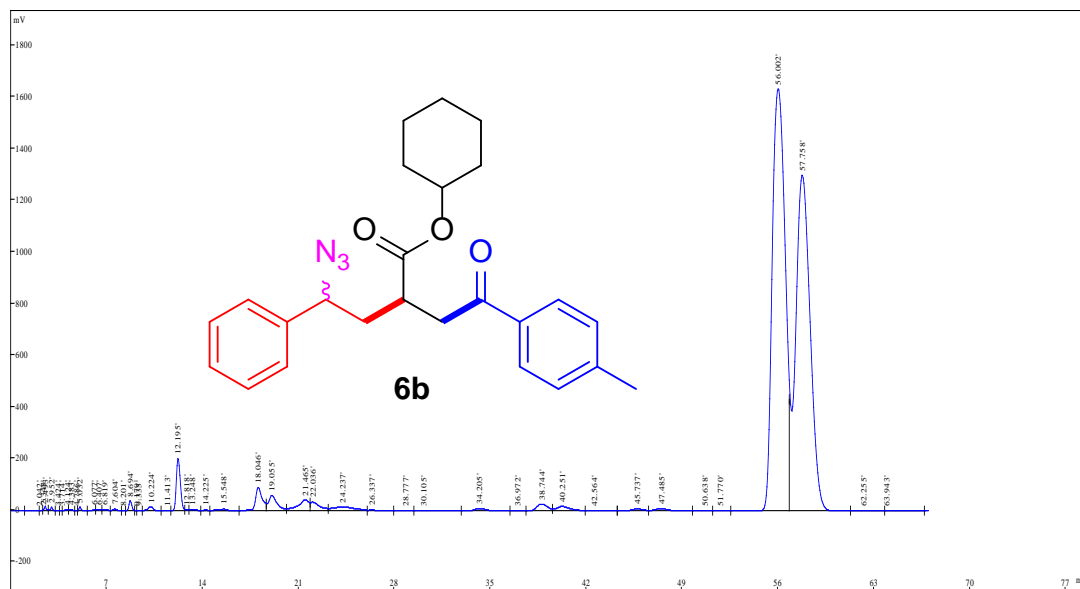
eluted by CH₃CN:H₂O=70:30

序号	保留时间	名称	浓度	峰面积
22	20.711		45.59	30917715
23	21.514		37.84	25671790



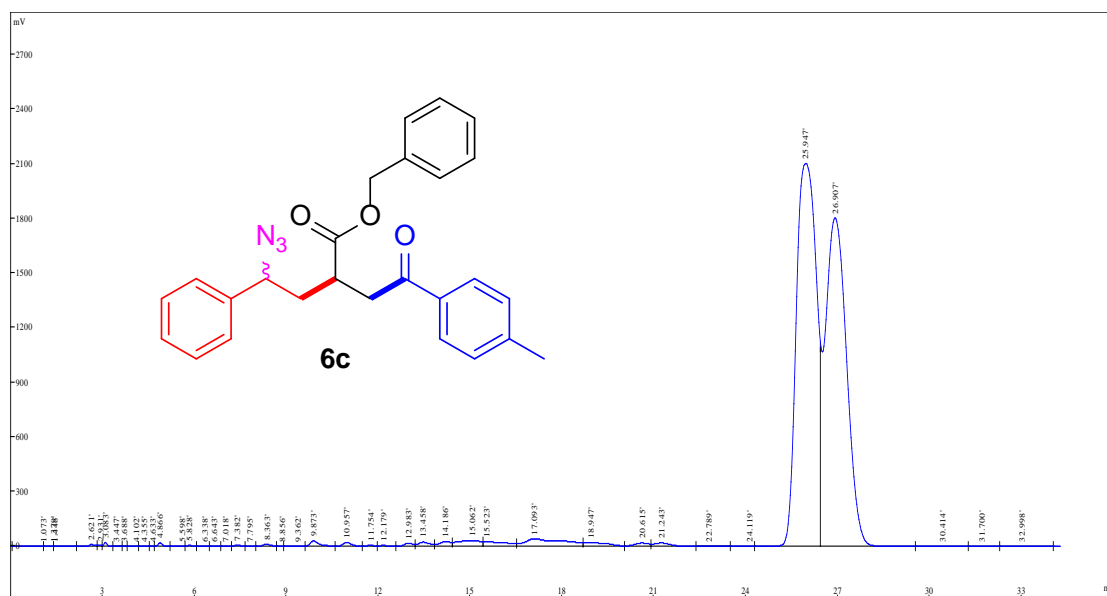
eluted by CH₃CN:H₂O=70:30

序号	保留时间	名称	浓度	峰面积
29	25.722		29.6	18081656
30	26.664		25.45	15550032



