Palladium-Catalyzed Hydroarylation of Diazocarboxylates and Diazophosphonates

Sergey M. Golitsin

Irina P. Beletskaya

Igor D. Titanyuk*

Department of Chemistry, Moscow State University, 119991,
Leninskie gory 1-3, Moscow, Russian Federation
titanyuk@org.chem.msu.ru

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Abstract A simple synthetic procedure for the Pd-catalyzed hydroarylation of diazoacetic ester has been previously developed in our laboratory. Now we have applied this methodology for hydroarylation of α -diazocarboxylates/ α -diazophosphonates. Diazo compounds reacted with aryl iodides and formic acid to afford diarylated esters or phosphonates in yields up to 71%.

Key words hydroarylation, diazo compounds, arylacetates, palladium catalysis, cross coupling, phosphonates

The transition-metal-catalyzed transformation of α -diazocarbonyl compounds has become a standard method in organic synthesis. The approach has traditionally been used for carbene generation in reactions such as X–H insertion (X = C, N, O, S), cyclopropanation, and cycloaddition to nitriles and carbonyl compounds.¹ More recently, the scope of their application was widened significantly to include Pd-catalyzed cross-coupling reactions, mostly due to the important contributions made by J. Wang and co-workers.² Depending on the reaction conditions, two types of cross-coupling reactions can be carried out: (i) with retention of diazo group leading to formation of aryl-substituted diazo compound;³ (ii) with the loss of diazo function (Scheme 1).⁴

Scheme 1

In the latter case, a organopalladium intermediate that is generated can be captured with a nucleophile.^{4–6} The hydride ion generated from formic acid is a suitable nucleophile for this type reaction. Our research group has elaborated Pd-catalyzed three-component hydroarylation coupling: aryl iodides reacted with α -diazocarboxylates/ α -diazophosphonates and formic acid to generate mono- or diarylacetates and diarylphosphonates.

Recently, J. Wang and co-workers have reported Pd-catalyzed reductive coupling of ethyl diazoacetate (EDA) with aryl iodides leading to the formation of α,α -diarylacetates. Although their methodology provides high yield and wide scope of products, it requires a stoichiometric amount of silver carbonate.⁷

The coupling of aryl iodides with EDA in the presence of formic acid and Et₃N was investigated previously by our research team (Scheme 2).⁸

Scheme 2 Hydroarylation of EDA with aryl iodides⁸

A number of aryl iodides were subjected to three-component hydroarylation under the optimized reaction conditions. Exploration of substrates containing electron-withdrawing groups (EWG) as well as iodobenzene allowed a range of ethyl arylacetates **2** to be synthesized in respectable yields (50–85%).

In this context, we have been interested in continuing our previous studies in an attempt to extend our method to a wider range of substrates. Herein we report a solution to this issue.

The coupling of methyl 4-iodobenzoate (**1a**) with phenyldiazoacetate (**3a**) in the presence of formic acid and Et₃N was investigated as a model reaction for the preparation of diarylated products (Table 1).

Table 1 Optimization of the Reaction Conditions in the Model Reaction^a

Entry	Catalyst	Base	Solvent	Yield (%) ^b
1	PdCl ₂ (PPh ₃) ₂	Et ₃ N	MeCN	38
2	Pd ₂ (dba) ₃ +PPh ₃	Et ₃ N	MeCN	29
3	PdCl ₂ (PCy ₃) ₂	Et ₃ N	MeCN	0
4	Pd(PPh ₃) ₄	Et ₃ N	MeCN	42
5	Pd(PPh ₃) ₄	Et ₃ N	1,2-DCE	60
6	Pd(PPh ₃) ₄	Et ₃ N	benzene	42
7	Pd(PPh ₃) ₄	Et ₃ N	EtOH	traces
8	Pd(PPh ₃) ₄	Et ₃ N	THF	52
9	Pd(PPh ₃) ₄	Et ₃ N	CHCl ₃	20
10	PdCl₂(PPh₃)₂	Et₃N	1,2-DCE	70
11	PdCl ₂ (PPh ₃) ₂	DBU	1,2-DCE	traces
12	PdCl ₂ (PPh ₃) ₂	Py	1,2-DCE	20
13	PdCl ₂ (PPh ₃) ₂	DIPEA	1,2-DCE	24
14	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	1,2-DCE	30
15 ^c	PdCl ₂ (PPh ₃) ₂	Et ₃ N	1,2-DCE	0
16 ^d	PdCl ₂ (PPh ₃) ₂	Et ₃ N	1,2-DCE	31
17 ^e	PdCl ₂ (PPh ₃) ₂	Et ₃ N	1,2-DCE	55

