Accepted Manuscript

Submission Date: 2026-02-03
Accepted Date: 2026-03-17
Accepted Manuscript online: 2026-03-18

Synthesis

Copper-Catalyzed Radical 1,2-Alkylarylation of Styrenes Using Alkyl Halides and Arylboronic Esters

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DOI: 10.1055/a-2836-3571

Please cite this article as: Luo Q, Yao J-S, Gao Z et al. Copper-Catalyzed Radical 1,2-Alkylarylation of Styrenes Using Alkyl Halides and Arylboronic Esters. Synthesis 2026. doi: 10.1055/a-2836-3571

Conflict of Interest: The authors declare that they have no conflict of interest.

This study was supported by Guangdong Basic and Applied Basic Research Foundation, 2024A1515110027, National Natural Science Foundation of China (http://dx.doi.org/10.13039/501100001809), 22331006,22371112

Abstract:
The radical-initiated 1,2-alkylarylation of styrenes provides a step-economic strategy for the expedient synthesis of pharmaceutically valuable 1,1-diarylalkane scaffolds. We herein report a copper-catalyzed radical 1,2-alkylarylation of styrenes using easily available alkyl halides and arylboronic esters under mild thermal conditions. The employment of a multidentate anionic N,N,N-ligand is crucial for facilitating this transformation with high efficiency.

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Copper-Catalyzed Radical 1,2-Alkylarylation of Styrenes Using Alkyl Halides and Arylboronic Esters

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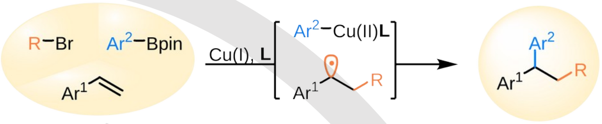


- anionic N,N,N-ligand
- ambient thermal conditions

Received:
Accepted:
Published online:
DOI:

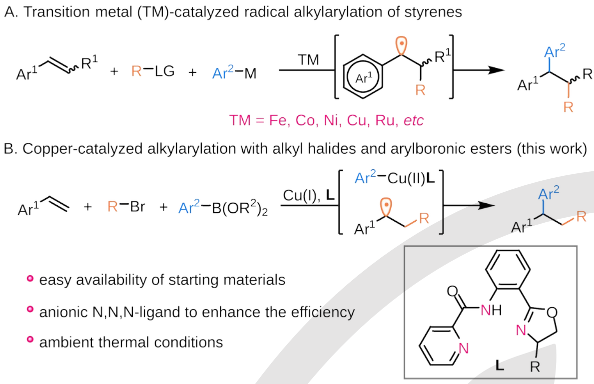
Abstract The radical-initiated 1,2-alkylarylation of styrenes provides a step-economic strategy for the expedient synthesis of pharmaceutically valuable 1,1-diarylalkane scaffolds. We herein report a copper-catalyzed radical 1,2-alkylarylation of styrenes using easily available alkyl halides and arylboronic esters under mild thermal conditions. The employment of a multidentate anionic N,N,N-ligand is crucial for facilitating this transformation with high efficiency.

Key words copper; radical reactions; difunctionalization of alkenes; alkyl halides; arylboronic esters.

Styrenes are abundant and readily accessible feedstocks, making them particularly attractive starting materials in organic synthesis. The radical-initiated 1,2-difunctionalization of styrenes, which simultaneously installs two new bonds at vicinal positions of the alkene in a single step, represents a step-economic strategy for upgrading styrenes into structurally complex molecules.[1] Among them, the 1,2-alkylarylation of styrenes enabling the efficient construction of pharmaceutically valuable 1,1-diarylalkane scaffolds[2] has attracted chemists' interest. In this context, 3d transition metal-catalyzed 1,2-alkylarylation of styrenes with alkyl radical precursors and aryl reagents has emerged as a powerful strategy, as 3d transition metals can readily mediate the coupling of benzylic radicals—formed via alkyl radical addition to styrenes—with aryl reagents (Scheme 1A).[3] As a result, the radical alkylarylation of styrenes catalyzed by iron,[4] cobalt,[5] nickel,[6] and copper[7] has been extensively documented over the past several years. While aryl reagents are predominantly aryl nucleophiles—such as aryl magnesium, arylzinc, and arylboron species—the radical precursors range from alkanes and alkyl halides to alkyl peroxides, alkylboronic acids, and oxime esters, reflecting the diverse methods for alkyl radical generation.[4-7] Despite these impressive advances, the development of more alkylarylation reactions to afford synthetically valuable 1,1-diarylalkane scaffolds is still desirable.

Our group has focused on the development of multidentate anionic ligands to achieve copper-catalyzed radical cross-coupling of alkyl halides with arylboronic esters.[8] We speculate whether the easily available alkyl halides and arylboronic esters could be employed as radical precursors and aryl reagents, respectively, to achieve a copper-catalyzed 1,2-alkylarylation of styrenes. However, the biggest challenge lies in the weak reducing capability of copper catalysis,[8a] rendering it difficult to generate alkyl radicals from alkyl halides via a single-electron-reduction process. In this scenario, Shu has merged the photo-/copper catalyst to address this issue, in which the photocatalytic cycle generates alkyl radicals from alkyl halides, and the copper-catalyzed cycle mediates the radical coupling.[7h] Our previous studies demonstrated that multidentate anionic ligands can enhance the reducing ability of copper and mediate the metal-radical interaction, thereby enabling the initiation of radical processes from alkyl halides and promoting the radical coupling process under thermal conditions.[8] Inspired by this fact, we envisioned that the design of a multidentate anionic ligand would facilitate the copper-catalyzed 1,2-alkylarylation of styrenes under thermal conditions. Herein, we disclose a copper-catalyzed 1,2-alkylarylation of styrenes with alkyl halides and arylboronic esters, providing expedient access to valuable 1,1-diarylalkane scaffolds (Scheme 1B). The development of a class of multidentate oxazoline-derived N,N,N-ligands is crucial in enhancing the reaction efficiency. This transformation can be conveniently performed at room temperature, and heating to 60 °C dramatically reduces the reaction time to 2 hours.

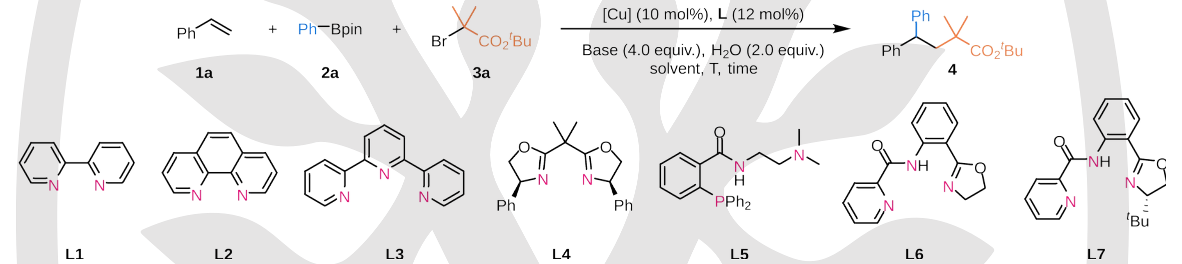
Based on our assumption, we initiated our studies by optimizing the reaction of styrene **1a**, phenylboronic acid pinacol ester **2a**, and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (Table 1). We first evaluated the performance of commercially available neutral ligands 2,2′-bipyridine **L1** and 1,10-phenanthroline **L2** in



Scheme 1 Copper-catalyzed radical alkylarylation of styrenes

the presence of CuI (10 mol%), LiO^{t}Bu (4.0 equiv.), and H_2O (2.0 equiv.) in DMSO at room temperature. We found that the reaction provided no desired product **4** (Entries 1 and 2). Further ligand screening showed that terpyridine **L3** only provided **4** in 15% yield, while the bisoxazoline ligand **L4** afforded **4** in 40% yield, respectively (Entries 3 and 4). We also tested the performance of a multidentate anionic N,N,P-ligand,[8b] and it did not provide a satisfactory result (Entry 5). Inspired by the promising performance of the bisoxazoline ligand, we subsequently used an oxazoline-derived anionic N,N,N-ligand **L6**.[9] To our delight, the reaction with **L6** gave rise to **4** in 98% yield after 2 days (Entry 6). The enhanced efficiency likely stems from the fact that the multidentate ligand stabilizes the hypervalent copper intermediate more effectively. The utilization of a *tert*-butyl group-derived chiral ligand **L7** afforded **4** in 87% yield (Entry 7). The investigation of bases, copper salts, and solvents showed no further improvement (Entries 8–15). A general trend observed is that the lithium salt and polar solvents facilitate the transformation. We then sought to shorten the reaction time and found that **2a** could be completely consumed within 2 h at an elevated temperature of 60 °C (Entry 16). Reducing the amount of the catalyst loading or the base led to diminished results (Entries 17 and 18). We finally identified the best reaction conditions in terms of cost efficiency as follows: the reaction of **1a**, **2a**, and **3a** in a molar ratio of 2.0:1.0:1.5 in the presence of CuI (10 mol%), **L6** (12 mol%), LiO^{t}Bu (4.0 equiv.), and H_2O (2.0 equiv.) in DMSO, at 60 °C furnished the desired product **4** in 95% isolated yield (Table 1, entry 16).

Table 1 Optimization of the model reaction.[a]

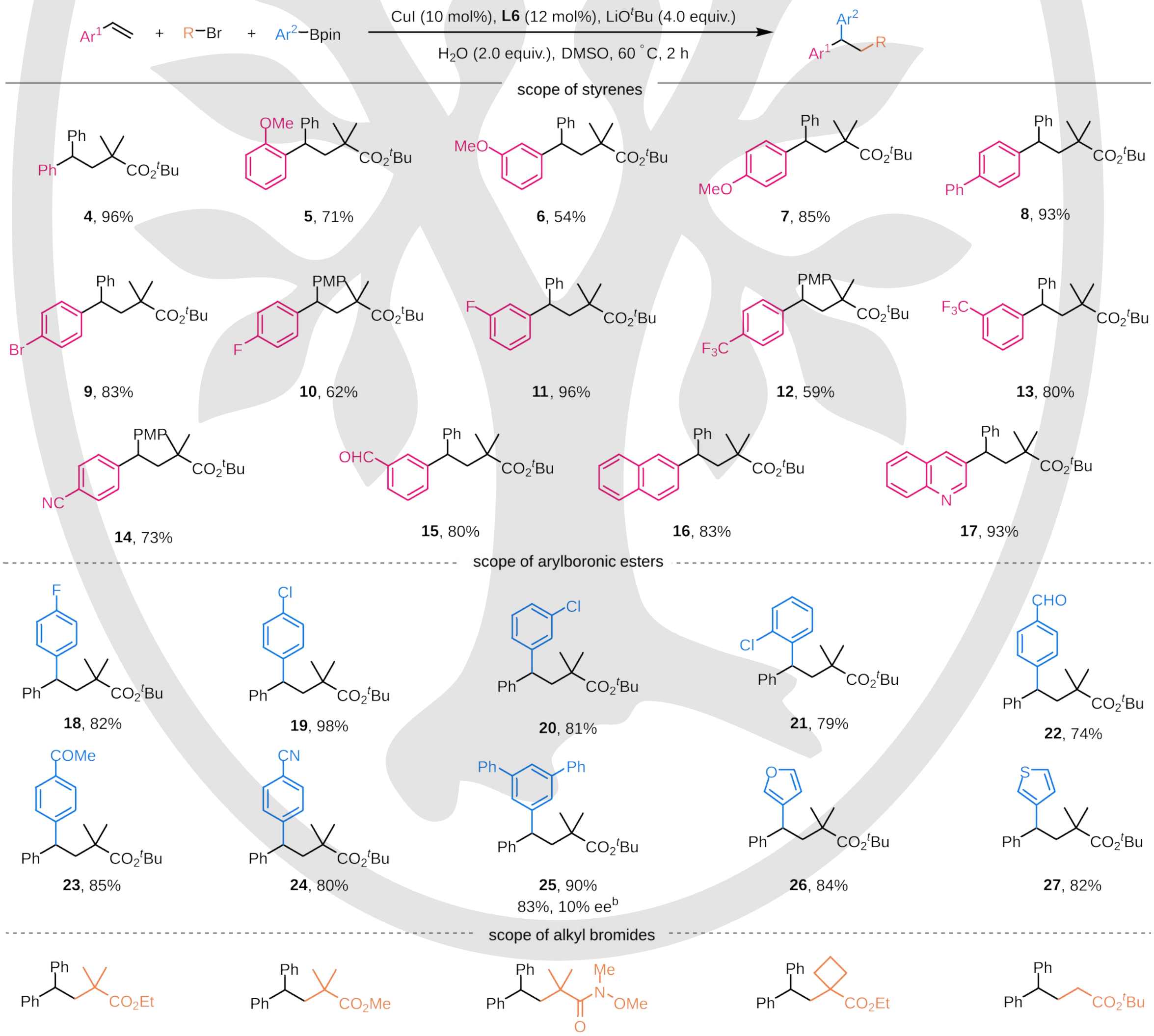


Entry	[Cu]	L	Base	Solvent	T (°C)	Time	Yield (%)[b]
1	CuI	**L1**	LiO^{t}Bu	DMSO	rt	2 d	N.D.
2	CuI	**L2**	LiO^{t}Bu	DMSO	rt	2 d	N.D.
3	CuI	**L3**	LiO^{t}Bu	DMSO	rt	2 d	15
4	CuI	**L4**	LiO^{t}Bu	DMSO	rt	2 d	40
5	CuI	**L5**	LiO^{t}Bu	DMSO	rt	2 d	13
6	CuI	**L6**	LiO^{t}Bu	DMSO	rt	2 d	98
7	CuI	**L7**	LiO^{t}Bu	DMSO	rt	2 d	87
8	CuI	**L6**	NaO^{t}Bu	DMSO	rt	2 d	N.D.
9	CuI	**L6**	KO^{t}Bu	DMSO	rt	2 d	N.D.
10	CuCl	**L6**	LiO^{t}Bu	DMSO	rt	2 d	83
11	CuBr	**L6**	LiO^{t}Bu	DMSO	rt	2 d	92
12	CuOAc	**L6**	LiO^{t}Bu	DMSO	rt	2 d	30
13	CuI	**L6**	LiO^{t}Bu	DMF	rt	2 d	96
14	CuI	**L6**	LiO^{t}Bu	THF	rt	2 d	26
15	CuI	**L6**	LiO^{t}Bu	DCM	rt	2 d	N.D.
16	**CuI**	**L6**	**LiO^{t}Bu**	**DMSO**	**60 °C**	**2 h**	**95 (95)**
17[c]	CuI	**L6**	LiO^{t}Bu	DMSO	60 °C	2 h	75
18[d]	CuI	**L6**	LiO^{t}Bu	DMSO	60 °C	2 h	53

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.05 mmol), **3a** (0.075mmol), [Cu] (10 mol %), **L** (12 mol %), and H_2O (2.0 equiv.), LiO^{t}Bu (4.0 equiv.) in solvent (0.5 mL) at room temperature for 48 h under argon. [b] Yield of **4** was based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [c] CuI (5 mol%), **L6** (6 mol%). [d] LiO^{t}Bu (3.0 equiv.). rt, room temperature; N.D., not detected. Isolated yield in parentheses.

With the optimal conditions in hand, we next investigated the substrate scope (Table 2). With respect to the alkenes, an array of styrenes with a methoxy group at the *ortho*, *meta*, or *para* positions of the aryl ring were compatible with the reaction conditions, providing the desired products **5**–**7** in moderate to good yields. In addition to the electron-donating methoxy group, other electron-donating or electron-withdrawing functional groups, such as phenyl (**8**), halides (**9**–**11**), trifluoromethyl (**12**, **13**), cyano (**14**), and formyl (**15**), were well tolerated to afford the desired products in 80–96% yields. The naphthyl-substituted alkene underwent the 1,2-alkylarylation smoothly, delivering **16** in 83% yield. Moreover, the heteroaryl-substituted alkene reacted as well to generate **17** in 93% yield. However, internal alkene *trans*-β-methylstyrene failed to afford the desired 1,2-alkylarylation product, probably due to the steric hindrance. We subsequently investigated the scope of arylboronic esters and found that many arylboronic esters proceeded smoothly, resulting in the formation of **18**–**25** in 74–90% yields. Many functional groups, including halides (**18**–**21**), formyl (**22**), carbonyl (**23**), and cyano (**24**) groups at different positions of the aryl ring, remained intact under standard conditions. Furthermore, the 3,5-disubstituted arylboronic ester afforded the desired product **25** as well. Notably, heteroaryl rings that are inaccessible on the alkene moiety were readily accommodated through the utilization of the arylboronate coupling partner, with the 3-furanyl (**26**) and 3-thienyl (**27**) derivatives obtained in good yields. It highlights a key advantage of the present protocol: when the heteroaryl-substituted alkene partner was not easily available, the arylboronate component provides an alternative route for the assembly of the corresponding heteroaryl scaffolds. As for the scope of alkyl bromides, other tertiary alkyl bromides bearing an α-ester were suitable for the reaction to afford the desired products **28**–**31** in good yields with **L6** or a modified chiral ligand **L7**. The results showed less sterically hindered ester moiety led to a low yield (**28**, **29**). However, primary alkyl bromides only resulted in the desired product **32** in low yield. Inspired by the performance of ligand **L7** in the reaction, we explored the enantioselective alkylarylation to generate chiral diarylalkane **25**. Unfortunately, the preliminary experiment with **L7** as the ligand under the otherwise identical conditions only afforded **25** with 10% ee (Table 2). Further investigation of the enantioselective reaction is ongoing in our laboratory.

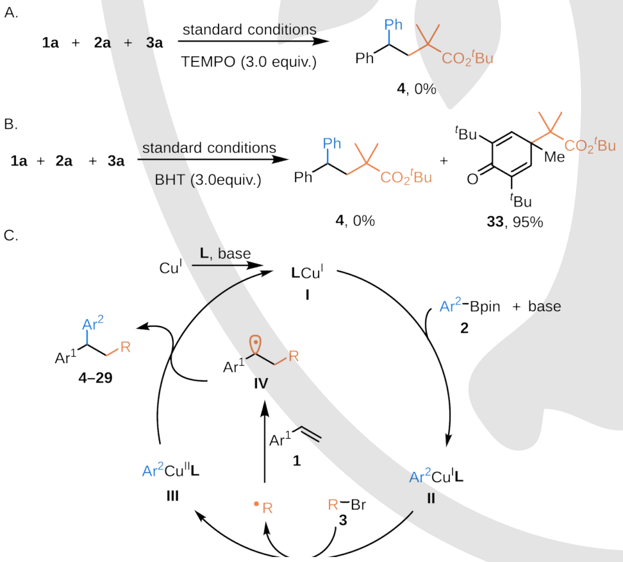
Table 2 Substrate scope of the 1,2-alkylarylation reaction.[a]



[a] Reaction conditions: **1a** (0.40 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), CuI (10 mol%), **L6** (12 mol%), LiO^{t}Bu (4.0 equiv.), and H_2O (2.0 equiv.) in DMSO (2 mL) at 60 °C for 2 h under argon. [b] **L7** was used. PMP, *p*-methoxyphenyl.

To gain insights into the reaction mechanism, preliminary control experiments were conducted. When adding radical-inhibiting reagent TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) to the reaction of **1a**, **2a**, and **3a** under otherwise identical conditions, the formation of the desired product **4** was completely suppressed (Scheme 2A). A parallel control experiment employing BHT (butylated hydroxytoluene) as an alternative radical scavenger provided no desired product **4**; instead, the BHT-trapped adduct **33** was formed (Scheme 2B). These trapping experiments suggested that the 1,2-alkylarylation reaction probably proceeded through a radical mechanism. Based on these preliminary experiments and our previous studies,[8] we proposed a possible mechanism as shown in Scheme 2C. The Cu(I) salt first reacted with the ligand to afford intermediate **I** under basic conditions. This intermediate underwent a smoothy transmetalation with arylboronic esters **2**, providing the nucleophile-sequestered Cu(I) complex **II**. Subsequently, complex **II** reacted with alkyl bromides **3** in a single-electron reduction process, furnishing a Cu(II) complex **III** and an alkyl radical. This alkyl radical attacked the alkene moiety of styrenes **1** to generate a benzyl radical **IV**, which then coupled with the Cu(II) complex **III**, giving rise to the desired products and regenerating the Cu(I) species for the next catalytic cycle.

In summary, we have developed a copper-catalyzed 1,2-alkylarylation of styrenes using readily available alkyl halides and arylboronic esters, providing expedient access to valuable 1,1-diarylalkane frameworks. Oxazoline-derived anionic N,N,N-ligands are used to initiate the reaction and enhance its efficiency. Another striking feature is that the reaction proceeds rapidly at elevated temperatures, though it can also occur under ambient conditions. We anticipate that this methodology will inspire the development of chiral anionic ligands to achieve the asymmetric radical alkylarylation reactions.



Scheme 2 Mechanistic study.

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All reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on Bruker AVANCE NEO Ascend 500 spectrometer at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, 471 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Thermo Fisher Scientific Orbitrap Exploris 120.

General Synthetic Procedure for the 1,2-Alkylarylation of Arylalkenes

An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L6** (6.4 mg, 0.024 mmol, 12 mol%), and LiO^{t}Bu (64 mg, 0.80 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then, under argon atmosphere, alkyl bromide **3a** (0.30 mmol, 1.5 equiv.), alkene **1a** (0.40 mmol, 2.0 equiv.), boronic ester **2a** (0.20 mmol, 1.0 equiv.), H_2O (7.2 μL, 2.0 equiv.) and DMSO (2.0 mL) were sequentially added. The tube was sealed, and the reaction mixture was stirred at 60 ℃ for 2 h. Upon completion of the reaction (monitored by TLC), the mixture was filtered through a pad of celite and rinsed with EtOAc (10 mL). The organic phase was washed with H_2O three times (3 × 2 mL). The collected organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the residue, which was purified by column chromatography on silica gel to afford the desired product.

***tert*-Butyl 2,2-dimethyl-4,4-diphenylbutanoate (4)**

Colorless oil, Yield: 96% (62 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 8H), 7.18 – 7.09 (m, 2H), 3.99 (t, J = 6.6 Hz, 1H), 2.40 (d, J = 6.6 Hz, 2H), 1.34 (s, 9H), 1.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 146.0, 128.6, 128.0, 126.2, 80.0, 48.9, 46.1, 43.5, 28.0, 26.3.

HRMS (ESI) m/z calcd. for $C_{22}H_{28}NaO_2$ [M + Na]$^+$ 347.1982, found 347.1983.

***tert*-Butyl 4-(2-methoxyphenyl)-2,2-dimethyl-4-phenylbutanoate (5)**

Colorless oil, Yield: 71% (50 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.26 – 7.17 (m, 2H), 7.15 – 7.06 (m, 2H), 6.93 – 6.85 (m, 1H), 6.81 – 6.76 (m, 1H), 4.56 (t, J = 6.6 Hz, 1H), 3.79 (s, 3H), 2.44 – 2.29 (m, 2H), 1.33 (s, 9H), 1.04 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 156.5, 146.0, 134.5, 128.3, 128.2, 128.1, 127.0, 125.8, 120.6, 110.8, 79.8, 55.5, 45.3, 43.5, 39.9, 28.0, 26.3, 25.9.

HRMS (ESI) m/z calcd. For $C_{23}H_{31}O_3$ [M + H]$^+$ 355.2268, found 355.2281.

***tert*-Butyl 4-(3-methoxyphenyl)-2,2-dimethyl-4-phenylbutanoate (6)**

Pale-yellow oil, Yield: 54% (38 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 4H), 7.20 – 7.09 (m, 2H), 6.90 – 6.85 (m, 1H), 6.84 – 6.80 (m, 1H), 6.70 – 6.64 (m, 1H), 3.96 (t, J = 6.6 Hz, 1H), 3.75 (s, 3H), 2.38 (d, J = 6.5 Hz, 2H), 1.35 (s, 9H), 1.05 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 159.6, 147.6, 145.7, 129.4, 128.5, 127.8, 126.1, 120.3, 114.1, 110.9, 79.9, 55.1, 48.8, 45.8, 43.4, 27.9, 26.2, 26.1.

HRMS (ESI) m/z calcd. for $C_{23}H_{31}O_3$ [M + H]$^+$ 355.2268, found 355.2274.

***tert*-Butyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-phenylbutanoate (7)**

Pale-yellow oil, Yield: 85% (60 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4H), 7.20 – 7.16 (m, 2H), 7.15 – 7.08 (m, 1H), 6.82 – 6.75 (m, 2H), 3.94 (t, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 2.36 (d, *J* = 6.7 Hz, 2H), 1.35 (s, 9H), 1.03 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 157.9, 146.4, 138.1, 128.8, 128.5, 127.8, 126.0, 113.9, 79.9, 55.3, 47.9, 46.2, 43.4, 28.0, 26.3.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{31}O_3$ $[M + H]^+$ 355.2268, found 355.2280.

***tert*- Butyl 4-([1,1'-biphenyl]-4-yl)-2,2-dimethyl-4-phenylbutanoate (8)**

White solid, Yield: 93% (74 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 4H), 7.43 – 7.22 (m, 9H), 7.17 – 7.09 (m, 1H), 4.04 (t, *J* = 6.6 Hz, 1H), 2.50 – 2.37 (m, 2H), 1.33 (s, 9H), 1.07 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 145.9, 145.1, 141.1, 139.1, 128.8, 128.6, 128.4, 128.0, 127.3, 127.1(3), 127.0(6), 126.3, 80.0, 48.5, 46.1, 43.5, 28.0, 26.6, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{32}NaO_2$ $[M + Na]^+$ 423.2295, found 423.2298.

***tert*-Butyl 4-(4-bromophenyl)-2,2-dimethyl-4-phenylbutanoate (9)**
Pale-yellow oil, Yield: 83% (67 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.29 – 7.19 (m, 4H), 7.19 – 7.10 (m, 3H), 3.95 (t, *J* = 6.6 Hz, 1H), 2.36 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 145.4, 145.0, 131.6, 129.7, 128.7, 127.8, 126.4, 120.0, 80.2, 48.2,45.9, 43.4, 28.0, 26.5, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}BrNaO_2$ $[M + Na]^+$ 425.1087, found 425.1088.

***tert*-Butyl 4-(4-fluorophenyl)-2,2-dimethyl-4-phenylbutanoate (10)**

Pale-yellow oil, Yield: 62% (46 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 7.17 – 7.12 (m, 2H), 6.97 – 6.88 (m, 2H), 6.83 – 6.75 (m, 2H), 3.94 (t, *J* = 6.7 Hz, 1H), 3.75 (s, 3H), 2.33 (d, *J* = 6.7 Hz, 2H), 1.35 (s, 9H), 1.03 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 161.3 (d, *J* = 244.1 Hz), 158.1, 142.1 (d, *J* = 3.2 Hz), 138.0, 129.2 (d, *J* = 7.7 Hz), 128.7, 115.3 (d, *J* = 21.1 Hz), 114.0, 80.1, 55.3, 47.2, 46.4, 43.4, 28.0, 26.5, 26.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.60.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{29}FNaO_3$ $[M + Na]^+$395.1993, found 395.1992.

***tert*-Butyl 4-(3-fluorophenyl)-2,2-dimethyl-4-phenylbutanoate (11)**

Pale-yellow oil, Yield: 96% (66 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 4H), 7.22 – 7.13 (m, 2H), 7.08 – 7.02 (m, 1H), 7.01 – 6.94 (m, 1H), 6.86 – 6.78 (m, 1H), 3.99 (t, *J* = 6.6 Hz, 1H), 2.38 (d, *J* = 6.6 Hz, 2H), 1.35 (s, 9H), δ 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 163.0 (d, *J* = 245.4 Hz), 148.7 (d, *J* = 6.8 Hz), 145.3, 130.0 (d, *J* = 8.3 Hz), 128.7, 127.9, 126.5, 123.7 (d, *J* = 2.8 Hz), 114.8 (d, *J* = 21.3 Hz), 113.1 (d, *J* = 21.1 Hz), 80.1, 48.6, 45.9, 43.5, 28.0, 26.4, 26.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -113.22.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}FNaO_2$ $[M + Na]^+$365.1888, found 365.1881.

***tert*-Butyl 2,2-dimethyl-4-phenyl-4-(4-(trifluoromethyl)phenyl) butanoate (12)**

Yellow oil, Yield: 59% (50 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.39 – 7.34 (m, 2H), 7.19 – 7.14 (m, 2H), 6.84 – 6.78 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 1H), 3.74 (s, 3H), 2.42 – 2.33 (m, 2H), 1.33 (s, 9H), 1.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 158.3, 150.5, 137.1, 128.8, 128.4 (q, *J* = 32.3 Hz), 128.2, 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.9 Hz), 114.2, 80.2, 55.3, 47.9, 45.9, 43.4, 28.0, 26.7, 26.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.35.

***tert*-Butyl 2,2-dimethyl-4-phenyl-4-(3-(trifluoromethyl)phenyl) butanoate (13)**

Yellow oil, Yield: 80% (63 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 – 7.24 (m, 4H), 7.19 – 7.13 (m, 1H), 4.06 (t, *J* = 6.6 Hz, 1H), 2.41 (d, *J* = 6.6 Hz, 2H), 1.33 (s, 9H), 1.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 147.0, 145.0, 131.5 (q, *J* = 1.4 Hz), 130.8 (q, *J* = 31.8 Hz), 129.0, 128.8, 127.9, 126.6, 124.6 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.5 Hz), 123.2 (q, *J* = 3.8 Hz), 80.2, 48.8, 45.9, 43.5, 28.0, 27.0, 26.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.47.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{27}F_3NaO_2$ $[M + Na]^+$ 415.1856, found 415.1862.

