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Fluorous bis(oxazolines) ligand: Synthesis and application in Kabachnik-Fields reaction

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ABSTRACT

A novel fluorous bis(oxazolines) ligand was synthesized with 70% overall yield in 5 steps starting from 5-aminoisophthalic acid. The ligand was applied in the one-pot synthesis of α-aminophosphonates via copper-catalyzed Kabachnik-Fields reaction, giving the corresponding products in moderate to excellent yields under mild conditions. Furthermore, the fluorous ligand could be easily recovered and reused for four times without significant loss of activity.

1. Introduction

Organophosphorus compounds have been widely used in organic synthesis, biological, pharmaceutical, and materials sciences as valuable building blocks [1,2]. As an important class of organophosphorus compounds, α-aminophosphonates have attracted considerable attention because they are considered to be structural analogs of the corresponding α-amino acids and transition-satate mimics of peptide hydrolysis [3]. α-Aminophosphonates display a broad spectrum of biological activities that include peptide mimetics [4], enzyme inhibitors [5], antibiotics [6], herbicides [7], catalytic antibodies [8], anti HIV [9], anti cancer [10] and thrombotic agents [11].

Considering the wide range of biological property of α-aminophosphonates, a large number of methods for the preparation of α-aminophosphonates have been published. In recent years, a three-component synthesis that starts from aldehydes, amines, and diethyl phosphite has been reported by using metal catalysts such as $Mg(ClO_4)_2$, $ZrOCl_2{\cdot}8H_2O$, $FeCl_3$, $LiClO_4$, $ZrCl_4$ [12]. However, the harsh reaction conditions, expensive reagents, long reaction times, complicated workup procedures, relatively low yields and large amount of catalysts limit the use of these methods. Therefore, it is necessary to find an effective metal catalyst for the synthesis of α-aminophosphonates. An effective metal catalyst has to be stable and highly selective, but also highly active to ensure high turnover numbers and permit low catalyst loadings. Moreover, it needs to be amenable to rational design, giving the possibility for fine-tuning the catalytic properties of the metal center. These issues can usually be solved by an appropriate choice of ligands [13]. In 2007, Muraki and co-workers reported the synthesis of α-aminophosphonates employing a novel copper-2,2′-bipyridine derivative complex [14]. In 2012, the gold-2,2′-bipyridine complex was successfully synthesized and applied in the formation of α-aminophosphonates by Zhang et al. [15]. In the same year, Zhu et al. carried out the reaction in the presence of lanthanide amido complexes [16].

As an important nitrogen based ligands, a large number of bis(oxazolines) have been reported because of their ready accessibility, modular nature and applicability in a wide range of metal catalyzed transformations [17,18]. However, most of the bis(oxazolines) ligands are difficult to be recovered and reused. Fluorous technology provides the possibility to design recyclable and subsequently reusable versions of ligands. Fluorous synthesis has been widely utilized in organic synthesis since the pioneering works of Horváth in 1994 [19]. In 1997, Curran's group further substantiated this concept by introducing a perfluoroalkyl chain as fluorous tag [20]. Fluorous-tagged molecules are easily separated from non-fluorous molecules by a fluorous liquid–liquid extraction (F-LLE) using fluorous solvents or a fluorous solid phase extraction (F-SPE) using perfluorinated silica gel [21].

However, there were few reports describing the recyclability of fluorous bis(oxazolines) [22]. As a follow up to our previous work [23], a novel fluorous bis(oxazolines) ligand was synthesized and applied in copper-catalyzed asymmetric α-hydrophosphonylation

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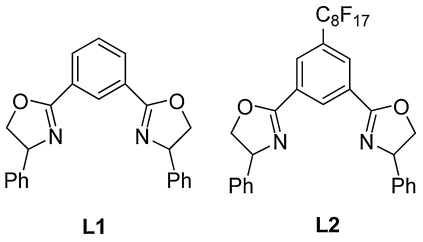


Fig. 1. Bis(oxazolines) ligands.

[24]. In this literature, the racemic fluorous bis(oxazolines) (Fig. 1 **L2**) was investigated in the synthesis of α-aminophosphonates via copper-catalyzed Kabachnik-Fields reaction. Compared to the silica supported or polymer supported bis(oxazolines) [25], the modified bis(oxazolines) with long perfluoroalkyl groups are soluble in organic solvents, yet they could be easily separated and recovered from the reaction mixture by F-SPE.

