PEG-Mediated Catalyst-Free Expeditious Synthesis of Polysubstituted Anilines and Benzenes *via* the Reaction of Malononitrile and β-Ketoester Derivatives in the Presence of Activated Acetylenes

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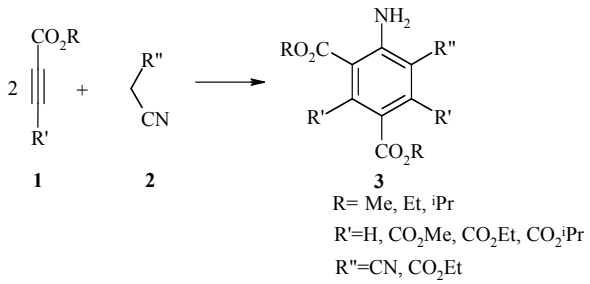
Abstract: Poly(ethylene glycol) (PEG) has been used as a sustainable, non-volatile, and environmentally friendly reaction solvent for synthesis of functionalized anilines and benzenes *via* the reaction of malononitrile and β-ketoester derivatives in the presence of activated acetylenes at 80° C. No additional solvent and catalyst are required.



Keywords: Activated acetylenes, functionalized anilines and benzenes, malononitrile, PEG, β-ketoester.

1. INTRODUCTION

The concept of "green chemistry" has been widely adopted to meet the fundamental scientific challenges of protecting human health and the environment while simultaneously achieving commercial viability. One of the thrust areas for achieving this target is to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimum byproducts and waste generation, as well as eliminating the use of volatile and toxic organic solvents [1].

Volatile, toxic and hazardous organic solvents are continuously being replaced either by the use of solvent-free techniques [2], or by using ionic liquids [3], water [4] or phase-transfer catalysts [5].

Recently PEG is found to be an interesting solvent system. The important difference between using PEG and other neoteric solvents is that all of the toxicological properties, the short and long-term hazards, and the biodegradability, etc., are established and known. The application of PEG as a reaction medium is highly beneficial as the system remains neutral, which helps in maintaining a wide variety of functional groups unchanged that are either acid or base susceptible [6].

Aromatic amines are very important compounds, being the structural units of some medicinally important molecules and many other industrially relevant materials. The amino function can be introduced into the benzene ring by a wide variety of methods, i.e., by the reduction of a nitro moiety, by the replacement of a halogen atom, by rearrangement reactions, etc. [7, 8]. Different anilines have also been obtained by the amination of arenes with azodicarboxylates, followed by the reduction of the primary-formed hydrazino intermediates [9, 10], by the Buchwald-Hartwig cross-coupling reaction [11-13], by the microwave-assisted replacement of a halogen atom with the amino moiety [14], etc. Numerous approaches for the synthesis of aromatic compounds from acyclic precursors have received growing interest due to their short synthetic steps and the avoidance of regioisomeric problems.

According to the literature, cyanoanilines are the building blocks of artificial photosynthetic systems [15]. Due to their semiconducting or nonlinear optical properties [16], these compounds are useful in fabrication of molecular electronic devices [17].

Recently a green one-pot multicomponent synthesis of polysubstituted aniline derivatives of biological, pharmacological, and optical applications using silica nanoparticles as reusable catalyst has been reported by Banerjee *et al*. [18].

2. RESULTS AND DISCUSSION

As part of our current studies on the development of new routes to heterocyclic systems [19-23], we now report the results of our studies involving the reactions of activated

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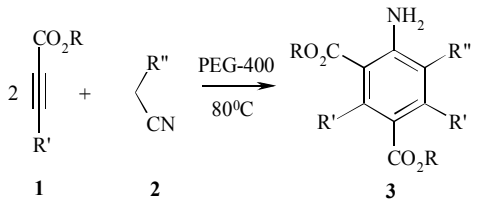
acetylenes (**1**) and malononitrile derivatives (**2**) in PEG at 80^0C which led to high polysubstituted aniline derivatives (**3**) in the absence catalyst (Scheme **1**).



Scheme 1. Synthesis of high polysubstituted aniline derivatives.

