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Supporting Information

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$FeCl_2$-Catalyzed Selective C-C Bond Formation via Oxidative Activation of Benzylic C-H Bond

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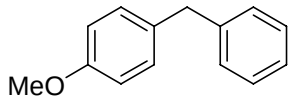
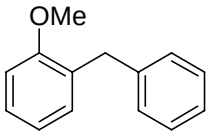
1) Experimental details and characterization data for all compounds

General information: ^{1}H NMR spectra were recorded on JEOL 300 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at JEOL 75.4 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. Elementary analyses were obtained on an Elementar Vario EL (Germany). IR spectra were recorded by a Nicolet 5MX-S infrared spectrometer. Melting points were recorded by Melting Point Apparatus. Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air at room temperature. Unless otherwise noted, all reactions were performed under a nitrogen atmosphere. All reagents were purchased from Acros, Aldrich, TCI, and Strem and used without further purification.

General Procedure for 4-Benzyl anisole (1c)[1]**:** 4-Benzylphenol (1.5 g, 8 mmol) in THF (3 ml) was added dropwise, under an nitrogen atmosphere, to sodium hydride (60% dispersion in mineral oils) (0.36 g, 9 mmol) in THF (18 ml) at 0 ^{o}C. The mixture was refluxed for 1 hour followed by cooling to room temperature and the addition of methyl iodide (1.36 g, 10 mmol) in THF (2.5 ml). The mixture was stirred at room temperature for 15 hours, quenched by saturated aq ammonium chloride (10 ml), diluted with water (15 ml) and extracted with methylene chloride. The combined organic phases were washed with 1 M sodium hydroxide and brine, dried over $MgSO_4$. Solvent was concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with ethyl acetate/petroleum ether = 1:9) and the fraction with an R_f = 0.8 was collected and concentrated to give the title product **1c**.

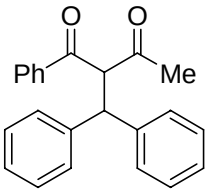


4-Benzyl anisole (1c). Isolated by flash column chromatography (ethyl acetate/petroleum ether = 1:9, R_f = 0.8). IR (neat): $\tilde{\nu}$ = 3027, 2959, 2928, 1611, 1511, 1494, 1454, 1301, 1247, 1176, 1106, 1074, 1037, 837, 797, 770, 725, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.66-7.48(m, 7H), 7.23(d, *J* = 8.1 Hz, 2H), 4.30(s, 2H), 4.05(s, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 157.8, 141.4, 133.0, 129.6, 128.6, 128.2, 125.8, 113.7, 54.7, 40.8 ppm; MS (EI) *m/z* (%) 199, 198(100), 183, 167, 153, 139, 128, 121, 115, 102, 92, 91, 77, 76, 63, 62, 51, 39, 27; HRMS calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1047.

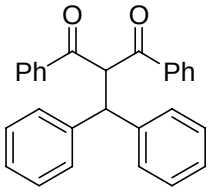


2-Benzyl anisole (1d).[1] Isolated by flash column chromatography (ethyl acetate/petroleum ether = 1:9, R_f = 0.7). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.16-7.06(m, 6H), 6.97-6.95(m, 1H), 6.79-6.73(m, 2H), 3.88(s, 2H), 3.68(m, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 157.3, 141.0, 130.3, 129.6, 128.9, 128.2, 127.4, 125.7, 120.4, 110.3, 55.3, 35.8 ppm.

General procedure for products 3: To a mixture of 1-benzoylacetone (81 mg, 0.5 mmol) and $FeCl_2$ (12.6 mg, 0.1 mmol), diphenylmethane (1 mL, 6.0 mmol) was added under a nitrogen atmosphere at room temperature. *t*-Butyl peroxide (0.188 mL, 1.0 mmol) was added dropwise into the mixture. The resulting mixture was stirred at room temperature for 36 h or at 80^{o}C for 8 h. The resulting solid was diluted with dichloromethane and purified by flash column chromatography on silica gel (eluent: dichloromethane/petroleum ether = 2:1). The fraction with an R_f = 0.5 was collected to give the desired product **3a**.

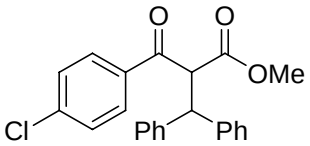


2-Benzhydryl-1-phenyl-butane-1,3-dione (3a).[2] Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). m.p. 149.8-150.7 ^{o}C; IR (neat): $\tilde{\nu}$ = 3063, 3028, 2922, 2843, 1722, 1675, 1596, 1494, 1449, 1356, 1273, 1203, 1179, 973, 769, 747, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.95(d, *J* = 7.8 Hz, 2H), 7.53-7.03(m, 13H), 5.62(d, *J* = 12.0 Hz, 1H), 5.10(d, *J* = 12.0 Hz, 1H), 2.04(s, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 203.0, 194.2, 141.7, 141.2, 136.9, 133.6, 129.0, 128.7, 128.6, 128.1, 127.7, 127.1, 126.7, 68.9, 51.5, 27.8 ppm.

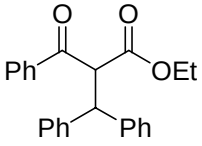


2-Benzhydryl-1,3-diphenyl-propane-1,3-dione (3b).[2,3] Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). m.p. 228.6-230.2 ^{o}C; IR (neat): $\tilde{\nu}$ = 3059, 3013, 1691, 1660, 1595, 1495, 1448, 1321, 1290, 1264, 1202, 1182, 1029, 994, 774, 748, 705, 689 cm^{-1};

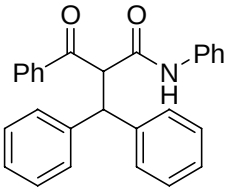
^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.82(dd, J = 8.7, 1.5 Hz, 4H), 7.48-7.43(m, 2H), 7.35-7.29(m, 4H), 7.27-7.24(m, 4H), 7.16-7.11(m, 4H), 7.07-7.02(m, 2H), 6.35(d, J = 11.7 Hz, 1H), 5.32(d, J = 11.7 Hz, 1H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 194.1, 141.7, 136.9, 133.2, 128.6, 128.5, 128.4, 128.3, 126.6, 62.3, 52.4 ppm.



Methyl 2-benzhydryl-3-(4-chlorophenyl)-3-oxopropanoate (3c). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). IR (neat): $\tilde{\nu}$ = 3092, 3028, 2951, 1743, 1687, 1588, 1570, 1494, 1452, 1434, 1401, 1289, 1264, 1206, 1154, 1093, 1012, 969, 840, 821, 758, 748, 703 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.92(d, J = 8.4 Hz, 2H), 7.38-7.01(m, 12H), 5.38(d, J = 11.7 Hz, 1H), 5.07(d, J = 11.7 Hz, 1H), 3.44(s, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 191.7, 167.9, 141.4, 141.3, 140.1, 134.8, 130.0, 129.0, 128.6, 128.5, 127.9, 127.6, 126.9, 126.6, 59.2, 52.6, 50.9 ppm; MS (EI) *m/z* (%) 378, 360, 347, 319, 301, 239, 207, 179, 167, 152, 139(100), 115, 111, 91, 75, 59, 51, 39, 28; HRMS calcd for $C_{23}H_{19}O_3{}^{35}Cl$: 378.1023; found: 378.1018.

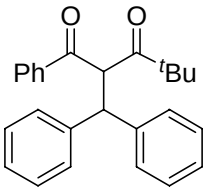


Ethyl 2-benzhydryl-3-oxo-3-phenylpropanoate (3d).[3] Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.6). m.p. 141.9-143.1 ^{o}C; IR (neat): $\tilde{\nu}$ = 3407, 3064, 3027, 2917, 2852, 1596, 1492, 1460, 1423, 1374, 1305, 1215, 1129, 1019, 937, 912, 750, 741, 692, 599 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 8.01(d, J = 7.2 Hz, 2H), 7.57-7.02(m, 13), 5.41(d, J = 12.0 Hz, 1H), 5.08(d, J = 12.0 Hz, 1H), 3.94-3.88(m, 2H), 0.92(t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 192.9, 167.8, 141.8, 136.7, 133.7, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.0, 126.7, 61.7, 59.5, 51.0, 13.8 ppm.

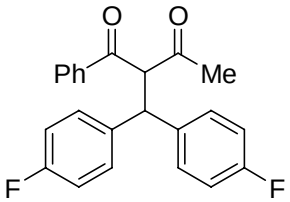


2-Benzhydryl-3-oxo-N,3-diphenylpropanamide (3e). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.3). m.p. 202.2-202.8 ^{o}C; IR (neat): $\tilde{\nu}$ = 3283, 3060, 3027, 2919, 1687, 1651, 1597, 1540, 1498, 1446, 1328, 1266, 1205, 1087, 1029, 1001, 741, 695

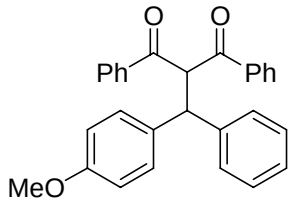
cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 8.04-7.96(m, 4H), 7.58-7.02(m, 16H), 5.42(d, J = 12.0 Hz, 1H), 4.95(d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 198.4, 164.7, 141.1, 140.6, 137.1, 136.9, 134.0, 128.8, 128.7, 128.6, 128.2, 127.7, 127.2, 126.9, 124.6, 120.2, 62.7, 54.1 ppm; MS (EI) *m/z* (%) 405, 300(100), 207, 178, 167, 152, 131, 105, 93, 77, 51, 39, 28; HRMS calcd for $C_{28}H_{23}O_2N$: 405.1729; found: 405.1717.



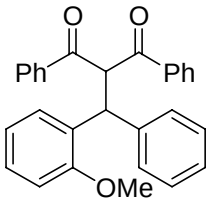
2-Benzhydryl-4,4-dimethyl-1-phenylpentane-1,3-dione (3f). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). m.p. 218.5-218.9 ^{o}C; IR (neat): $\tilde{\nu}$ = 3059, 2971, 2925, 2864, 1712, 1661, 1590, 1450, 1291, 1264, 1196, 1061, 991, 768, 745, 708, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.80(dd, J = 7.2, 1.5 Hz, 2H), 7.47-7.42(m, 10H), 7.05-7.00(m, 2H), 6.96-6.91(m, 1H), 5.95(d, J = 11.4 Hz, 1H), 5.10(d, J = 11.4 Hz, 1H), 0.90(s, 9H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 207.3, 194.6, 142.0, 140.6, 137.2, 132.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 126.7, 126.6, 60.8, 53.6, 45.4, 26.5 ppm; MS (EI) *m/z* (%) 316(100), 287, 273, 261, 245, 229, 215, 203, 189, 129, 115, 101, 88, 84, 55, 47, 29; MS (MALDI-TOF) *m/z* 393 $[M+Na]^+$ or 409 $[M+K]^+$.



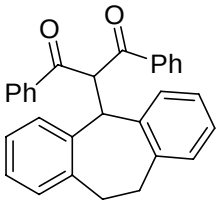
2-(bis(4-Fluorophenyl)methyl)-1-phenylbutane-1,3-dione (3g). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). m.p. 166.0-166.6 ^{o}C; IR (neat): $\tilde{\nu}$ = 1725, 1677, 1603, 1508, 1449, 1416, 1357, 1272, 1226, 1202, 1160, 1106, 1015, 972, 827, 788, 769, 717, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.84(d, J = 7.5 Hz, 2H), 7.45-7.41(m, 1H), 7.33-7.20(m, 4H), 7.07(dd, J = 8.7, 5.4 Hz, 2H), 6.89(dd, J = 8.7, 8.7 Hz, 2H), 6.72(dd, J = 8.4, 8.4 Hz, 2H), 5.44(d, J = 12.0 Hz, 1H), 5.01(d, J = 12.0 Hz, 1H), 1.94(s, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 202.3, 193.8, 163.3, 163.0, 160.1, 159.8, 137.3, 137.2, 136.8, 136.7, 136.6, 133.8, 129.6, 129.5, 129.2, 129.1, 128.7, 128.6, 116.0, 115.7, 115.6, 115.3, 68.9, 49.8, 27.8 ppm; MS (EI) *m/z* (%) 321 [100, $(M-MeCO)^+$], 259 $[M-PhCO]^+$, 203, 183, 120, 105, 95, 77, 43; Anal. Calcd for $C_{23}H_{18}F_2O_2$: C, 75.81%; H, 4.98%. Found: C, 75.49%; H, 5.19%.



2-[(4-Methoxy-phenyl)-phenyl-methyl]-1,3-diphenyl-propane-1,3-dione (3h). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.2). m.p. 202.7-203.6 ^oC; IR (neat): $\tilde{\nu}$ = 3060, 3017, 2931, 2835, 1696, 1664, 1610, 1596, 1580, 1512, 1495, 1448, 1320, 1260, 1199, 1179, 1114, 1078, 1033, 971, 934, 821, 804, 759, 724, 700, 688 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.83(d, J = 7.8 Hz, 4H), 7.48-7.02(m, 13H), 6.67(d, J = 8.4 Hz, 2H), 6.31(d, J = 11.7 Hz, 1H), 5.28(d, J = 11.7 Hz, 1H), 3.66(s, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 194.2, 194.0, 158.1, 142.0, 137.0, 136.9, 133.8, 133.2, 129.2, 128.6, 128.5, 128.4, 128.1, 126.5, 113.9, 62.5, 55.1, 51.6 ppm; MS (EI) *m/z* (%) 420, 315, 297, 237, 224, 197, 165, 153, 128, 115, 105(100), 77, 51, 39, 28; HRMS calcd for $C_{29}H_{24}O_3$: 420.1725; found: 420.1733.

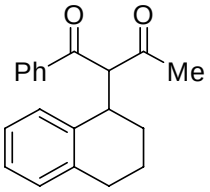


2-[(2-Methoxy-phenyl)-phenyl-methyl]-1,3-diphenyl-propane-1,3-dione (3i). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.3). m.p. 160.5-161.6 ^oC; IR (neat): $\tilde{\nu}$ = 3061, 2923, 2835, 1697, 1665, 1596, 1492, 1462, 1448, 1320, 1246, 1200, 1180, 1118, 1076, 1028, 972, 806, 755, 736, 700, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.78(d, J = 7.5 Hz, 4H), 7.41-7.17(m, 9H), 7.05-6.91(m, 4H), 6.71(dd, J = 7.5, 7.5 Hz, 1H), 6.57(d, J = 8.1 Hz, 1H), 6.44(d, J = 11.4 Hz, 1H), 5.53(d, J = 11.7 Hz, 1H), 3.55(s, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 194.9, 194.1, 156.9, 141.6, 137.1, 137.0, 133.1, 132.9, 130.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 126.2, 120.5, 111.1, 61.5, 55.2, 47.0 ppm; MS (EI) *m/z* (%) 420, 315, 297, 285, 223, 197, 181, 165, 149, 115, 105(100), 91, 77, 51, 41, 29; HRMS calcd for $C_{29}H_{24}O_3$: 420.1725; found: 420.1739.