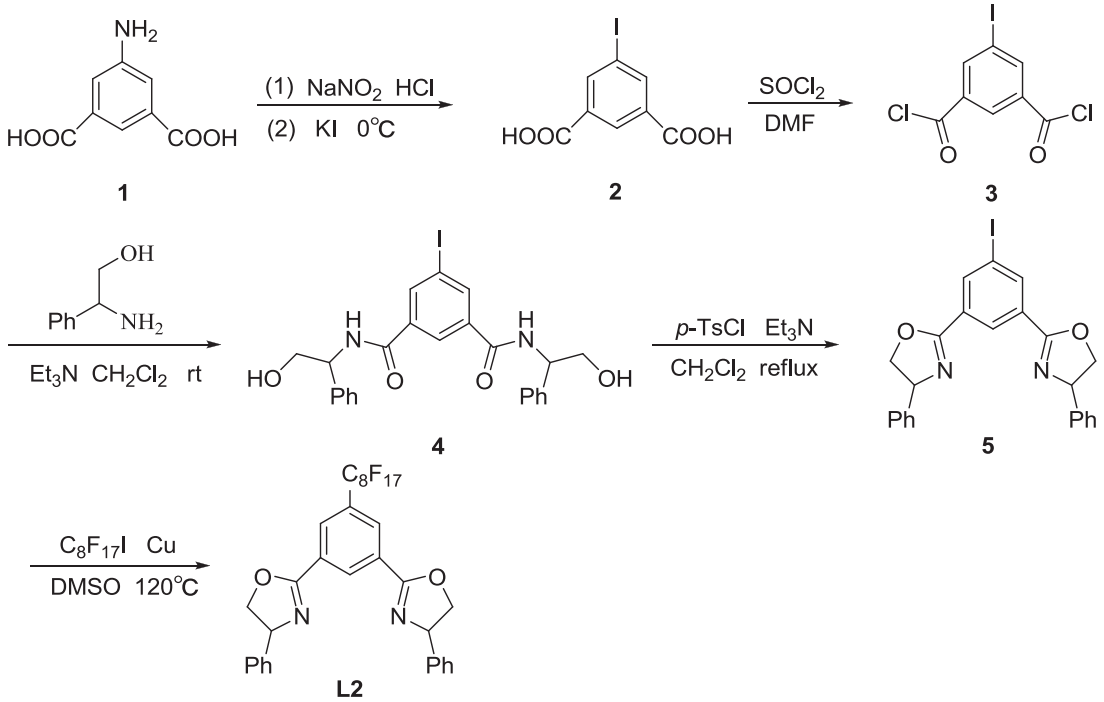
2. Results and discussion

The fluorous bis(oxazolines) ligand (Fig. 1 **L2**) was successfully synthesized in 5 steps starting from 5-aminoisophthalic acid (Scheme 1). The 5-iodoisophthalic acid **(2)** was synthesized through diazotization and halogenation from commercially available 5-aminoisophthalic acid **(1)**. Compound **2** was refluxed in thionyl chloride with catalytic amount of N,N-dimethylformamide to give 5-iodoisophthaloyl dichloride **(3)**. Treatment of **3** with phenylglycinol in the presence of triethylamine gave compound **4**. A solution of compound **4**, *p*-toluenesulfonyl chloride and triethylamine was refluxed in dichloromethane to give bis(oxazolines) **5**. The introduction of perfluoroalkyl chain was performed by a copper-catalyzed coupling reaction. The desired fluorous bis(oxazolines) ligand **(L2)** was obtained in 70% overall yield.

The fluorous bis(oxazolines) **(L2)** was applied in copper-catalyzed Kabachnik-Fields reaction. The reaction of benzaldehyde, aniline, and diethyl phosphite was selected as a model for the synthesis of α-aminophosphonate. Table 1 summarizes the results of the reaction. Initially, different metal catalysts were investigated in the reaction (Table 1, entries 2–10). The product was obtained in 28% yield without any catalyst, but no significant promoting effects were obtained in the presence of metal catalysts (Table 1, entries 2–8) because the water was generated during the course of the reaction which can deactivate or decompose the catalysts [26]. However, the product was obtained in 62% yield when using zinc(II) triflate and 66% yield in the presence of copper(II) triflate (Table 1, entries 9 and 10). Probably due to their high reactivity and inertness toward water. As a result, copper(II) triflate was selected as catalyst for this reaction.

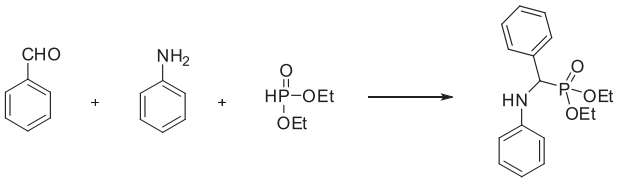
In order to probe the influence of the ligand, two different bis(oxazolines) ligand (Fig. 1) were then examined in the reaction. It was found that the yields were obviously increased by the addition of bis(oxazolines) ligands (Table 1, entries 13 and 14). Compared to the non-fluorous bis(oxazolines) ligand **(L1)** [27], the similar result was obtained when using the fluorous bis(oxazolines) ligand **(L2)**. After that, we studied the reaction time and the best result was obtained when reacted for 6 h (Table 1, entries 14–17). On the other hand, the amount of catalyst was also investigated. The yield was not obviously changed when the amount of catalyst was reduced to 5 mol% (Table 1, entries 14 and 19). Finally, different solvents were tested in the reaction (Table 1, entries 18 and 20–28). The results showed that dichloromethane was the best solvent for this reaction.