The choice of an appropriate reaction medium is of crucial importance for successful synthesis. Different solvents, such as methanol, ethanol, acetonitrile, and tetrahydrofuran (THF) were explored. The results are summarized in Table **1**.

Table 1. Synthetic Results of 3a Under Different Reactions Conditions

Entry	Solvent	Temp/°C	Time/h	Isolated Yield (%)
1	PEG-400	80	18	90
2	Methanol	Reflux	20	-
3	Ethanol	Reflux	24	-
4	THF	Reflux	20	-
5	Acetonitrile	Reflux	20	-

As can be seen from Table **1**, the best results were obtained by heating the reaction mixture in PEG-400 at 80^0C, which yielded product **3a** in high yield (Table **1**, entry 1). Encouraged by this success we investigated the scope of the reaction activated acetylenic compounds (**1a-g**) with malononitrile derivatives (**2a–b**) in PEG-400 at 80 ^{0}C which led to high polysubstituted aniline derivatives (**3a–g**) in 32-90% yields (Table **2**). The reaction proceeded smoothly in Poly (ethylene glycol) (PEG) and was complete within 18 h at 80^0C.

The ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of high functionalized aniline derivatives (**3a–g**). The structures of compounds (**3a-g**) were deduced from their elemental analyses and their IR, ^{1}H NMR and ^{13}C NMR analyses. For example, the ^{1}H NMR spectrum of (**3a**) exhibited four singlets identified (δ= 3.84, 3.91, 3.92 and 4.00 ppm) as methoxy groups and a broad signal for aniline protons. The ^{1}H decoupled ^{13}C NMR spectrum of (**3a**) showed 15 distinct resonances which further confirmed the proposed structure. The IR spectrum of (**3a**) displayed characteristic ester carbonyl bands. The ^{1}H NMR and ^{13}C NMR spectra of (**3b–g**) were similar to those for (**3a**) except for the ester moieties, which exhibited characteristic resonances in appropriate regions of the spectrum.

The reaction of β-ketoesters with activated acetylenes in PEG-400 also was investigated at 80^0C for 12 h that lead to functionalized benzenes in good yields. The results are summarized in Table **3**.

The structures of compounds **4a-4c** were assigned based on their IR, ^{1}H-NMR and ^{13}C-NMR spectral data. In the IR spectrum of (**4a**) observed characteristic ester carbonyl bands. In the ^{1}H-NMR spectrum of (**4a**), the methoxy protons resonated at (δ= 3.46, 3.89 and 3.92 ppm). The ^{1}H decoupled ^{13}C-NMR spectrum of (**4a**) showed 23 distinct resonances which further confirmed the proposed structure. The ^{1}H NMR and ^{13}C NMR spectra of (**4a–c**) were similar to those for (**4a**) except for the ester moieties, which exhibited characteristic resonances in appropriate regions of the spectrum. The abovementioned reactions in PEG run in the absence catalyst and products obtained with good yields. It seems the high viscosity of PEG can increase the contact surface between the reagents and generate the adequate position for the reactions to occure.

Although the mechanistic details of the reaction are not known, a plausible rationalization maybe advanced to explain the product formation (Scheme **2**).

Presumably, the intermediate (**5**) formed from malononitrile and dimethylacetylenedicarboxylate attacks to another dimethylacetylenedicarboxylate to furnish intermediate (**6**), which is converted to heterocyclic compound (**7**). Intermediate (**7**) then undergoes a proton-transfer reaction to generate product (**3a**). In summary, we have reported a transformation involving activated acetylenes (**1a-e**) and malononitrile and β-ketoester deravatives (**2a-c**) in PEG, which leads to the regioselective synthesis of polysubstituted anilines and benzenes.

3. CONCLUSION

In conclusion, we have described a convenient route to polysubstituted anilines and benzenes from malononitrile and β-ketoester derivatives and activated acetylenes. The polysubstituted anilines and benzenes reported in this work may be considered as potentially useful synthetic intermediates because they possess atoms with different oxidation states. The advantage of the present procedure is that the reaction is performed under neutral conditions by simple mixing of the starting materials. No additional solvent and catalyst are required. The simplicity of the present procedure makes it an interesting alternative to other approaches.