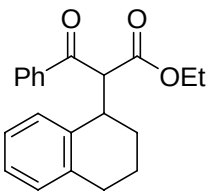


2-(10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-yl)-1,3-diphenyl-propane-1,3-dione (3j). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.4). m.p.

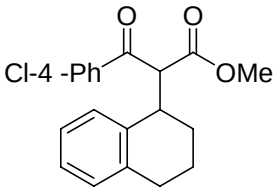
145.6-147.0 °C; IR (neat): $\tilde{\nu}$ = 3062, 3010, 2933, 1698, 1663, 1596, 1579, 1493, 1447, 1316, 1260, 1197, 1180, 1104, 1018, 986, 806, 763, 754, 740, 688 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.73(d, J = 7.5 Hz, 4H), 7.44-7.39(m, 2H), 7.31-7.25(m, 5H), 6.97-6.91(m, 7H), 6.51(d, J = 10.8 Hz, 1H), 5.28(d, J = 10.8 Hz, 1H), 3.67-3.62(m, 2H), 3.02-2.95(m, 2H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 194.0, 138.9, 137.8, 137.4, 133.0, 132.6, 130.4, 128.5, 128.3, 127.2, 126.0, 63.7, 54.7, 33.2 ppm; MS (EI) *m/z* (%) 398, 311, 293, 225, 223, 193(100), 192, 165, 152, 139, 115, 105, 91, 77, 51, 39, 28; MS (MALDI-TOF) *m/z* 439 $[M+Na]^+$; Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51%; H, 5.81%. Found: C, 86.49%; H, 5.84%.



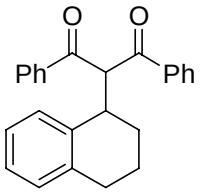
1-Phenyl-2-(1,2,3,4-tetrahydro-naphthalen-1-yl)-butane-1,3-dione (3k). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.6). The ratio of two diasteromers is 1.2:1. **Two diasteromers:** ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.86(d, J = 7.2 Hz, 2H), 7.68(d, J = 7.2 Hz, 2H), 7.51-7.24(m, 6H), 7.08-6.77(m, 8H), 4.91(d, J = 9.6 Hz, 1H), 4.86(d, J = 9.9 Hz, 1H), 3.92-3.88(m, 2H), 2.81-2.68(m, 4H), 2.14(s, 3H), 1.96(s, 3H), 1.83-1.64(m, 8H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 203.9, 203.5, 196.6, 195.3, 137.4, 137.3, 137.2, 136.8, 133.6, 133.3, 129.4, 129.3, 128.9, 128.8, 128.6, 128.4, 126.7, 126.5, 125.6, 125.5, 68.4, 67.2, 38.9, 38.4, 30.5, 28.5, 28.4, 28.3, 26.2, 26.0, 19.2, 18.8 ppm. **One isomer** (recrystallized from dichloromethane and petroleum ether): m.p. 113.2-114.5 °C; IR (neat): $\tilde{\nu}$ = 3062, 2937, 2871, 1719, 1676, 1596, 1491, 1448, 1356, 1278, 1261, 1209, 1158, 1080, 972, 769, 757, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.94(d, J = 8.1 Hz, 2H), 7.60-7.43(m, 3H), 7.16-7.00(m, 4H), 4.99(d, J = 9.3 Hz, 1H), 4.00-3.96(m, 1H), 2.88-2.73(m, 2H), 2.04(s, 3H), 1.83-1.74(m, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 204.0, 195.4, 137.4, 137.3, 133.7, 129.5, 128.9, 128.6, 128.5, 126.8, 125.7, 67.2, 38.9, 30.6, 28.5, 26.2, 19.2 ppm; MS (EI) *m/z* (%) 292, 274, 249(100), 231, 215, 202, 187, 169, 130, 128, 115, 105, 91, 77, 65, 63, 43, 39, 28; HRMS calcd for $C_{20}H_{20}O_2$: 292.1463; found: 292.1469.



Ethyl 2-(1,2,3,4-tetrahydronaphthalen-1-yl)-3-oxo-3-phenylpropanoate (3l). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.6). The ratio of two diasteromers is 1:1. **Two diasteromers:** IR (neat): $\tilde{\nu}$ = 3059, 2936, 2868, 1733, 1687, 1597, 1580, 1491, 1448, 1367, 1330, 1280, 1263, 1238, 1211, 1174, 1151, 1114, 1096, 1031, 1001, 741, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.90(d, J = 7.2 Hz, 2H), 7.74(d, J = 7.2 Hz, 2H), 7.47-7.24(m, 6H), 7.05-6.80(m, 8H), 4.77(d, J = 9.0 Hz, 1H), 4.65(d, J = 9.6 Hz, 1H), 4.03(q, J = 7.2 Hz, 2H), 3.92-3.79(m, 4H), 2.77-2.65(m, 4H), 1.90-1.60(m, 8H), 1.05(t, J = 7.2 Hz, 3H), 0.92(t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 195.0, 193.8, 168.9, 168.4, 137.2, 137.1, 137.0, 136.9, 136.8, 136.7, 133.4, 133.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 126.5, 126.2, 125.4, 125.2, 61.2, 61.1, 59.0, 58.9, 37.9, 37.8, 28.7, 28.5, 26.1, 26.0, 19.7, 18.9, 13.8, 13.6 ppm; MS (EI) *m/z* (%) 322, 304, 277, 249, 231, 217, 193, 171, 147, 130(100), 115, 105, 91, 77, 63, 51, 39, 29; HRMS calcd for $C_{21}H_{22}O_3$: 322.1569; found: 322.1562.

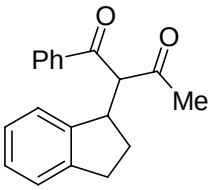


Methyl 3-(4-chlorophenyl)-2-(1,2,3,4-tetrahydronaphthalen-1-yl)-3-oxopropanoate (3m). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.6). The ratio of two diasteromers is 1:1. **Two diasteromers:** IR (neat): $\tilde{\nu}$ = 3059, 2949, 1737, 1687, 1588, 1571, 1489, 1452, 1434, 1400, 1334, 1282, 1262, 1209, 1153, 1093, 1011, 959, 844, 775, 759, 739, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.83(d, J = 8.7 Hz, 2H), 7.64(d, J = 8.7 Hz, 2H), 7.33(d, J = 8.7 Hz, 2H), 7.23(d, J = 8.7 Hz, 2H), 7.10-6.77(m, 8H), 4.72(d, J = 9.6 Hz, 1H), 4.63(d, J = 9.6 Hz, 1H), 3.88-3.80(m, 2H), 3.59(s, 3H), 3.45(s, 3H), 2.79(m, 4H), 1.88-1.62(m, 8H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 193.9, 192.6, 169.2, 168.7, 140.1, 139.8, 137.2, 137.0, 136.8, 136.7, 135.1, 129.8, 129.7, 129.3, 129.2, 129.1, 128.8, 128.7, 128.5, 126.7, 126.5, 125.4, 125.3, 59.0, 58.7, 52.4, 52.3, 38.1, 38.0, 28.6, 28.5, 26.1, 26.0, 19.4, 19.0 ppm; MS (EI) *m/z* (%) 342, 324, 283, 265, 247, 230, 203, 171, 143, 130(100), 128, 111, 91, 75, 57, 51, 39, 27; HRMS calcd for $C_{20}H_{19}O_3{}^{35}Cl$: 342.1023; found: 342.1018.

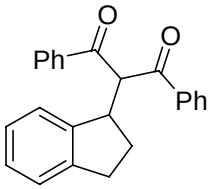


1,3-Diphenyl-2-(1,2,3,4-tetrahydro-naphthalen-1-yl)-propane-1,3-dione (3n). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). m.p. 119.5-120.2 ^oC;

IR (neat): $\tilde{\nu}$ = 3063, 3013, 2938, 1697, 1669, 1596, 1581, 1492, 1448, 1330, 1279, 1199, 1181, 1002, 760, 739, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.86(d, J = 7.8 Hz, 2H), 7.71(d, J = 7.8 Hz, 2H), 7.60-7.27(m, 7H), 7.03-6.79(m, 3H), 5.87(d, J = 8.7 Hz, 1H), 4.20-4.14(m, 1H), 2.94-2.72(m, 2H), 2.00-1.74(m, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 196.1, 194.7, 137.3, 137.2, 136.9, 136.8, 133.3, 133.1, 129.3, 128.9, 128.7, 128.6, 128.4, 126.4, 125.5, 60.9, 39.1, 28.9, 26.4, 19.9 ppm; MS (EI) *m/z* (%) 354, 336, 249(100), 231, 225, 202, 191, 178, 171, 153, 130, 115, 105, 91, 77, 69, 51, 39, 28; HRMS calcd for $C_{25}H_{22}O_2$: 354.1620; found: 354.1629.

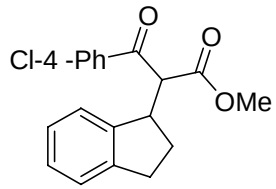


2-Indan-1-yl-1-phenyl-butane-1,3-dione (3o). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.6). The ratio of two diasteromers is 1.2:1. **Two diasteromers:** IR (neat): $\tilde{\nu}$ = 3067, 2946, 2843, 1721, 1673, 1596, 1579, 1477, 1448, 1357, 1278, 1204, 1180, 1025, 1001, 978, 755, 720, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.99(d, J = 8.1 Hz, 2H), 7.94(d, J = 8.1 Hz, 2H), 7.61-7.39(m, 6H), 7.24-7.07(m, 6H), 6.98-6.91(m, 2H), 4.75(d, J = 9.9 Hz, 1H), 4.67(d, J = 10.2 Hz, 1H), 4.34-4.19(m, 2H), 3.03-2.75(m, 4H), 2.33-2.15(m, 2H), 2.23(s, 3H), 2.20(s, 3H), 1.90-1.65(m, 2H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 203.4, 203.2, 195.8, 195.5, 144.2, 143.9, 143.8, 143.6, 137.0, 136.9, 133.8, 133.7, 128.9, 128.8, 127.2, 127.1, 126.4, 126.3, 124.8, 124.7, 124.5, 124.2, 68.9, 67.9, 45.3, 44.7, 31.0, 30.9, 30.8, 30.0, 29.3, 27.7 ppm; MS (EI) *m/z* (%) 278, 250, 236, 235(100), 217, 202, 173, 163, 157, 147, 129, 128, 116, 105, 91, 77, 65, 63, 43, 39, 28; HRMS calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1309.



2-Indan-1-yl-1,3-diphenyl-propane-1,3-dione (3p). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.5). m.p. 117.1-121.8 ^oC; IR (neat): $\tilde{\nu}$ = 2960, 2934, 2901, 1698, 1666, 1597, 1581, 1479, 1449, 1322, 1269, 1200, 1182, 1098, 1027, 1002, 816, 797, 765, 754, 707, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.85(d, J = 8.4 Hz, 2H), 7.73(d, J = 8.1 Hz, 2H), 7.45-6.78(m, 10H), 5.46(d, J = 9.3 Hz, 1H), 4.38-4.33(m, 1H), 2.90-2.71(m, 2H), 2.20-2.13(m, 1H), 1.86-1.79(m, 1H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 195.2, 194.7, 144.2, 143.9, 136.9, 136.6, 133.4, 133.3, 128.8, 128.7, 128.6, 128.5, 127.0, 126.1, 124.7, 124.6,

61.3, 45.8, 31.0, 30.7 ppm; MS (EI) *m/z* (%) 338, 337, 235(100), 217, 202, 157, 147, 128, 116, 105, 91, 77, 69, 51, 43, 27; HRMS calcd for $C_{24}H_{20}O_2$: 340.1463; found: 340.1461.



Methyl 3-(4-chlorophenyl)-2-(2,3-dihydro-1H-inden-1-yl)-3-oxopropanoate (3q). Isolated by flash column chromatography (dichloromethane/petroleum ether = 2:1, R_f = 0.7). The ratio of two diasteromers is 1:1. **Two diasteromers:** IR (neat): $\tilde{\nu}$ = 2952, 1740, 1686, 1588, 1571, 1478, 1458, 1434, 1401, 1264, 1206, 1179, 1154, 1093, 1012, 954, 910, 826, 756, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.85(d, *J* = 8.7 Hz, 2H), 7.79(d, *J* = 8.4 Hz, 2H), 7.31(d, *J* = 8.7 Hz, 2H), 7.7.28(d, *J* = 8.7 Hz, 2H), 7.13-6.83(m, 8H), 4.44(d, *J* = 9.3 Hz, 1H), 4.41(d, *J* = 9.1 Hz, 1H), 4.15-4.05(m, 2H), 3.58(s, 6H), 2.95-2.68(m, 4H), 2.30-2.16(m, 2H), 1.93-1.84(m, 1H), 1.67-1.58(m, 1H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS) δ = 193.0, 192.9, 168.9, 168.7, 144.1, 143.8, 143.5, 143.4, 140.2, 140.0, 134.8, 134.7, 130.0, 129.9, 129.0, 128.9, 127.2, 127.1, 126.2, 126.1, 124.7, 124.6, 124.4, 124.2, 58.5, 58.3, 52.5, 52.4, 44.7, 44.4, 30.8, 30.6, 30.5, 30.2 ppm; MS (EI) *m/z* (%) 328, 269, 251, 233, 213, 189, 181, 157, 139, 129, 116(100), 111, 91, 75, 69, 57, 43, 29; HRMS calcd for $C_{19}H_{17}O_3{}^{35}Cl$: 328.0866; found: 328.0856.

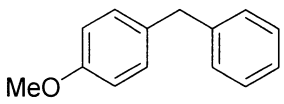
References:

[1] J. A. Wilkinson, S. B. Rossington, S. Ducki, J. Leonard, N. Hussain, *Tetrahedron* **2006**, *62*, 1833.

[2] A. Gonzalez, J. Marquet, M. Moreno-Manas, *Tetrahedron Lett.* **1988**, *29*, 1469.

[3] K. Yamamura, *J. Org. Chem.* **1978**, *43*, 724.

