Rapid Construction of Tetralin, Chromane, and Indane Motifs via Cyclative C−H/C−H Coupling: Four-Step Total Synthesis of (±)-Russujaponol F

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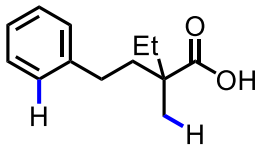
General Information

$Pd(OAc)_2$, LiOAc, Ag_2CO_3, and sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) were purchased from Sigma-Aldrich. $Pd(CH_3CN)_4(BF_4)_2$ was purchased from Strem. 1-Fluoro-2,4,6-trimethylpyridinium tetrafluoroborate was purchased from TCI. HFIP was purchased from Oakwood. Other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with short-wave UV light or $KMnO_4$ and heat as developing agents. ^1H NMR spectra were recorded on Bruker DRX-600 instrument. Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for TMS. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-600 was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of $CDCl_3$. Column chromatography was performed using E. Merck silica (60, particle size 0.043–0.063 mm), and preparative thin layer chromatography (pTLC) was performed on Merck silica plates (60F-254). High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

Preparation of aliphatic acids



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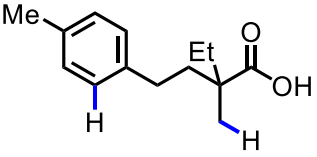

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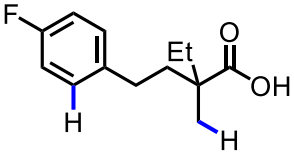

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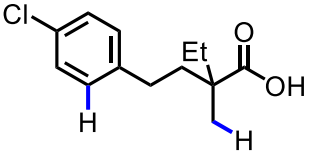

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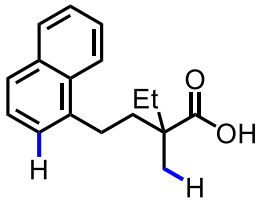

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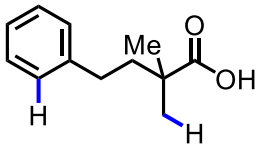

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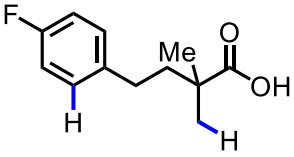

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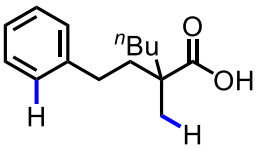

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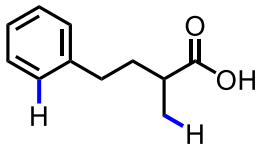

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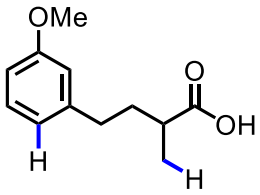

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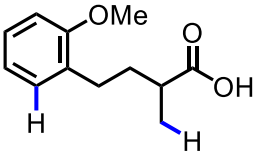

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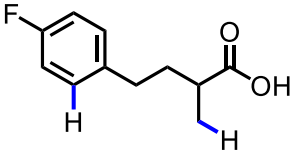

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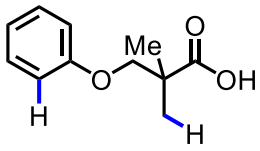

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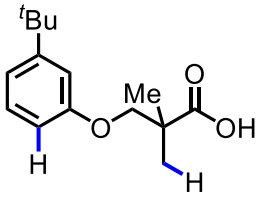

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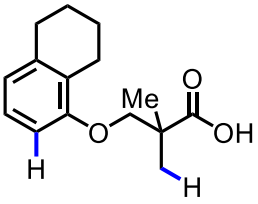

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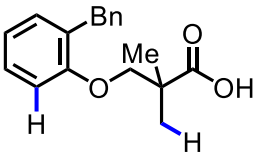

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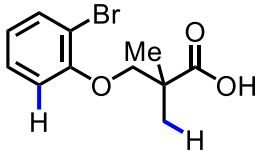

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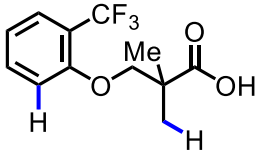

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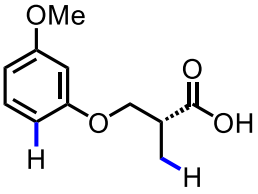

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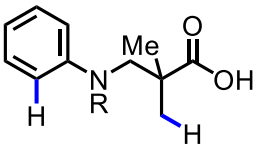
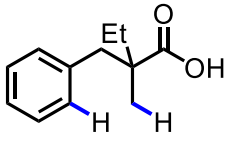


R = Boc or Ts

1t



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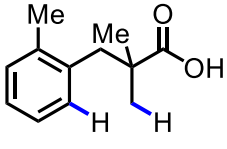

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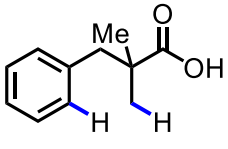

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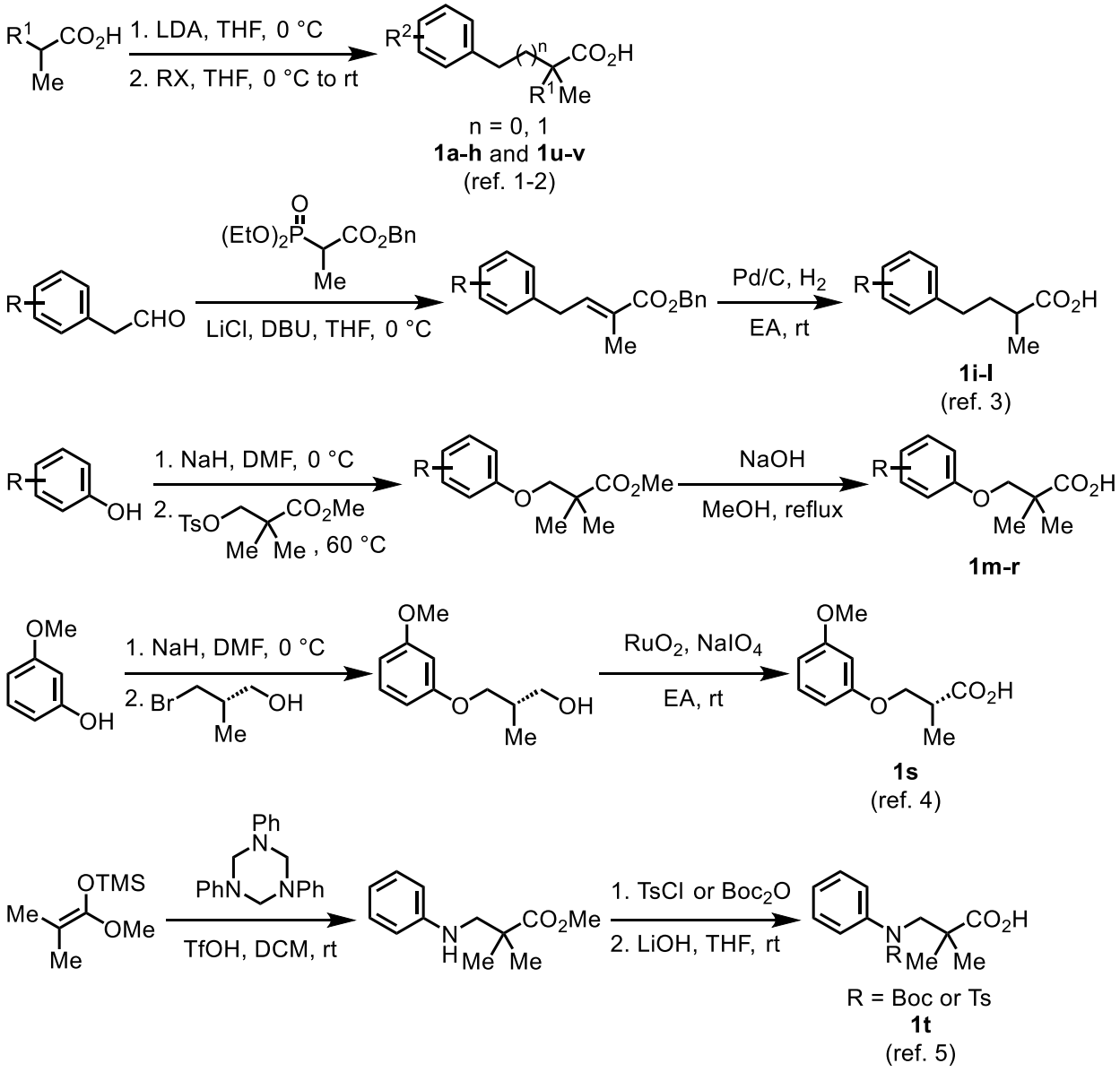
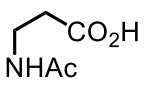
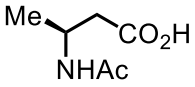


Aliphatic carboxylic acids were synthesized following literature procedures[1–5] (**1a**–**1v**) or obtained from the commercial source (**1w**).

Preparation of mono-*N*-protected β-amino acid ligand



L4



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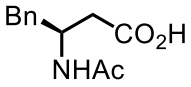

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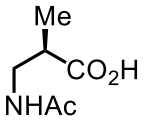
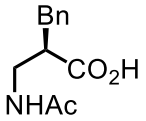
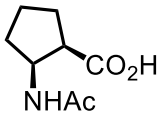


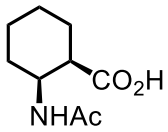
L7



L8



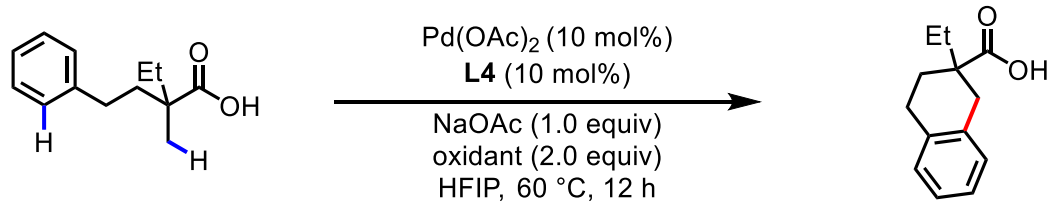
(±)-L9



(±)-L10

L4–**L10** were commercially available (**L4**) or synthesized following literature procedures[6–9] (**L5**–**L10**).

Table S1. Oxidant investigation for the cyclative C−H/C−H coupling reaction[a,b]

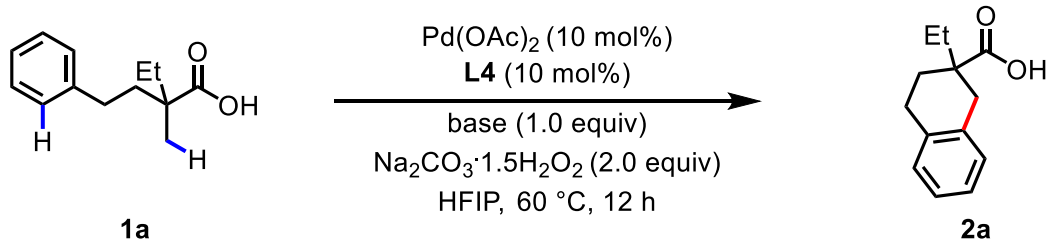


1a **2a**

entry	oxidant	yield (%)	entry	oxidant	yield (%)
1	w/o	0	10	CMHP	22
2	AcOO^{t}Bu	38	11	TBHP (70% in water)	50
3	BzOO^{t}Bu	0	12	TBHP (ca. 5.5 M in decane)	53
4	BzOOBz	0	13	$K_2S_2O_8$	5
5	Lauroyl peroxide	0	14	$Na_2S_2O_8$	0
6	^{t}BuOO^{t}Bu	0	15	Oxone	0
7	H_2O_2 in water	0	16	Selectfluor	32
8	UHP	0	17	NFSI	0
9	$Na_2CO_3{\cdot}1.5H_2O_2$	56	18	FTMP	0

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L4** (10 mol%), NaOAc (1.0 equiv), $Na_2CO_3{\cdot}1.5H_2O_2$ (2.0 equiv), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

Table S2. Base screening for the cyclative C−H/C−H coupling reaction[a,b]

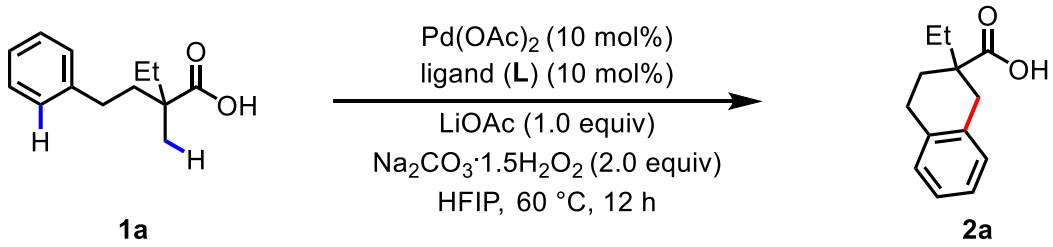


1a **2a**

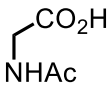
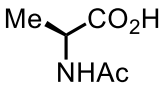
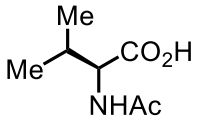
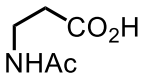
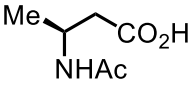
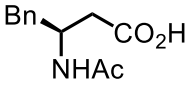
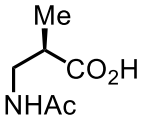
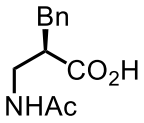
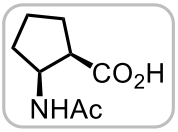
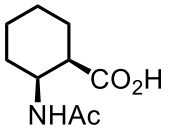
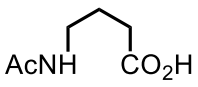
entry	base	yield (%)	entry	base	yield (%)
1	w/o	50	6	Na_3PO_4	49
2	$NaHCO_3$	45	7	NaOAc	56
3	Na_2CO_3	44	8	LiOAc	57
4	NaH_2PO_4	36	9	KOAc	50
5	Na_2HPO_4	45	10	CsOAc	41

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L4** (10 mol%), base (1.0 equiv), $Na_2CO_3·1.5H_2O_2$ (2.0 equiv), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The conversions were determined by ^1H NMR analysis of the remaining **1a**.

Table S3. Ligand investigation for the cyclative C−H/C−H coupling reaction[a,b]

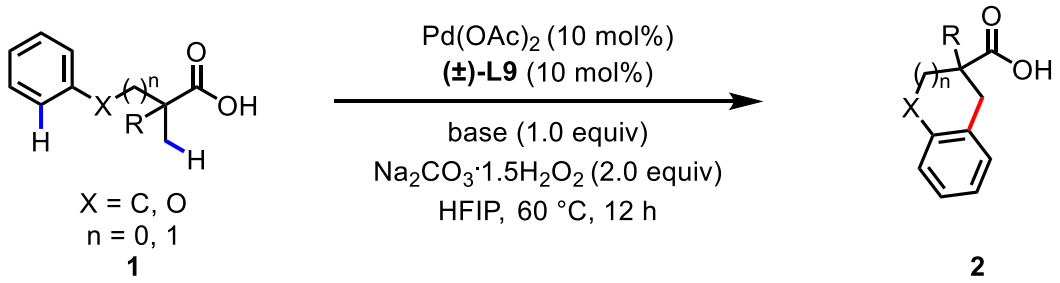


1a **2a**

w/o ligand(**L**)			
23%	**L1**, 19%	**L2**, 45%	**L3**, 39%
			
L4, 57%	**L5**, 53%	**L6**, 62%	**L7**, 63%
			
L8, 54%	**(±)-L9**, 75%(78%[c])	**(±)-L10**, 63%	**L11**, 20%

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), ligand (**L**) (10 mol%), LiOAc (1.0 equiv), $Na_2CO_3 \cdot 1.5H_2O_2$ (2.0 equiv), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. [c]Isolated yield.

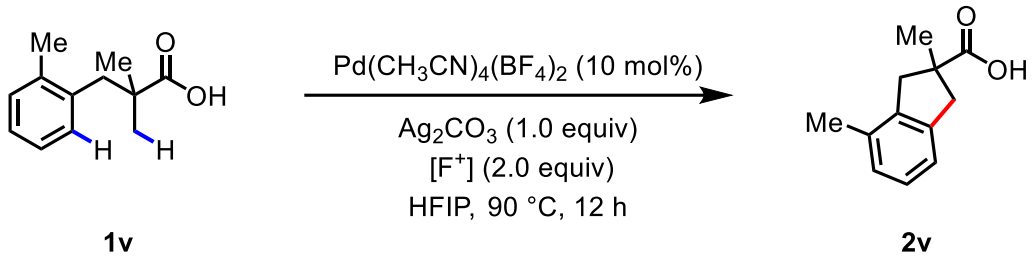
Table S4. Comparison between LiOAc and NaOAc under the standard conditions[a,b]



entry	1	yield using LiOAc (%)	yield using NaOAc (%)
1	**1a**	78	61
2	**1d**	58	45
3	**1i**	63	45
4	**1n**	80	77
5	**1u**	53	44

[a]Conditions: **1** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **(±)-L9** (10 mol%), base (1.0 equiv), $Na_2CO_3·1.5H_2O_2$ (2.0 equiv), HFIP (1.0 mL), 60 °C, 12 h. [b]Isolated yields.

Table S5. Conditions investigation for the cyclative C−H/C−H coupling reaction[a,b]

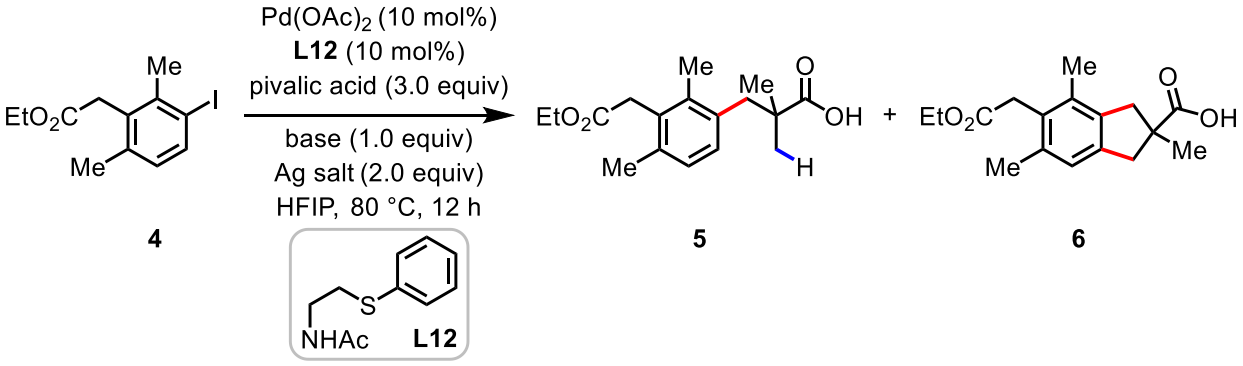


1v **2v**

entry	variation from standard conditions B	yield (%)
1	none	55 (61[c])
2	w/o Ag_2CO_3	0
3	Na_2CO_3 instead of Ag_2CO_3	0
4	LiOAc instead of Ag_2CO_3	0
5	$Pd(OAc)_2$ instead of $Pd(CH_3CN)_4(BF_4)_2$	23
6	w/ **(±)-L9** (10 mol%)	34
7	standard conditions A	23

[a]Conditions: **1v** (0.1 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (10 mol%), Ag_2CO_3 (1.0 equiv), [F^+] = 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (2.0 equiv), HFIP (1.0 mL), 90 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. [c]Isolated yield.

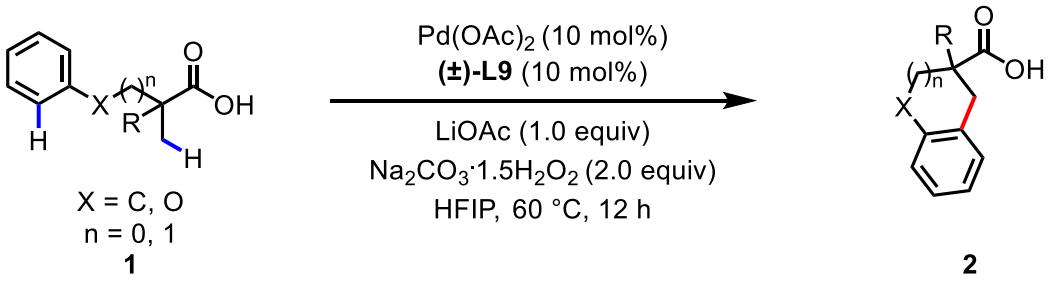
Table S6. Base and Ag salt investigation for arylation[a,b]



entry	base	Ag salt	**5** + **6** yield (%)
1	$Na_2HPO_4{\cdot}7H_2O$	Ag_2CO_3	52 + 4
2	$Na_2HPO_4{\cdot}7H_2O$	Ag_2O	52 + 3
3	$Na_2HPO_4{\cdot}7H_2O$	AgOAc	44 + 0
4	$NaHCO_3$	Ag_2CO_3	41 + 5
5	Na_2CO_3	Ag_2CO_3	50 + 5
6	Na_2HPO_4	Ag_2CO_3	47 + 4
7	Na_3PO_4	Ag_2CO_3	46 + 2
8	NaOAc	Ag_2CO_3	65 + 5
9	LiOAc	Ag_2CO_3	64 + 8
10	KOAc	Ag_2CO_3	46 + 10
11	CsOAc	Ag_2CO_3	61(62[c]) + 12(12[c])
12	CsOAc	w/o	0
13	w/o	Ag_2CO_3	0

[a]Conditions: **4** (0.1 mmol), pivalic acid (3.0 equiv), $Pd(OAc)_2$ (10 mol%), **L12** (10 mol%), base (1.0 equiv), Ag salt (2.0 equiv), HFIP (1.0 mL), 80 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard. [c]Isolated yields.

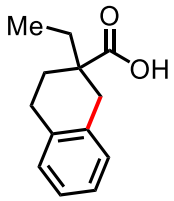
General procedure for the cyclative C−H/C−H coupling reaction



General Procedure A: In the culture tube, $Pd(OAc)_2$ (10 mol%, 2.2 mg), ligand **(±)-L9** (10 mol%, 1.7 mg), LiOAc (1.0 equiv, 6.6 mg), $Na_2CO_3·1.5H_2O_2$ (2.0 equiv, 31.4 mg), and **1** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (1.0 mL) was added. The reaction mixture was stirred at rt for 3 min, and then heated to 60 °C for 12 h (600 rpm). After being allowed to cool to room temperature, the mixture was treated with HCO_2H (0.1 mL) and concentrated *in vacuo*. The crude mixture was purified by pTLC (hexane/EA with 1% AcOH) to afford the product **2**.

General Procedure B: In the culture tube, $Pd(CH_3CN)_4(BF_4)_2$ (10 mol%, 4.4 mg), Ag_2CO_3 (1.0 equiv, 27.4 mg), 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (2.0 equiv, 45.4 mg), and **1** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (1.0 mL) was added. The reaction mixture was stirred at rt for 3 min, and then heated to 90 °C for 12 h (600 rpm). After being allowed to cool to room temperature, the mixture was treated with HCO_2H (0.1 mL), diluted with DCM, filtered through a Celite plug, and concentrated *in vacuo*. The crude mixture was purified by pTLC (hexane/EA with 1% AcOH) to afford the product **2**.

Substrate scope of the cyclative C−H/C−H coupling reaction



2-Ethyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2a)

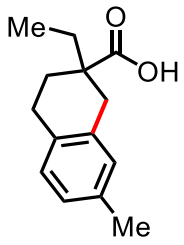
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 16.0 mg, 78% yield).

Following **General Procedure A** on 2.0 mmol scale. Purification by column chromatography afforded the title compound (282.0 mg, 69% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.03 (m, 4H), 3.22 (d, *J* = 16.5 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.83 – 2.75 (m, 1H), 2.67 (d, *J* = 16.5 Hz, 1H), 2.20 – 2.12 (m, 1H), 1.85 – 1.77 (m, 1H), 1.79 – 1.69 (m, 1H), 1.70 – 1.61 (m, 1H), 0.94 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.5, 135.5, 134.9, 129.3, 128.8, 126.0, 125.9, 46.0, 36.6, 31.1, 30.1, 26.3, 8.9.

HRMS (ESI-TOF) Calcd for $C_{13}H_{15}O_2^-$ [M-H]$^-$: 203.1078; found: 203.1072.