Material and Methods

IR Spectra: *Shimadzu IR-460* spectrometer. ^{1}H- and ^{13}C-NMR spectra: Bruker DRX-500 AVANCE instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp.; δ in ppm, J in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in *m/z*. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. All chemicals were used as-received from the appropriate suppliers.

General Procedure

General procedure for the preparation of compounds **3** and **4**: To a stirred solution of **2** (2 mmol) in 1 mL of PEG-400 was added activated acetylenes (4 mmol) at room temperature. The reaction mixture was heated at 80^0C for 12 or 18 h. the product was extracted from the mixture with diethyl ether (3 × 4 ml) to afford pure title compound.

Table 2. Reaction of Activated Acetylenic Compounds and Malononitrile Deravatives in PEG-400 at 80 ^{0}C

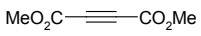
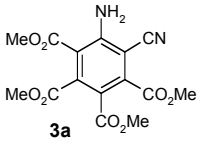
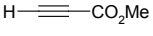
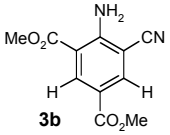
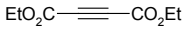
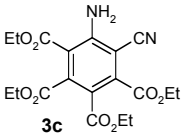
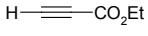
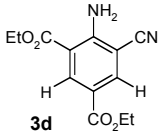
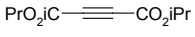
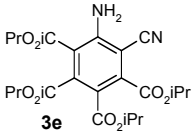
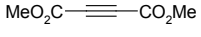
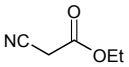
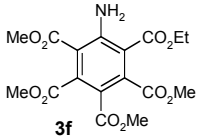
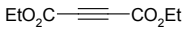
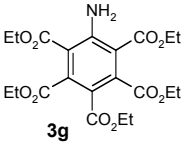
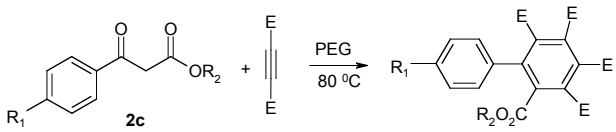
Entry	Activated Acetylene	Malononitrile Derivative	Product	Yield%
a	 **1a**	 **2a**	 **3a**	**90**
b	 **1b**	**2a**	 **3b**	**88**
c	 **1c**	**2a**	 **3c**	**84**
d	 **1d**	**2a**	 **3d**	**81**
e	 **1e**	**2a**	 **3e**	**72**
f	 **1a**	 **2b**	 **3f**	**35**
g	 **1c**	**2b**	 **3g**	**32**

Table 3. PEG-400 Catalyzed Reaction of β-Ketoesters with Activated Acetyls



2c **4**

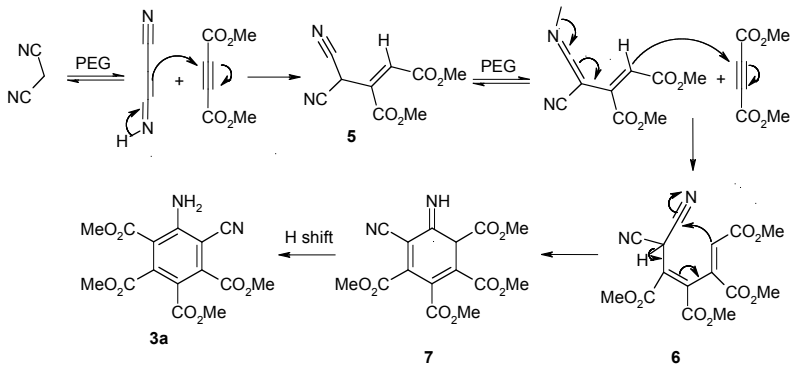
4	R_1	R_2	E	Yield%
a	H	Et	CO_2Me	95
b	H	Et	CO_2Et	92
c	Br	Me	CO_2Me	93