^a Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), base (2.5 mmol), HCO₂H (0.5 mmol), Pd catalyst (0.05 mmol), reflux.

^b Isolated yield.

^c Carried out at 20 °C.

^d Carried out at 40 °C.

^e Carried out at 60 °C.

Screening of catalytic systems revealed that application of palladium catalysts Pd(PPh₃)₄ and PdCl₂(PPh₃)₂ was more effective than Pd₂(dba)₃ (Table 1, entries 1–3). The investigated chemical reaction appeared to be sensitive not only to the selected catalyst but also to the choice of solvent and base. The reaction afforded hydroarylated product **4a** with higher yield (entries 5, 10) using 1,2-DCE as solvent. Triethylamine appeared to be the best base for this reaction; other bases such as K₂CO₃, pyridine, DIPEA or DBU were found to be ineffective or less effective in this reaction.

Reaction temperature variation was further investigated. Attempts to obtain hydroarylated product **4a** at room temperature failed. Increase of reaction temperature greatly influenced the amount of synthesized product. In summary, it was found that the most favorable conditions were:

PdCl₂(PPh₃)₂ as the catalyst, triethylamine as the base, 1,2-DCE as the solvent, and reflux temperature (Table 1, entry 10).

The coupling of aryl iodides **1** with α-aryldiazoacetates **3** in the presence of formic acid and triethylamine provided diarylacetates **4a–l** in a yield up to 71% (Table 2). The scope of the proposed method was examined by application of ethyl α-aryldiazocarboxylates (**3a–d**) in the hydroarylation reaction with a series of aryl iodides **1** under the optimized reaction conditions.

Table 2 Hydroarylation of α-Aryldiazoacetates **3** with Aryl Iodides **1**^a

Entry	R	Ar	Product	Yield (%) ^b
1	H (3a)	<i>p</i> -MeO ₂ CC ₆ H ₄ (1a)	4a	70
2	H (3a)	<i>m</i> -MeO ₂ CC ₆ H ₄ (1b)	4b	45
3	H (3a)	3-C ₅ H ₄ N (1c)	4c	53
4	H (3a)	<i>p</i> -NCC ₆ H ₄ (1d)	4d	66
5	H (3a)	<i>p</i> -O ₂ NC ₆ H ₄ (1e)	4e	71
6	H (3a)	<i>p</i> -F ₃ CC ₆ H ₄ (1f)	4f	55
7	H (3a)	<i>p</i> -AcC ₆ H ₄ (1g)	4g	69
8	H (3a)	<i>m</i> -MeC ₆ H ₄ (1h)	4h	trace
9	<i>p</i> -CN (3b)	<i>p</i> -O ₂ NC ₆ H ₄ (1e)	4i	37
10	<i>p</i> -CN (3b)	<i>m</i> -MeO ₂ CC ₆ H ₄ (1b)	4j	35
11	<i>p</i> -MeO ₂ C (3c)	<i>p</i> -MeO ₂ CC ₆ H ₄ (1a)	4k	43
12	<i>m</i> -Me (3d)	<i>p</i> -NCC ₆ H ₄ (1d)	4l	64

^a Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), Et₃N (1.25 mmol), HCO₂H (0.5 mmol), Pd(PPh₃)₂Cl₂ (0.025 mmol), DCE, reflux for 2 h.

^b Isolated yield.