To demonstrate the generality of this method, we next investigated the scope of this reaction, and the results were summarized in Table 2. The reactions of various aldehydes, amines and diethyl phosphite under the optimized conditions giving the corresponding α-aminophosphonates in moderate to excellent yields (68–95%). The aromatic aldehydes containing electron-donating and electron-withdrawing substituent reacted with aniline and diethyl phosphite provide good to excellent yields



Scheme 1. Synthesis of fluorous bis(oxazolines).

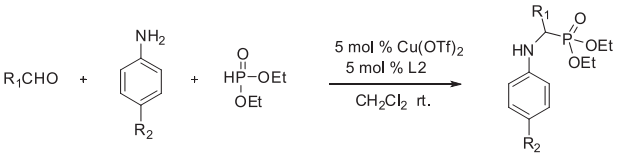
Table 1
Optimization of reaction conditions including catalyst, solvent and ligand.[a]



Entry	Catalyst	Amount of cat. (mol%)	Ligand	Solvent	Time (h)	Yield[b] (%)
1	None	5	–	CH_2Cl_2	6	28
2	$Cu(OAc)_2$	5	–	CH_2Cl_2	6	35
3	$CuSO_4$	5	–	CH_2Cl_2	6	34
4	$CuCl_2$	5	–	CH_2Cl_2	6	55
5	CuCl	5	–	CH_2Cl_2	6	43
6	$AlCl_3$	5	–	CH_2Cl_2	6	43
7	$FeCl_3$	5	–	CH_2Cl_2	6	52
8	$Zn(OAc)_2$	5	–	CH_2Cl_2	6	23
9	$Zn(OTf)_2$	5	–	CH_2Cl_2	6	62
10	$Cu(OTf)_2$	5	–	CH_2Cl_2	6	66
11	$CuCl_2$	5	**L1**	CH_2Cl_2	6	85
12	$FeCl_3$	5	**L1**	CH_2Cl_2	6	82
13	$Cu(OTf)_2$	5	**L1**	CH_2Cl_2	6	93
14	$Cu(OTf)_2$	5	**L2**	CH_2Cl_2	6	94
15	$Cu(OTf)_2$	5	**L2**	CH_2Cl_2	3	88
16	$Cu(OTf)_2$	5	**L2**	CH_2Cl_2	9	92
17	$Cu(OTf)_2$	5	**L2**	CH_2Cl_2	12	91
18	$Cu(OTf)_2$	2	**L2**	CH_2Cl_2	6	89
19	$Cu(OTf)_2$	10	**L2**	CH_2Cl_2	6	94
20	$Cu(OTf)_2$	5	**L2**	THF	6	91
21	$Cu(OTf)_2$	5	**L2**	$PhCH_3$	6	90
22	$Cu(OTf)_2$	5	**L2**	Dioxane	6	89
23	$Cu(OTf)_2$	5	**L2**	CH_3CN	6	86
24	$Cu(OTf)_2$	5	**L2**	MeOH	6	87
25	$Cu(OTf)_2$	5	**L2**	EtOH	6	85
26	$Cu(OTf)_2$	5	**L2**	DMF	6	62
27	$Cu(OTf)_2$	5	**L2**	DMSO	6	65
28	$Cu(OTf)_2$	5	**L2**	H_2O	6	38

[a] Rcaction conditions: 1 mmol benzaldehyde, 1 mmol aniline, 1.5 mmol diethyl phosphite, metal catalyst, ligand (same scale of metal catalyst), 1 mL solvent, room temperature.
[b] Isolated yields.

Table 2
Scope of substrates.[a]

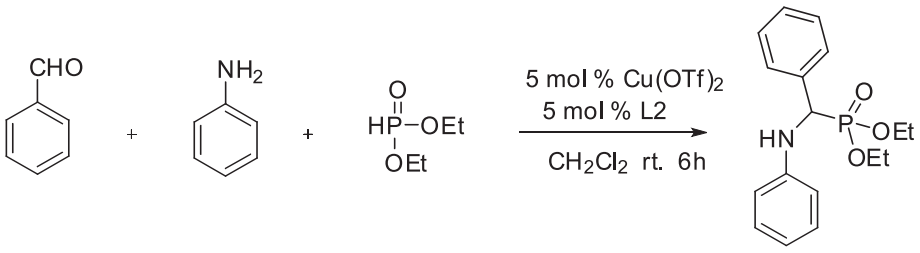


Entry	R_1	R_2	Product	Yield[b] (%)
1	C_6H_5-	H	**6a**	94
2	4-CH_3-C_6H_4-	H	**6b**	92
3	4-Cl-C_6H_4-	H	**6c**	93
4	4-F-C_6H_4-	H	**6d**	92
5	4-OCH_3-C_6H_4-	H	**6e**	90
6	4-NO_2-C_6H_4-	H	**6f**	91
7	4-NMe_2-C_6H_4-	H	**6g**	85
8	4-CF_3-C_6H_4-	H	**6h**	92
9	3-CF_3-C_6H_4-	H	**6i**	90
10	3-NO_2-C_6H_4-	H	**6j**	87
11	3-Cl-C_6H_4-	H	**6k**	90
12	3-Br-C_6H_4-	H	**6l**	91
13	2-CF_3-C_6H_4-	H	**6m**	73
14	2-NO_2-C_6H_4-	H	**6n**	85
15	2-Br-C_6H_4-	H	**6o**	87
16	1-Naphthyl	H	**6p**	91
17	2-Furyl	H	**6q**	Trace
18	2-Thienyl	H	**6r**	68
19	C_6H_5-	Cl	**6s**	92
20	C_6H_5-	CH_3	**6t**	95
21	C_6H_5-	OCH_3	**6u**	90
22	C_6H_5-	NO_2	**6v**	86

