Electronic supplementary information

Regio- and stereo-selective decarbonylative alkylative arylation of terminal alkynes with aliphatic aldehydes and arenes via dual C-H bond functionalization

Yong Peng, Feng Zhang, Ting-Ting Qin, Cong-Ling Xu and Luo Yang*

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I. General information

Unless otherwise noted, all commercially available compounds were used as purchased without further purification. Dry solvents (toluene, ethyl acetate, dichloromethane, acetonitrile, chlorobenzene, fluorobenzene, trifluoromethyl benzene) were used as commercially available. 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. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 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.

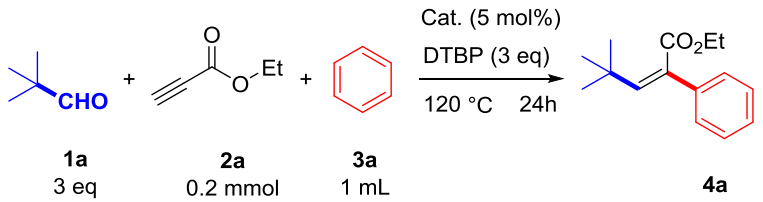
The Z/E ratio was determined by GC of reaction mixtures by assuming the Z/E-isomers with the same responses under the FID detector. The ratio of regio-isomers for the products from mono-substituted arenes was determined by ^{1}H NMR.

II. Genneral experimental procedure

An oven-dried reaction vessel was successively charged with $CuBr_2$ (0.05 mmol, 25 mol%), benzene (**3a**, 4 mL), ethyl propiolate (**2a**, 0.2 mmol, 1.0 equiv), pivalaldehyde (**1a**, 0.6 mmol, 3 equiv) and di-*tert*-butyl peroxide (DTBP, 0.6 mmol, 3 equiv). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 24 h. Afterwards the resulting mixture was cooled to room temperature, the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether (1:3) as eluent to give products **4a**.

III. Condition optimization

Table S1. Optimization of the catalyst[a]



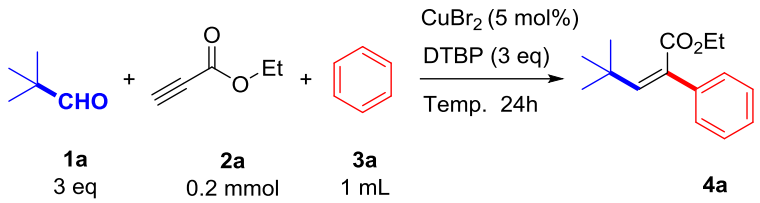
1a 3 eq | **2a** 0.2 mmol | **3a** 1 mL | **4a**

entry	Cat. (mol%)	Yield[%][b]
1	--	10
2	$Fe(OAc)_2$	10
3	$Fe(acac)_2$	7
4	$FeCl_2$	11
5	$CoCl_2$	12
6	$Co(OAc)_2$	8
7	$Co(acac)_2$	9
8	$NiCl_2$	8
9	$Ni(acac)_2$	8
10	$Ni(OAc)_2$	10
11	CuBr	20
12	$Cu(OAc)_2$	13
13	$Cu(acac)_2$	4
14	$CuBr_2$	25
15	Cu_2O	17

16	CuCl	19
17	$CuF_2 \cdot 2H_2O$	14
18	CuCN	11
19	$CuSO_4$	8

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (0.6 mmol, 3.0 equiv), **3a** (1 mL), DTBP (0.6 mmol, 3.0 equiv), Cat. (0.01 mmol, 5 mol%), stirred at 120 °C for 24 h under air. [b] Isolated yields.

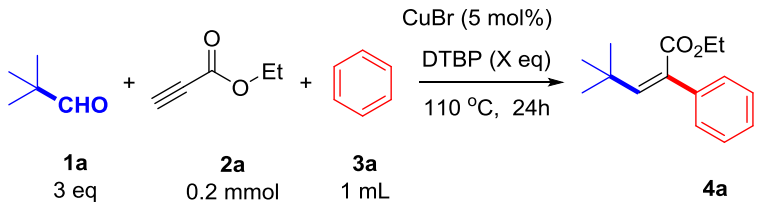
Table S2. Optimization of the temperature[a]



entry	Temp. (℃)	Yield[%][b]
1	80	19
2	90	31
3	100	42
4	110	49
5	120	25
6	130	17

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (0.6 mmol, 3.0 equiv), **3a** (1 mL), DTBP (0.6 mmol, 3.0 equiv), $CuBr_2$ (0.01 mmol, 5 mol%), for 24 h under air. [b] Isolated yields.

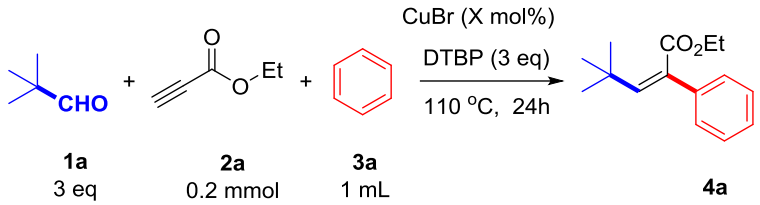
Table S3. Optimization of the amounts of oxidants[a]



entry	[O] (X equiv)	Yield[%][b]
1	TBHP in water	17
2	TBHP in decane	0
3	H_2O_2	0
4	DTBP（3 eq)	49
5	DTBP（2 eq)	28
6	DTBP（4 eq)	41

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (0.6 mmol, 3.0 equiv), **3a** (1 mL), DTBP (X equiv), $CuBr_2$ (0.01 mmol, 5 mol%), stirred at 120 °C for 24 h under air. [b] Isolated yields.

Table S4. Optimization of the amounts of catalysts [a]

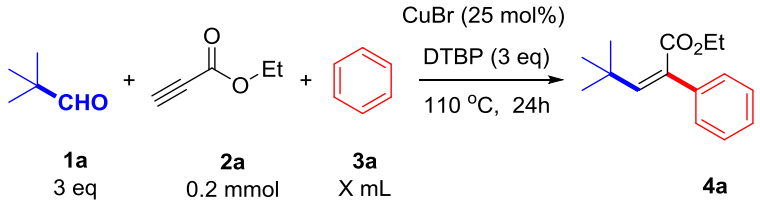


1a 3 eq | **2a** 0.2 mmol | **3a** 1 mL | **4a**

entry	$CuBr_2$ (X %)	Yield[%][b]
1	5	49
2	10	52
3	15	55
4	20	60
5	25	76
6	30	48

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (0.6 mmol, 3.0 equiv), **3a** (1 mL), DTBP (0.6 mmol, 3.0 equiv), $CuBr_2$ (X %), stirred at 120 °C for 24 h under air. [b] Isolated yields.

Table S5. Optimization of the amounts of solvent[a]

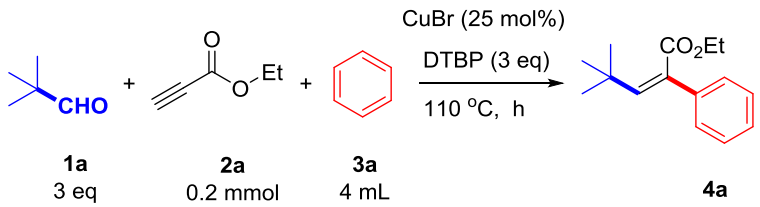


1a 3 eq | **2a** 0.2 mmol | **3a** X mL | **4a**

entry	Sol (X mL)	Yield[%][b]
1	1	76
2	2	78
3	3	83
4	4	88

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (0.6 mmol, 3.0 equiv), **3a** (X mL), DTBP (0.6 mmol, 3.0 equiv), $CuBr_2$ (25 %), stirred at 120 °C for 24 h under air. [b] Isolated yields.

Table S6. Optimization of the time[a]



1a 3 eq | **2a** 0.2 mmol | **3a** 4 mL | **4a**

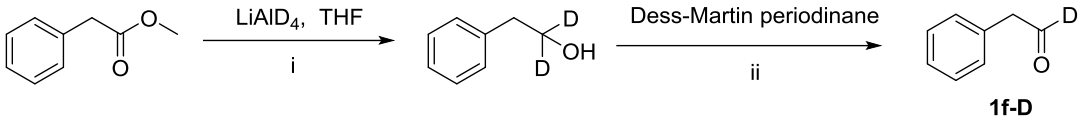
entry	h	Yield[%][b]
1	12	57
2	16	74

3	20	84
4	24	88

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (3 equiv), **3a** (4 mL), DTBP (0.6 mmol, 3.0 equiv), $CuBr_2$ (25 %), stirred at 120 °C under air. [b] Isolated yields.

IV. KIE experiments

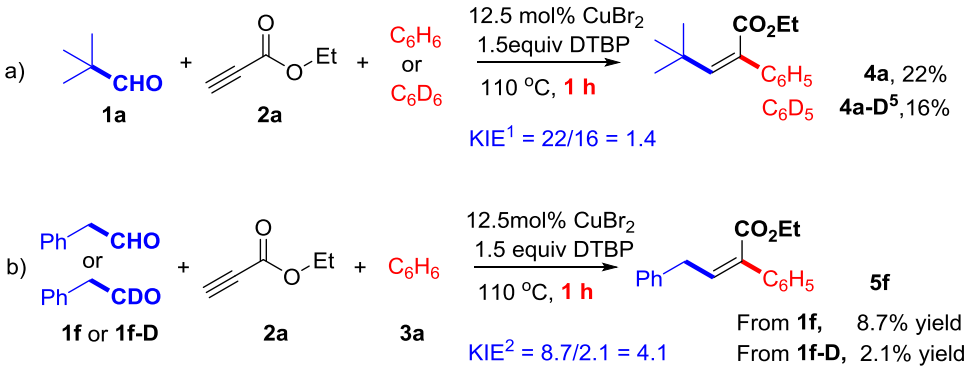
(a) Synthesis of 2-phenylacetaldehyde-D[1] (D[1]–1f)



(i) To a stirred suspension of $LiAlD_4$ (0.23 g, 6 mmol) in dry THF (3 ml) was added dropwise a solution of methyl methyl 2-phenylacetate (0.75 g, 5 mmol) in dry THF (10 ml) at 0 °C. After 1.5 h at room temperature, the reaction was quenched by addition with 40% KOH at 0 °C. The precipitate was filtered off and washed with ether. The combined filtrates were evaporated and the residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 10 : 1) to give 2-phenylethan-1-ol-D[2] (0.52 g, 85%) as a yellow oil.

(ii) Dess-Martin periodinane (2.12 g, 5 mmol) was added to a solution of above 2-phenylethan-1-ol-D[2] (4.3 mmol) in 15 mL of CH_2Cl_2. The reaction mixture was stirred until the alcohol was no longer detectable (TLC). The mixture was suction filtered and concentrated under reduced pressure. The residue was further purified by column chromatography on silica gel to give 2-phenylacetaldehyde-D[1] (**1f-D**) (0.49 g, 95%) as a colorless oil.

(b) Competing experiments

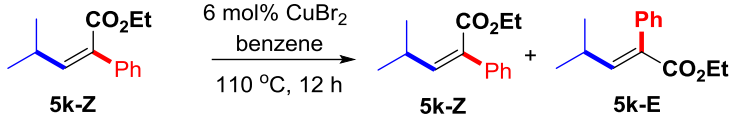


[a] Two microwave reaction vessels was separately charged with charged with $CuBr_2$ (0.025 mmol, 12.5 mmol%), benzene (**3a**, 2 mL), (or benzene **D[6]-3a**) ethyl propiolate (**2a**, 0.1 mmol, 1.0 equiv), pivalaldehyde (**1a**, 0.3 mmol, 1.5 equiv) and di-*tert*-butyl peroxide (DTBP, 0.3 mmol, 1.5 equiv). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 1 h. Yield of **4a** and **4a-D[5]** was detected by GC.

[b] Two microwave reaction vessels was separately charged with charged with $CuBr_2$ (0.025 mmol, 12.5 mol%), benzene (**3a**, 2 mL), ethyl propiolate (**2a**, 0.1 mmol, 1.0 equiv), 2-phenylacetaldehyde (**1f**, 0.3 mmol, 1.5 equiv) (or 2-phenylacetaldehyde **D[1]-1f)** and di-*tert*-butyl peroxide (DTBP, 0.3 mmol, 1.5 equiv). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 1 h. Yield

of **5f** was detected by GC.

(c)



with $CuBr_2$: **Z:E** = 2.5:1
without $CuBr_2$: **Z:E** = 7:1

[a] A microwave reaction vessels was separately charged with charged with $CuBr_2$ (0.006 mmol, 6 mmol%), benzene (**3a**, 1 mL) and ethyl (Z)-4-methyl-2-phenylpent-2-enoate (**5k-Z**, 0.05 mmol). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 12 h. Yield of **5k-Z** and **5k-E** was detected by GC.

[b] A microwave reaction vessels was separately charged with charged with benzene (**3a**, 1 mL) and ethyl (Z)-4-methyl-2-phenylpent-2-enoate (**5k-Z**, 0.05 mmol). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 12 h. Yield of **5k-Z** and **5k-E** was detected by GC.

V. DFT calculations

Computational Details

All DFT calculations were carried out with Gaussian03 quantum chemical package.[1] The geometry optimizations were performed with B3LYP functional and the 6-311+G(d) basis set. For those structures having various conformations, the most stable conformer was searched and utilized. Vibrational frequency calculations were carried out at the same level of theory as the geometry optimizations. Free energy changes were calculated based on the optimized gas phase structures.

The calculation out-put files and coordinates were included in the separated zipped file.

References

Gaussian 03, Revision B.05,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,
K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,
V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,
G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota,
R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,
H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,
C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,
A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala,
K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg,
V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain,
O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari,
J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford,
J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,
I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,
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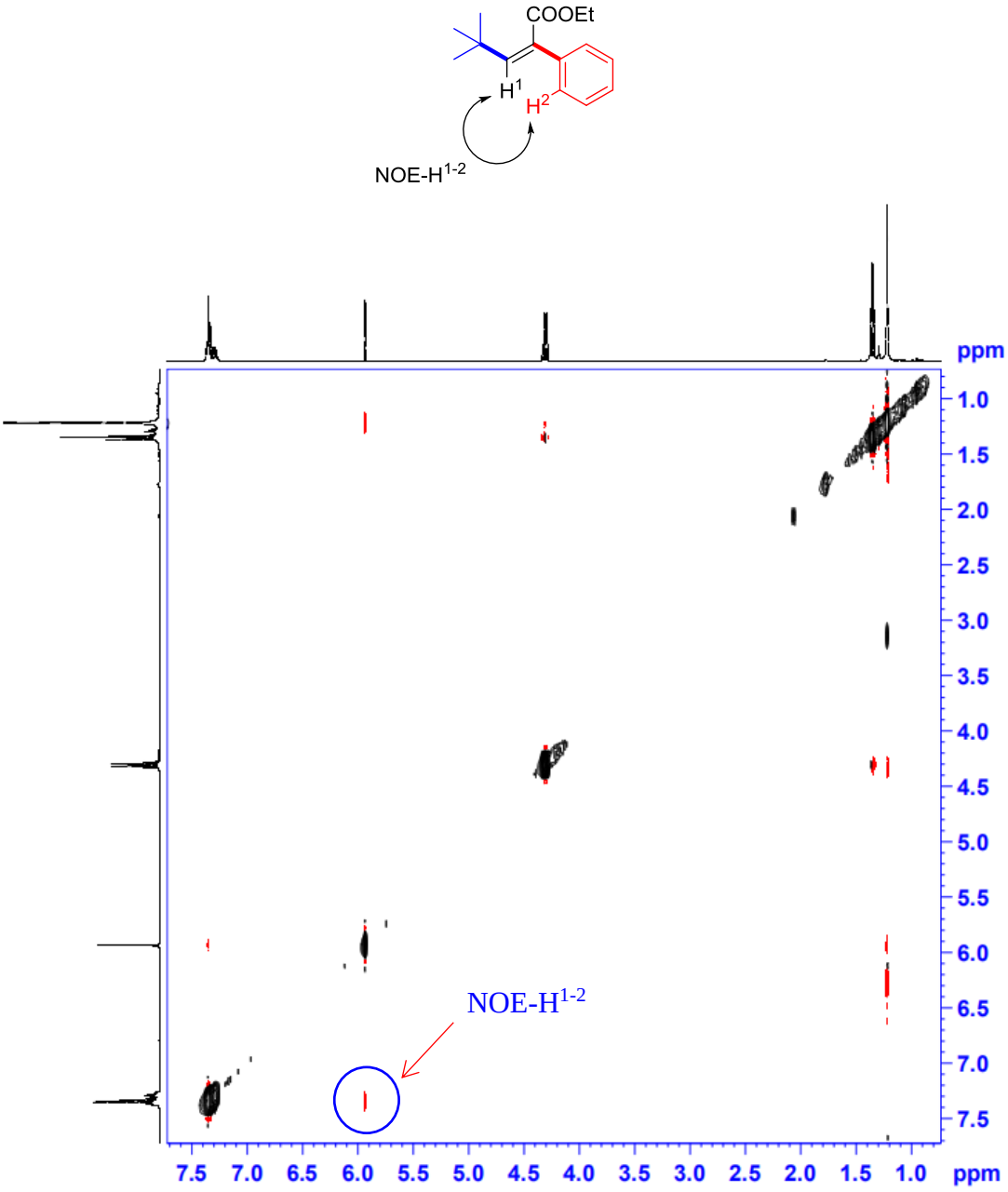
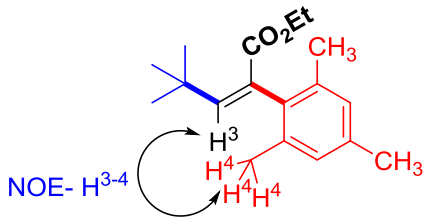
Gaussian, Inc., Pittsburgh PA, 2003.

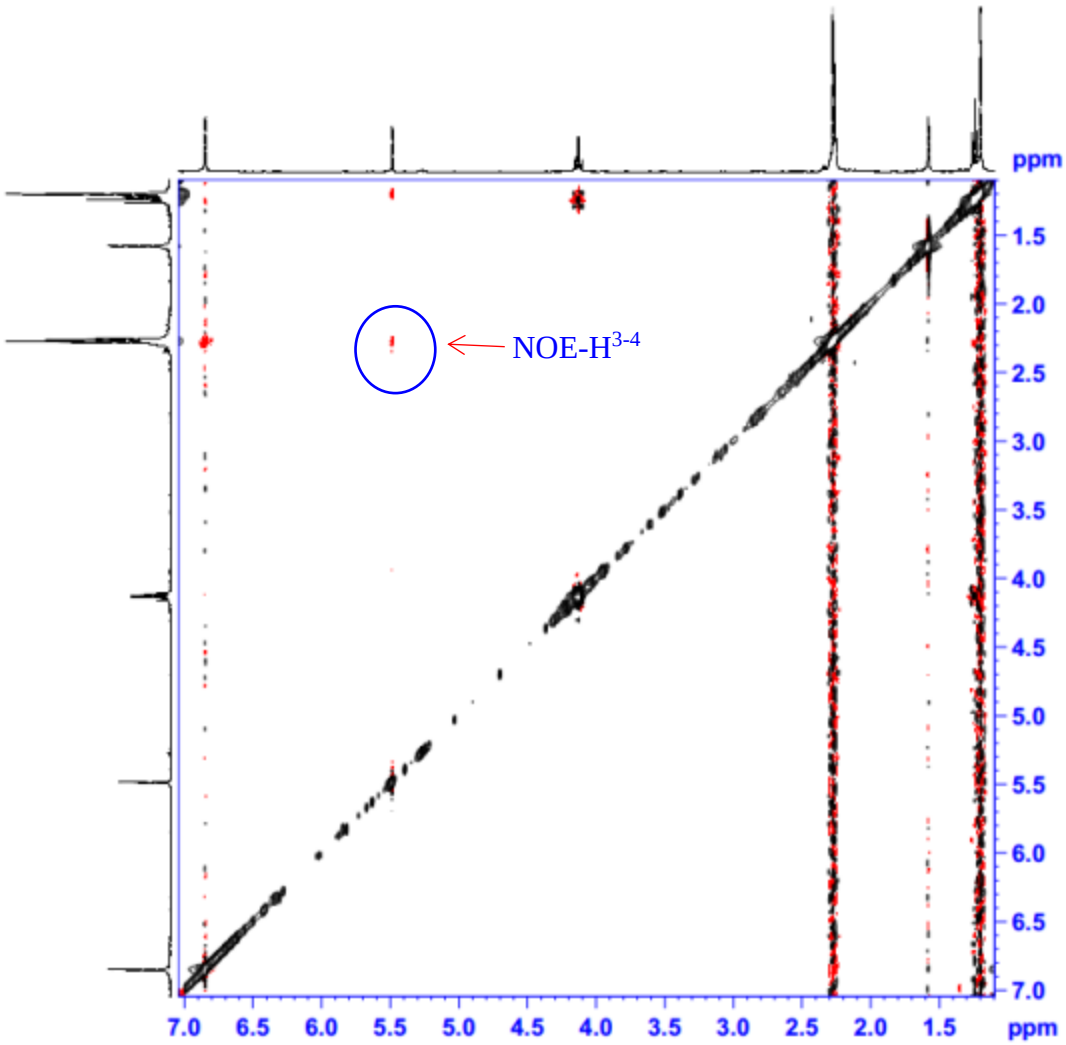
VI. The assignment of the configuration by NOE

(a) ethyl (Z)-4,4-dimethyl-2-phenylpent-2-enoat (4a)



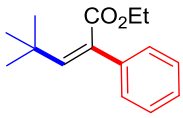
(b) ethyl (Z)-2-mesityl-4,4-dimethylpent-2-enoate (6g)





VII Spectra data of products 4a-4i, 5b-5m, 6b-6m

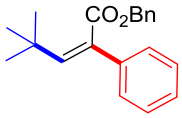
(4a) ethyl (Z)-4,4-dimethyl-2-phenylpent-2-enoate[1]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (40.8 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 5.90 (s, 1H), 4.27 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.02, 142.45, 138.08, 132.29, 128.57, 127.68, 126.09, 61.05, 33.98, 29.86, 14.15. IR (cm^{-1}): 3083, 3059, 2905, 2870, 1727, 1540, 751.

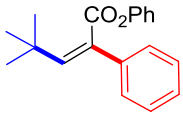
(4b) benzyl (Z)-4,4-dimethyl-2-phenylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between benzyl propiolate (**2b**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow oil (50.6 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 5H), 7.29 – 7.25 (m, 5H), 5.92 (s, 1H), 5.25 (s, 2H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.85, 142.94, 137.93, 135.37, 131.88, 128.78, 128.64, 128.60, 128.46, 127.75, 126.18, 67.06, 34.05, 29.88. IR (cm^{-1}): 3096, 3054, 2936, 2867, 1776, 1540, 694. HRMS: calcd. for $C_{20}H_{22}NaO_2^+$ $[M+Na]^+$: 317.1512; Found: 317.1497.

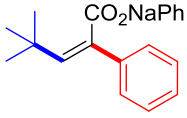
(4c) phenyl (Z)-4,4-dimethyl-2-phenylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between phenyl propiolate (**2c**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow oil (60 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 8H), 7.16 (d, J = 8.0 Hz, 2H), 6.05 (s, 1H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.17, 150.69, 144.12, 137.91, 131.65, 129.66, 128.82, 128.00, 126.36, 126.17, 121.52, 34.33, 30.06. IR (cm^{-1}): 3089, 3066, 2954, 2843, 1647, 1558,747. HRMS: calcd. for $C_{19}H_{20}NaO_2^+$ $[M+Na]^+$: 303.1356; Found: 303.1337

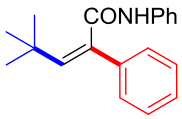
(4d) naphthalen-2-yl (Z)-4,4-dimethyl-2-phenylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between naphthalen-2-yl propiolate (**2d**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow oil (52.8 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 5H), 7.49 (d, J = 8.0 Hz, 4H), 7.41 (t, J = 8.0 Hz, 2H), 7.30 (dd, J = 8.0, 1.8 Hz, 1H), 6.08 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.31, 159.20, 148.33, 144.29, 137.94, 133.88, 131.67, 131.59, 130.35, 129.64, 128.87, 128.57, 128.05, 127.92, 127.83, 126.75, 126.41, 125.94, 124.70, 122.00, 120.96, 118.49, 34.38, 30.10. IR (cm^{-1}): 3362, 3209, 2937, 2844, 1646, 1570, 745. HRMS: calcd. for $C_{19}H_{20}Na_2O_2^+$ $[M+Na]^+$: 353.1512; Found: 353.1517.

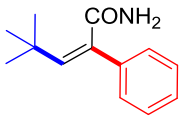
(4e) (Z) -4,4-dimethyl-N,2-diphenylpent-2-enamide[2]



The title compound was prepared according to the general procedure described above by the reaction between N-phenyl-O-propioloylhydroxylamine (**2e**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow solid (45.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.46 – 7.44 (m, 2H), 7.36 – 7.28 (m, 5H), 7.26 (s, 1H), 7.14 (t, J = 6.0 Hz, 1H), 6.00 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.11, 142.32, 138.06, 137.72, 135.34, 129.25, 128.84, 127.95, 126.10, 124.69, 119.87, 34.40, 30.20. IR (cm^{-1}): 3061, 3043, 2906,2748, 1751, 1615, 748. Melting point: 158-162 ℃.

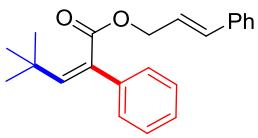
(4f) (Z)-O-(4,4-dimethyl-2-phenylpent-2-enoyl)hydroxylamine



The title compound was prepared according to the general procedure described above by the reaction between propiolamide (**2f**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow solid (21.9 mg, 50%).

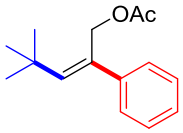
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 6.18 (s, 1H), 6.05 (s, 1H), 5.91 (s, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.50, 142.47, 137.95, 132.10, 128.56, 127.67, 126.01, 33.94, 29.78. IR (cm^{-1}): 3297, 3060, 2958, 2870, 1727, 1635, 1478, 754. HRMS: calcd. for $C_{13}H_{17}NNaO^+$ $[M+Na]^+$: 226.1202; Found: 226.1229.

(4g) cinnamyl (Z)-4,4-dimethyl-2-phenylpent-2-enoate



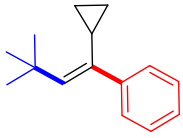
The title compound was prepared according to the general procedure described above by the reaction between cinnamyl propiolate (**2g**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow oil (33.3 mg, 52%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 6.4 Hz, 5H), 7.33 (t, J = 7.2 Hz, 5H), 6.70 (d, J = 15.6 Hz, 1H), 6.30 – 6.26 (m, 1H), 5.93 (s, 1H), 4.85 (t, J = 6.4 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.92, 152.65, 143.79, 137.92, 135.98, 135.73, 128.79, 128.67, 128.49, 127.89, 126.86, 126.48, 121.74, 66.91, 34.05, 29.86. IR (cm^{-1}): 3297, 3092, 2976, 2861, 1703, 1647, 755. HRMS: calcd. for $C_{22}H_{24}NaO_2^+$ [M+Na]$^+$: 343.1669; Found: 343.1670.

(4h) (Z)-4,4-dimethyl-2-phenylpent-2-en-1-yl acetate



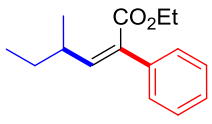
The title compound was prepared according to the general procedure described above by the reaction between prop-2-yn-1-yl acetate (**2h**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (33.9 mg, 73%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 5.98 (s, 1H), 5.10 (s, 2H), 2.00 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.28, 145.94, 142.58, 133.43, 128.36, 127.08, 126.56, 61.58, 33.56, 31.53, 21.15. IR (cm^{-1}): 3104, 3063, 2978, 2863, 1699, 1487, 756. HRMS: calcd. for $C_{14}H_{18}Na^+$ [M+Na]$^+$: 255.1356; Found: 255.1341.

(4i) (Z)-(1-cyclopropyl-3,3-dimethylbut-1-en-1-yl)benzene



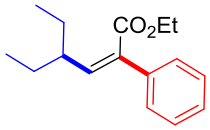
The title compound was prepared according to the general procedure described above by the reaction between ethynylcyclopropane (**2i**) with pivalaldehyde (**1a**) and benzene (**3a**), and purified by flash column chromatography as yellow oil (24 mg, 60%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.08 (m, 5H), 5.23 – 5.10 (m, 1H), 2.37 – 2.27 (m, 1H), 1.25 (s, 2H), 1.11 (s, 2H), 1.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.44, 137.87, 133.79, 128.42, 127.61, 127.07, 36.35, 30.22, 20.49, 14.41, 12.08. IR (cm^{-1}): 3185, 3073, 2988, 2813, 1699, 1487, 756. HRMS: calcd. for $C_{14}H_{18}Na^+$ [M+Na]$^+$: 208.1222; Found: 208.1230.

(5b) ethyl (Z)-4-methyl-2-phenylhex-2-enoate



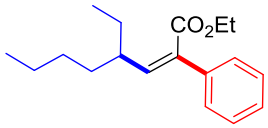
The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2-methylbutanal (**1b**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (35.7 mg, 77%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 5H), 5.91 (d, J = 10.4 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.75 – 2.64 (m, 1H), 1.49 – 1.37 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.08 (d, J = 6.4 Hz, 3H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.72, 144.44, 137.87, 133.79, 128.42, 127.61, 127.07, 77.48, 77.16, 76.84, 60.84, 36.35, 30.22, 20.49, 14.41, 12.08. IR (cm^{-1}): 3143, 3069, 2965, 2870, 1697, 1560, 755. HRMS: calcd. for $C_{15}H_{20}NaO_2^+$ [M+Na]$^+$: 255.1356; Found: 255.1347.

(5c) ethyl (Z)-4-ethyl-2-phenylhex-2-enoate



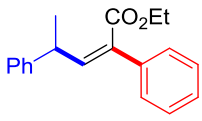
The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2-ethylbutanal (**1c**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (38.4 mg, 78%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 5.85 (d, J = 10.4 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.56 – 2.47 (m, 1H), 1.57 – 1.50(m, 3H), 1.32 (t, J = 7.0 Hz, 4H), 0.91 (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.82, 143.04, 137.95, 135.28, 128.44, 127.61, 127.02, 60.78, 43.36, 28.15, 14.42, 12.02. IR (cm^{-1}): 3179, 3086, 2929, 2874, 1722, 1643, 755. HRMS: calcd. for $C_{15}H_{19}NaO_2^+$ [M+Na]$^+$: 269.1512; Found: 269.1484.

(5d) ethyl (Z)-4-ethyl-2-phenyloct-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2-ethylhexanal (**1d**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (41.6 mg, 76%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 5H), 5.85 (dd, J = 10.4, 0.8 Hz, 1H), 4.31 – 4.26 (m, 2H), 2.62 – 2.55 (m, 1H), 1.55 – 1.48 (m, 2H), 1.29 (dd, J = 7.2, 6 Hz, 9H), 0.92 – 0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.80, 143.39, 138.02, 134.98, 128.44, 127.60, 127.05, 60.78, 41.68, 35.12, 29.75, 28.50, 23.02, 14.42, 14.21, 11.98. IR (cm^{-1}): 3085, 3029, 2928, 2873, 1722, 1634, 748. HRMS: calcd. for $C_{17}H_{23}NaO_2^+$ [M+Na]$^+$: 297.1825; Found: 297.1803.

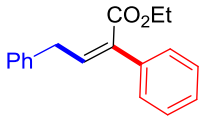
(5e) ethyl (Z)-2,4-diphenylpent-2-enoate[3]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2-phenylpropanal (**1e**) and benzene (**3a**), and purified by flash column chromatography as yellow oil (41.4 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 10H), 6.19 (d, J = 10.4 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.21 – 4.14 (m, 1H), 1.48 (d, J = 6.8 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.39, 144.74, 142.73, 137.64, 133.27, 128.72, 128.42, 127.80, 127.27, 127.19, 126.55, 61.04, 39.66, 21.33, 14.41. IR (cm^{-1}): 3244, 3085, 3029, 2928, 2873, 1722, 748.

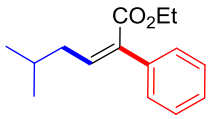
(5f) ethyl (Z)-2,4-diphenylbut-2-enoate[4]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2-phenylacetaldehyde (**1f**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (28.7 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 10H), 6.29 (t, J = 7.6 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 3.76 (t, J = 8.6 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.32, 147.42, 137.18, 129.15, 128.93, 128.80, 128.75, 128.43, 127.84, 127.27, 126.52, 61.09, 36.41, 14.42. IR (cm^{-1}): 3125, 3112, 2948, 2893, 1732, 1635, 755.

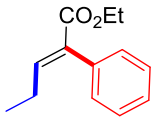
(5g) ethyl (Z)-5-methyl-2-phenylhex-2-enoat



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2**a**) with 3-methylbutanal (**1g**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (29.2 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 5H), 6.19 (t, J = 7.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.30 (t, J = 7.2 Hz, 2H), 1.85 – 1.75 (m, 1H), 1.32 (t, J = 7.0 Hz, 3H), 0.97 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.55, 138.44, 138.09, 135.45, 128.42, 127.62, 127.18, 60.84, 39.07, 28.93, 22.61, 14.43. IR (cm^{-1}): 3085, 3062, 2957, 2869, 1721, 1636, 754. HRMS: calcd. for $C_{15}H_{20}NaO_2^+$ $[M+Na]^+$: 255.1356; Found: 255.1368.

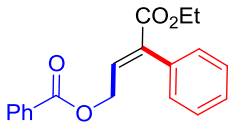
(5h) ethyl (E)-2-phenylpent-2-enoate[5]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2**a**) with propionaldehyde (**1h**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (22.9 mg, 56% (Z:E = 1:9)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.04 (t, J = 7.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.13 – 2.04 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.44, 146.37, 139.76, 129.90, 129.79, 128.00, 127.40, 60.87, 23.01, 14.34, 13.46. IR (cm^{-1}): 3083, 3072, 2950, 2871, 1732, 1633, 755.

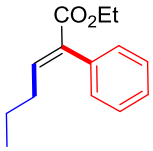
(5i) (E)-4-ethoxy-4-oxo-3-phenylbut-2-en-1-yl benzoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2-oxoethyl benzoate (**1i**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (42.1 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (t, J = 4.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 6.4 Hz, 4H), 7.42 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 5.37 (s, 2H), 4.31 (dq, J = 53.6, 7.2 Hz, 2H), 1.28 (dd, J = 14.0, 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.94, 166.59, 136.19, 133.18, 130.26, 129.85, 129.51, 128.95, 128.74, 128.52, 128.31, 128.22, 66.84, 61.90, 14.30. IR (cm^{-1}): 3065, 3033, 2926, 2956, 2853, 1720, 1654, 735. HRMS: calcd. for $C_{18}H_{16}NaO_4^+$ [M+Na]$^+$: 333.1097; Found: 333.1090.

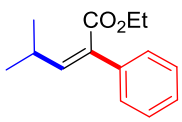
(5j) ethyl (E)-2-phenylhex-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with cyclopropanecarbaldehyde (**1j**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (18.7 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3H), 7.18 – 7.16 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.06 (dd, J = 14.8, 7.6 Hz, 2H), 1.45 (dd, J = 14.8, 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 145.06, 135.69, 134.20, 129.89, 128.03, 127.40, 60.92, 31.63, 22.28, 14.40, 14.00. IR (cm^{-1}): 3012, 3001, 2958, 2837, 1736, 1073, 749. HRMS: calcd. for $C_{14}H_{18}NaO_2^+$ [M+Na]$^+$: 225.1244; Found: 225.1253.

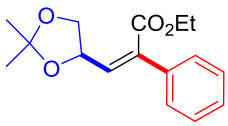
(5k) ethyl (Z)-4-methyl-2-phenylpent-2-enoate[1]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with isobutyraldehyde (**1k**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (34.9 mg, 80%).

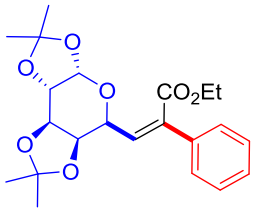
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.17 (d, J = 7.2 Hz, 1H), 6.84 (d, J = 10.8 Hz, 0.7×1H), 5.95 (d, J = 10.0 Hz, 0.3×1H), 4.32 – 4.27 (m, 0.65×1H), 4.22 – 4.17 (m, 1.35×1H), 2.97 – 2.88 (m, 1H), 2.45 – 2.36 (m, 2H), 1.32 (t, J = 7.0 Hz, 1H), 1.26 (t, J = 6.6 Hz, 2H), 1.10 (d, J = 6.4 Hz, 2H), 0.99 (d, J = 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.62, 167.62, 151.32, 145.47, 137.74, 135.80, 132.68, 131.84, 129.91, 129.66, 128.39, 128.03, 127.59, 127.37, 127.07, 60.92, 60.86, 29.56, 28.64, 22.83, 22.33, 14.35. IR (cm^{-1}): 3012, 3001, 2958, 2837, 1736, 1073, 749.

(5l) ethyl (Z)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-phenylacrylate



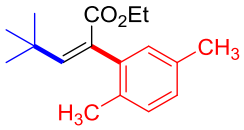
The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with 2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (**1l**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (39.7 mg, 72%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 5H), 6.27 (d, J = 7.2 Hz, 1H), 5.14 (q, J = 7.2 Hz, 1H), 4.35 (dd, J = 8.4, 6.8 Hz, 1H), 4.32 – 4.26 (m, 2H), 3.74 (dd, J = 8.4, 7.2 Hz, 1H), 1.44 (d, J = 19.6 Hz, 6H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.19, 139.88, 136.96, 136.38, 128.44, 128.30, 127.83, 109.96, 74.32, 69.83, 61.39, 26.75, 25.77, 14.36. IR (cm^{-1}): 3433, 3031, 2985, 2935, 2874, 1716, 1637, 761. HRMS: calcd. for $C_{15}H_{17}NaO_4^+$ $[M+Na]^+$: 299.1254; Found: 299.1267.

(5m) Ethyl(Z)-2-phenyl-3-(2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)acrylate[6]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with D-galactopyranose (**1m**) and benzene (**3a**), and purified by flash column chromatography as colorless oil (48.5 mg, 72%, d.r. = 1:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 6.28 (d, J = 8.0 Hz, 0.5×1H), 6.08 (d, J = 7.2 Hz, 0.5×1H), 5.59 (d, J = 5.2 Hz, 0.5×1H), 5.33 (d, J = 2.4 Hz, 0.5×1H), 5.05 (dd, J = 8.0, 2.0 Hz, 0.5×1H), 4.71 – 4.66 (m, 0.5×1H), 4.59 (dd, J = 5.2, 3.6 Hz, 0.5×1H), 4.50 (dd, J = 7.6, 2.0 Hz, 0.5×1H), 4.40 – 4.35 (m, 1H), 4.33 – 4.27 (m, 2H), 4.24 (dd, J = 8.8, 5.2 Hz, 0.5×1H), 4.09 (dd, J = 9.6, 5.2 Hz, 0.5×1H), 1.58 – 1.48 (m, 6H), 1.44 – 1.36 (m, 6H), 1.34 – 1.26(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.40, 138.87, 137.73, 134.54, 129.77, 127.98, 111.01, 109.10, 100.01, 96.25, 75.53, 74.18, 72.96, 70.30, 61.26, 27.97, 27.11, 25.84, 25.60, 14.20. HRMS: calcd. for $C_{21}H_{25}NaO_7^+$ [M+Na]+: 427.1727; Found: 427.1775.

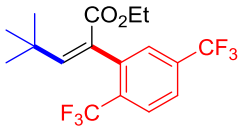
(6b) ethyl (Z)-2-(2,5-dimethylphenyl)-4,4-dimethylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and *p*-xylene (**3b**), and purified by flash column chromatography as colorless oil (38.5 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.06 – 6.98 (m, 2H), 5.59 (s, 1H), 4.17 (d, J = 7.2 Hz, 2H), 2.30 (t, J = 9.4 Hz, 6H), 1.27 (t, J = 7.0 Hz, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.64, 146.64, 139.06, 135.19, 130.24, 130.13, 129.43, 128.63, 128.45, 60.85, 33.97, 29.92, 20.98, 19.56, 14.18. IR (cm^{-1}): 3098, 3017, 2957, 2868, 1721, 1683, 1646, 747. HRMS: calcd. for $C_{16}H_{22}O_2^+$ $[M+H]^+$: 247.1693; Found:247.1689.

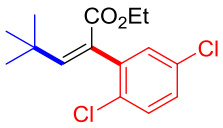
(6c) ethyl (Z)-2-(2,5-bis(trifluoromethyl)phenyl)-4,4-dimethylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,4-bis(trifluoromethyl)benzene (**3c**), and purified by flash column chromatography as colorless oil (53.7 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.65 (m, 3H), 5.84 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 1.25 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.23, 156.95, 147.20, 144.73, 142.94, 120.42,119.01 (t, J = 9.2 Hz), 105.10(t, J = 89.6 Hz,), 61.41, 34.75, 29.75, 14.02. IR (cm^{-1}): 2961, 2929 2872, 2856, 1731, 1647, 753. HRMS: calcd. for $C_{16}H_{15}F_6NaO_2^+$ $[M+Na]^+$: 391.1103; Found: 391.1120.

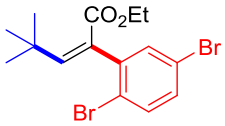
(6d) ethyl (Z)-2-(2,5-dichlorophenyl)-4,4-dimethylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,4-dichlorobenzene (**3d**), and purified by flash column chromatography as colorless oil (55.8 mg, 93%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, J = 8.8, 2.8 Hz, 2H), 7.19 (dd, J = 8.4, 2.4 Hz, 1H), 5.94 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.28 (d, J = 7.2 Hz, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.26, 152.51, 140.46, 132.51, 131.75, 131.22, 130.66, 129.99, 128.88, 61.17, 34.22, 29.88, 14.10. IR (cm^{-1}): 3018, 2989, 2876, 2813, 1712, 1688, 748. HRMS: calcd. for $C_{14}H_{15}Cl_2NaO_2^+$ $[M+Na]^+$: 323.0576; Found: 323.0570.