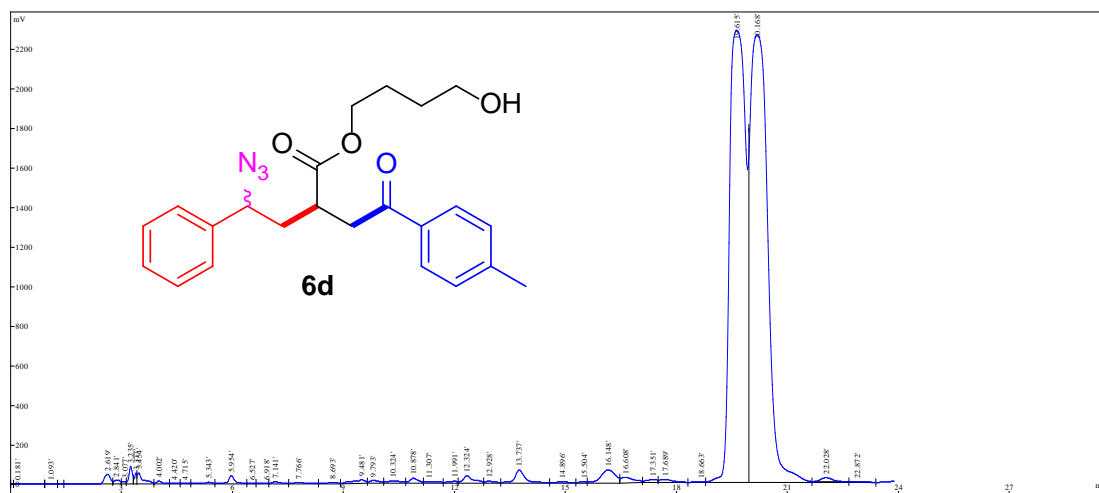
eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
43	56.002		46.61	107026285
44	57.754		41.42	95137466



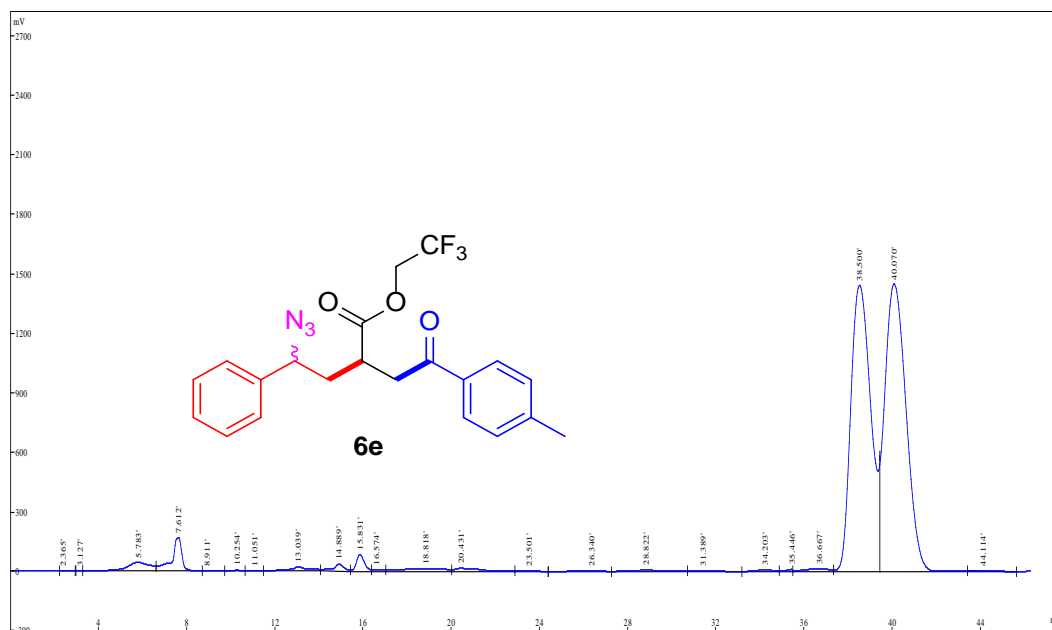
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
38	25.947		48.32	95754989
39	26.907		44.21	87646214