[a] Reaction conditions: 1 mmol aldehyde, 1 mmol amine, 1.5 mmol diethyl phosphite, 5 mol% $Cu(OTf)_2$, 5 mol% **L2**, 1 mL CH_2Cl_2, room temperature, 6 h.
[b] Isolated yields.

(Table 2, entries 1–8). The similar results were obtained when using aromatic amines containing electron-donating and electron-withdrawing substituent reacted with benzaldehyde and diethyl phosphite (Table 2, entries 19–22). The steric effect showed slight influences on the reactions (Table 2, entries 6, 10 and 14). 2-Thenaldehyde afforded α-aminophosphonate in 68% yield while 2-furaldehyde gave no product which are probably due to the instability of the intermediate (Table 2, entries 17 and 18).

Table 3
Recycling and reuse of the fluorous ligand[a]



Run	Recovery of ligand[b] (%)	Yield[c] (%)
–	–	94
1	94	93
2	95	91
3	92	92
4	93	90

[a] Rcaction conditions: 1 mmol benzaldehyde, 1 mmol aniline, 1.5 mmol diethyl phosphite, 5 mol% $Cu(OTf)_2$, 5 mol% **L2**, 1 mL CH_2Cl_2, room temperature, 6 h.
[b] Recovered by F-SPE.
[c] Isolated yields.

The recyclability of the fluorous bis(oxazolines) ligand was studied by choosing the reaction of benzaldehyde, aniline and diethyl phosphite as a model. After the reaction was finished, the ligand was recovered by FluoroFlash silica gel. The non-fluorous component was eluted by the mixture of methanol and water, then fluorous bis(oxazolines) was eluted by pure methanol. The recovered ligand could be used directly for the next run. As listed in Table 3, the fluorous bis(oxazolines) ligand could be reused for four times without significant loss of activity.

3. Conclusion

In summary, a novel fluorous bis(oxazolines) ligand was synthesized and used in copper-catalyzed Kabachnik-Fields reaction to give the corresponding α-aminophosphonates. The reactions proceeded smoothly to provide products in moderate to excellent yields (68–95%). This facile and efficient method was applicable for a wide range of substrates. Furthermore, the fluorous bis(oxazolines) ligand could be easily recovered by F-SPE and reused for four times without significant loss of activity.

4. Experimental

All reagents were purchased from commercial sources and without further purification, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H and ^{13}C NMR were recorded on a Bruker Avance III (500 MHz) spectrometer and tetramethylsilane (TMS) was used as a reference. Melting points were determined in open capillary tubes. Elemental analysis was performed on a Vario EL III recorder.

4.1. 5-Iodoisophthalic acid **(2)**

5-Aminoisophthalic acid (1.75 g, 9.6 mmol) was suspended in water (5 ml) at 0–5 °C. Dilute HCl (10%, 30 mL, 30 mmol) and $NaNO_2$ (701 mg, 10.1 mmol) solutions were added successively, and then the solution was stirred for 1 h to complete diazotization. Then KI (6.37 g, 38.4 mmol) was slowly added, and the mixture was stirred overnight at room temperature. After the reaction, the precipitate was collected by filtration, washed with water several times, and dried in vacuo. Yellow solid. Yield: 96%. Mp: 304–306 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.40 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 164.72, 140.90, 132.63, 128.59, 94.26.

4.2. 5-Iodoisophthaloyl dichloride **(3)**

5-Iodoisophthalic acid **2** (2.63 g, 9.0 mmol) was suspended in thionyl chloride (20 mL). Two drops of DMF was added and the mixture was heated to reflux for 3 h. The excess $SOCl_2$ was removed under reduced pressure to afford the 5-iodoisophthaloyl dichloride **3** as a yellow solid which was used directly for the next step.

4.3. 5-Iodo-N,N′-bis(1-hydroxy-3-phen-2-yl)benzene-1,3-dicarbonamide **(4)**

The above 5-iodoisophthaloyl dichloride in CH_2Cl_2 (20 mL) was added dropwise to a solution of phenylglycinol (22.5 mmol) and Et_3N (4.9 mL) in CH_2Cl_2 (20 mL) at 0 °C, then the mixture was stirred overnight at room temperature. The reaction mixture was successively washed with saturated NH_4Cl (aq), HCl (1 M), saturated $NaHCO_3$ (aq) and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (MeOH/CH_2Cl_2, 1:30). White solid, Yield: 91%. Mp: 129–131 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.97 (d, J = 8.1 Hz, 2H), 8.39 (d, J = 1.1 Hz, 2H), 8.36 (s, 1H), 7.38 (d, J = 7.4 Hz, 4H), 7.32 (t, J = 7.6 Hz, 4H), 7.23 (t, J = 7.3 Hz, 2H), 5.07–5.02 (m, 2H), 4.98 (t, J = 5.9 Hz, 2H), 3.72–3.67 (m, 2H), 3.65–3.60 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 163.83, 140.50, 137.55, 136.08, 127.62, 126.47, 126.38, 125.90, 93.82, 63.86, 55.78.