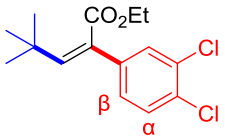
(6e) ethyl (Z)-2-(2,5-dibromophenyl)-4,4-dimethylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,4-dibromobenzene (**3e**), and purified by flash column chromatography as colorless oil (65.0 mg, 84%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 10.0, 2.4 Hz, 2H), 7.26 (dd, J = 8.4, 2.0 Hz, 1H), 5.89 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 1.27 (d, J = 7.2 Hz, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.94, 152.72, 142.73, 134.14, 134.03, 131.99, 131.31, 122.34, 121.07, 61.17, 34.17, 29.81, 14.11. IR (cm^{-1}): 3016, 2957, 2870, 2844, 1719, 1648, 754. HRMS: calcd. for $C_{14}H_{15}Br_2NaO_2^+$ $[M+Na]^+$: 410.9566; Found: 410.9571.

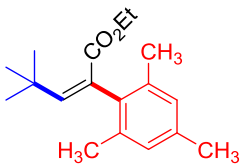
(6f) ethyl (Z)-2-(2,3-dichlorophenyl)-4,4-dimethylpent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,2-dichlorobenzene (**3f**), and purified by flash column chromatography as colorless oil (47.4 mg, 79% (α:β = 1:1)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1.5×1H), 7.21 – 7.14 (m, 4.0 Hz, 1.5×1H), 5.93 (s, 0.5×1H), 5.90 (s, 0.5×1H), 4.31 – 4.18 (m, 2H), 1.35 – 1.26 (m, 3H), 1.21 (d, J = 26.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.17, 167.40, 152.17, 144.31, 141.32, 138.20, 133.17, 132.70, 131.90, 131.73, 130.81, 130.45, 129.73, 129.67, 128.17, 127.24, 125.57, 61.44, 61.13, 34.20, 34.15, 29.88, 29.73, 14.14, 14.10. IR (cm^{-1}): 3019, 2961, 2906, 2870, 1720, 1635, 743. HRMS: calcd. for $C_{14}H_{15}Cl_2NaO_2^+$ $[M+Na]^+$: 323.0576; Found: 323.0557.

(6g) ethyl (Z)-2-mesityl-4,4-dimethylpent-2-enoate

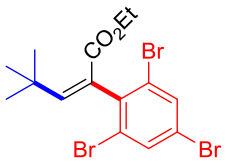


The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and mesitylene (**3g**), and purified by flash column chromatography as colorless oil (35.1 mg, 64%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.49 (s, 1H), 4.13 (q, J = 6.8 Hz, 2H), 2.27 (d, J = 7.2 Hz, 9H), 1.24 (t, J = 7.2 Hz, 3H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.24, 147.33, 137.14, 136.93, 136.16, 130.14, 128.28, 60.64, 33.91, 29.83, 21.13, 20.30, 14.18. IR (cm^{-1}): 3098,

2987, 2957, 2868, 1721, 1646, 747. HRMS: calcd. for $C_{17}H_{24}O_2^+$ $[M+H]^+$: 275.2006; Found: 275.2007.

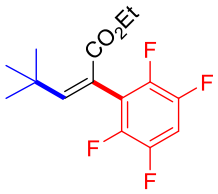
(6h) ethyl (Z)-4,4-dimethyl-2-(2,4,6-tribromophenyl)pent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,3,5-tribromobenzene (**3h**), and purified by flash column chromatography as yellow oil (53.0 mg, 57%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 36.4 Hz, 2H), 5.94 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.31 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.65, 158.11, 140.94, 134.22, 133.15, 130.96, 125.70, 121.72, 60.93, 34.16, 29.66, 14.15. IR (cm^{-1}): 3105, 3056, 2976, 2870, 1698, 1639, 748. HRMS: calcd. for $C_{14}H_{15}Br_3O_2^+$ $[M+H]^+$: 466.8851; Found: 466.8851.

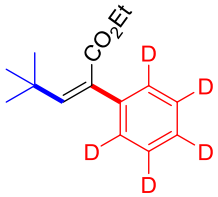
(6i) ethyl (Z)-4,4-dimethyl-2-(2,3,5,6-tetrafluorophenyl)pent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,2,4,5-tetrafluorobenzene (**3i**), and purified by flash column chromatography as yellow oil (40.1 mg, 66%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.98 (m, 1H), 6.17 (s, 1H), 4.23 (d, J = 7.2 Hz, 2H), 1.29 (d, J = 7.2 Hz, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.78, 152.52, 139.86, 128.95, 128.38, 127.04, 124.60, 61.23, 34.21,29.62, 14.00. ^{19}F NMR (400 MHz, $CDCl_3$) δ -139.43, -139.46, -139.49, -139.52, -141.97, -142.01, -142.03, -142.07. IR (cm^{-1}): 3108, 3093, 2976, 2862, 1868, 1646, 755. HRMS: calcd. for $C_{14}H_{13}F_4NaO_2^+$ $[M+Na]^+$: 327.0979; Found: 327.0970.

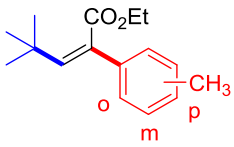
(6j) ethyl (Z)-4,4-dimethyl-2-(phenyl-*d*$_5$)pent-2-enoate



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and benzene-d_6 (**3j**), and purified by flash column chromatography as yellow oil (18.8 mg, 79%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.11, 142.49, 137.94, 132.24, 128.11, 127.87 (t, J = 48.4 Hz), 125.71 (t, J = 48.2 Hz), 61.12, 34.04, 29.90, 14.20. IR (cm^{-1}): 3093, 3039, 2915, 2820, 1727, 1540, 755. HRMS: calcd. for $C_{14}H_{12}D_5NaO_2^+$ $[M+Na]^+$: 260.1669; Found: 260.1670.

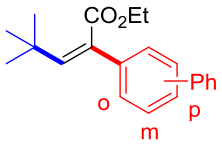
(6k) ethyl (Z)-4,4-dimethyl-2-(p-tolyl)pent-2-enoate[7,8]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and toluene (**3k**), and purified by flash column chromatography as colorless oil (34.4 mg, 70%, *o:m:p* = 6:2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 4H), 5.88 (s, 0.2×1H), 5.86 (s, 0.1×1H), 5.60 (s, 0.6×1H), 4.29 – 4.14 (m, 2H), 2.33 (d, J = 6.8 Hz, 3H), 1.33 – 1.24 (m, 3H), 1.20 – 1.18 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.52, 146.89, 146.73, 142.36, 141.73, 139.33, 136.42, 131.75, 130.33, 129.57, 129.33, 128.53, 127.71, 126.86, 126.02, 125.75, 123.28, 60.86, 34.00, 29.91, 20.06, 14.18. IR (cm^{-1}): 3053, 3019, 2910, 2872, 1717, 1640, 754 .. HRMS: calcd. for $C_{14}H_{18}O_2^+$ $[M+H]^+$: 247.1693 Found: 247.1689.

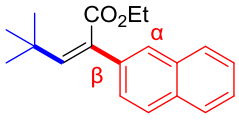
(6l) ethyl (Z)-2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpent-2-enoate[8]



The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and 1,1'-biphenyl (**3m**), and purified by flash column chromatography as colorless oil (50.5 mg, 82%, *o:p* =5:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 12.0, 7.6 Hz, 3H), 7.45 – 7.33 (m, 6H), 5.69 (d, J = 225.2 Hz, 1H), 4.34 – 4.00 (m, 2H), 1.37 – 1.32 (m, 2.5×1H), 1.20 (s, 6H), 1.18 (s, 0.5×1H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.10, 169.28, 149.39, 142.53, 138.43, 137.09, 131.93, 130.59, 130.09, 129.37, 128.92, 128.89, 127.97, 127.76, 127.50, 127.38, 127.35, 127.22, 127.14, 126.77, 126.53, 125.13, 61.20, 60.81, 34.11, 33.79, 29.93, 29.39, 14.23, 14.06. IR (cm^{-1}): 3058, 3029, 2957, 2869, 1718, 1636, 751. HRMS: calcd. for $C_{21}H_{25}O_2^+$ $[M+H]^+$: 309.1849; Found: 309.1850.

(6m) ethyl (Z)-4,4-dimethyl-2-(naphthalen-1-yl)pent-2-enoate[8,9]



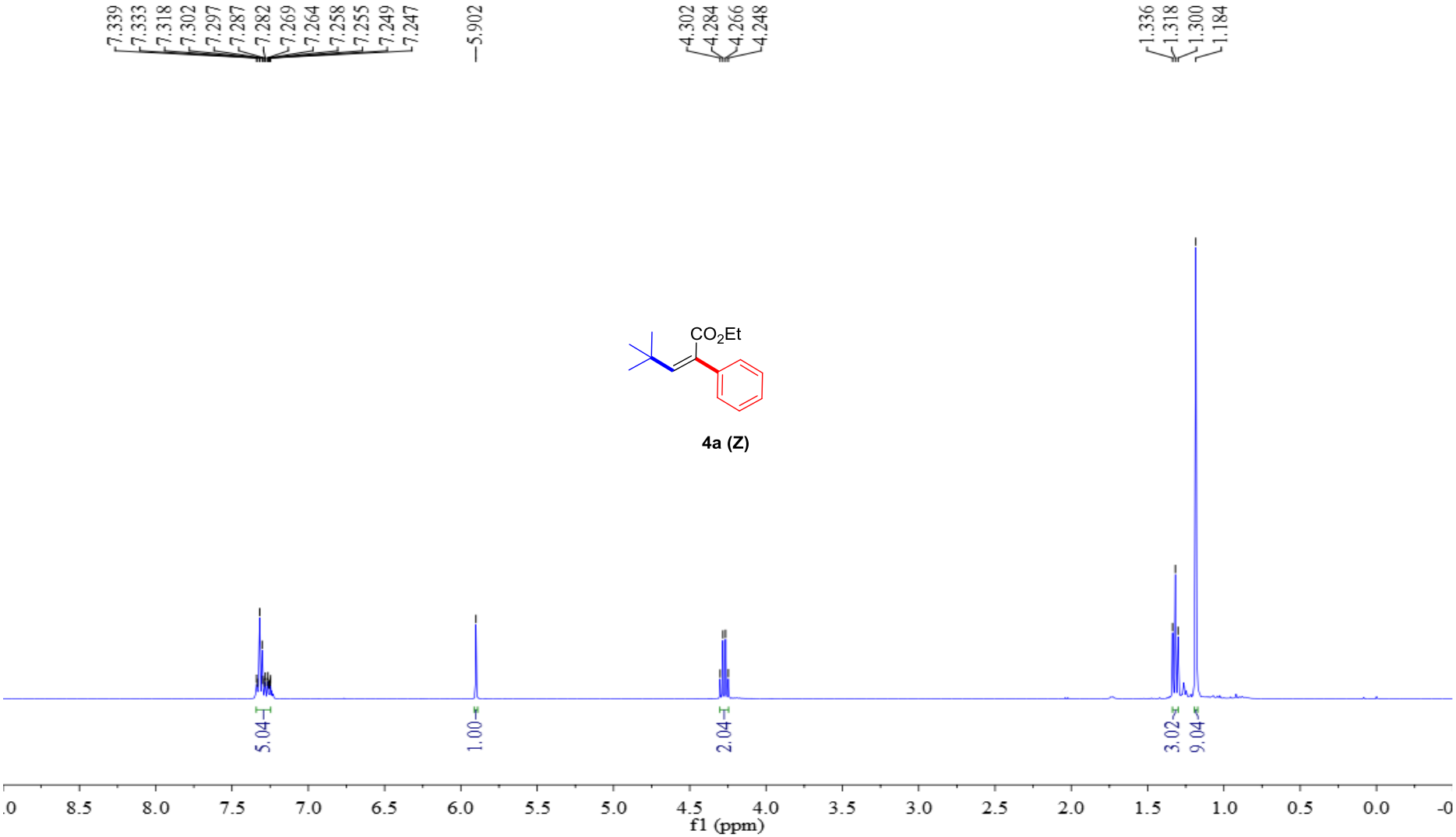
The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (**2a**) with pivalaldehyde (**1a**) and naphthalene (**3n**), and purified by flash column chromatography as colorless oil (34.4 mg, 61%, α:β= 1:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 7.78 (m, 3H), 7.52 – 7.42 (m, 4H), 5.92 (d, J = 101.6 Hz, 1H), 4.24 (dq, J = 70.4, 7.2 Hz, 2H), 1.22 (q, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.66, 147.83, 137.25, 133.81, 132.10, 130.76, 128.29, 128.16, 126.88, 126.26, 125.89, 125.82, 125.39, 61.04, 34.24, 29.96, 14.13. IR (cm^{-1}): 3132, 3059, 2917, 2826, 1712, 1620, 755. HRMS: calcd. for $C_{19}H_{23}O_2^+$ $[M+H]^+$: 283.1693; Found: 283.1692.

VIII. References

1. A. K. Gupta, K. S. Kim and H. O. Chang, *Synlett*, 2005, **3**, 457.
2. C. Schoellkopf and W. Hoppe; *Justus Liebigs Annalen der Chemie*, 1974, 1657.
3. Y. Wan, Z. Shao, K. Zhang and Q. Liu, *Angewandte Chemie International Edition*, 2018, **57**, 15143.
4. R. Rossi, A. Carpita and P. cossi, *Tetrahedron*, 1992, **48**, 8801.
5. N. Slougu and G. Rousseau, *Synthetic Communications*, 1982, **12**, 401.
6. C. Romano and C. Mazet, *Journal of the American Chemical Society*, 2018, **140**, 4743.
7. N. Jiang, Z.-H. Qu and J.-B. Wang, *Organic Letters*, 2001, **3**, 2989.
8. S.-J. Song, P. Lu, H. Liu, S.-H. Cai, C. Feng and T.-P. Loh, *Organic Letters*, 2017, **19**, 2869.
9. D. A. Rooke and E. M. Ferreira, *Organic Letters*, 2012, **14**, 1552.

IX. Copies of ^{1}H and ^{13}C NMR spectra of products 4a-4i, 5b-5m, 6b-6m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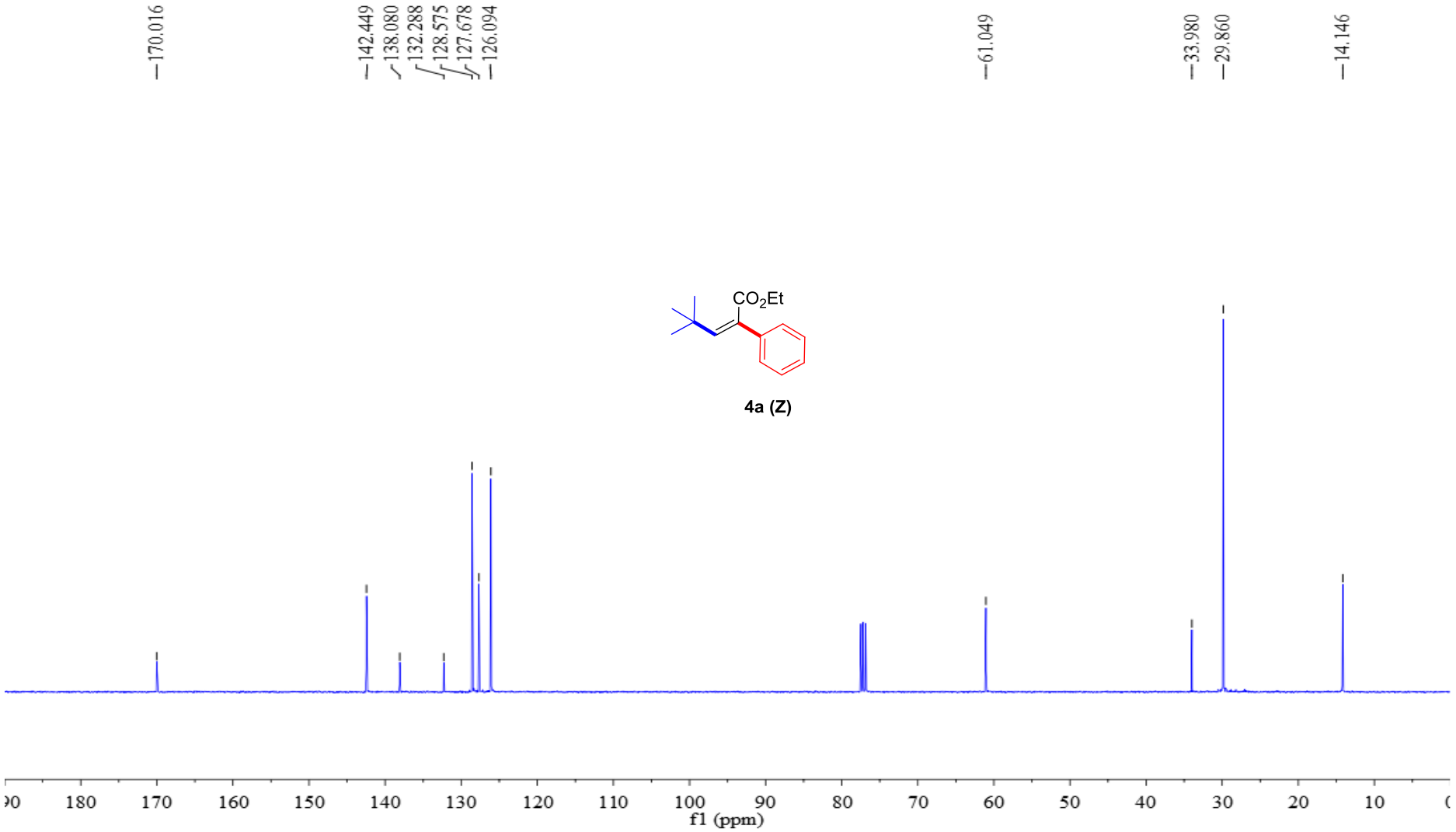
7.318
7.302
7.297
7.287
7.282
7.269
7.264
7.258
7.255
7.249
7.247
5.902
4.302
4.284
4.266
4.248
1.336
1.318
1.300
1.184
CO2Et
4a (Z)
5.04
1.00
2.04
3.02
9.04
f1 (ppm)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142.449
138.080
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127.678
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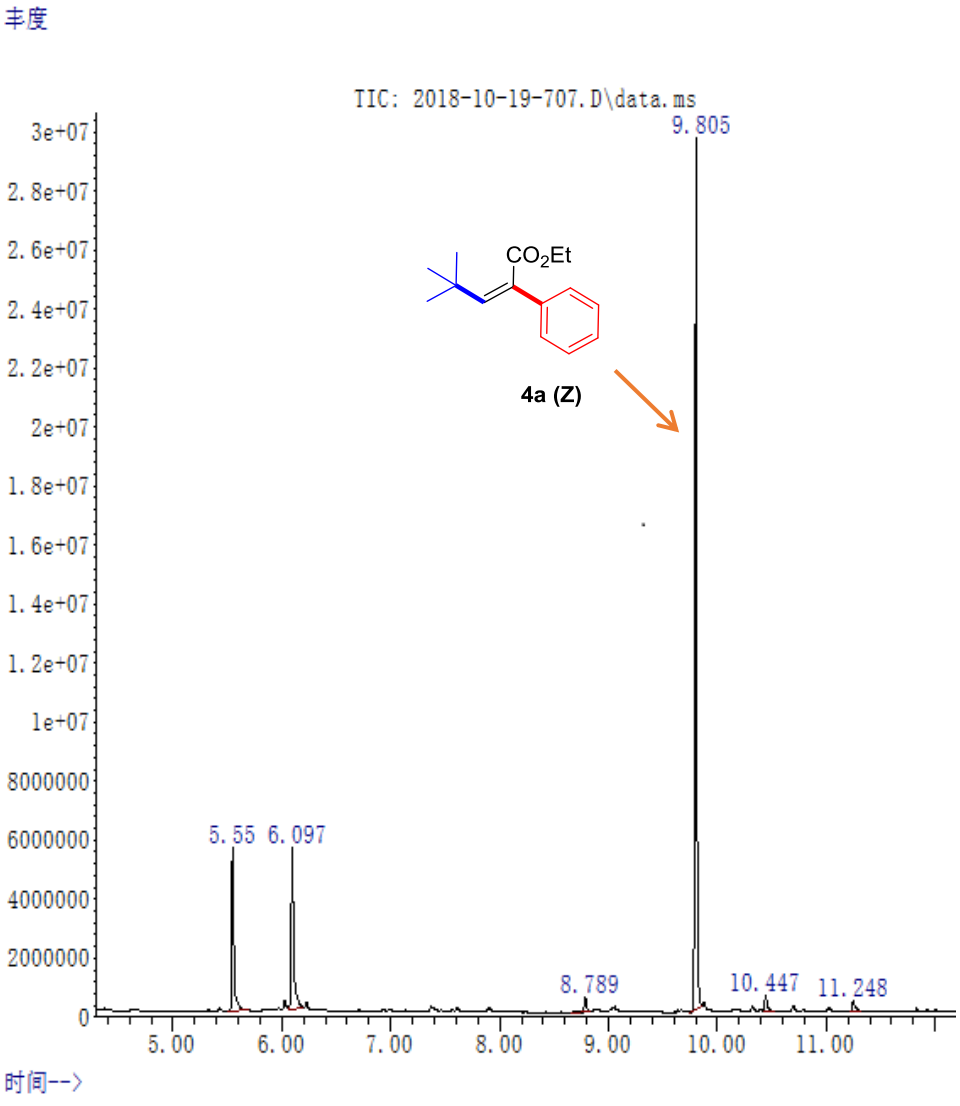
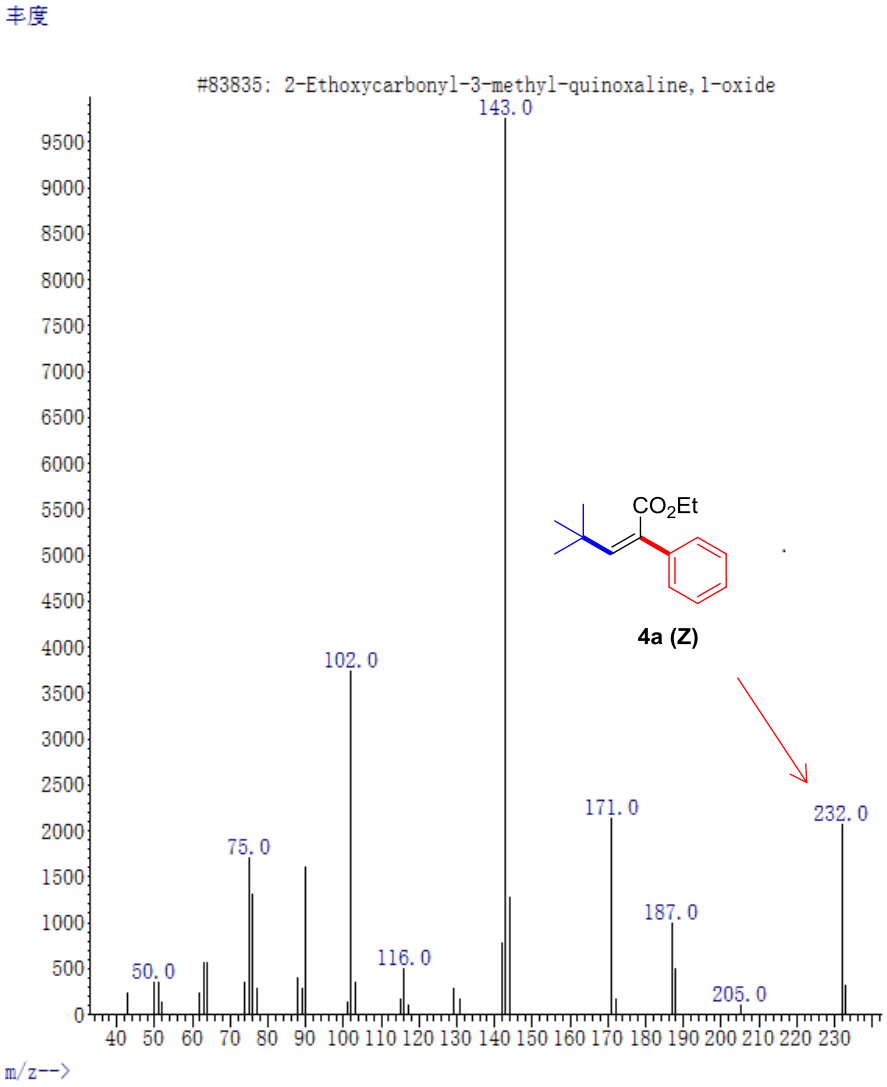
61.049
33.980
29.860
14.146
CO2Et
4a (Z)
f1 (ppm)


丰度
TIC: 2018-10-19-707.D\data.ms
9.805
5.55
6.097
8.789
10.447
11.248
4a (Z)
时间-->