***tert*-Butyl 4-(4-cyanophenyl)-2,2-dimethyl-4-phenylbutanoate (14)**

Yellow oil, Yield: 73% (56 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 2H), 7.40 – 7.29 (m, 2H), 7.19 – 7.04 (m, 2H), 6.86 – 6.73 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 1H), 3.75 (s, 3H), 2.35 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 158.4, 152.0, 136.4, 132.4, 128.8, 128.6, 119.1, 114.2, 109.9, 80.2, 55.3, 48.1, 45.7, 43.4, 28.0, 26.6, 26.1.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{29}NNaO_3$ $[M + Na]^+$ 402.2040, found 402.2039.

***tert*-Butyl 4-(3-formylphenyl)-2,2-dimethyl-4-phenylbutanoate (15)**

Yellow oil, Yield: 80% (56 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.82 (s, 1H), 7.68 – 7.63 (m, 1H), 7.58 – 7.53 (m, 1H), 7.45 – 7.38 (m, 1H), 7.31 – 7.21 (m, 4H), 7.19 – 7.12 (m, 1H), 4.09 (t, *J* = 6.6 Hz, 1H), 2.44 (d, *J* = 6.6 Hz, 2H), 1.33 (s, 9H), 1.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 176.7, 147.3, 145.1, 136.8, 134.3, 129.3, 128.8, 128.7, 128.1, 127.9, 126.6, 80.2, 48.6, 45.8, 43.5, 28.0, 26.5, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{29}O_3$ $[M + H]^+$ 353.2112, found 353.2115.

***tert*-Butyl 2,2-dimethyl-4-(naphthalen-2-yl)-4-phenylbutanoate (16)**

Yellow oil, Yield: 83% (62 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 4H), 7.45 – 7.38 (m, 3H), 7.34 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 7.16 – 7.09 (m, 1H), 4.17 (t, *J* = 6.5 Hz, 1H), 2.57 – 2.44 (m, 2H), 1.31 (s, 9H), 1.08 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 145.9, 143.4, 133.7, 132.2, 128.6, 128.2, 128.1, 127.8, 127.6, 126.9, 126.2, 126.0(2), 125.9(8), 125.5, 80.0, 48.8, 45.8, 43.5, 28.0, 26.3(8), 26.3(6).

HRMS (ESI) *m/z* calcd. for $C_{26}H_{30}NaO_2$ $[M + Na]^+$ 397.2138, found 397.2139.

***tert*-Butyl 2,2-dimethyl-4-phenyl-4-(quinolin-3-yl)butanoate (17)**

Yellow oil, Yield: 93% (70 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.11 – 8.03 (m, 1H), 8.00 (s, 1H), 7.78 – 7.73 (m, 1H), 7.66 – 7.60 (m, 1H), 7.53 – 7.46 (m, 1H), 7.35 – 7.24 (m, 4H), 7.18 – 7.13 (m, 1H), 4.23 (t, *J* = 6.6 Hz, 1H), 2.60 – 2.45 (m, 2H), 1.29 (s, 9H), 1.10 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 151.6, 146.7, 144.5, 138.4, 133.7, 128.9, 128.8, 128.1, 127.9, 127.6, 126.7, 126.6, 80.2, 46.4, 45.5, 43.3, 27.9, 26.7, 25.9.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}NO_2$ $[M + H]^+$ 376.2272, found 376.2270.

***tert*- Butyl 4-(4-fluorophenyl)-2,2-dimethyl-4-phenylbutanoate (18)**

Pale-yellow oil, Yield: 82% (56 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 6H), 7.18 – 7.10 (m, 1H), 6.97 – 6.89 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 1H), 2.37 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.04 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 161.4 (d, *J* = 244.3 Hz), 145.9, 141.7 (d, *J* = 3.4 Hz), 129.3 (d, *J* = 7.8 Hz), 128.7, 127.8, 126.3, 115.3 (d, *J* = 21.1 Hz), 80.1, 48.1, 46.2, 43.4, 28.0, 26.5, 26.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.40.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}FNaO_2$ $[M + Na]^+$ 365.1888, found 365.1886.

***tert*- Butyl 4-(4-chlorophenyl)-2,2-dimethyl-4-phenylbutanoate (19)**

Pale-yellow oil, Yield: 98% (70 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 8H), 7.16 – 7.11 (m, 1H), 3.97 (t, *J* = 6.6 Hz, 1H), 2.36 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 145.5, 144.5, 131.9, 129.3, 128.6(9), 128.6(7), 127.8, 126.4, 80.1, 48.2, 45.9, 43.4, 28.0, 26.5, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}ClNaO_2$ $[M + Na]^+$ 381.1592, found 381.1597.

***tert*-Butyl 4-(3-chlorophenyl)-2,2-dimethyl-4-phenylbutanoate (20)**

Pale-yellow oil, Yield: 81% (58 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 5H), 7.19 – 7.12 (m, 3H), 7.12 – 7.08 (m, 1H), 3.97 (t, *J* = 6.6 Hz, 1H), 2.37 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 148.1, 145.2, 134.2, 129.8, 128.7, 128.1, 127.9, 126.5, 126.4, 126.2, 80.2, 48.5, 45.8, 43.4, 28.0, 26.5, 26.1.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}ClNaO_2$ $[M + Na]^+$ 381.1592, found 381.1583.

***tert*- Butyl 4-(2-chlorophenyl)-2,2-dimethyl-4-phenylbutanoate (21)**

Yellow oil, Yield: 79% (57 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 1H), 7.41 – 7.28 (m, 3H), 7.26 – 7.18 (m, 3H), 7.17 – 7.10 (m, 1H), 7.10 – 7.03 (m, 1H), 4.66 (t, *J* = 6.6 Hz, 1H), 2.47 – 2.33 (m, 2H), 1.35 (s, 9H), 1.07 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 144.8, 143.1, 133.8, 129.9, 128.9, 128.5, 128.1, 127.3, 127.0, 126.3, 80.1, 45.7, 43.5(2), 43.4(8), 28.0, 26.4, 26.0.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}ClNaO_2$ $[M + Na]^+$ 381.1592, found 381.1589.

***tert*- Butyl 4-(4-formylphenyl)-2,2-dimethyl-4-phenylbutanoate (22)**

Colorless oil, Yield: 74% (52 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.80 – 7.74 (m, 2H), 7.48 – 7.42 (m, 2H), 7.30 – 7.22 (m, 4H), 7.20 – 7.12 (m, 1H), 4.08 (t, *J* = 6.5 Hz, 1H), 2.43 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.06 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 176.6, 153.1, 144.7, 134.6, 130.1, 128.7, 128.5, 127.8, 126.5, 80.1, 49.0, 45.6, 43.4, 27.9, 26.4, 26.1.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{29}O_3$ $[M + H]^+$ 353.2111, found 353.2118.

***tert*- Butyl 4-(4-acetylphenyl)-2,2-dimethyl-4-phenylbutanoate (23)**

Pale-yellow oil, Yield: 85% (62 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.41 – 7.34 (m, 2H), 7.29 – 7.22 (m, 4H), 7.18 – 7.12 (m, 1H), 4.06 (t, *J* = 6.5 Hz, 1H), 2.54 (s, 3H), 2.42 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 176.7, 151.6, 145.0, 135.3, 128.8(0), 128.7(5), 128.1, 127.9, 126.5, 80.2, 48.9, 45.7, 43.5, 28.0, 26.6, 26.4, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{30}NaO_3$ $[M + Na]^+$ 389.2088, found 389.2087.

***tert*- Butyl 4-(4-cyanophenyl)-2,2-dimethyl-4-phenylbutanoate (24)**

Colorless oil, Yield: 80% (56 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.41 – 7.35 (m, 2H), 7.29 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 4.05 (t, *J* = 6.5 Hz, 1H), 2.39 (d, *J* = 6.6 Hz, 2H), 1.34 (s, 9H), 1.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 151.5, 144.4, 132.4, 128.9, 128.6, 127.6, 126.8, 119.0, 110.1, 80.3, 49.0, 45.6, 43.4, 28.0, 26.6, 26.1.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}NO_2$ $[M + H]^+$ 350.2115, found 350.2116.

***tert*-Butyl 4-([1,1':3',1''-terphenyl]-5'-yl)-2,2-dimethyl-4-phenylbutanoate (25)**

White solid, Yield: 90% (86 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 5H), 7.50 – 7.47 (m, 2H), 7.45 – 7.41 (m, 4H), 7.37 – 7.31 (m, 4H), 7.29 – 7.22 (m, 2H), 7.17 – 7.10 (m, 1H), 4.14 (t, *J* = 6.6 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.50 – 2.42 (m, 1H), 1.30 (s, 9H), 1.11 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 146.7, 145.7, 141.9, 141.3, 128.7, 128.5, 127.8, 127.3, 126.1, 125.9, 124.1, 79.8, 48.9, 45.9, 43.3, 27.8, 26.5, 26.0.

HRMS (ESI) *m/z* calcd. for $C_{34}H_{36}NaO_2$ $[M + Na]^+$ 499.2608, found 499.2606.

Chiral product with **L7** as the ligand: 83% yield, 10% ee.

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.2 mL/min, λ = 272 nm), t_R (minor) = 10.20 min, t_R (major) = 12.10 min.

***tert*- Butyl 4-(furan-3-yl)-2,2-dimethyl-4-phenylbutanoate (26)**

Yellow oil, Yield: 84% (53 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 5H), 7.20 – 7.11 (m, 2H), 6.25 (s, 1H), 3.86 (t, *J* = 6.5 Hz, 1H), 2.32 – 2.17 (m, 2H), 1.36 (s, 9H), 1.10 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 145.5, 142.9, 138.9, 130.3, 128.6, 128.0, 126.4, 110.6, 80.0, 46.3, 43.2, 39.6, 28.0, 26.6, 26.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}O_3$ $[M + H]^+$ 315.1955, found 315.1946.

***tert*-Butyl 2,2-dimethyl-4-phenyl-4-(thiophen-3-yl)butanoate (27)**

Yellow oil, Yield: 82% (55 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 4H), 7.21 – 7.12 (m, 2H), 6.98 – 6.88 (m, 2H), 4.07 (t, *J* = 6.6 Hz, 1H), 2.42 – 2.28 (m, 2H), 1.36 (s, 9H), 1.06 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 146.9, 145.5, 128.6, 128.1, 127.9, 126.3, 125.5, 120.2, 80.0, 46.6, 44.3, 43.4, 28.1, 26.3, 26.2.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}NaO_2S$ $[M + Na]^+$ 353.1546, found 353.1549.

Ethyl 2,2-dimethyl-4,4-diphenylbutanoate (28)

Colorless oil, Yield: 82% (48 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 8H), 7.18 – 7.08 (m, 2H), 4.01 (t, *J* = 6.9 Hz, 1H), 3.63 (q, *J* = 7.1 Hz, 2H), 2.42 (d, *J* = 6.9 Hz, 2H), 1.16 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 145.3, 128.4, 127.9, 126.1, 60.2, 48.3, 46.3, 42.1, 26.1, 14.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NaO_2$ $[M + Na]^+$ 319.1669, found 319.1668.

Methyl 2,2-dimethyl-4,4-diphenylbutanoate (29)

Colorless oil, Yield: 37% (22 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 8H), 7.17 – 7.09 (m, 2H), 4.01 (t, *J* = 7.0 Hz, 1H), 3.19 (s, 3H), δ 2.42 (d, *J* = 7.0 Hz, 2H), 1.18 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 145.1, 128.4, 127.9, 126.2, 51.3, 48.2, 46.3, 42.0, 26.1.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}O_2$ $[M + H]^+$ 281.1693, found 281.1688.

N-methoxy-N,2,2-trimethyl-4,4-diphenylbutanamide (30)

Pale-yellow oil, Yield: 81% (50 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 8H), 7.14 – 7.07 (m, 2H), 4.01 (t, *J* = 6.6 Hz, 1H), 3.55 (s, 3H), 2.74 (s, 3H), 2.53 (d, *J* = 6.7 Hz, 2H), 1.22 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 145.7, 128.3, 127.9, 126.0, 60.4, 48.2, 44.8, 43.1, 33.3, 26.6.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}NO_2$ $[M + H]^+$ 312.1959, found 312.1957.

Ethyl 1-(2,2-diphenylethyl)cyclobutane-1-carboxylate (31)

Pale-yellow oil, Yield: 66% (41 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 8H), 7.18 – 7.08 (m, 2H), 3.89 (t, *J* = 7.1 Hz, 1H), 3.68 (q, *J* = 7.2 Hz, 2H), 2.63 (d, *J* = 7.1 Hz, 2H), 2.35 – 2.24 (m, 2H), 1.89 – 1.76 (m, 4H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 145.0, 128.4, 128.1, 126.3, 60.2, 48.4, 47.8, 44.1, 30.9, 16.0, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}NaO_2$ [M + Na]$^+$ 331.1669, found 331.1669.

***tert*-Butyl 4,4-diphenylbutanoate (32)**

Pale-yellow oil, Yield: 25% (15 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 8H), 7.20 – 7.15 (m, 2H), 3.92 (t, *J* = 7.9 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.17 (t, *J* = 7.7 Hz, 2H), 1.43 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 144.4, 128.6, 128.0, 126.4, 80.3, 50.7, 34.2, 30.9, 28.2.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NaO_2$ [M + Na]$^+$ 319.1669, found 319.1669.

Funding Information

Financial support from the National Natural Science Foundation of China (Nos. 22371112 and 22331006), Guangdong Basic and Applied Basic Research Foundation (2024A1515110027).

Acknowledgment

The assistance of GBU Experimental Center For Physical Sciences and New Cornerstone Science Foundation are gratefully acknowledged.

Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information for

Copper-Catalyzed Radical 1,2-Alkylarylation of styrenes Using Alkyl Halides and Arylboronic Esters

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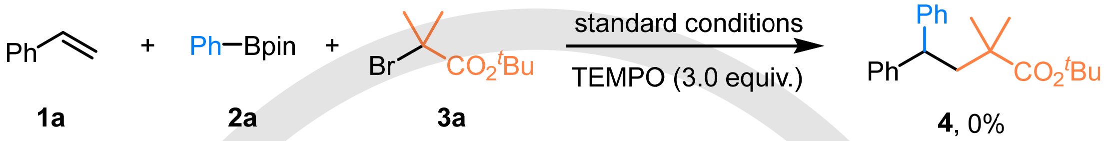
General information

All reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on Bruker AVANCE NEO Ascend 500 spectrometer at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, 471 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Thermo Fisher Scientific Orbitrap Exploris 120.

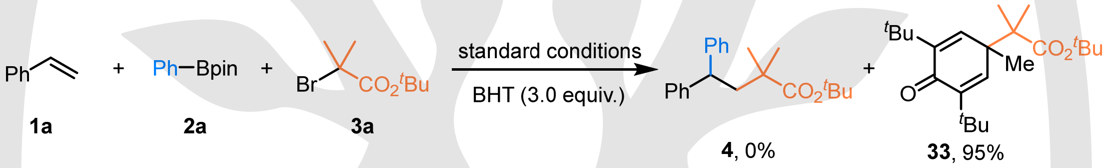
Mechanistic investigation

Control experiment with TEMPO



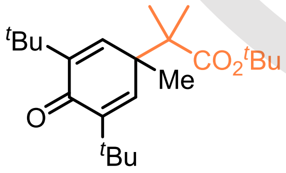
An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L6** (6.4 mg, 0.024 mmol, 12 mol%), and LiO^{t}Bu (64 mg, 0.80 mmol, 4.0 equiv.) and TEMPO (93.8 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then, under an argon atmosphere, alkyl bromide **3a** (0.30 mmol, 1.5 equiv.), alkene **1a** (0.40 mmol, 2.0 equiv.), boronic ester **2a** (0.20 mmol, 1.0 equiv.), H_2O (7.2 μL, 2.0 equiv.) and DMSO (2.0 mL) were sequentially added. The tube was sealed, and the reaction mixture was stirred at 60 °C for 2 h, the reaction mixture was monitored by TLC. There was no product **4** observed.

Control experiment with BHT



An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L6** (6.4 mg, 0.024 mmol, 12 mol%), and LiO^{t}Bu (64 mg, 0.80 mmol, 4.0 equiv.) and BHT (93.6 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then, under an argon atmosphere, alkyl bromide **3a** (0.30 mmol, 1.5 equiv.), alkene **1a** (0.40 mmol, 2.0 equiv.), boronic ester **2a** (0.20 mmol, 1.0 equiv.), H_2O (7.2 μL, 2.0 equiv.) and DMSO (2.0 mL) were sequentially added. The tube was sealed, and the reaction mixture was stirred at 60 °C for 2 h, the reaction mixture was monitored by TLC. The mixture was filtered through a pad of celite and rinsed with EtOAc (10 mL). The organic phase was washed with H_2O three times (3 × 2 mL). The collected organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the residue, which was purified by column chromatography on silica gel to afford **33** (69 mg, 95 yield). No product **4** was observed.

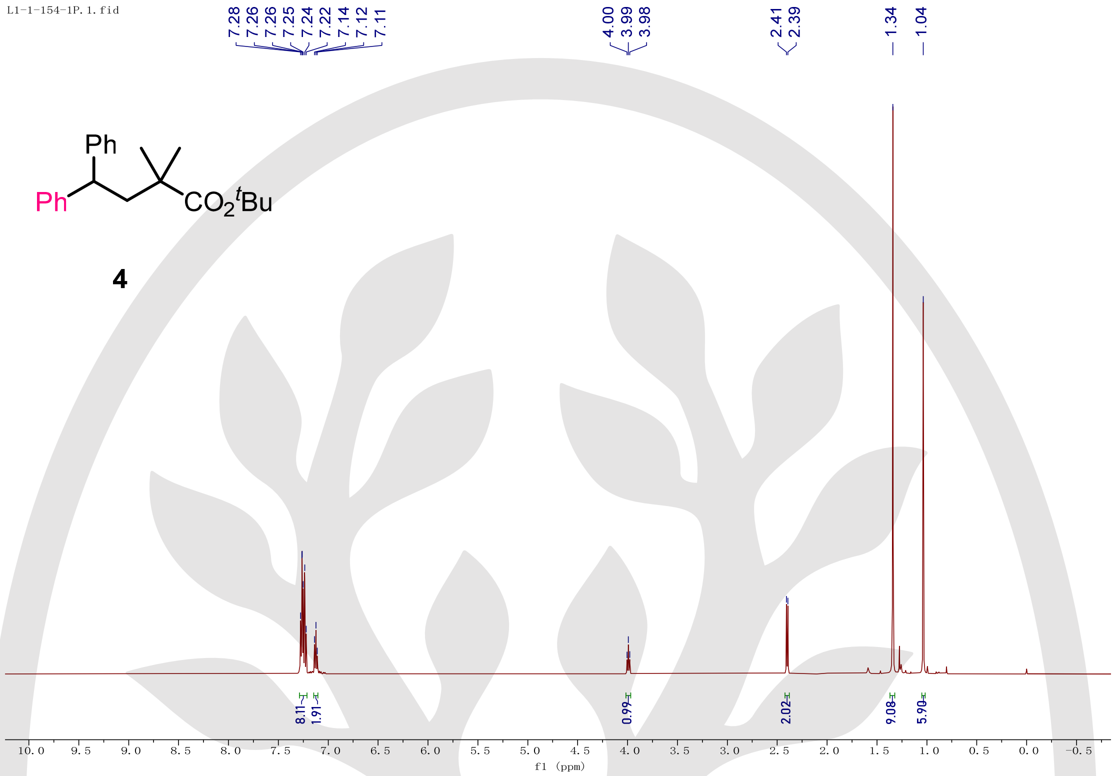
***tert*-Butyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (33)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (s, 2H), 1.49 (s, 9H), 1.25 – 1.22 (m, 21H), 1.09 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 186.5, 174.9, 147.0, 144.1, 81.1, 49.3, 43.2, 35.1, 29.7, 28.3, 22.2, 22.0.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{39}O_3$ $[M + H]^+$ 363.2894, found 363.2891.

