Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of Benzil Derivatives via Oxidation of Alkynes Catalyzed by Pd–Fe_3O_4 Heterodimer Nanocrystals

Sangmoon Byun,[a] Jooyoung Chung,[a] Jungmin Kwon,[a] Taehyun Lim [a] and B. Moon Kim,*[a]

[a] *Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea.*
E-mail: kimbm@snu.ac.kr;
Fax: +82 2-872-7505; Tel: +82-2-880-6644

General

All commercially available chemicals were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry Co. and used without further purification unless otherwise noted. All reaction products were identified through comparison with the authentic compounds and quantified through GC analysis using a Hewlett Packard 5890 Gas Chromatograph with mesitylene as an internal standard. All Transmission Electron Microscopy (TEM) images were obtained on a JEOL EM-2010 microscope at an accelerating voltage of 200 kV. The powder X-ray diffraction (XRD) was performed using a Bruker AXS D8 FOCUS (2theta : 5-100, scanspeed : 2degree/min, Cu Kαradiation: λ=1.54056nm, Generator : 40kV, 40m)

Experimental

Synthesis of substrates

-General Procedure for the Sonogashira Reaction.[1]

An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with Bu_4NOAc (1.5 mmol) and $Pd(OAc)_2$ (1-3 mol%) or $Pd_2(dba)_3$ (2 mol % for aryl bromides) inside a nitrogen-filled flask. The flask was capped with a rubber septum, and then it was removed from the glove box. An aryl iodide or bromide (1.0 mmol) and DMF (3.0 mL) were then successively added, and after 5 min of stirring, the alkyne (1.0 mmol) was added. Stirring was continued at room temperature under argon for the corresponding reaction times indicated in the tables, after which time the reaction mixture was diluted with water (10 mL) and extracted with diethyl ether (4x10 mL). The combined ether layers were dried over Na_2SO_4, filtered, concentrated, and purified through alumina gel flash chromatography using hexanes or hexanes/ether to elute the desired coupling product.[1]

-General procedure for Wacker-type oxidation

Pd–Fe_3O_4 nanocrystal catalyst (1.0 mmol) in 1,4-dioxane (5.0 mL) was put to a vial. Phenylacetylene (1 mmol), $CuBr_2$ (0.1 mmol) and H_2O (1 mL) were added to the mixture and an O_2 balloon was attached to the sealed vial. The vial was sonicated for 3 minute for dispersion of the catalyst and the reaction mixture was stirred for 28 h at 95 ^oC. After the reaction mixture was cooled to room temperature, the catalyst was separated from the mixture through the use of an external magnet. The solution containing the product was diluted with EtOAc (15 mL) and H_2O (15 mL) and extracted with EtOAc (3x15 mL).And dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using n-hexane/EtOAc as an eluent.

-General procedure for recycling

After the reaction was complete, 1,4-dioxane (5 mL) was added and the mixture was sonicated 3 min for dispersion. Then the Pd–Fe_3O_4 catalyst was separated with the use of an external magnet. The recovered catalyst was washed five times with EtOAc (20 mL), twice with water H_2O (20 mL) and dried in vacuo.

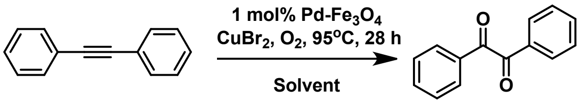
-Synthesis of Pd-Fe_3O_4 heterodimer nanocrystals.

The Pd-Fe_3O_4 synthesis was performed by two-step thermal decomposition of a mixture solution composed of iron acetate, palladium acetate, oleic acid and oleylamine. In a general synthesis, 10 mg of $Pd(acac)_2$ (0.033 mmol) and 0.7 g of $Fe(acac)_3$ (2.00 mmol) was added into a solution 4.0 mL of containing oleic acid (12.5 mmol) and 6.0 mL of oleylamine (17.5 mmol) and the mixture was heated to 120 ^{o}C in a vacuum with vigorous stirring for 3 h. Under Ar atmosphere, the dark mixture was heated to 220 ^{o}C at a heating rate of 2 ^{o}C /min and kept at this temperature for 30 min, and then it was further heated to 300 ^{o}C at the same heating rate and aged at 300 ^{o}C for 30 min. After cooling 3h, the mixture solution was precipitated by adding EtOH and 140 mg of the powdery Pd-Fe_3O_4 were obtained after the washing and vacuum drying processes. The nanocrystals were dispersible in many organic solvents such as chloroform and hexane.

Additional Discussion

Effect of water in the solvent

Table S1. Study on the effect of H_2O content in solvent.



1

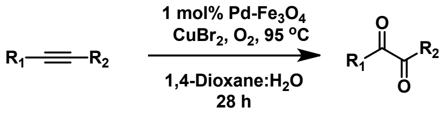
Entry	Solvnet	Yield (%)[a]
1	1,4-Dioxane	14
2	1,4-Dioxane : H_2O = 5 : 1	98
3	1,4-Dioxane : H_2O = 3 : 2	82
4	1,4-Dioxane : H_2O = 2 : 3	52
5	1,4-Dioxane : H_2O = 1 : 5	26
6	H_2O	6

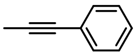
[a] isolated yield.

Oxidation alkyl-substituted acetylene derivatives

When 1-phenylpropyne was employed as substrate, only 20% yield of the desired product was isolated along with several other side products (Table S2, entry 1). When 5-nonyne, a dialkyl-substituted acetylene, was used, the reaction was very sluggish, leaving almost unreacted starting material (Table S2, entry 2).

Table S2. Oxidation of alkyl-substituted acetylene derivatives

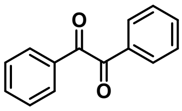


Entry	Substrate	Yield (%)[a]
1		20
2	$CH_3(CH_2)_3{-}{\equiv}{-}(CH_2)_3CH_3$	-

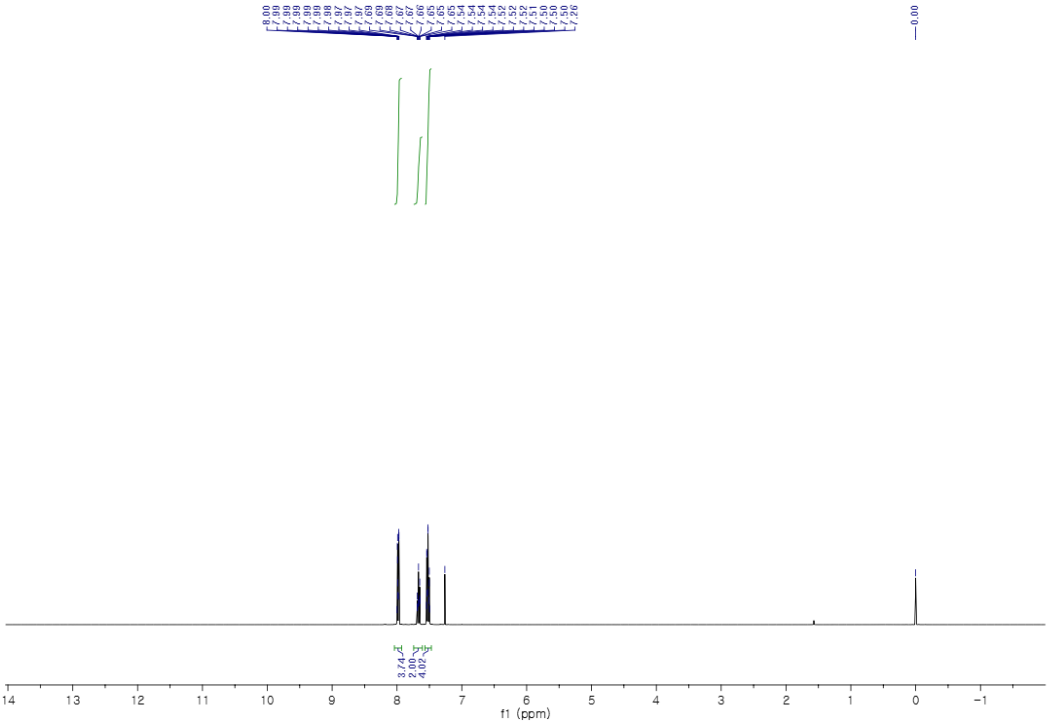
[a] isolated yield.

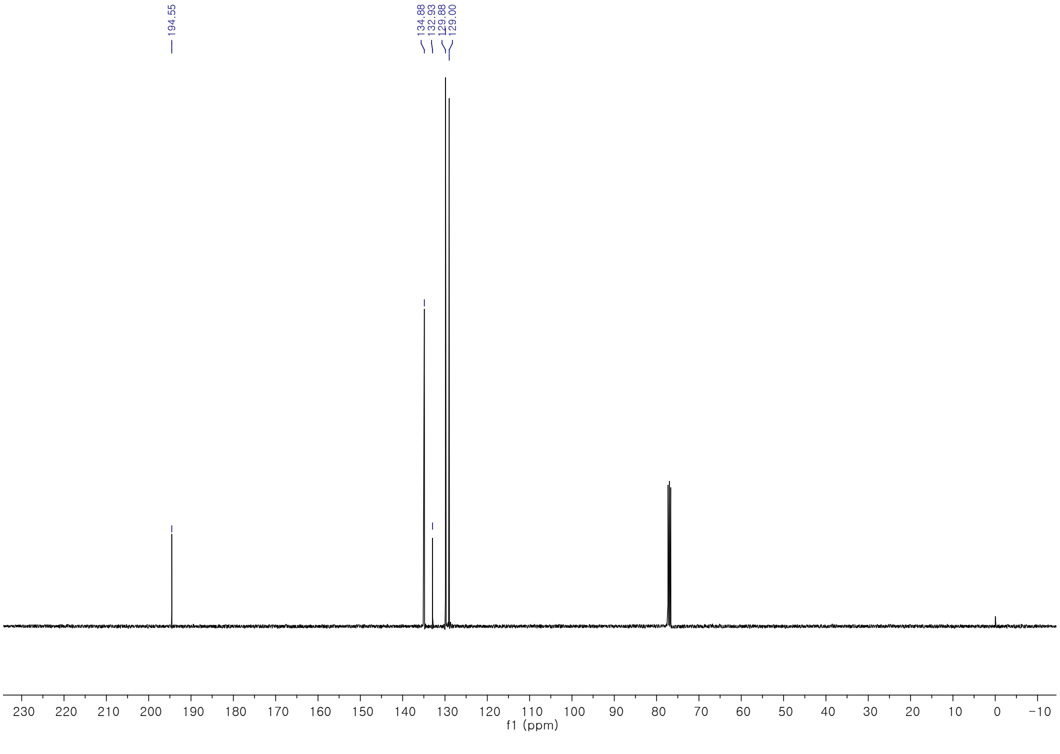
NMR data

T2-1. Benzil

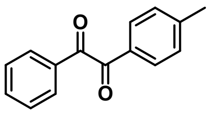


^{1}H NMR (CD_3Cl_3) δ 7.49 (4H, dd, *J* = 6.8, 7.3 Hz), 7.64 (2H, t, *J* = 6.8 Hz), 7.89 (4H, t, *J* = 7.3 Hz); ^{13}C NMR (CD_3Cl_3) δ 128.9, 129.8, 132.9, 134.8, 194.5; MS (EI) m/z 210 (M^+, 10%),105 (100), 77 (50), 51 (20); HRMS (EI) calcd for $C_{14}H_{10}O_2$ (M^+) 210.06808. Found 210.06771. These ^{1}H NMR and ^{13}C NMR were identical with those reported in the literature.[1]