丰度
#83835: 2-Ethoxycarbonyl-3-methyl-quinoxaline,1-oxide
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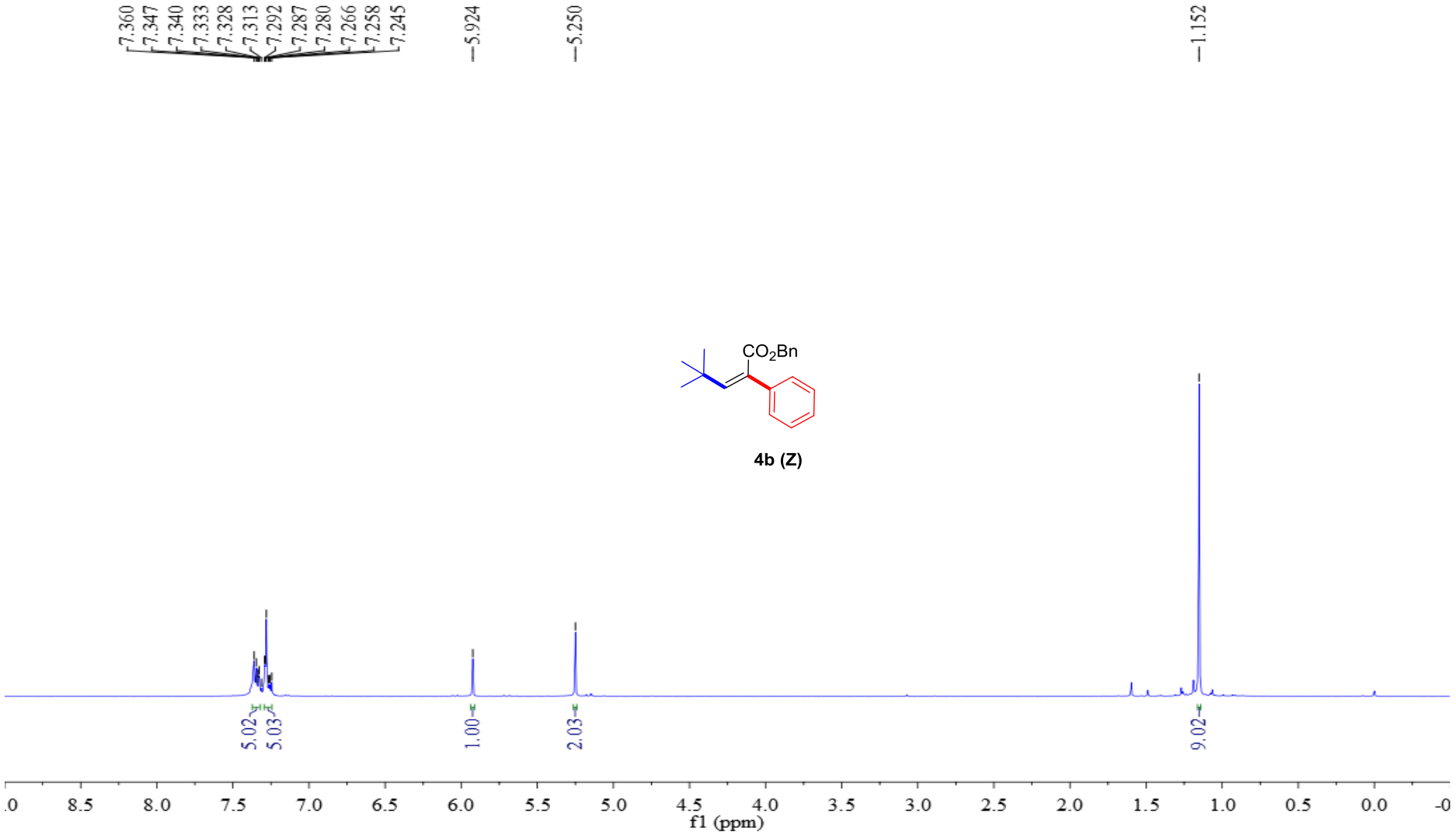
102.0
75.0
171.0
232.0
187.0
116.0
50.0
205.0
4a (Z)
m/z-->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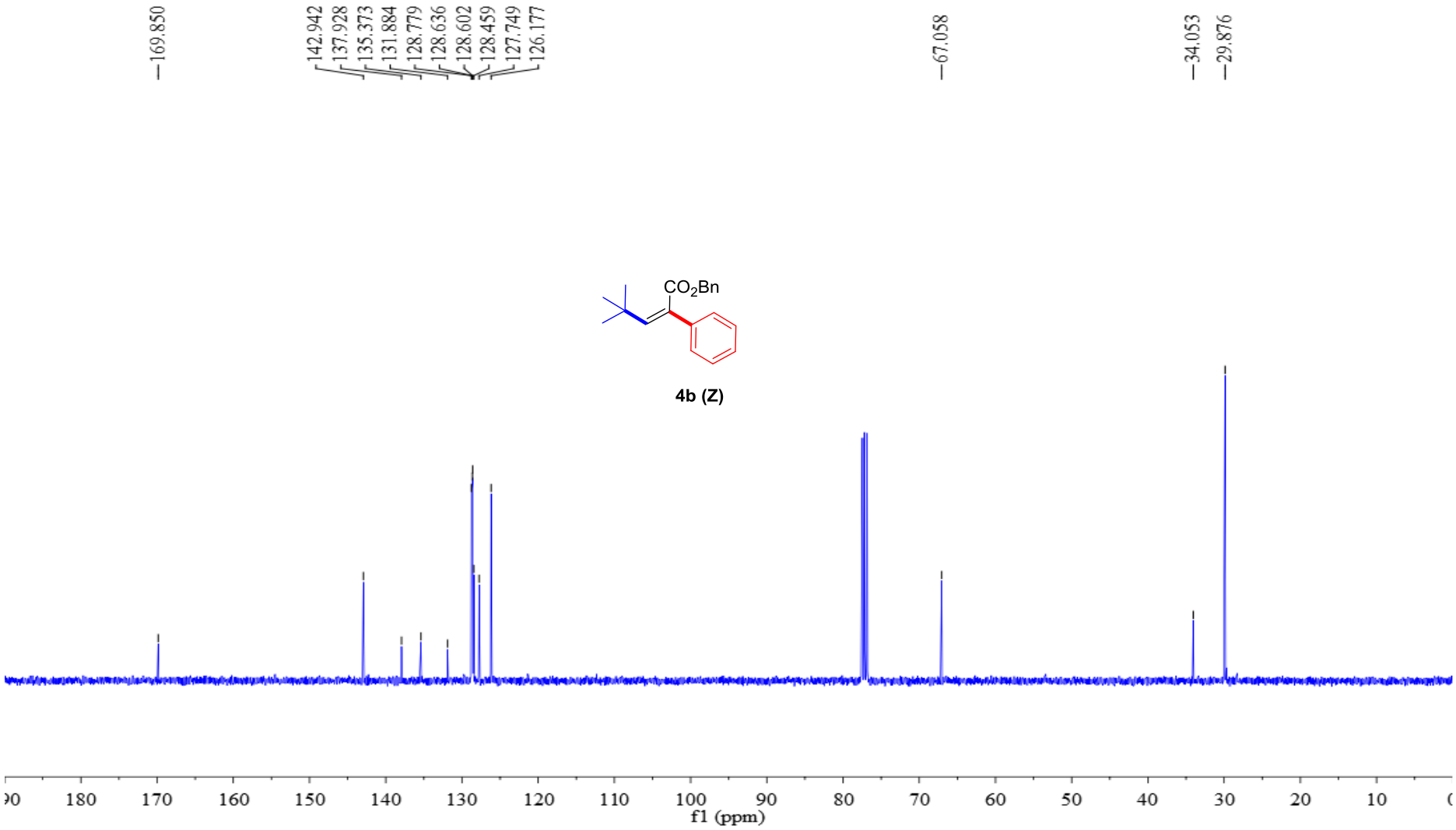
7.347
7.340
7.333
7.328
7.313
7.292
7.287
7.280
7.266
7.258
7.245
5.924
5.250
1.152
CO2Bn
4b (Z)
5.02
5.03
1.00
2.03
9.02
f1 (ppm)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142.942
137.928
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131.884
128.779
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126.177
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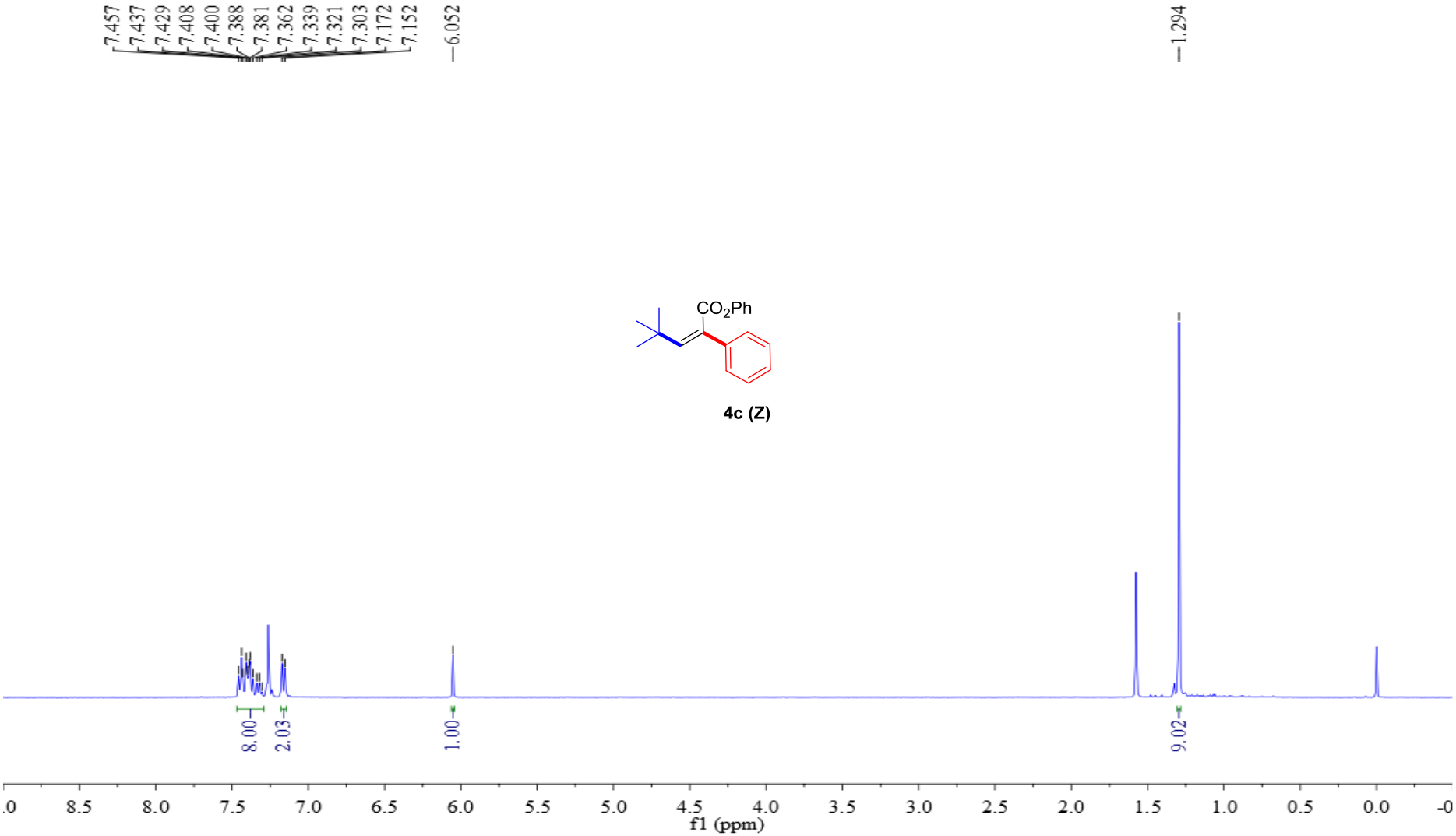
34.053
29.876
CO2Bn
4b (Z)
f1 (ppm)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7.437
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7.408
7.400
7.388
7.381
7.362
7.339
7.321
7.303
7.172
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6.052
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4c (Z)
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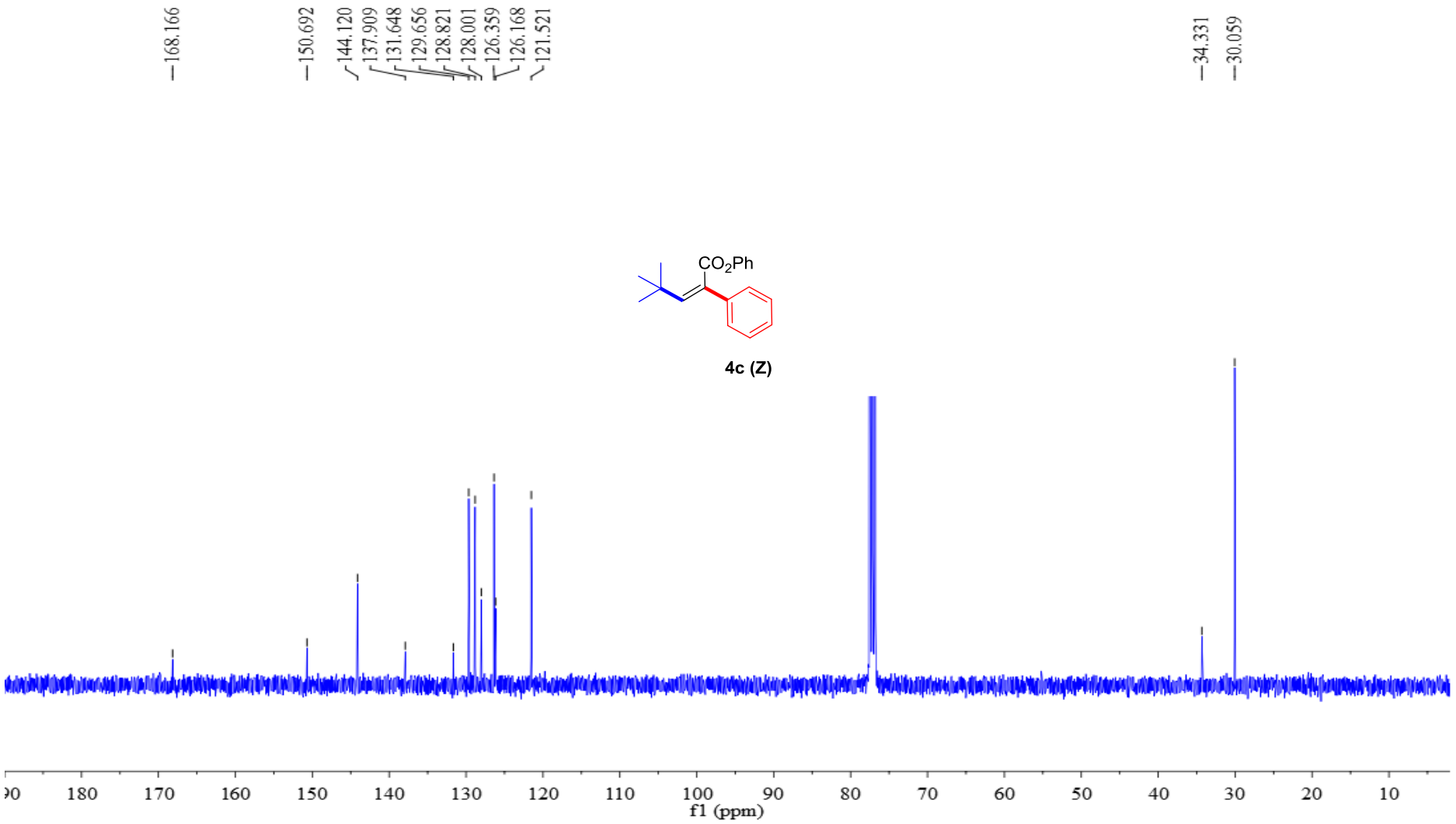
2.03
1.00
9.02
f1 (ppm)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128.001
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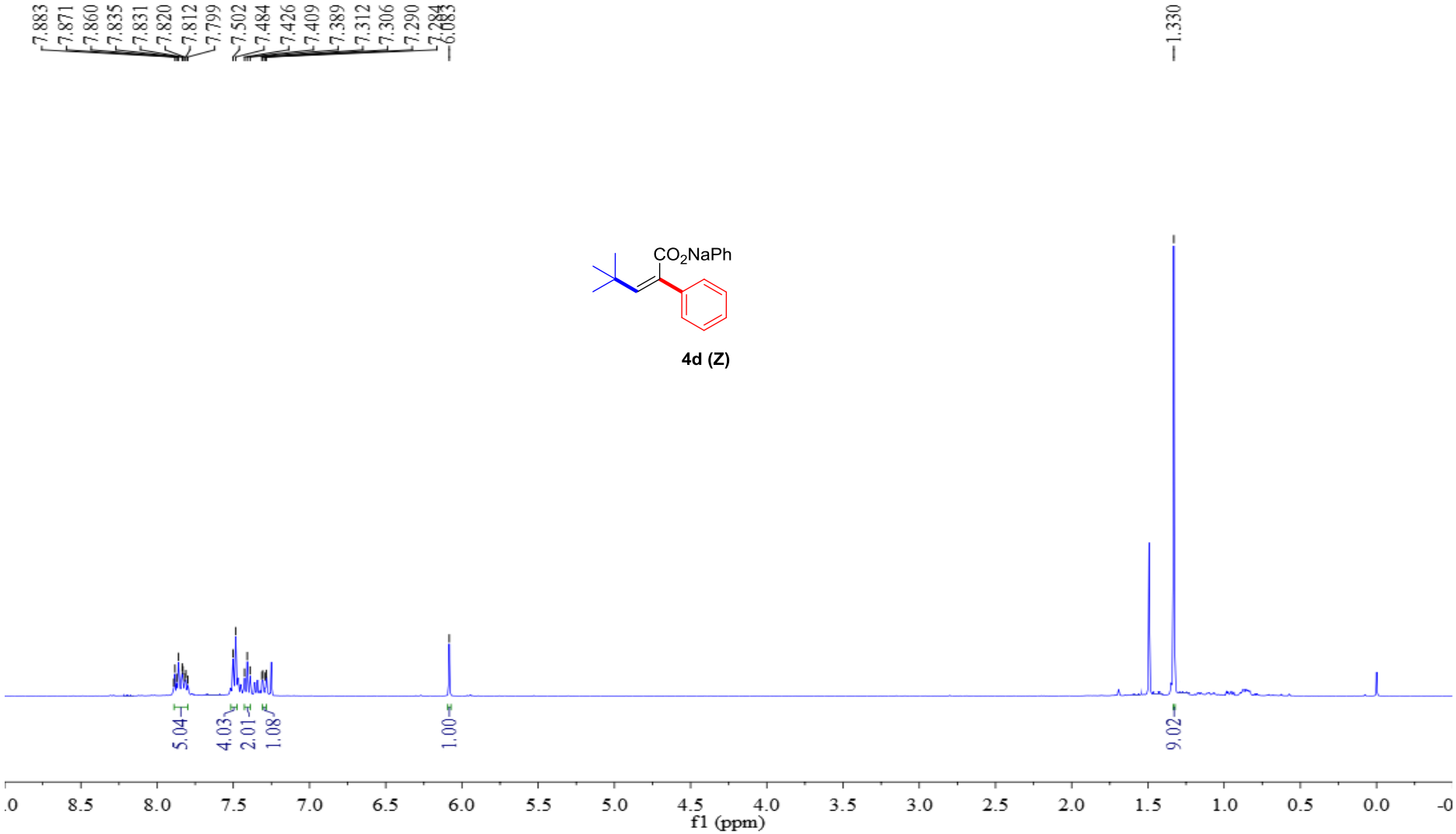
30.059
CO2Ph
4c (Z)
f1 (ppm)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7.799
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7.426
7.409
7.389
7.312
7.306
7.290
7.284
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CO2NaPh
4d (Z)
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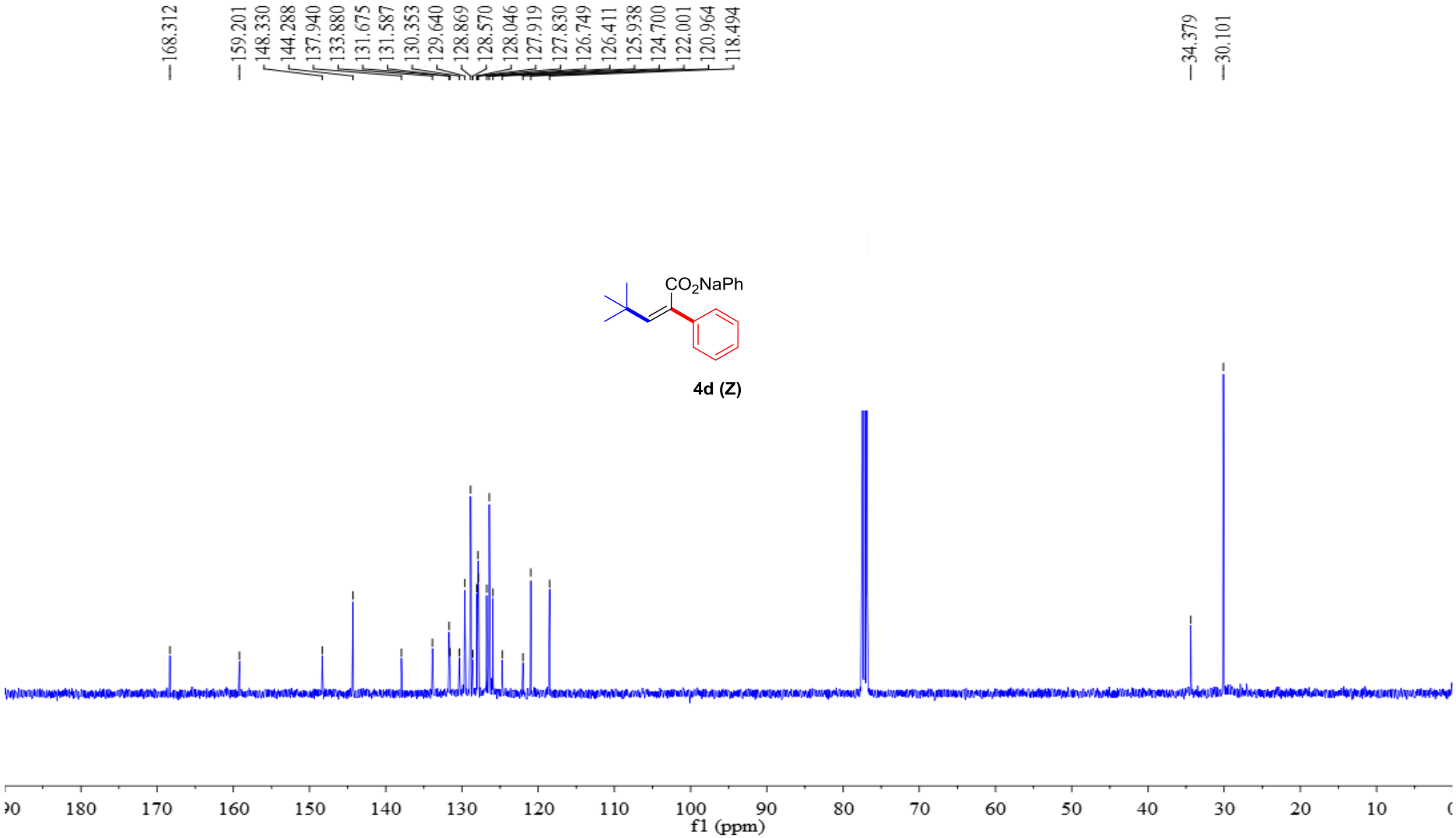
4.03
2.01
1.08
1.00
9.02
f1 (ppm)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127.830
126.749
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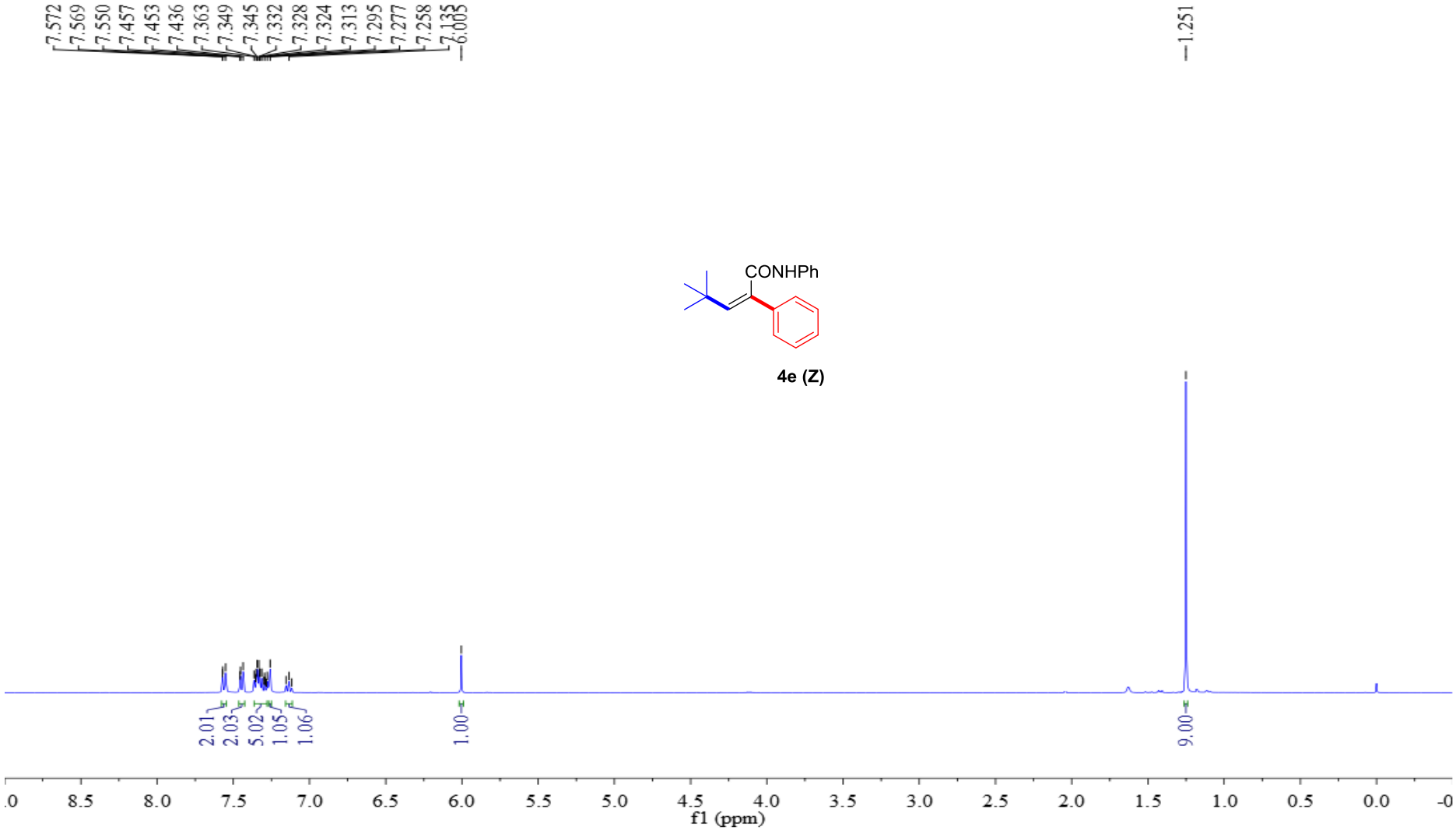
34.379
30.101
CO2NaPh
4d (Z)
f1 (ppm)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7.332
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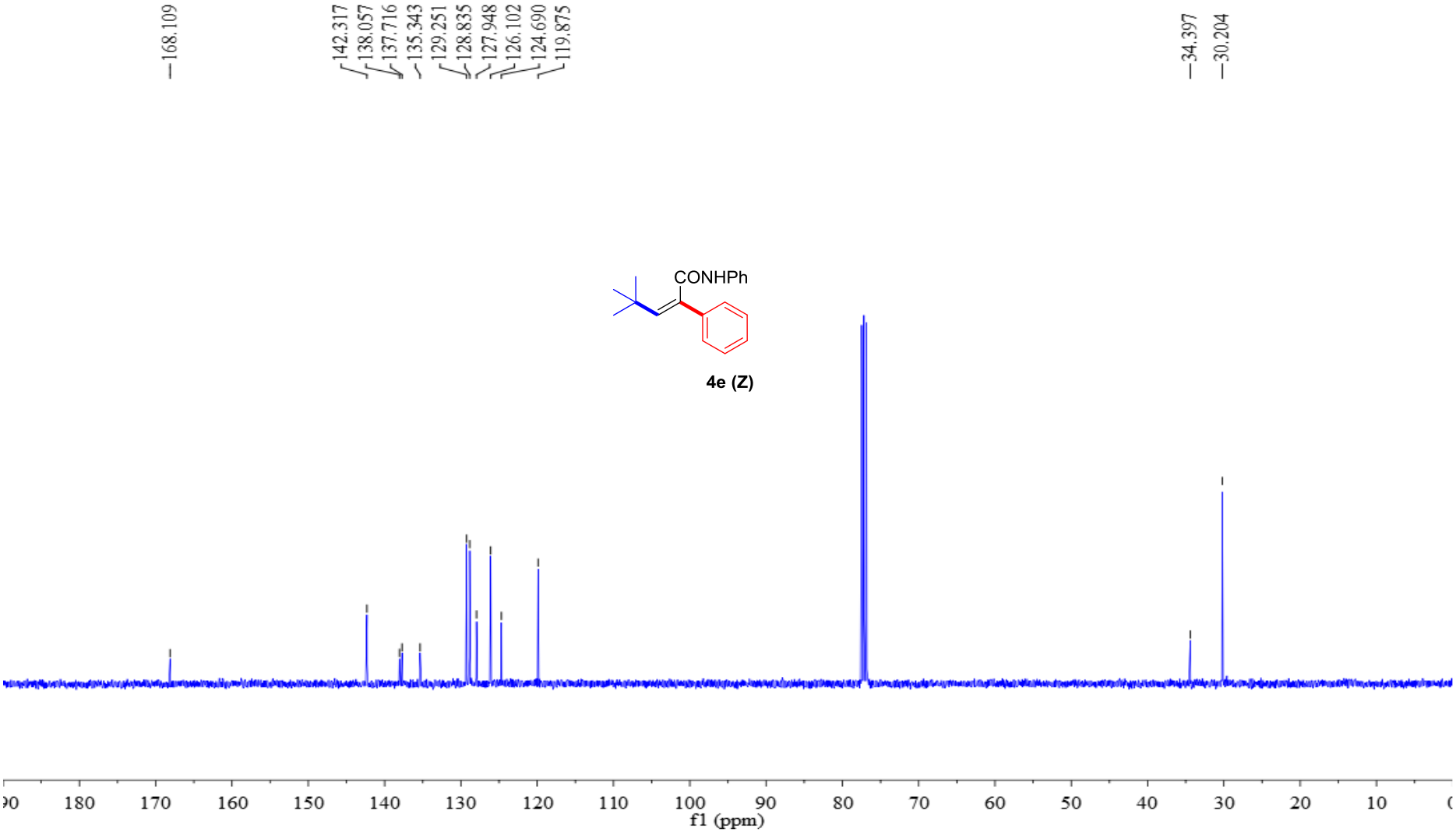
7.295
7.277
7.258
7.135
6.003
1.251
CONHPh
4e (Z)
2.01
2.03
5.02
1.05
1.06
1.00
9.00
f1 (ppm)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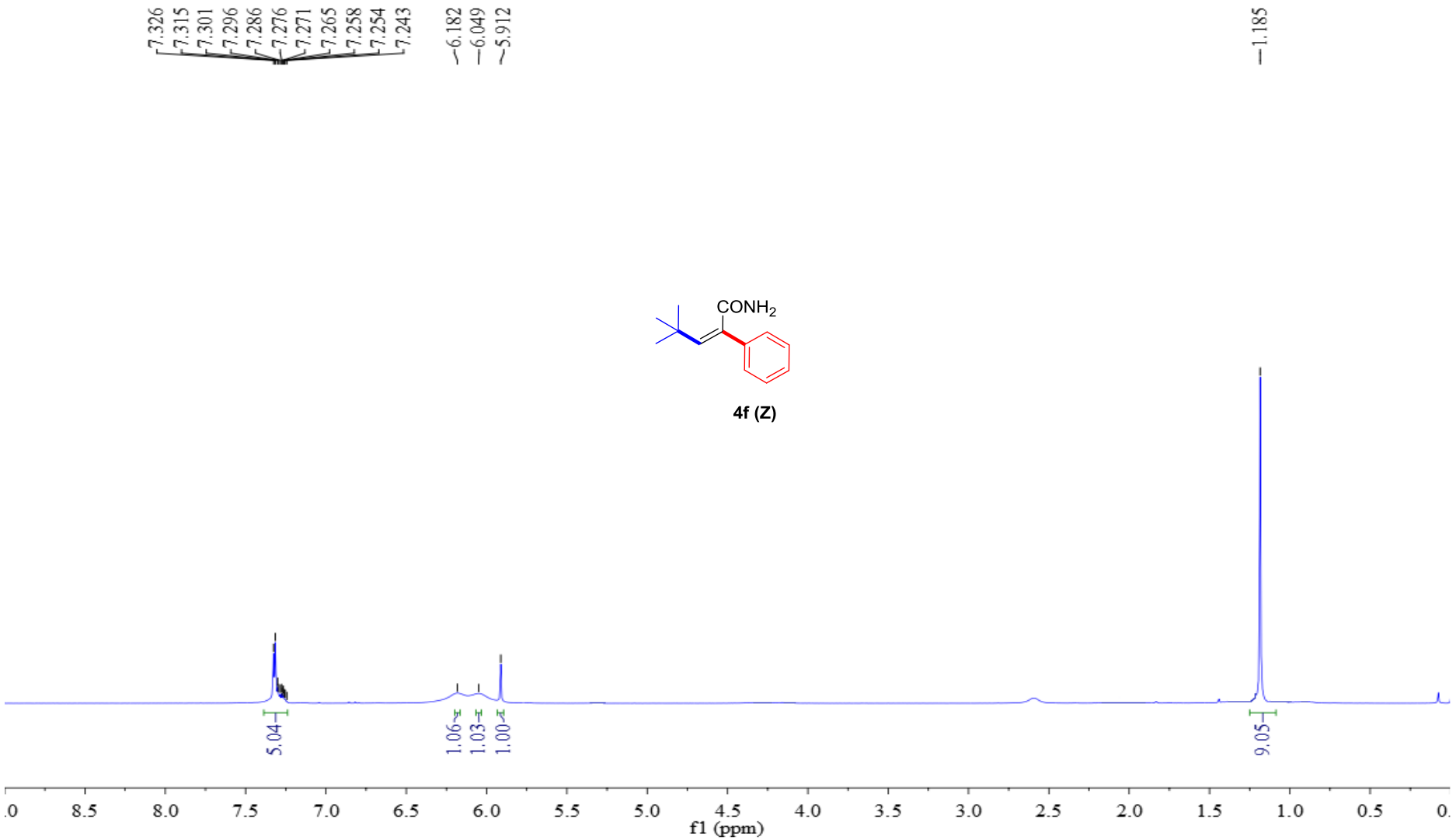
142.317
138.057
137.716
135.343
129.251
128.835
127.948
126.102
124.690
119.875
34.397
30.204
CONHPh
4e (Z)
f1 (ppm)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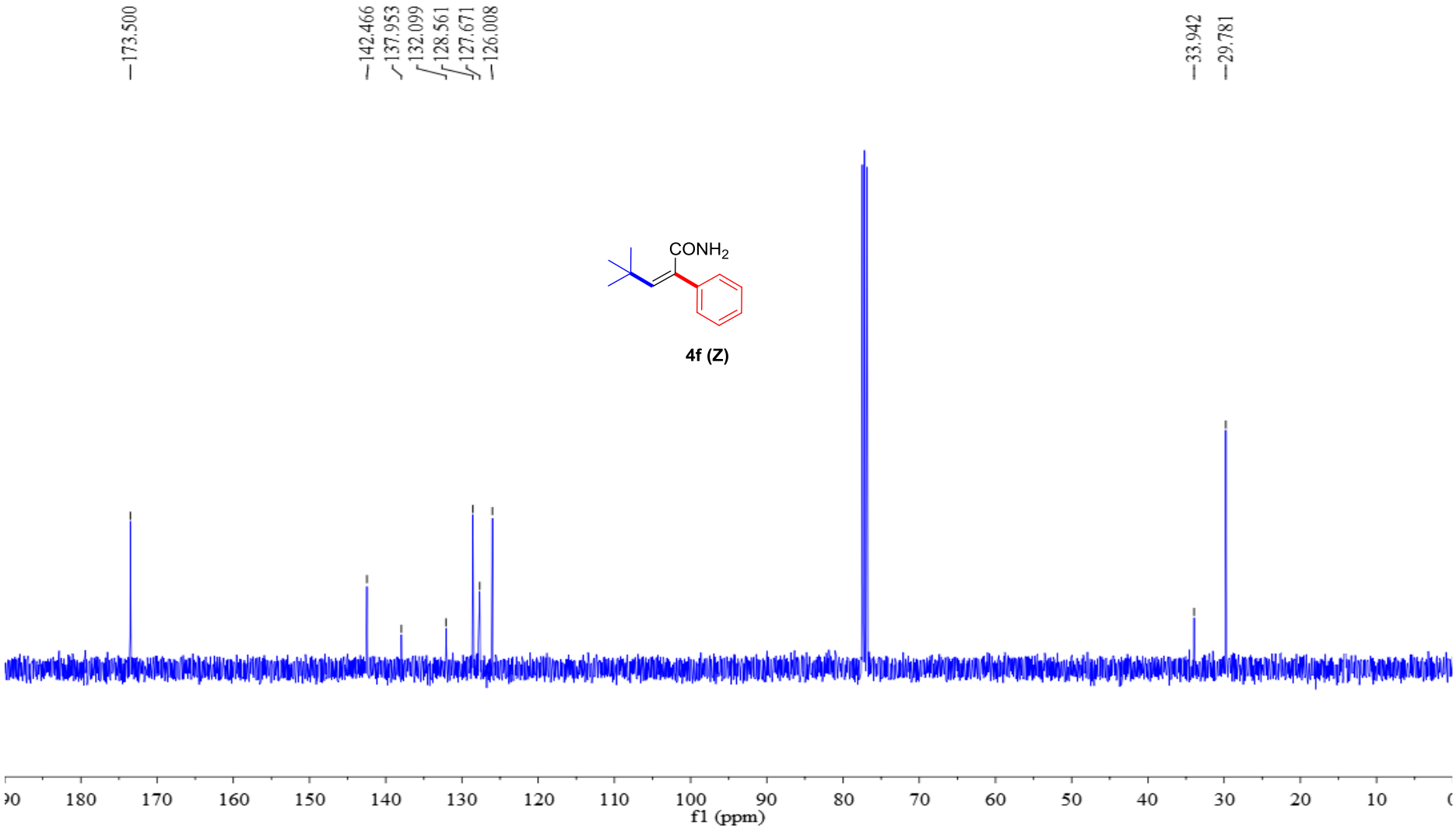
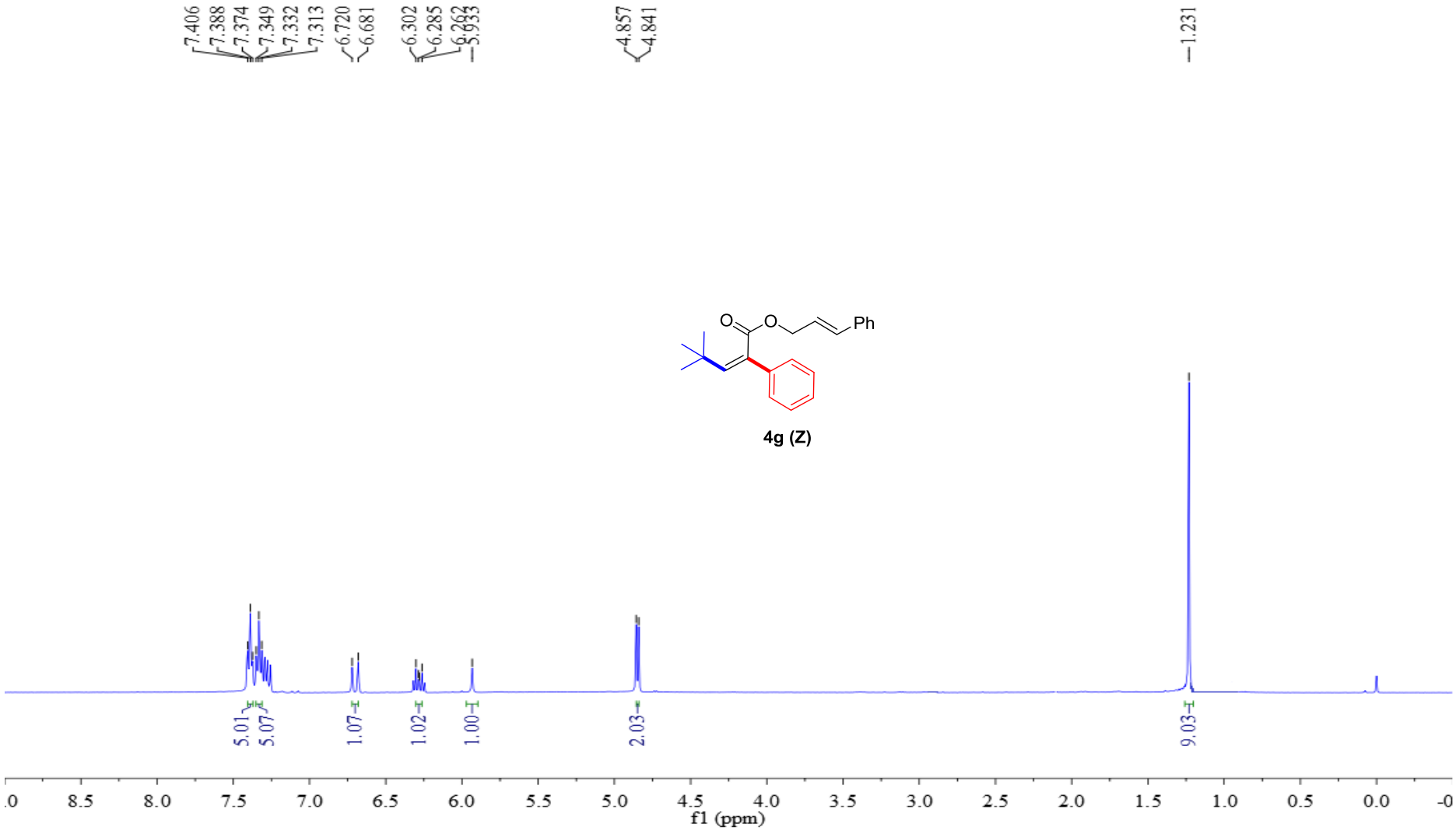
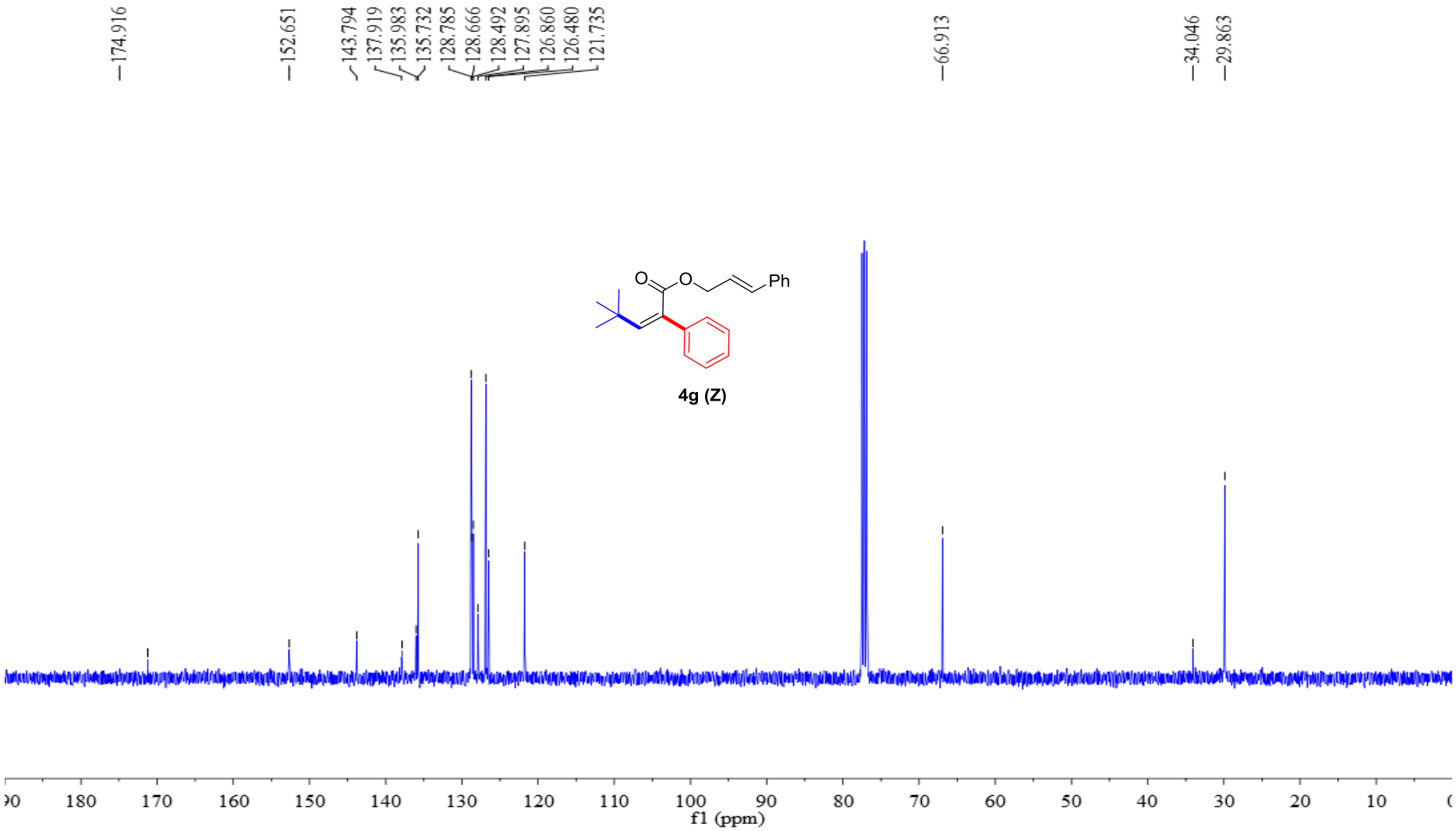
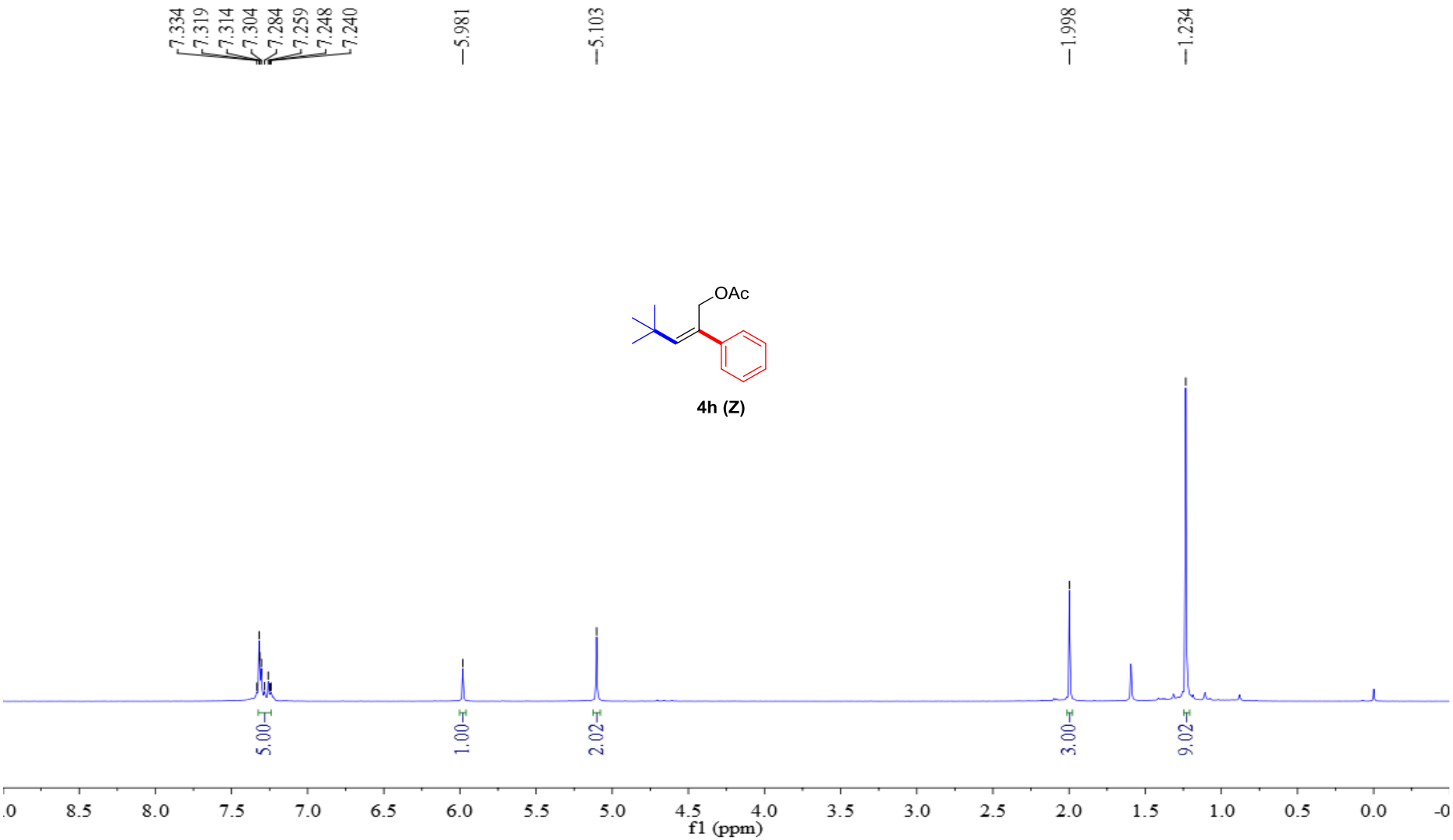
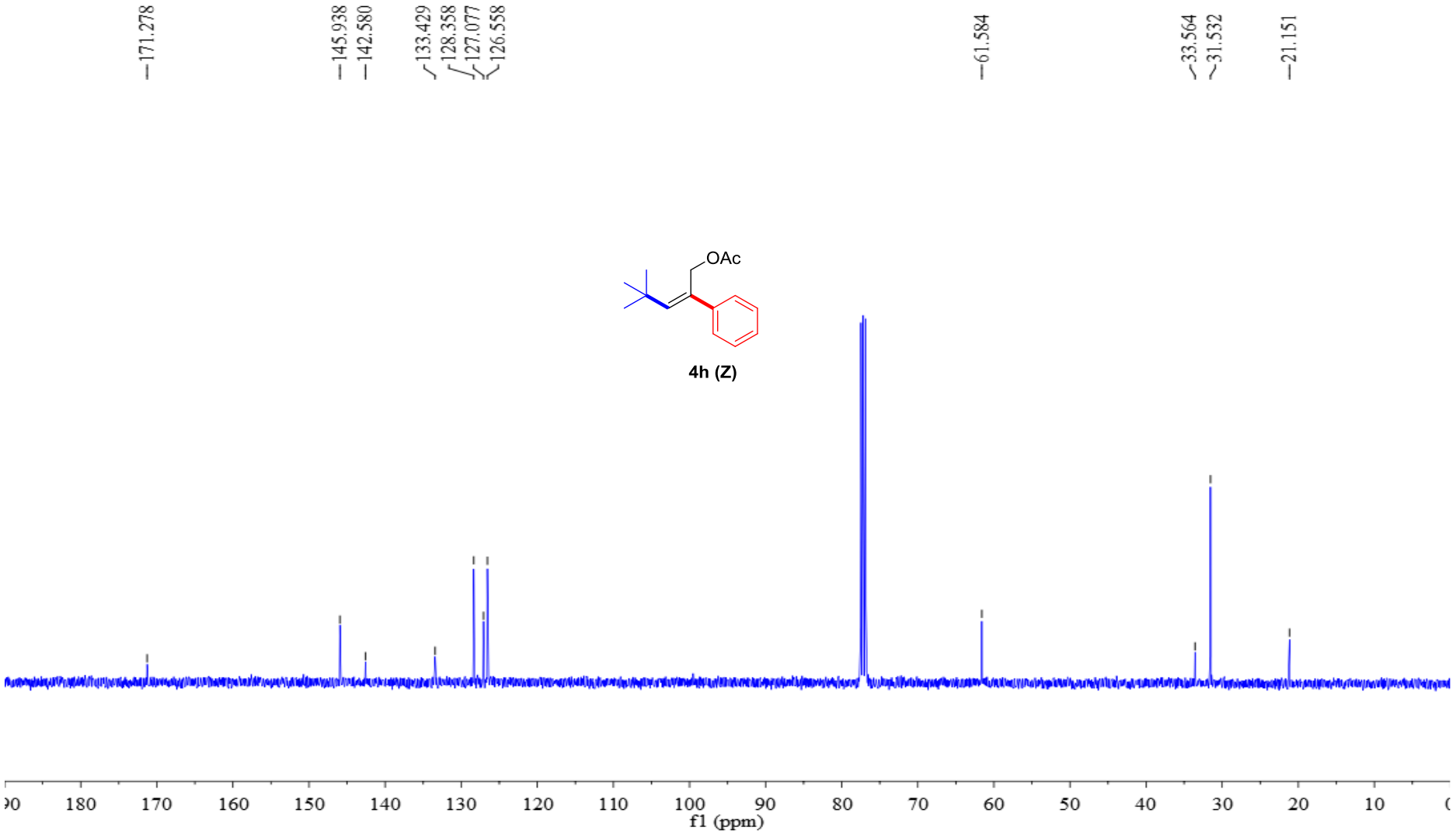
7.315
7.301
7.296
7.286
7.276
7.271
7.265
7.258
7.254
7.243
6.182
6.049
5.912
1.185
CONH2
4f (Z)
5.04
1.06
1.03
1.00
9.05
f1 (ppm)

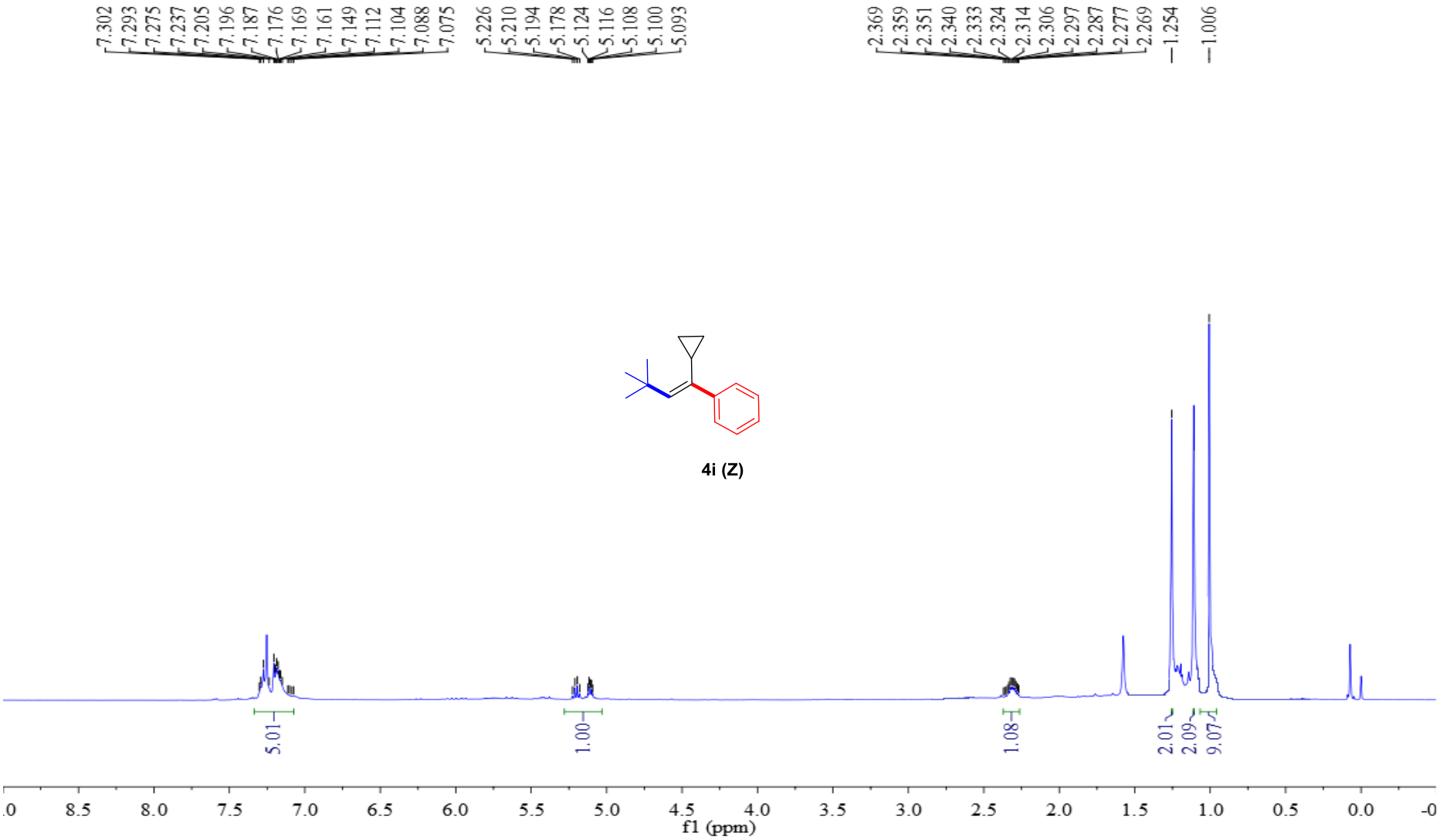

173.500
142.466
137.953
132.099
128.561
127.671
126.008
33.942
29.781
CONH2
4f (Z)
f1 (ppm)


7.406
7.388
7.374
7.349
7.332
7.313
6.720
6.681
6.302
6.285
6.262
5.933
4.857
4.841
1.231
O
O
Ph
4g (Z)
5.01
5.07
1.07
1.02
1.00
2.03
9.03
f1 (ppm)


174.916
152.651
143.794
137.919
135.983
135.732
128.785
128.666
128.492
127.895
126.860
126.480
121.735
66.913
34.046
29.863
O
O
Ph
4g (Z)
f1 (ppm)


7.334
7.319
7.314
7.304
7.284
7.259
7.248
7.240
5.981
5.103
1.998
1.234
OAc
4h (Z)
5.00
1.00
2.02
3.00
9.02
f1 (ppm)