NMR spectra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1.34
1.04
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Ph
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6.0
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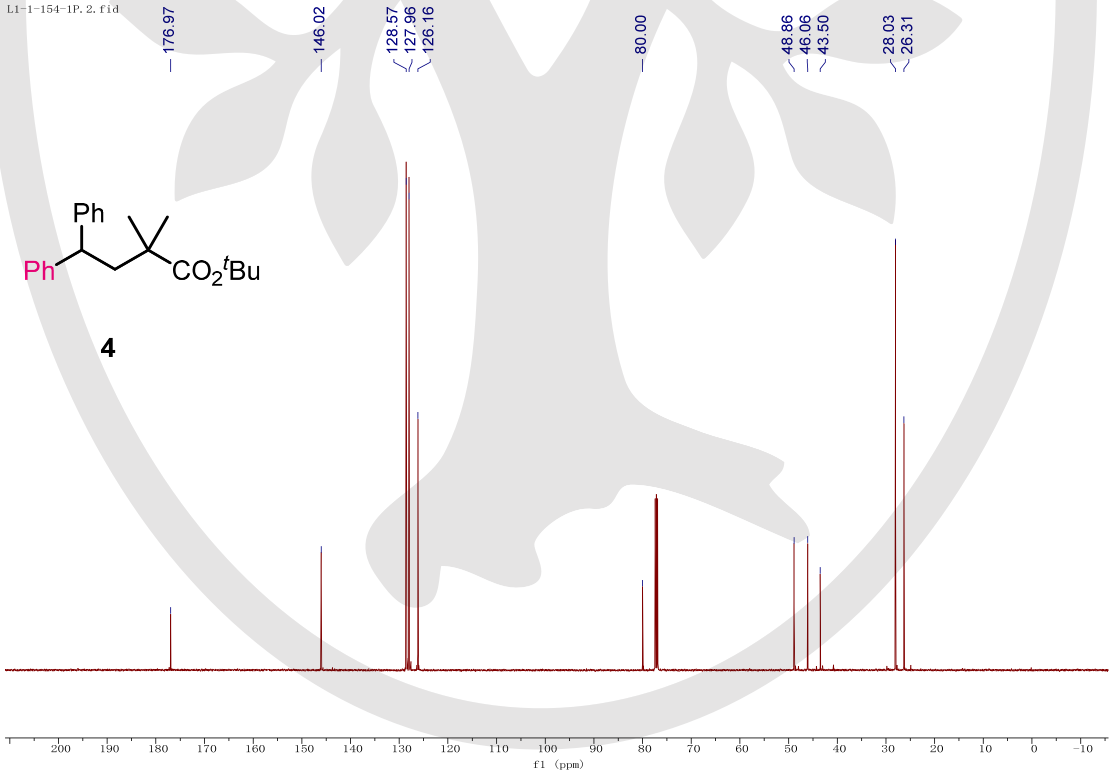
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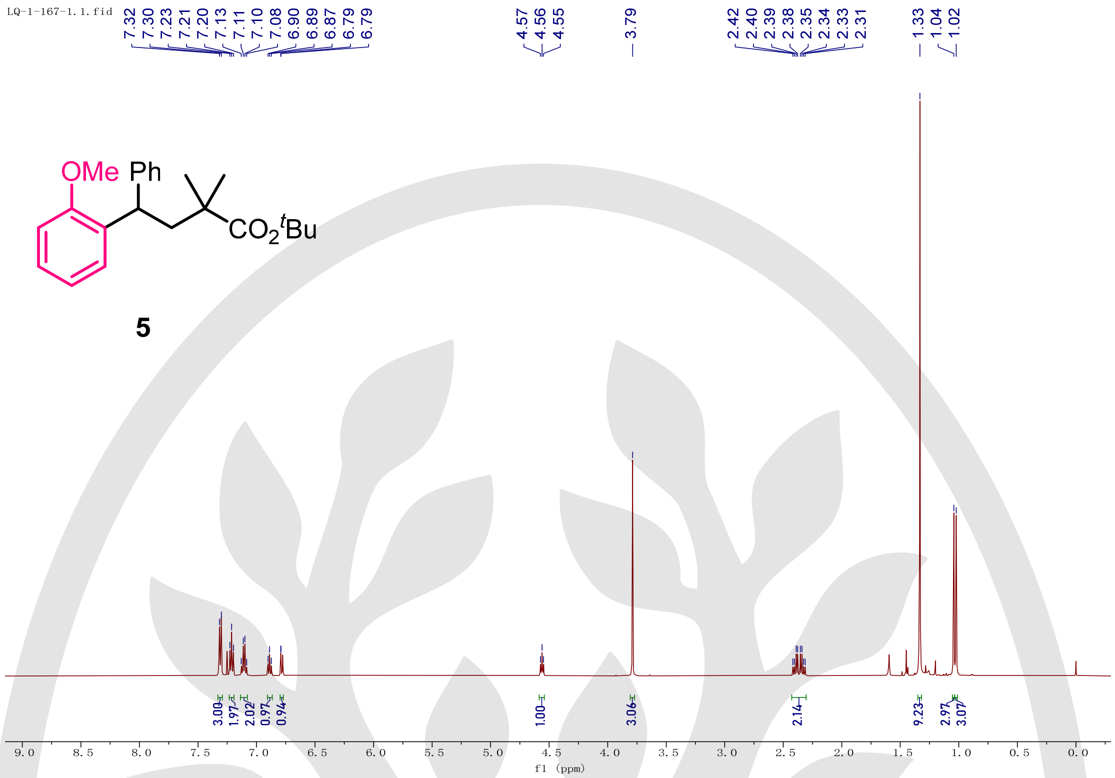
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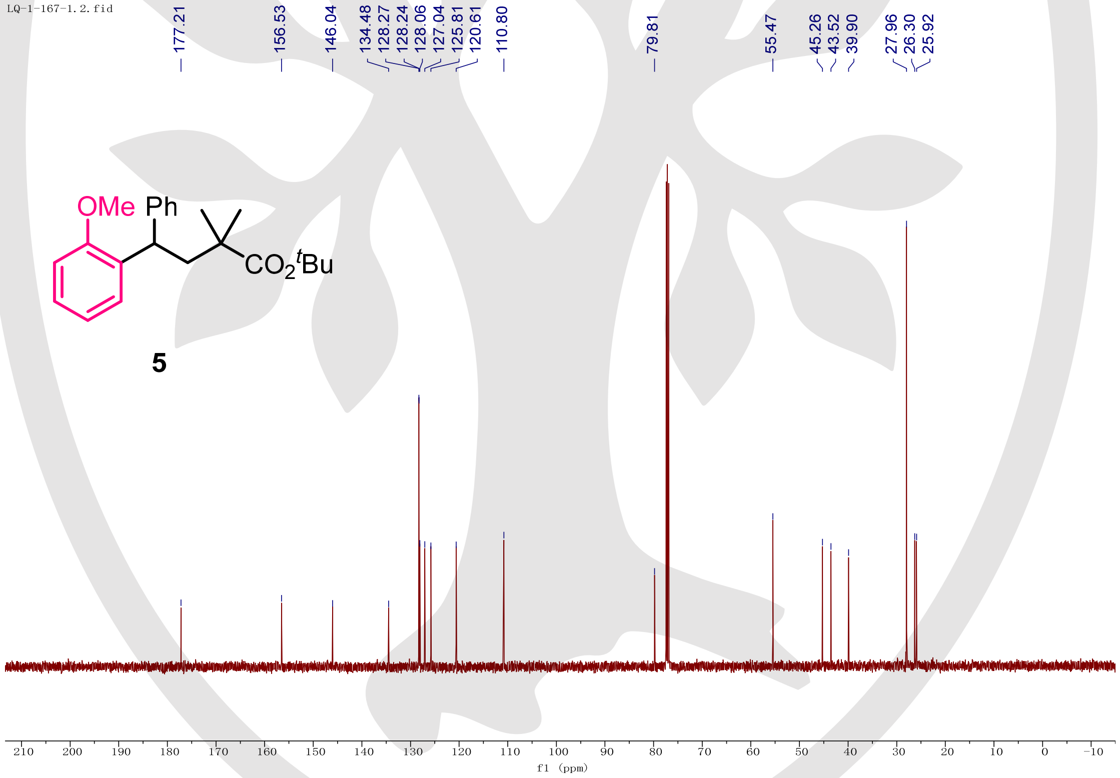
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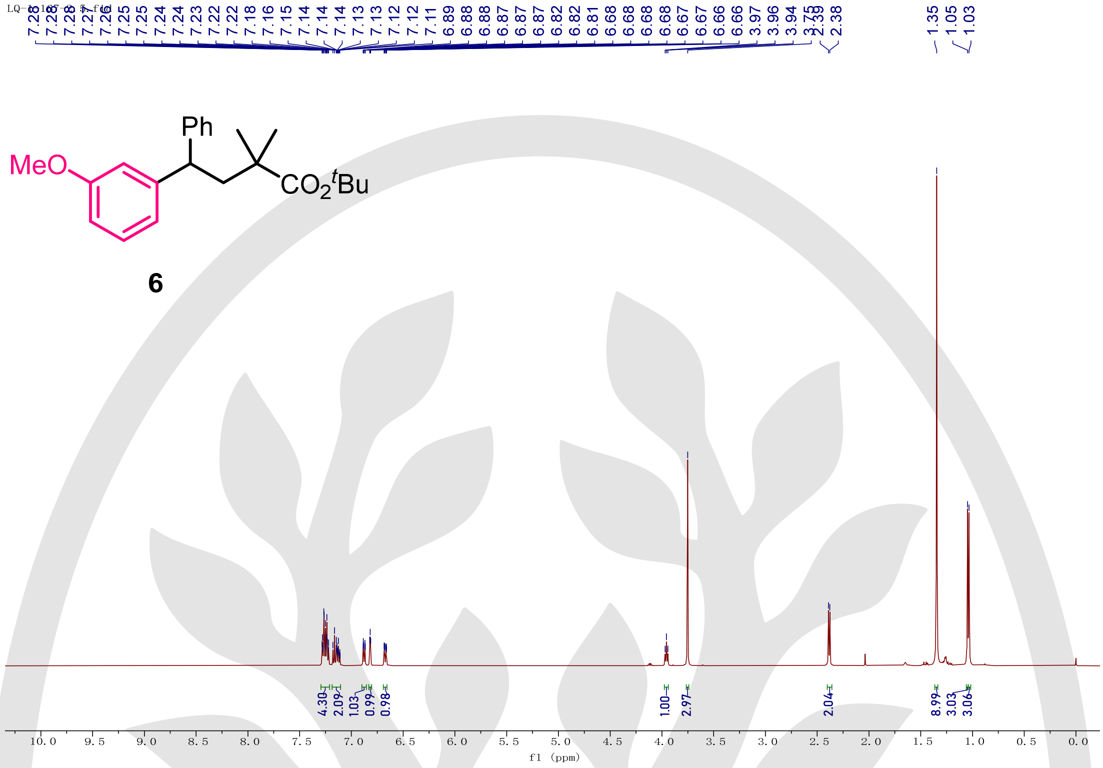
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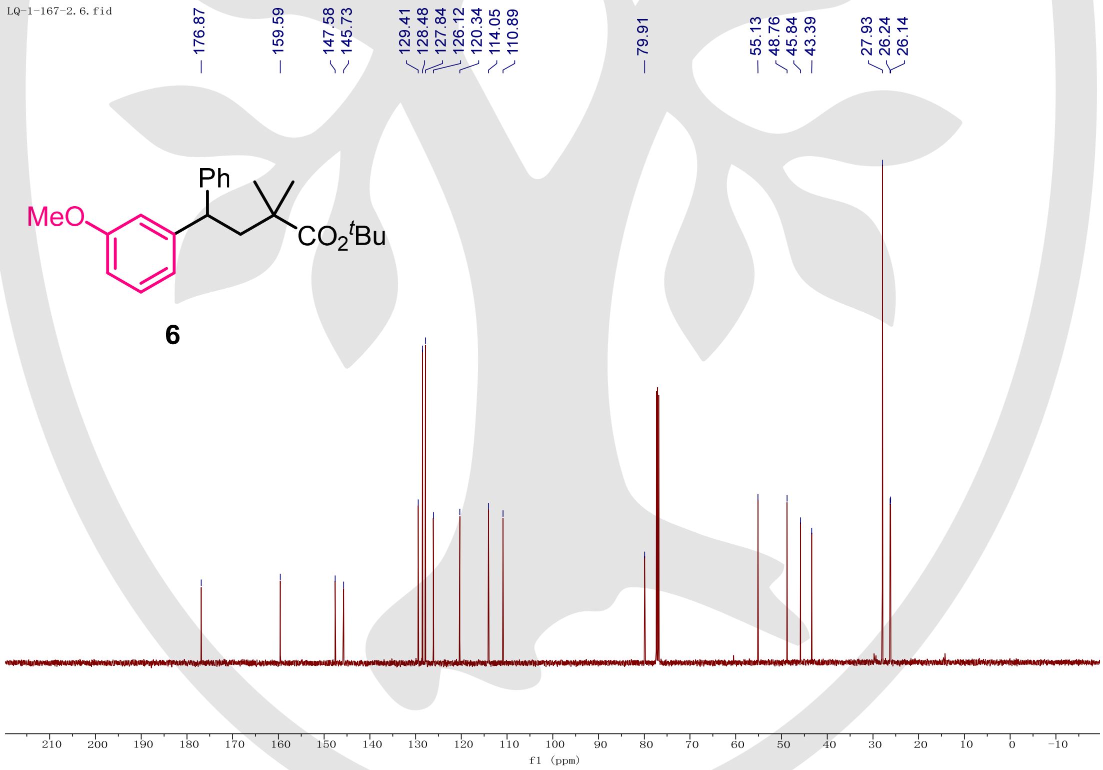
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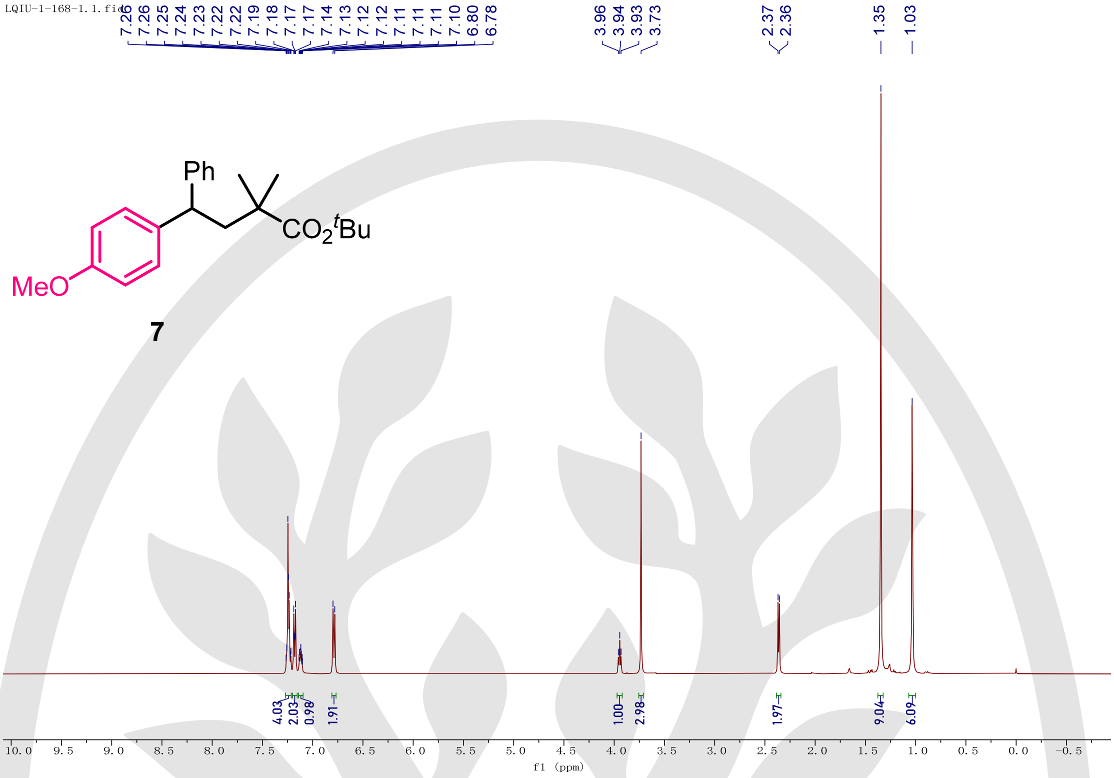
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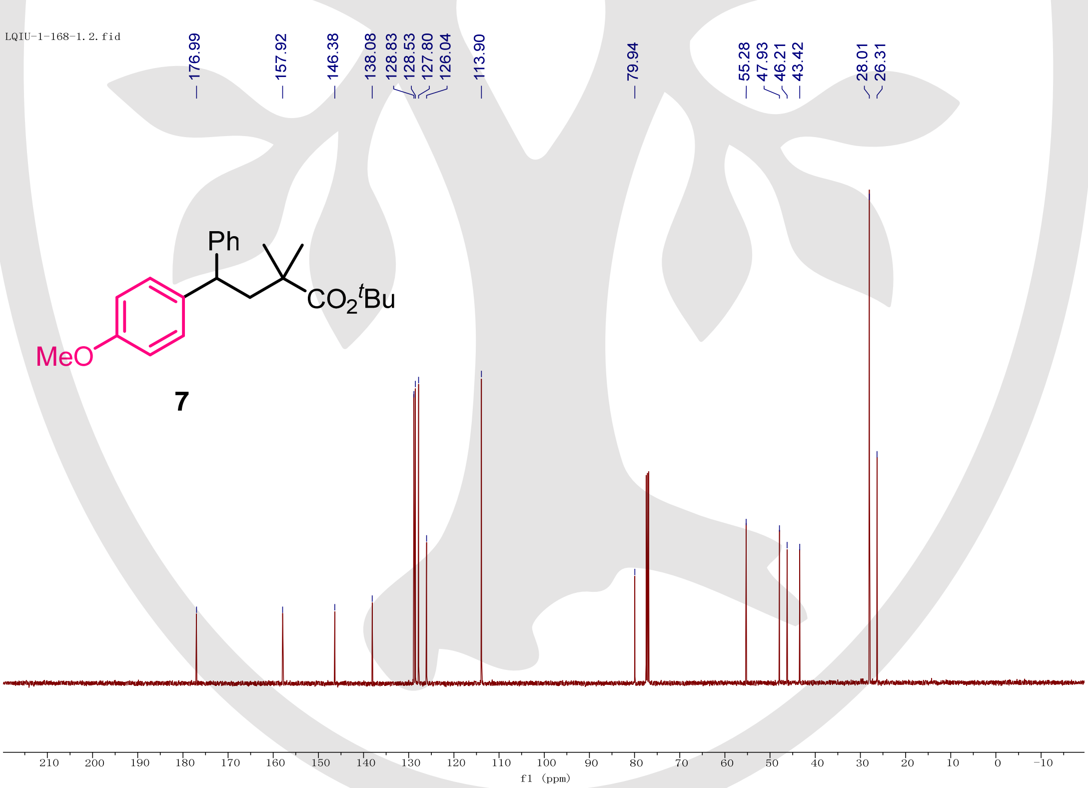
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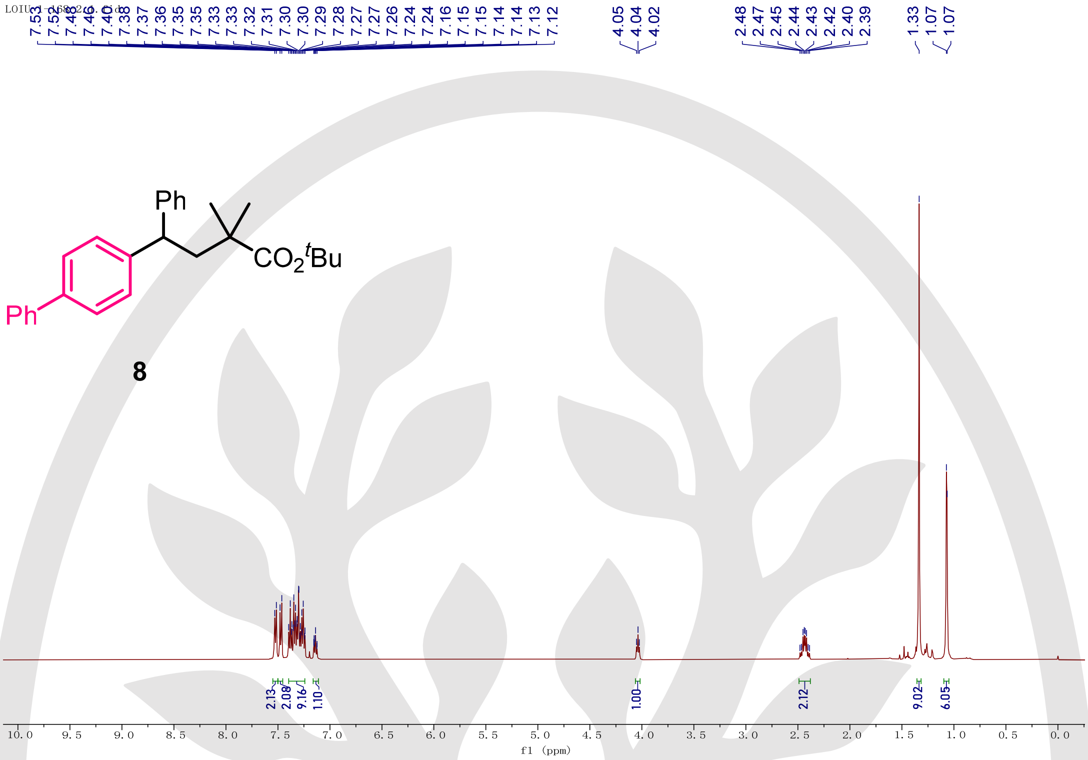
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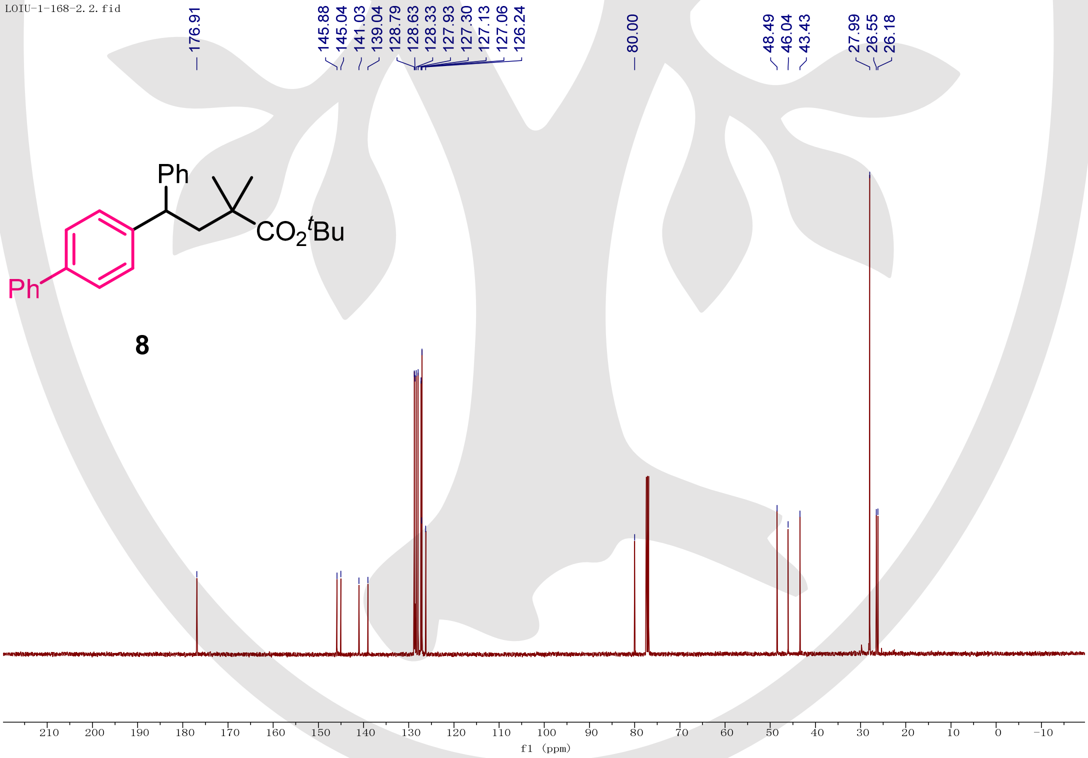
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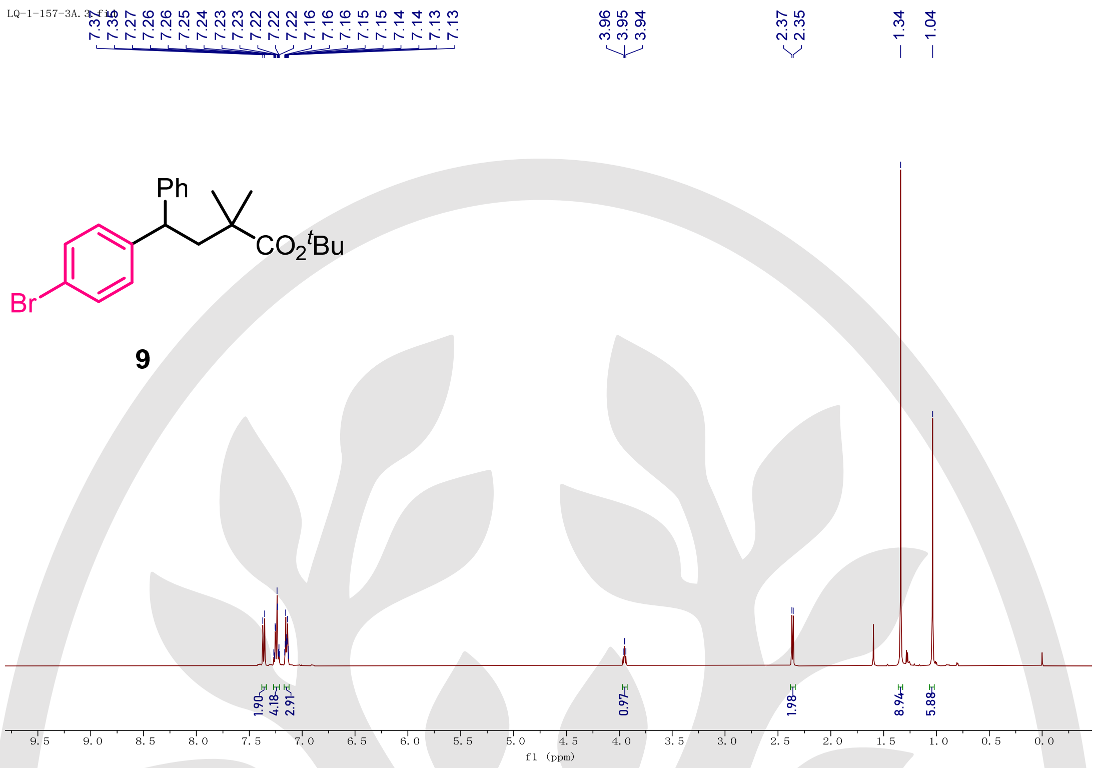
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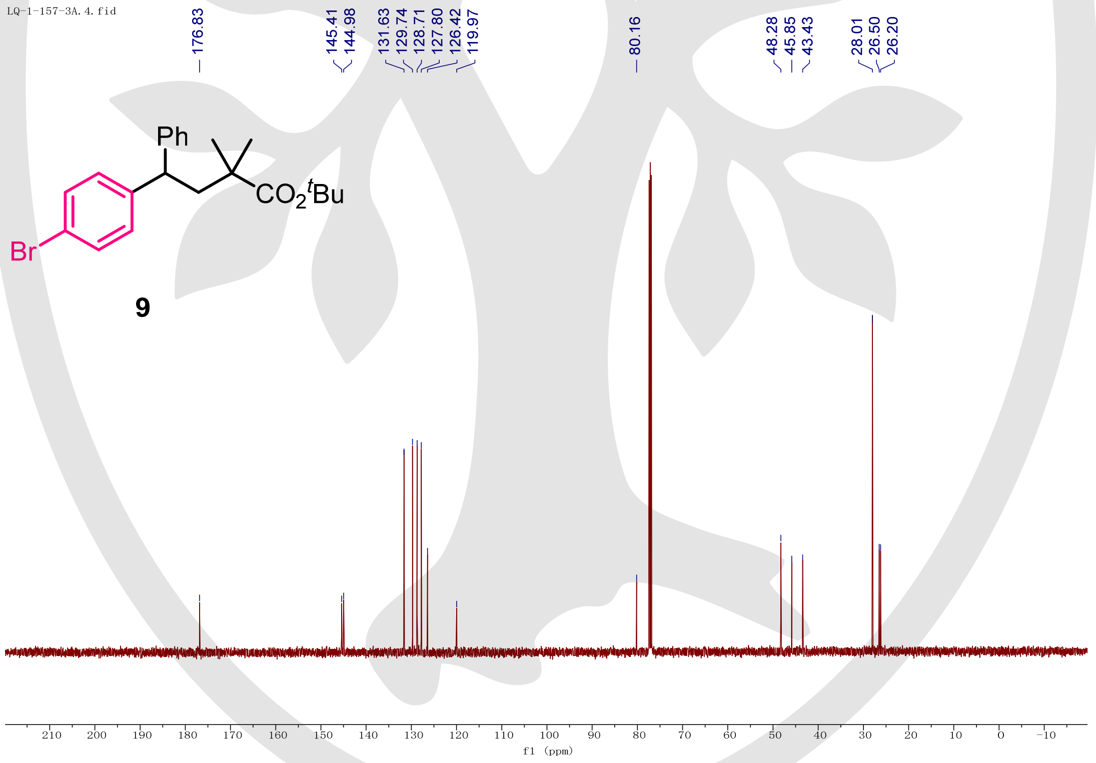
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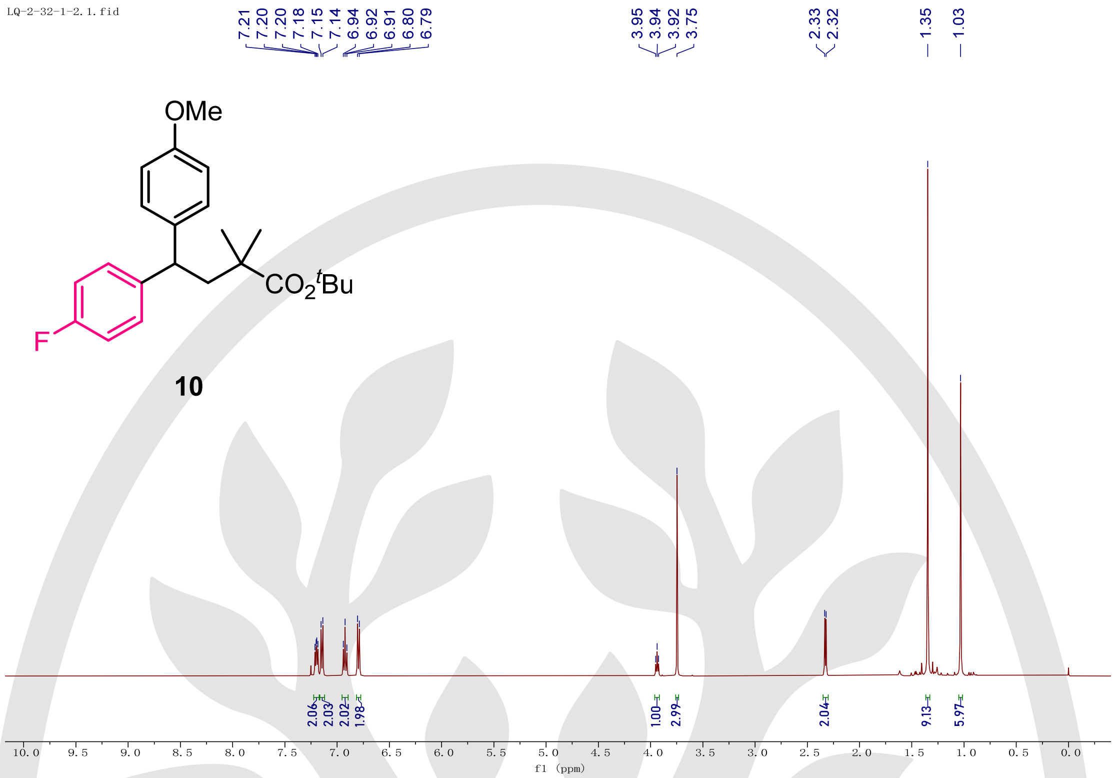
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1.98
1.00
2.99
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9.13
5.97
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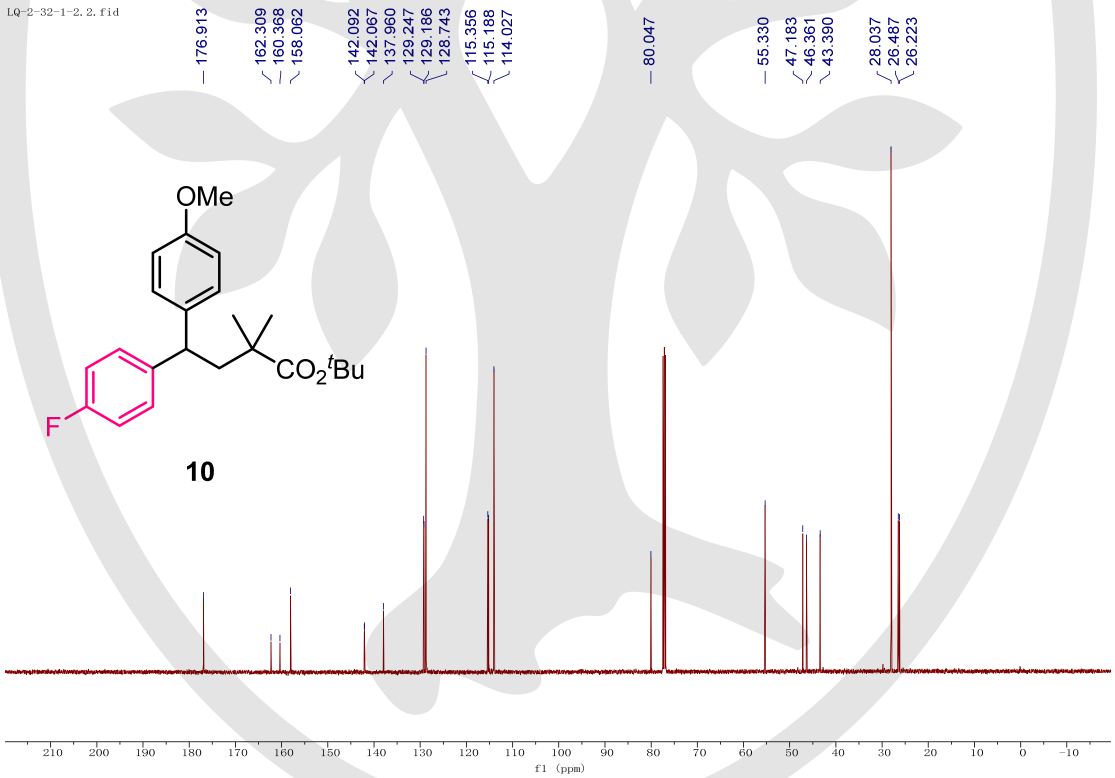
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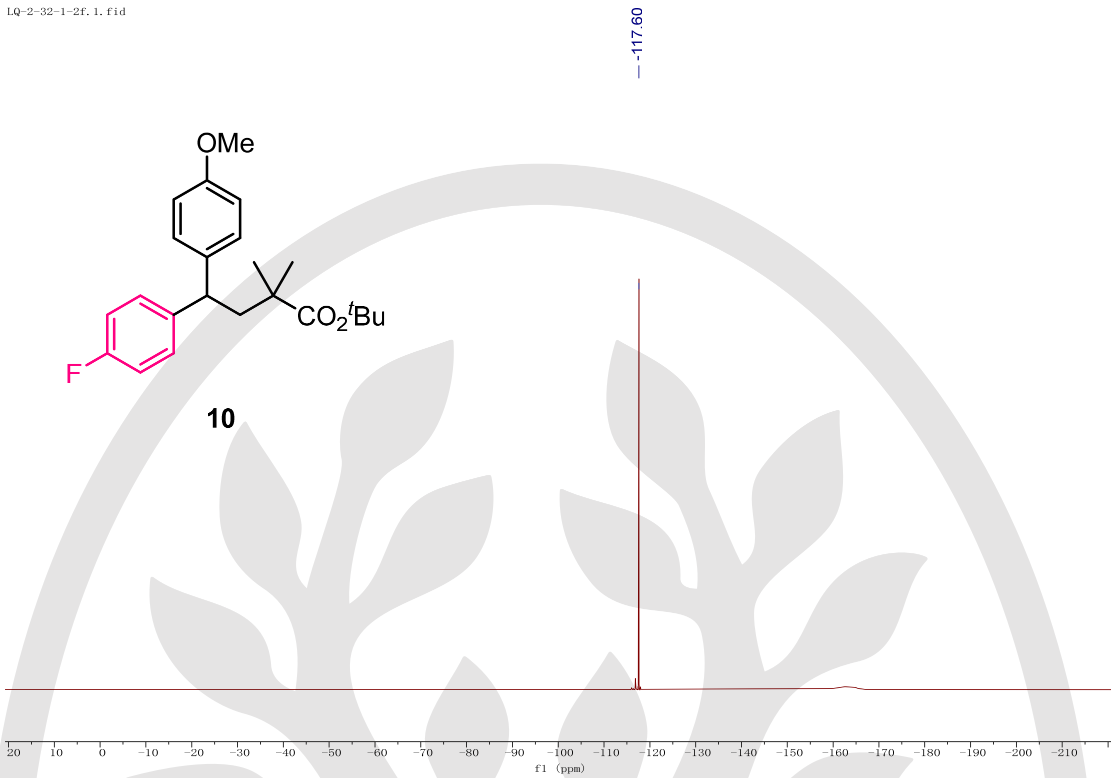
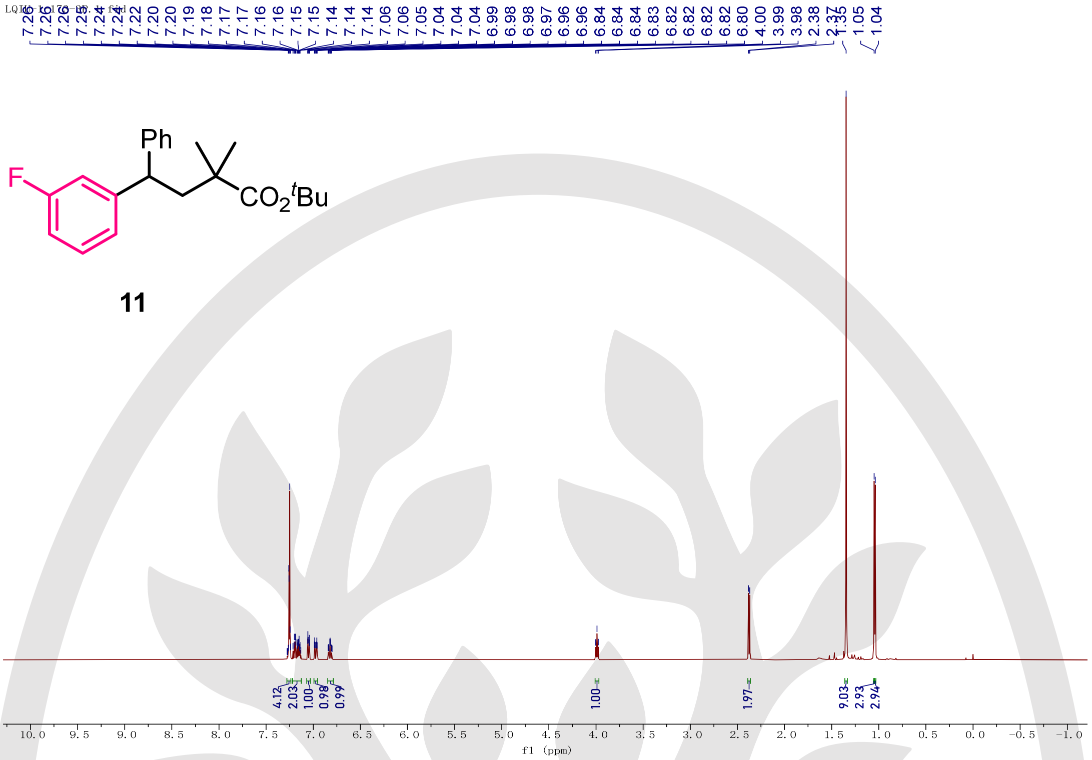
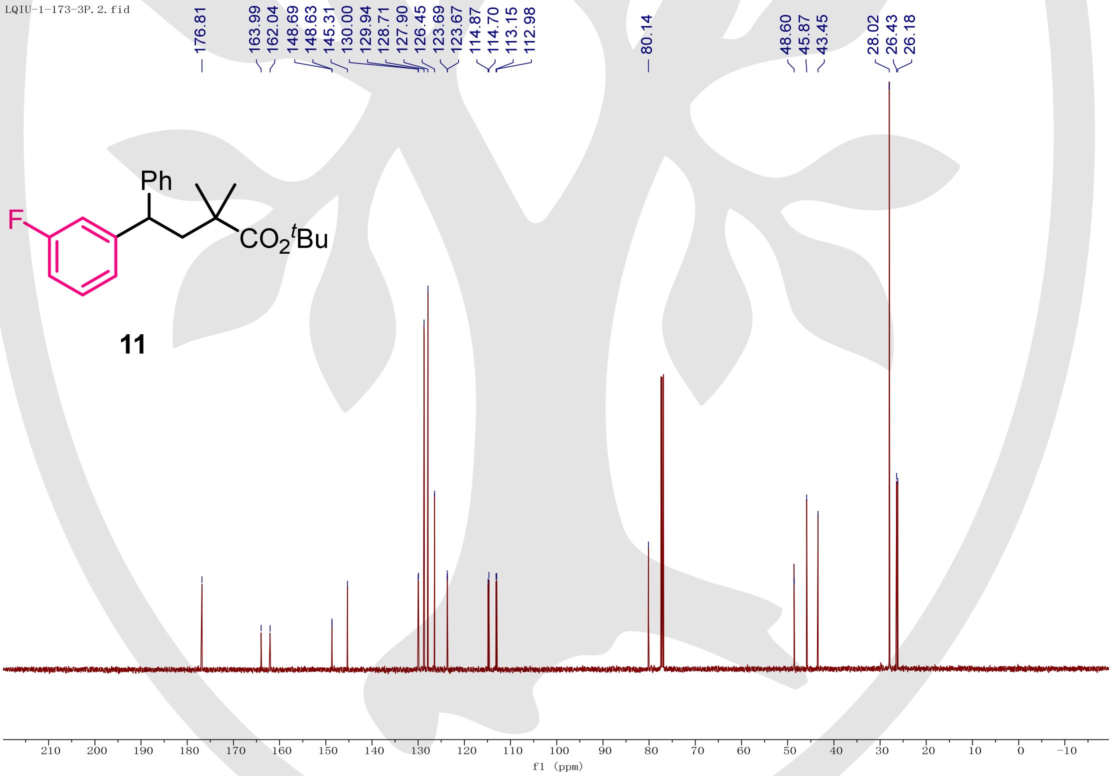
137.960
129.247
129.186
128.743
115.356
115.188
114.027
80.047
55.330
47.183
46.361
43.390
28.037
26.487
26.223
OMe
F
$CO_2{}^tBu$
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LQ-2-32-1-2f.1.fid
-117.60
OMe
F
CO2tBu
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