4.4. 1,3-Bis(4,4-diphenyl-2-oxazolin-2-yl)-5-iodobenzene **(5)**

p-Toluenesulfonyl chloride (15 mmol) was added to the solution of 5-iodo-N,N′-bis(1-hydroxy-3-phen-2-yl)benzene-1,3-dicarbonamide **4** (6 mmol) and Et_3N (2.3 mL) in CH_2Cl_2 (30 mL). The reaction mixture was allowed to reflux for 24 h. Saturated NH_4Cl solution was then poured into the reaction mixture. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3× 15 mL). The combined extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (ethyl acetate/petroleum ether, 1:8). Yellow oil, Yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.63 (s, 1H), 8.55 (d, J = 1.0 Hz, 2H), 7.41–7.34 (m, 4H), 7.31 (t, J = 3.1 Hz, 4H), 7.29 (s, 2H), 5.44–5.37 (m, 2H), 4.82 (dd, J = 10.0, 8.7 Hz, 2H), 4.31 (t, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.73, 140.86, 138.99, 128.64, 127.87, 126.83, 126.64, 125.74, 92.52, 74.15, 69.27.

4.5. 1,3-Bis(4,4-diphenyl-2-oxazolin-2-yl)-5-perfluorooctyl benzene **(L2)**

A mixture of **5** (5.0 mmol), $C_8F_{17}I$ (5.0 mmol) and Cu powder (1.6 g, 25.0 mmol) in DMSO (10 ml) was stirred for 22 h at 120 °C. The mixture was filtered by Celite and washed with Et_2O and water. The aqueous layer was extracted with Et_2O (3× 15 ml). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by short-path silica gel column chromatography (ethyl acetate/petroleum ether, 1:6). White solid, Yield: 91%. Mp: 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (s, 1H), 8.41 (s, 2H), 7.42–7.35 (m, 4H), 7.34–7.28 (m, 6H), 5.48–5.41 (m, 2H), 4.90–4.84 (m, 2H), 4.35 (t, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.99, 141.85, 131.93, 130.16, 129.67, 129.20, 129.03, 128.02, 126.88, 75.42, 70.53; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −80.72 (t, J = 9.8 Hz, 3F), −110.62 (dt, J = 64.3, 13.1 Hz, 2F), −121.00 to −121.27 (m, 4F), −121.83 (s, 4F), −122.67 (s, 2F), −125.99 to −126.14 (m, 2F). Anal. Calc. for $C_{32}H_{19}F_{17}N_2O_2$: C, 48.85; H, 2.44; Found: C, 48.64; H, 2.53.

4.6. General procedure for synthesis of α-aminophosphonates and recovery of fluorous bis(oxazolines)

5 mol% $Cu(OTf)_2$ and 5 mol% ligand was stirred in CH_2Cl_2 at room temperature for 30 min. Aldehyde (1 mmol), amine (1 mmol) and diethyl phosphite (1.5 mmol) was added respectively and then the mixture was stirred for 6 h at room temperature. After the reaction was finished, the mixture was separated by FluoroFlash silica gel. The non-fluorous component was eluted by the mixture of methanol and water (methanol/water, 4:1), then fluorous bis(oxazolines) was eluted by pure methanol. The elutant was concentrated in vacuo and the recovered ligand could be used directly for the next run. The non-fluorous mixture was concentrated in vacuo and then purified by short-path silica gel column chromatography (ethyl acetate/petroleum ether, 1:4).

4.6.1. Diethyl (phenylamino)(phenyl)methylphosphonate **(6a)** [28]

White solid; Mp: 92–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, H), 7.26 (t, J = 7.2 Hz, 1H), 7.10 (t, J = 7.8 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.9 Hz, 2H), 4.79 (br, s, 1H), 4.74 (s, 1H), 4.19–4.04 (m, 2H), 3.98–3.90 (m, 1H), 3.73–3.63 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.46 (d, J = 14.6 Hz), 136.04, 129.29, 128.71,

128.00, 118.53, 114.00, 63.40, 56.83, 55.63, 16.55 (d, J = 3.3 Hz), 16.31 (d, J = 4.0 Hz).

4.6.2. Diethyl (phenylamino)(4-methylphenyl)methylphosphonate ***(6b)*** *[28]*

White solid; Mp: 64–65 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (dd, J = 8.0, 2.0 Hz, 2H), 7.17–7.06 (m, 4H), 6.69 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.9 Hz, 2H), 4.76 (br, s, 1H), 4.71 (s, 1H), 4.18–4.04 (m, 2H), 3.99–3.91 (m, 1H), 3.74–3.66 (m, 1H), 2.31 (d, J = 0.9 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.51 (d, J = 14.4 Hz), 137.70, 132.85, 129.43, 129.25, 127.82, 118.44, 113.98, 63.33, 56.48, 55.28, 21.25, 16.55 (d, J = 3.2 Hz), 16.34 (d, J = 3.2 Hz).