Exploration of EWG-containing aryl iodides and 3-iodopyridine allowed phenylarylates **4a–g** to be synthesized in good yields (40–71%). Aryl iodide containing electron-donating groups (*m*-tolyl iodide) exhibited poor reactivity and provided product **4h** in trace amounts (Table 2, entry 8). A significant influence of the electronic effects of substituents on the aromatic ring of the diazo compound was observed. It was opposite to that of aryl iodides: the presence of electron-withdrawing group on the benzene ring of diazo compound **3** decreased the yield of product compared with that of unsubstituted phenyldiazoacetate **3a** (entries 9–11). In contrast, diazocarboxylate **3d**, containing an electron-donating *m*-CH₃ group, provided good yield of product **4l** (entry 12).

The phosphonate (PO₃²⁻) moiety is a common structural fragment that is present in a wide range of biologically active compounds.^{9,10} Despite structural and electronic differences between phosphonate and carboxylic functionalities (in terms of size, shape, acidity, and geometry) the

phosphonate functionality is regarded as a bioisostere of the carboxylic group. α -Diazophosphonates have received much more attention in organic synthesis in recent years; they are widely used for the preparation of derivatives of phosphonic acids.¹¹

We also applied the above procedure for the synthesis of diarylmethylphosphonates **6a–e** (Table 3). Diazophosphonates **5** exhibited comparable reactivity under analogous reaction conditions yielding the corresponding α,α -diarylphosphonates **6a–e** in good yield.

Table 3 Hydroarylation of Diazophosphonates **5** with Aryl Iodides **1**^a

Entry	R ¹	R	Product	Yield (%) ^b
1	<i>p</i> -MeO (5a)	<i>p</i> -MeO ₂ C	6a	66
2	H (5b)	<i>p</i> -O ₂ N	6b	60
3	H (5b)	<i>p</i> -MeO ₂ C	6c	54
4	H (5b)	<i>p</i> -NC	6d	63
5	H (5b)	<i>p</i> -Ac	6e	71

^a Reaction conditions: **1** (0.5 mmol), **5** (0.5 mmol), Et₃N (1.25 mmol), HCO₂H (0.5 mmol), Pd(PPh₃)₂Cl₂ (0.025 mmol), DCE, reflux for 4 h.

^b Isolated yield.

The proposed mechanism of hydroarylation is presented in Scheme 3. Palladium dichloride complex can be easily reduced by formic acid resulting in Pd(0) species. The catalytic cycle starts with oxidative addition to form arylpalladium iodide complex **A**. Then addition of diazo compound to this complex could generate carbene complex **B**.¹² Migration of the aryl group to the carbene center, which is now described in several publications,^{13,14} would produce benzylic intermediate **C**. The exchange complex **D** can be easily produced by substitution of halogen with formate anion followed by liberation of carbon dioxide (complex **E**). Reductive elimination should provide the product simultaneously with regeneration of the Pd(0) species.

In conclusion, this report describes a simple method for palladium-catalyzed hydroarylation of diazocarboxylates and diazophosphonates in the presence of formic acid. The proposed reaction can serve as a pathway for the preparation of diarylated carboxylic acid and phosphonic acid derivatives that are otherwise difficult to access. A range of arylated products were synthesized in 35–71% yield by applying this methodology.

Scheme 3 Mechanism of hydroarylation

All solvents were distilled prior to use. Acetonitrile and 1,2-dichloroethane were dried by distillation over P₂O₅. Chromatography was carried out using 230–400 mesh silica gel (Merck 40/60). ¹H NMR spectra were recorded with a commercial Agilent 400-MR (400 MHz) instrument. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 7.26 ppm). ¹³C{¹H} NMR spectra were collected with commercial Agilent 400-MR (100 MHz) instrument with complete proton decoupling. ³¹P and ¹⁹F NMR spectra were recorded with a commercial Agilent 400-MR (162 MHz and 376 MHz respectively) instrument. HRMS (ESI) were recorded with a commercial apparatus. Published procedures were applied for the synthesis of aryldiazocarboxylates (**3**)^{3a} and aryldiazophosphonates (**5**).^{3b}

Pd-Catalyzed Cross-Coupling between Aryl Iodides and Aryldiazoacetates; Typical Procedure A

To a mixture of aryl iodide (**1a–h**; 0.5 mmol), aryldiazoacetate (**3a–d**; 0.75 mmol), and PdCl₂(PPh₃)₂ (18 mg, 0.025 mmol) in a Schlenk flask under argon atmosphere, Et₃N (127 mg, 1.25 mmol) and formic acid (23 mg, 0.5 mmol) in DCE (3 mL) were added. The mixture was stirred and heated at 80 °C until **1a–h** disappeared (2–4 h, monitoring by TLC). Solvent was evaporated under reduced pressure. Pure product **4** was isolated by column chromatography (EtOAc/petrol ether, 1:5 v/v).