Tetramethyl 5-amino-6-cyano-1,2,3,4-benzenete tetracarboxylate (3a)

Yield: 0.31 g (90%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3386, 3332 (NH_2), 2351(CN), 1734, 1726, 1720, 1713, (C=O), 1282 (C–O) cm^{-1}.^{1}H NMR: 3.84 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3) 6.89 (broad, 2H, NH_2).^{13}C NMR: 53.0 (OCH_3), 53.1 (OCH_3), 53.2 (OCH_3), 53.6 (OCH_3), 97.6 (C), 111.1 (C), 113.7 (C), 123.4 (C), 124.3 (C), 128.8 (C), 152.5 (C), 165.2, 165.5, 166.8, 167.8 (4 C=O, ester). EI-MS: 350 (M^+, 6), 114 (34), 59 (100). Anal. Calcd for $C_{15}H_{14}N_2O_8$ (350.28): C, 51.43; H, 4.03; N, 8.00. Found: C, 51.48; H, 4.01; N, 7.91.

Dimethyl 4-amino-5-cyano isophthalate (3b)

Yield: 0.20 g (88%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3412, 3342 (NH_2), 2341(CN), 1732, 1717, (C=O), 1261



Scheme 2. Proposed mechanism for the formation of compound **3a**.

(C–O) cm^{-1}.^{1}H NMR: 3.81 (s, 3H, OCH_3), 3.85.(s, 3H, OCH_3), 6.77 (broad, 2H, NH_2), 8.52(s, 1H, CH), 8.85(s, 1H, CH) ^{13}C NMR: 53.1 (OCH_3), 53.3 (OCH_3), 98.2 (C), 114.1 (C), 116.7 (C), 123.4 (C), 128.6 (CH), 132.3 (CH), 151.2 (C), 164.2, 165.5, (2 C=O, ester). EI-MS: 234 (M^+, 5), 116 (48), 59 (100). Anal. Calcd for $C_{11}H_{10}N_2O_4$ (234.21): C, 56.41; H, 4.30; N, 11.96. Found: C, 56.45; H, 4.38; N, 11.90.

Tetraethyl 5-amino-6-cyano-1,2,3,4-benzenete tetracarboxylate (3c)

Yield: 0.34 g (84%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3512, 3435 (NH_2), 2289(CN), 1728, 1722, 1720, 1714, (C=O), 1251 (C–O) cm^{-1}. ^{1}H NMR: 1.17-1.46 (m, 12H, CH_3), 3.47 (q, ^{3}J = 7.0 Hz, 2H, OCH_2), 3.70 (q, ^{3}J = 6.9 Hz, 2H, OCH_2), 4.22-4.32 (m, 4H, OCH_2), 6.79 (broad, 2H, NH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.2 (Me), 14.3 (Me), 15.4 (Me), 15.6 (Me), 62.5 (OCH_2), 62.6 (OCH_2), 63.0 (OCH_2), 63.4 (OCH_2), 97.8 (C), 111.9 (C), 114.2 (C), 119.1 (C), 142.1 (C), 144.1 (C), 152.7 (C), 164.5, 165.0, 165.7, 166.6 (4 C=O, ester). EI-MS: 406 (M^+, 9), 114 (52), 73 (100). Anal. Calcd for $C_{19}H_{22}N_2O_8$ (406.39): C, 56.15; H, 5.46; N, 6.89. Found: C, 56.20; H, 5.40; N, 6.83.

Diethyl 4-amino-5-cyano isophthalate (3d)

Yield: 0.21 g (81%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3487, 3451 (NH_2), 2355(CN), 1728, 1718, (C=O), 1241 (C–O) cm^{-1}. ^{1}H NMR: 1.22 (t, ^{3}J = 6.9 Hz, 3H, CH_3), 1.44 (t, ^{3}J = 7.1 Hz, 3H, CH_3), 3.48 (q, ^{3}J = 6.9 Hz,2H, OCH_2), 4.45 (q, ^{3}J = 7.1 Hz, 2H, OCH_2), 6.67 (broad, 2H, NH_2), 8.37(s, 1H, CH), 8.73 (s, 1H, CH). ^{13}C NMR: 14.7 (Me), 14.9 (Me), 62.1 (OCH_2), 62.3 (OCH_2), 97.1 (C), 112.5 (C), 115.2 (C), 121.3 (C), 131.0 (CH), 134.8 (CH), 145.7 (C), 165.5, 165.9, (2 C=O, ester). Anal. Calcd for $C_{13}H_{14}N_2O_4$ (262.26): C, 59.54; H, 5.38; N, 10.68. Found: C, 59.50; H, 5.42; N, 10.65.