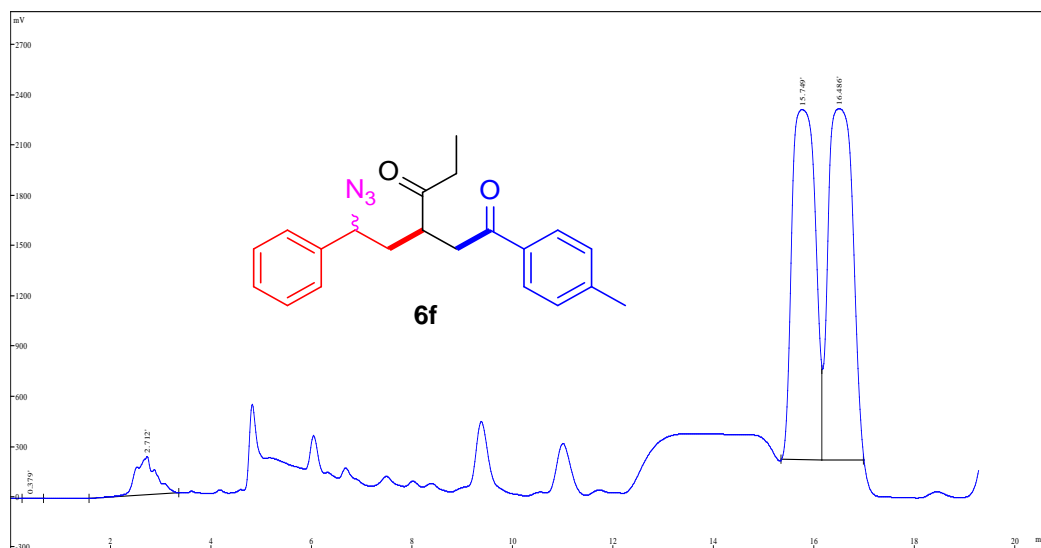
eluted by CH3CN:H2O=70:30

序号	保留时间	名称	浓度	峰面积
36	19.615		46.35	72553306
37	20.168		45.43	71099027



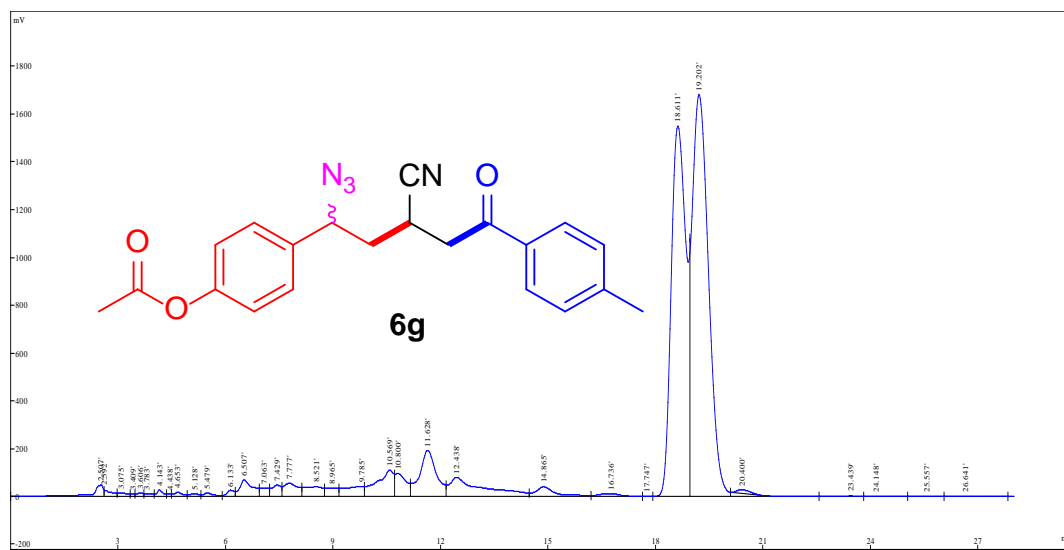
eluted by CH3CN:H2O=50:50

序号	保留时间	名称	浓度	峰面积
21	38.500		43.11	92855936
22	40.070		44.56	95974534



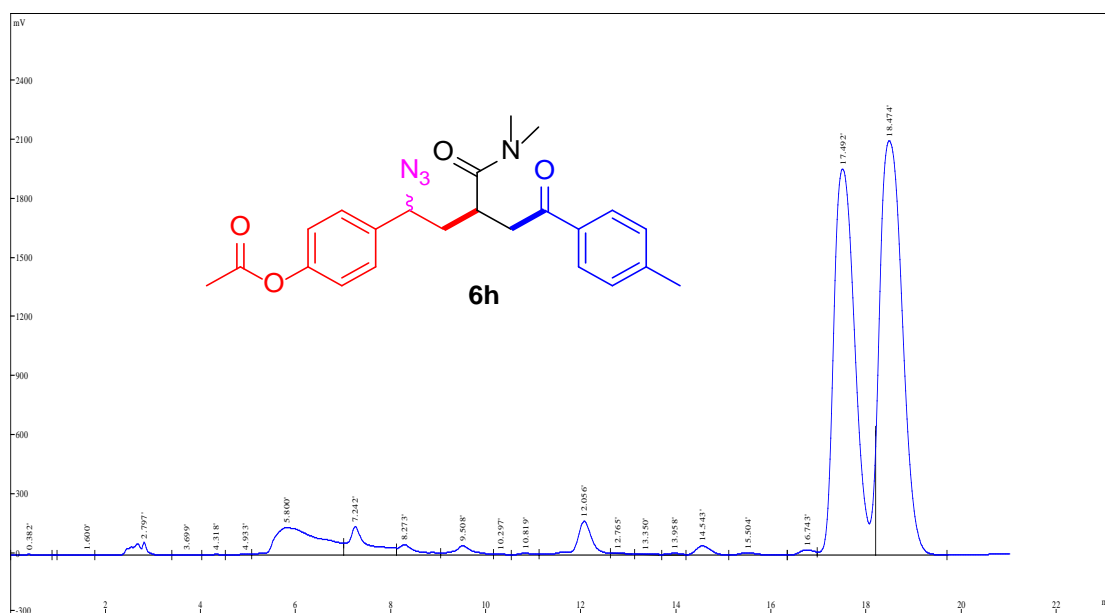