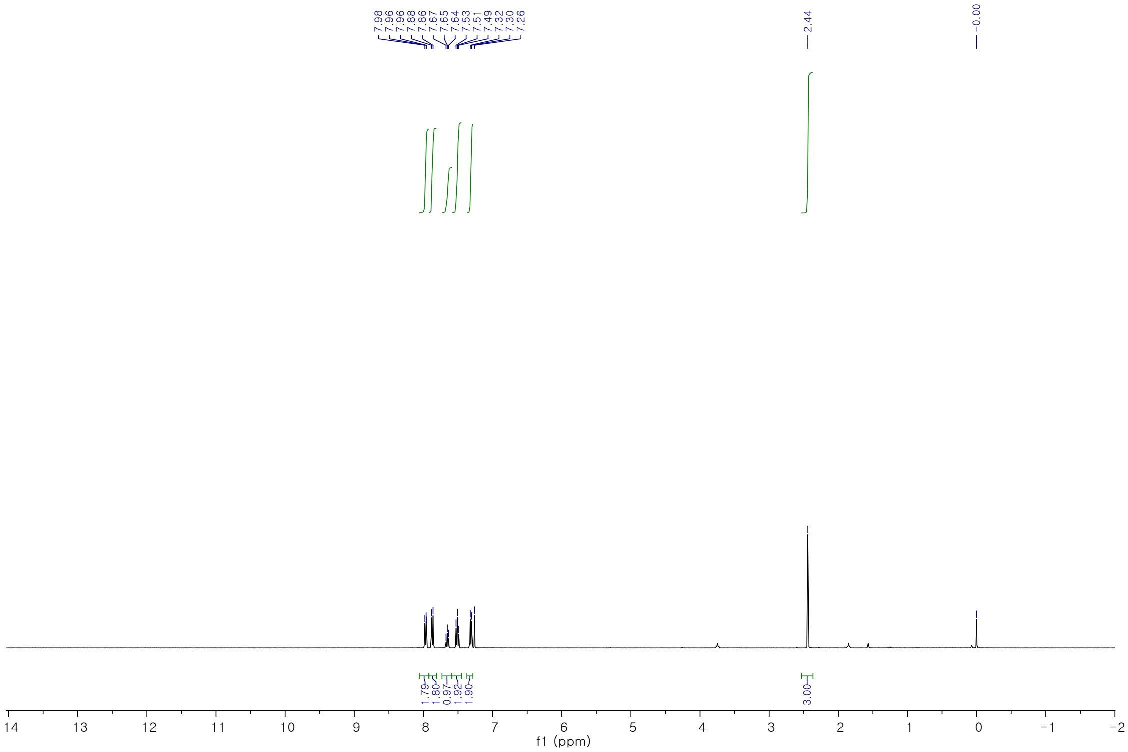


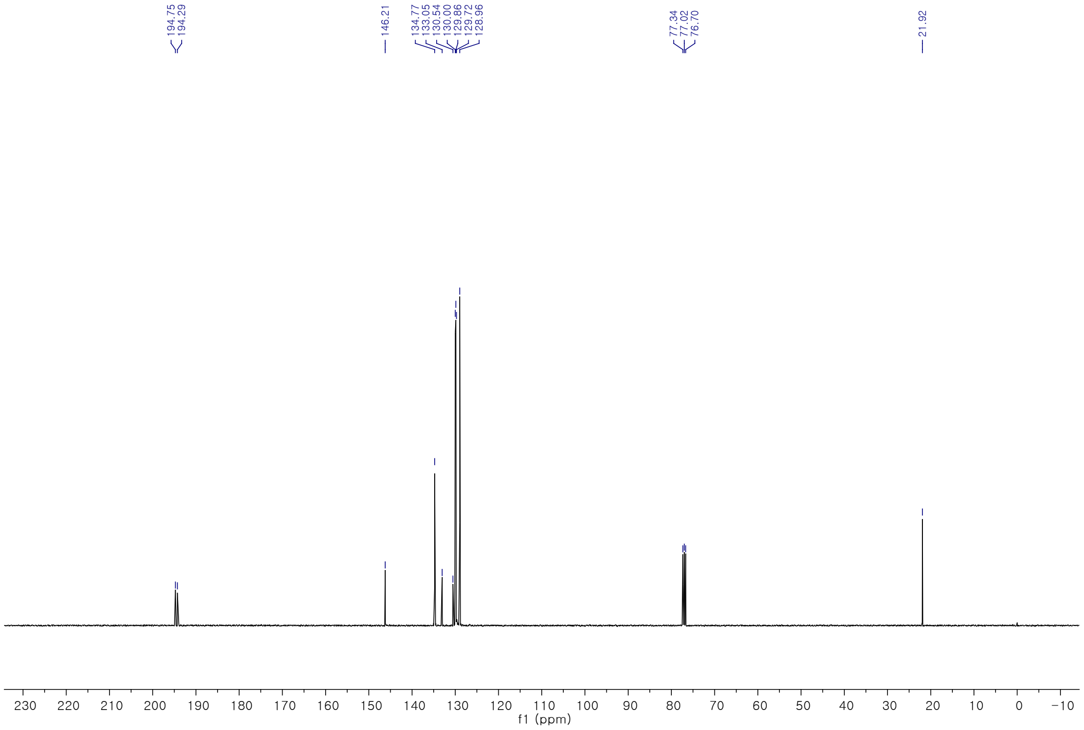


T2-2. 1-Phenyl-2-*p*-tolylethane-1,2-dione

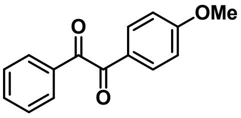


^{1}H NMR (CDCl$_3$) δ 2.41 (3H, s), 7.29 (2H, d, *J* = 8.3 Hz),7.48 (2H, dd, *J* = 7.2, 7.3 Hz), 7.63 (1H, t, *J* = 7.3 Hz), 7.86 (2H, d, *J* = 8.3 Hz), 7.96 (2H, d, *J* = 7.2Hz); ^{13}C NMR (CDCl$_3$) δ 21.8, 128.9, 129.6, 129.7, 129.9, 130.4, 133.0, 134.7, 194.2, 194.7; MS (EI) m/z 224 (M$^+$, 10%), 119 (100), 105 (20), 77 (15); HRMS (EI) calcd for $C_{15}H_{12}O_2$ (M$^+$) 224.06808. Found 224.08295. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[2]

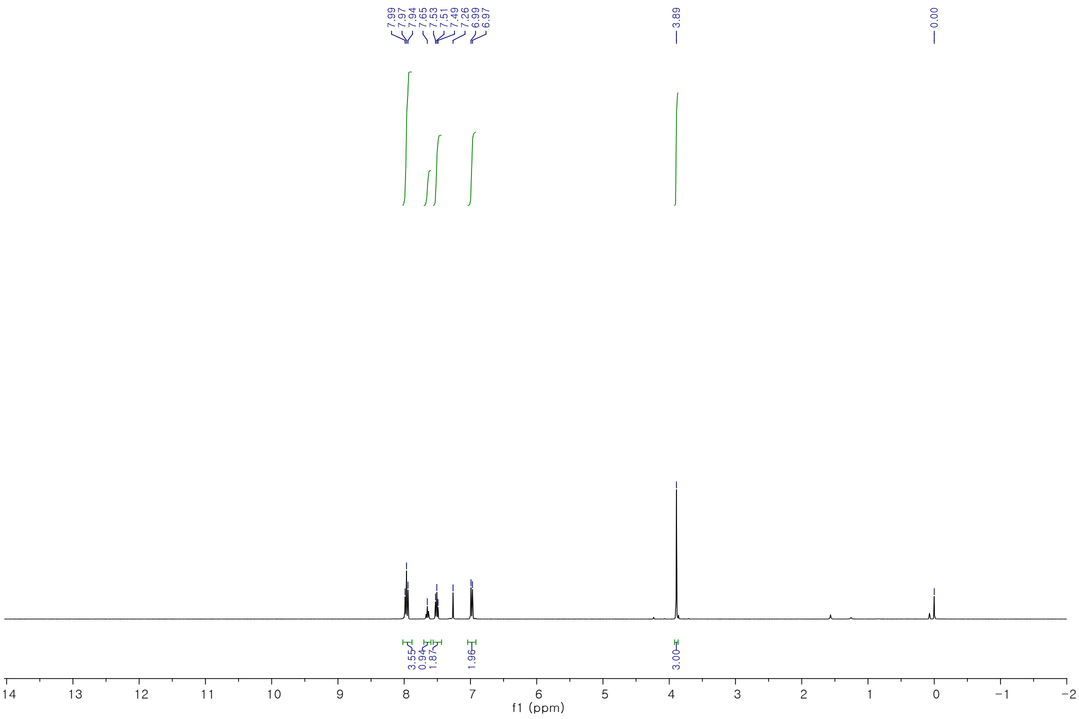


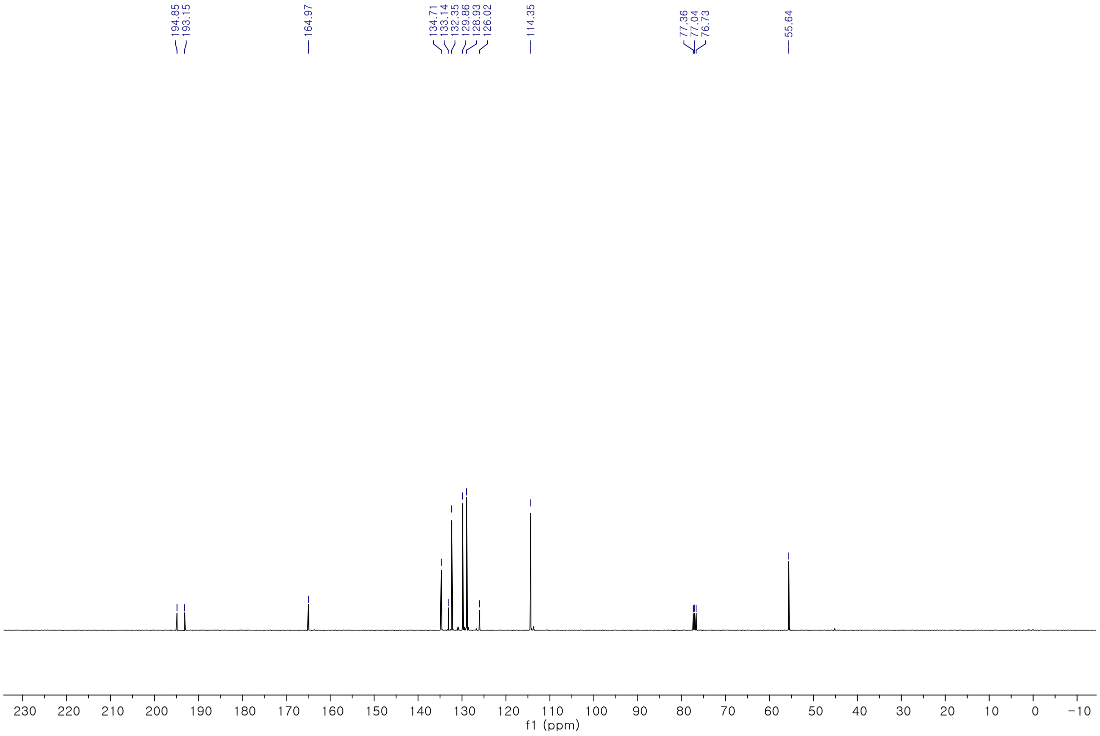


T2-3. 1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione

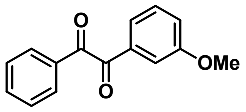


^{1}H NMR (CDCl$_3$) δ 3.88 (3H, s), 6.97 (2H, d, *J* = 8.8 Hz),7.50 (2H, dd, *J* = 7.9, 8.0 Hz), 7.64 (1H, t, *J* = 8.0 Hz), 7.94–7.98 (4H, m); ^{13}C NMR (CDCl$_3$) δ 55.6,114.3, 126.1, 128.9, 129.9, 132.3, 133.2, 134.7, 165.0, 193.1, 194.7; MS (EI) m/z 240 (M$^+$, 5%), 135(100), 92 (10), 77 (20); HRMS (EI) calcd for $C_{15}H_{12}O_3$ (M$^+$) 240.07865. Found 240.07806. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[2]