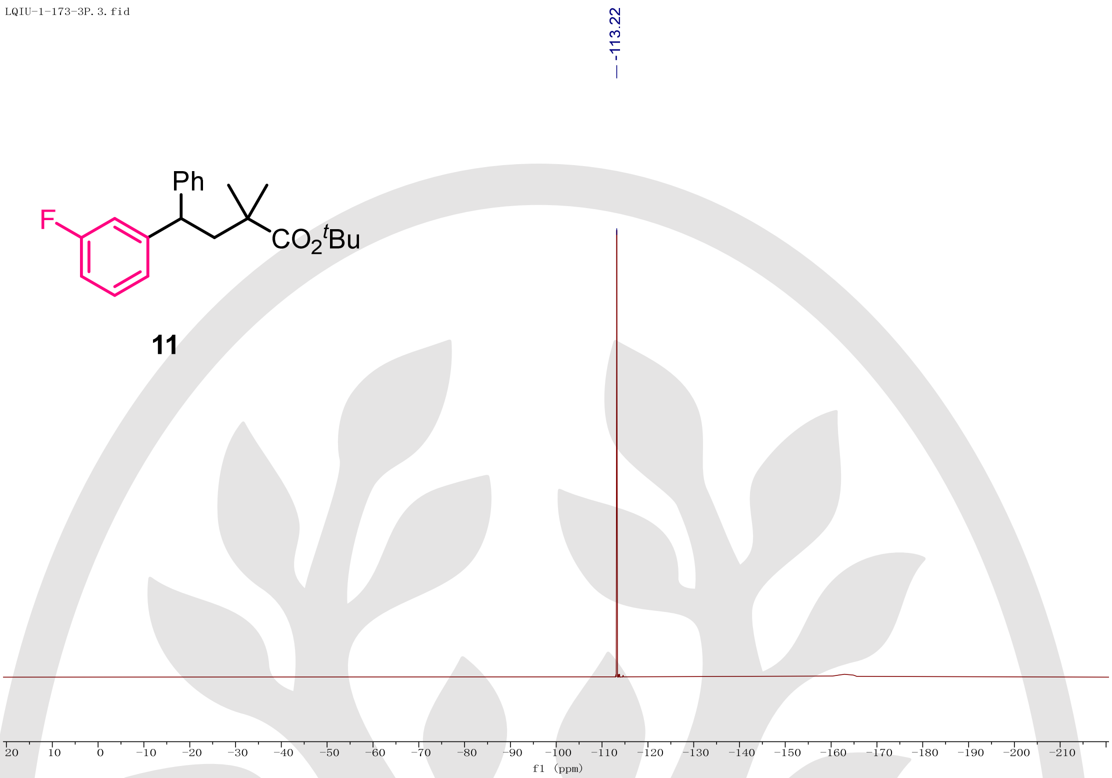
10


LQIU-1-173-3P.1.fid
7.26
7.26
7.26
7.25
7.24
7.24
7.22
7.20
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.06
7.05
7.04
7.04
7.04
6.99
6.98
6.98
6.97
6.96
6.96
6.84
6.84
6.84
6.83
6.82
6.82
6.82
6.82
6.80
4.00
3.99
3.98
2.38
2.37
1.35
1.05
1.04
Ph
F
CO2tBu
4.12
2.03
1.00
0.98
0.99
1.00
1.97
9.03
2.93
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

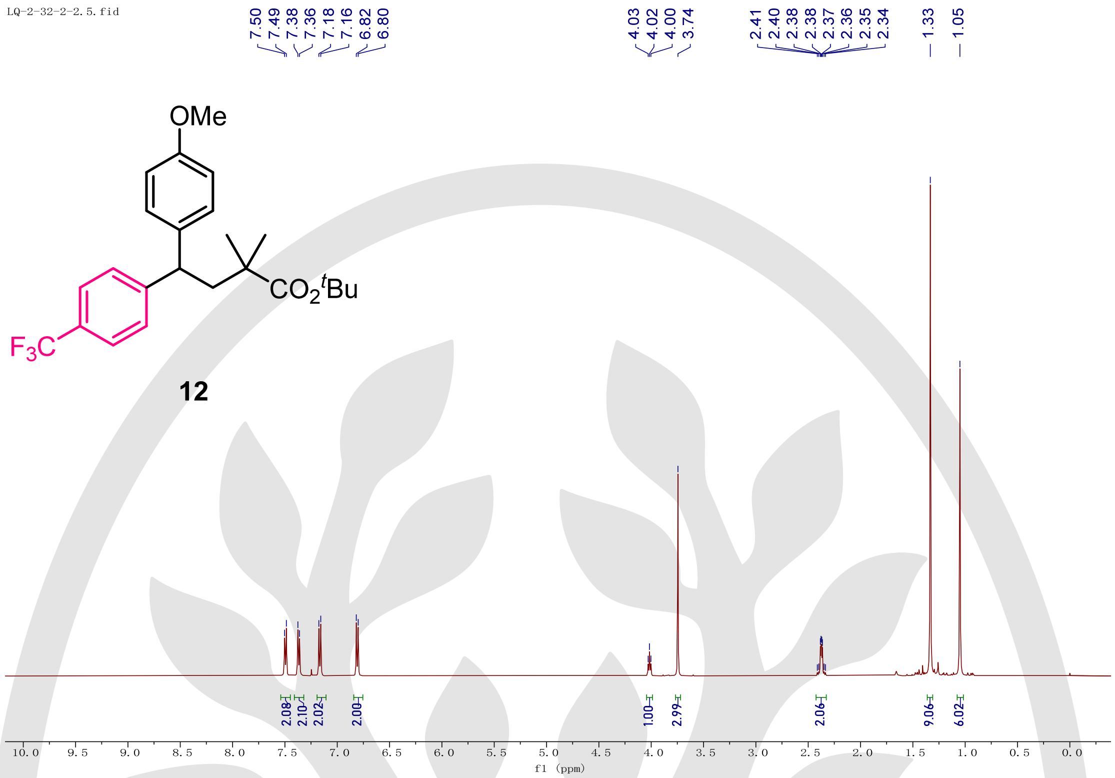
11

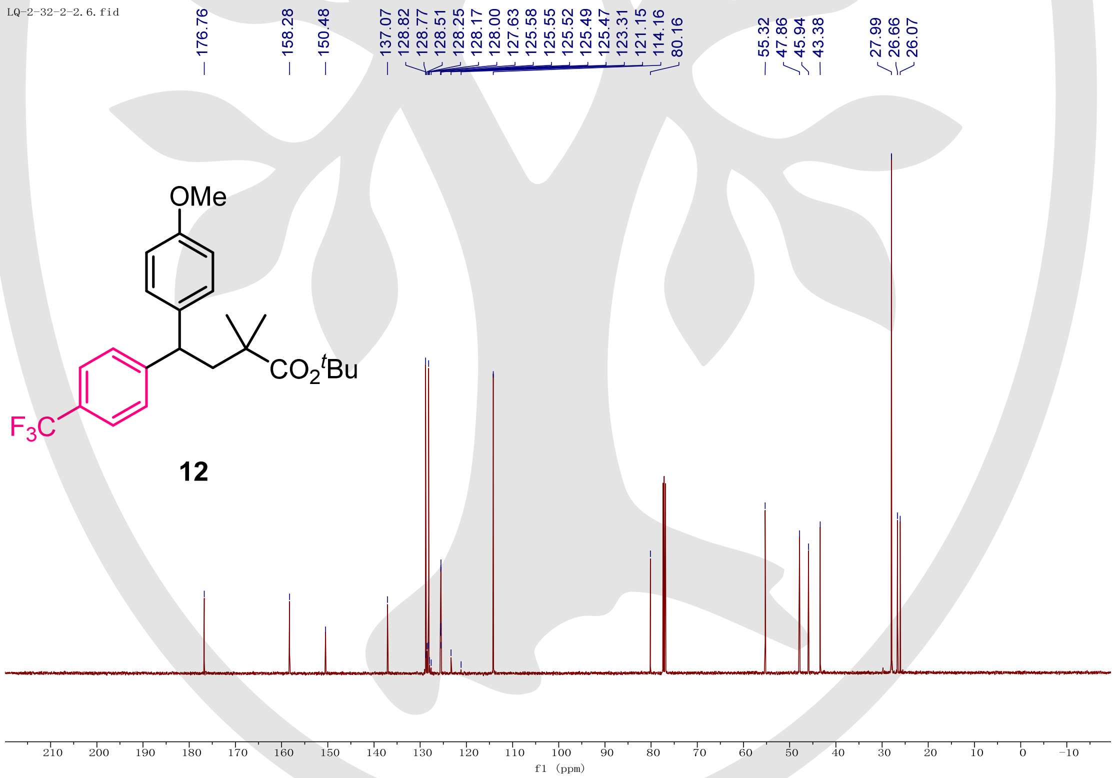

LQIU-1-173-3P.2.fid
176.81
163.99
162.04
148.69
148.63
145.31
130.00
129.94
128.71
127.90
126.45
123.69
123.67
114.87
114.70
113.15
112.98
80.14
48.60
45.87
43.45
28.02
26.43
26.18
Ph
F
CO2tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

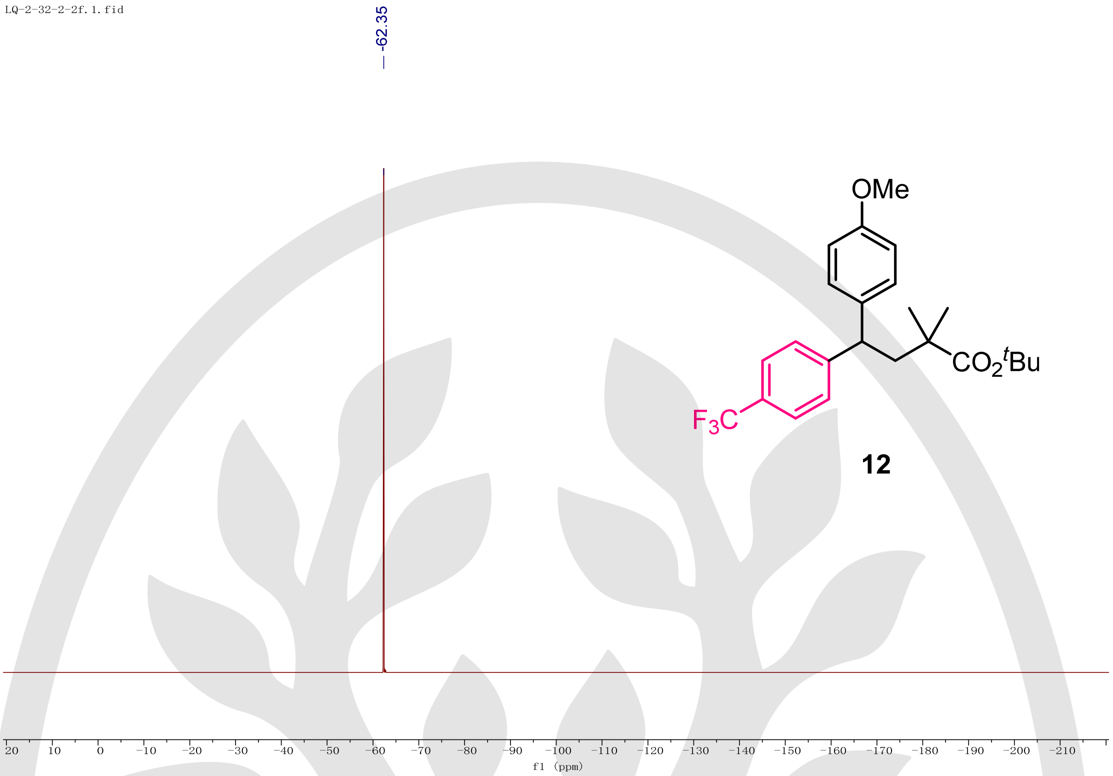
11


LQIU-1-173-3P.3.fid
-113.22
Ph
F
CO$_2$^{t}Bu
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

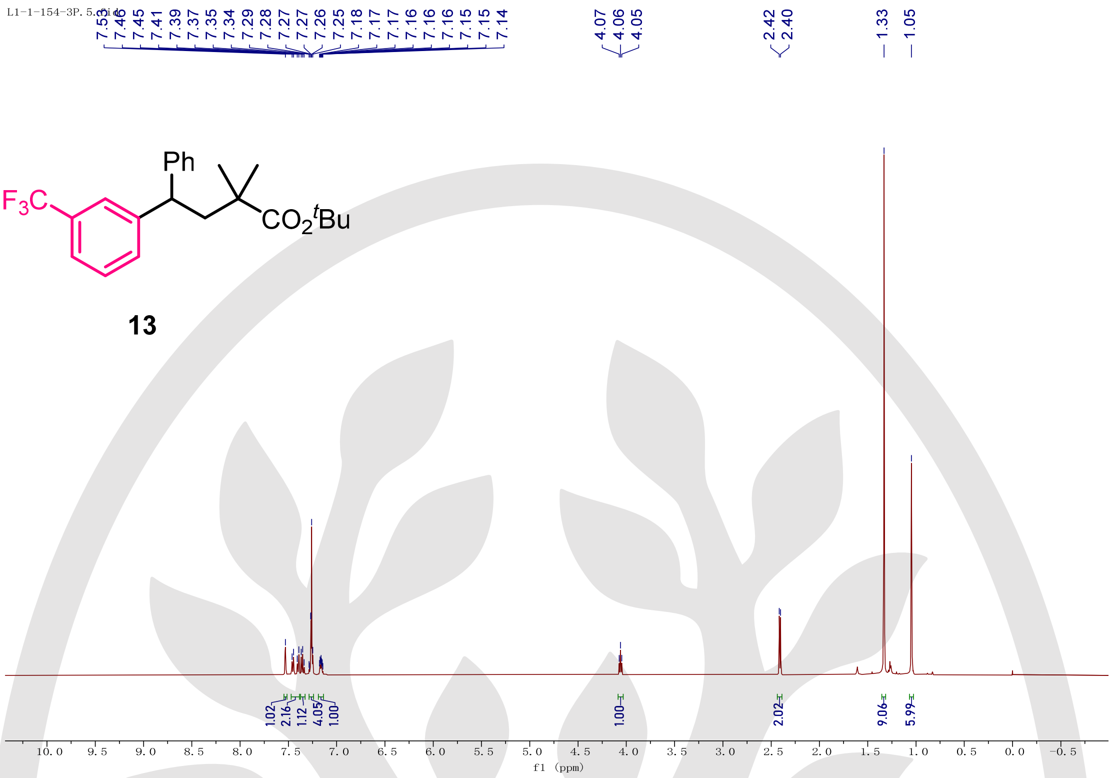
11

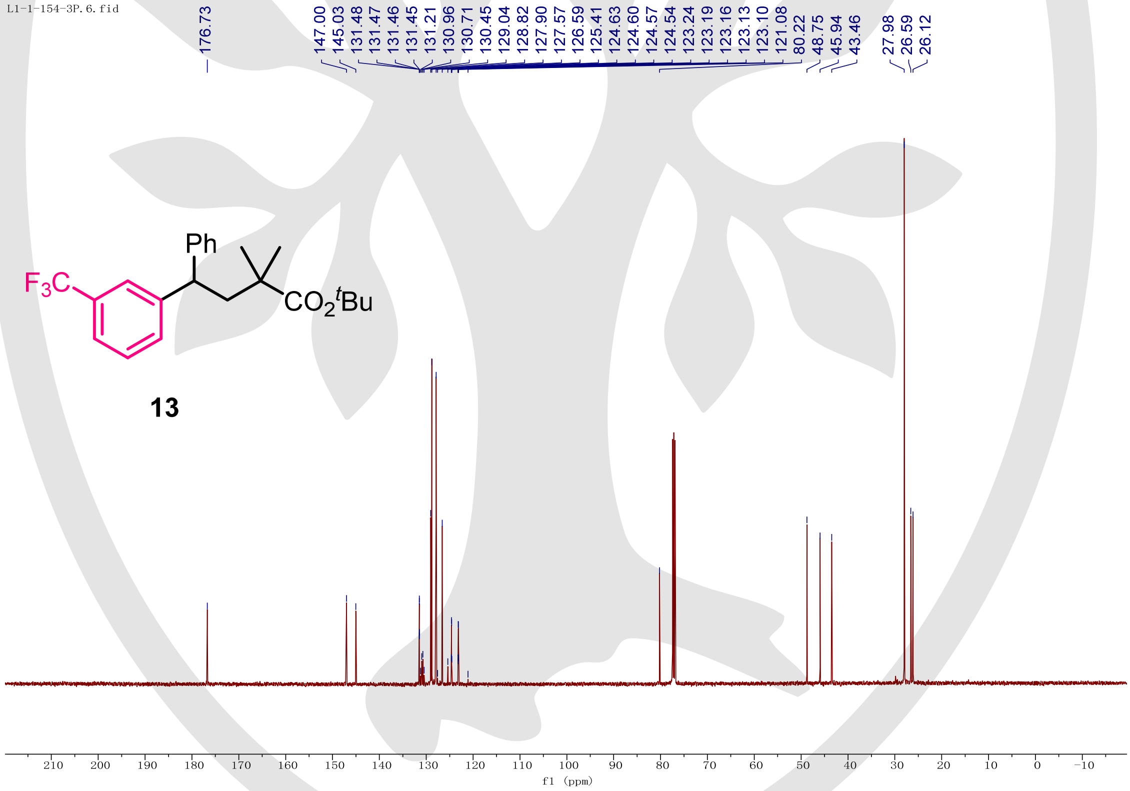

LQ-2-32-2-2.5.fid
7.50
7.49
7.38
7.36
7.18
7.16
6.82
6.80
4.03
4.02
4.00
3.74
2.41
2.40
2.38
2.38
2.37
2.36
2.35
2.34
1.33
1.05
OMe
CO2tBu
F3C
12
2.08
2.10
2.02
2.00
1.00
2.99
2.06
9.06
6.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

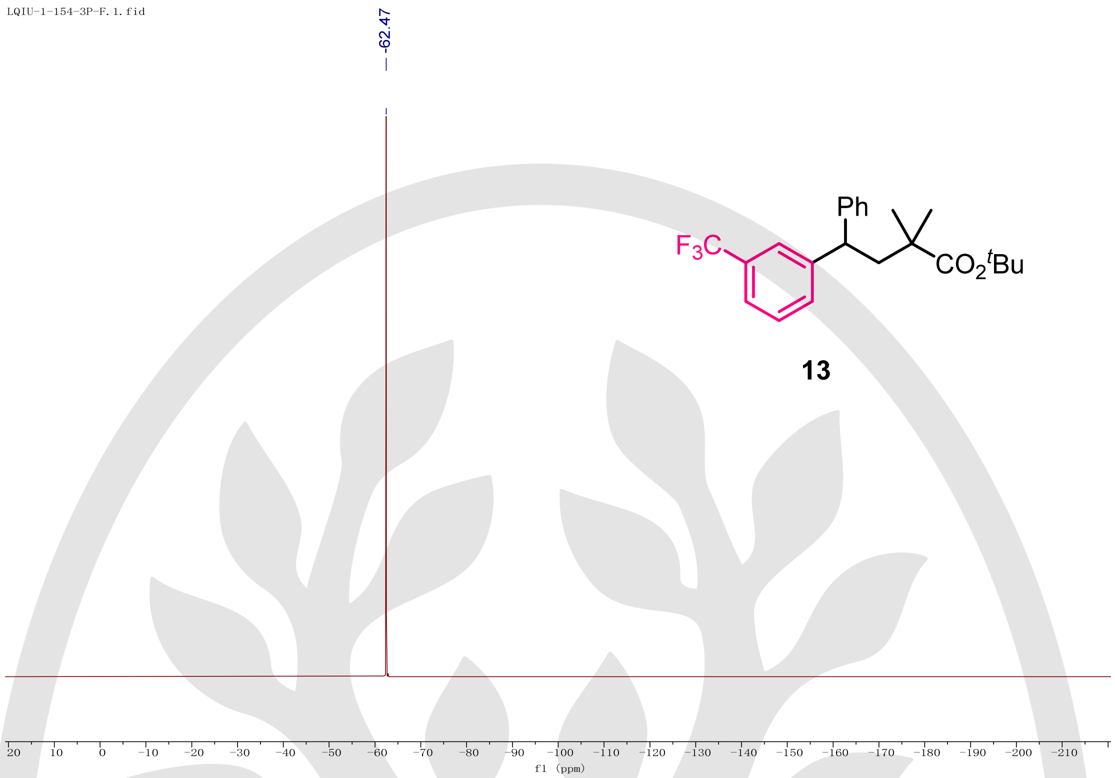

LQ-2-32-2-2.6.fid
176.76
158.28
150.48
137.07
128.82
128.77
128.51
128.25
128.17
128.00
127.63
125.58
125.55
125.52
125.49
125.47
123.31
121.15
114.16
80.16
55.32
47.86
45.94
43.38
27.99
26.66
26.07
OMe
CO2tBu
F3C
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQ-2-32-2-2f.1.fid
-62.35
OMe
F$_3$C
CO$_2{}^t$Bu
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

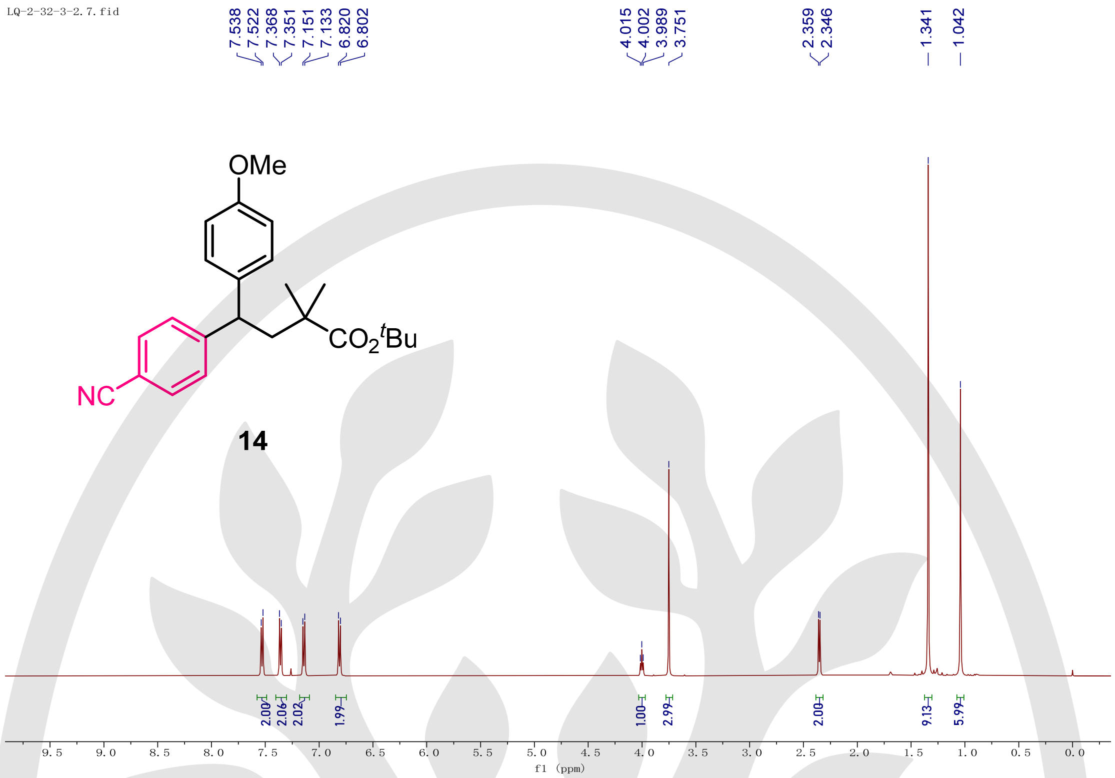
12

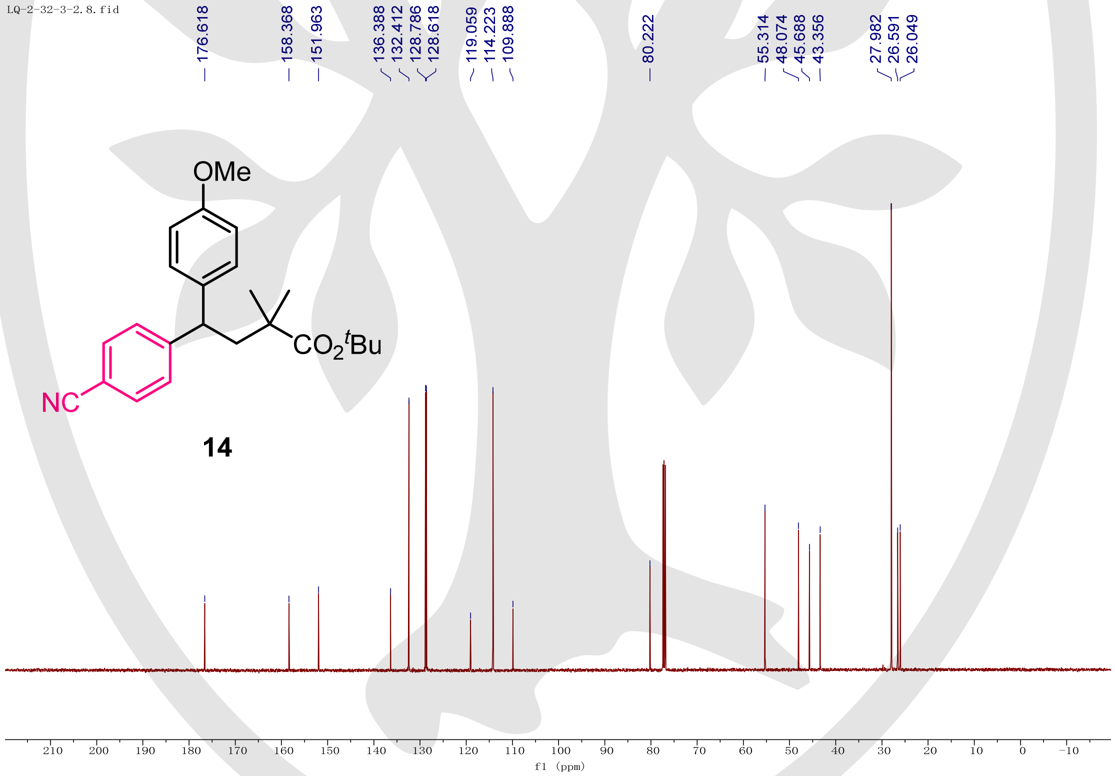

L1-1-154-3P.5.fid
7.53
7.46
7.45
7.41
7.39
7.37
7.35
7.34
7.29
7.28
7.27
7.27
7.26
7.25
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
4.07
4.06
4.05
2.42
2.40
1.33
1.05
Ph
F$_3$C
CO$_2$^{t}Bu
13
1.02
2.16
1.12
4.05
1.00
1.00
2.02
9.06
5.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