Pd-Catalyzed Cross-Coupling between Aryl Iodides and Aryldiazophosphonates; Typical Procedure B

To a mixture of aryl iodide **1** (0.5 mmol), aryldiazophosphonate (**5a–b**; 0.5 mmol), and PdCl₂(PPh₃)₂ (18 mg, 0.025 mmol) in a Schlenk flask under argon atmosphere, Et₃N (127 mg, 1.25 mmol) and formic acid (23 mg, 0.5 mmol) in DCE (3 mL) were added. The mixture was stirred and heated at 80 °C for 3 h. Solvent was evaporated under reduced pressure. Pure product **6** was isolated by column chromatography (EtOAc/petrol ether, 1:1 v/v).

Characterization of Synthesized Products

Ethyl [4-(Methoxycarbonyl)phenyl](phenyl)acetate (4a)

Prepared according to general procedure **A** from methyl 4-iodobenzoate and phenyldiazoacetate. Reaction time 2 h.

Yield: 104 mg (70%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.99 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.3 Hz, 2 H), 7.26–7.38 (m, 5 H), 5.05 (s, 1 H), 4.26 (q, J = 7.1 Hz, 2 H), 3.94 (s, 3 H), 1.30 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.9, 166.8, 143.8, 138.0, 129.8, 129.2, 128.7, 128.5, 127.5, 127.2, 61.4, 57.1, 52.1, 14.1.

IR (film): 1733, 1615, 1290 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$: C, 72.48; H, 6.04. Found: C, 72.67; H, 5.91.

NMR spectral data for this compound were consistent with those in the literature.⁷

Ethyl [3-(Methoxycarbonyl)phenyl](phenyl)acetate (4b)

Prepared according to general procedure **A** from methyl 3-iodobenzoate and phenyldiazoacetate. Reaction time 2.5 h.

Yield: 67 mg (45%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.02 (bs, 1 H), 7.95 (dt, 1J = 7.7 Hz, 2J = 1.3 Hz, 1 H), 7.53 (dt, 1J = 7.7 Hz, 2J = 1.9 Hz, 1 H), 7.43–7.25 (m, 6 H), 5.06 (s, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 3.90 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 172.1, 166.8, 139.2, 138.3, 133.1, 130.5, 129.8, 128.9, 128.7, 128.6, 128.3, 127.5, 61.4, 56.9, 52.1, 14.1.

IR (film): 1740, 1610, 1281 cm^{-1} .

HRMS (ESI): m/z [$\text{M} + \text{H}$]⁺ calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$: 299.1283; found: 299.1278.

Ethyl (Pyridin-3-yl)(phenyl)acetate (4c)

Prepared according to general procedure **A** from 3-iodopyridine and phenyldiazoacetate. Reaction time 2.5 h.

Yield: 64 mg (53%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.57 (d, J = 2.0 Hz, 1 H), 8.50 (dd, 1J = 4.7 Hz, 2J = 1.5 Hz, 1 H), 7.68 (dt, 1J = 1.7 Hz, 2J = 8.0 Hz, 1 H), 7.21–7.36 (m, 6 H), 5.01 (s, 1 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.25 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.7, 149.9, 148.7, 137.8, 136.1, 134.6, 128.9, 128.4, 127.6, 123.4, 61.6, 54.6, 14.1.

IR (film): 1730, 1600 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$: C, 74.69; H, 6.22; N, 5.81. Found: C, 74.33; H, 6.24; N, 5.51.