2) PDF file of copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds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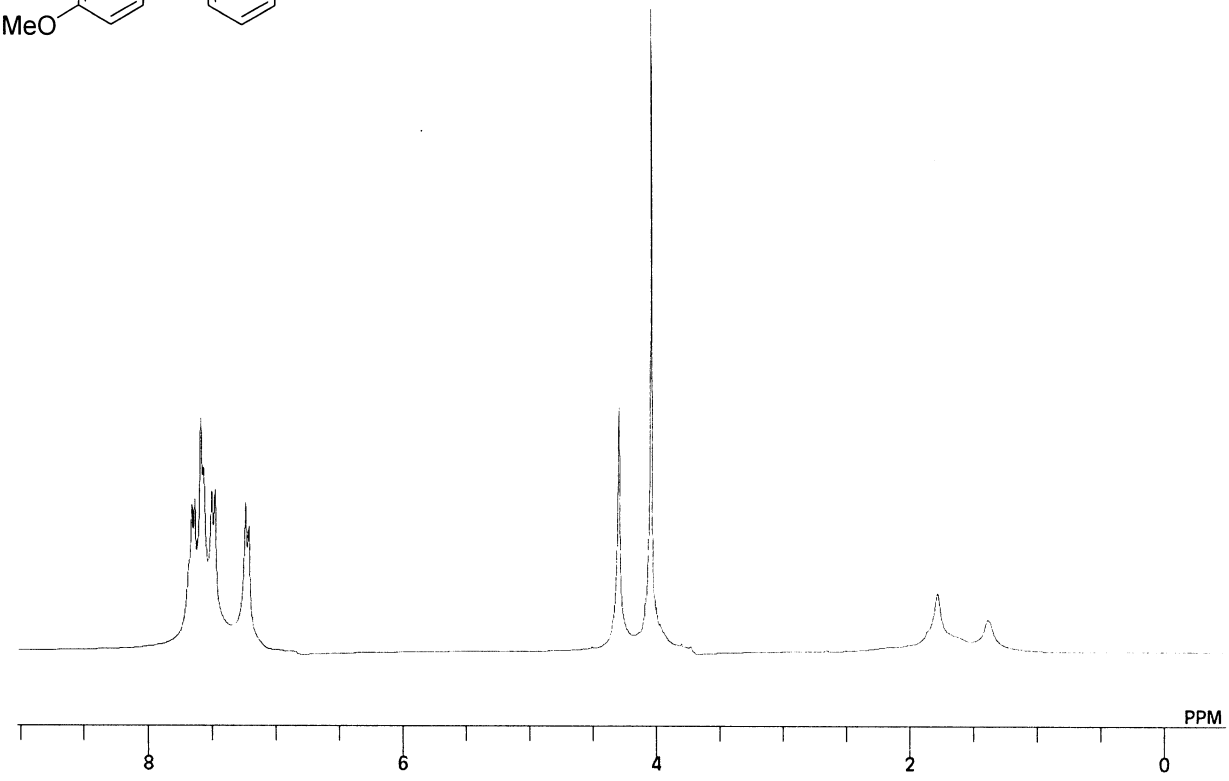
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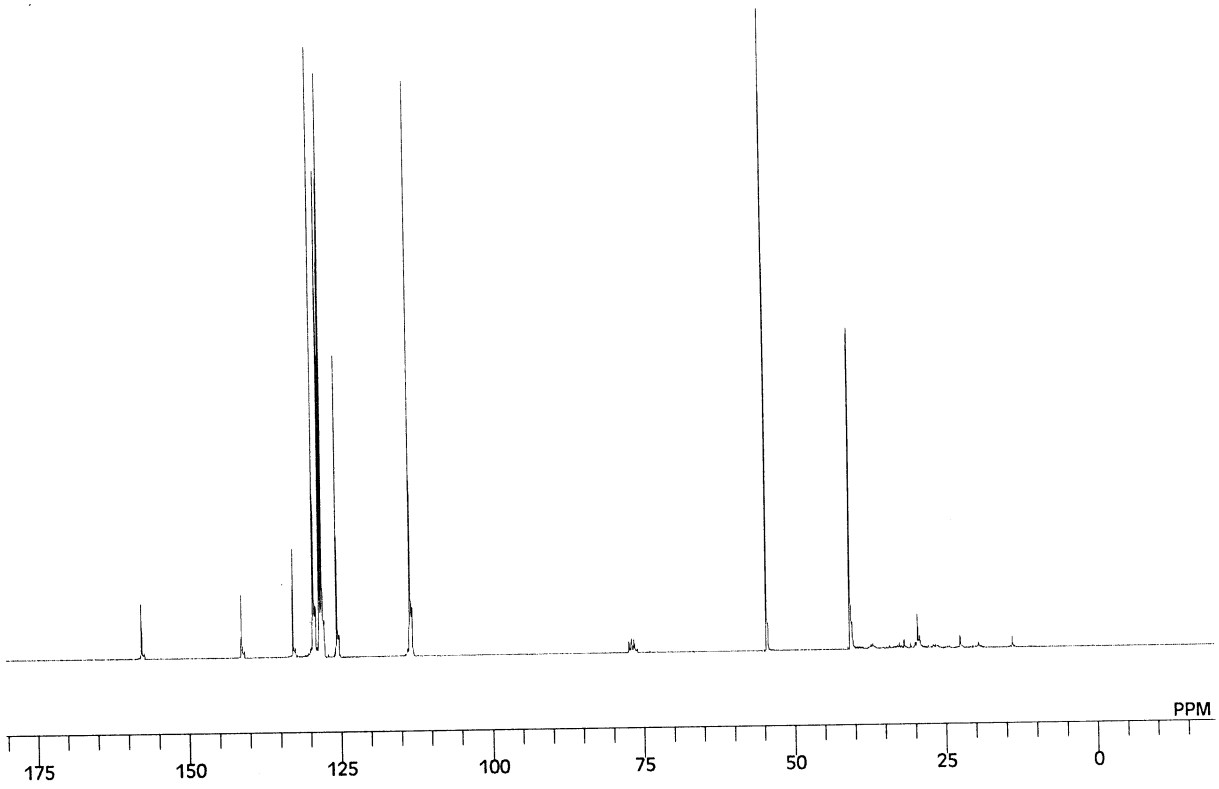
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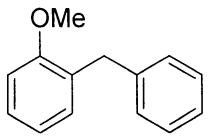
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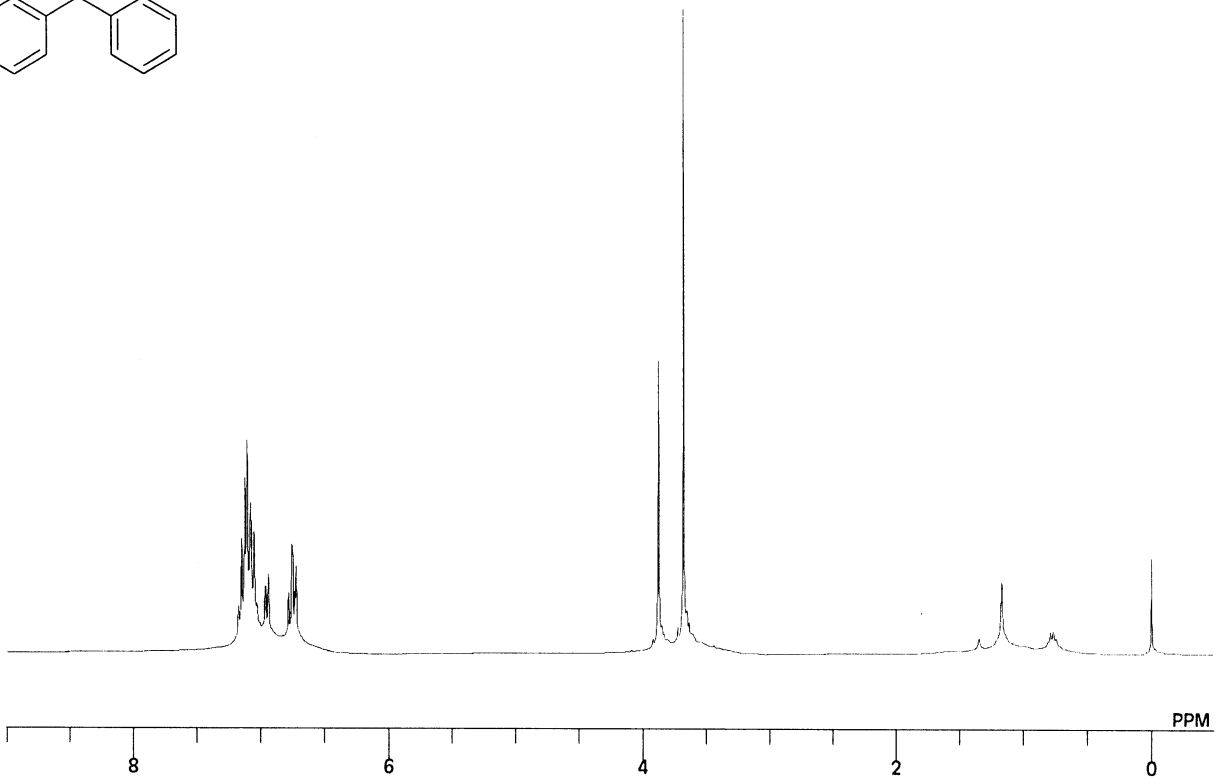
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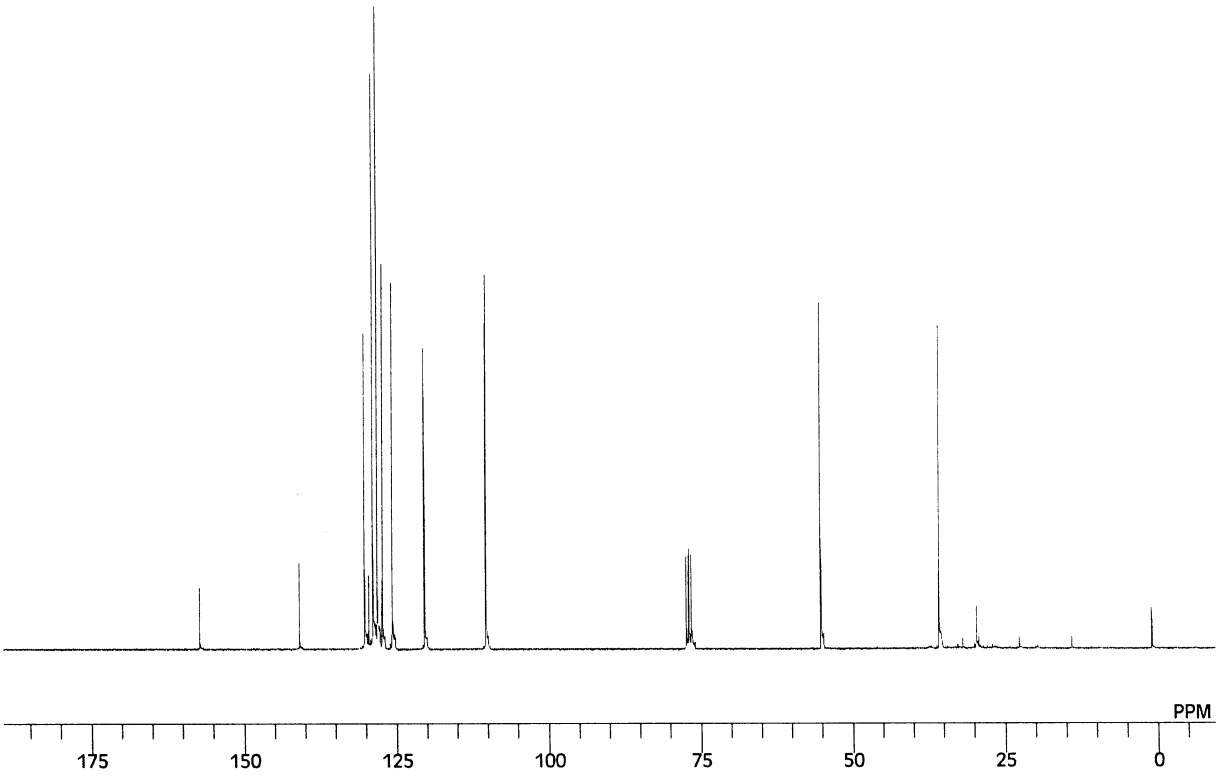
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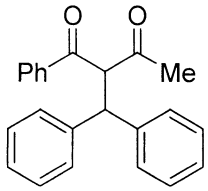
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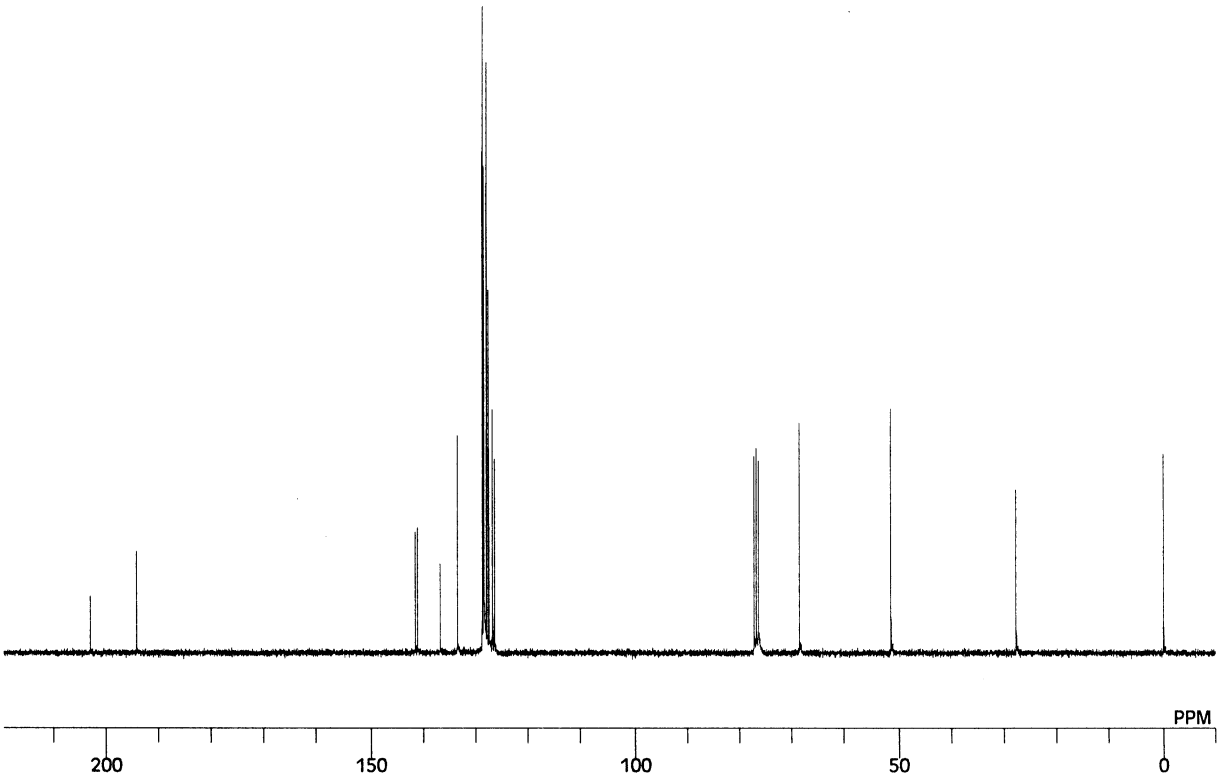
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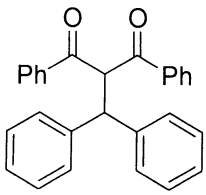
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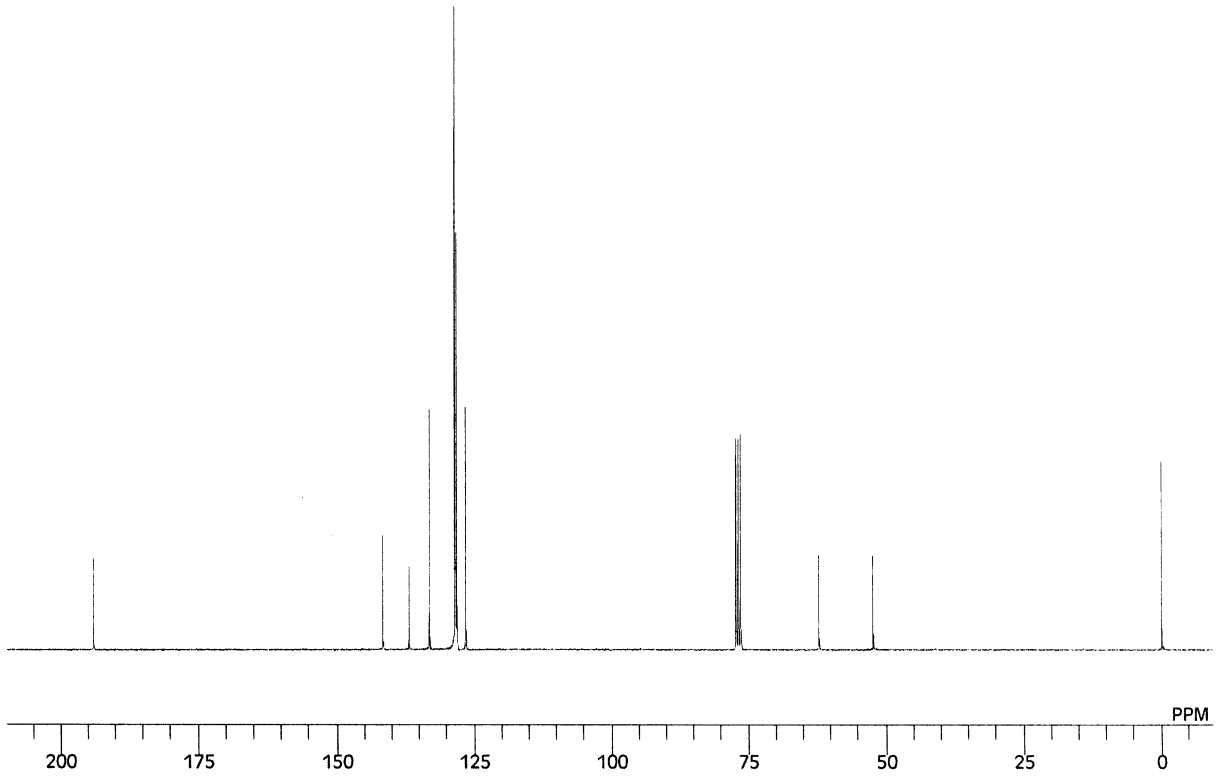