eluted by CH₃CN:H₂O=60:40

序号	保留时间	名称	浓度	峰面积
3	15.749		46.66	67610835
4	16.486		48.84	70759226



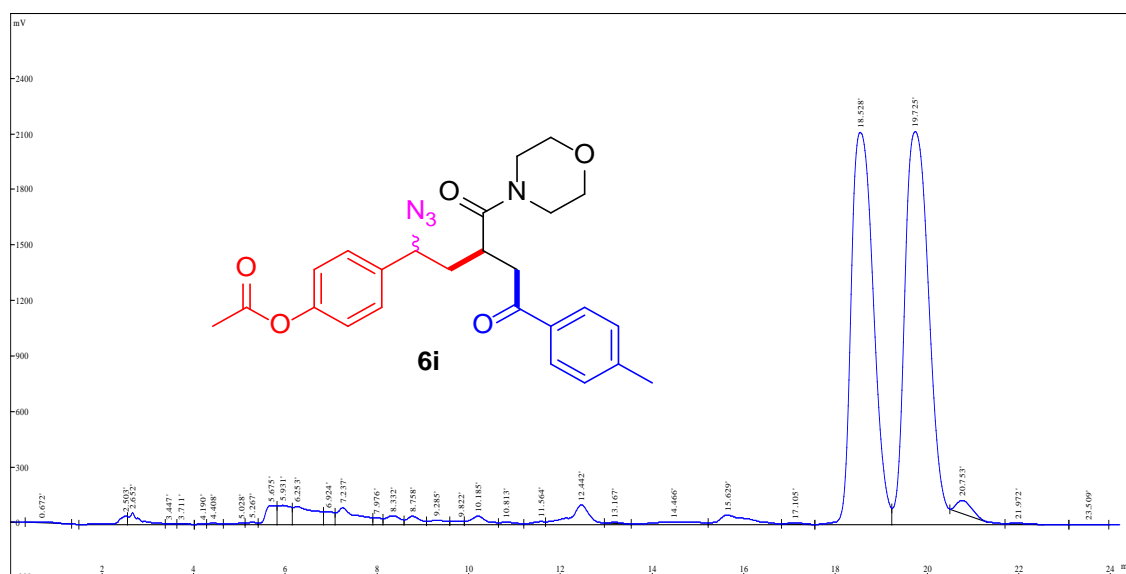
eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
27	18.611		35.24	46625856
28	19.202		39.29	51963405



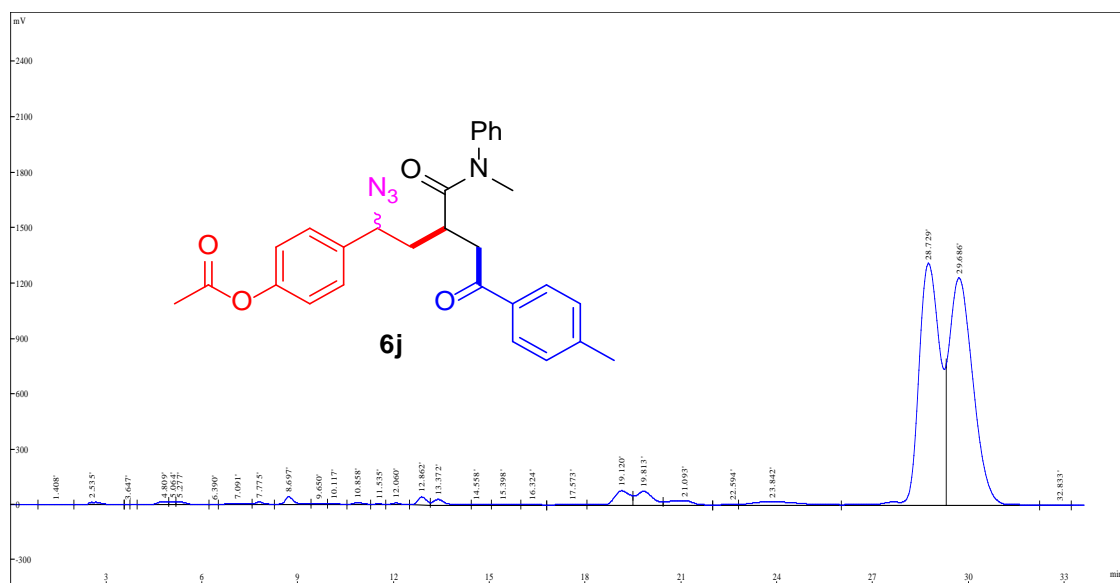
eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
20	17.492		39.57	61709952
21	18.474		43.23	67430765



eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
28	18.528		39.58	71258368
29	19.725		44.67	80424378



eluted by CH₃CN:H₂O=50:50

序号	保留时间	名称	浓度	峰面积
27	28.729		42.64	61472883
28	29.686		43.45	62646003