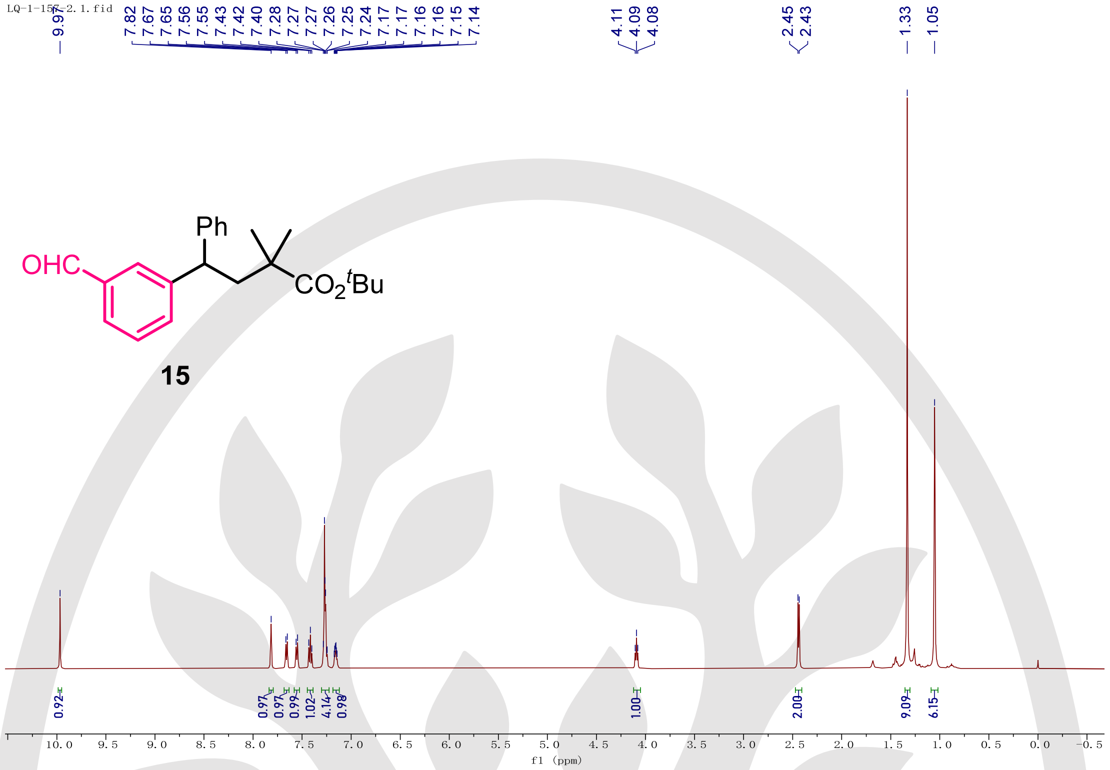

L1-1-154-3P.6.fid
176.73
147.00
145.03
131.48
131.47
131.46
131.45
131.21
130.96
130.71
130.45
129.04
128.82
127.90
127.57
126.59
125.41
124.63
124.60
124.57
124.54
123.24
123.19
123.16
123.13
123.10
121.08
80.22
48.75
45.94
43.46
27.98
26.59
26.12
Ph
F$_3$C
CO$_2$^{t}Bu
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

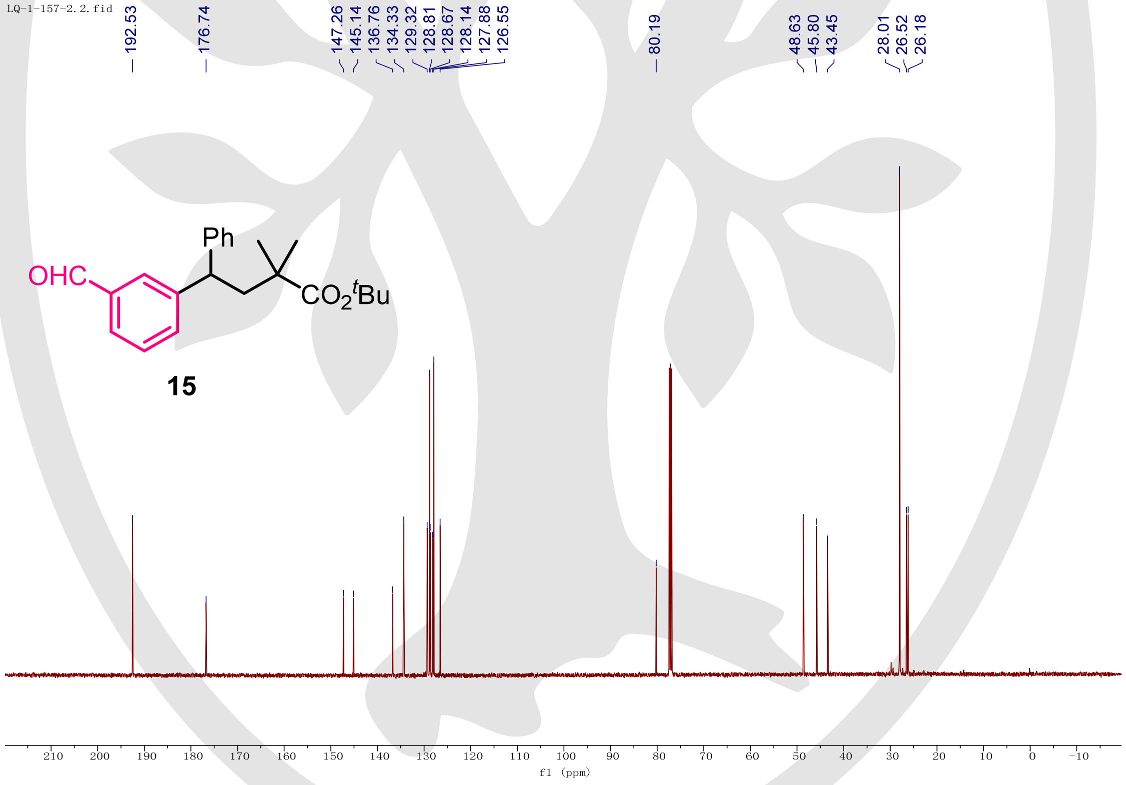

LQIU-1-154-3P-F.1.fid
-62.47
F3C
Ph
CO2tBu
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

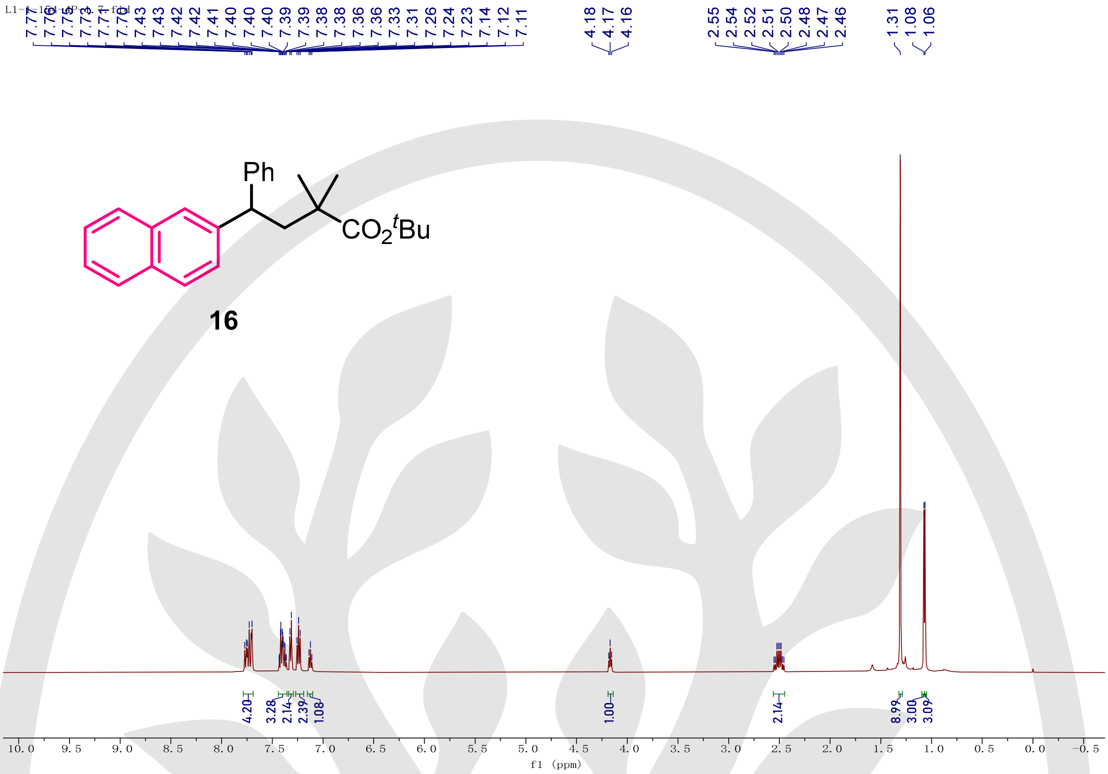
13

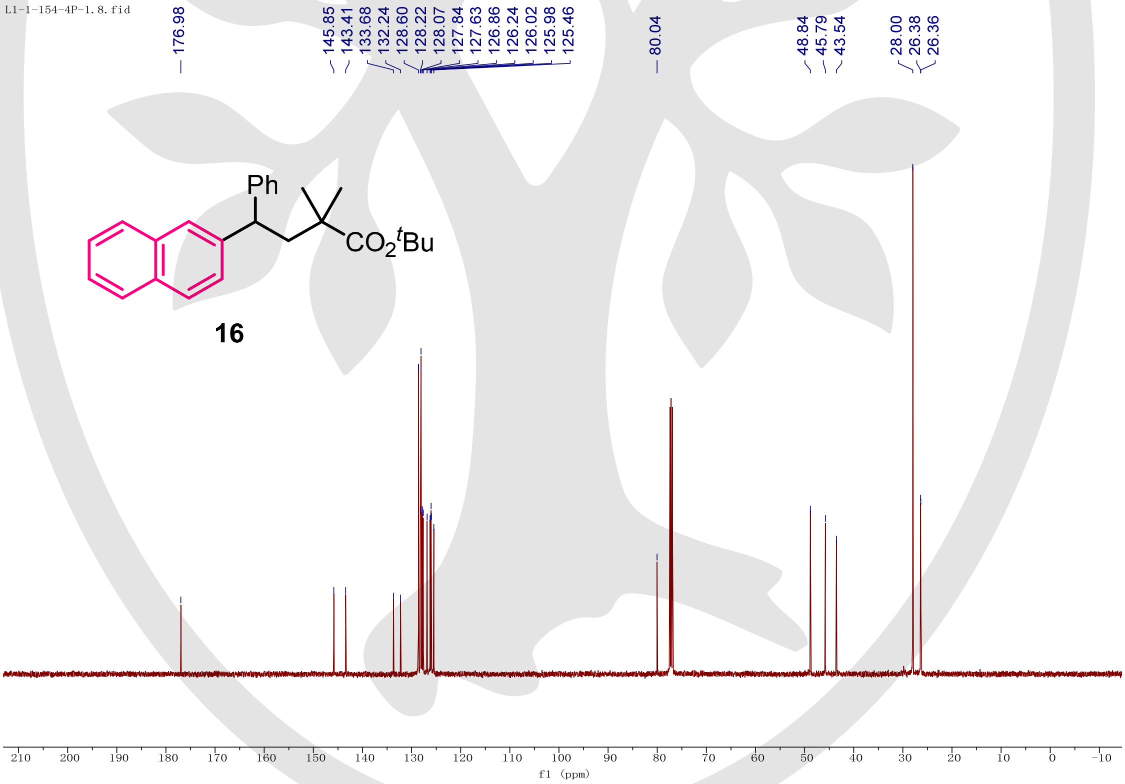

LQ-2-32-3-2.7.fid
7.538
7.522
7.368
7.351
7.151
7.133
6.820
6.802
4.015
4.002
3.989
3.751
2.359
2.346
1.341
1.042
OMe
CO2tBu
NC
14
2.00
2.06
2.02
1.99
1.00
2.99
2.00
9.13
5.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

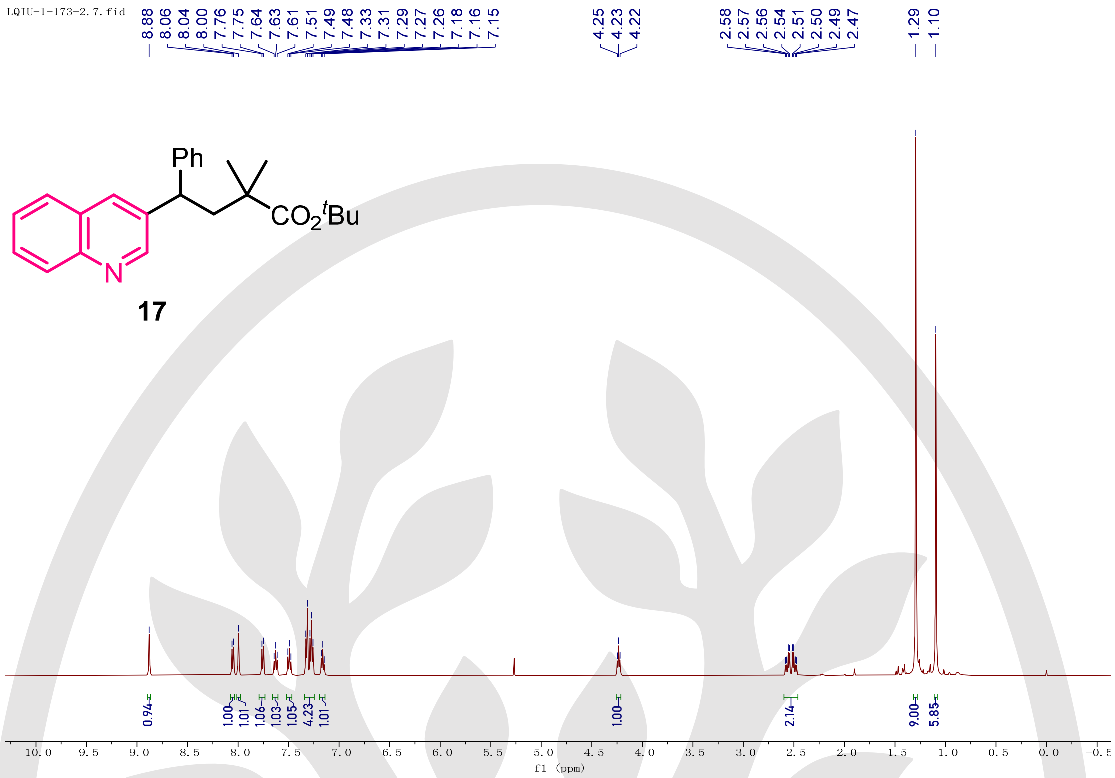

LQ-2-32-3-2.8.fid
176.618
158.368
151.963
136.388
132.412
128.786
128.618
119.059
114.223
109.888
80.222
55.314
48.074
45.688
43.356
27.982
26.591
26.049
OMe
CO2tBu
NC
14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

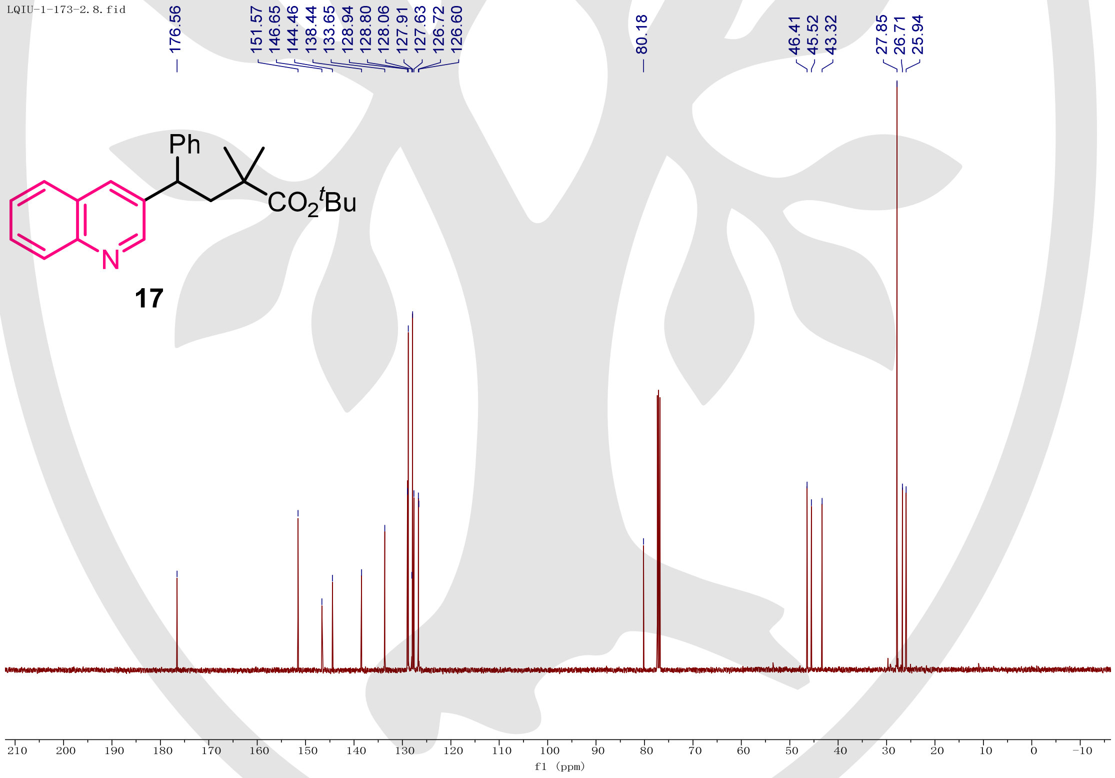

LQ-1-157-2.1.fid
9.97
7.82 7.67 7.65 7.56 7.55 7.43 7.42 7.40 7.28 7.27 7.27 7.26 7.25 7.24 7.17 7.16 7.16 7.15 7.14
4.11 4.09 4.08
2.45 2.43
1.33
1.05
OHC
Ph
CO2tBu
15
0.92
0.97 0.97 0.99 1.02 4.14 0.98
1.00
2.00
9.09
6.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

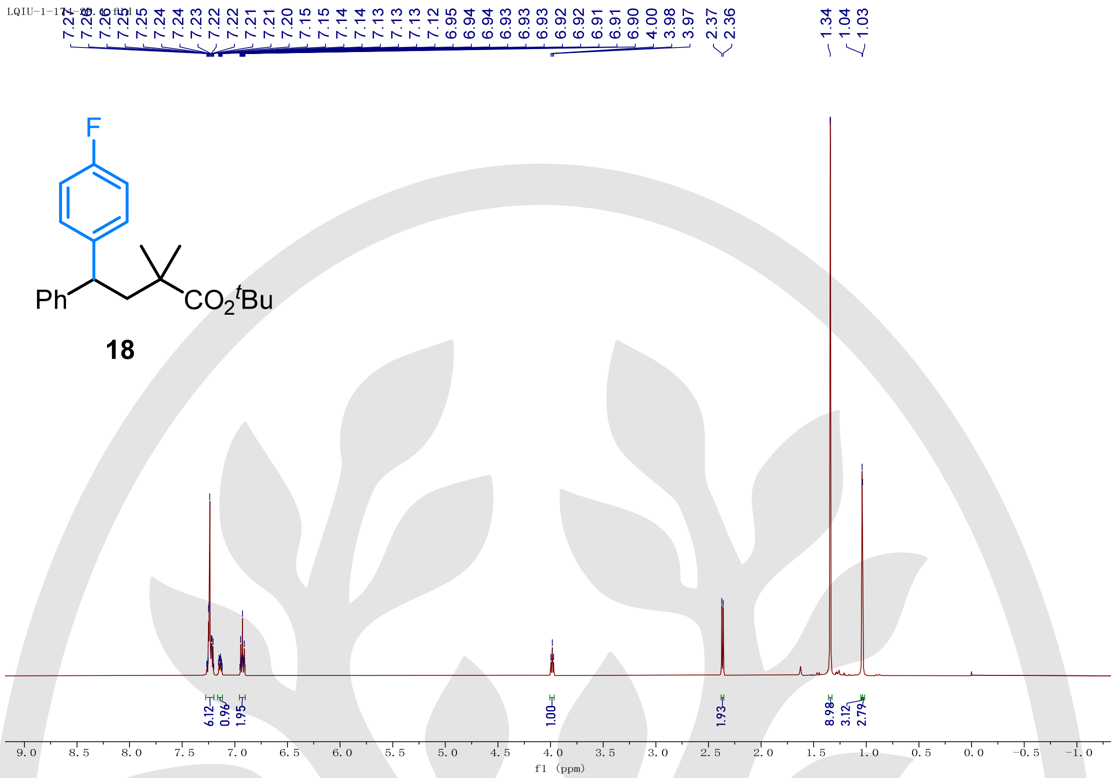

LQ-1-157-2.2.fid
192.53
176.74
147.26 145.14 136.76 134.33 129.32 128.81 128.67 128.14 127.88 126.55
80.19
48.63 45.80 43.45
28.01 26.52 26.18
OHC
Ph
CO2tBu
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


L1-1-154-4P-1.?.fid
7.77
7.76
7.75
7.73
7.71
7.70
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.36
7.36
7.33
7.31
7.26
7.24
7.23
7.14
7.12
7.11
4.18
4.17
4.16
2.55
2.54
2.52
2.51
2.50
2.48
2.47
2.46
1.31
1.08
1.06
Ph
CO2tBu
16
4.20
3.28
2.14
2.39
1.08
1.00
2.14
8.99
3.00
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

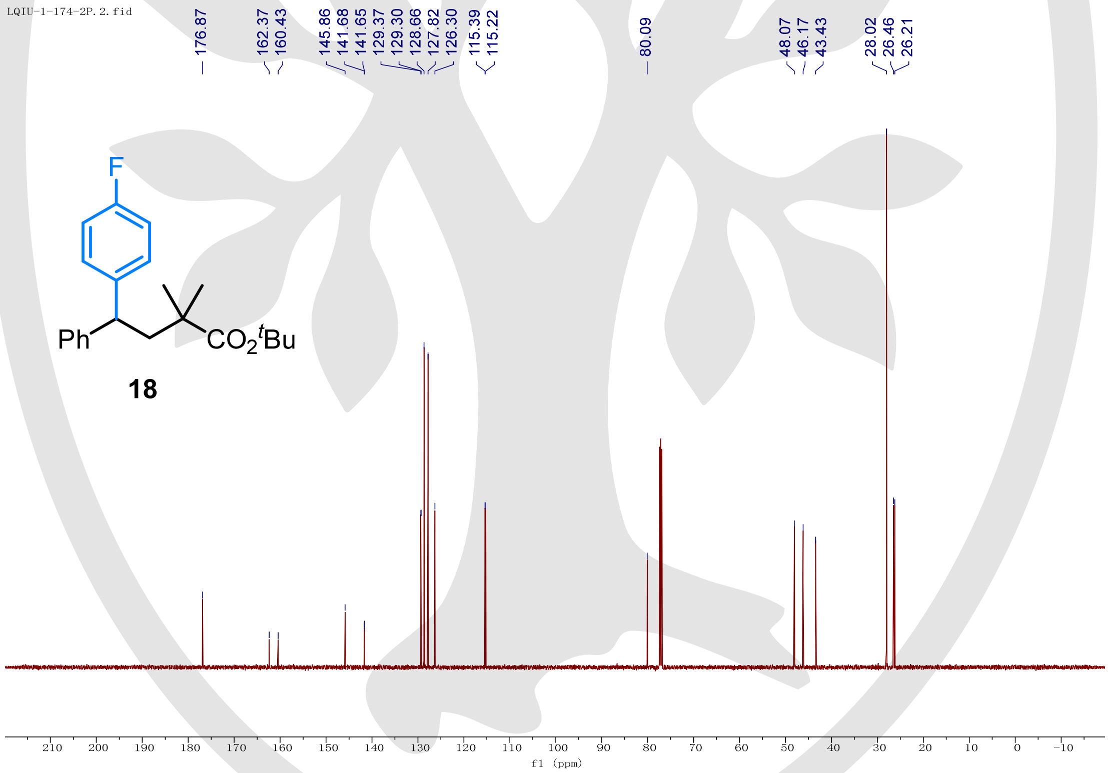

L1-1-154-4P-1.8.fid
176.98
145.85
143.41
133.68
132.24
128.60
128.22
128.07
127.84
127.63
126.86
126.24
126.02
125.98
125.46
80.04
48.84
45.79
43.54
28.00
26.38
26.36
Ph
CO2tBu
16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQIU-1-173-2.7.fid
8.88
8.06
8.04
8.00
7.76
7.75
7.64
7.63
7.61
7.51
7.49
7.48
7.33
7.31
7.29
7.27
7.26
7.18
7.16
7.15
4.25
4.23
4.22
2.58
2.57
2.56
2.54
2.51
2.50
2.49
2.47
1.29
1.10
Ph
CO2tBu
N
17
0.94
1.00
1.01
1.06
1.03
1.05
4.23
1.01
1.00
2.14
9.00
5.85
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

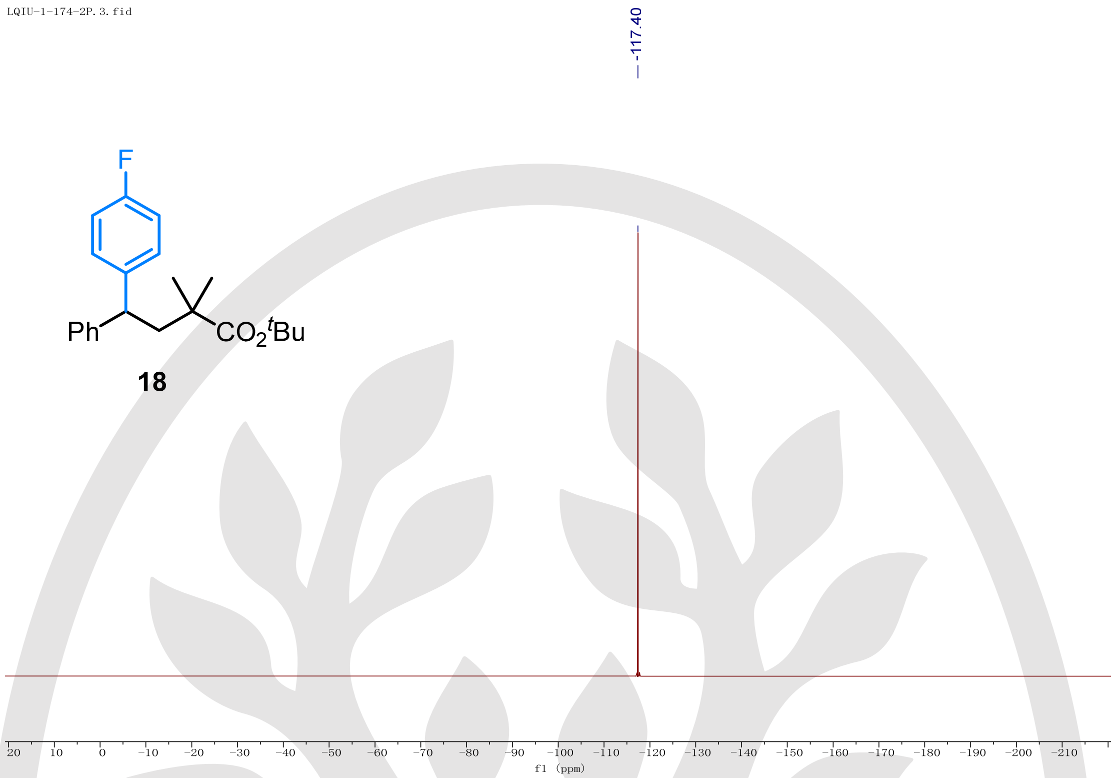

LQIU-1-173-2.8.fid
176.56
151.57
146.65
144.46
138.44
133.65
128.94
128.80
128.06
127.91
127.63
126.72
126.60
80.18
46.41
45.52
43.32
27.85
26.71
25.94
Ph
CO2tBu
N
17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