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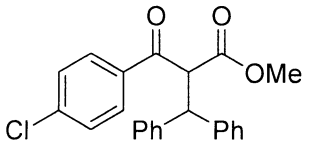
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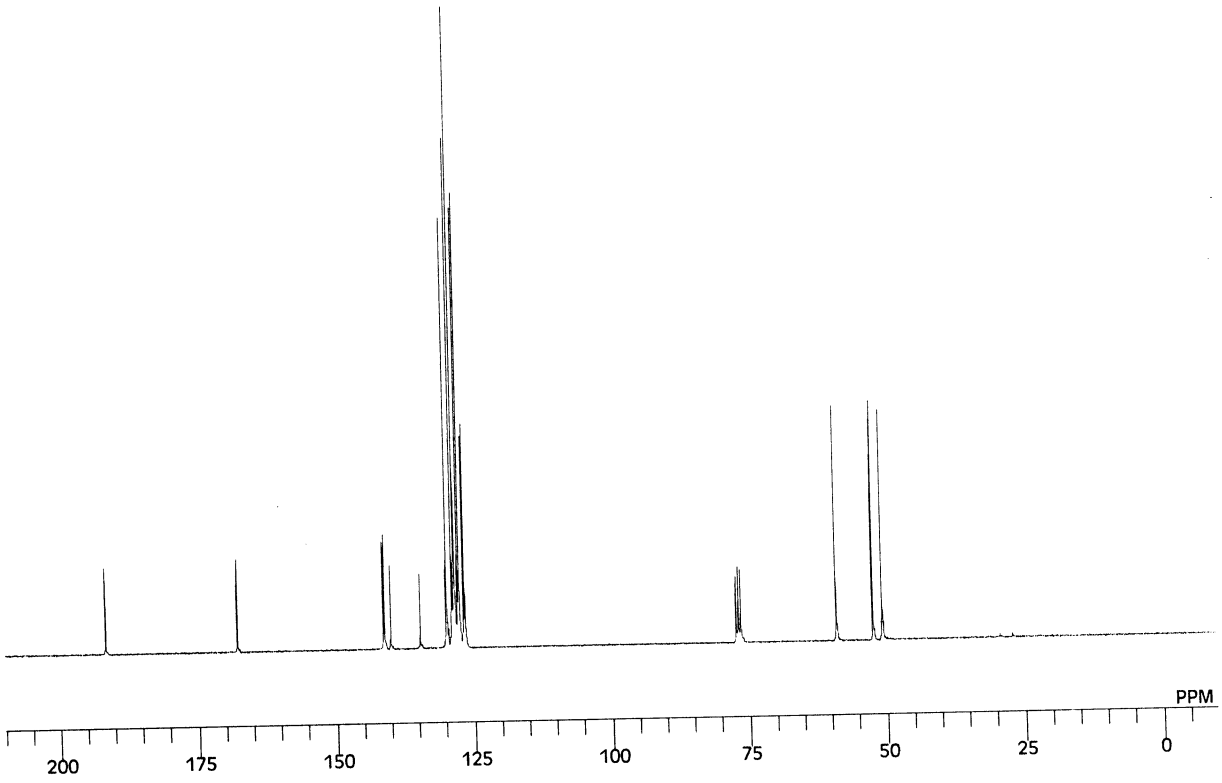
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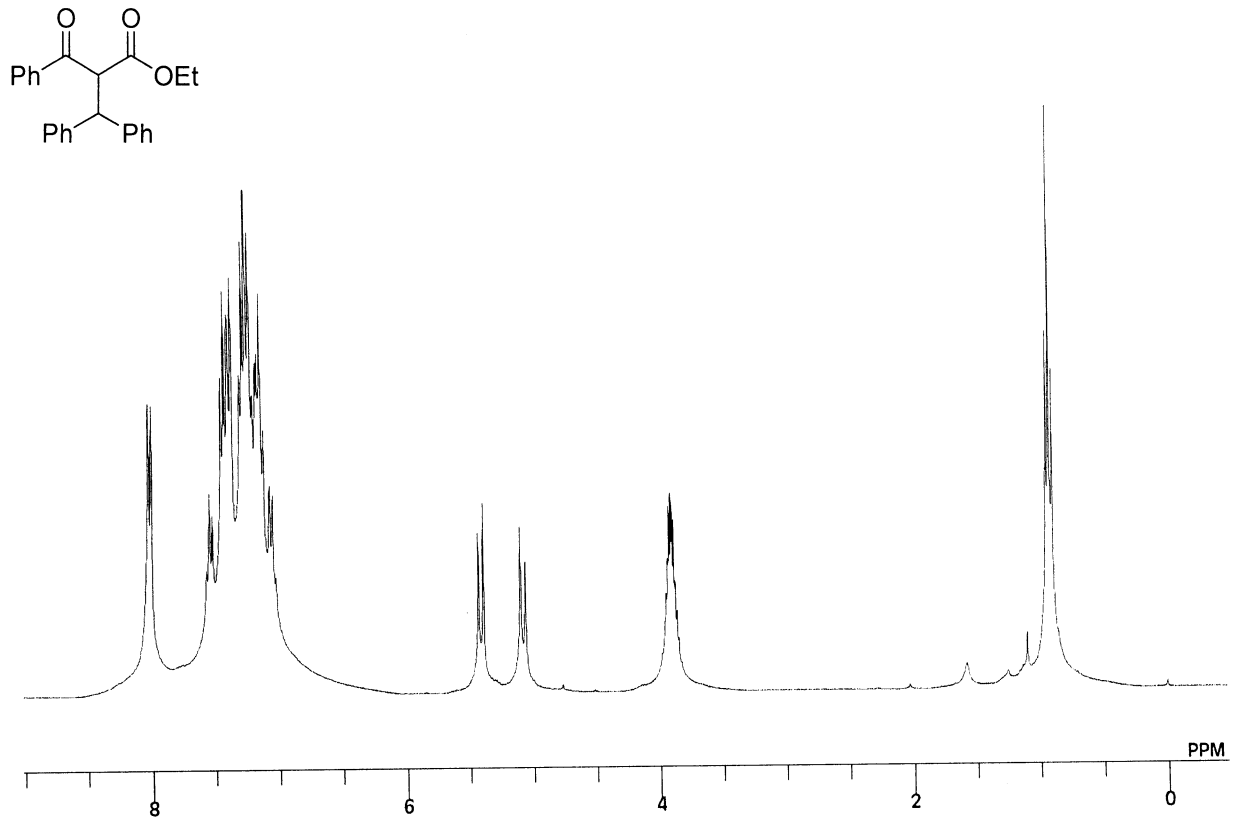
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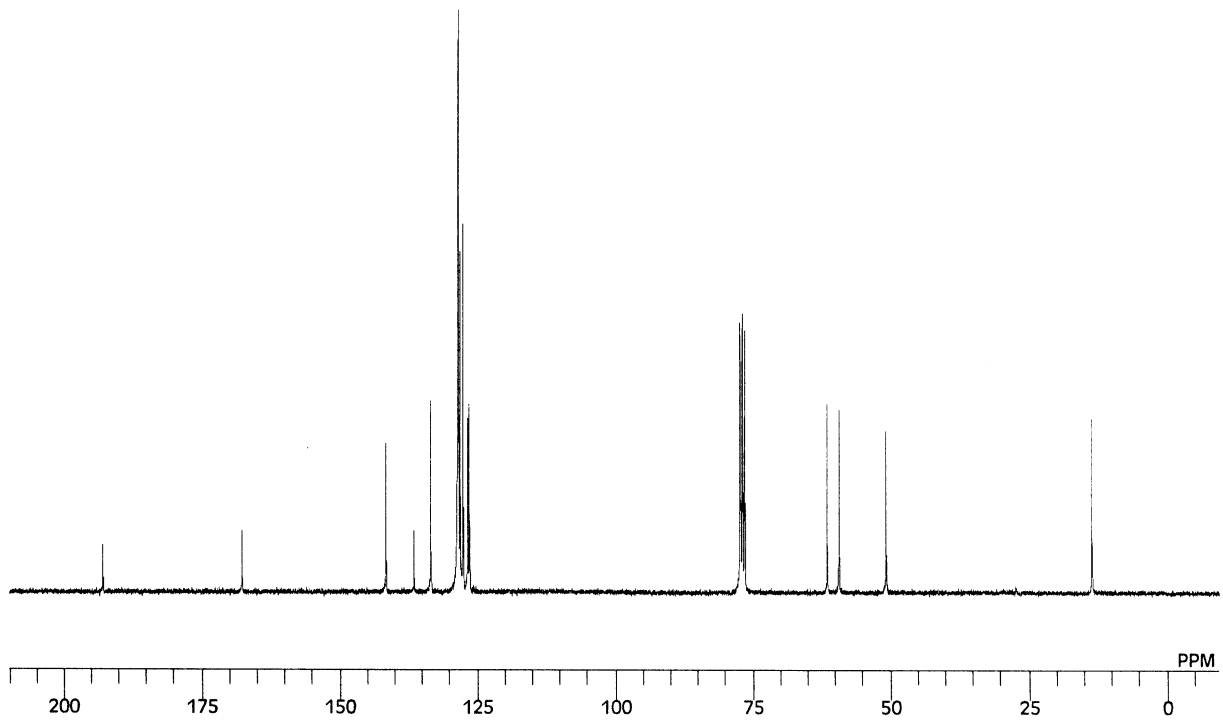
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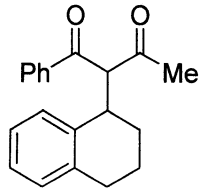
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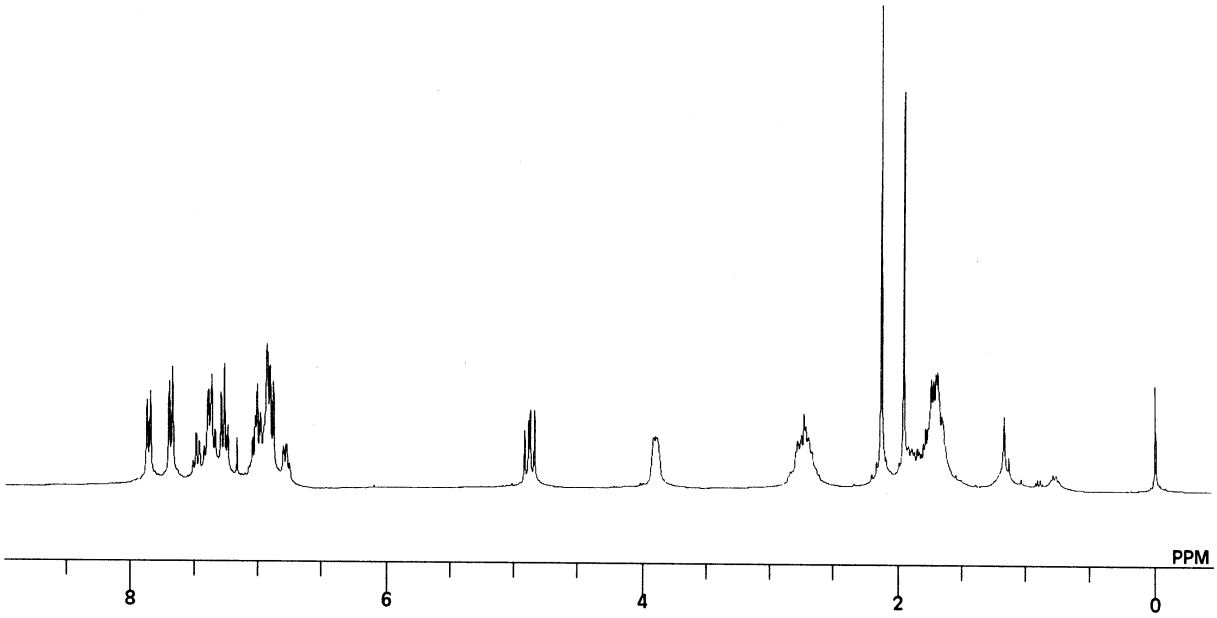
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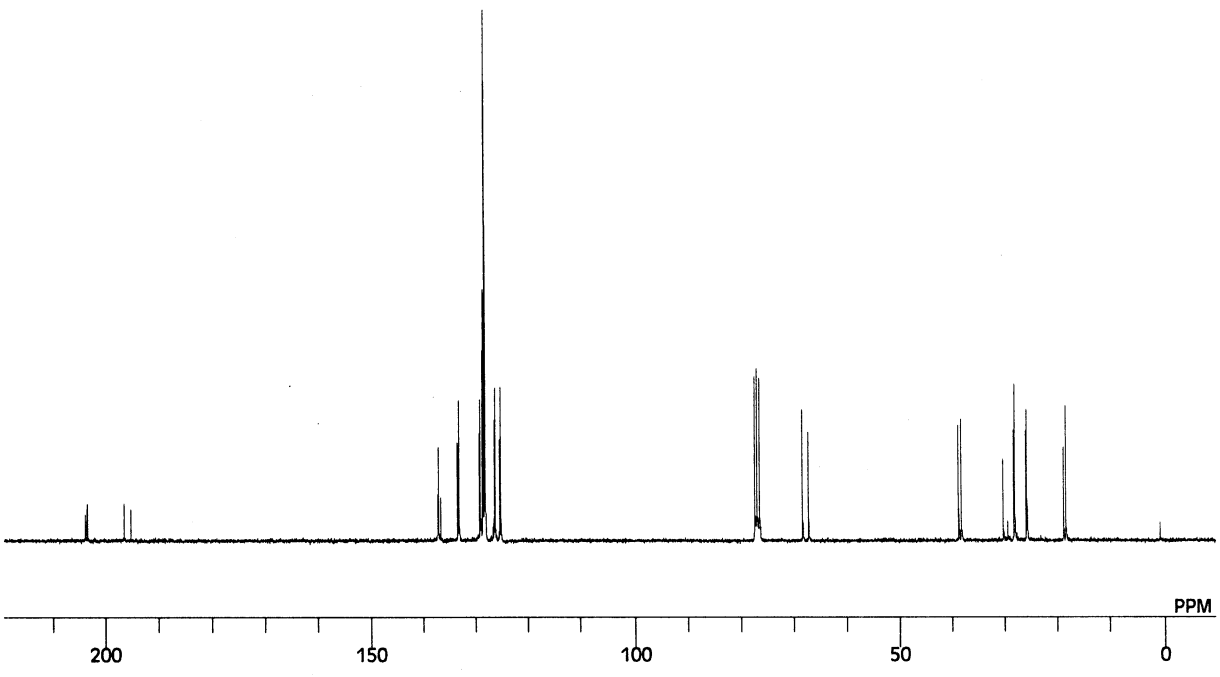
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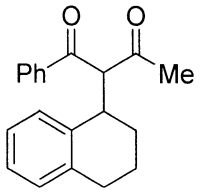
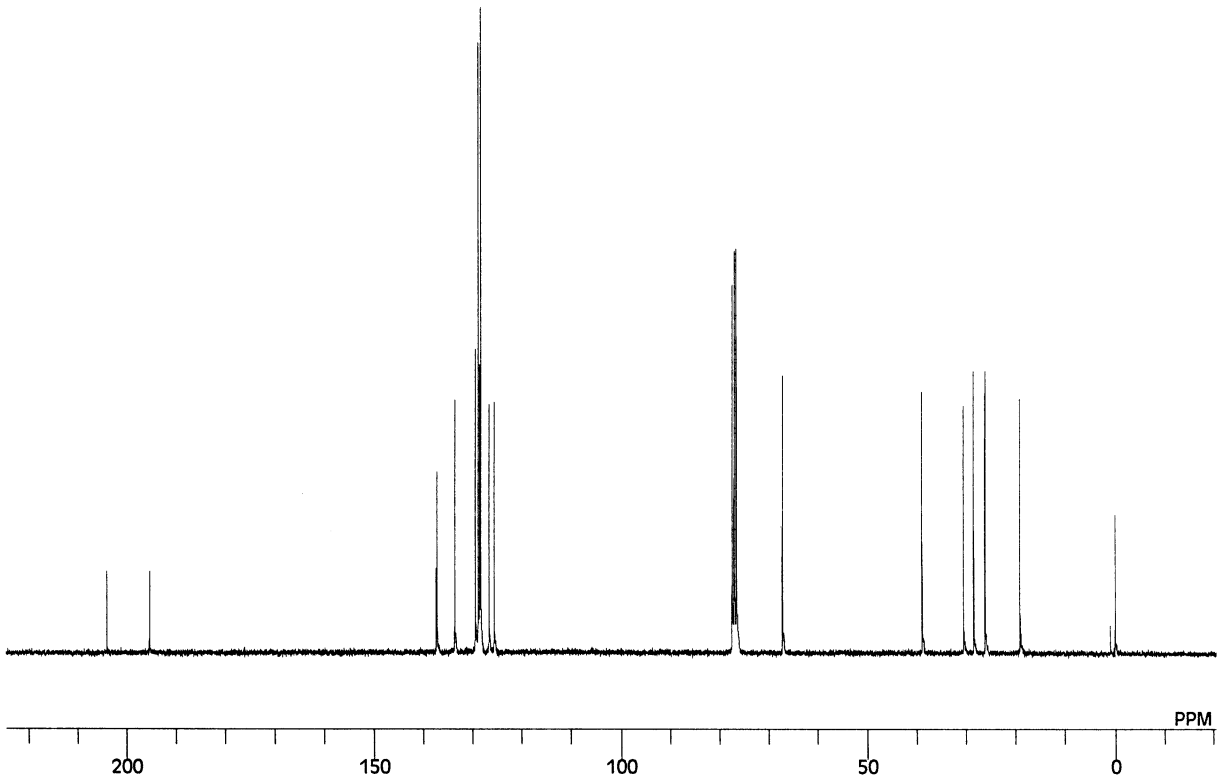
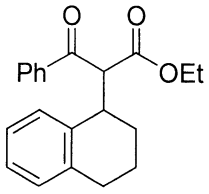