171.278
145.938
142.580
133.429
128.358
127.077
126.558
61.584
33.564
31.532
21.151
OAc
4h (Z)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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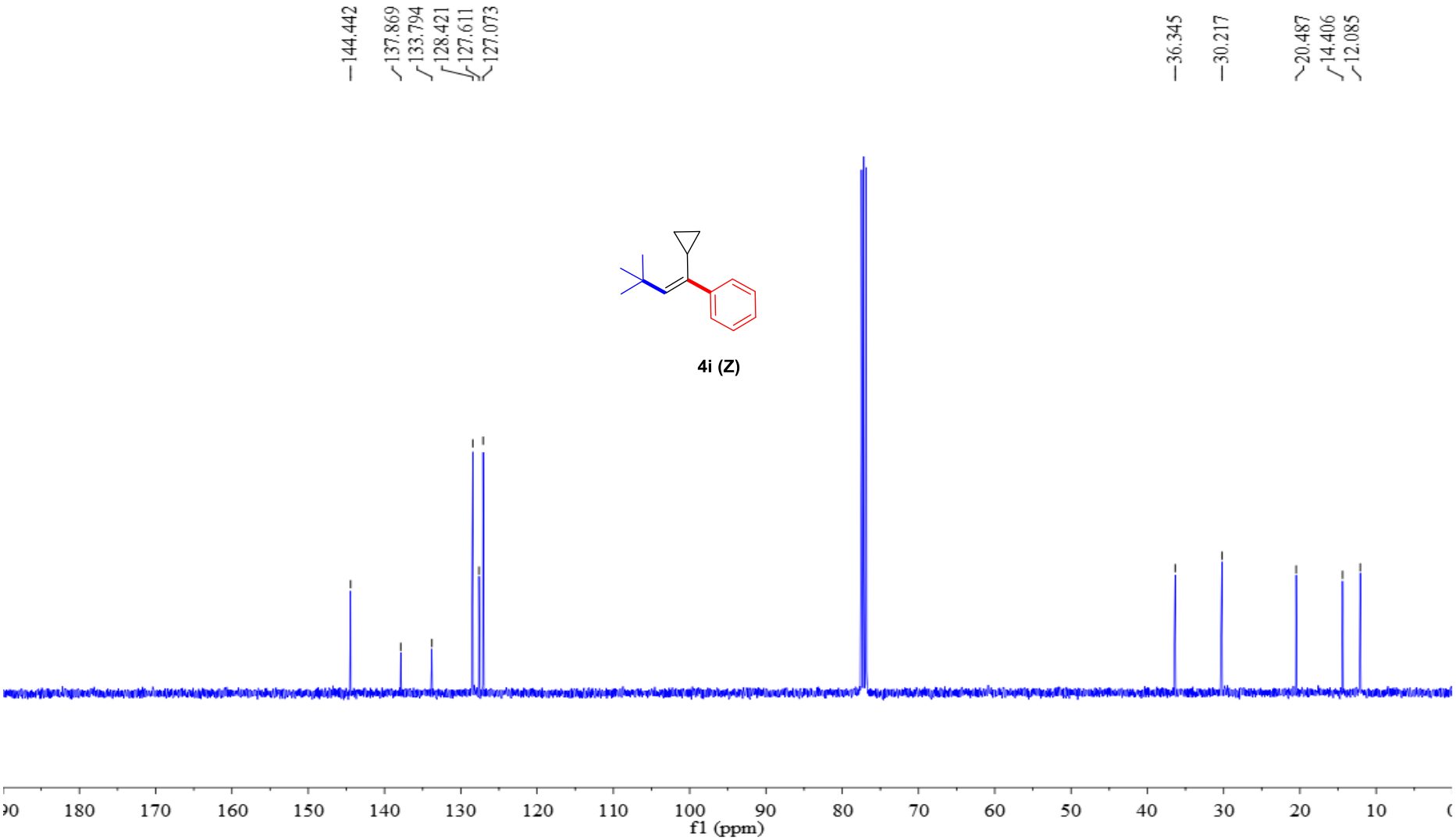
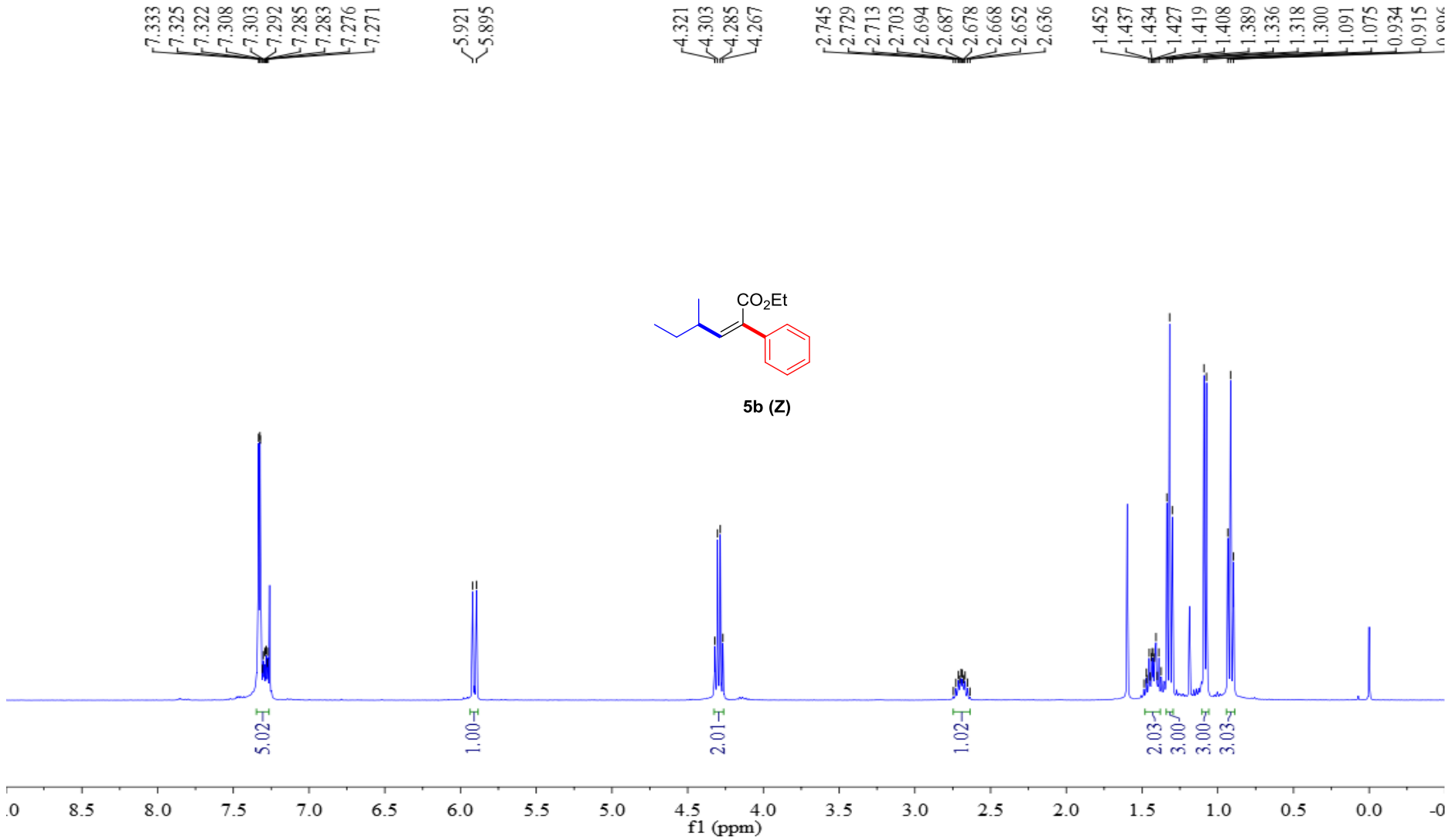
7.293
7.275
7.237
7.205
7.196
7.187
7.176
7.169
7.161
7.149
7.112
7.104
7.088
7.075
5.226
5.210
5.194
5.178
5.124
5.116
5.108
5.100
5.093
2.369
2.359
2.351
2.340
2.333
2.324
2.314
2.306
2.297
2.287
2.277
2.269
1.254
1.006
4i (Z)
5.01
1.00
1.08
2.01
2.09
9.07
f1 (ppm)


144.442
137.869
133.794
128.421
127.611
127.073
36.345
30.217
20.487
14.406
12.085
4i (Z)
f1 (ppm)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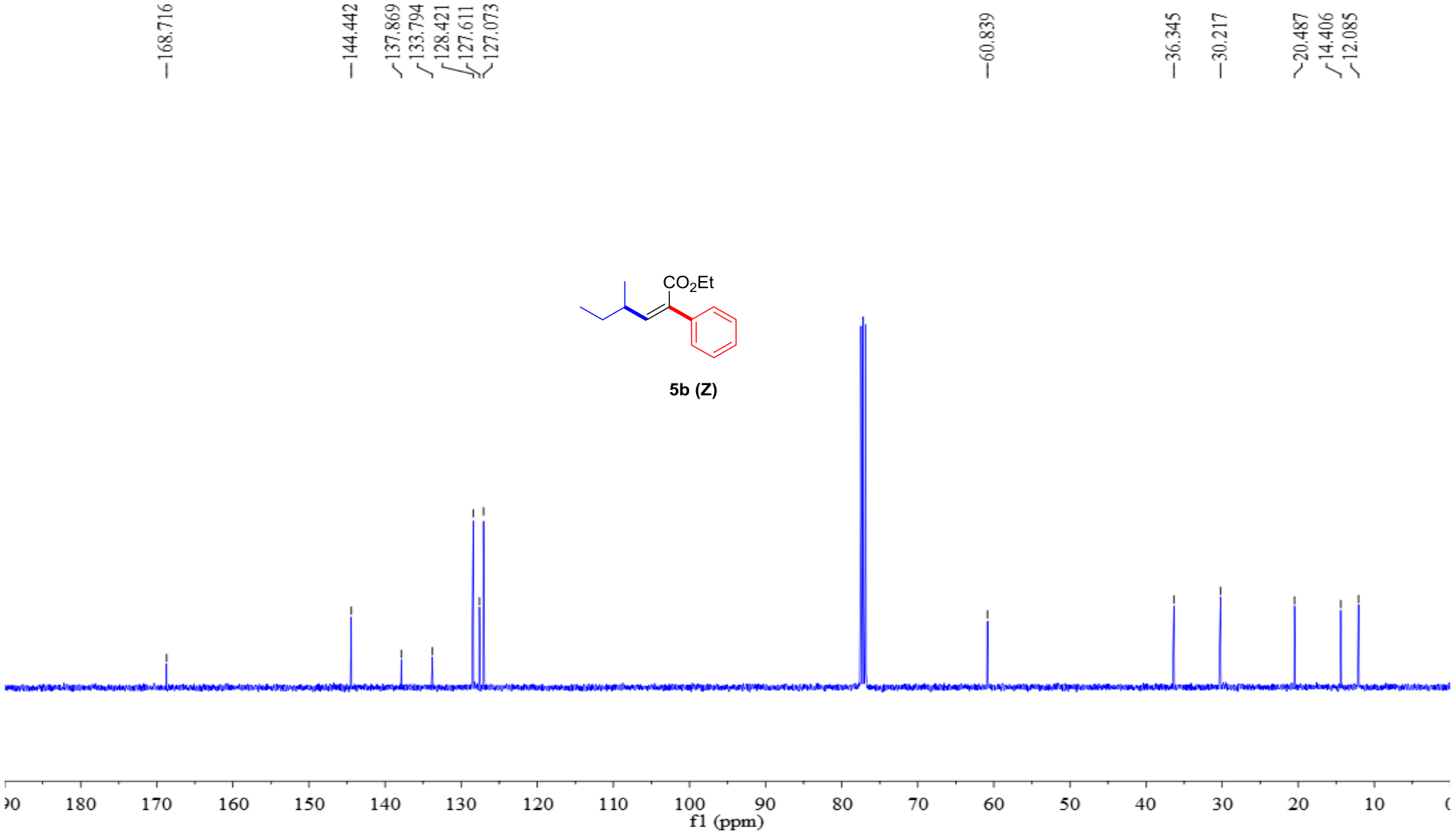
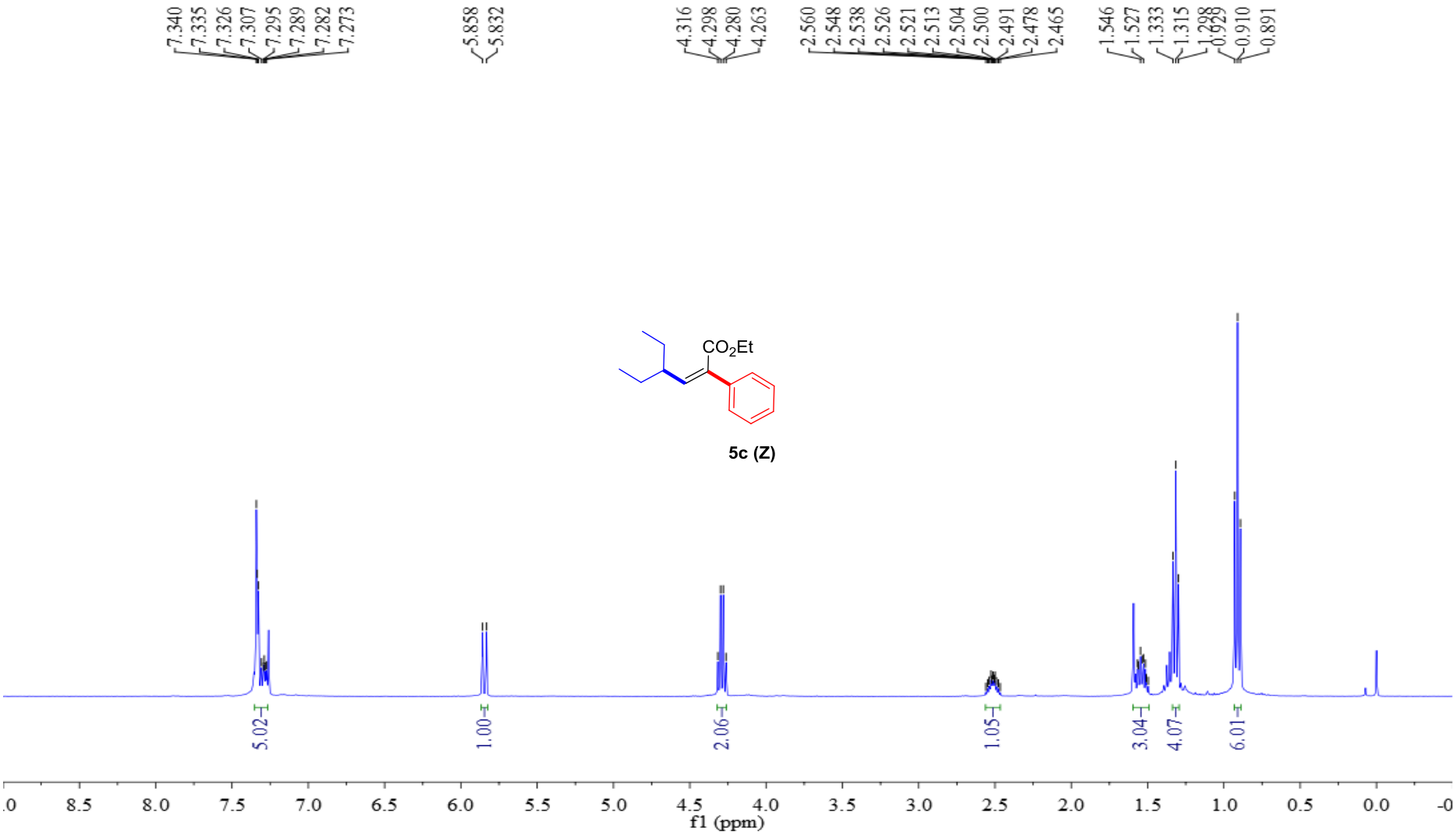
7.325
7.322
7.308
7.303
7.292
7.285
7.283
7.276
7.271
5.921
5.895
4.321
4.303
4.285
4.267
2.745
2.729
2.713
2.703
2.694
2.687
2.678
2.668
2.652
2.636
1.452
1.437
1.434
1.427
1.419
1.408
1.389
1.336
1.318
1.300
1.091
1.075
0.934
0.915
CO2Et
5b (Z)
5.02
1.00
2.01
1.02
2.03
3.00
3.00
3.03
f1 (ppm)


168.716
144.442
137.869
133.794
128.421
127.611
127.073
60.839
36.345
30.217
20.487
14.406
12.085
CO2Et
5b (Z)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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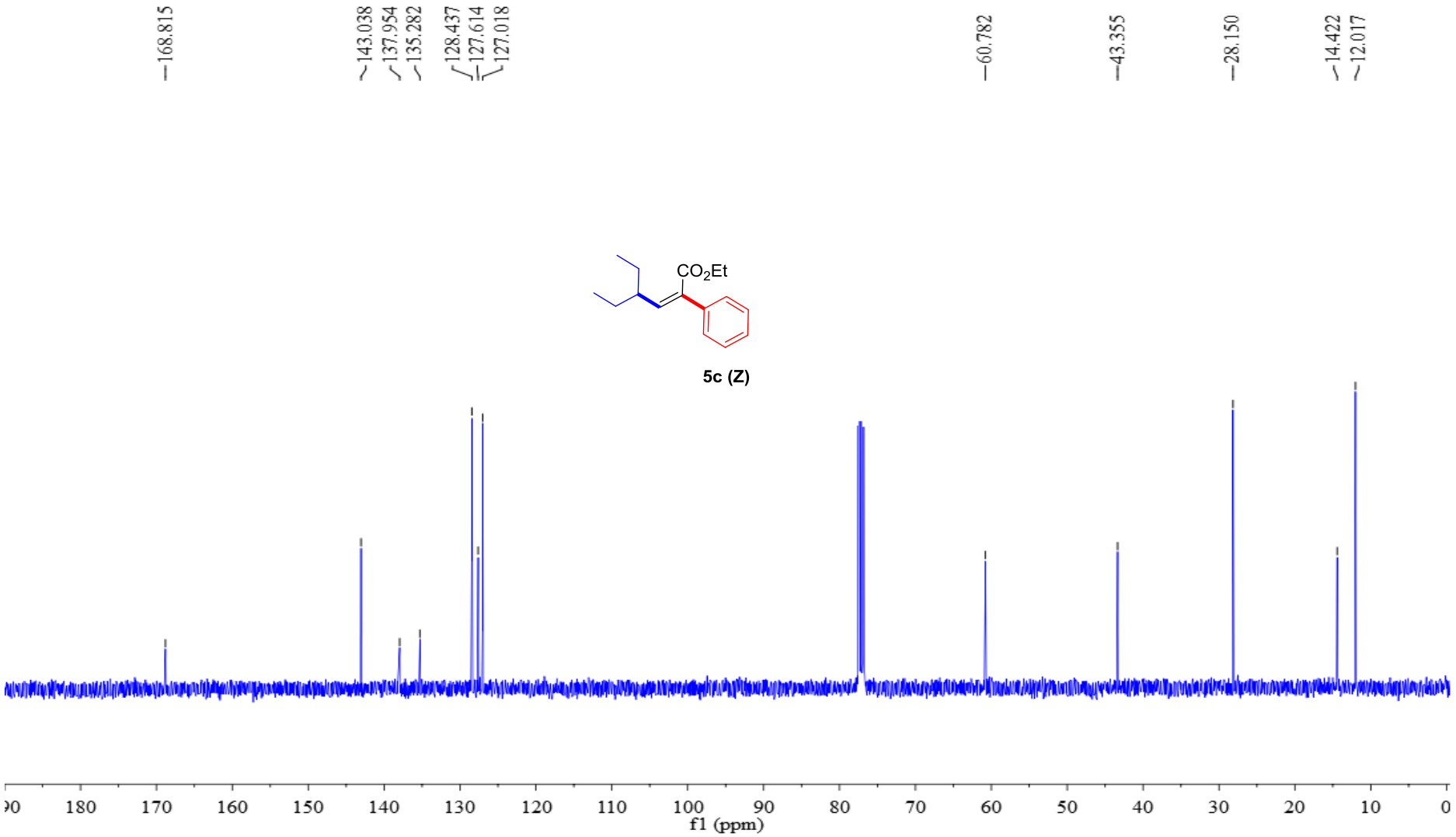
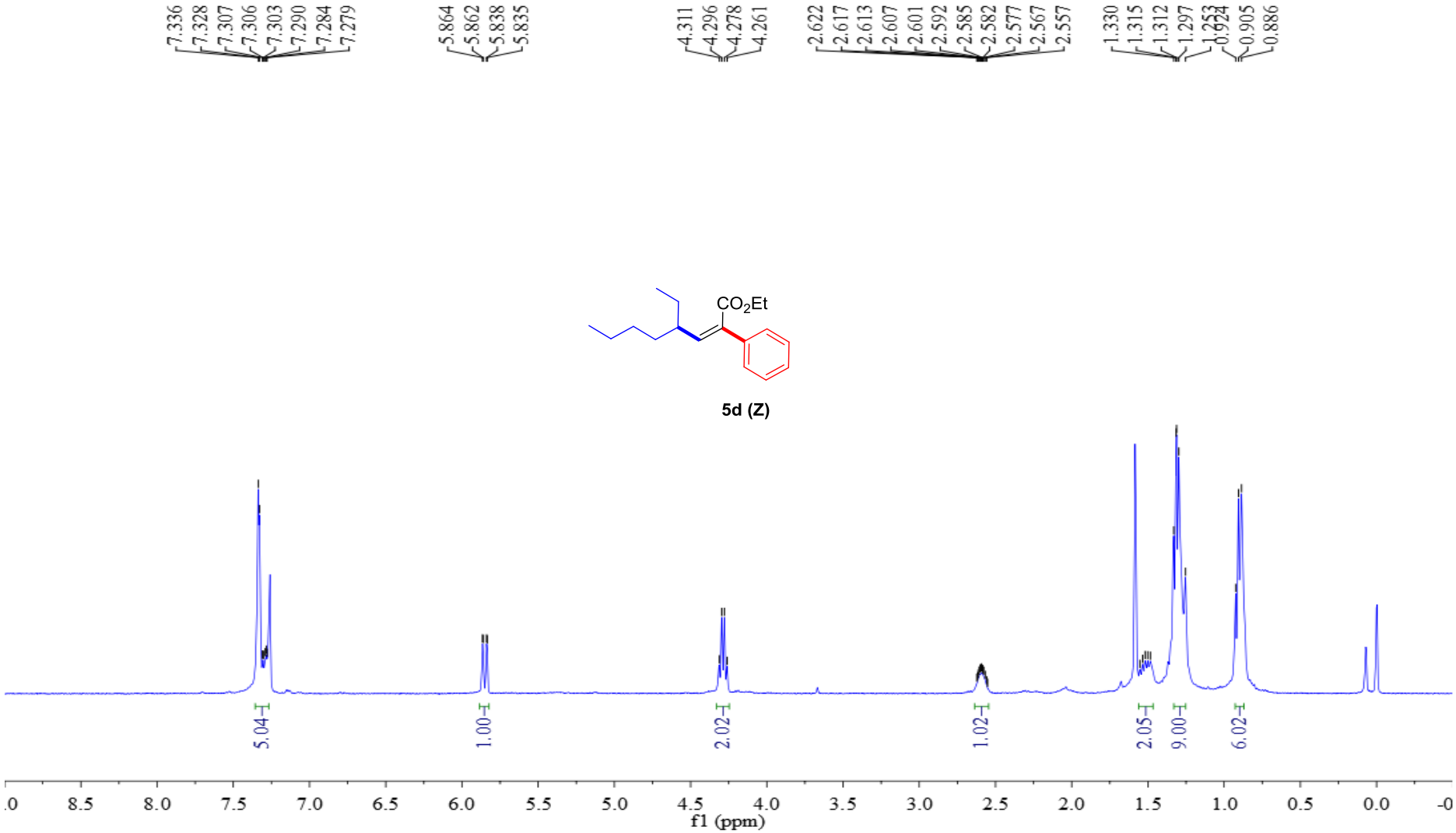
7.335
7.326
7.307
7.295
7.289
7.282
7.273
5.858
5.832
4.316
4.298
4.280
4.263
2.560
2.548
2.538
2.526
2.521
2.513
2.504
2.500
2.491
2.478
2.465
1.546
1.527
1.333
1.315
1.298
0.929
0.910
0.891
CO2Et
5c (Z)
5.02
1.00
2.06
1.05
3.04
4.07
6.01
f1 (ppm)


168.815
143.038
137.954
135.282
128.437
127.614
127.018
60.782
43.355
28.150
14.422
12.017
CO2Et
5c (Z)
f1 (ppm)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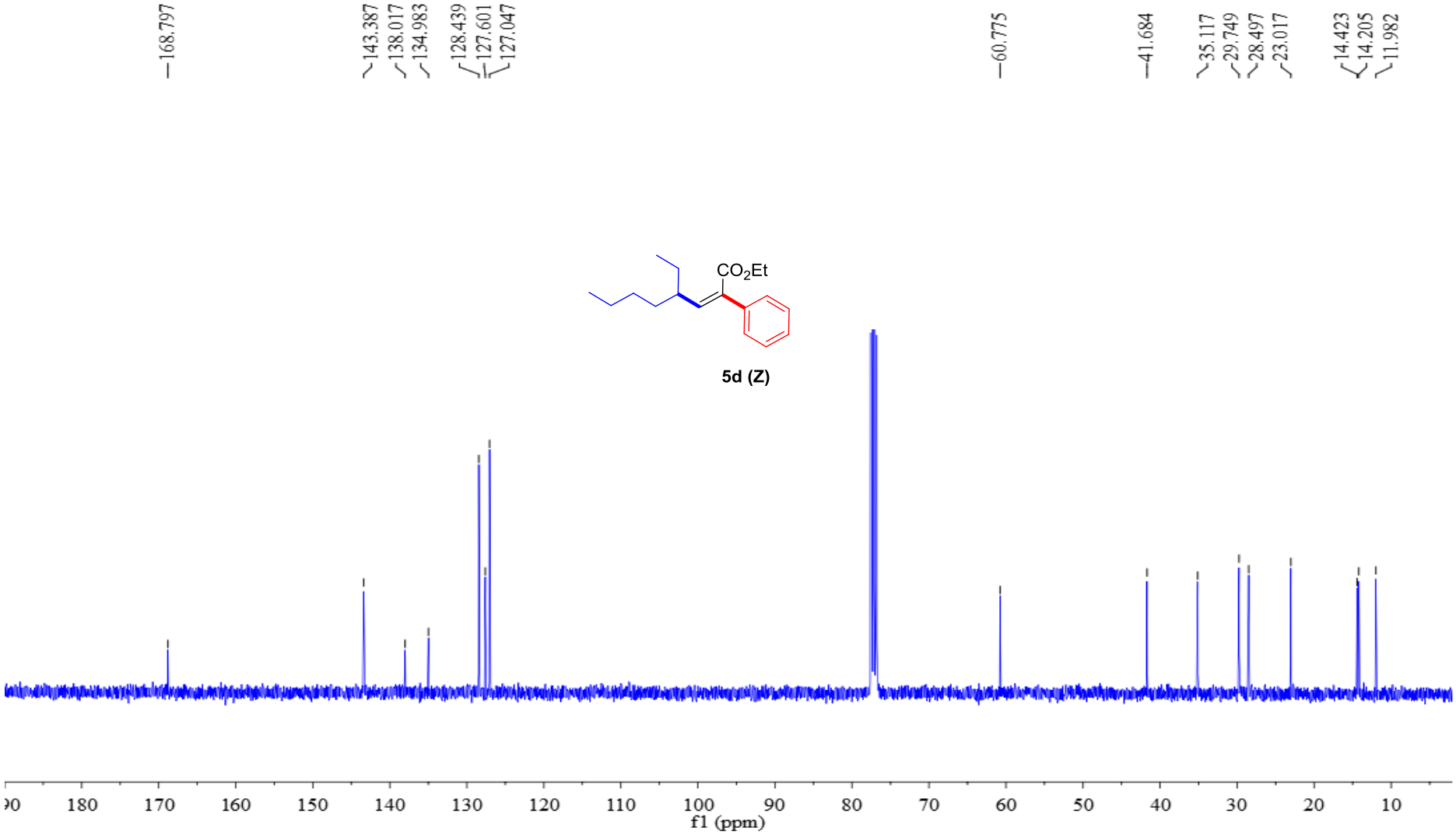
7.328
7.307
7.306
7.303
7.290
7.284
7.279
5.864
5.862
5.838
5.835
4.311
4.296
4.278
4.261
2.622
2.617
2.613
2.607
2.601
2.592
2.585
2.582
2.577
2.567
2.557
1.330
1.315
1.312
1.297
0.924
0.905
0.886
CO2Et
5d (Z)
5.04
1.00
2.02
1.02
2.05
9.00
6.02
f1 (ppm)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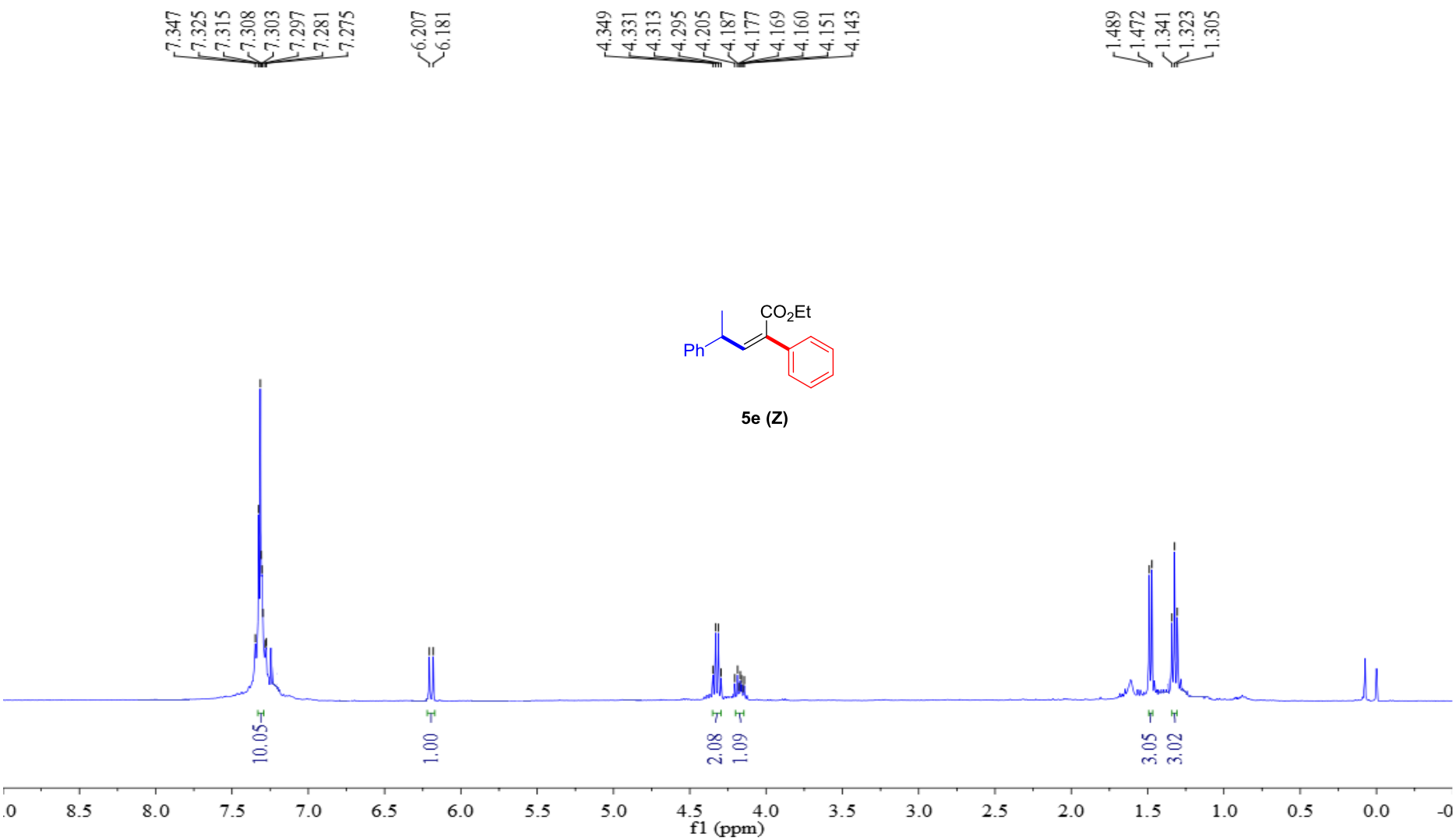
143.387
138.017
134.983
128.439
127.601
127.047
60.775
41.684
35.117
29.749
28.497
23.017
14.423
14.205
11.982
CO2Et
5d (Z)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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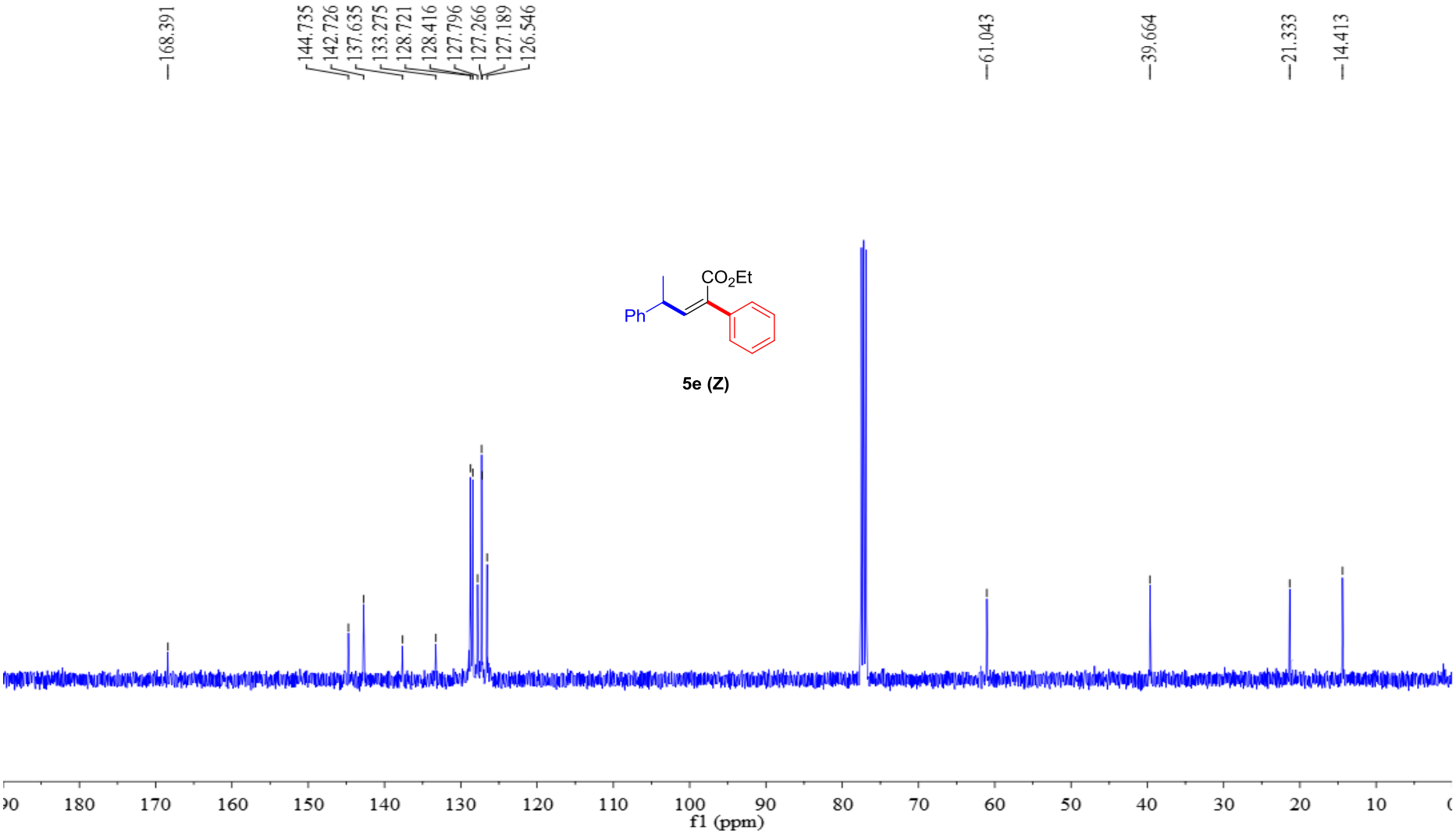
7.325
7.315
7.308
7.303
7.297
7.281
7.275
6.207
6.181
4.349
4.331
4.313
4.295
4.205
4.187
4.177
4.169
4.160
4.151
4.143
1.489
1.472
1.341
1.323
1.305
CO2Et
Ph
10.05
1.00
2.08
1.09
3.05
3.02
f1 (ppm)

5e (Z)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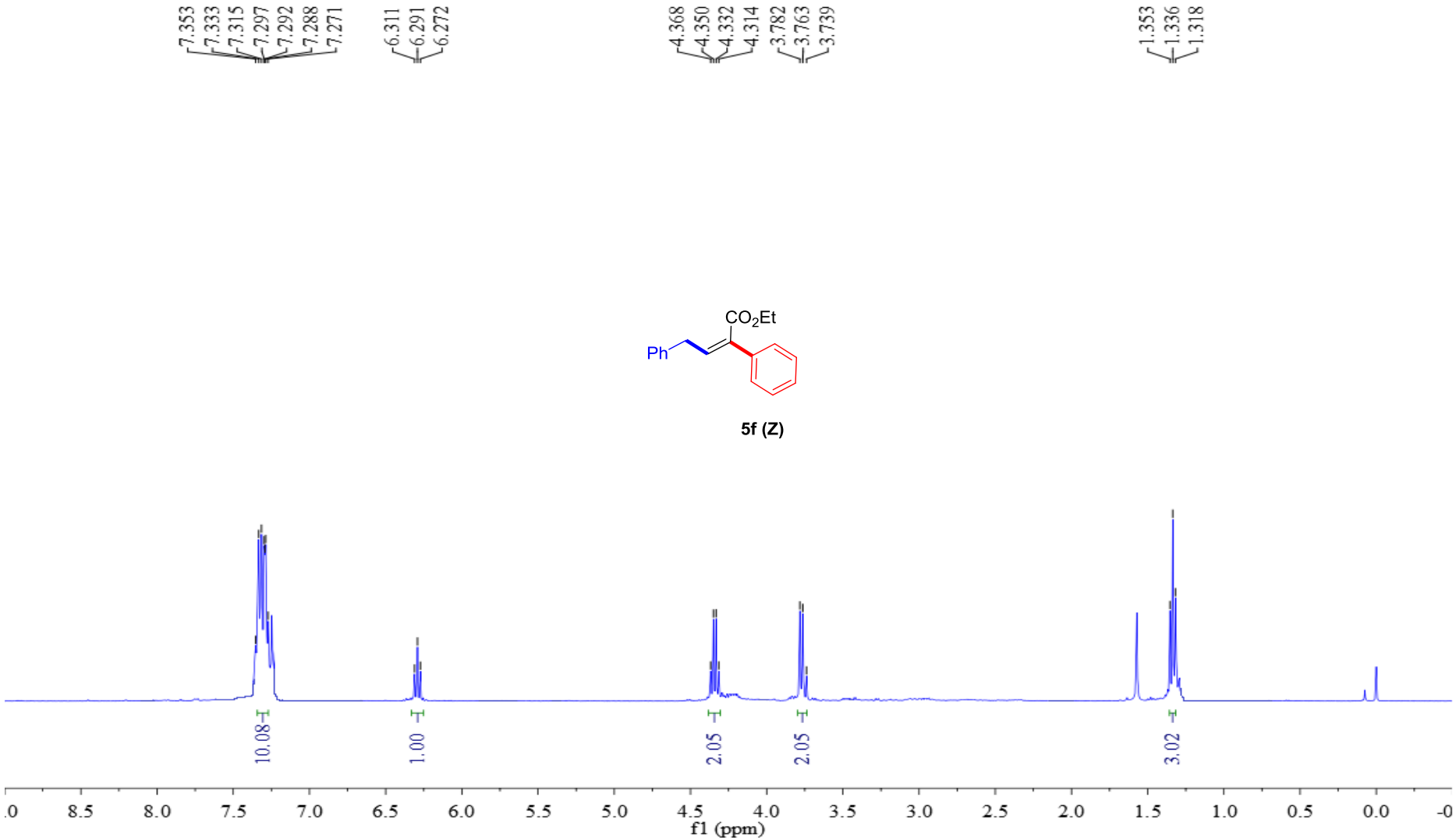
144.735
142.726
137.635
133.275
128.721
128.416
127.796
127.266
127.189
126.546
61.043
39.664
21.333
14.413
CO2Et
Ph
5e (Z)
f1 (ppm)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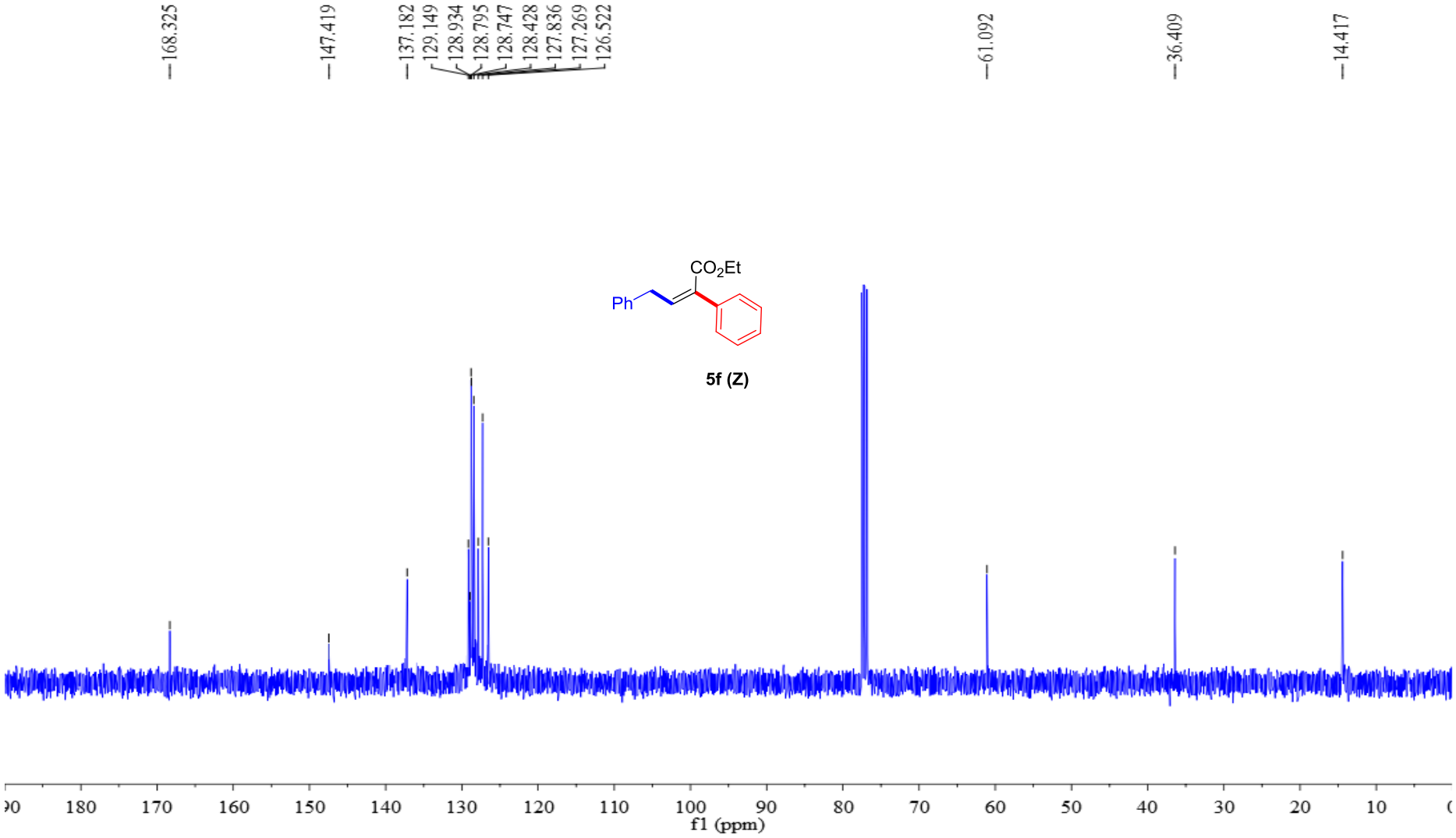
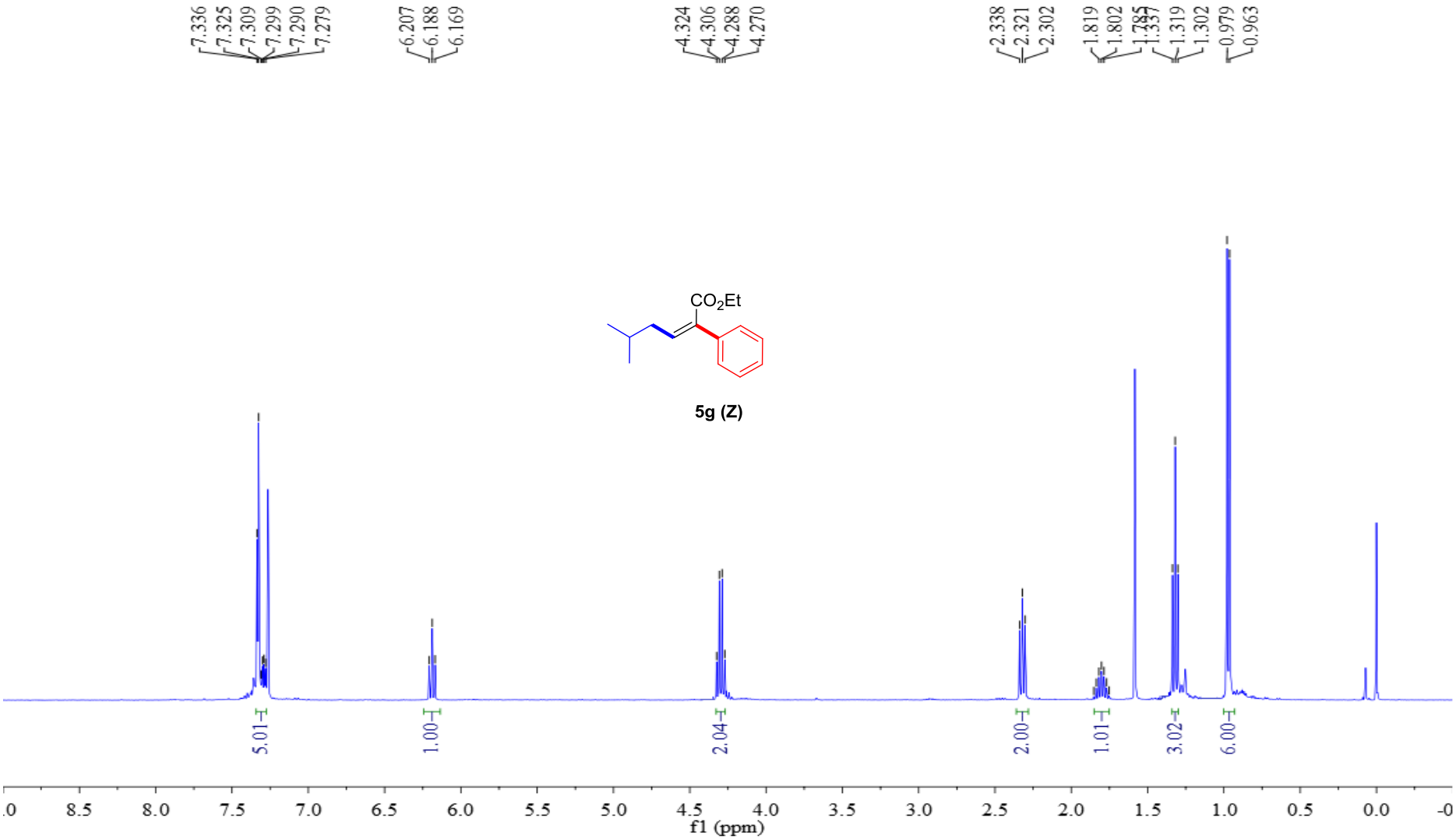
7.333
7.315
7.297
7.292
7.288
7.271
6.311
6.291
6.272
4.368
4.350
4.332
4.314
3.782
3.763
3.739
1.353
1.336
1.318
CO2Et
Ph
10.08
1.00
2.05
2.05
3.02
f1 (ppm)