4.6.3. Diethyl (phenylamino)(4-chlorophenyl)methylphosphonate ***(6c)*** *[29]*

White solid; Mp: 58–59 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (dd, J = 8.5, 2.1 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.11 (t, J = 7.8 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 8.0 Hz, 2H), 4.75 (br, s, 1H), 4.70 (d, J = 6.8 Hz, 1H), 4.18–4.05 (m, 2H), 4.03–3.95 (m, 1H), 3.83–3.73 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.15 (d, J = 14.3 Hz), 134.74, 133.84, 129.35, 129.28, 128.92, 118.80, 113.97, 63.99–62.95, 56.29, 55.09, 16.55 (d, J = 3.8 Hz), 16.37 (d, J = 3.5 Hz).

4.6.4. Diethyl (phenylamino)(4-fluorophenyl)methylphosphonate ***(6d)*** *[30]*

White solid; Mp: 83–84 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49–7.42 (m, 2H), 7.11 (t, J = 7.9 Hz, 2H), 7.03 (t, J = 8.6 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.1 Hz, 2H), 4.77 (br, s, 1H), 4.72 (s, 1H), 4.19–4.04 (m, 2H), 4.01–3.93 (m, 1H), 3.80–3.71 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.50, 161.53, 146.19 (d, J = 14.3 Hz), 131.74, 129.62, 129.51, 129.28, 118.66, 115.72, 115.55, 113.92, 63.40, 56.05, 54.85, 16.49 (d, J = 3.0 Hz), 16.30 (d, J = 3.4 Hz).

4.6.5. Diethyl (phenylamino)(4-methoxyphenyl)methylphosphonate ***(6e)*** *[28]*

White solid; Mp: 101–103 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38 (dd, J = 8.7, 2.1 Hz, 2H), 7.10 (t, J = 7.8 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 8.3 Hz, 2H), 4.73 (br, s, 1H), 4.69 (s, 1H), 4.17–4.04 (m, 2H), 3.98–3.91 (m, 1H), 3.77 (s, 3H), 3.74–3.65 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.41, 146.47 (d, J = 14.0 Hz), 129.26, 129.05, 127.80, 118.46, 114.17, 114.00, 63.33, 56.09, 55.34, 54.89, 16.57 (d, J = 3.4 Hz), 16.40.

4.6.6. Diethyl (phenylamino)(4-nitrophenyl)methylphosphonate ***(6f)*** *[28]*

Yellow solid; Mp: 124–125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.20 (d, J = 8.6 Hz, 2H), 7.66 (dd, J = 8.7, 2.1 Hz, 2H), 7.11 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 8.1 Hz, 2H), 4.88 (s, 1H), 4.83 (s, 1H), 4.20–4.09 (m, 2H), 4.07–3.99 (m, 1H), 3.92–3.84 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.65, 144.66 (d, J = 13.9 Hz), 143.09, 128.38, 127.67, 122.78, 118.14, 112.83, 62.75 (d, J = 5.8 Hz), 62.50 (d, J = 5.8 Hz), 55.66, 54.49, 15.43 (d, J = 3.3 Hz), 15.28.

4.6.7. Diethyl (phenylamino)[4-(dimethylamino)phenyl]methylphosphonate ***(6g)*** *[30]*

Yellow solid; Mp: 109–111 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (dd, J = 8.7, 2.0 Hz, 2H), 7.09 (t, J = 7.8 Hz, 2H), 6.67 (t, J = 7.6 Hz, 3H), 6.61 (d, J = 8.1 Hz, 2H), 4.69 (br, s, 1H), 4.65 (d, J = 4.5 Hz, 1H), 4.17–4.04 (m, 2H), 3.98–3.90 (m, 1H), 3.73–3.63 (m, 1H), 2.92 (s, 6H), 1.28 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.35, 146.73 (d, J = 14.3 Hz), 129.21, 128.71, 123.07, 118.25, 114.04, 112.67, 63.23 (dd, J = 13.5, 5.9 Hz), 56.09, 54.87, 40.61, 16.58, 16.45.

4.6.8. Diethyl (phenylamino)[4-(trifluoromethyl)phenyl]methylphosphonate ***(6h)*** *[31]*

White solid; Mp: 121–123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65–7.54 (m, 4H), 7.12 (t, J = 7.9 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 4.86 (br, s, 1H), 4.81 (d, J = 6.1 Hz, 1H), 4.21–4.07 (m, 2H), 4.05–3.97 (m, 1H), 3.87–3.77 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.02 (d, J = 14.0 Hz), 140.53, 129.36, 128.25, 125.59, 118.88, 113.88, 63.65 (d, J = 5.4 Hz), 63.44 (d, J = 5.4 Hz), 56.58, 55.39, 16.46, 16.26.

