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Experimental and Theoretical Studies on Nickel-Zinc-Catalyzed Cross-Coupling of *gem*-Dibromoalkenes with P(O)—H Compounds

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Table of Contents

General:

All reactions were carried out under argon atmosphere. All the metal reagents and P(O)H compounds were purchased and used without further purification. The *gem*-dibromoalkenes were prepared from the aldehydes, triphenylphosphine and carbon tetrabromide in CH_2Cl_2. The dry K_3PO_4 was made from $K_3PO_4 \cdot 3H_2O$ by heating under vacuum. The solvent was freshly distilled. All new compounds were further characterized by HRMS. ^{31}P, ^{1}H and ^{13}C NMR spectra were measured on Bruker 400M spectrometers or Bruker 500M spectrometers. ^{1}H NMR and ^{13}C NMR were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm) and 85% H_3PO_4 as external standard for ^{31}P NMR. All coupling constants (J values) were reported in Hertz (Hz). HRMS spectra were recorded on a Bruker En Apex ultra 7.0 FT-MS apparatus. The CAS number of the known compound was listed.

Experimental section:

General procedure for the preparation of *gem*-dibromoalkenes (1a-1f).

To an ice cooled stirred solution of aldehyde (1.0 mmol) and carbon tetrabromide (1.5 mmol) in anhydrous CH2Cl2 (20 mL) was added triphenylphosphine (4.0 mmol) by several portions. The reaction was monitored by TLC. After the reaction was complete, the mixture was diluted with hexane (100 mL) and purified directly by column chromatography on silica gel. If it is not specified, hexane was used as an eluent for the column chromatography.

General procedure for the preparation of alkenyl-phosphorus compounds (3a-3n).

An oven-dried Schlenk tube containing $NiCl_2$ (0.02 mmol), Zn powder (0.4 mmol), 2,2'-bipyridine (0.04 mmol), P(O)H (0.44 mmol), *gem*-dibromoalkenes (0.2 mmol) and K_3PO_4 (1.0 mmol) was evacuated and purged with argon three times. Dry DMF (2.0 mL) was added at room temperature, and the resulting mixture was stirred at room temperature for 30 minutes. Then the mixture was heated at 80 ^{o}C for 20 hours. The mixture was cooled to room temperature and then transferred to a round-bottom flask. Silica gel (3.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column and purified by flash chromatography to yield the desired product.

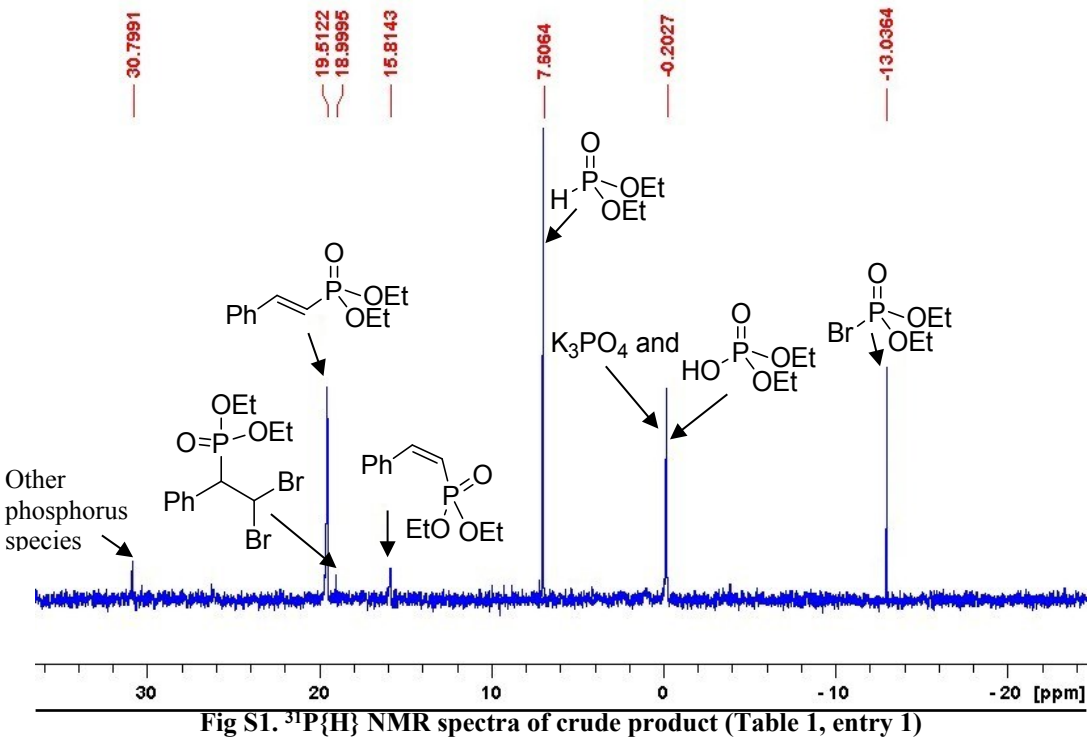

Fig S1. $^{31}P\{H\}$ NMR spectra of crude product (Table 1, entry 1)

Inspired by one of the referees, we tried to identify how Ni(II) is reduced in the absence of Zn powder by means of $^{31}P\{H\}$ NMR. 2,2-dibromovinyl benzene (**1a**, 0.2 mmol) was treated with diethyl phosphonate (**2a**, 0.44 mmol) in DMF at 80 °C under catalysis of $NiCl_2$ (0.02 mmol), bpy (**L3**, 0.04 mmol) and K_3PO_4 (1.0 mmol) system for 20 hours. The corresponding species and signals are as above.

Herein, we proposed a possible reduction pathway: The reaction of tetracoordinated $R_2P(O)H$ with a base generates a three coordinated R_2POH. Both of them bear phosphorus atom in the +3 oxidation state. Ni(II) might be reduced by these P(III) species in the reaction mixture (A. Kraszewski, J. Stawinski, *Pure Appl. Chem.* 2007, 79, 2217), forming P(V) species such as $XP(O)(OEt)_2$ (X = Cl, OH). However, it is difficult to differentiate K_3PO_4 and $HOP(O)(OEt)_2$ because they have almost same chemical shift (approximately 0.0 ppm) ((1) Kundu, Soumen; *Catalysis Science & Technology* 2012, 2, 1165-1172 (2) Seo, Donghwan; *Advanced Functional Materials* 2010, 20, 1397-1403 (3) Kachkovskyi, Georgiy O.; *Phosphorus, Sulfur and Silicon and the Related Elements* 2010, 185, 2441-2448)

Spectral Data

1-(*tert*-butyl)-4-(4,4-dibromo-2-methylbut-3-en-1-yl)benzene. (1d, New compound)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.00 (m, 4H, $C^{Ar}H$), 6.33-6.23 (m, 1H, C*H*), 2.82-2.70 (m, 2H, CH_2), 2.60-2.50 (m, 1H, C*H*(CH_3)(CH_2)(C^{alkene}H)), 1.37-1.33 (s, 9H, CH_3) ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1 (C^{Ar}), 143.6 (C^{alkene}H), 136.0 (C^{Ar}), 128.8 (C^{Ar}), 125.2 (C^{Ar}), 87.9(*C*Br_2), 41.3 (*C*H_2), 39.8 (*C*(CH_3)$_3$), 34.4 (*C*H(CH_3)(CH_2)(C^{alkene}H)), 31.4 ((*C*H_3)$_3$), 18.4 (*C*H_3). Anal. calcd for $C_{15}H_{20}Br_2$: C, 50.03; H, 5.60. Found: C, 50.07; H, 5.55.

(*E*)-diethyl styrylphosphonate. (3a, CAS Number: 20408-33-7)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.35 (m, 6H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.25 (t app., J = 17.5 Hz, 1H, $PC^{alkene}H$), 4.20-3.98 (m, 4H, OCH_2), 1.35 (t, J = 6.9 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7 (d, J = 6.4 Hz, $C^{Ar}C^{alkene}$), 135.0 (d, J = 23.8 Hz, $C^{Ar}C^{alkene}$), 130.2 (C^{Ar}), 128.8 (C^{Ar}), 127.7 (C^{Ar}), 114.1 (d, J = 190.5 Hz, PC^{alkene}H), 61.8 (d, 5.4 Hz, O*C*H_2), 16.4 (d, J = 6.4 Hz, *C*H_3). ^{31}P NMR (203 MHz, $CDCl_3$), δ 19.4. ESI-MS: $[M+H]^+$ *m/z* calcd for $C_{12}H_{17}O_3PNa^+$: 263.1, found: 263.1.

(*E*)-diisopropyl styrylphosphonate (3b, CAS Number: 78463-00-0)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.35 (m, 6H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.26 (t app., J = 17.5 Hz, 1H, $PC^{alkene}H$), 4.75-4.60 (m, 2H, OC*H*(CH_3)$_2$), 1.38 and 1.32 (d, J = 6.2 Hz, d, J = 6.2 Hz, 12H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (d, J = 6.5 Hz, $C^{Ar}C^{alkene}$), 135.2 (d, J = 23.1 Hz, $C^{Ar}C^{alkene}$), 130.0 (C^{Ar}), 128.8 (C^{Ar}), 127.6 (C^{Ar}), 115.7 (d, J = 190.5 Hz, PC^{alkene}H), 70.5 (d, J = 5.6 Hz, O*C*H(CH_3)$_2$), 24.1 (d, J = 4.1 Hz, *C*H_3), 24.0 (d, J = 4.6 Hz, *C*H_3).^{31}P NMR (203 MHz, $CDCl_3$) δ 17.2. ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{14}H_{21}O_3PNa^+$: 291.1, found: 291.1.

(*E*)-dipropyl styrylphosphonate. (3c, CAS Number: 146896-98-2)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.33 (m, 6H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 7.25 (t app., J = 17.5 Hz, 1H, $PC^{alkene}H$), 4.06-3.85 (m, 4H, OCH_2CH_2CH_3), 1.75-1.65 (m, 4H, OCH_2CH_2CH_3), 0.93 (t, J = 7.4 Hz, 6H, OCH_2CH_2CH_3) ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6 (d, J = 6.7 Hz, $C^{Ar}C^{alkene}$), 134.9 (d, J = 23.6 Hz, $C^{Ar}C^{alkene}$), 130.2 (C^{Ar}), 128.8 (C^{Ar}), 127.7 (C^{Ar}), 113.9 (d, J = 190.7 Hz, PC^{alkene}H), 67.4 (d, J = 5.8 Hz, O*C*H_2CH_2CH_3), 23.8 (d, J = 6.6 Hz, OCH_2*C*H_2CH_3), 10.0 (OCH_2CH_2*C*H_3), ^{31}P NMR (203 MHz, $CDCl_3$) δ 19.3. ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{14}H_{21}O_3PNa^+$: 291.1, found: 291.1.

(*E*)-dibenzyl styrylphosphonate. (3d, CAS Number: 848420-33-7)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.30 (m, 16H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.23 (dd, J = 17.6 Hz, 18.2 Hz, 1H, $PC^{alkene}H$), 5.08 (d, J = 8.2 Hz, 4H, OCH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0 (d, J = 6.3 Hz, $C^{Ar}C^{alkene}$), 136.5 (d, J = 19.0 Hz, $C^{Ar}C^{alkene}$), 130.3 (C^{Ar}), 128.8 (C^{Ar}), 128.6 (C^{Ar}), 128.4 (C^{Ar}), 128.0 (C^{Ar}), 127.9 (C^{Ar}), 127.7 (C^{Ar}), 113.6 (d, J = 191.5 Hz, PC^{alkene}H), 67.4 (d, J = 5.4 Hz, O*C*H_2). ^{31}P NMR (203 MHz, $CDCl_3$) δ 20.5. ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{22}H_{21}O_3PNa^+$: 364.1, found: 364.1.

(*E*)-benzyl phenyl(styryl)phosphinate. (3e, New compound)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.80 (m, 2H, $C^{Ar}H$), 7.65-7.50 (m, 2H, $C^{Ar}H$), 7.50-7.43 (m, 4H, $C^{Ar}H$), 7.40-7.28 (m, 8H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.49 (dd, J = 17.4 Hz, 20.6 Hz, 1H, $PC^{alkene}H$), 5.17-4.97 (m, 2H, OCH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1 (d, J = 5.6 Hz, $C^{Ar}C^{alkene}$), 136.5 (d, J = 7.1 Hz, $C^{Ar}C^{alkene}$), 135.0 (d, J = 20.0 Hz, $C^{Ar}C^{alkene}$), 132.3 (d, J = 2.4 Hz, C^{Ar}), 131.5 (d, J = 100.1 Hz, PC^{Ar}), 130.2 (C^{Ar}), 128.8 (C^{Ar}), 128.7 (C^{Ar}), 128.6 (C^{Ar}), 128.6 (C^{Ar}), 128.3 (C^{Ar}), 128.0 (C^{Ar}), 127.8 (C^{Ar}), 117.8 (d, J = 137.7 Hz, PC^{alkene}H), 66.2 (d, J = 5.4 Hz, O*C*H_2) . ^{31}P NMR (203 MHz, $CDCl_3$) δ 32.2. HR-ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{21}H_{20}O_2P^+$: 335.11954, found: 335.11851.

(*E*)-diphenyl(styryl)phosphine oxide. (3f, CAS Number: 3582-82-9)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.70 (m, 4H, $C^{Ar}H$), 7.56-7.44 (m, 9H, $C^{Ar}H$), 7.40-7.32 (m, 3H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.84 (dd, J = 17.4 Hz, 22.3 Hz, 1H, $PC^{alkene}H$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5 (d, J = 3.6 Hz, C^{Ar}), 135.2 (d, J = 16.3 Hz, $C^{Ar}C^{alkene}$), 133.1 (d, J = 105.1 Hz, PC^{Ar}), 131.8 (d, J = 2.8 Hz, C^{Ar}), 131.4 (d, J = 9.9 Hz, C^{Ar}), 130.1, 128.8 (d, J = 23.7 Hz, $C^{Ar}C^{alkene}$), 128.6 (C^{Ar}), 127.8 (C^{Ar}), 119.4 (d, J = 102.8 Hz, PC^{alkene}H). ^{31}P NMR ($CDCl_3$, 203 MHz) δ 24.3. ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{20}H_{17}OPNa^+$: 327.1, found: 327.1.