5f (Z)


168.325
147.419
137.182
129.149
128.934
128.795
128.747
128.428
127.836
127.269
126.522
61.092
36.409
14.417
CO2Et
Ph
5f (Z)
f1 (ppm)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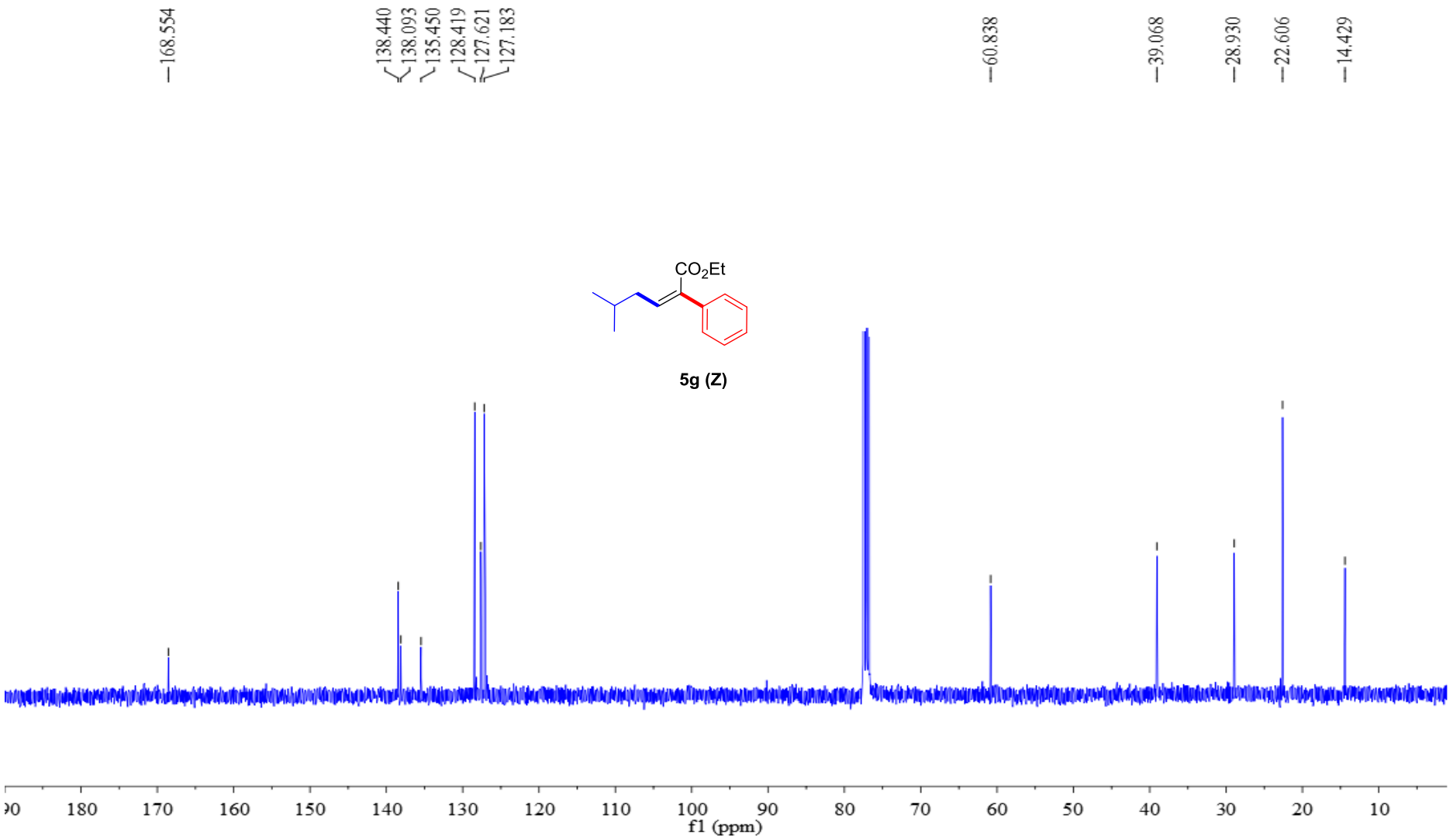
7.325
7.309
7.299
7.290
7.279
6.207
6.188
6.169
4.324
4.306
4.288
4.270
2.338
2.321
2.302
1.819
1.802
1.785
1.337
1.319
1.302
0.979
0.963
CO2Et
5g (Z)
5.01
1.00
2.04
2.00
1.01
3.02
6.00
f1 (ppm)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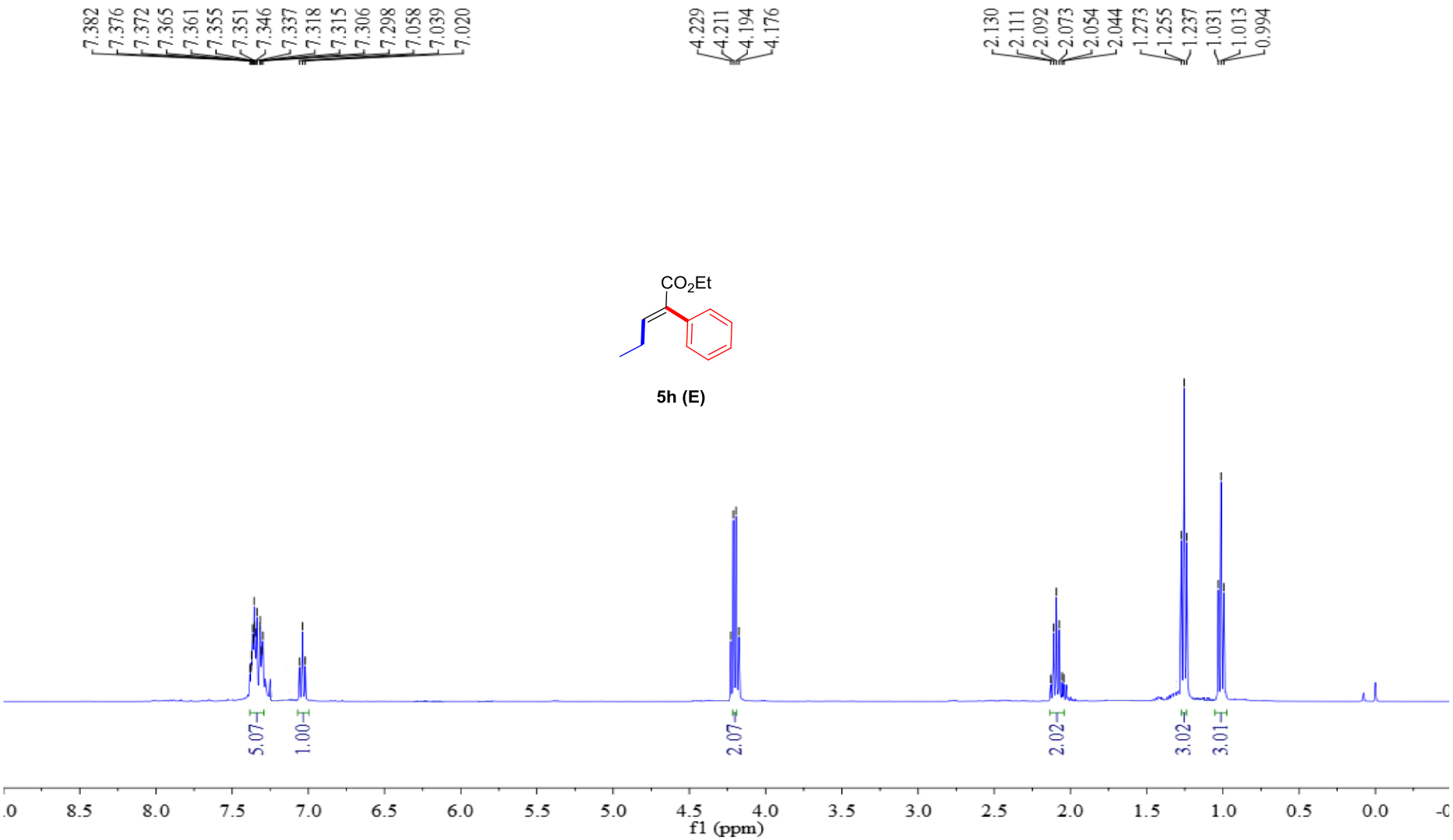
138.093
135.450
128.419
127.621
127.183
60.838
39.068
28.930
22.606
14.429
CO2Et
5g (Z)
f1 (ppm)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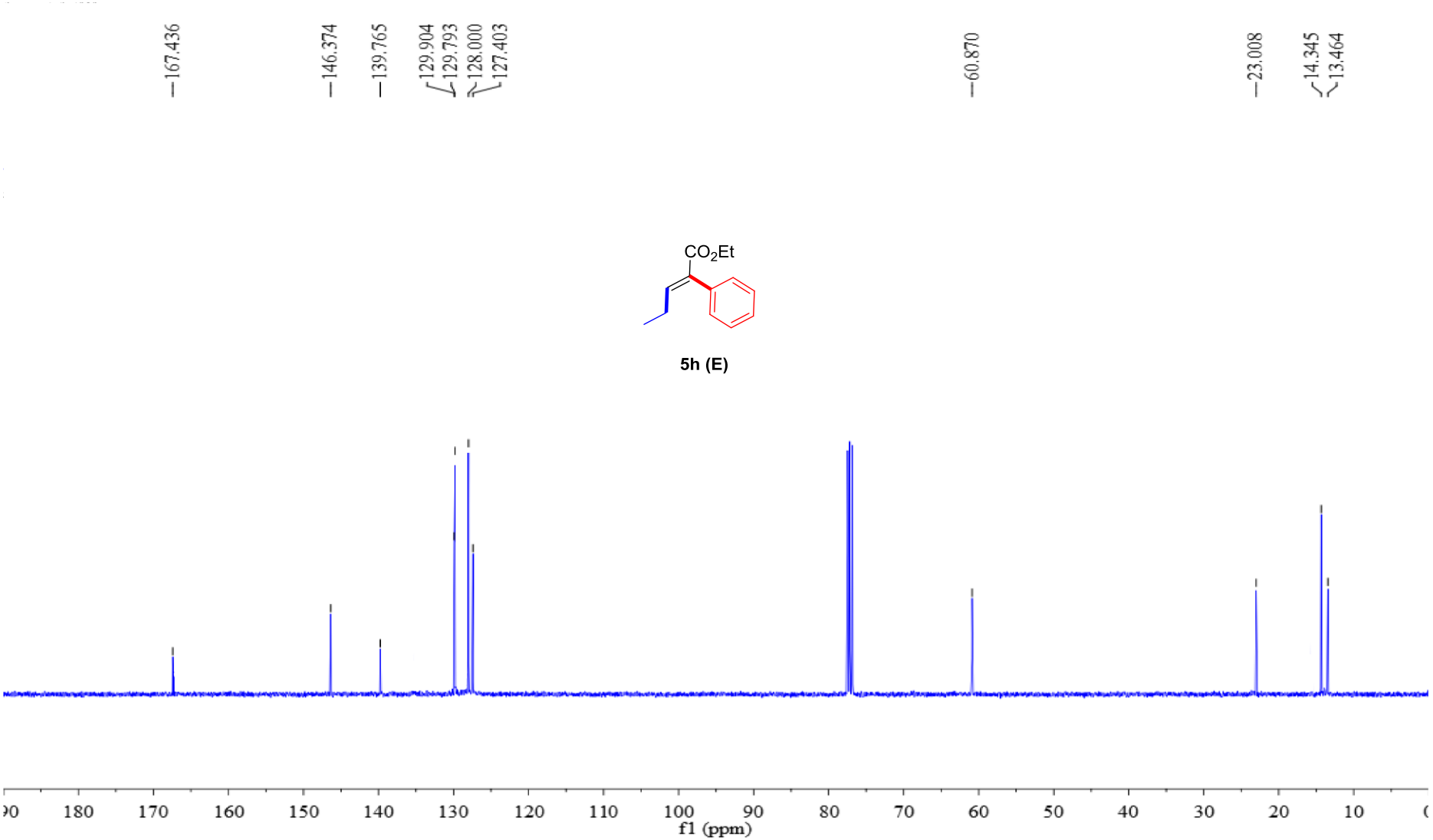
7.372
7.365
7.361
7.355
7.351
7.346
7.337
7.318
7.315
7.306
7.298
7.058
7.039
7.020
4.229
4.211
4.194
4.176
2.130
2.111
2.092
2.073
2.054
2.044
1.273
1.255
1.237
1.031
1.013
0.994
CO2Et
5h (E)
5.07
1.00
2.07
2.02
3.02
3.01
f1 (ppm)


167.436
146.374
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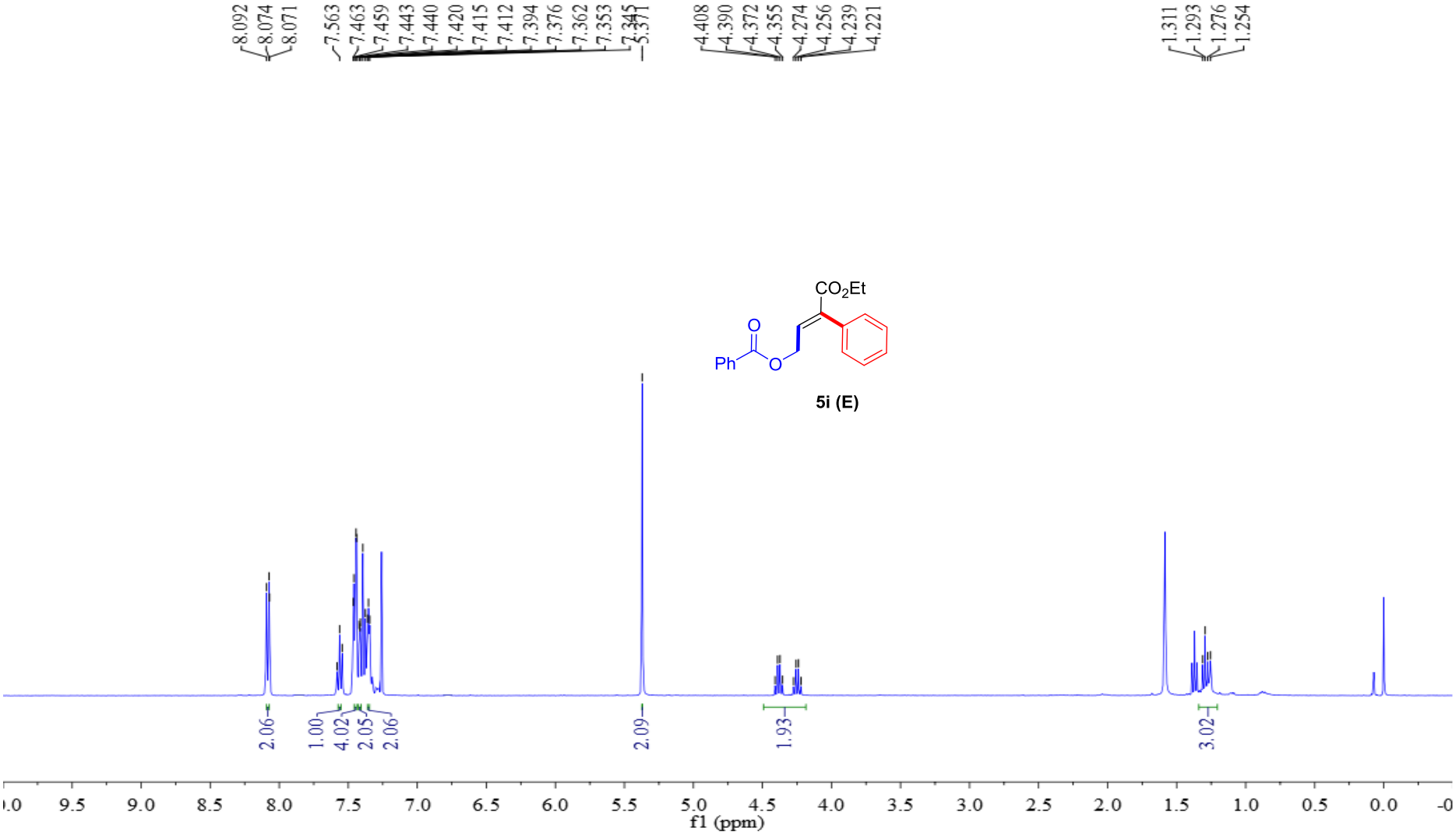
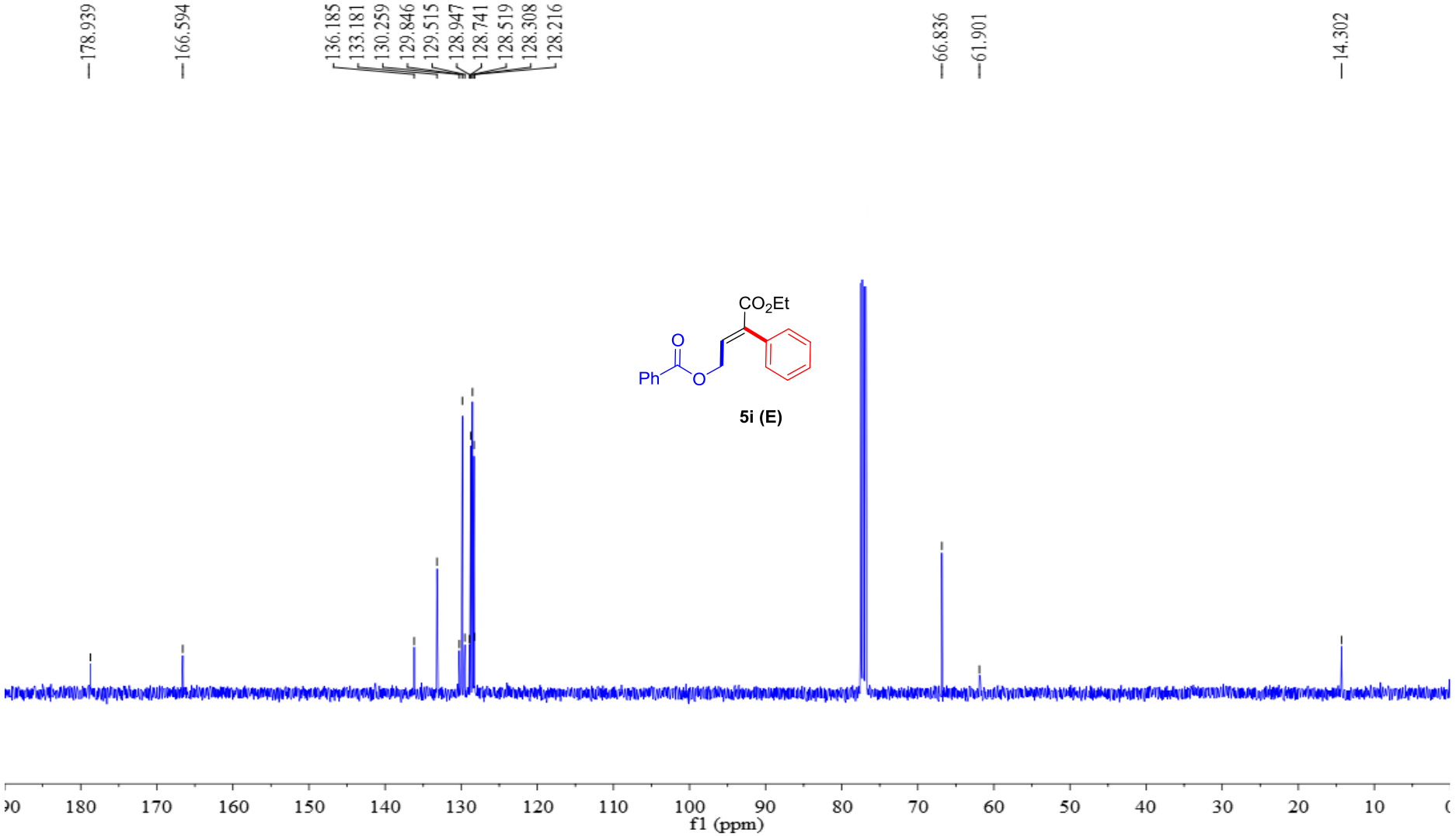
129.793
128.000
127.403
60.870
23.008
14.345
13.464
CO2Et
5h (E)
f1 (ppm)


8.092
8.074
8.071
7.563
7.463
7.459
7.443
7.440
7.420
7.415
7.412
7.394
7.376
7.362
7.353
5.371
4.408
4.390
4.372
4.355
4.274
4.256
4.239
4.221
1.311
1.293
1.276
1.254
CO2Et
O
Ph
O
5i (E)
2.06
1.00
4.02
2.05
2.06
2.09
1.93
3.02
f1 (ppm)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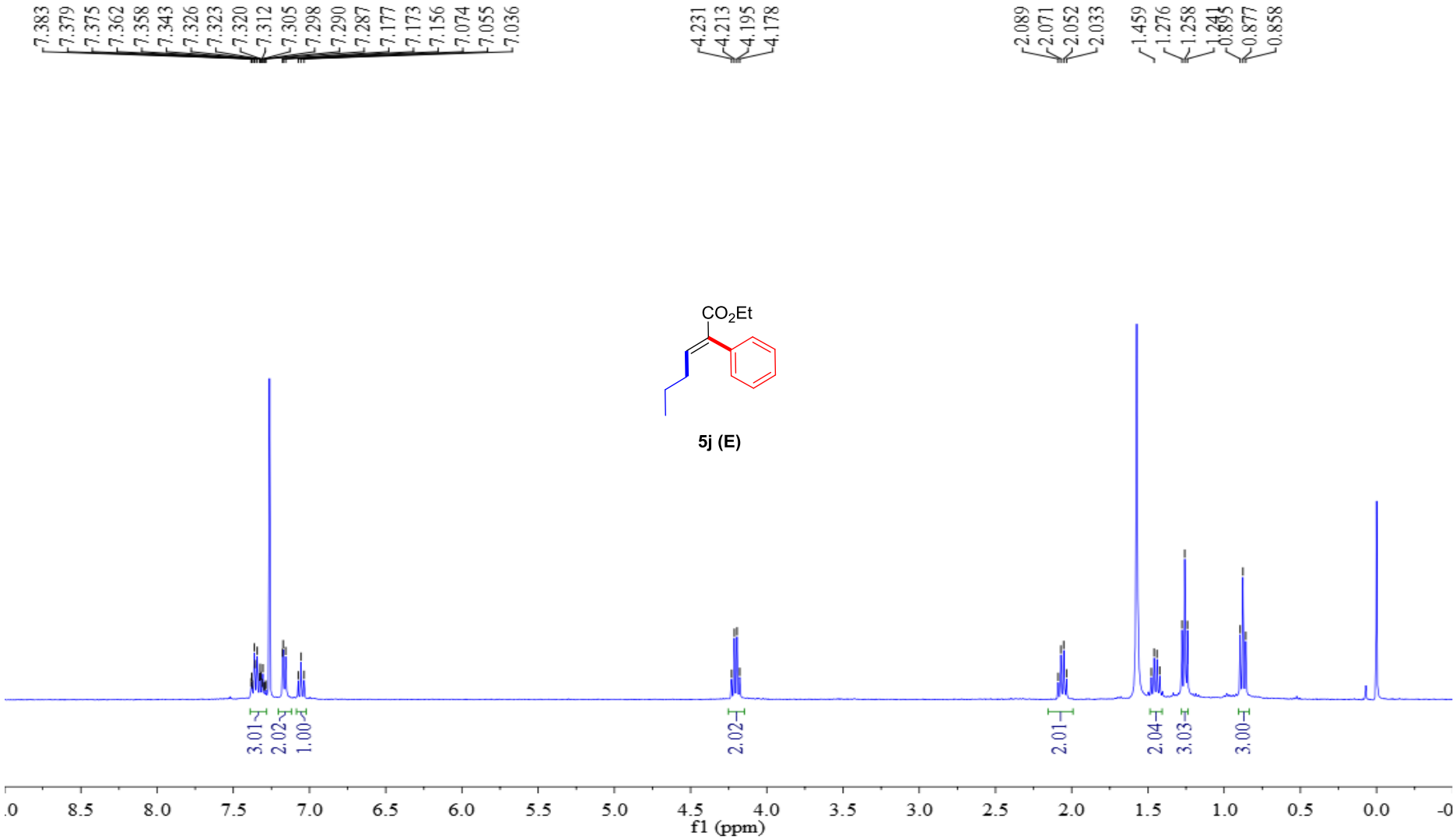
136.185
133.181
130.259
129.846
129.515
128.947
128.741
128.519
128.308
128.216
66.836
61.901
14.302
CO2Et
O
Ph
O
5i (E)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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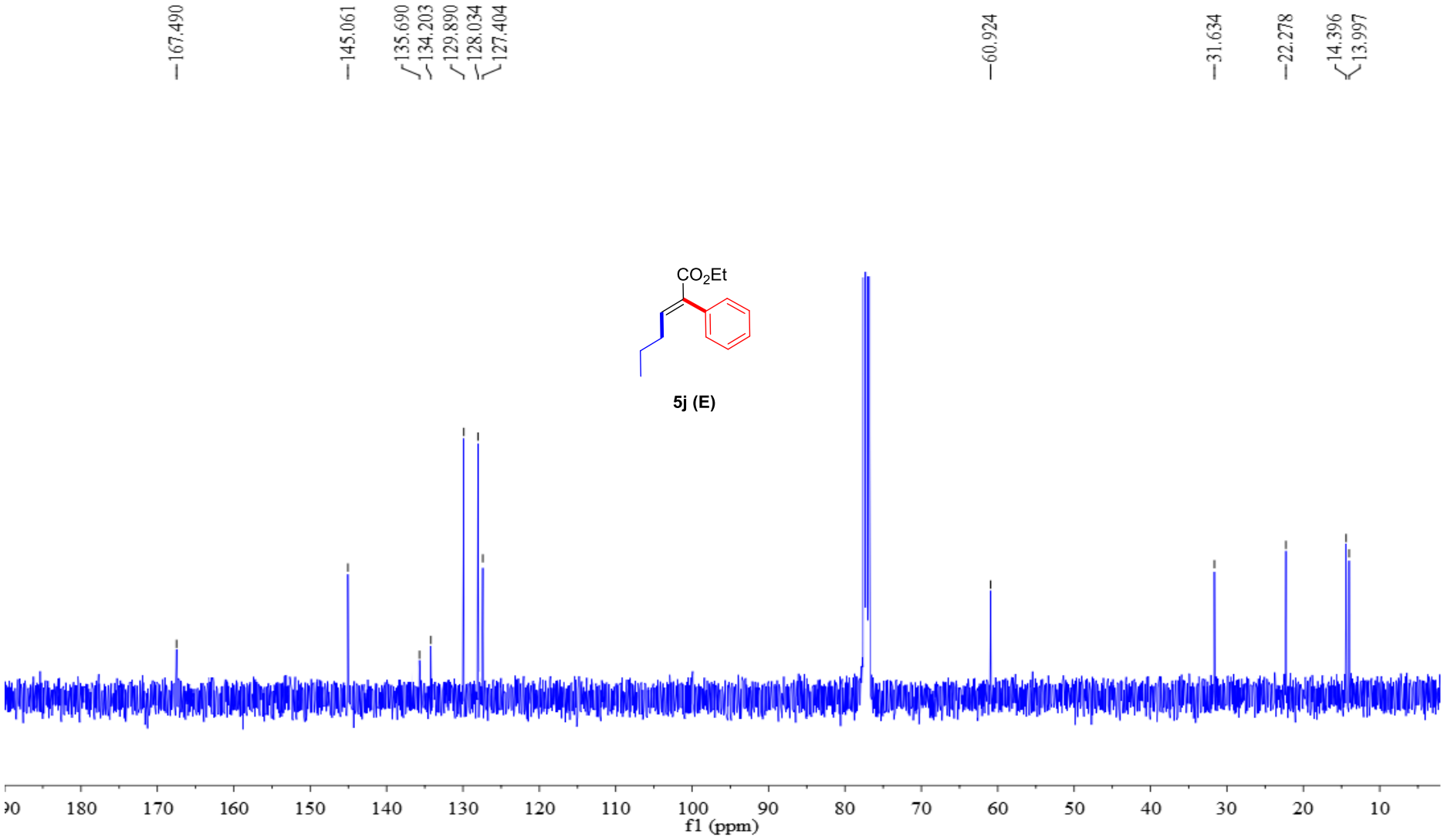
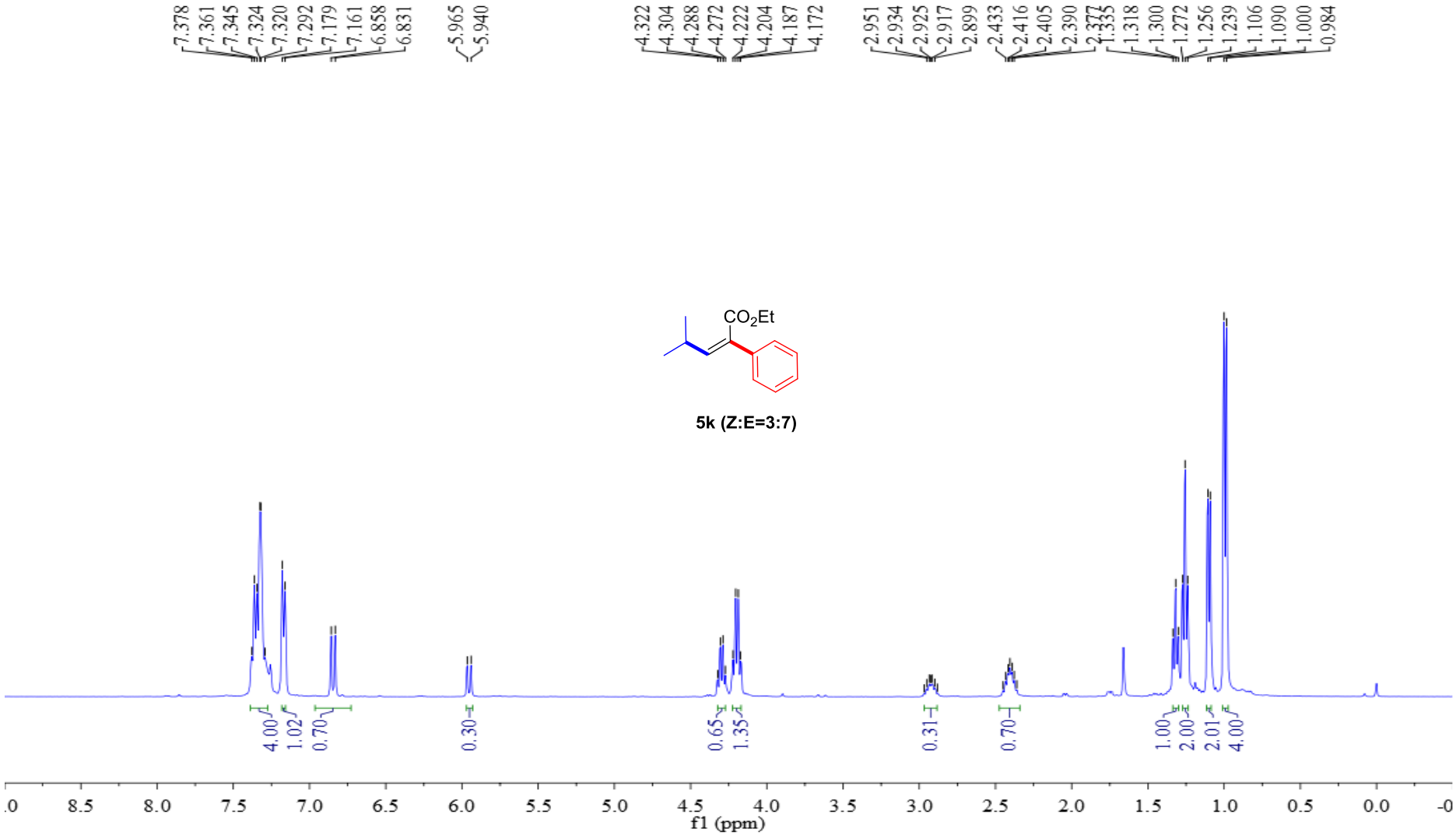
7.379
7.375
7.362
7.358
7.343
7.326
7.323
7.320
7.312
7.305
7.298
7.290
7.287
7.177
7.173
7.156
7.074
7.055
7.036
4.231
4.213
4.195
4.178
2.089
2.071
2.052
2.033
1.459
1.276
1.258
1.241
0.895
0.877
0.858
CO2Et
5j (E)
3.01
2.02
1.00
2.02
2.01
2.04
3.03
3.00
f1 (ppm)