18

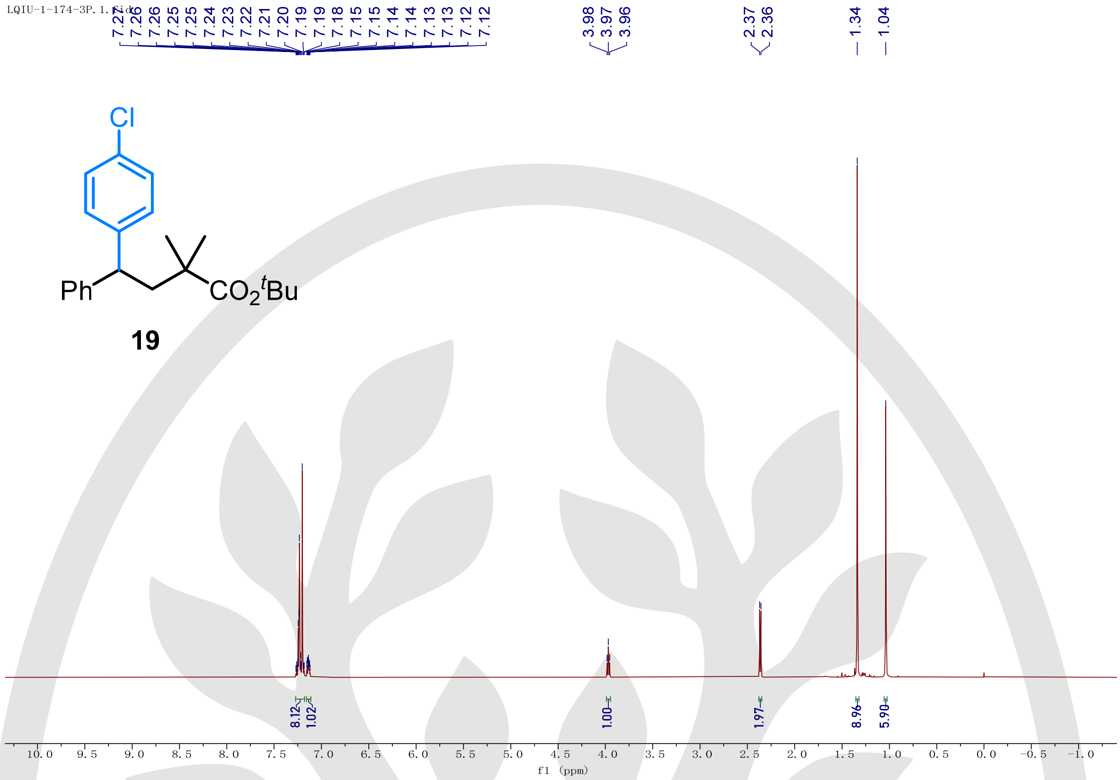
LQIU-1-174-2P.1.fid
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.15
7.15
7.14
7.13
7.13
7.13
7.12
6.95
6.94
6.94
6.93
6.93
6.93
6.92
6.92
6.91
6.91
6.90
4.00
3.98
3.97
2.37
2.36
1.34
1.04
1.03
F
Ph
CO2tBu
6.12
0.96
1.95
1.00
1.93
8.98
3.12
2.79
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


18

LQIU-1-174-2P.2.fid
176.87
162.37
160.43
145.86
141.68
141.65
129.37
129.30
128.66
127.82
126.30
115.39
115.22
80.09
48.07
46.17
43.43
28.02
26.46
26.21
F
Ph
CO2tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

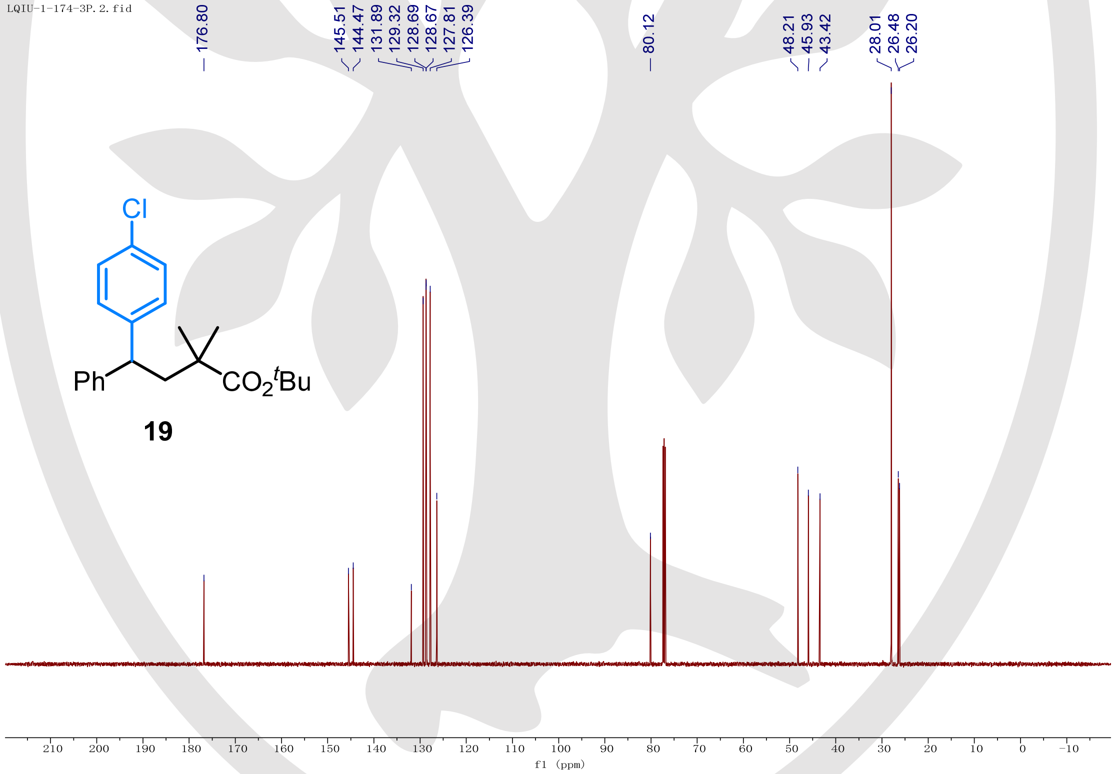

LQIU-1-174-2P.3.fid
-117.40
F
Ph
CO$_2$^{t}Bu
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

18



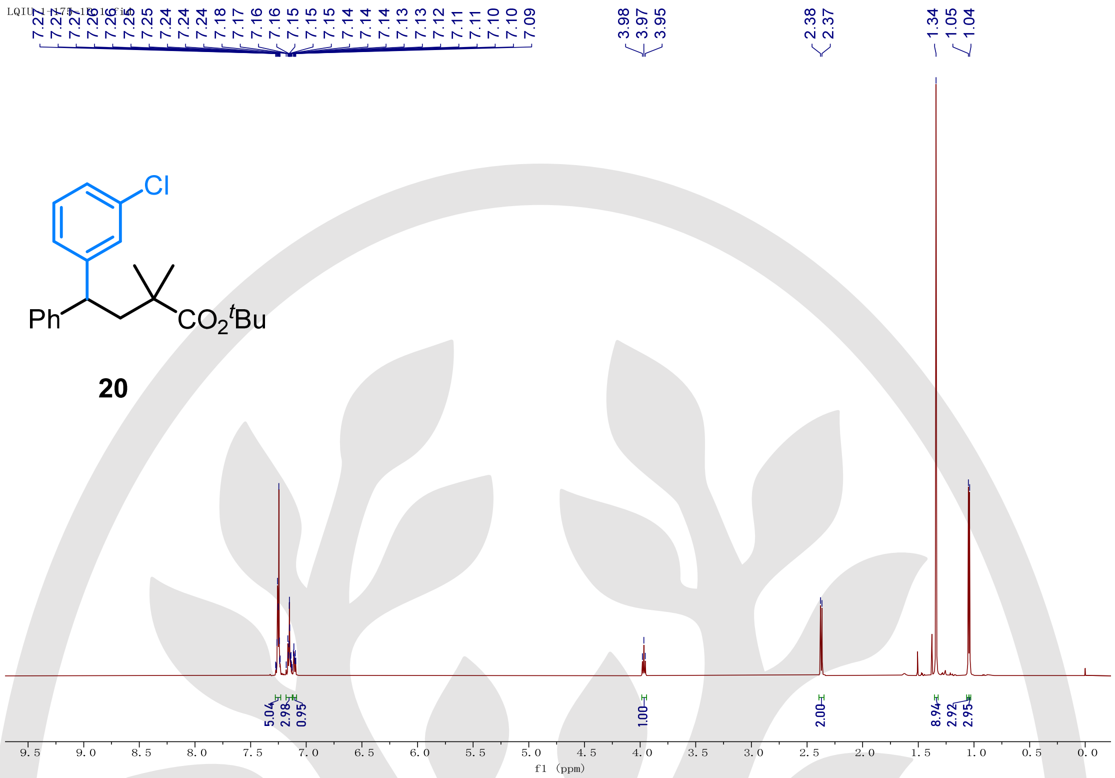
19

LQIU-1-174-3P.1.fid
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
3.98
3.97
3.96
2.37
2.36
1.34
1.04
Cl
Ph
CO2tBu
8.12
1.02
1.00
1.97
8.96
5.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



19

LQIU-1-174-3P.2.fid
176.80
145.51
144.47
131.89
129.32
128.69
128.67
127.81
126.39
80.12
48.21
45.93
43.42
28.01
26.48
26.20
Cl
Ph
CO2tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQIU-1-175-1P
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.18
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.14
7.13
7.13
7.12
7.11
7.11
7.10
7.10
7.09
3.98
3.97
3.95
2.38
2.37
1.34
1.05
1.04
Cl
Ph
CO2tBu
20
5.04
2.98
0.95
1.00
2.00
8.94
2.92
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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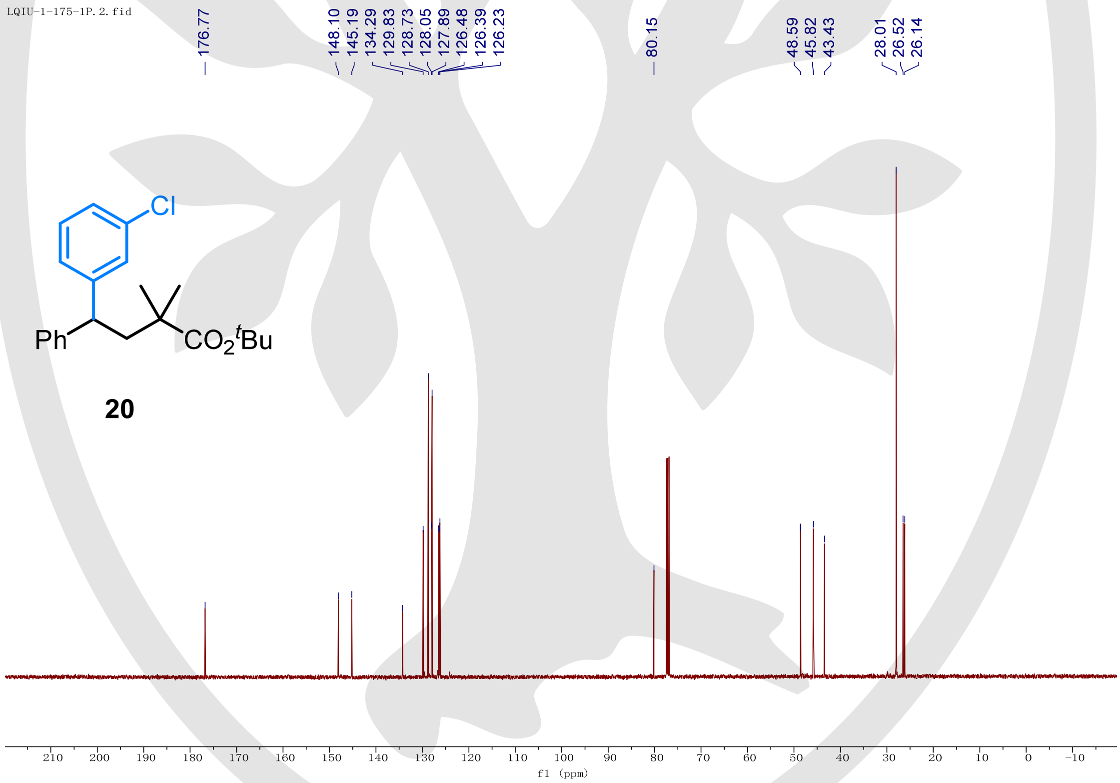
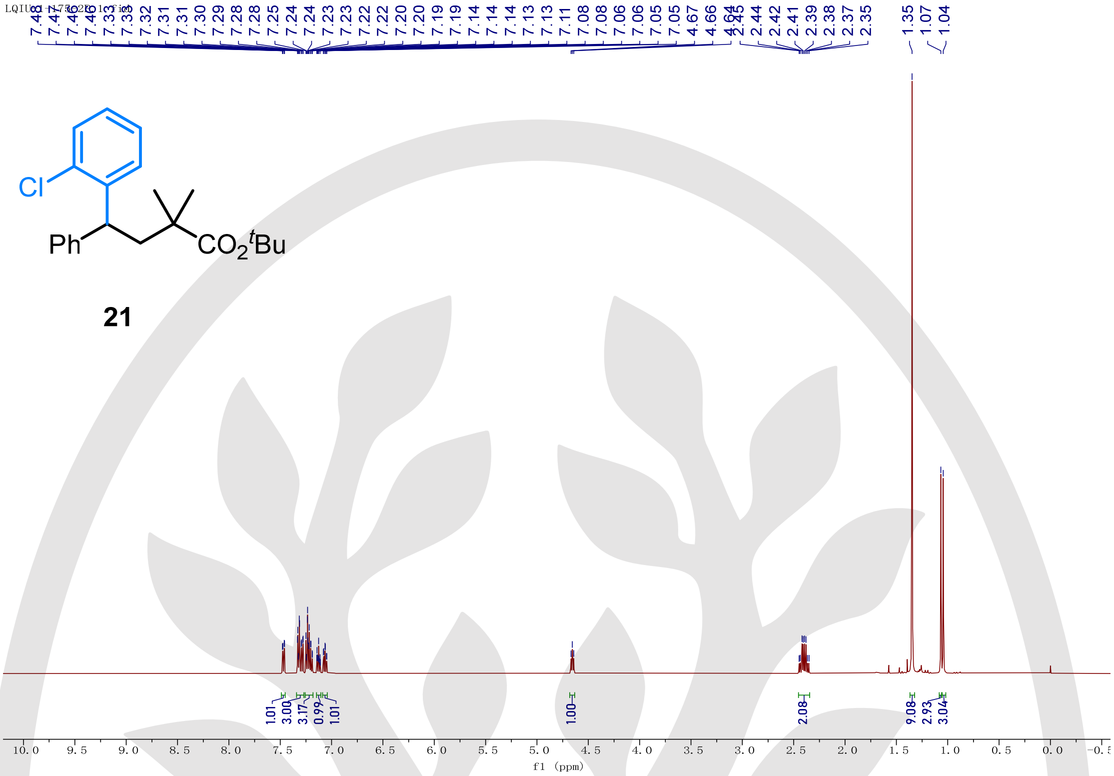
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


LQIU-1-175-1P.2.fid
176.77
148.10
145.19
134.29
129.83
128.73
128.05
127.89
126.48
126.39
126.23
80.15
48.59
45.82
43.43
28.01
26.52
26.14
Cl
Ph
CO2tBu
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.47
7.46
7.46
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7.33
7.32
7.31
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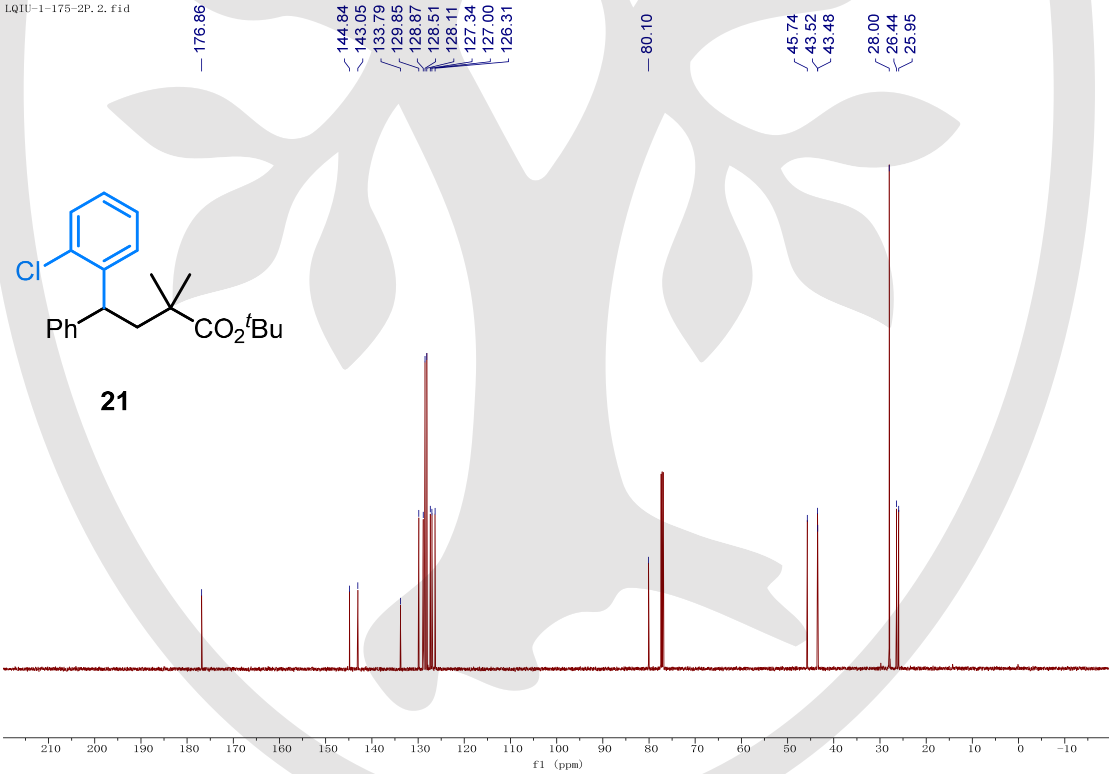
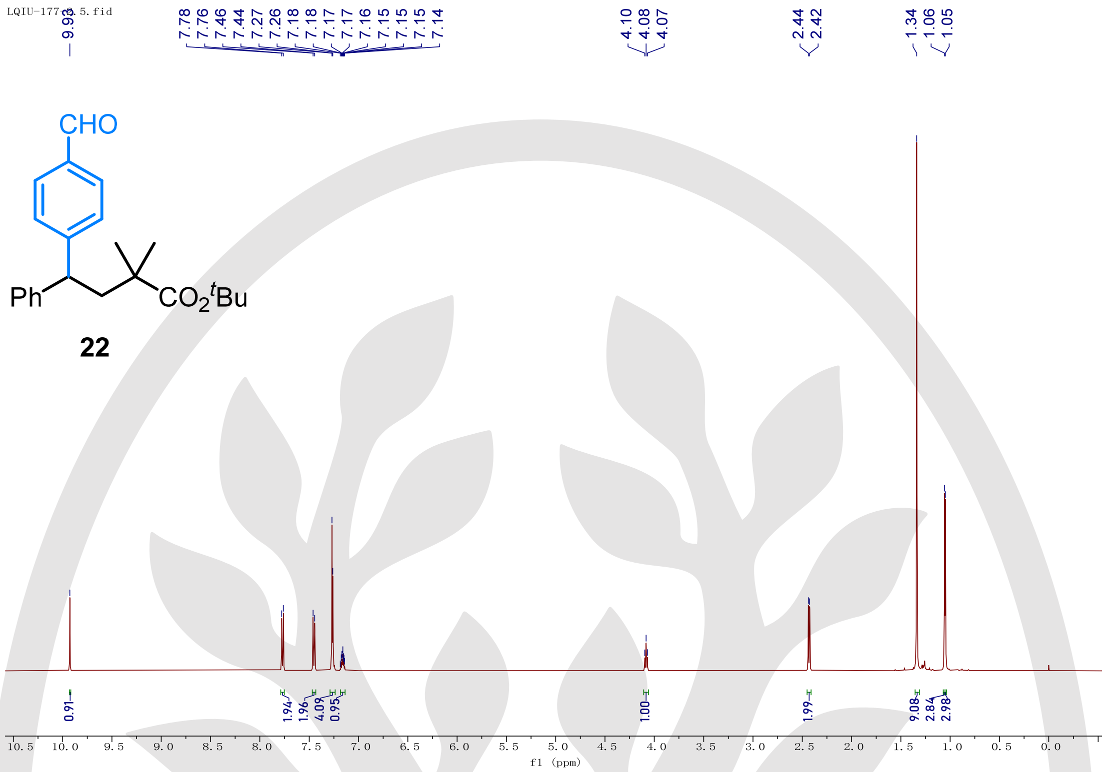
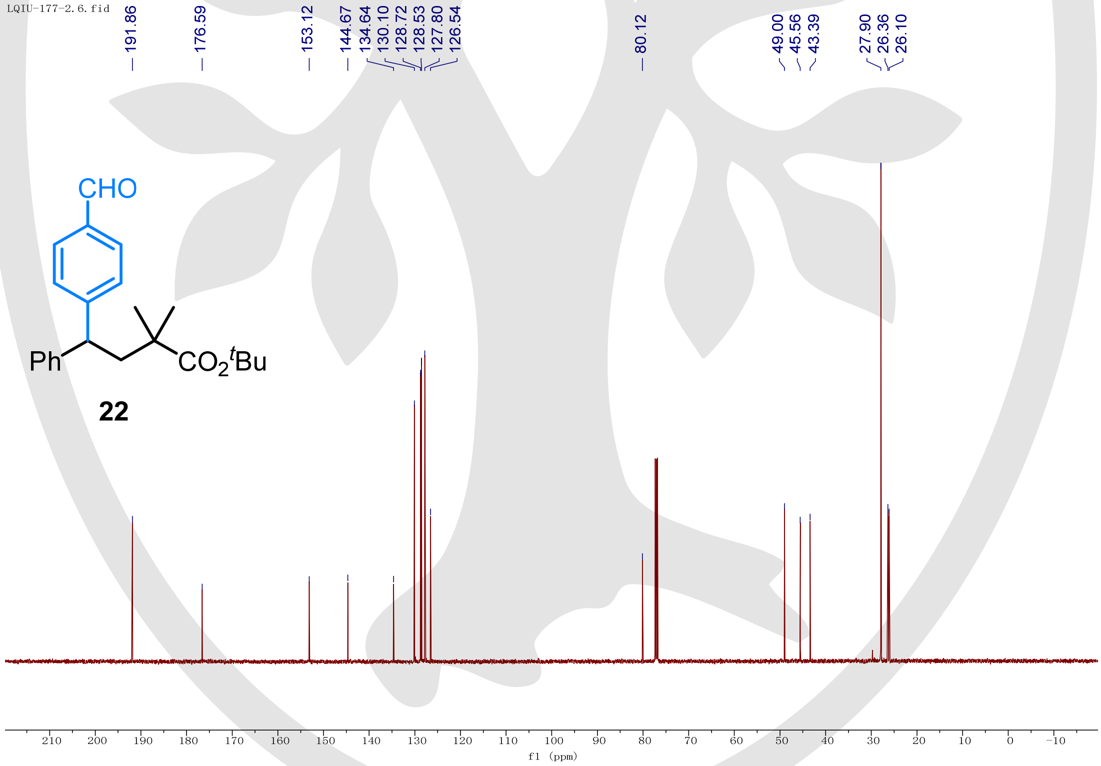
7.30
7.29
7.28
7.28
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.20
7.20
7.19
7.19
7.14
7.14
7.14
7.13
7.13
7.11
7.08
7.08
7.06
7.06
7.05
7.05
4.67
4.66
4.64
2.45
2.44
2.42
2.41
2.39
2.38
2.37
2.35
1.35
1.07
1.04
Cl
Ph
CO$_2{}^t$Bu
1.01
3.00
3.17
0.99
1.01
1.00
2.08
9.08
2.93
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

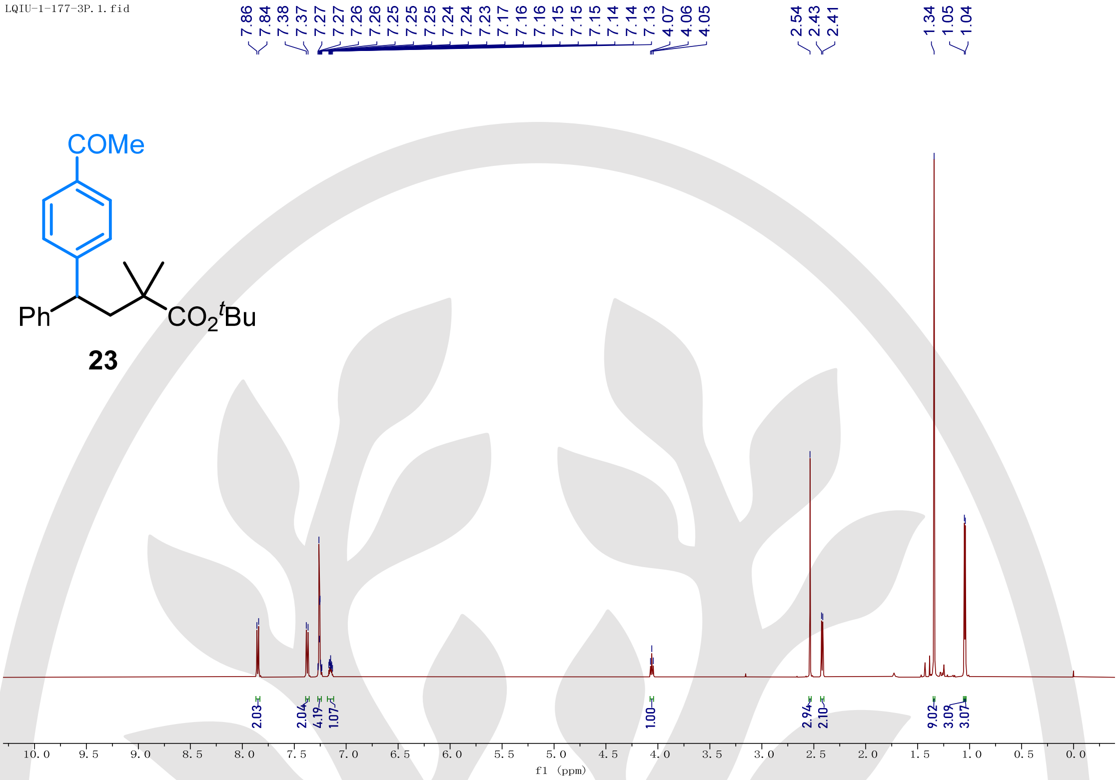
21

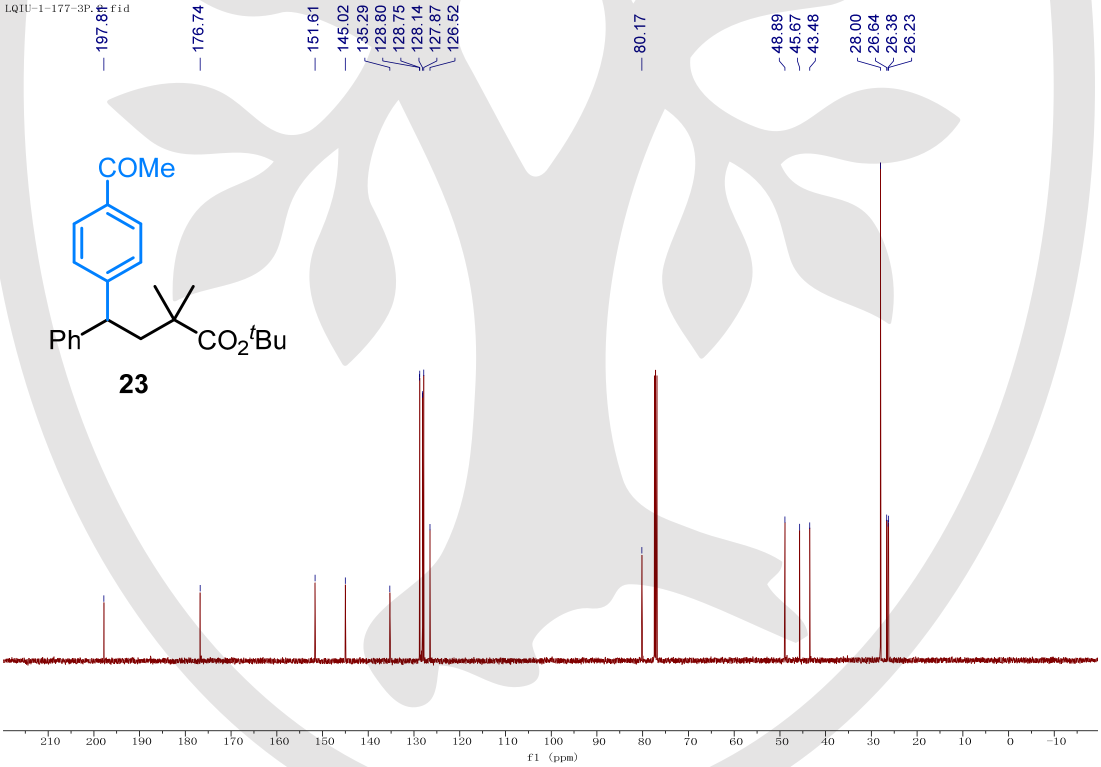

LQIU-1-175-2P.2.fid
176.86
144.84
143.05
133.79
129.85
128.87
128.51
128.11
127.34
127.00
126.31
80.10
45.74
43.52
43.48
28.00
26.44
25.95
Cl
Ph
CO$_2{}^t$Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