(*E*)-dipropyl 4-(trifluoromethyl)styrylphosphonate. (3g, New Compound)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.50 (m, 5H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.35 (t app., J = 17.1 Hz, 1H, $PC^{alkene}H$), 4.07-3.97 (m, 4H, OCH_2CH_2CH_3), 1.78-1.69 (m, 4H, OCH_2CH_2CH_3), 0.96 (t, J = 7.4 Hz, 6H, OCH_2CH_2CH_3) ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6 (d, J = 6.5 Hz, C^{Ar}), 138.3 (d, J = 23.3 Hz, $C^{Ar}C^{alkene}$), 131.8 (d, J = 32.5 Hz, C^{Ar}), 127.8 (C^{Ar}), 125.8 (q, J = 3.7 Hz, CF_3C^{Ar}), 123.7 (q, J = 271.2 Hz, CF_3), 117.4 (d, J = 190.1 Hz, PC^{alkene}H), 67.5 (d, J = 5.6 Hz, O*C*H_2CH_2CH_3), 23.8 (d, J = 6.4 Hz, OCH_2*C*H_2CH_3), 10.0 (*C*H_3), ^{31}P NMR (203 MHz, $CDCl_3$) δ 18.1. HR-ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{15}H_{21}O_3F_3P^+$: 337.11749, found: 337.11697.

(*E*)-benzyl phenyl(4-(trifluoromethyl)styryl)phosphinate. **(3h, New compound)**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.80 (m, 2H, $C^{Ar}H$), 7.65-7.45 (m, 8H, $C^{Ar}H$), 7.40-7.30 (m, 5H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.59 (dd, J = 17.5 Hz, 19.9 Hz, 1H, $PC^{alkene}H$), 5.18-4.95 (m, 2H, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (d, J = 5.5 Hz, C^{Ar}), 138.2 (d, J = 22.3 Hz, $C^{Ar}C^{alkene}$), 136.3 (d, J = 6.9 Hz, C^{Ar}), 132.6 (d, J = 105.3 Hz, PC^{Ar}), 131.5 (d, J = 12.8 Hz, C^{Ar}), 129.8 (C^{Ar}), 128.8 (C^{Ar}), 128.7 (C^{Ar}), 128.6 (C^{Ar}), 128.4 (C^{Ar}), 128.3 (q, J = 250.0 Hz, *C*F_3), 127.9 (d, J = 9.9 Hz, C^{Ar}), 127.8 (C^{Ar}),

125.8 (q, J = 3.6 Hz, CF_3C^{Ar}), 121.1 (d, J = 136.1 Hz, $PC^{alkene}H$), 66.2 (d, J = 5.5 Hz, OCH_2) . ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2. HR-ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}O_2PF_3^+$: 403.10693, found: 403.10626.

(*E*)-diphenyl(4-(trifluoromethyl)styryl)phosphine oxide. (3i, CAS Number: 1469762-73-1)
^1H NMR (500 MHz, $CDCl_3$) δ 7.78-7.71 (m, 4H, $C^{Ar}H$), 7.60 (s, 4H, $C^{Ar}H$), 7.56-7.50 (m, 3H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 7.50-7.42 (m, 4H, $C^{Ar}H$), 6.95 (dd, J = 17.3 Hz, 21.9 Hz, 1H, $PC^{alkene}H$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7 (d, J = 3.6 Hz, C^{Ar}), 138.4 (d, 18.6 Hz, $C^{Ar}C^{alkene}$), 132.1 (d, J = 2.8 Hz, C^{Ar}), 131.6 (d, J = 105.3 Hz, PC^{Ar}), 131.3 (d, J = 9.9 Hz, C^{Ar}), 128.8 (C^{Ar}), 128.7 (C^{Ar}), 127.9 (C^{Ar}), 125.8 (q, J = 3.7 Hz, C^{Ar}), 123.9 (q, J = 270.9 Hz, CF_3), 122.6 (d, J = 101.4 Hz, $PC^{alkene}H$). ^{31}P NMR ($CDCl_3$, 203 MHz) δ 23.4. ESI-MS: $[M+Na]^+$ m/z calcd for $C_{21}H_{16}OPF_3Na^+$: 395.1, found: 395.1.

(*E*)-dipropyl 4-methylstyrylphosphonate. (3j, New compound)
^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.35 (m, 3H, $C^{Ar}H$), 7.20-7.15 (m, 2H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.20 (t app., J = 17.6, 1H, $PC^{alkene}H$), 4.06-3.95 (m, 4H, $OCH_2CH_2CH_3$), 2.37-2.35 (s, 3H, $C^{Ar}CH_3$), 1.75-1.68 (m, 4H, $OCH_2CH_2CH_3$), 0.96 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_3$) ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6 (d, J = 6.5 Hz, C^{Ar}), 140.5 (C^{Ar}), 129.5 (C^{Ar}), 129.0 (C^{Ar}), 127.7 (C^{Ar}), 112.6 (d, J = 191.3 Hz, $PC^{alkene}H$), 67.3 (d, J = 5.8 Hz, $OCH_2CH_2CH_3$), 23.8 (d, J = 6.5 Hz, CH_2CH_3), 21.4 ($C^{Ar}CH_3$), 10.1 (CH_2CH_3), ^{31}P NMR ($CDCl_3$, 162 MHz) δ 20.0. ESI-MS: $[M+Na]^+$ *m/z* calcd for $C_{15}H_{24}O_3P^+$: 283.14576, found: 283.14526.

(*E*)-(p-methyl)styryl diphenylphosphine oxide. (3k, CAS Number: 72095-43-3)
^1H NMR (500 MHz, $CDCl_3$) δ 7.80-7.70 (m, 4H, $C^{Ar}H$), 7.55-7.39 (m, 9H, $C^{Ar}H$), 7.20-7.16 (m, 2H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.77 (dd, J = 17.4 Hz, 22.3 Hz, 1H, $PC^{alkene}H$), 2.38-2.34 (s, 3H, $C^{Ar}CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5 (d, J = 3.8 Hz, C^{Ar}), 140.4 (C^{Ar}), 133.2 (d, J = 105.3 Hz, PC^{Ar}), 132.6, 131.8 (d, J = 2.7 Hz, C^{Ar}), 131.4 (d, J = 9.9 Hz, C^{Ar}), 129.6 (C^{Ar}), 128.6 (d, J = 11.9 Hz, C^{Ar}), 127.8 (C^{Ar}), 117.9 (d, J = 104.7 Hz, $PC^{alkene}H$), 21.4 ($C^{Ar}CH_3$). ^{31}P NMR ($CDCl_3$, 203 MHz) δ 24.6. ESI-MS: $[M+Na]^+$ m/z calcd for $C_{21}H_{19}OPNa^+$: 341.1, found: 341.1.

(*E*)-dipropyl (4-(4-(*tert*-butyl)phenyl)-3-methylbut-1-en-1-yl)phosphonate. (3l, New Compound)
^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 1H, $C^{Ar}C^{alkene}H$), 7.27-7.00 (m, 4H, $C^{Ar}H$), 5.96 (ddd, J = 23.6 Hz, 17.5 Hz and 5.7 Hz, 1H, $PC^{alkene}H$), 4.11-3.90 (m, 4H, OCH_2), 3.71-3.69 (s, 1H, CH), 2.55-2.75 (m, 2H, CH_2), 1.72-1.62 (m, 4H, CH_2CH_3), 1.32-1.29 (s, 9H, $C(CH_3)_3$), 1.20-1.15 (d, J = 7.0 Hz, 3H, CH_3), 0.98-0.89 (m, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (C^{Ar}), 149.4 (C^{Ar}), 128.2 (d, J = 146.4 Hz, $PC^{alkene}H$), 125.0 (C^{Ar}), 124.4 (C^{Ar}), 123.4 (d, J = 2.6 Hz, C^{alkene}), 67.3 (d, J = 7.8 Hz, CH_2), 34.9 (d, J = 70.3 Hz, OCH_2), 31.4 ($C(CH_3)_3$), 30.0 (d, J = 15.6 Hz, CH_2CH_3), 23.8 (d, J = 6.1 Hz, CH), 19.2 (CH_3), 10.1 ($CHCH_3$), 10.1 ($C(CH_3)_3$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.6. HR-ESI-MS: $[M+Na]^+$ m/z calcd for $C_{21}H_{36}O_3P^+$: 367.23966, found: 363.23931.

(*E*)-(2-cyclohexylviyl) diphenylphosphine oxide. (3m, CAS Number: 112863-51-1)
^1H NMR (500 MHz, $CDCl_3$) δ 7.72-7.65 (m, 4H, $C^{Ar}C^{alkene}H$), 7.54-7.40 (m, 6H, $C^{Ar}H$, $C^{Ar}C^{alkene}H$), 6.70 (ddd, J = 6.3 Hz, 17.2 Hz, 20.0 Hz, 1H, $PC^{alkene}H$), 6.15 (ddd, J = 1.3 Hz, 17.2 Hz, 24.6 Hz, 1H, $C^{cy}C^{alkene}H$), 1.85-1.63 (m, 5H, $C^{cy}H$), 1.15-1.30 (m, 6H, $C^{cy}H$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (C^{Ar}), 133.0 (C^{Ar}), 131.6 (d, J = 2.6 Hz, C^{Ar}), 131.3 (d, J = 98 Hz, PC^{Ar}), 128.5 (d, J = 11.9 Hz, C^{Ar}), 118.9 (d, J = 103.1 Hz, PC^{alkene}), 42.3 (d, J = 15.4Hz, $C^{cy}C^{alkene}$), 31.7 (C^{cy}), 25.9 (C^{cy}), 25.7 (C^{cy}). ^{31}P NMR (203 MHz, $CDCl_3$) δ 24.2. ESI-MS: $[M+Na]^+$ m/z calcd for $C_{20}H_{23}OPNa^+$: 333.1, found: 333.1.

(*E*)-(4-hydroxystyryl)diphenylphosphine oxide. (3n, New compound)
^1H NMR (400 MHz, DMSO) δ 9.94-9.90 (s, 1H, OH), 7.88-7.72 (m, 4H, $C^{Ar}H$), 7.60-7.45 (m, 8H, $C^{Ar}H$), 7.40-7.10 (m, 2H, $C^{alkene}H$), 7.00-6.70 (m, 2H, $C^{Ar}H$). ^{13}C NMR (100 MHz, DMSO) δ 159.8 (C^{Ar}), 146.4 (C^{Ar}), 135.1 (d, J = 102.7 Hz, PC^{Ar}), 132.0 (C^{Ar}), 131.1 (d, J = 9.6 Hz, $C^{Ar}C^{alkene}$), 130.3 (C^{Ar}), 129.1 (d, J = 11.6 Hz, $C^{Ar}C^{alkene}$), 116.3 (d, J = 126.8 Hz, PC^{alkene}), 116.1 (C^{Ar}), 115.8 ((C^{Ar})). ^{31}P NMR (162 MHz, DMSO) δ 21.0. HR-ESI-MS: $[M+Na]^+$ m/z calcd for $C_{20}H_{17}O_2PNa^+$: 343.08584, found: 343.08621.

NMR Spectra Copies

1d

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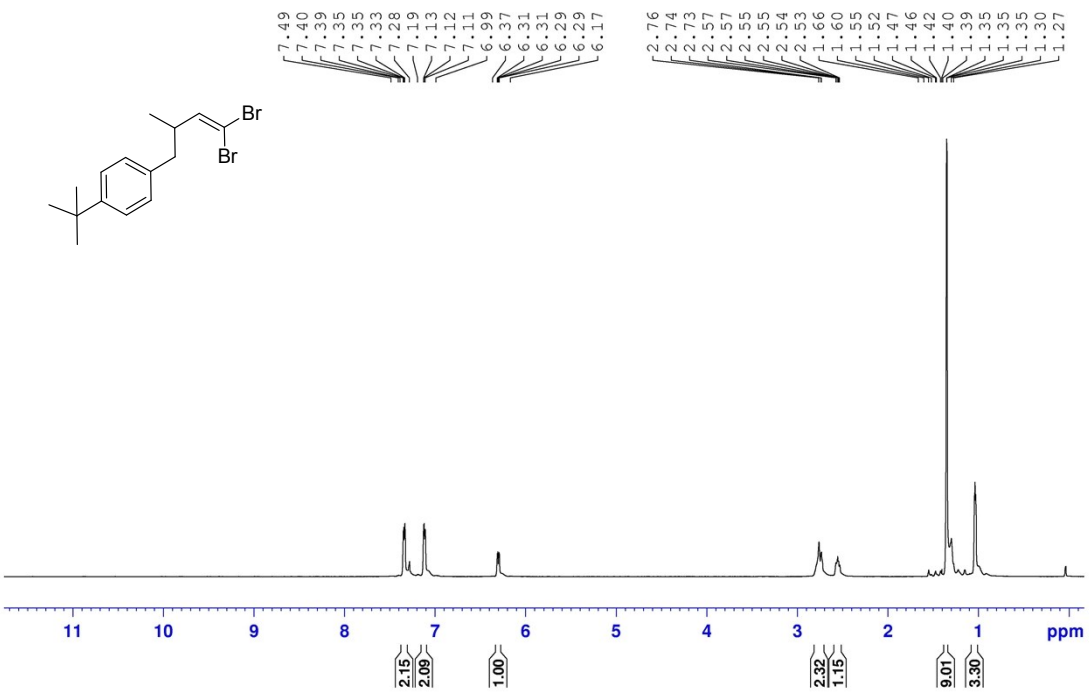