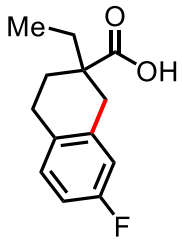
2-Ethyl-7-methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2b)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 16.5 mg, 76% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 – 6.93 (m, 1H), 6.93 – 6.85 (m, 2H), 3.17 (d, *J* = 16.4 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.78 – 2.70 (m, 1H), 2.63 (d, *J* = 16.4 Hz, 1H), 2.28 (s, 3H), 2.18 – 2.08 (m, 1H), 1.84 – 1.75 (m, 1H), 1.77 – 1.68 (m, 1H), 1.69 – 1.59 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) (major and minor rotamers) δ 182.8, 135.6, 135.6, 135.5, 134.8, 132.6, 132.0, 130.1, 129.6, 129.4, 128.9, 127.1, 127.0, 46.3, 46.2, 36.8, 36.5, 31.3, 31.3, 30.5, 30.3, 26.4, 26.1, 21.3, 9.1.

HRMS (ESI-TOF) Calcd for $C_{14}H_{17}O_2^-$ [M-H]$^-$: 217.1234; found: 217.1232.



2-Ethyl-7-fluoro-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2c)

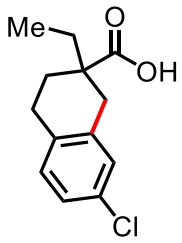
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 13.0 mg, 59% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 6.97 (m, 1H), 6.84 – 6.73 (m, 2H), 3.24 – 3.12 (m, 1H), 2.90 – 2.71 (m, 2H), 2.68 – 2.58 (m, 1H), 2.20 – 2.11 (m, 1H), 1.83 – 1.68 (m, 2H), 1.68 – 1.60 (m, 1H), 0.98 – 0.90 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) (major rotamer) δ 182.2, 161.2 (d, *J* = 243.4 Hz), 136.9 (d, *J* = 7.2 Hz), 130.9 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 8.2 Hz), 115.0 (d, *J* = 20.4 Hz), 113.1 (d, *J* = 21.3 Hz), 45.8, 36.6, 31.3, 30.3, 25.7, 8.9.

^{13}C NMR (150 MHz, $CDCl_3$) (minor rotamer) δ 182.3, 161.2 (d, *J* = 243.4 Hz), 137.4 (d, *J* = 7.2 Hz), 130.5 (d, *J* = 7.8 Hz), 130.4 (d, *J* = 2.9 Hz), 115.4 (d, *J* = 20.8 Hz), 115.2 (d, *J* = 21.0 Hz), 46.1, 36.0, 31.2, 29.8, 26.5, 8.9.

HRMS (ESI-TOF) Calcd for $C_{13}H_{14}FO_2^-$ $[M-H]^-$: 221.0983; found: 221.0990.



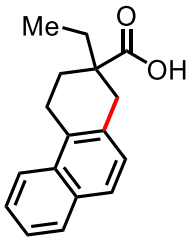
7-Chloro-2-ethyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2d)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 13.8 mg, 58% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.03 (m, 2H), 7.03 – 6.96 (m, 1H), 3.25 – 3.13 (m, 1H), 2.91 – 2.71 (m, 2H), 2.71 – 2.58 (m, 1H), 2.21 – 2.12 (m, 1H), 1.83 – 1.70 (m, 2H), 1.69 – 1.60 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) (major and minor rotamers) δ 182.0, 182.0, 137.3, 136.8, 133.9, 133.4, 131.4, 131.4, 130.6, 130.1, 129.0, 128.6, 126.1, 126.1, 46.0, 45.8, 36.4, 36.1, 31.3, 31.3, 30.1, 29.9, 26.3, 25.8, 8.9.

HRMS (ESI-TOF) Calcd for $C_{13}H_{14}ClO_2^-$ [M-H]$^-$: 237.0688; found: 237.0684.



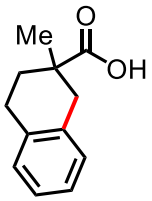
2-Ethyl-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid (2e)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 11.5 mg, 45% yield, *ortho*/*peri* = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) (*ortho*-product) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 3.36 (d, *J* = 16.6 Hz, 1H), 3.25 – 3.13 (m, 2H), 2.84 (d, *J* = 16.6 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.01 – 1.92 (m, 1H), 1.83 – 1.75 (m, 1H), 1.76 – 1.67 (m, 1H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) (*ortho*-product) δ 182.5, 132.3, 132.2, 132.1, 130.1, 128.6, 128.2, 126.3, 126.1, 125.0, 123.0, 45.7, 37.5, 30.9, 29.8, 23.2, 9.0.

HRMS (ESI-TOF) Calcd for $C_{17}H_{17}O_2^-$ [M-H]$^-$: 253.1234; found: 253.1230.



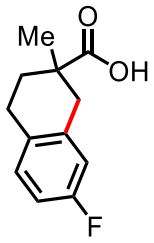
2-Methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2f)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 12.5 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 – 7.02 (m, 4H), 3.24 (d, *J* = 16.4 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.87 – 2.78 (m, 1H), 2.67 (d, *J* = 16.4 Hz, 1H), 2.21 – 2.13 (m, 1H), 1.85 – 1.75 (m, 1H), 1.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.7, 135.1, 134.7, 129.4, 128.9, 126.0, 126.0, 41.6, 38.5, 31.8, 26.2, 24.4.

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}O_2^-$ [M-H]$^-$: 189.0921; found: 189.0919.



7-Fluoro-2-methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2g)

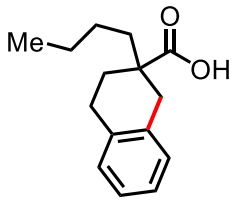
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 11.0 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 6.99 (m, 1H), 6.84 – 6.74 (m, 2H), 3.26 – 3.14 (m, 1H), 2.93 – 2.74 (m, 2H), 2.67 – 2.57 (m, 1H), 2.22 – 2.12 (m, 1H), 1.81 – 1.72 (m, 1H), 1.31 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) (major rotamer) δ 183.1, 161.2 (d, *J* = 243.6 Hz), 136.7 (d, *J* = 7.3 Hz), 130.5 (d, *J* = 1.8 Hz), 130.2 (d, *J* = 7.8 Hz), 115.4 (d, *J* = 20.8 Hz), 113.2 (d, *J* = 21.1 Hz), 41.5, 38.5, 31.9, 25.6, 24.5.

^{13}C NMR (150 MHz, $CDCl_3$) (minor rotamer) δ 183.2, 161.2 (d, *J* = 243.6 Hz), 137.0 (d, *J* = 7.2 Hz), 130. 6 (d, *J* = 6.2 Hz), 130.2 (d, *J* = 3.1 Hz), 115.0 (d, *J* = 20.5 Hz), 113.1 (d, *J* = 21.3 Hz), 41.7, 37.8, 31.5, 26.5, 24.5.

HRMS (ESI-TOF) Calcd for $C_{12}H_{12}FO_2^-$ [M-H]$^-$: 207.0827; found: 207.0825.



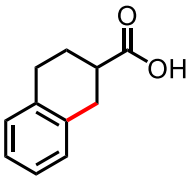
2-Butyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2h)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 16.5 mg, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.03 (m, 4H), 3.22 (d, *J* = 16.4 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.82 – 2.74 (m, 1H), 2.69 (d, *J* = 16.4 Hz, 1H), 2.20 – 2.10 (m, 1H), 1.87 – 1.77 (m, 1H), 1.73 – 1.63 (m, 1H), 1.63 – 1.55 (m, 1H), 1.35 – 1.23 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 181.4, 135.3, 134.7, 129.1, 128.6, 125.7, 125.7, 45.3, 37.9, 37.0, 30.2, 26.5, 26.1, 23.0, 13.9.

HRMS (ESI-TOF) Calcd for $C_{15}H_{19}O_2^-$ [M-H]$^-$: 231.1391; found: 231.1390.



1,2,3,4-Tetrahydronaphthalene-2-carboxylic acid (2i)

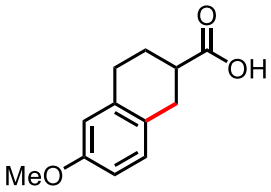
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 11.0 mg, 63% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 – 7.05 (m, 4H), 3.10 – 2.98 (m, 2H), 2.95 – 2.84 (m, 2H), 2.84 – 2.77 (m, 1H), 2.29 – 2.22 (m, 1H), 1.95 – 1.85 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 181.7, 135.7, 134.7, 129.2, 129.0, 126.2, 126.0, 39.9, 31.5, 28.5, 25.8.

HRMS (ESI-TOF) Calcd for $C_{11}H_{11}O_2^-$ [M-H]$^-$: 175.0765; found: 175.0757.

The NMR data matches the reported data[11].



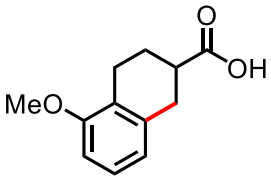
6-Methoxy-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2j)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 10.2 mg, 50% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, J = 8.4 Hz, 1H), 6.71 (dd, J = 8.4, 2.4 Hz, 1H), 6.63 (s, 1H), 3.77 (s, 3H), 3.04 – 2.91 (m, 2H), 2.91 – 2.81 (m, 2H), 2.81 – 2.73 (m, 1H), 2.27 – 2.18 (m, 1H), 1.93 – 1.82 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 181.2, 157.9, 136.8, 130.1, 126.8, 113.6, 112.4, 55.4, 40.1, 30.7, 28.8, 25.7.

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}O_3^-$ [M-H]$^-$: 205.0870; found: 205.0869.



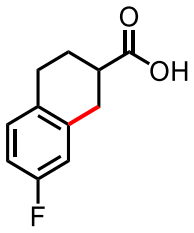
5-Methoxy-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2k)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 7.3 mg, 35% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 3.18 – 3.08 (m, 1H), 2.93 – 2.80 (m, 2H), 2.79 – 2.70 (m, 2H), 2.25 – 2.18 (m, 1H), 1.92 – 1.78 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 179.1, 157.5, 137.1, 126.4, 123.7, 121.1, 107.2, 55.4, 39.4, 28.7, 25.6, 25.4.

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}O_3^-$ [M-H]$^-$: 205.0870; found: 205.0869.



7-Fluoro-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (2l)

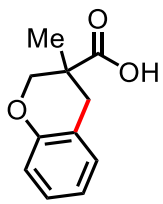
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 10.1 mg, 52% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 – 6.99 (m, 1H), 6.90 – 6.75 (m, 2H), 3.09 – 2.93 (m, 2H), 2.93 – 2.75 (m, 3H), 2.29 – 2.19 (m, 1H), 1.96 – 1.84 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) (major rotamer) δ 180.7, 161.2 (d, *J* = 243.7 Hz), 136.6 (d, *J* = 7.4 Hz), 131.2 (d, *J* = 2.7 Hz), 130.3 (d, *J* = 8.2 Hz), 115.3 (d, *J* = 20.6 Hz), 113.3 (d, *J* = 21.4 Hz), 39.5, 31.4, 27.8, 25.8.

^{13}C NMR (150 MHz, $CDCl_3$) (minor rotamer) δ 180.8, 161.3 (d, *J* = 244.2 Hz), 137.6 (d, *J* = 7.3 Hz), 130.5 (d, *J* = 7.8 Hz), 130.2 (d, *J* = 2.8 Hz), 115.1 (d, *J* = 20.7 Hz), 113.2 (d, *J* = 21.1 Hz), 39.7, 30.8, 28.6, 25.4.

HRMS (ESI-TOF) Calcd for $C_{11}H_{10}FO_2^-$ [M-H]$^-$: 193.0670; found: 193.0666.



3-Methylchromane-3-carboxylic acid (2m)

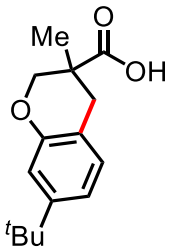
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 13.0 mg, 68% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.31 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.95 (d, *J* = 10.8 Hz, 1H), 3.27 (d, *J* = 16.4 Hz, 1H), 2.70 (d, *J* = 16.4 Hz, 1H), 1.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 180.7, 153.5, 130.0, 127.7, 121.1, 120.1, 116.8, 71.0, 40.8, 34.5, 21.1.

HRMS (ESI-TOF) Calcd for $C_{11}H_{11}O_3^-$ [M-H]$^-$: 191.0714; found: 191.0713.

The NMR data matches the reported data[12].



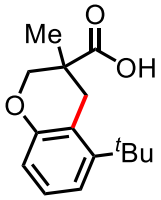
7-(*tert*-Butyl)-3-methylchromane-3-carboxylic acid (2n)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 20.0 mg, 80% yield, **2n**/**2n'** = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 4.29 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.93 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.24 (d, *J* = 16.3 Hz, 1H), 2.66 (d, *J* = 16.3 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 180.8, 153.0, 151.2, 129.4, 118.4, 117.0, 113.7, 71.0, 40.9, 34.6, 34.1, 31.4, 21.2.

HRMS (ESI-TOF) Calcd for $C_{15}H_{19}O_3^-$ [M-H]$^-$: 247.1340; found: 247.1339.

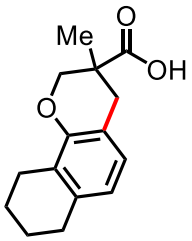


5-(*tert*-Butyl)-3-methylchromane-3-carboxylic acid (2n')

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 10.5 Hz, 1H), 3.91 (d, *J* = 10.5 Hz, 1H), 3.51 (d, *J* = 16.0 Hz, 1H), 2.90 (d, *J* = 16.0 Hz, 1H), 1.42 (s, 9H), 1.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 180.9, 154.0, 149.4, 127.1, 119.0, 118.9, 115.6, 70.4, 40.8, 36.2, 34.9, 31.2, 21.5.

HRMS (ESI-TOF) Calcd for $C_{15}H_{19}O_3^-$ [M-H]$^-$: 247.1340; found: 247.1337.



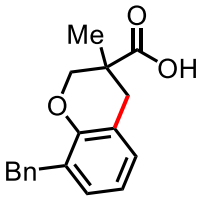
3-Methyl-3,4,7,8,9,10-hexahydro-2*H*-benzo[*h*]chromene-3-carboxylic acid (2o)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 21.0 mg, 85% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.29 (d, *J* = 10.8 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.23 (d, *J* = 16.3 Hz, 1H), 2.70 (t, *J* = 5.8 Hz, 2H), 2.65 (d, *J* = 16.3 Hz, 1H), 2.64 – 2.58 (m, 2H), 1.80 – 1.69 (m, 4H), 1.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 181.2, 151.1, 136.7, 126.5, 125.4, 121.6, 116.2, 70.9, 40.7, 34.5, 29.6, 23.1, 23.0, 22.9, 21.1.

HRMS (ESI-TOF) Calcd for $C_{15}H_{17}O_3^-$ [M-H]$^-$: 245.1183; found: 245.1183.



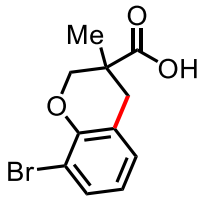
8-Benzyl-3-methylchromane-3-carboxylic acid (2p)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 20.0 mg, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 4.31 (d, *J* = 10.7 Hz, 1H), 4.03 – 3.88 (m, 3H), 3.28 (d, *J* = 16.4 Hz, 1H), 2.71 (d, *J* = 16.4 Hz, 1H), 1.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 180.5, 151.2, 141.1, 129.1, 129.0, 128.5, 128.4, 128.1, 125.9, 120.7, 119.9, 71.0, 40.7, 35.7, 34.7, 21.0.

HRMS (ESI-TOF) Calcd for $C_{18}H_{17}O_3^-$ [M-H]$^-$: 281.1183; found: 281.1184.



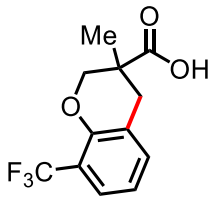
8-Bromo-3-methylchromane-3-carboxylic acid (2q)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 8.5 mg, 31% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.76 (t, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.07 (d, *J* = 10.8 Hz, 1H), 3.29 (d, *J* = 16.4 Hz, 1H), 2.72 (d, *J* = 16.4 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 179.8, 150.1, 131.5, 129.2, 121.9, 110.9, 71.7, 40.7, 34.6, 21.0 (1 carbon signal was not assigned due to overlaps).

HRMS (ESI-TOF) Calcd for $C_{11}H_{10}BrO_3^-$ [M-H]$^-$: 268.9819; found: 268.9820.



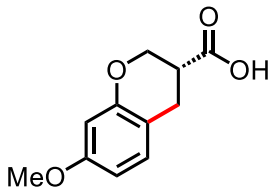
3-Methyl-8-(trifluoromethyl)chromane-3-carboxylic acid (2r)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 4.5 mg, 17% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 10.9 Hz, 1H), 4.08 (d, *J* = 10.9 Hz, 1H), 3.31 (d, *J* = 16.4 Hz, 1H), 2.75 (d, *J* = 16.4 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 179.5, 151.6, 133.8, 125.4 (q, *J* = 5.4 Hz), 123.7 (q, *J* = 272.3 Hz), 121.6, 120.2, 118.2 (q, *J* = 30.9 Hz), 71.2, 40.3, 34.3, 21.0.

HRMS (ESI-TOF) Calcd for $C_{12}H_{10}F_3O_3^-$ [M-H]$^-$: 259.0588; found: 259.0587.



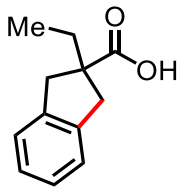
(*R*)-7-Methoxychromane-3-carboxylic acid (2s)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 15.0 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.39 (d, *J* = 2.6 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.21 – 4.14 (m, 1H), 3.75 (s, 3H), 3.10 – 3.04 (m, 1H), 3.03 – 2.96 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 159.4, 154.8, 130.3, 112.1, 108.1, 101.7, 66.3, 55.5, 38.4, 26.8.

HRMS (ESI-TOF) Calcd for $C_{11}H_{11}O_4^-$ [M-H]$^-$: 207.0663; found: 207.0660.



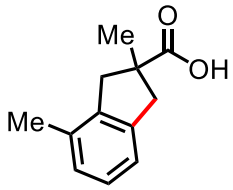
2-Ethyl-2,3-dihydro-1*H*-indene-2-carboxylic acid (2u)

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 10.0 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 2H), 7.16 – 7.11 (m, 2H), 3.48 (d, *J* = 16.2 Hz, 2H), 2.92 (d, *J* = 16.2 Hz, 2H), 1.83 (q, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.3, 141.4, 126.7, 124.6, 54.7, 41.8, 31.5, 10.0.

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}O_2^-$ [M-H]$^-$: 189.0921; found: 189.0918.



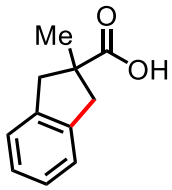
2,4-Dimethyl-2,3-dihydro-1*H*-indene-2-carboxylic acid (2v)

Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 11.5 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 3.53 (d, *J* = 15.9 Hz, 1H), 3.43 (d, *J* = 16.0 Hz, 1H), 2.86 (d, *J* = 15.9 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.24 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 184.2, 141.0, 140.0, 134.2, 127.6, 127.0, 122.1, 49.0, 44.2, 42.8, 25.4, 19.2.

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}O_2^-$ [M-H]$^-$: 189.0921; found: 189.0915.



2-Methyl-2,3-dihydro-1*H*-indene-2-carboxylic acid (2w)

Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 8.0 mg, 48% yield).

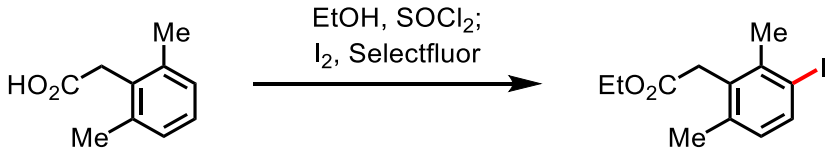
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 7.18 – 7.14 (m, 2H), 3.52 (d, *J* = 15.8 Hz, 2H), 2.85 (d, *J* = 15.8 Hz, 2H), 1.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.5, 141.2, 126.8, 124.8, 49.5, 44.0, 25.0.

HRMS (ESI-TOF) Calcd for $C_{11}H_{11}O_2^-$ $[M-H]^-$: 175.0765; found: 175.0762.

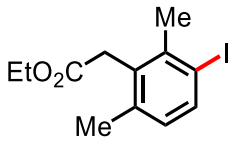
The NMR data matches the reported data[13].

Total synthesis of (±)-russujaponol F



3 **4**

To the EtOH (5.0 mL) solution of **3** (1.0 mmol, 164 mg) was added $SOCl_2$ (2.0 equiv, 0.15 mL) at 0 °C and then the mixture was stirred under reflux overnight. After being allowed to cool to room temperature, the mixture was concentrated *in vacuo* to afford the corresponding ethyl ester. Following literature procedure[10] with slight modification, to the CH_3CN solution (10.0 mL) of the ethyl ester was added I_2 (0.5 equiv, 127 mg) and Selectfluor (0.5 equiv, 177 mg) and the mixture was stirred at 60 °C for 3 h. After being allowed to cool to room temperature, the mixture was diluted with EA, washed with saturated $Na_2S_2O_3$, and concentrated *in vacuo*. The crude mixture was purified by column chromatography to afford the iodination product **4** (250 mg, 79% yield).

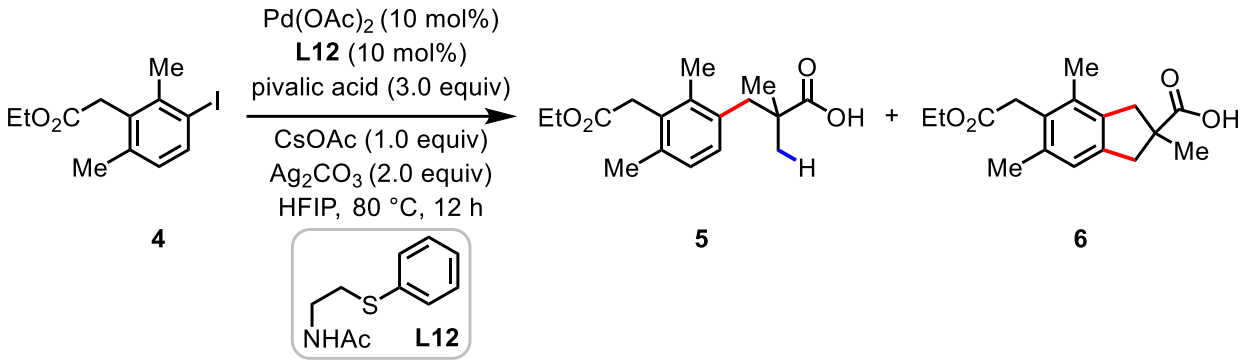


Ethyl 2-(3-iodo-2,6-dimethylphenyl)acetate (4)

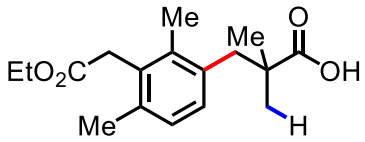
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 2H), 2.48 (s, 3H), 2.29 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 139.9, 138.1, 137.8, 133.0, 129.8, 99.7, 61.1, 37.1, 26.0, 20.5, 14.3.

HRMS (ESI-TOF) Calcd for $C_{12}H_{16}IO_2^+$ $[M+H]^+$: 319.0189; found: 319.0196.



In the culture tube, $Pd(OAc)_2$ (10 mol%, 2.2 mg), ligand **L12** (10 mol%, 2.0 mg), CsOAc (1.0 equiv, 19.2 mg), Ag_2CO_3 (2.0 equiv, 55.1 mg), pivalic acid (3.0 equiv, 30.6 mg) and **4** (0.1 mmol, 31.8 mg) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (1.0 mL) was added. The reaction mixture was stirred at rt for 3 min, and then heated to 80 °C for 12 h (600 rpm). After being allowed to cool to room temperature, the mixture was treated with HCO_2H (0.1 mL), diluted with DCM, filtered through a Celite plug, and concentrated *in vacuo*. The crude mixture was purified by pTLC (hexane/EA) to afford the arylation product **5** (18.0 mg, 62% yield) and the product **6** (3.5 mg, 12% yield).

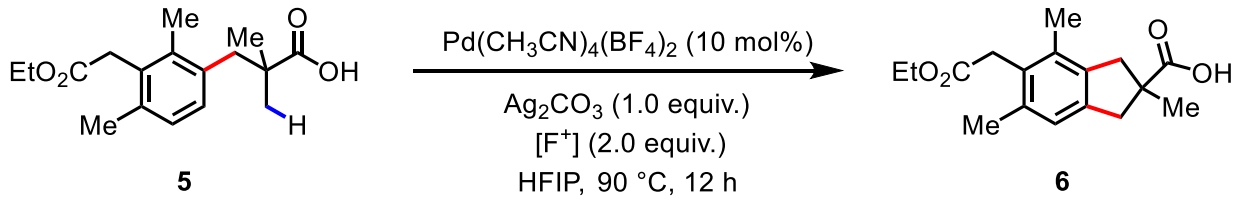


3-(3-(2-Ethoxy-2-oxoethyl)-2,4-dimethylphenyl)-2,2-dimethylpropanoic acid (5)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 2H), 2.99 (s, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 6H).