4.6.9. Diethyl (phenylamino)[3-(trifluoromethyl)phenyl]methylphosphonate ***(6i)***

White solid; Mp: 108–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.9 Hz, 2H), 6.75–6.60 (m, 3H), 5.26 (d, J = 23.7 Hz, 1H), 4.98 (br, s, 1H), 4.26–4.10 (m, 2H), 3.90–3.82 (m, 1H), 3.56–3.48 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.63 (d, J = 12.4 Hz), 135.00, 131.34, 128.25, 128.01, 127.56, 127.00, 125.31, 117.68, 112.85, 62.43, 51.11, 49.90, 15.39 (d, J = 3.1 Hz), 14.92 (d, J = 3.2 Hz).

4.6.10. Diethyl (phenylamino)(3-nitrophenyl)methylphosphonate ***(6j)*** *[30]*

Yellow solid; Mp: 96–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.35 (d, J = 1.6 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.11 (t, J = 7.9 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 4.90 (s, 1H), 4.85 (s, 1H), 4.21–4.10 (m, 2H), 4.08–4.01 (m, 1H), 3.94–3.85 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.50, 145.75 (d, J = 13.6 Hz), 138.95, 133.86, 129.61, 129.39, 122.93 (d, J = 16.6 Hz), 119.06, 113.86, 63.81 (d, J = 5.4 Hz), 63.48 (d, J = 5.3 Hz), 56.30, 55.11, 16.47 (d, J = 2.9 Hz), 16.29.

4.6.11. Diethyl (phenylamino)(3-chlorophenyl)methylphosphonate ***(6k)*** *[29]*

White solid; Mp: 90–91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (s, 1H), 7.40–7.35 (m, 1H), 7.29–7.22 (m, 2H), 7.12 (t, J = 7.9 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 7.9 Hz, 2H), 4.86 (s, 1H), 4.74 (dd, J = 24.4, 5.5 Hz, 1H), 4.20–4.07 (m, 2H), 4.03–3.95 (m, 1H), 3.83–3.74 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.08 (d, J = 14.1 Hz), 138.42, 134.55, 129.87, 129.28, 128.16, 127.98, 126.02, 118.69, 113.83, 63.47, 56.36, 55.17, 16.44 (d, J = 2.9 Hz), 16.22 (d, J = 3.3 Hz).

4.6.12. Diethyl (phenylamino)(3-bromophenyl)methylphosphonate ***(6l)*** *[32]*

White solid; Mp: 96–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J = 1.2 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.0 Hz, 2H), 4.82 (s, 1H), 4.72 (dd, J = 24.5, 4.5 Hz, 1H), 4.19–4.06 (m, 2H), 4.03–3.95 (m, 1H), 3.82–3.74 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.07 (d, J = 13.9 Hz), 138.69, 131.11, 130.89, 130.19, 129.31, 126.45, 122.75, 118.74, 113.85, 63.51, 56.34, 55.15, 16.47 (d, J = 3.0 Hz), 16.25 (d, J = 3.3 Hz).

4.6.13. Diethyl (phenylamino)[2-(trifluoromethyl)phenyl]methylphosphonate ***(6m)*** *[31]*

White solid; Mp: 123–125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.9 Hz, 2H), 6.76–6.61 (m, 3H), 5.26 (d, J = 23.7 Hz, 1H), 4.99 (br, s, 1H), 4.24–4.12 (m, 2H), 3.90–3.82

(m, 1H), 3.56–3.48 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.73 (d, J = 12.4 Hz), 136.10, 132.44, 129.35, 129.11, 128.66, 128.10, 126.41, 118.78, 113.95, 63.53, 52.21, 51.00, 16.49 (d, J = 3.1 Hz), 16.02 (d, J = 3.2 Hz).

4.6.14. Diethyl (phenylamino)(2-nitrophenyl)methylphosphonate **(6n)** [30]

Yellow solid; Mp: 155–157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.7 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 8.0 Hz, 2H), 6.18 (d, J = 26.2 Hz, 1H), 5.07 (s, 1H), 4.23–4.10 (m, 2H), 4.00–3.89 (m, 1H), 3.86–3.76 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.52, 145.48 (d, J = 14.0 Hz), 133.57, 132.01, 129.48, 128.89, 128.61, 125.30, 118.87, 113.64, 63.95 (d, J = 5.2 Hz), 63.44 (d, J = 5.9 Hz), 50.58, 49.38, 16.42 (d, J = 2.8 Hz), 16.01 (d, J = 2.9 Hz).

4.6.15. Diethyl (phenylamino)(2-bromophenyl)methylphosphonate **(6o)** [31]

White solid; Mp: 120–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (t, J = 8.3 Hz, 2H), 7.26 (dd, J = 8.9, 6.1 Hz, 1H), 7.11 (t, J = 7.9 Hz, 3H), 6.69 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.9 Hz, 2H), 5.36 (d, J = 24.6 Hz, 1H), 5.07 (br, s, 1H), 4.28–4.17 (m, 2H), 3.94–3.86 (m, 1H), 3.67–3.57 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.79 (d, J = 14.4 Hz), 135.78, 132.82, 129.47, 129.27 (d, J = 9.7 Hz), 128.03, 124.83 (d, J = 6.2 Hz), 118.53, 113.68, 63.54, 54.92, 53.70, 16.50 (d, J = 3.2 Hz), 16.16 (d, J = 3.2 Hz).