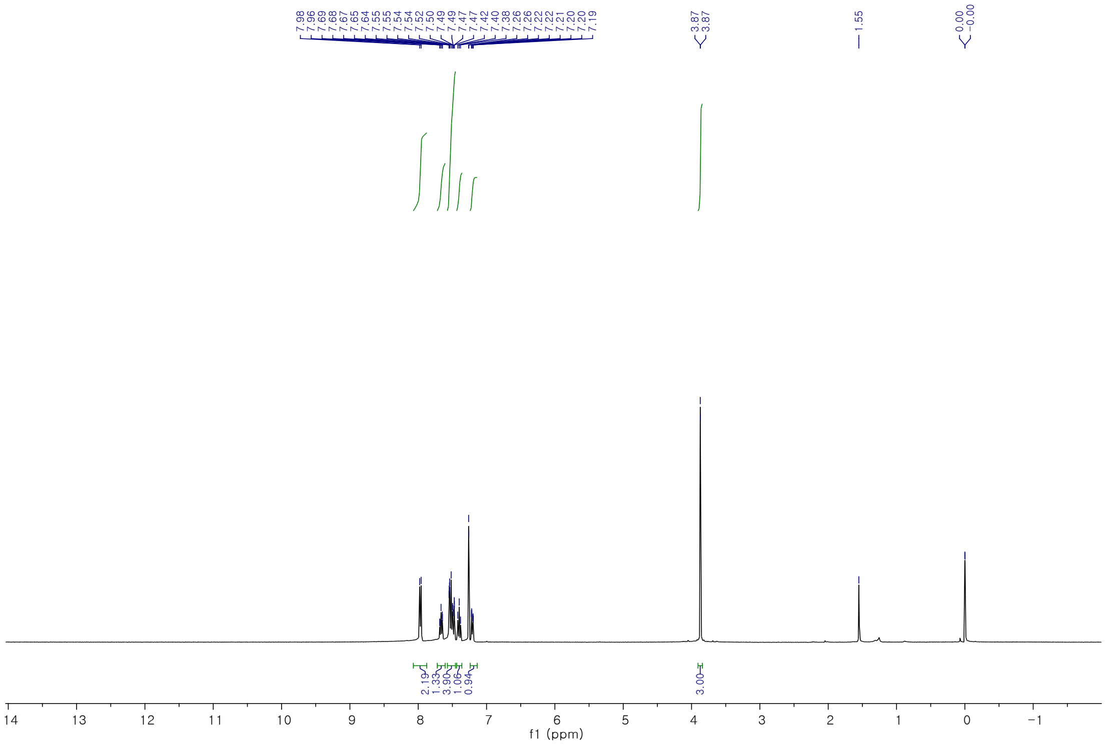


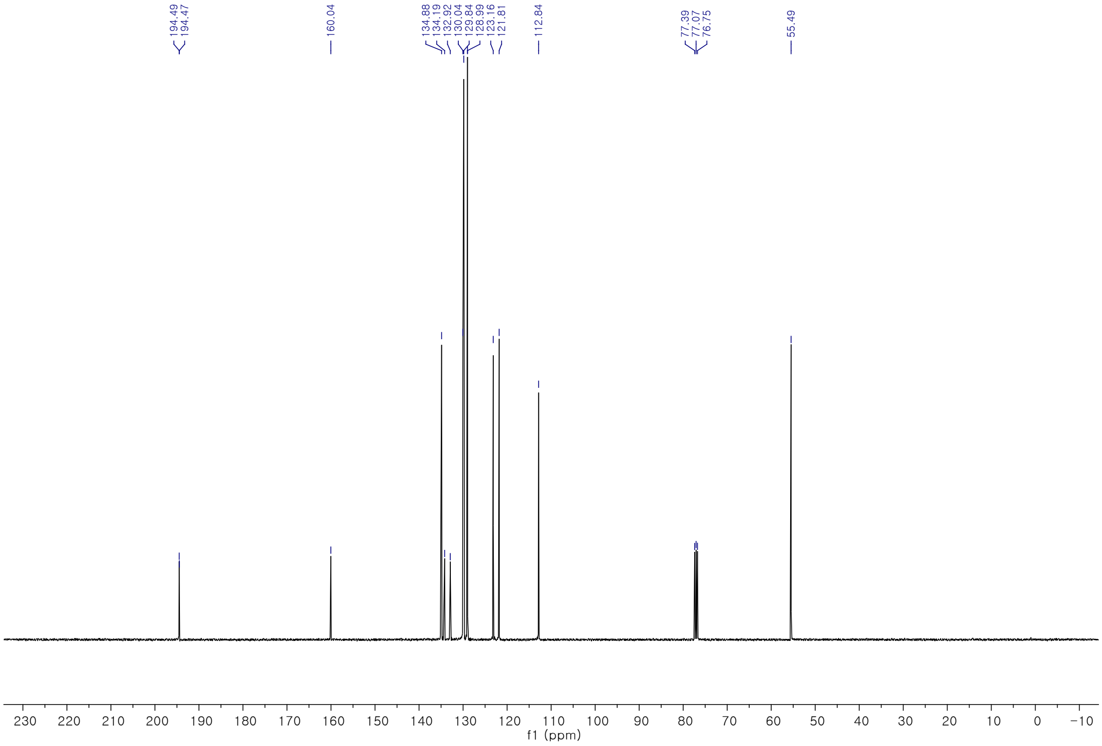


T2-4. 1-(3-Methoxyphenyl)-2-phenylethane-1,2-dione

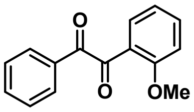


^{1}H NMR (CDCl$_3$) δ 3.86 (3H, s), 7.21 (1H, dd, *J* = 1.6, 8.2 Hz), 7.40 (1H, t, *J* = 8.2 Hz), 7.47–7.55 (4H, m), 7.66 (1H, t, *J* = 7.2 Hz), 7.97 (2H, d, 7.7 Hz); ^{13}C NMR (CDCl$_3$) δ 55.4, 112.8, 121.8, 123.1, 129.0, 129.8, 130.0, 132.9, 134.2, 134.8, 160.0, 194.4, 194.4; MS (EI) m/z 240 (M$^+$, 20%), 135 (100), 105 (40), 77 (40); HRMS (EI) calcd for $C_{15}H_{12}O_3$ (M$^+$) 240.07865. Found 240.07833. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[2]

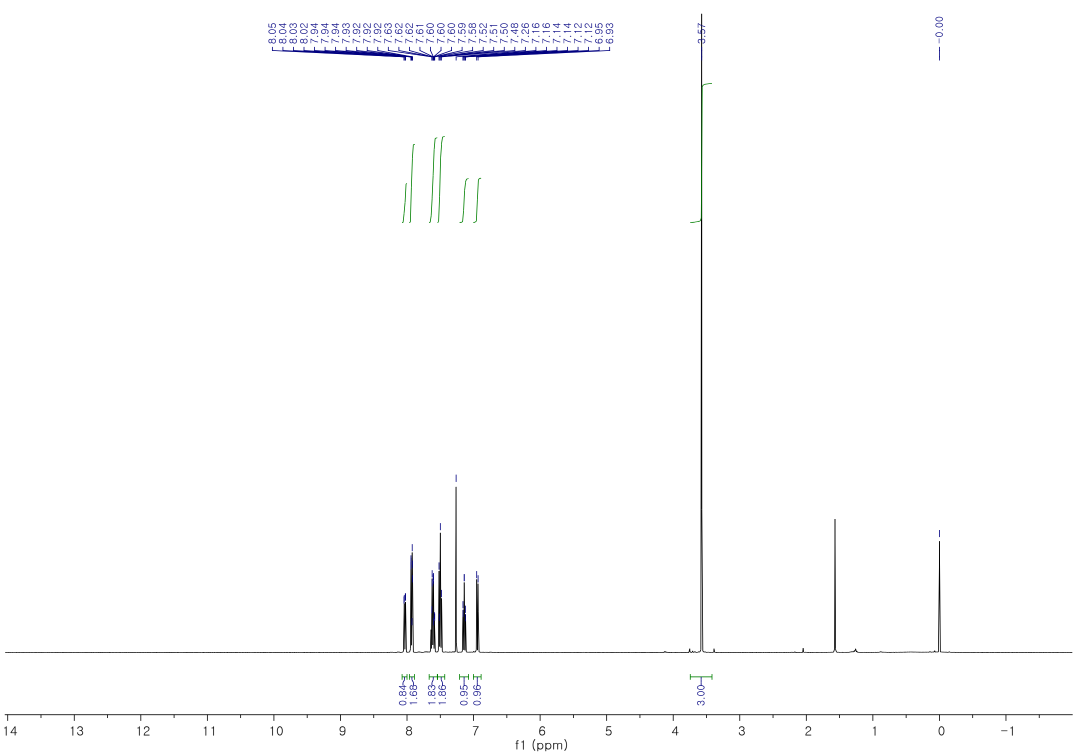


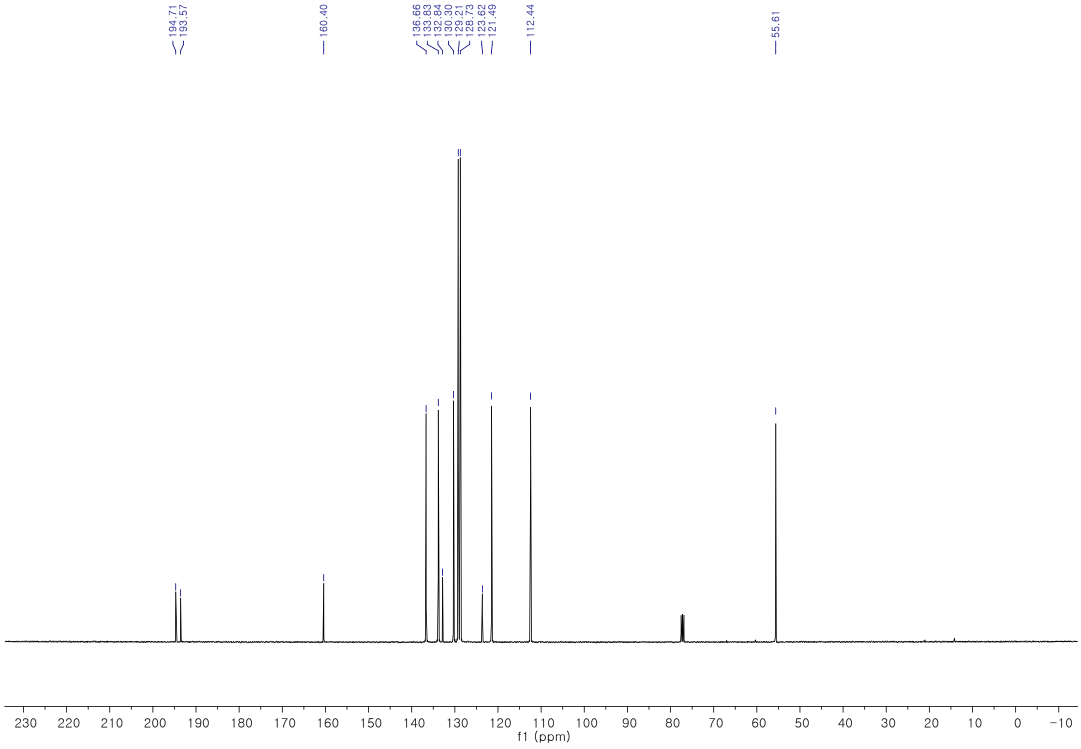


T2-5. 1-(2-Methoxyphenyl)-2-phenylethane-1,2-dione

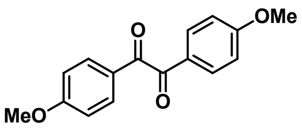


^{1}H NMR ($CDCl_3$) δ 3.56 (3H, s), 6.93 (1H, d, *J* = 8.0 Hz), 7.13 (1H, t, *J* = 8.0 Hz), 7.49 (2H, dd, *J* = 1.2, 8.1 Hz), 7.58–7.63 (2H, m), 7.92 (2H, dd, *J* = 8.0, 8.1 Hz), 8.03 (1H, dd, *J* = 1.2, 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 55.7, 112.4, 121.6, 123.9, 128.7, 129.3, 130.6, 133.0,133.7, 136.4, 160.4, 193.4, 194.6; MS (EI) m/z 240 (M^+, 20%), 135 (100), 105 (45), 77 (40); HRMS (EI) calcd for $C_{15}H_{12}O_3$ (M^+) 240.07865. Found 240.07912. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[2]