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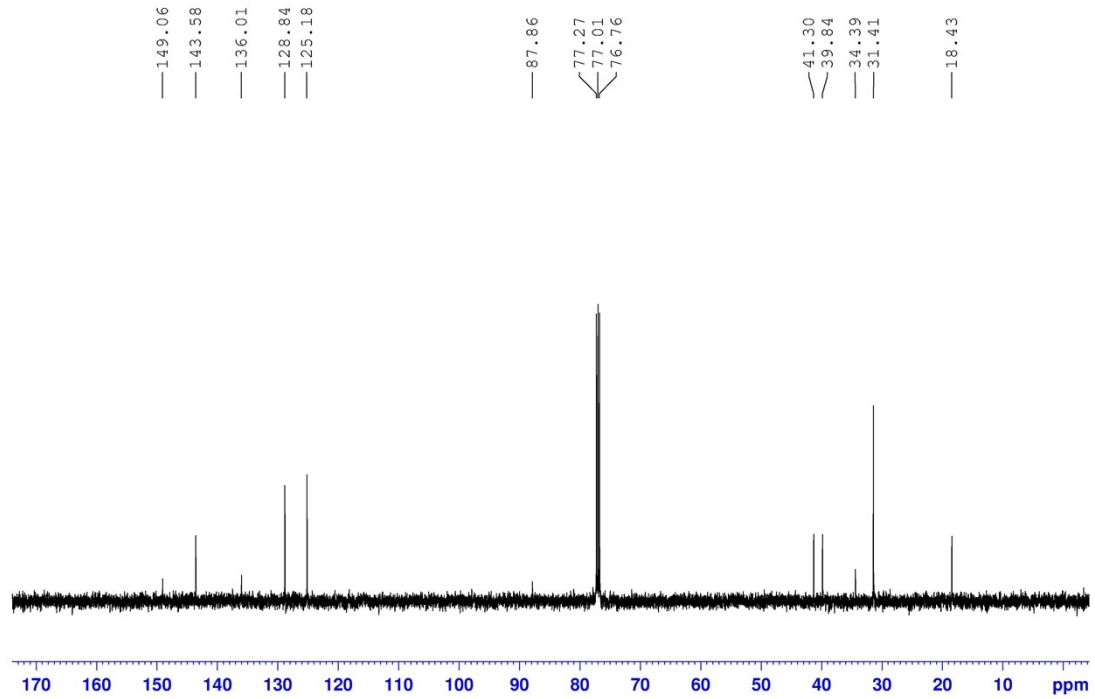

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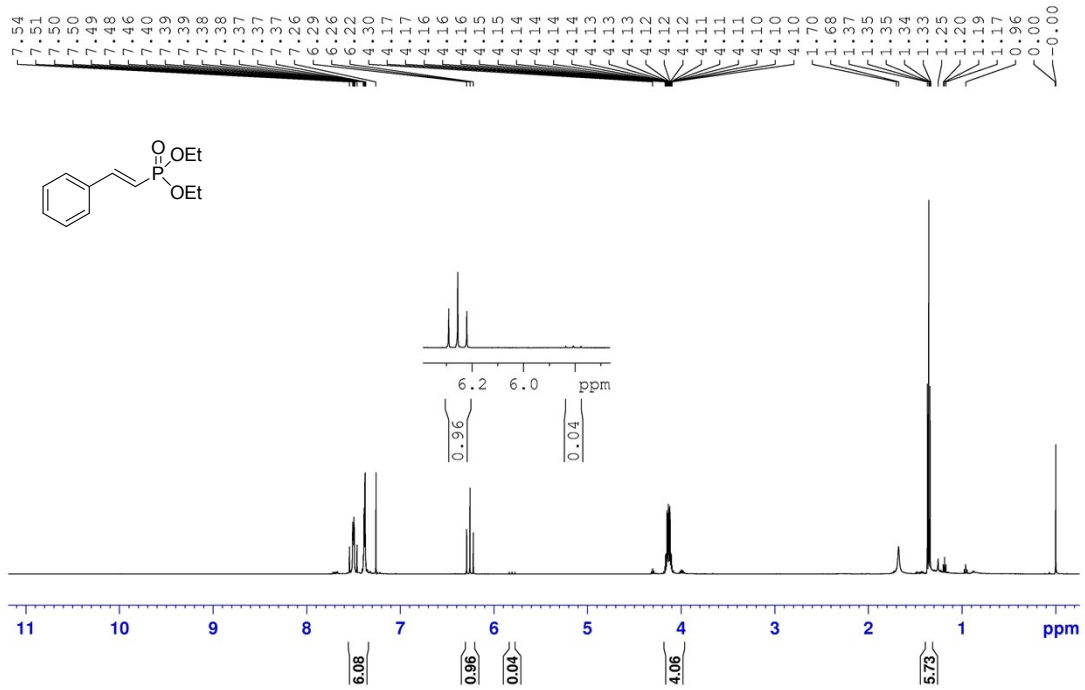

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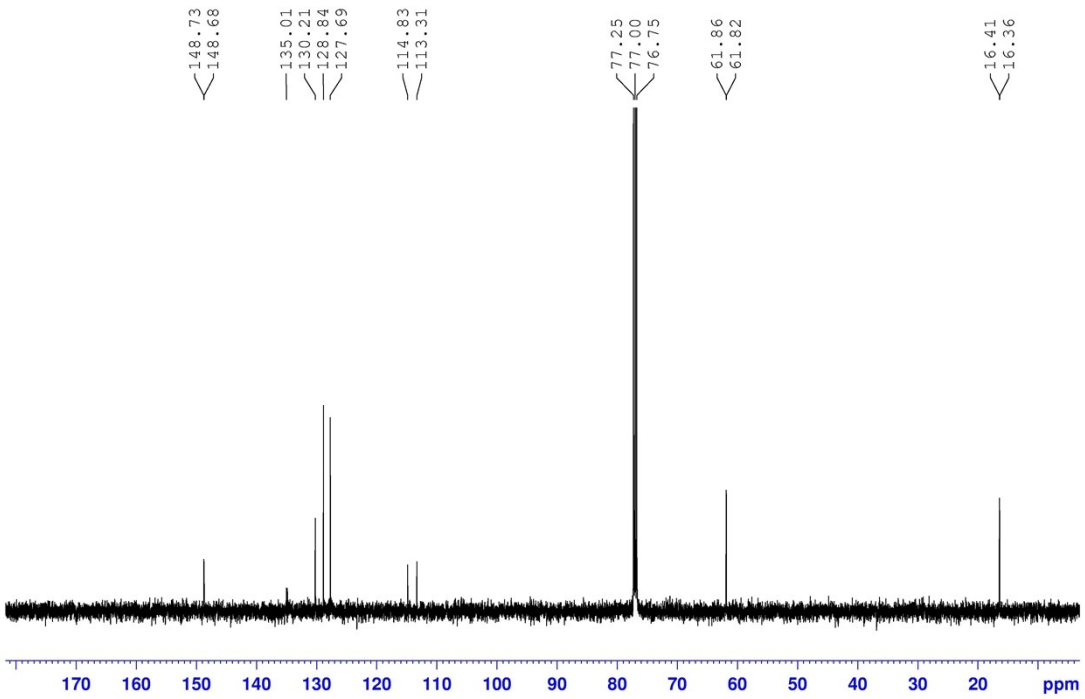

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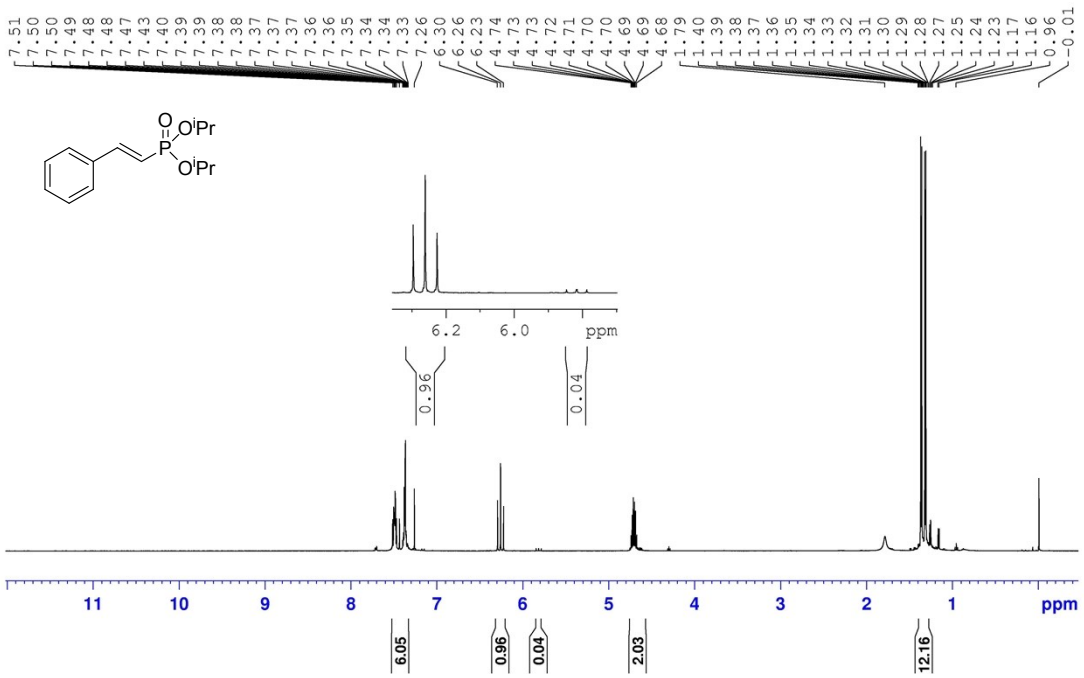

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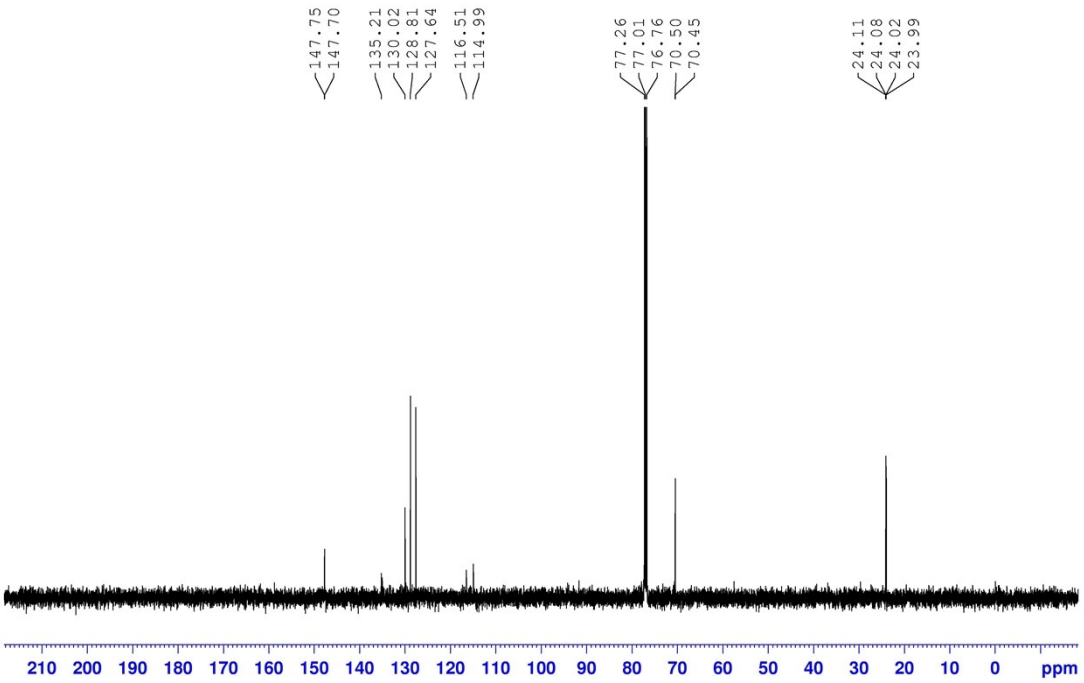

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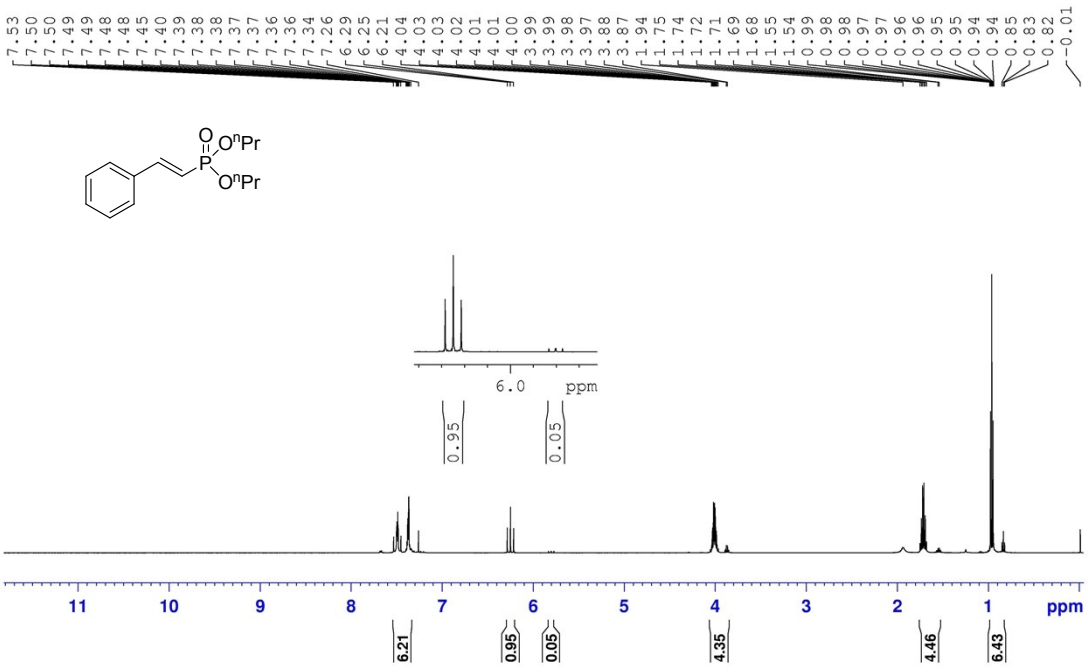