NMR spectral data for this compound were consistent with those in the literature.¹⁵

Ethyl (4-Cyanophenyl)(phenyl)acetate (4d)

Prepared according to general procedure **A** from 4-iodobenzonitrile and phenyldiazoacetate. Reaction time 2 h.

Yield: 87 mg (66%); yellow oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.60 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.38–7.26 (m, 5 H), 5.06 (s, 1 H), 4.23 (d, J = 7.1 Hz, 2 H), 1.26 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.5, 144.1, 137.5, 132.3, 129.5, 128.9, 128.5, 127.8, 118.7, 111.2, 61.6, 57.0, 14.1.

IR (film): 2230, 1738, 1612 cm^{-1} .

Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$: C, 76.68; H, 5.66; N, 5.28. Found: C, 76.91; H, 5.54; N, 5.13.

NMR spectral data for this compound were consistent with those in the literature.⁷

Ethyl (4-Nitrophenyl)(phenyl)acetate (4e)

Prepared according to general procedure **A** from 4-iodo-1-nitrobenzene and phenyldiazoacetate. Reaction time 1.5 h.

Yield: 100 mg (71%); yellow oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.17 (d, J = 8.8 Hz, 2 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.39–7.28 (m, 5 H), 5.10 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 1.27 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.4, 146.0, 137.4, 129.6, 129.0, 128.9, 128.5, 127.8, 123.7, 61.7, 56.8, 14.1.

IR (film): 1735, 1520, 1355 cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.49; H, 5.31; N, 4.86.

NMR spectral data for this compound were consistent with those in the literature.⁷

Ethyl [4-(Trifluoromethyl)phenyl](phenyl)acetate (4f)

Prepared according to general procedure **A** from 4-trifluoromethyl-1-iodobenzene and phenyldiazoacetate. Reaction time 3 h.

Yield: 85 mg (55%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.57 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.38–7.28 (m, 5 H), 5.05 (s, 1 H), 4.23 (d, J = 7.0 Hz, 2 H), 1.25 (t, J = 7.0 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.8, 142.7, 137.9, 129.0, 128.8, 128.7 (q, $J_{\text{C-F}}$ = 33.4 Hz), 128.5, 127.6, 125.5 (q, $J_{\text{C-F}}$ = 3.8 Hz), 123.9 (q, $J_{\text{C-F}}$ = 244 Hz, CF_3), 61.5, 56.8, 14.1.

^{19}F NMR (376 MHz, CDCl_3): δ = 62.6.

Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_2$: C, 66.23; H, 4.90. Found: C, 66.31; H, 5.01.

Ethyl (4-Acetylphenyl)(phenyl)acetate (4g)

Prepared according to general procedure **A** from 4-iodoacetophenone and phenyldiazoacetate. Reaction time 2 h.

Yield: 98 mg (69%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.92 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.36–7.26 (m, 5 H), 5.08 (s, 1 H), 4.23 (d, J = 7.1 Hz, 2 H), 2.58 (s, 3 H), 1.27 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 197.6, 171.7, 143.9, 137.9, 135.9, 128.9, 128.7, 128.5, 128.4, 127.4, 61.4, 56.9, 26.5, 14.0.

Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.57; H, 6.43. Found: C, 76.67; H, 6.51.

NMR spectral data for this compound were consistent with those in the literature.¹⁶

Ethyl (4-Nitrophenyl)(4-cyanophenyl)acetate (4i)

Prepared according to general procedure **A** from 4-iodo-1-nitrobenzene and (4-cyanophenyl)diazoacetate. Reaction time 3 h.

Yield: 57 mg (37%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.19 (d, J = 8.2 Hz, 2 H), 7.64 (d, J = 8.1 Hz, 2 H), 7.48 (d, J = 8.2 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 5.14 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 1.26 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 170.4, 147.4, 144.5, 142.5, 132.7, 129.6, 129.4, 124.1, 118.3, 111.9, 62.2, 56.5, 14.0.

IR (film): 2235, 1739, 1542, 1347 cm^{-1} .

Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$: C, 65.81; H, 4.52; N, 9.03. Found: C, 65.93; H, 4.73; N, 8.93.