(one isomer)

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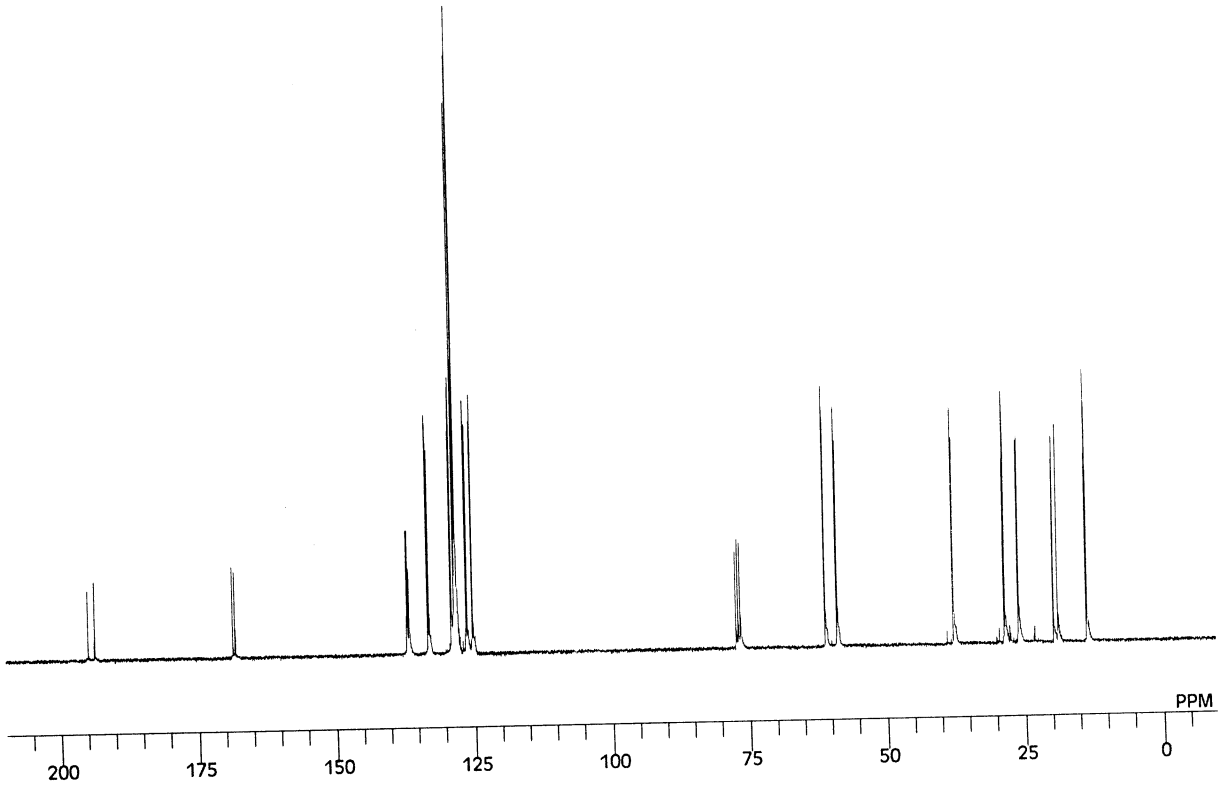
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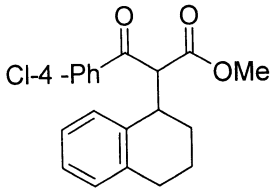
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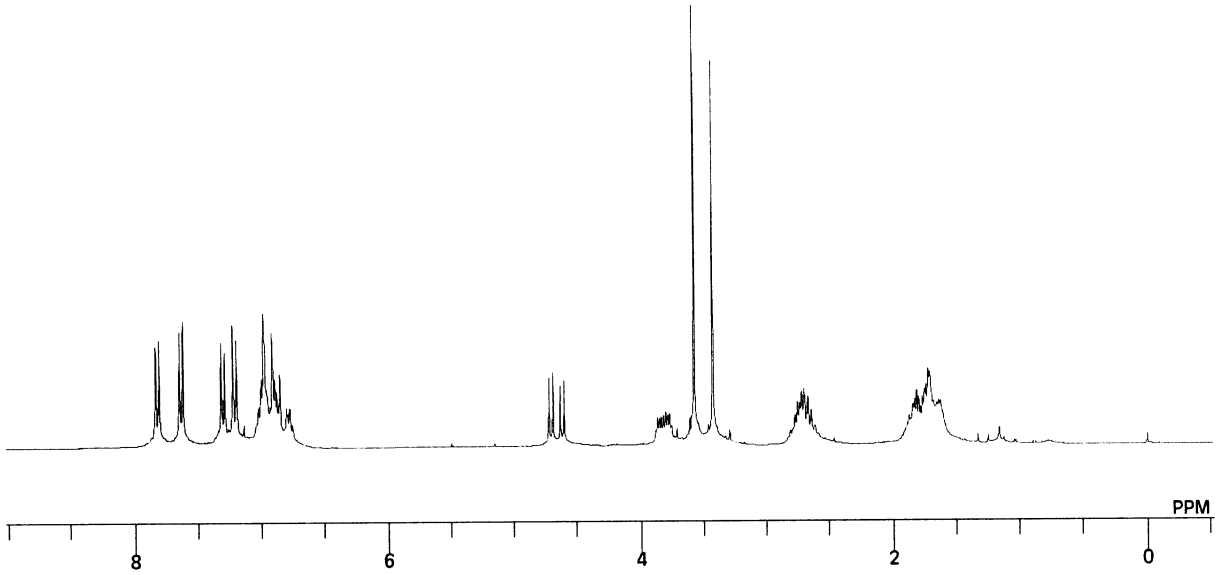
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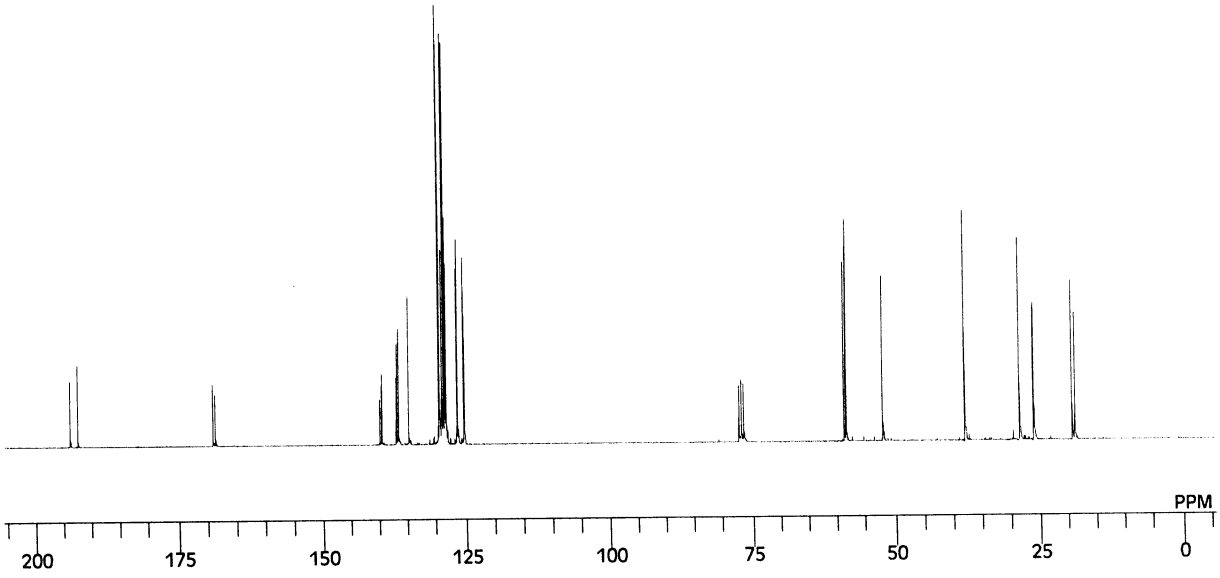
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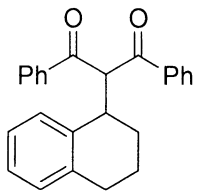
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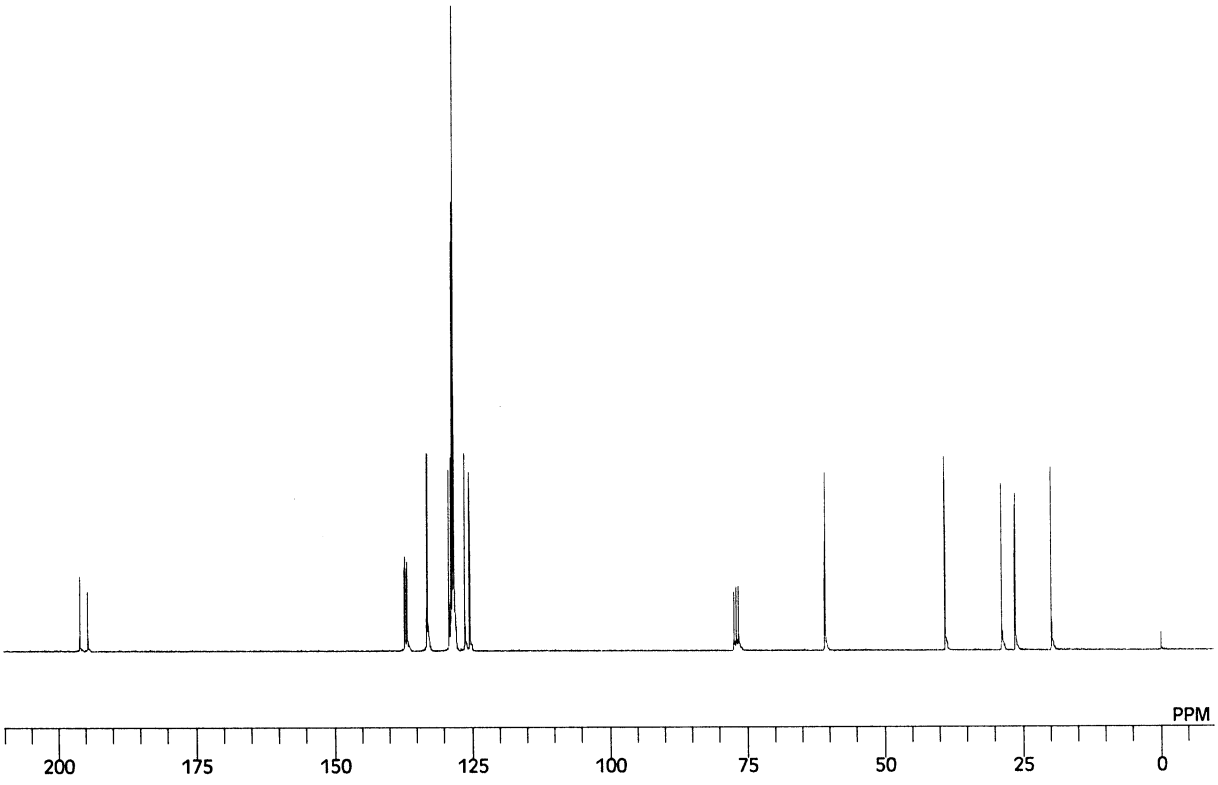
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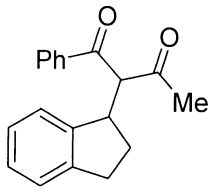