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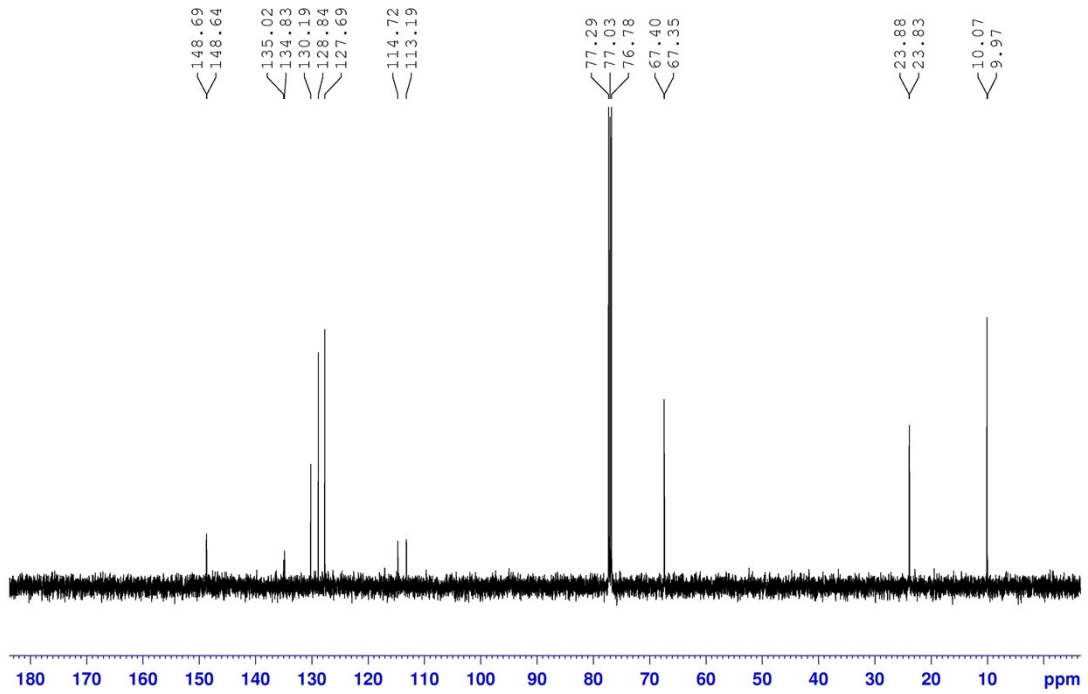

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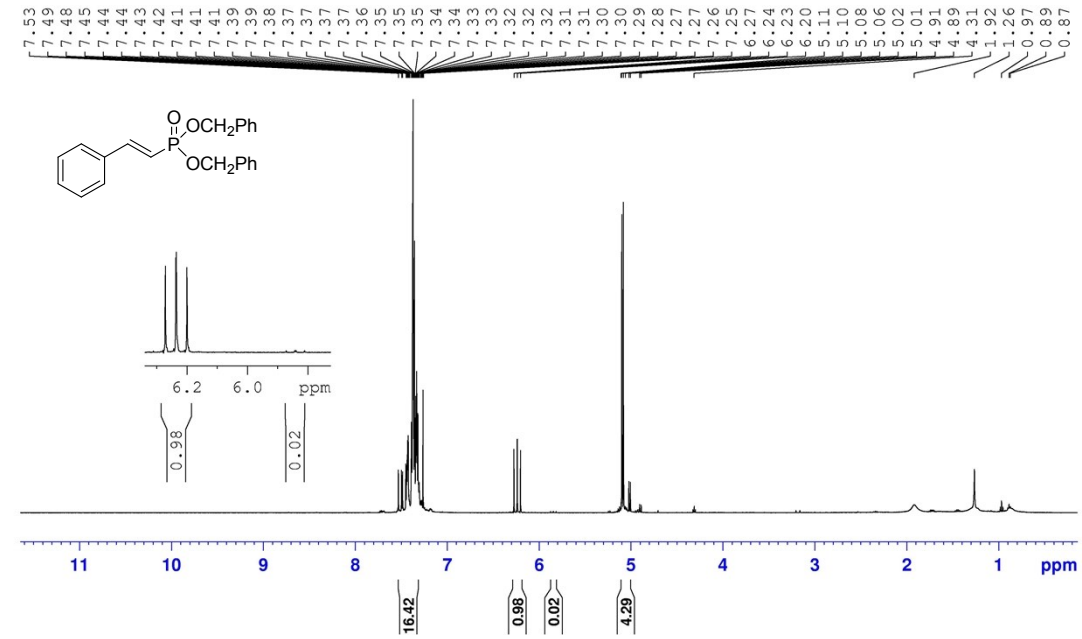

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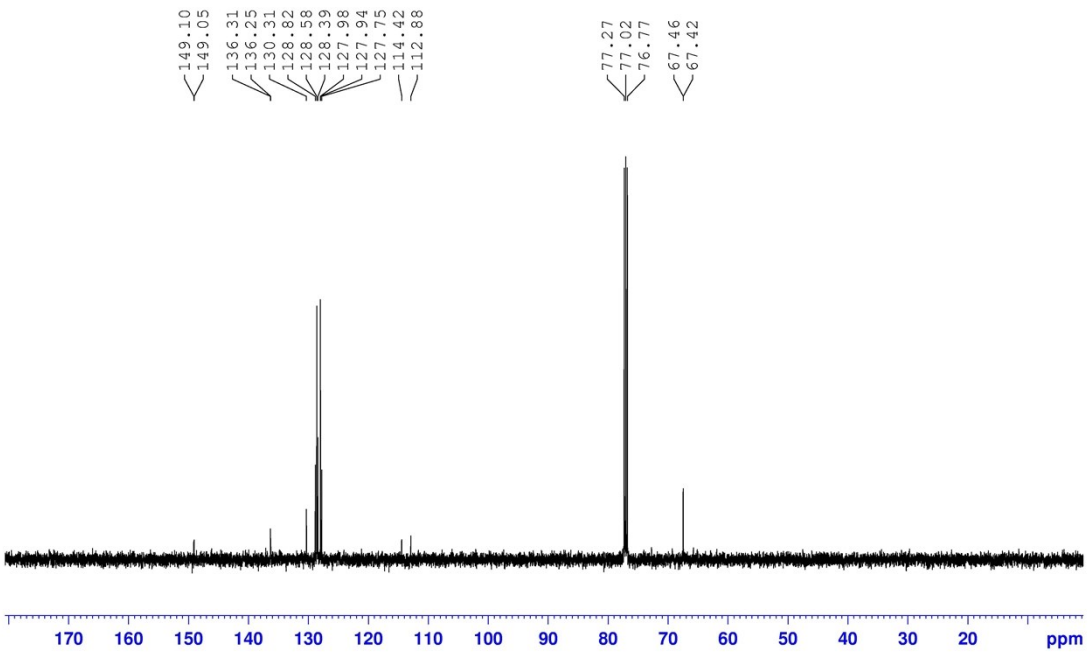

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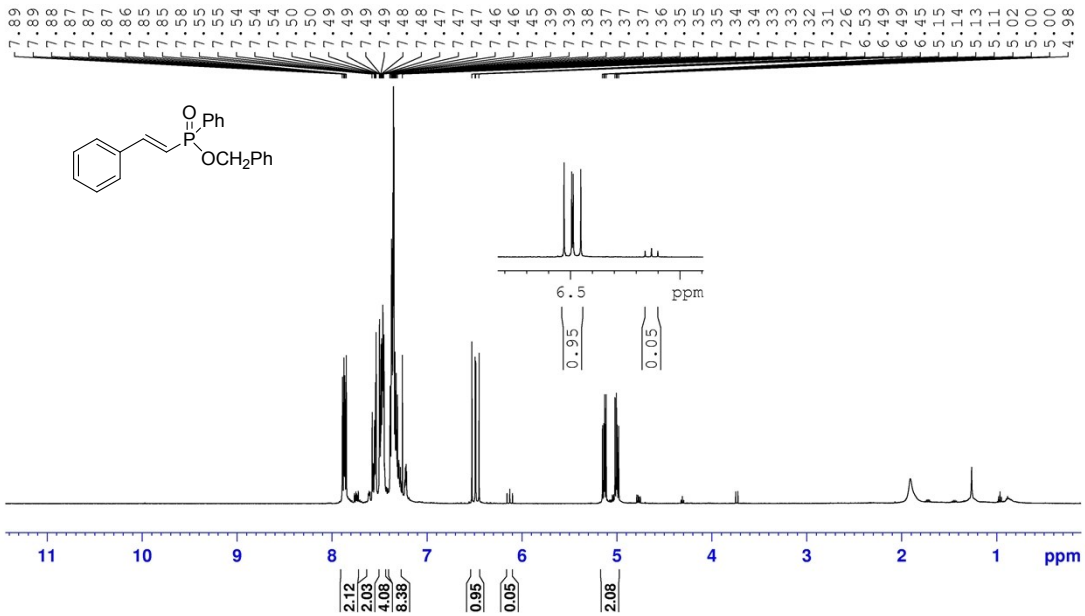

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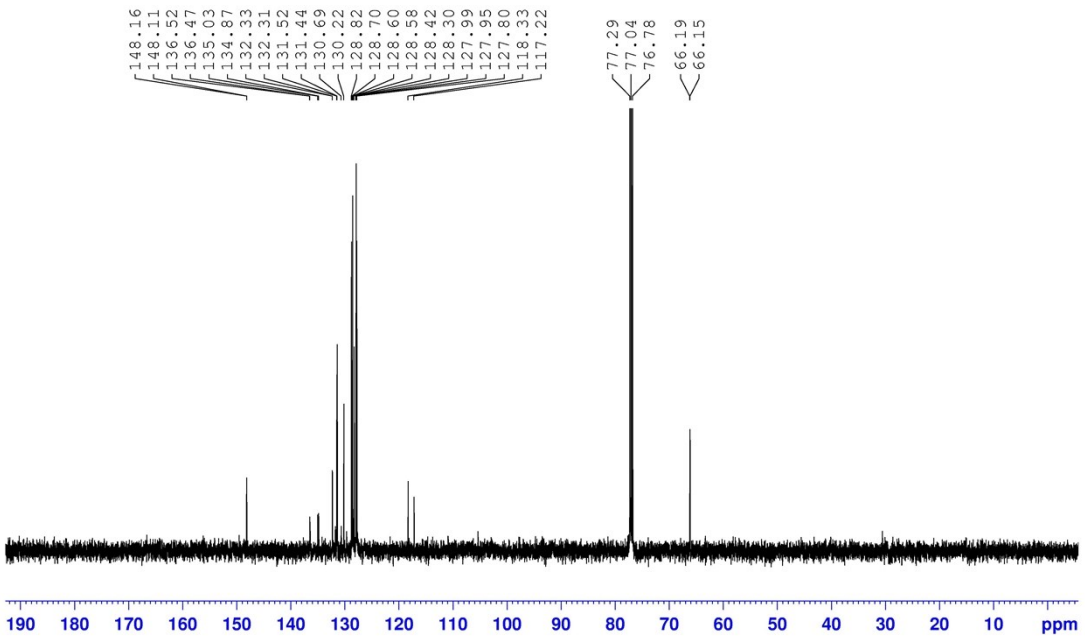

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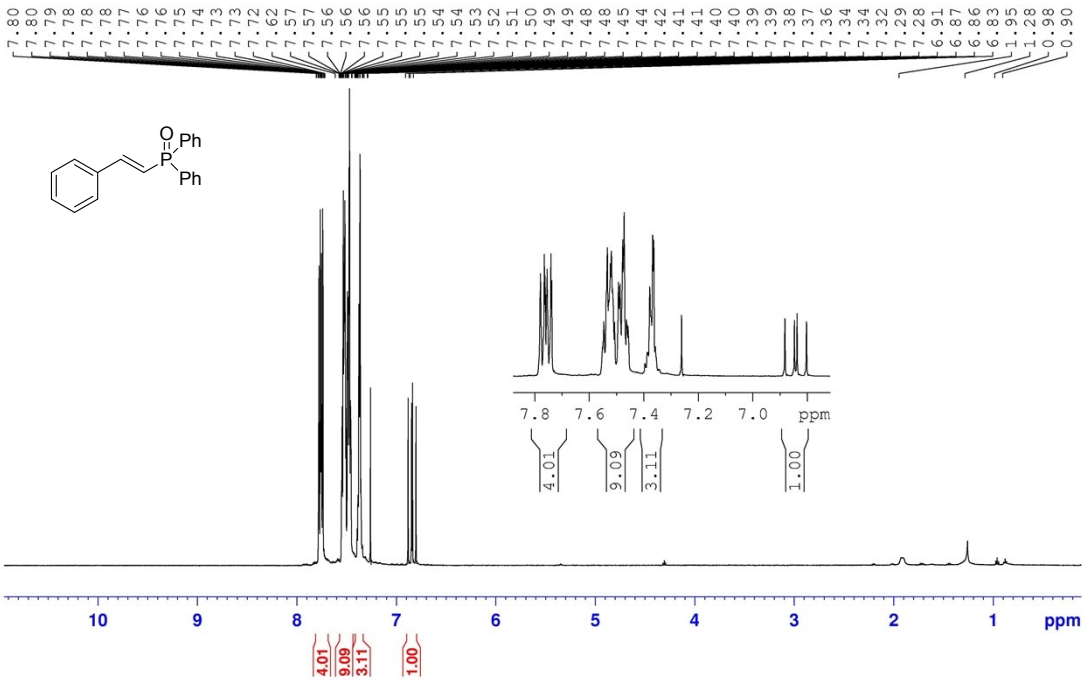