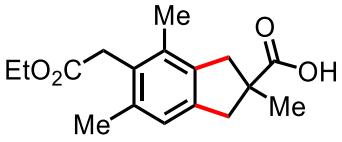
^{13}C NMR (150 MHz, $CDCl_3$) δ 183.1, 171.6, 136.5, 135.7, 134.0, 132.5, 130.1, 127.5, 60.9, 44.1, 42.3, 36.2, 27.3, 24.7, 20.7, 17.0, 14.4.

HRMS (ESI-TOF) Calcd for $C_{17}H_{23}O_4^-$ [M-H]$^-$: 291.1602; found: 291.1605.



5 **6**

In the culture tube, $Pd(CH_3CN)_4(BF_4)_2$ (10 mol%, 2.2 mg), Ag_2CO_3 (1.0 equiv, 13.8 mg), 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (2.0 equiv, 22.7 mg), and **5** (0.05 mmol, 14.6 mg) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (0.5 mL) was added. The reaction mixture was stirred at rt for 3 min, and then heated to 90 °C for 12 h (600 rpm). After being allowed to cool to room temperature, the mixture was treated with HCO_2H (0.05 mL), diluted with DCM, filtered through a Celite plug, and concentrated *in vacuo*. The crude mixture was purified by pTLC (hexane/EA) to afford the product **6** (6.0 mg, 41% yield).

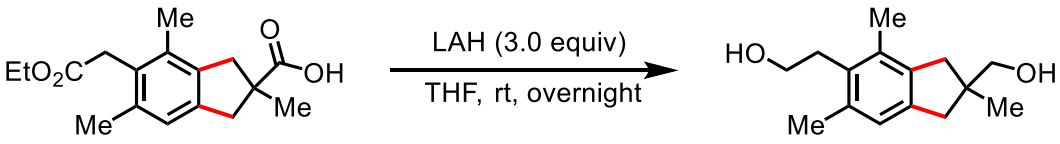


5-(2-Ethoxy-2-oxoethyl)-2,4,6-trimethyl-2,3-dihydro-1*H*-indene-2-carboxylic acid (6)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (s, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.66 (s, 2H), 3.49 (d, *J* = 16.0 Hz, 1H), 3.44 (d, *J* = 16.0 Hz, 1H), 2.81 (d, *J* = 16.0 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 3H), 2.21 (s, 3H), 1.41 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

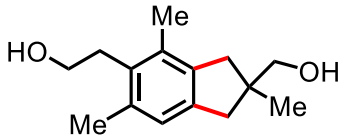
^{13}C NMR (150 MHz, $CDCl_3$) δ 181.9, 171.7, 139.7, 138.3, 136.0, 133.3, 130.0, 124.1, 60.9, 48.8, 44.2, 43.5, 35.4, 25.5, 20.8, 16.5, 14.4.

HRMS (ESI-TOF) Calcd for $C_{17}H_{21}O_4^-$ $[M-H]^-$: 289.1445; found: 289.1447.



6 (±)-russujaponol F

In the culture tube, to the THF (1.0 mL) solution of **6** (0.02 mmol, 6.0 mg) was added LAH (3.0 equiv, 1.0 M in THF, 0.06 mL) at 0 °C. The reaction mixture was warmed to rt and stirred at rt overnight. The mixture was diluted with ether, washed with saturated NH_4Cl, and concentrated *in vacuo*. The crude mixture was purified by pTLC (hexane/EA) to afford the (±)-russujaponol F (4.5 mg, 96% yield). The NMR data matches the reported data[14,15].



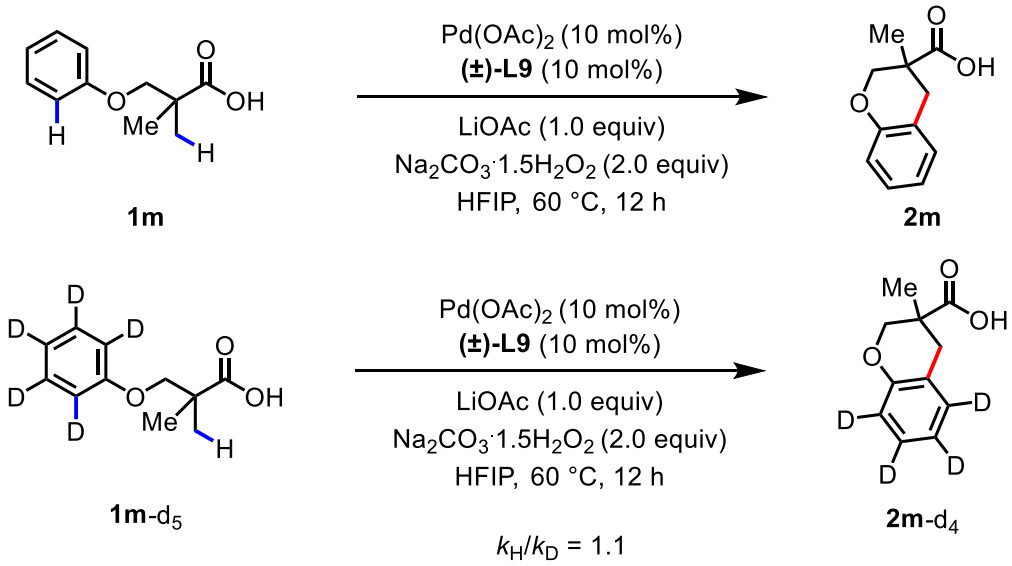
(±)-Russujaponol F

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (s, 1H), 3.74 (t, *J* = 7.4 Hz, 2H), 3.52 (s, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), δ 2.88 (d, *J* = 15.9 Hz, 1H), 2.84 (d, *J* = 15.9 Hz, 1H), 2.63 (d, *J* = 15.9 Hz, 1H), 2.59 (d, *J* = 15.9 Hz, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.3, 139.8, 135.4, 133.2, 132.3, 124.4, 71.1, 62.1, 44.3, 43.1, 42.4, 32.9, 24.6, 20.6, 16.3.

HRMS (ESI-TOF) Calcd for $C_{15}H_{21}O_2^-$ $[M-H]^-$: 233.1547; found: 233.1544.

KIE experiments



Following **General Procedure A** on 0.05 mmol scale. After being heated to 60 °C for the appropriate time, the mixture was diluted with DCM, treated with HCO_2H (0.1 mL), and concentrated *in vacuo*. The yield was determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The obtained yields were plotted as concentration vs. time (Figure S1 and S2). Representative initial data are shown below:

entry	t(min)	**2m** (10^{-3} M)	**2m**-d_4 (10^{-3} M)
1	0	0.0	0.0
2	20	22.5	19.3
3	40	107.7	116.2
4	60	161.0	141.3
5	80	250.2	241.4

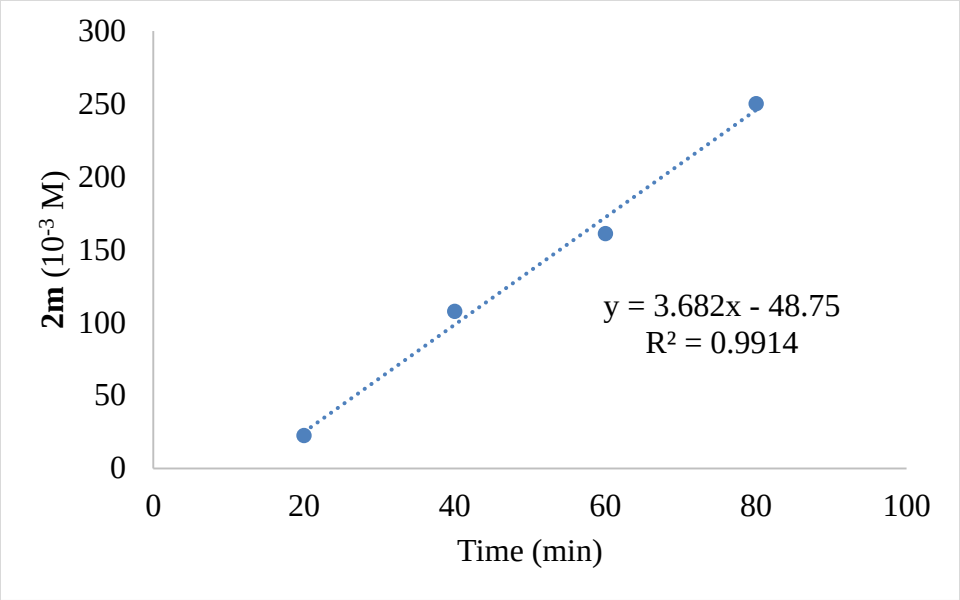


Figure S1. Representative initial data of **2m**

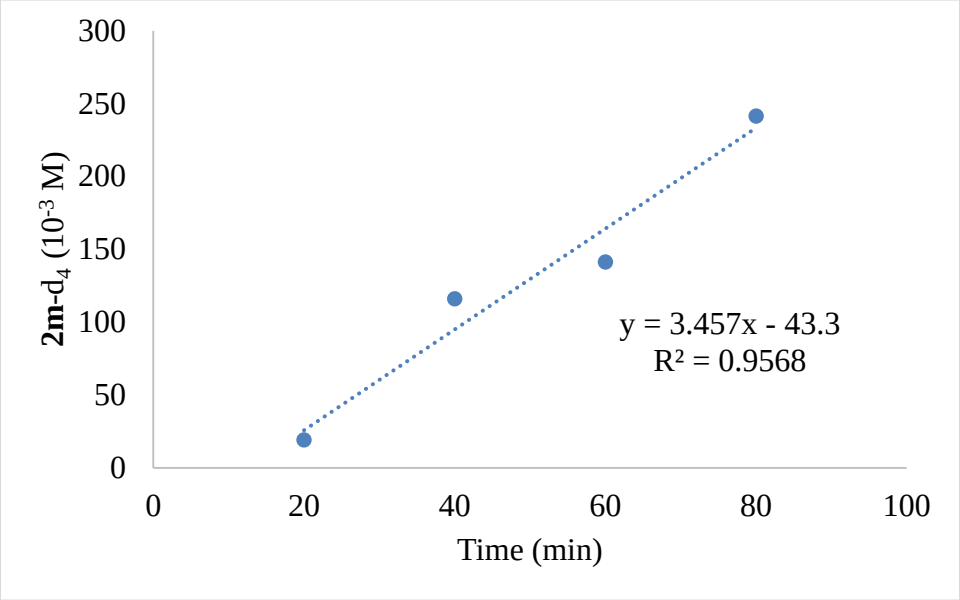


Figure S2. Representative initial data of **2m**-d_4

Reference:

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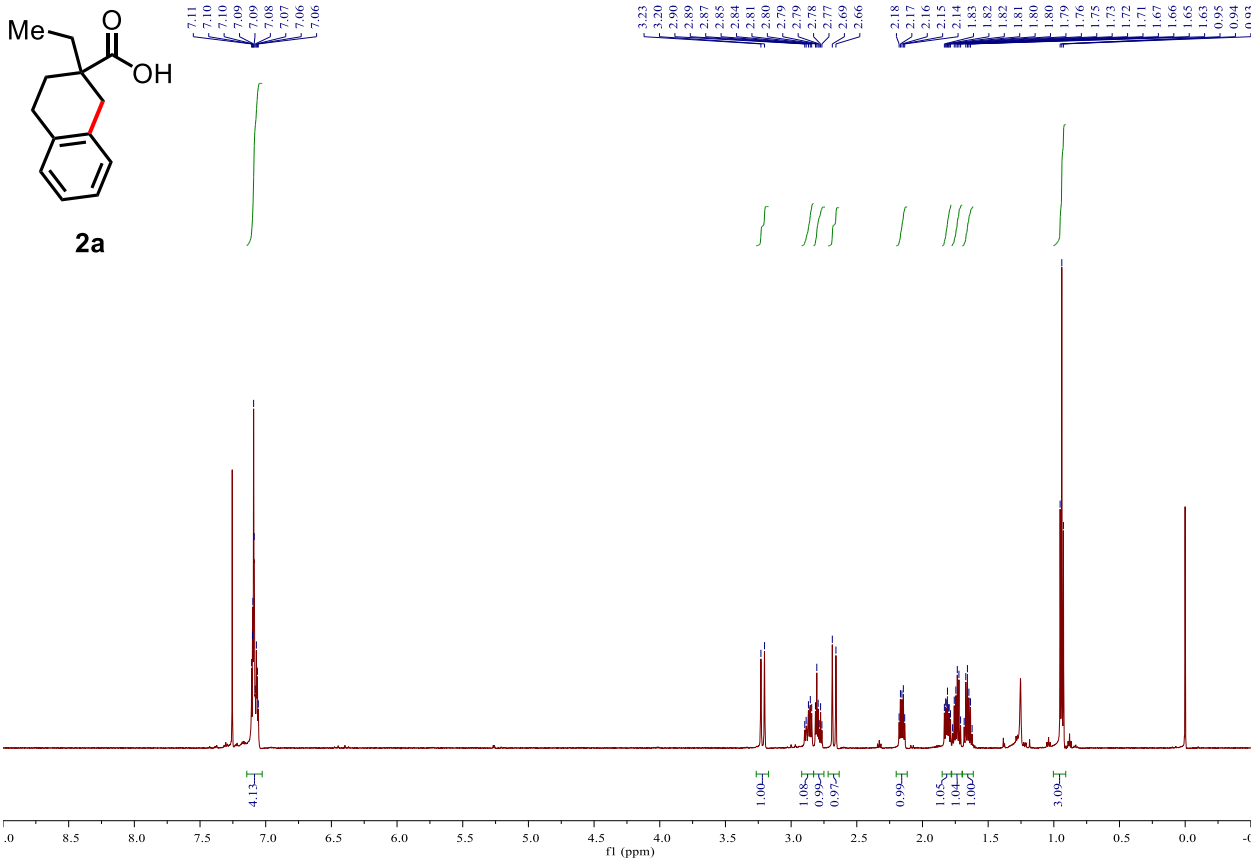
15. Melot, R.; Craveiro, M. V.; Baudoin, O. Total synthesis of (nor)illudalane sesquiterpenes based on a C(sp^3)−H activation strategy. *J. Org. Chem.* **2019**, *84*, 12933−12945.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2.87
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2.81
2.80
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2.79
2.78
2.77
2.69
2.66
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1.63
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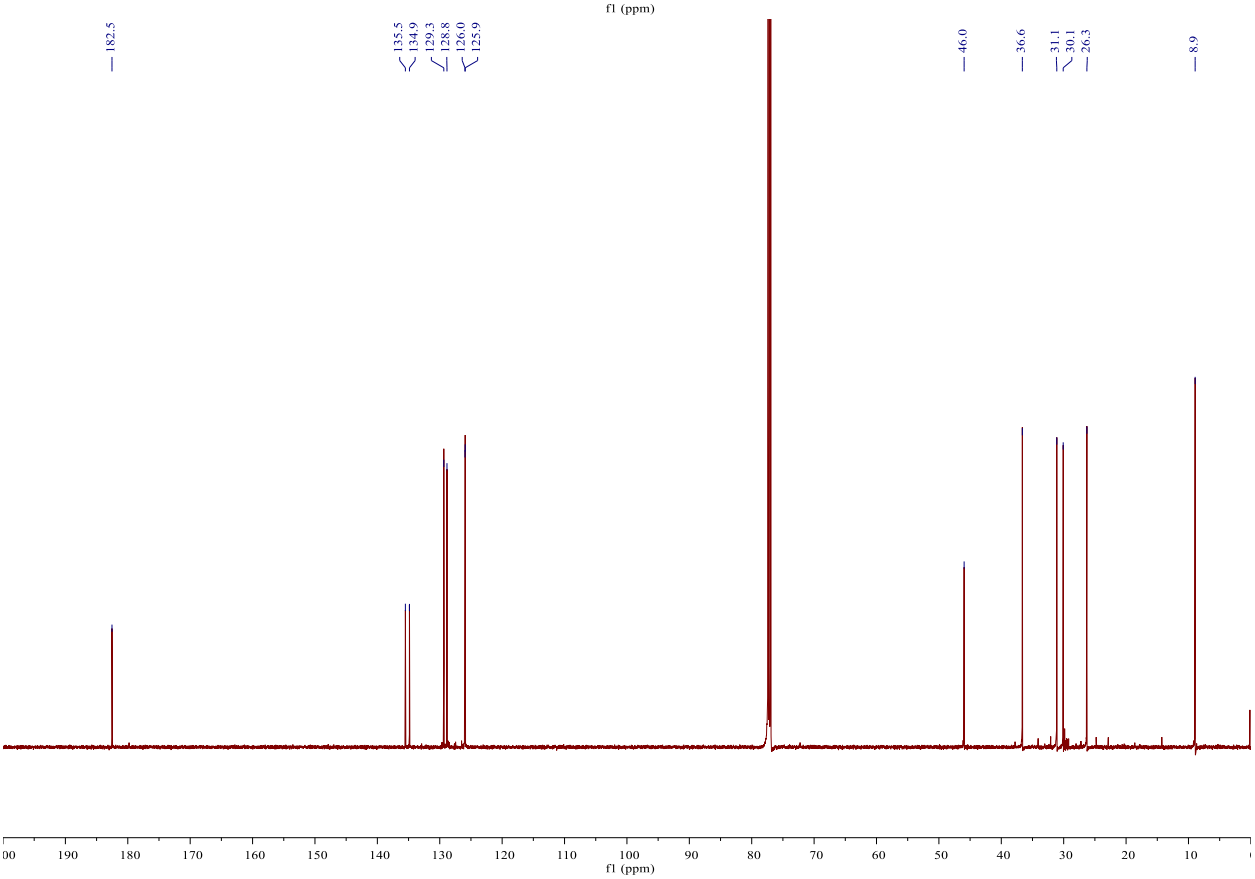
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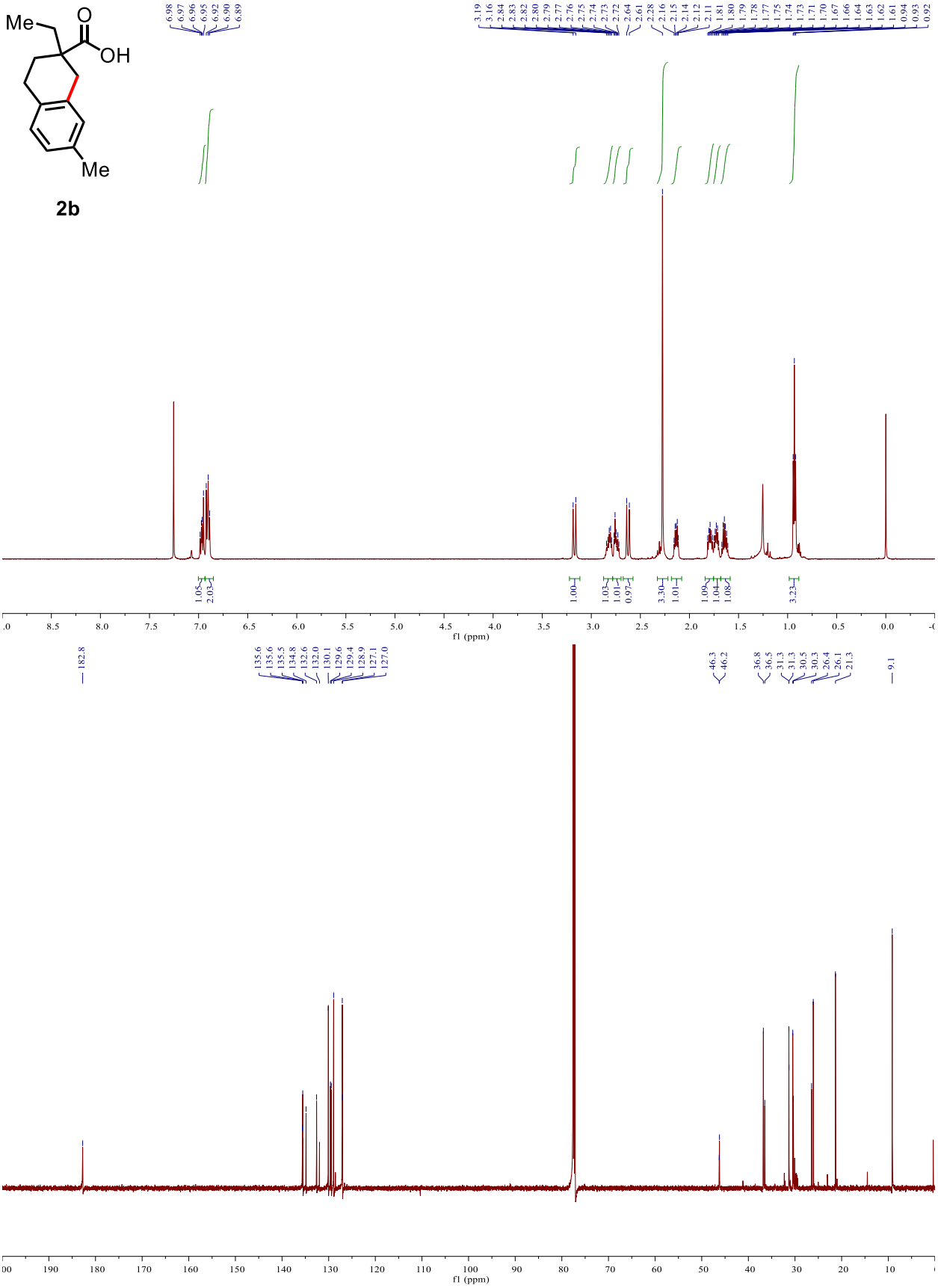
f1 (ppm)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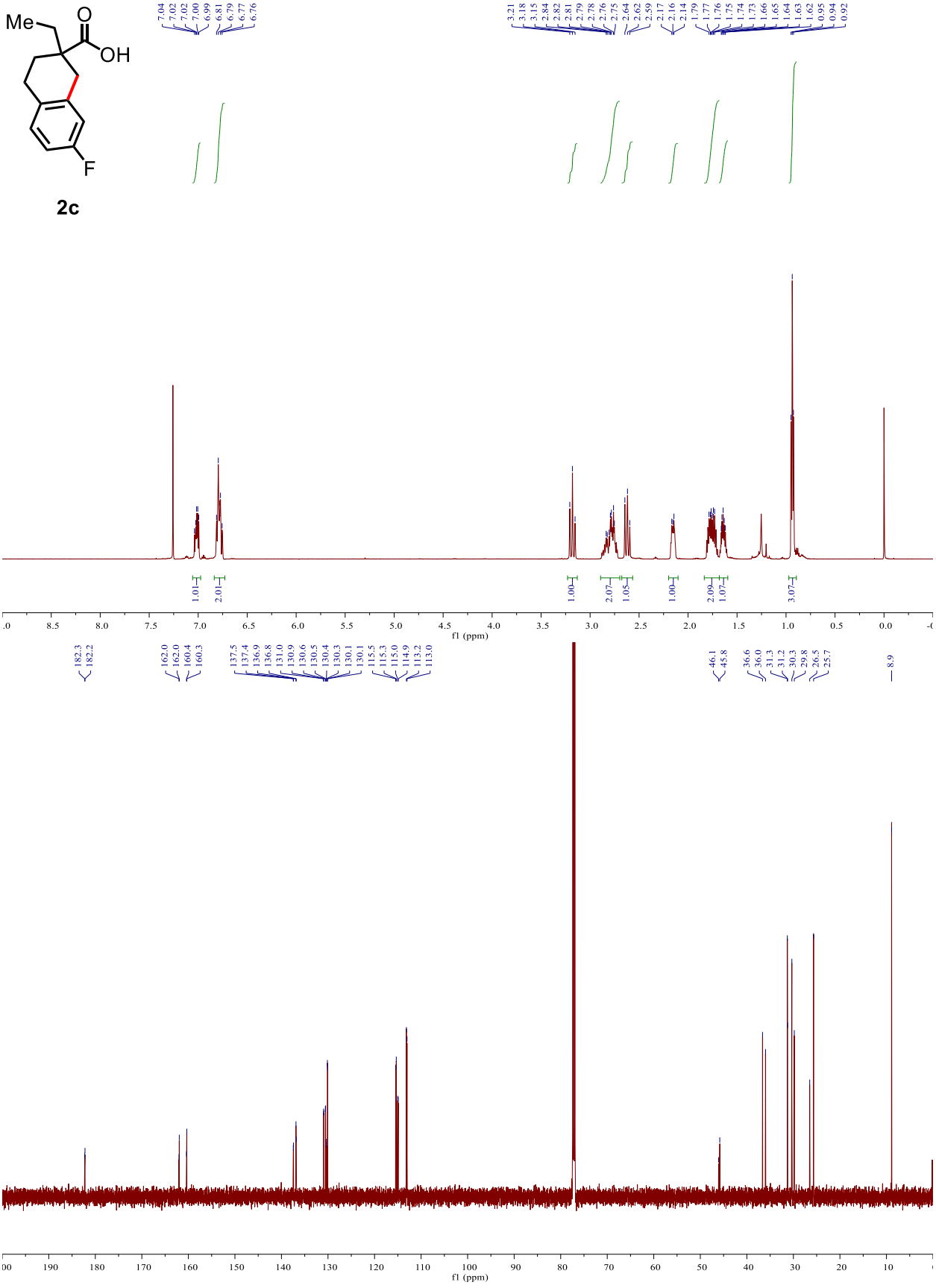
f1 (ppm)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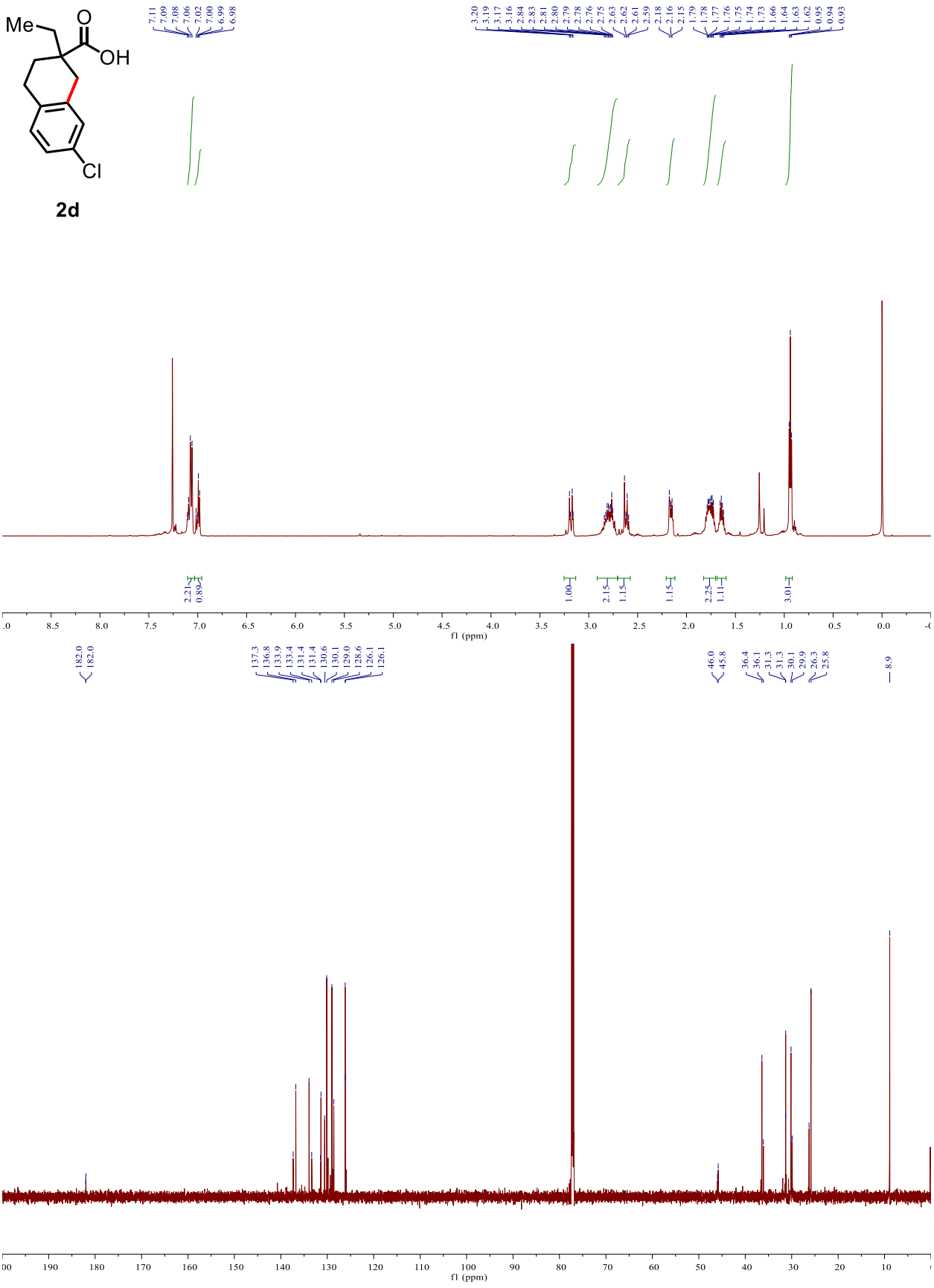
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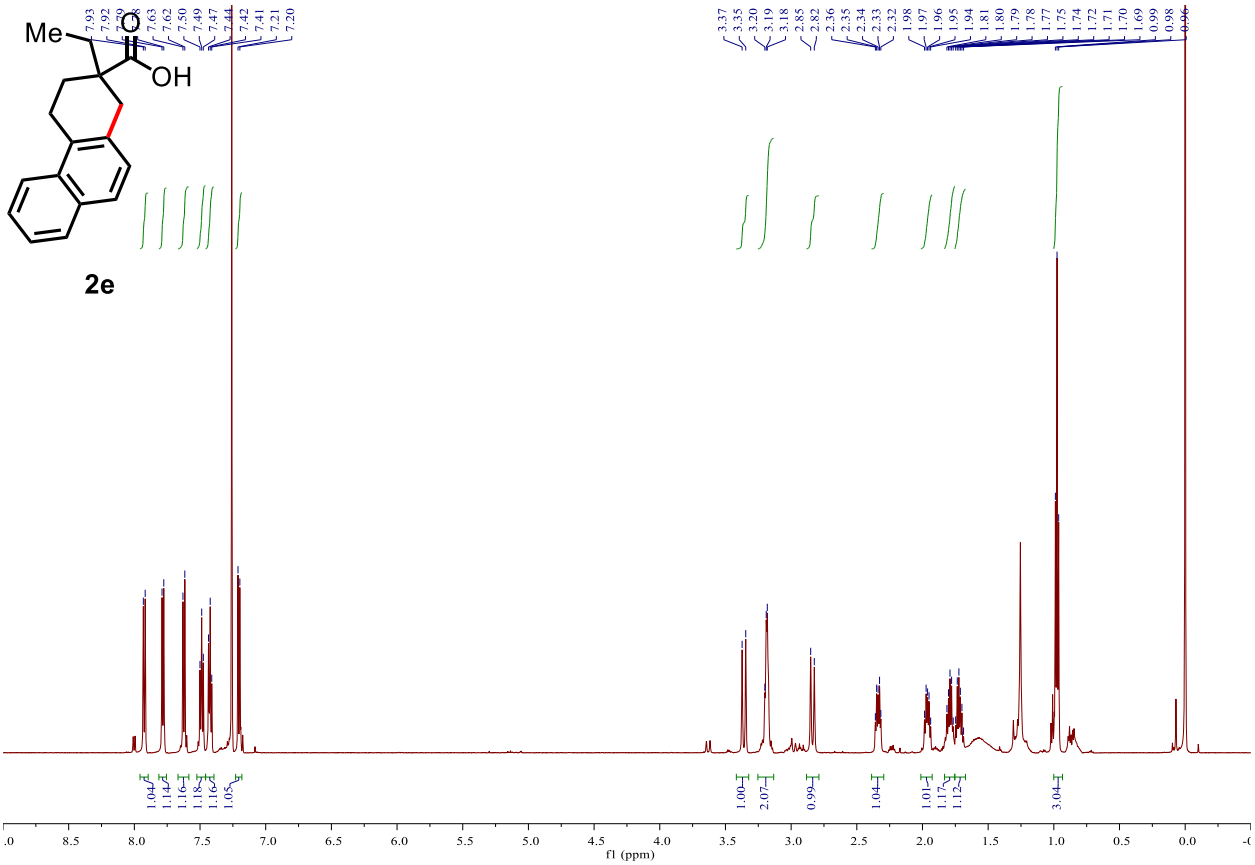
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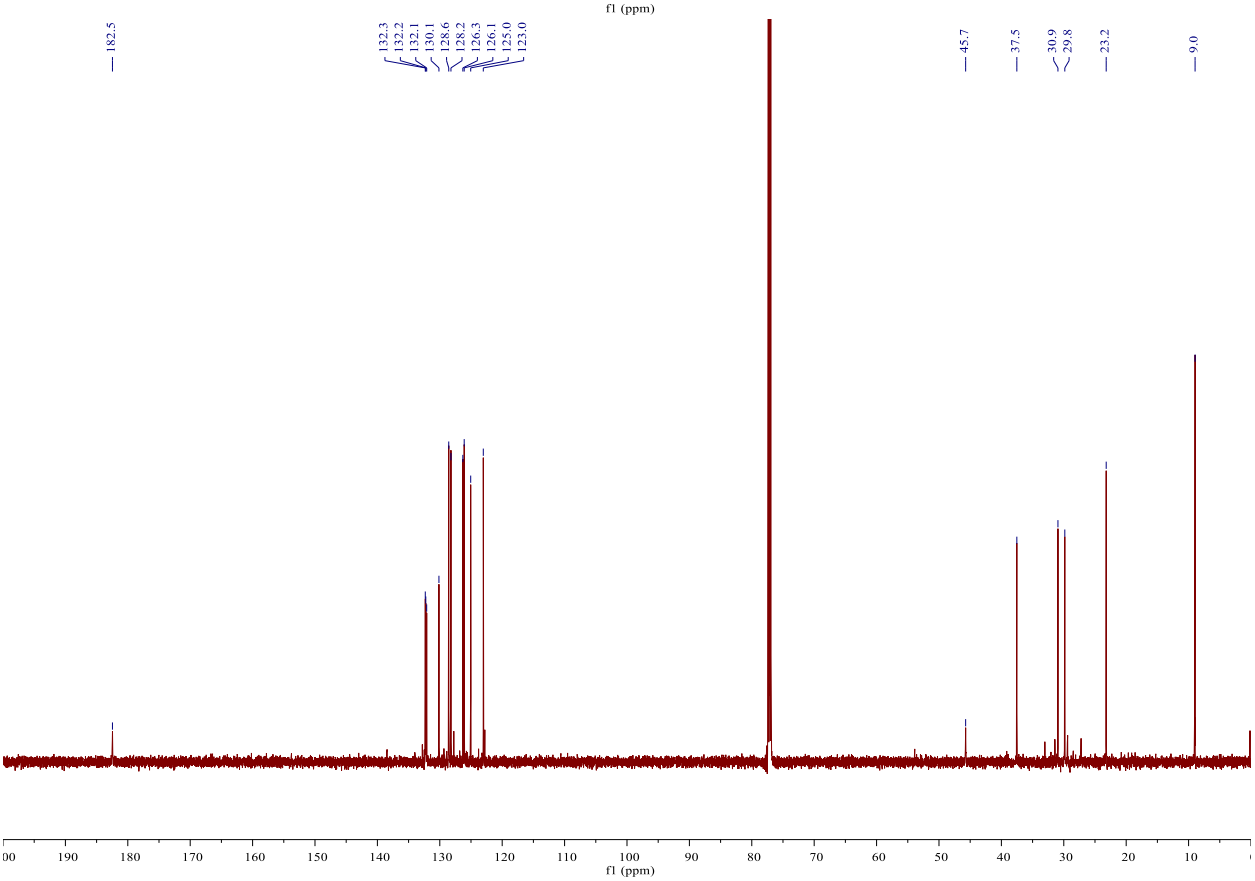
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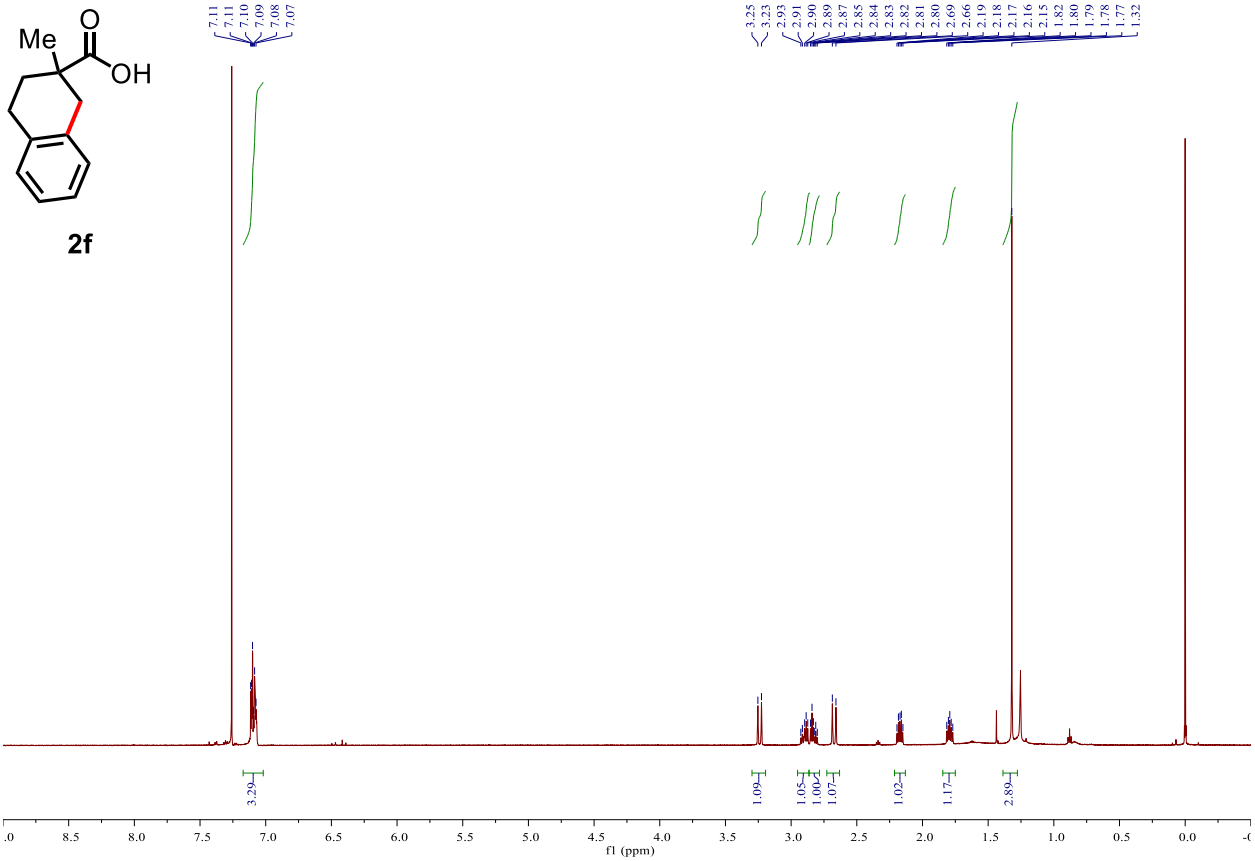
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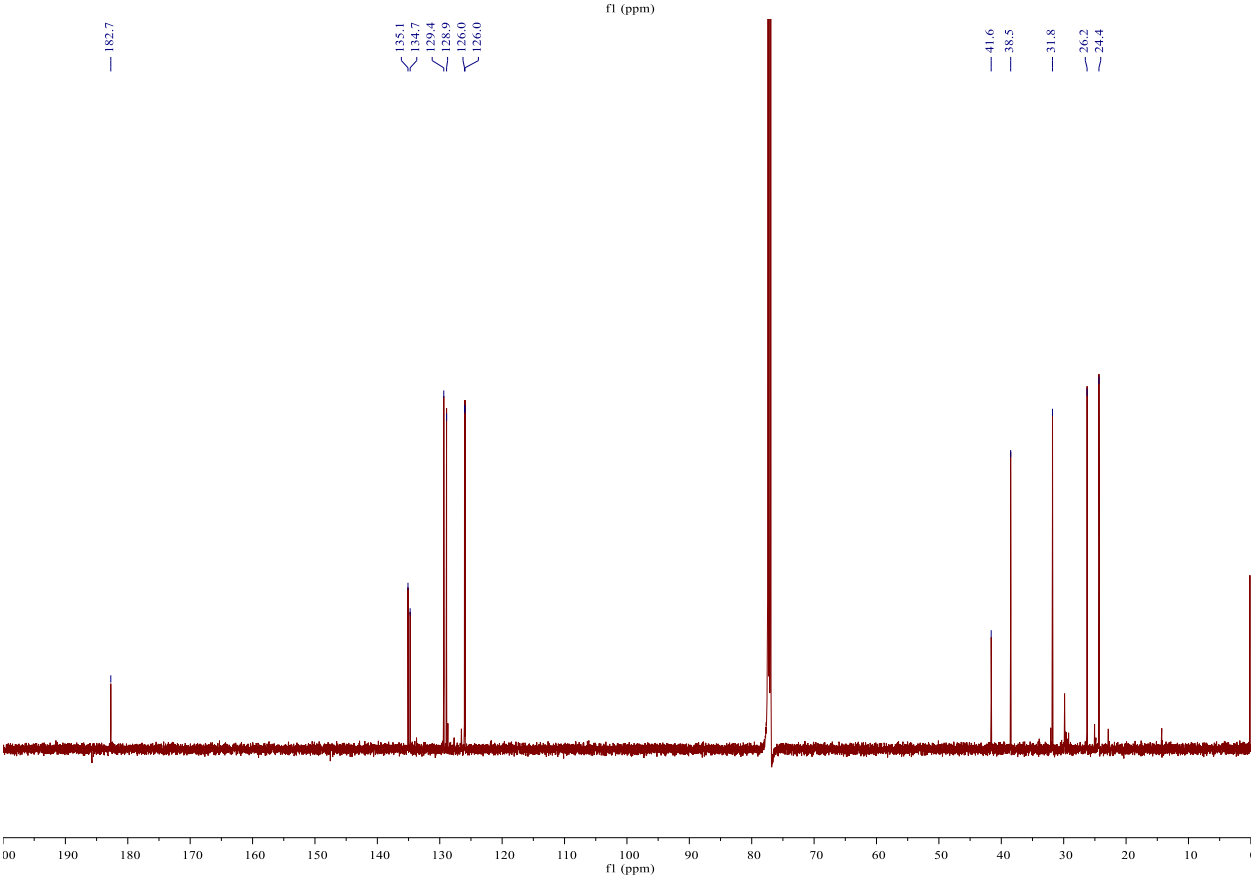
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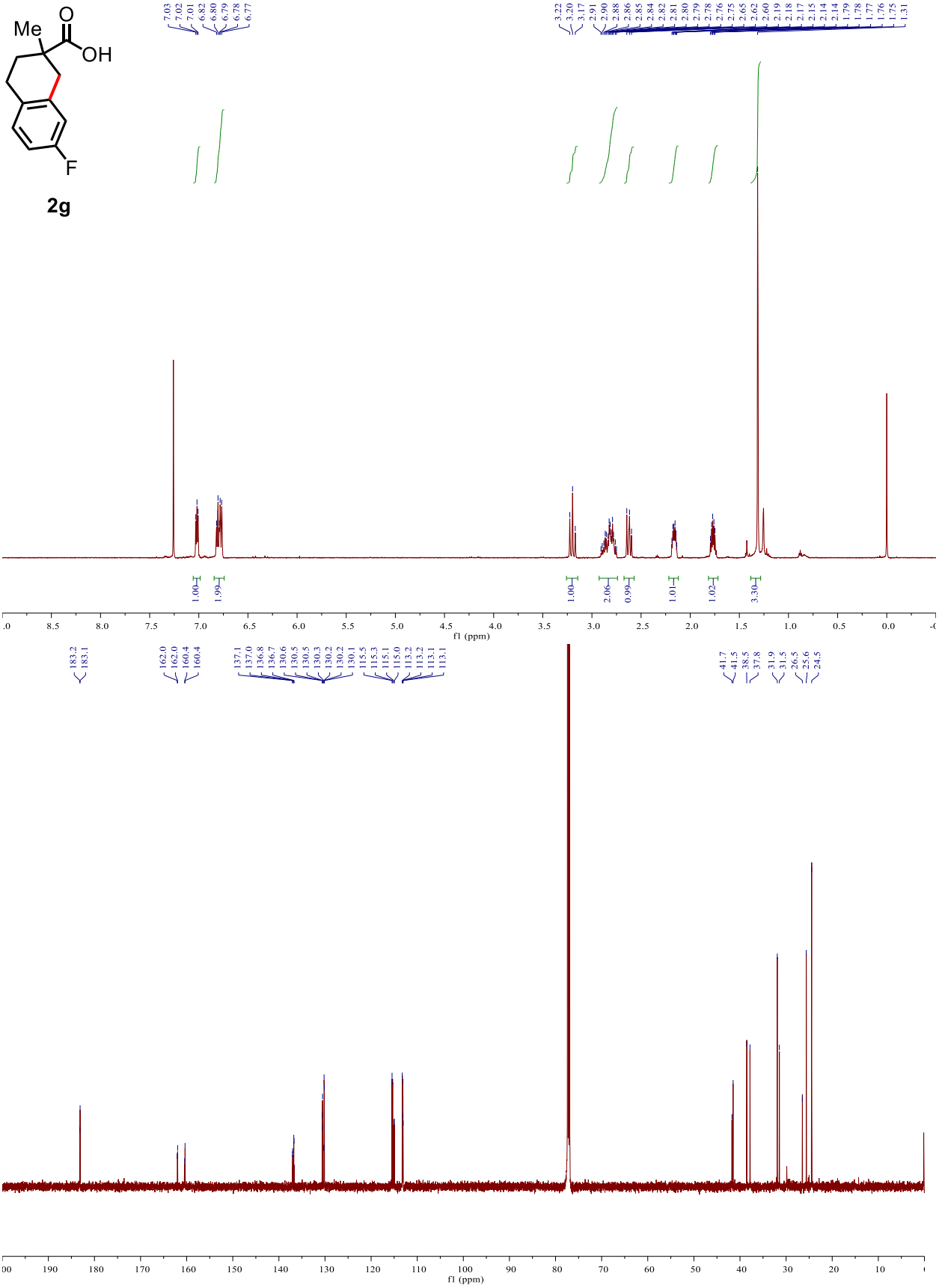