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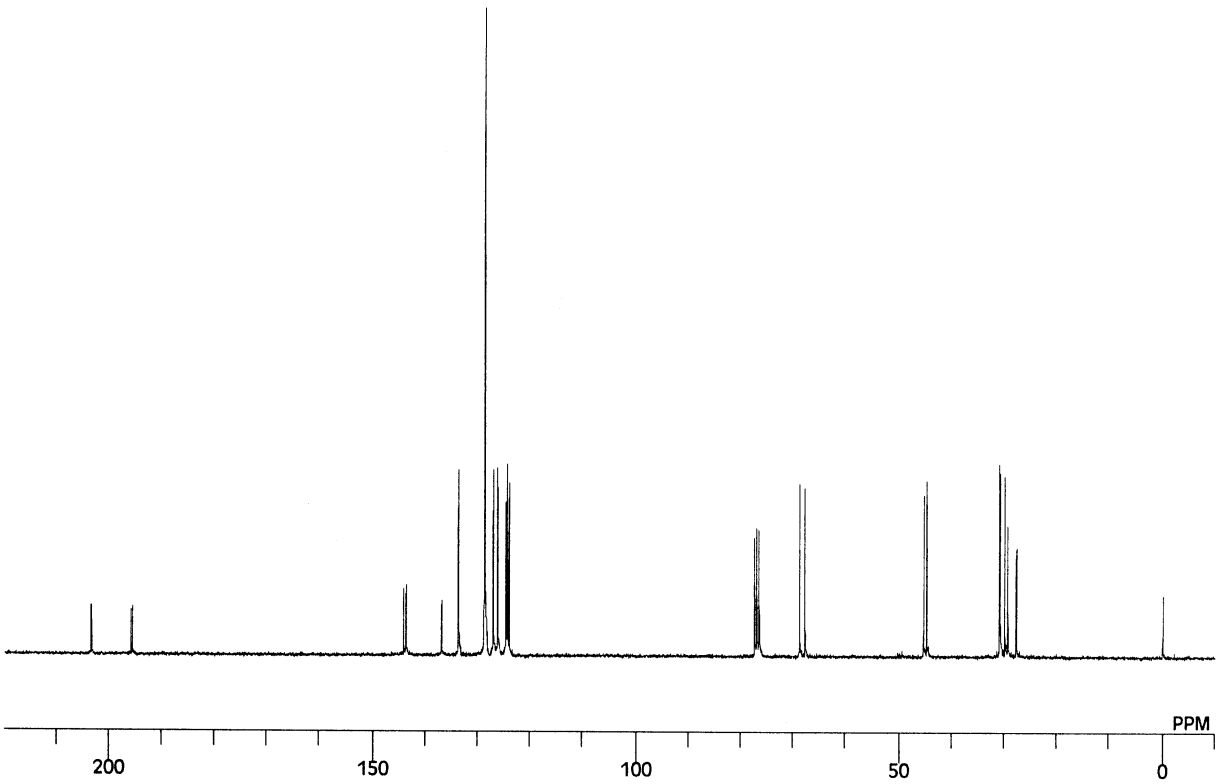
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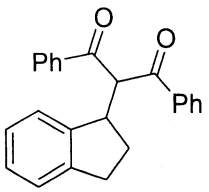
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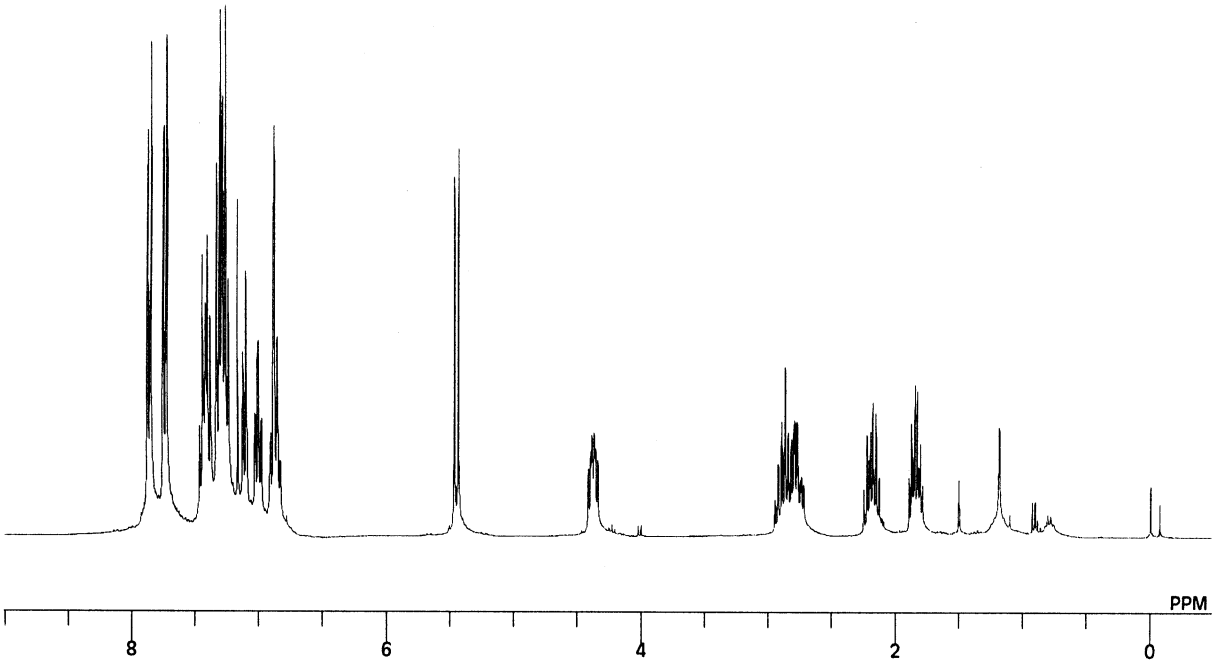
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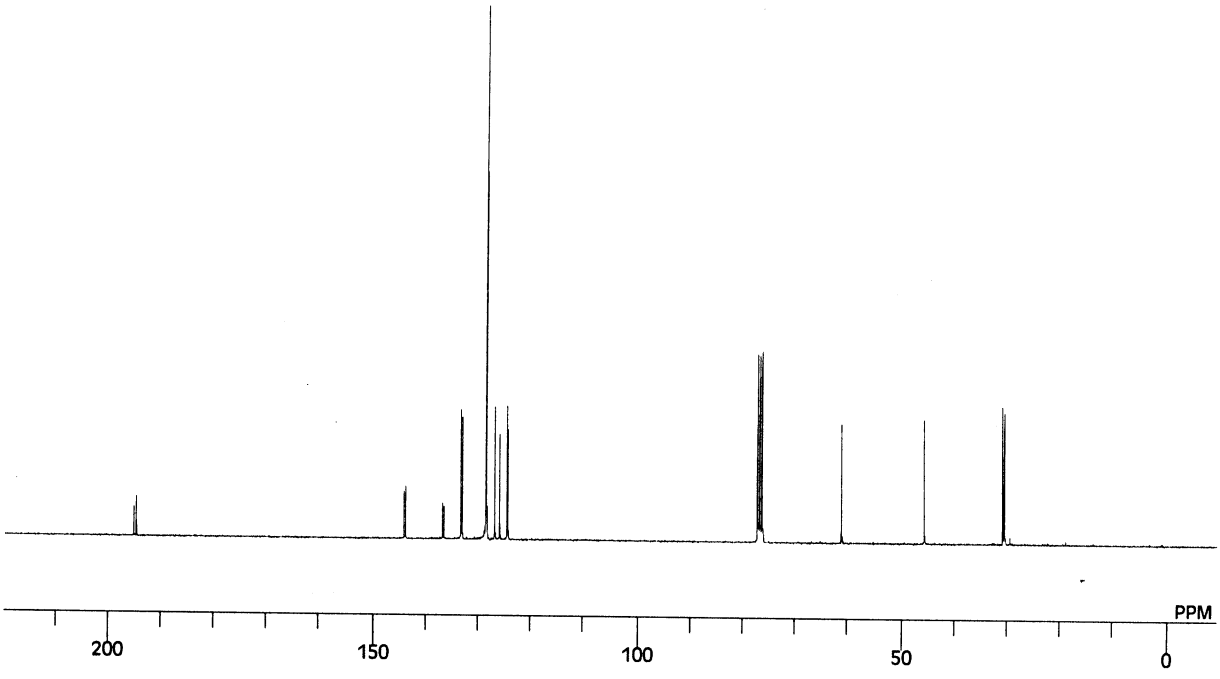
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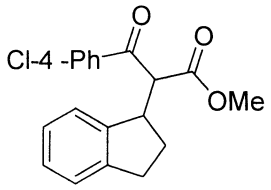
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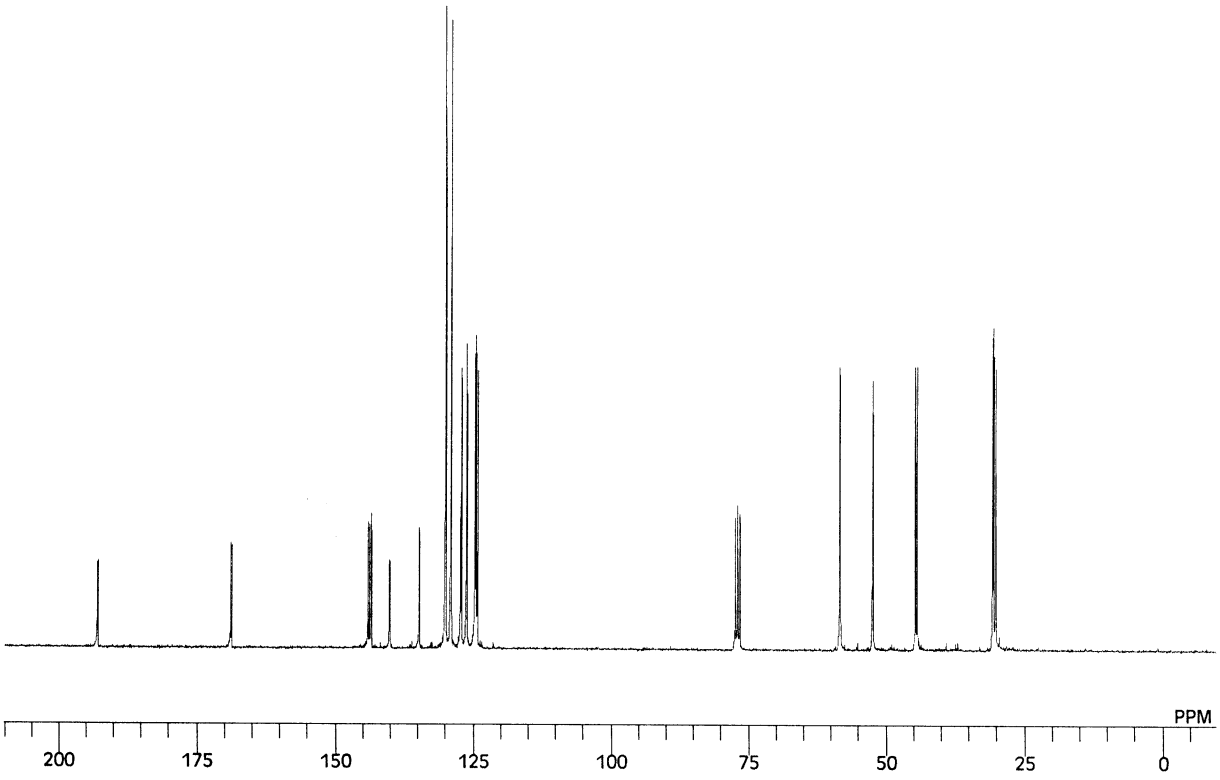
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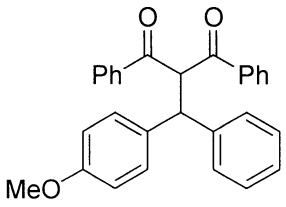