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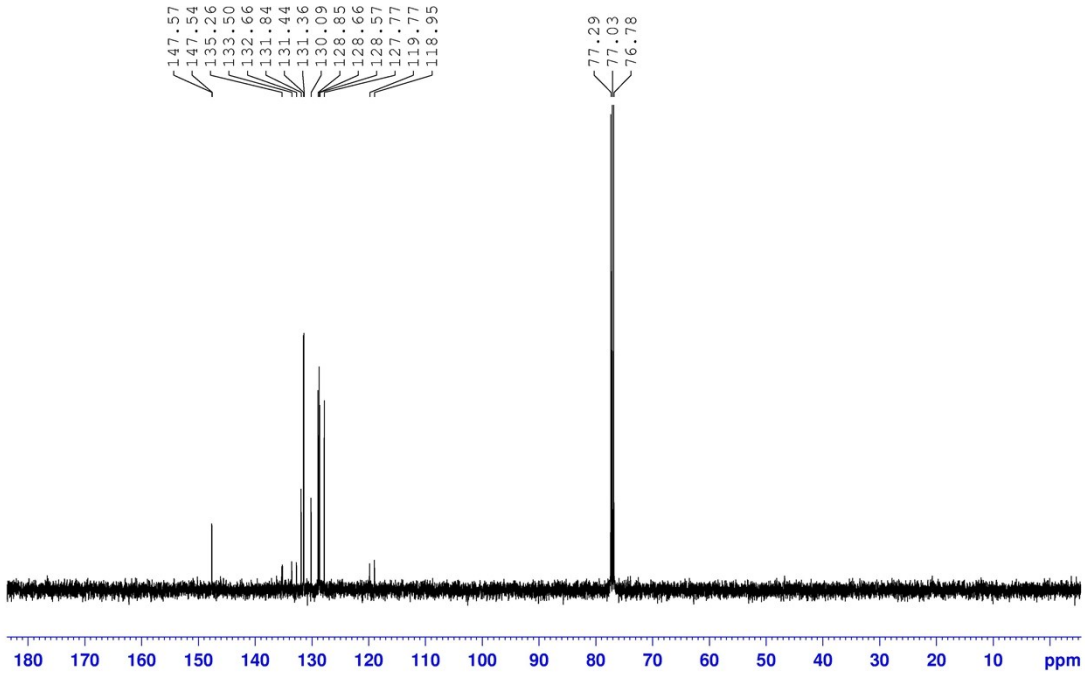

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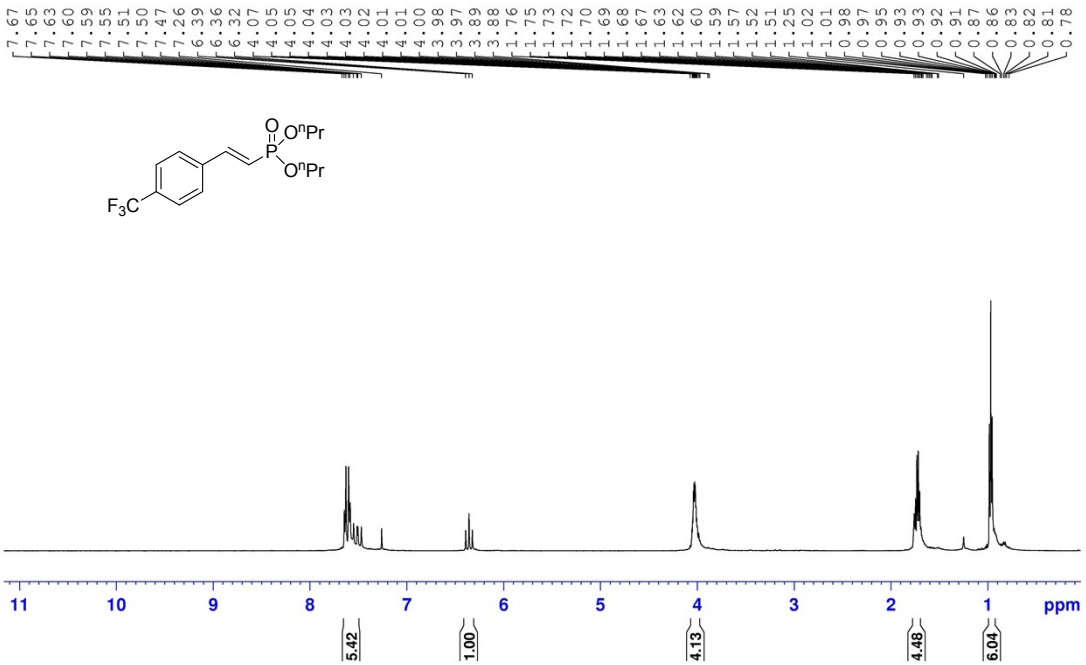
LIUL-20130905-CF3NPRP-H1



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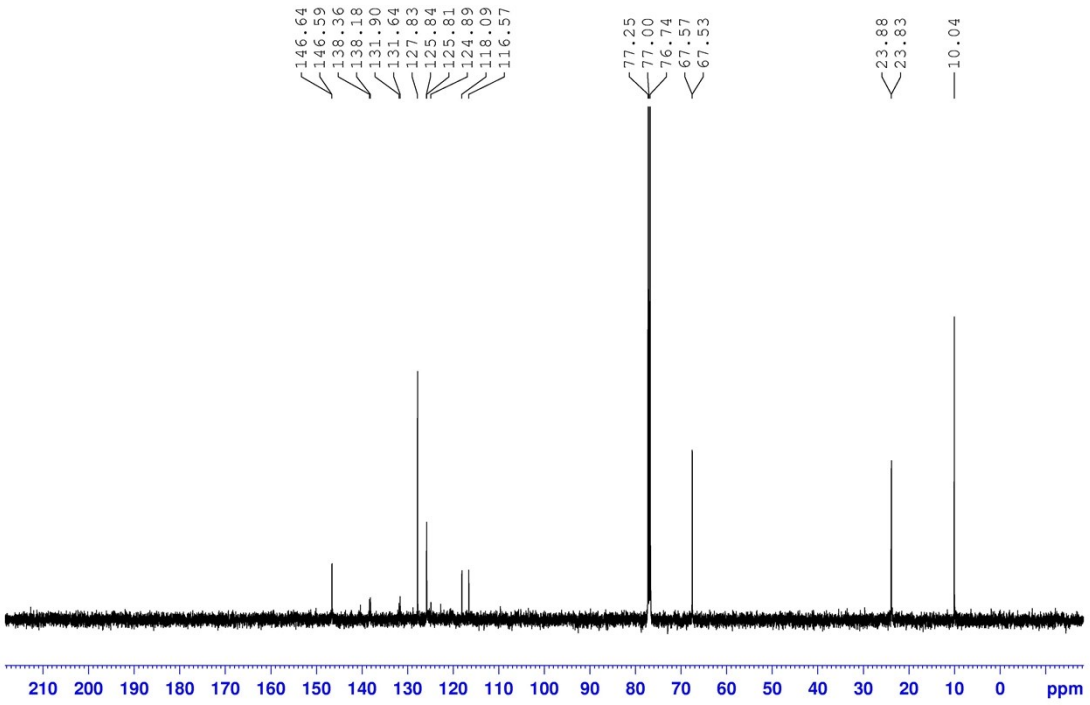

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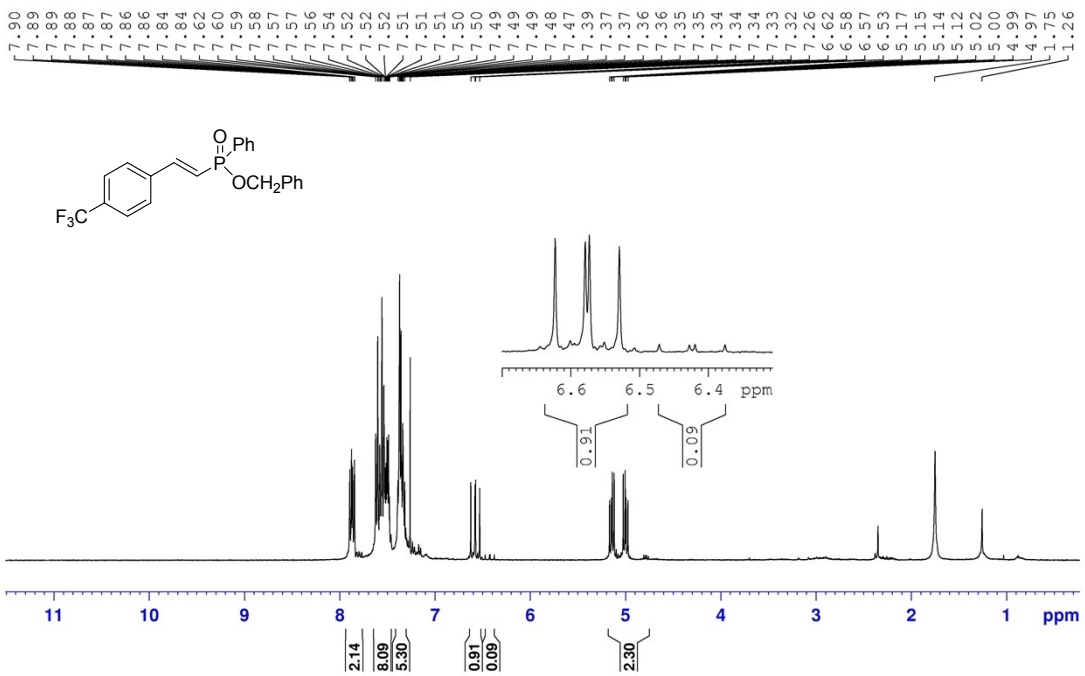

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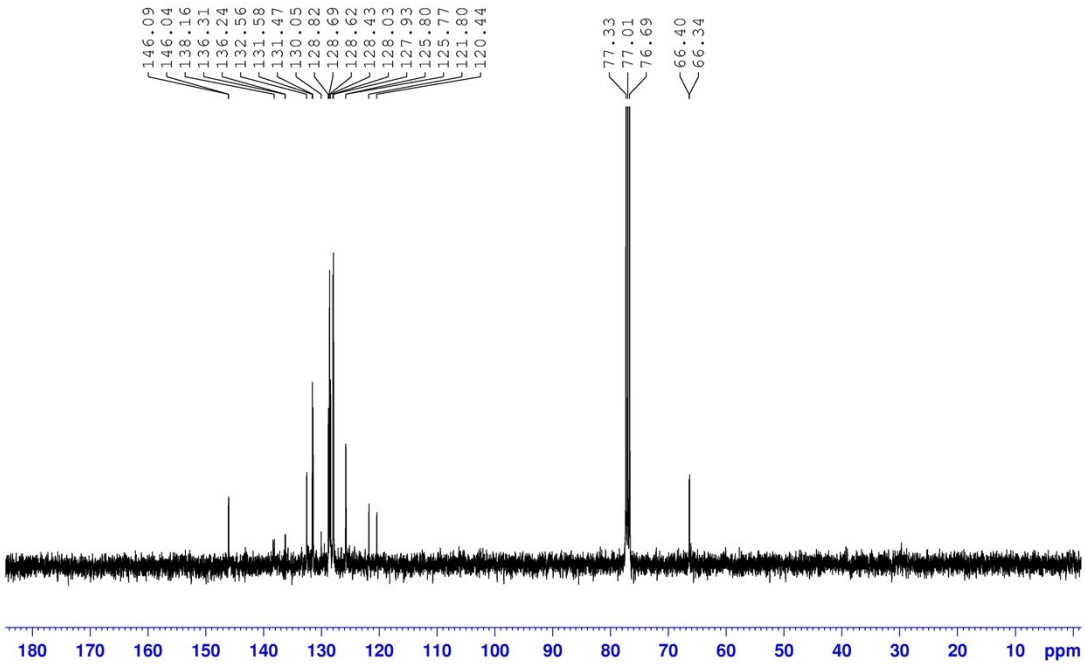

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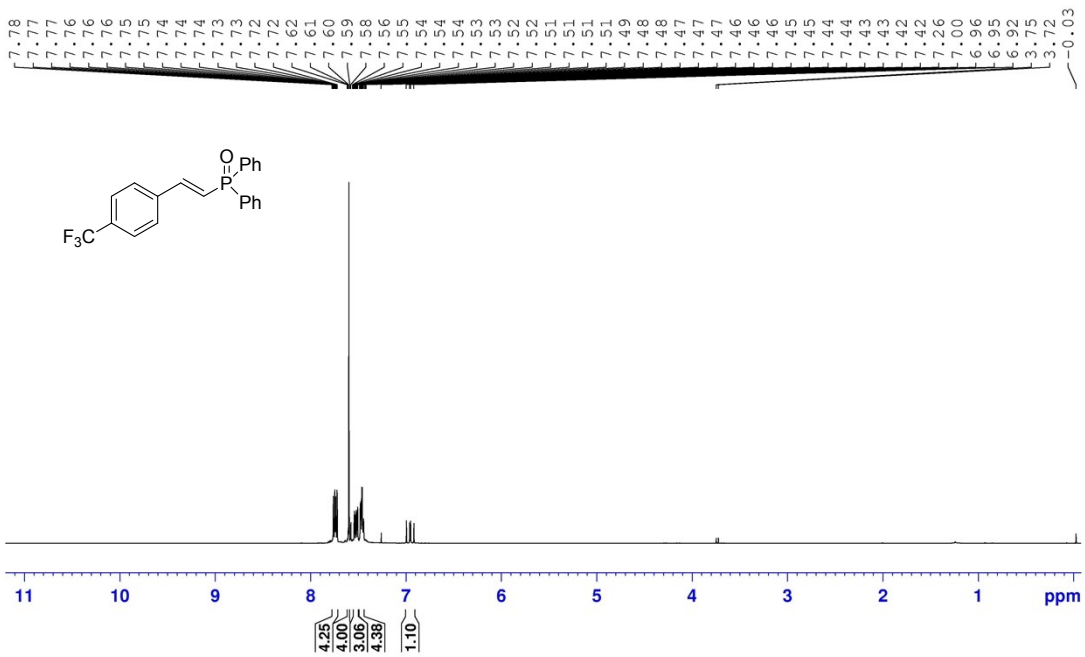