167.490
145.061
135.690
134.203
129.890
128.034
127.404
60.924
31.634
22.278
14.396
13.997
CO2Et
5j (E)
f1 (ppm)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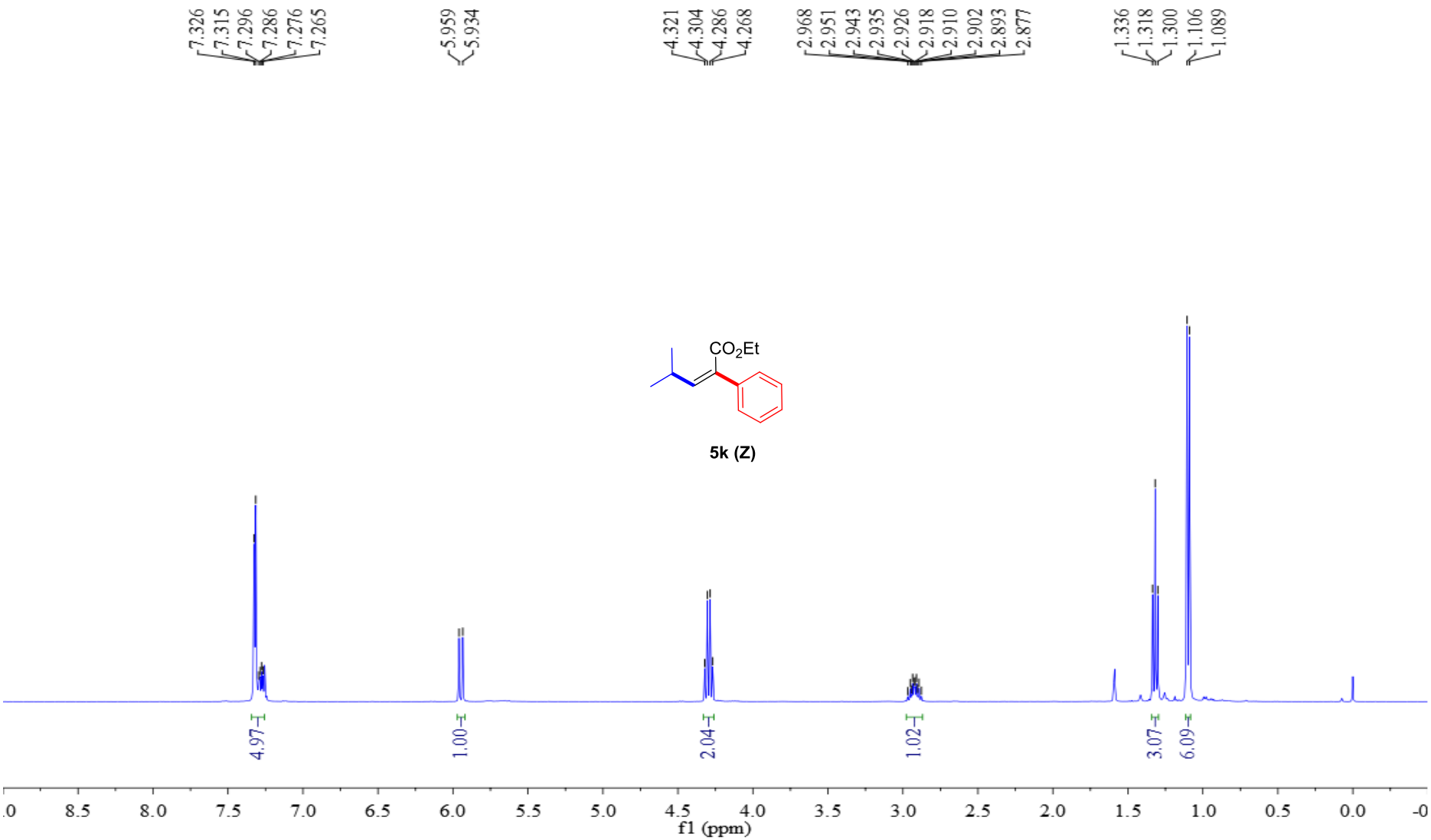
7.361
7.345
7.324
7.320
7.292
7.179
7.161
6.858
6.831
5.965
5.940
4.322
4.304
4.288
4.272
4.222
4.204
4.187
4.172
2.951
2.934
2.925
2.917
2.899
2.433
2.416
2.405
2.390
2.377
1.335
1.318
1.300
1.272
1.256
1.239
1.106
1.090
1.000
0.984
CO2Et
5k (Z:E=3:7)
4.00
1.02
0.70
0.30
0.65
1.35
0.31
0.70
1.00
2.00
2.01
4.00
f1 (ppm)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7.315
7.296
7.286
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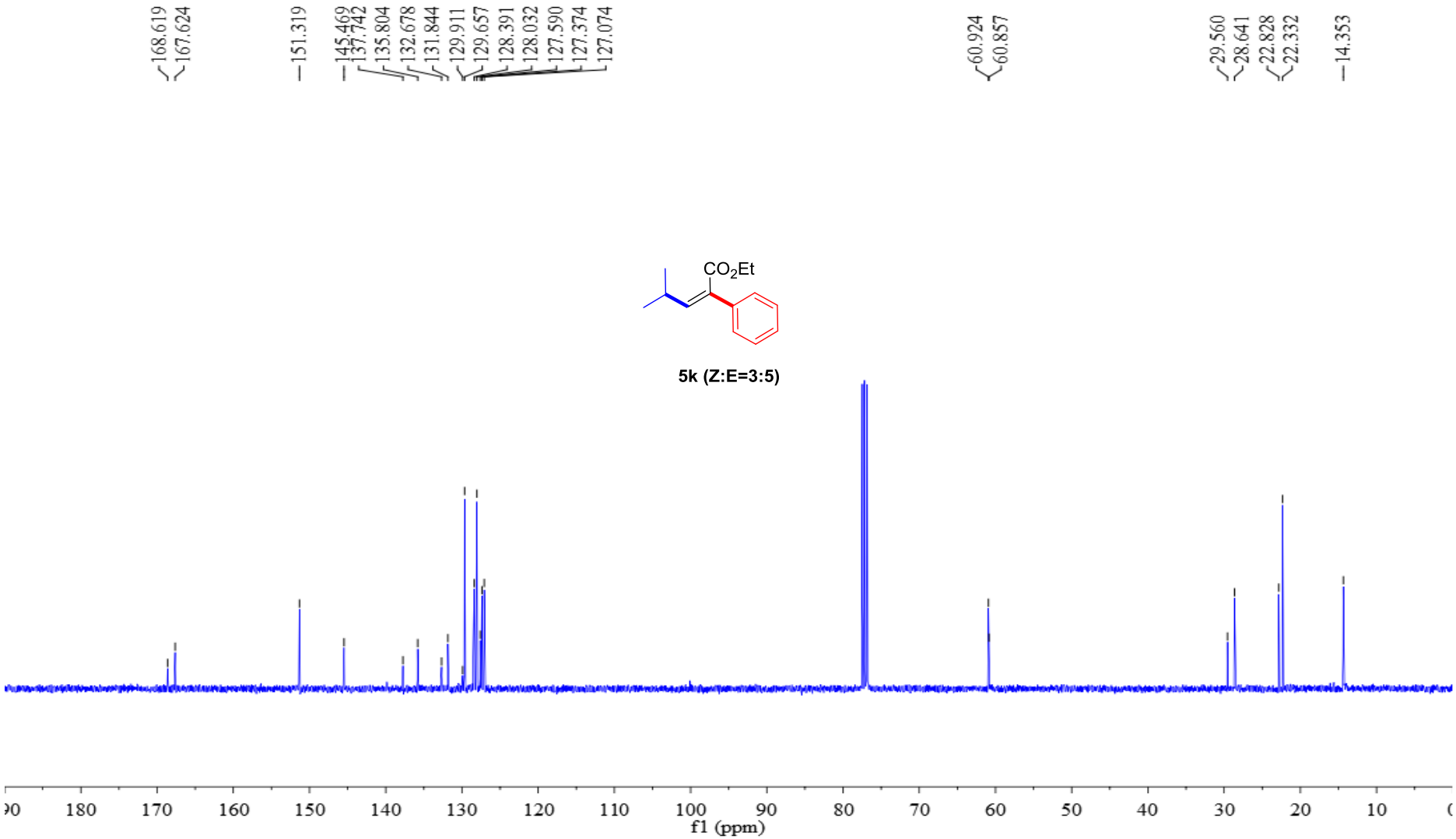
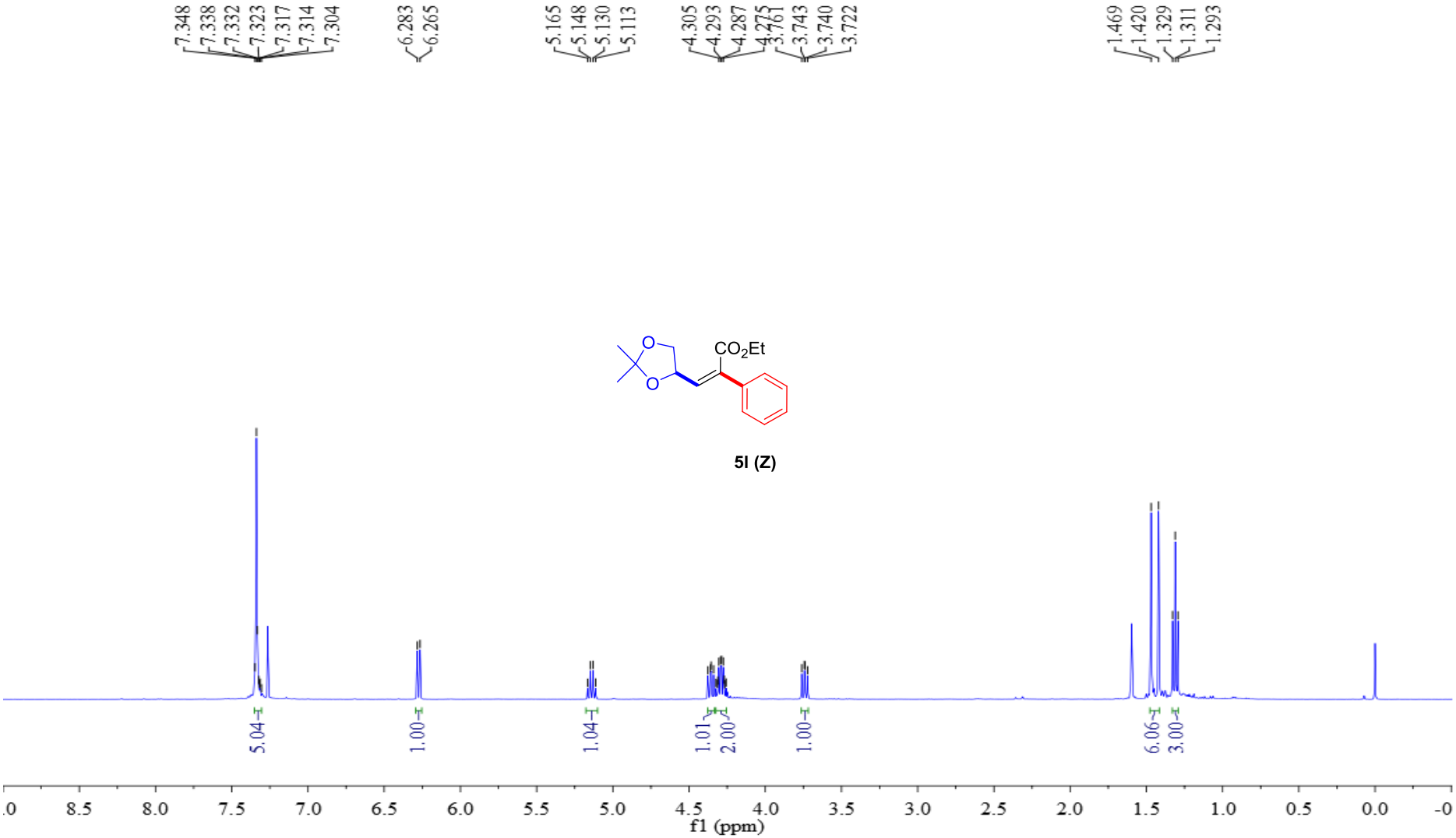
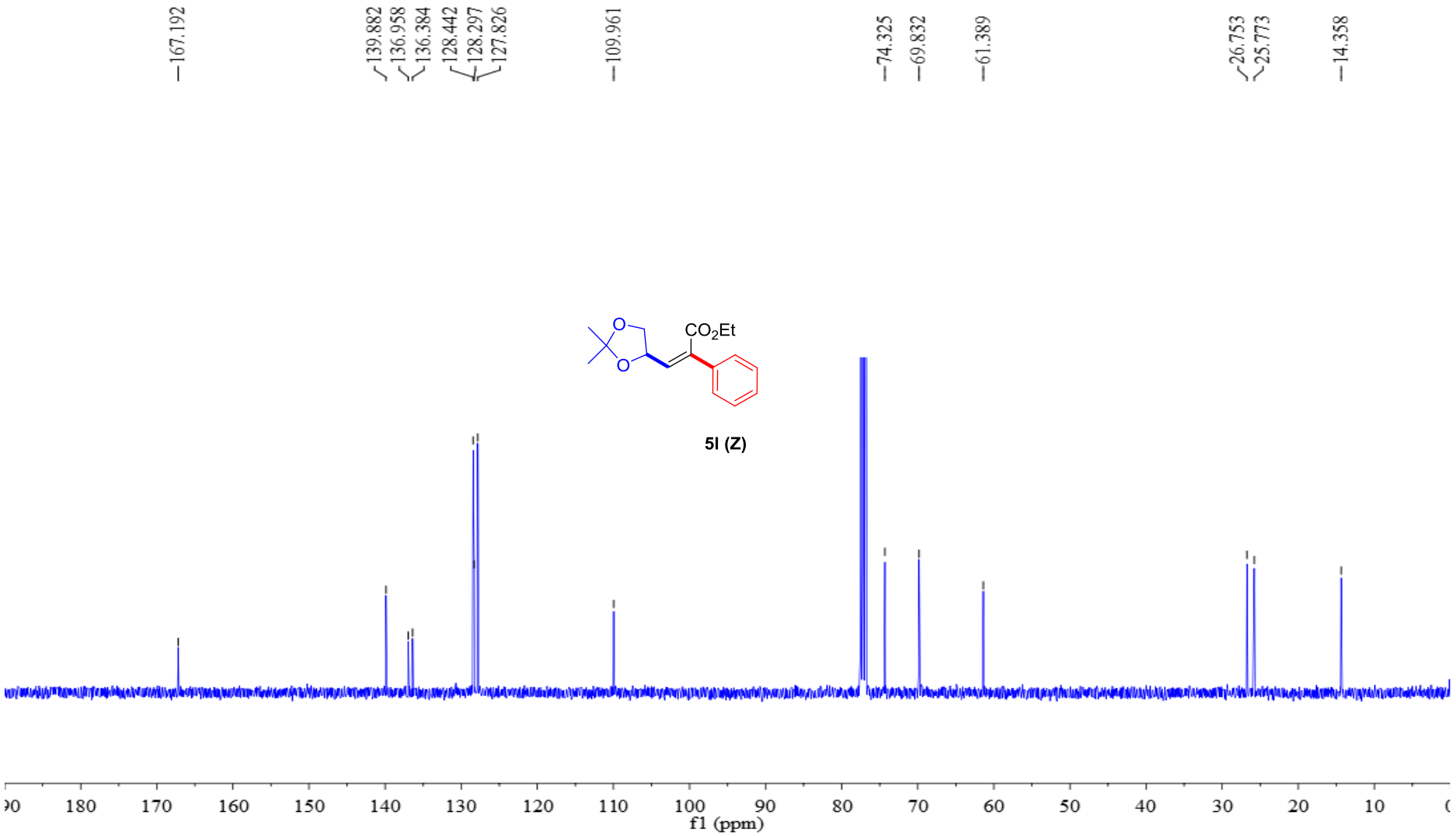
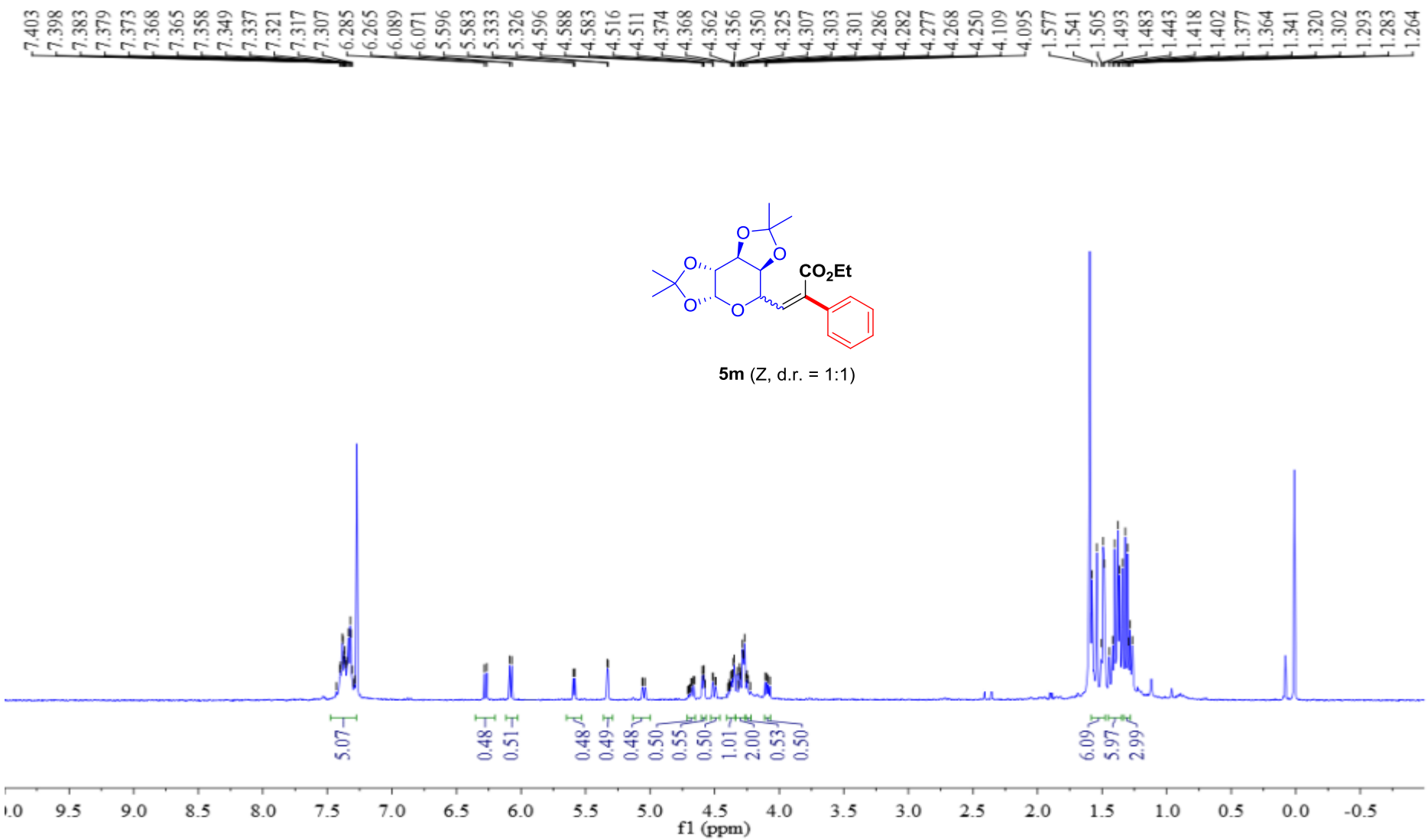
7.265
5.959
5.934
4.321
4.304
4.286
4.268
2.968
2.951
2.943
2.935
2.926
2.918
2.910
2.902
2.893
2.877
1.336
1.318
1.300
1.106
1.089
CO2Et
5k (Z)
4.97
1.00
2.04
1.02
3.07
6.09
f1 (ppm)


168.619
167.624
151.319
145.469
137.742
135.804
132.678
131.844
129.911
129.657
128.391
128.032
127.590
127.374
127.074
60.924
60.857
29.560
28.641
22.828
22.332
14.353
CO2Et
5k (Z:E=3:5)
f1 (ppm)

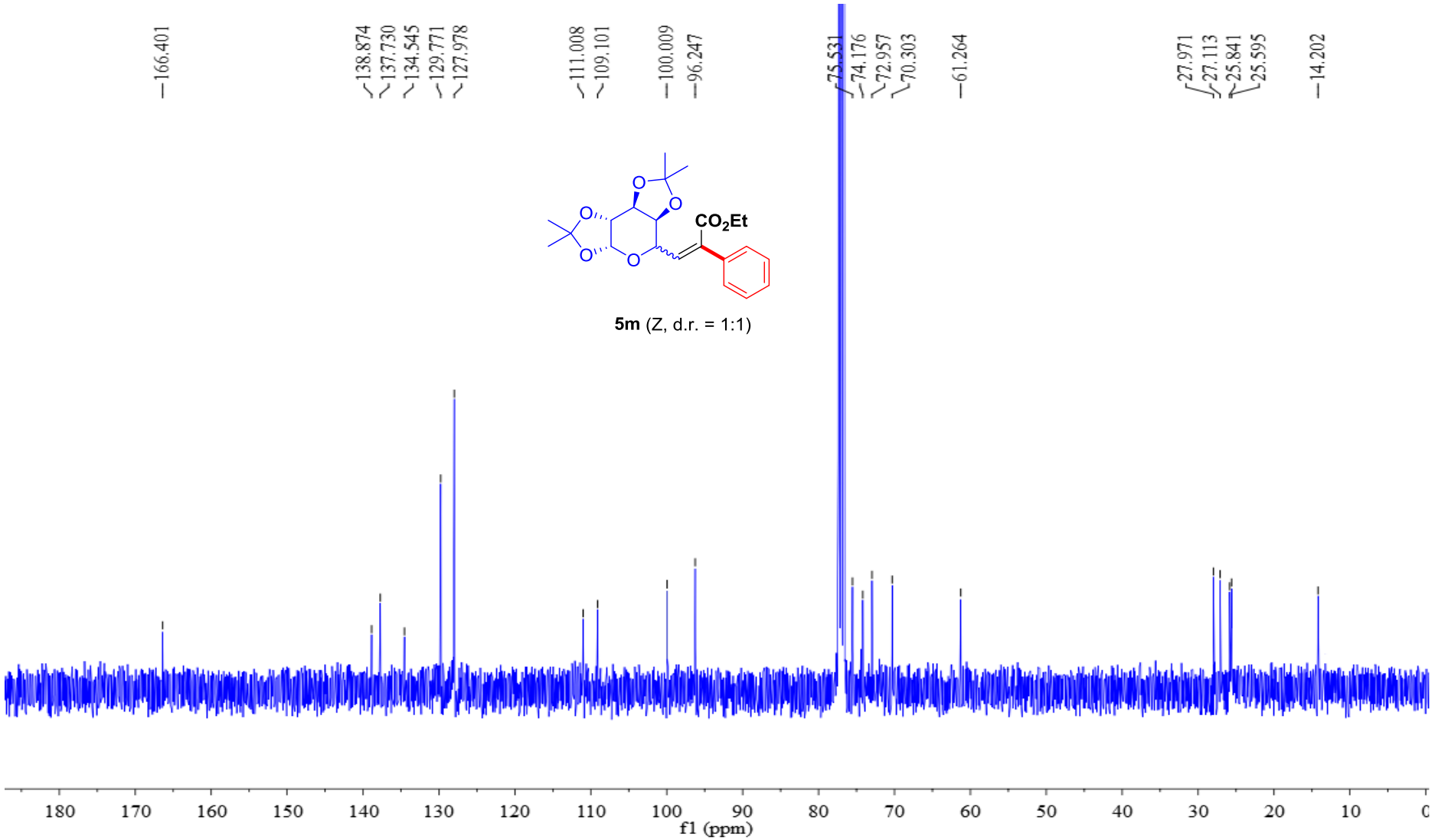

7.348
7.338
7.332
7.323
7.317
7.314
7.304
6.283
6.265
5.165
5.148
5.130
5.113
4.305
4.293
4.287
4.275
3.761
3.743
3.740
3.722
1.469
1.420
1.329
1.311
1.293
CO2Et
5.04
1.00
1.04
1.01
2.00
1.00
6.06
3.00
f1 (ppm)

5l (Z)

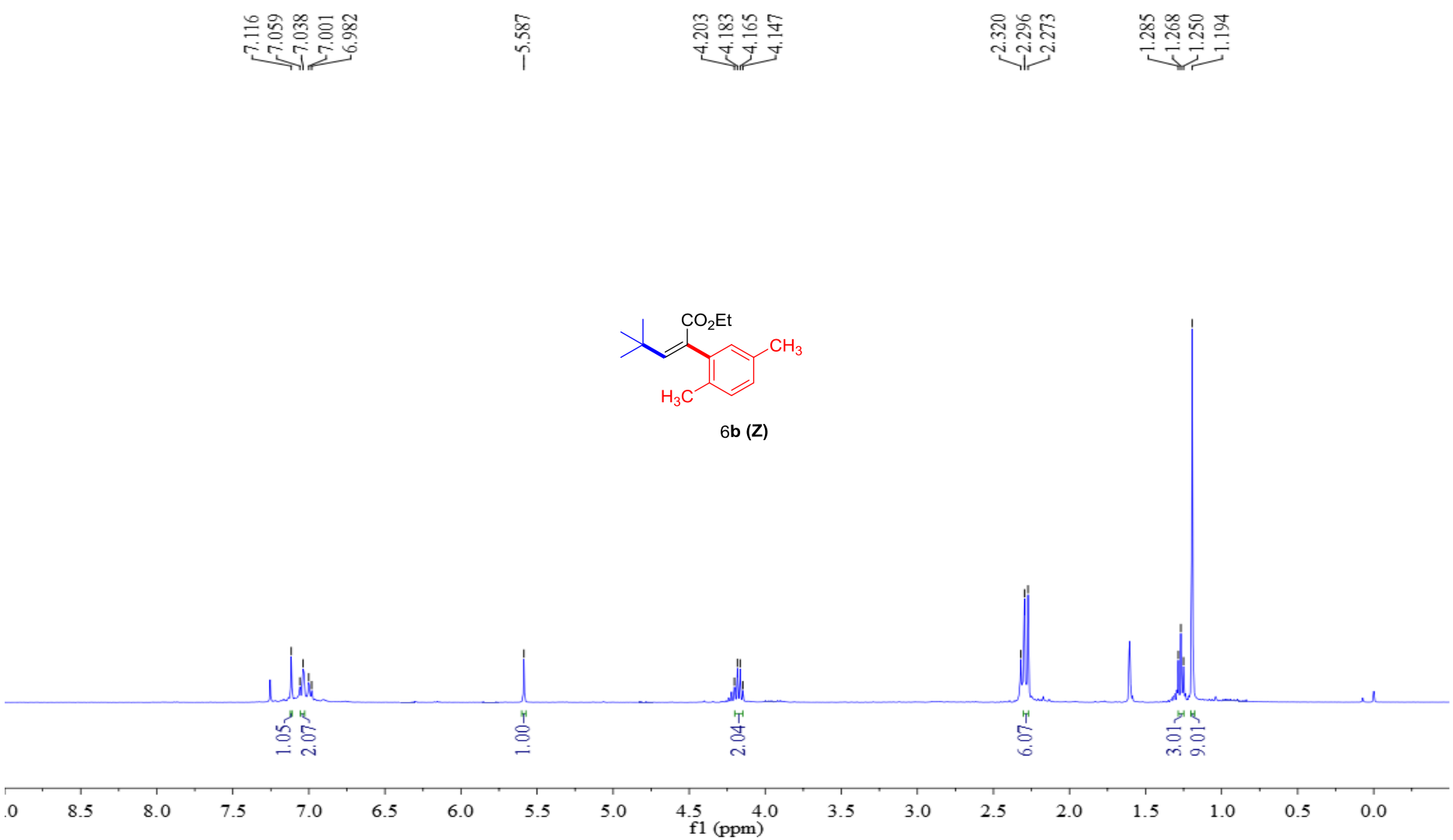

167.192
139.882
136.958
136.384
128.442
128.297
127.826
109.961
74.325
69.832
61.389
26.753
25.773
14.358
CO2Et
O
O
5l (Z)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.403
7.398
7.383
7.379
7.373
7.368
7.365
7.358
7.349
7.337
7.321
7.317
7.307
6.285
6.265
6.089
6.071
5.596
5.583
5.333
5.326
4.596
4.588
4.583
4.516
4.511
4.374
4.368
4.362
4.356
4.350
4.325
4.307
4.303
4.301
4.286
4.282
4.277
4.268
4.250
4.109
4.095
1.577
1.541
1.505
1.493
1.483
1.443
1.418
1.402
1.377
1.364
1.341
1.320
1.302
1.293
1.283
1.264
CO2Et
5.07
0.48
0.51
0.48
0.49
0.48
0.50
0.55
0.50
1.01
2.00
0.53
0.50
6.09
5.97
2.99
f1 (ppm)

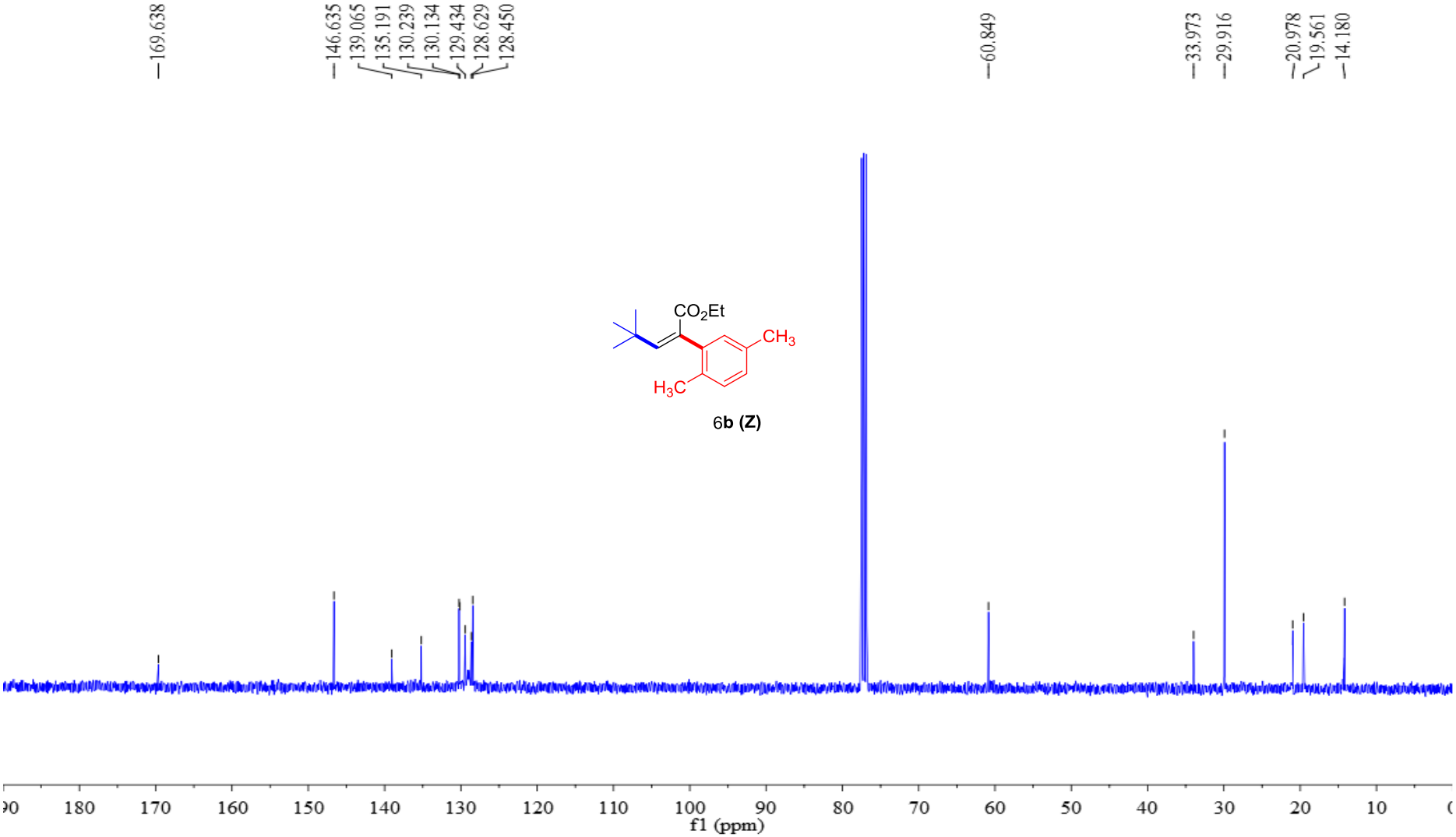
5m (Z, d.r. = 1:1)

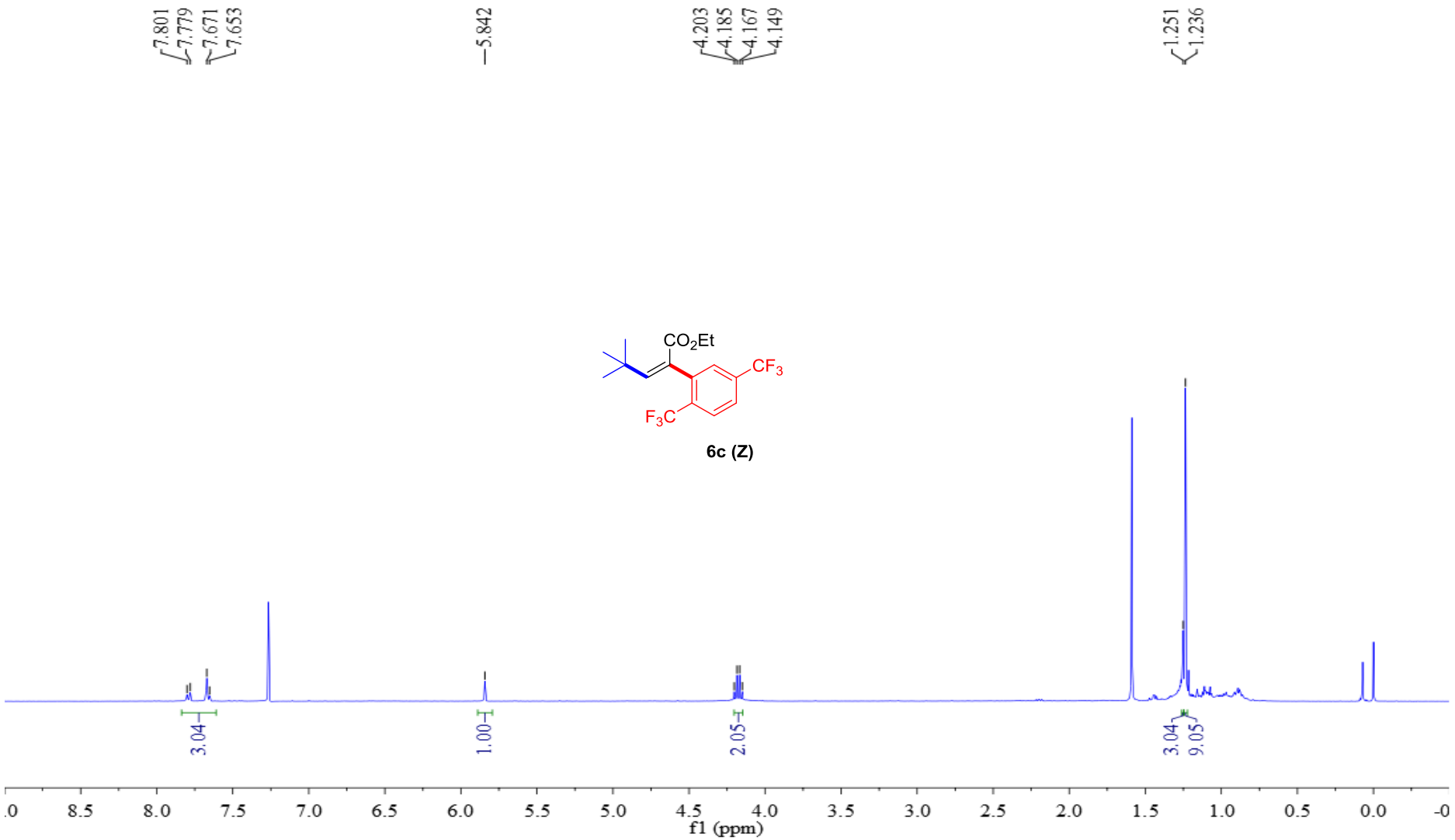

166.401
138.874
137.730
134.545
129.771
127.978
111.008
109.101
100.009
96.247
75.531
74.176
72.957
70.303
61.264
27.971
27.113
25.841
25.595
14.202
CO2Et
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

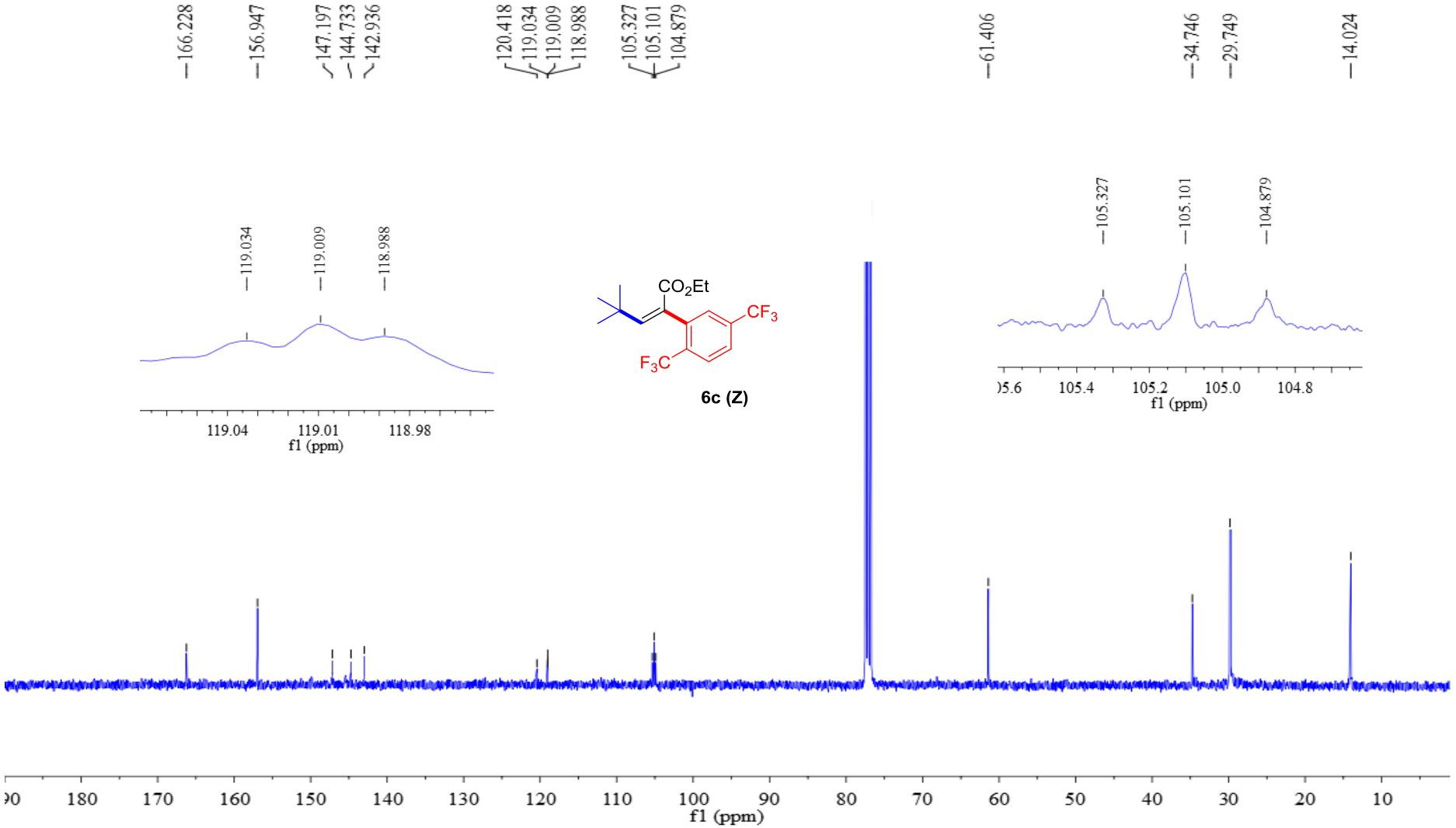
5m (Z, d.r. = 1:1)

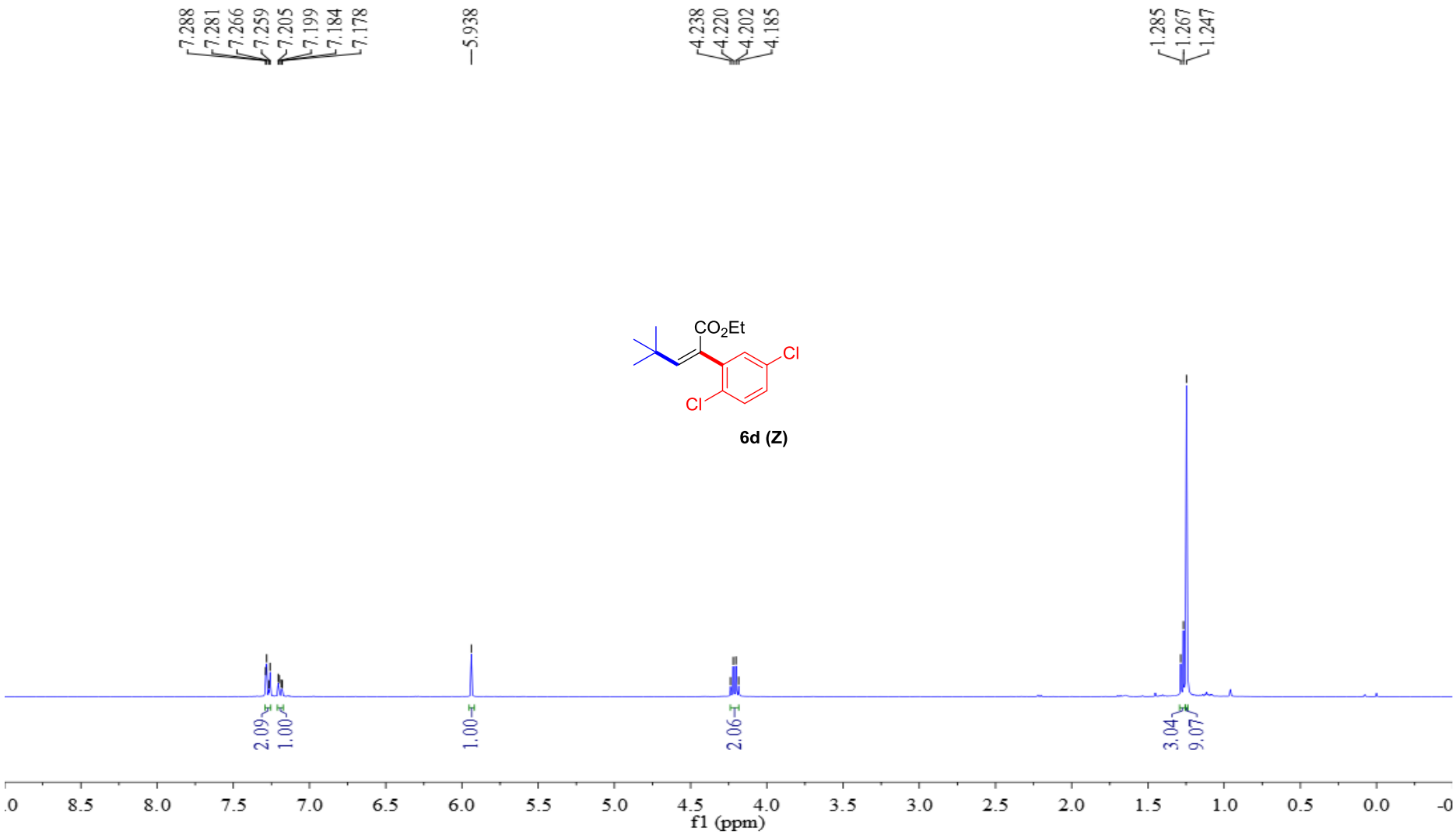

7.116
7.059
7.038
7.001
6.982
5.587
4.203
4.183
4.165
4.147
2.320
2.296
2.273
1.285
1.268
1.250
1.194
CO2Et
CH3
H3C
1.05
2.07
1.00
2.04
6.07
3.01
9.01
f1 (ppm)

6**b (Z)**

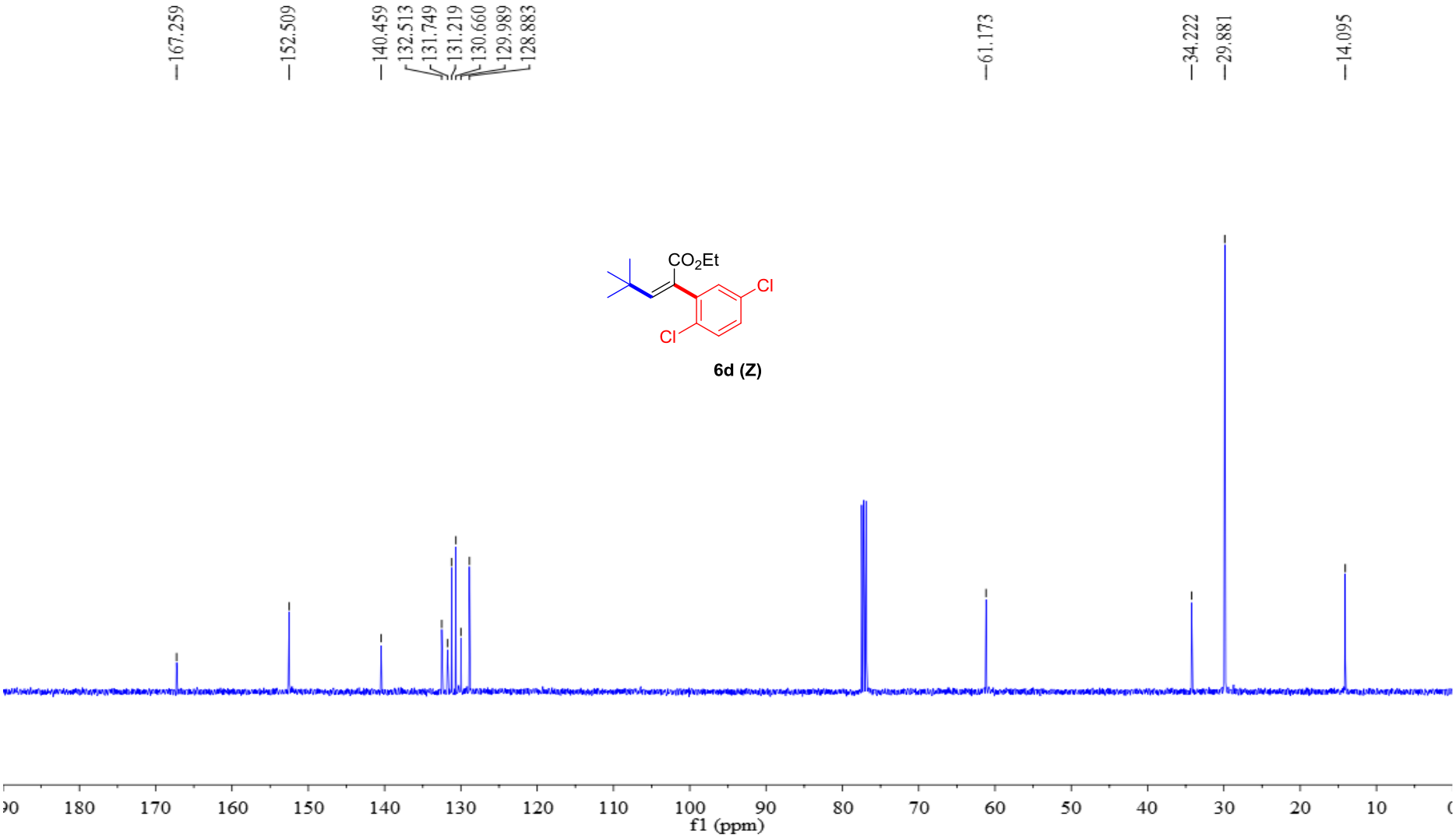

169.638
146.635
139.065
135.191
130.239
130.134
129.434
128.629
128.450
60.849
33.973
29.916
20.978
19.561
14.180
CO2Et
CH3
H3C
6b (Z)
f1 (ppm)