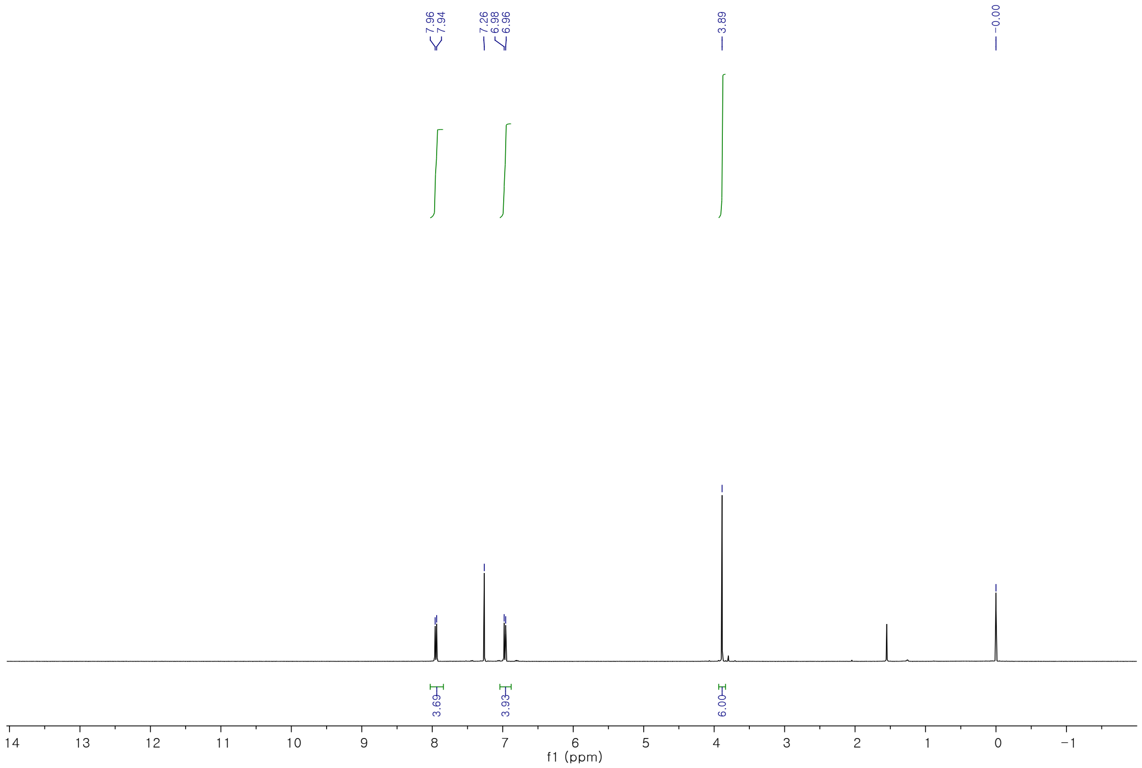


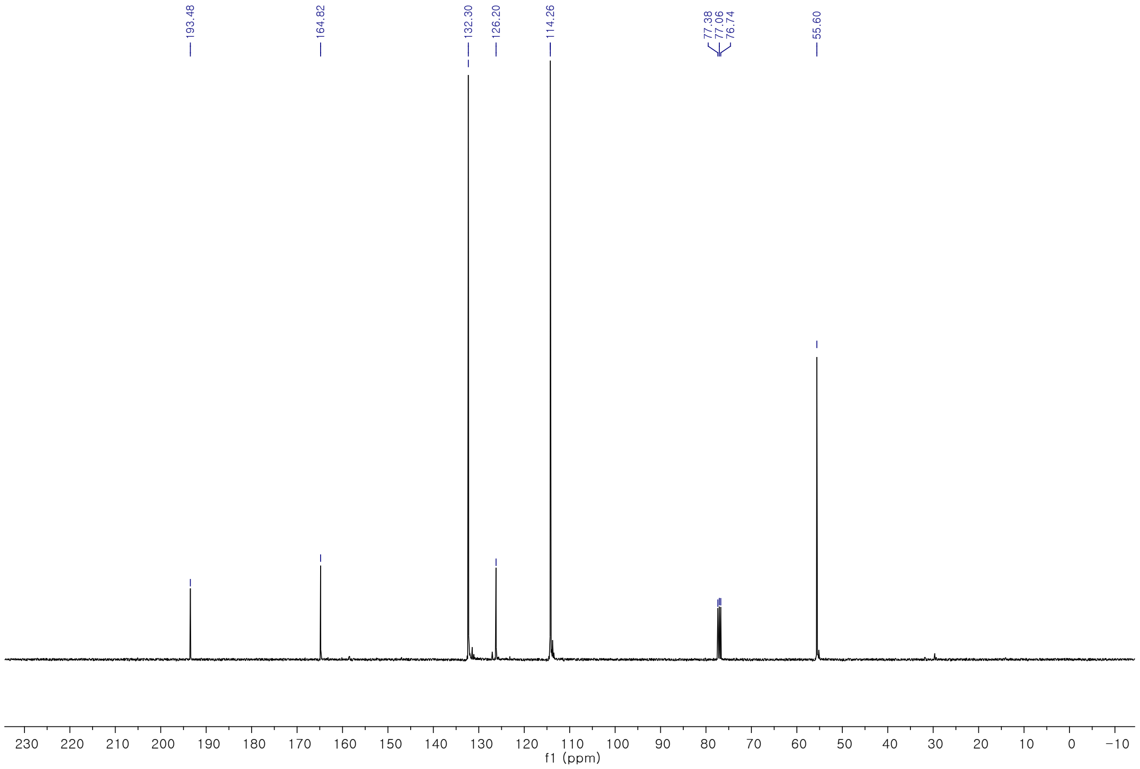


T2-6. 1,2-Bis(4-methoxyphenyl)ethane-1,2-dione

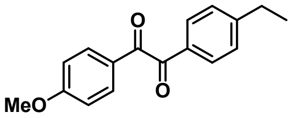


^{1}H NMR (CDCl$_3$) δ 3.88 (6H, s), 6.97 (4H, d, *J* = 9.0 Hz), 7.96 (4H, d, *J* = 9.0 Hz); ^{13}C NMR (CDCl$_3$) δ 55.6, 114.2, 126.2, 132.1, 132.3, 164.8, 193.4; MS (EI) m/z 270 (M$^+$, 10%), 135 (100), 120 (10), 105 (20), 77 (20); HRMS (EI) calcd for $C_{16}H_{14}O$ (M$^+$) 270.08921. Found 270.08973. The ^{1}H and ^{13}C NMR spectra were identical with those reported in theliterature.[2]

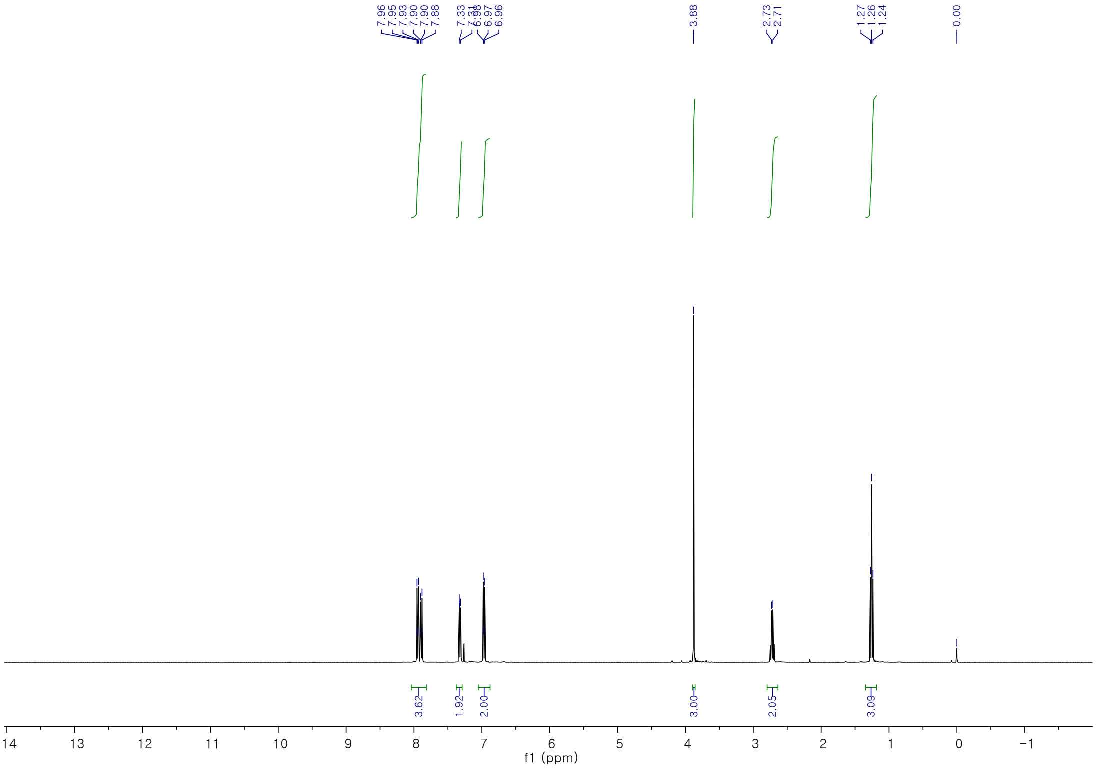


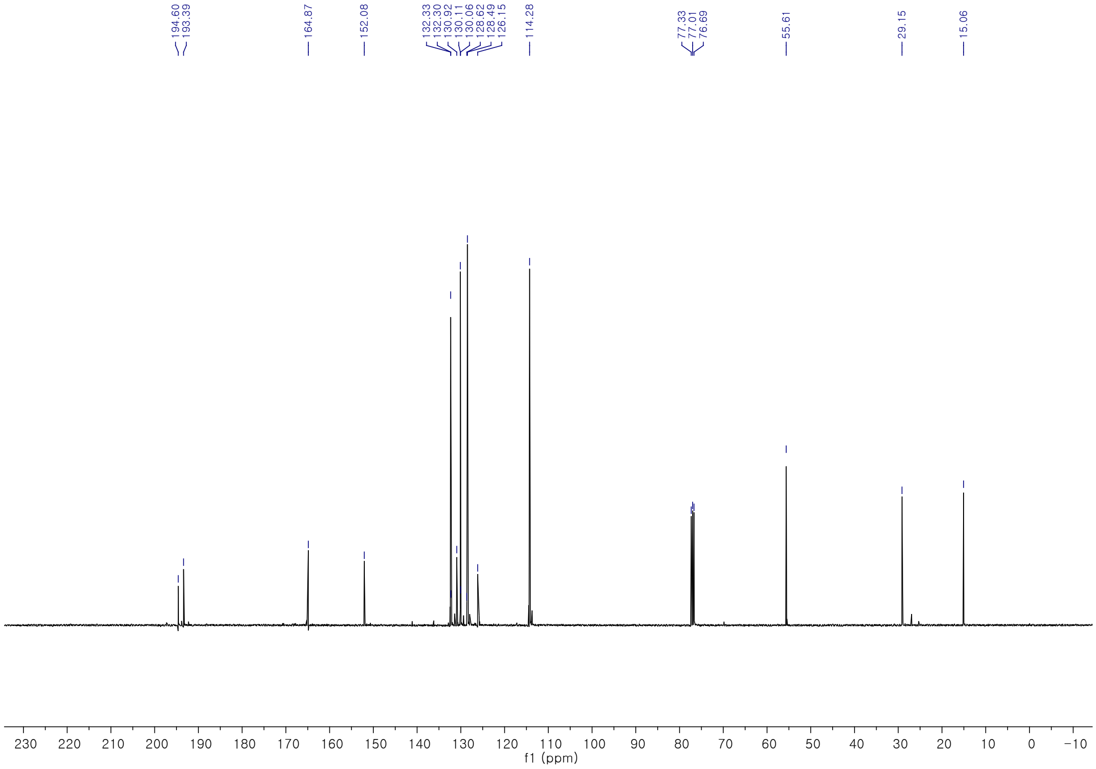


T2-7. 1-(4-Ethylphenyl)-2-(4-methoxyphenyl)ethane-1,2-dione

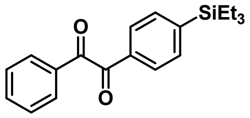


^{1}H NMR (CDCl$_3$): δ 7.94-7.89 (m, 2H),7.86 (d, 2H, *J*=8.2 Hz), 7.29 (d, 2H, *J*=8.2 Hz), 6.96-6.92 (m, 2H), 3.85 (s, 3H), 2.69 (q, 2H, *J*=7.6 Hz), 1.22 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (CDCl$_3$): δ 194.59, 193.37, 164.86, 152.06, 132.29, 130.93, 130.08, 128.46, 126.14, 114.27, 55.57, 29.11, 15.00; IR (KBr, cm^{-}1): ν 2968, 2934, 2841, 1665; HRMS-ESI (m/z): [M$^+$Na]$^+$ calcd for $C_{17}H_{16}O_3Na$ 291.0997; found 291.0994.[3]