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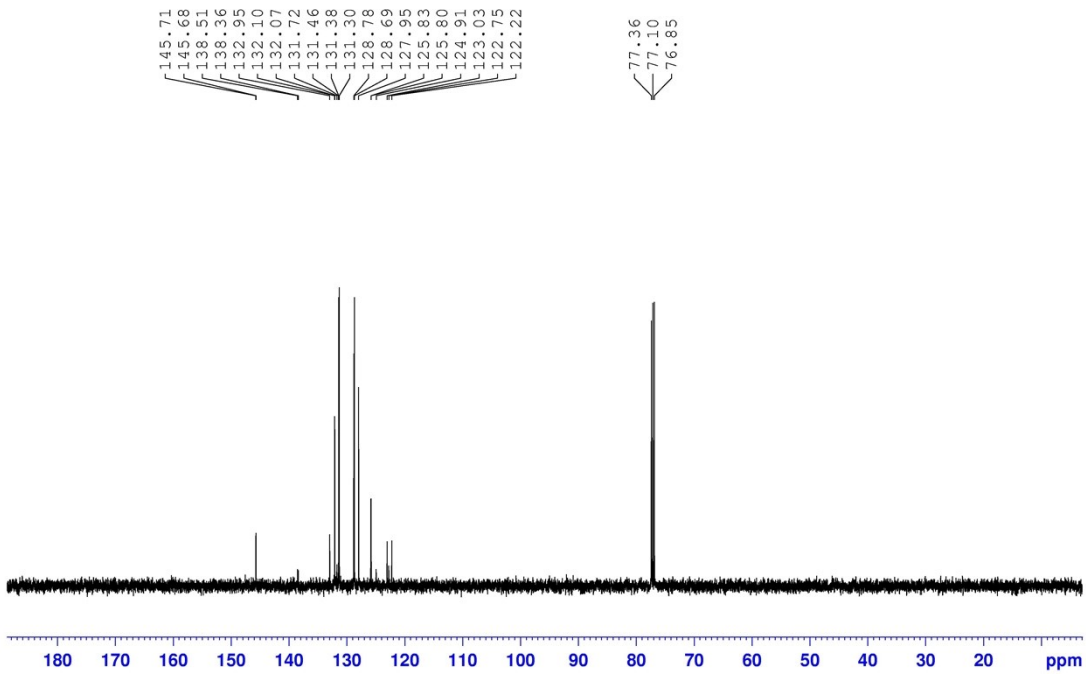

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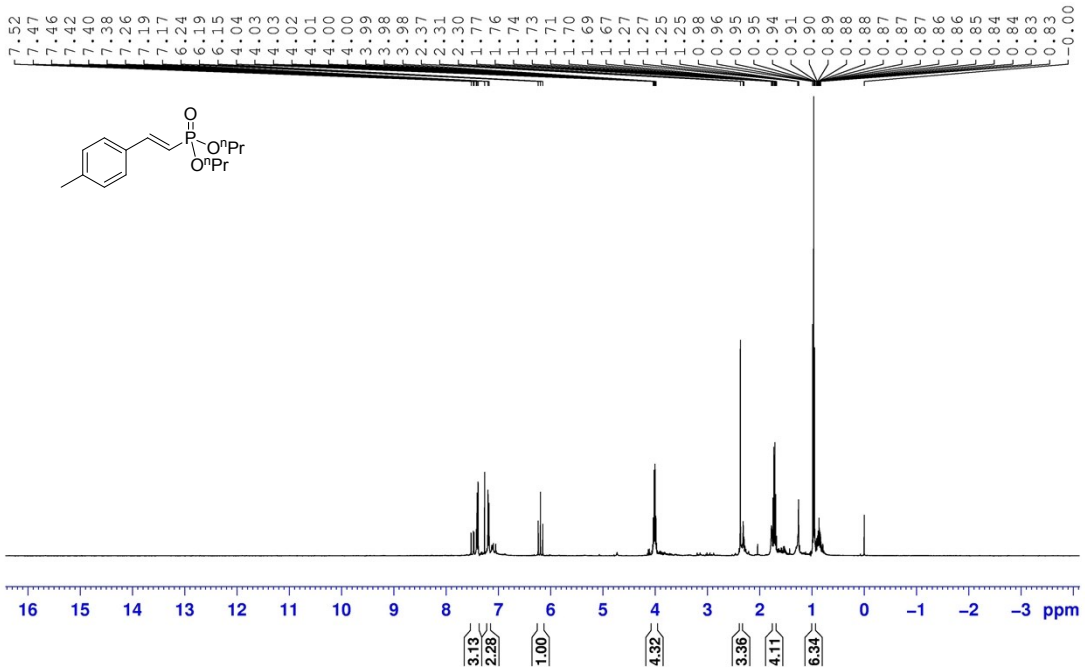

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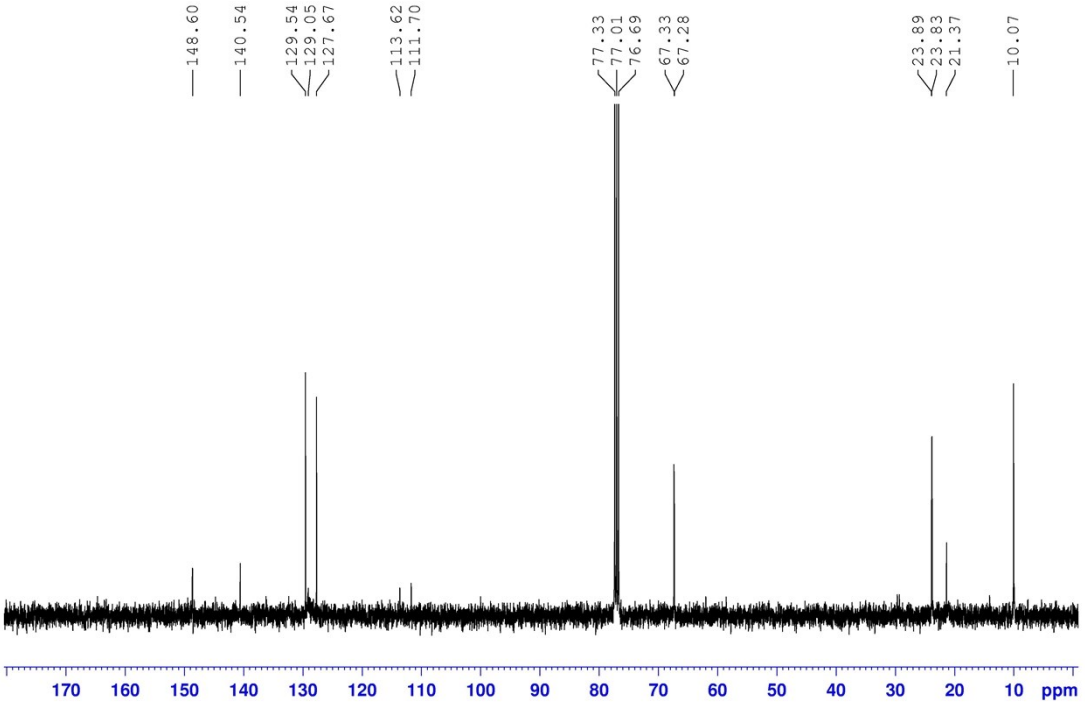

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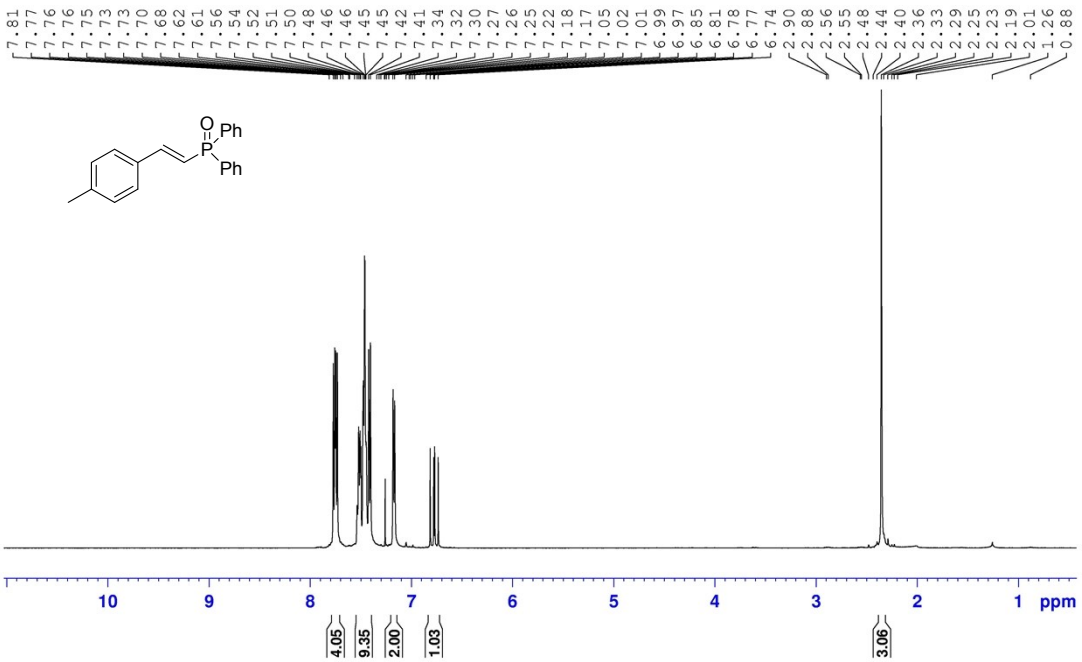

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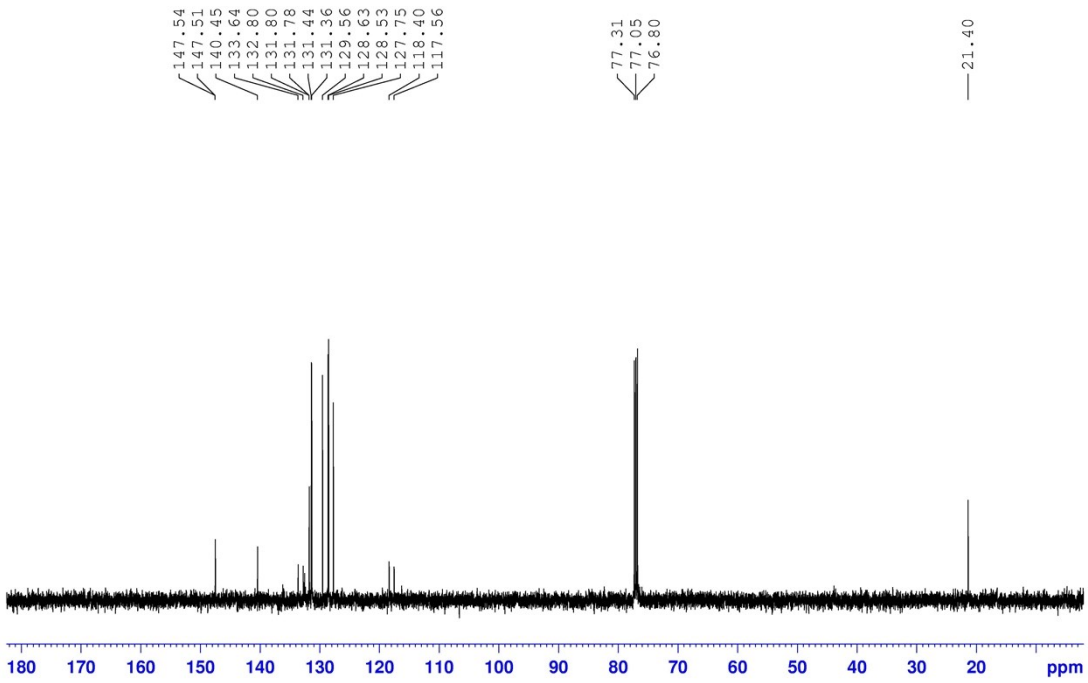

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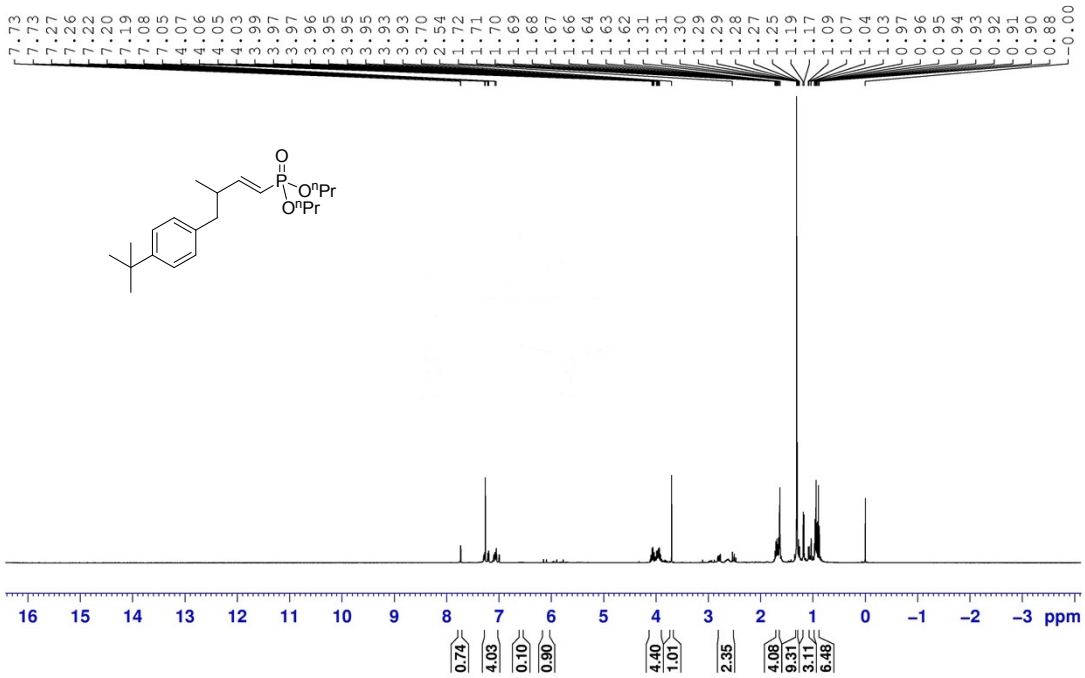