Ethyl [3-(Methoxycarbonyl)phenyl](4-cyanophenyl)acetate (4j)

Prepared according to general procedure **A** from methyl 3-iodobenzoate and (4-cyanophenyl)diazoacetate. Reaction time 4 h.

Yield: 56 mg (35%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.98 (m, 2 H), 7.62 (d, J = 8.3 Hz, 2 H), 7.52–7.48 (m, 1 H), 7.46–7.40 (m, 3 H), 5.09 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 3.91 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 172.0, 165.7, 143.5, 136.1, 132.9, 132.4, 131.6, 130.8, 129.7, 129.4, 129.0, 118.5, 108.9, 65.4, 57.2, 51.4, 14.0.

IR (film): 2232, 1736, 1614 cm^{-1} .

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.41; H, 5.34; N, 4.24.

Ethyl Bis[4-(methoxycarbonyl)phenyl]acetate (4k)

Prepared according to general procedure **A** from methyl 4-iodobenzoate and (4-(methoxycarbonyl)phenyl)diazoacetate. Reaction time 2 h.

Yield: 76 mg (43%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.99 (d, J = 8.0 Hz, 4 H), 7.37 (d, J = 8.0 Hz, 4 H), 5.09 (s, 1 H), 4.23 (q, J = 7.1 Hz, 2 H), 3.89 (s, 6 H), 1.24 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.2, 166.6, 142.9, 129.9, 129.4, 128.6, 61.6, 56.9, 52.1, 14.1.

IR (film): 1725, 1610, 1280 cm^{-1} .

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_6$: C, 67.41; H, 5.66. Found: C, 67.44; H, 5.69.

NMR spectral data for this compound were consistent with those in the literature.⁷

Ethyl (3-Methylphenyl)(4-cyanophenyl)acetate (4l)

Prepared according to general procedure **A** from 4-iodobenzonitrile and (3-methylphenyl)diazoacetate. Reaction time 2 h.

Yield: 89 mg (64%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.61 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.52–7.48 (m, 1 H), 7.46–7.40 (m, 3 H), 5.09 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 3.91 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 171.5, 144.1, 138.7, 137.3, 132.3, 129.4, 129.1, 128.8, 128.5, 125.4, 118.7, 111.1, 61.6, 56.9, 21.4, 14.1.

IR (film): 2227, 1731, 1607 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.18; H, 5.94; N, 4.88.

Diethyl [4-(Methoxycarbonyl)phenyl](4-methoxyphenyl)methylphosphonate (6a)

Prepared according to general procedure **B** from methyl 4-iodobenzoate and diethyl 1-diazo-(4-methoxyphenyl)methylphosphonate.

Yield: 129 mg (66%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.96 (d, J = 8.2 Hz, 2 H), 7.57 (d, J = 8.2 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 6.84 (d, J = 8.5 Hz, 2 H), 4.43 (d, J = 25.0 Hz, 1 H), 4.00–3.92 (m, 2 H), 3.87 (s, 3 H), 3.87–3.79 (m, 2 H), 3.76 (s, 3 H), 1.11 (t, J = 7.1 Hz, 6 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.8, 158.8, 142.5, 130.5, 129.8, 129.4, 128.8, 128.0, 114.1, 62.9 (d, J = 6.5 Hz), 62.6 (d, J = 6.5 Hz), 55.2, 52.1, 51.3 (d, J = 138.2 Hz), 16.2.

^{31}P NMR (162 MHz, CDCl_3): δ = 24.5.

Anal. Calcd for $\text{C}_{20}\text{H}_{25}\text{O}_6\text{P}$: C, 61.22; H, 6.42. Found: C, 61.18; H, 6.49.

Diethyl (4-Nitrophenyl)(phenyl)methylphosphonate (6b)

Prepared according to general procedure **B** from 4-iodo-1-nitrobenzene and diethyl 1-diazo-phenylmethylphosphonate.