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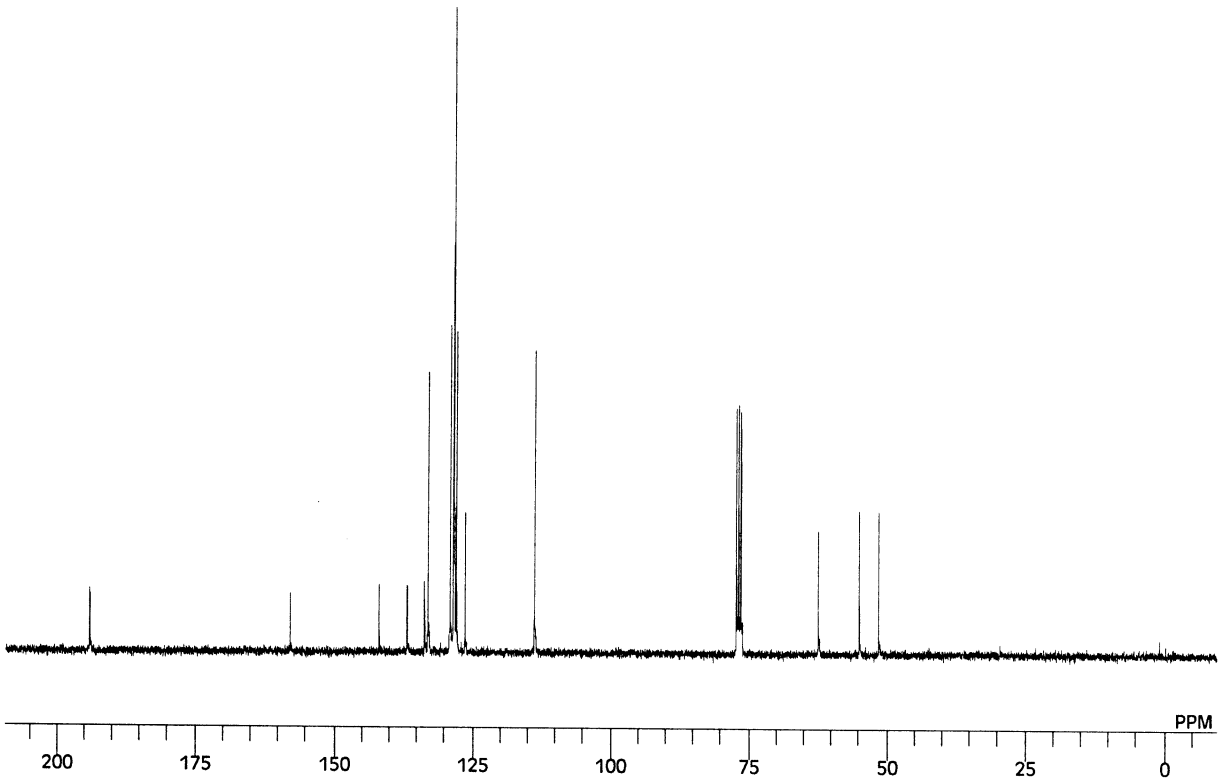
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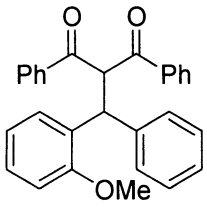
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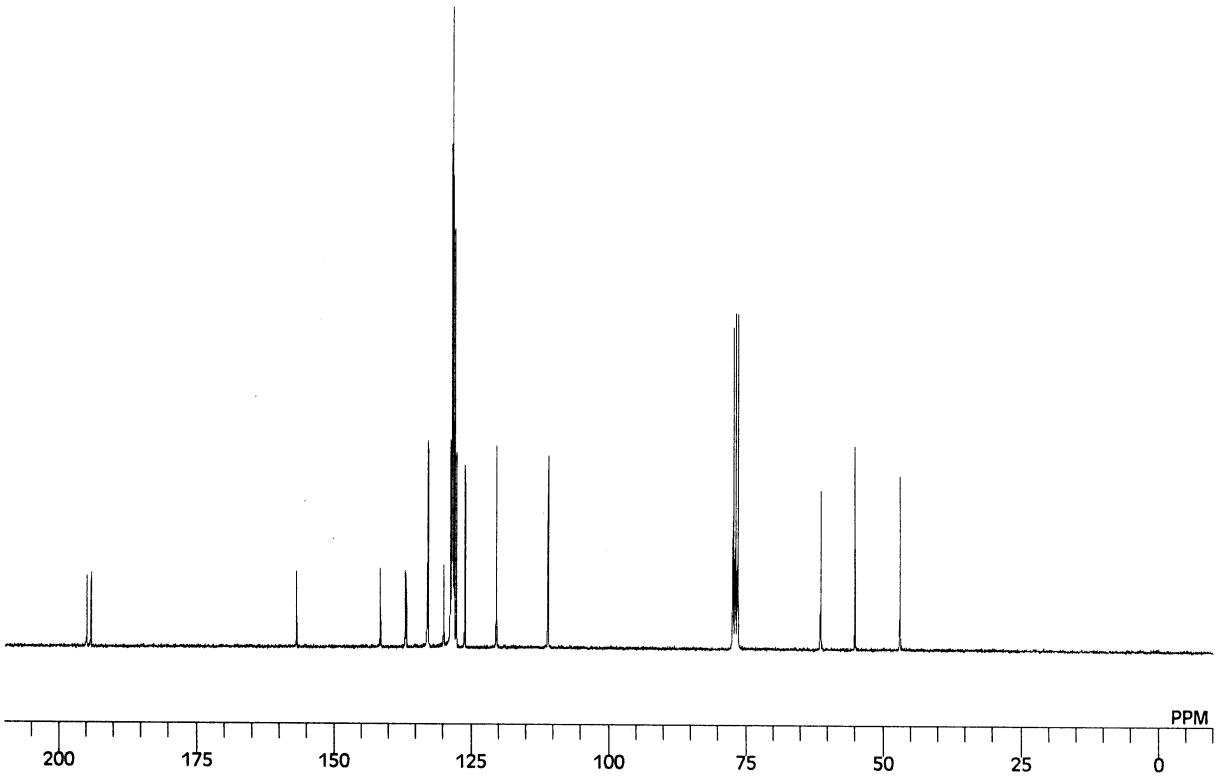
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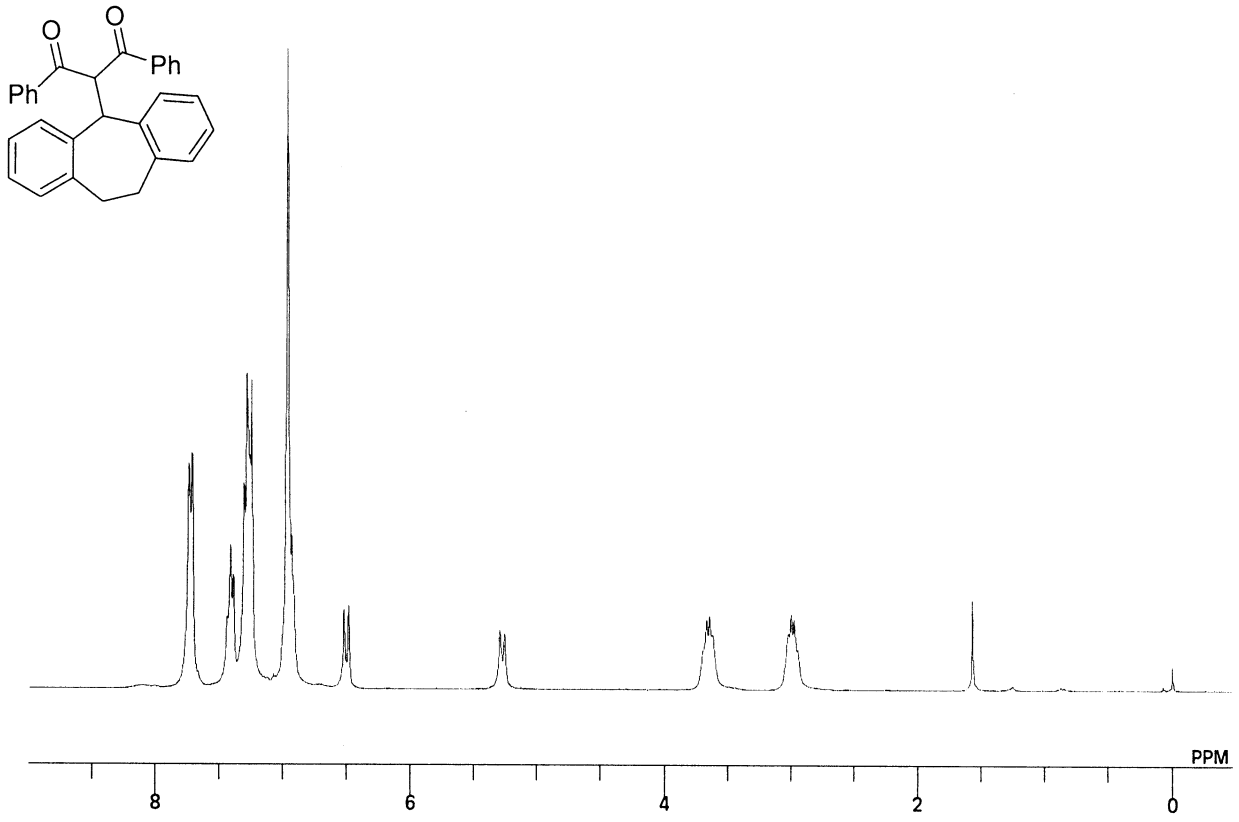
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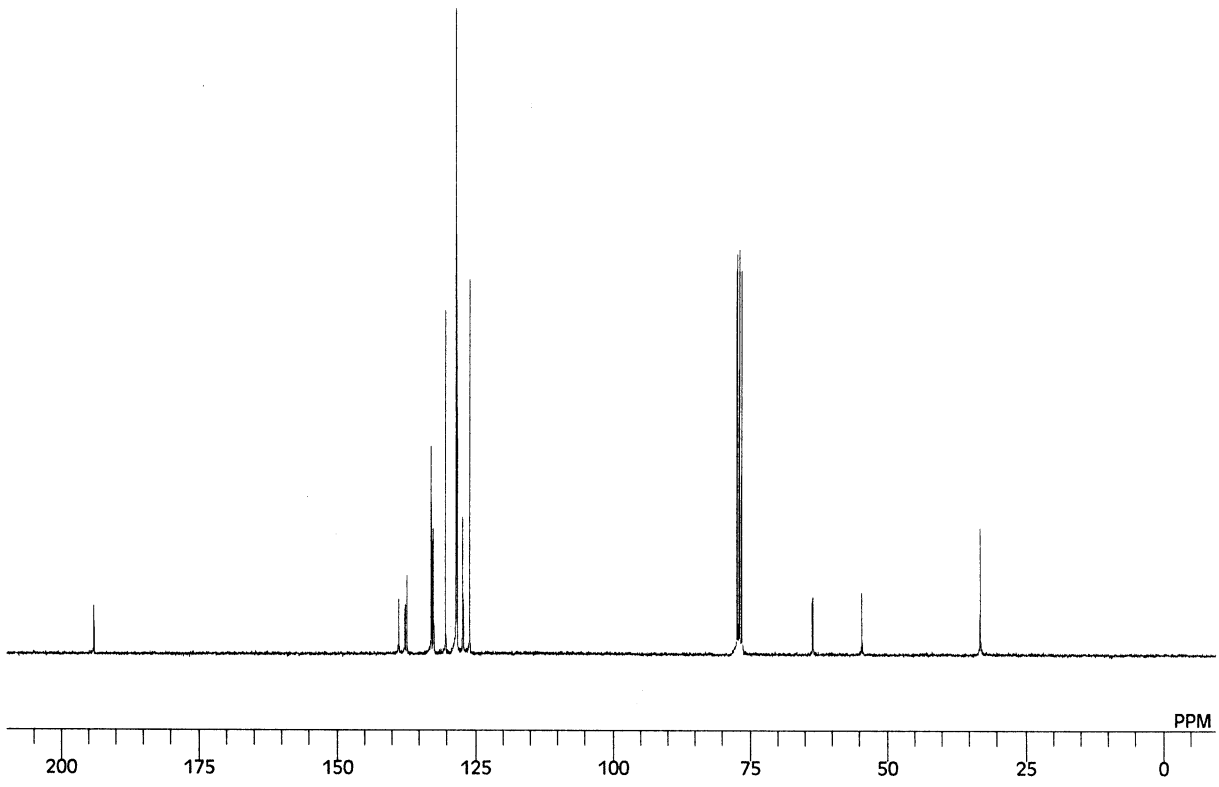
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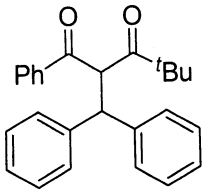
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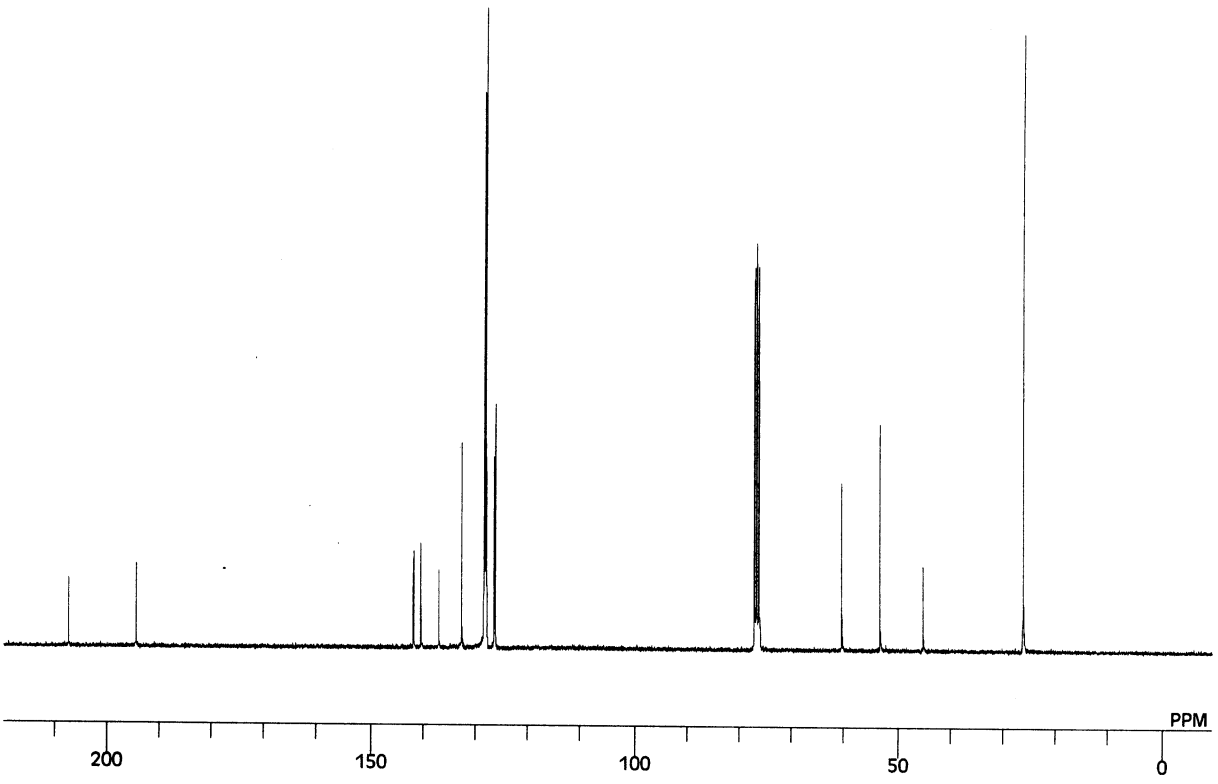