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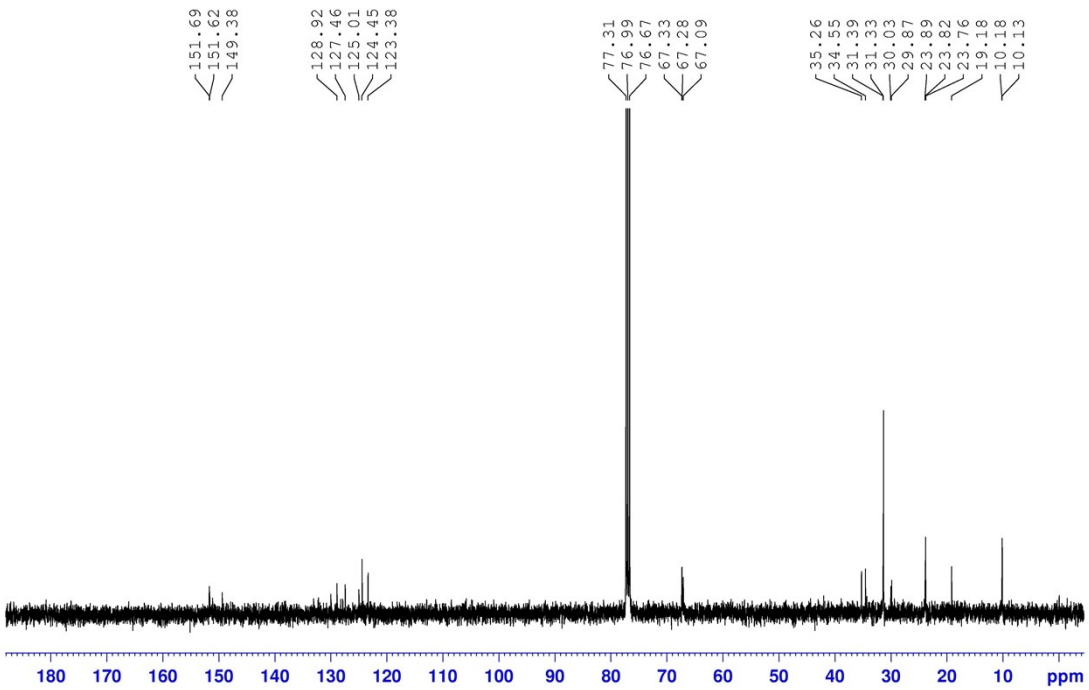

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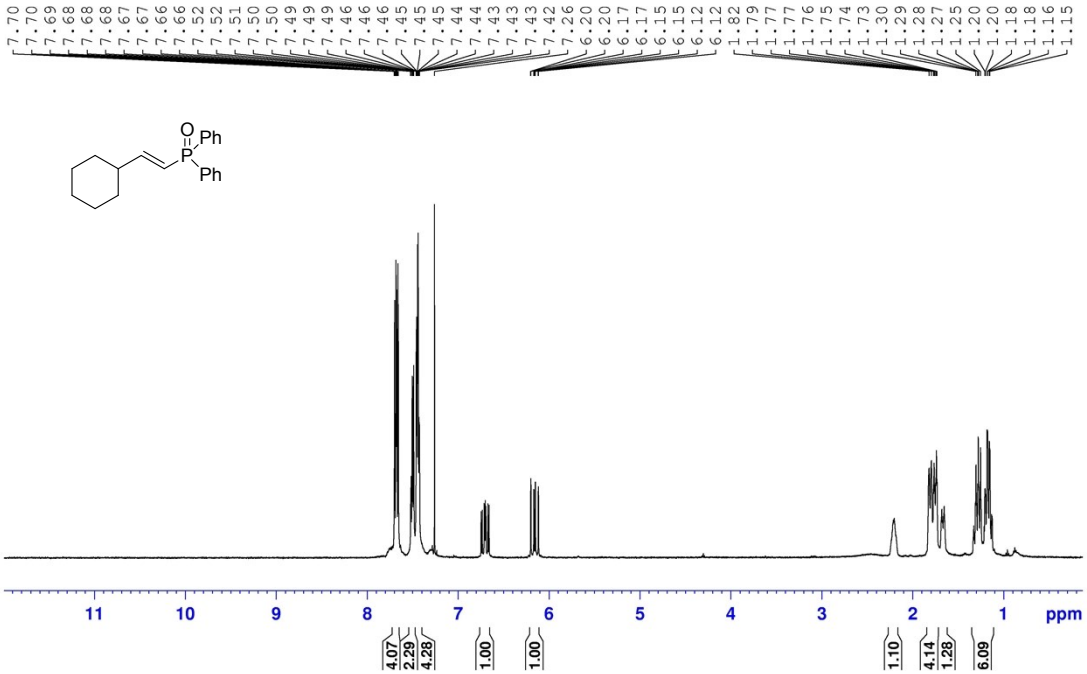

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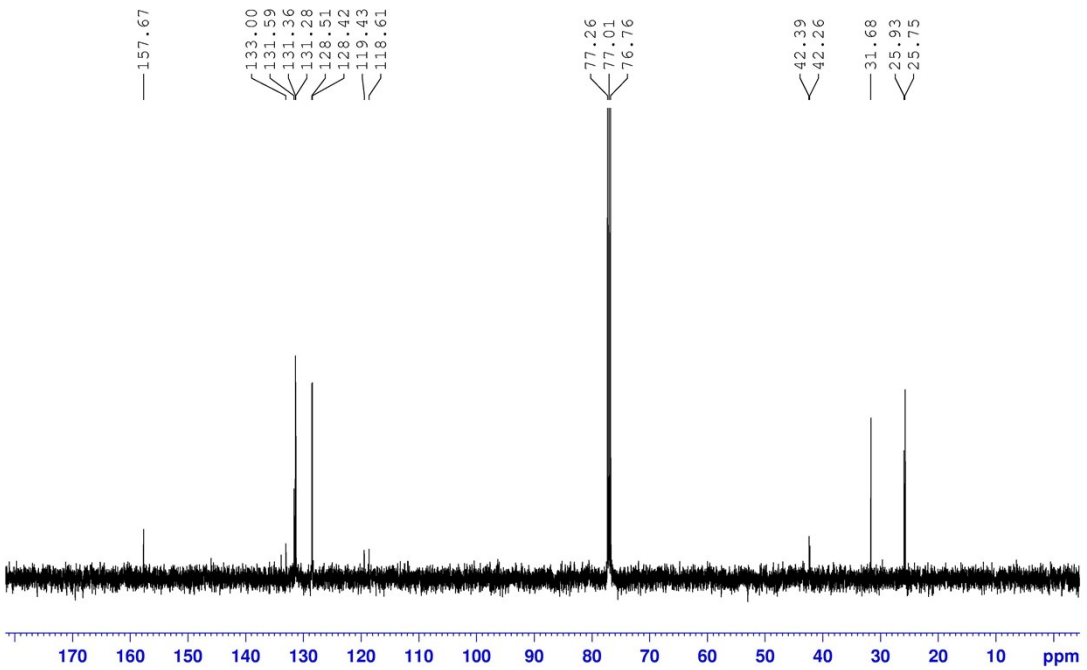

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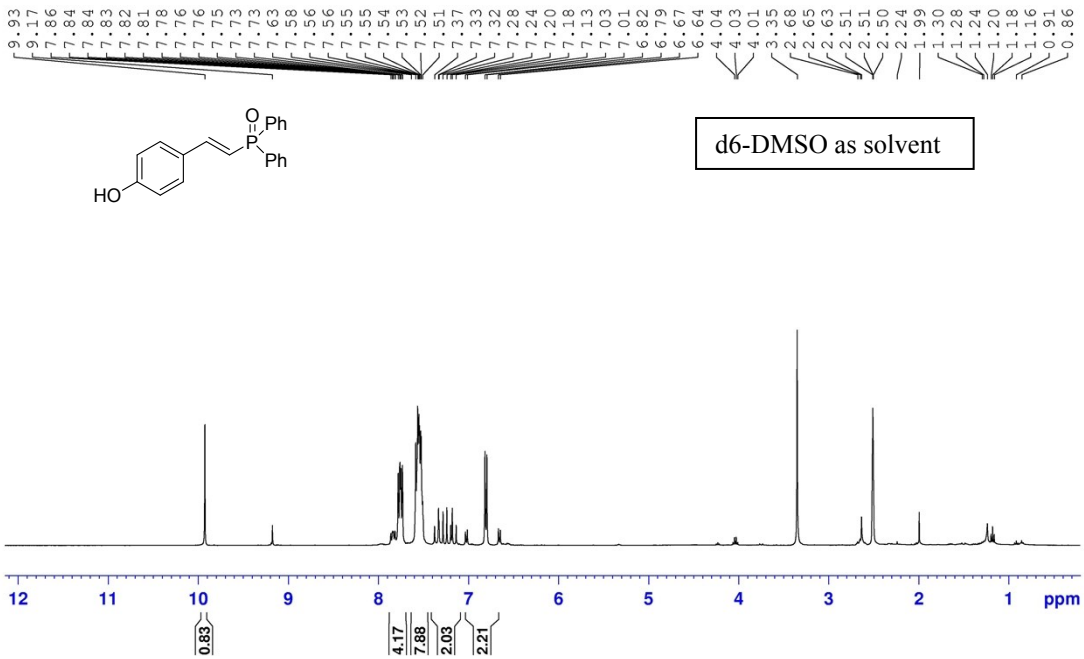
liul-20130524-OAcP-H1-DMSO



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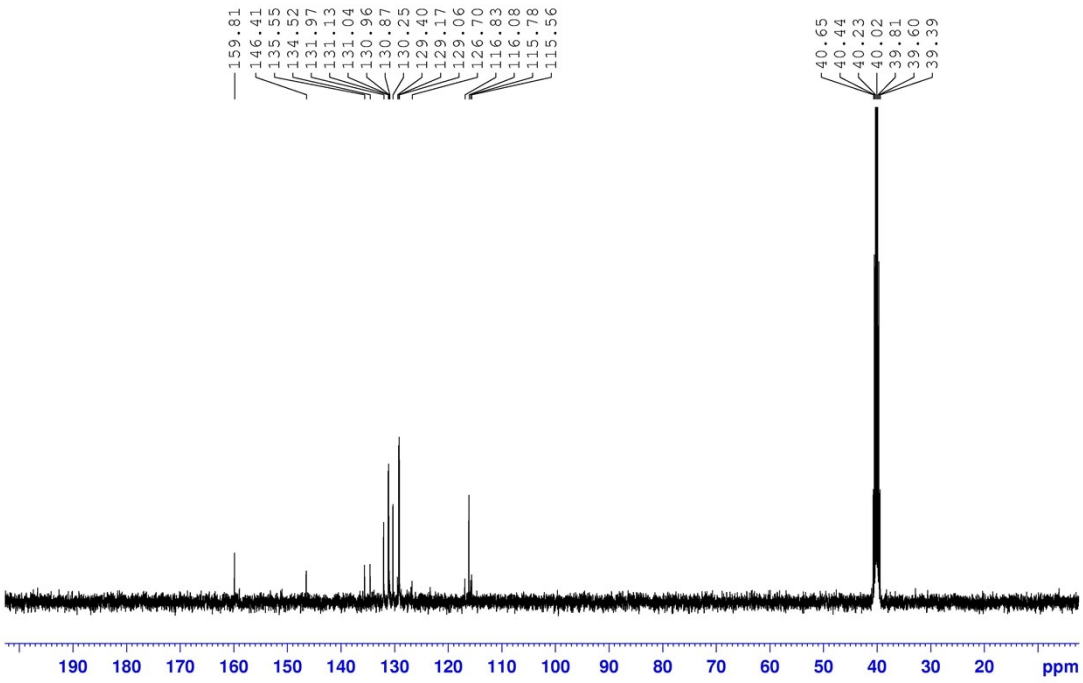

Computational details

In the density functional theory (DFT) calculations, geometry optimizations and frequency calculations were performed using the Gaussian 03 programs.[1a] DFT method B3LYP[2] with a mixed basis set employing D95v(d) for C, H, O, N and LANL2DZ for P, Br, Ni were used. Polarization functions were added for P (ξ_d = 0.387), Br (ξ_d = 0.428) and Ni (ξ_f = 3.13) to the standard LANL2DZ basis set.[3] Transition states were examined by vibrational analysis and then submitted to intrinsic reaction coordinate (IRC) calculations to determine which minima they connect. For compounds that had multiple conformations, searches were performed to find the lowest-energy conformation by comparing the structures optimized from different starting geometries. Energies in solution have been calculated by means of single point calculations (IEF-PCM method with the Bondi radii)[4] using the Gaussian 09 program[1b] with the B3LYP method using SDD[5] pseudo-potential for the metal center and the extended 6-311++G(2d,p) basis set for the other atoms. The gas-phase geometry was used for all of the solution phase calculations. The free energy correction from frequency calculation was added to the single-point energy to obtain the free energy in solution. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298 K.