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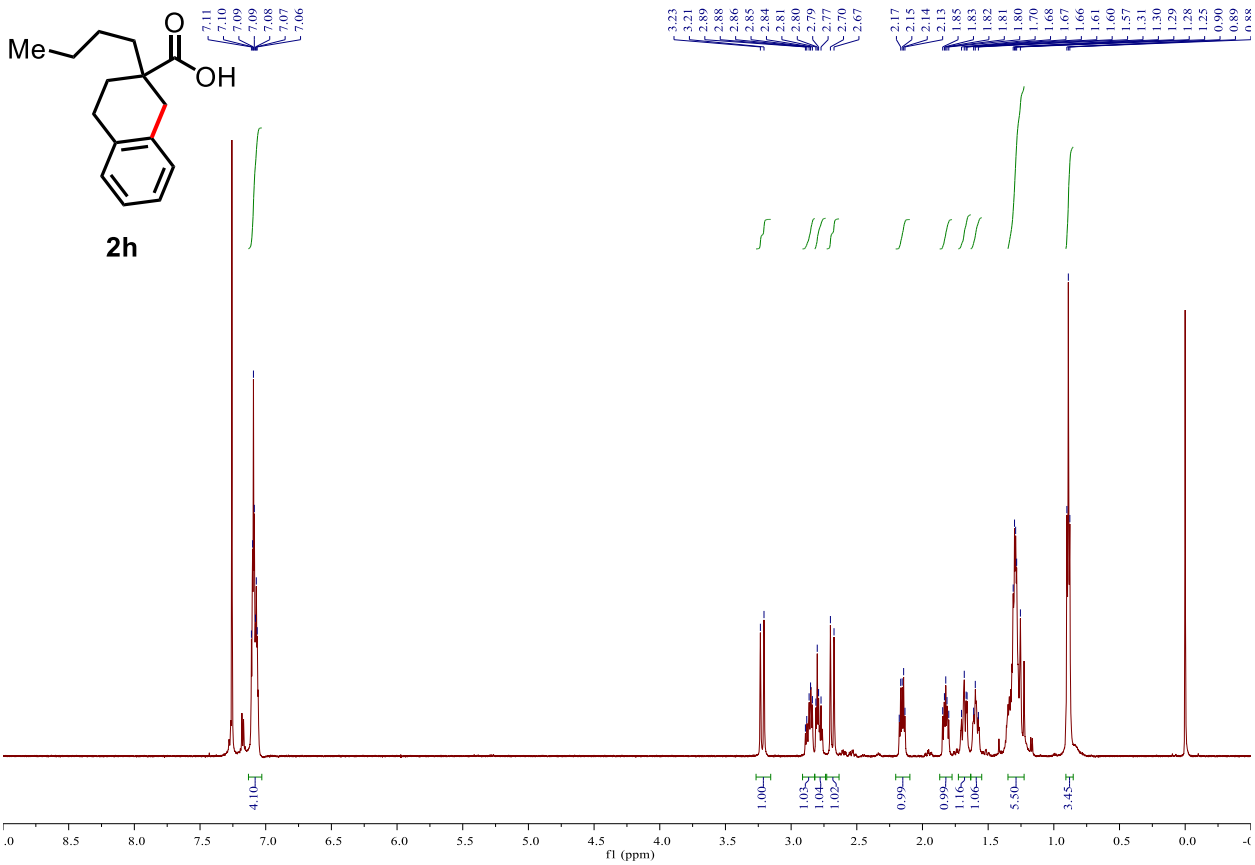
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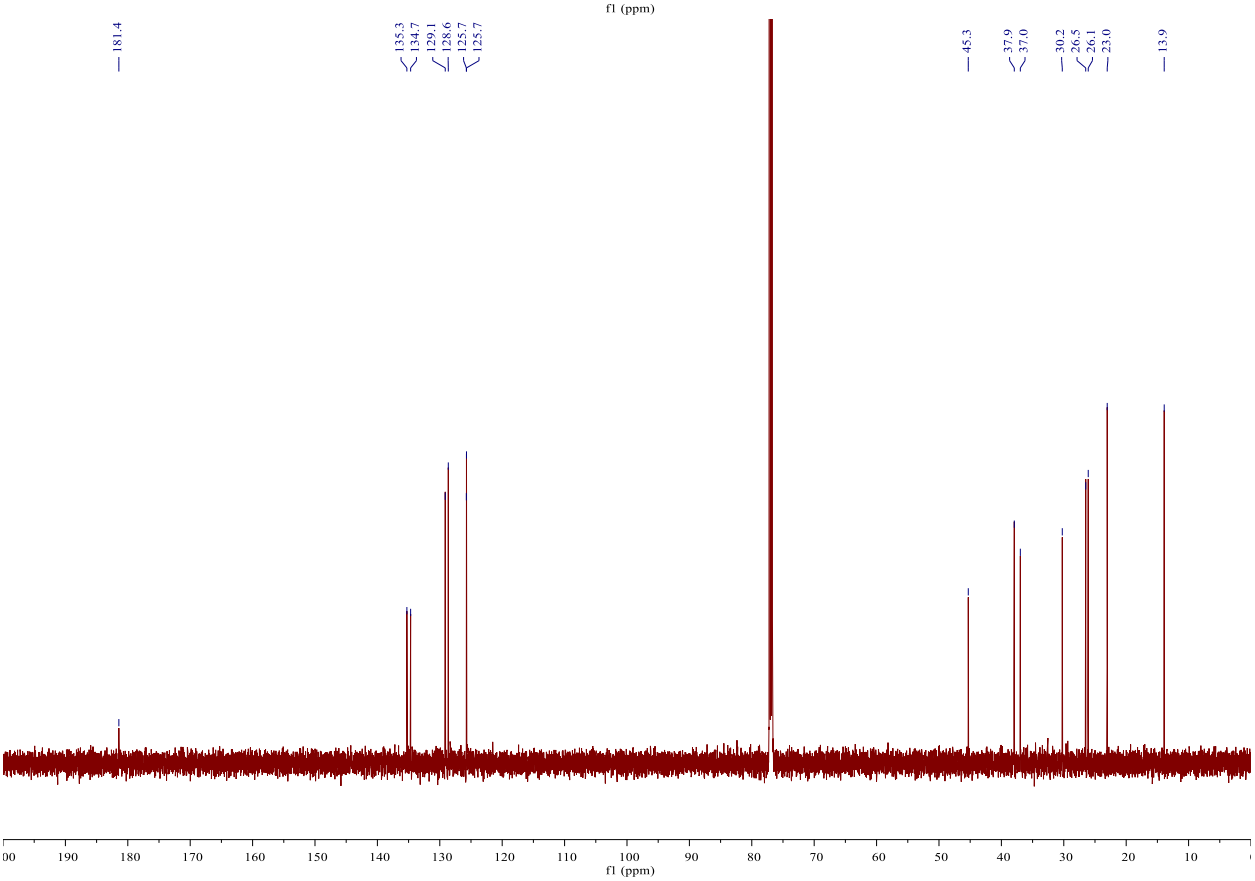
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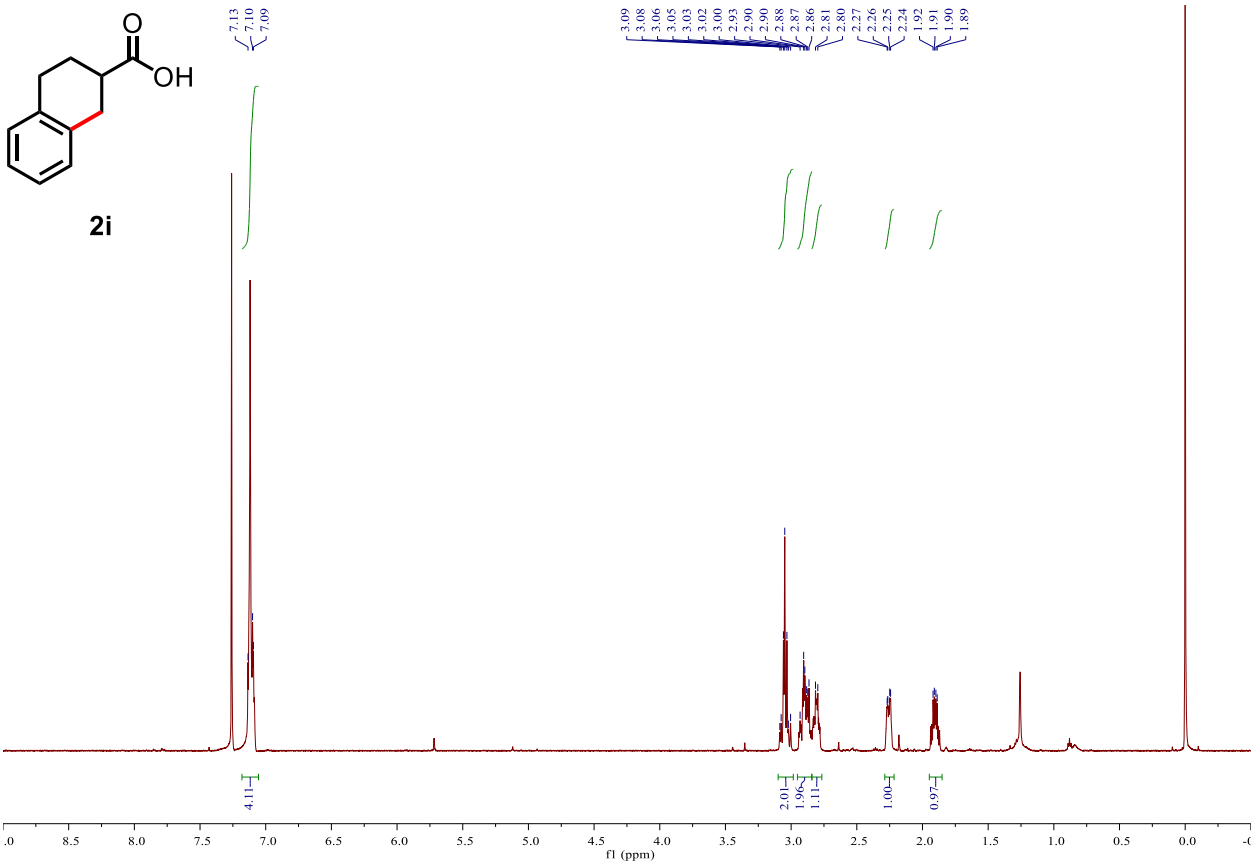
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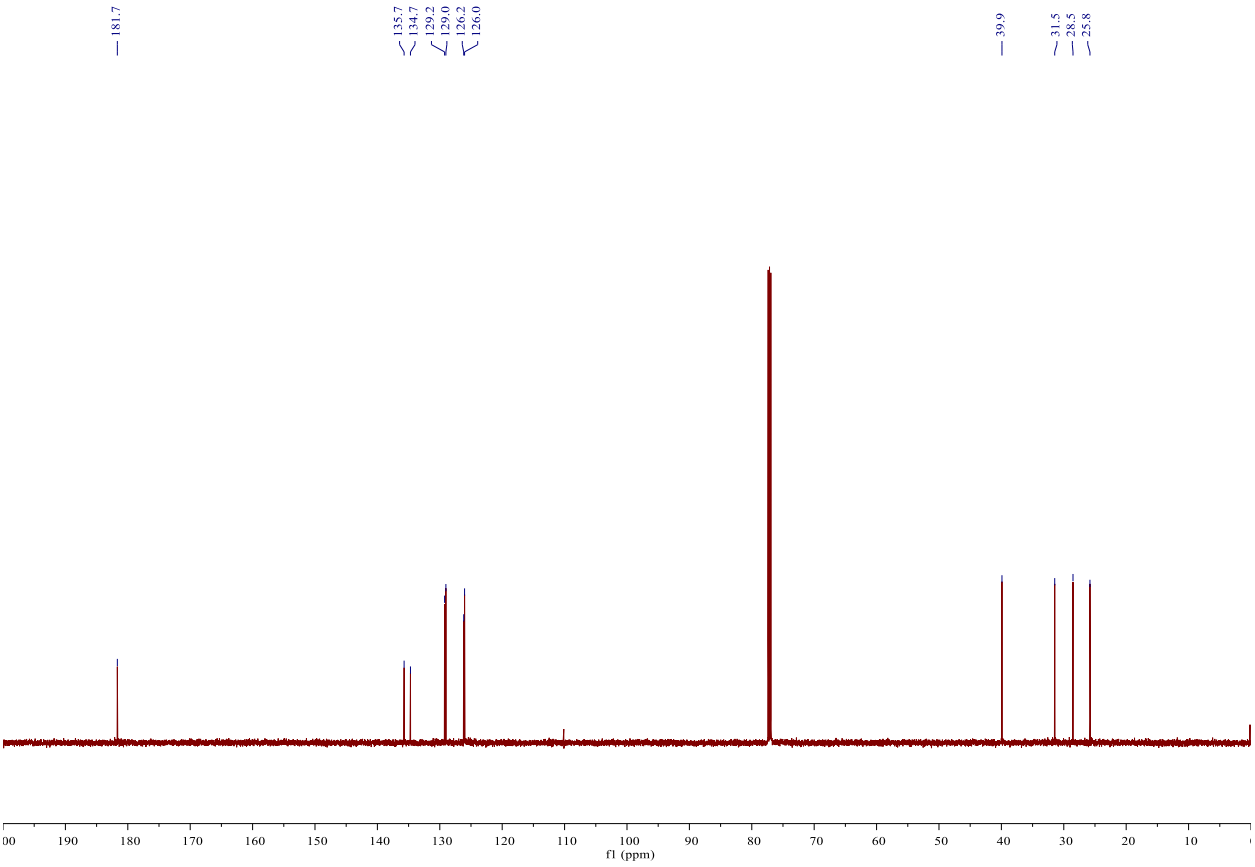
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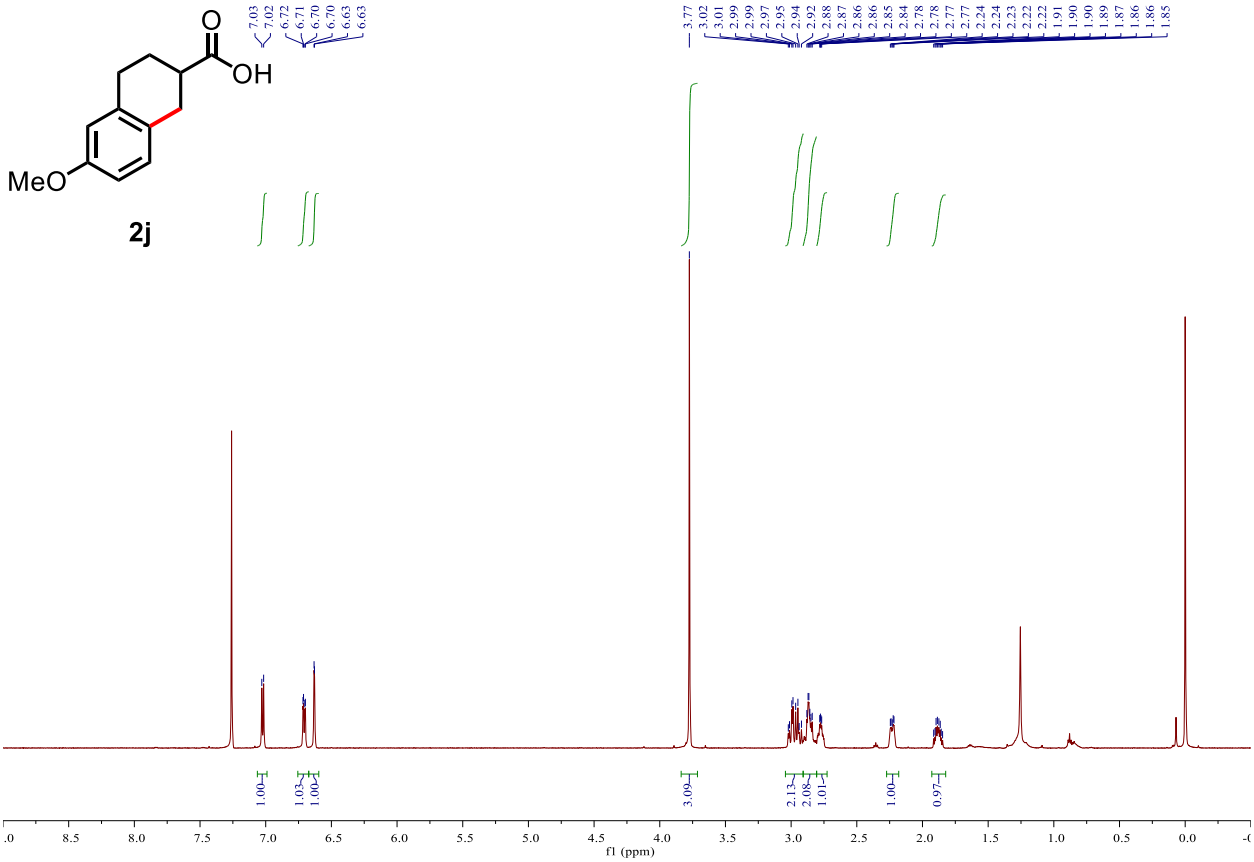
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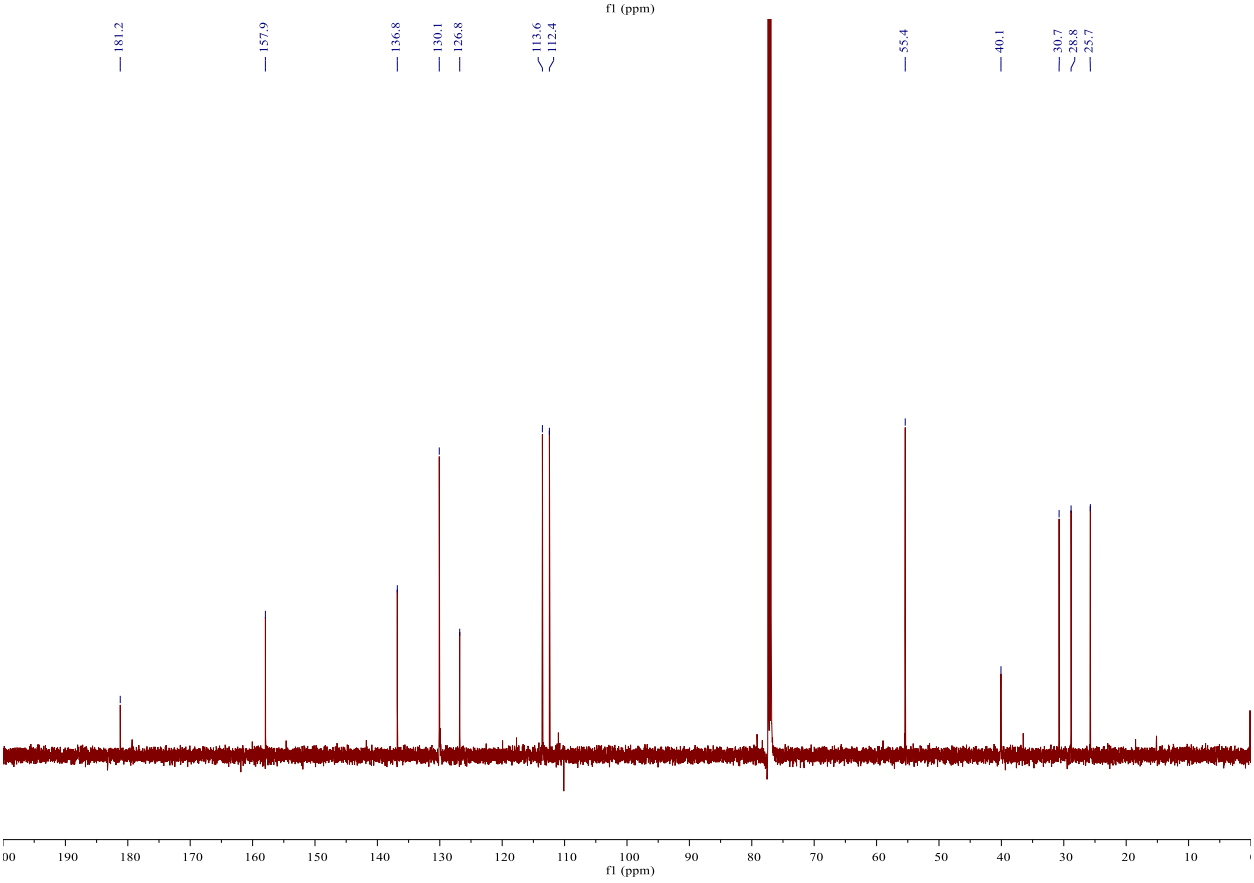
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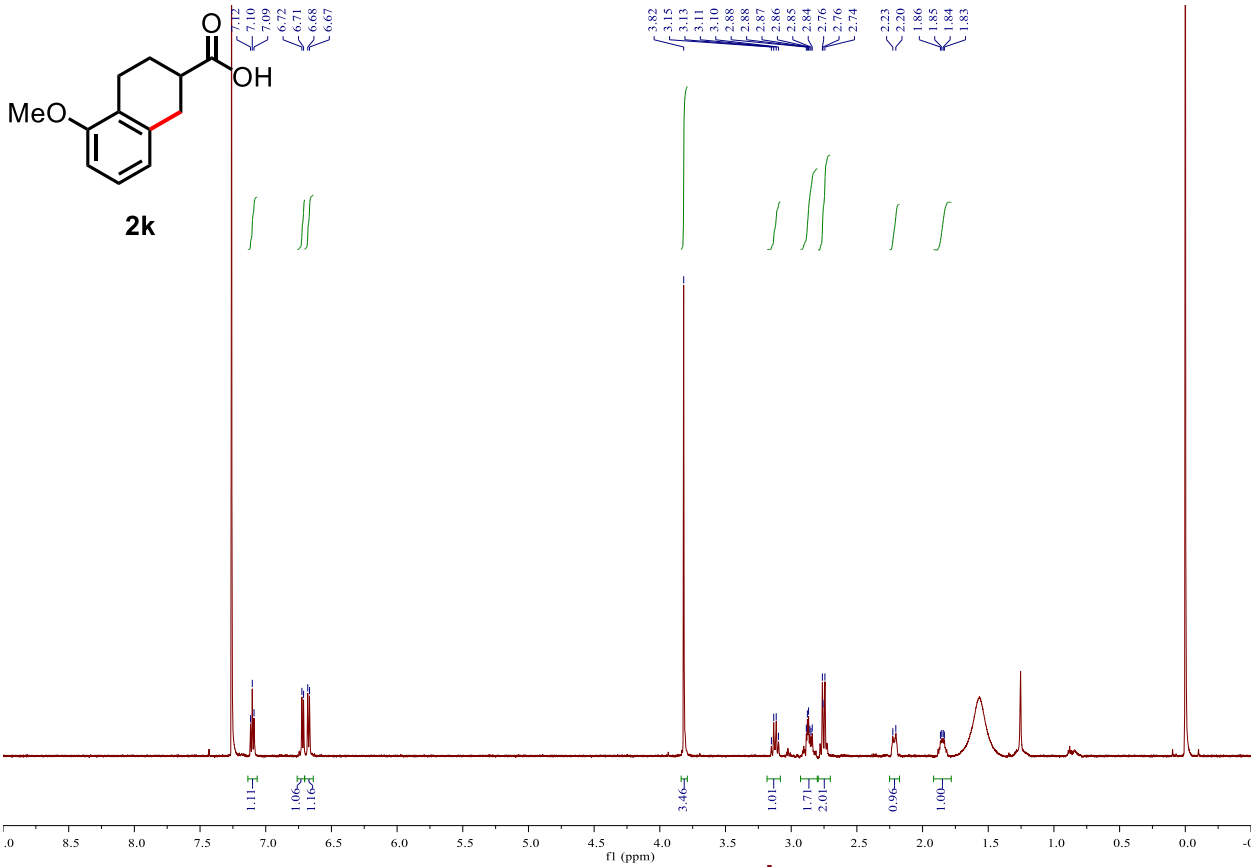
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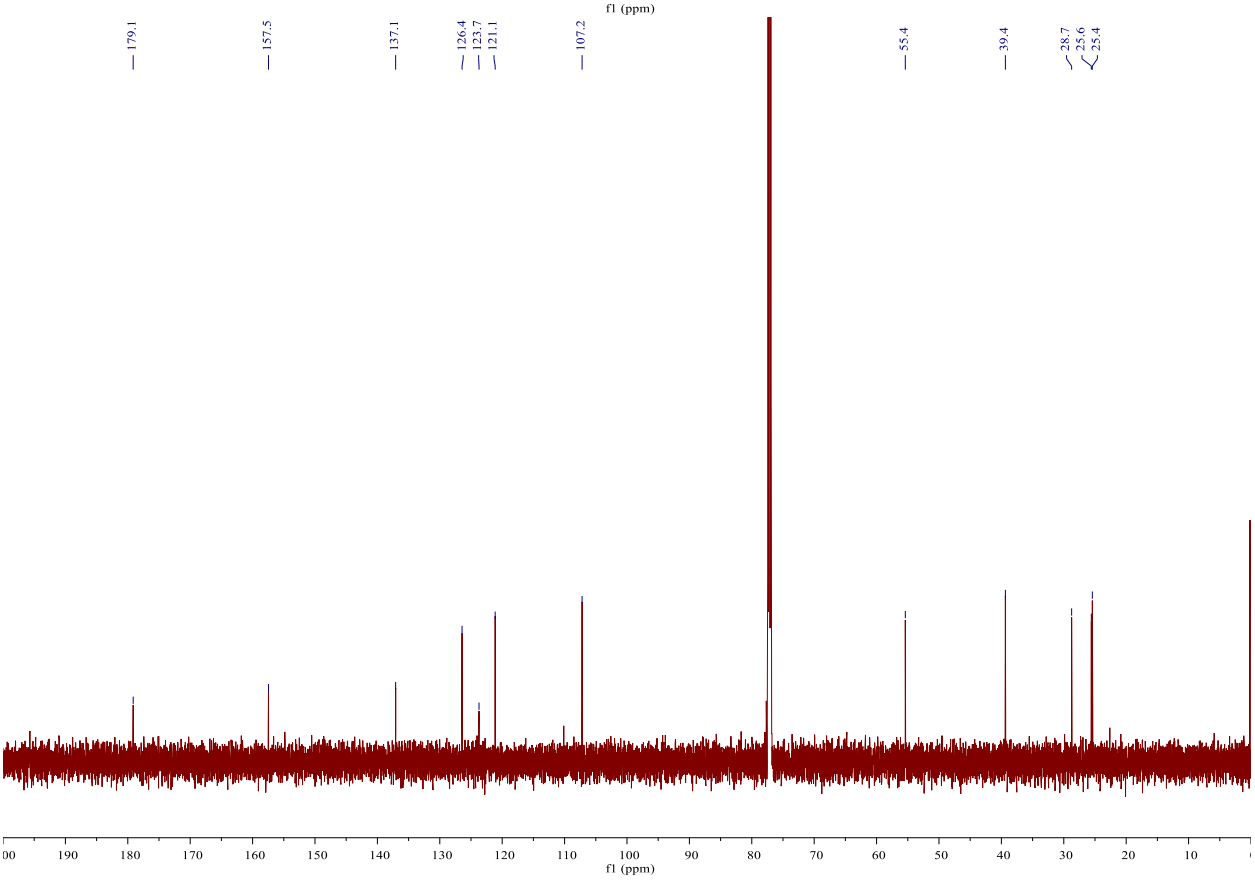
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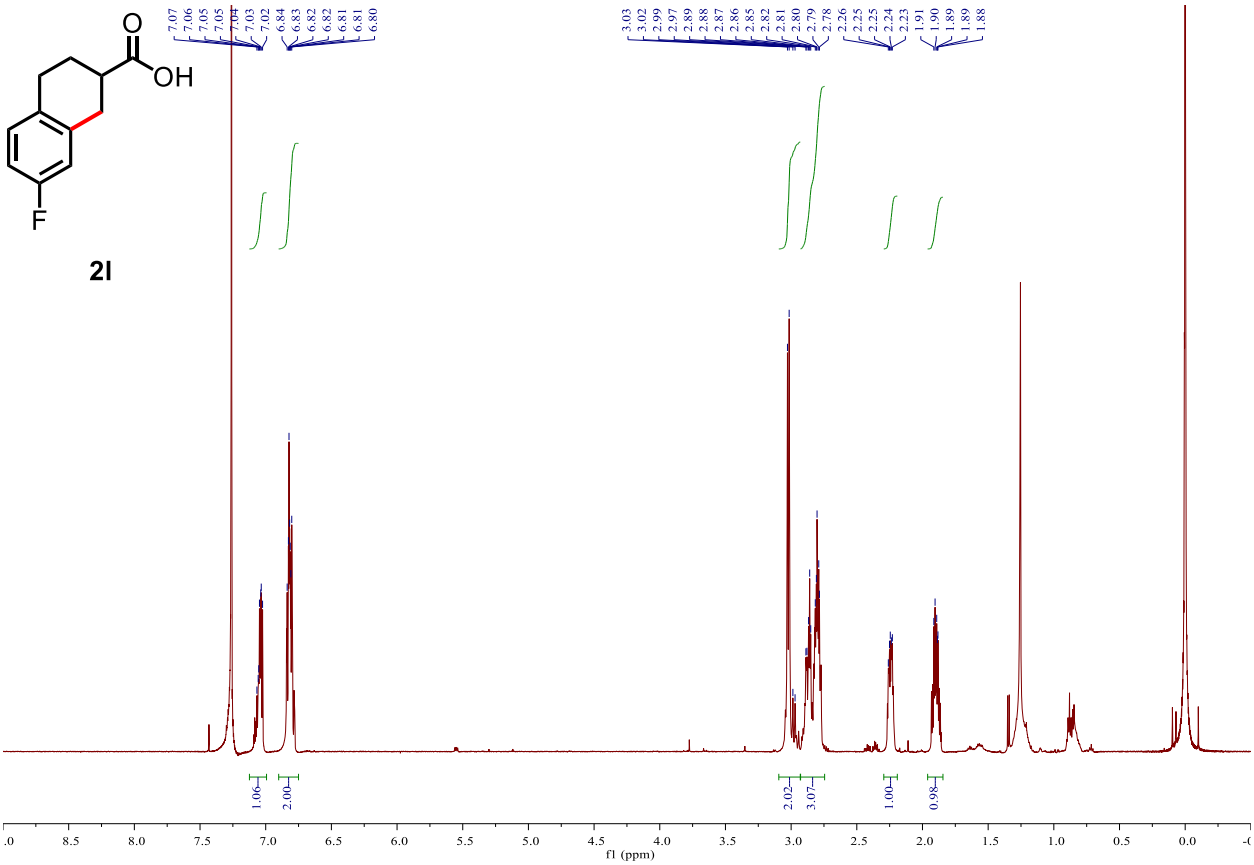
f1 (ppm)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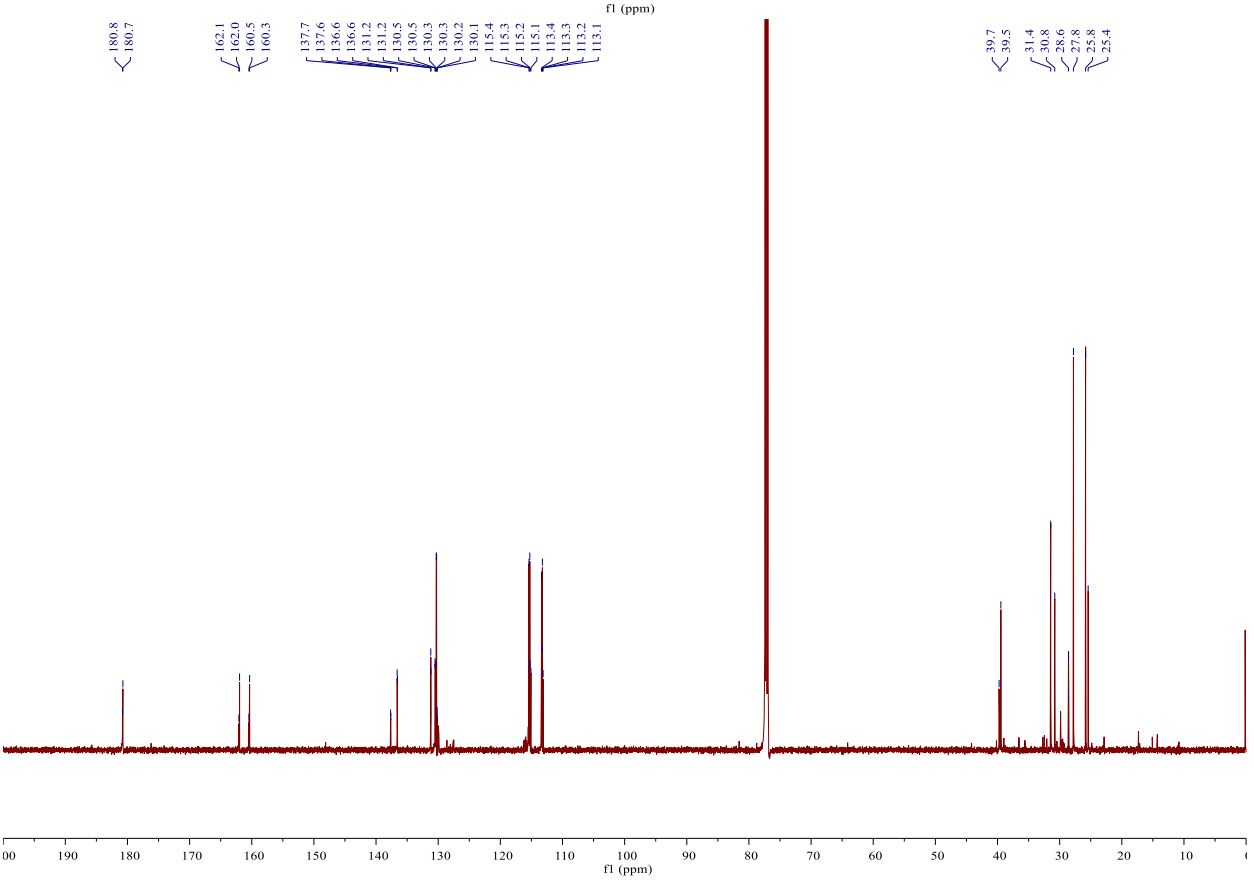
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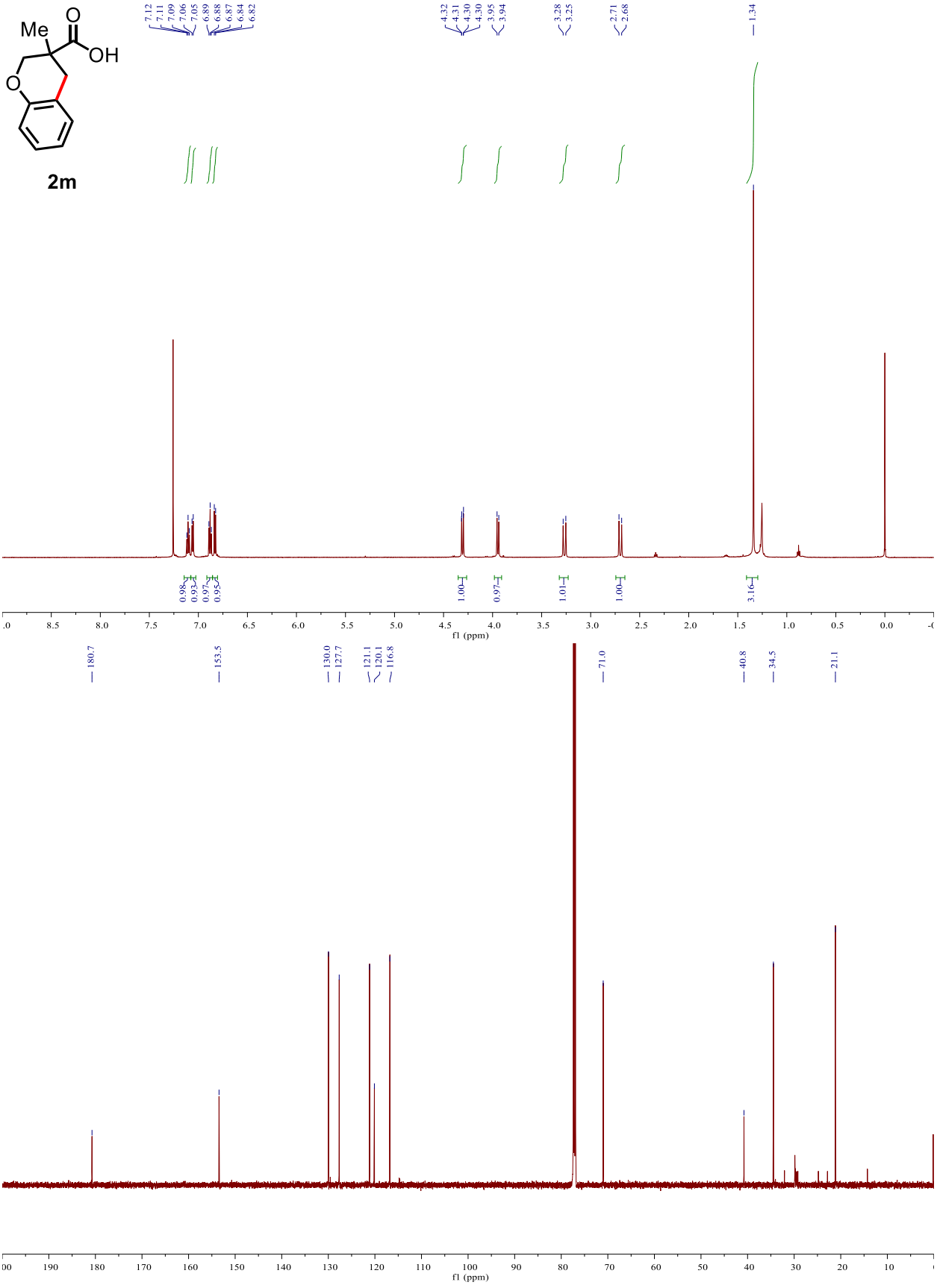
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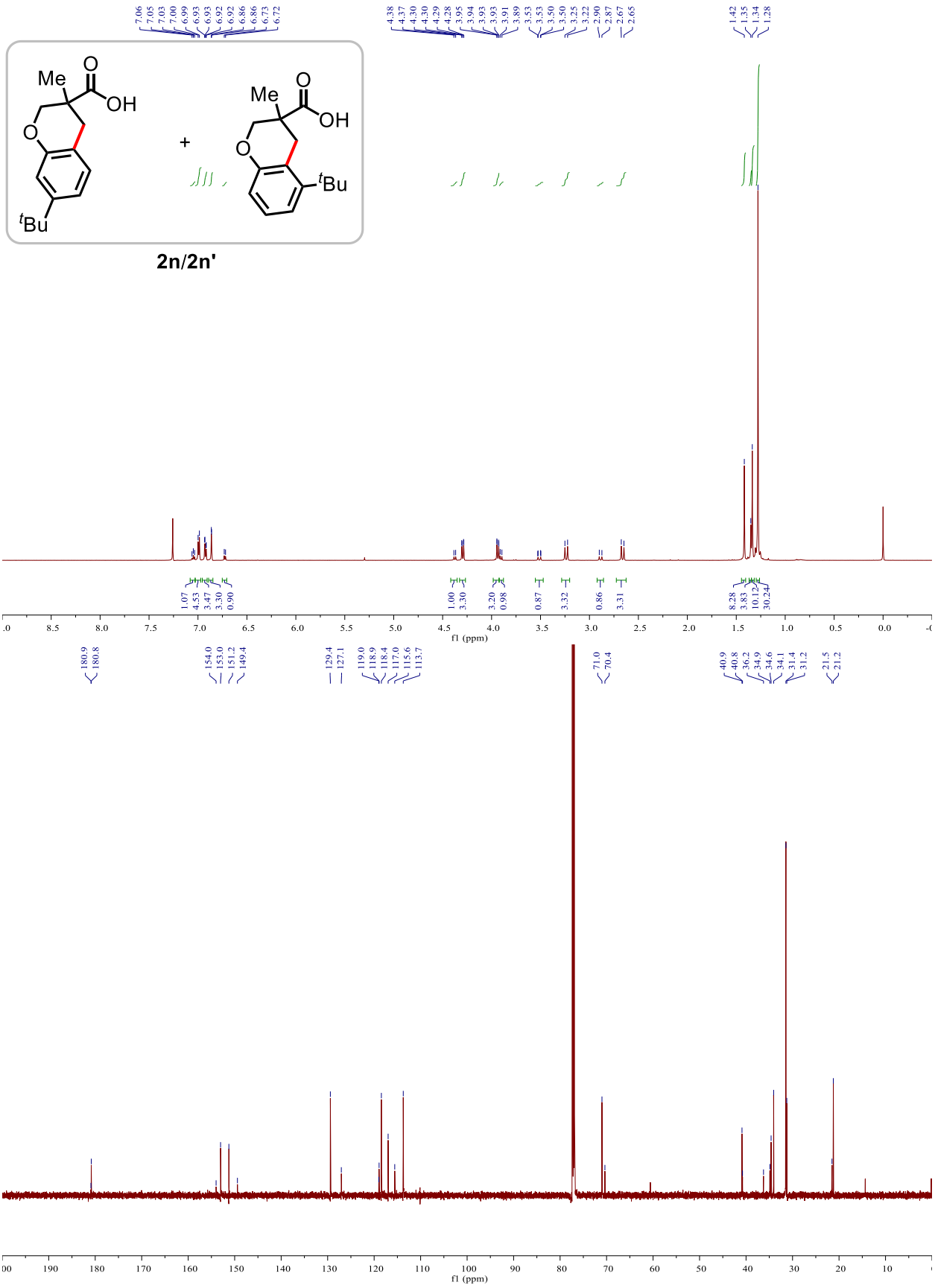
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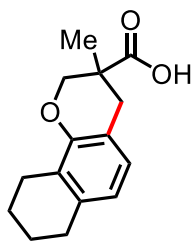
fl (ppm)
fl (ppm)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2o