Yield: 104 mg (60%); yellow oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.15 (d, J = 8.7 Hz, 2 H), 7.70 (d, J = 8.7 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.35–7.30 (m, 2 H), 7.28–7.24 (m, 1 H), 4.52 (d, J = 25.1 Hz, 1 H), 4.06–3.75 (m, 4 H), 1.14 (t, J = 7.1 Hz, 3 H), 1.09 (t, J = 7.0 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 147.0, 144.6, 135.4, 130.3, 129.4, 128.9, 127.8, 123.7, 63.2 (d, J = 6.7 Hz), 62.7 (d, J = 6.7 Hz), 51.0 (d, J = 139.1 Hz), 16.2.

^{31}P NMR (162 MHz, CDCl_3): δ = 23.4.

Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_5\text{P}$: C, 58.45; H, 5.77; N, 4.01. Found: C, 58.28; H, 5.69; N, 4.09.

NMR spectral data for this compound were consistent with those in the literature.¹⁷

Diethyl[4-(Methoxycarbonyl)phenyl](phenyl)methylphosphonate (6c)

Prepared according to general procedure **B** from methyl 4-iodobenzoate and diethyl 1-diazo-phenylmethylphosphonate.

Yield: 97 mg (54%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.97 (d, J = 8.1 Hz, 2 H), 7.60 (d, J = 7.7 Hz, 2 H), 7.51 (d, J = 7.3 Hz, 2 H), 7.35–7.27 (m, 2 H), 7.27–7.21 (m, 1 H), 4.48 (d, J = 25.0 Hz, 1 H), 4.03–3.92 (m, 2 H), 3.88 (s, 3 H), 3.89–3.79 (m, 2 H), 1.10 (q, J = 6.7 Hz, 6 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.8, 142.2, 136.0, 129.8, 129.5, 129.4, 128.9, 128.7, 127.4, 62.9 (d, J = 6.7 Hz), 62.7 (d, J = 6.7 Hz), 52.1, 51.3 (d, J = 138.2 Hz), 16.2.

^{31}P NMR (162 MHz, CDCl_3): δ = 24.2.

HRMS (ESI): m/z [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5\text{P}$: 363.1361; found: 363.1361.

Diethyl (4-Cyanophenyl)(phenyl)methylphosphonate (6d)

Prepared according to general procedure **B** from 4-iodobenzonitrile and diethyl 1-diazo-phenylmethylphosphonate.

Yield: 86 mg (63%); colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.65 (d, J = 8.3 Hz, 2 H), 7.60 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.2 Hz, 2 H), 7.37–7.30 (m, 2 H), 7.30–7.24 (m, 1 H), 4.48 (d, J = 25.1 Hz, 1 H), 4.06–3.76 (m, 4 H), 1.14 (t, J = 7.0 Hz, 3 H), 1.09 (t, J = 7.0 Hz, 3 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 142.4, 135.4, 132.2, 130.1, 129.4, 128.8, 127.6, 118.6, 110.9, 63.1 (d, J = 6.6 Hz), 62.6 (d, J = 6.6 Hz), 51.2 (d, J = 138.9 Hz), 16.1.

^{31}P NMR (162 MHz, CDCl_3): δ = 23.6.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{21}NO_3P$: 330.1259; found: 330.1260.

Diethyl (4-Acetylphenyl)(phenyl)methylphosphonate (6e)

Prepared according to general procedure **B** from 4-iodoacetophenone and diethyl 1-diazo-phenylmethylphosphonate.

Yield: 100 mg (71%); colorless oil.

1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.2 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H), 7.51 (d, J = 8.2 Hz, 2 H), 7.35–7.30 (m, 2 H), 7.28–7.23 (m, 1 H), 4.49 (d, J = 25.0 Hz, 1 H), 4.03–3.93 (m, 2 H), 3.92–3.77 (m, 2 H), 2.57 (s, 3 H), 1.13 (t, J = 7.1 Hz, 3 H), 1.10 (t, J = 7.1 Hz, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 197.6, 142.3, 135.8, 129.6, 129.4, 129.3, 128.7, 128.5, 127.4, 62.9 (d, J = 6.6 Hz), 62.6 (d, J = 6.6 Hz), 51.2 (d, J = 138.4 Hz), 26.5, 16.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.2.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{24}O_4P$: 347.1412; found: 347.1414.

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Supporting Information

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