1. (a) Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb; J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, **2004**. (b) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.
2. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
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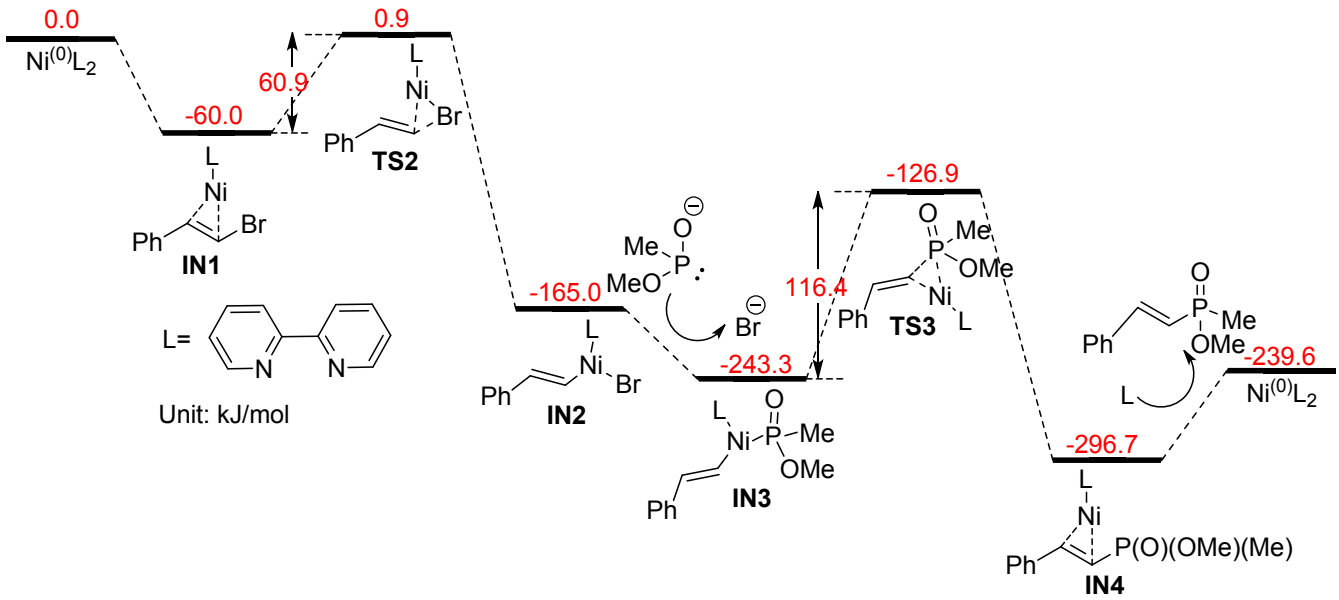

Fig S2 Free energy profile for the cross-coupling step

IN1

28	0.151322	-0.220896	-0.070802
6	-0.848826	-1.785664	0.218539
1	-1.096148	-2.088384	1.236721
6	-1.662677	-0.824890	-0.488325
1	-1.749499	-0.960210	-1.569362
6	-2.777843	-0.057183	0.110981
6	-3.684971	0.620622	-0.737254
6	-2.981533	0.066927	1.506645
6	-4.739531	1.385953	-0.222442
1	-3.567115	0.527246	-1.818149
6	-4.037764	0.825548	2.020906
1	-2.302926	-0.432528	2.196976
6	-4.925797	1.495799	1.162986
1	-5.424905	1.887852	-0.905979
1	-4.170350	0.897381	3.100736
35	-0.248640	-3.425871	-0.740370
6	2.725306	-1.374973	0.847830
6	4.097450	-1.354083	1.118734
6	4.797057	-0.152077	0.950427
6	4.100151	0.979960	0.515029
6	2.723797	0.881924	0.268107
7	2.051224	-0.285512	0.440389
1	5.866327	-0.097071	1.147421
1	2.139118	-2.286417	0.943771
1	4.596961	-2.262109	1.448619
1	4.624990	1.919510	0.364147
6	1.876949	2.006900	-0.203188
6	2.331904	3.323053	-0.363990
6	1.437046	4.305321	-0.801193
6	0.108071	3.944056	-1.057540
6	-0.271635	2.610792	-0.871470
7	0.588900	1.662426	-0.462561
1	1.770408	5.333425	-0.931792
1	3.364029	3.582964	-0.144875
1	-0.626384	4.673289	-1.391514
1	-1.295341	2.283786	-1.042094
1	-5.747586	2.085511	1.567286

TS2

28	-0.293347	-0.496939	-0.241891
6	1.316227	-0.572251	-1.072432
1	1.670616	-0.010545	-1.940308
6	2.032743	-0.751280	0.109244
1	1.826198	-1.641515	0.701645
6	3.149521	0.076638	0.573731
6	3.856197	-0.306918	1.739211
6	3.572609	1.254827	-0.089718
6	4.936842	0.442280	2.214788
1	3.550117	-1.209111	2.270237
6	4.660118	1.996220	0.380224
1	3.039565	1.596879	-0.976064
6	5.351053	1.599541	1.537063
1	5.462057	0.120710	3.114127
1	4.968431	2.896202	-0.152097
35	0.348472	-2.432544	-1.758892
6	-0.820464	2.130294	-1.683553
6	-1.448471	3.364591	-1.854763
6	-2.571434	3.661363	-1.065604
6	-3.019193	2.704611	-0.152768
6	-2.342619	1.477314	-0.051303
7	-1.245980	1.200809	-0.808022
1	-3.082175	4.618154	-1.157823
1	0.056158	1.864283	-2.271989
1	-1.064411	4.071771	-2.586745
1	-3.877063	2.915013	0.480412
6	-2.741684	0.392372	0.871182
6	-3.941071	0.386967	1.602506
6	-4.234245	-0.694806	2.434420
6	-3.319210	-1.756918	2.508982
6	-2.150879	-1.684093	1.749751
7	-1.856611	-0.638101	0.952912
1	-5.160037	-0.714895	3.006661
1	-4.644348	1.210243	1.511521
1	-3.502388	-2.624155	3.139132
1	-1.416939	-2.487205	1.770452
1	6.193295	2.184029	1.904987

IN2

28	-0.550645	-0.462093	-0.195877
6	1.312901	-0.367584	-0.437478
1	1.668316	-0.651755	-1.434201
6	2.205637	-0.004098	0.508561
1	1.837123	0.243877	1.509654
6	3.675316	0.104758	0.365878
6	4.424854	0.675924	1.417823
6	4.379898	-0.335667	-0.777935
6	5.815896	0.816140	1.331081
1	3.905138	1.011922	2.316226
6	5.767978	-0.195443	-0.866744
1	3.837399	-0.807710	-1.595513
6	6.497636	0.384012	0.184984
1	6.368385	1.259663	2.159472
1	6.288896	-0.548453	-1.756843
35	-0.265921	-2.792728	-0.246607
6	0.062498	2.414972	-0.498408
6	-0.240399	3.777093	-0.578572
6	-1.565924	4.185579	-0.397921
6	-2.536050	3.212223	-0.145033
6	-2.160067	1.863714	-0.080433
7	-0.868535	1.473040	-0.254705
1	-1.841783	5.237156	-0.454215
1	1.077021	2.048038	-0.619970
1	0.555843	4.489980	-0.778897
1	-3.573778	3.499985	-0.004964
6	-3.113602	0.759814	0.168143
6	-4.480009	0.944932	0.423393
6	-5.286478	-0.175817	0.642922
6	-4.702482	-1.446567	0.598806
6	-3.331202	-1.549125	0.338422
7	-2.555641	-0.473559	0.129841
1	-6.349640	-0.056160	0.844913
1	-4.910419	1.941658	0.454776
1	-5.287613	-2.348534	0.761986
1	-2.818615	-2.508354	0.288646
1	7.579829	0.487238	0.113828

IN3

28	0.633998	-0.216500	-0.220962
6	-1.210239	0.009764	-0.491594
6	-2.220515	0.030775	0.406461
6	-3.633213	0.405615	0.169533
6	-4.540541	0.357264	1.251185
6	-5.888533	0.702029	1.090961
6	-6.369067	1.107389	-0.162084
6	-5.481231	1.160046	-1.249746
6	-4.135981	0.815950	-1.087226
15	0.163881	-2.385189	-0.313755
8	1.363305	-3.336658	-0.447374
1	-1.442685	0.268756	-1.536626
1	-2.005771	-0.277600	1.432217
1	-4.178218	0.039009	2.229360
1	-6.565115	0.652324	1.944079
1	-7.416890	1.375553	-0.292171
1	-5.844037	1.469570	-2.230053
1	-3.468483	0.860963	-1.946931
6	3.431982	-1.359513	-0.117865
6	4.829889	-1.287156	-0.045502

6	5.443043	-0.038456	0.077468
6	4.633781	1.101371	0.125566
6	3.242674	0.956058	0.050945
7	2.652161	-0.261958	-0.069627
1	6.526665	0.053618	0.133585
1	2.894920	-2.308368	-0.222340
1	5.410826	-2.205661	-0.088231
1	5.083634	2.085494	0.218042
6	2.305537	2.102662	0.098538
6	2.710563	3.436592	0.258849
6	1.742816	4.443634	0.305814
6	0.393973	4.087117	0.197120
6	0.070156	2.735915	0.040415
7	0.998438	1.766362	-0.014325
1	2.038126	5.484262	0.429708
1	3.762764	3.688664	0.350752
1	-0.398936	4.830379	0.234029
1	-0.961401	2.402121	-0.034022
8	-0.623694	-2.659214	1.141235
6	-0.729403	-4.008586	1.607434
1	0.222728	-4.542056	1.497064
1	-1.005024	-3.959413	2.667289
1	-1.514183	-4.557431	1.064498
6	-1.078446	-2.920605	-1.587095
1	-2.053152	-2.450338	-1.430171
1	-0.697397	-2.648334	-2.579325
1	-1.173103	-4.012740	-1.545773

TS3

28	-0.433922	0.211719	-0.197171
6	1.356464	0.398664	-0.705017
6	2.016538	0.123753	0.481908
6	3.140791	-0.793414	0.677911
6	3.725490	-0.896860	1.962662
6	4.811605	-1.744972	2.200587
6	5.348860	-2.514163	1.156964
6	4.779971	-2.425250	-0.124878
6	3.688763	-1.585238	-0.360560
15	0.567488	2.254275	-0.616444
8	0.436940	3.013185	0.699177
1	1.804749	0.103534	-1.660459
1	1.701249	0.666414	1.375327
1	3.320037	-0.296037	2.777299
1	5.243588	-1.804387	3.199312
1	6.195829	-3.174709	1.338446
1	5.189420	-3.020473	-0.941043
1	3.255831	-1.538938	-1.358746
6	-2.370052	1.517472	1.596859
6	-3.563914	1.626932	2.315845
6	-4.531692	0.621978	2.176647
6	-4.267243	-0.456390	1.326761
6	-3.044993	-0.504574	0.639578
7	-2.115622	0.476567	0.777516
1	-5.473901	0.675128	2.719574
1	-1.581378	2.268652	1.655029
1	-3.723774	2.483771	2.966631
1	-5.003286	-1.246891	1.207032
6	-2.649130	-1.609026	-0.273454
6	-3.467452	-2.713292	-0.560496
6	-3.001464	-3.704829	-1.428773
6	-1.721543	-3.569049	-1.984462
6	-0.966815	-2.442141	-1.644910
7	-1.412279	-1.480857	-0.819435
1	-3.623322	-4.567073	-1.663535
1	-4.454287	-2.802070	-0.114477
1	-1.312058	-4.315366	-2.661743
1	0.036689	-2.298856	-2.043032
8	1.892462	2.826055	-1.481279
6	2.186854	4.225198	-1.408404
1	2.193070	4.572678	-0.368601
1	3.180849	4.359785	-1.849870
1	1.463345	4.825586	-1.982512
6	-0.751118	2.674943	-1.865951
1	-0.594460	2.109260	-2.791771
1	-1.744100	2.446893	-1.465938
1	-0.696008	3.748489	-2.092144

IN4

28	-0.222872	-0.138912	0.036211
6	1.633876	-0.567865	0.401779
6	1.487336	0.723844	-0.253982
6	1.640441	2.034244	0.414076
6	1.873772	3.189134	-0.368999
6	1.993551	4.458243	0.211930
6	1.888244	4.613451	1.601488
6	1.664209	3.477047	2.396689
6	1.540196	2.211577	1.814834
15	2.339900	-1.879545	-0.601644
8	2.100435	-1.804597	-2.089712
1	1.932840	-0.605251	1.453989
1	1.714466	0.741342	-1.323874
1	1.988300	3.079344	-1.448881
1	2.182657	5.325831	-0.420719
1	1.986158	5.597628	2.058131
1	1.586009	3.580894	3.479204
1	1.361401	1.348063	2.454087
6	-1.642898	2.083556	-1.312572
6	-2.756625	2.718293	-1.870959
6	-4.011984	2.110164	-1.742757
6	-4.105094	0.897089	-1.053288
6	-2.943174	0.323317	-0.518775
7	-1.727041	0.911603	-0.658543
1	-4.901779	2.571074	-2.168028
1	-0.651100	2.524765	-1.374979
1	-2.633071	3.665506	-2.390870
1	-5.068323	0.407291	-0.939599
6	-2.917752	-0.946823	0.246754
6	-4.063605	-1.682478	0.581931
6	-3.931351	-2.849961	1.339414
6	-2.650889	-3.246999	1.745889
6	-1.556647	-2.464066	1.366278
7	-1.675991	-1.344599	0.630855
1	-4.809597	-3.433358	1.610189
1	-5.047142	-1.347980	0.263757
1	-2.494144	-4.143087	2.342001
1	-0.545535	-2.733861	1.658091
8	3.951342	-1.820531	-0.192819
6	4.903972	-2.439859	-1.064424
1	4.681087	-2.214006	-2.113943
1	5.887584	-2.036094	-0.799495
1	4.921672	-3.532385	-0.926969
6	1.831337	-3.502528	0.115879
1	1.946522	-3.511219	1.207087
1	0.790229	-3.711424	-0.151948
1	2.459171	-4.294630	-0.309555