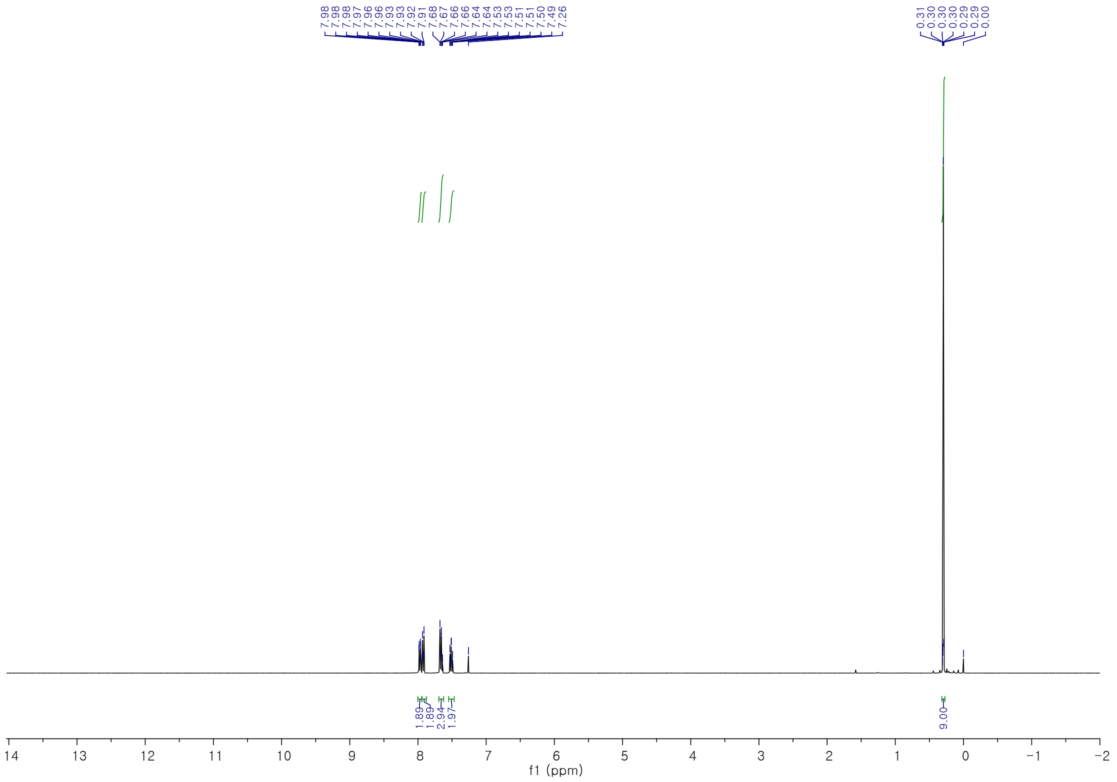


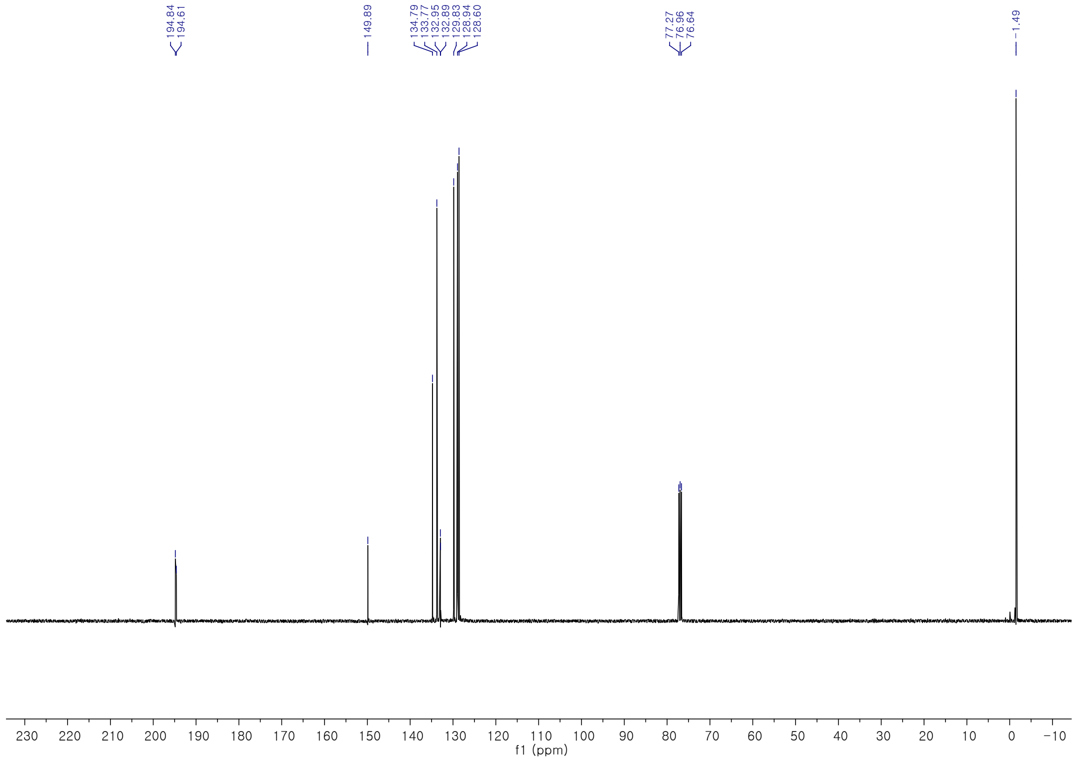


T2-8. 1-(4-Trimethylsilylphenyl)-2-phenylethane-1,2-dione

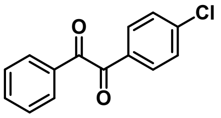


Yellow solid, mp 60-63°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97-7.90 (m, 4H), 7.67-7.63 (m, 3H), 7.48 (t, 2H, *J* = 7.8 Hz), 0.29(s, 9H); ^{13}C NMR ($CDCl_3$): δ 194.85, 194.61, 149.89, 134.79,133.79, 133.00, 132.96, 129.83, 128.96, 128.61, -1.49; IR (KBr, cm-1): ν 3066, 2957, 2897, 2802, 1675; HRMS-ESI (m/z): $[M^{+}Na]^+$ calcd for $C_{17}H_{18}O_2SiNa$ 305.0974; found 305.0971.[3]

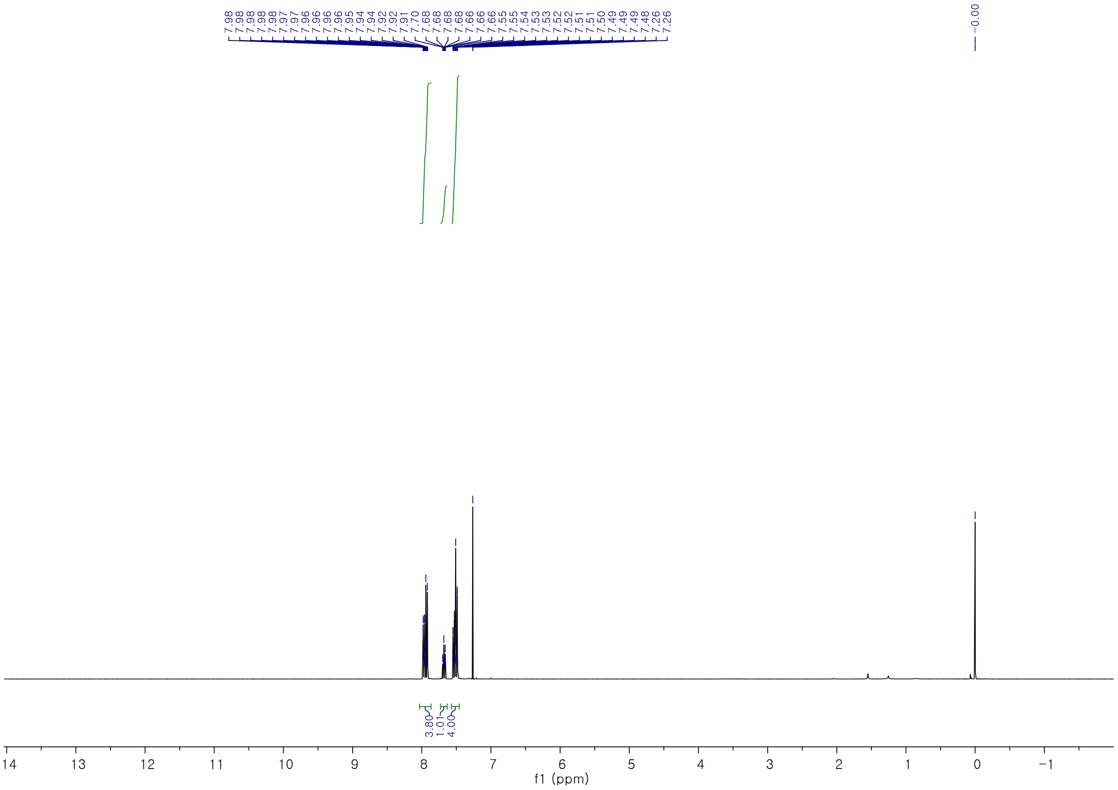


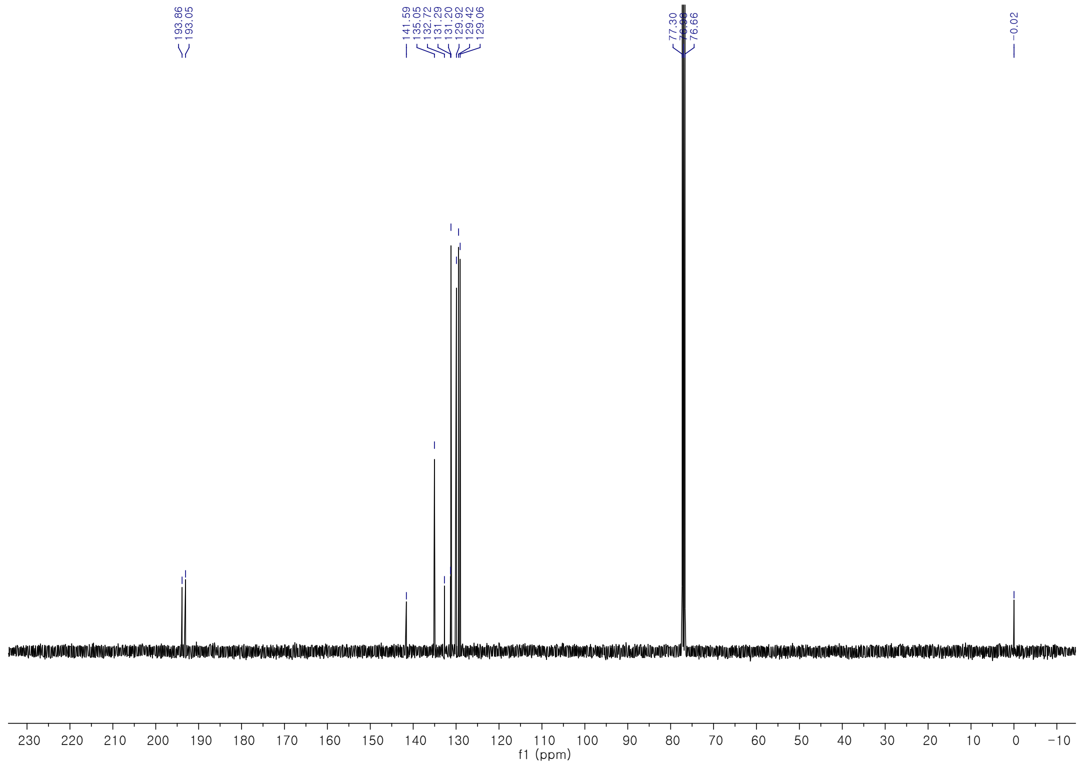


T2-9. 1-(4-Chlorophenyl)-2-phenylethane-1,2-dione

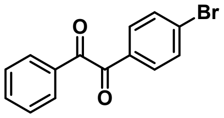


^{1}H NMR (CDCl$_3$) δ 7.45–7.51 (4H, m), 7.64 (1H, t, 7.4 Hz), 7.89–7.96 (4H, m); ^{13}C NMR (CDCl$_3$) δ 129.0, 129.4, 129.9, 131.1, 131.2, 131.3, 132.7, 135.0, 141.5, 193.0, 193.8; MS (EI) m/z 244 (M$^+$, 5%), 139 (40), 105 (100), 77 (40); HRMS (EI) calcd for C$_{14}$H$_9$Cl (M$^+$) 244.02911. Found 240.03001. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[2]