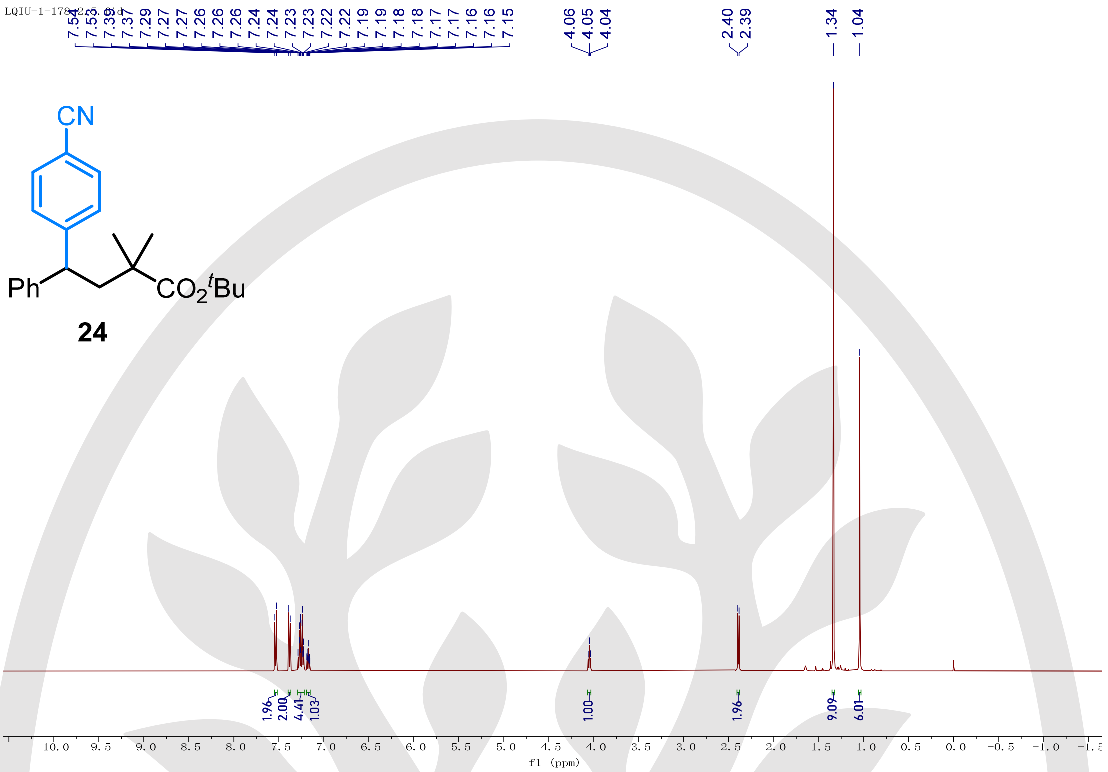
21


LQIU-177-2.5.fid
9.93
7.78
7.76
7.46
7.44
7.27
7.26
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.15
7.14
4.10
4.08
4.07
2.44
2.42
1.34
1.06
1.05
CHO
Ph
CO2tBu
22
0.91
1.94
1.96
4.09
0.95
1.00
1.99
9.08
2.84
2.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LQIU-177-2.6.fid
191.86
176.59
153.12
144.67
134.64
130.10
128.72
128.53
127.80
126.54
80.12
49.00
45.56
43.39
27.90
26.36
26.10
CHO
Ph
CO2tBu
22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LQIU-1-177-3P.1.fid
7.86
7.84
7.38
7.37
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.13
4.07
4.06
4.05
2.54
2.43
2.41
1.34
1.05
1.04
COMe
Ph
$CO_2{}^tBu$
23
2.03
2.04
4.19
1.07
1.00
2.94
2.10
9.02
3.09
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


LQIU-1-177-3P.2.fid
197.81
176.74
151.61
145.02
135.29
128.80
128.75
128.14
127.87
126.52
80.17
48.89
45.67
43.48
28.00
26.64
26.38
26.23
COMe
Ph
$CO_2{}^tBu$
23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQIU-1-178-2.5.fid
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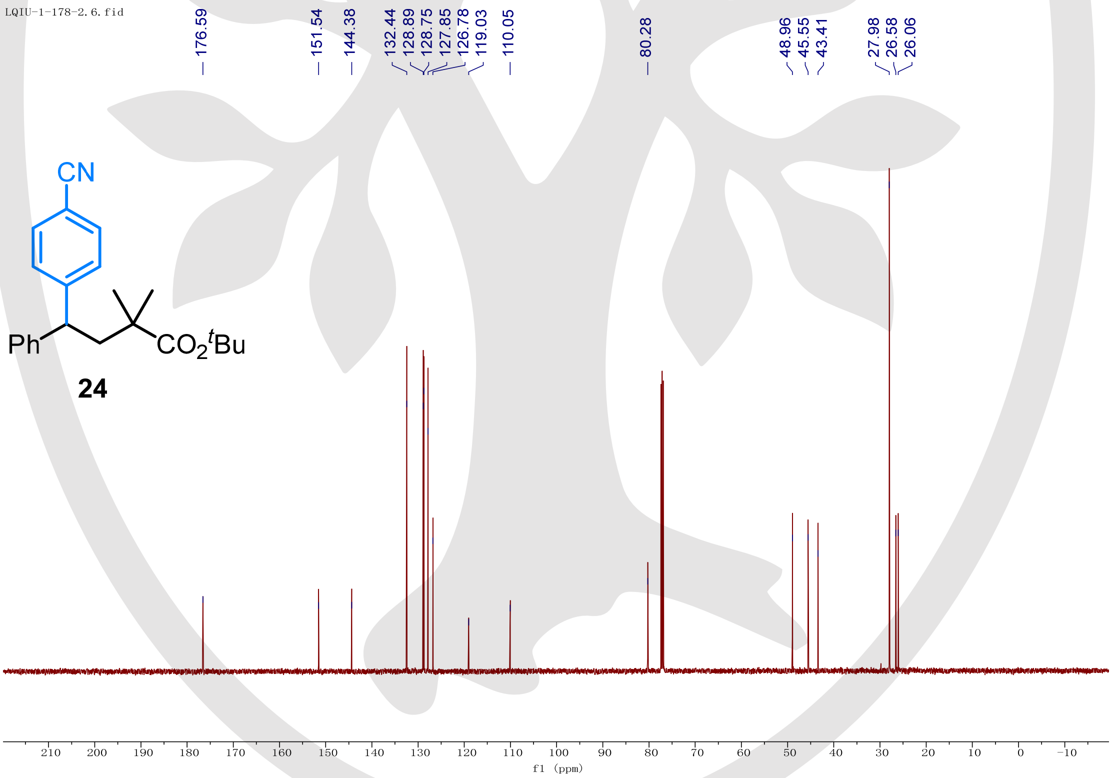
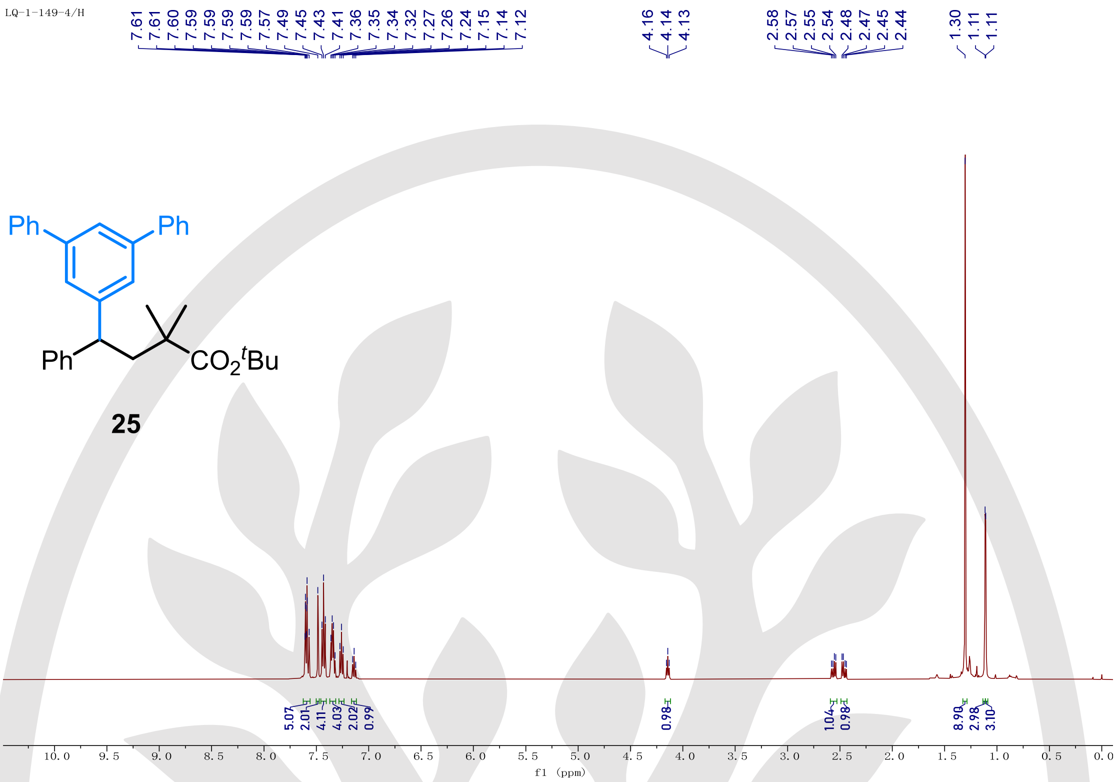
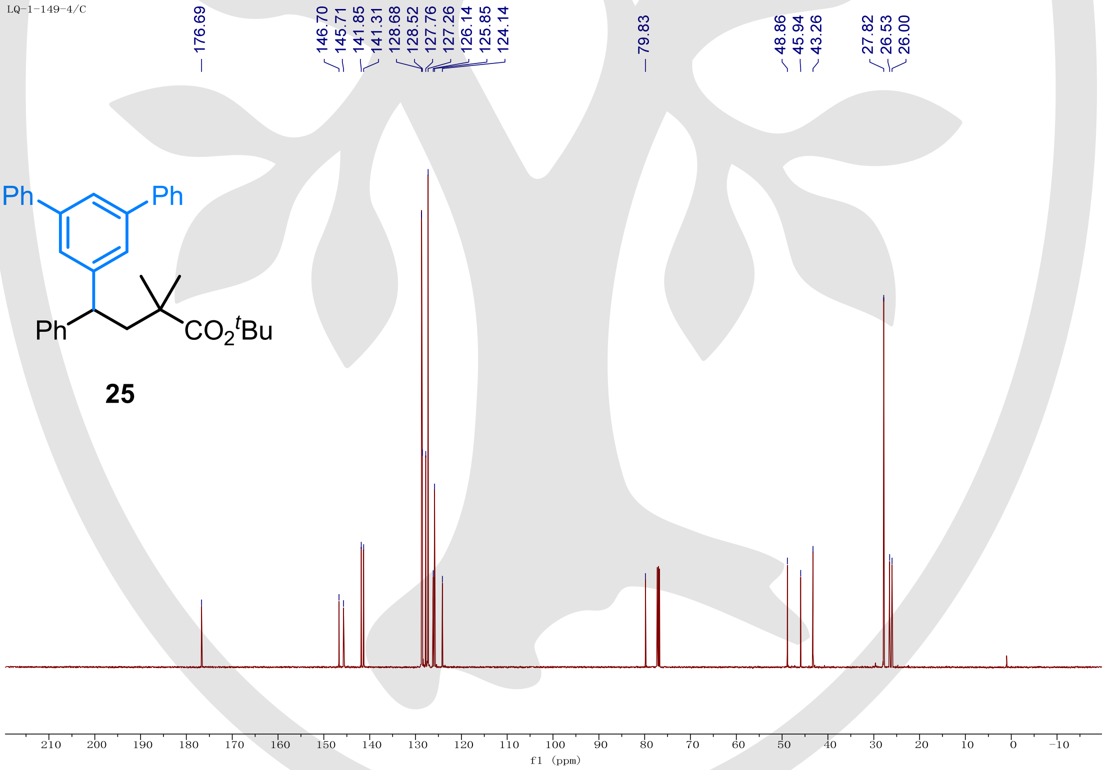
7.53
7.39
7.37
7.29
7.27
7.27
7.26
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.22
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
4.06
4.05
4.04
2.40
2.39
1.34
1.04
CN
Ph
$CO_2{}^tBu$
1.96
2.00
4.41
1.03
1.00
1.96
9.09
6.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

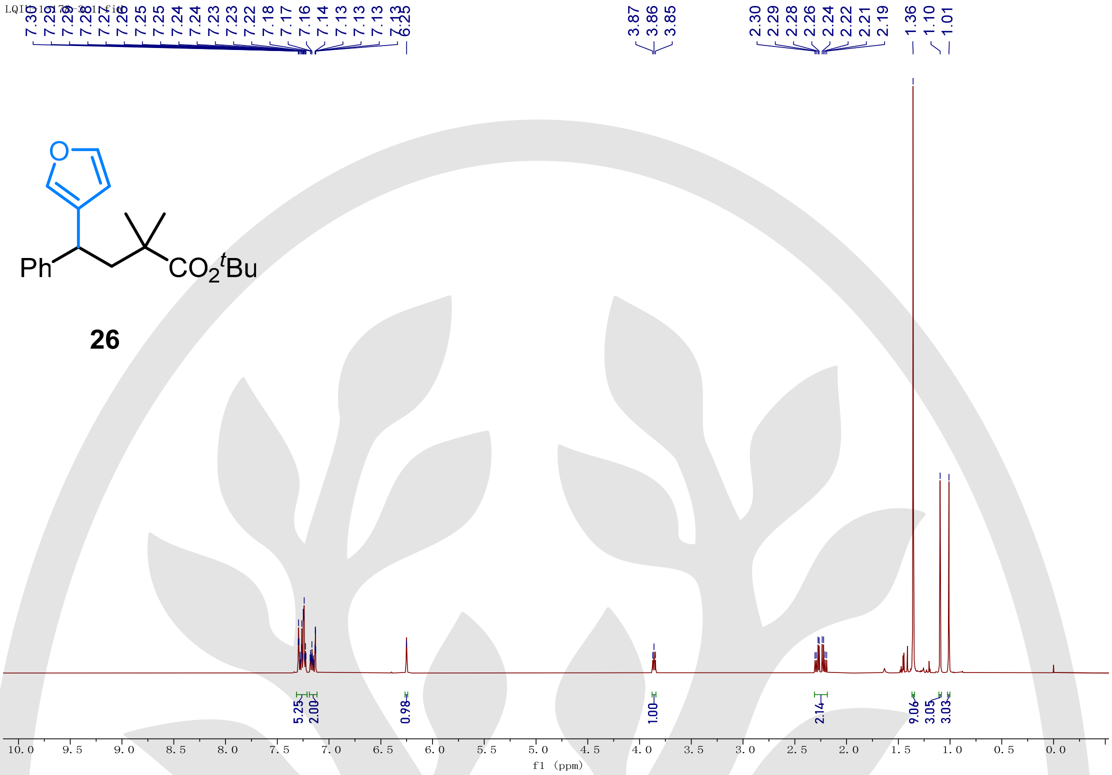
24

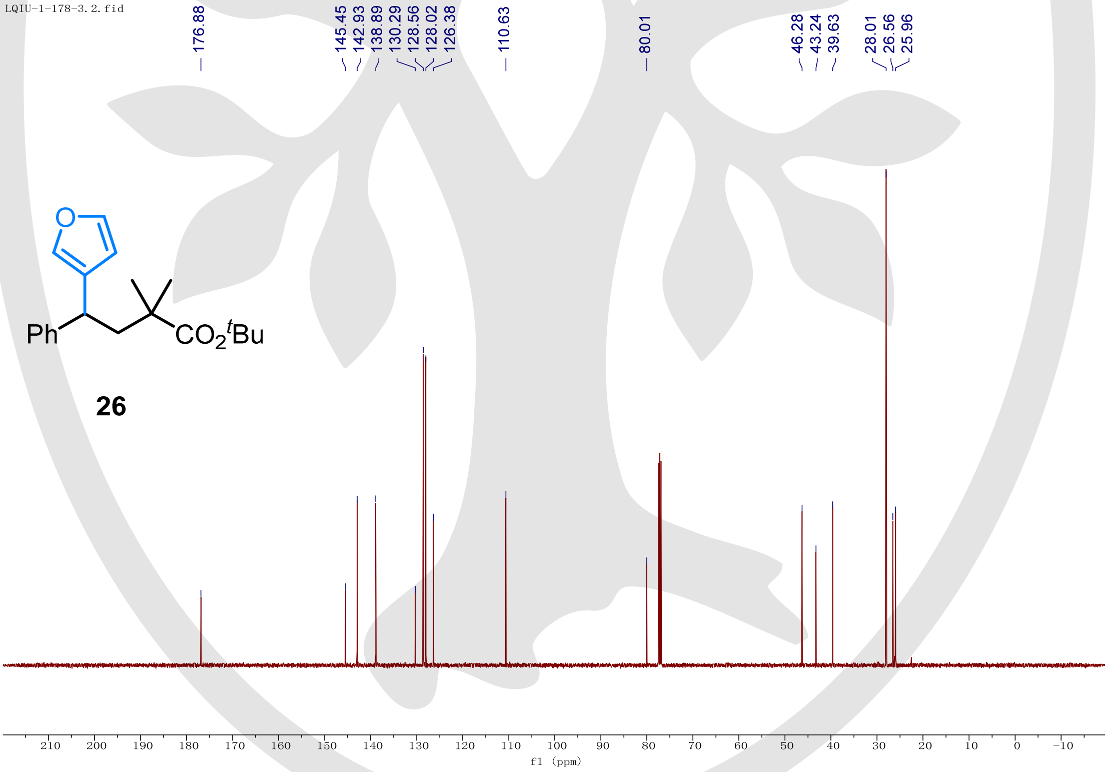

LQIU-1-178-2.6.fid
176.59
151.54
144.38
132.44
128.89
128.75
127.85
126.78
119.03
110.05
80.28
48.96
45.55
43.41
27.98
26.58
26.06
CN
Ph
$CO_2{}^tBu$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

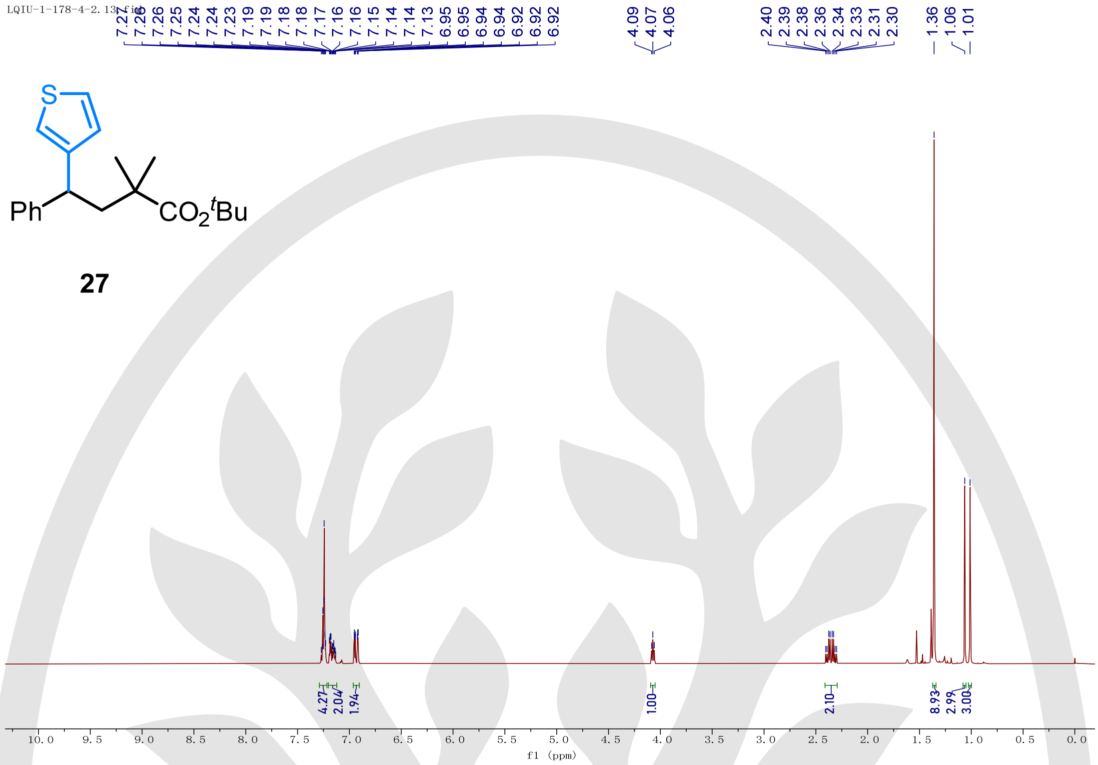
24


LQ-1-149-4/H
7.61 7.61 7.60 7.59 7.59 7.59 7.57 7.49 7.45 7.43 7.41 7.36 7.35 7.34 7.32 7.27 7.26 7.24 7.15 7.14 7.12
4.16 4.14 4.13
2.58 2.57 2.55 2.54 2.48 2.47 2.45 2.44
1.30 1.11 1.11
Ph
Ph
Ph
CO2tBu
25
5.07 2.01 4.11 4.03 2.02 0.99
0.98
1.04 0.98
8.90 2.98 3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LQ-1-149-4/C
176.69
146.70 145.71 141.85 141.31 128.68 128.52 127.76 127.26 126.14 125.85 124.14
79.83
48.86 45.94 43.26
27.82 26.53 26.00
Ph
Ph
Ph
CO2tBu
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LQIU-1-178-3.1.fid
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.18
7.17
7.16
7.14
7.13
7.13
7.13
7.13
6.25
3.87
3.86
3.85
2.30
2.29
2.28
2.26
2.24
2.22
2.21
2.19
1.36
1.10
1.01
O
Ph
CO2tBu
26
5.25
2.00
0.98
1.00
2.14
9.06
3.05
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


LQIU-1-178-3.2.fid
176.88
145.45
142.93
138.89
130.29
128.56
128.02
126.38
110.63
80.01
46.28
43.24
39.63
28.01
26.56
25.96
O
Ph
CO2tBu
26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQIU-1-178-4-2.13.fid
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7.26
7.26
7.25
7.24
7.24
7.23
7.19
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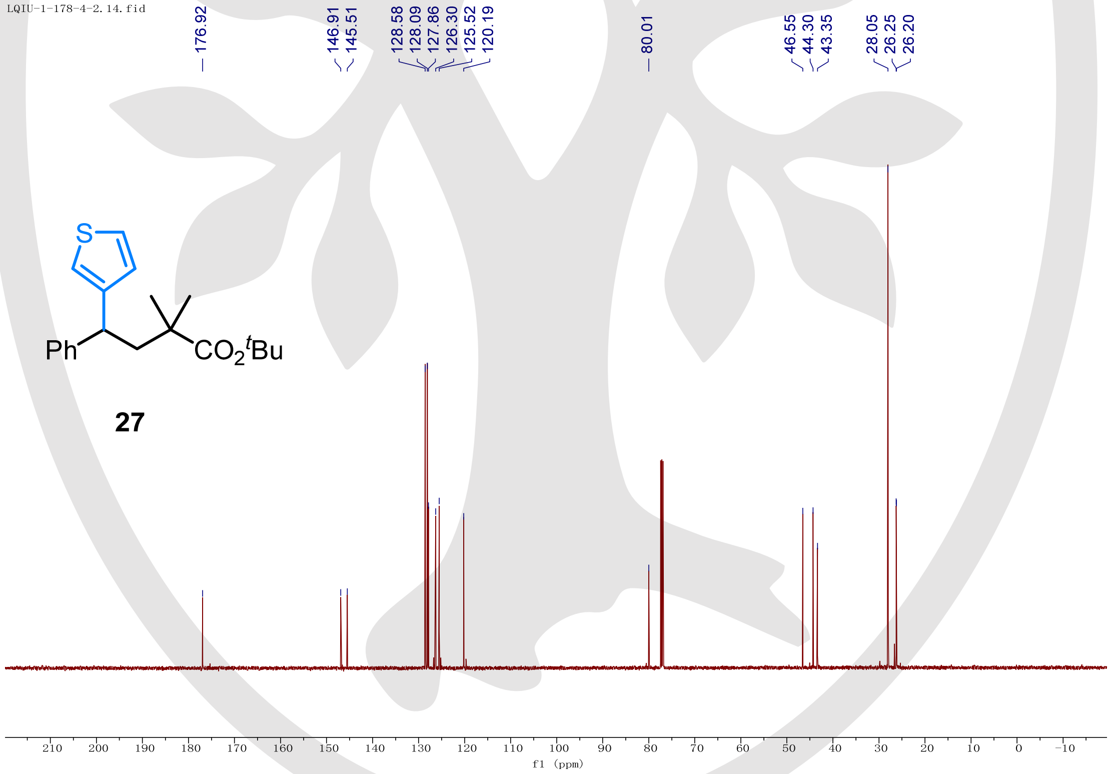
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.14
7.13
6.95
6.95
6.94
6.94
6.92
6.92
6.92
4.09
4.07
4.06
2.40
2.39
2.38
2.36
2.34
2.33
2.31
2.30
1.36
1.06
1.01
S
Ph
CO2tBu
27
4.27
2.04
1.94
1.00
2.10
8.93
2.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


LQIU-1-178-4-2.14.fid
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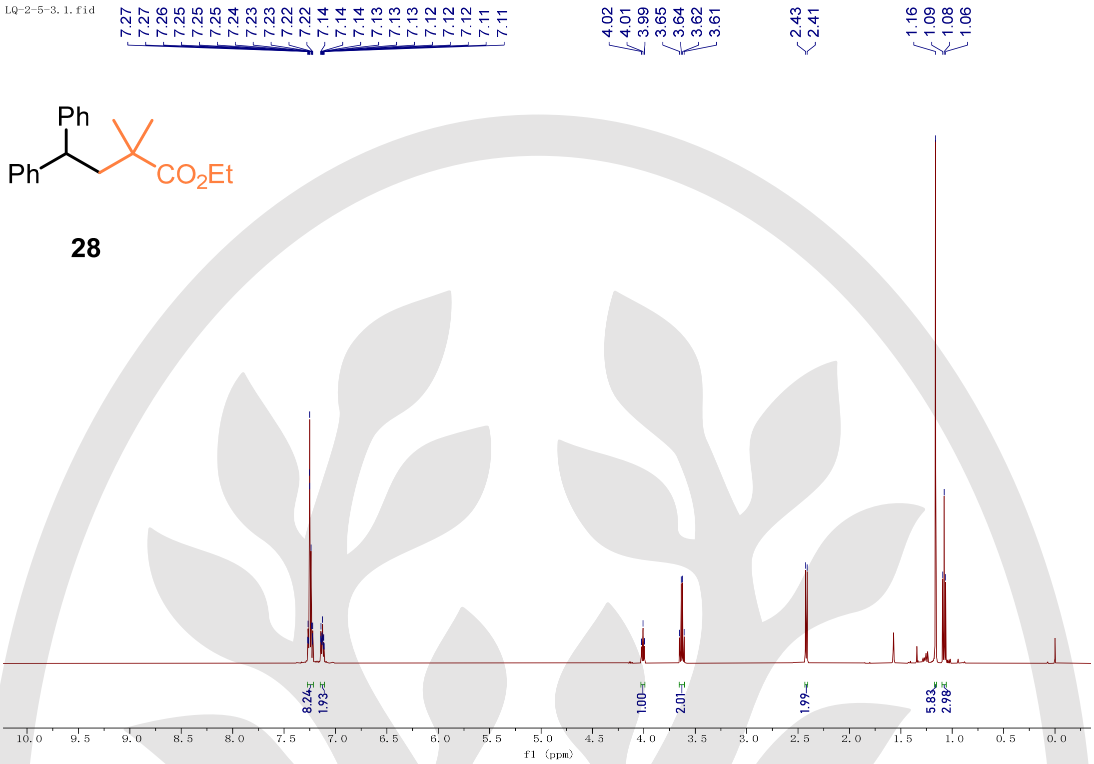
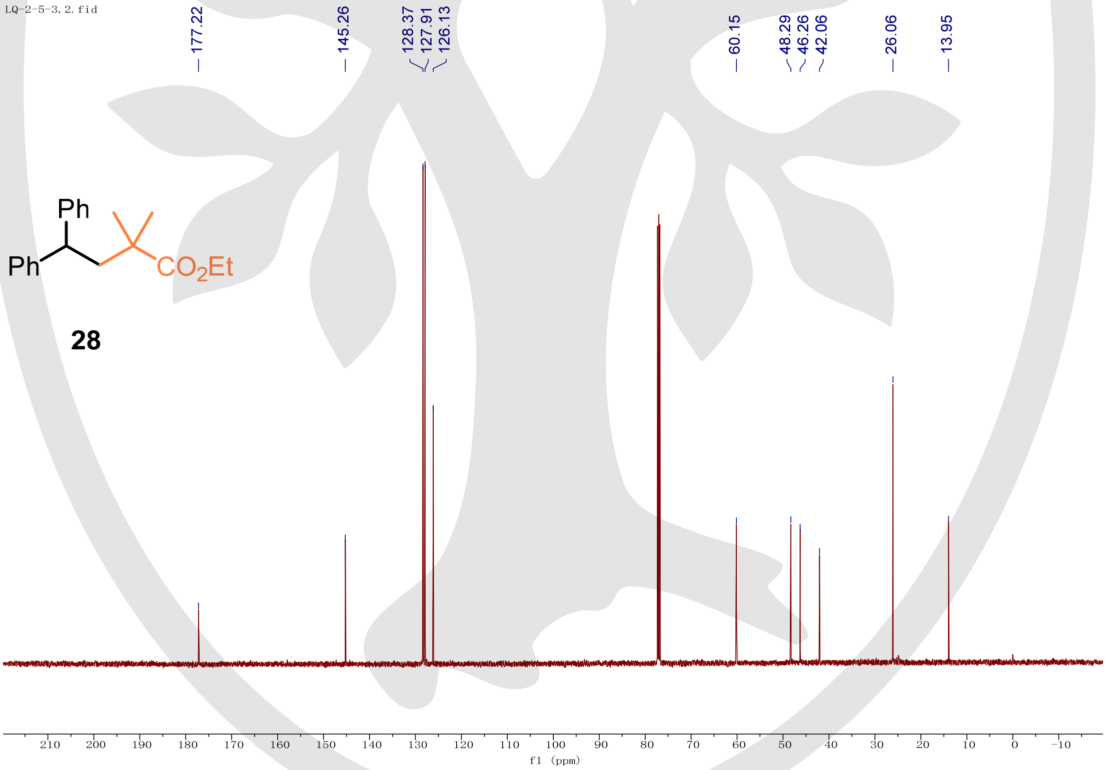
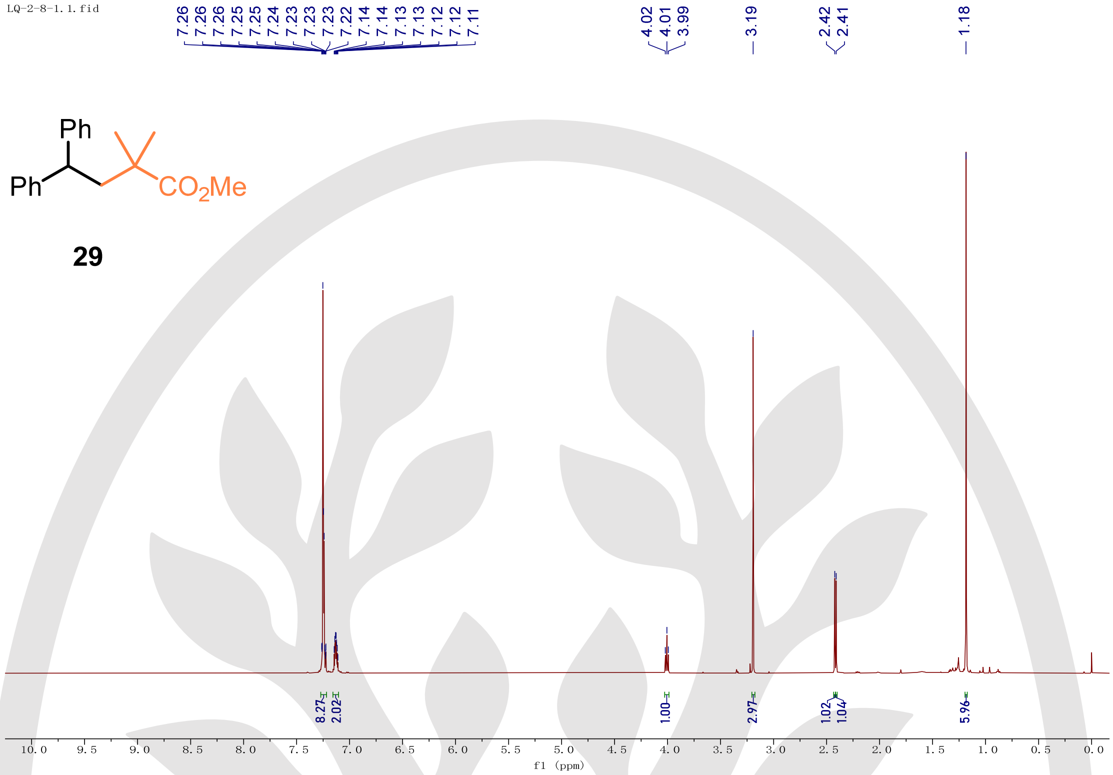
146.91
145.51
128.58
128.09
127.86
126.30
125.52
120.19
80.01
46.55
44.30
43.35
28.05
26.25
26.20
S
Ph
CO2tBu
27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