4.6.16. Diethyl (phenylamino)(1-naphthalenyl)methylphosphonate **(6p)** [33]

White solid; Mp: 123–125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.27 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.79 (dd, J = 7.6, 2.8 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.05 (t, J = 7.9 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 8.1 Hz, 2H), 5.66 (d, J = 24.1 Hz, 1H), 5.13 (br, s, 1H), 4.25–4.12 (m, 1H), 3.80–3.67 (m, 1H), 3.27–3.17 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.22 (d, J = 14.3 Hz), 133.92, 131.81, 131.62, 129.28, 129.12, 128.58, 126.37, 125.75, 125.50, 125.05, 123.04, 118.37, 113.68, 63.39 (dd, J = 23.0, 5.4 Hz), 52.13, 50.92, 16.54, 15.85 (d, J = 3.5 Hz).

4.6.17. Diethyl (phenylamino)(2-thienyl)methylphosphonate **(6r)** [14]

Brown solid; Mp: 59–61 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22 (d, J = 4.9 Hz, 1H), 7.19–7.10 (m, 3H), 7.01–6.93 (m, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 8.0 Hz, 2H), 5.05 (d, J = 23.7 Hz, 1H), 4.65 (br, s, 1H), 4.23–4.01 (m, 3H), 3.93–3.81 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.20 (d, J = 12.9 Hz), 139.93, 129.31, 127.16, 126.24 (d, J = 5.7 Hz), 125.36, 119.03, 114.07, 63.63 (dd, J = 22.5, 5.4 Hz), 52.78, 51.52, 16.50, 16.35 (d, J = 3.1 Hz).

4.6.18. Diethyl (4-chlorophenylamino)(phenyl)methylphosphonate **(6s)** [31]

White solid; Mp: 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.27 (dd, J = 6.7, 5.2 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 4.89 (br, s, 1H), 4.70 (d, J = 24.1 Hz, 1H), 4.18–4.04 (m, 2H), 3.96–3.88 (m, 1H), 3.70–3.61 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.00 (d, J = 14.2 Hz), 135.53, 129.10, 128.76, 128.18, 127.90, 123.14, 115.09, 63.45 (dd, J = 16.3, 5.6 Hz), 56.85, 55.65, 16.51 (d, J = 2.4 Hz), 16.26 (d, J = 3.2 Hz).

4.6.19. Diethyl (4-methylphenylamino)(phenyl)methylphosphonate **(6t)** [31]

White solid; Mp: 117–119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, J = 7.4 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.26 (dd, J = 8.0, 6.1 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 6.52 (d, J = 8.3 Hz, 2H), 4.77 (s, 1H), 4.72 (s, 1H), 4.17–4.07 (m, 2H), 3.98–3.91 (m, 1H), 3.74–3.64 (m, 1H), 2.18 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.06 (d, J = 15.3 Hz), 136.10, 129.75, 128.64, 127.94, 127.70, 114.09, 63.36, 57.03, 55.83(s), 20.43, 16.51 (d, J = 3.0 Hz), 16.27 (d, J = 2.9 Hz).

4.6.20. Diethyl (4-methoxyphenylamino)(phenyl)methylphosphonate **(6u)** [34]

Gray solid; Mp: 70–72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.28–7.20 (m, 1H), 6.68 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 4.69 (d, J = 24.0 Hz, 1H), 4.17–4.06 (m, 2H), 3.97–3.90 (m, 1H), 3.73–3.64 (m, 4H), 1.28 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.71, 140.41 (d, J = 15.6 Hz), 136.09, 128.61, 127.93, 115.29, 114.79, 63.30, 57.63, 56.43, 55.68, 16.48 (d, J = 3.0 Hz), 16.24 (d, J = 3.1 Hz).

4.6.21. Diethyl (4-nitrophenylamino)(phenyl)methylphosphonate **(6v)** [31]

Yellow solid; Mp: 145–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, J = 9.1 Hz, 2H), 7.46 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.30 (dd, J = 8.0, 6.4 Hz, 1H), 6.59 (d, J = 9.2 Hz, 2H), 6.09 (t, J = 8.6 Hz, 1H), 4.82 (dd, J = 24.0, 7.8 Hz, 1H), 4.22–4.07 (m, 2H), 3.95–3.87 (m, 1H), 3.67–3.56 (m, 1H), 1.96 (s, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.14 (d, J = 13.5 Hz), 138.96, 134.71, 129.15, 128.96, 128.57, 127.89, 126.13, 112.47, 63.99, 63.70 (dd, J = 63.6, 5.3 Hz), 56.18, 54.98, 16.50 (d, J = 2.7 Hz), 16.24 (d, J = 2.3 Hz).

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