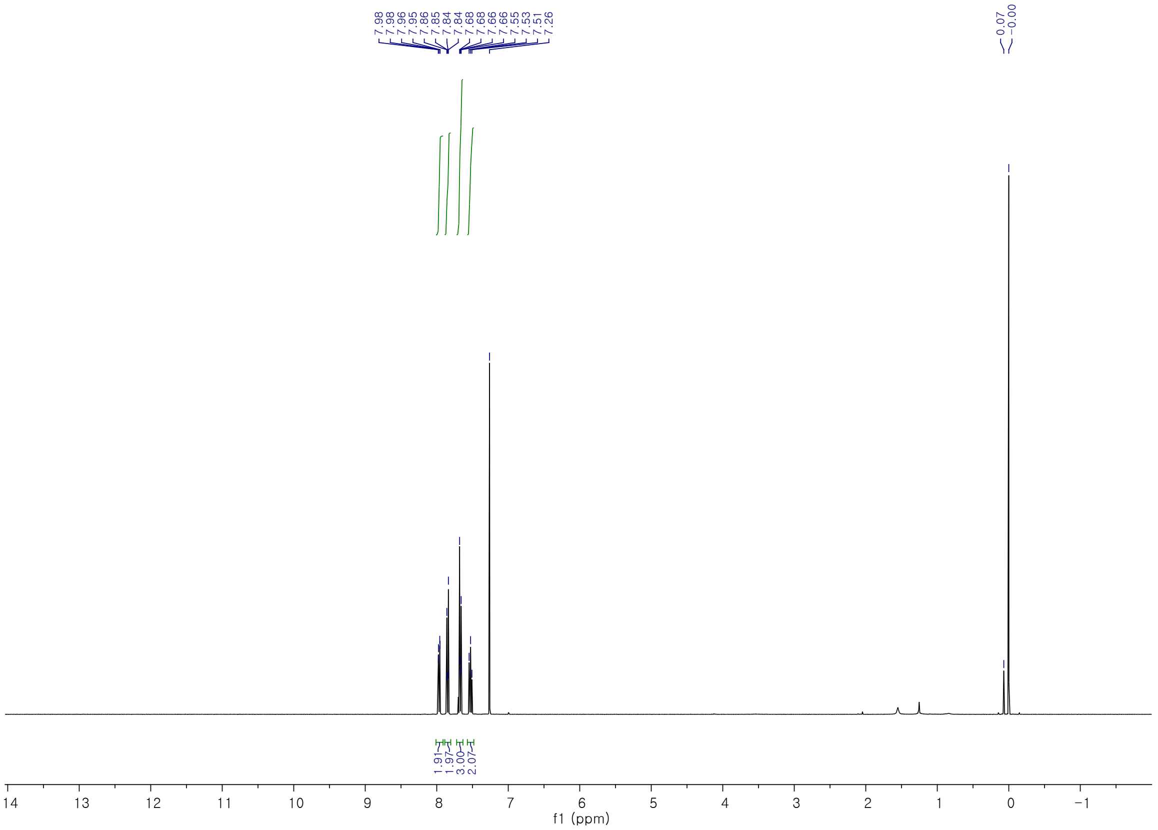


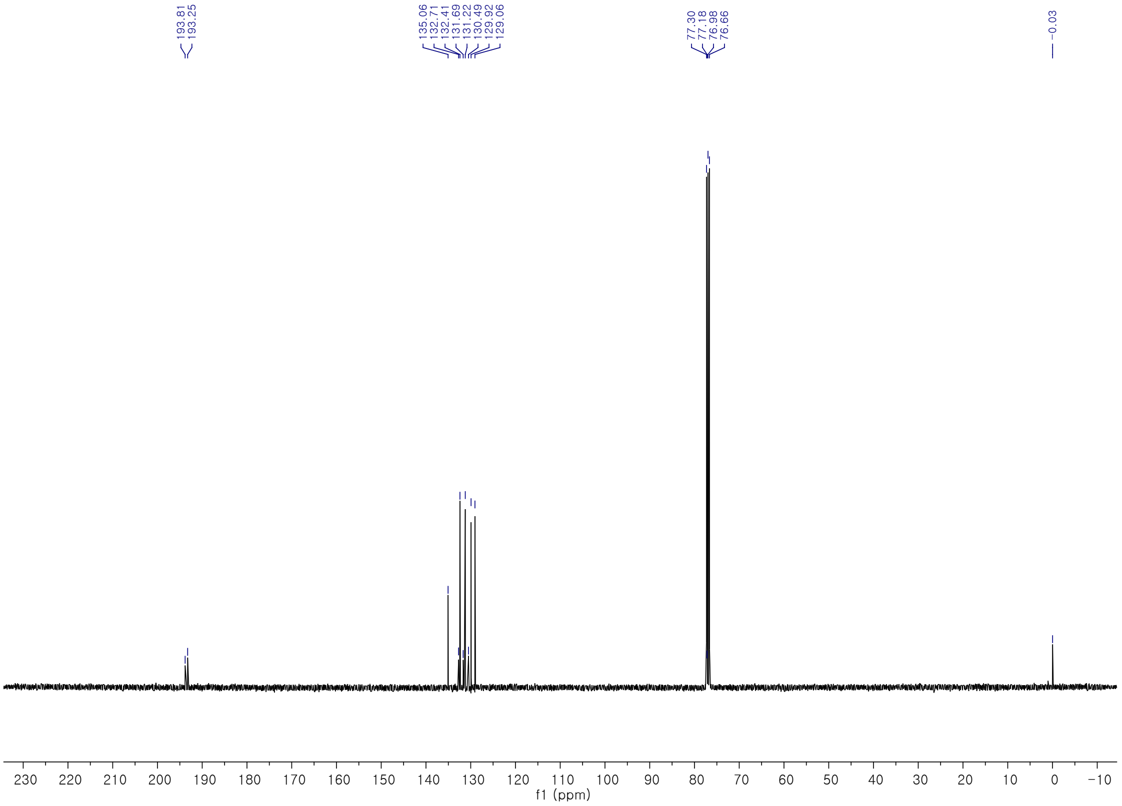


T2-10. 1-(4-bromophenyl)-2-phenylethane-1,2-dione

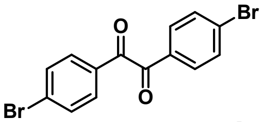


^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, J = 7.6Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.60 (t, J = 8.4 Hz, 3H), 7.45 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101MHz, CDCl3) δ 193.8, 193.3, 135.1, 132.7, 132.4, 131.7, 131.2, 130.5, 129.9, 129.1.[4]

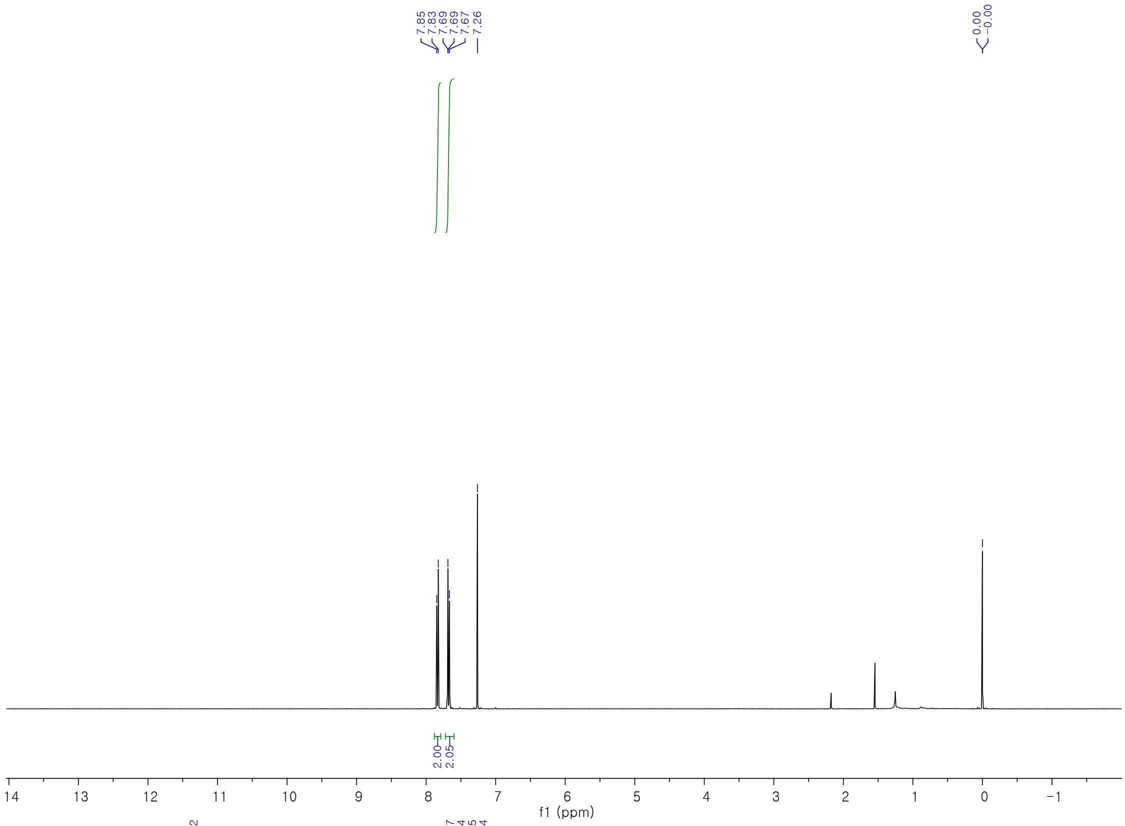


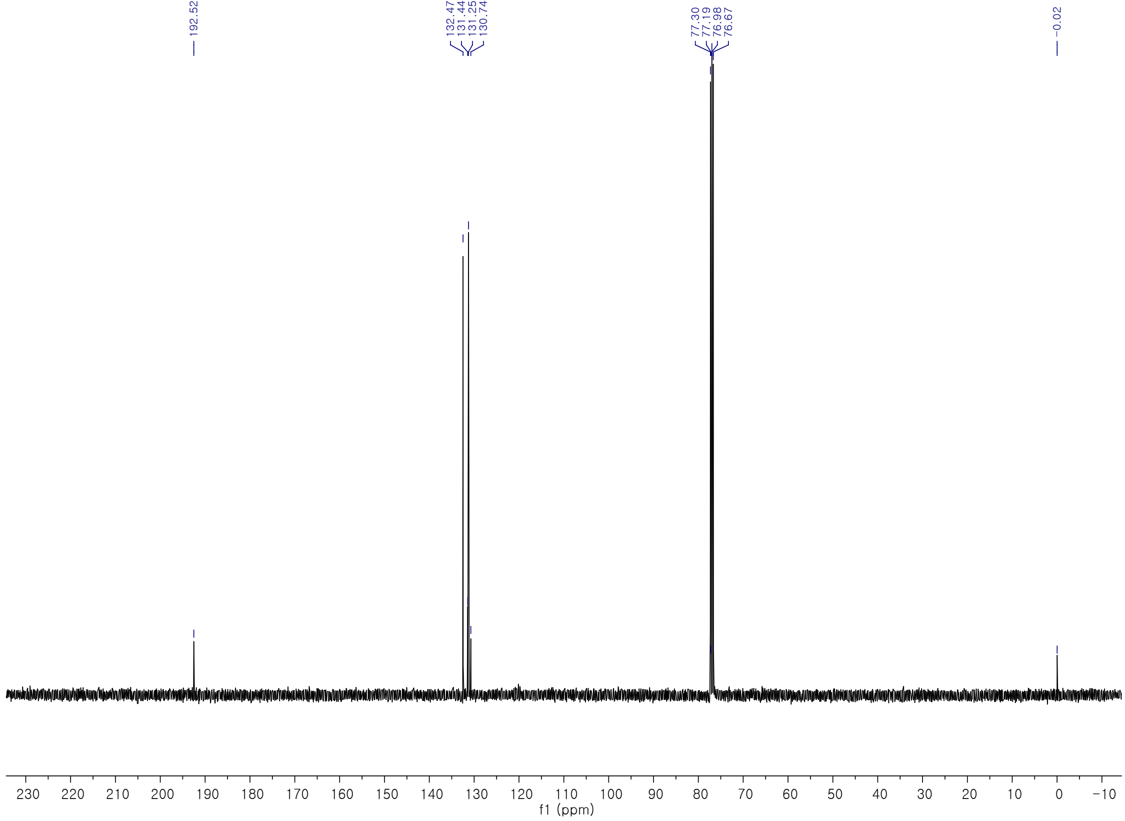


T2-11. 1,2-Bis(4-bromophenyl)ethane-1,2-dione

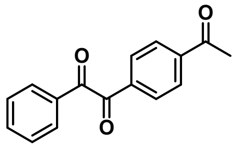


H NMR ($CDCl_3$) δ 7.83 (4H, d, *J* = 8.5 Hz), 7.67 (4H, d, *J* = 8.5 Hz)ppm.[5]