Tetraisopropyl 5-amino-6-cyano-1,2,3,4-benzenete tetracarboxylate (3e)

Yield: 0.33 g (72%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3436, 3379 (NH_2), 2286(CN), 1731, 1724, 1713, 1696, (C=O), 1267 (C–O) cm^{-1}. ^{1}H NMR: 1.32 (d, ^{3}J = 7.0 Hz, 6 H, CHMe_2), 1.37 (d, ^{3}J = 7.0 Hz, 6 H, CHMe_2), 1.42 (d, ^{3}J = 7.0 Hz, 6 H, CHMe_2), 1.48 (d, ^{3}J = 7.0 Hz, 6 H, CHMe_2), 5.01–5.12 (m, 2H, 2*CH*Me_2), 5.23–5.34 (m, 2H, 2*CH*Me_2), 6.75 (broad, 2H, NH_2). ^{13}C NMR: 21. (CHMe_2), 214 (CHMe_2), 21.6 (CHMe_2), 21.8 (CHMe_2), 67.3 (*CH*Me_2), 67.5 (*CH*Me_2), 67.8 (*CH*Me_2), 68.1 (*CH*Me_2), 98.1 (C), 115.3 (C), 117.1 (C), 125.2 (C), 127.8 (C), 128.3 (C), 153.0 (C), 164.6, 165.1, 165.4, 166.3 (4 C=O, ester). EI-MS: 462 (M^+, 7), 114 (60), 87 (100). Anal. Calcd for $C_{23}H_{30}N_2O_8$ (462.49): C, 59.73; H, 6.54; N, 6.06. Found: C, 59.70; H, 6.59; N, 6.12.

1-ethyl 2,3,4,5-tetramethyl 6-amino-1,2,3,4,5-benzene pentacarboxylate (3f)

Yield: 0.14 g (35%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3462, 3409 (NH_2), 1734, 1723, 1716, 1710, 1704, (C=O), 1250 (C–O) cm^{-1}.^{1}H NMR: 1.32 (*t*, ^{3}J = 7.0 Hz, 3H, CH_3), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.31 (q, ^{3}J = 7.0 Hz, 2H, OCH_2), 6.41 (broad, 2H, NH_2).^{13}C NMR: 13.5 (CH_3), 51.8 (OCH_3), 51.9 (OCH_3), 52.0 (OCH_3), 52.4 (OCH_3), 62.8 (OCH_2), 119.5 (C), 120.1 (C), 126.7 (C), 140.4 (C), 141.8 (C), 151.2 (C), 155.5, 159.2, 161.5, 165.8, 167.8 (5C=O). EI-MS: 397 (M^+, 7), 88 (56), 73 (40), 59 (100). Anal. Calcd for $C_{17}H_{19}NO_{10}$ (397.33): C, 51.39; H, 4.82; N, 3.53. Found: C, 51.42; H, 4.85; N, 3.63.