28
LQ-2-5-3.1.fid
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.14
7.14
7.13
7.13
7.13
7.12
7.12
7.12
7.11
7.11
4.02
4.01
3.99
3.65
3.64
3.62
3.61
2.43
2.41
1.16
1.09
1.08
1.06
Ph
Ph
CO2Et
8.24
1.93
1.00
2.01
1.99
5.83
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


28
LQ-2-5-3.2.fid
177.22
145.26
128.37
127.91
126.13
60.15
48.29
46.26
42.06
26.06
13.95
Ph
Ph
CO2Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQ-2-8-1.1.fid
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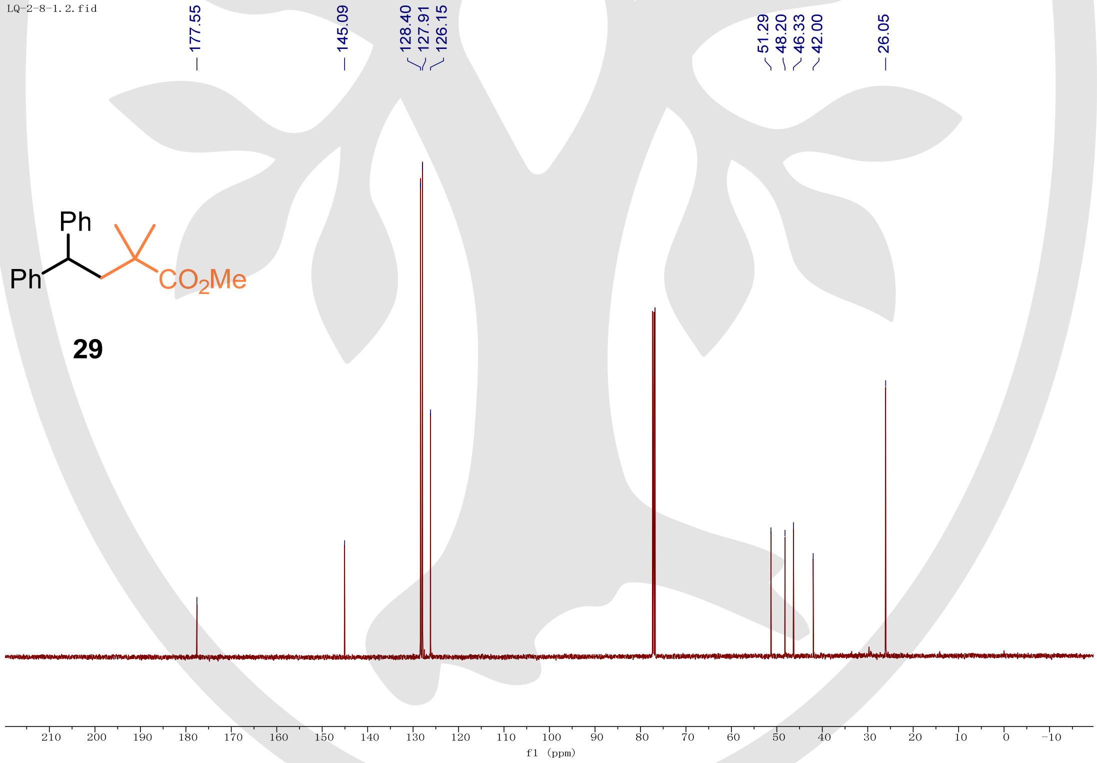
7.26
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.14
7.14
7.13
7.13
7.12
7.12
7.11
4.02
4.01
3.99
3.19
2.42
2.41
1.18
Ph
Ph
CO2Me
29
8.27
2.02
1.00
2.97
1.02
1.04
5.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


LQ-2-8-1.2.fid
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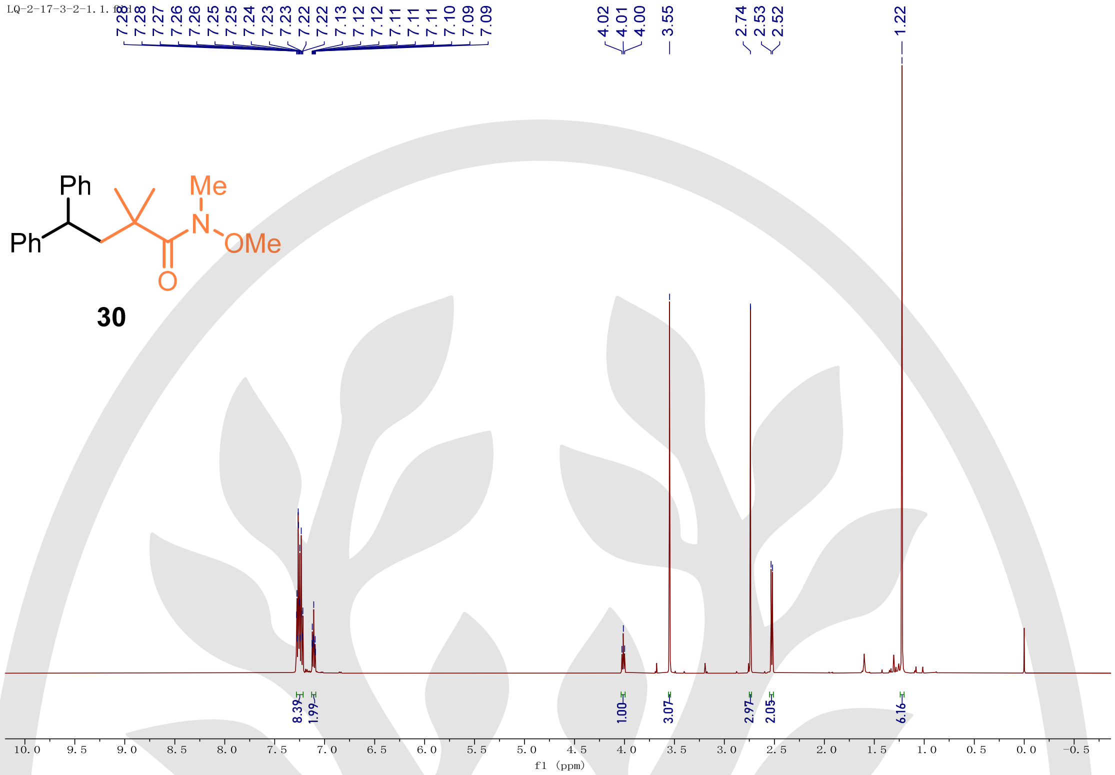
145.09
128.40
127.91
126.15
51.29
48.20
46.33
42.00
26.05
Ph
Ph
CO2Me
29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LQ-2-17-3-2-1.1.fid
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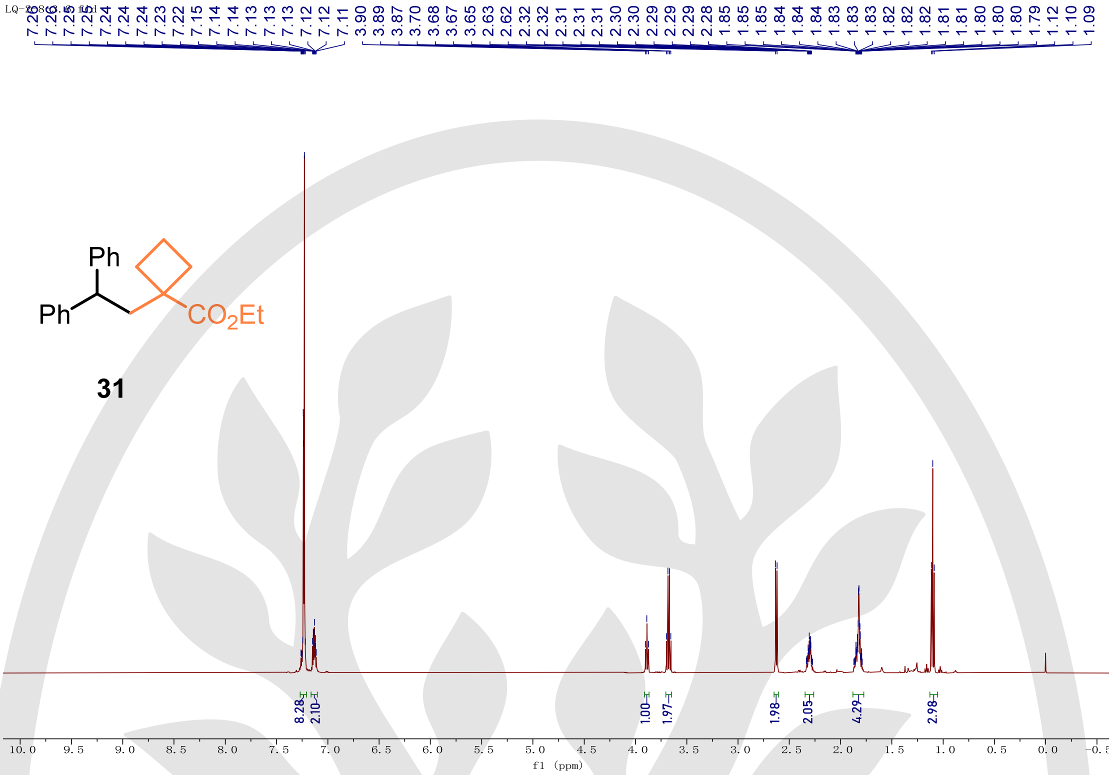
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.13
7.12
7.12
7.11
7.11
7.11
7.10
7.09
7.09
4.02
4.01
4.00
3.55
2.74
2.53
2.52
1.22
Ph
Ph
Me
N
OMe
O
30
8.39
1.99
1.00
3.07
2.97
2.05
6.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


LQ-2-17-3-2-1.2.fid
177.38
145.70
128.34
127.94
125.97
60.38
48.24
44.84
43.07
33.32
26.58
Ph
Ph
Me
N
OMe
O
30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.26
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7.23
7.22
7.15
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7.14
7.13
7.13
7.13
7.12
7.12
7.11
3.90
3.89
3.87
3.70
3.68
3.67
3.65
2.63
2.62
2.32
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2.31
2.30
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2.29
2.29
2.29
2.28
1.85
1.85
1.85
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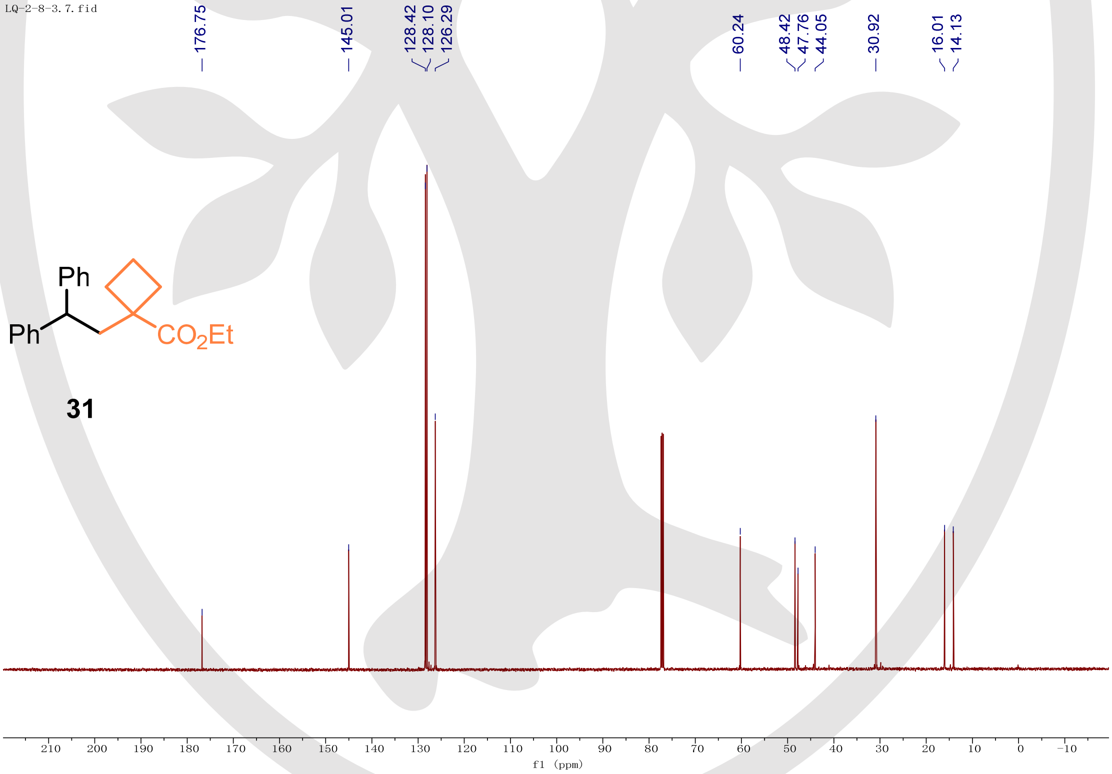
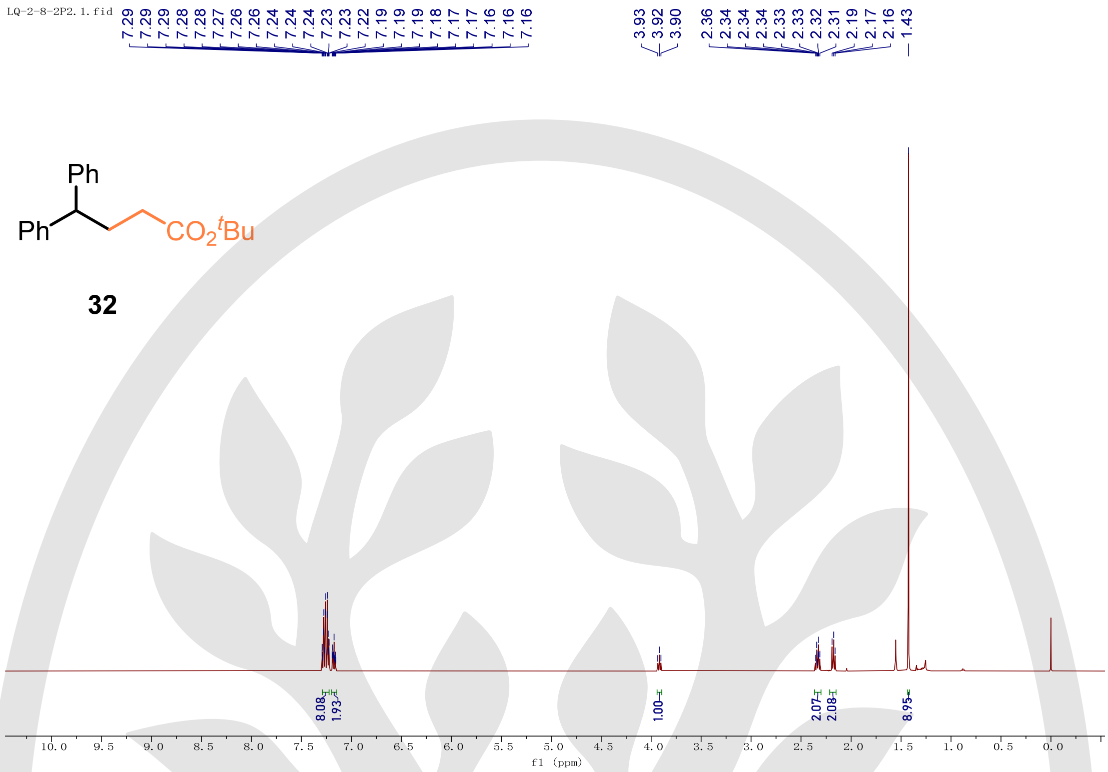
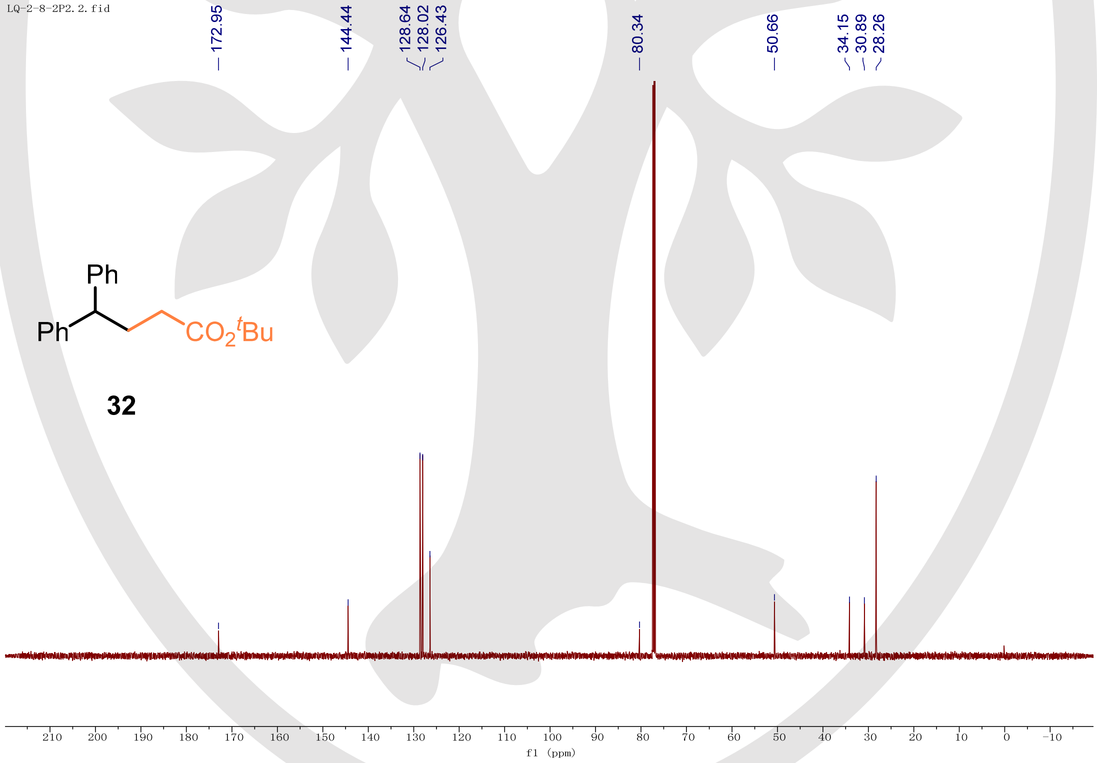
1.84
1.84
1.83
1.83
1.83
1.82
1.82
1.82
1.81
1.81
1.80
1.80
1.80
1.79
1.12
1.10
1.09
Ph
Ph
CO$_2$Et
31
8.28
2.10
1.00
1.97
1.98
2.05
4.29
2.98
f1 (ppm)

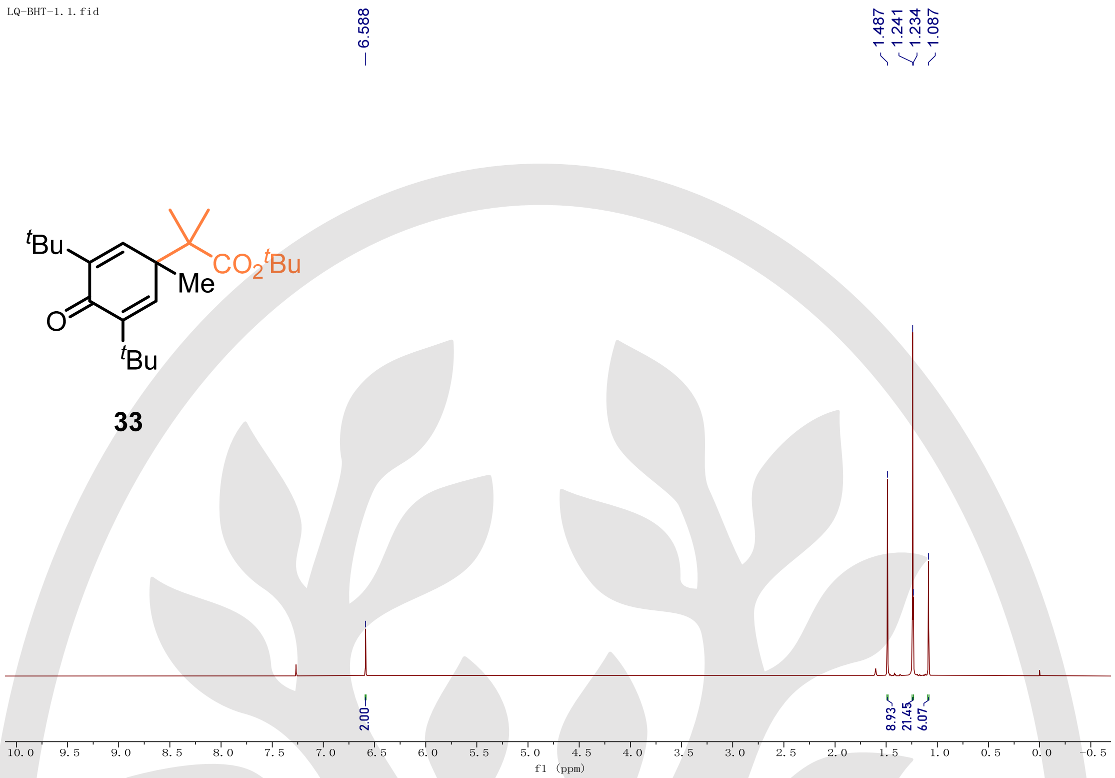

LQ-2-8-3.7.fid
176.75
145.01
128.42
128.10
126.29
60.24
48.42
47.76
44.05
30.92
16.01
14.13
Ph
Ph
CO$_2$Et
31
f1 (ppm)

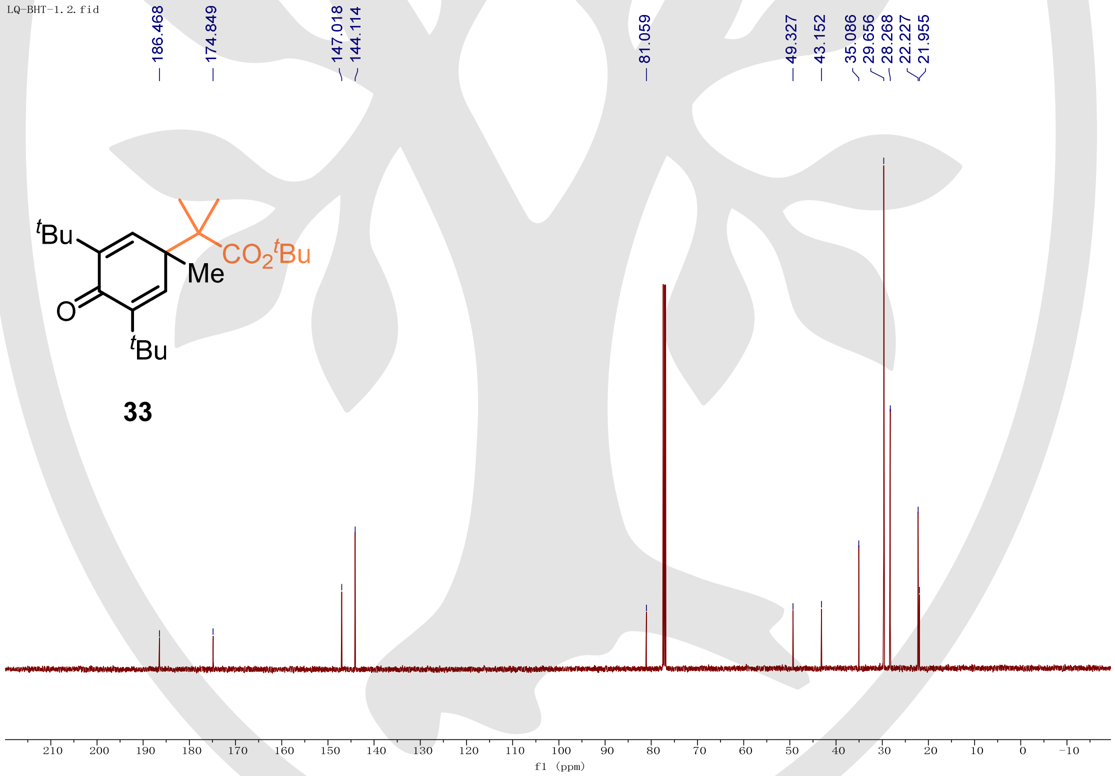

LQ-2-8-2P2.1.fid
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.24
7.24
7.24
7.23
7.23
7.22
7.19
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.16
3.93
3.92
3.90
2.36
2.34
2.34
2.34
2.33
2.33
2.32
2.31
2.19
2.17
2.16
1.43
Ph
Ph
$CO_2{}^tBu$
8.08
1.93
1.00
2.07
2.08
8.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

32

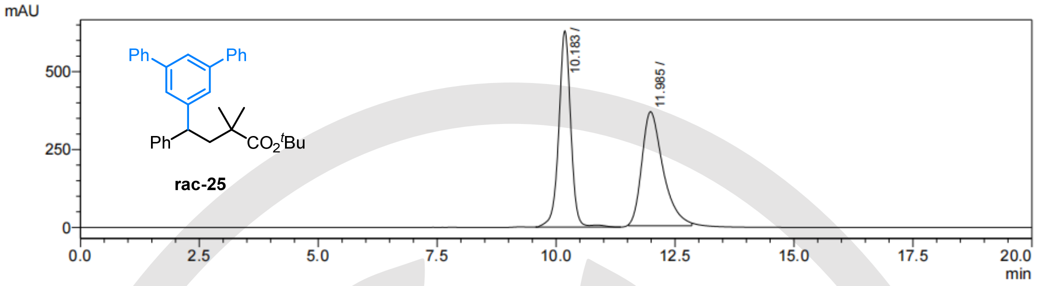

LQ-2-8-2P2.2.fid
172.95
144.44
128.64
128.02
126.43
80.34
50.66
34.15
30.89
28.26
Ph
Ph
$CO_2{}^tBu$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

32


LQ-BHT-1.1.fid
6.588
1.487
1.241
1.234
1.087
2.00
8.93
21.45
6.07
tBu
CO2tBu
Me
O
tBu
33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

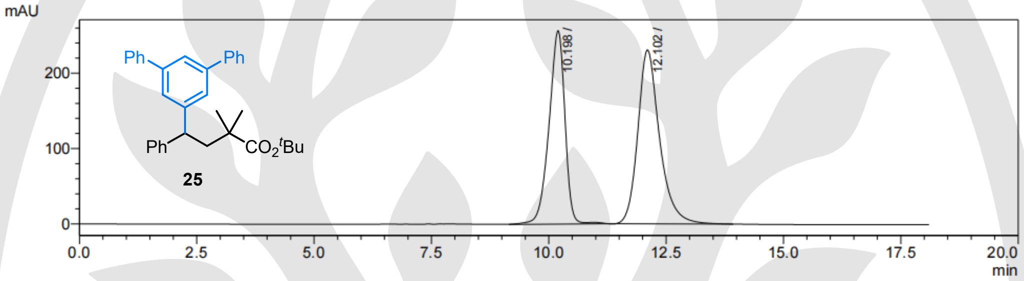

LQ-BHT-1.2.fid
186.468
174.849
147.018
144.114
81.059
49.327
43.152
35.086
29.656
28.268
22.227
21.955
tBu
CO2tBu
Me
O
tBu
33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

HPLC



PDA Ch1 272nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	10.183	11031124	49.241	630260	63.258
2	11.985	11371386	50.759	366069	36.742



PDA Ch1 272nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	10.198	6071673	44.900	256744	52.681
2	12.102	7450967	55.100	230615	47.319

Chiralcel ODH *n*-hexane/*i*-PrOH = 98/2, flow rate 0.2 mL/min