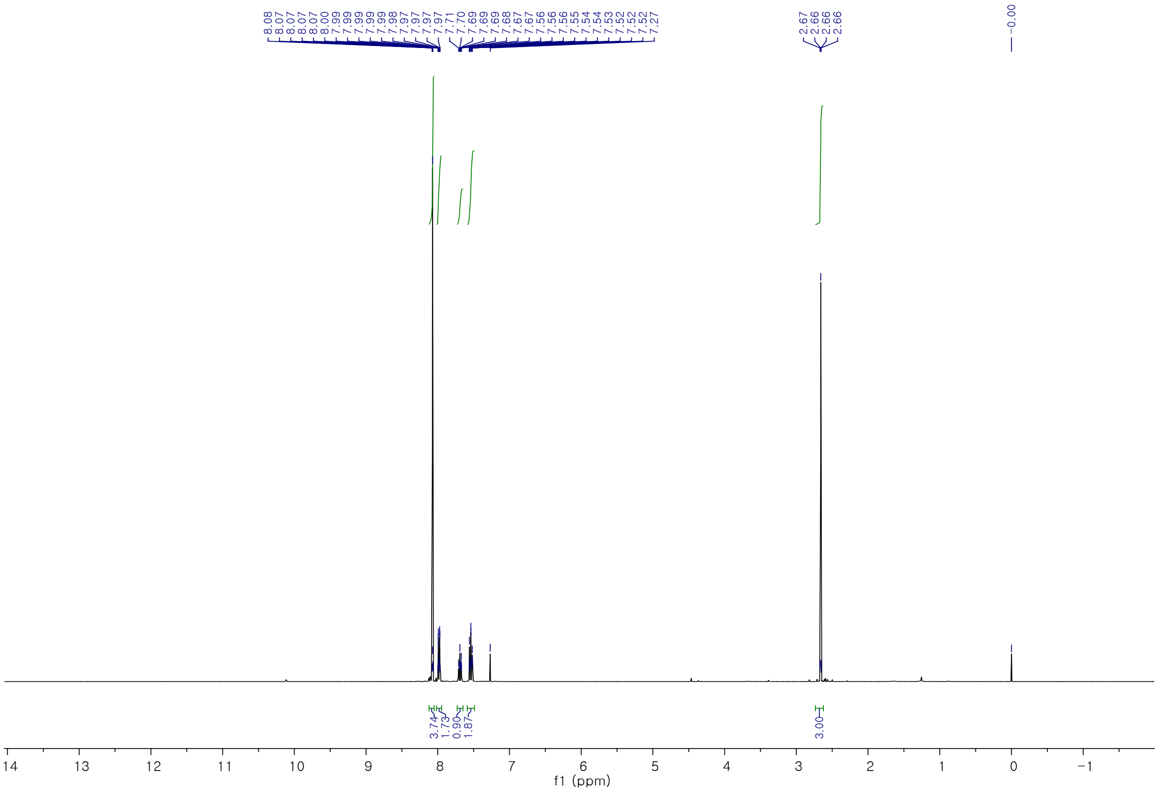


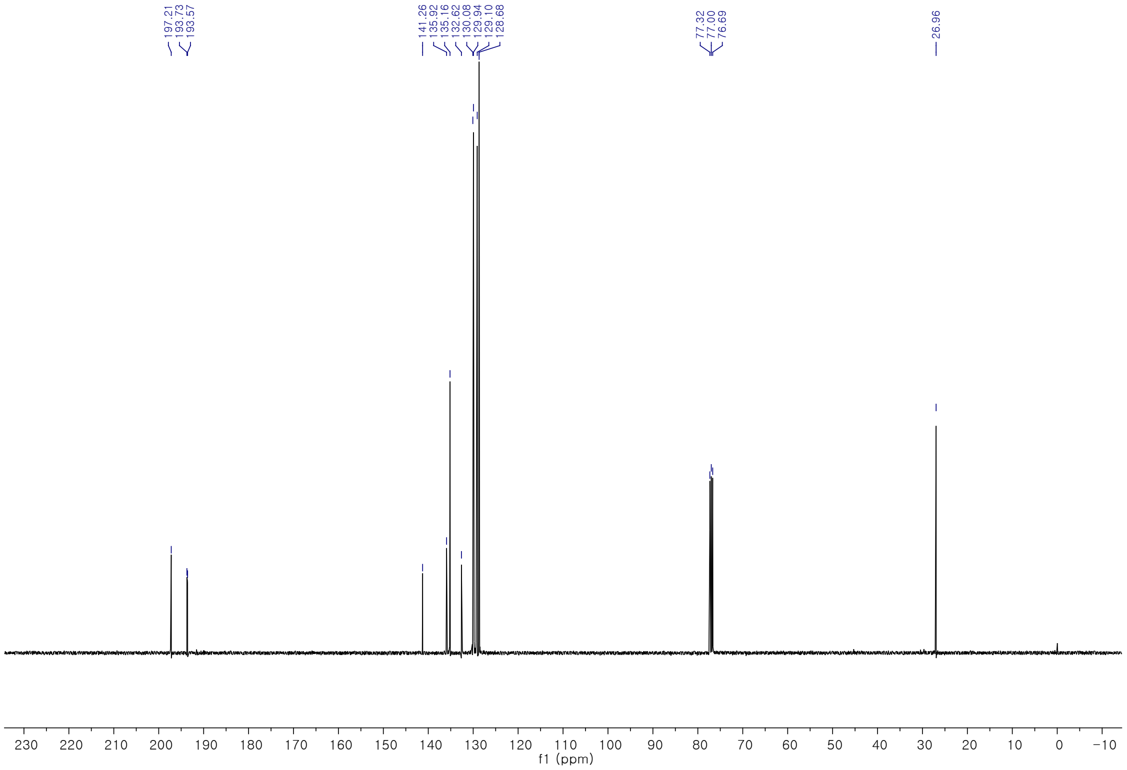


T2-12. 1-(4-acetylphenyl)-2-phenylethane-1,2-dione

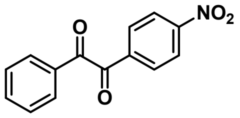


^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (s, 4H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 2.66 (s, 3H).[6]

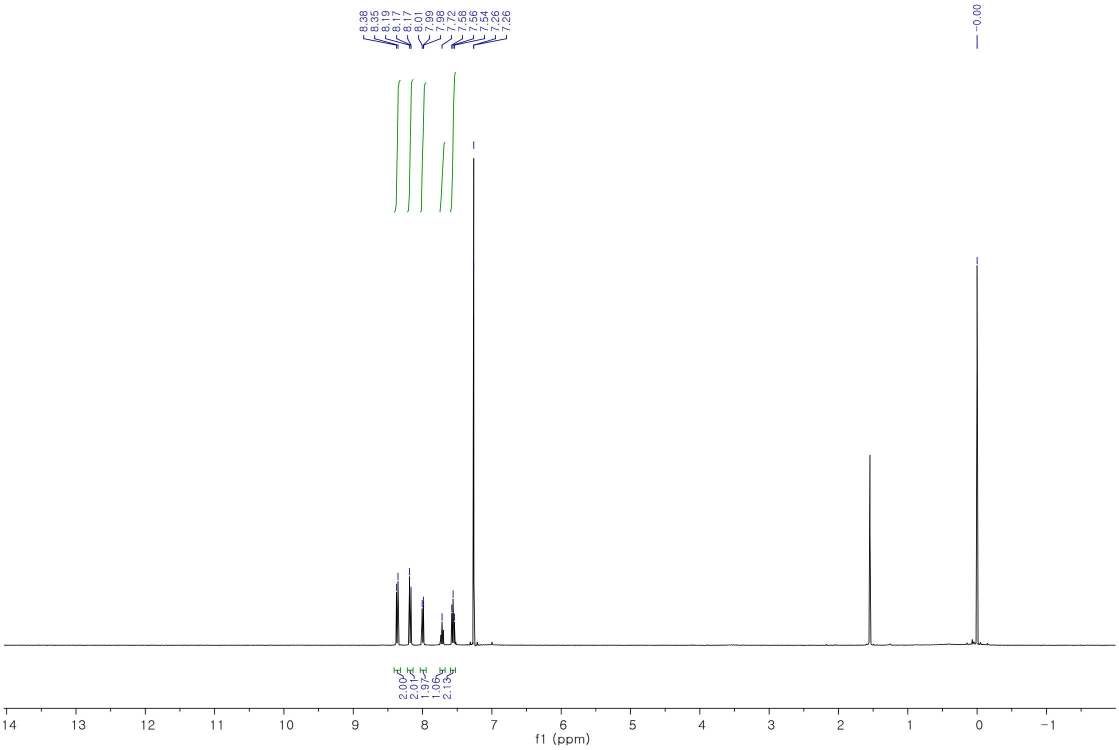


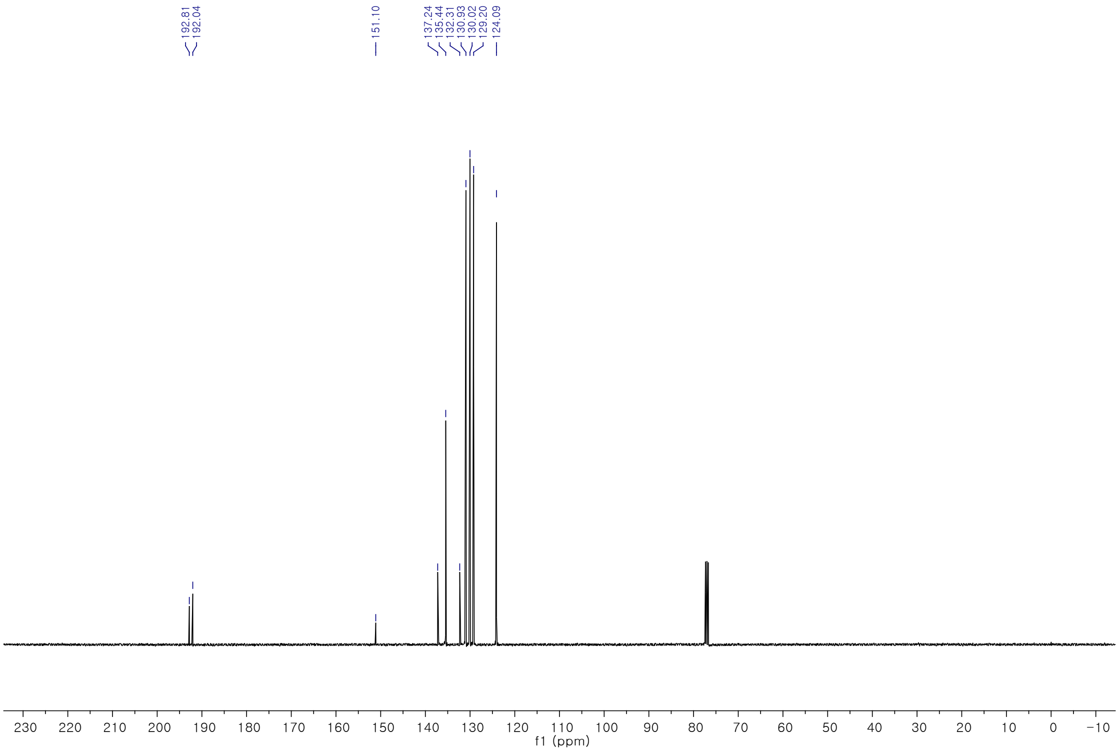


T2-13. 1-(4-Nitrophenyl)-2-phenylethane-1,2-dione

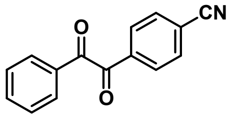


^{1}H NMR (CDCl$_3$) δ 7.55 (2H, dd, *J* = 7.2, 7.7 Hz), 7.71 (1H, t, *J* = 7.2 Hz), 7.99 (2H, d, *J* = 7.7 Hz), 8.17 (2H, d, 8.8 Hz), 8.34 (2H, d, 8.8 Hz); ^{13}C NMR (CDCl$_3$) δ 124.1, 129.2, 130.0, 130.9, 132.4, 135.4, 137.3, 151.1, 192.0, 192.8; MS (M$^+$H$^+$ m/z 256 (M$^+$, 10%), 154 (100), 136 (70), 105 (60); HRMS (FAB$^+$, m-nitrobenzylalchol) calcd for $C_{14}H_9NO_4$ (M$^+$H$^+$) 256.06098. Found 256.06021. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[2]