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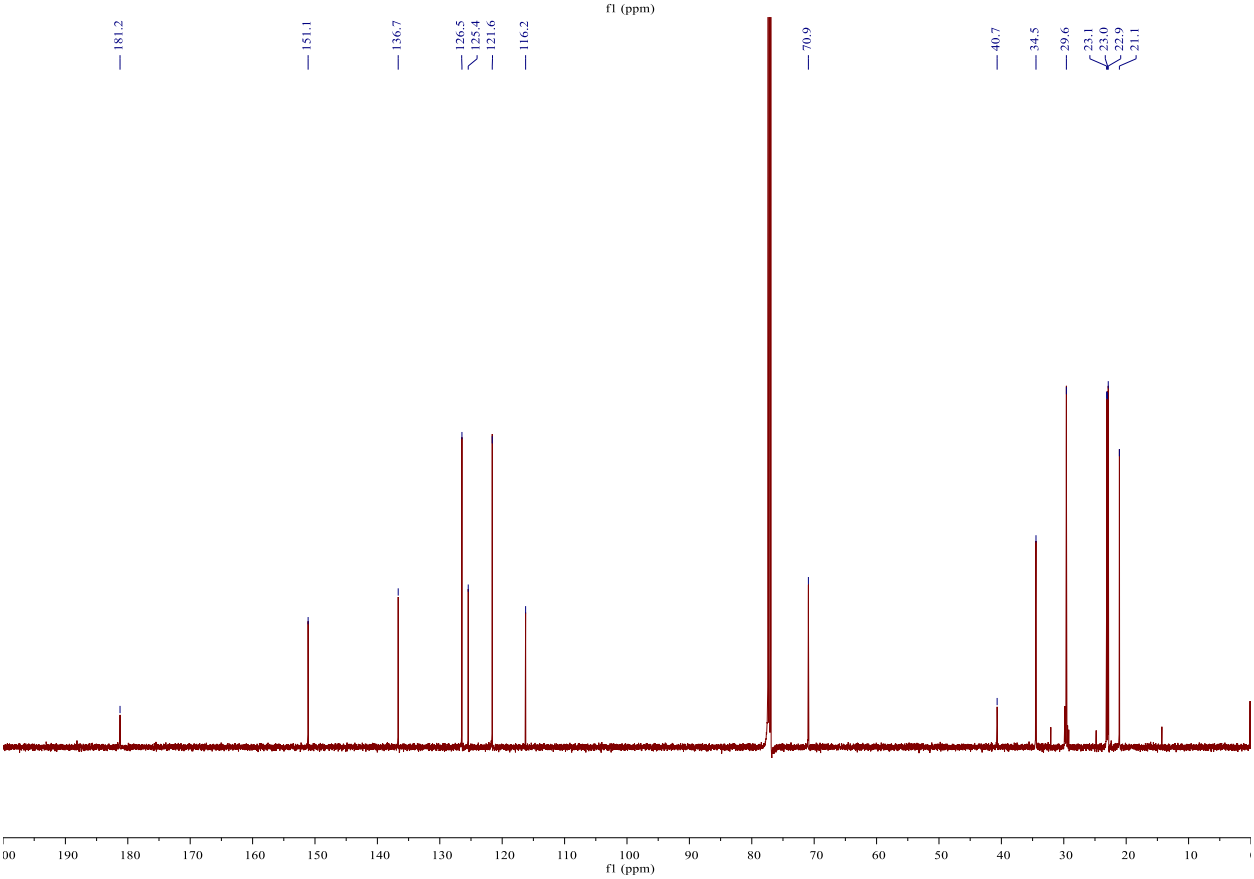
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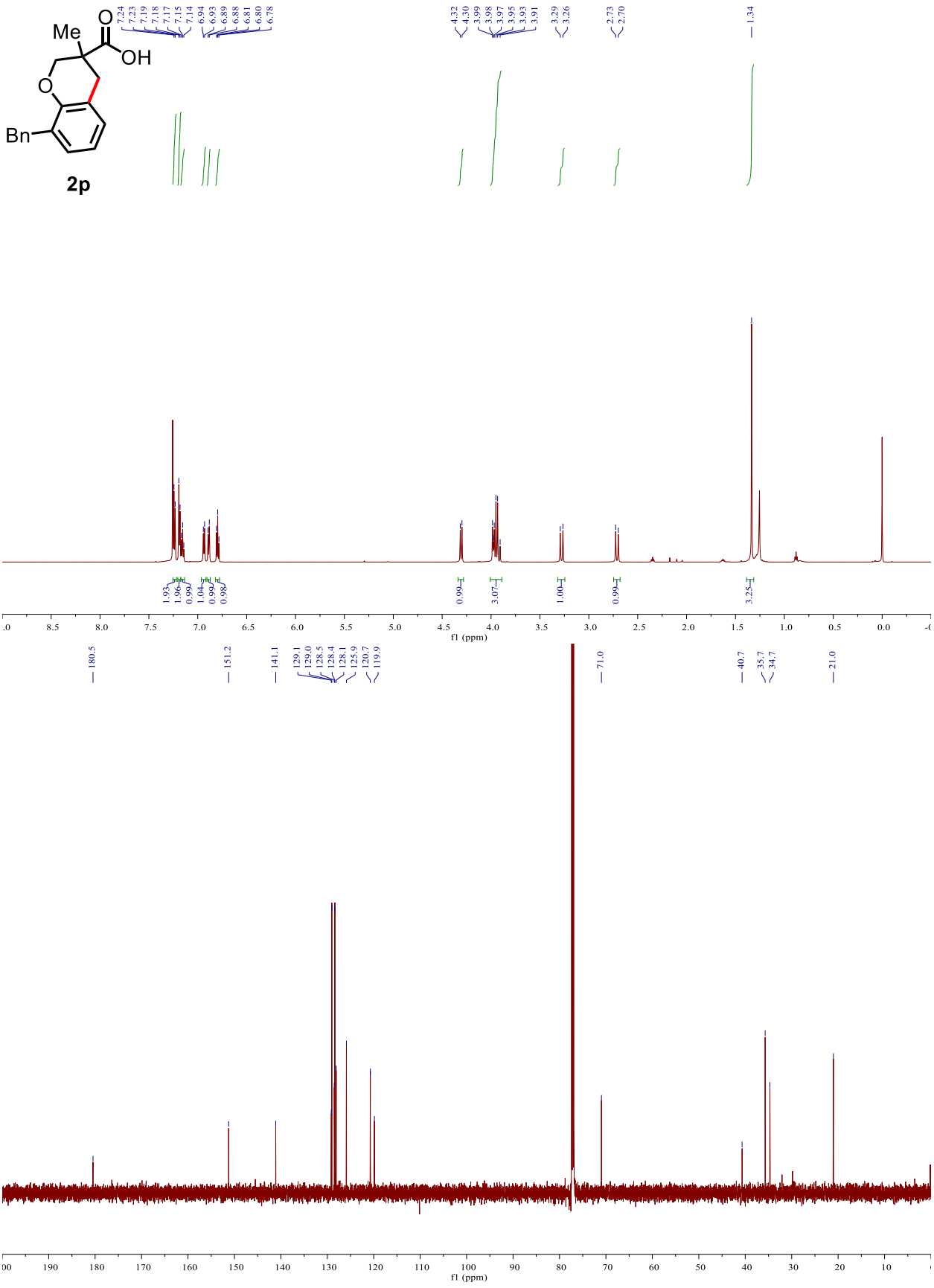
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OH
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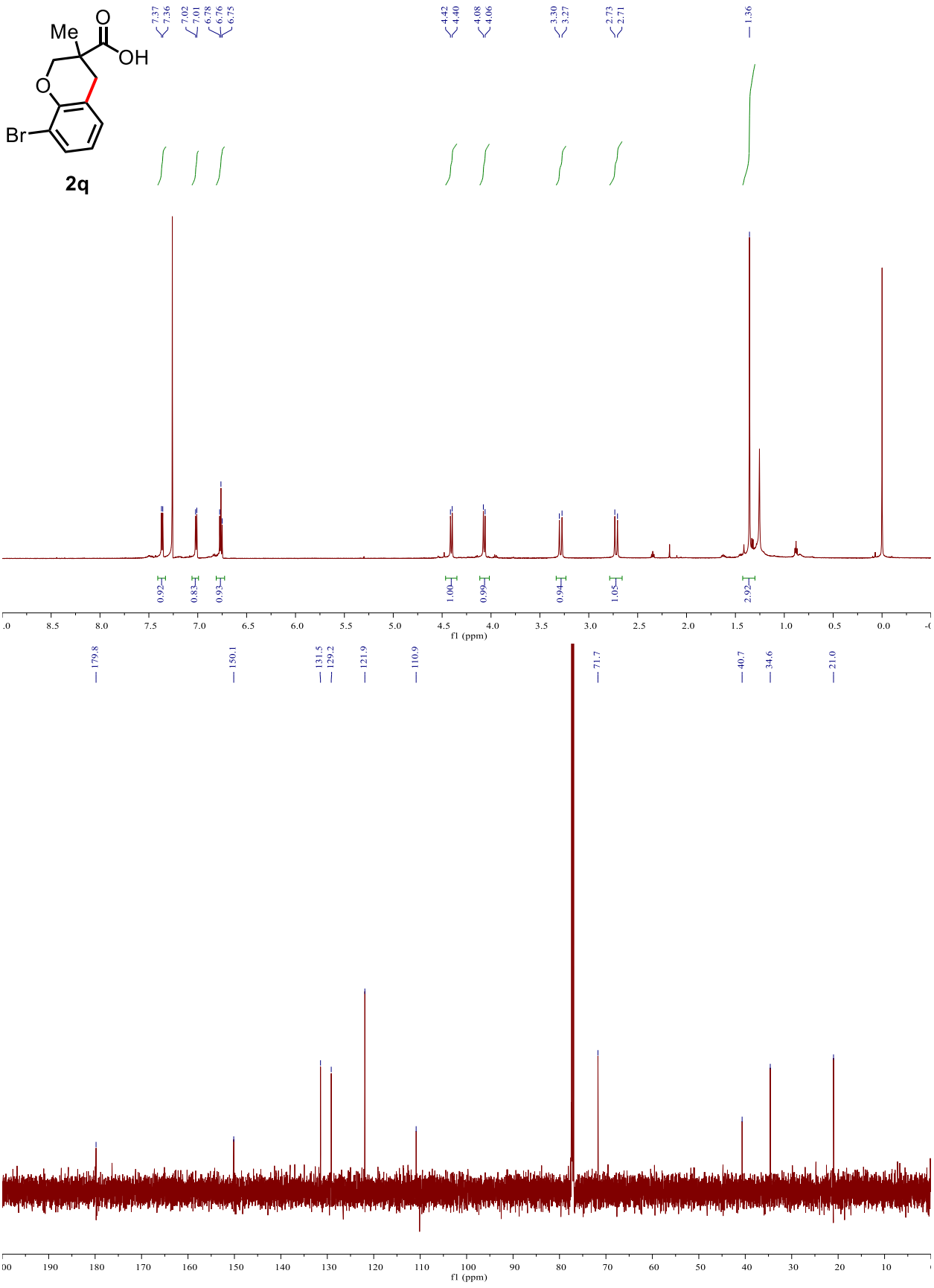
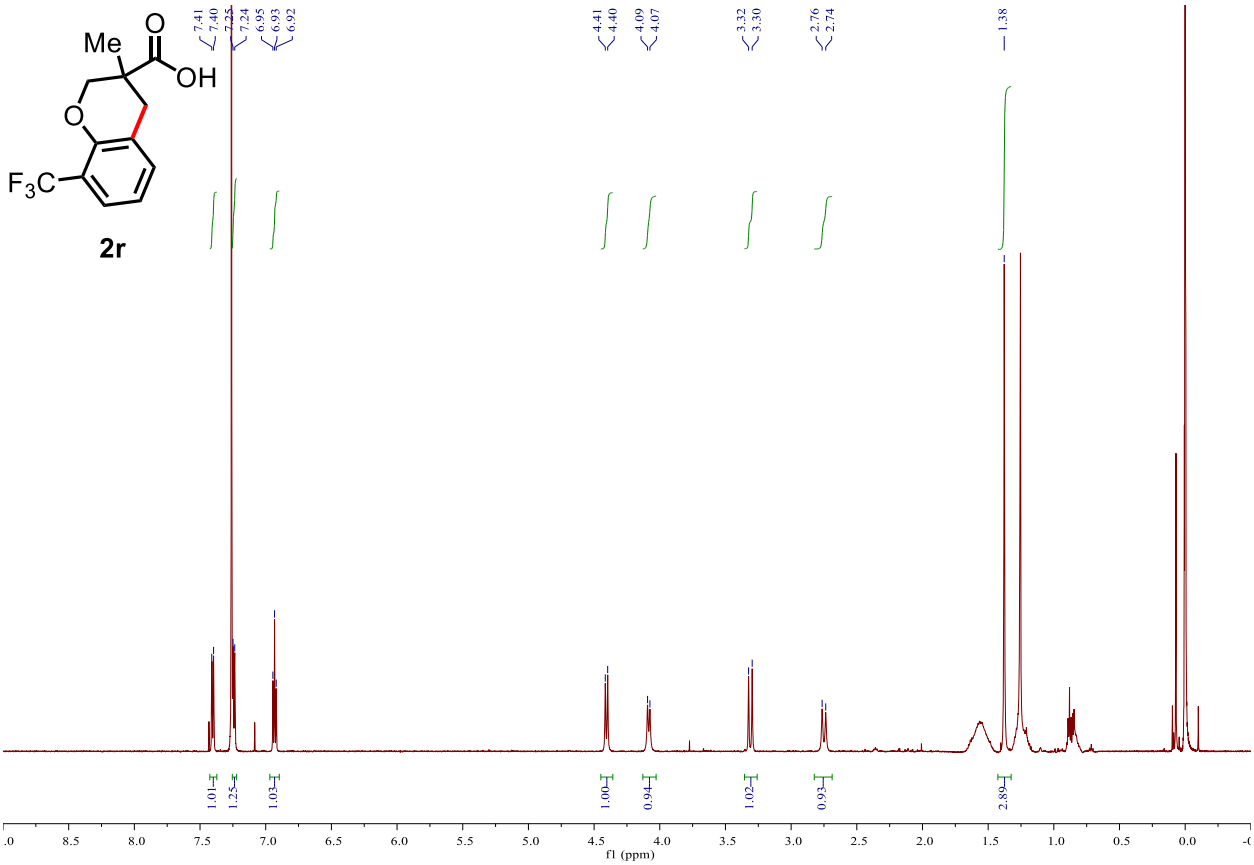
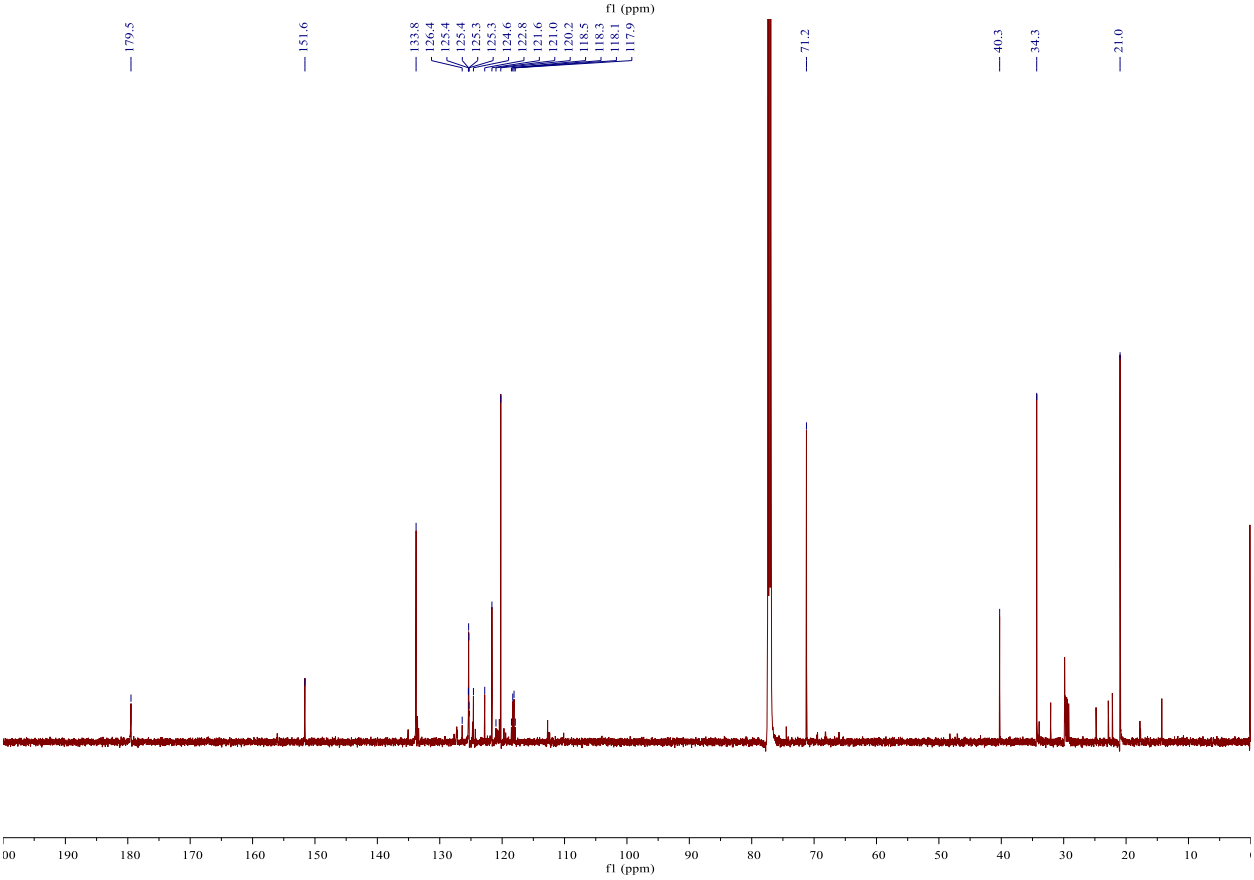
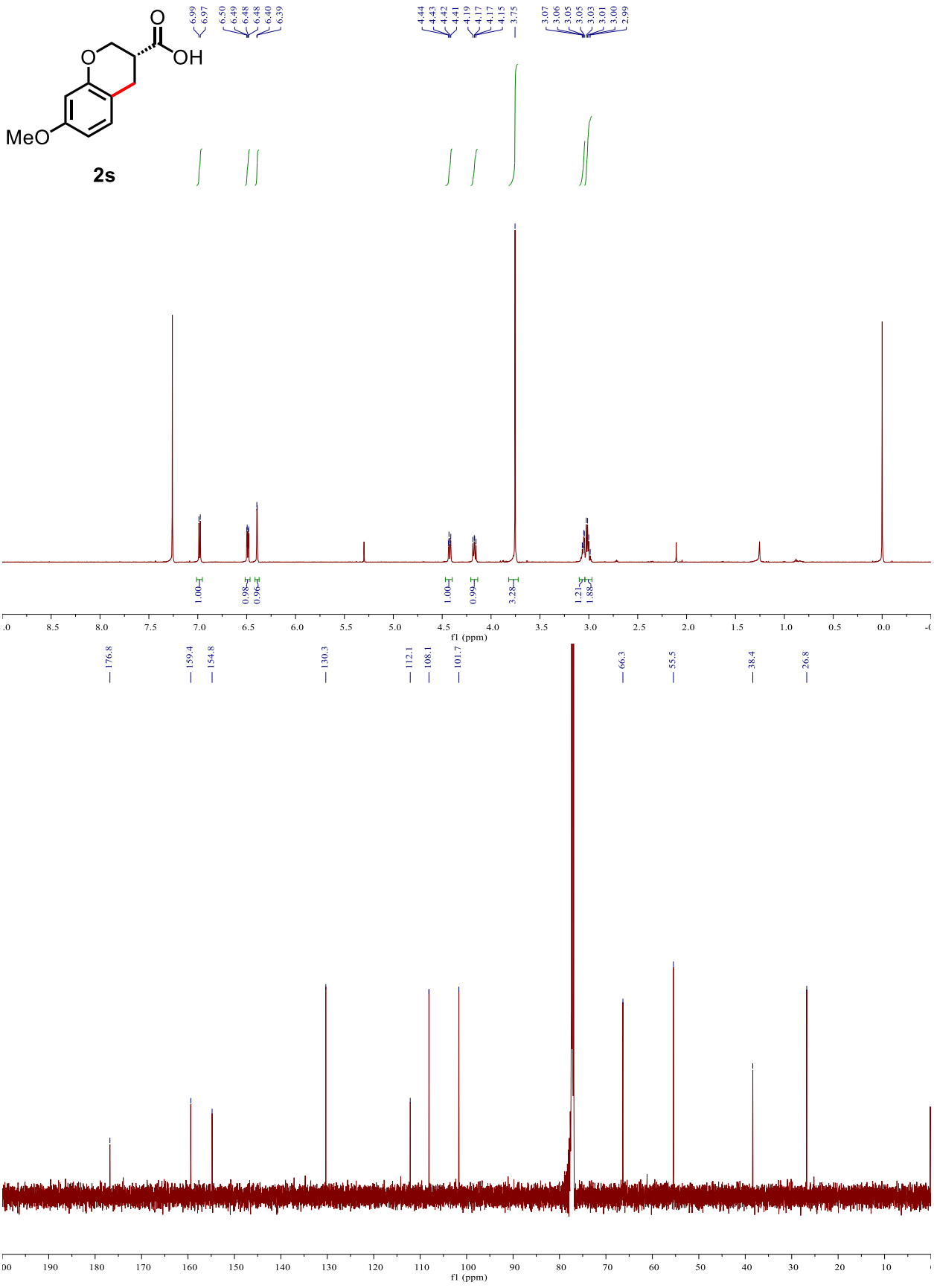
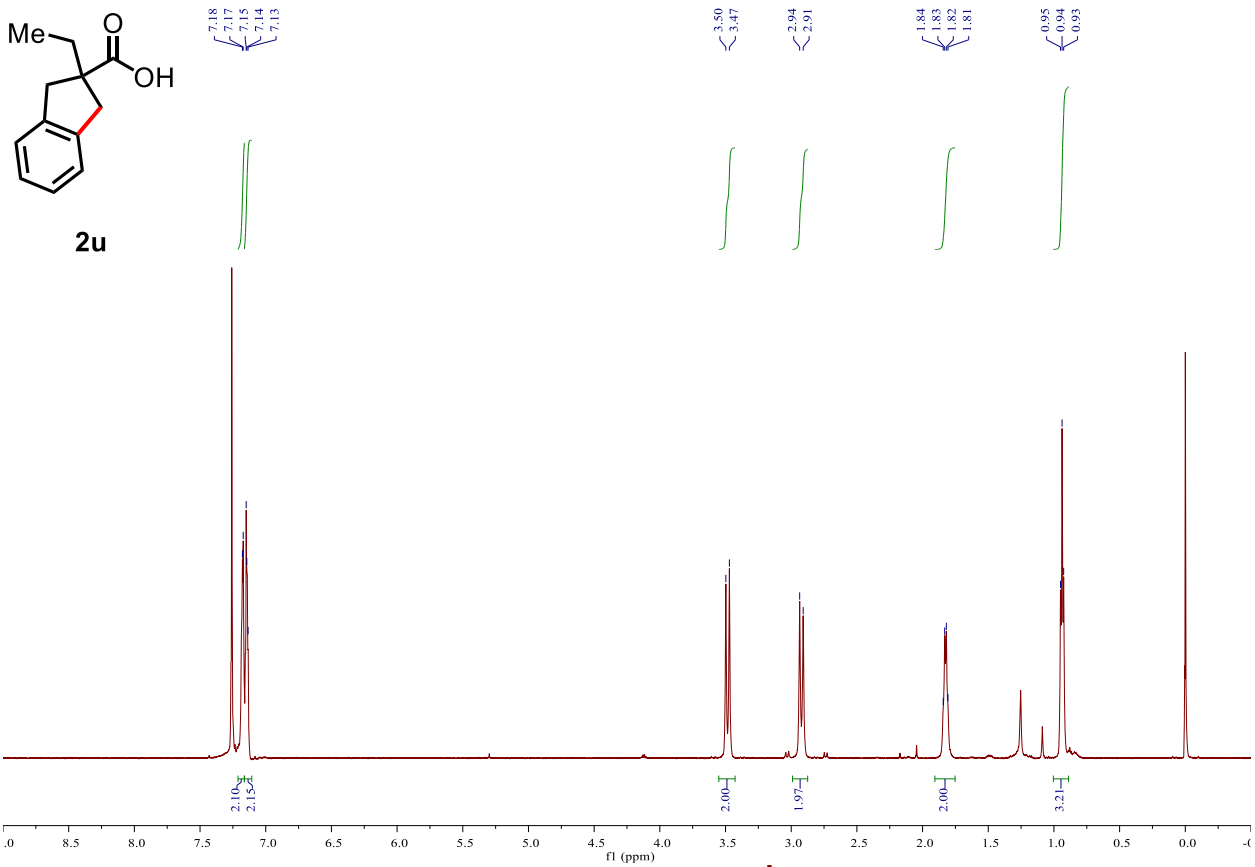
Bn
2p
f1 (ppm)