Pentaethyl 6-amino-1,2,3,4,5-benzene pentacarboxylate (3g)

Yield: 0.14 g (32%), yellow oil. IR (KBr) (v_{max}/cm^{-1}): 3446, 3361 (NH_2), 1729, 1722, 1716, 1711 1705 (C=O), 1278 (C–O) cm^{-1}. ^{1}H NMR: 1.32-1.42 (m, 15H, CH_3), 4.30-4.38 (m, 4H, 2OCH_2), 4.42-4.48 (m, 4H, 2OCH_2), 4.45 (q, ^{3}J = 7.01 Hz, 2H, OCH_2), 6.35 (broad, 2H, NH_2). ^{13}C NMR: 13.5 (Me), 14.2 (Me), 14.3 (Me), 14.4 (Me), 15.2 (Me), 60.5 (OCH_2), 61.6 (OCH_2), 62.6 (OCH_2), 63.0 (OCH_2), 63.4 (OCH_2), 119.6 (C), 122.6 (C), 125.6 (C), 140.5 (C), 146.6 (C), 151.2 (C), 163.2, 164.5, 165.0, 165.7,166.6 (5C=O). MS (EI, 70 eV): EI-MS: 453 (M^+, 8), 88 (51), 73 (100). Anal. Calcd for $C_{21}H_{27}NO_{10}$ (453.44): C, 55.6; H, 6.00; N, 3.09. Found: C, 55.7; H, 5.96; N, 3.12.

Biphenyl-2,3,4,5,6-pentacarboxylic acid 6-ethyl ester 2,3, 4,5-tetramethyl ester (4a)

Yield 0.43g (95%). Colorless crystalline solid, mp 125–127^{o}C. IR (KBr) (v_{max}/cm^{-1}): 1738, 1725, 1723, 1712, 1708 (C=O), 1251 (C–O) cm^{-1}. ^{1}H NMR: 0.89 (m, 3H, CH_3), 3.46 (s, 3H, OCH_3), 3.89 (s, 6H, 2OCH_3), 3.92 (s, 3H, OCH_3), 3.95–3.99 (m, 2H, OCH_2), 7.21–7.40 (m, 5H, 5CH). ^{13}C NMR: 13.8, 52.3, 53.4, 54.5, 55.7, 66.1, 127.6, 127.9 (2CH), 128.4 (2CH), 131.1, 131.4, 132.1, 135.9, 136.4, 136.6, 140.3, 165.2, 165.3, 165.7, 165.8, 166.2. Anal. Calcd for $C_{23}H_{22}O_{10}$ (458.41): C, 60.26; H, 4.84. Found: C, 60.18; H, 4.80.

Biphenyl-2,3,4,5,6-pentacarboxylic acid pentaethyl ester (4b)

Yield 0.47g (92%). Colorless crystalline solid, mp 122–124 ^{o}C. IR (KBr) (ν_{max}/cm^{-1}): 1738, 1725, 1718 (C=O), 1259 (C–O) cm^{-1}. ^{1}H NMR: 0.89-1.04 (m, 15H, 5 CH_3), 3.91–4.30 (m, 10H, 5OCH_2), 7.20–7.38 (m, 5H, 5CH). ^{13}C NMR: 13.2, 13.5, 13.6, 62.1, 62.2, 62.4, 126.6, 128.3, 128.2, 131.2, 132.2, 135.8, 136.3, 140.2, 165.4, 165.8, 166.3. Anal. Calcd for $C_{27}H_{30}O_{10}$ (514.52): C, 63.03; H, 5.88. Found: C, 63.11; H, 5.83.

4'-Bromo-biphenyl-2,3,4,5,6-pentacarboxylic acid pentamethyl ester (4c)

Yield 0.50g (93%). Colorless crystalline solid, mp 147–148 ^{o}C. IR (KBr) (ν_{max}/cm^{-1}): 1742, 1731, 1724 (C=O), 1252 (C–O) cm^{-1}. ^{1}H NMR: 3.51 (s, 6H, 2 OCH_3), 3.85 (s, 3H, OCH_3), 3,90 (s, 6H, 2 OCH_3), 7.07 (2H, d, ^{3}J= 8.2 Hz, 2CH), 7.49 (d, 2H, ^{3}J= 8.3 Hz, 2CH). ^{13}C NMR: 52.3, 53.5, 53.6, 123.1, 130.2, 131.6, 131.7, 133.1, 134.3, 135.9, 138.2, 165.3, 165.8, 166.2. Anal. Calcd for $C_{22}H_{19}BrO_{10}$ (537.31): C, 50.50; H, 3.66. Found: C, 50.61; H, 3.68.

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