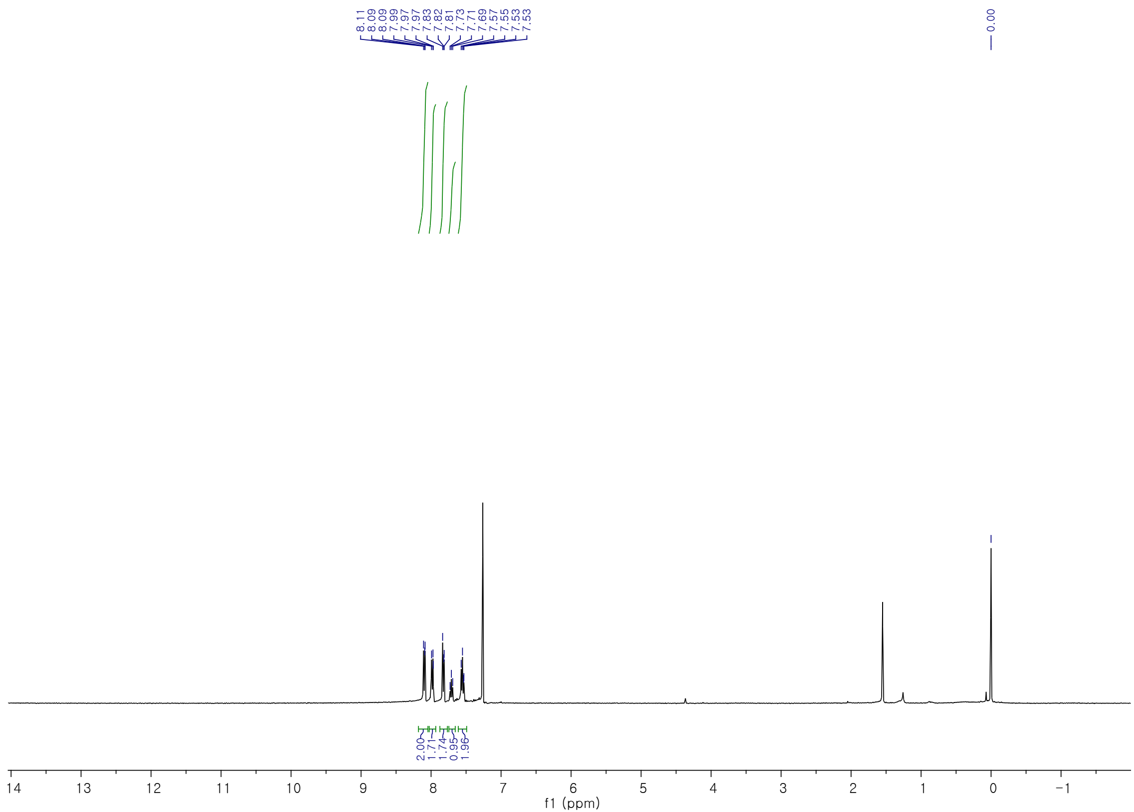


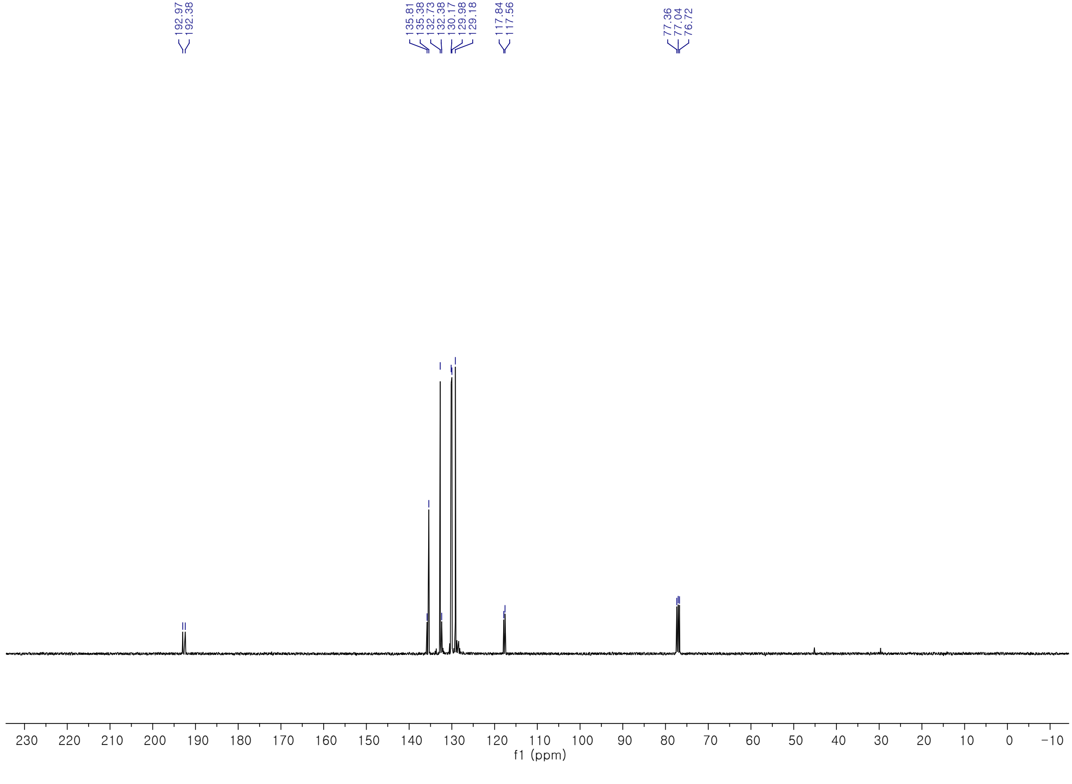


T2-14. 4-(2-Oxo)-2-phenylacetyl benzonitrile



^{1}H NMR ($CDCl_3$) δ 7.55 (2H, t, *J* = 8.0 Hz), 7.69 (1H, t, *J* = 8.0Hz), 7.80 (2H, d, *J* = 8.6 Hz), 7.96 (2H, d, 8.6 Hz), 8.08 (2H, d, 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 117.4,117.8, 129.1, 129.9, 130.1, 132.3, 132.6, 135.2, 135.7, 192.2, 192.8; MS (EI) m/z 235 (M^+, 5%), 135(10), 105 (100), 77 (40); HRMS (EI) calcd for $C_{15}H_9NO_2$ (M^+) 235.06333. Found 235.06300. The ^{1}H and ^{13}C NMR spectra were identical with those reported in the literature.[1]





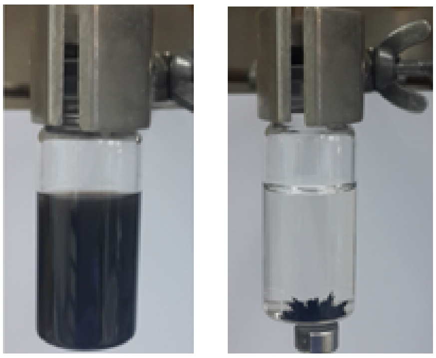


Figure S1. Magnetic separation of the Pd-Fe_3O_4 after the reaction.

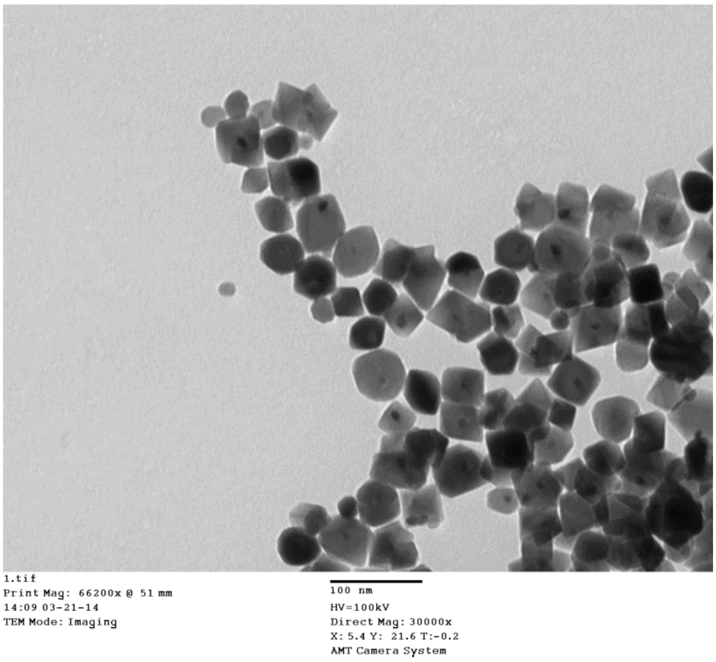


Figure S2. TEM images of the pristine Pd-Fe_3O_4

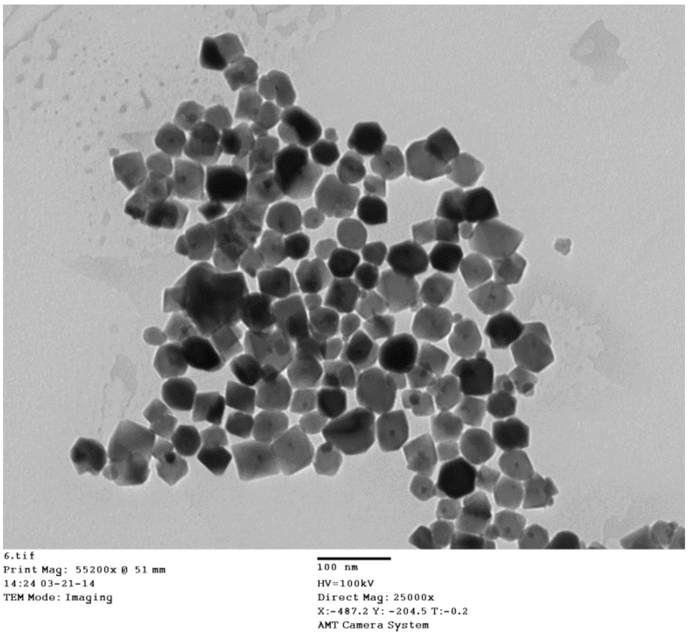


Figure S3. TEM images of the Pd-Fe3O4 after fifth recycling experiment

Pattern #	Compound Name	Formula	S-Q	System	Space Group	a	b	c	alpha	beta	gamma	Z
PDF 03-065-2867	Palladium, syn	Pd	0.97%	Cubic	Fm-3m (225)	3.8908						4
PDF 01-083-0112	Iron Oxide	Fe21.34 O32	99.03%	Cubic	P4332 (212)	8.3474						1

Figure S4. XRD pattern of the pristine Pd-Fe_3O_4 heterodimer nanocrystals

Pattern #	Compound Name	Formula	S-Q	System	Space Group	a	b	c	alpha	beta	gamma	Z
PDF 03-065-2867	Palladium, syn	Pd	1.43%	Cubic	Fm-3m (225)	3.8908						4
PDF 01-087-0246	Magnetite, syn	Fe2.9 O4	98.57%	Cubic	Fd-3m (227)	8.391						8

Figure S5. XRD pattern of Pd-Fe_3O_4 heterodimer nanocrystals after the fifth recycling experiment

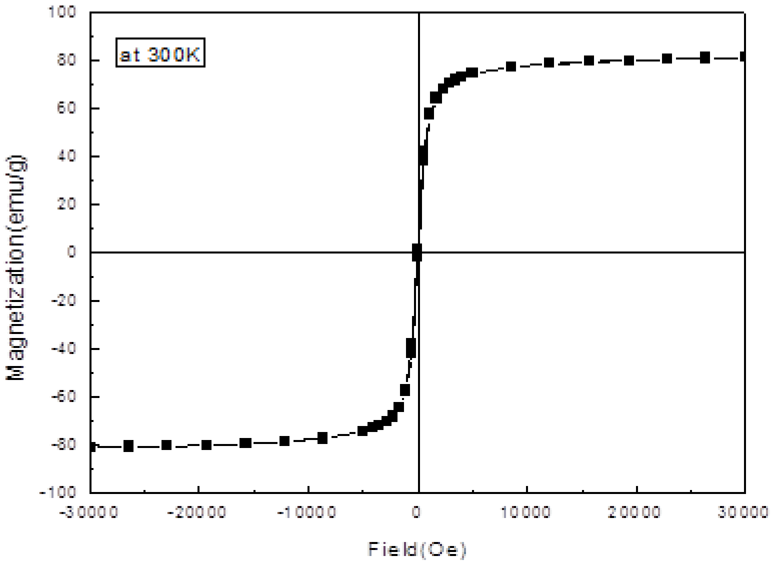


Figure S6. Magnetic behavior of the pristine Pd-Fe_3O_4

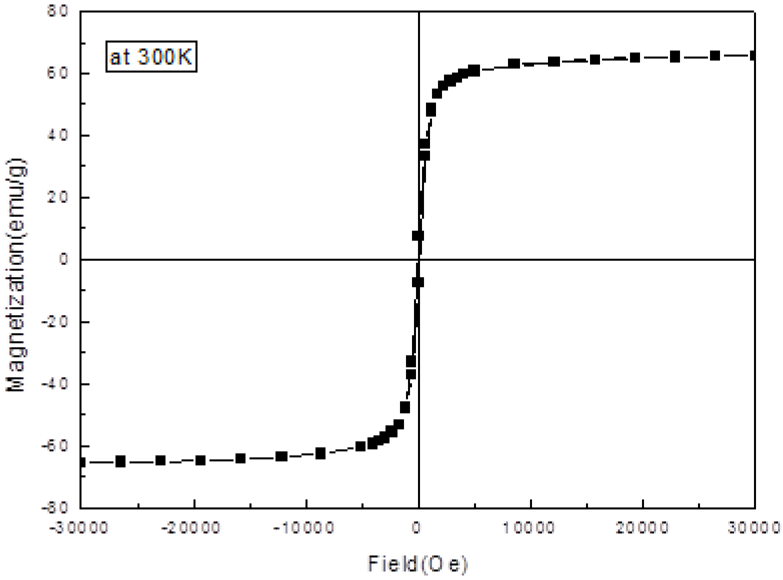


Figure S7. Magnetic behavior of the Pd-Fe_3O_4 after the fifth recycling experiment

References

1. S. Urgaonkar and J. G. Verkade, *J. Org. Chem.*, 2004, **69**, 5752-5755.
2. A. Giraud, O. Provot, J.-F. Peyrat, M. Alami and J.-D. Brion, *Tetrahedron*, 2006, **62**, 7667-7673.
3. A. Gao, F. Yang, J. Li and Y. Wu, *Tetrahedron*, 2012, **68**, 4950-4954.
4. W. Ren, Y. Xia, S. J. Ji, Y. Zhang, X. Wan and J. Zhao, *Org. Lett.*, 2009, **11**, 1841-1844.
5. F. Romanov-Michailidis, C. Besnard and A. Alexakis, *Org. Lett.*, 2012, **14**, 4906-4909.
6. M.-J. Wu, J.-H. Chu and Y.-J. Chen, *Synthesis*, 2009, **2009**, 2155-2162.