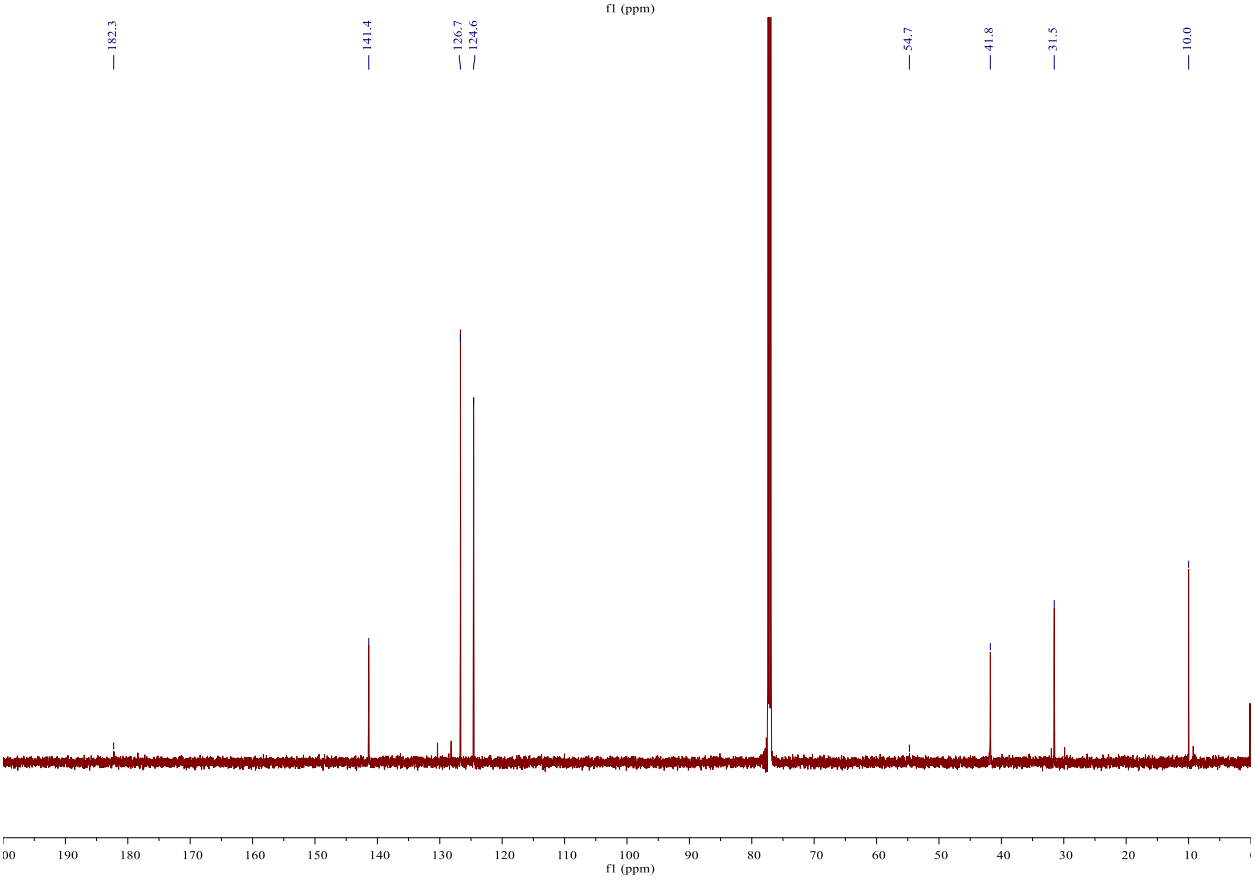

Me
O
OH
O
Br
2q
7.37
7.36
7.02
7.01
6.78
6.76
6.75
4.42
4.40
4.08
4.06
3.30
3.27
2.73
2.71
1.36
0.92
0.83
0.93
1.00
0.99
0.94
1.05
2.92
f1 (ppm)
179.8
150.1
131.5
129.2
121.9
110.9
71.7
40.7
34.6
21.0
f1 (ppm)

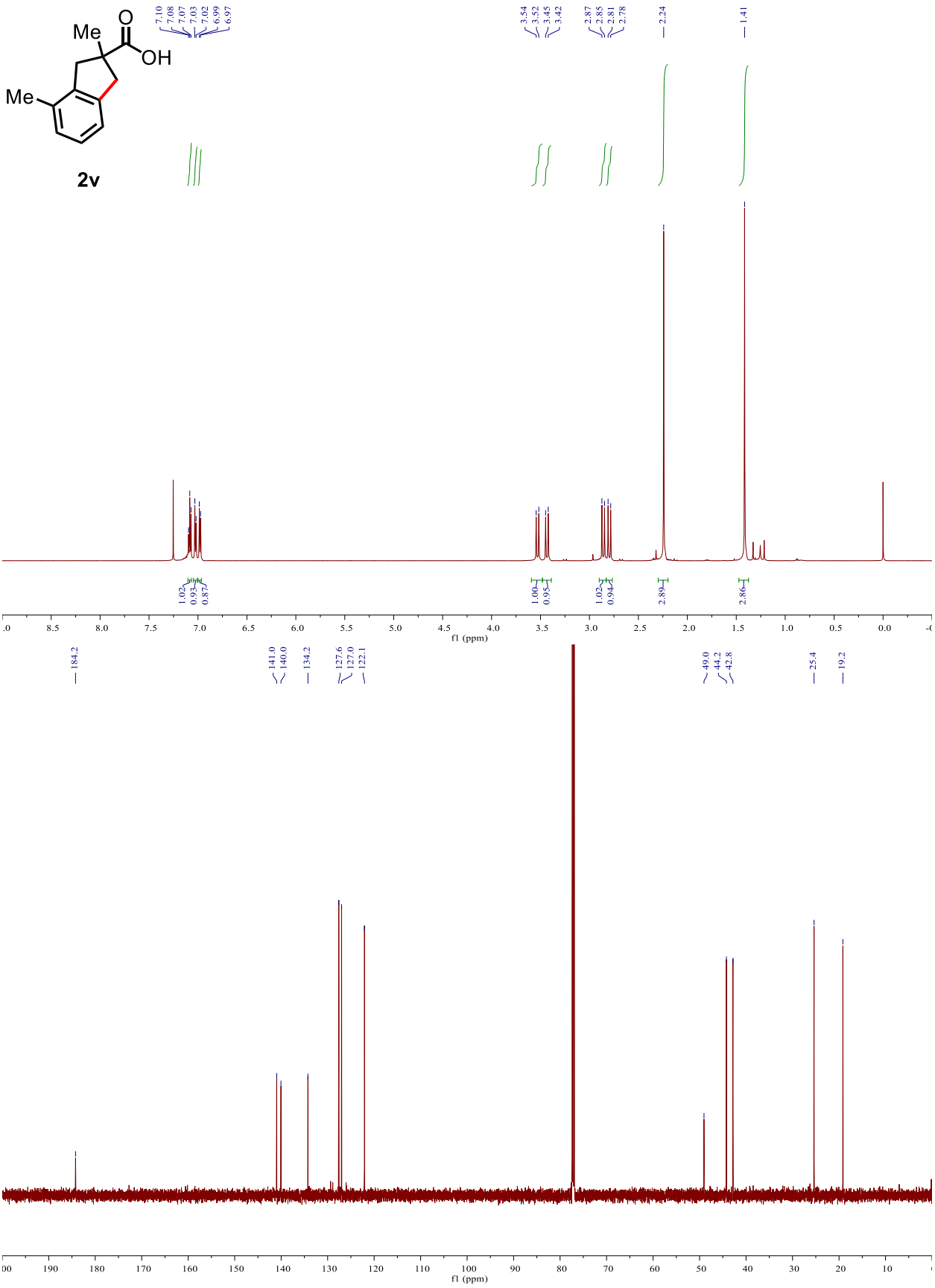

Me
O
OH
O
F3C
2r
7.41
7.40
7.25
7.24
6.95
6.93
6.92
4.41
4.40
4.09
4.07
3.32
3.30
2.76
2.74
1.38
1.01
1.25
1.03
1.00
0.94
1.02
0.93
2.89
f1 (ppm)