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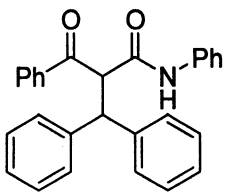
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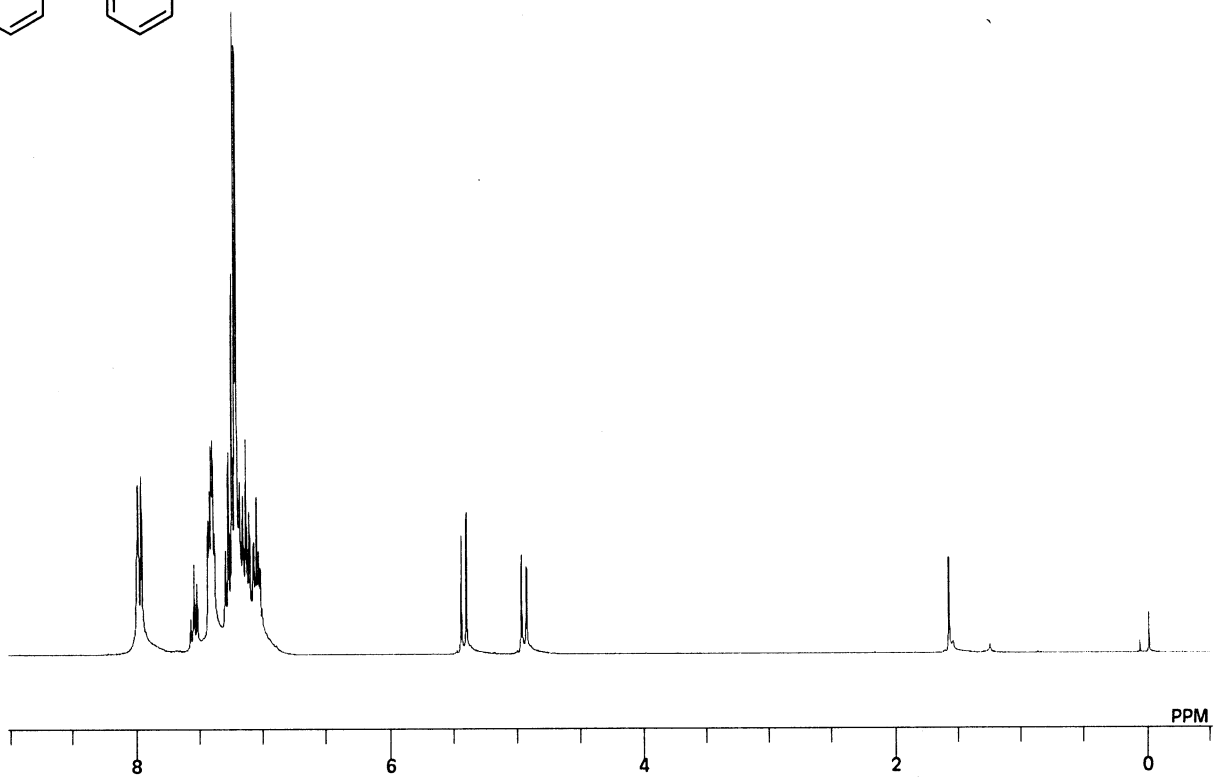
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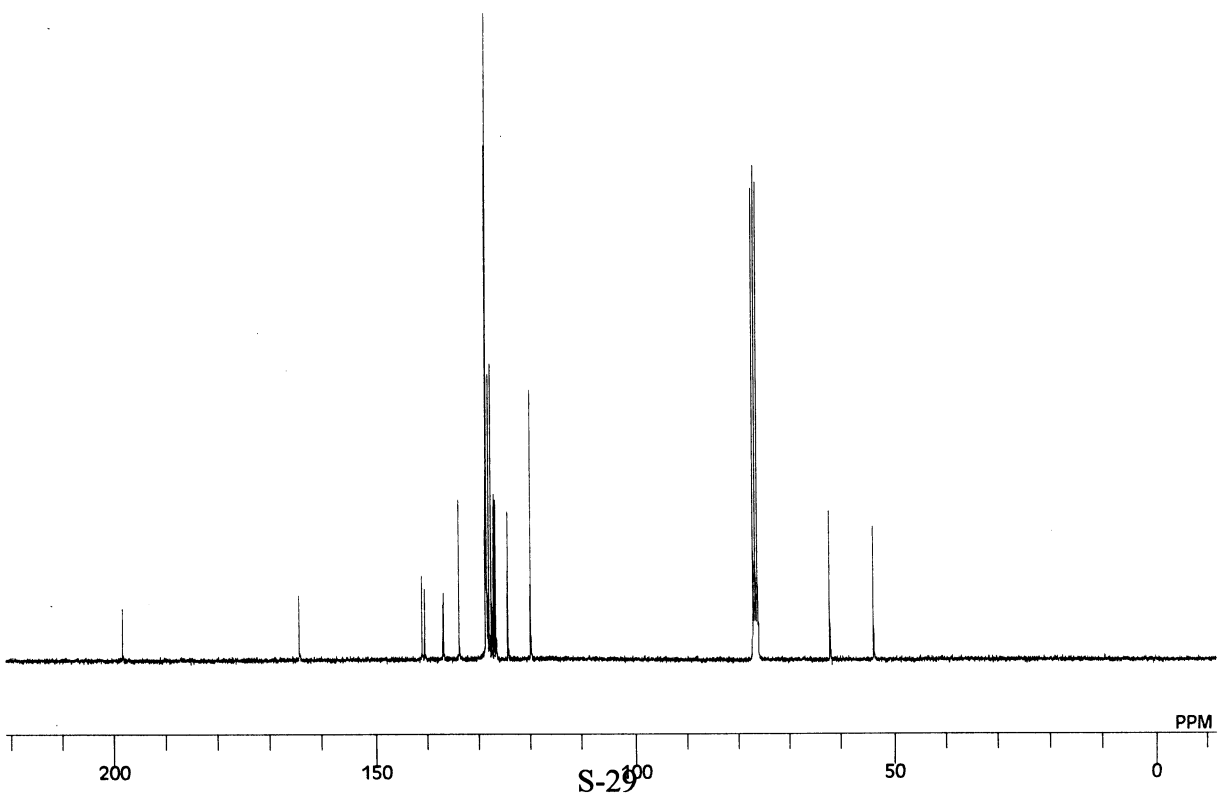
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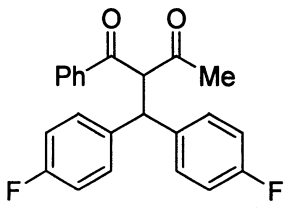
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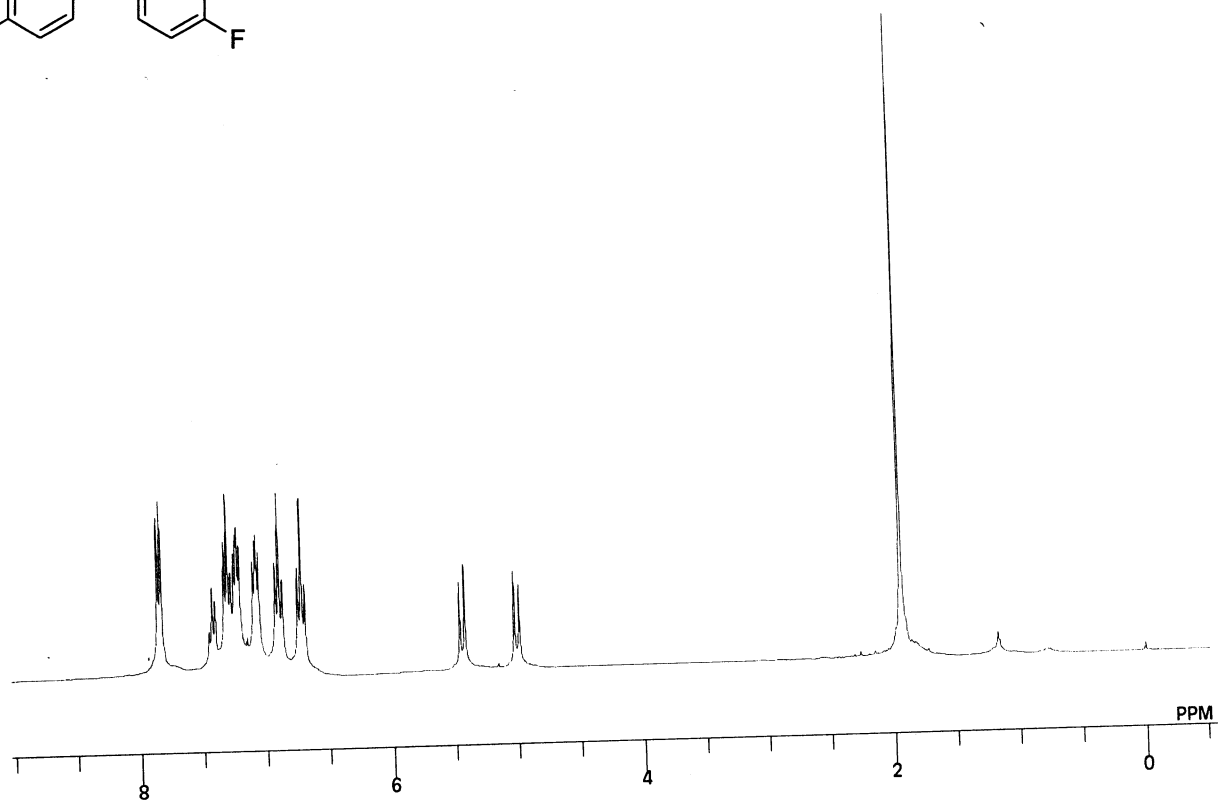
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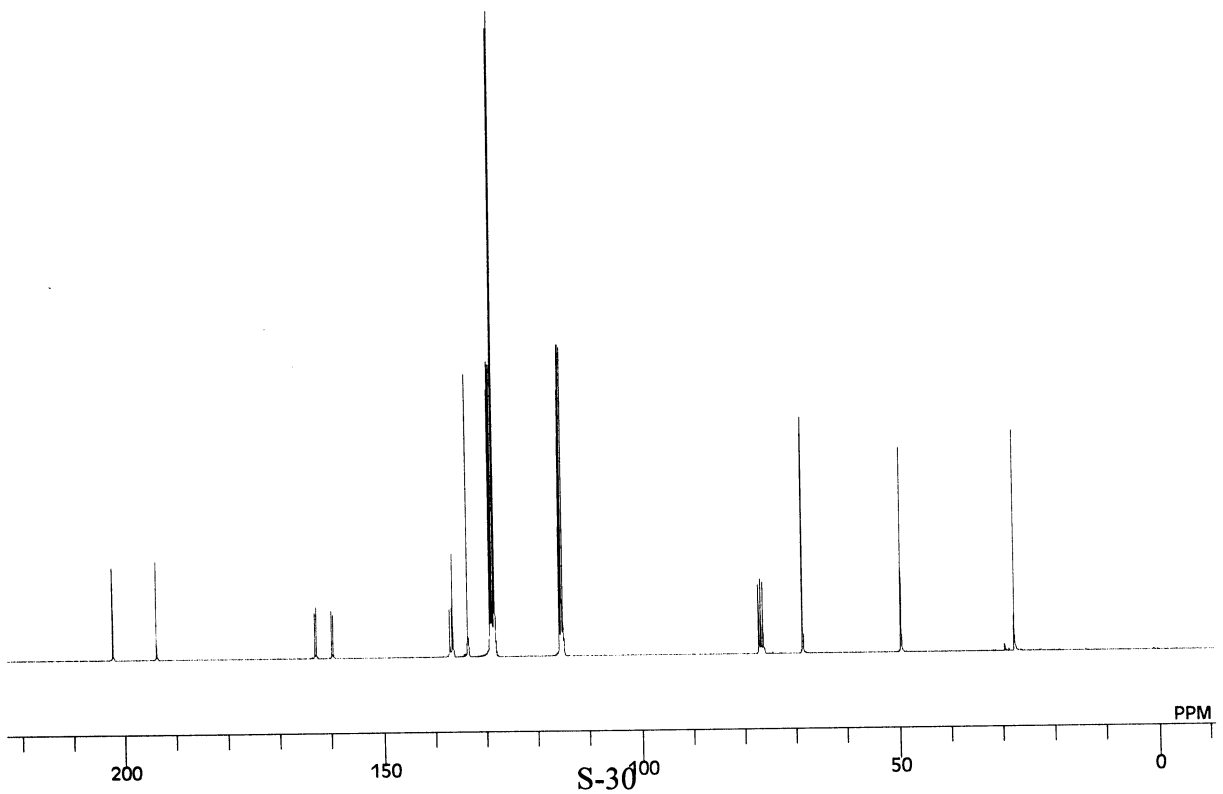
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