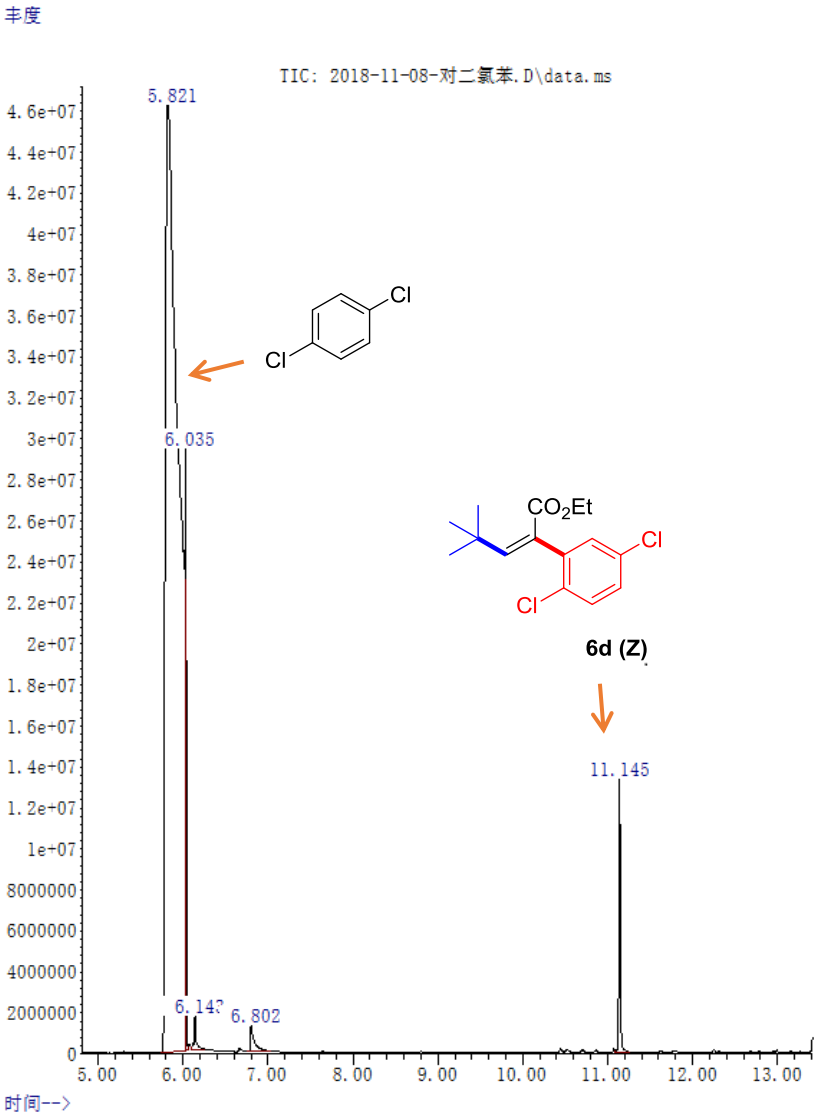

7.801
7.779
7.671
7.653
5.842
4.203
4.185
4.167
4.149
1.251
1.236
CO2Et
CF3
F3C
6c (Z)
3.04
1.00
2.05
3.04
9.05
f1 (ppm)


166.228
156.947
147.197
144.733
142.936
120.418
119.034
119.009
118.988
105.327
105.101
104.879
61.406
34.746
29.749
14.024
119.034
119.009
118.988
119.04
119.01
118.98
f1 (ppm)
CO2Et
CF3
F3C
6c (Z)
105.327
105.101
104.879
105.6
105.4
105.2
105.0
104.8
f1 (ppm)
f1 (ppm)


7.288
7.281
7.266
7.259
7.205
7.199
7.184
7.178
5.938
4.238
4.220
4.202
4.185
1.285
1.267
1.247
CO2Et
Cl
Cl
2.09
1.00
1.00
2.06
3.04
9.07
f1 (ppm)

6d (Z)


167.259
152.509
140.459
132.513
131.749
131.219
130.660
129.989
128.883
61.173
34.222
29.881
14.095
CO2Et
Cl
Cl
6d (Z)
f1 (ppm)


丰度
TIC: 2018-11-08-对二氯苯.D\data.ms
5.821
6.035
6.147
6.802
11.145
Cl
Cl
CO2Et
Cl
Cl
6d (Z)
4.6e+07
4.4e+07
4.2e+07
4e+07
3.8e+07
3.6e+07
3.4e+07
3.2e+07
3e+07
2.8e+07
2.6e+07
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
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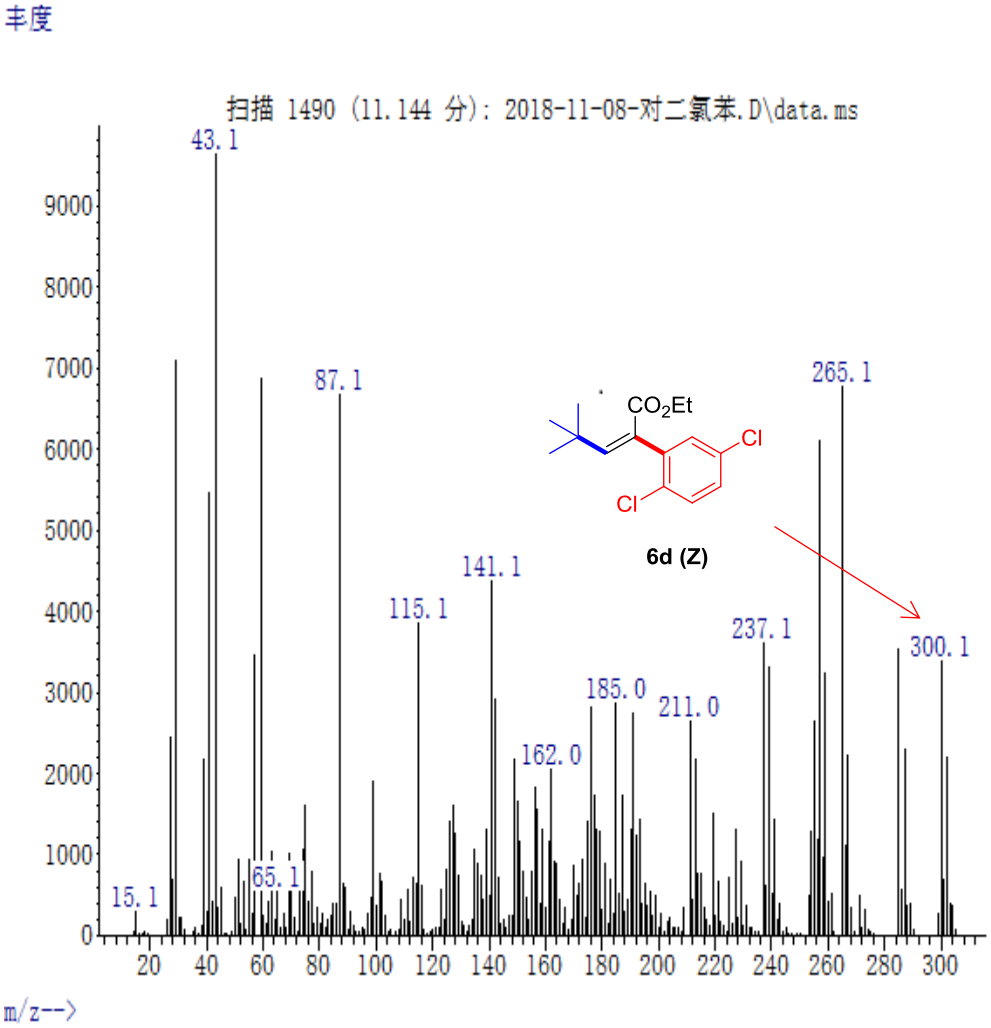
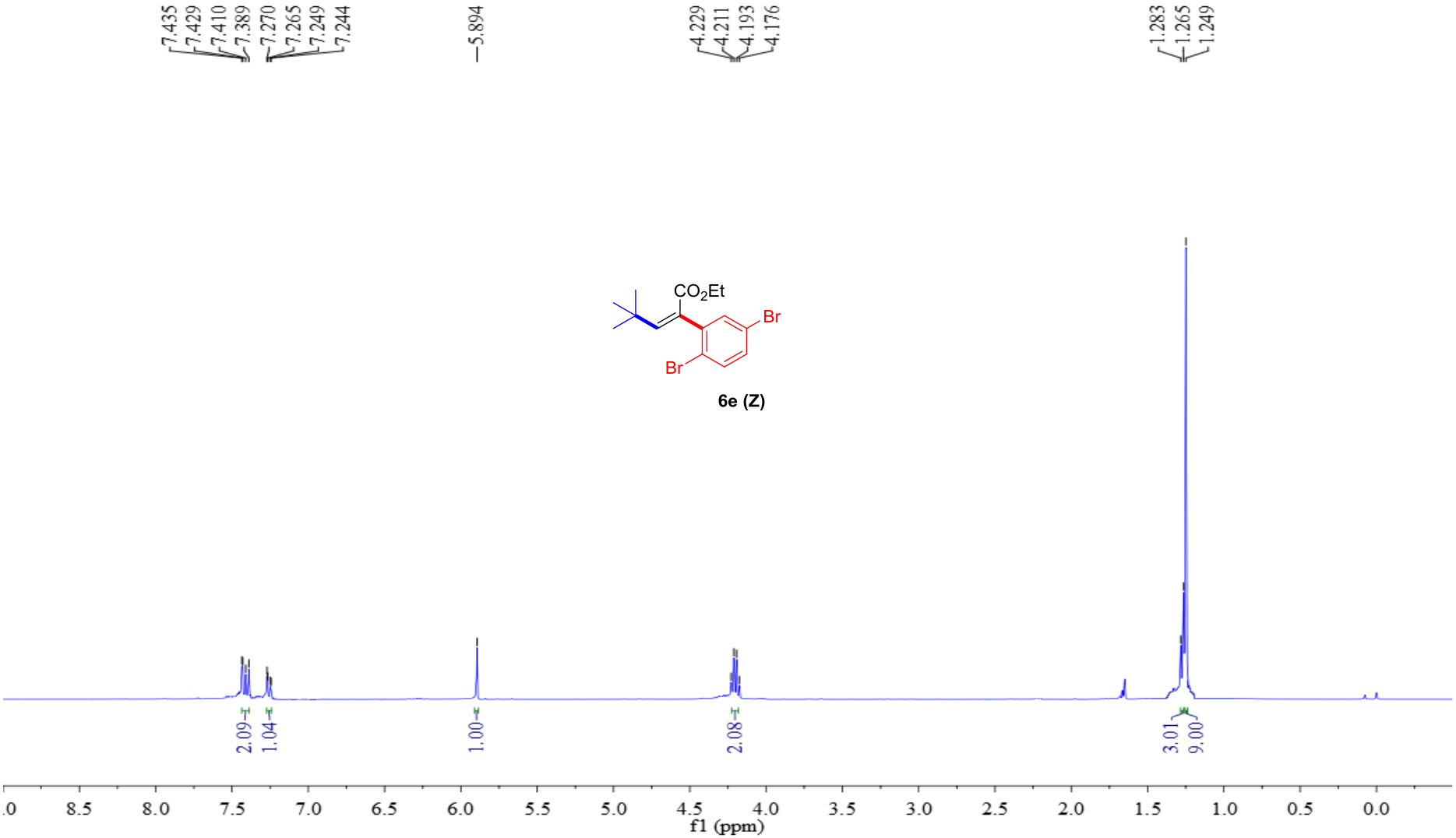
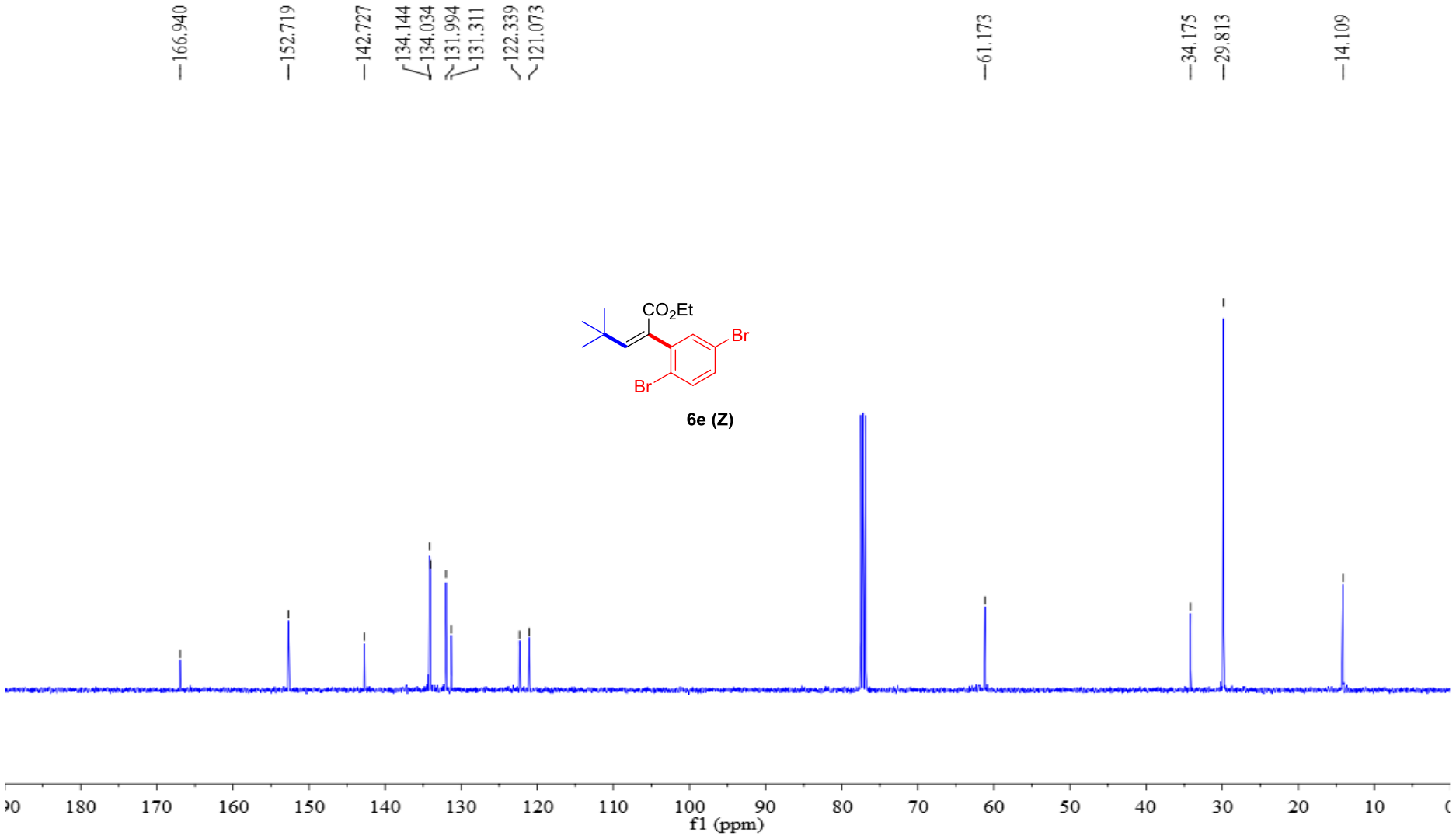
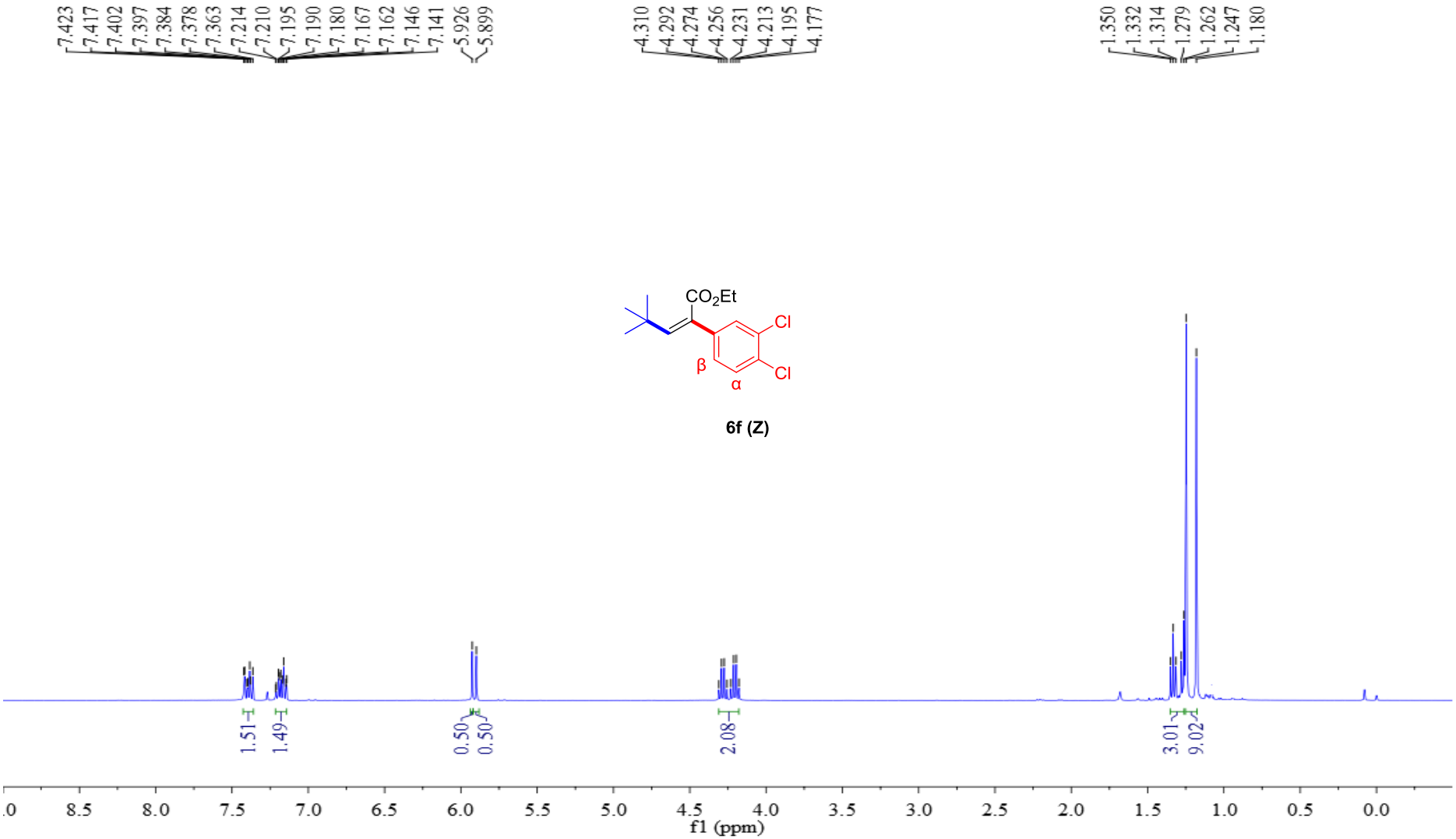
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
时间-->


丰度
扫描 1490 (11.144 分): 2018-11-08-对二氯苯.D\data.ms
43.1
87.1
265.1
141.1
115.1
237.1
300.1
185.0
211.0
162.0
65.1
15.1
CO2Et
Cl
Cl
6d (Z)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z-->

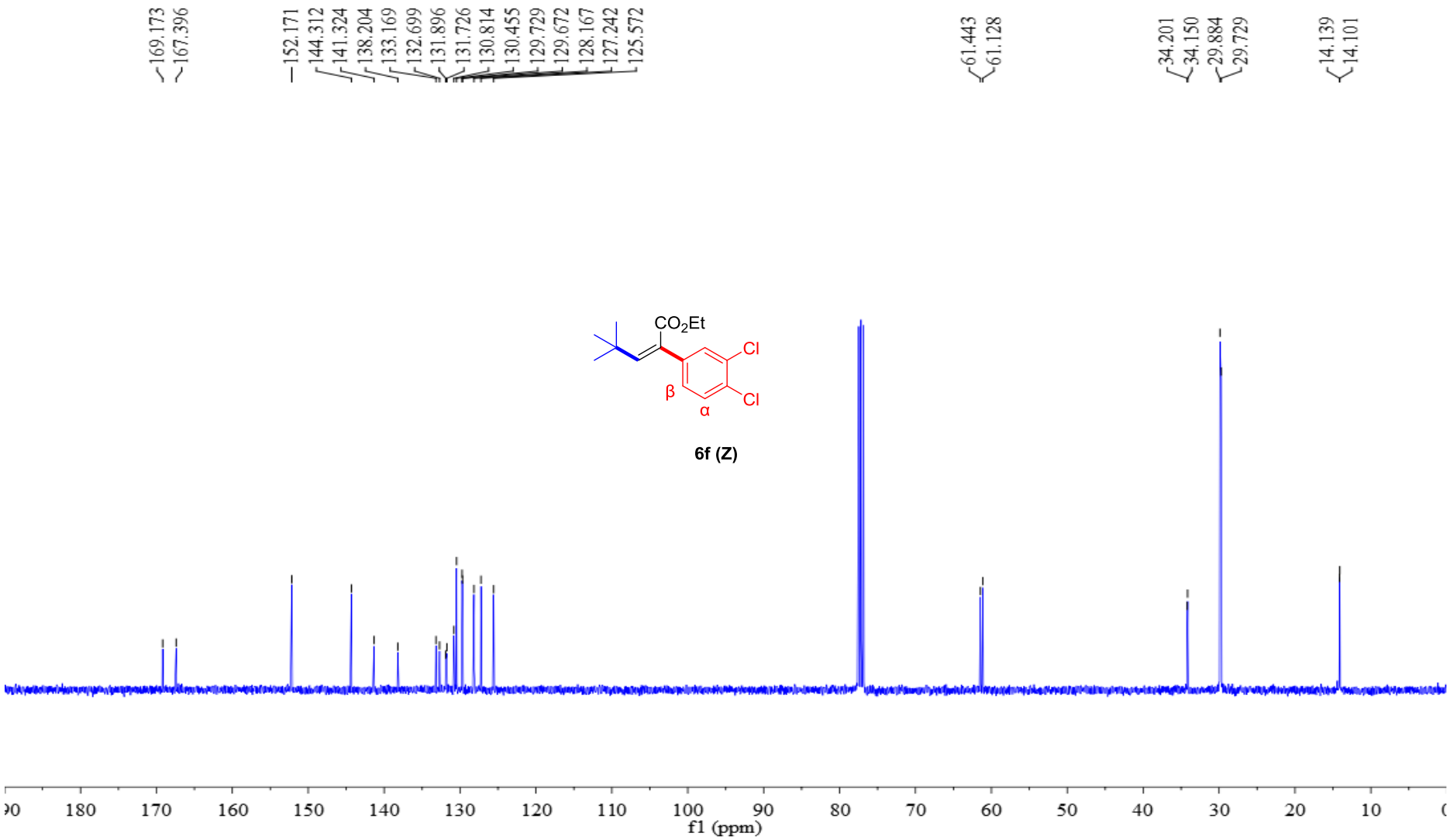

7.435
7.429
7.410
7.389
7.270
7.265
7.249
7.244
5.894
4.229
4.211
4.193
4.176
1.283
1.265
1.249
CO2Et
Br
Br
2.09
1.04
1.00
2.08
3.01
9.00
f1 (ppm)

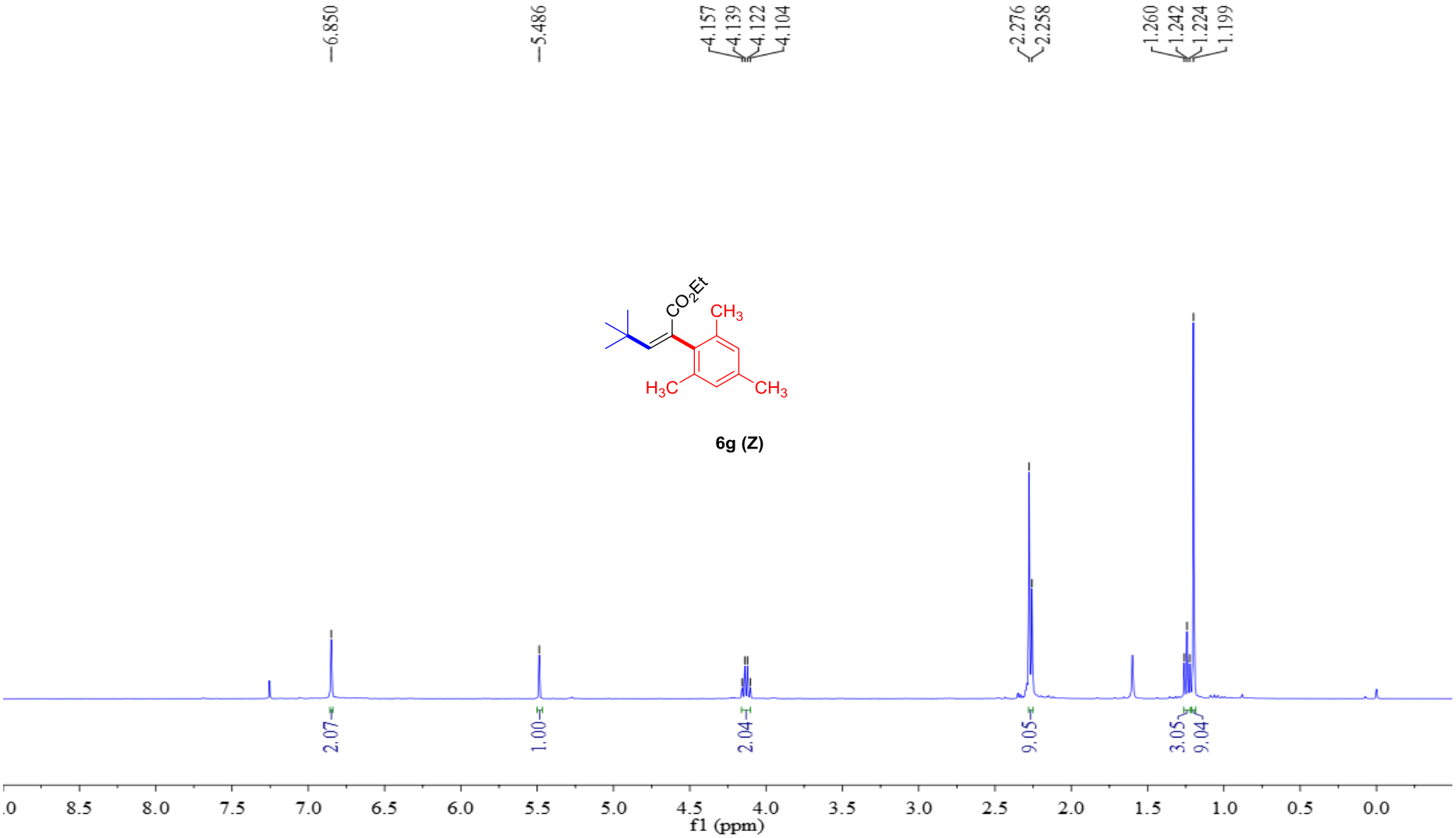
6e (Z)

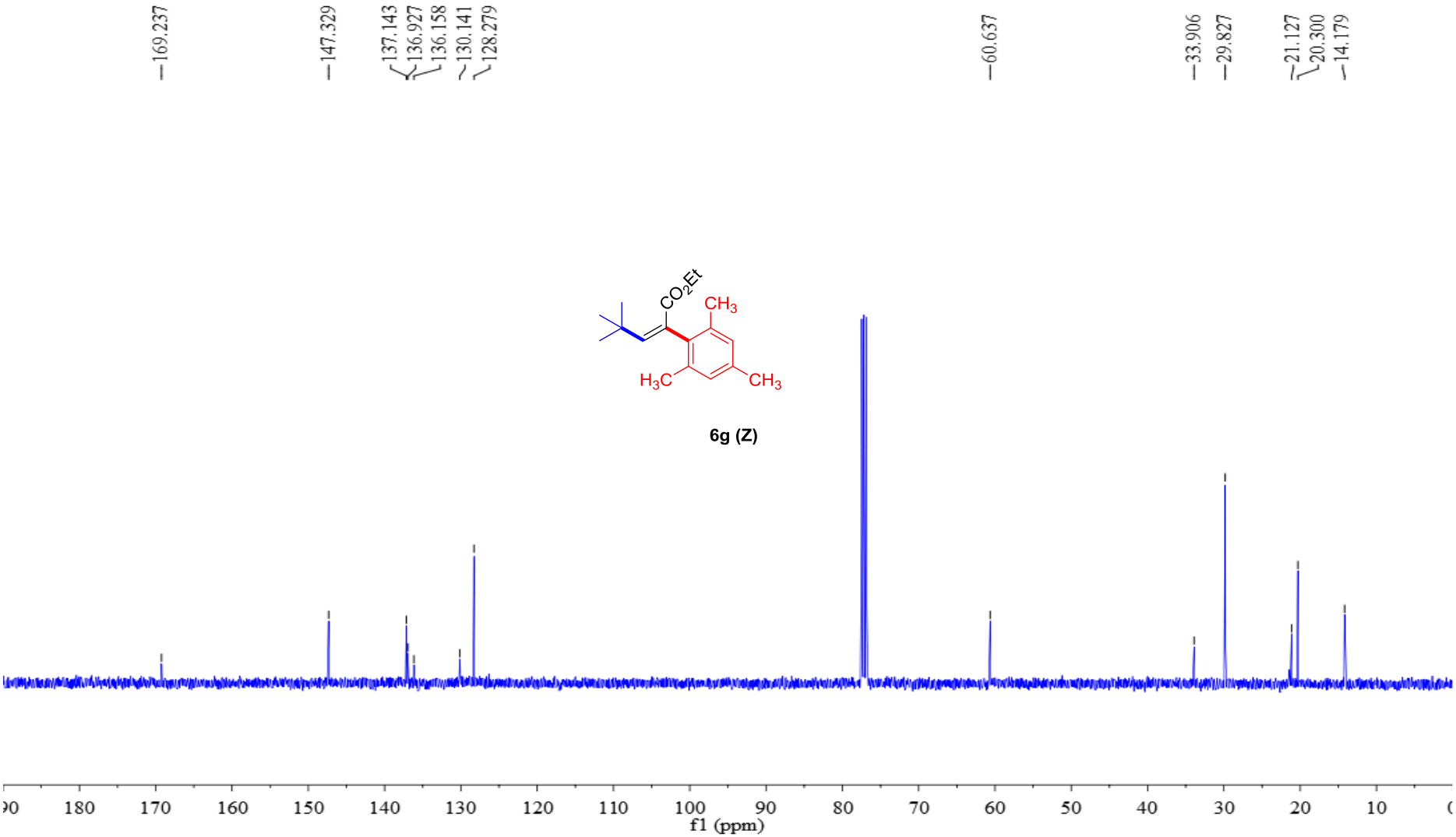

166.940
152.719
142.727
134.144
134.034
131.994
131.311
122.339
121.073
61.173
34.175
29.813
14.109
CO2Et
Br
Br
6e (Z)
f1 (ppm)

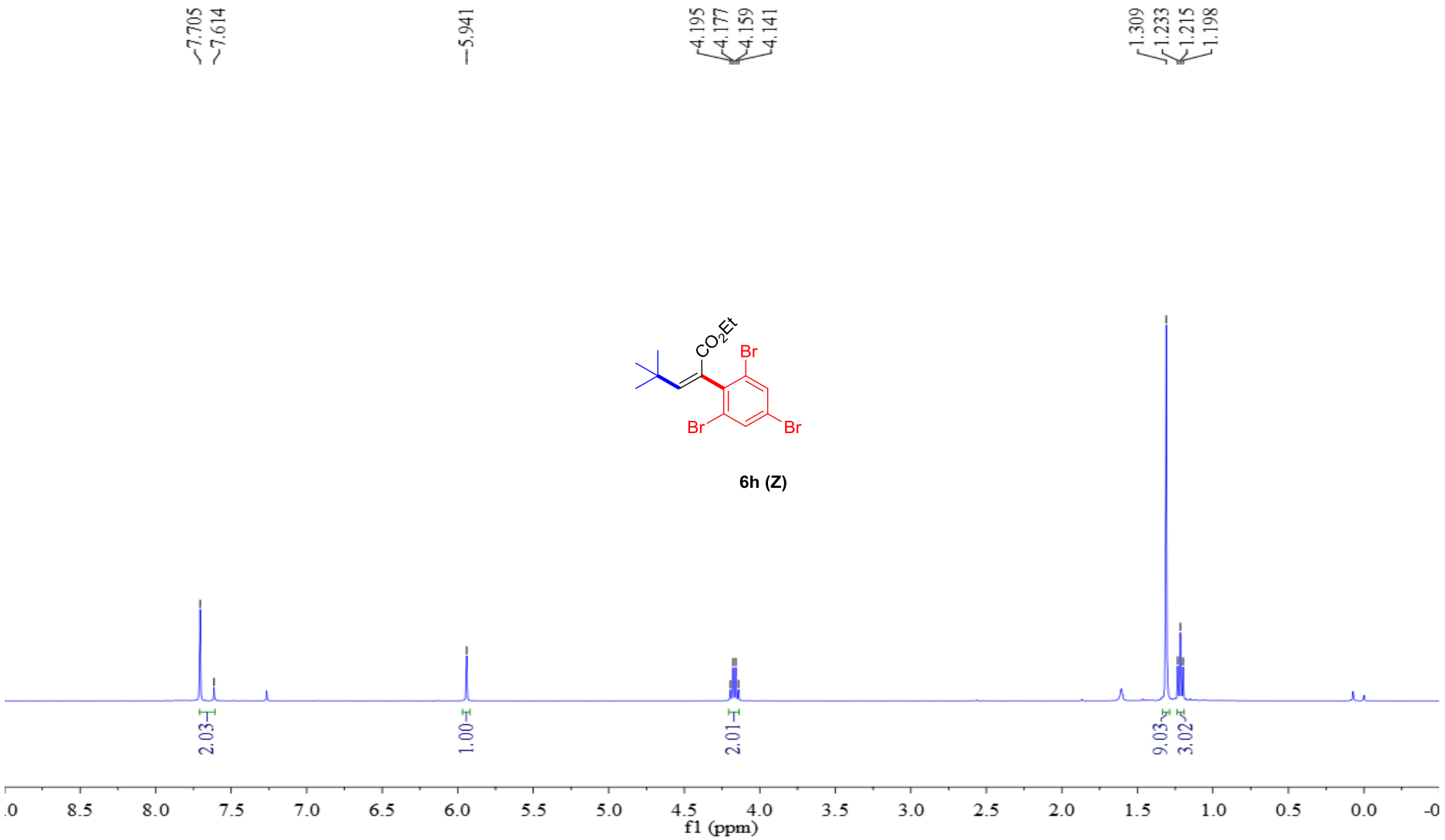

7.423
7.417
7.402
7.397
7.384
7.378
7.363
7.214
7.210
7.195
7.190
7.180
7.167
7.162
7.146
7.141
5.926
5.899
4.310
4.292
4.274
4.256
4.231
4.213
4.195
4.177
1.350
1.332
1.314
1.279
1.262
1.247
1.180
CO2Et
Cl
Cl
β
α
1.51
1.49
0.50
0.50
2.08
3.01
9.02
f1 (ppm)

6f (Z)

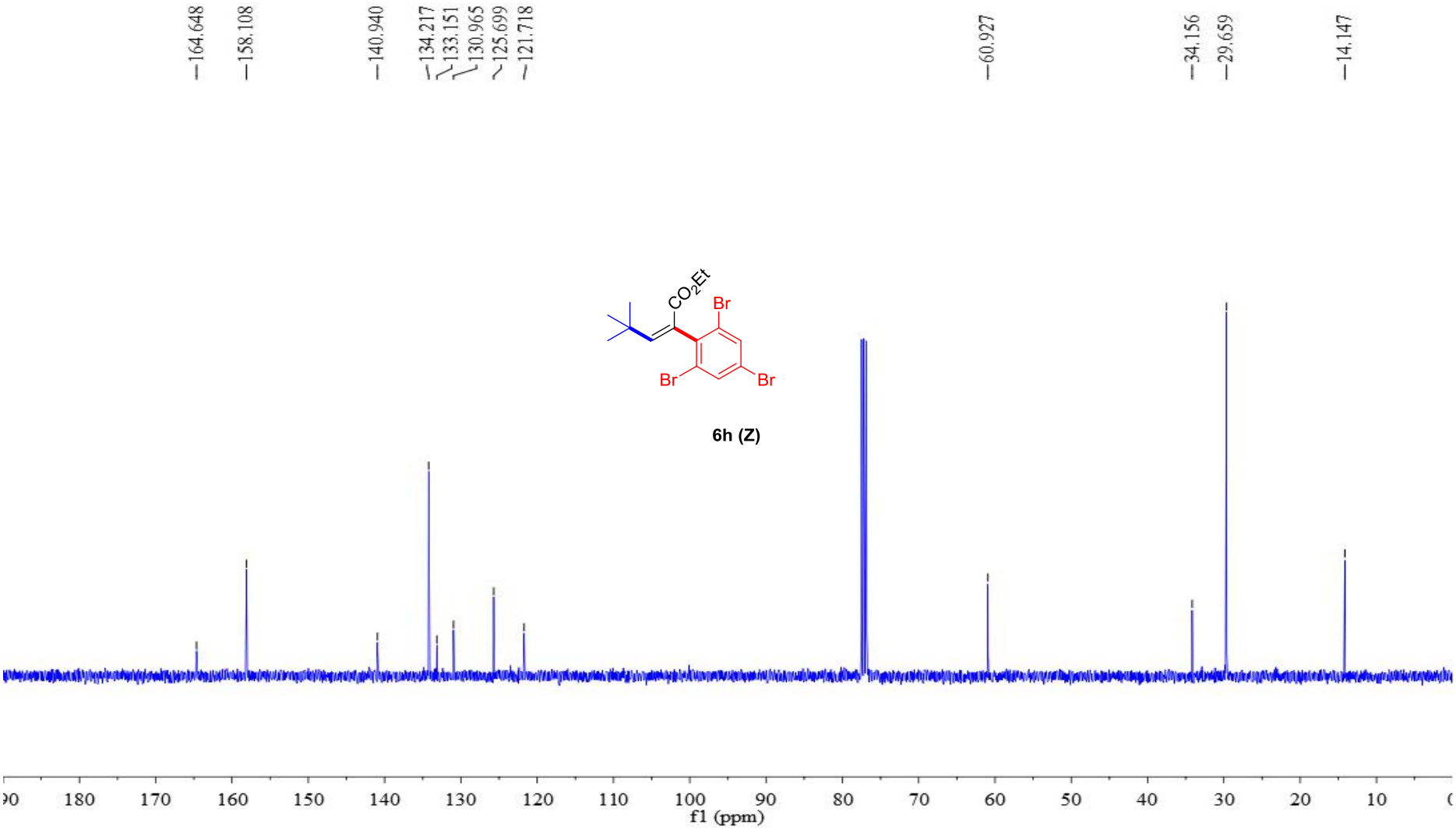

169.173
167.396
152.171
144.312
141.324
138.204
133.169
132.699
131.896
131.726
130.814
130.455
129.729
129.672
128.167
127.242
125.572
61.443
61.128
34.201
34.150
29.884
29.729
14.139
14.101
CO2Et
Cl
Cl
β
α
6f (Z)
f1 (ppm)

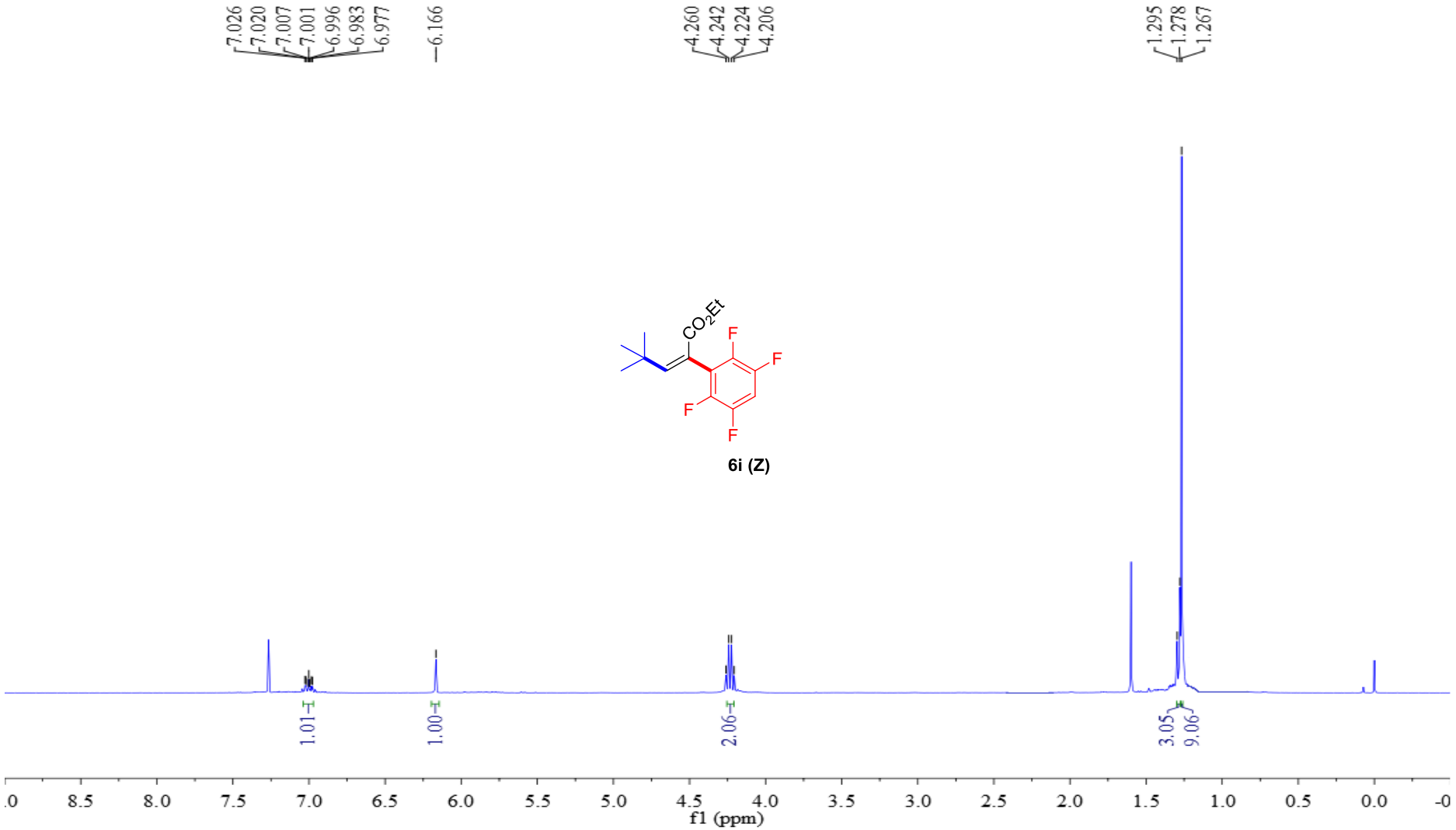

6.850
5.486
4.157
4.139
4.122
4.104
2.276
2.258
1.260
1.242
1.224
1.199
CO2Et
CH3
H3C
CH3
6g (Z)
2.07
1.00
2.04
9.05
3.05
9.04
f1 (ppm)