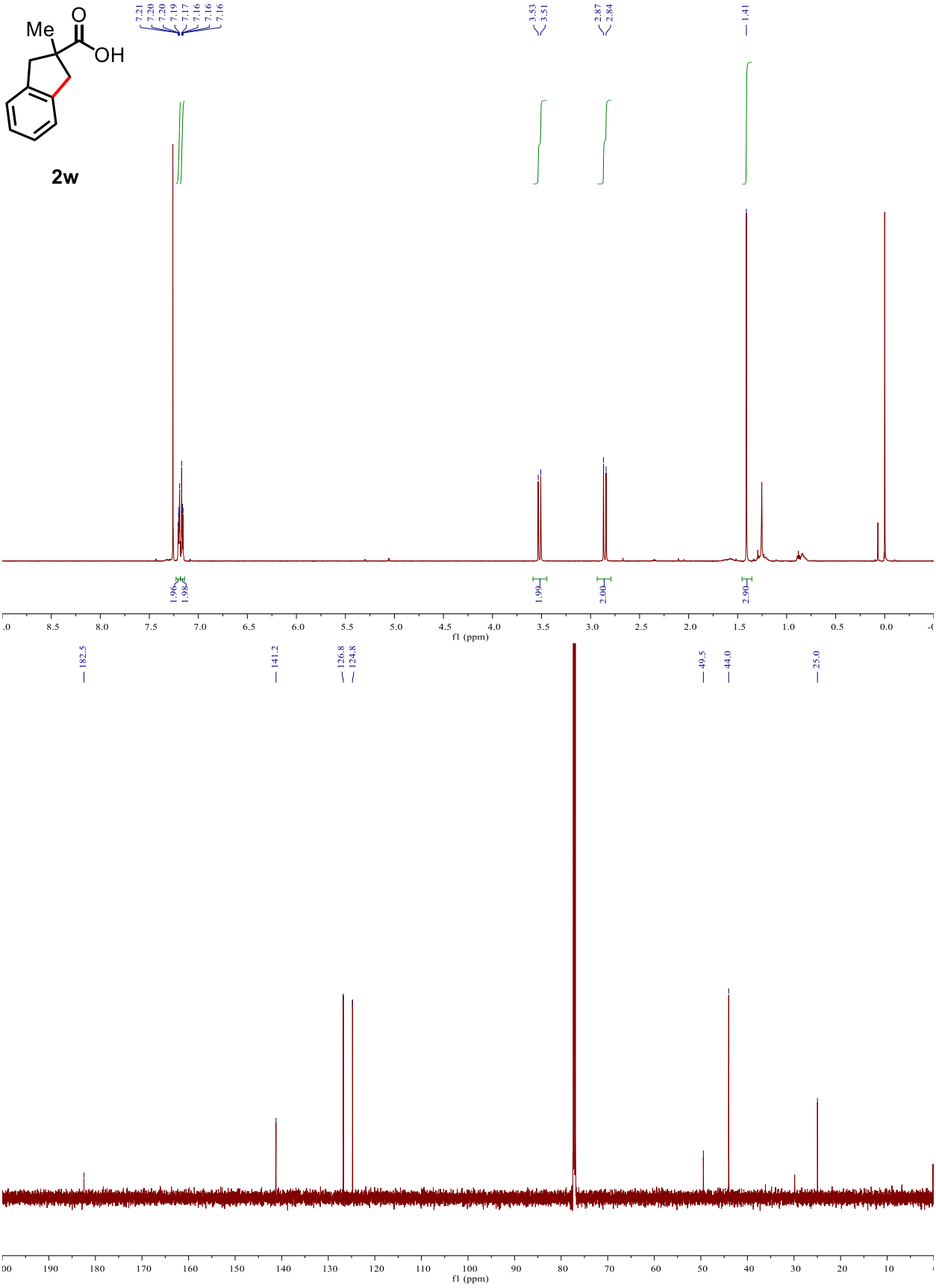

179.5
151.6
133.8
126.4
125.4
125.4
125.3
125.3
124.6
122.8
121.6
121.0
120.2
118.5
118.3
118.1
117.9
71.2
40.3
34.3
21.0
f1 (ppm)

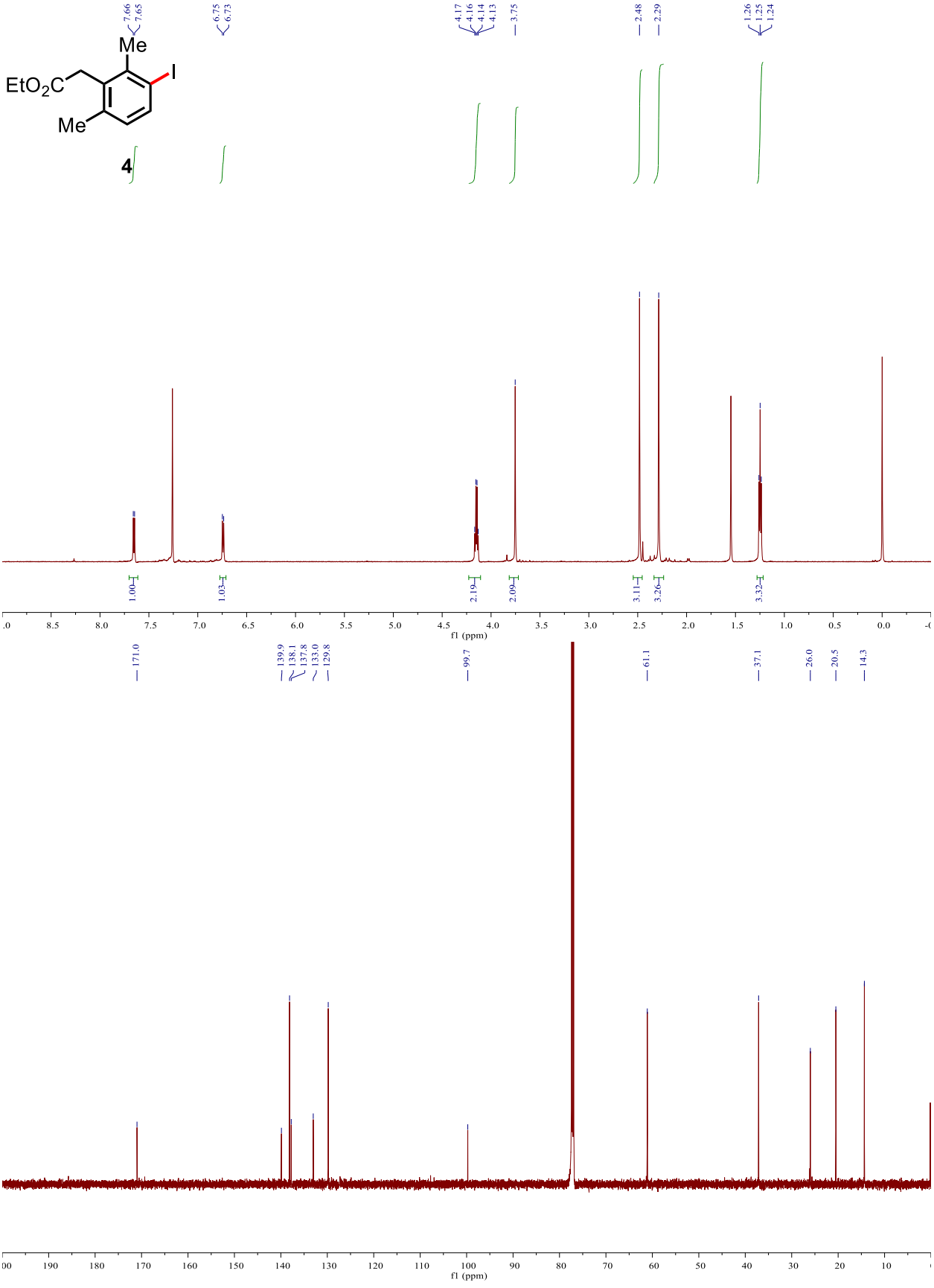

O
OH
O
MeO
2s
6.99
6.97
6.50
6.49
6.48
6.48
6.40
6.39
4.44
4.43
4.42
4.41
4.19
4.17
4.17
4.15
3.75
3.07
3.06
3.05
3.05
3.03
3.01
3.00
2.99
1.00
0.98
0.96
1.00
0.99
3.28
1.21
1.88
f1 (ppm)
176.8
159.4
154.8
130.3
112.1
108.1
101.7
66.3
55.5
38.4
26.8
f1 (ppm)

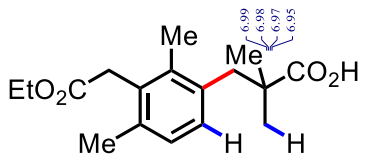

Me
O
OH
2u
7.18
7.17
7.15
7.14
7.13
3.50
3.47
2.94
2.91
1.84
1.83
1.82
1.81
0.95
0.94
0.93
2.10
2.15
2.00
1.97
2.00
3.21
f1 (ppm)


182.3
141.4
126.7
124.6
54.7
41.8
31.5
10.0
f1 (ppm)


Me
O
OH
Me
2v
7.10
7.08
7.07
7.03
7.02
6.99
6.97
3.54
3.52
3.45
3.42
2.87
2.85
2.81
2.78
2.24
1.41
1.02
0.93
0.87
1.00
0.95
1.02
0.94
2.89
2.86
f1 (ppm)
184.2
141.0
140.0
134.2
127.6
127.0
122.1
49.0
44.2
42.8
25.4
19.2
f1 (ppm)

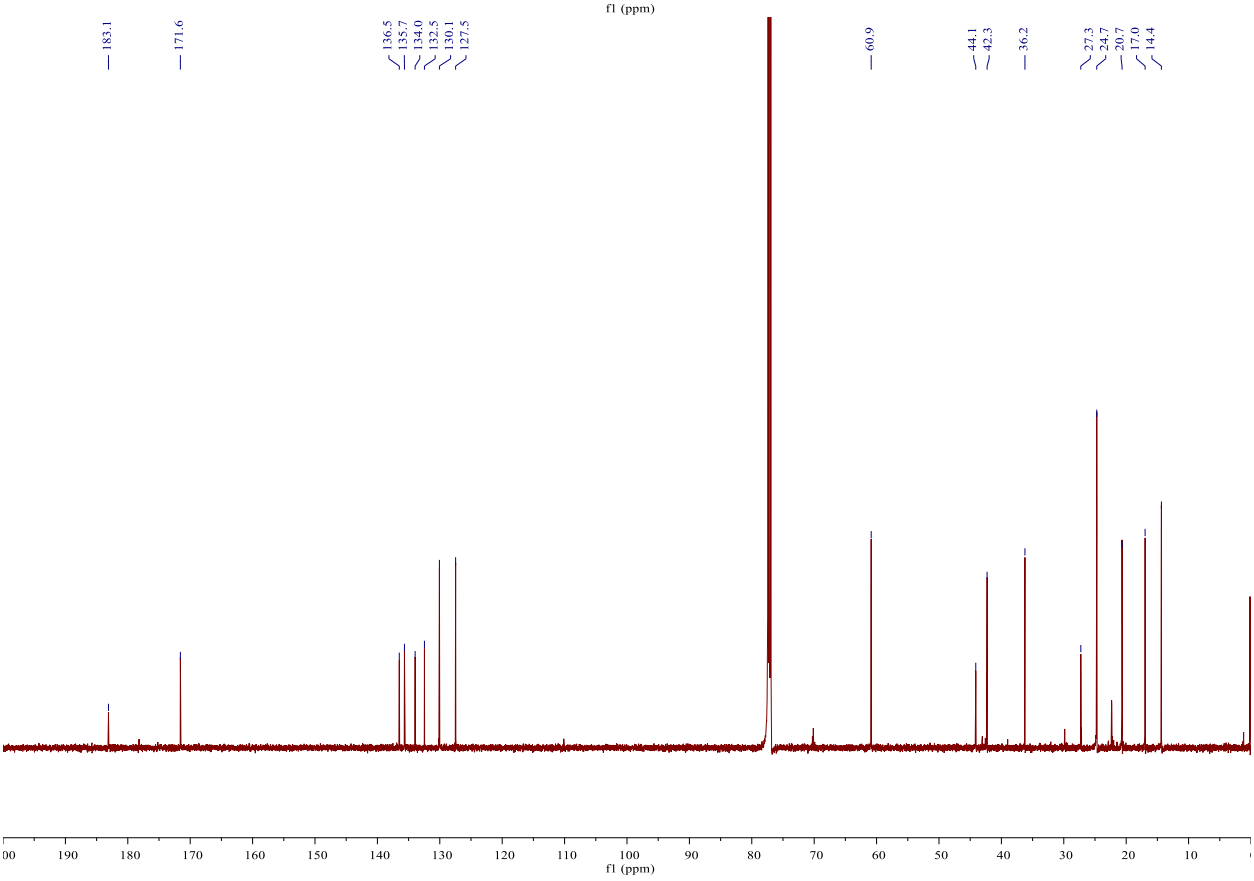

Me
O
OH
2w
7.21
7.20
7.20
7.19
7.17
7.16
7.16
7.16
3.53
3.51
2.87
2.84
1.41
1.96
1.98
1.99
2.00
2.90
f1 (ppm)
182.5
141.2
126.8
124.8
49.5
44.0
25.0
f1 (ppm)

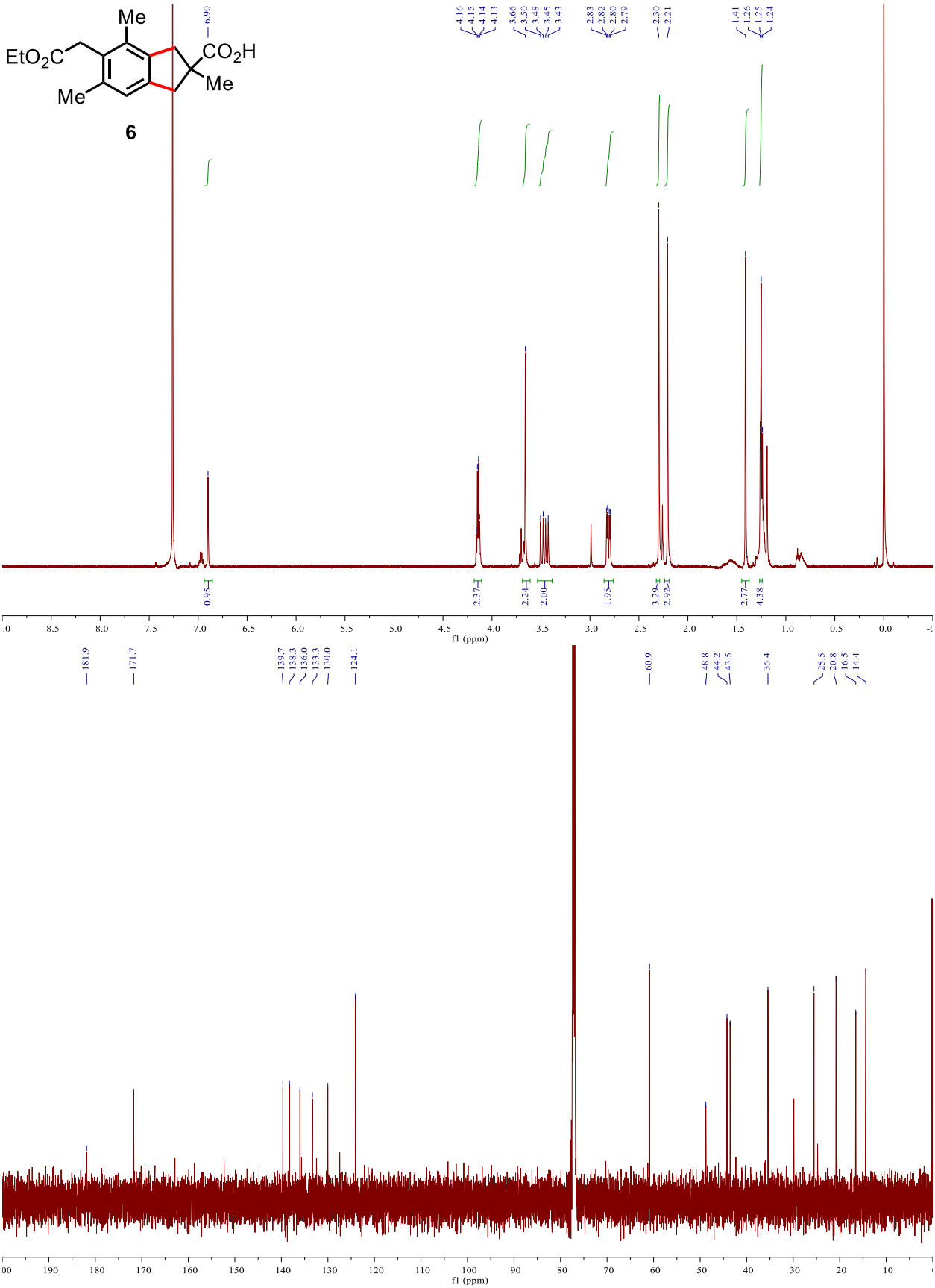

7.66
7.65
6.75
6.73
4.17
4.16
4.14
4.13
3.75
2.48
2.29
1.26
1.25
1.24
Me
EtO2C
I
Me
4
1.00
1.03
2.19
2.09
3.11
3.26
3.32
f1 (ppm)
171.0
139.9
138.1
137.8
133.0
129.8
99.7
61.1
37.1
26.0
20.5
14.3
f1 (ppm)

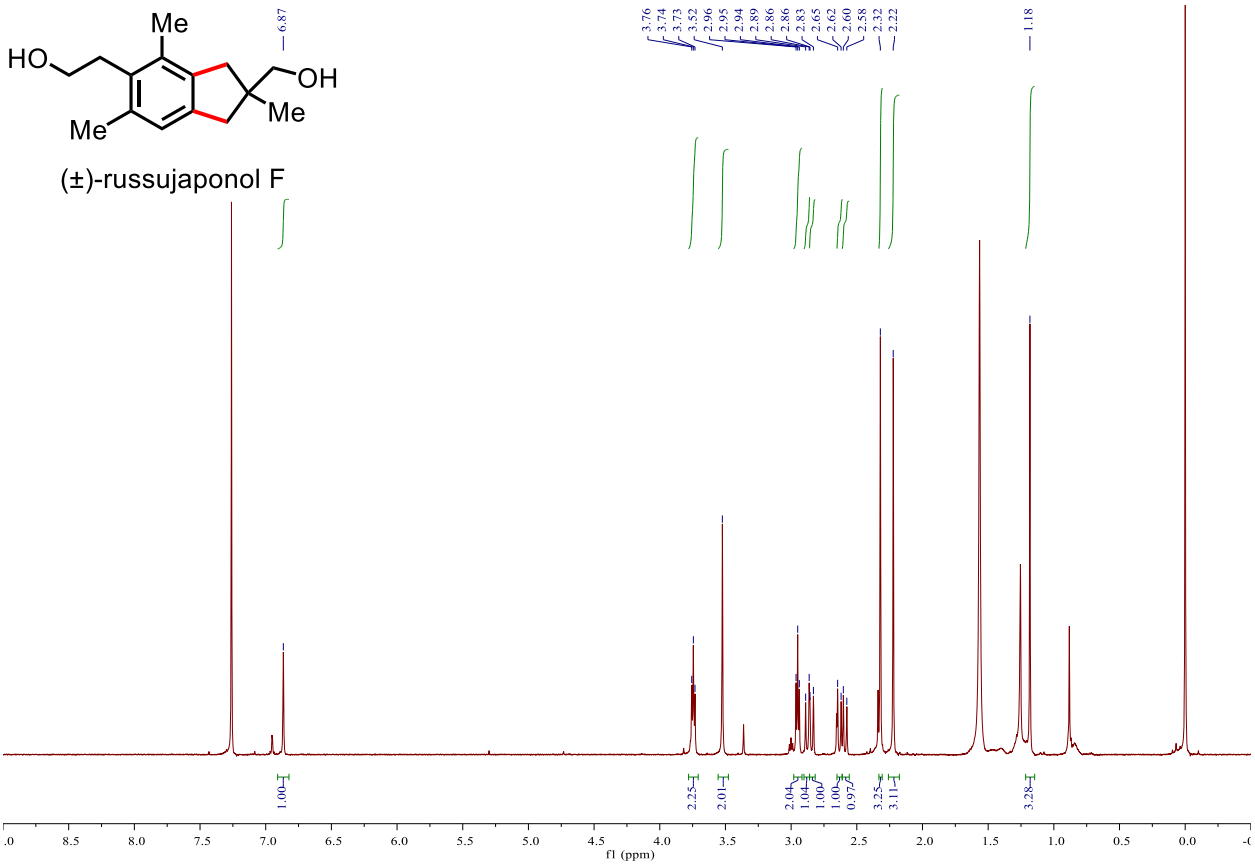

Me
Me
EtO2C
CO2H
Me
H
H

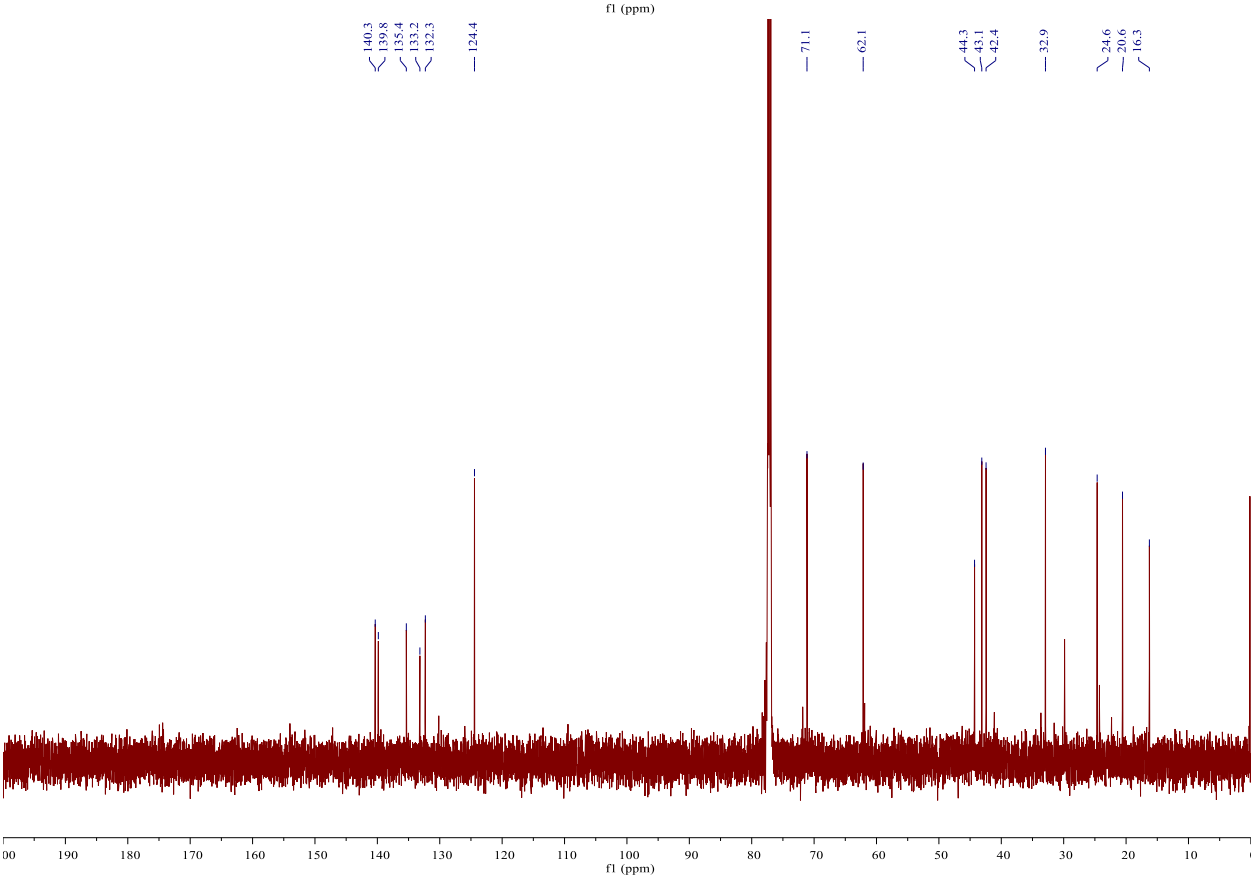
5

6.99
6.98
6.97
6.95
4.15
4.14
4.13
4.12
3.70
2.99
2.30
2.26
1.24
1.23
1.22
1.19
1.03
0.95
2.35
2.00
1.96
3.22
2.96
3.47
5.96
f1 (ppm)


183.1
171.6
136.5
135.7
134.0
132.5
130.1
127.5
60.9
44.1
42.3
36.2
27.3
24.7
20.7
17.0
14.4
f1 (ppm)


Me
EtO2C
CO2H
Me
Me
6
6.90
4.16
4.15
4.14
4.13
3.66
3.50
3.48
3.45
3.43
2.83
2.82
2.80
2.79
2.30
2.21
1.41
1.26
1.25
1.24
0.95
2.37
2.24
2.00
1.95
3.29
2.92
2.77
4.38
f1 (ppm)
181.9
171.7
139.7
138.3
136.0
133.3
130.0
124.1
60.9
48.8
44.2
43.5
35.4
25.5
20.8
16.5
14.4
f1 (ppm)


Me
HO
OH
Me
Me
(±)-russujaponol F
6.87
3.76
3.74
3.73
3.52
2.96
2.95
2.94
2.89
2.86
2.86
2.83
2.65
2.62
2.60
2.58
2.32
2.22
1.18
1.00
2.25
2.01
2.04
1.04
1.00
1.00
0.97
3.25
3.11
3.28
f1 (ppm)


140.3
139.8
135.4
133.2
132.3
124.4
71.1
62.1
44.3
43.1
42.4
32.9
24.6
20.6
16.3
f1 (ppm)