169.237
147.329
137.143
136.927
136.158
130.141
128.279
60.637
33.906
29.827
21.127
20.300
14.179
CO2Et
CH3
H3C
CH3
6g (Z)
f1 (ppm)

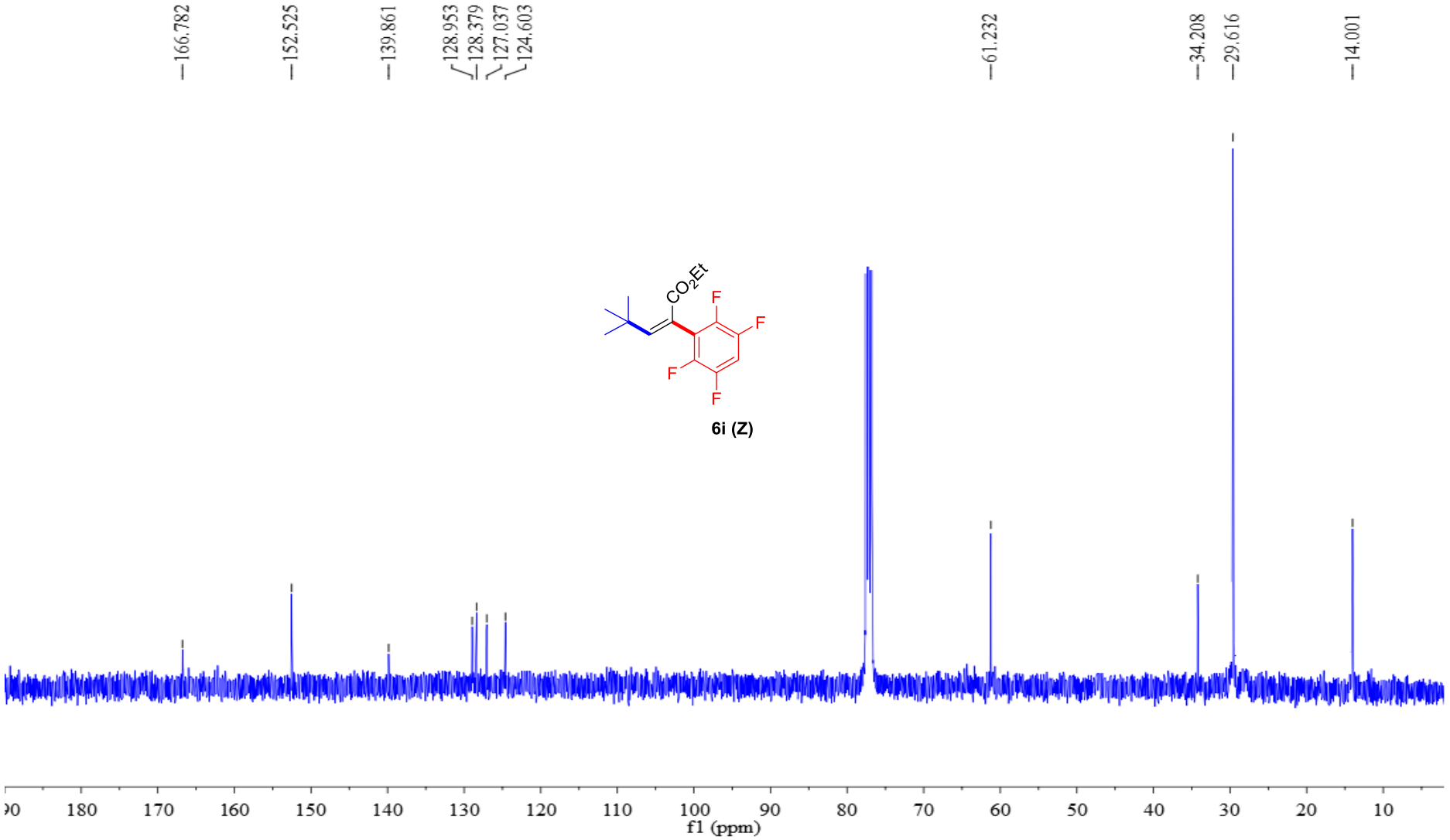

7.705
7.614
5.941
4.195
4.177
4.159
4.141
1.309
1.233
1.215
1.198
CO2Et
Br
Br
Br
2.03
1.00
2.01
9.03
3.02
f1 (ppm)

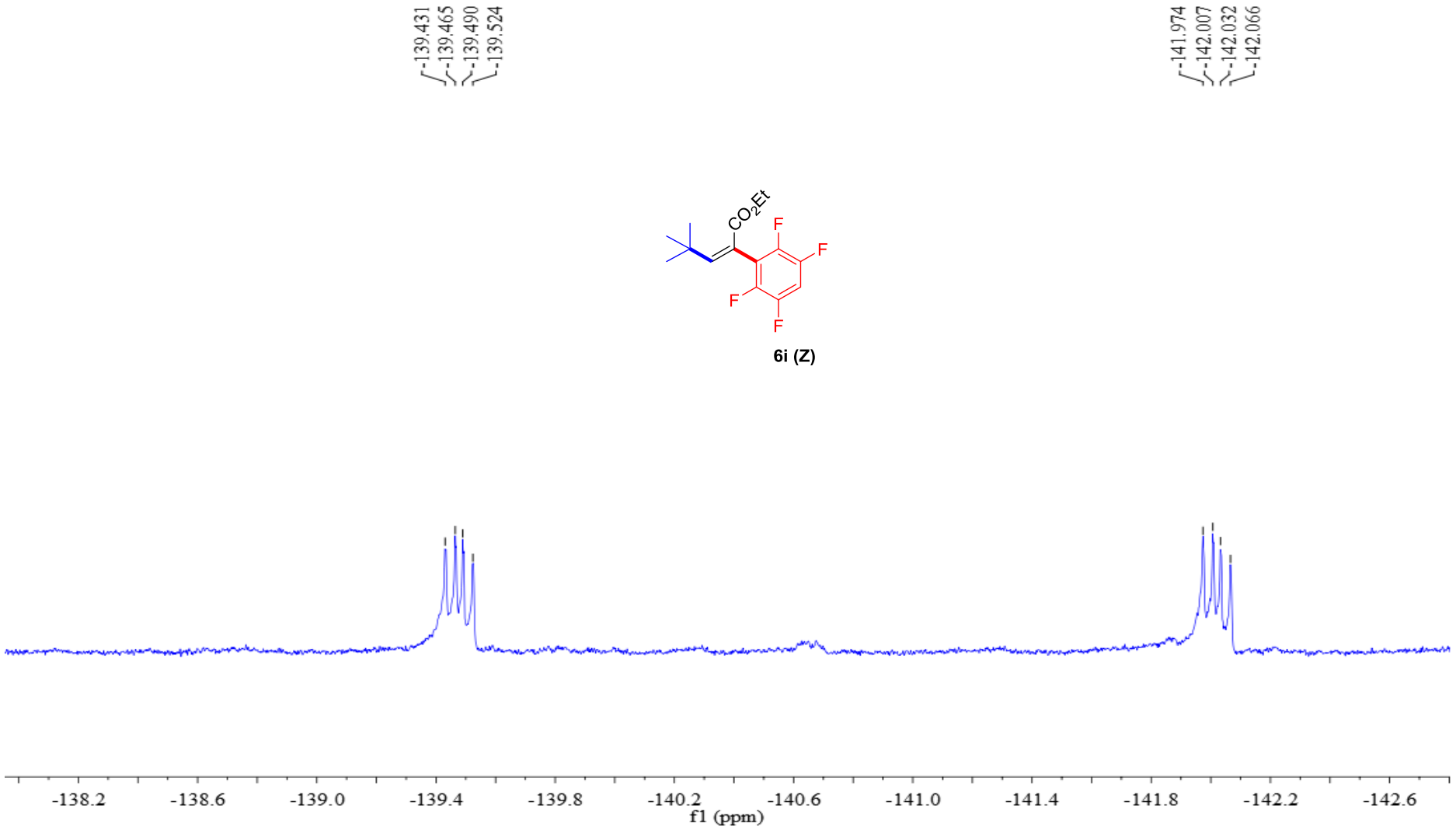
6h (Z)


164.648
158.108
140.940
134.217
133.151
130.965
125.699
121.718
60.927
34.156
29.659
14.147
CO2Et
Br
Br
Br
6h (Z)
f1 (ppm)

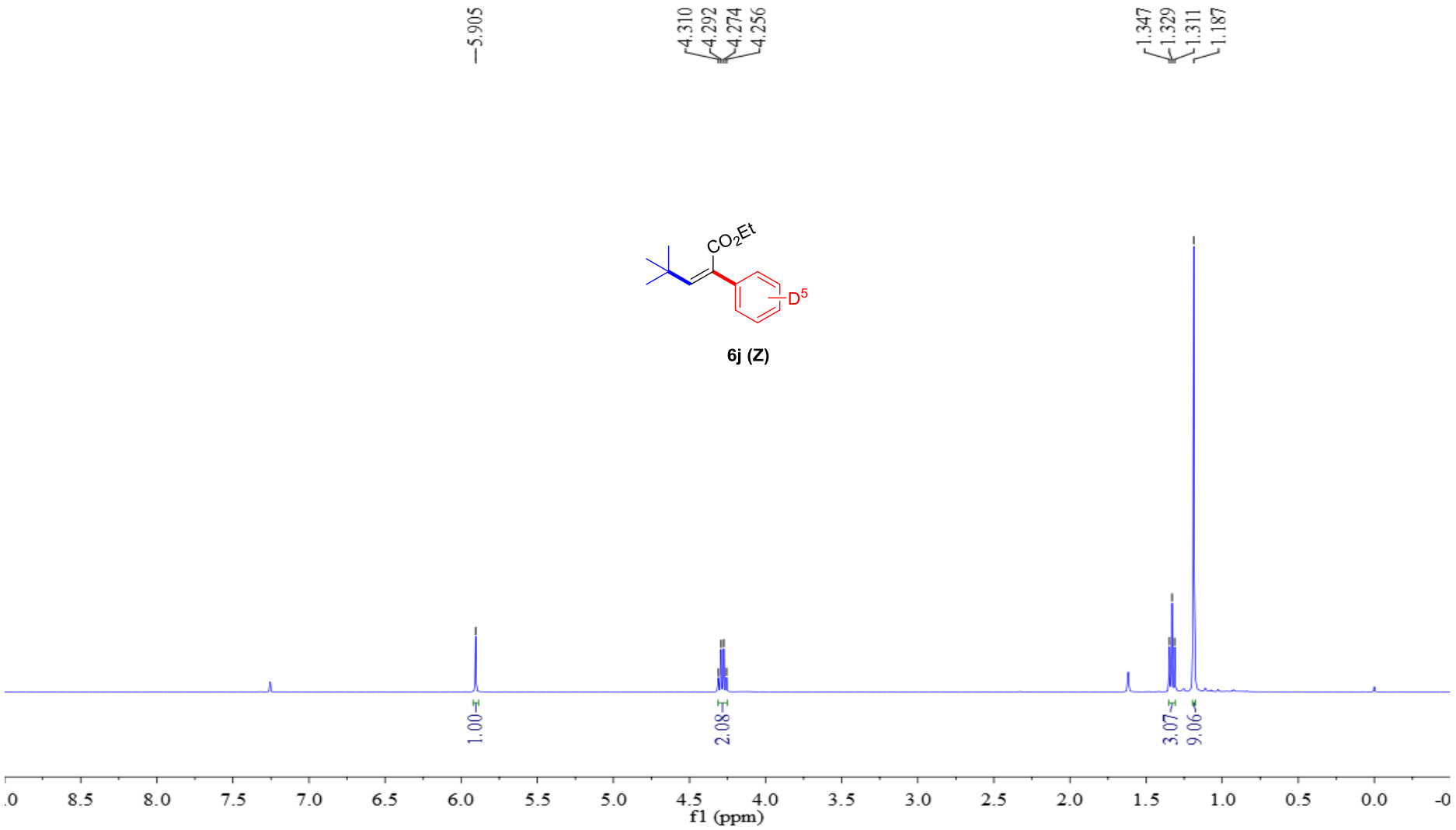

7.026
7.020
7.007
7.001
6.996
6.983
6.977
6.166
4.260
4.242
4.224
4.206
1.295
1.278
1.267
CO2Et
F
F
F
F
1.01
1.00
2.06
3.05
9.06
f1 (ppm)

6i (Z)

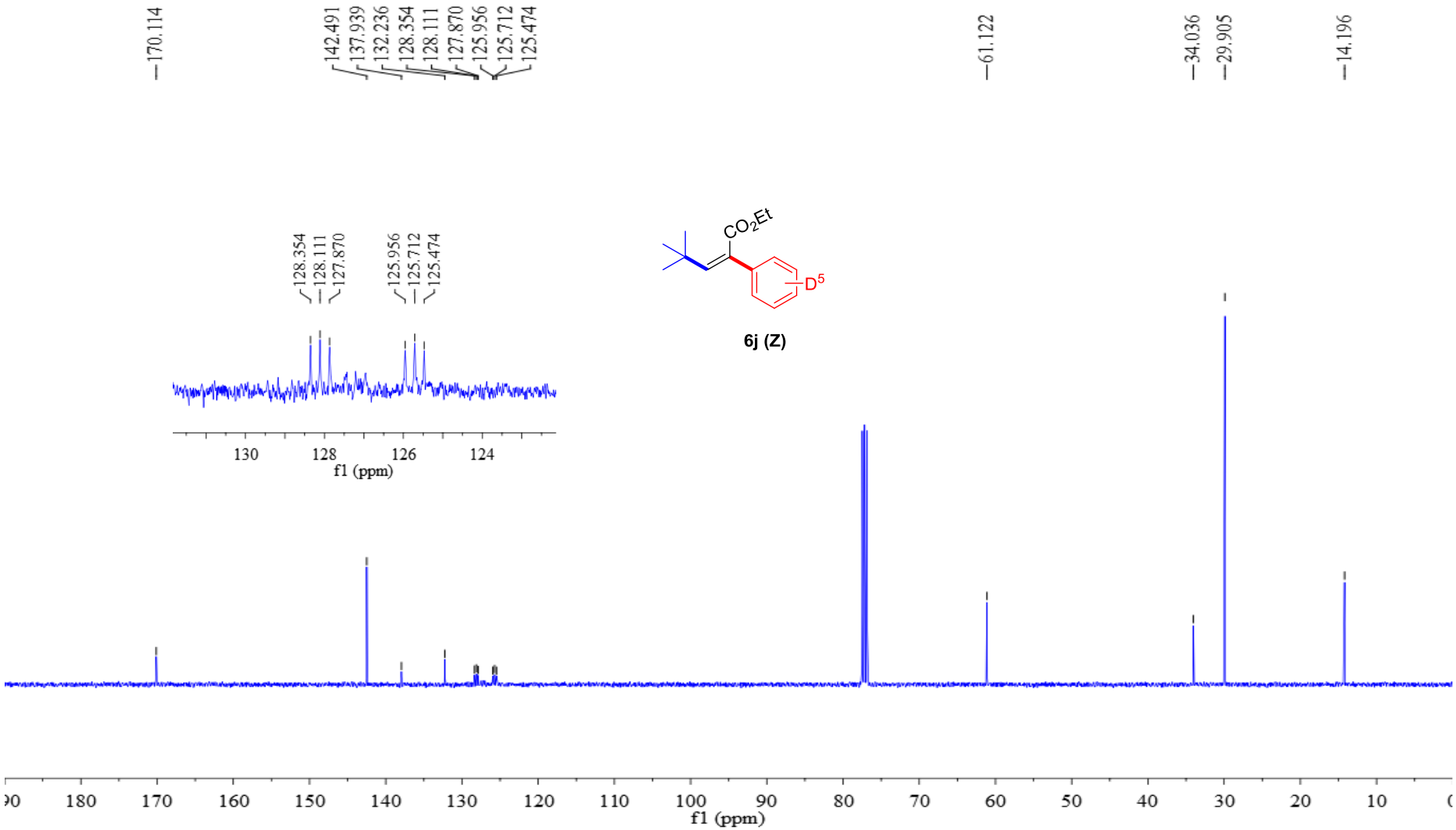

166.782
152.525
139.861
128.953
128.379
127.037
124.603
61.232
34.208
29.616
14.001
CO2Et
F
F
F
F
6i (Z)
f1 (ppm)

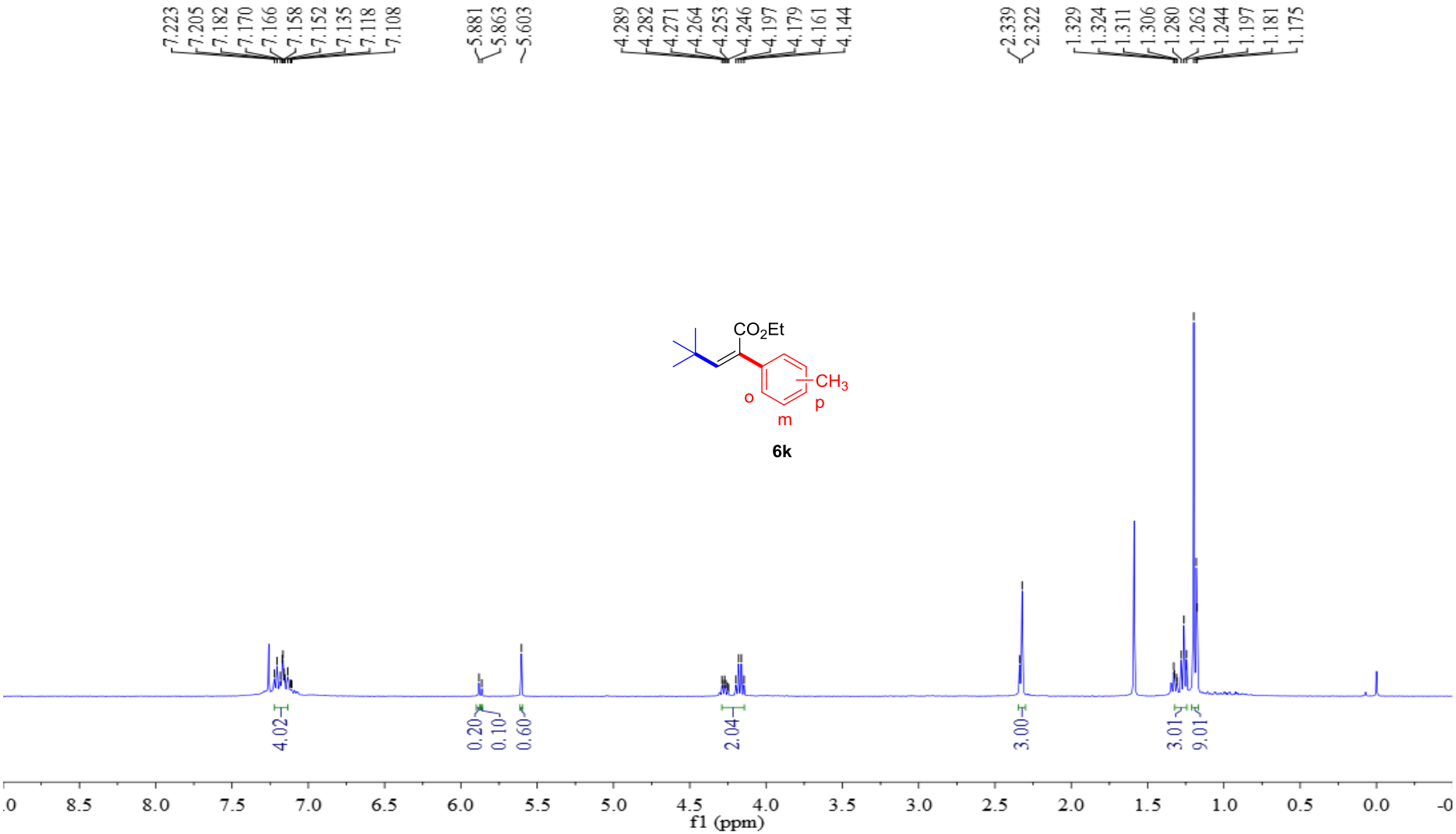

-139.431
-139.465
-139.490
-139.524
-141.974
-142.007
-142.032
-142.066
CO2Et
F
F
F
F
-138.2
-138.6
-139.0
-139.4
-139.8
-140.2
-140.6
-141.0
-141.4
-141.8
-142.2
-142.6
f1 (ppm)

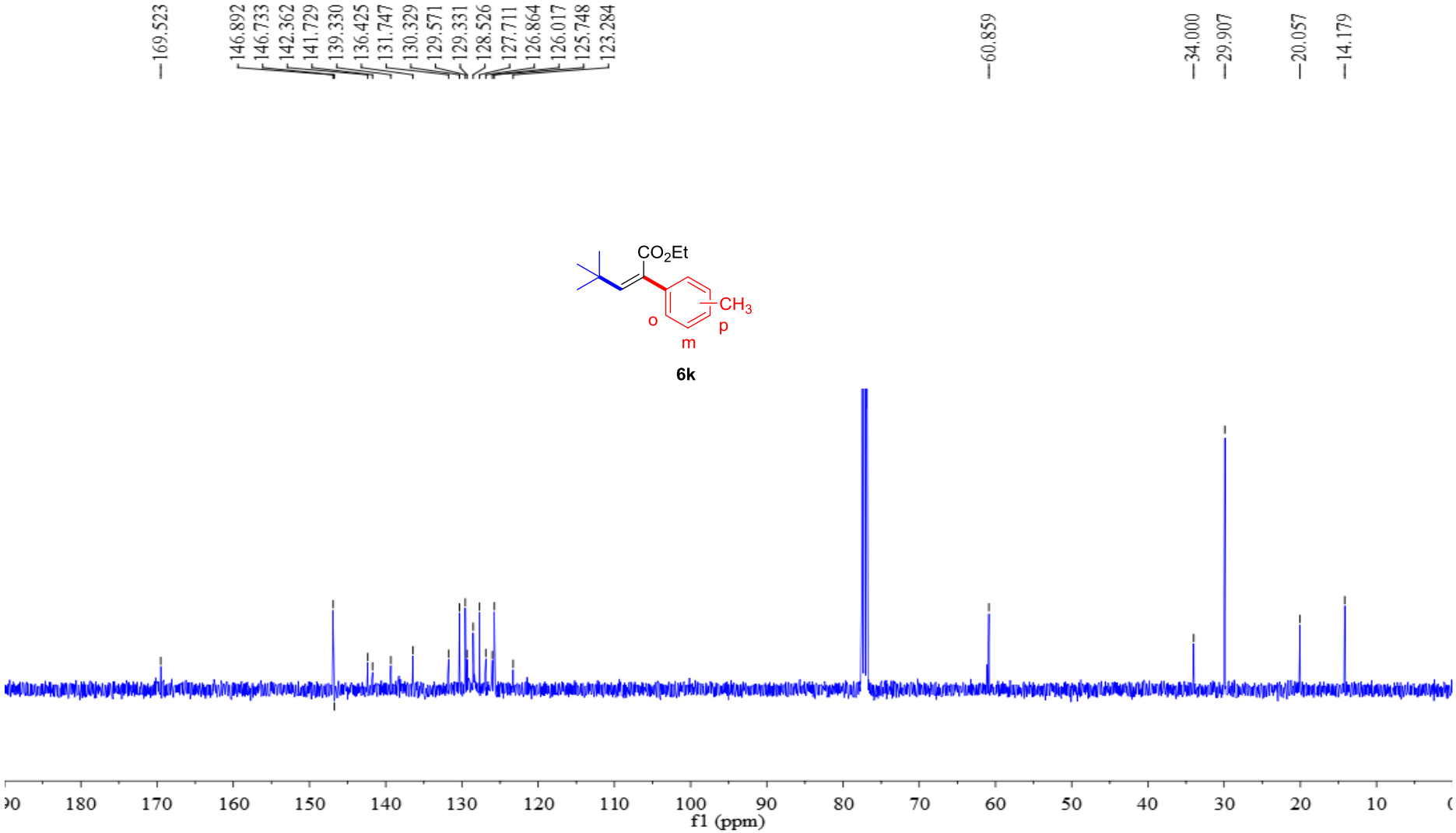
6i (Z)

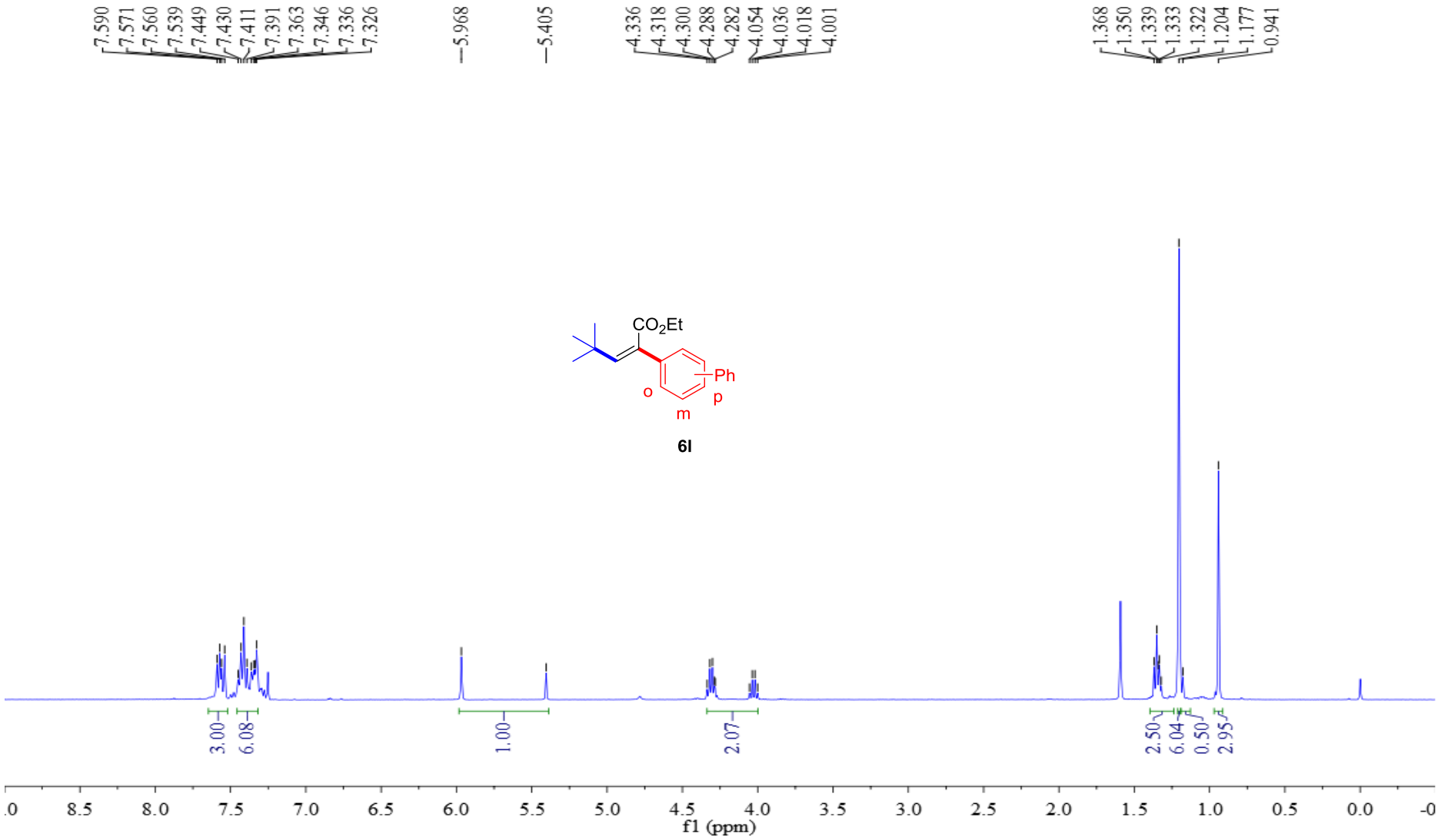

5.905
4.310
4.292
4.274
4.256
1.347
1.329
1.311
1.187
CO2Et
D5
1.00
2.08
3.07
9.06
f1 (ppm)

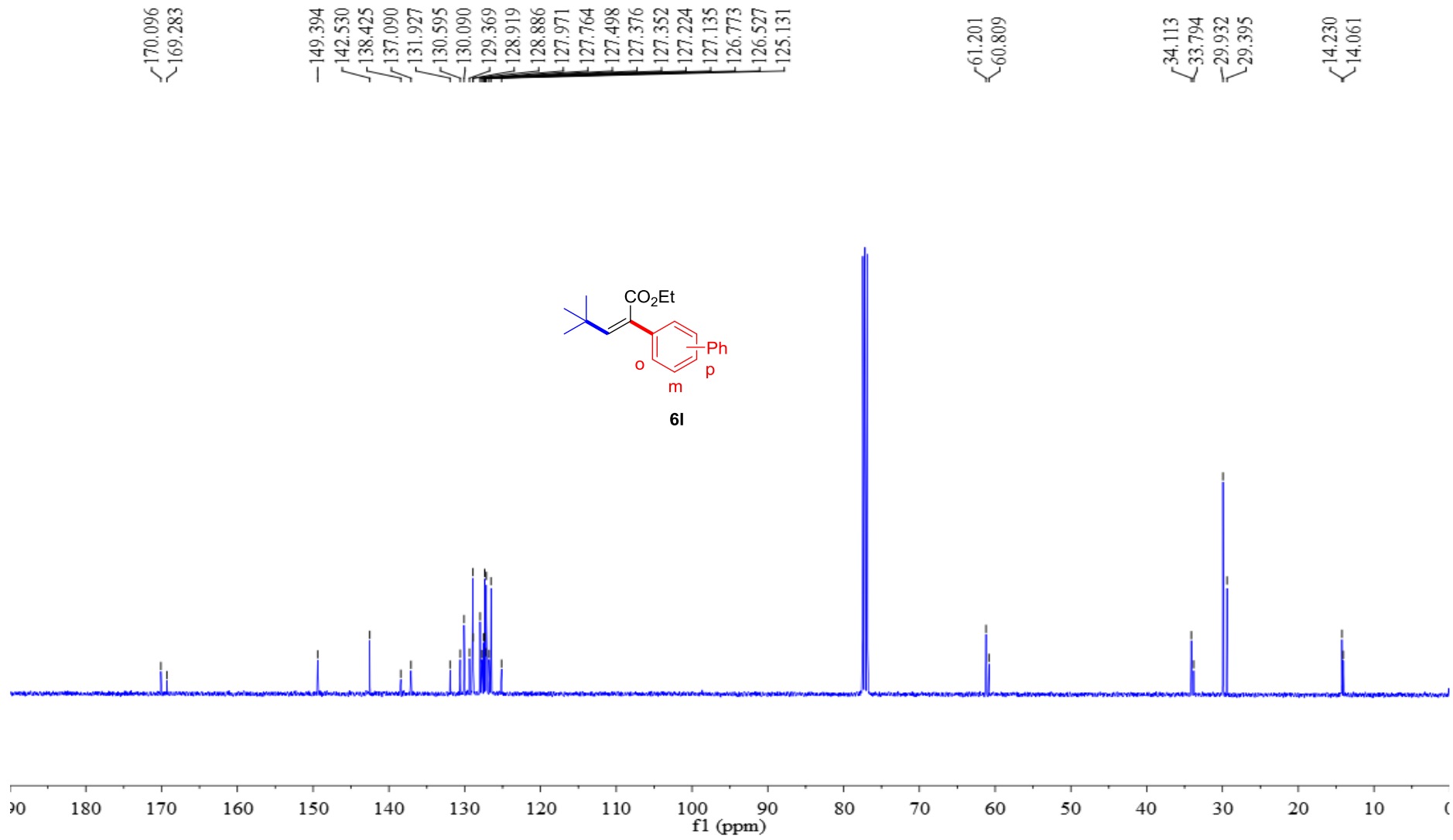
6j (Z)

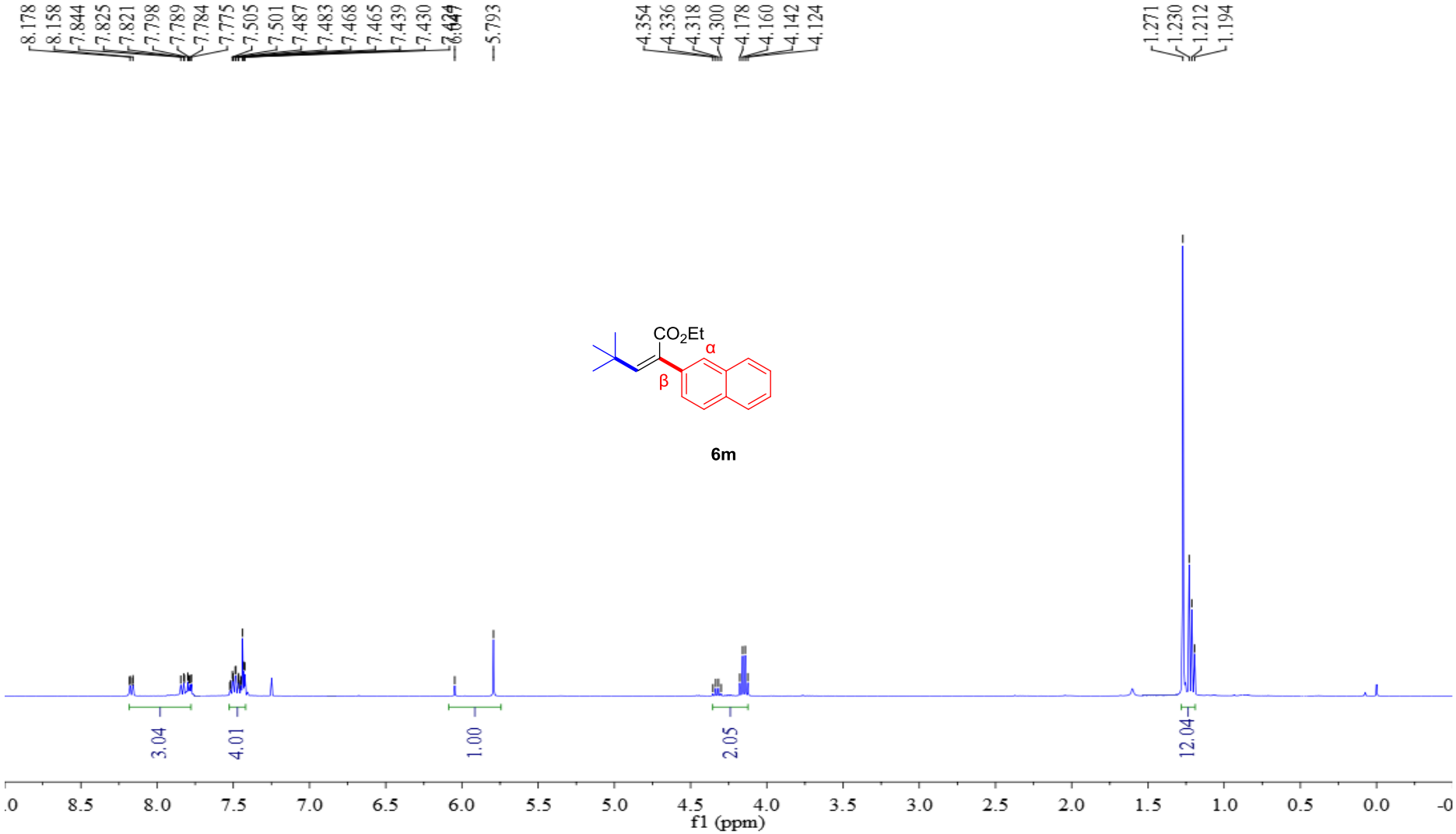

170.114
142.491
137.939
132.236
128.354
128.111
127.870
125.956
125.712
125.474
61.122
34.036
29.905
14.196
128.354
128.111
127.870
125.956
125.712
125.474
130
128
126
124
f1 (ppm)
CO2Et
D5
6j (Z)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

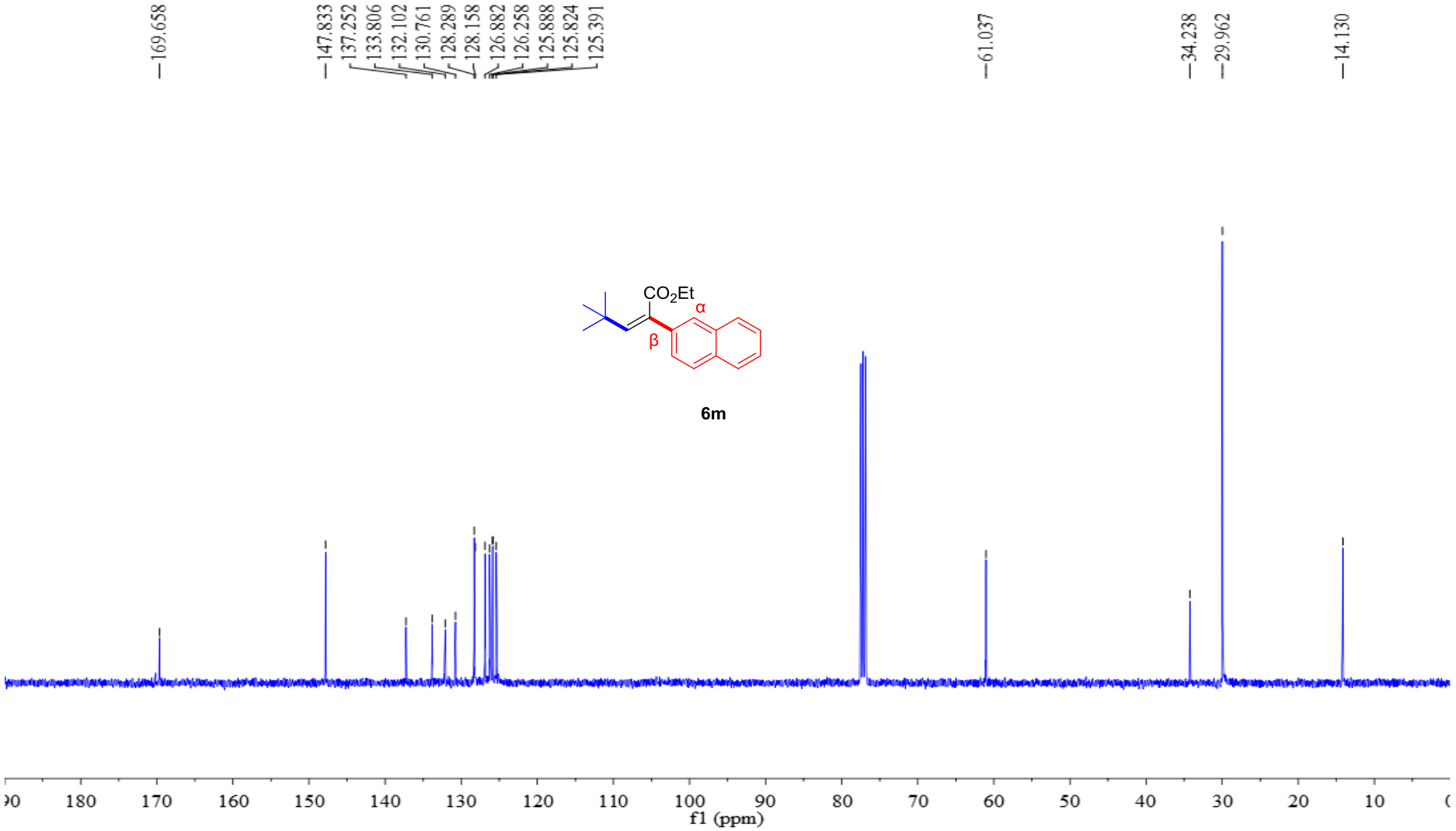

7.223
7.205
7.182
7.170
7.166
7.158
7.152
7.135
7.118
7.108
5.881
5.863
5.603
4.289
4.282
4.271
4.264
4.253
4.246
4.197
4.179
4.161
4.144
2.339
2.322
1.329
1.324
1.311
1.306
1.280
1.262
1.244
1.197
1.181
1.175
CO2Et
CH3
o
m
p
6k
4.02
0.20
0.10
0.60
2.04
3.00
3.01
9.01
f1 (ppm)


169.523
146.892
146.733
142.362
141.729
139.330
136.425
131.747
130.329
129.571
129.331
128.526
127.711
126.864
126.017
125.748
123.284
60.859
34.000
29.907
20.057
14.179
CO2Et
CH3
o
m
p
6k
f1 (ppm)


7.590
7.571
7.560
7.539
7.449
7.430
7.411
7.391
7.363
7.346
7.336
7.326
5.968
5.405
4.336
4.318
4.300
4.288
4.282
4.054
4.036
4.018
4.001
1.368
1.350
1.339
1.333
1.322
1.204
1.177
0.941
CO2Et
Ph
o
m
p
6l
3.00
6.08
1.00
2.07
2.50
6.04
0.50
2.95
f1 (ppm)


170.096
169.283
149.394
142.530
138.425
137.090
131.927
130.595
130.090
129.369
128.919
128.886
127.971
127.764
127.498
127.376
127.352
127.224
127.135
126.773
126.527
125.131
61.201
60.809
34.113
33.794
29.932
29.395
14.230
14.061
CO2Et
Ph
o
m
p
6l
f1 (ppm)


8.178
8.158
7.844
7.825
7.821
7.798
7.789
7.784
7.775
7.505
7.501
7.487
7.483
7.468
7.465
7.439
7.430
5.793
4.354
4.336
4.318
4.300
4.178
4.160
4.142
4.124
1.271
1.230
1.212
1.194
CO2Et
α
β
6m
3.04
4.01
1.00
2.05
12.04
f1 (ppm)


169.658
147.833
137.252
133.806
132.102
130.761
128.289
128.158
126.882
126.258
125.888
125.824
125.391
61.037
34.238
29.962
14.130
CO2Et
α
β
6m
f1 (ppm)